Supporting Information for

A General Copper-Catalyzed Radical Cross-Coupling of Unactivated Alkyl Halides

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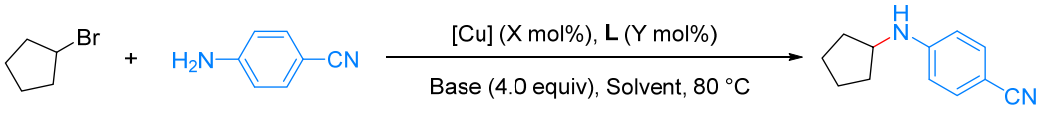
1. Supplementary tables for experiments

Table S1. Reaction condition optimization with cyclopentyl bromide **E1** and 4-aminobenzonitrile **N1**[a]

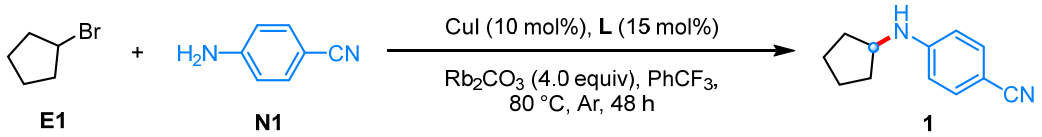


E1 **N1** **1**

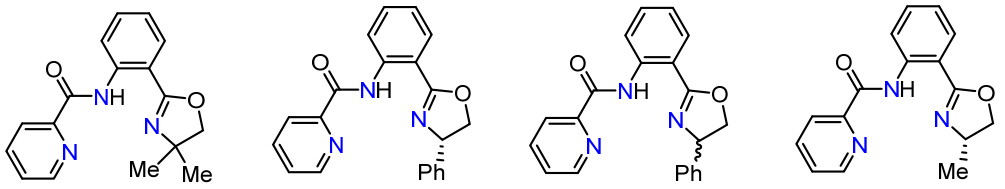
Entry	**L** (X mol%)	Base	Solvent	[Cu] (Y mol%)	Yield (%)
1	**L12** (15)	Rb_2CO_3	$PhCF_3$	CuI (10)	97
2	**L12** (15)	K_2CO_3	$PhCF_3$	CuI (10)	85
3	**L12** (15)	Cs_2CO_3	$PhCF_3$	CuI (10)	94
4	**L12** (15)	K_3PO_4	$PhCF_3$	CuI (10)	95
5	**L12** (15)	KOMe	$PhCF_3$	CuI (10)	trace
6	**L12** (15)	KO^{t}Bu	$PhCF_3$	CuI (10)	trace
7	**L12** (15)	Rb_2CO_3	PhH	CuI (10)	92
8	**L12** (15)	Rb_2CO_3	EtOAc	CuI (10)	52
9	**L12** (15)	Rb_2CO_3	CH_3CN	CuI (10)	80
10	**L12** (15)	Rb_2CO_3	1,4-dioxane	CuI (10)	85
11	**L12** (15)	Rb_2CO_3	$PhCF_3$	CuBr·Me_2S (10)	96
12	**L12** (15)	Rb_2CO_3	$PhCF_3$	CuTc (10)	95
13	**L12** (15)	Rb_2CO_3	$PhCF_3$	$Cu(CH_3CN)_4PF_6$ (10)	88
14	**L12** (15)	Rb_2CO_3	$PhCF_3$	$CuBr_2$ (10)	90
15	**L12** (15)	Rb_2CO_3	$PhCF_3$	$Cu(OAc)_2$ (10)	80
16[b,c]	**L12** (15)	Rb_2CO_3	$PhCF_3$	CuI (10)	65
17[c]	**L12** (7.5)	Rb_2CO_3	$PhCF_3$	CuI (5)	95

[a]Reaction conditions: cyclopentyl bromide **E1** (0.060 mmol, 1.2 equiv.), 4-aminobenzonitrile **N1** (0.050 mmol), CuI (10 mol%), L (15 mol%), and Rb_2CO_3 (4.0 equiv) in dry $PhCF_3$ (0.50 mL) at 80 °C for 48 h under argon; yield of **1** was based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. [b]at 60 °C. [c]for 72 h.

Table S2. Evaluation of *N,N,N*-ligands in the model reaction [a]



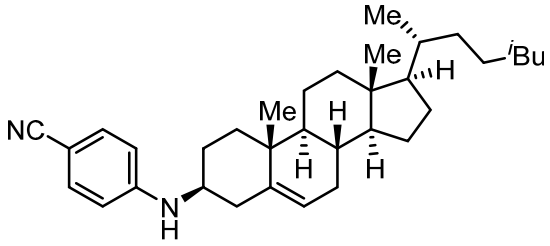
E1 N1 1



L11: 64% **L12**: 97% **L13**: 96% **L14**: 90%

[a]Reaction conditions: cyclopentyl bromide **E1** (0.060 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (0.050 mmol), CuI (10 mol%), L (15 mol%), and Rb_2CO_3 (4.0 equiv) in dry $PhCF_3$ (0.50 mL) at 80 °C for 48 h under argon; yield of **1** was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

2. Supplementary figures for experiments



87-major

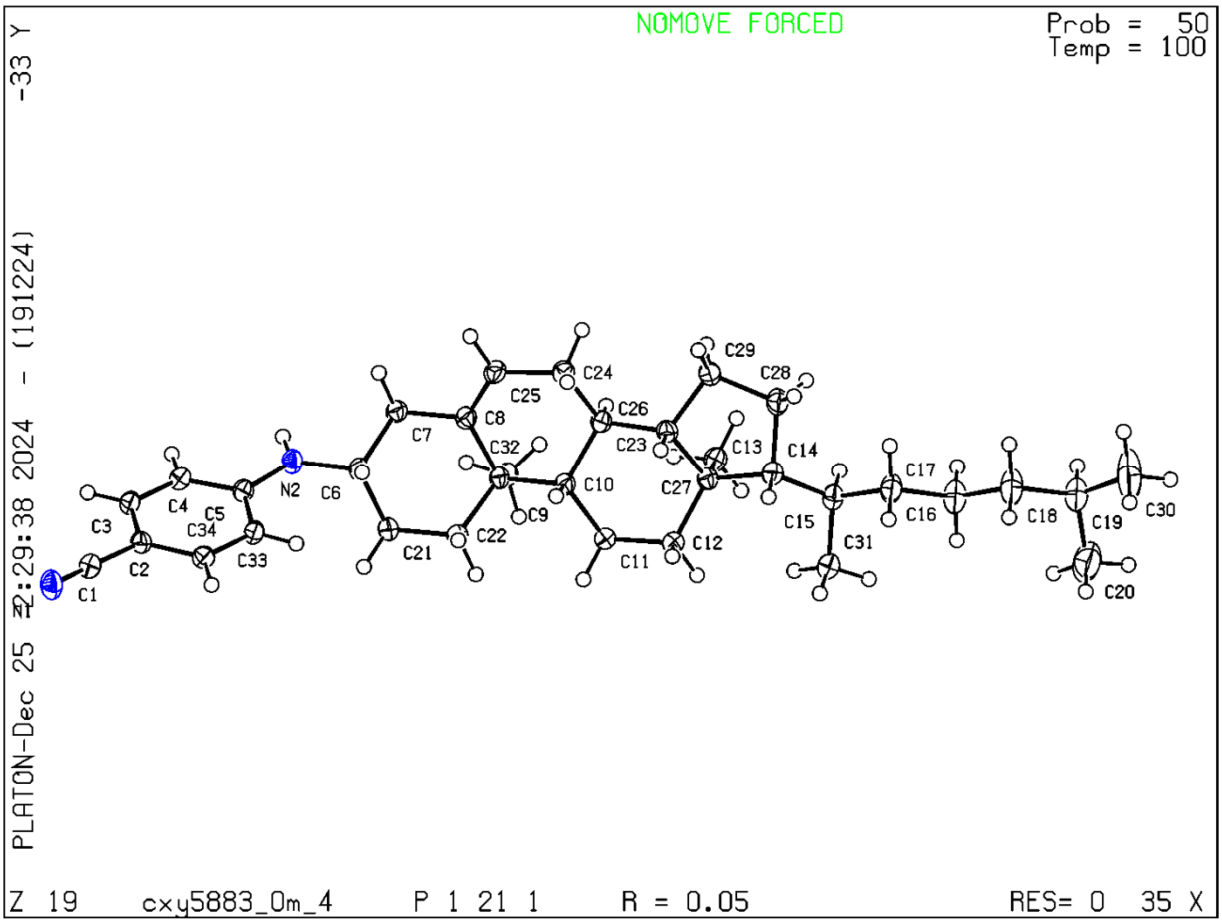
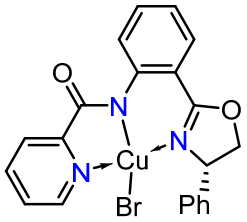


Figure S1. The X-ray structure of **87-major**.



CatA

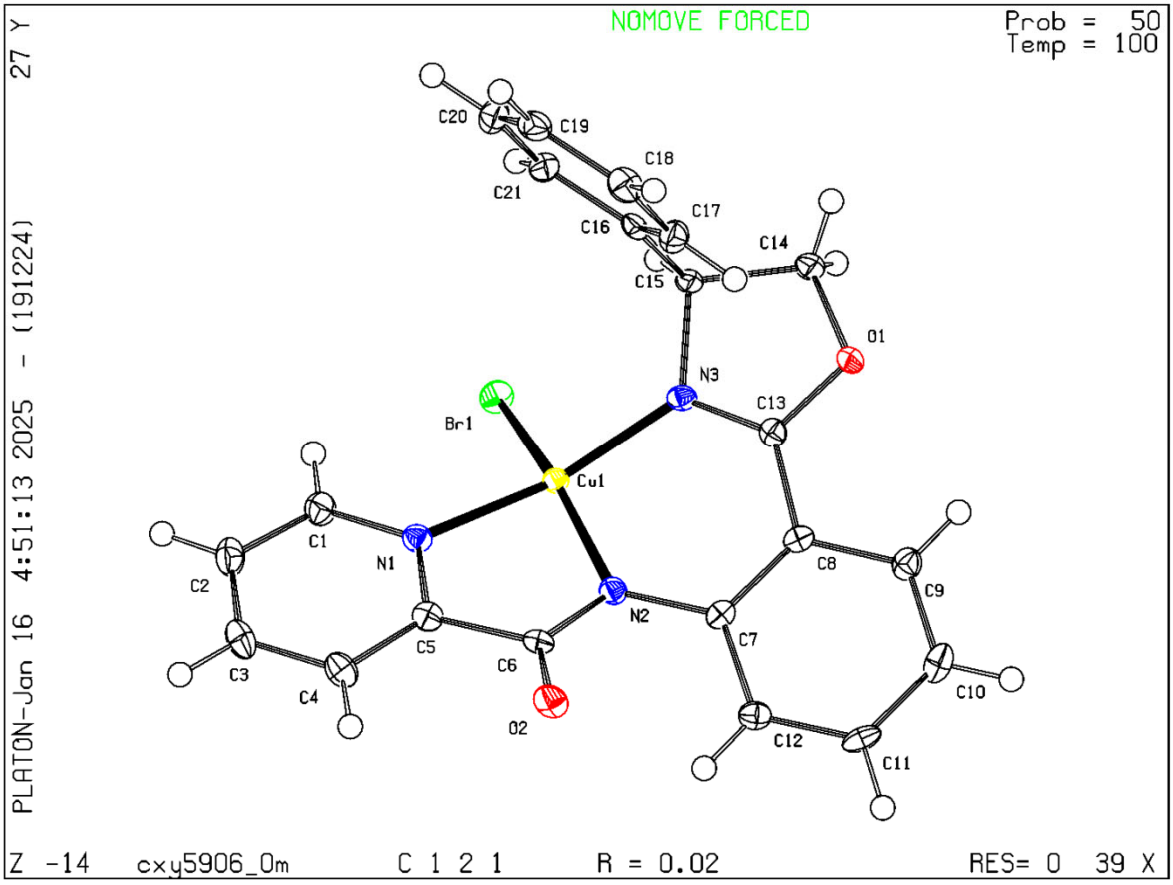
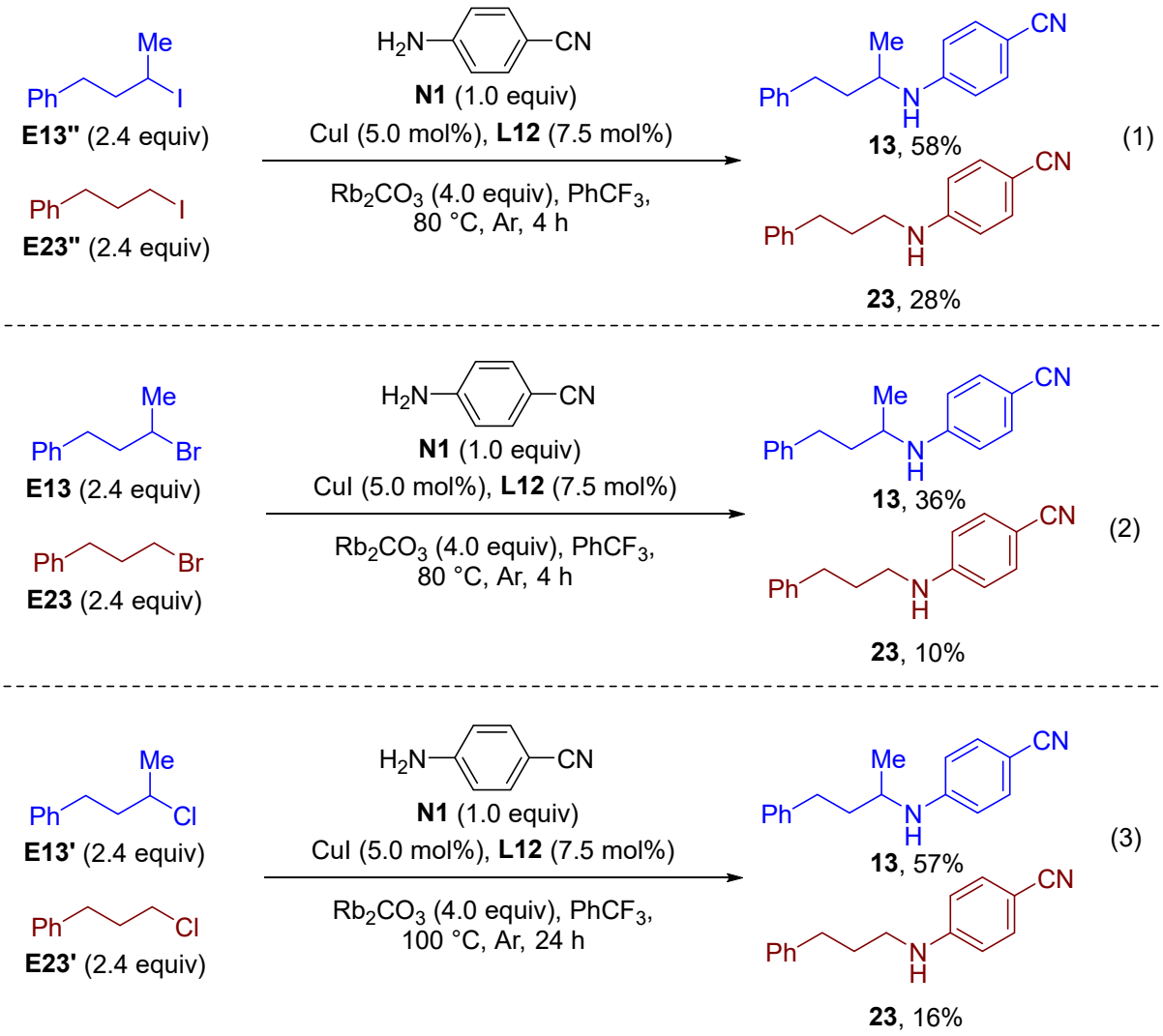
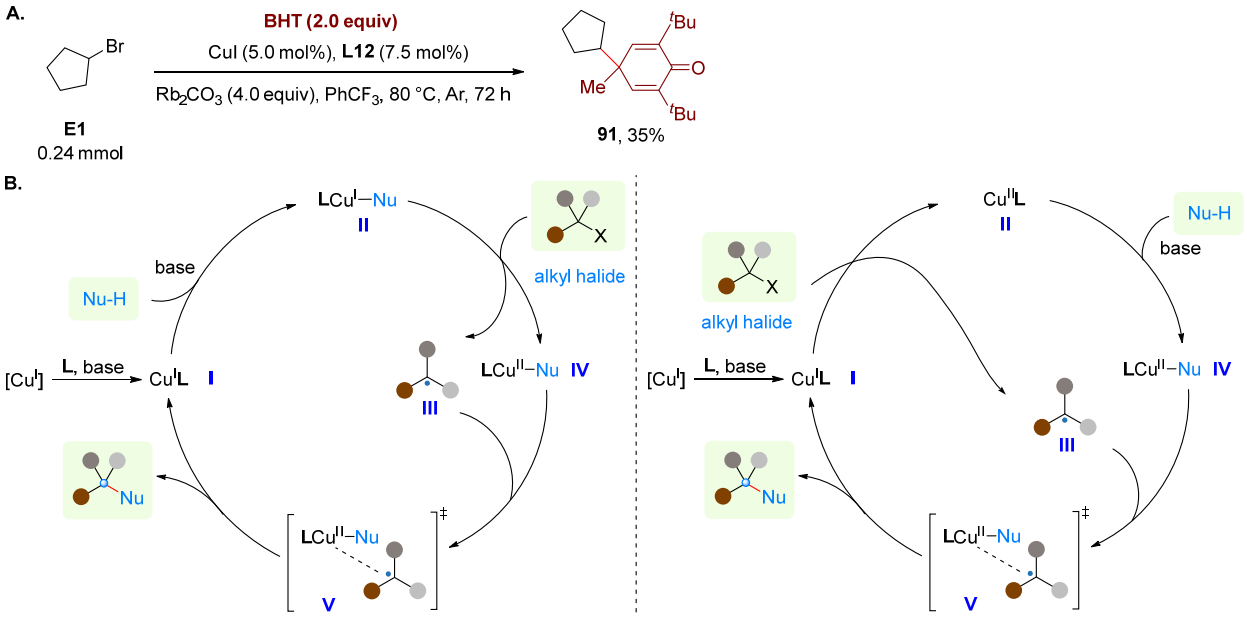


Figure S2. The X-ray structure of **CatA**.

3. Supplementary schemes for experiments



Scheme S1. Competition experiments.



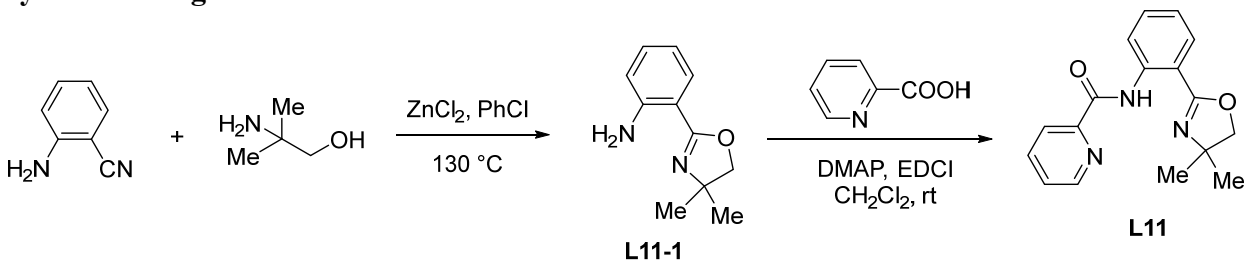
Scheme S2. Control experiments and mechanistic Proposal.

4. General information

Most of reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Anhydrous CH_2Cl_2 was purified and dried using a solvent-purification system that contained activated alumina under argon. CuI was purchased from Sigma-Aldrich. Rb_2CO_3 was purchased from Bide Pharmatech Ltd. and treated by hot gun (approximate 300 to 400 °C) for 2 minutes in vacuum. Anhydrous $PhCF_3$ was purchased from J&K Scientific. For cyclic voltammetry (CV) experiments tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was purchased from J&K Scientific and CH_3CN was purchased from TCI. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). As the eluent, the petroleum ether, EtOAc, CH_2Cl_2 and CH_3OH were purchased from Shanghai Titan Scientific Co. Ltd without further purification. Visualization on TLC was achieved by use of UV light (254 nm), iodine on silica gel or basic $KMnO_4$ indicator. NMR spectra were recorded on Bruker DRX-400 and DPX-600 spectrometers at 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR respectively, in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^1H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet, m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. The diastereoselectivity value (dr) was determined by ^1H NMR analysis of the crude product unless otherwise noted. Enantiomeric excess (ee) was determined using Agilent high-performance liquid chromatography (HPLC) with a Hatachi detector (at appropriate wavelength). Column conditions are reported in the experimental section below. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with Cu–Kα radiation.

5. The synthesis of ligands and alkyl halides

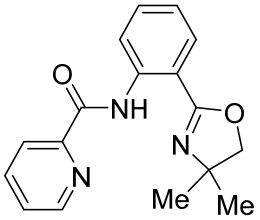
Synthesis of ligands L11 and L12



According to the literature reported procedure.[1,2] Under an argon atmosphere, to a solution of 2-aminobenzonitrile (1.18 g, 10.0 mmol, 1.0 equiv) and 2-amino-2-methylpropan-1-ol (1.24 g, 15.0 mmol, 1.5 equiv) in chlorobenzene (30 mL) was added dry $ZnCl_2$ (4.02 g, 30.0 mmol, 3.0 equiv) at once at rt. Then, the reaction mixture was reflux for 24 h. After completion (monitored by TLC), the reaction mixture was dissolved in water, EtOAc, and 2 mL ethylenediamine. Next, the reaction was extracted with EtOAc three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtrated and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford the product **L11-1** as a white solid (1.65 g, 87% yield).

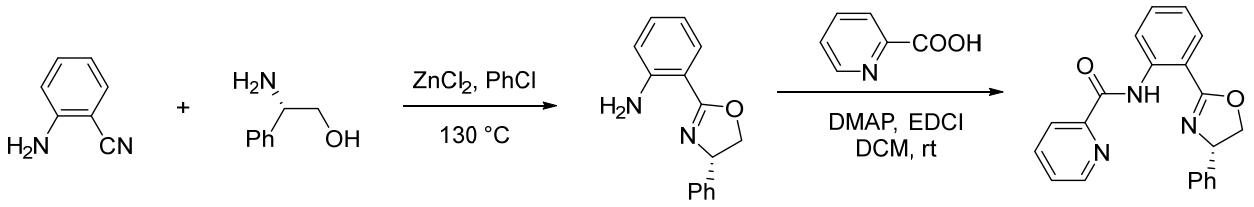
Under an argon atmosphere, to a solution of 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)aniline **L11-1** (1.14 g, 6.0 mmol, 1.0 equiv), picolinic acid (0.81 g, 6.6 mmol, 1.1 equiv), DMAP (1.17 g, 9.6 mmol, 1.6 equiv) in anhydrous CH_2Cl_2 (20 mL, 0.3 M) was added EDCI (1.84 g, 9.6 mmol, 1.6 equiv) at room temperature. Then the reaction mixture was stirred overnight. After completion (monitored by TLC), the reaction was quenched by water and extracted with EtOAc three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtrated and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford the product **L11** as a white solid (1.44 g, 81% yield).

***N*-(2-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)picolinamide (L11)**



L11

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.84 (s, 1H), 8.99 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.73 – 8.59 (m, 1H), 8.28 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.88 (td, *J* = 7.8, 1.7 Hz, 2H), 7.56 – 7.49 (m, 1H), 7.45 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.13 (td, *J* = 7.6, 1.2 Hz, 1H), 4.12 (s, 2H), 1.49 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 161.3, 151.3, 148.2, 139.5, 137.3, 132.2, 129.1, 126.2, 122.8, 122.7, 120.2, 115.1, 78.0, 68.2, 28.7.
HRMS (ESI) m/z calcd. for $C_{17}H_{18}N_3O_2$ $[M + H]^+$ 296.1394, found 296.1393.

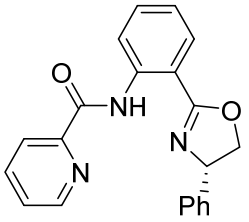


L12-1 **L12**

According to the literature reported procedure.[2,3] Under an argon atmosphere, to a solution of 2-aminobenzonitrile (1.18 g, 10.0 mmol, 1.0 equiv) and (*S*)-2-amino-2-phenylethan-1-ol (2.06 g, 15.0 mmol, 1.5 equiv) in chlorobenzene (30 mL) was added dry $ZnCl_2$ (4.02 g, 30.0 mmol, 3.0 equiv) at once at rt. Then, the reaction mixture was refluxed for 24 h. After completion (monitored by TLC), the reaction mixture was dissolved in water, EtOAc, and 2 mL ethylenediamine. Next, the reaction was extracted with EtOAc three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtrated and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford the product **L12-1** as a white solid (2.17 g, 91% yield).

Under an argon atmosphere, to a solution of (*S*)-2-(4-phenyl-4,5-dihydrooxazol-2-yl)aniline **L12-1** (1.43 g, 6.0 mmol, 1.0 equiv), picolinic acid (0.81 g, 6.6 mmol, 1.1 equiv), DMAP (1.17 g, 9.6 mmol, 1.6 equiv) in anhydrous CH_2Cl_2 (20 mL, 0.3 M) was added EDCI (1.84 g, 9.6 mmol, 1.6 equiv) at room temperature. Then the reaction mixture was stirred overnight. After completion (monitored by TLC), the reaction was quenched by water and extracted with EtOAc three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtrated and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford the product **L12** as a white solid (1.77 g, 86% yield).

(*S*)-*N*-(2-(4-Phenyl-4,5-dihydrooxazol-2-yl)phenyl)picolinamide (L12)

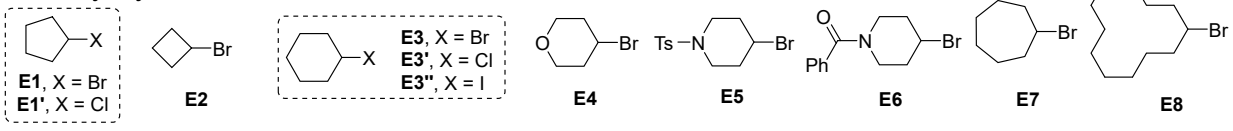


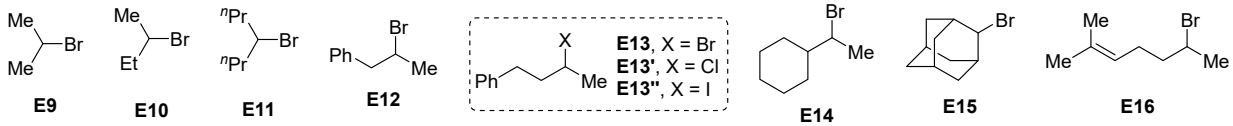
L12

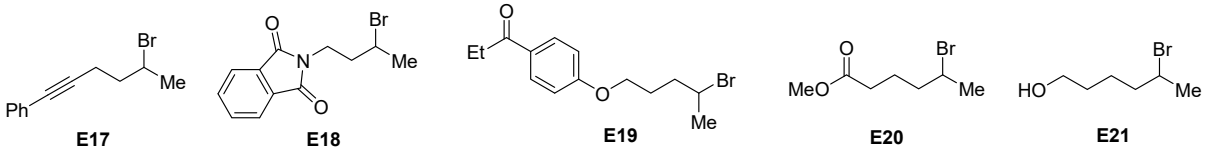
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.87 (s, 1H), 9.07 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.33 – 8.17 (m, 2H), 7.96 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.82 (td, *J* = 7.7, 1.5 Hz, 1H), 7.62 – 7.48 (m, 3H), 7.41 – 7.27 (m, 4H), 7.16 (td, *J* = 7.6, 1.2 Hz, 1H), 5.67 (t, *J* = 9.7 Hz, 1H), 4.85 (dd, *J* = 10.1, 8.2 Hz, 1H), 4.24 (dd, *J* = 9.3, 8.2 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 164.1, 150.9, 148.2, 142.1, 139.8, 137.2, 132.7, 129.6, 128.7, 127.5, 126.8, 126.1, 122.8, 122.7, 120.3, 114.5, 73.2, 70.2.
HRMS (ESI) m/z calcd. for $C_{21}H_{18}N_3O_2$ $[M + H]^+$ 344.1394, found 344.1395.

Scope of alkyl halides

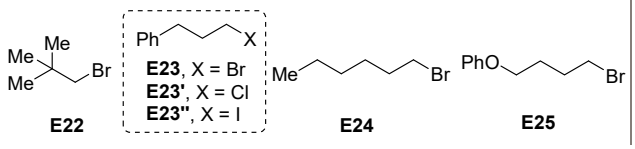
Secondary alkyl halides



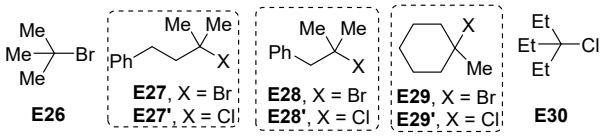




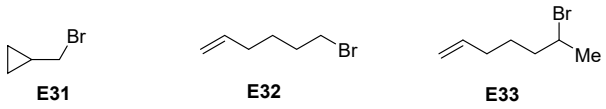
Primary alkyl halides



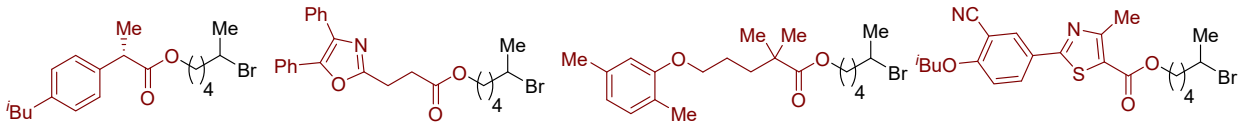
Tertiary alkyl halides

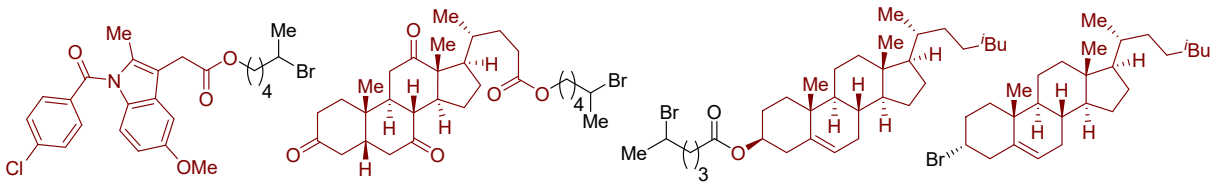


Clock substrates



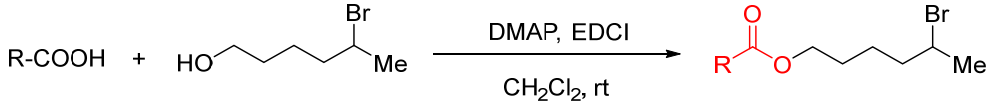
Alkyl halides based on bioactive molecules





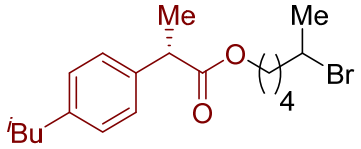
Compounds **E1**–**E4**, **E1′**, **E3′**, **E3′′**, **E7**–**E12**, **E15**, **E22**–**E26**, **E23′**, **E23′′**, and **E31**–**E32** were purchased from commercial sources. **E5**,[4] **E6**,[5] **E13**,[5] **E13′**,[6] **E13′′**,[7] **E14**,[4] **E16**,[8] **E17**–**E19**,[9] **E20**,[10] **E21**,[11] **E27**,[12] **E27′**,[13] **E28**,[14] **E28′**,[15] **E29**,[16] **E29′**,[15] **E30**,[17] **E33**,[18] and **E37**[19] were prepared according to the literature procedures.

General procedure (GP1) for the synthesis of complex alkyl bromides



To a solution of 5-bromohexan-1-ol (0.80 g, 4.4 mmol, 1.1 equiv), bioactive acid compound (4.0 mmol, 1.0 equiv), DMAP (0.73 g, 6.0 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (20 mL, 0.2 M) was added EDCI (1.15 g, 6.0 mmol, 1.5 equiv) at room temperature. Then the reaction mixture was stirred overnight. After completion (monitored by TLC), the reaction was quenched by water and extracted with EtOAc three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtrated and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel to afford the product.

2-Bromopropyl (*2S*)-2-(4-isobutylphenyl)propanoate (E34)



E34

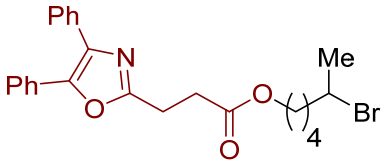
According to **General procedure (GP1)** with 5-bromohexan-1-ol (0.80 g, 4.4 mmol, 1.1 equiv), and (*S*)-Ibuprofen (0.82 g, 4.0 mmol, 1.0 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **E34** as a colorless oil (1.33 g, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.13 – 3.98 (m, 3H), 3.68 (q, *J* = 7.2 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.91 – 1.80 (m, 1H), 1.79 – 1.68 (m, 2H), 1.66 (d, *J* = 6.6 Hz, 3H), 1.63 – 1.55 (m, 2H), 1.53 – 1.43 (m, 4H), 1.42 – 1.29 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 140.5, 137.8, 129.4, 127.2, 64.3, 64.3, 51.35, 51.32, 45.2, 45.1, 40.57, 40.55, 30.2, 27.9, 26.44, 26.42, 24.1, 22.4, 18.5.

HRMS (ESI) m/z calcd. for $C_{19}H_{30}BrO_2$ $[M + H]^+$ 369.1424, found 369.1423.

2-Bromopropyl 3-(4,5-diphenyloxazol-2-yl)propanoate (E35)



E35

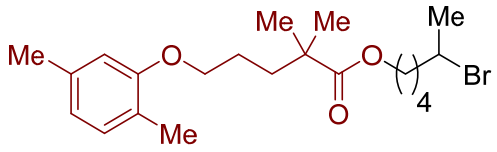
According to **General procedure (GP1)** with 5-bromohexan-1-ol (0.80 g, 4.4 mmol, 1.1 equiv), and Oxaprozin (1.17 g, 4.0 mmol, 1.0 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **E35** as light-yellow oil (1.68 g, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.59 – 7.54 (m, 2H), 7.40 – 7.28 (m, 6H), 4.14 (t, *J* = 6.4 Hz, 2H), 4.11 – 4.02 (m, 1H), 3.19 (t, *J* = 7.5 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 1.86 – 1.70 (m, 3H), 1.67 (d, *J* = 6.7 Hz, 3H), 1.65 – 1.54 (m, 2H), 1.53 – 1.44 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 161.8, 145.4, 135.1, 132.5, 129.0, 128.7, 128.6, 128.5, 128.1, 127.9, 126.5, 64.6, 51.3, 40.6, 31.2, 28.0, 26.5, 24.3, 23.6.

HRMS (ESI) m/z calcd. for $C_{24}H_{27}BrNO_3$ $[M + H]^+$ 456.1169, found 456.1172.

2-Bromopropyl 4-(2,5-dimethylphenoxy)-2,2-dimethylbutanoate (E36)



E36

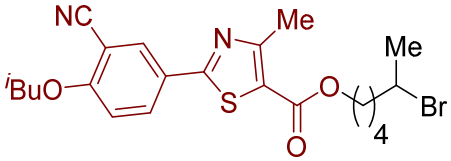
According to **General procedure (GP1)** with 5-bromohexan-1-ol (0.80 g, 4.4 mmol, 1.1 equiv) and Gemfibrozil (1.00 g, 4.0 mmol, 1.0 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **E36** as a colorless oil (1.24 g, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.60 (s, 1H), 4.14 – 4.03 (m, 3H), 3.91 (t, *J* = 3.6 Hz, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 1.90 – 1.76 (m, 2H), 1.76 – 1.71 (m, 4H), 1.70 (d, *J* = 6.6 Hz, 3H), 1.67 – 1.40 (m, 4H), 1.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 157.0, 136.5, 130.3, 123.6, 120.7, 111.9, 67.9, 64.1, 51.4, 42.2, 40.6, 37.2, 28.0, 26.5, 25.2, 24.3, 21.5, 15.8.

HRMS (ESI) m/z calcd. for $C_{21}H_{34}BrO_3$ $[M + H]^+$ 413.1686, found 413.1682.

2-Bromopropyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (E37)



E37

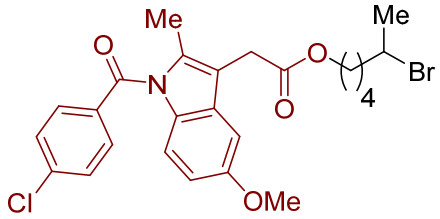
According to **General procedure (GP1)** with 5-bromohexan-1-ol (0.80 g, 4.4 mmol, 1.1 equiv), and Febuxostat (1.27 g, 4.0 mmol, 1.0 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc/CH_2Cl_2 = 20/1/1) to yield the product **E37** as a white solid (1.63 g, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.3 Hz, 1H), 8.09 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 4.31 (t, *J* = 6.4 Hz, 2H), 4.20 – 4.11 (m, 1H), 3.90 (d, *J* = 6.4 Hz, 2H), 2.77 (s, 3H), 2.28 – 2.14 (m, 1H), 1.96 – 1.75 (m, 4H), 1.74 (d, *J* = 6.6 Hz, 3H), 1.72 – 1.64 (m, 1H), 1.61 – 1.51 (m, 1H), 1.09 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 162.6, 162.1, 161.3, 132.6, 132.2, 126.0, 121.8, 115.5, 112.7, 103.0, 75.8, 65.1, 51.3, 40.6, 28.2, 28.1, 26.6, 24.4, 19.1, 17.6.

HRMS (ESI) m/z calcd. for $C_{22}H_{28}BrN_2O_3S$ $[M + H]^+$ 479.0999, found 479.1002.

2-Bromopropyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (E38)

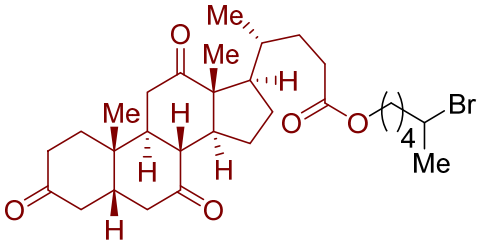


E38

According to **General procedure (GP1)** with 5-bromohexan-1-ol (0.80 g, 4.4 mmol, 1.1 equiv), and Indometacin (1.43 g, 4.0 mmol, 1.0 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc/CH_2Cl_2 = 20/1/1) to yield the product **E38**

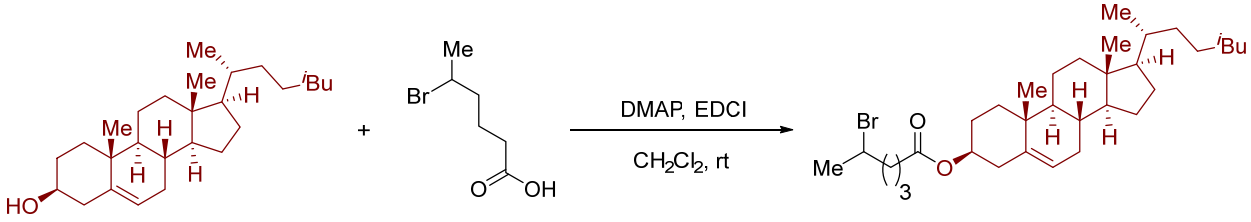
as a light-yellow oil (1.58 g, 76% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.13 – 4.07 (m, 2H), 4.07 – 3.97 (m, 1H), 3.82 (s, 3H), 3.66 (s, 2H), 2.38 (s, 3H), 1.84 – 1.69 (m, 2H), 1.68 – 1.58 (m, 5H), 1.58 – 1.32 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 168.3, 156.0, 139.2, 135.9, 133.9, 131.2, 130.8, 130.7, 129.1, 115.0, 112.6, 111.6, 101.3, 64.7, 55.7, 51.3, 40.5, 30.4, 28.0, 26.4, 24.2, 13.4.
HRMS (ESI) m/z calcd. for $C_{25}H_{28}BrClNO_4$ $[M + H]^+$ 520.0885, found 520.0888.

2-Bromopropyl (*4R*)-4-((*5S,8R,9S,10S,13R,14S,17R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (E39)



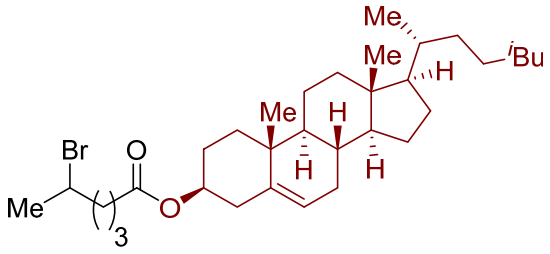
E39

According to **General procedure (GP1)** with 5-bromohexan-1-ol (0.80 g, 4.4 mmol, 1.1 equiv), and Dehydrocholic acid (1.61 g, 4.0 mmol, 1.0 equiv), the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 100/1) to yield the product **E39** as a white solid (1.76 g, 78% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 – 4.09 (m, 1H), 4.07 (t, *J* = 6.3 Hz, 2H), 2.97 – 2.80 (m, 3H), 2.49 – 1.77 (m, 18H), 1.72 (d, *J* = 6.6 Hz, 3H), 1.69 – 1.16 (m, 12H), 1.08 (s, 3H), 0.85 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 212.0, 209.1, 208.8, 174.2, 64.0, 56.9, 51.8, 51.4, 49.0, 46.9, 45.7, 45.6, 45.0, 42.8, 40.7, 38.7, 36.6, 36.0, 35.6, 35.3, 31.5, 30.5, 28.0, 27.7, 26.5, 25.2, 24.3, 22.0, 18.7, 11.9.
HRMS (ESI) m/z calcd. for $C_{30}H_{46}BrO_5$ $[M + H]^+$ 565.2523, found 565.2526.



To a solution of 5-bromohexanoic acid (0.86 g, 4.4 mmol, 1.1 equiv), Cholesterol (1.55 g, 4.0 mmol, 1.0 equiv), DMAP (0.73 g, 6.0 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 (20 mL, 0.2 M) was added EDCI (1.15 g, 6.0 mmol, 1.5 equiv) at room temperature. Then the reaction mixture was stirred overnight. After completion (monitored by TLC), the reaction was quenched by water and extracted with EtOAc three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtrated and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 100/1) to afford the product **E40** as a white solid (2.01 g, 89% yield).

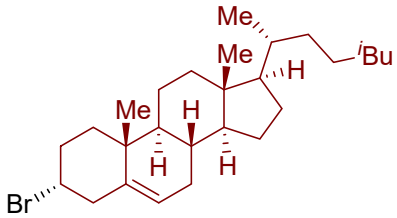
(*3S,8S,9S,10R,13R,14S,17R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 3-bromobutanoate (E40)



E40

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (d, *J* = 5.0 Hz, 1H), 4.69 – 4.51 (m, 1H), 4.20 – 4.03 (m, 1H), 2.38 – 2.24 (m, 4H), 2.07 – 1.92 (m, 2H), 1.92 – 1.74 (m, 7H), 1.71 (d, *J* = 6.7 Hz, 3H), 1.65 – 1.43 (m, 7H), 1.40 – 1.22 (m, 5H), 1.19 – 1.06 (m, 6H), 1.02 (s, 3H), 0.96 (d, *J* = 6.6 Hz, 2H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.7, 1.7 Hz, 6H), 0.67 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 139.7, 122.8, 74.0, 56.7, 56.2, 50.9, 50.1, 42.4, 40.3, 39.8, 39.6, 38.2, 37.0, 36.7, 36.2, 35.9, 33.9, 32.0, 31.9, 28.3, 28.1, 27.9, 26.5, 24.4, 23.9, 23.3, 22.9, 22.6, 21.1, 19.4, 18.8, 11.9.
HRMS (ESI) m/z calcd. for $C_{33}H_{56}BrO_2$ $[M + H]^+$ 563.3458, found 563.3449.

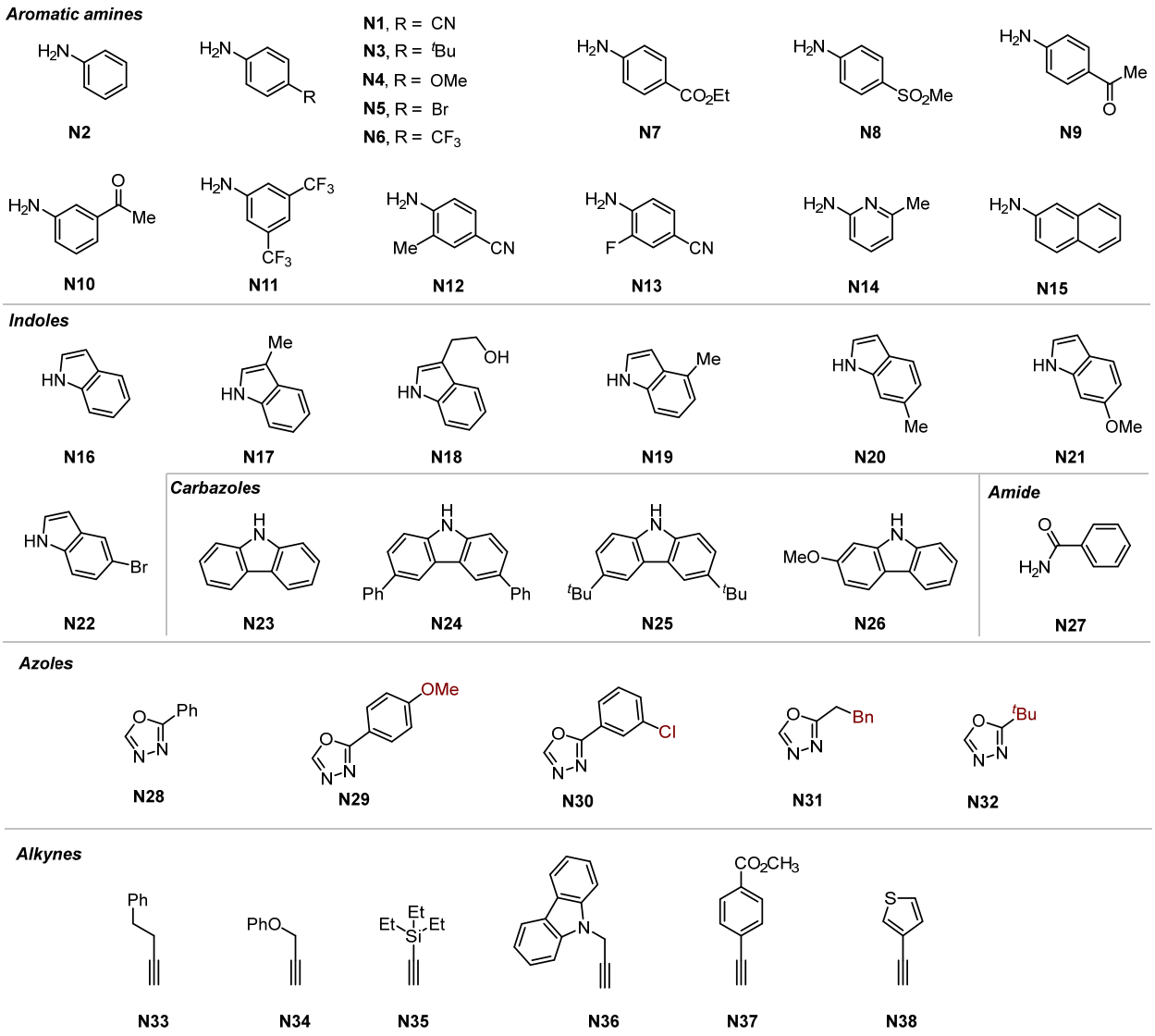
(*3R,8S,9S,10R,13R,14S,17R*)-3-Bromo-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene (E41)



E41

E37 was prepared according to the literature procedure.[19]
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 – 5.32 (m, 1H), 3.98 – 3.87 (m, 1H), 2.82 – 2.68 (m, 1H), 2.64 – 2.53 (m, 1H), 2.24 – 2.12 (m, 1H), 2.09 – 1.93 (m, 3H), 1.92 – 1.76 (m, 2H), 1.64 – 1.23 (m, 11H), 1.20 – 1.06 (m, 6H), 1.04 (s, 3H), 1.02 – 0.93 (m, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.67 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 122.4, 56.7, 56.2, 52.6, 50.2, 44.4, 42.4, 40.4, 39.7, 39.6, 36.4, 36.3, 35.9, 34.4, 31.9, 31.8, 28.3, 28.1, 24.3, 23.9, 22.9, 22.7, 21.0, 19.3, 18.8, 11.9.
HRMS (ESI) m/z calcd. for $C_{27}H_{46}Br$ $[M + H]^+$ 449.2777, found 449.2768.

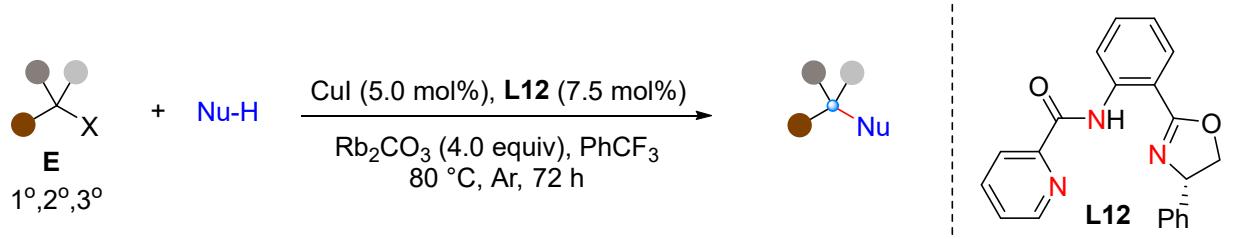
Scope of nucleophiles



Compounds **N1**–**N27**, **N33**–**N38** were purchased from commercial sources. **N28**–**N32** were prepared according to the literature method.[20]

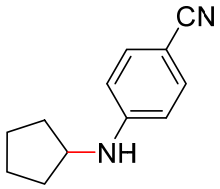
6. Cross-coupling of unactivated alkyl halides with C/N-nucleophiles

General procedure (GP):



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.01 mmol, 5 mol%), **L12** (5.2 mg, 0.015 mmol, 7.5 mol%), Rb_2CO_3 (184.8 mg, 0.80 mmol, 4.0 equiv), unactivated alkyl halide **E** (0.24 mmol, 1.2 equiv), C/N-nucleophile **Nu-H** (0.20 mmol, 1.0 equiv), and anhydrous $PhCF_3$ (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at 80 ℃ for 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

4-(Cyclopentylamino)benzonitrile (1)



1

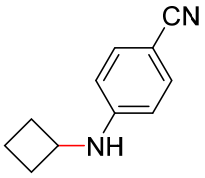
According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **1** as a colorless oil (33.5 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.9 Hz, 1H), 6.53 (d, *J* = 8.8 Hz, 1H), 4.27 (s, 1H), 3.85 – 3.73 (m, 1H), 2.09 – 1.95 (m, 2H), 1.80 – 1.57 (m, 4H), 1.54 – 1.41 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 133.7, 120.8, 112.6, 98.1, 54.2, 33.4, 24.1.

HRMS (ESI) m/z calcd. for $C_{12}H_{15}N_2$ $[M + H]^+$ 187.1230, found 187.1231.

4-(Cyclobutylamino)benzonitrile (2)



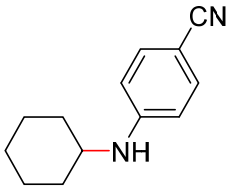
2

According to **General procedure (GP)** with cyclobutyl bromide **E2** (32.4 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **2** as a white solid (26.2 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 6.44 – 6.37 (m, 2H), 4.37 (s, 1H), 3.91 – 3.81

(m, 1H), 2.42 – 2.29 (m, 2H), 1.87 – 1.70 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 133.7, 120.6, 112.3, 98.4, 48.2, 30.9, 15.3.
HRMS (ESI) m/z calcd. for $C_{11}H_{13}N_2$ $[M + H]^+$ 173.1073, found 173.1073.

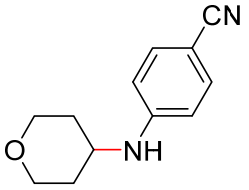
4-(Cyclohexylamino)benzonitrile (3)



3

According to **General procedure (GP)** with bromocyclobutane **E3** (39.1 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3** as a colorless oil (38.0 mg, 95% yield).
According to **General procedure (GP)** with chlorocyclohexane **E3′** (28.5 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) at 100 ℃ for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3** as a colorless oil (22.6 mg, 56% yield).
According to **General procedure (GP)** with iodocyclohexane **E3′′** (50.4 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3** as a colorless oil (36.9 mg, 92% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 6.56 – 6.49 (m, 2H), 4.18 (s, 1H), 3.35 – 3.23 (m, 1H), 2.08 – 1.96 (m, 2H), 1.83 – 1.73 (m, 2H), 1.71 – 1.61 (m, 1H), 1.44 – 1.31 (m, 2H), 1.29 – 1.12 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 133.7, 120.7, 112.3, 97.8, 51.2, 33.0, 25.6, 24.8.
HRMS (ESI) m/z calcd. for $C_{13}H_{17}N_2$ $[M + H]^+$ 201.1386, found 201.1387.

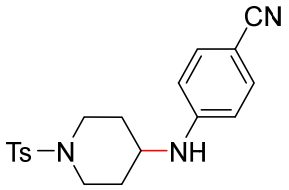
4-((Tetrahydro-2*H*-pyran-4-yl)amino)benzonitrile (4)



4

According to **General procedure (GP)** with 4-bromotetrahydro-2*H*-pyran **E4** (39.6 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **4** as a white solid (39.6 mg, 98% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 6.57 (d, J = 8.4 Hz, 2H), 4.22 (s, 1H), 4.07 – 3.96 (m, 2H), 3.52 (m, 3H), 3.62 – 3.46 (m, 2H), 1.60 – 1.46 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 133.8, 120.4, 112.5, 98.7, 66.6, 48.6, 33.1.
HRMS (ESI) m/z calcd. for $C_{12}H_{15}N_2O$ $[M + H]^+$ 203.1179, found 203.1178.

4-((1-Tosylpiperidin-4-yl)amino)benzonitrile (5)



5

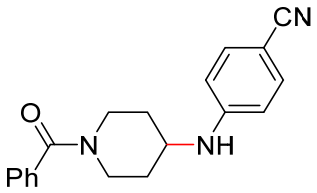
According to **General procedure (GP)** with 4-bromo-tosylpiperidine **E5** (73.0 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1 to 5/1) to yield the product **5** as a colorless oil (56.8 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.31 (m, 4H), 6.48 (d, *J* = 8.5 Hz, 2H), 4.07 (s, 1H), 3.82 – 3.68 (m, 2H), 3.34 – 3.19 (m, 1H), 2.56 – 2.39 (m, 5H), 2.16 – 2.02 (m, 2H), 1.68 – 1.49 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 143.9, 133.9, 132.8, 129.8, 127.8, 120.3, 112.5, 99.1, 48.9, 45.2, 31.4, 21.6.

HRMS (ESI) m/z calcd. for $C_{19}H_{22}N_3O_2S$ $[M + H]^+$ 356.1427, found 356.1427.

4-((1-Benzoylpiperidin-4-yl)amino)benzonitrile (6)



6

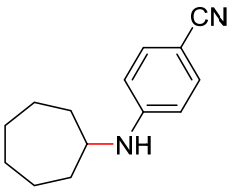
According to **General procedure (GP)** with (4-bromopiperidin-1-yl)(phenyl)methanone **E6** (64.4 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1 to 5/1) to yield the product **6** as a colorless oil (44.4 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 7H), 6.60 – 6.53 (m, 2H), 4.80 – 4.37 (m, 2H), 3.78 (s, 1H), 3.66 – 3.53 (m, 1H), 3.28 – 2.98 (m, 2H), 2.28 – 1.91 (m, 2H), 1.66 – 1.29 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 150.0, 135.7, 133.8, 129.8, 128.6, 126.8, 120.4, 112.5, 98.6, 49.4, 46.3, 40.9, 32.4, 31.8.

HRMS (ESI) m/z calcd. for $C_{19}H_{20}N_3O$ $[M + H]^+$ 306.1601, found 306.1599.

4-(Cycloheptylamino)benzonitrile (7)



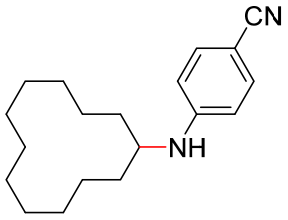
7

According to **General procedure (GP)** with bromocycloheptane **E7** (42.5 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **7** as a colorless oil (41.1 mg, 96% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 6.52 – 6.44 (m, 2H), 4.23 (s, 1H), 3.52 – 3.43

(m, 1H), 2.05 – 1.93 (m, 2H), 1.74 – 1.43 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 133.7, 120.7, 112.5, 97.8, 53.3, 34.6, 28.2, 24.2.
HRMS (ESI) m/z calcd. for $C_{14}H_{19}N_2$ $[M + H]^+$ 215.1543, found 215.1543.

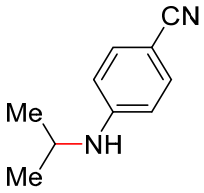
4-(Cyclododecylamino)benzonitrile (8)



8

According to **General procedure (GP)** with bromocyclododecane **E8** (59.3 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **8** as a colorless oil (33.0 mg, 58% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 6.56 – 6.47 (m, 2H), 4.07 (s, 1H), 3.60 – 3.50 (m, 1H), 1.70 – 1.61 (m, 2H), 1.51 – 1.30 (m, 20H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 133.8, 120.7, 112.3, 97.8, 49.2, 29.7, 24.2, 23.8, 23.31, 23.27, 21.3.
HRMS (ESI) m/z calcd. for $C_{19}H_{29}N_2$ $[M + H]^+$ 285.2325, found 285.2323.

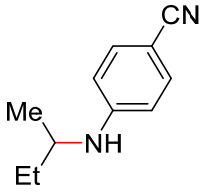
4-(Isopropylamino)benzonitrile (9)



9

According to **General procedure (GP)** with 2-bromopropane **E9** (29.5 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **9** as a colorless oil (29.1 mg, 91% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 6.55 – 6.47 (m, 2H), 4.10 (s, 1H), 3.72 – 3.58 (m, 1H), 1.23 (d, J = 6.3 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 133.8, 120.7, 112.4, 98.0, 43.9, 22.6.
HRMS (ESI) m/z calcd. for $C_{10}H_{13}N_2$ $[M + H]^+$ 161.1073, found 161.1072.

4-(*sec*-Butylamino)benzonitrile (10)

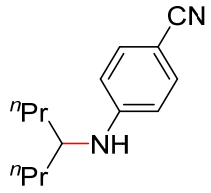


10

According to **General procedure (GP)** with 2-bromobutane **E10** (32.9 mg, 0.24 mmol, 1.2 equiv)

and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **10** as a colorless oil (33.1 mg, 95% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 2H), 6.56 – 6.48 (m, 2H), 4.10 (s, 1H), 3.49 – 3.37 (m, 1H), 1.66 – 1.45 (m, 2H), 1.19 (d, *J* = 6.3 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 133.8, 120.7, 112.3, 97.8, 49.5, 29.4, 20.0, 10.4.
HRMS (ESI) m/z calcd. for $C_{11}H_{15}N_2$ $[M + H]^+$ 175.1230, found 175.1231.

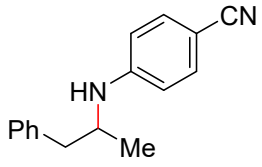
4-(Heptan-4-ylamino)benzonitrile (11)



11

According to **General procedure (GP)** with 4-bromoheptane **E11** (43.0 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **11** as a colorless oil (41.5 mg, 96% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 2H), 6.55 – 6.48 (m, 2H), 4.02 (s, 1H), 6.49 – 3.35 (m, 1H), 1.61 – 1.49 (m, 2H), 1.49 – 1.28 (m, 6H), 0.91 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 133.8, 120.7, 112.1, 97.6, 52.2, 37.2, 19.1, 14.1.
HRMS (ESI) m/z calcd. for $C_{14}H_{21}N_2$ $[M + H]^+$ 217.1699, found 217.1700.

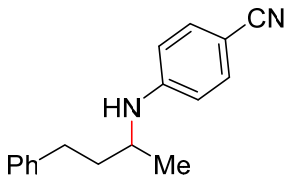
4-((1-phenylpropan-2-yl)amino)benzonitrile (12)



12

According to **General procedure (GP)** with (2-bromopropyl)benzene **E12** (47.8 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **12** as a colorless oil (45.8 mg, 97% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.34 – 7.26 (m, 2H), 7.26 – 7.20 (m, 1H), 7.19 – 7.12 (m, 2H), 6.57 – 6.51 (m, 2H), 4.15 – 4.05 (m, 1H), 3.80 (p, *J* = 6.4 Hz, 1H), 2.89 (dd, *J* = 13.5, 5.1 Hz, 1H), 2.76 (dd, *J* = 13.6, 7.0 Hz, 1H), 1.19 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 137.7, 133.9, 129.5, 128.6, 126.7, 120.6, 112.6, 98.5, 49.1, 42.2, 20.1.
HRMS (ESI) m/z calcd. for $C_{16}H_{21}N_2Na$ $[M + Na]^+$ 259.1205, found 259.1207.

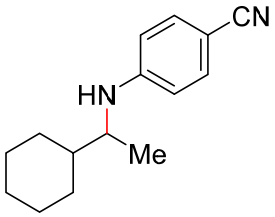
4-((4-Phenylbutan-2-yl)amino)benzonitrile (13)



13

According to **General procedure (GP)** with (3-bromobutyl)benzene **E13** (51.1 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **13** as a white solid (49.5 mg, 99% yield).
According to **General procedure (GP)** with (3-chlorobutyl)benzene **E13′** (40.5 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) at 100 °C for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **13** as a white solid (34.9 mg, 70% yield).
According to **General procedure (GP)** with (3-iodobutyl)benzene **E13′′** (62.4 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **13** as a colorless oil (47.6 mg, 95% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.32 – 7.24 (m, 2H), 7.23 – 7.18 (m, 1H), 7.15 (dd, *J* = 7.0, 1.7 Hz, 2H), 6.43 (d, *J* = 8.7 Hz, 2H), 4.09 (d, *J* = 7.8 Hz, 1H), 3.63 – 3.36 (m, 1H), 2.70 (t, *J* = 7.7 Hz, 2H), 1.94 – 1.73 (m, 2H), 1.23 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 141.4, 133.8, 128.5, 128.4, 126.1, 120.7, 112.4, 98.0, 47.5, 38.3, 32.3, 20.5.
HRMS (ESI) m/z calcd. for $C_{17}H_{19}N_2$ $[M + H]^+$ 251.1543, found 251.1541.

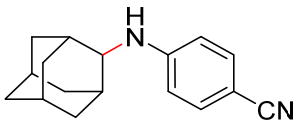
4-((1-Cyclohexylethyl)amino)benzonitrile (14)



14

According to **General procedure (GP)** with (1-bromoethyl)cyclohexane **E14** (45.9 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **14** as a colorless oil (38.8 mg, 85% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 2H), 6.56 – 6.46 (m, 2H), 4.12 (s, 1H), 3.41 – 3.35 (m, 1H), 1.83 – 1.65 (m, 5H), 1.48 – 1.37 (m, 1H), 1.30 – 1.17 (m, 3H), 1.14 (d, *J* = 6.6 Hz, 3H), 1.08 – 0.96 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 133.8, 120.8, 112.2, 97.6, 52.7, 43.0, 29.6, 28.6, 26.5, 26.3, 26.2, 17.3.
HRMS (ESI) m/z calcd. for $C_{15}H_{21}N_2$ $[M + H]^+$ 229.1699, found 229.1699.

4-(((1*r*,3*r*,5*r*,7*r*)-adamantan-2-yl)amino)benzonitrile (15)



15

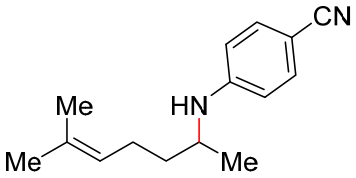
According to **General procedure (GP)** with 2-bromoadamantane **E15** (51.6 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **15** as a white solid (29.8 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 2H), 6.59 – 6.48 (m, 2H), 4.53 (d, *J* = 7.1 Hz, 1H), 3.57 (dt, *J* = 6.4, 2.9 Hz, 1H), 2.05 – 1.98 (m, 2H), 1.96 – 1.79 (m, 8H), 1.79 – 1.74 (m, 2H), 1.67 – 1.62 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 133.9, 120.8, 112.5, 97.9, 56.5, 37.6, 37.2, 31.6, 31.4, 27.3, 27.2.

HRMS (ESI) m/z calcd. for $C_{17}H_{20}N_2Na$ $[M + Na]^+$ 275.1518, found 275.1519.

4-((6-Methylhept-5-en-2-yl)amino)benzonitrile (16)



16

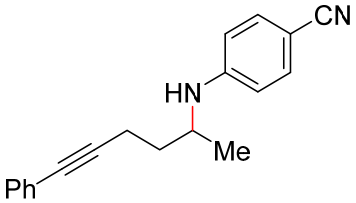
According to **General procedure (GP)** with 6-bromo-2-methylhept-2-ene **E16** (45.9 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **16** as a colorless oil (43.4 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 2H), 6.51 (d, *J* = 8.4 Hz, 2H), 5.10 (t, *J* = 7.2 Hz, 1H), 4.08 (s, 1H), 3.61 – 3.44 (m, 1H), 2.16 – 1.98 (m, 2H), 1.69 (s, 3H), 1.67 – 1.45 (m, 5H), 1.20 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 133.8, 132.6, 123.4, 120.7, 112.3, 97.8, 47.7, 36.8, 25.8, 24.6, 20.5, 17.7.

HRMS (ESI) m/z calcd. for $C_{15}H_{21}N_2$ $[M + H]^+$ 229.1699, found 229.1699.

4-((6-Phenylhex-5-yn-2-yl)amino)benzonitrile (17)



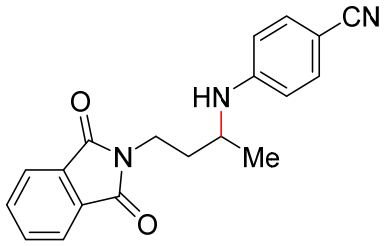
17

According to **General procedure (GP)** with (5-bromohex-1-yn-1-yl)benzene **E17** (56.9 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **17** as a colorless oil (43.9 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 4H), 7.33 – 7.26 (m, 3H), 6.58 (d, *J* = 7.6 Hz, 2H),

4.19 (d, J = 7.4 Hz, 1H), 3.78 (h, J = 6.4 Hz, 1H), 2.61 – 2.42 (m, 2H), 1.92 – 1.72 (m, 2H), 1.26 (d, J = 6.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 133.8, 131.5, 128.4, 127.9, 123.5, 120.6, 112.5, 98.2, 89.0, 81.5, 47.4, 35.3, 20.4, 16.4.
HRMS (ESI) m/z calcd. for $C_{19}H_{19}N_2$ $[M + H]^+$ 275.1543, found 275.1542.

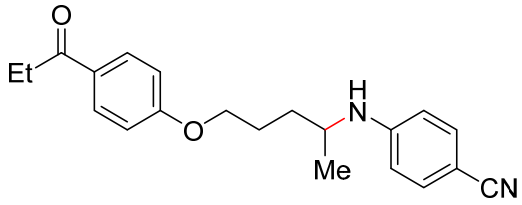
4-((4-(1,3-Dioxoisoindolin-2-yl)butan-2-yl)amino)benzonitrile (18)



18

According to **General procedure (GP)** with 2-(3-bromobutyl)isoindoline-1,3-dione **E18** (67.7 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 1/1) to yield the product **18** as a colorless oil (51.1 mg, 80% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.77 – 7.69 (m, 2H), 7.39 – 7.31 (m, 2H), 6.55 – 6.47 (m, 2H), 4.27 (s, 1H), 3.79 (t, J = 7.2 Hz, 2H), 3.64 (h, J = 6.4 Hz, 1H), 2.02 – 1.85 (m, 2H), 1.28 (d, J = 6.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 150.4, 134.1, 133.7, 131.9, 123.3, 120.5, 112.5, 98.4, 46.4, 34.99, 34.98, 20.7.
HRMS (ESI) m/z calcd. for $C_{19}H_{18}N_3O_2$ $[M + H]^+$ 320.1394, found 320.1393.

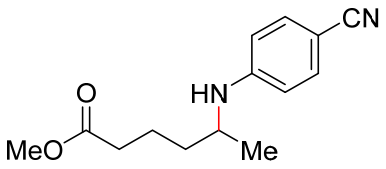
4-((5-(4-Propionylphenoxy)pentan-2-yl)amino)benzonitrile (19)



19

According to **General procedure (GP)** with 1-(4-((4-bromopentyl)oxy)phenyl)propan-1-one **E19** (71.8 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **19** as a colorless oil (39.0 mg, 58% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 7.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.54 (d, J = 6.8 Hz, 2H), 4.23 (s, 1H), 4.03 (t, J = 6.1 Hz, 2H), 3.60 (h, J = 6.3 Hz, 1H), 2.95 (q, J = 7.2 Hz, 2H), 1.96 – 1.84 (m, 2H), 1.81 – 1.67 (m, 2H), 1.25 (d, J = 6.3 Hz, 3H), 1.21 (t, J = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 162.6, 150.7, 133.8, 130.2, 130.0, 120.6, 114.1, 112.4, 98.0, 67.7, 47.9, 33.2, 31.4, 25.7, 20.6, 8.4.
HRMS (ESI) m/z calcd. for $C_{21}H_{25}N_2O_2$ $[M + H]^+$ 337.1911, found 337.1910.

Methyl 5-((4-cyanophenyl)amino)hexanoate (20)



20

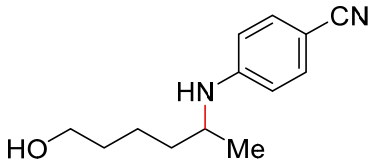
According to **General procedure (GP)** with methyl 5-bromohexanoate **E20** (50.2 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **20** as a colorless oil (42.8 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 6.56 – 6.48 (m, 2H), 4.17 (s, 1H), 3.67 (s, 3H), 3.52 (h, *J* = 5.9, 5.4 Hz, 1H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.81 – 1.66 (m, 2H), 1.64 – 1.48 (m, 2H), 1.21 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 150.7, 133.8, 120.6, 112.3, 98.0, 51.6, 48.0, 36.1, 33.7, 21.3, 20.5.

HRMS (ESI) m/z calcd. for $C_{14}H_{19}N_2O_2$ $[M + H]^+$ 247.1441, found 247.1441.

4-((6-Hydroxyhexan-2-yl)amino)benzonitrile (21)



21

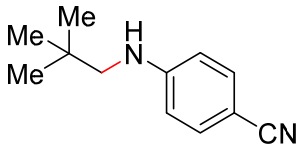
According to **General procedure (GP)** with 5-bromohexan-1-ol **E21** (43.4 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **21** as a colorless oil (35.3 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 6.56 – 6.49 (m, 2H), 4.16 (s, 1H), 3.64 (t, *J* = 6.3 Hz, 2H), 3.51 (h, *J* = 6.3 Hz, 1H), 1.81 (s, 1H), 1.65 – 1.41 (m, 6H), 1.20 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 133.8, 120.7, 112.3, 97.7, 62.5, 48.1, 36.6, 32.5, 22.3, 20.5.

HRMS (ESI) m/z calcd. for $C_{13}H_{19}N_2O$ $[M + H]^+$ 219.1492, found 219.1493.

4-(Neopentylamino)benzonitrile (22)



22

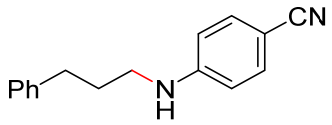
According to **General procedure (GP)** with 1-bromo-2,2-dimethylpropane **E22** (36.3 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **22** as a colorless oil (34.6 mg, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 4.30 (s, 1H), 2.94 (s, 2H), 0.99 (s, 9H).

^{13}C NMR (100 MHz, CDCl3) δ 152.1, 133.7, 120.7, 112.1, 98.0, 54.8, 27.5.

HRMS (ESI) m/z calcd. for $C_{12}H_{17}N_2$ $[M + H]^+$ 189.1386, found 189.1387.

4-((3-Phenylpropyl)amino)benzonitrile (23)



23

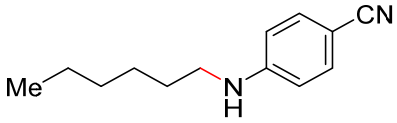
According to **General procedure (GP)** with (3-bromopropyl)benzene **E23** (47.8 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **23** as a colorless oil (44.9 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.34 – 7.14 (m, 5H), 6.52 – 6.44 (m, 2H), 4.20 (s, 1H), 3.17 (t, *J* = 7.1 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 1.96 (p, *J* = 7.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 141.1, 133.7, 128.6, 128.4, 126.2, 120.6, 112.1, 98.4, 42.61, 33.3, 30.6.

HRMS (ESI) m/z calcd. for $C_{16}H_{17}N_2$ $[M + H]^+$ 237.1386, found 237.1384.

4-(Hexylamino)benzonitrile (24)



24

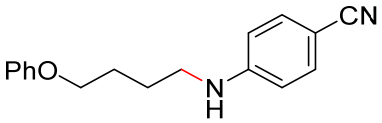
According to **General procedure (GP)** with 1-bromohexane **E24** (39.6 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **24** as a colorless oil (38.8 mg, 96% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 6.58 – 6.49 (m, 2H), 4.25 (s, 1H), 3.13 (t, *J* = 7.2 Hz, 2H), 1.67 – 1.57 (m, 2H), 1.44 – 1.27 (m, 6H), 0.94 – 0.84 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 133.7, 120.7, 112.0, 98.1, 43.2, 31.6, 29.1, 26.7, 22.6, 14.0.

HRMS (ESI) m/z calcd. for $C_{13}H_{19}N_2$ $[M + H]^+$ 203.1543, found 203.1544.

4-((4-Phenoxybutyl)amino)benzonitrile (25)



25

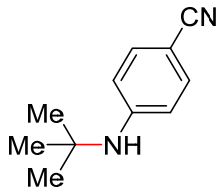
According to **General procedure (GP)** with (4-bromobutoxy)benzene **E25** (55.0 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **25** as a colorless oil (39.9 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 7.34 – 7.26 (m, 2H), 6.97 (m, 1H), 6.90 (m, 2H), 6.59 – 6.52 (m, 2H), 4.58 (s, 1H), 4.09 (t, *J* = 5.7 Hz, 2H), 3.39 (t, *J* = 6.6 Hz, 2H), 2.16 – 2.05 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 151.4, 133.8, 129.6, 121.1, 120.6, 114.4, 112.1, 98.5, 65.7, 40.8, 28.6.

HRMS (ESI) m/z calcd. for $C_{17}H_{19}N_2O$ $[M + H]^+$ 267.1492, found 267.1498.

4-(*tert*-Butylamino)benzonitrile (26)



26

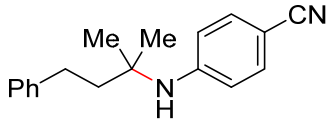
According to **General procedure (GP)** with 2-bromo-2-methylpropane **E26** (32.9 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%), **L11** (8.9 mg, 0.03 mmol, 15 mol%) for 4 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **26** as a white solid (26.1 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 4.24 (s, 1H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 133.5, 120.6, 114.2, 98.1, 51.4, 29.6.

HRMS (ESI) m/z calcd. for $C_{11}H_{15}N_2$ $[M + H]^+$ 175.1230, found 175.1229.

4-((2-Methyl-4-phenylbutan-2-yl)amino)benzonitrile (27)



27

According to **General procedure (GP)** with (3-bromo-3-methylbutyl)benzene **E27** (54.5 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%), **L11** (8.9 mg, 0.03 mmol, 15 mol%) for 4 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **27** as a white solid (34.3 mg, 65% yield).

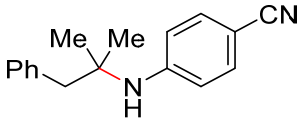
According to **General procedure (GP)** with (3-chloro-3-methylbutyl)benzene **E27′** (43.8 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%), **L11** (8.9 mg, 0.03 mmol, 15 mol%) for 4 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **27** as a white solid (41.4 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 2H), 7.31 – 7.22 (m, 2H), 7.22 – 7.14 (m, 1H), 7.14 – 7.05 (m, 2H), 6.69 – 6.56 (m, 2H), 4.16 (s, 1H), 2.69 – 2.51 (m, 2H), 2.09 – 1.94 (m, 2H), 1.42 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 142.0, 133.6, 128.6, 128.3, 126.0, 120.6, 114.1, 98.4, 54.0, 42.6, 30.7, 28.2.

HRMS (ESI) m/z calcd. for $C_{18}H_{21}N_2$ $[M + H]^+$ 265.1699, found 265.1690.

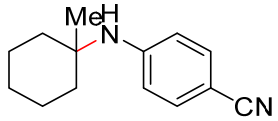
4-((2-Methyl-1-phenylpropan-2-yl)amino)benzonitrile (28)



28

According to **General procedure (GP)** with (2-bromo-2-methylpropyl)benzene **E28** (51.1mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%), **L11** (8.9 mg, 0.03 mmol, 15 mol%) for 4 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **28** as a white solid (38.5 mg, 77% yield).
According to **General procedure (GP)** with (2-chloro-2-methylpropyl)benzene **E28′** (40.3mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%), **L11** (8.9 mg, 0.03 mmol, 15 mol%) for 4 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **28** as a white solid (41.3 mg, 82% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.37 (m, 2H), 7.29 – 7.20 (m, 3H), 7.08 – 7.00 (m, 2H), 6.72 – 6.62 (m, 2H), 4.09 (s, 1H), 3.00 (s, 2H), 1.38 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 137.3, 133.7, 130.5, 128.2, 126.7, 120.6, 114.4, 98.4, 54.3, 45.4, 28.3.
HRMS (ESI) m/z calcd. for $C_{17}H_{19}N_2$ $[M + H]^+$ 251.1543, found 251.1542.

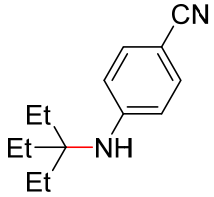
4-((1-methylcyclohexyl)amino)benzonitrile (29)



29

According to **General procedure (GP)** with 1-bromo-1-methylcyclohexane **E29** (42.5 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%), **L11** (8.9 mg, 0.03 mmol, 15 mol%) for 4 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **29** as a colorless oil (27.0 mg, 63% yield).
According to **General procedure (GP)** with 1-chloro-1-methylcyclohexane **E29′** (53.1 mg, 0.40 mmol, 2.0 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%), **L11** (8.9 mg, 0.03 mmol, 15 mol%) for 5 days, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **29** as a colorless oil (30.7 mg, 72% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 6.66 – 6.60 (m, 2H), 4.11 (s, 1H), 1.94 – 1.84 (m, 2H), 1.58 – 1.47 (m, 7H), 1.40 – 1.32 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 133.5, 120.8, 114.3, 97.9, 53.4, 37.8, 26.3, 25.6, 22.0.
HRMS (ESI) m/z calcd. for $C_{14}H_{18}N_2Na$ $[M + Na]^+$ 237.1362, found 237.1363.

4-((3-ethylpentan-3-yl)amino)benzonitrile (30)

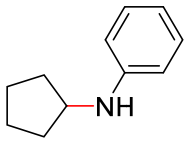


30

According to **General procedure (GP)** with 3-chloro-3-ethylpentane **E30** (32.3 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%), **L11** (8.9 mg, 0.03 mmol, 15 mol%) for 4 days, the reaction mixture was purified by column

chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **30** as a colorless oil (26.0 mg, 60% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 6.65 – 6.57 (m, 2H), 3.84 (s, 1H), 1.64 (q, *J* = 7.4 Hz, 6H), 0.80 (t, *J* = 7.4 Hz, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 133.6, 120.8, 114.0, 98.0, 59.7, 27.5, 7.7.
HRMS (ESI) m/z calcd. for $C_{14}H_{20}N_2Na$ $[M + Na]^+$ 239.1518, found 239.1519.

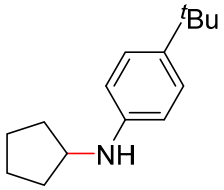
_N_-Cyclopentylaniline (31)



31

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and aniline **N2** (18.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **31** as a colorless oil (25.8 mg, 80% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.11 (m, 2H), 6.67 (td, *J* = 7.3, 1.4 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 3.78 (p, *J* = 6.2 Hz, 1H), 2.09 – 1.96 (m, 2H), 1.78 – 1.67 (m, 2H), 1.66 – 1.56 (m, 2H), 1.53 – 1.40 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 129.2, 117.0, 113.3, 54.8, 33.6, 24.1.
HRMS (ESI) m/z calcd. for $C_{11}H_{16}N$ $[M + H]^+$ 162.1277, found 162.1277.

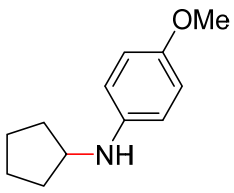
4-(*tert*-Butyl)-*N*-cyclopentylaniline (32)



32

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 4-(*tert*-butyl)aniline **N3** (29.8 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 60/1) to yield the product **32** as a colorless oil (30.4 mg, 70% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 3.83 – 3.72 (m, 1H), 3.50 (s, 1H), 2.09 – 1.96 (m, 2H), 1.81 – 1.56 (m, 4H), 1.55 – 1.42 (m, 2H), 1.30 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 139.7, 126.1, 112.9, 54.9, 33.9, 33.8, 31.7, 24.2.
HRMS (ESI) m/z calcd. for $C_{15}H_{24}N$ $[M + H]^+$ 218.1903, found 218.1903.

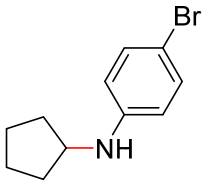
_N_-Cyclopentyl-4-methoxyaniline (33)



33

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 4-methoxyaniline **N4** (24.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **33** as a colorless oil (19.1 mg, 50% yield).
According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 4-methoxyaniline **N4** (24.6 mg, 0.20 mmol, 1.0 equiv), and K_3PO_4 (169.8 mg, 0.80 mmol, 4.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **33** as a colorless oil (28.8 mg, 75% yield).
^{1}H NMR (400 MHz, CDCl3) δ 6.78 (d, J = 8.9 Hz, 2H), 6.58 (d, J = 8.9 Hz, 2H), 3.78 – 3.68 (m, 4H), 2.61 (s, 1H), 2.07 – 1.93 (m, 2H), 1.80 – 1.56 (m, 4H), 1.51 – 1.39 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 142.5, 115.0, 114.7, 56.0, 55.7, 33.7, 24.2.
HRMS (ESI) m/z calcd. for $C_{12}H_{18}NO$ $[M + H]^+$ 192.1383, found 192.1378.

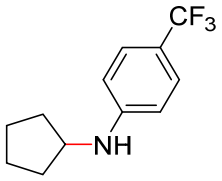
4-Bromo-*N*-cyclopentylaniline (34)



34

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 4-bromoaniline **N5** (34.4 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **34** as a colorless oil (38.4 mg, 80% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 2H), 6.52 – 6.43 (m, 2H), 3.82 – 3.59 (m, 2H), 2.10 – 1.94 (m, 2H), 1.80 – 1.56 (m, 4H), 1.54 – 1.39 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 131.9, 114.8, 108.4, 54.7, 33.5, 24.1.
HRMS (ESI) m/z calcd. for $C_{11}H_{15}BrN$ $[M + H]^+$ 240.0382, found 240.0382.

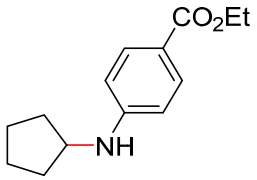
***N*-Cyclopentyl-4-(trifluoromethyl)aniline (35)**



35

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 4-(trifluoromethyl)aniline **N6** (32.2 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **35** as a colorless oil (39.9 mg, 87% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.3 Hz, 2H), 6.58 (d, *J* = 8.5 Hz, 2H), 4.00 (s, 1H), 3.86 – 3.76 (m, 1H), 2.11 – 1.98 (m, 2H), 1.80 – 1.58 (m, 4H), 1.53 – 1.41 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 126.59 (q, *J* = 3.8 Hz), 125.15 (q, *J* = 270.2 Hz), 118.23 (q, *J* = 32.6 Hz), 112.2, 54.4, 33.5, 24.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -60.9.
HRMS (ESI) m/z calcd. for $C_{12}H_{15}F_3N$ $[M + H]^+$ 230.1151, found 230.1152.

Ethyl 4-(cyclopentylamino)benzoate (36)



36

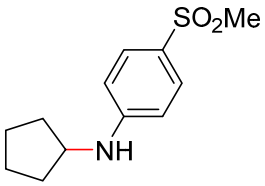
According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and ethyl 4-aminobenzoate **N7** (33.0 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **36** as a colorless oil (43.9 mg, 94% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 8.9 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.17 (s, 1H), 3.88 – 3.77 (m, 1H), 2.10 – 1.97 (m, 2H), 1.79 – 1.56 (m, 4H), 1.54 – 1.40 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 151.7, 131.5, 118.2, 111.8, 60.2, 54.3, 33.5, 24.1, 14.6.

HRMS (ESI) m/z calcd. for $C_{14}H_{20}NO_2$ $[M + H]^+$ 234.1489, found 234.1486.

***N*-Cyclopentyl-4-(methylsulfonyl)aniline (37)**



37

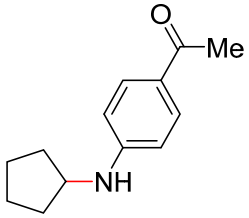
According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 4-(methylsulfonyl)aniline **N8** (34.2 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **37** as a white solid (34.9 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.9 Hz, 1H), 6.59 (d, *J* = 8.9 Hz, 1H), 4.35 (s, 1H), 3.87 – 3.76 (m, 1H), 2.99 (s, 3H), 2.11 – 1.96 (m, 2H), 1.80 – 1.57 (m, 4H), 1.55 – 1.39 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 129.4, 126.6, 112.1, 54.3, 45.2, 33.4, 24.0.

HRMS (ESI) m/z calcd. for $C_{12}H_{18}NO_2S$ $[M + H]^+$ 240.1053, found 240.1051.

1-(4-(Cyclopentylamino)phenyl)ethan-1-one (38)

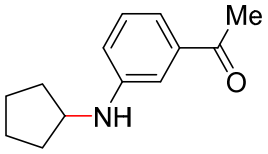


38

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 1-(4-aminophenyl)ethan-1-one **N9** (27.0 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **38** as a colorless oil (38.6 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.8 Hz, 1H), 6.54 (d, *J* = 8.8 Hz, 1H), 4.28 (s, 1H), 3.90 – 3.79 (m, 1H), 2.48 (s, 3H), 2.11 – 1.97 (m, 2H), 1.81 – 1.55 (m, 4H), 1.55 – 1.43 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 152.0, 130.9, 126.3, 111.8, 54.3, 33.6, 26.1, 24.1.
HRMS (ESI) m/z calcd. for $C_{13}H_{18}NO$ $[M + H]^+$ 204.1383, found 204.1384.

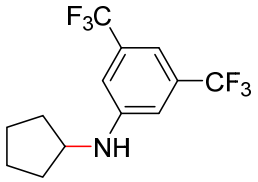
1-(3-(Cyclopentylamino)phenyl)ethan-1-one (39)



39

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 1-(3-aminophenyl)ethan-1-one **N10** (27.0 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **39** as a colorless oil (34.2 mg, 84% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 2H), 6.83 – 6.73 (m, 1H), 3.88 – 3.78 (m, 2H), 2.56 (s, 3H), 2.11 – 1.96 (m, 2H), 1.81 – 1.56 (m, 4H), 1.53 – 1.40 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.89, 148.3, 138.2, 129.3, 117.9, 117.4, 112.0, 54.7, 33.6, 26.8, 24.1.
HRMS (ESI) m/z calcd. for $C_{13}H_{18}NO$ $[M + H]^+$ 204.1383, found 204.1383.

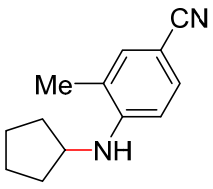
***N*-Cyclopentyl-3,5-bis(trifluoromethyl)aniline (40)**



40

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 3,5-bis(trifluoromethyl)aniline **N11** (45.8 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **40** as a colorless oil (51.0 mg, 86% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 1H), 6.91 (s, 2H), 4.17 – 4.05 (m, 1H), 3.88 – 3.76 (m, 1H), 2.14 – 1.99 (m, 2H), 1.82 – 1.61 (m, 4H), 1.53 – 1.43 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 132.4 (q, *J* = 32.6 Hz), 123.7 (q, *J* = 272.6 Hz), 112.1 (d, *J* = 4.2 Hz), 110.6 – 108.4 (m), 54.5, 33.4, 24.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2.
HRMS (ESI) m/z calcd. for $C_{13}H_{14}F_6N$ $[M + H]^+$ 298.1025, found 298.1026.

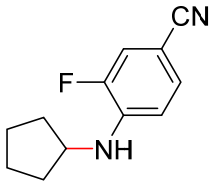
4-(Cyclopentylamino)-3-methylbenzonitrile (41)



41

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 4-amino-3-methylbenzonitrile **N12** (26.4 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **41** as a colorless oil (32.0 mg, 80% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.26 (s, 1H), 6.58 (d, *J* = 8.4 Hz, 1H), 4.00 (s, 1H), 3.90 – 3.80 (m, 1H), 2.15 – 2.02 (m, 5H), 1.83 – 1.61 (m, 4H), 1.56 – 1.45 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 133.3, 132.1, 121.7, 120.9, 109.7, 97.7, 54.2, 33.6, 24.1, 17.2.
HRMS (ESI) m/z calcd. for $C_{13}H_{17}N_2$ $[M + H]^+$ 201.1386, found 201.1385.

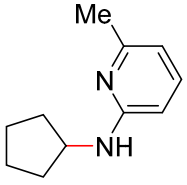
4-(Cyclopentylamino)-3-fluorobenzonitrile (42)



42

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 4-amino-3-fluorobenzonitrile **N13** (27.2 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **42** as a colorless oil (39.2 mg, 96% yield).
^{1}H NMR (400 MHz, $CDCl_3$ δ 7.29 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.18 (dd, *J* = 11.5, 1.9 Hz, 1H), 6.67 (t, *J* = 8.5 Hz, 1H), 4.44 (s, 1H), 3.88 – 3.77 (m, 1H), 2.14 – 1.99 (m, 2H), 1.83 – 1.61 (m, 4H), 1.59 – 1.47 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8 (d, *J* = 240.9 Hz), 140.6 (d, *J* = 11.2 Hz), 130.1 (d, *J* = 2.9 Hz), 119.5 (d, *J* = 2.6 Hz), 117.4 (d, *J* = 21.6 Hz), 111.6 (d, *J* = 4.4 Hz), 97.0 (d, *J* = 9.0 Hz), 54.0, 33.3, 24.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -135.4.
HRMS (ESI) m/z calcd. for $C_{12}H_{14}FN_2$ $[M + H]^+$ 205.1136, found 205.1135.

***N*-Cyclopentyl-6-methylpyridin-2-amine (43)**

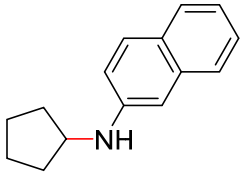


43

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 6-methylpyridin-2-amine **N14** (21.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1 to 5/1) to yield the product **43** as a colorless oil (28.2 mg, 80% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.3, 7.3 Hz, 1H), 6.42 (d, *J* = 7.3 Hz, 1H), 6.22 (d, *J* = 8.3 Hz, 1H), 4.80 (s, 1H), 3.93 – 3.79 (m, 1H), 2.36 (s, 3H), 2.06 – 1.94 (m, 2H), 1.80 – 1.68 (m, 2H), 1.68 – 1.56 (m, 2H), 1.55 – 1.45 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 156.6, 138.3, 111.9, 102.6, 53.6, 33.4, 24.1, 23.9.
HRMS (ESI) m/z calcd. for $C_{11}H_{17}N_2$ $[M + H]^+$ 177.1386, found 177.1386.

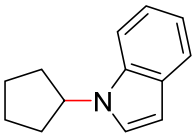
_N_-Cyclopentylnaphthalen-2-amine (44)



44

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and naphthalen-2-amine **N15** (28.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 40/1) to yield the product **44** as a colorless oil (35.0 mg, 83% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 8.4, 2H), 7.36 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.19 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 6.86 (dd, J = 8.7, 2.4 Hz, 1H), 6.82 (d, J = 2.3 Hz, 1H), 3.99 – 3.84 (m, 2H), 2.18 – 2.03 (m, 2H), 1.87 – 1.61 (m, 4H), 1.60 – 1.47 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 135.4, 129.0, 127.7, 127.4, 126.4, 126.0, 121.9, 118.4, 105.0, 54.8, 33.7, 24.3.
HRMS (ESI) m/z calcd. for $C_{15}H_{18}N$ $[M + H]^+$ 212.1434, found 212.1434.

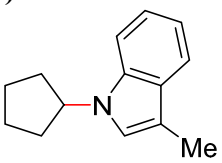
1-Cyclopentyl-1*H*-indole (45)



45

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 1*H*-indole **N16** (23.4 mg, 0.20 mmol, 1.0 equiv) and **L11** (4.4 mg, 0.015 mmol, 7.5 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **45** as a colorless oil (30.4 mg, 82% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.23 – 7.14 (m, 2H), 7.14 – 7.03 (m, 1H), 6.49 (d, J = 3.2 Hz, 1H), 4.84 – 4.72 (m, 1H), 2.27 – 2.10 (m, 2H), 2.01 – 1.82 (m, 4H), 1.81 – 1.67 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 128.8, 124.6, 121.3, 121.0, 119.4, 109.9, 101.1, 57.0, 32.7, 24.2.
HRMS (ESI) m/z calcd. for $C_{13}H_{16}N$ $[M + H]^+$ 186.1277, found 186.1277.

1-Cyclopentyl-3-methyl-1*H*-indole (46)

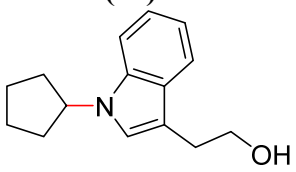


46

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 3-methyl-1*H*-indole **N17** (26.2 mg, 0.20 mmol, 1.0 equiv) and **L11** (4.4 mg, 0.015 mmol, 7.5 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel

(petroleum ether/EtOAc = 30/1) to yield the product **46** as a colorless oil (37.8 mg, 95% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 6.9 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.96 (s, 1H), 4.79 – 4.68 (m, 1H), 2.33 (s, 3H), 2.23 – 2.08 (m, 2H), 1.96 – 1.77 (m, 4H), 1.77 – 1.65 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 128.8, 122.3, 121.22, 119.1, 118.6, 110.2, 109.7, 56.7, 32.7, 24.2, 9.8.
HRMS (ESI) m/z calcd. for $C_{14}H_{18}N$ $[M + H]^+$ 200.1434, found 200.1434.

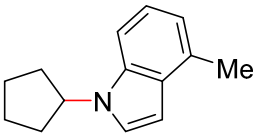
2-(1-Cyclopentyl-1*H*-indol-3-yl)ethan-1-ol (47)



47

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 2-(1*H*-indol-3-yl)ethan-1-ol **N18** (32.2 mg, 0.20 mmol, 1.0 equiv) and **L11** (4.4 mg, 0.015 mmol, 7.5 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **47** as a colorless oil (35.3 mg, 77% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.16 (m, 1H), 7.14 – 6.98 (m, 2H), 4.82 – 4.66 (m, 1H), 3.87 (t, *J* = 6.4 Hz, 2H), 3.01 (t, *J* = 6.3 Hz, 2H), 2.30 – 2.12 (m, 2H), 1.98 – 1.82 (m, 4H), 1.82 – 1.70 (m, 2H), 1.64 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 128.1, 123.1, 121.5, 119.1, 119.0, 110.7, 110.0, 62.8, 56.9, 32.7, 29.0, 24.2.
HRMS (ESI) m/z calcd. for $C_{15}H_{20}NO$ $[M + H]^+$ 230.1539, found 230.1540.

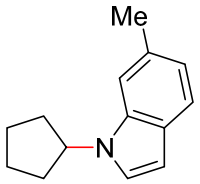
1-Cyclopentyl-4-methyl-1*H*-indole (48)



48

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 4-methyl-1*H*-indole **N19** (26.2 mg, 0.20 mmol, 1.0 equiv) and **L11** (4.4 mg, 0.015 mmol, 7.5 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **48** as a colorless oil (30.3 mg, 76% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.3 Hz, 1H), 7.24 (d, *J* = 3.2 Hz, 1H), 7.16 (t, 1H), 6.95 (d, *J* = 7.0 Hz, 1H), 6.56 (d, *J* = 3.2 Hz, 1H), 4.86 – 4.78 (m, 1H), 2.60 (s, 3H), 2.29 – 2.19 (m, 2H), 2.05 – 1.88 (m, 4H), 1.87 – 1.72 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 130.4, 128.6, 124.0, 121.5, 119.6, 107.6, 99.5, 57.2, 32.7, 24.2, 18.9.
HRMS (ESI) m/z calcd. for $C_{14}H_{18}N$ $[M + H]^+$ 200.1434, found 200.1433.

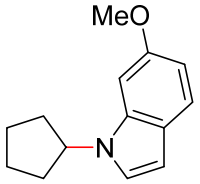
1-Cyclopentyl-6-methyl-1*H*-indole (49)



49

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 6-methyl-1*H*-indole **N20** (26.2 mg, 0.20 mmol, 1.0 equiv) and **L11** (4.4 mg, 0.015 mmol, 7.5 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **49** as a colorless oil (33.9 mg, 85% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 3.2 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.43 (d, *J* = 3.2 Hz, 1H), 4.80 – 4.69 (m, 1H), 2.49 (s, 3H), 2.24 – 2.12 (m, 2H), 1.97 – 1.81 (m, 4H), 1.81 – 1.66 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 131.0, 126.6, 124.0, 121.1, 120.6, 109.9, 100.8, 56.9, 32.7, 24.2, 22.1.
HRMS (ESI) m/z calcd. for $C_{14}H_{18}N$ $[M + H]^+$ 200.1434, found 200.1433.

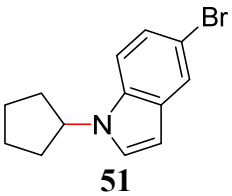
1-Cyclopentyl-6-methoxy-1*H*-indole (50)



50

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 6-methoxy-1*H*-indole **N21** (29.4 mg, 0.20 mmol, 1.0 equiv) and **L11** (4.4 mg, 0.015 mmol, 7.5 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **50** as a colorless oil (37.0 mg, 86% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 3.3 Hz, 1H), 6.90 (d, *J* = 2.3 Hz, 1H), 6.81 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 4.78 – 4.69 (m, 1H), 3.91 (s, 3H), 2.28 – 2.17 (m, 2H), 2.01 – 1.86 (m, 4H), 1.85 – 1.73 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 136.9, 123.5, 123.1, 121.5, 109.2, 101.0, 93.7, 57.0, 55.9, 32.6, 24.2.
HRMS (ESI) m/z calcd. for $C_{14}H_{18}NO$ $[M + H]^+$ 216.1383, found 216.1382.

5-Bromo-1-cyclopentyl-1*H*-indole (51)

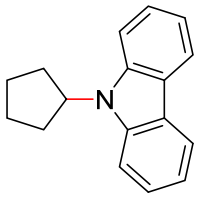


51

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 5-bromo-1*H*-indole **N22** (39.2 mg, 0.20 mmol, 1.0 equiv) and **L11** (4.4 mg, 0.015 mmol, 7.5 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **51** as a colorless oil (25.9 mg, 49% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.27 (d, *J* = 5.3 Hz, 2H), 7.20 (d, *J* = 3.3 Hz, 1H), 6.44 (d, *J* = 3.2 Hz, 1H), 4.81 – 4.69 (m, 1H), 2.27 – 2.14 (m, 2H), 1.99 – 1.84 (m, 4H), 1.84 – 1.72 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9, 130.4, 125.8, 124.1, 123.4, 112.6, 111.4, 100.70, 57.3, 32.7, 24.2.
HRMS (ESI) m/z calcd. for $C_{13}H_{15}BrN$ $[M + H]^+$ 264.0382, found 264.0383.

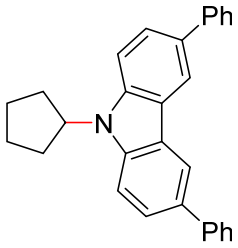
9-Cyclopentyl-9*H*-carbazole (52)



52

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 9*H*-carbazole **N23** (33.4 mg, 0.20 mmol, 1.0 equiv) and **L11** (4.4 mg, 0.015 mmol, 7.5 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **52** as a white solid (37.7 mg, 80% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.51 – 7.40 (m, 4H), 7.25 – 7.18 (m, 2H), 5.21 – 5.09 (m, 1H), 2.45 – 2.30 (m, 2H), 2.17 – 2.04 (m, 4H), 1.91 – 1.78 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 125.4, 123.3, 120.4, 118.6, 109.9, 55.8, 29.1, 25.4.
HRMS (ESI) m/z calcd. for $C_{17}H_{18}N$ $[M + H]^+$ 236.1434, found 236.1434.

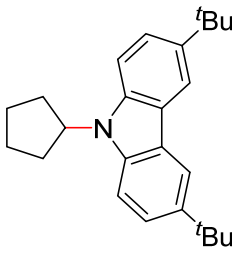
9-Cyclopentyl-3,6-diphenyl-9*H*-carbazole (53)



53

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv.), 3,6-diphenyl-9*H*-carbazole **N24** (63.9 mg, 0.20 mmol, 1.0 equiv.) and **L11** (4.4 mg, 0.015 mmol, 7.5 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 40/1) to yield the product **53** as a white solid (54.3 mg, 70% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.32 (m, 2H), 7.79 – 7.65 (m, 6H), 7.57 – 7.42 (m, 6H), 7.36 – 7.29 (m, 2H), 5.12 (p, *J* = 8.9 Hz, 1H), 2.45 – 2.28 (m, 2H), 2.21 – 2.04 (m, 4H), 1.91 – 1.76 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 139.6, 132.3, 128.8, 127.3, 126.5, 125.1, 124.0, 118.9, 110.2, 56.0, 29.3, 25.4.
HRMS (ESI) m/z calcd. for $C_{29}H_{26}N$ $[M + H]^+$ 388.2060, found 388.2057.

3,6-Di-*tert*-butyl-9-cyclopentyl-9*H*-carbazole (54)



54

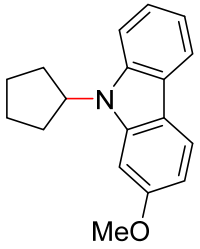
According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 3,6-di-*tert*-butyl-9*H*-carbazole **N25** (55.9 mg, 0.20 mmol, 1.0 equiv) and **L11** (4.4 mg, 0.015 mmol, 7.5 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 40/1) to yield the product **54** as a white solid (55.6 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.9 Hz, 1H), 7.52 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 5.18 – 5.02 (m, 1H), 2.70 – 2.21 (m, 2H), 2.19 – 2.01 (m, 4H), 1.92 – 1.80 (m, 2H), 1.49 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 138.2, 123.2, 123.1, 116.4, 109.3, 55.8, 34.7, 31.8, 29.3, 25.5.

HRMS (ESI) m/z calcd. for $C_{25}H_{34}N$ $[M + H]^+$ 348.2686, found 348.2686.

9-Cyclopentyl-2-methoxy-9*H*-carbazole (55)



55

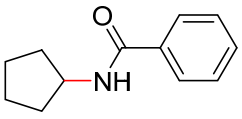
According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv.), 2-methoxy-9*H*-carbazole **N26** (39.4 mg, 0.20 mmol, 1.0 equiv.) and **L11** (4.4 mg, 0.015 mmol, 7.5 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **55** as a white solid (40.8 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.93 (m, 2H), 7.45 – 7.39 (m, 1H), 7.38 – 7.31 (m, 1H), 7.23 – 7.14 (m, 1H), 6.95 – 6.91 (m, 1H), 6.83 (dd, *J* = 8.5, 2.2 Hz, 1H), 5.06 (p, *J* = 8.9 Hz, 1H), 3.92 (s, 2H), 2.42 – 2.26 (m, 2H), 2.17 – 2.01 (m, 4H), 1.91 – 1.78 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 141.0, 139.8, 124.1, 123.5, 121.0, 119.6, 118.8, 117.3, 109.7, 106.7, 94.7, 55.7, 55.7, 28.9, 25.5.

HRMS (ESI) m/z calcd. for $C_{18}H_{20}NO$ $[M + H]^+$ 266.1539, found 266.1537.

***N*-Cyclopentylbenzamide (56)**

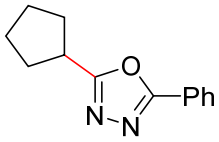


56

According to **General procedure (GP)** with cyclopentyl bromide **E1** (44.8 mg, 0.30 mmol, 1.5 equiv), benzamide **N27** (24.2 mg, 0.20 mmol, 1.0 equiv), K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv),

CuI (3.8 mg, 0.02 mmol, 10 mol%), **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **56** as a colorless oil (18.9 mg, 50% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.67 (m, 2H), 7.52 – 7.35 (m, 3H), 6.07 (s, 1H), 4.47 – 4.34 (m, 1H), 2.16 – 2.04 (m, 2H), 1.80 – 1.59 (m, 4H), 1.56 – 1.43 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 135.0, 131.3, 128.6, 126.9, 51.8, 33.3, 23.9.
HRMS (ESI) m/z calcd. for $C_{12}H_{16}NO$ $[M + H]^+$ 190.1226, found 190.1227.

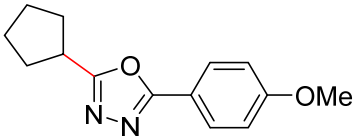
2-Cyclopentyl-5-phenyl-1,3,4-oxadiazole (57)



57

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 2-phenyl-1,3,4-oxadiazole **N28** (29.2 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **57** as a colorless oil (38.6 mg, 90% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 2H), 7.56 – 7.45 (m, 3H), 3.39 (p, J = 8.0 Hz, 1H), 2.22 – 2.10 (m, 2H), 2.05 – 1.95 (m, 2H), 1.91 – 1.81 (m, 2H), 1.79 – 1.67 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 164.6, 131.4, 129.0, 126.8, 124.2, 36.1, 31.2, 25.5.
HRMS (ESI) m/z calcd. for $C_{13}H_{15}N_2O$ $[M + H]^+$ 215.1179, found 215.1180.

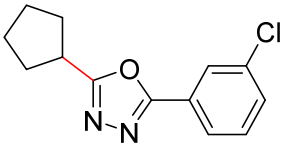
2-Cyclopentyl-5-(4-methoxyphenyl)-1,3,4-oxadiazole (58)



58

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 2-(4-methoxyphenyl)-1,3,4-oxadiazole **N29** (35.2 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **58** as a colorless oil (46.4 mg, 95% yield).
According to **General procedure (GP)** with cyclopentyl chloride **E1′** (25.1 mg, 0.24 mmol, 1.2 equiv) and 2-(4-methoxyphenyl)-1,3,4-oxadiazole **N29** (35.2 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **58** as a colorless oil (40.4 mg, 83% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.92 (m, 2H), 7.03 – 6.95 (m, 2H), 3.87 (s, 3H), 3.37 (p, J = 8.0 Hz, 1H), 2.21 – 2.08 (m, 2H), 2.05 – 1.92 (m, 2H), 1.91 – 1.79 (m, 2H), 1.79 – 1.67 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 164.6, 162.1, 128.5, 116.7, 114.4, 55.4, 36.0, 31.2, 25.5.
HRMS (ESI) m/z calcd. for $C_{14}H_{17}N_2O_2$ $[M + H]^+$ 245.1285, found 245.1285.

2-(3-Chlorophenyl)-5-cyclopentyl-1,3,4-oxadiazole (59)



59

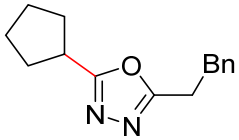
According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 2-(3-chlorophenyl)-1,3,4-oxadiazole **N30** (36.1 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **59** as a light-yellow solid (35.8 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (t, *J* = 1.9 Hz, 1H), 7.93 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 3.38 (p, *J* = 8.0 Hz, 1H), 2.22 – 2.08 (m, 2H), 2.04 – 1.92 (m, 2H), 1.91 – 1.82 (m, 2H), 1.81 – 1.70 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 163.6, 135.1, 131.5, 130.4, 126.8, 125.8, 124.9, 36.1, 31.2, 25.6.

HRMS (ESI) m/z calcd. for $C_{13}H_{14}ClN_2O$ $[M + H]^+$ 249.0789, found 249.0791.

2-Cyclopentyl-5-phenethyl-1,3,4-oxadiazole (60)



60

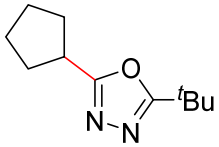
According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 2-phenethyl-1,3,4-oxadiazole **N31** (34.8 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **60** as a colorless oil (38.8 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.25 – 7.17 (m, 3H), 3.34 – 3.21 (m, 1H), 3.17 – 3.05 (m, 4H), 2.13 – 2.02 (m, 2H), 1.92 – 1.74 (m, 4H), 1.74 – 1.59 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 166.1, 140.3, 128.7, 128.3, 126.0, 35.9, 32.7, 31.0, 27.3, 25.5.

HRMS (ESI) m/z calcd. for $C_{15}H_{19}N_2O$ $[M + H]^+$ 243.1492, found 243.1493.

2-(*tert*-Butyl)-5-cyclopentyl-1,3,4-oxadiazole (61)



61

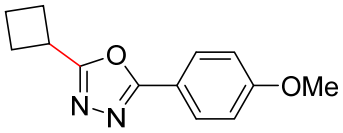
According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv) and 2-(*tert*-butyl)-1,3,4-oxadiazole **N32** (25.2 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **61** as a colorless oil (29.1 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.28 (p, *J* = 8.0 Hz, 1H), 2.16 – 2.02 (m, 2H), 1.96 – 1.75 (m, 4H), 1.73 – 1.66 (m, 2H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 170.1, 36.1, 32.4, 31.1, 28.2, 25.5.

HRMS (ESI) m/z calcd. for $C_{11}H_{19}N_2O$ $[M + H]^+$ 195.1492, found 195.1494.

2-Cyclobutyl-5-(4-methoxyphenyl)-1,3,4-oxadiazole (62)



62

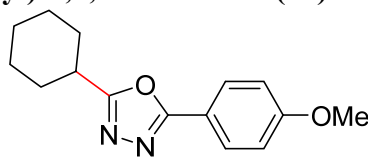
According to **General procedure (GP)** with bromocyclobutane **E2** (32.4 mg, 0.24 mmol, 1.2 equiv) and 2-(4-methoxyphenyl)-1,3,4-oxadiazole **N29** (35.2 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **62** as a white solid (21.2 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 2H), 7.04 – 6.96 (m, 2H), 3.88 (s, 3H), 3.79 (p, *J* = 8.5 Hz, 1H), 2.57 – 2.40 (m, 4H), 2.22 – 2.00 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 164.6, 162.1, 128.6, 116.7, 114.4, 55.5, 30.6, 27.1, 18.9.

HRMS (ESI) m/z calcd. for $C_{13}H_{15}N_2O_2$ $[M + H]^+$ 231.1128, found 231.1129.

2-Cyclohexyl-5-(4-methoxyphenyl)-1,3,4-oxadiazole (63)



59

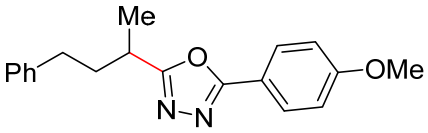
According to **General procedure (GP)** with bromocyclohexane **E3** (39.1 mg, 0.24 mmol, 1.2 equiv) and 2-(4-methoxyphenyl)-1,3,4-oxadiazole **N29** (35.2 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **63** as a white solid (35.6 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.02 – 6.96 (m, 2H), 3.87 (s, 3H), 2.97 (tt, *J* = 11.4, 3.6 Hz, 1H), 2.19 – 2.08 (m, 2H), 1.87 (m, 2H), 1.78 – 1.61 (m, 3H), 1.50 – 1.25 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 164.3, 162.1, 128.5, 116.8, 114.4, 55.5, 35.3, 30.3, 25.6, 25.5.

HRMS (ESI) m/z calcd. for $C_{15}H_{19}N_2O_2$ $[M + H]^+$ 259.1441, found 259.1441.

2-(4-Methoxyphenyl)-5-(4-phenylbutan-2-yl)-1,3,4-oxadiazole (64)



64

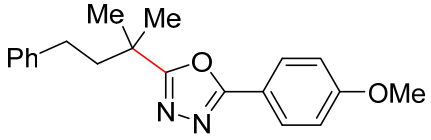
According to **General procedure (GP)** with (3-bromobutyl)benzene **E13** (51.1 mg, 0.24 mmol, 1.2 equiv) and 2-(4-methoxyphenyl)-1,3,4-oxadiazole **N29** (35.2 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **64** as a colorless oil (58.6 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 7.06 – 6.99 (m, 2H), 3.90 (s, 3H), 3.26 – 3.15 (m, 1H), 2.79 – 2.66 (m, 2H), 2.31 – 2.19 (m, 1H), 2.09 – 1.98 (m, 1H), 1.48 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 164.6, 162.1, 141.2, 128.53, 128.46, 128.44, 126.0, 116.6, 114.4, 55.4, 36.3, 33.2, 31.0, 18.3.

HRMS (ESI) m/z calcd. for $C_{19}H_{21}N_2O_2$ $[M + H]^+$ 309.1598, found 309.1597.

2-(4-Methoxyphenyl)-5-(2-methyl-4-phenylbutan-2-yl)-1,3,4-oxadiazole (65)



65

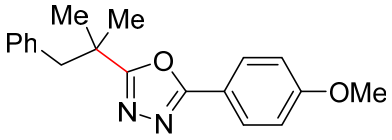
According to **General procedure (GP)** with (3-bromo-3-methylbutyl)benzene **E27** (54.5 mg, 0.24 mmol, 1.2 equiv), 2-(4-methoxyphenyl)-1,3,4-oxadiazole **N29** (35.2 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%), **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **65** as a colorless oil (36.8 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.9 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.17 – 7.11 (m, 3H), 7.00 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 2.64 – 2.55 (m, 2H), 2.12 – 2.05 (m, 2H), 1.53 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 164.6, 162.2, 141.8, 128.6, 128.4, 128.3, 125.9, 116.8, 114.4, 55.5, 43.5, 35.9, 31.2, 26.2.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}N_2O_2$ $[M + H]^+$ 323.1754, found 323.1753.

2-(4-Methoxyphenyl)-5-(2-methyl-1-phenylpropan-2-yl)-1,3,4-oxadiazole (66)



66

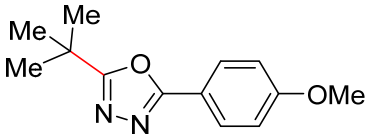
According to **General procedure (GP)** with (2-bromo-2-methylpropyl)benzene **E28** (51.1 mg, 0.24 mmol, 1.2 equiv), 2-(4-methoxyphenyl)-1,3,4-oxadiazole **N29** (35.2 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%), **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **66** as a white solid (30.8 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.24 – 7.17 (m, 3H), 7.00 (m, 4H), 3.88 (s, 3H), 3.07 (s, 2H), 1.47 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 164.4, 162.1, 136.8, 130.1, 128.5, 128.1, 126.7, 116.7, 114.3, 55.4, 47.5, 37.0, 25.8.

HRMS (ESI) m/z calcd. for $C_{19}H_{21}N_2O_2$ $[M + H]^+$ 309.1598, found 309.1595.

2-(*tert*-Butyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (67)



67

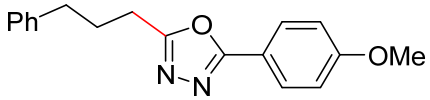
According to **General procedure (GP)** with 2-bromo-2-methylpropane **E26** (32.9 mg, 0.24 mmol, 1.2 equiv), 2-(4-methoxyphenyl)-1,3,4-oxadiazole **N29** (35.2 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%), **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **67** as a colorless oil (30.7 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 2H), 7.04 – 6.97 (m, 2H), 3.88 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 164.6, 162.1, 128.6, 116.8, 114.4, 55.5, 32.5, 28.3.

HRMS (ESI) m/z calcd. for $C_{13}H_{17}N_2O_2$ $[M + H]^+$ 233.1285, found 233.1284.

2-(4-Methoxyphenyl)-5-(3-phenylpropyl)-1,3,4-oxadiazole (68)



68

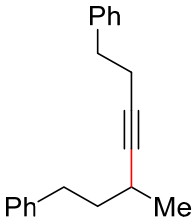
According to **General procedure (GP)** with (3-bromopropyl)benzene **E23** (47.8 mg, 0.24 mmol, 1.2 equiv), 2-(4-methoxyphenyl)-1,3,4-oxadiazole **N29** (35.2 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%), **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **68** as a colorless oil (34.0 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.9 Hz, 2H), 7.40 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 6.99 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 2.92 (t, J = 7.6 Hz, 2H), 2.77 (t, J = 7.5 Hz, 2H), 2.18 (p, J = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 164.7, 162.2, 140.9, 128.6, 128.5, 126.2, 116.6, 114.5, 55.5, 35.0, 28.1, 24.8.

HRMS (ESI) m/z calcd. for $C_{18}H_{19}N_2O_2$ $[M + H]^+$ 295.1441, found 295.1441.

(5-Methylhept-3-yne-1,7-diyl)dibenzene (69)



69

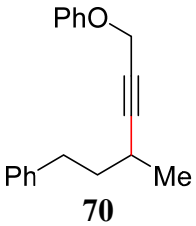
According to **General procedure (GP)** with (3-bromobutyl)benzene **E13** (51.1 mg, 0.24 mmol, 1.2 equiv), but-3-yn-1-ylbenzene **N33** (26.0 mg, 0.20 mmol, 1.0 equiv), Rb_2CO_3 (138.6 mg, 0.60 mmol, 3.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200/1) to yield the product **69** as a colorless oil (36.2 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.13 (m, 10H), 2.83 (t, J = 7.5 Hz, 2H), 2.79 – 2.70 (m, 1H), 2.68 – 2.57 (m, 1H), 2.53 – 2.44 (m, 2H), 2.42 – 2.30 (m, 1H), 1.73 – 1.60 (m, 2H), 1.14 (d, J = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 141.1, 128.7, 128.6, 128.42, 128.40, 126.3, 125.8, 85.3, 80.3, 39.1, 35.8, 33.8, 25.6, 21.6, 21.1.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}$ $[M + H]^+$ 263.1794, found 263.1795.

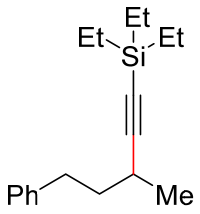
(3-Methyl-6-phenoxyhex-4-yn-1-yl)benzene (70)



70

According to **General procedure (GP)** with (3-bromobutyl)benzene **E13** (51.1 mg, 0.24 mmol, 1.2 equiv), (prop-2-yn-1-yloxy)benzene **N34** (26.4 mg, 0.20 mmol, 1.0 equiv), Rb_2CO_3 (138.6 mg, 0.60 mmol, 3.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200/1) to yield the product **70** as a colorless oil (37.0 mg, 70% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 4H), 7.21 – 7.09 (m, 3H), 7.03 – 6.94 (m, 3H), 4.72 (d, *J* = 2.0 Hz, 4H), 2.82 – 2.70 (m, 1H), 2.70 – 2.58 (m, 1H), 2.51 – 2.40 (m, 1H), 1.80 – 1.65 (m, 2H), 1.17 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 142.0, 129.4, 128.5, 128.4, 125.8, 121.3, 114.7, 92.1, 75.8, 56.4, 38.5, 33.6, 25.5, 20.9.
HRMS (ESI) m/z calcd. for $C_{19}H_{21}O$ $[M + H]^+$ 265.1587, found 265.1585.

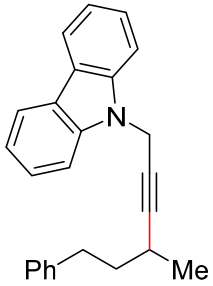
Triethyl(3-methyl-5-phenylpent-1-yn-1-yl)silane (71)



71

According to **General procedure (GP)** with (3-bromobutyl)benzene **E13** (51.1 mg, 0.24 mmol, 1.2 equiv), triethyl(ethynyl)silane **N35** (28.0 mg, 0.20 mmol, 1.0 equiv), Rb_2CO_3 (138.6 mg, 0.60 mmol, 3.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200/1) to yield the product **71** as a colorless oil (40.9 mg, 75% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 1H), 7.22 – 7.14 (m, 3H), 2.90 – 2.79 (m, 1H), 2.78 – 2.66 (m, 1H), 2.53 – 2.40 (m, 1H), 1.78 – 1.66 (m, 2H), 1.19 (d, *J* = 6.9 Hz, 1H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.60 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (100 MHz, CDCl3) δ 142.3, 128.7, 128.5, 125.9, 113.0, 81.9, 39.0, 33.8, 26.6, 21.3, 7.7, 4.8.
HRMS (ESI) m/z calcd. for $C_{18}H_{29}Si$ $[M + H]^+$ 273.2033, found 273.2033.

9-(4-Methyl-6-phenylhex-2-yn-1-yl)-9*H*-carbazole (72)

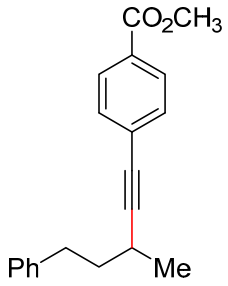


72

According to **General procedure (GP)** with (3-bromobutyl)benzene **E13** (51.1 mg, 0.24 mmol, 1.2 equiv), 9-(prop-2-yn-1-yl)-9*H*-carbazole **N36** (41.0 mg, 0.20 mmol, 1.0 equiv), Rb_2CO_3 (138.6 mg, 0.60 mmol, 3.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 4/1) to yield the product **72** as a white solid (44.5 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.56 – 7.45 (m, 4H), 7.29 – 7.16 (m, 4H), 7.16 – 7.10 (m, 1H), 7.01 (d, *J* = 7.3 Hz, 2H), 5.06 (d, *J* = 2.1 Hz, 2H), 2.71 – 2.47 (m, 2H), 2.41 – 2.28 (m, 1H), 1.67 – 1.58 (m, 2H), 1.10 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 140.1, 128.6, 128.4, 125.9, 125.8, 123.3, 120.5, 119.4, 109.1, 88.7, 75.0, 38.6, 33.7, 33.0, 25.5, 21.0.
HRMS (ESI) m/z calcd. for $C_{25}H_{24}N$ $[M + H]^+$ 338.1903, found 338.1907.

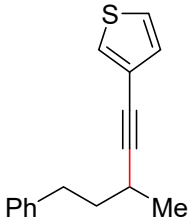
Methyl 4-(3-methyl-5-phenylpent-1-yn-1-yl)benzoate (73)



73

According to **General procedure (GP)** with (3-bromobutyl)benzene **E13** (51.1 mg, 0.24 mmol, 1.2 equiv), methyl 4-ethynylbenzoate **N37** (32.0 mg, 0.20 mmol, 1.0 equiv), Rb_2CO_3 (138.6 mg, 0.60 mmol, 3.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **73** as a colorless oil (22.2 mg, 38% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.15 (m, 5H), 3.91 (s, 3H), 2.94 – 2.73 (m, 2H), 2.72 – 2.61 (m, 1H), 1.94 – 1.75 (m, 2H), 1.29 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 142.0, 131.7, 129.5, 129.0, 128.9, 128.6, 128.5, 126.02, 97.8, 81.0, 52.3, 38.6, 33.9, 26.3, 21.0.
HRMS (ESI) m/z calcd. for $C_{20}H_{21}O_2$ $[M + H]^+$ 293.1536, found 293.1535.

3-(3-Methyl-5-phenylpent-1-yn-1-yl)thiophene (74)

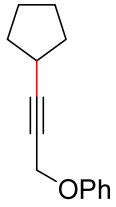


74

According to **General procedure (GP)** with (3-bromobutyl)benzene **E13** (51.1 mg, 0.24 mmol, 1.2 equiv), 3-ethynylthiophene **N38** (21.6 mg, 0.20 mmol, 1.0 equiv), Rb_2CO_3 (138.6 mg, 0.60 mmol, 3.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200/1) to yield the product **74** as a colorless oil (20.2 mg, 42% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.26 – 7.14 (m, 4H), 7.09 (dd, *J* = 5.0, 1.2 Hz, 1H), 2.93 – 2.82 (m, 1H), 2.81 – 2.72 (m, 1H), 2.69 – 2.57 (m, 1H), 1.90 – 1.72 (m, 2H), 1.27 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 130.2, 128.7, 128.5, 127.7, 125.9, 125.1, 123.0, 93.8, 38.8, 33.9, 26.2, 21.2.

HRMS (ESI) m/z calcd. for $C_{16}H_{17}S$ $[M + H]^+$ 241.1045, found 241.1042.

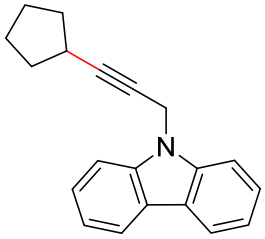
((3-Cyclopentylprop-2-yn-1-yl)oxy)benzene (75)



75

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), (prop-2-yn-1-yloxy)benzene **N34** (26.4 mg, 0.20 mmol, 1.0 equiv), Rb_2CO_3 (138.6 mg, 0.60 mmol, 3.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 200/1) to yield the product **75** as a colorless oil (32.8 mg, 82% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.01 – 6.93 (m, 3H), 4.68 (d, J = 2.1 Hz, 2H), 2.74 – 2.55 (m, 1H), 1.98 – 1.80 (m, 2H), 1.78 – 1.46 (m, 6H).
^{13}C NMR (100 MHz, CDCl3) δ 158.0, 129.5, 121.3, 115.1, 92.6, 74.5, 56.7, 33.7, 30.3, 25.1.
HRMS (ESI) m/z calcd. for $C_{14}H_{17}O$ $[M + H]^+$ 201.1274, found 201.1274.

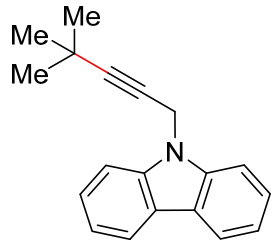
9-(3-Cyclopentylprop-2-yn-1-yl)-9*H*-carbazole (76)



76

According to **General procedure (GP)** with cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 9-(prop-2-yn-1-yl)-9*H*-carbazole **N36** (41.0 mg, 0.20 mmol, 1.0 equiv), Rb_2CO_3 (138.6 mg, 0.60 mmol, 3.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/Ch_2Cl_2 = 4/1) to yield the product **76** as a white solid (39.4 mg, 72% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.7 Hz, 2H), 7.59 – 7.49 (m, 4H), 7.34 – 7.26 (m, 2H), 5.06 (d, J = 2.1 Hz, 2H), 2.65 – 2.53 (m, 1H), 1.94 – 1.80 (m, 2H), 1.77 – 1.64 (m, 2H), 1.62 – 1.47 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 125.8, 123.2, 120.4, 119.3, 109.1, 89.1, 73.6, 33.8, 33.0, 30.2, 25.0.
HRMS (ESI) m/z calcd. for $C_{20}H_{20}N$ $[M + H]^+$ 274.1590, found 274.1591.

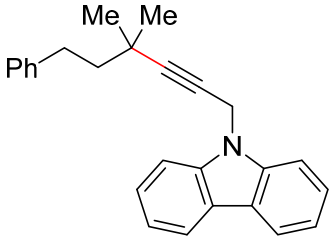
9-(4,4-Dimethylpent-2-yn-1-yl)-9*H*-carbazole (77)



77

According to **General procedure (GP)** with 2-bromo-2-methylpropane **E26** (32.9 mg, 0.24 mmol, 1.2 equiv), 9-(prop-2-yn-1-yl)-9*H*-carbazole **N36** (41.0 mg, 0.20 mmol, 1.0 equiv), Rb_2CO_3 (138.6 mg, 0.60 mmol, 3.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 80/1) to yield the product **77** as a white solid (44.4 mg, 85% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.44 (m, 4H), 7.29 – 7.20 (m, 2H), 5.00 (s, 2H), 1.15 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 125.7, 123.2, 120.4, 119.2, 109.1, 93.1, 72.5, 33.0, 30.9, 30.1, 27.5.
HRMS (ESI) m/z calcd. for $C_{19}H_{20}N$ $[M + H]^+$ 262.1590, found 262.1590.

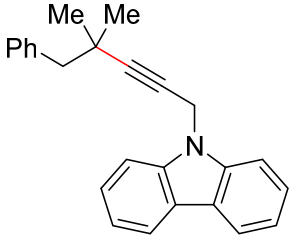
9-(4,4-Dimethyl-6-phenylhex-2-yn-1-yl)-9*H*-carbazole (78)



78

According to **General procedure (GP)** with (3-bromo-3-methylbutyl)benzene **E27** (54.5 mg, 0.24 mmol, 1.2 equiv), 9-(prop-2-yn-1-yl)-9*H*-carbazole **N36** (41.0 mg, 0.20 mmol, 1.0 equiv), Rb_2CO_3 (138.6 mg, 0.60 mmol, 3.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 80/1) to yield the product **78** as a white solid (48.5 mg, 69% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.57 – 7.43 (m, 4H), 7.29 – 7.17 (m, 4H), 7.16 – 7.09 (m, 1H), 7.01 – 6.93 (m, 2H), 5.04 (s, 2H), 2.65 – 2.53 (m, 2H), 1.64 – 1.51 (m, 2H), 1.17 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 140.1, 128.4, 128.3, 125.8, 125.7, 123.2, 120.4, 119.3, 109.1, 91.4, 74.4, 45.4, 32.9, 32.0, 31.4, 29.1.
HRMS (ESI) m/z calcd. for $C_{26}H_{26}N$ $[M + H]^+$ 352.2060, found 352.2057.

9-(4,4-Dimethyl-5-phenylpent-2-yn-1-yl)-9*H*-carbazole (79)



79

According to **General procedure (GP)** with (2-bromo-2-methylpropyl)benzene **E28** (51.1 mg, 0.24 mmol, 1.2 equiv), 9-(prop-2-yn-1-yl)-9*H*-carbazole **N36** (41.0 mg, 0.20 mmol, 1.0 equiv), Rb_2CO_3 (138.6 mg, 0.60 mmol, 3.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 80/1) to yield the product **79** as a white solid (39.1 mg, 58% yield).

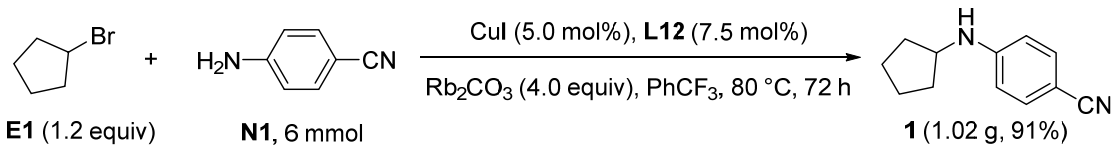
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.51 – 7.42 (m, 4H), 7.29 – 7.23 (m, 2H), 7.18 – 7.07 (m, 1H), 7.06 – 6.96 (m, 4H), 4.99 (s, 2H), 2.56 (s, 2H), 1.11 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 138.0, 130.4, 127.6, 126.2, 125.8, 123.2, 120.4, 119.3, 109.0, 91.1, 75.4, 48.8, 32.8, 32.4, 29.0.

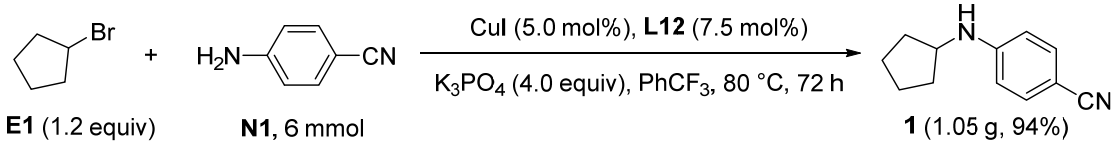
HRMS (ESI) m/z calcd. for $C_{25}H_{24}N$ $[M + H]^+$ 338.1903, found 338.1904.

7. Procedure for synthetic applications

Gram-scale reaction

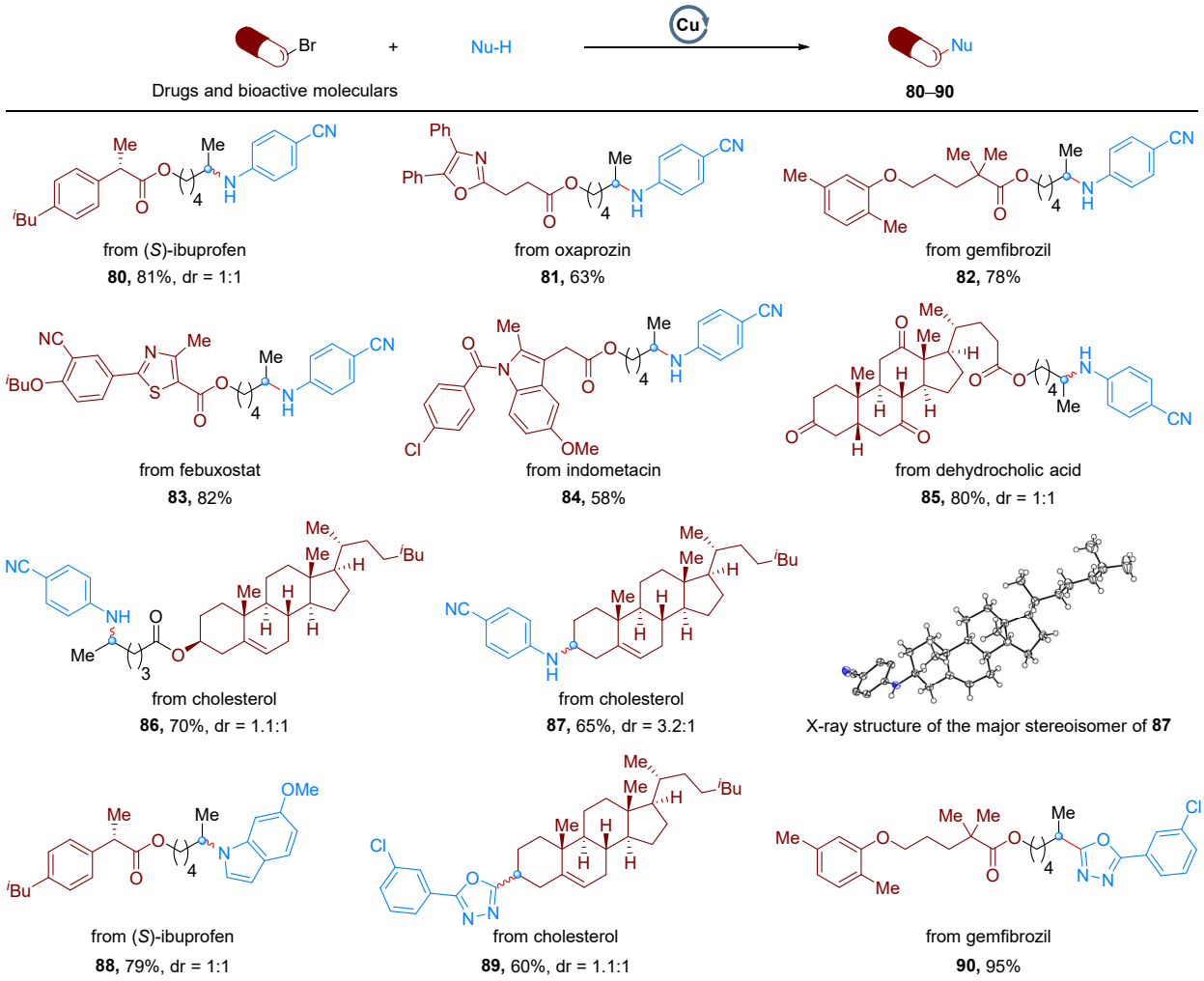


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged CuI (57.1 mg, 0.30 mmol, 5.0 mol%), **L12** (154.5 mg, 0.45 mmol, 7.5 mol%), Rb_2CO_3 (5.54 g, 24.0 mmol, 4.0 equiv), cyclopentyl bromide **E1** (1.07 g, 7.2 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (0.709 g, 6.0 mmol, 1.0 equiv), and anhydrous $PhCF_3$ (50 mL) were sequentially added into the mixture and the reaction mixture was stirred at 80 ℃ for 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **1** as a colorless oil (1.02 g, 91% yield).

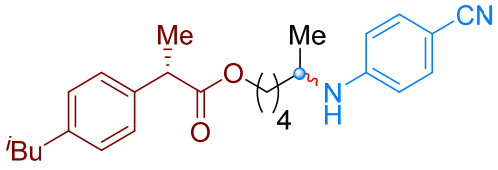


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged CuI (57.1 mg, 0.30 mmol, 5.0 mol%), **L12** (154.5 mg, 0.45 mmol, 7.5 mol%), K_3PO_4 (5.10 g, 24.0 mmol, 4.0 equiv), cyclopentyl bromide **E1** (1.07 g, 7.2 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (0.709 g, 6.0 mmol, 1.0 equiv), and anhydrous $PhCF_3$ (50 mL) were sequentially added into the mixture and the reaction mixture was stirred at 80 ℃ for 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **1** as a colorless oil (1.05 g, 94% yield).

Late-stage modification of complex molecules



2-((4-Cyanophenyl)amino)propyl (*2S*)-2-(4-isobutylphenyl)propanoate (80)

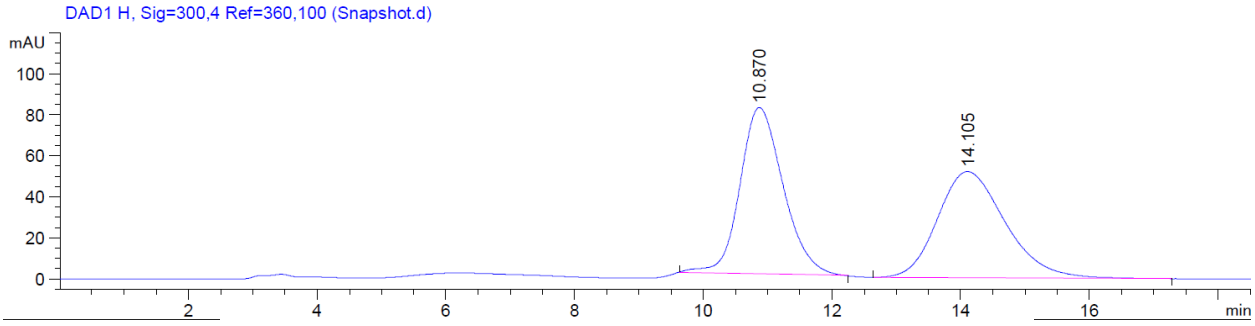


80

According to **General procedure (GP)** with **E34** (88.6 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **80** as a colorless oil (65.9 mg, 81% yield, 1:1 dr, the diastereoselectivity value was determined by HPLC analysis).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 7.1 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.48 (d, *J* = 8.4 Hz, 1H), 4.15 – 3.98 (m, 3H), 3.72 – 3.62 (m, 1H), 3.48 – 3.36 (m, 1H), 2.43 (d, *J* = 7.1 Hz, 2H), 1.90 – 1.75 (m, 1H), 1.64 – 1.53 (m, 2H), 1.56 – 1.37 (m, 5H), 1.37 – 1.23 (m, 2H), 1.13 (d, *J* = 6.3 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 6H).

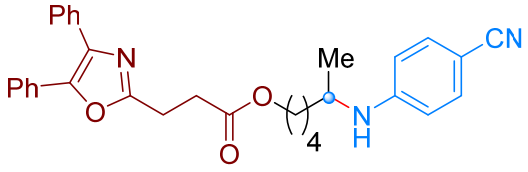
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 150.7, 140.5, 137.8, 133.7, 129.3, 127.1, 120.6, 112.3, 97.9, 64.2, 48.00, 47.98, 45.2, 45.0, 36.21, 36.17, 30.2, 28.4, 22.4, 22.3, 22.2, 20.4, 18.5, 18.4.
HRMS (ESI) m/z calcd. for $C_{26}H_{35}N_2O_2$ $[M + H]^+$ 407.2693, found 407.2693.
HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 300 nm), t_R = 10.87 min, t_R = 14.11 min.



Signal 8: DAD1 H, Sig=300,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.870	MM R	0.7789	3790.22778	81.09756	50.0402
2	14.105	BB	1.1192	3784.13452	51.74215	49.9598

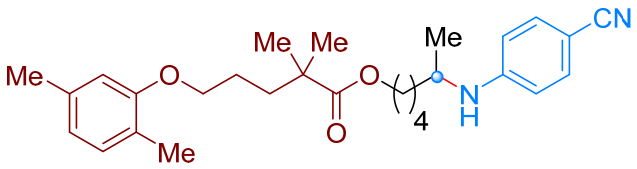
2-((4-Cyanophenyl)amino)propyl 3-(4,5-diphenyloxazol-2-yl)propanoate (81)



81

According to **General procedure (GP)** with **E35** (109.5 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **81** as a colorless oil (62.2 mg, 63% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.58 – 7.53 (m, 2H), 7.40 – 7.30 (m, 8H), 6.52 – 6.44 (m, 2H), 4.21 – 4.04 (m, 3H), 3.43 (s, 1H), 3.18 (t, *J* = 7.4 Hz, 2H), 2.90 (t, *J* = 7.4 Hz, 2H), 1.69 – 1.57 (m, 2H), 1.54 – 1.35 (m, 4H), 1.13 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 161.7, 150.7, 145.4, 135.0, 133.7, 132.4, 128.9, 128.7, 128.6, 128.5, 128.1, 127.8, 126.4, 120.6, 112.2, 97.8, 64.4, 47.9, 36.2, 32.7, 31.1, 28.8, 28.5, 23.6, 22.4, 20.4, 17.8.
HRMS (ESI) m/z calcd. for $C_{31}H_{32}N_3O_3$ $[M + H]^+$ 494.2438, found 494.2436.

2-((4-Cyanophenyl)amino)propyl 4-(2,5-dimethylphenoxy)-2,2-dimethylbutanoate (82)



82

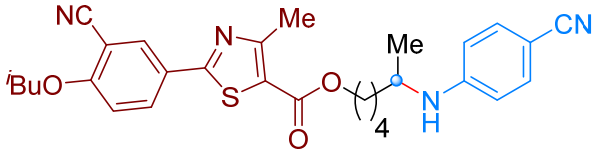
According to **General procedure (GP)** with **E36** (102.6 mg, 0.24 mmol, 1.2 equiv) and 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **82** as a colorless oil (70.3 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 6.60 (s, 1H), 6.48 (d, *J* = 8.7 Hz, 2H), 4.14 – 3.98 (m, 3H), 3.94 – 3.86 (m, 2H), 3.53 – 3.40 (m, 1H), 2.30 (s, 3H), 2.16 (s, 3H), 1.78 – 1.67 (m, 4H), 1.67 – 1.59 (m, 2H), 1.59 – 1.36 (m, 4H), 1.20 (s, 6H), 1.18 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 156.9, 150.7, 136.5, 133.8, 130.4, 123.5, 120.8, 120.6, 112.3, 112.0, 98.1, 67.9, 64.0, 48.0, 42.1, 37.1, 36.4, 28.6, 25.2, 25.2, 22.5, 21.5, 20.5, 15.8.

HRMS (ESI) m/z calcd. for $C_{28}H_{39}N_2O_3$ $[M + H]^+$ 451.2955, found 451.2955.

2-((4-Cyanophenyl)amino)propyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (83)



83

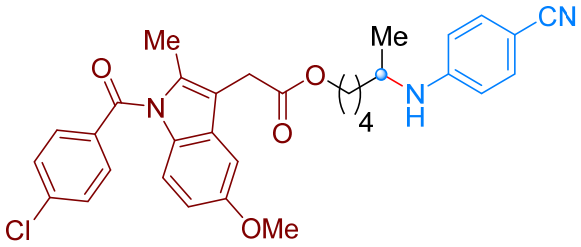
According to **General procedure (GP)** with **E37** (115.1 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) in 3 mL $PhCF_3$ for 72 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 150/1) to yield the product **83** as a white solid (84.7 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.2 Hz, 1H), 8.07 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.03 (d, *J* = 8.9 Hz, 1H), 6.56 – 6.50 (m, 2H), 4.35 – 4.25 (m, 2H), 4.10 (s, 1H), 3.91 (d, *J* = 6.5 Hz, 2H), 3.59 – 3.50 (m, 1H), 2.75 (s, 3H), 2.27 – 2.15 (m, 1H), 1.83 – 1.73 (m, 2H), 1.70 – 1.48 (m, 4H), 1.23 (d, *J* = 6.4 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 162.6, 162.1, 161.2, 150.7, 133.8, 132.6, 132.1, 125.9, 121.7, 120.6, 115.5, 112.7, 112.3, 102.9, 98.1, 75.7, 65.0, 48.0, 36.4, 28.6, 28.2, 22.5, 20.6, 19.1, 17.5.

HRMS (ESI) m/z calcd. for $C_{29}H_{33}N_4O_3S$ $[M + H]^+$ 517.2268, found 517.2269.

2-((4-Cyanophenyl)amino)propyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (84)



84

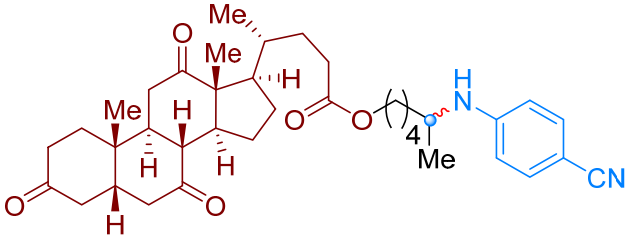
According to **General procedure (GP)** with **E38** (125.0 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) in 3 mL $PhCF_3$ for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **84** as a colorless oil (64.7 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.47 (d, *J* = 8.8 Hz, 2H), 4.18 – 4.03 (m, 3H), 3.82 (s, 3H), 3.65 (s, 2H), 3.47 – 3.36 (m, 1H), 2.38 (s, 3H), 1.69 – 1.57 (m, 3H), 1.53 – 1.31 (m, 3H), 1.12 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 168.4, 156.0, 150.7, 139.4, 136.0, 133.8, 131.2, 130.9, 130.7, 129.2, 120.6, 115.0, 112.7, 112.3, 111.3, 101.7, 98.1, 64.7, 55.8, 48.0, 36.3, 30.5, 28.6, 22.4, 20.4, 13.4.

HRMS (ESI) m/z calcd. for $C_{32}H_{33}ClN_3O_4$ $[M + H]^+$ 558.2154, found 558.2147.

2-((4-Cyanophenyl)amino)propyl (*4R*)-4-((*5S,8R,9S,10S,13R,14S,17R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (85)



85

According to **General procedure (GP)** with **E39** (135.7 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) in 3 mL $PhCF_3$ for 72 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 150/1) to yield the product **85** as a white solid (96.5 mg, 80% yield, 1:1 dr, the diastereoselectivity value was determined by HPLC analysis).

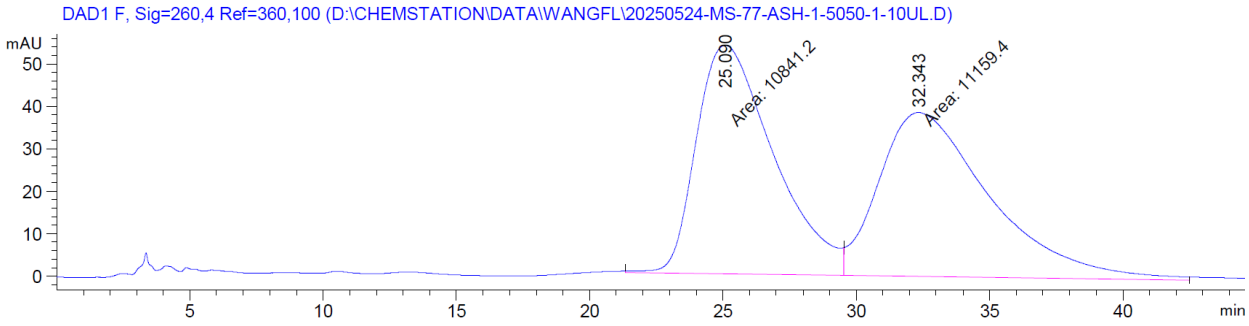
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.5 Hz, 2H), 6.49 (d, *J* = 8.5 Hz, 2H), 4.17 (s, 1H), 4.09 – 3.96 (m, 2H), 3.54 – 3.41 (m, 1H), 2.94 – 2.76 (m, 3H), 2.40 – 2.04 (m, 10H), 2.03 – 1.88 (m, 4H), 1.86 – 1.72 (m, 2H), 1.67 – 1.38 (m, 7H), 1.37 (s, 3H), 1.36 – 1.19 (m, 4H), 1.17 (d, *J* = 6.3 Hz, 3H), 1.03 (d, *J* = 2.5 Hz, 3H), 0.80 (dd, *J* = 6.6, 2.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 212.0, 209.1, 208.8, 174.1, 150.7, 133.7, 120.6, 112.2, 97.8, 97.8, 63.9, 56.8, 51.7, 48.9, 47.98, 47.96, 46.7, 45.50, 45.47, 44.9, 42.7, 38.6, 36.4, 36.3, 35.9, 35.4, 35.2, 31.4, 30.4, 28.5, 27.6, 25.0, 22.4, 21.8, 20.5, 18.58, 18.56, 11.8, 11.7.

HRMS (ESI) m/z calcd. for $C_{37}H_{51}N_2O_5$ $[M + H]^+$ 603.3792, found 603.3795.

HPLC analysis: Chiralcel ASH (*n*-hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 260 nm), t_R

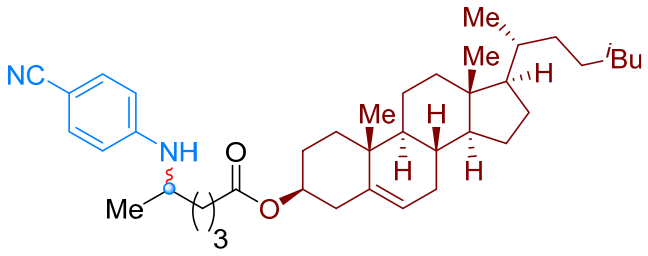
= 25.09 min, t_R = 32.34 min.



Signal 6: DAD1 F, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.090	MF	3.3628	1.08412e4	53.73147	49.2768
2	32.343	FM	4.8222	1.11594e4	38.56953	50.7232

(*3S,8S,9S,10R,13R,14S,17R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 3-((4-cyanophenyl)amino)butanoate (86)



86

According to **General procedure (GP)** with **E40** (135.3 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) in 3 mL $PhCF_3$ for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **86** as a white solid (84.1 mg, 70% yield, 1.1:1 dr, the diastereoselectivity value was determined by HPLC analysis).

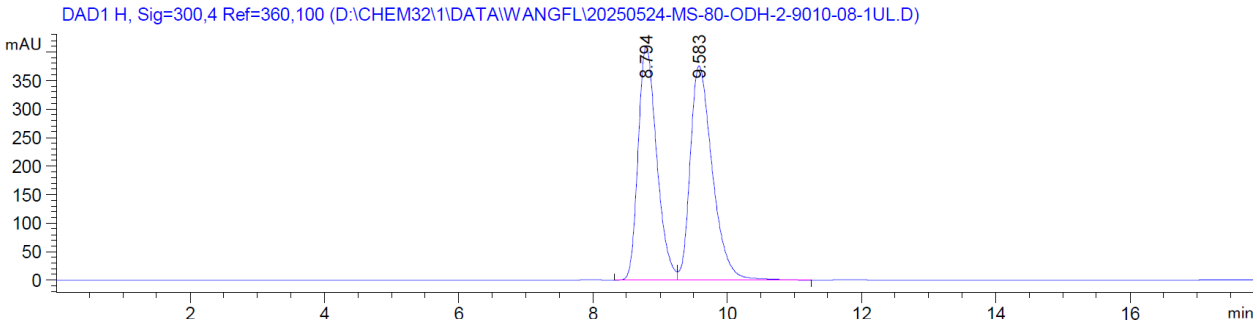
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.9 Hz, 2H), 6.52 (d, *J* = 8.9 Hz, 2H), 5.37 (d, *J* = 3.6 Hz, 1H), 4.70 – 4.51 (m, 1H), 4.16 (s, 1H), 3.60 – 3.41 (m, 1H), 2.38 – 2.21 (m, 4H), 2.06 – 1.91 (m, 2H), 1.89 – 1.77 (m, 3H), 1.75 – 1.64 (m, 2H), 1.62 – 1.41 (m, 9H), 1.39 – 1.24 (m, 4H), 1.23 – 1.18 (m, 4H), 1.18 – 1.05 (m, 6H), 1.05 – 0.95 (m, 6H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.9 Hz, 6H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 150.6, 139.5, 133.8, 122.8, 120.6, 112.3, 98.10, 74.1, 56.7, 56.1, 50.0, 48.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 36.0, 35.8, 34.3, 31.92, 31.86, 28.3, 28.0, 27.8, 24.3, 23.9, 22.9, 22.6, 21.4, 21.1, 20.5, 19.3, 18.8, 11.9.

HRMS (ESI) m/z calcd. for $C_{40}H_{61}N_2O_2$ $[M + H]^+$ 601.4728, found 601.4722.

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 300 nm),

t_R = 8.79 min, t_R = 9.58 min.

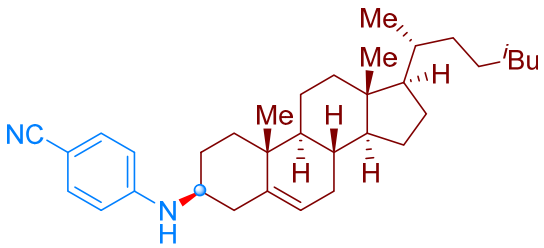


Signal 6: DAD1 F, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.794	BV	0.2964	3950.07397	205.33391	47.8102
2	9.583	VB	0.3504	4311.90967	187.45468	52.1898

4-(((*3S,8R,9S,10S,13R,14S,17R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)amino)benzonitrile (87-major)

According to **General procedure (GP)** with **E41** (107.9 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) in 3 mL $PhCF_3$ for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **87** as a white solid (63.3 mg, 65% yield, 3.2:1 dr).



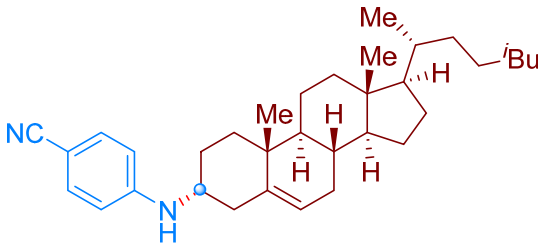
87-major

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.7 Hz, 2H), 6.51 (d, *J* = 8.7 Hz, 2H), 5.46 – 5.31 (m, 1H), 4.13 (s, 1H), 3.30 – 3.11 (m, 1H), 2.46 – 2.35 (m, 1H), 2.12 (t, *J* = 13.9 Hz, 1H), 2.07 – 1.74 (m, 5H), 1.67 – 1.04 (m, 20H), 1.02 (s, 3H), 1.01 – 0.94 (m, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.9 Hz, 6H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 140.4, 133.8, 122.2, 120.7, 112.4, 98.2, 56.8, 56.2, 52.9, 50.3, 42.4, 39.8, 39.6, 39.5, 38.0, 36.9, 36.2, 35.9, 31.9, 31.9, 29.3, 28.3, 28.1, 24.3, 23.9, 22.9, 22.6, 21.1, 19.5, 18.8, 11.9.

HRMS (ESI) m/z calcd. for $C_{34}H_{51}N_2$ $[M + H]^+$ 487.4047, found 487.4046.

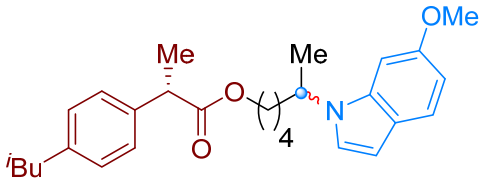
4-(((*3R,8R,9S,10S,13R,14S,17R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)amino)benzonitrile (87-minor)



87-minor

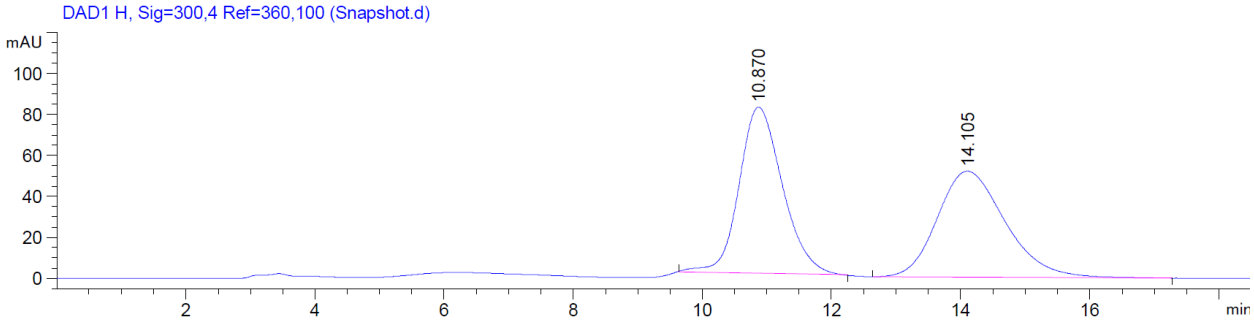
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.7 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 5.46 – 5.39 (m, 1H), 4.31 (s, 1H), 3.73 (s, 1H), 2.69 (d, *J* = 14.4 Hz, 1H), 2.08 – 1.95 (m, 3H), 1.90 – 1.78 (m, 2H), 1.76 – 1.55 (m, 5H), 1.54 – 1.40 (m, 4H), 1.39 – 1.06 (m, 12H), 1.05 (s, 3H), 1.03 – 0.94 (m, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 2.0 Hz, 6H), 0.68 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 138.6, 133.8, 124.2, 120.7, 112.5, 97.9, 56.8, 56.2, 50.5, 47.9, 42.4, 39.8, 39.6, 37.6, 37.4, 36.3, 35.9, 33.8, 32.0, 31.9, 28.3, 28.1, 24.6, 24.3, 23.9, 22.9, 22.6, 20.8, 19.0, 18.8, 11.9.
HRMS (ESI) m/z calcd. for $C_{34}H_{51}N_2$ $[M + H]^+$ 487.4047, found 487.4045.

2-(6-Methoxy-1*H*-indol-1-yl)propyl (*2S*)-2-(4-isobutylphenyl)propanoate (88)



88

According to **General procedure (GP)** with **E34** (88.4 mg, 0.24 mmol, 1.2 equiv), 6-methoxy-1*H*-indole **N21** (29.4 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L11** (8.8 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **88** as a light-yellow oil (68.8 mg, 79% yield, 1:1 dr, the diastereoselectivity value was determined by HPLC analysis).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 3.3 Hz, 1H), 6.84 – 6.74 (m, 2H), 6.44 (d, *J* = 3.2 Hz, 1H), 4.40 – 4.23 (m, 1H), 3.99 (t, *J* = 6.5 Hz, 2H), 3.86 (s, 3H), 3.62 (q, *J* = 7.1 Hz, 1H), 2.43 (d, *J* = 7.1 Hz, 2H), 1.90 – 1.68 (m, 3H), 1.58 – 1.49 (m, 2H), 1.43 (d, *J* = 7.0 Hz, 6H), 1.31 – 1.08 (m, 2H), 0.89 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 156.0, 140.5, 137.9, 137.8, 136.6, 129.3, 127.2, 122.84, 122.81, 121.5, 108.94, 108.92, 101.4, 93.4, 64.3, 64.2, 55.8, 51.29, 51.26, 45.2, 45.1, 36.5, 30.2, 28.29, 28.26, 22.7, 22.4, 21.22, 21.20, 18.4.
HRMS (ESI) m/z calcd. for $C_{28}H_{38}NO_3$ $[M + H]^+$ 436.2846, found 436.2838.
HPLC analysis: Chiralcel OJ (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 300 nm), t_R = 10.87 min, t_R = 14.12 min.

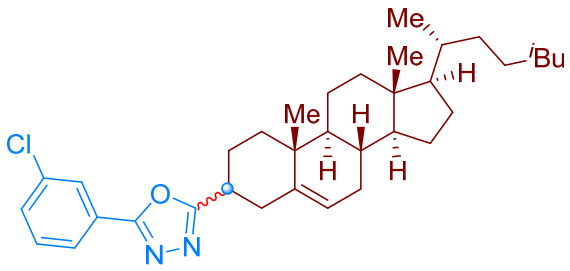


Signal 8: DAD1 H, Sig=300,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.870	MM R	0.7789	3790.22778	81.09756	50.0402
2	14.105	BB	1.1192	3784.13452	51.74215	49.9598

2-(3-Chlorophenyl)-5-((*8S,9S,10R,13R,14S,17R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)-1,3,4-oxadiazole (89)

According to **General procedure (GP)** with **E41** (107.9 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) in 3 mL $PhCF_3$ for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **89** as a white solid (66.0 mg, 60% yield, 1.1:1 dr).



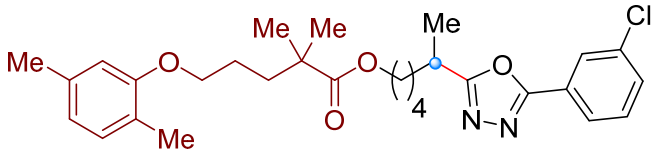
89

For one stereoisomer of 89: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 1.8 Hz, 1H), 7.92 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 5.47 – 5.32 (m, 1H), 3.44 – 3.35 (m, 1H), 2.86 – 2.74 (m, 1H), 2.58 (d, *J* = 14.7 Hz, 1H), 2.25 (d, *J* = 13.7 Hz, 1H), 2.13 – 1.89 (m, 3H), 1.86 – 1.73 (m, 2H), 1.59 – 1.29 (m, 10H), 1.29 – 1.10 (m, 5H), 1.08 (s, 3H), 1.07 – 0.92 (m, 5H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.85 (dd, *J* = 6.6, 1.9 Hz, 6H), 0.66 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 163.4, 138.5, 135.2, 131.5, 130.4, 126.8, 126.0, 124.9, 123.0, 56.7, 56.1, 50.1, 42.3, 39.7, 39.6, 37.1, 36.2, 35.9, 35.1, 34.4, 33.6, 31.9, 31.8, 28.3, 28.1, 24.3, 24.2, 23.9, 22.9, 22.6, 20.7, 19.4, 18.8, 11.9.
HRMS (ESI) m/z calcd. for $C_{35}H_{50}ClN_2O$ $[M + H]^+$ 549.3606, found 549.3602.

For the other stereoisomer of 89: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 5.52 – 5.36 (m, 1H), 3.00 – 2.87 (m,

1H), 2.64 (t, *J* = 13.9 Hz, 1H), 2.52 – 2.42 (m, 1H), 2.12 – 1.97 (m, 4H), 1.96 – 1.90 (m, 1H), 1.89 – 1.77 (m, 1H), 1.62 – 1.45 (m, 6H), 1.40 – 1.20 (m, 7H), 1.19 – 1.09 (m, 5H), 1.08 (s, 3H), 1.05 – 0.96 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.69 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 163.4, 140.2, 135.2, 131.6, 130.4, 126.9, 125.8, 125.0, 122.1, 56.8, 56.2, 50.3, 42.4, 39.8, 39.6, 38.7, 37.0, 36.9, 36.3, 36.1, 35.9, 31.9, 31.8, 28.3, 28.1, 26.5, 24.4, 23.9, 22.9, 22.6, 21.0, 19.5, 18.8, 12.0.
HRMS (ESI) m/z calcd. for $C_{35}H_{50}ClN_2O$ $[M + H]^+$ 549.3606, found 549.3602.

2-(5-(3-Chlorophenyl)-1,3,4-oxadiazol-2-yl)propyl 4-(2,5-dimethylphenoxy)-2,2-dimethylbutanoate (90)

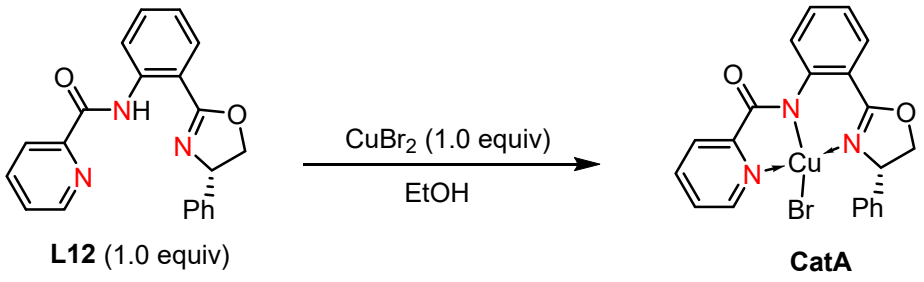


90

According to **General procedure (GP)** with **E36** (102.6 mg, 0.24 mmol, 1.2 equiv), 2-(3-chlorophenyl)-1,3,4-oxadiazole **N30** (36.1 mg, 0.20 mmol, 1.0 equiv), CuI (3.8 mg, 0.02 mmol, 10 mol%) and **L12** (10.3 mg, 0.03 mmol, 15 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **90** as a colorless oil (97.5 mg, 95% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 1.9 Hz, 1H), 7.93 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.51 – 7.38 (m, 2H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.59 (s, 1H), 4.06 (t, *J* = 6.5 Hz, 2H), 3.94 – 3.80 (m, 2H), 3.25 – 3.06 (m, 1H), 2.29 (s, 3H), 2.16 (s, 3H), 1.97 – 1.85 (m, 1H), 1.79 – 1.60 (m, 7H), 1.49 – 1.35 (m, 5H), 1.19 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 170.3, 163.5, 156.9, 136.4, 135.1, 131.5, 130.4, 130.2, 126.7, 125.7, 124.9, 123.5, 120.6, 111.9, 67.8, 63.9, 42.0, 37.0, 34.1, 31.6, 28.4, 25.2, 23.5, 21.4, 18.1, 15.8.
HRMS (ESI) m/z calcd. for $C_{29}H_{38}ClN_2O_4$ $[M + H]^+$ 513.2515, found 513.2508.

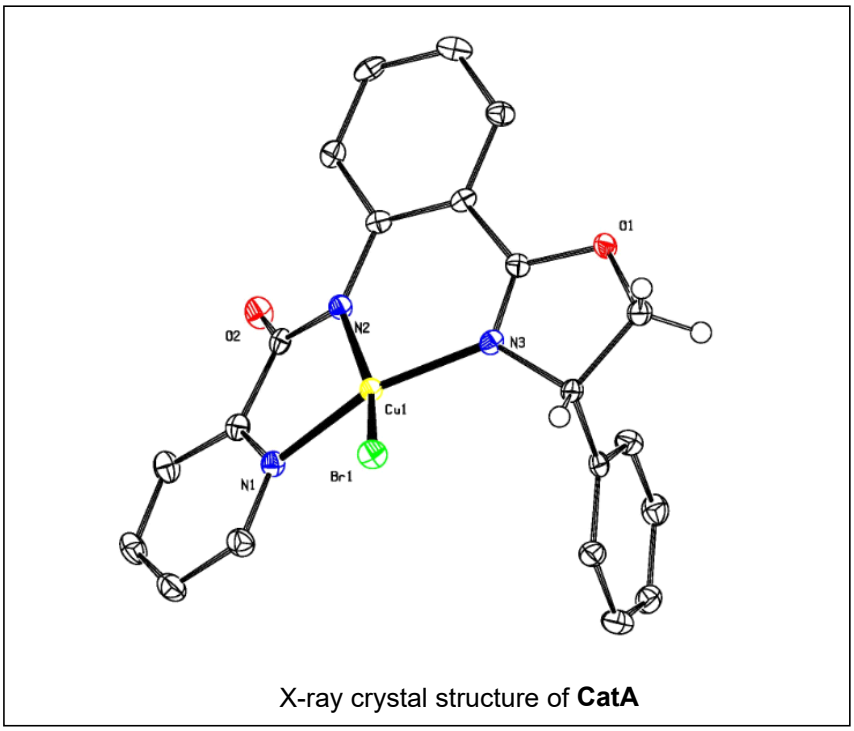
8. Mechanistic studies

Preparation and characterization of Cu(II) complex CatA



L12 (1.0 equiv)

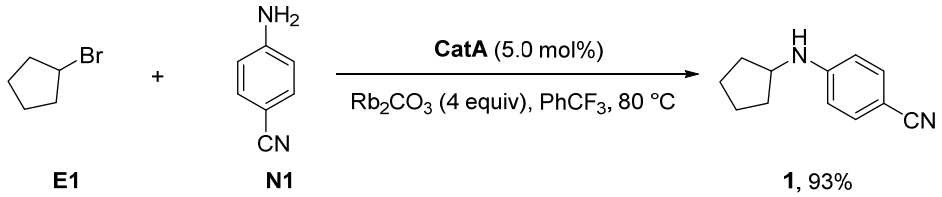
CatA



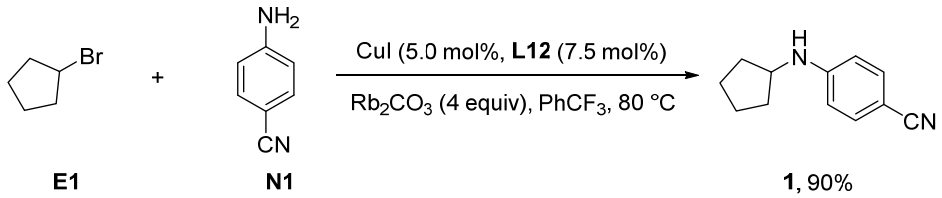
X-ray crystal structure of **CatA**

To a solution of $CuBr_2$ (11.2 mg, 0.05 mmol) in EtOH (1 mL) was added **L12** (17.2 mg, 0.05 mmol) at room temperature. The reaction mixture was stirred overnight, then concentrated under reduced pressure to yield a green precipitate. The precipitate was dissolved in CH_2Cl_2 (2 mL), filtered to remove any insoluble impurities, and the filtrate was transferred to a sealed vial. Slow diffusion crystallization was performed by carefully layering Et_2O (3.0 mL) over the CH_2Cl_2 solution. After 48 hours, green crystals suitable for X-ray analysis were collected by filtration, washed with cold Et_2O (2 × 1 mL), and dried under vacuum to afford the desired product (11.5 mg, 47% yield).

Reaction of Cu(II) complex CatA



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **CatA** (4.9 mg, 0.01 mmol, 5.0 mol%), Rb_2CO_3 (184.8 mg, 0.80 mmol, 4.0 equiv), cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), and anhydrous $PhCF_3$ (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at 80 ℃ for 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **1** as a colorless oil (34.6 mg, 93% yield).



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged CuI (1.9 mg, 0.01 mmol, 5.0 mol%), **L12** (5.2 mg, 0.015 mmol, 7.5 mol%), Rb_2CO_3 (184.8 mg, 0.80 mmol, 4.0 equiv), cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), and anhydrous $PhCF_3$ (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at 80 ℃ for 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **1** as a colorless oil (33.5 mg, 90% yield).

Cyclic voltammograms

Cyclic voltammetry (CV) experiments were performed using a CHI 650E potentiostat with a three-electrode cell configuration. The setup consisted of a glassy carbon working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode. The measurements were conducted at a scan rate of 0.1 V/s. Ferrocene (Fc, $E_{1/2}$ = +0.40 V vs SCE) was added at the end of the measurements as an internal standard to calibrate the potential scale.[21] The samples $CuBr_2$ (1 mM), $CuBr_2$/**L12** (1 mM), were prepared under the protection of the N_2 by dissolving them in degassed CH_3CN (0.1 M $TBAPF_6$) and stirred at 50 °C for 1 h, $CuBr_2$/**L12** with base (1 mM) were prepared under the protection of the N_2 by dissolving them in degassed CH_3CN (0.1 M $TBAPF_6$) directly with 10 equiv. Rb_2CO_3 and stirred at 50 °C for 1 h. $CuBr_2$/**L12** with base (1 mM) and nucleophile 3,5-bis(trifluoromethyl)aniline **N11** (3 mM) were prepared under the protection of the N_2 by dissolving them in degassed CH_3CN (0.1 M $TBAPF_6$) directly with 10 equiv. Rb_2CO_3 and stirred at 50 °C for 1 h. All samples were used for CV test directly. All potential values are reported relative to the

saturated calomel electrode (SCE).

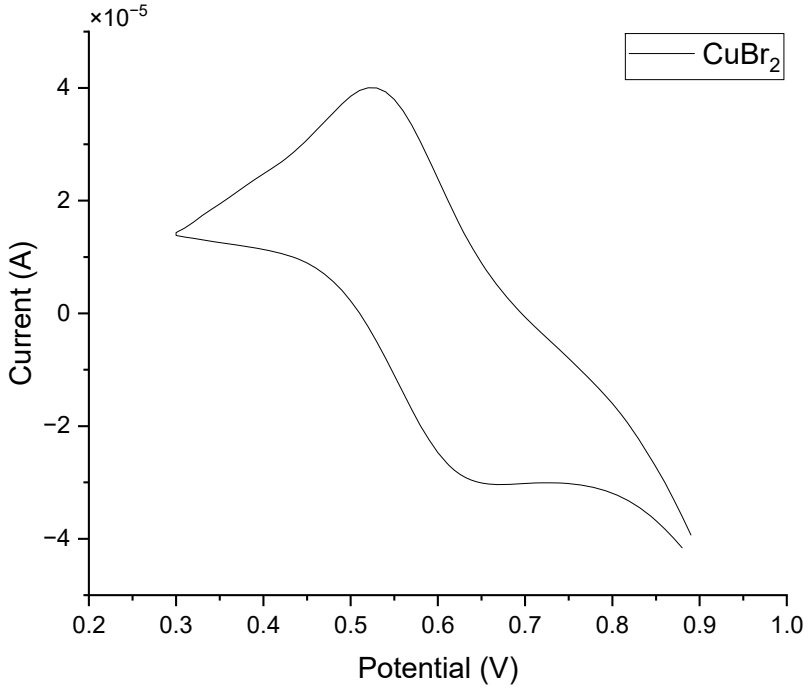


Figure S3. CVs of the $CuBr_2$ (1 mM), calibrated with Fc as an internal standard, $E(Cu^{I}/Cu^{II})$ = 0.58 V.

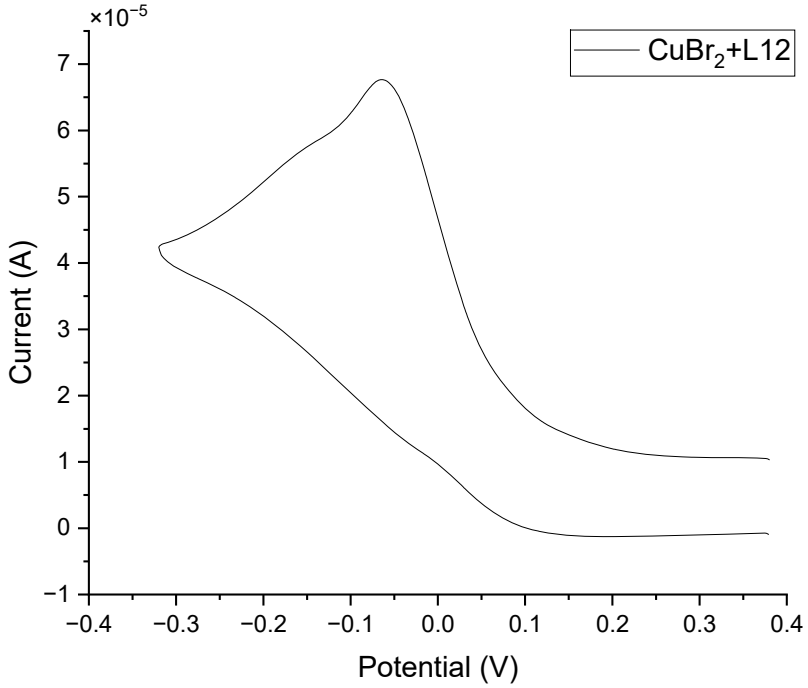


Figure S4. CVs of the $CuBr_2$/**L12** (1 mM), calibrated with Fc as an internal standard, E_{peak} = –0.06 V.

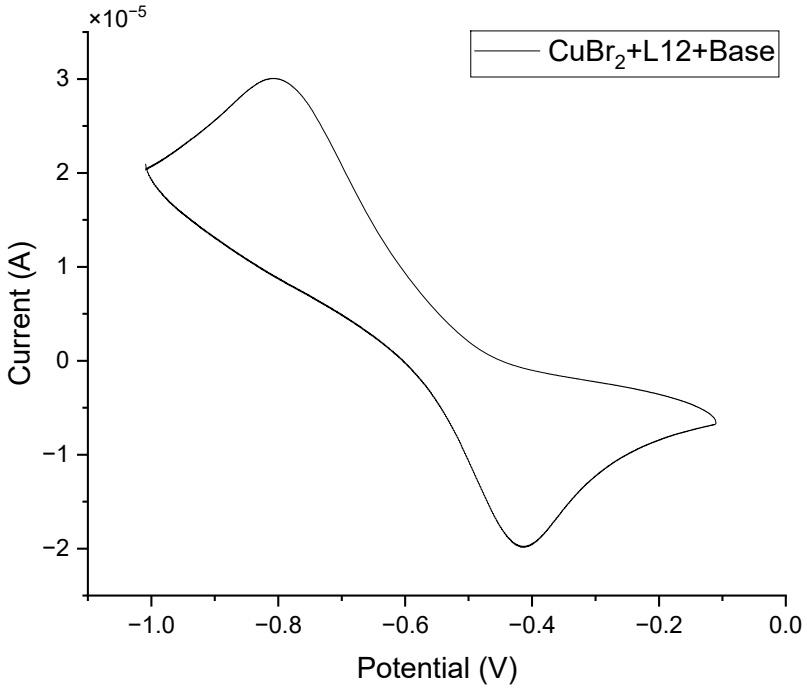


Figure S5. CVs of the $CuBr_2$/**L12** with base (1 mM), calibrated with Fc as an internal standard, $E(Cu^{I}/Cu^{II})$ = –0.61 V.

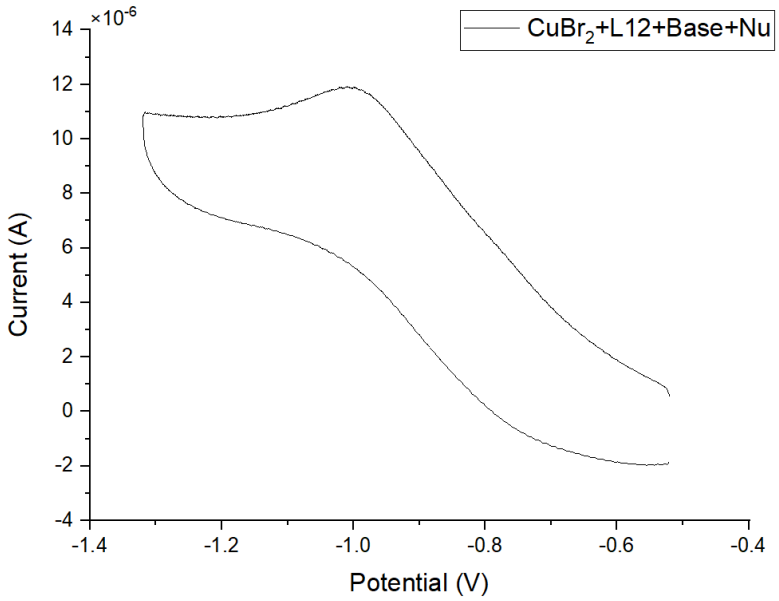
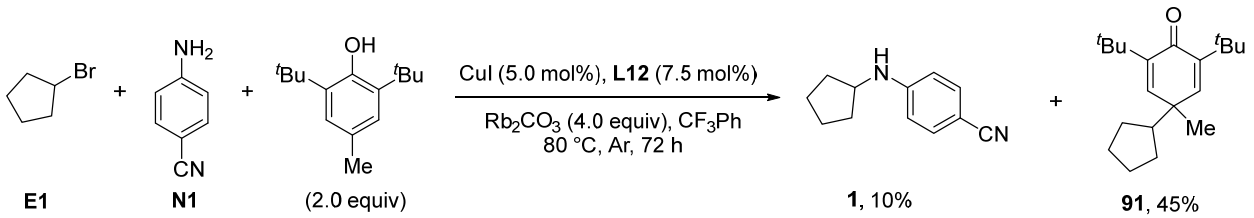
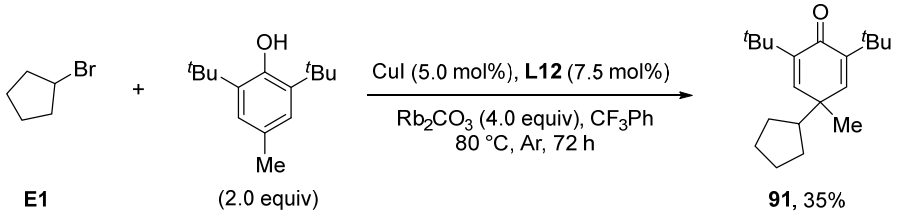


Figure S6. CVs of the $CuBr_2$/**L12** with base (1 mM) and nucleophile **N11** (3 mM), calibrated with Fc as an internal standard, E_{peak} = –0.98 V.

Radical trapping experiment

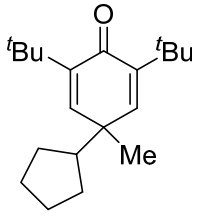


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged CuI (1.9 mg, 0.01 mmol, 5.0 mol%), **L12** (5.2 mg, 0.015 mmol, 7.5 mol%), Rb_2CO_3 (184.8 mg, 0.80 mmol, 4.0 equiv), cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), BHT (88.1 mg, 0.40 mmol, 2.0 equiv) and anhydrous $PhCF_3$ (3.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at 80 ℃ for 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 to 15/1) to yield the product **1** as a colorless oil (3.7 mg, 10% yield) and **91** as a colorless oil (26.0 mg, 45% yield).



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged CuI (1.9 mg, 0.01 mmol, 5.0 mol%), **L12** (5.2 mg, 0.015 mmol, 7.5 mol%), Rb_2CO_3 (184.8 mg, 0.80 mmol, 4.0 equiv), cyclopentyl bromide **E1** (35.8 mg, 0.24 mmol, 1.2 equiv), BHT (88.1 mg, 0.40 mmol, 2.0 equiv) and anhydrous $PhCF_3$ (3.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at 80 ℃ for 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 to 15/1) to afford **91** as a colorless oil (20.1 mg, 35% yield).

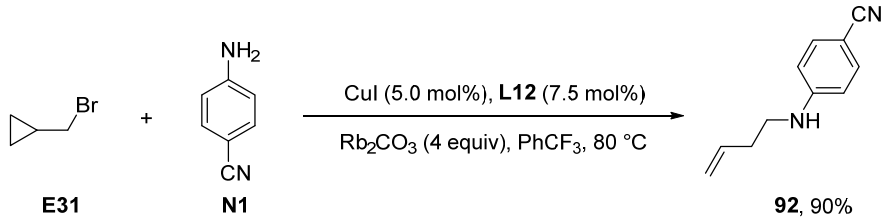
2,6-Di-*tert*-butyl-4-cyclopentyl-4-methylcyclohexa-2,5-dien-1-one (91)



91

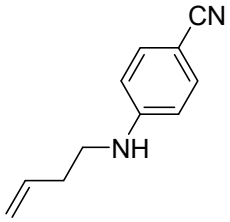
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (s, 2H), 2.08 – 1.95 (m, 1H), 1.63 – 1.52 (m, 2H), 1.51 – 1.42 (m, 4H), 1.22 (s, 18H), 1.18 (s, 3H), 1.15 – 1.07 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 186.8, 146.6, 145.9, 49.1, 41.5, 34.8, 29.6, 27.7, 26.0, 25.1.
HRMS (ESI) m/z calcd. for $C_{20}H_{33}O$ $[M + H]^+$ 289.2526, found 289.2519.

Radical clock experiments



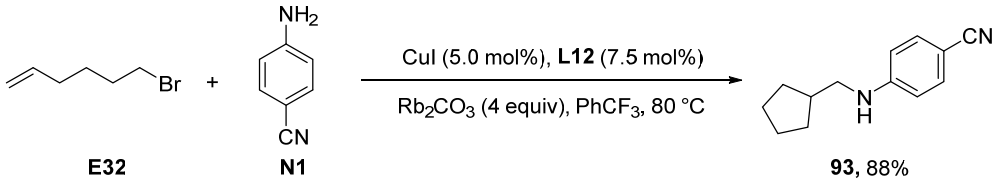
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.01 mmol, 5.0 mol%), **L12** (5.2 mg, 0.015 mmol, 7.5 mol%), Rb_2CO_3 (184.8 mg, 0.80 mmol, 4.0 equiv), (bromomethyl)cyclopropane **E31** (32.4 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), and anhydrous $PhCF_3$ (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at 80 ℃ for 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **92** as a colorless oil (31.0 mg, 90% yield).

4-(But-3-en-1-ylamino)benzonitrile (92)



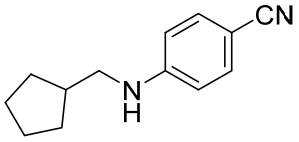
92

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2H), 6.60 – 6.52 (m, 2H), 5.87 – 5.75 (m, 1H), 5.20 – 5.12 (m, 2H), 4.26 (s, 1H), 3.22 (t, *J* = 6.7 Hz, 2H), 2.45 – 2.36 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 135.0, 133.7, 120.6, 117.8, 112.2, 98.6, 42.0, 33.2.
HRMS (ESI) m/z calcd. for $C_{11}H_{13}N_2$ $[M + H]^+$ 173.1073, found 173.1073.



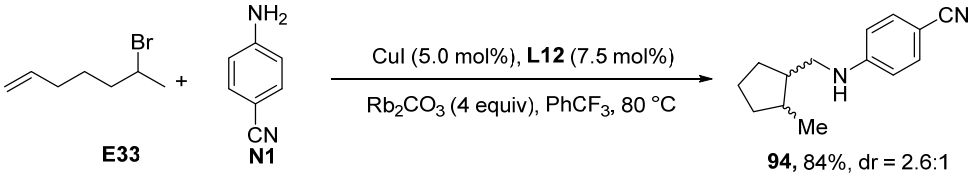
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.01 mmol, 5.0 mol%), **L12** (5.2 mg, 0.015 mmol, 7.5 mol%), Rb_2CO_3 (184.8 mg, 0.80 mmol, 4.0 equiv), 6-bromohex-1-ene **E32** (39.1 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), and anhydrous $PhCF_3$ (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at 80 ℃ for 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **93** as a colorless oil (35.3 mg, 88% yield).

4-((Cyclopentylmethyl)amino)benzonitrile (93)



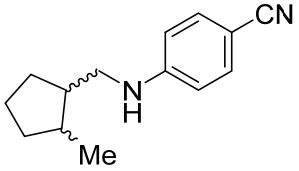
93

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 2H), 6.60 – 6.48 (m, 2H), 4.22 (s, 1H), 3.06 (d, *J* = 7.2 Hz, 2H), 2.24 – 2.08 (m, 1H), 1.90 – 1.78 (m, 2H), 1.72 – 1.51 (m, 4H), 1.34 – 1.20 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 133.7, 120.7, 112.1, 98.2, 48.6, 39.2, 30.6, 25.3.
HRMS (ESI) m/z calcd. for $C_{13}H_{17}N_2$ $[M + H]^+$ 201.1386, found 201.1387.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.9 mg, 0.01 mmol, 5.0 mol%), **L12** (5.2 mg, 0.015 mmol, 7.5 mol%), Rb_2CO_3 (184.8 mg, 0.80 mmol, 4.0 equiv), 6-bromohept-1-ene **E33** (42.5 mg, 0.24 mmol, 1.2 equiv), 4-aminobenzonitrile **N1** (23.6 mg, 0.20 mmol, 1.0 equiv), and anhydrous $PhCF_3$ (2.0 mL) were sequentially added into the mixture and the reaction mixture was stirred at 80 ℃ for 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to yield the product **94** as a colorless oil (36.0 mg, 84% yield, 2.6:1 dr).

4-(((2-Methylcyclopentyl)methyl)amino)benzonitrile (94)



94

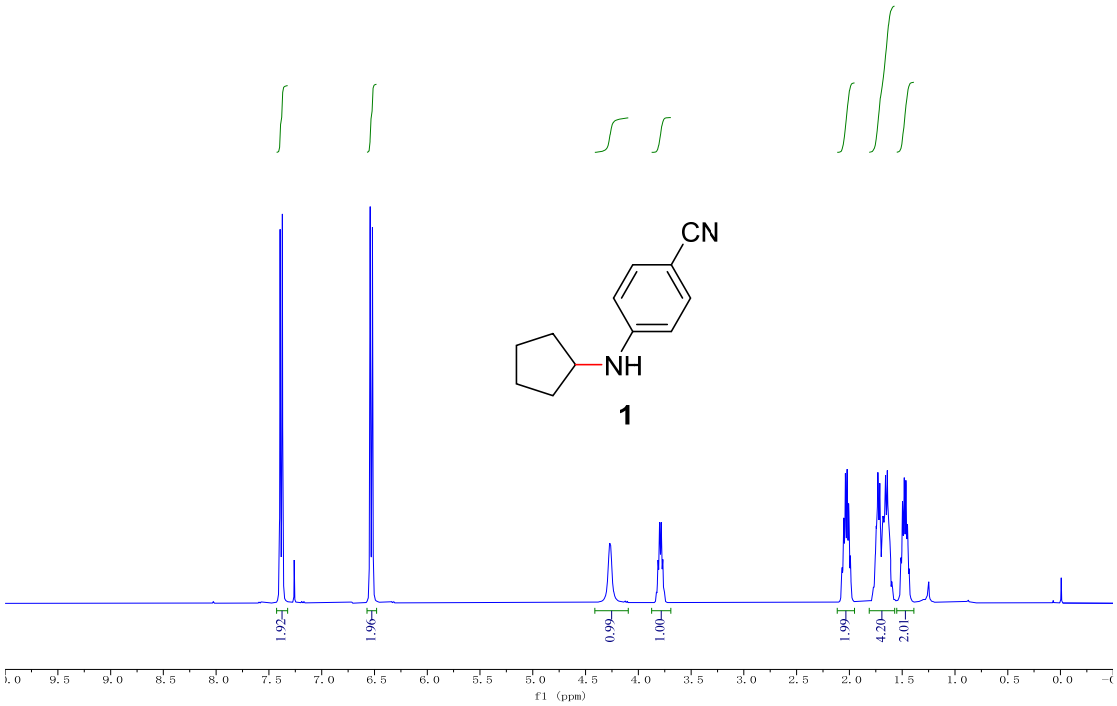
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 2H), 4.20 (s, 1H), 3.35 – 3.09 (m, 1H), 3.06 – 2.84 (m, 1H), 2.25 – 1.13 (m, 8H), 1.11 – 0.78 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 133.7, 120.7, 112.0, 98.2, 47.7, 46.8, 44.4, 42.5, 38.6, 35.2, 34.8, 33.6, 30.9, 28.5, 23.8, 22.6, 19.9, 14.9.
HRMS (ESI) m/z calcd. for $C_{14}H_{19}N_2$ $[M + H]^+$ 215.1543, found 215.1544.

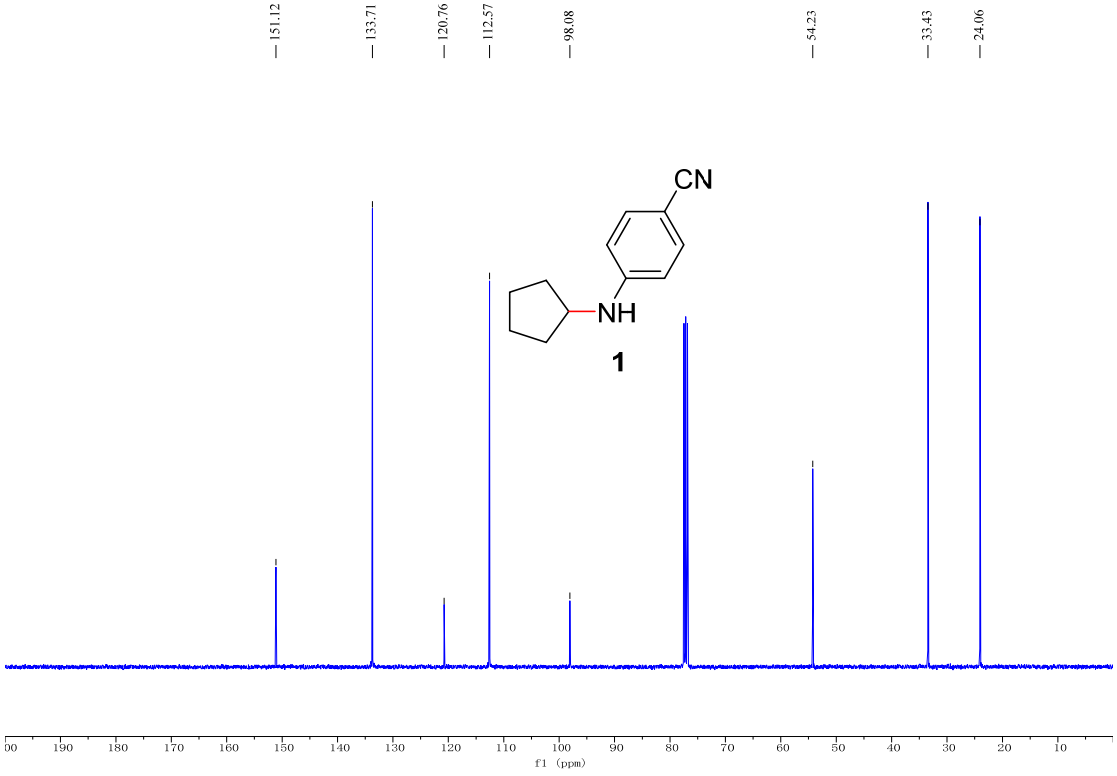
9. References

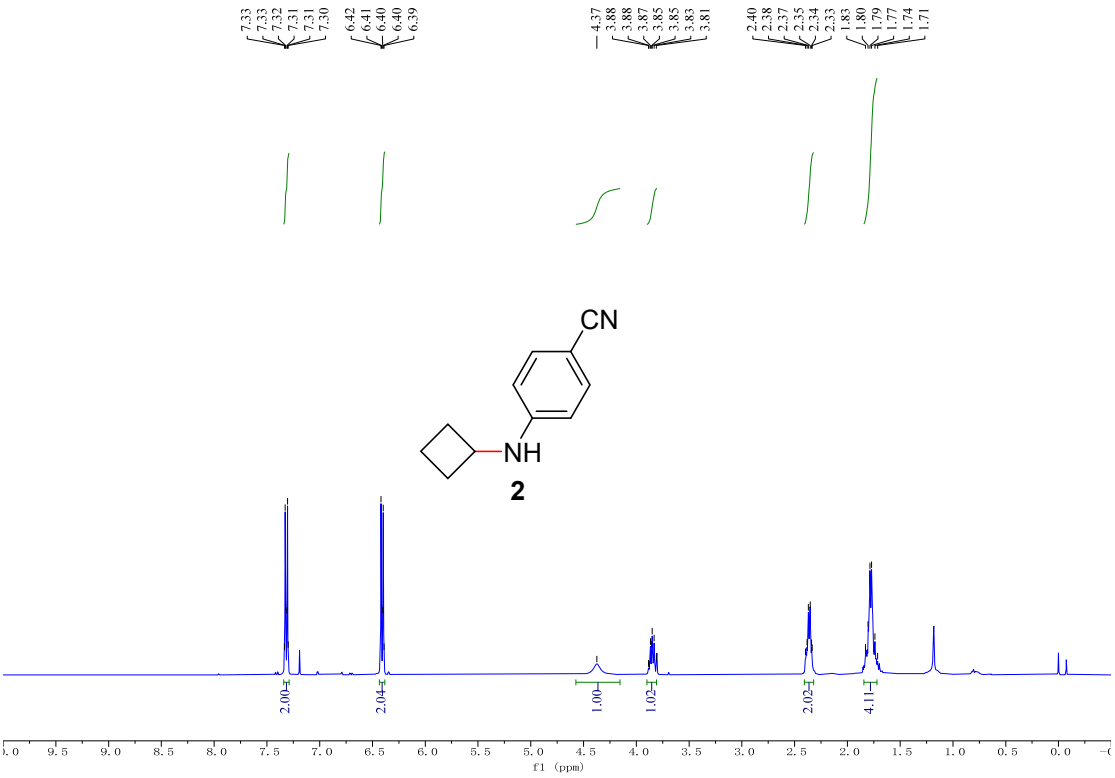
1. Decken, A.; Gossage, R. A.; Yadav, P. N. Oxazoline Chemistry. Part VIII. Synthesis and Characterization of a New Class of Pincer Ligands Derived from the 2-(*o*-Anilinyl)-2-Oxazoline Skeleton–Applications to the Synthesis of Group X Transition Metal Catalysts. *Can. J. Chem.* **2005**, *83*, 1185–1189.
2. Liu, L.; Guo, K.-X.; Tian, Y.; Yang, C.-J.; Gu, Q.-S.; Li, Z.-L.; Ye, L.; Liu, X.-Y. Copper-Catalyzed Intermolecular Enantioselective Radical Oxidative $C(sp^3)$−H/C(sp)−H Cross-Coupling with Rationally Designed Oxazoline-Derived *N,N,P*(*O*)-Ligands. *Angew. Chem., Int. Ed*. **2021**, *60*, 26710–26717.
3. Chen, X.; Cheng, Z.; Guo, J.; Lu, Z. Asymmetric Remote C–H Borylation of Internal Alkenes via Alkene Isomerization. *Nat. Commun.* **2022**, *13*, 650.
4. Zhu, C.; Liu, Z.-Y.; Tang, L.; Zhang, H.; Zhang, Y.-F.; Walsh, P. J.; Feng, C. Migratory Functionalization of Unactivated Alkyl Bromides for Construction of All-Carbon Quaternary Centers via Transposed *tert*-C-Radicals. *Nat. Commun.* **2020**, *11*, 4860.
5. Chen, F.; Chen, K.; Zhang, Y.; He, Y.; Wang, Y.-M.; Zhu, S. Remote Migratory Cross-Electrophile Coupling and Olefin Hydroarylation Reactions Enabled by in Situ Generation of NiH. *J. Am. Chem. Soc.* **2017**, *139*, 13929–13935.
6. Stach, T.; Dräger, J.; Huy, P. H. Nucleophilic Substitutions of Alcohols in High Levels of Catalytic Efficiency. *Org. Lett.* **2018**, *20*, 2980–2983.
7. Dang, H.; Cox, N.; Lalic, G. Copper-Catalyzed Reduction of Alkyl Triflates and Iodides: An Efficient Method for the Deoxygenation of Primary and Secondary Alcohols. *Angew. Chem., Int. Ed.* **2014**, *53*, 752–756.
8. Vyvyan, J. R.; Loitz, C.; Looper, R. E.; Mattingly, C. S.; Peterson, E. A.; Staben, S. T. Synthesis of Aromatic Bisabolene Natural Products via Palladium-Catalyzed Cross-Couplings of Organozinc Reagents. *J. Org. Chem*. **2004**, *69*, 2461–2468.
9. Zhou, Y.; Qiu, L.; Xie, W. A General Copper Catalytic System for Suzuki-Miyaura Cross-Coupling of Unactivated Secondary and Primary Alkyl Halides with Arylborons. *J. Am. Chem. Soc.* **2023**, *145*, 28146–28155.
10. Quinn, R. K.; Könst, Z. A.; Michalak, S. E.; Schmidt, Y.; Szklarski, A. R.; Flores, A. R.; Nam, S.; Horne, D. A.; Vanderwal, C. D.; Alexanian, E. J. Site-Selective Aliphatic C–H Chlorination Using *N*-Chloroamides Enables a Synthesis of Chlorolissoclimide. *J. Am. Chem. Soc*. **2016**, *138*, 696–702.
11. Sargent, B. T.; Alexanian, E. J. Palladium-Catalyzed Alkoxycarbonylation of Unactivated Secondary Alkyl Bromides at Low Pressure. *J. Am. Chem. Soc*. **2016**, *138*, 7520–7523.
12. Zhao, H.; McMillan, A. J.; Constantin, T.; Mykura, R. C.; Juliá, F.; Leonori, D. Merging Halogen-Atom Transfer (XAT) and Cobalt Catalysis to Override E2-Selectivity in the Elimination of Alkyl Halides: A Mild Route toward contra-Thermodynamic Olefins. *J. Am. Chem. Soc*. **2021**, *143*, 14806–14813.
13. Wu, X.; Hao, W.; Ye, K.-Y.; Jiang, B.; Pombar, G.; Song, Z.; Lin, S. Ti-Catalyzed Radical Alkylation of Secondary and Tertiary Alkyl Chlorides Using Michael Acceptors. *J. Am. Chem. Soc.* **2018**, *140*, 14836–14843.
14. Kyasa, S. K.; Meier, R. N.; Pardini, R. A.; Truttmann, T. K.; Kuwata, K. T.; Dussault, P. H. Synthesis of Ethers via Reaction of Carbanions and Monoperoxyacetals. *J. Org. Chem*. **2015**, *80*, 12100–12114.

15. Charki, P.; Cordier, M.; Ylijoki, K. E. O.; Müller, D. S. Reactions of Tertiary Aliphatic Cations with Silylated Alkynes: Substitution, Cyclization and Unexpected C−H Activation Products. *Chem. Eur. J.* **2025**, *31*, e202403979.
16. Chu, C.; Liang, Y.; Fu, G. Silicon-Carbon Bond Formation via Nickel-Catalyzed Cross-Coupling of Silicon Nucleophiles with Unactivated Secondary and Tertiary Alkyl Electrophiles. *J. Am. Chem. Soc.* **2016**, *138*, 6404–6407.
17. Zubaydi, S. AI.; Onuigbo, I. O.; Truesdell, B. L.; Sevov, Christo S. Cobalt-Catalyzed Electroreductive Alkylation of Unactivated Alkyl Chlorides with Conjugated Olefins. *Angew. Chem., Int. Ed.* **2024**, *63*, e202313830.
18. Ahn, J. M.; Ratani, T. S.; Hannoun, K. I.; Fu, G. C.; Peters, J. C. Photoinduced, Copper-Catalyzed Alkylation of Amines: A Mechanistic Study of the Cross-Coupling of Carbazole with Alkyl Bromides. *J. Am. Chem. Soc*. **2017**, *139*, 12716–12723.
19. Aly, M. R. E. S.; Saad, H. A.; Abdel-Hafez, S. H. Synthesis, Antimicrobial and Cytotoxicity Evaluation of New Cholesterol Congeners. *Beilstein J. Org. Chem.* **2015**, *11,* 1922–1932.
20. Su, X.-L.; Ye, L.; Chen, J.-J.; Liu, X.-D.; Jiang, S.-P.; Wang, F.-L.; Liu, L.; Yang, C.-J.; Chang, X.-Y.; Li, Z.-L.; Gu, Q.-S.; Liu, X.-Y. Copper-Catalyzed Enantioconvergent Cross-Coupling of Racemic Alkyl Bromides with Azole C(sp^2)−H Bonds. *Angew. Chem., Int. Ed.* **2021**, *60*, 380–384.
21. Pavlishchuk, V. V.; Addison, A. W. Conversion Constants for Redox Potentials Measured Versus Different Reference Electrodes in Acetonitrile Solutions at 25°C. *Inorg. Chim. Acta* **2000**, *298*, 97–102.

10. NMR spectra



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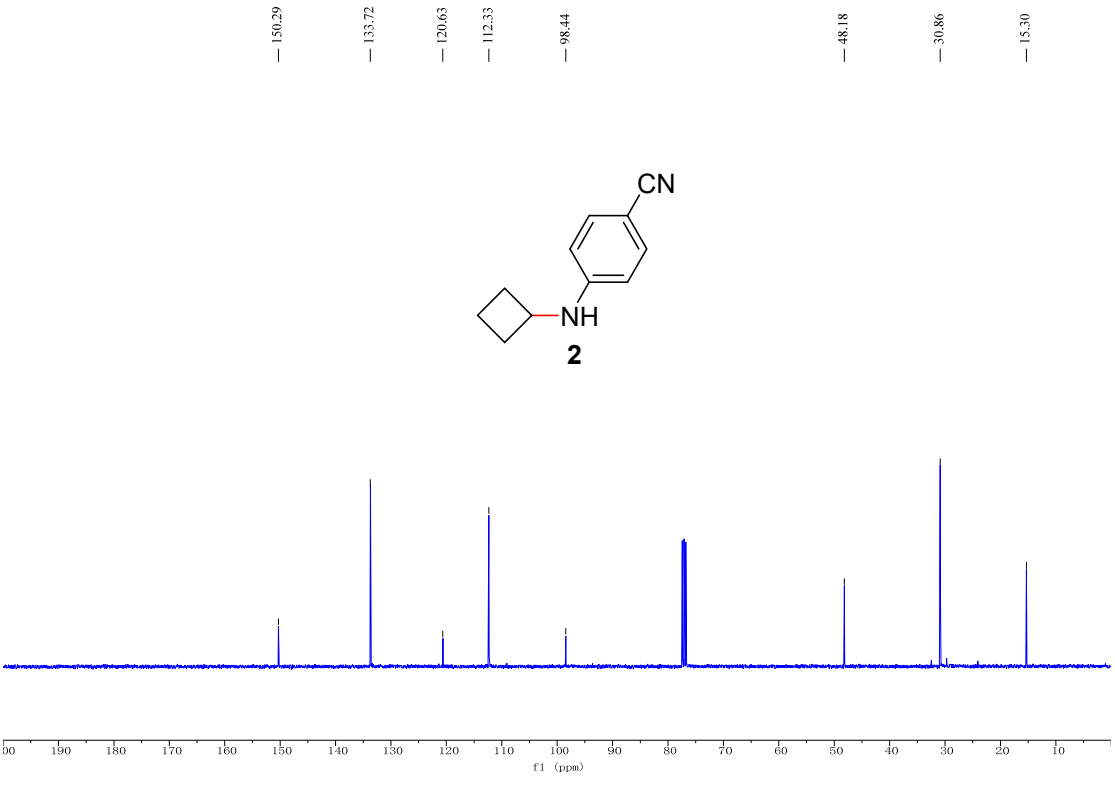
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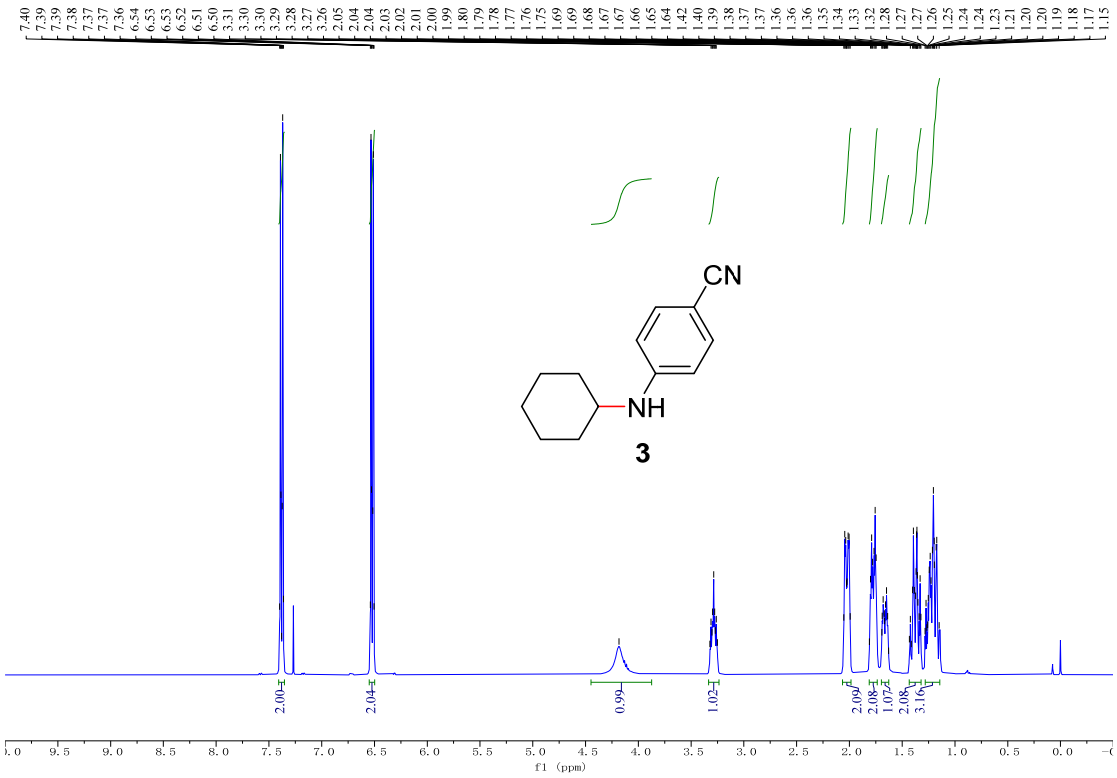
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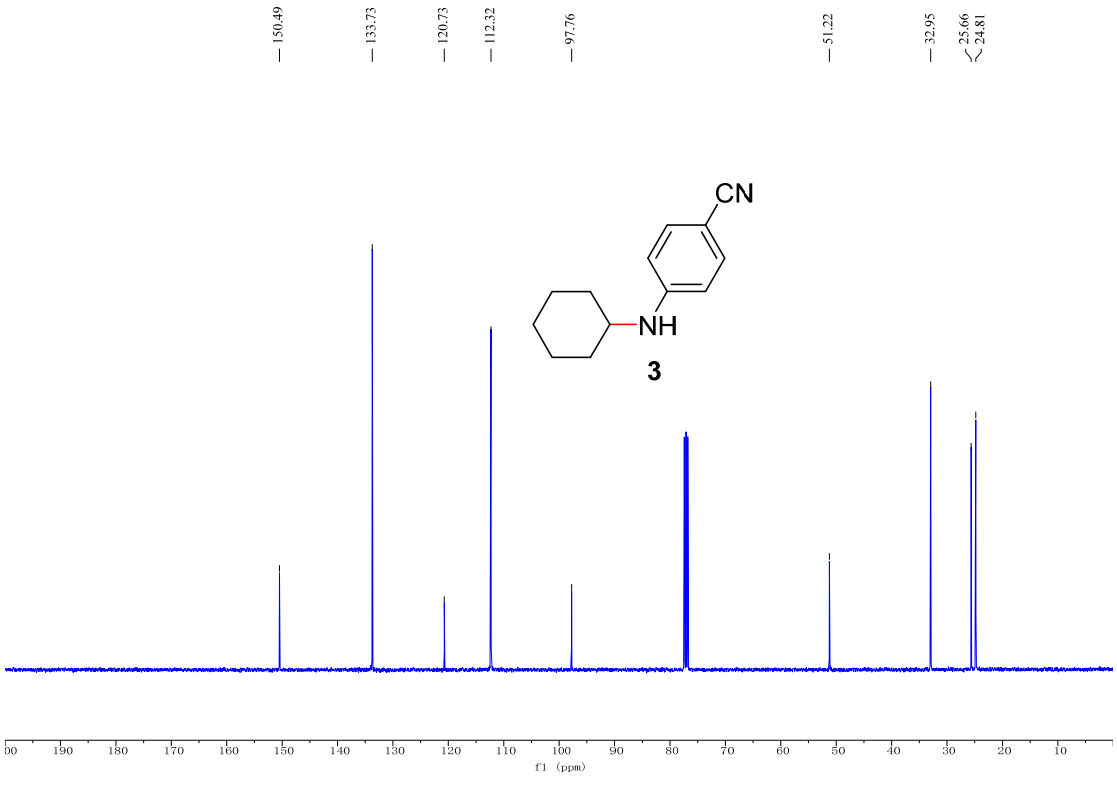
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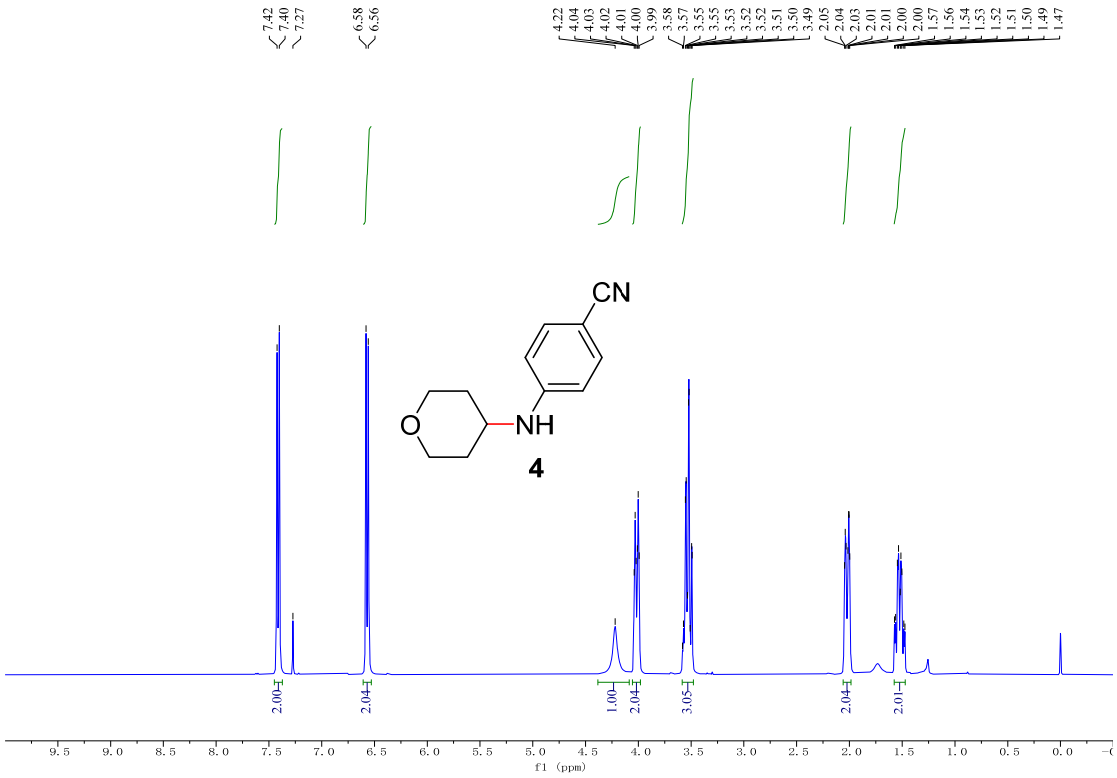
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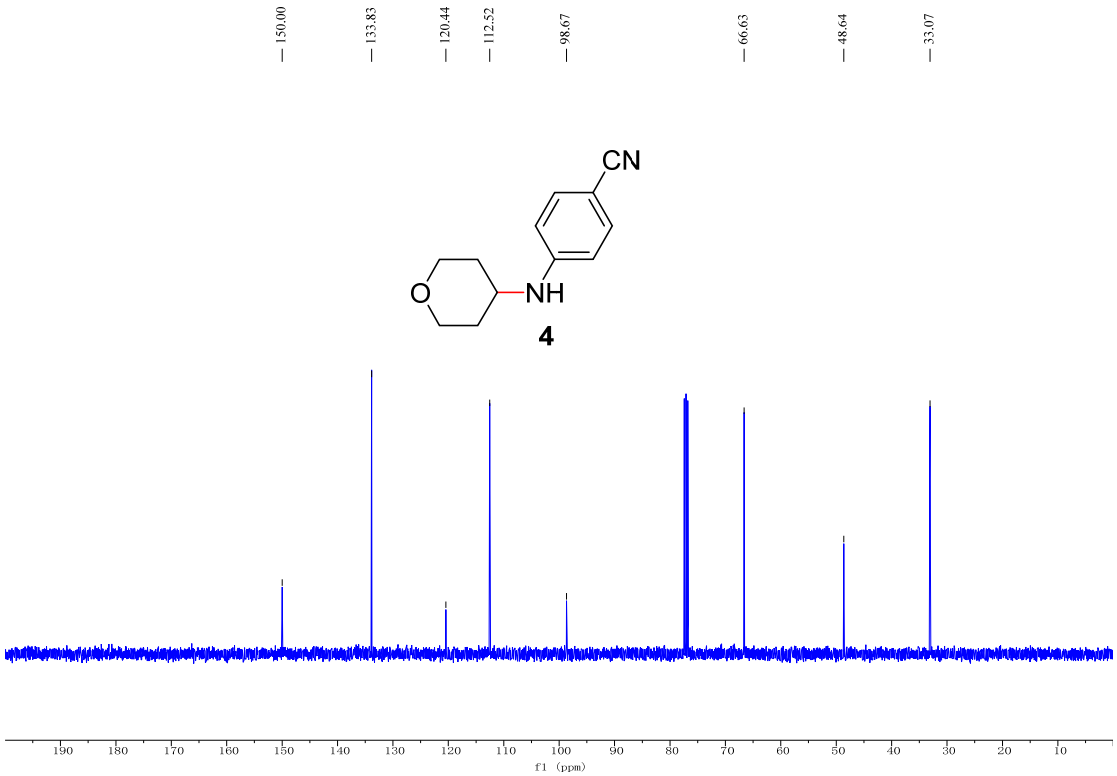
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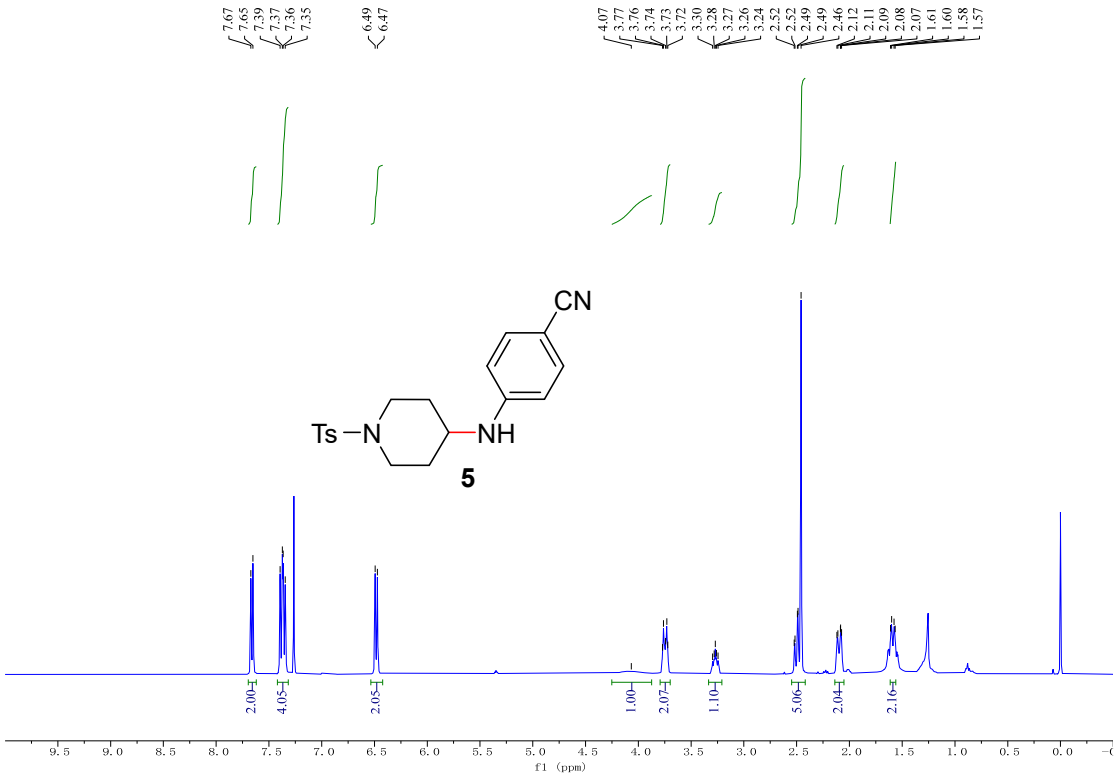
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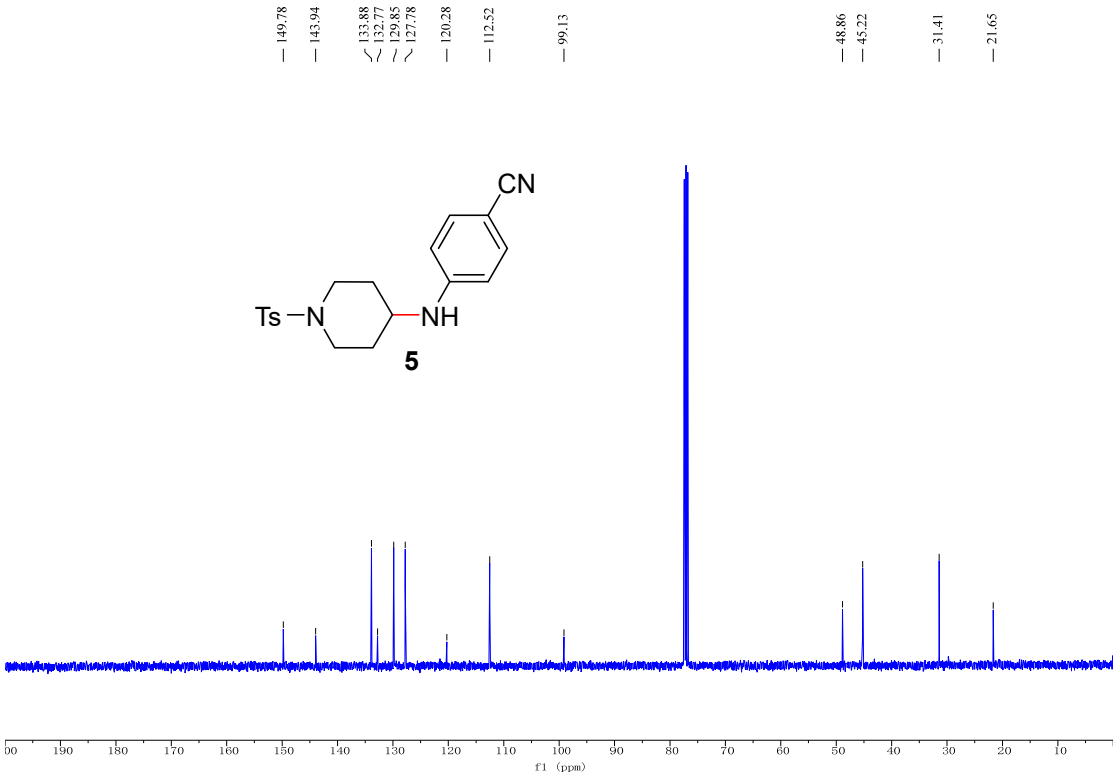
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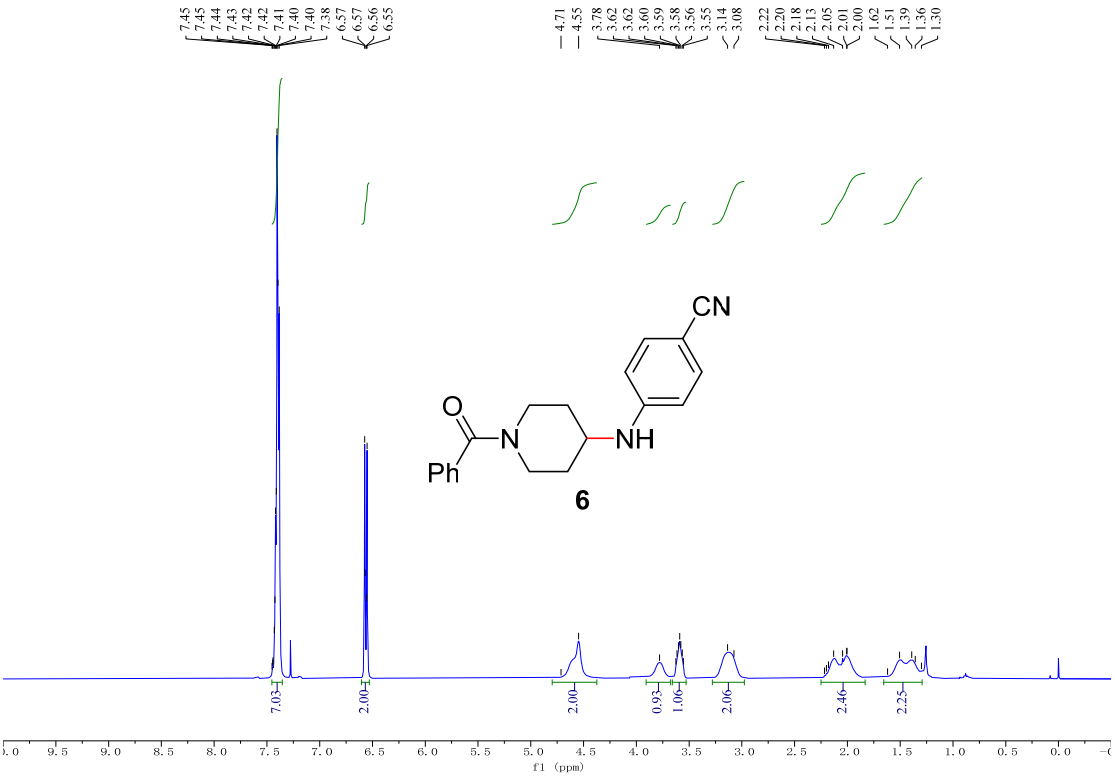
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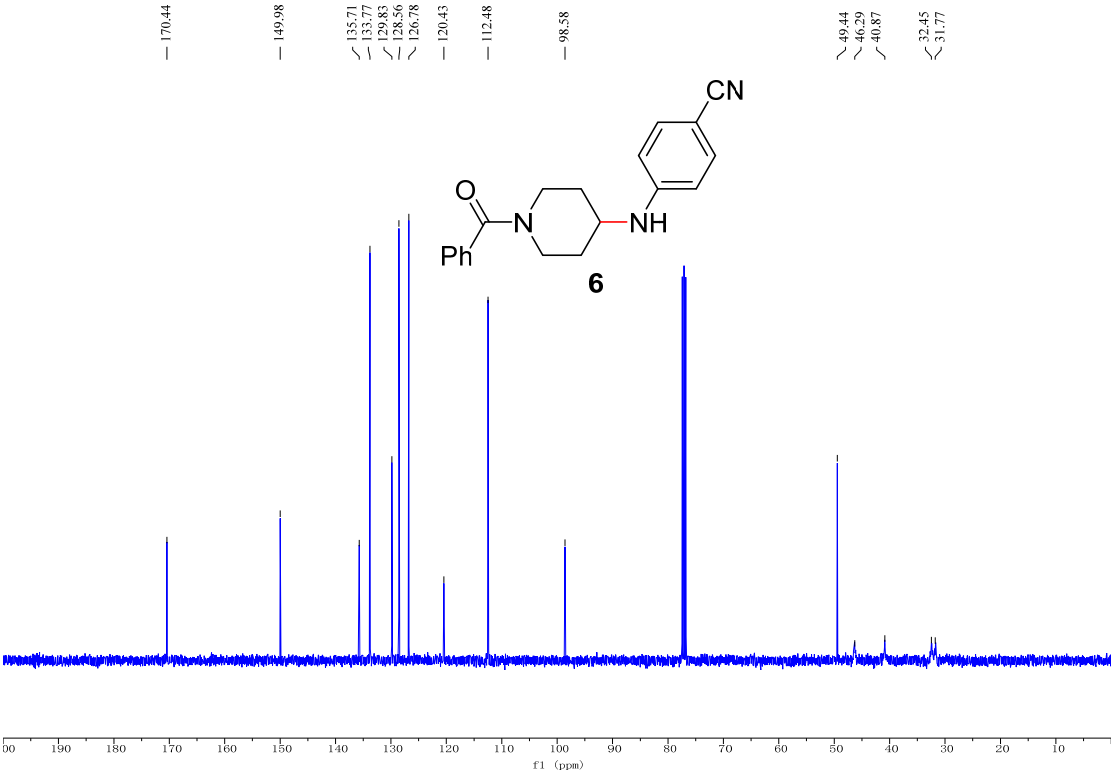
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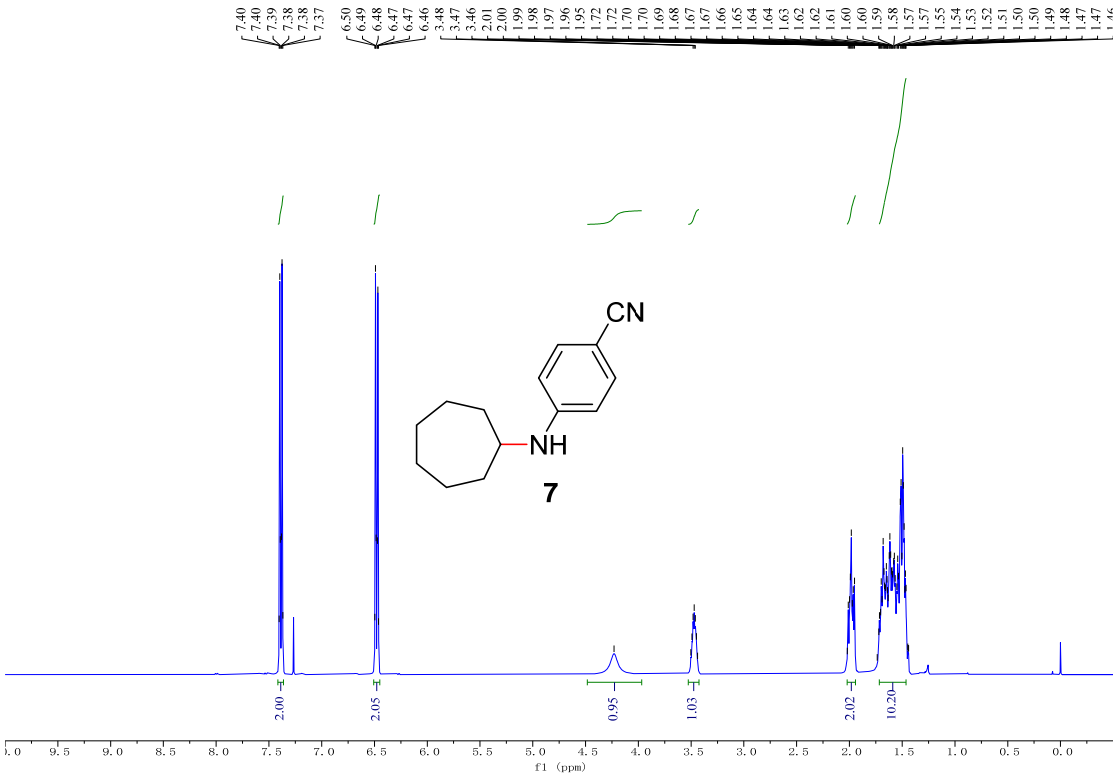
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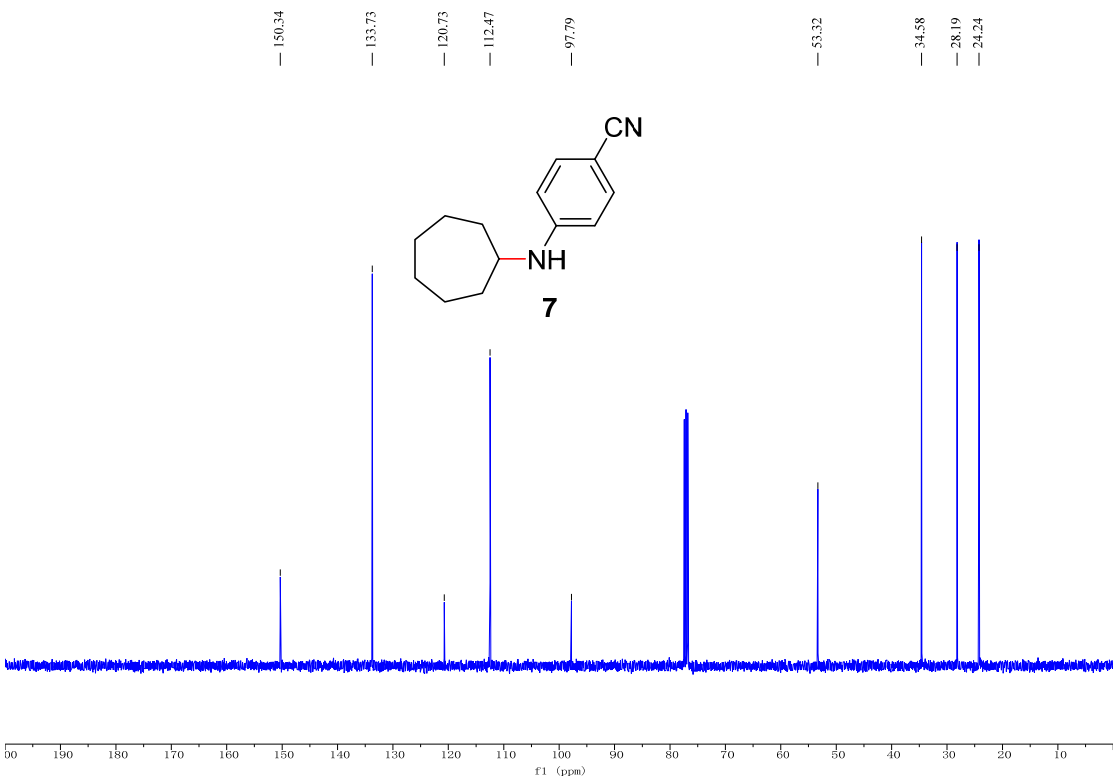
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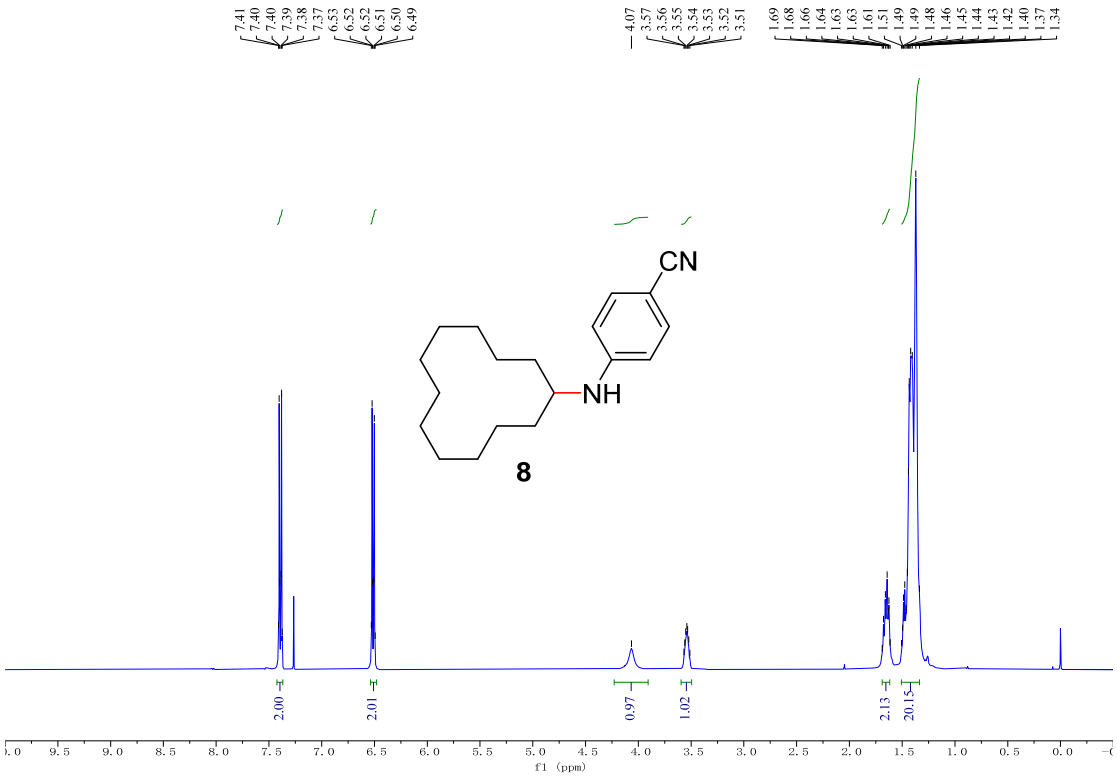
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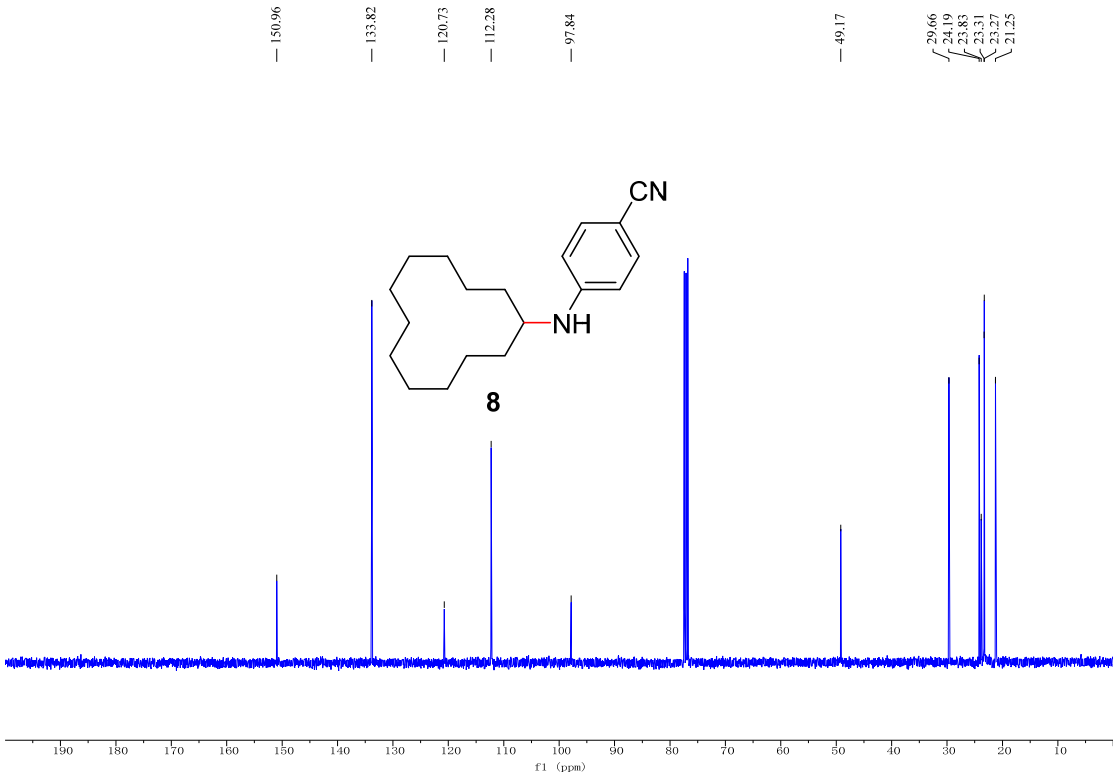
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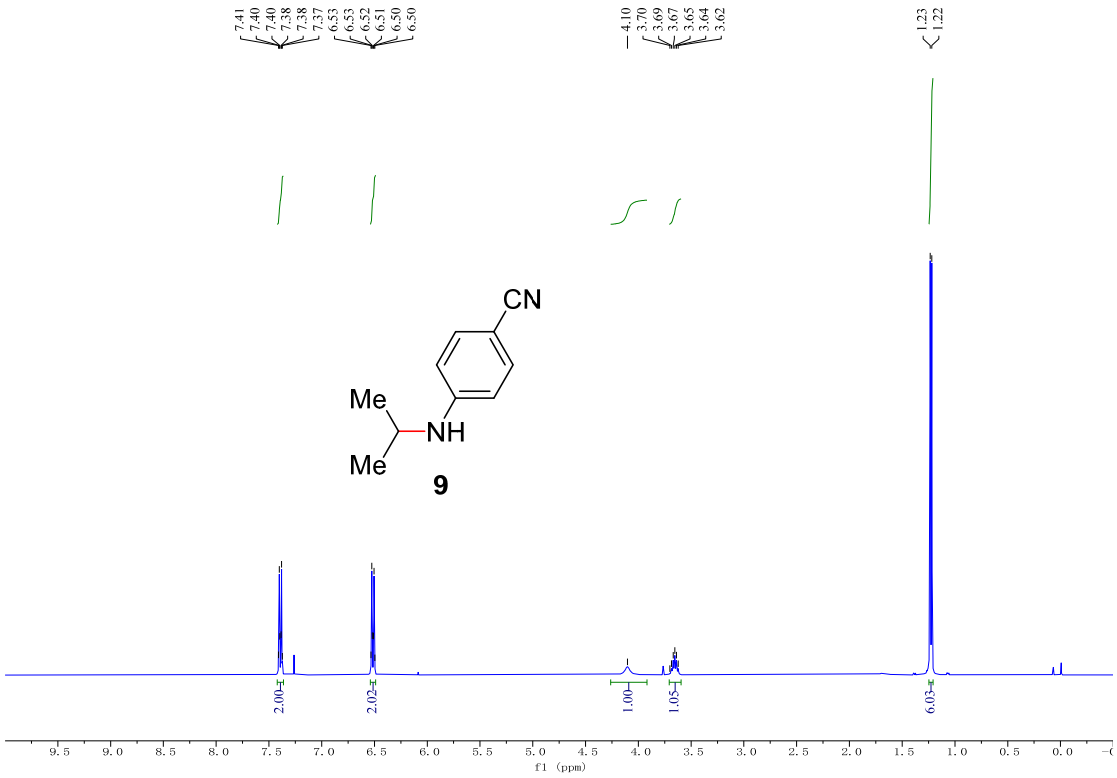
f1 (ppm)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3.69
3.67
3.65
3.64
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Me
NH
Me
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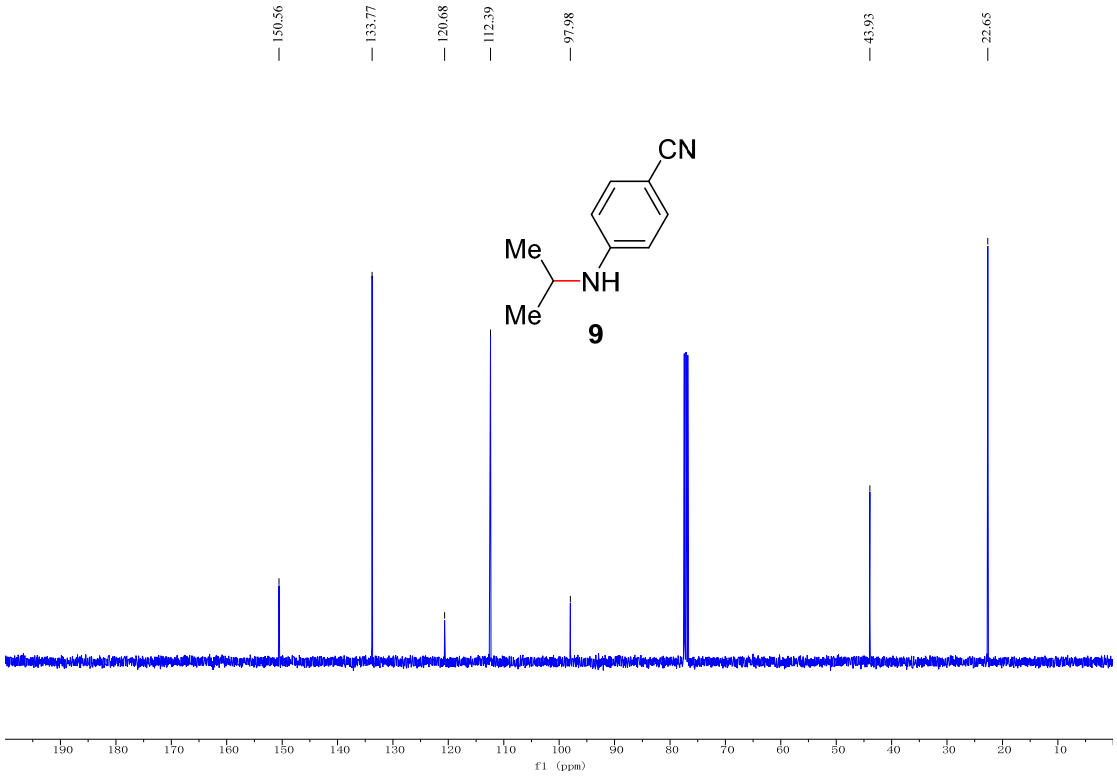
1.00
1.05
6.03
f1 (ppm)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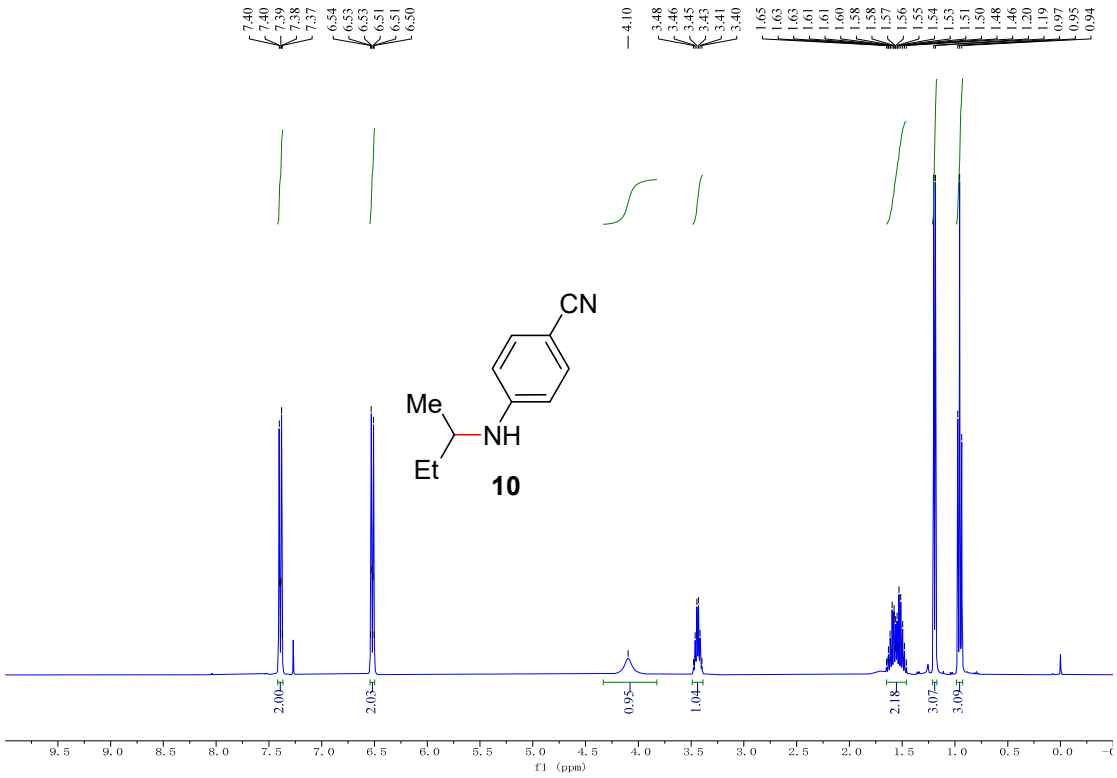
9
f1 (ppm)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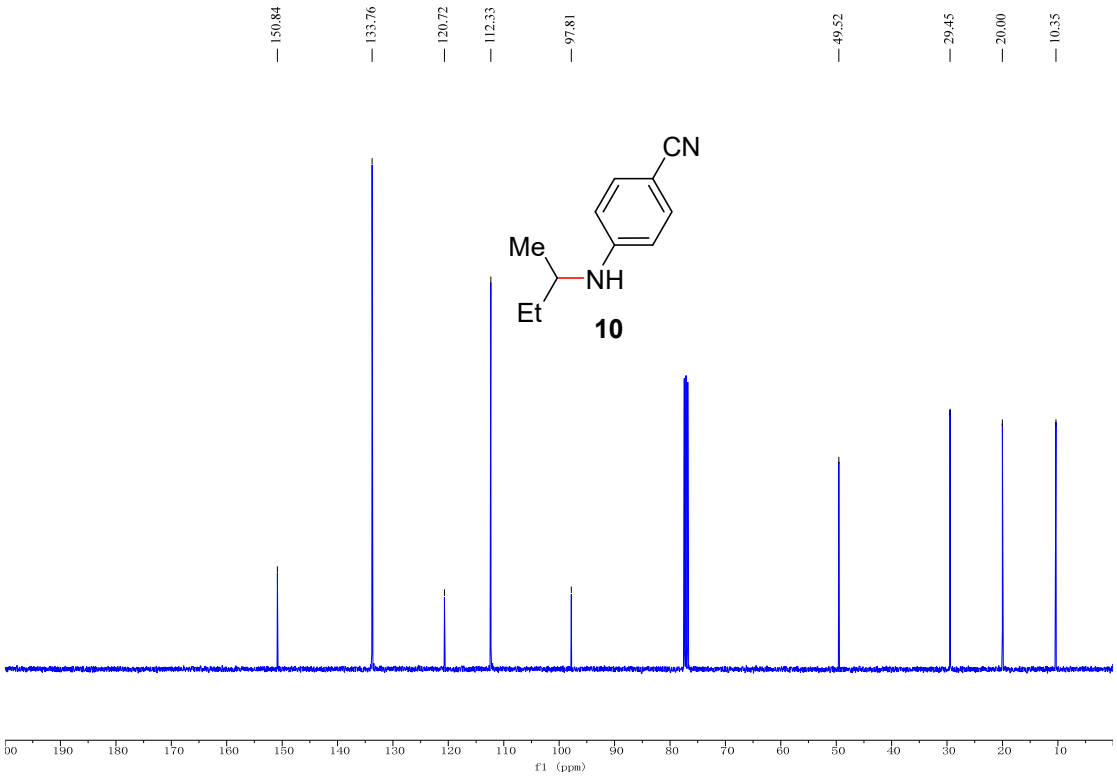
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NH
Et
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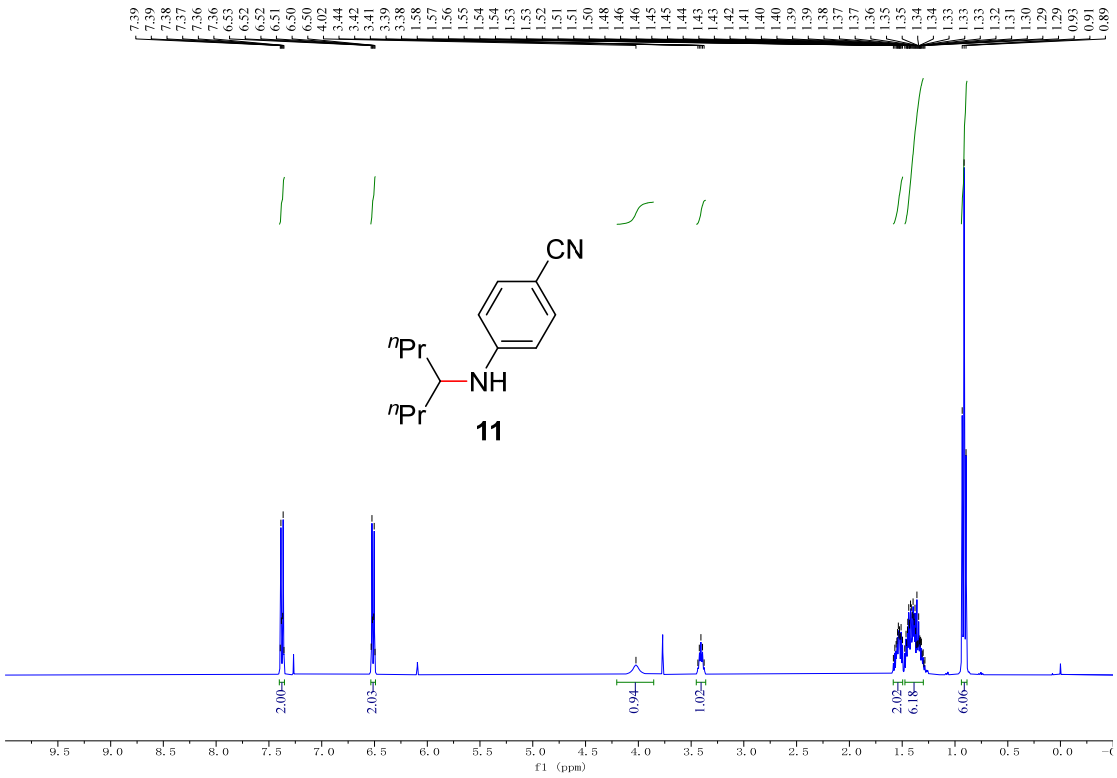
f1 (ppm)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6.06
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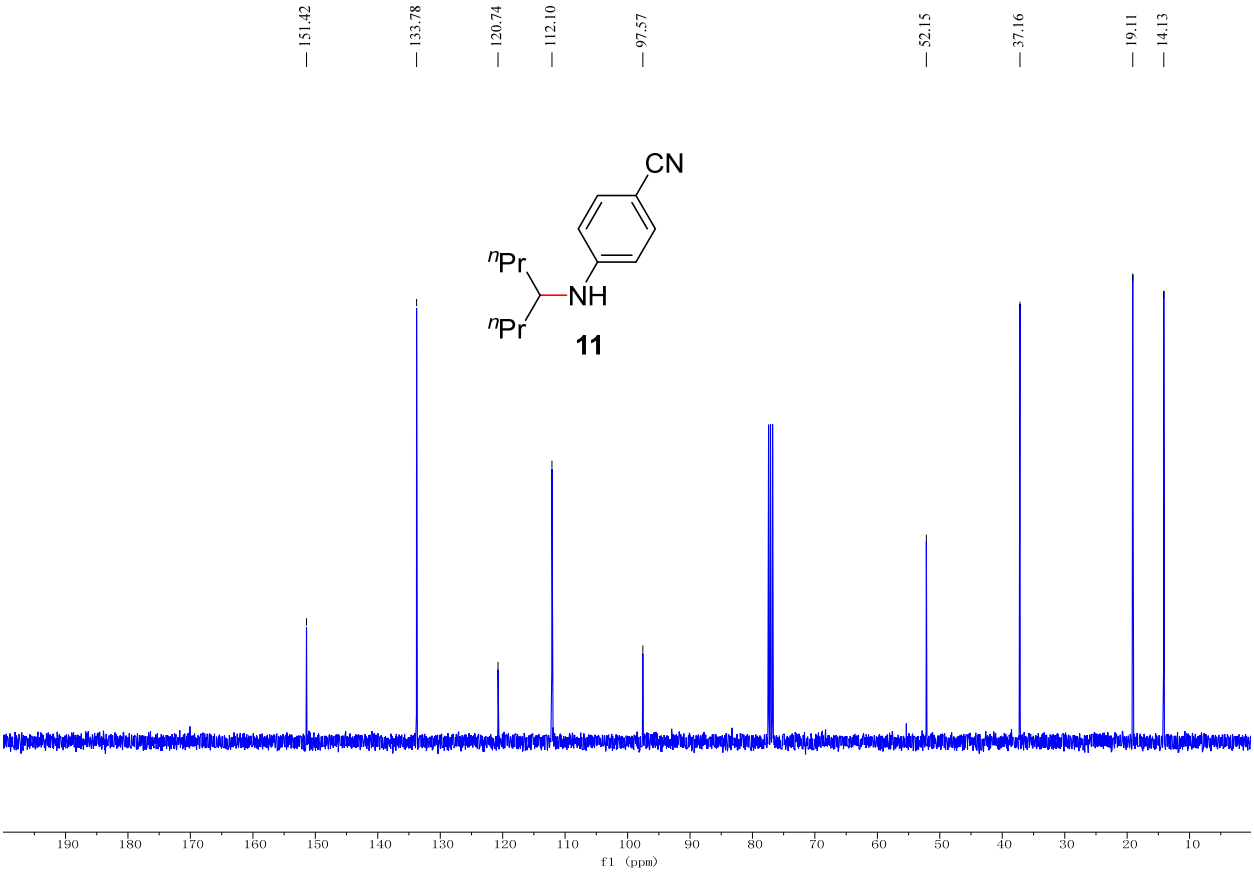
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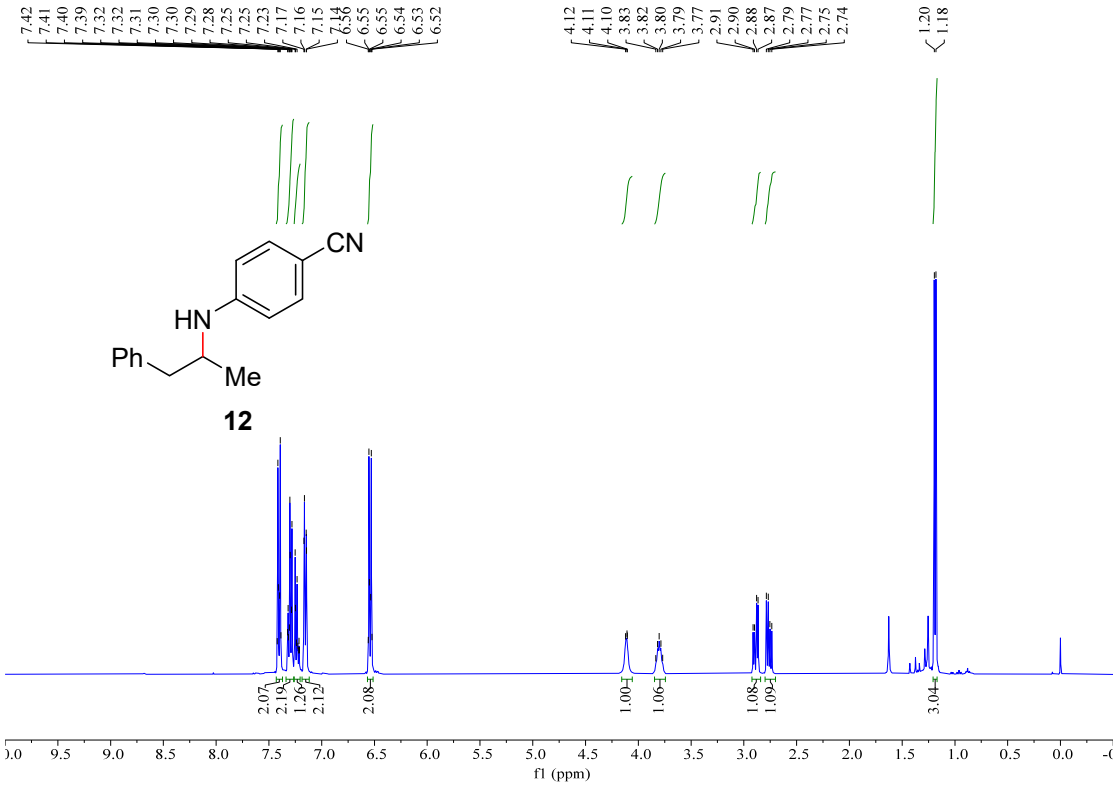
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2.75
2.74
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Ph
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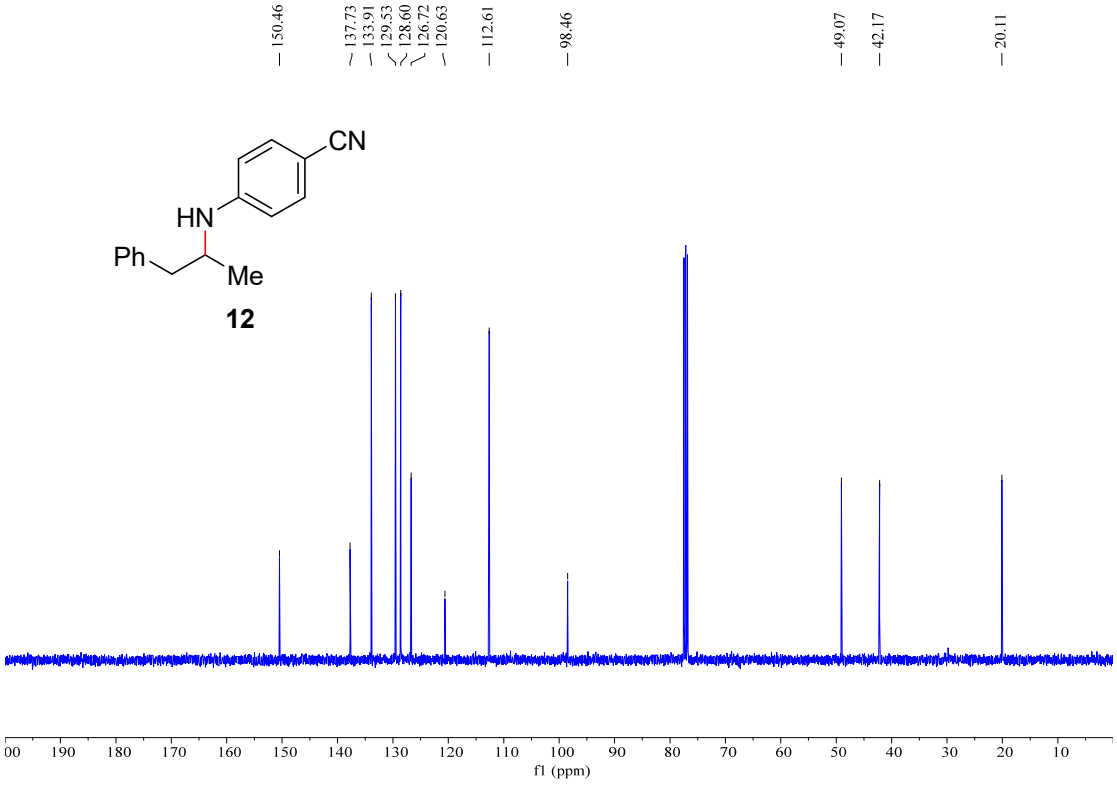
f1 (ppm)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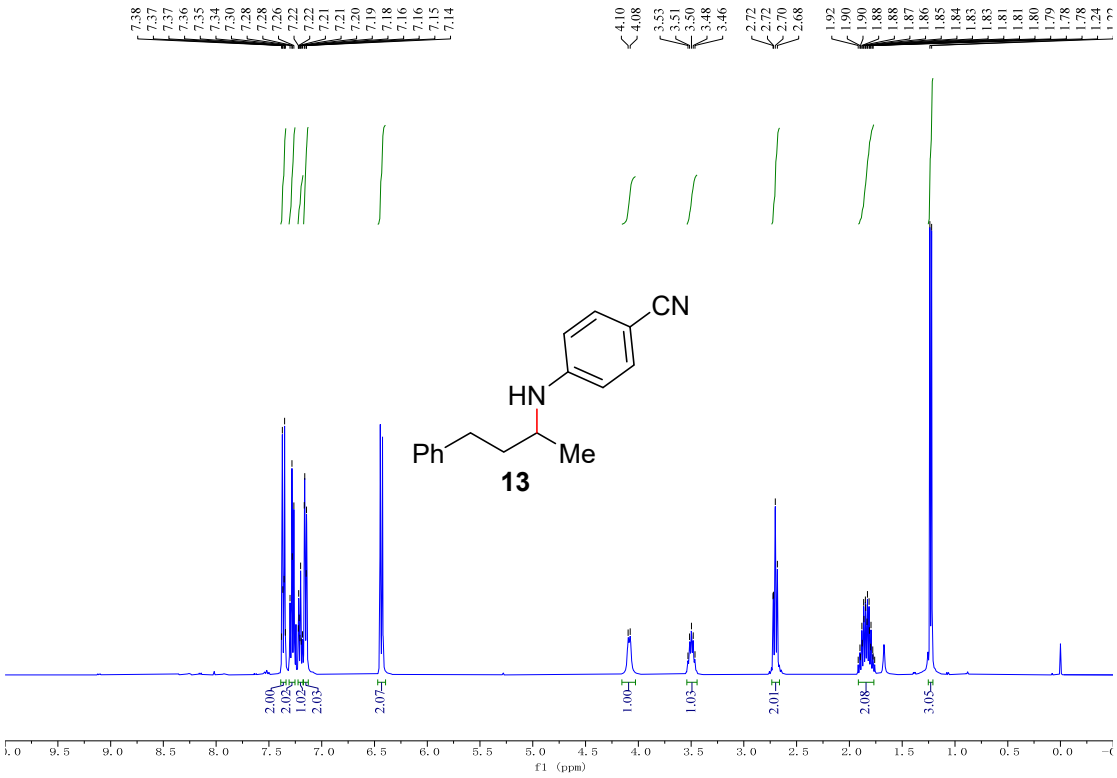
CN
HN
Ph
Me
12
f1 (ppm)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7.18
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7.15
7.14
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1.80
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1.24
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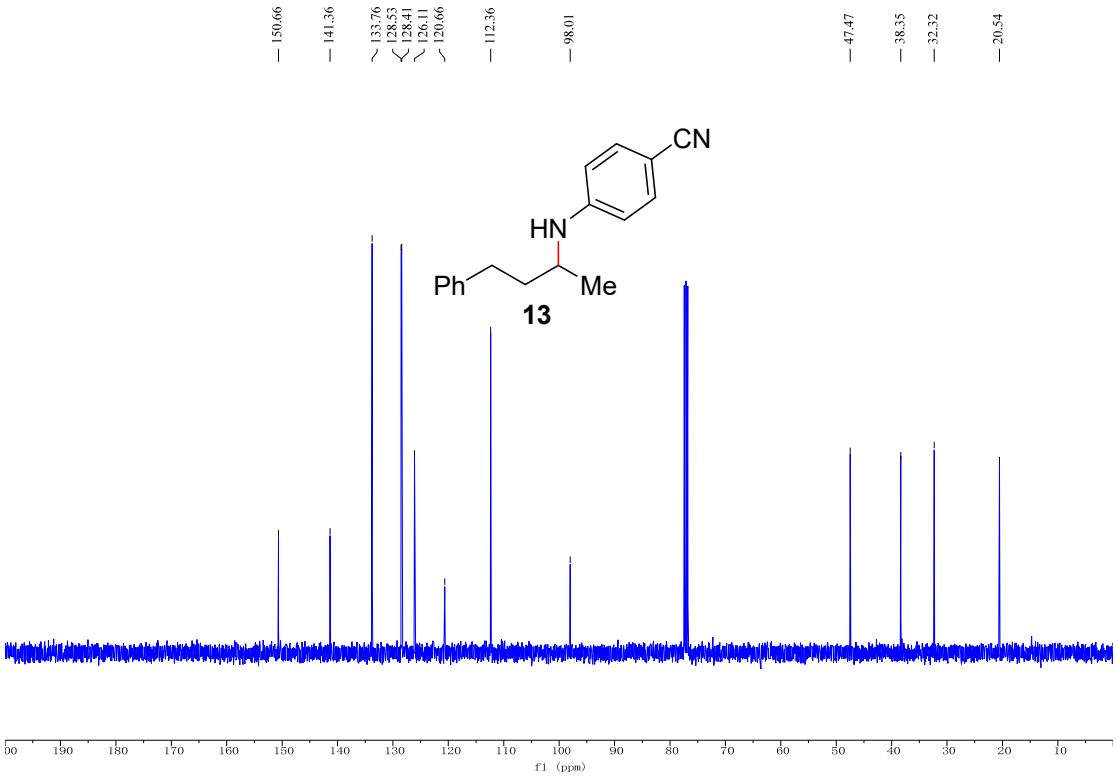
3.05
f1 (ppm)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20.54
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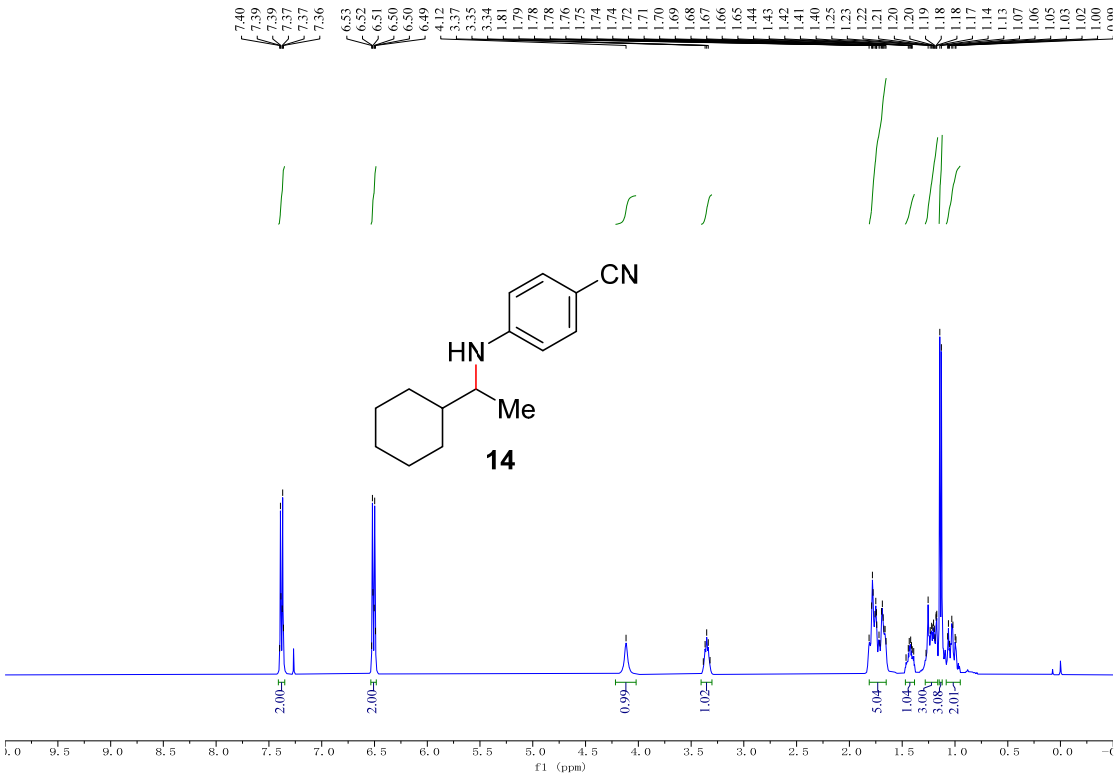
HN
Ph
Me
13
f1 (ppm)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1.04
3.00
3.08
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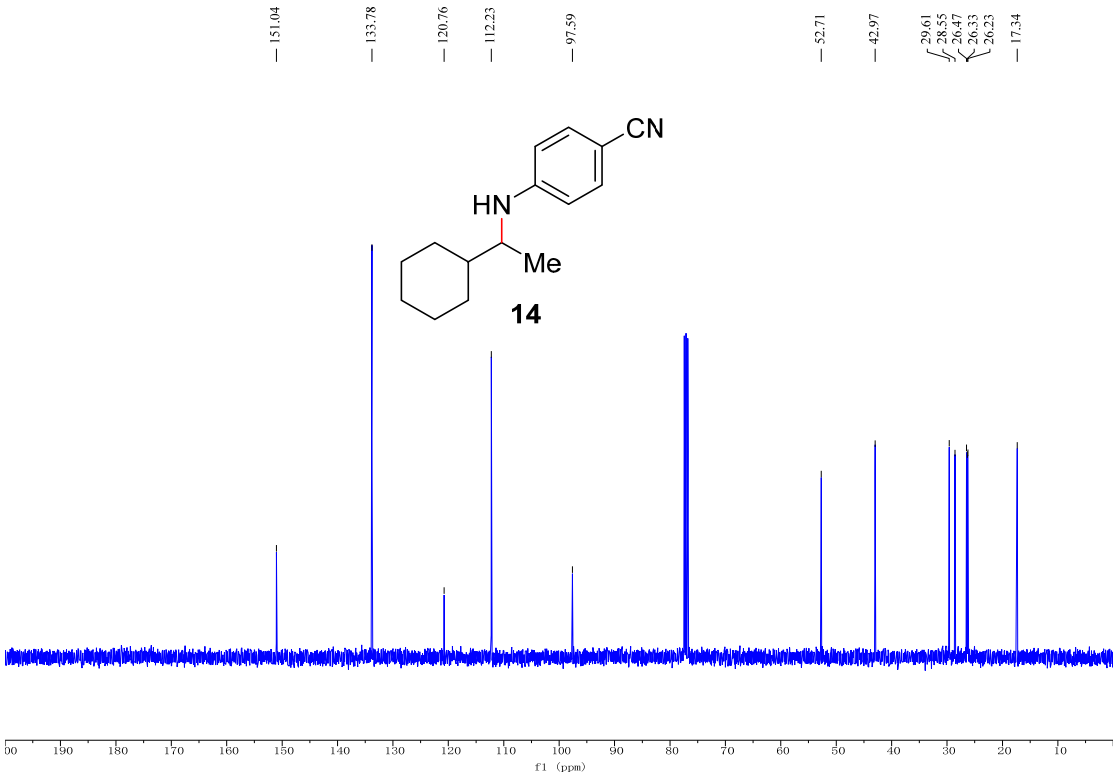
f1 (ppm)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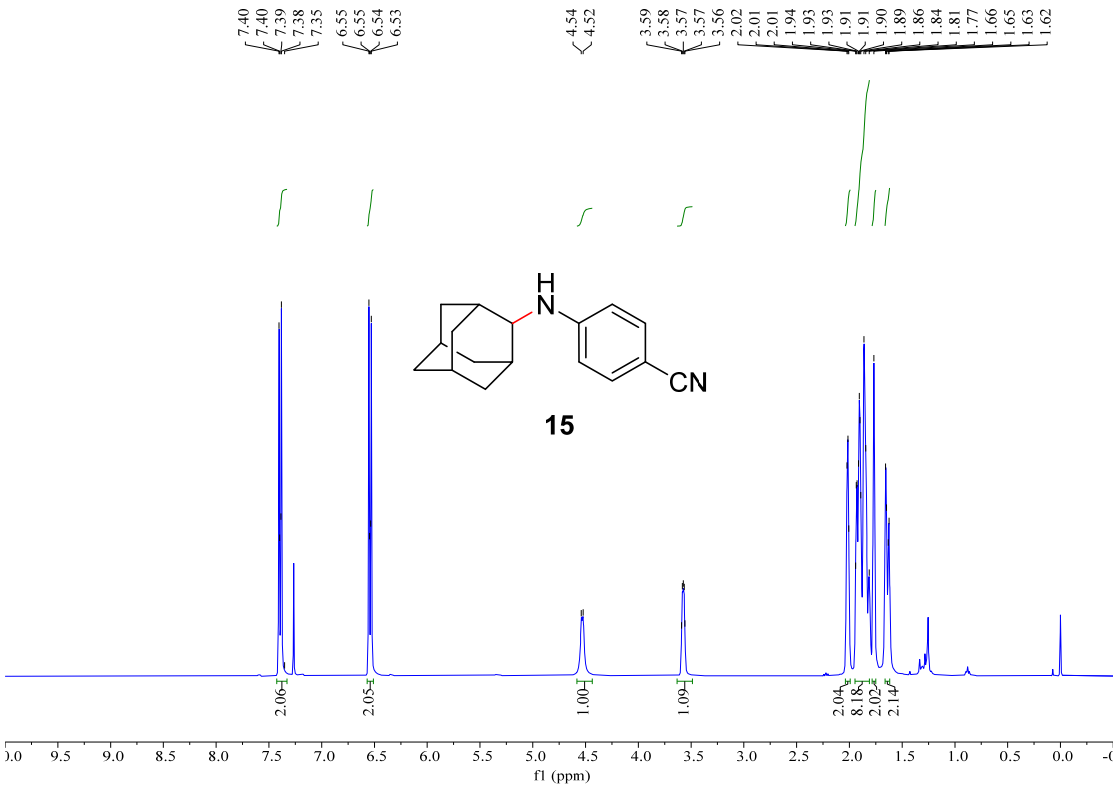
HN
Me
14
f1 (ppm)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1.63
1.62
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1.00
1.09
2.04
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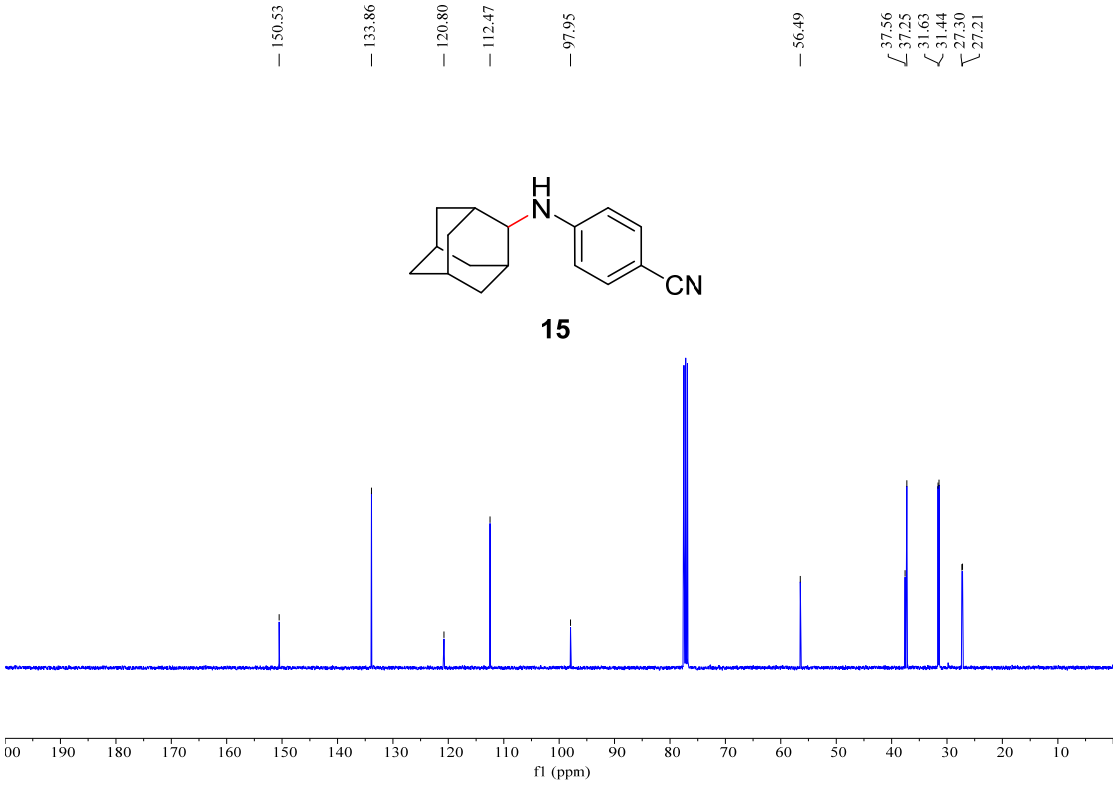
2.14
f1 (ppm)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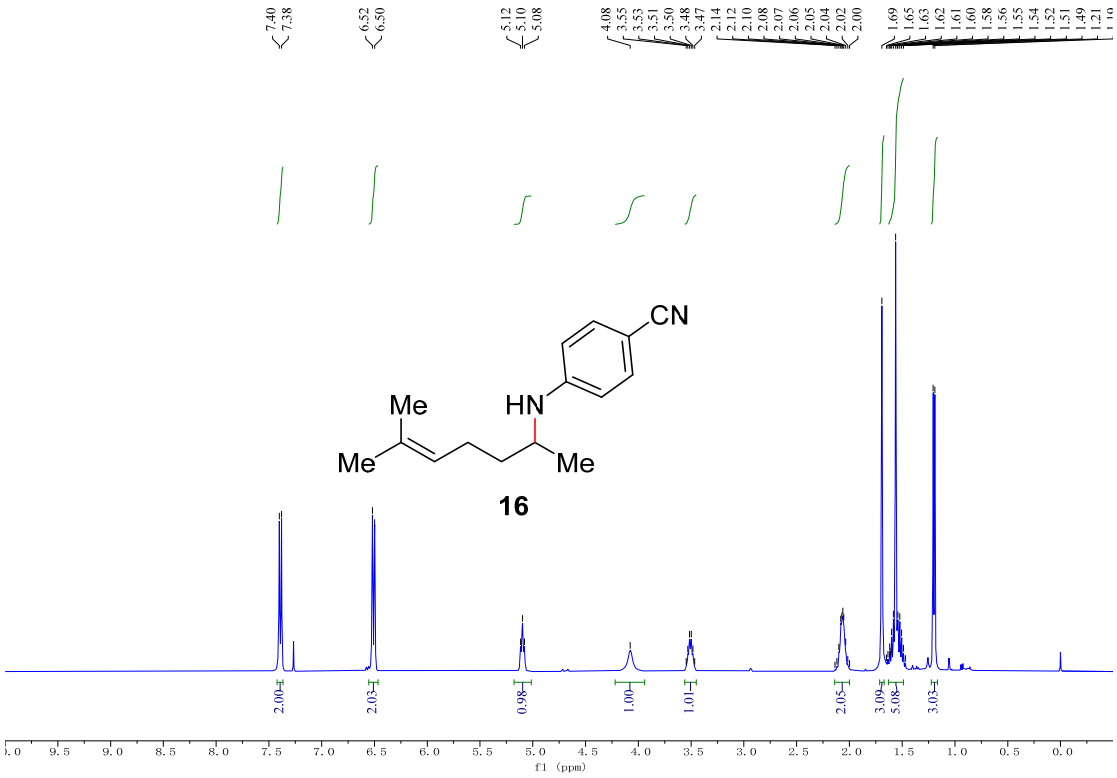
f1 (ppm)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2.08
2.07
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2.05
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2.02
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1.56
1.55
1.54
1.52
1.51
1.49
1.21
CN
HN
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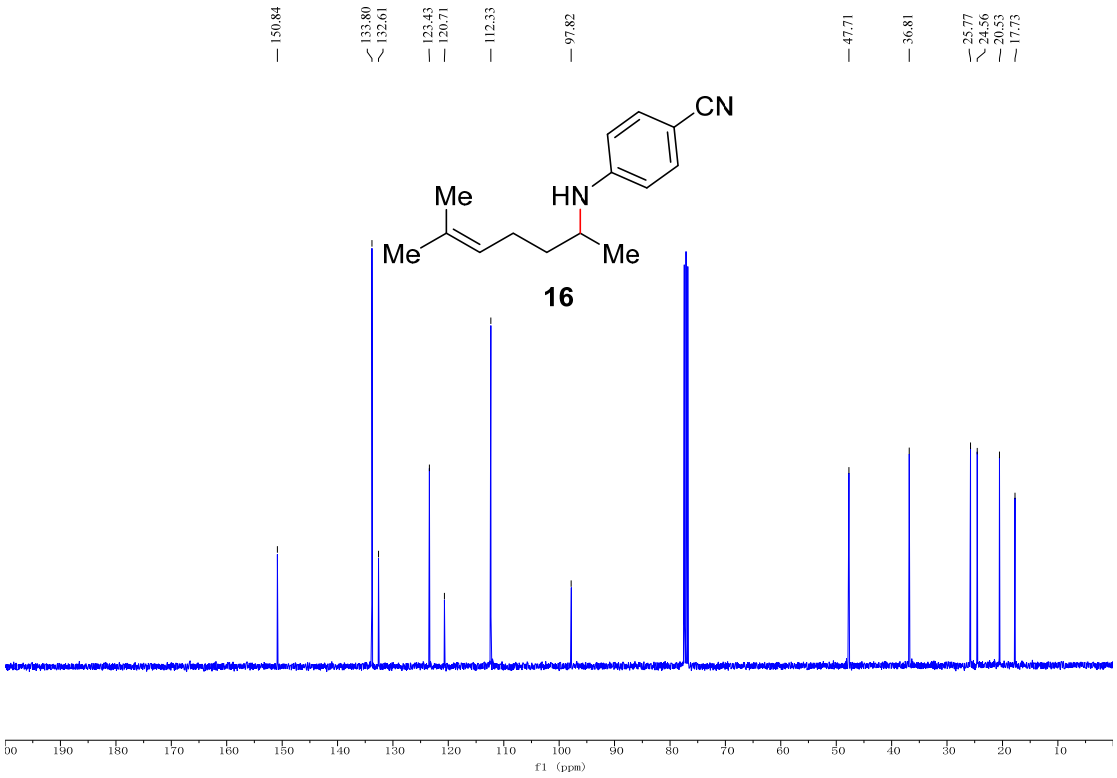
3.09
5.08
3.03
f1 (ppm)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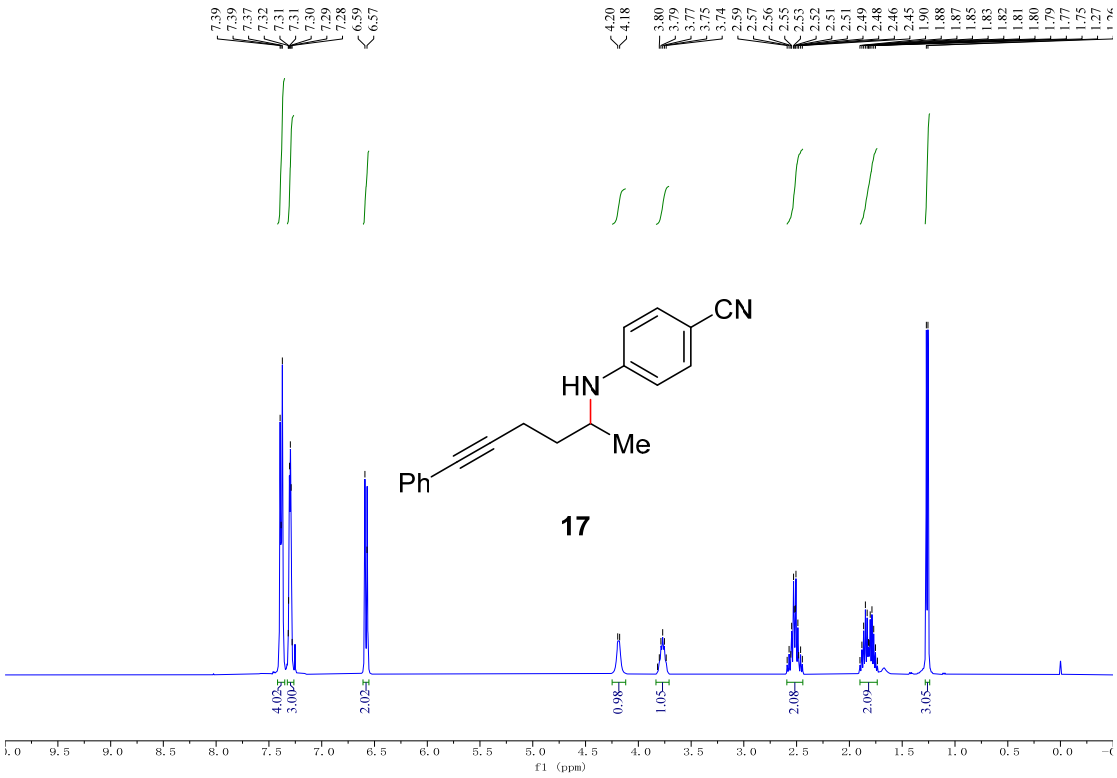
Me
Me
16
f1 (ppm)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3.77
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2.56
2.55
2.53
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2.51
2.49
2.48
2.46
2.45
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1.85
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1.82
1.81
1.80
1.79
1.77
1.75
1.27
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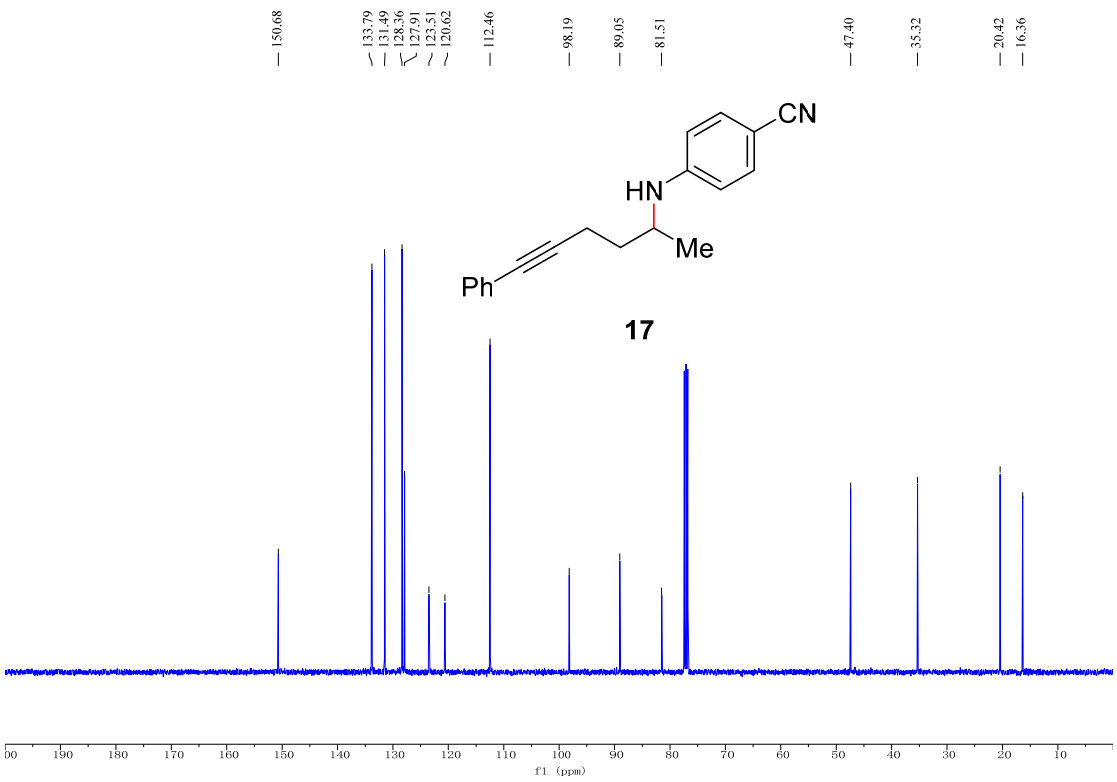
3.05
f1 (ppm)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Ph
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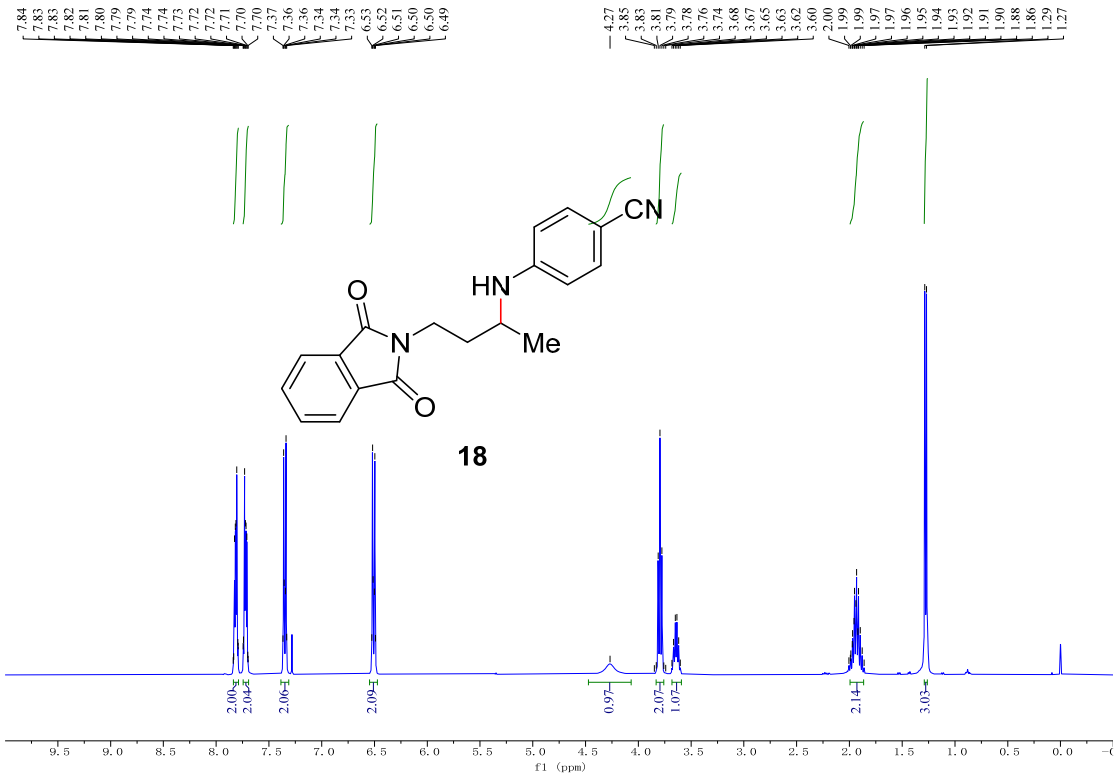
f1 (ppm)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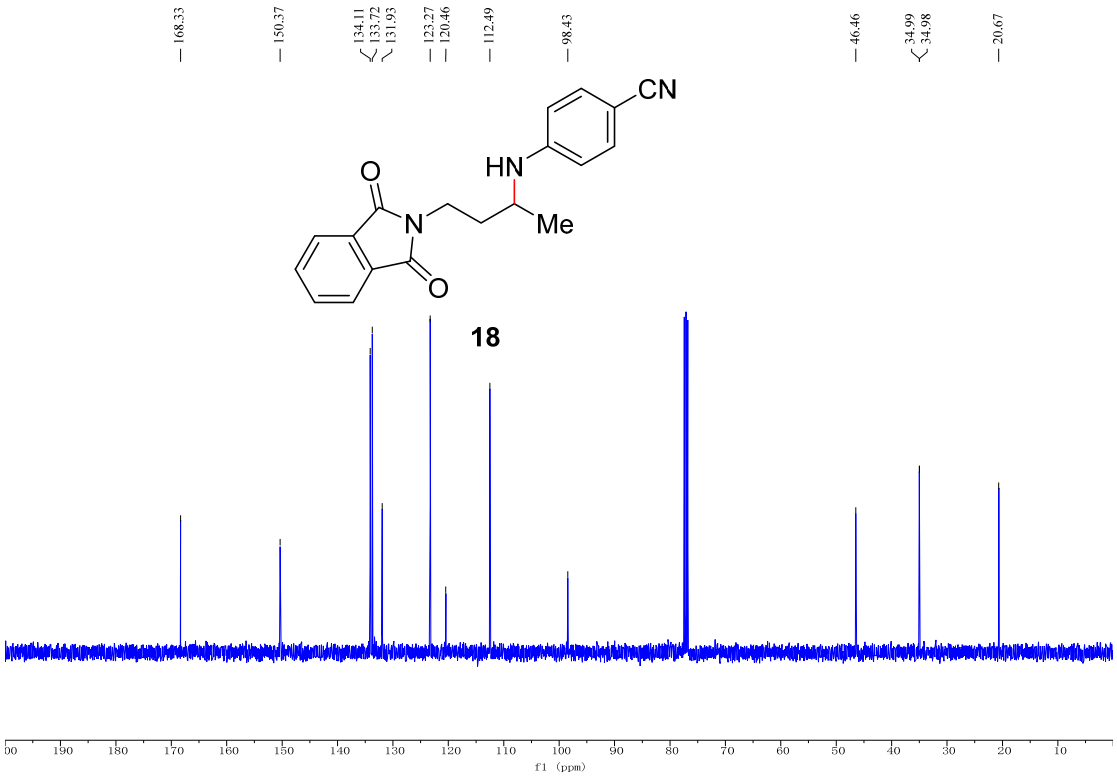
f1 (ppm)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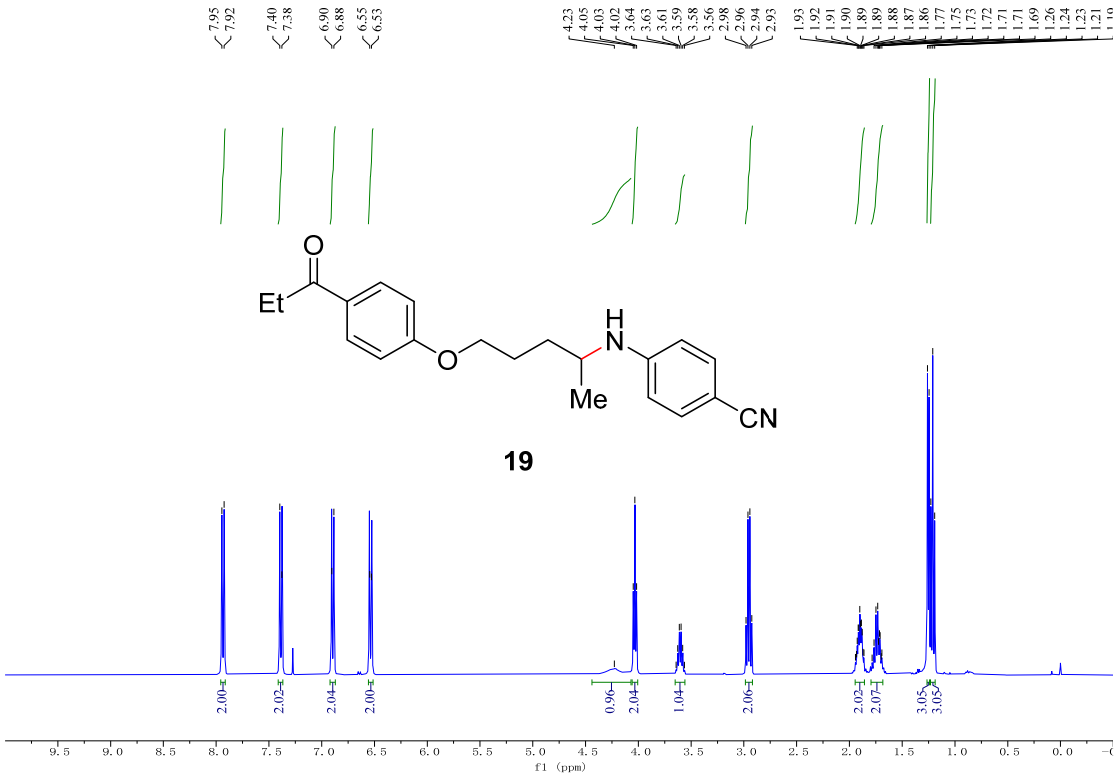
O
18
f1 (ppm)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2.07
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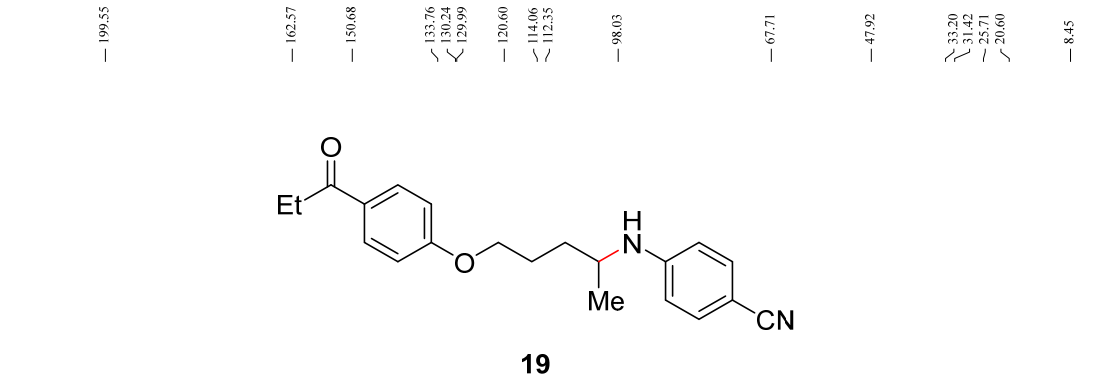
3.05
f1 (ppm)

19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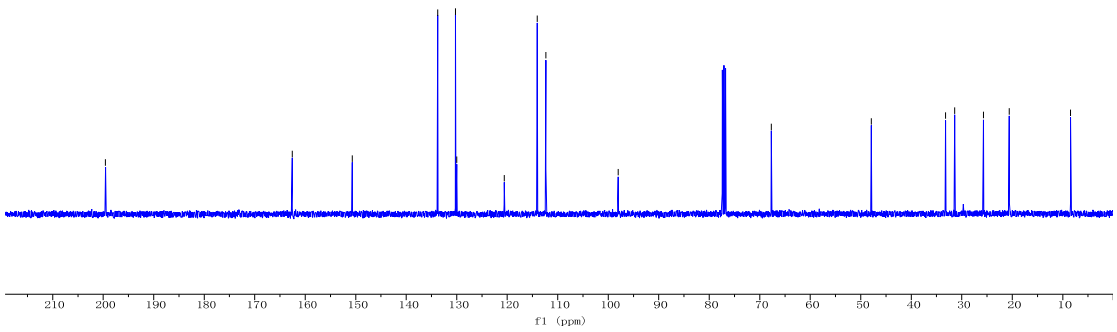
Et
O
H
N
Me
CN
f1 (ppm)

19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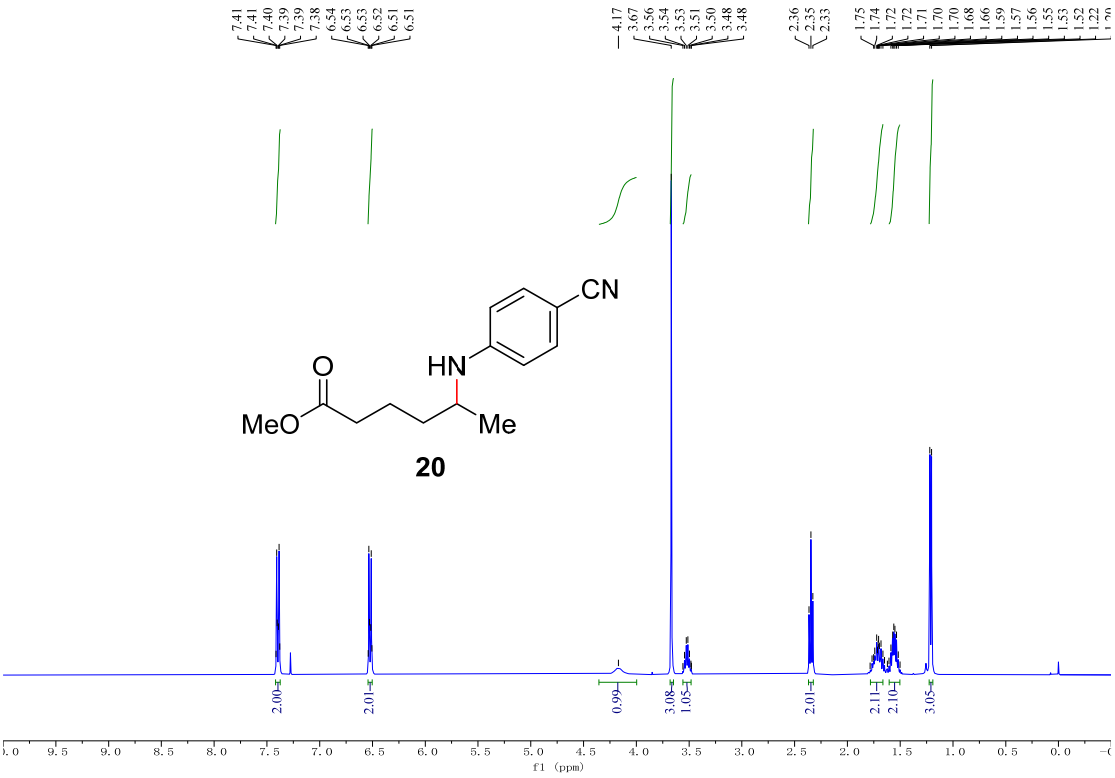
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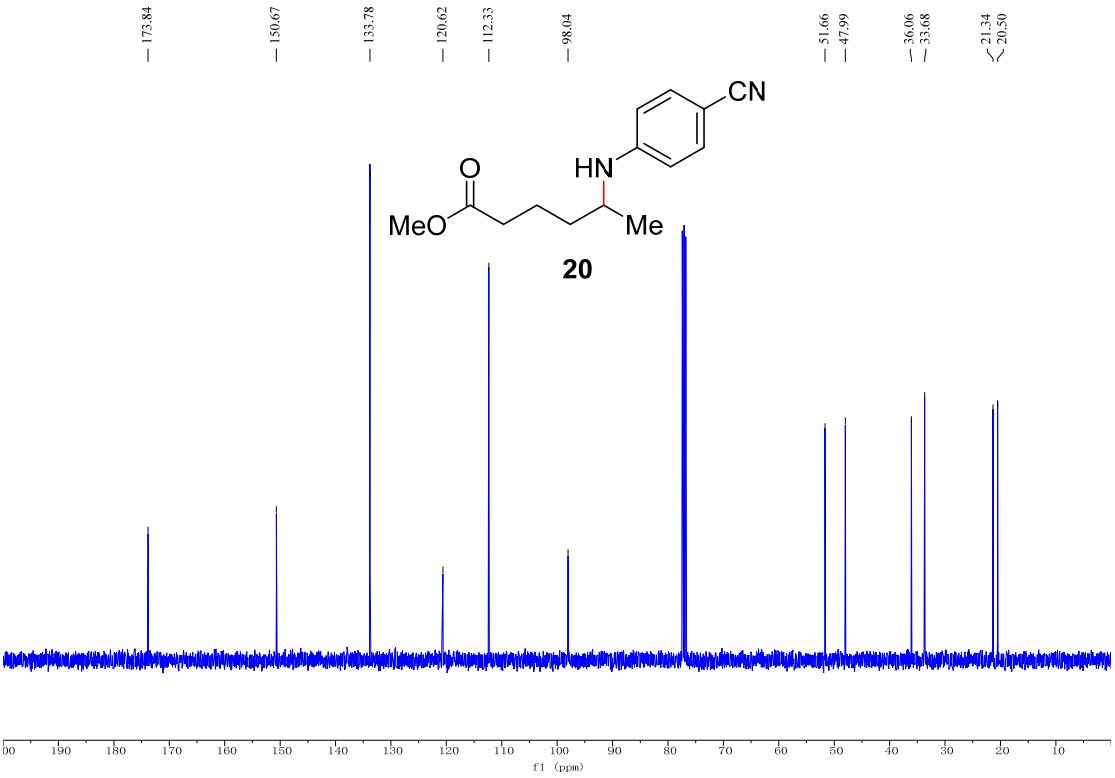
3.05
f1 (ppm)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HN
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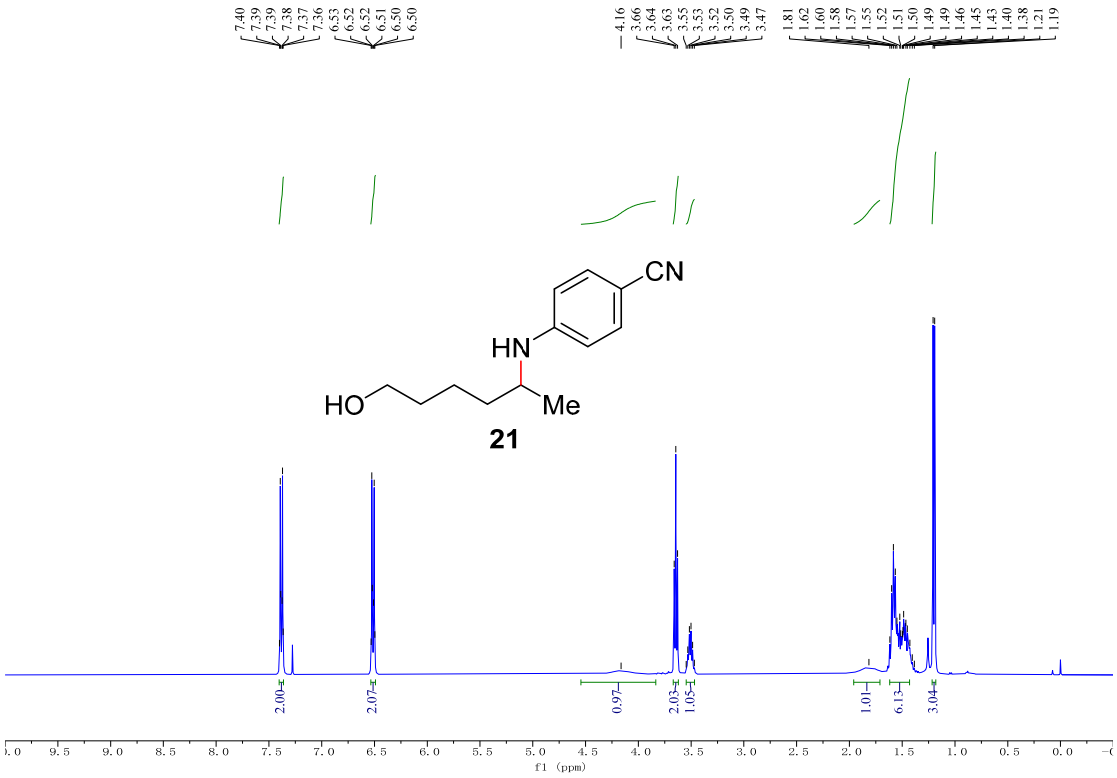
MeO
Me
20
f1 (ppm)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1.21
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1.01
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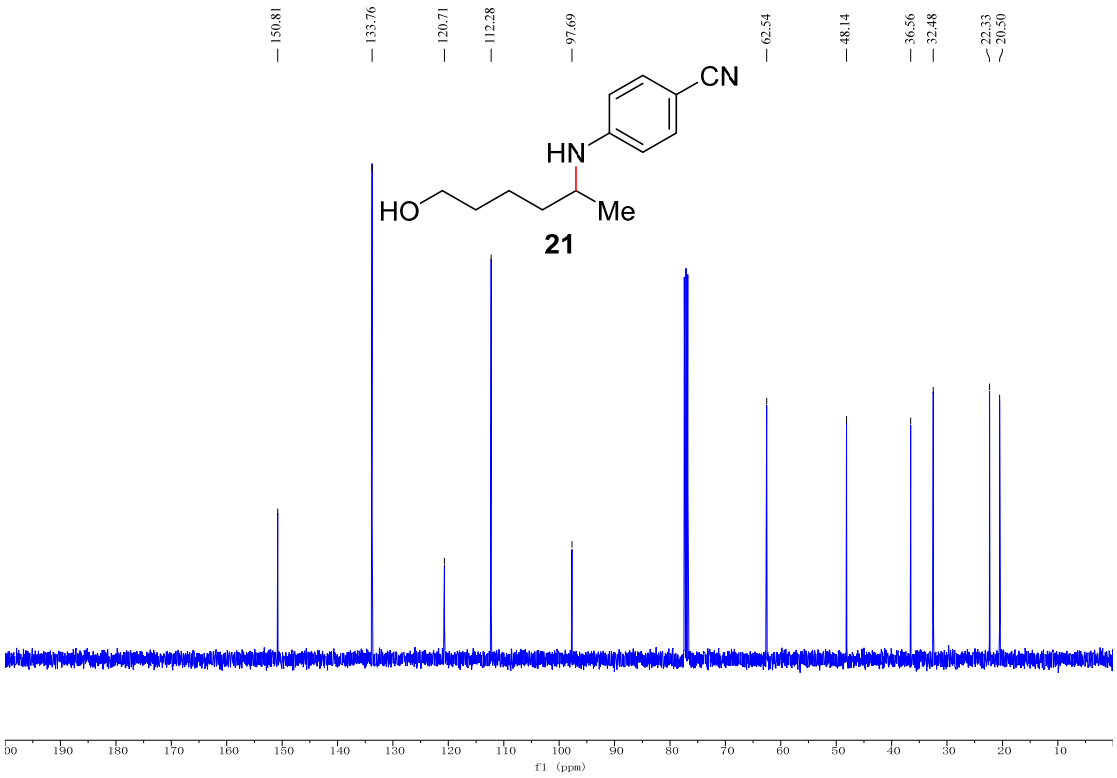
3.04
f1 (ppm)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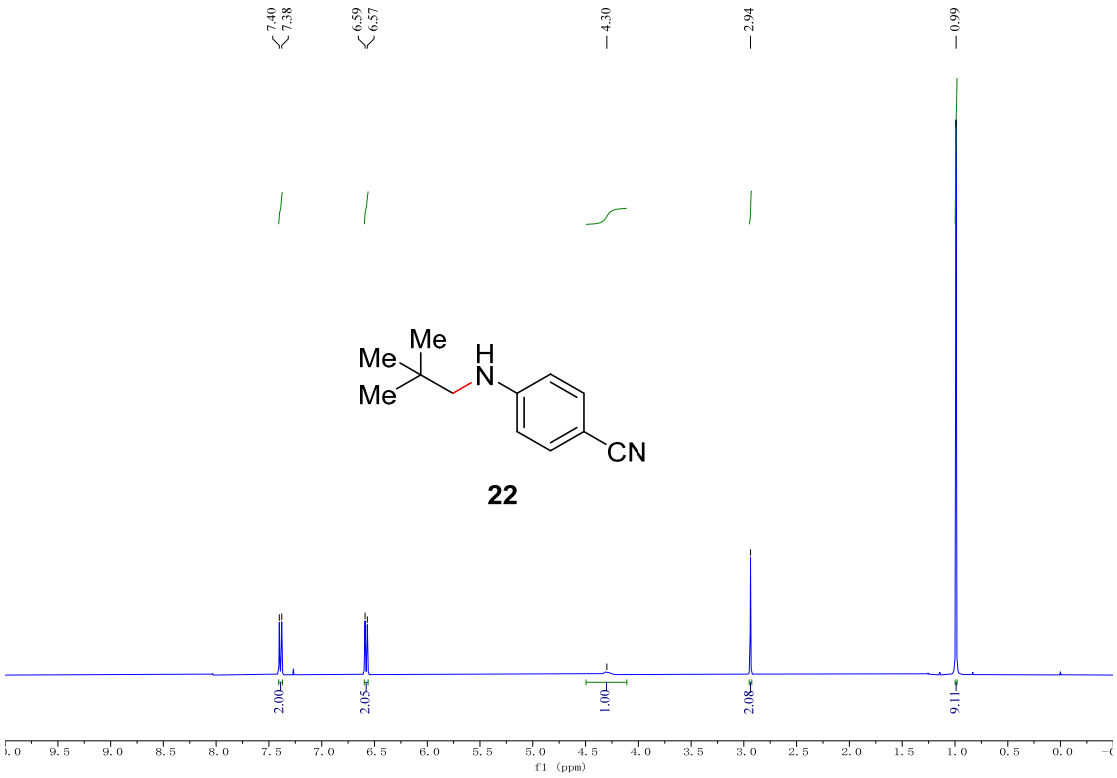
f1 (ppm)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Me
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H
N
CN
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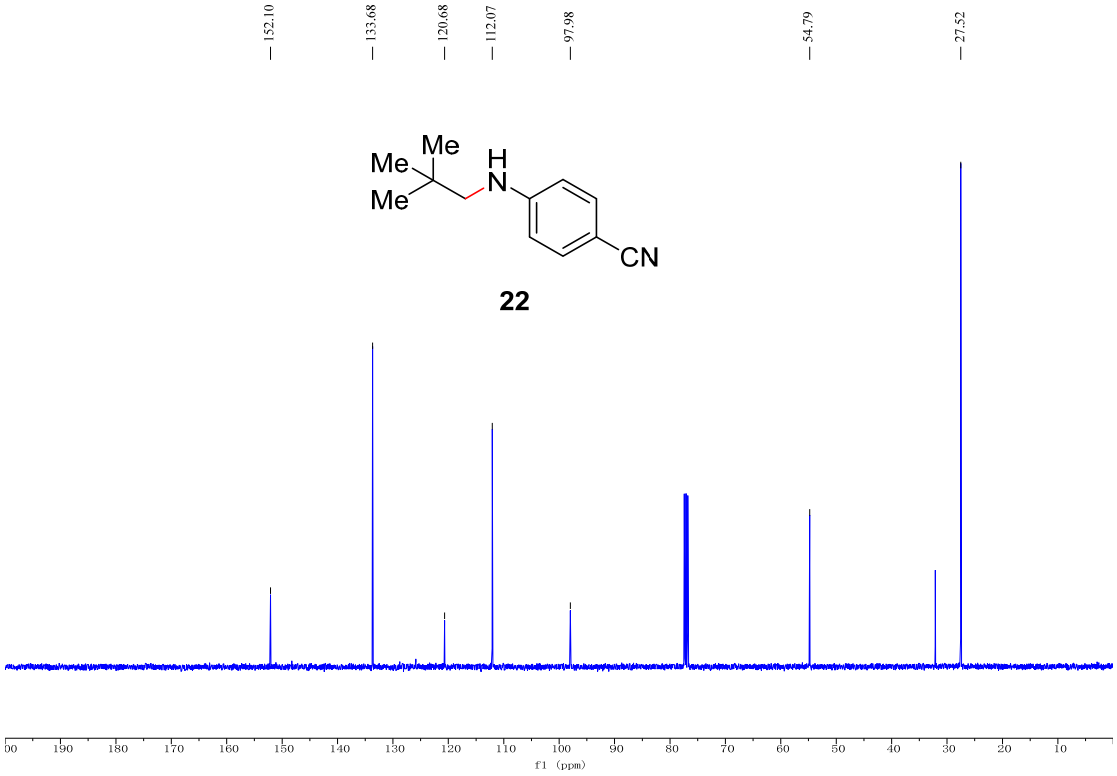
2.05
1.00
2.08
9.11
f1 (ppm)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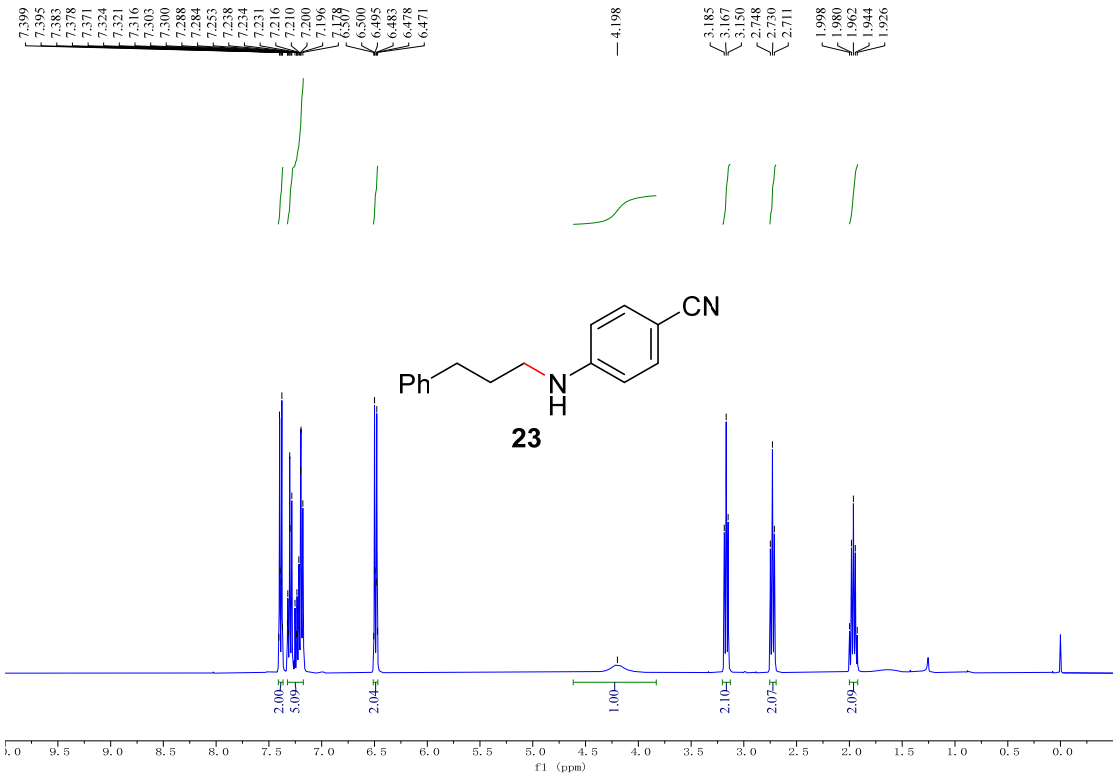
133.68
120.68
112.07
97.98
54.79
27.52
Me
Me
Me
H
N
CN
22
f1 (ppm)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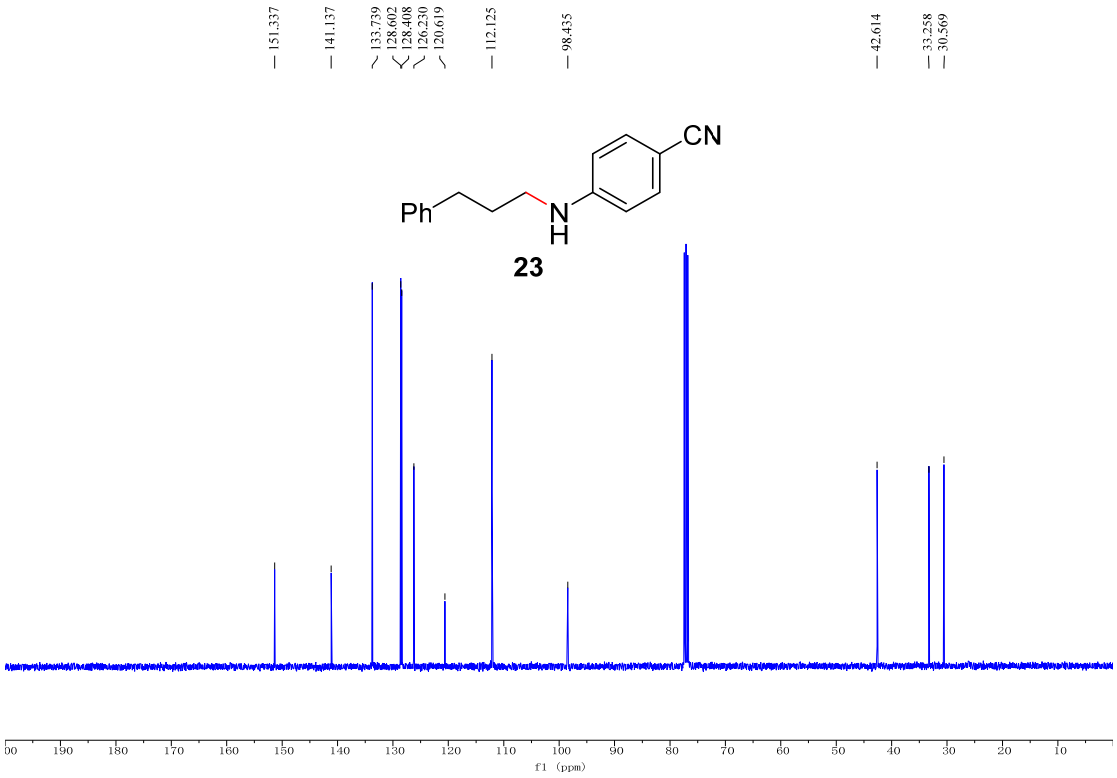
7.284
7.253
7.238
7.234
7.231
7.216
7.210
7.200
7.196
6.507
6.500
6.495
6.483
6.478
6.471
4.198
3.185
3.167
3.150
2.748
2.730
2.711
1.998
1.980
1.962
1.944
1.926
CN
Ph
N
H
23
2.00
5.09
2.04
1.00
2.10
2.07
2.09
f1 (ppm)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42.614
33.258
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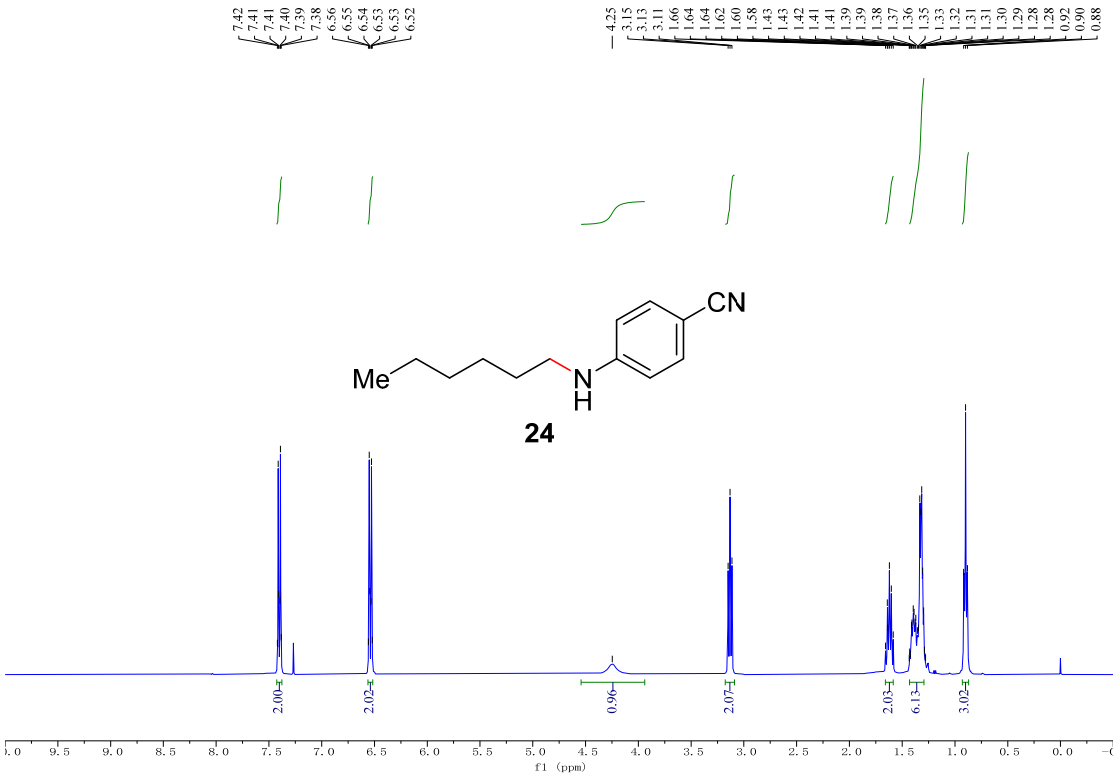
CN
Ph
N
H
23
f1 (ppm)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6.56
6.55
6.54
6.53
6.53
6.52
4.25
3.15
3.13
3.11
1.66
1.64
1.64
1.62
1.60
1.58
1.43
1.43
1.42
1.41
1.41
1.39
1.39
1.38
1.37
1.36
1.35
1.33
1.32
1.31
1.31
1.30
1.29
1.28
1.28
0.92
0.90
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CN
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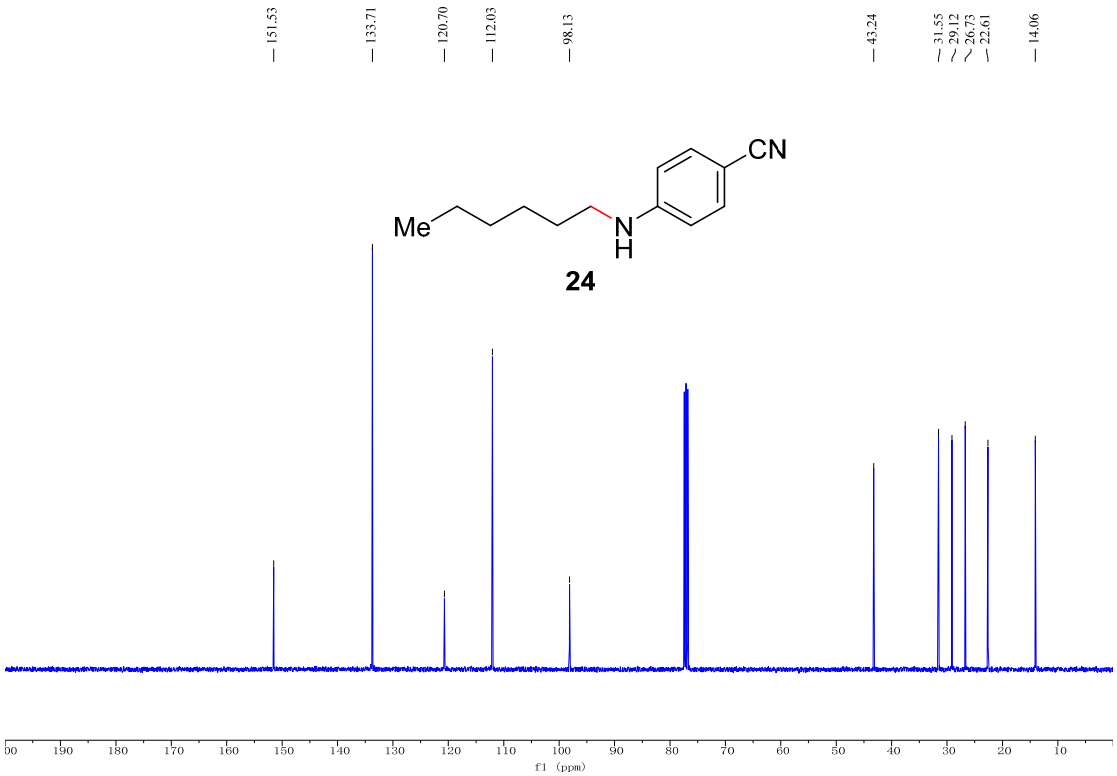
H
24
2.00
2.02
0.96
2.07
2.03
6.13
3.02
f1 (ppm)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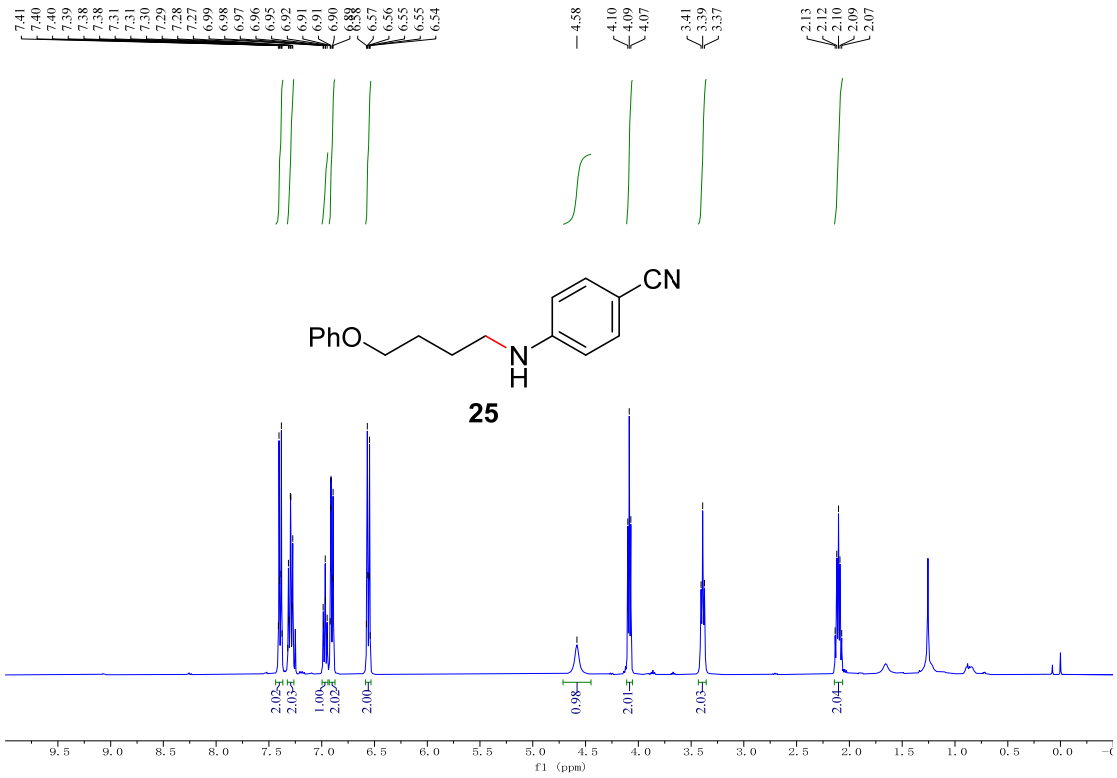
22.61
14.06
CN
Me
N
H
24
f1 (ppm)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7.31
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7.29
7.28
7.27
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6.98
6.97
6.96
6.95
6.92
6.91
6.91
6.90
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6.56
6.55
6.54
4.58
4.10
4.09
4.07
3.41
3.39
3.37
2.13
2.12
2.10
2.09
2.07
CN
PhO
N
H
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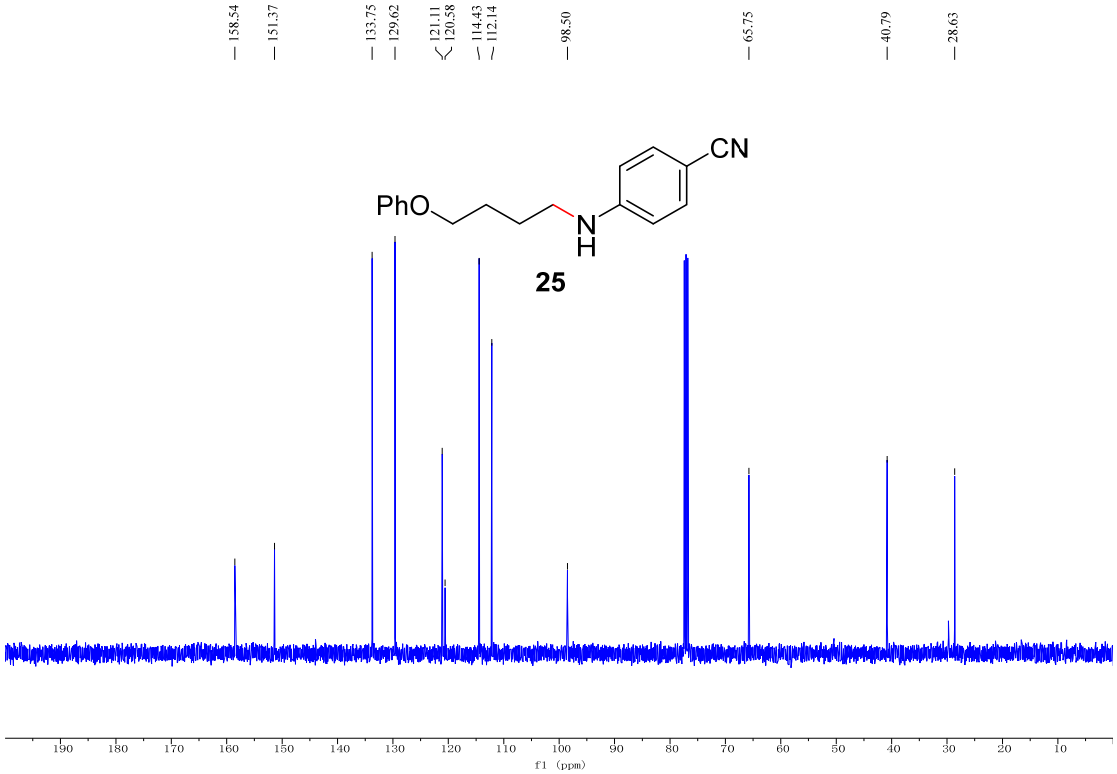
2.03
2.03
1.00
2.02
2.00
0.98
2.01
2.03
2.04
f1 (ppm)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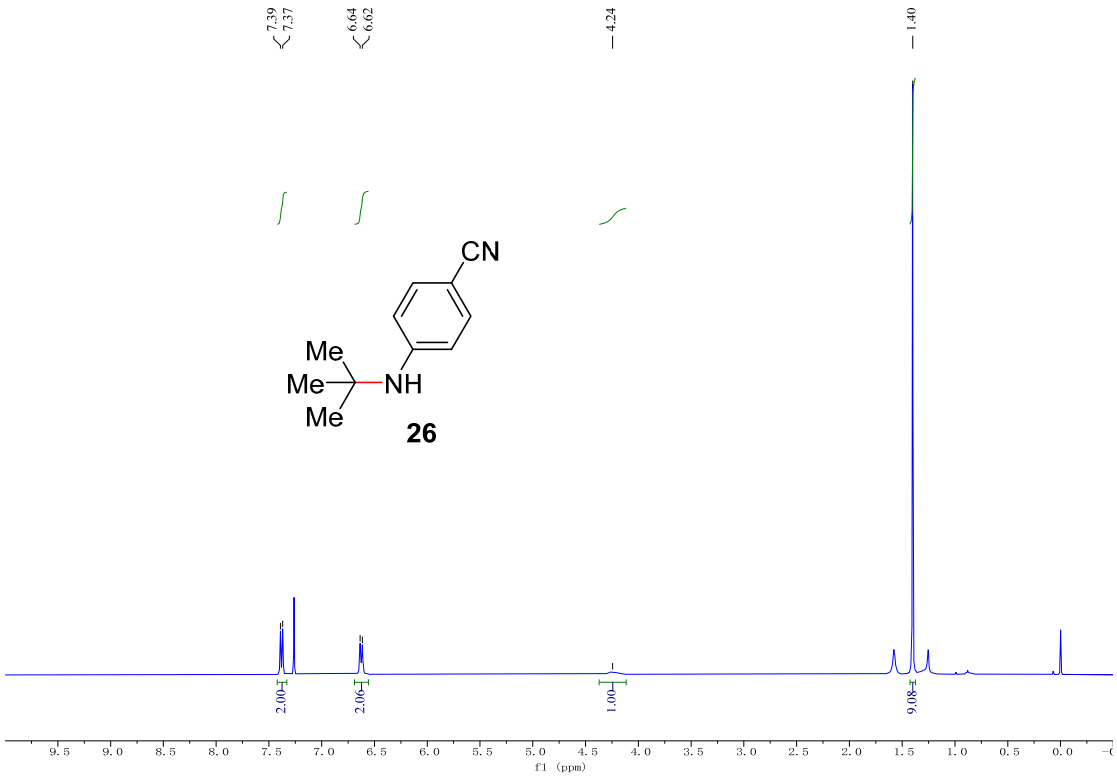
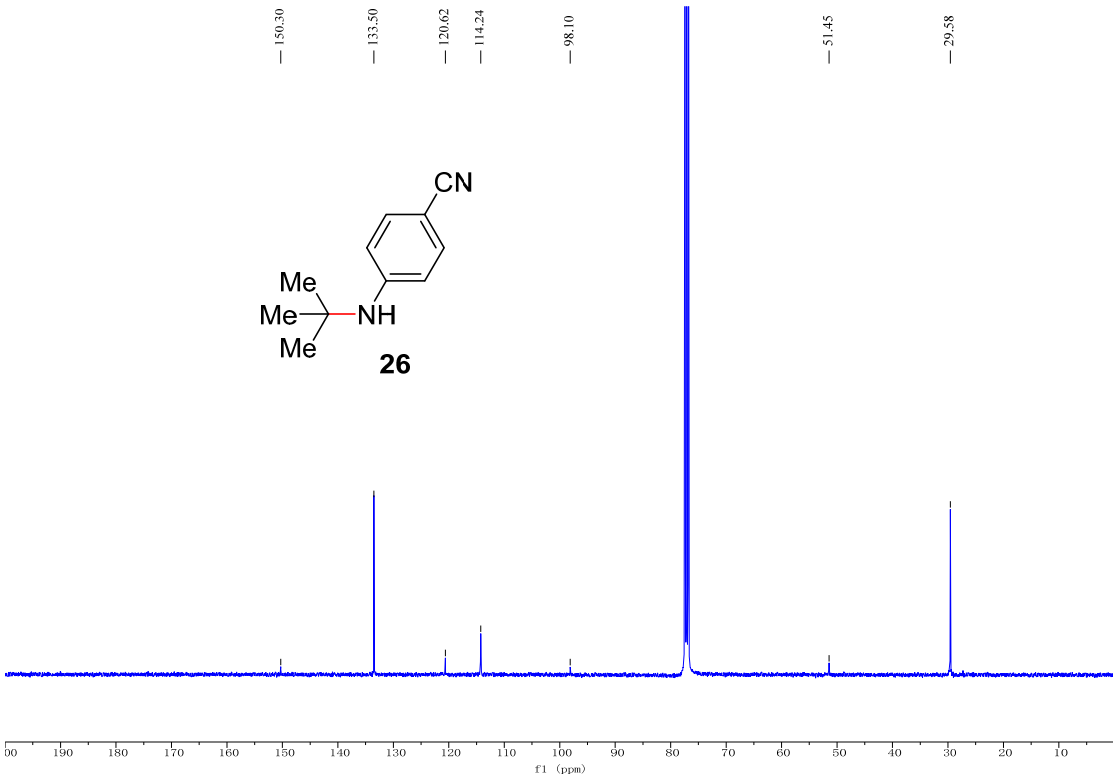
121.11
120.58
114.43
112.14
98.50
65.75
40.79
28.63
CN
PhO
N
H
25
f1 (ppm)


7.39
7.37
6.64
6.62
4.24
1.40
CN
Me
Me
NH
Me
26
2.00
2.04
1.00
9.08
f1 (ppm)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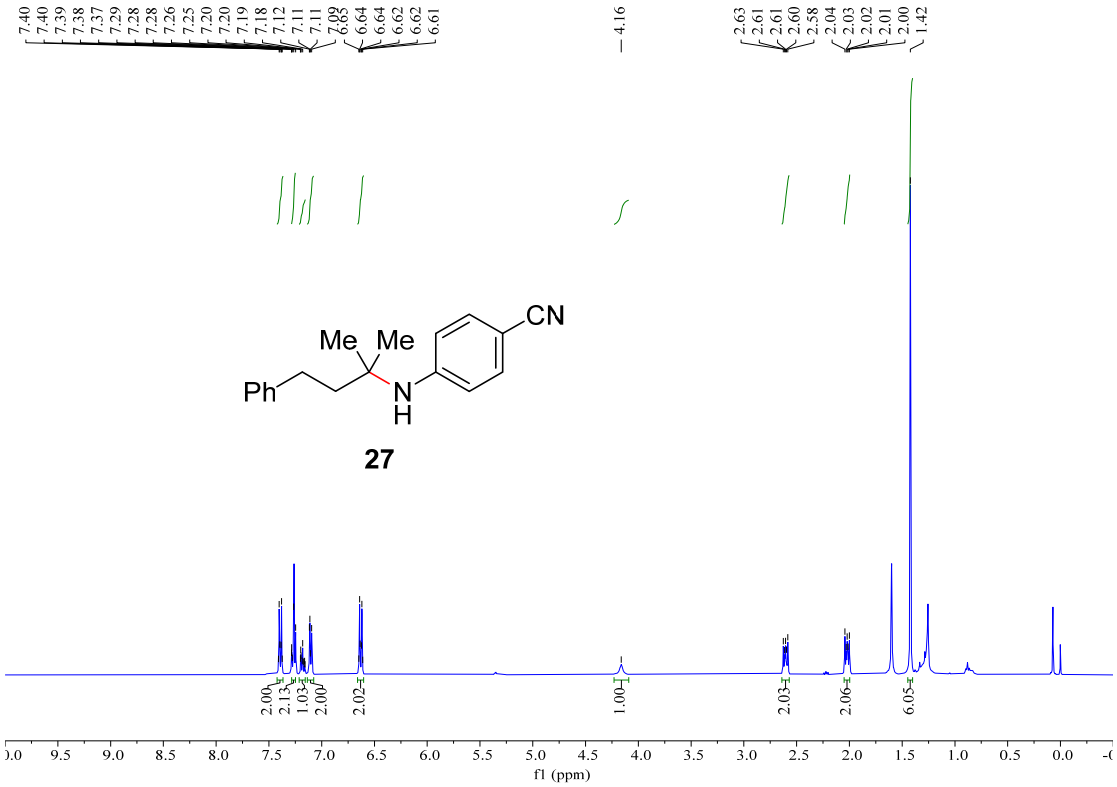
120.62
114.24
98.10
51.45
29.58
CN
Me
Me
NH
Me
26
f1 (ppm)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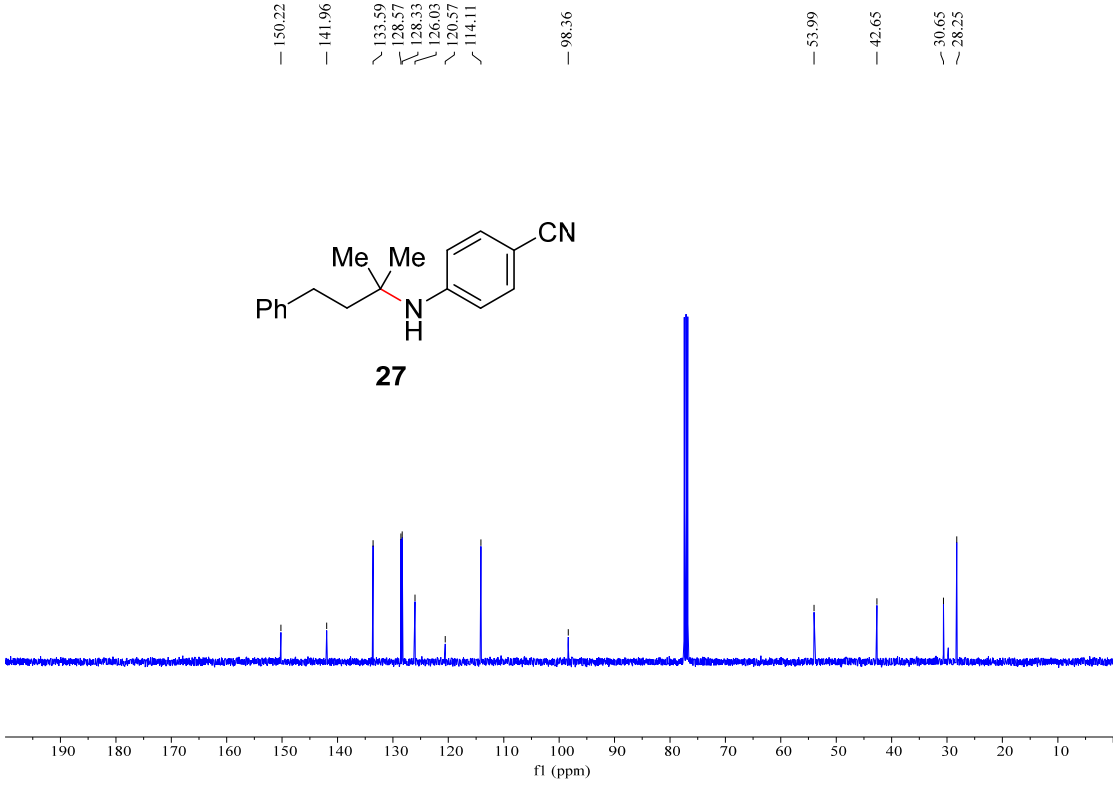
7.38
7.37
7.29
7.28
7.28
7.26
7.25
7.20
7.19
7.18
7.12
7.11
7.11
7.08
6.64
6.64
6.62
6.62
6.61
4.16
2.63
2.61
2.61
2.60
2.58
2.04
2.03
2.02
2.01
2.00
1.42
CN
Me Me
Ph
N
H
27
2.00
2.13
1.03
2.00
2.02
1.00
2.03
2.06
6.05
f1 (ppm)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126.03
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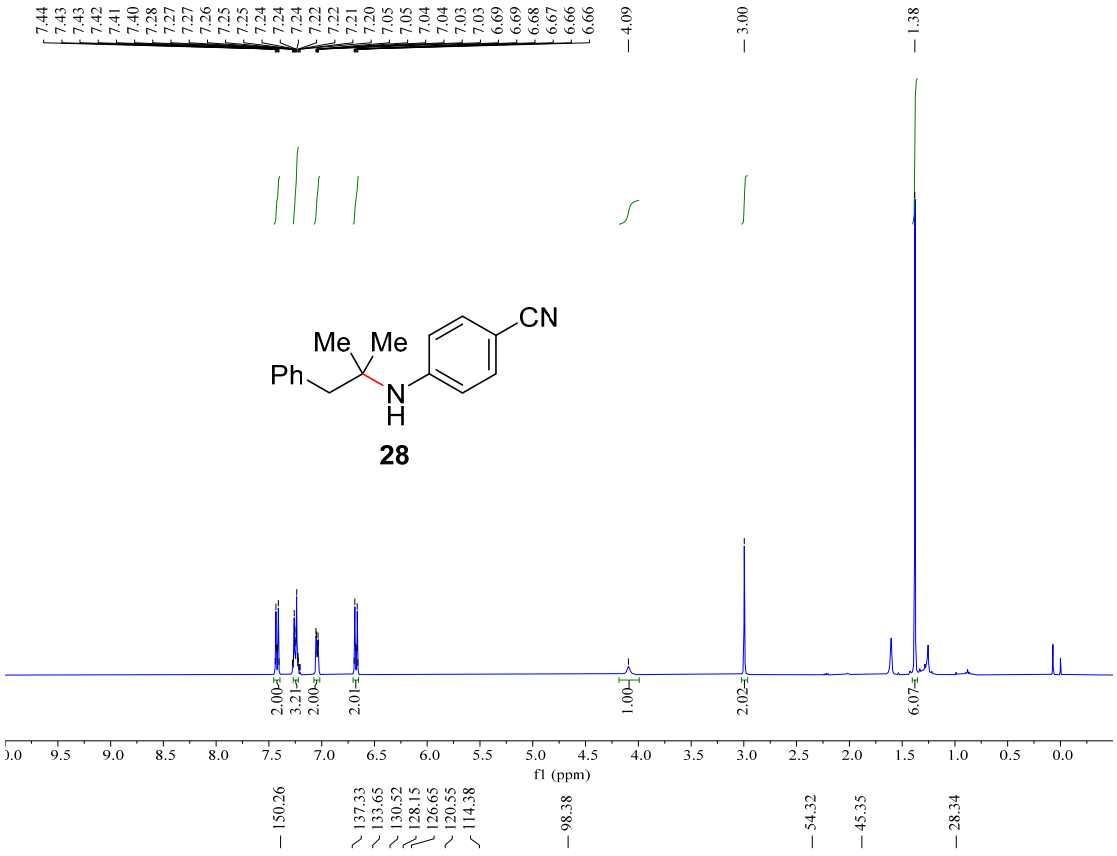
98.36
53.99
42.65
30.65
28.25
CN
Me Me
Ph
N
H
27
f1 (ppm)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7.26
7.25
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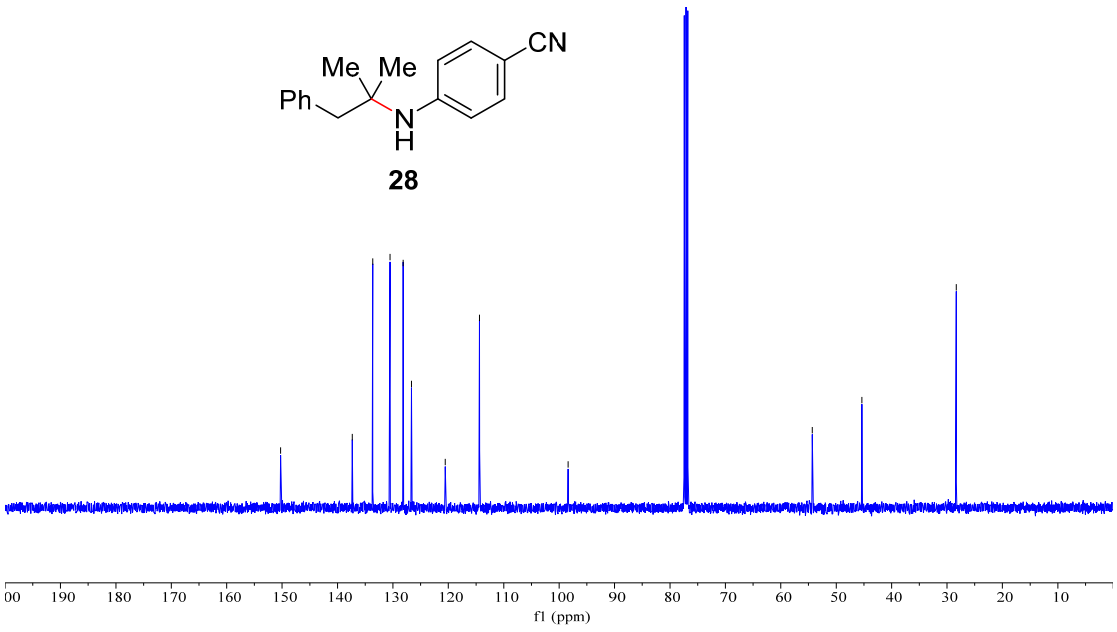
7.24
7.24
7.24
7.22
7.21
7.20
7.05
7.05
7.04
7.04
7.03
7.03
6.69
6.69
6.68
6.67
6.66
6.66
4.09
3.00
1.38
CN
Me
Me
Ph
N
H
28
2.00
3.21
2.00
2.01
1.00
2.02
6.07
f1 (ppm)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128.15
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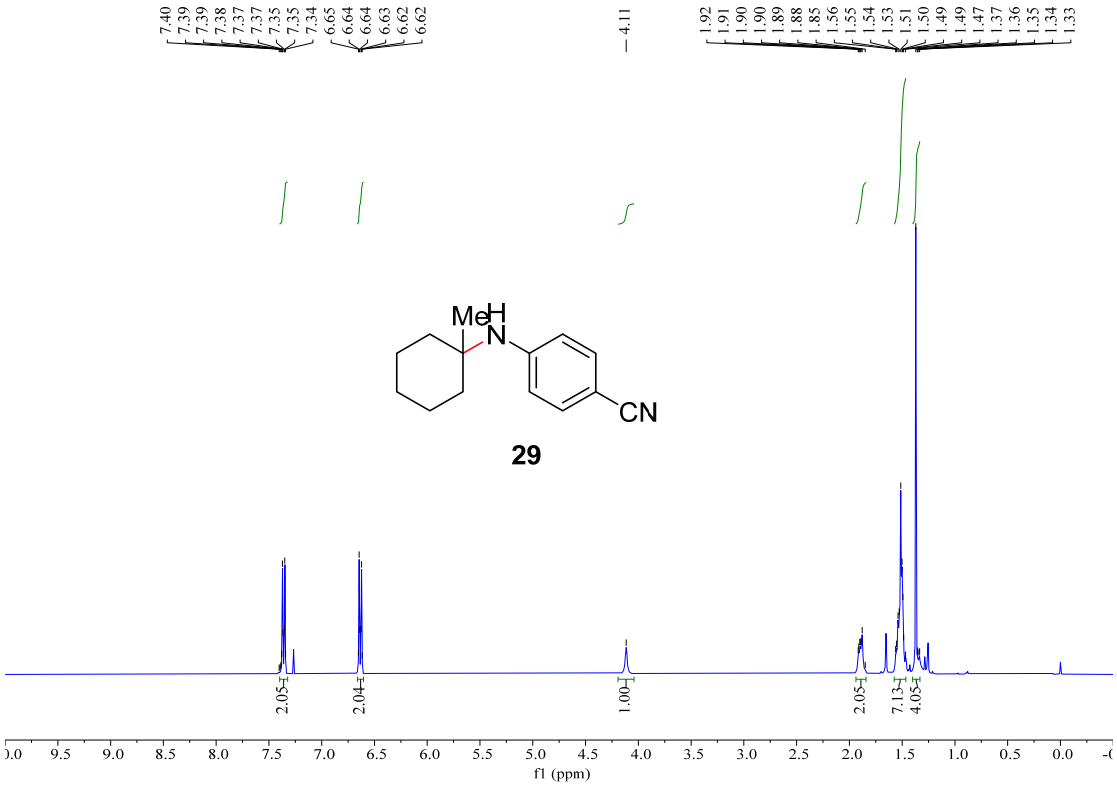
54.32
45.35
28.34
CN
Me
Me
Ph
N
H
28
f1 (ppm)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7.39
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7.38
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7.37
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7.34
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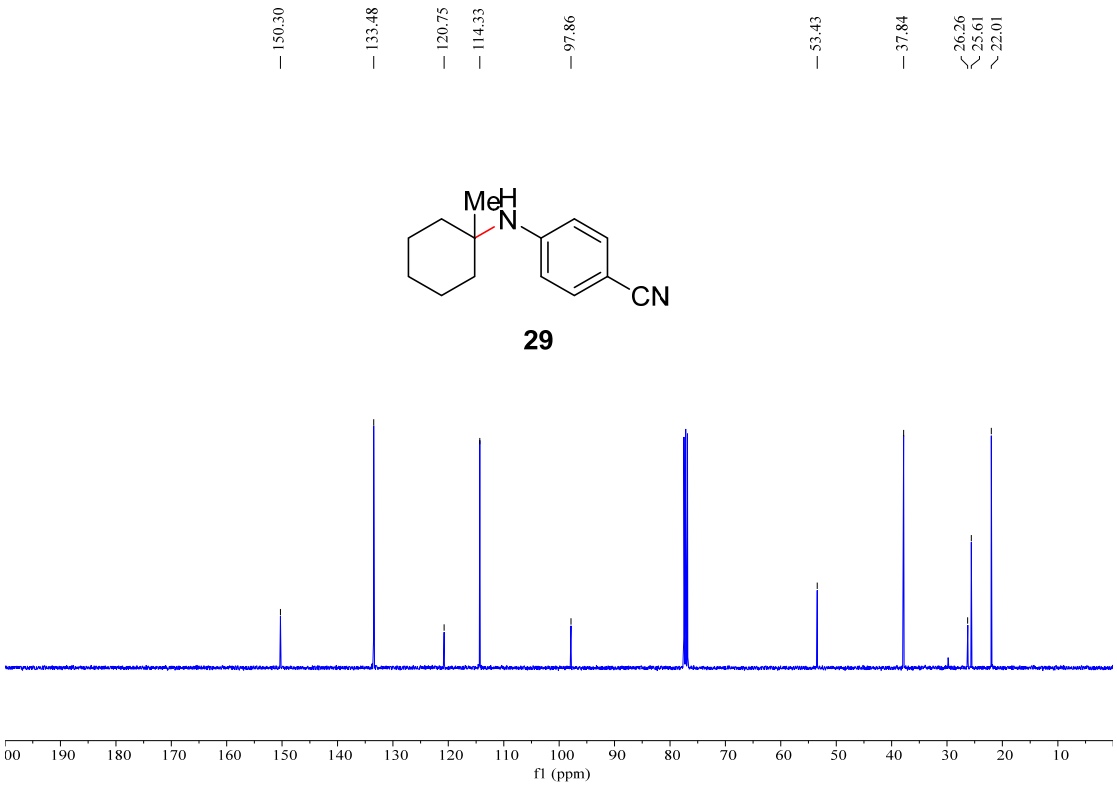
6.64
6.64
6.63
6.62
6.62
4.11
1.92
1.91
1.90
1.90
1.89
1.88
1.85
1.56
1.55
1.54
1.53
1.51
1.50
1.49
1.49
1.47
1.37
1.36
1.35
1.34
1.33
Me
H
N
CN
2.05
2.04
1.00
2.05
7.13
4.05
f1 (ppm)

29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133.48
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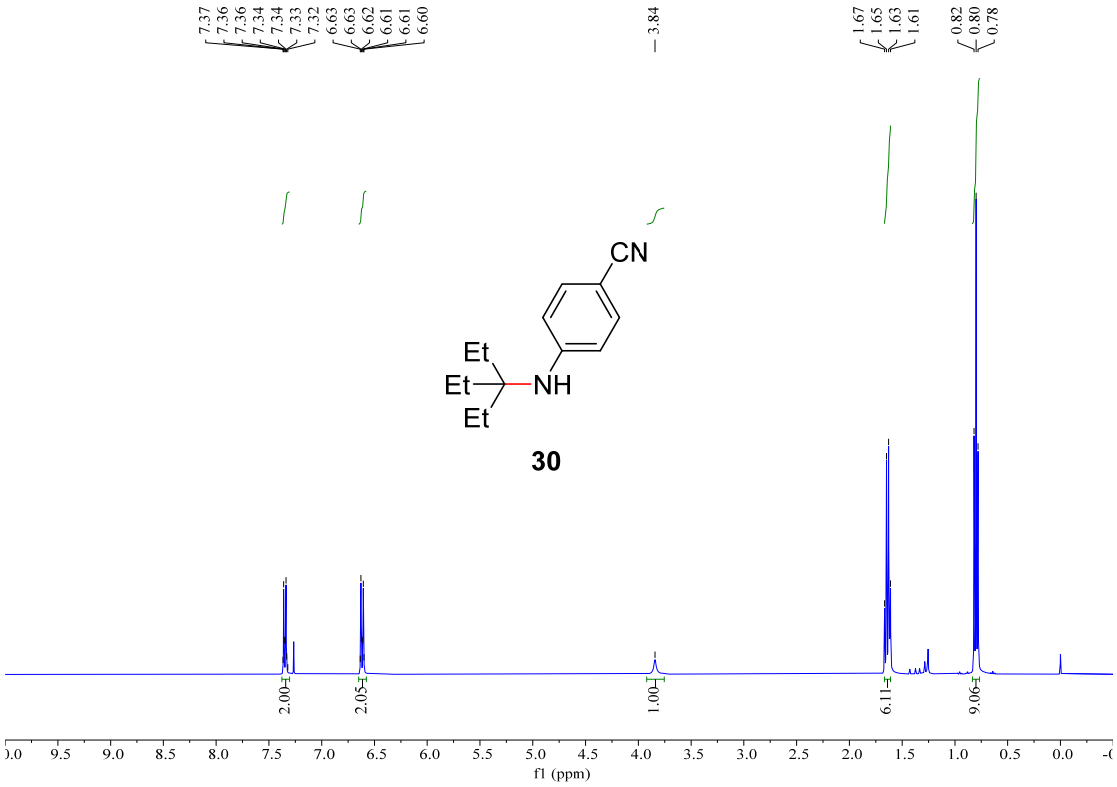
53.43
37.84
26.26
25.61
22.01
Me
H
N
CN
f1 (ppm)

29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7.36
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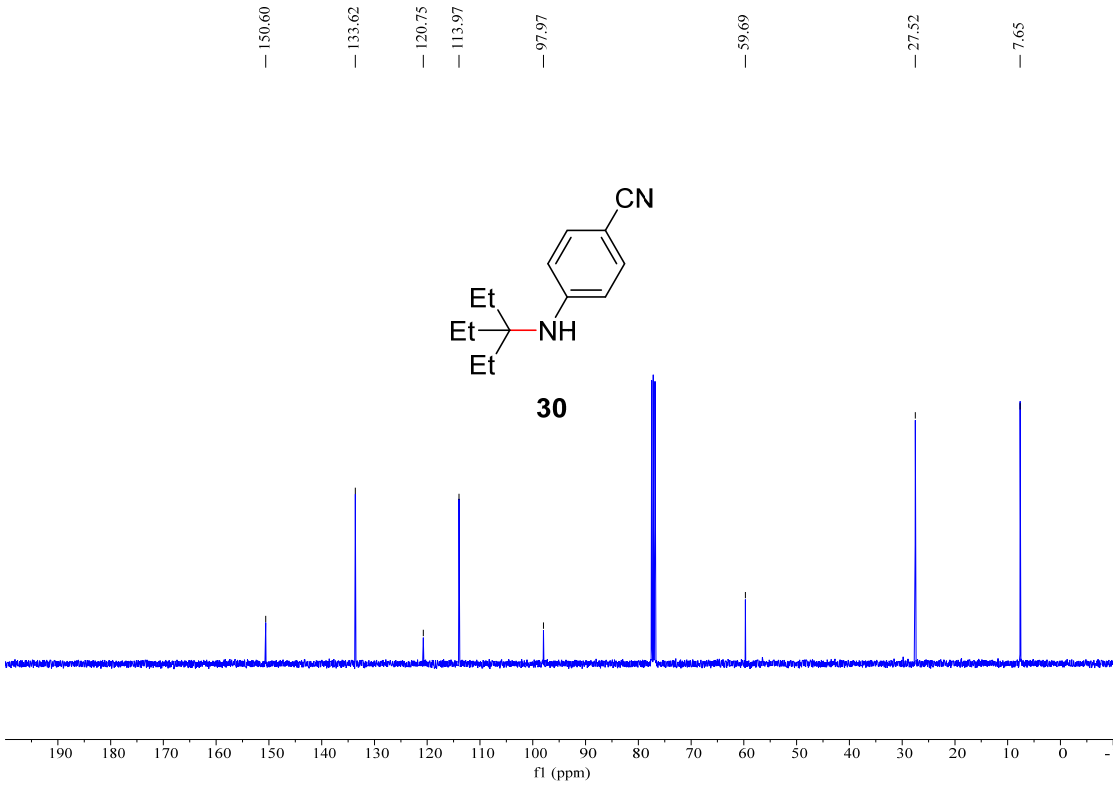
7.34
7.33
7.32
6.63
6.63
6.62
6.61
6.61
6.60
3.84
1.67
1.65
1.63
1.61
0.82
0.80
0.78
CN
Et
Et
NH
Et
30
2.00
2.05
1.00
6.11
9.06
f1 (ppm)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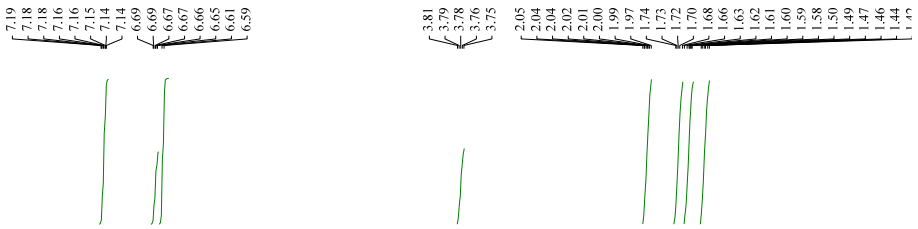
113.97
97.97
59.69
27.52
7.65
CN
Et
Et
NH
Et
30
f1 (ppm)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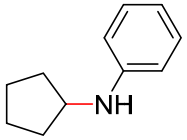
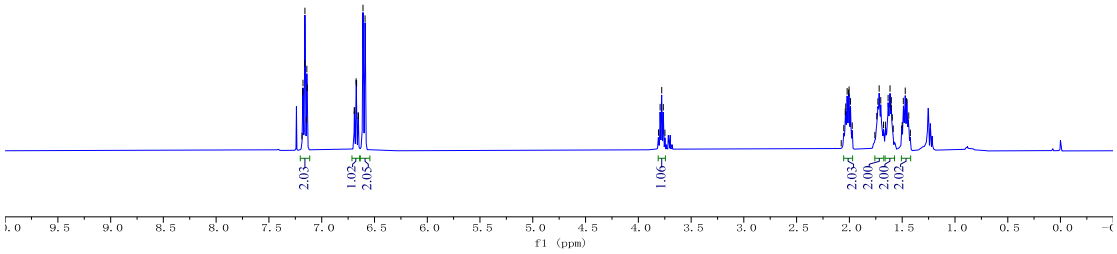
7.18
7.18
7.16
7.16
7.15
7.14
7.14
6.69
6.69
6.67
6.67
6.66
6.65
6.61
6.59
3.81
3.79
3.78
3.76
3.75
2.05
2.04
2.04
2.02
2.01
2.00
1.99
1.97
1.74
1.73
1.72
1.70
1.68
1.66
1.63
1.62
1.61
1.60
1.59
1.58
1.50
1.49
1.47
1.46
1.44


NH

31


2.03
1.02
2.05
1.06
2.03
2.00
2.00
2.02
f1 (ppm)


148.015
129.245
117.015
113.274
54.752
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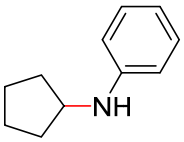
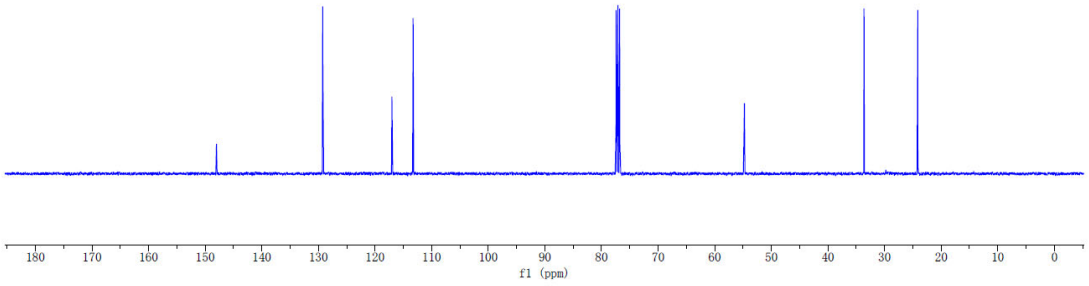
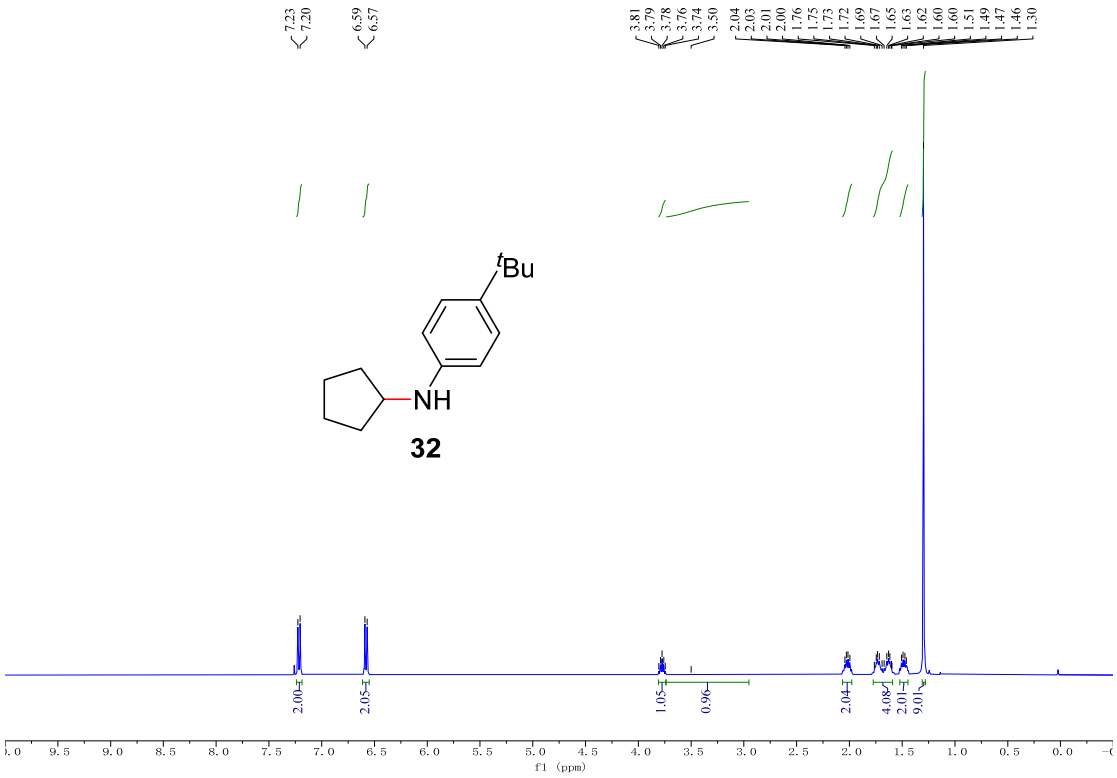
29.778
24.129


NH

31


f1 (ppm)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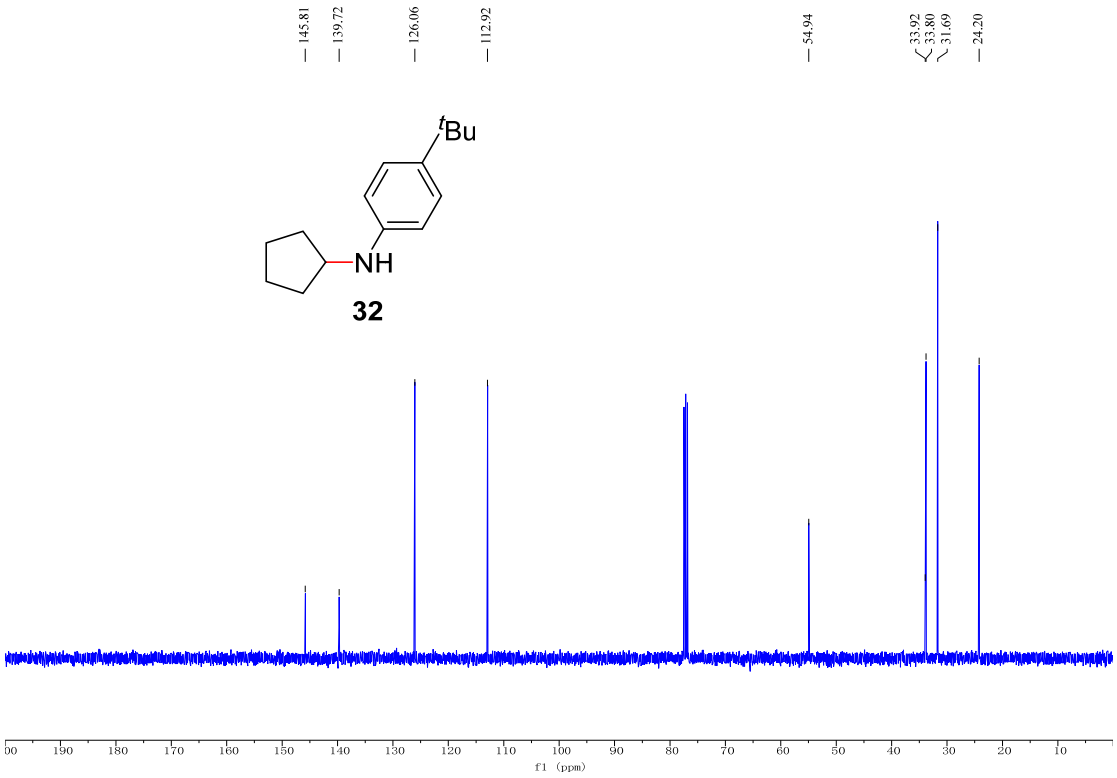
3.76
3.74
3.50
2.04
2.03
2.01
2.00
1.76
1.75
1.73
1.72
1.69
1.67
1.65
1.63
1.62
1.60
1.60
1.51
1.49
1.47
1.46
1.30
tBu
NH
32
2.00
2.05
1.05
0.96
2.04
4.08
2.01
9.01
f1 (ppm)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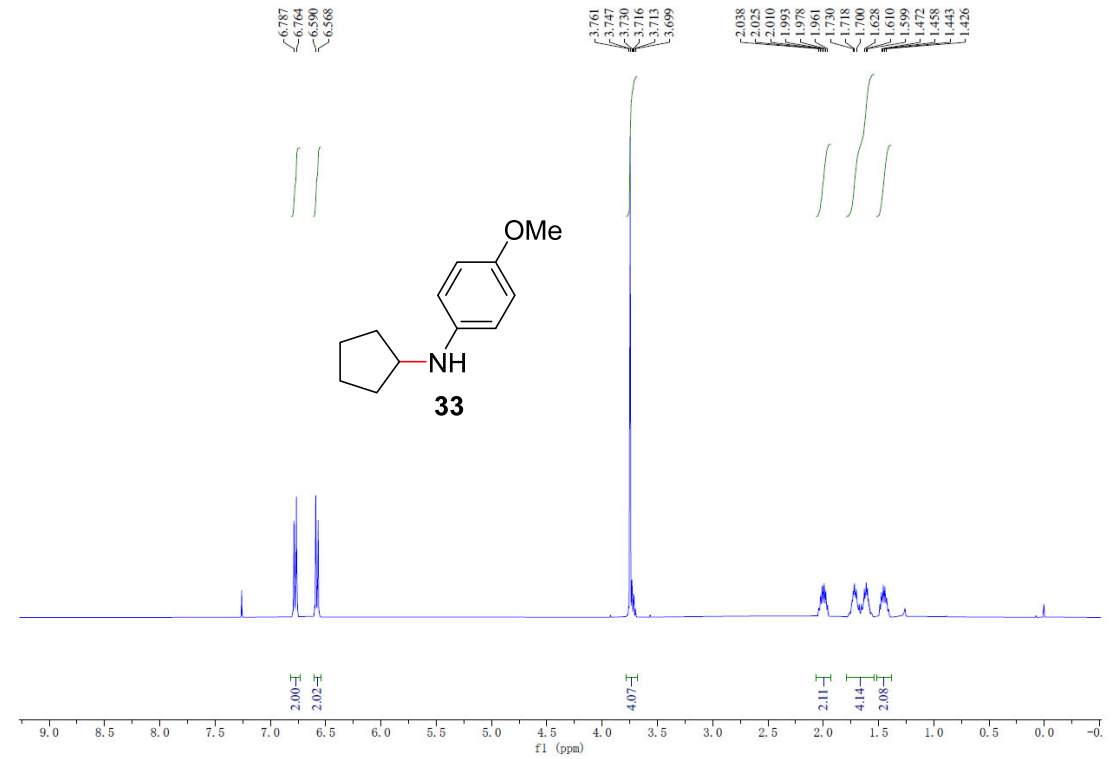
33.92
33.80
31.69
24.20
tBu
NH
32
f1 (ppm)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6.590
6.568
3.761
3.747
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3.716
3.713
3.699
2.038
2.025
2.010
1.993
1.978
1.961
1.730
1.718
1.700
1.628
1.610
1.599
1.472
1.458
1.443
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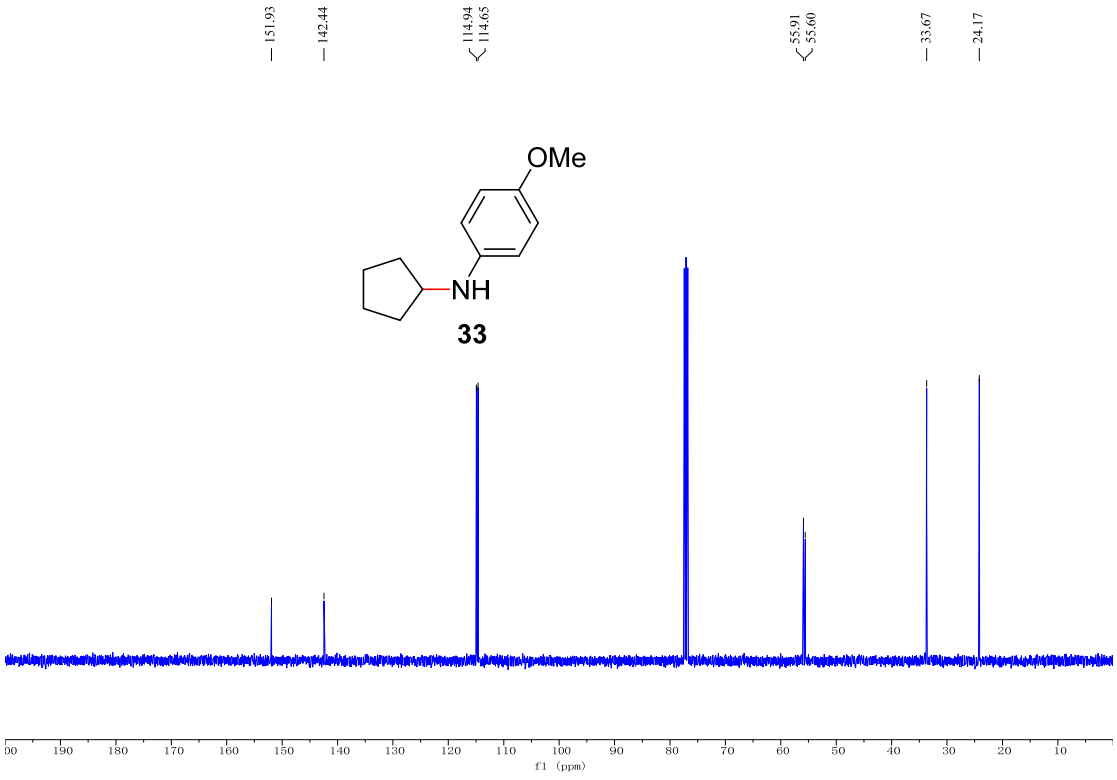
OMe
NH
33
2.00
2.02
4.07
2.11
4.14
2.08
f1 (ppm)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142.44
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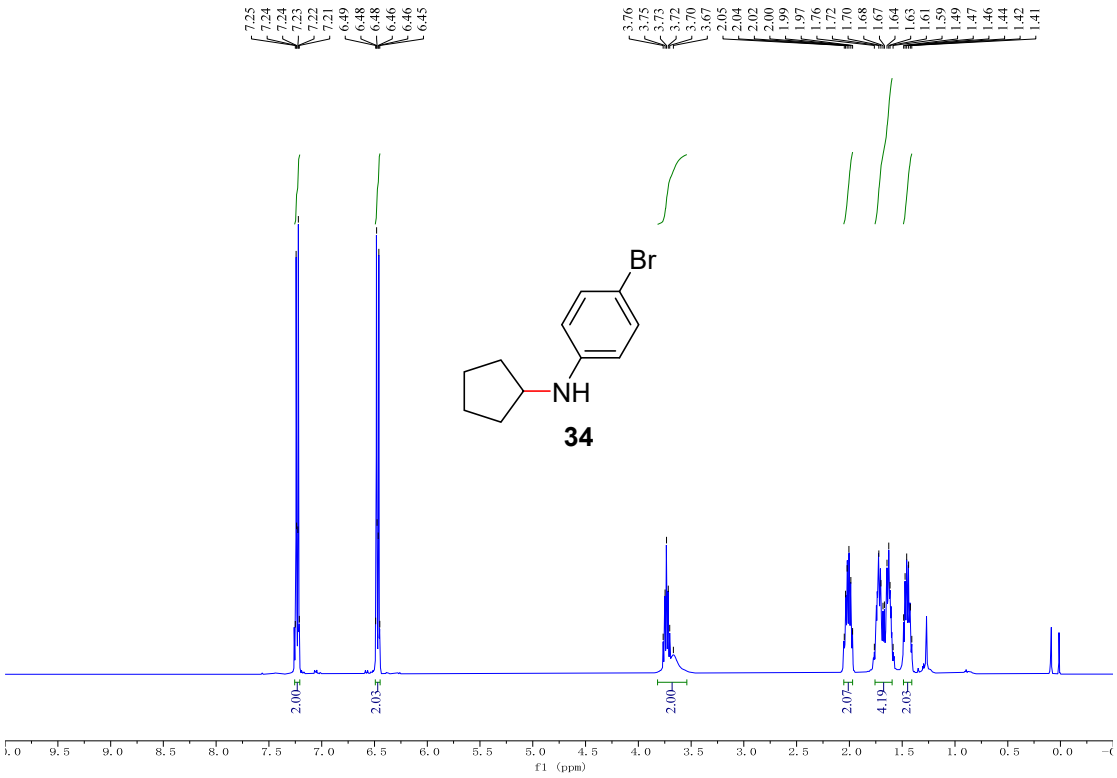
114.65
55.91
55.60
33.67
24.17
OMe
NH
33
f1 (ppm)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7.24
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7.22
7.21
6.49
6.48
6.48
6.46
6.46
6.45
3.76
3.75
3.73
3.72
3.70
3.67
2.05
2.04
2.02
2.00
1.99
1.97
1.76
1.72
1.70
1.68
1.67
1.64
1.63
1.61
1.59
1.49
1.47
1.46
1.44
1.42
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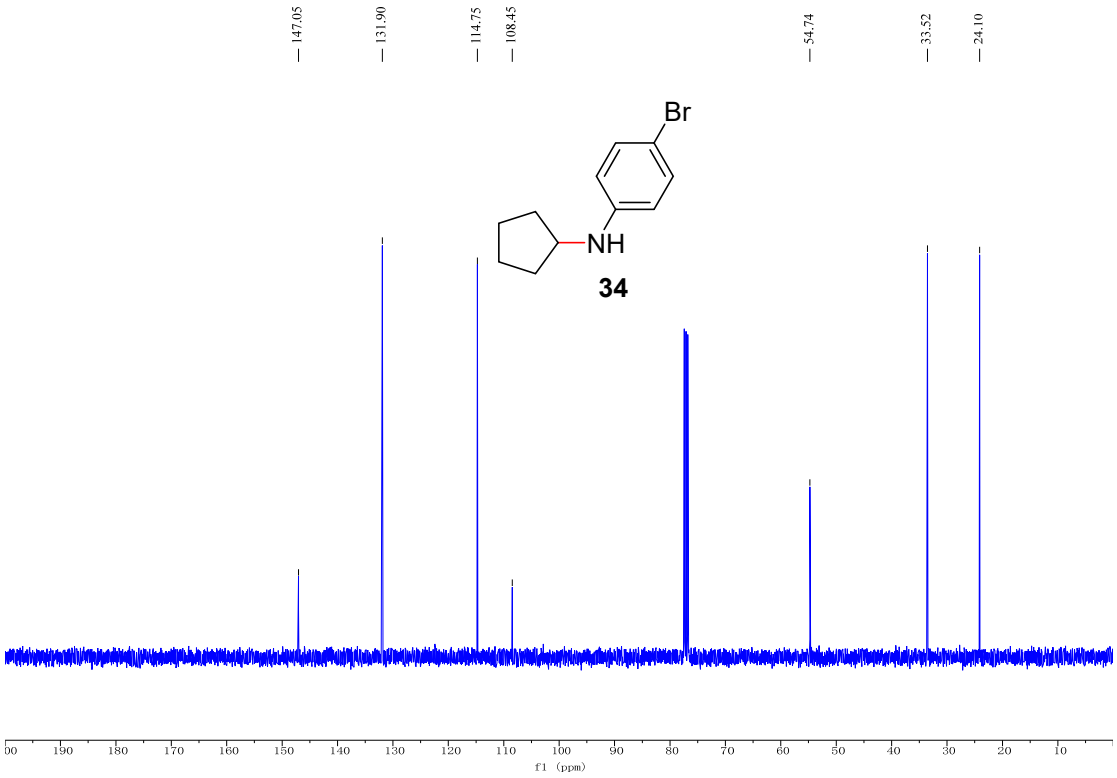
Br
NH
34
2.00
2.03
2.00
2.07
4.19
2.03
f1 (ppm)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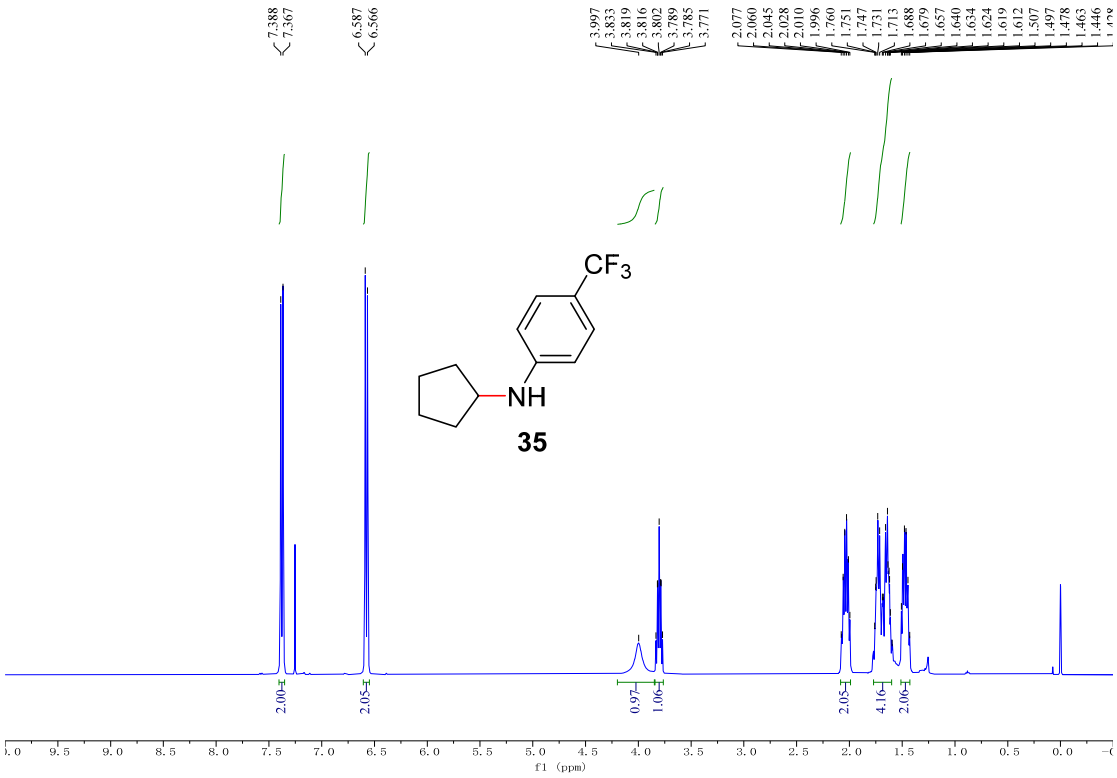
131.90
114.75
108.45
54.74
33.52
24.10
Br
NH
34
f1 (ppm)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6.566
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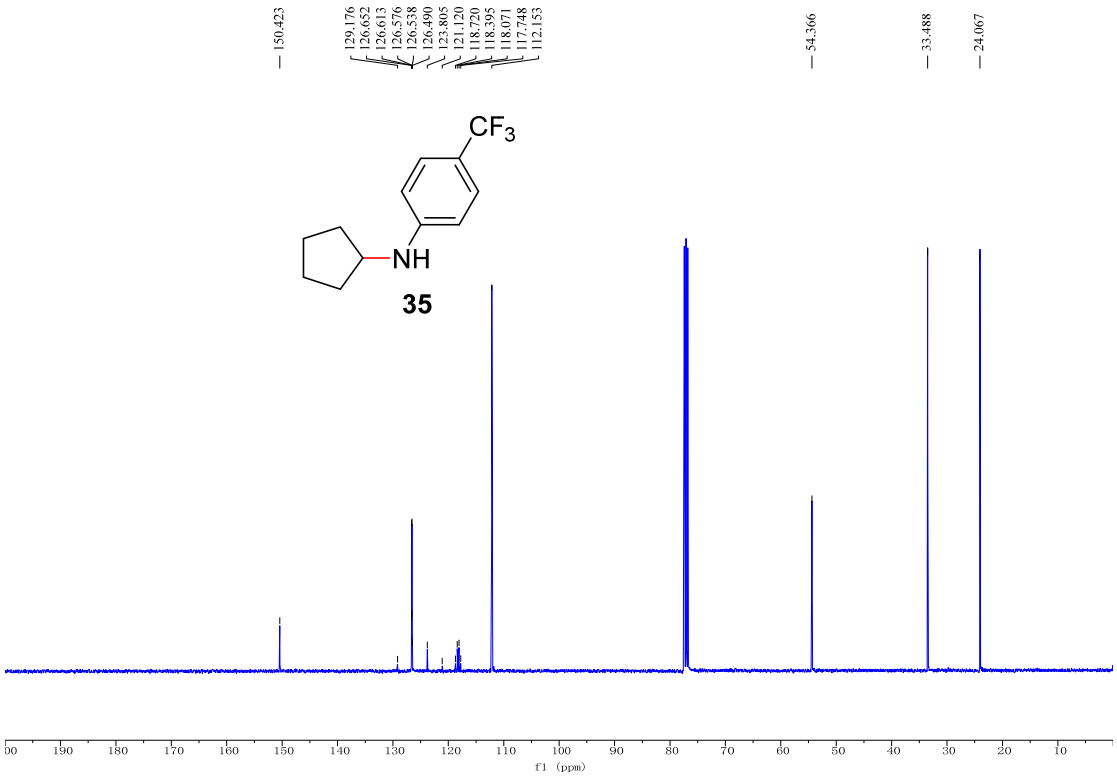
3.833
3.819
3.816
3.802
3.789
3.785
3.771
2.077
2.060
2.045
2.028
2.010
1.996
1.760
1.751
1.747
1.731
1.713
1.688
1.679
1.657
1.640
1.634
1.624
1.619
1.612
1.507
1.497
1.478
1.463
1.446
CF3
NH
35
2.00
2.05
0.97
1.06
2.05
4.16
2.06
f1 (ppm)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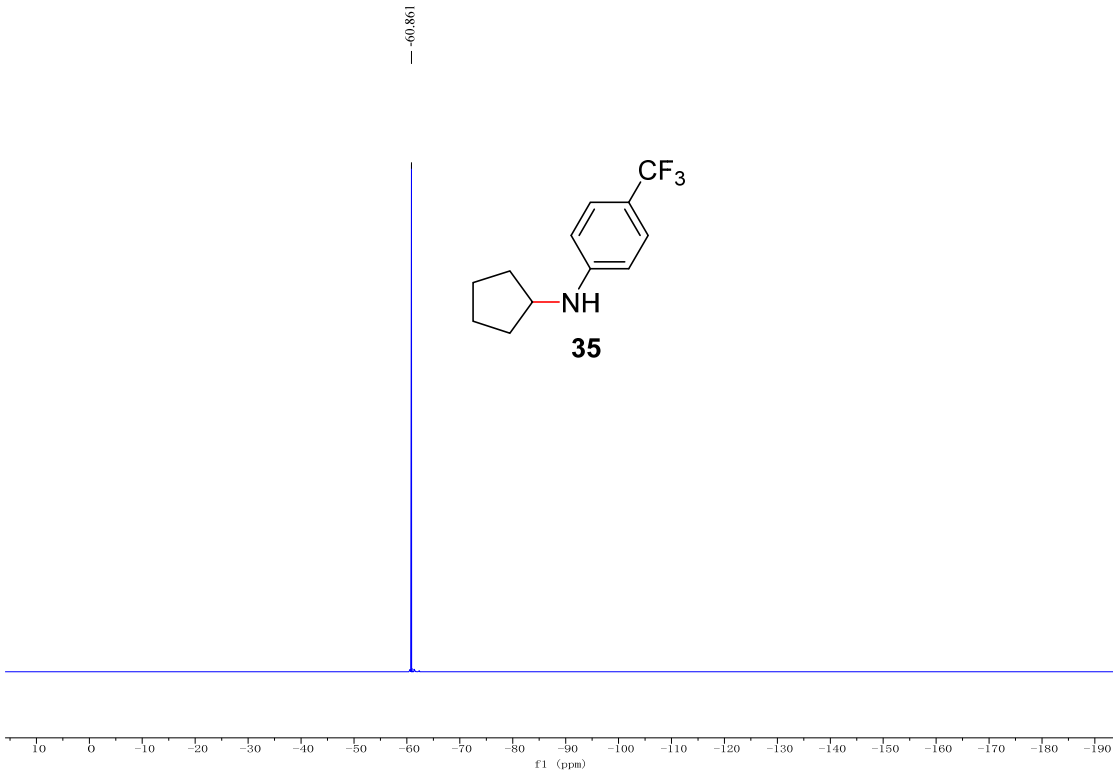
118.071
117.748
112.153
54.366
33.488
24.067
CF3
NH
35
f1 (ppm)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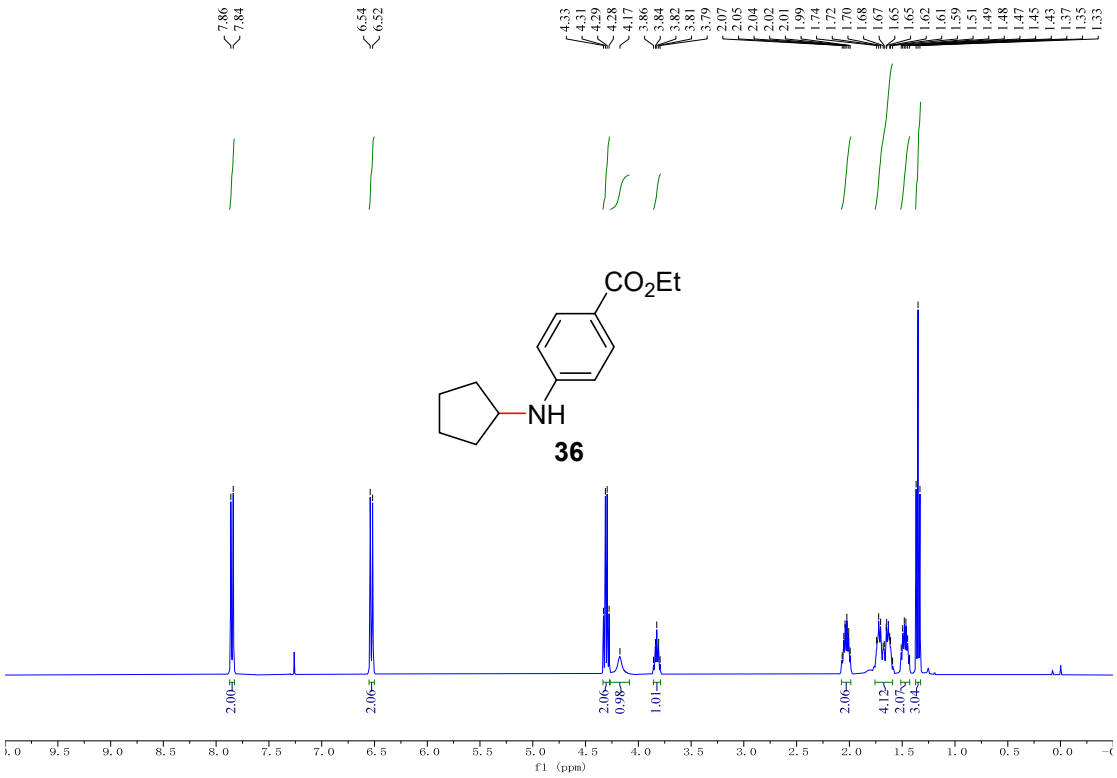
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)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7.84
6.54
6.52
4.33
4.31
4.29
4.28
4.17
3.86
3.84
3.82
3.81
3.79
2.07
2.05
2.04
2.02
2.01
1.99
1.74
1.72
1.70
1.68
1.67
1.65
1.65
1.62
1.61
1.59
1.51
1.49
1.48
1.47
1.45
1.43
1.37
1.35
1.33
CO2Et
NH
36
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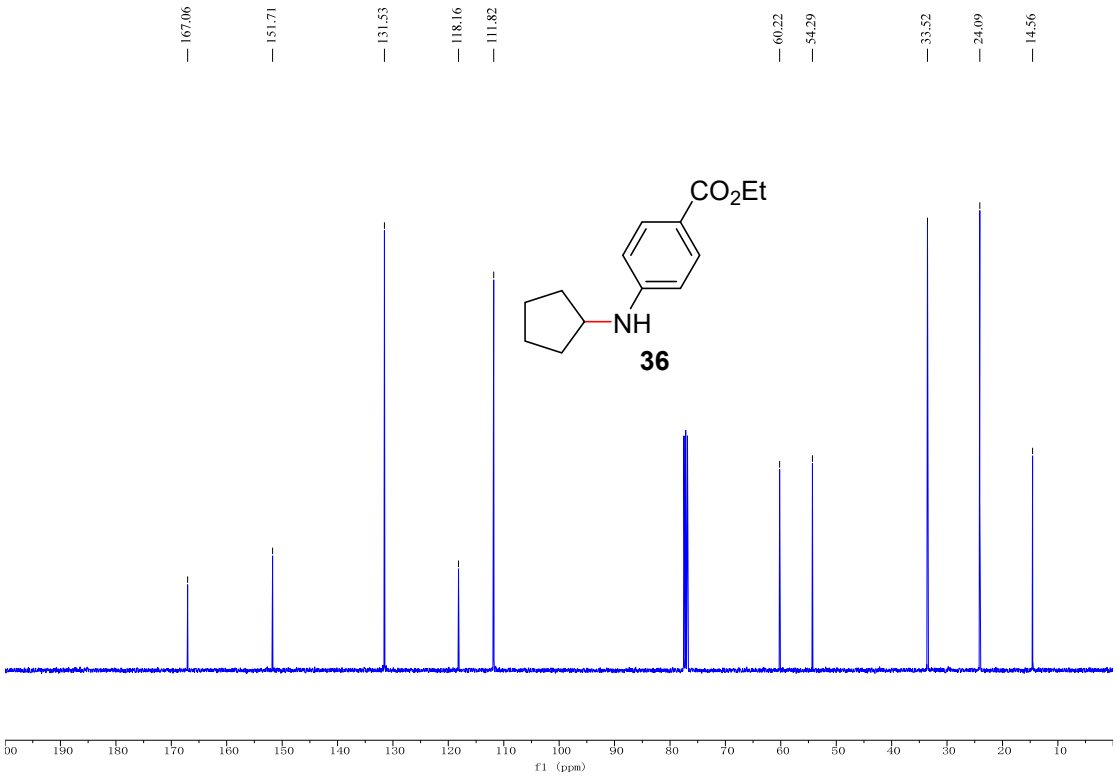
2.06
2.06
0.98
1.01
2.06
4.12
2.07
3.04
f1 (ppm)


167.06
151.71
131.53
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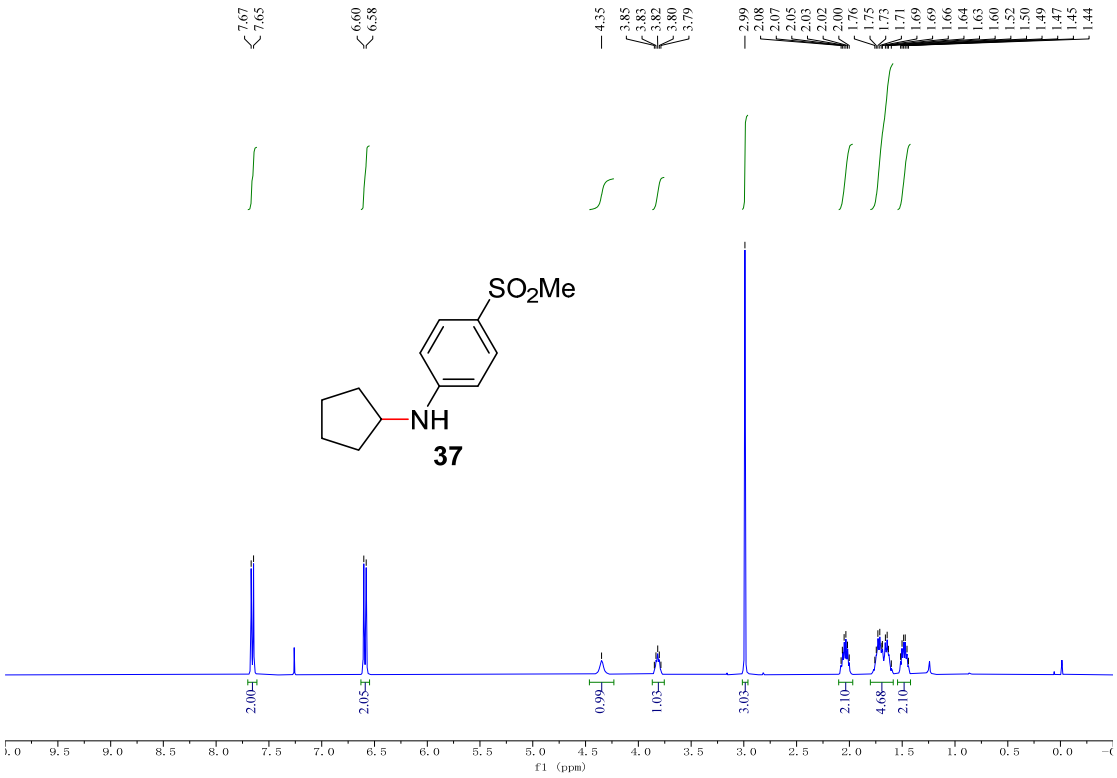
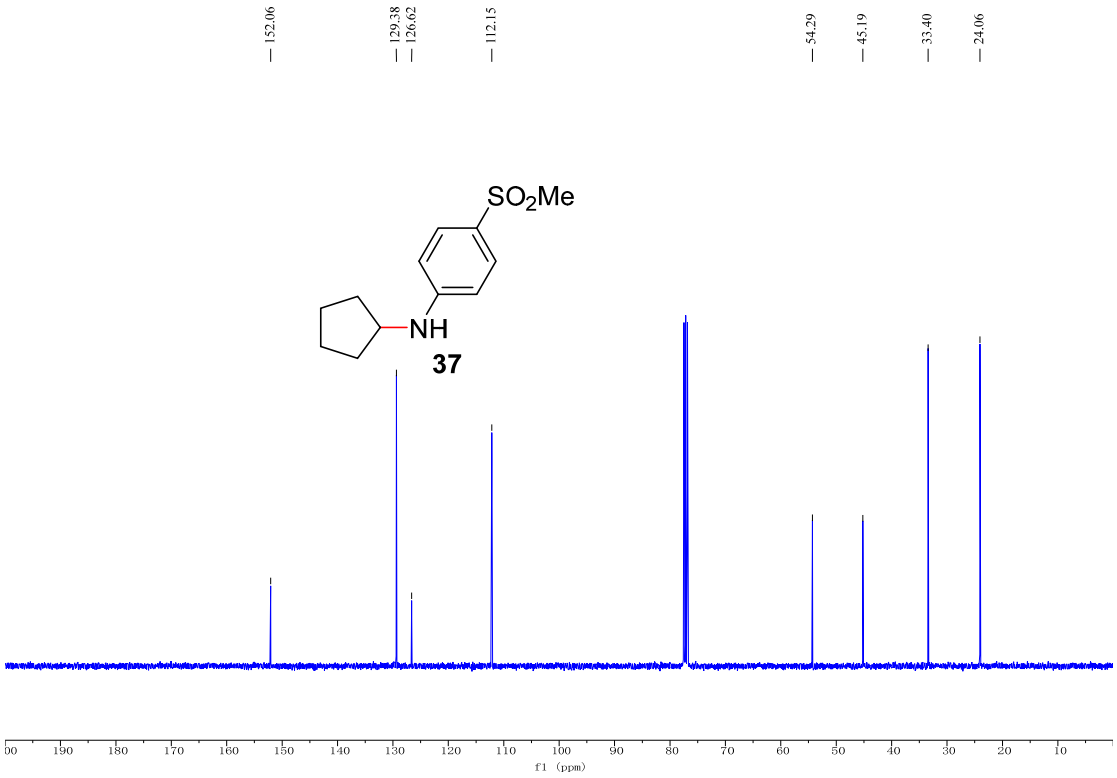
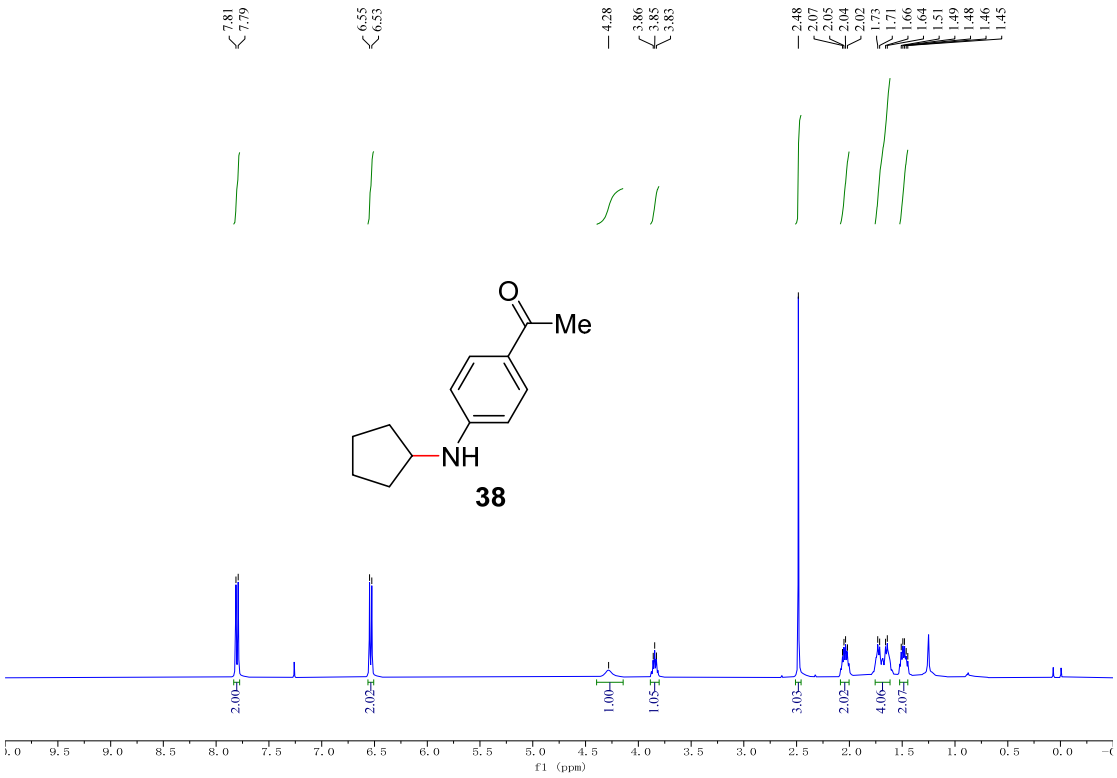
60.22
54.29
33.52
24.09
14.56
CO2Et
NH
36
f1 (ppm)


7.67
7.65
6.60
6.58
4.35
3.85
3.83
3.82
3.80
3.79
2.99
2.08
2.07
2.05
2.03
2.02
2.00
1.76
1.75
1.73
1.71
1.69
1.69
1.66
1.64
1.63
1.60
1.52
1.50
1.49
1.47
1.45
1.44
SO2Me
NH
37
2.00
2.05
0.99
1.03
3.03
2.10
4.68
2.10
f1 (ppm)


152.06
129.38
126.62
112.15
54.29
45.19
33.40
24.06
SO2Me
NH
37
f1 (ppm)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3.86
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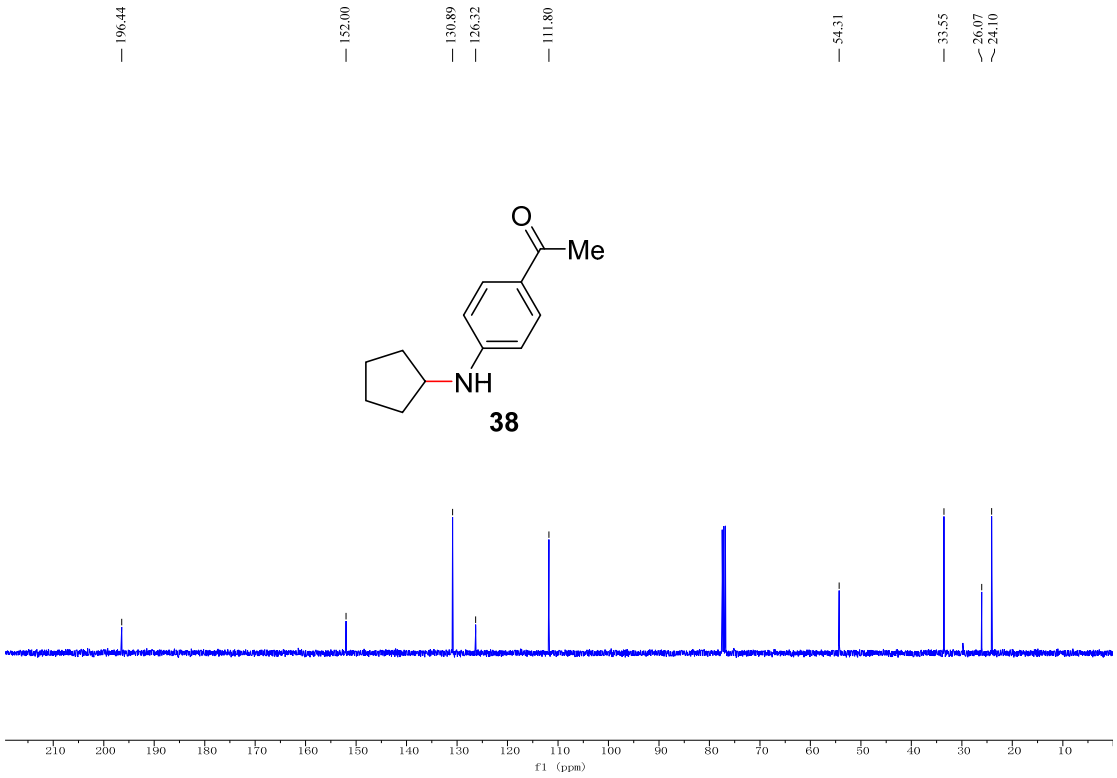
3.83
2.48
2.07
2.05
2.04
2.02
1.73
1.71
1.66
1.64
1.51
1.49
1.48
1.46
1.45
O
Me
NH
38
2.00
2.02
1.00
1.05
3.03
2.02
4.06
2.07
f1 (ppm)


196.44
152.00
130.89
126.32
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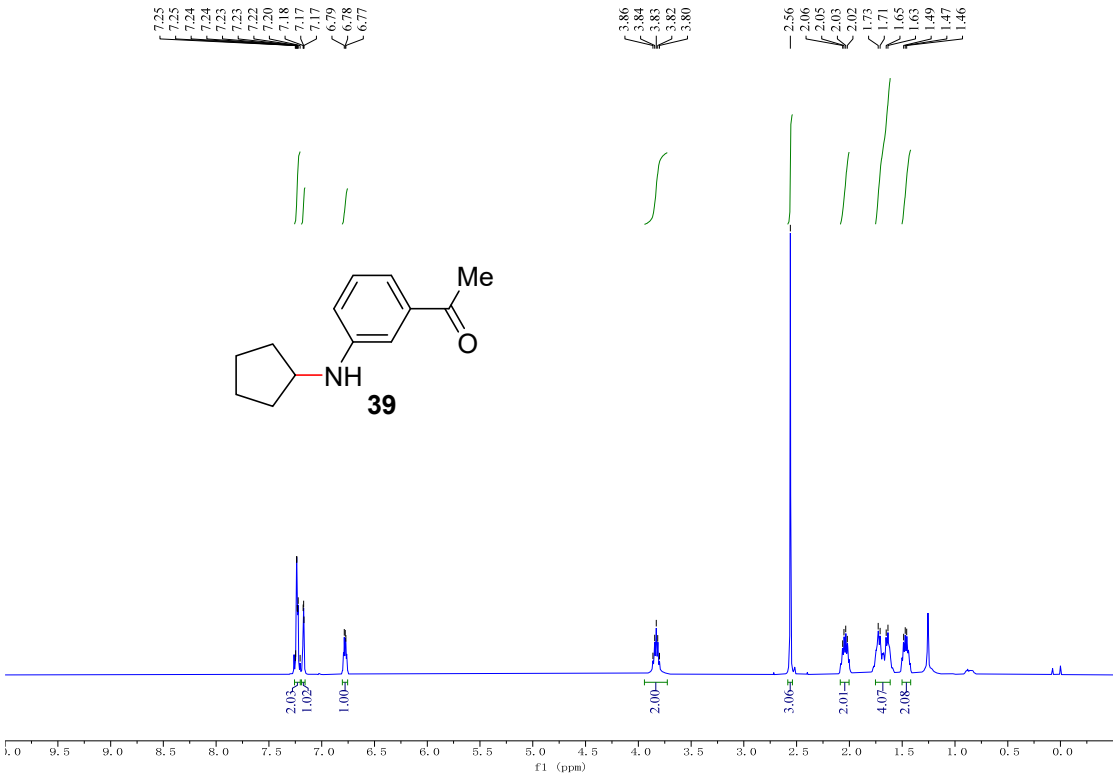
54.31
33.55
26.07
24.10
O
Me
NH
38
f1 (ppm)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7.24
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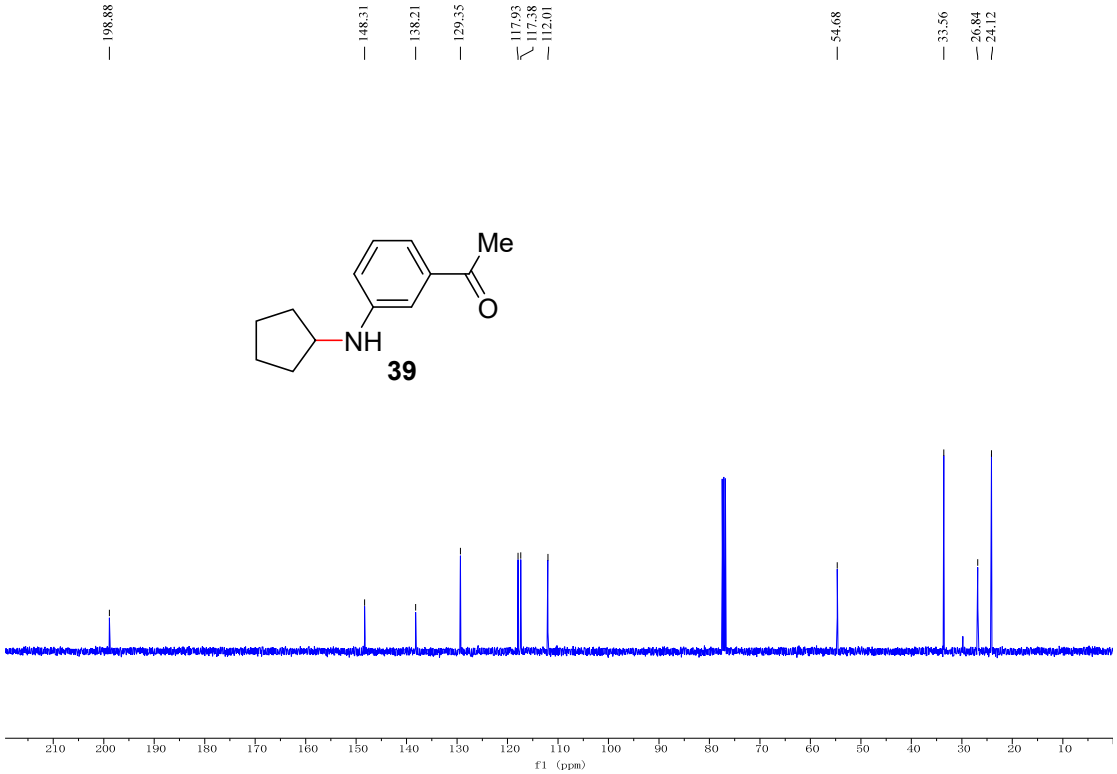
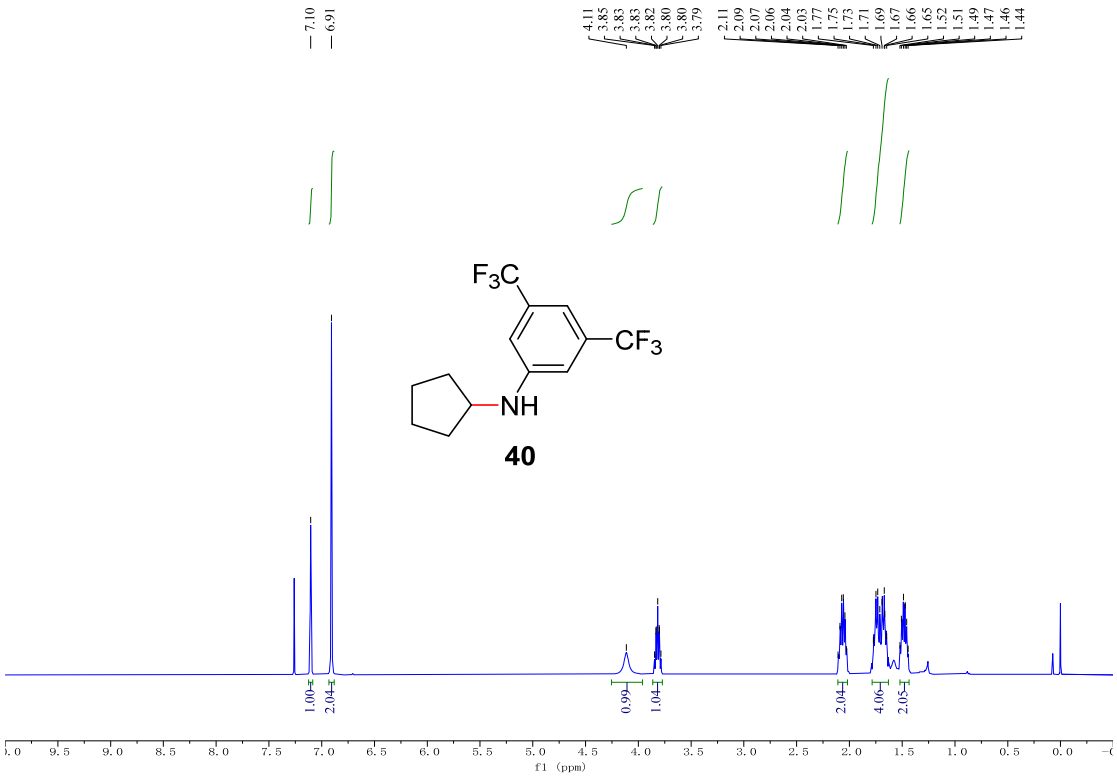
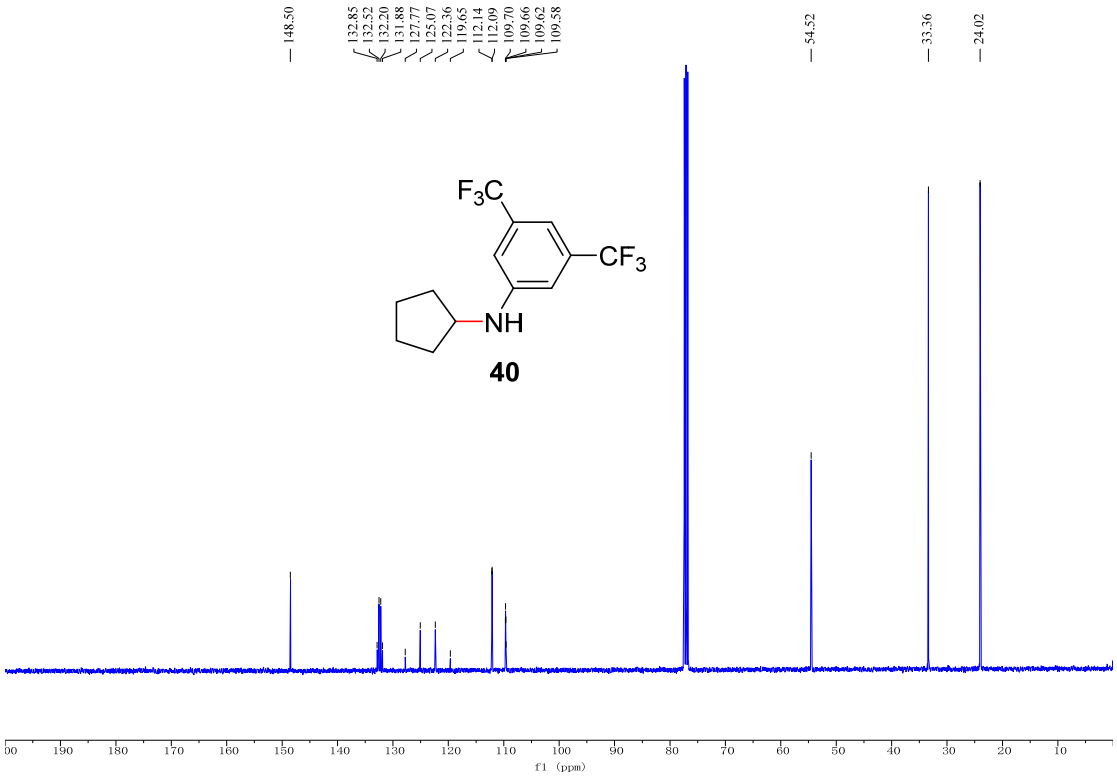
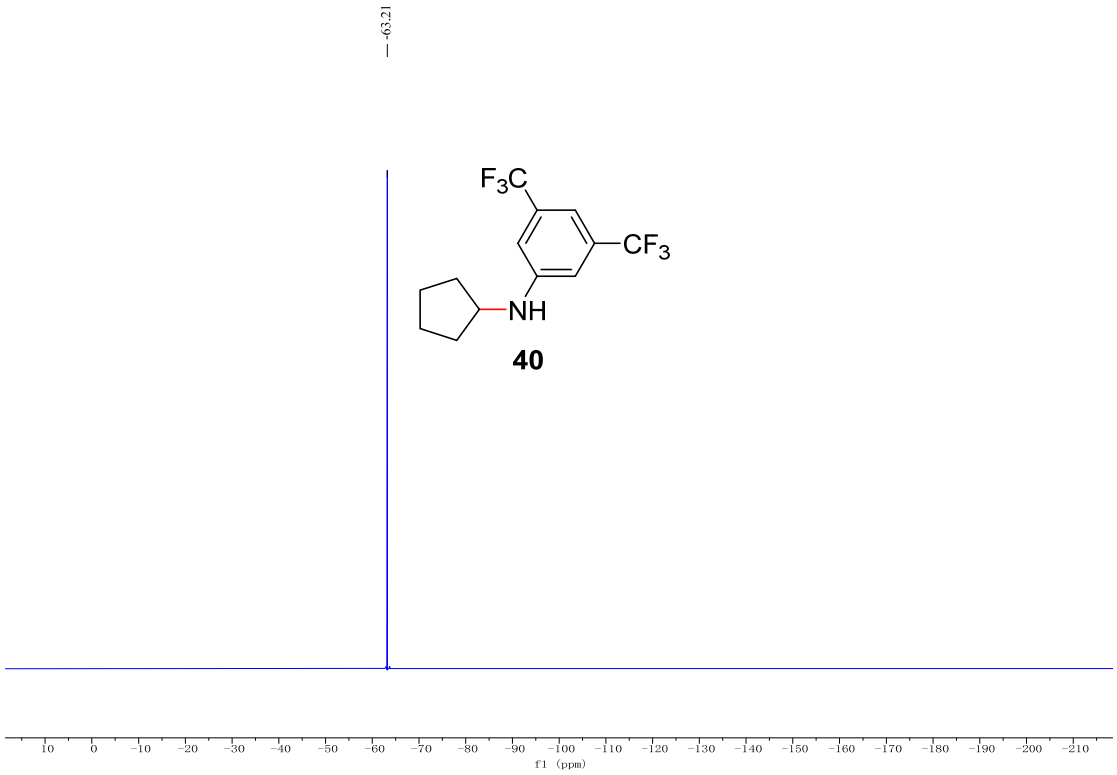
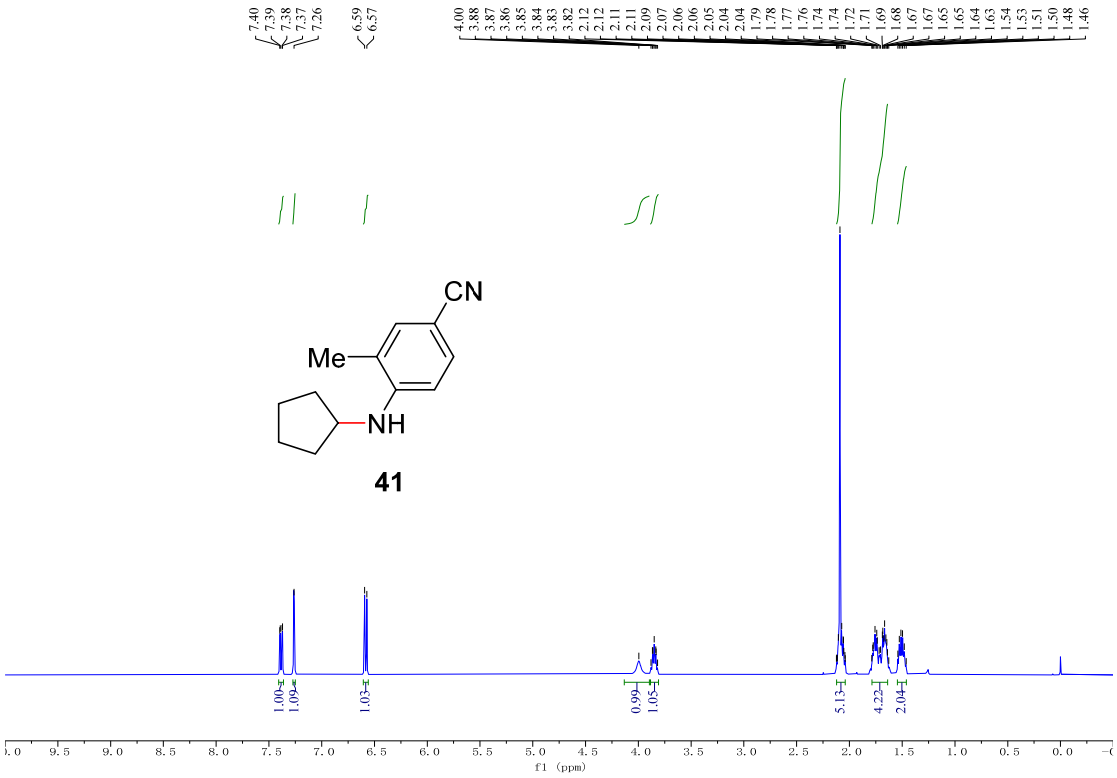
7.23
7.22
7.20
7.18
7.17
7.17
6.79
6.78
6.77
3.86
3.84
3.83
3.82
3.80
2.56
2.06
2.05
2.03
2.02
1.73
1.71
1.65
1.63
1.49
1.47
1.46
Me
O
NH
39
2.03
1.02
1.00
2.00
3.06
2.01
4.07
2.08
f1 (ppm)


198.88
148.31
138.21
129.35
117.93
117.38
112.01
54.68
33.56
26.84
24.12
Me
O
NH
39
f1 (ppm)


7.10
6.91
4.11
3.85
3.83
3.83
3.82
3.80
3.80
3.79
2.11
2.09
2.07
2.06
2.04
2.03
1.77
1.75
1.73
1.71
1.69
1.67
1.66
1.65
1.52
1.51
1.49
1.47
1.46
1.44
F3C
CF3
NH
40
1.00
2.04
0.99
1.04
2.04
4.06
2.05
f1 (ppm)


148.50
132.85
132.52
132.20
131.88
127.77
125.07
122.36
119.65
112.14
112.09
109.70
109.66
109.62
109.58
54.52
33.36
24.02
F3C
CF3
NH
40
f1 (ppm)


-63.21
F3C
CF3
NH
40
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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6.57
4.00
3.88
3.87
3.86
3.85
3.84
3.83
3.82
2.12
2.12
2.11
2.11
2.09
2.07
2.06
2.06
2.05
2.04
2.04
1.79
1.78
1.77
1.76
1.74
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1.68
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1.67
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1.63
1.54
1.53
1.51
1.50
1.48
1.46
CN
Me
NH
41
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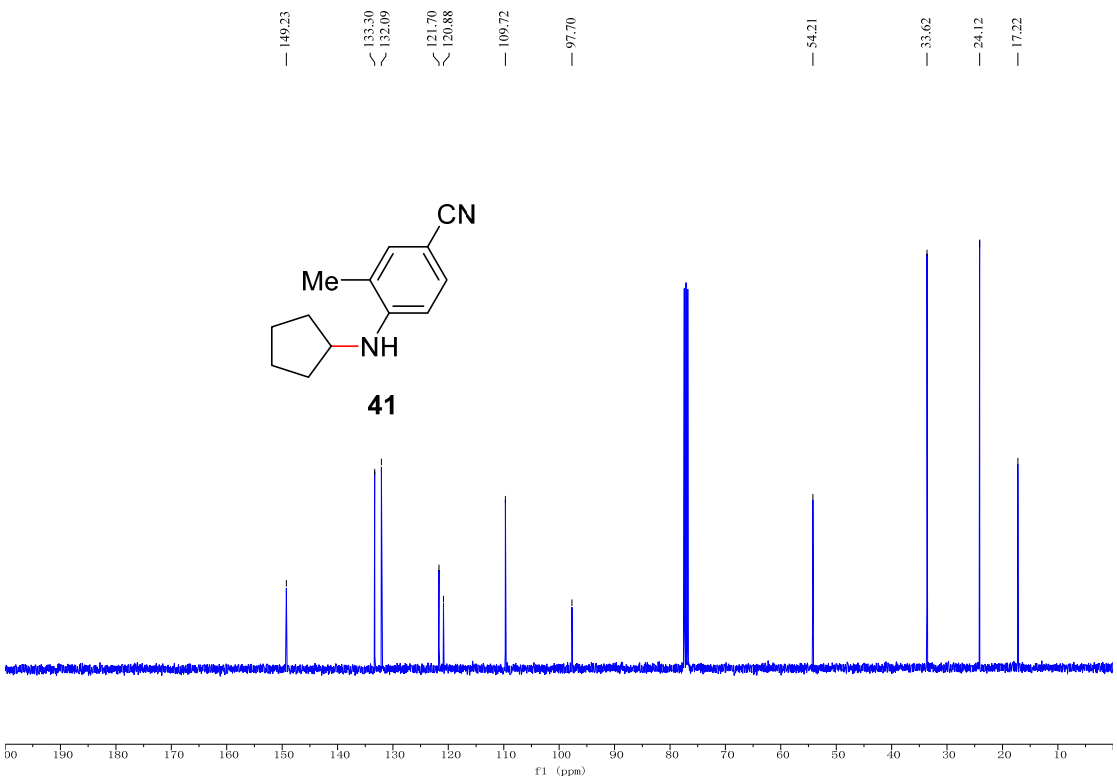
1.09
1.03
0.99
1.05
5.13
4.23
2.04
f1 (ppm)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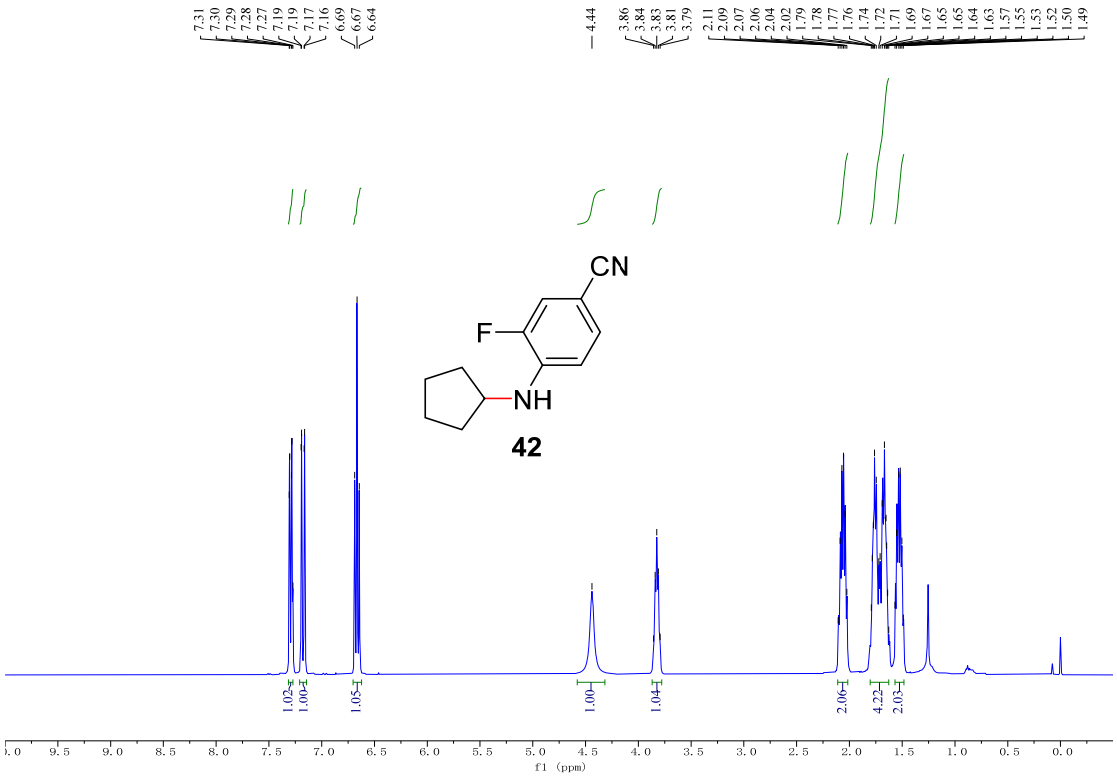
97.70
54.21
33.62
24.12
17.22
CN
Me
NH
41
f1 (ppm)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7.28
7.27
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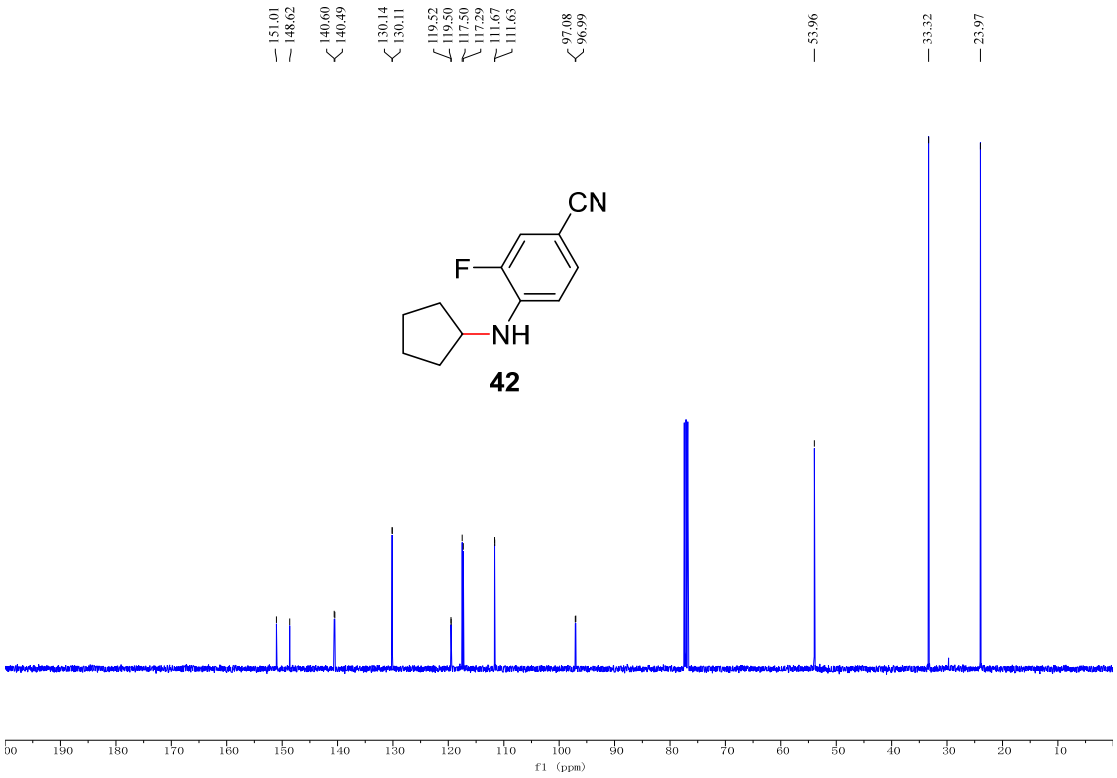
7.19
7.17
7.16
6.69
6.67
6.64
4.44
3.86
3.84
3.83
3.81
3.79
2.11
2.09
2.07
2.06
2.04
2.02
1.79
1.78
1.77
1.76
1.74
1.72
1.71
1.69
1.67
1.65
1.65
1.64
1.63
1.57
1.55
1.53
1.52
1.50
1.49
CN
F
NH
42
1.03
1.00
1.05
1.00
1.04
2.06
4.22
2.03
f1 (ppm)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148.62
140.60
140.49
130.14
130.11
119.52
119.50
117.50
117.29
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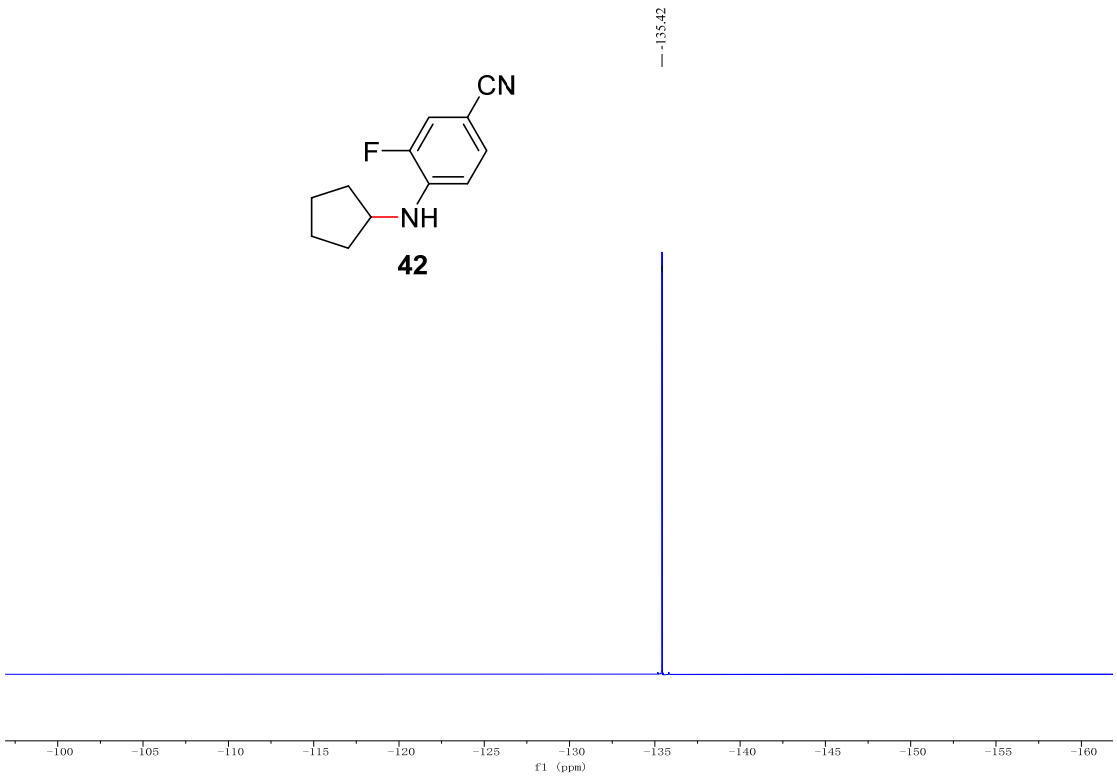
111.63
97.08
96.99
53.96
33.32
23.97
CN
F
NH
42
f1 (ppm)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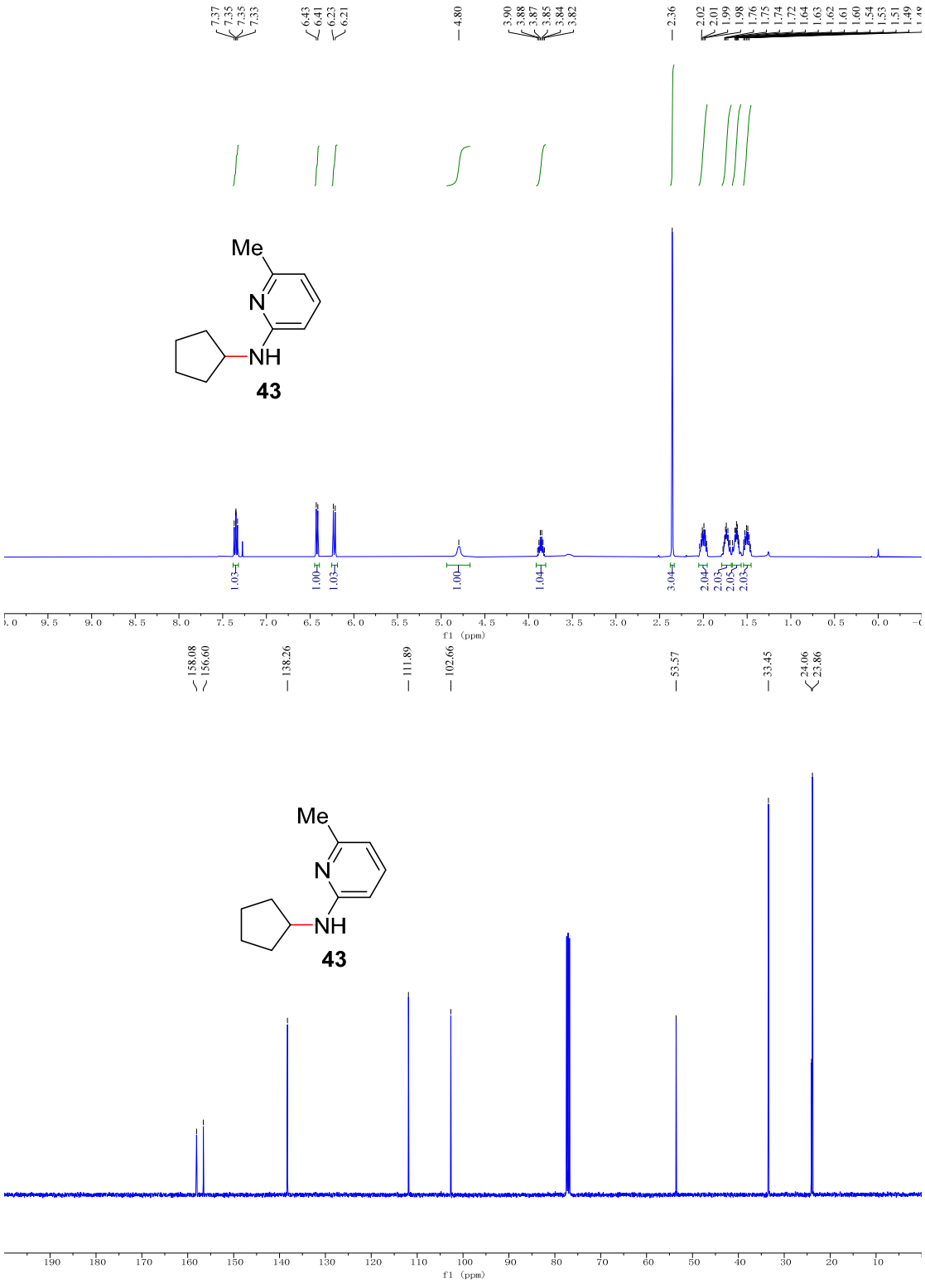
CN
F
NH
42
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
f1 (ppm)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7.35
7.33
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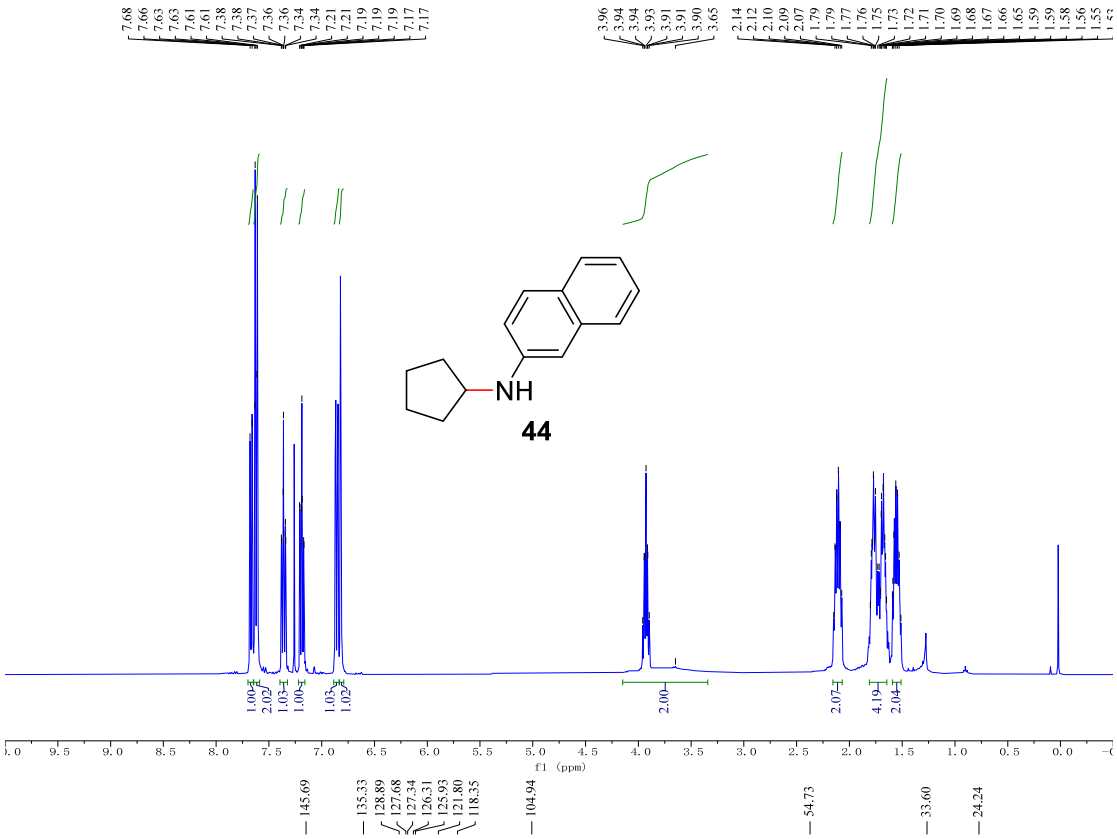
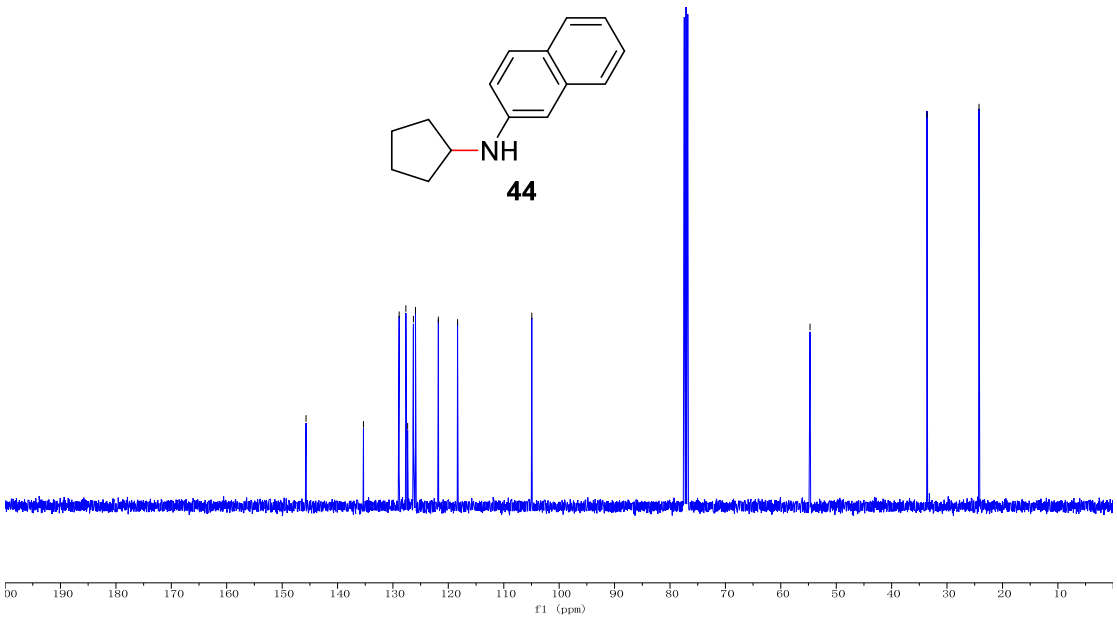
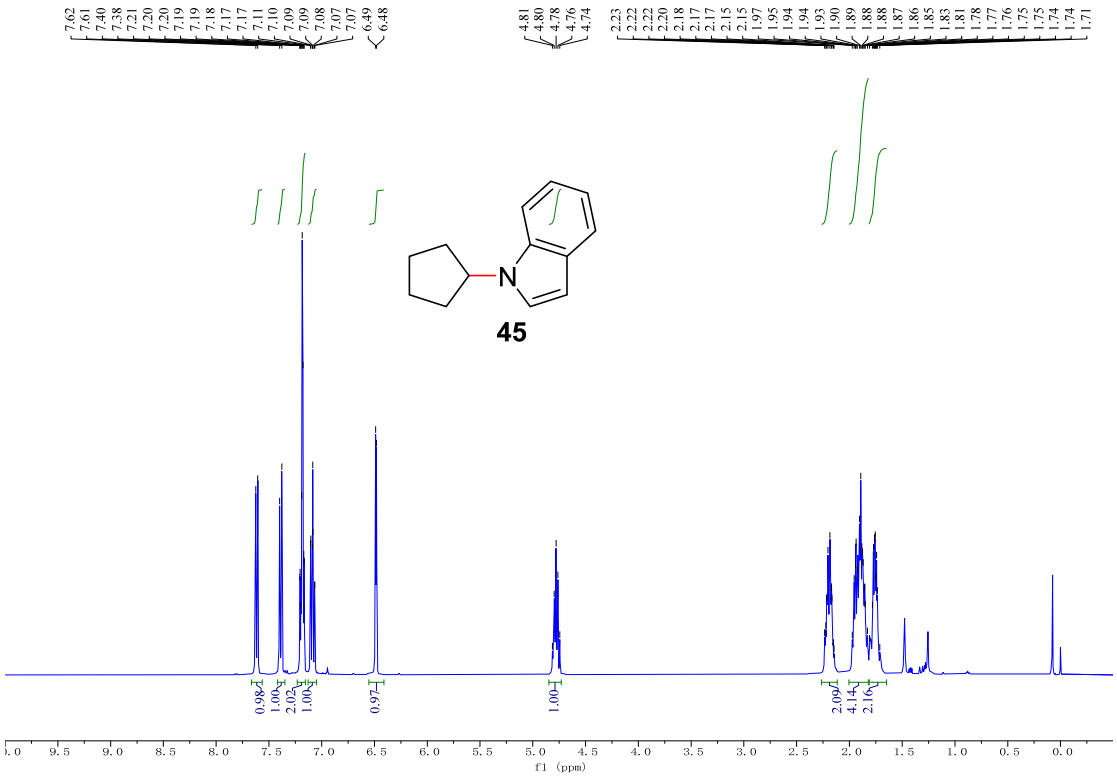
6.41
6.23
6.21
4.80
3.90
3.88
3.87
3.85
3.84
3.82
2.36
2.02
2.01
1.99
1.98
1.76
1.75
1.74
1.72
1.64
1.63
1.62
1.61
1.60
1.54
1.53
1.51
1.49
Me
N
NH
43
1.03
1.00
1.03
1.00
1.04
3.04
2.04
2.05
2.05
2.03
f1 (ppm)
158.08
156.60
138.26
111.89
102.66
53.57
33.45
24.06
23.86
Me
N
NH
43
f1 (ppm)


NH
44
f1 (ppm)


NH
44
f1 (ppm)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7.19
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7.18
7.17
7.17
7.17
7.11
7.10
7.09
7.09
7.08
7.07
7.07
6.49
6.48
4.81
4.80
4.78
4.76
4.74
2.23
2.22
2.22
2.20
2.18
2.17
2.17
2.15
2.15
1.97
1.95
1.94
1.94
1.93
1.90
1.89
1.88
1.88
1.87
1.86
1.85
1.83
1.81
1.78
1.77
1.76
1.75
1.75
1.74
1.74
1.71
N
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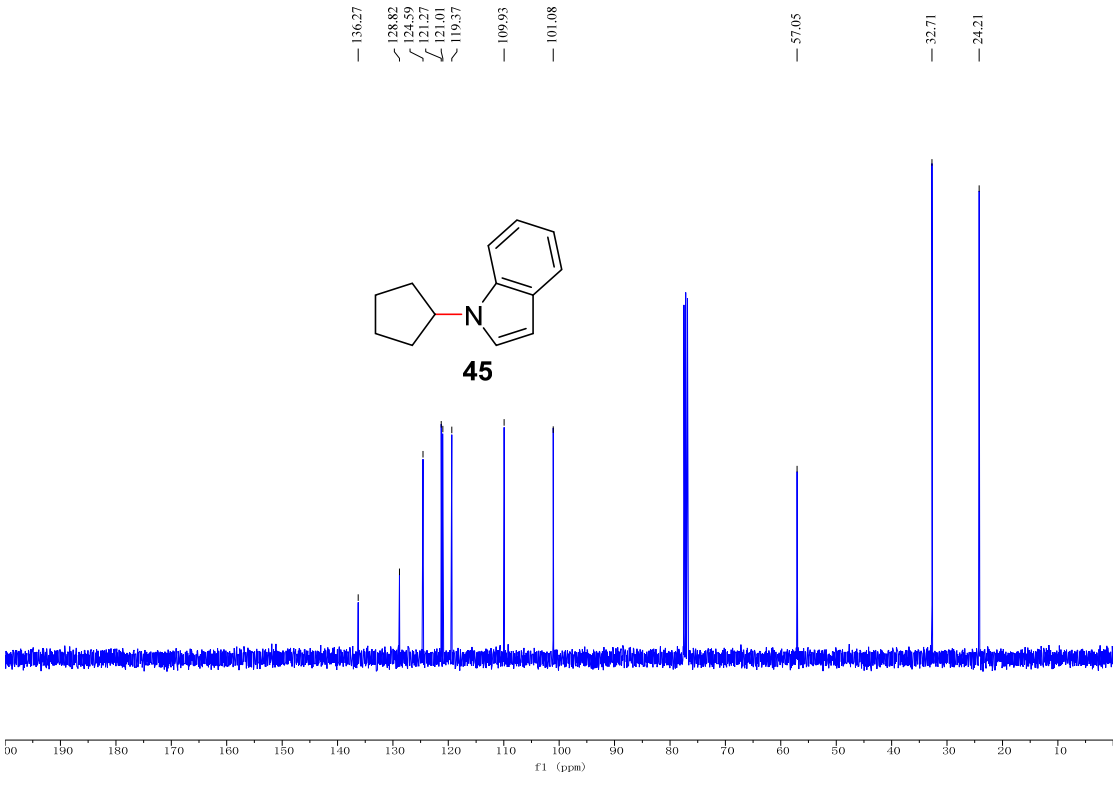
1.06
2.02
1.00
0.97
1.00
2.09
4.14
2.16
f1 (ppm)


136.27
128.82
124.59
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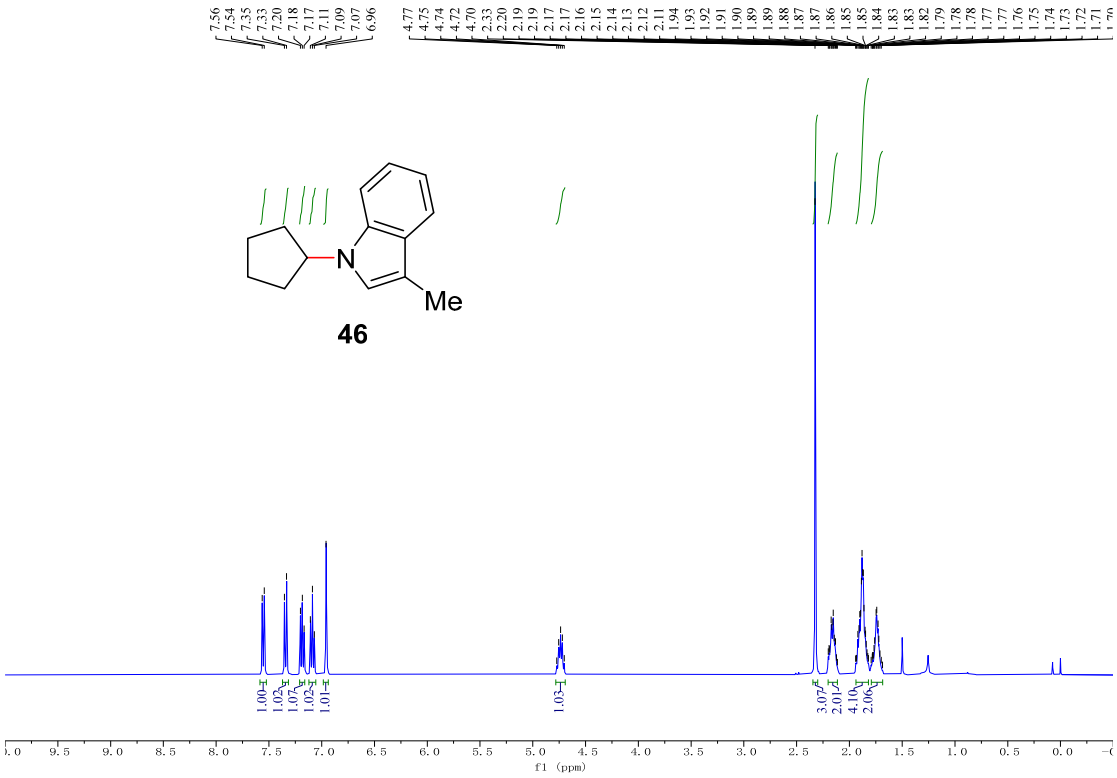
121.01
119.37
109.93
101.08
57.05
32.71
24.21
N
45
f1 (ppm)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7.18
7.17
7.11
7.09
7.07
6.96
4.77
4.75
4.74
4.72
4.70
2.33
2.20
2.19
2.19
2.17
2.17
2.16
2.15
2.14
2.13
2.12
2.11
1.94
1.93
1.92
1.91
1.90
1.89
1.89
1.88
1.87
1.87
1.86
1.85
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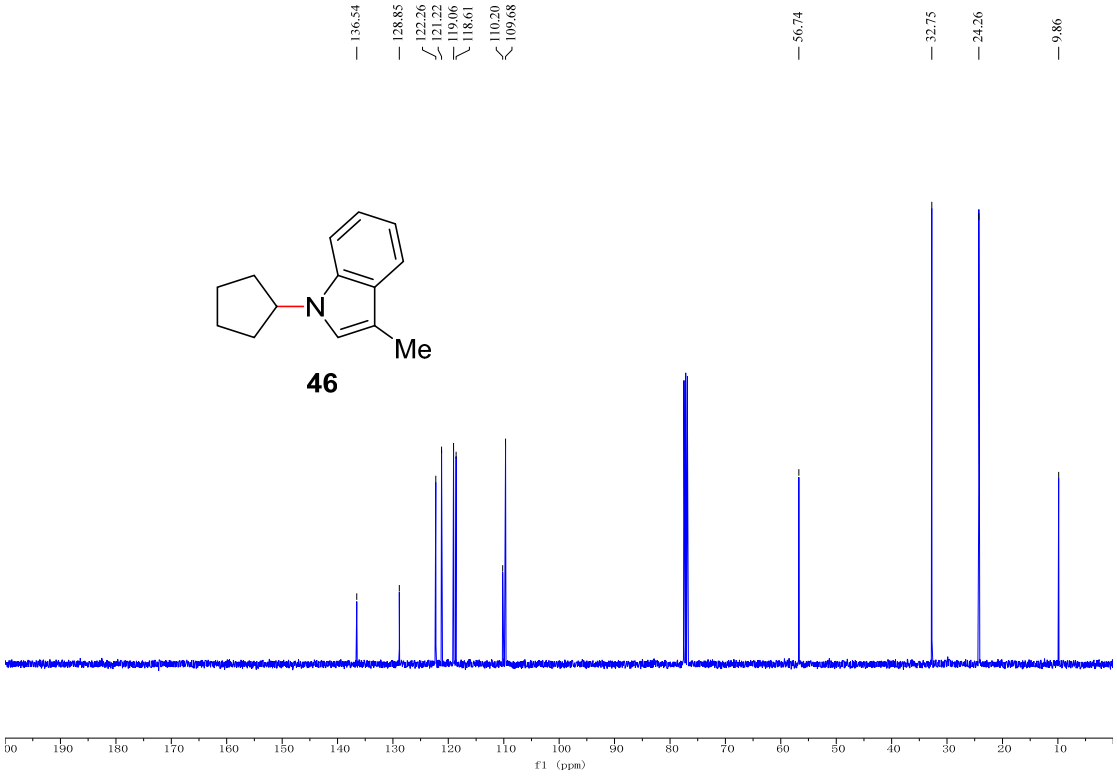
1.83
1.82
1.79
1.78
1.78
1.77
1.77
1.76
1.75
1.74
1.73
1.72
1.71
N
Me
46
1.00
1.02
1.07
1.02
1.01
1.03
3.07
2.01
4.10
2.06
f1 (ppm)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128.85
122.26
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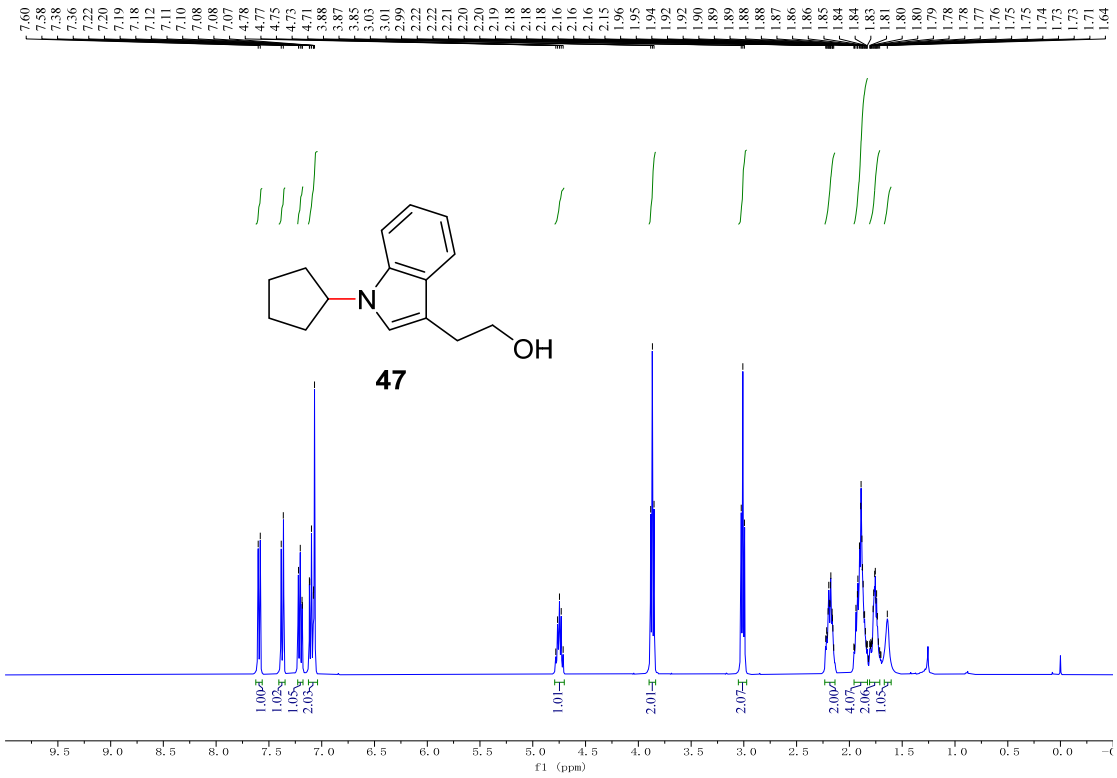
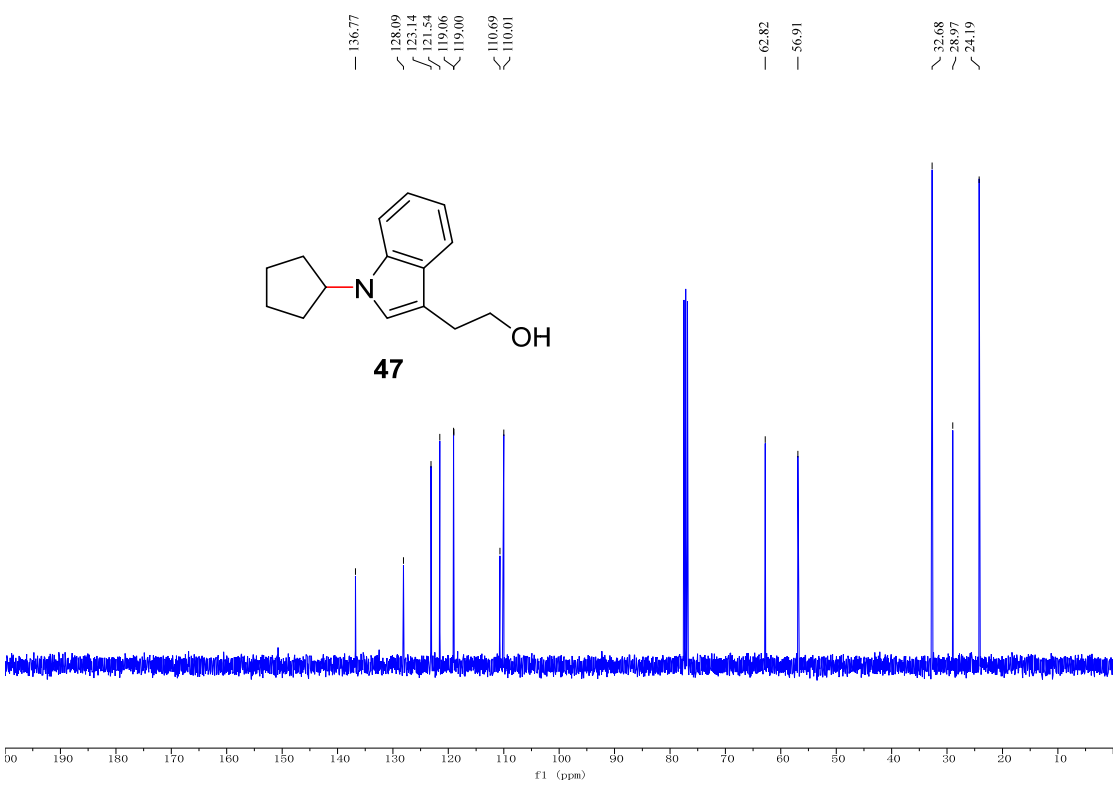
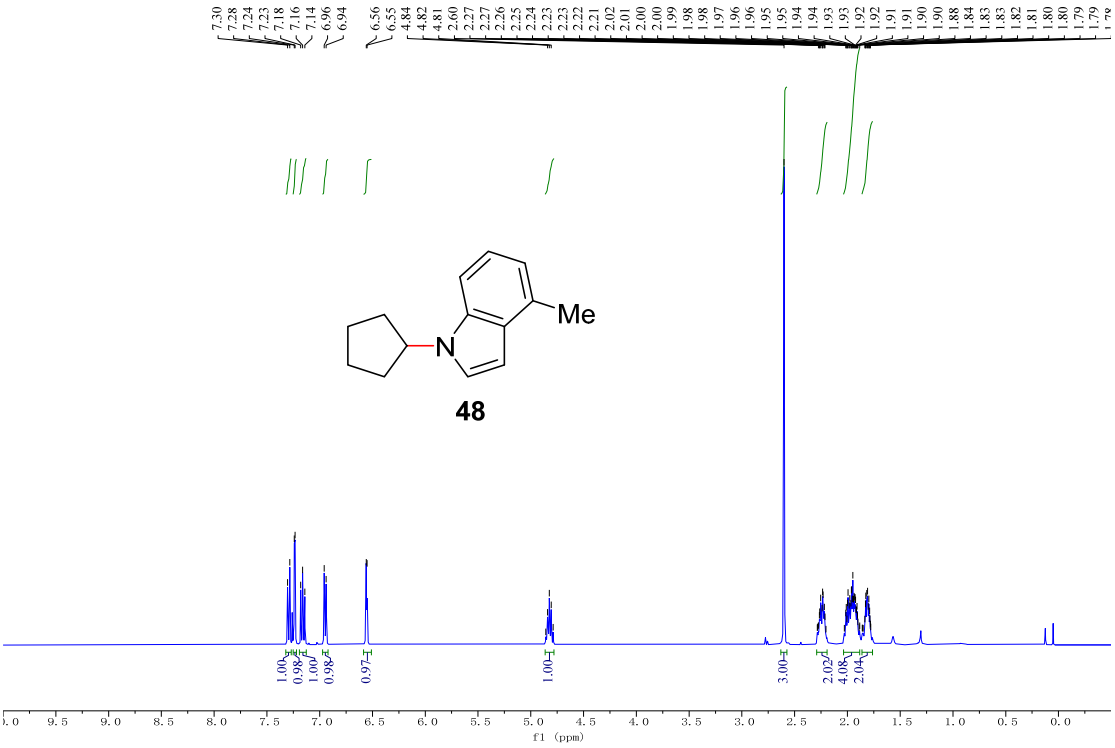
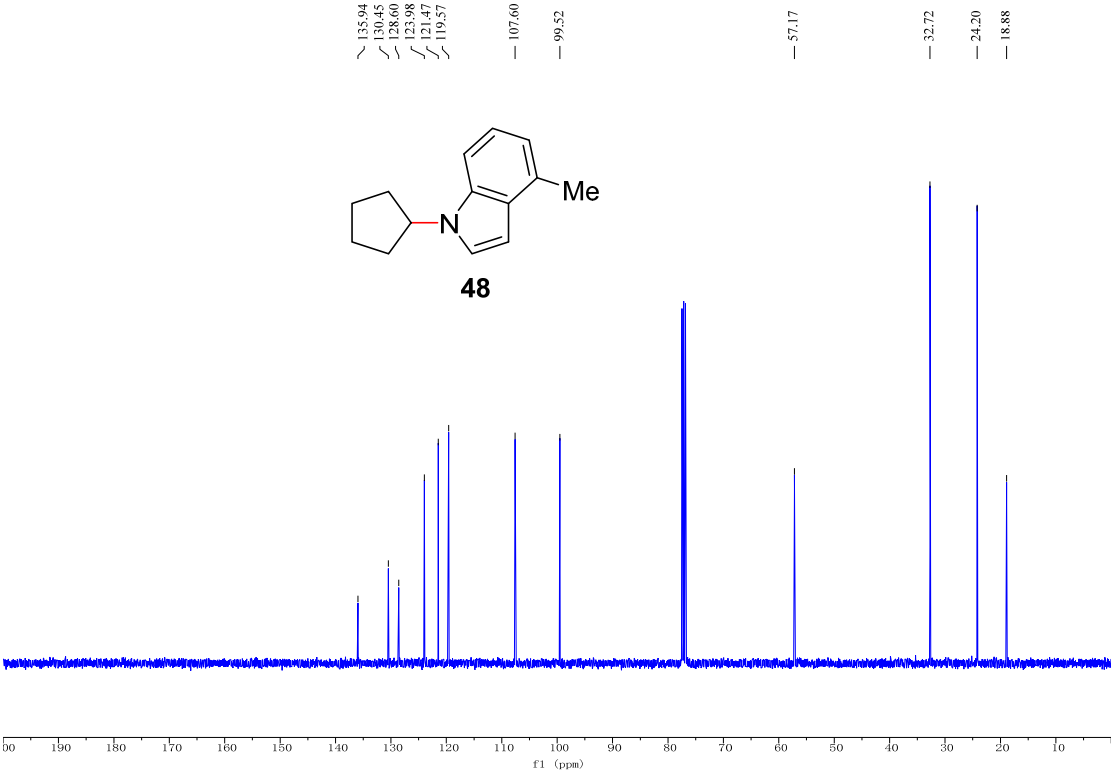
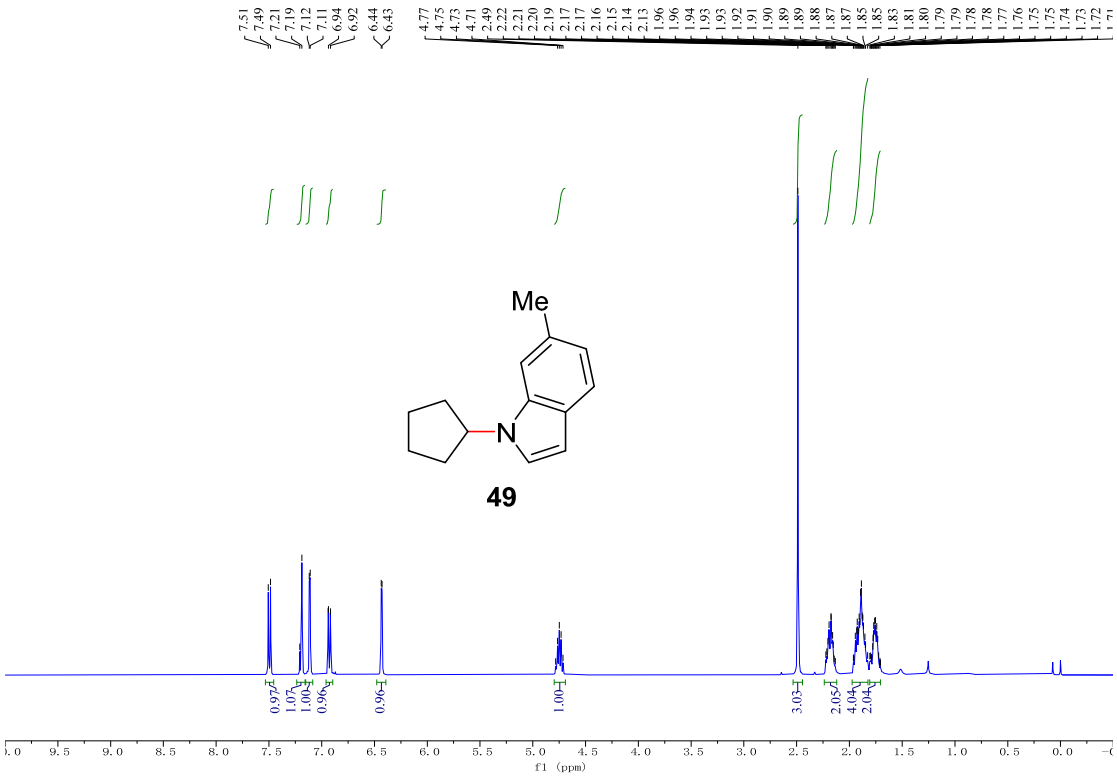
109.68
56.74
32.75
24.26
9.86
N
Me
46
f1 (ppm)

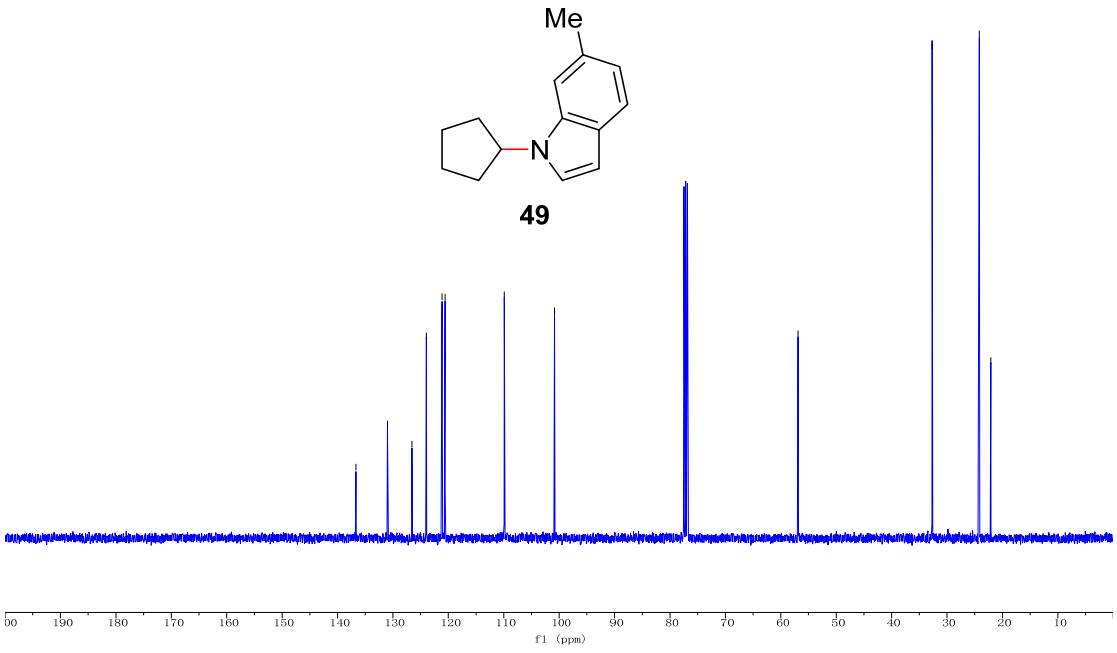

7.60 7.58 7.38 7.36 7.22 7.20 7.19 7.18 7.12 7.11 7.10 7.08 7.08 7.07 4.78 4.77 4.75 4.73 4.71 3.88 3.87 3.85 3.03 3.01 2.99 2.22 2.21 2.20 2.20 2.19 2.18 2.18 2.18 2.16 2.16 2.16 2.15 1.96 1.95 1.94 1.92 1.90 1.89 1.89 1.88 1.88 1.87 1.86 1.86 1.85 1.84 1.84 1.83 1.81 1.80 1.80 1.79 1.78 1.78 1.77 1.76 1.75 1.75 1.74 1.73 1.73 1.71 1.64
N
OH
47
1.00 1.02 1.05 2.03 1.01 2.01 2.07 2.00 4.07 2.06 1.05
f1 (ppm)

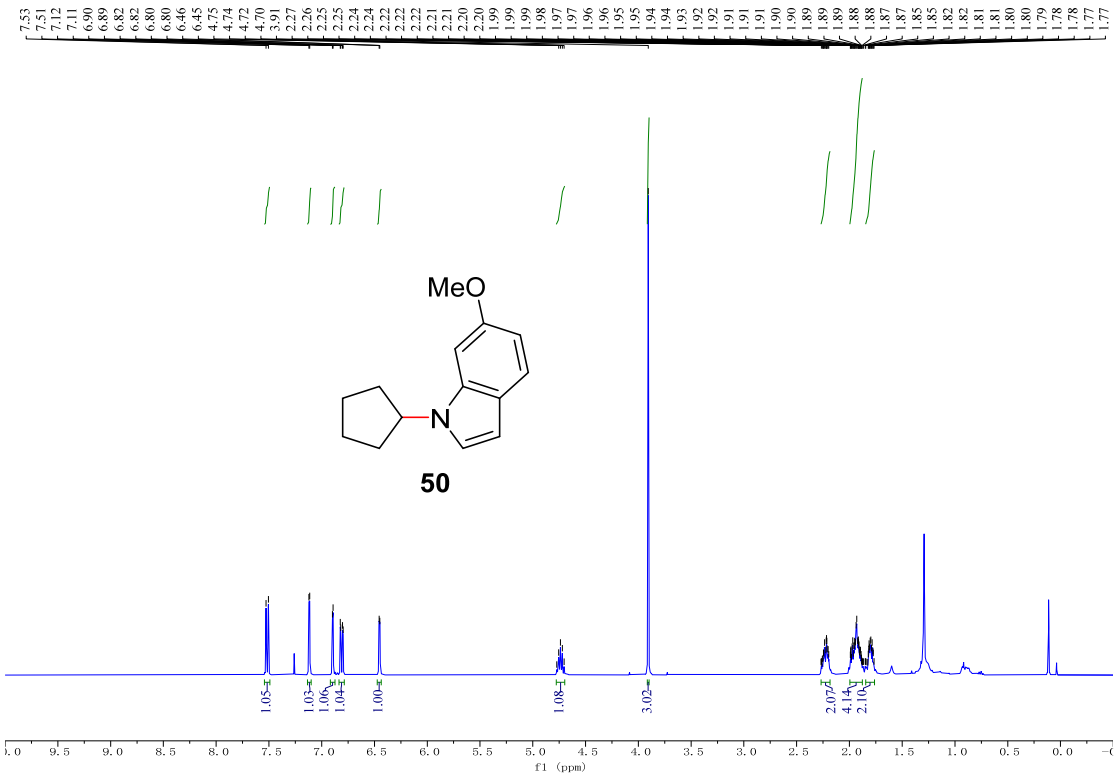

136.77
128.09
123.14
121.54
119.06
119.00
110.69
110.01
62.82
56.91
32.68
28.97
24.19
N
OH
47
f1 (ppm)

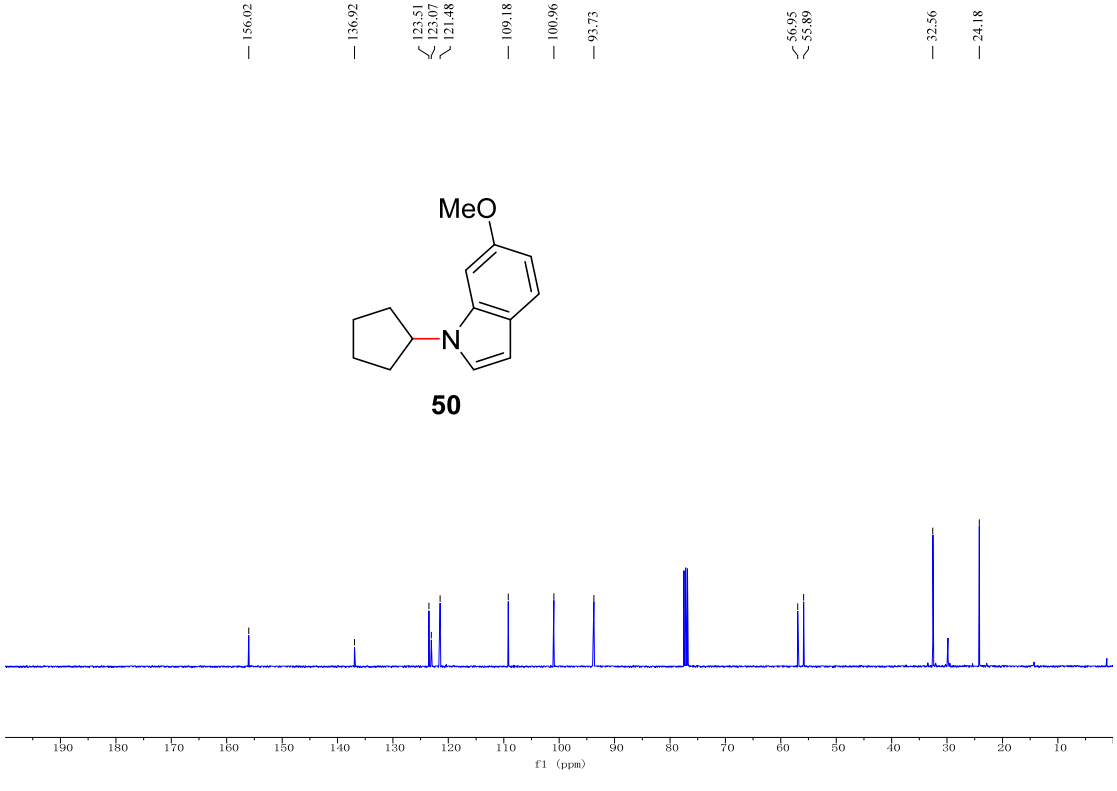

Me
N
48
f1 (ppm)


Me
N
48
f1 (ppm)


Me
N
49
f1 (ppm)


Me
N
49
f1 (ppm)


MeO
N
50
1.05
1.03
1.06
1.04
1.00
1.08
3.02
2.07
4.14
2.10
f1 (ppm)


156.02
136.92
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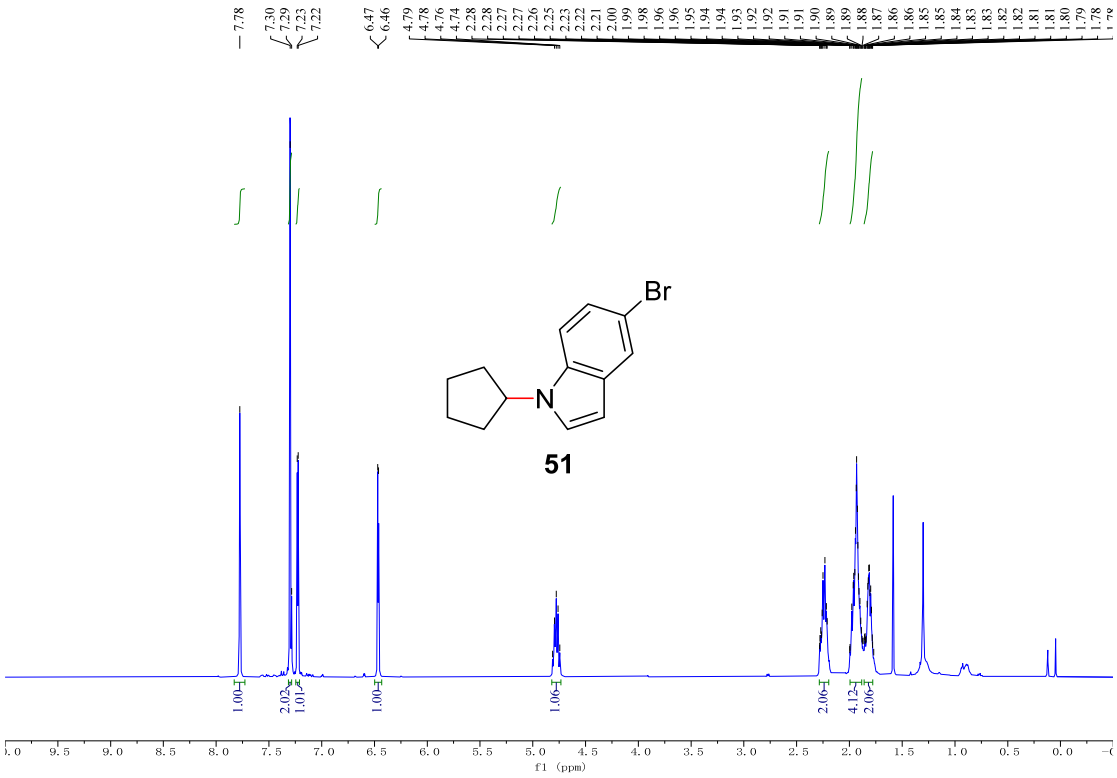
123.07
121.48
109.18
100.96
93.73
56.95
55.89
32.56
24.18
MeO
N
50
f1 (ppm)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1.00
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2.06
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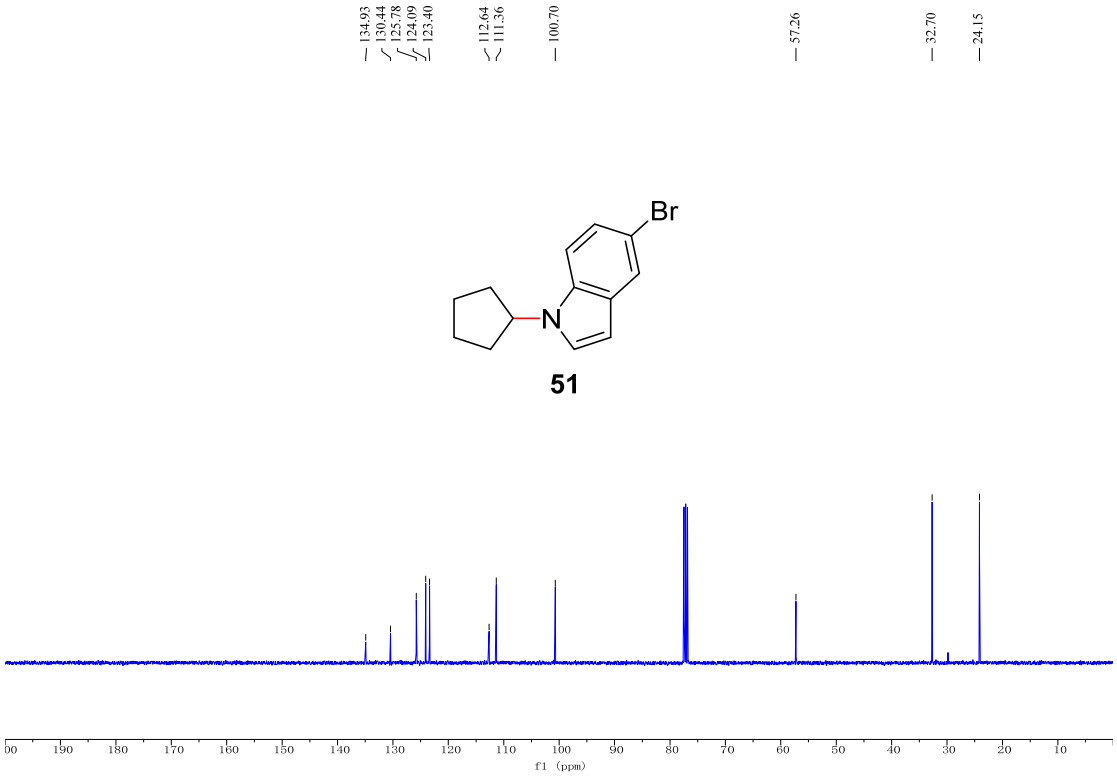
2.06
f1 (ppm)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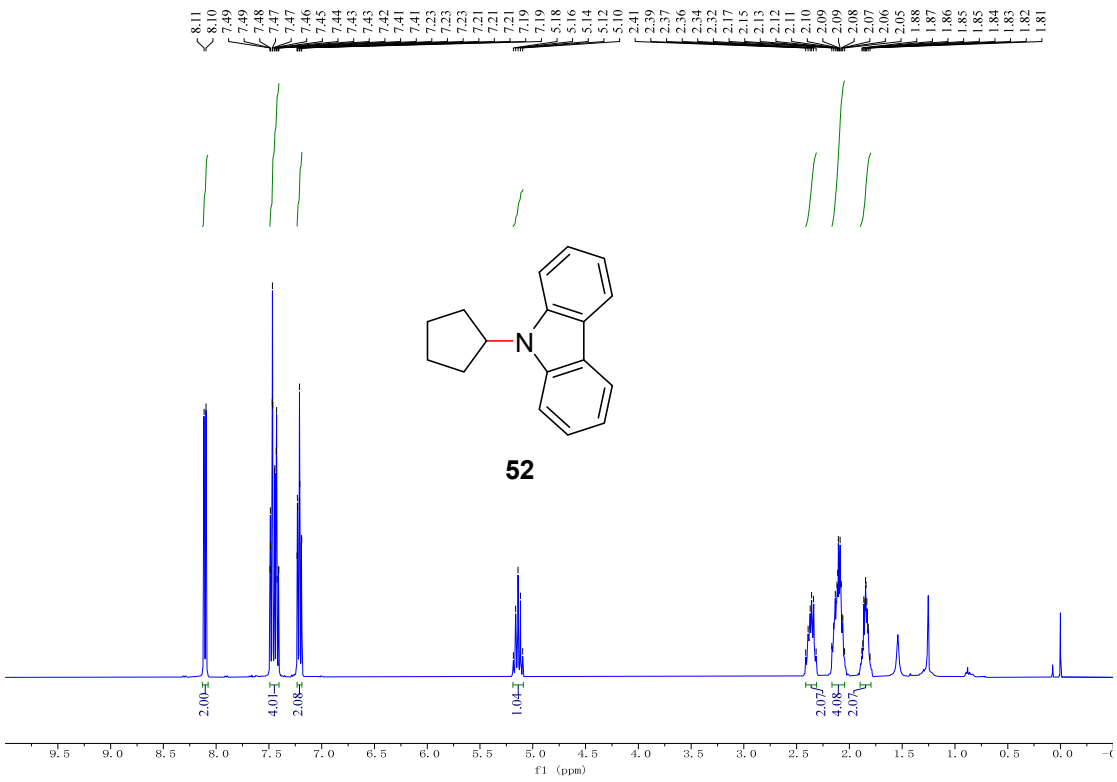
f1 (ppm)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5.12
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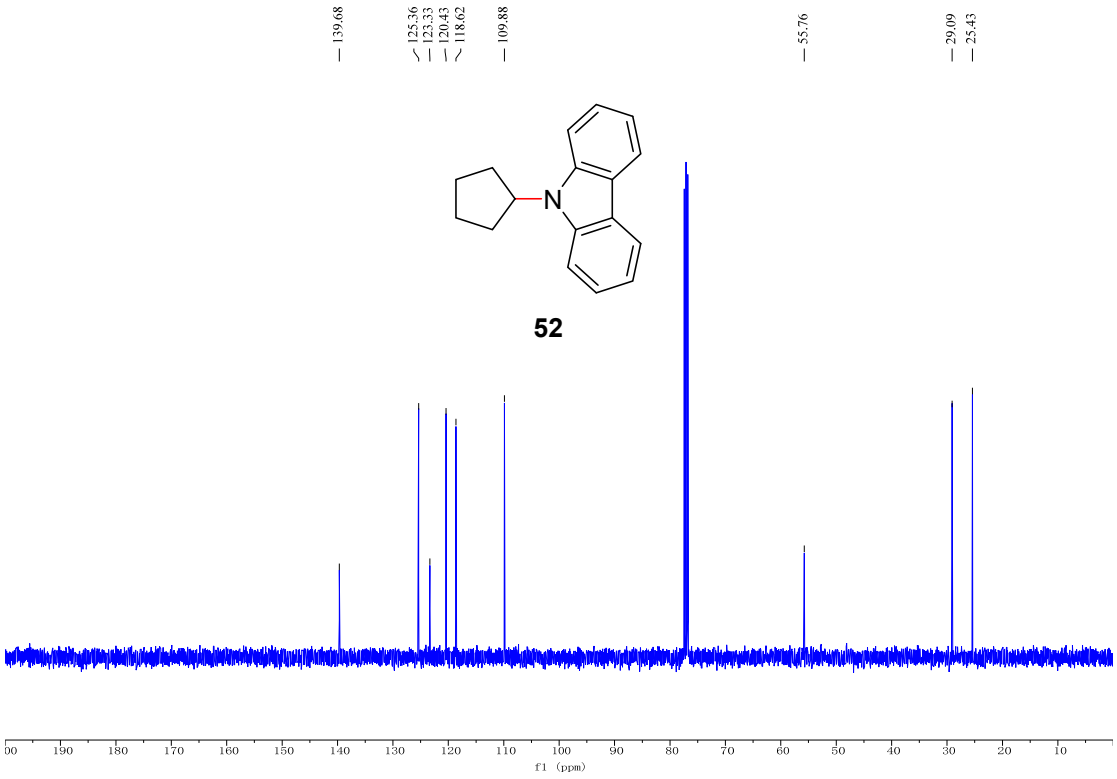
2.07
f1 (ppm)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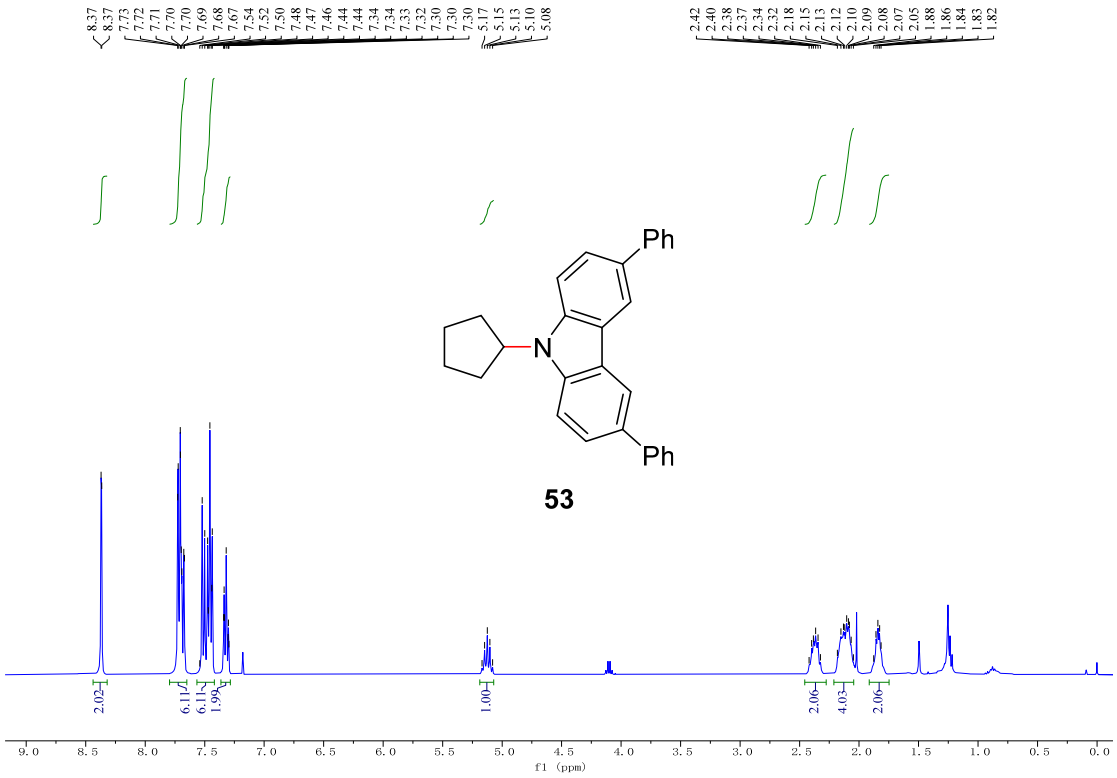
f1 (ppm)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2.07
2.05
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1.86
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1.83
1.82
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2.06
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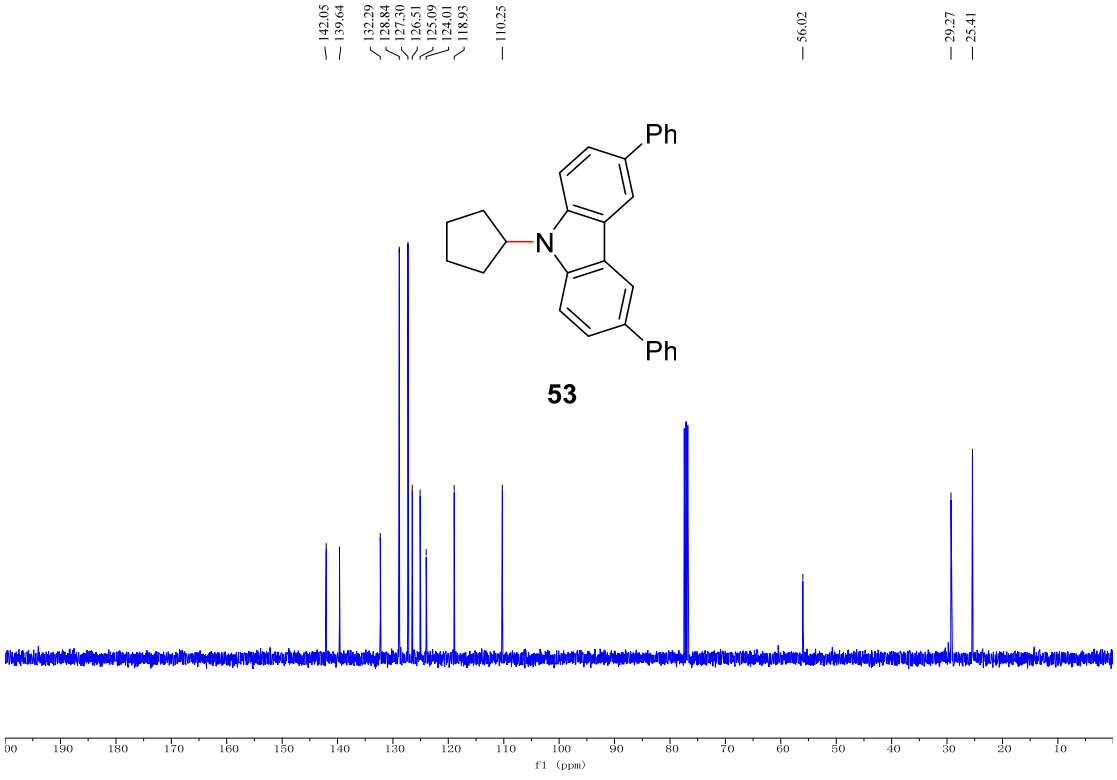
2.06
f1 (ppm)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25.41
Ph
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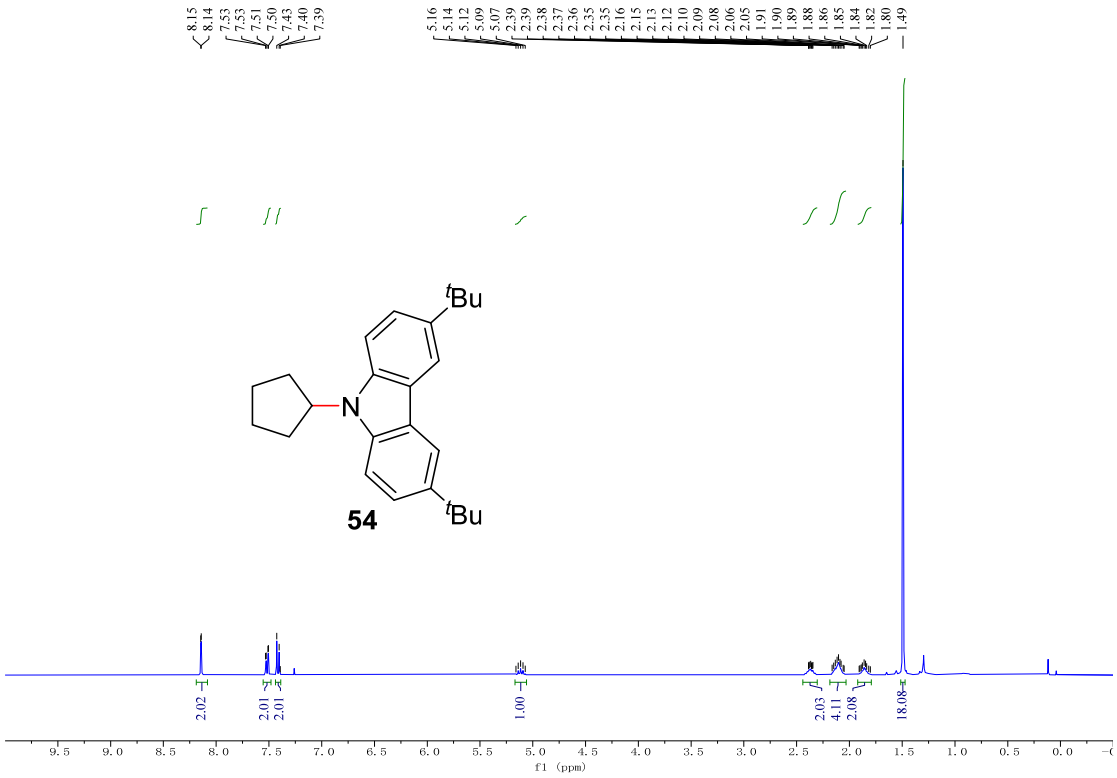
Ph
53
f1 (ppm)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2.13
2.12
2.10
2.09
2.08
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2.05
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1.90
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1.88
1.86
1.85
1.84
1.82
1.80
1.49
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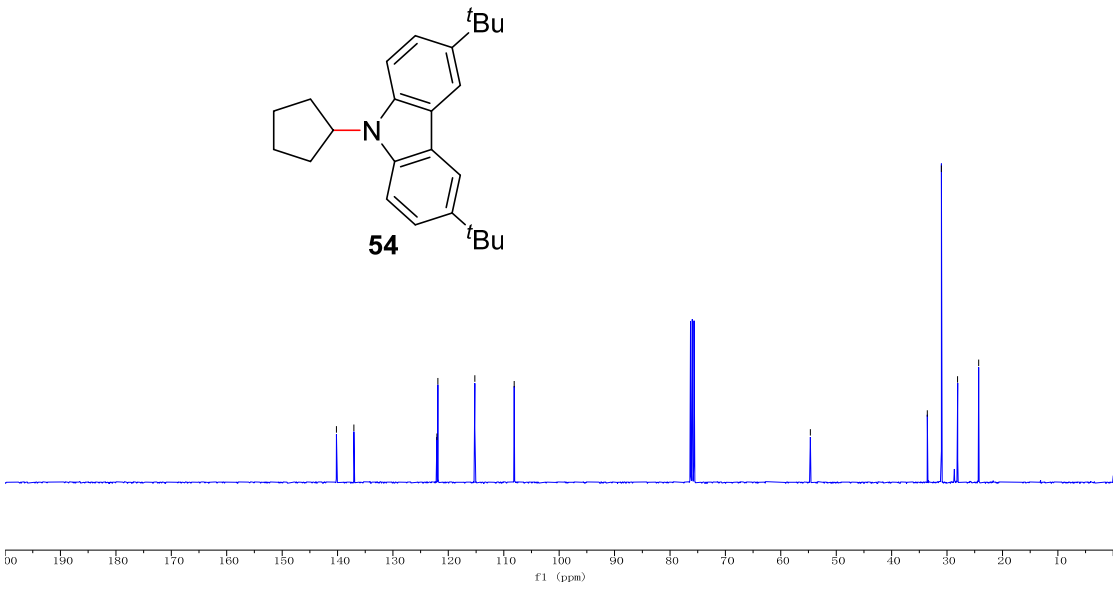
18.08
f1 (ppm)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28.09
24.30
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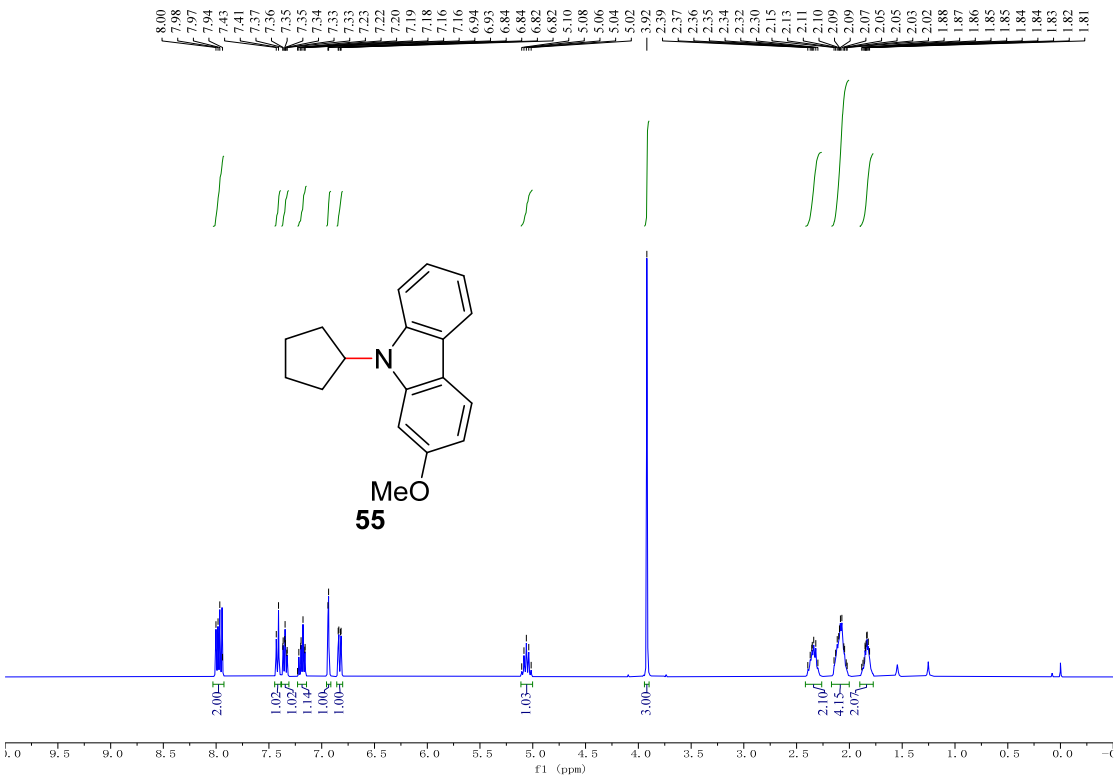
N
tBu
54
f1 (ppm)


MeO
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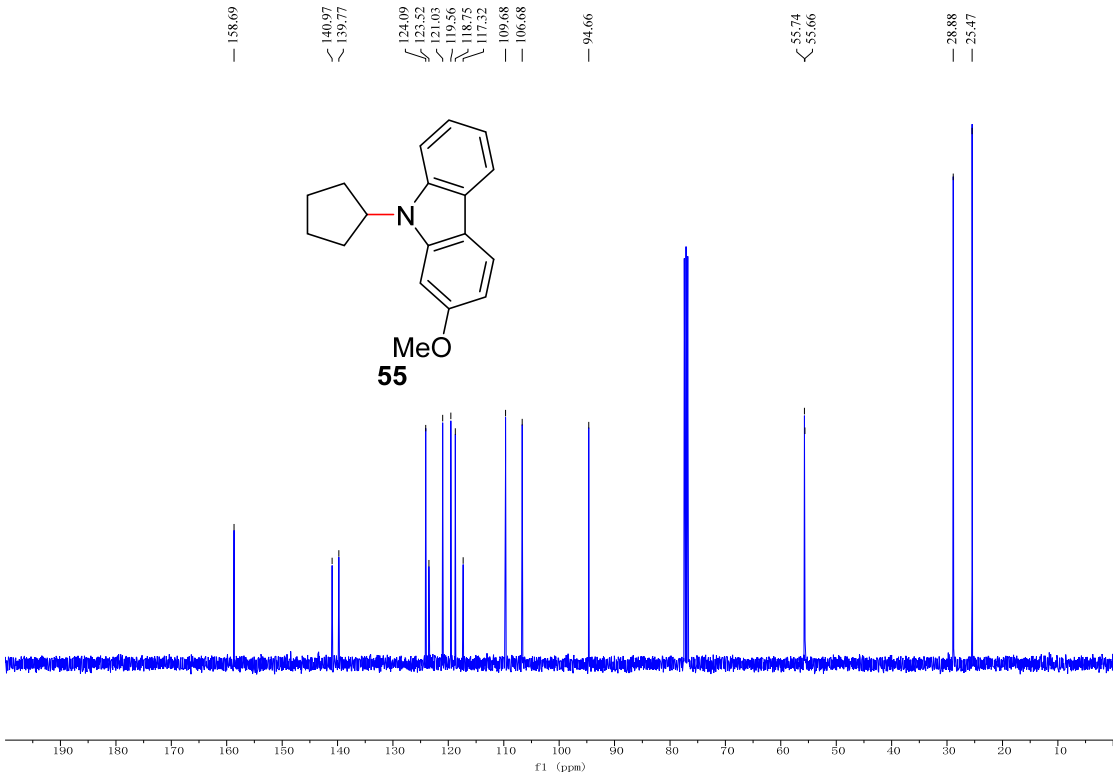
f1 (ppm)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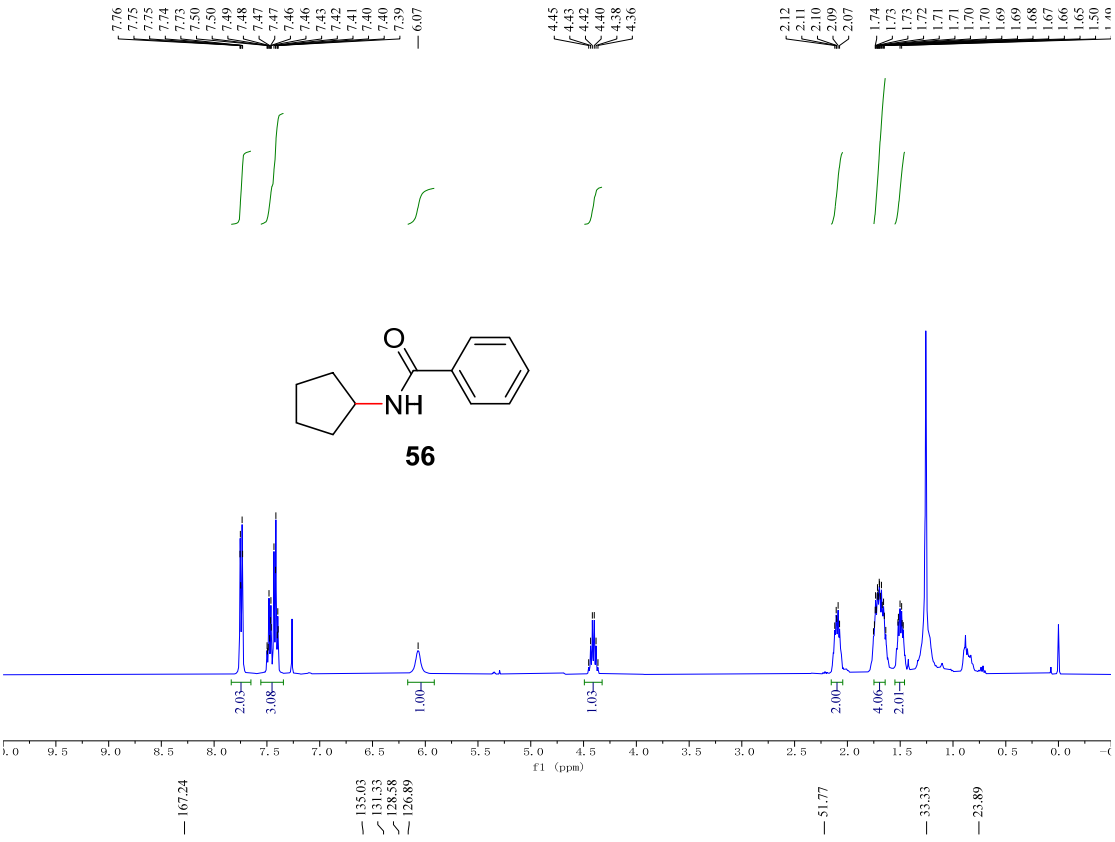
f1 (ppm)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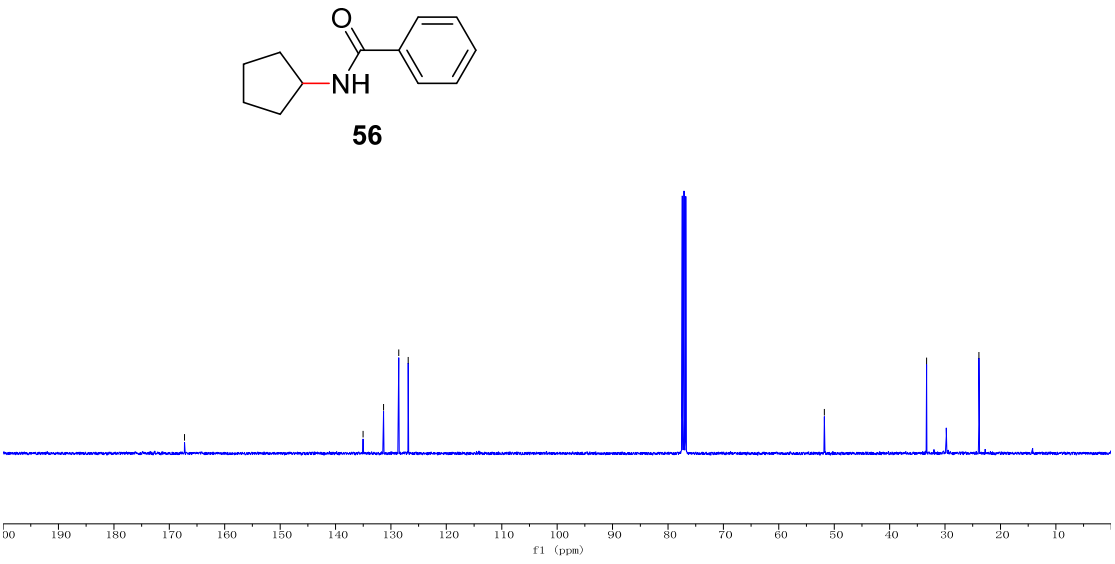
1.03
2.00
4.06
2.01
f1 (ppm)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23.89
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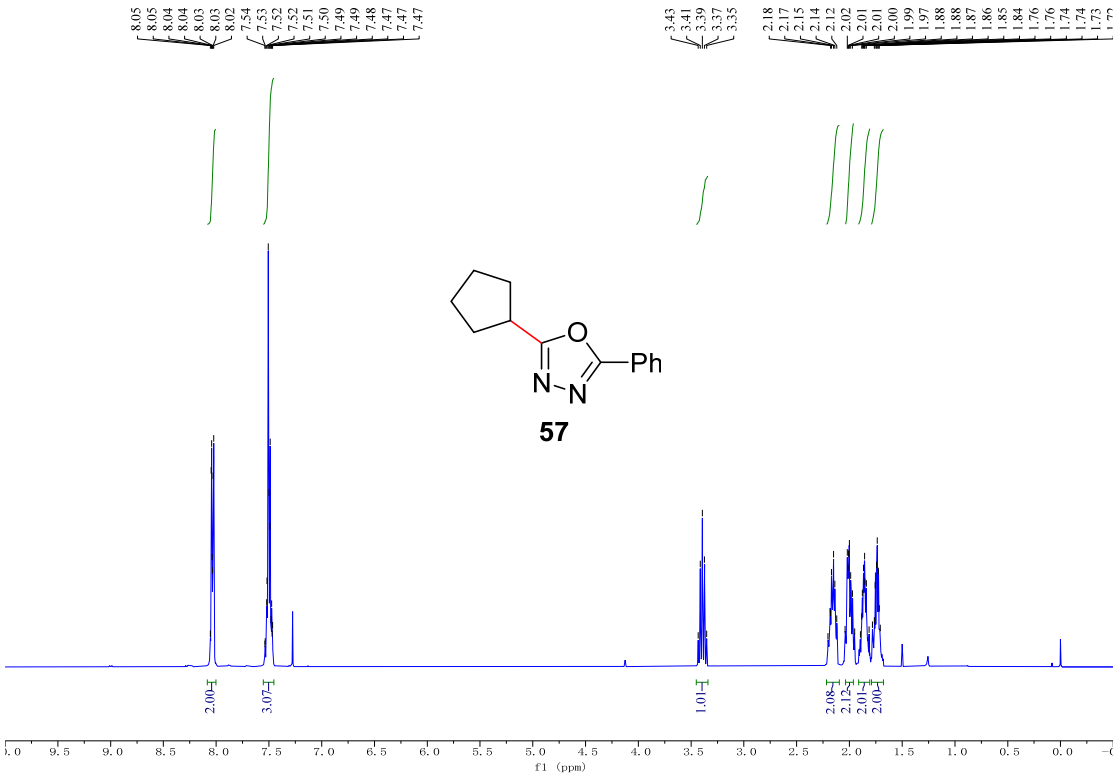
56
f1 (ppm)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1.76
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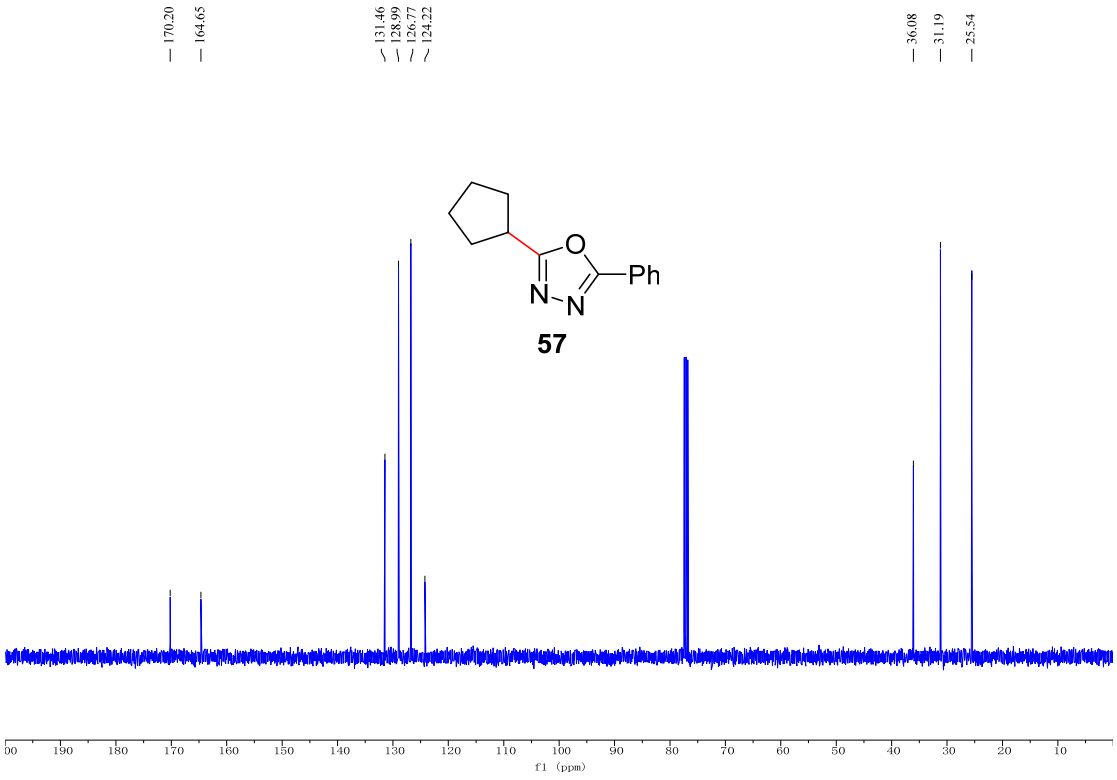
2.00
f1 (ppm)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Ph
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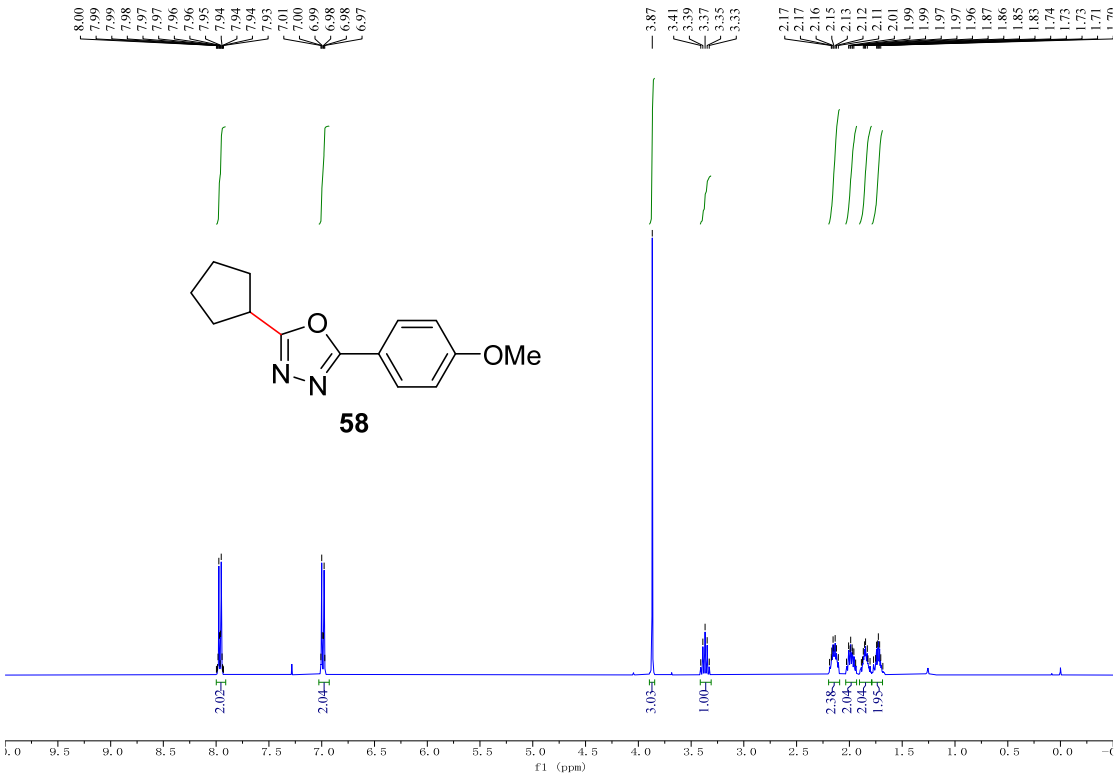
f1 (ppm)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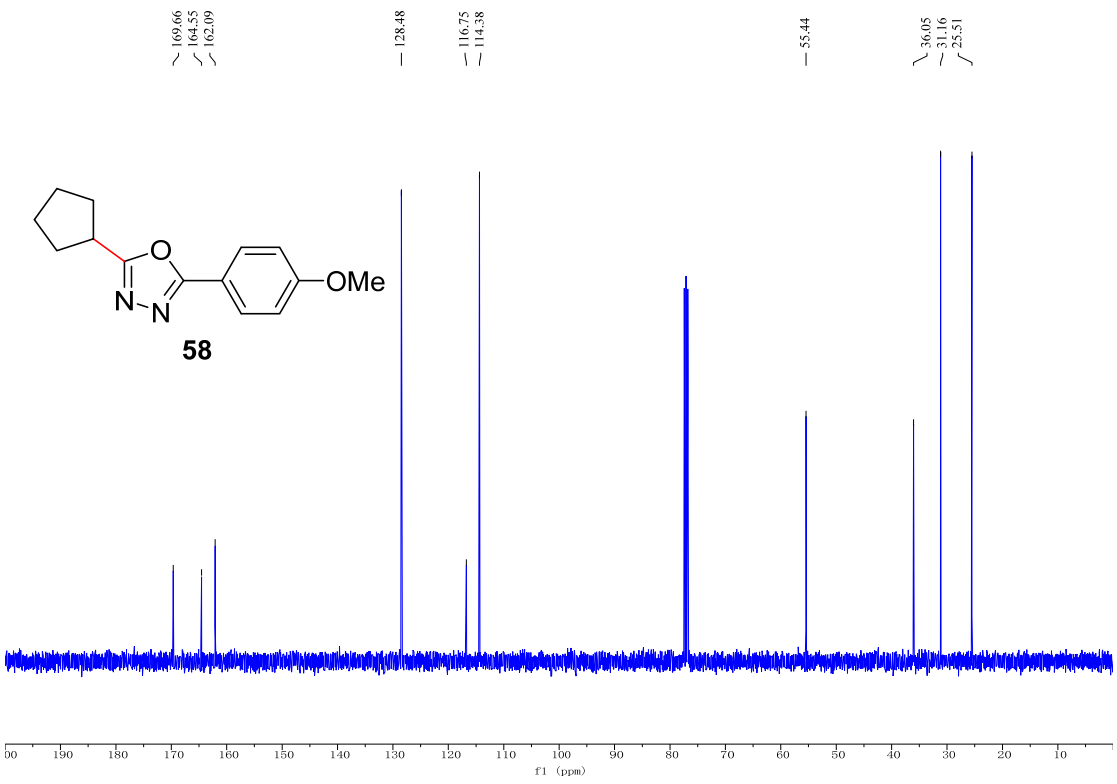
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OMe
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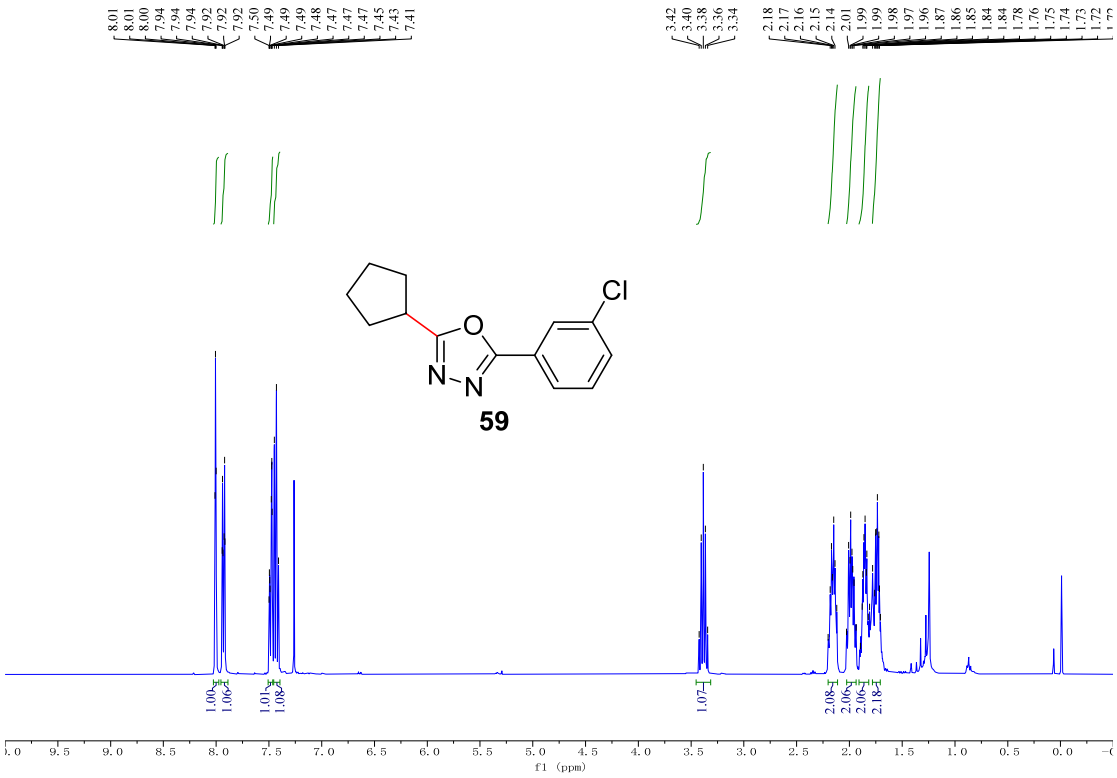
f1 (ppm)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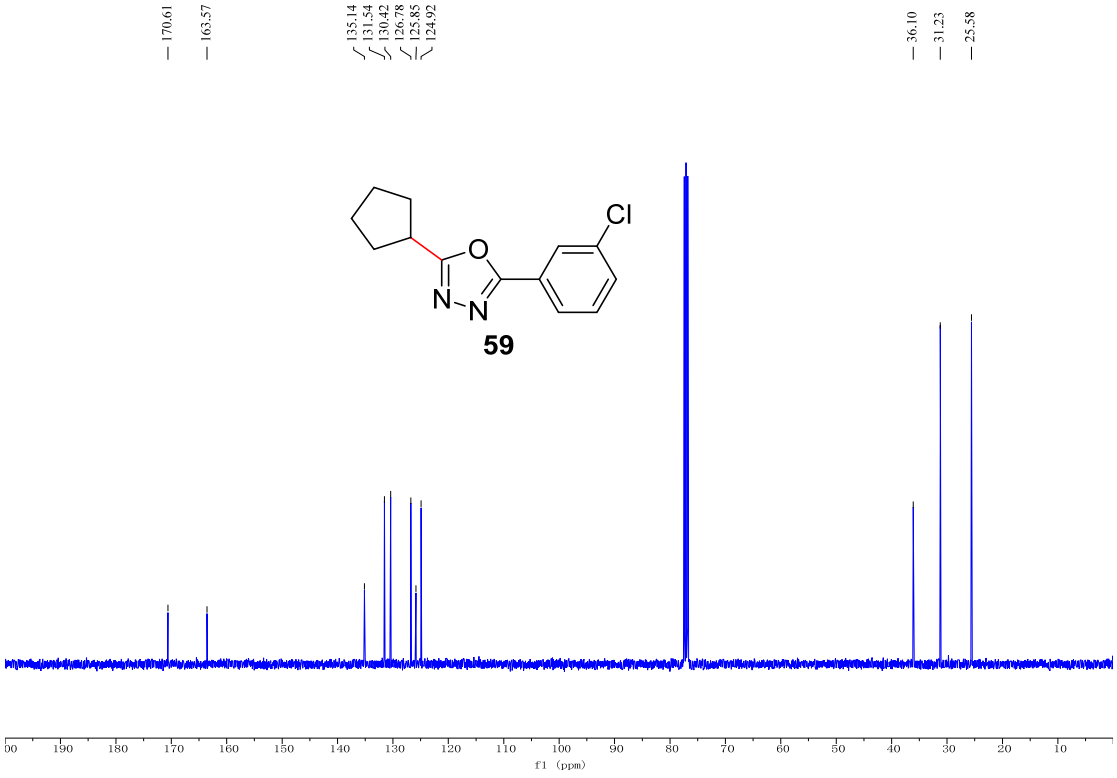
2.06
2.18
f1 (ppm)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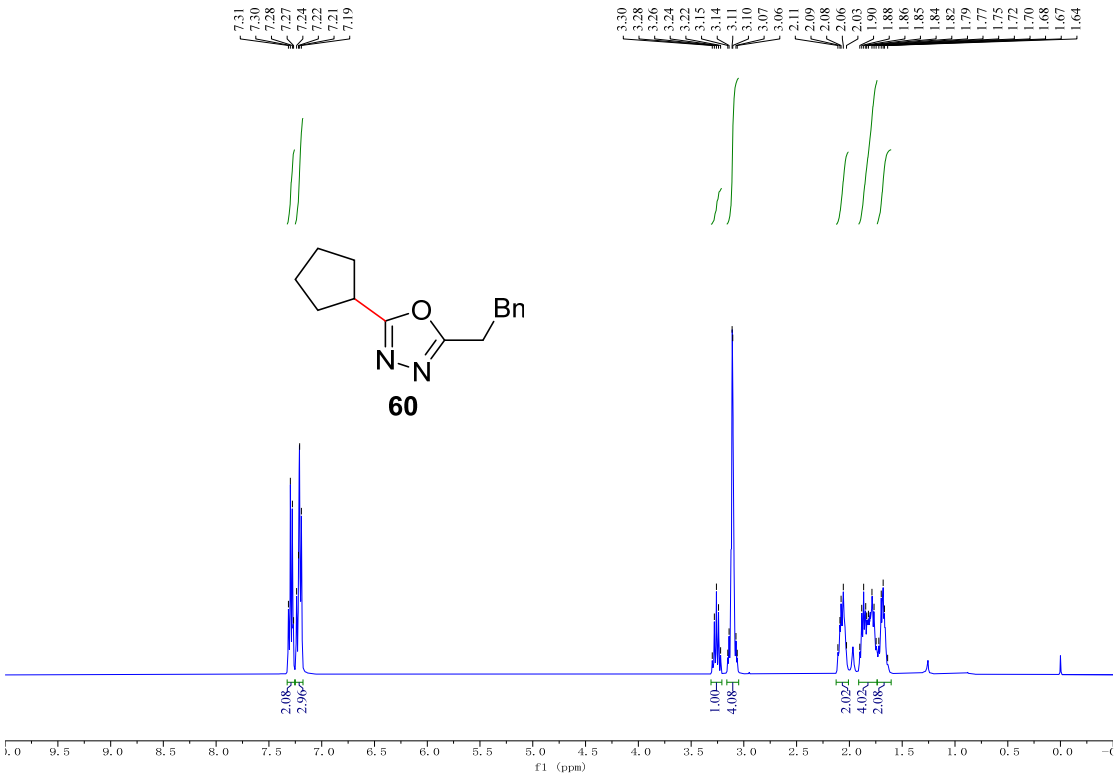
f1 (ppm)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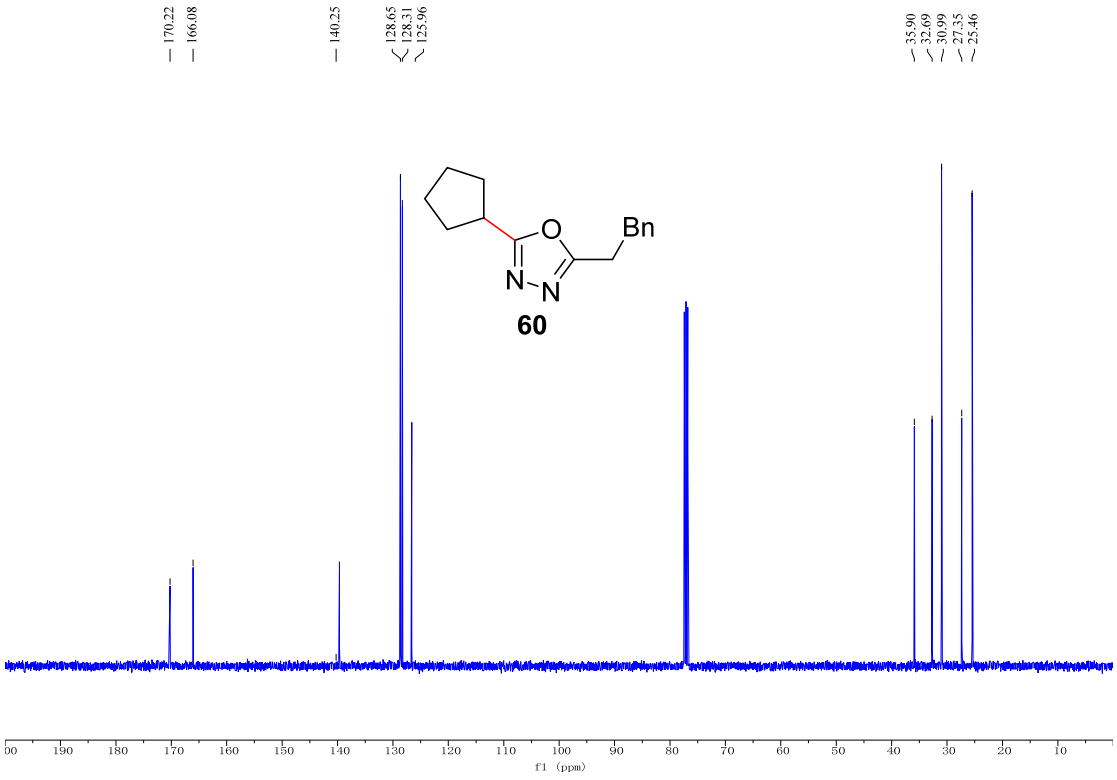
f1 (ppm)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27.35
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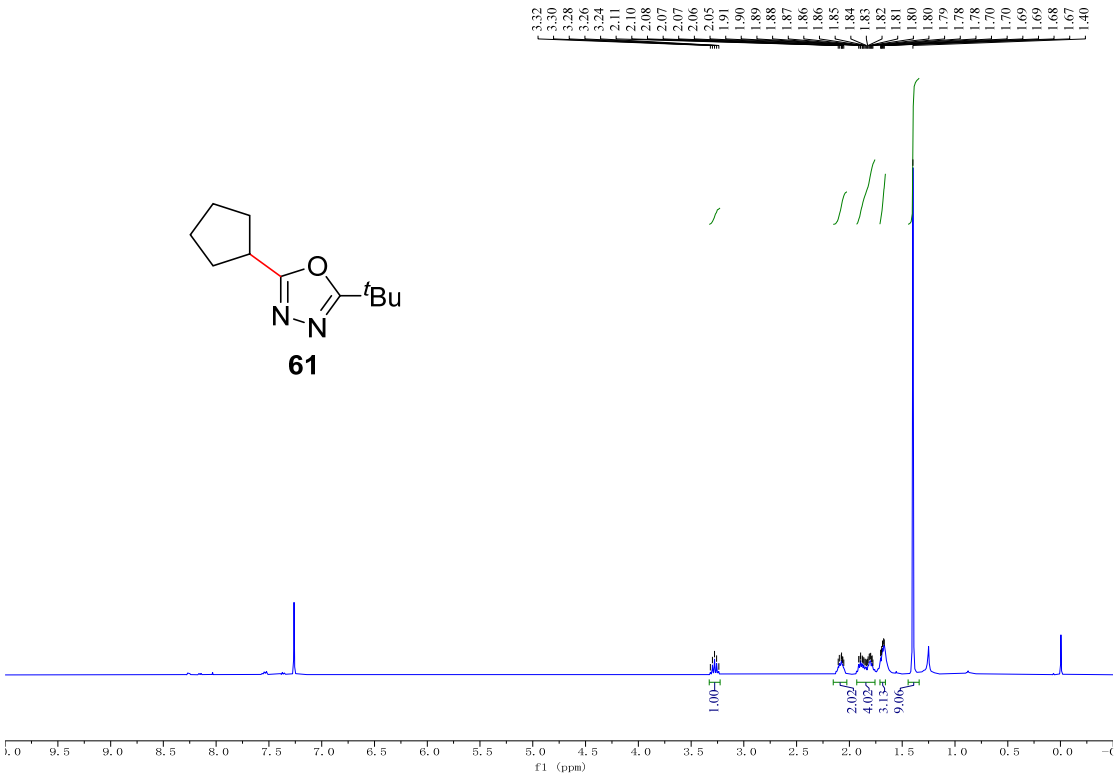
O
Bn
N
N
60
f1 (ppm)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2.05
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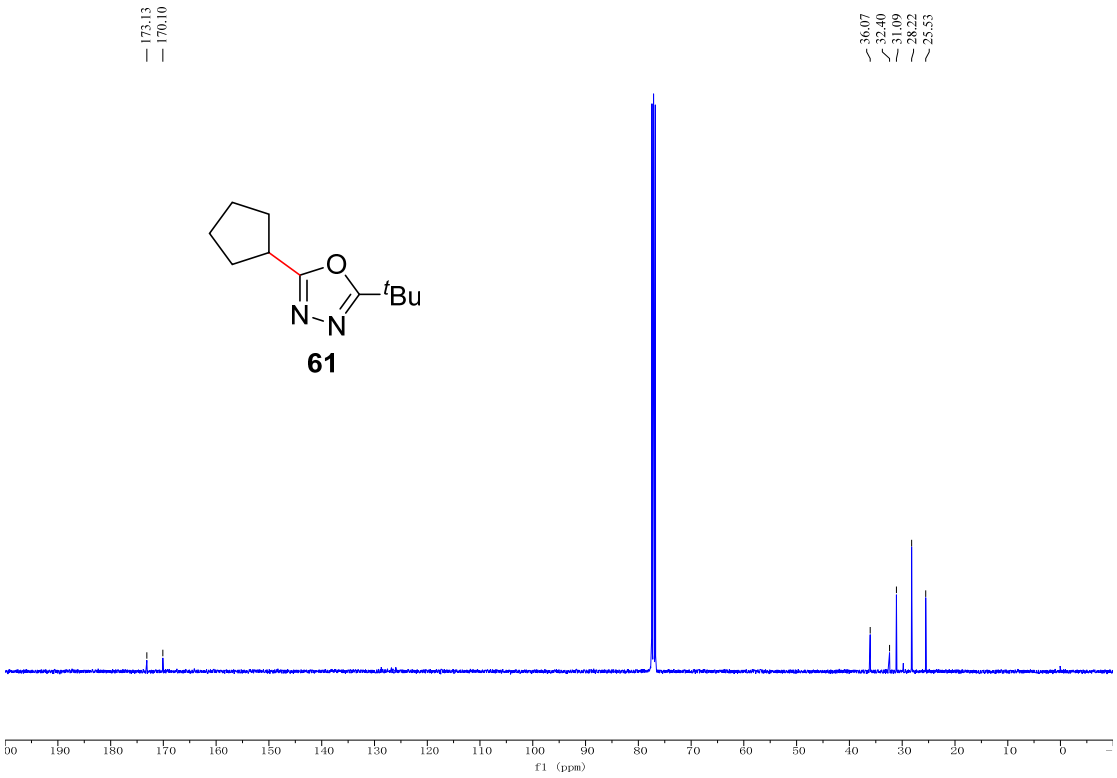
4.02
3.13
9.06
f1 (ppm)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tBu
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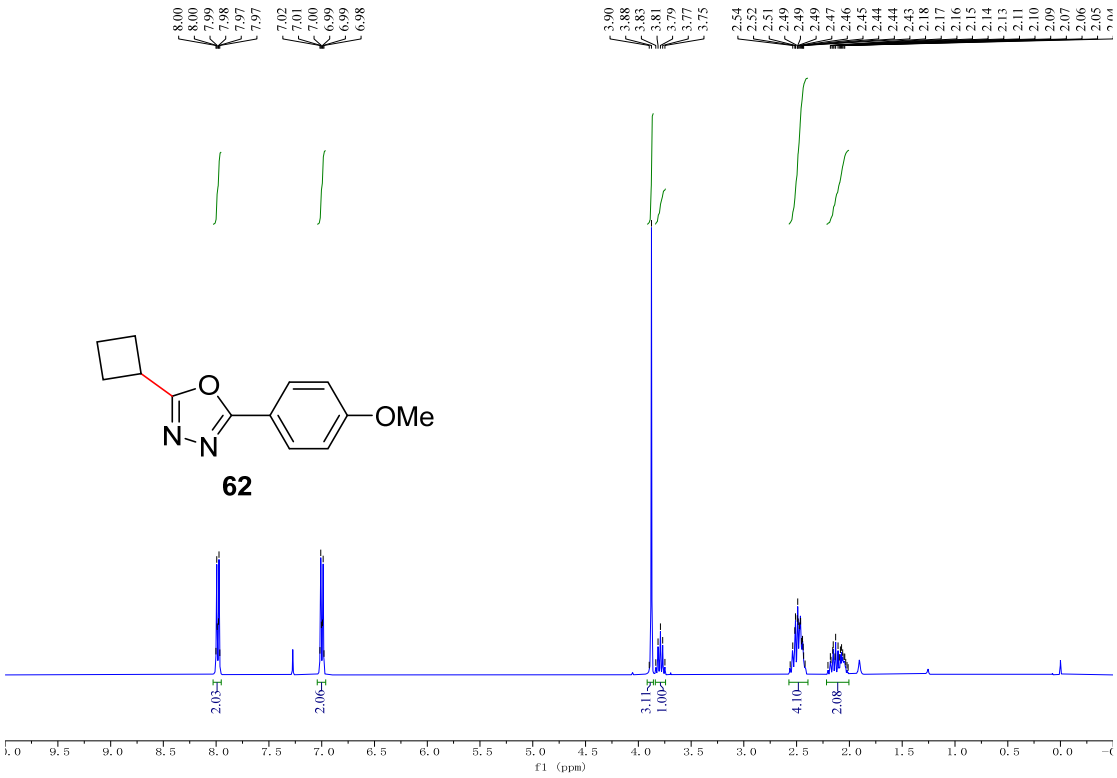
f1 (ppm)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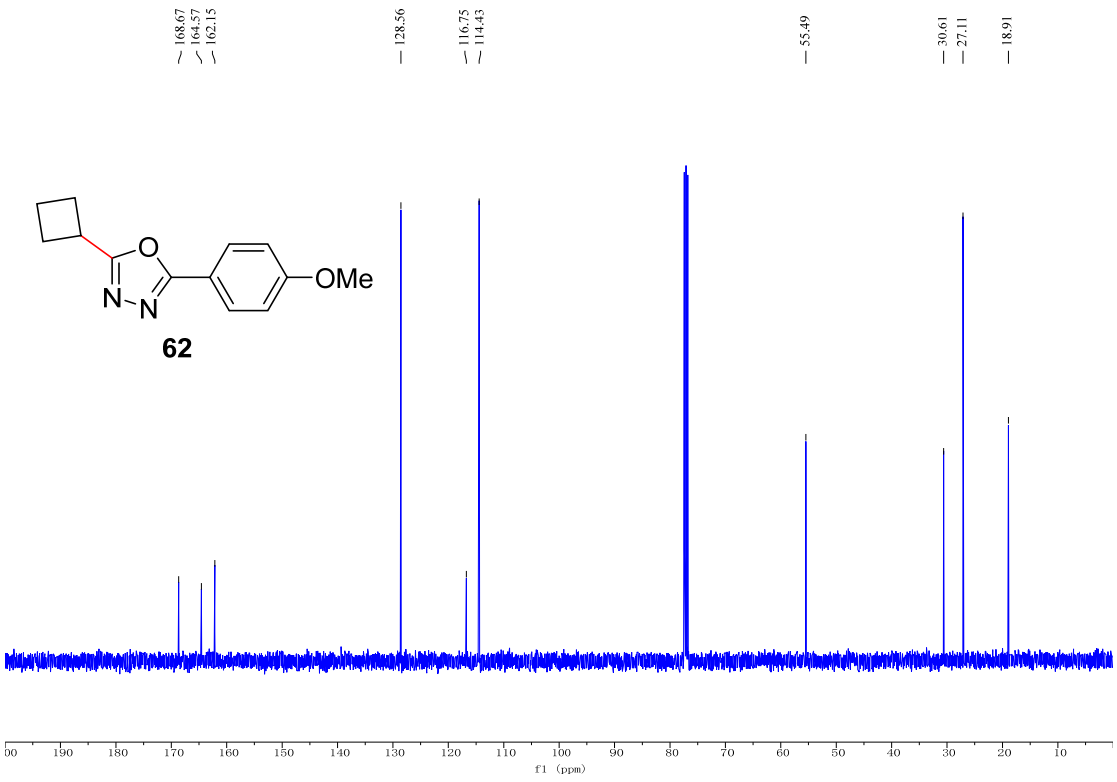
2.08
f1 (ppm)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O
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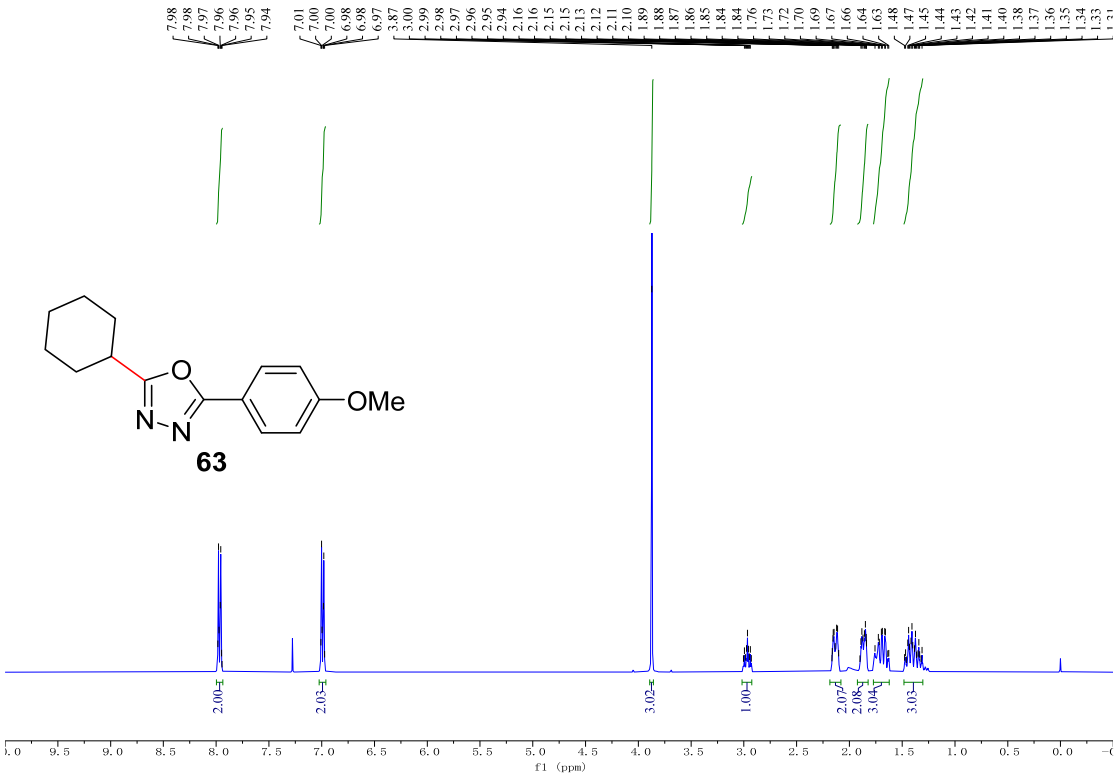
f1 (ppm)


OMe
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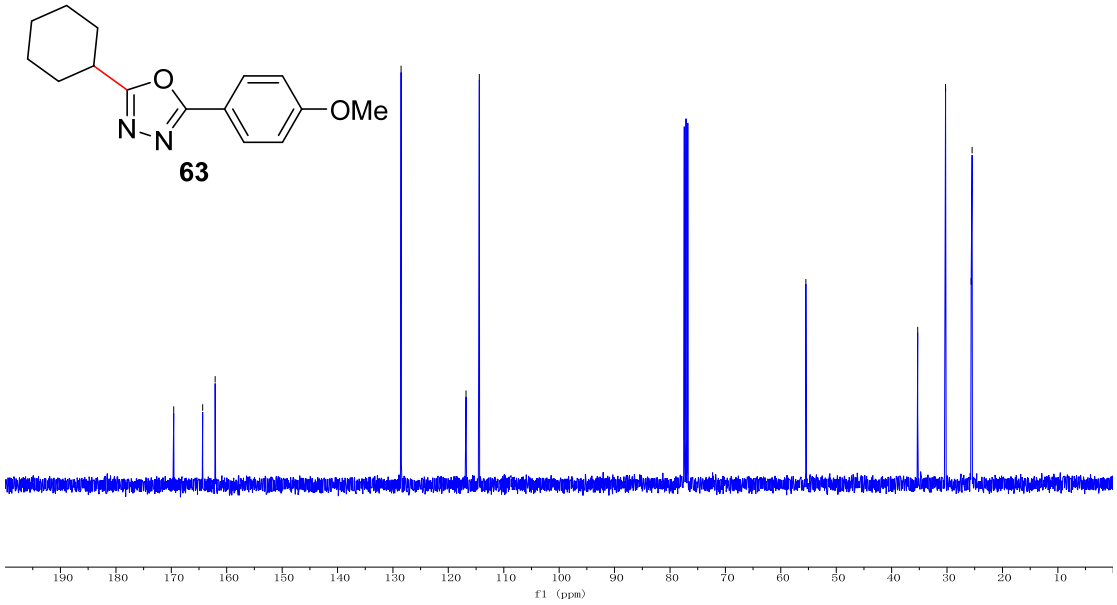
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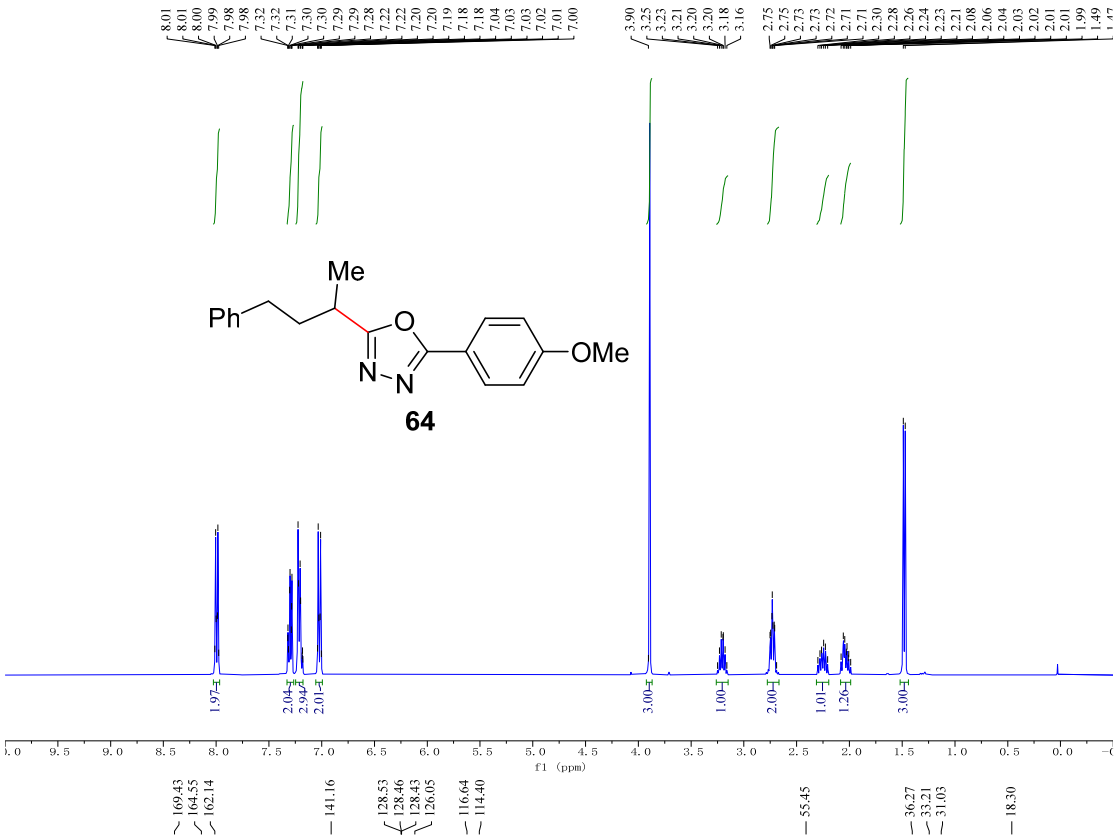
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Ph
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OMe
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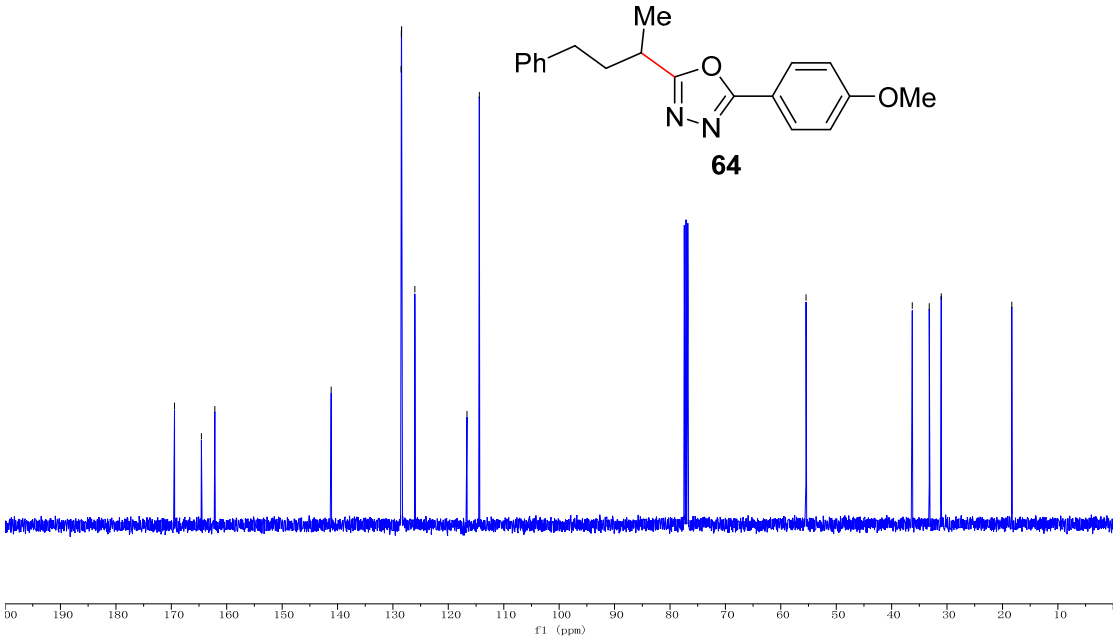
f1 (ppm)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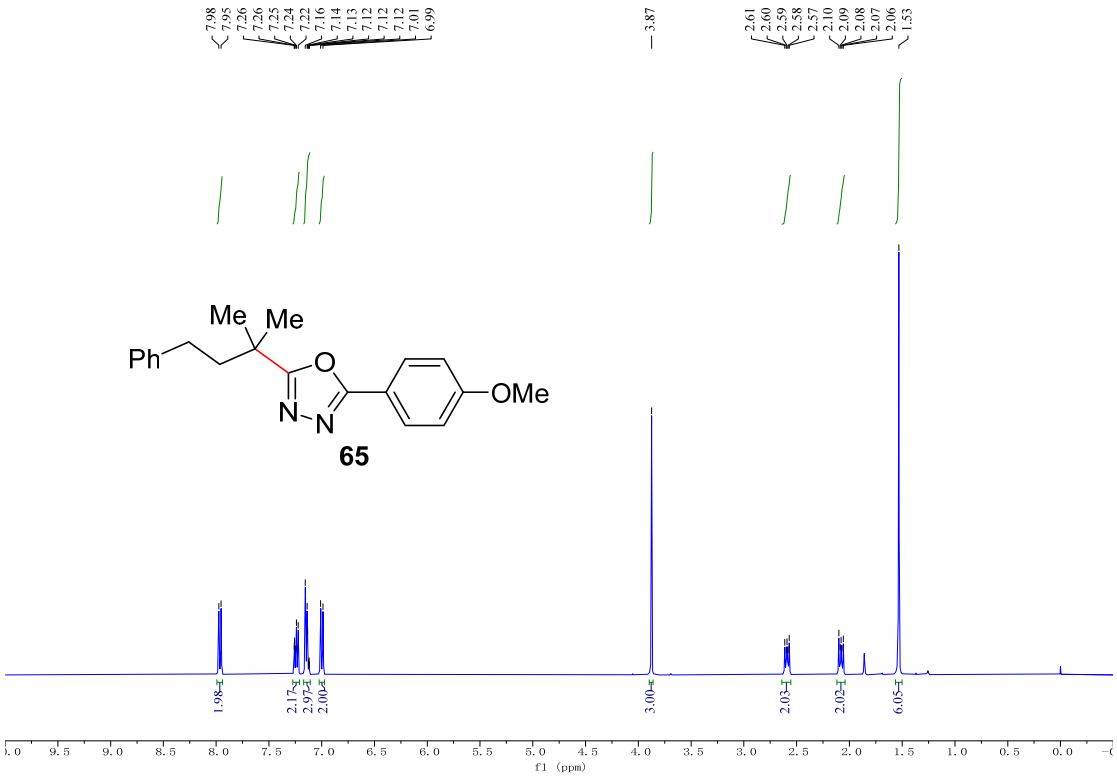
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2.60
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2.06
1.53
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Ph
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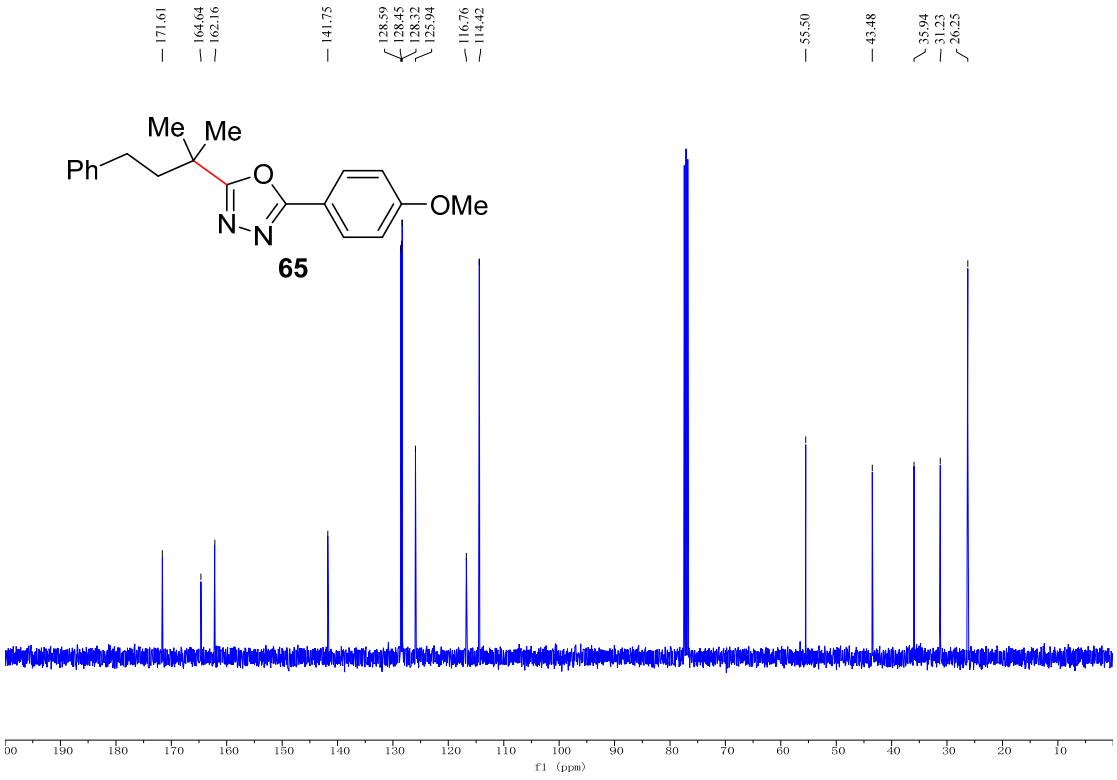
f1 (ppm)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26.25
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O
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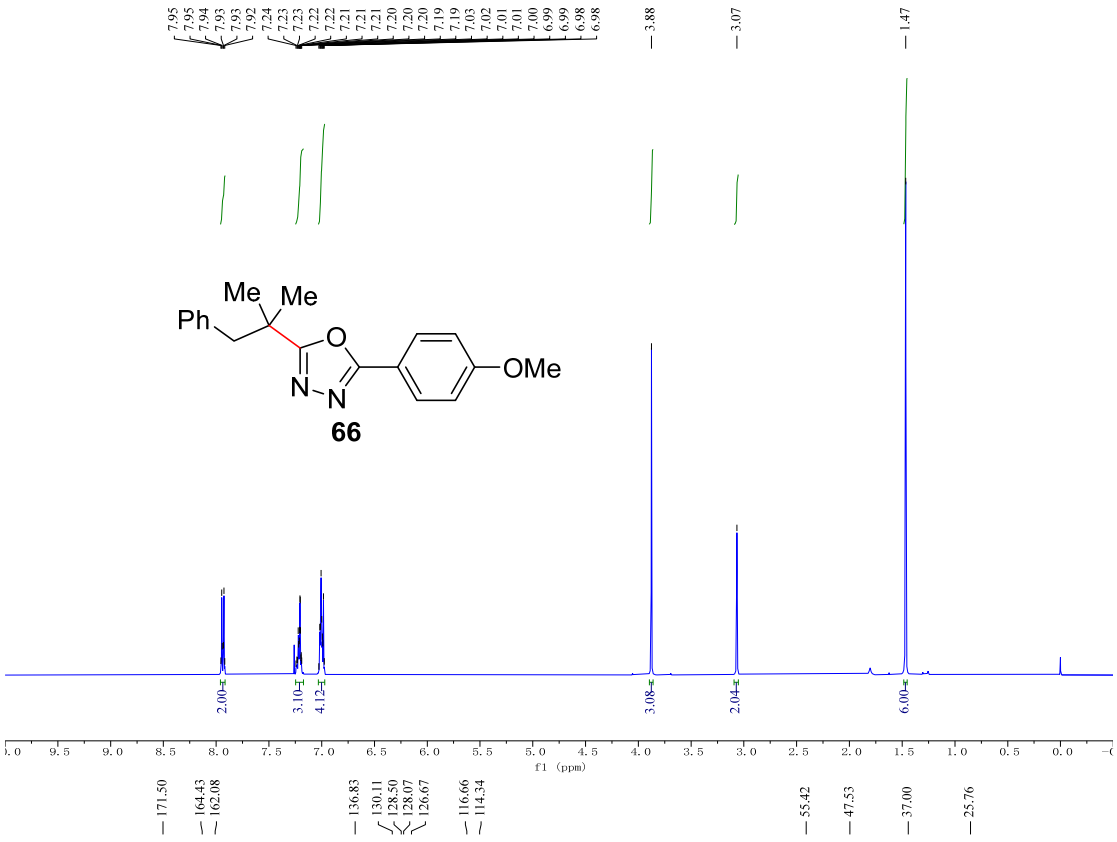
OMe
65
f1 (ppm)


7.95
7.95
7.94
7.93
7.93
7.92
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.20
7.20
7.20
7.19
7.19
7.03
7.02
7.01
7.01
7.00
6.99
6.99
6.98
6.98
3.88
3.07
1.47
Me
Me
Ph
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N
N
OMe
66
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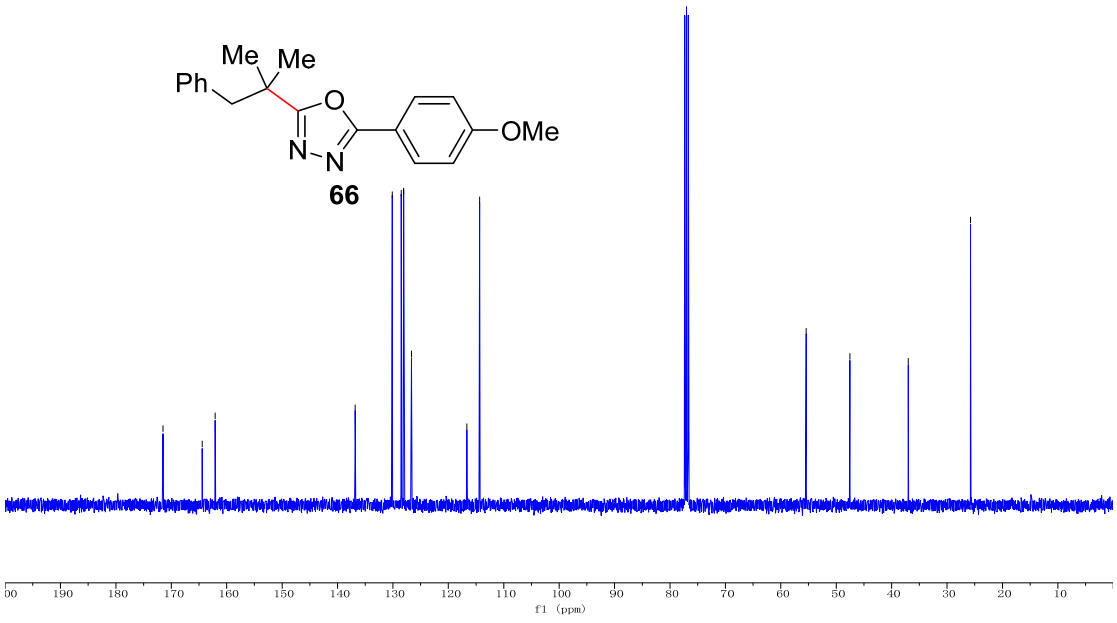
3.10
4.12
3.08
2.04
6.00
f1 (ppm)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164.43
162.08
136.83
130.11
128.50
128.07
126.67
116.66
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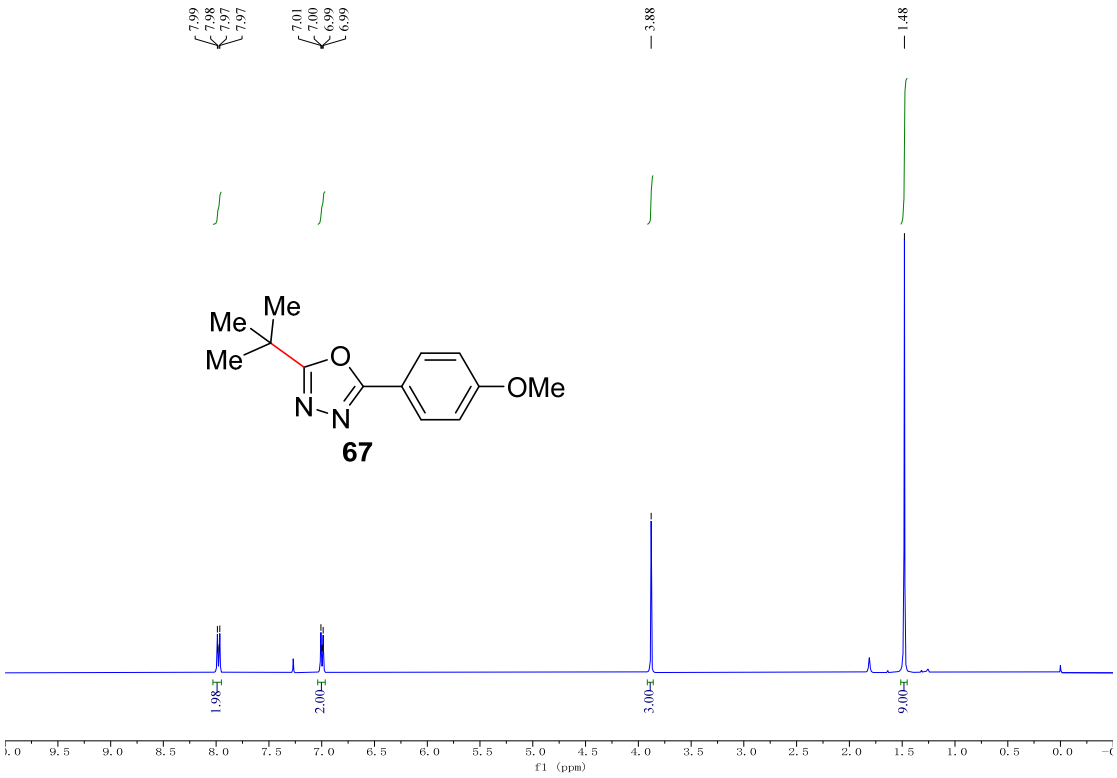
47.53
37.00
25.76
Me
Me
Ph
O
N
N
OMe
66
f1 (ppm)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7.98
7.97
7.97
7.01
7.00
6.99
6.99
3.88
1.48
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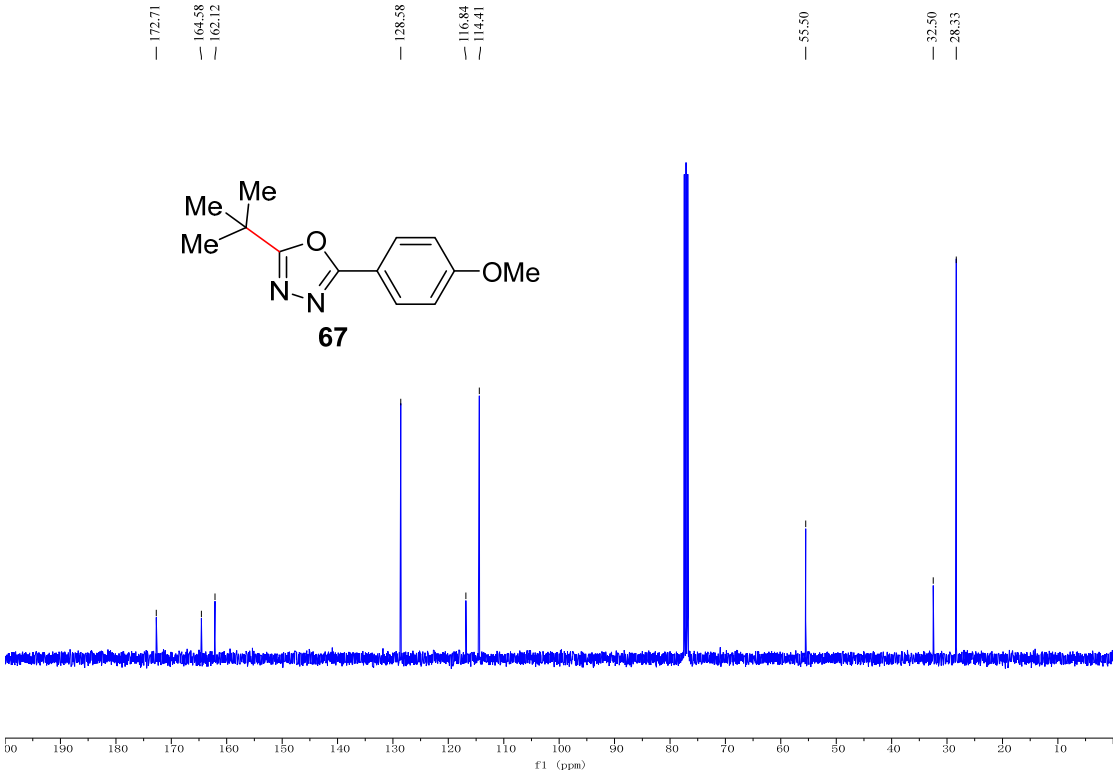
Me
Me
O
N
N
OMe
67
1.98
2.00
3.00
9.00
f1 (ppm)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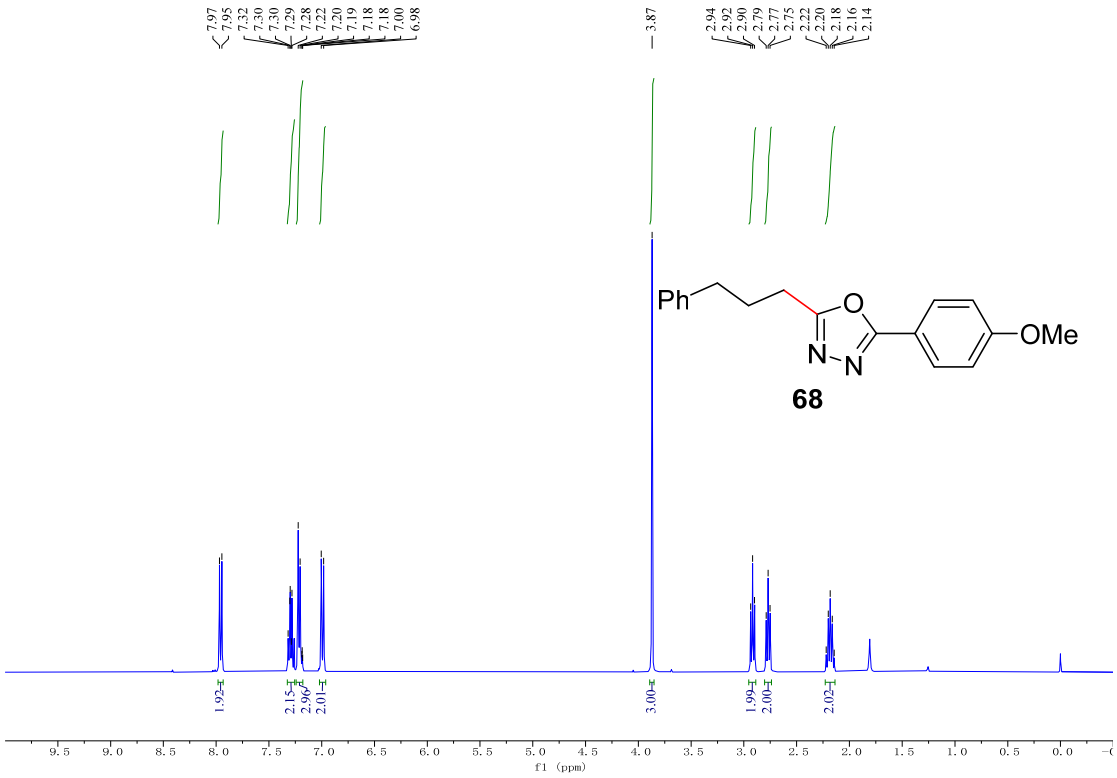
Me
Me
Me
O
N
N
OMe
67
f1 (ppm)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7.28
7.22
7.20
7.19
7.18
7.18
7.00
6.98
3.87
2.94
2.92
2.90
2.79
2.77
2.75
2.22
2.20
2.18
2.16
2.14
Ph
O
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N
OMe
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1.92
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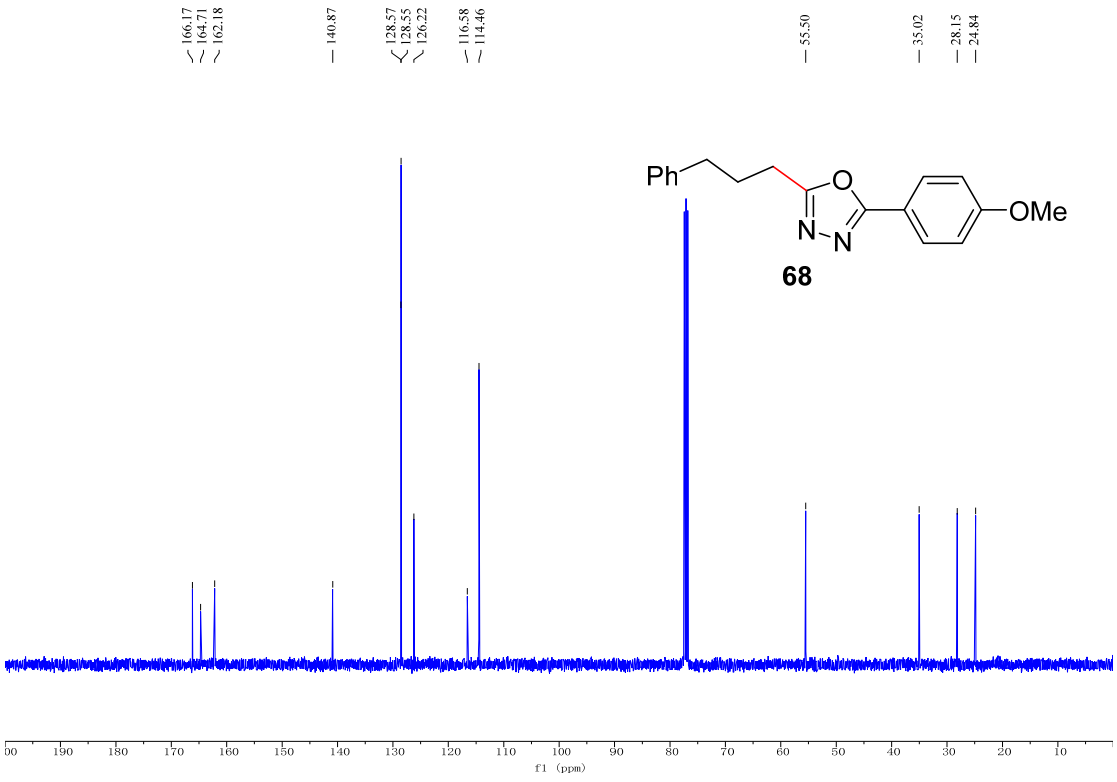
2.96
2.01
3.00
1.99
2.00
2.02
f1 (ppm)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Ph
O
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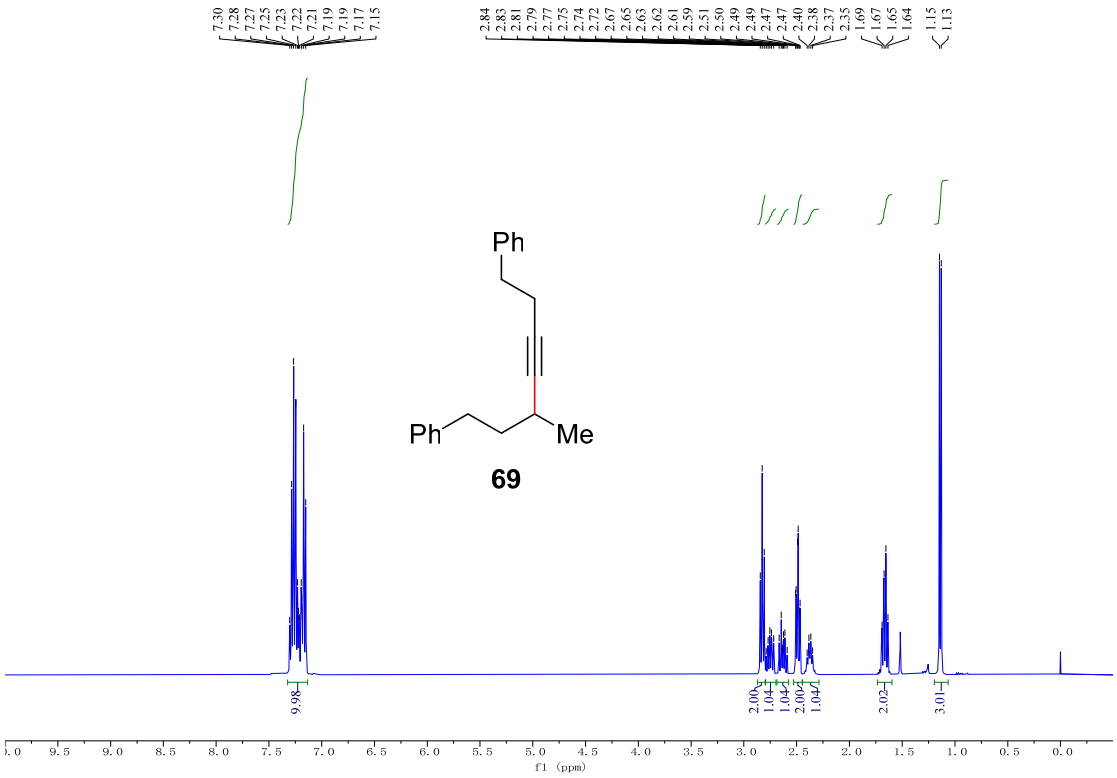
N
OMe
68
f1 (ppm)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7.28
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7.19
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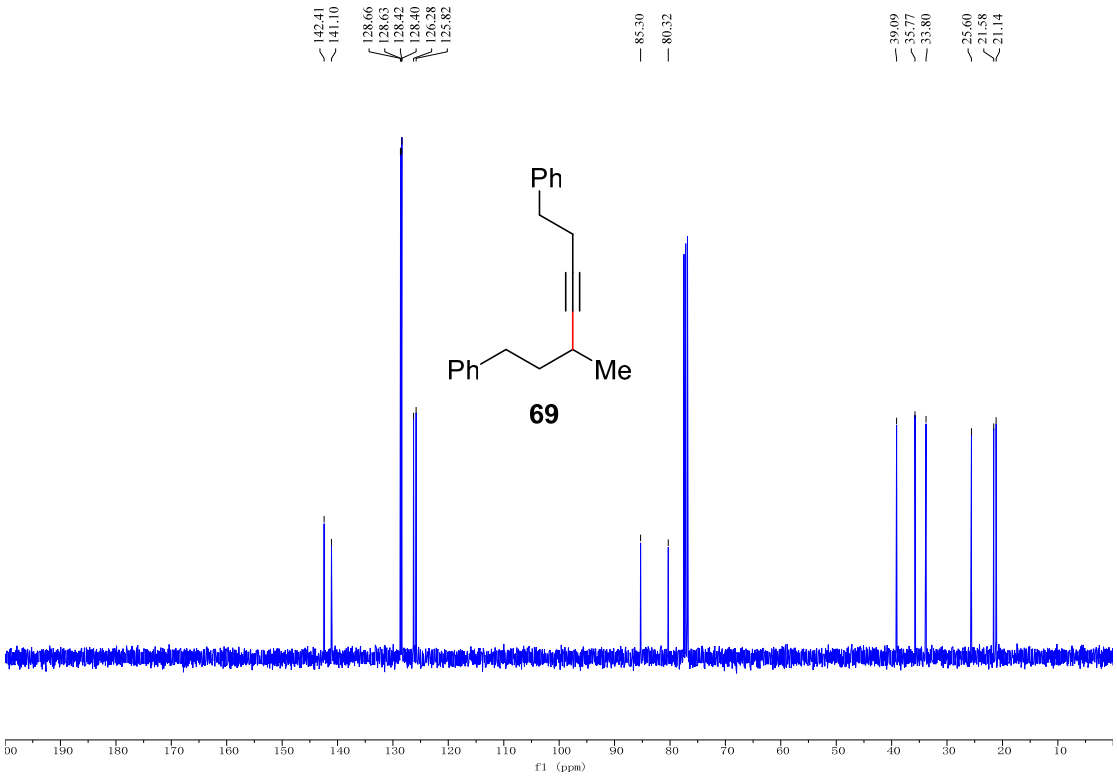
7.17
7.15
2.84
2.83
2.81
2.79
2.77
2.75
2.74
2.72
2.67
2.65
2.63
2.62
2.61
2.59
2.51
2.50
2.49
2.49
2.47
2.47
2.40
2.38
2.37
2.35
1.69
1.67
1.65
1.64
1.15
1.13
Ph
Ph
Me
69
9.98
2.00
1.04
1.04
2.00
1.04
2.02
3.01
f1 (ppm)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33.80
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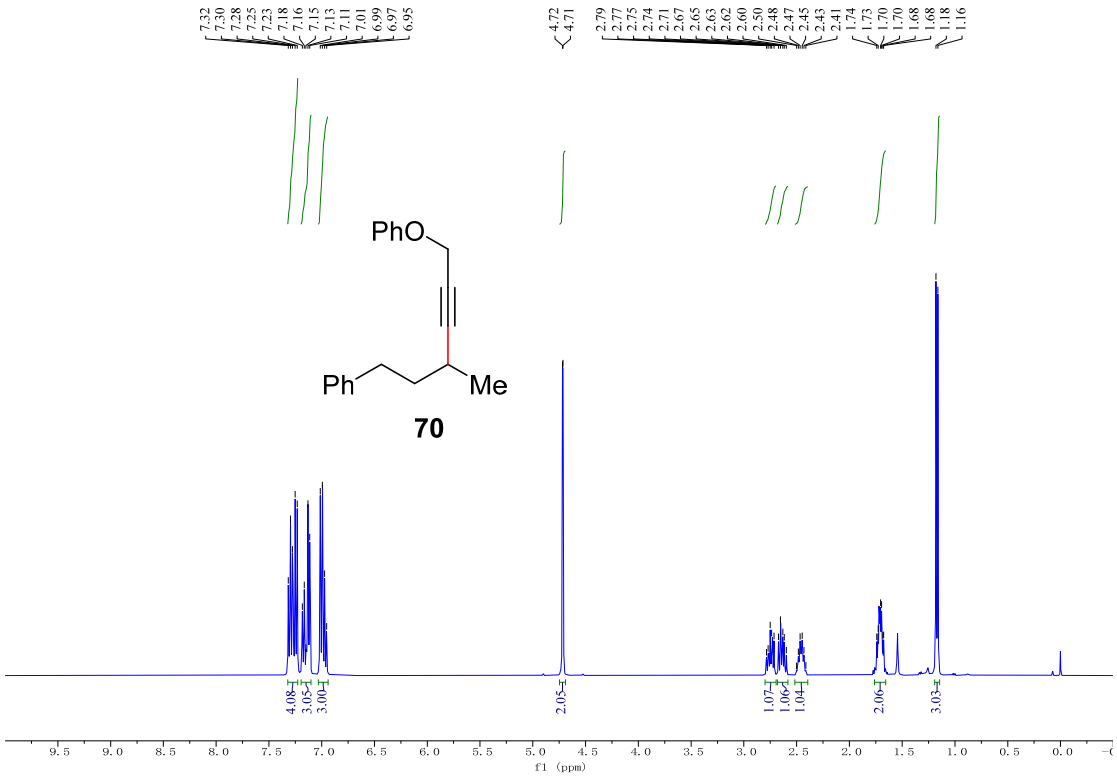
21.14
Ph
Ph
Me
69
f1 (ppm)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7.25
7.23
7.18
7.16
7.15
7.13
7.11
7.01
6.99
6.97
6.95
4.72
4.71
2.79
2.77
2.75
2.74
2.71
2.67
2.65
2.63
2.62
2.60
2.50
2.48
2.47
2.45
2.43
2.41
1.74
1.73
1.70
1.70
1.68
1.68
1.18
1.16
PhO
Ph
Me
70
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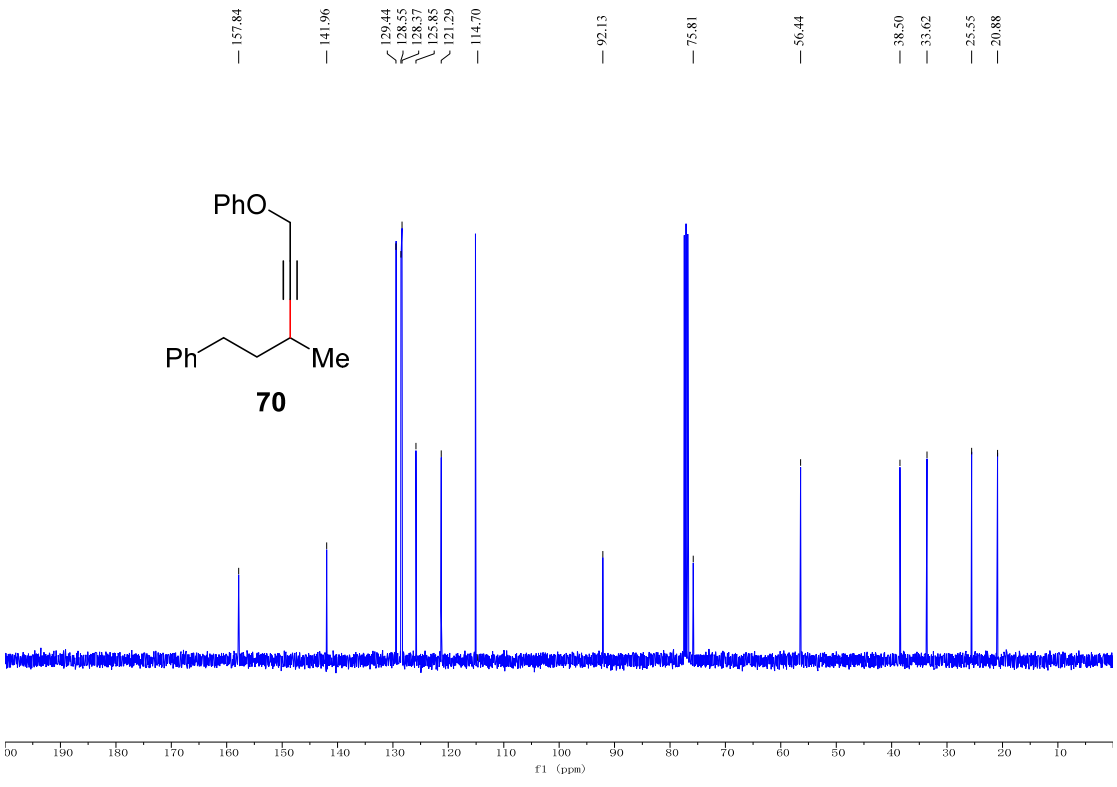
3.05
3.00
2.05
1.07
1.06
1.04
2.06
3.03
f1 (ppm)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128.37
125.85
121.29
114.70
92.13
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56.44
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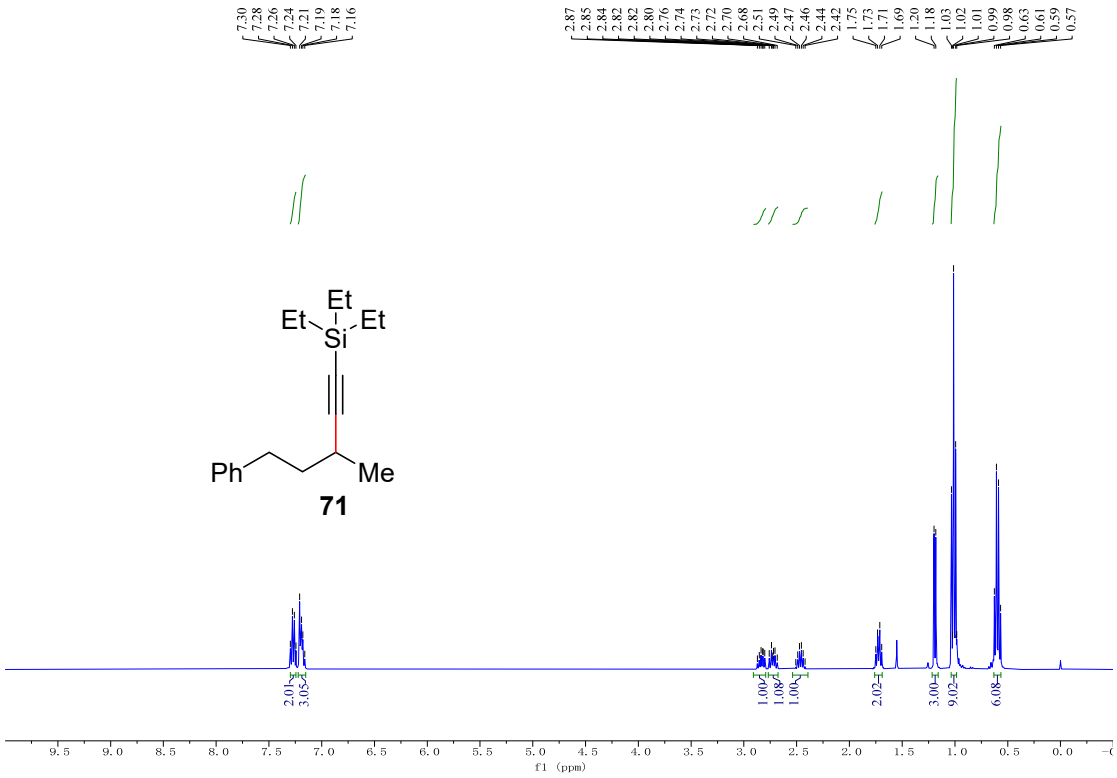
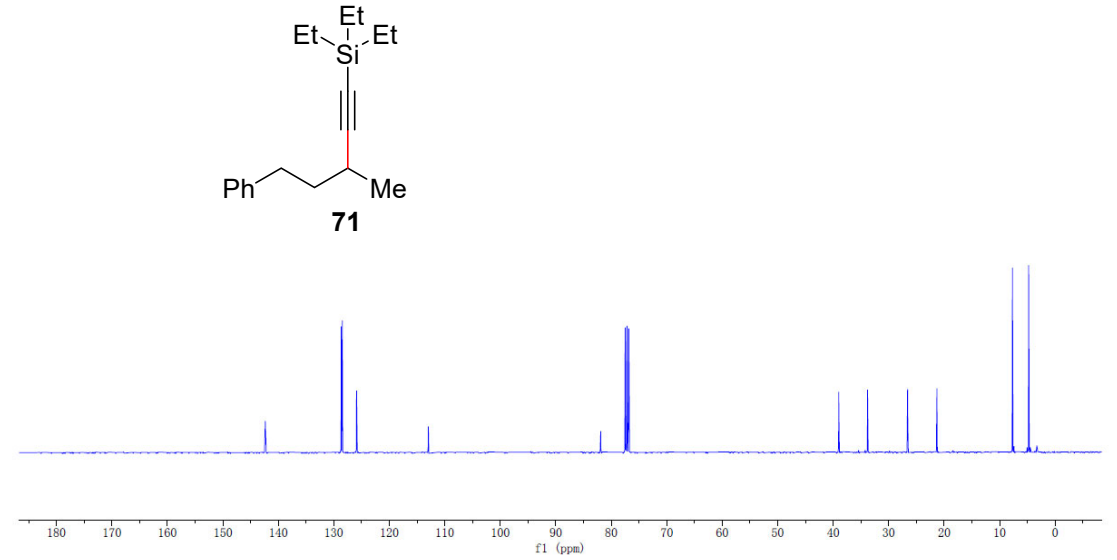
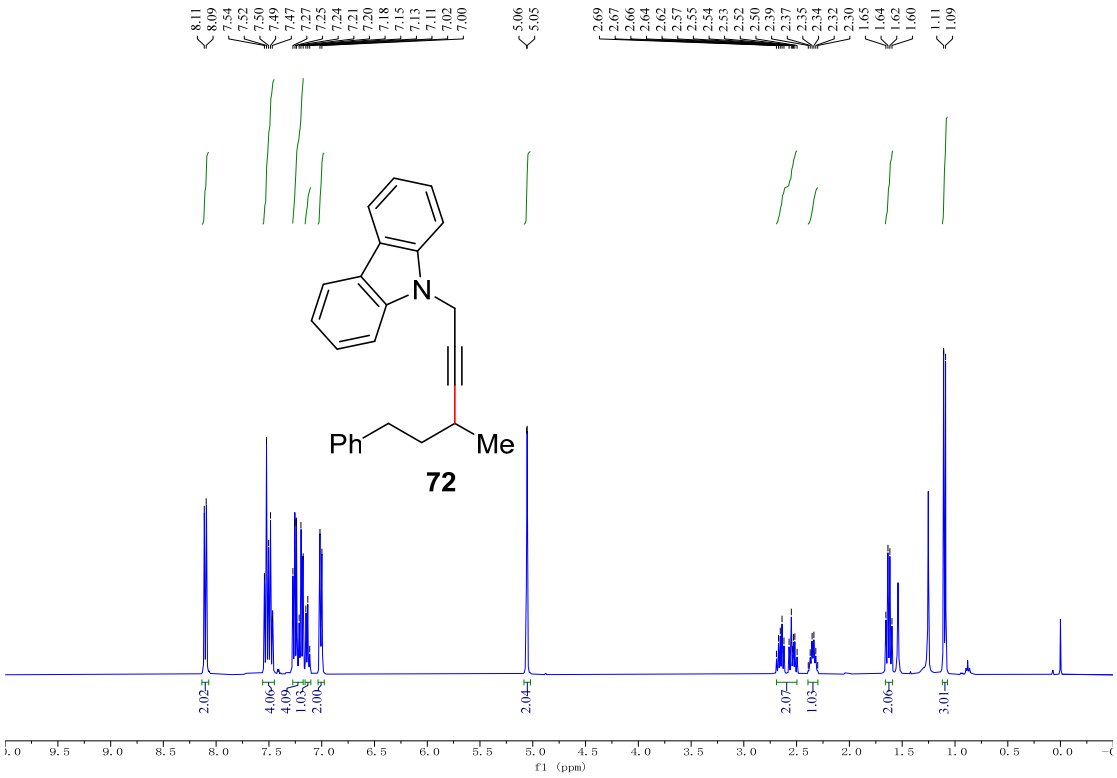
33.62
25.55
20.88
PhO
Ph
Me
70
f1 (ppm)


Et
Et
Et
Si
Ph
Me
71
f1 (ppm)


Et
Et
Et
Si
Ph
Me
71
f1 (ppm)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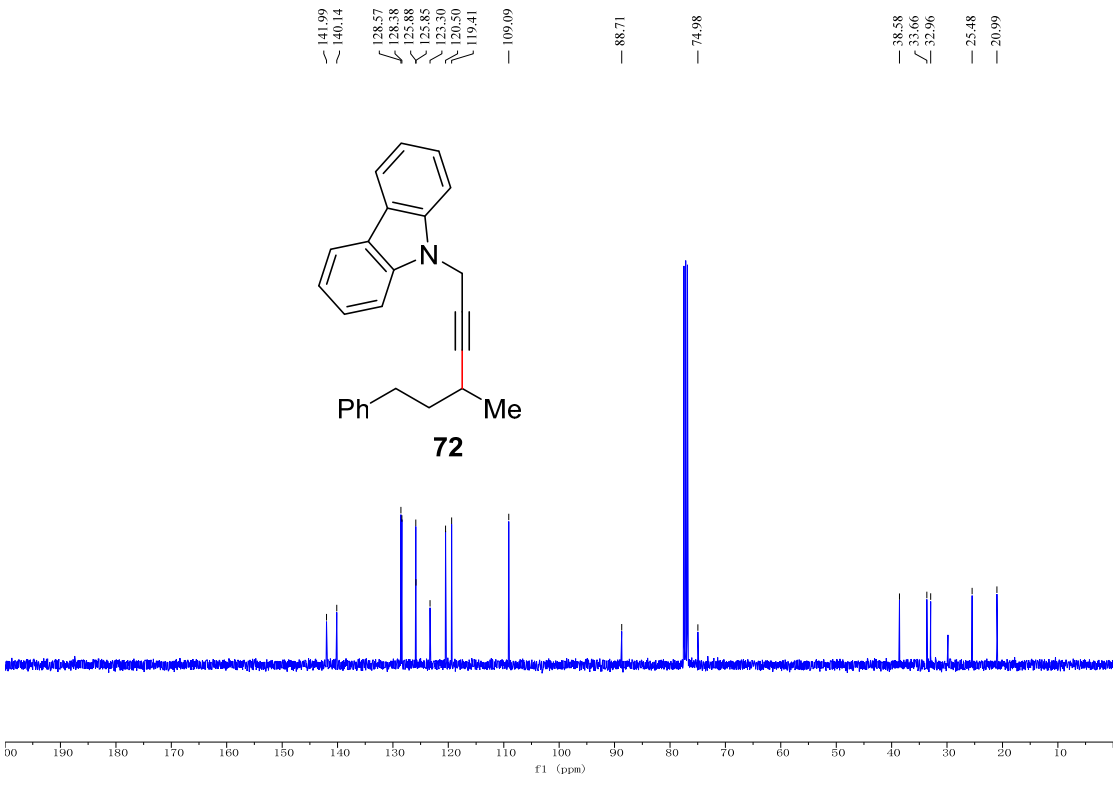
7.20
7.18
7.15
7.13
7.11
7.02
7.00
5.06
5.05
2.69
2.67
2.66
2.64
2.62
2.57
2.55
2.54
2.53
2.52
2.50
2.39
2.37
2.35
2.34
2.32
2.30
1.65
1.64
1.62
1.60
1.11
1.09
N
Ph
Me
72
2.02
4.06
4.09
1.03
2.00
2.04
2.07
1.03
2.06
3.01
f1 (ppm)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140.14
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125.85
123.30
120.50
119.41
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74.98
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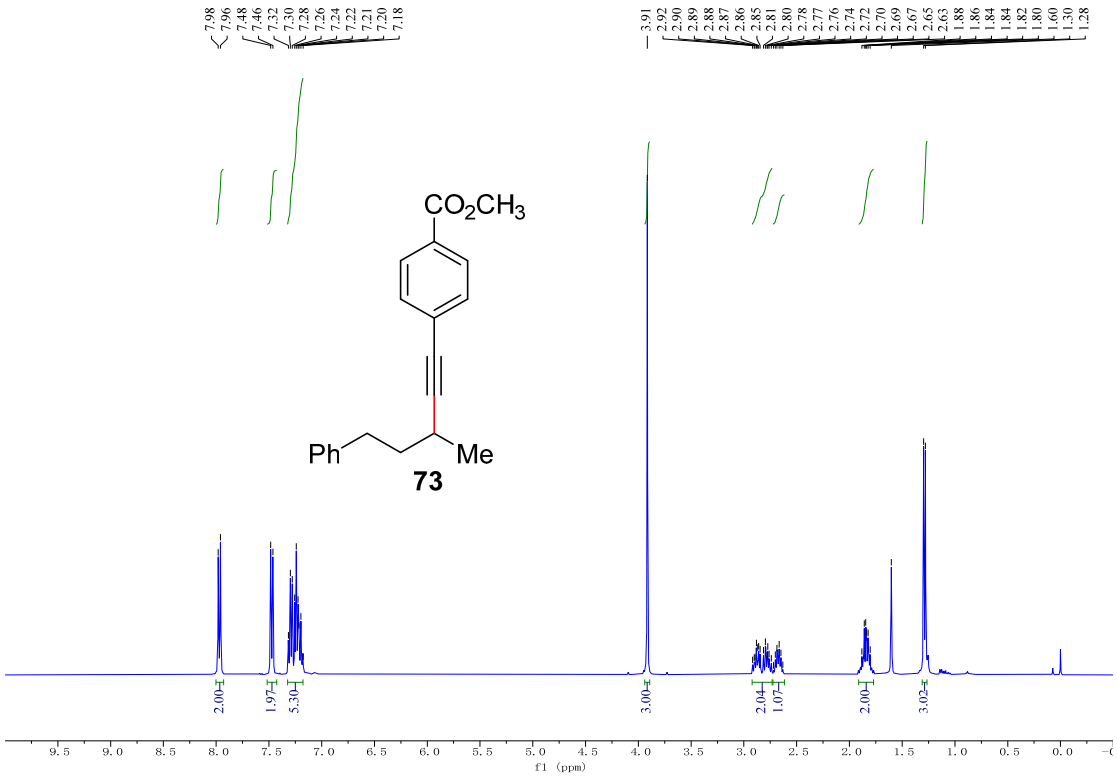
25.48
20.99
N
Ph
Me
72
f1 (ppm)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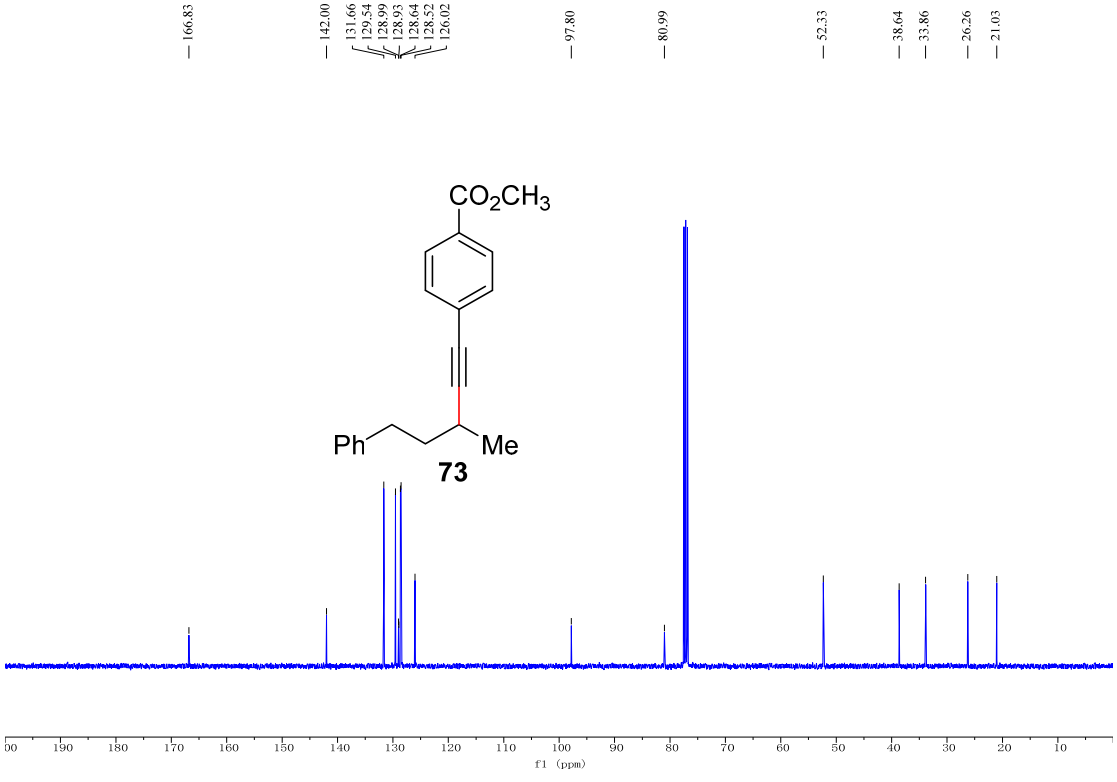
7.96
7.48
7.46
7.32
7.30
7.28
7.26
7.24
7.22
7.21
7.20
7.18
3.91
2.92
2.90
2.89
2.88
2.87
2.86
2.85
2.81
2.80
2.78
2.77
2.76
2.74
2.72
2.70
2.69
2.67
2.65
2.63
1.88
1.86
1.84
1.82
1.80
1.60
1.30
1.28
CO2CH3
Ph
Me
73
2.00
1.97
5.30
3.00
2.04
1.07
2.00
3.02
f1 (ppm)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128.99
128.93
128.64
128.52
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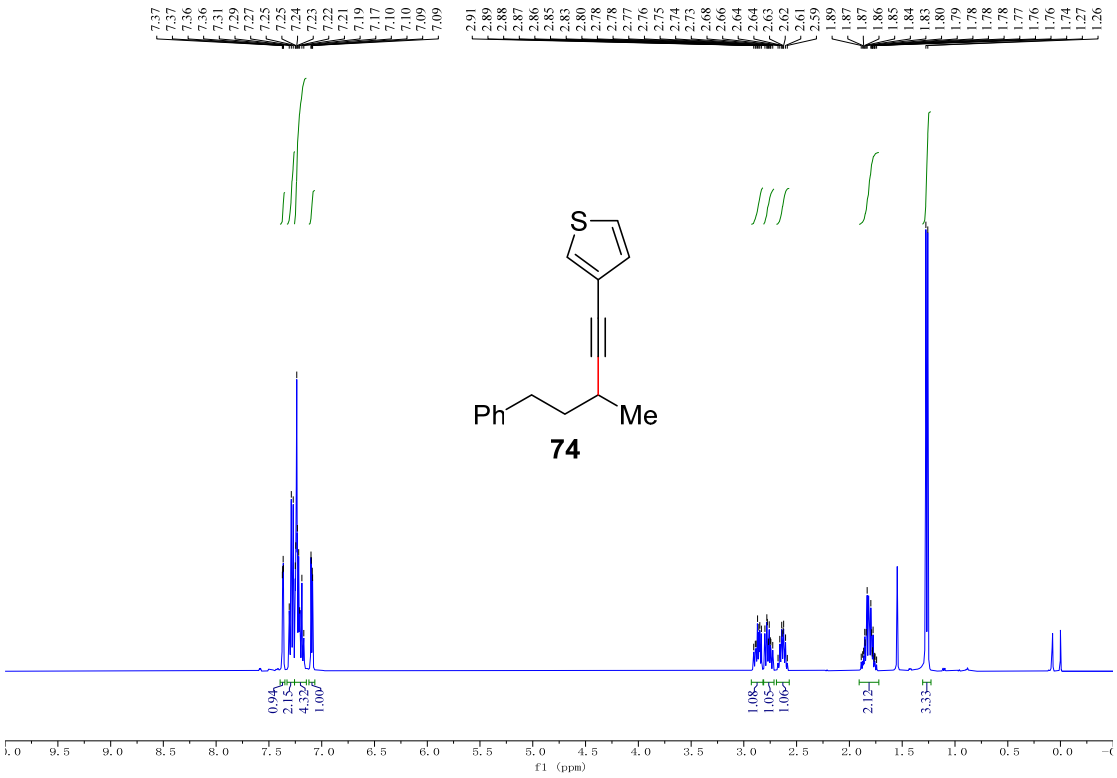
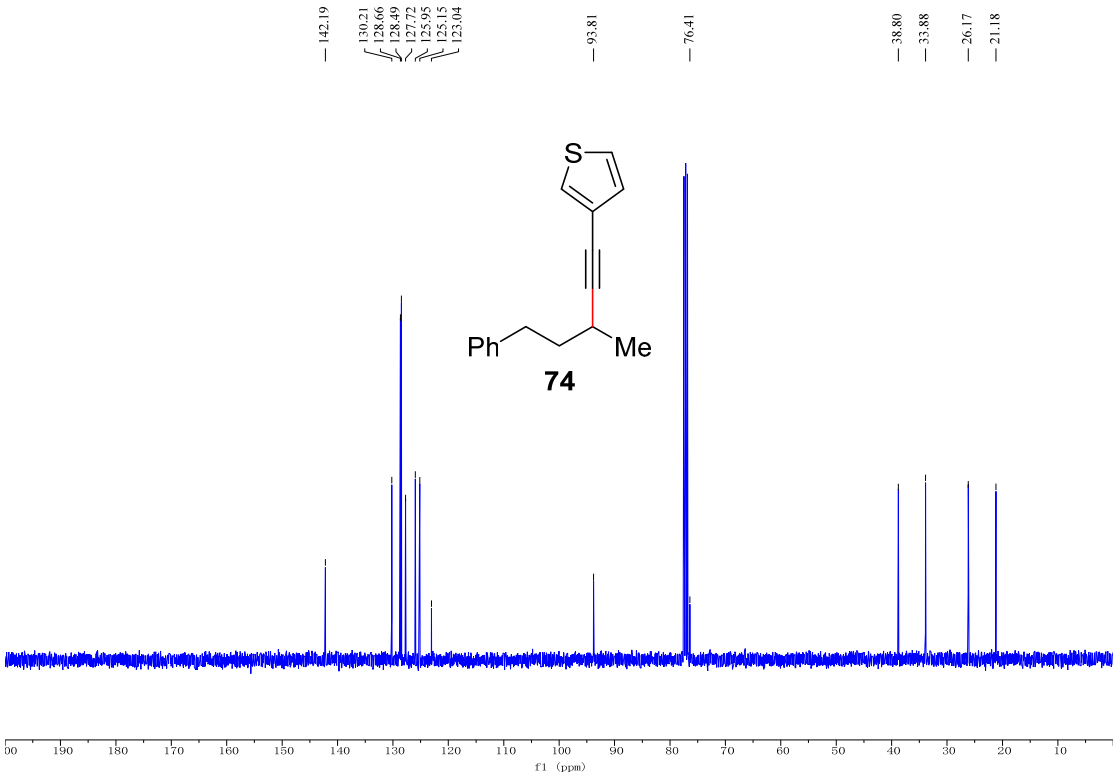
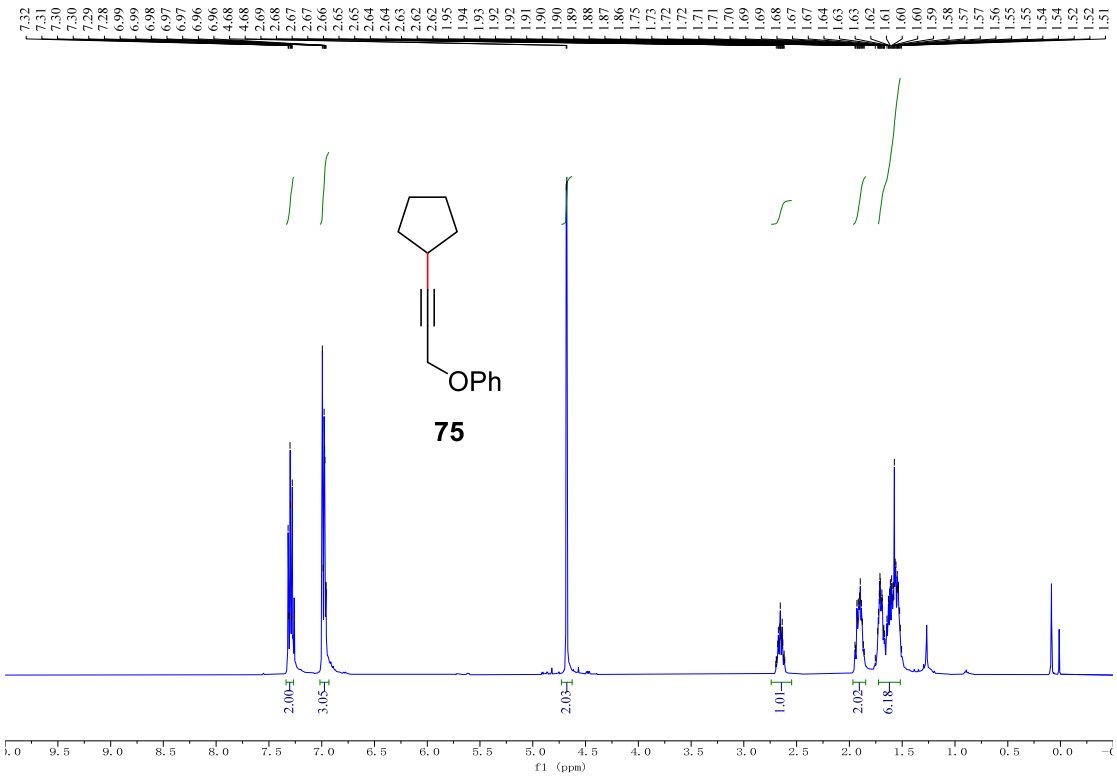
52.33
38.64
33.86
26.26
21.03
CO2CH3
Ph
Me
73
f1 (ppm)


S
Ph
Me
74
f1 (ppm)


S
Ph
Me
74
f1 (ppm)


OPh
75
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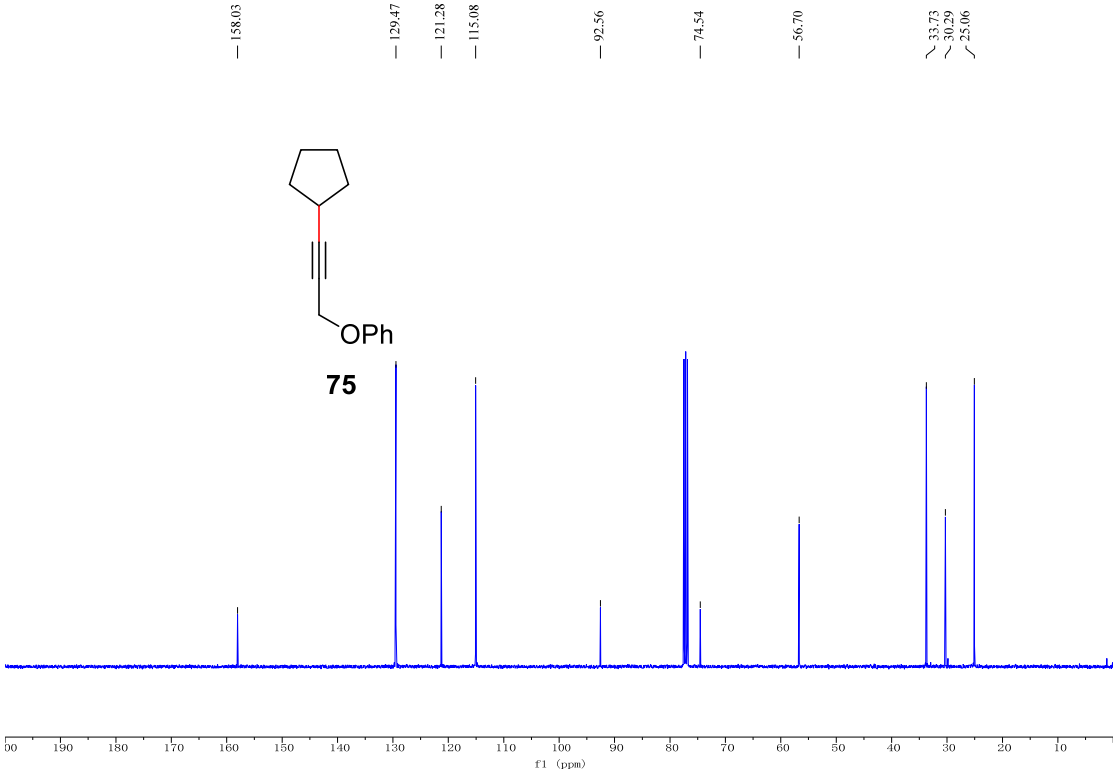
2.02
6.18
f1 (ppm)


158.03
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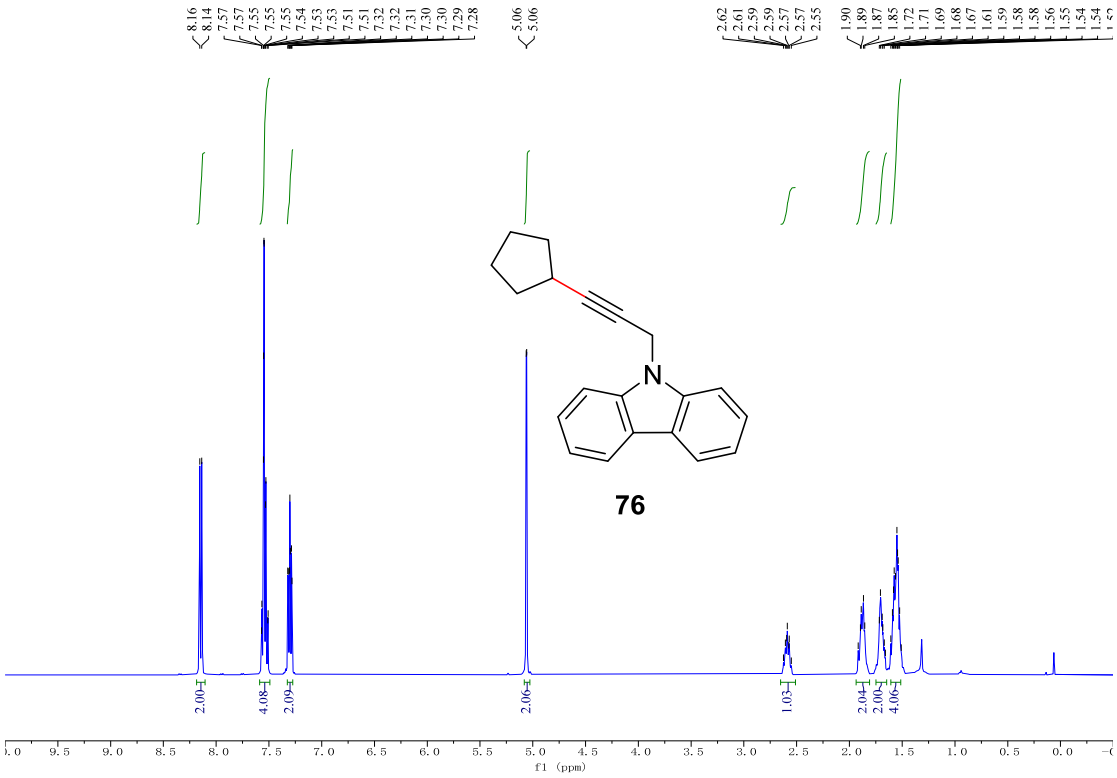
115.08
92.56
74.54
56.70
33.73
30.29
25.06
OPh
75
f1 (ppm)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7.31
7.30
7.30
7.29
7.28
5.06
5.06
2.62
2.61
2.59
2.59
2.57
2.57
2.55
1.90
1.89
1.87
1.85
1.72
1.71
1.69
1.68
1.67
1.61
1.59
1.58
1.56
1.55
1.54
1.54
N
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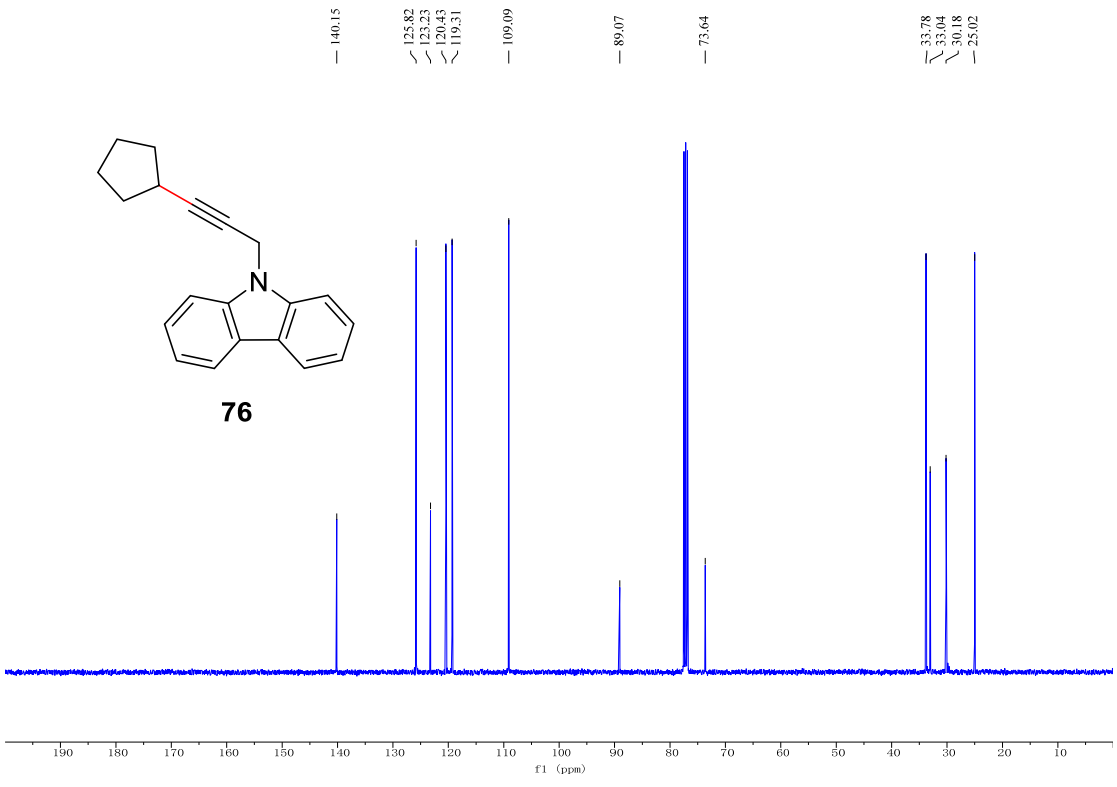
2.00
4.08
2.09
2.06
1.03
2.04
2.00
4.06
f1 (ppm)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125.82
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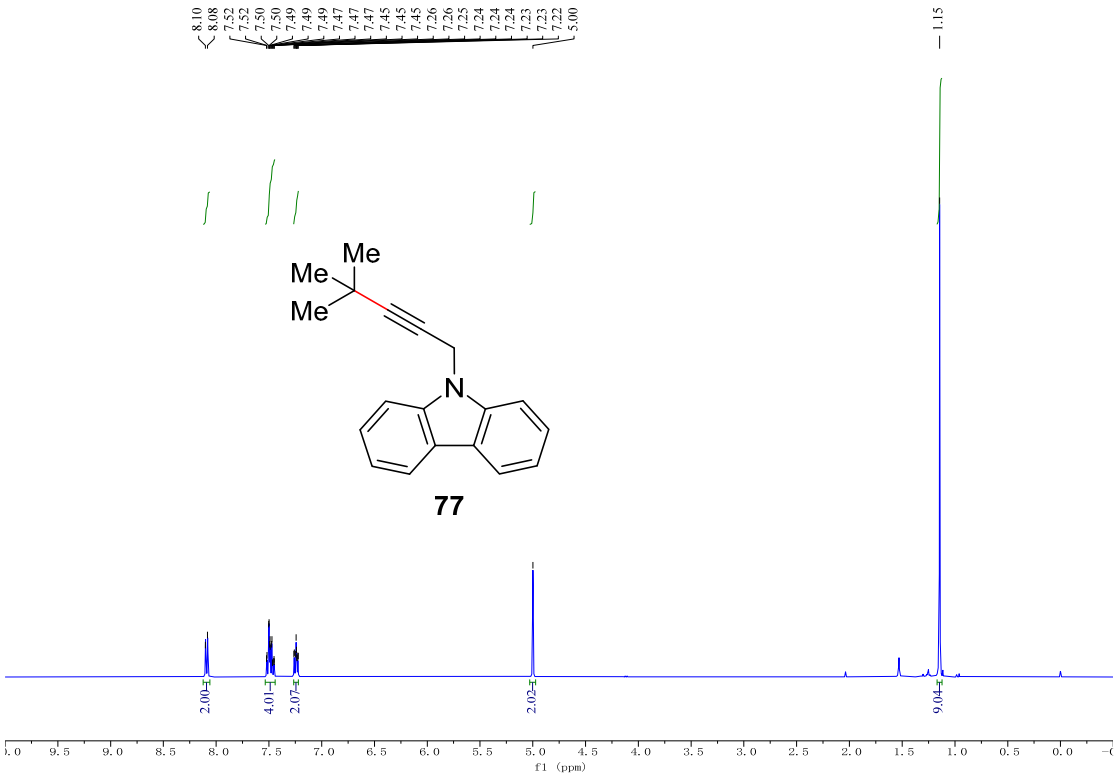
109.09
89.07
73.64
33.78
33.04
30.18
25.02
N
76
f1 (ppm)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8.08
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7.52
7.50
7.50
7.49
7.49
7.49
7.47
7.47
7.47
7.45
7.45
7.45
7.26
7.26
7.25
7.24
7.24
7.24
7.23
7.23
7.22
5.00
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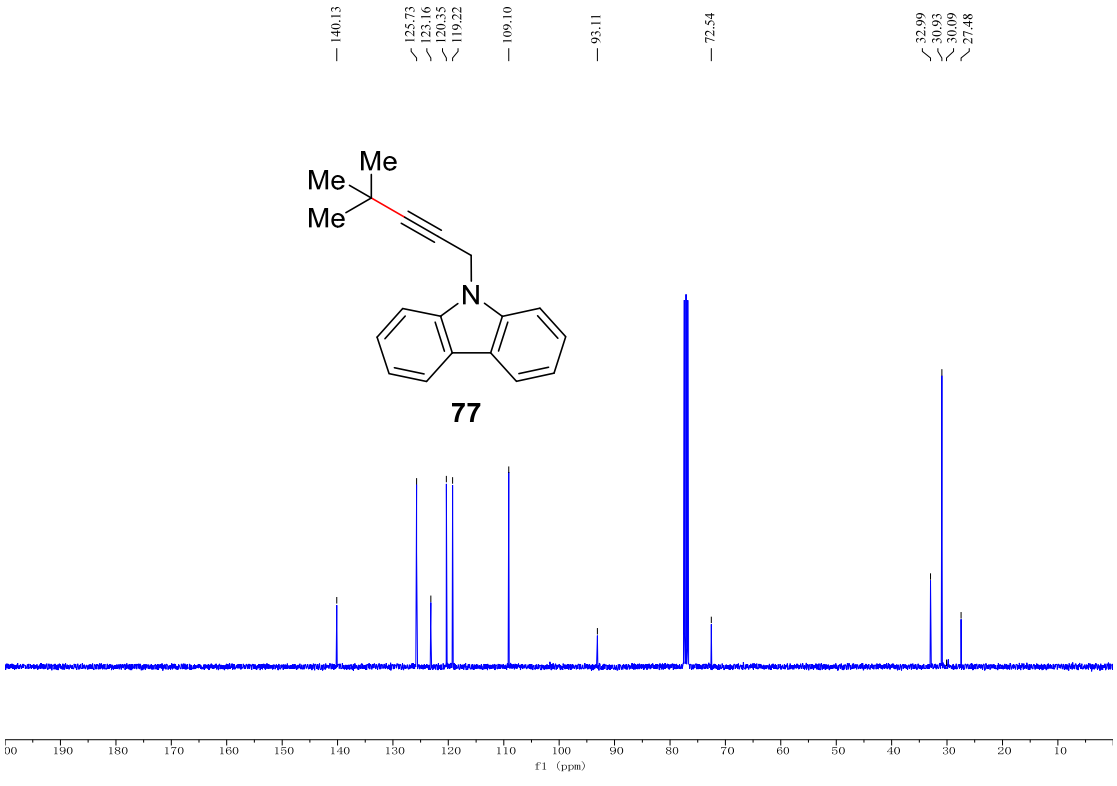
Me
Me
Me
N
77
2.00
4.01
2.07
2.02
9.04
f1 (ppm)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125.73
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120.35
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109.10
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72.54
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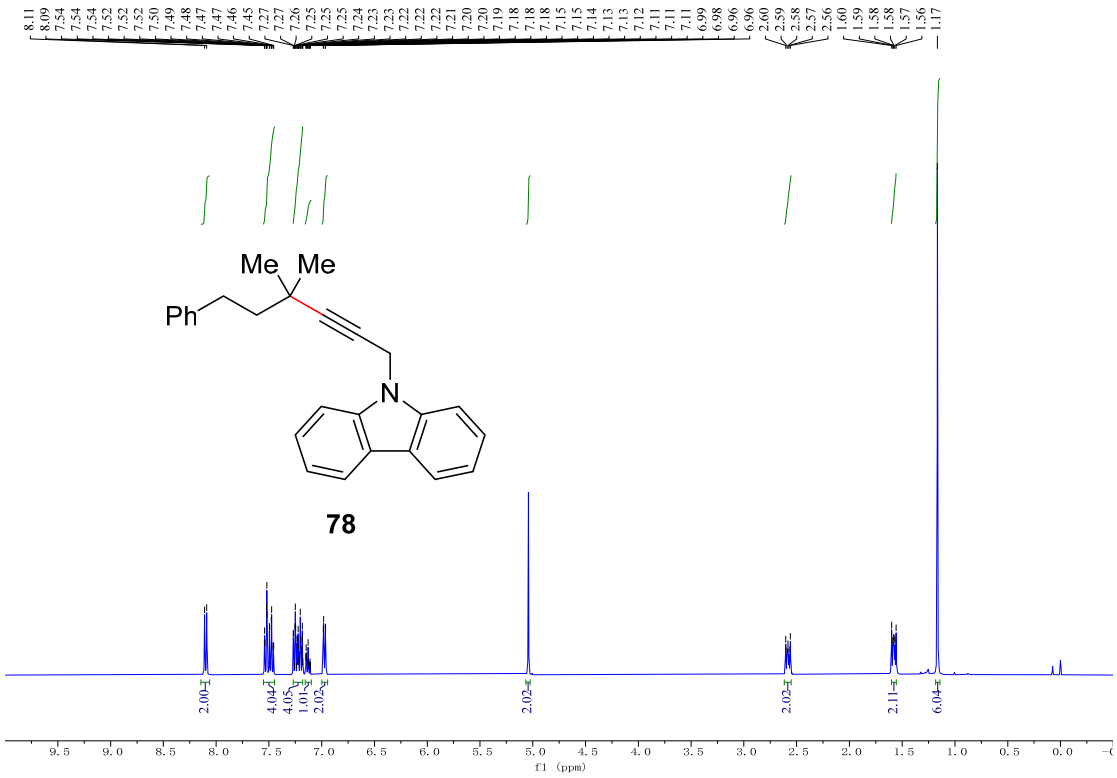
30.93
30.09
27.48
Me
Me
Me
N
77
f1 (ppm)


Me Me
Ph
N
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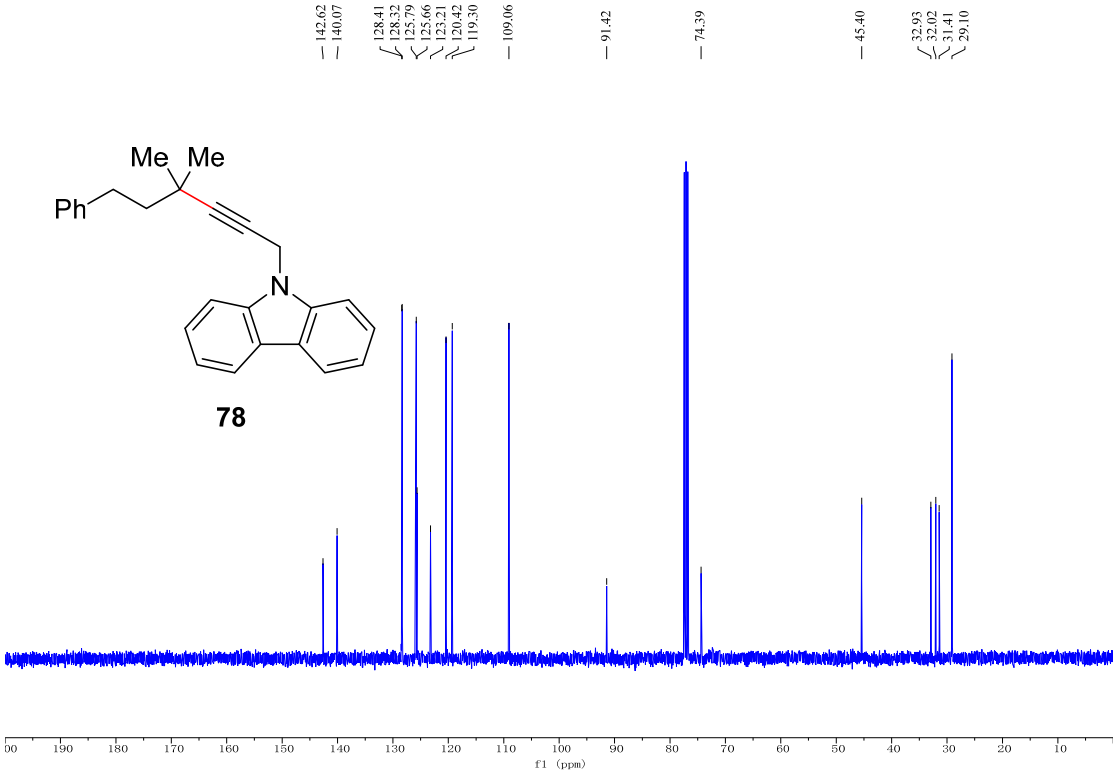
4.04
4.05
1.01
2.02
2.02
2.02
2.11
6.04
f1 (ppm)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119.30
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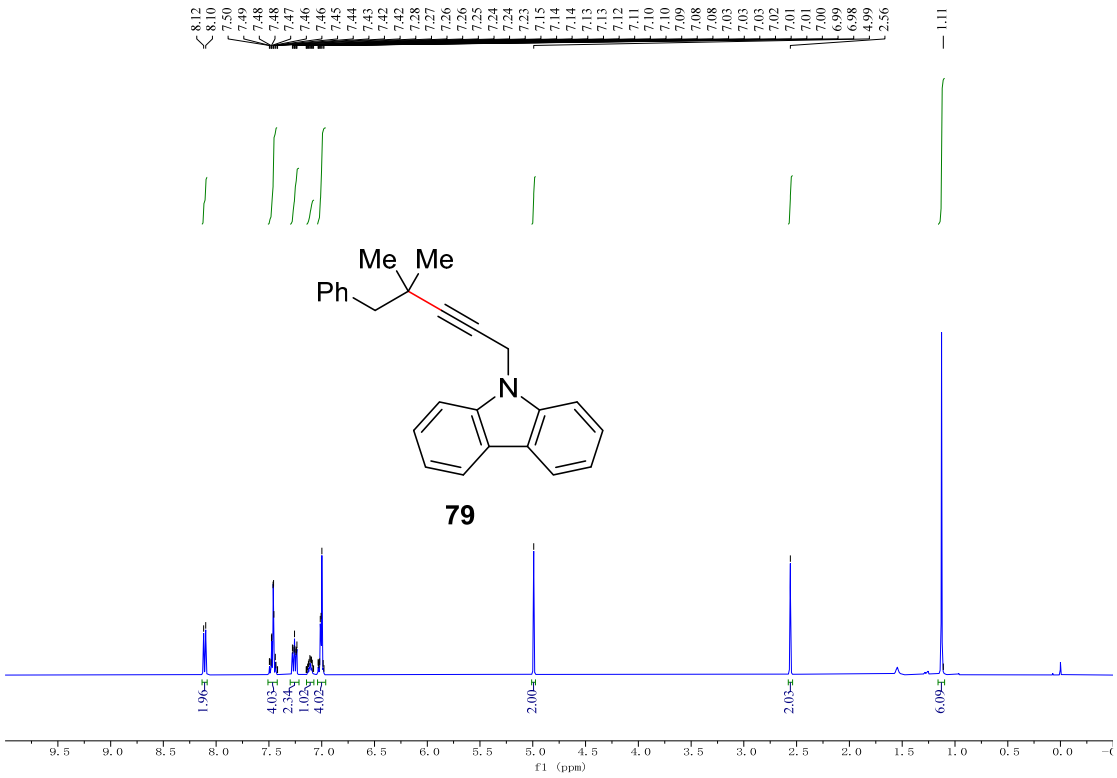
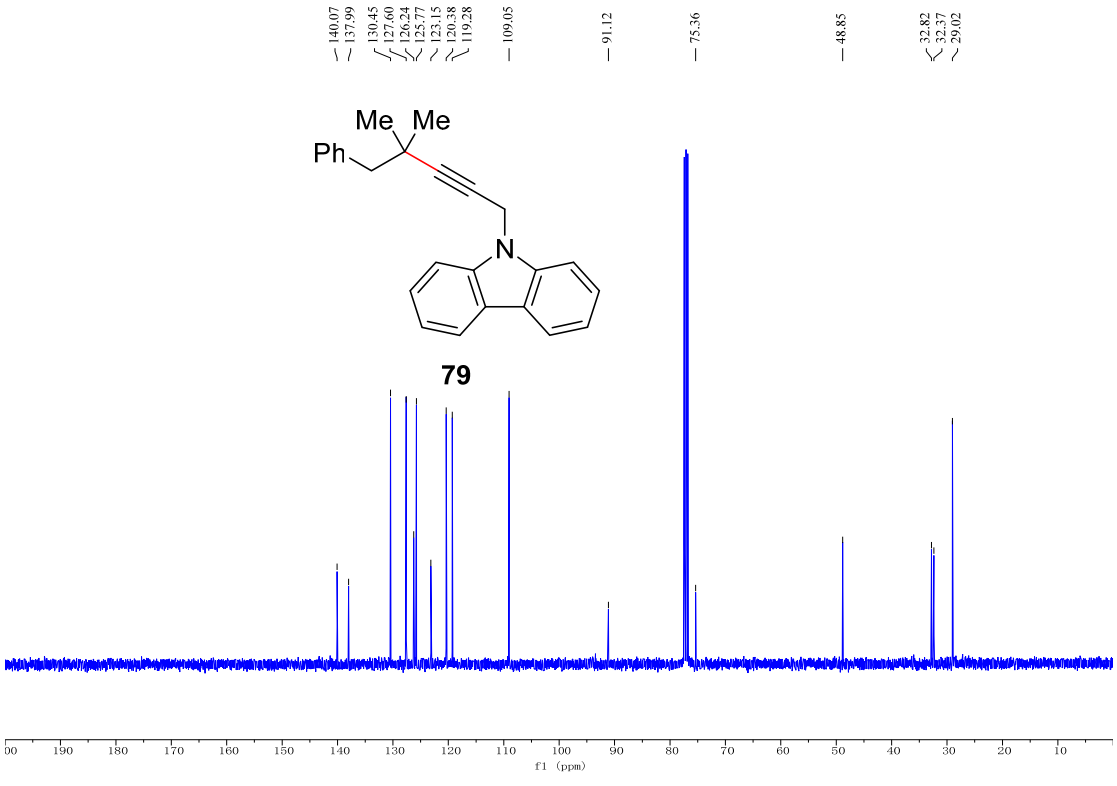
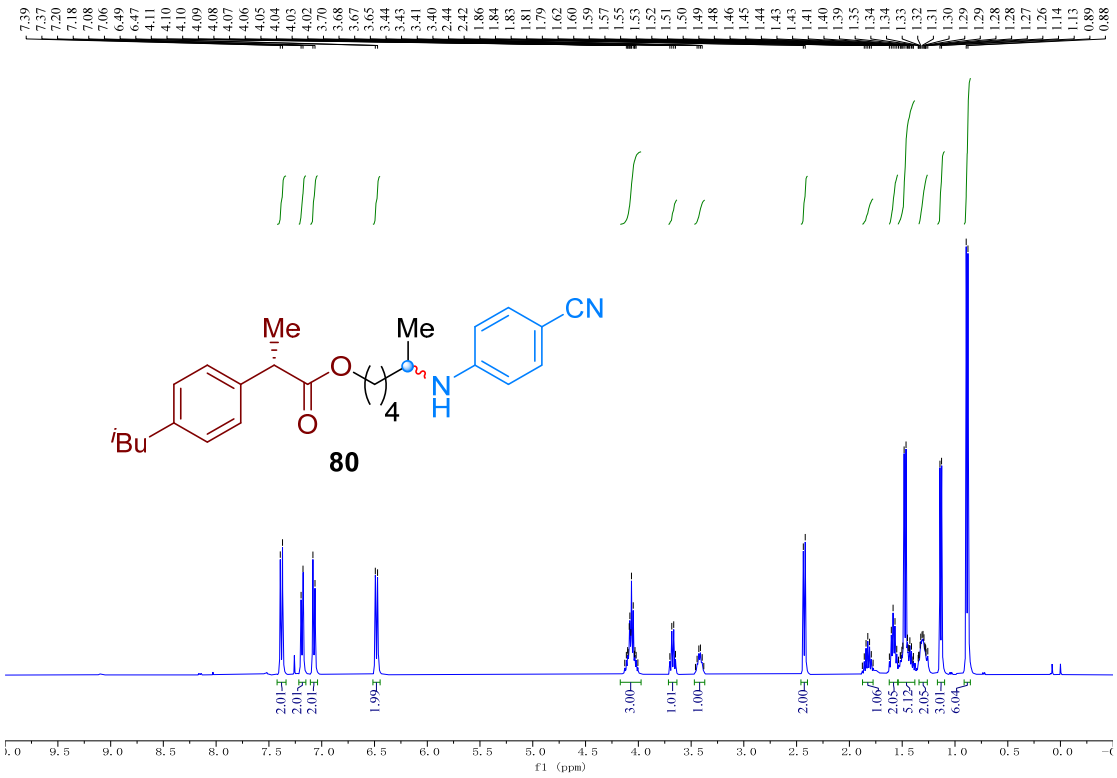
45.40
32.93
32.02
31.41
29.10
Me Me
Ph
N
78
f1 (ppm)


Me Me
Ph
N
79
f1 (ppm)


Me Me
Ph
N
79
f1 (ppm)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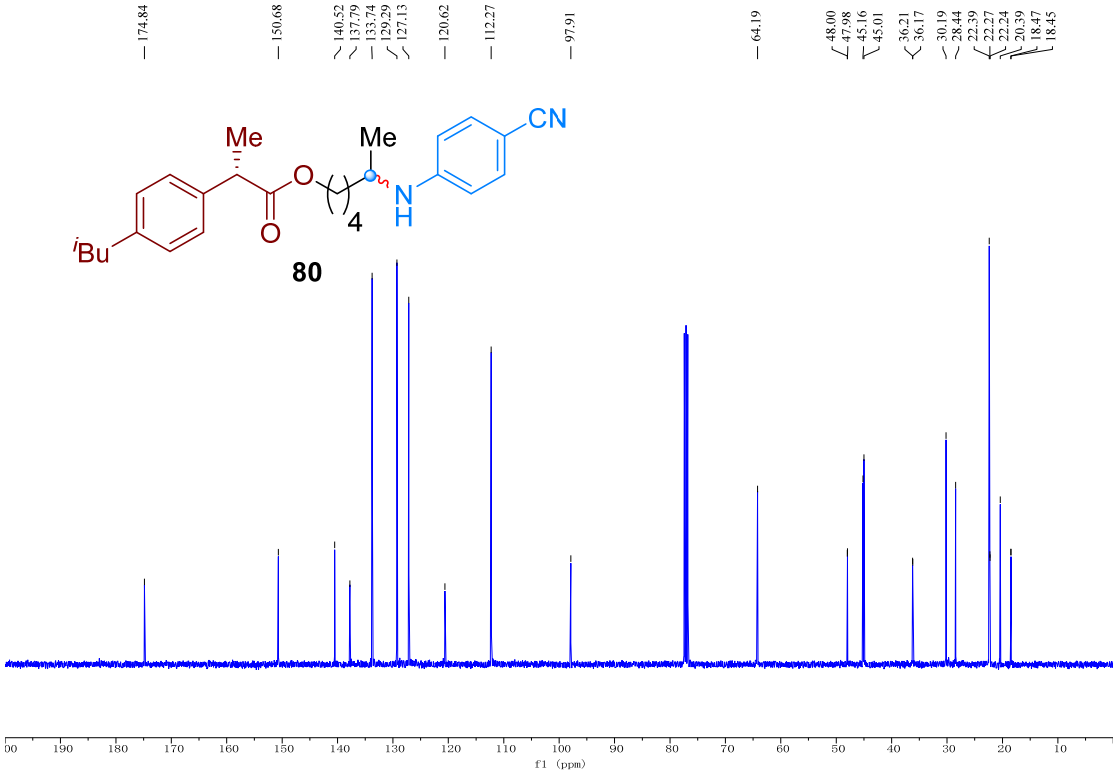
Me
CN
O
O
N
H
4
iBu
80
f1 (ppm)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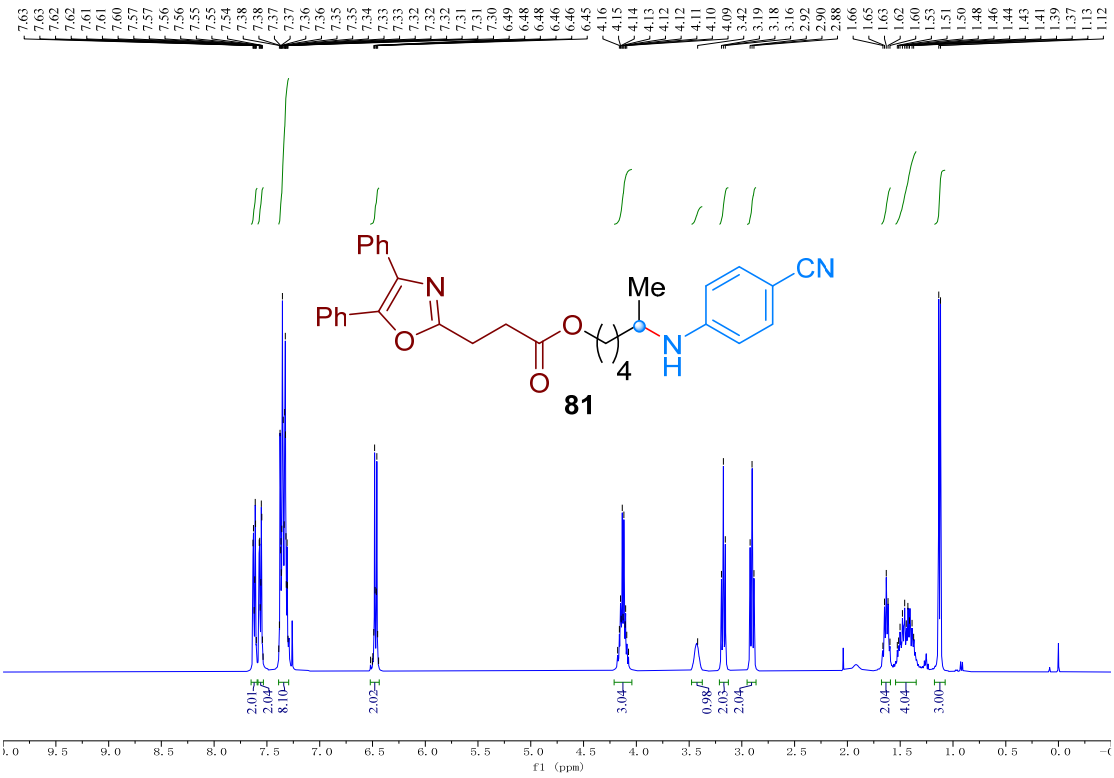
Me
CN
O
O
N
H
4
iBu
80
f1 (ppm)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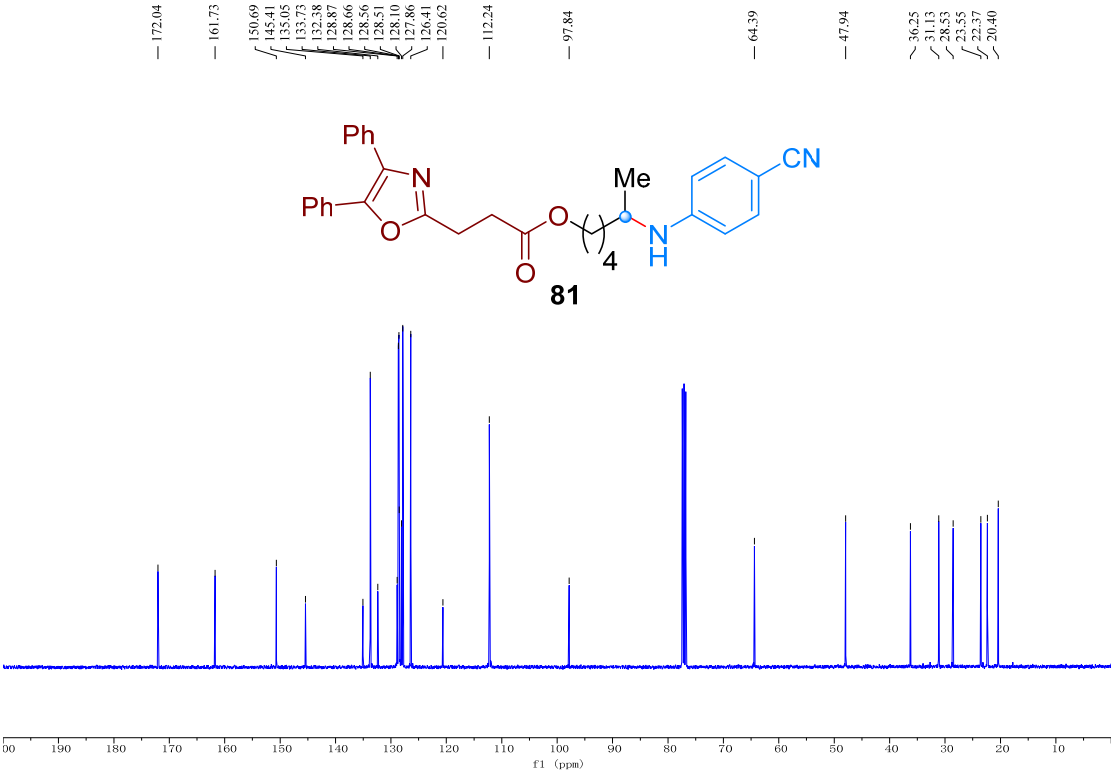
N
Ph
O
O
O
Me
4
N
H
CN
81
f1 (ppm)


Ph
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Ph
O
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O
Me
4
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CN
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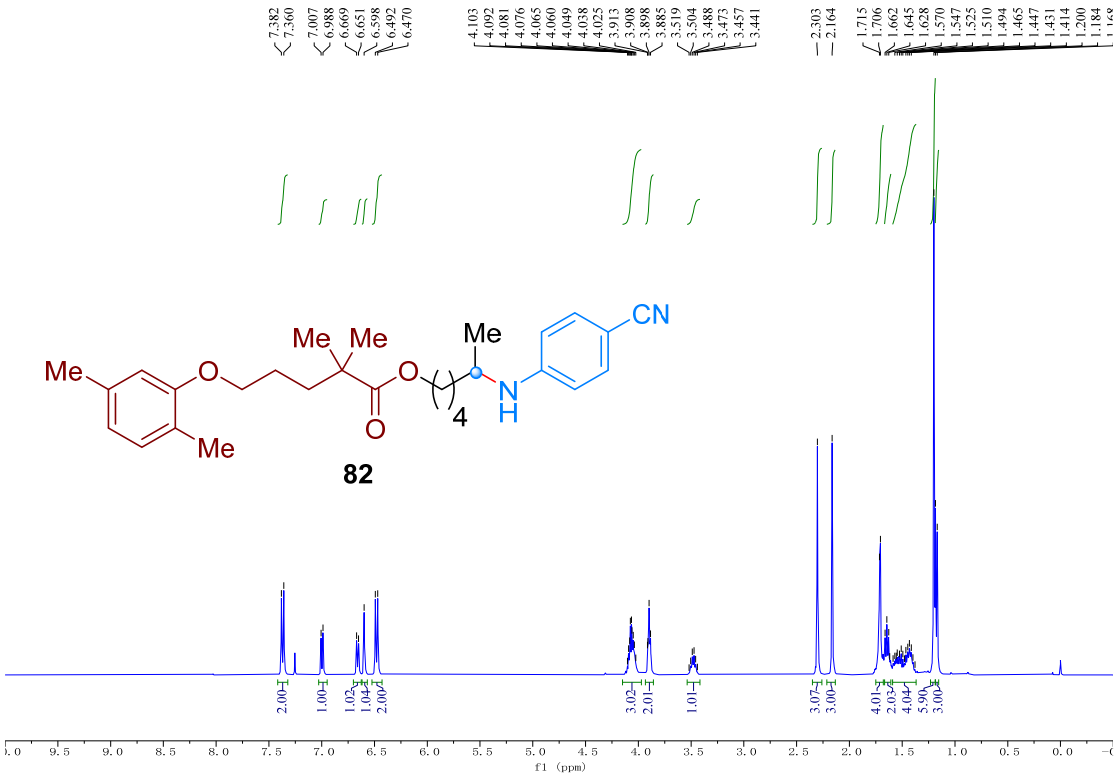
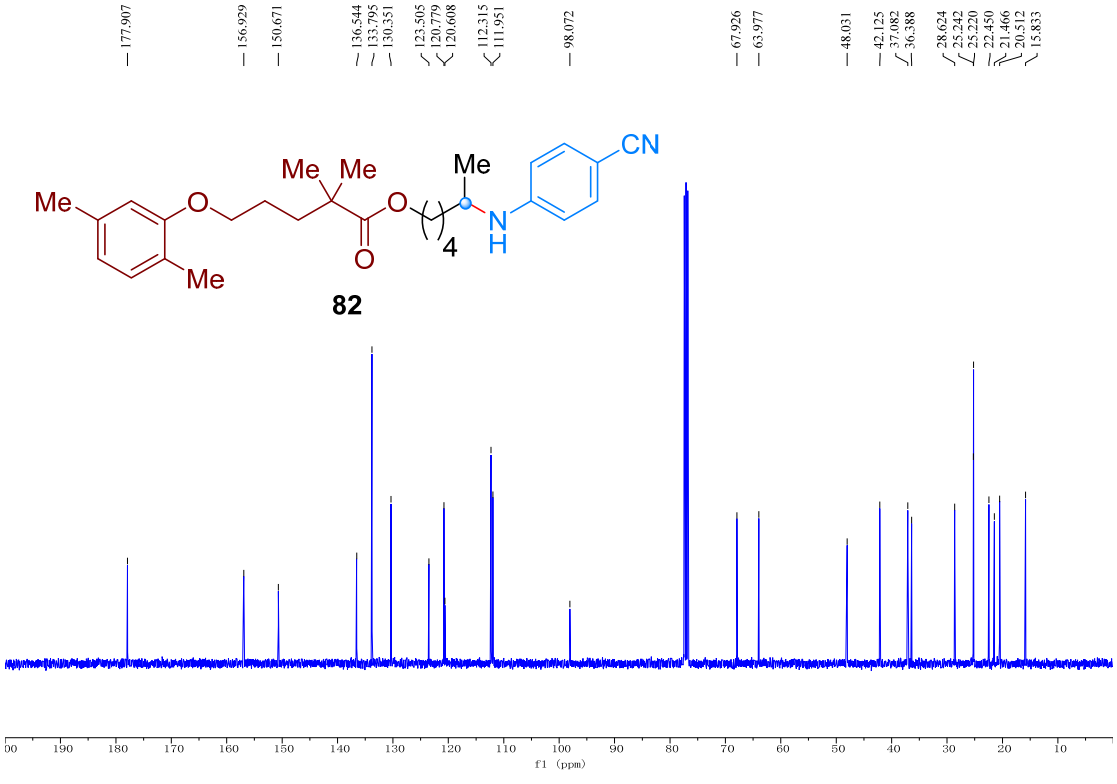
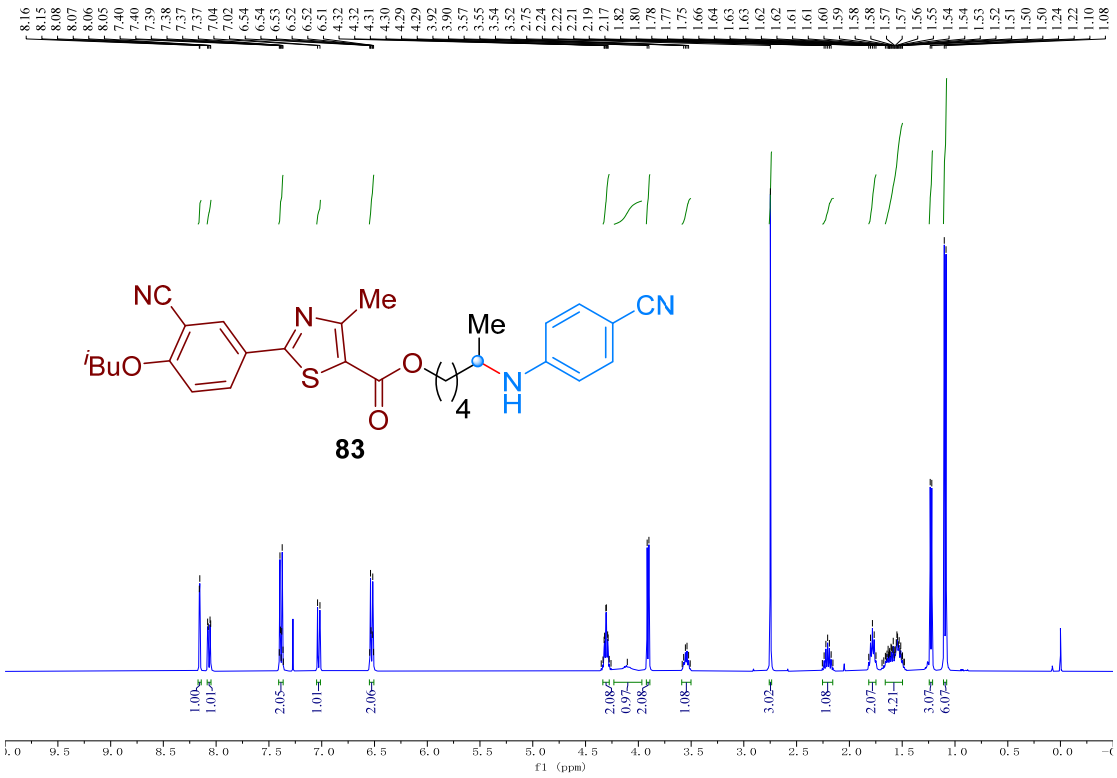
f1 (ppm)


Me
Me
Me
Me
O
O
O
O
4
N
H
CN
82
f1 (ppm)


Me
Me
Me
Me
O
O
O
O
4
N
H
CN
82
f1 (ppm)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S
O
Me
CN
O
4
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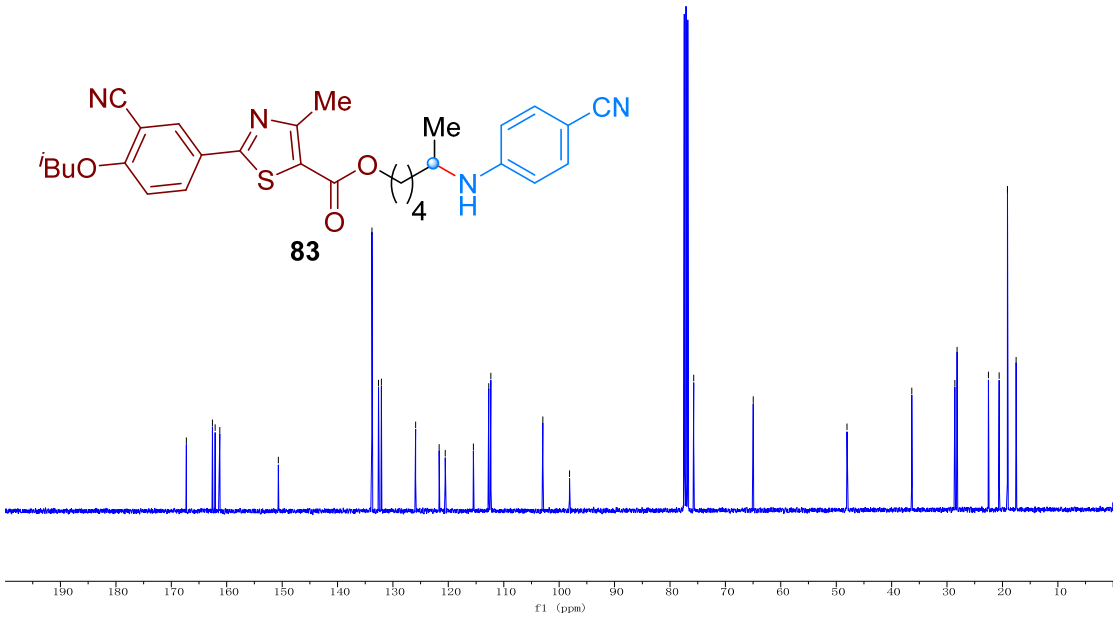
H
83


NC
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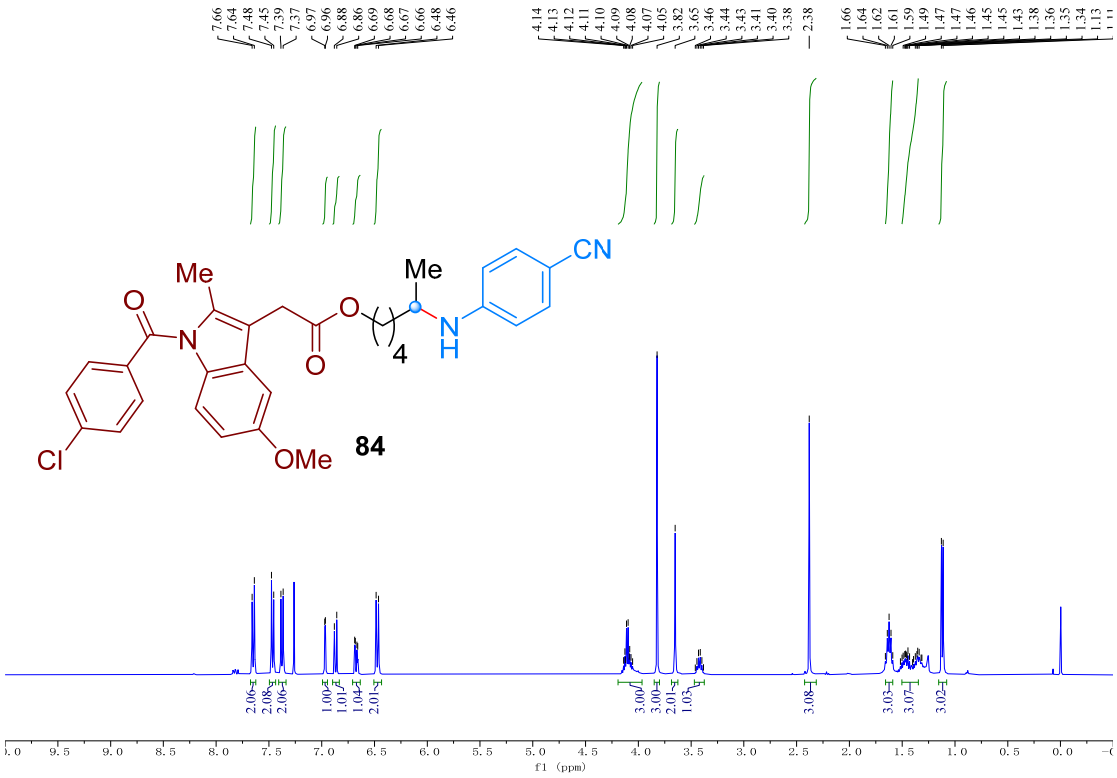
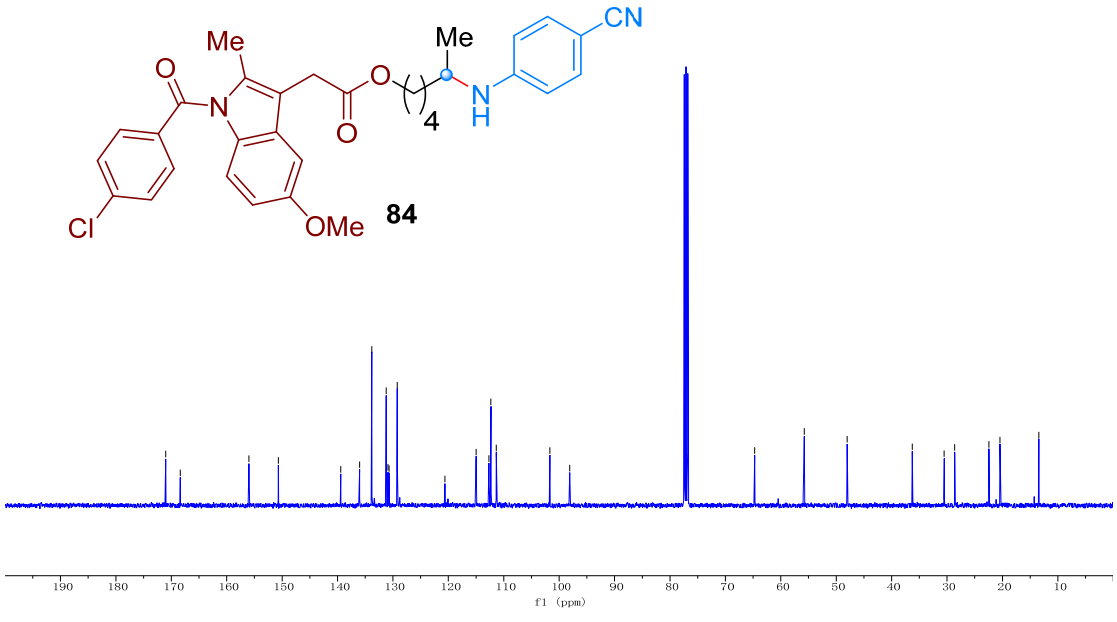
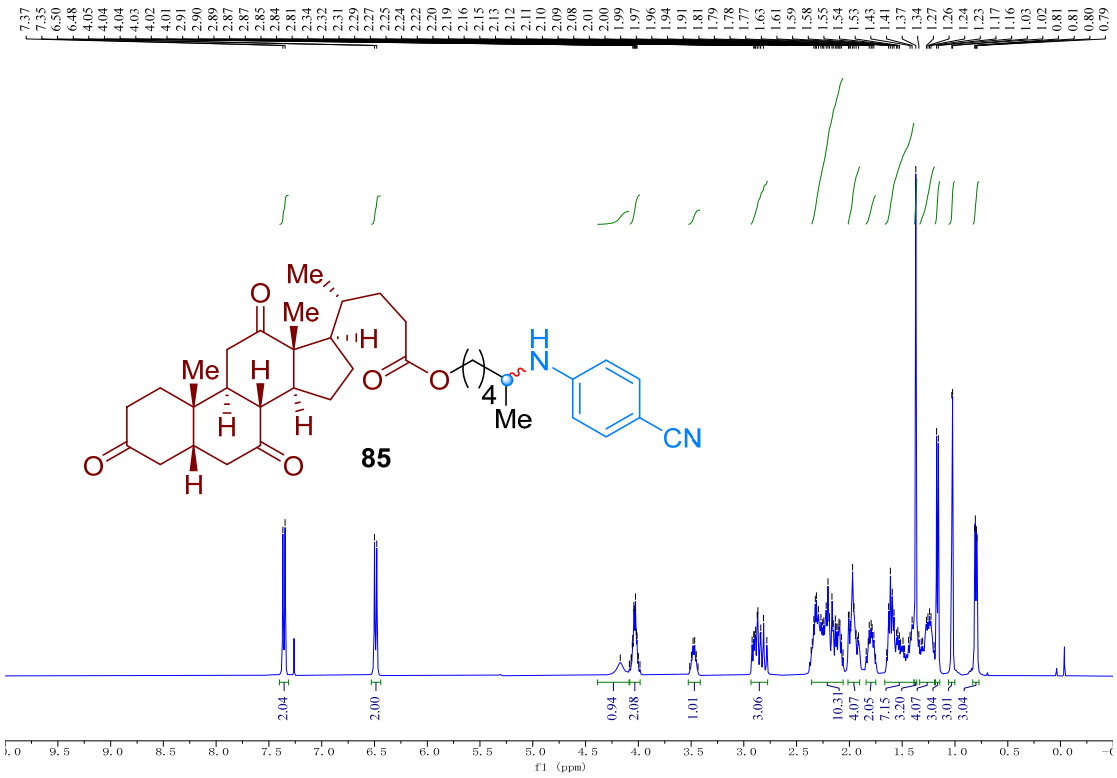
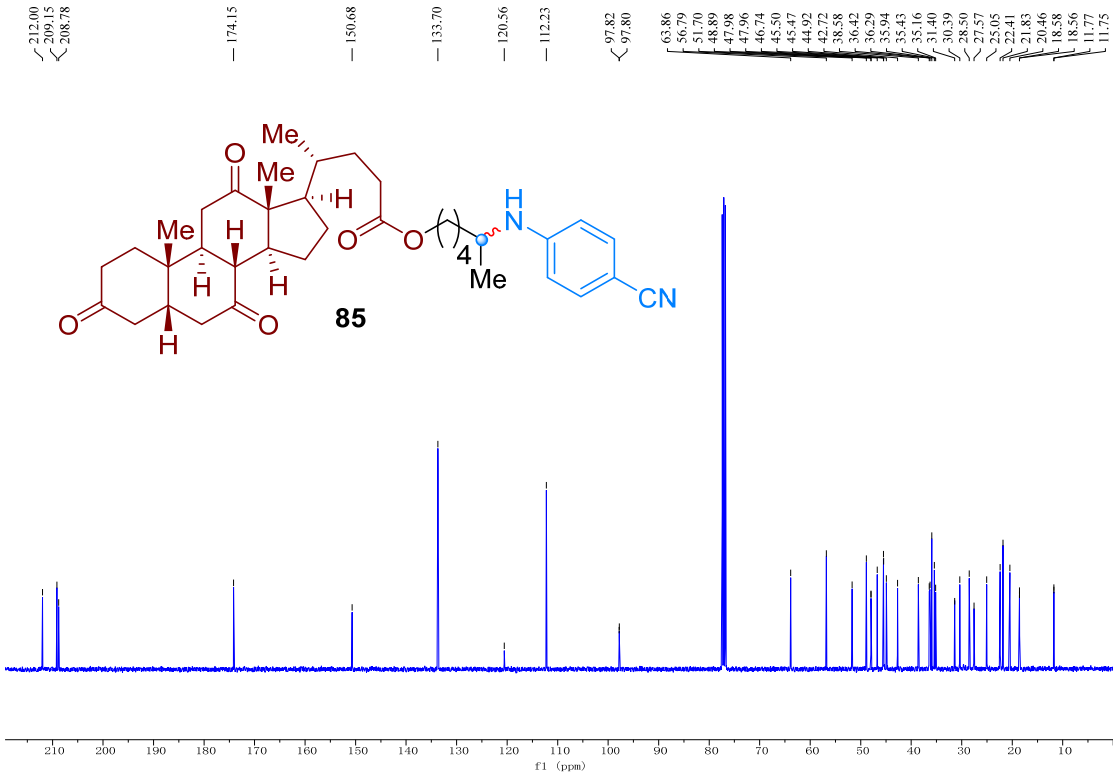
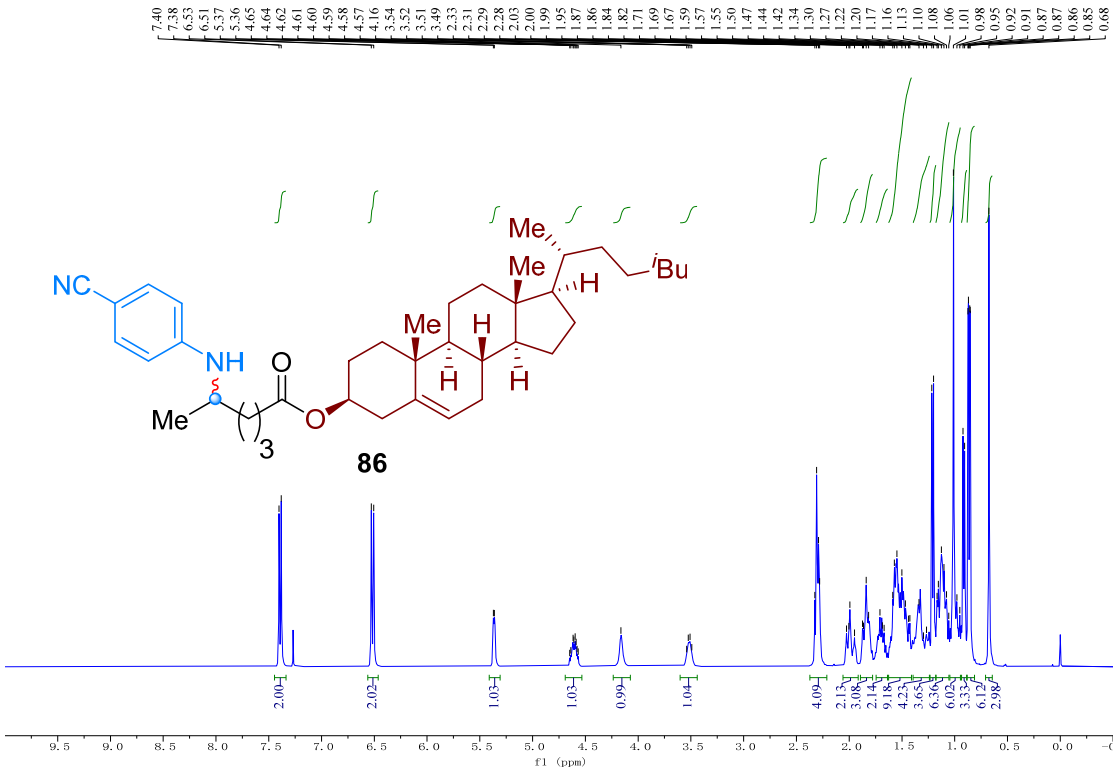
N
^{i}BuO
S
O
Me
CN
O
4
N
H
83

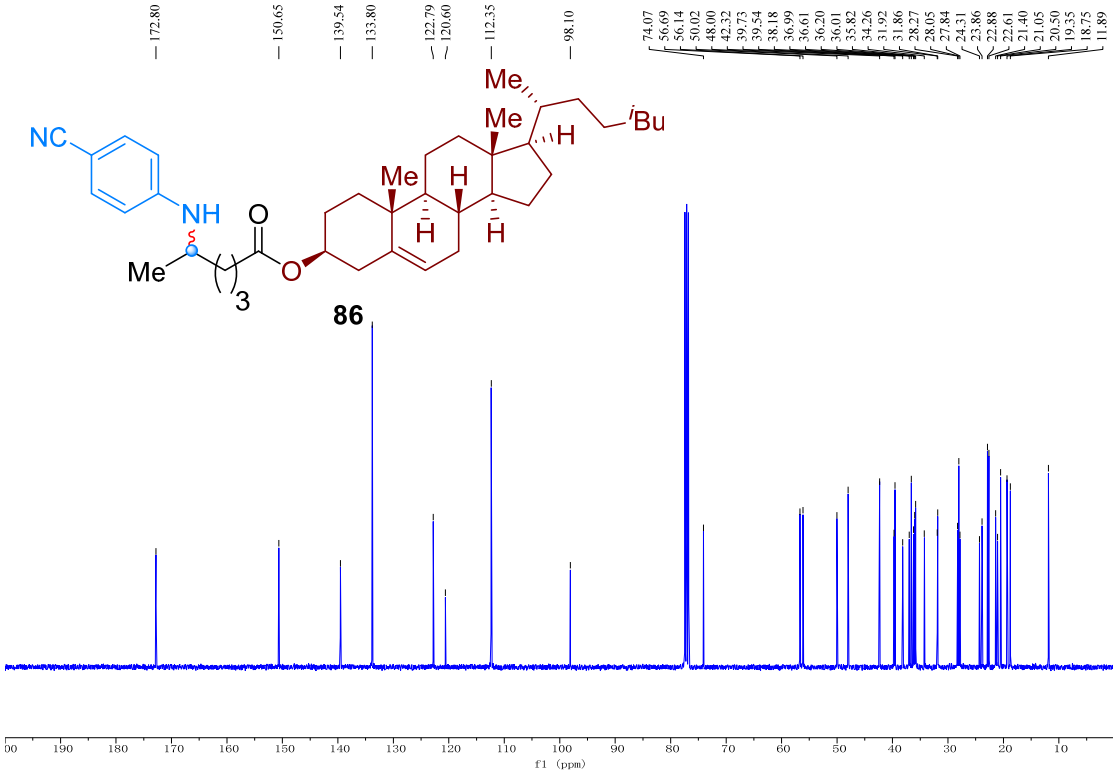

Me
O
N
O
O
Me
4
N
H
CN
Cl
OMe
84
f1 (ppm)

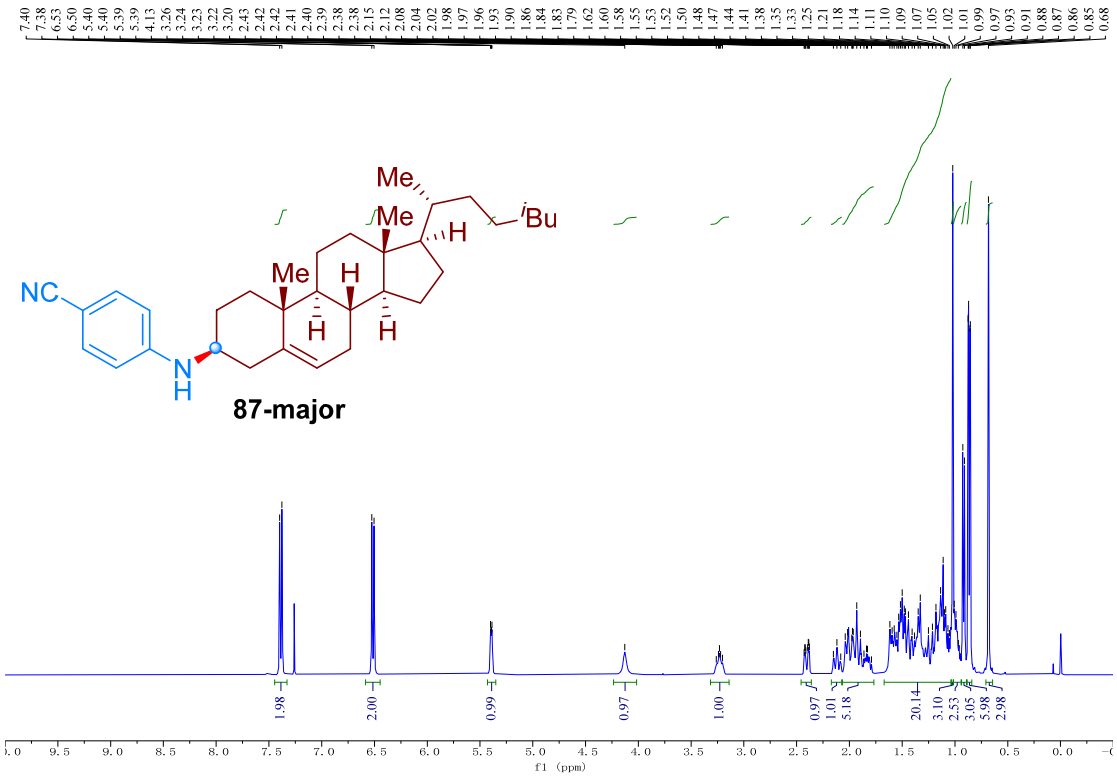

Me
O
N
O
O
Me
4
N
H
CN
Cl
OMe
84
f1 (ppm)

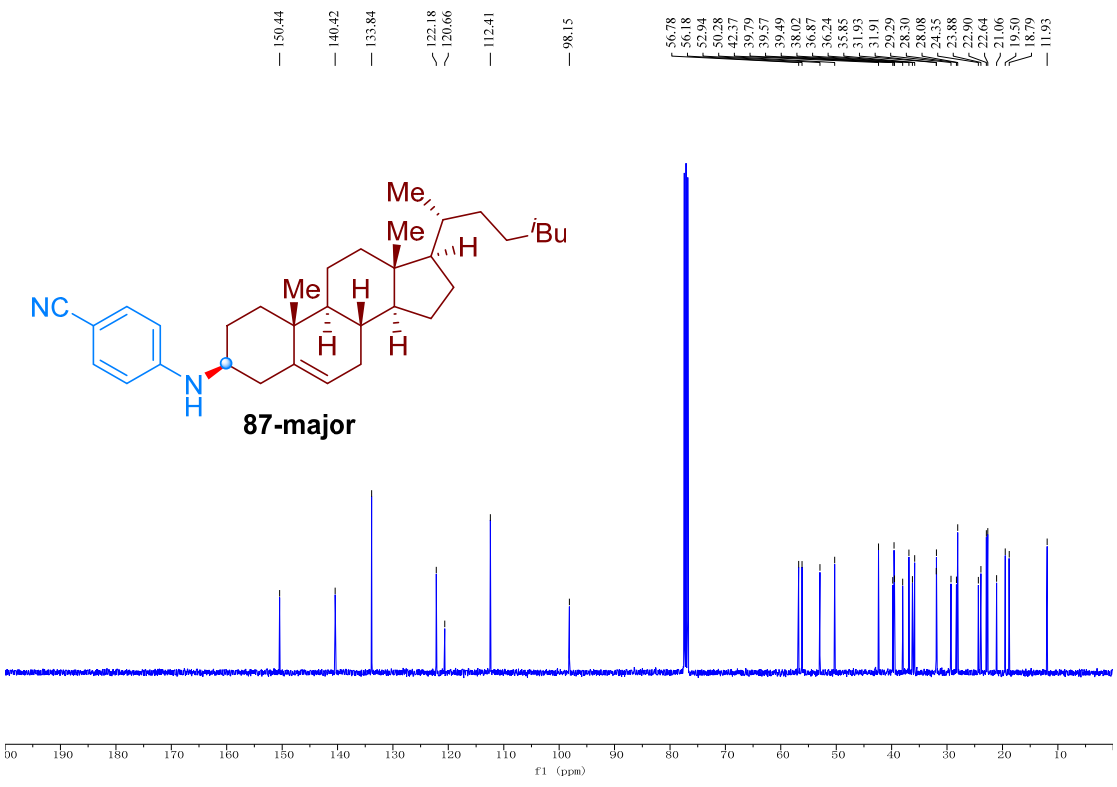

85
f1 (ppm)

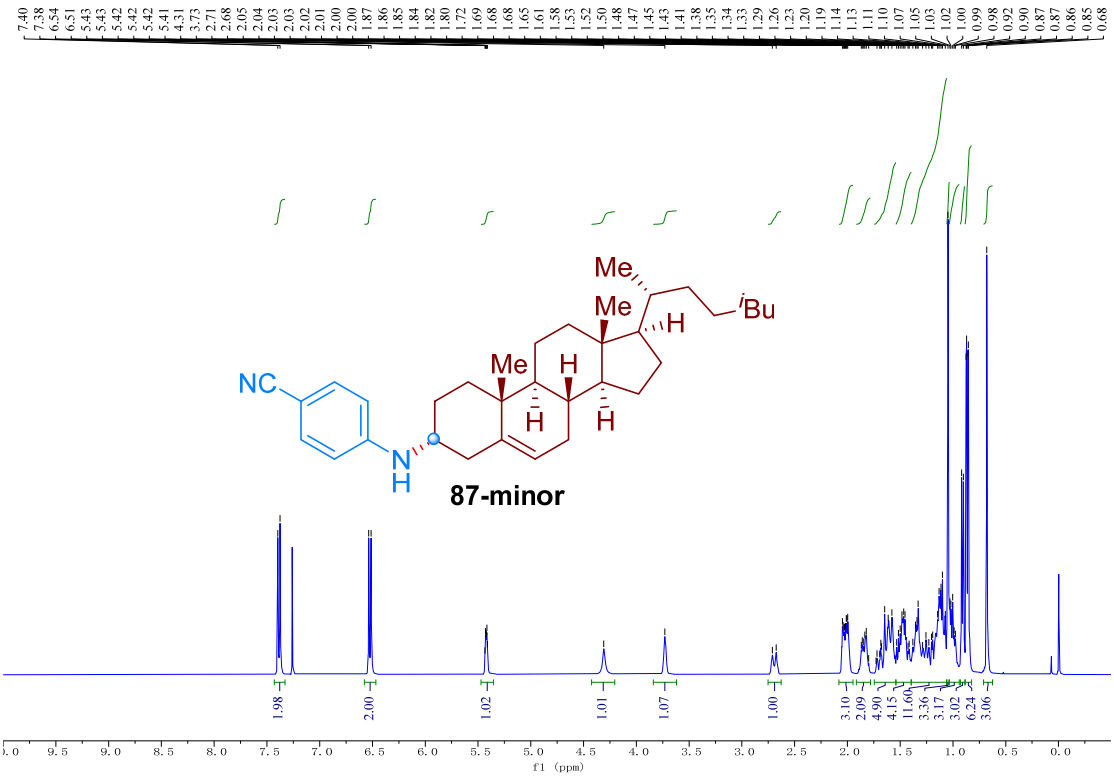

85
f1 (ppm)

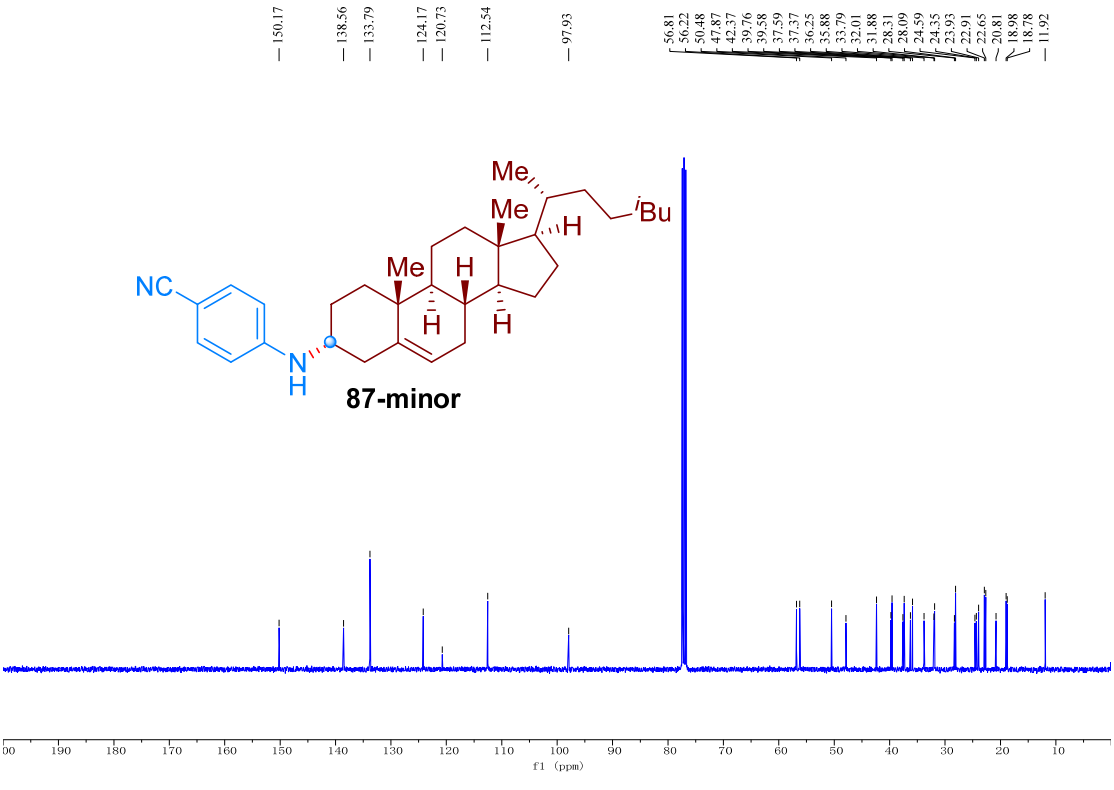

NC
NH
O
Me
3
O
Me
Me
H
iBu
Me
H
H
H
86
f1 (ppm)

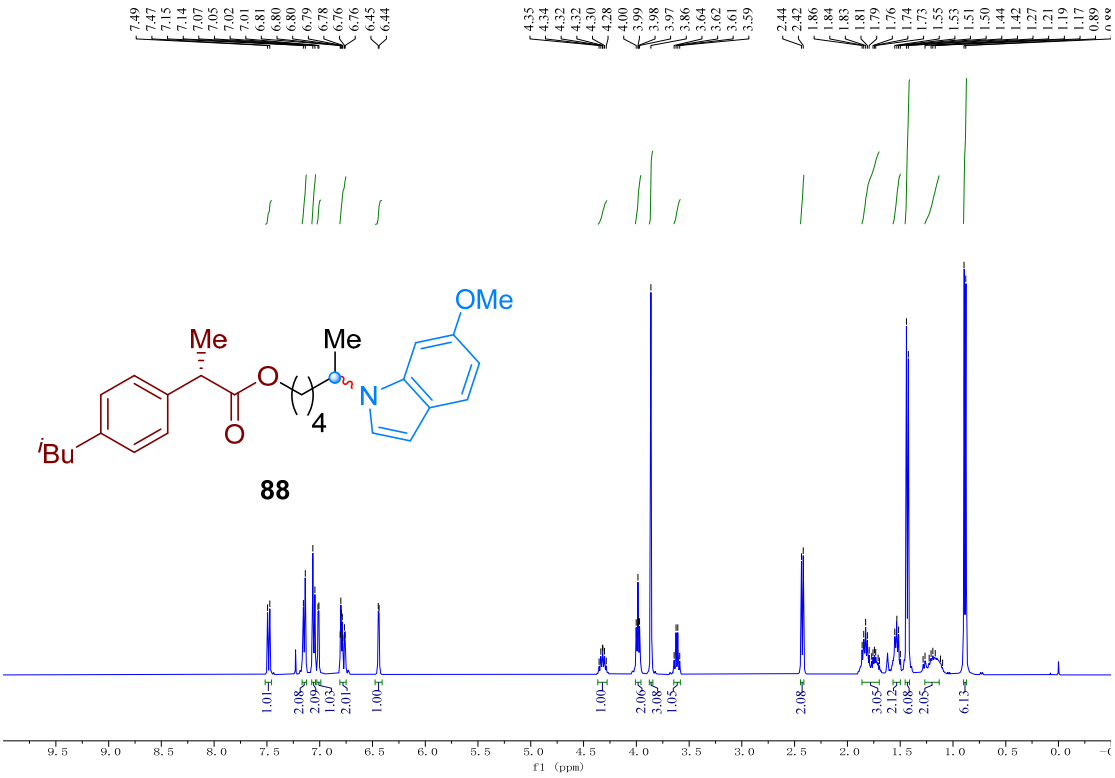

NC
NH
O
Me
3
O
Me
Me
H
iBu
Me
H
H
H
86
f1 (ppm)

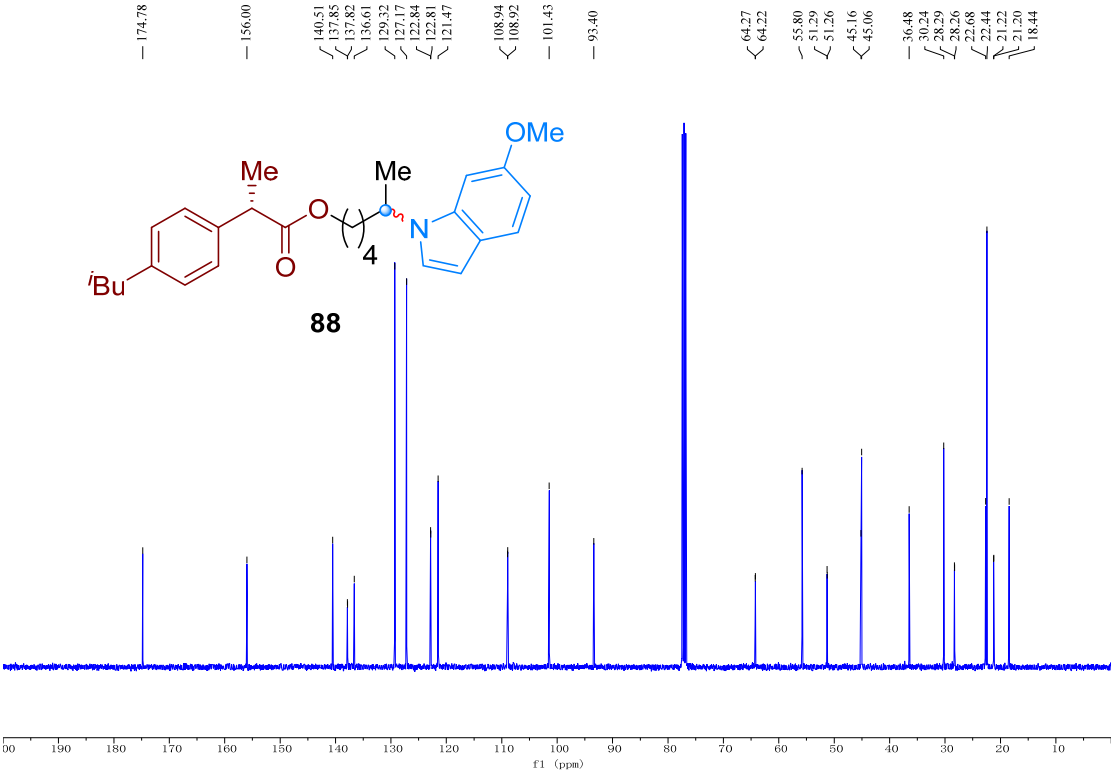

Me
Me
iBu
H
Me
H
H
H
NC
N
H
87-major
1.98
2.00
0.99
0.97
1.00
0.97
1.01
5.18
20.14
3.10
2.53
3.05
5.98
2.98
f1 (ppm)

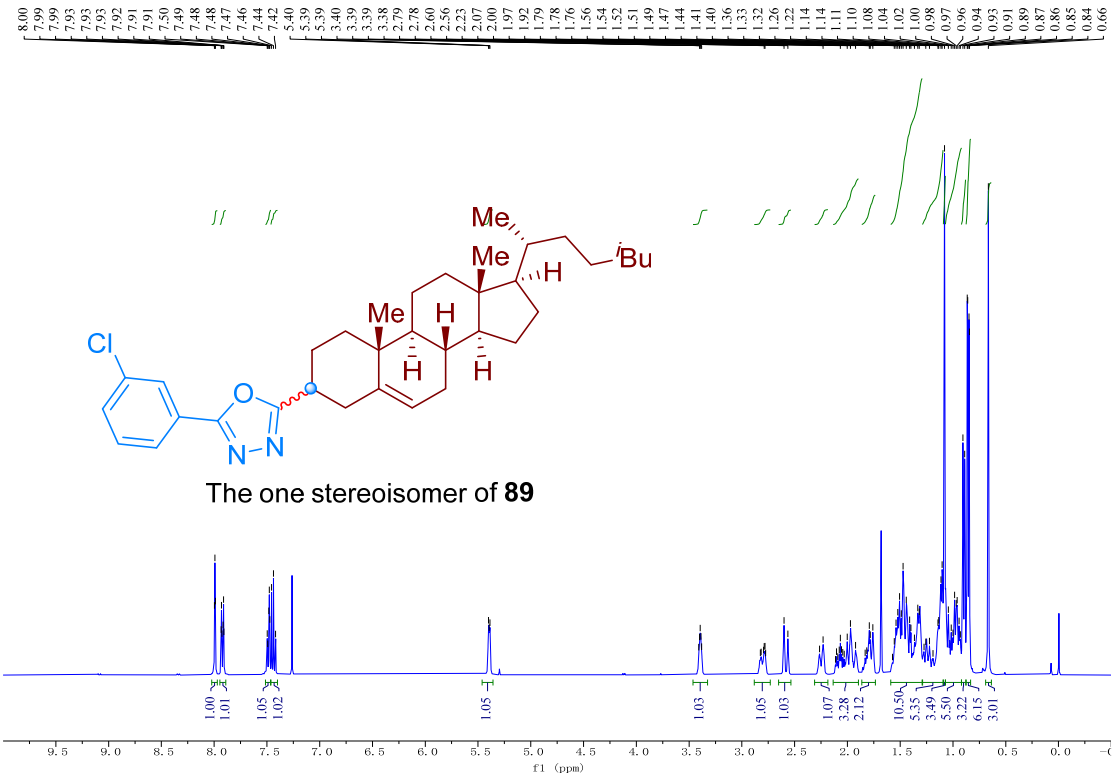

Me
Me
iBu
H
Me
H
H
H
NC
N
H
87-major
f1 (ppm)


Me
Me
H
iBu
Me
H
H
H
NC
N
H
87-minor
1.98
2.00
1.02
1.01
1.07
1.00
3.10
2.09
4.90
4.15
11.60
3.36
3.17
3.02
6.24
3.06
f1 (ppm)

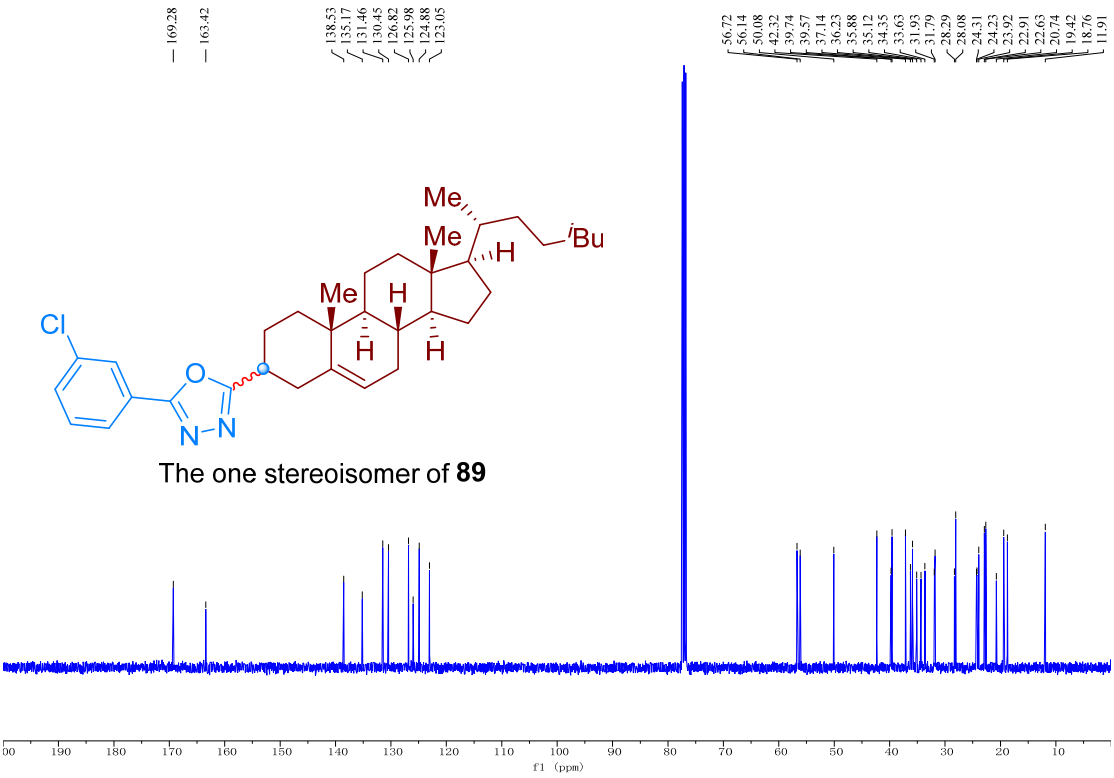

150.17
138.56
133.79
124.17
120.73
112.54
97.93
56.81
56.22
50.48
47.87
42.37
39.76
39.58
37.59
37.37
36.25
35.88
33.79
32.01
31.88
28.31
28.09
24.59
24.35
23.93
22.91
22.65
20.81
18.98
18.78
11.92
Me
Me
H
iBu
Me
H
H
H
NC
N
H
87-minor
f1 (ppm)


OMe
Me
Me
O
O
4
N
iBu
88
f1 (ppm)

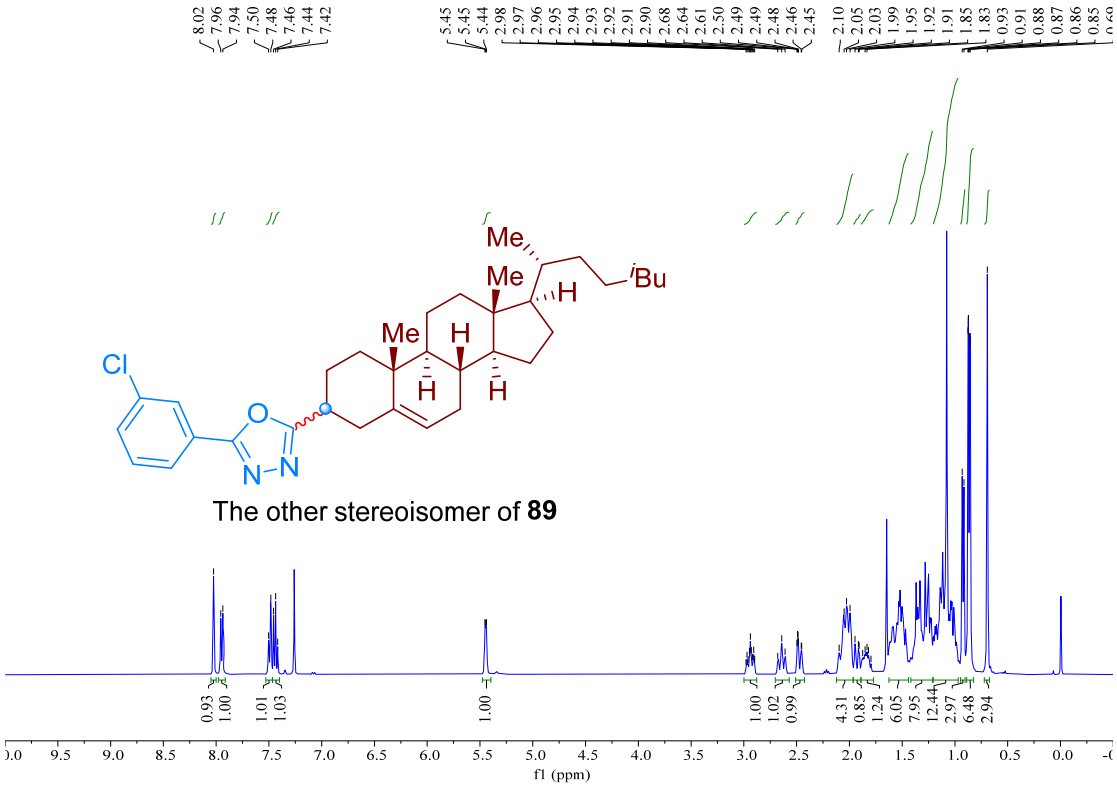

OMe
Me
Me
O
O
4
N
iBu
88
f1 (ppm)

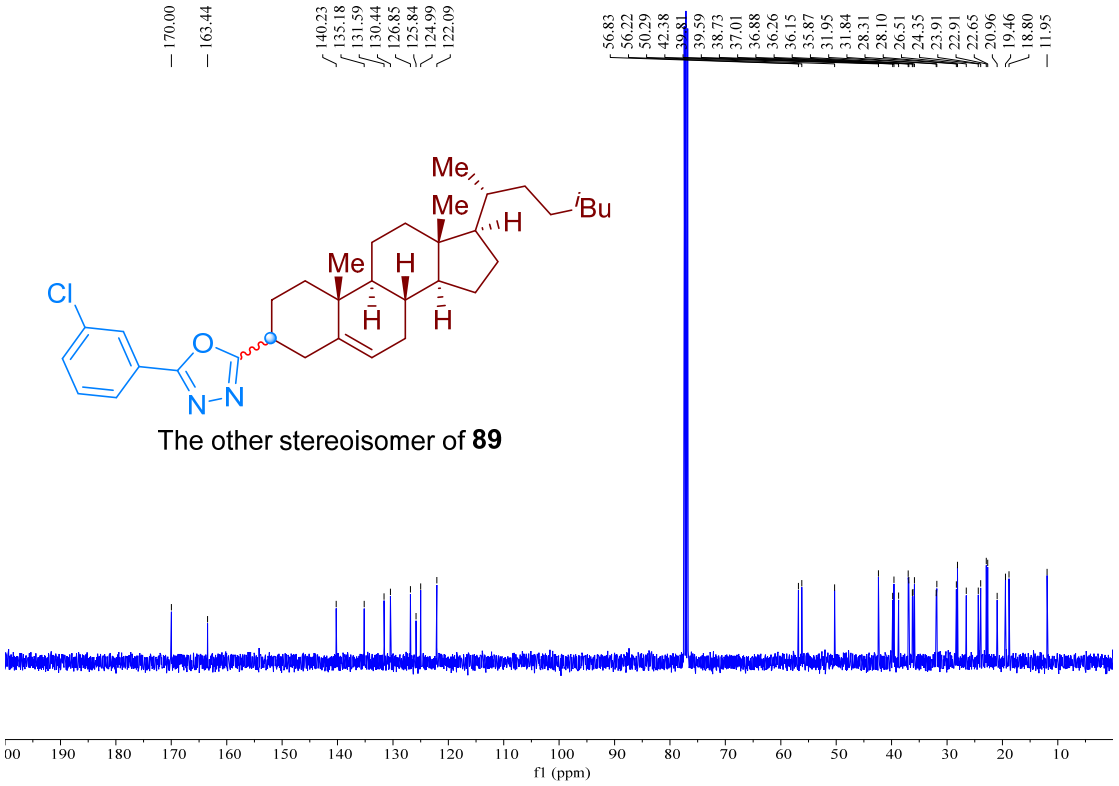


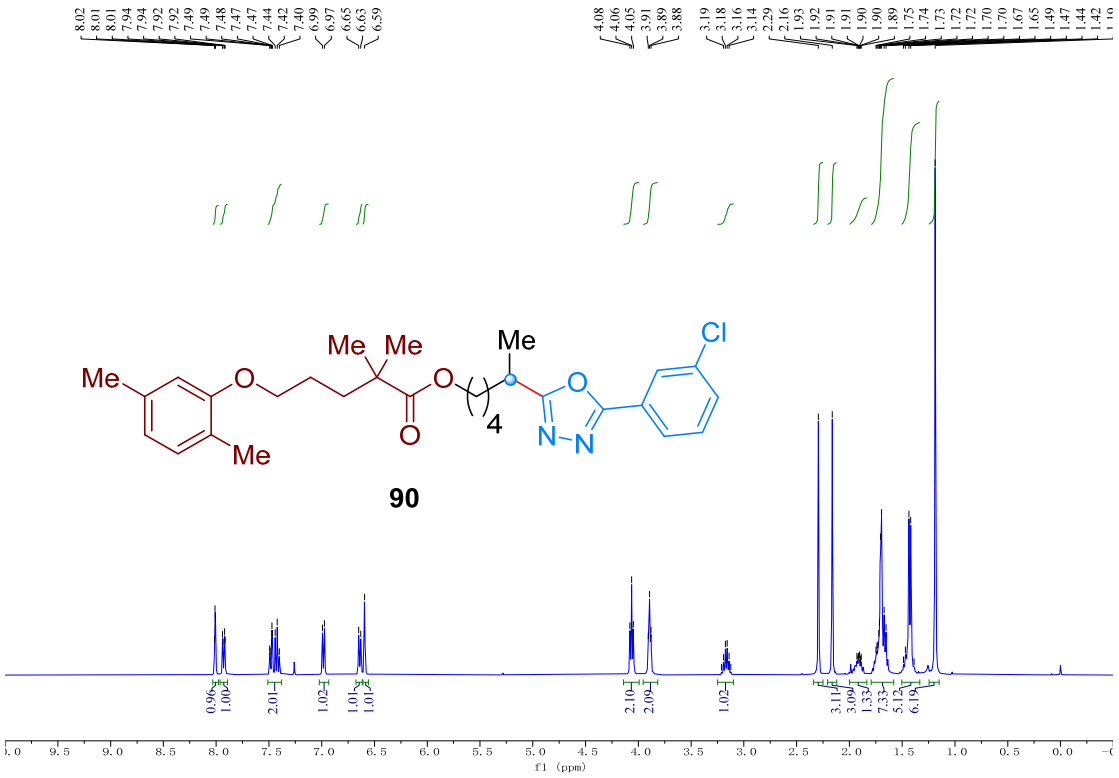
The one stereoisomer of **89**

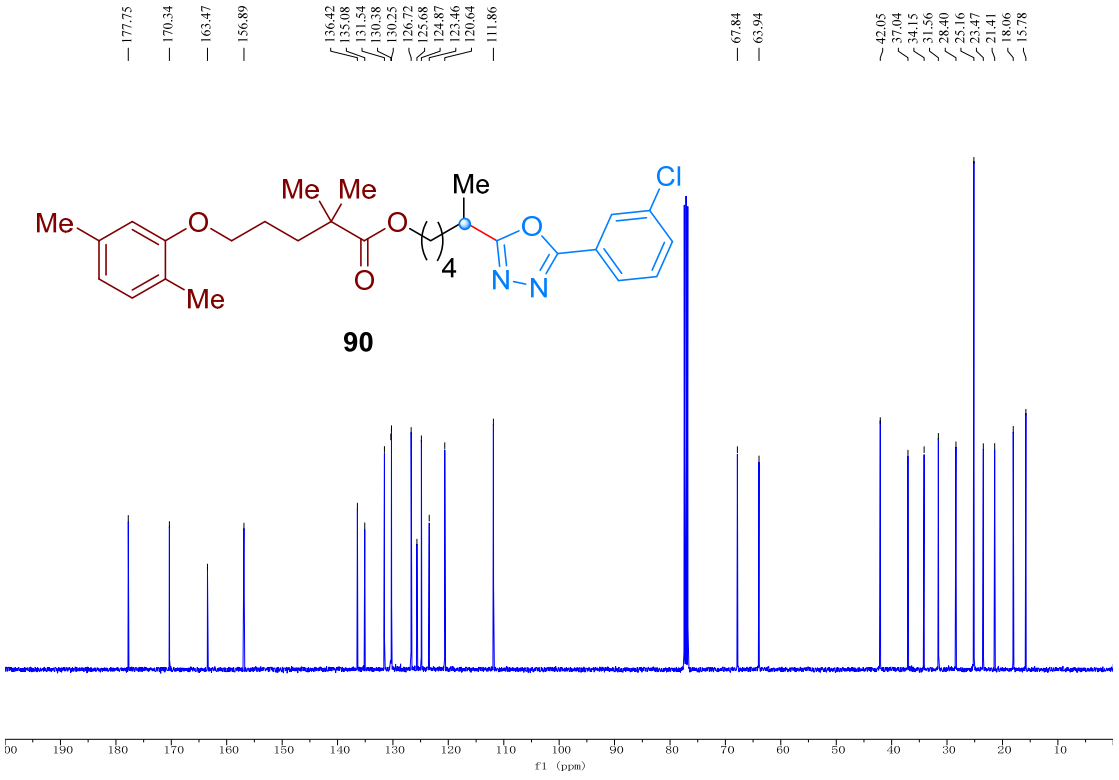


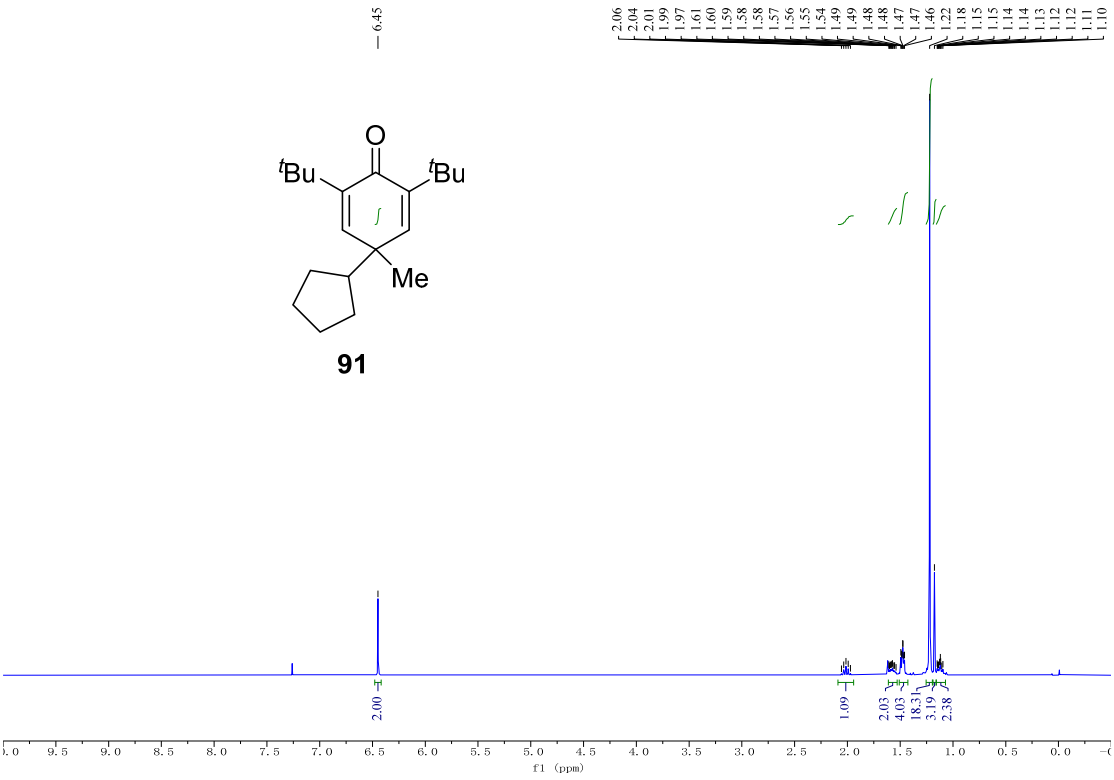
The one stereoisomer of **89**

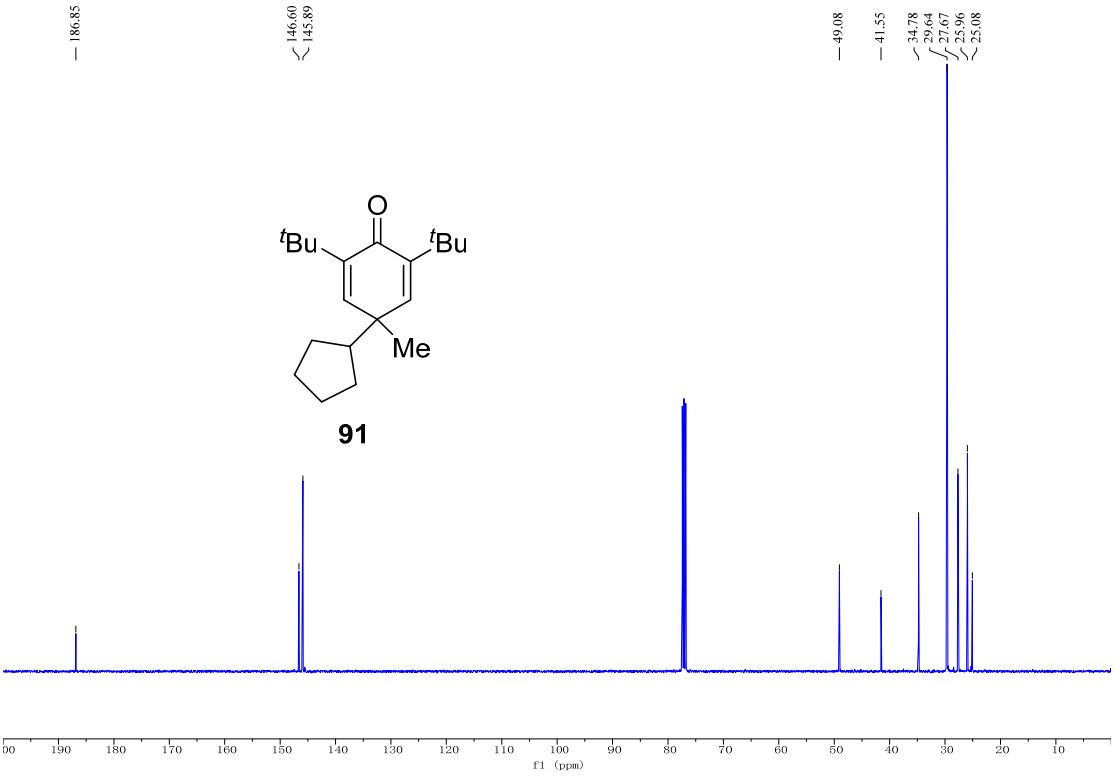

Me
Me
H
iBu
Me
H
H
H
Cl
O
N-N
The other stereoisomer of 89
fl (ppm)

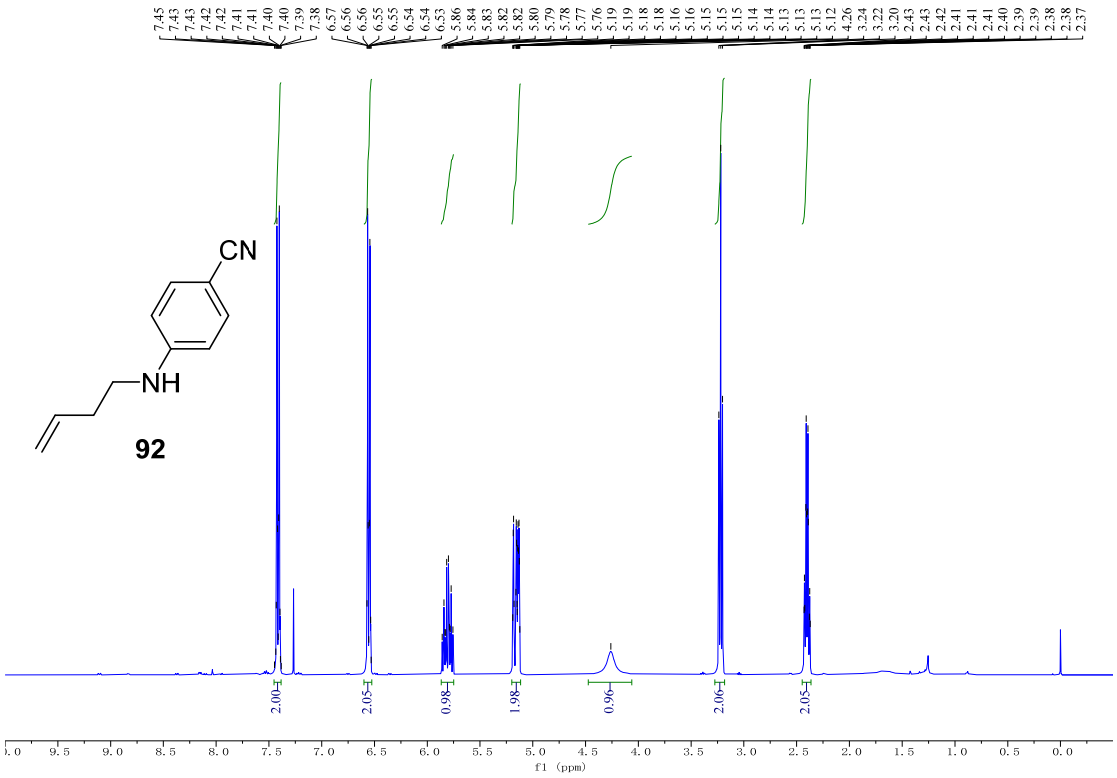

Me
Me
H
iBu
Me
H
H
H
Cl
O
N-N
The other stereoisomer of 89
fl (ppm)

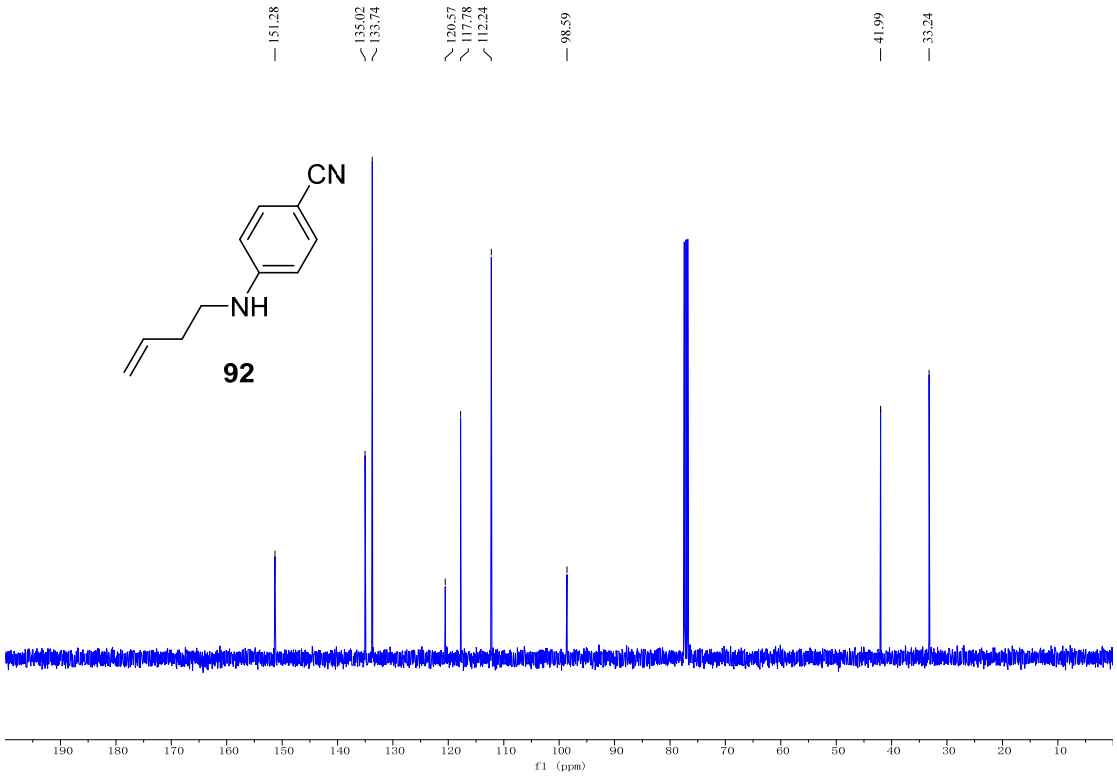

Me
Me
Me
O
O
O
4
Me
O
N-N
Cl
Me
90
f1 (ppm)

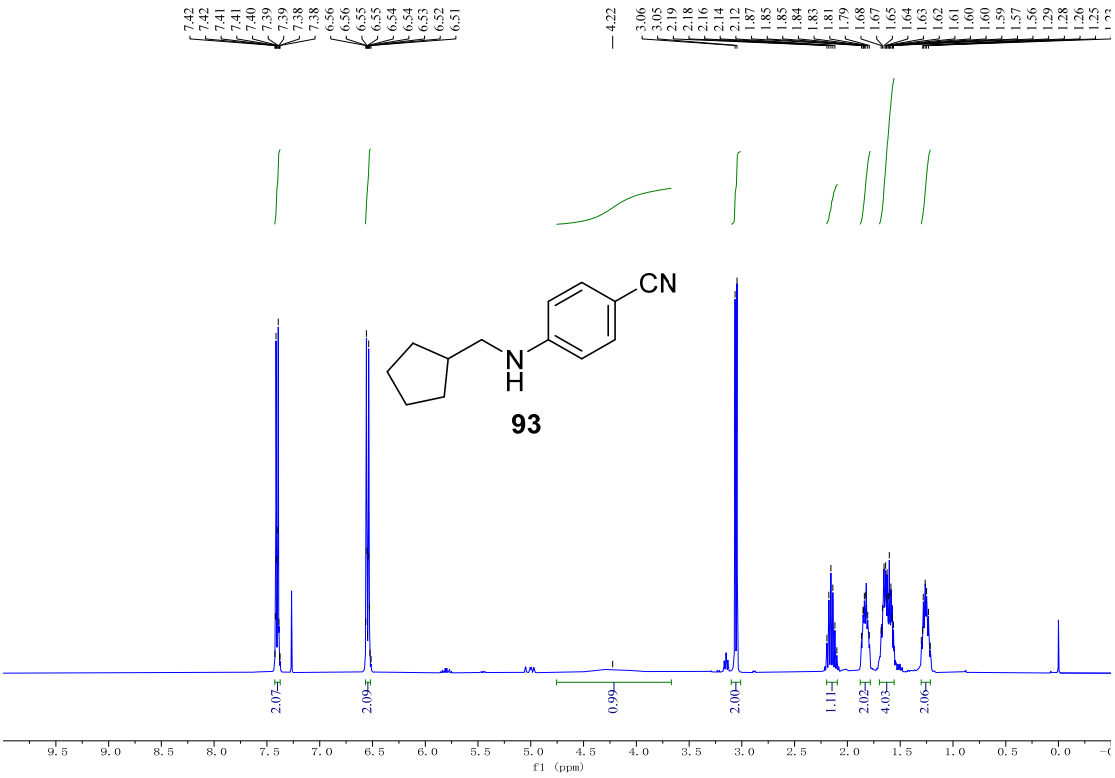

Me
Me
Me
O
O
O
4
Me
O
N-N
Cl
Me
90
f1 (ppm)

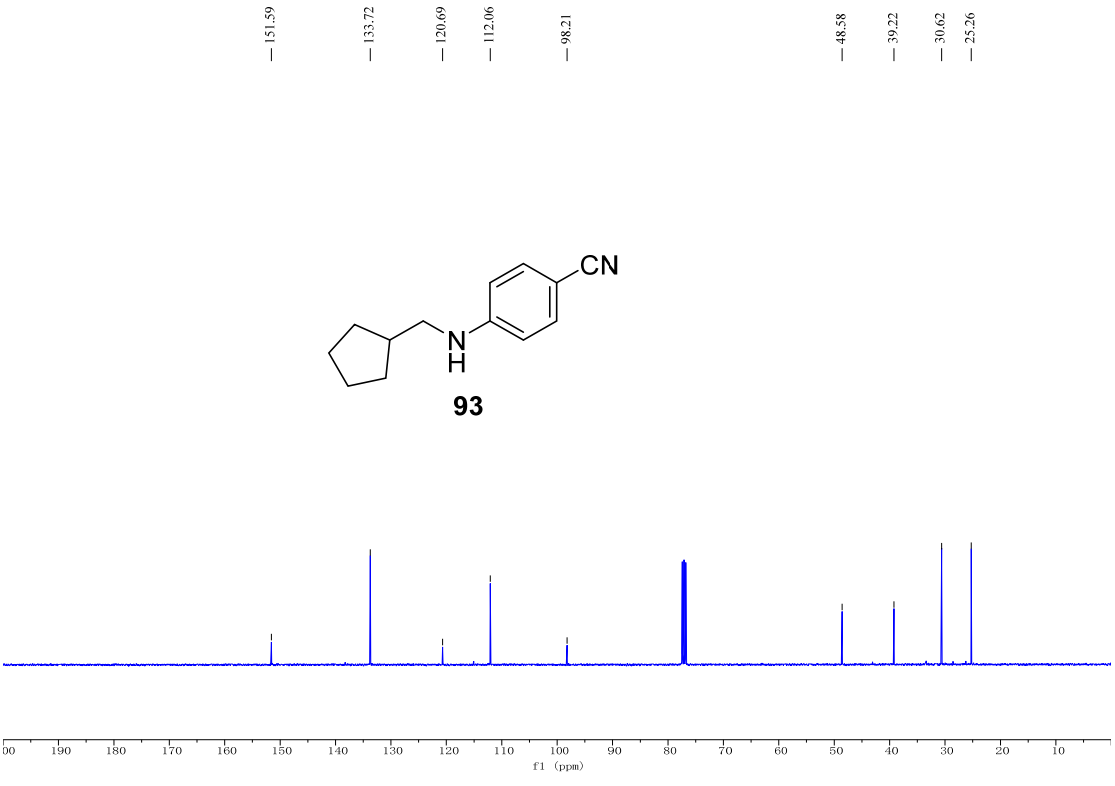

6.45
2.06
2.04
2.01
1.99
1.97
1.61
1.60
1.59
1.58
1.58
1.57
1.56
1.55
1.54
1.49
1.49
1.48
1.48
1.47
1.47
1.46
1.22
1.18
1.15
1.15
1.14
1.14
1.13
1.12
1.12
1.11
1.10
O
tBu
tBu
Me
91
2.00
1.09
2.03
4.03
18.31
3.19
2.38
f1 (ppm)

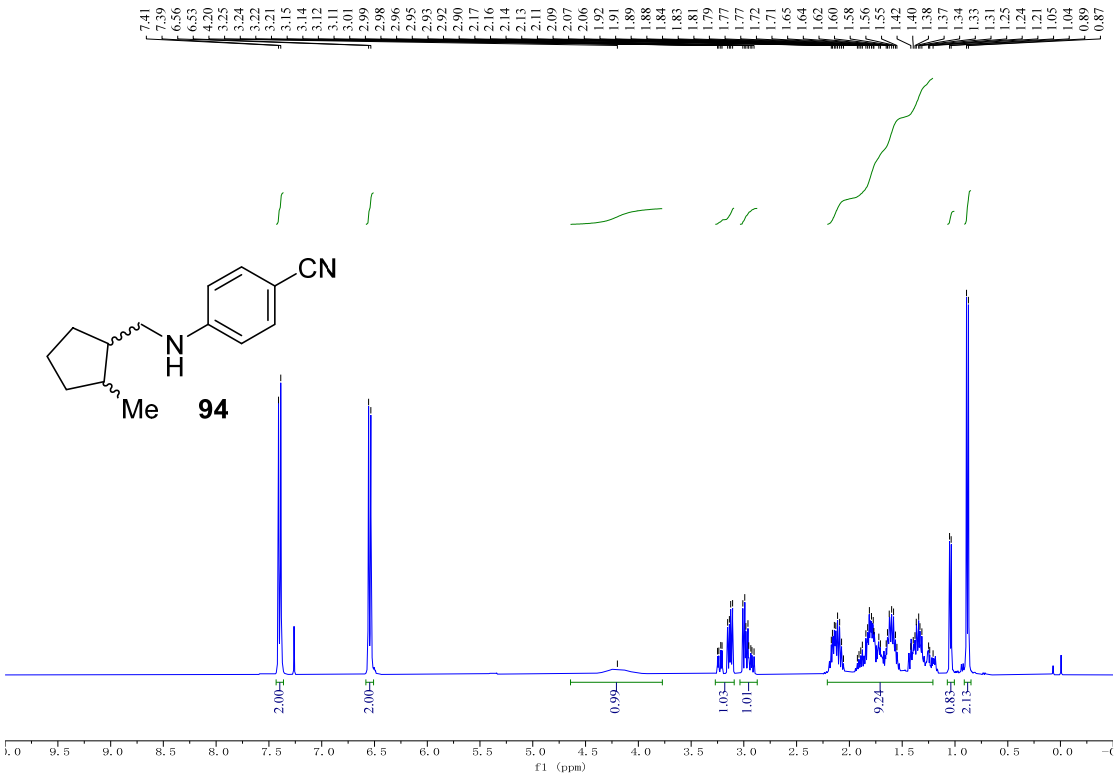

186.85
146.60
145.89
49.08
41.55
34.78
29.64
27.67
25.96
25.08
O
tBu
tBu
Me
91
f1 (ppm)

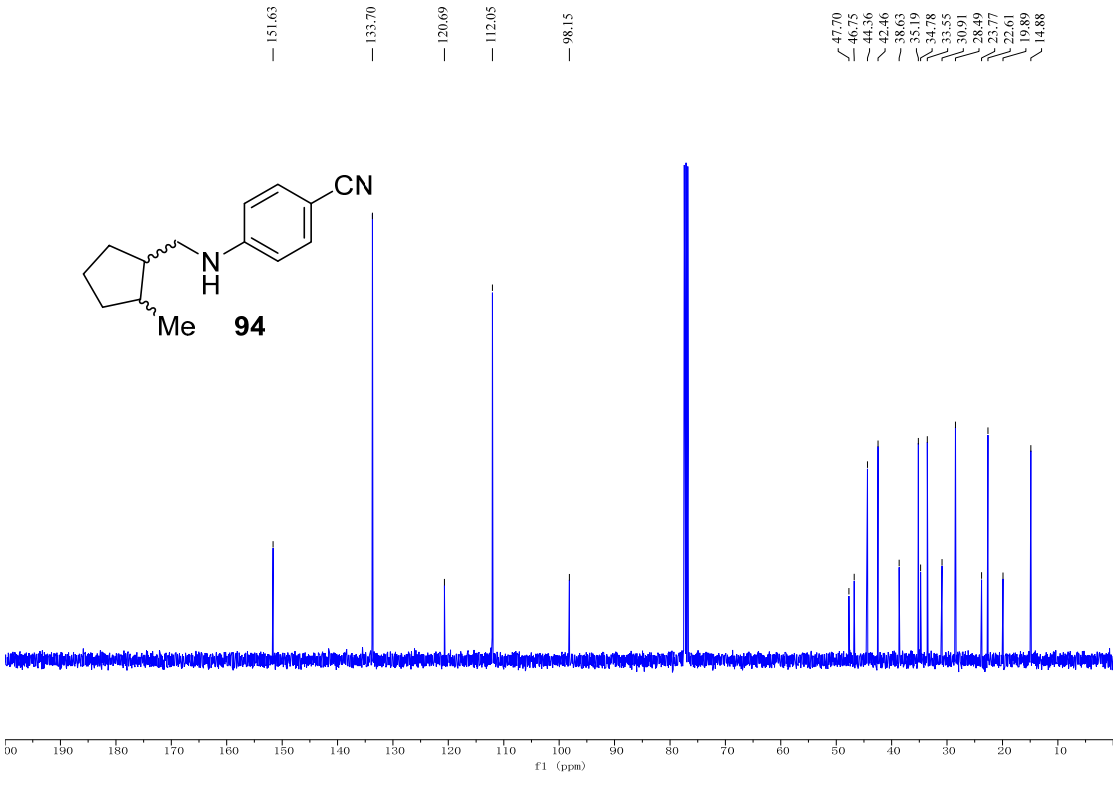

CN
NH
92
f1 (ppm)


151.28
135.02
133.74
120.57
117.78
112.24
98.59
41.99
33.24
CN
NH
92
f1 (ppm)


7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.38
6.56
6.56
6.55
6.55
6.54
6.54
6.53
6.52
6.51
4.22
3.06
3.05
2.19
2.18
2.16
2.14
2.12
1.87
1.85
1.85
1.84
1.83
1.81
1.79
1.68
1.67
1.65
1.64
1.63
1.62
1.61
1.60
1.60
1.59
1.57
1.56
1.29
1.28
1.26
1.25
CN
N
H
93
2.07
2.09
0.99
2.00
1.11
2.02
4.03
2.06
f1 (ppm)


151.59
133.72
120.69
112.06
98.21
48.58
39.22
30.62
25.26
CN
N
H
93
f1 (ppm)


7.41
7.39
6.56
6.53
4.20
3.25
3.24
3.22
3.21
3.15
3.14
3.12
3.11
3.01
2.99
2.98
2.96
2.95
2.93
2.92
2.90
2.17
2.16
2.14
2.13
2.11
2.09
2.07
2.06
1.92
1.91
1.89
1.88
1.84
1.83
1.81
1.79
1.77
1.77
1.72
1.71
1.65
1.64
1.62
1.60
1.58
1.56
1.55
1.42
1.40
1.38
1.37
1.34
1.33
1.31
1.25
1.24
1.21
1.05
1.04
0.89
0.87
CN
N
H
Me
94
2.00
2.00
0.99
1.03
1.01
9.24
0.83
2.13
f1 (ppm)


151.63
133.70
120.69
112.05
98.15
47.70
46.75
44.36
42.46
38.63
35.19
34.78
33.55
30.91
28.49
23.77
22.61
19.89
14.88
CN
N
H
Me
94
f1 (ppm)