Manganese-Catalyzed α-Alkylation of Ketones with Primary Alcohols

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Table of Contents

1. General Information:

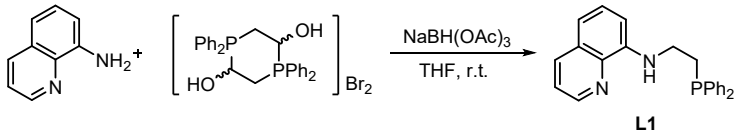
General. Unless otherwise noted, all oxygen- and moisture-sensitive reactions were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230-400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200-300 mesh) using standard methods.

Structural Analysis. NMR spectra were measured on a Bruker Avance-500 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 500 MHz in NMR solvents and referenced internally to corresponding solvent resonance, ^{13}C NMR spectra were recorded at 126 MHz, ^{31}P NMR spectra were recorded at 202 MHz. The signals were referenced to residual chloroform (7.26 ppm, ^{1}H, 77.00 ppm, ^{13}C). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), bs (broad singlet) and bq (broad quartet). High resolution mass spectra (HRMS) data were obtained on a Thermo Fisher TSQ Quantis LC/MS spectrometer with ESI source. X-ray crystallography was measured on an APEXIJ DVO diffractometer.

Materials. Commercial reagents and solvent were purchased from J&K, Sigma-Aldrich, Alfa Aesar, TCI, Energy chemicals and used as received unless otherwise stated.

2. Preparation of Quinoline-derived NNP Ligand Chelated Catalyst Mn-1

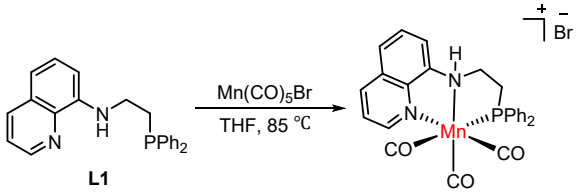
2.1 Synthesis of quinoline-derived NNP ligand (L1)



L1

A vial was charged with 8-aminoquinoline (1.44 g, 10 mmol), the α-phosphinoacetaldehydes dimer[1] (3.09 g, 5 mmol), sodium(triacetoxy)borohydride (4.24 g, 20 mmol), 3Å molecular sieves and degas THF (40 mL). The blood-red mixture was stirred for overnight under ambient atmosphere at room temperature. The reaction mixture was filtered, the filter cake was rinsed with degas DCM (40 mL) and concentrated under reduced pressure. The residue was purified by neutral alumina fast under ambient atmosphere (*n*-hexane: EtOAc = 10:1) to give the desired product **L1** as a yellow oil (2.14 g, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, J = 2.6 Hz, 1H), 8.00 (d, J = 6.6 Hz, 1H), 7.46 (m, 4H), 7.32 (m, 8H), 7.01 (d, J = 8.1 Hz, 1H), 6.51 (d, J = 7.6 Hz, 1H), 6.31 (s, 1H), 3.45 (dt, J = 11.4, 5.5 Hz, 2H), 2.60 – 2.46 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8, 144.2, 138.2, 138.1, 135.9, 132.9, 132.7, 128.8, 128.7, 128.6, 128.5, 128.1, 127.7, 121.4, 113.9, 104.7, 40.5, 40.3, 28.4, 28.3. ^{31}P{1H} NMR (202 MHz, $CDCl_3$): δ -21.01. HRMS-ESI m/z: $[M+H]^+$ calculated for $C_{23}H_{22}N_2P$: 357.1515, found: 357.1523.

2.2 Synthesis of catalyst Mn-1



L1 **Mn-1**

A flame dried Schlenk tube was charged with manganese pentacarbonyl bromide (825 mg, 3.0 mmol, 1.0 eq.) and the NNP ligand **L1** (1.18 g, 3.3 mmol, 1.1 eq.). The tube was evacuated and backfilled with nitrogen for three times. THF (30 mL) was added and the resulting orange suspension was heated to 80 °C and stirred for 20 h. The solution was allowed to cool to room temperature and THF was removed in vacuo. The reaction mixture was filtered, and the solid was washed with diethyl ether and *n*-hexane (3 x 5 mL), which on evaporation gave a yellow solid product **Mn-1** (1.6 g, 86% yield). Yellow single crystals were obtained by slow diffusion of *n*-hexane into a saturated solution of **Mn-1** in $CHCl_3$ at 0 °C. ^{1}H NMR (500 MHz, DMSO-d6) δ 9.61 (s, 1H), 8.61 (dd, J = 16.1, 6.5 Hz, 2H), 8.31 (d, J = 7.4 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.92 (m, 3H), 7.65 (m, 3H), 7.52 – 7.33 (m, 2H), 7.26 (t, J = 7.6 Hz, 2H), 6.98 (t, J = 8.9 Hz, 2H), 4.11 (m, 1H), 3.22 (m, 2H), 1.84 – 1.57 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d6) δ 156.6, 146.1, 142.6, 139.2, 132.5, 132.4, 132.0, 131.4, 131.0, 131.0, 130.9, 130.0, 129.9, 129.9, 129.6, 129.5, 129.3, 128.6, 128.2, 124.5, 57.1, 57.0, 20.7, 20.5. ^{31}P NMR (202 MHz, DMSO-d6) δ 67.37. HRMS-ESI m/z: $[M-Br]^+$ calculated for $C_{26}H_{21}MnN_2O_3P$: 495.0670, found: 495.0683.

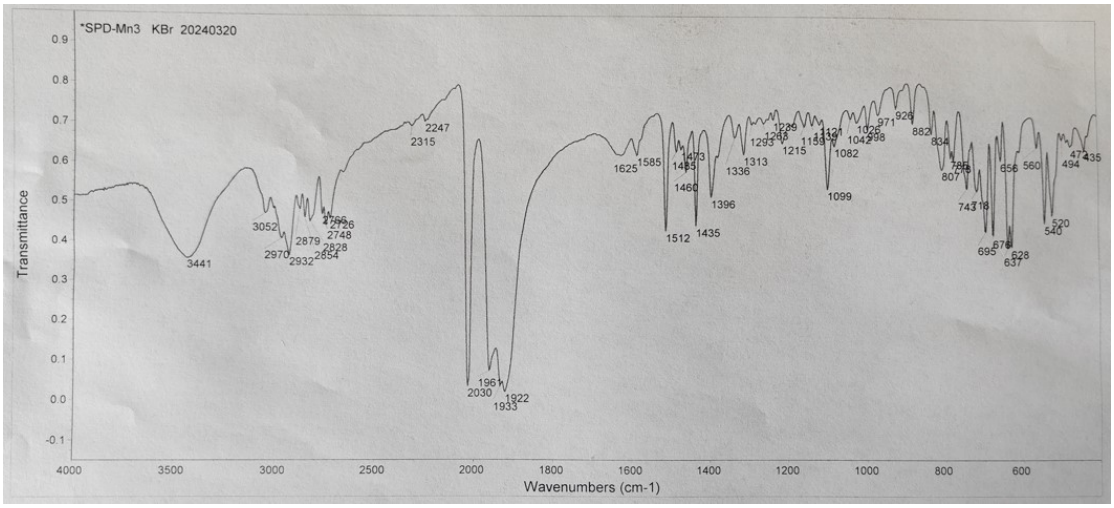
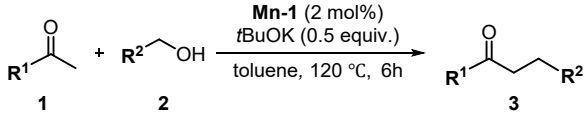


Figure S1. IR spectrum of **Mn-1** on KBr plate.

3. Procedures for Manganese-Catalyzed α-Alkylation of Ketones with Primary Alcohols

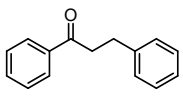


A flame dried Schlenk tube was charged with **Mn-1** (0.01 mmol), *t*BuOK (0.25 mmol), ketone **1** (0.5 mmol) and alcohol **2** (0.6 mmol). The tube was evacuated and backfilled with nitrogen for three times. Toluene (1 mL) was added and the mixture was stirred at 120 °C for 6 h. After completion of the reaction, the reaction mixture was cooled to ambient temperature and 5 mL of water was added and the aqueous solution extracted with EtOAc (3 × 5 mL). Combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by silica gel column chromatography (*n*-hexane/EtOAc = 10:1) to give the corresponding product **3**.

Gram-scale synthesis of 3a

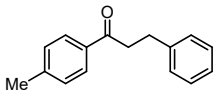
A flame dried Schlenk tube equipped with a stir bar was charged with **Mn-1** (95.5 mg, 0.17 mmol), *t*BuOK (466 mg, 4.15 mmol), acetophenone **1a** (1 g, 8.3 mmol), phenylmethanol **2a** (984 mg, 9.1 mmol) and toluene (15 mL) under nitrogen. Then the reaction mixture was stirred for 10 h at 120 °C. After this time, the reaction mixture was cooled to ambient temperature and 30 mL of water was added and the aqueous solution extracted with EtOAc (3 × 30 mL). Combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. the reaction mixture was purified by silica gel column chromatography (n-hexane/EtOAc = 10:1) to afford the desired product **3a** as a white solid (1.52 g, 87% yield).

1,3-Diphenylpropan-1-one (3a) [2]:



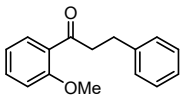
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.27 (m, 4H), 7.19 (t, *J* = 7.0 Hz, 1H), 3.45 – 3.22 (m, 2H), 3.13 – 2.95 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 141.3, 136.8, 133.1, 128.6, 128.5, 128.4, 128.0, 126.1, 40.4, 30.1.

3-Phenyl-1-(p-tolyl)propan-1-one (3b) [2]:



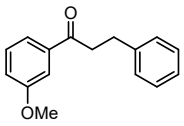
White solid, 98.7 mg, 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 8.2 Hz, 2H), 7.31 – 7.29 (m, 2H), 7.28 –7.24 (m, 4H), 7.21 (t, J = 7.0 Hz, 1H), 3.28 – 3.25 (m, 2H), 3.07 – 3.04 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 143.8, 141.4, 134.4, 129.3, 128.5, 128.4, 128.2, 126.1, 40.4, 30.2, 21.6.

1-(2-Methoxyphenyl)-3-phenylpropan-1-one (3c) [6]:



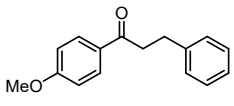
White solid, 110.5 mg, 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.30 – 7.23 (m, 4H), 7.19 (t, *J* = 7.2 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.87 (s, 3H), 3.30 (t, *J* = 7.6 Hz, 2H), 3.02 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.7, 158.5, 141.7, 133.4, 130.4, 128.5, 128.4, 128.4, 125.9, 120.7, 111.5, 55.5, 45.4, 30.5.

1-(3-Methoxyphenyl)-3-phenylpropan-1-one (3d) [3]:



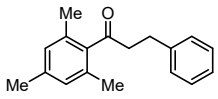
Pale yellow solid, 106.9 mg, 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 1H), 7.48 (s, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.30 (t, J = 7.6 Hz, 2H), 7.25 (d, J = 7.6 Hz, 2H), 7.20 (t, J = 7.6 Hz, 1H), 7.09 (dd, J = 8.0 Hz, J = 3.0 Hz, 1H), 3.84 (s, 3H), 3.28 (t, J = 7.6 Hz, 2H), 3.06 (t, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 159.9, 141.3, 138.3, 129.6, 128.5, 128.4, 126.1, 120.7, 119.6, 112.3, 55.4, 40.6, 30.2.

1-(4-Methoxyphenyl)-3-phenylpropan-1-one (3e) [3]:



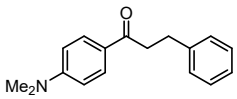
Pale yellow solid, 112.9 mg, 94% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 2 H), 7.29 (t, J = 7.6 Hz, 2 H), 7.25 (d, J = 7.0 Hz, 2H), 7.19 (t, J = 7.0 Hz, 1 H), 6.92 (d, J = 8.0 Hz, 2 H), 3.84 (s, 3 H), 3.24 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 163.5, 141.5, 130.3, 130.0, 128.5, 128.4, 126.1, 113.7, 55.5, 40.1, 30.4.

1-Mesityl-3-phenylpropan-1-one (3f) [4]:



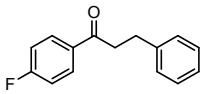
Colorless liquid, 117.3 mg, 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.29 – 7.18 (m, 5H), 6.81 (s, 2H), 3.06 – 2.99 (m, 4H), 2.26 (s, 3H), 2.11 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.7, 141.0, 139.5, 138.4, 132.6, 128.5, 128.5, 126.1, 46.4, 29.5, 21.0, 19.0.

1-(4-(Dimethylamino)phenyl)-3-phenylpropan-1-one (3g) [7]:



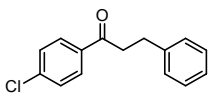
White solid, 116.5 mg, 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.0 Hz, 2H), 7.30 – 7.24 (m, 4H), 7.18 (t, *J* = 7.0 Hz, 1H), 6.63 (d, *J* = 9.0 Hz, 2H), 3.19 (t, J = 7.6 Hz, 2H), 3.06 – 3.03 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.4, 153.4, 141.9, 130.3, 128.5, 126.0, 124.9, 110.7, 40.0, 39.8, 30.7.

1-(4-Fluorophenyl)-3-phenylpropan-1-one (3h) [4]:



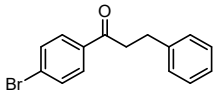
Colorless liquid, 89 mg, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 – 7.95 (m, 2H), 7.31 – 7.20 (m, 5H), 7.11 (t, J=8.6, 2H), 3.26 (t, J=7.8, 2H), 3.06 (t, J=7.8, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.6, 165.6 (d, $^1J_{CF}$=253), 141.1, 133.2 (d, $^4J_{CF}$=3), 130.7 (d, $^3J_{CF}$=9), 128.4, 128.4, 126.2, 115.6 (d, $^2J_{CF}$=21), 40.4, 30.1.

1-(4-Chlorophenyl)-3-phenylpropan-1-one (3i) [4]:



Pale yellow solid, 99.1 mg, 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87 (d, J=8.6, 2H), 7.40 (d, J=8.6, 2H), 7.31 – 7.19 (m, 5H), 3.26 (t, J=7.6, 2H), 3.06 (t, J=7.6, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.0, 141.1, 139.5, 135.2, 129.5, 128.9, 128.6, 128.4, 126.2, 40.4, 30.1.

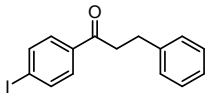
1-(4-Bromophenyl)-3-phenylpropan-1-one (3j) [4]:



Pale yellow solid, 120 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (d,

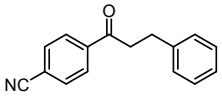
J=8.4, 2H), 7.58 (d, J=8.4, 2H), 7.31 – 7.20 (m, 5H), 3.25 (t, J=7.6, 1H), 3.05 (t, J=7.6, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1, 141.0, 135.6, 131.9, 129.6, 128.6, 128.4, 128.2, 126.2, 40.4, 30.1.

1-(4-Iodophenyl)-3-phenylpropan-1-one (3k) [8]:



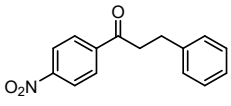
Pale yellow solid, 141.2 mg, 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J=8.4, 2H), 7.66 (d, J=8.4, 2H), 7.32 – 7.20 (m, 5H), 3.25 (t, J=7.6, 1H), 3.05 (t, J=7.6, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.5, 141.0, 137.9, 136.1, 129.4, 128.6, 128.4, 126.2, 101.0, 40.3, 30.0.

4-(3-Phenylpropanoyl)benzonitrile (3l) [17]



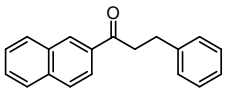
Yellow oil, 72.9 mg, 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.34 – 7.26 (m, 2H), 7.24 – 7.18 (m, 3H), 3.31 (t, J = 7.5 Hz, 2H), 3.07 (t, J = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 197.8, 140.7, 139.8, 132.5, 128.6, 128.5, 128.4, 126.4, 117.9, 116.3, 40.7, 29.9;

1-(4-Nitrophenyl)-3-phenylpropan-1-one (3m) [17]



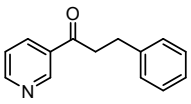
Yellow oil, 61.3 mg, 48% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (d, J = 8.8 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H), 7.36-7.27 (m, 2H), 7.27-7.20 (m, 3H), 3.35 (t, J = 7.5 Hz, 2H), 3.09 (t, J = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 197.6, 150.3, 141.2, 140.6, 129.1, 128.7, 128.4, 126.4, 123.9, 41.0, 29.9;

1-(Naphthalen-2-yl)-3-phenylpropan-1-one (3n) [4]:



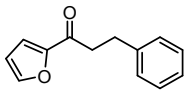
Yellow solid, 115.8 mg, 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.45 (s, 1H), 8.02 (m, 1H), 7.93 – 7.85 (m, 3H), 7.59 – 7.51 (m, 2H), 7.33 – 7.20 (m, 5H), 3.43 (t, J=7.6, 2H), 3.12 (t, J=7.6, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 141.4, 135.6, 134.2, 132.5, 129.7, 129.6, 128.6, 128.5, 128.5, 127.8, 126.8, 126.2, 123.9, 40.6, 30.3.

3-Phenyl-1-(pyridin-3-yl)propan-1-one (3o) [2]:



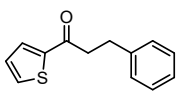
Yellowish oil, 82.4 mg, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (s, 1 H), 8.77 (d, J = 4.5 Hz, 1 H), 8.22 (d, J = 8.0 Hz, 1 H), 7.40 (dd, J = 8.0, 4.5 Hz, 1 H), 7.30 (t, J = 7.5 Hz, 2 H), 7.25 (d, J = 7.5 Hz, 2 H), 7.20 (t, J = 7.5 Hz, 1 H), 3.32 (t, J = 7.6 Hz, 2 H), 3.08 (t, J = 7.6 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.0, 153.5, 149.6, 140.7, 135.3, 132.1, 128.6, 128.4, 126.3, 123.6, 40.7, 29.8.

1-(Furan-2-yl)-3-phenylpropan-1-one (3p) [2]:



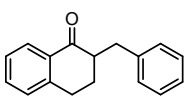
Slightly yellow oil, 71.1 mg, 71% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, J = 1.6, 0.6 Hz, 1H), 7.30 – 7.16 (m, 6H), 6.52 (dd, J = 3.6, 1.7 Hz, 1H), 3.21 – 3.13 (m, 2H), 3.08 – 3.02 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.5, 152.7, 146.3, 141.0, 128.5, 128.4, 126.2, 117.0, 112.2, 40.2, 30.0.

3-Phenyl-1-(thiophen-2-yl)propan-1-one (3q) [2]:



Slightly yellow oil, 87.6 mg, 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 3.7 Hz, 1H), 7.61 (d, J = 4.9 Hz, 1H), 7.31 – 7.18 (m, 5H), 7.10 (dd, J = 3.8, 4.8 Hz, 1H), 3.22 (t, J = 7.7 Hz, 2H), 3.07 (dd, J = 6.8, 8.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.1, 144.2, 141.0, 133.5, 131.8, 128.6, 128.4, 128.1, 126.2, 41.2, 30.4.

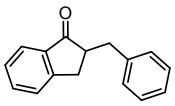
2-Benzyl-3,4-dihydronaphthalen-1(2*H*)-one (3r) [3]:



Pale yellow solid, 100.4 mg, 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 1 H), 7.46 (t, J = 7.5 Hz, 1 H), 7.33 – 7.29 (m, 3 H), 7.25 – 7.20 (m, 4 H), 3.50 (dd, J = 14.0, 4.0 Hz, 1 H), 2.95 – 2.91 (m, 2 H), 2.77 – 2.73 (m, 1 H), 2.64 (dd, J = 14.0, 10.0 Hz, 1 H), 2.13 – 2.09 (m, 1 H), 1.83 – 1.75 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ

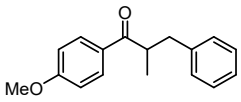
199.3, 144.0, 140.1, 133.2, 132.5, 129.3, 128.7, 128.4, 127.6, 126.6, 126.1, 49.5, 35.7, 28.6, 27.7.

2-Benzyl-2,3-dihydro-1*H*-inden-1-one (3s) [9]:



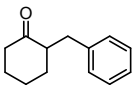
Pale yellow oil, 91.1 mg, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.32 – 7.18 (m, 5H), 3.40 (dd, *J* = 14.0, 4.0 Hz, 1H), 3.16 (dd, *J* = 17.2, 8.0 Hz, 1H), 3.04 – 2.95 (m, 1H), 2.86 (dd, *J* = 17.0, 3.8 Hz, 1H), 2.67 (dd, *J* = 13.8, 10.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.8, 153.6, 139.7, 136.6, 134.8, 128.9, 128.5, 127.4, 126.6, 126.4, 124.0, 49.0, 37.0, 32.2.

1-(4-Methoxyphenyl)-2-methyl-3-phenylpropan-1-one (3t) [18]:



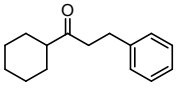
Colorless oil, 91.1 mg, 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.22 – 7.17 (m, 3H), 6.94 – 6.92 (m, 2H), 3.86 (s, 3H), 3.75 – 3.68 (m,1H), 3.19 – 3.15 (m, 1H), 2.72 – 2.68 (m, 1H), 1.20 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 202.2, 163.3, 140.0, 130.5, 129.0, 129.1, 128.3, 126.0, 113.7, 55.4, 42.3, 39.5, 17.5.

2-Benzylcyclohexan-1-one (3u) [19]:



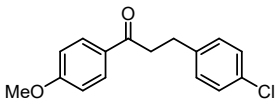
Colorless oil, 54.6 mg, 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.18 (m, 2H), 7.16 – 7.05 (m, 3H), 3.14 (dd, J = 13.8 Hz, J = 5.2 Hz, 1H), 2.48 – 2.43 (m, 1H), 2.36 – 2.22 (m, 3H), 1.99 – 1.90 (m, 2H), 1.75 – 1.71 (m, 1H), 1.61 – 1.46 (m, 2H), 1.27 – 1.20 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.6, 140.4, 129.2, 128.3, 126.0, 52.5, 42.2, 35.5, 33.4, 28.1, 25.1.

1-Cyclohexyl-3-phenylpropan-1-one (3v) [20]:



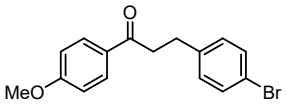
Colorless oil, 71.4 mg, 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (t, J = 6.5 Hz, 2H), 7.18 (t, J = 6.3 Hz, 3H), 2.88 (t, J = 7.6 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 2.30 (td, J = 11.1, 3.2 Hz, 1H), 1.82-1.75 (m, 4H), 1.68 – 1.62 (m, 1H), 1.35 – 1.13 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 213.1, 141.4, 128.4, 128.3, 126.0, 51.0, 42.2, 29.7, 28.4, 25.9, 25.7;

3-(4-Chlorophenyl)-1-(4-methoxyphenyl)propan-1-one (3w) [5]:



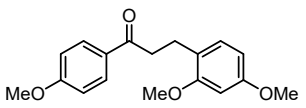
Pale yellow solid, 108.5 mg, 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 9.2 Hz, 2H), 3.86 (s, 3H), 3.22 (t, *J* = 7.6 Hz, 2H), 3.02 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.4, 163.5, 139.9, 131.8, 130.3, 129.9, 129.8, 128.6, 113.8, 55.5, 39.8, 29.6.

3-(4-Bromophenyl)-1-(4-methoxyphenyl)propan-1-one (3x) [10]:



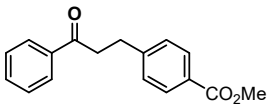
White solid, 121.3 mg, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 3.22 (t, *J* = 7.6 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 163.5, 140.4, 131.5, 130.3, 130.2, 129.9, 119.8, 113.8, 55.5, 39.7, 29.6.

3-(2,4-Dimethoxyphenyl)-1-(4-methoxyphenyl)propan-1-one (3y):



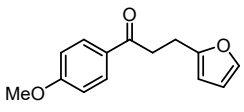
Pale yellow solid, 135.2 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.45 – 6.41 (m, 2H), 3.85 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.16 (t, *J* = 7.6 Hz, 2H), 2.96 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.8, 163.3, 159.5, 158.4, 130.4, 130.3, 130.1, 122.0, 113.6, 103.9, 98.6, 55.4, 55.3, 55.2, 39.0, 25.3. HRMS-ESI m/z: $[M+H]^+$ calculated for $C_{18}H_{21}O_4$: 301.1434, found: 301.1445.

Methyl 4-(3-oxo-3-phenylpropyl)benzoate (3z) [17]:



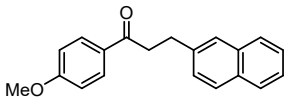
White solid, 93.9 mg, 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) 7.97 – 7.94 (m, 4H), 7.60 – 7.54 (m, 1H), 7.50 – 7.42 (m, 2H), 7.36 – 7.31 (m, 2H), 3.90 (s, 3H), 3.32 (t, J = 7.6 Hz, 2H), 3.13 (t, J = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) 198.7, 167.0, 146.8, 136.7, 133.2, 129.9, 128.7, 128.5, 128.2, 128.0, 52.0, 39.8, 30.0.

3-(Furan-2-yl)-1-(4-methoxyphenyl)propan-1-one (3aa):



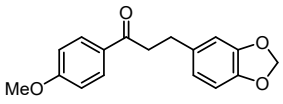
Pale yellow solid, 81.8 mg, 71% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.31 (s, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.28 (s, 1H), 6.05 (s, 1H), 3.86 (s, 3H), 3.28 (t, *J* = 7.6 Hz, 2H), 3.08 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 163.5, 155.0, 141.1, 130.3, 129.9, 113.8, 110.2, 105.2, 55.5, 36.6, 22.7. HRMS-ESI m/z: $[M+H]^+$ calculated for $C_{14}H_{15}O_3$: 231.1016, found: 231.1011.

1-(4-Methoxyphenyl)-3-(naphthalen-2-yl)propan-1-one (3ab) [10]:



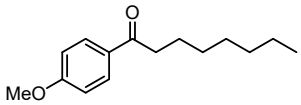
White solid, 122 mg, 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 5.0 Hz, 2H), 7.79 – 7.76 (m, 3H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.44 – 7.36 (m, 3H), 6.90 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 3.31 (t, *J* = 7.6 Hz, 2H), 3.21 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7, 163.5, 139.0, 133.7, 132.1, 130.3, 130.0, 128.1, 127.6, 127.5, 127.2, 126.5, 126.0, 125.3, 113.8, 55.5, 40.0, 30.5.

3-(Benzo[*d*][1,3]dioxol-5-yl)-1-(4-methoxyphenyl)propan-1-one (3ac) [11]:



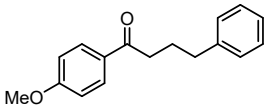
White solid, 122.2 mg, 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 5.0 Hz, 2H), 6.73 (d, *J* = 5.0 Hz, 2H), 6.69 (dd, *J* = 8.0, 1.8 Hz, 1H), 5.91 (s, 2H), 3.86 (s, 3H), 3.20 (t, *J* = 7.6 Hz, 2H), 2.97 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 163.5, 147.6, 145.8, 135.3, 130.3, 129.9, 121.2, 113.7, 108.9, 108.3, 100.8, 55.5, 40.3, 30.1.

1-(4-Methoxyphenyl)octan-1-one (3ad) [13]:



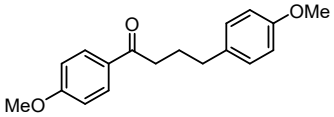
Pale yellow oil, 67.9 mg, 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.90 (t, *J* = 7.4 Hz, 2H), 1.76 – 1.70 (m, 2H), 1.37 – 1.27 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 163.3, 130.3, 130.2, 113.6, 55.4, 38.3, 31.7, 29.4, 29.2, 24.7, 22.6, 14.1.

1-(4-Methoxyphenyl)-4-phenylbutan-1-one (3ae) [12]:



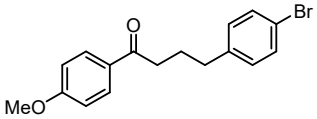
Pale yellow oil, 91.5 mg, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 5.0 Hz, 2H), 7.29 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.21 – 7.19 (m, 3H), 6.91 (d, *J* = 5.0 Hz, 2H), 3.86 (s, 3H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.13 – 2.00 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 163.4, 141.8, 130.3, 130.1, 128.5, 128.4, 125.9, 113.7, 55.5, 37.4, 35.3, 25.9.

1,4-Bis(4-methoxyphenyl)butan-1-one (3af) [13]:



White solid, 106.6 mg, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 2H), 3.85 (s, 3H), 3.78 (s, 3H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.06 – 2.01 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.8, 163.4, 157.9, 133.9, 130.3, 130.2, 129.4, 113.8, 113.7, 55.5, 55.3, 37.3, 34.4, 26.2.

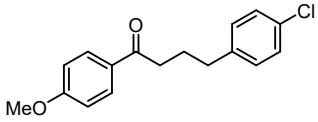
4-(4-Bromophenyl)-1-(4-methoxyphenyl)butan-1-one (3ag):



Pale yellow solid, 116.6 mg, 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ

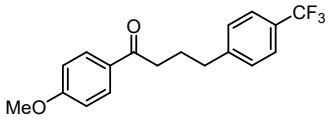
7.90 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.07 – 2.01 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.4, 163.4, 140.8, 131.4, 130.3, 130.3, 130.0, 119.7, 113.7, 55.5, 37.1, 34.6, 25.7. HRMS-ESI m/z: $[M+H]^+$ calculated for $C_{17}H_{18}BrO_2$: 333.0485, found: 333.0472.

4-(4-Chlorophenyl)-1-(4-methoxyphenyl)butan-1-one (3ah):



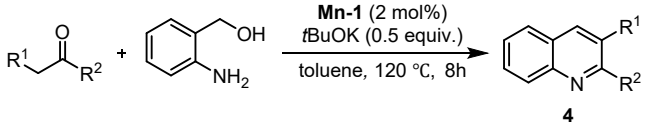
Pale yellow solid, 98.2 mg, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 3.86 (s, 3H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.07 – 2.01 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.4, 163.4, 140.2, 131.6, 130.3, 130.1, 129.9, 128.5, 113.7, 55.5, 37.1, 34.6, 25.8. HRMS-ESI m/z: $[M+H]^+$ calculated for $C_{17}H_{18}ClO_2$: 289.0990, found: 289.0997.

1-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)butan-1-one (3ai):



Pale yellow solid, 98.3 mg, 61% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.11 – 2.05 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3, 163.5, 146.0, 130.2, 130.0, 128.8, 128.4, 128.2, 125.4, 125.3, 125.3, 125.3, 125.2, 123.3, 113.7, 55.5, 37.1, 35.1, 25.5. HRMS-ESI m/z: $[M+H]^+$ calculated for $C_{18}H_{18}F_3O_2$: 323.1253, found: 323.1261.

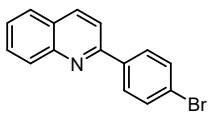
4. Procedures for Synthesis of Quinolones



4

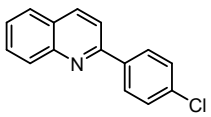
A flame dried Schlenk tube was charged with **Mn-1** (0.01 mmol), *t*BuOK (0.25 mmol), ketone (0.5 mmol) and 2-aminobenzyl alcohol (0.5 mmol). The tube was evacuated and backfilled with nitrogen for three times. Toluene (1 mL) was added and the mixture was stirred at 120 °C for 8 h. After completion of the reaction, the reaction mixture was cooled to ambient temperature and 5 mL of water was added and the aqueous solution extracted with EtOAc (3 × 5 mL). Combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by silica gel column chromatography (*n*-hexane/EtOAc = 10:1) to give the corresponding product **4**.

2-(4-Bromophenyl)quinolone (4a) [2]:



White solid, 119.4 mg, 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J = 8.6 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 8.6 Hz, 2H), 7.74 (dd, J = 8.0, 3.4 Hz, 2H), 7.66 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.656 (d, J = 8.6 Hz, 2H), 7.45 (t, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 148.2, 138.5, 137.0, 132.0, 129.9, 129.7, 129.1, 128.5, 127.5, 126.5, 124.0, 118.5.

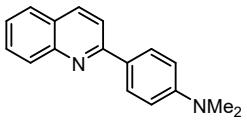
2-(4-Chlorophenyl)quinolone (4b) [2]:



White solid, 97.1 mg, 81% yield. ^{1}H NMR (500 MHz, CDCl3) δ 8.19 (d, J = 8.6 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 8.11 (d, J = 7.0 Hz, 2H), 7.84 (d, J = 8.6 Hz,

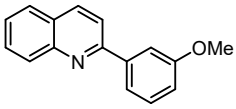
2H), 7.74 (t, J = 7.7 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.48 (d, J = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 148.3, 138.1, 137.6, 135.6, 129.8, 129.7, 129.0, 128.8, 127.5, 127.2, 126.5, 118.5.

_N,N_-Dimethyl-4-(quinolin-2-yl)aniline (4c) [14]:



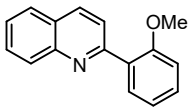
Yellow solid, 84.4 mg, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 9.0 Hz, 3H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.67 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.47 – 7.42 (m, 1H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.73 (d, *J* = 9.0 Hz, 1H), 3.04 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 151.4, 148.4, 136.3, 129.3, 128.5, 127.4, 127.3, 127.1, 126.7, 125.3, 118.3, 112.3, 40.4.

2-(3-Methoxyphenyl)quinolone (4d) [5]:



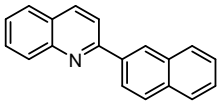
White solid, 77.6 mg, 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 – 8.17 (m, 2H), 7.85 (d, J = 8.6 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.77 (t, J = 2.0 Hz, 1H), 7.73 – 7.69 (m, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.42 (t, J =7.9 Hz, 1H), 7.02 (m, 1H), 3.93 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 157.1, 148.2, 141.2, 136.7, 129.8, 129.8, 129.6, 127.5, 127.3, 126.3, 120.0, 119.1, 115.4, 112.7, 55.4.

2-(2-Methoxyphenyl)quinolone (4e) [15]:



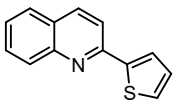
Pale yellow oil, 67.1 mg, 57% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.5 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.85 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.70 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.41 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.13 (t, *J* = 6.9 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 157.1, 148.3, 135.1, 131.5, 130.3, 129.8, 129.7, 129.2, 127.4, 127.1, 126.2, 123.5, 121.3, 111.5, 55.7.

2-(Naphthalen-2-yl)quinolone (4f) [3]:



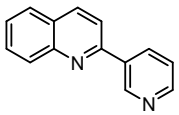
White solid, 102.1 mg, 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.37 (dd, J = 8.5, 1.5 Hz, 1H), 8.22 (d, J = 8.5 Hz, 2H), 8.00 (m, 3 H), 7.88 (dd, J = 6.0, 3.0 Hz, 1H), 7.82 (d, J = 8.5 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.52 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 148.3, 136.9, 136.7, 133.9, 133.5, 129.8, 129.7, 128.8, 128.6, 127.7, 127.5, 127.2, 127.2, 126.7, 126.4, 126.3, 125.1, 119.2.

2-(Thiophen-2-yl)quinolone (4g) [2]:



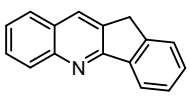
White solid, 75 mg, 71% yield. 1H NMR (500 MHz, CDCl3) δ 8.12 – 8.07 (m, 2H), 7.78 – 7.67 (m, 4H), 7.49 – 7.45 (m, 2H), 7.14 (dd, *J* = 5.0, 3.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4, 148.1, 145.4, 136.6, 129.8, 129.3, 128.6, 128.1, 127.5, 127.2, 126.1, 125.9, 117.7.

2-(Pyridin-3-yl)quinolone (4h) [3]:



Pale yellow solid, 80.4 mg, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.70 (d, J = 4.5 Hz, 1H), 8.51 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 8.5 Hz, 1H), 8.17 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.75 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.45 (dd, J = 8.0, 5.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6, 150.2, 148.8, 148.4, 137.2, 135.1, 134.9, 130.0, 129.8, 127.6, 127.4, 126.8, 123.7, 118.5.

11*H*-Indeno[1,2-*b*]quinoline (4i) [16]:



Pale yellow solid, 65.2 mg, 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.26 (m, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.15 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.58 (m, 1H), 7.51 – 7.47 (m, 3H), 4.00 (s, 2H). ^{13}C NMR

(126 MHz, $CDCl_3$) δ 161.7, 148.0, 145.1, 140.3, 134.6, 131.1, 130.0, 129.1, 128.8, 127.8, 127.5, 127.4, 125.7, 125.4, 122.1, 34.0.

5. X-Ray Crystallographic Data of Mn-1

Figure S2. X-Ray Structure of **Mn-1** (CCDC 2082641).

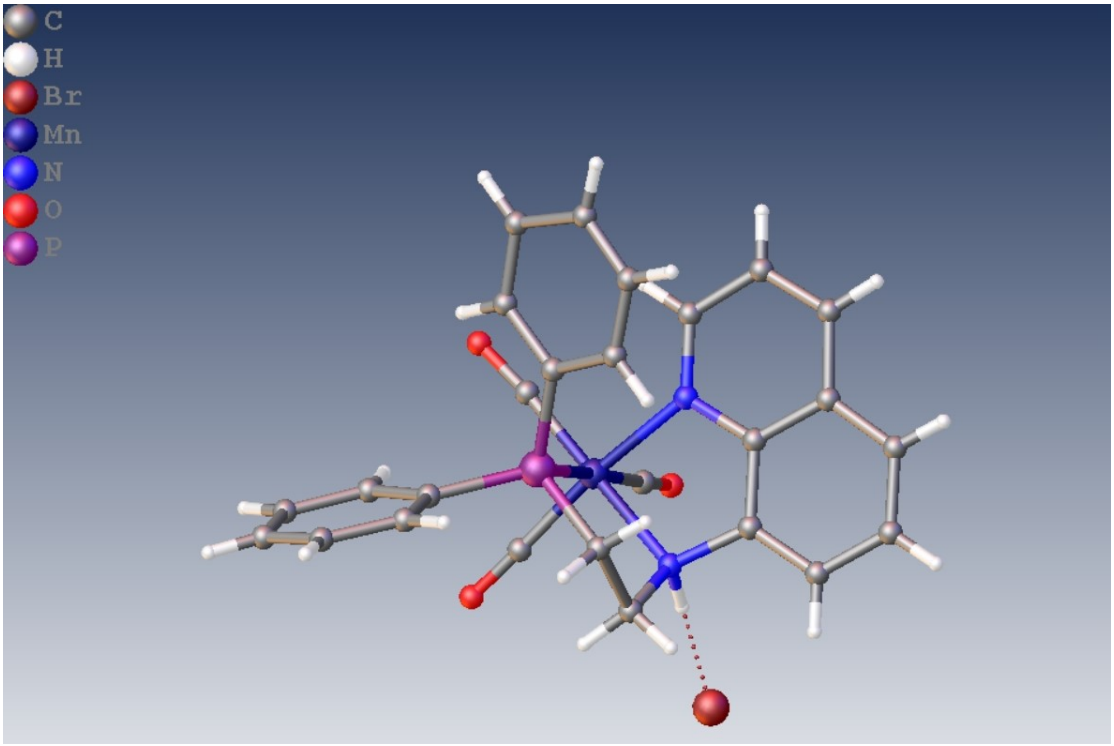


Table S1. Crystal data and structure refinement for **Mn-1**.

Identification code	SPD
Empirical formula	$C_{26}H_{21}BrMnN_2O_3P$
Formula weight	575.27
Temperature/K	303.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.1364(4)
b/Å	20.0961(7)
c/Å	15.2761(5)
α/°	90
β/°	93.171(2)
γ/°	90
Volume/Å^3	3413.5(2)
Z	4
ρ_{calc}g/cm^3	1.119
μ/mm^{-1}	5.143
F(000)	1160.0
Crystal size/mm^3	0.30 × 0.28 × 0.26

Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.95 to 136.912
Index ranges	$-13 \leq h \leq 13$, $-24 \leq k \leq 12$, $-16 \leq l \leq 18$
Reflections collected	21467
Independent reflections	6205 [R_{int} = 0.0706, R_{sigma} = 0.0755]
Data/restraints/parameters	6205/7/307
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0654, wR_2 = 0.2128
Final R indexes [all data]	R_1 = 0.0914, wR_2 = 0.2343
Largest diff. peak/hole / e $Å^{-3}$	0.46/-0.51

6. References

[1] A. A. Mikhailine, E. Kim, C. Dingels, A. J. Lough, R. H. Morris, *Inorg. Chem.* 2008, **47**, 6587.

[2] X. Lan, Z. Ye, M. Huang, Y. Liu, Z. Ke, *Org. Lett.*, 2019, **21**, 8065.

[3] G. Zhang, J. Wu, H. Zeng, S. Zhang, Z. Yin, S. Zheng, *Org. Lett.*, 2017, **19**, 1080.

[4] S. Elangovan, J.-B. Sortais, M. Beller, C. Darcel, *Angew. Chem., Int. Ed.*, 2015, 54, 14483.

[5] A. Maji, A. Singh, N. Singh and K. Ghosh, *ChemCatChem.*, 2020, **12**, 3108.

[6] P. Colbon, J. Ruan, M. Purdie, J. Xiao, *Org. Lett.*, 2010, **12**, 3670.

[7] L. Li, Z. Niu, Y. Liang, *Org. Biomol. Chem.*, 2018, **16**, 7792.

[8] W. Li, X. Wu, *Eur. J. Org. Chem.*, 2015, **2**, 331.

[9] P. Liu, R. Liang, L. Lu, Z. Yu, F. Li, *J. Org. Chem.*, 2017, **82**, 1943.

[10] M. Vellakkaran, M. M. S. Andappan, N. Kommu, *Eur. J. Org. Chem.*, 2012, **25**, 4694.

[11] G. Balamurugan, S. Balaji, R. Ramesh, N. S. P. Bhuvanesh, *Appl. Organomet. Chem.*, 2019, **33**, 4696.

[12] M. Das, M. D. Vu, Q. Zhang, X. Liu, *Chem. Sci.*, 2019, **10**, 1687.

[13] O. Vechorkin, X. Hu, *Angew. Chem., Int. Ed.*, 2009, **48**, 2937.

[14] M. J. Iglesias, A. Prieto, M. C. Nicasio, *Org. Lett.*, 2012, **14**, 4318.

[15] B. Hu, Y. Li, W. Dong, Z. Zhang, *RSC Adv.*, 2016, **6**, 48315.

[16] L. Xi, R. Zhang, S. Chen, X. Yu, *Org. Biomol. Chem.*, 2015, **13**, 3924.

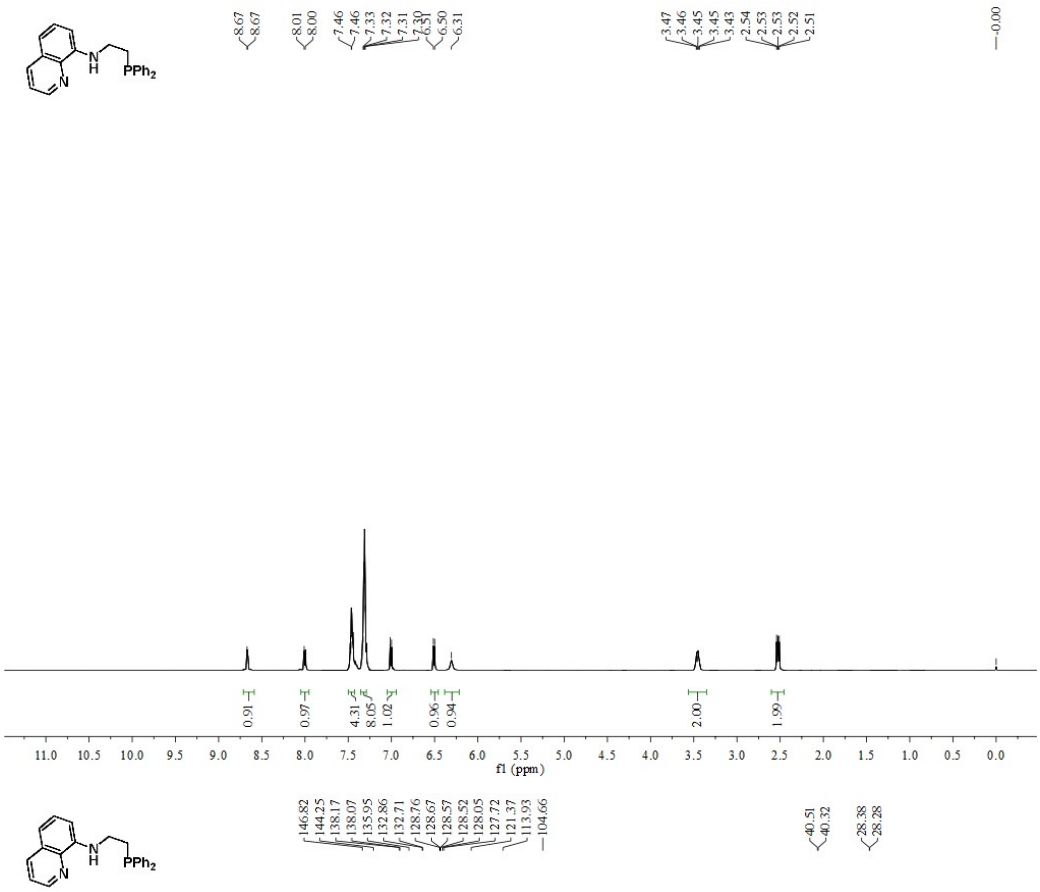
[17] X. Wang, X. Wang, Z. Zhang, T. Wang, *J. Org. Chem.*, 2022, **87**, 10173.

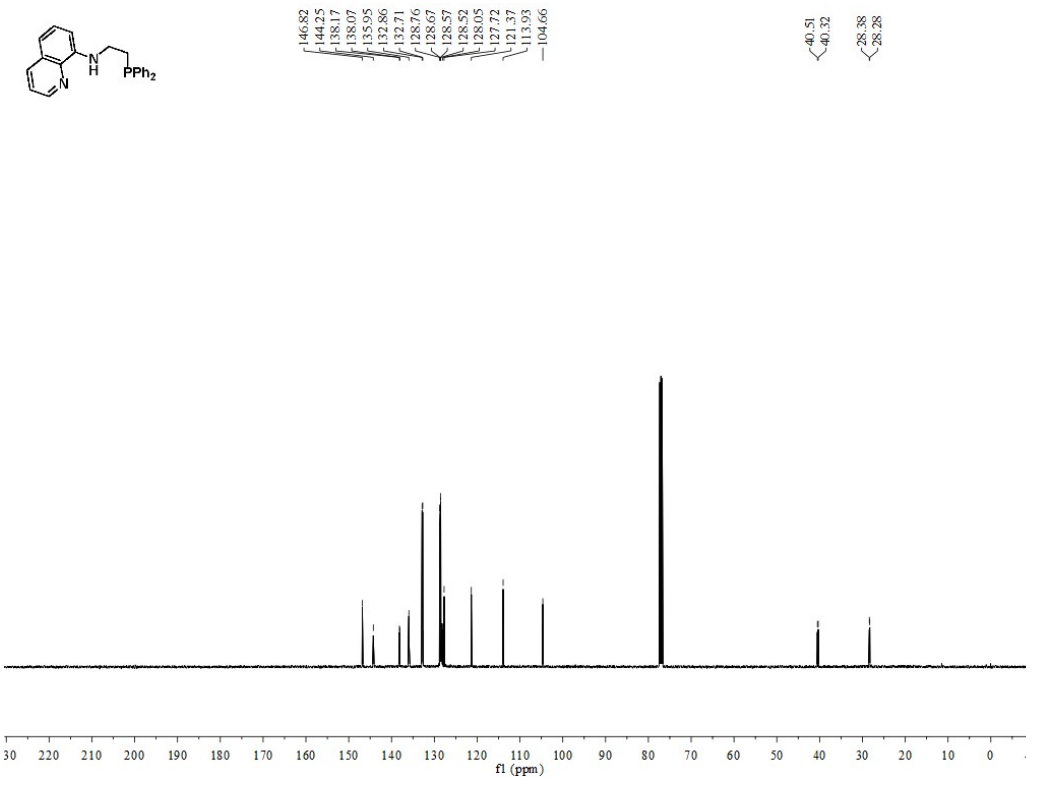
[18] B. Emayavaramban, P. Chakraborty, B. Sundararaju, *Org. Lett.*, 2022, **24**, 6219.

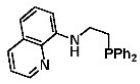
[19] X. Wang, T. Pei, X. Han, R. A. Widenhoefer, *Org. Lett.*, 2003, **5**, 2699.

[20] K. Nicholson, T. Langer, S. P. Thomas, *Org. Lett.*, 2021, **23**, 2498.

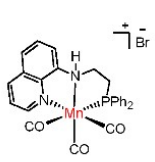
7. NMR Spectra



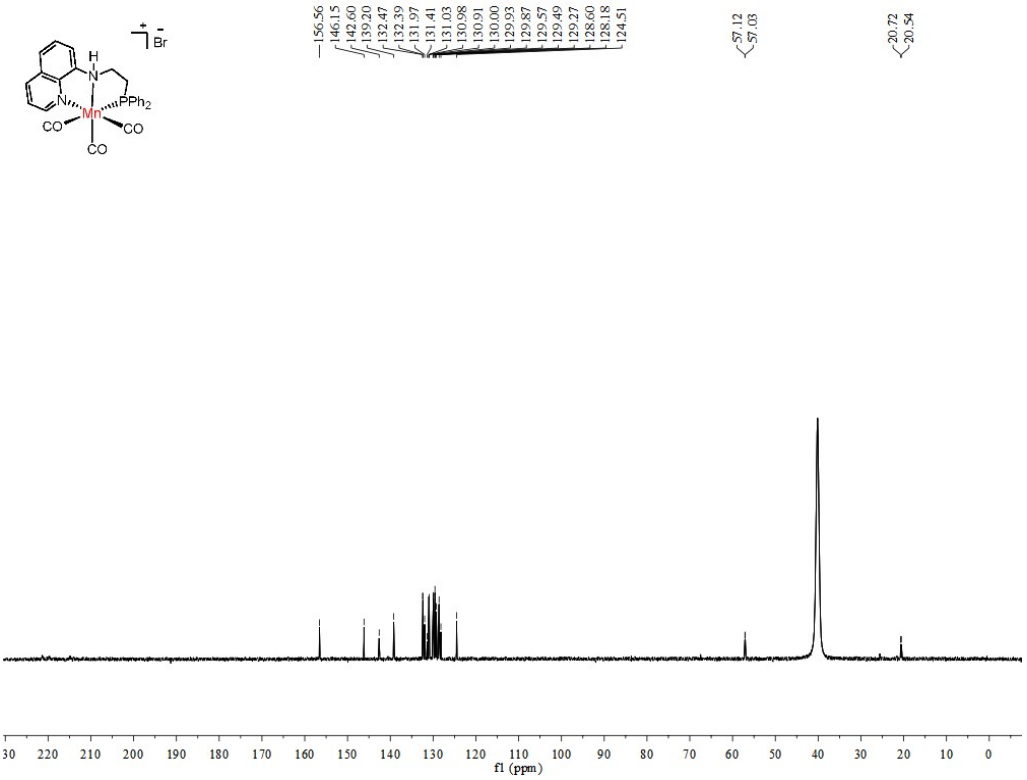



N
H
PPh2
N

-21.01
260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)


H
N
N
Mn
PPh2
CO
CO
CO
Br

9.61
8.63 8.62 8.60 8.59 8.32 8.30 8.13 7.94 7.92 7.91 7.65 7.64 7.37 7.28 7.26 7.00 6.98 4.17 4.16 4.15 4.14 4.09 4.08 4.06 4.05 3.28 3.23 3.22 3.19 3.16 1.75 1.72 1.70 1.69 1.68 1.66 1.65
0.97 2.01 1.00 1.05 3.10 3.15 2.19 2.10 2.05 0.99 2.11 1.20
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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146.15
142.60
139.20
132.47
132.39
131.97
131.41
131.03
130.98
130.91
130.00
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129.27
128.60
128.18
124.51
57.12
57.03
20.72
20.54
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H
N
N
Mn
PPh2
CO
CO
CO
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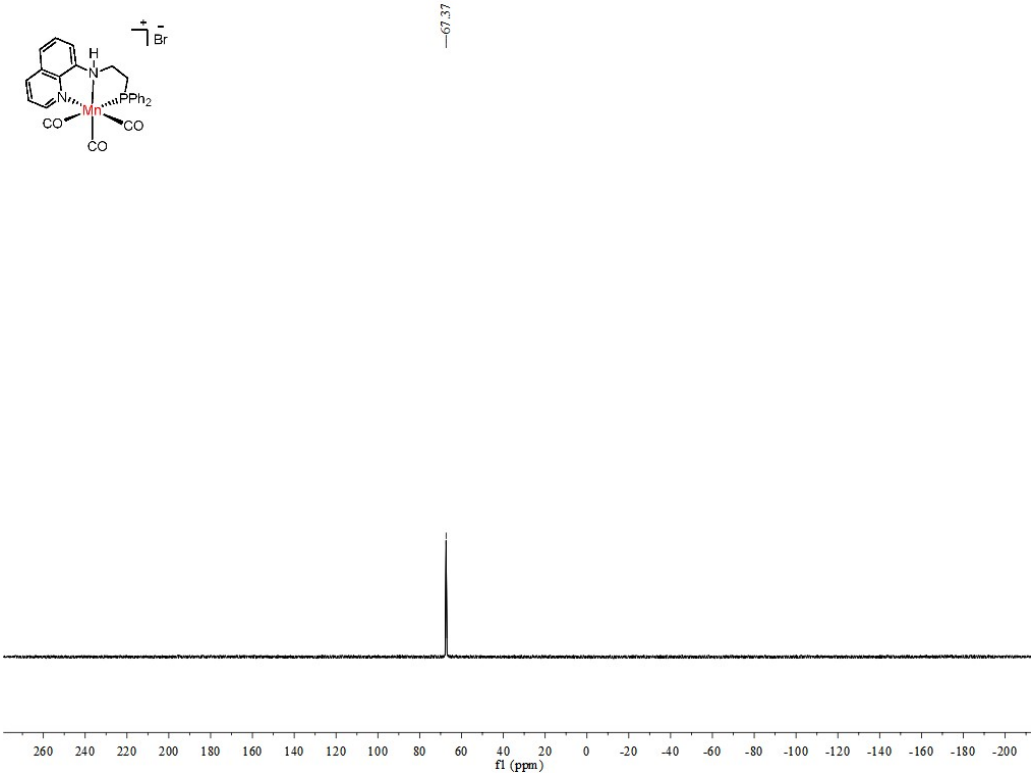
f1 (ppm)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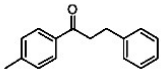
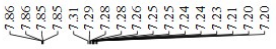
N
N
Mn
PPh2
CO
CO
CO
260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

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7.85
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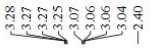
7.25
7.25
7.24
7.24
7.23
7.21
7.20
7.20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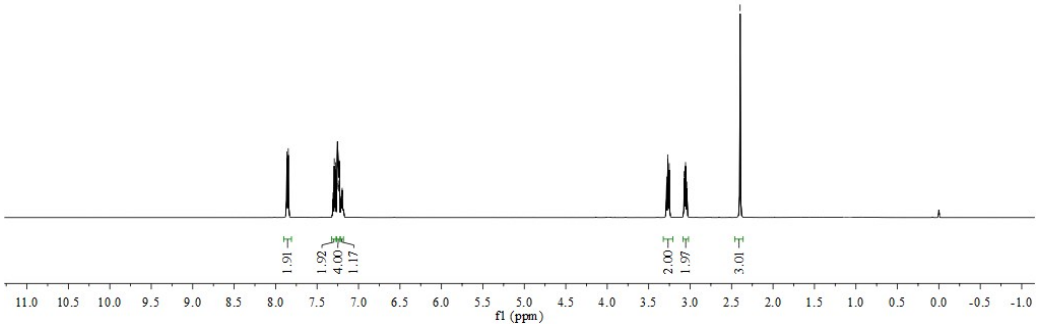
3.27
3.25
3.07
3.06
3.06
3.04
2.40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1.92
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1.17
2.00
1.97
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


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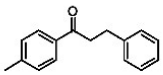

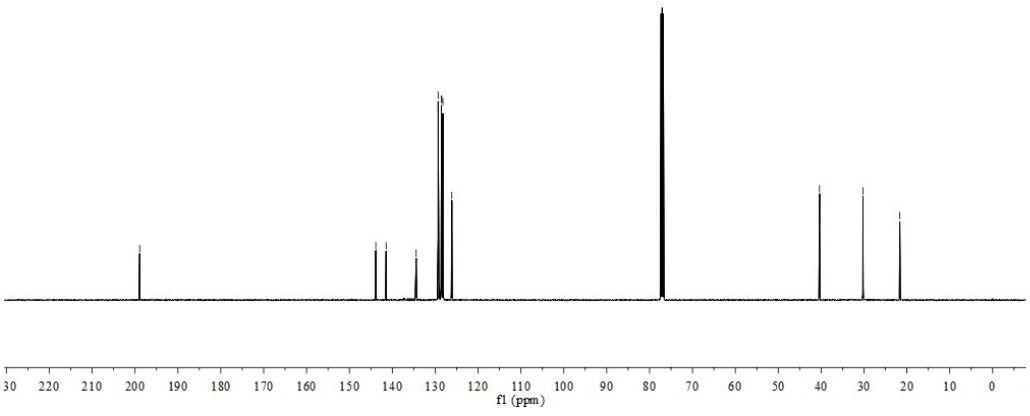
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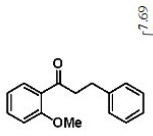
O
OMe

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6.99
6.98
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3.30
3.29
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3.02
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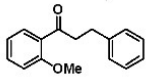
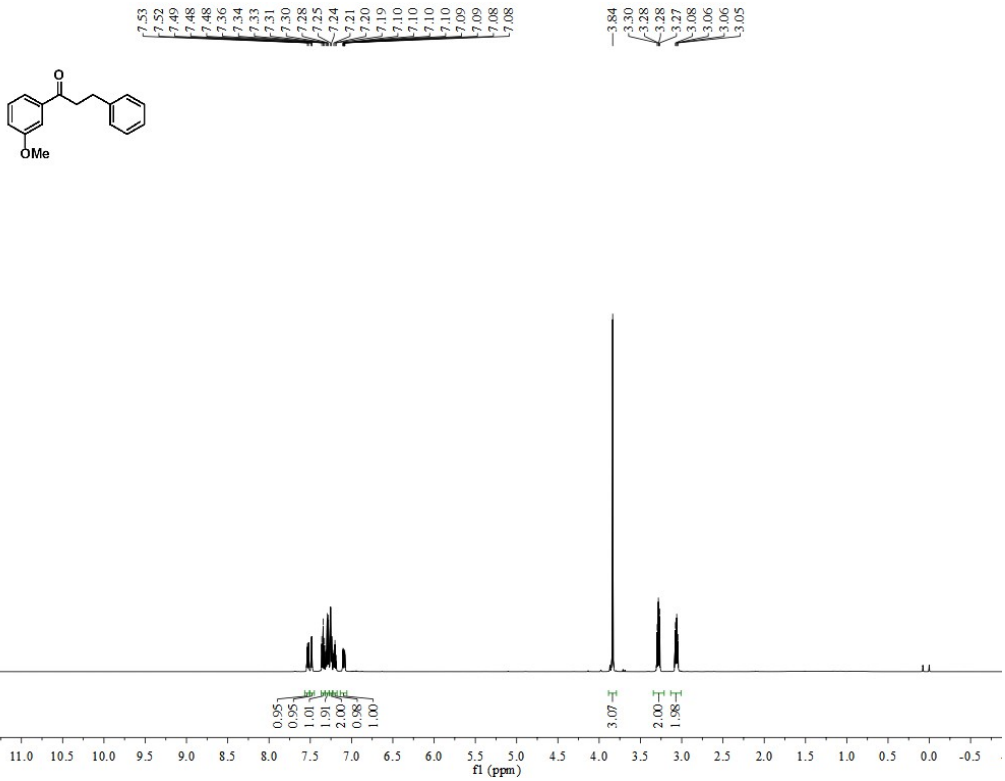
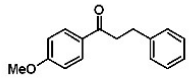
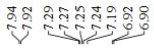
2.06
1.04
0.99
0.97
3.05
2.00
2.00
fl (ppm)

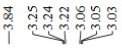

O
OMe

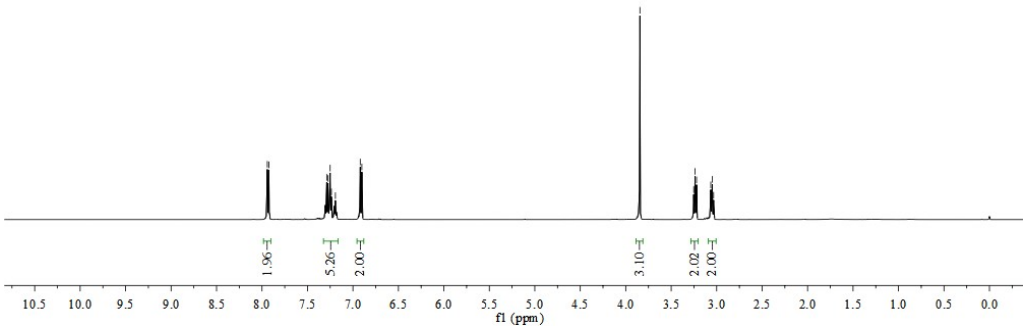
201.72
158.54
141.74
133.40
130.37
128.46
128.40
128.35
125.90
120.68
111.51
55.50
45.44
30.50
fl (ppm)


7.53
7.52
7.49
7.48
7.48
7.36
7.34
7.33
7.31
7.30
7.28
7.25
7.24
7.21
7.20
7.19
7.10
7.10
7.10
7.09
7.09
7.08
7.08
3.84
3.30
3.28
3.28
3.27
3.08
3.06
3.06
3.05
O
OMe
0.95
0.95
1.01
1.91
2.00
0.98
1.00
3.07
2.00
1.98
11.0 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 0.0 -0.5
f1 (ppm)
199.03
159.87
141.29
138.26
129.59
128.54
128.44
126.15
120.68
119.58
112.29
55.45
40.57
30.21
O
OMe
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

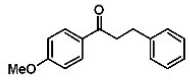

MeO

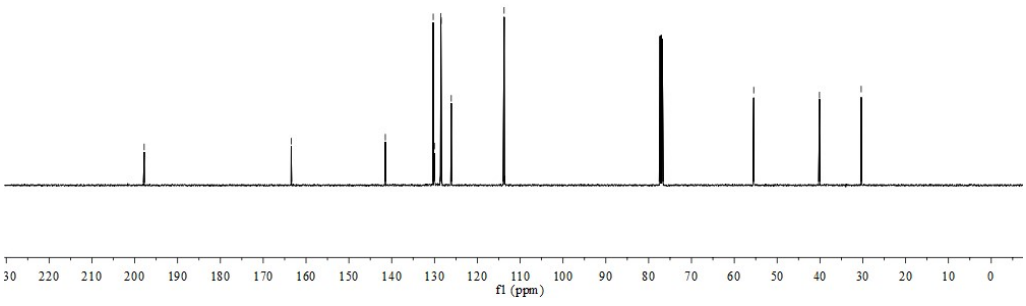

7.94
7.92
7.29
7.27
7.25
7.24
7.19
6.92
6.90


3.84
3.25
3.24
3.22
3.06
3.05
3.03

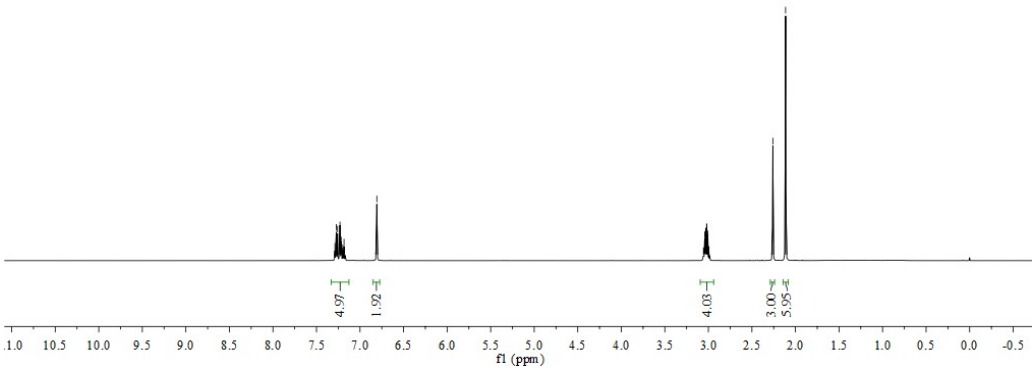

1.96
5.26
2.00
3.10
2.02
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

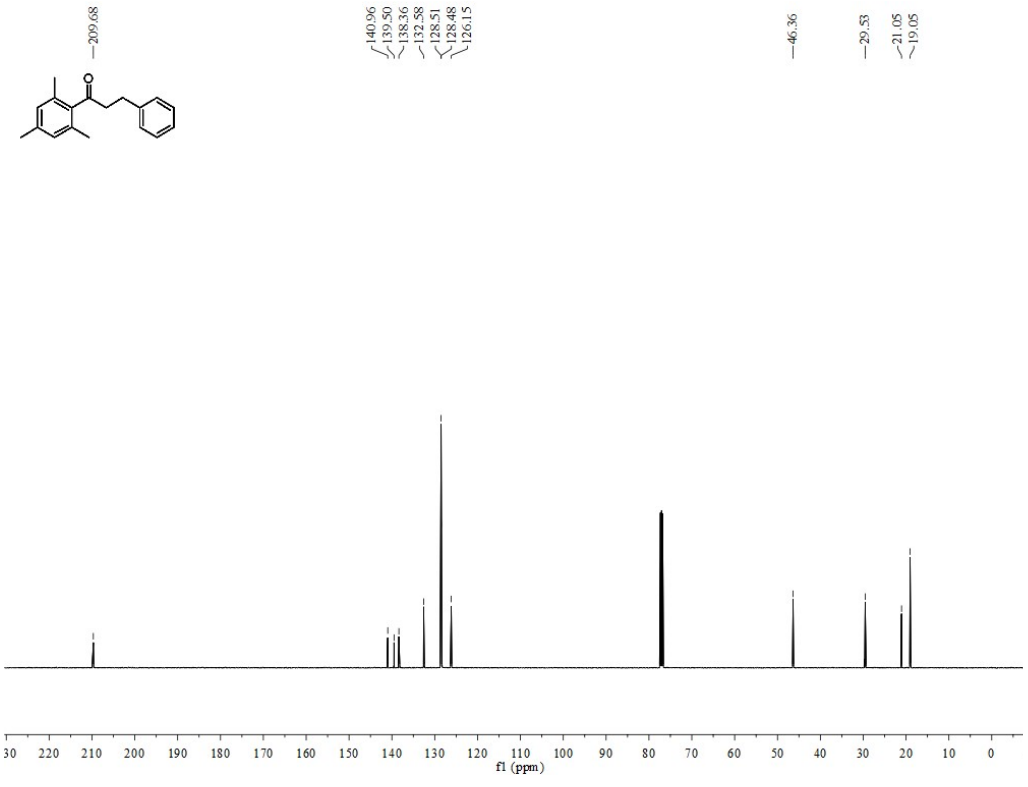

197.80
163.47
141.49
130.31
130.02
128.51
128.43
126.09
113.75
55.46
40.11
30.37

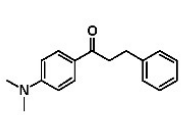

MeO


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

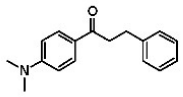

7.29
7.27
7.26
7.26
7.24
7.23
7.23
7.23
7.22
7.22
7.21
7.20
7.20
7.19
7.18
6.81
3.06
3.05
3.04
3.03
3.03
3.02
3.02
3.01
3.01
3.00
2.99
2.26
2.11


4.97
1.92
4.03
3.00
5.95
f1 (ppm)

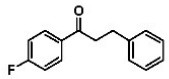

209.68
140.96
139.50
138.36
132.58
128.51
128.48
126.15
46.36
29.53
21.05
19.05
f1 (ppm)



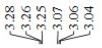
7.88
7.86
7.28
7.27
7.25
7.24
6.64
6.62
3.21
3.19
3.18
3.06
3.04
3.03
2.00
3.96
0.94
2.02
2.10
8.15
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

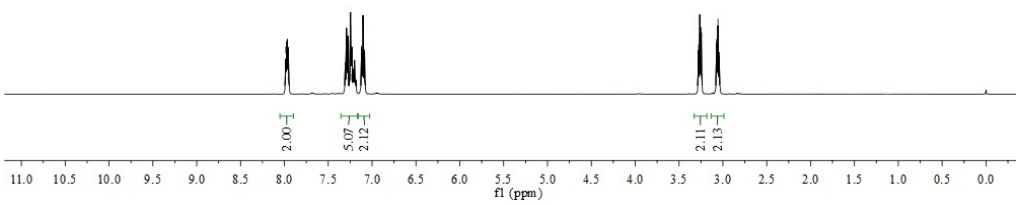


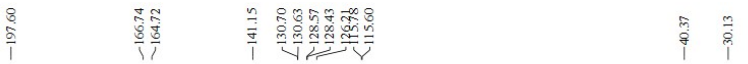
197.41
153.39
141.87
130.27
128.47
125.97
124.90
110.70
40.04
39.76
30.75
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

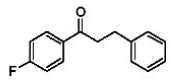


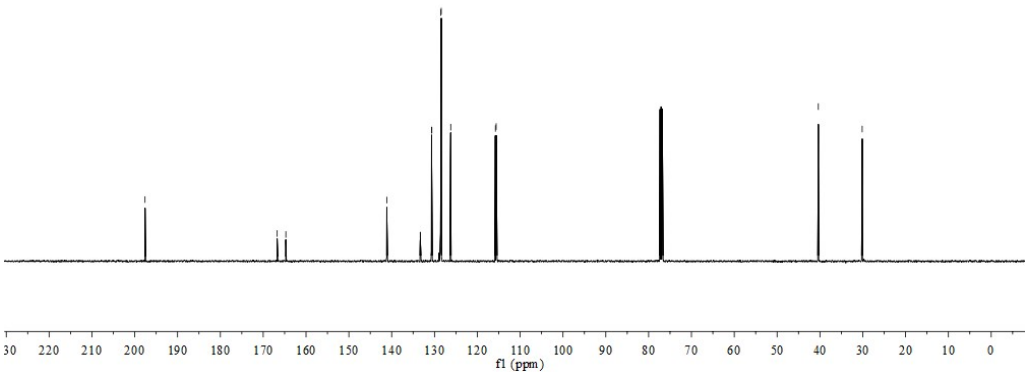

7.98
7.97
7.97
7.95
7.31
7.29
7.28
7.25
7.23
7.21
7.20
7.19
7.12
7.10
7.09

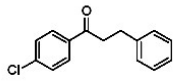

3.28
3.26
3.25
3.07
3.06
3.04

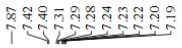

2.00
5.07
2.12
2.11
2.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


197.60
166.74
164.72
141.15
130.70
130.63
128.57
128.43
115.60
40.37
30.13

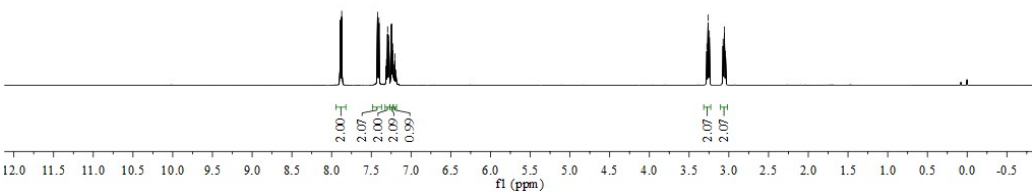



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

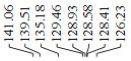

O
Cl


7.87
7.42
7.40
7.31
7.29
7.28
7.24
7.23
7.22
7.20
7.19

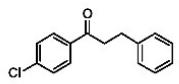

3.28
3.26
3.25
3.07
3.06
3.04

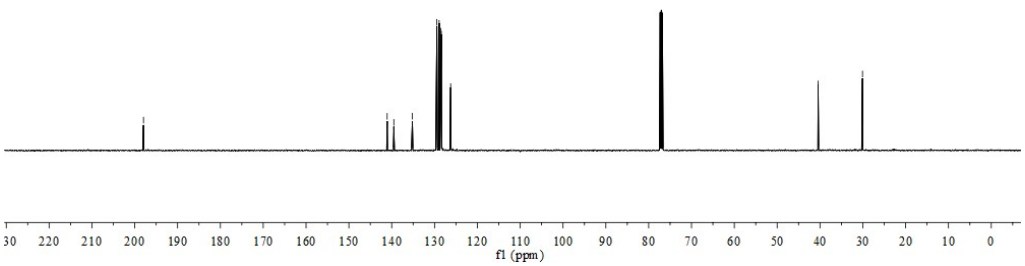

2.00
2.07
2.00
2.09
0.99
2.07
2.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


197.96

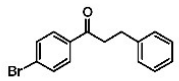

141.06
139.51
135.18
129.46
128.93
128.58
128.41
126.23

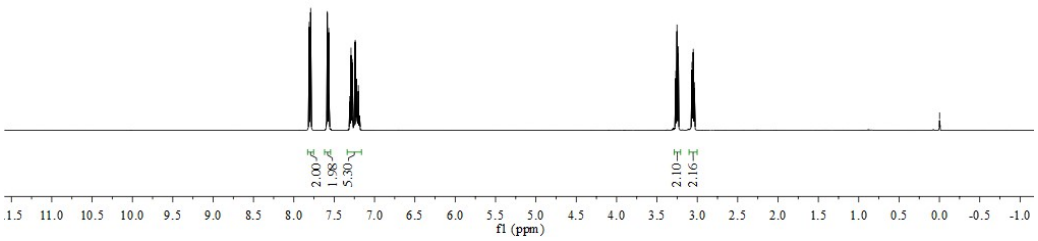

40.44
30.07


O
Cl

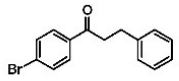

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

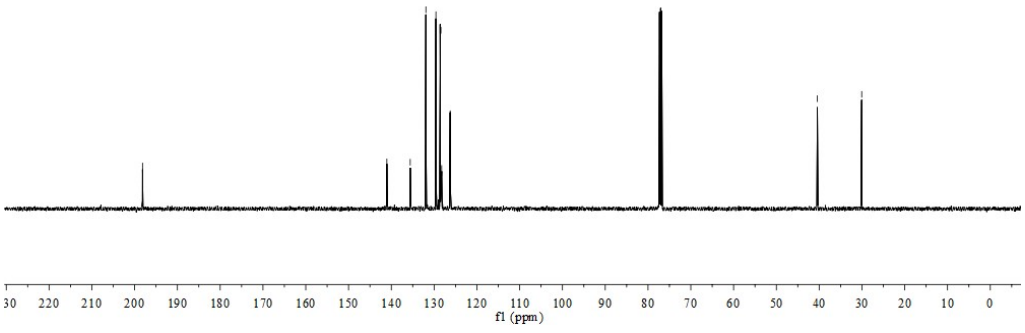

7.81
7.80
7.80
7.79
7.59
7.59
7.58
7.57
7.57
7.31
7.29
7.28
7.28
7.27
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.22
7.20
3.27
3.25
3.25
3.24
3.07
3.05
3.05
3.04
0.00

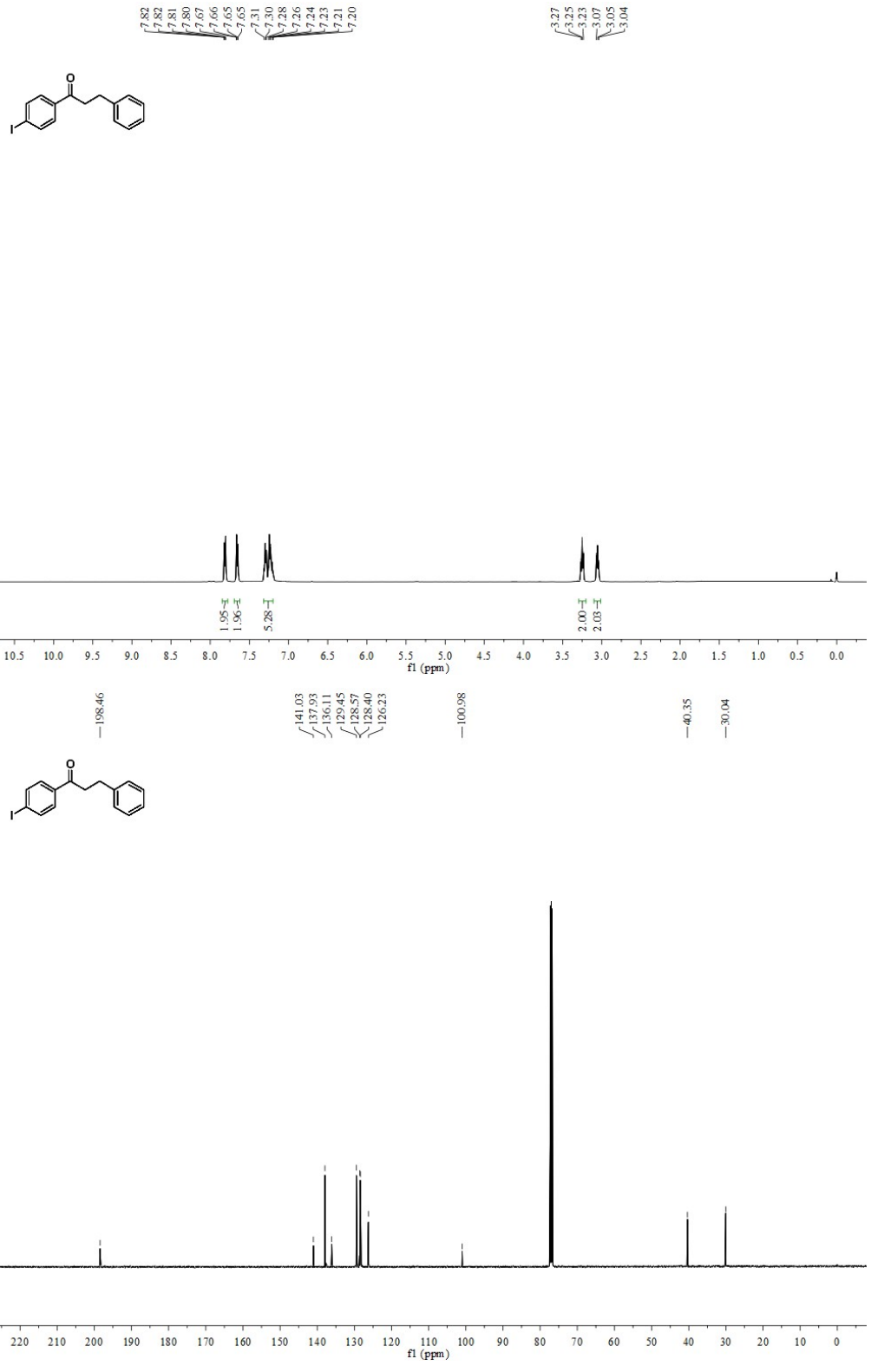

O
Br

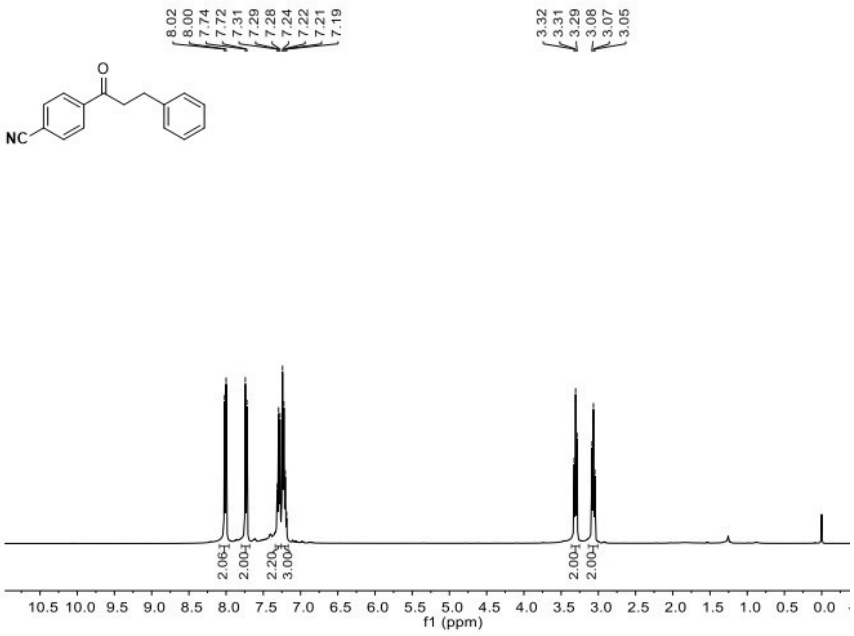

2.00
1.98
5.30
2.10
2.16
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

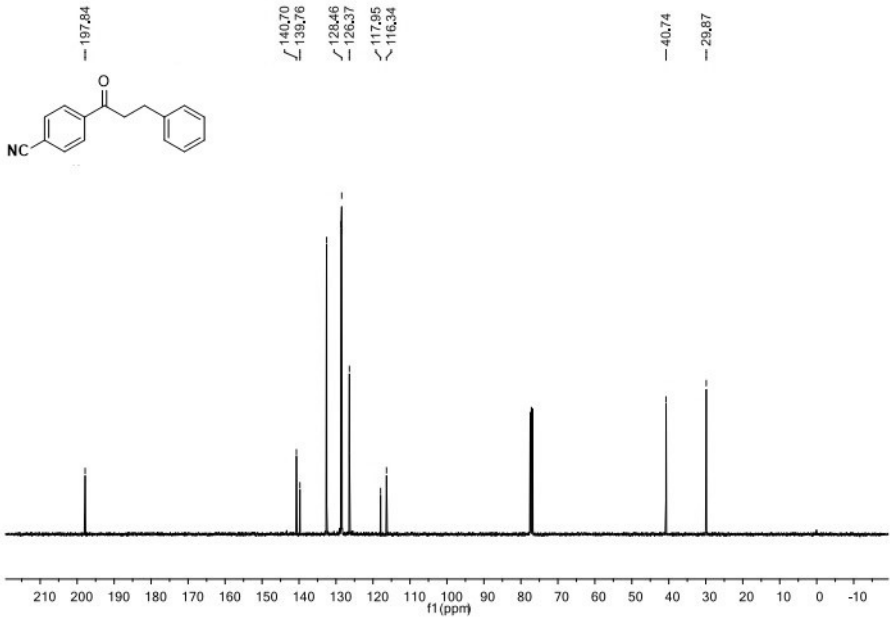

198.15
141.04
135.58
131.92
129.57
128.58
128.41
128.23
126.24
40.42
30.06

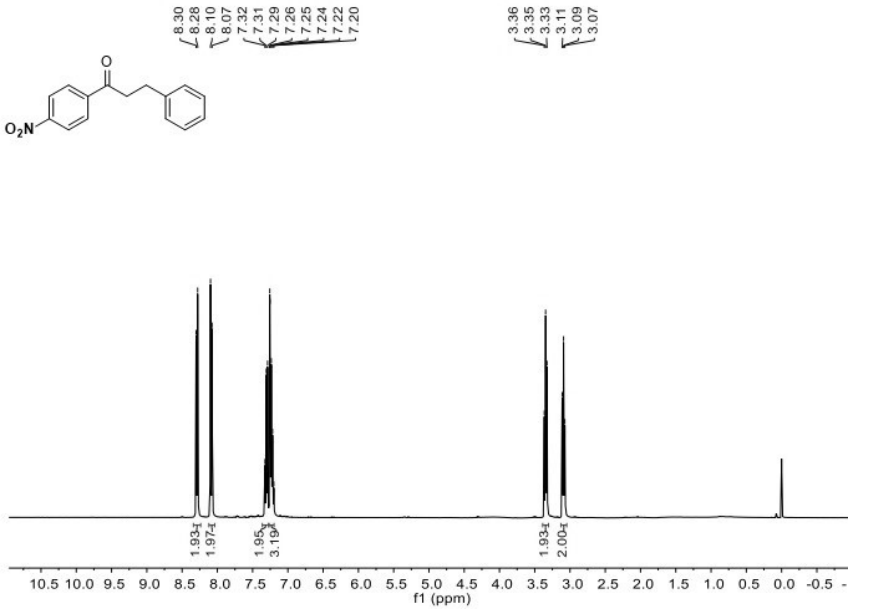

O
Br

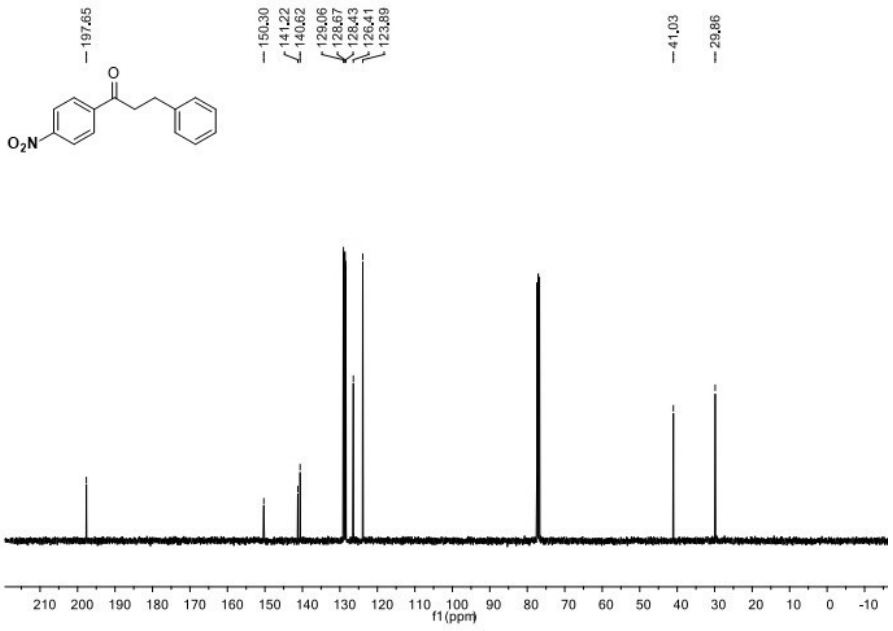

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

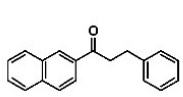

7.82
7.82
7.81
7.80
7.67
7.66
7.65
7.65
7.31
7.30
7.28
7.26
7.24
7.23
7.21
7.20
3.27
3.25
3.23
3.07
3.05
3.04
O
I
1.95
1.96
5.28
2.00
2.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
198.46
141.03
137.93
136.11
129.45
128.57
128.40
126.23
100.98
40.35
30.04
O
I
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

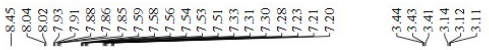

8.02
8.00
7.74
7.72
7.31
7.29
7.28
7.24
7.22
7.21
7.19
3.32
3.31
3.29
3.08
3.07
3.05
O
NC
2.06
2.00
2.20
3.00
2.00
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

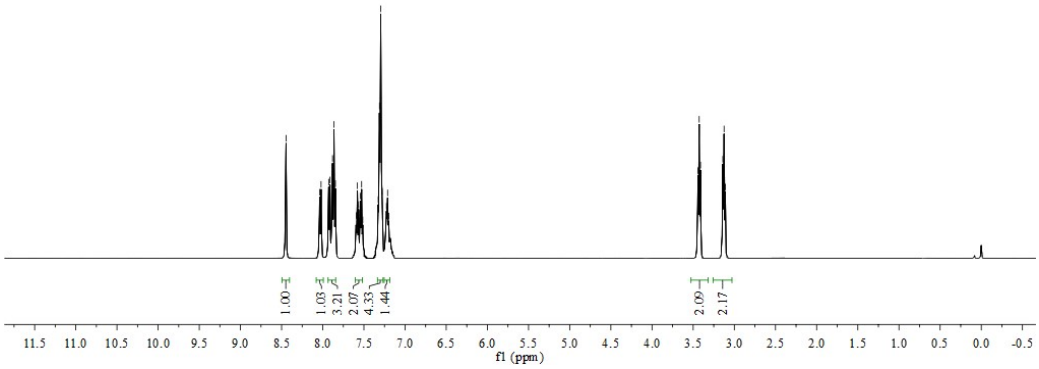

197.84
140.70
139.76
128.46
126.37
117.95
116.34
40.74
29.87
O
NC
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

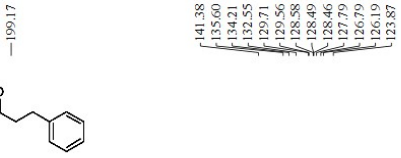

8.30
8.28
8.10
8.07
7.32
7.31
7.29
7.26
7.25
7.24
7.22
7.20
3.36
3.35
3.33
3.11
3.09
3.07
O
O2N
1.93
1.97
1.95
3.19
1.93
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


197.65
150.30
141.22
140.62
129.06
128.67
128.43
126.41
123.89
41.03
29.86
O
O2N
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)




8.45
8.04
8.02
7.93
7.91
7.88
7.86
7.85
7.59
7.58
7.56
7.54
7.53
7.51
7.33
7.31
7.30
7.28
7.23
7.21
7.20
3.44
3.43
3.41
3.14
3.12
3.11


1.00
1.03
3.21
2.07
4.33
1.44
2.09
2.17
11.5 11.0 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 0.0 -0.5
f1 (ppm)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141.38
135.60
134.21
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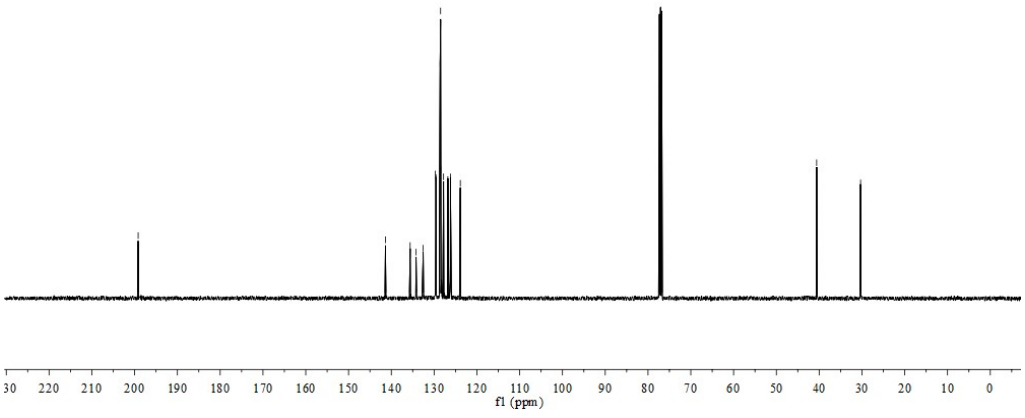
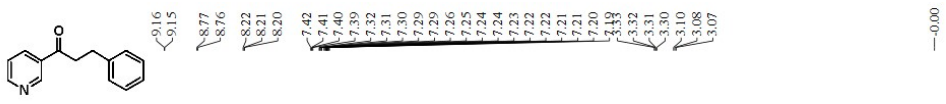
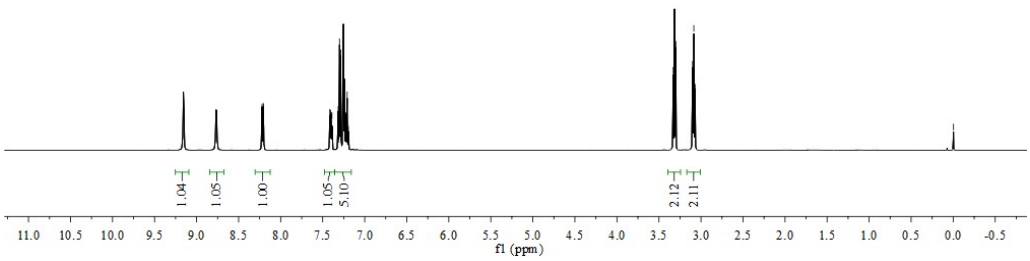
129.56
128.58
128.49
128.46
127.79
126.79
126.19
123.87
40.89
30.32


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


9.16
9.15
8.77
8.76
8.22
8.21
8.20
7.42
7.41
7.40
7.39
7.32
7.31
7.30
7.29
7.29
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.21
7.20
3.33
3.32
3.31
3.30
3.10
3.08
3.07
0.00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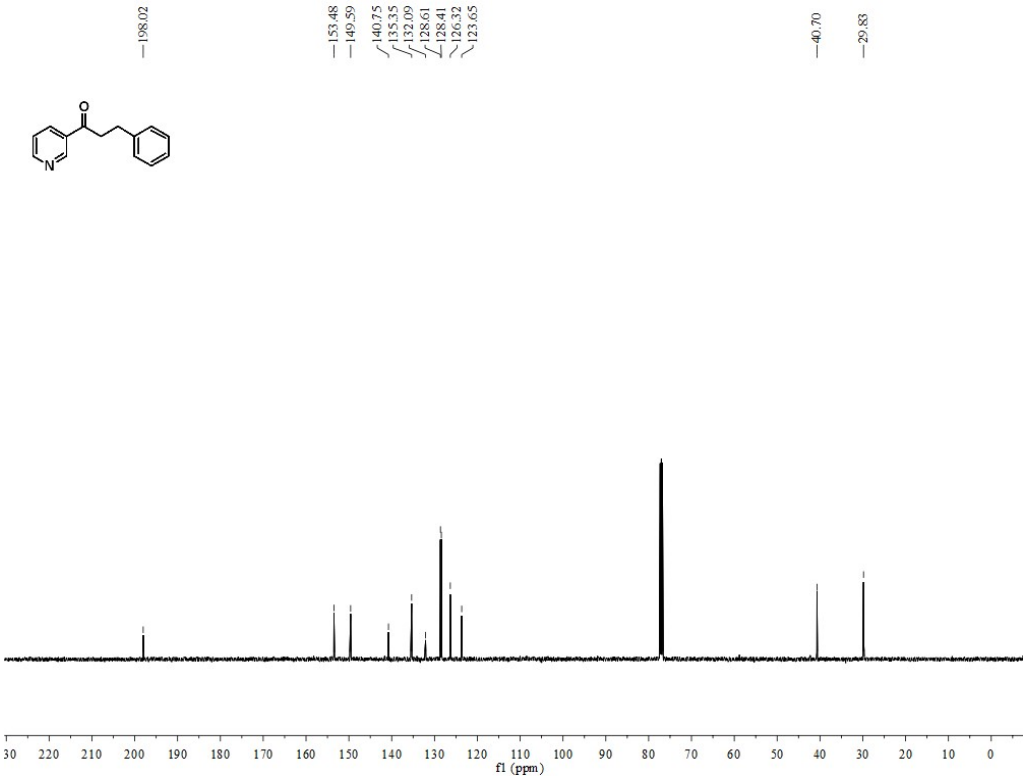
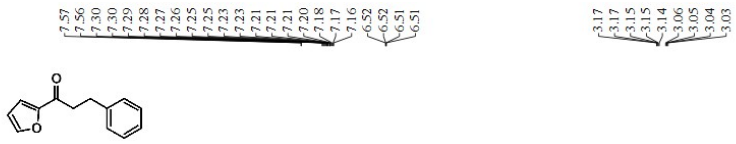
1.05
1.00
1.05
5.10
2.12
2.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


198.02
153.48
149.59
140.75
135.35
132.09
128.61
128.41
126.32
123.65
40.70
29.83
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.56
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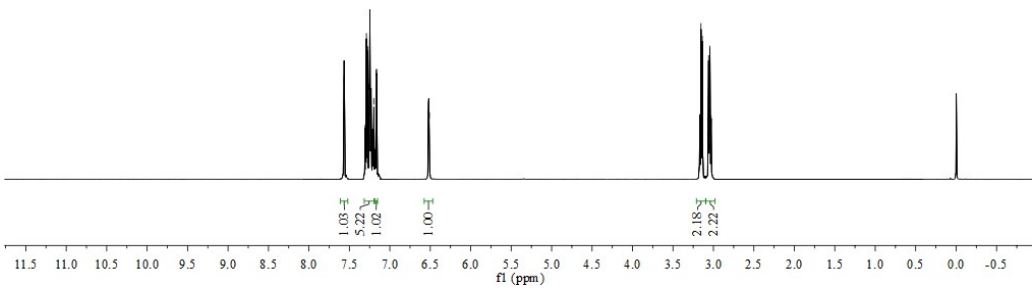
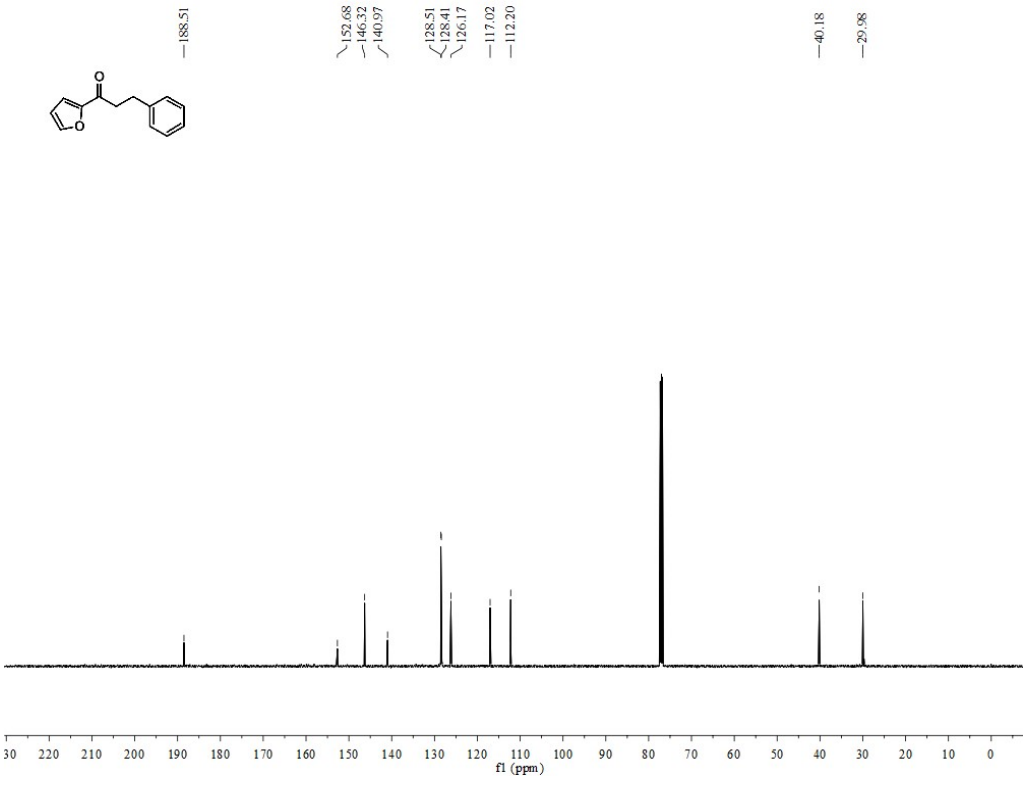
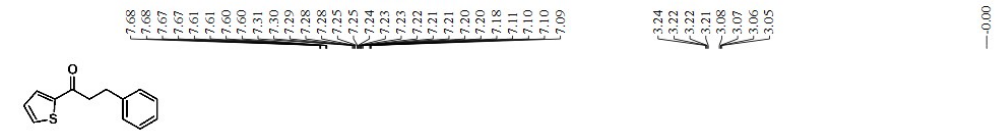
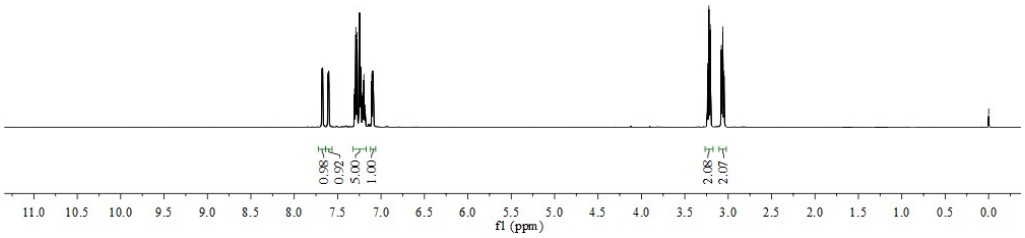
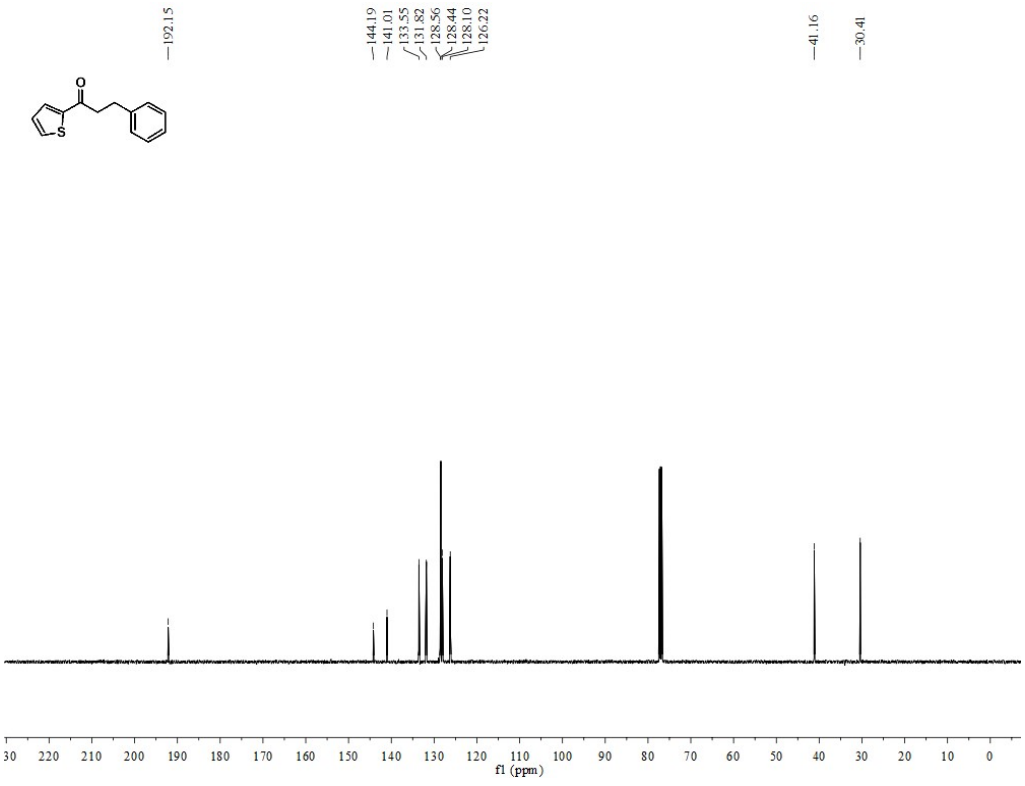
7.28
7.27
7.26
7.25
7.25
7.23
7.23
7.21
7.21
7.21
7.20
7.18
7.17
7.16
6.52
6.51
6.51
3.17
3.17
3.15
3.15
3.14
3.06
3.05
3.04
3.03

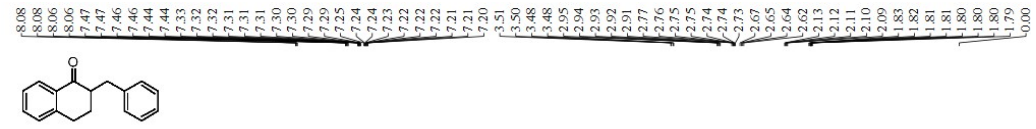

1.03
5.22
1.02
1.00
2.18
2.22
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

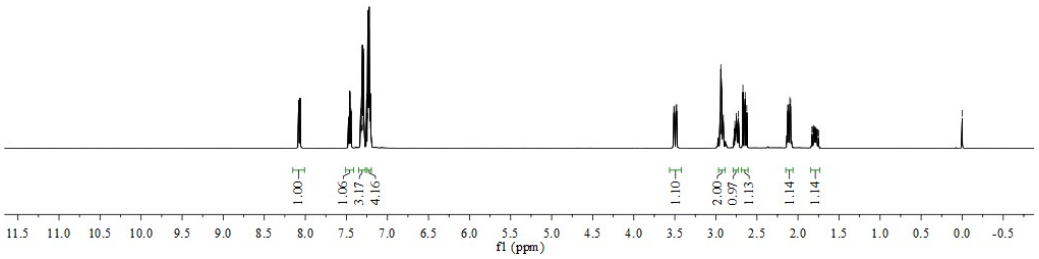

188.51
152.68
146.32
140.97
128.51
128.41
126.17
117.02
112.20
40.18
29.98
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

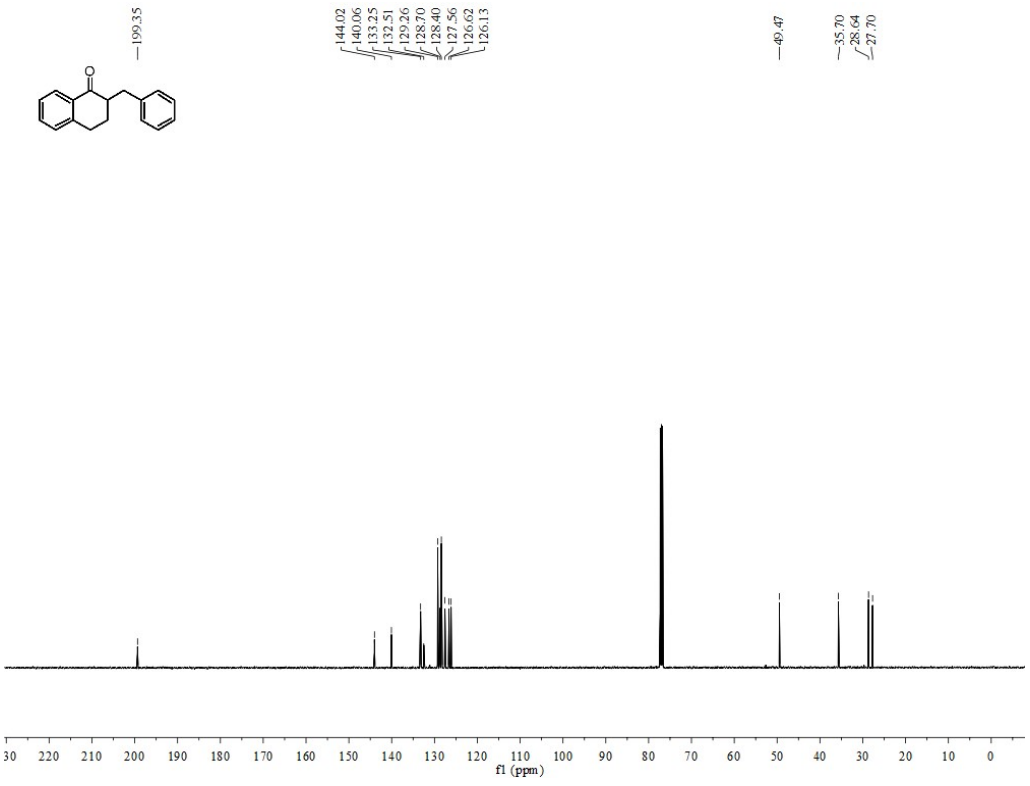

7.68
7.68
7.67
7.67
7.61
7.61
7.60
7.60
7.31
7.30
7.29
7.28
7.28
7.25
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.20
7.20
7.18
7.11
7.10
7.10
7.09
3.24
3.22
3.22
3.21
3.08
3.07
3.06
3.05
0.00

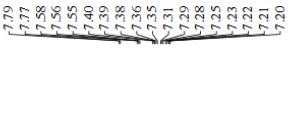

0.98
0.92
5.00
1.00
2.08
2.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

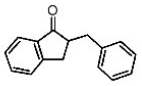

192.15
144.19
141.01
133.55
131.82
128.56
128.44
128.10
126.22
41.16
30.41
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

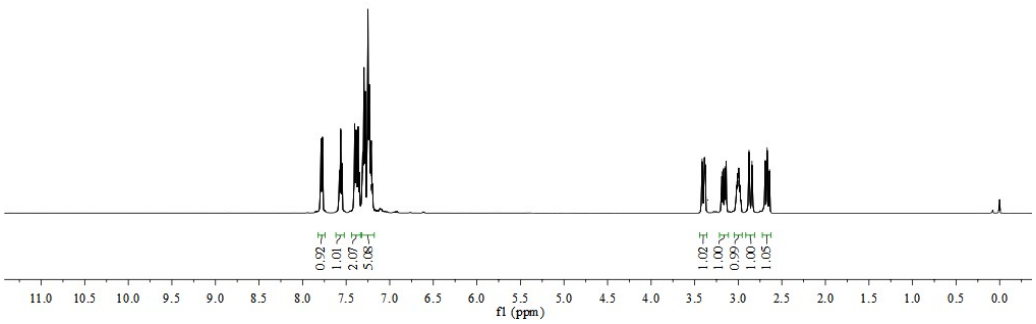

8.08
8.08
8.06
8.06
7.47
7.47
7.46
7.46
7.44
7.44
7.33
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.21
7.20
3.51
3.50
3.48
2.95
2.94
2.93
2.92
2.91
2.77
2.76
2.75
2.75
2.74
2.74
2.73
2.67
2.65
2.64
2.62
2.13
2.12
2.11
2.10
2.09
1.83
1.82
1.81
1.81
1.80
1.80
1.80
1.79
0.00

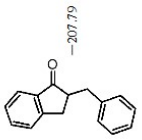

1.00
1.06
3.17
4.16
1.10
2.00
0.97
1.13
1.14
1.14
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


199.35
144.02
140.06
133.25
132.51
129.26
128.70
128.40
127.56
126.62
126.13
49.47
35.70
28.64
27.70
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

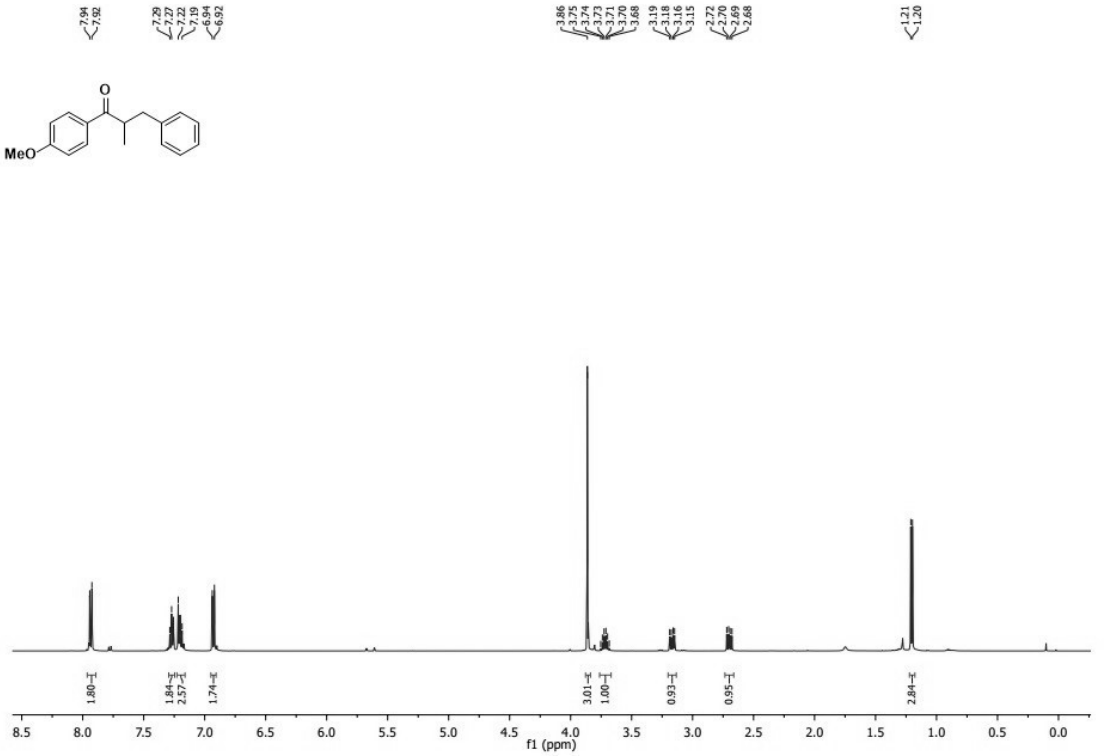


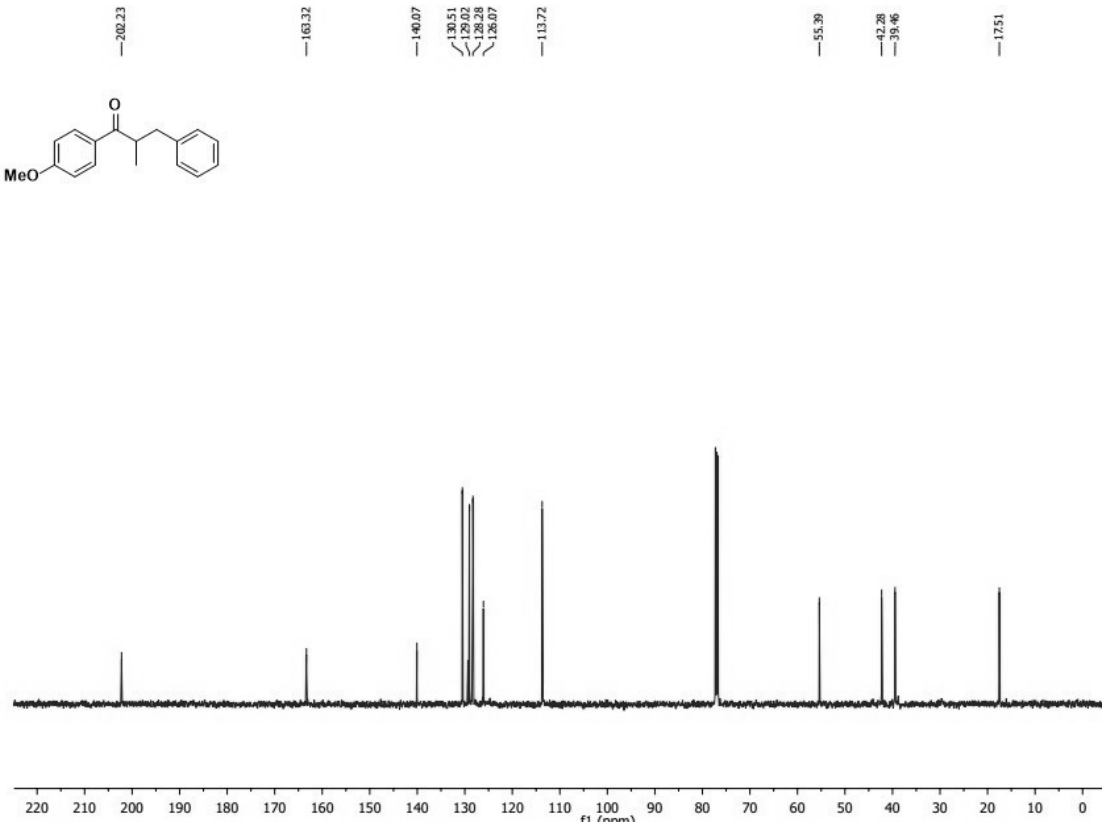


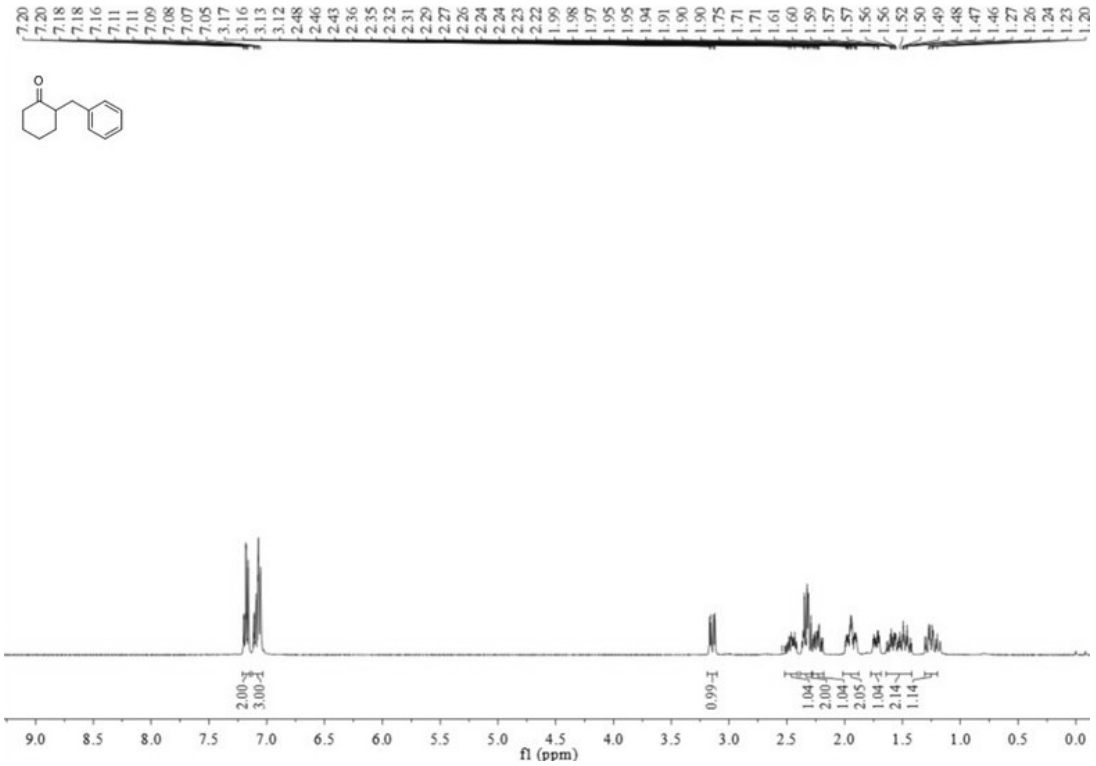

0.92
1.01
2.07
5.08
1.02
1.00
0.99
1.00
1.05
f1 (ppm)

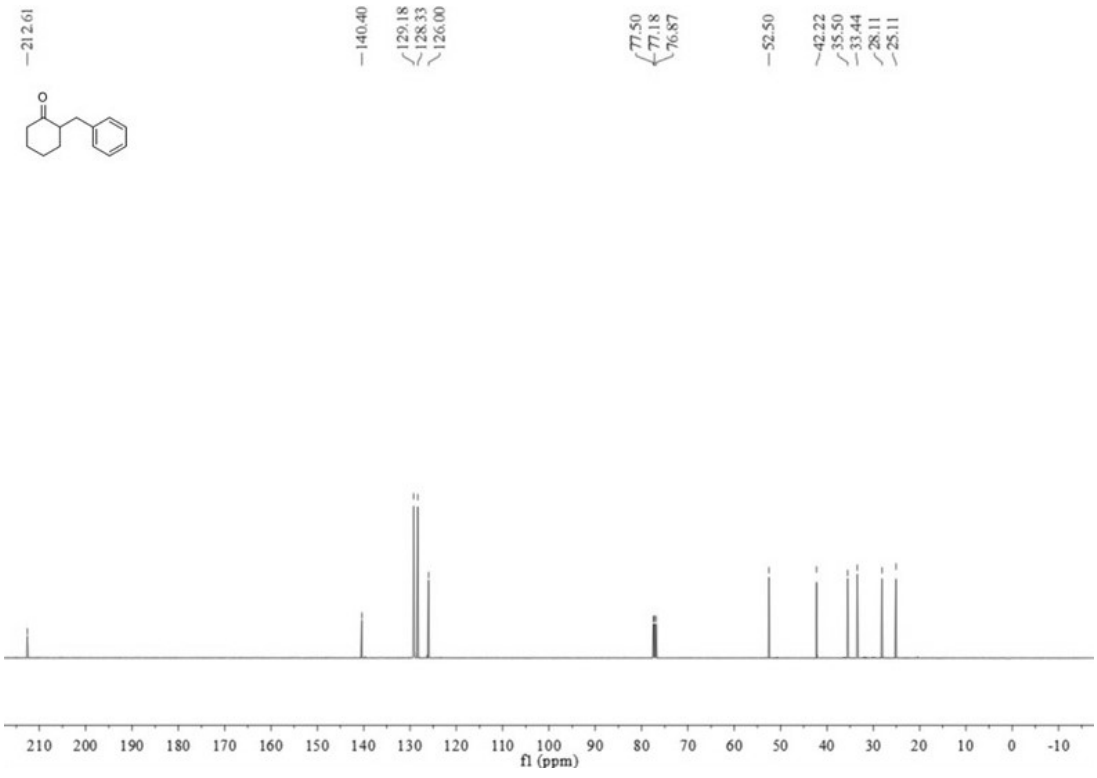


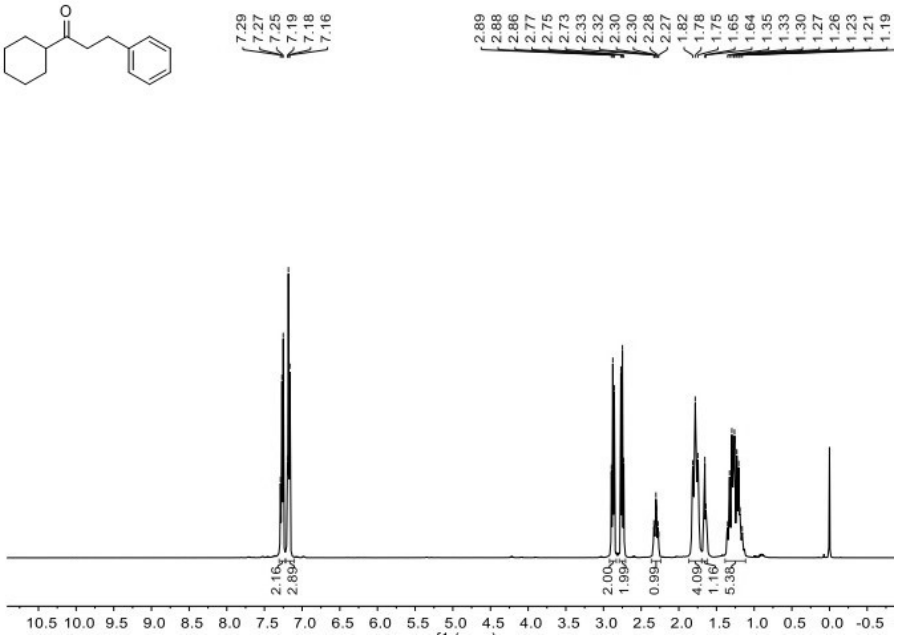
207.79
153.63
139.66
136.58
134.82
128.92
128.54
127.44
126.60
126.36
124.04
48.96
37.02
32.22
f1 (ppm)

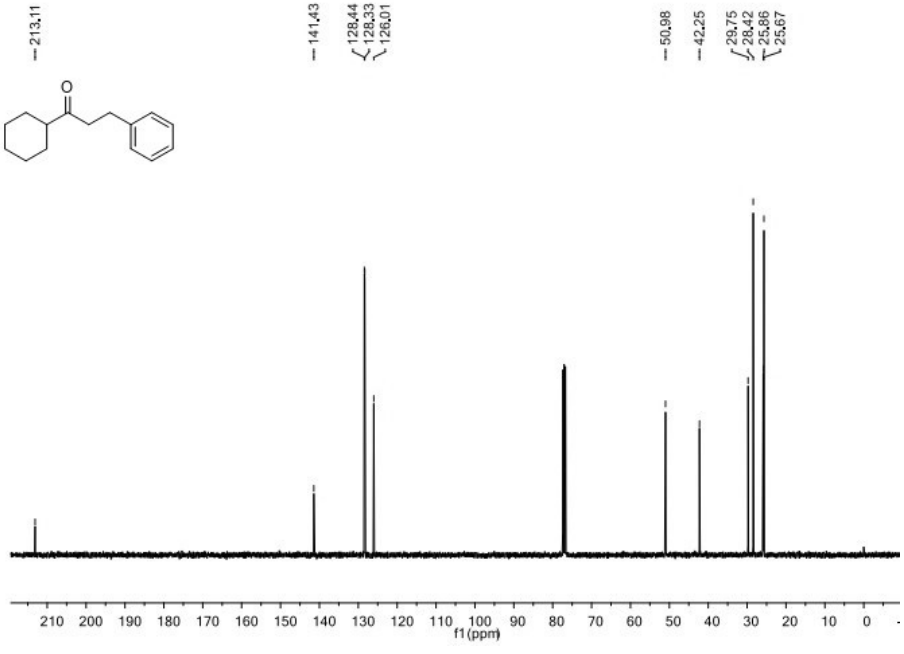

7.94
7.92
7.29
7.27
7.22
7.19
6.94
6.92
3.86
3.75
3.74
3.73
3.71
3.70
3.68
3.19
3.18
3.16
3.15
2.72
2.70
2.69
2.68
1.21
1.20
O
MeO
1.80
1.84
2.57
1.74
3.01
1.00
0.93
0.95
2.84
f1 (ppm)

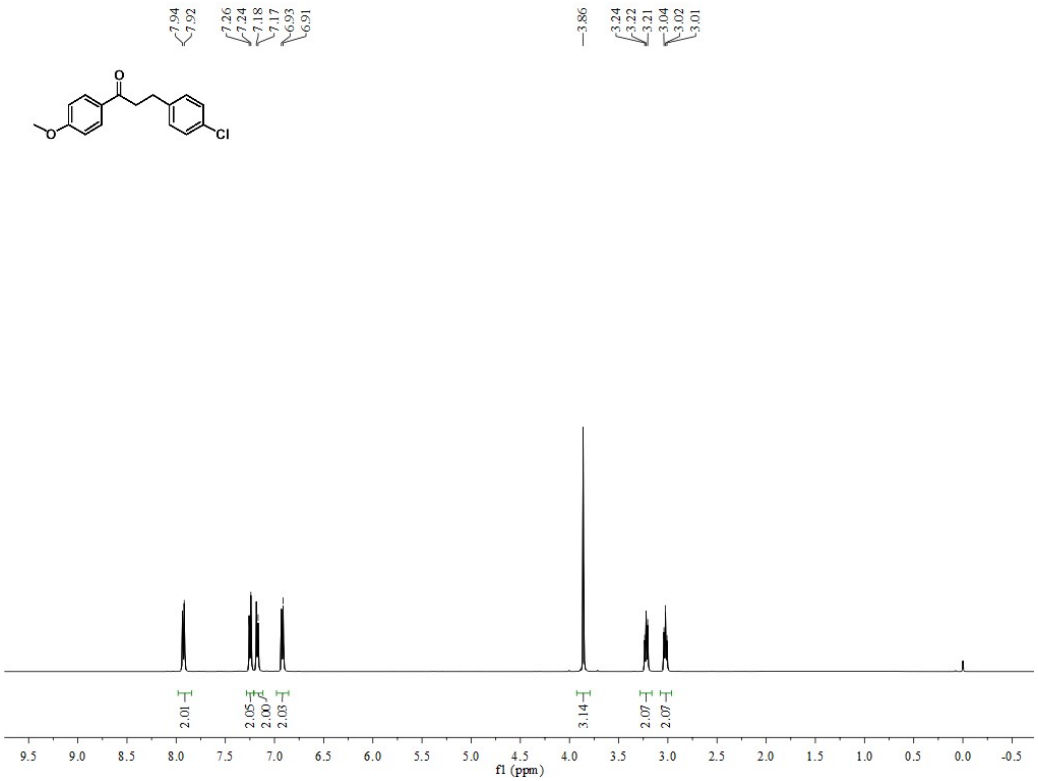

202.23
163.32
140.07
130.51
129.02
128.28
126.07
113.72
55.39
42.28
39.46
17.51
O
MeO
f1 (ppm)

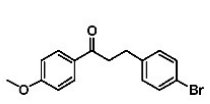

7.20
7.20
7.18
7.18
7.16
7.11
7.11
7.09
7.08
7.07
7.05
3.17
3.16
3.13
3.12
2.48
2.46
2.43
2.36
2.35
2.32
2.31
2.29
2.27
2.26
2.24
2.24
2.23
2.22
1.99
1.98
1.97
1.95
1.95
1.94
1.91
1.90
1.90
1.75
1.71
1.71
1.61
1.60
1.59
1.57
1.57
1.56
1.56
1.52
1.50
1.49
1.48
1.47
1.46
1.27
1.26
1.24
1.23
1.20
2.00
3.00
0.99
1.04
2.00
1.04
2.05
1.04
2.14
1.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


212.61
140.40
129.18
128.33
126.00
77.50
77.18
76.87
52.50
42.22
35.50
33.44
28.11
25.11
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)

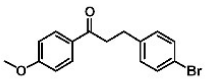

7.29
7.27
7.25
7.19
7.18
7.16
2.89
2.88
2.86
2.77
2.75
2.73
2.33
2.32
2.30
2.30
2.28
2.27
1.82
1.78
1.75
1.65
1.64
1.35
1.33
1.30
1.27
1.26
1.23
1.21
1.19
2.16
2.89
2.00
1.99
0.99
4.09
1.16
5.38
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


213,11
141,43
128,44
128,33
126,01
50,98
42,25
29,75
28,42
25,86
25,67
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

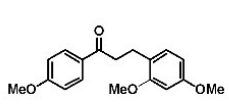

7.94
7.92
7.26
7.24
7.18
7.17
6.93
6.91
3.86
3.24
3.22
3.21
3.04
3.02
3.01
O
O
Cl
2.01
2.05
2.00
2.03
3.14
2.07
2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
197.39
163.53
139.92
131.81
130.28
129.88
129.82
128.56
113.77
55.47
39.79
29.59
O
O
Cl
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
Br

7.93
7.92
7.41
7.39
7.13
7.12
6.93
6.91
3.86
3.24
3.22
3.21
3.03
3.01
3.00
2.00
1.92
1.99
2.01
3.12
2.07
2.07
11.5 11.0 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 0.0
f1 (ppm)


O
O
Br

197.35
163.54
140.44
131.52
130.27
130.23
129.88
119.83
113.77
55.47
39.71
29.64
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MeO
MeO
OMe

7.96
7.94
7.09
7.08
6.92
6.90
6.45
6.45
6.42
6.41
3.85
3.80
3.78
3.18
3.17
3.16
3.16
3.15
2.97
2.96
2.96
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1.01
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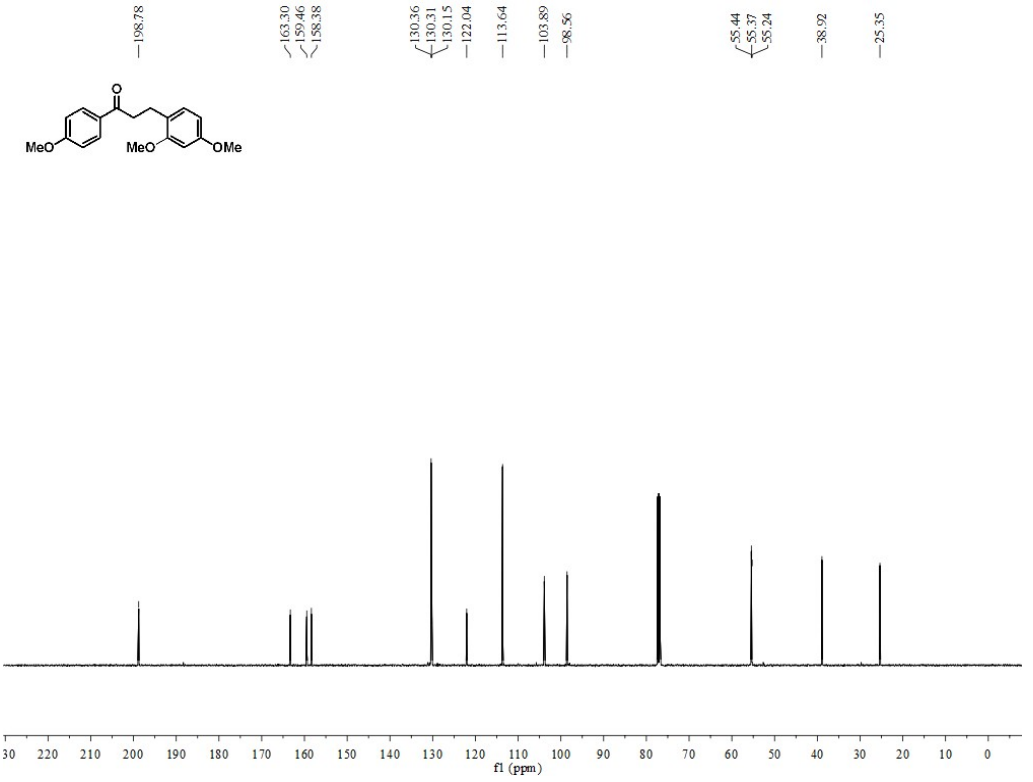
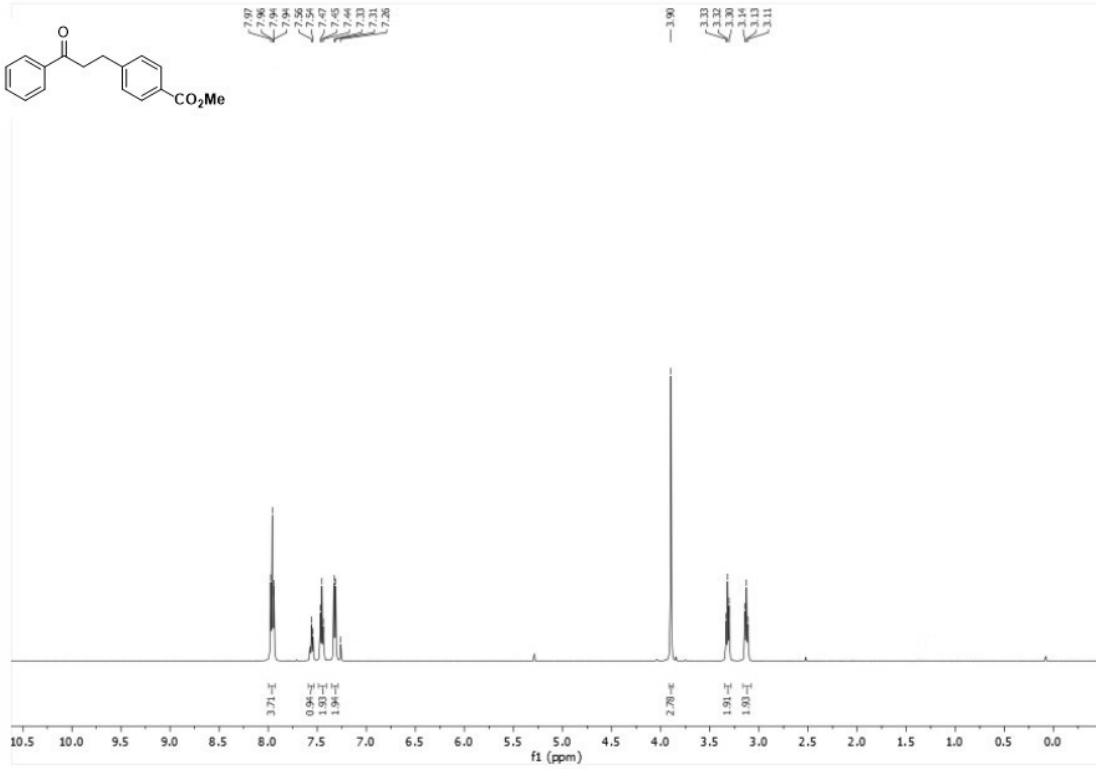
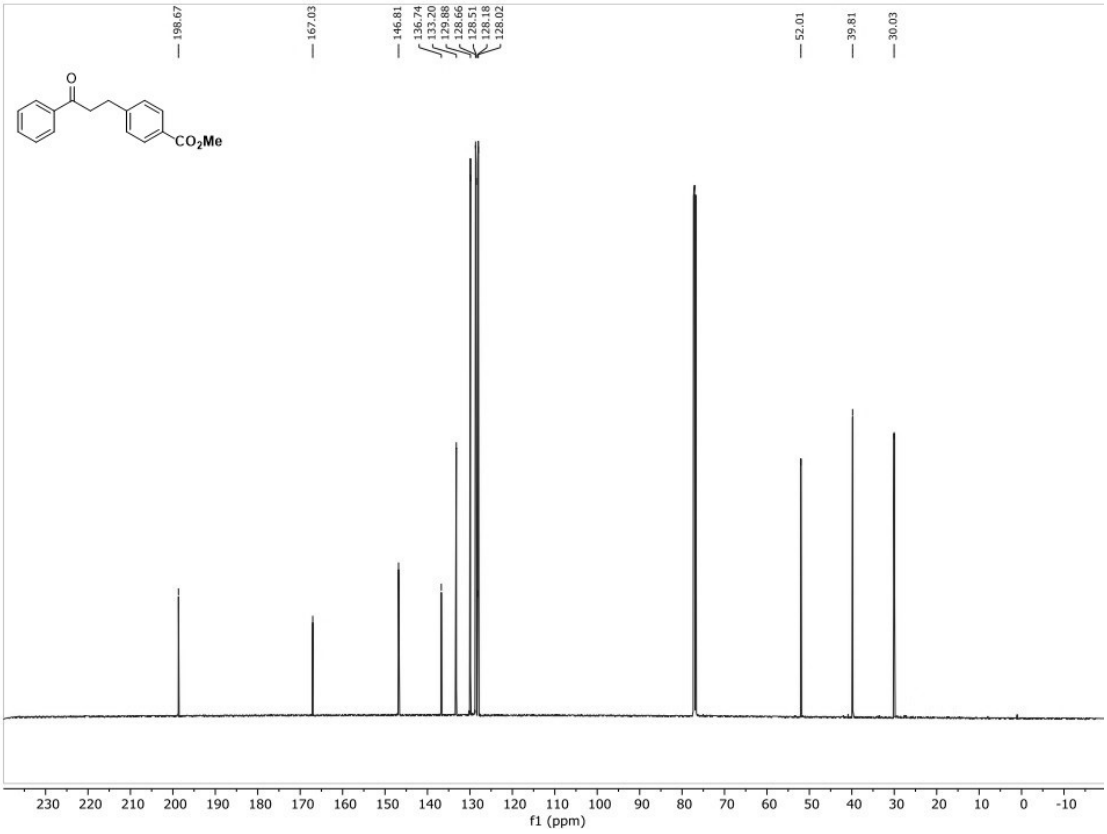
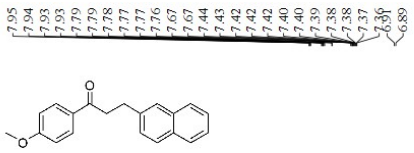
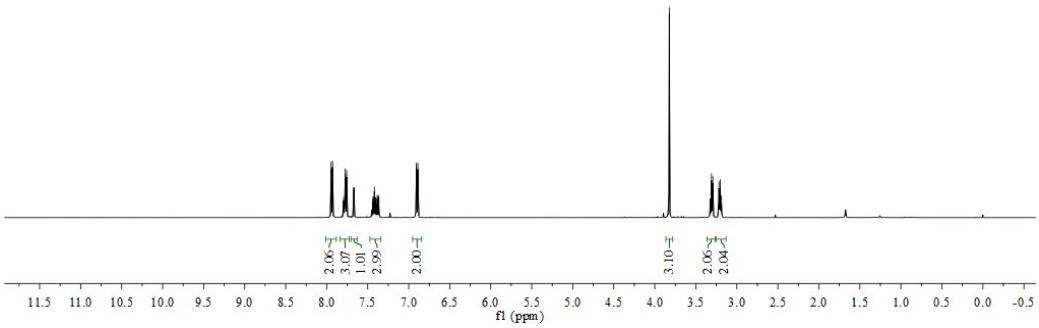
2.02
3.15
6.09
2.06
2.07
f1 (ppm)

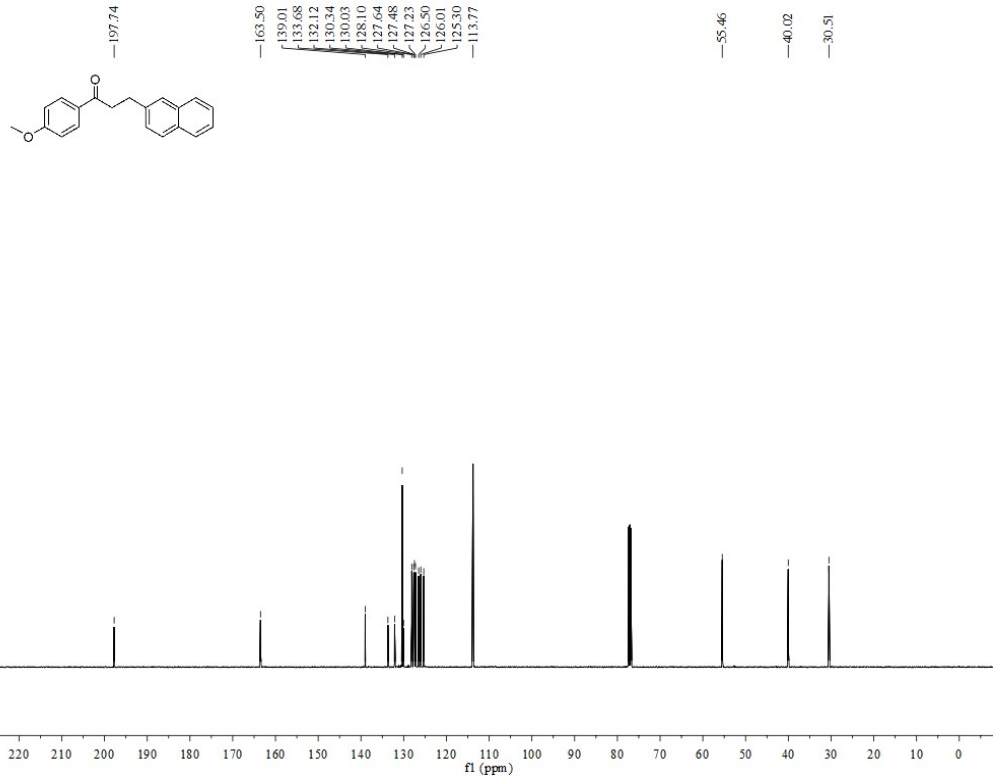

198.78
163.30
159.46
158.38
130.36
130.31
130.15
122.04
113.64
103.89
98.56
55.44
55.37
55.24
38.92
25.35
MeO
MeO
OMe
f1 (ppm)

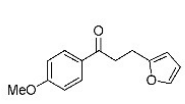

O
CO2Me
7.97
7.96
7.94
7.94
7.56
7.54
7.47
7.45
7.44
7.33
7.31
7.26
3.90
3.33
3.32
3.30
3.14
3.13
3.11
3.71
0.94
1.93
1.94
2.78
1.91
1.93
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


198.67
167.03
146.81
136.74
133.20
129.88
128.66
128.51
128.18
128.02
52.01
39.81
30.03
O
CO2Me
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)

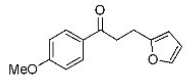

7.95
7.94
7.93
7.93
7.79
7.79
7.78
7.77
7.77
7.76
7.67
7.67
7.44
7.43
7.42
7.42
7.42
7.40
7.40
7.39
7.38
7.38
7.37
7.36
6.91
6.89
3.82
3.32
3.32
3.31
3.31
3.29
3.22
3.21
3.20
3.19


2.06
3.07
1.01
2.99
2.00
3.10
2.06
2.04
11.5 11.0 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 0.0 -0.5
f1 (ppm)

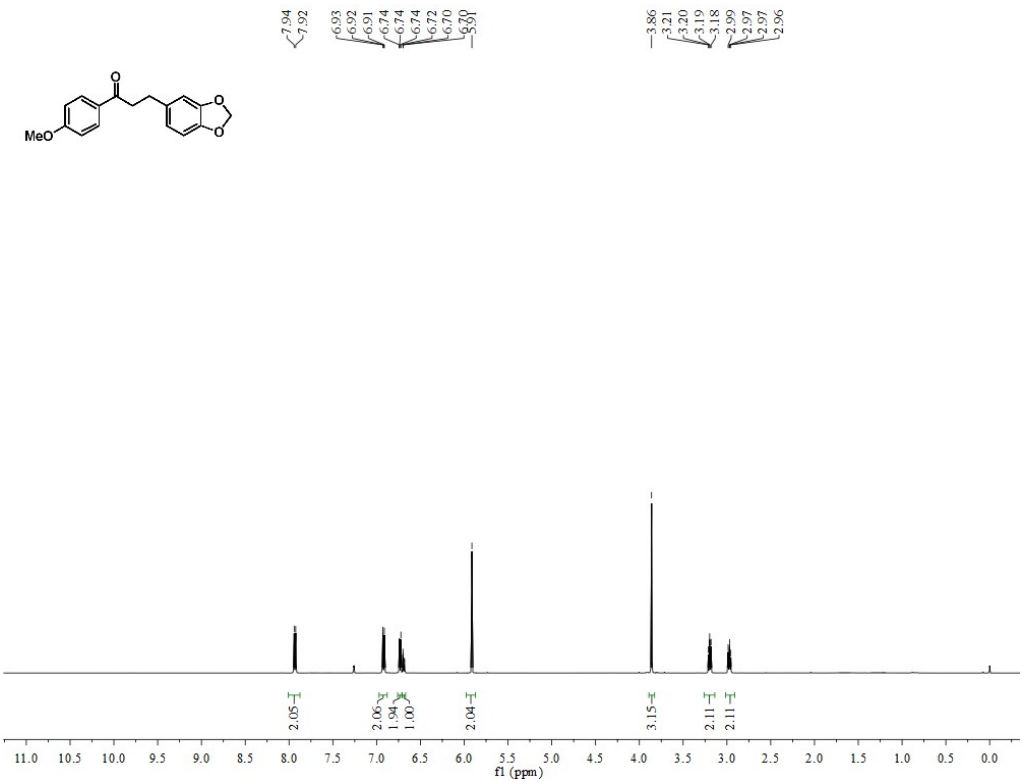

197.74
163.50
139.01
133.68
132.12
130.34
130.03
128.10
127.64
127.48
127.23
126.50
126.01
125.30
113.77
55.46
40.02
30.51
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

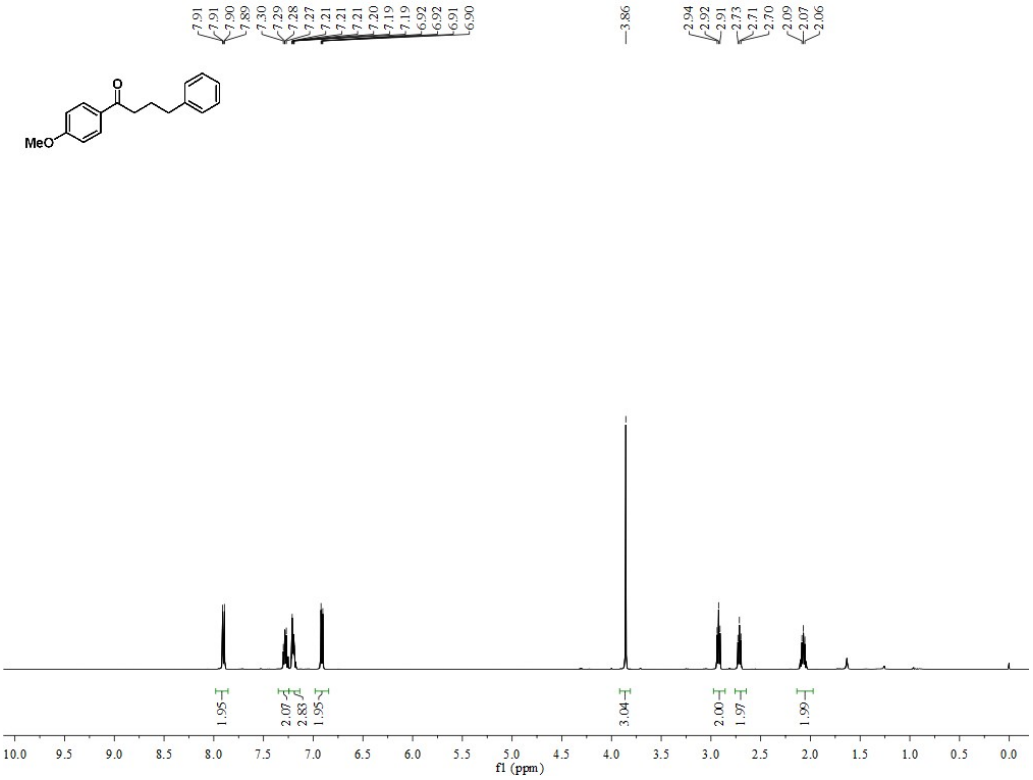

MeO

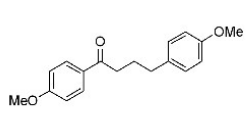
7.96
7.95
7.31
6.94
6.92
6.28
6.28
6.05
3.86
3.29
3.28
3.26
3.09
3.08
2.15
1.02
2.17
1.00
0.99
3.37
2.18
2.13
f1 (ppm)

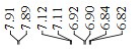

MeO

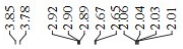
197.24
163.53
154.97
141.06
130.31
129.88
113.76
110.25
105.25
55.48
36.57
22.69
f1 (ppm)

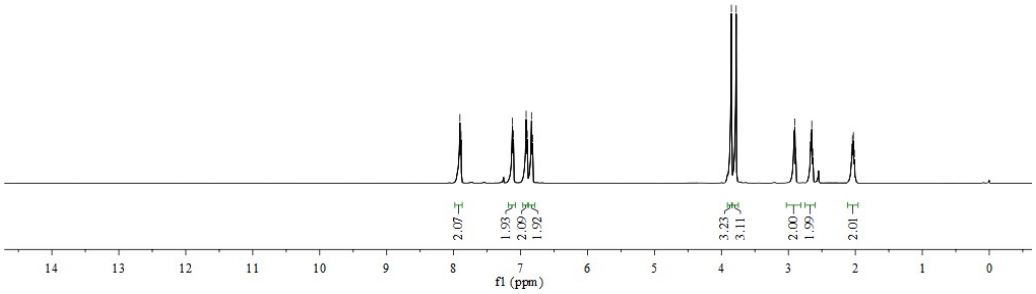

7.94
7.92
6.93
6.92
6.91
6.74
6.74
6.74
6.72
6.70
6.70
5.91
3.86
3.21
3.20
3.19
3.18
2.99
2.97
2.97
2.96
MeO
2.05
2.06
1.94
1.00
2.04
3.15
2.11
2.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
197.77
163.46
147.63
145.80
135.26
130.30
129.97
121.16
113.73
108.93
108.26
100.81
55.47
40.34
30.09
MeO
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

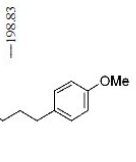

7.91
7.91
7.90
7.89
7.30
7.29
7.28
7.27
7.21
7.21
7.21
7.20
7.19
7.19
6.92
6.91
6.90
3.86
2.94
2.92
2.91
2.73
2.71
2.70
2.09
2.07
2.06
MeO
1.95
2.07
2.83
1.95
3.04
2.00
1.97
1.99
f1 (ppm)
198.73
163.37
141.79
130.29
130.14
128.53
128.38
125.92
113.68
55.46
37.38
35.28
25.95
MeO
f1 (ppm)


OMe
MeO

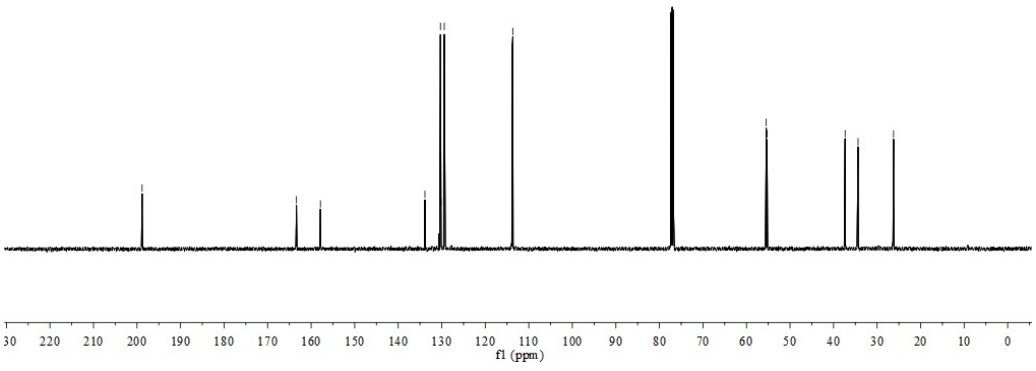

7.91
7.89
7.12
7.11
6.92
6.90
6.84
6.82

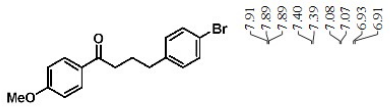

3.85
3.78
2.92
2.90
2.89
2.67
2.65
2.06
2.04
2.03
2.01


2.07
1.93
2.09
1.92
3.23
3.11
2.00
1.99
2.01
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

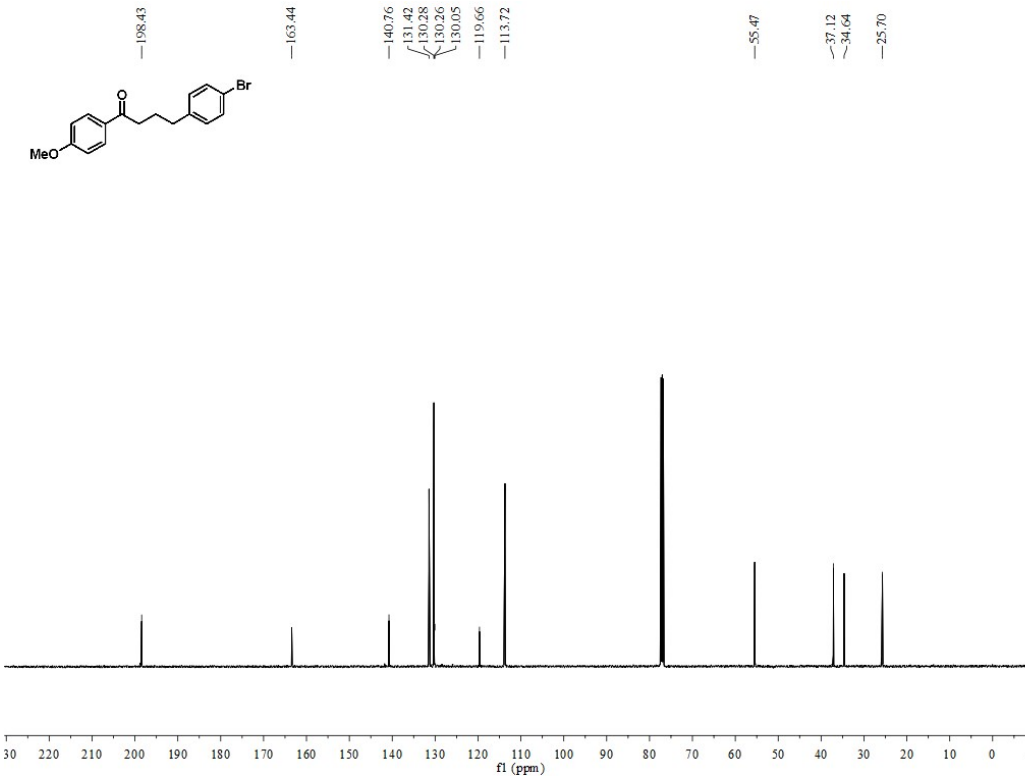

OMe
MeO

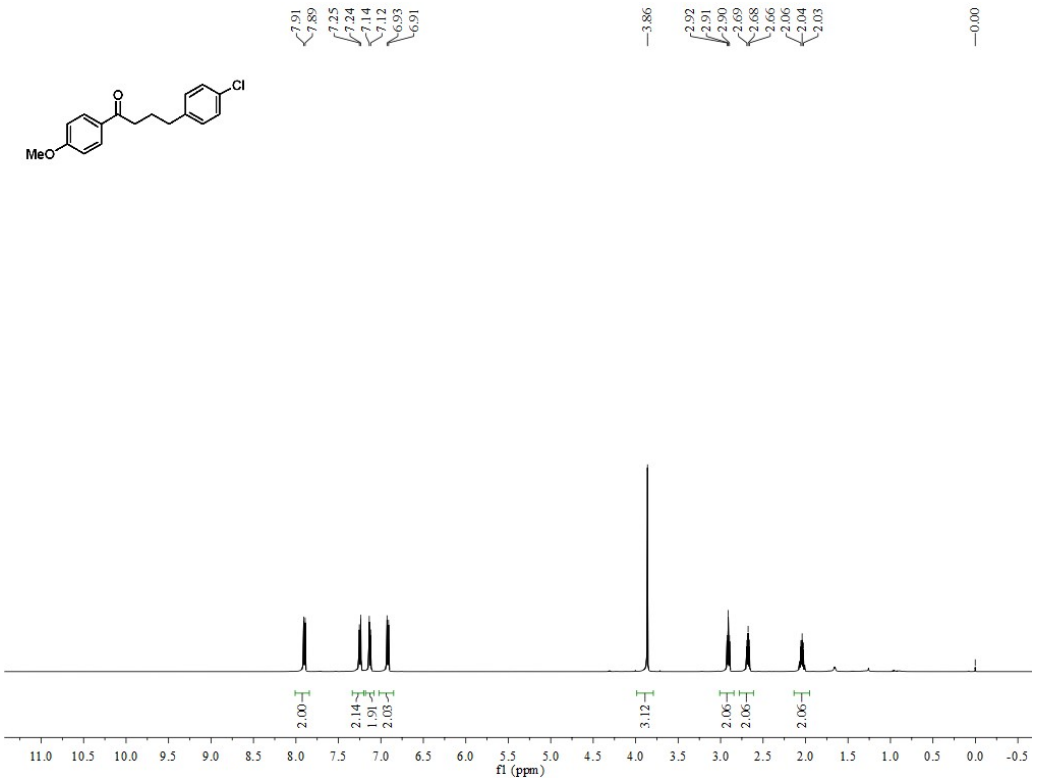

198.83
163.37
157.87
133.86
130.30
130.16
129.42
113.81
113.69
55.46
55.27
37.34
34.37
26.21

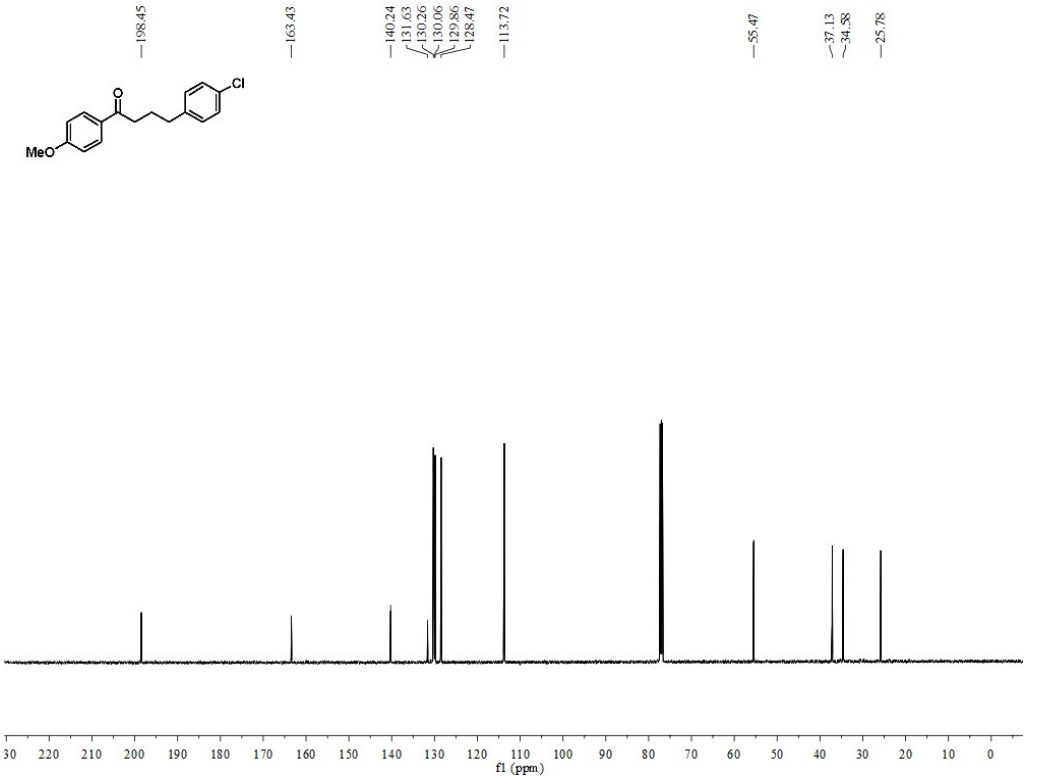

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

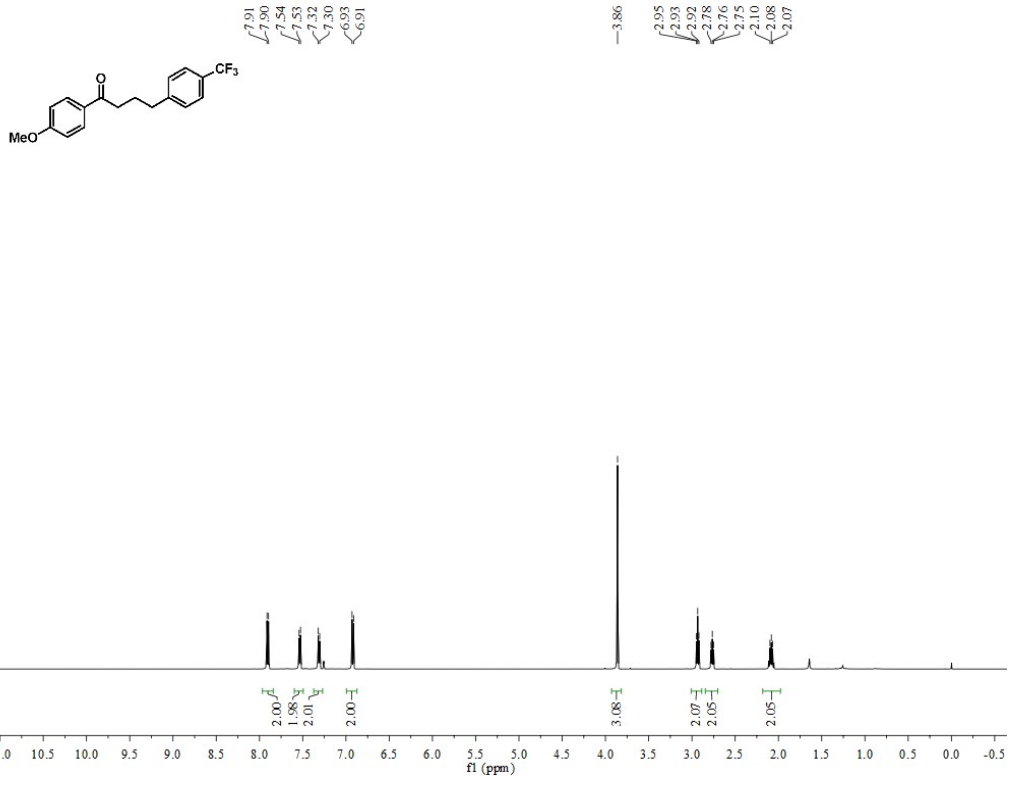

O
Br
MeO

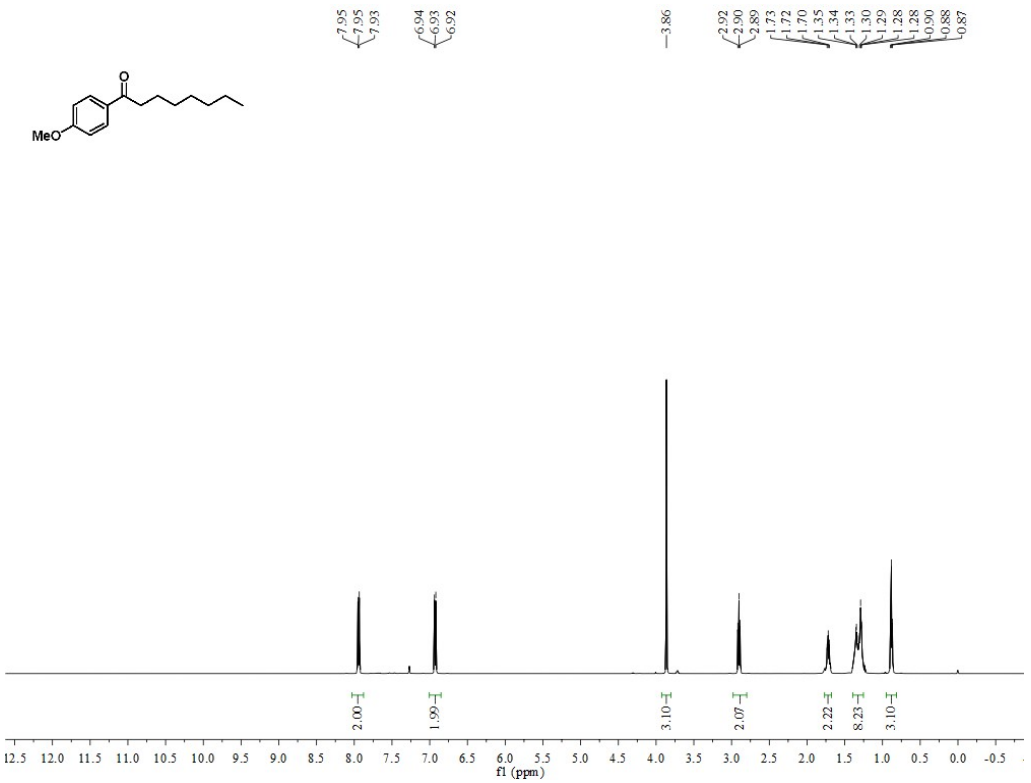
7.91
7.89
7.89
7.40
7.39
7.08
7.07
6.93
6.91
3.86
2.92
2.91
2.89
2.67
2.66
2.64
2.05
2.04
2.02
2.00
1.78
1.84
2.01
3.09
2.05
1.88
2.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

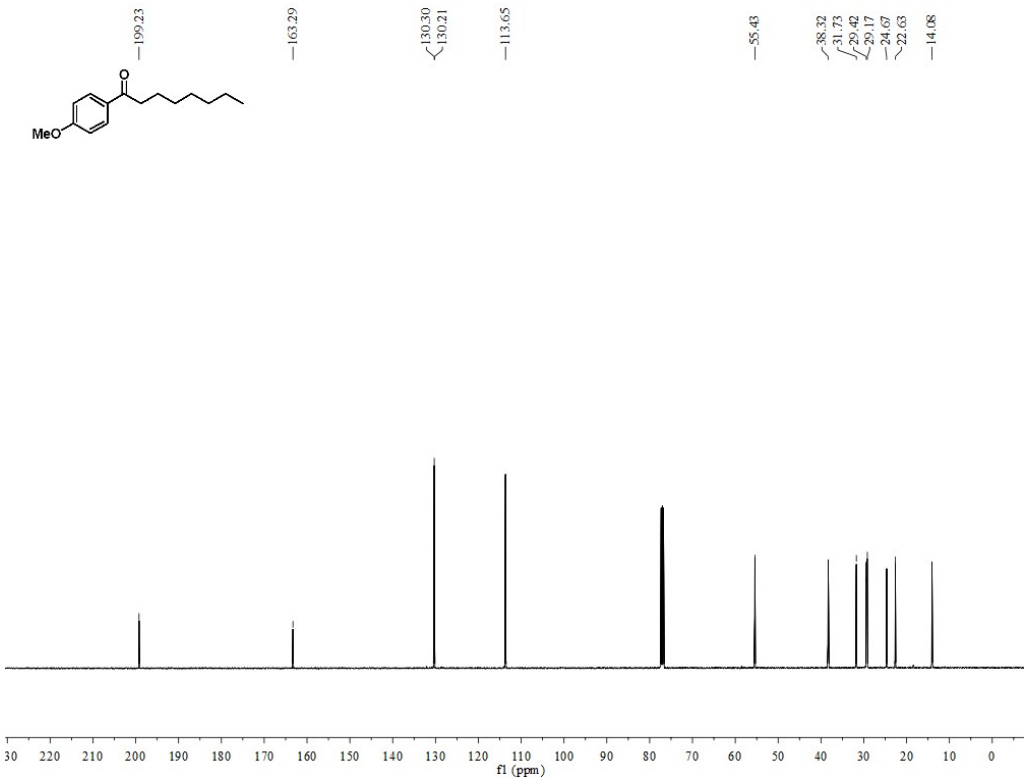

198.43
163.44
140.76
131.42
130.28
130.26
130.05
119.66
113.72
55.47
37.12
34.64
25.70
O
Br
MeO
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

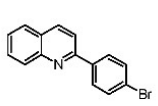

7.91
7.89
7.25
7.24
7.14
7.12
6.93
6.91
3.86
2.92
2.91
2.90
2.69
2.68
2.66
2.06
2.04
2.03
0.00
Cl
O
MeO
2.00
2.14
1.91
2.03
3.12
2.06
2.06
2.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


198.45
163.43
140.24
131.63
130.26
130.06
129.86
128.47
113.72
55.47
37.13
34.58
25.78
Cl
O
MeO
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.91
7.90
7.54
7.53
7.32
7.30
6.93
6.91
3.86
2.95
2.93
2.92
2.78
2.76
2.75
2.10
2.08
2.07
CF3
O
MeO
2.00
1.98
2.01
2.00
3.08
2.07
2.05
2.05
11.0 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 0.0 -0.5
f1 (ppm)
198.27
163.47
145.96
130.25
130.02
128.80
125.35
125.32
125.28
55.46
37.10
35.06
25.55
CF3
O
MeO
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

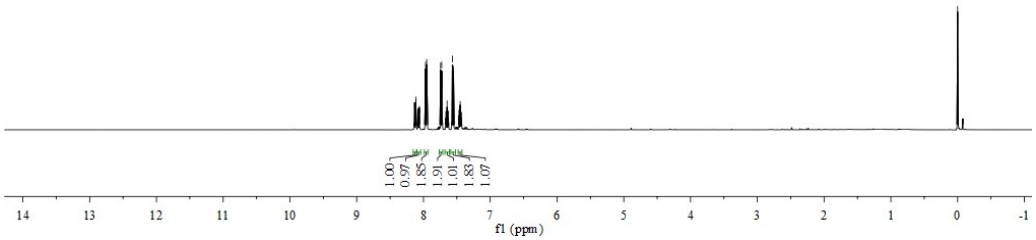

7.95
7.95
7.93
6.94
6.93
6.92
3.86
2.92
2.90
2.89
1.73
1.72
1.70
1.35
1.34
1.33
1.30
1.29
1.28
1.28
0.90
0.88
0.87
MeO
2.00
1.99
3.10
2.07
2.22
8.23
3.10
f1 (ppm)

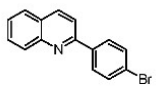

199.23
163.29
130.30
130.21
113.65
55.43
38.32
31.73
29.42
29.17
24.67
22.63
14.08
MeO
f1 (ppm)

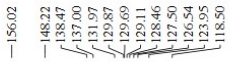

Br

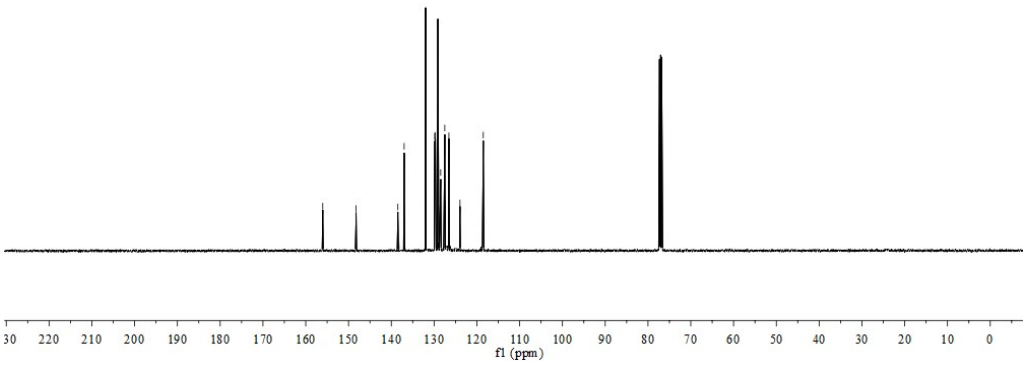

8.13
8.11
8.08
8.06
7.97
7.95
7.74
7.73
7.66
7.65
7.65
7.64
7.63
7.63
7.57
7.55
7.47
7.46
7.45
7.45
7.45
7.44
7.43

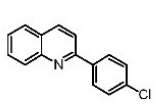
0.00


1.00
0.97
1.85
1.91
1.01
1.83
1.07
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

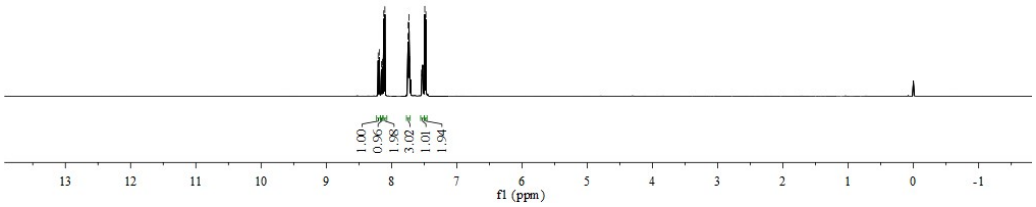

Br

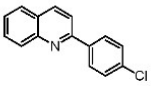

156.02
148.22
138.47
137.00
131.97
129.87
129.69
129.11
128.46
127.50
126.54
123.95
118.50

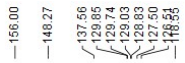

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

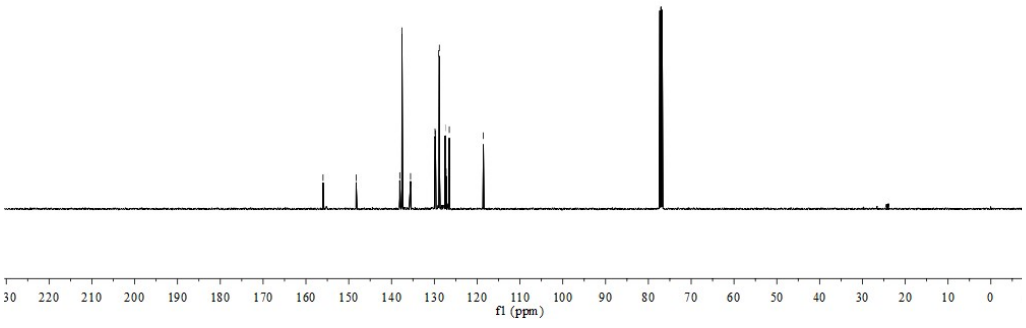

N
Cl

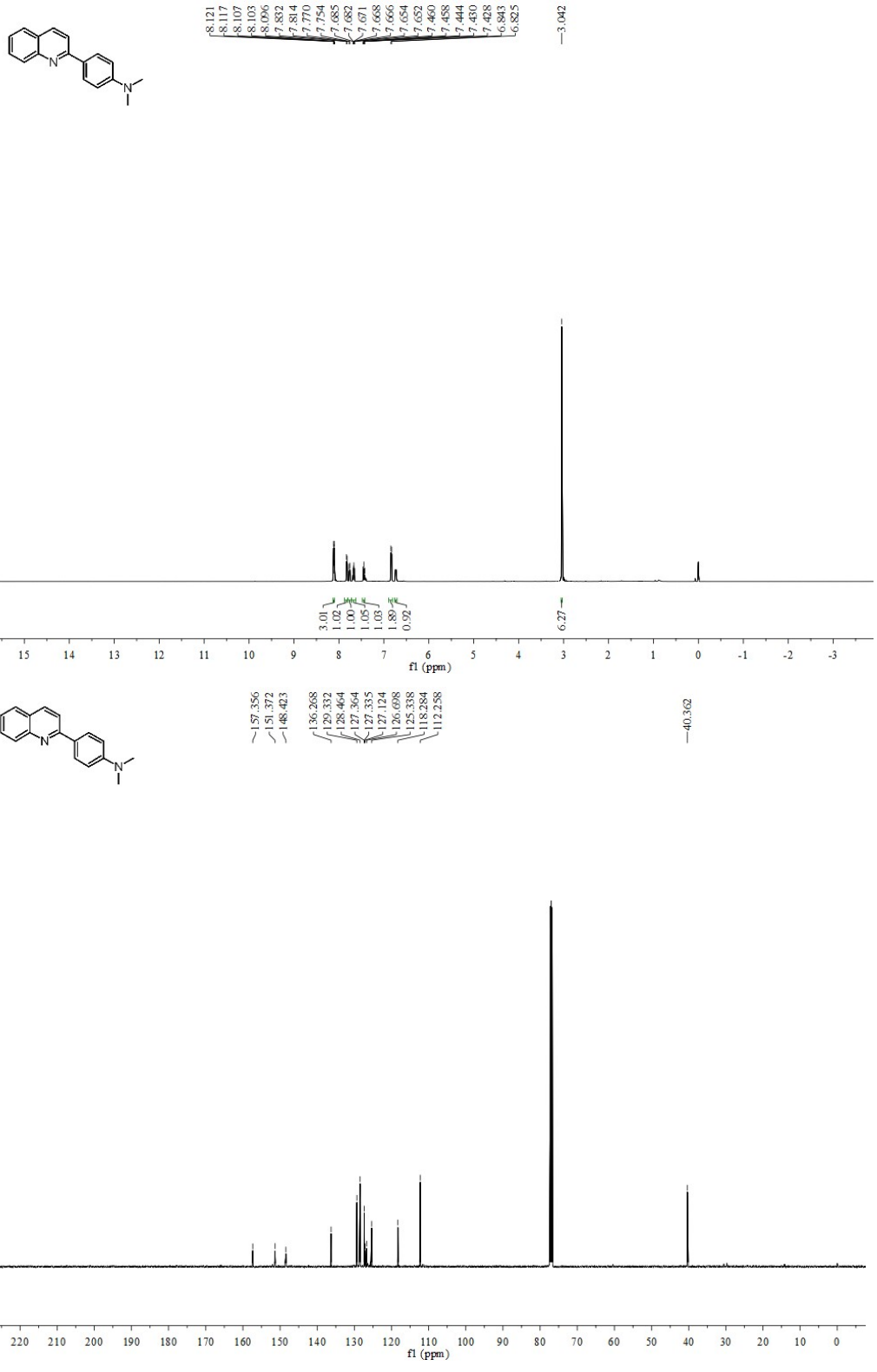

8.205
8.188
8.156
8.139
8.120
8.116
8.106
8.102
7.747
7.745
7.732
7.729
7.726
7.723
7.538
7.536
7.491
7.473

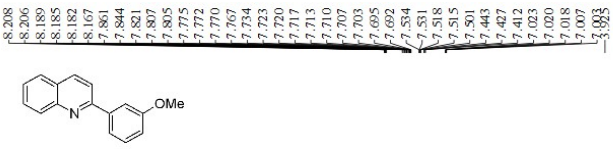

1.00
0.96
1.98
3.02
1.01
1.94
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

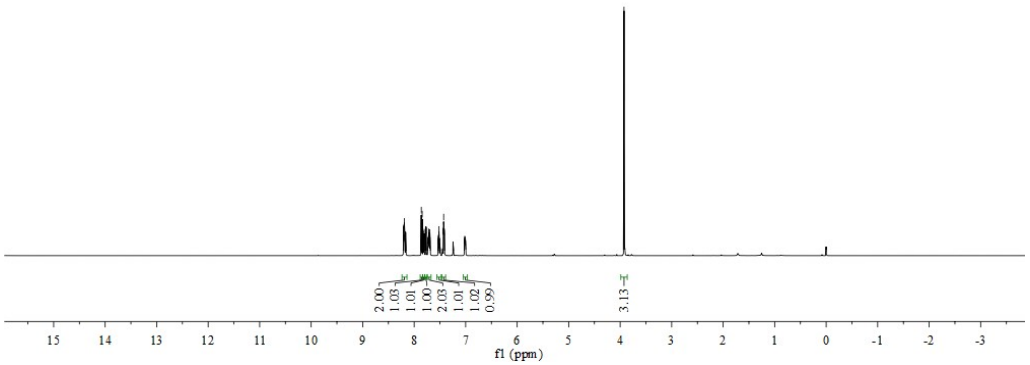

N
Cl

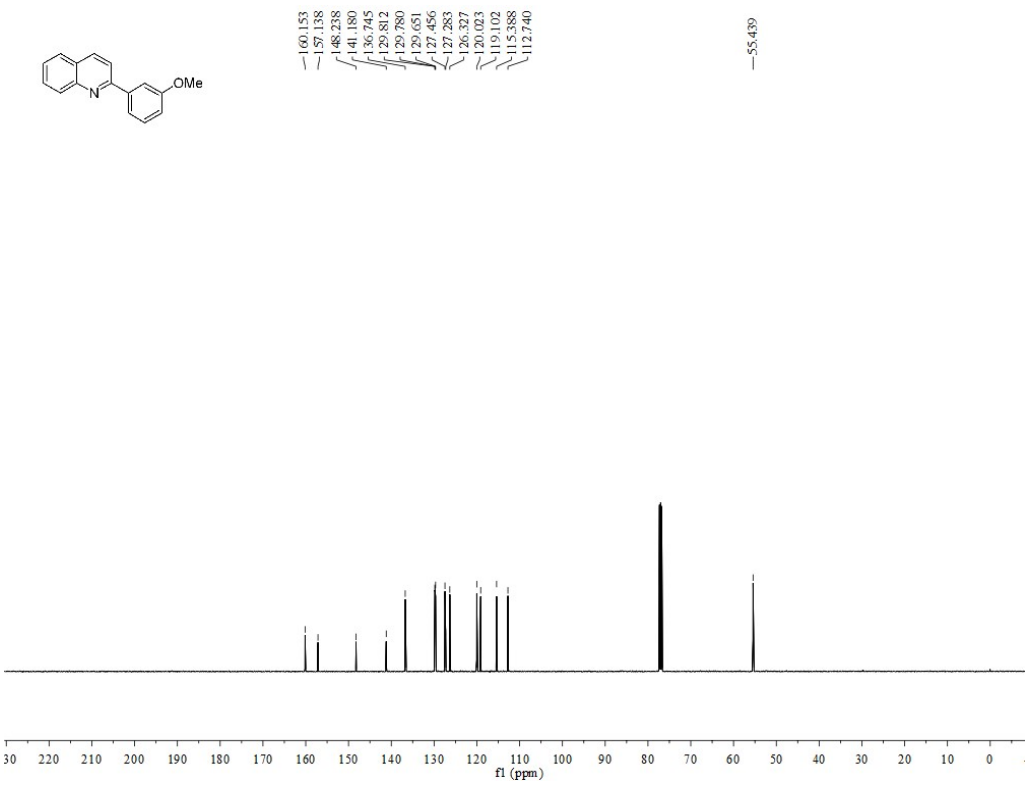

156.00
148.27
137.56
129.85
129.74
129.03
128.83
127.50
126.51
118.55

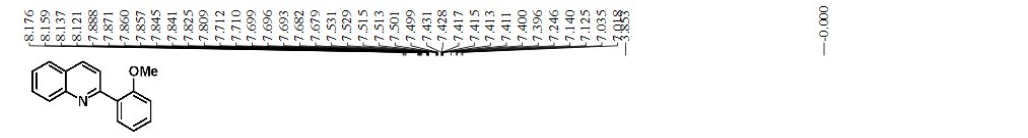

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.121
8.117
8.107
8.103
8.096
7.832
7.814
7.770
7.754
7.685
7.682
7.671
7.668
7.666
7.654
7.652
7.460
7.458
7.444
7.430
7.428
6.843
6.825
3.042
3.01
1.02
1.00
1.05
1.03
1.89
0.92
6.27
f1 (ppm)
157.356
151.372
148.423
136.268
129.332
128.464
127.364
127.335
127.124
126.698
125.338
118.284
112.258
40.362
f1 (ppm)

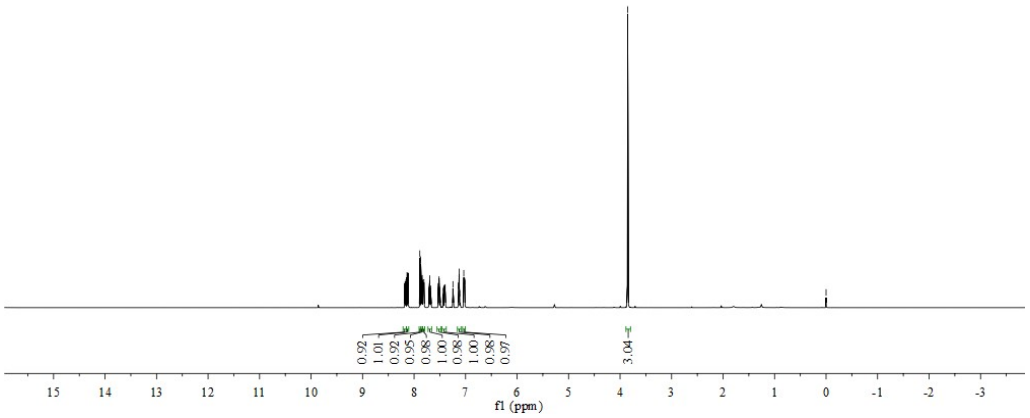

8.208
8.206
8.189
8.185
8.182
8.167
7.861
7.844
7.821
7.807
7.805
7.775
7.772
7.770
7.767
7.734
7.723
7.720
7.717
7.713
7.710
7.707
7.703
7.695
7.692
7.534
7.531
7.518
7.515
7.501
7.443
7.427
7.412
7.023
7.020
7.018
7.007
3.993
OMe

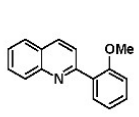

2.00
1.03
1.01
1.00
2.03
1.01
1.02
0.99
3.13
f1 (ppm)


160.153
157.138
148.238
141.180
136.745
129.812
129.780
129.651
127.456
127.283
126.327
120.023
119.102
115.388
112.740
55.439
OMe
f1 (ppm)

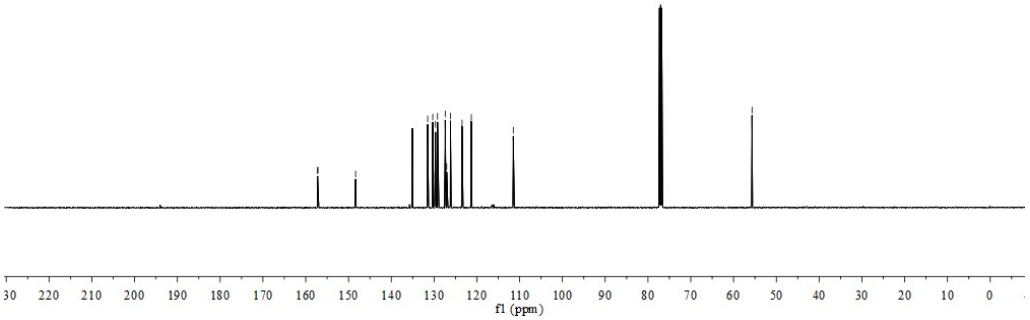

8.176
8.159
8.137
8.121
7.888
7.871
7.860
7.857
7.845
7.841
7.825
7.809
7.712
7.710
7.699
7.696
7.693
7.682
7.679
7.531
7.529
7.515
7.513
7.501
7.499
7.431
7.428
7.417
7.415
7.413
7.411
7.400
7.396
7.246
7.140
7.125
7.035
3.853
3.838
-0.000

OMe
N


0.92
1.01
0.92
0.95
0.98
1.00
0.98
1.00
0.98
0.97
3.04
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


OMe
N


157.230
157.147
148.349
131.503
130.313
129.671
129.195
127.393
126.169
123.462
121.293
111.484
55.681


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


8.61
8.61
8.37
8.37
8.36
8.35
8.24
8.23
8.22
8.22
8.02
8.00
7.99
7.98
7.89
7.89
7.88
7.88
7.84
7.84
7.82
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7.76
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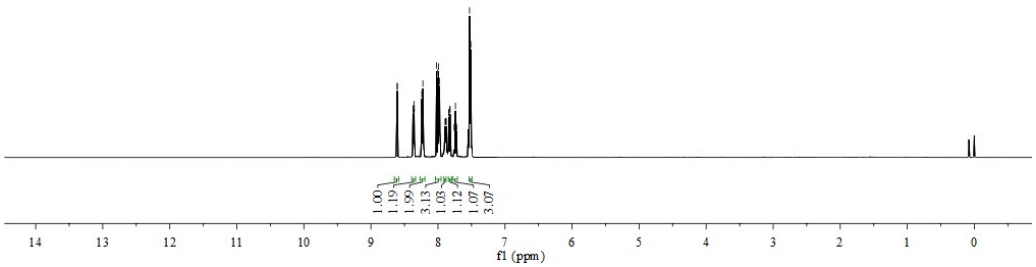
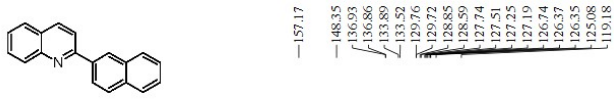
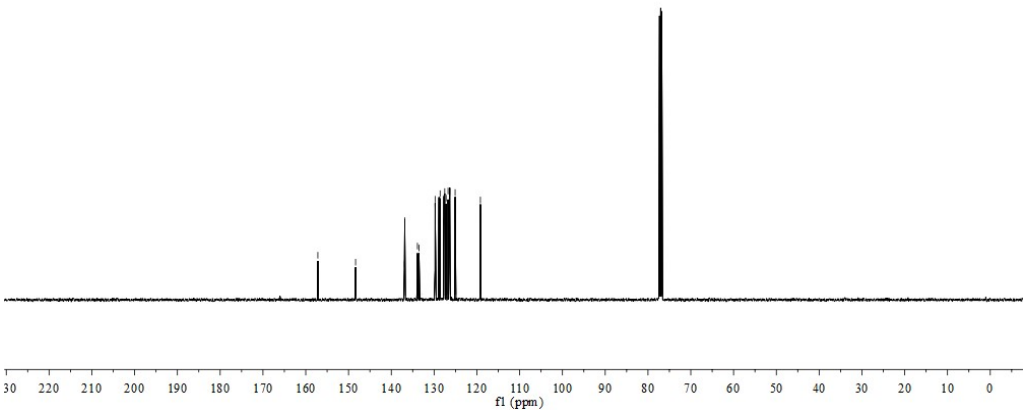
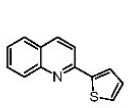
7.74
7.74
7.74
7.73
7.72
7.53
7.51

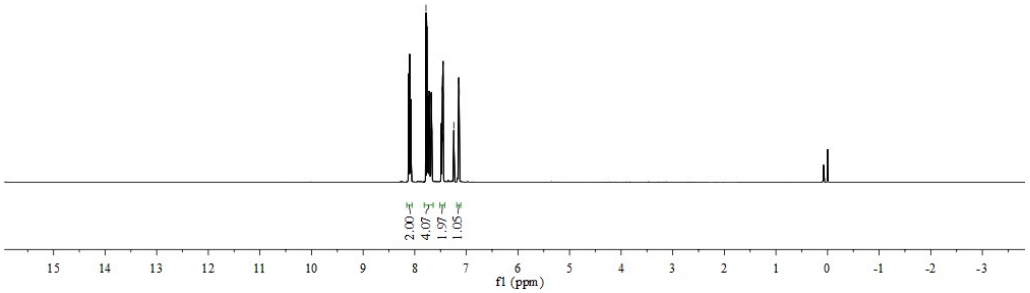

1.00
1.19
1.99
3.13
1.03
1.12
1.07
3.07
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

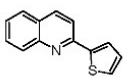

157.17
148.35
136.93
136.86
133.89
133.52
129.76
129.72
128.85
128.59
127.74
127.51
127.25
127.19
126.74
126.37
126.35
125.08
119.18

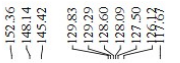

30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



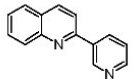

8.115
8.098
8.092
8.073
7.782
7.764
7.756
7.740
7.722
7.715
7.697
7.683
7.680
7.677
7.666
7.485
7.482
7.471
7.468
7.466
7.461
7.458
7.454
7.451
7.448
7.243
7.153
7.146
7.143
7.136

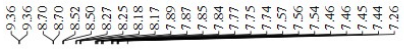

2.00
4.07
1.97
1.05
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)




152.36
148.14
145.42
129.83
129.29
128.60
128.09
127.50
119.12
119.07

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)




9.36
9.36
8.70
8.70
8.52
8.50
8.27
8.25
8.18
8.17
7.89
7.87
7.85
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7.74
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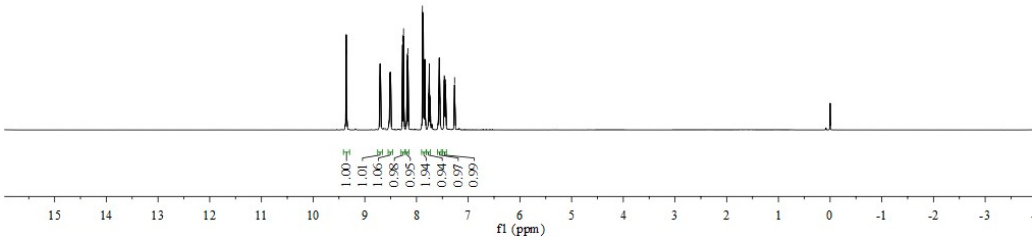
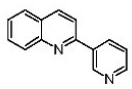
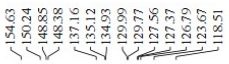
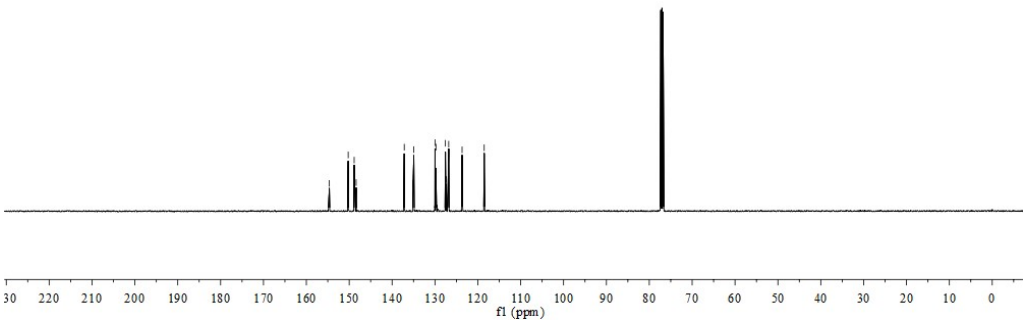
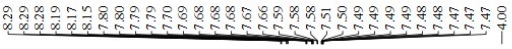
7.54
7.46
7.46
7.45
7.44
7.26


1.00
1.01
1.06
0.98
0.95
1.94
0.94
0.97
0.99
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)




154.63
150.24
148.85
148.38
137.16
135.12
134.93
129.99
129.77
127.56
127.37
126.79
123.67
118.51


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


8.29
8.29
8.28
8.19
8.17
8.15
7.80
7.80
7.79
7.79
7.70
7.69
7.68
7.68
7.68
7.67
7.66
7.59
7.58
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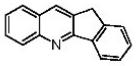
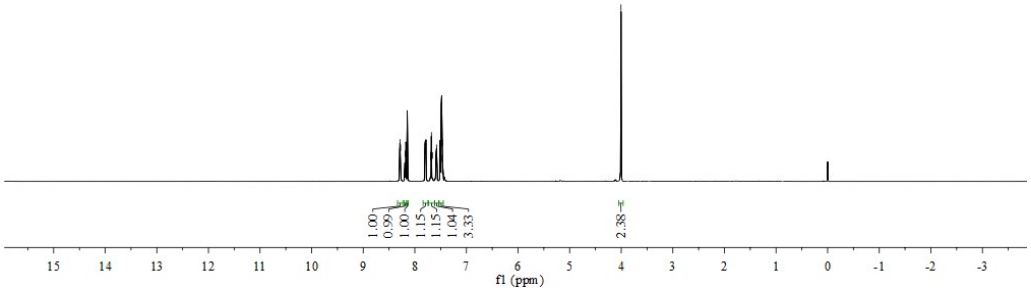
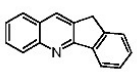
7.49
7.48
7.47
7.47
7.47
4.00

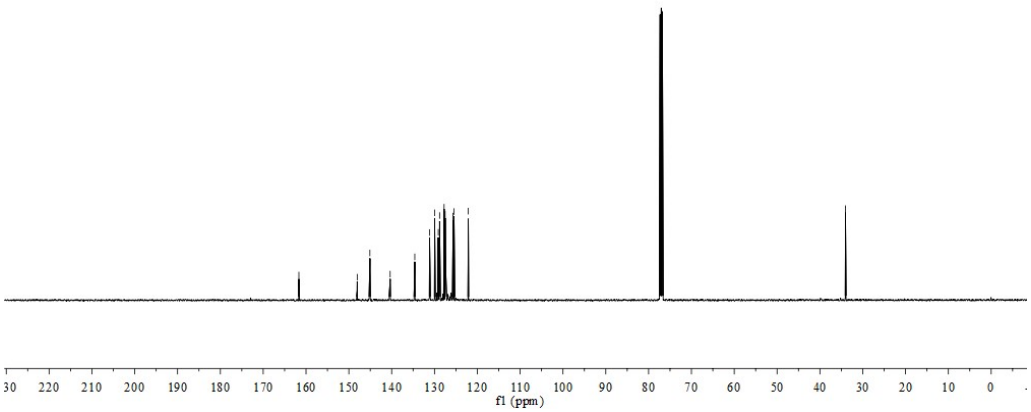



1.00
0.99
1.00
1.15
1.15
1.04
3.33
2.38
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)




161.67
148.04
145.09
140.35
134.60
131.15
129.96
129.11
128.81
127.76
127.52
127.40
125.67
125.44
122.11

34.02


230
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)