Supporting Information

Copper-Catalyzed *anti*-Selective Radical 1,2-Alkylarylation of Terminal Alkynes

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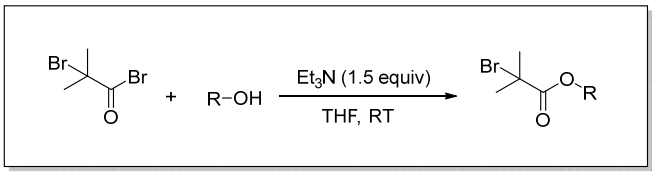
General information

All reactions were carried out under argon atmosphere using Schlenk techniques unless otherwise noted. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. CuI and **L3** were purchased from Bide Pharmatech Ltd. K_2CO_3 was purchased from Aladdin. Toluene and Et_2O was purchased from Aladdin, which was distilled with sodium and benzophenone under argon atmosphere. Anhydrous THF, DMF and DCE were purchased from J&K Scientific. Other solvents and reagents were purchased from Aladdin, J&K Scientific, Tansoole, and Bidepharm. For reactions that need heating, an oil bath was employed and the temperature of the oil bath was denoted. 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 colorless (254 nm), iodine, or basic $KMnO_4$ indicator.

NMR spectra were recorded on Bruker DRX-400 and DPX-600 spectrometers at 400 or 600 MHz for ^1H NMR, 100 or 150 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. The chemical shifts were expressed in ppm and coupling constants were given in Hz. Data for ^1H NMR were recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR were reported in terms of chemical shift (δ, ppm). HRMS measurements were performed with a Thermo Q Exactive mass spectrometer with an orbitrap mass analyzer. X-ray diffraction was measured on a Bruker D8 VENTURE diffractometer with MoKα (λ = 0.71073) radiation.

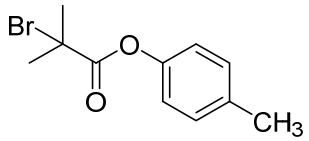
The synthesis of substrates

All alkynes and aryl boronic acids and most of radical precursors were purchased from commercial sources. The radical precursors **2b** and **2c** were synthesized according to the reported literature.[1]



To a solution of phenol or alcohol (10 mmol, 1.0 equiv) and Et_3N (2.08 mL, 15 mmol, 1.5 equiv) in THF (30 mL) in an ice bath was added a solution of 2-bromoisobutyryl bromide (1.8 mL, 15 mmol, 1.5 equiv) dropwise under argon for 5 min. The reaction mixture was stirred at room temperature for 12 h, and then filtrated through a short pad of silica. The filtrate was concentrated in *vacuo*, and the residue was diluted in DCM (60 mL), washed with 0.1 M HCl aq. (40 mL), and sat. $NaHCO_3$ solution (40 mL) sequentially. The organic layer was dried with Na_2SO_4 and concentrated in *vacuo*. Further purification by flash column chromatography.

_p_-tolyl 2-bromo-2-methylpropanoate (2b)



2b

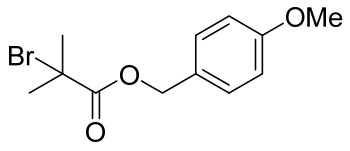
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1) to afford **2b** (2.31 g, 90% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H), 2.05 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 148.6, 135.9, 130.1, 120.8, 55.6, 30.8, 21.0.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{14}BrO_2$ $[M + H]^+$ 257.0099, found 257.0010.

4-methoxybenzyl 2-bromo-2-methylpropanoate (2c)



2c

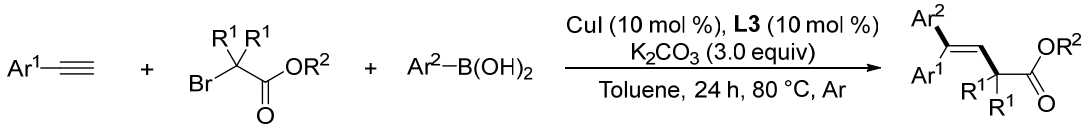
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **2c** (2.53 g, 88% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 5.14 (s, 2H), 3.79 (s, 3H), 1.93 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 159.7, 129.9, 127.5, 113.9, 67.5, 55.9, 55.2, 30.8.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{16}BrO_3$ $[M + H]^+$ 287.0277, found 287.0281.

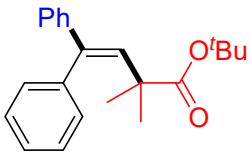
Typical procedure for 1,2-alkylarylation of alkynes



1 **2** **3** **4-39**

To a 10 mL sealable tube were sequentially added alkene **1** (0.20 mmol), **2** (0.40 mmol, 2.0 equiv), **3** (0.40 mmol, 2.0 equiv), CuI (3.81 mg, 0.020 mmol, 10 mol %), **L3** (8.02 mg, 0.020 mmol, 10 mol %), K_2CO_3 (82.9 mg, 0.60 mmol, 3.0 equiv), and toluene (2.0 mL) under argon atmosphere. Then the tube was sealed and the reaction mixture was stirred in an oil bath at 80 °C for 24 h. After the completion of reaction, the pure product was isolated by flash column chromatography.

tert-Butyl 2,2-dimethyl-4,4-diphenylbut-3-enoate (4)



4

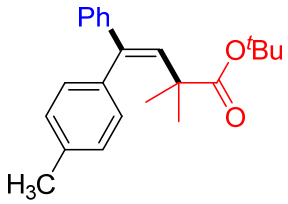
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40/1) to afford **4** (65.7 mg, 98% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.27 (m, 3H), 7.27 – 7.14 (m, 7H), 6.13 (s, 1H), 1.38 (s, 9H), 1.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 144.0, 141.7, 140.2, 134.1, 130.3, 128.1, 128.0, 127.4, 127.3, 127.1, 80.3, 45.0, 28.0, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{26}NaO_2$ $[M + Na]^+$ 345.1825, found 345.1831.

tert-Butyl-2,2-dimethyl-4-phenyl-4-(*p*-tolyl)but-3-enoate (5)



5

The product mixture was purified by silica gel column chromatography (petroleum

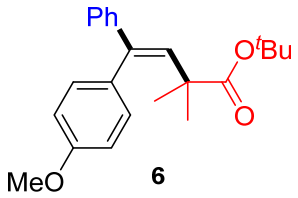
ether/ethyl acetate = 30/1) to afford **5** (65.3 mg, *anti/syn* = 17/1, 97% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.15 (m, 5H), 7.13 – 7.11 (m, 2H), 7.06 – 7.03 (m, 2H), 6.10 (s, 1H), 2.35 (s, 3H), 1.38 (s, 9H), 1.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 144.2, 141.7, 137.2, 136.9, 134.0, 130.1, 128.8, 128.1, 127.5, 127.0, 80.2, 45.0, 28.0, 27.5, 21.4.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{28}NaO_2$ $[M + Na]^+$ 359.1982, found 359.1988.

tert-Butyl-4-(4-methoxyphenyl)-2,2-dimethyl-4-phenylbut-3-enoate (6)



6

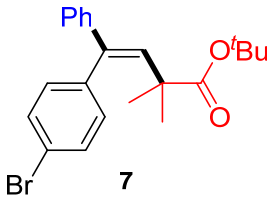
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **6** (63.4 mg, *anti/syn* = 5/1, 90% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.16 (m, 5H), 7.11 – 7.03 (m, 2H), 6.87 – 6.84 (m, 2H), 6.09 (s, 1H), 3.81 (s, 3H), 1.38 (s, 9H), 1.18 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 158.9, 144.3, 141.4, 134.1, 132.5, 131.3, 128.1, 127.5, 127.1, 113.5, 80.2, 55.3, 45.0, 28.0, 26.8.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{28}NaO_3$ $[M + Na]^+$ 375.1931, found 375.1938.

tert-Butyl-4-(4-bromophenyl)-2,2-dimethyl-4-phenylbut-3-enoate (7)



7

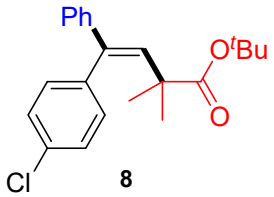
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **7** (62.0 mg, *anti/syn* > 20/1, 77% yield) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.0 Hz, 2H), 7.27 – 7.19 (m, 3H), 7.19 – 7.10 (m, 2H), 7.05 (d, J = 7.9 Hz, 2H), 6.12 (s, 1H), 1.38 (s, 9H), 1.18 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 143.4, 140.5, 139.2, 134.7, 132.0, 131.3, 128.2, 127.4, 127.4, 121.5, 80.5, 45.0, 28.0, 27.6.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}BrNaO_2$ $[M + Na]^+$ 423.0930, found 423.0940.

tert-Butyl-4-(4-chlorophenyl)-2,2-dimethyl-4-phenylbut-3-enoate (8)



8

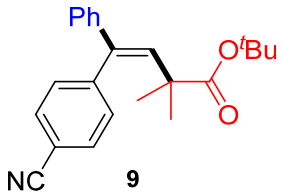
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **8** (71.0 mg, *anti/syn* > 20/1, 97% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.28 (m, 2H), 7.28 – 7.19 (m, 3H), 7.18 – 7.08 (m, 4H), 6.13 (s, 1H), 1.38 (s, 9H), 1.18 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 143.5, 140.6, 138.7, 134.8, 133.3, 131.6, 128.3, 128.2, 127.4, 127.4, 80.5, 45.0, 28.0, 27.6.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}ClNaO_2$ $[M + Na]^+$ 379.1435, found 379.1442.

tert-Butyl-4-(4-cyanophenyl)-2,2-dimethyl-4-phenylbut-3-enoate (9)



9

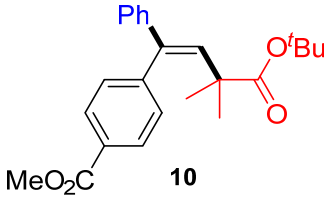
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 15/1) to afford **9** (57.0 mg, *anti/syn* = 6/1, 82% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.60 (m, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.23 (m, 3H), 7.16 – 7.06 (m, 2H), 6.17 (s, 1H), 1.37 (s, 9H), 1.18 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 145.4, 142.8, 140.1, 135.5, 131.9, 131.1, 128.4, 127.7, 127.4, 118.9, 111.3, 80.7, 45.1, 28.0, 27.6.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{26}NO_2$ $[M + H]^+$ 348.1958, found 348.1966.

Methyl-4-(4-(*tert*-butoxy)-3,3-dimethyl-4-oxo-1-phenylbut-1-en-1-yl)benzoate (10)



10

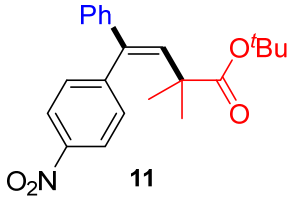
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 15/1) to afford **10** (62.3 mg, *anti/syn* = 12/1, 82% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 7.97 (m, 2H), 7.31 – 7.19 (m, 5H), 7.19 – 7.11 (m, 2H), 6.17 (s, 1H), 3.92 (s, 3H), 1.38 (s, 9H), 1.16 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 167.1, 145.4, 143.2, 140.8, 134.8, 130.3, 129.6, 129.1, 129.0, 128.3, 127.4, 80.5, 52.2, 45.1, 28.0, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{28}NaO_4$ $[M + Na]^+$ 403.1880, found 403.1888.

***tert*-Butyl-2,2-dimethyl-4-(4-nitrophenyl)-4-phenylbut-3-enoate (11)**



11

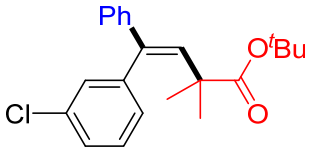
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **11** (44.8 mg, *anti/syn* = 16/1, 61% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H), 7.31 – 7.22 (m, 3H), 7.19 – 7.03 (m, 2H), 6.20 (s, 1H), 1.38 (s, 9H), 1.19 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 147.5, 147.3, 142.6, 139.9, 135.8, 131.2, 128.5, 127.8, 127.4, 123.4, 80.8, 45.1, 28.0, 27.6.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}NO_4Na$ $[M + Na]^+$ 390.1676, found 390.1683.

tert-Butyl-4-(3-chlorophenyl)-2,2-dimethyl-4-phenylbut-3-enoate (12)



12

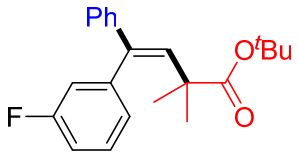
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **12** (43.7 mg, *anti/syn* > 20/1, 60% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.18 (m, 5H), 7.14 – 7.19 (m, 3H), 7.08 (ddd, J = 6.1, 2.4, 1.6 Hz, 1H), 6.13 (s, 1H), 1.39 (s, 9H), 1.18 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 143.3, 142.0, 140.4, 134.9, 134.0, 130.2, 129.4, 128.5, 128.3, 127.6, 127.4, 80.6, 45.0, 28.0, 27.6.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}ClNaO_2$ $[M + Na]^+$ 379.1435, found 379.1442.

tert-Butyl-4-(3-fluorophenyl)-2,2-dimethyl-4-phenylbut-3-enoate (13)



13

The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **13** (65.8 mg, *anti/syn* = 7/1, 96% yield) as a pale yellow oil.

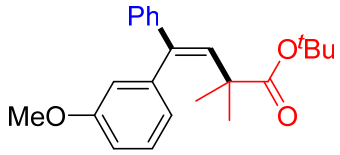
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.19 (m, 4H), 7.22 – 7.14 (m, 2H), 7.07 – 6.93 (m, 2H), 6.90 (ddd, J = 9.6, 2.6, 1.5 Hz, 1H), 6.13 (s, 1H), 1.39 (s, 9H), 1.18 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.0, 162.6 (d, J = 246.3 Hz), 143.3, 142.4 (d, J = 7.6 Hz), 140.5, 138.8, 134.7, 129.6 (d, J = 8.4 Hz), 128.3, 127.4, 126.1 (d, J = 3.1 Hz), 117.3 (d, J = 21.1 Hz), 114.3 (d, J = 21.0 Hz), 80.5, 45.0, 28.0, 27.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ −113.6.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}FNaO_2$ $[M + Na]^+$ 363.1731, found 363.1737.

tert-Butyl-4-(3-methoxyphenyl)-2,2-dimethyl-4-phenylbut-3-enoate (14)



14

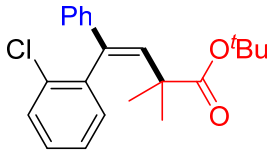
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to afford **14** (41.4 mg, *anti/syn* = 20/1, 57% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.16 (m, 6H), 6.84 (ddd, J = 8.3, 2.6, 1.0 Hz, 1H), 6.77 (dt, J = 7.5, 1.2 Hz, 1H), 6.71 (dd, J = 2.6, 1.4 Hz, 1H), 6.11 (s, 1H), 3.78 (s, 3H), 1.38 (s, 9H), 1.19 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 159.4, 143.8, 141.5(1), 141.4(5), 134.0, 129.0, 128.1, 127.4, 127.1, 122.9, 115.9, 112.9, 80.3, 55.3, 45.1, 28.0, 27.4.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{28}NaO_3$ $[M + Na]^+$ 375.1931, found 375.1938.

tert-Butyl-4-(2-chlorophenyl)-2,2-dimethyl-4-phenylbut-3-enoate (15)



15

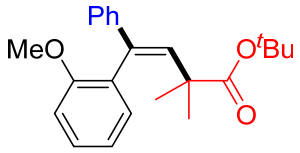
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **15** (55.8 mg, *anti/syn* = 16/1, 78% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.33 (m, 1H), 7.31 – 7.20 (m, 6H), 7.23 – 7.16 (m, 2H), 6.26 (s, 1H), 1.43 (s, 9H), 1.23 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 142.0, 138.9, 138.5, 134.9, 134.3, 132.2, 129.8, 129.0, 128.3, 127.3, 126.8, 126.3, 80.5, 45.4, 28.1, 27.2, 25.0.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}ClNaO_2$ $[M + Na]^+$ 379.1435, found 379.1442.

***tert*-Butyl-4-(2-methoxyphenyl)-2,2-dimethyl-4-phenylbut-3-enoate (16)**



16

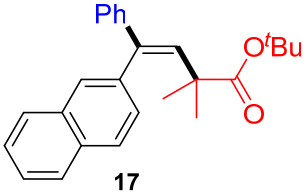
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 15/1) to afford **16** (65.0 mg, *anti/syn* = 16/1, 92% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (ddd, J = 8.2, 7.4, 1.8 Hz, 1H), 7.27 – 7.14 (m, 5H), 7.11 (dd, J = 7.4, 1.8 Hz, 1H), 6.94 (td, J = 7.4, 1.0 Hz, 1H), 6.88 (dd, J = 8.2, 1.1 Hz, 1H), 6.24 (s, 1H), 3.68 (s, 3H), 1.42 (s, 9H), 1.11 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 157.2, 143.2, 138.0, 134.3, 131.7, 129.1, 129.0, 128.1, 126.9, 126.6, 120.3, 110.9, 80.2, 55.5, 45.1, 28.1.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{28}NaO_3$ $[M + Na]^+$ 375.1931, found 375.1938.

***tert*-Butyl-2,2-dimethyl-4-(naphthalen-2-yl)-4-phenylbut-3-enoate (17)**



17

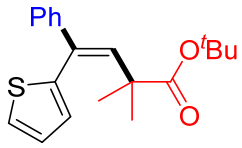
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **17** (66.5 mg, *anti/syn* = 9/1, 88% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 – 7.76 (m, 4H), 7.69 (s, 1H), 7.52 – 7.43 (m, 2H), 7.26 – 7.18 (m, 5H), 6.21 (s, 1H), 1.34 (s, 9H), 1.19 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 143.8, 141.6, 137.7, 134.6, 133.2, 132.7, 128.9, 128.5, 128.2, 128.1, 127.8, 127.7, 127.6, 127.2, 126.2, 126.1, 80.3, 45.1, 28.0, 27.6.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{28}NaO_2$ $[M + Na]^+$ 395.1982, found 395.1989.

***tert*-Butyl-2,2-dimethyl-4-phenyl-4-(thiophen-2-yl)but-3-enoate (18)**



18

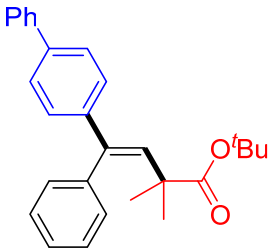
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **18** (48.0 mg, *anti/syn* = 20/1, 73% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, J = 5.1, 1.2 Hz, 1H), 7.30 – 7.21 (m, 5H), 7.00 (dd, J = 5.1, 3.5 Hz, 1H), 6.94 (dd, J = 3.5, 1.2 Hz, 1H), 6.10 (s, 1H), 1.35 (s, 9H), 1.30 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 144.1, 141.1, 137.5, 134.6, 128.6, 128.1, 127.6, 127.5, 126.7, 126.3, 80.4, 45.1, 28.0, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}NaO_2S$ $[M + Na]^+$ 351.1389, found 351.1396.

***tert*-Butyl-4-([1,1'-biphenyl]-4-yl)-2,2-dimethyl-4-phenylbut-3-enoate (19)**



19

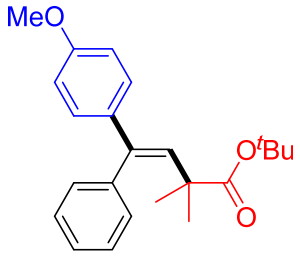
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **19** (36.0 mg, *anti/syn* > 20/1, 44% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 7.1 Hz, 2H), 7.48 (d, J = 8.3 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.37 – 7.28 (m, 4H), 7.29 – 7.22 (m, 2H), 7.20 (d, J = 7.0 Hz, 2H), 6.21 (s, 1H), 1.39 (s, 9H), 1.18 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 142.9, 141.2, 140.9, 140.1, 140.0, 134.1, 130.3, 128.9, 128.1, 127.8, 127.3(8), 127.3(5), 127.1, 126.9, 80.3, 45.1, 28.0, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{30}NaO_2$ $[M + Na]^+$ 421.2138, found 421.2145.

***tert*-Butyl-4-(4-methoxyphenyl)-2,2-dimethyl-4-phenylbut-3-enoate (20)**



20

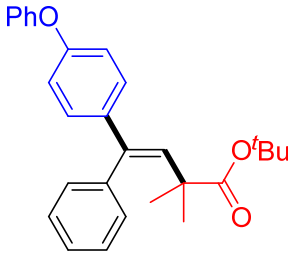
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to afford **20** (50.4 mg, *anti/syn* > 20/1, 71% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.26 (m, 3H), 7.17 (d, J = 2.0 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 6.05 (s, 1H), 3.77 (s, 3H), 1.38 (s, 9H), 1.15 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 158.9, 141.1, 140.5, 136.7, 132.5, 130.2, 128.5, 128.0, 127.2, 113.5, 80.2, 55.4, 45.0, 28.0, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{28}NaO_3$ $[M + Na]^+$ 375.1931, found 375.1937.

***tert*-Butyl-2,2-dimethyl-4-(4-phenoxyphenyl)-4-phenylbut-3-enoate (21)**



21

The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **21** (54.1 mg, *anti/syn* > 20/1, 65% yield) as a colorless oil.

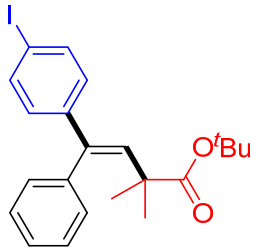
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.24 (m, 5H), 7.21 – 7.10 (m, 4H), 7.10 – 7.02 (m, 1H), 6.99 (dt, J = 7.8, 1.1 Hz, 2H), 6.92 – 6.83 (m, 2H), 6.10 (s, 1H), 1.38 (s, 9H), 1.16 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 157.3, 156.5, 141.0, 140.2, 139.1, 133.4, 130.2,

129.8, 128.7, 128.1, 127.3, 123.4, 119.0, 118.4, 80.3, 45.0, 28.0, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{30}NaO_3$ $[M + Na]^+$ 437.2087, found 437.2095.

tert-Butyl-4-(4-iodophenyl)-2,2-dimethyl-4-phenylbut-3-enoate (22)



22

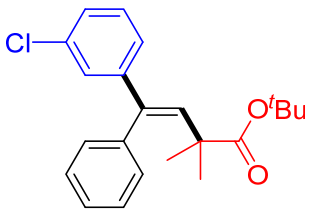
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **22** (63.7 mg, *anti/syn* = 6/1, 70% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.5 Hz, 1H), 7.36 – 7.27 (m, 4H), 7.17 – 7.10 (m, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.12 (s, 1H), 1.37 (s, 9H), 1.15 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.0, 143.6, 140.8, 139.6, 137.2, 134.6, 130.2, 129.3, 128.2, 127.5, 92.8, 80.4, 45.1, 28.0, 27.4.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}NaO_2I$ $[M + Na]^+$ 471.0791, found 471.0802.

tert-Butyl-4-(3-chlorophenyl)-2,2-dimethyl-4-phenylbut-3-enoate (23)



23

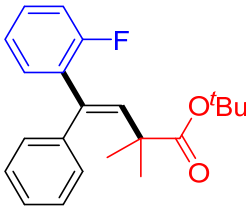
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **23** (50.8 mg, *anti/syn* > 20/1, 71% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.27 (m, 3H), 7.21 – 7.11 (m, 5H), 7.04 (dt, J = 6.8, 1.9 Hz, 1H), 6.13 (s, 1H), 1.38 (s, 9H), 1.16 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 145.9, 140.6, 139.4, 135.3, 134.1, 130.1, 129.3, 128.2, 127.6, 127.5, 127.1, 125.7, 80.4, 45.1, 28.0, 27.4.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}ClNaO_2$ $[M + Na]^+$ 379.1435, found 379.1442.

tert-Butyl-4-(2-fluorophenyl)-2,2-dimethyl-4-phenylbut-3-enoate (24)



24

The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **24** (55.6 mg, *anti/syn* > 20/1, 81% yield) as a colorless oil.

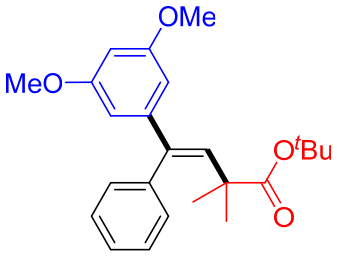
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.22 (m, 3H), 7.24 – 7.09 (m, 4H), 7.07 – 6.92 (m, 2H), 5.97 (s, 1H), 1.36 (s, 9H), 1.20 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.0, 160.0 (d, J = 247.8 Hz), 140.2, 137.9 (d, J = 3.0 Hz), 136.4, 132.6 (d, J = 13.3 Hz), 131.2 (d, J = 3.3 Hz), 129.6, 128.7 (d, J = 8.2 Hz), 128.0, 127.3, 123.8 (d, J = 3.7 Hz), 115.9 (d, J = 22.6 Hz), 80.3, 45.1, 27.9, 27.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ −114.9 ppm.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}FNaO_2$ $[M + Na]^+$ 363.1731, found 363.1738.

tert-Butyl-4-(3,5-dimethoxyphenyl)-2,2-dimethyl-4-phenylbut-3-enoate (25)



25

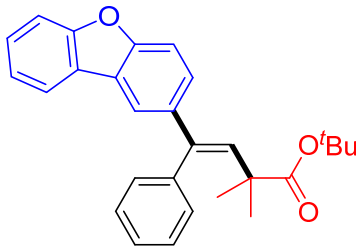
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 15/1) to afford **25** (32.0 mg, *anti/syn* > 20/1, 40% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.22 (m, 3H), 7.23 – 7.10 (m, 2H), 6.36 – 6.33 (m, 3H), 6.13 (s, 1H), 3.73 (s, 6H), 1.37 (s, 9H), 1.15 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 160.5, 146.3, 141.6, 139.9, 134.3, 130.1, 128.0, 127.3, 106.1, 98.9, 80.3, 55.4, 45.0, 28.0, 27.4.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{30}NaO_4$ $[M + Na]^+$ 405.2036, found 405.2044.

tert-Butyl-4-(dibenzo[b,d]furan-2-yl)-2,2-dimethyl-4-phenylbut-3-enoate (26)



26

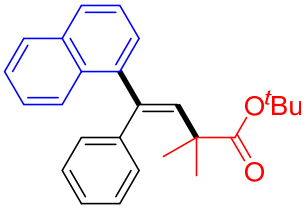
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **26** (31.2 mg, *anti/syn* > 20/1, 36% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 1.9 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.46 – 7.40 (m, 2H), 7.37 – 7.27 (m, 5H), 7.26 – 7.20 (m, 2H), 6.17 (s, 1H), 1.40 (s, 9H), 1.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 156.8, 155.7, 141.8, 140.5, 139.4, 134.1, 130.3, 128.2, 127.4, 127.2(4), 127.1(6), 124.4, 124.1, 122.8, 120.9, 119.6, 111.8, 111.1, 80.4, 45.1, 28.1, 27.6.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{28}NaO_3$ $[M + Na]^+$ 435.1931, found 435.1941.

tert-Butyl-2,2-dimethyl-4-(naphthalen-1-yl)-4-phenylbut-3-enoate (27)



27

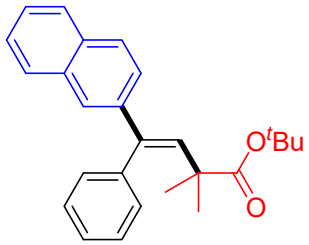
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1) to afford **27** (45.8 mg, *anti/syn* > 20/1, 60% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 – 8.23 (m, 1H), 7.86 – 7.77 (m, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.48 – 7.35 (m, 3H), 7.33 – 7.26 (m, 3H), 7.26 – 7.15 (m, 3H), 5.82 (s, 1H), 1.35 (s, 9H), 1.33 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.0, 143.0, 141.1, 139.7, 137.7, 134.1, 132.1, 129.1, 128.3, 128.1, 127.4, 127.2, 126.8, 126.3, 126.0, 125.7, 125.4, 80.4, 45.0, 28.0, 27.9.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{28}NaO_2$ $[M + Na]^+$ 395.1982, found 395.1990.

tert-Butyl-2,2-dimethyl-4-(naphthalen-2-yl)-4-phenylbut-3-enoate (28)



28

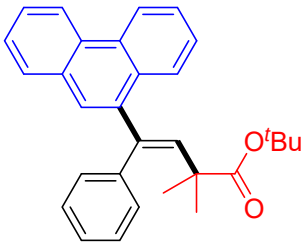
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1) to afford **28** (36.0 mg, *anti/syn* > 20/1, 47% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.71 (m, 3H), 7.57 (s, 1H), 7.48 – 7.42 (m, 3H), 7.42 – 7.35 (m, 3H), 7.29 – 7.23 (m, 2H), 6.31 (s, 1H), 1.43 (s, 9H), 1.25 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 141.7, 141.4, 140.1, 134.7, 133.4, 132.7, 130.4, 128.3, 128.1, 127.6(1), 127.5(9), 127.4, 126.5, 126.2, 125.9, 125.6, 80.4, 45.1, 28.0, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{28}NaO_2$ $[M + Na]^+$ 395.1982, found 395.1989.

tert-Butyl-2,2-dimethyl-4-(phenanthren-9-yl)-4-phenylbut-3-enoate (29)



29

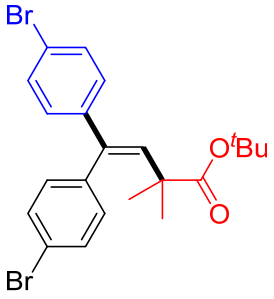
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1) to afford **29** (40.6 mg, *anti/syn* > 20/1, 47% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 – 8.63 (m, 2H), 8.28 (dd, J = 8.1, 1.5 Hz, 1H), 7.88 – 7.82 (m, 1H), 7.64 – 7.51 (m, 5H), 7.39 – 7.33 (m, 2H), 7.26 – 7.20 (m, 2H), 7.20 – 7.14 (m, 1H), 5.91 (s, 1H), 1.37 (s, 6H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 141.5, 140.7, 140.0, 137.7, 131.7, 131.6, 130.9, 130.0, 129.1, 128.7, 128.1, 127.3(4), 127.2(6), 127.2(1), 126.8, 126.6, 126.5, 126.4, 122.9, 122.6, 80.4, 44.9, 28.1, 27.9.

HRMS (ESI) *m/z* calcd. for $C_{30}H_{30}NaO_2$ $[M + Na]^+$ 445.2138, found 445.2148.

***tert*-Butyl 4,4-bis(4-bromophenyl)-2,2-dimethylbut-3-enoate (30)**



30

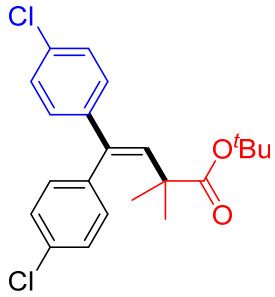
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40/1) to afford **30** (92.0 mg, 96% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.02 (dd, J = 8.5, 5.1 Hz, 4H), 6.11 (s, 1H), 1.37 (s, 9H), 1.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 142.4, 139.6, 138.6, 135.2, 131.9, 131.5, 131.3, 129.0, 121.8, 121.5, 80.7, 45.1, 28.0, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{24}Br_2NaO_2$ $[M + Na]^+$ 501.0035, found 501.0048.

***tert*-Butyl 4,4-bis(4-chlorophenyl)-2,2-dimethylbut-3-enoate (31)**



31

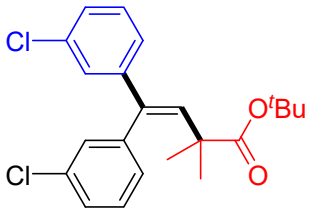
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **31** (45.4 mg, 57% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 7.08 (dd, J = 8.5, 4.6 Hz, 4H), 6.11 (s, 1H), 1.37 (s, 9H), 1.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8, 142.0, 139.6, 138.2, 135.2, 133.6, 133.3, 131.5, 128.7, 128.5, 128.4, 80.6, 45.1, 28.0, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{24}Cl_2NaO_2$ $[M + Na]^+$ 413.1046, found 413.1054.

***tert*-Butyl 4,4-bis(3-chlorophenyl)-2,2-dimethylbut-3-enoate (32)**



32

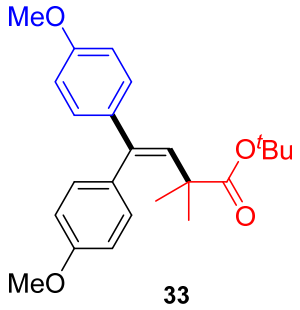
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **32** (58.0 mg, 74% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.24 (m, 2H), 7.23 – 7.12 (m, 4H), 7.06 (dt, J = 6.5, 1.8 Hz, 1H), 7.01 (dt, J = 6.9, 1.9 Hz, 1H), 6.13 (s, 1H), 1.39 (s, 9H), 1.18 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 145.1, 141.3, 139.3, 136.1, 134.3, 134.2, 130.1, 129.5(4), 129.4(7), 128.4, 127.9, 127.4, 125.7, 80.7, 45.1, 28.0, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{24}Cl_2NaO_2$ $[M + Na]^+$ 413.1046, found 413.1054.

***tert*-Butyl 4,4-bis(4-methoxyphenyl)-2,2-dimethylbut-3-enoate (33)**



33

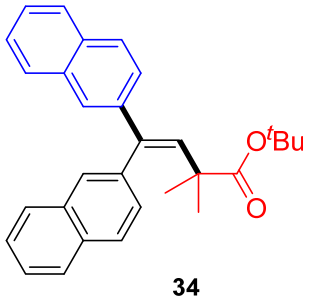
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to afford **33** (40.8 mg, 52% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 6.01 (s, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 1.38 (s, 9H), 1.16 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 158.9(2), 158.8(5), 140.8, 137.1, 132.7, 132.5, 131.3, 128.6, 113.45, 113.42, 80.2, 55.4, 55.3, 44.9, 28.0, 27.6.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{30}NaO_4$ $[M + Na]^+$ 405.2036, found 405.2044.

***tert*-Butyl 2,2-dimethyl-4,4-di(naphthalen-2-yl)but-3-enoate (34)**



34

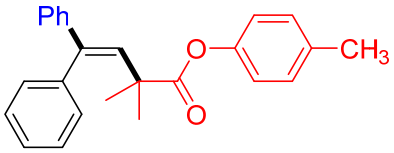
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **34** (56.4 mg, 66% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.65 (m, 7H), 7.54 (s, 1H), 7.52 – 7.37 (m, 5H), 7.29 (dd, J = 8.4, 1.6 Hz, 1H), 6.35 (s, 1H), 1.35 (s, 9H), 1.23 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 141.6, 141.2, 137.7, 135.2, 133.4, 133.2, 132.8, 132.7, 129.0, 128.6, 128.3, 128.2, 127.9, 127.7(4), 127.6(6), 127.6, 126.7, 126.3, 126.2, 126.1, 126.0, 125.8, 80.4, 45.2, 28.0, 27.7.

HRMS (ESI) *m/z* calcd. for $C_{30}H_{30}NaO_2$ $[M + Na]^+$ 445.2138, found 445.2146.

***p*-Tolyl 2,2-dimethyl-4,4-diphenylbut-3-enoate (35)**



35

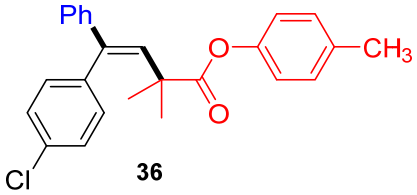
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **35** (66.0 mg, 92% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.35 (m, 3H), 7.25 – 7.19 (m, 7H), 7.10 (d, J = 8.3 Hz, 2H), 6.74 (d, J = 8.5 Hz, 2H), 6.22 (s, 1H), 2.31 (s, 3H), 1.41 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.2, 148.9, 143.5, 142.6, 139.6, 135.2, 133.3, 130.3, 129.8, 128.3, 128.2, 127.6, 127.5, 127.4, 121.1, 44.5, 27.9, 21.0.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{24}NaO_2$ $[M + Na]^+$ 379.1609, found 379.1677.

***p*-Tolyl-4-(4-chlorophenyl)-2,2-dimethyl-4-phenylbut-3-enoate (36)**



36

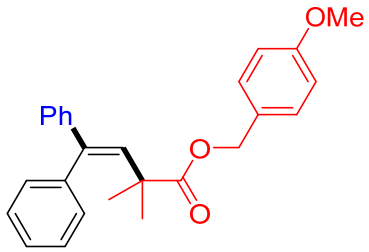
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **36** (40.2 mg, *anti/syn* > 20/1, 51% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.22 (m, 4H), 7.22 – 7.06 (m, 7H), 6.73 (d, J = 8.5 Hz, 2H), 6.21 (s, 1H), 2.32 (s, 3H), 1.42 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 148.8, 143.1, 141.5, 138.0, 135.3, 133.9, 133.7, 131.7, 129.9, 128.6, 128.3, 127.6, 127.4, 120.9, 44.5, 27.9, 21.0.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{23}ClNaO_2$ $[M + H]^+$ 391.1459, found 391.1466.

4-Methoxybenzyl 2,2-dimethyl-4,4-diphenylbut-3-enoate (37)



37

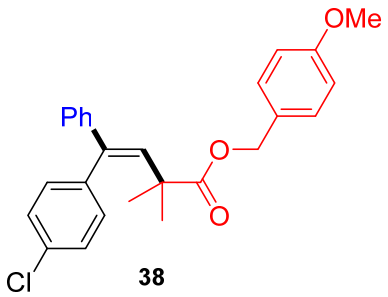
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to afford **37** (71.4 mg, 92% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.26 (m, 3H), 7.26 – 7.14 (m, 7H), 7.12 – 7.06 (m, 2H), 6.90 – 6.81 (m, 2H), 6.09 (s, 1H), 4.67 (s, 2H), 3.79 (s, 3H), 1.29 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 159.5, 143.4, 141.8, 139.4, 134.1, 130.3, 129.8, 128.5, 128.2, 128.0, 127.4, 127.3(4), 127.2(6), 113.9, 66.0, 55.4, 44.3, 27.8.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{26}NaO_3$ $[M + Na]^+$ 409.1774, found 409.1782.

4-Methoxybenzyl-4-(4-chlorophenyl)-2,2-dimethyl-4-phenylbut-3-enoate (38)



38

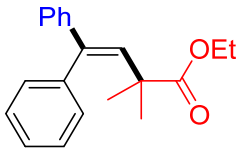
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to afford **38** (74.3 mg, *anti/syn* = 20/1, 88% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 – 7.17 (m, 6H), 7.17 – 7.10 (m, 2H), 7.05 – 6.96 (m, 2H), 6.94 – 6.79 (m, 3H), 6.09 (s, 1H), 4.71 (s, 2H), 3.80 (s, 3H), 1.29 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 159.6, 143.0, 140.7, 137.8, 134.7, 133.4, 131.60, 129.8, 128.3, 128.3, 127.5, 127.3, 114.0, 66.2, 55.4, 44.3, 30.9, 27.8.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{25}ClNaO_3$ $[M + Na]^+$ 443.1384, found 443.1383.

Ethyl 2,2-dimethyl-4,4-diphenylbut-3-enoate (39)



39

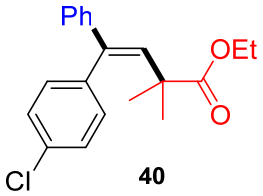
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **39** (44.8 mg, 76% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.27 (m, 3H), 7.27 – 7.16 (m, 5H), 7.16 – 7.09 (m, 2H), 6.09 (s, 1H), 3.73 (q, J = 7.1 Hz, 2H), 1.29 (s, 6H), 1.13 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 143.5, 141.6, 139.4, 134.3, 130.2, 128.2, 128.0, 127.4, 127.4, 127.2, 60.5, 44.2, 27.9, 14.1.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{22}NaO_2$ $[M + Na]^+$ 317.1512, found 317.1518.

Ethyl-4-(4-chlorophenyl)-2,2-dimethyl-4-phenylbut-3-enoate (40)



40

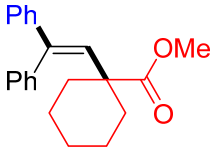
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **40** (51.2 mg, *anti/syn* > 20/1, 77% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.19 (m, 5H), 7.18 – 7.11 (m, 2H), 7.11 – 7.02 (m, 2H), 6.09 (s, 1H), 3.76 (q, J = 7.1 Hz, 2H), 1.30 (s, 6H), 1.14 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 143.0, 140.5, 137.9, 134.9, 133.4, 131.6, 128.3, 128.2, 127.5, 127.3, 60.7, 44.2, 27.9, 14.1.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}ClNaO_2$ $[M + Na]^+$ 351.1122, found 351.1118.

Methyl 1-(2,2-diphenylvinyl)cyclohexane-1-carboxylate (41)



41

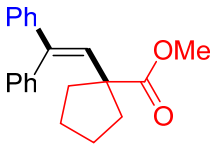
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **41** (50.2 mg, 78% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.28 (m, 3H), 7.28 – 7.16 (m, 5H), 7.12 – 7.06 (m, 2H), 6.04 (s, 1H), 3.39 (s, 3H), 1.91 – 1.85 (m, 2H), 1.64 – 1.47 (m, 4H), 1.47 – 1.32 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.0, 143.7, 142.4, 139.4, 133.2, 130.0, 128.8, 128.2, 128.0, 127.4, 127.3(3), 127.2(7), 126.5, 51.6, 48.3, 35.8, 25.7, 22.7.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}O_2$ $[M + H]^+$ 321.1849, found 321.1856.

Methyl 1-(2,2-diphenylvinyl)cyclopentane-1-carboxylate (42)



42

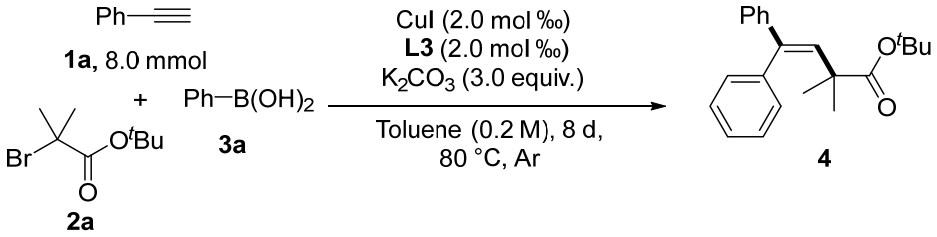
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **42** (45.6 mg, 73% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.28 (m, 3H), 7.28 – 7.17 (m, 5H), 7.14 – 7.06 (m, 2H), 6.16 (s, 1H), 3.31 (s, 3H), 2.23 – 2.11 (m, 2H), 1.79 – 1.58 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 143.3, 142.0, 139.6, 134.0, 130.3, 128.2, 128.0, 127.49, 127.46, 127.3, 55.4, 51.7, 39.3, 24.7.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{23}O_2$ $[M + H]^+$ 307.1693, found 307.1699.

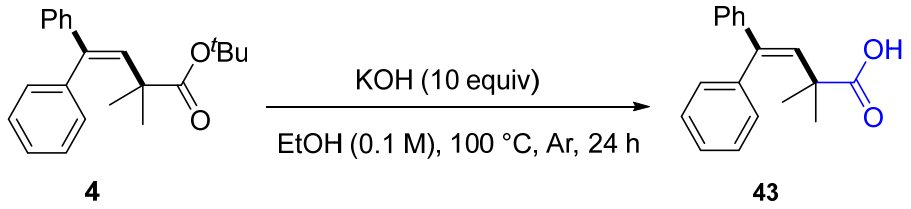
Gram-scale reaction



To a 100 mL Schlenk bottle were sequentially added alkene **1a** (0.82 g, 8.0 mmol), **2a** (3.57 g, 16.0 mmol, 2.0 equiv), **3a** (1.95 g, 16.0 mmol, 2.0 equiv), CuI (3.04 mg, 0.016 mmol, 2.0 mol ‰) , **L3** (6.44 mg, 0.016 mmol, 2.0 mol ‰), K_2CO_3 (3.32 g, 24.0 mmol, 3.0 equiv), and toluene (40 mL) under argon atmosphere. Then the bottle was sealed and the reaction mixture was stirred in an oil bath at 80 °C for 8 d. After the completion of reaction, the pure product **4** was isolated by flash column chromatography (2.14 g, 83% yield).

Transformations of trisubstituted alkenes (4 and 35)

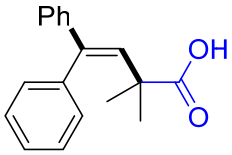
Procedure a: Hydrolysis[2] of ester group in **4**



4 **43**

To a 25 mL Schlenk bottle containing a mixture of product **4** (322 mg, 1.0 mmol) and KOH (561 mg, 10.0 mmol, 10.0 equiv) was added EtOH (5.0 mL) under argon. Then the reaction bottle was sealed and heated to 100 °C in an oil bath for 24 h under argon. After completion of the reaction (as indicated by TLC), the solvent was removed and the residue was dissolved in water. The aqueous solution was extracted with Et_2O, acidified, and then extracted again with Et_2O. The second combined organic layer was dried over $MgSO_4$, filtered, and concentrated to dryness. The crude residue was purified by silica-gel column chromatography to afford desired the product **43**.

2,2-Dimethyl-4,4-diphenylbut-3-enoic acid (43)



43

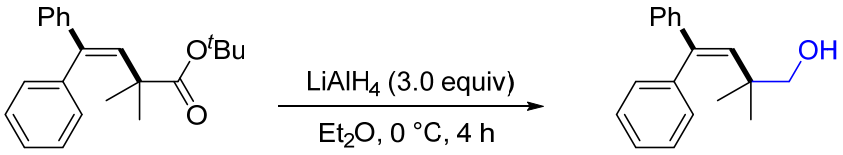
The product mixture was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 3/1) to afford **43** (232.0 mg, 87% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.39 (s, 1H), 7.35 – 7.12 (m, 10H), 6.13 (s, 1H), 1.28 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 183.3, 143.1, 142.4, 139.2, 133.2, 130.3, 128.2, 128.0, 127.5, 127.4, 127.2, 44.2, 27.4.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}O_2$ $[M + H]^+$ 267.1380, found 267.1376.

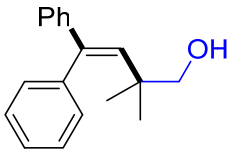
Procedure b: Reduction[1] of ester group in **4**



4 **44**

To a dry tube containing **4** (322 mg, 1.0 mmol) in anhydrous Et_2O (20.0 mL) was added $LiAlH_4$ (113.8 mg, 3.0 mmol, 3.0 equiv) at 0 °C. The mixture was allowed to warm to room temperature. After being stirred for 4 h, the reaction was slowly quenched with sat. NH_4Cl and then extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford desired the product **44**.

2,2-Dimethyl-4,4-diphenylbut-3-en-1-ol (44)



44

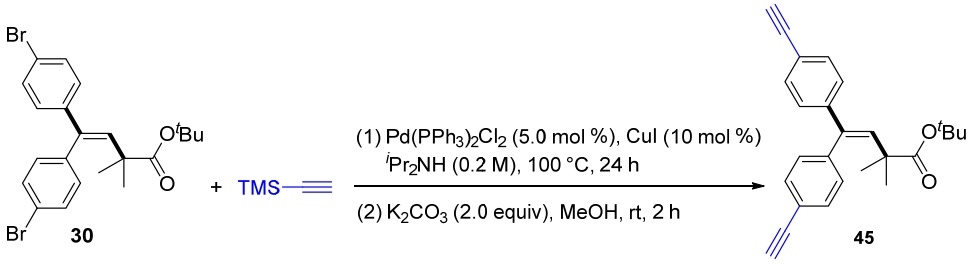
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **44** (242.2 mg, 96% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.27 (m, 3H), 7.27 – 7.13 (m, 7H), 6.03 (s, 1H), 3.29 (s, 2H), 0.93 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 141.9, 140.5, 135.8, 130.1, 128.2, 1281, 127.2, 127.02, 126.99, 72.4, 39.5, 25.9.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{21}O$ $[M + H]^+$ 253.1587, found 253.1585.

Procedure c: Sonogashira coupling of **30**

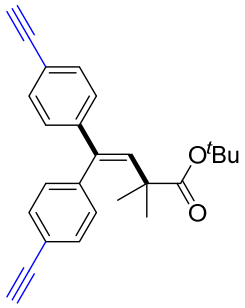


30 **45**

To a 25 mL Schlenk bottle containing a mixture of product **30** (480 mg, 1.0 mmol), CuI (19 mg, 0.10 mmol, 10 mol %) and $Pd(PPh_3)_2Cl_2$ (35 mg, 0.050 mmol, 5.0 mol %) was added diisopropylamine (5.0 mL) under nitrogen and the mixture was degassed for 3 times. Then ethynyltrimethylsilane (294.6 mg, 3.0 mmol, 3.0 equiv) was added via syringe and the reaction was heated to 100 °C in an oil bath for 24 h under argon. After completion of the reaction, the mixture was filtered through frits and the filtrate was collected and concentrated. After evaporation of the solvent, the crude product was purified by silica gel column chromatography to afford the TMS-aryl acetylene.

Next, the obtained TMS-aryl acetylene and K_2CO_3 (276.4 mg, 2.0 mmol, 2.0 equiv) were mixed with MeOH (10 mL) and stirred at rt for 2 h. Upon completion, the mixture was diluted with water and extracted with DCM. The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography to afford desired the product **45**.

***tert*-Butyl 4,4-bis(4-ethynylphenyl)-2,2-dimethylbut-3-enoate (45)**



45

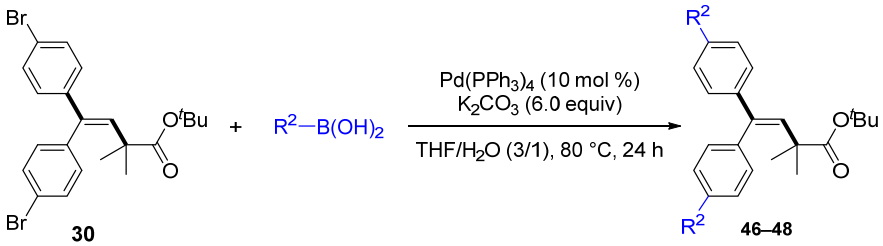
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford **45** (340.8 mg, 92% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.12 (dd, J = 8.4, 7.5 Hz, 4H), 6.17 (s, 1H), 3.10 (s, 1H), 3.08 (s, 1H), 1.37 (s, 9H), 1.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 143.8, 140.4, 140.3, 135.5, 131.9(8), 131.9(6), 130.2, 127.3, 121.3, 120.9, 83.6(3), 83.5(5), 80.6, 77.9, 77.7, 45.1, 28.0, 27.4.

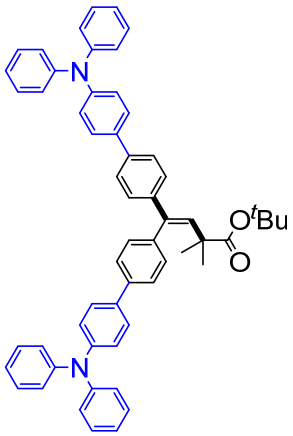
HRMS (ESI) *m/z* calcd. for $C_{26}H_{27}O_2$ $[M + H]^+$ 371.2006, found 371.2009.

Procedure d: Suzuki[3] coupling of **30**



To a mixture of **30** (240 mg, 0.50 mmol), aryl boronic acid (1.1 mmol, 2.2 equiv), $Pd(PPh_3)_2Cl_2$ (58 mg, 0.050 mmol, 10 mol %), and K_2CO_3 (415 mg, 3.0 mmol, 6.0 equiv) was added THF/H_2O (3/1, 4.0 mL) under argon. Then the reaction was stirred in an oil bath at 80 °C under argon for 24 h. After completion of the reaction, the reaction mixture was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography to give the desired product.

***tert*-Butyl 4,4-bis(4'-(diphenylamino)-[1,1'-biphenyl]-4-yl)-2,2-dimethylbut-3-enoate (46)**



46

The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 15/1) to afford **46** (332.0 mg, 82% yield) as a pale yellow solid.

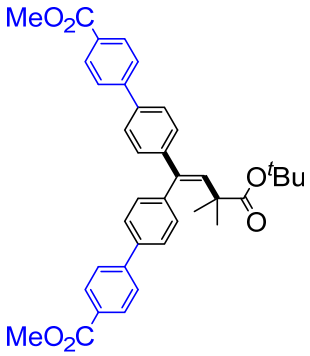
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.48 – 7.41 (m, 4H), 7.30 – 7.20 (m, 12H), 7.16 – 7.09 (m, 12H), 7.04 – 6.99 (m, 4H), 6.20 (s, 1H), 1.38 (s, 9H), 1.23 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 147.8(0), 147.7(7), 147.3(2), 147.2(6), 142.5,

141.0, 139.5, 139.4, 138.7, 134.8, 134.7, 134.1, 130.7, 129.4, 129.3, 127.9, 127.8, 127.7, 126.4, 126.2, 124.6, 124.5, 124.1, 123.9, 123.1, 123.0, 80.4, 45.1, 28.0, 27.6.

HRMS (ESI) *m/z* calcd. for $C_{58}H_{52}NaO_2N_2$ $[M + Na]^+$ 831.3921, found 831.3910.

Dimethyl 4',4'''-(4-(*tert*-butoxy)-3,3-dimethyl-4-oxobut-1-ene-1,1-diyl)bis([1,1'-biphenyl]-4-carboxylate) (47)



47

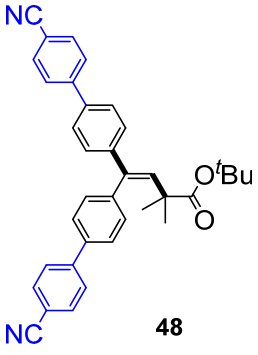
The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **47** (272.0 mg, 92% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (dd, J = 13.2, 8.4 Hz, 4H), 7.70 (d, J = 8.5 Hz, 2H), 7.63 (dd, J = 8.3, 2.9 Hz, 4H), 7.54 (d, J = 8.5 Hz, 2H), 7.31 (dd, J = 8.3, 4.6 Hz, 4H), 6.24 (s, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 1.39 (s, 9H), 1.25 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 167.0(9), 167.0(6), 145.2(3), 145.1(5), 143.7, 140.5, 140.0, 139.0, 138.8, 135.0, 130.8, 130.2(4), 130.2(2), 129.0, 128.9, 128.0, 127.1, 127.0(2), 126.9(8), 126.9(2), 80.5, 52.3, 52.2, 45.1, 28.0, 27.6.

HRMS (ESI) *m/z* calcd. for $C_{38}H_{38}NaO_6$ $[M + Na]^+$ 613.2561, found 613.2555.

***tert*-Butyl 4,4-bis(4'-cyano-[1,1'-biphenyl]-4-yl)-2,2-dimethylbut-3-enoate (48)**



48

The product mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford **48** (231.0 mg, 88% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.43 (m, 12H), 7.43 – 7.12 (m, 4H), 6.27 (s, 1H), 1.39 (s, 9H), 1.25 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 147.9, 145.2, 145.1, 144.0, 140.3, 140.2, 139.6, 138.2, 137.9, 137.7, 135.5, 132.7, 132.0, 130.9(4), 130.8(8), 128.1, 128.0, 119.0, 111.0, 110.9, 80.5, 45.1, 27.9, 27.6.

HRMS (ESI) *m/z* calcd. for $C_{36}H_{33}N_2O_2$ $[M + H]^+$ 525.2537, found 525.2528.

X-Ray crystallography data of 9 and 11

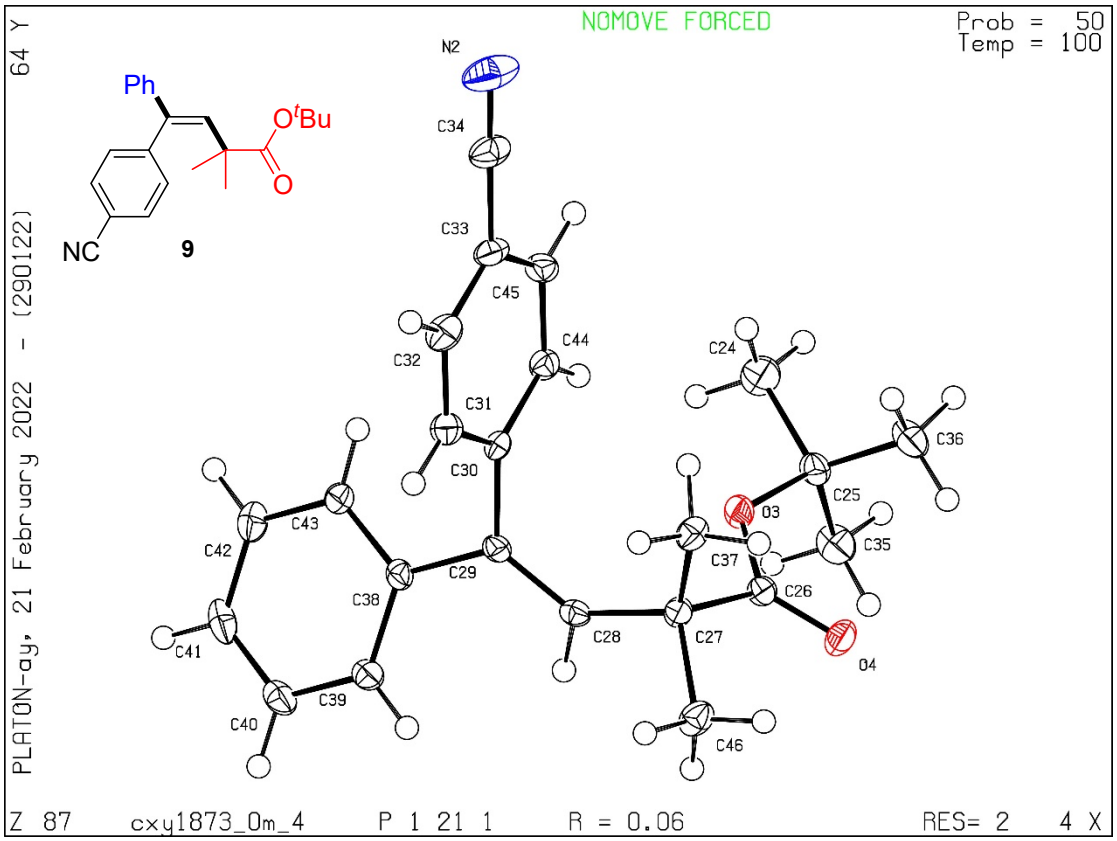


Figure S1. ORTEP diagram of **9** (CCDC: 2142776). Thermal ellipsoids are shown at the 50% probability level. A colorless square-shaped crystal of **9** for X-ray diffraction was obtained by slowly volatilizing a saturated solution of **9** in dichloromethane. The single crystal was then subjected to X-ray diffraction analysis.

Table S1. Crystal data and structure refinement for 9

Identification code	**9**
Empirical formula	$C_{23}H_{25}NO_2$
Formula weight	347.44
Temperature/K	100.05
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.6624(5)
b/Å	19.1106(12)
c/Å	11.8131(8)
α/°	90
β/°	94.569(2)
γ/°	90

Volume/Å^3	1949.4(2)
Z	4
ρ_{calc}g/cm^3	1.184
μ/mm^{-1}	0.075
F(000)	744.0
Crystal size/mm^3	0.33 × 0.26 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.262 to 56.87
Index ranges	? ≤ h ≤ ?, ? ≤ k ≤ ?, ? ≤ l ≤ ?
Reflections collected	9740
Independent reflections	9740 [R_{int} = 0.085, R_{sigma} = 0.0774]
Data/restraints/parameters	9740/1/481
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0592, wR_2 = 0.1328
Final R indexes [all data]	R_1 = 0.0834, wR_2 = 0.1432
Largest diff. peak/hole / e Å^{-3}	0.33/-0.33
Flack parameter	0.4(16)

Table S2. Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 9. Ueq is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	6681(3)	6205.9(13)	7097(2)	20.0(5)
O2	5354(3)	6450.3(14)	8617(2)	23.7(6)
O3	8180(3)	6134.1(13)	2410(2)	18.9(5)
O4	9691(3)	6832.2(13)	1429(2)	22.9(6)
N1	4371(4)	4259(2)	13072(3)	33.6(9)
N2	9939(5)	4322(2)	8250(3)	39.8(10)
C1	7497(5)	7410(2)	7588(5)	36.5(11)
C2	8020(4)	6658(2)	7478(3)	22.6(8)
C3	5459(4)	6162.0(18)	7723(3)	16.0(6)
C4	4179(4)	5703.7(18)	7135(3)	15.5(6)
C5	4817(4)	5010.9(17)	6753(3)	15.4(6)
C6	5152(4)	4426.4(17)	7356(3)	13.1(6)
C7	5027(4)	4374.1(17)	8602(3)	14.1(6)
C8	3915(4)	3932.9(19)	9028(3)	19.7(7)
C9	3761(4)	3890(2)	10180(3)	21.3(7)
C10	4730(4)	4280.5(19)	10921(3)	19.2(7)
C11	4541(4)	4261(2)	12120(3)	24.6(8)
C12	8813(4)	6372(2)	8571(4)	28.1(9)

Atom	*x*	*y*	*z*	U(eq)
C13	5879(4)	4706.1(19)	10527(3)	18.5(7)
C14	6022(4)	4747.7(18)	9367(3)	17.5(7)
C15	5747(4)	3790.0(17)	6808(3)	15.2(6)
C16	5365(4)	3639.2(18)	5659(3)	17.1(7)
C17	6040(4)	3073.1(19)	5151(3)	20.9(7)
C18	7110(5)	2657.1(19)	5761(3)	22.3(8)
C19	7473(4)	2790.6(19)	6907(3)	21.7(8)
C20	6788(4)	3349.4(18)	7424(3)	18.4(7)
C21	2857(4)	5634.1(19)	7918(3)	21.5(7)
C22	3548(4)	6104.3(19)	6061(3)	21.2(7)
C23	9071(5)	6585(3)	6513(4)	35.3(10)
C24	5829(5)	6296(2)	3235(4)	30.9(9)
C25	6949(4)	6670.9(18)	2507(3)	19.2(7)
C26	9461(4)	6285.9(17)	1903(3)	16.4(7)
C27	10664(4)	5692.8(18)	2053(3)	16.5(7)
C28	9913(4)	4991.3(17)	1769(3)	15.3(6)
C29	9573(4)	4444.9(18)	2418(3)	15.0(6)
C30	9697(4)	4432.9(18)	3696(3)	15.8(6)
C31	10873(4)	4060.5(19)	4295(3)	19.9(7)
C32	10944(4)	4027(2)	5473(3)	22.9(8)
C33	9812(4)	4358(2)	6058(3)	20.2(7)
C34	9874(4)	4330(2)	7286(3)	25.5(8)
C35	6179(5)	6839(2)	1341(3)	26.7(8)
C36	7619(5)	7315(2)	3115(3)	26.6(8)
C37	11446(4)	5766.0(19)	3265(3)	19.4(7)
C38	8942(4)	3786.1(17)	1875(3)	16.0(7)
C39	9334(4)	3576.6(19)	803(3)	18.6(7)
C40	8677(5)	2981.1(19)	289(3)	22.7(8)
C41	7603(5)	2590.6(19)	827(3)	25.4(8)
C42	7211(5)	2788.2(19)	1892(3)	23.8(8)
C43	7897(4)	3372.4(18)	2423(3)	18.2(7)
C44	8568(4)	4759.8(18)	4285(3)	17.6(7)
C45	8615(4)	4726.0(19)	5461(3)	19.9(7)
C46	11885(4)	5816(2)	1198(3)	22.3(7)

Table S3. Anisotropic Displacement Parameters ($Å^2×10^3$) for 9. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	17.7(12)	22.7(13)	19.9(12)	-2.0(11)	2.6(10)	-4.8(10)
O2	23.4(13)	28.4(14)	19.0(13)	-6.4(11)	0.5(10)	2.2(11)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O3	16.6(12)	15.6(11)	24.9(13)	0.9(10)	5.8(10)	3.2(9)
O4	24.8(13)	17.5(12)	27.0(14)	6.7(11)	5.5(11)	0.2(10)
N1	32.0(19)	54(2)	14.7(15)	8.4(16)	4.0(14)	12.1(17)
N2	40(2)	60(3)	19.5(17)	4.2(18)	0.9(15)	-22(2)
C1	28(2)	19.2(19)	61(3)	-2(2)	-3(2)	-5.2(16)
C2	18.6(17)	21.2(17)	27.8(19)	-4.9(16)	0.9(14)	-4.1(14)
C3	16.0(15)	14.4(14)	17.3(15)	0.9(13)	0.0(12)	3.0(12)
C4	15.7(15)	15.0(15)	15.6(15)	1.3(13)	0.8(12)	0.2(12)
C5	16.0(15)	16.4(15)	13.6(15)	-0.5(13)	0.8(12)	-1.1(12)
C6	14.4(14)	15.8(15)	9.2(14)	0.5(13)	1.9(12)	-2.3(13)
C7	16.7(15)	13.9(15)	11.7(14)	-0.9(13)	1.7(12)	3.7(13)
C8	22.2(17)	18.0(17)	18.6(17)	-0.7(14)	-0.1(14)	-2.8(14)
C9	20.3(17)	22.2(18)	22.4(18)	6.1(15)	7.3(14)	-0.7(14)
C10	22.1(17)	21.2(17)	15.1(16)	3.7(14)	5.3(13)	8.9(14)
C11	21.4(18)	29(2)	23.8(19)	5.1(16)	3.4(15)	7.9(15)
C12	18.5(17)	33(2)	32(2)	-3.6(18)	-4.2(15)	-3.0(16)
C13	20.0(17)	20.5(16)	14.4(15)	-1.3(14)	-1.8(13)	3.0(14)
C14	16.3(16)	17.8(16)	18.7(17)	1.5(14)	2.3(13)	0.7(13)
C15	17.2(16)	13.7(15)	14.9(15)	0.8(13)	2.9(13)	-0.8(12)
C16	21.1(17)	18.3(16)	11.8(15)	1.9(13)	1.3(13)	-2.9(13)
C17	29.1(19)	20.7(17)	13.8(16)	-3.4(14)	6.1(14)	-7.5(15)
C18	29.4(19)	14.0(16)	24.3(18)	-3.7(14)	7.7(15)	-0.5(14)
C19	23.1(18)	17.9(17)	23.9(18)	-1.9(15)	1.3(15)	2.8(14)
C20	20.9(17)	15.9(15)	18.5(17)	0.1(14)	1.0(13)	-1.9(13)
C21	17.8(17)	19.6(17)	27.4(18)	-0.7(15)	4.6(14)	1.4(14)
C22	23.5(17)	18.2(16)	21.0(17)	2.8(14)	-2.9(14)	3.8(14)
C23	25(2)	50(3)	32(2)	-1(2)	4.8(17)	-15.7(19)
C24	25.4(19)	28(2)	41(2)	4.9(18)	15.0(17)	7.2(16)
C25	20.1(16)	17.2(16)	20.6(17)	-0.3(14)	3.0(13)	5.3(14)
C26	17.5(16)	16.0(16)	15.7(15)	-0.7(13)	0.9(12)	-1.2(13)
C27	16.3(16)	14.5(15)	19.2(16)	1.8(13)	3.7(13)	0.6(13)
C28	14.6(15)	17.6(15)	13.8(15)	-0.9(13)	2.5(12)	2.7(12)
C29	14.3(15)	15.1(15)	15.9(15)	-0.7(13)	3.5(12)	3.1(13)
C30	17.5(15)	12.9(14)	17.6(16)	1.0(13)	3.9(13)	-3.4(13)
C31	20.7(17)	19.2(16)	19.8(17)	1.6(14)	2.6(14)	2.6(14)
C32	22.7(18)	24.6(18)	20.6(18)	5.8(15)	-3.5(14)	0.2(15)
C33	24.4(17)	23.3(18)	13.1(16)	1.1(14)	2.4(14)	-8.3(15)
C34	24.6(19)	32(2)	19.7(18)	0.6(17)	2.4(15)	-12.5(17)
C35	27(2)	28.0(19)	24.0(19)	-0.8(16)	-3.3(16)	7.1(16)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C36	32(2)	23.9(19)	23.4(19)	-7.1(16)	0.5(16)	5.1(16)
C37	19.4(17)	19.5(17)	18.8(16)	2.5(14)	-1.6(13)	-3.4(14)
C38	20.0(16)	13.2(15)	14.4(15)	0.5(13)	-1.1(13)	3.9(13)
C39	22.7(17)	18.5(16)	14.4(16)	0.6(13)	-0.1(13)	5.0(14)
C40	32.4(19)	20.1(17)	14.8(16)	-1.9(14)	-3.1(15)	9.5(15)
C41	31(2)	14.9(17)	28(2)	-6.1(15)	-7.8(16)	2.9(15)
C42	26.2(19)	16.9(17)	27.8(19)	0.7(15)	-0.9(16)	-3.5(15)
C43	23.0(17)	15.3(16)	16.4(16)	1.8(13)	1.5(13)	1.5(13)
C44	17.1(16)	16.4(15)	19.5(17)	1.1(14)	3.6(13)	-0.3(13)
C45	19.6(17)	20.9(16)	20.1(17)	-2.8(15)	7.4(14)	-3.9(14)
C46	17.7(16)	22.4(17)	27.3(19)	5.2(15)	5.4(14)	-0.1(14)

Table S4. Bond Lengths for 9.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C2	1.488(4)	C16	C17	1.389(5)
O1	C3	1.342(4)	C17	C18	1.381(6)
O2	C3	1.201(4)	C18	C19	1.388(5)
O3	C25	1.491(4)	C19	C20	1.387(5)
O3	C26	1.334(4)	C24	C25	1.525(5)
O4	C26	1.209(4)	C25	C35	1.517(5)
N1	C11	1.146(5)	C25	C36	1.517(5)
N2	C34	1.136(5)	C26	C27	1.540(5)
C1	C2	1.516(6)	C27	C28	1.516(5)
C2	C12	1.516(6)	C27	C37	1.541(5)
C2	C23	1.521(6)	C27	C46	1.538(5)
C3	C4	1.535(5)	C28	C29	1.342(5)
C4	C5	1.517(5)	C29	C30	1.506(4)
C4	C21	1.534(5)	C29	C38	1.497(5)
C4	C22	1.545(5)	C30	C31	1.390(5)
C5	C6	1.344(5)	C30	C44	1.392(5)
C6	C7	1.488(4)	C31	C32	1.389(5)
C6	C15	1.489(5)	C32	C33	1.396(5)
C7	C8	1.403(5)	C33	C34	1.448(5)
C7	C14	1.395(5)	C33	C45	1.397(5)
C8	C9	1.381(5)	C38	C39	1.395(5)
C9	C10	1.382(5)	C38	C43	1.399(5)
C10	C11	1.440(5)	C39	C40	1.390(5)
C10	C13	1.393(5)	C40	C41	1.386(6)
C13	C14	1.388(5)	C41	C42	1.381(6)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C15	C16	1.401(4)	C42	C43	1.391(5)
C15	C20	1.395(5)	C44	C45	1.388(5)

Table S5. Bond Angles for 9.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	O1	C2	120.0(3)	C19	C20	C15	121.1(3)
C26	O3	C25	120.7(3)	O3	C25	C24	102.2(3)
O1	C2	C1	110.2(3)	O3	C25	C35	109.9(3)
O1	C2	C12	109.7(3)	O3	C25	C36	110.3(3)
O1	C2	C23	102.6(3)	C35	C25	C24	111.0(3)
C1	C2	C23	110.7(4)	C35	C25	C36	112.4(3)
C12	C2	C1	112.8(4)	C36	C25	C24	110.6(3)
C12	C2	C23	110.3(3)	O3	C26	C27	111.6(3)
O1	C3	C4	111.0(3)	O4	C26	O3	124.7(3)
O2	C3	O1	125.1(3)	O4	C26	C27	123.6(3)
O2	C3	C4	123.8(3)	C26	C27	C37	106.5(3)
C3	C4	C22	106.6(3)	C28	C27	C26	110.5(3)
C5	C4	C3	111.4(3)	C28	C27	C37	115.8(3)
C5	C4	C21	114.3(3)	C28	C27	C46	107.2(3)
C5	C4	C22	107.6(3)	C46	C27	C26	107.8(3)
C21	C4	C3	108.9(3)	C46	C27	C37	108.8(3)
C21	C4	C22	107.8(3)	C29	C28	C27	132.2(3)
C6	C5	C4	129.5(3)	C28	C29	C30	125.7(3)
C5	C6	C7	123.4(3)	C28	C29	C38	119.9(3)
C5	C6	C15	121.1(3)	C38	C29	C30	114.3(3)
C7	C6	C15	115.5(3)	C31	C30	C29	120.6(3)
C8	C7	C6	120.1(3)	C31	C30	C44	119.4(3)
C14	C7	C6	121.1(3)	C44	C30	C29	119.9(3)
C14	C7	C8	118.8(3)	C32	C31	C30	120.4(3)
C9	C8	C7	120.8(3)	C31	C32	C33	119.8(3)
C8	C9	C10	119.4(3)	C32	C33	C34	120.5(3)
C9	C10	C11	119.9(3)	C32	C33	C45	120.1(3)
C9	C10	C13	121.2(3)	C45	C33	C34	119.4(3)
C13	C10	C11	118.9(3)	N2	C34	C33	178.5(4)
N1	C11	C10	178.5(4)	C39	C38	C29	121.5(3)
C14	C13	C10	119.0(3)	C39	C38	C43	118.1(3)
C13	C14	C7	120.8(3)	C43	C38	C29	120.3(3)
C16	C15	C6	121.7(3)	C40	C39	C38	120.7(3)
C20	C15	C6	119.9(3)	C41	C40	C39	120.4(3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C20	C15	C16	118.3(3)	C42	C41	C40	119.6(3)
C17	C16	C15	120.3(3)	C41	C42	C43	120.2(4)
C18	C17	C16	120.7(3)	C42	C43	C38	120.9(3)
C17	C18	C19	119.6(3)	C45	C44	C30	120.9(3)
C20	C19	C18	119.9(3)	C44	C45	C33	119.4(3)

Table S6. Torsion Angles for 9.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C3	C4	C5	49.6(4)	C16	C17	C18	C19	2.4(5)
O1	C3	C4	C21	176.5(3)	C17	C18	C19	C20	-1.5(6)
O1	C3	C4	C22	-67.4(3)	C18	C19	C20	C15	-0.9(5)
O2	C3	C4	C5	-131.6(4)	C20	C15	C16	C17	-1.4(5)
O2	C3	C4	C21	-4.7(5)	C21	C4	C5	C6	-43.2(5)
O2	C3	C4	C22	111.3(4)	C22	C4	C5	C6	-162.8(3)
O3	C26	C27	C28	48.3(4)	C25	O3	C26	O4	-5.0(5)
O3	C26	C27	C37	-78.3(3)	C25	O3	C26	C27	171.7(3)
O3	C26	C27	C46	165.2(3)	C26	O3	C25	C24	-174.4(3)
O4	C26	C27	C28	-134.9(3)	C26	O3	C25	C35	67.7(4)
O4	C26	C27	C37	98.6(4)	C26	O3	C25	C36	-56.8(4)
O4	C26	C27	C46	-18.0(5)	C26	C27	C28	C29	-109.0(4)
C2	O1	C3	O2	-2.2(5)	C27	C28	C29	C30	8.4(6)
C2	O1	C3	C4	176.5(3)	C27	C28	C29	C38	-174.7(3)
C3	O1	C2	C1	-59.2(4)	C28	C29	C30	C31	-107.2(4)
C3	O1	C2	C12	65.6(4)	C28	C29	C30	C44	76.9(4)
C3	O1	C2	C23	-177.1(3)	C28	C29	C38	C39	30.5(5)
C3	C4	C5	C6	80.7(4)	C28	C29	C38	C43	-147.6(3)
C4	C5	C6	C7	-3.9(5)	C29	C30	C31	C32	-177.3(3)
C4	C5	C6	C15	178.8(3)	C29	C30	C44	C45	176.8(3)
C5	C6	C7	C8	113.5(4)	C29	C38	C39	C40	-176.8(3)
C5	C6	C7	C14	-67.8(4)	C29	C38	C43	C42	175.1(3)
C5	C6	C15	C16	-28.9(5)	C30	C29	C38	C39	-152.2(3)
C5	C6	C15	C20	147.2(3)	C30	C29	C38	C43	29.6(4)
C6	C7	C8	C9	-178.5(3)	C30	C31	C32	C33	1.2(5)
C6	C7	C14	C13	178.8(3)	C30	C44	C45	C33	-0.1(5)
C6	C15	C16	C17	174.7(3)	C31	C30	C44	C45	0.9(5)
C6	C15	C20	C19	-173.9(3)	C31	C32	C33	C34	-179.7(3)
C7	C6	C15	C16	153.6(3)	C31	C32	C33	C45	-0.4(5)
C7	C6	C15	C20	-30.3(4)	C32	C33	C45	C44	-0.2(5)
C7	C8	C9	C10	-0.9(5)	C34	C33	C45	C44	179.2(3)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C8	C7	C14	C13	-2.5(5)	C37	C27	C28	C29	12.2(5)
C8	C9	C10	C11	177.6(3)	C38	C29	C30	C31	75.7(4)
C8	C9	C10	C13	-1.2(5)	C38	C29	C30	C44	-100.1(4)
C9	C10	C13	C14	1.4(5)	C38	C39	C40	C41	0.9(5)
C10	C13	C14	C7	0.5(5)	C39	C38	C43	C42	-3.2(5)
C11	C10	C13	C14	-177.4(3)	C39	C40	C41	C42	-1.3(6)
C14	C7	C8	C9	2.8(5)	C40	C41	C42	C43	-0.4(6)
C15	C6	C7	C8	-69.0(4)	C41	C42	C43	C38	2.7(6)
C15	C6	C7	C14	109.7(4)	C43	C38	C39	C40	1.4(5)
C15	C16	C17	C18	-0.9(5)	C44	C30	C31	C32	-1.4(5)
C16	C15	C20	C19	2.3(5)	C46	C27	C28	C29	133.8(4)

Table S7. Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for 9.

Atom	*x*	*y*	*z*	U(eq)
H1A	6913.26	7556	6882.76	55
H1B	8403.94	7713.15	7733.6	55
H1C	6833.79	7448.44	8220.35	55
H5	5008.16	4986.82	5973.33	18
H8	3261.07	3660.01	8516.97	24
H9	2995.31	3595.49	10461.49	26
H12A	8111.84	6408.83	9179.29	42
H12B	9755.87	6642.17	8776.71	42
H12C	9085.39	5880.11	8463.36	42
H13	6554.2	4963.96	11045.57	22
H14	6806.95	5033.83	9091.31	21
H16	4641.35	3925.39	5225.97	20
H17	5761.48	2971	4374.18	25
H18	7595.09	2281.53	5400	27
H19	8190.82	2499.56	7336.31	26
H20	7031.12	3433.57	8210.45	22
H21A	2061.26	5319.74	7569.02	32
H21B	2402.18	6095.69	8033.24	32
H21C	3262.31	5442.35	8651.68	32
H22A	4390.61	6187.12	5570.87	32
H22B	3116.22	6553.66	6281.22	32
H22C	2735.04	5826.38	5647.95	32
H23A	9327.94	6090.75	6414.3	53
H23B	10024.15	6852.68	6693.61	53
H23C	8537.93	6765.12	5809.93	53

Atom	*x*	*y*	*z*	U(eq)
H24A	5471.14	5862.09	2856.85	46
H24B	4939.28	6599.3	3337.42	46
H24C	6357.8	6184.83	3977.56	46
H28	9629.27	4926.17	982.33	18
H31	11633.48	3827.64	3896.8	24
H32	11762.07	3778.72	5879.26	27
H35A	6931.35	7063.07	879.92	40
H35B	5306.25	7157.45	1418.14	40
H35C	5801.68	6406.28	970.23	40
H36A	8245.32	7173.13	3804.22	40
H36B	6774.05	7619.27	3321.07	40
H36C	8270.15	7569.97	2612.88	40
H37A	10659.07	5739.32	3814.95	29
H37B	11979.16	6218.01	3340.27	29
H37C	12198.8	5387.27	3410.76	29
H39	10058.33	3843.59	421.44	22
H40	8966.2	2841.04	-436.59	27
H41	7139.85	2189.65	466.68	30
H42	6470.3	2524.26	2262.76	29
H43	7653.64	3492.11	3169.02	22
H44	7754.38	5009.25	3876.51	21
H45	7840.2	4950.99	5855.62	24
H46A	12679.42	5450.7	1287.73	33
H46B	12368.11	6275.14	1337.4	33
H46C	11387.17	5801.16	423.85	33

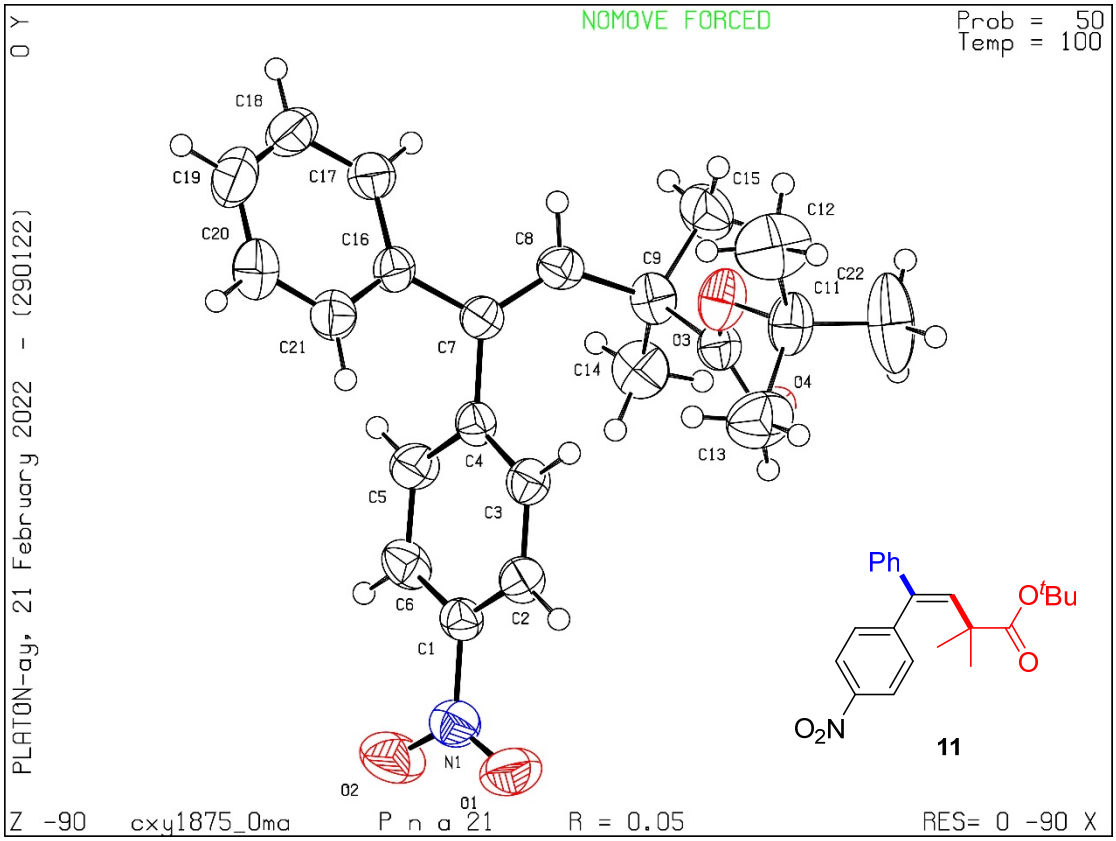


Figure S2. ORTEP diagram of **11** (CCDC: 2142777). Thermal ellipsoids are shown at the 50% probability level. A colorless stick-shaped crystal of **11** for X-ray diffraction was obtained by slowly volatilizing a saturated solution of **11** in dichloromethane. The single crystal was then subjected to X-ray diffraction analysis.

Table S8. Crystal data and structure refinement for 11

Identification code	**11**
Empirical formula	$C_{22}H_{25}NO_4$
Formula weight	367.43
Temperature/K	100
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	11.598(4)
b/Å	8.730(3)
c/Å	19.743(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1999.0(12)

Z	4
ρ_{calc}g/cm^3	1.221
μ/mm^{-1}	0.084
F(000)	784.0
Crystal size/mm^3	0.32 × 0.31 × 0.28
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.102 to 55.218
Index ranges	-12 ≤ h ≤ 15, -11 ≤ k ≤ 8, -25 ≤ l ≤ 24
Reflections collected	15392
Independent reflections	4399 [R_{int} = 0.0370, R_{sigma} = 0.0407]
Data/restraints/parameters	4399/28/281
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0481, wR_2 = 0.1015
Final R indexes [all data]	R_1 = 0.0793, wR_2 = 0.1154
Largest diff. peak/hole / e Å^{-3}	0.19/-0.16
Flack parameter	-0.7(18)

Table S9. Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 11. Ueq is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

Atom	*x*	*y*	*z*	U(eq)
O3	7781(2)	6753(2)	6493.3(12)	55.7(6)
O1	2076(2)	5639(3)	4991.9(14)	68.5(7)
O4	6350(3)	5237(4)	6789.6(18)	76.4(10)
O2	2248(2)	4101(3)	4152.9(16)	75.1(8)
N1	2659(2)	4910(3)	4595.5(15)	49.3(6)
C12	8419(6)	9201(7)	6853(4)	90(2)
C11	7486(8)	8035(9)	6980(5)	54.3(15)
C10	7210(4)	5465(4)	6473(2)	44.2(9)
C9	7793(3)	4278(3)	6006.2(16)	45.4(7)
C7	7561(2)	5297(3)	4787.2(15)	38.3(6)
C4	6281(2)	5180(3)	4743.9(14)	37.8(6)
C3	5581(3)	6150(3)	5116.6(15)	41.3(7)
C2	4394(3)	6069(3)	5072.6(16)	42.8(7)
C1	3918(2)	5007(3)	4643.2(15)	38.6(6)
C14	6934(5)	2947(5)	5914(3)	61.6(14)
C13	6326(5)	8686(8)	6760(4)	77.3(18)
C15	8835(5)	3675(6)	6383(3)	64.2(14)
C16	8144(3)	5859(3)	4164.8(15)	40.8(7)
C17	9271(3)	5428(4)	4003.5(16)	49.5(8)

Atom	*x*	*y*	*z*	U(eq)
C18	9804(3)	6021(5)	3436(2)	62.2(10)
C19	9258(4)	7054(5)	3033(2)	66.9(10)
C20	8147(4)	7478(4)	3182.1(18)	62.8(10)
C21	7592(3)	6873(4)	3732.2(17)	50.3(8)
C5	5765(3)	4148(4)	4308.8(17)	48.7(8)
C6	4580(3)	4052(3)	4251.8(17)	48.5(8)
C8	8165(3)	4989(3)	5345.0(16)	41.6(7)
C22	7496(9)	7430(8)	7693(3)	111(3)
C10A	8009(16)	5404(15)	6594(7)	44.2(9)
O4A	8475(12)	5055(15)	7124(8)	76.4(10)
C15A	8838(19)	3070(30)	6127(12)	64.2(14)
C14A	6683(19)	3420(30)	6075(16)	61.6(14)
C22A	6730(30)	7200(40)	7591(14)	111(3)
C13A	6740(30)	9000(40)	6647(19)	77.3(18)
C12A	8580(20)	8590(30)	7223(17)	90(2)
C11A	7480(30)	7750(50)	6990(20)	54.3(15)

Table S10. Anisotropic Displacement Parameters ($Å^2×10^3$) for 11. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O3	78.6(16)	40.7(11)	47.8(13)	-4.1(10)	8.2(13)	5.9(11)
O1	46.6(15)	79.3(17)	79.5(19)	-4.5(15)	9.0(13)	7.8(12)
O4	80(2)	64.8(19)	84(2)	-6.9(17)	33.2(19)	-6.2(16)
O2	54.2(15)	82.0(18)	89(2)	-15.1(17)	-14.2(15)	-14.6(13)
N1	45.7(16)	48.1(14)	54.0(16)	7.7(13)	-2.1(14)	-3.9(14)
C12	90(4)	59(4)	122(6)	-33(3)	8(4)	-6(3)
C11	82(3)	40(4)	41.6(18)	-7(3)	5.0(18)	9(2)
C10	46(3)	47(2)	40(2)	5.0(17)	0(2)	1.0(18)
C9	55(2)	37.4(15)	44.0(17)	1.3(14)	-3.2(15)	2.7(13)
C7	38.4(16)	36.8(13)	39.6(16)	-7.0(12)	-0.9(13)	4.7(12)
C4	41.2(16)	38.2(14)	34.0(15)	1.1(12)	-2.0(13)	2.8(12)
C3	44.7(18)	39.6(14)	39.5(16)	-6.0(12)	0.9(14)	1.5(12)
C2	44.9(19)	40.5(14)	43.0(17)	-3.5(13)	-0.7(14)	5.6(12)
C1	37.3(15)	39.5(13)	38.9(15)	5.4(13)	-2.6(13)	-0.1(12)
C14	69(3)	49(3)	67(4)	7(3)	-1(2)	-1(3)
C13	67(5)	72(4)	93(5)	-20(3)	11(4)	12(3)
C15	65(3)	68(3)	59(3)	10(2)	-12(3)	15(3)
C16	43.1(17)	43.4(15)	36.0(16)	-9.4(13)	0.7(13)	-2.4(13)
C17	45.6(19)	55.6(17)	47.3(18)	-10.7(15)	-0.8(15)	-1.0(14)
C18	49(2)	81(3)	56(2)	-20(2)	12.3(18)	-11.7(18)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C19	76(3)	80(2)	46(2)	-6(2)	14(2)	-17(2)
C20	77(3)	67(2)	44.5(19)	5.5(18)	0.1(18)	1.3(19)
C21	52(2)	55.4(19)	43.3(17)	-1.8(15)	-0.4(15)	4.6(15)
C5	43.6(18)	51.4(17)	50.9(19)	-13.5(15)	0.5(15)	8.1(14)
C6	51(2)	43.7(16)	50.7(19)	-12.9(14)	-11.3(16)	-1.3(14)
C8	38.8(17)	39.9(14)	46.1(17)	-5.7(13)	-1.6(14)	3.1(13)
C22	208(9)	81(4)	45(3)	-13(3)	-15(4)	4(5)
C10A	46(3)	47(2)	40(2)	5.0(17)	0(2)	1.0(18)
O4A	80(2)	64.8(19)	84(2)	-6.9(17)	33.2(19)	-6.2(16)
C15A	65(3)	68(3)	59(3)	10(2)	-12(3)	15(3)
C14A	69(3)	49(3)	67(4)	7(3)	-1(2)	-1(3)
C22A	208(9)	81(4)	45(3)	-13(3)	-15(4)	4(5)
C13A	67(5)	72(4)	93(5)	-20(3)	11(4)	12(3)
C12A	90(4)	59(4)	122(6)	-33(3)	8(4)	-6(3)
C11A	82(3)	40(4)	41.6(18)	-7(3)	5.0(18)	9(2)

Table S11. Bond Lengths for 11.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3	C11	1.513(11)	C7	C16	1.486(4)
O3	C10	1.305(4)	C7	C8	1.332(4)
O3	C10A	1.223(13)	C4	C3	1.384(4)
O3	C11A	1.36(5)	C4	C5	1.381(4)
O1	N1	1.214(4)	C3	C2	1.381(4)
O4	C10	1.194(5)	C2	C1	1.372(4)
O2	N1	1.221(4)	C1	C6	1.372(4)
N1	C1	1.465(4)	C16	C17	1.396(4)
C12	C11	1.507(9)	C16	C21	1.387(4)
C11	C13	1.524(9)	C17	C18	1.381(5)
C11	C22	1.504(10)	C18	C19	1.359(6)
C10	C9	1.542(5)	C19	C20	1.373(6)
C9	C14	1.541(6)	C20	C21	1.369(5)
C9	C15	1.514(5)	C5	C6	1.381(5)
C9	C8	1.508(4)	C10A	O4A	1.218(17)
C9	C10A	1.541(14)	C22A	C11A	1.54(3)
C9	C15A	1.627(16)	C13A	C11A	1.55(3)
C9	C14A	1.494(19)	C12A	C11A	1.54(3)
C7	C4	1.491(4)			

Table S12. Bond Angles for 11.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	O3	C11	122.8(4)	C3	C4	C7	120.7(2)
C10A	O3	C11A	123.7(17)	C5	C4	C7	120.8(2)
O1	N1	O2	123.2(3)	C5	C4	C3	118.4(3)
O1	N1	C1	118.9(3)	C2	C3	C4	121.3(3)
O2	N1	C1	118.0(3)	C1	C2	C3	118.3(3)
O3	C11	C13	107.1(6)	C2	C1	N1	118.7(3)
C12	C11	O3	103.4(7)	C6	C1	N1	119.1(3)
C12	C11	C13	109.6(6)	C6	C1	C2	122.2(3)
C22	C11	O3	109.4(6)	C17	C16	C7	121.7(3)
C22	C11	C12	112.8(7)	C21	C16	C7	120.6(3)
C22	C11	C13	113.8(8)	C21	C16	C17	117.6(3)
O3	C10	C9	112.0(3)	C18	C17	C16	120.2(3)
O4	C10	O3	123.4(4)	C19	C18	C17	121.0(3)
O4	C10	C9	124.5(3)	C18	C19	C20	119.4(3)
C14	C9	C10	107.1(3)	C21	C20	C19	120.5(4)
C15	C9	C10	106.8(3)	C20	C21	C16	121.2(3)
C15	C9	C14	108.2(3)	C6	C5	C4	121.4(3)
C8	C9	C10	111.5(2)	C1	C6	C5	118.3(3)
C8	C9	C14	113.1(3)	C7	C8	C9	130.4(3)
C8	C9	C15	109.9(3)	O3	C10A	C9	117.2(11)
C8	C9	C10A	110.0(6)	O4A	C10A	O3	118.5(13)
C8	C9	C15A	100.5(9)	O4A	C10A	C9	124.1(12)
C10A	C9	C15A	100.6(10)	O3	C11A	C22A	120(3)
C14A	C9	C8	122.0(13)	O3	C11A	C13A	106(3)
C14A	C9	C10A	113.0(12)	O3	C11A	C12A	108(3)
C14A	C9	C15A	107.6(14)	C22A	C11A	C13A	104(3)
C16	C7	C4	115.4(2)	C12A	C11A	C22A	113(3)
C8	C7	C4	123.9(3)	C12A	C11A	C13A	105(3)
C8	C7	C16	120.7(3)				

Table S13. Torsion Angles for 11.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	C10	C9	C14	-169.3(4)	C14	C9	C8	C7	39.6(5)
O3	C10	C9	C15	75.0(4)	C15	C9	C8	C7	160.6(3)
O3	C10	C9	C8	-45.0(4)	C16	C7	C4	C3	-111.5(3)
O1	N1	C1	C2	-8.5(4)	C16	C7	C4	C5	65.6(3)
O1	N1	C1	C6	172.3(3)	C16	C7	C8	C9	-173.6(3)
O4	C10	C9	C14	12.0(6)	C16	C17	C18	C19	1.4(5)
O4	C10	C9	C15	-103.7(5)	C17	C16	C21	C20	-2.6(5)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O4	C10	C9	C8	136.2(4)	C17	C18	C19	C20	-2.0(5)
O2	N1	C1	C2	171.0(3)	C18	C19	C20	C21	0.2(5)
O2	N1	C1	C6	-8.1(4)	C19	C20	C21	C16	2.1(5)
N1	C1	C6	C5	-179.3(3)	C21	C16	C17	C18	0.9(4)
C11	O3	C10	O4	6.9(7)	C5	C4	C3	C2	1.8(4)
C11	O3	C10	C9	-171.8(4)	C8	C9	C10A	O3	41.0(15)
C10	O3	C11	C12	175.8(5)	C8	C9	C10A	O4A	-132.8(16)
C10	O3	C11	C13	-68.4(6)	C8	C7	C4	C3	65.8(4)
C10	O3	C11	C22	55.4(8)	C8	C7	C4	C5	-117.1(3)
C10	C9	C8	C7	-81.1(4)	C8	C7	C16	C17	31.2(4)
C7	C4	C3	C2	179.0(3)	C8	C7	C16	C21	-147.0(3)
C7	C4	C5	C6	-178.5(3)	C10A	O3	C11A	C22A	-36(4)
C7	C16	C17	C18	-177.3(3)	C10A	O3	C11A	C13A	-153.9(18)
C7	C16	C21	C20	175.6(3)	C10A	O3	C11A	C12A	95(3)
C4	C7	C16	C17	-151.4(3)	C10A	C9	C8	C7	-119.9(8)
C4	C7	C16	C21	30.4(4)	C15A	C9	C8	C7	134.7(9)
C4	C7	C8	C9	9.2(5)	C15A	C9	C10A	O3	146.3(15)
C4	C3	C2	C1	-0.6(4)	C15A	C9	C10A	O4A	-27(2)
C4	C5	C6	C1	-0.3(5)	C14A	C9	C8	C7	16.0(12)
C3	C4	C5	C6	-1.3(5)	C14A	C9	C10A	O3	-99.2(18)
C3	C2	C1	N1	179.8(3)	C14A	C9	C10A	O4A	87(2)
C3	C2	C1	C6	-1.1(4)	C11A	O3	C10A	C9	152.8(19)
C2	C1	C6	C5	1.6(5)	C11A	O3	C10A	O4A	-33(3)

Table S14. Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for 11.

Atom	*x*	*y*	*z*	U(eq)
H12A	9175.28	8728.98	6926.59	135
H12B	8322.09	10065.02	7164.97	135
H12C	8366.65	9569.36	6385.02	135
H3	5924.66	6885.55	5408.27	50
H2	3919.75	6732.16	5333.04	51
H14A	6795.23	2453.68	6352.54	92
H14B	7254.45	2197.53	5596.61	92
H14C	6204.53	3345.04	5735.06	92
H13A	6362.91	8982.61	6281.99	116
H13B	6141.67	9586.18	7036.25	116
H13C	5725.71	7907.29	6821.28	116
H15A	9377.01	4516.12	6465.57	96
H15B	9212.59	2881.48	6111.65	96

Atom	*x*	*y*	*z*	U(eq)
H15C	8589.24	3238.56	6817.36	96
H17	9671.11	4723.41	4285.03	59
H18	10564.67	5702.43	3325.81	75
H19	9642.55	7479.55	2652.06	80
H20	7760.68	8197.19	2901.09	75
H21	6814.15	7153.11	3819.29	60
H5	6234.9	3491.05	4042.83	58
H6	4233.08	3341.95	3949.43	58
H8	8956.9	5260.6	5322.61	50
H22A	6908.08	6630.52	7739.57	167
H22B	7329.66	8266.31	8008.86	167
H22C	8256.67	6998.24	7794.19	167
H15D	9576.48	3609.39	6118.19	96
H15E	8826.23	2290.16	5768.17	96
H15F	8739.28	2565.86	6567.91	96
H14D	6712.07	2774.95	6479.8	92
H14E	6565.3	2780.16	5673.82	92
H14F	6045.04	4152.51	6115.85	92
H22D	6064.97	6633.04	7416.45	167
H22E	6468.91	8079.69	7854.11	167
H22F	7192.05	6519.68	7881.37	167
H13D	7122.12	9339.28	6230.36	116
H13E	6653.14	9875.48	6954.88	116
H13F	5979.49	8582.95	6538	116
H12D	9042.14	7908.63	7507.22	135
H12E	8365.98	9505.62	7482.62	135
H12F	9027.82	8896.25	6824.39	135
H22B	7329.66	8266.31	8008.86	167
H22C	8256.67	6998.24	7794.19	167
H15D	9576.48	3609.39	6118.19	96
H15E	8826.23	2290.16	5768.17	96
H15F	8739.28	2565.86	6567.91	96
H14D	6712.07	2774.95	6479.8	92
H14E	6565.3	2780.16	5673.82	92
H14F	6045.04	4152.51	6115.85	92
H22D	6064.97	6633.04	7416.45	167
H22E	6468.91	8079.69	7854.11	167
H12F	9027.82	8896.25	6824.39	135

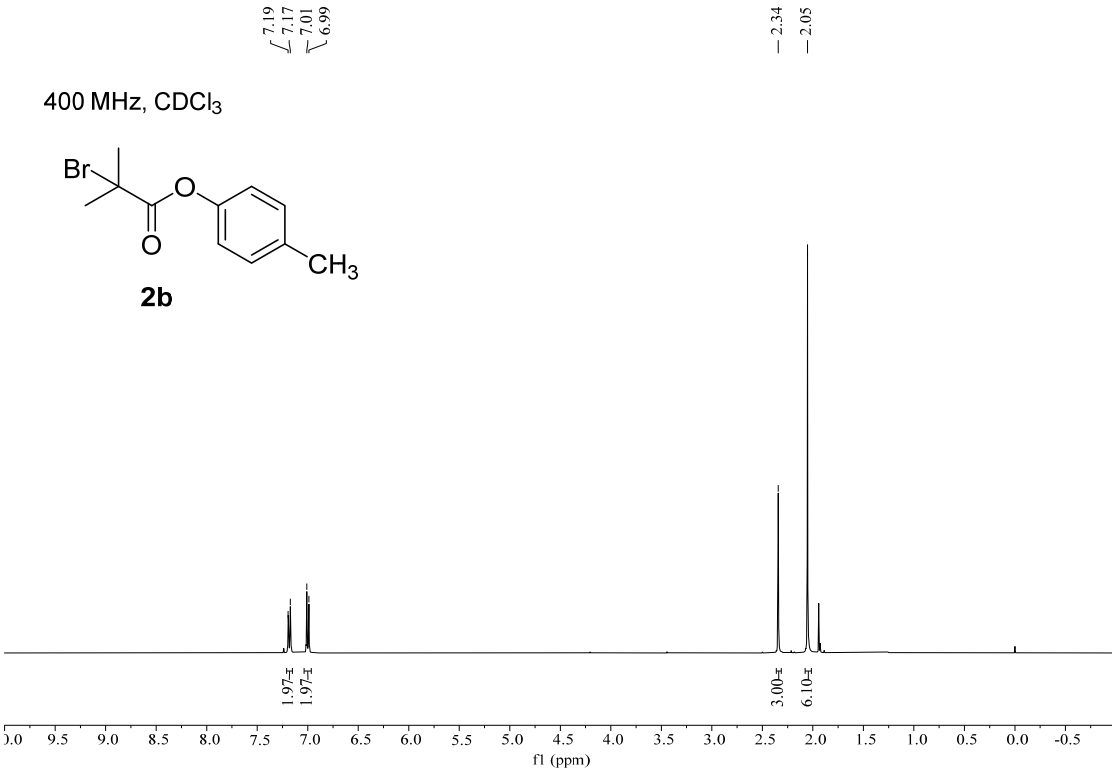
Table S15. Atomic Occupancy for 11.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
O4	0.802(3)	C12	0.802(3)	H12A	0.802(3)
H12B	0.802(3)	H12C	0.802(3)	C11	0.802(3)
C10	0.802(3)	C14	0.802(3)	H14A	0.802(3)
H14B	0.802(3)	H14C	0.802(3)	C13	0.802(3)
H13A	0.802(3)	H13B	0.802(3)	H13C	0.802(3)
C15	0.802(3)	H15A	0.802(3)	H15B	0.802(3)
H15C	0.802(3)	C22	0.802(3)	H22A	0.802(3)
H22B	0.802(3)	H22C	0.802(3)	C10A	0.198(3)
O4A	0.198(3)	C15A	0.198(3)	H15D	0.198(3)
H15E	0.198(3)	H15F	0.198(3)	C14A	0.198(3)
H14D	0.198(3)	H14E	0.198(3)	H14F	0.198(3)
C22A	0.198(3)	H22D	0.198(3)	H22E	0.198(3)
H22F	0.198(3)	C13A	0.198(3)	H13D	0.198(3)
H13E	0.198(3)	H13F	0.198(3)	C12A	0.198(3)
H12D	0.198(3)	H12E	0.198(3)	H12F	0.198(3)
C11A	0.198(3)				

Reference

1. Tang, C.; Zhang, R.; Zhu, B.; Fu, J.; Deng, Y.; Tian, L.; Guan, W.; Bi, X. Directed Copper-Catalyzed Intermolecular Heck-Type Reaction of Unactivated Olefins and Alkyl Halides. *J. Am. Chem. Soc.* **2018**, *140*, 16929−16935.
2. Armesto, D.; Ortiz, M. J.; Agarrabeitia, A. R.; Aparicio-Lara, S.; Martin-Fontecha, M.; Liras, M.; Martinez-Alcazar, M. P. Photochemical Reactivity of 1-Substituted-1-aza-1,4-dienes Promoted by Electron Acceptor Sensitizers. Di-π-methane Rearrangements and Alternative Reactions via Radical-Cation Intermediates. *J. Org. Chem.* **2002**, *67*, 9397−9405.
3. Zeng, X.; Lu, Z.; Liu, S.; Hammond, G. B.; Xu, B. Metal-free, Regio-, and Stereo-Controlled Hydrochlorination and Hydrobromination of Ynones and Ynamides. *J. Org. Chem.* **2017**, *82*, 13179−13187.

NMR spectra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6.99
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CH3
2b
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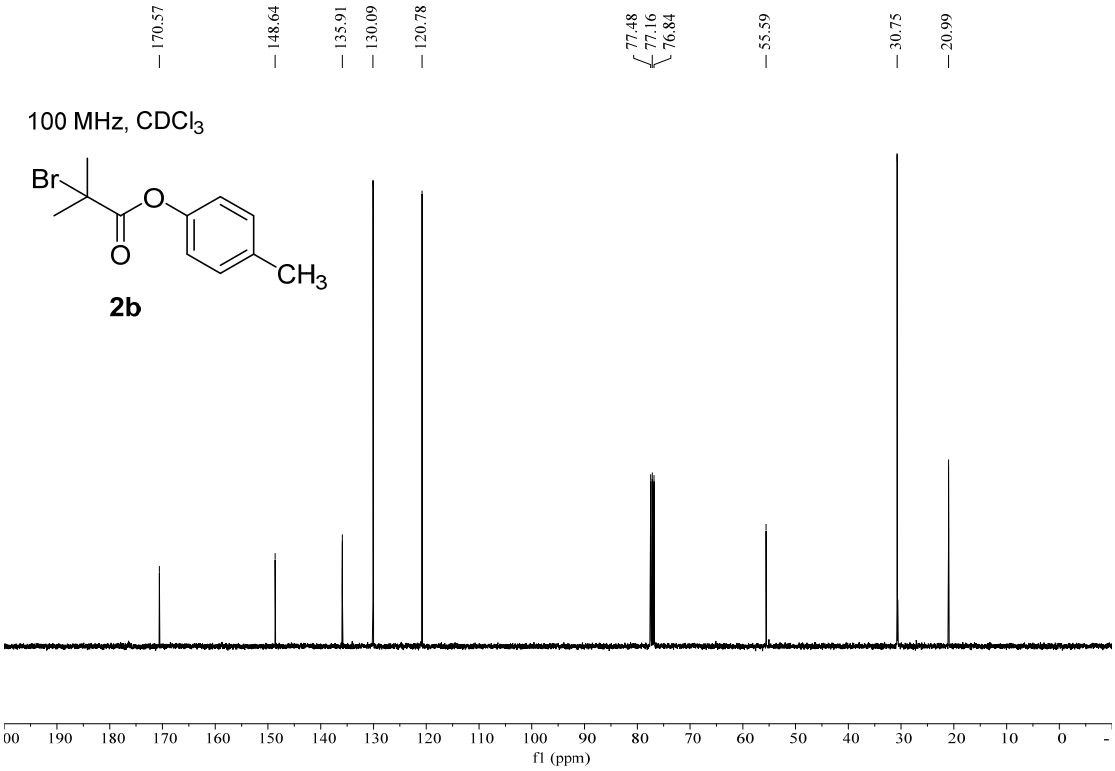
1.97
3.00
6.10
f1 (ppm)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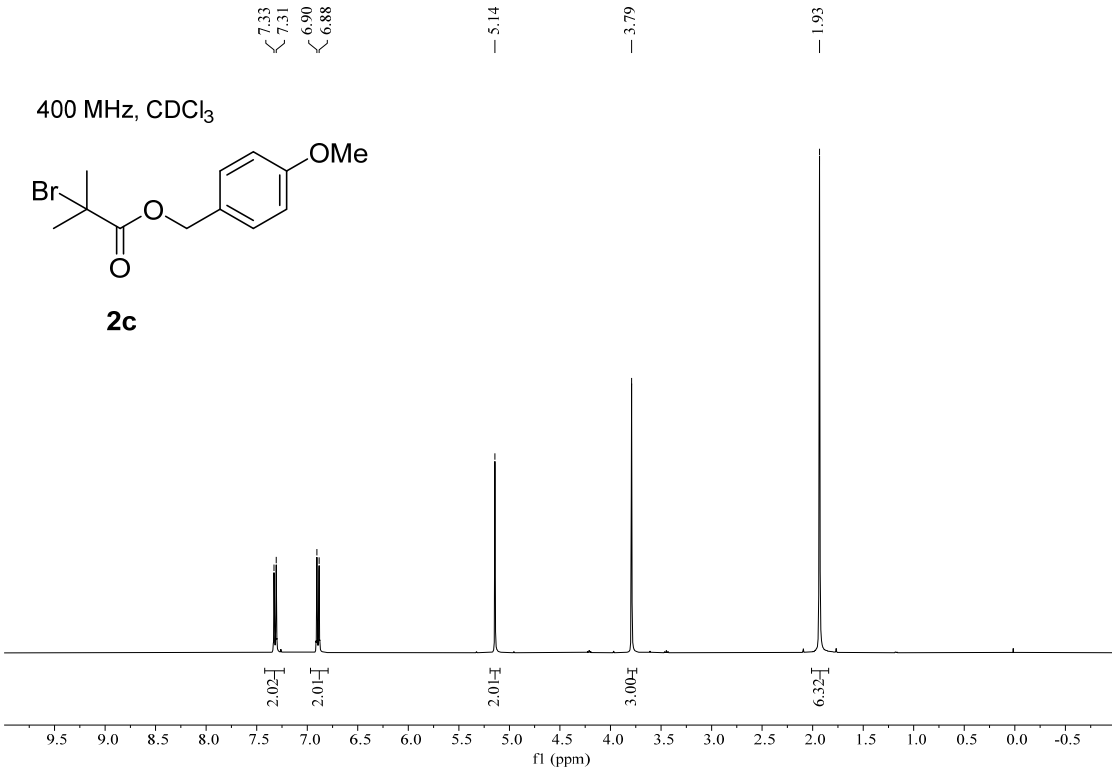
Br
O
O
CH3
2b
f1 (ppm)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O
OMe
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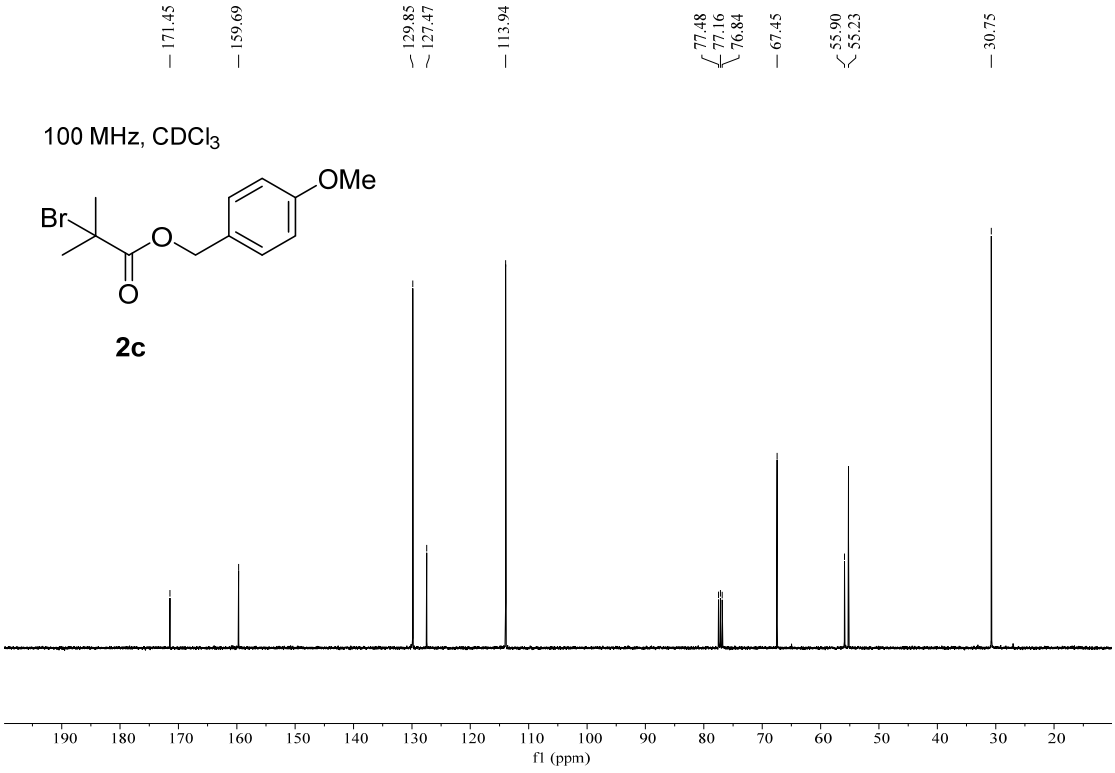
2.02
2.01
2.01
3.00
6.32
f1 (ppm)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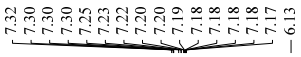
Br
O
O
OMe
2c
f1 (ppm)



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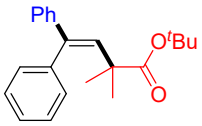

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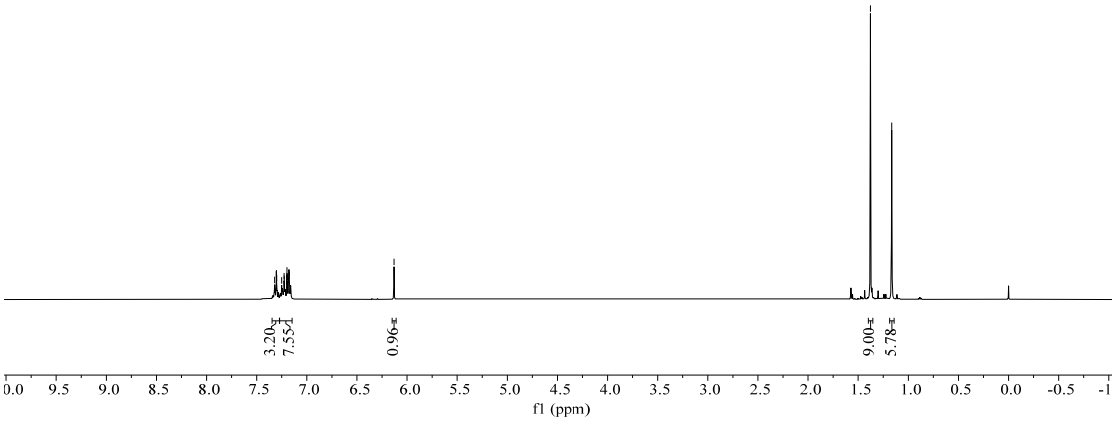

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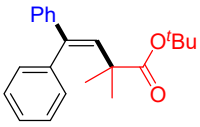

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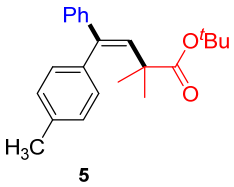

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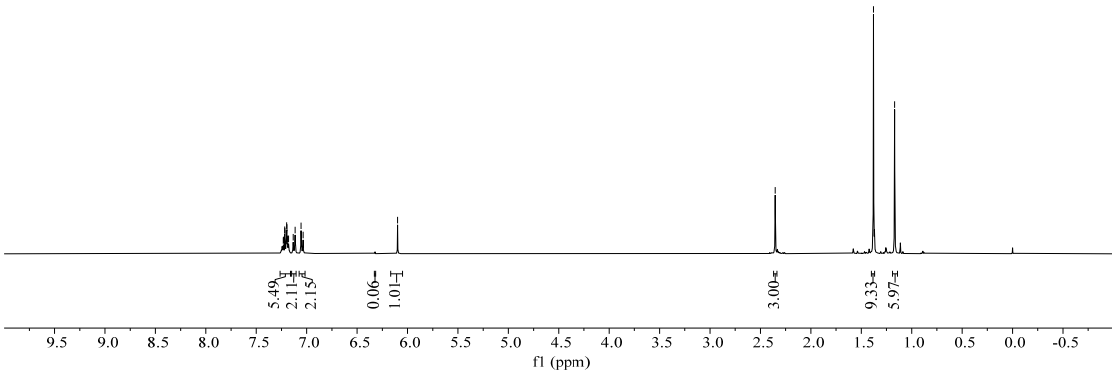

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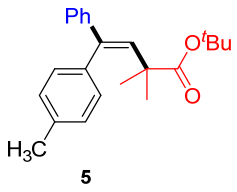

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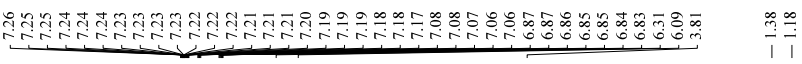

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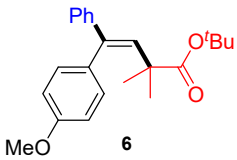

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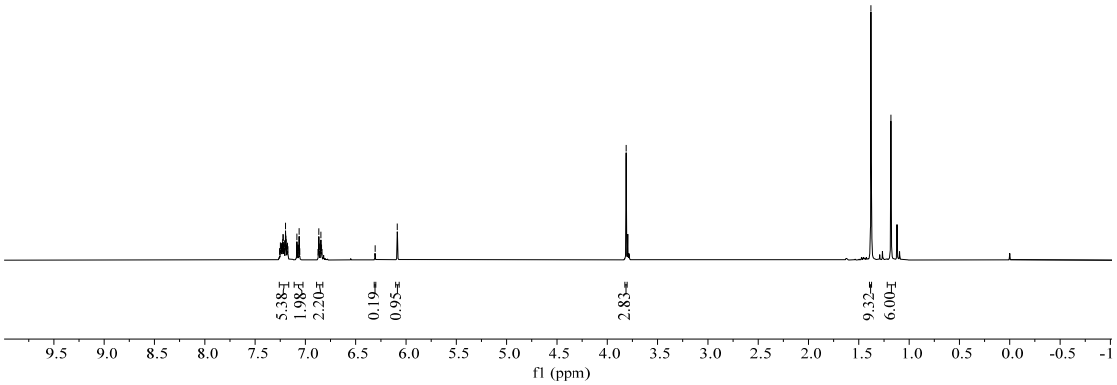

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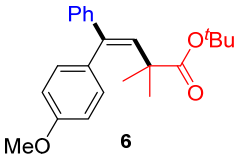

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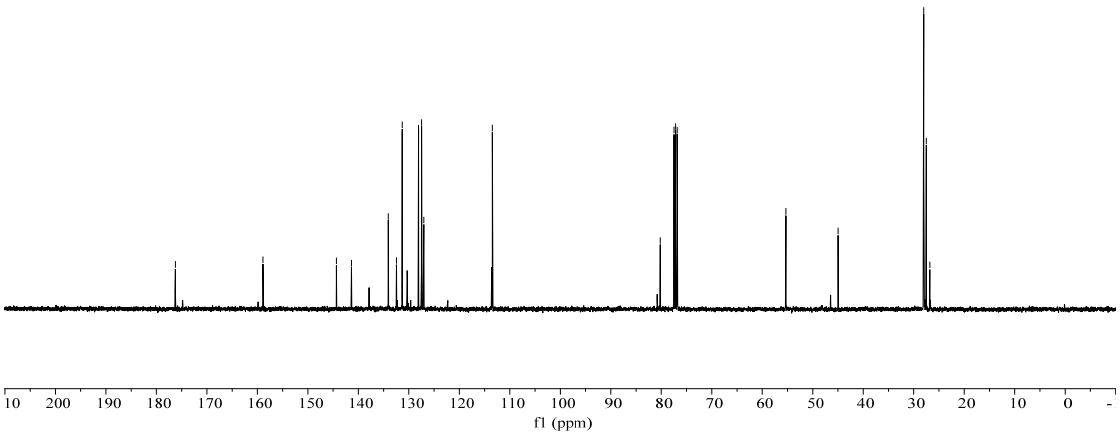

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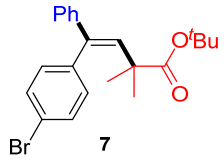

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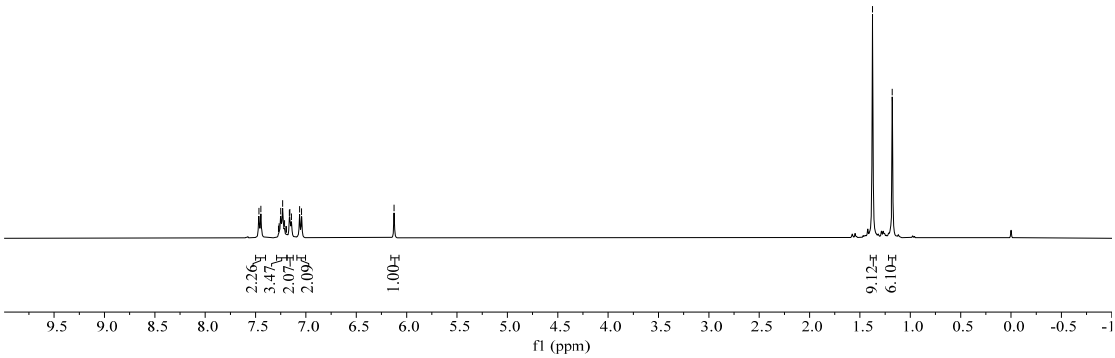

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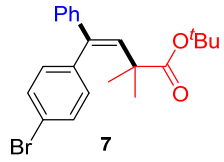

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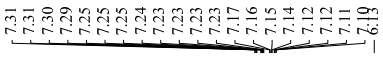

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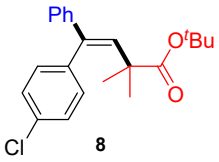

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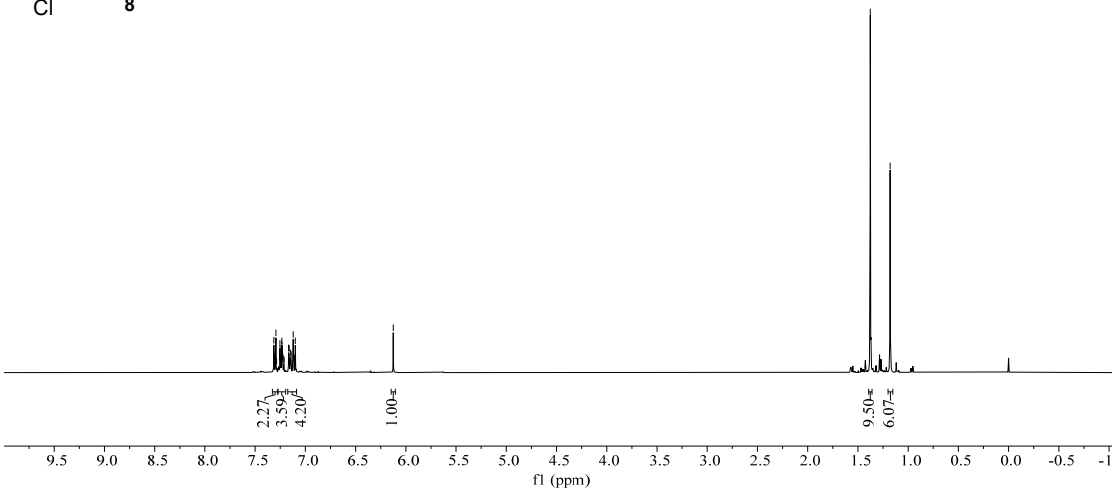

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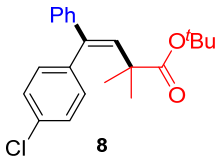

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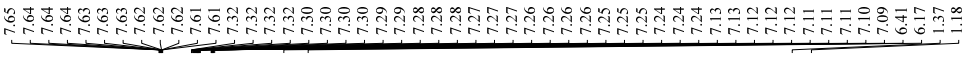

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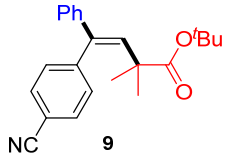

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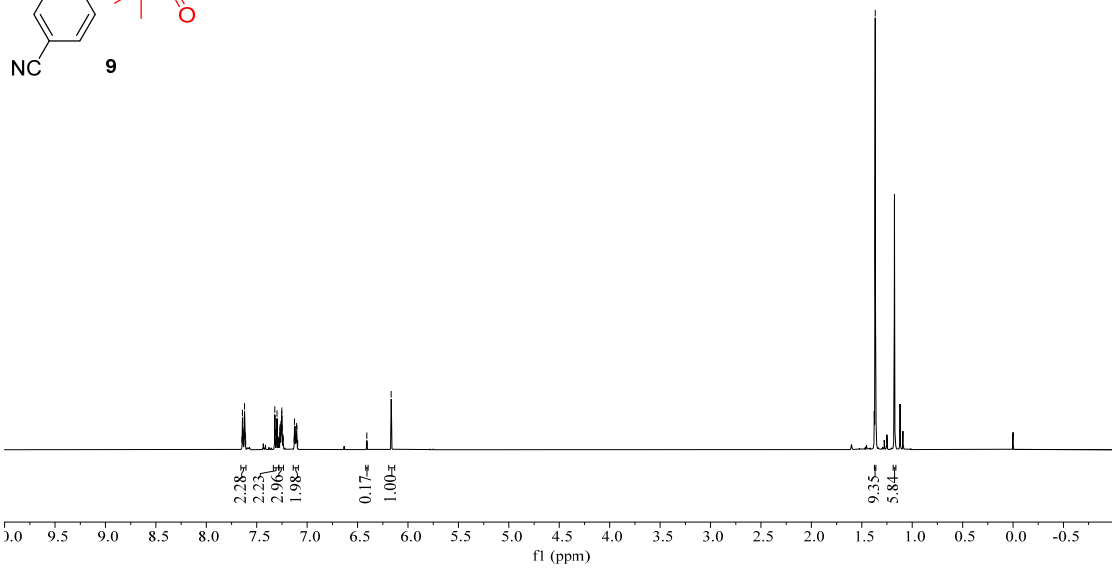

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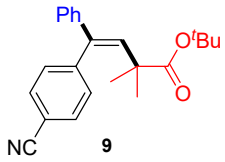

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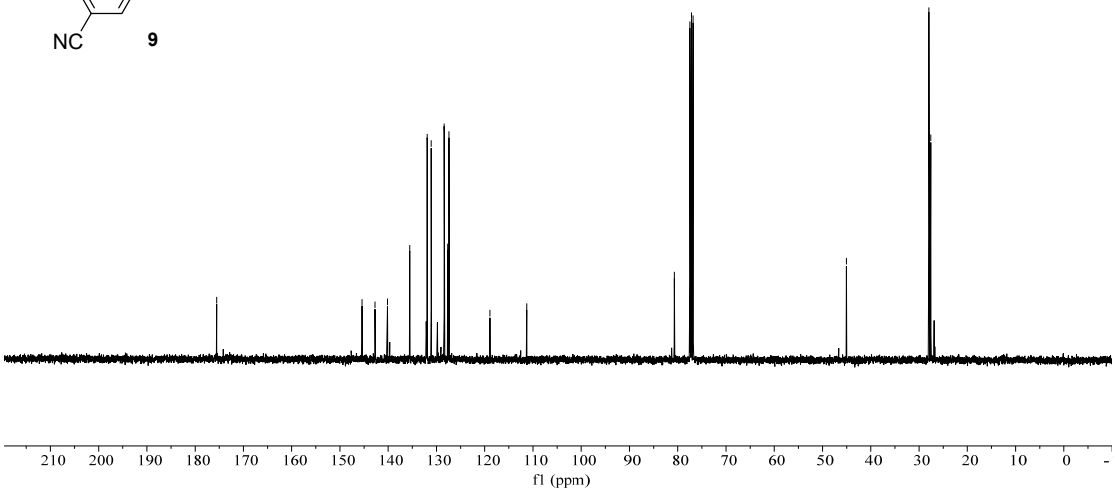

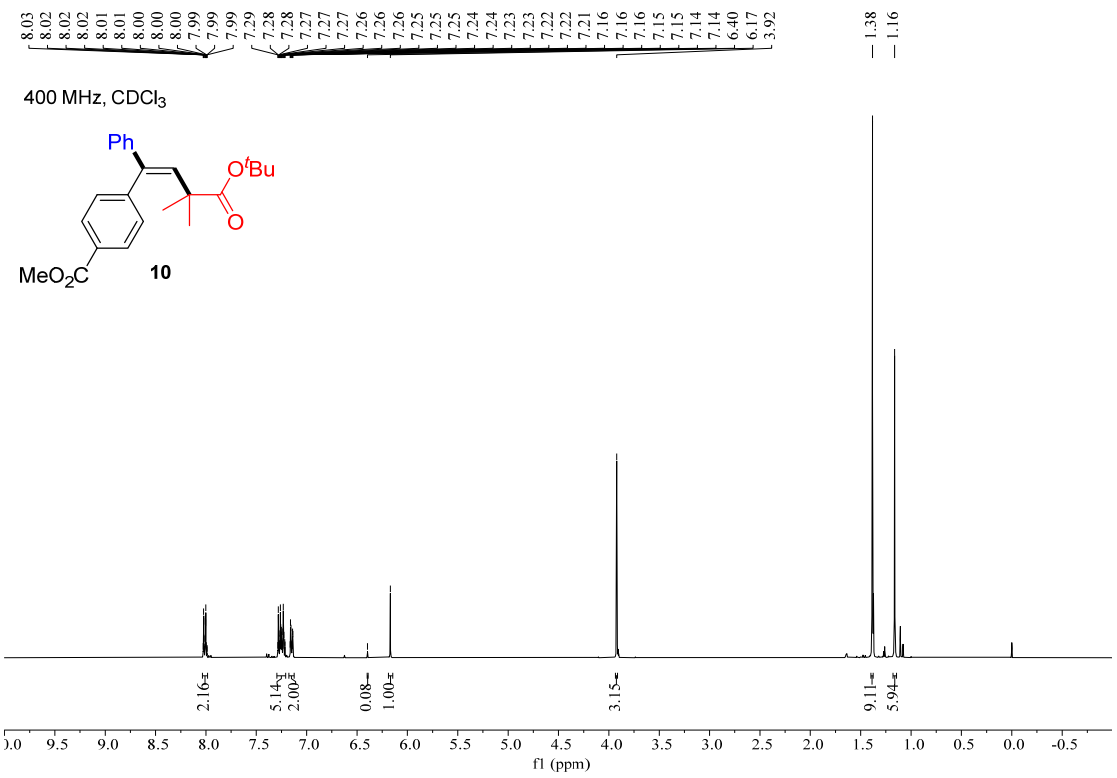
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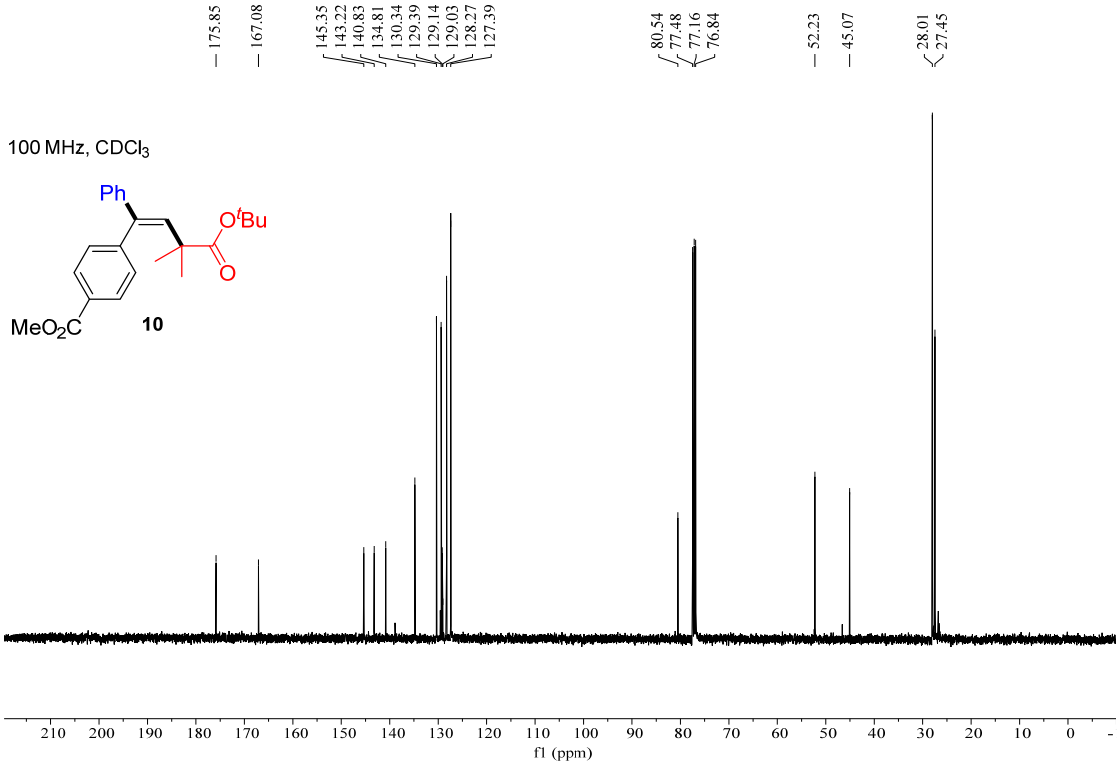
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O'Bu
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MeO2C
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fl (ppm)

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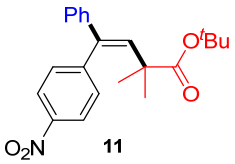

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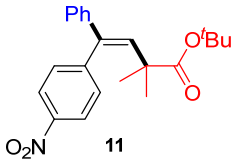
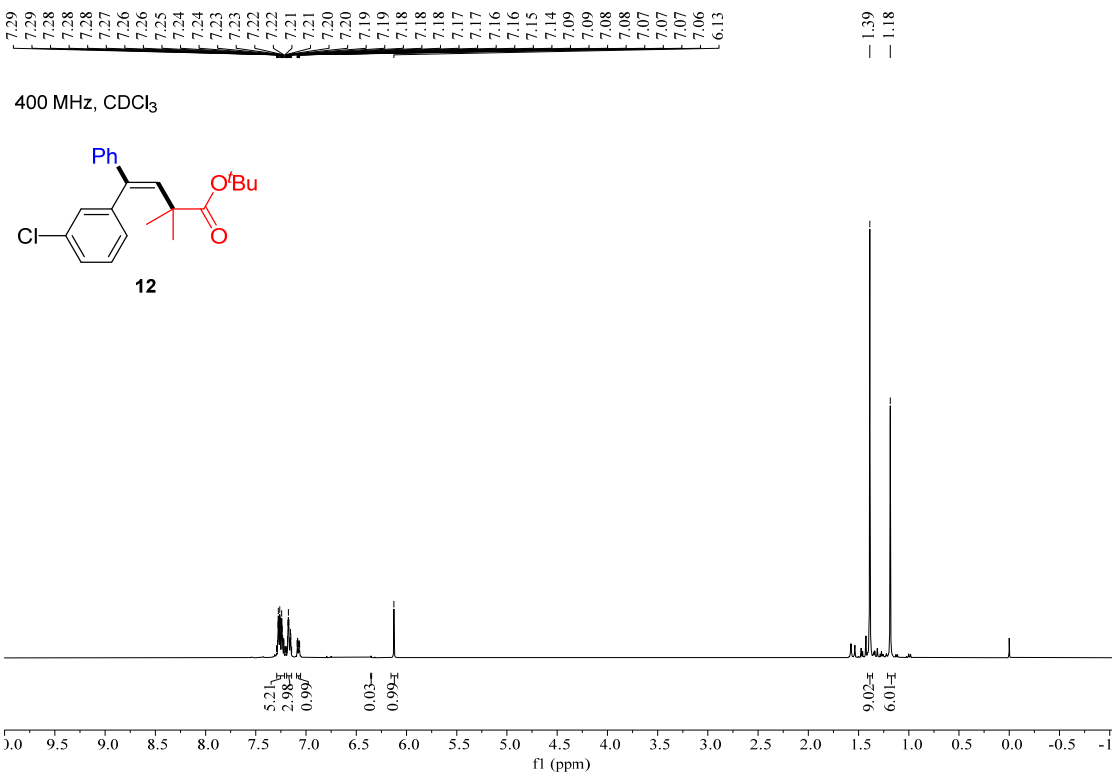


11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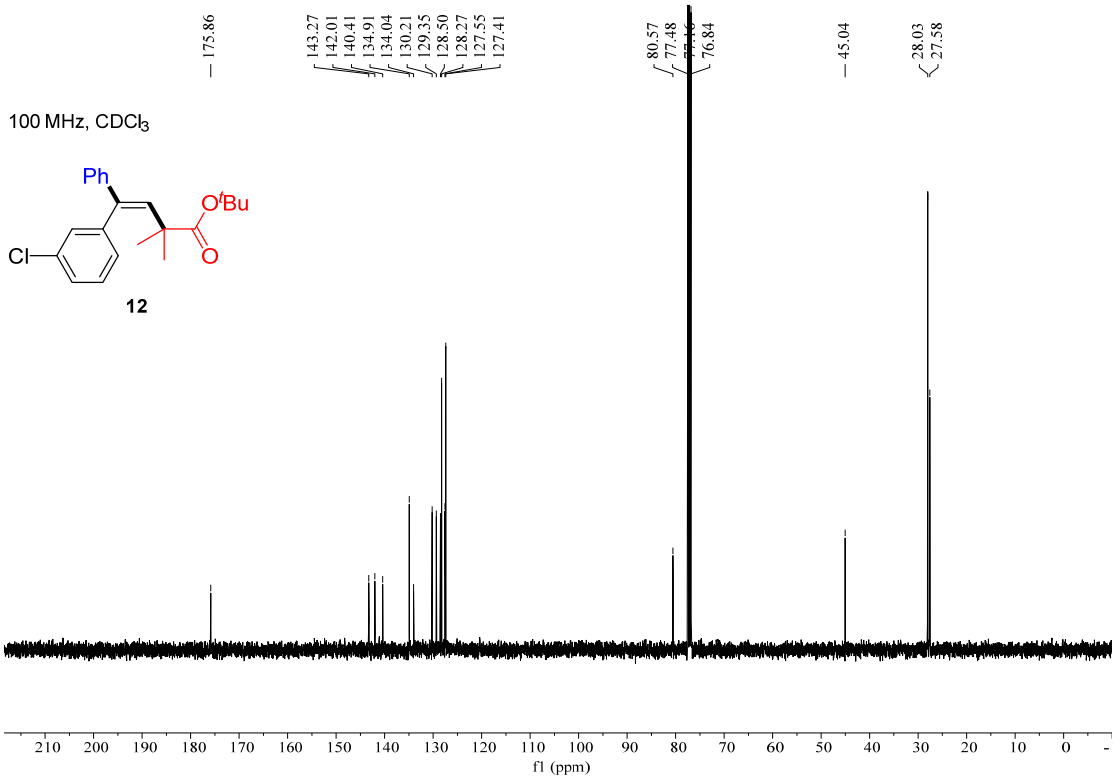
7.17
7.17
7.16
7.16
7.15
7.14
7.09
7.09
7.08
7.08
7.07
7.07
7.07
7.06
6.13
1.39
1.18
400 MHz, CDCl3
Ph
OtBu
Cl
O
12
5.21
2.98
0.99
0.03
0.99
9.02
6.01
f1 (ppm)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143.27
142.01
140.41
134.91
134.04
130.21
129.35
128.50
128.27
127.55
127.41
80.57
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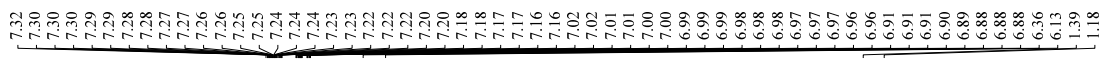
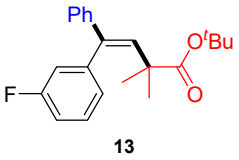
77.16
76.84
45.04
28.03
27.58
100 MHz, CDCl3
Ph
OtBu
Cl
O
12
f1 (ppm)



400 MHz, $CDCl_3$



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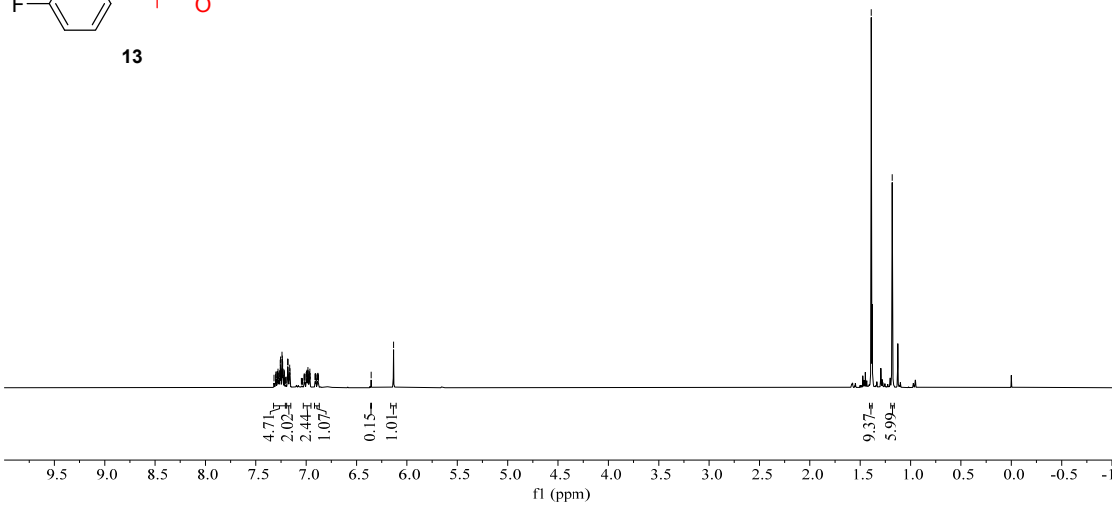
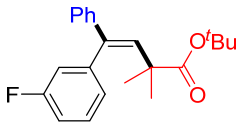


100 MHz, $CDCl_3$



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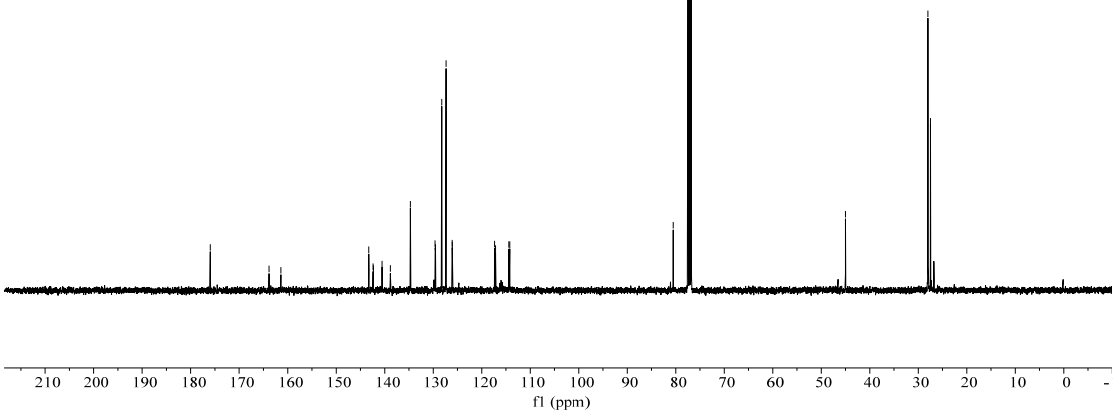
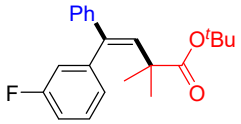


376 MHz, $CDCl_3$



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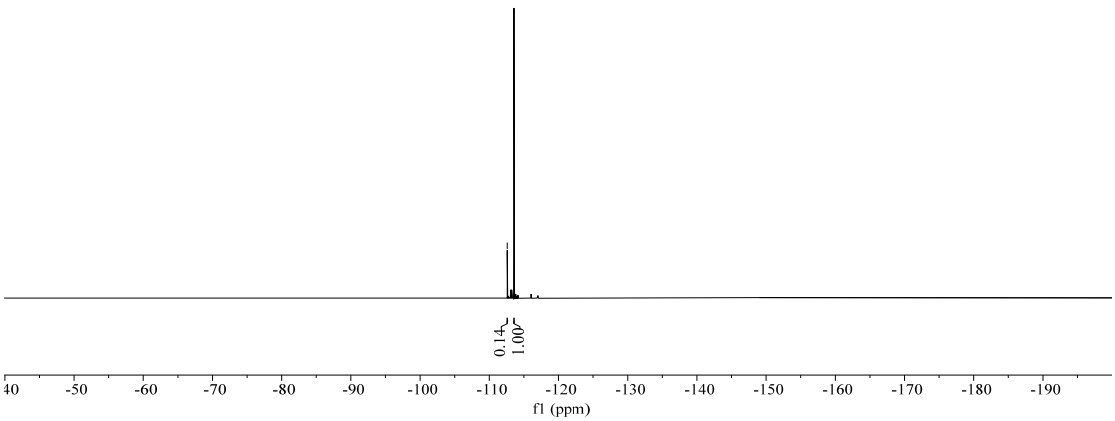
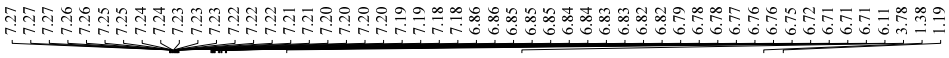
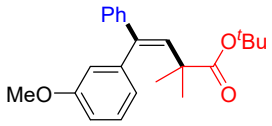
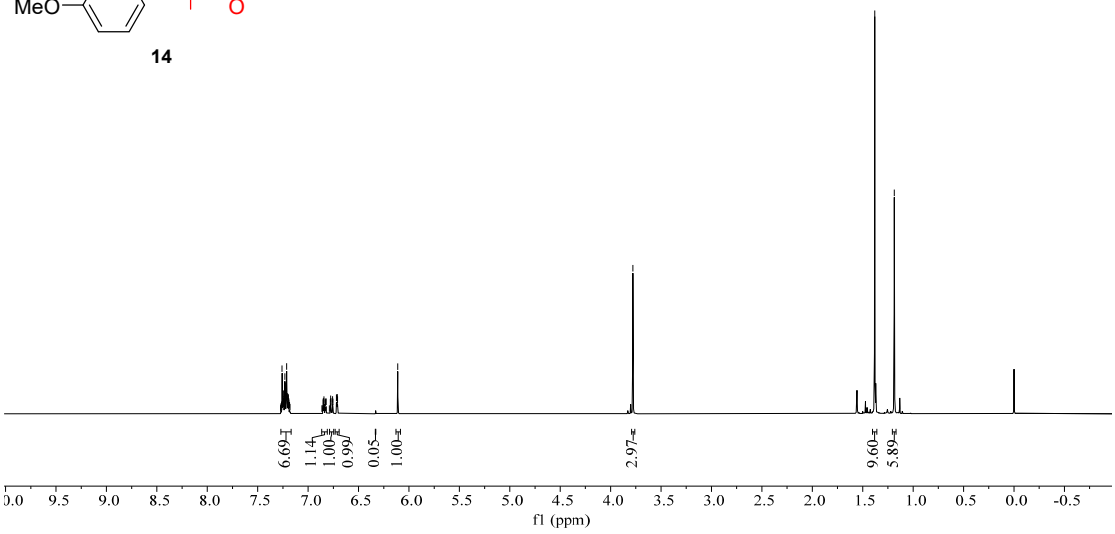


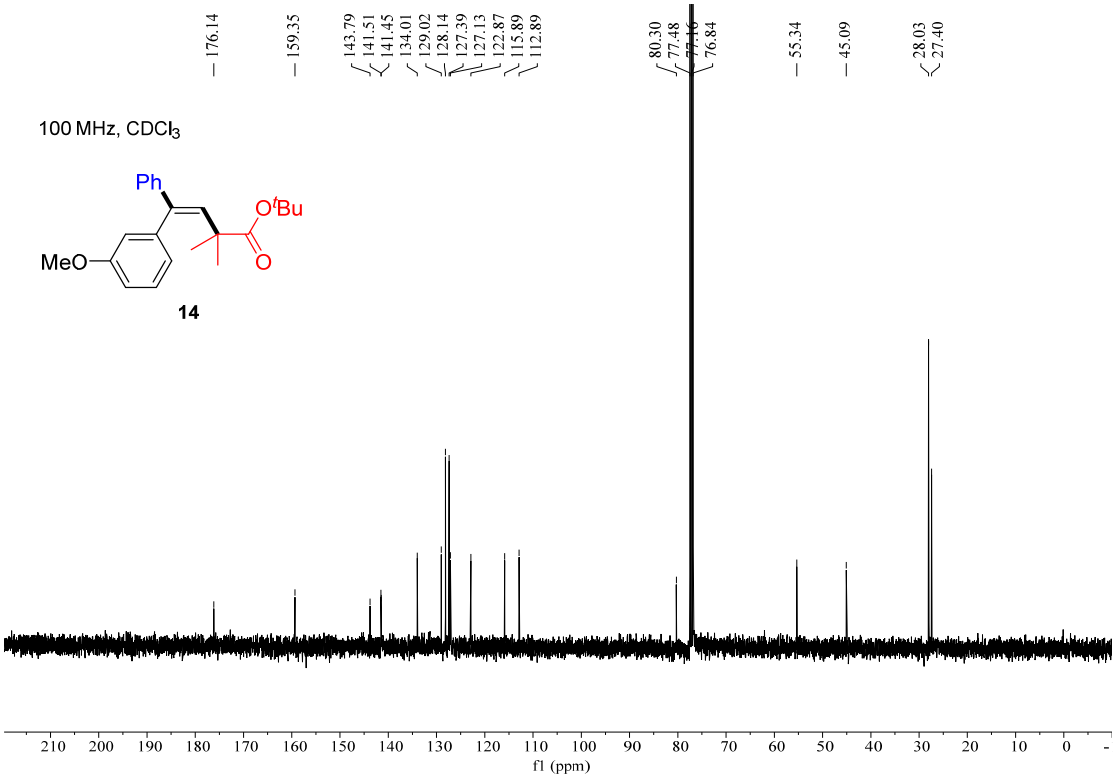


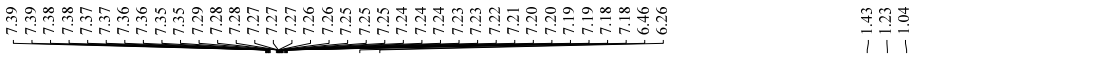
400 MHz, $CDCl_3$



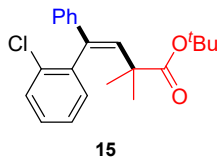
14







400 MHz, $CDCl_3$



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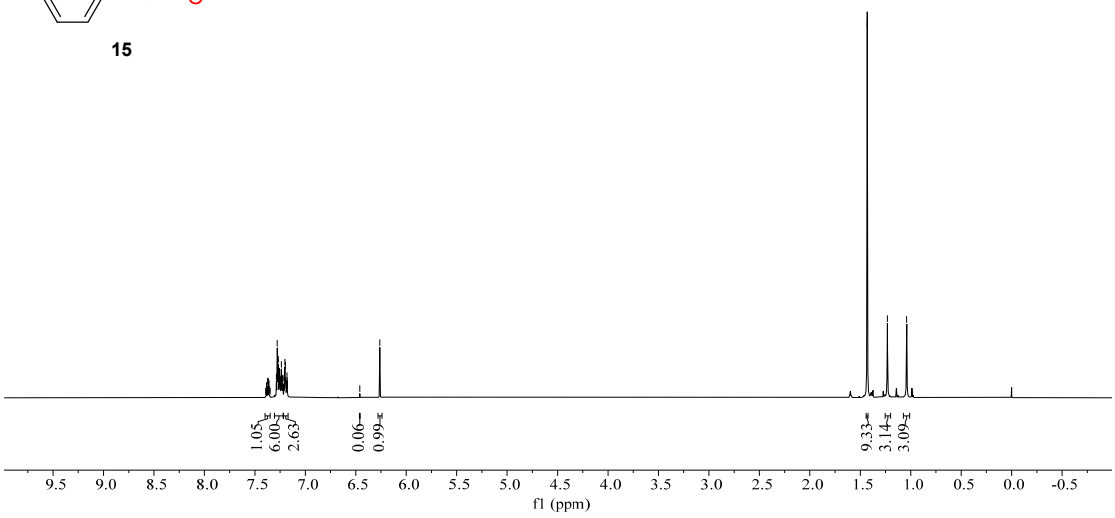
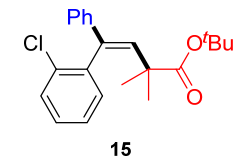
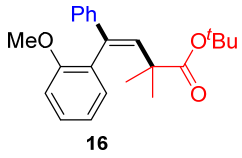


100 MHz, $CDCl_3$

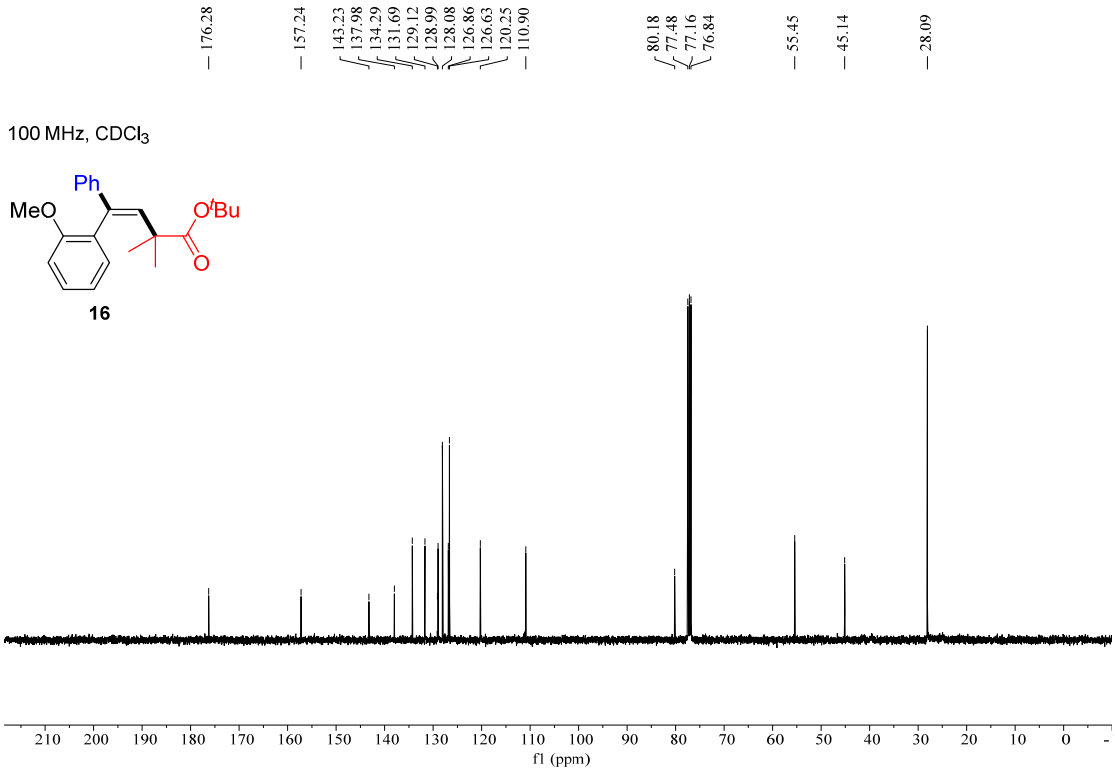


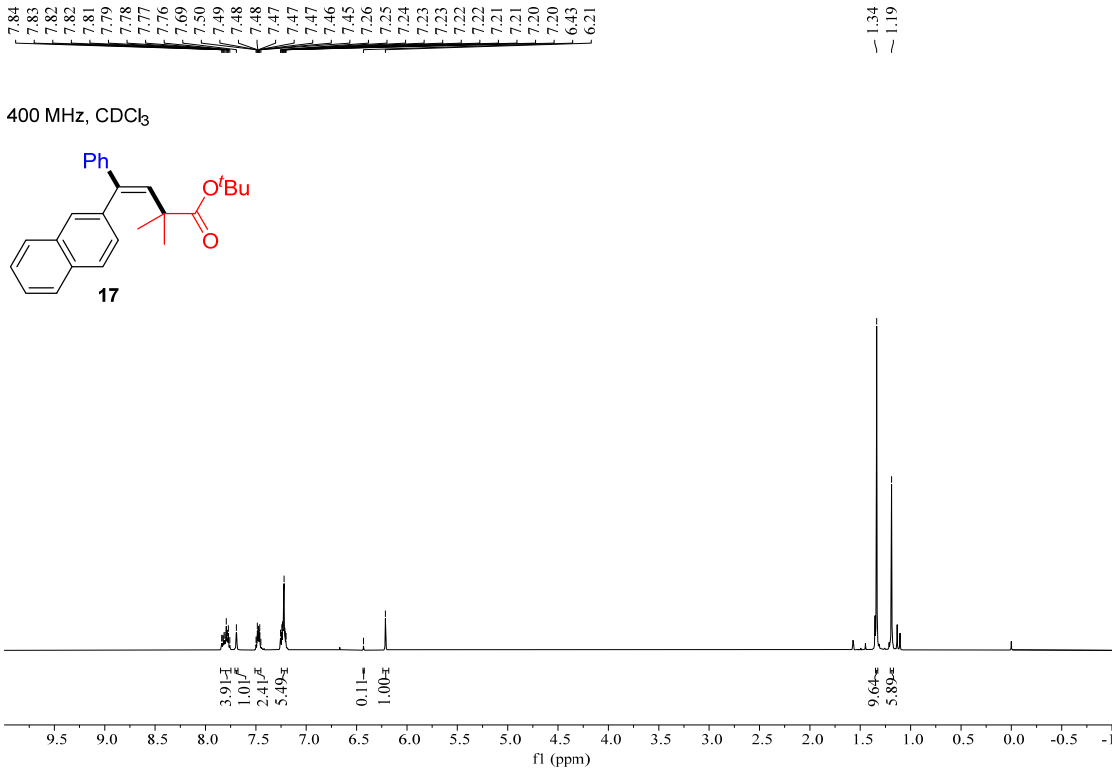
15

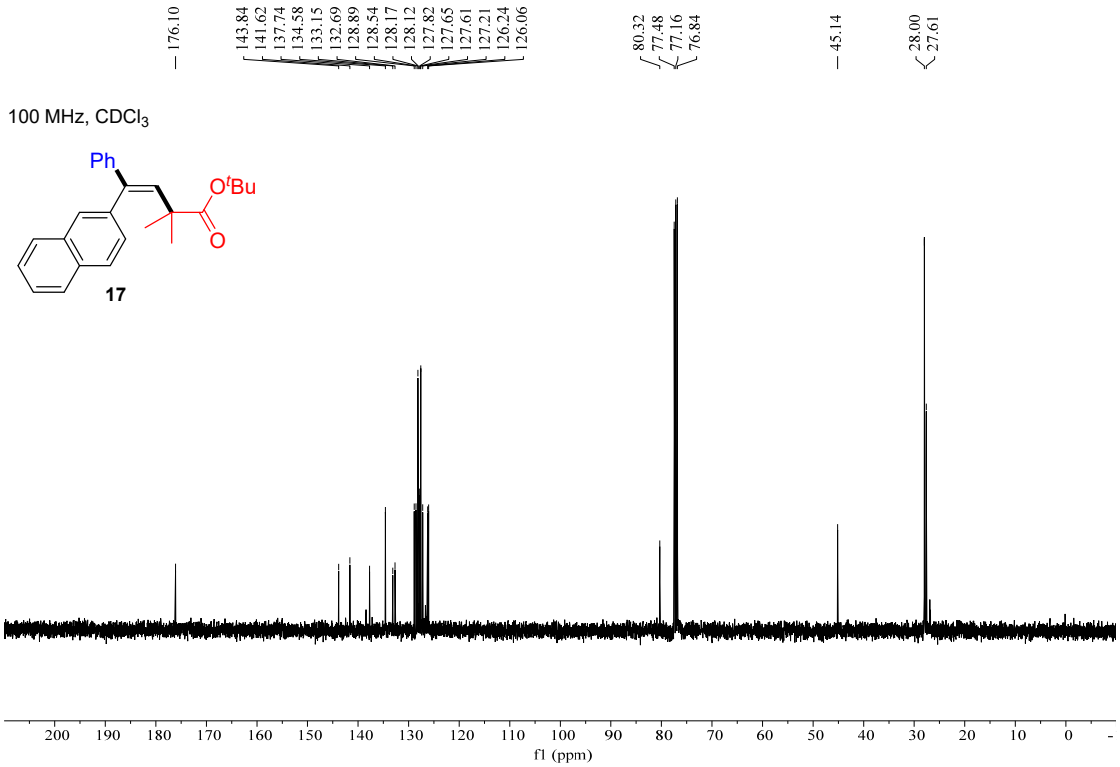
400 MHz, $CDCl_3$



16


176.28
157.24
143.23
137.98
134.29
131.69
129.12
128.99
128.08
126.86
126.63
120.25
110.90
80.18
77.48
77.16
76.84
55.45
45.14
28.09
100 MHz, CDCl3
Ph
MeO
O'Bu
O
16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.84
7.83
7.82
7.82
7.81
7.79
7.78
7.77
7.76
7.69
7.50
7.49
7.48
7.48
7.47
7.47
7.47
7.46
7.45
7.26
7.25
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.20
6.43
6.21
1.34
1.19
400 MHz, CDCl3
Ph
O'Bu
O
17
3.91
1.01
2.41
5.49
0.11
1.00
9.64
5.89
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
f1 (ppm)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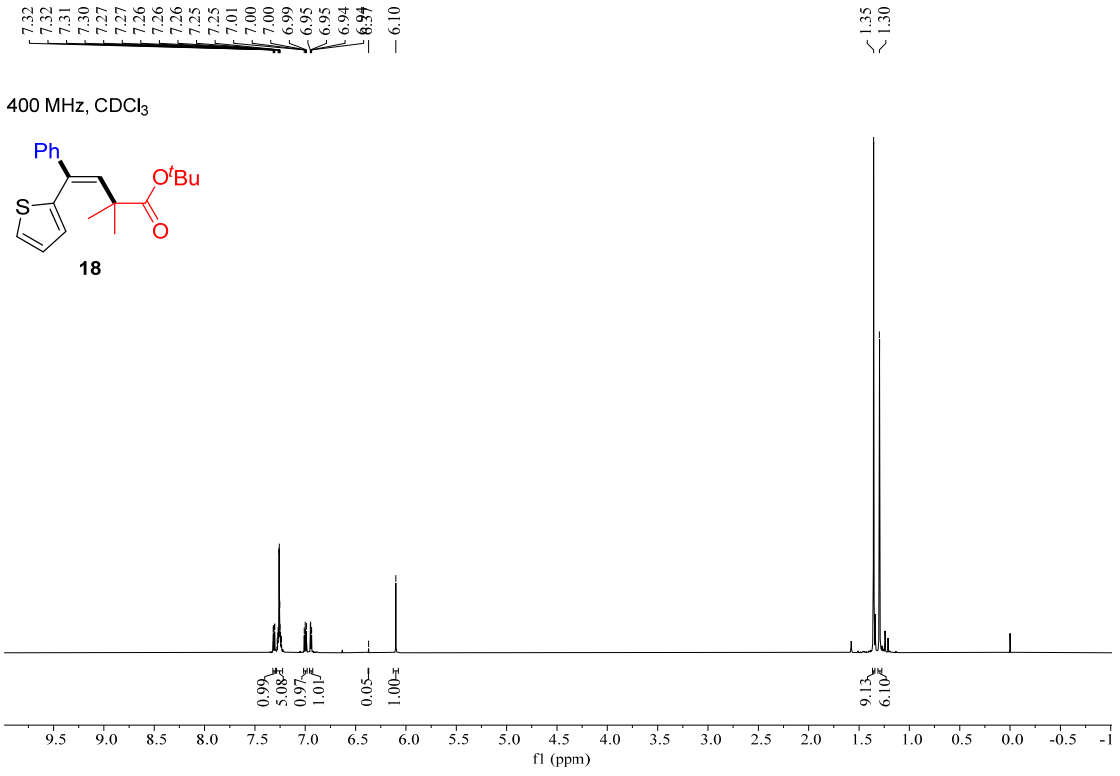
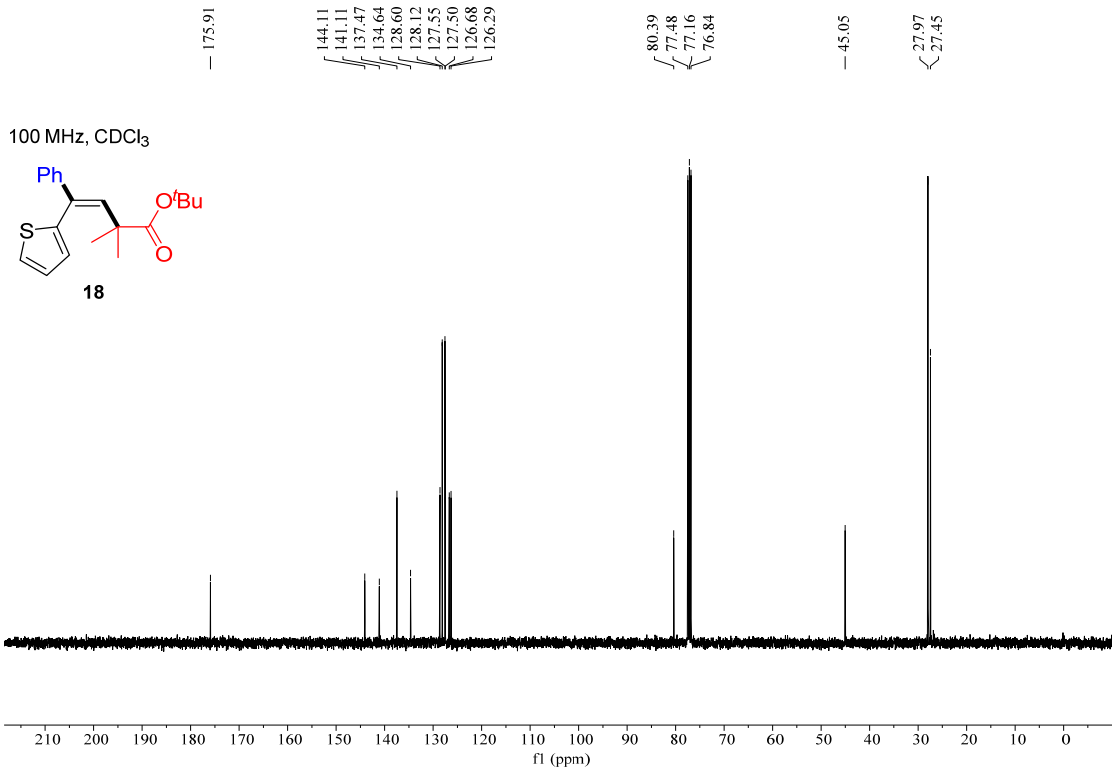
143.84
141.62
137.74
134.58
133.15
132.69
128.89
128.54
128.17
128.12
127.82
127.65
127.61
127.21
126.24
126.06
80.32
77.48
77.16
76.84
45.14
28.00
27.61
100 MHz, CDCl3
Ph
OtBu
O
17
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.32
7.32
7.31
7.30
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.01
7.00
7.00
6.99
6.95
6.95
6.94
6.94
6.10
1.35
1.30
400 MHz, CDCl3
Ph
S
OtBu
O
18
0.99
5.08
0.97
1.01
0.05
1.00
9.13
6.10
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
f1 (ppm)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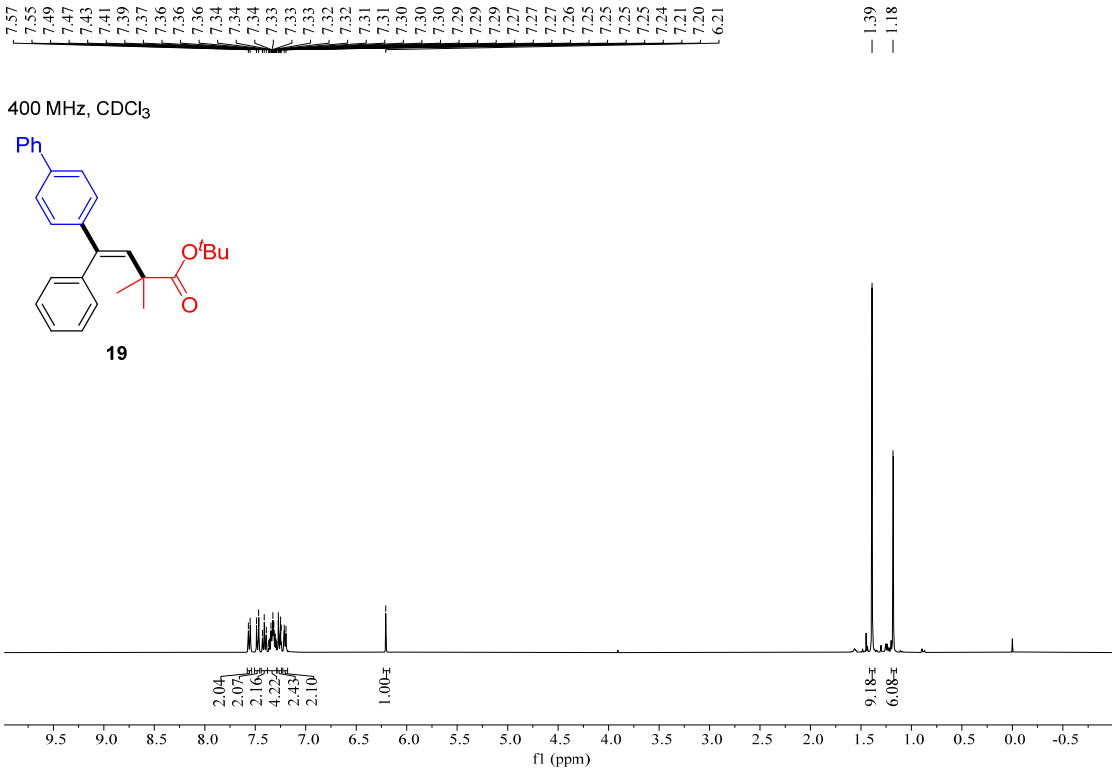
144.11
141.11
137.47
134.64
128.60
128.12
127.55
127.50
126.68
126.29
80.39
77.48
77.16
76.84
45.05
27.97
27.45
100 MHz, CDCl3
Ph
S
O
tBu
O
18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.34
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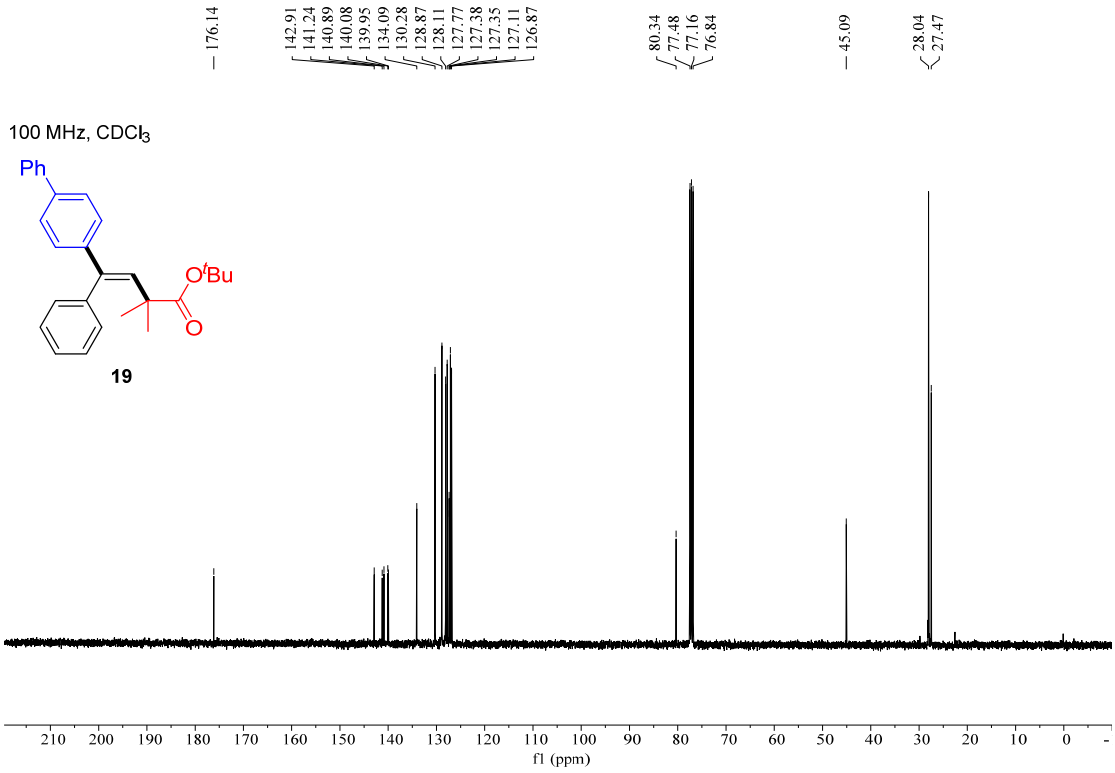
7.27
7.27
7.27
7.26
7.25
7.25
7.25
7.25
7.24
7.21
7.20
6.21
1.39
1.18
400 MHz, CDCl3
Ph
O
tBu
O
19
2.04
2.07
2.16
4.22
2.43
2.10
1.00
9.18
6.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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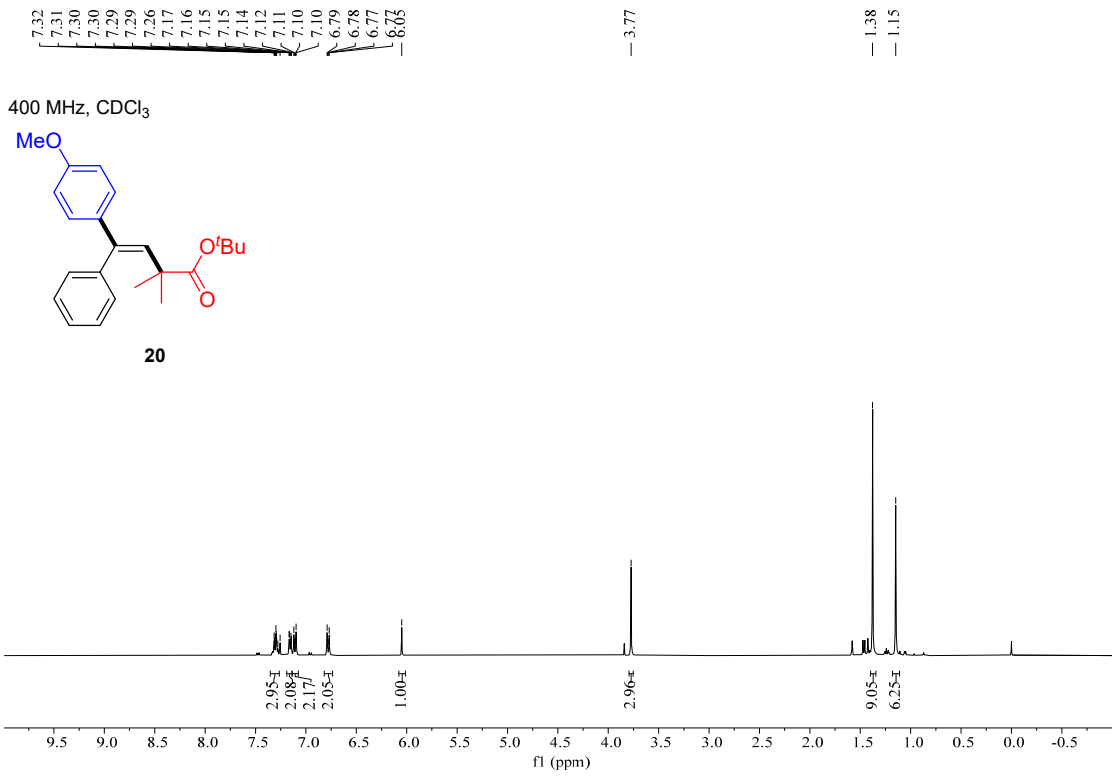
141.24
140.89
140.08
139.95
134.09
130.28
128.87
128.11
127.77
127.38
127.35
127.11
126.87
80.34
77.48
77.16
76.84
45.09
28.04
27.47
100 MHz, CDCl3
Ph
O'Bu
O
19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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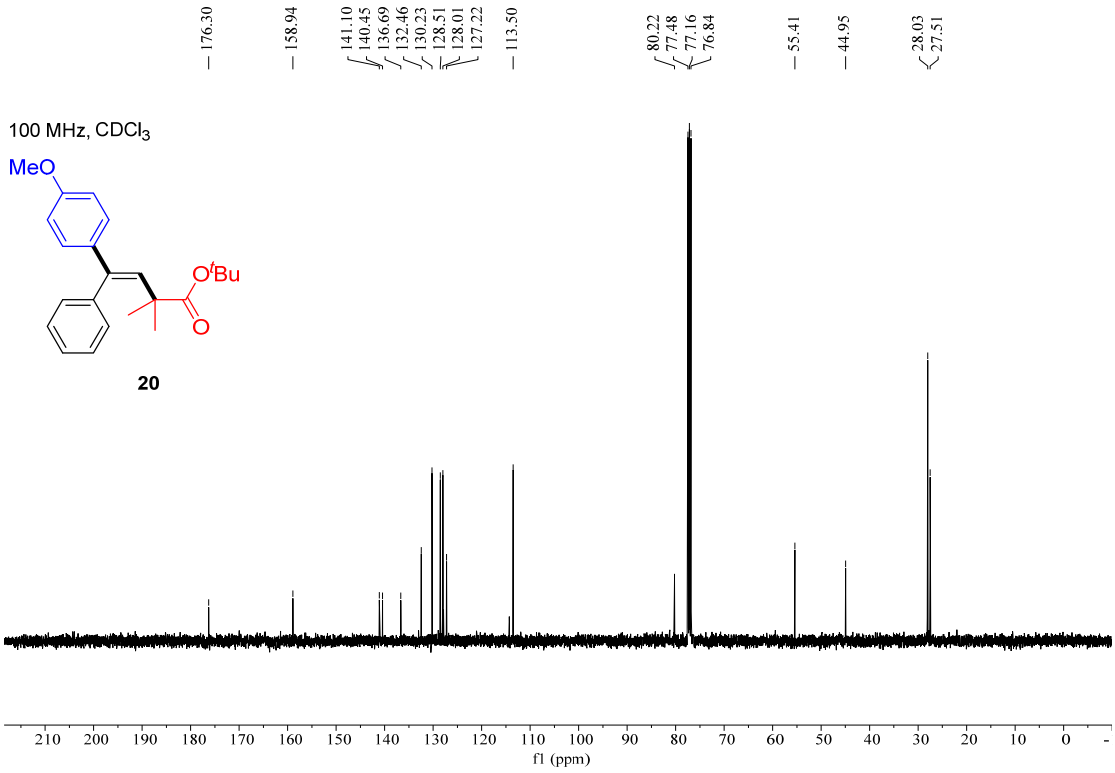
7.17
7.16
7.15
7.15
7.14
7.12
7.11
7.10
7.10
6.79
6.78
6.77
6.77
6.05
3.77
1.38
1.15
400 MHz, CDCl3
MeO
O'Bu
O
20
2.95
2.08
2.17
2.05
1.00
2.96
9.05
6.25
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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158.94
141.10
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132.46
130.23
128.51
128.01
127.22
113.50
80.22
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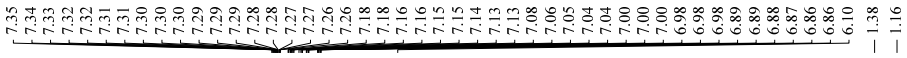
77.16
76.84
55.41
44.95
28.03
27.51
100 MHz, CDCl3
MeO
O
tBu
O
20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)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7.16
7.15
7.15
7.14
7.13
7.13
7.08
7.06
7.05
7.04
7.04
7.00
7.00
7.00
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6.89
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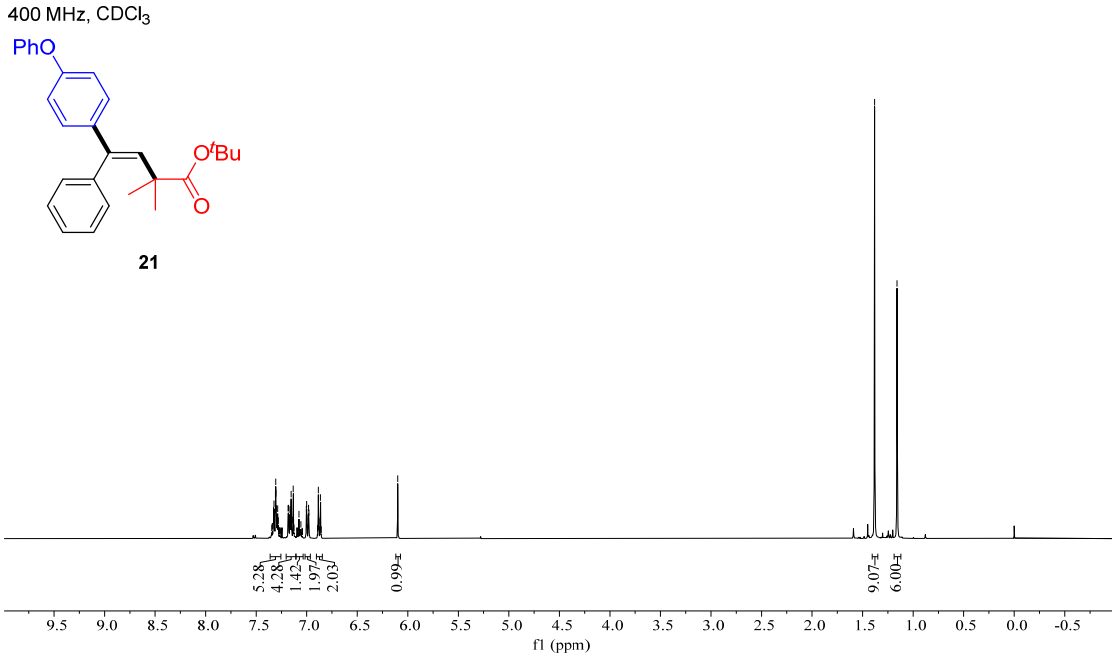
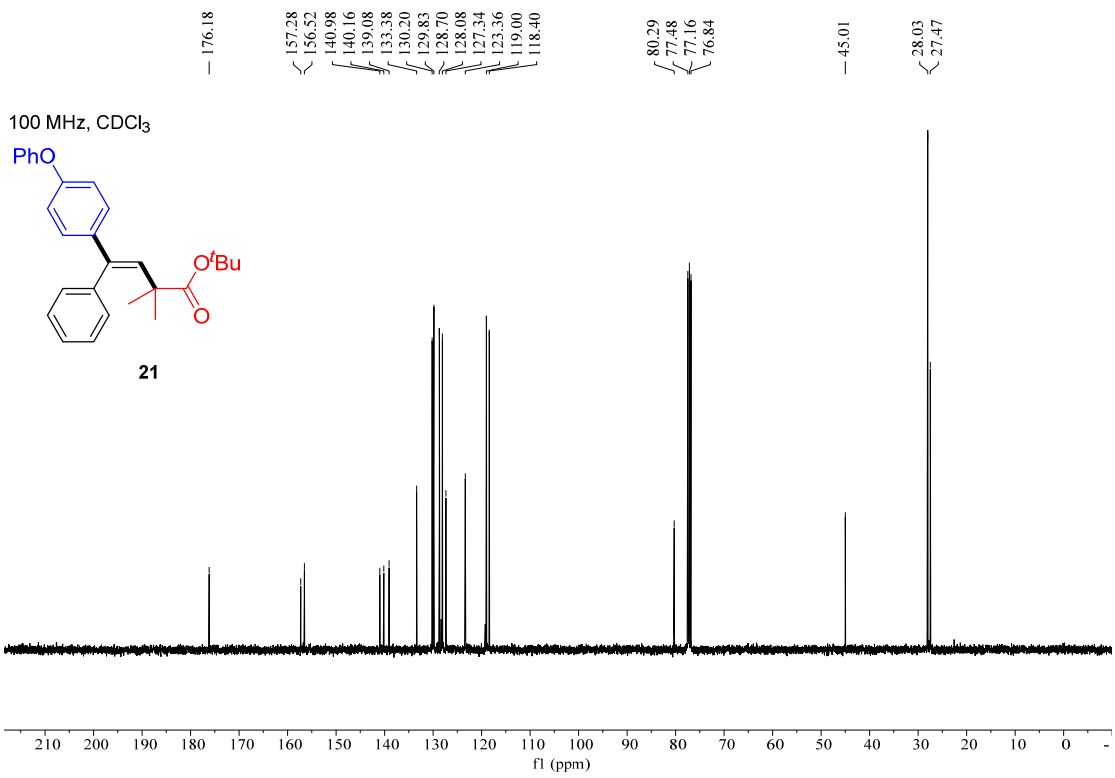
6.87
6.86
6.86
6.10
1.38
1.16


400 MHz, CDCl3
PhO
O
tBu
O
21
5.28
4.28
1.42
1.97
2.03
0.99
9.07
6.00
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
f1 (ppm)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139.08
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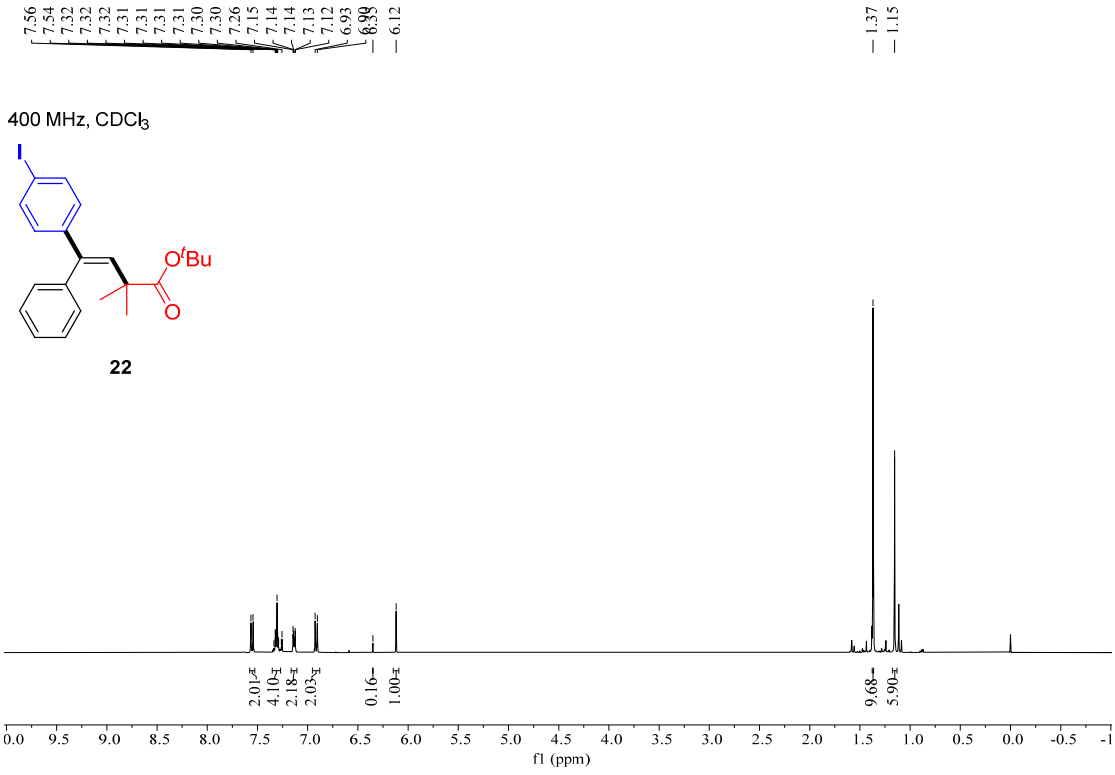
130.20
129.83
128.70
128.08
127.34
123.36
119.00
118.40
80.29
77.48
77.16
76.84
45.01
28.03
27.47
100 MHz, CDCl3
PhO
O'Bu
O
21
f1 (ppm)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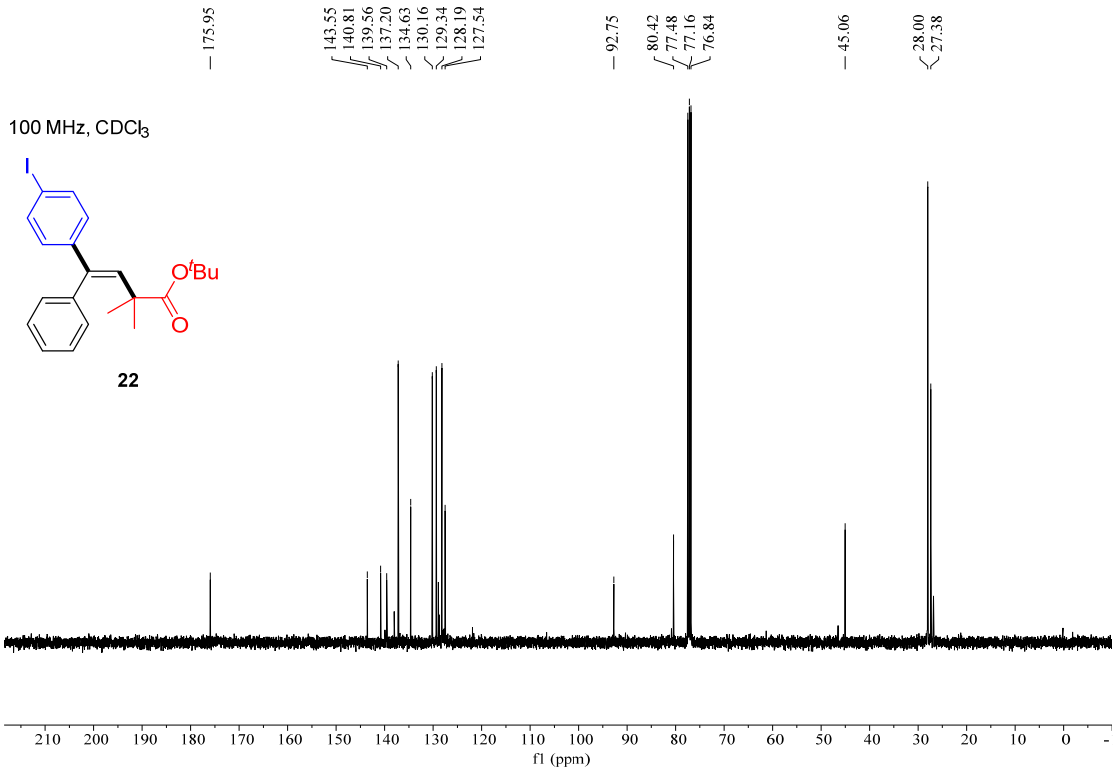
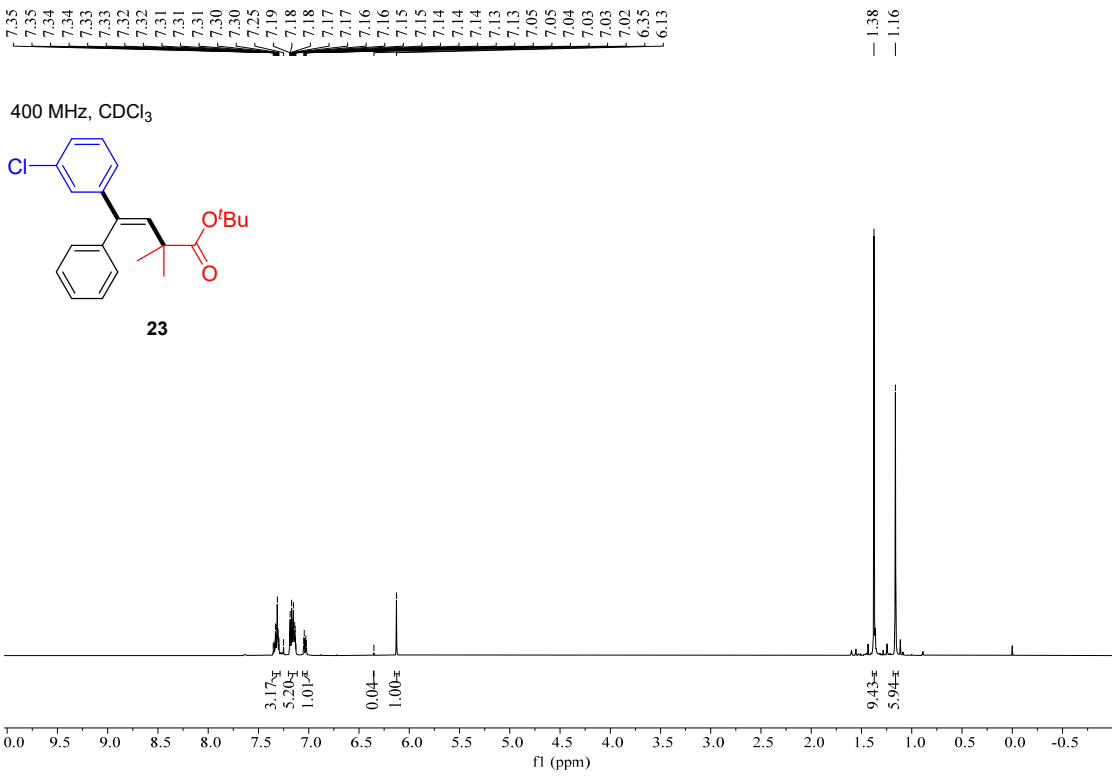
7.15
7.14
7.14
7.13
7.12
6.93
6.12
1.37
1.15
400 MHz, CDCl3
I
O'Bu
O
22
2.01
4.10
2.18
2.03
0.16
1.00
9.68
5.90
f1 (ppm)


100 MHz, CDCl3
I
O
tBu
O
22
175.95
143.55
140.81
139.56
137.20
134.63
130.16
129.34
128.19
127.54
92.75
80.42
77.48
77.16
76.84
45.06
28.00
27.38
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.35
7.34
7.34
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7.32
7.32
7.31
7.31
7.31
7.30
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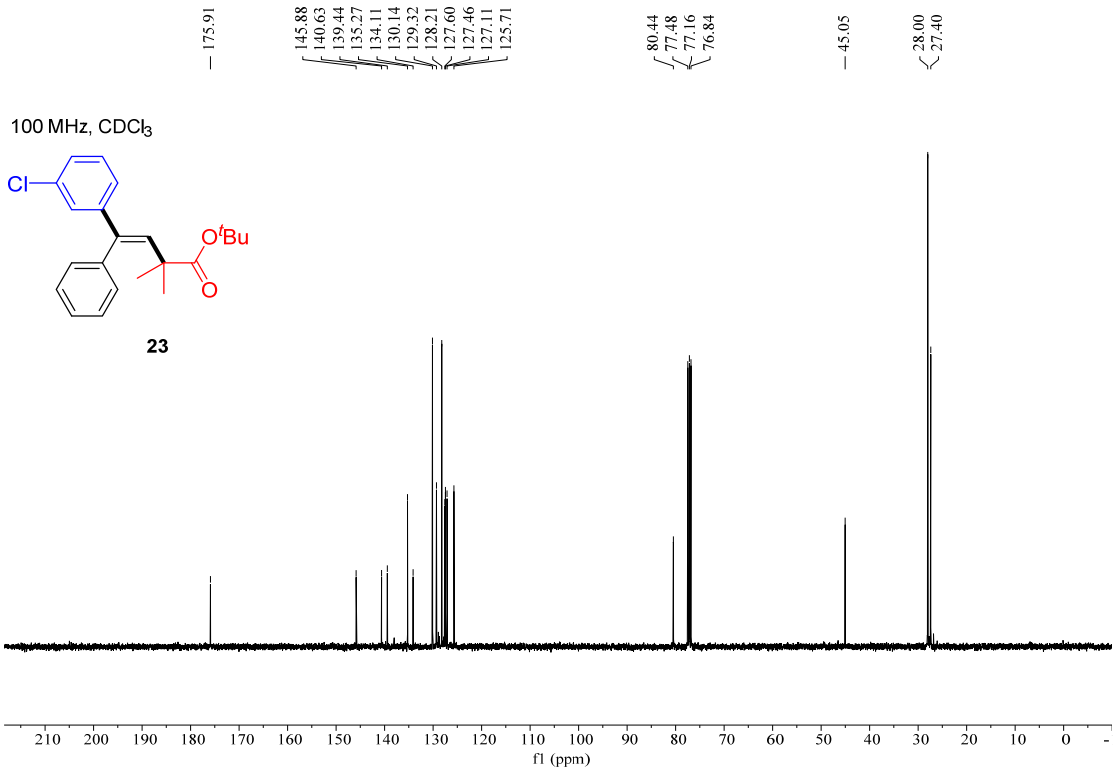
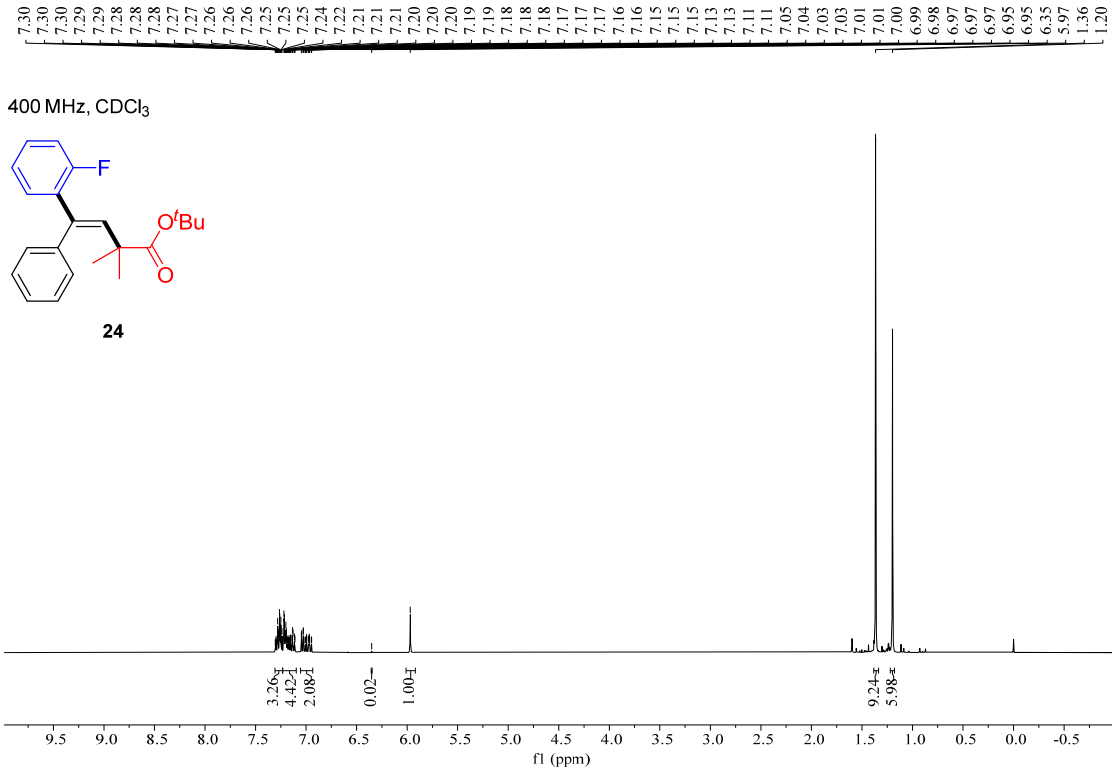
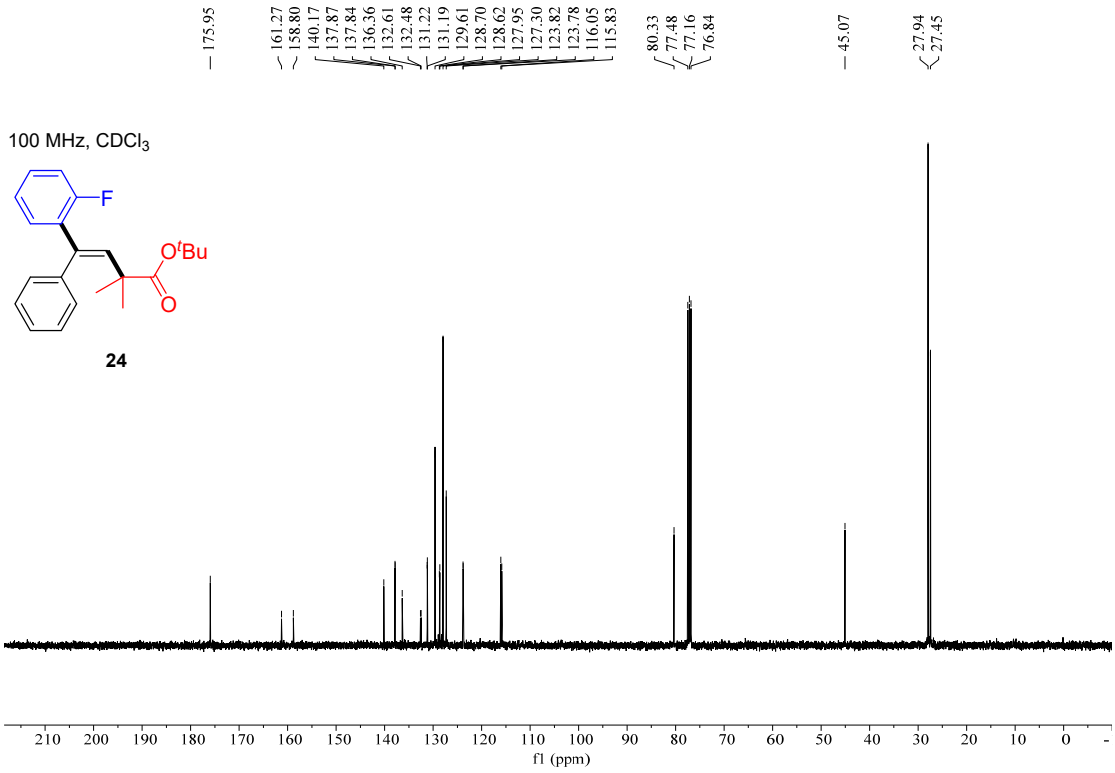
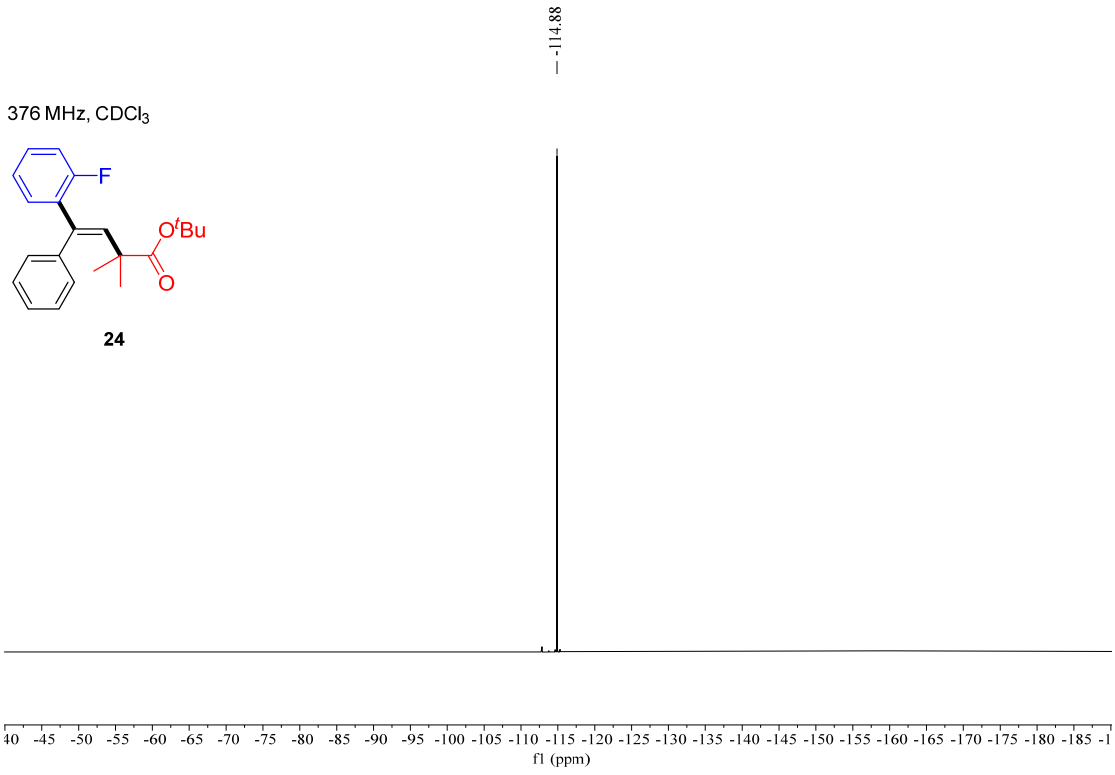
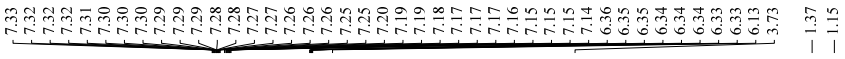
7.13
7.13
7.05
7.05
7.04
7.03
7.03
7.02
6.35
6.13
1.38
1.16
400 MHz, CDCl3
Cl
O
tBu
O
23
3.17
5.20
1.01
0.04
1.00
9.43
5.94
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


175.91
145.88
140.63
139.44
135.27
134.11
130.14
129.32
128.21
127.60
127.46
127.11
125.71
80.44
77.48
77.16
76.84
45.05
28.00
27.40
100 MHz, CDCl3
Cl
O
tBu
O
23
f1 (ppm)

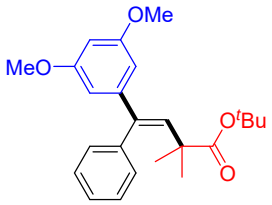

7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.25
7.24
7.22
7.21
7.21
7.21
7.20
7.20
7.20
7.19
7.19
7.18
7.18
7.18
7.17
7.17
7.17
7.16
7.16
7.15
7.15
7.15
7.13
7.13
7.11
7.11
7.05
7.04
7.03
7.03
7.01
7.01
7.00
6.99
6.98
6.97
6.97
6.97
6.95
6.35
5.97
1.36
1.20
400 MHz, CDCl3
F
O
tBu
O
24
3.26
4.42
2.08
0.02
1.00
9.24
5.98
f1 (ppm)


175.95
161.27
158.80
140.17
137.87
137.84
136.36
132.61
132.48
131.22
131.19
129.61
128.70
128.62
127.95
127.30
123.82
123.78
116.05
115.83
80.33
77.48
77.16
76.84
45.07
27.94
27.45
100 MHz, CDCl3
F
O'Bu
O
24
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)

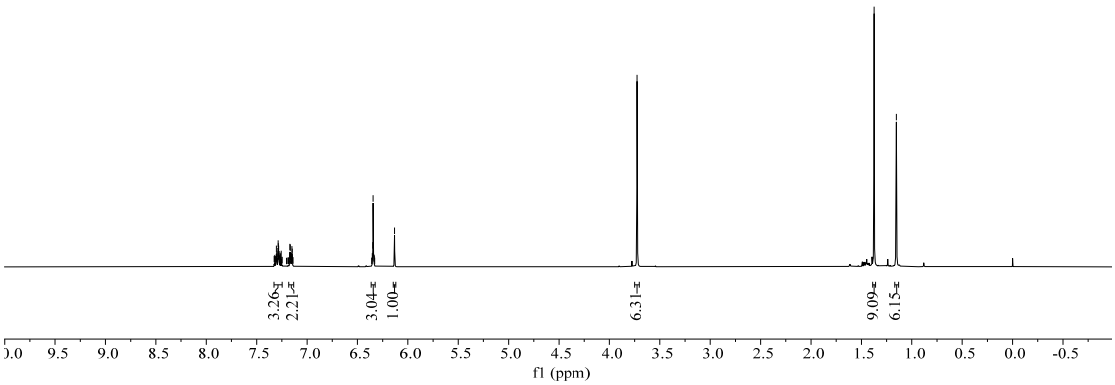

-114.88
376 MHz, CDCl3
F
O'Bu
O
24
40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -1
f1 (ppm)



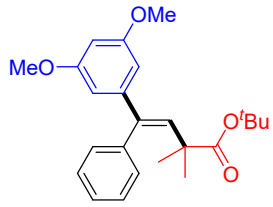
400 MHz, $CDCl_3$



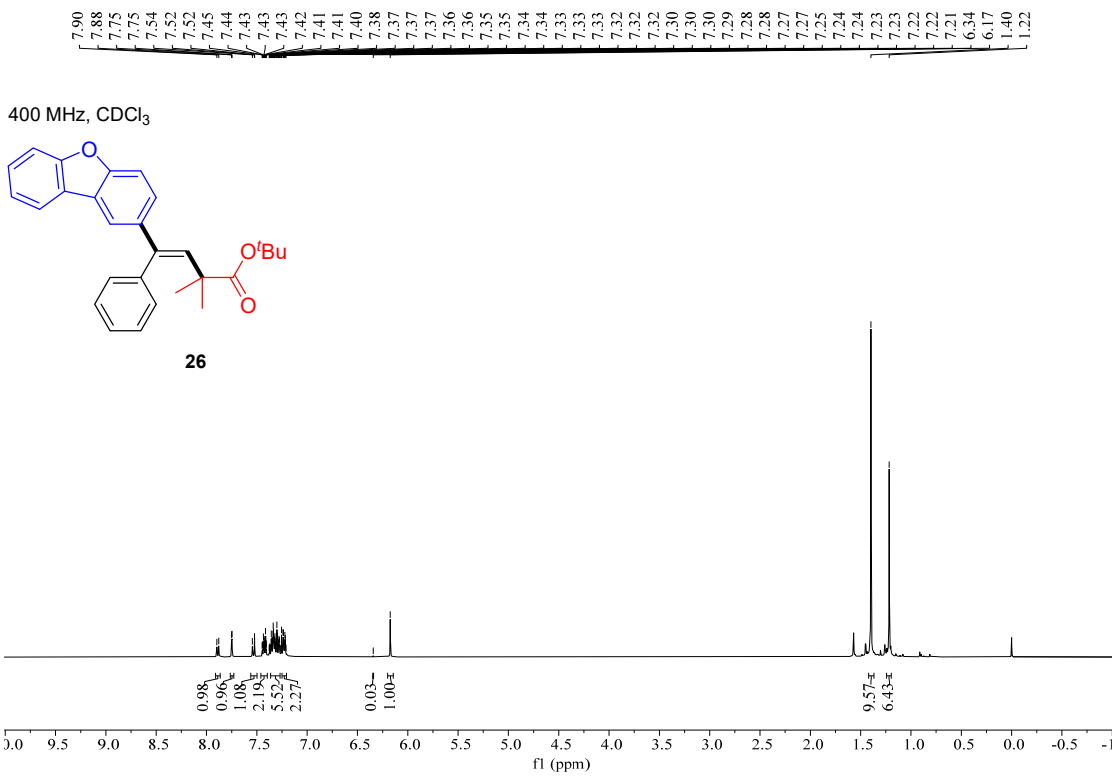
25

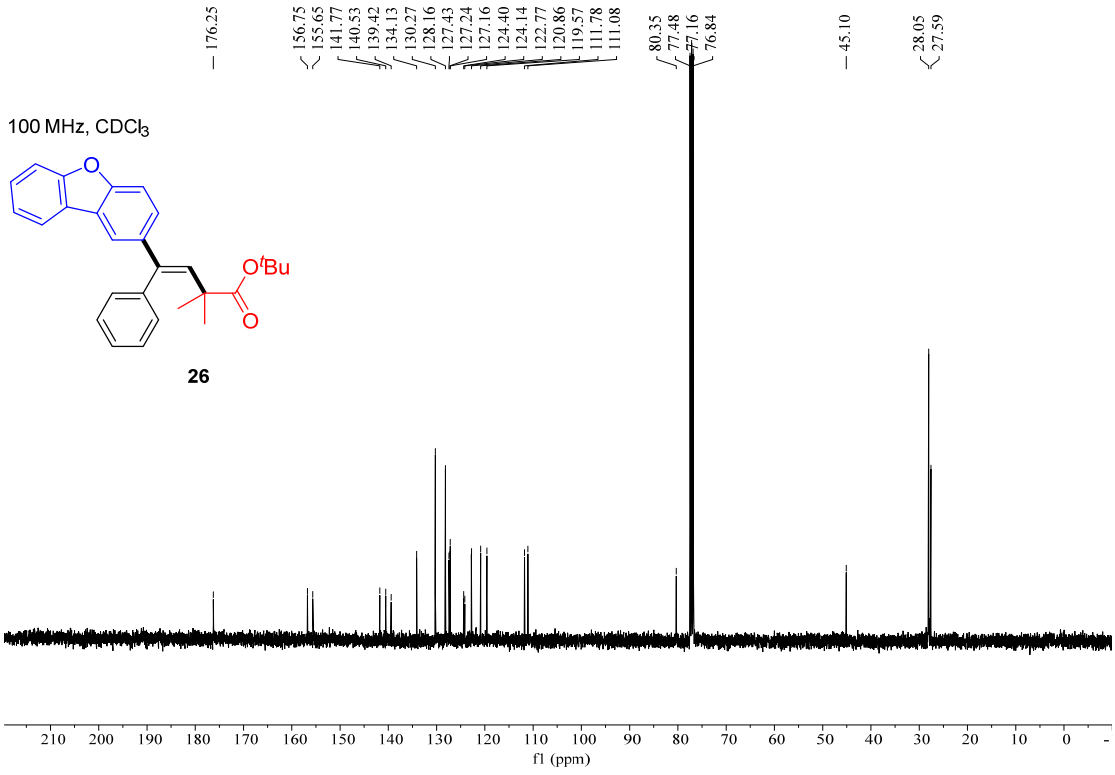


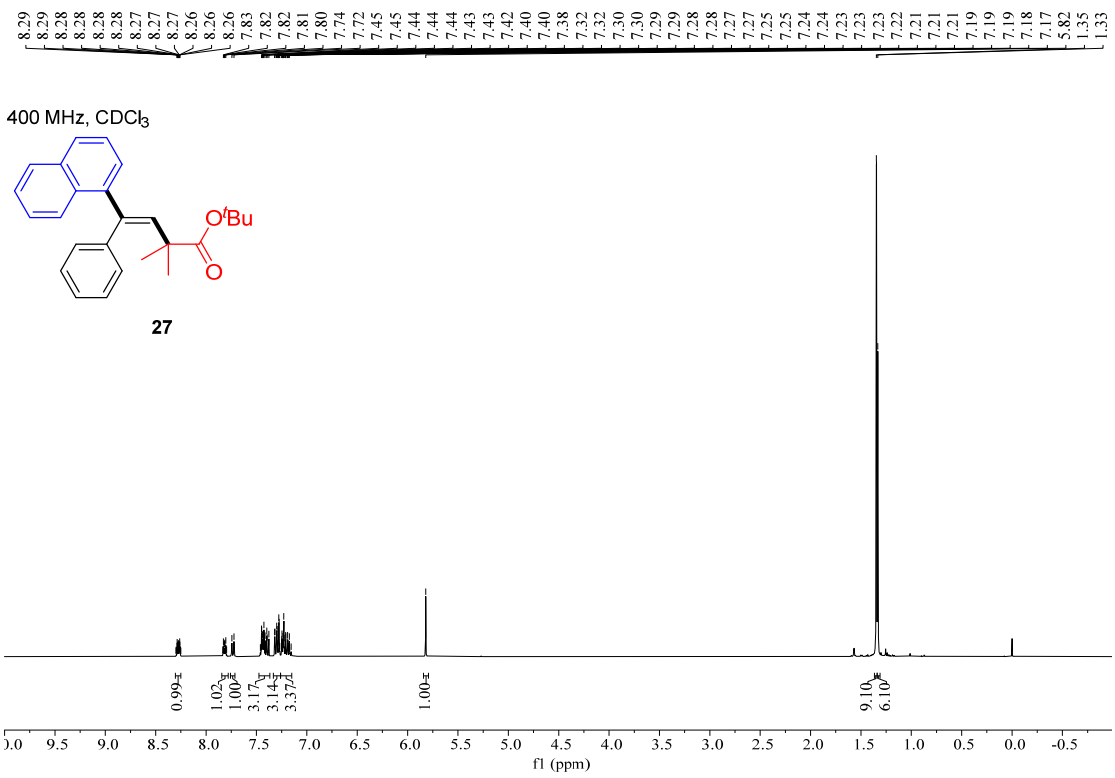
100 MHz, $CDCl_3$

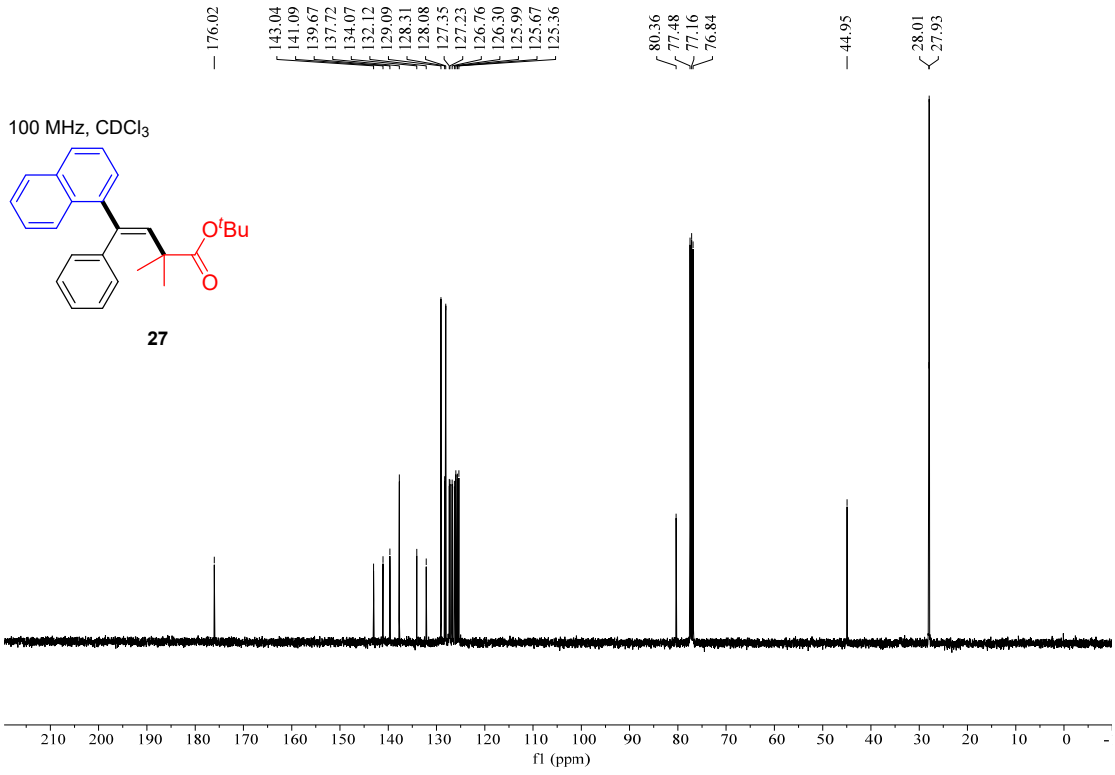


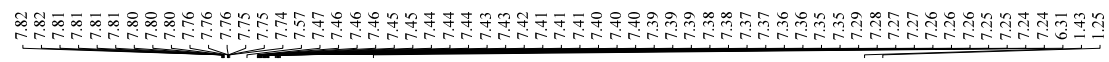
25


7.90
7.88
7.75
7.75
7.54
7.52
7.52
7.45
7.44
7.43
7.43
7.43
7.42
7.41
7.41
7.40
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.33
7.32
7.32
7.32
7.30
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
6.34
6.17
1.40
1.22
400 MHz, CDCl3
O
O
tBu
O
26
0.98
0.96
1.08
2.19
5.52
2.27
0.03
1.00
9.57
6.43
f1 (ppm)

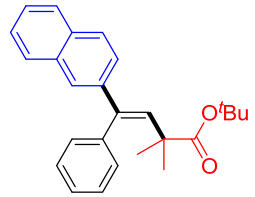

176.25
156.75
155.65
141.77
140.53
139.42
134.13
130.27
128.16
127.43
127.24
127.16
124.40
124.14
122.77
120.86
119.57
111.78
111.08
80.35
77.48
77.16
76.84
45.10
28.05
27.59
100 MHz, CDCl3
O
O
tBu
O
26
f1 (ppm)


400 MHz, CDCl3
O
tBu
O
27
f1 (ppm)

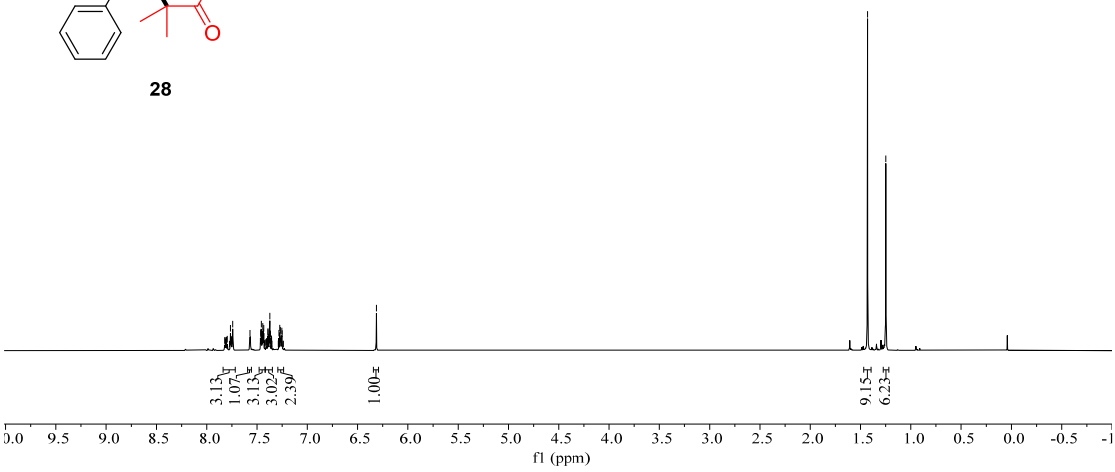

100 MHz, CDCl3
O
tBu
O
27
f1 (ppm)

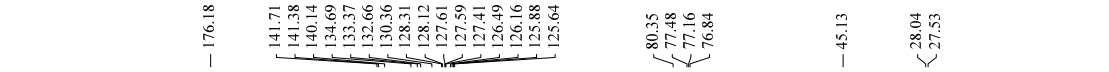


400 MHz, $CDCl_3$

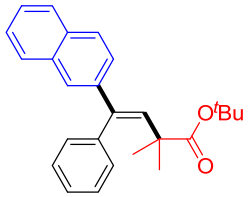


28

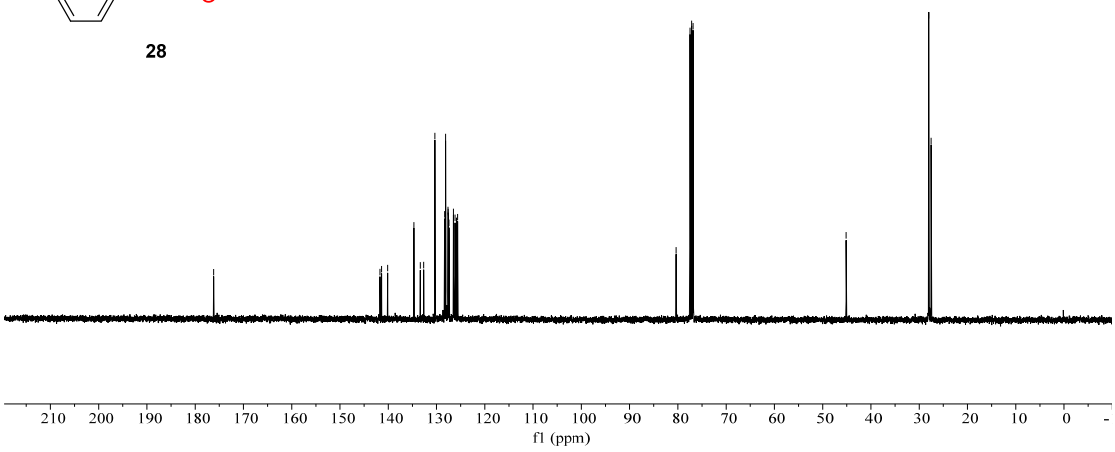


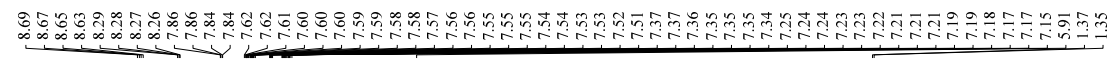


100 MHz, $CDCl_3$

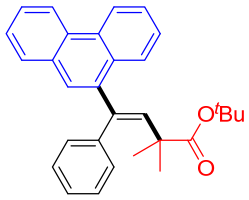


28

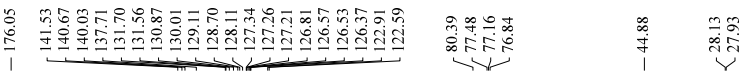




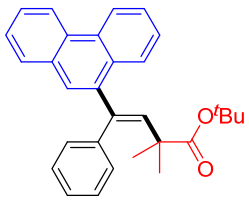
400 MHz, $CDCl_3$



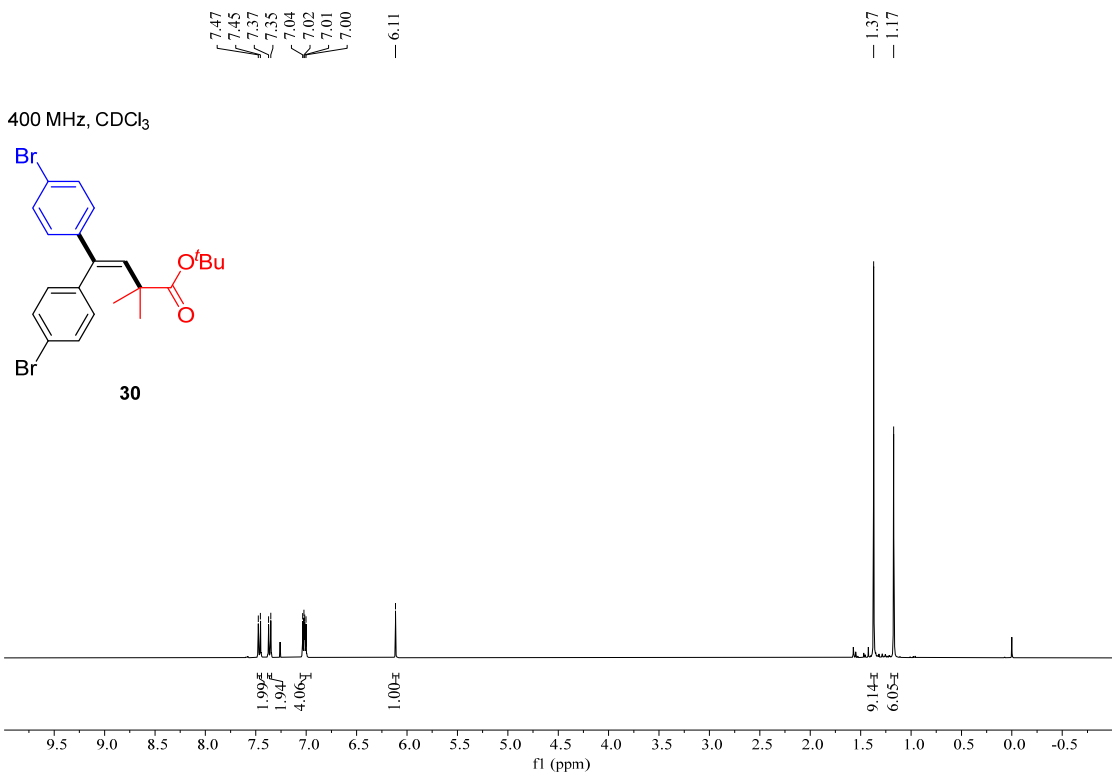
29

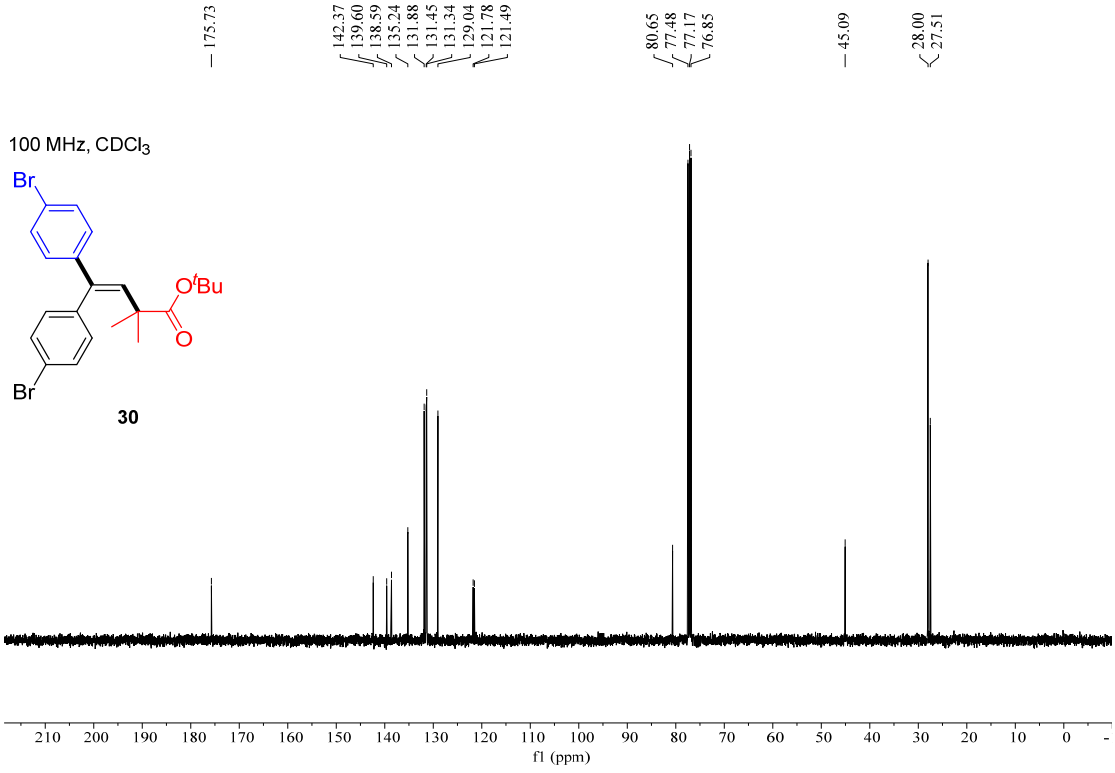


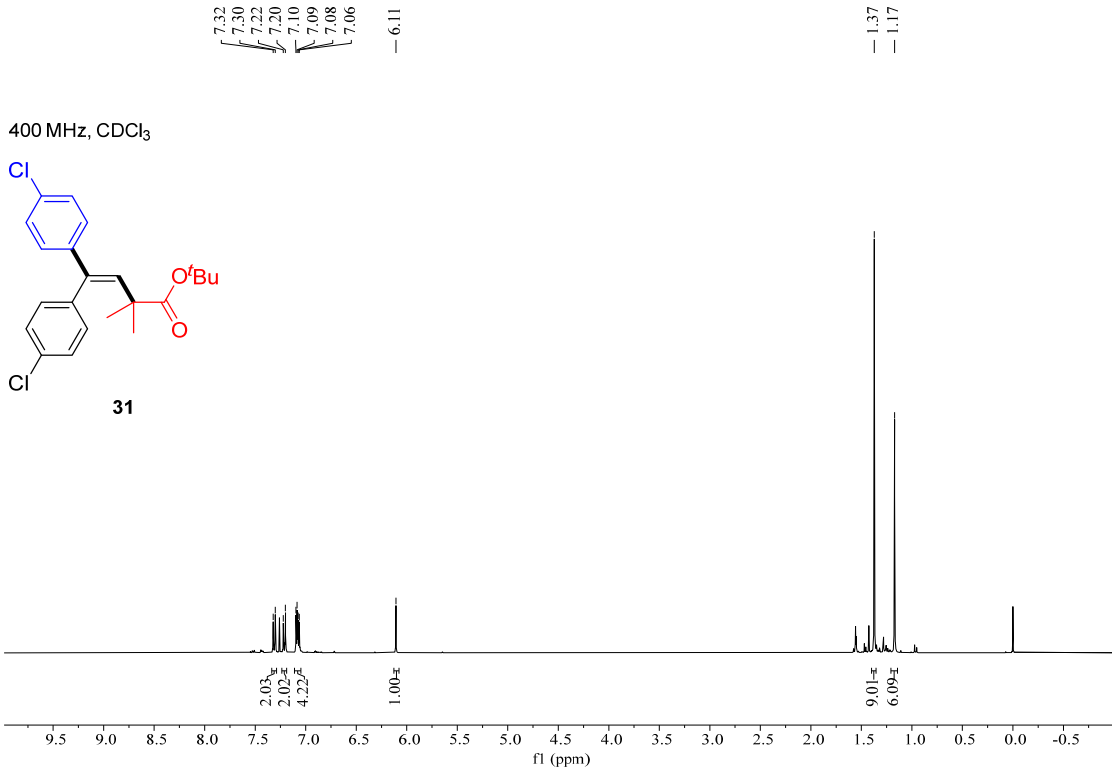
100 MHz, $CDCl_3$

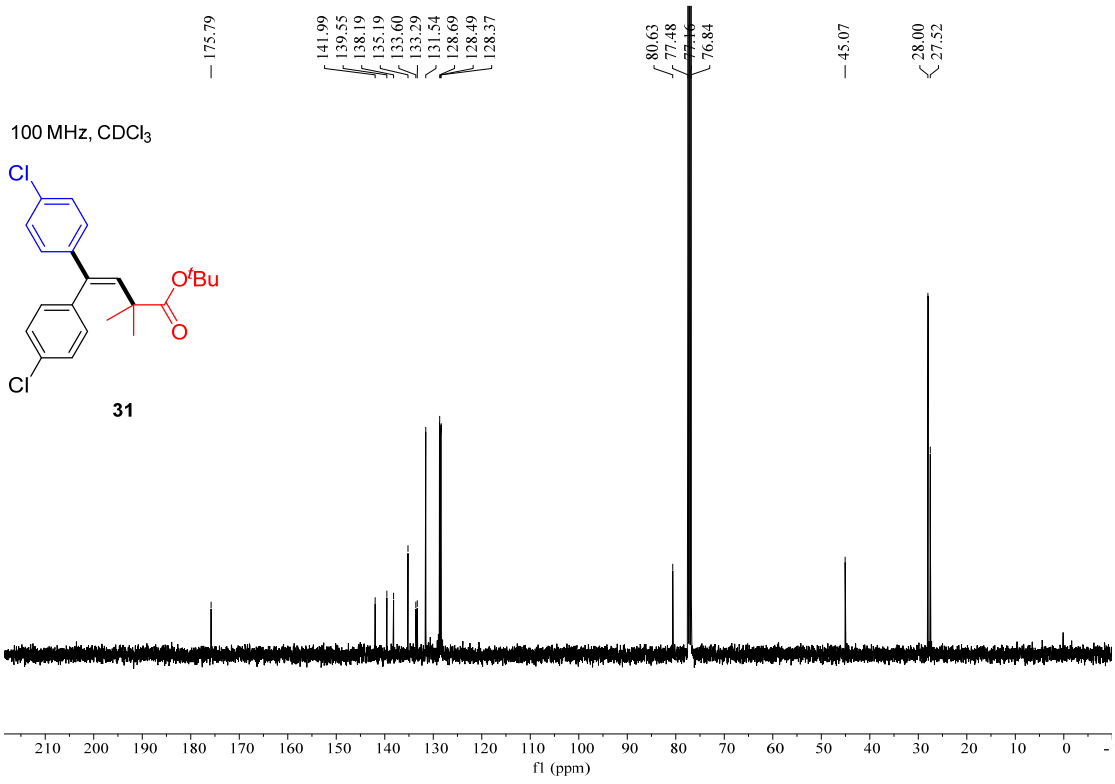


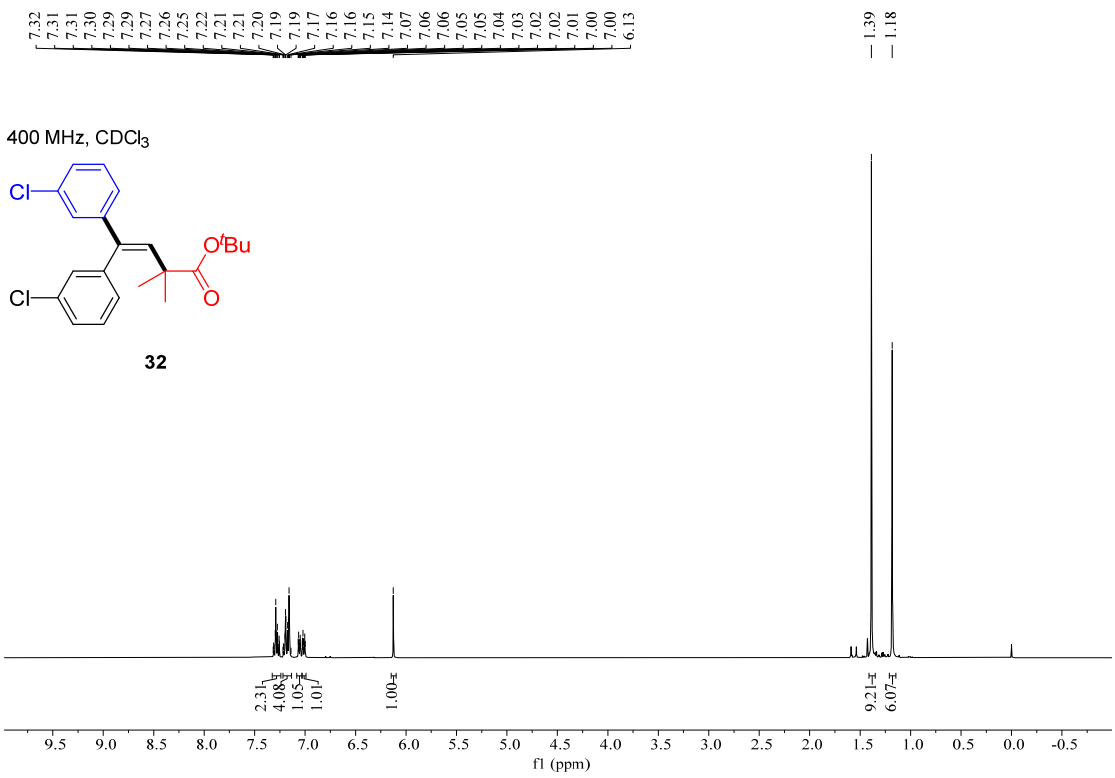
29

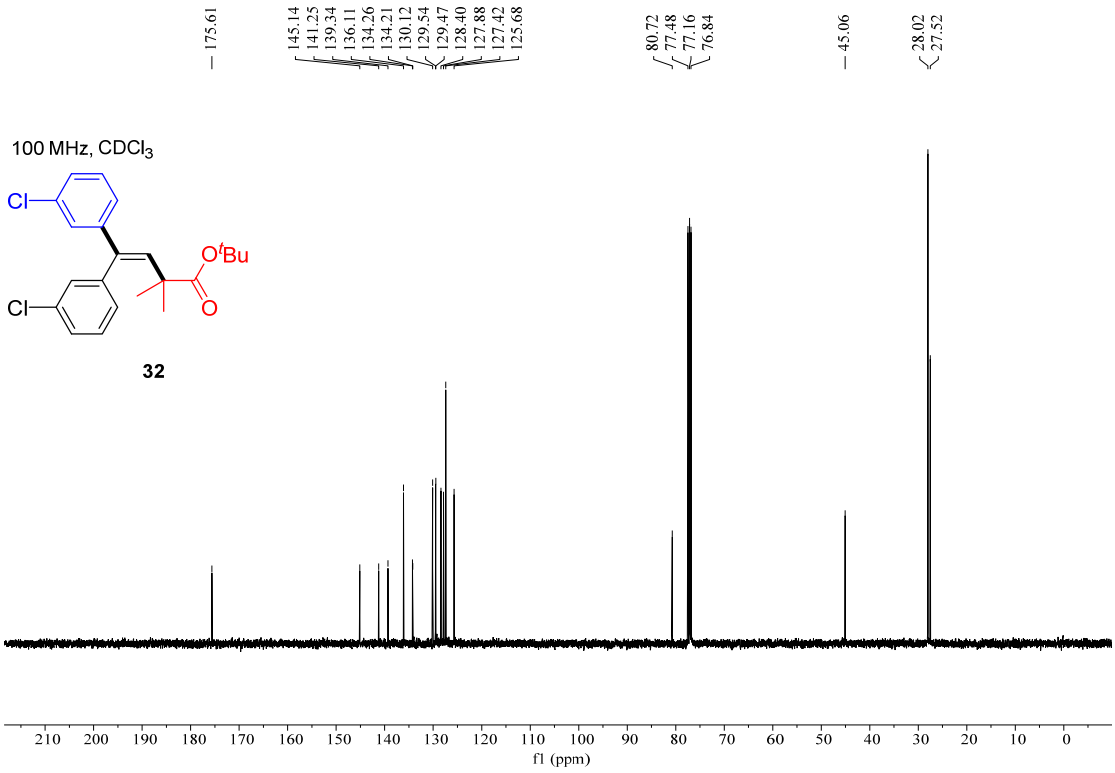

7.47
7.45
7.37
7.35
7.04
7.02
7.01
7.00
6.11
1.37
1.17
400 MHz, CDCl3
Br
O
tBu
O
Br
30
1.99
1.94
4.06
1.00
9.14
6.05
f1 (ppm)


175.73
142.37
139.60
138.59
135.24
131.88
131.45
131.34
129.04
121.78
121.49
80.65
77.48
77.17
76.85
45.09
28.00
27.51
100 MHz, CDCl3
Br
O
tBu
O
Br
30
f1 (ppm)

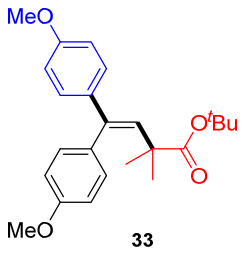

7.32
7.30
7.22
7.20
7.10
7.09
7.08
7.06
6.11
1.37
1.17
400 MHz, CDCl3
Cl
O
tBu
O
Cl
31
2.03
2.02
4.22
1.00
9.01
6.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


175.79
141.99
139.55
138.19
135.19
133.60
133.29
131.54
128.69
128.49
128.37
80.63
77.48
77.16
76.84
45.07
28.00
27.52
100 MHz, CDCl3
Cl
O
tBu
O
Cl
31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)


7.32
7.31
7.31
7.30
7.29
7.29
7.27
7.26
7.25
7.22
7.21
7.21
7.20
7.19
7.19
7.17
7.16
7.16
7.15
7.14
7.07
7.06
7.06
7.05
7.05
7.04
7.03
7.02
7.02
7.01
7.00
7.00
6.13
1.39
1.18
400 MHz, CDCl3
Cl
O'Bu
Cl
O
32
2.31
4.08
1.05
1.01
1.00
9.21
6.07
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
f1 (ppm)

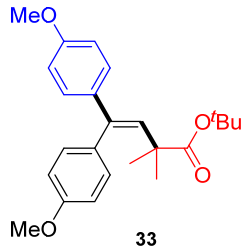

175.61
145.14
141.25
139.34
136.11
134.26
134.21
130.12
129.54
129.47
128.40
127.88
127.42
125.68
80.72
77.48
77.16
76.84
45.06
28.02
27.52
100 MHz, CDCl3
Cl
O'Bu
Cl
O
32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

400 MHz, $CDCl_3$

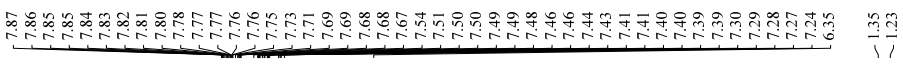


33

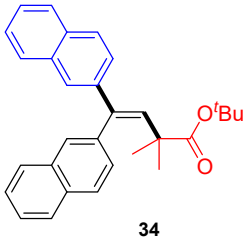
100 MHz, $CDCl_3$



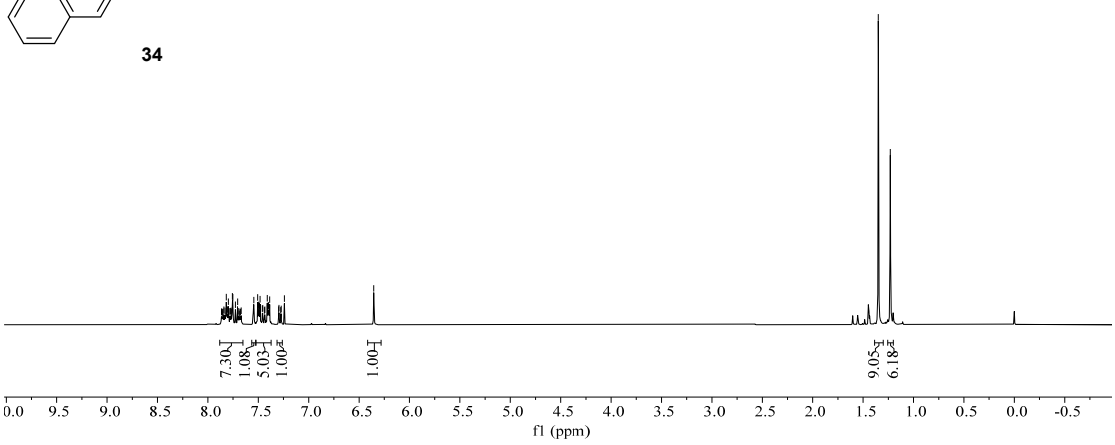
33

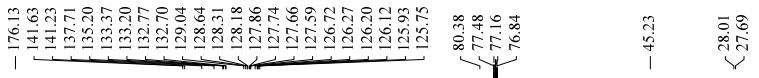


400 MHz, $CDCl_3$

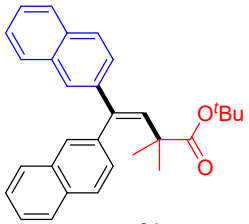


34

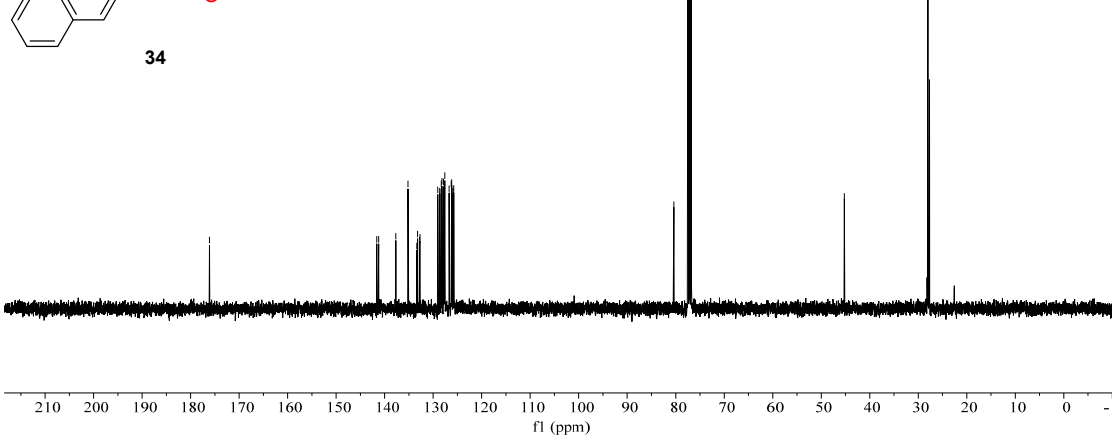


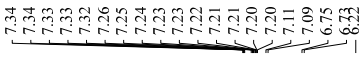


100 MHz, $CDCl_3$

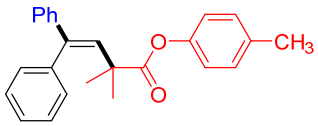


34

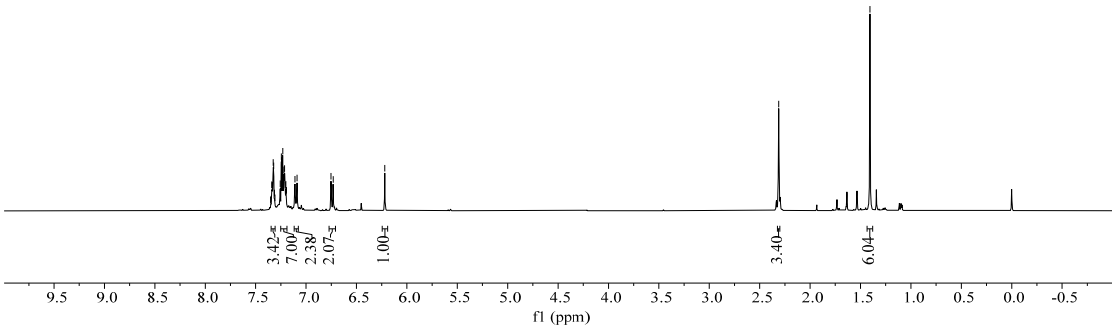




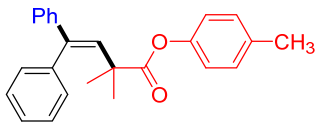
400 MHz, $CDCl_3$



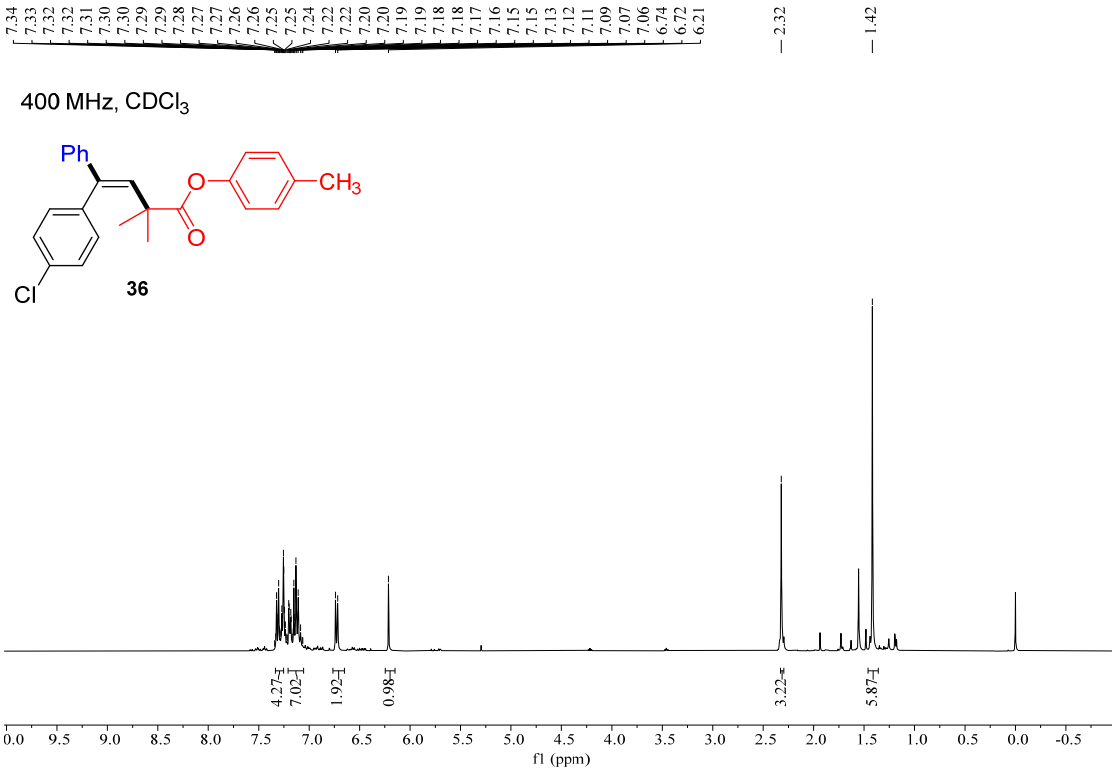
35

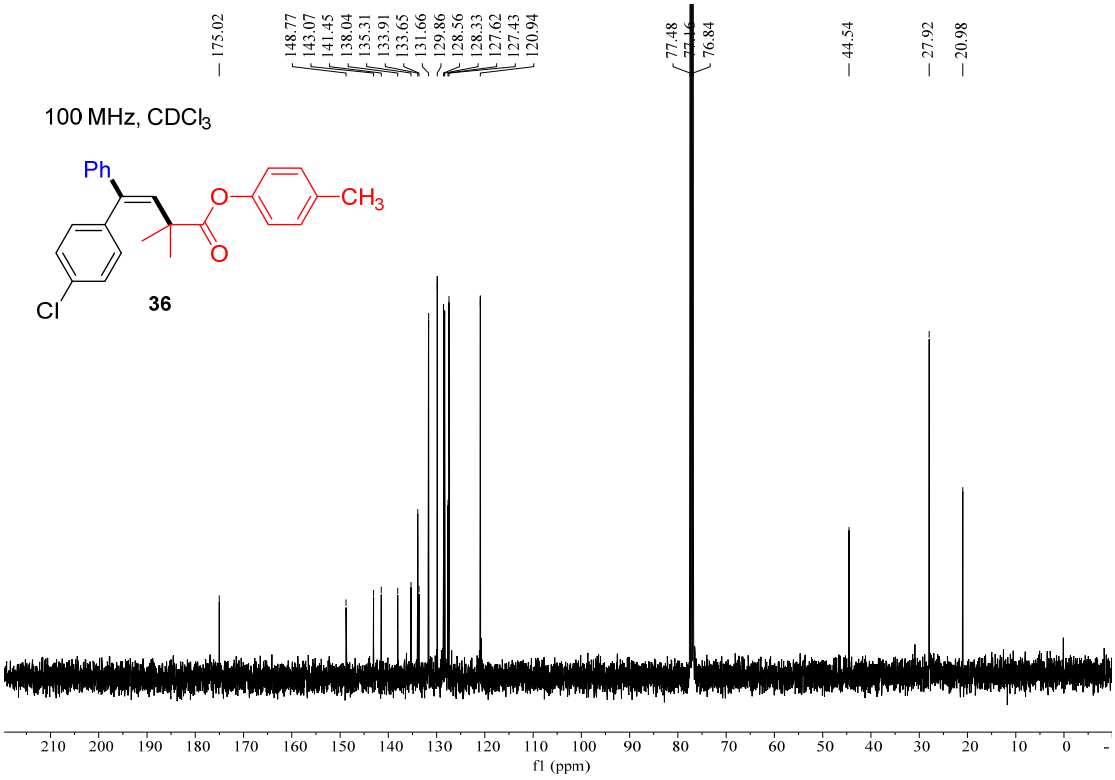


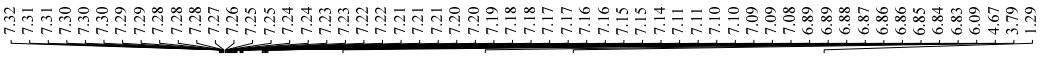
100 MHz, $CDCl_3$



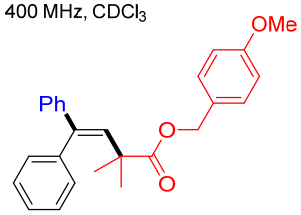
35


400 MHz, CDCl3
Ph
O
CH3
O
Cl
36
7.34 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.24 7.22 7.22 7.20 7.20 7.19 7.19 7.18 7.18 7.17 7.16 7.15 7.15 7.13 7.12 7.11 7.09 7.07 7.06 6.74 6.72 6.21
2.32
1.42
4.27
7.02
1.92
0.98
3.22
5.87
f1 (ppm)

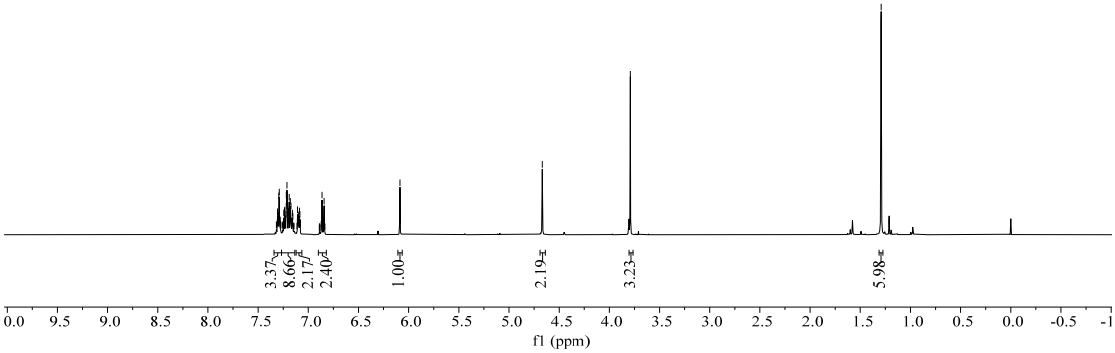

100 MHz, CDCl3
Ph
O
CH3
O
Cl
36
175.02
148.77 143.07 141.45 138.04 135.31 133.91 133.65 131.66 129.86 128.56 128.33 127.62 127.43 120.94
77.48 77.16 76.84
44.54
27.92
20.98
f1 (ppm)



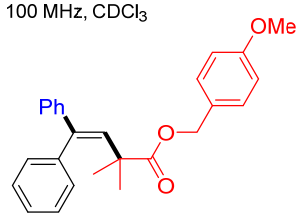
400 MHz, $CDCl_3$



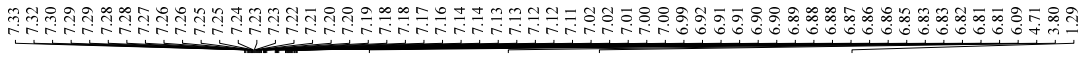
37



100 MHz, $CDCl_3$



37


7.33
7.32
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.21
7.20
7.20
7.19
7.18
7.18
7.17
7.16
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.02
7.02
7.01
7.00
7.00
6.99
6.92
6.91
6.91
6.90
6.90
6.89
6.88
6.88
6.87
6.86
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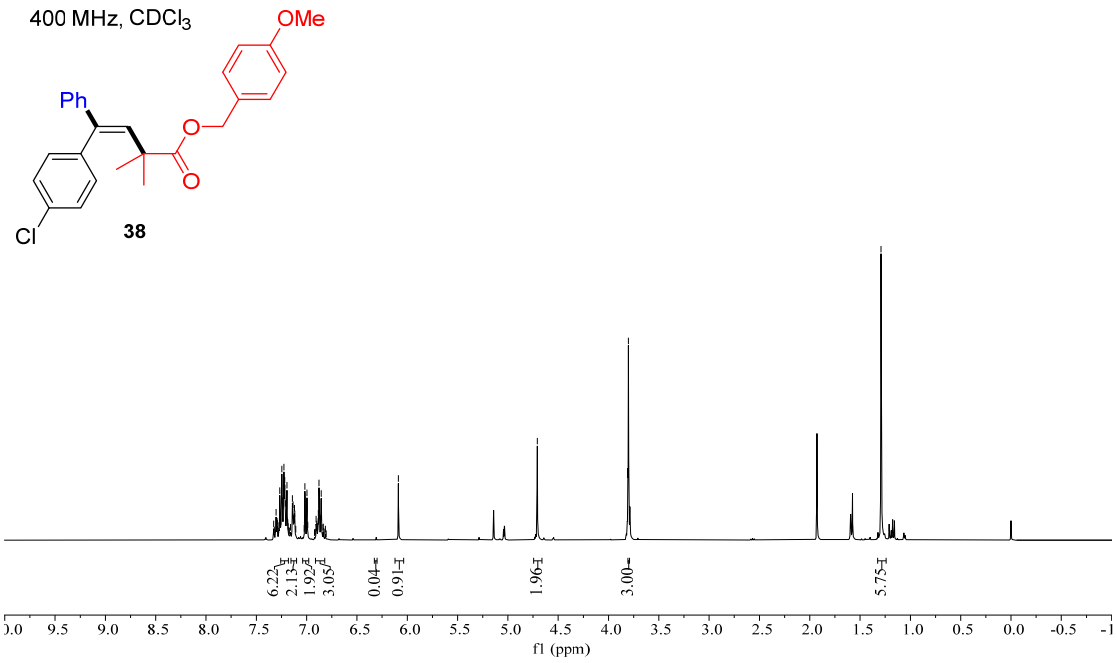
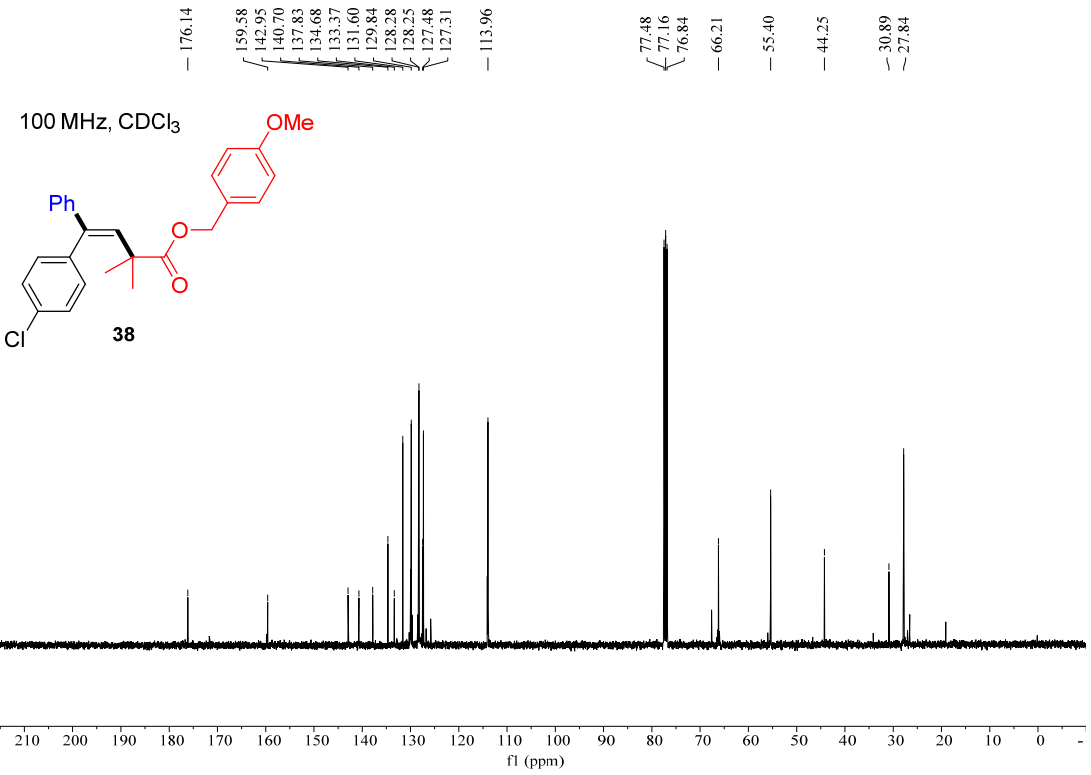
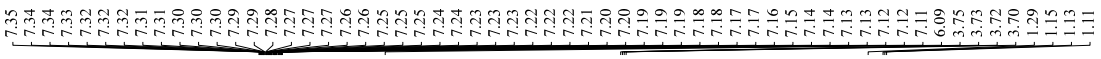
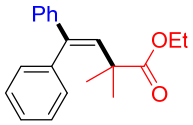
6.83
6.83
6.82
6.81
6.81
6.09
4.71
3.80
1.29


400 MHz, CDCl3
OMe
Ph
O
O
Cl
38
6.22
2.13
1.92
3.05
0.04
0.91
1.96
3.00
5.75
f1 (ppm)

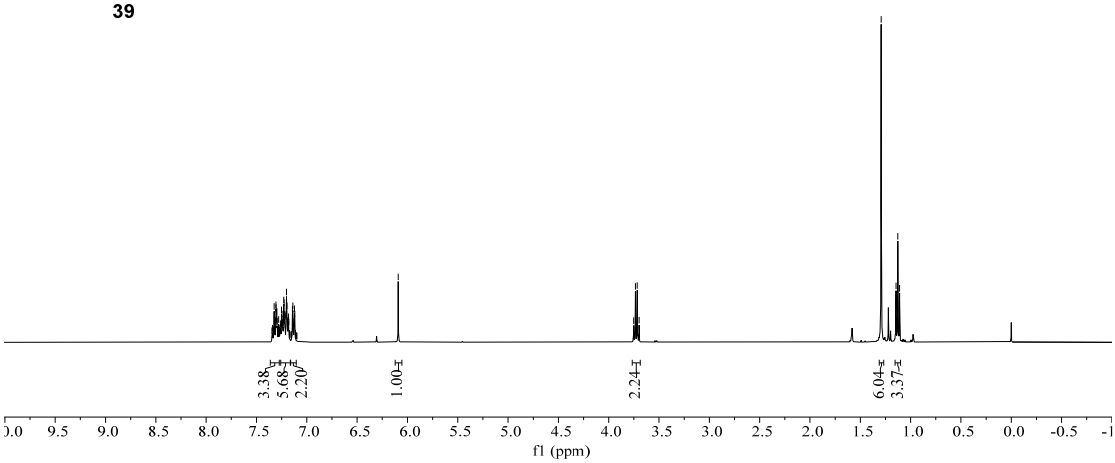

176.14
159.58
142.95
140.70
137.83
134.68
133.37
131.60
129.84
128.28
128.25
127.48
127.31
113.96
77.48
77.16
76.84
66.21
55.40
44.25
30.89
27.84
100 MHz, CDCl3
OMe
Ph
O
O
Cl
38
f1 (ppm)

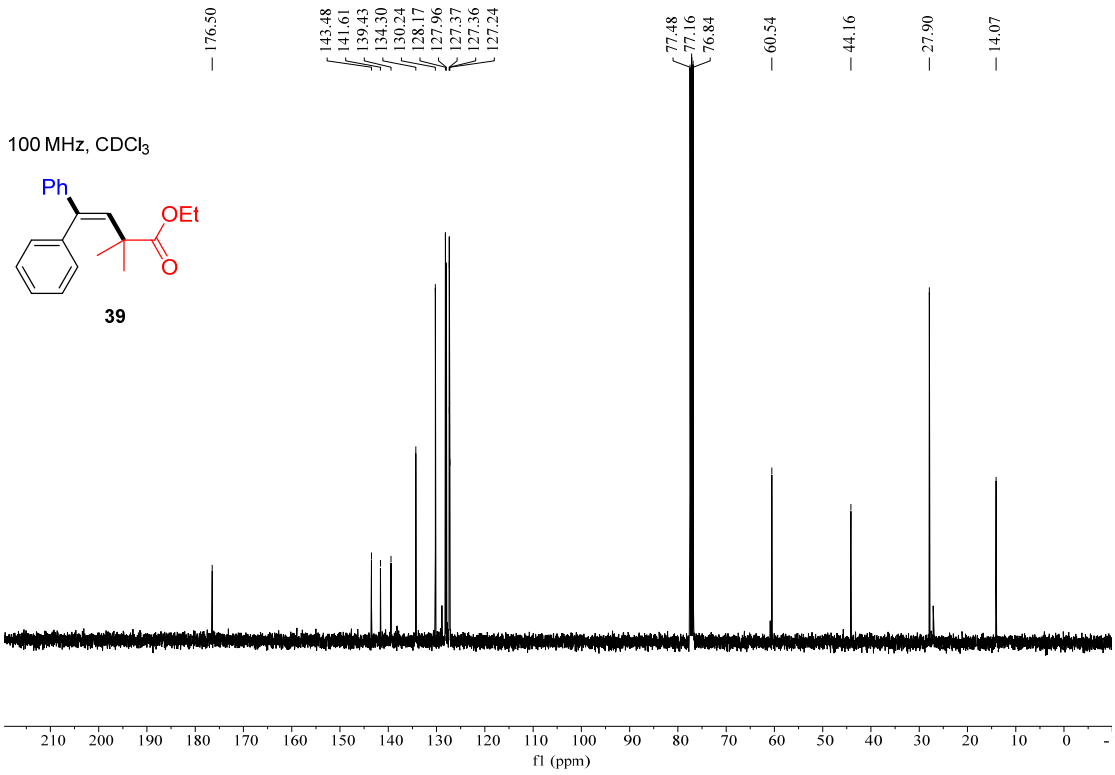


400 MHz, $CDCl_3$



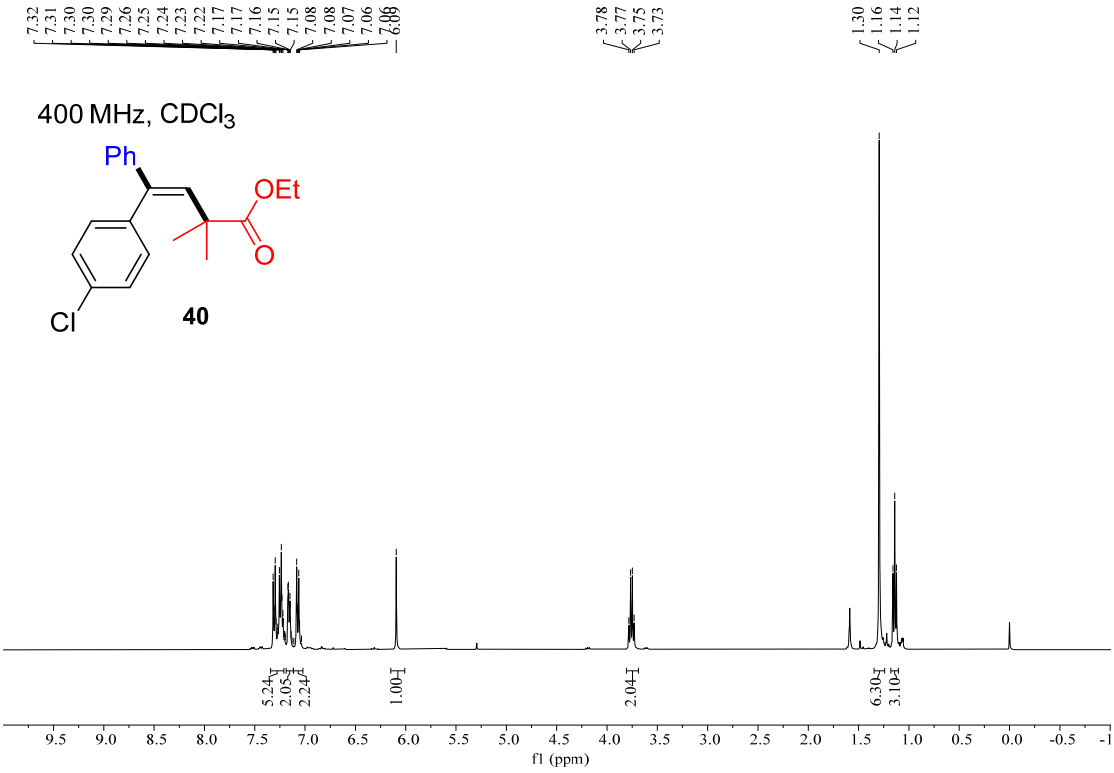
39

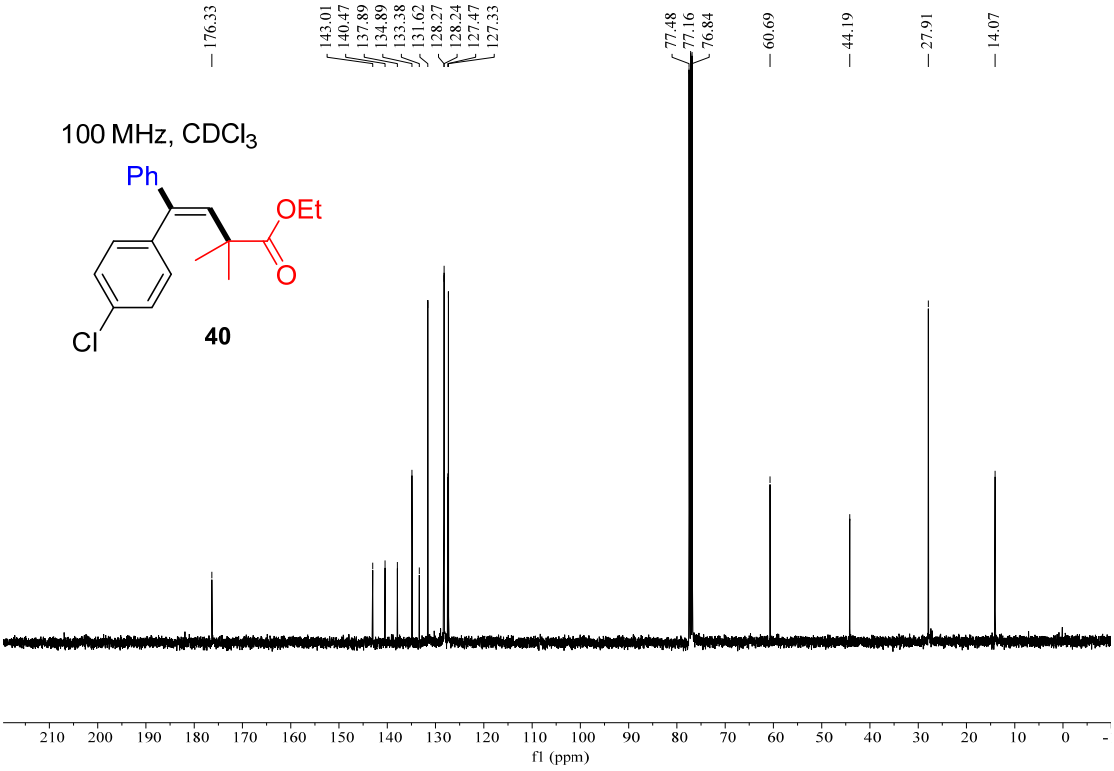




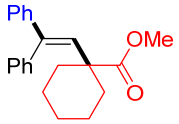
100 MHz, $CDCl_3$

39

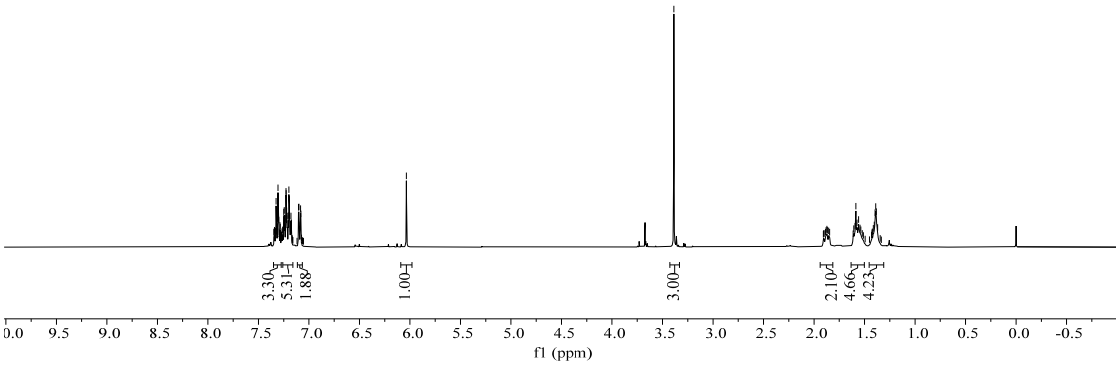

7.32
7.31
7.30
7.30
7.29
7.26
7.25
7.24
7.23
7.22
7.17
7.17
7.16
7.15
7.15
7.08
7.08
7.07
7.06
6.09
3.78
3.77
3.75
3.73
1.30
1.16
1.14
1.12
400 MHz, CDCl3
Ph
OEt
O
Cl
40
5.24
2.05
2.24
1.00
2.04
6.30
3.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

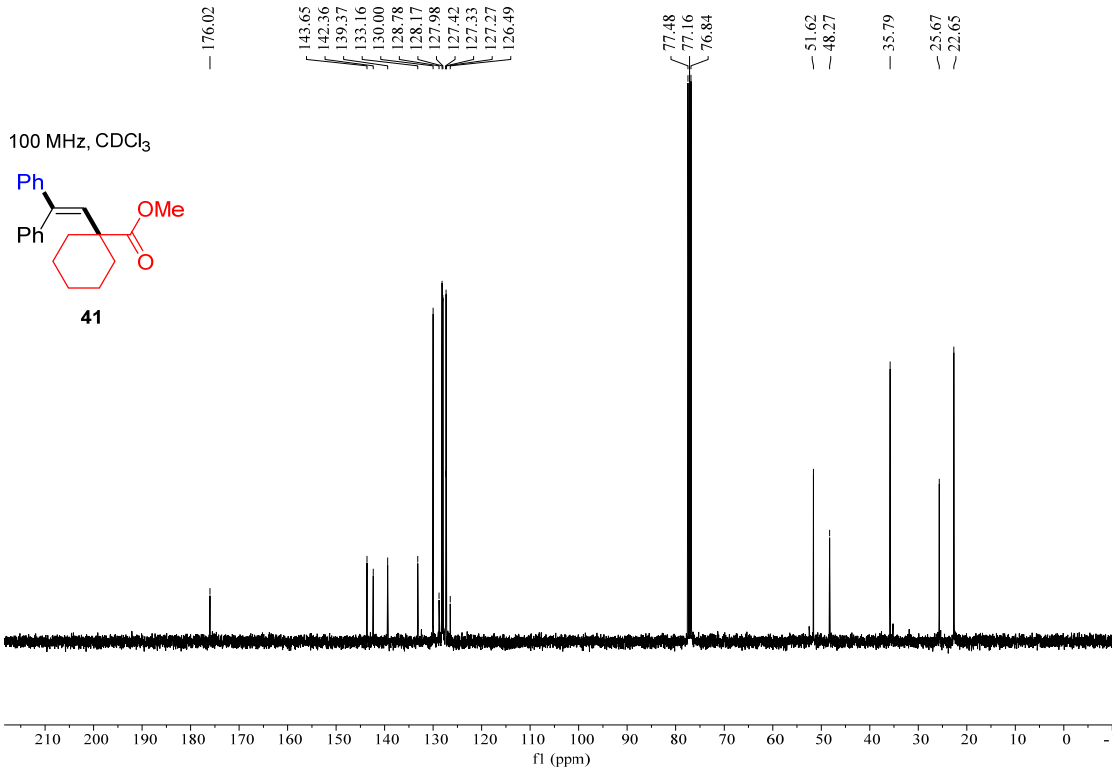

176.33
143.01
140.47
137.89
134.89
133.38
131.62
128.27
128.24
127.47
127.33
77.48
77.16
76.84
60.69
44.19
27.91
14.07
100 MHz, CDCl3
Ph
OEt
O
Cl
40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)

400 MHz, $CDCl_3$



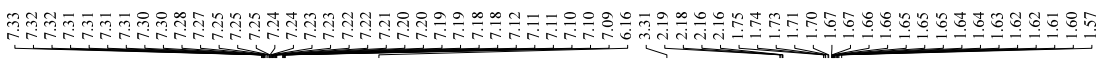
41



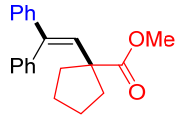


100 MHz, $CDCl_3$

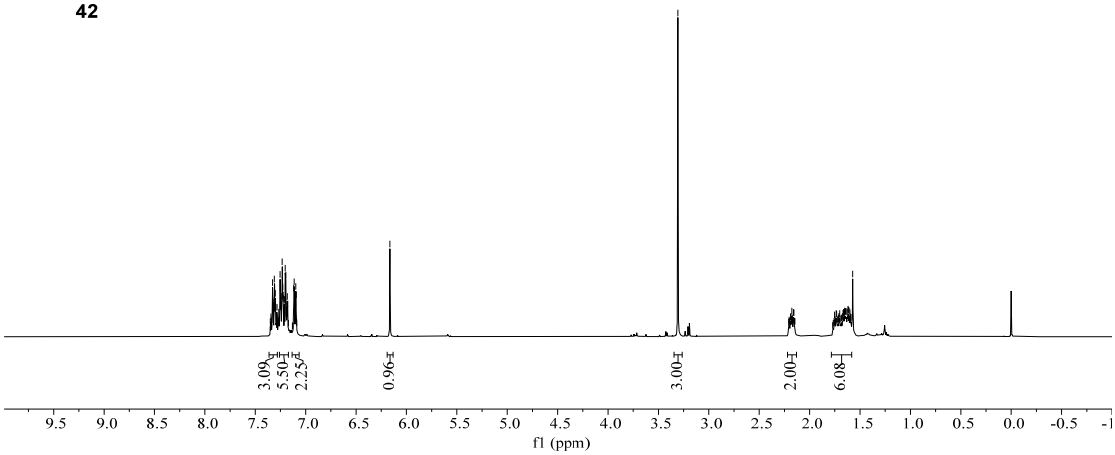
41



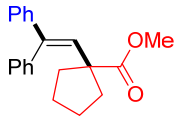
400 MHz, $CDCl_3$



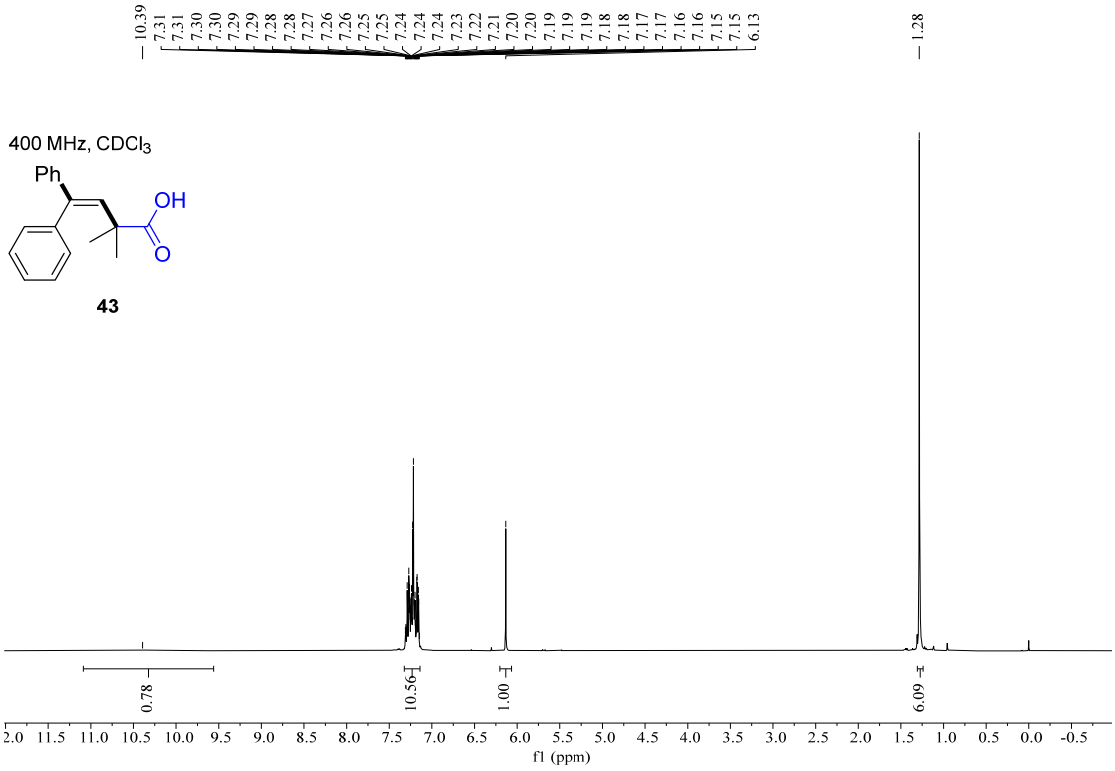
42

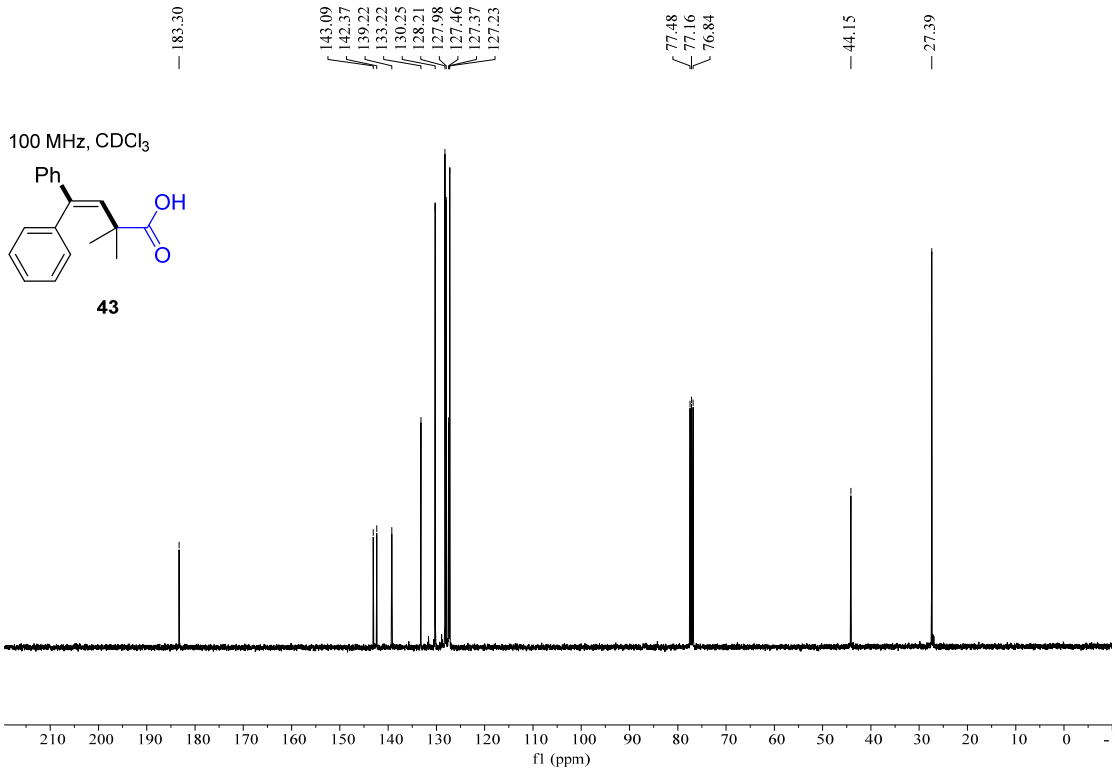


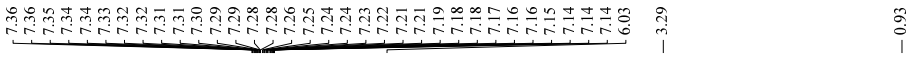
100 MHz, $CDCl_3$



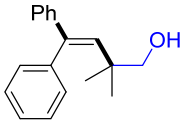
42


10.39
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.24
7.23
7.22
7.21
7.20
7.20
7.19
7.19
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.15
6.13
1.28
400 MHz, CDCl3
Ph
OH
O
43
0.78
10.56
1.00
6.09
f1 (ppm)

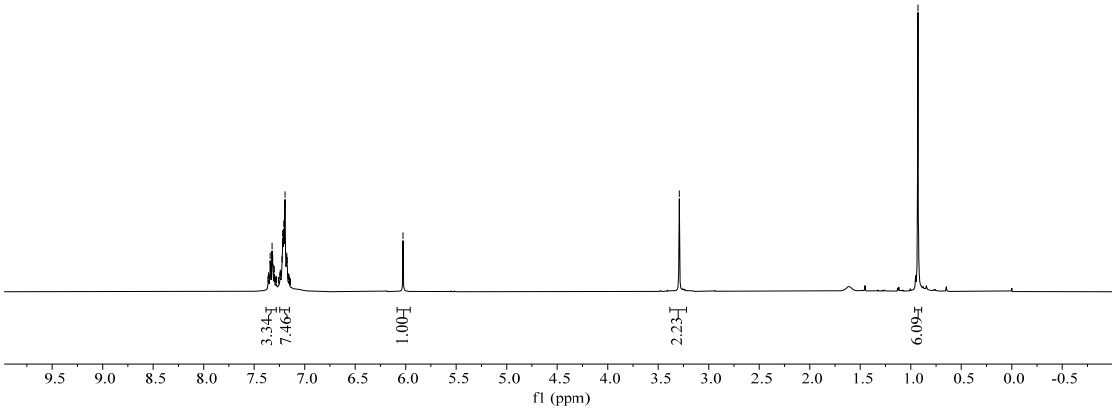

183.30
143.09
142.37
139.22
133.22
130.25
128.21
127.98
127.46
127.37
127.23
77.48
77.16
76.84
44.15
27.39
100 MHz, CDCl3
Ph
OH
O
43
f1 (ppm)

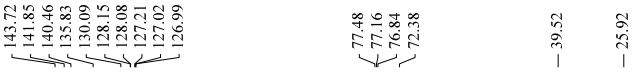


400 MHz, $CDCl_3$

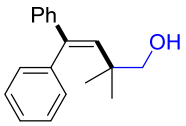


44

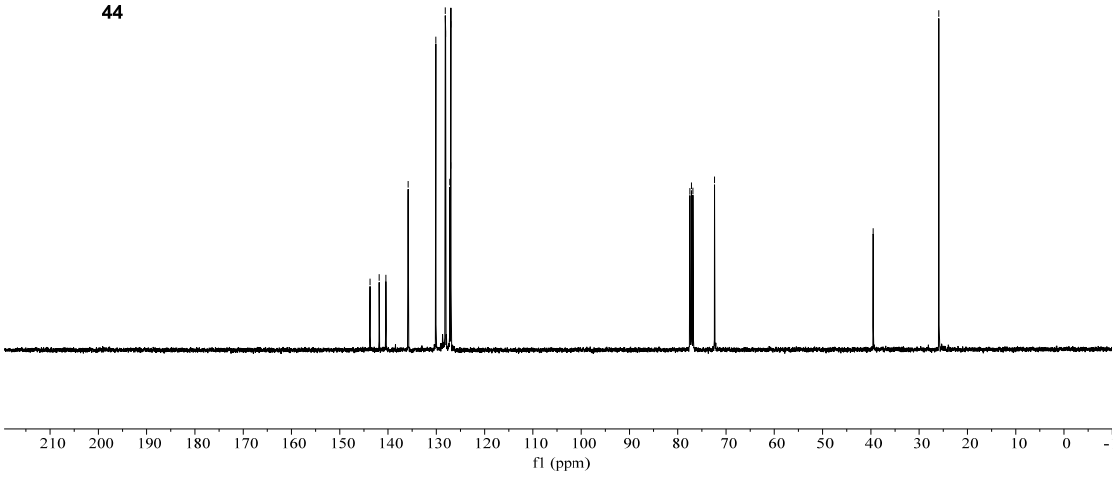




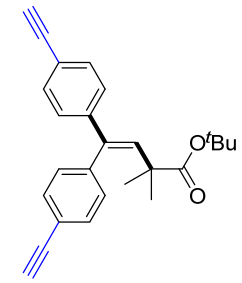
100 MHz, $CDCl_3$



44

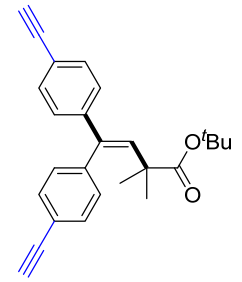


400 MHz, $CDCl_3$

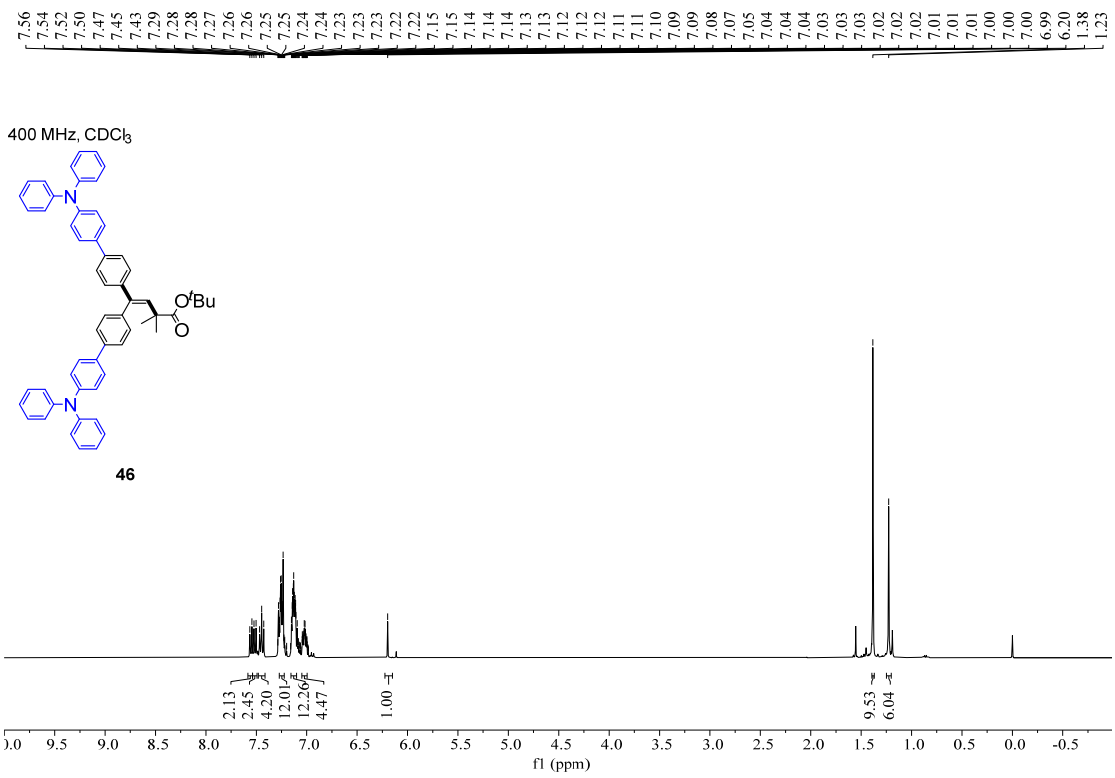


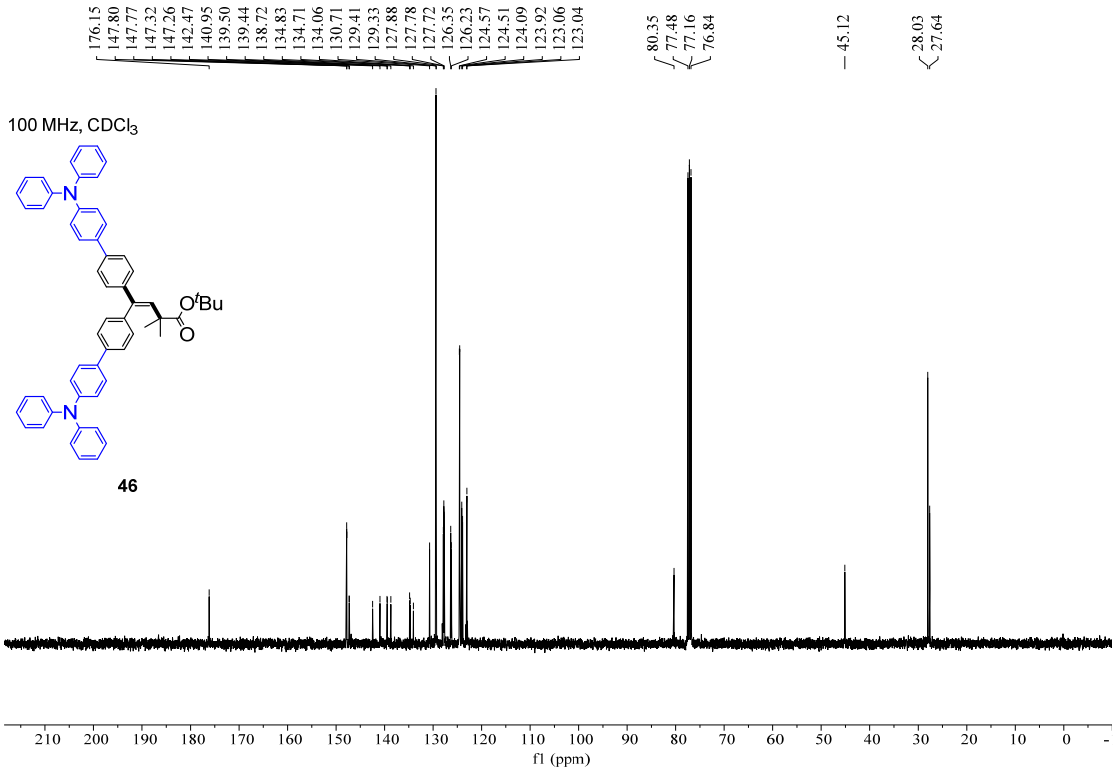
45

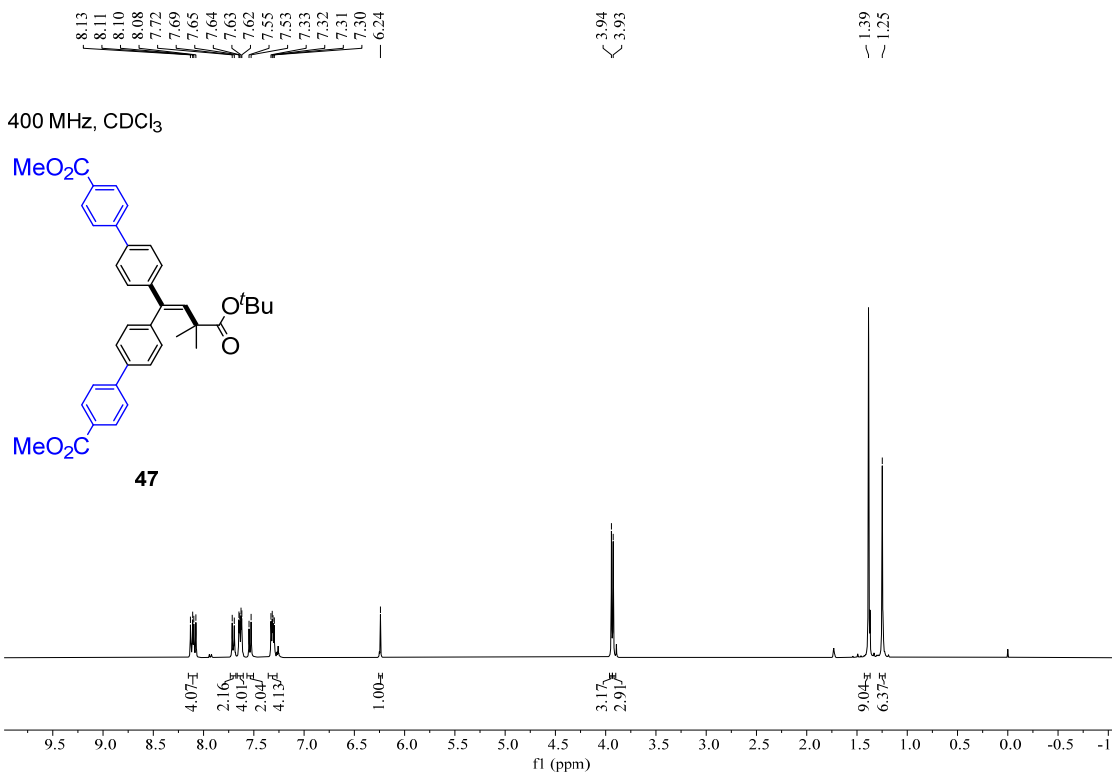
100 MHz, $CDCl_3$

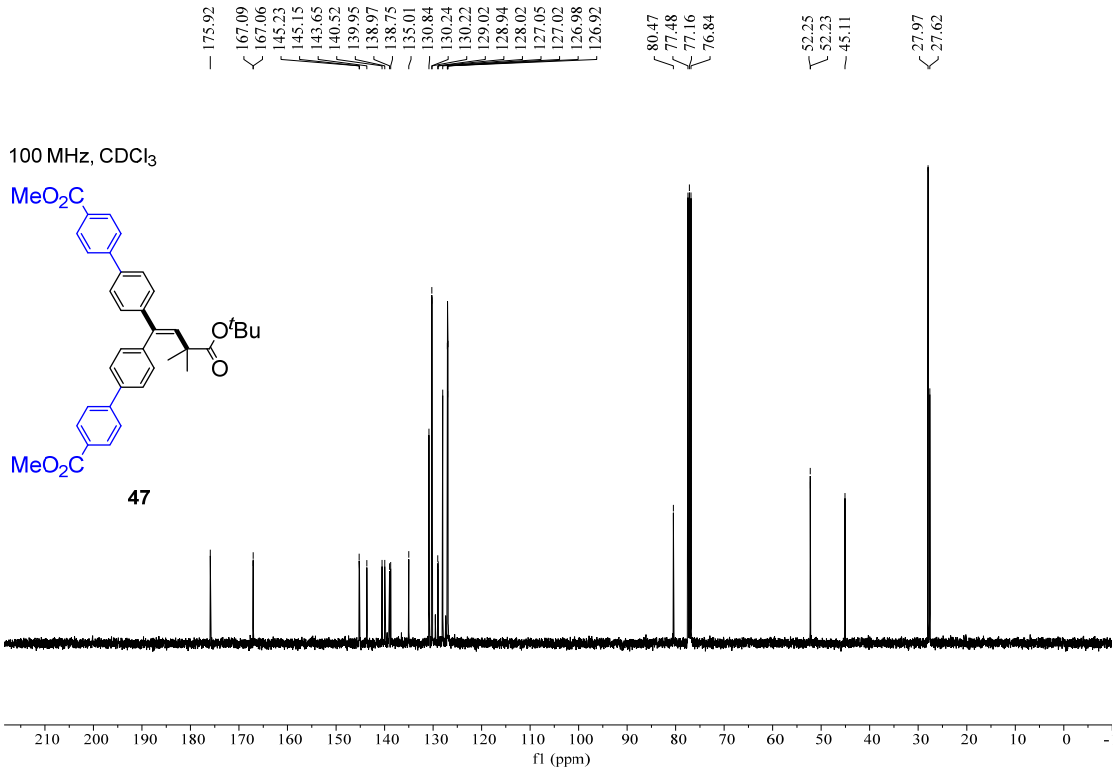


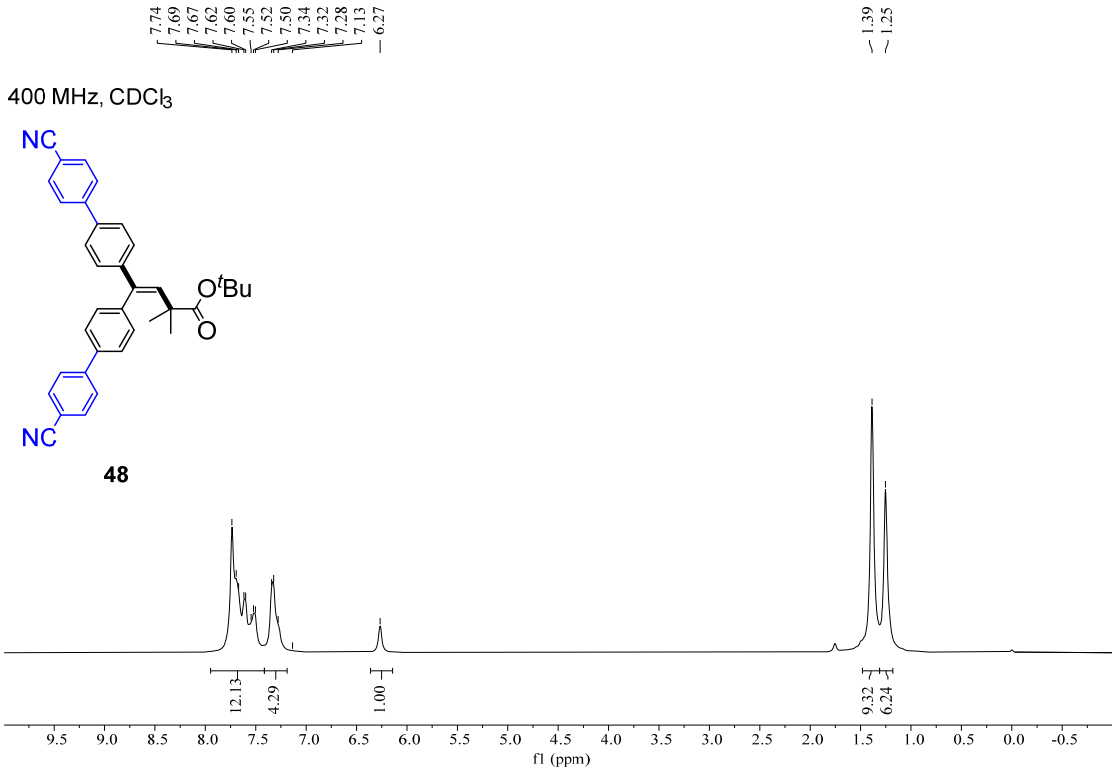
45

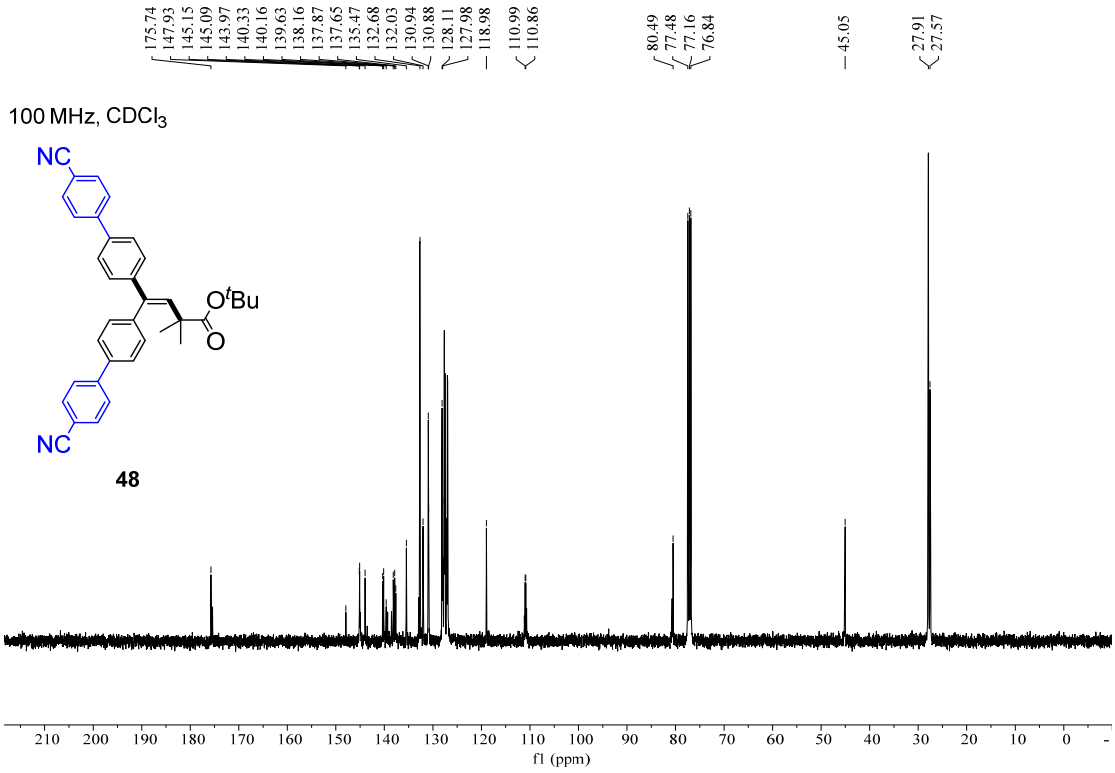

400 MHz, CDCl3
O'Bu
O
46
2.13
2.45
4.20
12.01
12.26
4.47
1.00
9.53
6.04
f1 (ppm)


100 MHz, CDCl3
O'Bu
O
46
45.12
f1 (ppm)


8.13
8.11
8.10
8.08
7.72
7.69
7.65
7.64
7.63
7.62
7.55
7.53
7.33
7.32
7.31
7.30
6.24
3.94
3.93
1.39
1.25
400 MHz, CDCl3
MeO2C
O^tBu
O
MeO2C
47
4.07
2.16
4.01
2.04
4.13
1.00
3.17
2.91
9.04
6.37
f1 (ppm)


175.92
167.09
167.06
145.23
145.15
143.65
140.52
139.95
138.97
138.75
135.01
130.84
130.24
130.22
129.02
128.94
128.02
127.05
127.02
126.98
126.92
80.47
77.48
77.16
76.84
52.25
52.23
45.11
27.97
27.62
100 MHz, CDCl3
MeO2C
O^tBu
O
MeO2C
47
f1 (ppm)


7.74
7.69
7.67
7.62
7.60
7.55
7.52
7.50
7.34
7.32
7.28
7.13
6.27
1.39
1.25
400 MHz, CDCl3
NC
O^tBu
O
NC
48
12.13
4.29
1.00
9.32
6.24
f1 (ppm)


175.74
147.93
145.15
145.09
143.97
140.33
140.16
139.63
138.16
137.87
137.65
135.47
132.68
132.03
130.94
130.88
128.11
127.98
118.98
110.99
110.86
80.49
77.48
77.16
76.84
45.05
27.91
27.57
100 MHz, CDCl3
NC
O^tBu
O
NC
48
f1 (ppm)