Supporting Information (SI)

HFIP-promoted synthesis of bicyclo[2.1.1]-hexanes through formal [2π+2σ] cycloaddition of bicyclo[1.1.0]butanes with α-cyano chalcones

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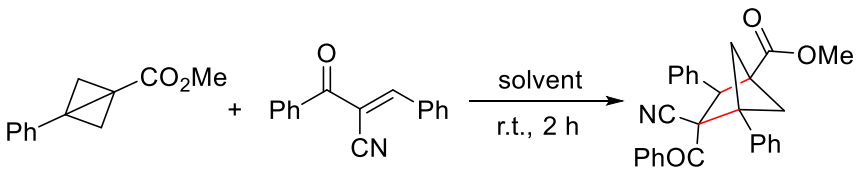
Content

General information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 instrument at 400 (^{1}H NMR), 100 (^{13}C NMR) as well as 376 MHz (^{19}F NMR). Tetramethylsilane (TMS) and $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.0 ppm for ^{13}C NMR) or THF-*d*8 (1.72 ppm and 3.58 ppm for ^{1}H NMR, 67.2 ppm and 25.3 ppm for ^{13}C NMR) were used as references. Data for ^{1}H NMR were reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz), and integration. Data for ^{13}C NMR were reported as ppm. High-resolution mass spectra (HRMS) analyses were performed by the electrospray ionization (ESI) method on a Waters SYNAPT G2-Si mass spectrometer with a Q-TOF analyzer. Melting points were determined using a X-4 digital micro melting point apparatus. Thin-layer chromatography (TLC) was performed, and visualization of the compounds was accomplished with UV light (254 nm). Flash column chromatography was performed on silica gel (200−300 mesh). Known BCBs **1**[1] and *α*-cyano chalcones **2**[2] were prepared according to literature procedures. Other purchased reagents and solvents were used without further purification, if not stated otherwise.

Table S1. Optimization of solvents[a]



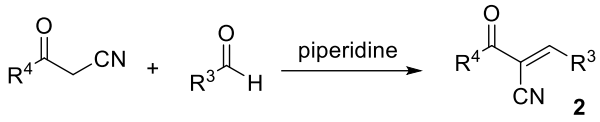
1a **2a** **3aa**

Entry	**1a**:**2a**	Solvent	Yield (%)[b]
1	1:1	toluene/HFIP (4:1)	50
2	1:1	*p*-xylene/HFIP (4:1)	24
3	1:1	CF_3Ph/HFIP (4:1)	40
4	1:1	MeCN/HFIP (4:1)	42
5	1:1	DCE/HFIP (4:1)	26
6	1:1	THF/HFIP (4:1)	43
7	1:1	1,4-dioxane/HFIP (4:1)	30
8	1:1	DMF/HFIP (4:1)	8

[a] Reaction conditions: **1a**, **2a** (0.2 mmol, 1.0 eq.) in solvent (4.0 mL) at room temperature for 2 h.

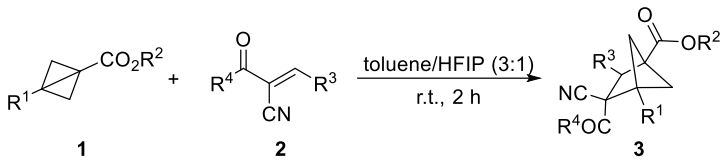
[b] Isolated yields with >20:1 dr.

General procedure for the synthesis of *α*-cyano chalcones



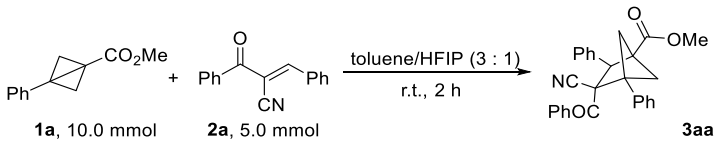
To a round-bottom flask with a magnetic stirring bar was added cyanoketone (10 mmol, 1.0 eq.), aldehyde (10 mmol, 1.0 eq.), piperidine (8.5 mg, 1.0 mmol, 0.1 eq.) and EtOH (40 mL). The reaction mixture was heated in an oil bath to reflux overnight. Upon completion, the reaction mixture was concentrated under the reduced pressure. The crude product was purified by recrystallisation from EtOH to afford the *α*-cyano chalcones **2**.

General procedure for preparation of products 3



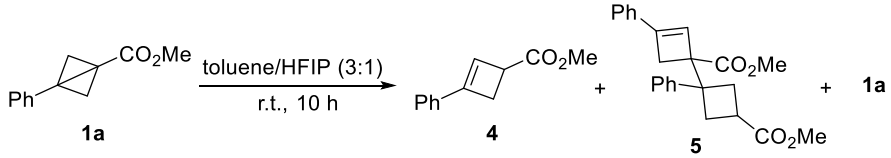
BCB **1** (0.4 mmol, 2.0 eq.) was added to a mixture of *α*-cyano chalcone **2** (0.2 mmol, 1.0 eq.) and toluene/HFIP (3.0 mL:1.0 mL) under room temperature. The resulting mixture was stirred for 2 hours until chalcone was used up by TLC monitoring. The solvent was removed in vacuo on a rotary evaporator and the residue was purified by silica gel column chromatography (PE/EA = 20/1) to give the pure product **3**.

Procedure for scale-up synthesis of compound 3aa



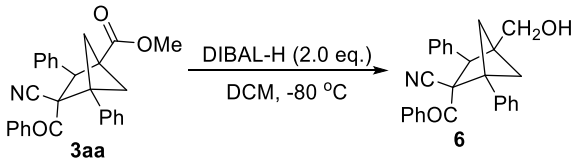
BCB **1a** (1.88 g, 10.0 mmol, 2.0 eq.) was added to a mixture of *α*-cyano chalcone **2a** (1.17 g, 5.0 mmol, 1.0 eq.) and toluene/HFIP (75 mL:25 mL) under room temperature. The resulting mixture was stirred for 2 hours until chalcone was used up by TLC monitoring. The solvent was removed in vacuo on a rotary evaporator and the residue was purified by silica gel column chromatography (PE/EA = 20/1) to give the pure product **3aa** in 80% yield (1.68 g) as a white solid.

Control experiment



A mixture of BCB **1a** (75.2 mg, 0.4 mmol) and toluene/HFIP (3.0 mL:1.0 mL) was stirred for 10 hours under room temperature. The solvent was removed in vacuo on a rotary evaporator and the residue was purified by silica gel column chromatography (PE/EA = 20/1) to give product **4** (26.3 mg, 35% yield), product **5** (5.3 mg, 7% yield) and unreacted **1a** (30.1 mg, 40%). Physical and spectral properties of products **4** and **5** were identical to those previously reported in literature.[3]

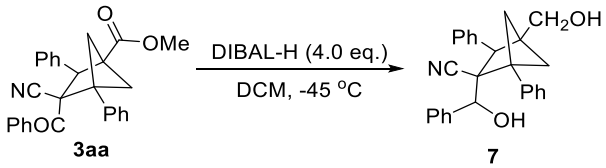
Procedure for preparation of compound 6



3aa **6**

An oven-dried 25 mL Schlenk tube was charged with **3aa** (84.2 mg, 0.2 mmol, 1.0 eq.) and dry DCM (2.0 mL) under N_2. The solution was cooled to -80 °C in a dry alcohol bath. A solution of DIBAL-H in toluene (0.4 mL, 0.4 mmol, 2.0 eq., 1.0 M) of was added dropwise to the reaction mixture over 10 min. After stirring at -80 °C for 0.5 h, the reaction was quenched with saturated NH_4Cl aqueous solution (5 mL). The aqueous layer was extracted with ethyl acetate (10 mL × 3), the combined organic layer was dried over Na_2SO_4, filtered and concentrated under the reduced pressure. The residue was purified by silica gel column chromatography (PE/EA = 8/1) to afford product **6** (67.7 mg, 86% yield) as a white solid.

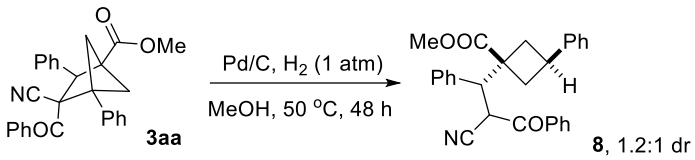
Procedure for preparation of compound 7



3aa **7**

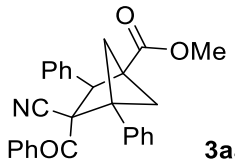
An oven-dried 25 mL Schlenk tube was charged with **3aa** (84.2 mg, 0.2 mmol, 1.0 eq.) and dry DCM (2.0 mL) under N_2. The solution was cooled to -45 °C in a dry alcohol bath. A solution of DIBAL-H in toluene (0.8 mL, 0.8 mmol, 4.0 eq., 1.0 M) of was added dropwise to the reaction mixture over 10 min. After stirring at -45 °C for 0.5 h, the reaction was quenched with saturated NH_4Cl aqueous solution (5 mL). The aqueous layer was extracted with ethyl acetate (10 mL × 3), the combined organic layer was dried over Na_2SO_4, filtered and concentrated under the reduced pressure. The residue was purified by silica gel column chromatography (PE/EA = 5/1) to afford product **7** (63.2 mg, 80% yield) as a white solid.

Procedure for preparation of compound 8

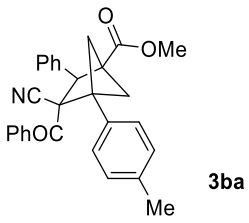


An oven-dried 25 mL Schlenk tube was charged with **3aa** (84.2 mg, 0.2 mmol, 1.0 eq.), Pd/C (64.0 mg, 10 wt %) and MeOH (4.0 mL). The mixture was degassed, and charged with hydrogen balloon and stirred at 50 °C for 48 h. Then the mixture was filtered by celite, concentrated and purified by silica gel column chromatography (PE/EA = 10/1) to give the product **8** (60.9 mg, 72% yield) as a colorless oil.

Characterization data of products

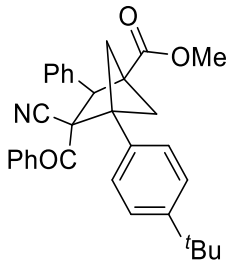


Methyl 3-benzoyl-3-cyano-2,4-diphenylbicyclo[2.1.1]hexane-1-carboxylate (3aa): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3aa** (white solid, 71.7 mg, 0.17 mmol, 85% yield). M.p.: 120 − 121 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 6H), 7.29 – 7.17 (m, 7H), 7.12 (t, J = 7.8 Hz, 2H), 4.99 (s, 1H), 3.64 (s, 3H), 3.21 (dd, J = 9.9, 8.3 Hz, 1H), 3.01 (dd, J = 9.9, 7.5 Hz, 1H), 2.66 (dd, J = 8.3, 2.2 Hz, 1H), 2.29 (d, J = 7.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.9, 171.1, 137.4, 136.9, 135.7, 133.1, 129.5, 129.0, 128.7, 128.3, 128.1, 128.0, 127.8, 126.6, 119.2, 64.3, 60.2, 56.9, 52.2, 50.7, 44.3, 44.1; **HRMS (ESI)** m/z $[M + Na]^+$ calcd for $C_{28}H_{23}NO_3Na$ 444.1570, found 444.1578.



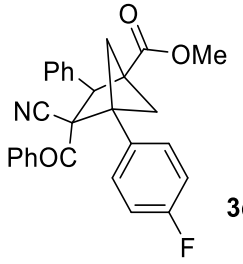
Methyl 3-benzoyl-3-cyano-2-phenyl-4-(*p*-tolyl)bicyclo[2.1.1]hexane-1-carboxylate (3ba): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ba** (white solid, 76.7 mg, 0.176 mmol, 88% yield). M.p.: 65 − 66 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 6H), 7.25 – 7.18 (m, 2H), 7.15 – 7.03 (m, 6H), 4.96 (d, J = 2.1 Hz, 1H), 3.63 (s, 3H), 3.19 (dd, J = 9.9, 8.3 Hz, 1H), 3.00 (dd, J = 9.9, 7.5 Hz, 1H), 2.62 (dd, J = 8.3, 2.2 Hz, 1H), 2.29 (s, 3H), 2.26 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.0, 171.2, 138.2, 137.0, 135.8, 134.4, 133.1, 129.6, 129.3, 129.0, 128.1, 128.0, 127.8, 126.5,

119.3, 64.3, 60.1, 57.0, 52.1, 50.7, 44.4, 44.1, 21.2; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{29}H_{25}NO_3Na$ 458.1727, found 458.1734.



3ca

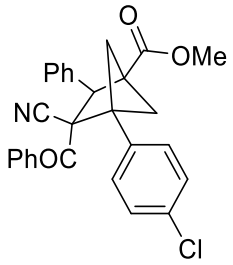
Methyl 3-benzoyl-4-(4-(*tert*-butyl)phenyl)-3-cyano-2-phenylbicyclo[2.1.1]hexane-1-carboxylate (3ca): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ca** (white solid, 85.9 mg, 0.18 mmol, 90% yield). M.p.: 125 – 126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.08 (m, 10H), 7.07 – 6.93 (m, 4H), 4.96 (s, 1H), 3.56 (s, 3H), 3.12 (t, J = 9.2 Hz, 1H), 2.88 (t, J = 8.8 Hz, 1H), 2.57 (d, J = 8.4 Hz, 1H), 2.18 (d, J = 7.6 Hz, 1H), 1.18 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.8, 171.2, 151.7, 137.1, 135.8, 134.4, 133.0, 129.6, 129.0, 128.0, 127.9, 127.7, 126.2, 125.6, 119. 3, 64.6, 60.2, 56.6, 52.2, 50.6, 44.2, 44.0, 34.6, 31.3; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{32}H_{31}NO_3Na$ 500.2196, found 500.2206.



3da

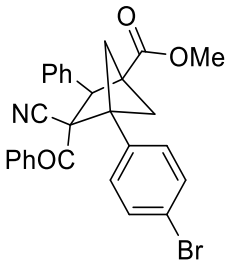
Methyl 3-benzoyl-3-cyano-4-(4-fluorophenyl)-2-phenylbicyclo[2.1.1]hexane-1-carboxylate (3da): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3da** (white solid, 67.7 mg, 0.154 mmol, 77% yield). M.p.: 160 − 161 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 5H), 7.32 – 7.28 (m, 1H), 7.25 – 7.15 (m, 6H), 6.96 – 6.91 (m, 2H), 4.90 (d, J = 2.1 Hz, 1H), 3.63 (s, 3H), 3.19 (dd, J = 9.9, 8.3 Hz, 1H), 2.97 (dd, J = 9.9, 7.5 Hz, 1H), 2.62 (dd, J = 8.4, 2.2 Hz, 1H), 2.28 (d, J = 7.5 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.04 (s, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.4, 170.9, 162.6 (d, J = 247.8 Hz), 136.7, 135.5, 133.4, 133.3 (d, J = 3.6 Hz), 129.5, 129.0, 128.5 (d, J = 8.0 Hz), 128.2,

128.1, 128.0, 119.2, 115.6 (d, J = 21.8 Hz), 63.9, 59.3, 56.9, 52.2, 50.8, 44.6, 44.1; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{28}H_{22}FNO_3Na$ 462.1476, found 462.1481.



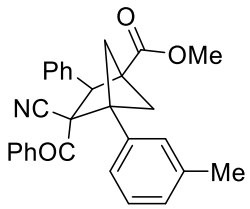
3ea

Methyl 3-benzoyl-4-(4-chlorophenyl)-3-cyano-2-phenylbicyclo[2.1.1]hexane-1-carboxylate (3ea): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ea** (white solid, 67.5 mg, 0.148 mmol, 74% yield). M.p.: 64 – 65 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 3H), 7.39 – 7.30 (m, 3H), 7.26 – 7.19 (m, 5H), 7.19 – 7.14 (m, 3H), 4.86 (d, J = 2.1 Hz, 1H), 3.63 (s, 3H), 3.19 (dd, J = 9.9, 8.3 Hz, 1H), 2.95 (dd, J = 9.9, 7.5 Hz, 1H), 2.60 (dd, J = 8.3, 2.2 Hz, 1H), 2.28 (d, J = 7.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.2, 170.8, 136.5, 135.9, 135.4, 134.3, 133.5, 129.6, 129. 0, 128.7, 128.23, 128.21, 128.20, 128.0, 119.1, 63.8, 59.1, 57.0, 52.2, 51.0, 44.6, 44.0; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{28}H_{22}ClNO_3Na$ 478.1180, found 478.1185.



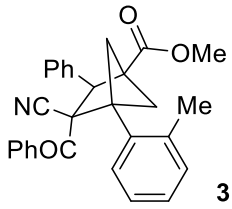
3fa

Methyl 3-benzoyl-4-(4-bromophenyl)-3-cyano-2-phenylbicyclo[2.1.1]hexane-1-carboxylate (3fa): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3fa** (white solid, 75.1 mg, 0.15 mmol, 75% yield). M.p.: 86 − 87 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 8H), 7.24 (d, J = 8.7 Hz, 2H), 7.18 (t, J = 7.2 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 4.85 (s, 1H), 3.62 (s, 3H), 3.19 (t, J = 9.1 Hz, 1H), 2.94 (dd, J = 9.9, 7.5 Hz, 1H), 2.60 (dd, J = 8.4, 2.2 Hz, 1H), 2.28 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.2, 170.8, 136.5, 136.4, 135.3, 133.5, 131.7, 129.6, 129.0, 128.5, 128.3, 128.1, 126.6, 122.4, 119.1, 63.7, 59.1, 57.0, 52.2, 51.0, 44.6, 44.0; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{28}H_{22}BrNO_3Na$ 522.0675, found 522.0685.



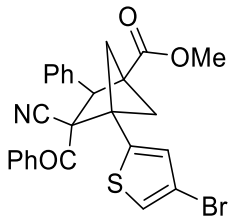
3ga

Methyl 3-benzoyl-3-cyano-2-phenyl-4-(*m*-tolyl)bicyclo[2.1.1]hexane-1-carboxylate (3ga): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ga** (white solid, 77.5 mg, 0.178 mmol, 89% yield). M.p.: 83 – 84 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 6H), 7.22 (d, J = 7.6 Hz, 2H), 7.17 – 7.09 (m, 3H), 7.08 – 7.00 (m, 2H), 6.94 (s, 1H), 5.00 (s, 1H), 3.65 (s, 3H), 3.19 (t, J = 9.1 Hz, 1H), 2.97 (dd, J = 9.9, 7.5 Hz, 1H), 2.64 (dd, J = 8.4, 2.2 Hz, 1H), 2.26 (d, J = 7.5 Hz, 1H), 2.20 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.9, 171.2, 138.4, 137.3, 137.0, 135.8, 133.1, 129.5, 129.04, 128.95, 128.6, 128.0, 127.9, 127.8, 127.2, 123.6, 119.2, 64.3, 60.2, 56.8, 52.1, 50.6, 44.3, 44.1, 21.3; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{29}H_{25}NO_3Na$ 458.1727, found 458.1729.



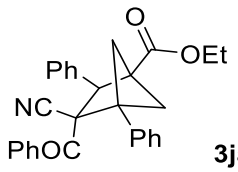
3ha

Methyl 3-benzoyl-3-cyano-2-phenyl-4-(*o*-tolyl)bicyclo[2.1.1]hexane-1-carboxylate (3ha): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ha** (white solid, 74.1 mg, 0.17 mmol, 85% yield). M.p.: 107 – 108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 5H), 7.28 – 7.14 (m, 6H), 7.09 (t, J = 7.8 Hz, 2H), 6.95 – 6.92 (m, 1H), 5.24 (s, 1H), 3.67 (s, 3H), 3.31 (t, J = 9.0 Hz, 1H), 3.02 (t, J = 8.7 Hz, 1H), 2.78 (d, J = 8.1 Hz, 1H), 2.38 (d, J = 7.6 Hz, 1H), 2.06 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.7, 171.2, 137.2, 136.8, 135.5, 135.3, 133.3, 131.7, 129.7, 129.0, 128.6, 128.1, 127.77, 127.76, 126.5, 119.5, 64.7, 61.0, 55.8, 52.2, 50.3, 45.9, 45.6, 20.4; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{29}H_{25}NO_3Na$ 458.1727, found 458.1731.



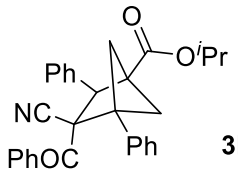
3ia

Methyl 3-benzoyl-4-(4-bromothiophen-2-yl)-3-cyano-2-phenylbicyclo[2.1.1]hexane-1-carboxylate (3ia): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ia** (white solid, 79.0 mg, 0.156 mmol, 78% yield). M.p.: 120 − 121 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.8 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.39 – 7.37 (m, 3H), 7.31 – 7.27 (m, 4H), 7.10 (s, 1H), 6.94 (s, 1H), 4.48 (s, 1H), 3.57 (s, 3H), 3.16 (t, J = 9.3 Hz, 1H), 2.86 (t, J = 8.8 Hz, 1H), 2.65 (d, J = 8.5 Hz, 1H), 2.41 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.3, 170.1, 141.2, 135.7, 134.9, 133.9, 129.7, 129.2, 129.0, 128.8, 128.6, 128.3, 123.0, 118.8, 109.6, 62.9, 57.5, 55.0, 52.3, 52.2, 46.9, 44.9; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{26}H_{20}BrNO_3SNa$ 528.0239, found 528.0247.



3ja

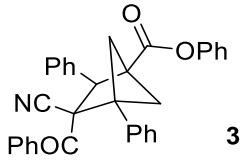
Ethyl 3-benzoyl-3-cyano-2,4-diphenylbicyclo[2.1.1]hexane-1-carboxylate (3ja): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ja** (white solid, 65.3 mg, 0.15 mmol, 75% yield). M.p.: 87 − 88 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 5H), 7.31 – 7.19 (m, 8H), 7.11 (d, J = 7.4 Hz, 2H), 4.95 (d, J = 2.1 Hz, 1H), 4.17 – 3.96 (m, 2H), 3.22 (dd, J = 9.9, 8.3 Hz, 1H), 3.01 (dd, J = 9.9, 7.5 Hz, 1H), 2.64 (dd, J = 8.3, 2.2 Hz, 1H), 2.29 (d, J = 7.5 Hz, 1H), 1.09 (t, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.9, 170.6, 137.5, 136.9, 135.7, 133.2, 129.5, 128.9, 128.7, 128.3, 128.2, 128.0, 127.9, 126.7, 119.3, 64.2, 60.9, 60.0, 57.1, 50.9, 44.4, 44.1, 14.0; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{29}H_{25}NO_3Na$ 458.1727, found 458.1737.



3ka

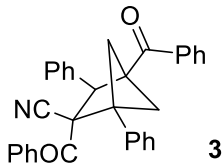
Isopropyl 3-benzoyl-3-cyano-2,4-diphenylbicyclo[2.1.1]hexane-1-carboxylate (3ka): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ka** (white solid, 71.9 mg, 0.16 mmol, 80% yield). M.p.: 75 − 76 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 5H), 7.31 – 7.21 (m, 8H), 7.13 (t, J = 7.7 Hz, 2H), 5.00 – 4.93 (m, 1H), 4.89 (s, 1H), 3.21 (t, J = 9.1 Hz, 1H), 2.99 (dd, J = 9.9, 7.5 Hz, 1H), 2.63 (dd, J = 8.4, 2.1 Hz, 1H), 2.28 (d, J = 7.5 Hz, 1H), 1.15 (d, J = 6.2 Hz, 1H), 0.97 (d, J = 6.2 Hz, 3H); **^{13}C**

NMR (100 MHz, $CDCl_3$) δ 193.9, 170.1, 137.5, 136.9, 135.6, 133.1, 129.5, 128.8, 128.6, 128.4, 128.2, 128.0, 127.8, 126. 7, 119.3, 68.4, 64.1, 59.9, 57.2, 51.2, 44.3, 44.0, 21.6, 21.4; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{30}H_{27}NO_3Na$ 472.1883, found 472.1886.



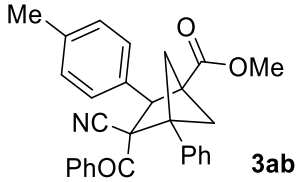
3la

Phenyl 3-benzoyl-3-cyano-2,4-diphenylbicyclo[2.1.1]hexane-1-carboxylate (3la): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3la** (white solid, 56.1 mg, 0.116 mmol, 58% yield). M.p.: 164 − 165 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.27 (m, 13H), 7.25 – 7.07 (m, 5H), 6.80 (d, J = 8.0 Hz, 2H), 5.09 (s, 1H), 3.34 (t, J = 9.1 Hz, 1H), 3.17 (t, J = 8.7 Hz, 1H), 2.77 (d, J = 8.4 Hz, 1H), 2.47 (d, J = 7.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.7, 169.2, 150.3, 137.3, 136.7, 135.6, 133.3, 129.6, 129.5, 129.1, 128.7, 128.5, 128.3, 127.9, 126.7, 126.1, 121.3, 119.2, 64.1, 60.2, 57.3, 51.1, 44.6, 44.1; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{33}H_{25}NO_3Na$ 506.1727, found 506.1729.



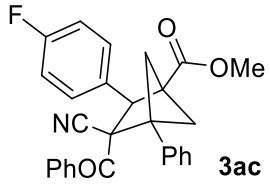
3ma

2,4-Dibenzoyl-1,3-diphenylbicyclo[2.1.1]hexane-2-carbonitrile (3ma): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ma** (white solid, 71.9 mg, 0.154 mmol, 77% yield). M.p.: 177 − 178 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.3 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.34 (d, J = 7.6 Hz, 2H), 7.29 – 7.20 (m, 10H), 7.14 (t, J = 7.9 Hz, 2H), 5.30 (d, J = 2.1 Hz, 1H), 3.43 – 3.37 (m, 2H), 2.77 (dt, J = 5.2, 2.4 Hz, 1H), 2.48 (dd, J = 5.2, 2.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.1, 194.4, 137.4, 136.5, 136.0, 135.6, 133.3, 129.6, 128.9, 128.84, 128.75, 128.43, 128.40, 128.2, 128.0, 127.9, 126.7, 119.2, 65.5, 59.7, 58.6, 58.1, 45.9, 45.2; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{33}H_{25}NO_2Na$ 490.1778, found 490.1785.



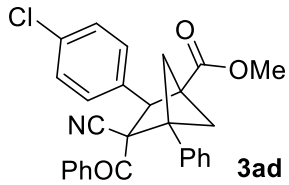
3ab

Methyl 2-([1,1'-biphenyl]-4-yl)-3-benzoyl-3-cyano-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (3ab): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ab** (white solid, 63.6 mg, 0.146 mmol, 73% yield). M.p.: 155 – 156 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 3H), 7.27 – 7.19 (m, 5H), 7.18 – 7.07 (m, 6H), 4.91 (s, 1H), 3.63 (s, 3H), 3.21 (t, J = 9.1 Hz, 1H), 3.01 (t, J = 8.7 Hz, 1H), 2.63 (d, J = 8.3 Hz, 1H), 2.31 (s, 3H), 2.28 (d, J = 6.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.0, 171.1, 137.7, 137.5, 135.8, 133.8, 133.1, 129.7, 129.5, 128.7, 128.3, 128.0, 127.9, 126.7, 119.4, 64.3, 60.1, 56.9, 52.1, 50.8, 44.4, 44.1, 21.2; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{29}H_{25}NO_3Na$ 458.1727, found 458.1732.



3ac

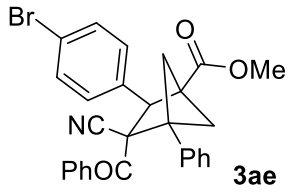
Methyl 3-benzoyl-3-cyano-2-(4-fluorophenyl)-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (3ac): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ac** (white solid, 56.3 mg, 0.128 mmol, 64% yield). M.p.: 160 − 161 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 3H), 7.28 – 7.16 (m, 7H), 7.12 (t, J = 7.8 Hz, 2H), 7.04 (t, J = 8.5 Hz, 2H), 4.97 (s, 1H), 3.65 (s, 3H), 3.19 (t, J = 9.1 Hz, 1H), 2.98 (dd, J = 9.9, 7.6 Hz, 1H), 2.65 (dd, J = 8.4, 2.2 Hz, 1H), 2.29 (d, J = 7.6 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.69 (s, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.5, 170.9, 162.2 (d, J = 247.1 Hz), 137.2, 135.5, 133.3, 132.7 (d, J = 3.6 Hz), 129.8 (d, J = 8.0 Hz), 129.5, 128.7, 128.4, 127.9, 126.6, 119.2, 116.0 (d, J = 21.8 Hz), 64.2, 60.1, 56.1, 52.2, 50.8, 44.2, 44.0; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{28}H_{22}FNO_3Na$ 462.1476, found 462.1485.



3ad

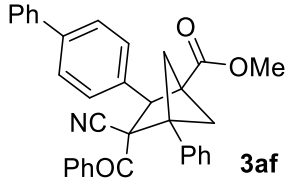
Methyl 3-benzoyl-2-(4-chlorophenyl)-3-cyano-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (3ad): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ad** (white solid, 63.8 mg, 0.14 mmol, 70% yield).

M.p.: 190 − 191 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 7.28 – 7.22 (m, 3H), 7.21 – 7.09 (m, 6H), 4.97 (d, J = 2.2 Hz, 1H), 3.65 (s, 3H), 3.17 (dd, J = 10.0, 8.4 Hz, 1H), 2.97 (dd, J = 9.9, 7.6 Hz, 1H), 2.66 (dd, J = 8.3, 2.2 Hz, 1H), 2.29 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.4, 170.9, 137.2, 135.51, 135.48, 133.9, 133.3, 129.6, 129.5, 129.2, 128.7, 128.5, 127.9, 126.6, 119.1, 64.1, 60.2, 56.1, 52.2, 50.7, 44.2, 44.1; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{28}H_{22}ClNO_3Na$ 478.1180, found 478.1190.



3ae

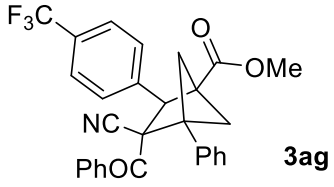
Methyl 3-benzoyl-2-(4-bromophenyl)-3-cyano-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (3ae): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ae** (white solid, 69.1 mg, 0.138 mmol, 69% yield). M.p.: 179 − 180 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.5 Hz, 2H), 7.38 – 7.35 (m, 1H), 7.33 – 7.30 (m, 2H), 7.26 – 7.22 (m, 3H), 7.19 – 7.17 (m, 2H), 7.14 – 7.08 (m, 4H), 4.96 (d, J = 2.1 Hz, 1H), 3.65 (s, 3H), 3.16 (dd, J = 9.9, 8.4 Hz, 1H), 2.97 (dd, J = 9.9, 7.6 Hz, 1H), 2.66 (dd, J = 8.4, 2.2 Hz, 1H), 2.29 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.4, 170.8, 137.1, 136.0, 135.5, 133.3, 132.2, 129.8, 129.5, 128.7, 128.5, 127.9, 126.5, 122.1, 119.1, 64.1, 60.2, 56.2, 52.3, 50.6, 44.2, 44.1; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{28}H_{22}BrNO_3Na$ 522.0675, found 522.0674.



3af

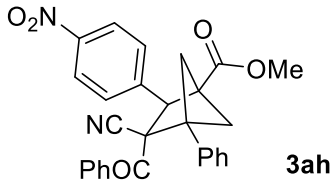
Methyl 2-([1,1'-biphenyl]-4-yl)-3-benzoyl-3-cyano-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (3af): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3af** (white solid, 67.7 mg, 0.136 mmol, 68% yield). M.p.: 125 − 126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.8 Hz, 4H), 7.44 – 7.28 (m, 8H), 7.28 – 7.18 (m, 5H), 7.12 (t, J = 7.8 Hz, 2H), 5.01 (d, J = 2.2 Hz, 1H), 3.66 (s, 3H), 3.25 (t, J = 9.1 Hz, 1H), 3.03 (dd, J = 9.9, 7.5 Hz, 1H), 2.68 (dd, J = 8.3, 2.3 Hz, 1H), 2.31 (d, J = 7.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.8, 171.1, 140.7, 140.5, 137.4, 135. 9, 135.7, 133.2,

129.6, 128.8, 128.7, 128.6, 128.4, 127.9, 127.6, 127.4, 127.1, 126.7, 119.3, 64.3, 60.2, 56.8, 52.2, 50.8, 44.4, 44.2; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{34}H_{27}NO_3Na$ 520.1883, found 520.1892.



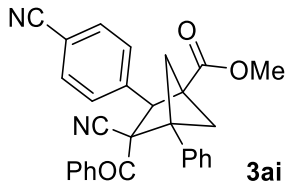
3ag

Methyl 3-benzoyl-3-cyano-4-phenyl-2-(4-(trifluoromethyl)phenyl)bicyclo[2.1.1]hexane-1-carboxylate (3ag): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ag** (white solid, 63.6 mg, 0.13 mmol, 65% yield). M.p.: 99 − 100 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.2 Hz, 2H), 7.39 – 7.29 (m, 5H), 7.27 – 7.23 (m, 3H), 7.20 – 7.15 (m, 2H), 7.12 (t, J = 7.9 Hz, 2H), 5.11 (s, 1H), 3.67 (s, 3H), 3.18 (dd, J = 10.0, 8.4 Hz, 1H), 2.99 (dd, J = 9.9, 7.6 Hz, 1H), 2.71 (dd, J = 8.4, 2.2 Hz, 1H), 2.31 (d, J = 7.6 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.64 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.3, 170.7, 141.2, 137.0, 135.4, 133.3, 130.1 (q, J = 32.5 Hz), 129.5, 128.8, 128.5, 128.4, 127.9, 126.5, 126.0 (q, J = 3.7 Hz), 124.0 (q, J = 273.4 Hz), 119.0, 64.2, 60.4, 56.1, 52.3, 50.5, 44.1; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{29}H_{22}F_3NO_3Na$ 512.1444, found 512.1453.



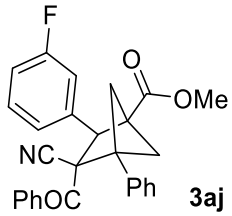
3ah

Methyl 3-benzoyl-3-cyano-2-(4-nitrophenyl)-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (3ah): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ah** (white solid, 62.5 mg, 0.134 mmol, 67% yield). M.p.: 135 − 136 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.3 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.33 (d, J = 7.9 Hz, 2H), 7.27 – 7.21 (m, 3H), 7.17 – 7.05 (m, 4H), 5.20 (s, 1H), 3.69 (s, 3H), 3.17 (t, J = 9.2 Hz, 1H), 2.96 (dd, J = 9.9, 7.7 Hz, 1H), 2.75 (dd, J = 8.4, 2.3 Hz, 1H), 2.33 (d, J = 7.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.7, 170.5, 147.4, 144.7, 136.7, 135.2, 133.5, 129.6, 129.0, 128.8, 128.7, 127.9, 126.4, 124.2, 118.9, 64.2, 60.5, 55.7, 52.4, 50.4, 44.2, 44.0; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{28}H_{22}N_2O_3Na$ 489.1421, found 489.1421.



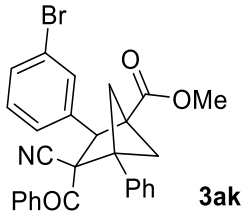
3ai

Methyl 3-benzoyl-3-cyano-2-(4-cyanophenyl)-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (3ai): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ai** (white solid, 64.3 mg, 0.144 mmol, 72% yield). M.p.: 142 − 143 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.40 – 7.29 (m, 5H), 7.29 – 7.20 (m, 3H), 7.16 – 7.08 (m, 4H), 5.14 (d, J = 2.1 Hz, 1H), 3.68 (s, 3H), 3.14 (dd, J = 9.9, 8.4 Hz, 1H), 2.95 (dd, J = 9.9, 7.7 Hz, 1H), 2.72 (dd, J = 8.4, 2.2 Hz, 1H), 2.31 (d, J = 7.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.8, 170.6, 142.7, 136.8, 135.2, 133.5, 132.8, 129.6, 128.83, 128.80, 128.6, 127.9, 126.4, 118.9, 118.5, 111.9, 64.2, 60.5, 56.0, 52.4, 50.3, 44.1, 44.0; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{28}H_{22}N_2O_3Na$ 469.1523, found 469.1531.



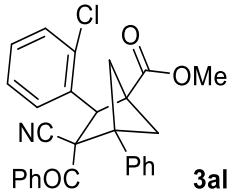
3aj

Methyl 3-benzoyl-3-cyano-2-(3-fluorophenyl)-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (3aj): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3aj** (white solid, 59.8 mg, 0.136 mmol, 68% yield). M.p.: 134 − 135 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 4H), 7.27 – 7.21 (m, 3H), 7.20 – 7.16 (m, 2H), 7.12 (t, J = 7.9 Hz, 2H), 7.02 – 6.90 (m, 3H), 5.03 (d, J = 2.2 Hz, 1H), 3.67 (s, 3H), 3.18 (dd, J = 9.9, 8.3 Hz, 1H), 2.97 (dd, J = 9.9, 7.6 Hz, 1H), 2.68 (dd, J = 8.3, 2.2 Hz, 1H), 2.28 (d, J = 7.6 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.69 (s, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.4, 170.8, 162.9 (d, J = 247.9 Hz), 139.5 (d, J = 7.2 Hz), 137.1, 135.5, 133.3, 130.6 (d, J = 8.0 Hz), 129.6, 128.7, 128.5, 127.9, 126.5, 123.8 (d, J = 2.9 Hz), 119.0, 115.2 (d, J = 5.8 Hz), 115.0 (d, J = 5.1 Hz), 64.2, 60.3, 56.2 (d, J = 1.5 Hz), 52.3, 50.5, 44.2, 44.1; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{28}H_{22}FNO_3Na$ 462.1476, found 462.1471.



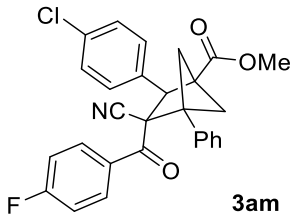
3ak

Methyl 3-benzoyl-3-cyano-4-phenyl-2-(p-tolyl)bicyclo[2.1.1]hexane-1-carboxylate (3ak): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ak** (white solid, 66.1 mg, 0.132 mmol, 66% yield). M.p.: 115 − 116 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 5H), 7.28 – 7.21 (m, 4H), 7.18 – 7.10 (m, 5H), 4.98 (s, 1H), 3.67 (s, 3H), 3.18 (t, J = 9.2 Hz, 1H), 2.94 (dd, J = 9.9, 7.6 Hz, 1H), 2.67 (dd, J = 8.4, 2.2 Hz, 1H), 2.28 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.1, 170.7, 139.3, 137.1, 135.4, 133.3, 131.3, 131.2, 130.5, 129.3, 128.7, 128.5, 127. 9, 126. 6, 126.5, 123.0, 119.0, 64.1, 60.2, 56.0, 52.3, 50.5, 44.2, 44.1; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{28}H_{22}BrNO_3Na$ 522.0675, found 522.0677.



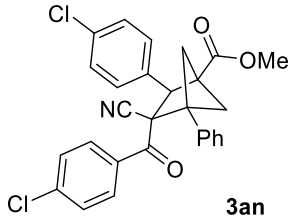
3al

Methyl 3-benzoyl-2-(2-chlorophenyl)-3-cyano-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (3al): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3al** (white solid, 79.3 mg, 0.174 mmol, 87% yield). M.p.: 180 − 181 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.7 Hz, 1H), 7.34 – 7.23 (m, 7H), 7.21 – 7.17 (m, 2H), 7.14 – 7.06 (m, 4H), 5.01 (d, J = 2.2 Hz, 1H), 3.70 (s, 3H), 3.39 (dd, J = 9.9, 7.5 Hz, 1H), 3.07 (dd, J = 9.9, 8.2 Hz, 1H), 2.72 (dd, J = 8.2, 2.3 Hz, 1H), 2.27 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.1, 171.2, 137.1, 136.4, 135.6, 135.5, 132.5, 130.2, 129.1, 129.0, 128.6, 127.2, 127.5, 127.3, 126.3, 118.8, 63.3, 60.9, 55.6, 52.3, 50.3, 43.9, 42.9; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{28}H_{22}ClNO_3Na$ 478.1180, found 478.1190.



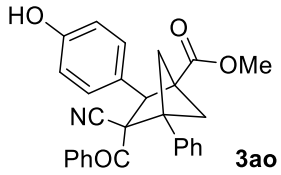
3am

Methyl 2-(4-chlorophenyl)-3-cyano-3-(4-fluorobenzoyl)-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (3am): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3am** (white solid, 61.6 mg, 0.13 mmol, 65% yield). M.p.: 160 − 161 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.28 – 7.21 (m, 3H), 7.18 – 7.13 (m, 4H), 6.78 (t, *J* = 8.6 Hz, 2H), 5.01 (d, *J* = 2.1 Hz, 1H), 3.66 (s, 3H), 3.16 (dd, *J* = 9.9, 8.4 Hz, 1H), 2.90 (dd, *J* = 9.9, 7.6 Hz, 1H), 2.67 (dd, *J* = 8.3, 2.2 Hz, 1H), 2.28 (d, *J* = 7.6 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* -103.46 (s, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 191.4, 170.8, 165.6 (d, *J* = 257.4 Hz), 137.1, 135.4, 133.9, 132.6 (d, *J* = 9.3 Hz), 131.7 (d, *J* = 3.4 Hz), 129.4, 129.2, 128.8, 128.6, 126.5, 119.1, 115.1 (d, *J* = 21.7 Hz), 64.1, 60.1, 55.7, 52.3, 50.6, 44.1, 44.0; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{28}H_{21}ClFNO_3Na$ 496.1086, found 496.1095.



3an

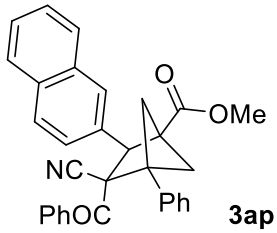
Methyl 3-(4-chlorobenzoyl)-2-(4-chlorophenyl)-3-cyano-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (3an): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3an** (white solid, 73.5 mg, 0.150 mmol, 75% yield). M.p.: 170 − 171 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.32 (d, *J* = 8.5 Hz, 2H), 7.29 – 7.22 (m, 5H), 7.18 – 7.12 (m, 4H), 7.08 (d, *J* = 8.7 Hz, 2H), 4.99 (d, *J* = 2.2 Hz, 1H), 3.66 (s, 3H), 3.16 (dd, *J* = 9.9, 8.4 Hz, 1H), 2.91 (dd, *J* = 9.9, 7.7 Hz, 1H), 2.67 (dd, *J* = 8.4, 2.2 Hz, 1H), 2.28 (d, *J* = 7.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 192.2, 170.7, 140.0, 137.0, 135.4, 133.9, 133.7, 131.0, 129.4, 129.3, 128.8, 128.6, 128.2, 126.5, 119.0, 64.2, 60.2, 55.9, 52.3, 50.6, 44.1, 44.0; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{28}H_{21}Cl_2NO_3Na$ 512.0791, found 512.0793.



3ao

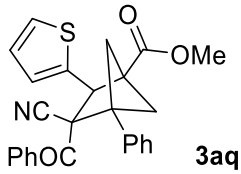
Methyl 3-benzoyl-3-cyano-2-(4-hydroxyphenyl)-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (3ao): The crude product was purified by column chromatography with petroleum ether/ethyl

acetate (5/1, v/v) as eluent to give compound **3ao** (white solid, 84.0 mg, 0.192 mmol, 96% yield). M.p.: 121 – 122 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (t, J = 7.4 Hz, 1H), 7.33 (d, J = 7.9 Hz, 2H), 7.26 – 7.20 (m, 5H), 7.17 – 7.07 (m, 4H), 6.76 (d, J = 8.5 Hz, 2H), 5.42 (s, 1H), 4.84 (s, 1H), 3.65 (s, 3H), 3.21 (t, J = 9.1 Hz, 1H), 3.00 (dd, J = 9.9, 7.6 Hz, 1H), 2.62 (dd, J = 8.4, 2.1 Hz, 1H), 2.29 (d, J = 7.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.7, 171.7, 155.8, 137.4, 135.6, 133.3, 129.5, 128.7, 128.6, 128.3, 128.1, 127.9, 126.7, 119.4, 115.9, 64.2, 59.9, 56.9, 52.3, 51.1, 44.5, 44.1; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{28}H_{23}NO_4Na$ 460.1519, found 460.1528.



3ap

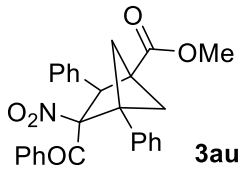
Methyl 3-benzoyl-3-cyano-2-(naphthalen-2-yl)-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (3ap): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3ap** (white solid, 78.3 mg, 0.166 mmol, 83% yield). M.p.: 119 − 120 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 3H), 7.71 (s, 1H), 7.51 – 7.43 (m, 2H), 7.38 – 7.32 (m, 3H), 7.28 – 7.20 (m, 6H), 7.11 (t, J = 7.7 Hz, 2H), 5.15 (s, 1H), 3.62 (s, 3H), 3.34 (t, J = 9.1 Hz, 1H), 3.06 (dd, J = 9.9, 7.6 Hz, 1H), 2.73 (dd, J = 8.4, 2.3 Hz, 1H), 2.33 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.8, 171.2, 137.4, 135.7, 134.5, 133.4, 133.2, 132.9, 129.6, 128.8, 128.7, 128.4, 128.2, 127.9, 127.8, 126.6, 126.4, 126.31, 126.28, 119.3, 64.2, 60.3, 57.0, 52.2, 50.8, 44.4, 44.2; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{32}H_{25}NO_3Na$ 494.1727, found 494.1735.



3aq

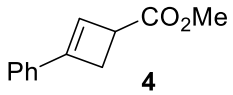
Methyl 3-benzoyl-3-cyano-4-phenyl-2-(thiophen-2-yl)bicyclo[2.1.1]hexane-1-carboxylate (3aq): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3aq** (white solid, 59.9 mg, 0.14 mmol, 70% yield). M.p.: 110 − 111 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.41 – 7.36 (m, 1H), 7.30 – 7.25 (m, 6H), 7.19 – 7.13 (m, 2H), 7.11 (d, J = 3.5 Hz, 1H), 7.02 (dd, J = 5.1, 3.6 Hz, 1H), 5.00

(d, J = 2.1 Hz, 1H), 3.62 (s, 3H), 3.24 (dd, J = 9.9, 8.6 Hz, 1H), 2.95 (dd, J = 9.9, 7.7 Hz, 1H), 2.59 (dd, J = 8.6, 2.2 Hz, 1H), 2.33 (d, J = 7.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.8, 170.3, 138.9, 137.2, 135.2, 133.4, 129.6, 128.6, 128.3, 128.0, 127.4, 127.1, 126.9, 125.7, 119.0, 63.8, 59.9, 53.1, 52.6, 52.2, 44.4, 44.0; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{26}H_{21}NO_3SNa$ 450.1134, found 450.1144.



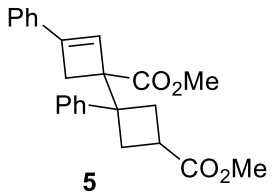
3au

Methyl 3-benzoyl-3-nitro-2,4-diphenylbicyclo[2.1.1]hexane-1-carboxylate (3au): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **3au** (Light yellow solid, 56.4 mg, 0.128 mmol, 64% yield). M.p.: 179 − 180 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 9H), 7.23 (d, J = 7.4 Hz, 1H), 7.12 – 7.03 (m, 5H), 5.29 (d, J = 2.7 Hz, 1H), 3.65 (dd, J = 10.2, 8.6 Hz, 1H), 3.52 (s, 3H), 2.87 (dd, J = 10.2, 7.8 Hz, 1H), 2.70 (dd, J = 8.6, 2.7 Hz, 1H), 2.19 (d, J = 7.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.8, 170.2, 136.7, 135.1, 134.7, 132.8, 129.5, 128.5, 128.2, 128.1, 127.9, 127.81, 127.80, 105.7, 60.2, 58.0, 52.6, 51.9, 46.1, 43.4; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{27}H_{23}NO_5Na$ 464.1468, found 464.1469.



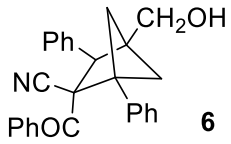
4

Methyl 3-phenylcyclobut-2-ene-1-carboxylate (4): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **4** (colorless liquid, 26.3 mg, 35% yield). **^{1}H NMR** (400 MHz, THF-d8) δ 7.23 (d, J = 7.0 Hz, 2H), 7.17 (t, J = 7.3 Hz, 2H), 7.11 (t, J = 7.1 Hz, 1H), 6.15 (d, J = 1.1 Hz, 1H), 3.50 (s, 3H), 3.48–3.44 (m, 1H), 2.91–2.82 (m, 2H); **^{13}C NMR** (100 MHz, THF-d8) δ 173.4, 149.0, 134.9, 129.1, 129.0, 125.7, 125.4, 51.7, 42.1, 33.0. Physical and spectral properties of this material were identical to those previously reported in literature.[3]



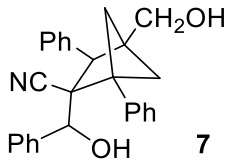
5

Dimethyl 1',3-diphenyl-[1,1'-bi(cyclobutan)]-2-ene-1,3'-dicarboxylate (5): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **5** (colorless liquid, 5.3 mg, 7% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.38 (m, 3H), 7.37–7.28 (m, 7H), 6.39 (s, 1H), 3.67 (s, 3H), 3.46 (s, 3H), 3.06–2.98 (m, 2H), 2.94–2.84 (m, 3H), 2.73–2.64 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.6, 173.6, 148.1, 143.5, 133.3, 128.6, 128.4, 128.1, 127.0, 126.7, 126.3, 125.0, 58.4, 51.7, 51.4, 46.3, 34.6, 33.2, 32.8, 31.6. Physical and spectral properties of this material were identical to those previously reported in literature.[3]



6

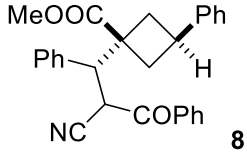
2-Benzoyl-4-(hydroxymethyl)-1,3-diphenylbicyclo[2.1.1]hexane-2-carbonitrile (6): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (8/1, v/v) as eluent to give compound **6** (white solid, 67.7 mg, 0.172 mmol, 86% yield). M.p.: 114 − 115 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 10H), 7.29 – 7.24 (m, 3H), 7.12 (t, J = 7.7 Hz, 2H), 4.38 (d, J = 2.1 Hz, 1H), 3.76 (d, J = 11.9 Hz, 1H), 3.67 (d, J = 11.8 Hz, 1H), 3.08 (dd, J = 10.2, 8.2 Hz, 1H), 2.61 (dd, J = 10.2, 7.6 Hz, 1H), 2.23 (dd, J = 8.3, 2.1 Hz, 1H), 2.09 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.5, 138.4, 136.7, 135.4, 133.1, 129.63, 129.57, 128.9, 128.4, 128.3, 127.84, 127.82, 127.1, 119.8, 64.3, 62.0, 59.4, 56.9, 52.1, 43.3, 41.9; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{27}H_{23}NO_2Na$ 416.1621, found 416.1618.



7

2-(Hydroxy(phenyl)methyl)-4-(hydroxymethyl)-1,3-diphenylbicyclo[2.1.1]hexane-2-carbonitrile (7): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (5/1, v/v) as eluent to give compound **7** (white solid, 63.2 mg, 0.16 mmol, 80% yield). M.p.: 104 – 105 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.49 – 7.45 (m, 4H), 7.41 – 7.32 (m, 4H), 7.13 (t, J = 7.3 Hz, 1H), 7.05 (t, J = 7.5 Hz, 2H), 6.41 (d, J = 7.5 Hz, 2H), 4.97 (s, 1H), 3.65 (d, J = 11.8 Hz, 1H), 3.56 (d, J = 11.7 Hz, 1H), 3.13 (d, J = 2.1 Hz, 1H), 3.03 (dd, J = 10.0, 8.1 Hz, 1H), 2.29 (dd, J = 10.0, 7.8 Hz, 1H), 2.19 (d, J = 7.8 Hz, 1H), 2.11 (dd, J = 8.1, 2.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.1, 138.6, 136.1, 129.4, 129.1, 128.9, 128.8, 128.3,

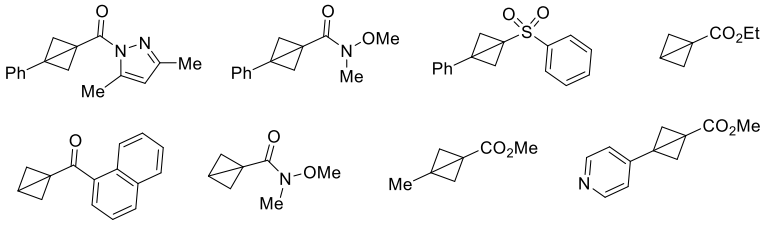
128.0, 127.5, 126.2, 119.9, 76.0, 63.1, 61.8, 56.4, 54.6, 52.2, 42.5, 42.3; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{27}H_{25}NO_2Na$ 418.1778, found 418.1776.



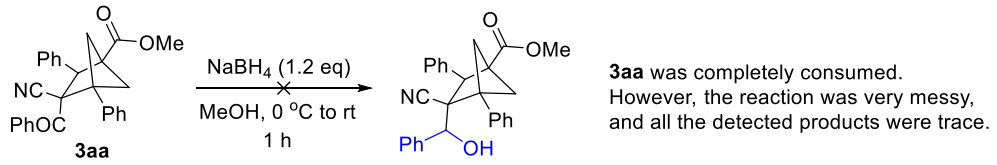
8, 1.2:1 dr

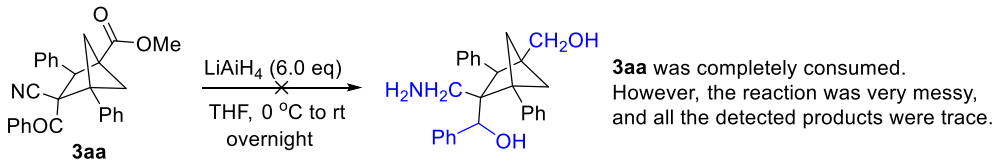
Methyl 1-(2-cyano-3-oxo-1,3-diphenylpropyl)-3-phenylcyclobutane-1-carboxylate (8): The crude product was purified by column chromatography with petroleum ether/ethyl acetate (10/1, v/v) as eluent to give compound **8** (colorless liquid, 60.9 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) For major isomer: δ 7.81 (d, J = 7.3 Hz, 2H), 7.52 (t, J = 7.8 Hz, 2H), 7.40 (t, J = 7.7 Hz, 2H), 7.37–7.08 (m, 9H), 5.49 (d, J = 11.0 Hz, 1H), 3.90 (s, 3H), 3.89 (d, J = 8.1 Hz, 1H), 3.67–3.60 (m, 1H), 3.11–3.05 (m, 1H), 2.80 (dd, J = 19.2, 10.4 Hz, 1H), 2.72–2.65 (m, 1H), 2.31 (dd, J = 19.6, 10.5 Hz, 1H); For major isomer: δ 7.98 (d, J = 7.2 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.37–7.08 (m, 9H), 6.91 (d, J = 7.1 Hz, 2H), 5.37 (d, J = 8.0 Hz, 1H), 3.98 (d, J = 8.0 Hz, 1H), 3.80 (s, 3H), 3.45–3.35 (m, 1H), 2.84–2.79 (m, 1H), 2.49–2.42 (m, 1H), 2.34–2.29 (m, 1H), 2.15 (t, J = 10.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.8, 190.3, 176.6, 176.3, 144.4, 143.9, 136.3, 135.9, 134.8, 134.7, 134.4, 134.3, 129.5, 129.1, 128.92, 128.90, 128.8, 128.7, 128.47, 128.45, 128.4, 128.0, 126.32, 126.26, 117.0, 116.7, 54.2, 52.64, 52.55, 52.0, 48.2, 48.0, 42.1, 41.5, 39.9, 39.7, 38.0, 36.9, 34.9, 34.7; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{28}H_{25}NO_3Na$ 446.1727, found 446.1733.

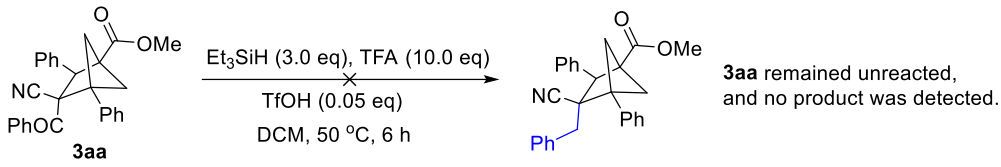
Inapplicable substrates

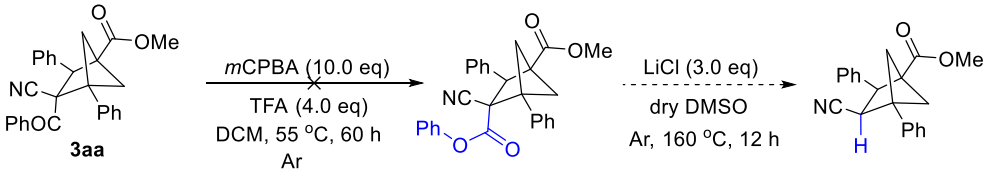


Unsuccessful transformations

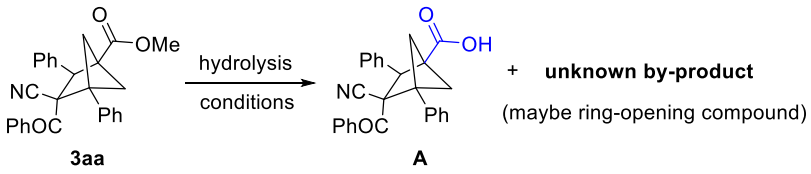








3aa remained unreacted, and
no product was detected.



conditions and result:

1) LiOH (1.0 eq),THF : H_2O (1:1), rt, 24 h; **3aa** was partially consumed. **A** was obtained in major, but an unknown by-product was also obtained which could not be separated.
2) LiOH (3.0 eq),THF : H_2O (1:1), rt, 24 h; **3aa** was completely consumed. The ratio of unknown by-product increase
3) LiOH (6.0 eq),THF : H_2O (1:1), rt, 24 h; **3aa** was completely consumed. But no desired product was obtained.
4) KOH (4.0 eq), EtOH : H_2O (1:1), 90 °C, 4 h; **3aa** was completely consumed. However, no product was detected.
5) 6N HCl aq., 100 °C, 5 h; **3aa** remained unreacted, and no product was detected.

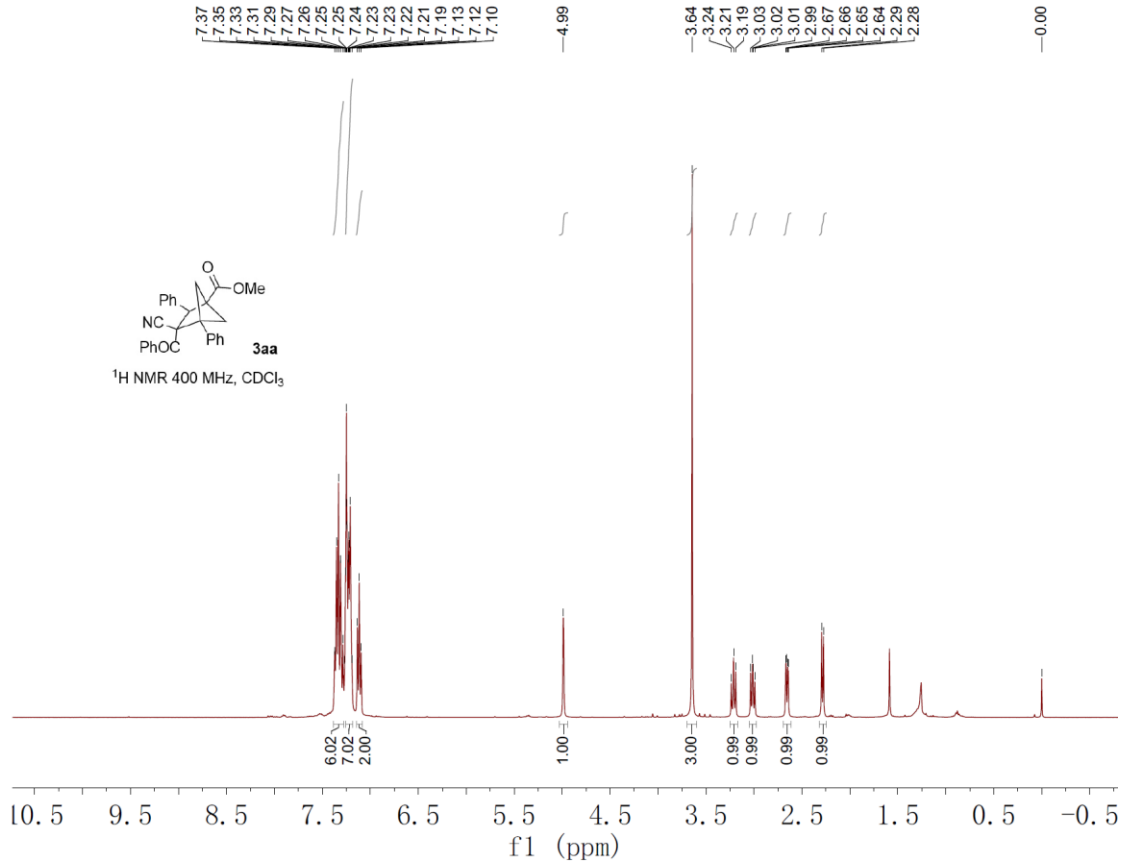
References

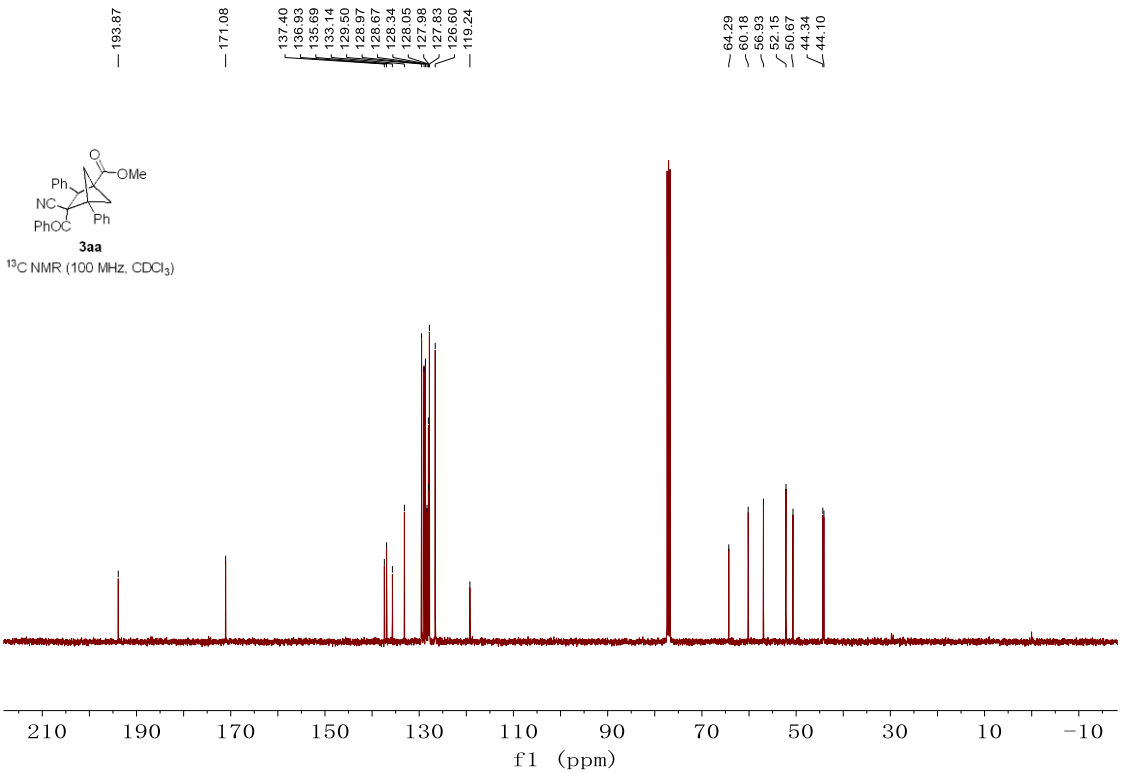
(1) S.-L. Lin, Y.-H. Chen, H.-H. Liu, S.-H. Xiang and B. Tan, *J. Am. Chem. Soc.*, 2023, **145**, 21152−21158.

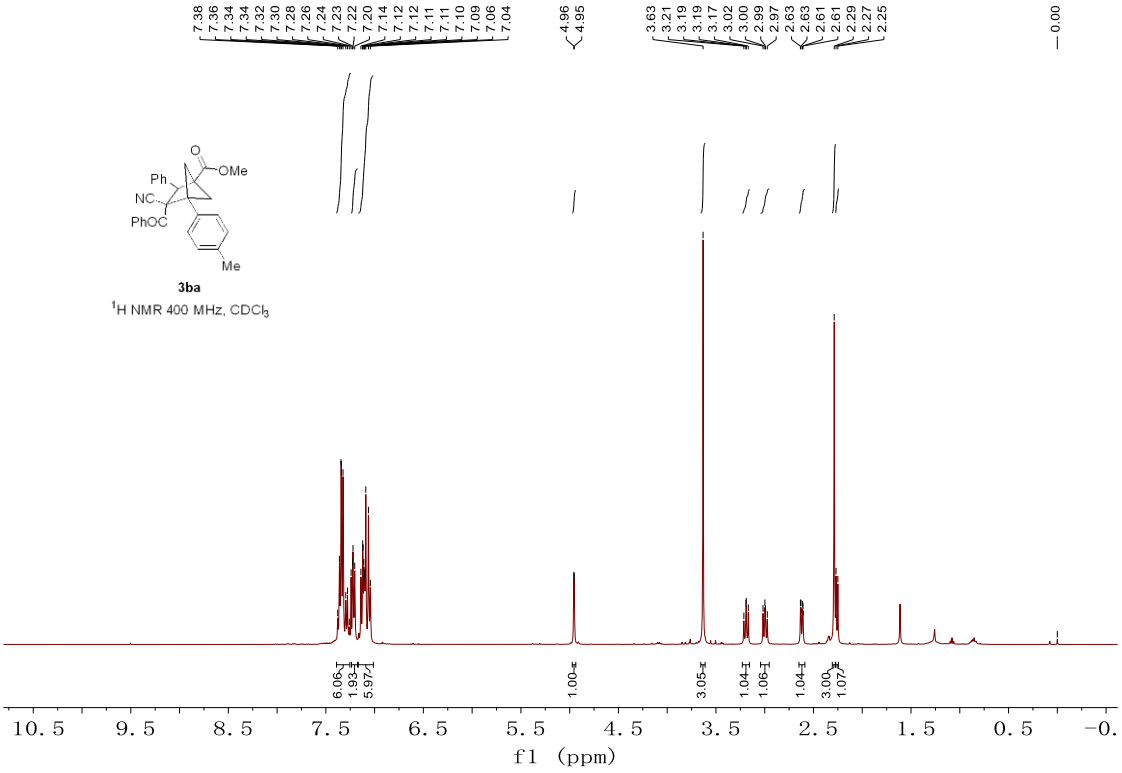
(2) J. Zhang, D. Xiong, Z. Jiang, S. Chen, G.-B. Huang, J. Li, Z. Wang and J. Yang, *Org. Lett.*, 2024, **26**, 1447−1451.

(3) H. Wu, M. Sun, J. Zhang, Z. Wang, J. Yang and G. Zhu, *Org. Chem. Front.*, 2025, **12**, 1951–1957.

NMR spectra of the related compounds



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7.10
7.09
7.06
7.04
4.96
4.95
3.63
3.21
3.19
3.19
3.17
3.02
3.00
2.99
2.97
2.63
2.63
2.61
2.61
2.29
2.27
2.25
0.00
O
OMe
Ph
NC
PhOC
Me
3ba
1H NMR 400 MHz, CDCl3
6.06
1.93
5.97
1.00
3.05
1.04
1.06
1.04
3.00
1.07
10.5
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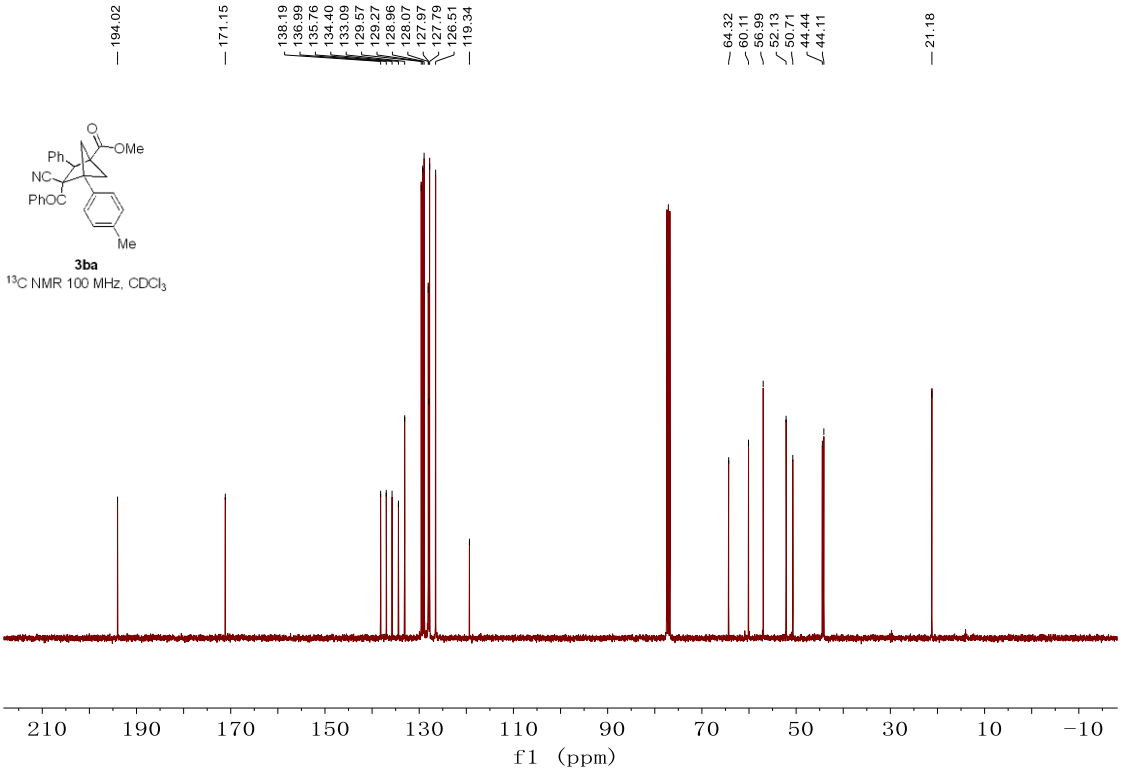
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126.51
119.34
64.32
60.11
56.99
52.13
50.71
44.44
44.11
21.18
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Ph
NC
PhOC
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210
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170
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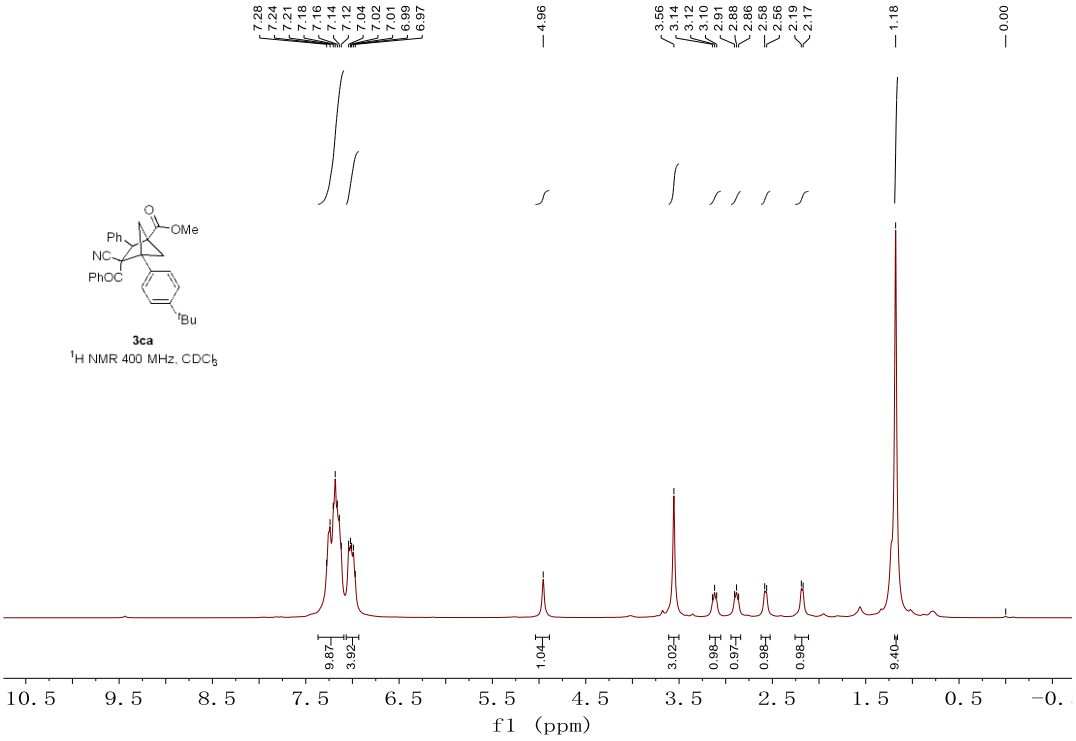
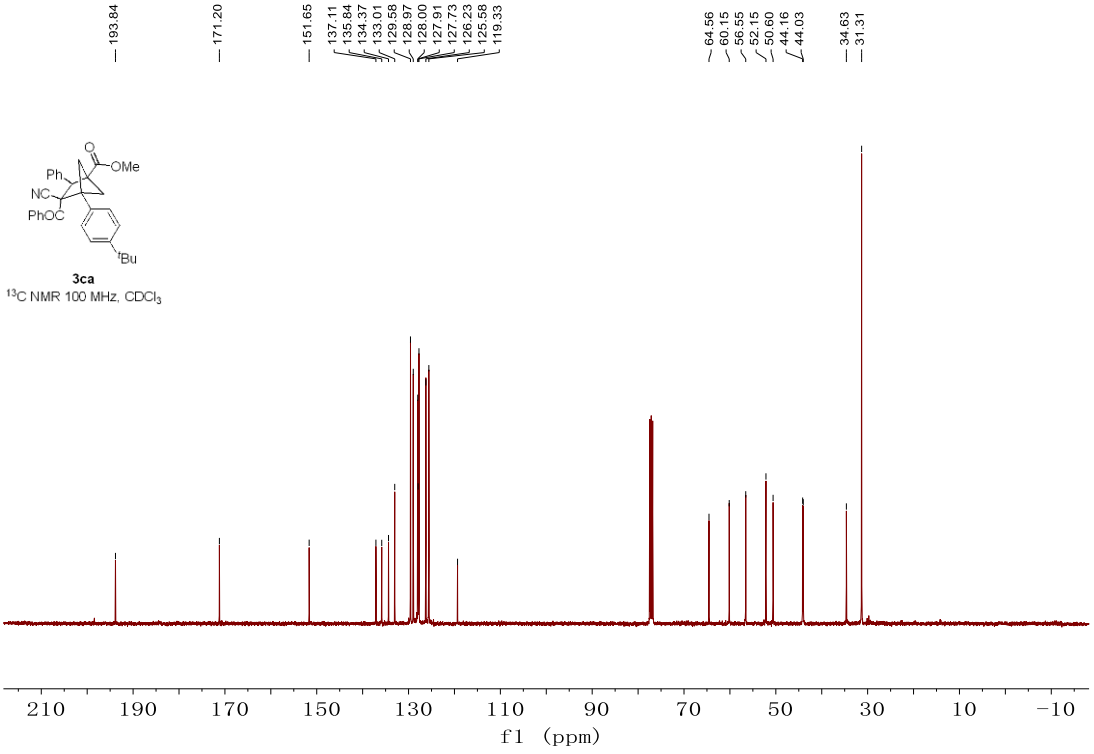
−10
f1 (ppm)



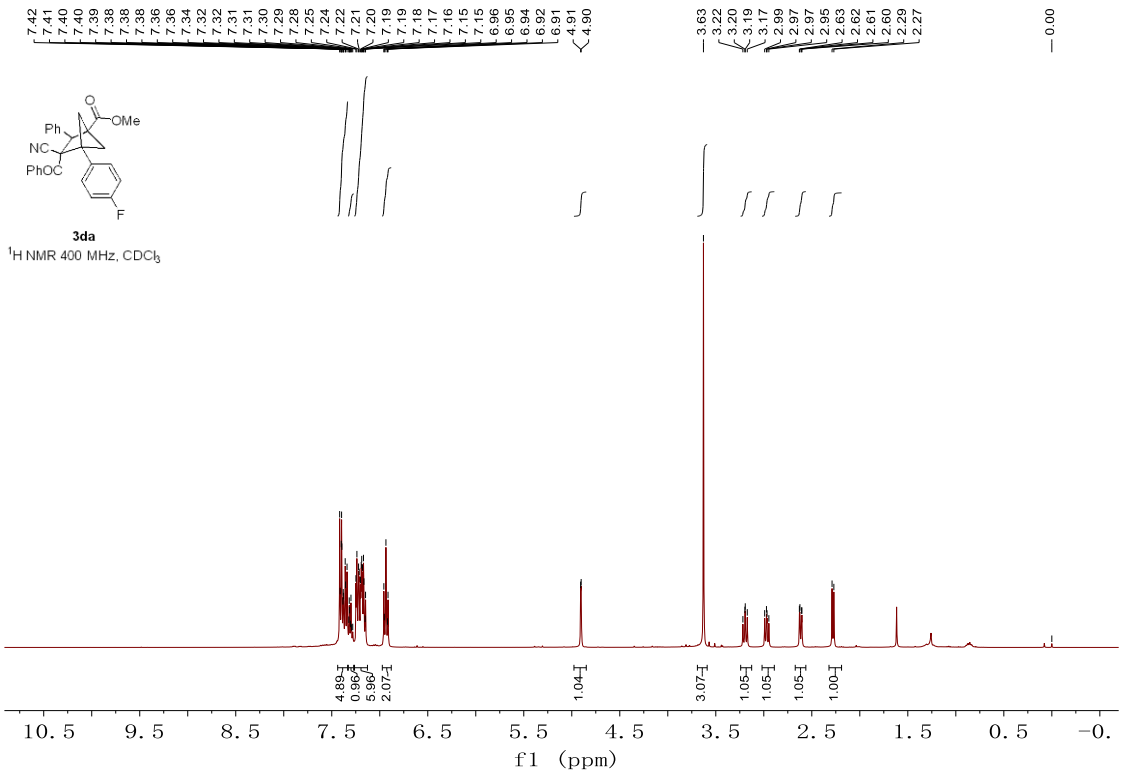
3ca

^{1}H NMR 400 MHz, $CDCl_3$



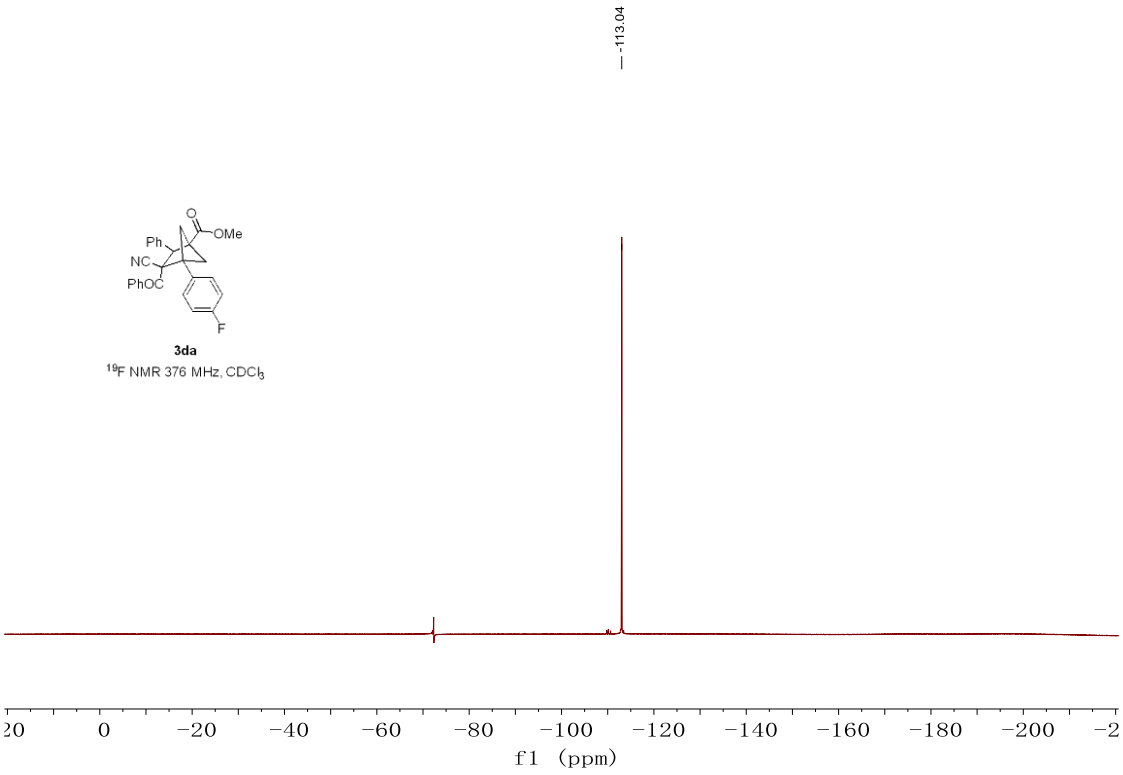
3ca

^{13}C NMR 100 MHz, $CDCl_3$



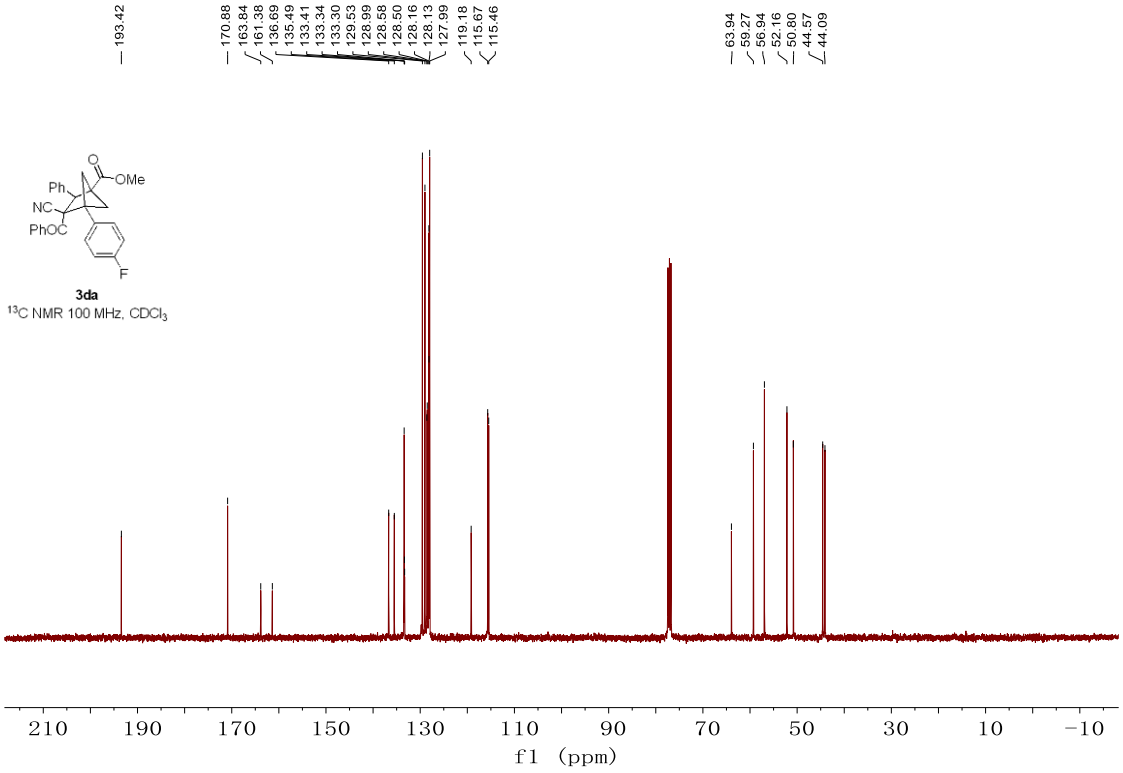
3da

^{1}H NMR 400 MHz, $CDCl_3$



3da

^{19}F NMR 376 MHz, $CDCl_3$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127.99
119.18
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63.94
59.27
56.94
52.16
50.80
44.57
44.09
Ph
NC
PhOC
OMe
F
3da
13C NMR 100 MHz, CDCl3
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130
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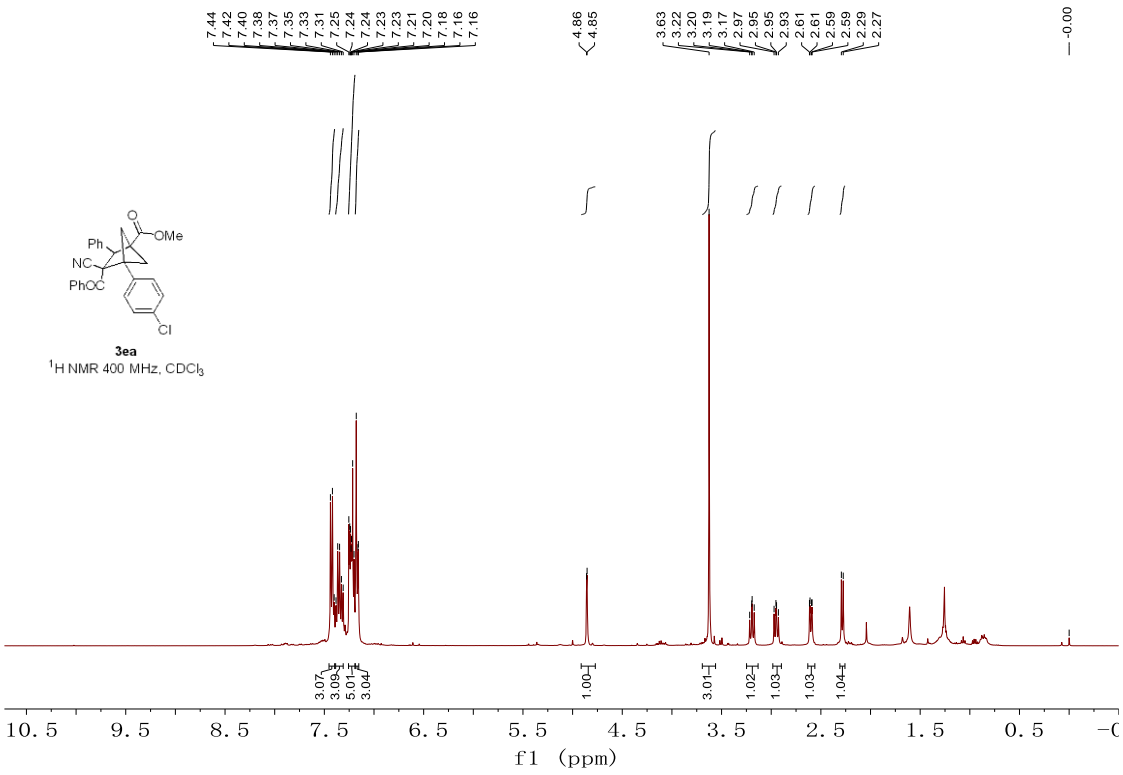
10
−10
f1 (ppm)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2.59
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2.29
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1.00
3.01
1.02
1.03
1.03
1.04
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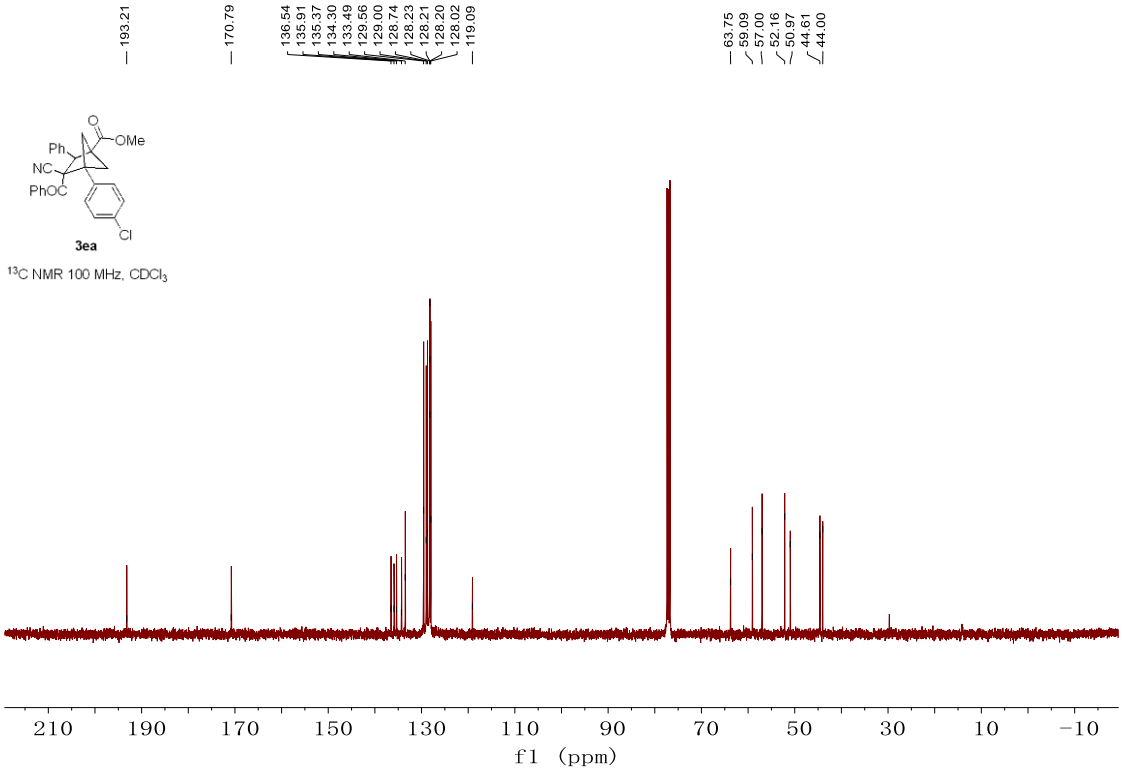
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NC
PhOC
OMe
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13C NMR 100 MHz, CDCl3
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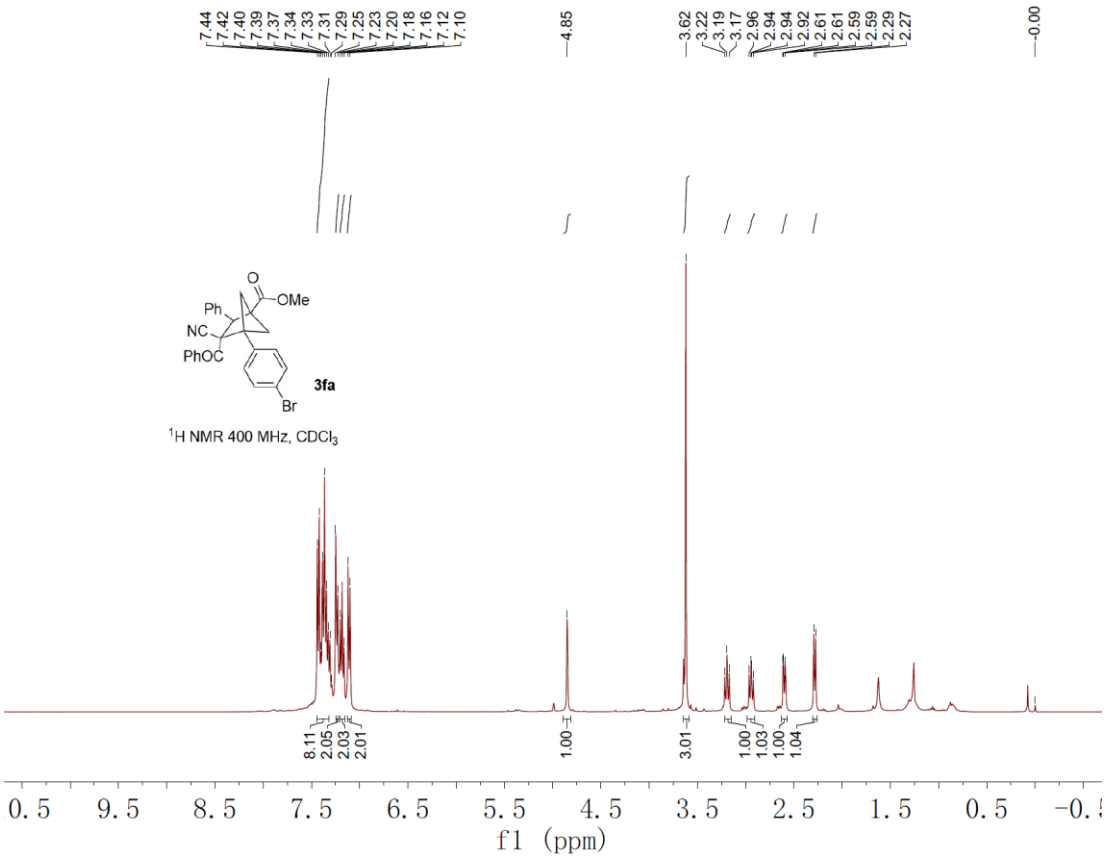
f1 (ppm)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7.16
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7.10
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2.94
2.94
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2.59
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2.29
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Ph
NC
PhOC
OMe
Br
3fa
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1.00
1.04
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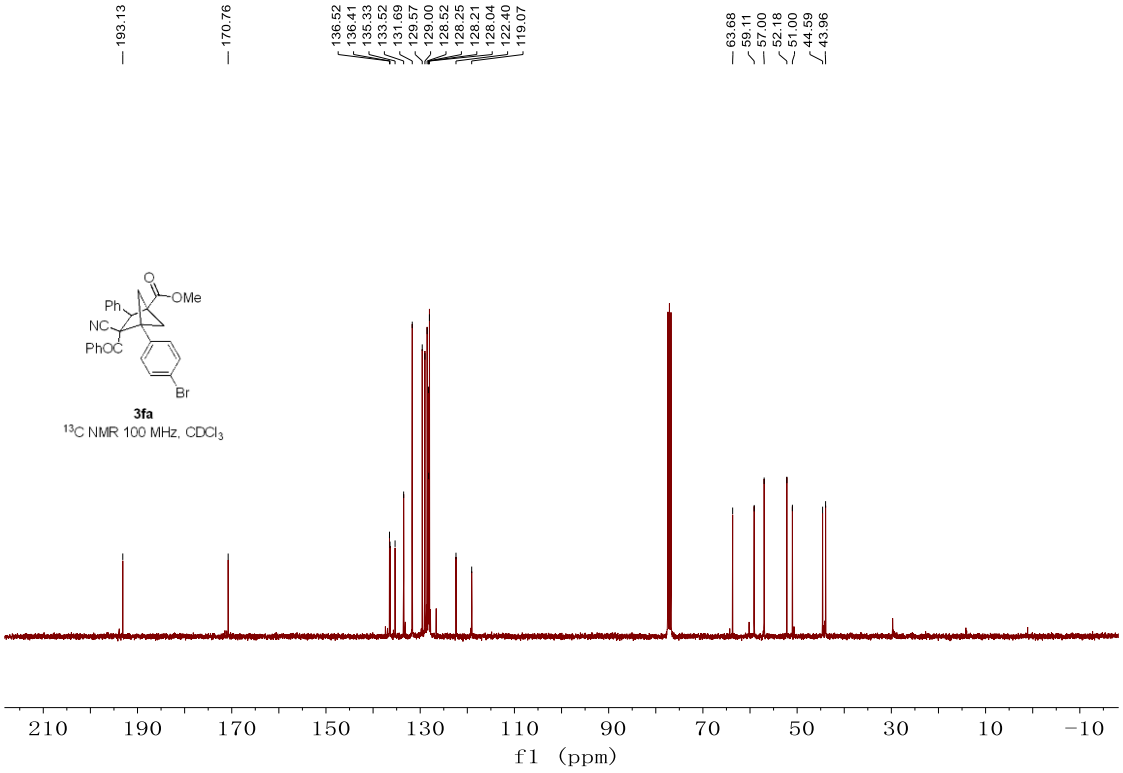
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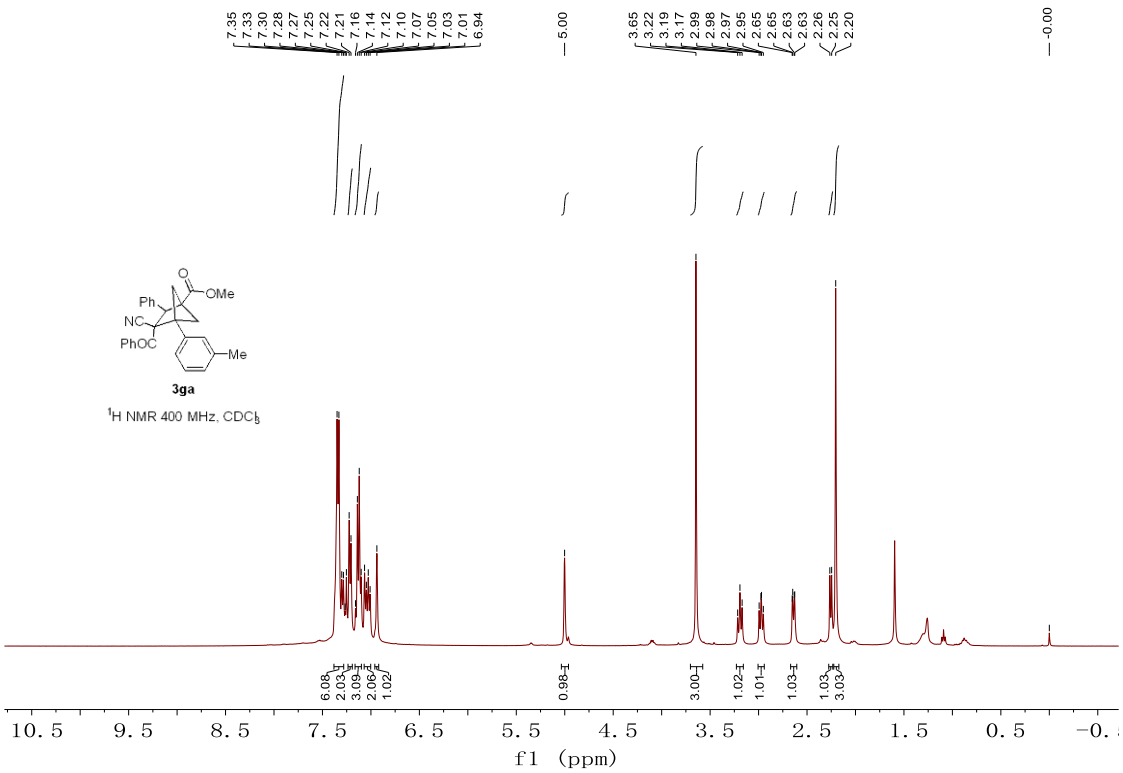
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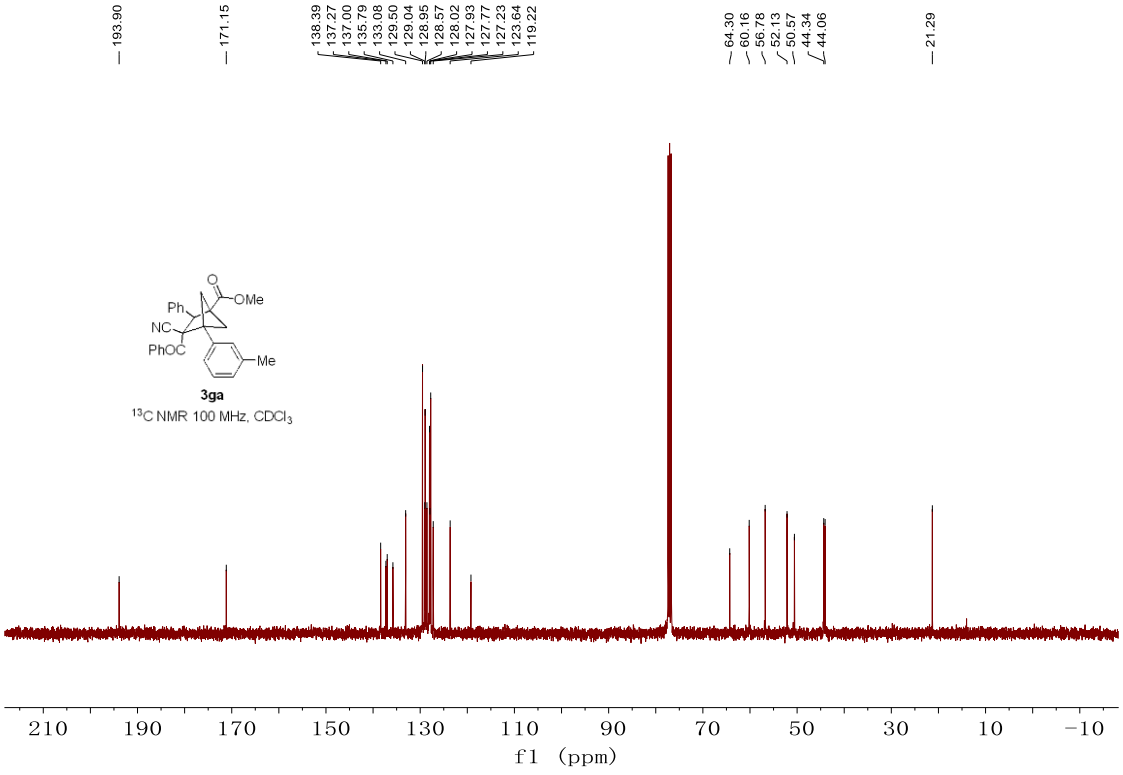
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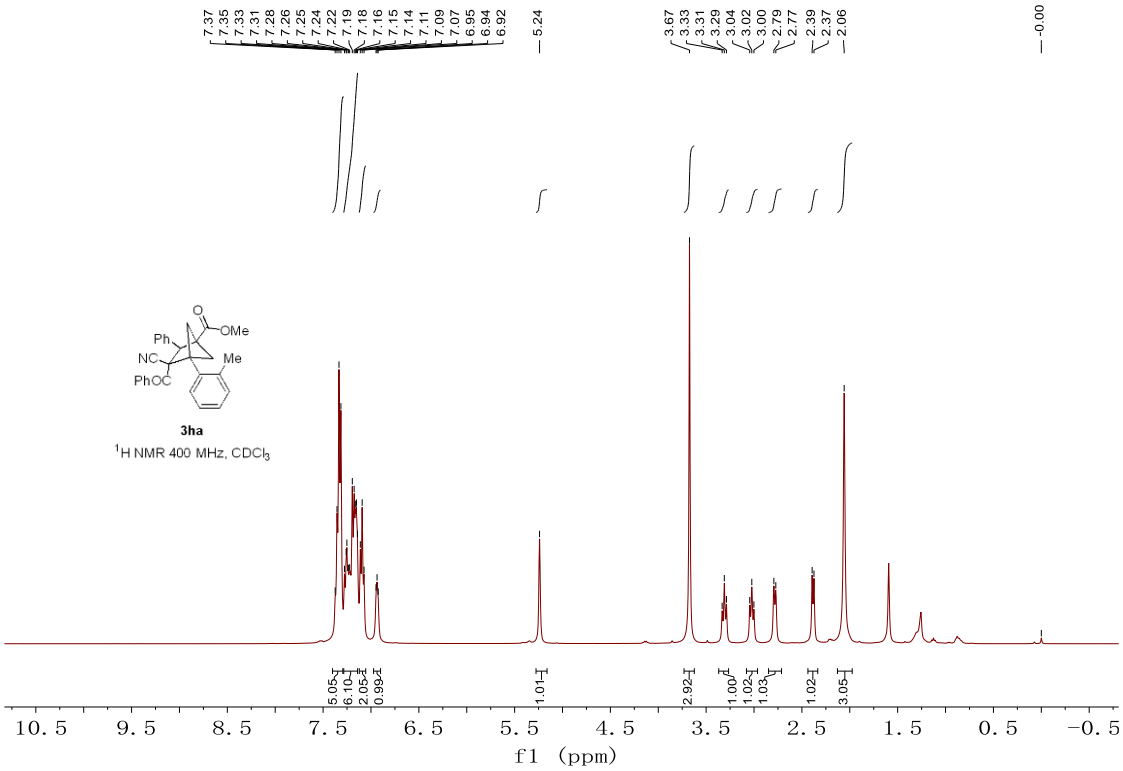
f1 (ppm)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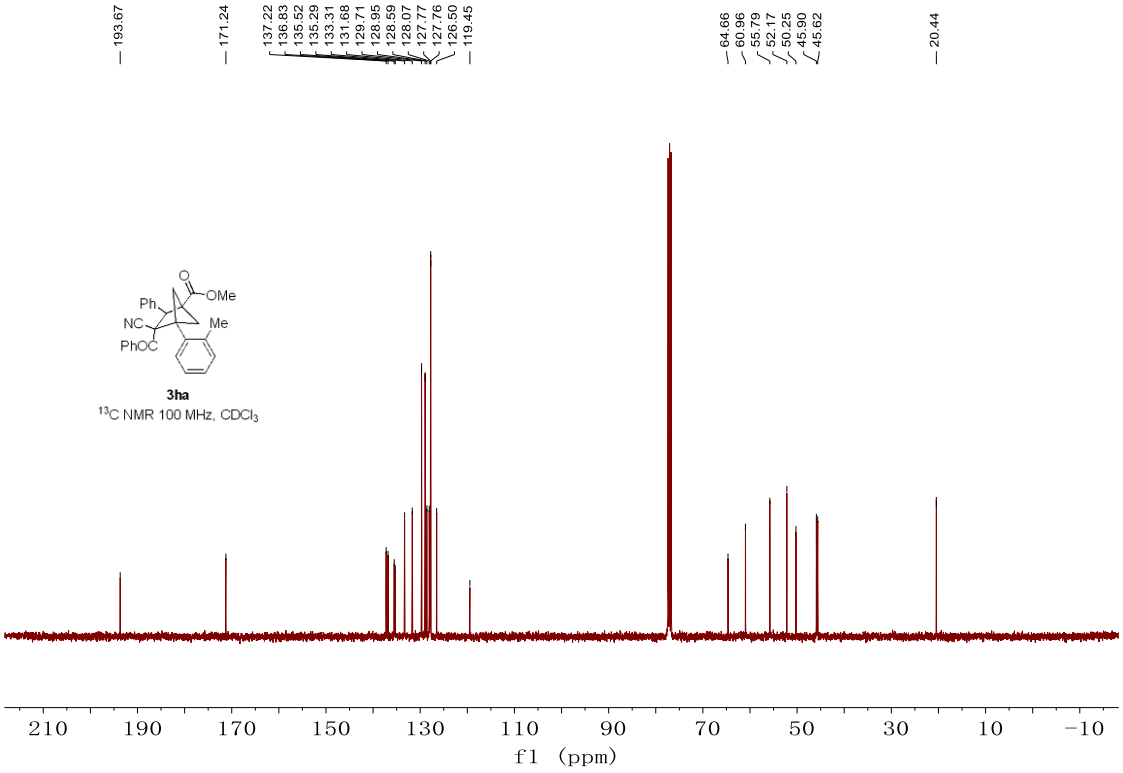
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55.79
52.17
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45.62
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Ph
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PhOC
OMe
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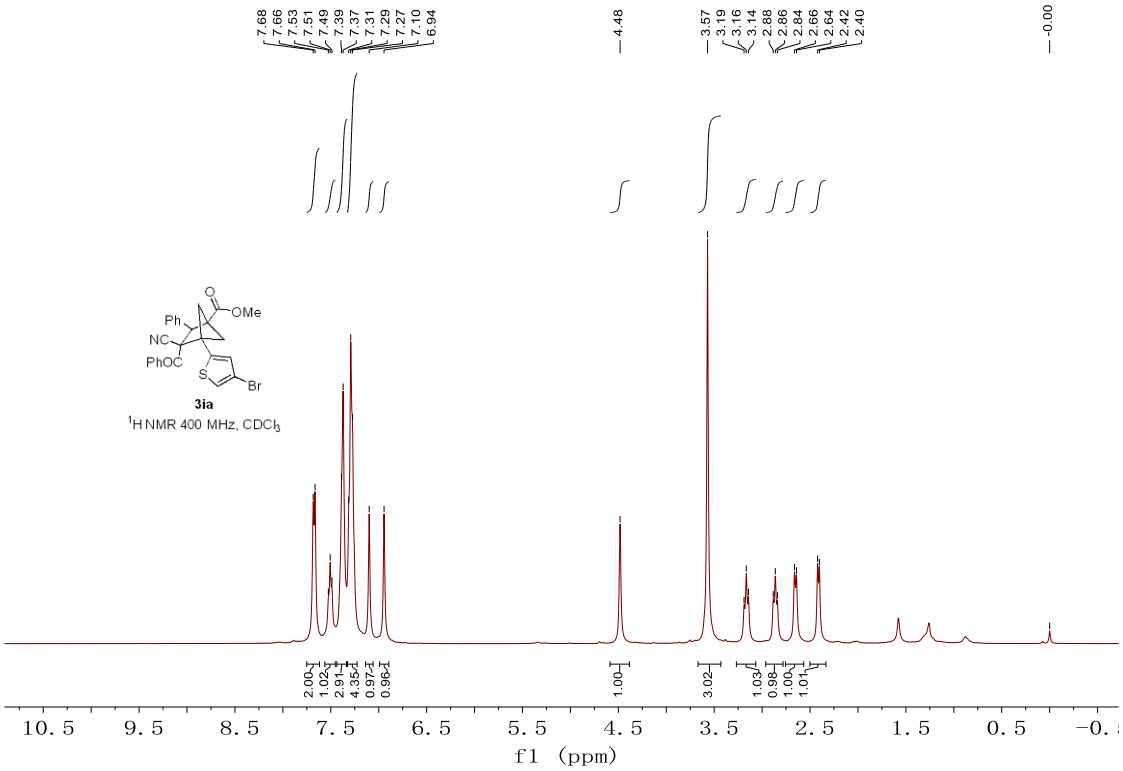
f1 (ppm)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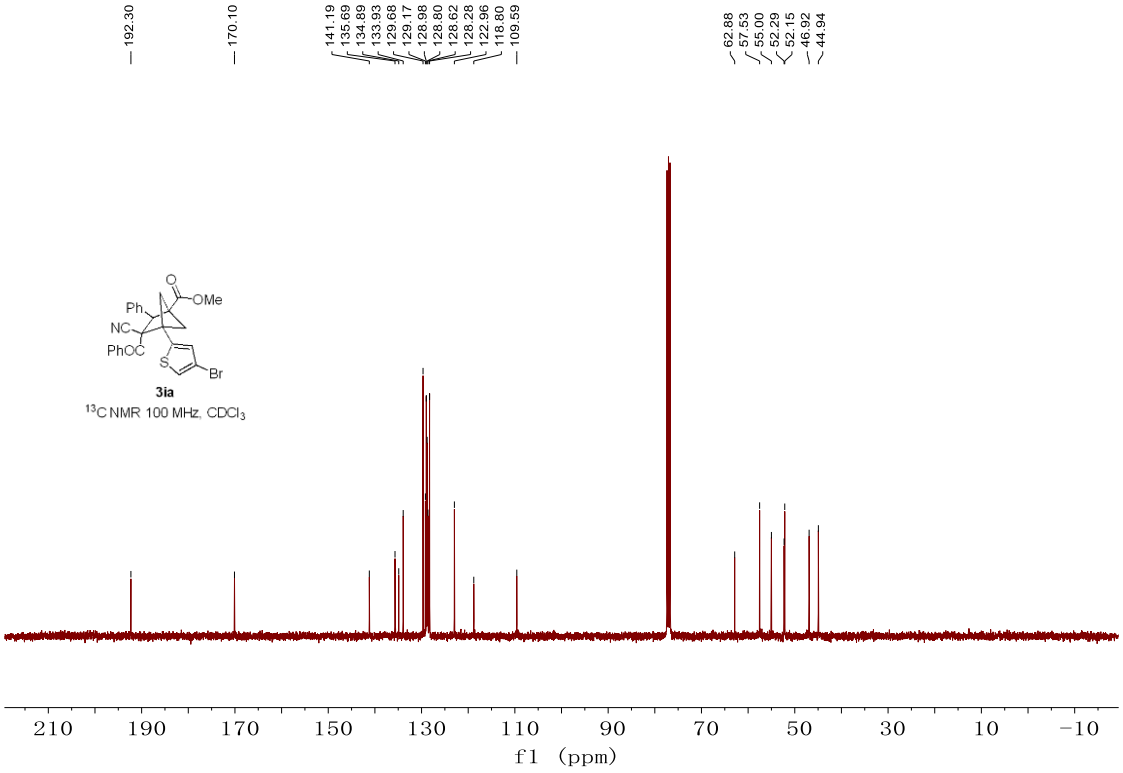
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52.15
46.92
44.94
O
OMe
Ph
NC
PhOC
S
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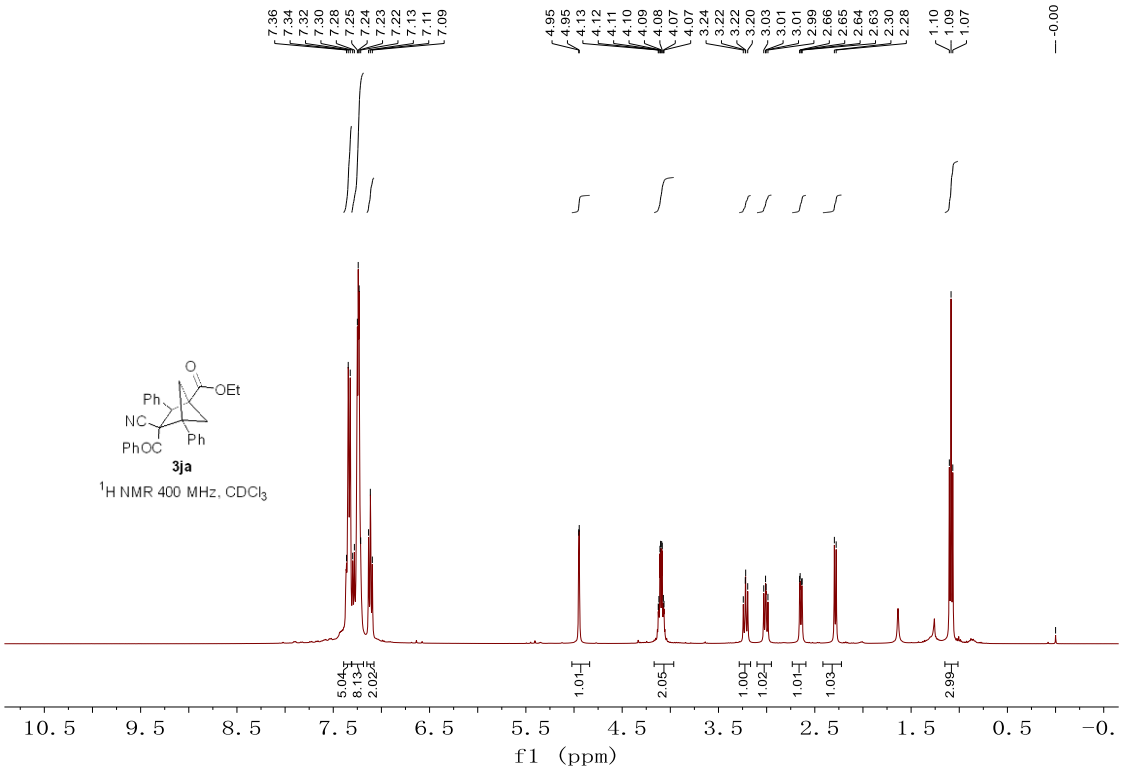
f1 (ppm)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1.07
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PhOC
Ph
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2.05
1.00
1.02
1.01
1.03
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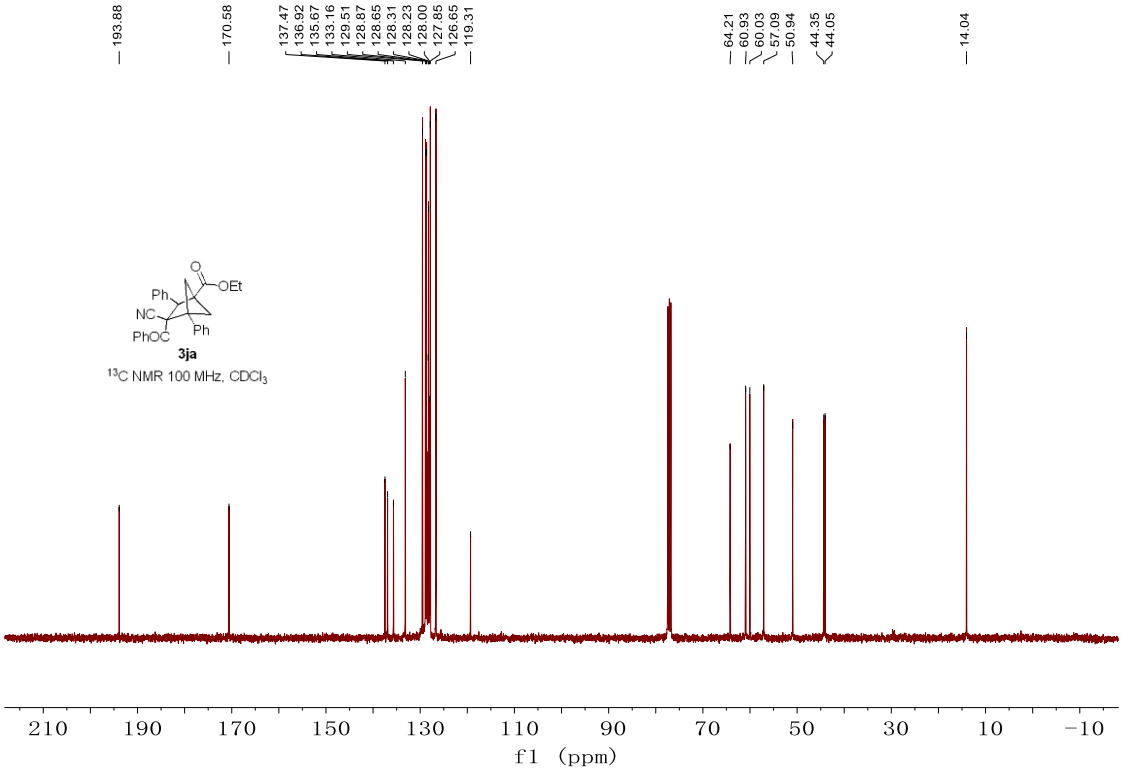
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Ph
NC
PhOC
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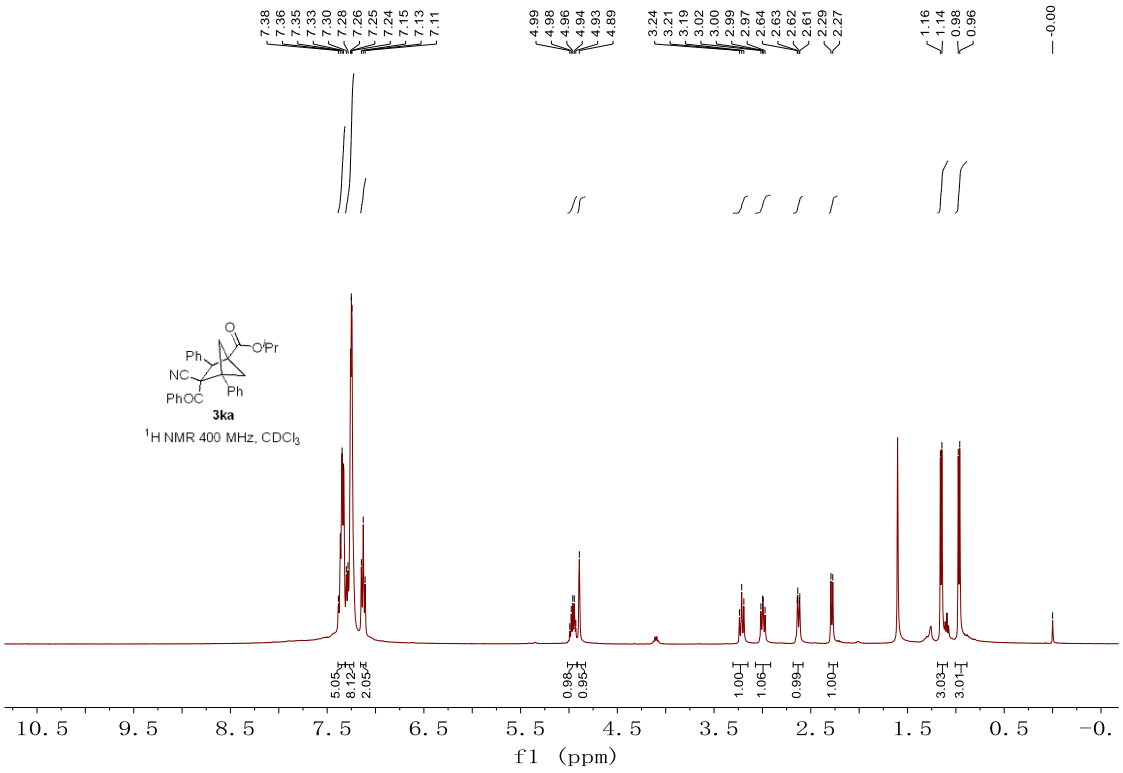
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0.96
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O'Pr
Ph
NC
PhOC
Ph
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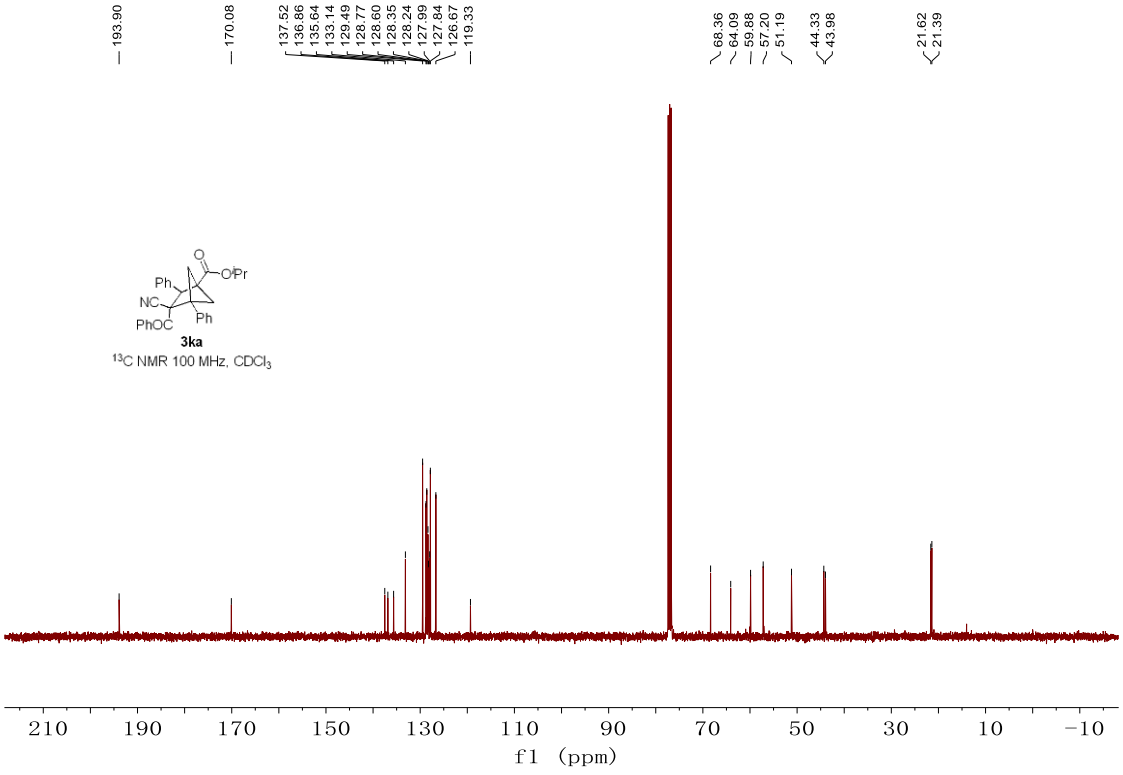
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PhOC
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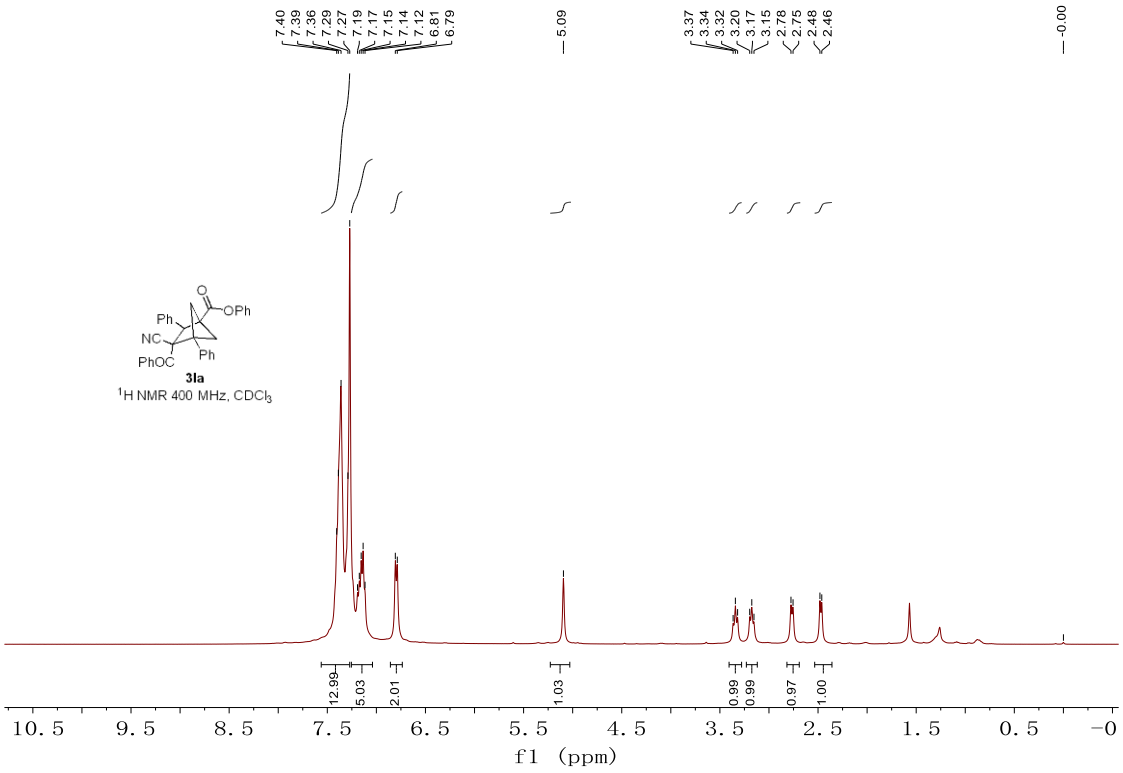
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3.34
3.32
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3.15
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2.48
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Ph
NC
PhOC
Ph
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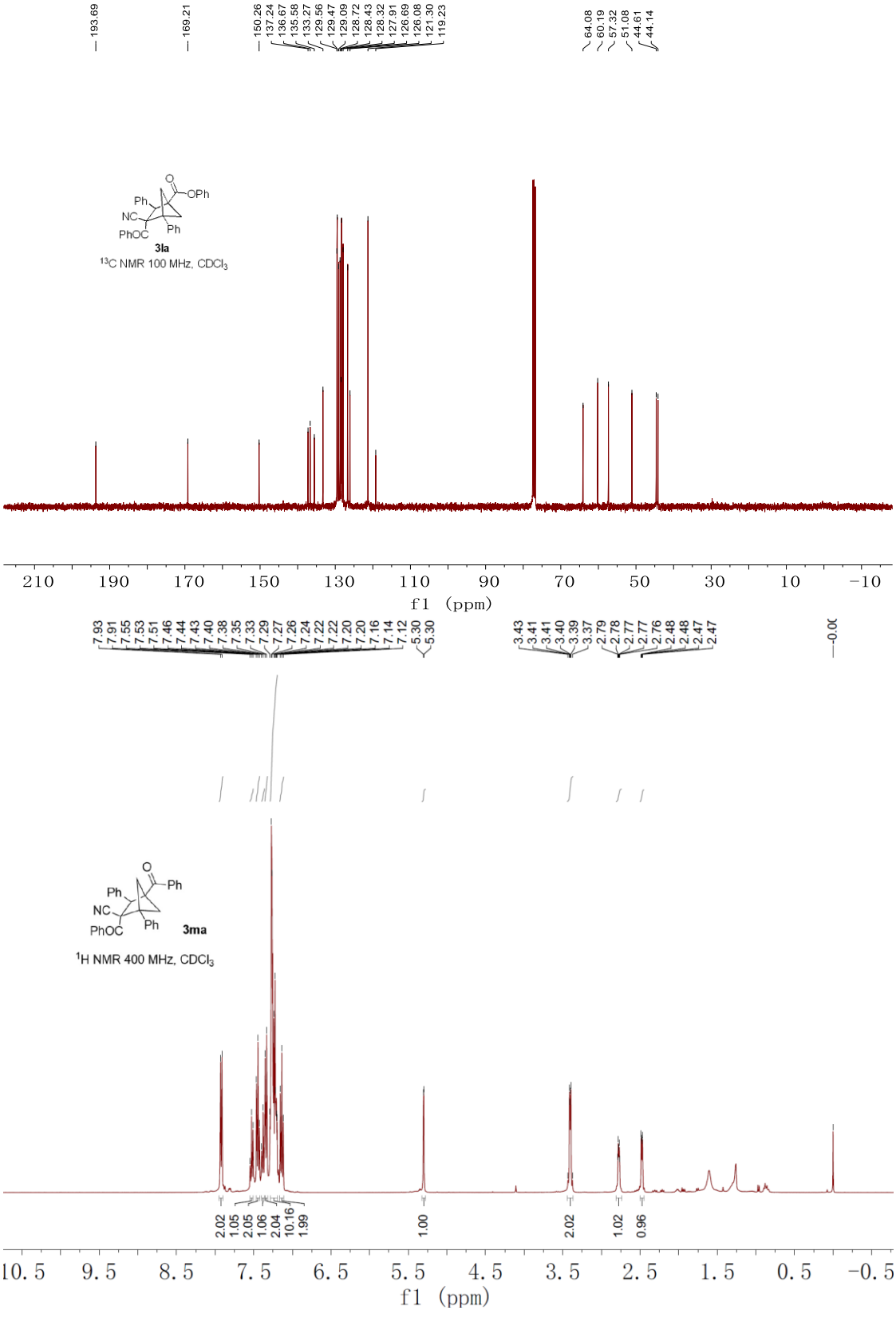
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OPh
Ph
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Ph
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−10
f1 (ppm)
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Ph
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PhOC
Ph
3ma
1H NMR 400 MHz, CDCl3
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2.05
1.06
2.04
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1.99
1.00
2.02
1.02
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10.5
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4.5
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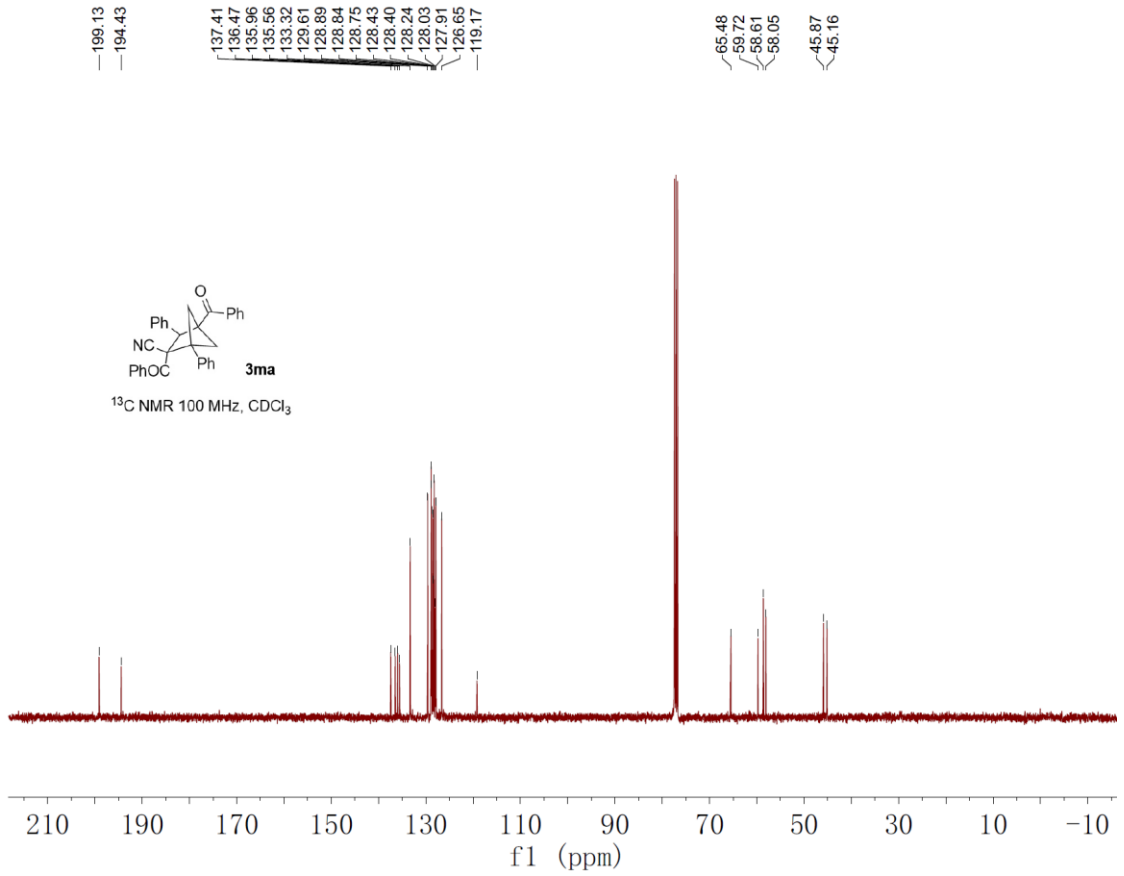
−0.5
f1 (ppm)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58.05
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45.16
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Ph
Ph
NC
PhOC
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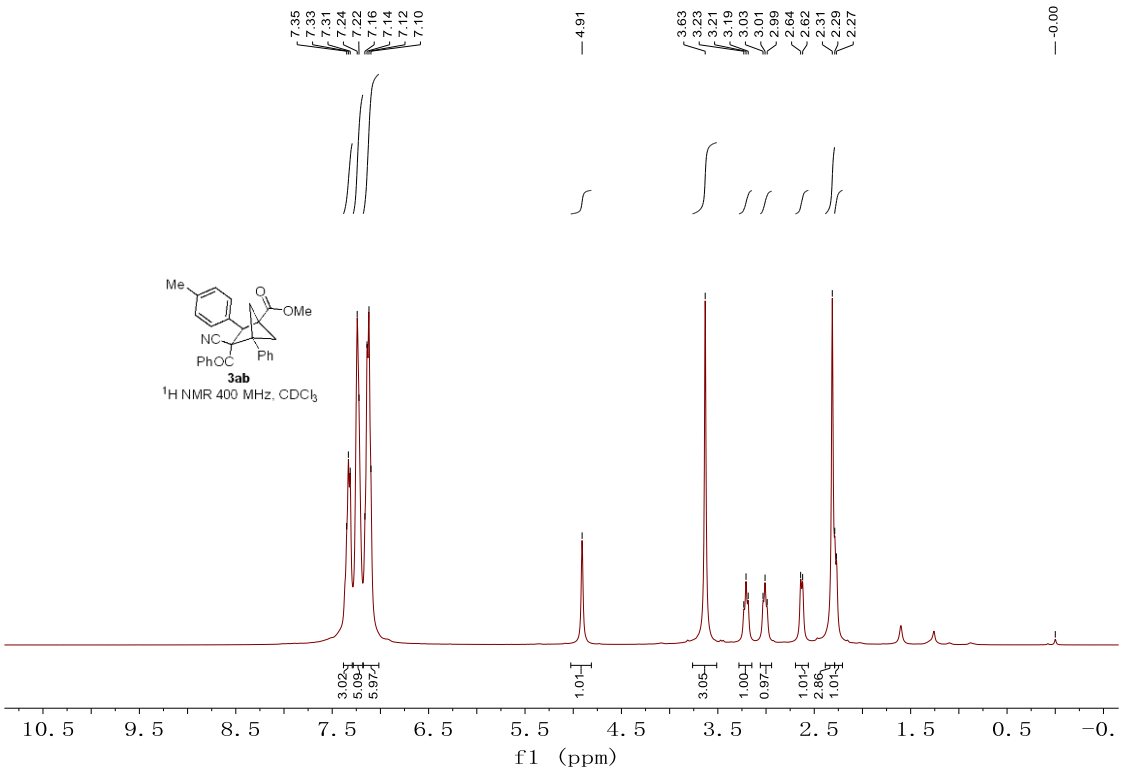
−10
f1 (ppm)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Me
O
OMe
NC
PhOC
Ph
3ab
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3.05
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1.01
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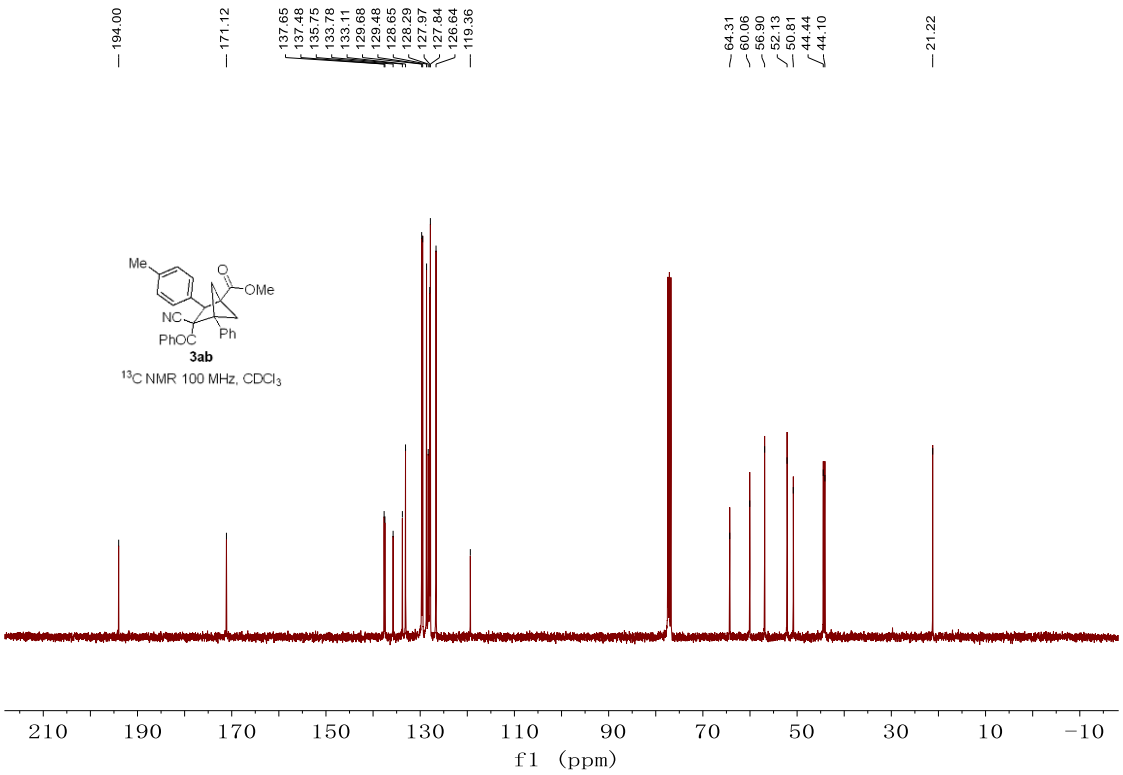
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60.06
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52.13
50.81
44.44
44.10
21.22
Me
O
OMe
NC
PhOC
Ph
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150
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90
70
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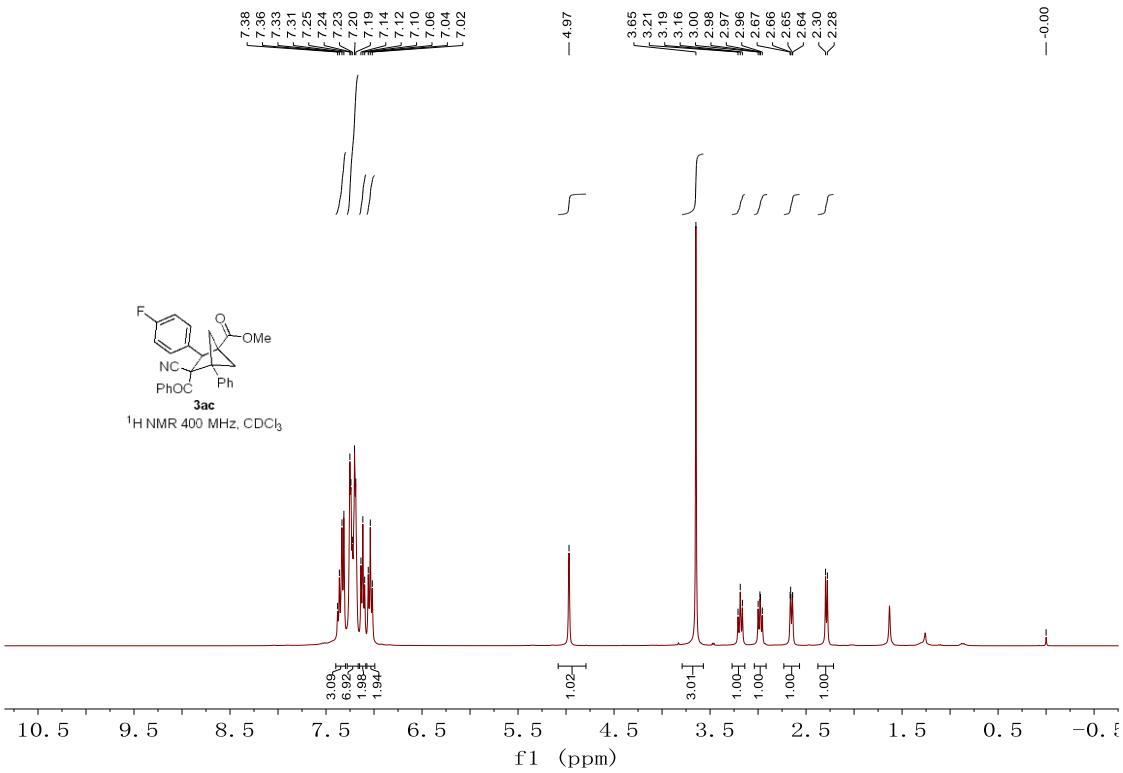
10
−10
f1 (ppm)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2.30
2.28
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OMe
NC
PhOC
Ph
3ac
1H NMR 400 MHz, CDCl3
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1.00
1.00
1.00
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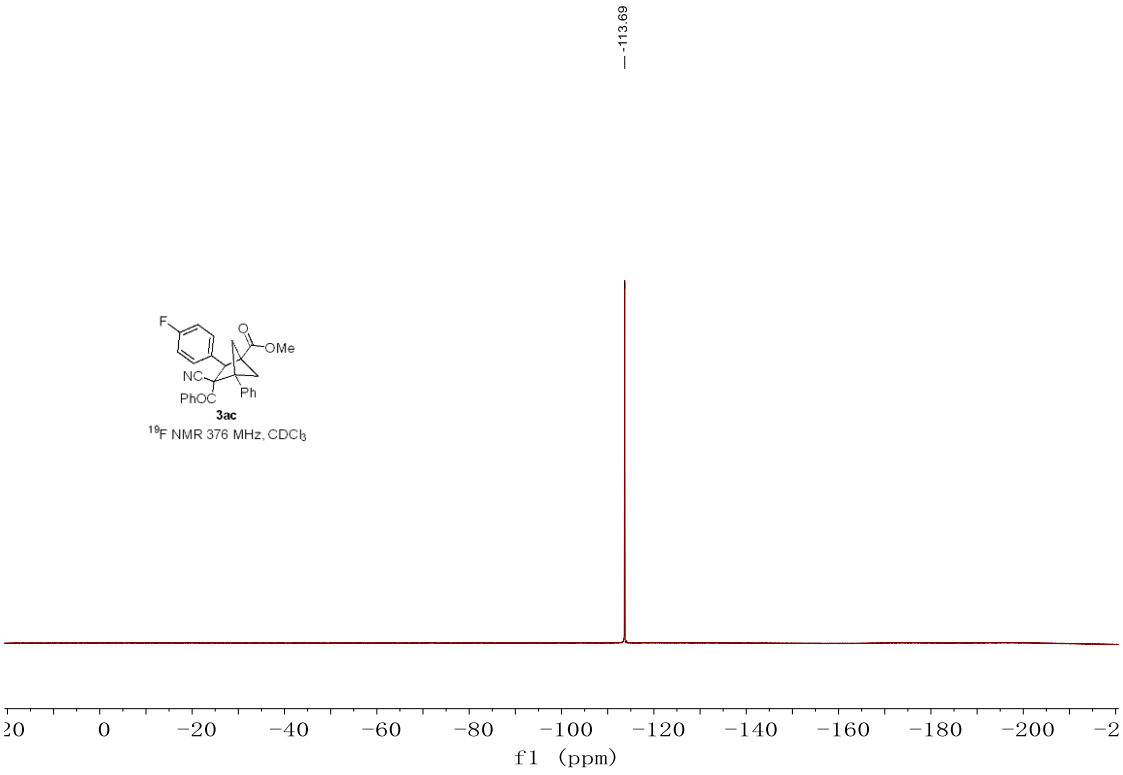
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Ph
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−2
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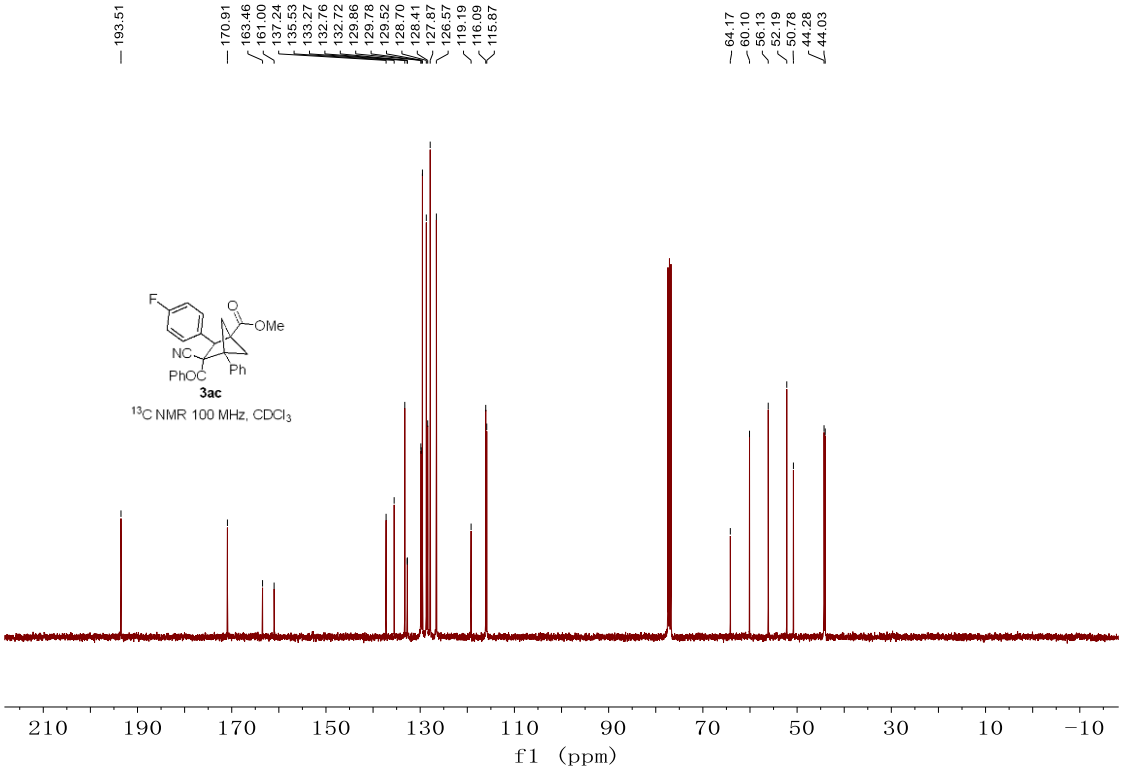
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60.10
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44.03
F
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OMe
NC
PhOC
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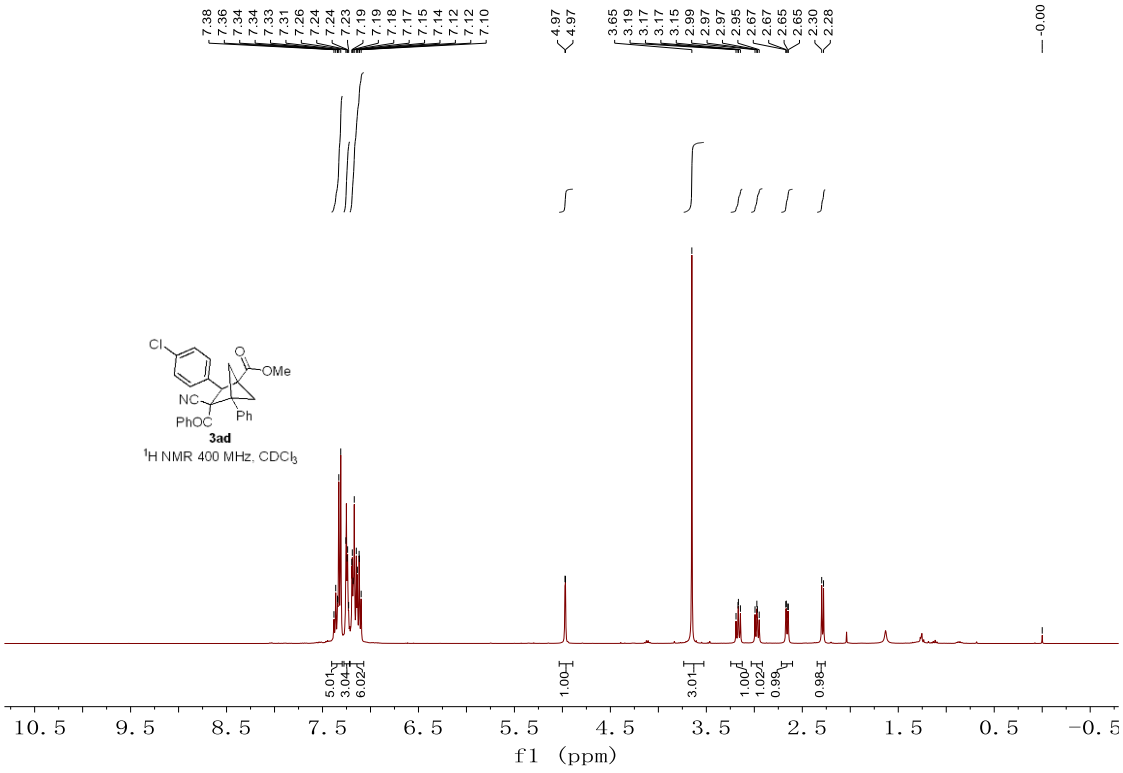
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7.10
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4.97
3.65
3.19
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3.17
3.15
2.99
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2.97
2.95
2.67
2.67
2.65
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Cl
OMe
NC
PhOC
Ph
3ad
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3.01
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1.02
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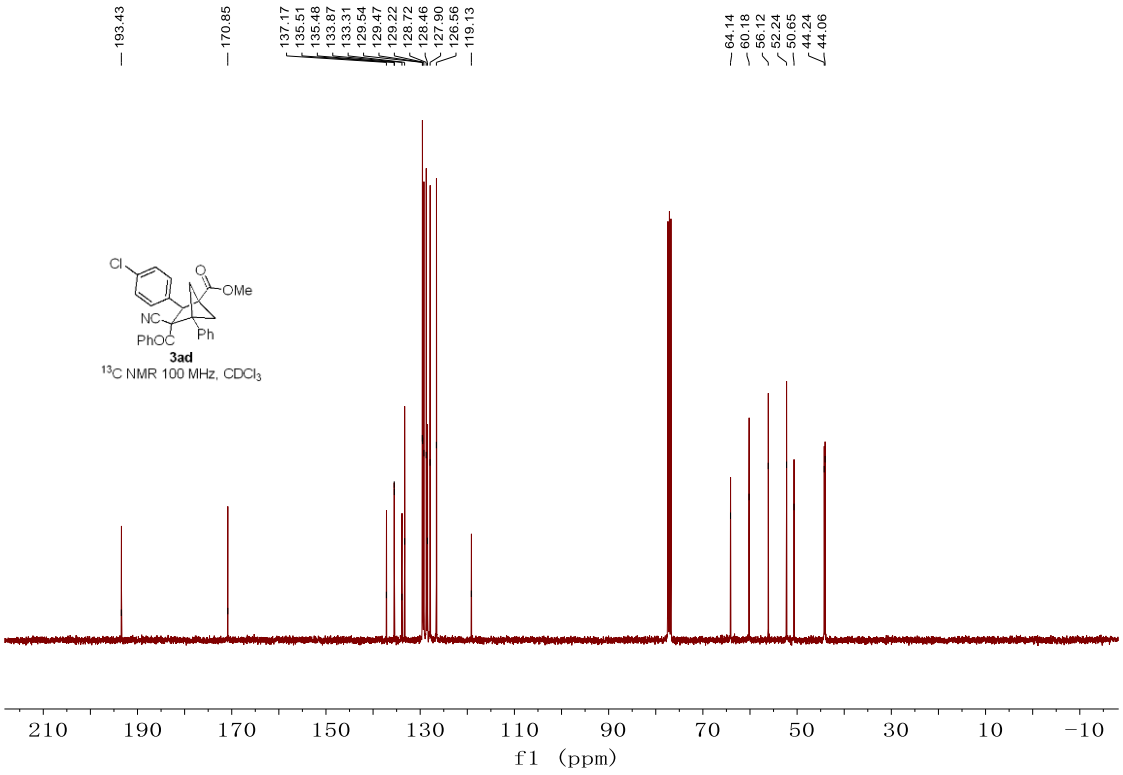
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Cl
OMe
NC
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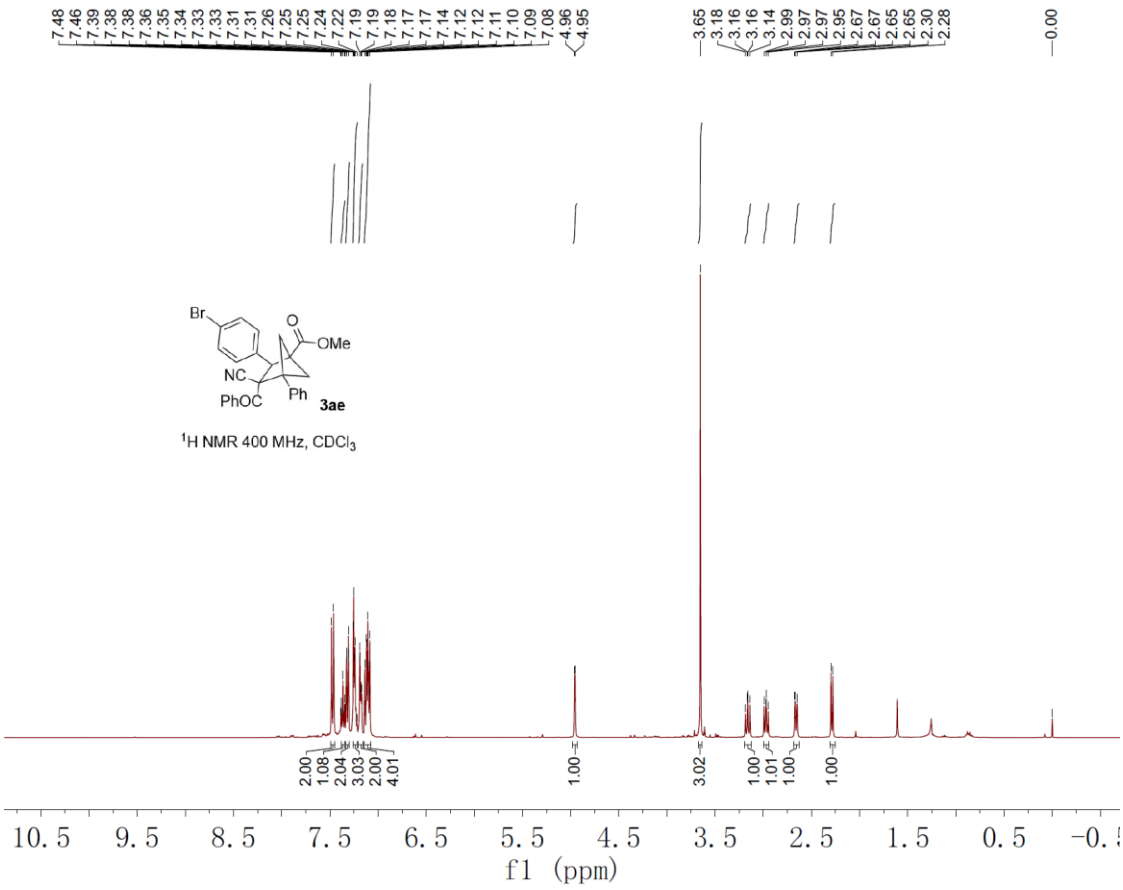
f1 (ppm)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OMe
NC
PhOC
Ph
3ae
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4.01
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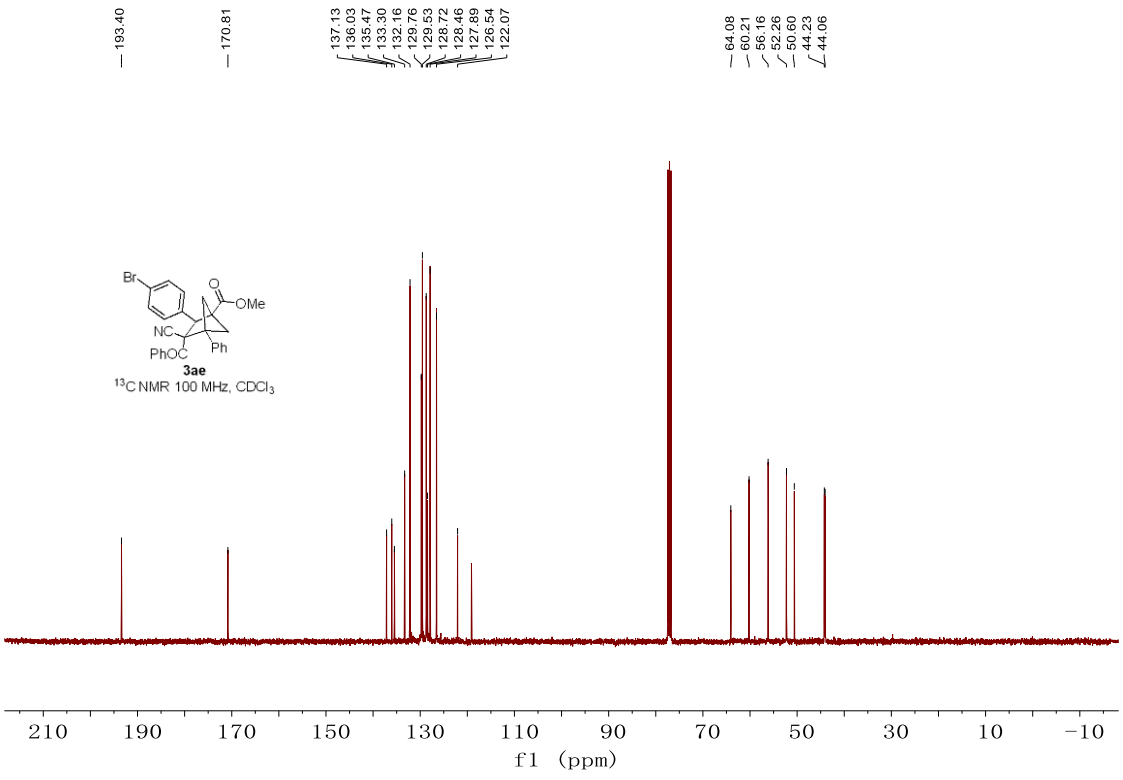
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Br
O
OMe
NC
PhOC
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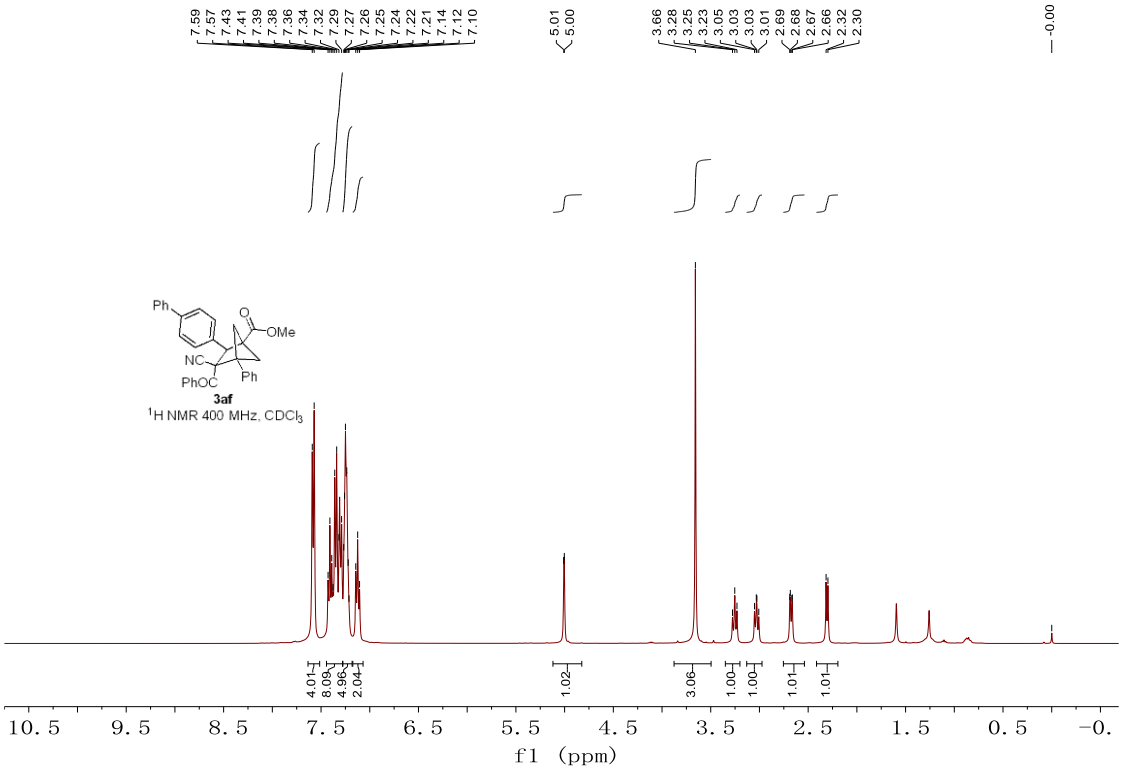
90
70
50
30
10
−10
f1 (ppm)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3.23
3.05
3.03
3.03
3.01
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2.32
2.30
-0.00
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OMe
NC
PhOC
Ph
3af
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3.06
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1.01
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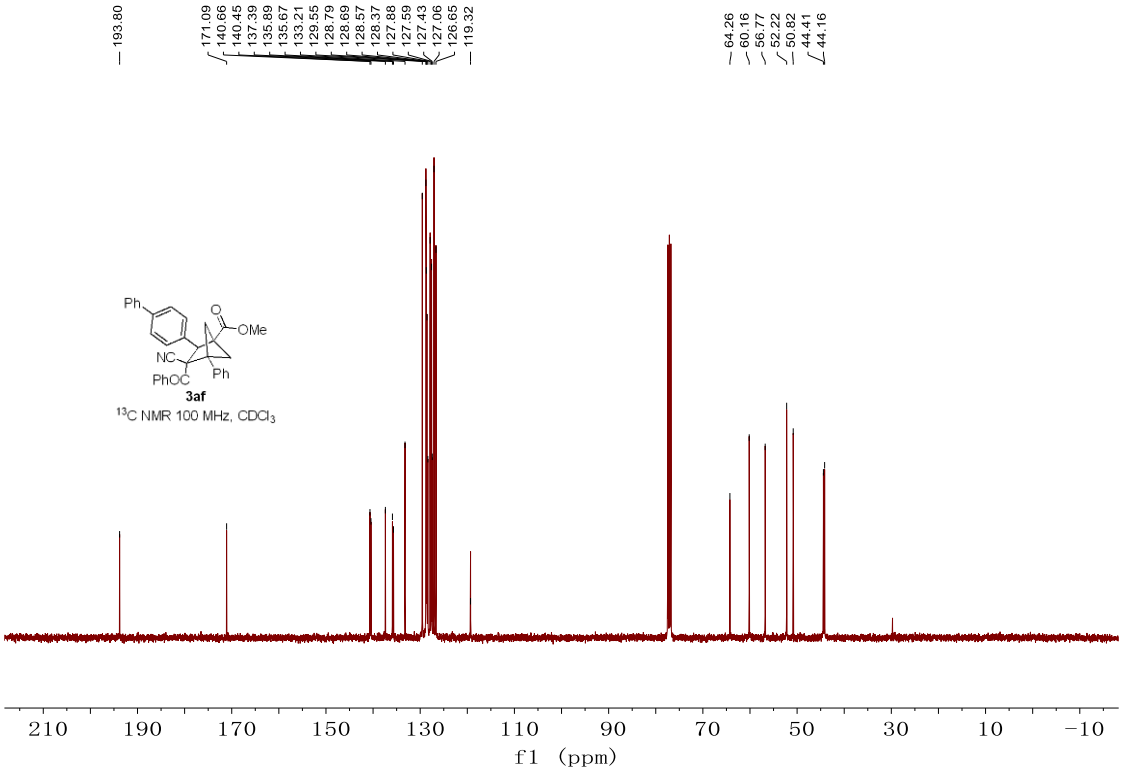
f1 (ppm)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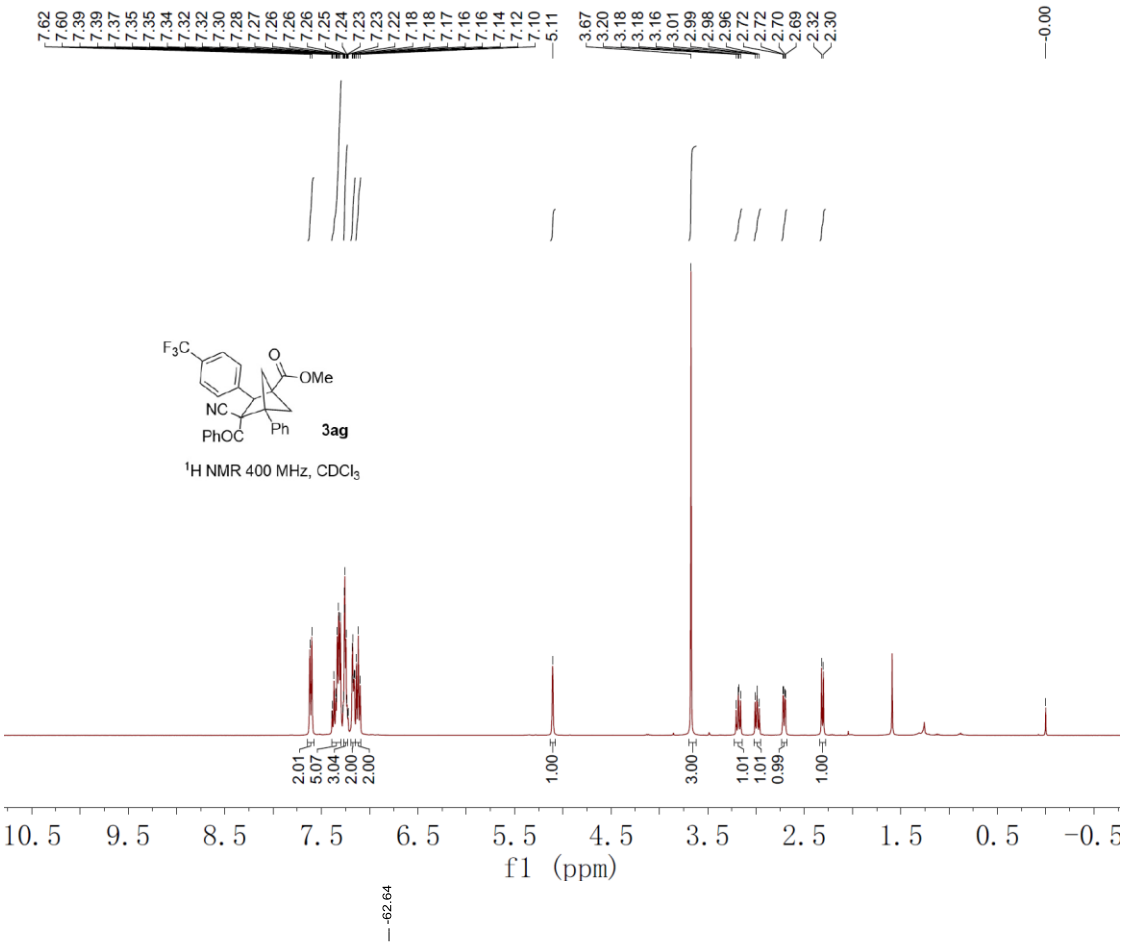
f1 (ppm)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Ph
3ag
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1.00
3.00
1.01
1.01
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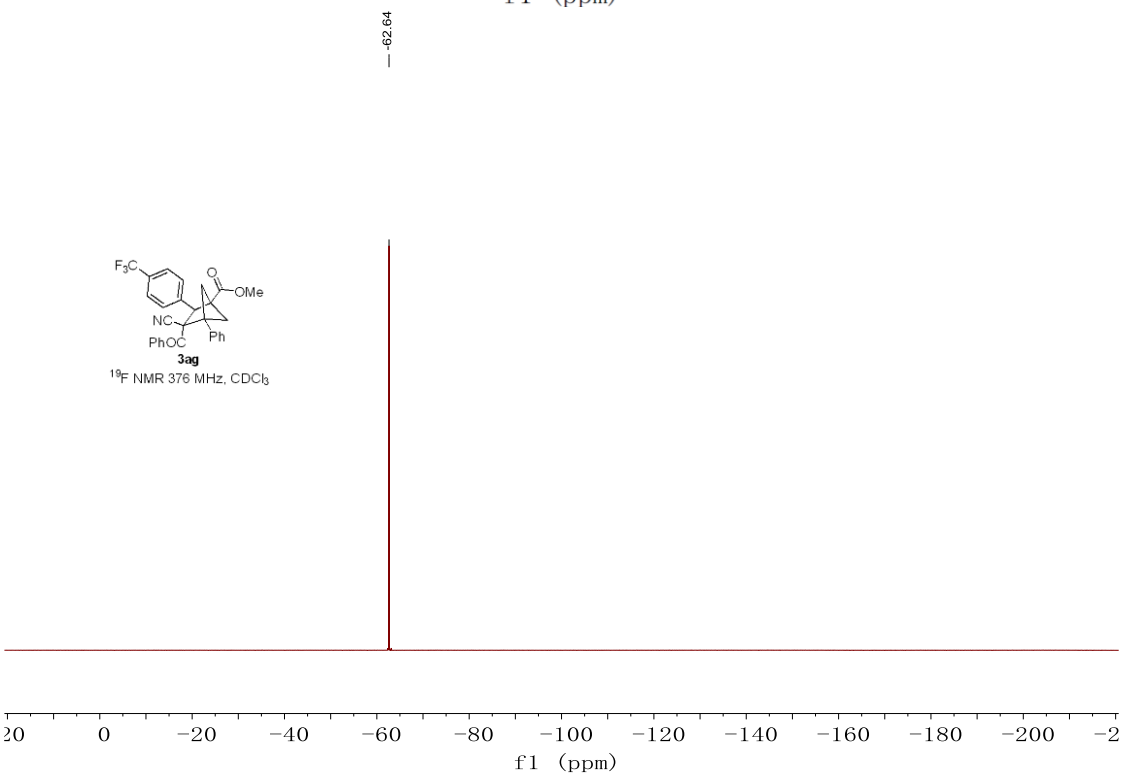
f1 (ppm)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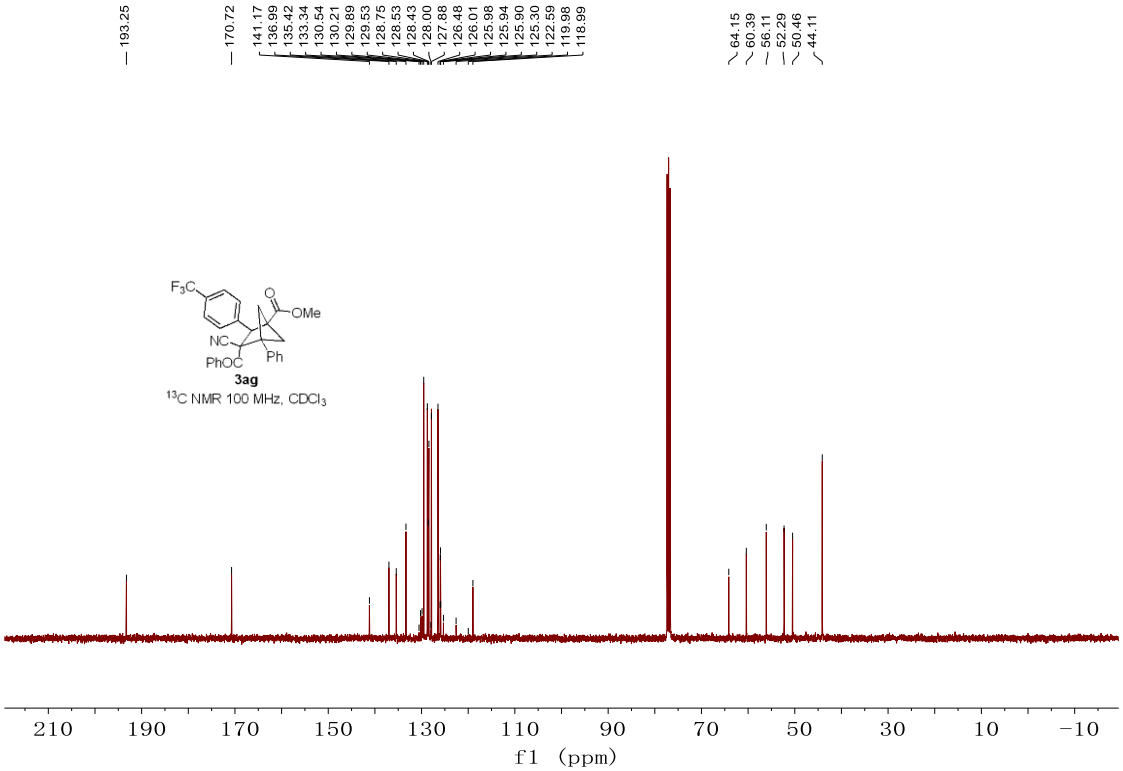
-2
f1 (ppm)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44.11
F3C
OMe
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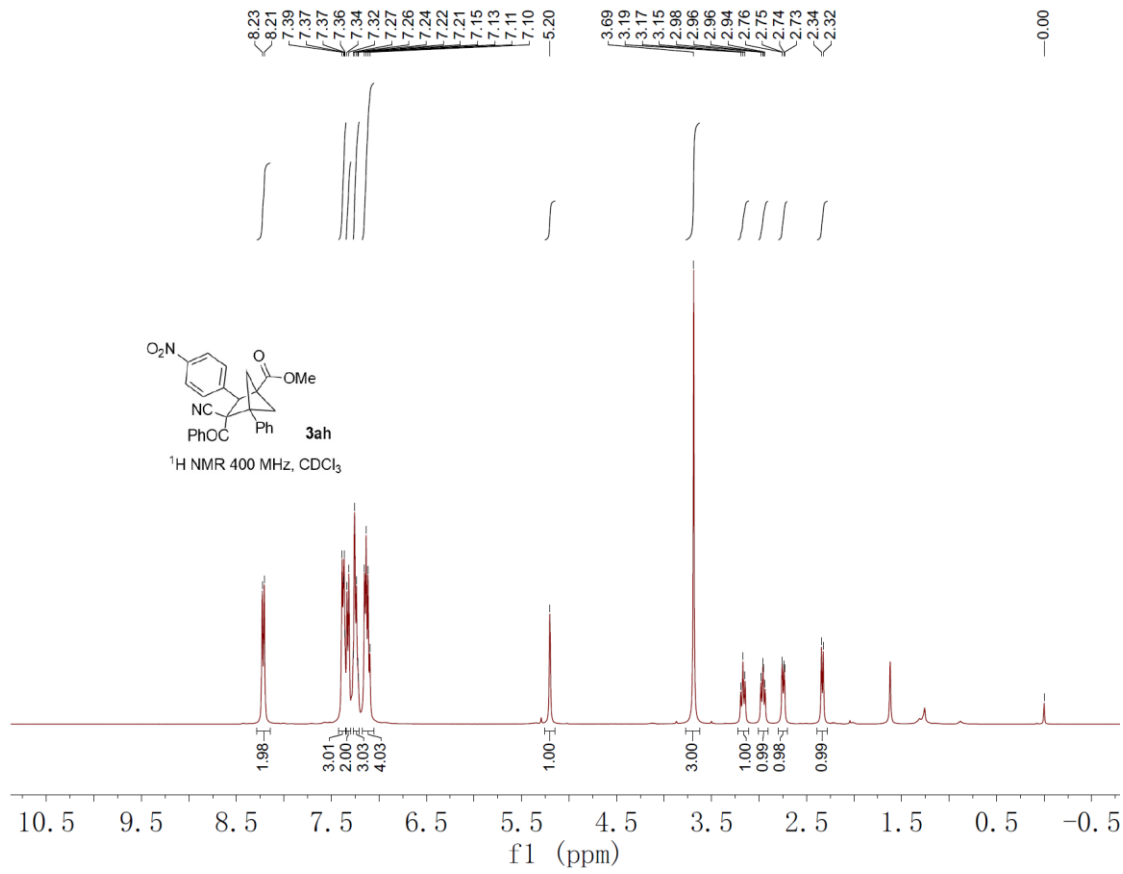
−10
f1 (ppm)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PhOC
Ph
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2.00
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4.03
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3.00
1.00
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0.98
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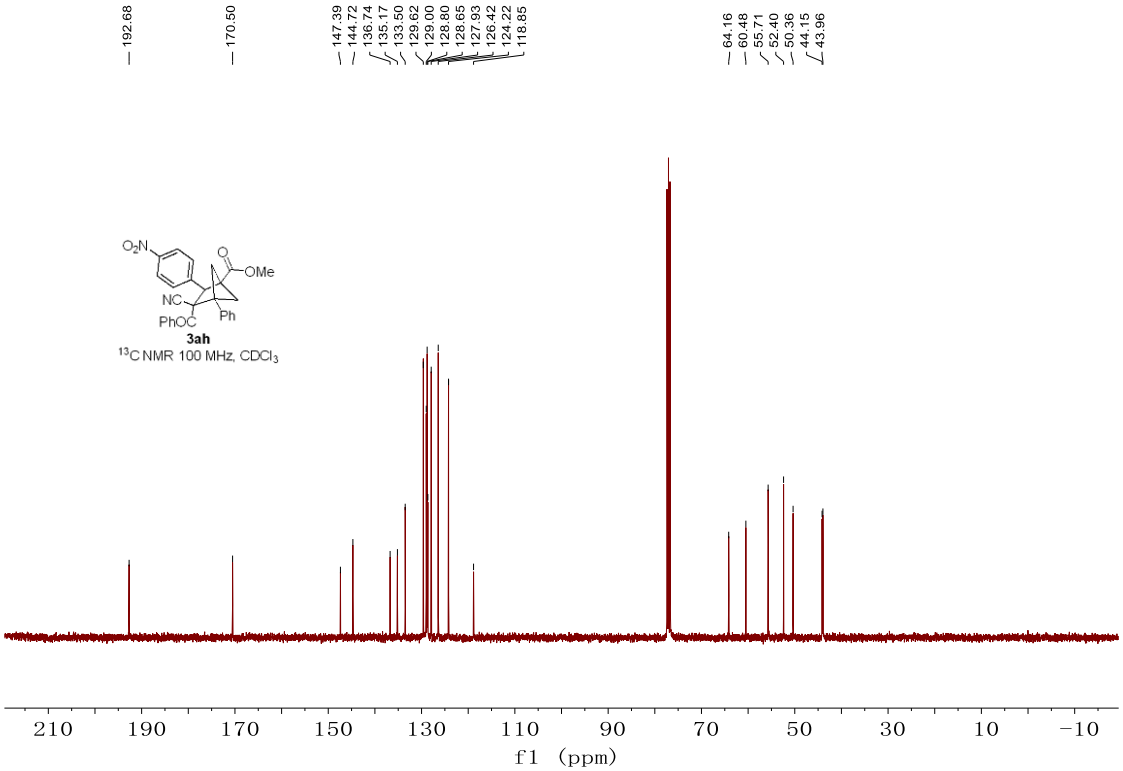
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43.96
O2N
OMe
NC
PhOC
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90
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30
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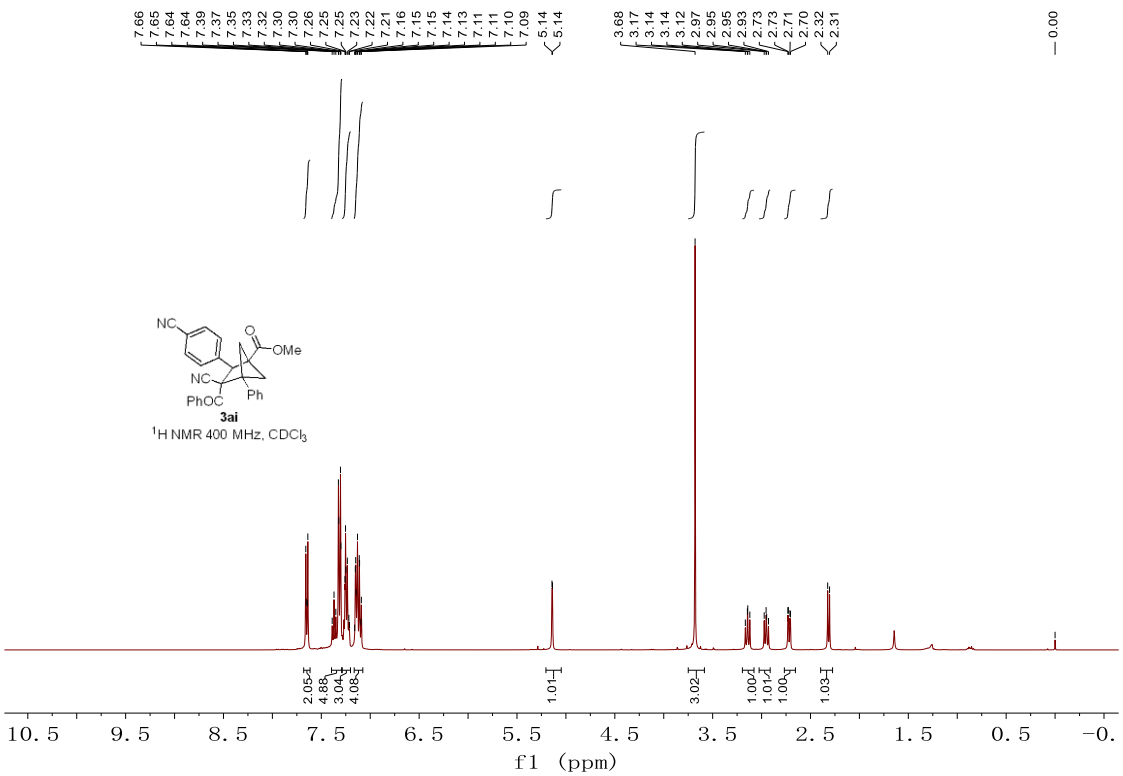
−10
f1 (ppm)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5.14
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2.95
2.93
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2.73
2.71
2.70
2.32
2.31
0.00
NC
OMe
NC
PhOC
Ph
3ai
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4.08
1.01
3.02
1.00
1.01
1.00
1.03
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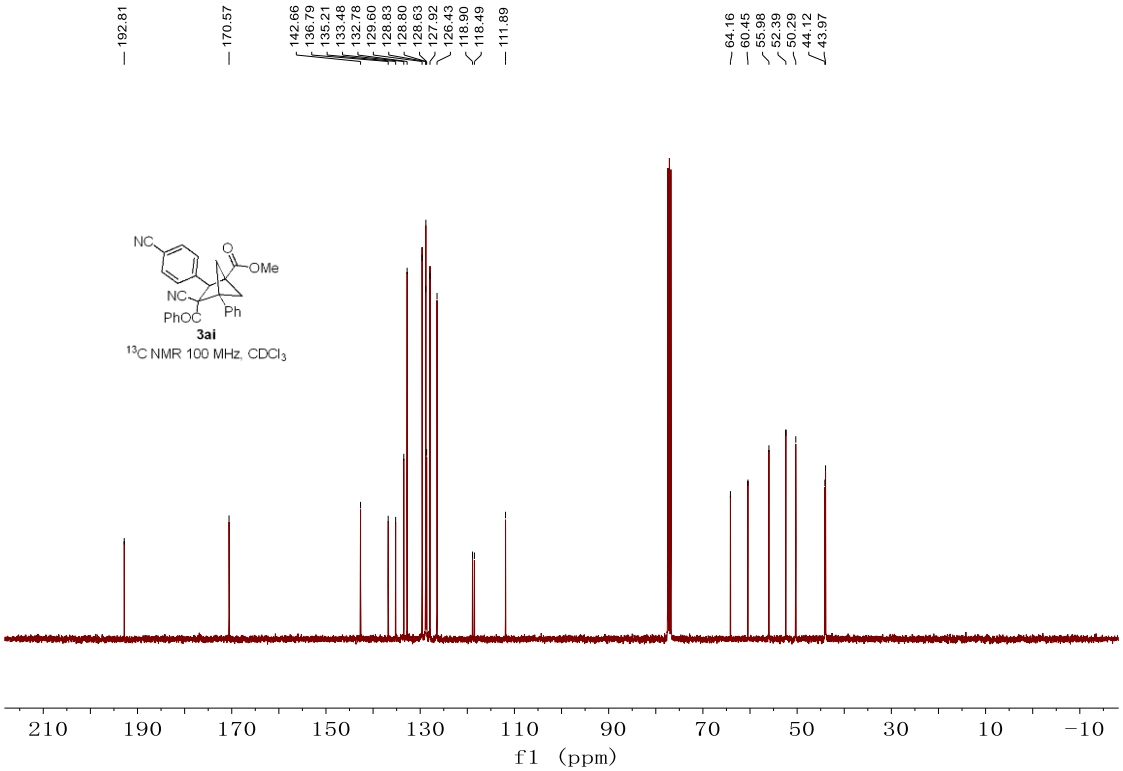
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64.16
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52.39
50.29
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43.97
NC
O
OMe
NC
PhOC
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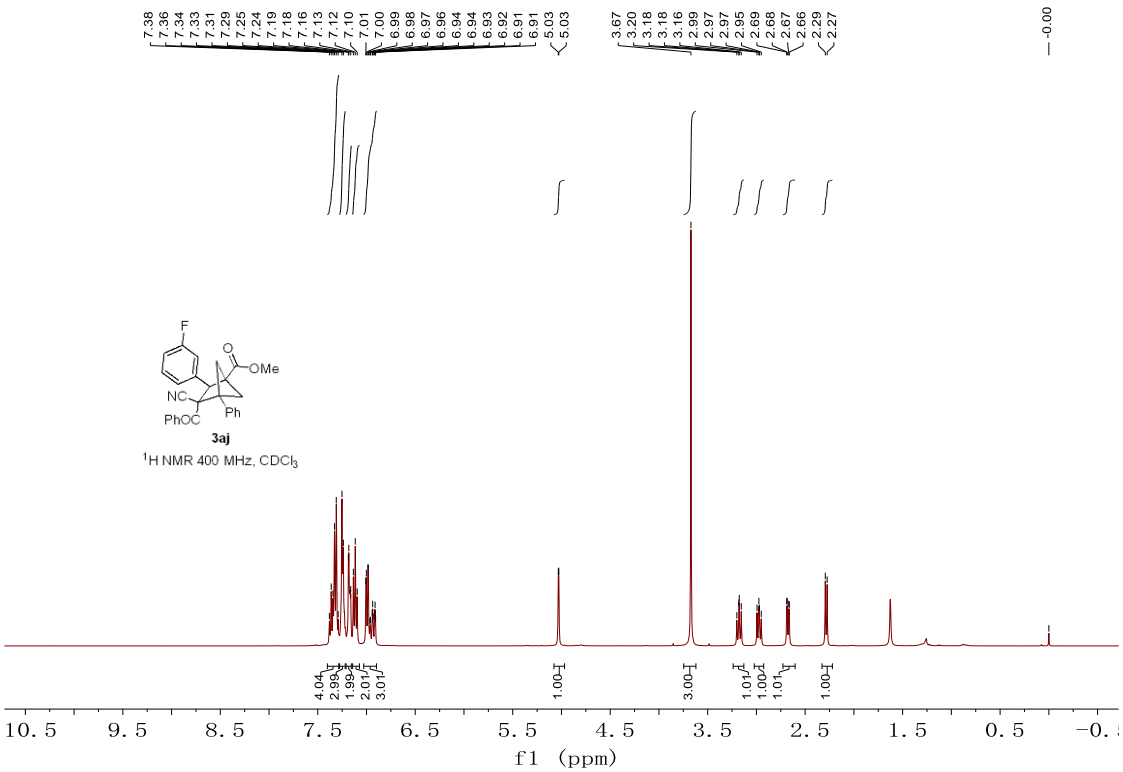
−10
f1 (ppm)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2.27
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O
OMe
NC
PhOC
Ph
3aj
1H NMR 400 MHz, CDCl3
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1.00
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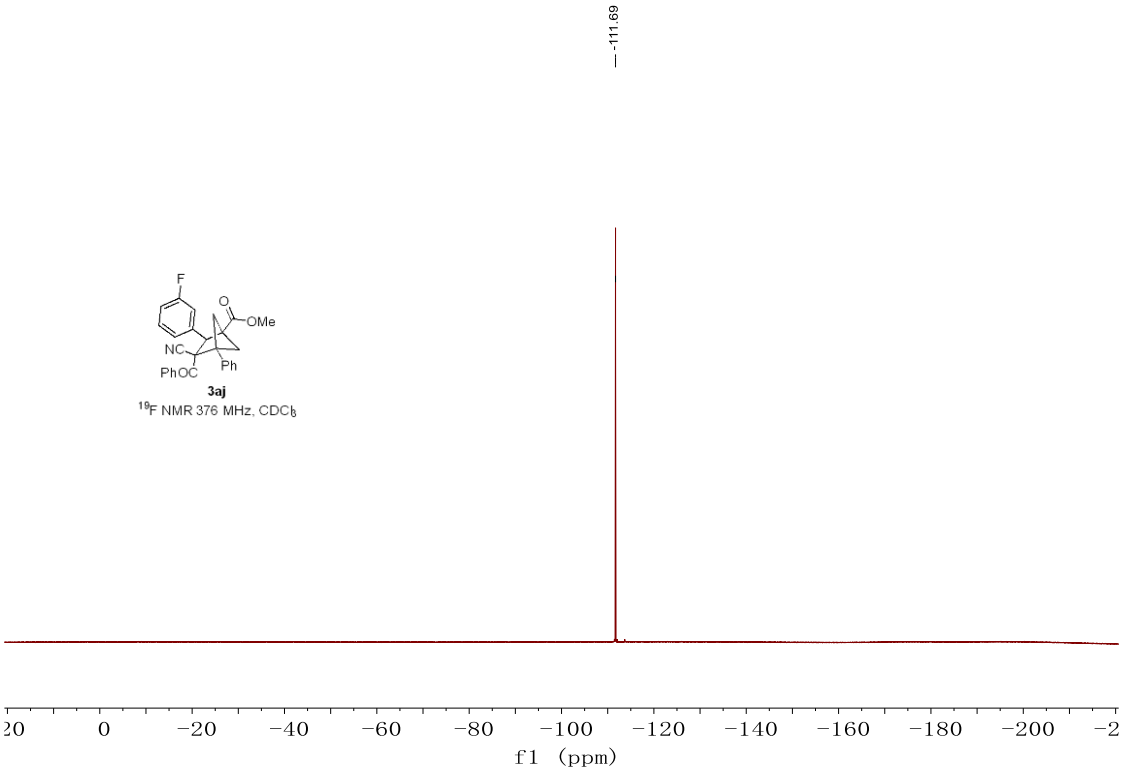
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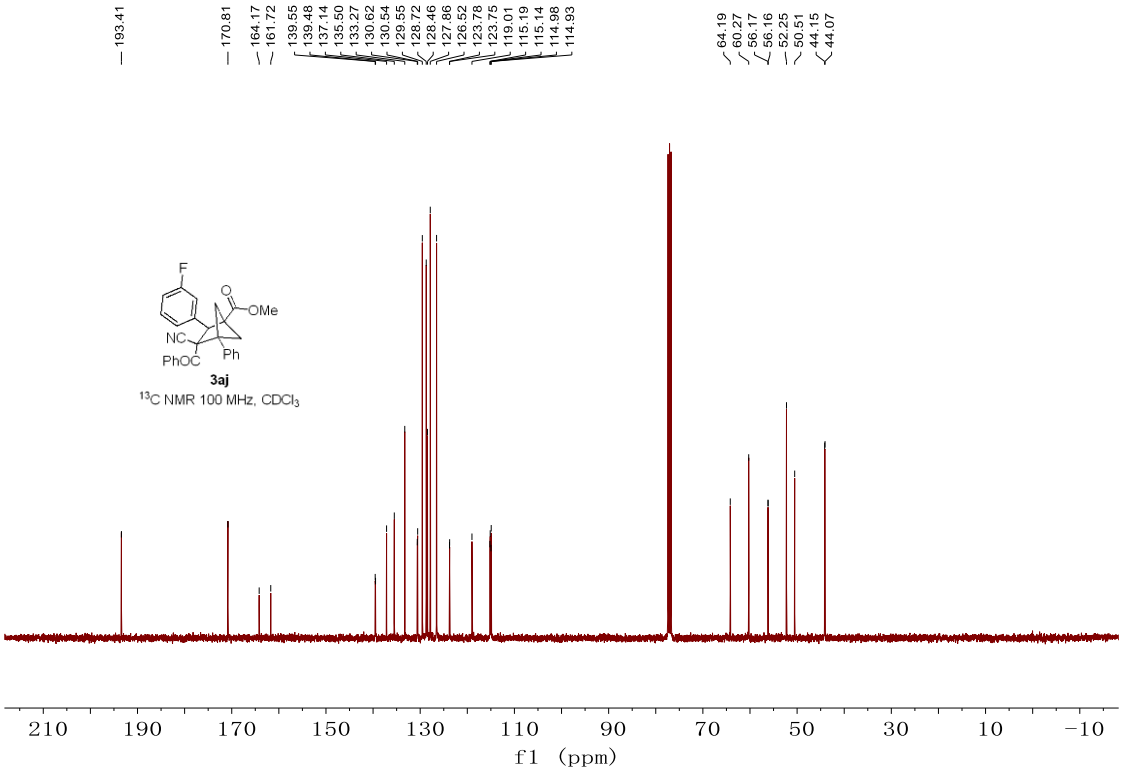
−200
−2
f1 (ppm)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114.93
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56.16
52.25
50.51
44.15
44.07
F
O
OMe
NC
PhOC
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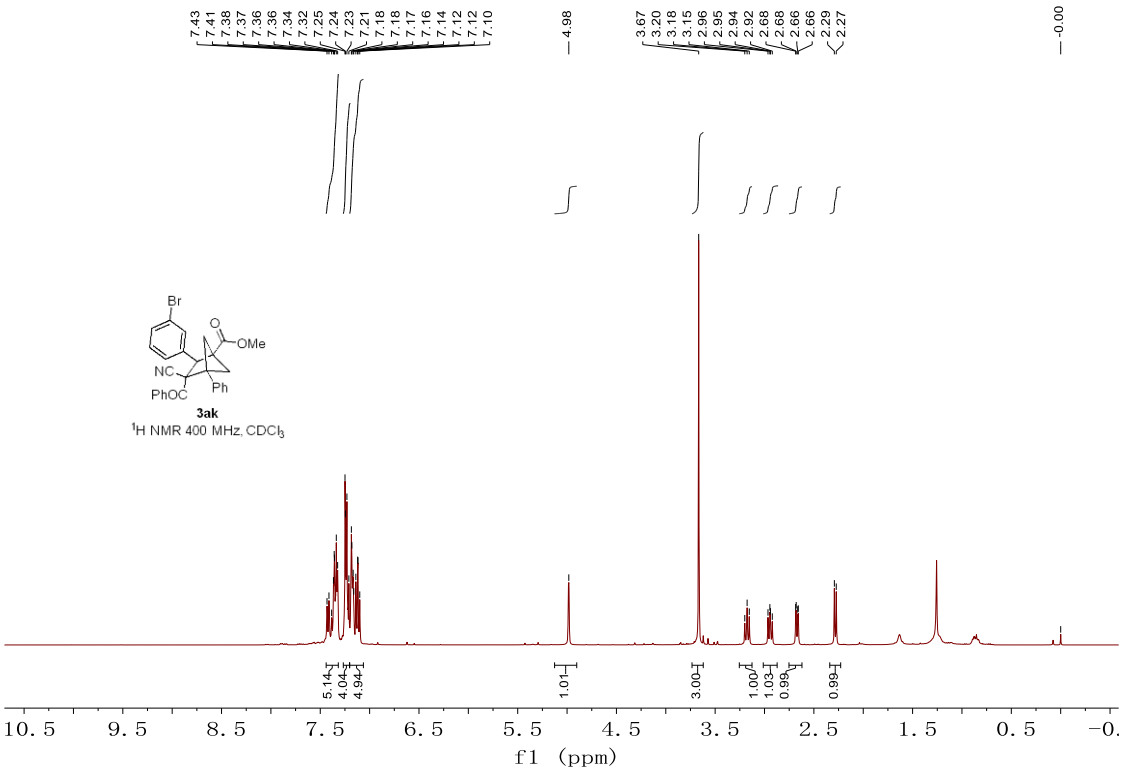
f1 (ppm)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7.10
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2.95
2.94
2.92
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2.66
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OMe
NC
PhOC
Ph
3ak
1H NMR 400 MHz, CDCl3
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4.94
1.01
3.00
1.00
1.03
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0.99
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6.5
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4.5
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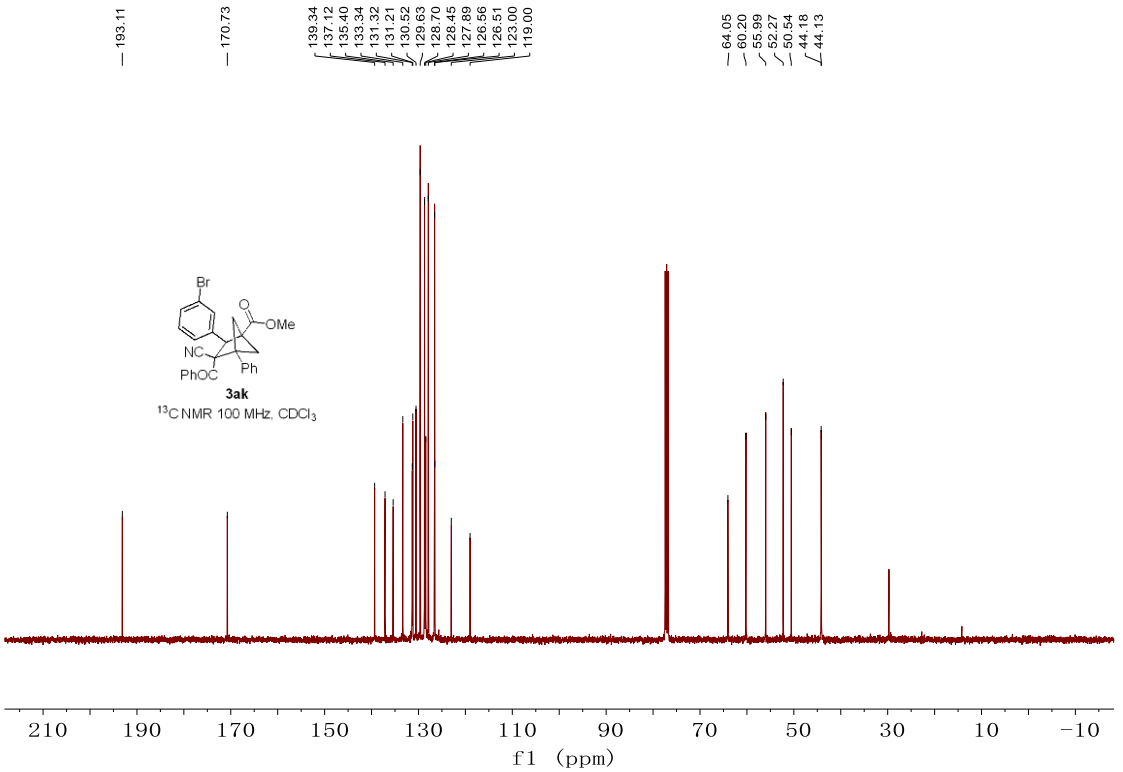
f1 (ppm)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64.05
60.20
55.99
52.27
50.54
44.18
44.13
Br
O
OMe
NC
PhOC
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70
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30
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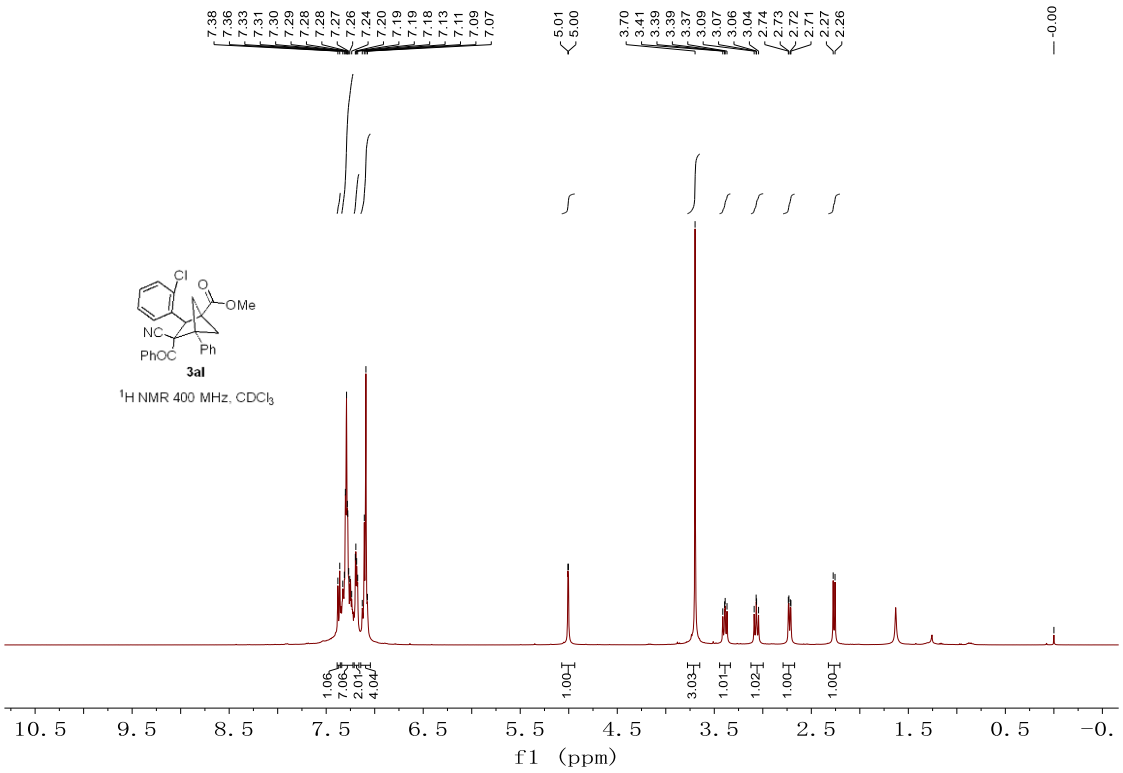
f1 (ppm)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7.18
7.13
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O
OMe
NC
PhOC
Ph
3al
1H NMR 400 MHz, CDCl3
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2.01
4.04
1.00
3.03
1.01
1.02
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1.00
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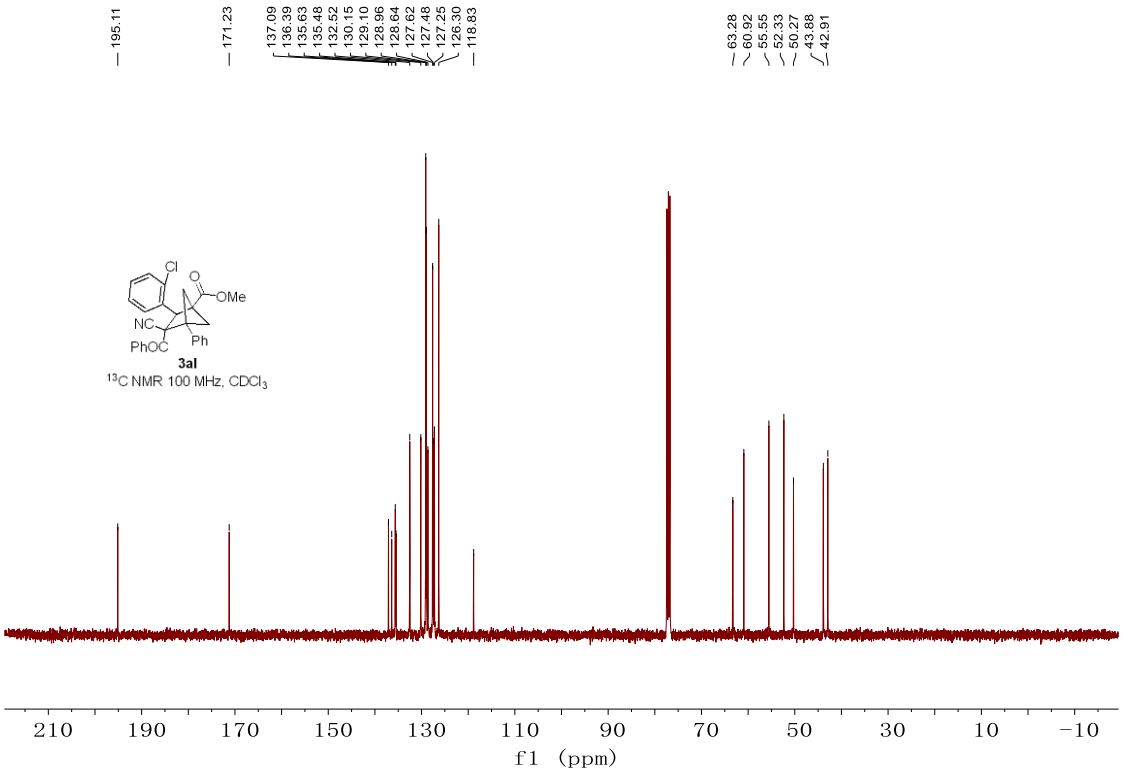
f1 (ppm)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126.30
118.83
63.28
60.92
55.55
52.33
50.27
43.88
42.91
Cl
O
OMe
NC
PhOC
Ph
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13C NMR 100 MHz, CDCl3
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90
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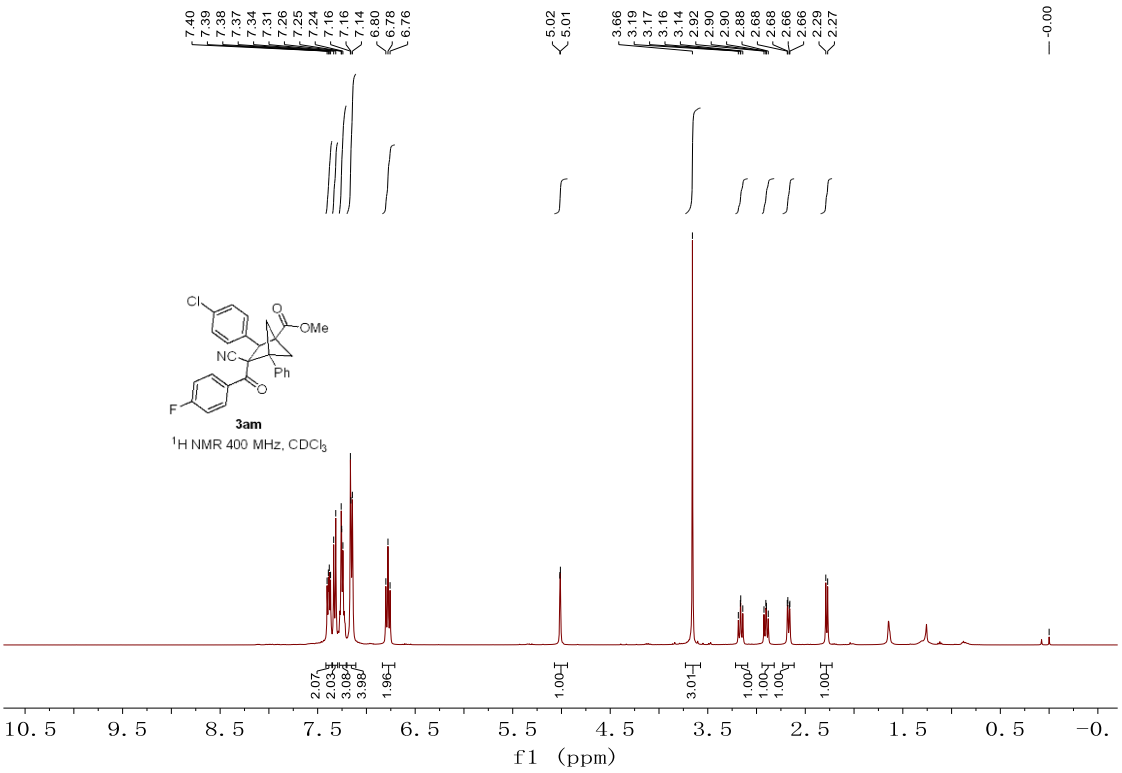
f1 (ppm)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5.01
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3.14
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2.68
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2.27
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O
OMe
NC
Ph
O
F
3am
1H NMR 400 MHz, CDCl3
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3.08
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3.01
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1.00
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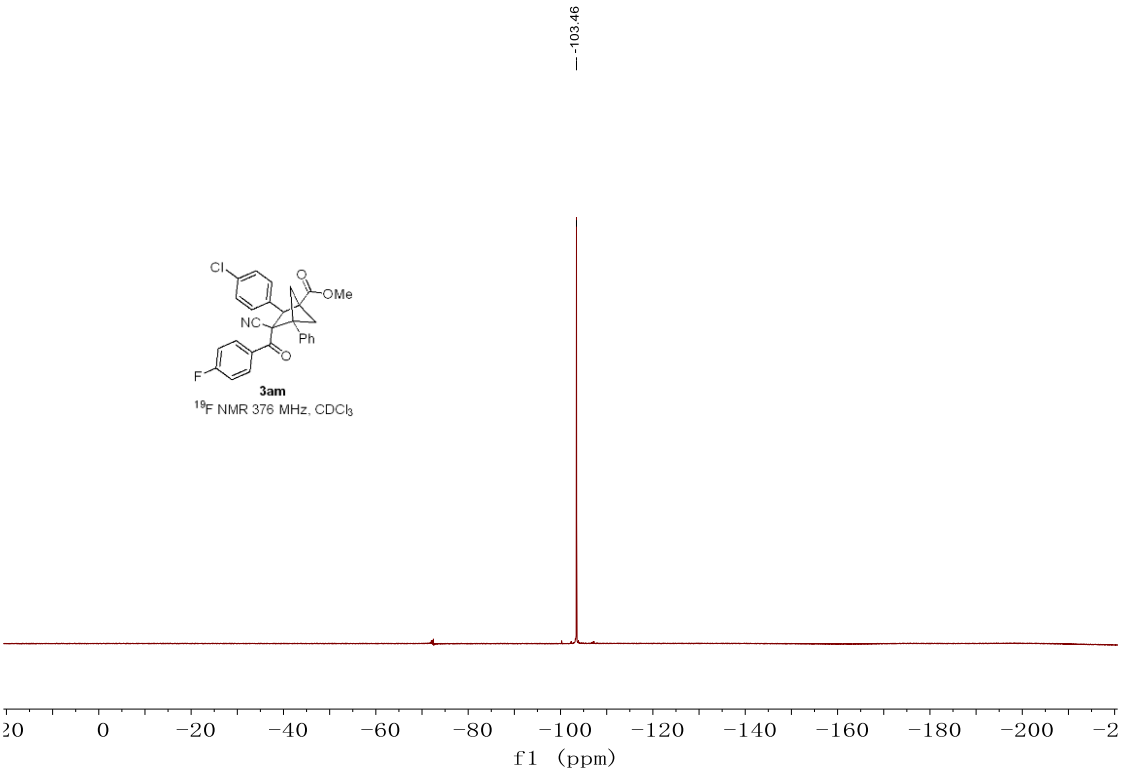
f1 (ppm)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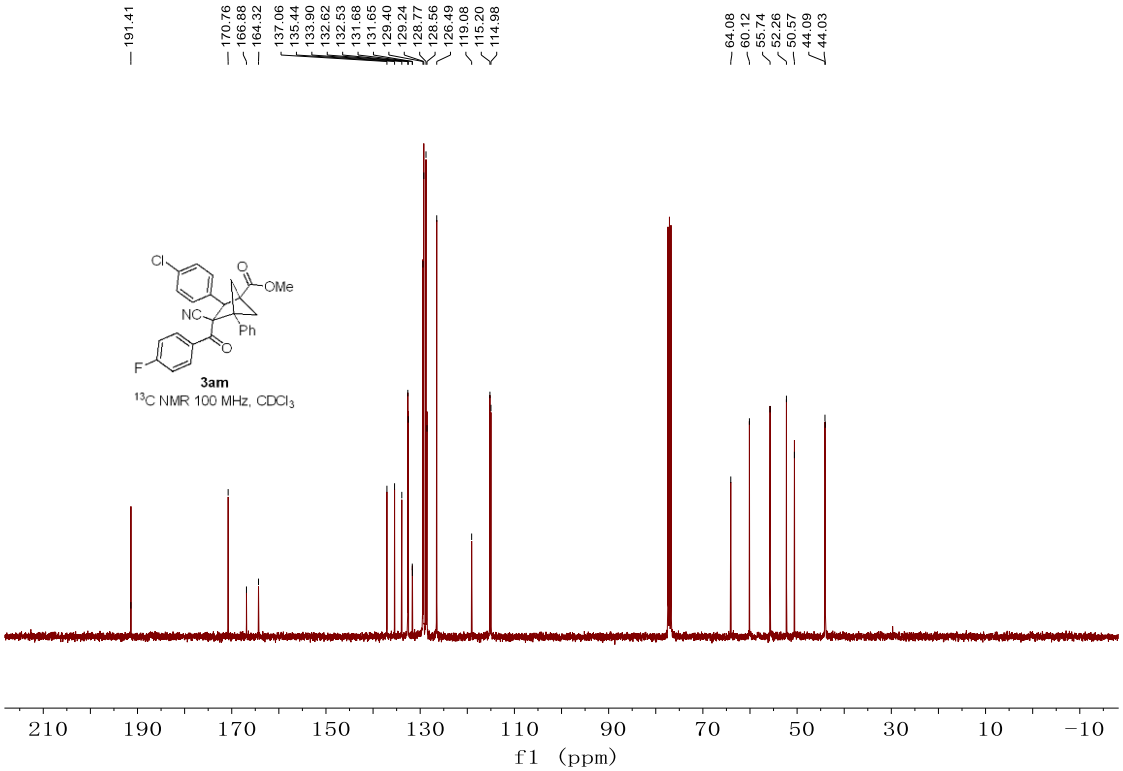
-140
-160
-180
-200
-2
f1 (ppm)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44.03
Cl
O
OMe
NC
Ph
O
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70
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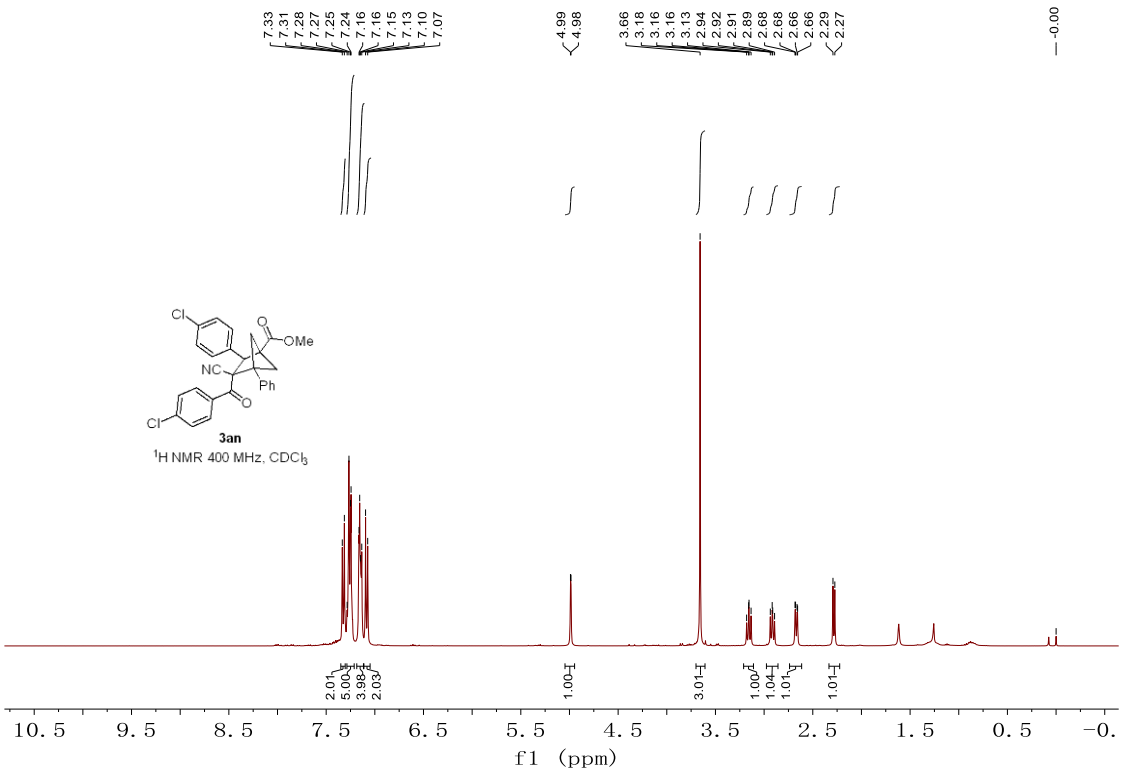
f1 (ppm)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2.92
2.91
2.89
2.68
2.68
2.66
2.66
2.29
2.27
-0.00
Cl
O
OMe
NC
Ph
O
Cl
3an
1H NMR 400 MHz, CDCl3
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3.01
1.00
1.04
1.01
1.01
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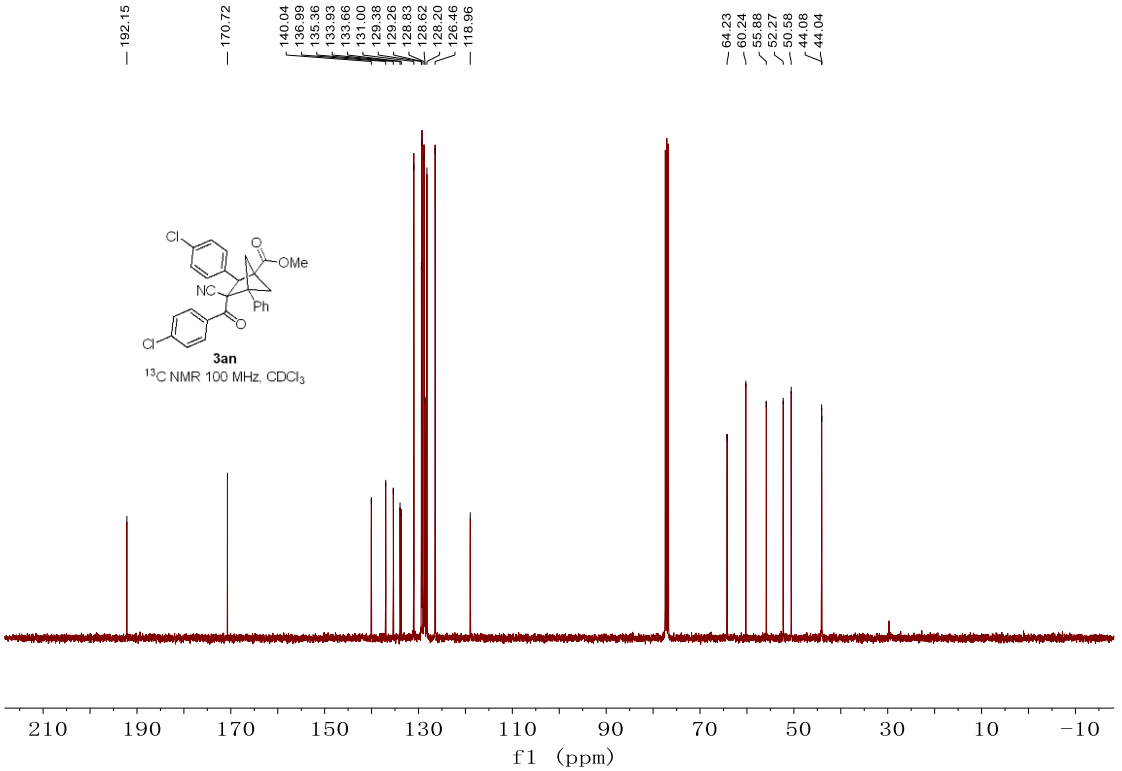
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44.08
44.04
Cl
O
OMe
NC
Ph
Cl
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210
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70
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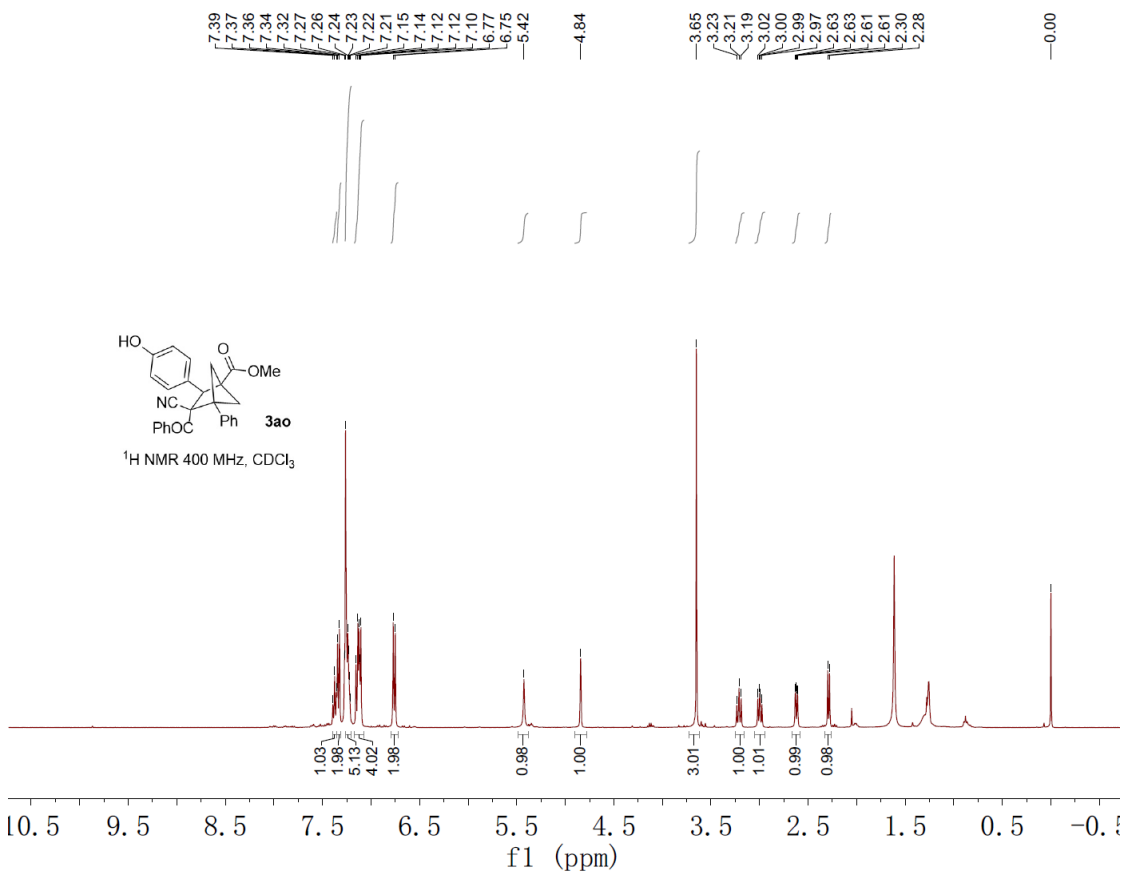
−10
f1 (ppm)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OMe
NC
PhOC
Ph
3ao
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1.00
1.01
0.99
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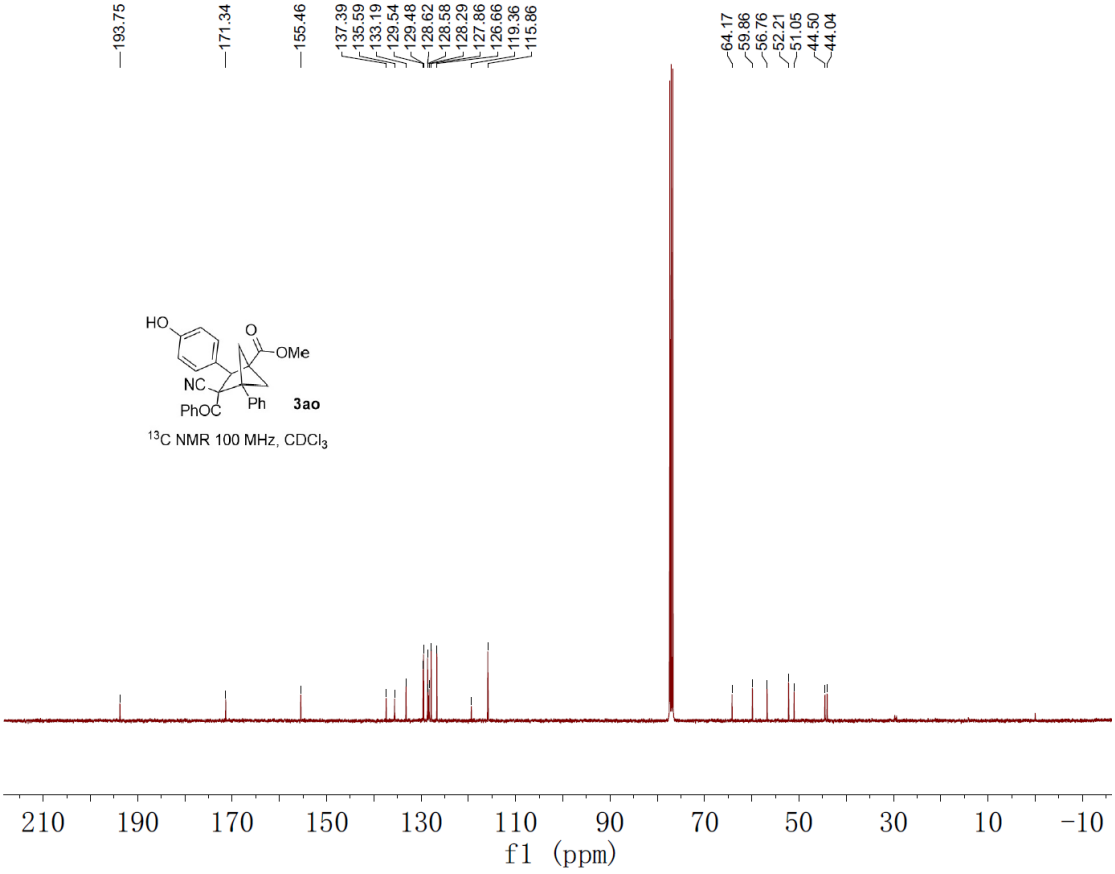
f1 (ppm)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56.76
52.21
51.05
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44.04
HO
O
OMe
NC
PhOC
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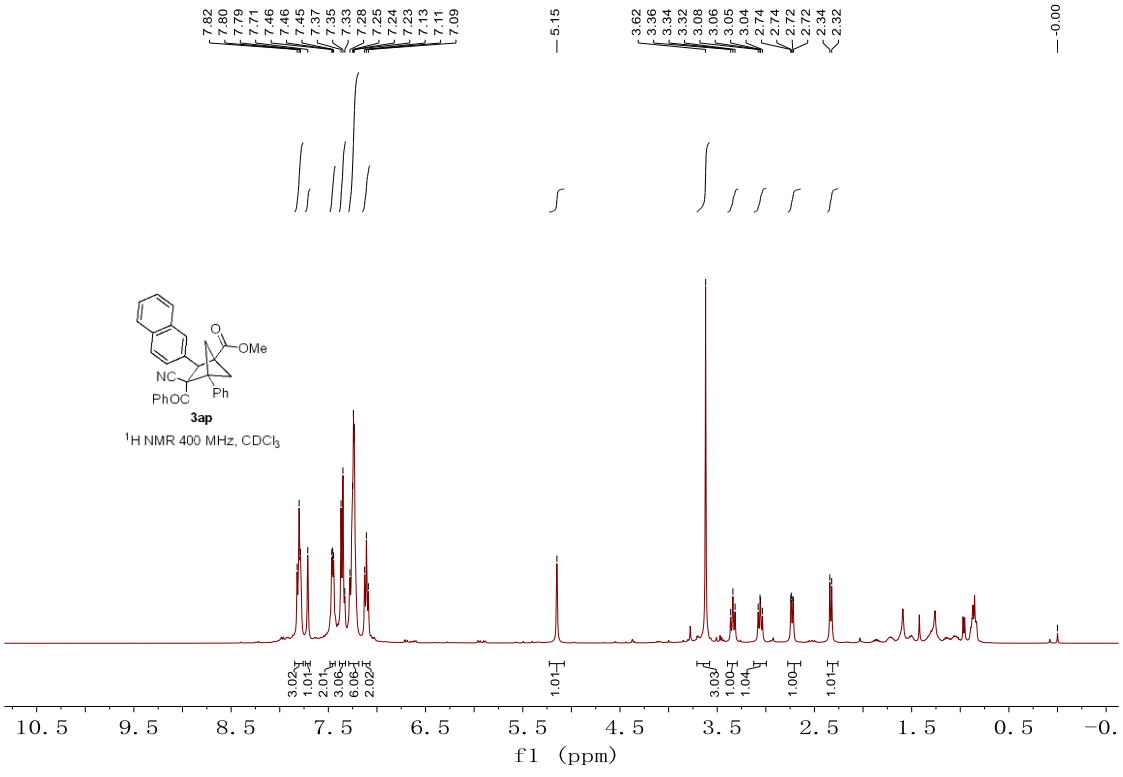
−10
f1 (ppm)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3.08
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3.04
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2.74
2.72
2.72
2.34
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0.00
O
OMe
NC
PhOC
Ph
3ap
1H NMR 400 MHz, CDCl3
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2.01
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1.01
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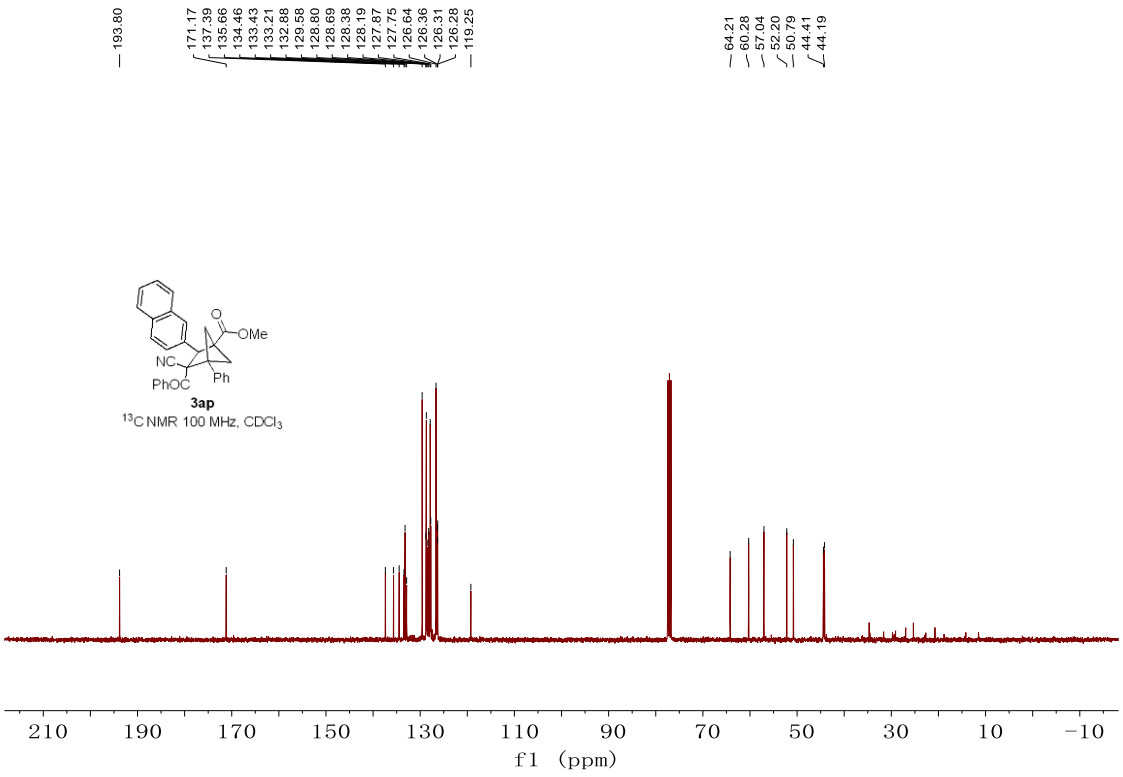
f1 (ppm)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OMe
NC
PhOC
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70
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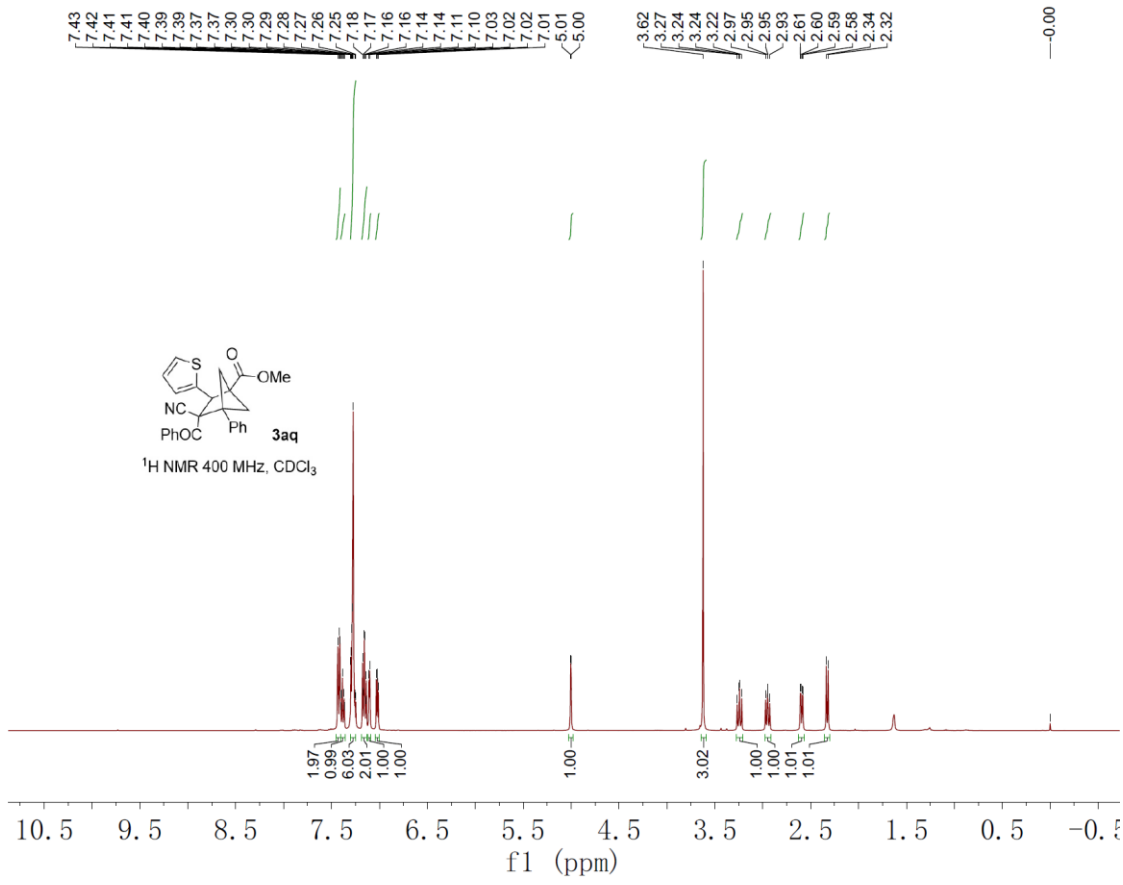
−10
f1 (ppm)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7.02
7.02
7.01
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S
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OMe
NC
PhOC
Ph
3aq
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1.00
1.00
1.00
3.02
1.00
1.00
1.01
1.01
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5.5
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2.5
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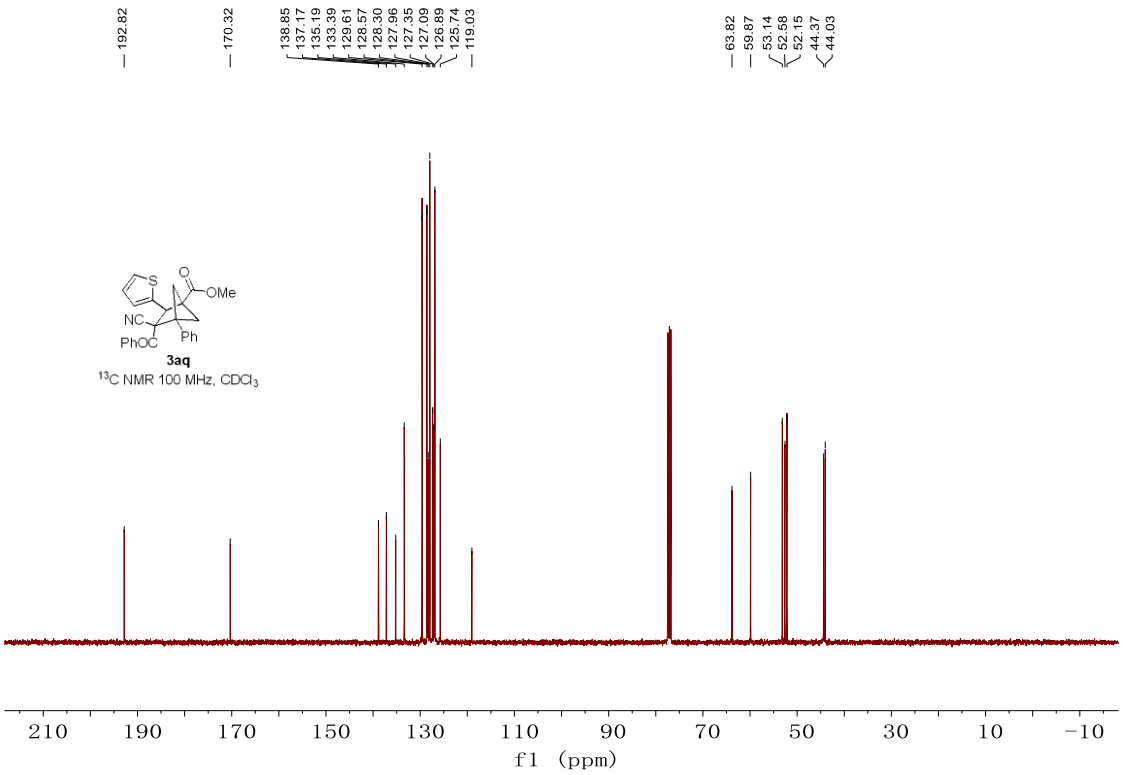
0.5
f1 (ppm)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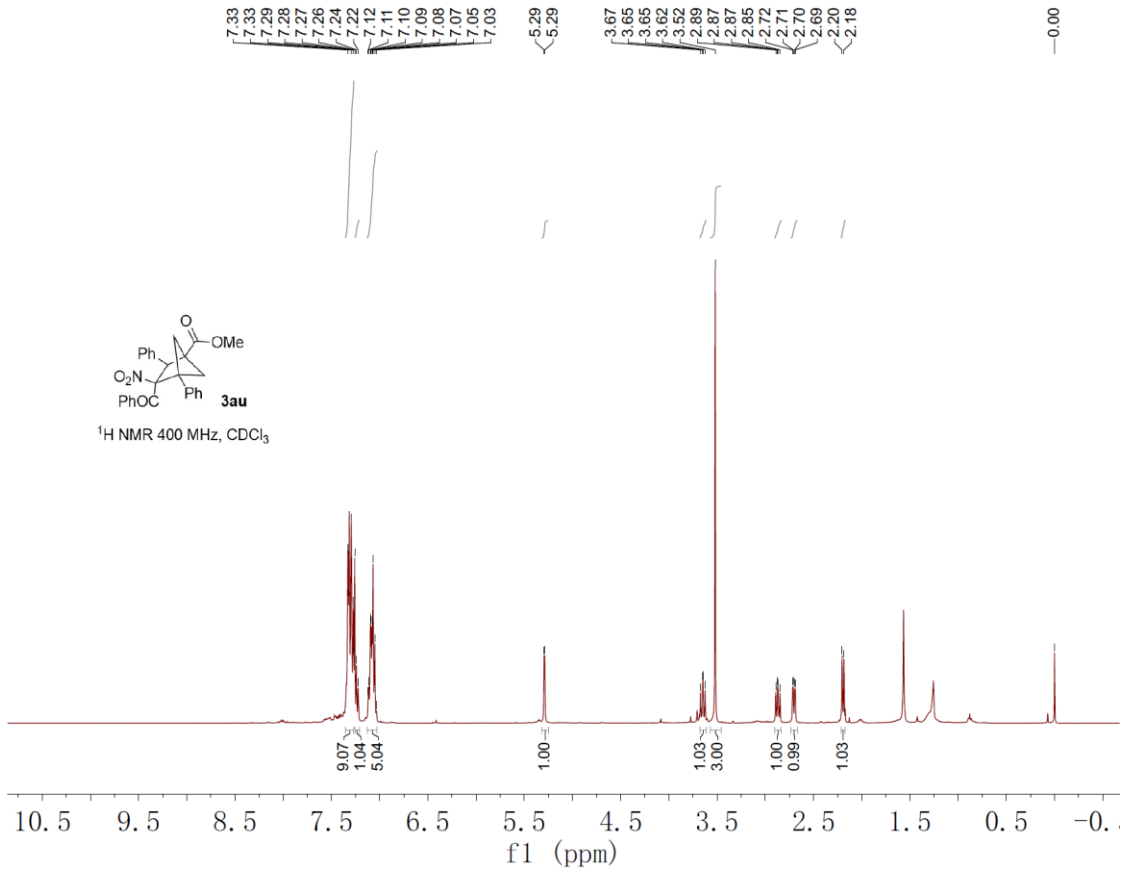
133.39
129.61
128.57
128.30
127.96
127.35
127.09
126.89
125.74
119.03
63.82
59.87
53.14
52.58
52.15
44.37
44.03
OMe
NC
PhOC
Ph
3aq
13C NMR 100 MHz, CDCl3
210
190
170
150
130
110
90
70
50
30
10
−10
f1 (ppm)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7.22
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7.11
7.10
7.09
7.08
7.07
7.05
7.03
5.29
5.29
3.67
3.65
3.65
3.62
3.52
2.89
2.87
2.87
2.85
2.72
2.71
2.70
2.69
2.20
2.18
0.00
OMe
Ph
O2N
PhOC
Ph
3au
1H NMR 400 MHz, CDCl3
9.07
1.04
5.04
1.00
1.03
3.00
1.00
0.99
1.03
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5.5
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3.5
2.5
1.5
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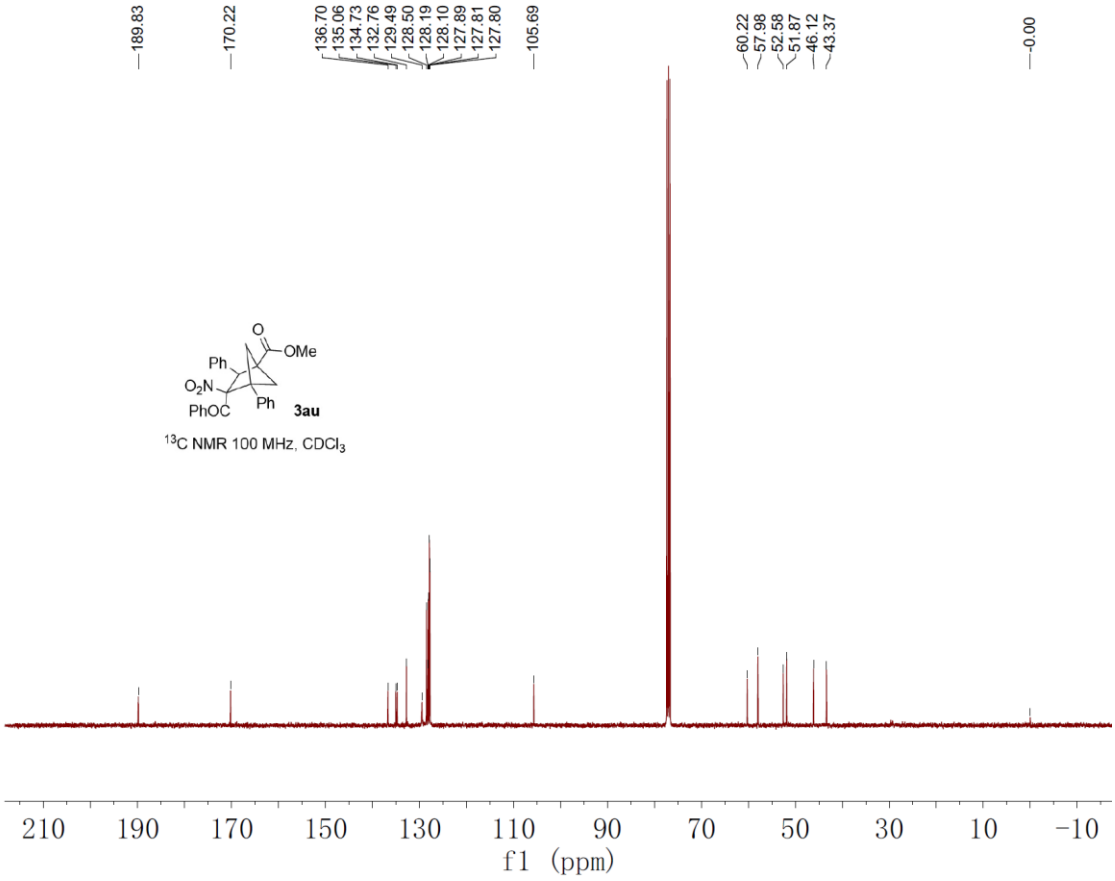
f1 (ppm)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132.76
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128.50
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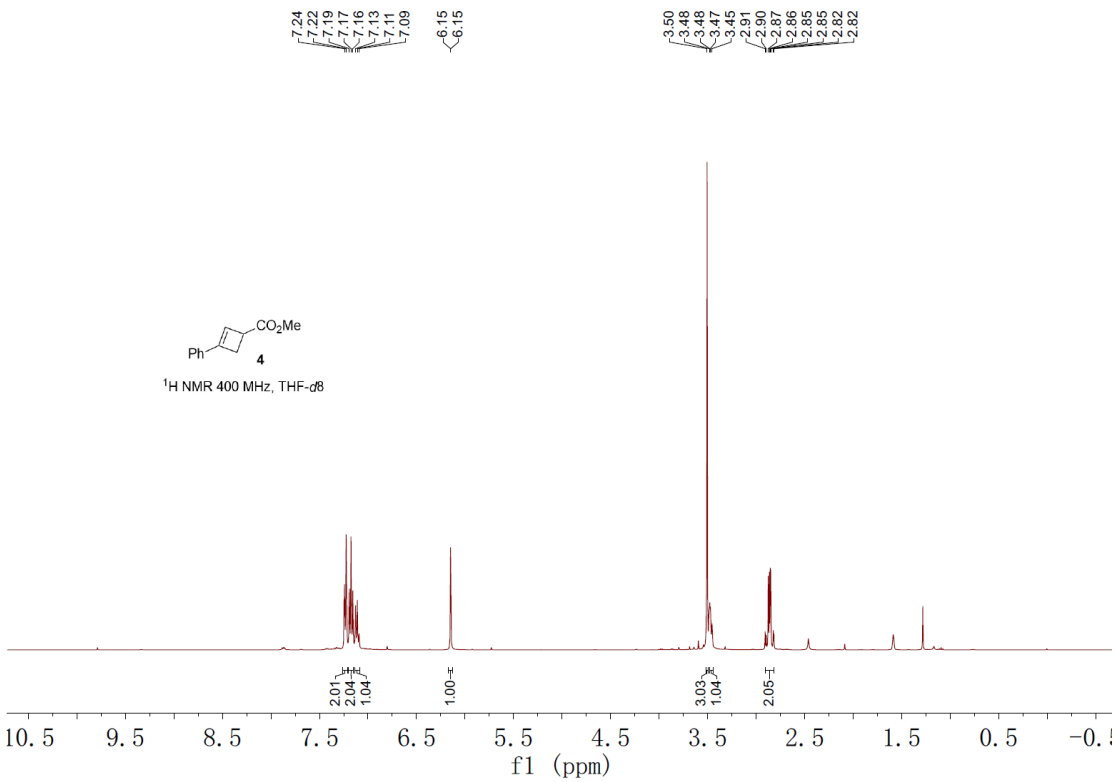
128.10
127.89
127.81
127.80
105.69
60.22
57.98
52.58
51.87
46.12
43.37
0.00
O
OMe
Ph
O2N
PhOC
Ph
3au
13C NMR 100 MHz, CDCl3
210
190
170
150
130
110
90
70
50
30
10
−10
f1 (ppm)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7.09
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6.15
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3.48
3.47
3.45
2.91
2.90
2.87
2.86
2.85
2.85
2.82
2.82
CO2Me
Ph
4
1H NMR 400 MHz, THF-d8
2.01
2.04
1.04
1.00
3.03
1.04
2.05
10.5
9.5
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7.5
6.5
5.5
4.5
3.5
2.5
1.5
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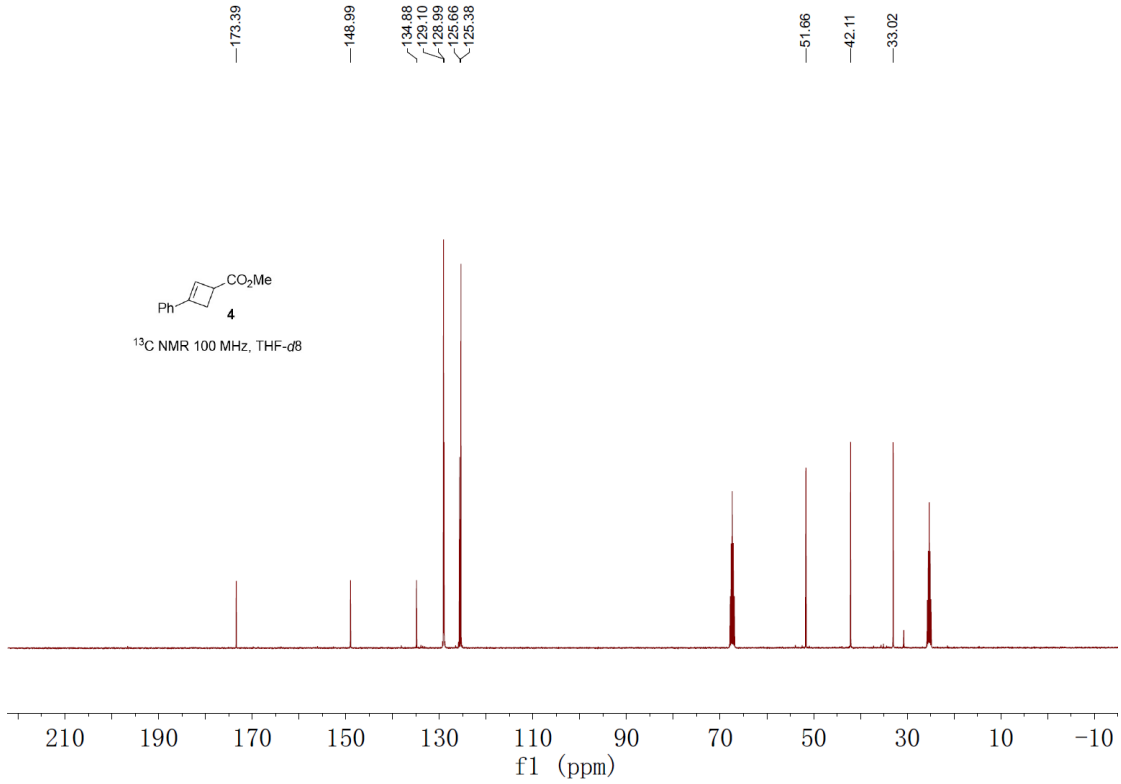
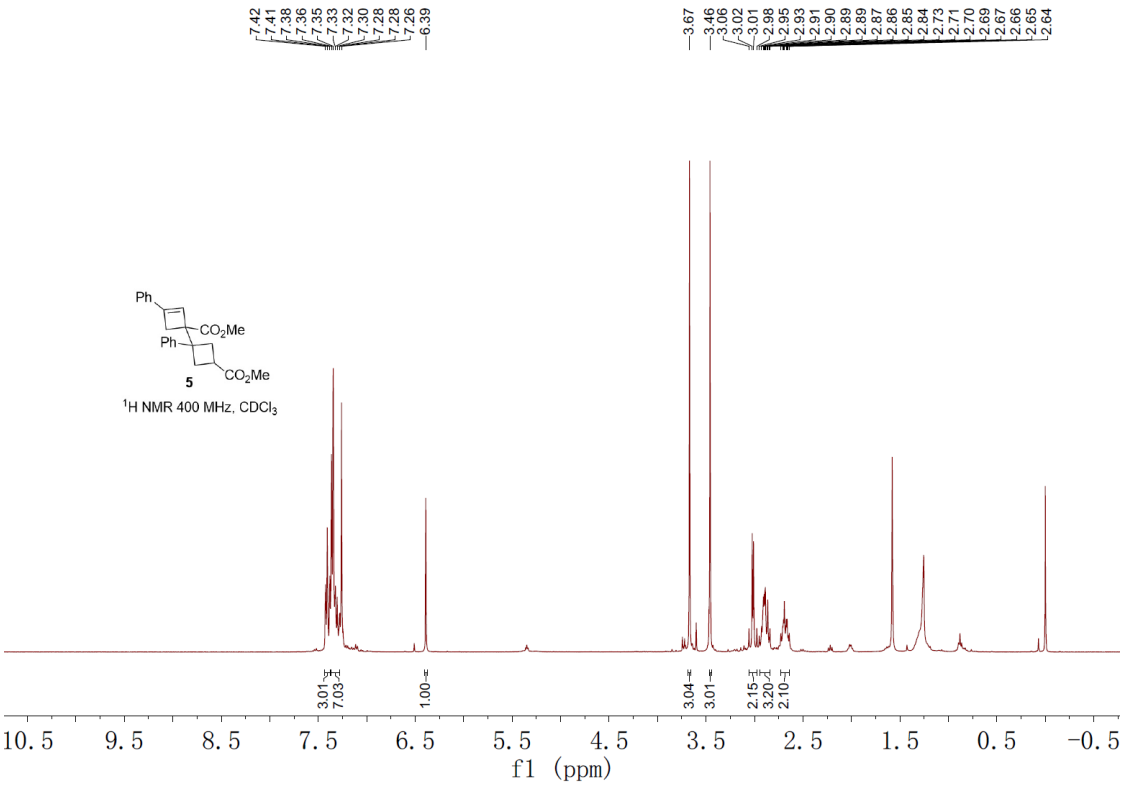
f1 (ppm)


173.39
148.99
134.88
129.10
128.99
125.66
125.38
51.66
42.11
33.02
CO2Me
Ph
4
13C NMR 100 MHz, THF-d8
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)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3.46
3.06
3.02
3.01
2.98
2.95
2.93
2.91
2.90
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2.89
2.87
2.86
2.85
2.84
2.73
2.71
2.70
2.69
2.67
2.66
2.65
2.64
Ph
CO2Me
Ph
CO2Me
5
1H NMR 400 MHz, CDCl3
3.01
7.03
1.00
3.04
3.01
2.15
3.20
2.10
10.5
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6.5
5.5
4.5
3.5
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1.5
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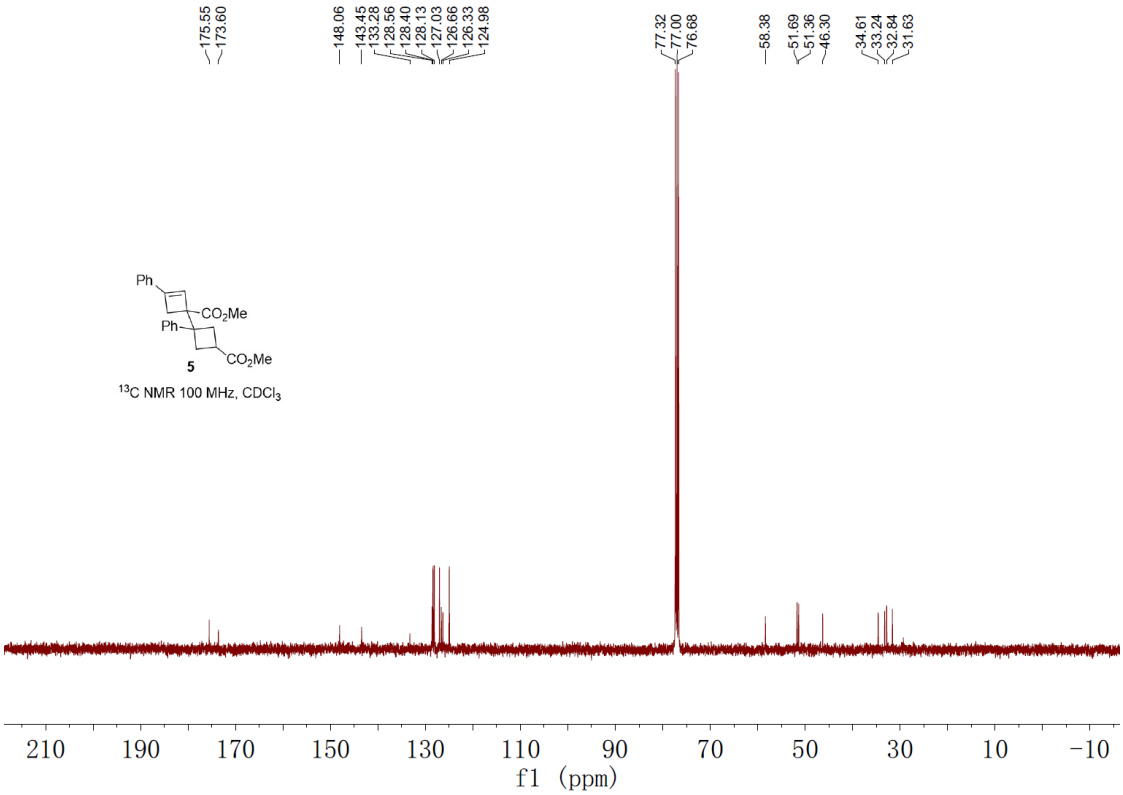
-0.5
f1 (ppm)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173.60
148.06
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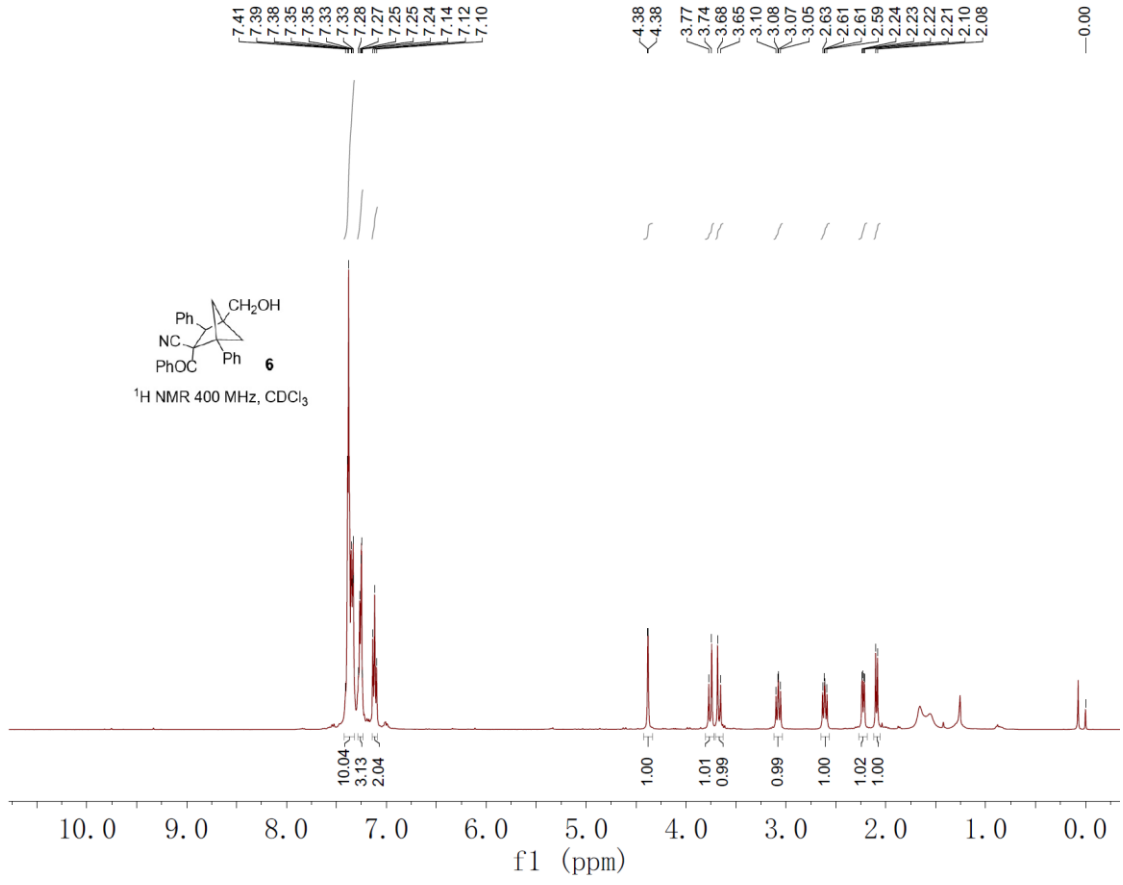
127.03
126.66
126.33
124.98
77.32
77.00
76.68
58.38
51.69
51.36
46.30
34.61
33.24
32.84
31.63
Ph
CO2Me
Ph
CO2Me
5
13C NMR 100 MHz, CDCl3
210
190
170
150
130
110
90
70
50
30
10
−10
f1 (ppm)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7.12
7.10
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4.38
3.77
3.74
3.68
3.65
3.10
3.08
3.07
3.05
2.63
2.61
2.61
2.59
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2.23
2.22
2.21
2.10
2.08
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CH2OH
Ph
NC
PhOC
Ph
6
1H NMR 400 MHz, CDCl3
10.04
3.13
2.04
1.00
1.01
0.99
0.99
1.00
1.02
1.00
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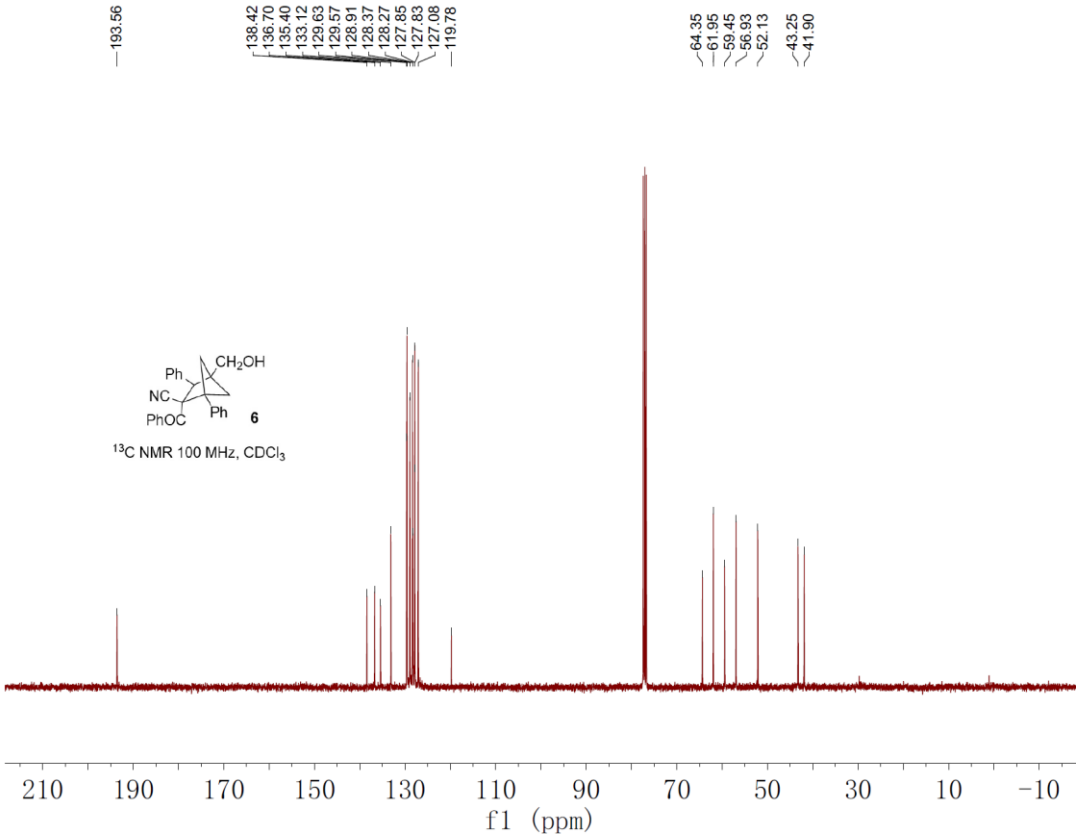
f1 (ppm)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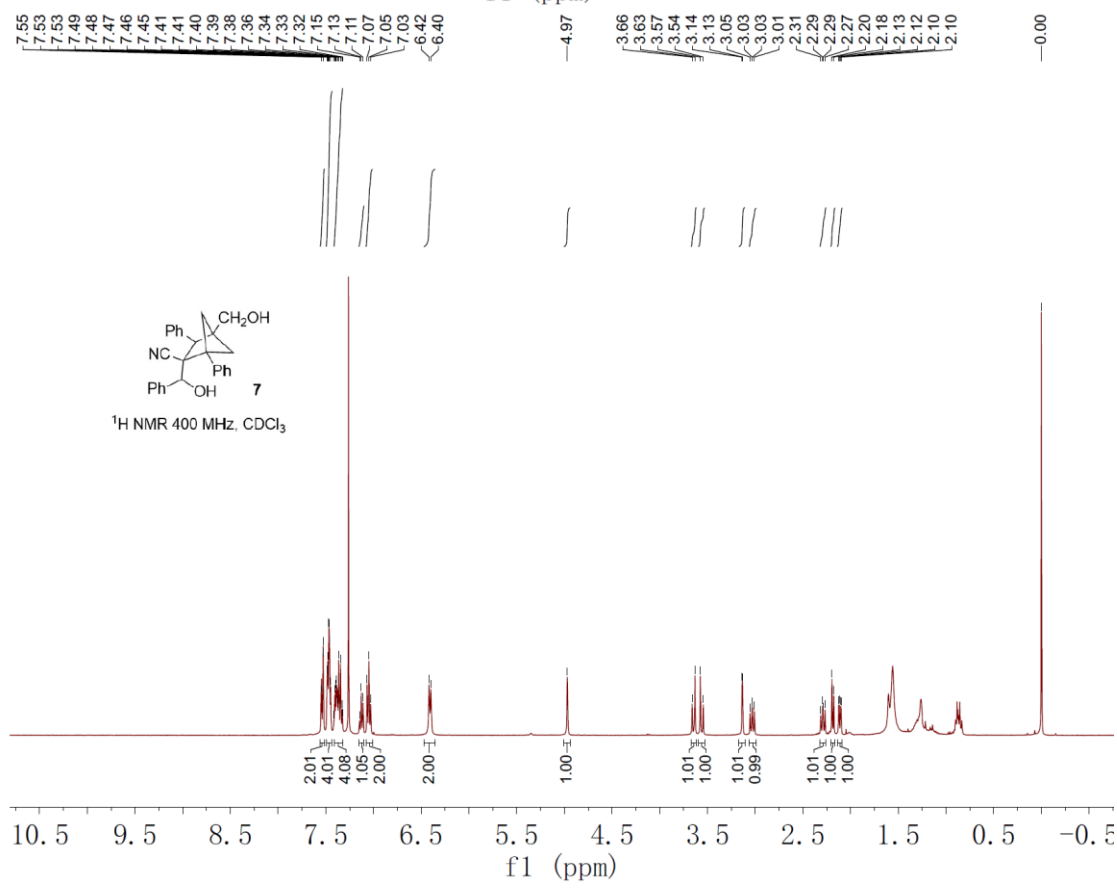
127.08
119.78
64.35
61.95
59.45
56.93
52.13
43.25
41.90
CH2OH
Ph
NC
PhOC
Ph
6
13C NMR 100 MHz, CDCl3
210
190
170
150
130
110
90
70
50
30
10
−10
f1 (ppm)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7.41
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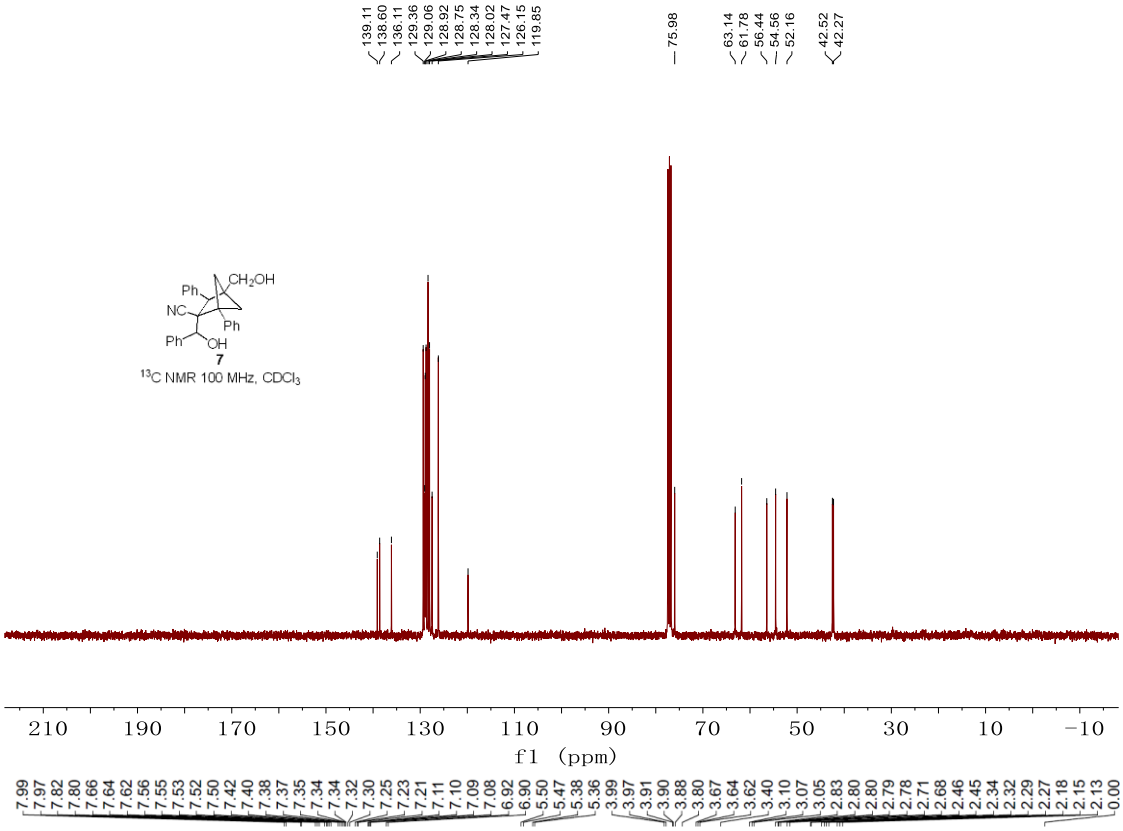
7.39
7.38
7.36
7.34
7.33
7.32
7.15
7.13
7.11
7.07
7.05
7.03
6.42
6.40
4.97
3.66
3.63
3.57
3.54
3.14
3.13
3.05
3.03
3.03
3.01
2.31
2.29
2.29
2.27
2.20
2.18
2.13
2.12
2.10
2.10
0.00
CH2OH
Ph
NC
Ph
Ph
OH
7
1H NMR 400 MHz, CDCl3
2.01
4.01
4.08
1.05
2.00
2.00
1.00
1.01
1.00
1.01
0.99
1.01
1.00
1.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)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136.11
129.36
129.06
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128.34
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127.47
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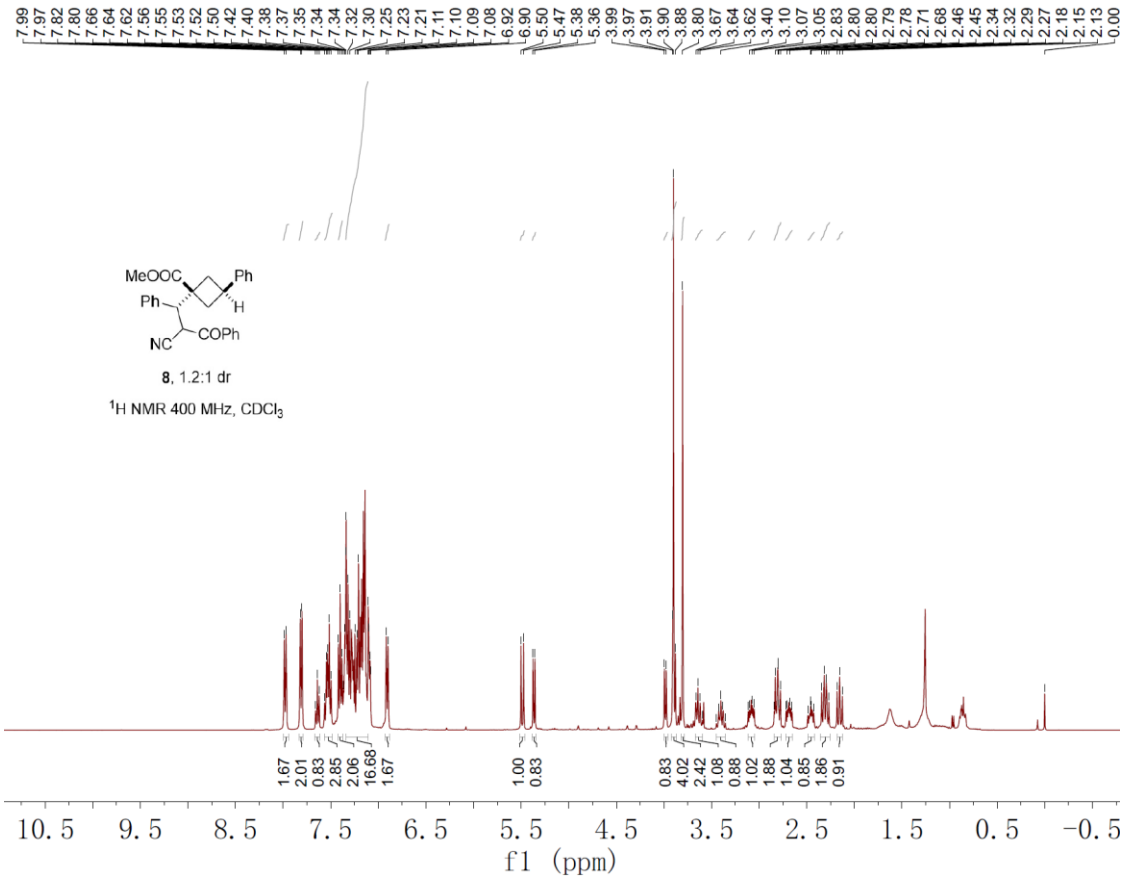
75.98
63.14
61.78
56.44
54.56
52.16
42.52
42.27
Ph
CH2OH
NC
Ph
Ph
OH
7
13C NMR 100 MHz, CDCl3
210
190
170
150
130
110
90
70
50
30
10
−10
f1 (ppm)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7.34
7.34
7.32
7.30
7.25
7.23
7.21
7.11
7.10
7.09
7.08
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5.47
5.38
5.36
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3.91
3.90
3.88
3.80
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3.64
3.62
3.40
3.10
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3.05
2.83
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2.46
2.45
2.34
2.32
2.29
2.27
2.18
2.15
2.13
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MeOOC
Ph
Ph
H
NC
COPh
8, 1.2:1 dr
1H NMR 400 MHz, CDCl3
1.67
2.01
0.83
2.85
2.06
16.68
1.67
1.00
0.83
0.83
4.02
2.42
1.08
0.88
1.02
1.88
1.04
0.85
1.86
0.91
10.5
9.5
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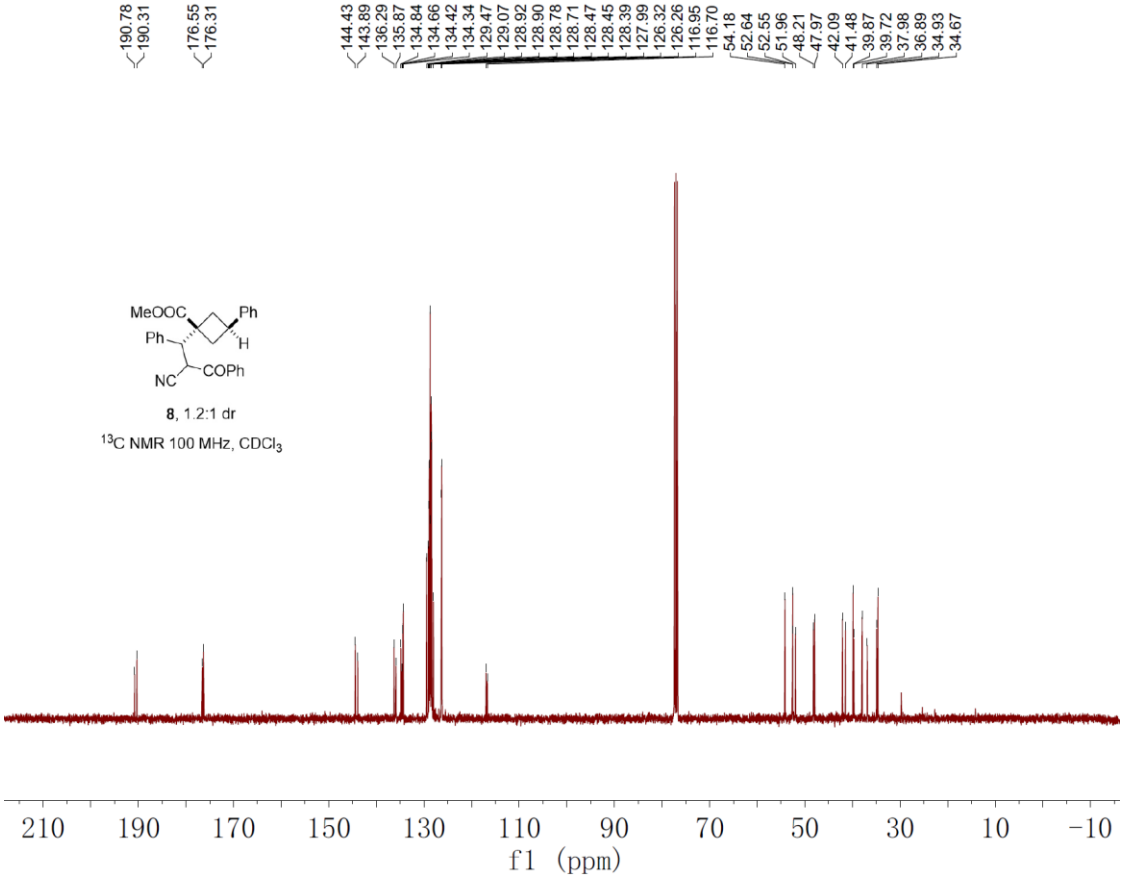
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)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176.31
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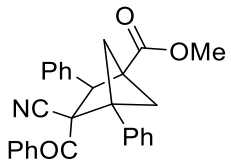
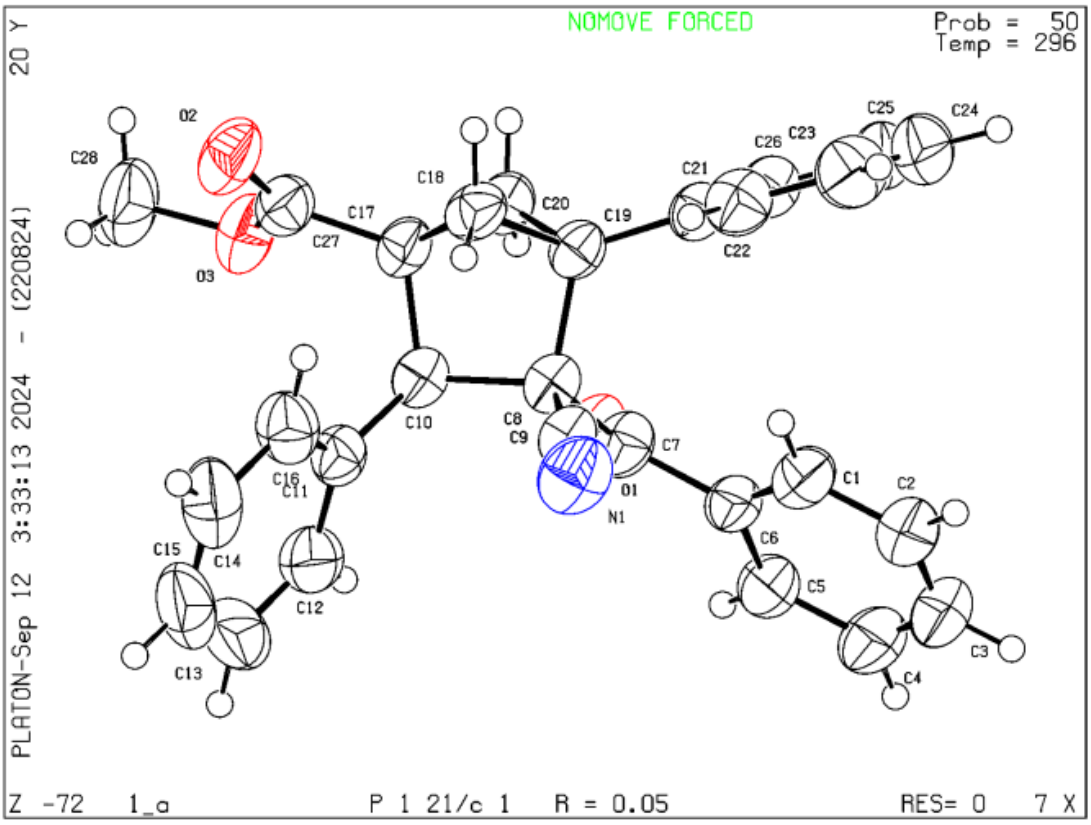
134.42
134.34
129.47
129.07
128.92
128.90
128.78
128.71
128.47
128.45
128.39
127.99
126.32
126.26
116.95
116.70
54.18
52.64
52.55
51.96
48.21
47.97
42.09
41.48
39.87
39.72
37.98
36.89
34.93
34.67
MeOOC
Ph
Ph
H
NC
COPh
8, 1.2:1 dr
13C NMR 100 MHz, CDCl3
210
190
170
150
130
110
90
70
50
30
10
−10
f1 (ppm)

X-Ray crystallographic data

X-ray structure of product **3aa** (thermal ellipsoids are shown at 50% probability level). The crystal of product **3aa** was obtained by slow evaporation in dichloromethane and petroleum ether. Crystal data have been deposited to CCDC, number 2428976.



3aa



Bond precision: C-C = 0.0039 A Wavelength=0.71073

Cell: a=13.893(14) b=20.91(2) c=7.841(8)
alpha=90 beta=100.45(3) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	2240(4)	2241(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C28 H23 N O3	C28 H23 N O3
Sum formula	C28 H23 N O3	C28 H23 N O3
Mr	421.47	421.47
Dx,g cm-3	1.250	1.249
Z	4	4
Mu (mm-1)	0.081	0.081
F000	888.0	888.0
F000'	888.40	
h,k,lmax	16,24,9	16,24,9
Nref	3980	3944
Tmin,Tmax	0.982,0.986	0.653,0.745
Tmin'	0.982	

Correction method= # Reported T Limits: Tmin=0.653 Tmax=0.745
AbsCorr = NONE

Data completeness= 0.991 Theta(max)= 25.055

R(reflections)= 0.0521(2323) wR2(reflections)= 0.1320(3944)

S = 1.016 Npar= 290