Supporting Information for

Nickel-catalyzed Asymmetric α-Arylation and Heteroarylation of Ketones with Chloroarenes: Effect of Halide on Selectivity, Oxidation State, and Room Temperature Reactions

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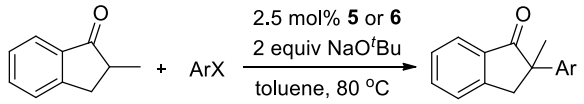
Additional Discussion of Reference 12:

As described in more detail previously (reference 4 in the manuscript: Liao, X.; Weng, Z.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 195.), we have not been able to reproduce the enantioselectivity and yields reported previously for a nickel-catalyzed asymmetric α-arylation (Chen, G. C.; Kwong, F. Y.; Chan, H. O.; Yub, W.-Y.; Chan, A. S. C. *Chem. Commun.* **2006**, 1413.). The much lower optical rotations for the products reported by Kwong and Chan than for analogous products we reported in reference 4 are consistent with this finding. Moreover, we find that the products from **α**-arylation of indanone catalyzed by the combination of $Ni(COD)_2$ and (*R*)-P-Phos have a levorotatory rotation, but they are reported to have a dextrorotatory rotation. The detailed studies in the current paper are consistent with our prior findings.

Table SI. Asymmetric **α**-Arylation of 2-Methyl-1-Indanone with Chloro- and Bromoarenes Catalyzed by $\{[(R)\text{-BINAP}]NiX\}_2$ (X = Cl and Br)[a].



	F_3C—Cl	Cl	MeO—Cl
$\{[(R)\text{-BINAP}]NiCl\}_2$ (**5**),	yield: 33%, ee: 50%	yield: 34%, ee: 81%	yield: 13%, ee: 89%
$Ni(COD)_2$/(R)-BINAP,	yield: 71%, ee: 95%	yield: 78%, ee: 93%	yield: 73%, ee: 94%
	F_3C—Br	Br	MeO—Br
$\{[(R)\text{-BINAP}]NiBr\}_2$ (**6**),	yield: 32%, ee: 7%	yield: 49%, ee: 34%	yield: 28%, ee: 51%
$Ni(COD)_2$/(R)-BINAP,	yield: 38%, ee: 39%	yield: 61%, ee: 76%	yield: 44%, ee: 77%

[a]Conditions: Indanones (0.200 mmol), chloro- or bromoarenes (0.400 mmol), NaO^{t}Bu (0.400 mmol), $\{[(R)\text{-BINAP}]NiCl\}_2$ (5.0 μmol, 2.5 mol%) for chloroarenes and $\{[(R)\text{-BINAP}]NiBr\}_2$ (5.0 μmol, 2.5 mol%) for bromoarenes; solvent: toluene (1.0 mL); temperature: 80 °C; reaction time: 24 h; ee was determined by chiral HPLC analysis.

General Remarks. All the manipulations were performed in a nitrogen-filled glovebox, unless mentioned otherwise. THF, toluene, benzene, and pentane were purified by passing the degassed solvents (Ar) through a column of activated alumina (solvent purification system purchased from Innovative Technologies, Newburyport, MA). $Ni(COD)_2$, (*R*)-DIFLUORPHOS, (*R*)-BINAP, (*R*)-P-PHOS, (*R*)-XylBINAP, (*R*)-SEGPHOS, and (*R*)-DM-SEGPHOS were purchased from Strem Chemical Co. and used as received. NaO^tBu, 2-methyl-1-tetralone, and 2-methyl-1-indanone were purchased from Aldrich and used as received. All other chemicals were used as received from commercial resources. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded using a Varian 400 MHz or 500 MHz NMR spectrometer. ^1H NMR spectra were referenced to resonances of the residual protons in the deuterated solvents; and $^{31}P\{^1H\}$ NMR shifts were reported in parts per million relative to an 85% H_3PO_4 external standard. Silica gel chromatography was performed using a Teledyne Isco Combiflash® R_f system with Redi*Sep* Gold™ columns. High-resolution mass spectra data were obtained from the University of Illinois SCS Mass Spectroscopy Laboratory. Elemental analyses were performed at Microanalysis Laboratory in the University of Illinois or by Robertson Microlab, Inc., Madison, NJ.

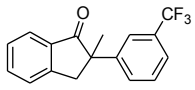
Screening of Ligands and Electrophiles for Ni-catalyzed Asymmetric α-Arylation of 2-Methyl-1-indanone

In a drybox, a 4-mL screw-capped vial was charged with $Ni(COD)_2$ (2.8 mg, 0.010 mmol), the bidentate phosphine ligand (0.012 mmol) [(*R*)-BINAP (7.5 mg), (*R*)-XylBINAP (8.8 mg), (*R*)-SEGPHOS (7.3 mg), (*R*)-DM-SEGPHOS (8.7 mg), (*R*)-P-PHOS (7.7 mg), or (*R*)-DIFLUORPHOS (8.2 mg)], NaO^tBu (38.4 mg, 0.400 mmol), the phenyl coupling partner (0.400 mmol) [PhBr (62.8 mg), PhCl (45.0 mg), PhI (81.6 mg), or PhOTf (90.5 mg)], 2-methyl-1-indanone (29.2 mg, 0.200 mmol), a magnetic stirring bar, and toluene (1.0 mL). The vial was sealed with a cap containing a PTFE septum and taken out of the drybox. The reaction mixture was stirred in an oil bath preheated to 80 ºC for 24 h and then cooled to room temperature. The mixture was quenched with a saturated aqueous NH_4Cl solution and extracted with Et_2O (2 × 10 mL). The combined extract was dried over Na_2SO_4, filtered, and dried under reduced pressure. The crude product was purified with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc). The ee of 2-methyl-2-phenyl-2,3-dihydro-*1H*-inden-1-one was checked by HPLC (OB-H column, 3% isopropanol in hexanes, flow rate 0.5 mL/min).

The General Procedure for the α-Arylation Reactions of Indanones and Tetralones with Aryl Chlorides

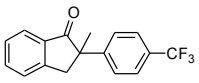
In a drybox, a 4-mL screw-capped vial was charged with $Ni(COD)_2$ (2.8 mg, 0.010 mmol, for indanones; 5.5 mg, 0.020 mmol for tetralones), (*R*)-BINAP (7.5 mg, 0.012 mmol for indanones; 14.9 mg, 0.024 mmol for tetralones), NaO^tBu (38.4 mg, 0.400 mmol), the corresponding aryl chloride (0.400 mmol), ketone (0.200 mmol), a magnetic stirring bar, and toluene (1.0 mL). The vial was sealed with a cap containing a PTFE septum and removed from the drybox. The reaction mixture was stirred in an oil bath (60 ºC for reactions of the indanones and 80 ºC for reactions of the tetralones) for 36 h (for reactions of indanones) or 48 h (for reactions of tetralones) and then cooled to room temperature. The mixture was quenched with a saturated aqueous NH_4Cl solution and extracted with Et_2O (2 × 10 mL). The combined extract was dried over Na_2SO_4, filtered, and dried under reduced pressure. The crude product was purified with a CombiFlash system with 5-20% ethyl acetate in hexanes as eluent. The conditions for chromatography and data for characterization of the products are given below.

2-Methyl-2-(3-(trifluoromethyl)phenyl)-2,3-dihydro-*1H*-inden-1-one (Table 2, Entry 1)



This reaction was conducted at 60 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→94:6 hexanes/EtOAc). The title compound was isolated as a colorless liquid in 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, 1H, J_{HH} = 7.6 Hz), 7.69 (t, 1H, J_{HH} = 7.5 Hz), 7.61 (s, 1H), 7.52 (m, 3H), 7.46 (t, 1H, J_{HH} = 7.6Hz), 7.43 (t, 1H, J_{HH} = 7.8 Hz), 3.59 (d, 1H, J_{HH} = 17.1 Hz), 3.37 (d, 1H, J_{HH} = 17.1 Hz), 1.69 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 208.1, 152.4, 145.1, 15.7, 135.5, 131.1 (q, J_{CF} = 32.2), 129.3, 128.2, 126.7, 125.3, 123.8 (q, J_{CF} = 3.9 Hz), 123.2 (q, J_{CF} = 3.7 Hz), 122.9 (q, J_{CF} = 271.0 Hz), 53.2, 44.8, 25.1. $[\alpha]^{24}_D$ = -30.3º (c = 0.60, $CHCl_3$). HPLC analysis: 96% ee, Chiralcel OJ-H column, 2% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 14.9 min, $t_{[minor]}$ = 17.8 min.

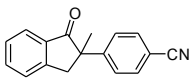
2-Methyl-2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-*1H*-inden-1-one (Table 2, Entry 2)



This reaction was conducted at 60 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→94:6 hexanes/EtOAc). The title compound was isolated as a colorless liquid in 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, 1H, J_{HH} = 7.6 Hz), 7.68 (td, 1H, J_{HH} = 7.4 Hz, J_{HH} = 1.2 Hz), 7.57 (d, 2H, J_{HH} = 8.3Hz), 7.52 (d, 1H, J_{HH} = 7.7 Hz), 7.46 (t, 1H, J_{HH} = 7.3 Hz), 7.45 (d, 2H, J_{HH} = 8.3 Hz), 3.57 (d, 1H, J_{HH} = 17.2 Hz), 3.36 (d, 1H, J_{HH} = 17.2 Hz), 1.69 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 208.0, 152.4, 148.1, 135.7, 135.5, 129.2 (q, J_{CF} = 33.5 Hz), 128.3,

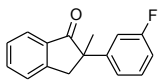
126.8, 126.7, 125.7 (q, J_{CF} = 3.1 Hz), 125.3, 124.2 (q, J_{CF} = 271.4), 53.3, 44.8, 24.8. $[\alpha]^{24}_{D}$ = -37.0º (c = 0.82, $CHCl_3$). HPLC analysis: 95% ee, Chiralcel OJ column, 2% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 17.0 min, $t_{[minor]}$ = 22.0 min.

4-(2-Methyl-1-oxo-2,3-dihydro-1*H*-inden-2-yl)benzonitrile (Table 2, Entry 3)



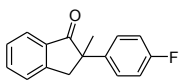
This reaction was conducted at 60 ºC for 16h. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→85:15 hexanes/EtOAc). The title compound was isolated as a yellow liquid in 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, 1H, J_{HH} = 7.7 Hz), 7.67 (td, 1H, J_{HH} = 7.4 Hz, J_{HH} = 1.1 Hz), 7.59 (dt, 2H, J_{HH} = 8.6 Hz, J_{HH} = 1.9 Hz), 7.51 (dt, 1H, J_{HH} = 7.7 Hz, J_{HH} = 1.0 Hz), 7.44 (m, 3H), 3.55 (d, 1H, J_{HH} = 17.3 Hz), 3.35 (d, 1H, J_{HH} = 17.3 Hz), 1.66 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 207.5, 152.3, 149.5, 135.9, 135.3, 132.6, 128.4, 127.4, 126.7, 125.4, 119.0, 110.8, 53.5, 44.6, 24.8. $[\alpha]^{22}_{D}$ = -49.7, (c = 0.80, $CHCl_3$). HPLC analysis: 92% ee, Chiralcel OB-H column, 20% isopropanol in hexane, 1.0 mL/min flow rate, 210 nm UV lamp, $t_{[major]}$ = 15.0 min, $t_{[minor]}$ = 23.0 min.

2-(3-Fluorophenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (Table 2, Entry 4)



This reaction was conducted at 80 ˚C. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→97:3 hexanes/EtOAc). The title compound was isolated as a colorless liquid in 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, 1H, J_{HH} = 7.7 Hz), 7.66 (t, 1H, J_{HH} = 7.5 Hz), 7.50 (d, 1H, J_{HH} = 7.5 Hz), 7.43 (t, 1H, J_{HH} = 7.5 Hz), 7.25 (m, 1H), 7.06 (m, 2H), 6.91 (m, 1H), 3.56 (d, 1H, J_{HH} = 17.4 Hz), 3.32 (d, 1H, J_{HH} = 17.4 Hz), 1.65 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 208.2, 164.1, 161.9, 152.5, 146.7 (d, J_{CF} = 3.2 Hz), 135.5, 130.2 (d, J_{CF} = 8.4 Hz), 128.1, 126.6, 125.2, 122.0 (d, J_{CF} = 2.6 Hz), 113.8 (d, J_{CF} = 8.7 Hz), 113.6 (d, J_{CF} = 10.0 Hz), 53.2 (d, J_{CF} = 1.5 Hz), 44.9, 24.7. $[\alpha]^{23}_{D}$ = -48.0º, (c = 0.94, $CHCl_3$). HPLC analysis: 94% ee, Chiralcel OB-H column, 1% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 28.0 min, $t_{[minor]}$ = 33.7 min. Anal. Calc'd for $C_{16}H_{13}FO$: C, 79.98; H, 5.45. Found: C, 79.89; H, 5.52.

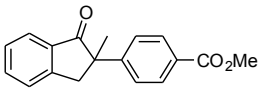
2-(4-Fluorophenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one (Table 2, Entry 5)



This reaction was conducted at 80 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→97:3 hexanes/EtOAc). The title compound was isolated as a colorless liquid in 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, 1H, J_{HH} = 7.7 Hz), 7.66 (td, 1H, J_{HH} = 7.6 Hz, J_{HH} = 1.1 Hz), 7.51 (dt, 1H, J_{HH} = 7.7 Hz, J_{HH} = 0.7 Hz), 7.44 (td, 1H, J_{HH} = 7.4 Hz, J_{HH} = 0.7 Hz), 7.29 (m, 2H), 5.99

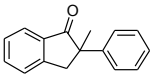
(m, 2H), 3.56 (d, 1H, J_{HH} = 17.4 Hz), 3.32 (d, 1H, J_{HH} = 17.4 Hz), 1.65 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 208.7, 162.8, 160.8, 152.6, 139.8 (d, J_{CF} = 3.3 Hz), 135.6, 135.5, 128.1, 128.0 (d, J_{CF} = 8.3 Hz), 126.7, 125.2, 115.5 (d, J_{CF} = 21.5 Hz), 52.8, 45.0, 25.0. $[\alpha]^{23}_D$ = -57.7, (c = 0.89, $CHCl_3$). HPLC analysis: 95% ee, Chiralcel OB-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 19.0 min, $t_{[minor]}$ = 27.0 min.

Methyl 4-(2-methyl-1-oxo-2,3-dihydro-1*H*-inden-2-yl)benzoate (Table 2, Entry 6)



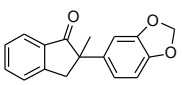
This reaction was conducted at 60 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc). The title compound was isolated as a white solid in 41% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, 2H, J_{HH} = 8.5 Hz), 7.83 (d, 1H, J_{HH} = 7.5 Hz), 7.67 (td, 1H, J_{HH} = 7.7 Hz, J_{HH} = 1.1 Hz), 7.51 (d, 1H, J_{HH} = 7.8 Hz), 7.44 (t, 1H, J_{HH} = 7.7 Hz), 7.39 (d, 1H, J_{HH} = 8.5 Hz), 3.89 (s, 3H), 3.59 (d, 1H, J_{HH} = 17.4 Hz), 3.34 (d, 1H, J_{HH} = 17.3 Hz), 1.68 (s, 3H). $^{13}C\{^1H\}$ NMR (126.7 Hz, $CDCl_3$): 208.1, 167.1, 152.5, 149.3, 135.6, 130.1, 128.7, 128.2, 126.7, 126.5, 125.2, 53.5, 52.3, 44.9, 24.8. $[\alpha]^{22}_D$ = -40.7º (c = 0.29, $CHCl_3$). HPLC analysis: 99% ee, Chiralcel AD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 29.9 min, $t_{[minor]}$ = 33.1 min. HRMS (ESI) exact mass calc'd for $C_{18}H_{16}O_3$: m/z 281.1178 ($[M+H]^+$). Found: 281.1176 ($[M+H]^+$).

2-Methyl-2-phenyl-2,3-dihydro-*1H*-inden-1-one (Table 2, Entry 7)



This reaction was conducted at 60 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc). The titled compound was isolated as a colorless liquid in 82% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, 1H, J_{HH} = 7.7 Hz), 7.65 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.0 Hz), 7.50 (d, 2H, J_{HH} = 7.8 Hz), 7.42 (t, 1H, J_{HH} = 7.4 Hz), 7.31 (m, 4H), 7.22 (m, 1H), 3.61 (d, 1H, J_{HH} = 17.3 Hz), 3.32 (d, 1H, J_{HH} = 17.3 Hz), 1.67 (s, 3H). $^{13}C\{^1H\}$ NMR (100.6 Hz, $CDCl_3$): 208.6, 152.5, 143.9, 135.6, 135.1, 128.6, 127.7, 126.6, 126.4, 126.1, 124.9, 53.1, 44.8, 24.5. $[\alpha]^{24}_D$ = -53.0º (c = 0.83, $CHCl_3$). HPLC analysis: 96% ee, Chiralcel OB-H column, 3% isopropanol in hexane, 0.5 mL/min low rate, 254 nm UV lamp, $t_{[major]}$ = 24.8 min, $t_{[minor]}$ = 30.6 min.

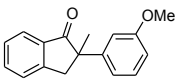
2-(Benzo[*d*][1,3]dioxol-5-yl)-2-methyl-2,3-dihydro-*1H*-inden-1-one (Table 2, Entry 8)



This reaction was conducted at 80 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→90:10 hexanes/EtOAc). The title compound was isolated as a colorless liquid in 73% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, 1H, J_{HH} = 7.6 Hz), 7.64 (td, 1H, J_{HH} = 7.4 Hz, J_{HH} = 1.0 Hz), 7.48

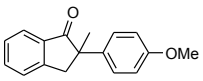
(d, 1H, J_{HH} = 7.8 Hz), 7.42 (t, 1H, J_{HH} = 7.4 Hz), 6.77 (m, 2H), 6.73 (t, 1H, J_{HH} = 8.1 Hz), 5.79 (s, 2H), 3.53 (d, 1H, J_{HH} = 17.5 Hz), 3.28 (d, 1H, J_{HH} = 17.5 Hz), 1.61 (s, 3H). $^{13}C\{^1H\}$ NMR (100.6 Hz, $CDCl_3$): 208.8, 152.7, 148.1, 146.4, 137.9, 135.7, 135.4, 128.0, 126.6, 125.2, 119.4, 108.3, 107.2, 101.2, 53.0, 45.2, 24.8. $[\alpha]^{24}_D$ = -85.3º (c = 0.63, $CHCl_3$). HPLC analysis: 98% ee, Chiralcel AD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 22.4 min, $t_{[minor]}$ = 24.5 min. HRMS (ESI) exact mass calc'd for $C_{17}H_{14}O_3$: m/z 267.1021 ($[M+H]^+$). Found: 267.1022 ($[M+H]^+$).

2-(3-Methoxyphenyl)-2-methyl-2,3-dihydro-*1H*-inden-1-one (Table 2, Entry 9)



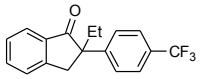
This reaction was conducted at 60 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→90:10 hexanes/EtOAc). The title compound was isolated as a white solid in 79% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, 1H, J_{HH} = 7.7 Hz), 7.64 (t, 1H, J_{HH} = 7.5 Hz), 7.49 (d, 1H, J_{HH} = 7.7 Hz), 7.42 (t, 1H, J_{HH} = 7.3 Hz), 7.22 (t, 1H, J_{HH} = 8.0 Hz), 6.89 (s, 1H), 6.88 (d, 1H, J_{HH} = 8.6 Hz), 6.76 (dd, 1H, J_{HH} = 8.3 Hz, J_{HH} = 2.5 Hz), 3.77 (s, 3H), 3.59 (d, 1H, J_{HH} = 17.3 Hz), 3.30 (d, 1H, J_{HH} = 17.3 Hz), 1.65 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 208.7, 159.9, 152.8, 145.7, 135.8, 135.4, 129.8, 128.0, 126.6, 125.2, 118.8, 112.9, 111.7, 55.4, 53.3, 45.1, 24.6. $[\alpha]^{24}_D$ = -58.2º (c = 0.78, $CHCl_3$). HPLC analysis: 96% ee, Chiralcel AD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 16.0 min, $t_{[minor]}$ = 17.3 min. Anal. Calc'd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.85; H, 6.59.

2-(4-Methoxyphenyl)-2-methyl-2,3-dihydro-*1H*-inden-1-one (Table 2, Entry 10)



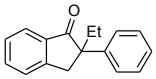
This reaction was conducted at 60 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→90:10 hexanes/EtOAc). The title compound was isolated as a white solid in 81% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, 1H, J_{HH} = 7.7 Hz), 7.64 (td, 1H, J_{HH} = 7.6 Hz, J_{HH} = 1.1 Hz), 7.49 (d, 1H, J_{HH} = 7.7 Hz), 7.41 (t, 1H, J_{HH} = 7.4 Hz), 7.23 (m, 2H), 6.83 (m, 2H), 3.77 (s, 3H), 3.57 (d, 1H, J_{HH} = 17.4 Hz), 3.29 (d, 1H, J_{HH} = 17.4 Hz), 1.64 (s, 3H). $^{13}C\{^1H\}$ NMR (100.6 Hz, $CDCl_3$): 208.7, 158.3, 152.5, 135.9, 135.6, 135.0, 127.7, 127.2, 126.3, 124.9, 113.9, 55.2, 52.5, 44.7, 24.6. $[\alpha]^{24}_D$ = -92.2 (c = 0.67, $CHCl_3$). HPLC analysis: 96% ee, Chiralcel AD-H column, 10% isopropanol in hexane, 0.5 mL/min low rate, 254 nm UV lamp, $t_{[major]}$ = 19.5 min, $t_{[minor]}$ = 23.9 min.

2-Ethyl-2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-inden-1-one (Table 2, Entry 11)



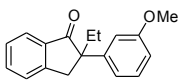
This reaction was conducted at 80 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc). The title compound was isolated as a colorless liquid in 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, 1H, J_{HH} = 7.6 Hz), 7.66 (td, 1H, J_{HH} = 7.5 Hz, 1.1 Hz), 7.56 (m, 4H), 7.53 (dt, 1H, J_{HH} = 7.7 Hz, J_{HH} = 1.0 Hz), 7.42 (t, 1H, J_{HH} = 7.5 Hz), 3.59 (d, 1H, J_{HH} = 17.5 Hz), 3.43 (d, 1H, J_{HH} = 17.5 Hz), 2.18 (dq, 1H, J_{HH} = 13.8 Hz, J_{HH} = 7.5 Hz), 2.08 (dq, 1H, J_{HH} = 13.8 Hz, J_{HH} = 7.5 Hz). 0.85 (t, 3H, J_{HH} = 7.3 Hz). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 207.5, 152.6, 146.6, 136.3, 135.6, 129.0 (q, J_{CF} = 32.3 Hz), 128.1, 127.4, 126.4, 125.6 (q, J_{CF} = 3.9 Hz), 124.9, 124.4 (q, J_{CF} = 271.6 Hz), 57.7, 40.6, 31.8, 9.4. $[\alpha]^{25}_D$ = -69.0º, (c = 0.99, $CHCl_3$). HPLC analysis: 92% ee, Chiralcel OJ column, 2% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 13.8 min, $t_{[minor]}$ = 12.0 min. Anal. Calc'd for $C_{18}H_{15}F_3O$: C, 71.04; H, 4.97. Found: C, 70.97; H, 5.06.

2-Ethyl-2-phenyl-2,3-dihydro-1*H*-inden-1-one (Table 2, Entry 12)



This reaction was conducted at 80 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc).The title compound was isolated as a colorless liquid in 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, 1H, J_{HH} = 7.7 Hz), 7.63 (td, 1H, J_{HH} = 7.6 Hz, J_{HH} = 1.0 Hz), 7.52 (d, 1H, J_{HH} = 7.7 Hz), 7.41 (m, 3H), 7.31 (m, 2H), 7.22 (t, 1H, J_{HH} = 7.3 Hz), 3.61 (d, 1H, J_{HH} = 17.6 Hz), 3.40 (d, 1H, J_{HH} = 17.6 Hz), 2.20 (dq, 1H, J_{HH} = 13.9 Hz, J_{HH} = 7.3 Hz), 2.08 (dq, 1H, J_{HH} = 13.9 Hz, J_{HH} = 7.3 Hz). 0.86 (t, 3H, J_{HH} = 7.4 Hz). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 208.3, 153.0, 142.5, 136.7, 135.2, 128.7, 127.9, 126.9, 126.8, 126.4, 124.8, 57.8, 40.8, 31.4, 9.5. $[\alpha]^{26}_D$ = -87.2º, (c = 0.94, $CHCl_3$). HPLC analysis: 95% ee, Chiralcel AD-H column, 2% isopropanol in hexane, 0.5 mL/min flow rare, 254 nm UV lamp, $t_{[major]}$ = 20.7 min, $t_{[minor]}$ = 22.5 min. Anal. Calc'd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.43; H, 6.98.

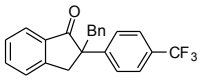
2-Ethyl-2-(3-methoxyphenyl)-2,3-dihydro-1*H*-inden-1-one (Table 2, Entry 13)



This reaction was conducted at 80 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc). The title compound was isolated as a colorless liquid in 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, 1H, J_{HH} = 7.8 Hz), 7.62 (td, 1H, J_{HH} = 7.4 Hz, J_{HH} = 1.1 Hz), 7.50 (d, 1H, J_{HH} = 7.7 Hz), 7.39 (t, 1H, J_{HH} = 7.4 Hz), 7.23 (t, 1H, J_{HH} = 8.0 Hz), 6.99 (m, 2H), 6.76 (dd, 1H, J_{HH} = 8.2 Hz, J_{HH} = 2.5 Hz), 3.79 (s, 3H), 3.59 (d, 1H, J_{HH} = 17.4 Hz), 3.37 (d, 1H, J_{HH} = 17.4 Hz), 2.17 (dq, 1H, J_{HH} = 13.7 Hz, J_{HH} = 7.4 Hz), 2.06 (dq, 1H, J_{HH} = 13.7 Hz, J_{HH}

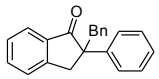
= 7.4 Hz). 0.86 (t, 3H, J_{HH} = 7.4 Hz). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 208.2, 159.9, 153.0, 144.2, 136.7, 135.2, 129.6, 127.8, 126.4, 124.8, 119.4, 113.4, 111.6, 57.7, 40.8, 31.5, 9.5. $[\alpha]^{26}_D$ = -91.9º, (c = 0.87, $CHCl_3$). HPLC analysis: 94% ee, Chiralcel AD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rare, 254 nm UV lamp, $t_{[major]}$ = 14.9 min, $t_{[minor]}$ = 17.4 min. Anal. Calc'd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.96; H, 6.91.

2-Benzyl-2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-inden-1-one (Table 2, Entry 14)



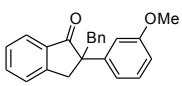
This reaction was conducted at 80 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc). The title compound was isolated as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, 1H, J_{HH} = 7.6 Hz), 7.59 (m, 5H), 7.40 (d, 1H, J_{HH} = 7.6 Hz), 7.35 (t, 1H, J_{HH} = 7.6 Hz), 7.15 (m, 3H), 7.00 (m, 2H), 3.58 (d, 1H, J_{HH} = 17.2 Hz), 3.54 (d, 1H, J_{HH} = 17.2 Hz), 3.51 (d, 1H, J_{HH} = 13.7 Hz), 3.33 (d, 1H, J_{HH} = 13.7 Hz). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 206.8, 152.4, 146.3, 136.8, 136.0, 135.5, 130.5, 129.3 (q, J_{CF} = 32.3 Hz), 128.4, 128.0, 127.6, 127.0, 126.3, 125.6 (q, J_{CF} = 3.8 Hz), 124.9, 124.3 (q, J_{CF} = 272.6 Hz), 58.4, 44.7, 38.9. $[\alpha]^{25}_D$ = -81.6º, (c = 0.97, $CHCl_3$). HPLC analysis: 98% ee, Chiralcel AD-H column, 2% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 24.9 min, $t_{[minor]}$ = 31.2 min. Anal. Calc'd for $C_{23}H_{17}F_3O$: C, 75.40; H, 4.68. Found: C, 75.59; H, 4.90.

2-Benzyl-2-phenyl-2,3-dihydro-1*H*-inden-1-one (Table 2, Entry 15)



This reaction was conducted at 80 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→96:4 hexanes/EtOAc). The title compound was isolated as a white solid in 77% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, 1H, J_{HH} = 7.6 Hz), 7.53 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.0 Hz), 7.47 (m, 2H), 7.37 (d, 1H, J_{HH} = 7.5 Hz), 7.32 (m, 3H), 7.24 (t, 1H, J_{HH} = 7.4 Hz), 7.14 (m, 3H), 7.02 (m, 2H), 3.55 (d, 1H, J_{HH} = 17.1 Hz), 3.54 (d, 1H, J_{HH} = 13.7 Hz), 3.50 (d, 1H, J_{HH} = 17.1 Hz), 3.34 (d, 1H, J_{HH} = 13.7 Hz). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 207.6, 152.8, 142.3, 137.5, 136.3, 135.2, 130.5, 128.7, 128.2, 127.7, 127.1, 127.0, 126.7, 126.2, 124.8, 58.5, 44.4, 39.0. $[\alpha]^{25}_D$ = -114.2º, (c = 1.01, $CHCl_3$). HPLC analysis: 98% ee, Chiralcel AD-H column, 3% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 22.5 min, $t_{[minor]}$ = 28.9 min. HRMS (ESI) exact mass calc'd for $C_{22}H_{18}O$: m/z 299.1436 ($[M+H]^+$). Found: 299.1434 ($[M+H]^+$).

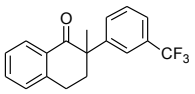
2-Benzyl-2-(3-methoxyphenyl)-2,3-dihydro-1*H*-inden-1-one (Table 2, Entry 16)



This reaction was conducted at 80 ºC. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→90:10

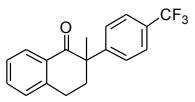
hexanes/EtOAc). The title compound was isolated as a yellow liquid in 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, 1H, J_{HH} = 7.7 Hz), 7.53 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.1 Hz), 7.37 (d, 1H, J_{HH} = 7.6 Hz), 7.32 (t, 1H, J_{HH} = 7.4 Hz), 7.24 (t, 1H, J_{HH} = 8.1 Hz), 7.15 (m, 3H), 7.08 (t, 1H, J_{HH} = 2.3 Hz), 7.05 (m, 3H), 6.88 (dd, 1H, J_{HH} = 8.3 Hz, J_{HH} = 2.4 Hz), 3.55 (d, 1H, J_{HH} = 17.2 Hz), 3.54 (d, 1H, J_{HH} = 13.2 Hz), 3.50 (d, 1H, J_{HH} = 17.2 Hz), 3.35 (d, 1H, J_{HH} = 13.2 Hz). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 207.5, 159.9, 152.8, 144.0, 137.5, 136.3, 135.2, 130.6, 129.7, 128.3, 127.8, 126.8, 126.3, 124.8, 119.6, 113.6, 112.1, 58.5, 44.4, 39.1. $[\alpha]^{25}_D$ = -94.0º, (c = 0.44, $CHCl_3$). HPLC analysis: 98% ee, Chiralcel AD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 18.2 min, $t_{[minor]}$ = 22.2 min. Anal. Calc'd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.15; H, 6.29.

2-Methyl-2-(3-(trifluoromethyl)phenyl)-3,4-dihydronaphthalen-1(2*H*)-one (Table 2, Entry 17)



This reaction was conducted at 80 ˚C for 48 h. The crude mixture was purified by preparative TLC (petroleum ether: CH_2Cl_2 = 7:3), yielding the title compound as a colorless liquid in 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, 1H, J_{HH} = 7.8 Hz), 7.56 (s, 1H), 7.44 (m, 1H), 7.46 (t, 1H, J_{HH} = 7.5 Hz), 7.40 (m, 2H), 7.34 (t, 1H, J_{HH} = 7.4 Hz), 7.16 (d, 1H, J_{HH} = 7.7 Hz), 2.91 (dt, 1H, J_{HH} = 12.5 Hz, J_{HH} = 4.8 Hz), 2.83 (ddd, 1H, J_{HH} = 17.3Hz, J_{HH} = 10.8 Hz, J_{HH} = 4.4 Hz), 2.65 (dt, 1H, J_{HH} = 14.2 Hz, J_{HH} = 4.4 Hz), 2.30 (ddd, 1H, J_{HH} = 14.2 Hz, J_{HH} = 10.8 Hz, J_{HH} = 4.8 Hz), 1.57 (s, 3H). ^{13}C NMR (125.6 Hz, $CDCl_3$): 200.7, 143.7, 143.5, 133.7, 132.6, 131.2 (q, J_{CF} = 32.2 Hz), 130.3, 129.3, 129.0, 128.4, 127.1, 124.4 (q, J_{CF} = 272.8 Hz), 123.9 (q, J_{CF} = 3.9 Hz), 123.3 (q, J_{CF} = 3.9 Hz), 50.6, 36.3, 26.8, 26.2. $[\alpha]^{23}_D$ = 191.3˚ (c = 1.30, $CHCl_3$). HPLC analysis: 96% ee, Chiralcel OJ-H column, 2% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 12.7 min, $t_{[minor]}$ = 17.6 min. HRMS (ESI) exact mass calc'd for $C_{18}H_{15}F_3O$: m/z 305.1153 ($[M+H]^+$). Found: 305.1154 ($[M+H]^+$).

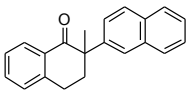
2-Methyl-2-(4-(trifluoromethyl)phenyl)-3,4-dihydronaphthalen-1(2*H*)-one (Table 2, Entry 18)



This reaction was conducted at 80 ˚C for 48 h. The crude mixture was purified by preparative TLC (petroleum ether: CH_2Cl_2 = 7:3), yielding the title compound as a colorless liquid in 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (dd, 1H, J_{HH} = 7.8 Hz, J_{HH} = 1.2 Hz), 7.55 (d, 2H, J_{HH} = 8.3 Hz), 7.46 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.4 Hz), 7.37 (d, 2H, J_{HH} = 8.3 Hz), 7.34 (t, 1H, J_{HH} = 7.5 Hz), 7.16 (d, 1H, J_{HH} = 7.7 Hz), 2.89 (dt, 1H, J_{HH} = 17.2 Hz, J_{HH} = 4.6 Hz), 2.82 (ddd, 1H, J_{HH} = 17.2Hz, J_{HH} = 11.2 Hz, J_{HH} = 4.4

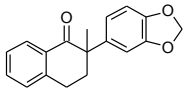
Hz), 2.64 (dt, 1H, J_{HH} = 14.1 Hz, J_{HH} = 4.4 Hz), 2.31 (ddd, 1H, J_{HH} = 14.1 Hz, J_{HH} = 11.2 Hz, J_{HH} = 4.9 Hz), 1.57 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 200.8, 146.8, 143.5, 133.7, 132.6, 129.2 (q, J_{CF} = 32.7 Hz), 129.1, 128.3, 127.0, 125.8 (q, J_{CF} = 3.9 Hz), 125.7, 124.3 (q, J_{CF} = 272.6 Hz), 50.8, 36.4, 26.8, 26.2. $[\alpha]^{23}_D$ = 164.9° (c = 1.38, $CHCl_3$). HPLC analysis: 94% ee, Chiralcel OJ-H column, 2% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 13.2 min, $t_{[minor]}$ = 20.7 min.

2-Methyl-3,4-dihydro-[2,2'-binaphthalen]-1(2*H*)-one (Table 2, Entry19)



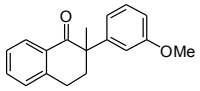
This reaction was conducted at 80 ˚C for 48 h. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc). This compound was isolated as a white solid in 76% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 8.25 (d, 1H, J_{HH} = 7.9 Hz), 7.82 (d, 1H, J_{HH} = 8.8 Hz), 7.79 (m, 1H), 7.73 (m, 1H), 7.58 (d, 1H, J_{HH} = 1.7 Hz), 7.44 (m, 4H), 7.35 (t, 1H, J_{HH} = 7.6 Hz), 7.11 (d, 1H, J_{HH} = 7.4 Hz), 2.87 (m, 2H), 2.77 (dt, 1H, J_{HH} = 14.1 Hz, J_{HH} = 4.2 Hz), 2.35 (ddd, 1H, J_{HH} = 14.1 Hz, J_{HH} = 9.8 Hz, J_{HH} = 6.5 Hz), 1.64 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 201.5, 143.8, 139.8, 133.5, 133.4, 133.0, 132.4, 128.9, 128.6, 128.3, 128.2, 127.6, 126.9, 126.3, 126.1, 125.6, 124.7, 50.9, 36.4, 27.2, 26.5. $[\alpha]^{25}_D$ = 138.6° (c = 0.58, $CHCl_3$). HPLC analysis: 90% ee, Chiralcel OB-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 50.3 min, $t_{[minor]}$ = 41.8 min. HRMS (ESI) exact mass calc'd for $C_{21}H_{18}O$: m/z 287.1436 ($[M+H]^+$). Found: 287.1435 ($[M+H]^+$).

2-(Benzo[*d*][1,3]dioxol-5-yl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (Table 2, entry 20)



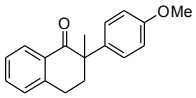
This reaction was conducted at 80 ˚C for 48 h. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc). The title compound was isolated as a white solid in 61% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 8.14 (dd, 1H, J_{HH} = 7.9 Hz, J_{HH} = 1.1 Hz), 7.41 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.3 Hz), 7.30 (t, 1H, J_{HH} = 7.4 Hz), 7.12 (d, 1H, J_{HH} = 7.7 Hz), 6.76 (d, 1H, J_{HH} = 1.8 Hz), 6.68 (d, 1H, J_{HH} = 8.2 Hz), 6.62 (dd, 1H, J_{HH} = 8.2 Hz, J_{HH} = 1.8 Hz), 5.89 (dd, 2H, J_{HH} = 6.4 Hz, J_{HH} = 1.4 Hz), 2.88 (ddd, 1H, J_{HH} = 16.9 Hz, J_{HH} = 11.7 Hz, J_{HH} = 4.4 Hz), 2.80 (dt, 1H, J_{HH} = 16.9 Hz, J_{HH} = 4.3 Hz), 2.53 (ddd, 1H, J_{HH} = 14.0 Hz, J_{HH} = 4.1 Hz, J_{HH} = 3.8 Hz), 2.23 (ddd, 1H, J_{HH} = 14.0 Hz, J_{HH} = 11.7 Hz, J_{HH} = 4.8 Hz), 1.49 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 201.4, 148.1, 146.4, 143.8, 136.1, 133.4, 132.8, 128.9, 128.2, 126.8, 119.8, 108.4, 107.3, 101.2, 50.4, 36.5, 27.5, 26.3. $[\alpha]^{23}_D$ = 231.4° (c = 1.24, $CHCl_3$). HPLC analysis: 96% ee, Chiralcel AD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 17.1 min, $t_{[minor]}$ = 14.5 min.

2-(4-Methoxyphenyl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (Table 2, Entry 21)



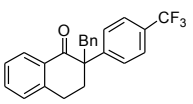
This reaction was conducted at 80 ˚C for 48 h. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc). The title compound was isolated as a colorless liquid in 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (dd, 1H, J_{HH} = 7.9 Hz, J_{HH} = 1.2 Hz), 7.41 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.4 Hz), 7.30 (t, 1H, J_{HH} = 7.4 Hz), 7.19 (t, 1H, J_{HH} = 8.0 Hz), 7.11 (d, 1H, J_{HH} = 7.6 Hz), 6.81 (d, 1H, J_{HH} = 8.2 Hz), 6.79 (t, 1H, J_{HH} = 1.8 Hz), 6.74 (dd, 1H, J_{HH} = 8.2 Hz , J_{HH} = 2.4 Hz), 2.88 (ddd, 1H, J_{HH} = 17.5 Hz, J_{HH} = 11.8 Hz, J_{HH} = 4.4 Hz), 2.80 (dt, 1H, J_{HH} = 17.0 Hz, J_{HH} = 4.0 Hz), 2.60 (dt, 1H, J_{HH} = 14.0 Hz, J_{HH} = 4.0 Hz), 2.25 (ddd, 1H, J_{HH} = 14.0 Hz, J_{HH} = 11.8 Hz, J_{HH} = 4.9 Hz), 1.53 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 201.4, 160.0, 144.0, 143.9, 133.3, 132.9, 129.7, 128.9, 128.2, 126.8, 119.1, 113.2, 111.6, 55.4, 50.7, 36.4, 27.3, 26.4. $[\alpha]^{23}_D$ = 215.7˚ (c = 1.46, $CHCl_3$). HPLC analysis: 92% ee, Chiralcel AD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 12.5 min, $t_{[minor]}$ = 11.6 min. HRMS (ESI) exact mass calc'd for $C_{18}H_{18}O_2$: m/z 267.1385 ($[M+H]^+$). Found: 267.1384 ($[M+H]^+$).

2-(4-Methoxyphenyl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (Table 2, Entry 22)



This reaction was conducted at 80 ˚C for 48 h. The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc). The title compound was isolated as a colorless liquid in 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (dd, 1H, J_{HH} = 7.8 Hz, J_{HH} = 1.1 Hz), 7.42 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.4 Hz), 7.32 (t, 1H, J_{HH} = 7.5 Hz), 7.16 (d, 2H, J_{HH} = 8.8 Hz), 7.13 (d, 1H, J_{HH} = 7.5 Hz), 6.82 (d, 2H, J_{HH} = 8.9 Hz), 2.84 (m, 2H), 2.59 (dt, 1H, J_{HH} = 14.0 Hz, J_{HH} = 4.2 Hz), 2.26 (ddd, 1H, J_{HH} = 14.0 Hz, J_{HH} = 11.2 Hz, J_{HH} = 5.1 Hz), 1.52 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 201.6, 158.5, 143.8, 134.2, 133.3, 132.9, 128.9, 128.2, 127.7, 126.8, 114.2, 55.4, 50.0, 36.5, 27.4, 26.3. $[\alpha]^{23}_D$ = 229.3˚ (c = 0.64, $CHCl_3$). HPLC analysis: 96% ee, Chiralcel AD-H column, 10% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 15.6 min, $t_{[minor]}$ = 13.9 min. HRMS (ESI) exact mass calc'd for $C_{18}H_{18}O_2$: m/z 267.1385 ($[M+H]^+$). Found: 267.1384 ($[M+H]^+$).

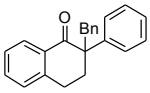
2-Benzyl-2-(4-(trifluoromethyl)phenyl)-3,4-dihydronaphthalen-1(2*H*)-one (Table 2, Entry 23)



This reaction was conducted at 80 ˚C for 48 h. The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column,

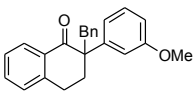
100:0→97:3 hexanes/EtOAc). The title compound was isolated as a white solid in 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, 1H, J_{HH} = 7.8 Hz), 7.54 (d, 2H, J_{HH} =8.4 Hz), 7.42 (t, 1H, J_{HH} = 8.1 Hz), 7.32 (t, 1H, J_{HH} = 7.7 Hz), 7.29 (d, 2H, 8.4 Hz), 7.21 (t, 3H, J_{HH} = 3.0 Hz), 7.09 (d, 1H, J_{HH} = 7.6 Hz), 6.93 (m, 2H), 3.43 (d, 1H, J_{HH} = 13.6 Hz), 3.21 (d, 1H, J_{HH} = 13.6 Hz), 2.85 (m, 2H), 2.65 (ddd, 1H, J_{HH} = 14.4 Hz, J_{HH} = 3.7 Hz, J_{HH} = 3.5 Hz), 2.30 (ddd, 1H, J_{HH} = 14.4 Hz, J_{HH} = 10.4 Hz, J_{HH} = 7.2 Hz). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 199.1, 143.3, 142.9, 137.1, 133.7, 132.8, 131.3, 129.5 (q, J_{CF} = 33.2 Hz), 128.9, 128.6, 128.1 (two peaks overlap), 126.9, 126.8, 12.5 (q, J_{CF} = 3.6 Hz), 124.3 (q, J_{CF} = 272.0 Hz), 54.8, 46.4, 31.0, 25.8. $[\alpha]^{22}_D$ = 240.3º, (c = 1.18, $CHCl_3$). HPLC analysis: 94% ee, Chiralcel AD-H column, 2% isopropanol in hexane, 0.5 mL/min flow rare, 254 nm UV lamp, $t_{[major]}$ = 14.3 min, $t_{[minor]}$ = 12.5 min. HRMS (ESI) exact mass calc'd for $C_{24}H_{19}F_3O$: m/z 381.1466 ($[M+H]^+$). Found: 381.1469 ($[M+H]^+$).

2-Benzyl-2-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (Table 2, Entry 24)



This reaction was conducted at 80 ˚C for 48 h. The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→97:3 hexanes/EtOAc). The title compound was isolated as a white solid in 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (dd, 1H, J_{HH} = 8.1 Hz, J_{HH} = 1.2 Hz), 7.38 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.5 Hz), 7.27 (m, 4H), 7.19 (m, 5H), 7.06 (d, 1H, 7.8 Hz), 6.94 (m, 2H), 3.43 (d, 1H, J_{HH} = 13.4 Hz), 3.19 (d, 1H, J_{HH} = 13.4 Hz), 2.92 (ddd, 1H, J_{HH} = 17.2 Hz, J_{HH} = 13.0 Hz, J_{HH} = 4.3 Hz), 2.80 (ddd, 1H, J_{HH} = 17.1 Hz, J_{HH} = 4.3 Hz, J_{HH} = 2.7 Hz), 2.61 (ddd, 1H, J_{HH} = 14.2 Hz, J_{HH} = 4.3 Hz, J_{HH} = 2.7 Hz), 2.24 (ddd, 1H, J_{HH} = 14.2 Hz, J_{HH} = 13.0 Hz, J_{HH} = 4.7 Hz). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 199.7, 143.5, 138.6, 137.8 (two peaks overlap), 133.4, 133.1, 131.4, 128.8, 128.6, 128.4, 127.9, 127.6, 127.3, 126.7, 126.5, 54.8, 46.6, 31.1, 26.0. $[\alpha]^{22}_D$ = 232.5º, (c = 0.32, $CHCl_3$). HPLC analysis: 98% ee, Chiralcel AD-H column, 3% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 14.7 min, $t_{[minor]}$ = 11.8 min. HRMS (ESI) exact mass calc'd for $C_{23}H_{20}O$: m/z 313.1952 ($[M+H]^+$). Found: 313.1951 ($[M+H]^+$).

2-Benzyl-2-(3-methoxyphenyl)-3,4-dihydronaphthalen-1(2*H*)-one (Table 2, Entry 25)



This reaction was conducted at 80 ˚C for 48 h. The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→95:5 hexanes/EtOAc). The title compound was isolated as a white solid in 53% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, 1H, J_{HH} = 8.0 Hz), 7.38 (t, 1H, J_{HH} = 7.7 Hz), 7.29 (t, 1H, J_{HH} = 7.5 Hz), 7.20 (m, 4H), 7.06 (d, 1H, 7.7 Hz), 6.98 (m, 2H), 6.78 (m, 2H), 6.73 (m, 1H), 3.73 (2, 3H), 3.44 (d, 1H, J_{HH} = 13.6 Hz), 3.19 (d, 1H, J_{HH} = 13.6 Hz), 2.96 (ddd, 1H, J_{HH} = 17.3 Hz, J_{HH} = 13.0 Hz, J_{HH} = 4.5 Hz), 2.79 (ddd, 1H, J_{HH} = 17.3 Hz, J_{HH} = 4.2

Hz, J_{HH} = 2.9 Hz), 2.58 (ddd, 1H, J_{HH} = 14.3 Hz, J_{HH} = 4.2 Hz, J_{HH} = 2.9 Hz), 2.22 (ddd, 1H, J_{HH} = 14.3 Hz, J_{HH} = 13.0 Hz, J_{HH} = 4.5 Hz). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 199.5, 159.9, 143.6, 140.3, 137.8, 133.4, 133.0, 131.4, 129.5, 128.8, 128.5, 127.9, 126.7, 126.5, 120.1, 113.9, 112.4, 55.4, 54.9, 46.5, 31.2, 26.0. $[\alpha]^{22}_D$ = 258.8º, (c = 0.36, $CHCl_3$). HPLC analysis: 99% ee, Chiralcel AD-H column, 10% isopropanol in hexane, 1.0 mL/min flow rare, 254 nm UV lamp, $t_{[major]}$ = 11.3 min, $t_{[minor]}$ = 13.3 min. HRMS (ESI) exact mass calc'd for $C_{24}H_{22}O_2$: m/z 343.1698 ($[M+H]^+$). Found: 343.1699 ($[M+H]^+$).

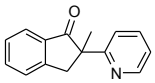
Ni-Catalyzed Arylation of 2-Methyl-1-Indanone with Chlorobenzene on a 2.00 mmol Scale

In a drybox, a 20-mL screw-capped vial was charged with $Ni(COD)_2$ (27.5 mg, 0.100 mmol), [(*R*)-BINAP (74.7 mg, 0.120 mmol), NaO^{t}Bu (384 mg, 4.00 mmol), PhCl (450 mg, 4.00), 2-methyl-1-indanone (292 mg, 2.00 mmol), a magnetic stirring bar, and toluene (10 mL). The vial was sealed with a cap containing a PTFE septum and taken out of the drybox. The reaction mixture was stirred in an oil bath preheated to 60 ºC for 36 h and then cooled to room temperature. The mixture was quenched with a saturated aqueous NH_4Cl solution (10 mL) and extracted with Et_2O (2 × 15 mL). The combined extract was dried over Na_2SO_4, filtered, and dried under reduced pressure. The crude product was purified with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc), yielding the 2-methyl-2-phenyl-2,3-dihydro-*1H*-inden-1-one (354 mg, 1.59 mmol, 80%) as a colorless liquid. The ee of this product was determined to be 96% by chiral HPLC analysis.

The General Procedure for the α-Heteroarylation Reactions of 2-Methyl-1-indanone and 2-Methyl-1-tetralone

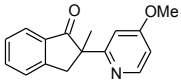
In a drybox, a 4-mL screw-capped vial was charged with $Ni(COD)_2$ (5.5 mg, 0.020 mmol), (*R*)-DIFOURPHOS (16.4 mg, 0.024 mmol), and toluene (1 mL), and the mixture was stirred for 30 min. The resulting solution was added to another 4-mL screw-capped vial containing 2-methyl-1-indanone (29.2 mg, 0.200 mmol) or 2-methyl-1-tetralone (32.0 mg, 0.200 mmol), chloro-heteroarene (0.400 mmol), and NaO^{t}Bu (38.4 mg, 0.400 mmol). The vial was sealed with a cap containing a PTFE spetum and taken out of the drybox. The mixture was stirred for 28 h in an oil bath preheated to 70 ºC and then cooled to room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution and extracted with Et_2O (2 × 10 mL). The combined extract was dried over Na_2SO_4, filtered, and dried under reduced pressure. The crude product was purified with a CombiFlash system with 5-20% ethyl acetate in hexanes as eluent. The conditions for chromatography and the data for characterization of the products are given below.

2-Methyl-2-(pyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (Table 3, Entry 2)



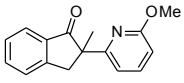
The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→90:10 hexanes/EtOAc). This compound was isolated as a colorless liquid in 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (ddd, 1H, J_{HH} = 4.8 Hz, J_{HH} = 1.8 Hz, J_{HH} = 0.8 Hz), 7.79 (d, 1H, J_{HH} = 7.6 Hz), 7.63 (td, 1H, J_{HH} = 7.7 Hz, J_{HH} = 1.8 Hz), 7.61 (td, 1H, J_{HH} = 7.4 Hz, J_{HH} = 1.0 Hz), 7.50 (t, 2H, J_{HH} = 7.5 Hz), 7.38 (t, 1H, J_{HH} = 7.6 Hz), 7.12 (ddd, 1H, J_{HH} = 7.5 Hz, J_{HH} = 4.8 Hz, J_{HH} = 1.0 Hz), 4.09 (d, 1H, J_{HH} = 17.3Hz), 3.19 (d, 1H, J_{HH} = 17.3Hz), 1.68 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 208.6, 162.5, 153.6, 149.4, 136.8, 135.5, 135.3, 127.8, 126.8, 125.0, 122.0, 121.3, 56.0, 42.6, 24.6. $[\alpha]^{22}_D$ = -71.6º, (c = 0.91, $CHCl_3$). HPLC analysis: 97% ee, Chiralcel OB-H column, 5% isopropanol in hexane, 1.0 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 12.5 min, $t_{[minor]}$ = 18.1 min. HRMS (ESI) exact mass calc'd for $C_{15}H_{13}NO$: m/z 224.1075 ($[M+H]^+$). Found: 224.1083 ($[M+H]^+$).

2-Methyl-2-(4-methoxypyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (Table 3, Entry 3)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→80:20 hexanes/EtOAc). This compound was isolated as a colorless solid in 54% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (d, 1H, J_{HH} = 5.8 Hz), 7.80 (d, 1H, J_{HH} = 7.8 Hz), 7.62 (t, 1H, J_{HH} = 7.6 Hz), 7.50 (d, 1H, J_{HH} = 7.8 Hz), 7.39 (t, 1H, J_{HH} = 7.5 Hz), 7.08 (d, 1H, J_{HH} = 2.4 Hz), 6.67 (dd, 1H, J_{HH} = 5.6 Hz, J_{HH} = 2.4 Hz), 4.08 (d, 1H, J_{HH} = 17.3 Hz), 3.85 (s, 3H), 3.19 (d, 1H, J_{HH} = 17.3Hz), 1.67 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 208.5, 166.4, 164.3, 153.6, 150.6, 135.5, 135.3, 127.7, 126.8, 125.0, 108.0, 107.7, 55.9, 55.3, 42.6, 24.7. $[\alpha]^{25}_D$ = -106.0º, (c = 0.70, $CHCl_3$). HPLC analysis: 91% ee, Chiralcel AD-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 30.7 min, $t_{[minor]}$ = 33.4 min. HRMS (ESI) exact mass calc'd for $C_{16}H_{15}NO_2$: m/z 254.1181 ($[M+H]^+$). Found: 254.1172 ($[M+H]^+$).

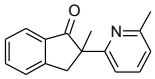
2-Methyl-2-(6-methoxypyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (Table 3, Entry 4)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→93:7 hexanes/EtOAc). This compound was isolated as a colorless liquid in 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, 1H, J_{HH} = 7.8 Hz), 7.62 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.1 Hz), 7.52 (dd, 1H, J_{HH} = 8.3 Hz, J_{HH} = 7.5 Hz), 7.50 (d, 1H, J_{HH} = 7.6 Hz), 7.39 (t, 1H, J_{HH} = 7.4 Hz), 7.03 (d, 1H, J_{HH} = 7.4 Hz), 6.57 (d, 1H, J_{HH} = 8.3 Hz), 4.02 (d, 1H, J_{HH} = 17.1 Hz), 3.71 (s, 3H), 3.15 (d, 1H, J_{HH} = 17.1Hz), 1.68 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 208.5, 163.3, 160.1, 153.9, 139.3, 135.9, 135.1, 127.6, 126.5, 124.8, 113.5, 108.8, 56.0, 53.2, 42.8, 23.8. $[\alpha]^{23}_D$ = -2.1º, (c = 1.02, $CHCl_3$). HPLC analysis: 41% ee, Chiralcel AD-H

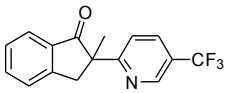
column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 12.7 min, $t_{[minor]}$ = 15.3 min. HRMS (ESI) exact mass calc'd for $C_{16}H_{15}NO_2$: m/z 224.1077 ($[M+H]^+$). Found: 224.1081 ($[M+H]^+$).

2-Methyl-2-(6-methylpyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (Table 3, Entry 5)



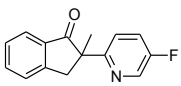
The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→90:10 hexanes/EtOAc). This compound was isolated as a colorless liquid in 87% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, 1H, J_{HH} = 7.8 Hz), 7.62 (t, 1H, J_{HH} = 7.5 Hz), 7.51 (t, 2H, J_{HH} = 7.7 Hz), 7.39 (t, 1H, J_{HH} = 7.4 Hz), 7.31 (d, 1H, J_{HH} = 7.9 Hz), 6.98 (d, 1H, J_{HH} = 7.6 Hz), 4.20 (d, 1H, J_{HH} = 17.2 Hz), 3.16 (d, 1H, J_{HH} = 17.2Hz), 2.46 (s, 3H), 1.68 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 209.0, 161.5, 157.9, 153.8, 136.8, 135.7, 135.2, 127.6, 126.8, 124.9, 121.4, 118.1, 56.1, 42.3, 25.0, 24.8. $[\alpha]^{22}_D$ = -27.5º, (c = 0.95, $CHCl_3$). HPLC analysis: 94% ee, Chiralcel AD-H column, 3% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 13.5 min, $t_{[minor]}$ = 17.5 min. HRMS (ESI) exact mass calc'd for $C_{16}H_{15}NO$: m/z 238.1232 ($[M+H]^+$). Found: 238.1223($[M+H]^+$).

2-Methyl-2-(5-(trifluoromethyl)pyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (Table 3, Entry 6)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→90:10 hexanes/EtOAc). This compound was isolated as a yellow liquid in 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.87 (s, 1H), 7.90 (dd, 1H, J_{HH} = 8.4 Hz, J_{HH} = 2.2 Hz), 7.81 (d, 1H, J_{HH} = 7.9 Hz), 7.71 (d, 1H, J_{HH} = 8.3 Hz), 7.66 (td, 1H, J_{HH} = 7.6 Hz, J_{HH} = 1.1 Hz), 7.53 (d, 1H, J_{HH} = 7.6 Hz), 7.42 (t, 1H, J_{HH} = 7.4 Hz), 4.13 (d, 1H, J_{HH} = 17.3 Hz), 3.23 (d, 1H, J_{HH} = 17.3Hz), 1.72 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 207.6, 166.3, 153.4, 146.2 (q, J_{CF} = 4.0 Hz), 135.6, 135.1, 133.9 (q, J_{CF} = 3.4 Hz), 128.0, 126.8, 125.1, 125.0 (q, J_{CF} = 32.8 Hz), 123.7 (q, J_{CF} = 271.2 Hz), 121.1, 56.2, 42.2, 24.8. $[\alpha]^{23}_D$ = -63.9º, (c = 1.02, $CHCl_3$). HPLC analysis: 81% ee, Chiralcel AD-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 13.1 min, $t_{[minor]}$ = 19.0 min. HRMS (ESI) exact mass calc'd for $C_{16}H_{12}F_3NO$: m/z 292.0949 ($[M+H]^+$). Found: 292.0943 ($[M+H]^+$).

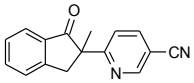
2-Methyl-2-(5-flouropyridin-2-yl)-2,3-dihydro-1*H*-inden-1-one (Table 3, Entry 7)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→95:5 hexanes/EtOAc). This compound was isolated as a colorless liquid in 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.35 (d, 1H, J_{HH} = 3.0 Hz), 7.79 (d, 1H, J_{HH} = 7.7 Hz), 7.63 (td, 1H, J_{HH} = 7.4 Hz, J_{HH} = 1.0 Hz), 7.55 (dd, 1H, J_{HH} = 8.7 Hz, J_{HF} =

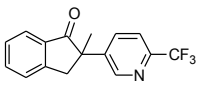
4.3 Hz), 7.51 (d, 1H, J_{HH} = 7.7 Hz), 7.40 (t, 1H, J_{HH} = 7.5 Hz), 7.36 (td, 1H, J_{HH} = 8.4 Hz, J_{HF} = 3.0 Hz), 4.08 (d, 1H, J_{HH} = 17.2 Hz), 3.20 (d, 1H, J_{HH} = 17.2Hz), 1.68 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 208.3, 159.6, 158.3, 158.2, 157.5, 153.4, 137.4, 137.2, 135.5, 135.3, 127.9, 126.8, 125.0, 123.5, 123.3, 122.2 (two peaks overlap), 55.5, 42.4, 25.1. $[\alpha]^{24}_D$ = -90.3º, (c = 1.11, $CHCl_3$). HPLC analysis: 98% ee, Chiralcel AS-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 11.6 min, $t_{[minor]}$ = 13.1 min. HRMS (ESI) exact mass calc'd for $C_{15}H_{12}FNO$: m/z 242.0981 ($[M+H]^+$). Found: 242.0974 ($[M+H]^+$).

6-(2-Methyl-1-oxo-2,3-dihydro-1*H*-inden-2-yl)nicotinonitrile (Table 3, Entry 8)



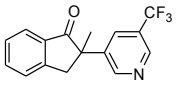
The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→90:10 hexanes/EtOAc). This compound was isolated as an off-white solid in 87% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 8.76 (d, 1H, J_{HH} = 2.1 Hz), 7.94 (dd, 1H, J_{HH} = 8.4 Hz, J_{HH} = 2.1 Hz), 7.79 (d, 1H, J_{HH} = 7.7 Hz), 7.72 (d, 1H, J_{HH} = 8.3 Hz), 7.66 (t, 1H, J_{HH} = 7.3 Hz), 7.53 (d, 1H, J_{HH} = 7.6 Hz), 7.42 (d, 1H, J_{HH} = 7.3 Hz), 4.11(d, 1H, J_{HH} = 17.2 Hz), 3.22 (d, 1H, J_{HH} = 17.2 Hz), 1.71 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 207.4, 166.7, 153.3, 151.9, 139.9, 135.8, 134.9, 128.1, 126.8, 125.1, 121.6, 117.0, 108.2, 56.5, 42.0, 24.8. $[\alpha]^{25}_D$ = -17.3º, (c = 1.22, $CHCl_3$). HPLC analysis: 21% ee, Chiralcel AS-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 37.4 min, $t_{[minor]}$ = 58.4 min. HRMS (ESI) exact mass calc'd for $C_{16}H_{12}N_2O$: m/z 249.1028 ($[M+H]^+$). Found: 249.1025 ($[M+H]^+$).

2-Methyl-2-(6-(trifluoromethyl)pyridin-3-yl)-2,3-dihydro-1*H*-inden-1-one (Table 3, Entry 9)



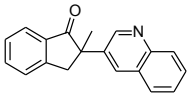
The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→90:10 hexanes/EtOAc). This compound was isolated as a colorless liquid in 76% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 8.71 (d, 1H, J_{HH} = 2.1 Hz), 7.90 (dd, 1H, J_{HH} = 8.4 Hz, J_{HH} = 2.1 Hz), 7.83 (d, 1H, J_{HH} = 7.7 Hz), 7.69 (td, 1H, J_{HH} = 7.4 Hz, J_{HH} = 1.0 Hz), 7.62 (d, 1H, J_{HH} = 8.3 Hz), 7.53 (d, 1H, J_{HH} = 7.9 Hz), 7.46 (t, 1H, J_{HH} = 7.3 Hz), 3.62 (d, 1H, J_{HH} = 17.3 Hz), 3.41 (d, 1H, J_{HH} = 17.3Hz), 1.70 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 206.8, 151.9, 148.6, 146.6 (q, J_{CF} = 35.3 Hz), 142.8, 136.0, 135.5, 135.0, 128.5, 126.8, 125.4, 121.7 (q, J_{CF} = 273.8 Hz), 120.4 (q, J_{CF} = 3.0 Hz), 51.9, 43.9, 25.3. $[\alpha]^{25}_D$ = -37.3º, (c = 0.98, $CHCl_3$). HPLC analysis: 96% ee, Chiralcel AD-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 19.5 min, $t_{[minor]}$ = 25.8 min. HRMS (ESI) exact mass calc'd for $C_{16}H_{12}F_3NO$: m/z 292.0949 ($[M+H]^+$). Found: 292.0952 ($[M+H]^+$).

2-Methyl-2-(5-(trifluoromethyl)pyridin-3-yl)-2,3-dihydro-1*H*-inden-1-one (Table 3, Entry 10)



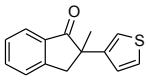
The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→80:20 hexanes/EtOAc). This compound was isolated as an off-white solid in 54% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.74 (s, 1H), 8.15 (dd, 1H, J_{HH} = 8.0 Hz, J_{HH} = 1.4 Hz), 7.83 (t, 1H, J_{HH} = 2.0 Hz), 7.49 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.4 Hz), 7.35 (t, 1H, J_{HH} = 7.6 Hz), 7.20 (d, 1H, J_{HH} = 7.7 Hz),), 3.02 (dt, 1H, J_{HH} = 17.4 Hz , J_{HH} = 5.2 Hz), 2.85 (ddd, 1H, J_{HH} = 17.4 Hz, J_{HH} = 9.7 Hz, J_{HH} = 4.3 Hz), 2.66 (ddd, 1H, J_{HH} = 14.1 Hz, J_{HH} = 5.8 Hz, J_{HH} = 4.6 Hz), 2.32 (ddd, 1H, J_{HH} = 14.1 Hz, J_{HH} = 9.7 Hz, J_{HH} = 4.6 Hz), 1.62 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 206.8, 151.7, 151.5, 145.2 (q, J_{CF} = 3.9 Hz), 139.9, 136.0, 135.0, 131.1 (q, J_{CF} = 3.9 Hz), 128.5, 126.8, 126.6 (q, J_{CF} = 33.3 Hz), 125.4, 123.6 (q, J_{CF} = 272.5 Hz), 51.6, 43.9, 25.5. $[\alpha]^{24}_D$ = -34.1° (c = 1.13, $CHCl_3$). HPLC analysis: 95% ee, Chiralcel OD-H column, 3% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 21.8 min, $t_{[minor]}$ = 19.3 min. HRMS (ESI) exact mass calc'd for $C_{16}H_{12}F_3NO$: m/z 292.0949 ($[M+H]^+$). Found: 292.0952 ($[M+H]^+$).

2-Methyl-2-(quinolin-3-yl)-2,3-dihydro-1*H*-inden-1-one (table 3, Entry 11)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→80:20 hexanes/EtOAc). This compound was isolated as an off-white solid in 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.84 (d, 1H, J_{HH} = 2.4 Hz), 8.15 (d, 1H, J_{HH} = 2.4 Hz), 8.06 (d, 1H, J_{HH} = 8.4 Hz), 7.87 (d, 1H, J_{HH} = 7.8 Hz), 7.78 (d, 1H, J_{HH} = 8.0 Hz), 7.67 (m, 2H), 7.52 (m, 2H), 7.45 (t, 1H, J_{HH} = 7.6 Hz), 3.71 (d, 1H, J_{HH} = 17.4 Hz), 3.44 (d, 1H, J_{HH} = 17.4Hz), 1.78 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 207.8, 152.2, 150.0, 147.2, 136.7, 135.8, 135.5, 132.8, 129.5, 129.2, 128.3, 128.1, 127.9, 127.1, 126.8, 125.3, 52.0, 44.3, 25.2. $[\alpha]^{24}_D$ = -98.4° (c = 0.97, $CHCl_3$). HPLC analysis: 99% ee, Chiralcel AS-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 33.8 min, $t_{[minor]}$ = 42.5 min. HRMS (ESI) exact mass calc'd for $C_{19}H_{15}NO$: m/z 274.1232 ($[M+H]^+$). Found: 274.1226 ($[M+H]^+$).

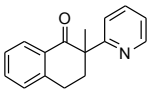
2-Methyl-2-(thiophen-3-yl)-2,3-dihydro-1*H*-inden-1-one (table 3, Entry 12)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→93:7 hexanes/EtOAc). This compound was isolated as a colorless liquid in 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, 1H, J_{HH} = 7.6 Hz), 7.64 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 0.9 Hz), 7.49 (t, 1H, J_{HH} = 7.7 Hz), 7.41 (t, 1H, J_{HH} = 7.4 Hz), 7.25 (dd, 1H, J_{HH} = 5.1 Hz, J_{HH} = 3.0 Hz), 7.16 (dd, 1H, J_{HH} = 3.0 Hz, J_{HH} = 1.4 Hz), 6.98 (dd, 1H, J_{HH} = 5.1 Hz, J_{HH} = 1.4 Hz), 3.58 (d, 1H, J_{HH} = 17.3 Hz), 3.29 (d, 1H, J_{HH} = 17.3 Hz), 1.65 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 207.8, 152.4, 144.6, 135.4, 128.0, 126.7, 126.4, 126.3, 125.2,

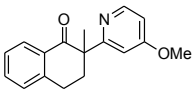
120.5, 51.4, 43.9, 25.4. $[\alpha]^{23}_{D}$ = -91.0° (c = 1.00, $CHCl_3$). HPLC analysis: 90% ee, Chiralcel AD-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 17.2 min, $t_{[minor]}$ = 18.9 min. HRMS (ESI) exact mass calc'd for $C_{14}H_{12}OS$: m/z 229.0687 ($[M+H]^+$). Found: 229.0688 ($[M+H]^+$).

2-Methyl-2-(pyridin-2-yl)-3,4-dihydronaphthalen-1(2*H*)-one (Table 3, Entry 14)



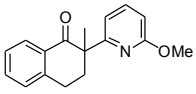
The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→90:10 hexanes/EtOAc). This compound was isolated as a colorless liquid in 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (ddd, 1H, J_{HH} = 4.8 Hz, J_{HH} = 1.8 Hz, J_{HH} = 1.0 Hz), 8.16 (dd, 1H, J_{HH} = 8.0 Hz, J_{HH} = 1.2 Hz), 7.54 (td, 1H, J_{HH} = 7.8 Hz, J_{HH} = 1.9 Hz), 7.42 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.4 Hz), 7.30 (t, 1H, J_{HH} = 7.7 Hz), 7.15 (dt, 1H, J_{HH} = 7.3 Hz, J_{HH} = 1.0 Hz), 7.13 (d, 1H, J_{HH} = 7.3 Hz), 7.10 (ddd, 1H, J_{HH} = 7.4 Hz, J_{HH} = 4.8 Hz, J_{HH} = 1.1 Hz), 2.90 (m, 2H), 2.85 (m, 1H), 2.21 (ddd, 1H, J_{HH} = 13.2 Hz, J_{HH} = 8.8 Hz, J_{HH} = 6.3 Hz), 1.58 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 201.2, 162.2, 149.4, 144.1, 136.7, 133.3, 132.9, 128.9, 128.2, 126.7, 121.9, 121.6, 53.2, 35.9, 26.4, 25.6. $[\alpha]^{22}_{D}$ = 280.0º, (c = 0.41, $CHCl_3$). HPLC analysis: 99% ee, Chiralcel OB-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 18.0 min, $t_{[minor]}$ = 21.2 min. HRMS (ESI) exact mass calc'd for $C_{16}H_{15}NO$: m/z 238.1232 ($[M+H]^+$). Found: 238.1233 ($[M+H]^+$).

2-(4-Methoxypyridin-2-yl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (Table 3, Entry 15)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→80:20 hexanes/EtOAc). This compound was isolated as a colorless sticky liquid in 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.36 (d, 1H, J_{HH} = 5.7 Hz), 8.14 (dd, 1H, J_{HH} = 8.0 Hz, J_{HH} = 1.2 Hz), 7.41 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.4 Hz), 7.29 (t, 1H, J_{HH} = 7.5 Hz), 7.13 (d, 1H, J_{HH} = 7.6 Hz), 6.66 (d, 1H, J_{HH} = 2.4 Hz), 6.64 (dd, 1H, J_{HH} = 5.7 Hz, J_{HH} = 2.4 Hz), 3.74 (s, 3H), 2.87 (m, 3H), 2.18 (m, 1H), 1.56 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 201.1, 166.3, 163.8, 150.7, 144.2, 133.3, 132.9, 128.9, 128.2, 126.7, 108.1, 107.8, 55.2, 53.2, 35.9, 26.5, 25.6. $[\alpha]^{23}_{D}$ = 167.1° (c = 0.81, $CHCl_3$). HPLC analysis: 94% ee, Chiralcel AD-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 20.3 min, $t_{[minor]}$ = 23.7 min. HRMS (ESI) exact mass calc'd for $C_{17}H_{17}NO_2$: m/z 268.1338 ($[M+H]^+$). Found: 268.1341 ($[M+H]^+$).

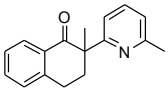
2-(6-Methoxypyridin-2-yl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (Table 3, entry 16)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→93:7 hexanes/EtOAc). This

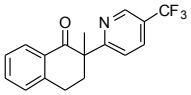
compound was isolated as a colorless liquid in 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (dd, 1H, J_{HH} = 8.0 Hz, J_{HH} = 1.2 Hz), 7.43 (dd, 1H, J_{HH} = 8.0 Hz, J_{HH} = 7.5 Hz), 7.41 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.4 Hz), 7.30 (t, 1H, J_{HH} = 7.7 Hz), 7.13 (d, 1H, J_{HH} = 7.7 Hz), 6.71 (d, 1H, J_{HH} = 7.6 Hz), 6.54 (d, 1H, J_{HH} = 8.4 Hz), 3.76 (s, 3H), 2.83 (m, 3H), 2.20 (m, 1H), 1.58 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 201.0, 163.4, 160.1, 144.1, 139.2, 133.4, 133.1, 128.9, 127.9, 126.6, 113.9, 108.7, 53.3, 52.9, 36.2, 26.5, 25.3. $[\alpha]^{23}_D$ = 109.1˚ (c = 0.93, $CHCl_3$). HPLC analysis: 35% ee, Chiralcel AD-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 12.0 min, $t_{[minor]}$ = 10.8 min. HRMS (ESI) exact mass calc'd for $C_{17}H_{17}NO_2$: m/z 268.1338 ($[M+H]^+$). Found: 268.1337 ($[M+H]^+$).

2-Methyl-2-(6-methylpyridin-2-yl)-3,4-dihydronaphthalen-1(2*H*)-one (Table 3, Entry 17)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→90:10 hexanes/EtOAc). This compound was isolated as a colorless liquid in 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (dd, 1H, J_{HH} = 7.9 Hz, J_{HH} = 1.2 Hz), 7.41 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.4 Hz), 7.40 (t, 1H, J_{HH} = 7.7 Hz), 7.29 (t, 1H, J_{HH} = 7.4 Hz), 7.13 (d, 1H, J_{HH} = 7.6 Hz), 6.94 (d, 1H, J_{HH} = 7.6 Hz), 6.90 (d, 1H, J_{HH} = 7.8 Hz), 2.96 (dt, 1H, J_{HH} = 13.3 Hz, J_{HH} = 4.3 Hz), 2.84 (m, 2H), 3.49 (s, 3H), 2.16 (m, 1H), 1.57 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 201.5, 161.2, 158.1, 144.3, 136.7, 133.2, 133.1, 128.9, 128.1, 126.6, 121.3, 118.4, 53.2, 35.8, 26.5, 25.7, 24.9. $[\alpha]^{23}_D$ = 286.7˚ (c = 0.77, $CHCl_3$). HPLC analysis: 98% ee, Chiralcel AD-H column, 3% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 13.9 min, $t_{[minor]}$ = 13.4 min. HRMS (ESI) exact mass calc'd for $C_{17}H_{17}NO$: m/z 252.1388 ($[M+H]^+$). Found: 252.1385 ($[M+H]^+$).

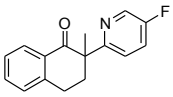
2-Methyl-2-(5-(trifluoromethyl)pyridin-2-yl)-3,4-dihydronaphthalen-1(2*H*)-one (Table 3, Entry 18)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→90:10 hexanes/EtOAc).This compound was isolated as a colorless liquid in 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.15 (dd, 1H, J_{HH} = 7.9 Hz, J_{HH} = 1.2 Hz), 7.81 (dd, 1H, J_{HH} = 8.4 Hz, J_{HH} = 2.3 Hz), 7.46 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.4 Hz), 7.33 (m, 2H), 7.17 (d, 1H, J_{HH} = 7.6 Hz), 2.90 (m, 3H), 2.24 (m, 1H), 1.62 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 200.3, 166.5, 146.3 (q, J_{CF} = 3.9 Hz), 143.9, 133.9 (q, J_{CF} = 3.3 Hz), 133.7, 132.6, 129.0, 128.3, 126.9, 124.9 (q, J_{CF} = 33.5 Hz), 123.8 (q, J_{CF} = 272.4 Hz), 121.5, 53.4, 35.7, 26.3, 25.2. $[\alpha]^{23}_D$ = 177.7˚ (c = 1.07, $CHCl_3$). HPLC analysis: 96% ee, Chiralcel AD-H column, 5% isopropanol in hexane, 0.5

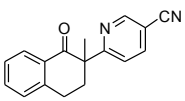
mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 10.3 min, $t_{[minor]}$ = 12.2 min. HRMS (ESI) exact mass calc'd for $C_{17}H_{14}F_3NO$: m/z 306.1106 ($[M+H]^+$). Found: 306.1105 ($[M+H]^+$).

2-(5-Fluoropyridin-2-yl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (Table 3, Entry 19)



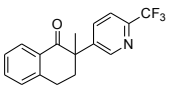
The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→95:5 hexanes/EtOAc). This compound was isolated as a colorless liquid in 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, 1H, J_{HH} = 3.0 Hz), 8.14 (d, 1H, J_{HH} = 7.9 Hz), 7.43 (t, 1H, J_{HH} = 7.4 Hz), 7.31 (t, 1H, J_{HH} = 7.7 Hz), 7.28 (td, 1H, J_{HH} = 8.5 Hz, J_{HF} = 3.0 Hz), 7.18 (dd, 1H, J_{HH} = 8.9 Hz, J_{HF} = 4.4 Hz), 7.15 (d, 1H, J_{HH} = 7.6 Hz), 2.86 (m, 3H), 2.21 (m, 1H), 1.57 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 200.9, 159.5, 158.1 (two peaks overlap), 157.4, 144.0, 137.6, 137.4, 133.5, 132.7, 129.0, 128.3, 126.8, 123.5, 123.4, 122.5 (two peaks overlap), 52.7, 35.9, 26.3, 25.6. $[\alpha]^{23}_D$ = 244.4° (c = 1.14, $CHCl_3$). HPLC analysis: 99% ee, Chiralcel AS-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 11.8 min, $t_{[minor]}$ = 13.9 min. HRMS (ESI) exact mass calc'd for $C_{16}H_{14}FNO$: m/z 256.1138 ($[M+H]^+$). Found: 256.1137 ($[M+H]^+$).

6-(2-Methyl-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)nicotinonitrile (Table 3, Entry 20)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→90:10 hexanes/EtOAc). This compound was isolated as an off-white solid in 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.80 (dd, 1H, J_{HH} = 2.2 Hz, J_{HH} = 0.9 Hz), 8.12 (dd, 1H, J_{HH} = 8.0 Hz, J_{HH} = 1.2 Hz), 7.85 (dd, 1H, J_{HH} = 8.3 Hz, J_{HH} = 2.2 Hz), 7.46 (td, 1H, J_{HH} = 7.6 Hz, J_{HH} = 1.2 Hz), 7.35 (dd, 1H, J_{HH} = 8.3 Hz, J_{HH} = 0.8 Hz), 7.32 (t, 1H, J_{HH} = 7.6 Hz), 7.17 (d, 1H, J_{HH} = 7.8 Hz), 2.88 (m, 3H), 2.23 (m, 1H), 1.60 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 199.9, 167.0, 152.1, 143.8, 139.8, 133.9, 132.4, 129.1, 128.3, 127.0, 121.9, 116.9, 108.2, 53.7, 35.5, 26.2, 25.0. $[\alpha]^{23}_D$ = 188.8° (c = 0.43, $CHCl_3$). HPLC analysis: 93% ee, Chiralcel AD-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 27.0 min, $t_{[minor]}$ = 41.3 min. HRMS (ESI) exact mass calc'd for $C_{17}H_{14}N_2O$: m/z 263.1184 ($[M+H]^+$). Found: 263.1188 ($[M+H]^+$).

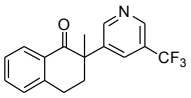
2-Methyl-2-(5-(trifluoromethyl)pyridin-2-yl)-3,4-dihydronaphthalen-1(2*H*)-one (Table 3, Entry 21)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→90:10 hexanes/EtOAc). This compound was isolated as an off-white solid in 54% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.67 (d, 1H, J_{HH} = 2.2 Hz), 8.15 (dd, 1H, J_{HH} = 7.9 Hz, J_{HH} = 1.0 Hz), 7.73 (dd, 1H, J_{HH} = 8.4 Hz, J_{HH} = 2.2 Hz), 7.60 (d, 1H,

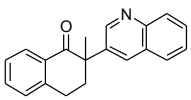
J_{HH} = 8.3 Hz), 7.48 (dt, 1H, J_{HH} = 7.6 Hz, J_{HH} = 1.3 Hz), 7.35 (t, 1H, J_{HH} = 7.6 Hz), 7.19 (d, 1H, J_{HH} = 7.7 Hz), 2.99 (dt, 1H, J_{HH} = 17.4 Hz, J_{HH} = 4.9 Hz), 2.83 (ddd, 1H, J_{HH} = 17.4 Hz, J_{HH} = 10.3 Hz, J_{HH} = 4.4 Hz), 2.67 (dt, 1H, J_{HH} = 14.1 Hz , J_{HH} = 4.9 Hz), 2.33 (ddd, 1H, J_{HH} = 14.1 Hz, J_{HH} = 10.3 Hz, J_{HH} = 4.7 Hz), 1.61 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 199.5, 148.7, 146.8 (q, J_{CF} = 35.1 Hz), 143.2, 141.9, 136.0, 134.1, 132.1, 129.1, 128.5, 127.3, 121.7 (q, J_{CF} = 273.2 Hz), 120.4 (q, J_{CF} = 3.0 Hz), 49.3, 36.0, 26.0, 25.9. $[\alpha]^{23}_D$ = 133.6° (c = 0.93, $CHCl_3$). HPLC analysis: 96% ee, Chiralcel AD-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 18.9 min, $t_{[minor]}$ = 20.0 min. HRMS (ESI) exact mass calc'd for $C_{17}H_{14}F_3NO$: m/z 306.1106 ($[M+H]^+$). Found: 306.1100 ($[M+H]^+$).

2-Methyl-2-(5-(trifluoromethyl)pyridin-3-yl)-3,4-dihydronaphthalen-1(2*H*)-one (Table 3, Entry 22)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→80:20 hexanes/EtOAc). This compound was isolated as an off-white solid in 45% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.74 (s, 1H), 8.15 (dd, 1H, J_{HH} = 8.0 Hz, J_{HH} = 1.4 Hz), 7.83 (t, 1H, J_{HH} = 2.0 Hz), 7.49 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.4 Hz), 7.35 (t, 1H, J_{HH} = 7.6 Hz), 7.20 (d, 1H, J_{HH} = 7.7 Hz),), 3.02 (dt, 1H, J_{HH} = 17.4 Hz , J_{HH} = 5.2 Hz), 2.85 (ddd, 1H, J_{HH} = 17.4 Hz, J_{HH} = 9.7 Hz, J_{HH} = 4.3 Hz), 2.66 (ddd, 1H, J_{HH} = 14.1 Hz, J_{HH} = 5.8 Hz, J_{HH} = 4.6 Hz), 2.32 (ddd, 1H, J_{HH} = 14.1 Hz, J_{HH} = 9.7 Hz, J_{HH} = 4.6 Hz), 1.62 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 199.4, 151.8, 145.2 (q, J_{CF} = 4.2 Hz), 143.1, 139.1, 134.1, 132.0, 131.6, 129.1, 128.6, 127.3, 126.7 (q, J_{CF} = 33.3 Hz), 123.6 (q, J_{CF} = 272.8 Hz), 49.1, 36.0, 26.0, 25.7. $[\alpha]^{23}_D$ = 152.4° (c = 0.74, $CHCl_3$). HPLC analysis: 97% ee, Chiralcel AD-H column, 3% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 19.7 min, $t_{[minor]}$ = 18.4 min. HRMS (ESI) exact mass calc'd for $C_{17}H_{14}F_3NO$: m/z 306.1106 ($[M+H]^+$). Found: 306.1101 ($[M+H]^+$).

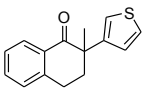
2-Methyl-2-(quinolin-3-yl)-3,4-dihydronaphthalen-1(2*H*)-one (Table 3, Entry 23)



The crude product was purified by silica gel chromatography with a CombiFlash system (4 g column, 100:0→80:20 hexanes/EtOAc). This compound was isolated as an off-white solid in 87% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 8.93 (d, 1H, J_{HH} = 2.4 Hz), 8.21 (dd, 1H, J_{HH} = 8.0 Hz, J_{HH} = 1.1 Hz), 8.06 (d, 1H, J_{HH} = 8.5 Hz), 7.87 (d, 1H, J_{HH} = 2.4 Hz), 7.69 (d, 1H, J_{HH} = 8.2 Hz), 7.65 (t, 1H, J_{HH} = 7.7 Hz), 7.48 (t, 1H, J_{HH} = 7.6 Hz), 7.43 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.5 Hz), 7.33 (t, 1H, J_{HH} = 7.4 Hz), 7.12 (d, 1H, J_{HH} = 7.7 Hz), 2.92 (m, 1H), 2.81 (m, 2H), 2.35 (m, 1H), 1.66 (s, 3H). $^{13}C\{^1H\}$ NMR (125.6 Hz, $CDCl_3$): 200.3, 149.6, 147.1, 143.5, 135.3, 133.8, 133.6, 132.4, 129.6, 129.2, 129.0, 128.4,

128.0, 127.9, 127.1, 127.0, 49.5, 36.1, 26.4, 26.3. $[\alpha]^{24}_D$ = +185.1° (c = 0.62, $CHCl_3$). HPLC analysis: 99% ee, Chiralcel AS-H column, 5% isopropanol in hexane, 0.5 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 22.7 min, $t_{[minor]}$ = 25.2 min. HRMS (ESI) exact mass calc'd for $C_{20}H_{17}NO$: m/z 288.1388 ($[M+H]^+$). Found: 288.1384 ($[M+H]^+$).

2-Methyl-2-(thiophen-3-yl)-3,4-dihydronaphthalen-1(2*H*)-one (Table 3, Entry 24)

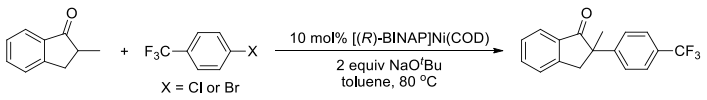


The crude product was purified by silica gel chromatography with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc). This compound was isolated as a colorless liquid in 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, 1H, J_{HH} = 8.0 Hz), 7.52 (td, 1H, J_{HH} = 7.5 Hz, J_{HH} = 1.3 Hz), 7.33 (t, 1H, J_{HH} = 7.6 Hz), 7.28 (d, 1H, J_{HH} = 5.1 Hz, J_{HH} = 2.9 Hz), 7.17 (d, 1H, J_{HH} = 7.6 Hz), 7.05 (dd, 1H, J_{HH} = 5.2 Hz, J_{HH} = 1.3 Hz), 6.91 (dd, 1H, J_{HH} = 2.9 Hz, J_{HH} = 1.4 Hz), 2.88 (m, 2H), 2.54 (dt, 1H, J_{HH} = 13.8 Hz, J_{HH} = 4.4 Hz), 2.28 (ddd, 1H, J_{HH} = 15.8 Hz, J_{HH} = 10.3 Hz, J_{HH} = 5.6 Hz), 1.56 (s, 3H). ^{13}C{^{1}H} NMR (125.6 Hz, $CDCl_3$): 200.3, 144.0, 143.4, 133.5, 132.4, 128.9, 128.3, 126.9, 126.5, 126.0, 121.0, 48.6, 36.9, 26.6, 26.4. $[\alpha]^{25}_D$ = 165.6° (c = 0.57, $CHCl_3$). HPLC analysis: 92% ee, Chiralcel OB-H column, 5% isopropanol in hexane, 1.0 mL/min flow rate, 254 nm UV lamp, $t_{[major]}$ = 8.8 min, $t_{[minor]}$ = 12.0 min. HRMS (ESI) exact mass calc'd for $C_{15}H_{14}OS$: m/z 243.0844 ($[M+H]^+$). Found: 243.0848 ($[M+H]^+$).

Aromatic Substitution Reaction of the Sodium Enolate of 2-Methyl-1-Indanone with Activated Heteroaryl Chloride

In a drybox, a 4-mL screw-capped vial was charged with 2-methyl-1-indanone (29.2 mg, 0.200 mmol), 2-chloro-5-(trifluoromethyl)pyridine (72.6 mg, 0.400 mmol) or 2-chloro-5-cyanopyridine (55.4 mg, 0.400 mmol), and NaO^{t}Bu (38.4 mg, 0.400 mmol). The vial was sealed with a cap containing a PTFE spetum and taken out of the drybox. The mixture was stirred for 28 h in an oil bath preheated to 70 ºC and then cooled to room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution. GC-MS analysis of these reaction mixtures indicated that 2-methyl-1-indanone was fully converted to the desired α-heteroaryl indanone.

Following the Enantiometric Excess of the Product *vs* Time for the Following Reactions



In a drybox, a 4-mL screw-capped vial was charged with $Ni(COD)_2$ (16.5 mg, 0.060 mmol), (*R*)-BINAP (44.8 mg, 0.072 mmol), and toluene (1.5 mL). The mixture was stirred for 8 h at room

temperature and then 10 min at 50 ºC. The resulting solution was added to another 4-mL screw-capped vial containing 2-methyl-1-indanone (87.7 mg, 0.600 mmol), 4-chlorobenzotrifluoride (216.6 mg, 1.200 mmol) or 4-bromobenzotrifluoride (270.0 mg, 1.2 mmol), NaO^{t}Bu (115.3 mg, 1.200 mmol), and toluene (1.5 mL). The vial was sealed with a cap containing a PTFE spectrum and removed from the drybox. The mixture was stirred in an oil bath preheated to 80 ºC, and an aliquot of the mixture (0.15 mL) was removed at 0.5 min, 1 min, 2 min, 2.5 min, 3 min, 5 min, 7 min, 10 min, 15min, 20 min, 30 min, 50 min, 70 min, 90 min, and 120 min. Each aliquot was filtered through a short silica column. The filtrate was diluted to ~2 mL, and the ee of the product was checked by HPLC (AD-H column, 2% isopropanol in hexanes, flow rate 0.5 mL/min).

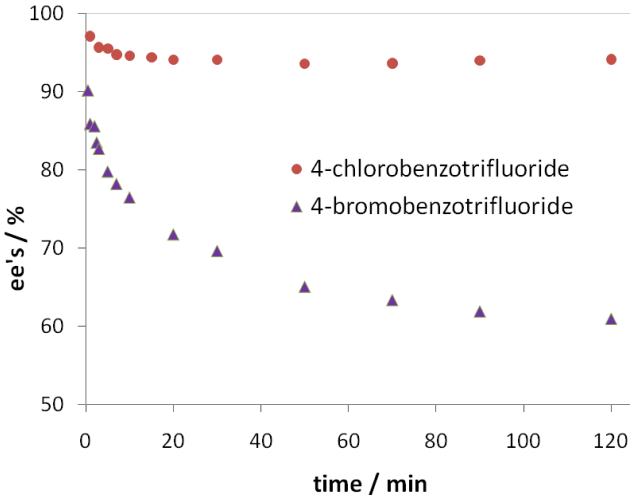


Figure S1. Enantiomeric excess vs time for reactions of 2-methyl-1-indanone with 4-chloro- and 4-bromobenzotrifluoride at 80 ˚C.

Synthesis of [(*R*)-BINAP]Ni(Cl)(C_6H_4-4-CN) (1)

To a mixture of $Ni(COD)_2$ (138 mg, 0.500 mmol) and (*R*)-BINAP (343 mg, 0.550 mmol) was added toluene (3 mL). The resulting suspension was stirred for 12 h at room temperature and then 10 min at 50 ºC. The mixture was cooled to room temperature, at which point 4-chlorobenzonitrile (206 mg, 1.50 mmol) was added. The resulting mixture was stirred 2 h at room temperature and then filtrated. The solid was washed with pentane (3 × 10 mL) and dried under vacuum, yielding the title compound (315 mg, 0.385 mmol, 77%) as a brown crystalline solid. ^{1}H NMR (500 MHz, CH_2Cl_2): δ 8.19 (broad s, 1H), 7.99 (broad s, 2H), 7.88 (broad s, 1H), 7.74-7.30 (m, 14H), 7.28-6.84 (m, 11H), 6.73 (broad s, 4H), 6.57 (broad s, 3H). ^{31}P{^{1}H} NMR (202.2 MHz, CH_2Cl_2): δ 31.4 (d, J_{PP} = 34.9 Hz), 16.7 (d, J_{PP} = 34.9 Hz). Anal. Calc'd for $C_{51}H_{36}ClNNiP_2$: C, 74.80; H, 4.43; N, 1.71. Found: C, 74.59; H, 4.23; N, 1.69.

Synthesis of [(*R*)-BINAP]Ni(Cl)(C_6H_4-4-CF_3) (2)

A mixture of $Ni(COD)_2$ (128 mg, 0.500 mol) and (*R*)-BINAP (343 mg, 0.550 mmol) in toluene (3 mL) was stirred for 6 h at room temperature. To the resulting purple suspension was added 4-chlorobenzotrifluoride (853 mg, 5.00 mmol) and benzonitrile (10 μL), and the mixture was stirred for 20 min. The suspension was filtered, and the resulting solid was dissolved in CH_2Cl_2 (2 mL) and diethyl ether (1 mL). To this mixture was added pentane (17 mL) with vigorous stirring, and the precipitate was collected by filtration and dried under vacuum, affording the title compound (322 mg, 0.373 mmol, 75%) as a brick red powder. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.20 (broad s, 1H), 7.97 (broad s, 2H), 7.89 (broad s, 1H), 7.67 (broad s, 5H), 7.55 (broad s, 6H), 7.39 (broad s, 3H), 7.00 (broad s, 9H), 6.70 (broad s, 4H), 6.54 (broad s, 3H). ^{31}P{^{1}H} (202.2 MHz, CD_2Cl_2): δ 31.45 (d, J_{PP} = 32.0 Hz), 16.54 (d, J_{PP} = 32.0 Hz). Anal. Calc'd for $C_{51}H_{36}ClF_3NiP_2$: C, 71.07; H, 4.21. Found: C, 70.90; H, 4.35. Crystallization of compound **2** for X-ray analysis: Pentane was carefully layered on top of a saturated solution of this compound in THF. Slow diffusion of pentane at -30 ºC afforded crystals suitable for single-crystal X-ray diffraction analysis.

Synthesis of [(*R*)-BINAP]Ni(Br)(C_6H_4-4-CF_3) (3)

A mixture of $Ni(COD)_2$ (128 mg, 0.500 mol) and R-BINAP (343mg, 0.550 mmol) in toluene (3 mL) was stirred for 6 h at room temperature. To the resulting purple suspension was added 4-bromobenzotrifluoride (563mg, 2.50 mmol) and benzonitrile (10 μL), and the mixture was stirred for 20 min. The suspension was filtered, and the resulting solid was dissolved in CH_2Cl_2 (2 mL) and diethyl ether (1 mL). To this mixture was added pentane (17 mL) with vigorous stirring, and the precipitate was isolated by filtration and dried under vacuum, affording the title compound (364.7 mg, 0.402 mmol, 80%) as a brick red powder. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.21 (broad s, 1H), 7.99 (broad s, 2H), 7.90 (broad s, 1H), 7.80 – 7.40 (m, 11H), 7.39 (broad s, 3H), 7.30 – 6.80 (m, 10H), 6.80 -6.60 (m, 8H). ^{31}P{^{1}H} (202.2 MHz, CD_2Cl_2): δ 31.8 (d, J_{PP} = 30.4 Hz), 15.6 (d, J_{PP} = 30.4 Hz). Anal. Calc'd for $C_{51}H_{36}BrF_3NiP_2$: C, 67.58; H, 4.00. Found: C, 67.30; H, 4.21.

Reaction of [(*R*)-BINAP]Ni(Cl)(C_6H_4-4-CF_3) with the Sodium Enolate of 2-Methyl-1-indanone

A mixture of [(*R*)-BINAP]Ni(Cl)(C_6H_4-4-CF_3) (43.1 mg, 50.0 μmol), the sodium enolate of 2-methyl-1-indanone (20.2 mg, 120 μmol), and (*R*)-BINAP (31.1 mg, 50.0 μmol) in toluene (0.5 mL) was stirred for 4 h at 80 ˚C. After the same workup procedure with the catalytic reaction, 2-methyl-2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-*1H*-inden-1-one was isolated in 72% yield with >99% ee.

Reaction of [(*R*)-BINAP]Ni(Br)(C_6H_4-4-CF_3) with the Sodium Enolate of 2-Methyl-1-indanone

A mixture of [(*R*)-BINAP]Ni(Br)(C_6H_4-4-CF_3) (45.3 mg, 50.0 μmol), the sodium enolate of 2-methyl-1-indanone (20.2 mg, 120 μmol), and (*R*)-BINAP (31.1 mg, 50.0 μmol) in toluene (0.5 mL) was stirred for 4 h at 80 ˚C. After the same workup procedure with the catalytic reaction, 2-methyl-2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-*1H*-inden-1-one was isolated in 72% yield with >99% ee.

Synthesis of [(*R*)-BINAP]Ni(η^2-N≡CPh) (4)

To a mixture of $Ni(COD)_2$ (138mg, 0.500 mmol) and (*R*)-BINAP (343mg, 0.550 mmol), was added toluene (3 mL), and the resulting suspension was stirred for 12 h at room temperature. Benzonitrile (1.02 g, 10.0 mmol) was added to the mixture, and stirring was continued for 1 h. The resulting precipitate was filtered, washed with pentane (5 ml) three times, and dried under vacuum, affording the title compound in its toluene-solvated form (1 toluene per Ni, 373 mg, 0.432 mmol, 86%) as a yellow powder. Crystals suitable for single-crystal X-ray diffraction analysis were grown by vapor diffusion of pentane into a concentrated solution of the title compound in benzene. ^{1}H NMR (500 MHz, THF-d_8): δ 8.60 (t, 2H, J_{HH} = 8.4 Hz), 7.76 (t, 2H, J_{HH} = 8.6 Hz), 7.50 (t, 3H, J_{HH} = 7.2 Hz), 7.48-7.18 (m, 17H), 7.13 (t, 1H, J_{HH} = 7.3 Hz), 7.10 (d, 2H, J_{HH} = 7.8 Hz), 7.05 (d, 2H, J_{HH} = 7.8 Hz), 6.98 (t, 1H, J_{HH} = 7.8 Hz), 6.91 (t, 3H, J_{HH} = 7.4 Hz), 6.70 (d, 1H, J_{HH} = 8.5 Hz), 6.65 (t, 1H, J_{HH} = 7.2 Hz), 6.56 (m, 3H), 6.42 (t, 2H, J_{HH} = 6.9 Hz). ^{31}P{^{1}H} NMR (202.2 MHz, toluene):): δ 42.3 (d, J_{PP} = 45.4 Hz), 28.4 (d, J_{PP} = 45.4 Hz). Anal. Calc'd for $C_{58}H_{45}NNiP_2$: C, 79.47; H, 5.17; N, 1.60. Found: C, 79.11; H, 5.30; N, 1.72.

Synthesis of {[(*R*)-BINAP]NiCl}$_2$ (5)

A solution of [(*R*)-BINAP]Ni(Cl)(C_6H_4-4-CF_3) (100 mg, 0.116 mmol) in THF was allowed to stand overnight at room temperature and then slow vapor diffusion of pentane into this mixture afforded dark red crystalline material. Parts of these crystals were suitable for X-ray analysis. The solid was filtered and dried under vacuum, yielding the title compound (57.3 mg, 0.040 mmol, 69%) as a dark red solid. Anal. Calc'd for $C_{88}H_{64}Cl_2Ni_2P_4$: C, 73.72; H, 4.50. Found: C, 73.65; H, 4.41.

Synthesis of {[(*R*)-BINAP]NiBr}$_2$ (6)

A solution of [(*R*)-BINAP](Br)Ni(C_6H_4-4-CF_3) (100 mg, 0.110 mmol) in THF was allowed to stand overnight at room temperature and then slow vapor diffusion of pentane into this mixture afforded dark red crystalline material. Parts of these crystals were suitable for X-ray analysis. The

solid was filtered and dried under vacuum, yielding the title compound (59.7 mg, 0.039 mmol, 72%) as a dark red solid. Anal. Calc'd for $C_{88}H_{64}Br_2Ni_2P_4$: C, 69.42; H, 4.24. Found: C, 69.47; H, 4.14.

Arylation of 2-Methyl-indanone with Chloro- and Bromoarenes Catalyzed by {[(*R*)-BINAP]NiX}$_2$ (X = Cl, 5; X = Br, 6)

In a drybox, a 4-mL screw-capped vial was charged with {[(*R*)-BINAP]NiX}$_2$ (X = Cl, 7.2 mg, 5.0 μmol; X = Br, 7.6 mg, 5.0 μmol), 2-methyl-1-indanone (29.2 mg, 0.200 mmol), chloroarenes (0.400 mmol) for {[(*R*)-BINAP]NiCl}$_2$ or bromoarene (0.400 mmol) for {[(*R*)-BINAP]NiBr}$_2$, a magnetic stirring bar, and toluene (1.0 mL). The vial was sealed with a cap containing a PTFE septum and taken out of the drybox. The reaction mixture was stirred in an oil bath preheated to 80 ºC for 24 h and then cooled to room temperature. The mixture was quenched with a saturated aqueous NH_4Cl solution and extracted with Et_2O (2 × 10 mL). The combined extract was dried over Na_2SO_4, filtered, and dried under reduced pressure. The crude product was purified with a CombiFlash system (12 g column, 100:0→95:5 hexanes/EtOAc). The isolated yields and ee's of the products were summarized in eq 5 in the manuscript.

The General Procedure for the α-Arylation Reactions of Indanones and Tetralones with Aryl Halides at Room Temperature Catalyzed by (*R*)-BINAP]Ni(η^2-N≡CPh) (4)

In a drybox, a 4-mL screw-capped vial was charged with (*R*)-BINAP]Ni(η^2-N≡CPh) (8.8 mg, 0.010 mmol for bromoarenes; 17.5 mg, 0.020 mmol for chloroarenes), NaO^{t}Bu (38.4 mg, 0.400 mmol), the corresponding chloroarene (0.400 mmol) or bromoarene (0.400 mmol), ketone (0.200 mmol), a magnetic stirring bar, and toluene (1.0 mL). The vial was sealed with a cap containing a PTFE septum and removed from the drybox. The reaction mixture was stirred at room temperature for 20 h. The mixture was quenched with a saturated aqueous NH_4Cl solution and extracted with Et_2O (2 × 10 mL). The combined extract was dried over Na_2SO_4, filtered, and dried under reduced pressure. The crude product was purified with a CombiFlash system with 5-20% ethyl acetate in hexanes as eluent. The conditions for chromatography and data for characterization of the products are given above.

Ortep Drawings of Complex 2, 4–6.

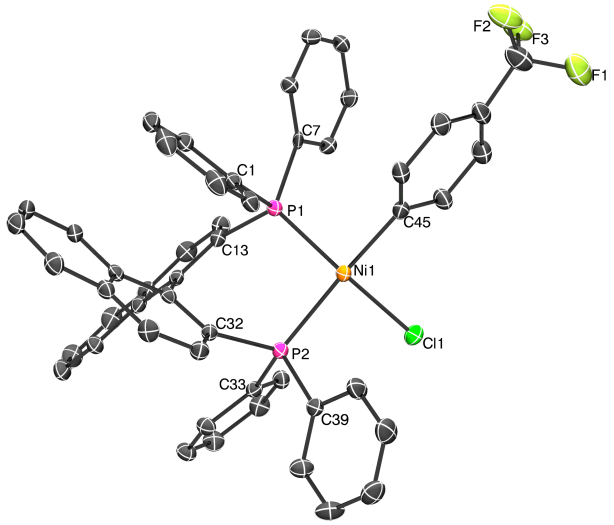


Figure S2. Ortep drawing of [(*R*)-BINAP]Ni(Cl)(C_6H_4-4-CF_3) (**2**). All hydrogens are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level.

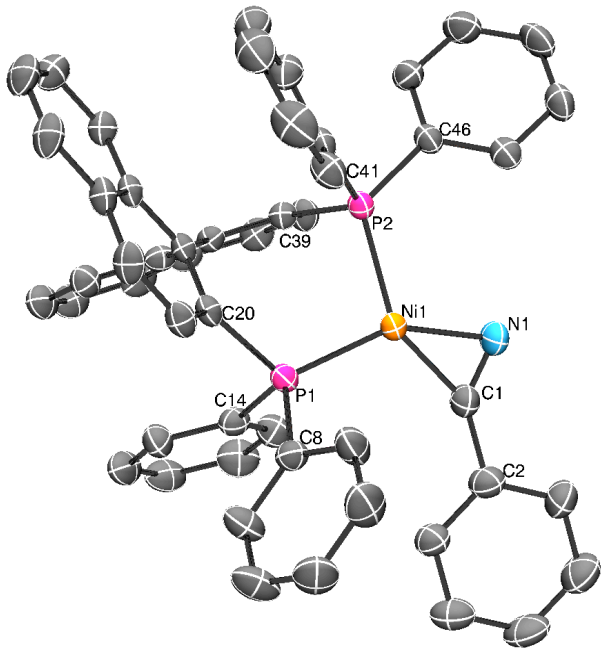


Figure S3. Ortep drawing of [(*R*)-BINAP]Ni(η^2-N≡C-Ph) (**4**). All hydrogens are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level.

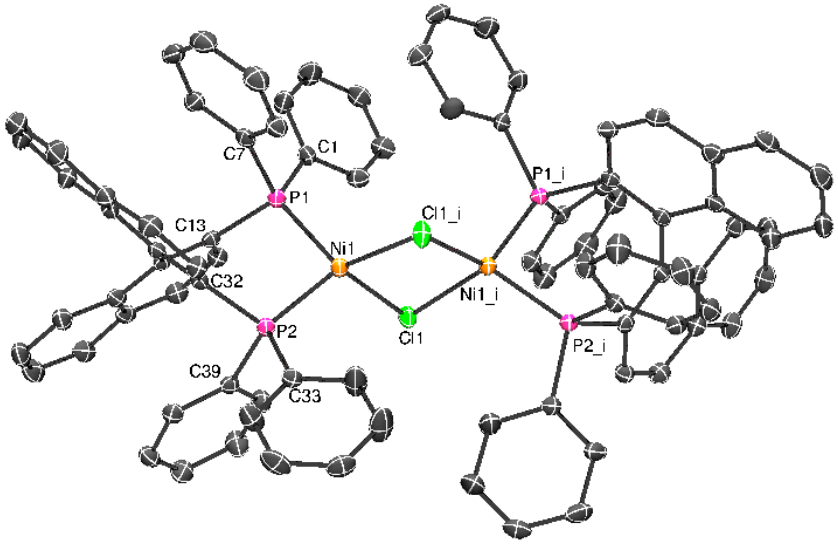


Figure S4. Ortep drawing of {[(*R*)-BINAP]Ni(μ-Cl)}$_2$ (**5**). All hydrogens are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level.

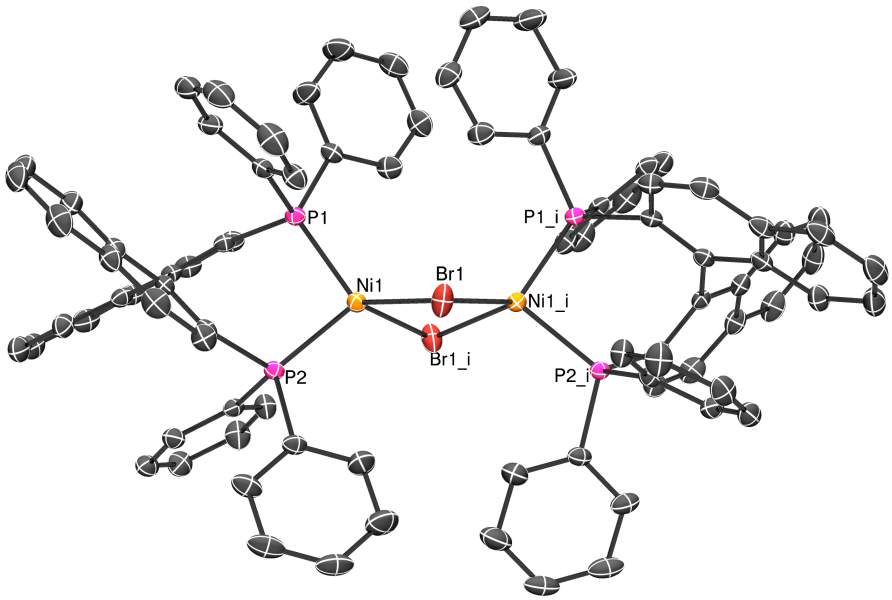
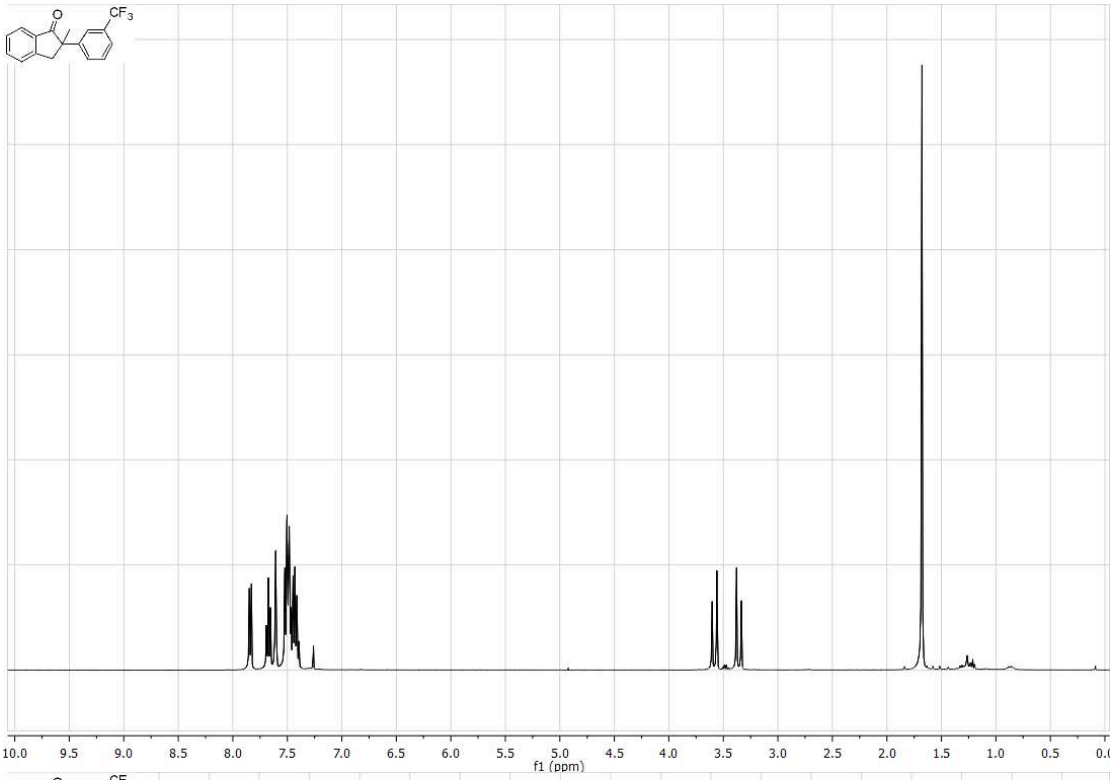


Figure S5. Ortep drawing of {[(*R*)-BINAP]Ni(μ-Br)}$_2$ (**6**). All hydrogens are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level.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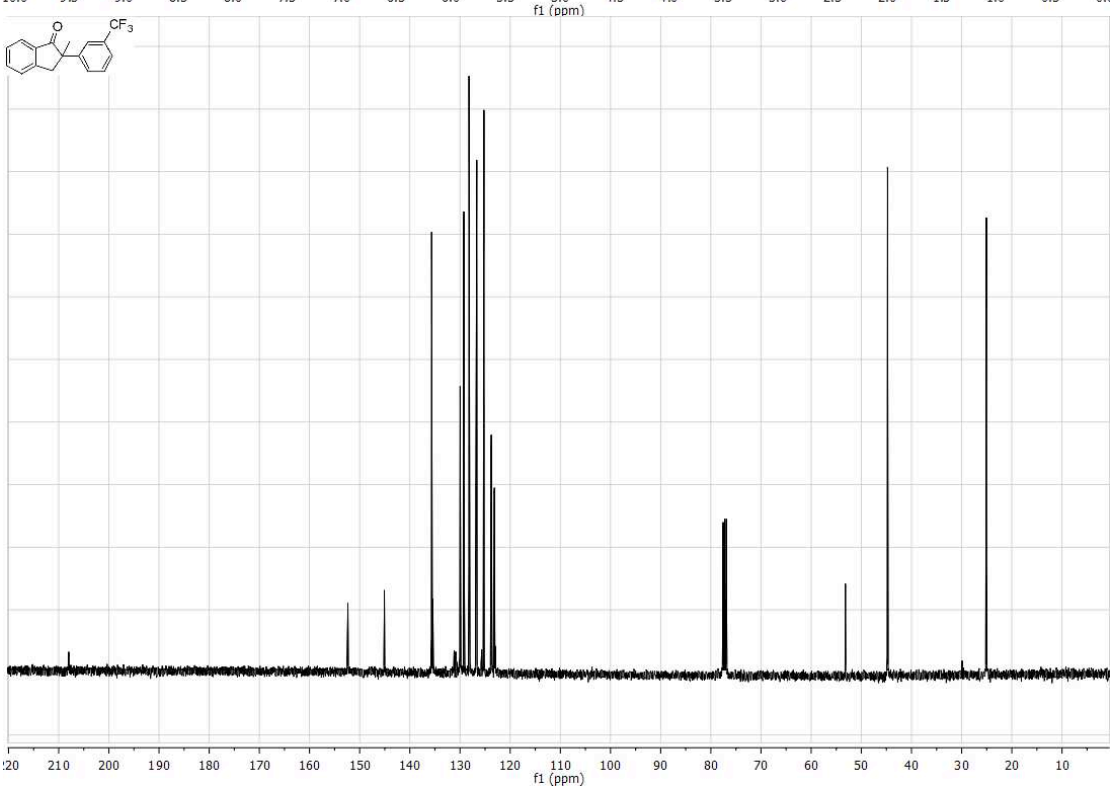
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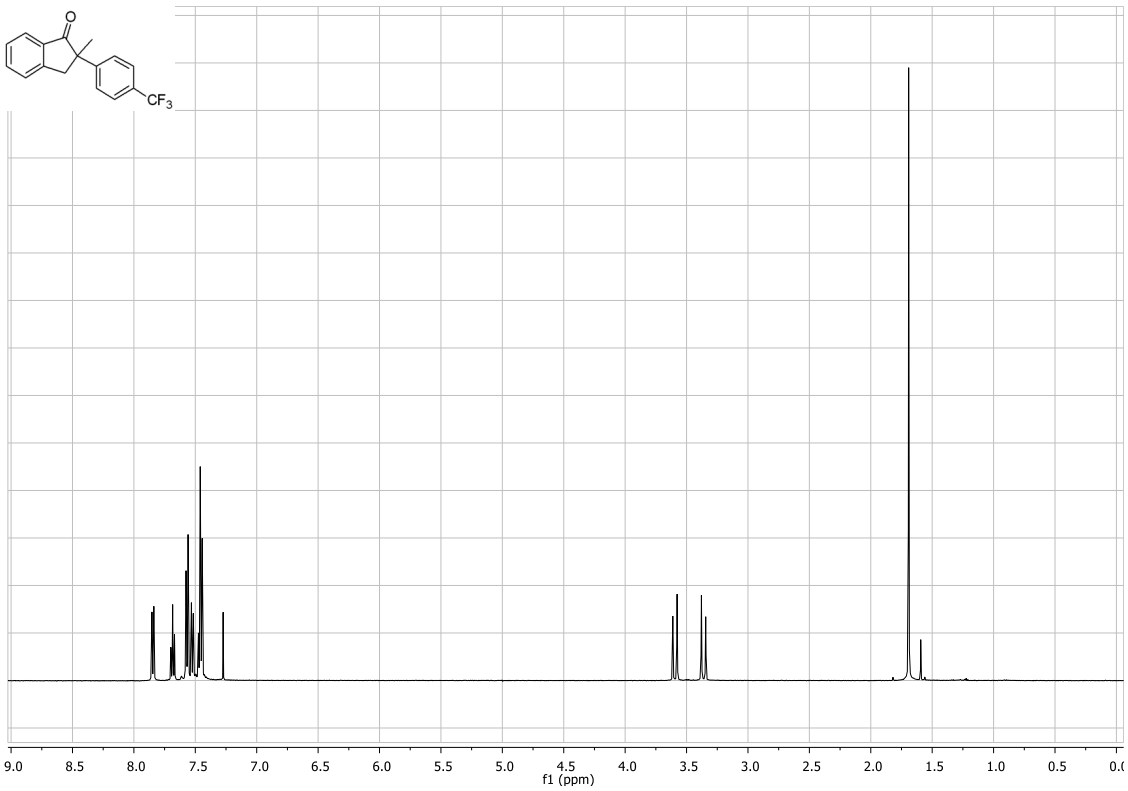
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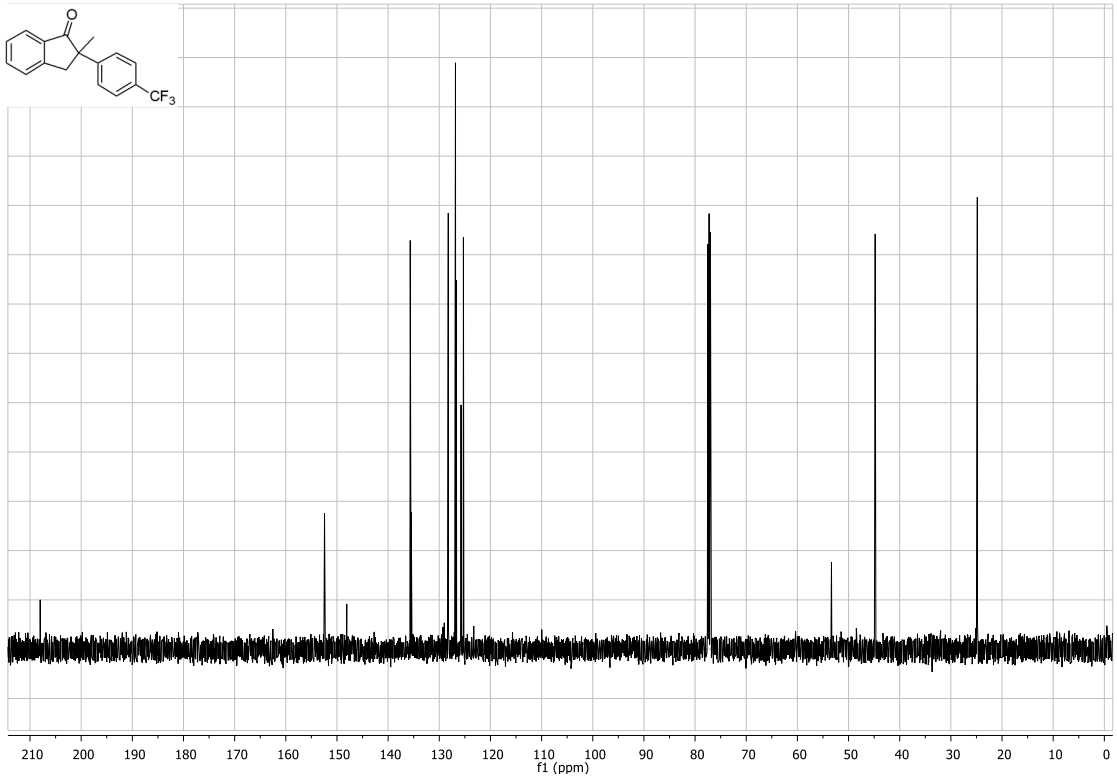
f1 (ppm)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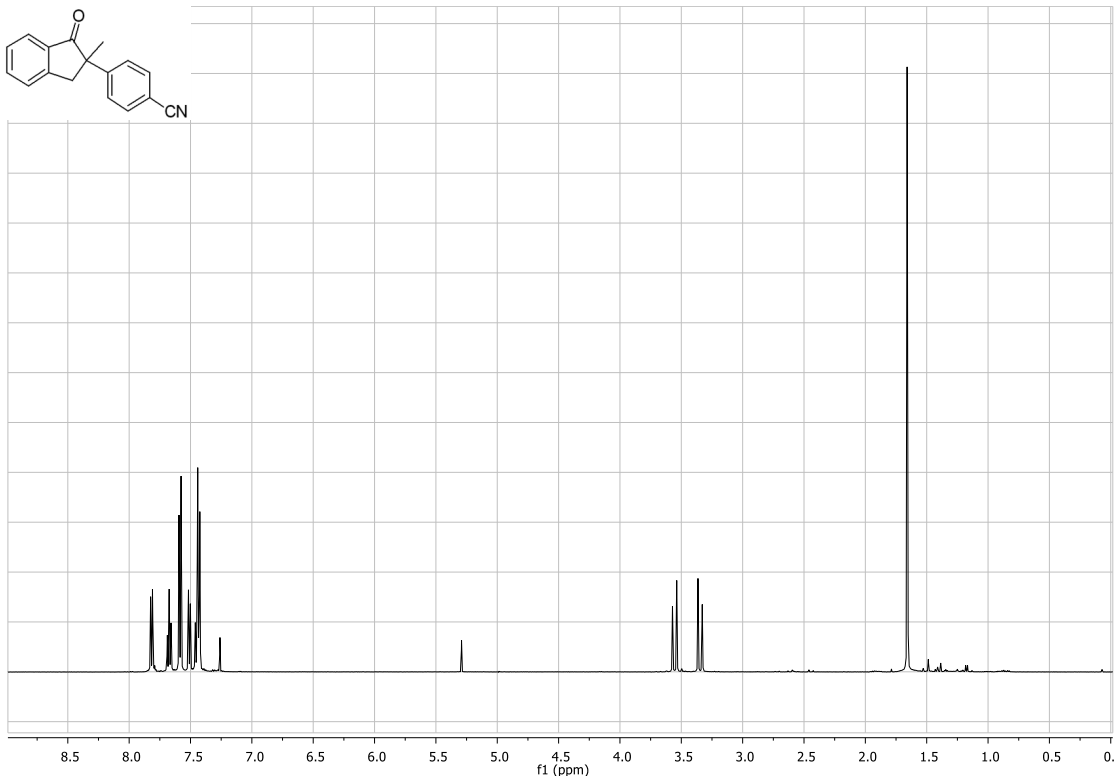
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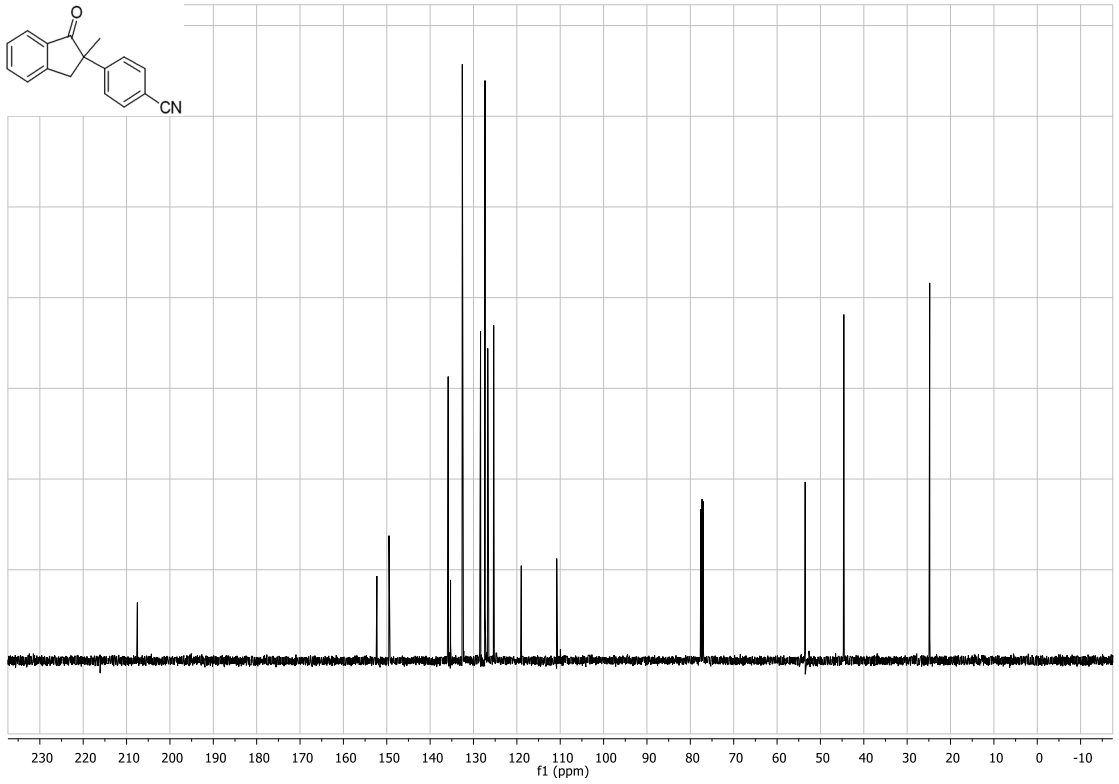
f1 (ppm)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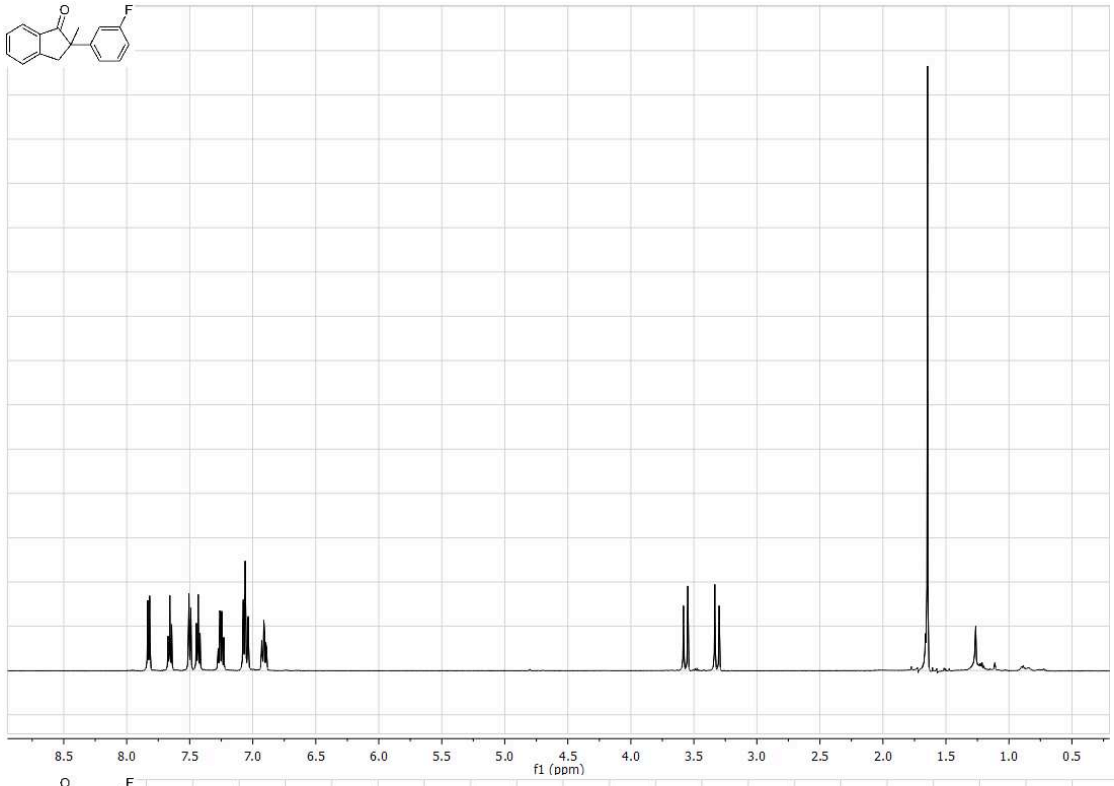
f1 (ppm)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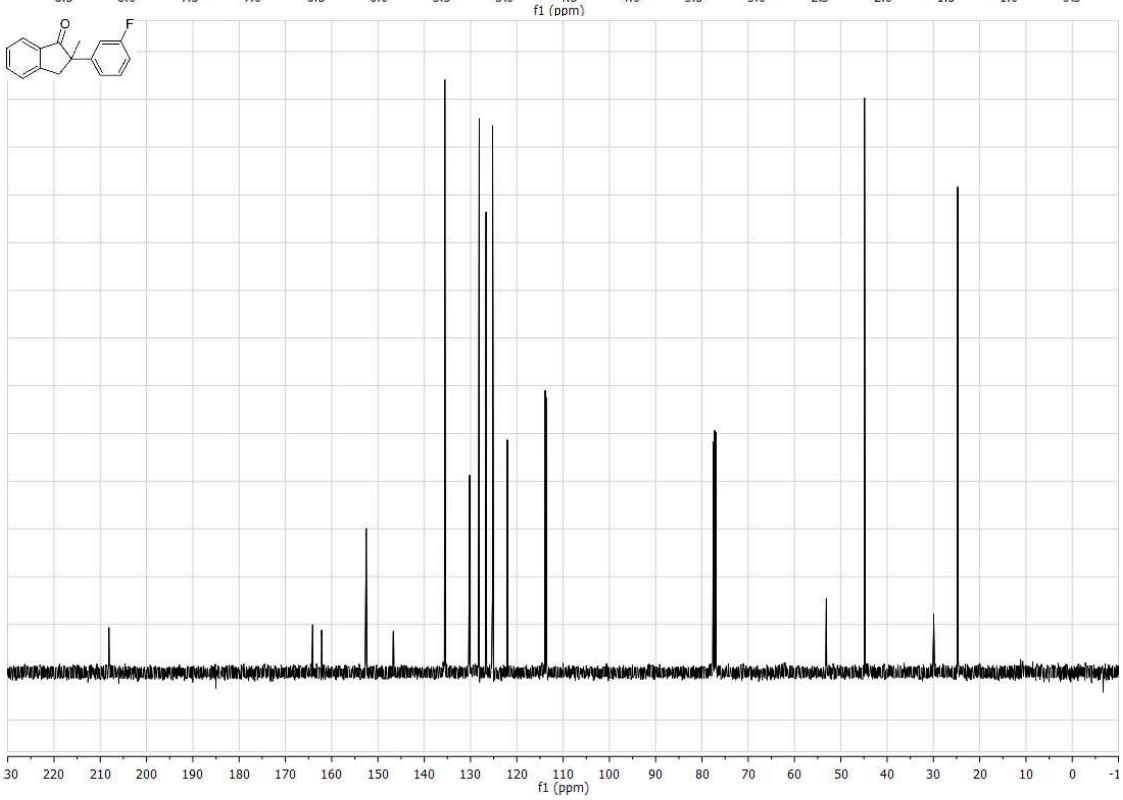
0.5
f1 (ppm)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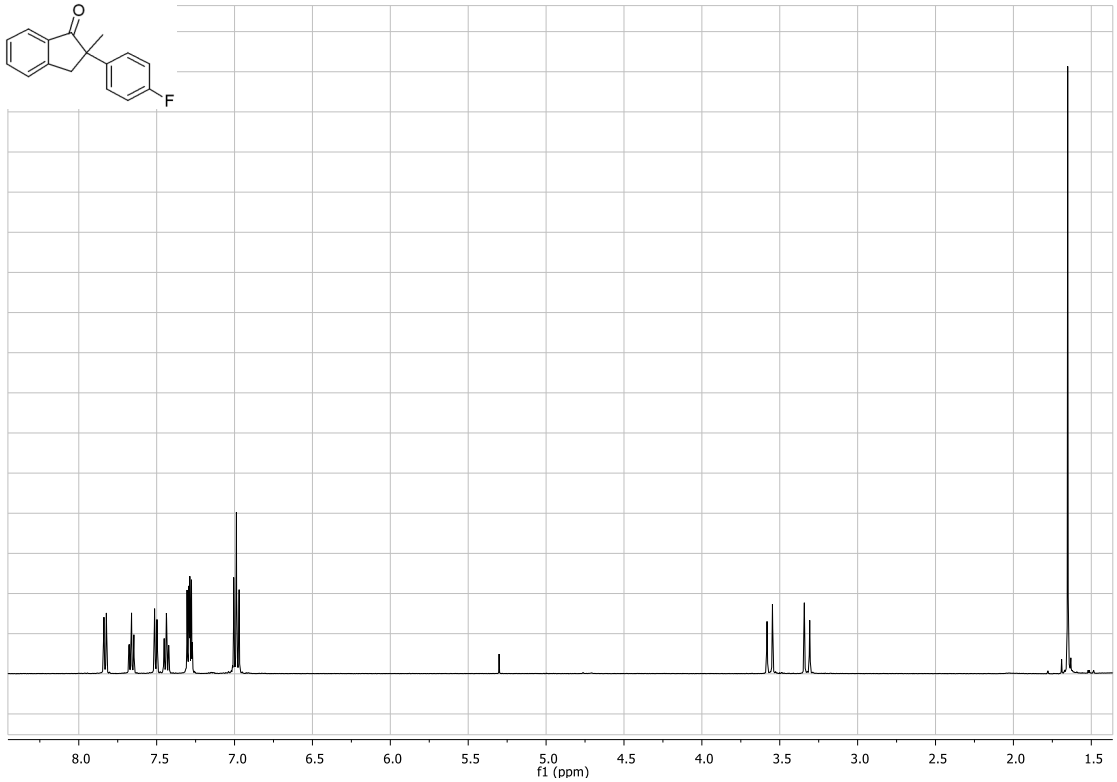
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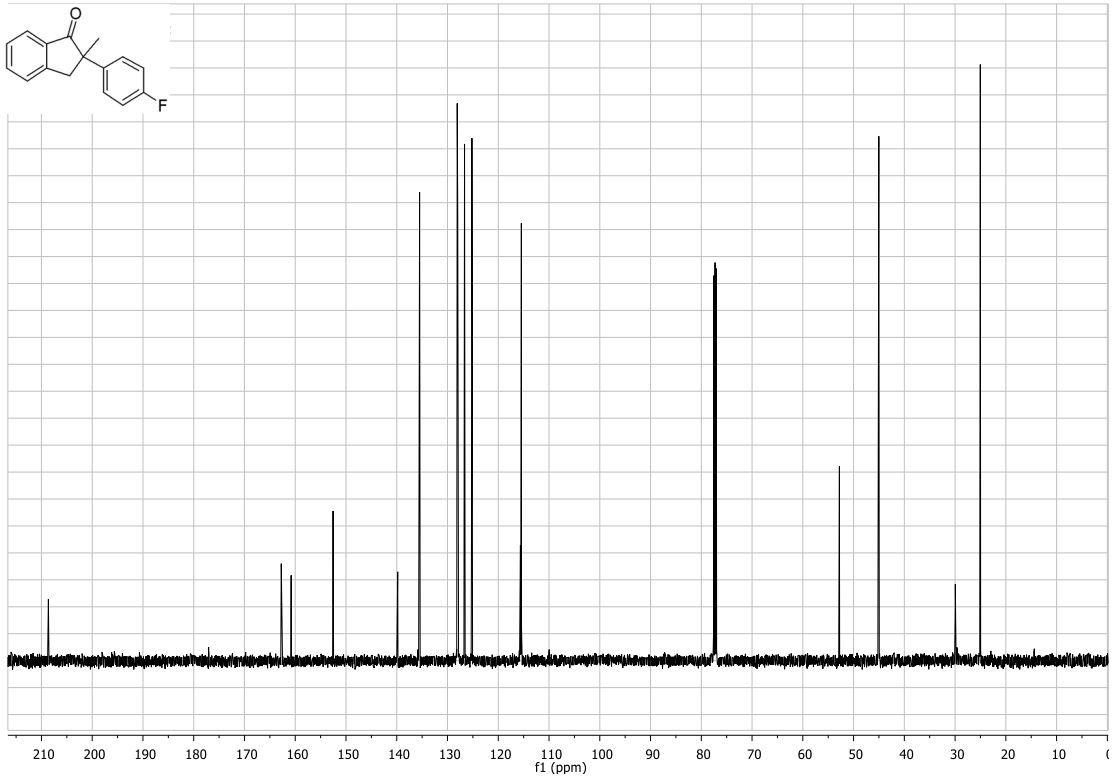
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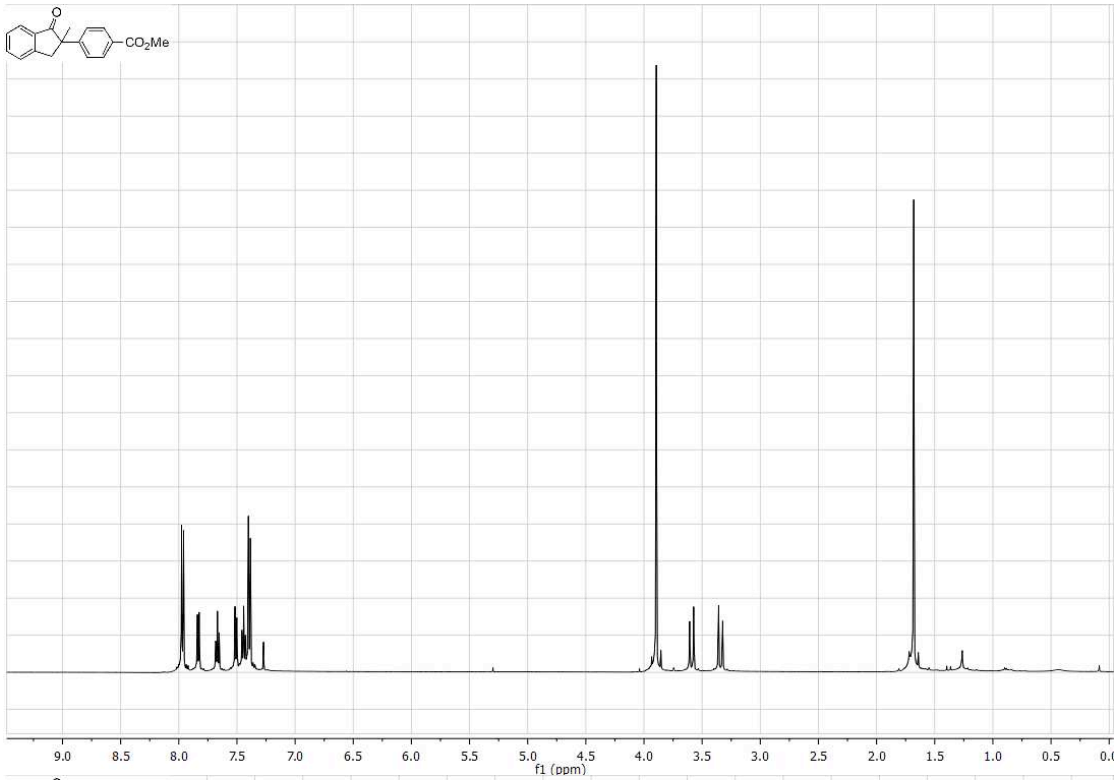
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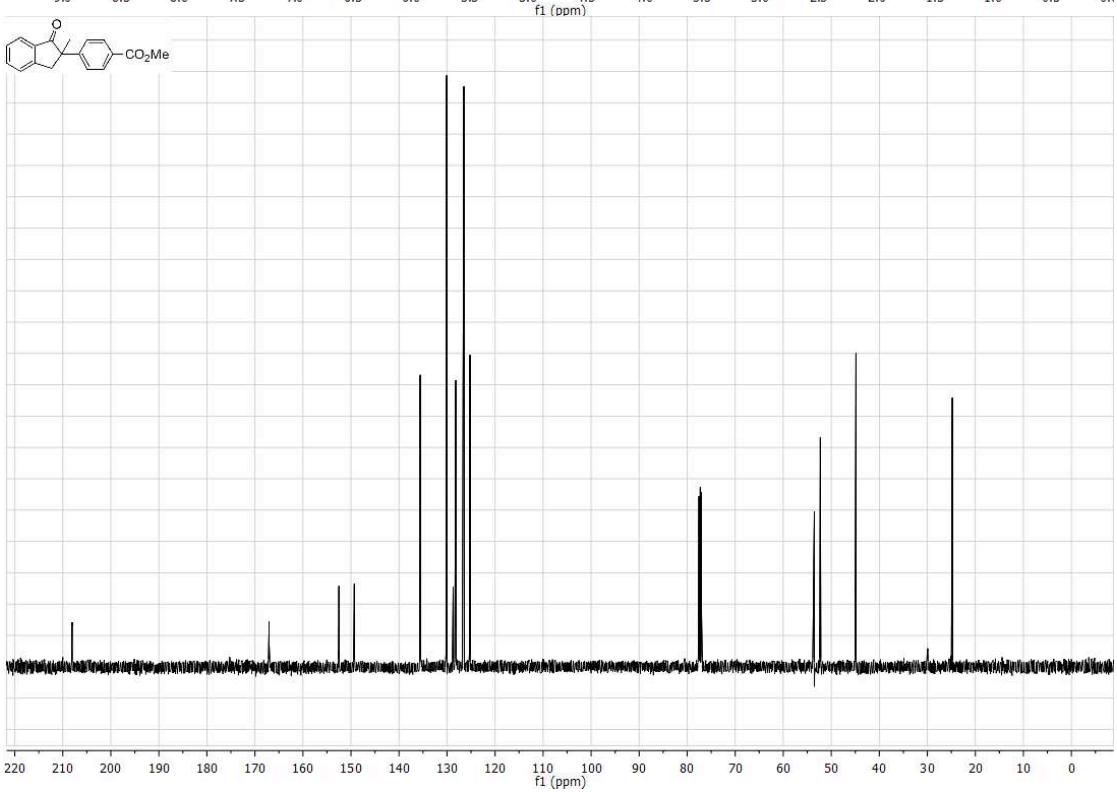
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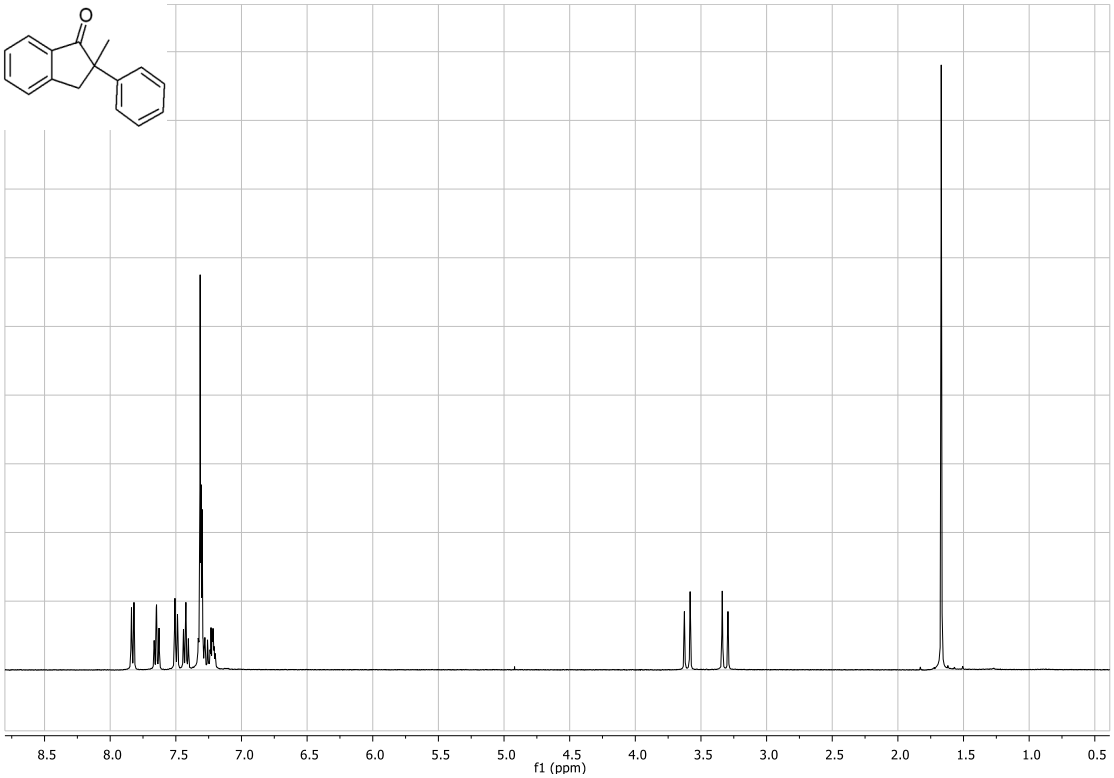
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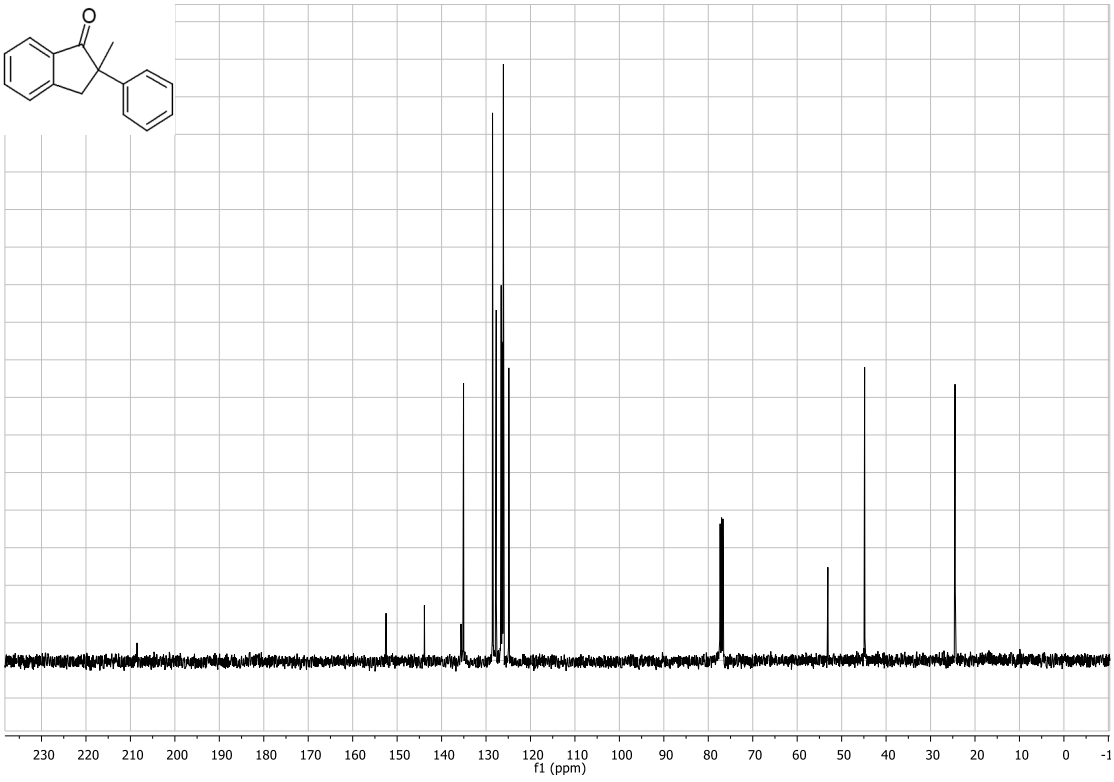
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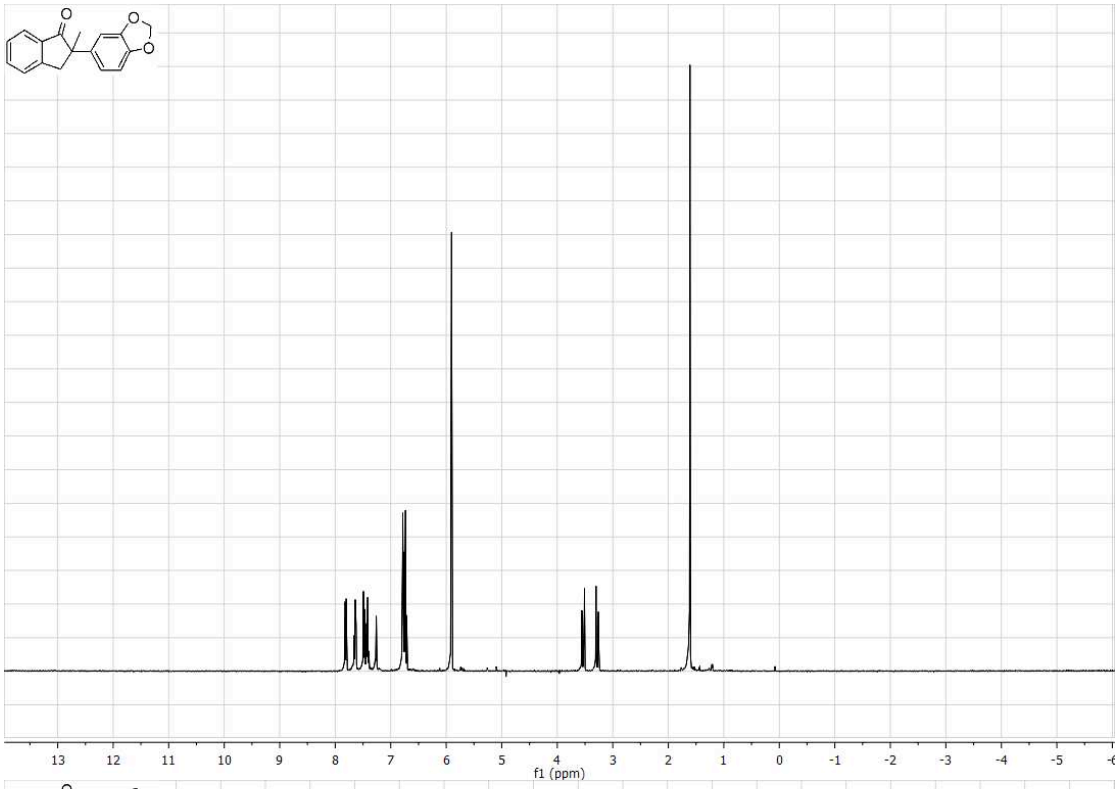
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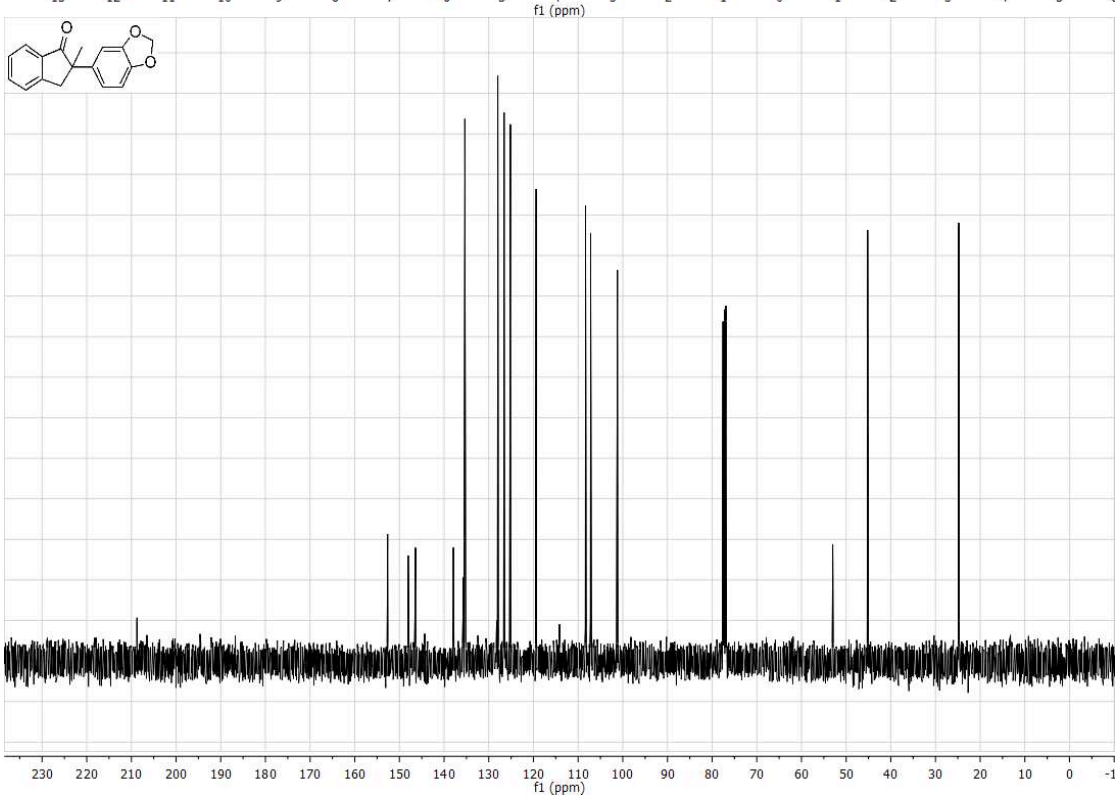
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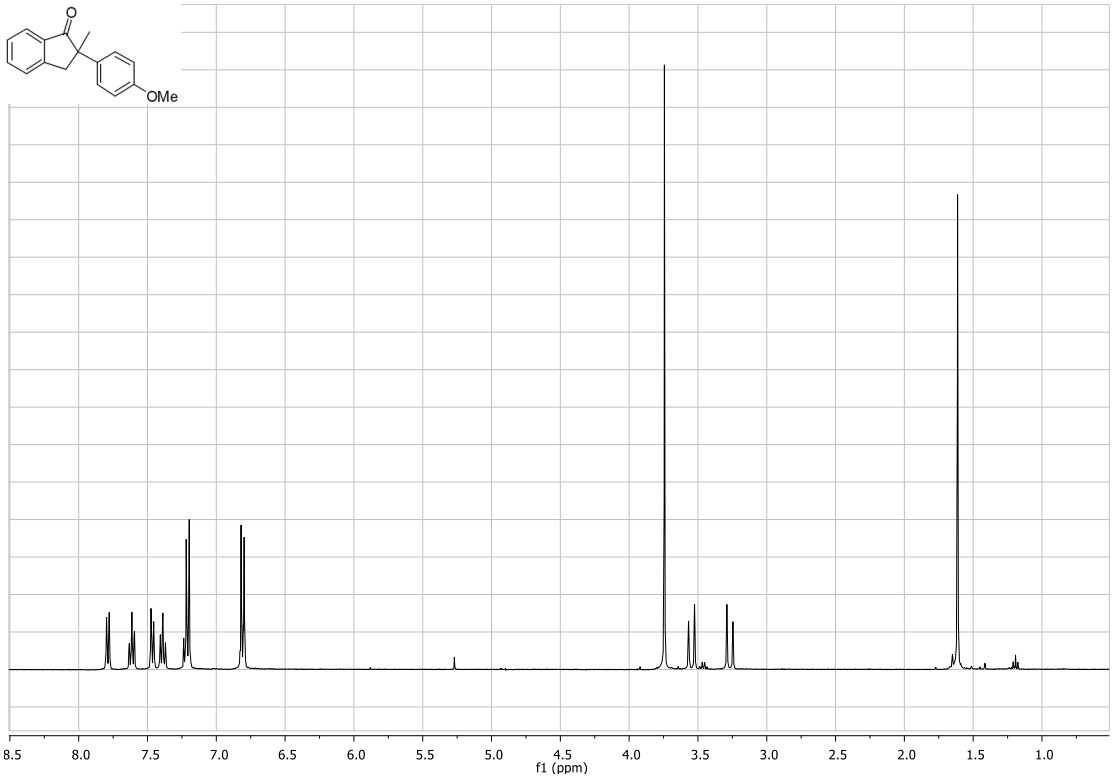
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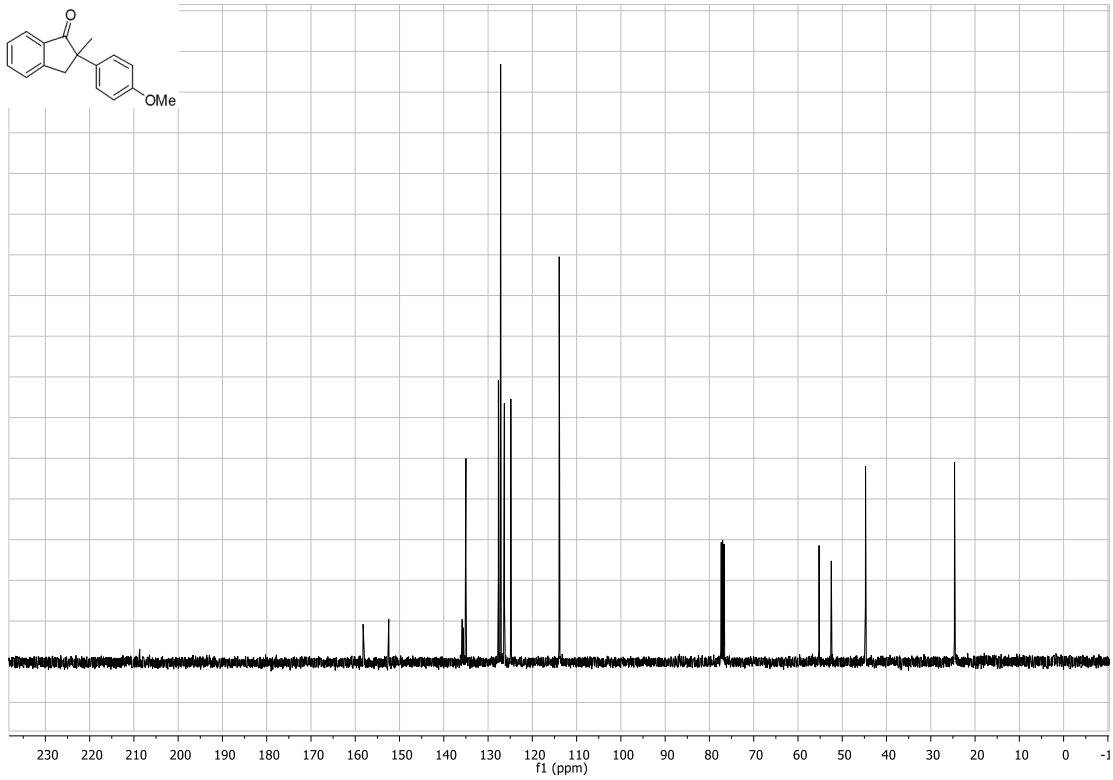
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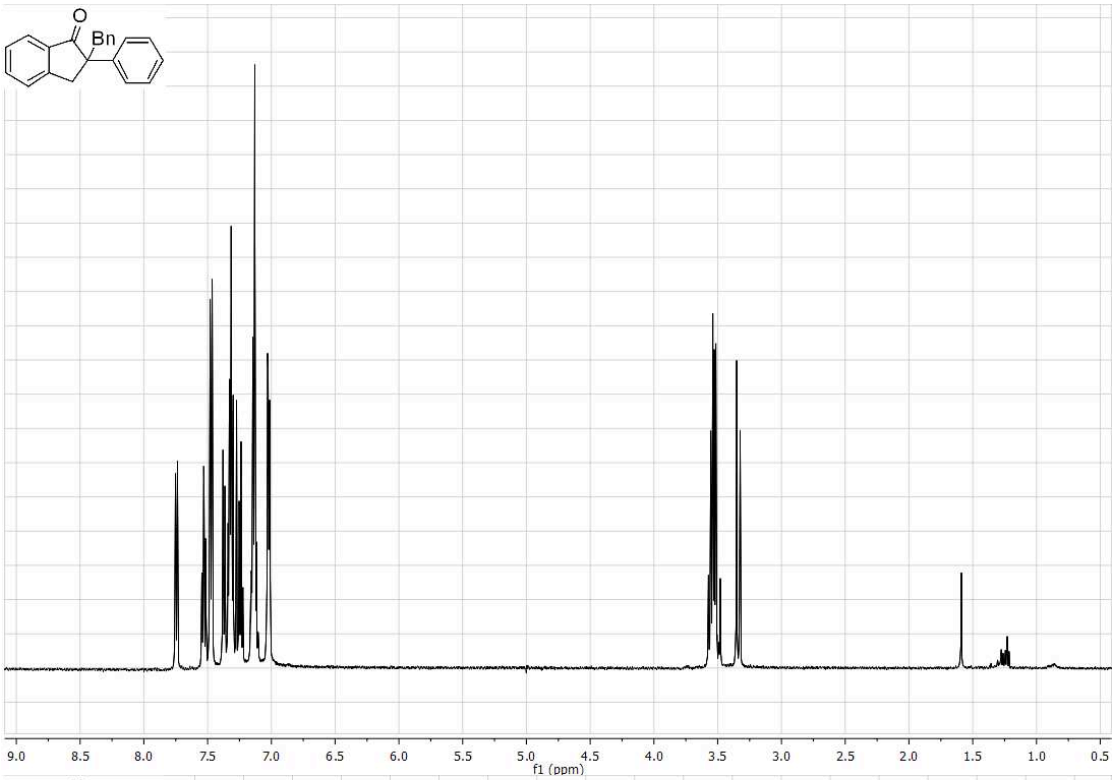
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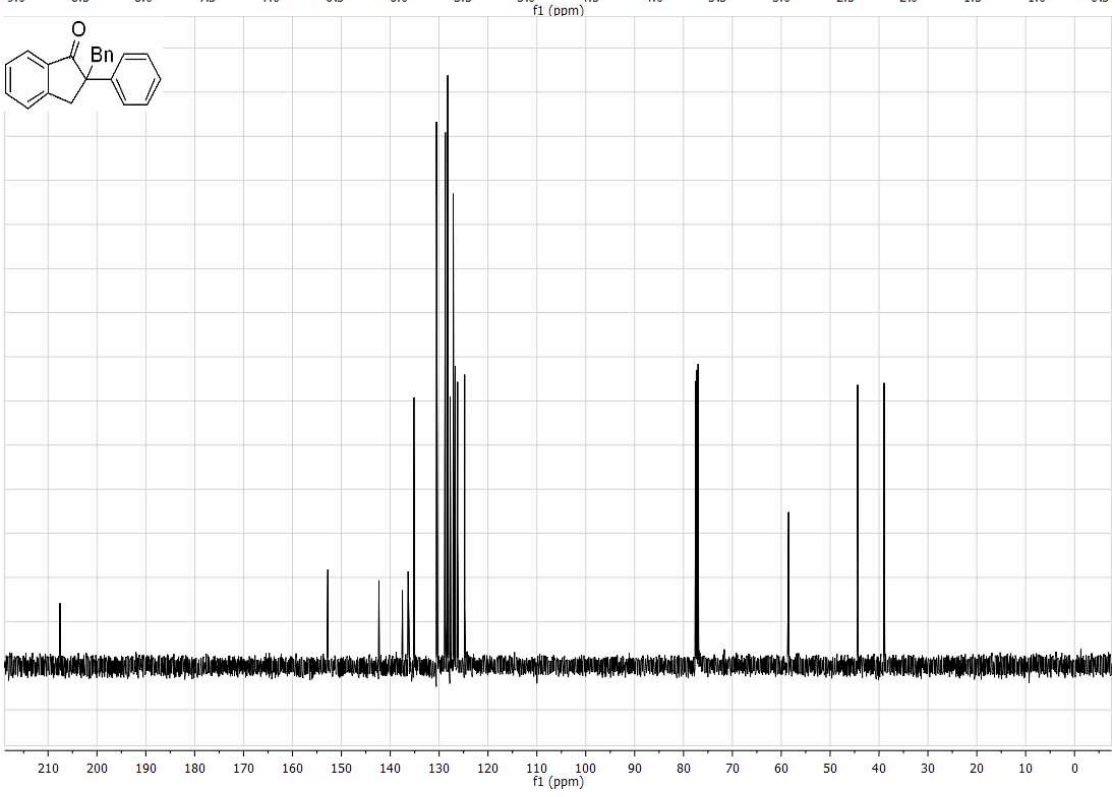
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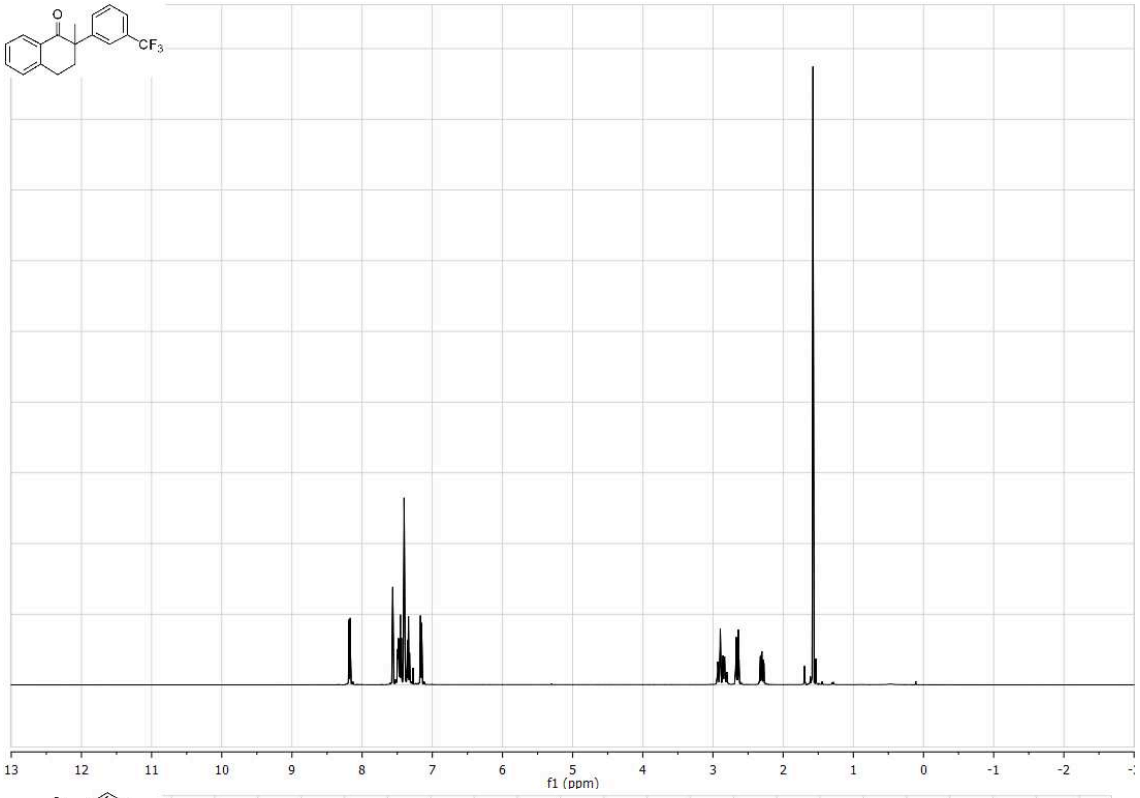
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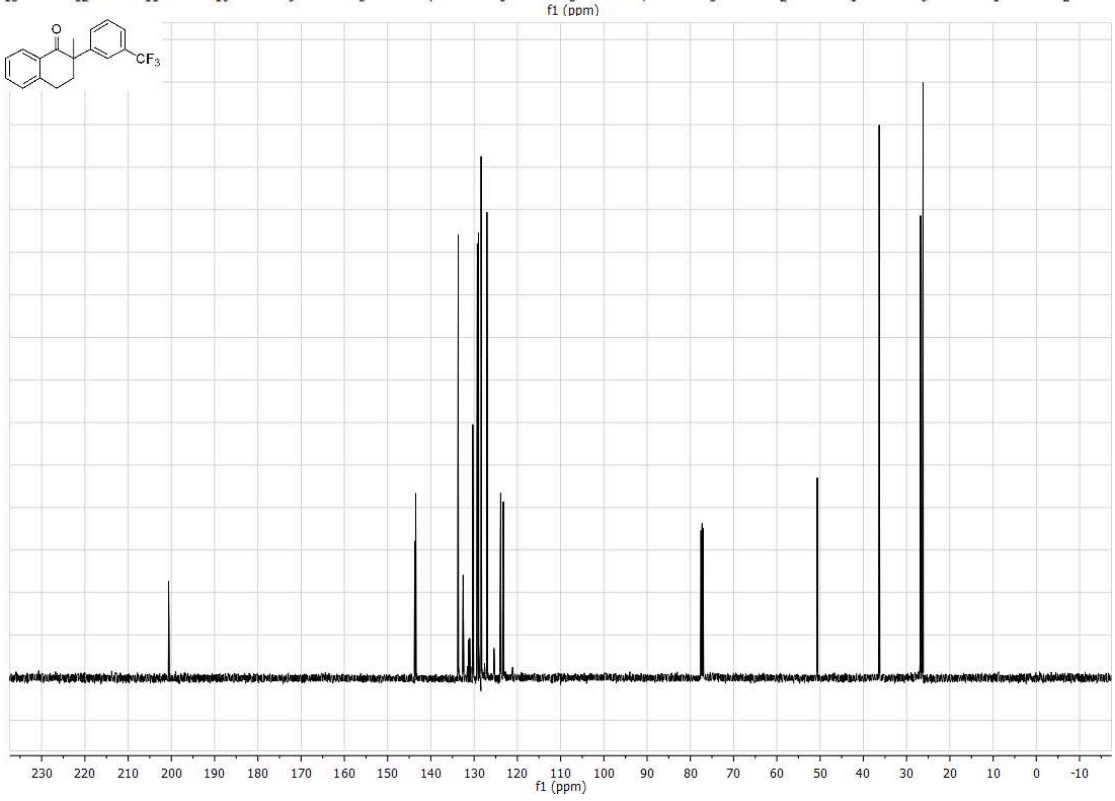
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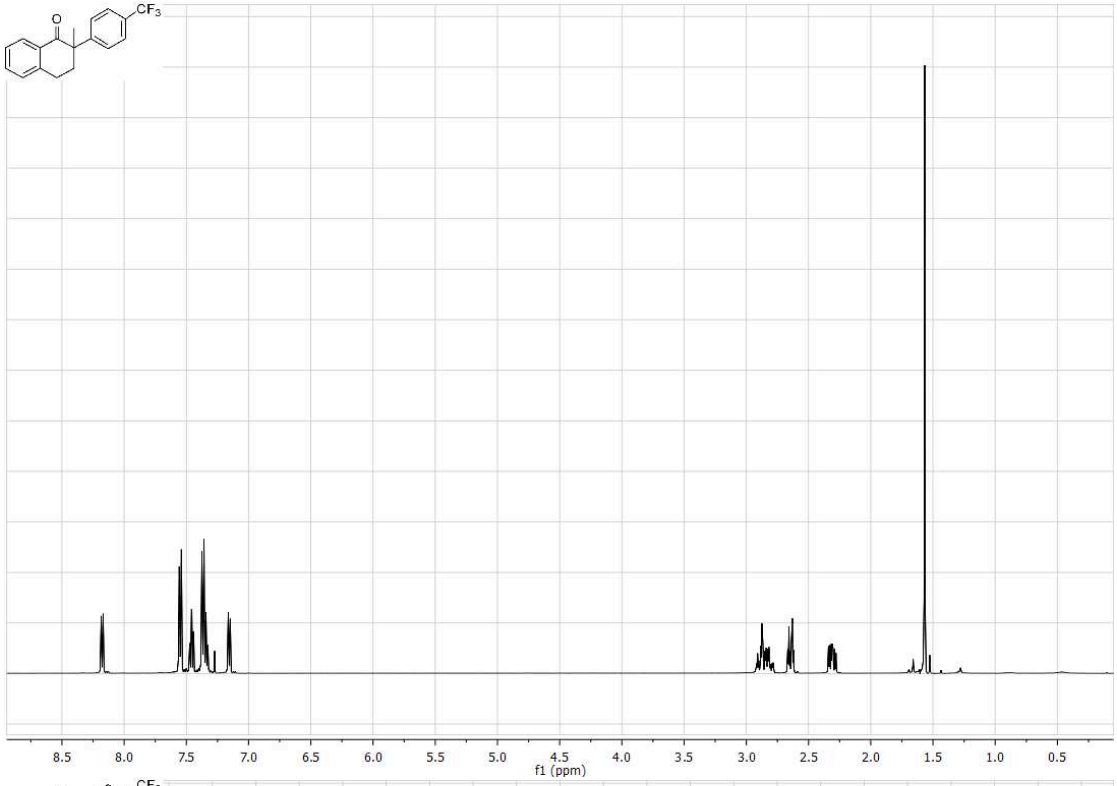
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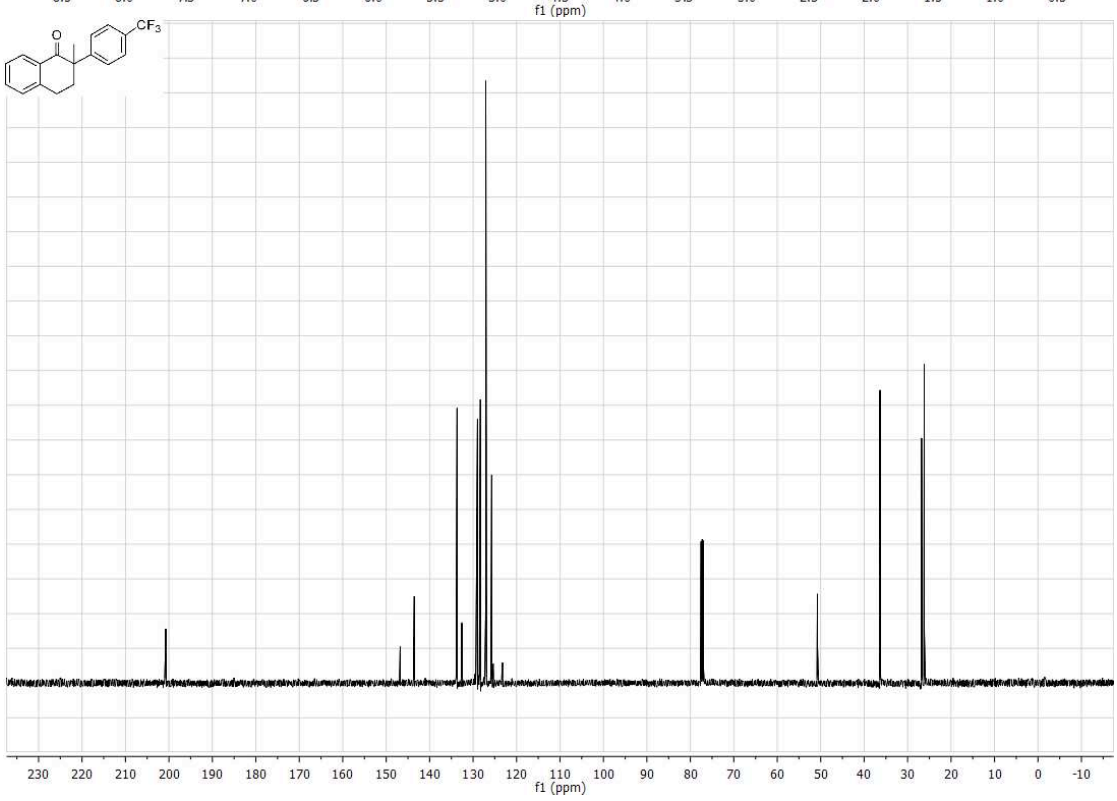
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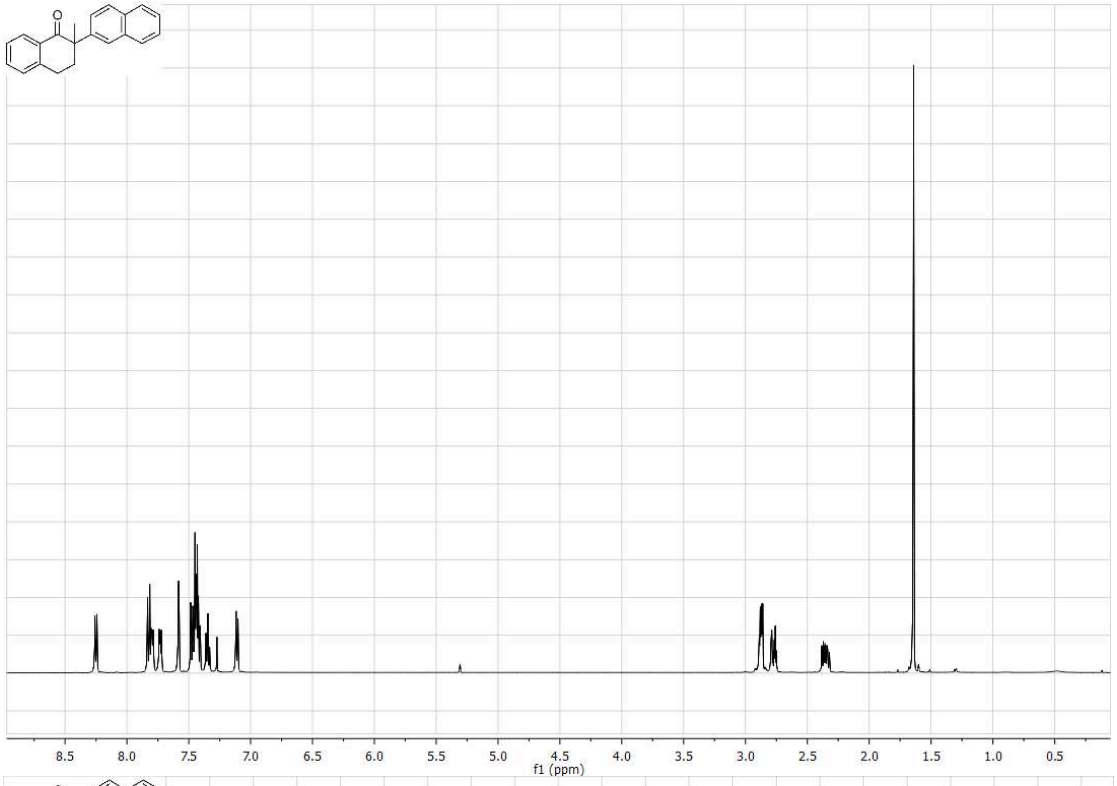
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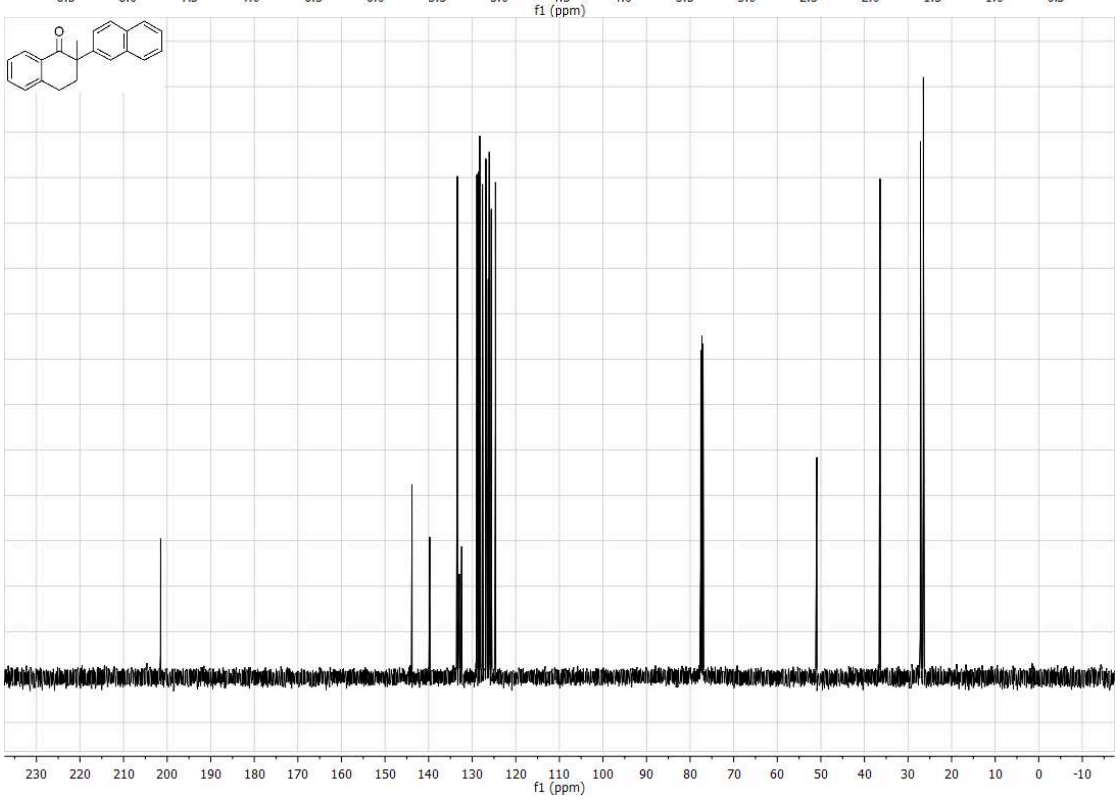
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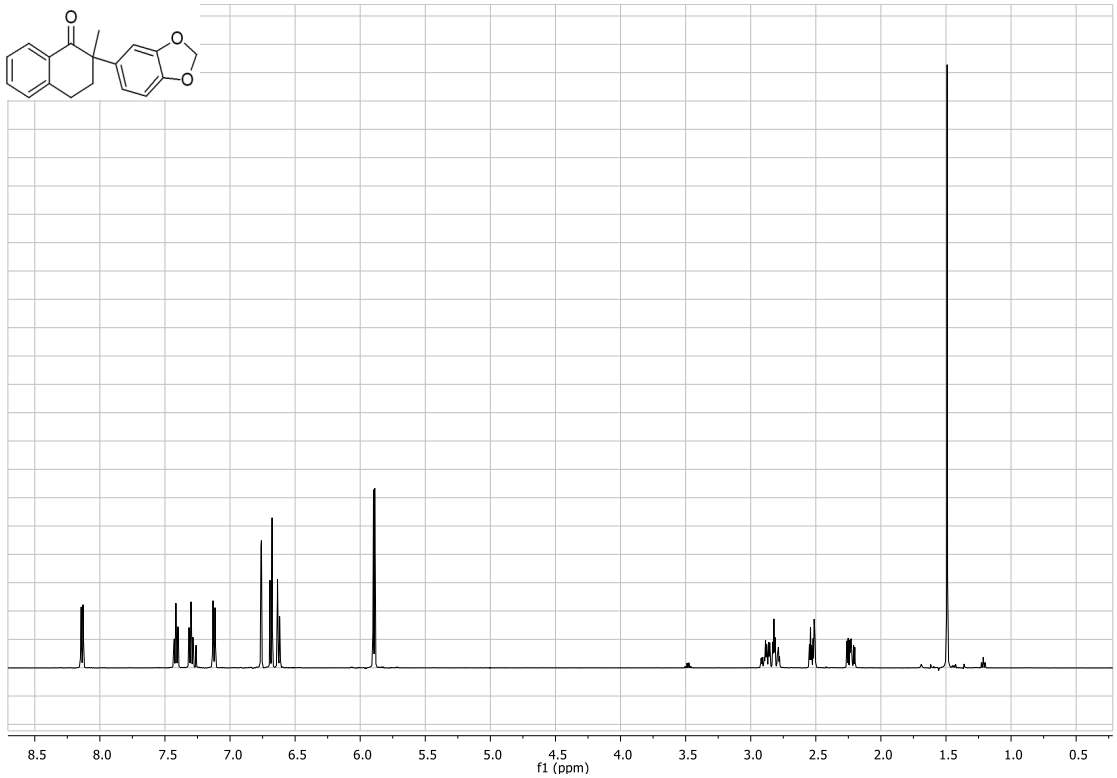
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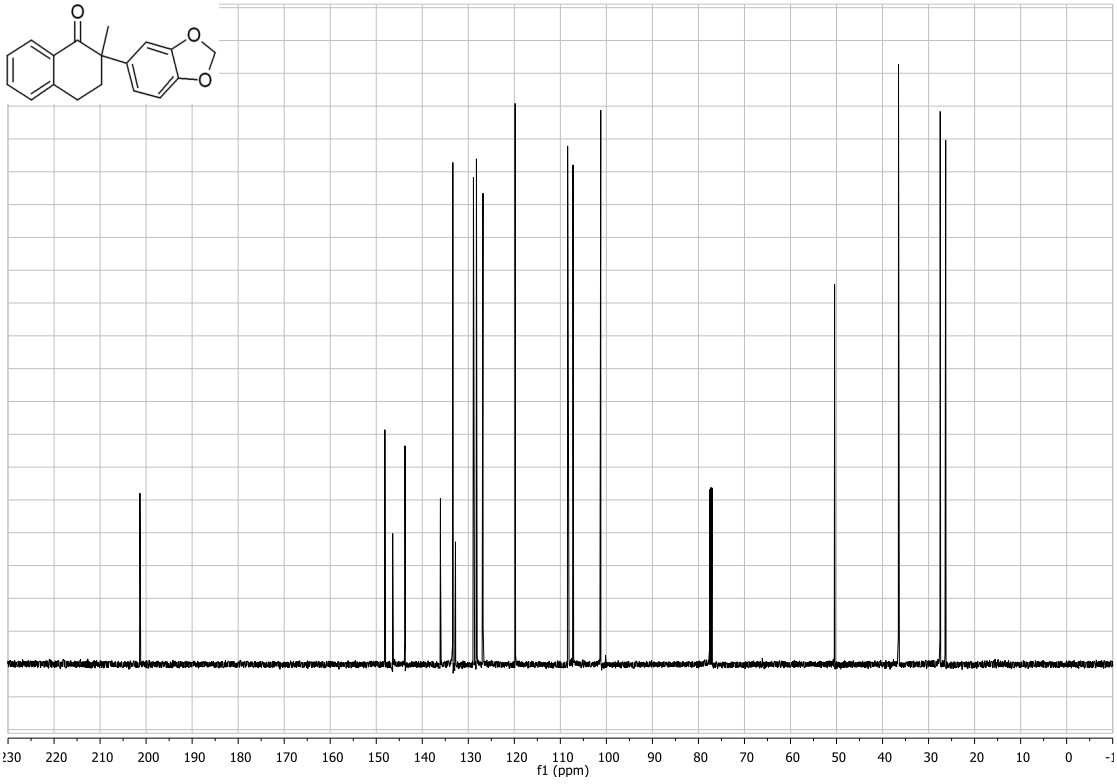
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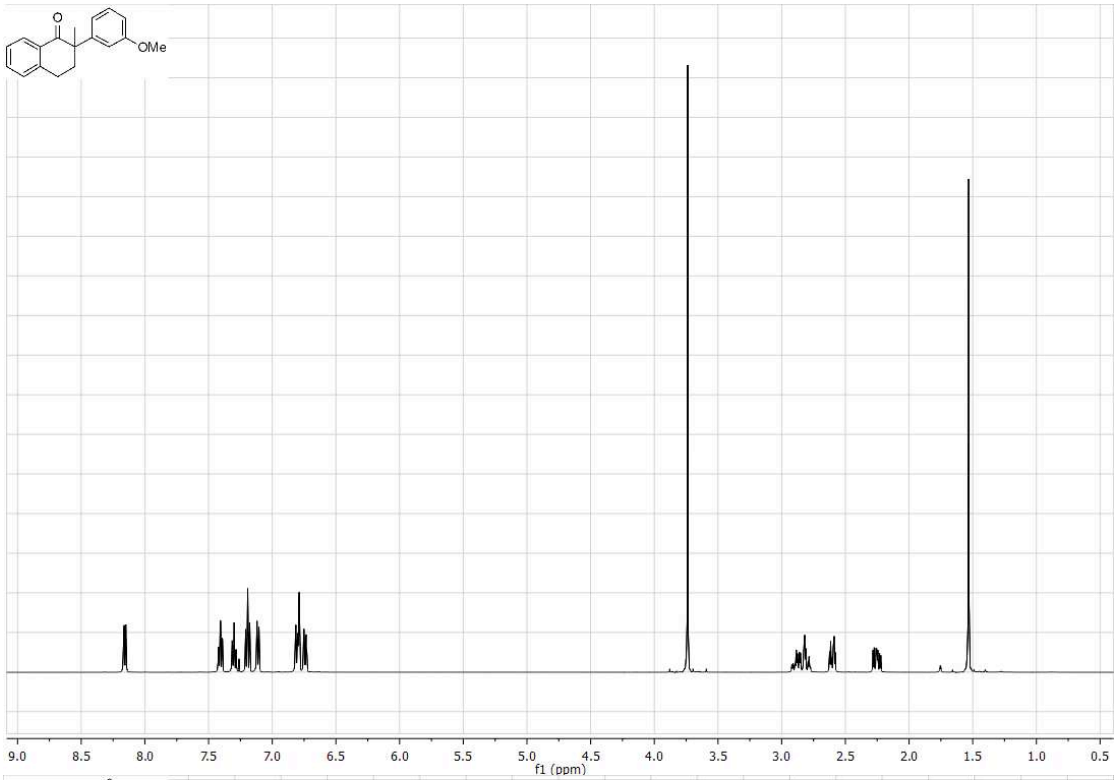
0
f1 (ppm)


O
OMe
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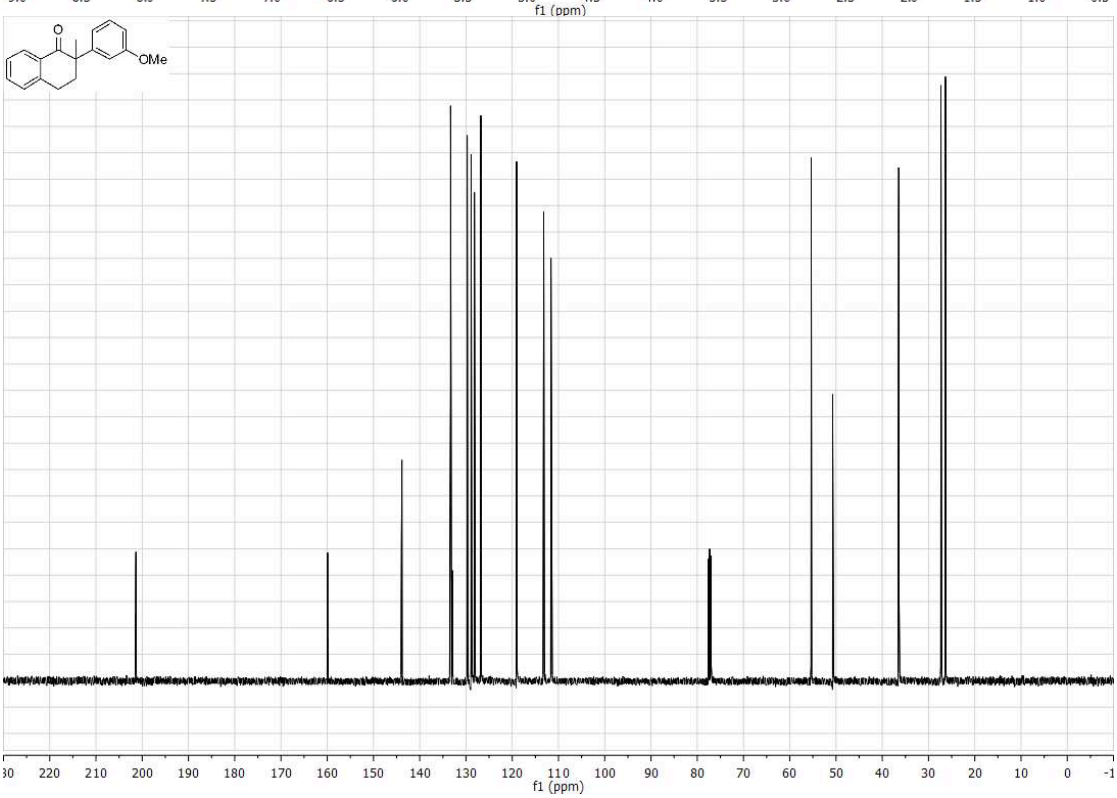
f1 (ppm)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OMe
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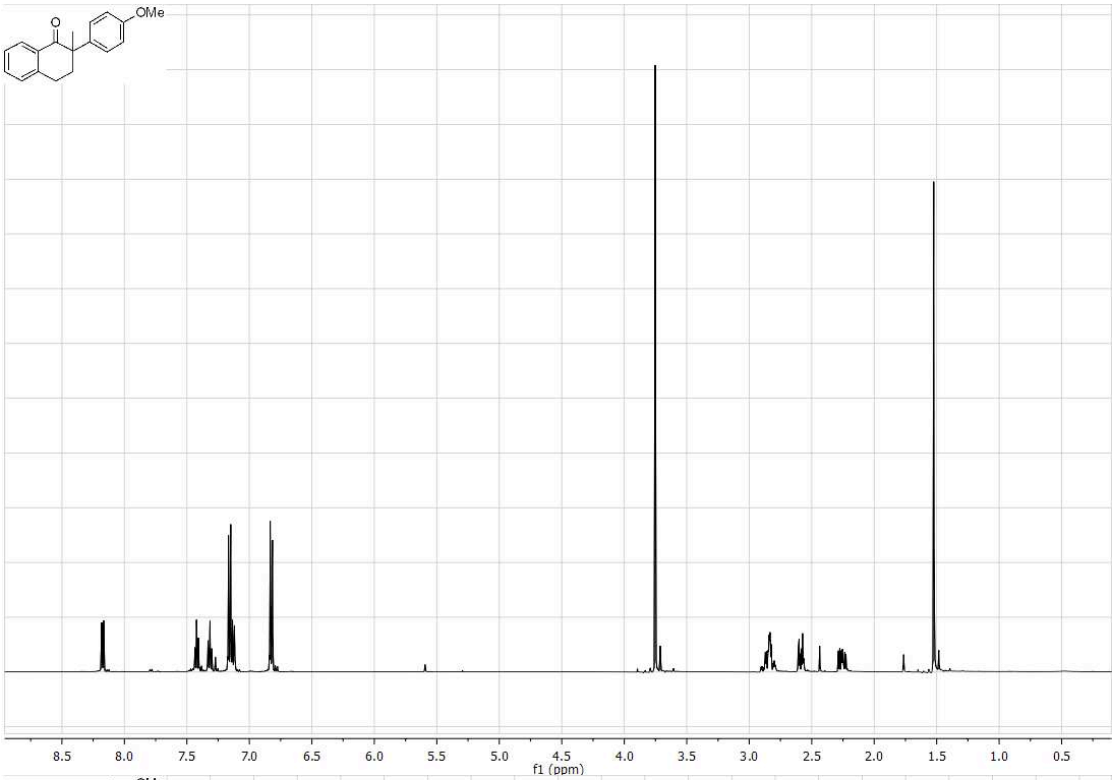
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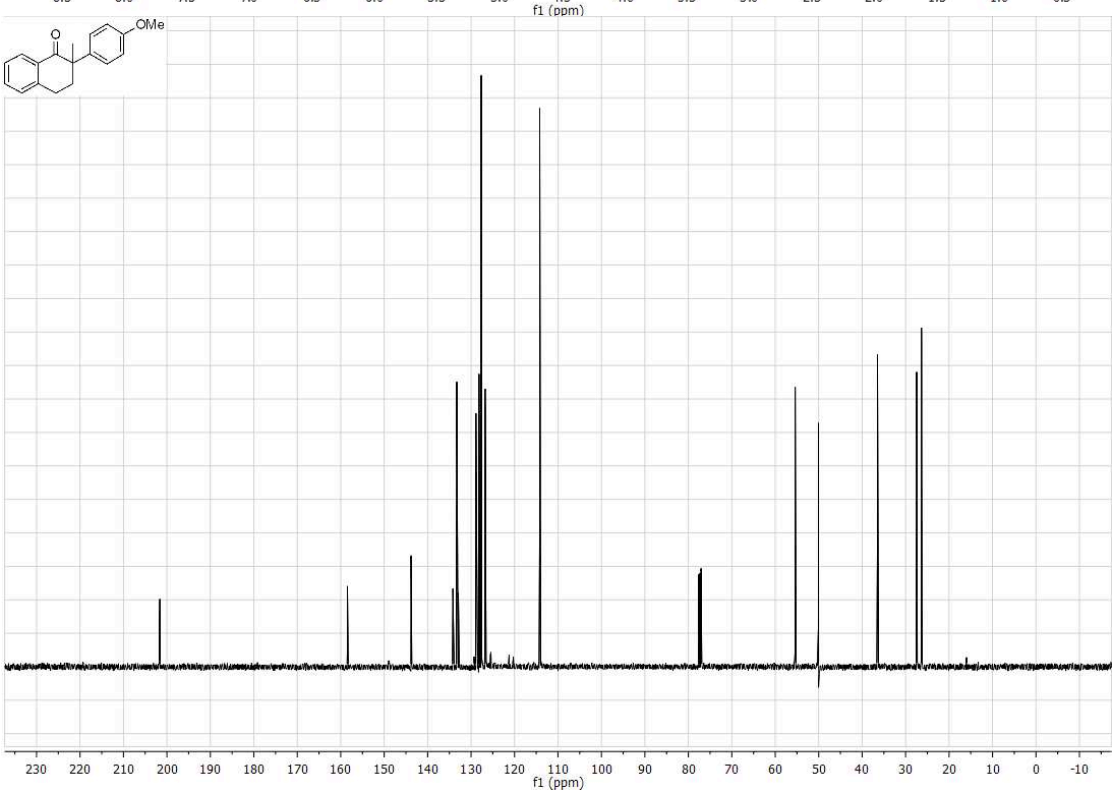
f1 (ppm)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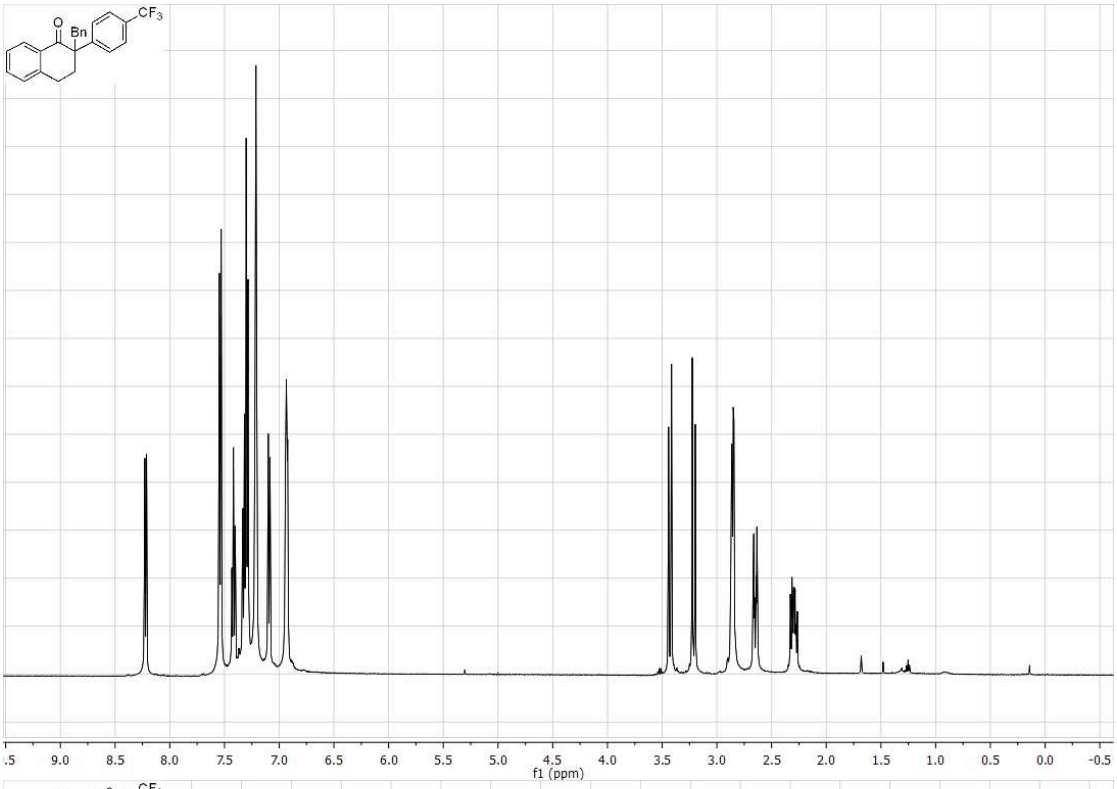
f1 (ppm)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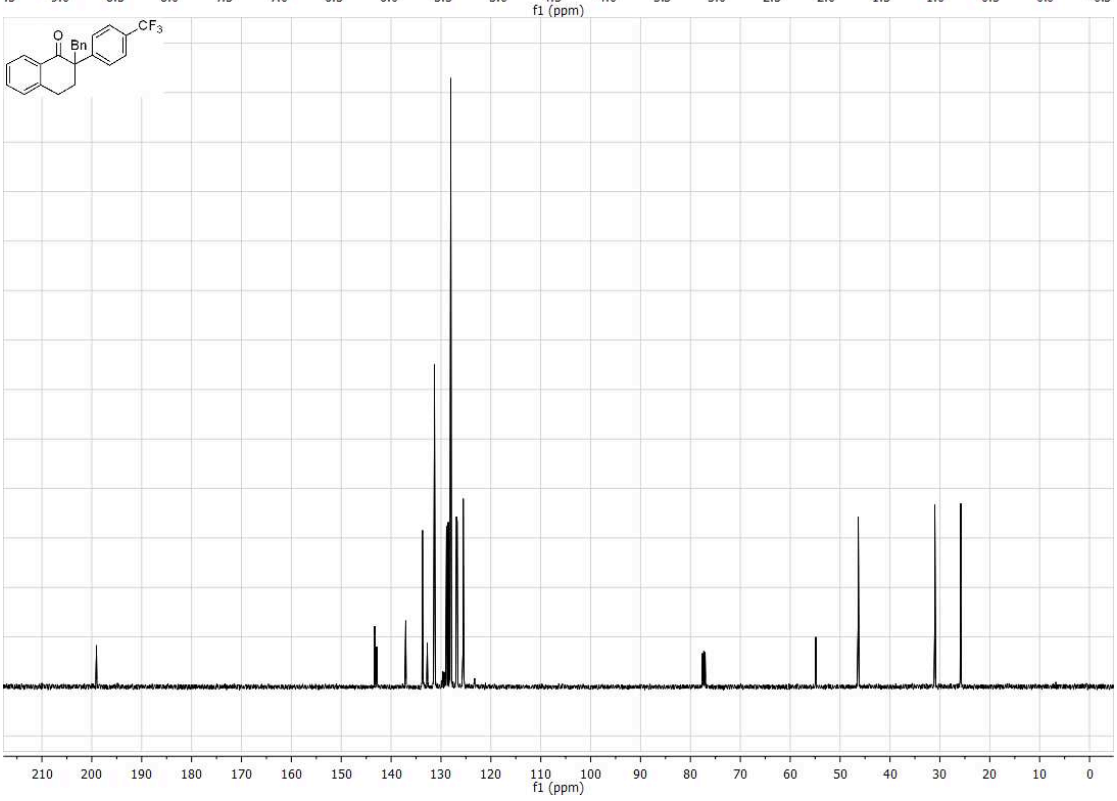
Bn
CF3
f1 (ppm)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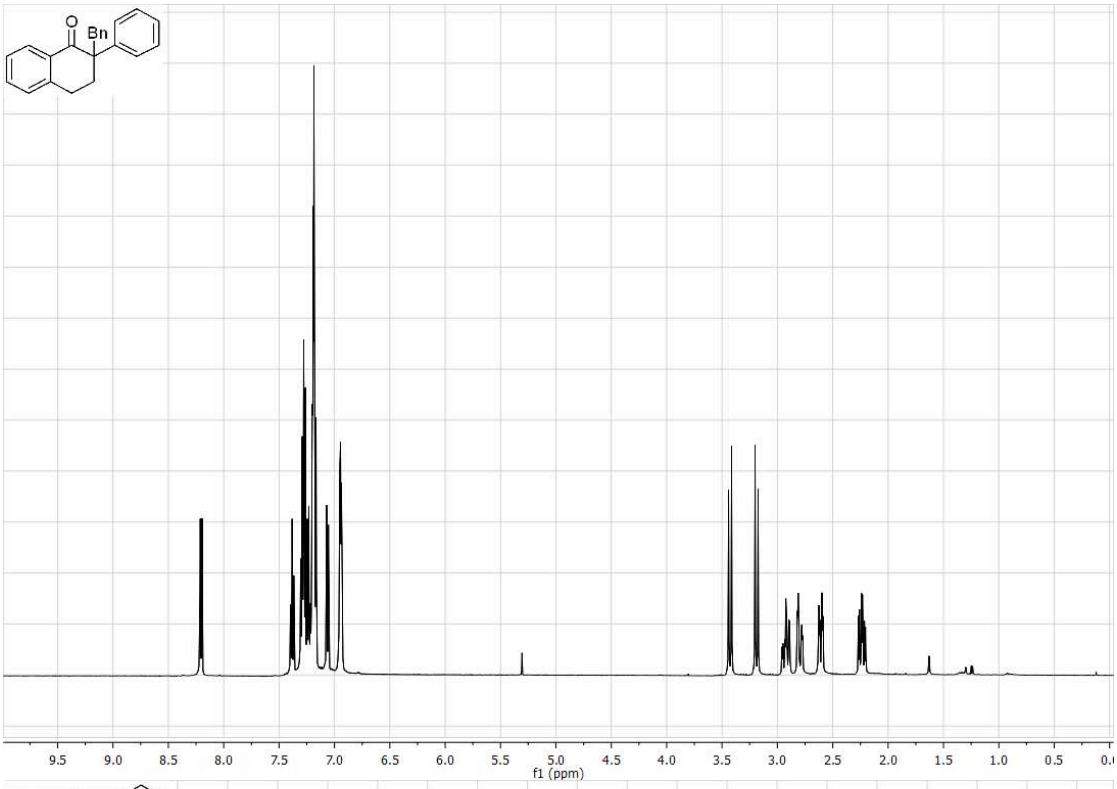
CF3
f1 (ppm)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Bn
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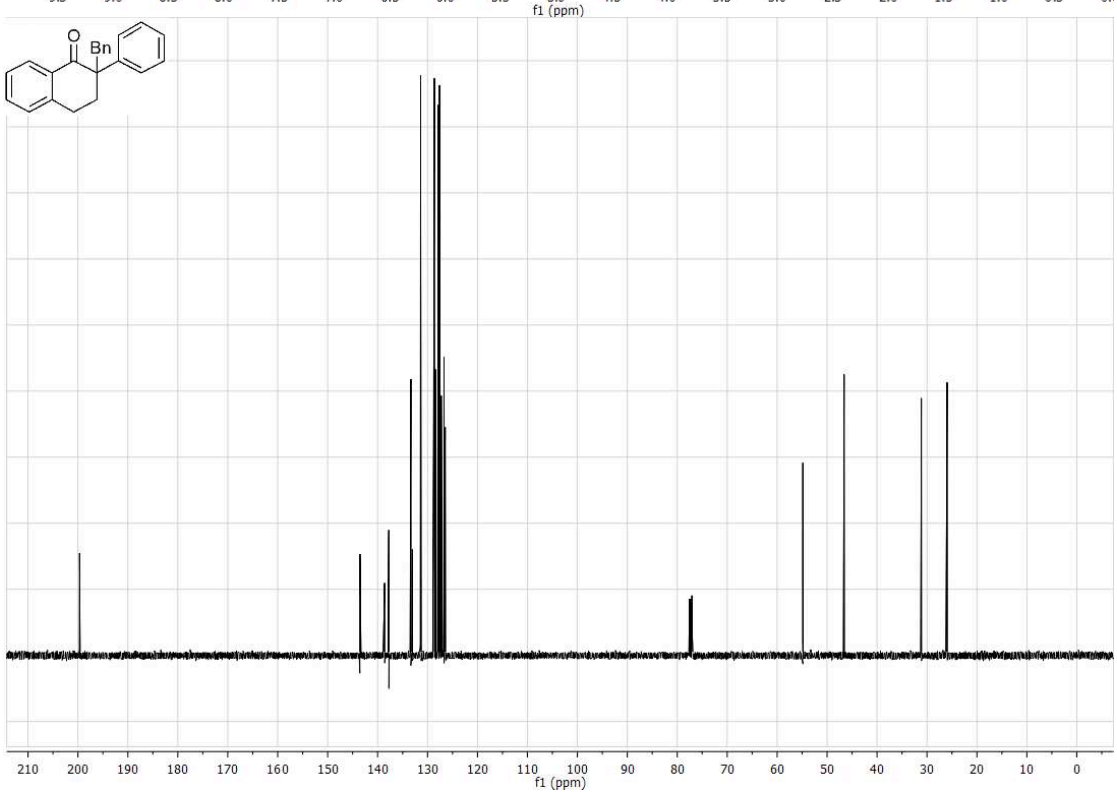
f1 (ppm)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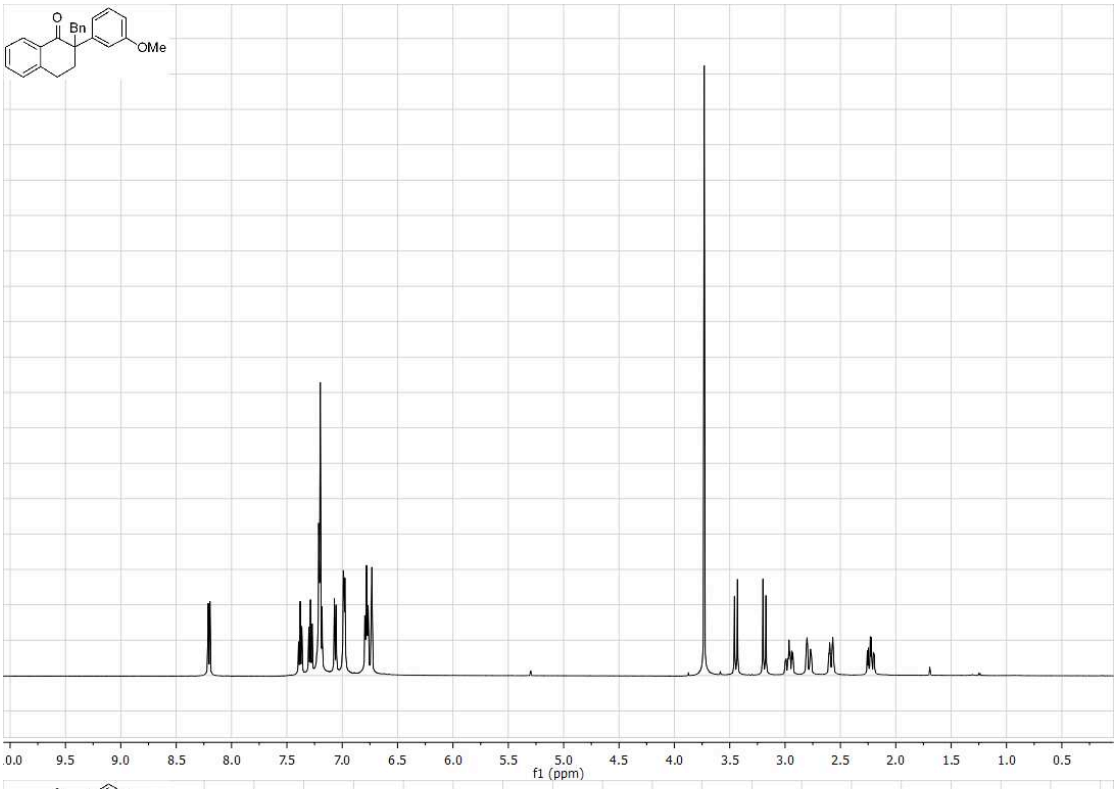
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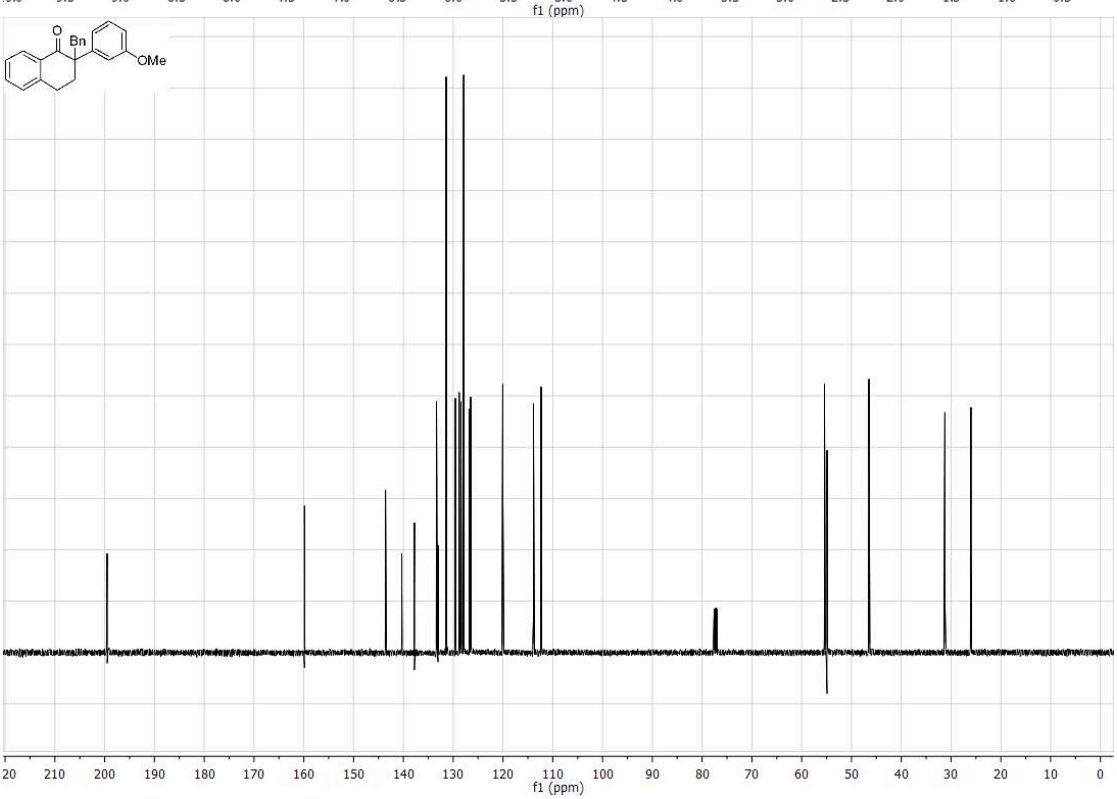
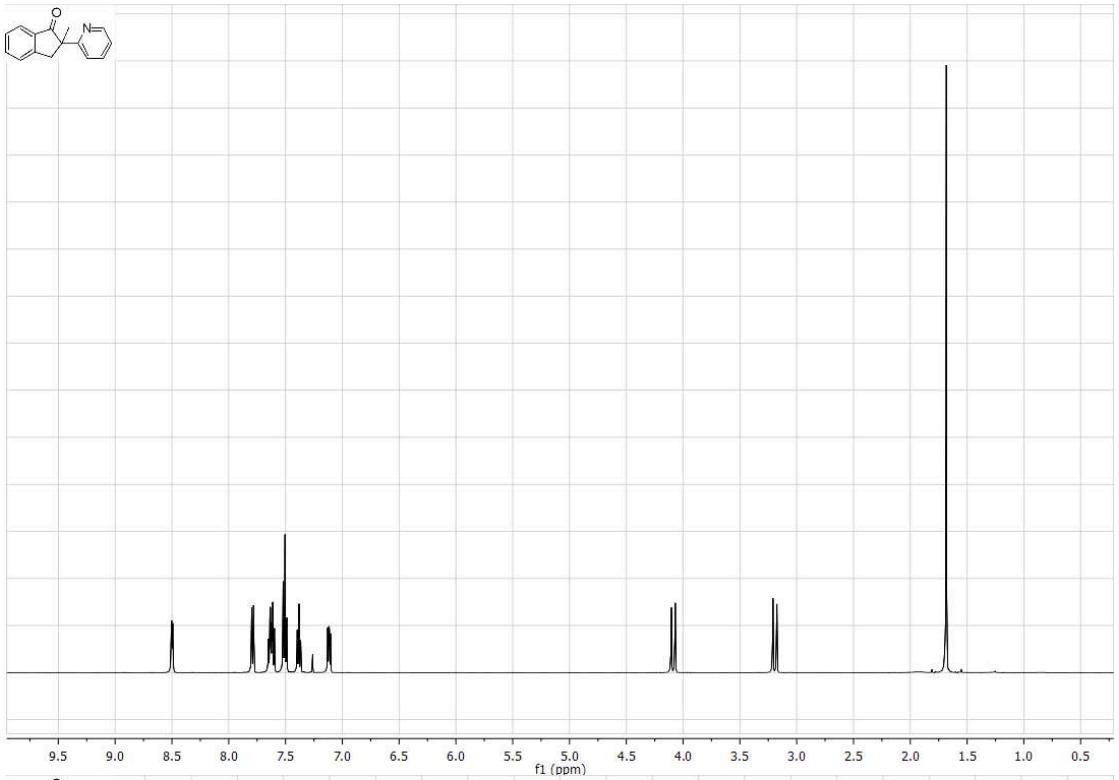
Bn
OMe
f1 (ppm)


O
Bn
OMe
f1 (ppm)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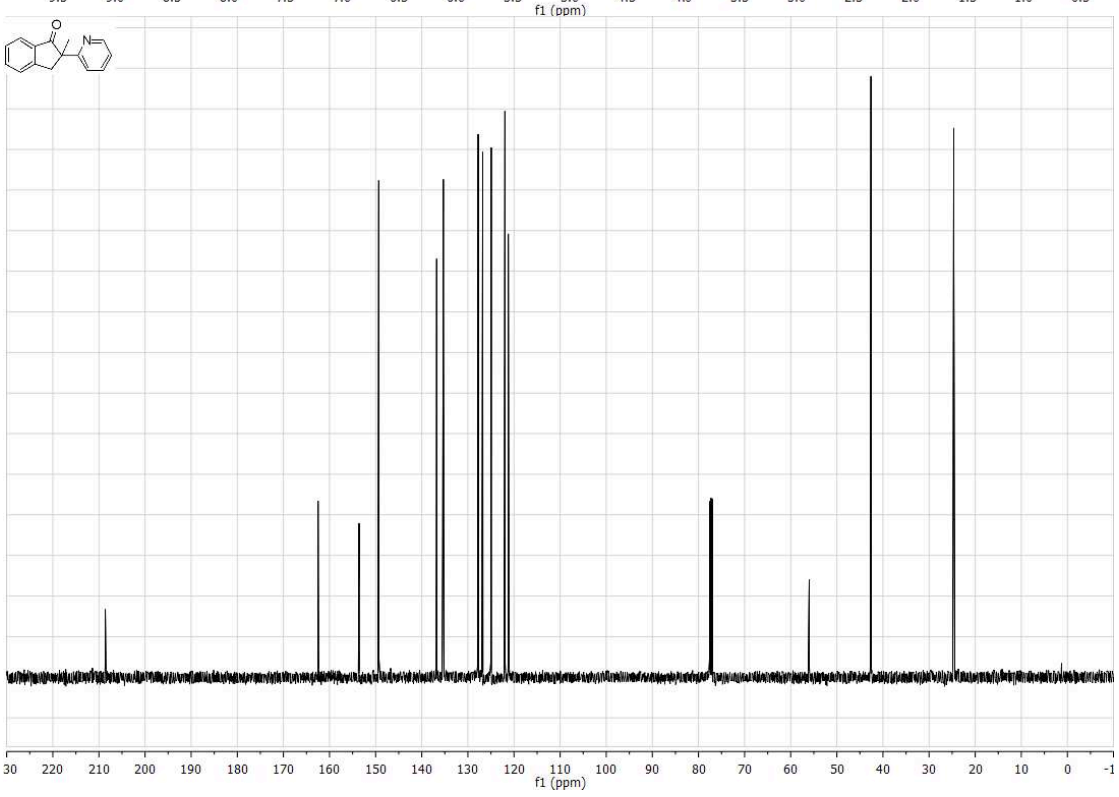
f1 (ppm)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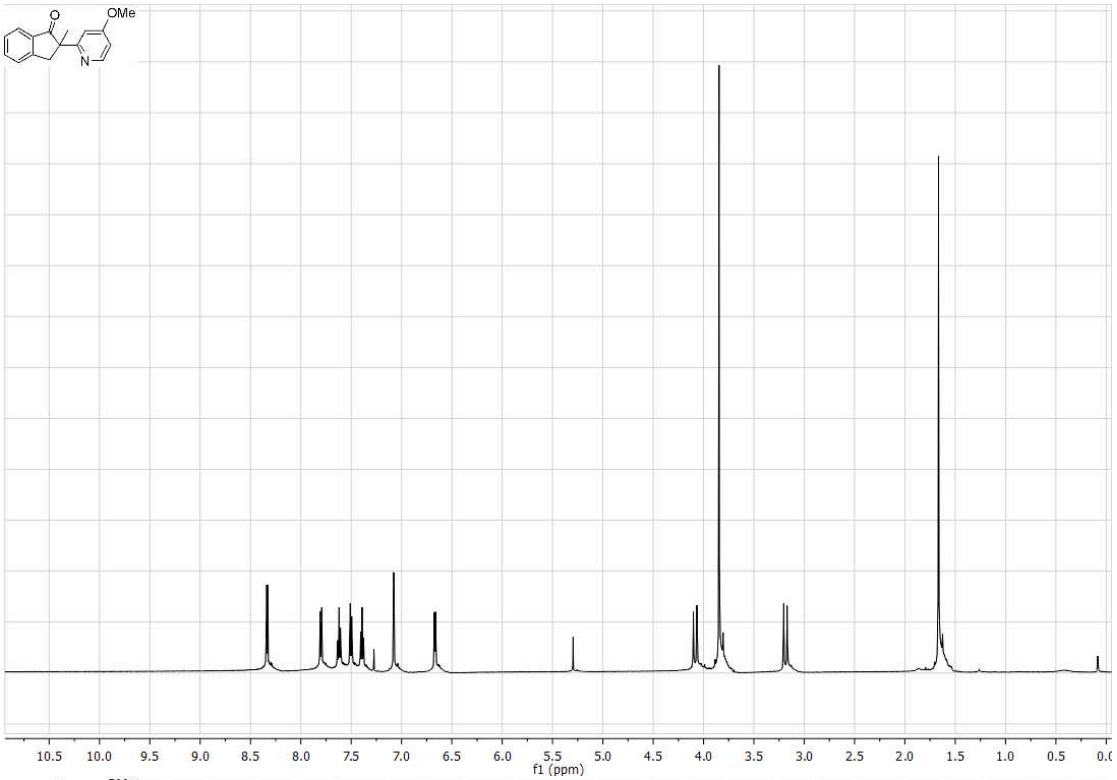
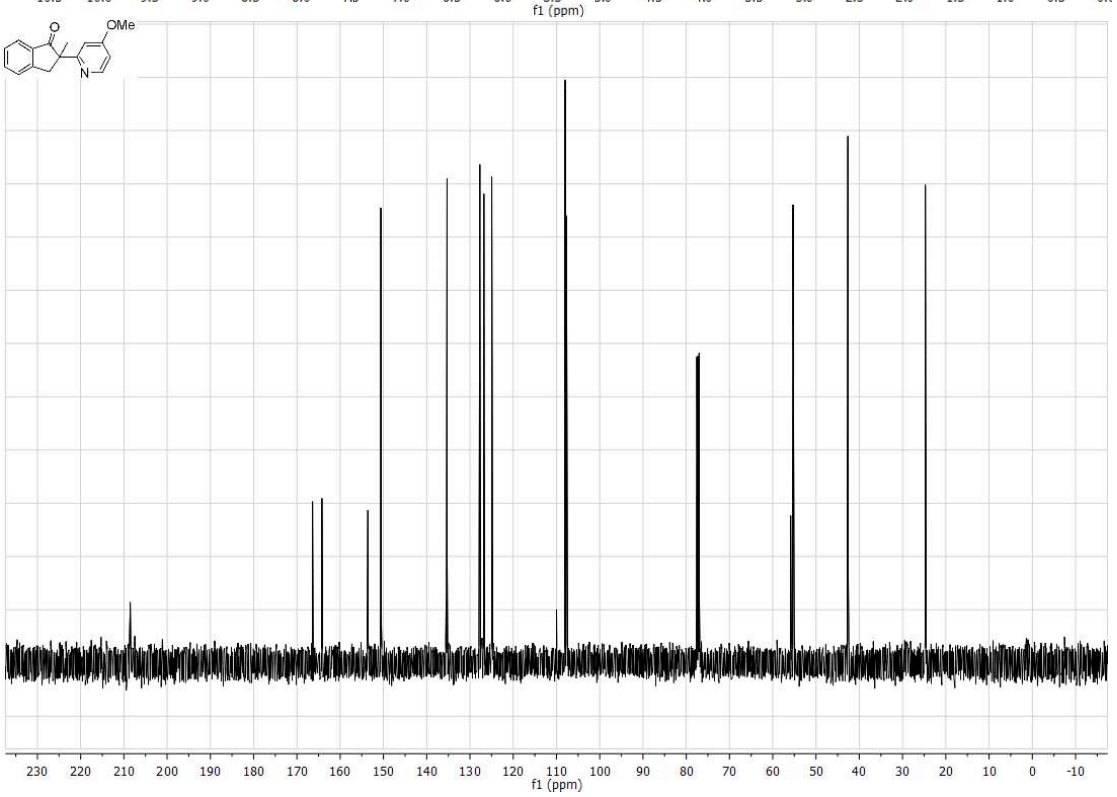
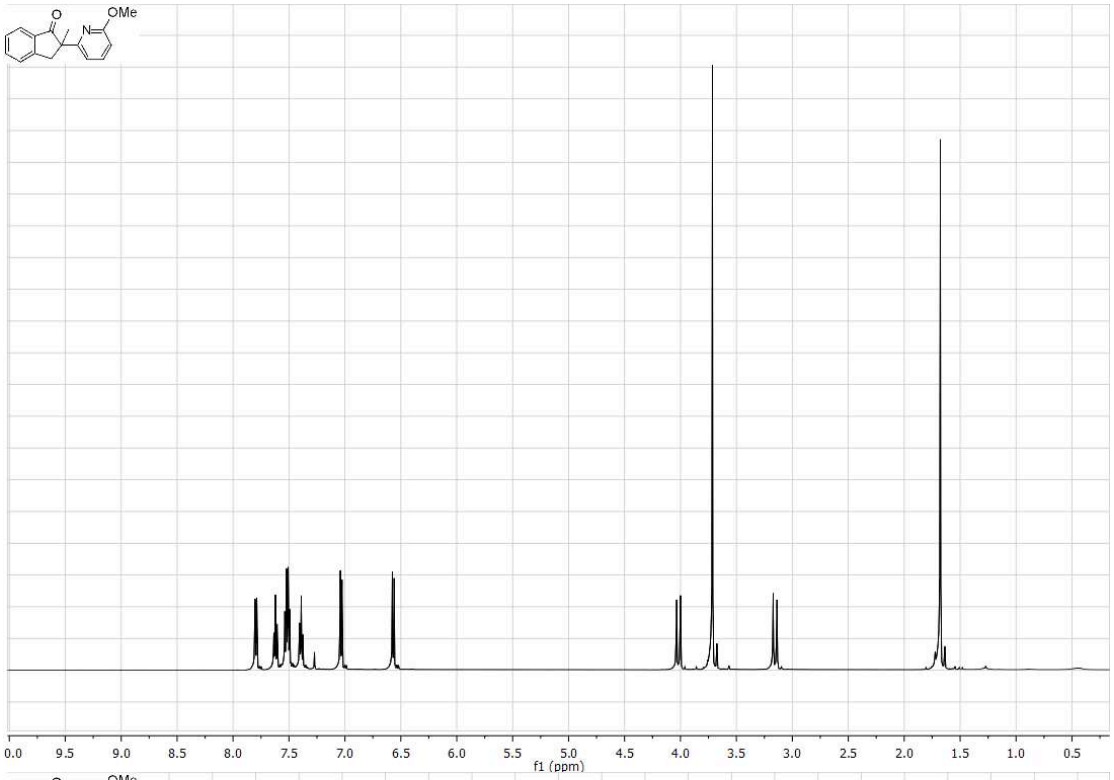
f1 (ppm)


OMe
O
N
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


OMe
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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OMe
N
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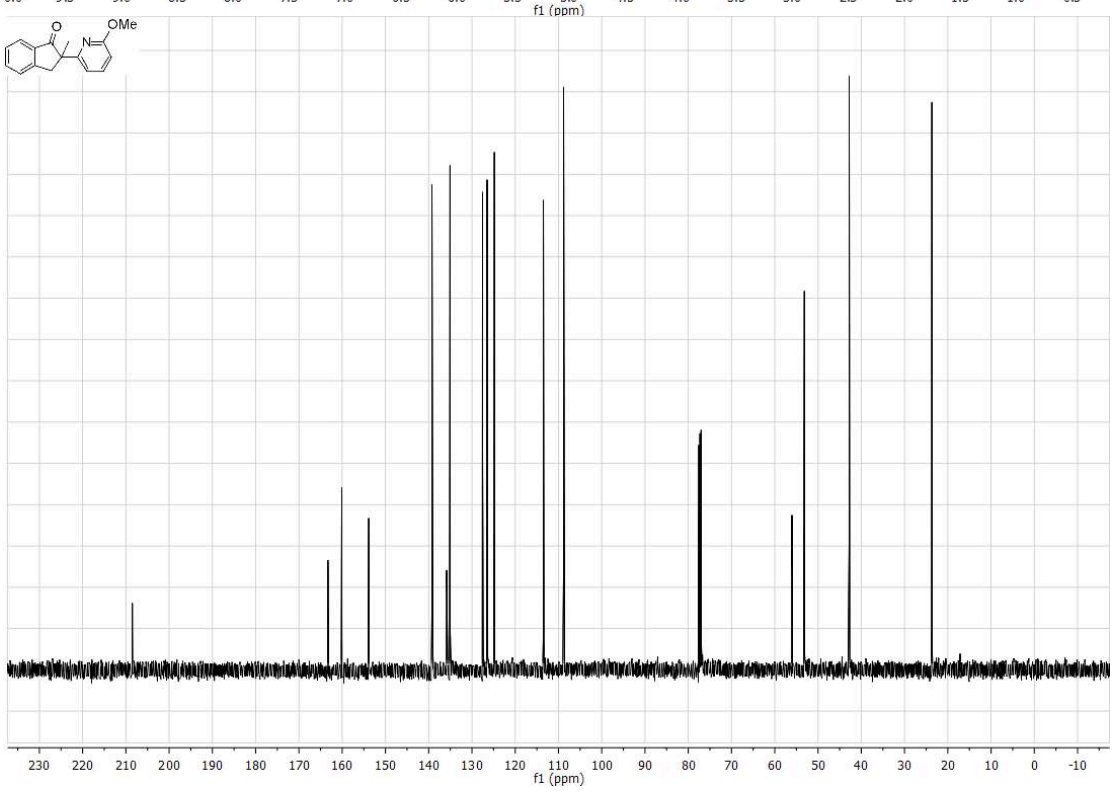
f1 (ppm)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OMe
N
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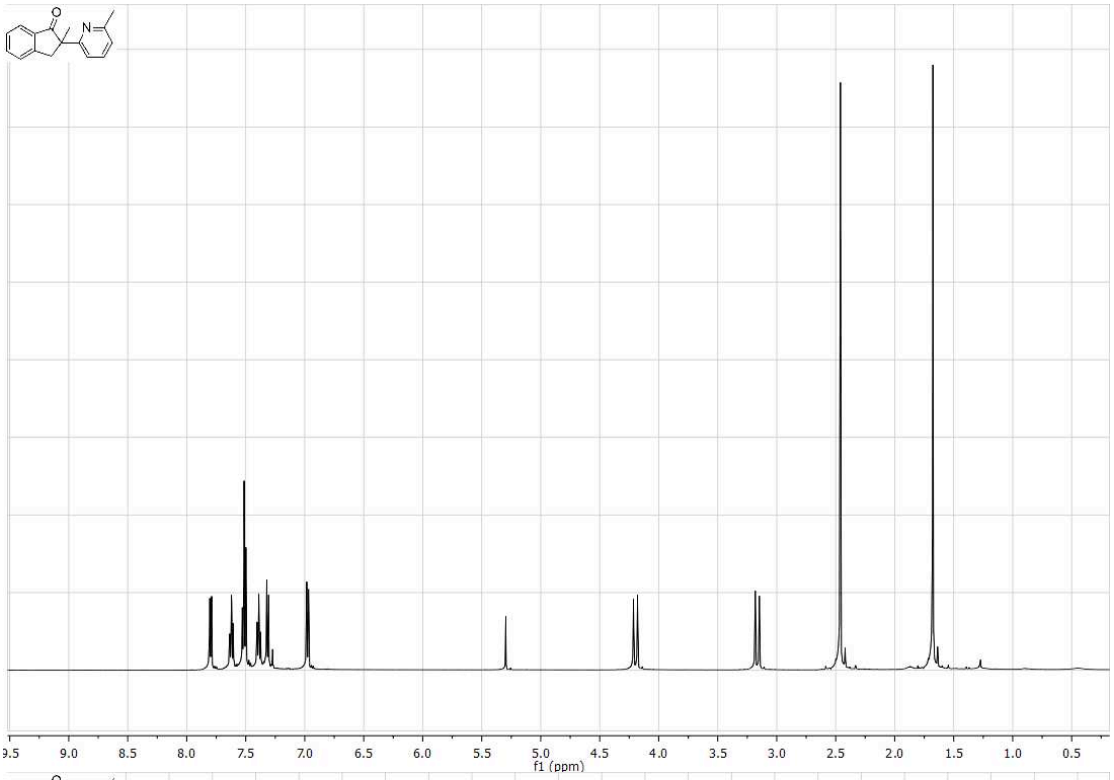
f1 (ppm)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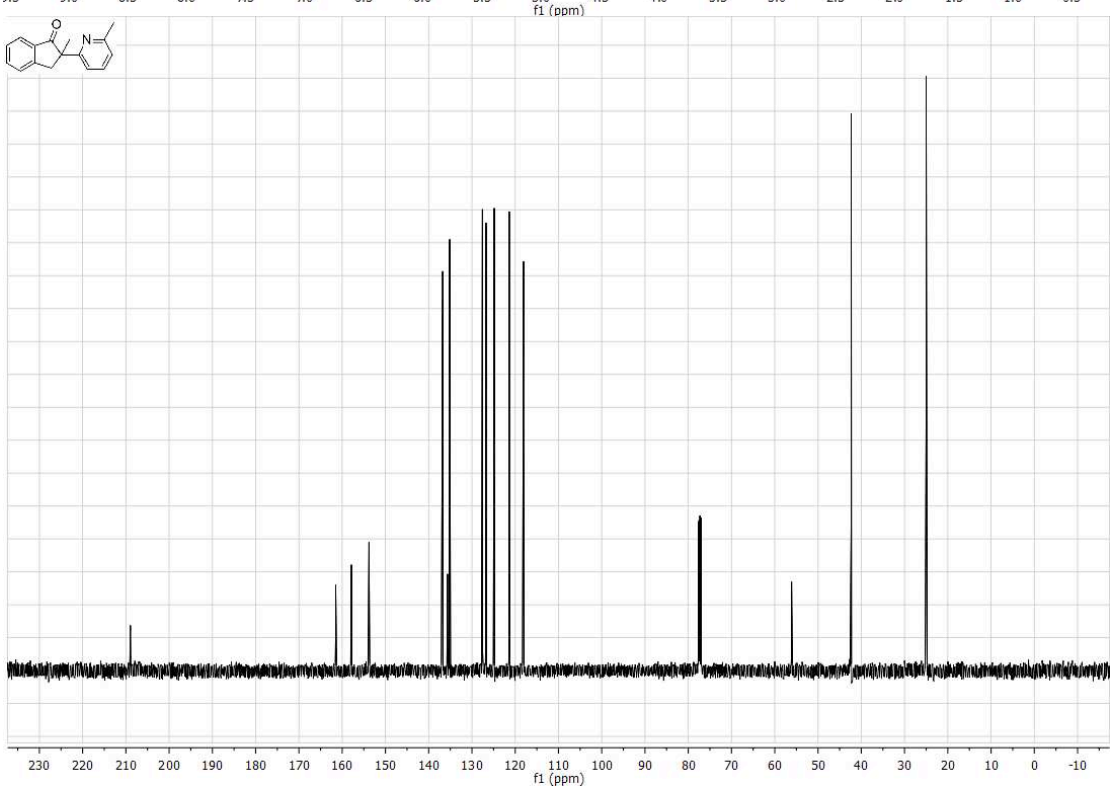
f1 (ppm)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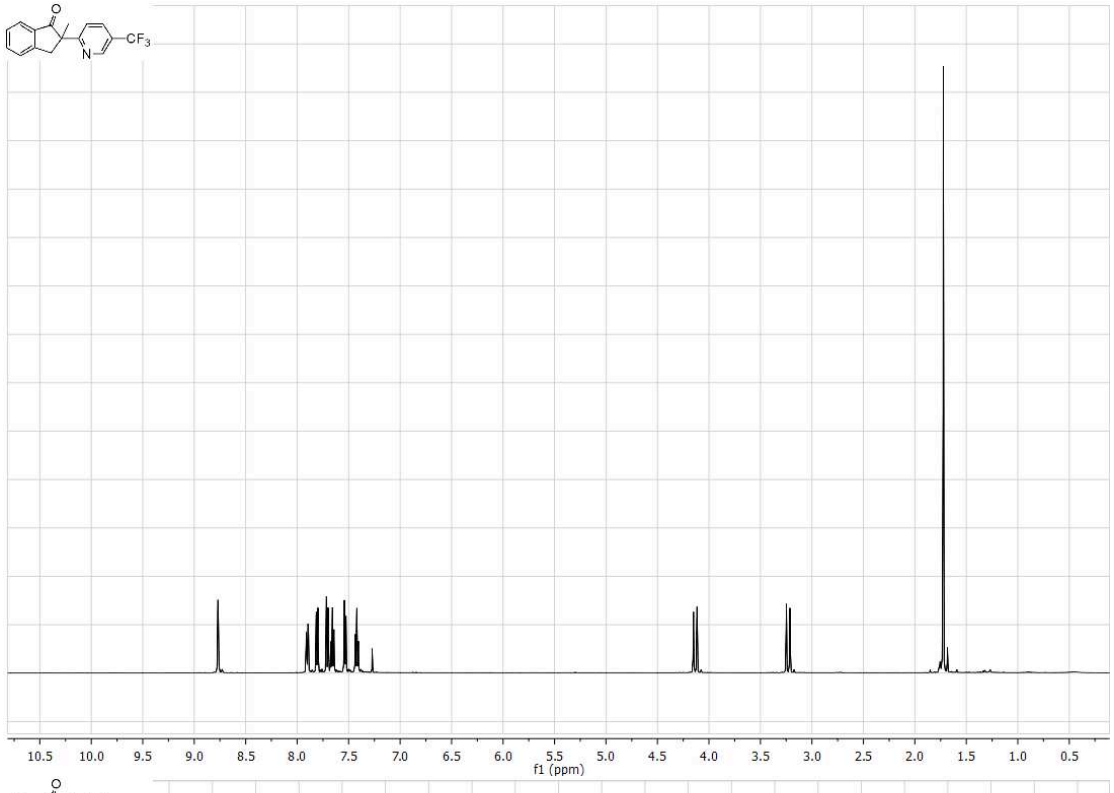
f1 (ppm)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CF3
N
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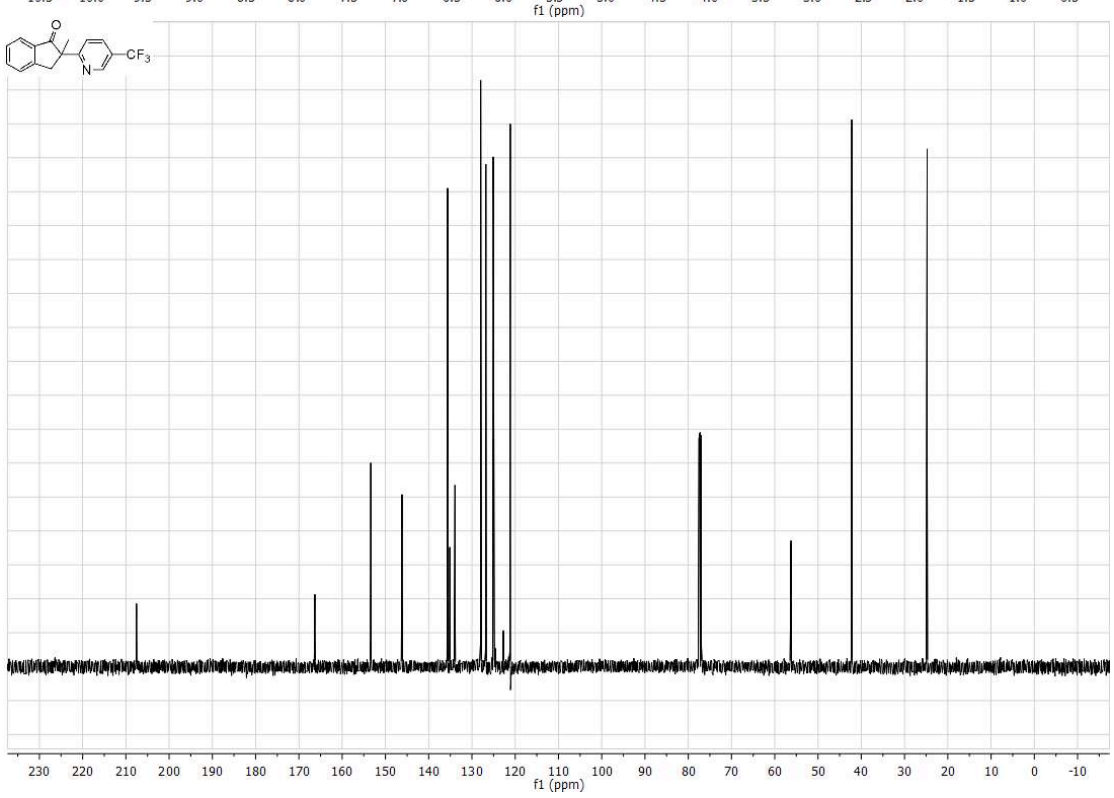
f1 (ppm)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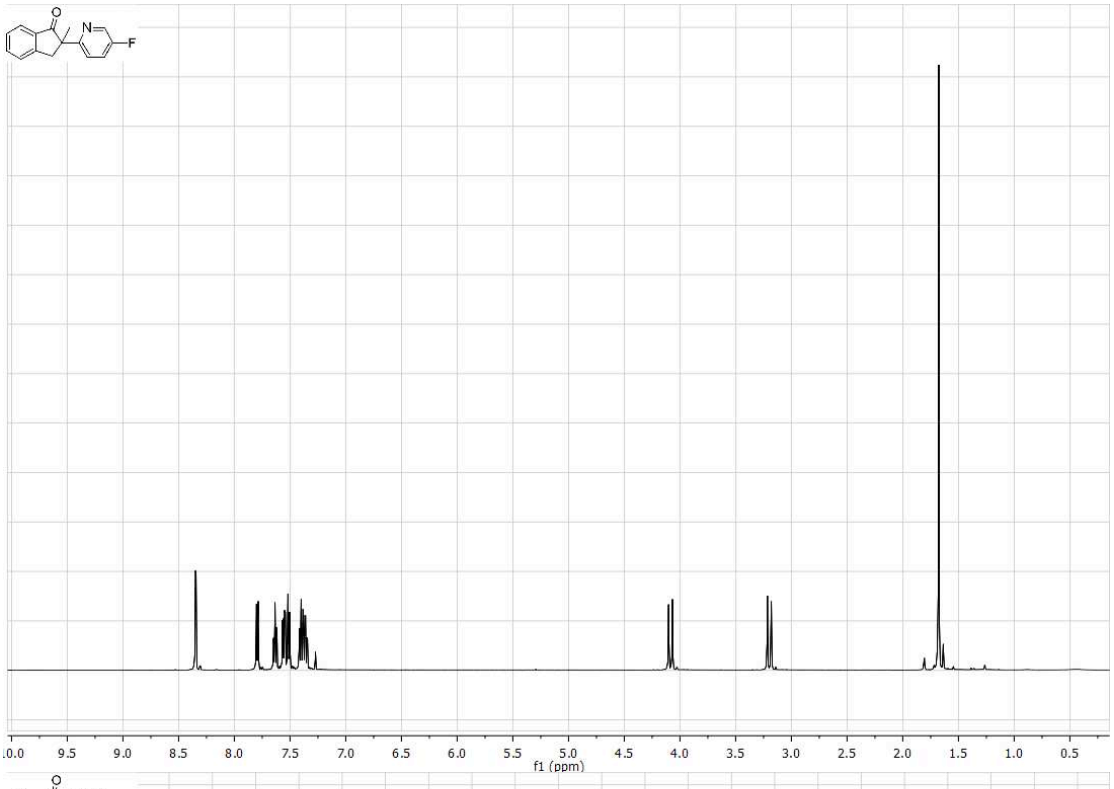
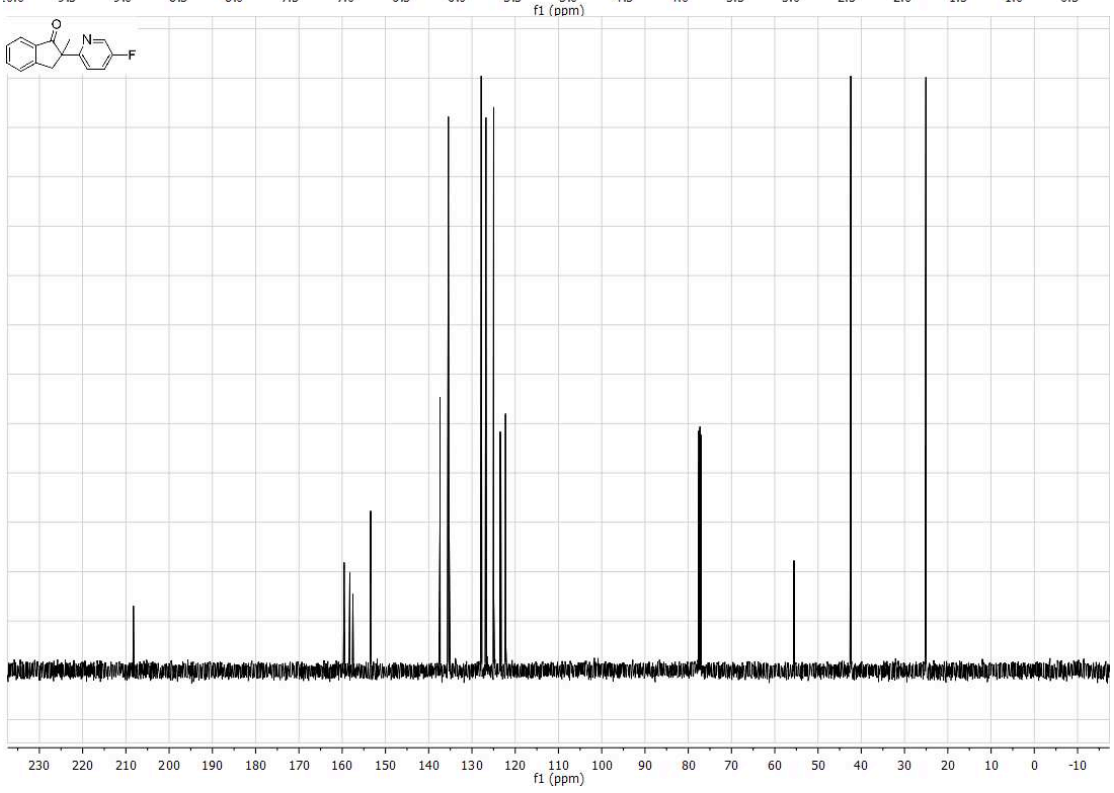
f1 (ppm)


O
N
F
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
f1 (ppm)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40
30
20
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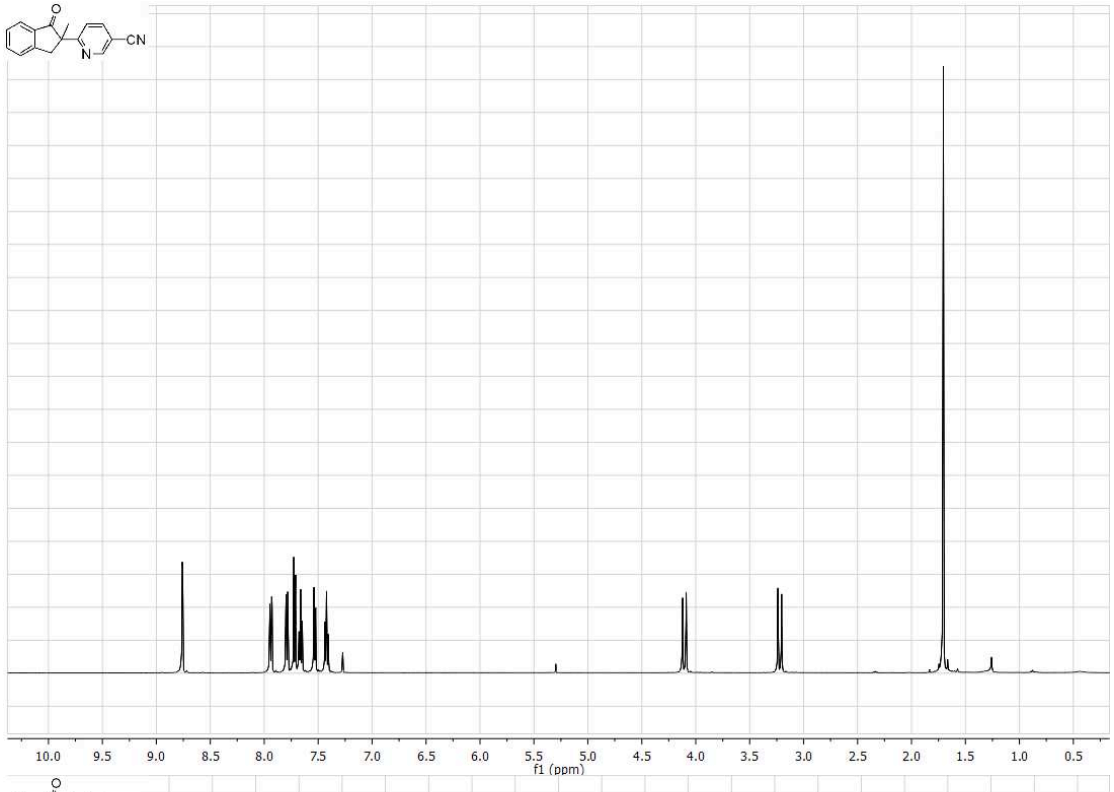
0
-10
f1 (ppm)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CN
N
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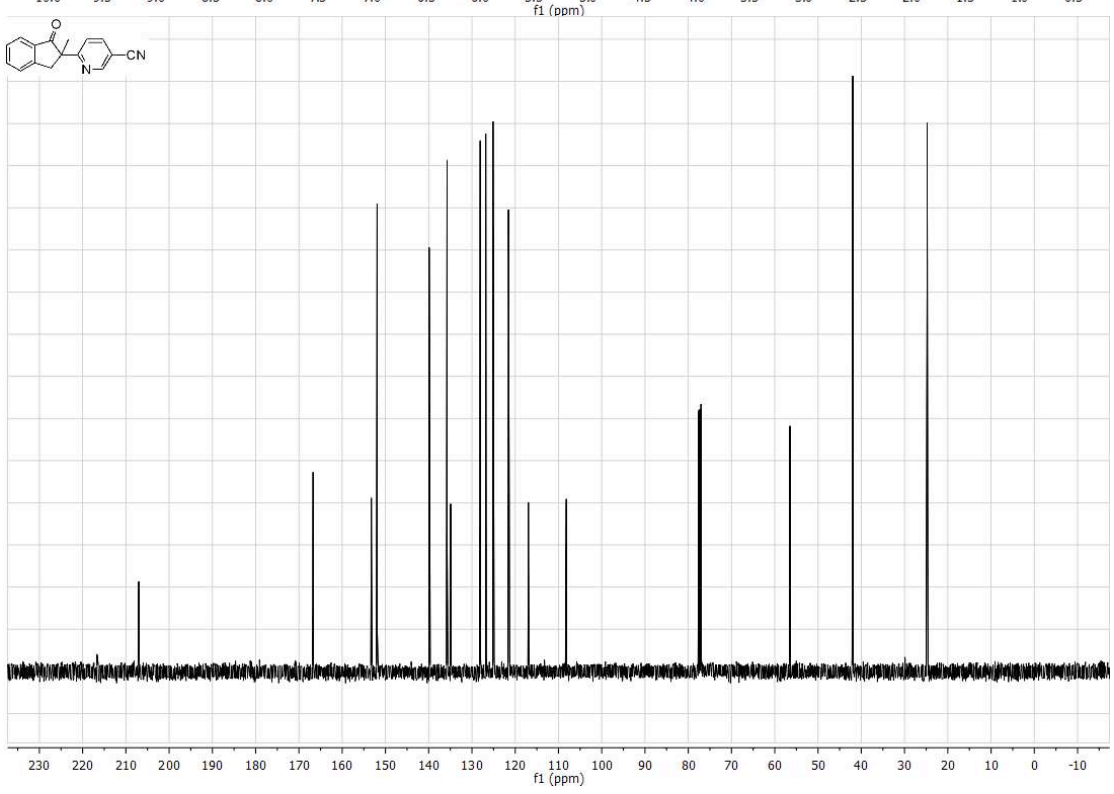
f1 (ppm)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CN
N
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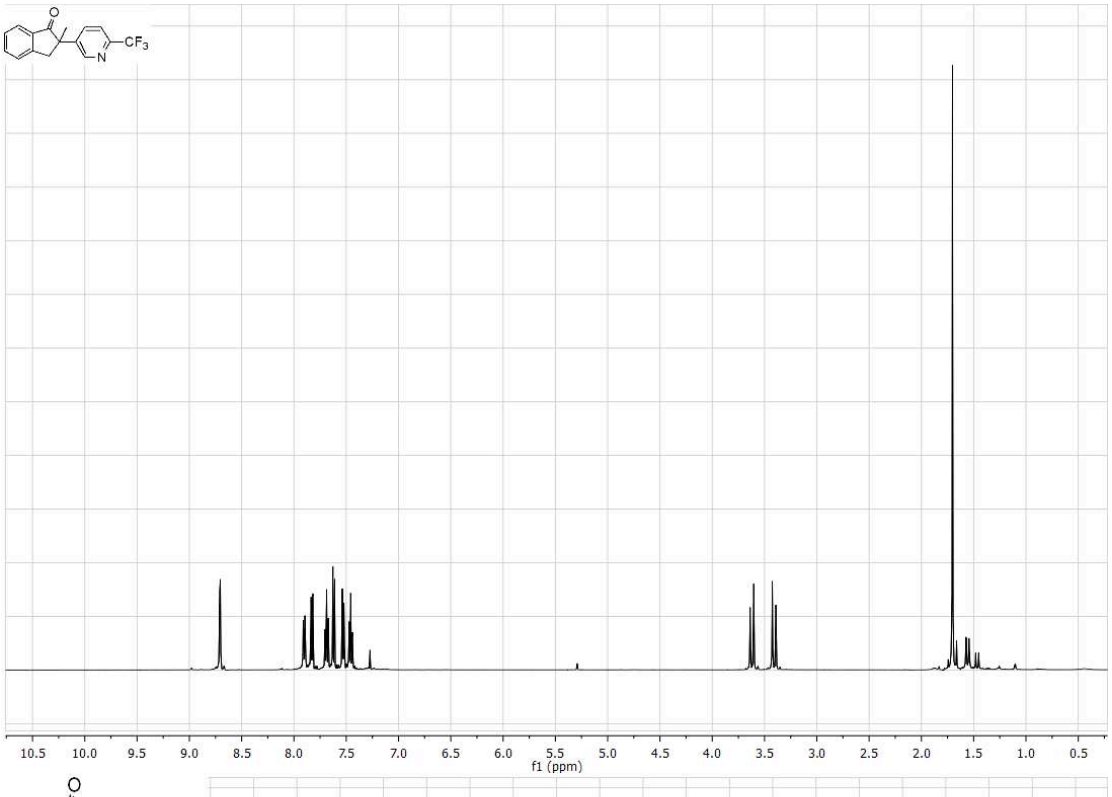
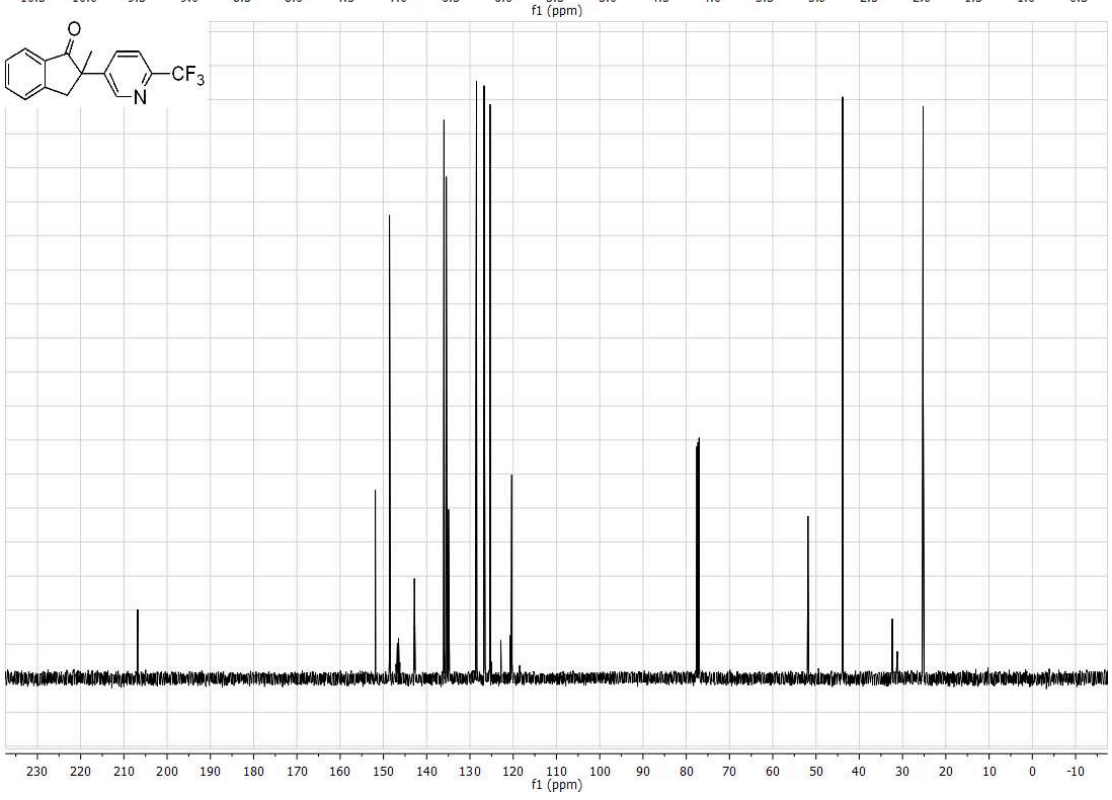
f1 (ppm)


O
CF3
N
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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N
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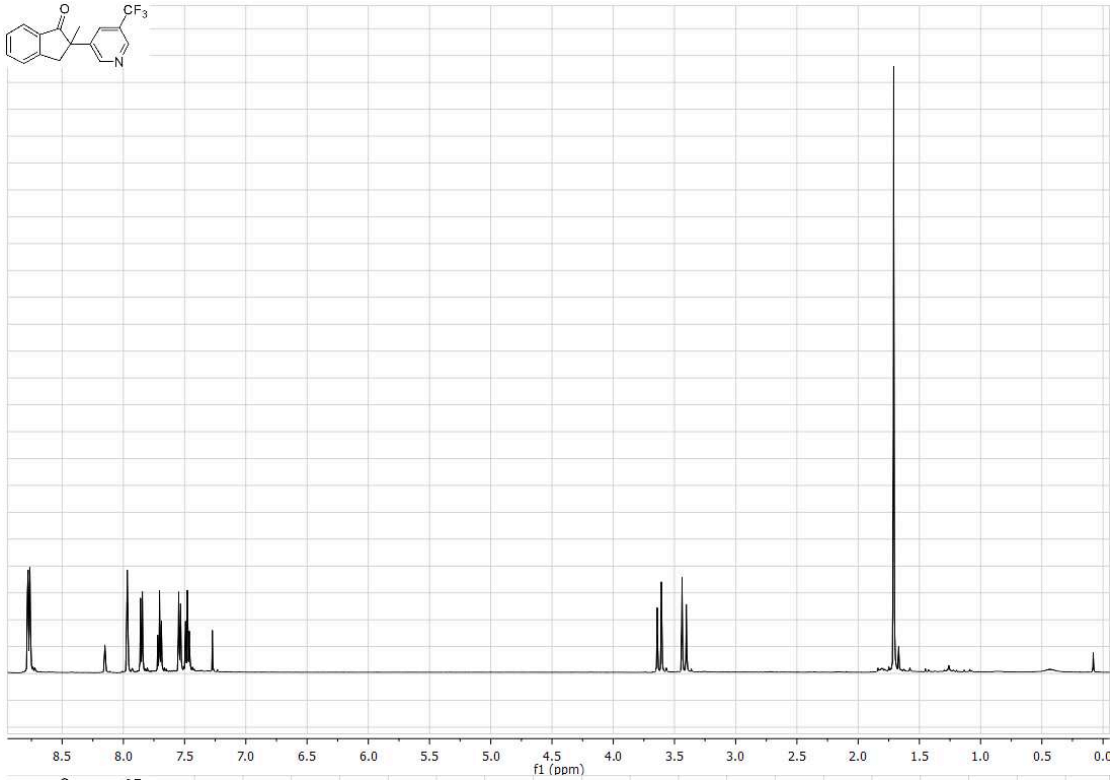
f1 (ppm)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7.0
6.5
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3.0
2.5
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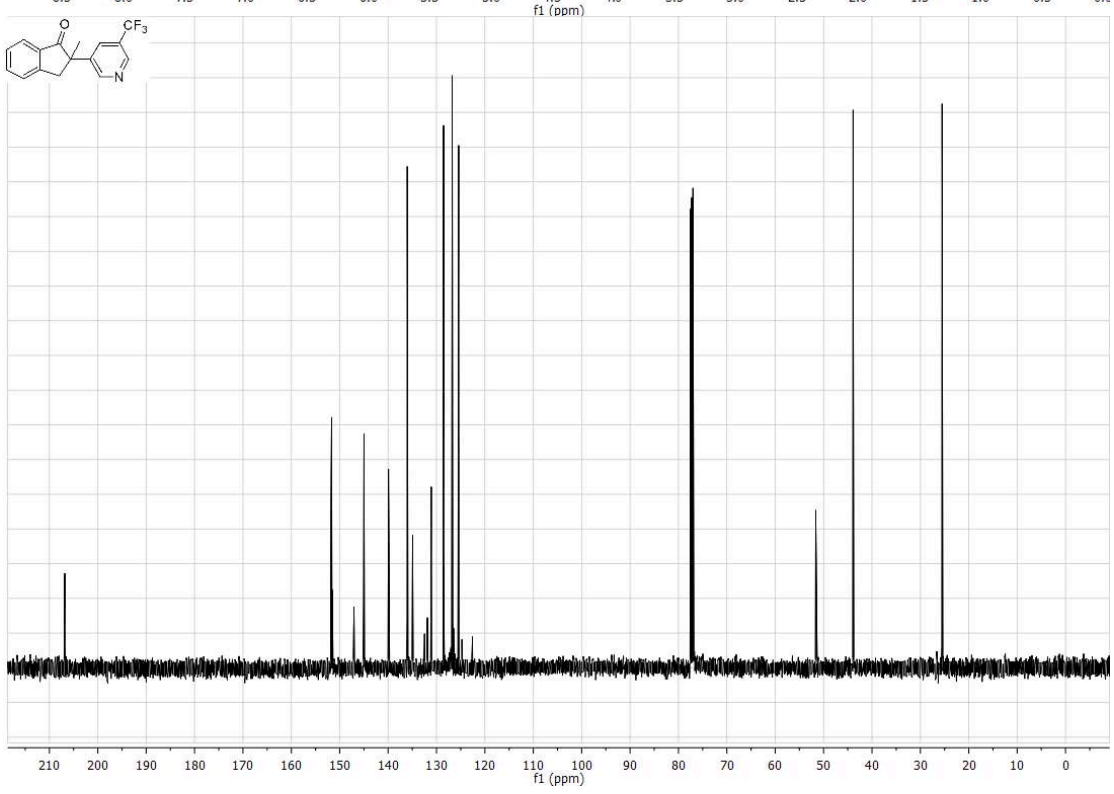
1.5
1.0
0.5
f1 (ppm)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CF3
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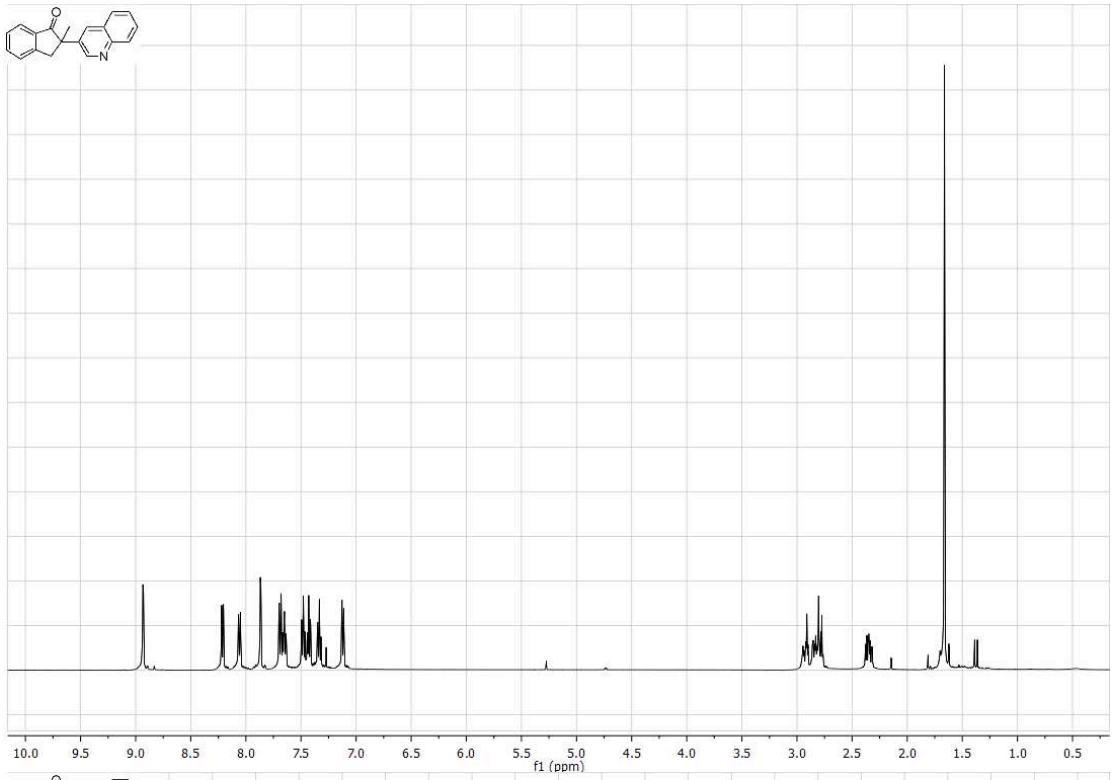
f1 (ppm)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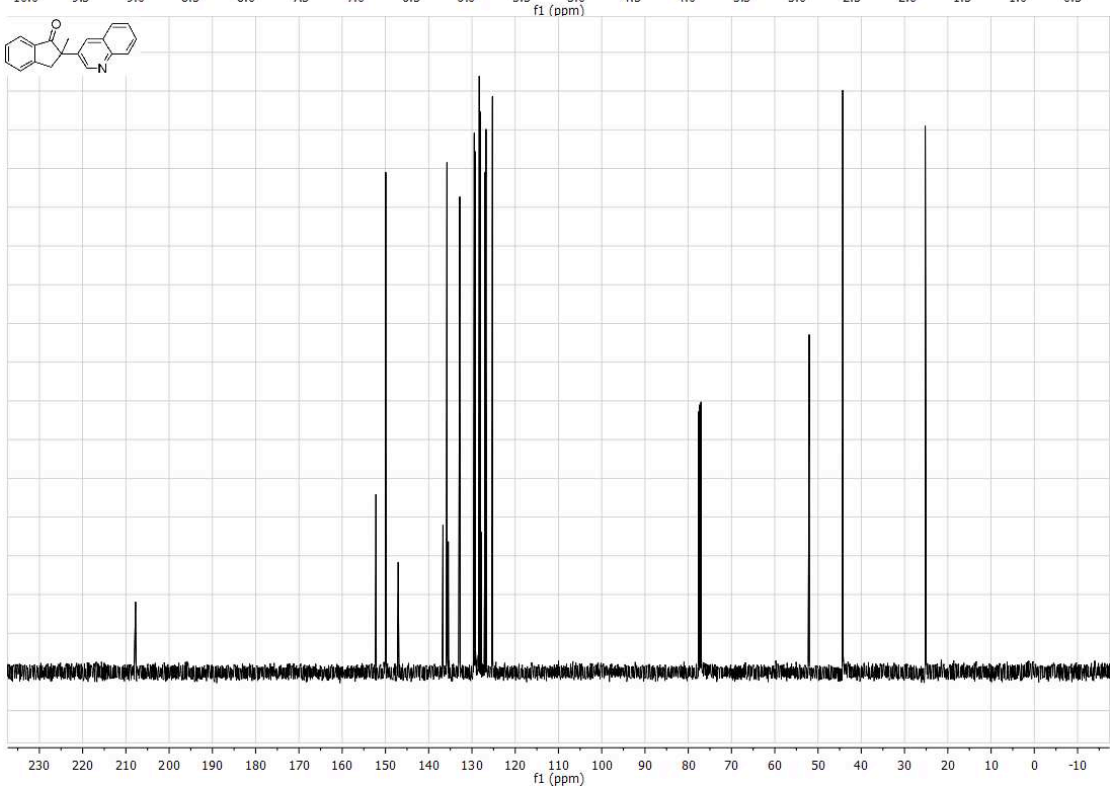
f1 (ppm)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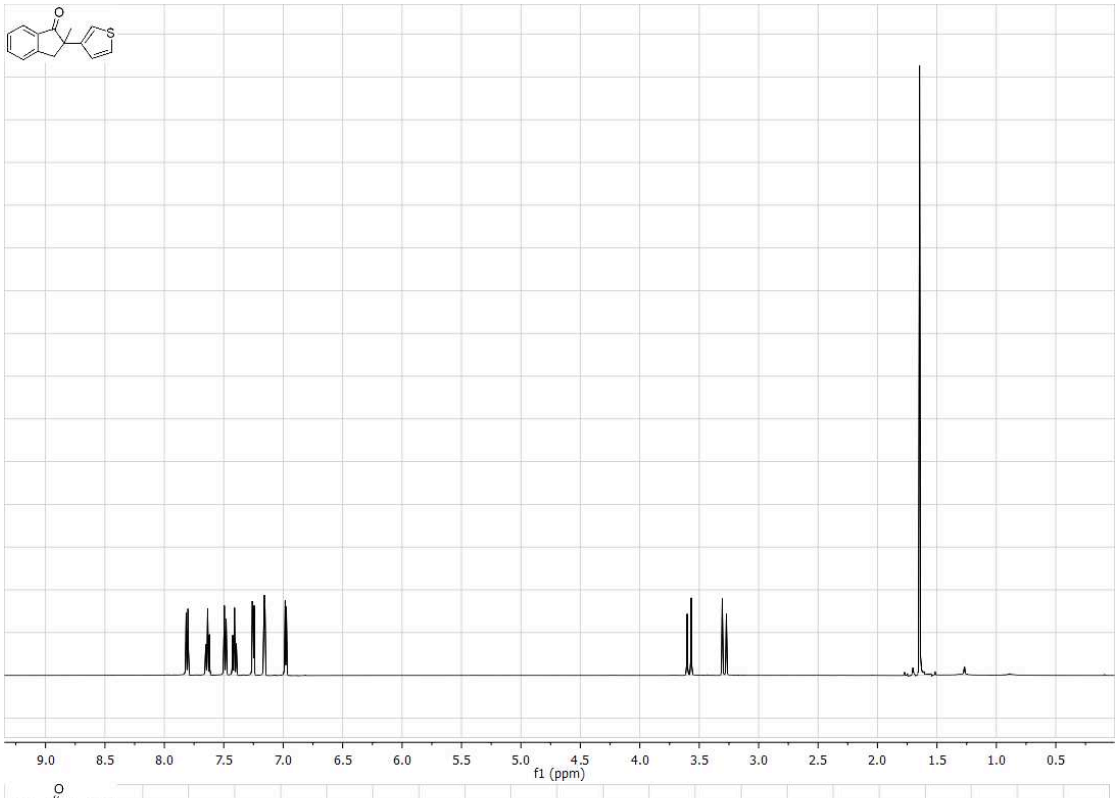
f1 (ppm)


O
S
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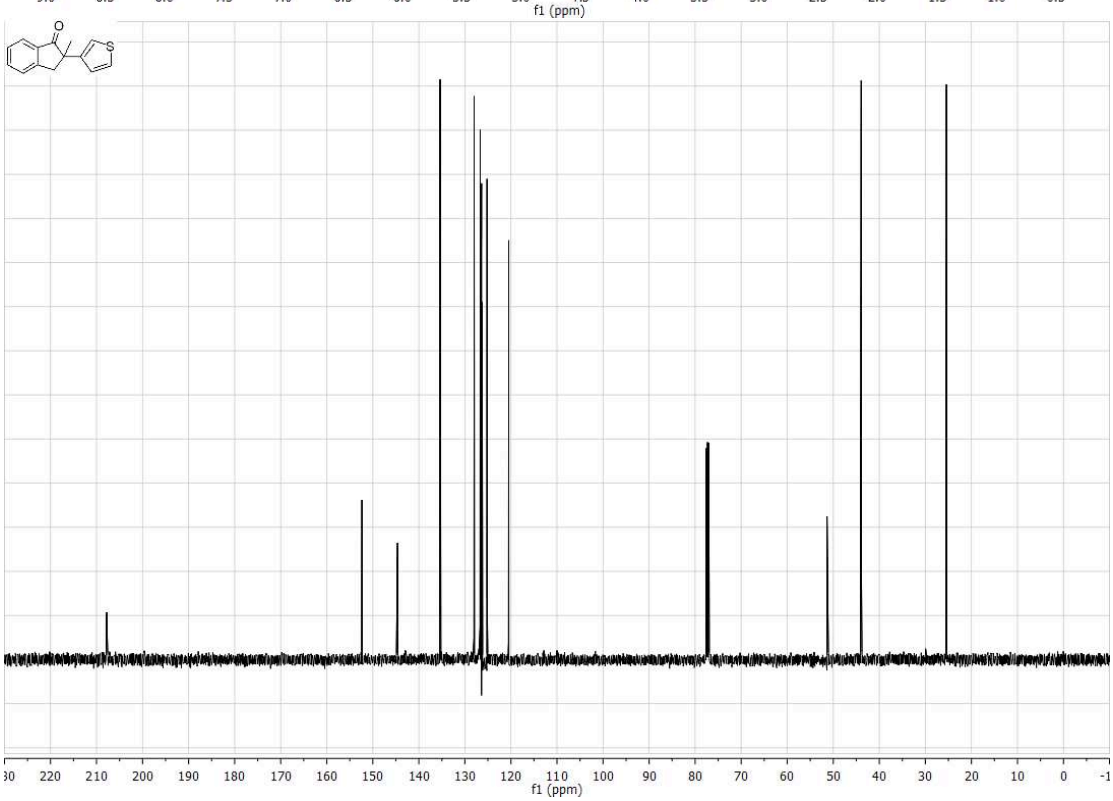
f1 (ppm)


O
S
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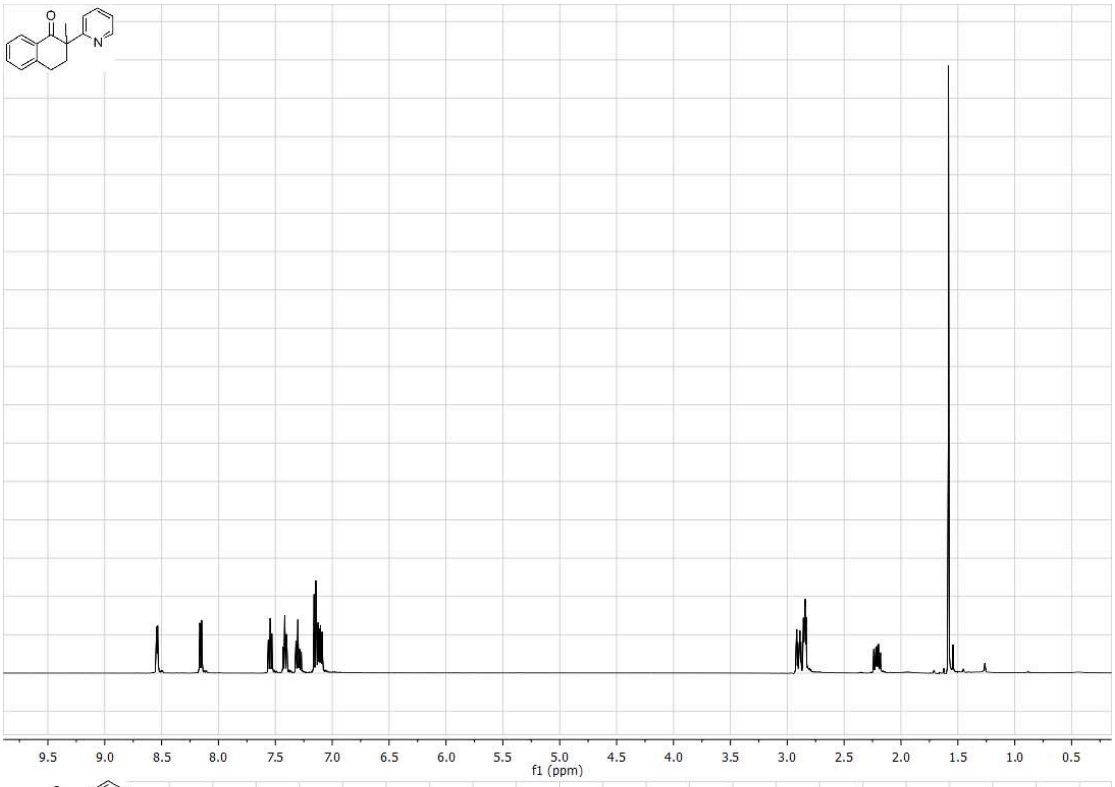
f1 (ppm)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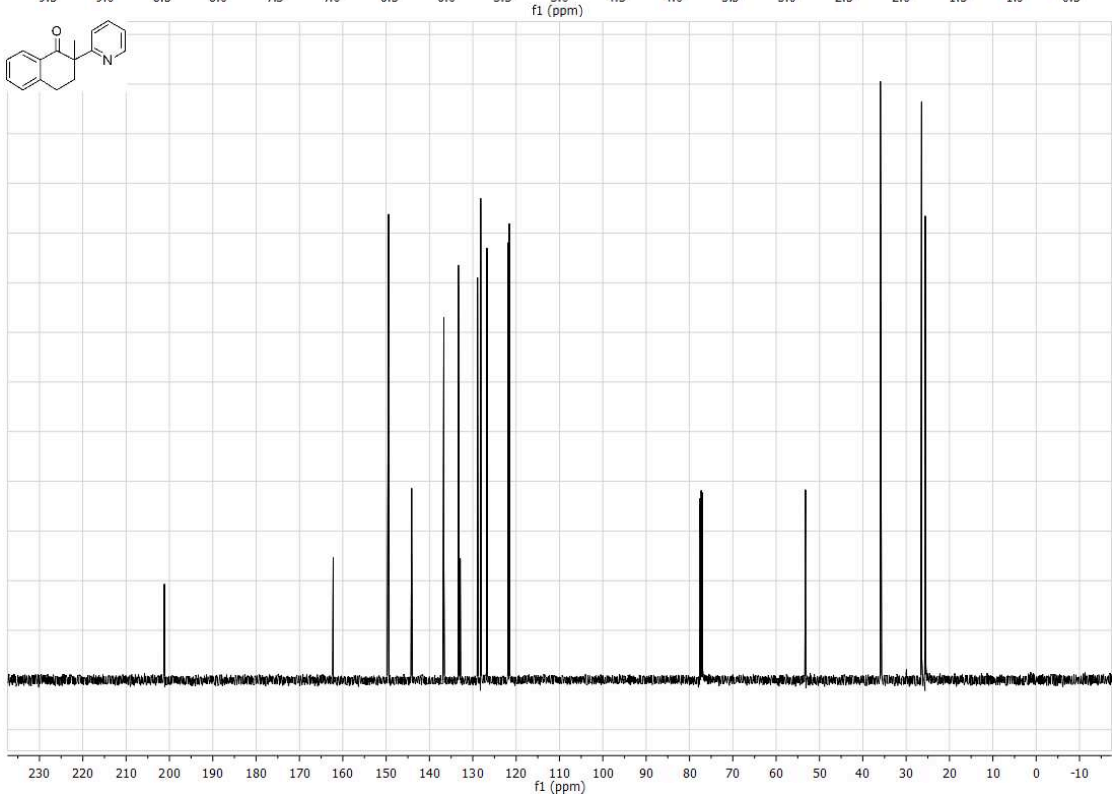
f1 (ppm)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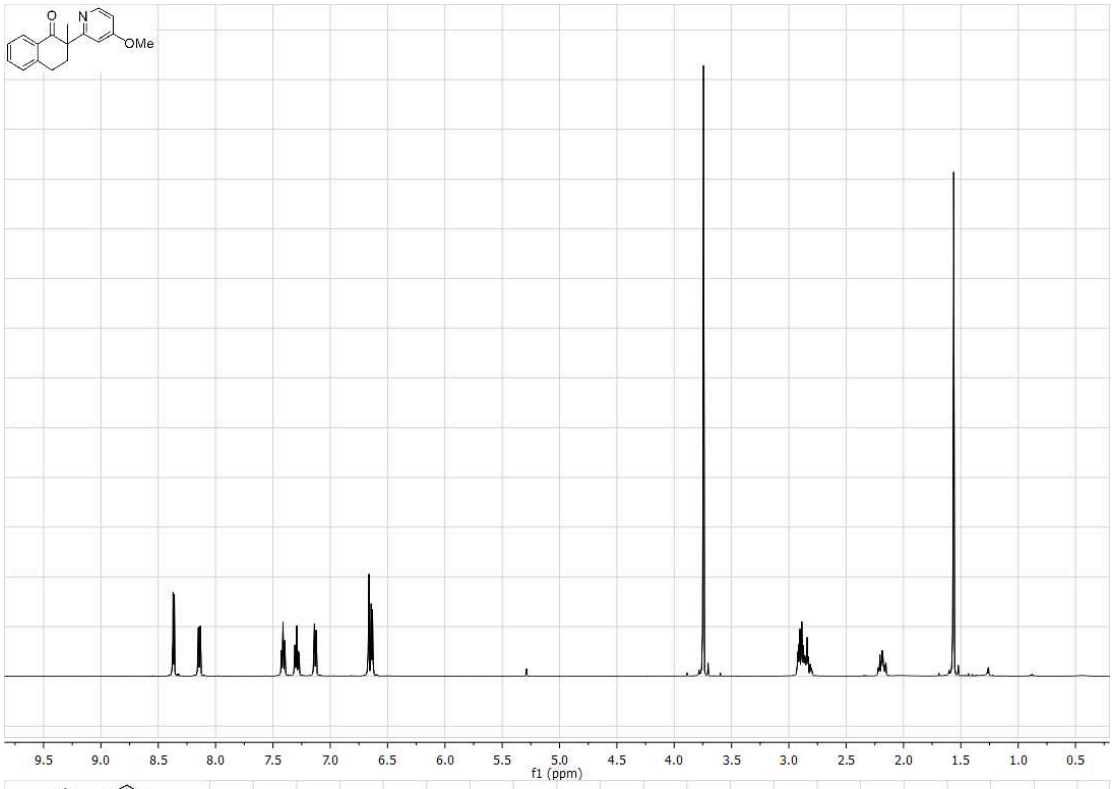
f1 (ppm)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N
OMe
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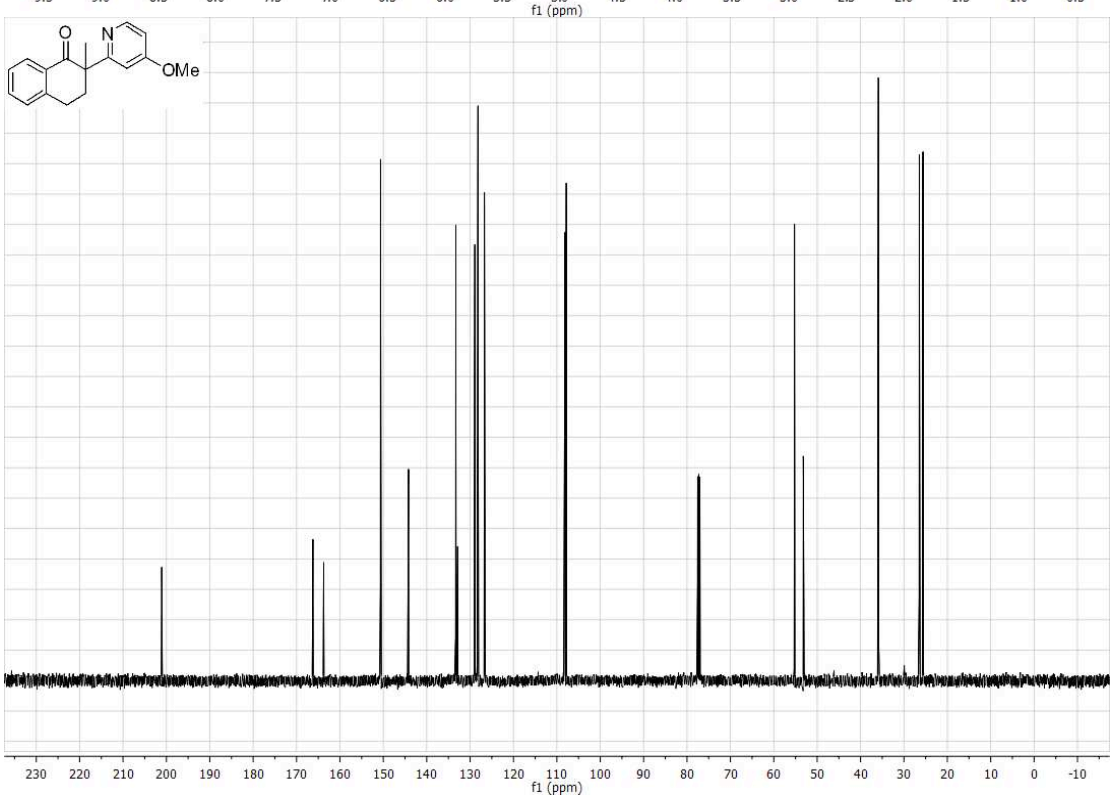
f1 (ppm)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N
OMe
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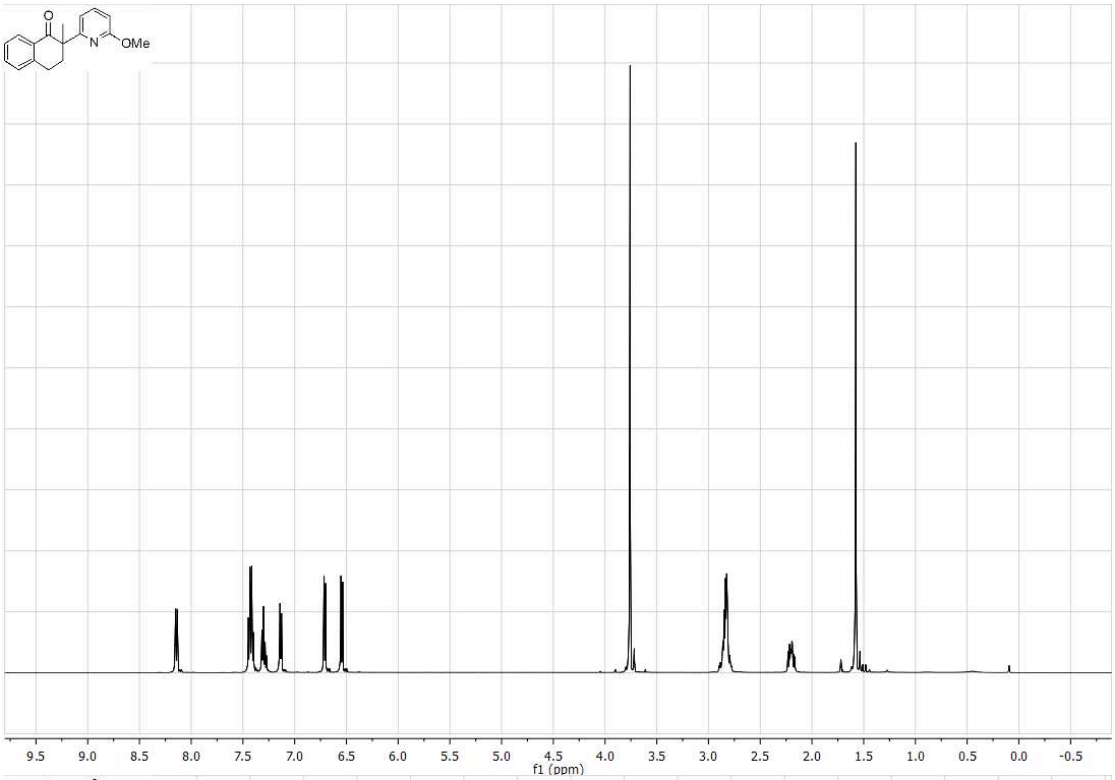
f1 (ppm)


OMe
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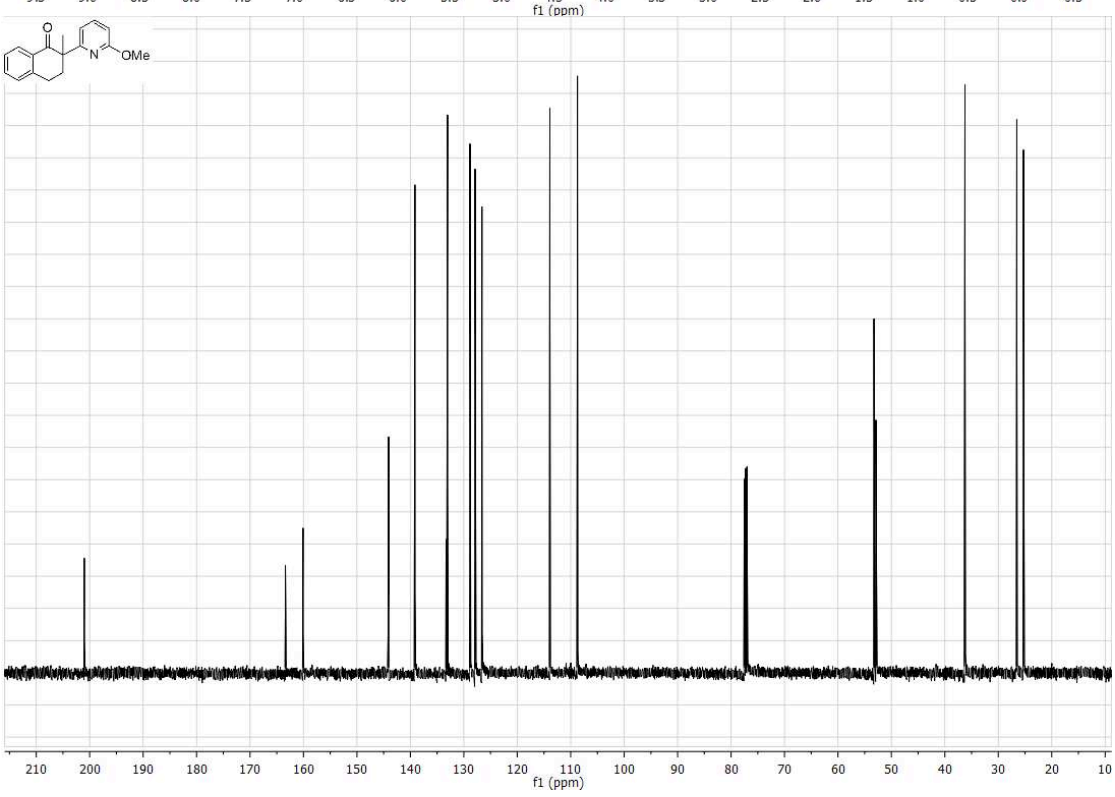
f1 (ppm)


OMe
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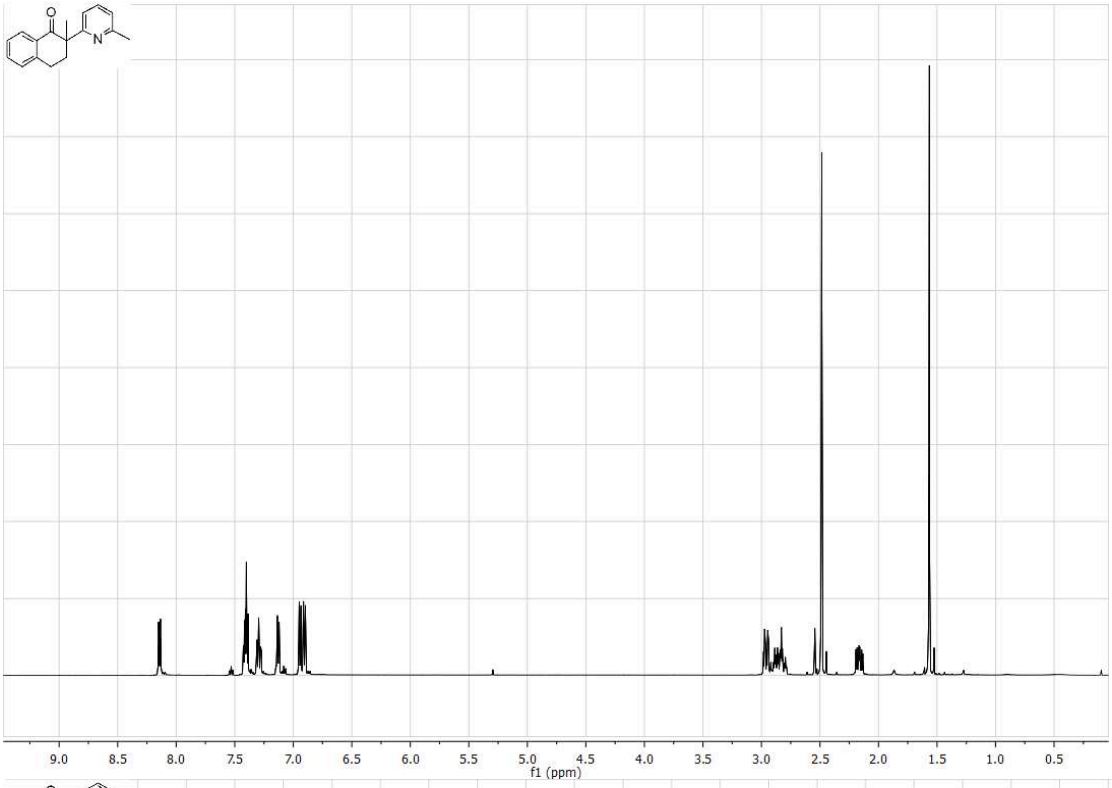
f1 (ppm)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7.5
7.0
6.5
6.0
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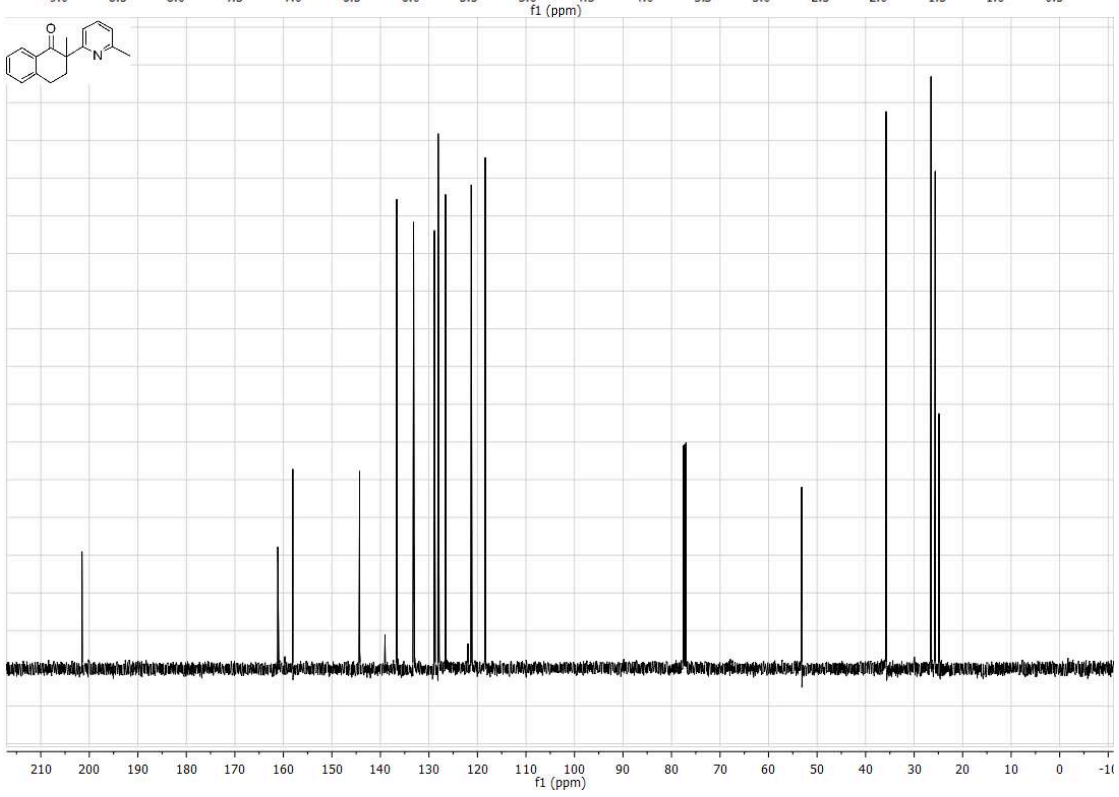
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


210
200
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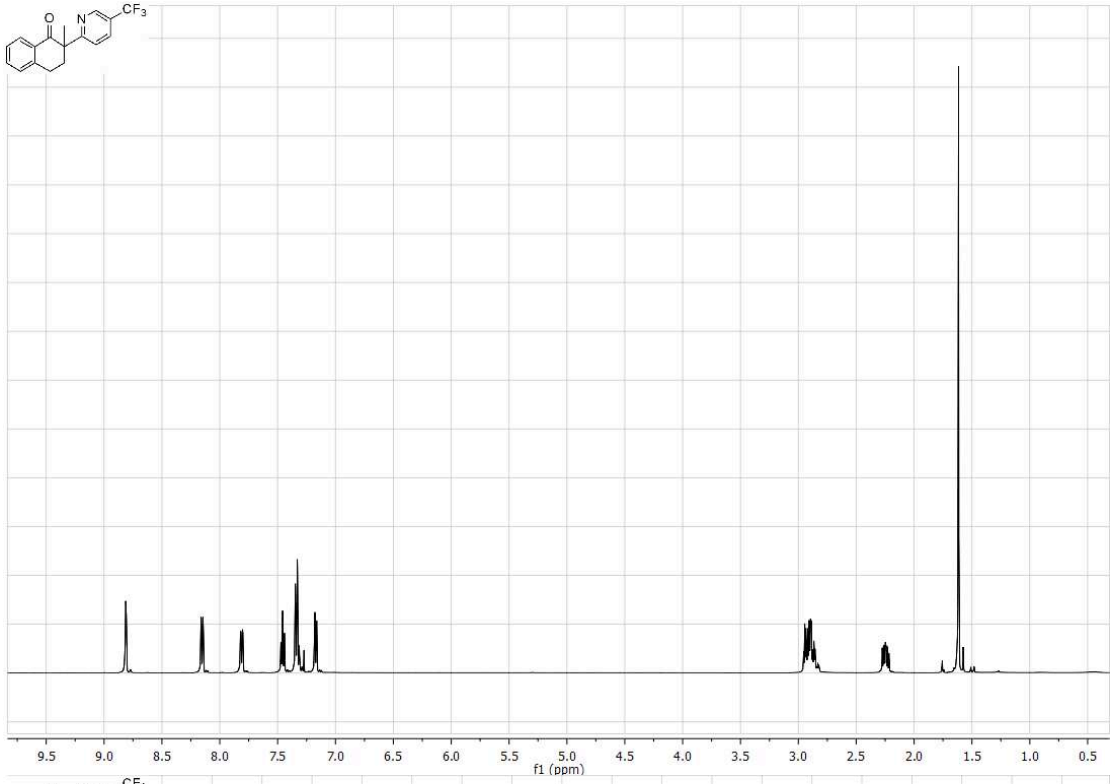
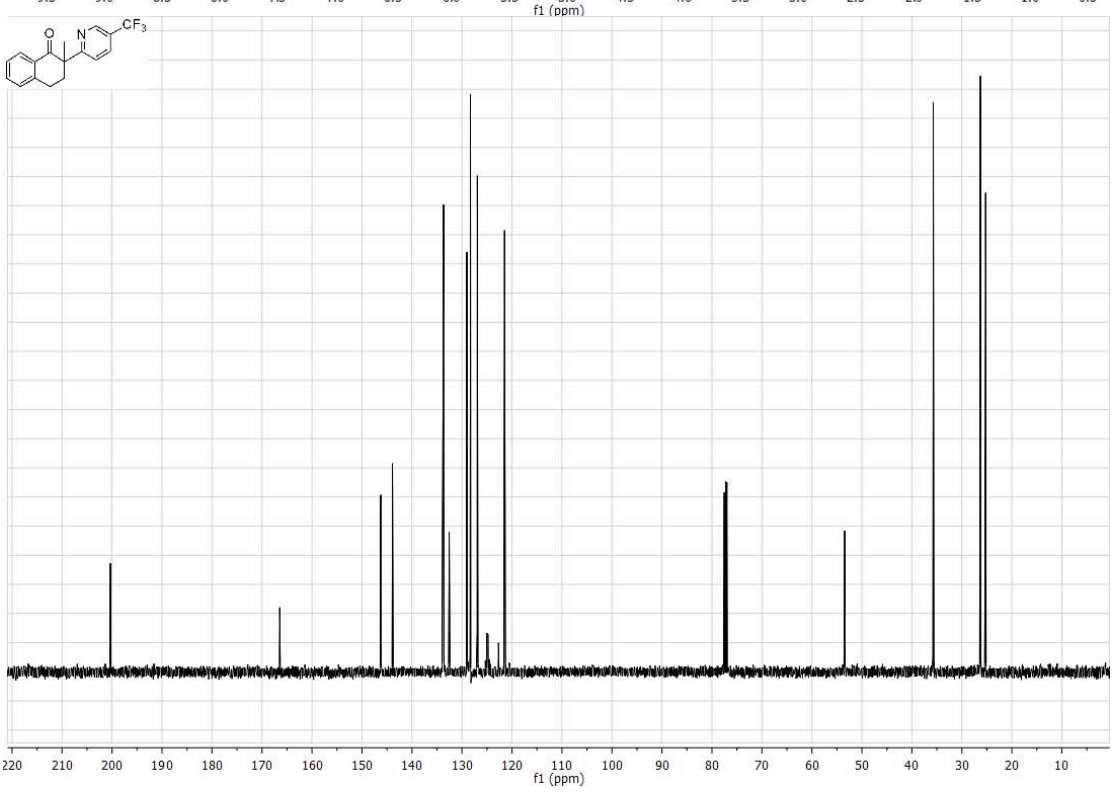
10
0
f1 (ppm)


O
N
CF3
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
f1 (ppm)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N
CF3
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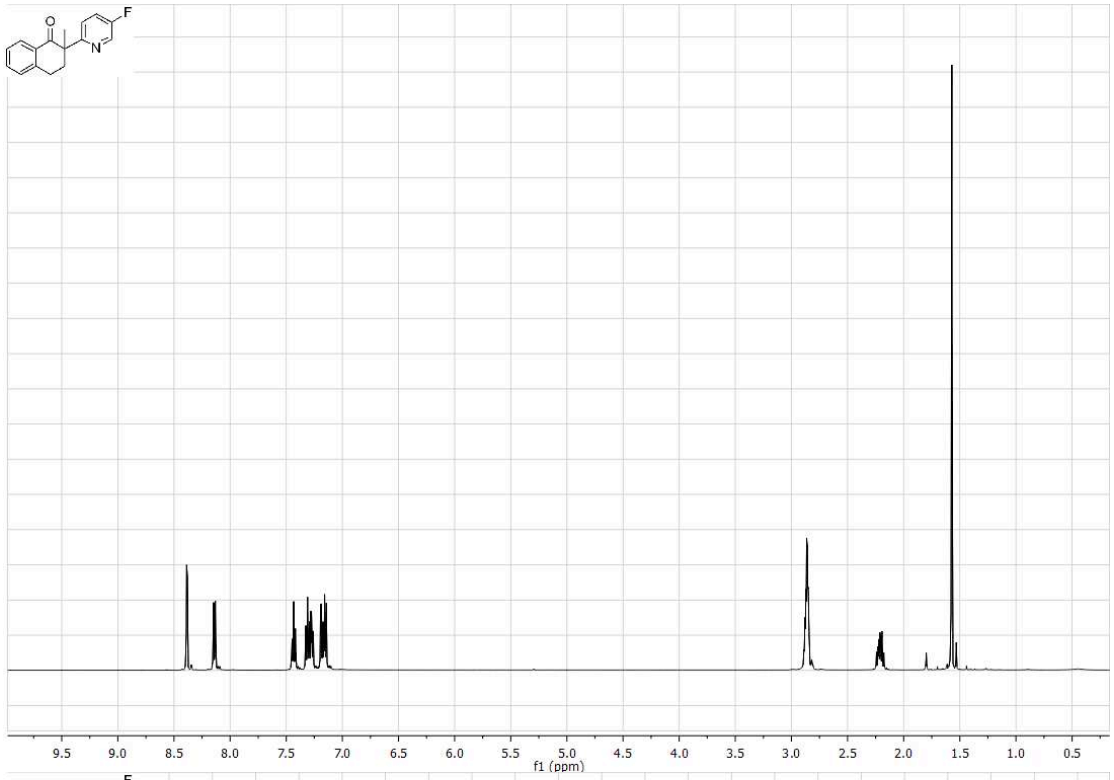
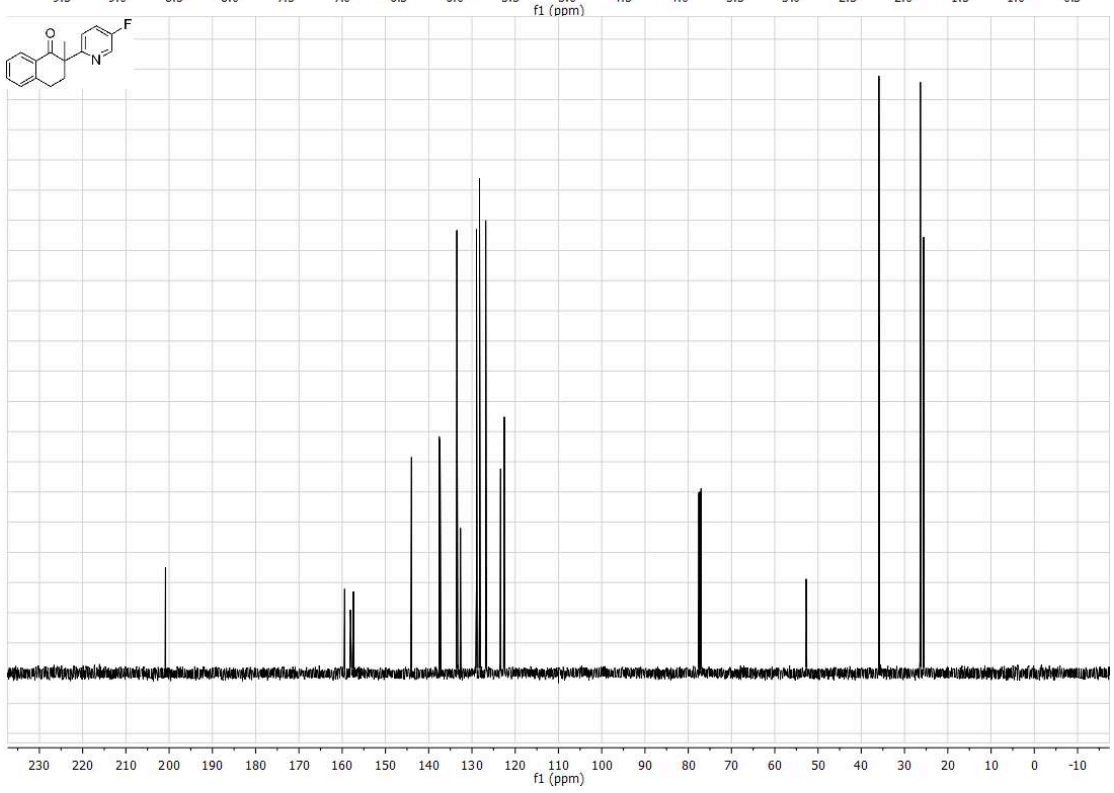
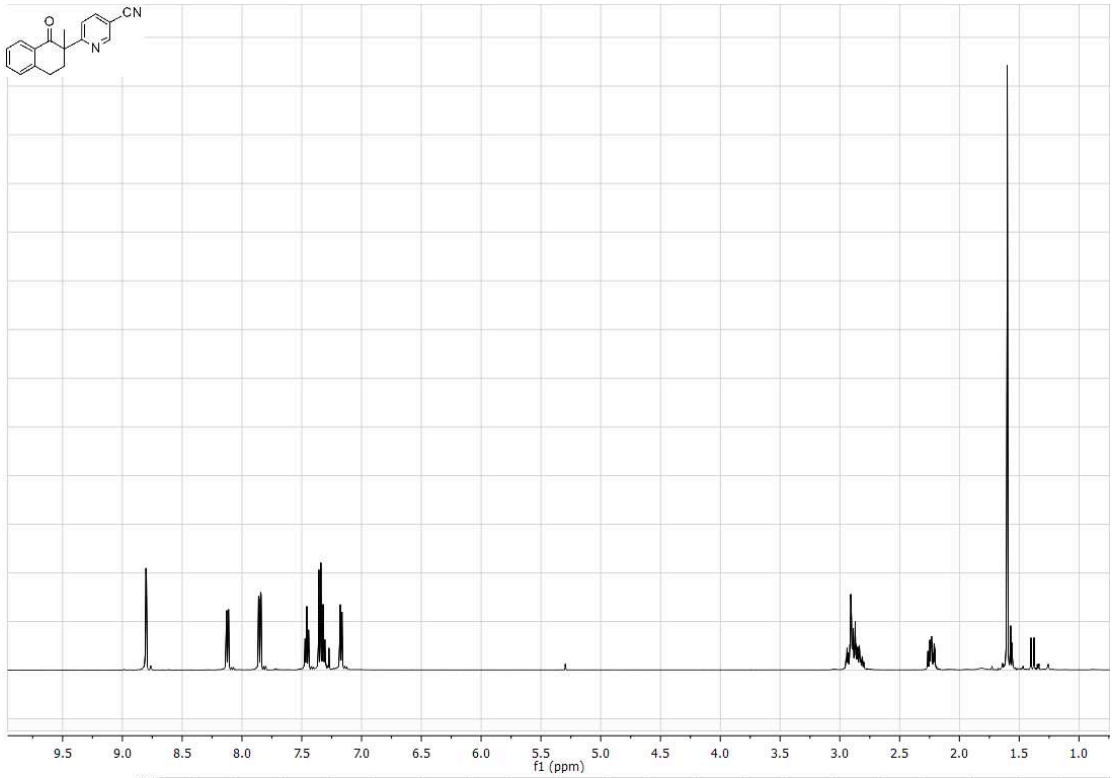
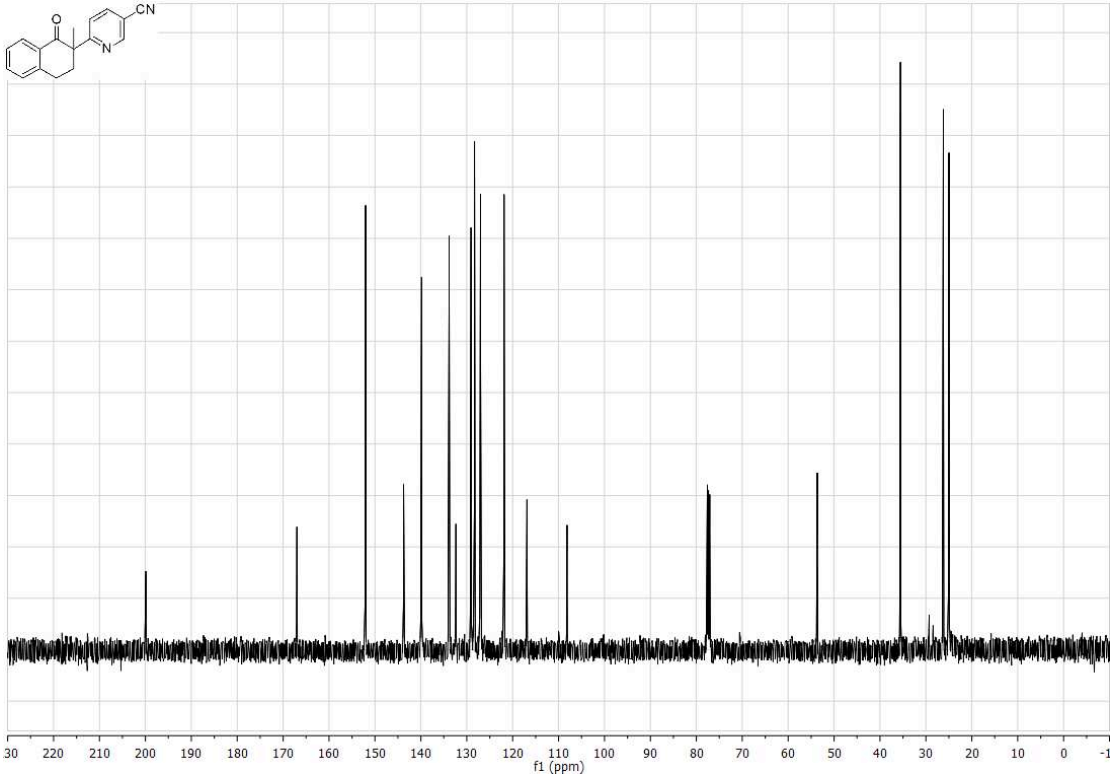
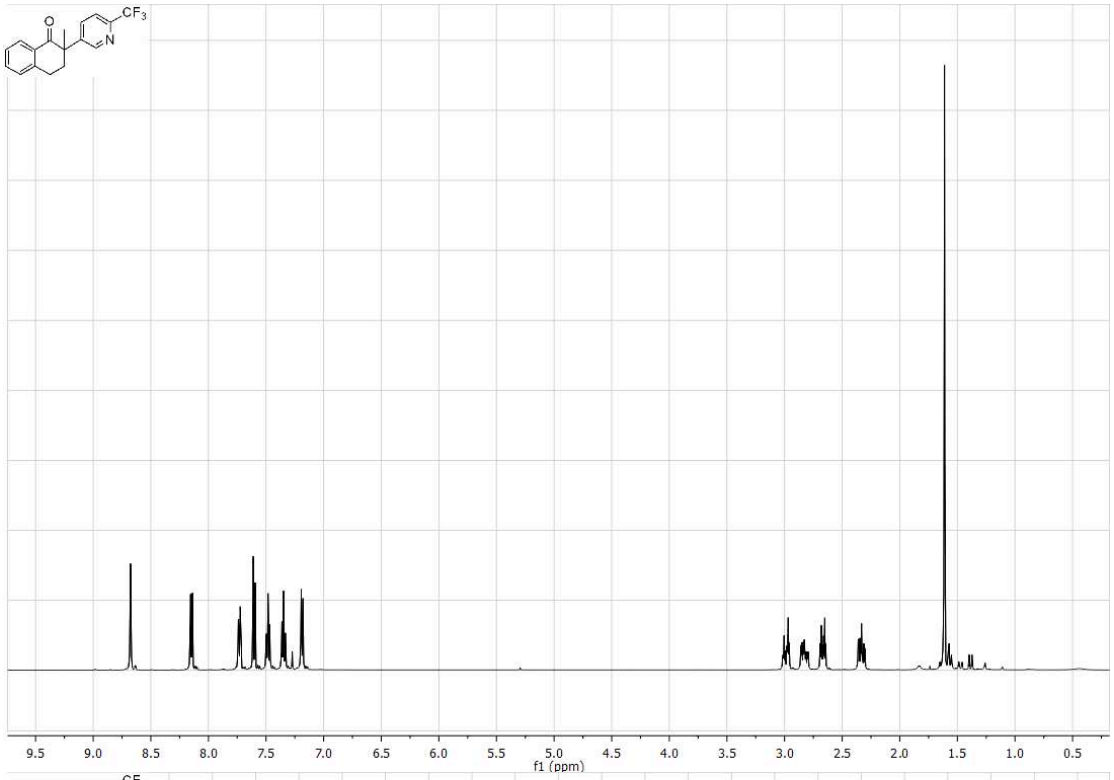
f1 (ppm)

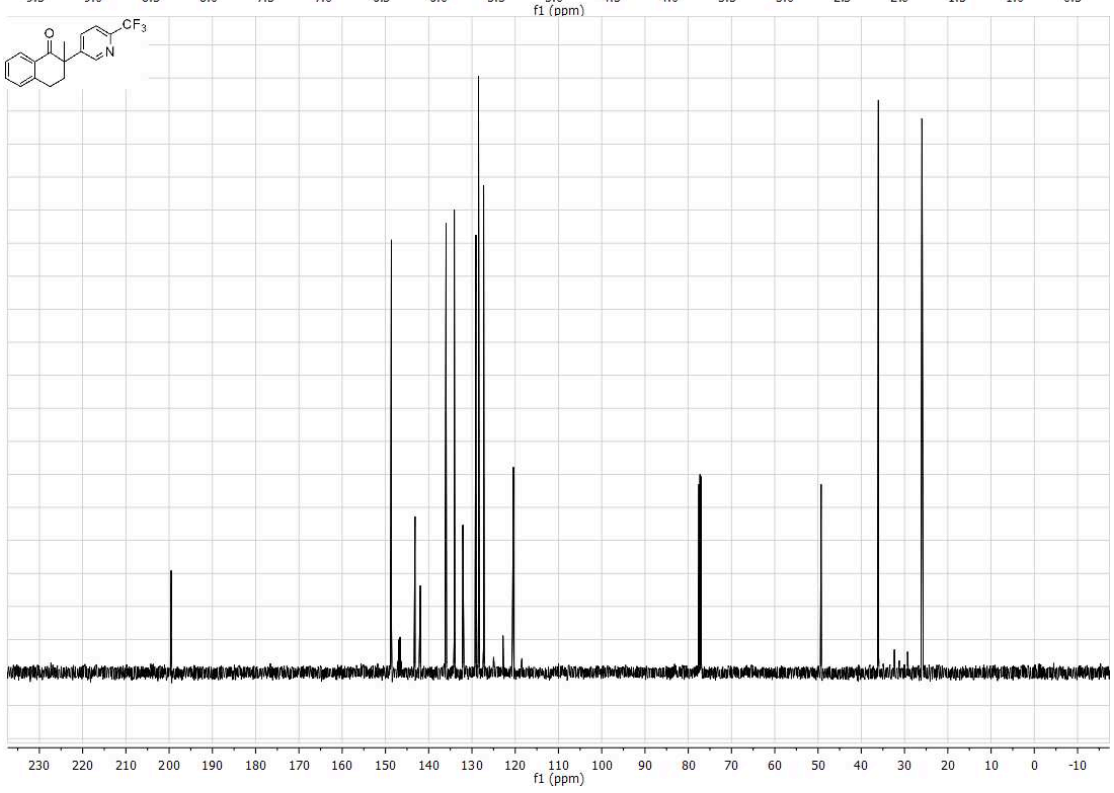

O
F
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

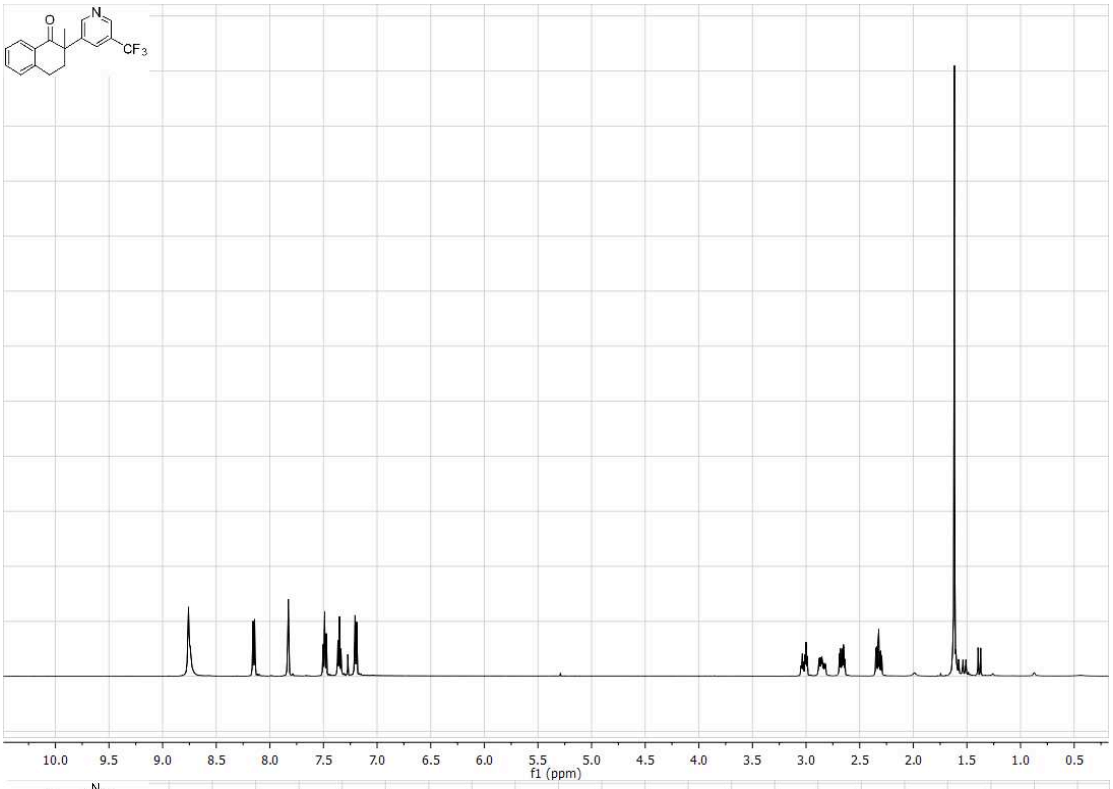

O
F
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

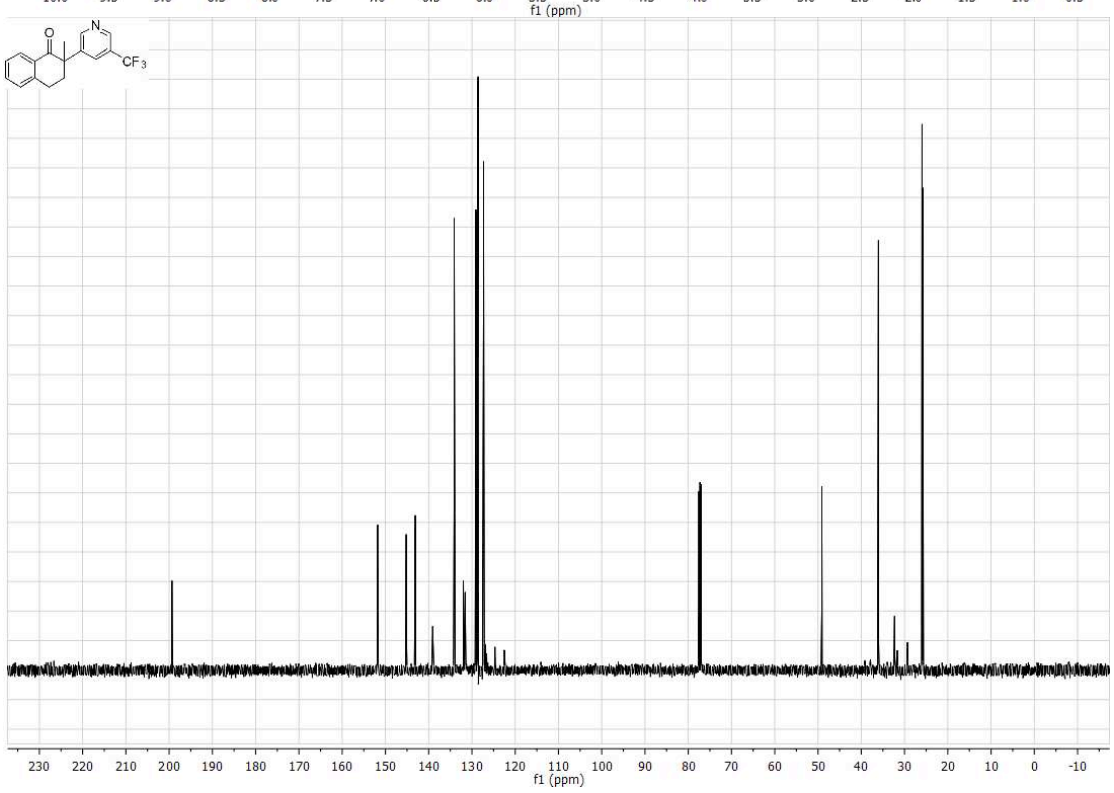

O
CN
N
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

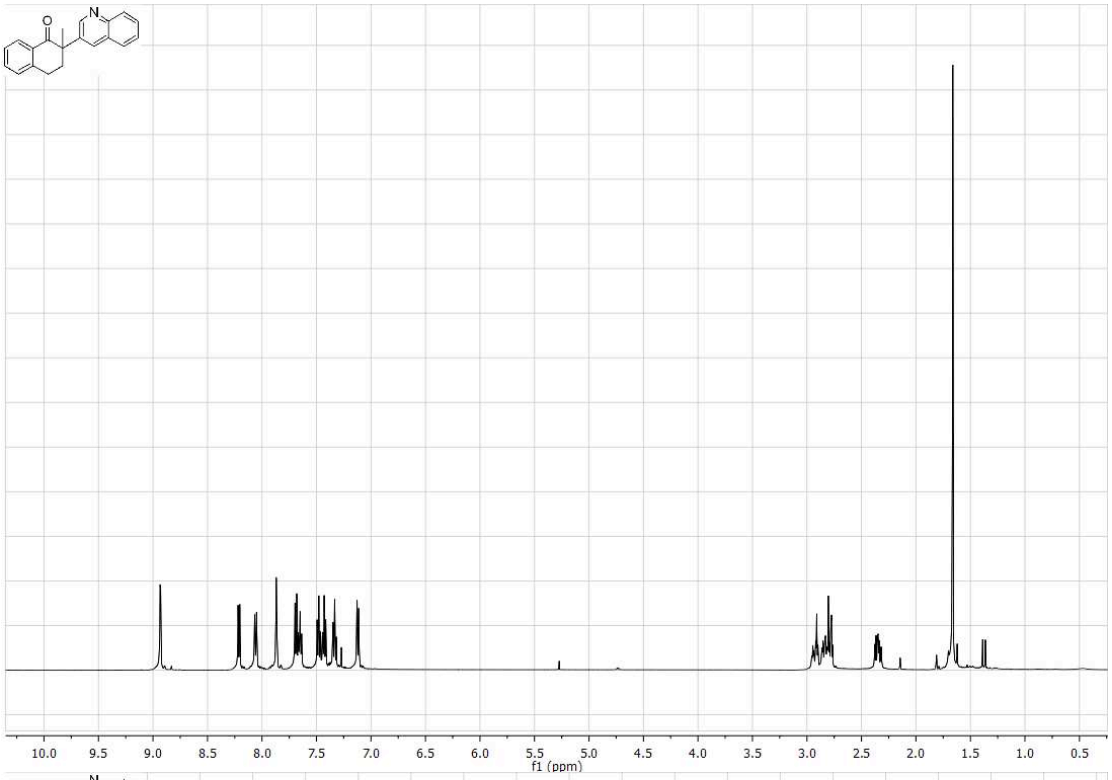

O
CN
N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

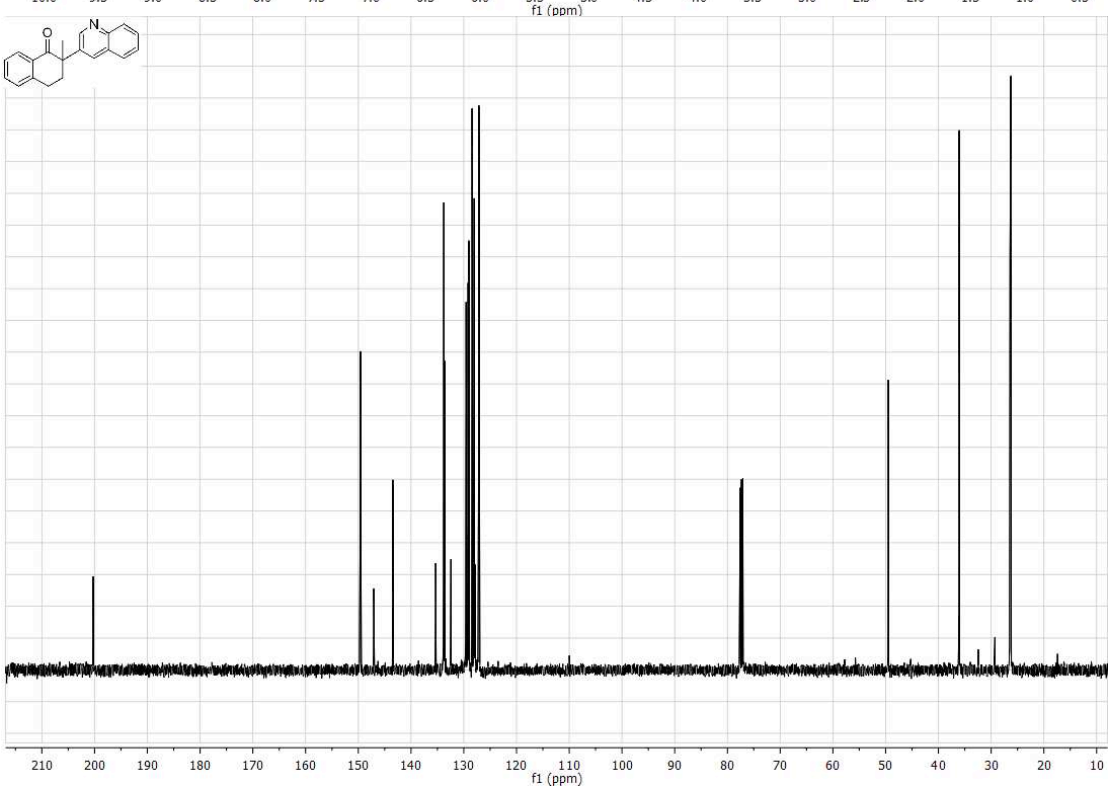

CF3
N
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

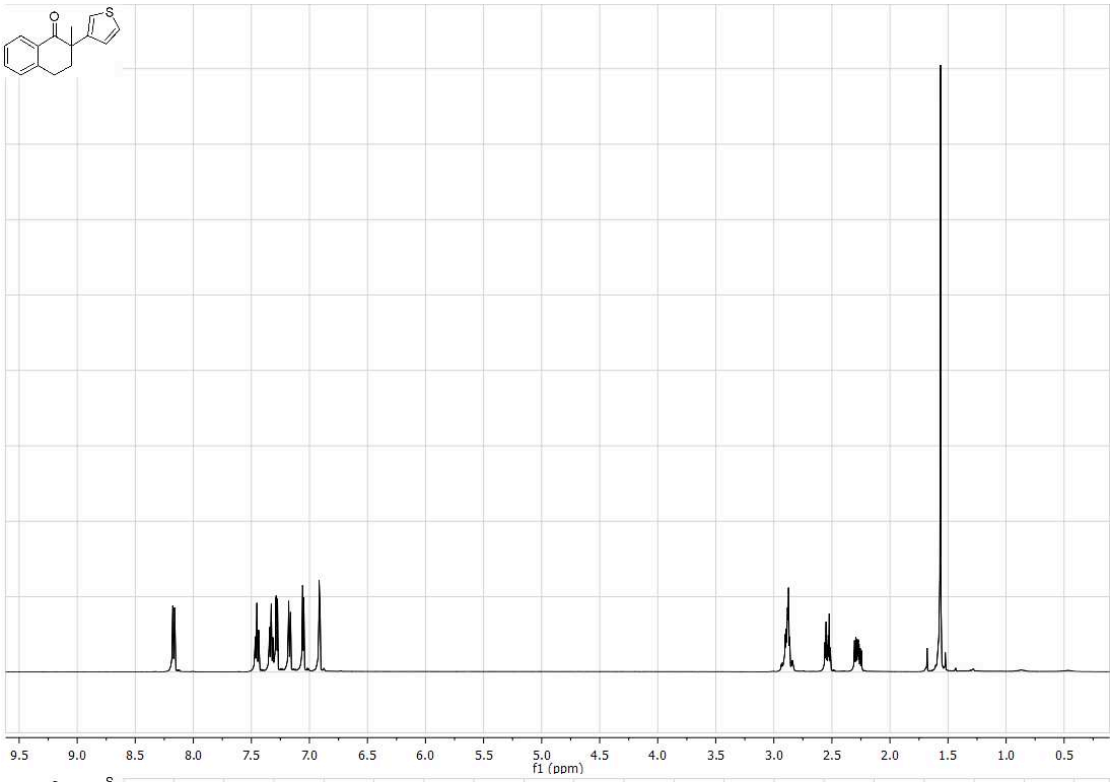

CF3
N
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

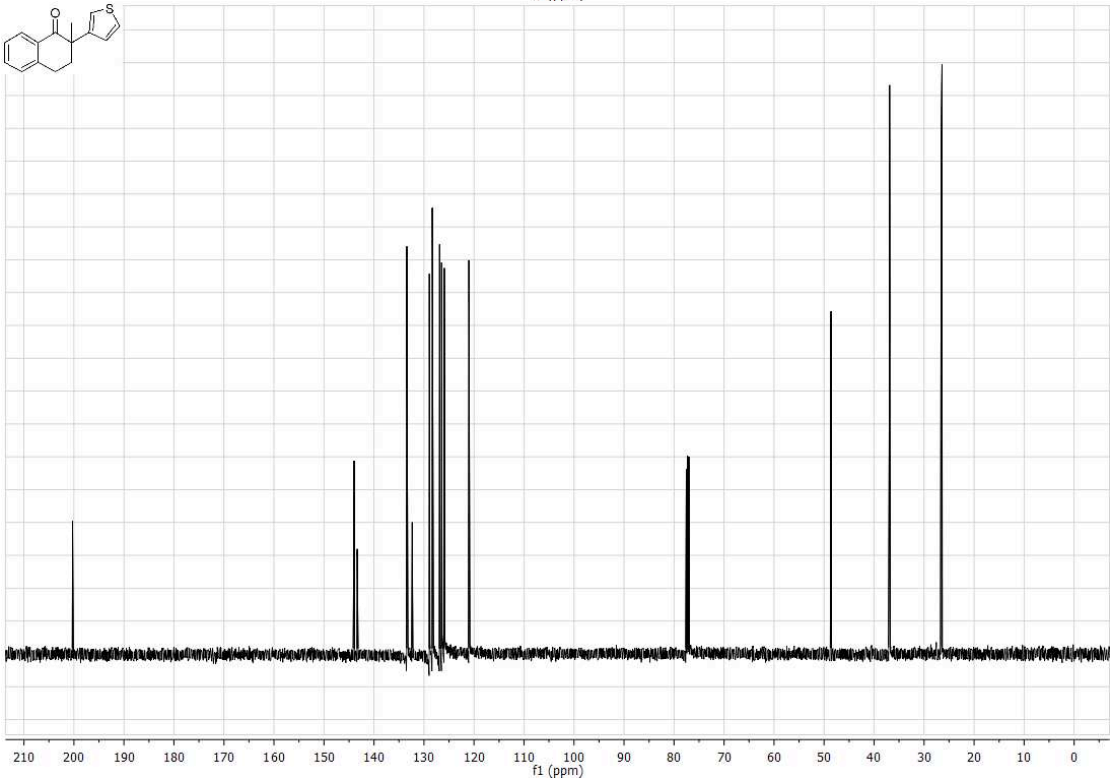

O
N
CF3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


O
N
CF3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


O
S
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
f1 (ppm)


O
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)