Supporting Information

Catalytic Diverse Radical-Mediated 1,2-Cyanofunctionalization of Unactivated Alkenes via Synergistic Remote Cyano Migration and Protected Strategies

Na Wang, Lei Li, Zhong-Liang Li, Ning-Yuan Yang, Zhen Guo*, Hong-Xia Zhang, and Xin-Yuan Liu*

liuxy3@sustc.edu.cn; guozhen@tyut.edu.cn

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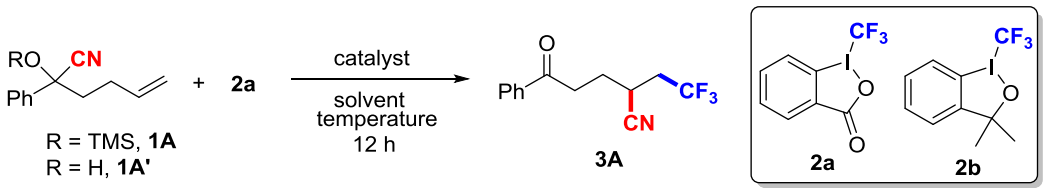
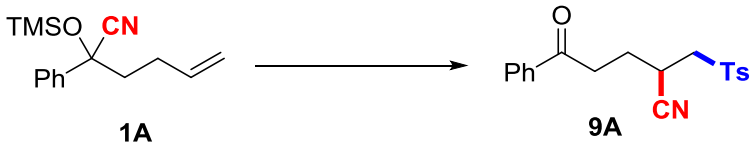
Table S1 Screening of Reaction Conditions for Trifluoromethylation Reactions:[a,b]



Entry	**2a** (X equiv)	Catalyst	Solvent	Temperature (°C)	Yield (%)
1	1.5	CuBr	EtOAc	60	58
2	1.5	CuCl	EtOAc	60	50
3	1.5	DBN	EtOAc	60	55
4	1.5	CuI	EtOAc	60	61
5	1.5	CuI	DMF	60	53
6	**1.5**	**CuI**	**CH_3CN**	**60**	**80(75)**[c]
7	1.5	CuI	CH_3CN	25	0
8	1.5	CuI	CH_3CN	80	63
9	1.5	CuI	CH_3CN	100	55
10	1.2	CuI	CH_3CN	60	50
11	2.0	CuI	CH_3CN	60	79
12[d]	1.5	CuI	CH_3CN	60	trace
13[e]	1.5	CuI	CH_3CN	60	78

[a]Reaction Conditions: **1A** (0.10 mmol), catalyst (20 mol%), **2a** in 1 mL solvent, under argon for 12 h. [b]Yield based on ^1H NMR spectroscopy with CH_2Br_2 as internal standard. [c]Isolated yield in parenthesis. [d]**2b** was used in place of **2a**. [e]TMS-removal **1A'** was employed as the substrate.

Table S2. Screening of Reaction Conditions for 1,2-Cyanosulfonylation.[a,b]



1A **9A**

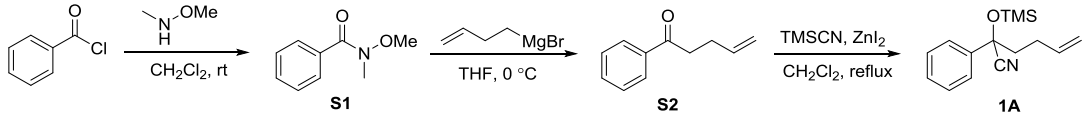
Entry	Ts source (X equiv)	Catalyst /Oxidant (Y equiv)	Solvent	T (°C)	Time	Blue LED	Yield
1	*p*-tolSO_2H (3.0)	$K_2S_2O_8$ (2.0)	EtOAc	80	12 h	No	trace
3	*p*-tolSO_2H (3.0)	$Na_2S_2O_8$ (2.0)	EtOAc	80	12 h	No	trace
4	$TsNHNH_2$ (3.0)	$Na_2S_2O_8$ (2.0)	EtOAc	80	12 h	No	trace
5	$TsNHNH_2$ (3.0)	$K_2S_2O_8$ (2.0)	EtOAc	80	12 h	No	trace
6[c]	TsCl (1.5)	$[Ir(ppy)_2(dtbbpy)]PF_6$ (0.005)	EtOAc	25	5 h	yes	82%

[a]Reaction conditions: **1A** (0.10 mmol), solvent (1 mL). [b]Isolated yield. [c]$Na_2HPO_4 \cdot 12H_2O$ (2.0 equiv) was added. [d]KOAc (2.0 equiv) was added. [e]Isolated yield in parenthesis.

General information.

All reactions were carried out under argon using Schlenk techniques. Reagents were purchased at the commercial quality and used without further purification. 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). Visualization on TLC was achieved by use of UV light (254 nm), $KMnO_4$ or iodine stain. NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400/500 MHz for ^1H NMR, 100/125 MHz for ^{13}C NMR and 376 MHz for ^{19}F NMR 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, quartet; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). ^{19}F NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer ($CFCl_3$ as an external reference (0 ppm)). ^{31}P NMR spectra were recorded on a Bruker DPX 400/500 MHz spectrometer. Mass spectrometric data were obtained using Bruker Apex IV RTMS.

Experimental procedure for synthesis of substrates

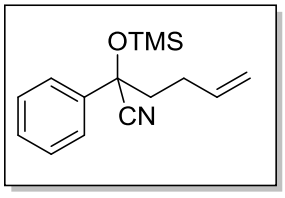


To a solution of *N*,*O*-dimethylhydroxylamine hydrochloride (2.93 g, 30 mmol) in anhydrous CH_2Cl_2 (40 mL) were added Et_3N (8.4 mL, 60 mmol) and benzoyl chloride (3.5 mL, 30 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1 h and quenched with saturated $NaHCO_3$ (20 mL). Dichloromethane (50 mL) was added to extract the product from the aqueous layer. The organic layer was washed with HCl (1M, 20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product **S1** (5.0 g).

To a solution of prepared Grignard reagent (1M, 45 mL) in THF was added **S1** (5.0 g, 30 mmol) in THF (10 mL) at 0 °C dropwisely. The reaction mixture was stirred at room temperature for 2 h and quenched with saturated NH_4Cl (20 mL). Diethyl ether was used to extract the product from the aqueous layer (3 × 50 mL). The combined organic layer was washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product **S2** (3.9 g, 80%).

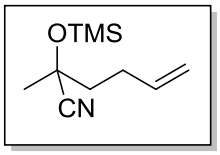
A solution of **S2** (3.9 g, 24 mmol), TMSCN (3.4 mL, 26 mmol) and ZnI_2 (0.41 g, 1.3 mmol) in anhydrous CH_2Cl_2 (40 mL) were heated to reflux for 4 h and cooled down to room temperature. The solvent was removed to afford the crude product, which was purified by flash column chromatography (PE:EtOAc = 100:1) to afford the product **1A** (4.8 g, 77%), as a colorless oil.[1]

2-phenyl-2-((trimethylsilyl)oxy)hex-5-enenitrile (1A)



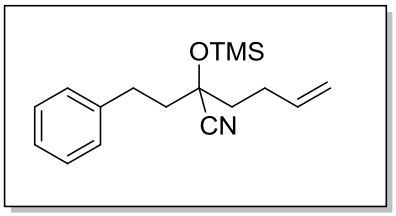
1A: (4.8 g, PE:EtOAc = 100:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 - 7.50 (m, 2H), 7.44 - 7.32 (m, 3H), 5.83 - 5.71 (m, 1H), 5.06 - 4.93 (m, 2H), 2.33 - 2.21 (m, 1H), 2.17 - 1.96 (m, 3H), 0.15 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.82, 136.64, 128.67, 128.54, 125.00, 120.68, 115.29, 75.19, 45.03, 28.58, 0.87.
HRMS (ESI) m/z calcd. for $C_{15}H_{22}ONSi$ $[M+H]^+$ 260.1465, found 260.1463.

2-methyl-2-((trimethylsilyl)oxy)hex-5-enenitrile (1B)



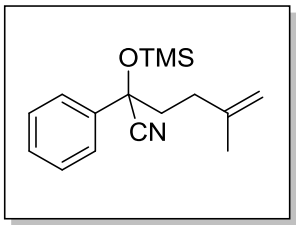
1B: (0.3 g, PE:EtOAc = 50:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 - 5.74 (m, 1H), 5.10 - 4.96 (m, 2H), 2.34 - 2.16 (m, 2H), 1.87 - 1.73 (m, 2H), 1.58 (s, 3H), 0.23 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.65, 121.50, 115.07, 68.94, 42.20, 28.69, 28.30, 0.97.
HRMS (ESI) m/z calcd. for $C_{10}H_{20}ONSi$ $[M+H]^+$ 198.1309, found 198.1307.

2-phenethyl-2-((trimethylsilyl)oxy)hex-5-enenitrile (1C)



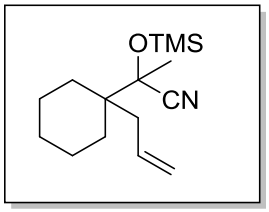
1C: (0.5 g, PE:EtOAc = 100:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 - 7.35 (m, 2H), 7.32 - 7.27 (m, 3H), 5.99 - 5.86 (m, 1H), 5.24 - 5.10 (m, 2H), 2.98 - 2.82 (m, 2H), 2.44 - 2.29 (m, 2H), 2.17 - 2.10 (m, 2H), 2.02 - 1.95 (m, 2H), 0.38 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 140.46, 136.61, 128.41, 128.16, 126.06, 120.94, 115.38, 72.39, 42.73, 40.01, 30.31, 28.14, 1.18.
HRMS (ESI) m/z calcd. for $C_{17}H_{25}ONNaSi$ $[M+Na]^+$ 310.1598, found 310.1588.

5-methyl-2-phenyl-2-((trimethylsilyl)oxy)hex-5-enenitrile (1D)



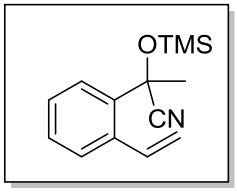
1D: (0.4 g, PE:EtOAc = 100:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 - 7.52 (m, 2H), 7.44 - 7.33 (m, 3H), 4.72 (s, 1H), 4.67 (s, 1H), 2.28 - 2.14 (m, 2H), 2.11 - 2.01 (m, 2H), 1.71 (s, 3H), 0.16 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.97, 140.81, 128.62, 128.50, 124.95, 120.59,110.24, 75.28, 44.11, 32.23, 22.60, 0.82.
HRMS (ESI) m/z calcd. for $C_{16}H_{24}ONSi$ $[M+H]^+$ 274.1622, found 274.1616.

2-(1-allylcyclohexyl)-2-((trimethylsilyl)oxy)propanenitrile (1E)



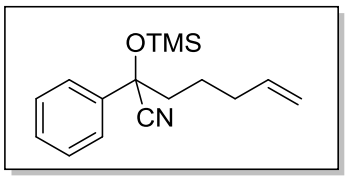
1E: (0.2 g, PE:EtOAc = 100:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 - 5.86 (m, 1H), 5.07 - 4.96 (m, 2H), 2.42 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.25 (dd, *J* = 15.6, 7.2 Hz, 1H), 1.78 - 1.58 (m, 4H), 1.55 (s, 3H), 1.53 - 1.34 (m, 5H), 1.21 - 1.08 (m, 1H), 0.23 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 135.86, 122.04, 116.08, 78.11, 43.46, 34.75, 30.61, 29.54, 25.37, 24.00, 21.54, 21.39, 1.18.
HRMS (ESI) m/z calcd. for $C_{14}H_{19}ONNaSi$ $[M+Na]^+$ 268.1128, found 268.1121.

2-((trimethylsilyl)oxy)-2-(2-vinylphenyl)acetonitrile (1F)



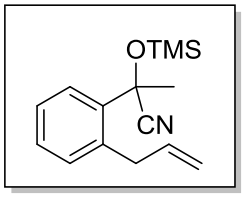
1F: (0.5 g, PE:EtOAc = 50:1, colorless oil) ^{1}H NMR (500 MHz, Chloroform-*d*) δ7.64 – 7.71 (m, 1H), 7.58 – 7.52 (m, 1H), 7.51 – 7.41 (m, 1H), 7.38 – 7.28 (m, 1H), 7.33 – 7.28 (m, 2H), 5.63 (dt, *J* = 17.3, 1.6 Hz, 1H), 5.36 (dt, *J* = 11.0, 1.6 Hz, 1H), 1.98 (s,3H), 0.18 (s, 9H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 137.20 , 136.45 , 135.61 , 129.05, 128.34 , 127.81 , 125.49 , 121.53 , 116.56 , 72.57 , 31.57 , 1.02 .
HRMS (ESI) m/z calcd. for $C_{14}H_{20}ONSi[M+H]^+$ 246.1309 , found 246.1304 .

2-phenyl-2-((trimethylsilyl)oxy)hept-6-enenitrile (1G)



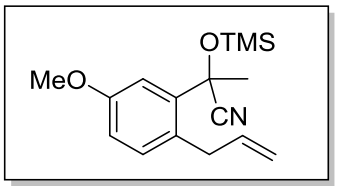
1G: (0.5 g, PE:EtOAc = 100:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.42 - 7.33 (m, 3H), 5.79 - 5.68 (m, 1H), 5.02 - 4.92 (m, 2H), 2.09 - 1.98 (m, 3H), 1.96 - 1.87 (m, 1H), 1.67 - 1.57 (m, 1H), 1.50 - 1.38 (m, 1H), 0.13 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.05, 137.86, 128.62, 128.54, 125.05, 120.89, 115.16, 75.54, 45.40, 33.07, 23.52, 0.93.
HRMS (ESI) m/z calcd. for $C_{16}H_{24}ONSi$ $[M+H]^+$ 274.1622, found 274.1618.

2-(2-allylphenyl)-2-((trimethylsilyl)oxy)propanenitrile (1H)



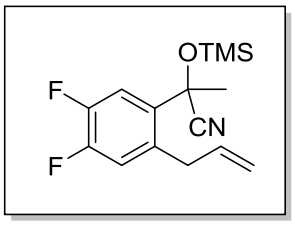
1H: (0.5 g, PE:EtOAc = 50:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 - 7.60 (m, 1H), 7.36 - 7.21 (m, 3H), 6.09 - 5.93 (m, 1H), 5.19 - 5.03 (m, 2H), 3.87 - 3.67 (m, 2H), 1.99 (s, 3H), 0.24 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.31, 137.50, 137.36, 132.09, 128.79, 126.35, 125.55, 121.88, 116.41, 72.02, 36.71, 31.52, 1.21.
HRMS (ESI) m/z calcd. for $C_{15}H_{21}ONNaSi$ $[M+Na]^+$ 282.1285, found 282.1278.

2-(2-allyl-5-methoxyphenyl)-2-((trimethylsilyl)oxy)propanenitrile (1I)



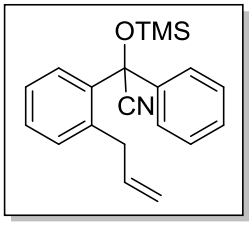
1I: (0.6 g, PE:EtOAc = 30:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 - 7.17 (m, 2H), 6.85 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.02 - 5.92 (m, 1H), 5.12 - 5.01 (m, 2H), 3.82 (s, 3H), 3.70 (dd, *J* = 16.0, 6.0 Hz, 1H), 3.61 (dd, *J* = 16.5, 6.0 Hz, 1H), 1.94 (s, 3H), 0.22 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 157.76, 139.56, 137.66, 133.11, 128.90, 121.72, 116.03, 113.51, 111.68, 71.64, 55.26, 35.89, 31.46, 1.16.
HRMS (ESI) m/z calcd. for $C_{16}H_{24}O_2NSi$ $[M+H]^+$ 290.1571, found 290.1565.

2-(2-allyl-4,5-difluorophenyl)-2-((trimethylsilyl)oxy)propanenitrile (1J)



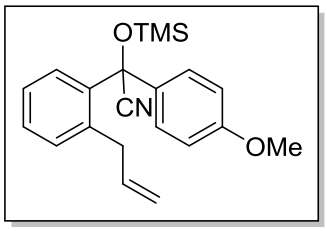
1J: (0.5 g, PE:EtOAc = 50:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 12.0, 8.0 Hz, 1H), 7.09 (dd, *J* = 11.4, 8.1 Hz, 1H), 5.93 (ddt, *J* = 16.6, 10.2, 6.4 Hz, 1H), 5.14 (ddd, *J* = 18.5, 13.6, 1.4 Hz, 2H), 3.66 (qd, *J* = 16.3, 6.3 Hz, 2H), 1.92 (s, 3H), 0.25 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 149.85 (dd, *J* = 221.7, 12.4 Hz), 147.88 (dd, *J* = 218.9, 12.3 Hz), 136.01, 135.45 (t, *J* = 3.9 Hz), 134.34 (dd, *J* = 5.3, 4.0 Hz), 121.11, 120.33 (d, *J* = 17.4 Hz), 117.35, 114.91 (d, *J* = 19.6 Hz), 70.18, 35.95, 31.16, 1.09.
HRMS (ESI) m/z calcd. for $C_{15}H_{20}ONF_2Si$ $[M+H]^+$ 296.1277, found 296.1270.

2-(2-allylphenyl)-2-phenyl-2-((trimethylsilyl)oxy)acetonitrile (1K)



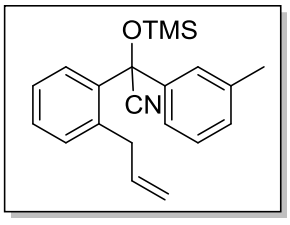
1K: (0.3 g, PE:EtOAc = 50:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.47 - 7.42 (m, 2H), 7.40 - 7.31 (m, 5H), 7.26 (dd, *J* = 7.2, 1.6 Hz, 1H), 5.46 - 5.34 (m, 1H), 4.89 - 4.79 (m, 2H), 3.30 - 3.14 (m, 2H), 0.15 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.48, 138.33, 137.92, 136.03, 131.54, 129.16, 128.69, 128.59, 127.05, 126.33, 125.95, 120.30, 116.02, 76.45, 36.58, 0.87.
HRMS (ESI) m/z calcd. for $C_{20}H_{23}ONNaSi$ $[M+Na]^+$ 344.1441, found 344.1432.

2-(2-allylphenyl)-2-(4-methoxyphenyl)-2-((trimethylsilyl)oxy)acetonitrile (1M)

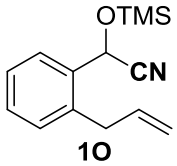


1M: (0.3 g, PE:EtOAc = 50:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.37 - 7.28 (m, 4H), 7.24 (d, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 5.50 - 5.40 (m, 1H), 4.91 - 4.82 (m, 2H), 3.80 (s, 3H), 3.27 (dd, *J* = 15.5, 6.5 Hz, 1H), 3.17 (dd, *J* = 15.5, 7.0 Hz, 1H), 0.12 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.78, 138.27, 138.08, 136.18, 133.51, 131.41, 129.04, 127.75, 126.89, 125.91, 120.46, 116.08, 113.85, 75.99, 55.24, 36.59, 0.89.
HRMS (ESI) m/z calcd. for $C_{21}H_{25}O_2NNaSi$ $[M+Na]^+$ 374.1547, found 374.1547.

2-(2-allylphenyl)-2-(m-tolyl)-2-((trimethylsilyl)oxy)acetonitrile (1N)

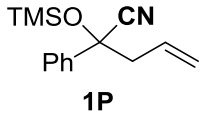


1N: (0.5 g, PE:EtOAc = 50:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 - 7.87 (m, 2H), 7.40 - 7.21 (m, 5H), 7.14 - 7.08 (m, 1H), 5.41 - 5.29 (s, 1H), 4.89 - 4.77 (m, 2H), 3.31 - 3.13 (m, 2H), 1.98 (s, 3H), 0.14 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.80, 151.05, 148.56, 148.44, 136.49, 136.42, 136.40, 136.36, 133.17, 133.13, 120.02, 119.85, 116.92, 116.47, 116.28, 78.84, 36.50 , 23.63.
HRMS (ESI) m/z calcd. for $C_{21}H_{25}ONNaSi$ $[M+Na]^+$ 358.1598, found 358.1585.



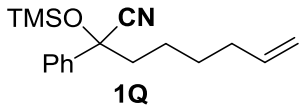
1O

1O: (0.4 g, PE:EtOAc = 50:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 1H), 7.35 – 7.24 (m, 3H), 6.10 – 5.93 (m, 1H), 5.68 (s, 1H), 5.17 (dd, *J* = 10.1, 1.2 Hz, 1H), 5.06 (dd, *J* = 17.1, 1.3 Hz, 1H), 3.55 (d, *J* = 5.9 Hz, 2H), 0.24 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.96, 136.10, 134.42, 130.54, 129.63, 127.35, 127.17, 119.14, 116.71, 61.21, 36.59, -0.17.
HRMS (ESI) m/z calcd. for $C_{14}H_{19}ONNaSi$ $[M+Na]^+$ 268.1128, found 268.1125.



1P

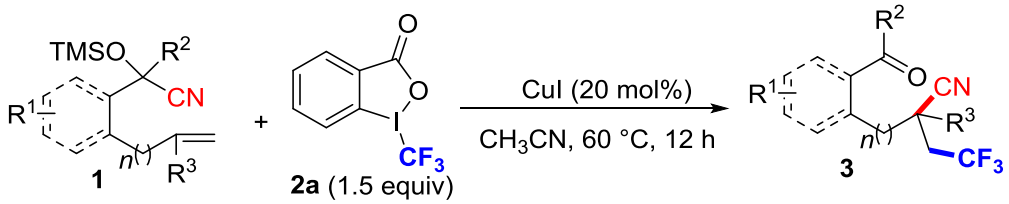
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.50 (m, 2H), 7.47 – 7.33 (m, 3H), 5.74 (ddt, *J* = 17.3, 10.3, 7.2 Hz, 1H), 5.26 – 5.11 (m, 2H), 2.81 (dd, *J* = 13.8, 7.0 Hz, 1H), 2.67 (dd, *J* = 13.8, 7.3 Hz, 1H), 0.17 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.49, 130.90, 128.76, 128.53, 125.21, 120.45, 120.41, 75.40, 50.24, 0.96.
HRMS (ESI) m/z calcd. for $C_{14}H_{19}ONNaSi$ $[M+Na]^+$ 268.1128, found 268.1125.



1Q

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.47 (m, 2H), 7.40 (tdd, *J* = 6.9, 4.6, 2.2 Hz, 3H), 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.08 – 4.89 (m, 2H), 2.11 – 1.91 (m, 4H), 1.61 – 1.52 (m, 1H), 1.47 – 1.35 (m, 3H), 0.16 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.14, 138.41, 128.62, 128.54, 125.08, 120.93, 114.64, 75.61, 45.87, 33.45, 28.41, 23.81, 0.96.
HRMS (ESI) m/z calcd. for $C_{17}H_{25}ONNaSi$ $[M+Na]^+$ 310.1598, found 310.1594.

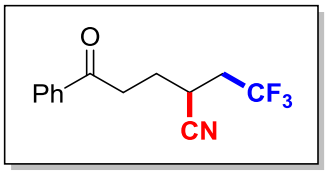
General procedure for 1,2-cyanotrifluoromethylation of alkenes 1



In an oven-dried 25 mL Schlenk tube were added **1** (0.20 mmol), CuI (8 mg, 0.04 mmol) and Togni's reagent **2a** (95 mg, 0.30 mmol). The tube was vacuumed and back-filled with argon three times and then added with CH_3CN (2 mL). The reaction mixture was heated to 60 °C for 12 h and cooled down to room temperature. EtOAc

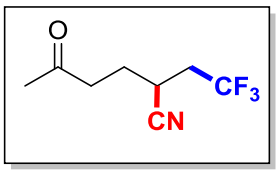
(30 mL) was added and the organic layer was washed with saturated $NaHCO_3$ solution (5 mL) and brine (5 mL) sequentially, dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **3**.

5-oxo-5-phenyl-2-(2,2,2-trifluoroethyl)pentanenitrile (3A)



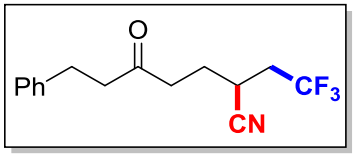
3A: (38 mg, PE:EtOAc = 20:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 3.28 (t, *J* = 7.0 Hz, 2H), 3.18 - 3.11 (m, 1H), 2.65 - 2.54 (m, 1H), 2.49 - 2.38 (m, 1H), 2.31 - 2.22 (m, 1H), 2.08 - 1.99 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 197.63, 136.12, 133.68, 128.78, 127.98, 125.01 (q, *J* = 275.6 Hz), 119.37, 36.72 (q, *J* = 29.9 Hz), 35.00, 26.31, 25.04 (q, *J* = 3.1 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.59.
HRMS (ESI) m/z calcd. for $C_8H_{11}ONF_3[M+H]^+$ 256.0944 , found 256.0950 .

5-oxo-2-(2,2,2-trifluoroethyl)hexanenitrile (3B)



3B: (28 mg, PE:EtOAc = 30:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.06 - 2.99 (m, 1H), 2.79 - 2.68 (m, 2H), 2.59 - 2.46 (m, 1H), 2.41 - 2.30 (m, 1H), 2.20 (s, 3H), 2.09 - 2.00 (m, 1H), 1.87 - 1.78 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 206.21, 124.91 (q, *J* = 275.6 Hz), 119.21, 39.80, 36.61 (q, *J* = 29.9 Hz), 30.01, 25.79, 24.77 (q, *J* = 3.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.83.
HRMS (ESI) m/z calcd. for $C_8H_{11}ONF_3$ $[M+H]^+$ 194.0787 , found 194.0784.

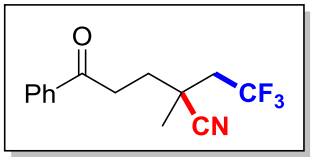
5-oxo-7-phenyl-2-(2,2,2-trifluoroethyl)heptanenitrile (3C)



3C: (44 mg, PE:EtOAc = 30:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 - 7.16 (m, 3H), 3.02 - 2.95 (m, 1H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.66 (t, *J* = 7.0 Hz, 2H), 2.55 - 2.43 (m, 1H), 2.38 - 2.27 (m, 1H), 2.08 - 2.00 (m, 1H), 1.86 - 1.77 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 207.67, 140.44, 128.57, 128.24, 126.29, 124.89 (q, *J* =

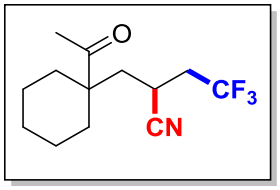
275.6 Hz), 119.19, 44.26, 39.19, 36.55 (q, *J* = 29.9 Hz), 29.66, 25.73, 24.77 (q, *J* = 2.9 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.81.
HRMS (ESI) m/z calcd. for $C_{15}H_{17}ONF_3$ $[M+H]^+$ 284.1257 , found 284.1249.

2-methyl-5-oxo-5-phenyl-2-(tosylmethyl)pentanenitrile (3D)



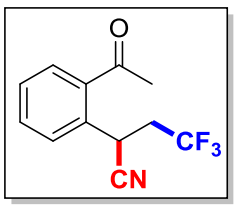
1C: (46 mg, PE:EtOAc = 30:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 - 7.96 (m, 2H), 7.62 - 7.57 (m, 1H), 7.51 - 7.46 (m, 2H), 3.24 (t, *J* = 8.0 Hz, 2H), 2.63 - 2.52 (m, 1H), 2.44 - 2.34 (m, 1H), 2.25 - 2.18 (m, 1H), 2.15 - 2.06 (m, 1H), 1.54 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 197.45, 136.17, 133.58, 128.75, 127.99, 124.89 (q, *J* = 276.6 Hz), 121.63, 42.23 (q, *J* = 28.5 Hz), 33.80, 33.60, 32.69 (q, *J* = 2.0 Hz), 23.84.
^{19}F NMR (376 MHz, $CDCl_3$) δ -60.76.
HRMS (ESI) m/z calcd. for $C_{14}H_{15}ONF_3$ $[M+H]^+$ 270.1100 , found 270.1091.

2-((1-acetylcyclohexyl)methyl)-4,4,4-trifluorobutanenitrile (3E)



3E: (30 mg, PE:EtOAc = 30:1, colorless oil)^{1}H NMR (500 MHz, $CDCl_3$) δ 2.79 - 2.71 (m, 1H), 2.58 - 2.45 (m, 1H), 2.40 - 2.29 (m, 1H), 2.21 (s, 3H), 2.16 (dd, J = 14.5, 10.0 Hz, 1H), 2.05 - 1.97 (m, 2H), 1.77 (dd, J = 14.5, 2.5 Hz, 1H), 1.62 - 1.57 (m, 1H), 1.54 - 1.38 (m, 6H), 1.37 - 1.30 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 212.19, 124.87 (q, *J* = 275.88 Hz), 119.97, 51.55, 38.30, 37.66 (q, *J* = 29.5 Hz), 32.97, 32.38, 25.66, 25.45, 22.25, 22.19, 20.86 (q, *J* = 3.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.40.
HRMS (ESI) m/z calcd. for $C_{13}H_{19}ONF_3$ $[M+H]^+$ 262.1413 , found 262.1405 .

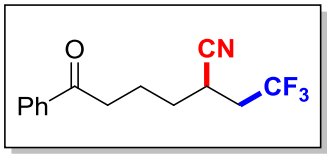
2-(2-acetylphenyl)-4,4,4-trifluorobutanenitrile (3F)



3F: (22 mg, PE:EtOAc = 100:1, pale yellow oil)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.5

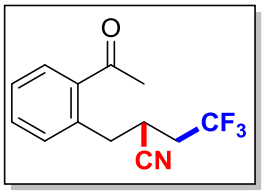
Hz, 1H), 5.14 (t, *J* = 7.0 Hz, 1H), 2.77 - 2.70 (m, 2H), 2.67 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 200.85, 134.88, 133.90, 133.32, 131.06, 130.04, 129.11, 124.81 (q, *J* = 276.4 Hz), 119.18, 38.99 (q, *J* = 29.4 Hz), 29.02, 28.53 (q, *J* = 3.1 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.70.
HRMS (ESI) m/z calcd. for $C_{12}H_{11}ONF_3[M+H]^+$ 242.0787 , found 242.0794 .

6-oxo-6-phenyl-2-(2,2,2-trifluoroethyl)hexanenitrile (3G)



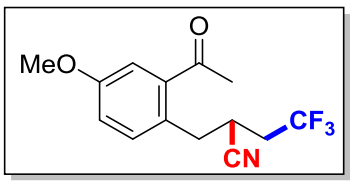
3G: (42 mg, PE:EtOAc = 100:1, pale yellow oil)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 3.08 (t, *J* = 7.0 Hz, 2H), 2.97 - 2.90 (m, 1H), 2.62 - 2.50 (m, 1H), 2.44 - 2.33 (m, 1H), 2.07 - 1.99 (m, 1H), 1.97 - 1.89 (m, 1H), 1.85 - 1.75 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 198.72, 136.51, 133.31, 128.67, 127.91, 125.06 (q, *J* = 275.6 Hz), 119.51, 37.12, 36.24 (q, *J* = 29.6 Hz), 31.43, 25.56 (q, *J* = 3.0 Hz), 20.98.
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.89.
HRMS (ESI) m/z calcd. for $C_{14}H_{15}ONF3[M+H]^+$ 270.1100 , found 270.1093 .

2-(2-acetylbenzyl)-4,4,4-trifluorobutanenitrile (3H)



3H: (36 mg, PE:EtOAc = 100:1, colorless oil)^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.55 (td, *J* = 7.6, 1.2 Hz, 1H), 7.48 - 7.38 (m, 2H), 3.44 - 3.32 (m, 2H), 3.03 - 2.94 (m, 1H), 2.66 - 2.49 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.25, 136.57, 136.18, 132.90, 132.72, 131.07, 128.15, 125.16 (q, *J* = 275.6 Hz), 119.62, 37.33, 36.36 (q, *J* = 29.7 Hz), 29.14, 27.41 (q, *J* = 2.8 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.45.
HRMS (ESI) m/z calcd. for $C_{13}H_{13}ONF_3$ $[M+H]^+$ 256.0944 , found 256.0937 .

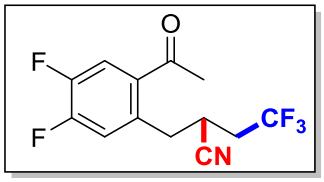
2-(2-acetyl-4-methoxybenzyl)-4,4,4-trifluorobutanenitrile (3I)



3I: (51 mg, PE:EtOAc = 100:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.05 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.86 (s, 3H),

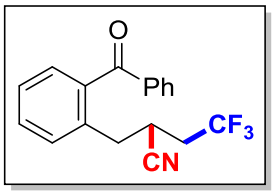
3.39 - 3.30 (m, 1H), 3.26 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.93 (dd, *J* = 12.8, 10.0 Hz , 1H), 2.61 (s, 3H), 2.58 - 2.44 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 201.06, 158.96, 137.21, 133.93, 128.25, 125.20 (q, *J* = 275.8 Hz), 119.80, 117.58, 116.82, 55.52, 36.56, 36.26 (q, *J* = 29.6 Hz), 29.08, 27.60 (q, *J* = 2.6 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.48.
HRMS (ESI) m/z calcd. for $C_{14}H_{15}O_2NF_3$ $[M+H]^+$ 286.1049 , found 286.1041.

2-(2-acetyl-4,5-difluorobenzyl)-4,4,4-trifluorobutanenitrile (3J)



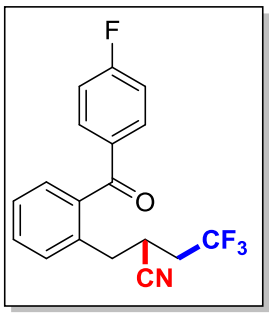
3J: (49 mg, PE:EtOAc = 100:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 10.5, 8.0 Hz, 1H), 7.24 (dd, *J* = 10.5, 8.0 Hz, 1H), 3.39 - 3.31 (m, 2H), 2.94 - 2.86 (m, 1H), 2.65 - 2.47 (m, 5H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 198.62, 152.07 (d, *J* = 257.1, 12.4 Hz), 149.09 (d, *J* = 250.3, 12.5 Hz), 134.74 (dd, *J* = 6.3, 4.0 Hz), 132.66 (t, *J* = 3.8 Hz), 125.02 (q, *J* = 275.6 Hz), 121.92 (d, *J* = 17.4 Hz), 120.48 (dd, *J* = 17.8, 1.8 Hz), 119.15, 36.59, 36.33 (d, *J* = 29.9 Hz), 29.02, 27.27.
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.43 (s, 3F), -129.09 (d, *J* = 21.8 Hz, 1F), -136.37 (d, *J* = 21.8 Hz, 1F).
HRMS (ESI) m/z calcd. for $C_{13}H_{11}ONF_5[M+H]^+$ 292.0755 , found 292.0746.

2-(2-benzoylbenzyl)-4,4,4-trifluorobutanenitrile (3K)



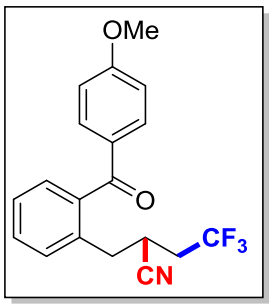
3K: (41 mg, PE:EtOAc = 100:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.53 - 7.43 (m, 4H), 7.40 (t, *J* = 7.5 Hz, 1H), 3.54 - 3.46 (m, 1H), 3.12 (dd, *J* = 13.5, 5.5 Hz, 1H), 3.03 (dd, *J* = 13.5, 10.0 Hz, 1H), 2.63 - 2.41 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 197.99, 137.62, 135.92, 133.40, 131.75, 131.46, 130.75, 130.32, 128.50, 127.17, 125.11 (q, *J* = 275.8 Hz), 119.49, 36.104 (q, *J* = 29.9 Hz), 36.097, 27.87 (q, *J* = 2.8 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.43.
HRMS (ESI) m/z calcd. for $C_{18}H_{15}ONF_3[M+H]^+$ 318.1100 , found 318.1109 .

4,4,4-trifluoro-2-(2-(4-fluorobenzoyl)benzyl)butanenitrile (3L)



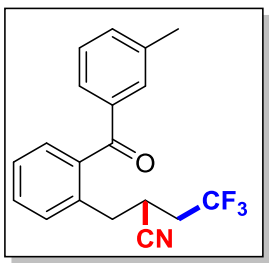
3L: (54 mg, PE:EtOAc = 100:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 - 7.78 (m, 2H), 7.59 - 7.49 (m, 2H), 7.45 - 7.37 (m, 2H), 7.19 - 7.11 (m, 2H), 3.53 - 3.43 (m, 1H), 3.13 - 2.98 (m, 2H), 2.63 - 2.40 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 196.32, 165.89 (d, *J* = 268.88 Hz), 137.42, 135.86, 133.88 (d, *J* = 2.9 Hz), 133.01 (d, *J* = 9.4 Hz), 131.81, 131.52, 130.42, 127.21, 125.08 (q, *J* = 275.8 Hz), 119.42, 115.70 (d, *J* = 21.9 Hz), 36.08 (q, *J* = 29.9 Hz), 35.97, 27.87 (q, *J* = 2.8 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.47 (s, 3F), -104.16 (s, 1F).
HRMS (ESI) m/z calcd. for $C_{18}H_{14}ONF_4[M+H]^+$ 336.1006 , found 336.0995.

4,4,4-trifluoro-2-(2-(4-methoxybenzoyl)benzyl)butanenitrile (3M)



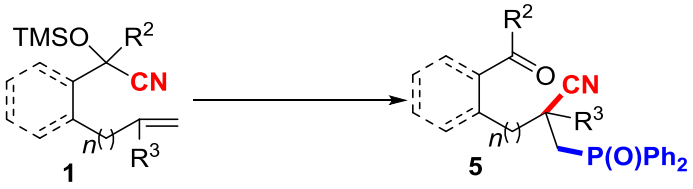
3M: (57 mg, PE:EtOAc = 100:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 9.0 Hz, 2H), 7.55 - 7.46 (m, 2H), 7.43 - 7.36 (m, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 3.88 (s, 3H), 3.50 - 3.42 (m, 1H), 3.08 - 2.97 (m, 2H), 2.58 - 2.39 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 196.50, 163.92, 138.36, 135.24, 132.74, 131.45, 130.87, 130.18, 129.92, 127.06, 125.09 (q, *J* = 275.8 Hz), 119.50, 113.75, 55.52, 35.96 (q, *J* = 29.8 Hz), 35.90, 27.75 (q, *J* = 2.8 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.46 (s).
HRMS (ESI) m/z calcd. for $C_{18}H_{14}ONF_4[M+H]^+$ 336.1006 , found 336.0995.

4,4,4-trifluoro-2-(2-(3-methylbenzoyl)benzyl)butanenitrile (3N)



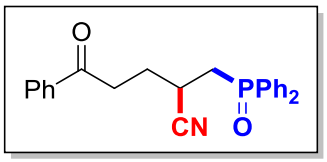
3N: (61 mg, PE:EtOAc = 100:1, pale yellow oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.44 - 7.32 (m, 3H), 7.32 - 7.22 (m, 3H), 3.61 - 3.54 (m, 1H), 3.33 (dd, *J* = 13.0, 5.0 Hz, 1H), 3.09 (dd, *J* = 13.0, 10.0 Hz, 1H), 2.67 - 2.50 (m, 2H), 2.38 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 200.53, 138.69, 137.84, 137.78, 136.73, 132.40, 132.22, 131.37, 131.19, 129.82, 127.59, 125.39, 125.16 (q, *J* = 275.8 Hz), 119.57, 36.65, 36.23 (q, *J* = 29.6 Hz), 27.65 (q, *J* = 2.6 Hz), 20.36.
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.32 (s).
HRMS (ESI) m/z calcd. for $C_{19}H_{17}ONF_3$ $[M+H]^+$ 332.1257 , found 332.1246.

Experimental procedure for 1,2-cyanophosphonylation of alkene of 1.



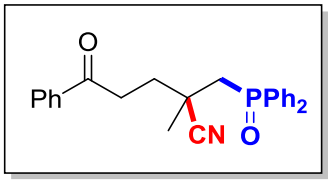
In an oven-dried 25 mL Schlenk tube were added **1** (0.20 mmol), $AgNO_3$ (14 mg, 0.04 mmol) and $H(O)PPh_2$ **4** (80 mg, 0.40 mmol). The tube was vacuumed and back-filled with argon three times and then added with DMF (2 mL). The reaction mixture was heated to 80 °C for 12 h and cooled down to room temperature. Diethyl ether (30 mL) was added and the organic layer was washed with water (3 × 8 mL), dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **5**.

2-((diphenylphosphoryl)methyl)-5-oxo-5-phenylpentanenitrile (5A)



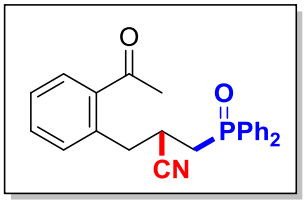
5A: (58 mg, PE:EtOAc = 1:1, white solid) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.81 – 7.76 (m, 4H), 7.64 – 7.45 (m, 9H), 3.35 – 3.11 (m, 3H), 2.82 – 2.76 (m, 1H), 2.62 – 2.55 (m, 1H), 2.35 – 2.26 (m, 1H), 2.15 – 2.07 (m, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.74, 136.32 , 133.42 , 132.55 (d, *J* = 2.9 Hz), 132.43 (d, *J* = 2.8 Hz), 132.27 (d, *J* = 101.58 Hz),131.08 (d, *J* = 9.5 Hz), 130.89 (d, *J* = 100.51 Hz),130.58 (d, *J* = 9.5 Hz), 129.04 (d, *J* = 4.0 Hz), 128.94 (d, *J* = 4.0 Hz), 128.69 , 128.02 , 120.49 (d, *J* = 9.1 Hz), 35.61 , 32.90 (d, *J* = 69.4 Hz), 28.09 (d, *J* = 7.1 Hz), 24.92 (d, *J* = 2.8 Hz).
^{31}P NMR (202 MHz, Chloroform-*d*) δ 28.44.
HRMS (ESI) m/z calcd. for $C_{24}H_{23}O_2NP[M+H]^+$ 388.1461 , found 388.1471.

2-((diphenylphosphoryl)methyl)-2-methyl-5-oxo-5-phenylpentanenitrile (5D)



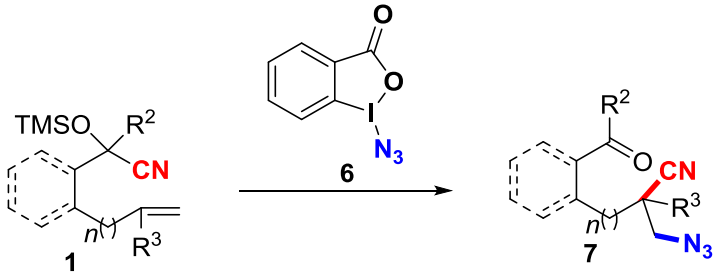
5D: (54 mg, PE:EtOAc = 1:1, white solid) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.88 – 7.76 (m, 4H), 7.62 – 7.44 (m, 9H), 3.17 (t, *J* = 7.8 Hz, 2H), 2.76 (d, *J* = 9.8 Hz, 1H), 2.68 (d, *J* = 11.5 Hz, 1H), 2.65 (d, *J* = 11.5 Hz, 1H), 2.40 – 2.30 (m, 1H), 2.25 – 2.15 (m, 1H), 1.59 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.97, 136.41 , 133.37 133.27, (d, *J* = 100.53 Hz), 132.54 (d, *J* = 100.56 Hz), 132.27 (d, *J* = 2.8 Hz), 132.17 (d, *J* = 2.9 Hz), 130.87 (d, *J* = 9.3 Hz), 130.57 (d, *J* = 9.3 Hz), 128.94 (d, *J* = 5.2 Hz), 128.85 (d, *J* = 5.3 Hz), 128.68 , 128.07 , 122.58 (d, *J* = 9.2 Hz), 38.43 (d, *J* = 68.6 Hz), 35.00 (d, *J* = 6.8 Hz), 34.63 (d, *J* = 3.7 Hz), 34.34 , 25.62 (d, *J* = 3.8 Hz).
^{31}P NMR (202 MHz, Chloroform-*d*) δ 25.78.
HRMS (ESI) m/z calcd. for $C_{25}H_{25}O_2NP[M+H]^+$ 402.1617 , found 402.1628.

2-(2-acetylbenzyl)-3-(diphenylphosphoryl)propanenitrile (5H)



5H: (55 mg, PE:EtOAc = 1:1, white solid) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 – 7.77 (m, 5H), 7.60 – 7.45 (m, 7H), 7.41 – 7.35 (m, 2H), 3.46 – 3.37 (m, 2H), 3.29 – 3.22 (m, 1H), 2.82 – 2.64 (m, 2H), 2.59 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 201.37, 136.94, 136.82, 132.67, 132.32 (d, *J* = 2.8 Hz), 132.31, 132.24 (d, *J* = 2.8 Hz), 132.14 (d, *J* = 100.76 Hz), 131.62 (d, *J* = 100.31 Hz), 131.03 (d, *J* = 9.5 Hz), 130.81 (d, *J* = 9.4 Hz), 130.45, 128.90 (d, *J* = 7.6 Hz), 128.81 (d, *J* = 7.6 Hz), 127.72, 120.30 (d, *J* = 6.5 Hz), 38.09 (d, *J* = 9.0 Hz), 32.54 (d, *J* = 69.8 Hz), 29.41 , 27.49 (d, *J* = 3.6 Hz).
^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.31.
HRMS (ESI) m/z calcd. for $C_{24}H_{23}O_2NP[M+H]^+$ 388.1461, found 388.1471.

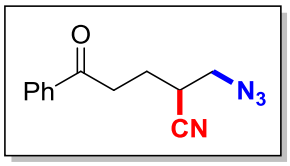
Experimental procedure for 1,2-cyanoazidation of alkene of 1



In an oven-dried 25 mL Schlenk tube were added **1** (0.20 mmol), CuI (8 mg, 0.04 mmol) and Togni's azide **6** (88 mg, 0.30 mmol). The tube was vacuumed and

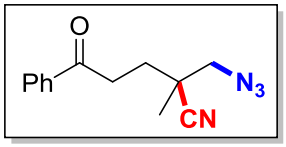
back-filled with argon three times and then added with EtOAc (2 mL). The reaction mixture was heated to 80 °C for 12 h and cooled down to room temperature. EtOAc (30 mL) was added and the organic layer was washed with saturated $NaHCO_3$ solution (5 mL) and brine (5 mL) sequentially, dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **7**.

2-(azidomethyl)-5-oxo-5-phenylpentanenitrile (7A)



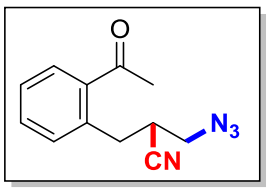
7A: (42 mg, PE:EtOAc = 15:1, white solid) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 - 7.95 (m, 2H), 7.63 - 7.58 (m, 1H), 7.52 - 7.46 (m, 2H), 3.65 - 3.57 (m, 2H), 3.30 - 3.20 (m, 2H), 3.08 - 3.00 (m, 1H), 2.24 - 2.15 (m, 1H), 2.08 - 1.99 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.88, 136.21, 133.63, 128.77, 127.99, 119.44, 52.10, 34.99, 31.63, 23.90.
HRMS (ESI) m/z calcd. for $C_{12}H_{12}ON_4Na[M+Na]^+$ 251.0903 , found 251.0908 .

2-(azidomethyl)-2-methyl-5-oxo-5-phenylpentanenitrile (7D)



7D: (30 mg, PE:EtOAc = 15:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 - 7.96 (m, 2H), 7.61 - 7.57 (m, 1H), 7.51 - 7.46 (m, 2H), 3.50 (dd, *J* = 31.00, 12.5 Hz, 2H), 3.30 - 3.14 (m, 2H), 2.21 - 2.14 (m, 1H), 2.02 - 1.95 (m, 1H), 1.43 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 197.74, 136.21, 133.48, 128.70, 127.97, 121.73, 57.93, 37.60, 33.91, 30.66, 22.21.
HRMS (ESI) m/z calcd. for $C_{13}H_{15}ON_2[M+H]^+$215.1179 , found 215.1186 .

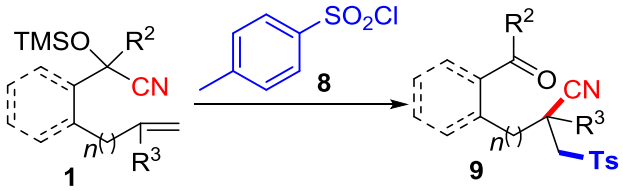
2-(2-acetylbenzyl)-3-azidopropanenitrile (7H)



7H: (29 mg, PE:EtOAc = 15:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.85 (m, 1H), 7.53 (td, *J* = 7.2, 1.2 Hz, 1H), 7.46 - 7.38 (m, 2H), 3.68 (dd, *J* = 12.4, 4.8 Hz, 1H), 3.60 (dd, *J* = 12.4, 6.0 Hz, 1H), 3.35 - 3.26 (m, 2H), 3.02 - 2.93 (m, 1H), 2.63 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.30, 136.90, 136.26, 132.87, 132.67, 130.94, 127.92, 119.77, 51.93, 35.05, 33.92, 29.20.

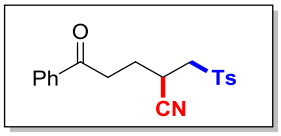
HRMS (ESI) m/z calcd. for $C_{12}H_{12}ON_4Na[M+ Na]^+$ 251.0903 , found 251.0908 .

General procedure for photoredox catalyzed 1,2-cyanosulfonylation of alkene 1



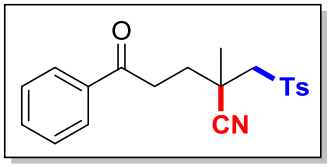
In an oven-dried 10 mL tube were added **1** (44 mg, 0.2 mmol), tosyl chloride (**8**, 57 mg, 0.3 mmol), $Na_2HPO_4·12H_2O$ (144 mg, 0.4 mmol) and $[Ir(dtbbpy)(ppy)_2]PF_6$ (1.6 mg, 0.002 mmol) sequentially. The tube was vacuumed and back-filled with argon three times and then added with anhydrous EtOAc (2 mL). The reaction mixture was irradiated with blue LED for 5 h. EtOAc (30 mL) was added and the organic layer was washed with water (5 mL) and brine (5 mL) sequentially, dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **9**.

5-oxo-5-phenyl-2-(tosylmethyl)pentanenitrile (9A)



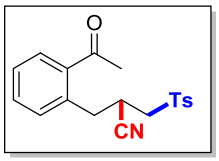
9A: (56 mg, PE:EtOAc = 3:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 - 7.92 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 3.54 - 3.46 (m 1H), 3.38 - 3.19 (m, 4H), 2.46 (s, 3H), 2.36 - 2.28 (m, 1H), 2.12 - 2.02 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 197.44, 145.85, 136.12, 135.15, 133.62, 130.30, 128.75, 128.34, 127.99, 118.79, 57.43, 35.03, 26.43, 26.04, 21.73.
HRMS (ESI) m/z calcd. for $C_{19}H_{20}O_3NS[M+H]^+$ 342.1169 , found 342.1168.

2-methyl-5-oxo-5-phenyl-2-(tosylmethyl)pentanenitrile (9D)



9D: (49 mg, PE:EtOAc = 3:1, white solid) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.43 (d, *J* = 14.5 Hz, 1H), 3.32 (d, *J* = 14.5 Hz, 1H), 3.19 (t, *J* = 7.5 Hz, 2H), 2.42 (s, 3H), 2.37 - 2.29 (m, 1H), 2.23 - 2.15 (m, 1H), 1.68 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 197.45, 145.50, 136.86, 136.14, 133.44, 130.10, 128.65, 128.00, 127.96, 121.00, 62.08, 34.51, 33.73, 33.48, 24.10, 21.60.
HRMS (ESI) m/z calcd. for $C_{14}H_{15}ONF_3$ $[M+H]^+$ 270.1100 , found 270.1091.

2-(2-acetylbenzyl)-3-tosylpropanenitrile (9H)

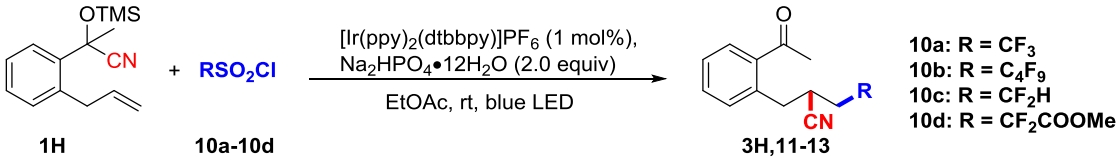


9H: (63 mg, PE:EtOAc = 2:1, colorless oil) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 3H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.35 (dd, *J* = 15.5, 8.0 Hz, 3H), 3.54 - 3.46 (m, 2H), 3.41 - 3.31 (m, 2H), 3.18 - 3.10 (m, 1H), 2.58 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 201.06, 145.45, 136.38, 135.98, 135.30, 132.77, 132.54, 130.88, 130.06, 128.31, 128.08, 118.87, 56.86, 36.82, 29.09, 28.23, 21.64.

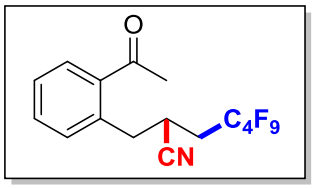
HRMS (ESI) m/z calcd. for$C_{19}H_{20}O_3NS[M+H]^+$ 342.1169 , found 342.1168 .

General procedure for photoredox catalyzed 1,2-cyanoperfluoroalkylation of alkene 1A with RSO_2Cl



In an oven-dried 10 mL tube were added **1H** (38 mg, 0.20 mmol), $Na_2HPO_4{\cdot}12H_2O$ (144 mg, 0.40 mmol) and $[Ir(dtbbpy)(ppy)_2]PF_6$ (1.6 mg, 0.002 mmol) sequentially. The tube was vacuumed and back-filled with argon three times and then added with anhydrous EtOAc (2 mL), followed by addition of **10a-10d** (0.30 mmol), The reaction mixture was irradiated with blue LED for 5 h. EtOAc (30 mL) was added and the organic layer was washed with water (5 mL) and brine (5 mL) sequentially, dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **3H** and **11-13**.

2-(2-acetylbenzyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptanenitrile (11)



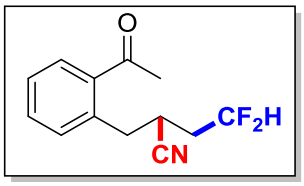
11: (73 mg, PE:EtOAc = 20:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.55 (td, *J* = 7.6, 1.2 Hz, 1H), 7.48 - 7.39 (m, 2H), 3.53 - 3.44 (m, 1H), 3.38 (dd, *J* = 12.8, 4.8 Hz, 1H), 3.03 (dd, *J* = 12.8, 10.0 Hz, 1H), 2.66 - 2.42 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 201.26, 136.46, 136.22, 132.92, 132.71, 131.08, 128.19, 119.83, 119.28 - 106.29 (m), 37.83, 33.41 (t, *J* = 21.5 Hz), 29.09, 26.06.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.93 - -81.10 (m), -111.96 - -114.69 (m), -124.13 - -124.55 (m), -125.81 - -126.05 (m).

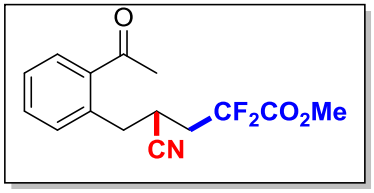
HRMS (ESI) m/z calcd. for $C_{16}H_{13}ONF_9[M+H]^+$ 406.0848 , found 406.0856.

2-(2-acetylbenzyl)-4,4-difluorobutanenitrile (12)



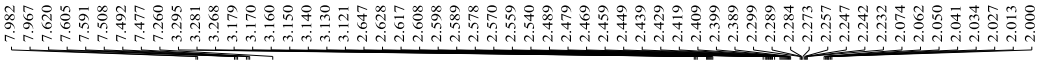
12: (42 mg, PE:EtOAc = 20:1, colorless oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.53 (td, *J* = 7.6, 1.6 Hz, 1H), 7.46 - 7.37 (m, 2H), 6.07 (tdd, *J* = 56.0, 5.2, 4.4 Hz, 1H), 3.35 (dd, *J* = 12.8, 4.8 Hz, 1H), 3.30 - 3.21 (m, 1H), 2.98 (dd, *J* = 12.8, 10.0 Hz, 1H), 2.63 (s, 3H), 2.34 - 2.21 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.21, 136.97, 136.28, 132.81, 132.60, 130.94, 127.96, 120.30, 114.99 (t, *J* = 238.9 Hz), 37.28, 36.54 (t, *J* = 22.7 Hz), 29.15, 27.72 (t, *J* = 5.8 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -115.10, -115.86, -116.00, -116.77.
HRMS (ESI) m/z calcd. for $C_{13}H_{14}ONF_2$ $[M+H]^+$ 238.1038 , found 238.1031.

methyl 5-(2-acetylphenyl)-4-cyano-2,2-difluoropentanoate (13)



13: (53 mg, PE:EtOAc = 3:1, pale yellow oil) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52 (td, *J* = 7.6, 1.6 Hz, 1H), 7.46 - 7.36 (m, 2H), 3.91 (s, 3H), 3.40 - 3.29 (m, 2H), 3.05 - 2.96 (m, 1H), 2.66 - 2.40 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.14, 163.55 (t, *J* = 32.1 Hz), 136.70, 136.38, 132.84, 132.54, 130.88, 127.99, 120.05, 114.39 (t, *J* = 261.2 Hz), 53.63, 37.63, 36.87 (t, *J* = 23.9 Hz), 29.13 (s), 26.95 (t, *J* = 4.2 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -103.38 (dd, *J* = 417.4, 267.3 Hz).
HRMS (ESI) m/z calcd. for $C_{15}H_{16}O_3NF_2$ $[M+H]^+$ 296.1093 , found 296.1084 .

NMR spectra:


7.982
7.967
7.620
7.605
7.591
7.508
7.492
7.477
7.260
3.295
3.281
3.268
3.179
3.170
3.160
3.150
3.140
3.130
3.121
2.647
2.628
2.617
2.608
2.598
2.589
2.578
2.570
2.559
2.540
2.489
2.479
2.469
2.459
2.449
2.439
2.429
2.419
2.409
2.399
2.389
2.299
2.289
2.284
2.273
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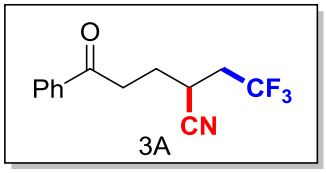
2.041
2.034
2.027
2.013
2.000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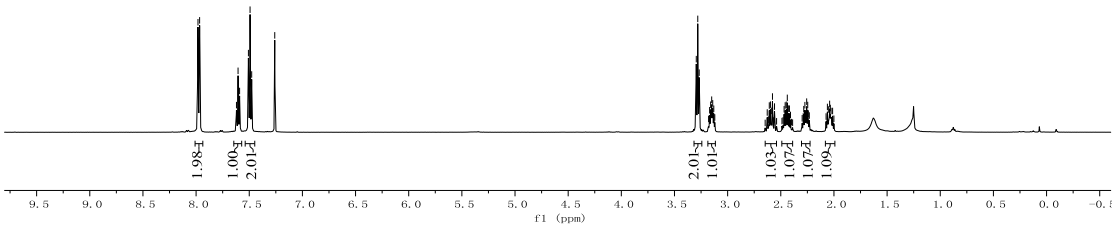
Ph
CF3
CN
3A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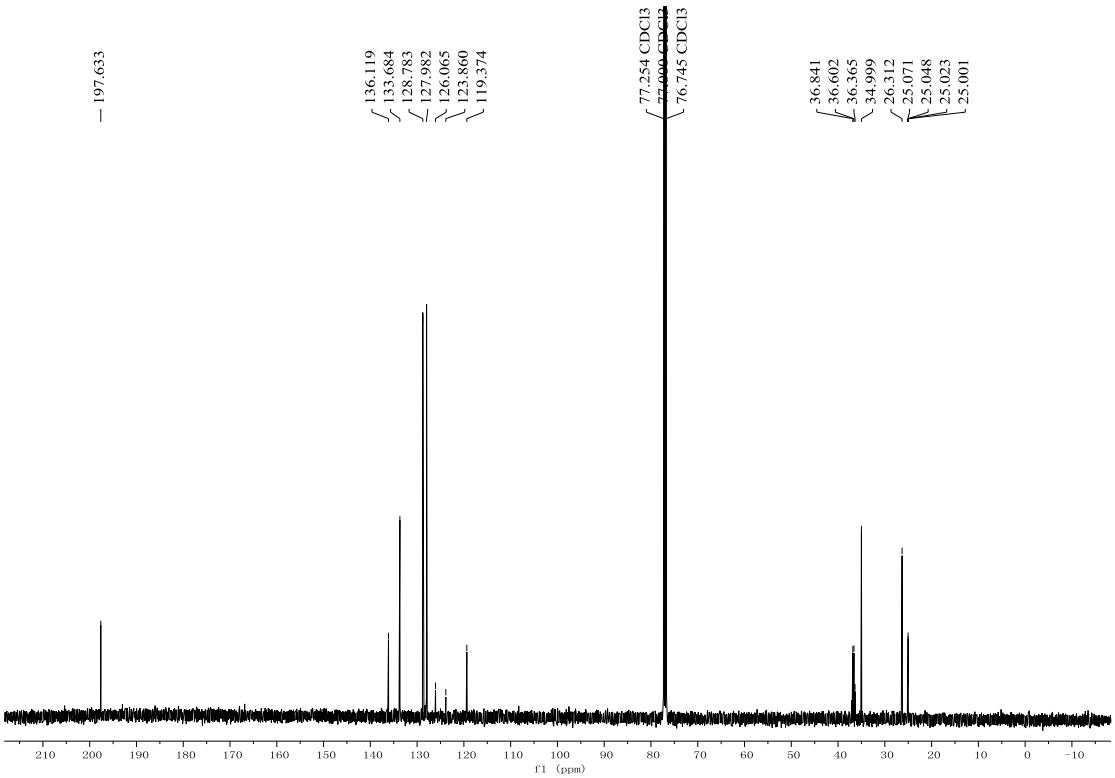
2.01
2.01
1.01
1.03
1.07
1.07
1.09
f1 (ppm)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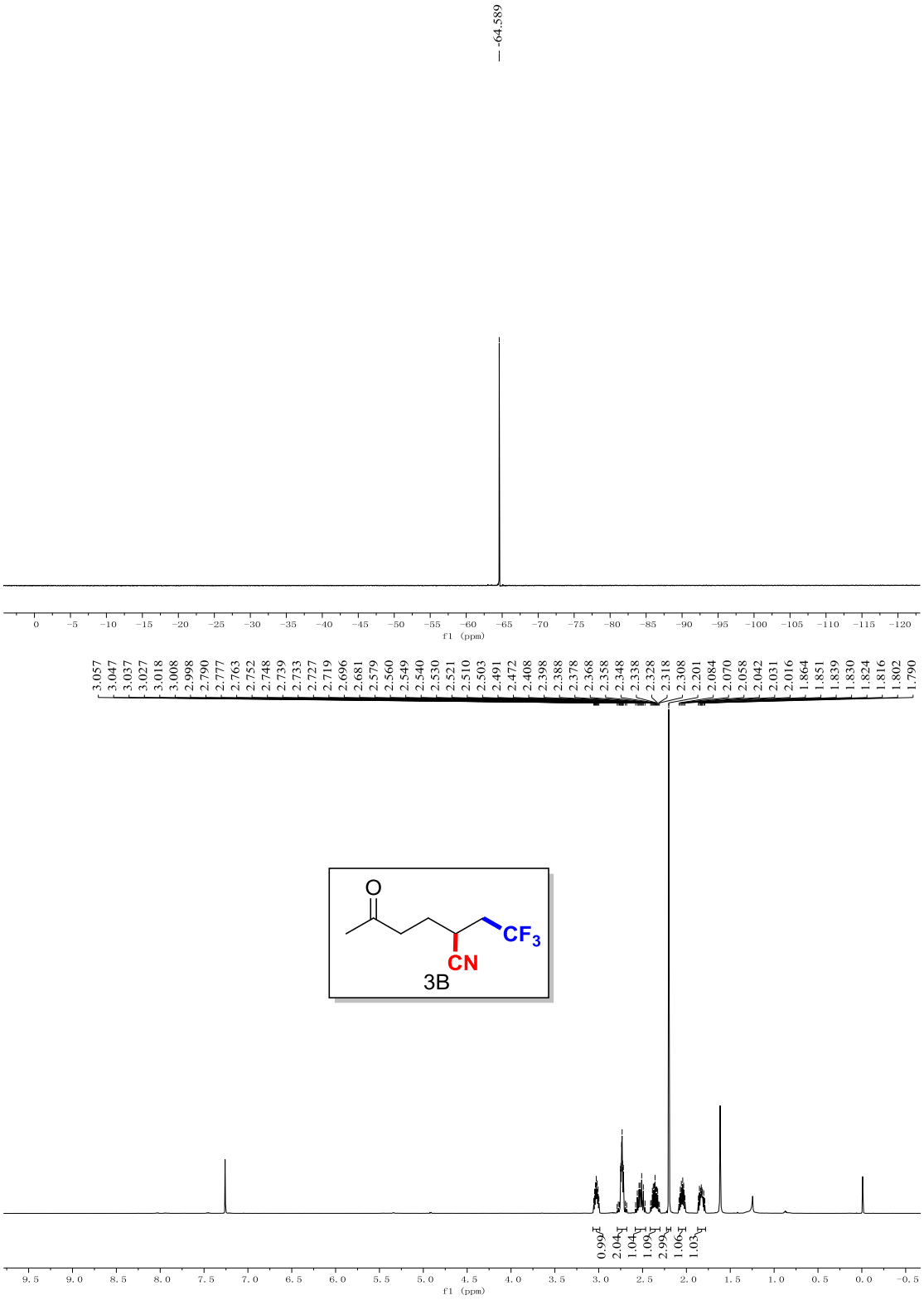
136.119
133.684
128.783
127.982
126.065
123.860
119.374
77.254 CDCl3
77.000 CDCl3
76.745 CDCl3
36.841
36.602
36.365
34.999
26.312
25.071
25.048
25.023
25.001
f1 (ppm)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f1 (ppm)
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3.047
3.037
3.027
3.018
3.008
2.998
2.790
2.777
2.763
2.752
2.748
2.739
2.733
2.727
2.719
2.696
2.681
2.579
2.560
2.549
2.540
2.530
2.521
2.510
2.503
2.491
2.472
2.408
2.398
2.388
2.378
2.368
2.358
2.348
2.338
2.328
2.318
2.308
2.201
2.084
2.070
2.058
2.042
2.031
2.016
1.864
1.851
1.839
1.830
1.824
1.816
1.802
1.790
O
CF3
CN
3B
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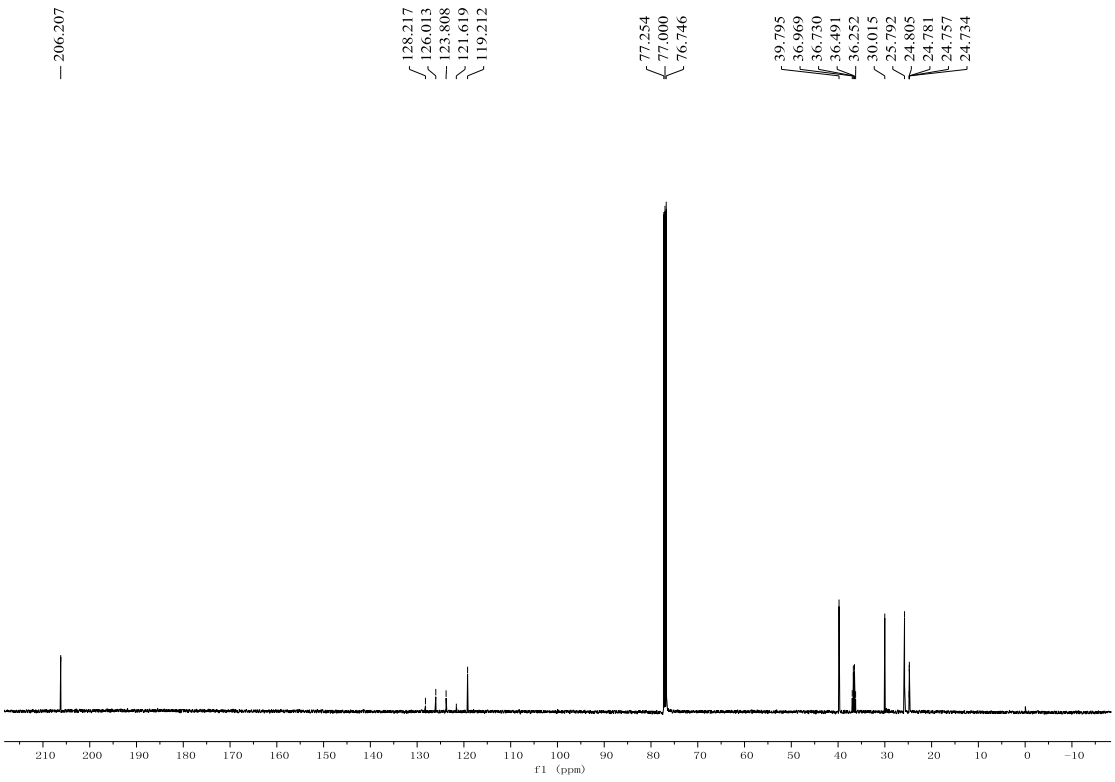
1.04
1.09
2.90
1.06
1.03
f1 (ppm)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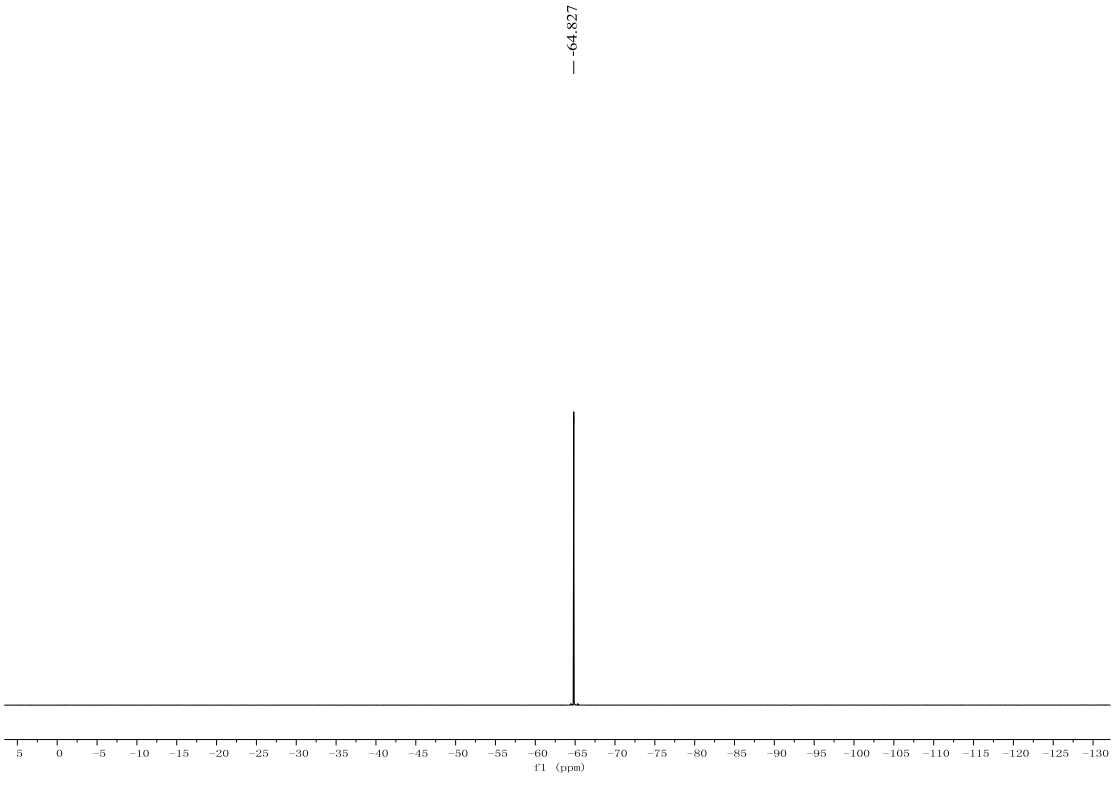
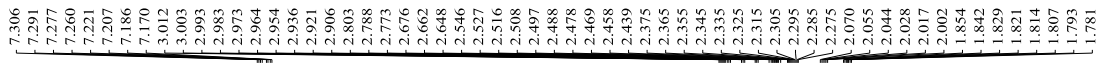
128.217
126.013
123.808
121.619
119.212
77.254
77.000
76.746
39.795
36.969
36.730
36.491
36.252
30.015
25.792
24.805
24.781
24.757
24.734
f1 (ppm)


-64.827
f1 (ppm)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7.291
7.277
7.260
7.221
7.207
7.186
7.170
3.012
3.003
2.993
2.983
2.973
2.964
2.954
2.936
2.921
2.906
2.803
2.788
2.773
2.676
2.662
2.648
2.546
2.527
2.516
2.508
2.497
2.488
2.478
2.469
2.458
2.439
2.375
2.365
2.355
2.345
2.335
2.325
2.315
2.305
2.295
2.285
2.275
2.070
2.055
2.044
2.028
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2.002
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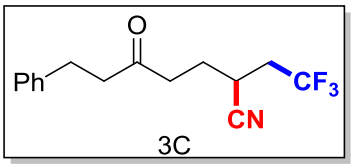
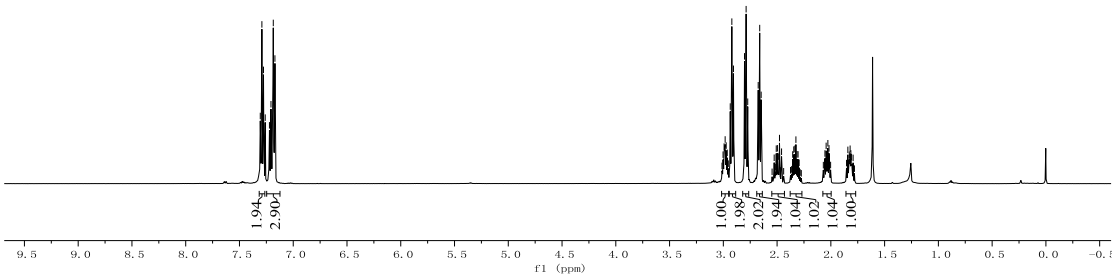
1.842
1.829
1.821
1.814
1.807
1.793
1.781


O
Ph
CF3
CN
3C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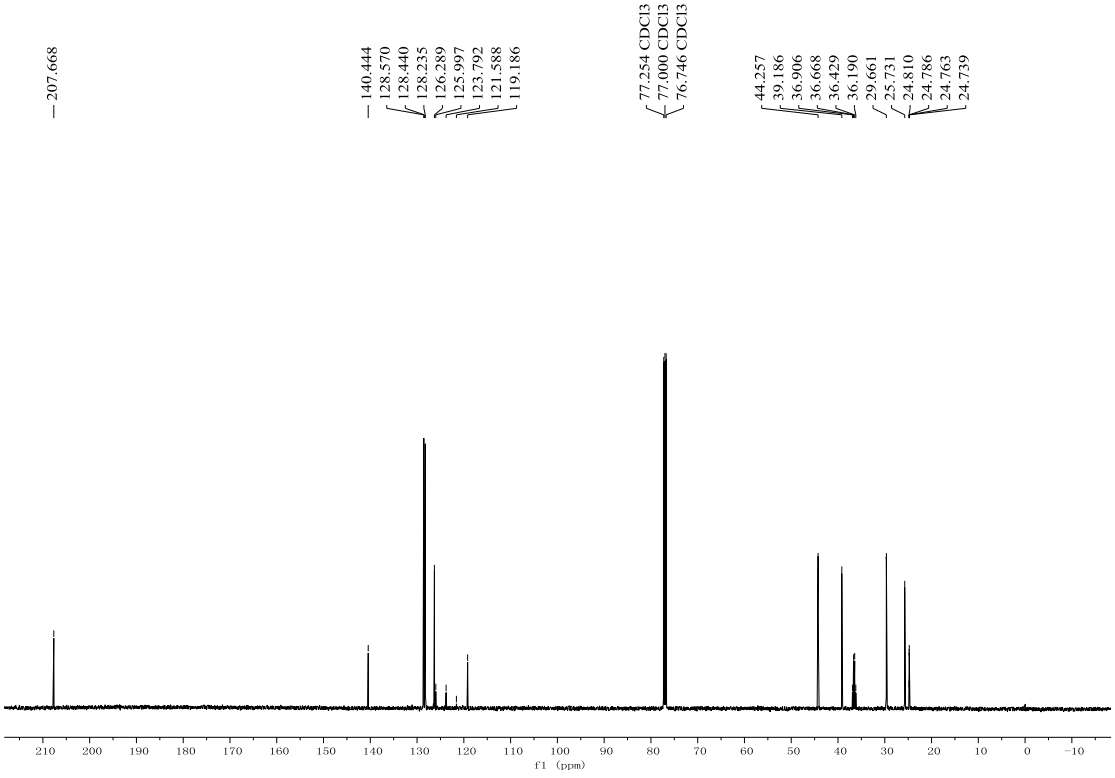
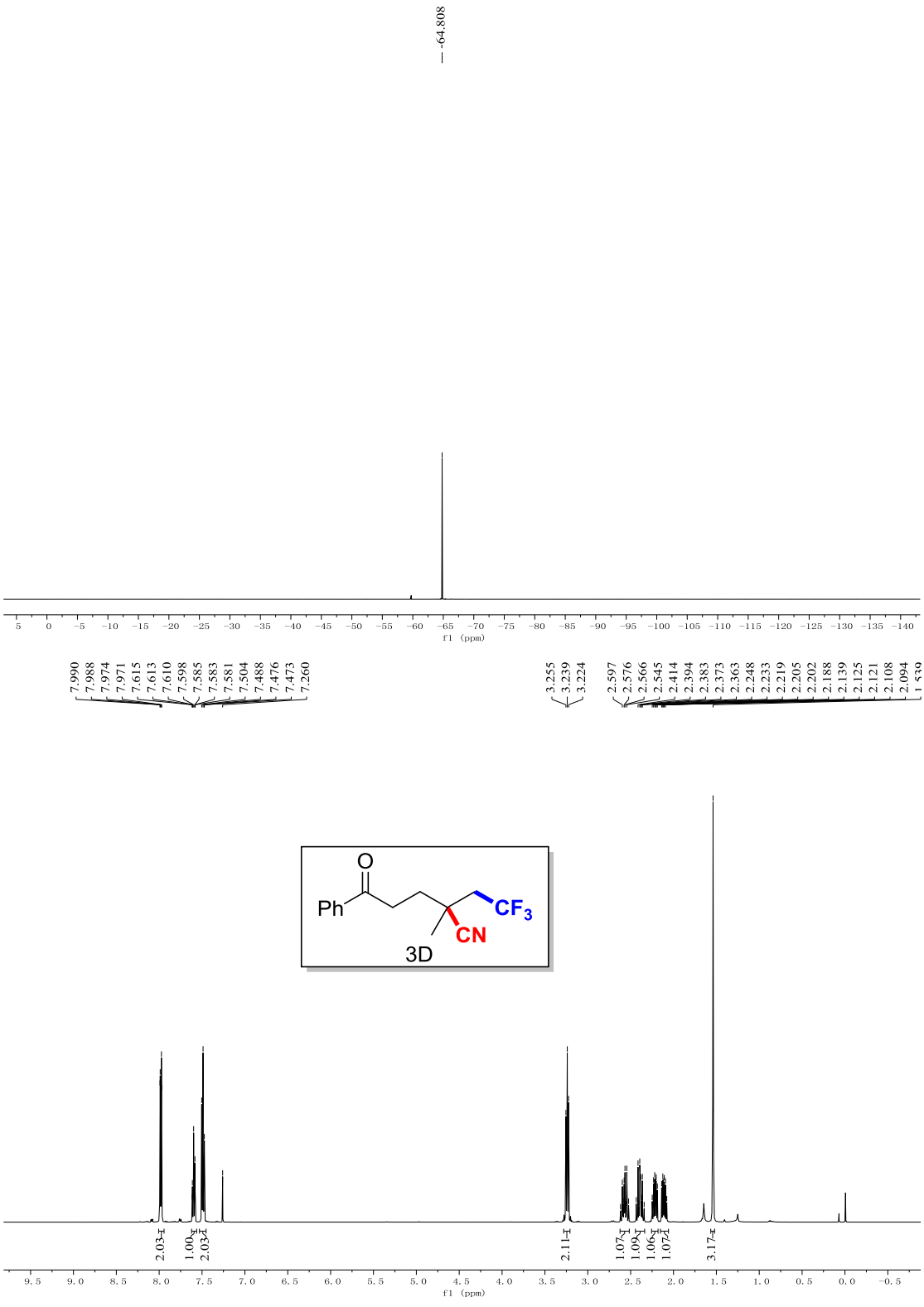
2.90
1.00
1.98
2.02
1.94
1.04
1.02
1.04
1.00
f1 (ppm)


207.668
140.444
128.570
128.440
128.235
126.289
125.997
123.792
121.588
119.186
77.254 CDCl3
77.000 CDCl3
76.746 CDCl3
44.257
39.186
36.906
36.668
36.429
36.190
29.661
25.731
24.810
24.786
24.763
24.739
f1 (ppm)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f1 (ppm)
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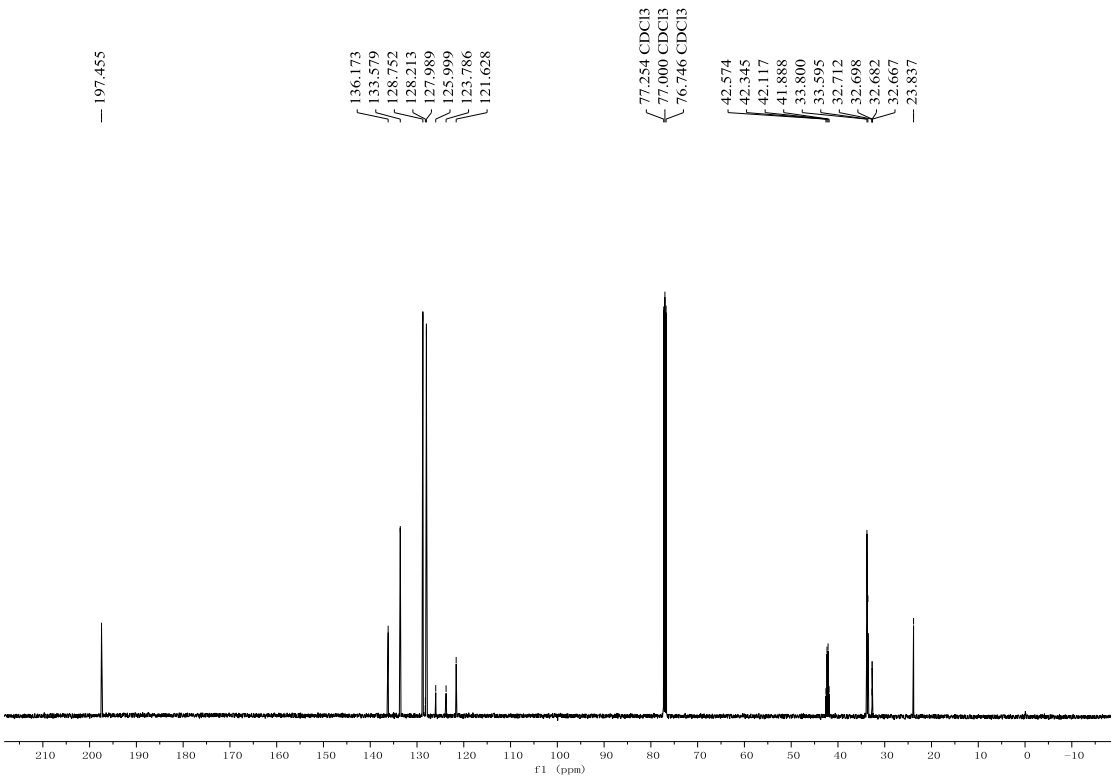
7.988
7.974
7.971
7.615
7.613
7.610
7.598
7.585
7.583
7.581
7.504
7.488
7.476
7.473
7.260
3.255
3.239
3.224
2.597
2.576
2.566
2.545
2.414
2.394
2.383
2.373
2.363
2.248
2.233
2.219
2.205
2.202
2.188
2.139
2.125
2.121
2.108
2.094
O
Ph
CF3
CN
3D
2.03
1.00
2.03
2.11
1.07
1.09
1.06
1.07
3.17
f1 (ppm)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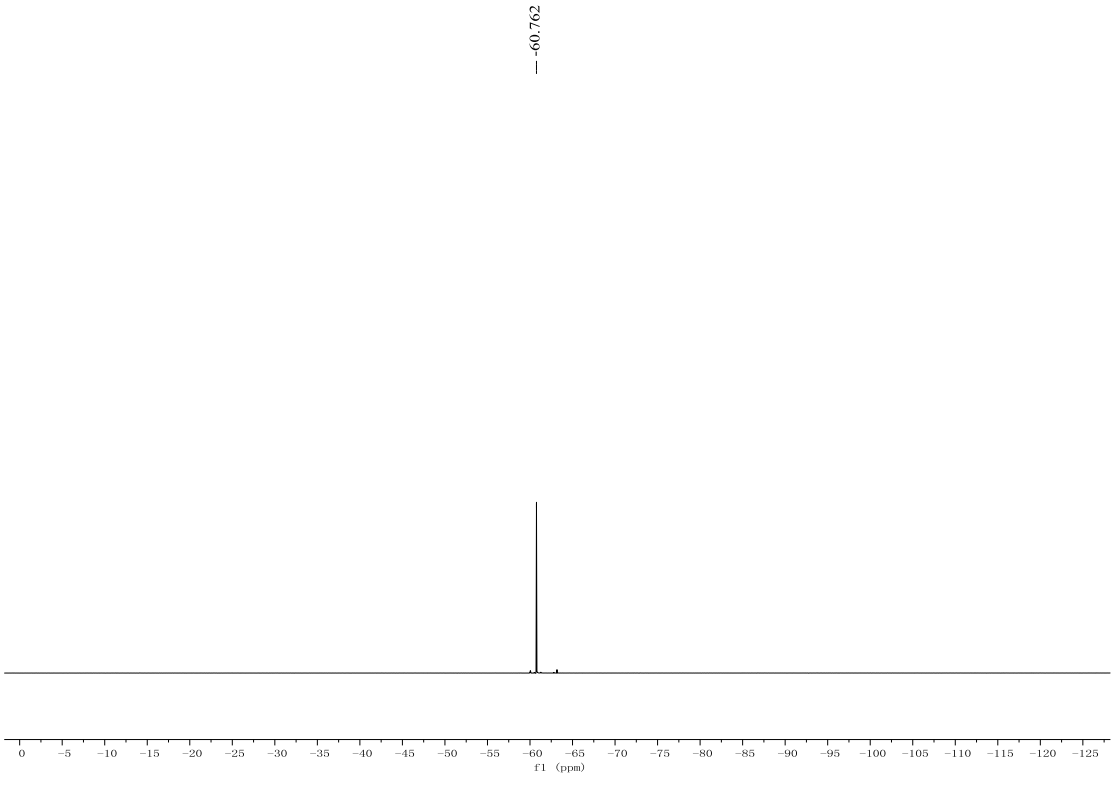
133.579
128.752
128.213
127.989
125.999
123.786
121.628
77.254 CDCl3
77.000 CDCl3
76.746 CDCl3
42.574
42.345
42.117
41.888
33.800
33.595
32.712
32.698
32.682
32.667
23.837
f1 (ppm)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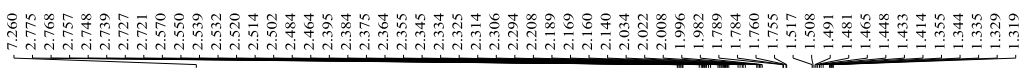
f1 (ppm)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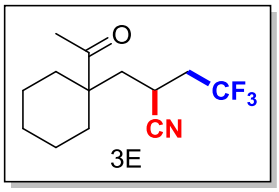
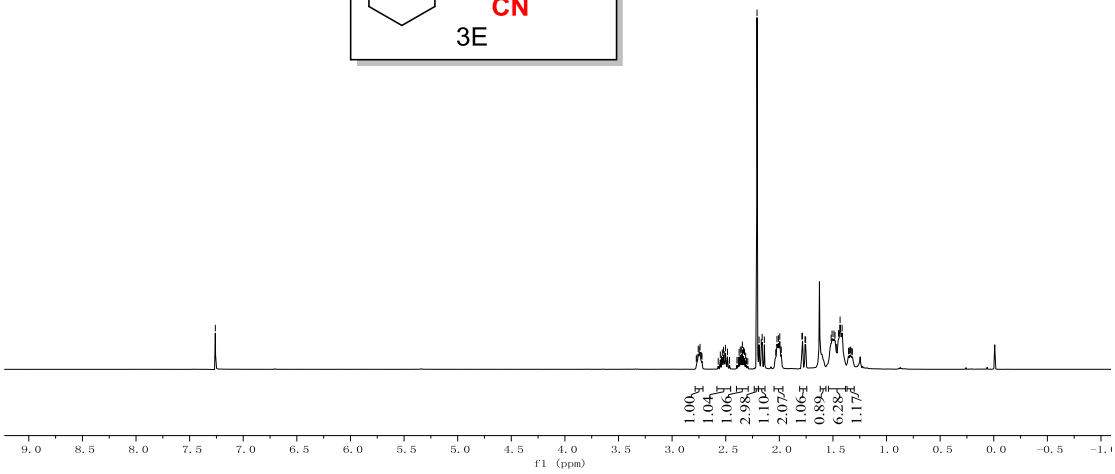
2.768
2.757
2.748
2.739
2.727
2.721
2.570
2.550
2.539
2.532
2.520
2.514
2.502
2.484
2.464
2.395
2.384
2.375
2.364
2.355
2.345
2.334
2.325
2.314
2.306
2.294
2.208
2.189
2.169
2.160
2.140
2.034
2.022
2.008
1.996
1.982
1.789
1.784
1.760
1.755
1.517
1.508
1.491
1.481
1.465
1.448
1.433
1.414
1.355
1.344
1.335
1.329
1.319


O
CF3
CN

3E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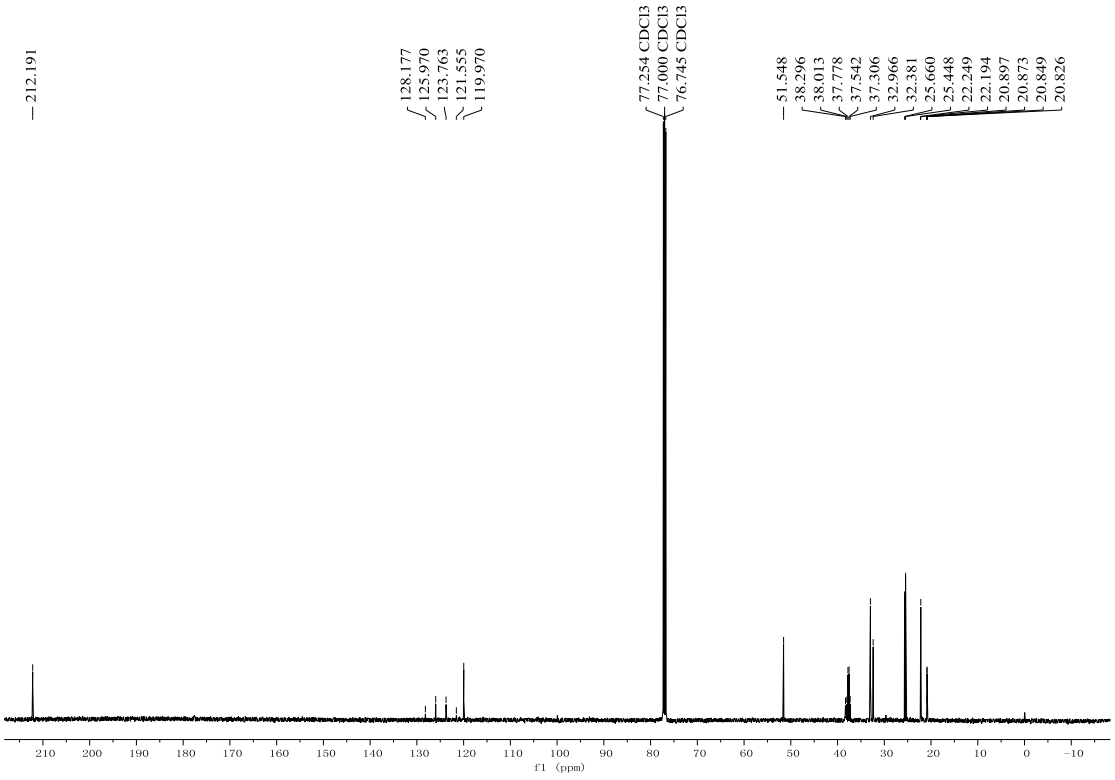
1.04
1.06
2.98
1.10
2.07
1.06
0.89
6.28
1.17
f1 (ppm)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125.970
123.763
121.555
119.970
77.254 CDCl3
77.000 CDCl3
76.745 CDCl3
51.548
38.296
38.013
37.778
37.542
37.306
32.966
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25.660
25.448
22.249
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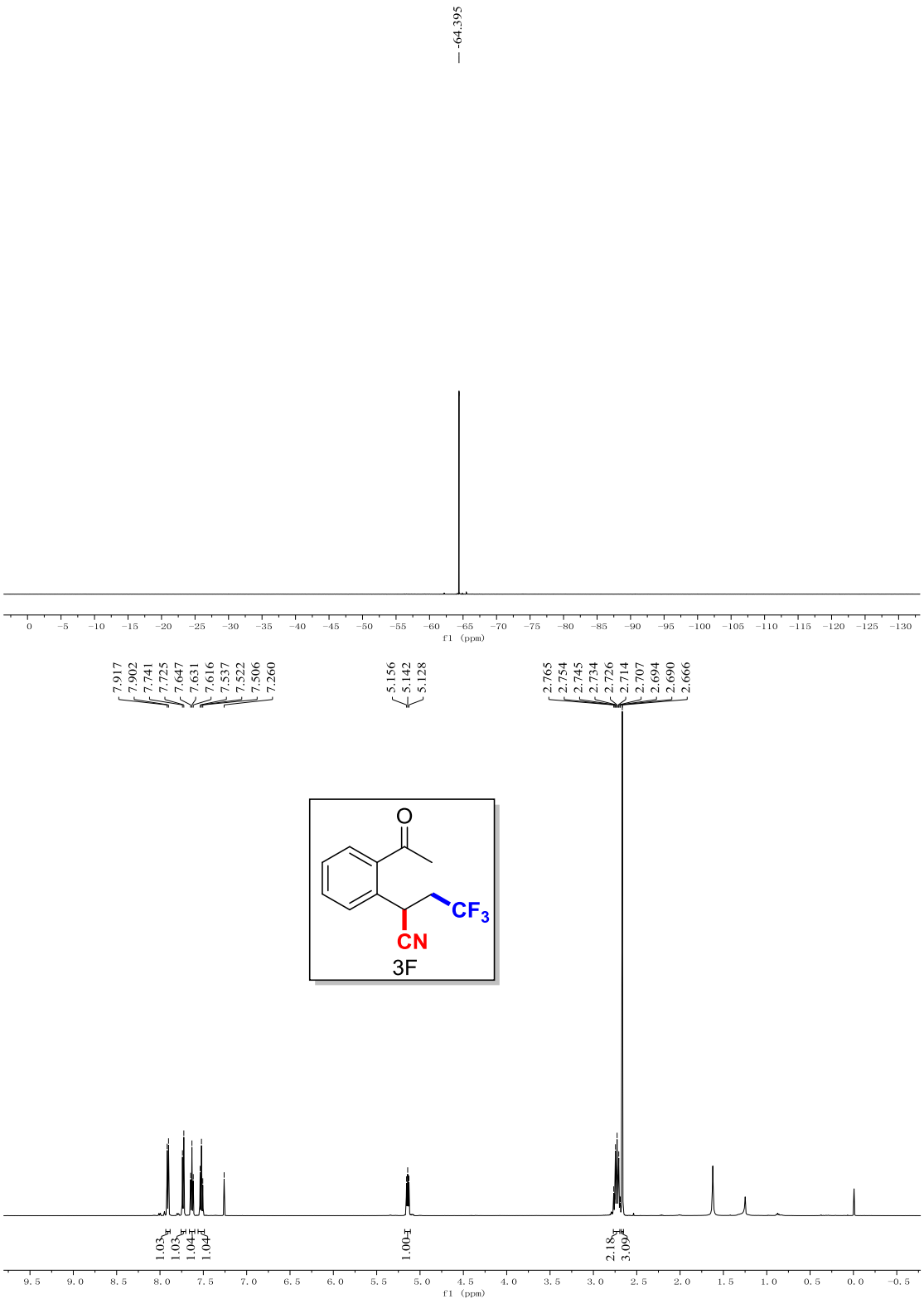
20.897
20.873
20.849
20.826
f1 (ppm)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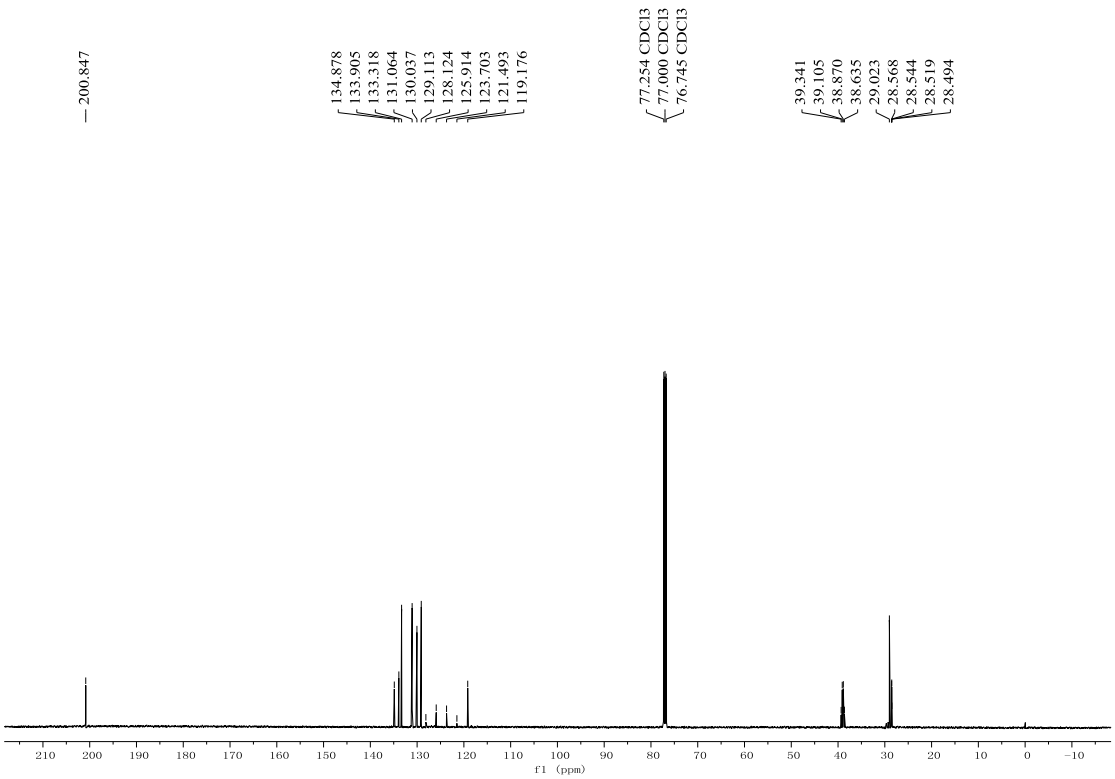
7.741
7.725
7.647
7.631
7.616
7.537
7.522
7.506
7.260
5.156
5.142
5.128
2.765
2.754
2.745
2.734
2.726
2.714
2.707
2.694
2.690
2.666
O
CF3
CN
3F
1.03
1.02
1.04
1.04
1.00
2.18
3.09
f1 (ppm)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133.905
133.318
131.064
130.037
129.113
128.124
125.914
123.703
121.493
119.176
77.254 CDCl3
77.000 CDCl3
76.745 CDCl3
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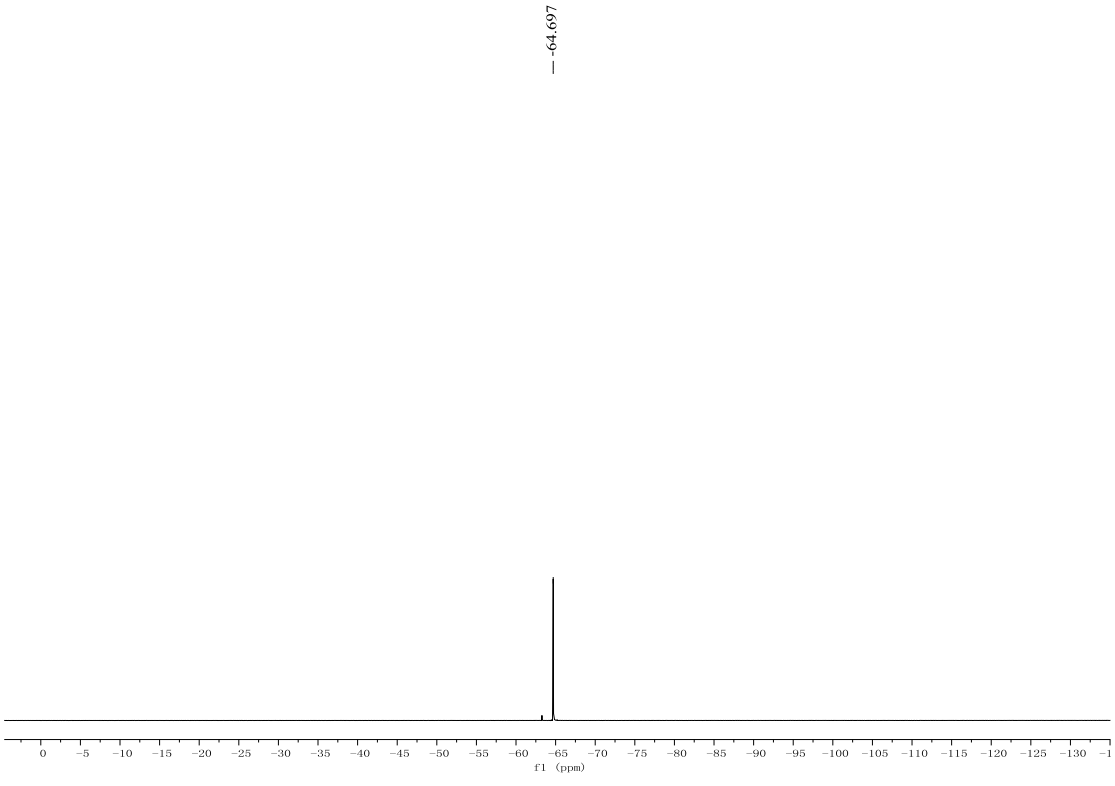
39.105
38.870
38.635
29.023
28.568
28.544
28.519
28.494
f1 (ppm)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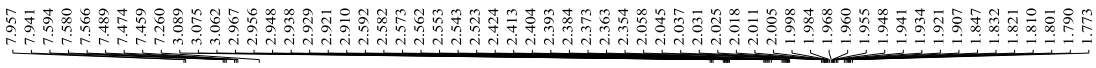
f1 (ppm)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7.459
7.260
3.089
3.075
3.062
2.967
2.956
2.948
2.938
2.929
2.921
2.910
2.592
2.582
2.573
2.562
2.553
2.543
2.523
2.424
2.413
2.404
2.393
2.384
2.373
2.363
2.354
2.058
2.045
2.037
2.031
2.025
2.018
2.011
2.005
1.998
1.984
1.968
1.960
1.955
1.948
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1.921
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1.847
1.832
1.821
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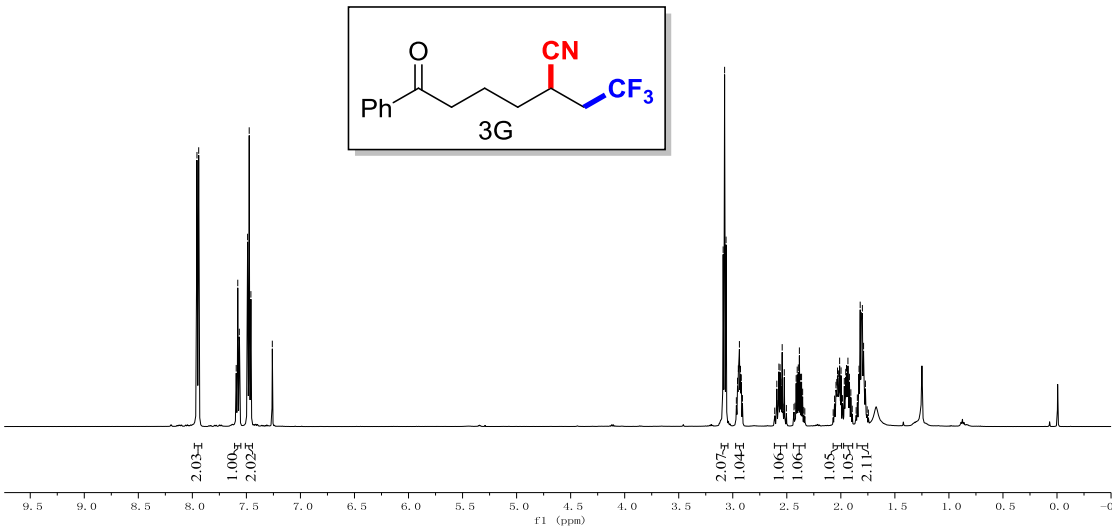
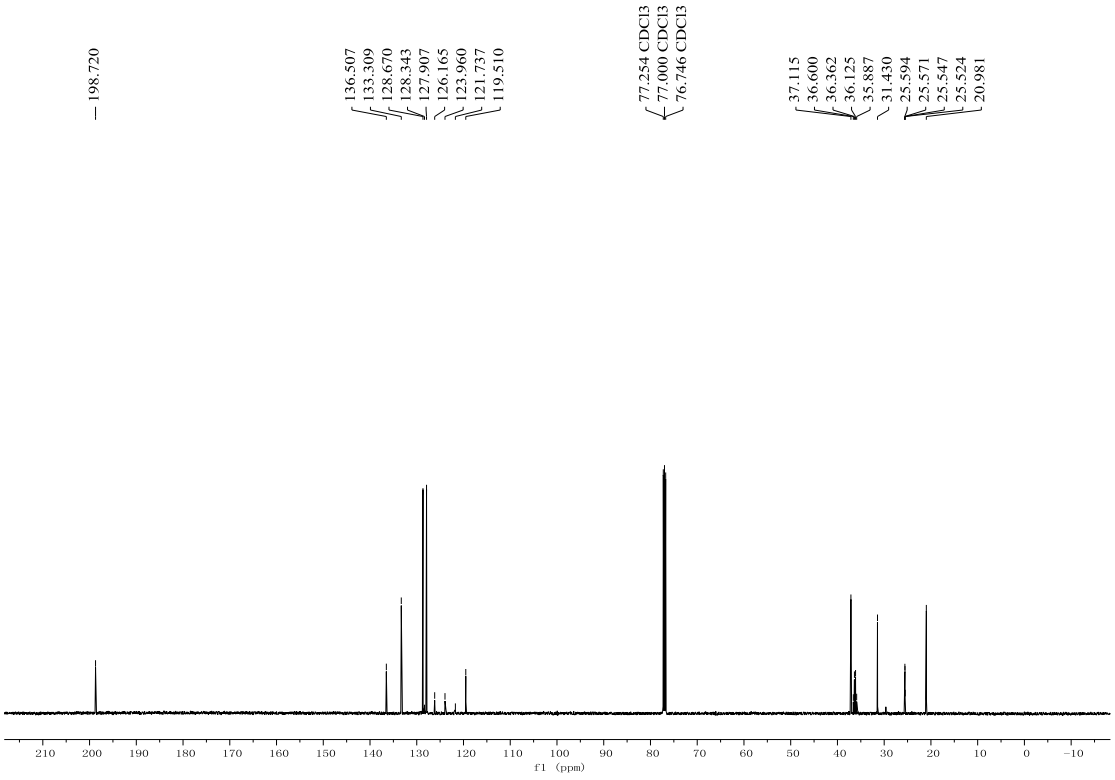
1.801
1.790
1.773


O
CN
Ph
CF3
3G
2.03
1.00
2.02
2.07
1.04
1.06
1.06
1.05
1.05
2.11
f1 (ppm)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128.343
127.907
126.165
123.960
121.737
119.510
77.254 CDCl3
77.000 CDCl3
76.746 CDCl3
37.115
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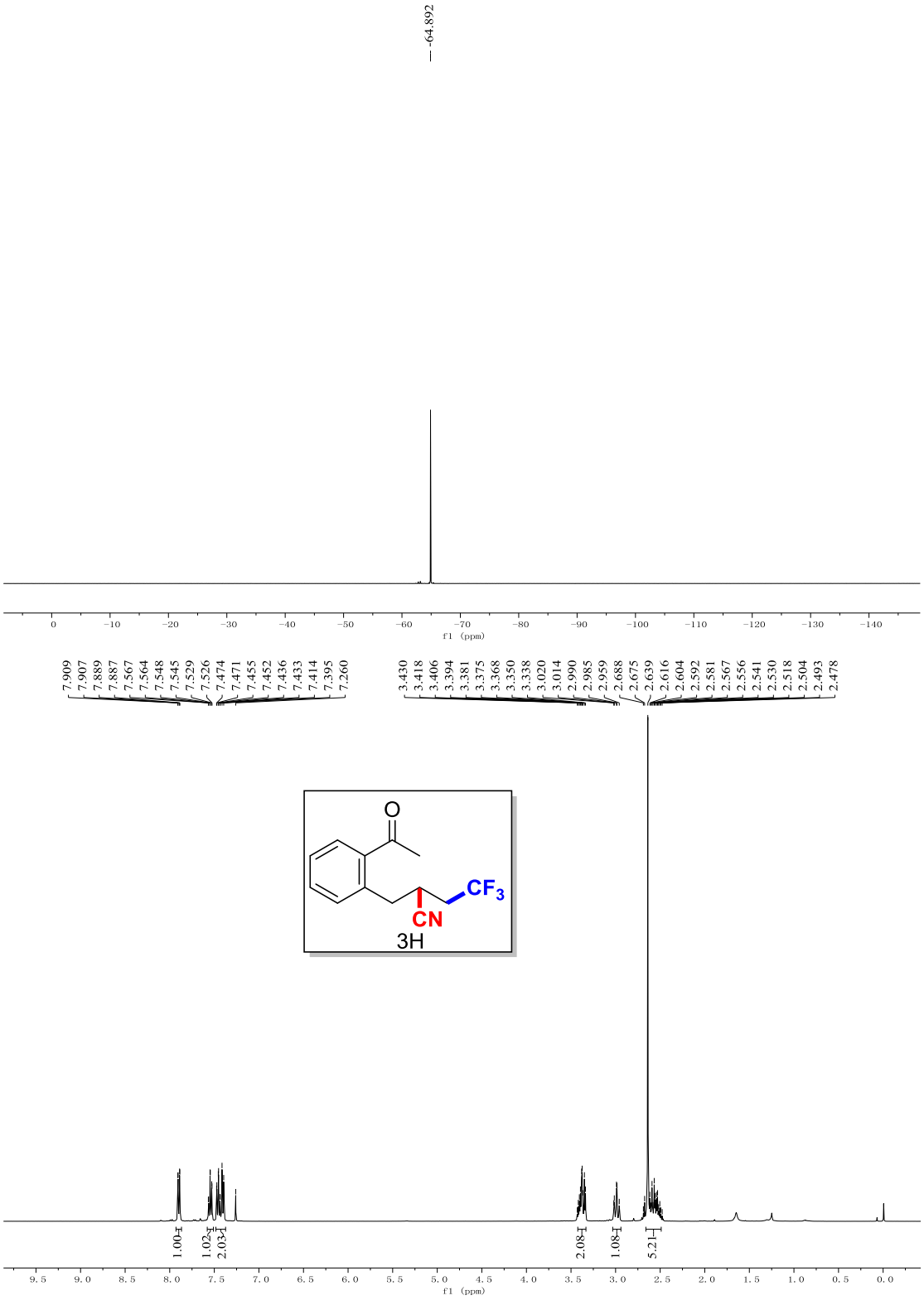
36.125
35.887
31.430
25.594
25.571
25.547
25.524
20.981
f1 (ppm)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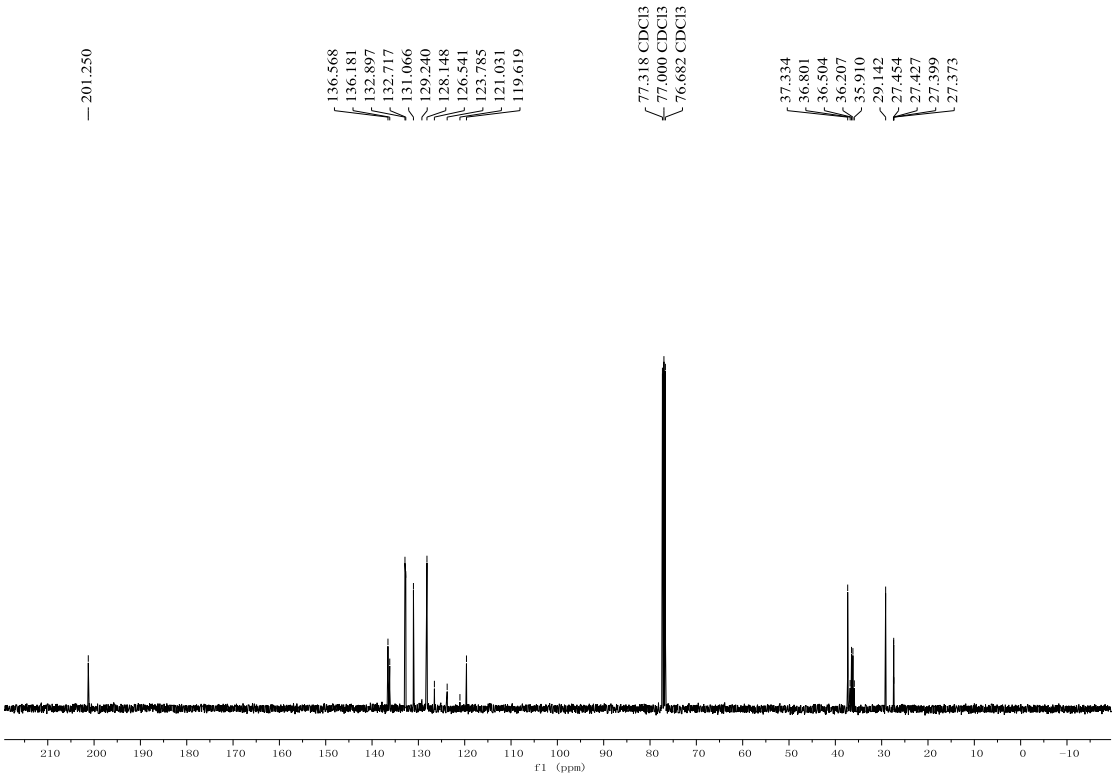
7.526
7.474
7.471
7.455
7.452
7.436
7.433
7.414
7.395
7.260
3.430
3.418
3.406
3.394
3.381
3.375
3.368
3.350
3.338
3.020
3.014
2.990
2.985
2.959
2.688
2.675
2.639
2.616
2.604
2.592
2.581
2.567
2.556
2.541
2.530
2.518
2.504
2.493
2.478
O
CF3
CN
3H
1.00
1.02
2.03
2.08
1.08
5.21
f1 (ppm)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132.717
131.066
129.240
128.148
126.541
123.785
121.031
119.619
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
37.334
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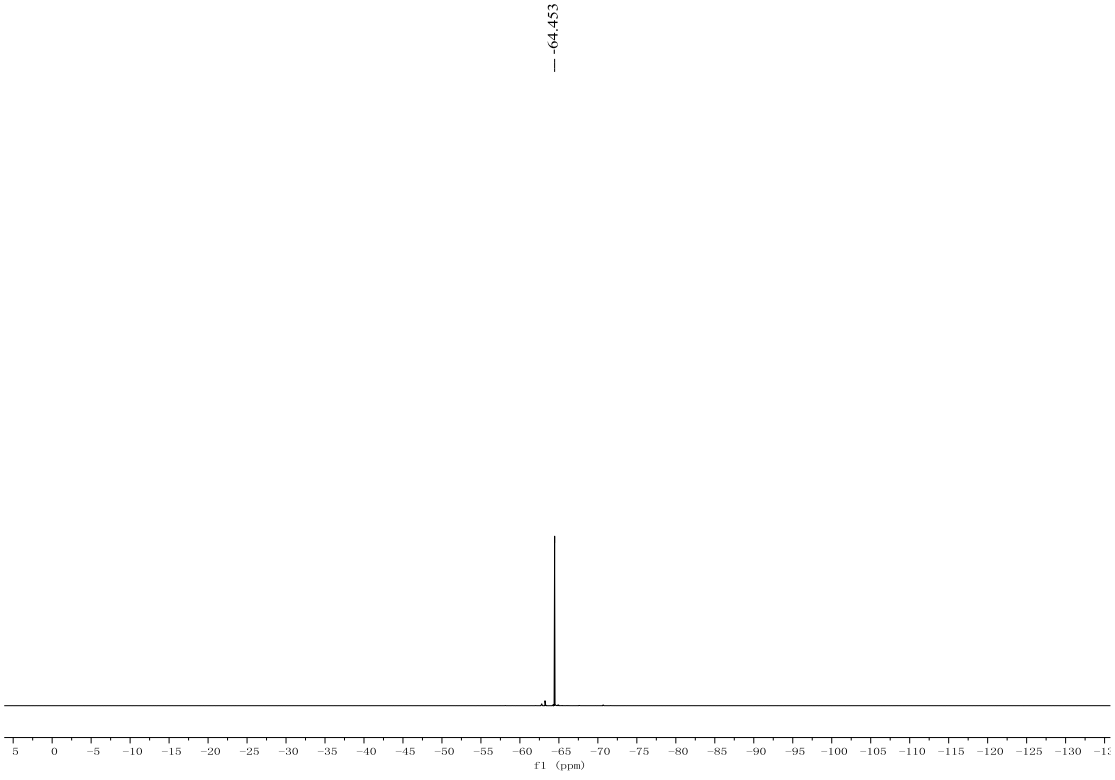
36.504
36.207
35.910
29.142
27.454
27.427
27.399
27.373
f1 (ppm)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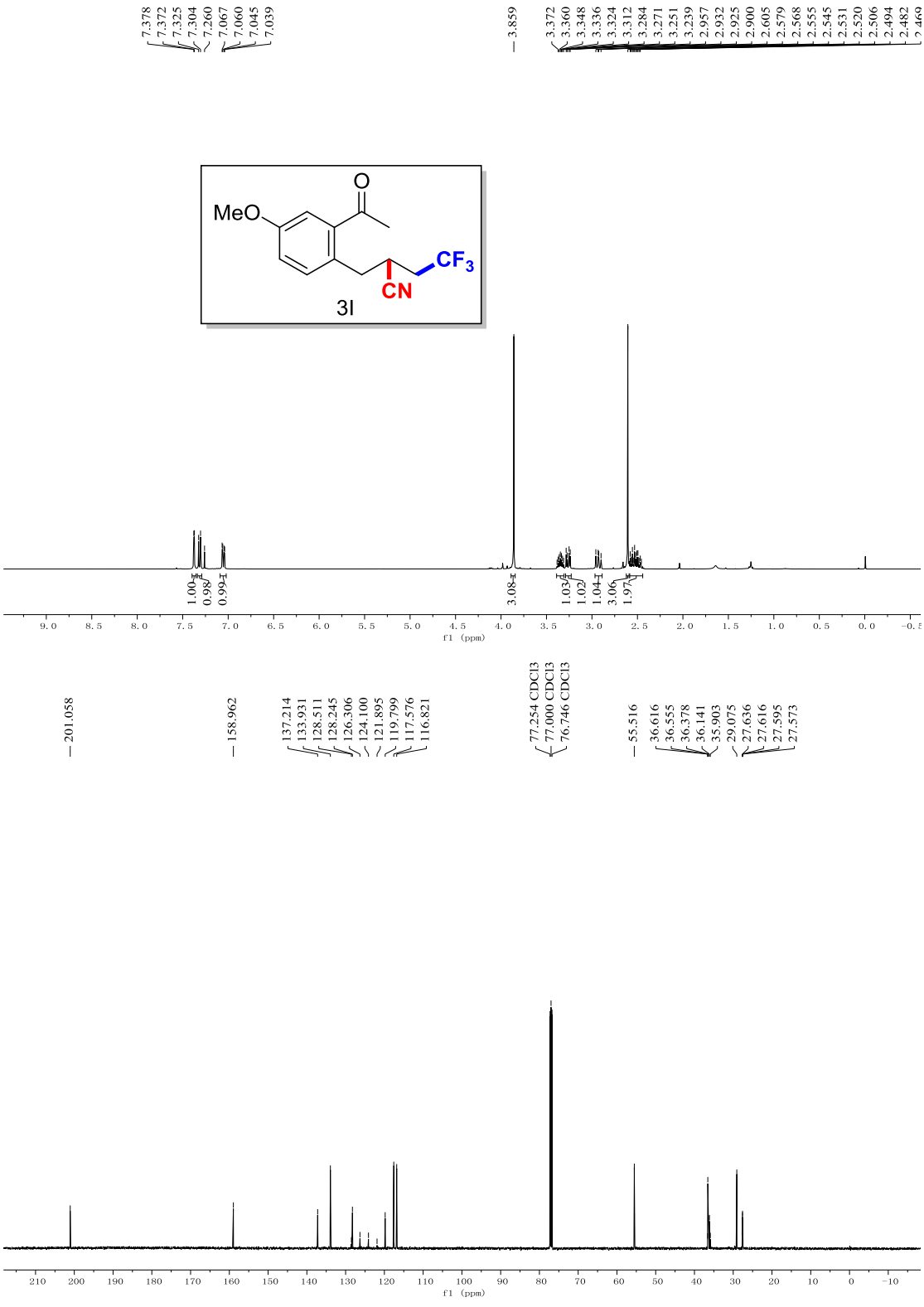
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7.067
7.060
7.045
7.039
3.859
3.372
3.360
3.348
3.336
3.324
3.312
3.284
3.271
3.251
3.239
2.957
2.932
2.925
2.900
2.605
2.579
2.568
2.555
2.545
2.531
2.520
2.506
2.494
2.482
2.469
MeO
O
CF3
CN
3l
1.00
0.98
0.99
3.08
1.03
1.02
1.04
3.06
1.97
f1 (ppm)
201.058
158.962
137.214
133.931
128.511
128.245
126.306
124.100
121.895
119.799
117.576
116.821
77.254 CDCl3
77.000 CDCl3
76.746 CDCl3
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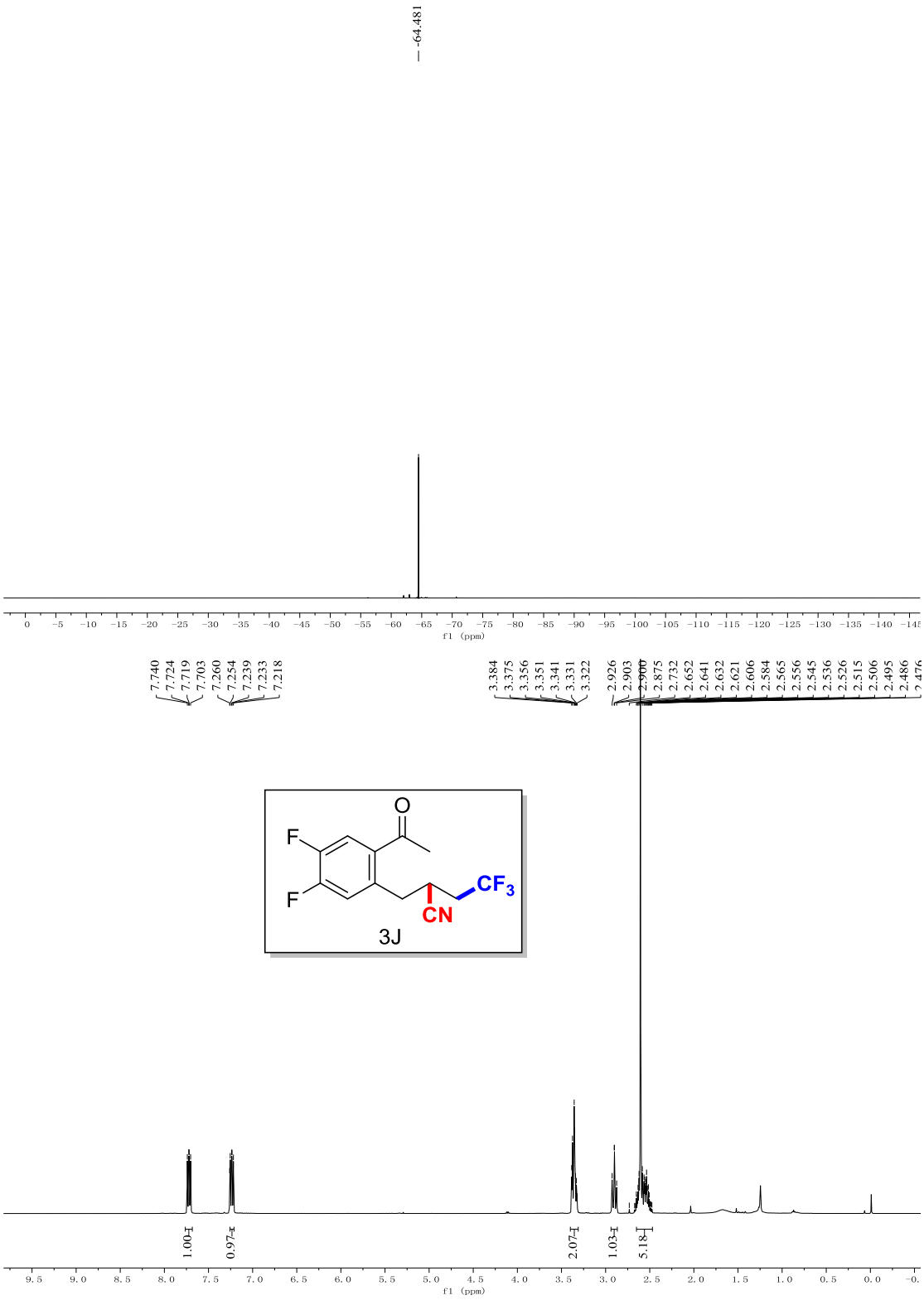
36.616
36.555
36.378
36.141
35.903
29.075
27.636
27.616
27.595
27.573
f1 (ppm)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f1 (ppm)
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7.239
7.233
7.218
3.384
3.375
3.356
3.351
3.341
3.331
3.322
2.926
2.903
2.900
2.875
2.732
2.652
2.641
2.632
2.621
2.606
2.584
2.565
2.556
2.545
2.536
2.526
2.515
2.506
2.495
2.486
O
F
F
CF3
CN
3J
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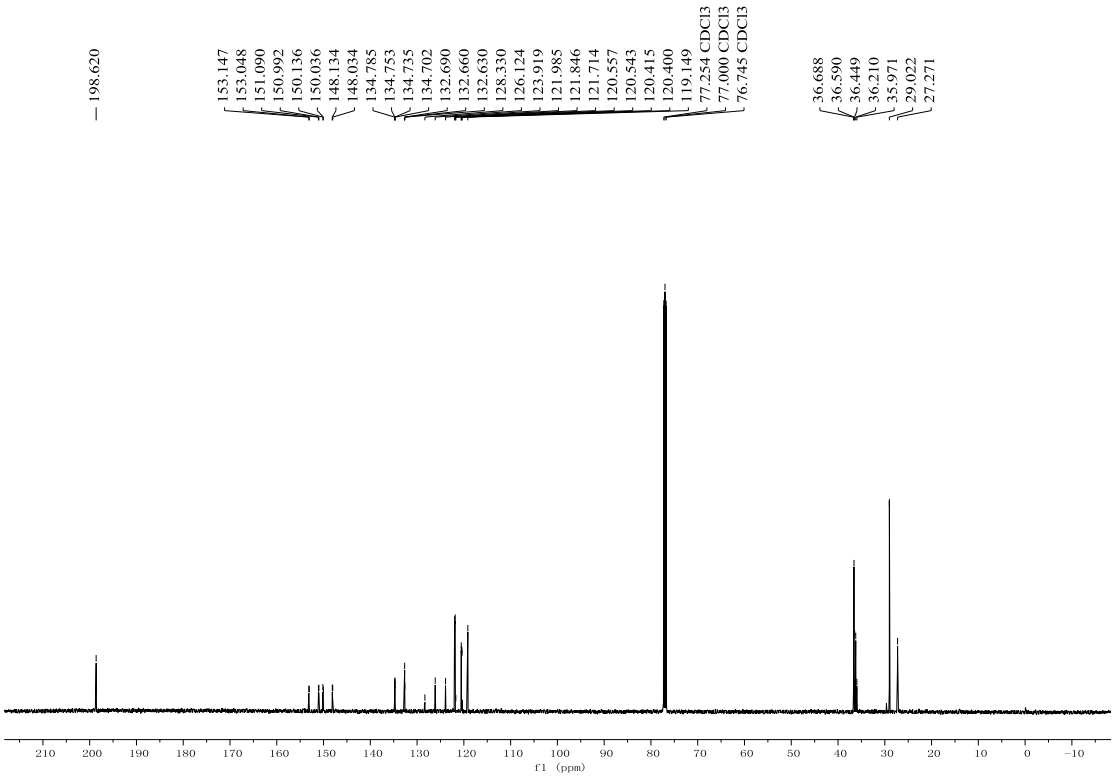
0.97
2.07
1.03
5.18
f1 (ppm)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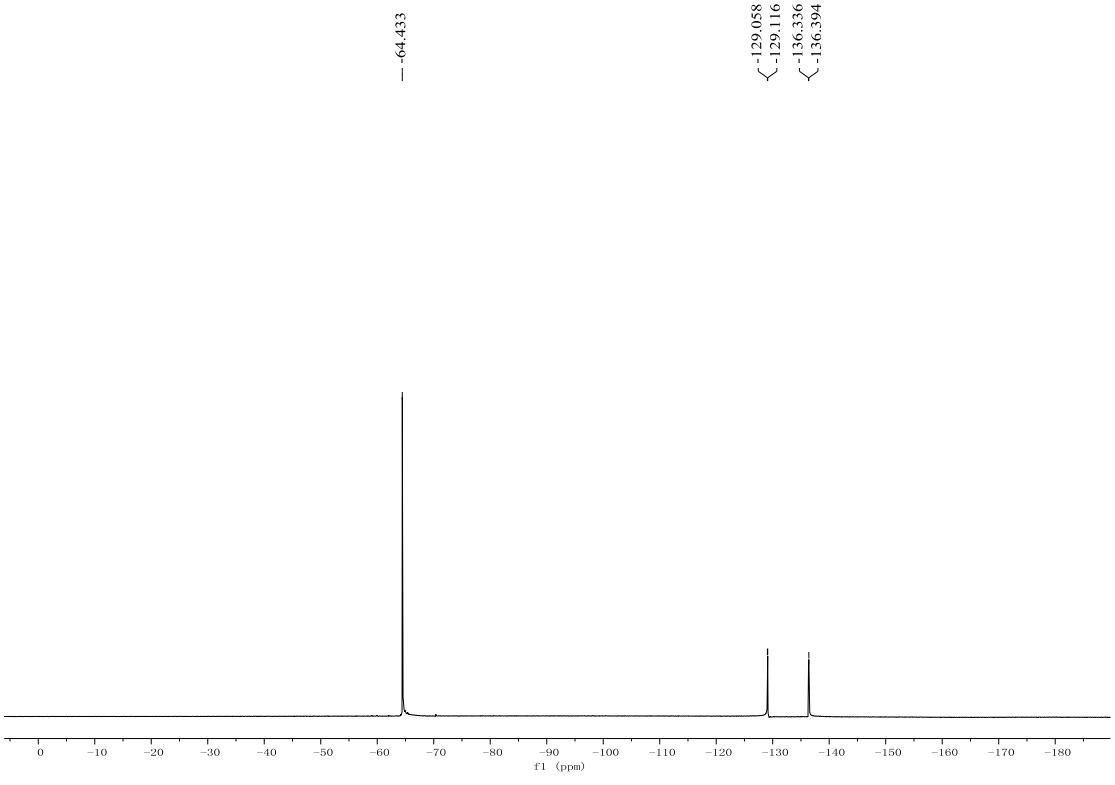
151.090
150.992
150.136
150.036
148.134
148.034
134.785
134.753
134.735
134.702
132.690
132.660
132.630
128.330
126.124
123.919
121.985
121.846
121.714
120.557
120.543
120.415
120.400
119.149
77.254 CDCl3
77.000 CDCl3
76.745 CDCl3
36.688
36.590
36.449
36.210
35.971
29.022
27.271
f1 (ppm)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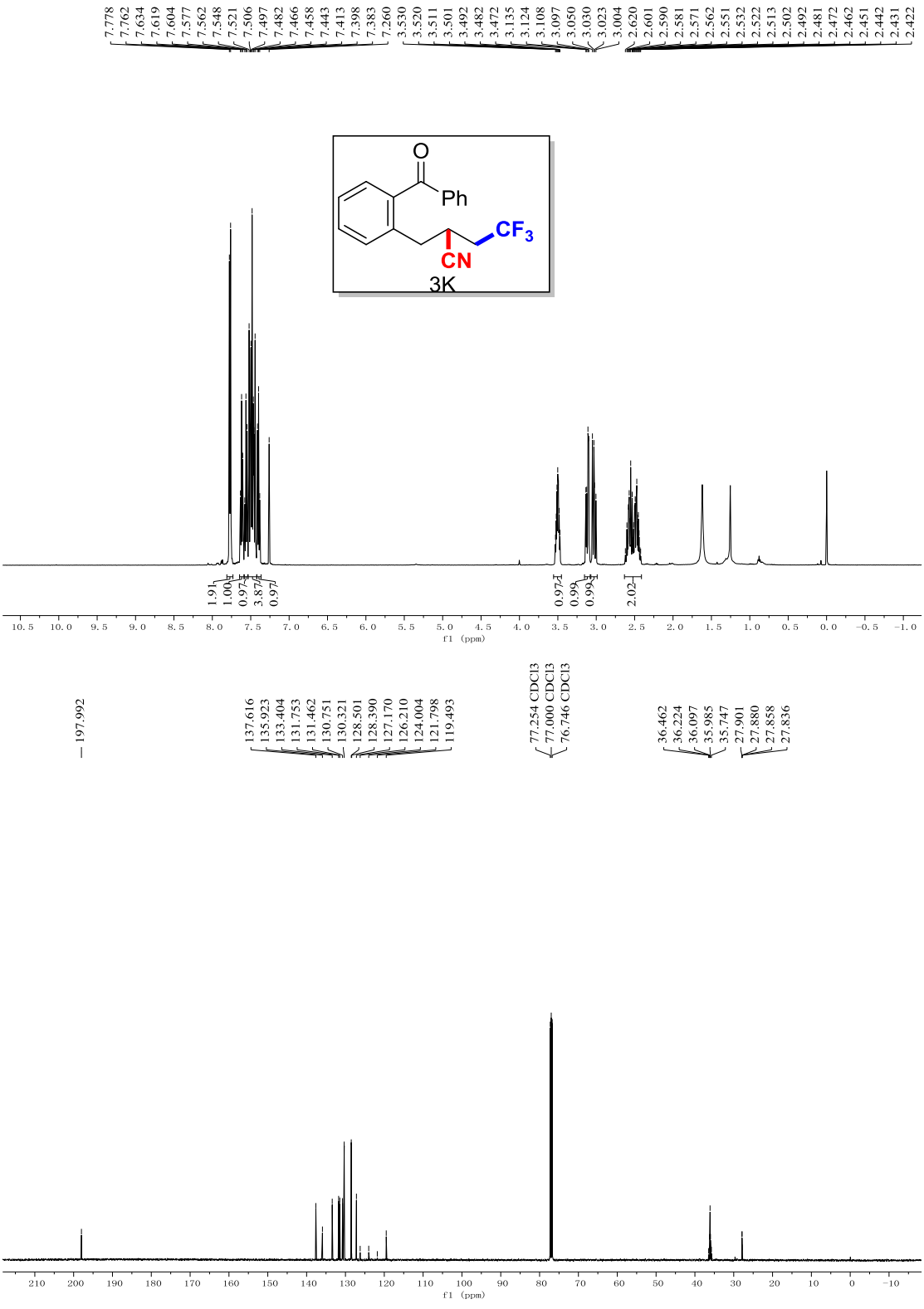
-129.058
-129.116
-136.336
-136.394
f1 (ppm)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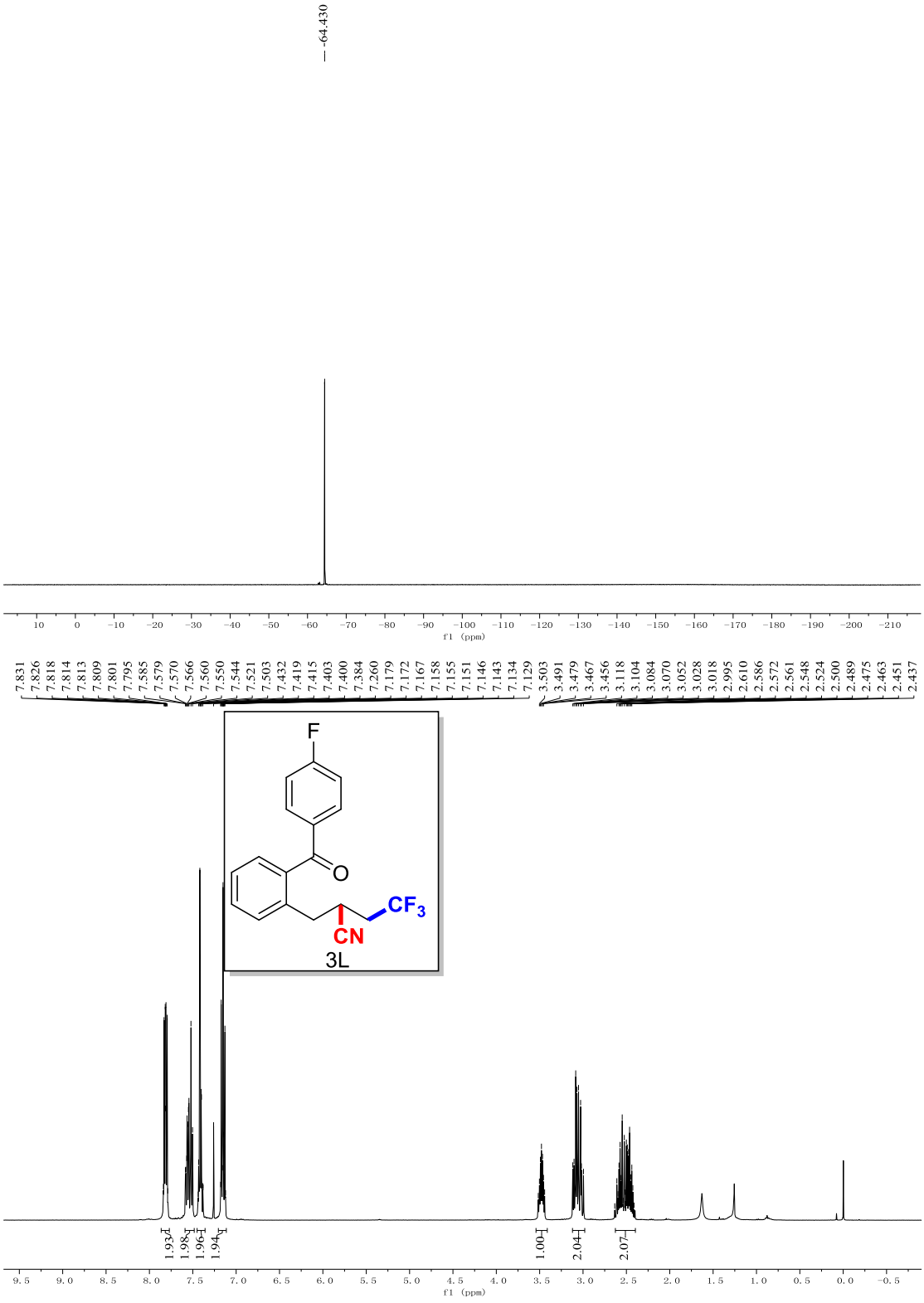
7.762
7.634
7.619
7.604
7.577
7.562
7.548
7.521
7.506
7.497
7.482
7.466
7.458
7.443
7.413
7.398
7.383
7.260
3.530
3.520
3.511
3.501
3.492
3.482
3.472
3.135
3.124
3.108
3.097
3.050
3.030
3.023
3.004
2.620
2.601
2.590
2.581
2.571
2.562
2.551
2.532
2.522
2.513
2.502
2.492
2.481
2.472
2.462
2.451
2.442
2.431
2.422
O
Ph
CF3
CN
3K
1.91
1.00
0.97
3.87
0.97
0.97
0.99
0.99
2.02
f1 (ppm)
197.992
137.616
135.923
133.404
131.753
131.462
130.751
130.321
128.501
128.390
127.170
126.210
124.004
121.798
119.493
77.254 CDCl3
77.000 CDCl3
76.746 CDCl3
36.462
36.224
36.097
35.985
35.747
27.901
27.880
27.858
27.836
f1 (ppm)


-64.430
f1 (ppm)
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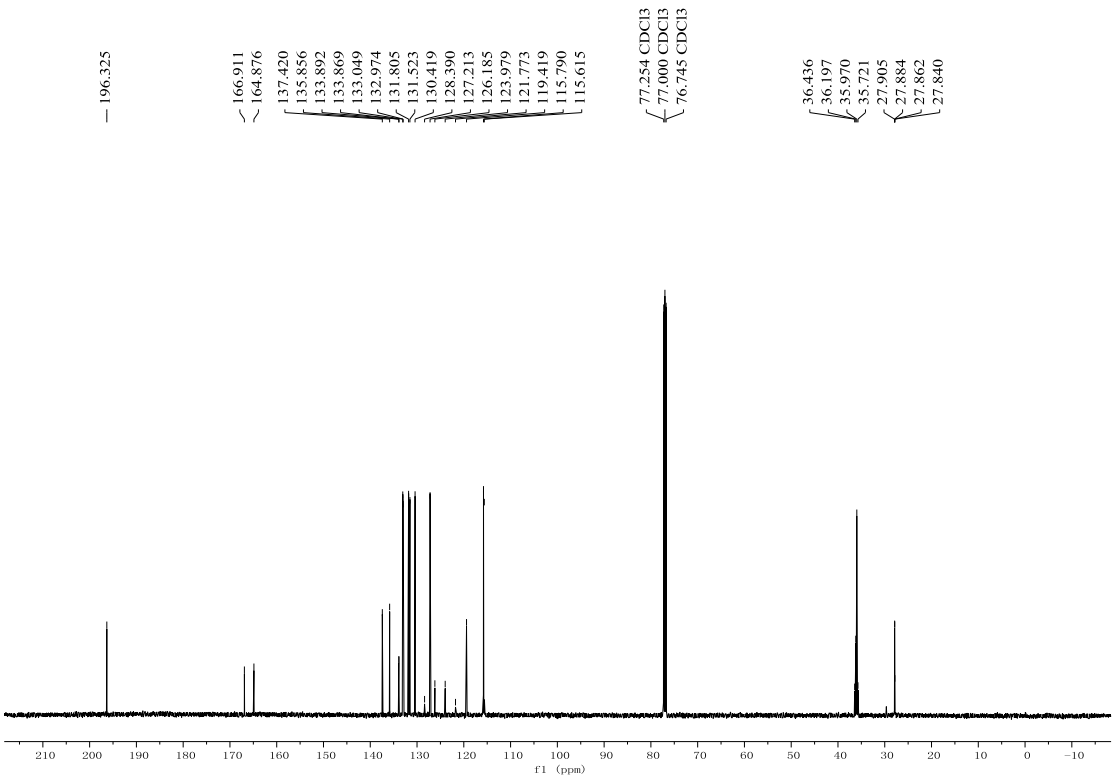
7.826
7.818
7.814
7.813
7.809
7.801
7.795
7.585
7.579
7.570
7.566
7.560
7.550
7.544
7.521
7.503
7.432
7.419
7.415
7.403
7.400
7.384
7.260
7.179
7.172
7.167
7.158
7.155
7.151
7.146
7.143
7.134
7.129
3.503
3.491
3.479
3.467
3.456
3.118
3.104
3.084
3.070
3.052
3.028
3.018
2.995
2.610
2.586
2.572
2.561
2.548
2.524
2.500
2.489
2.475
2.463
2.451
2.437
F
O
CF3
CN
3L
1.93
1.98
1.96
1.94
1.00
2.04
2.07
f1 (ppm)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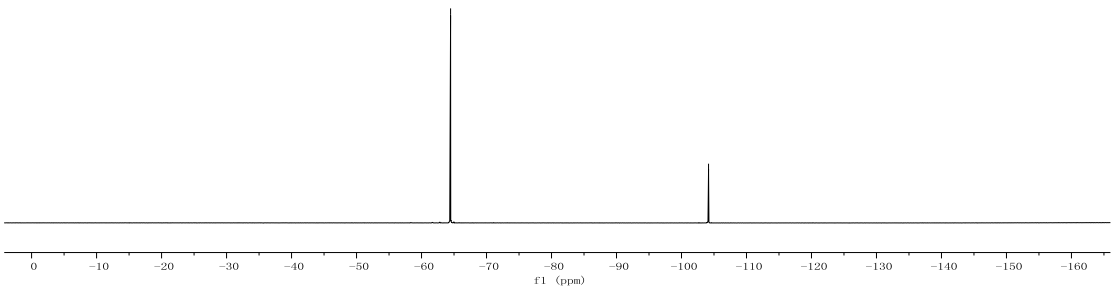
166.911
164.876
137.420
135.856
133.892
133.869
133.049
132.974
131.805
131.523
130.419
128.390
127.213
126.185
123.979
121.773
119.419
115.790
115.615
77.254 CDCl3
77.000 CDCl3
76.745 CDCl3
36.436
36.197
35.970
35.721
27.905
27.884
27.862
27.840
f1 (ppm)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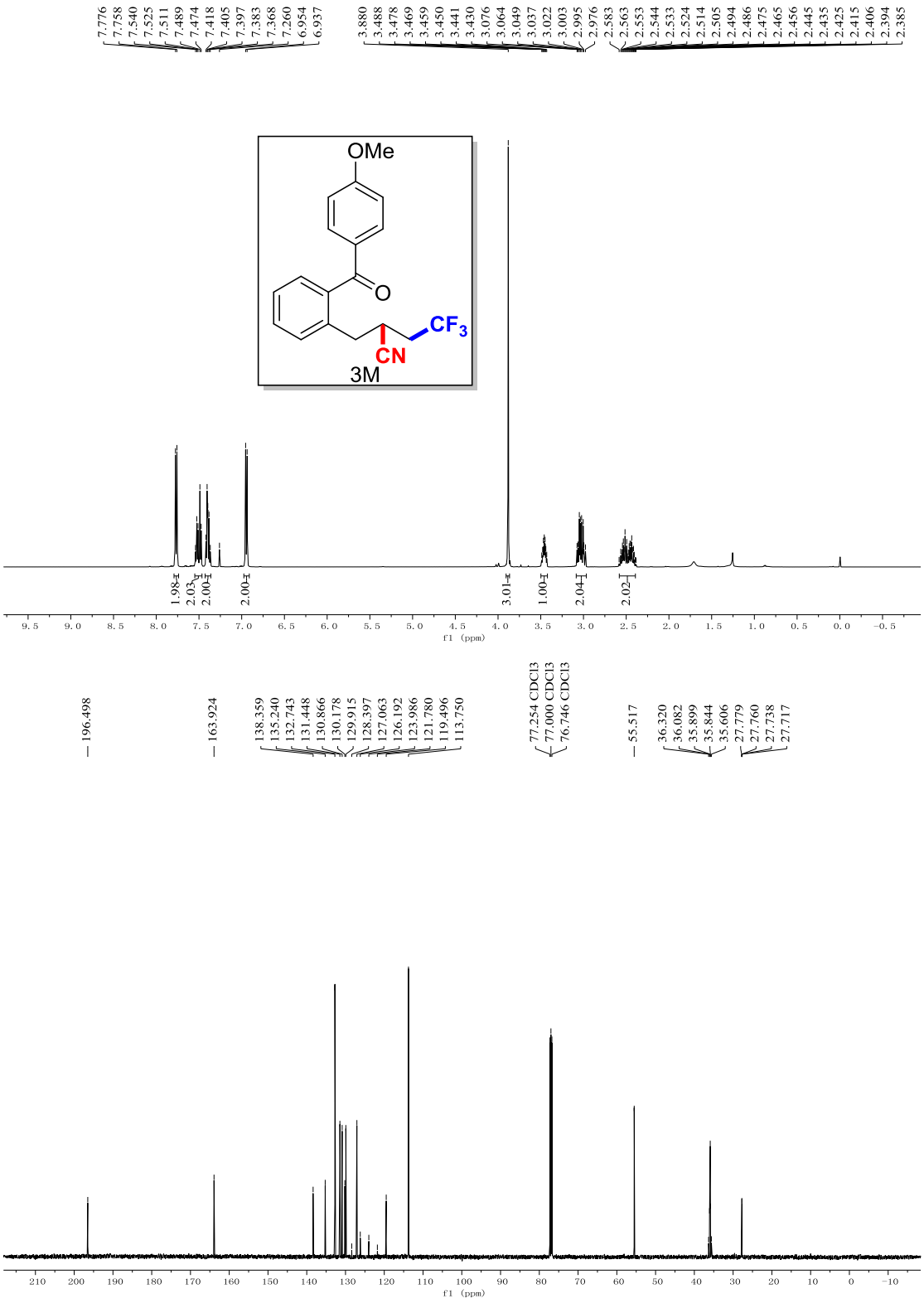
-104.161
f1 (ppm)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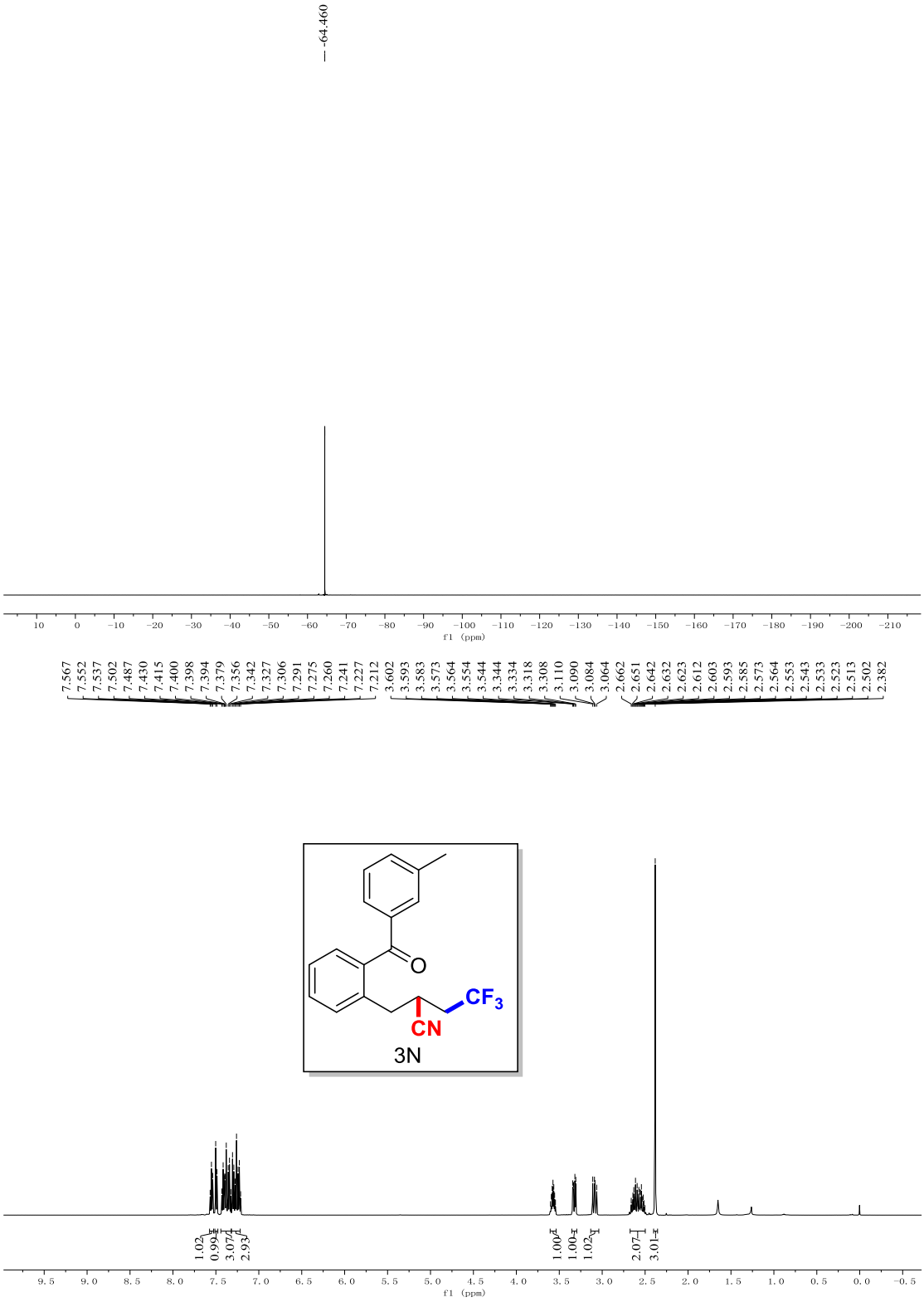
7.758
7.540
7.525
7.511
7.489
7.474
7.418
7.405
7.397
7.383
7.368
7.260
6.954
6.937
3.880
3.488
3.478
3.469
3.459
3.450
3.441
3.430
3.076
3.064
3.049
3.037
3.022
3.003
2.995
2.976
2.583
2.563
2.553
2.544
2.533
2.524
2.514
2.505
2.494
2.486
2.475
2.465
2.456
2.445
2.435
2.425
2.415
2.406
2.394
2.385
OMe
O
CF3
CN
3M
1.98
2.03
2.00
2.00
3.01
1.00
2.04
2.02
f1 (ppm)
196.498
163.924
138.359
135.240
132.743
131.448
130.866
130.178
129.915
128.397
127.063
126.192
123.986
121.780
119.496
113.750
77.254 CDCl3
77.000 CDCl3
76.746 CDCl3
55.517
36.320
36.082
35.899
35.844
35.606
27.779
27.760
27.738
27.717
f1 (ppm)


-64.460
f1 (ppm)
7.567
7.552
7.537
7.502
7.487
7.430
7.415
7.400
7.398
7.394
7.379
7.356
7.342
7.327
7.306
7.291
7.275
7.260
7.241
7.227
7.212
3.602
3.593
3.583
3.573
3.564
3.554
3.544
3.344
3.334
3.318
3.308
3.110
3.090
3.084
3.064
2.662
2.651
2.642
2.632
2.623
2.612
2.603
2.593
2.585
2.573
2.564
2.553
2.543
2.533
2.523
2.513
2.502
2.382
O
CF3
CN
3N
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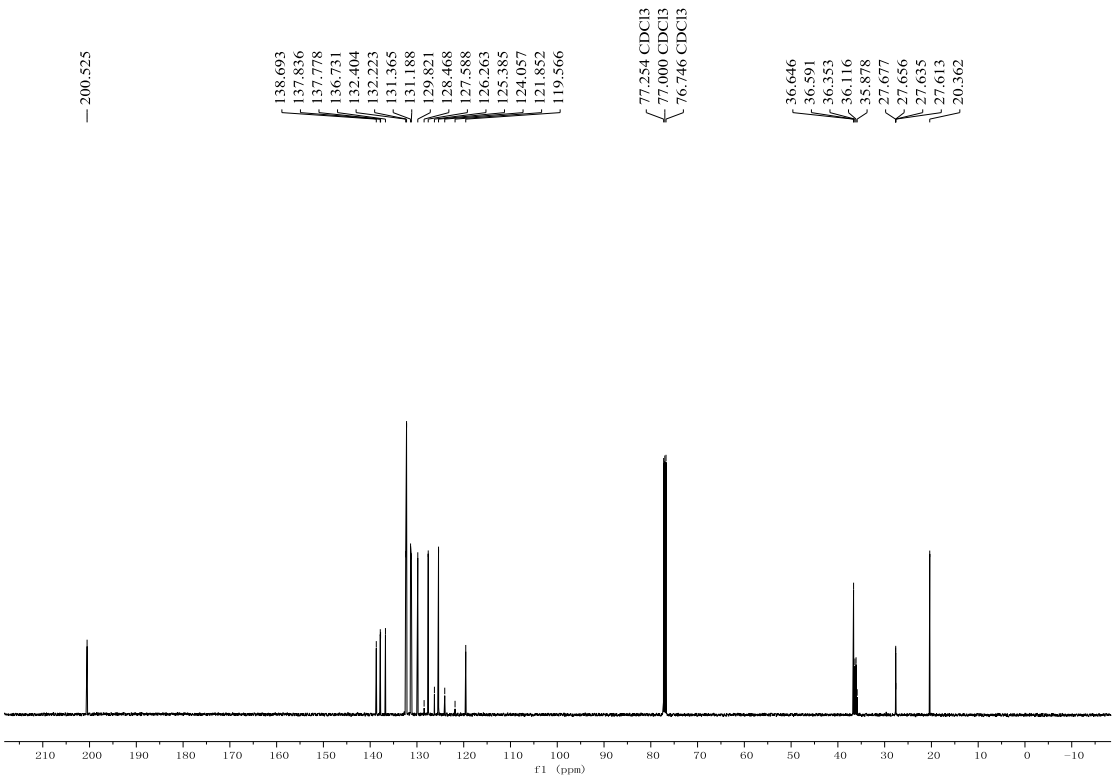
0.99
3.07
2.93
1.00
1.00
1.02
2.07
3.01
f1 (ppm)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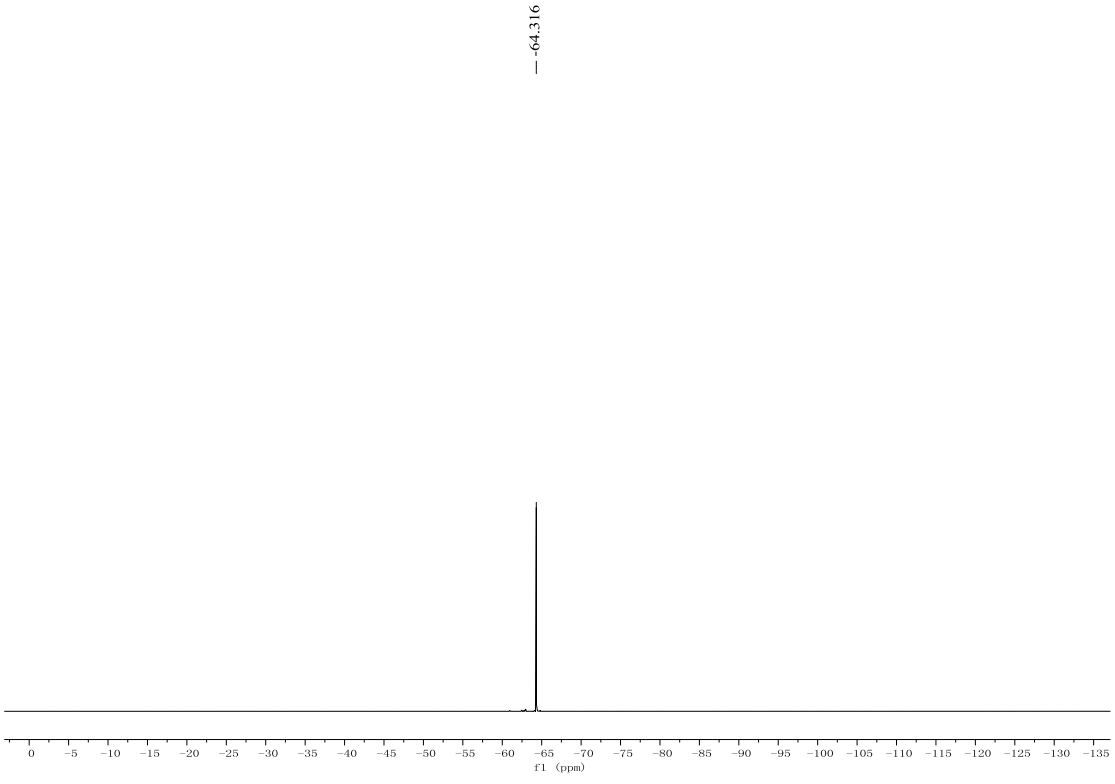
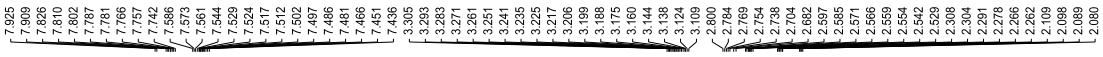
137.836
137.778
136.731
132.404
132.223
131.365
131.188
129.821
128.468
127.588
126.263
125.385
124.057
121.852
119.566
77.254 CDCl3
77.000 CDCl3
76.746 CDCl3
36.646
36.591
36.353
36.116
35.878
27.677
27.656
27.635
27.613
20.362
f1 (ppm)


-64.316
f1 (ppm)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7.909
7.826
7.810
7.802
7.787
7.781
7.766
7.757
7.742
7.586
7.573
7.561
7.544
7.529
7.524
7.517
7.512
7.502
7.497
7.486
7.481
7.466
7.451
7.436
3.305
3.293
3.283
3.271
3.261
3.251
3.241
3.235
3.225
3.217
3.206
3.199
3.188
3.175
3.160
3.144
3.138
3.124
3.109
2.800
2.784
2.769
2.754
2.738
2.704
2.682
2.597
2.585
2.571
2.566
2.559
2.554
2.542
2.529
2.308
2.304
2.291
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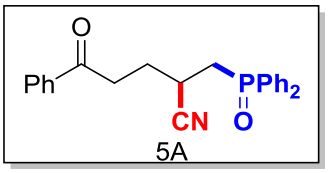
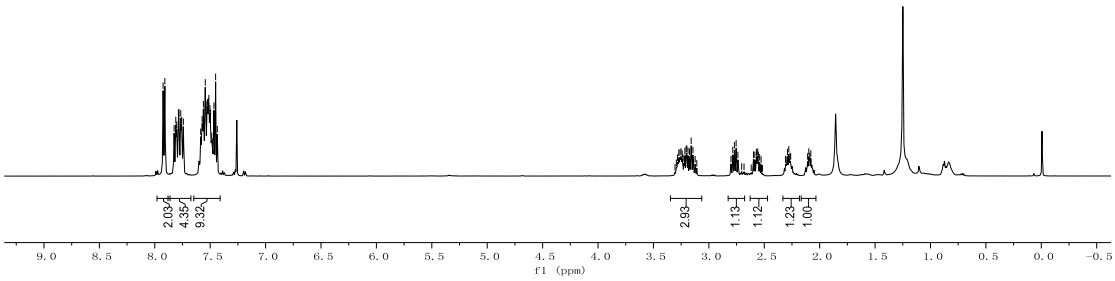
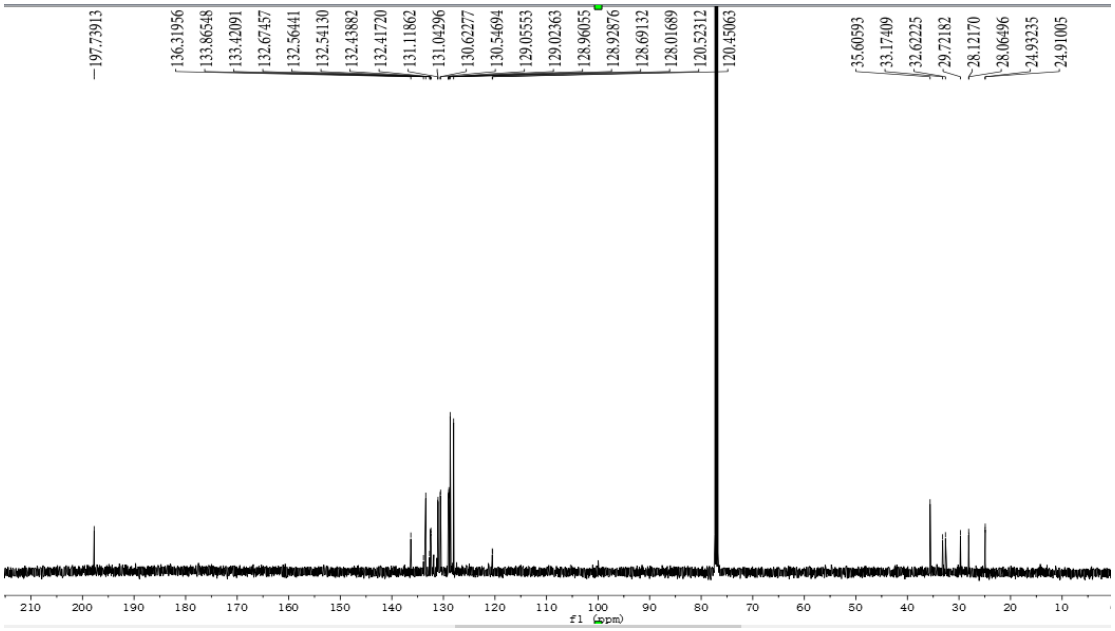
2.266
2.262
2.109
2.098
2.089
2.080


O
Ph
PPh2
CN
O
5A


2.03
4.35
9.32
2.93
1.13
1.12
1.23
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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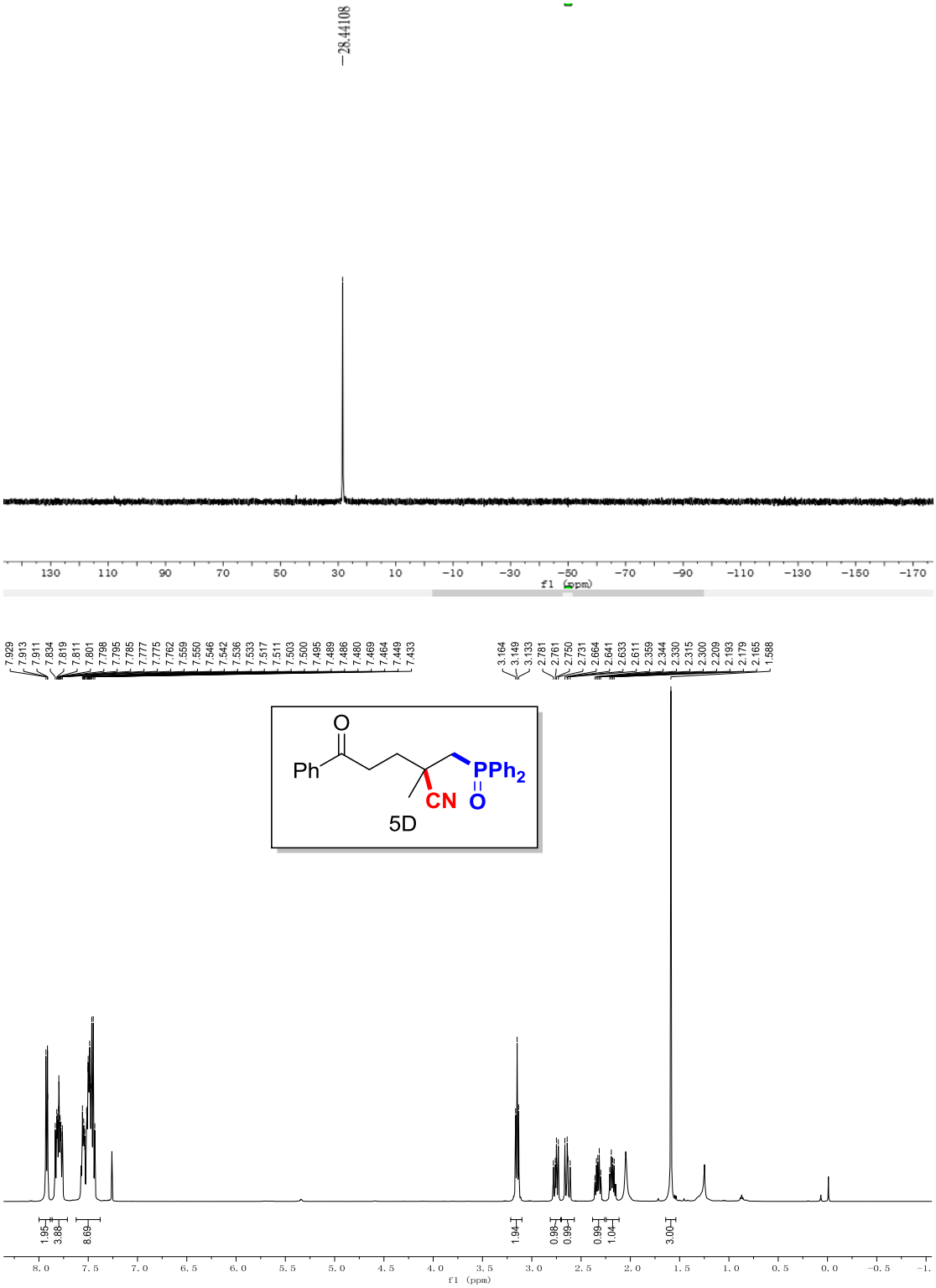
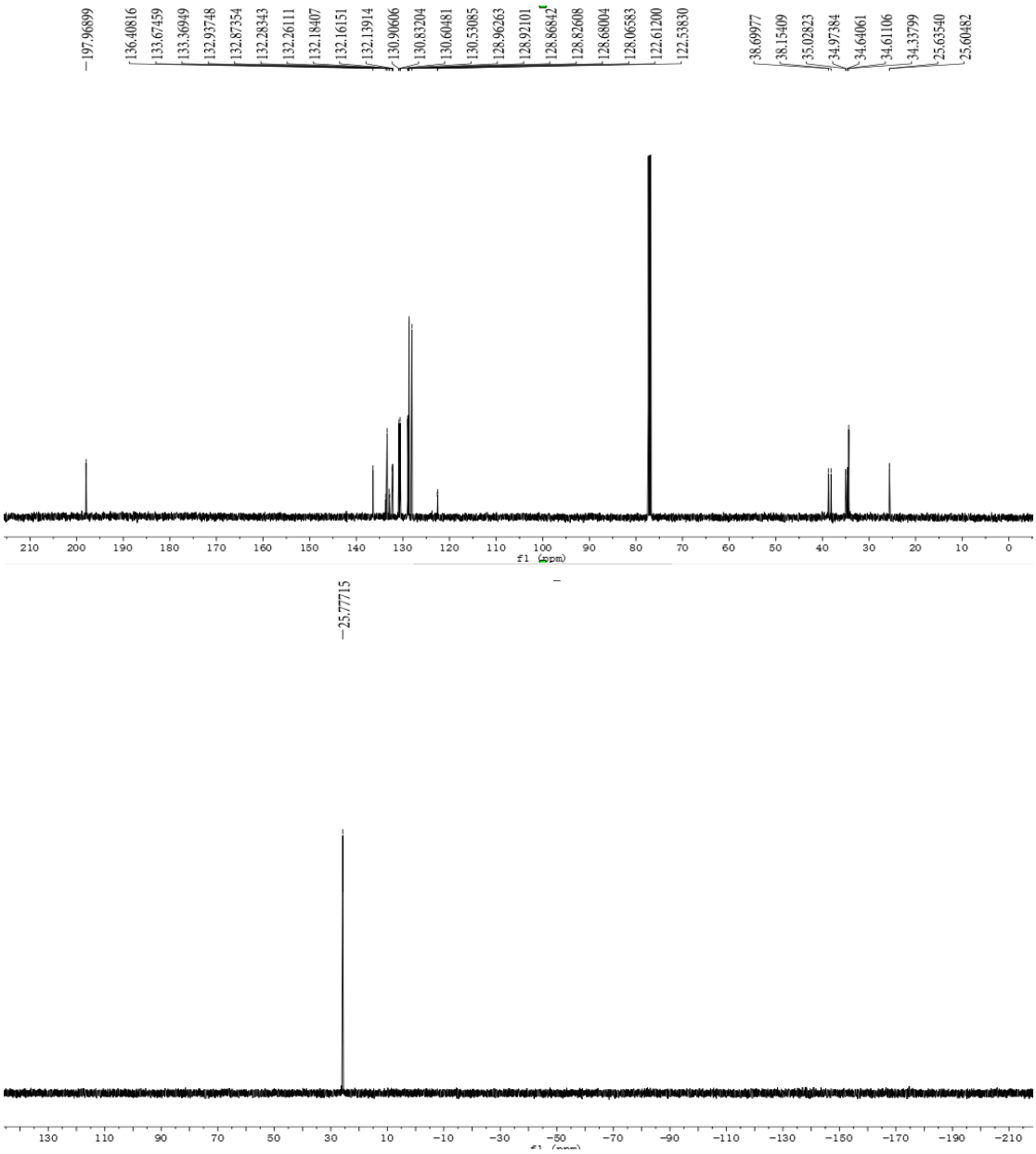
133.42091
132.67457
132.56441
132.54130
132.43882
132.41720
131.11862
131.04296
130.62277
130.54694
129.05553
129.02363
128.96055
128.92876
128.69132
128.01689
120.52312
120.45063
35.60593
33.17409
32.62225
29.72182
28.12170
28.06496
24.93235
24.91005
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


28.44108
f1 (ppm)
7.929
7.913
7.911
7.834
7.819
7.811
7.801
7.798
7.795
7.785
7.777
7.775
7.762
7.559
7.550
7.546
7.542
7.536
7.533
7.517
7.511
7.503
7.500
7.495
7.489
7.486
7.480
7.469
7.464
7.449
7.433
3.164
3.149
3.133
2.781
2.761
2.750
2.731
2.664
2.641
2.633
2.611
2.359
2.344
2.330
2.315
2.300
2.209
2.193
2.179
2.165
1.588
Ph
O
PPh2
CN
O
5D
1.95
3.88
8.69
1.94
0.98
0.99
0.99
1.04
3.00
f1 (ppm)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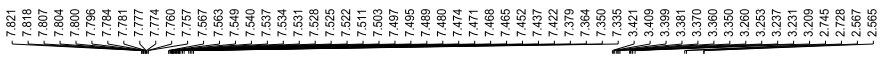
132.87354
132.28343
132.26111
132.18407
132.16151
132.13914
130.90606
130.83204
130.60481
130.53085
128.96263
128.92101
128.86842
128.82608
128.68004
128.06583
122.61200
122.53830
38.69977
38.15409
35.02823
34.97384
34.64061
34.61106
34.33799
25.63540
25.60482
25.77715
f1 (ppm)


7.821
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7.807
7.804
7.800
7.796
7.784
7.781
7.777
7.774
7.760
7.757
7.567
7.563
7.549
7.540
7.537
7.534
7.531
7.528
7.525
7.522
7.511
7.503
7.497
7.495
7.489
7.480
7.474
7.471
7.468
7.465
7.452
7.437
7.422
7.379
7.364
7.350
7.335
3.421
3.409
3.399
3.381
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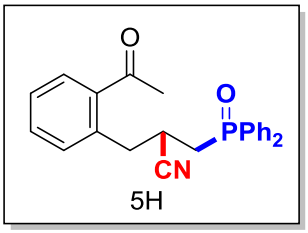
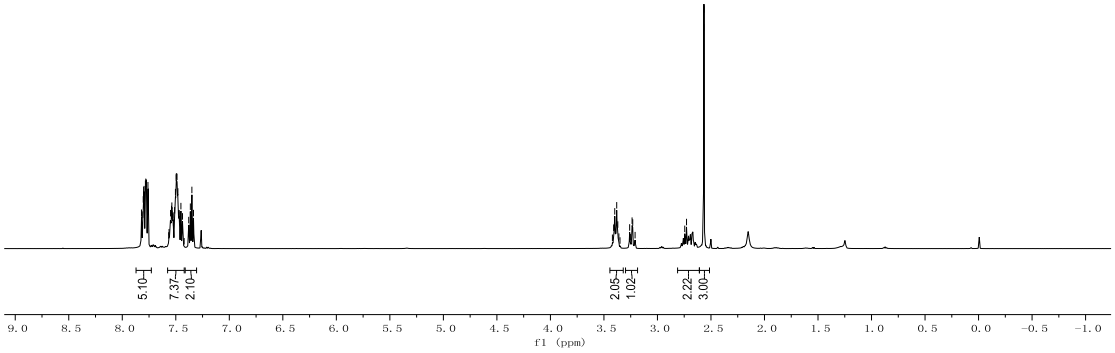
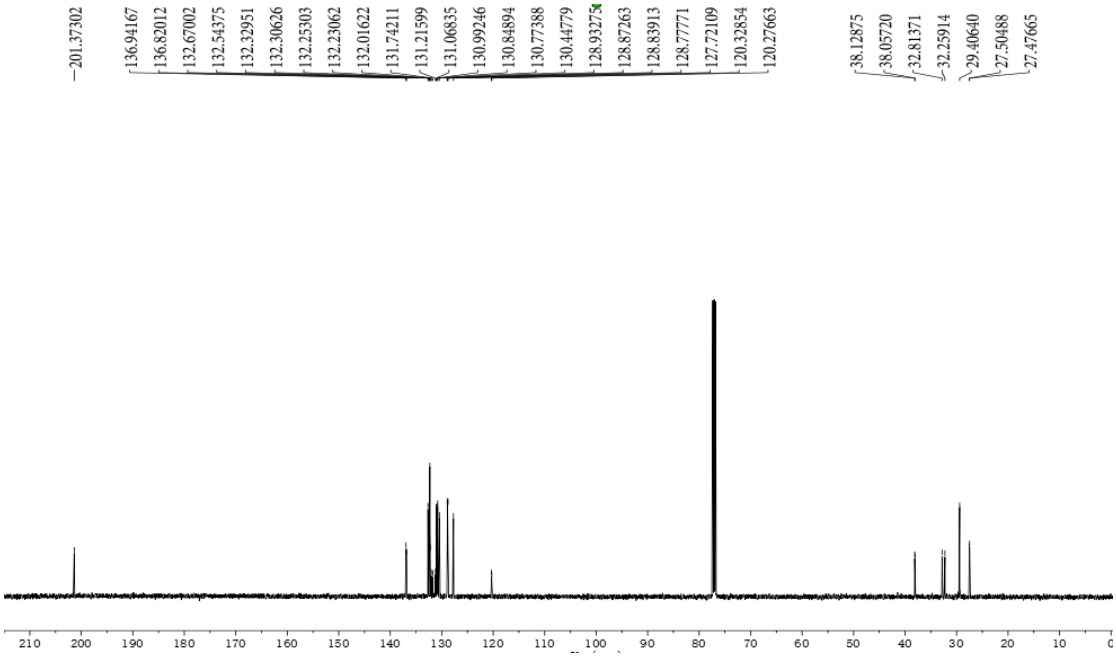
3.260
3.253
3.237
3.231
3.209
2.745
2.728
2.567
2.565


O
O
PPh2
CN
5H


5.10
7.37
2.10
2.05
1.02
2.22
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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136.82012
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132.54375
132.32951
132.30626
132.25303
132.23062
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131.21599
131.06835
130.99246
130.84894
130.77388
130.44779
128.93275
128.87263
128.83913
128.77771
127.72109
120.32854
120.27663
38.12875
38.05720
32.81371
32.25914
29.40640
27.50488
27.47665
210
200
190
180
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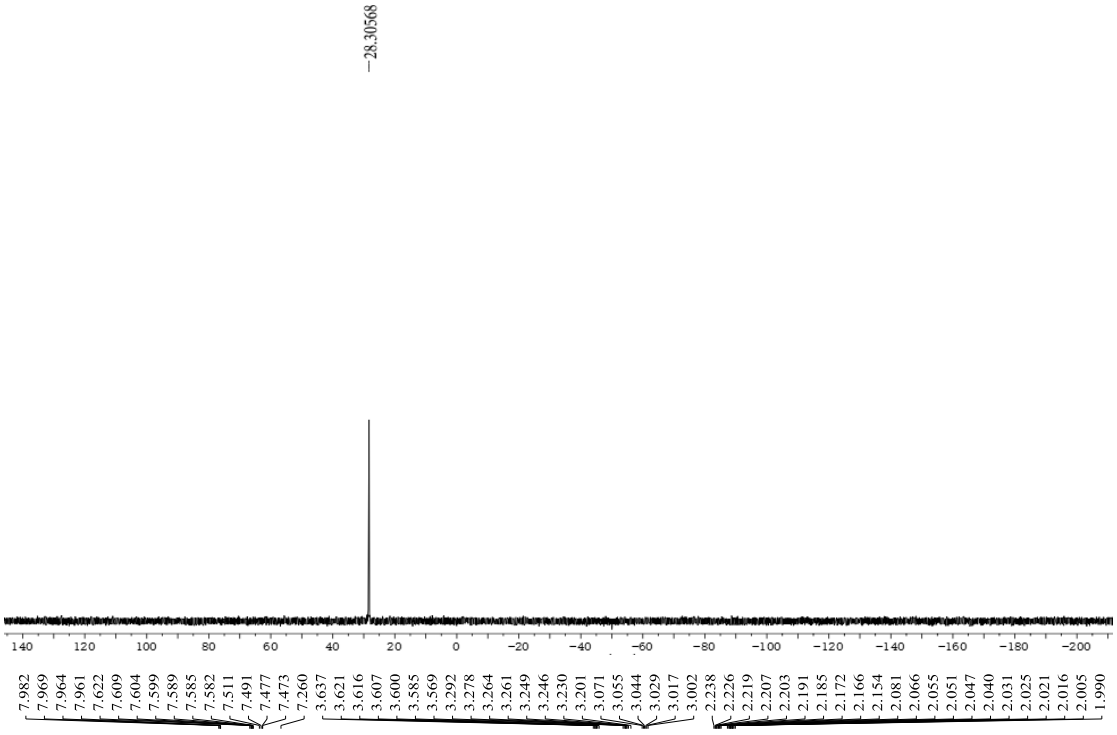
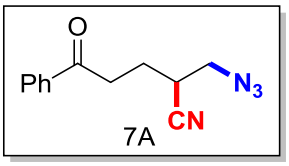
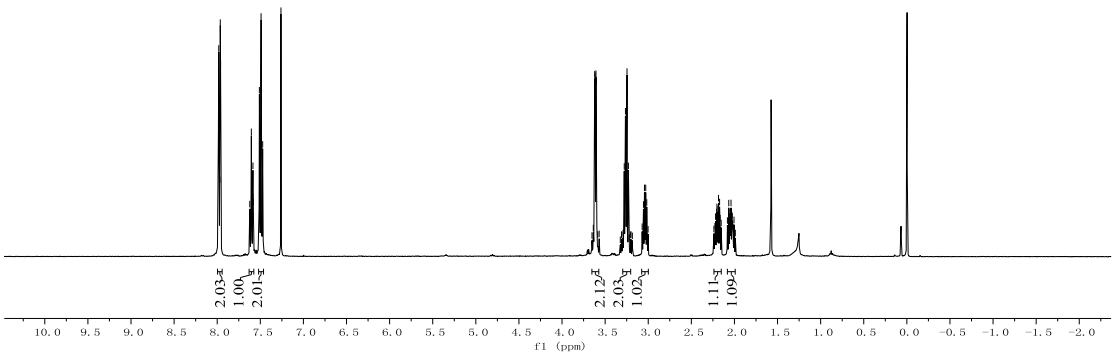
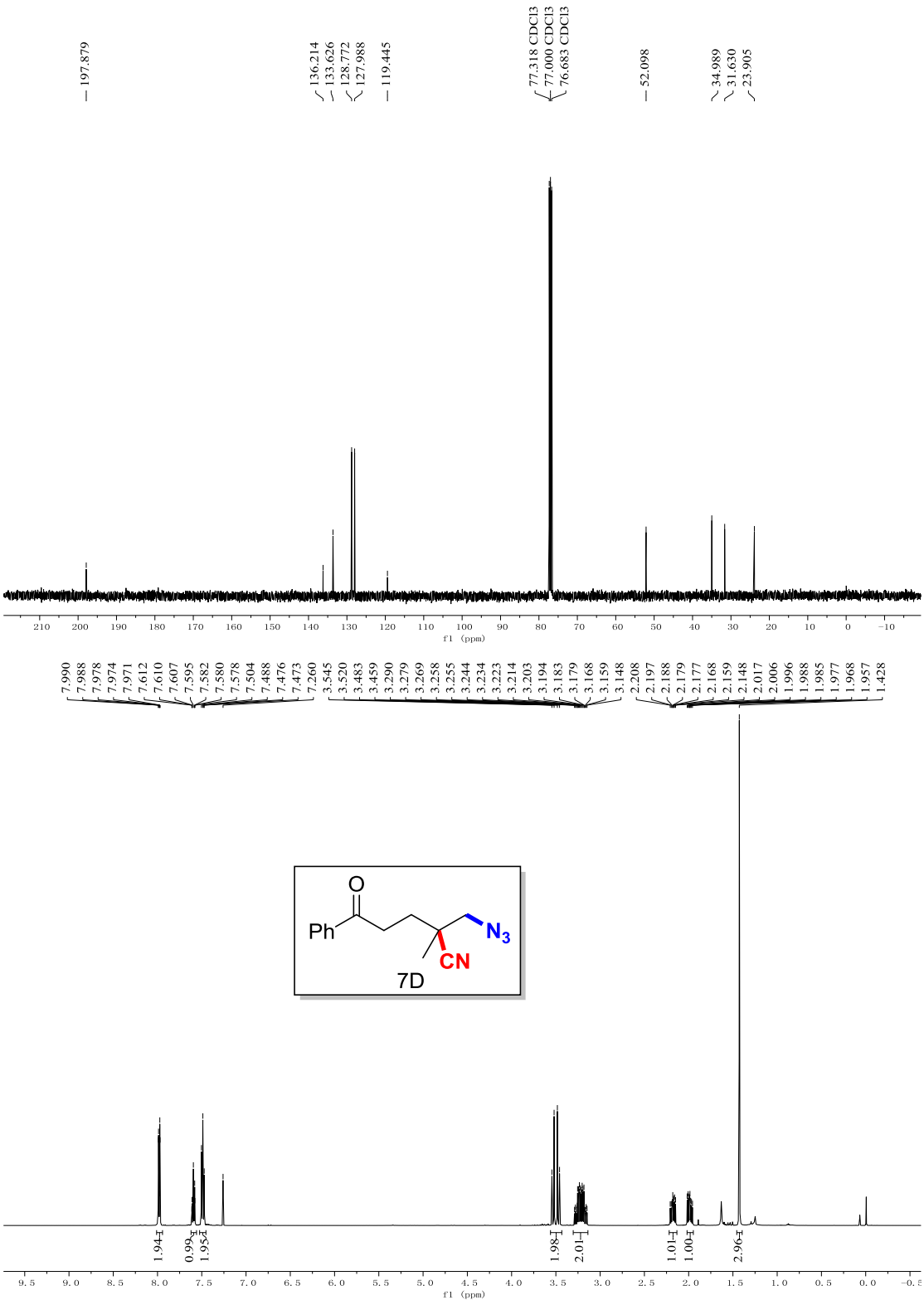
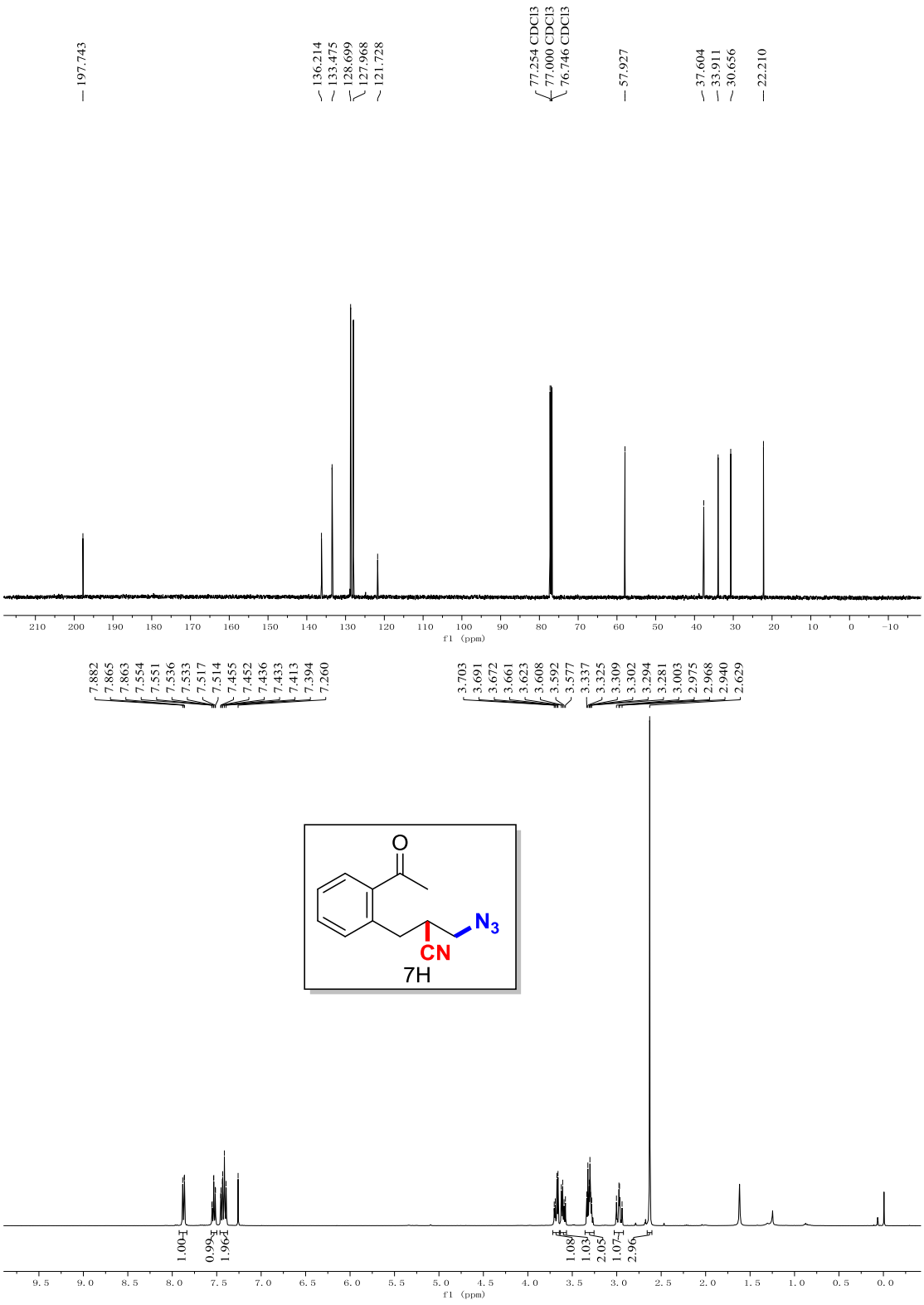
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


-28.30568
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
7.982 7.969 7.964 7.961 7.622 7.609 7.604 7.599 7.589 7.585 7.582 7.511 7.491 7.477 7.473 7.260
3.637 3.621 3.616 3.607 3.600 3.585 3.569 3.292 3.278 3.264 3.261 3.249 3.246 3.230 3.201 3.071 3.055 3.044 3.029 3.017 3.002
2.238 2.226 2.219 2.207 2.203 2.191 2.185 2.172 2.166 2.154 2.081 2.066 2.055 2.051 2.047 2.040 2.031 2.025 2.021 2.016 2.005 1.990


O
Ph
N3
CN
7A


2.03
1.00
2.01
2.12
2.03
1.02
1.11
1.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)


197.879
136.214
133.626
128.772
127.988
119.445
77.318 CDCl3
77.000 CDCl3
76.683 CDCl3
52.098
34.989
31.630
23.905
f1 (ppm)
7.990
7.988
7.978
7.974
7.971
7.612
7.610
7.607
7.595
7.582
7.580
7.578
7.504
7.488
7.476
7.473
7.260
3.545
3.520
3.483
3.459
3.290
3.279
3.269
3.258
3.255
3.244
3.234
3.223
3.214
3.203
3.194
3.183
3.179
3.168
3.159
3.148
2.208
2.197
2.188
2.179
2.177
2.168
2.159
2.148
2.017
2.006
1.996
1.988
1.985
1.977
1.968
1.957
1.428
O
Ph
N3
CN
7D
1.94
0.99
1.95
1.98
2.01
1.01
1.00
2.96
f1 (ppm)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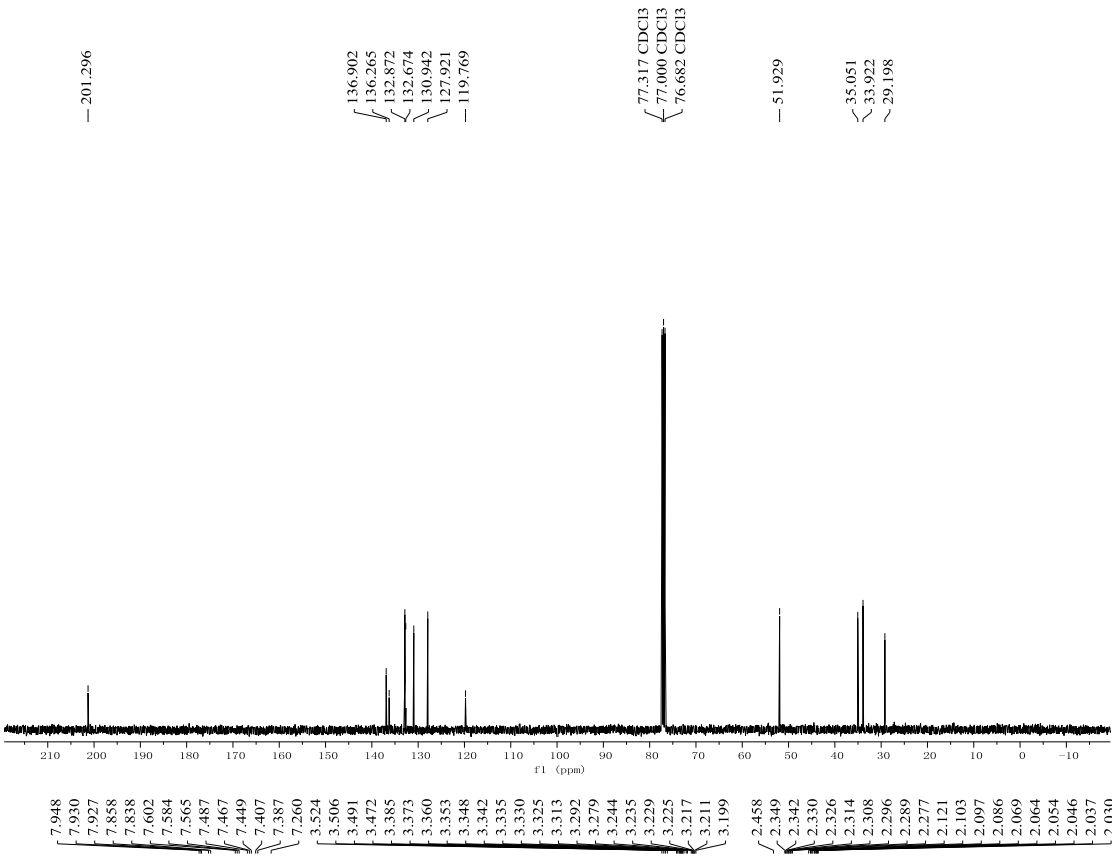
133.475
128.699
127.968
121.728
77.254 CDCl3
77.000 CDCl3
76.746 CDCl3
57.927
37.604
33.911
30.656
22.210
f1 (ppm)
7.882
7.865
7.863
7.554
7.551
7.536
7.533
7.517
7.514
7.455
7.452
7.436
7.433
7.413
7.394
7.260
3.703
3.691
3.672
3.661
3.623
3.608
3.592
3.577
3.337
3.325
3.309
3.302
3.294
3.281
3.003
2.975
2.968
2.940
2.629
O
N3
CN
7H
1.00
0.99
1.96
1.08
1.03
2.05
1.07
2.96
f1 (ppm)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136.902
136.265
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130.942
127.921
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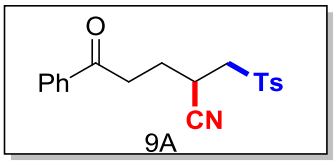
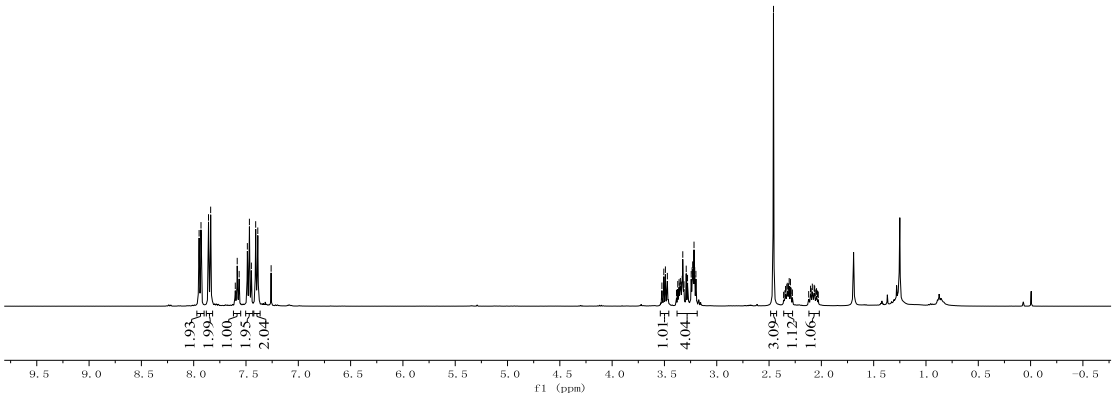
77.000 CDCl3
76.682 CDCl3
51.929
35.051
33.922
29.198
f1 (ppm)


O
Ph
Ts
CN
9A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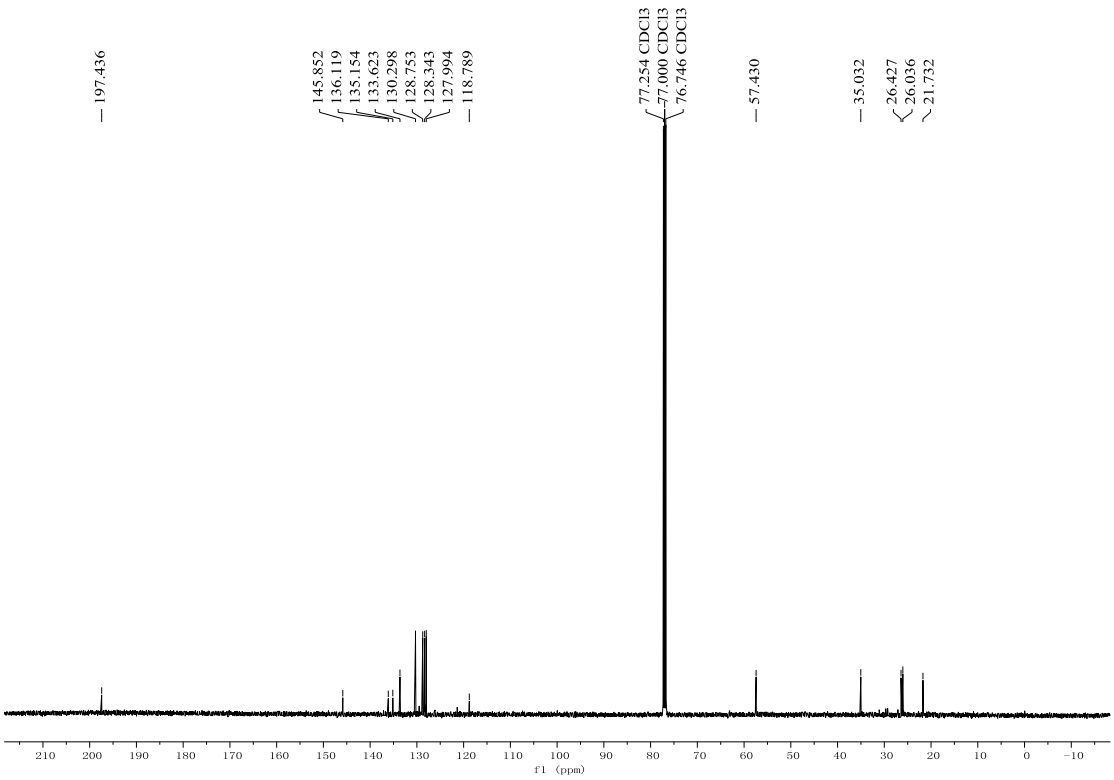
1.99
1.00
1.95
2.04
1.01
4.04
3.09
1.12
1.06
f1 (ppm)


197.436
145.852
136.119
135.154
133.623
130.298
128.753
128.343
127.994
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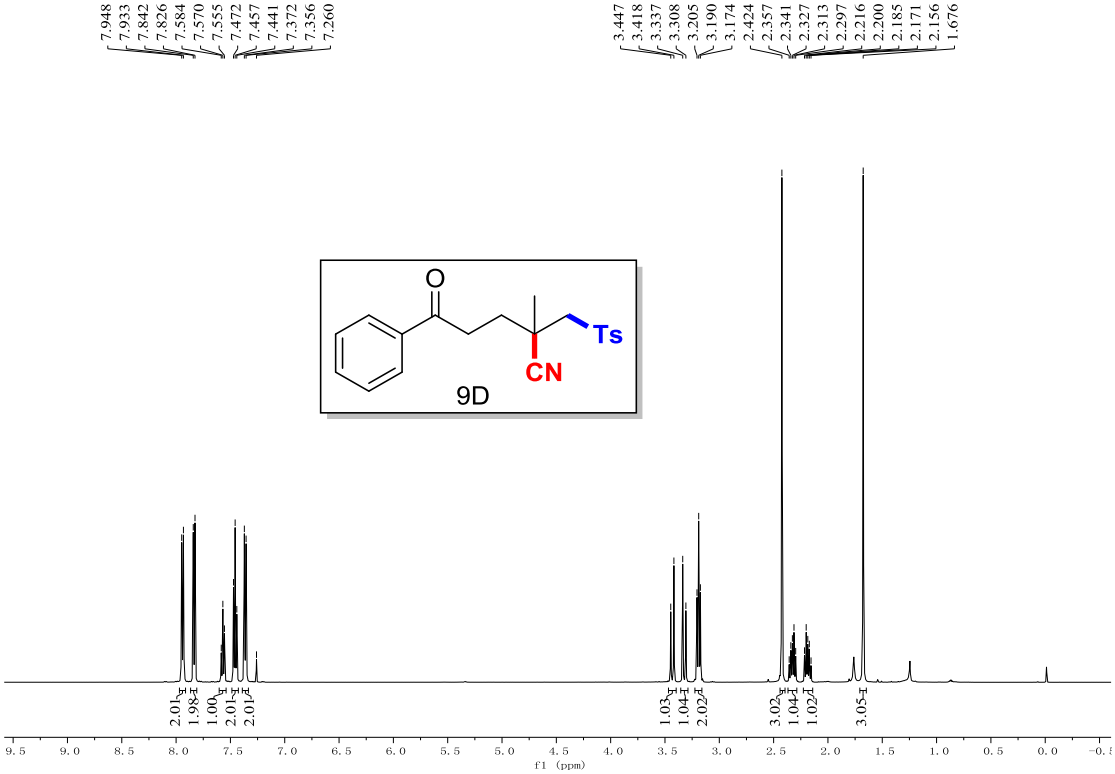
77.254 CDCl3
77.000 CDCl3
76.746 CDCl3
57.430
35.032
26.427
26.036
21.732
f1 (ppm)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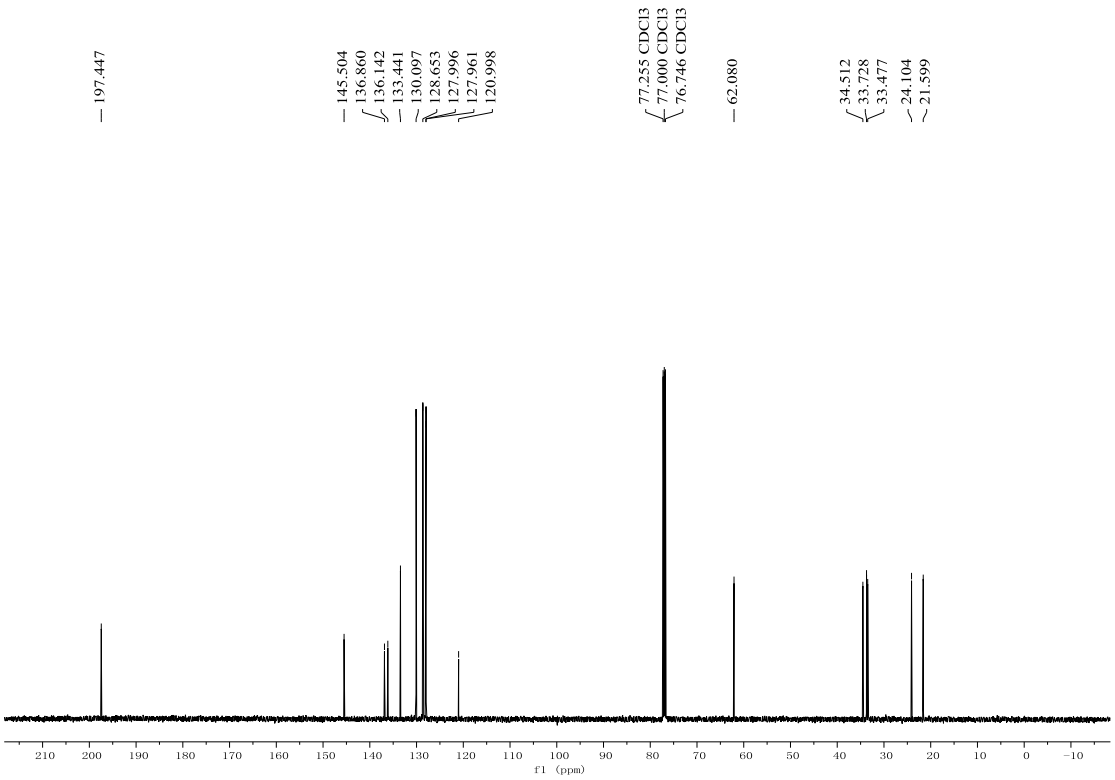
7.933
7.842
7.826
7.584
7.570
7.555
7.472
7.457
7.441
7.372
7.356
7.260
3.447
3.418
3.337
3.308
3.205
3.190
3.174
2.424
2.357
2.341
2.327
2.313
2.297
2.216
2.200
2.185
2.171
2.156
1.676
O
Ts
CN
9D
2.01
1.98
1.00
2.01
2.01
1.03
1.04
2.02
3.02
1.04
1.02
3.05
f1 (ppm)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145.504
136.860
136.142
133.441
130.097
128.653
127.996
127.961
120.998
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77.000 CDCl3
76.746 CDCl3
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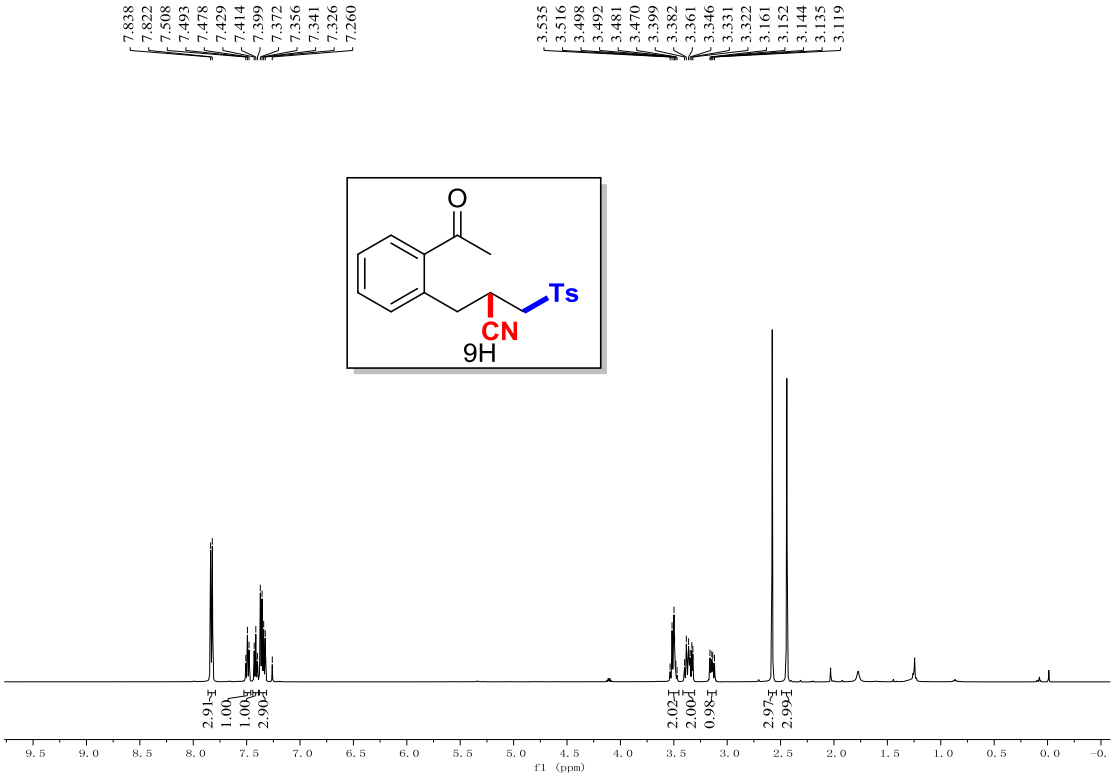
34.512
33.728
33.477
24.104
21.599
f1 (ppm)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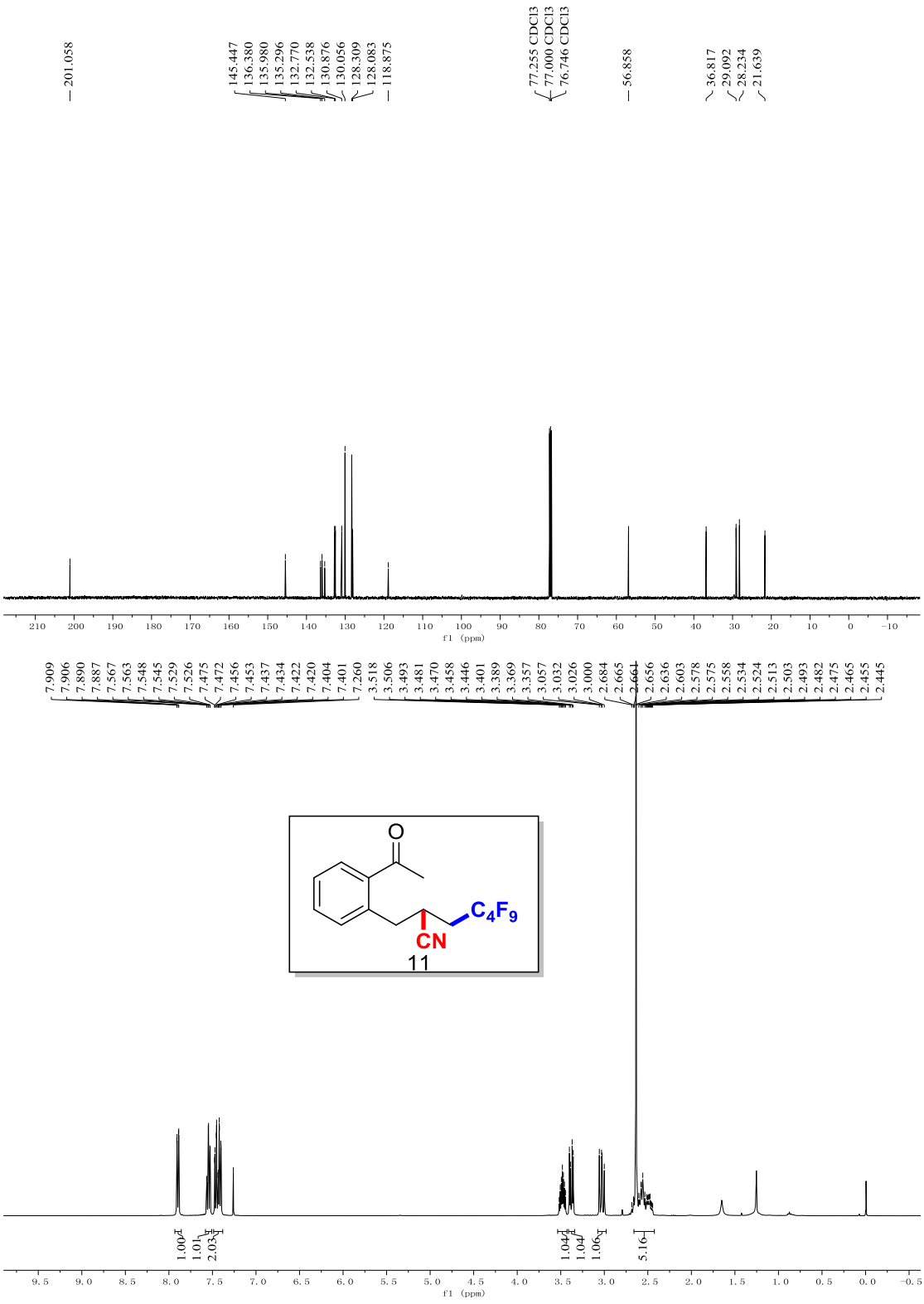
7.822
7.508
7.493
7.478
7.429
7.414
7.399
7.372
7.356
7.341
7.326
7.260
3.535
3.516
3.498
3.492
3.481
3.470
3.399
3.382
3.361
3.346
3.331
3.322
3.161
3.152
3.144
3.135
3.119
O
Ts
CN
9H
2.91
1.00
1.00
2.90
2.02
2.00
0.98
2.97
2.99
f1 (ppm)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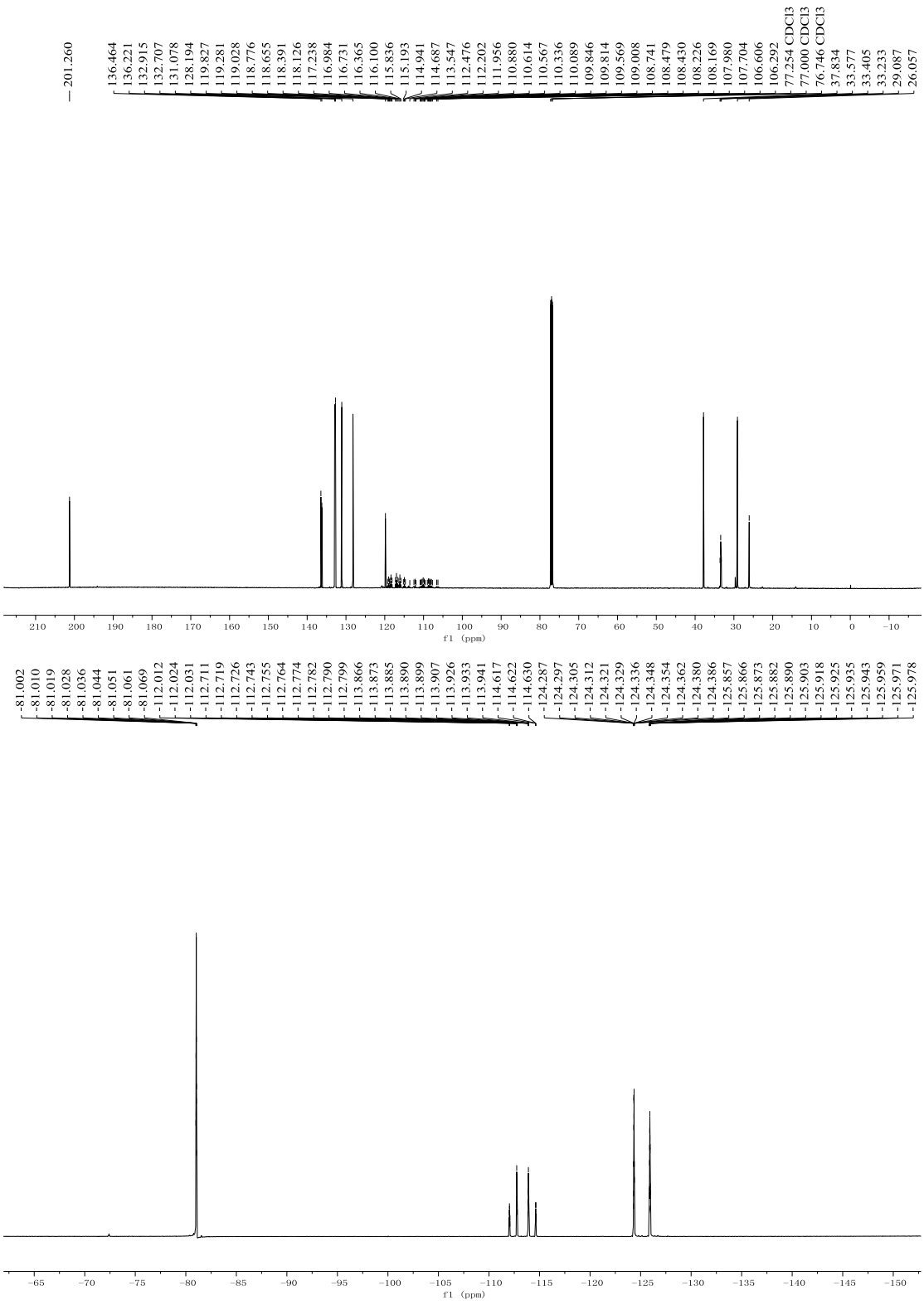
136.380
135.980
135.296
132.770
132.538
130.876
130.056
128.309
128.083
118.875
77.255 CDCl3
77.000 CDCl3
76.746 CDCl3
56.858
36.817
29.092
28.234
21.639
f1 (ppm)
7.909
7.906
7.890
7.887
7.567
7.563
7.548
7.545
7.529
7.526
7.475
7.472
7.456
7.453
7.437
7.434
7.422
7.420
7.404
7.401
7.260
3.518
3.506
3.493
3.481
3.470
3.458
3.446
3.401
3.389
3.369
3.357
3.057
3.032
3.026
3.000
2.684
2.665
2.661
2.656
2.636
2.603
2.578
2.575
2.558
2.534
2.524
2.513
2.503
2.493
2.482
2.475
2.465
2.455
2.445
O
C4F9
CN
11
1.00
1.01
2.03
1.04
1.04
1.06
5.16
f1 (ppm)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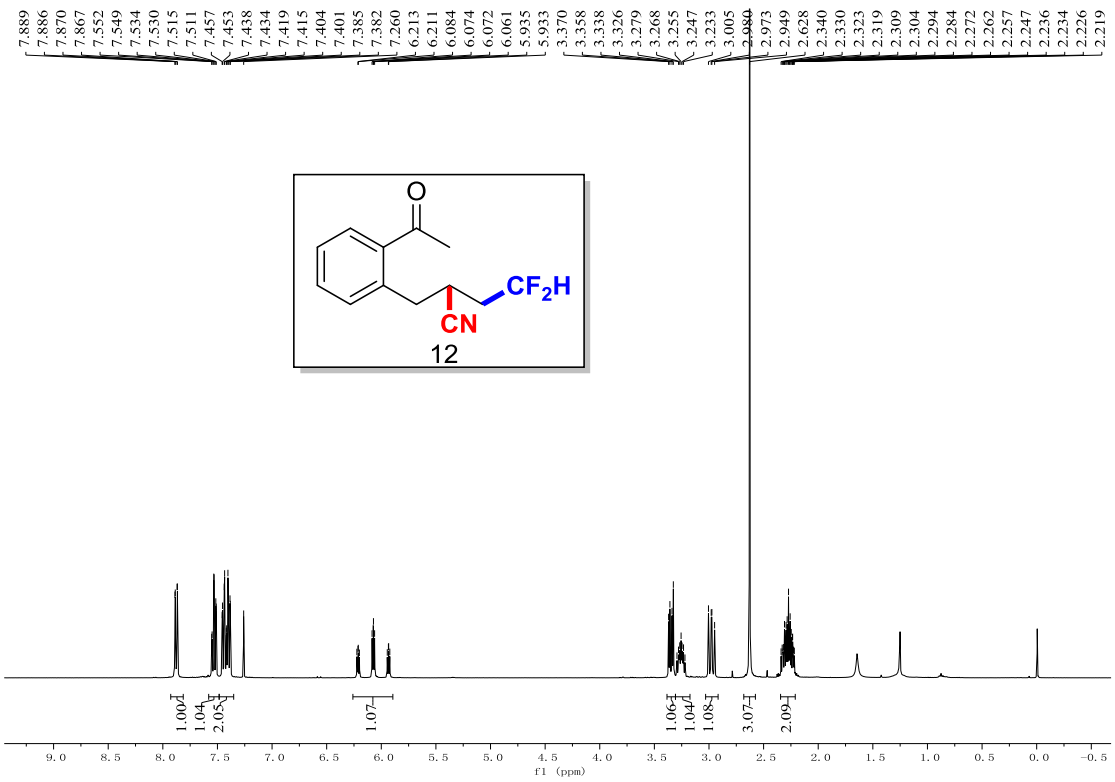
118.655
118.391
118.126
117.238
116.984
116.731
116.365
116.100
115.836
115.193
114.941
114.687
113.547
112.476
112.202
111.956
110.880
110.614
110.567
110.336
110.089
109.846
109.814
109.569
109.008
108.741
108.479
108.430
108.226
108.169
107.980
107.704
106.606
106.292
77.254 CDCl3
77.000 CDCl3
76.746 CDCl3
37.834
33.577
33.405
33.233
29.087
26.057
f1 (ppm)
-81.002
-81.010
-81.019
-81.028
-81.036
-81.044
-81.051
-81.061
-81.069
-112.012
-112.024
-112.031
-112.711
-112.719
-112.726
-112.743
-112.755
-112.764
-112.774
-112.782
-112.790
-112.799
-113.866
-113.873
-113.885
-113.890
-113.899
-113.907
-113.926
-113.933
-113.941
-114.617
-114.622
-114.630
-124.287
-124.297
-124.305
-124.312
-124.321
-124.329
-124.336
-124.348
-124.354
-124.362
-124.380
-124.386
-125.857
-125.866
-125.873
-125.882
-125.890
-125.903
-125.918
-125.925
-125.935
-125.943
-125.959
-125.971
-125.978
f1 (ppm)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7.867
7.552
7.549
7.534
7.530
7.515
7.511
7.457
7.453
7.438
7.434
7.419
7.415
7.404
7.401
7.385
7.382
7.260
6.213
6.211
6.084
6.074
6.072
6.061
5.935
5.933
3.370
3.358
3.338
3.326
3.279
3.268
3.255
3.247
3.233
3.005
2.973
2.949
2.628
2.340
2.330
2.323
2.319
2.309
2.304
2.294
2.284
2.272
2.262
2.257
2.247
2.236
2.234
2.226
2.219
O
CF2H
CN
12
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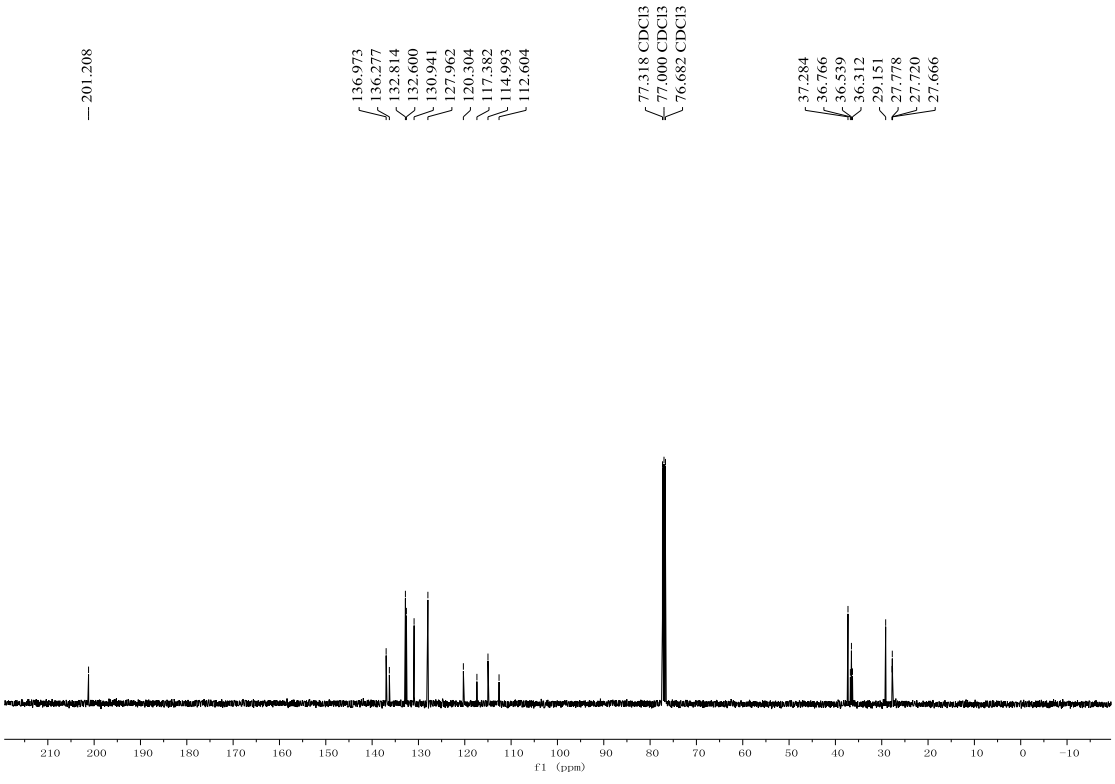
1.04
2.05
1.07
1.06
1.04
1.08
3.07
2.09
f1 (ppm)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136.277
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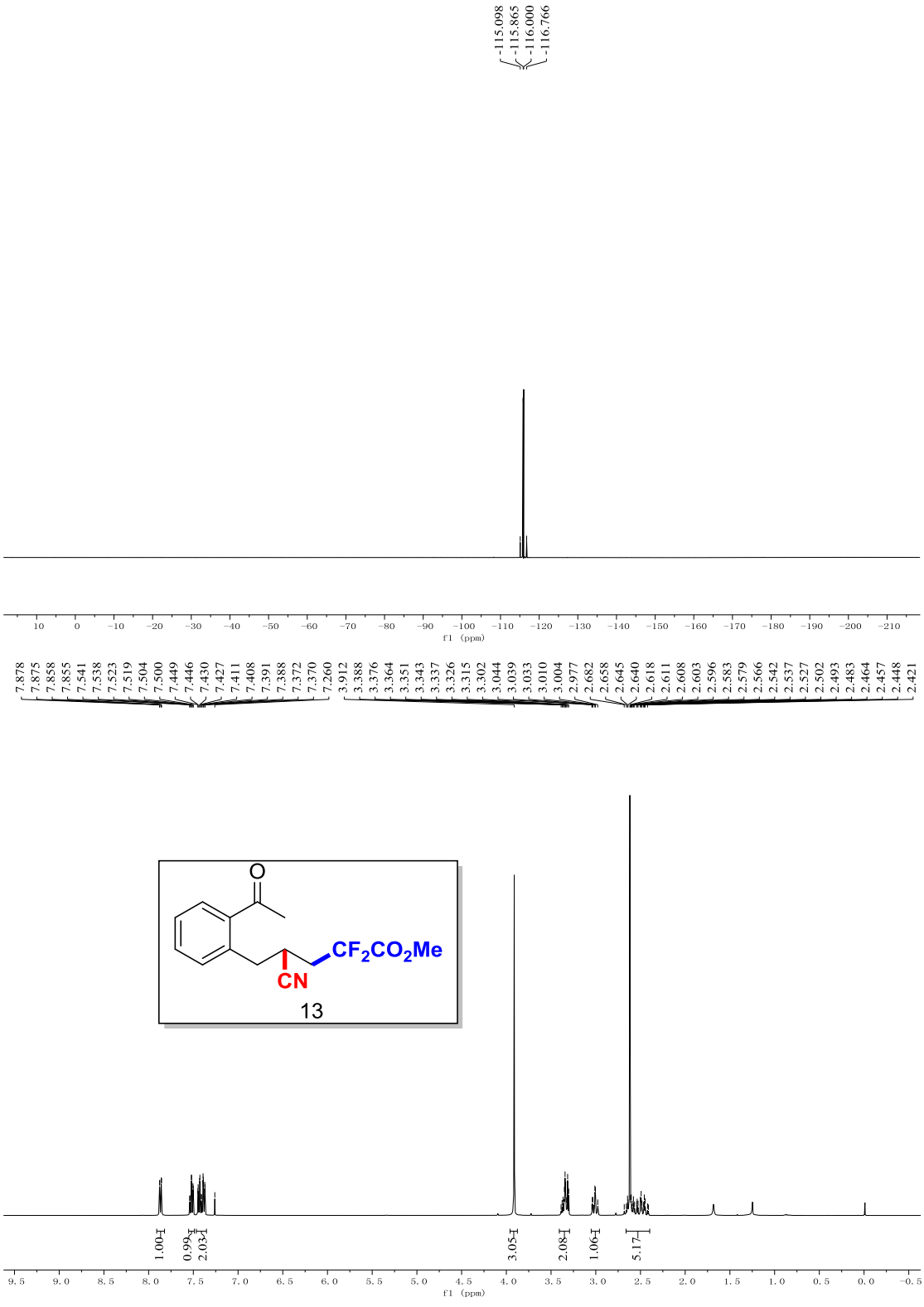
132.600
130.941
127.962
120.304
117.382
114.993
112.604
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
37.284
36.766
36.539
36.312
29.151
27.778
27.720
27.666
f1 (ppm)


-115.098
-115.865
-116.000
-116.766
f1 (ppm)
7.878
7.875
7.858
7.855
7.541
7.538
7.523
7.519
7.504
7.500
7.449
7.446
7.430
7.427
7.411
7.408
7.391
7.388
7.372
7.370
7.260
3.912
3.388
3.376
3.364
3.351
3.343
3.337
3.326
3.315
3.302
3.044
3.039
3.033
3.010
3.004
2.977
2.682
2.658
2.645
2.640
2.618
2.611
2.608
2.603
2.596
2.583
2.579
2.566
2.542
2.537
2.527
2.502
2.493
2.483
2.464
2.457
2.448
2.421
O
CF2CO2Me
CN
13
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0.99
2.03
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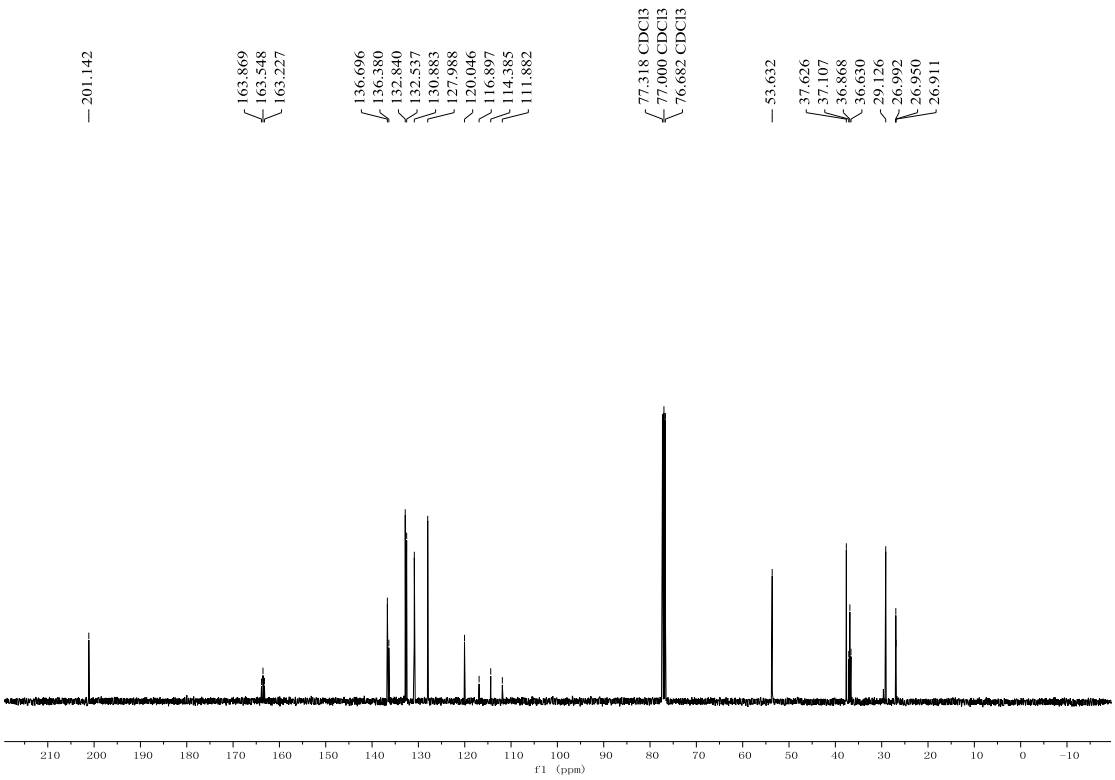
2.08
1.06
5.17
f1 (ppm)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132.537
130.883
127.988
120.046
116.897
114.385
111.882
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
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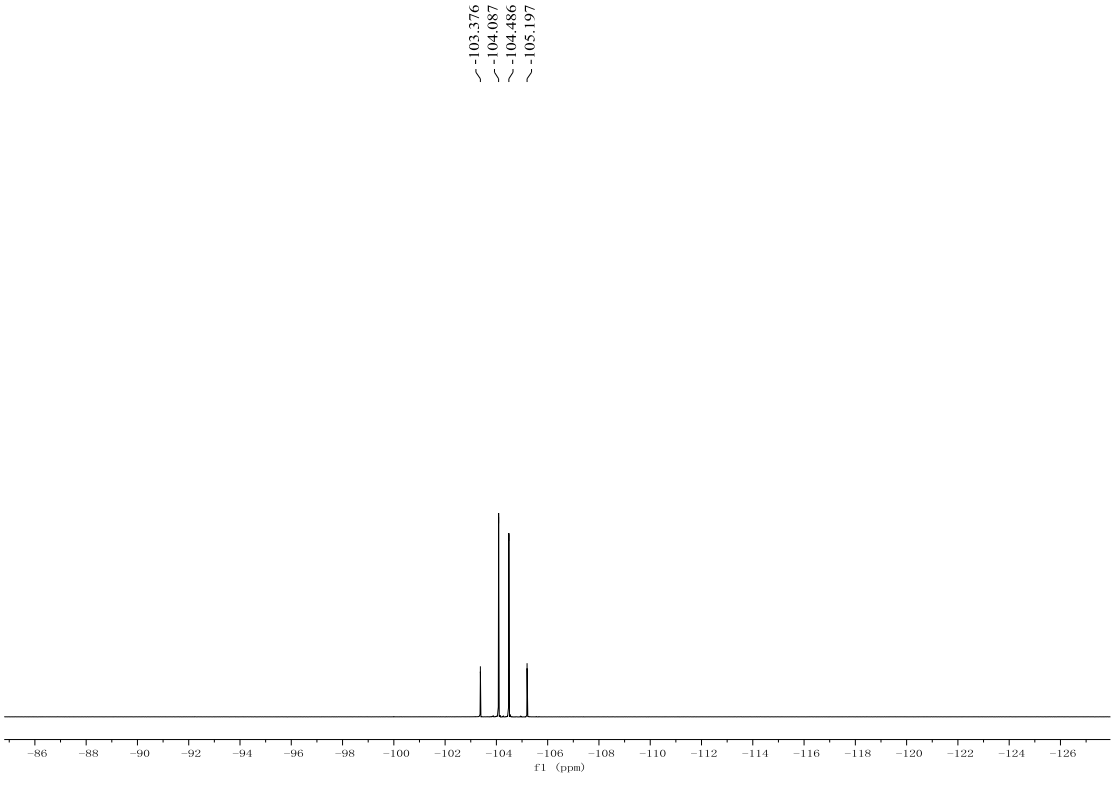
37.107
36.868
36.630
29.126
26.992
26.950
26.911
f1 (ppm)


-103.376
-104.087
-104.486
-105.197
f1 (ppm)

Reference

(1) Evans, D. A.; Truesdale, L. K.; Carroll, G. L. *J. Chem. Soc, Chem. Commun.* **1973**, 55.