Supporting Information

Palladium-Catalyzed Carbonylative Addition of Aryl Bromides to Arylalkynes: A Simple and Efficient Method for Chalcone Synthesis

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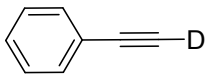
1. General Information

Solvents were dried and degassed before use by standard procedures. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) or a Bruker Avance II-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C); $CDCl_3$ and TMS were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on either a Q-TOF mass spectrometry or a GC-TOF mass spectrometry. TLC was carried out on SiO_2 (silica gel 60 F_{254}, Merck), and the spots were located with UV light, iodoplatinate reagent or 1% aqueous $KMnO_4$. Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 mesh). The starting materials **1a**–**1k** and **2a**–**2l** are commercially available.

2. Preparation and Characterization of Deuterium-labeled Phenyl Acetylene 2b-d_1[1]

A 50 mL round bottomed flask was charged with phenyl acetylene (1.02 g, 10 mmol), potassium carbonate (2.07 g, 15 mmol), and MeCN (20 mL). After the resulting mixture was stirred under a nitrogen atmosphere for 30 min, D_2O (1.0 mL, 50 mmol) was added, and the resulting mixture was stirred for 1 h. The deuterium-labeled product was extracted with CH_2Cl_2 (10 mL×3), and the combined organic layers were washed with brine (10 mL × 2), dried over $MgSO_4$. The solvent was removed under reduced pressure to afford deuterium-labeled phenyl acetylene (**2b-d_1**) as a colorless oil (887.0 mg, 86% yield).

Deuterium-labeled Phenyl Acetylene (2b-d_1)

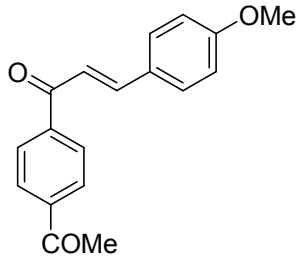


Colorless oil (887.0 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 6.0 Hz, 2H), 7.35–7.32 (m, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3, 129.0, 128.5, 122.4, 83.5, 83.4.

3. Representative Procedure for Palladium-Catalyzed Carbonylative Addition Reaction of Aryl Bromides to Arylalkynes.

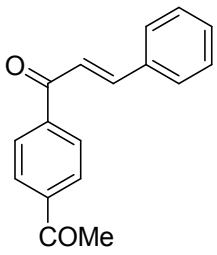
4-Acetylphenyl bromide (**1a**, 99.5 mg, 0.5 mmol), 4-methoxyphenyl acetylene (**2a**, 198.2 mg, 1.5 mmol), $^{i}Pr_2NEt$ (248 μL, 1.5 mmol), $PdCl_2$ (8.7 mg, 0.05 mmol), DPPB (42.6 mg, 0.1 mmol), and DMF (3.0 mL) were placed in a 25 mL autoclave with a magnetic stir bar under a N_2 atmosphere. The autoclave was purged with CO three times, filled with CO to 15 atm pressure, and heated to 120 ºC for 36 h. The autoclave was allowed to cool to room temperature and the remaining CO was vented. Then water (5 mL) was added to the resultant mixture. The product was extracted with ethyl acetate (5 mL × 3), and the combined organic layers were washed with brine (5mL × 2), dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 5:1) to afford (*E*)-1-(4-acetylphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one (**3a**) as a pale yellow solid (123.3 mg, 88% yield).

(*E*)-1-(4-Acetylphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (3a)[2]



Pale yellow solid (123.3 mg, 88% yield), mp 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 4H), 7.95 (d, J = 15.6 Hz, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 15.6 Hz, 1H), 7.10 (d, J = 8.4 Hz, 2H), 4.02 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 190.1, 162.1, 145.8, 39.7, 130.6, 128.7, 128.6, 127.4, 119.5, 114.6, 55.6, 27.0.

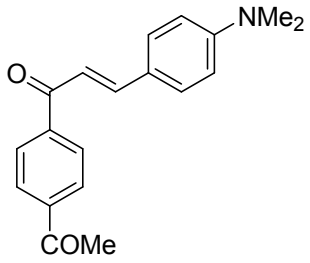
(*E*)-1-(4-Acetylphenyl)-3-phenylprop-2-en-1-one (3b)



White solid (105.1 mg, 84% yield), mp 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 4H), 7.82 (d, J = 15.6 Hz, 1H), 7.67–7.64 (m, 2H), 7.51 (d, J = 15.6 Hz, 1H), 7.45–7. 42 (m, 3H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 190.1, 146.0, 141.7, 139.9, 134.7, 131.0, 129.2, 128.8, 128.73, 128.65, 121.9, 27.1; IR (KBr) 3041,

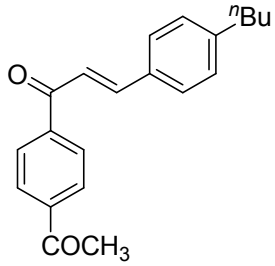
3000, 1681, 1656, 1607, 1594, 1573, 770 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{16}O_2$: 250.0994 $[M]^+$; found: 250.0982.

(*E*)-1-(4-Acetylphenyl)-3-(4-(dimethylamino)phenyl)prop-2-en-1-one (3c)



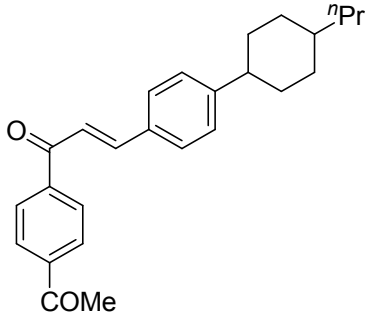
Yellow solid (129.1 mg, 88% yield), mp 116–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 4H), 7.80 (d, J = 15.6 Hz, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 15.2 Hz, 1H), 6.69 (d, J = 8.8 Hz, 2H), 3.05 (s, 6H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 190.2, 152.5, 147.1, 142.9, 139.5, 128.62, 128.59, 122.5, 116.7, 112.0, 40.3, 27.1; IR (KBr) 2911, 1751, 1684, 1650, 1674, 1550, 1525, 1367, 1186, 1169, 812 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{19}NO_2$: 293.1416 $[M]^+$; found: 293.1418.

(*E*)-1-(4-Acetylphenyl)-3-(4-butylphenyl)prop-2-en-1-one (3d)



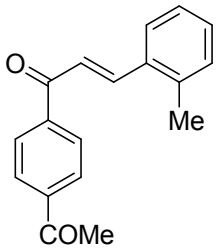
Pale yellow solid (131.8 mg, 86% yield), mp 132–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 4H), 7.81 (d, J = 15.6 Hz, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 15.6 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 2.66–2.63 (m, 5H), 1.65–1.58 (m, 2H), 1.41–1.32 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 190.1, 146.7, 146.1, 141.9, 139.8, 132.1, 129.2, 128.8, 128.7, 128.6, 120.9, 35.7, 33.5, 27.0, 22.4, 14.1; IR (KBr) 2955, 2923, 2855, 1677, 1657, 1610, 1600, 981, 961, 840, 820 cm^{-1}; HRMS (ES^+) calcd for $C_{21}H_{22}O_2Na$: 329.1517 $[M+Na]^+$; found: 329.1515.

(*E*)-1-(4-Acetylphenyl)-3-(4-(4-propylcyclohexyl)phenyl)prop-2-en-1-one (3e)



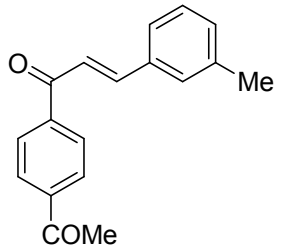
Pale yellow solid (149.8 mg, 80% yield), mp 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 4H), 7.81 (d, J = 15.6 Hz, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 15.6 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 2.67 (s, 3H), 2.54–2.47 (m, 1H), 1.91–1.86 (m, 4H), 1.51–1.00 (m, 9H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 190.2, 151.6, 146.2, 139.8, 128.7, 127.1, 120.9, 44.8, 37.1, 33.5, 27.0, 20.1, 14.6; IR (KBr) 2953, 2919, 2846, 1681, 1656, 1592, 1562, 1309, 1262, 988, 819 cm^{-1}; HRMS (ES$^+$) calcd for $C_{26}H_{30}O_2Na$: 397.2144 [M+Na]$^+$; found: 397.2148.

(*E*)-1-(4-Acetylphenyl)-3-(o-tolyl)prop-2-en-1-one (3f)



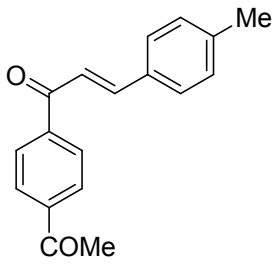
Pale yellow solid (108.4 mg, 82% yield), mp 102–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 15.6 Hz, 1H), 8.09 (s, 4H), 7.71 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 15.6 Hz, 1H), 7.35–7.24 (m, 3H), 2.67 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 190.7, 143.6, 141.8, 140.0, 138.7, 133.7, 131.2, 130.8, 128.8, 128.7, 126.60, 126.57, 122.9, 27.1, 20.0; IR (KBr) 3054, 1680, 1658, 1595, 1313, 976, 761 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{16}O_2$: 264.1150 [M]$^+$; found: 264.1159.

(*E*)-1-(4-Acetylphenyl)-3-(m-tolyl)prop-2-en-1-one (3g)



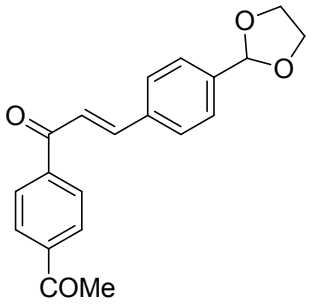
Pale yellow solid (103.1 mg, 78% yield), mp 98–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 4H), 7.80 (d, J = 16.0 Hz, 1H), 7.52–7.45 (m, 3H), 7.32 (dd, J = 8.0, 8.0 Hz, 1H), 7.25 (d, J = 7.6 Hz, 1H), 2.67 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 190.1, 146.2, 141.7, 139.8, 138.8, 134.6, 131.9, 129.3, 129.0, 128.7, 128.6, 125.9, 121.6, 27.0, 21.4; IR (KBr) 3015, 2920, 1686, 1663, 1596, 1264, 1239, 1031, 1012, 784 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{16}O_2$: 264.1150 [M]$^+$; found: 264.1143.

(*E*)-1-(4-Acetylphenyl)-3-(p-tolyl)prop-2-en-1-one (3h)



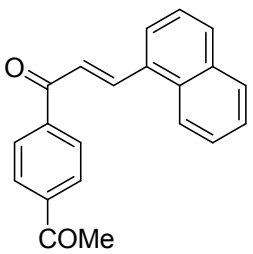
Pale yellow solid (113.7 mg, 86% yield), mp 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 4H), 7.80 (d, J = 15.6 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 15.6 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 2.66 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 190.2, 146.1, 141.9, 141.7, 139.8, 131.9, 129.9, 128.74, 128.72, 128.6, 120.9, 27.0, 21.7; IR (KBr) 2927, 1679, 1652, 1593, 1561, 981, 809 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{16}O_2$: 264.1150 $[M]^+$; found: 264.1138.

(*E*)-3-(4-(1,3-Dioxolan-2-yl)phenyl)-1-(4-acetylphenyl)prop-2-en-1-one (3k)



Pale yellow solid (129.0 mg, 80% yield), mp 136–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 4H), 7.83 (d, J = 16.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.56–7.51 (m, 3H), 5.85 (s, 1H), 4.11 (t, J = 17.2 Hz, 4H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 189.9, 145.3, 141.5, 140.6, 139.9, 135.4, 128.7, 128.62, 128.55, 127.2, 122.2, 65.4, 27.0; IR (KBr) 2957, 2888, 1680, 1657, 1597, 1077, 1012, 952, 818 cm^{-1}; HRMS (ES$^+$) calcd for $C_{20}H_{18}O_4Na$: 345.1103 $[M+Na]^+$; found: 345.1109.

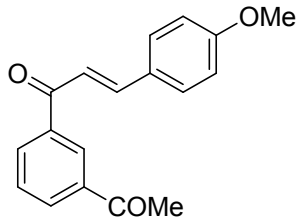
(*E*)-1-(4-Acetylphenyl)-3-(naphthalen-1-yl)prop-2-en-1-one (3l)



Pale yellow solid (123.2 mg, 82% yield), mp 118–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 15.2 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.8 Hz, 2H), 8.08 (d, J = 8.4 Hz, 2H), 7.95–7.88 (m, 3H), 7.62–7.51 (m, 4H), 2.66 (s, 3H); ^{13}C

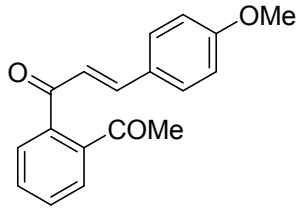
NMR (100 MHz, $CDCl_3$) δ 197.7, 189.9, 142.8, 141.7, 140.0, 133.9, 132.1, 131.9, 131.4, 129.0, 128.9, 128.7, 127.3, 126.5, 125.6, 125.4, 124.3, 123.5, 27.1; IR (KBr) 3055, 1686, 1660, 1595, 1500, 1433, 1401, 1348, 1310, 1258, 1216, 798, 775 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{16}O_2$: 300.1150 $[M]^+$; found: 300.1147.

(*E*)-1-(3-Acetylphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (4b)



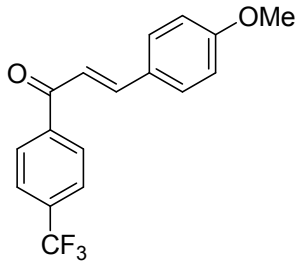
Pale yellow solid (98.1 mg, 70% yield), mp 78–80 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.22 (d, J = 7.6 Hz, 1H), 8.17 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 15.6 Hz, 1H), 7.64–7.60 (m, 3H), 7.45 (d, J = 15.6 Hz, 1H), 6.95 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 189.7, 162.0, 145.7, 137.5, 132.2, 129.2, 127.5, 119.2, 114.6, 114.3, 55.6, 27.0; IR (KBr) 3008, 2933, 2838, 1687, 1660, 1596, 1511, 1423, 1255, 1196, 1172, 1030, 830 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{16}O_3$: 280.1099 $[M]^+$; found: 280.1094.

(*E*)-1-(2-Acetylphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (4c)



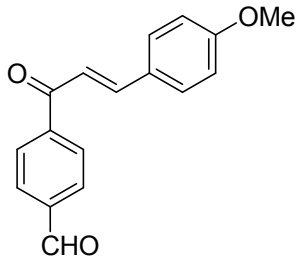
Pale yellow solid (100.9 mg, 72% yield), mp 106–108 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 4H), 7.80 (d, J = 15.6 Hz, 1H), 7.62 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 15.6 Hz, 1H), 6.95 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 190.1, 162.1, 145.9, 142.1, 139.8, 130.6, 128.7, 128.6, 127.5, 119.6, 114.6, 55.6, 27.0; IR (KBr) 3000, 2933, 2836, 1680, 1657, 1589, 1510, 1256, 1214, 1171, 1031, 818 cm^{-1}; HRMS (ES^+) calcd for $C_{18}H_{16}O_3Na$: 303.0997 $[M+Na]^+$; found: 303.0990.

(*E*)-3-(4-Methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (4d)



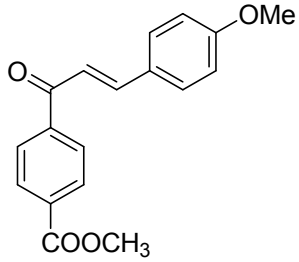
Yellow solid (119.5 mg, 78% yield), mp 116–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 2H), 7.83–7.75 (m, 3H), 7.62 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 15.6 Hz, 1H), 6.95 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 162.0, 146.0, 141.4, 133.4 (q, ^2J = 32.5 Hz), 130.5, 128.7, 127.2, 125.6, 123.7 (q, ^1J = 270.7 Hz), 119.2, 114.5, 55.4; IR (KBr) 2963, 2841, 1659, 1600, 1572, 1512, 1328, 1257, 1159, 1116, 983, 831 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{13}O_2F_3$: 306.0868 $[M]^+$; found: 306.0874.

(*E*)-4-(3-(4-Methoxyphenyl)acryloyl)benzaldehyde (4e)



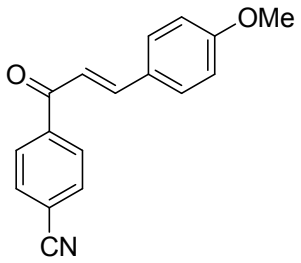
Pale yellow solid (106.6 mg, 80% yield), mp 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.13 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 16.0 Hz, 1H), 7.61 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 16.0 Hz, 1H), 6.94 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 189.9, 162.0, 146.0, 143.1, 138.5, 130.5, 129.8, 128.9, 127.2, 119.3, 114.5, 55.4; IR (KBr) 2838, 1703, 1659, 1590, 1570, 1511, 1257, 1212, 1174, 1032, 818, 807 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{14}O_3$: 266.0943 $[M]^+$; found: 266.0942.

(*E*)-Methyl 4-(3-(4-methoxyphenyl)acryloyl)benzoate (4f)



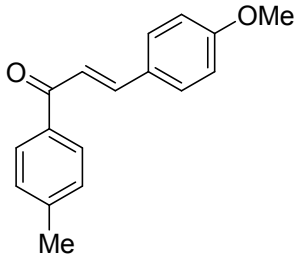
Yellow solid (120.0 mg, 81% yield), mp 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 15.6 Hz, 1H), 7.61 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 15.6 Hz, 1H), 6.95 (d, J = 8.8 Hz, 2H), 3.96 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 166.5, 162.0, 145.8, 142.1, 130.5, 129.9, 128.4, 127.4, 119.6, 114.6, 55.6, 52.6; IR (KBr) 2951, 2844, 1713, 1655, 1593, 1511, 1281, 1106, 829 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{16}O_4$: 296.1049 $[M]^+$; found: 296.1096.

(*E*)-4-(3-(4-Methoxyphenyl)acryloyl)benzonitrile (4g)



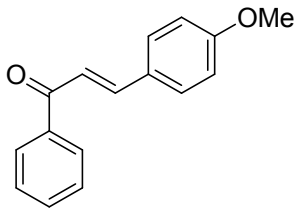
Yellow solid (118.5 mg, 90% yield), mp 122–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.8 Hz, 2H), 7.83–7.79 (m, 3H), 7.61 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 15.6 Hz, 1H), 6.95 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.7, 159.8, 144.1, 139.5, 128.2, 126.4, 124.7, 116.4, 115.7, 113.3, 112.2, 53.1; IR (KBr) 2938, 2839, 2224, 1657, 1597, 1573, 1512, 1424, 1293, 1252, 1212, 1176, 1035, 814 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{13}NO_2$: 263.0946 $[M]^+$; found: 263.0943.

(*E*)-3-(4-Methoxyphenyl)-1-(p-tolyl)prop-2-en-1-one (4i)[3]



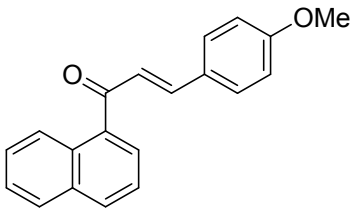
White solid (50.5 mg, 40% yield), mp 82–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.6 Hz, 2H), 7.78 (d, J = 15.6 Hz, 1H), 7.60 (d, J = 7.2 Hz, 2H), 7.42 (d, J = 15.6 Hz, 1H), 7.29 (d, J = 7.6 Hz, 2H), 6.93 (d, J = 7.2 Hz, 2H), 3.85 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 161.8, 144.4, 143.6, 136.1, 129.5, 127.9, 112.0, 114.6, 55.6, 21.9.

(*E*)-3-(4-Methoxyphenyl)-1-phenylprop-2-en-1-one (4j)[4]



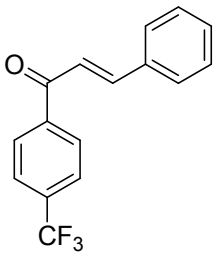
Colorless oil (62.0 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.6 Hz, 2H), 7.79 (d, J = 15.6 Hz, 1H), 7.61–7.49 (m, 5H), 7.42 (d, J = 15.6 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 161.8, 144.9, 138.6, 128.7, 128.6, 127.7, 112.0, 114.6, 55.6.

(*E*)-3-(4-Methoxyphenyl)-1-(naphthalen-1-yl)prop-2-en-1-one (4k)[5]



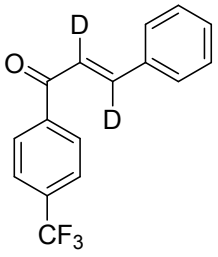
Colorless oil (83.6 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.8 Hz 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 7.73 (d, J = 6.4 Hz, 1H), 7.57–7.50 (m, 6H), 7.17 (d, J = 16.0 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 161.9, 146.1, 137.6, 133.9, 130.6, 130.4, 128.5, 127.42, 127.36, 127.0, 126.5, 125.8, 125.1, 124.7, 114.6, 55.5.

(*E*)-3-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (5d)



White solid (89.8 mg, 65% yield), mp 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 15.6 Hz, 1H), 7.76 (d, J =8.0 Hz, 2H), 7.65–7.63 (m, 2H), 7.49 (d, J =15.6 Hz, 1H), 7.43–7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 146.0, 141.1, 134.6, 134.2 (q, ^2J = 32.1 Hz), 131.0, 129.1, 128.8, 128.6, 125.7, 123.8 (q, ^1J = 271.2 Hz), 121.6; IR (KBr) 3060, 3037, 1943, 1666, 1604, 1574, 1450, 1409, 1334, 1164, 1112, 985, 840 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{11}F_3O$: 276.0762 $[M]^+$; found: 276.0754.

(*E*)-3-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one-d_2 (5d-d_2)



White solid (94.6 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0Hz, 2H), 7.66 (dd, J = 2.4, 6.0 Hz, 2H), 7.45–7.43 (m, 3H); HRMS (EI) calcd for $C_{16}H_9D_2F_3O$: 278.0888 $[M]^+$; found: 278.0897.

4. References

(1) S. P. Bew, G. D. Hiatt-Gipson, J. A. Lovell, C. Poullain, *Org. Lett*., 2012, **14**, 456.

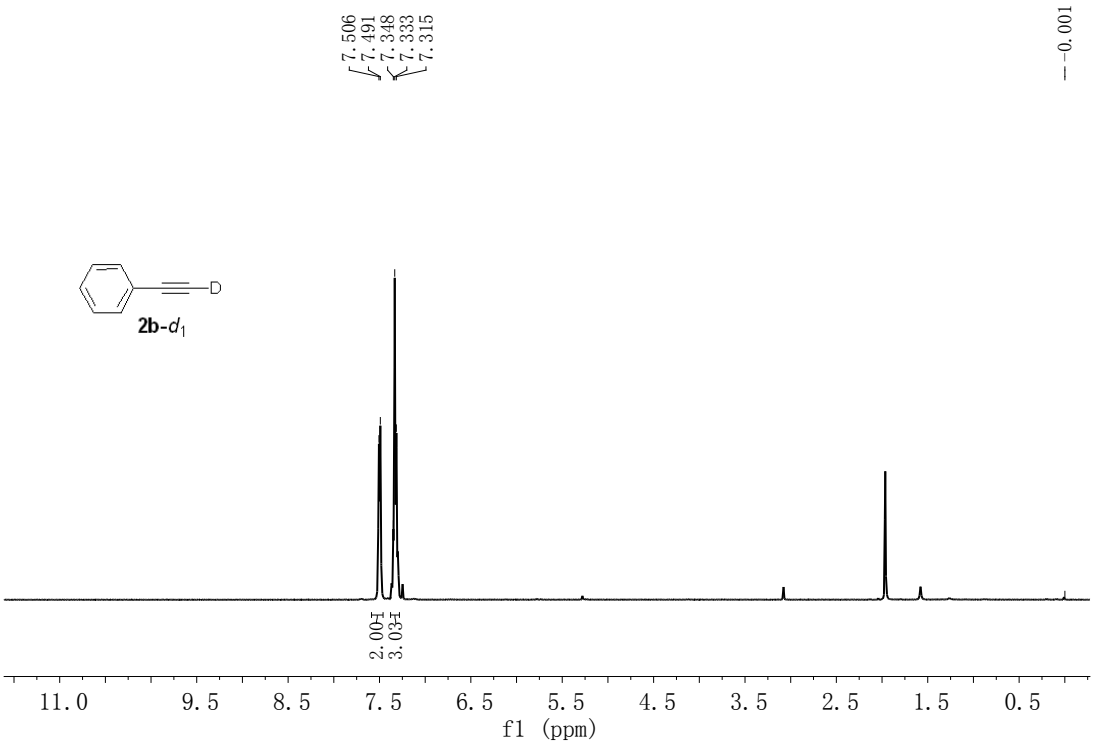
(2) A. Khatyr, H. Maas, G. Calzaferri, *J. Org. Chem*., 2002, **67**, 6705.

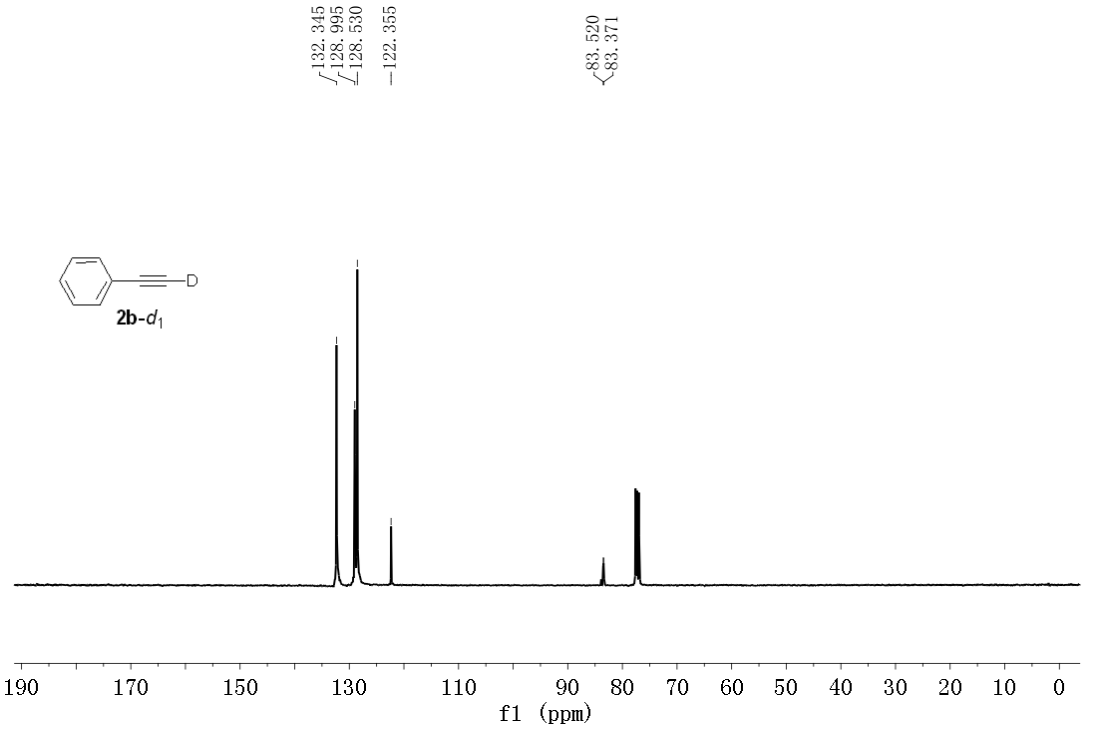
(3) X.-F. Wu, H. Neumann, A. Spannenberg, T. Schulz, H. Jiao, M. Beller, *J. Am. Chem. Soc*., 2010, **132**, 14596.

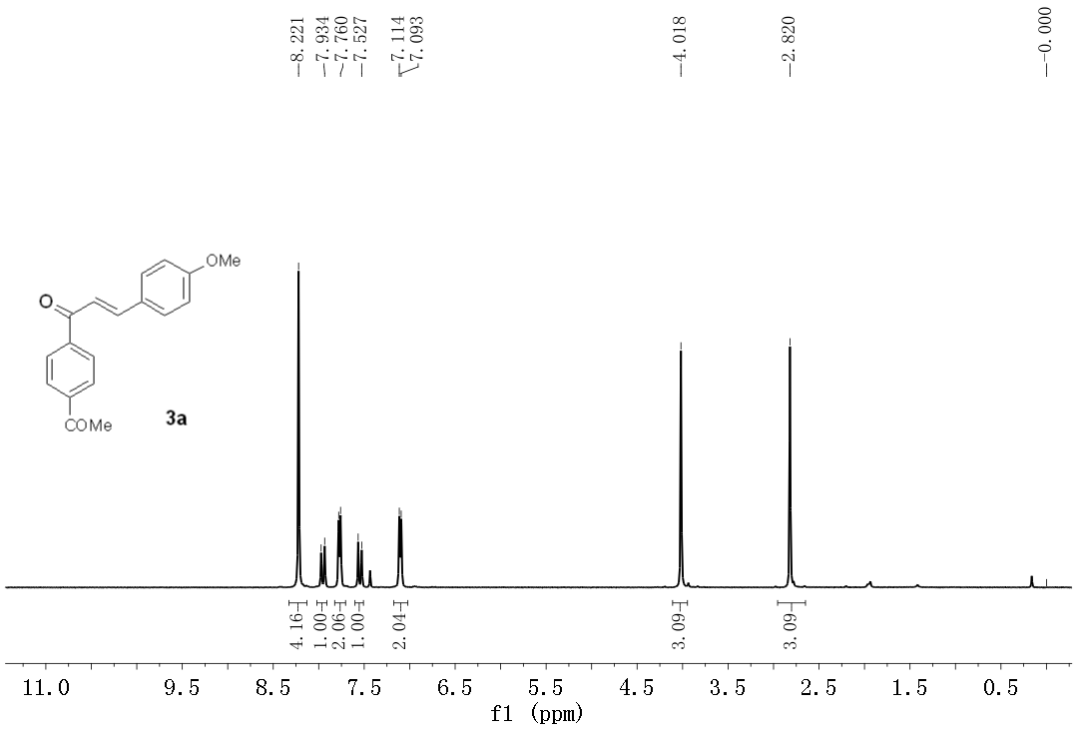
(4) K. R. Buszek, N. Brown, *Org. Lett*., 2007, **9**, 707.

(5) N. Ingarsal, G. Saravanan, P. Amutha, S. Nagarajan, *Eur. J. Med. Chem*., 2007, **42**, 517.

5. Copies of ^{1}H and ^{13}C NMR Spectra of Starting Materials and Products



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7.093
4.018
2.820
0.000
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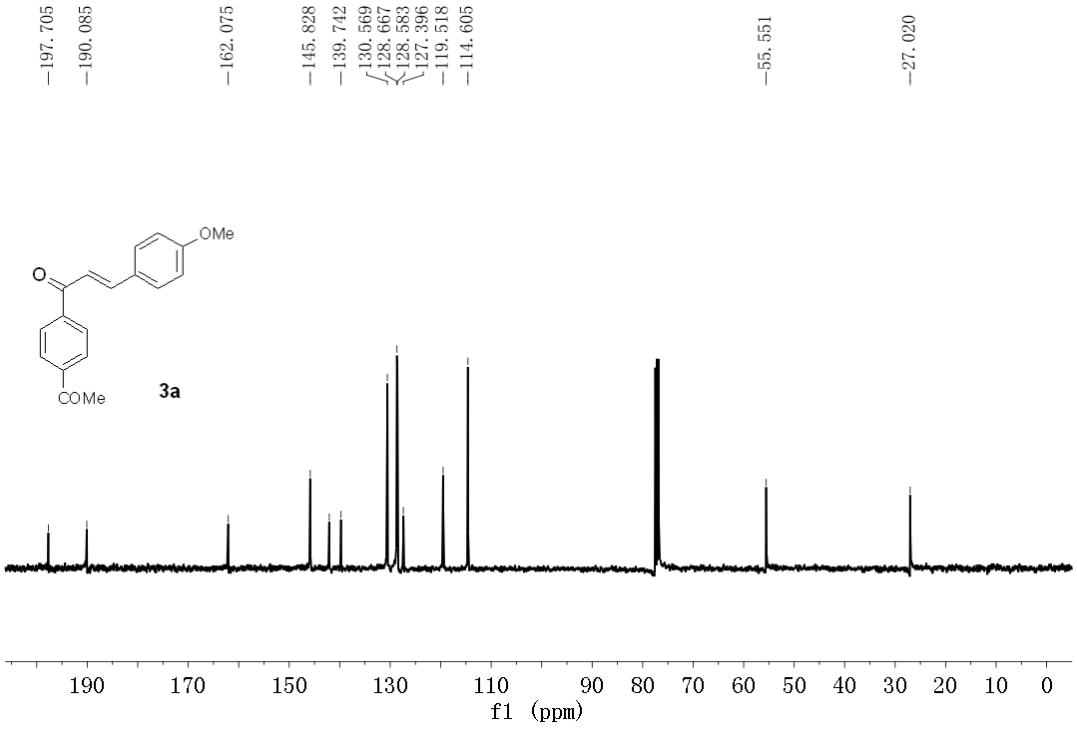
O
COMe
3a
4.16
1.00
2.06
1.00
2.04
3.09
3.09
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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162.075
145.828
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130.569
128.667
128.583
127.396
119.518
114.605
55.551
27.020
OMe
O
COMe
3a
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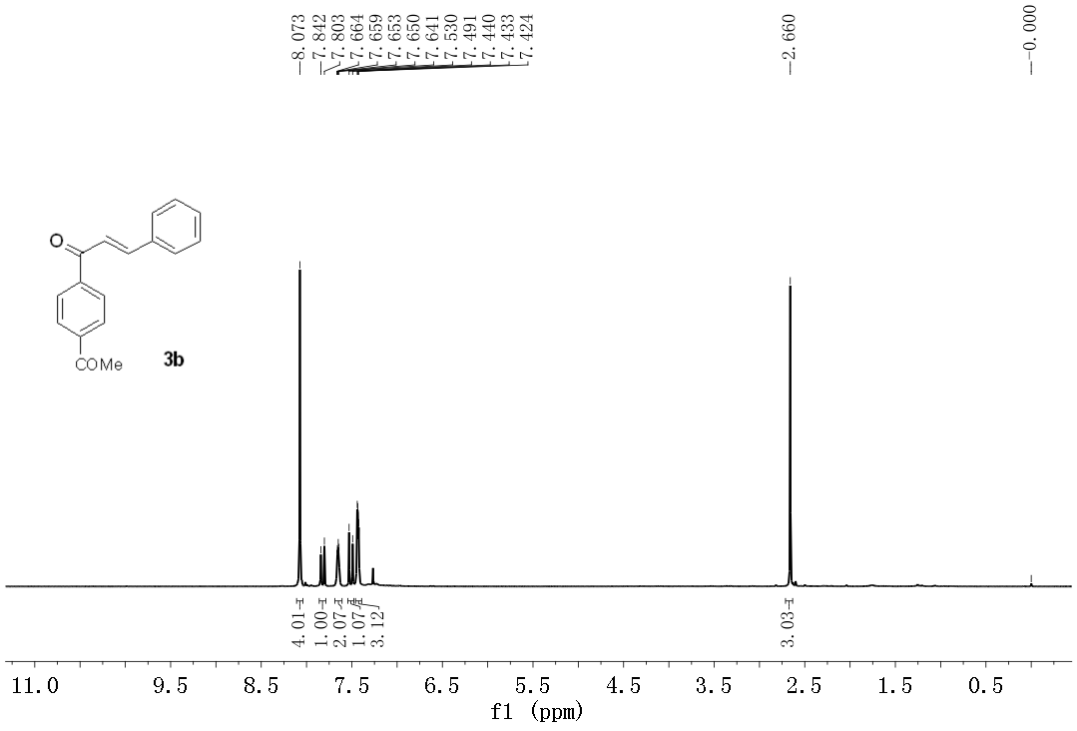
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.650
7.641
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7.491
7.440
7.433
7.424
2.660
0.000
O
COMe
3b
4.01
1.00
2.07
1.07
3.12
3.03
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
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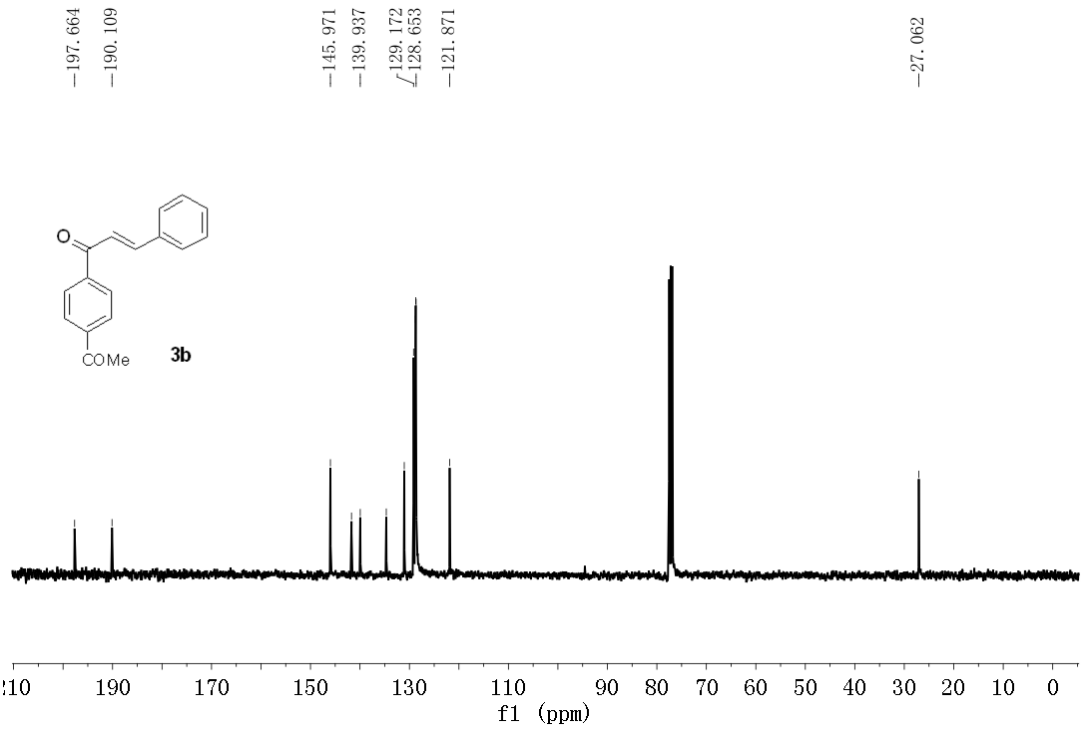
f1 (ppm)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110
90
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60
50
40
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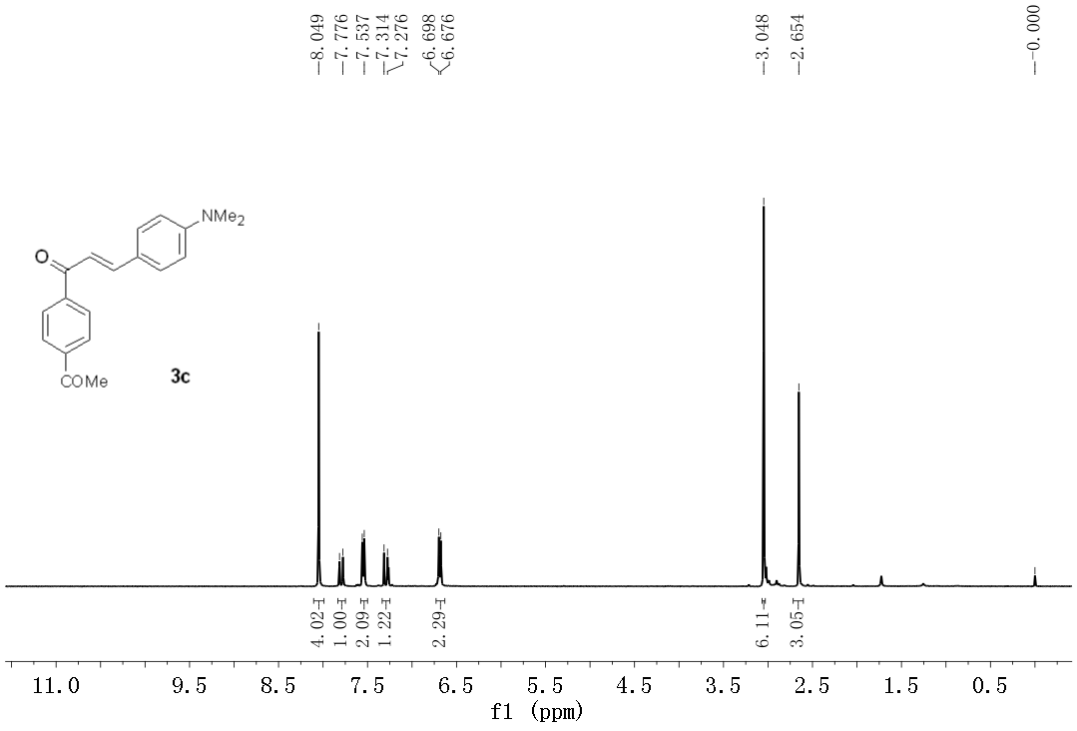
20
10
0
f1 (ppm)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6.698
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O
COMe
3c
4.02
1.00
2.09
1.22
2.29
6.11
3.05
11.0
9.5
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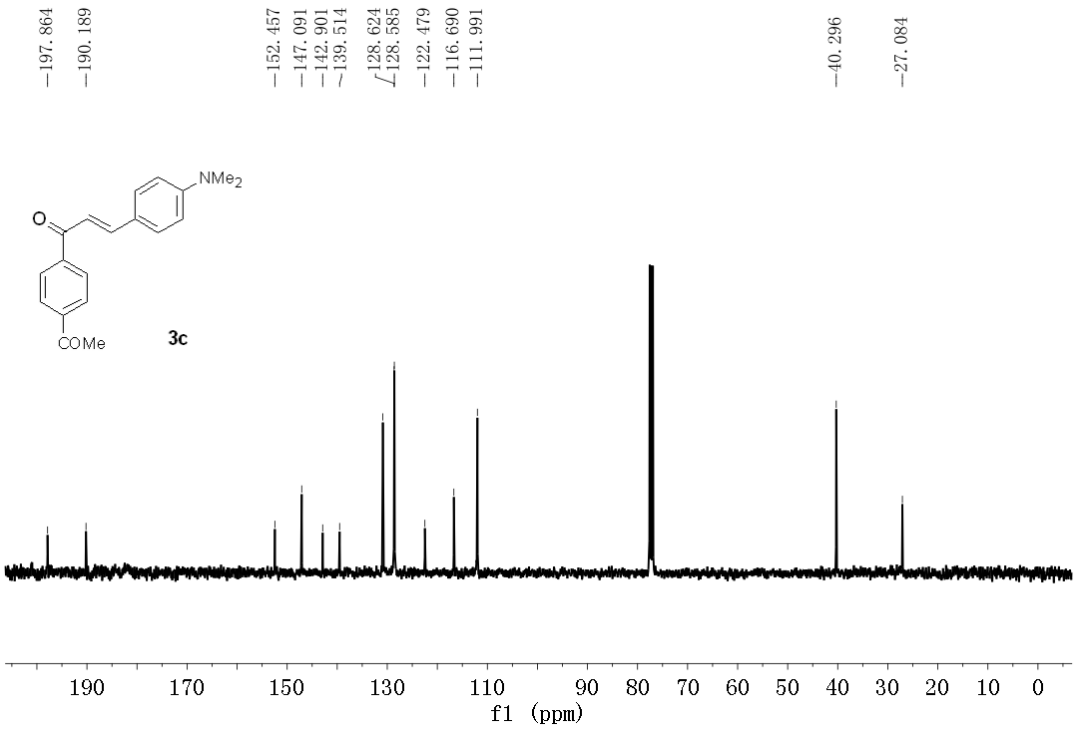
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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NMe2
O
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3c
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150
130
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90
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50
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30
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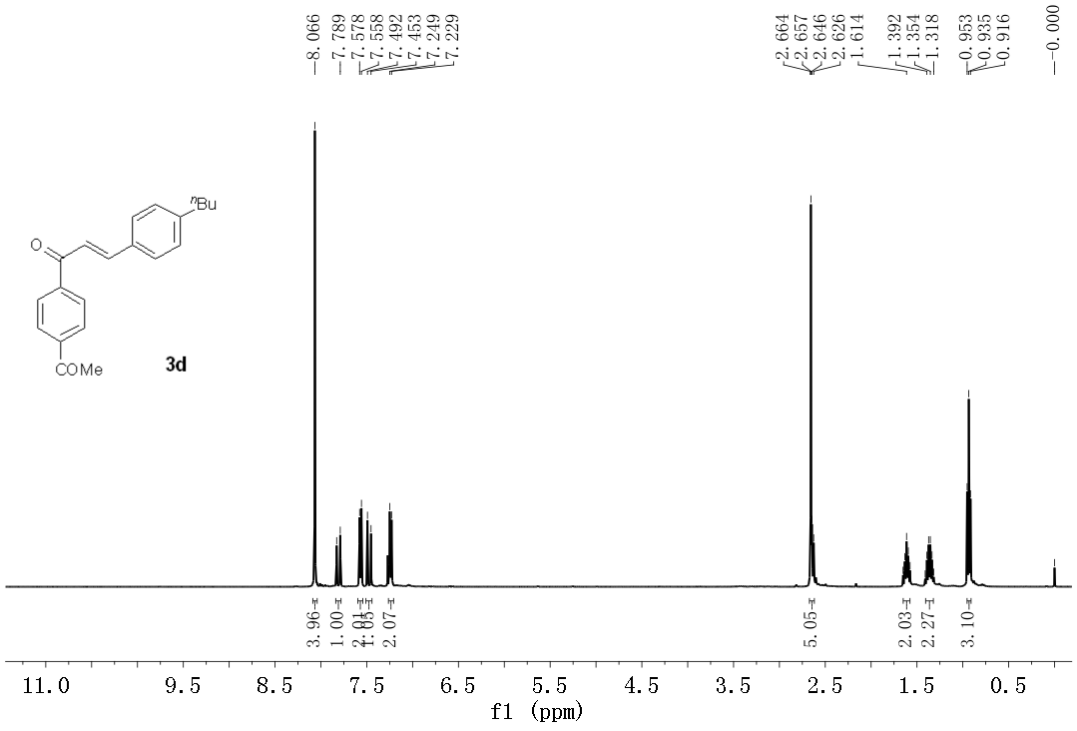
f1 (ppm)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1.392
1.354
1.318
0.953
0.935
0.916
0.000
3.96
1.00
2.07
5.05
2.03
2.27
3.10
11.0
9.5
8.5
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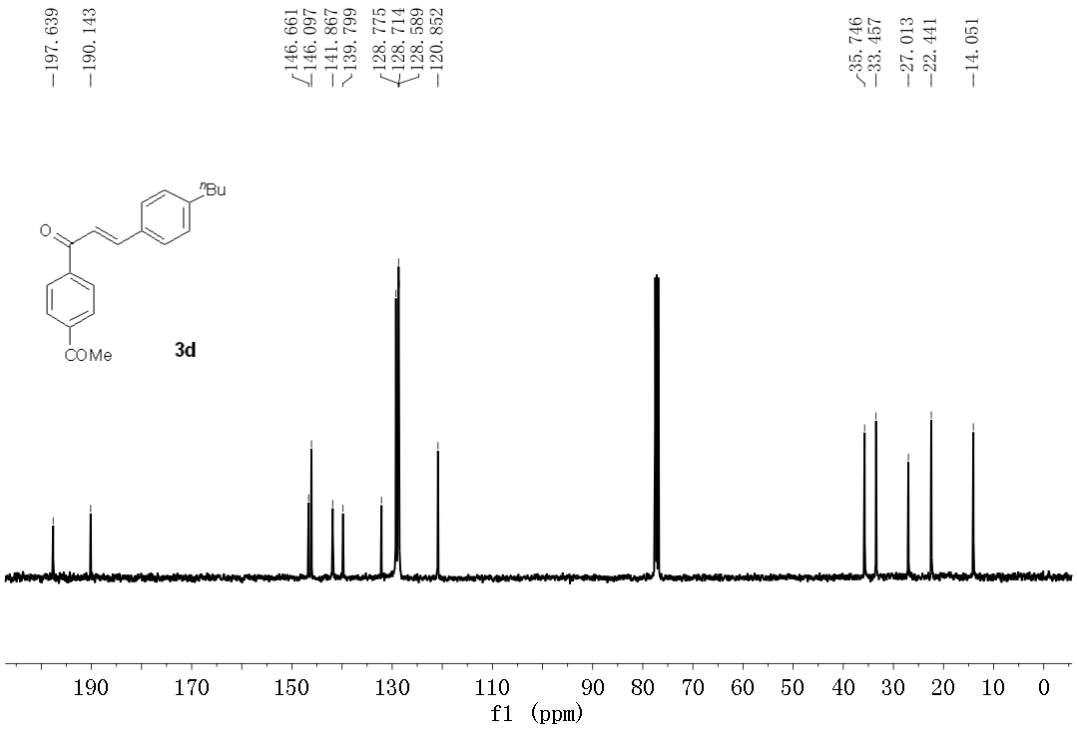
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
nBu
O
COMe
3d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22.441
14.051
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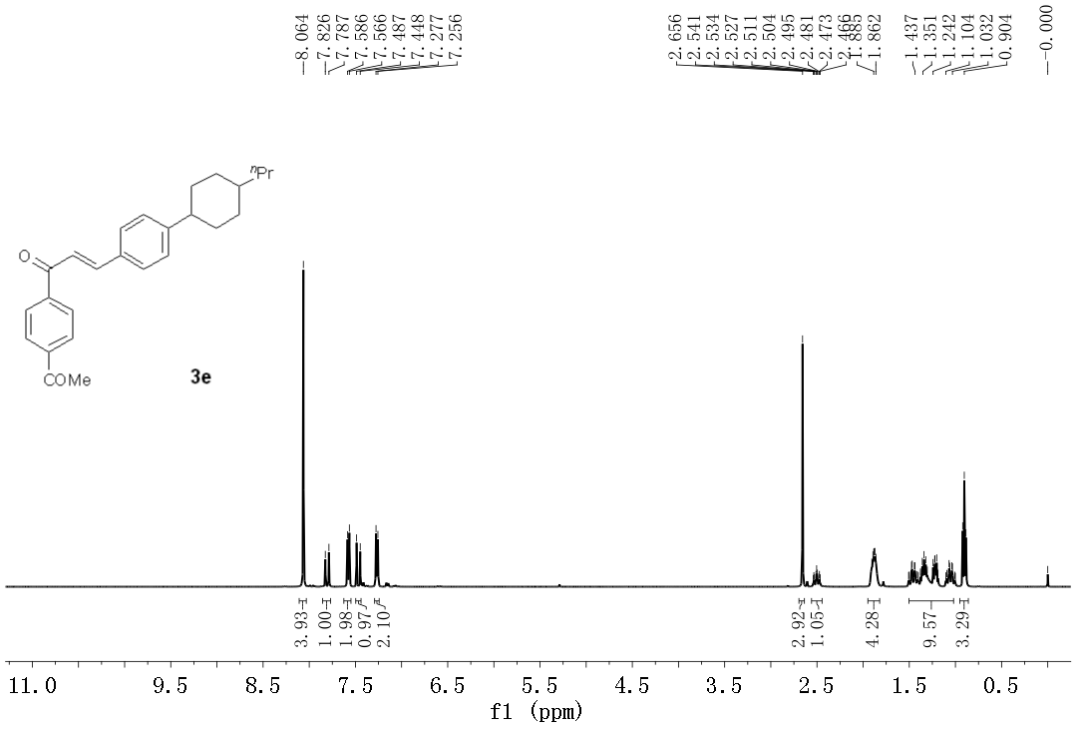
nBu
O
COMe
3d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COMe
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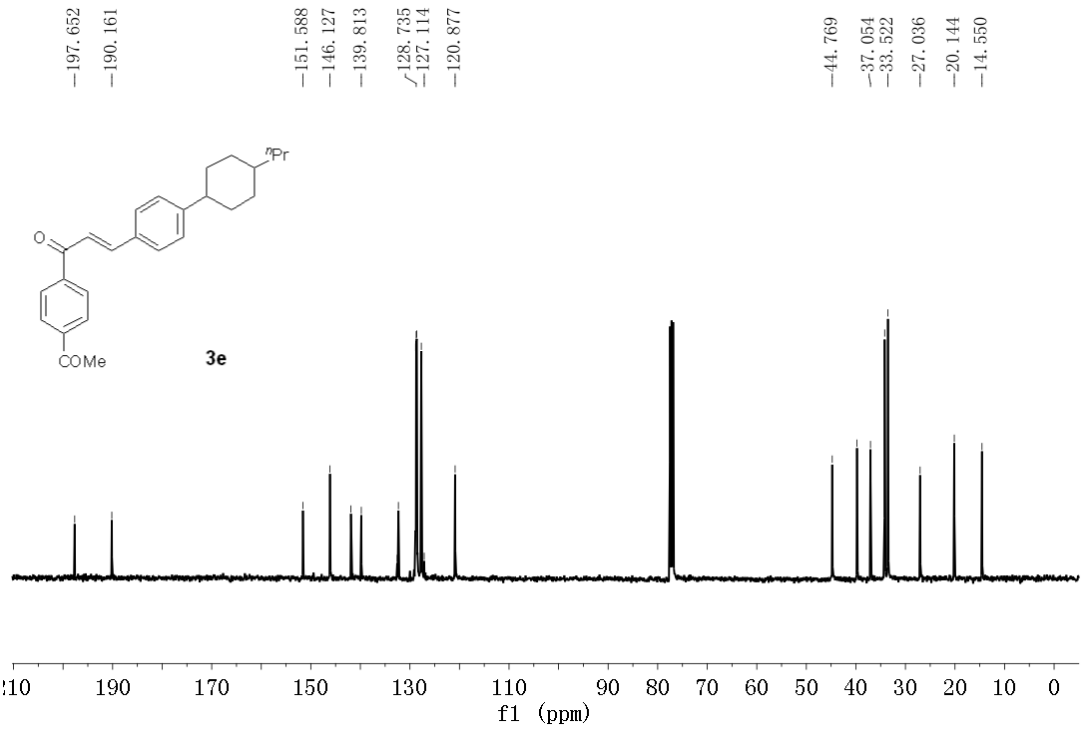
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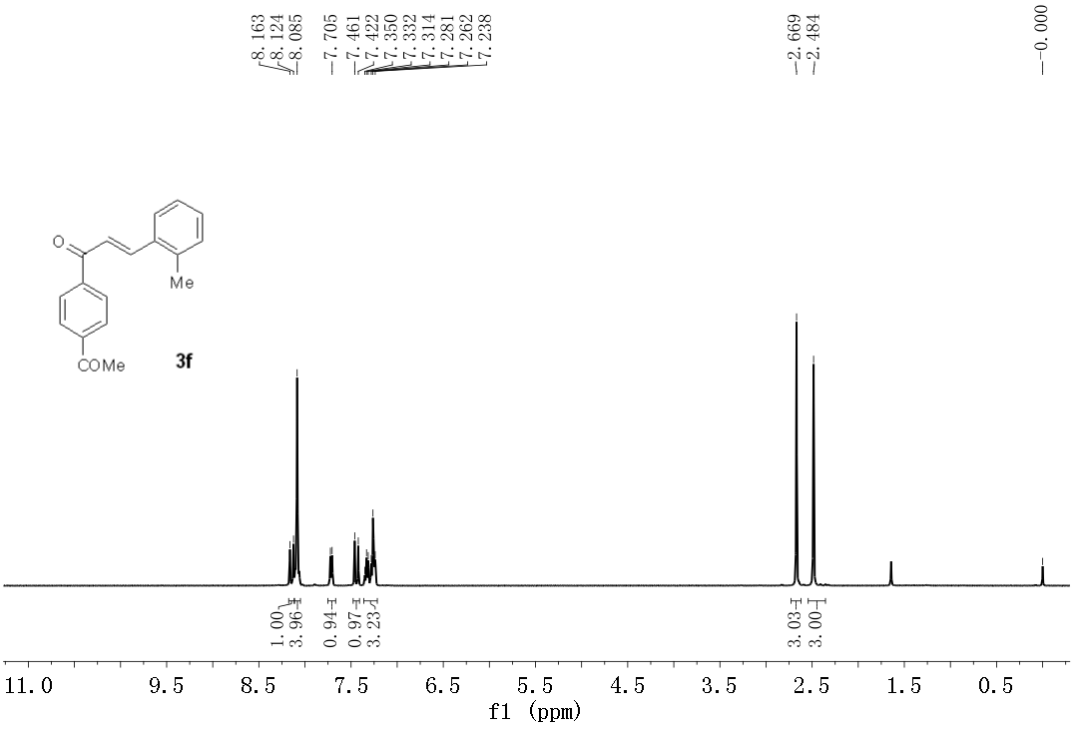
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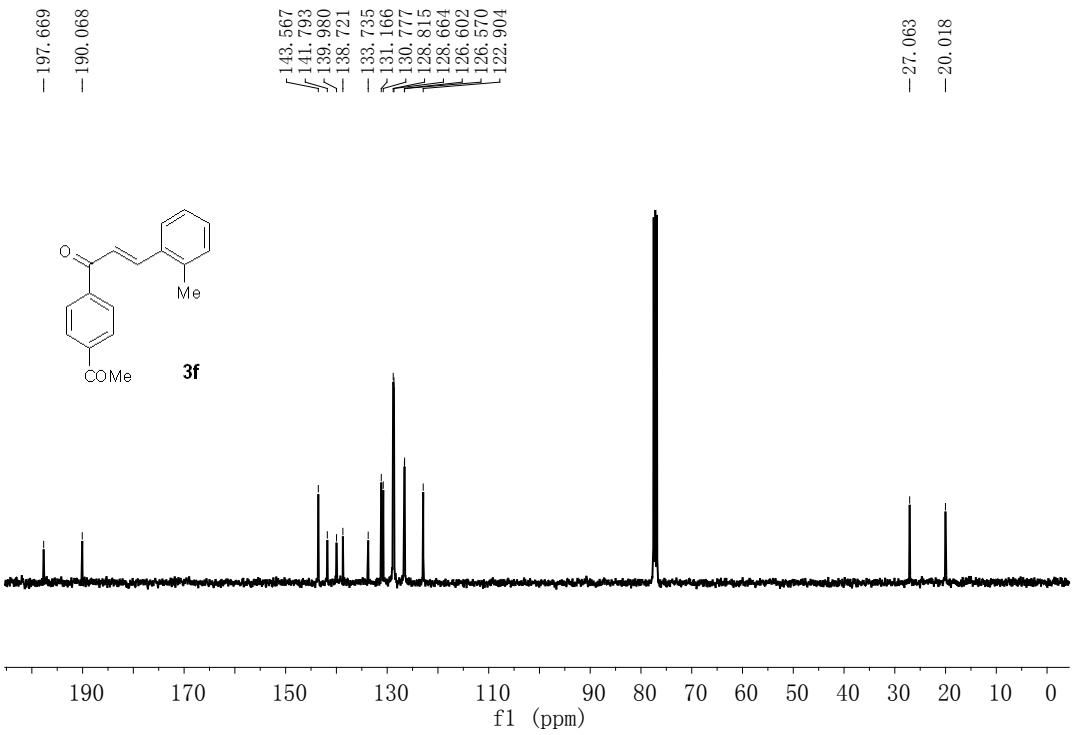
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126.570
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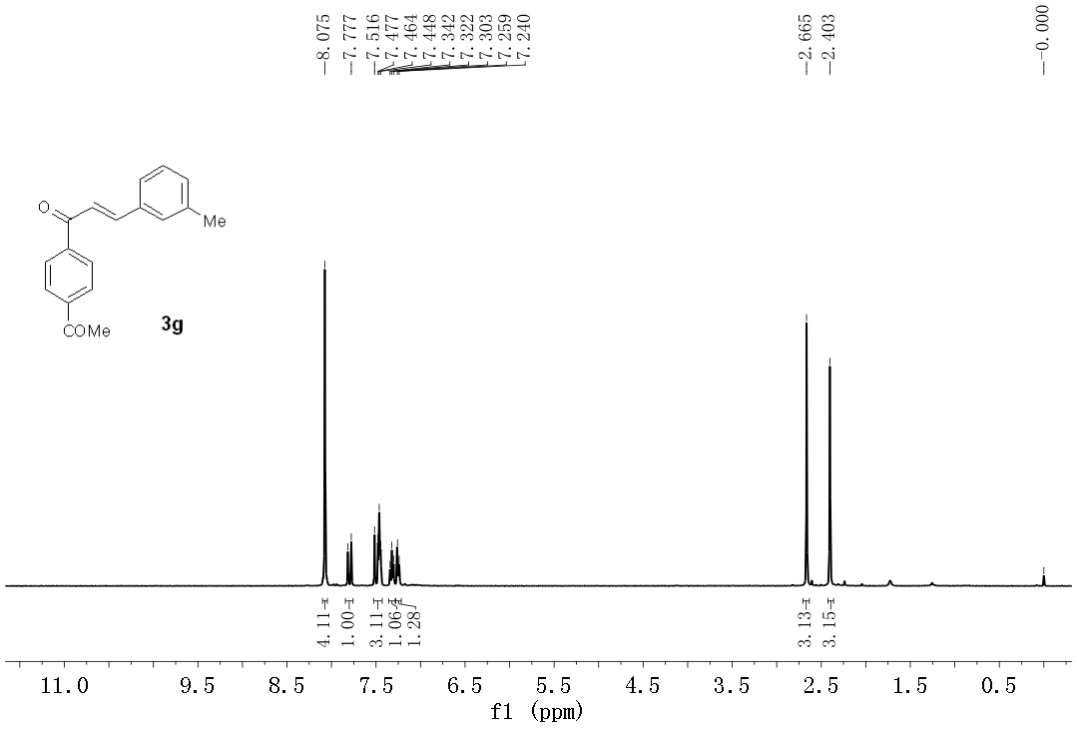
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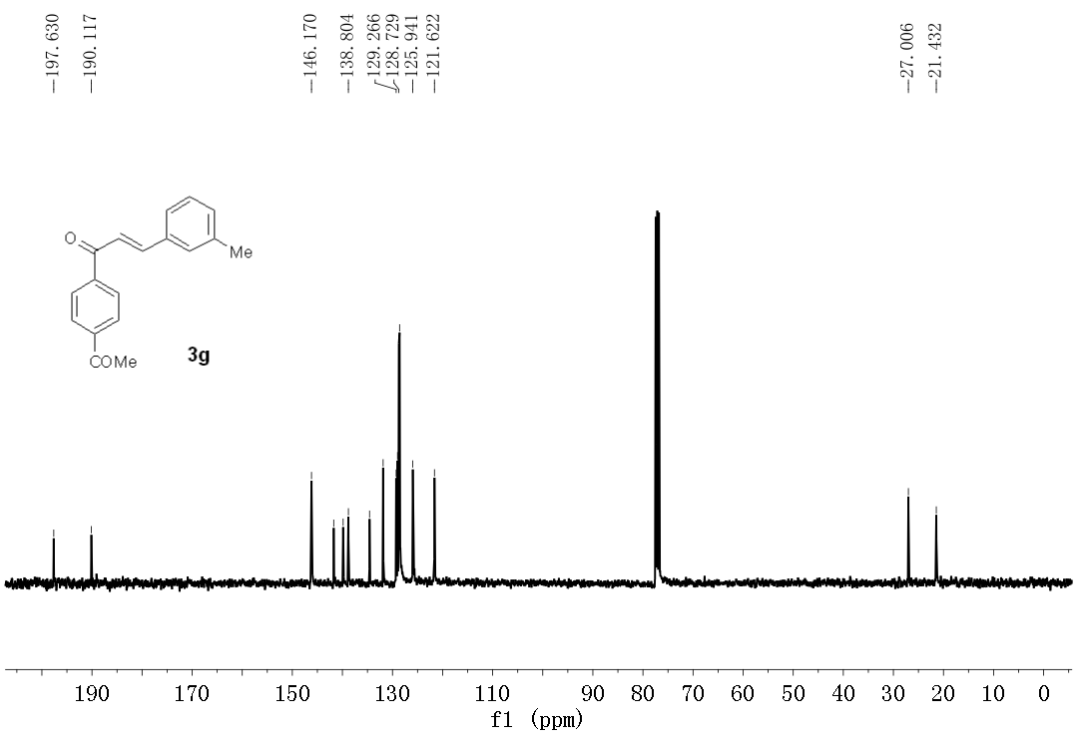
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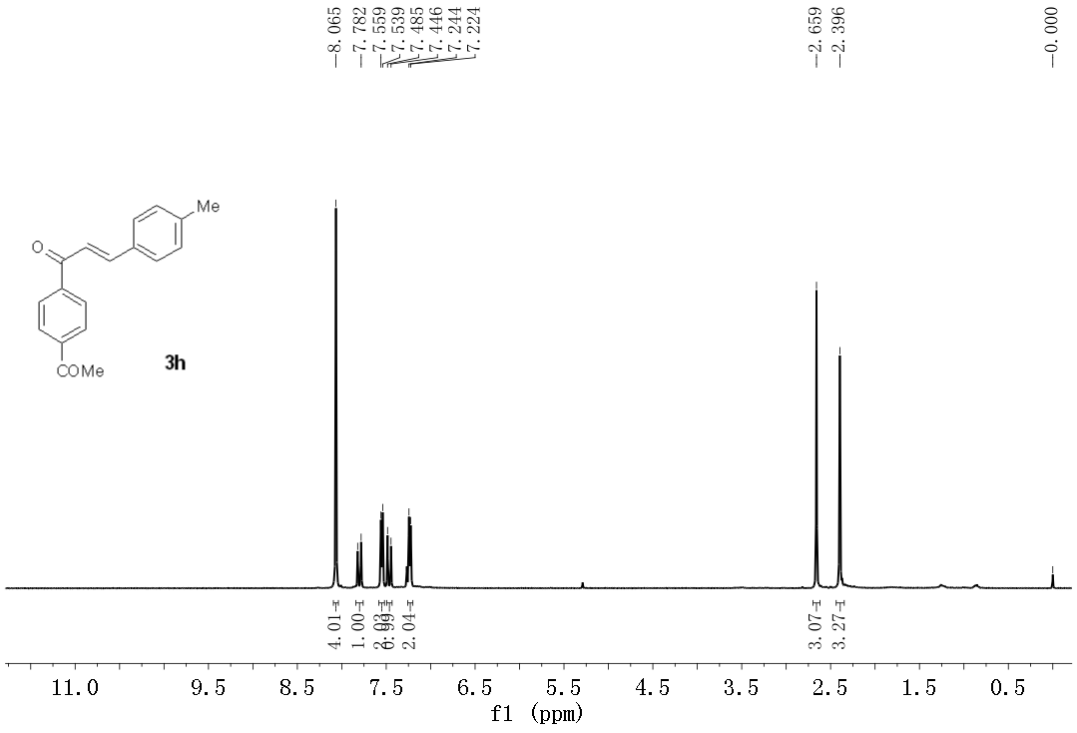
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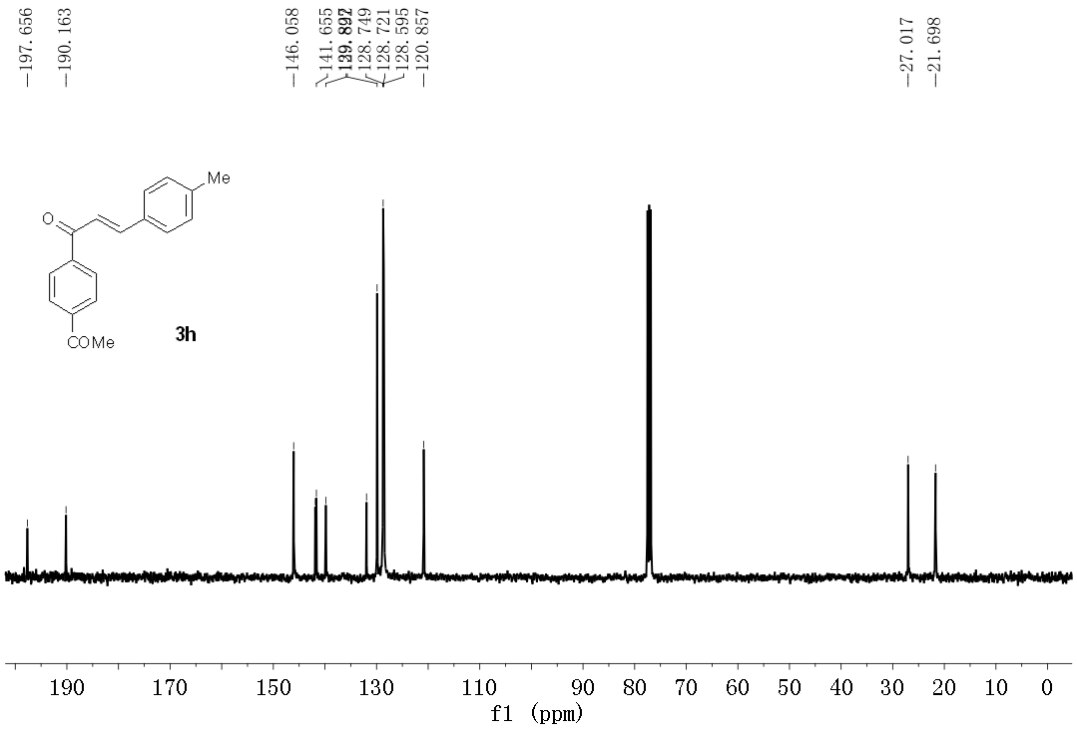
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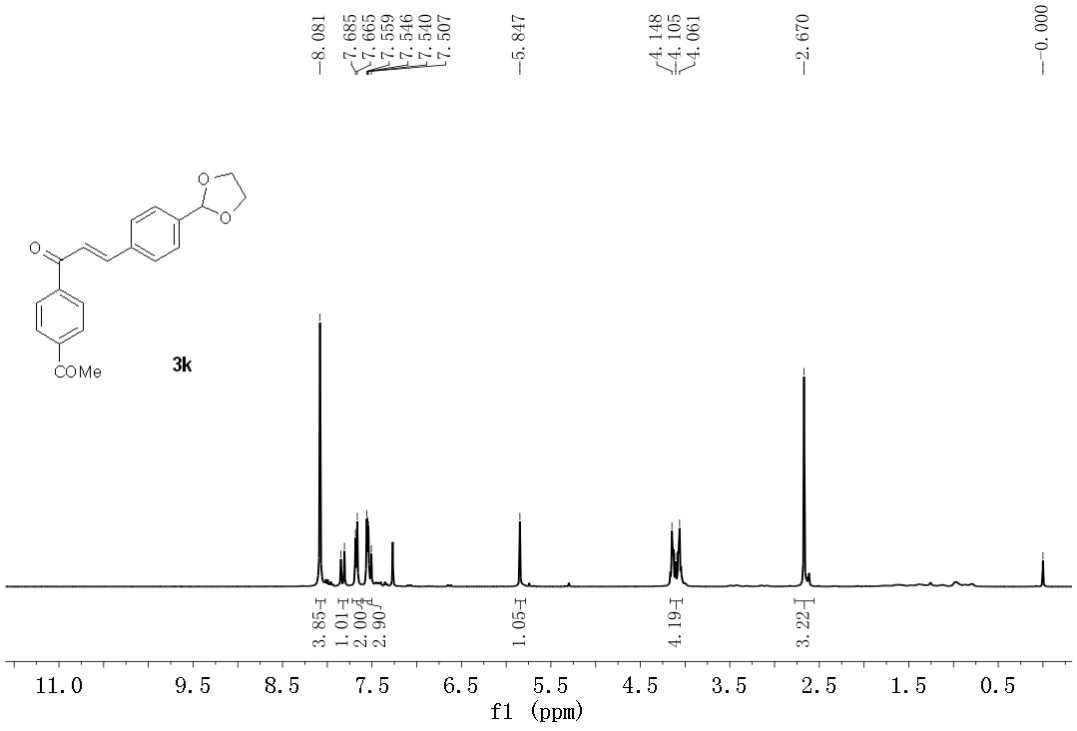
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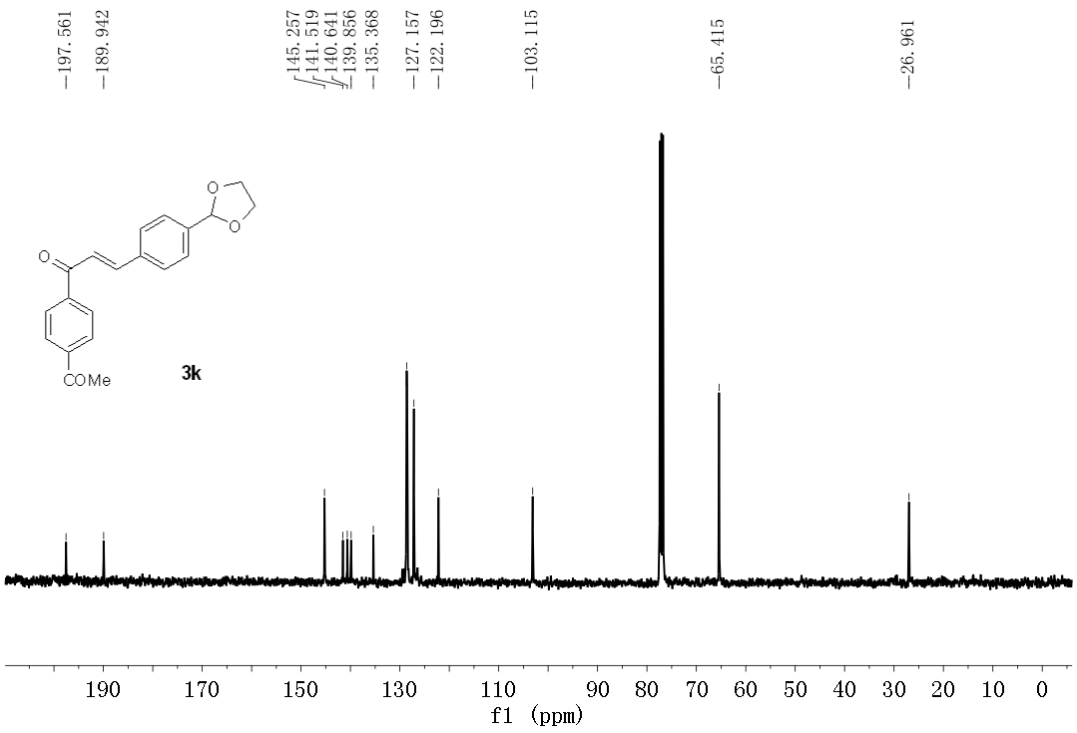
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130
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90
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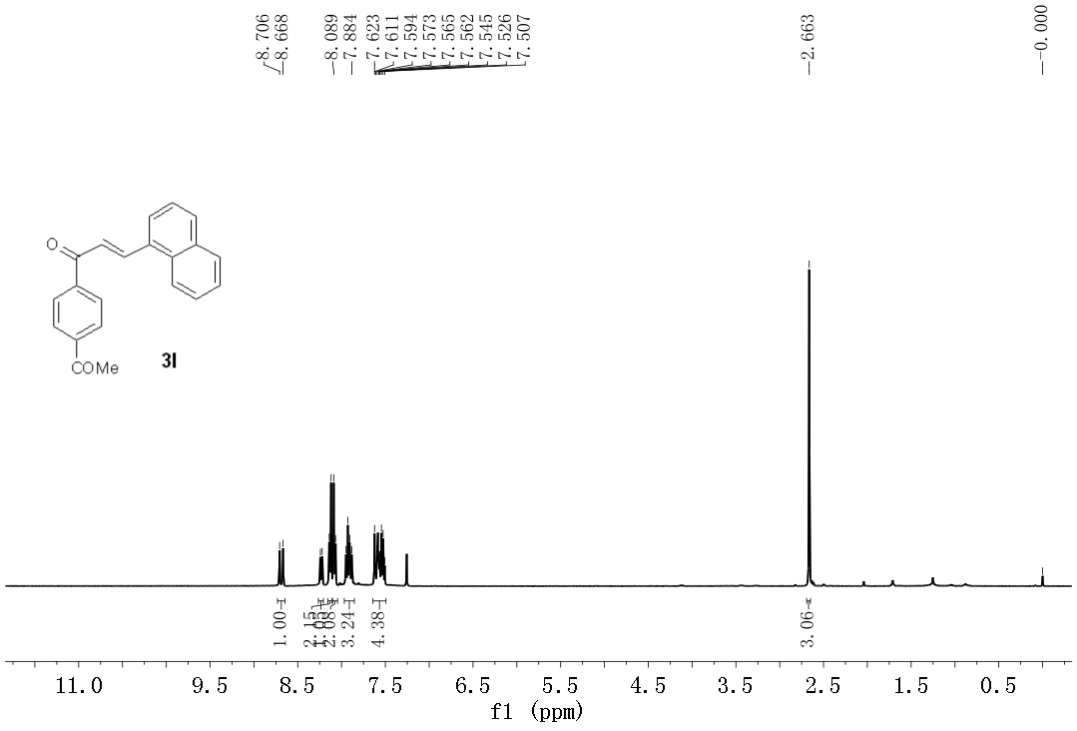
50
40
30
20
10
0
f1 (ppm)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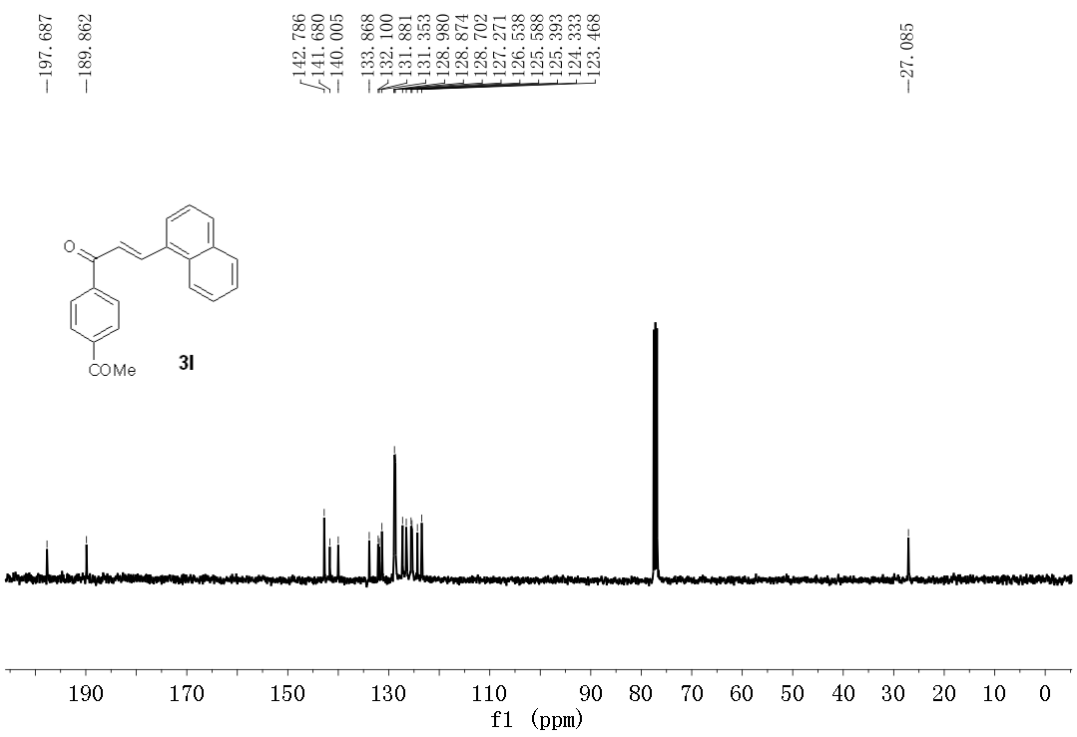
8.668
8.089
7.884
7.623
7.611
7.594
7.573
7.565
7.562
7.545
7.526
7.507
2.663
0.000
O
COMe
3l
1.00
2.15
2.08
3.24
4.38
3.06
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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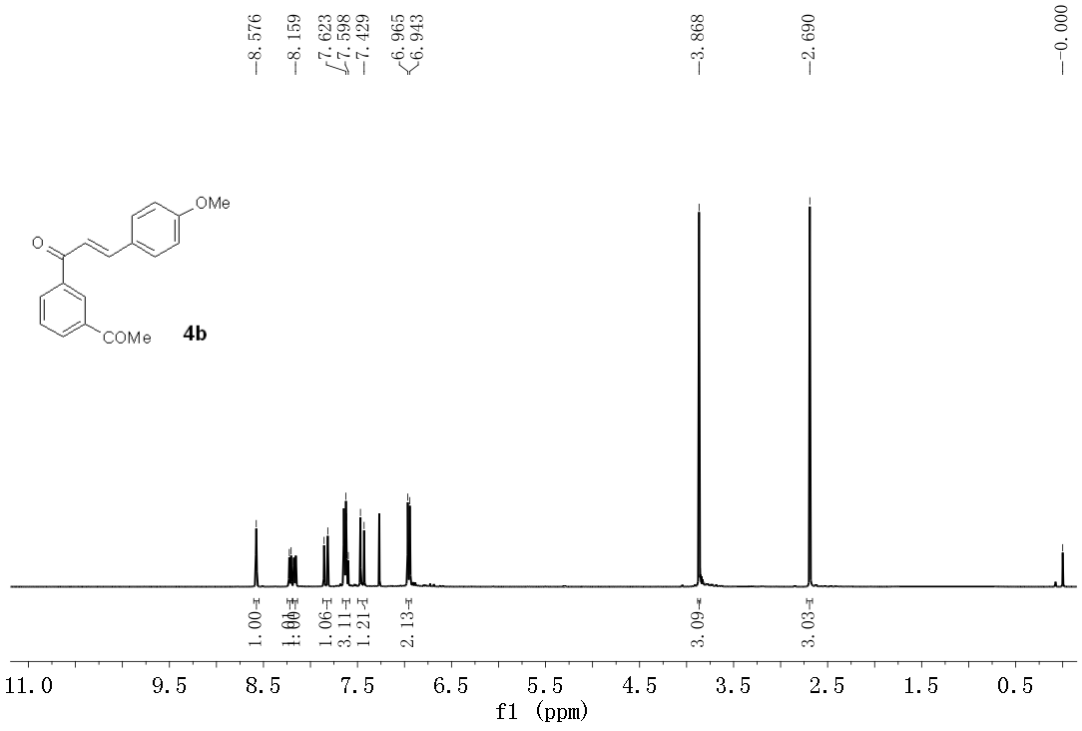
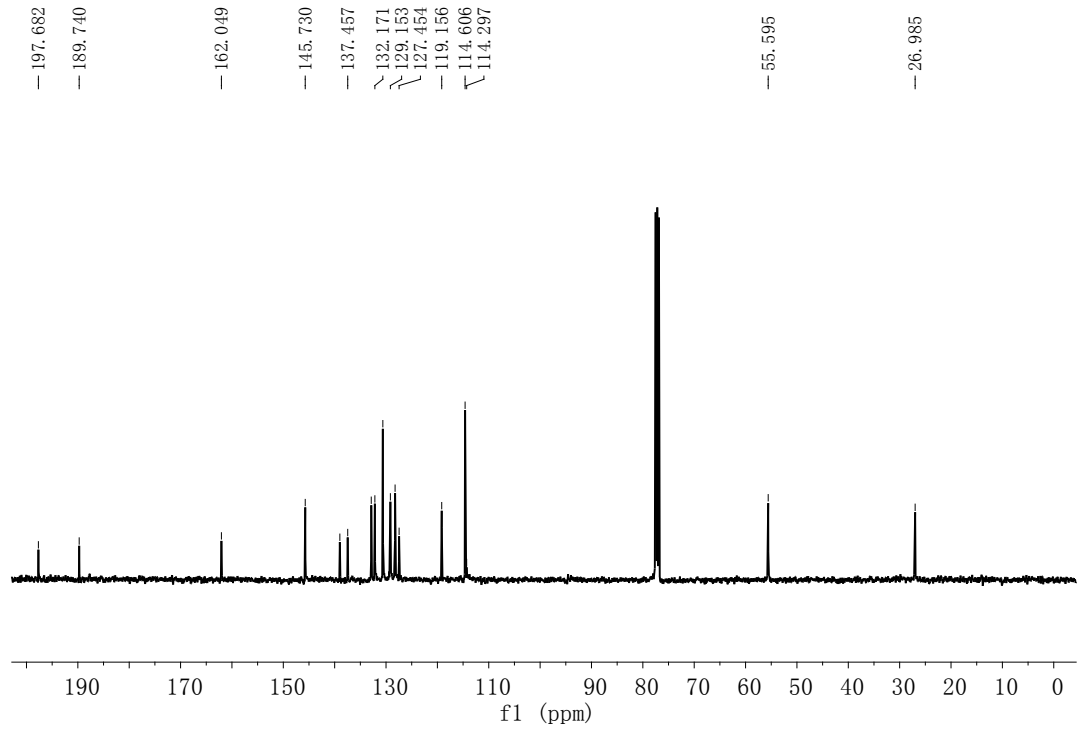
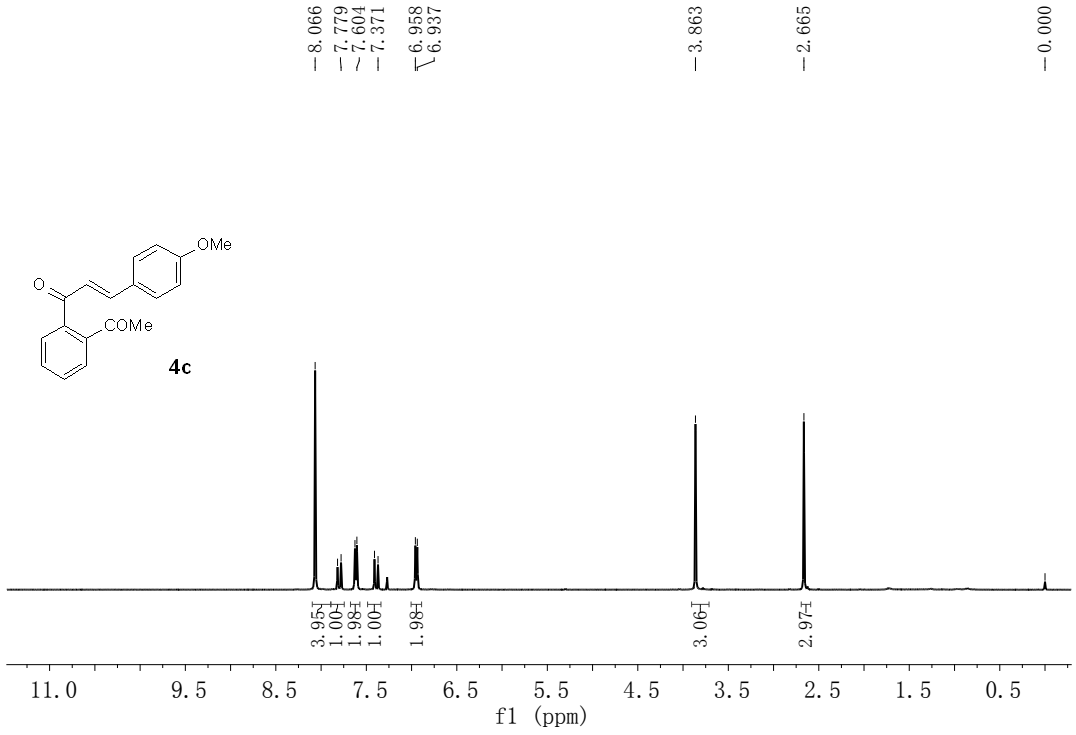
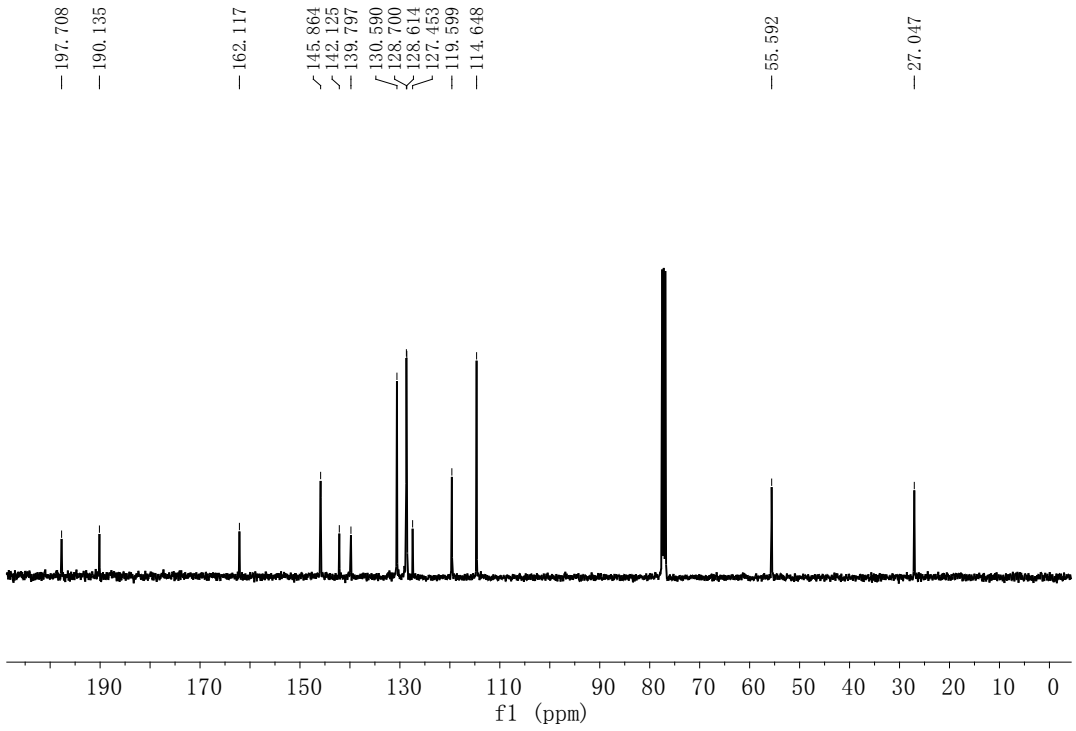
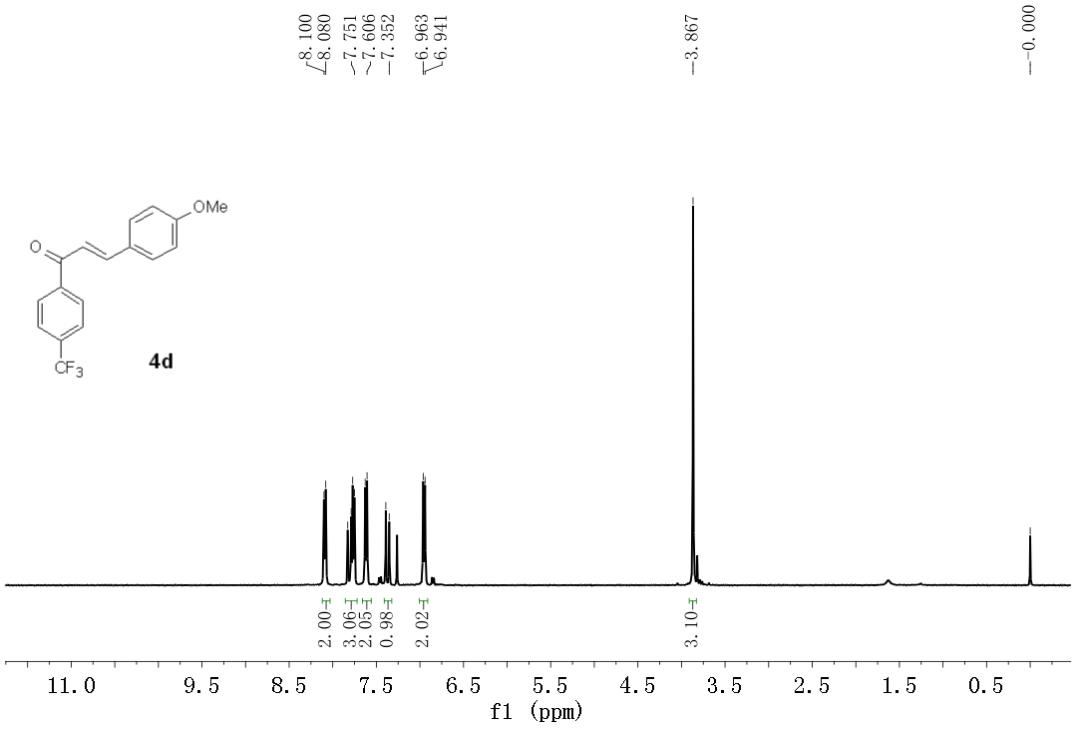
189.862
142.786
141.680
140.005
133.868
132.100
131.881
131.353
128.980
128.874
128.702
127.271
126.538
125.588
125.393
124.333
123.468
27.085
O
COMe
3l
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

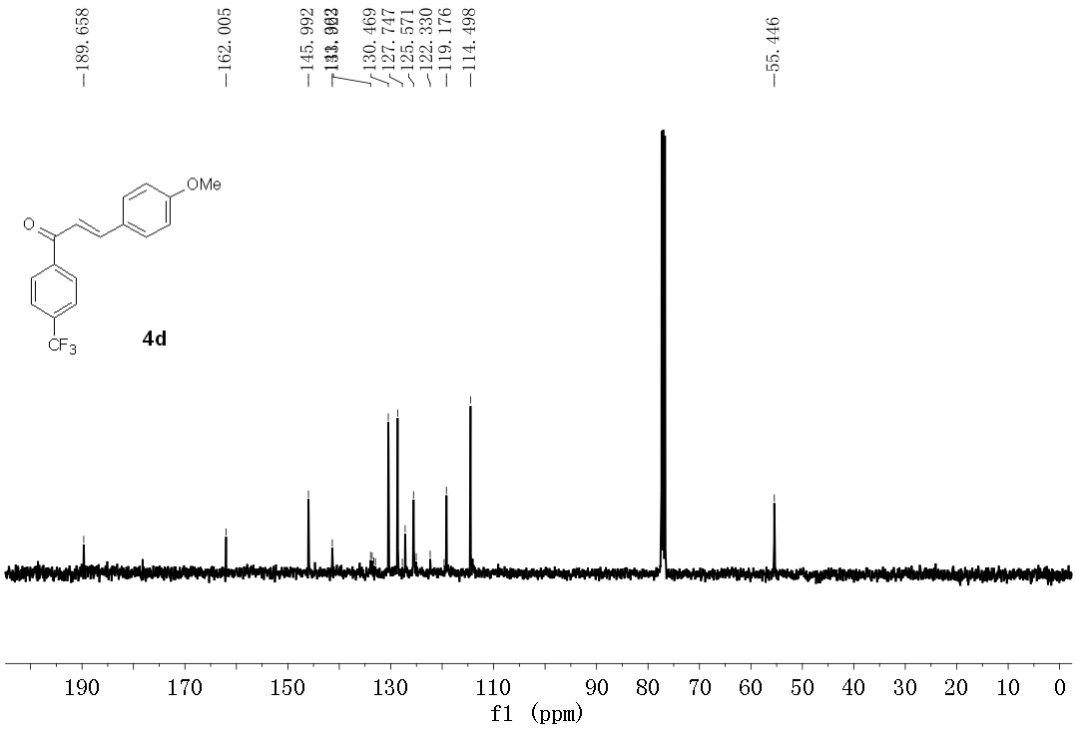

8.576
8.159
7.623
7.598
7.429
6.965
6.943
3.868
2.690
0.000
OMe
O
COMe
4b
1.00
1.00
1.06
3.11
1.21
2.13
3.09
3.03
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

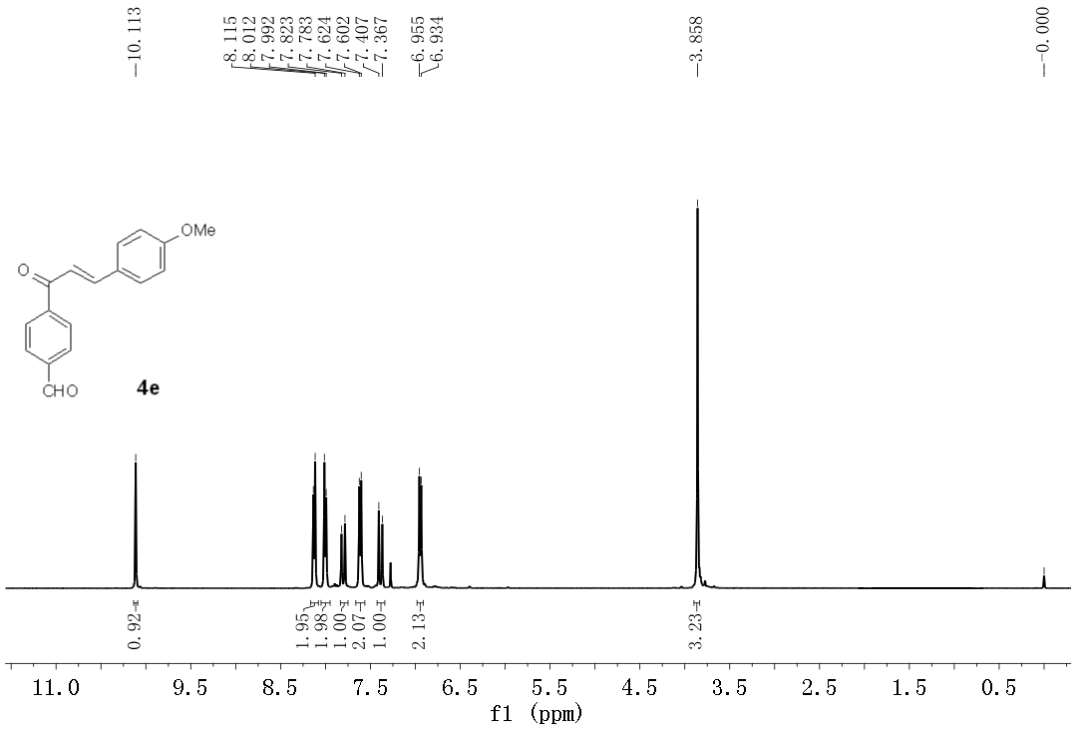

197.682
189.740
162.049
145.730
137.457
132.171
129.153
127.454
119.156
114.606
114.297
55.595
26.985
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

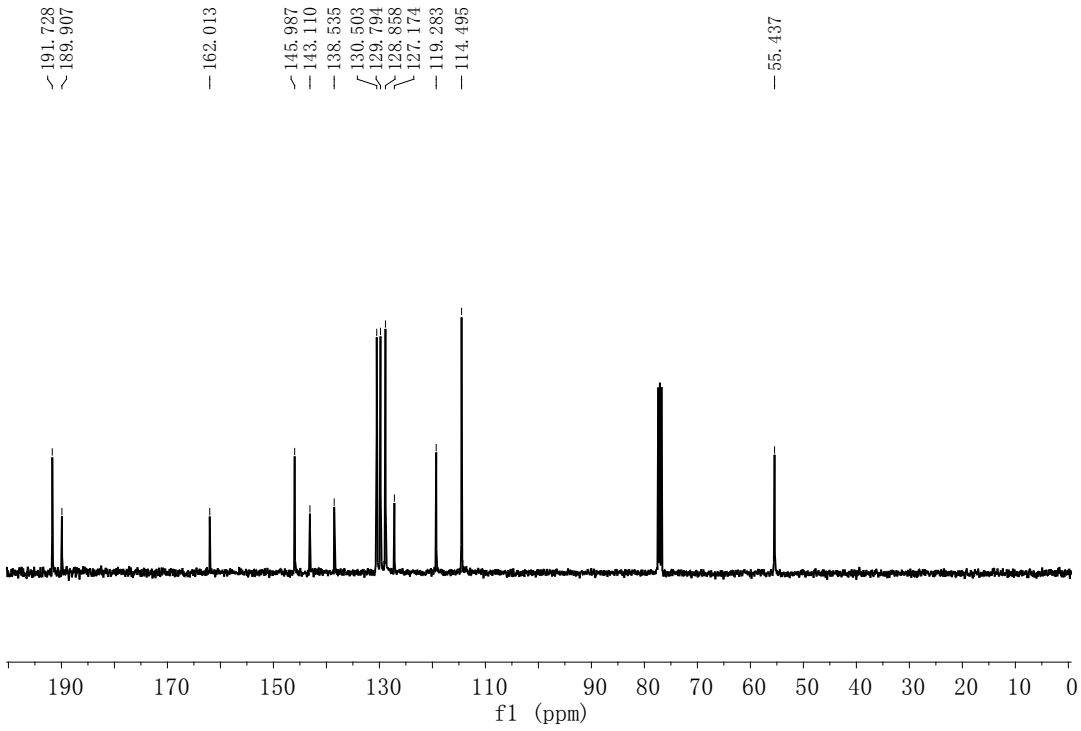

8.066
7.779
7.604
7.371
6.958
6.937
3.863
2.665
0.000
OMe
O
COMe
4c
3.95
1.00
1.98
1.00
1.98
3.06
2.97
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

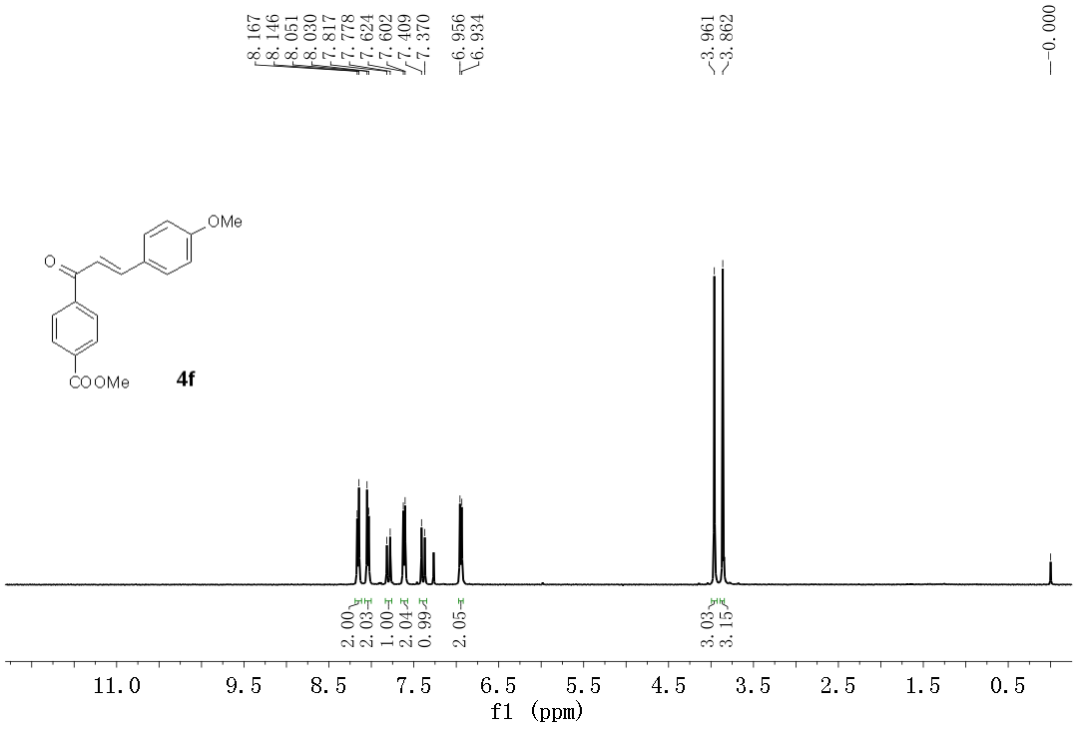

197.708
190.135
162.117
145.864
142.125
139.797
130.590
128.700
128.614
127.453
119.599
114.648
55.592
27.047
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

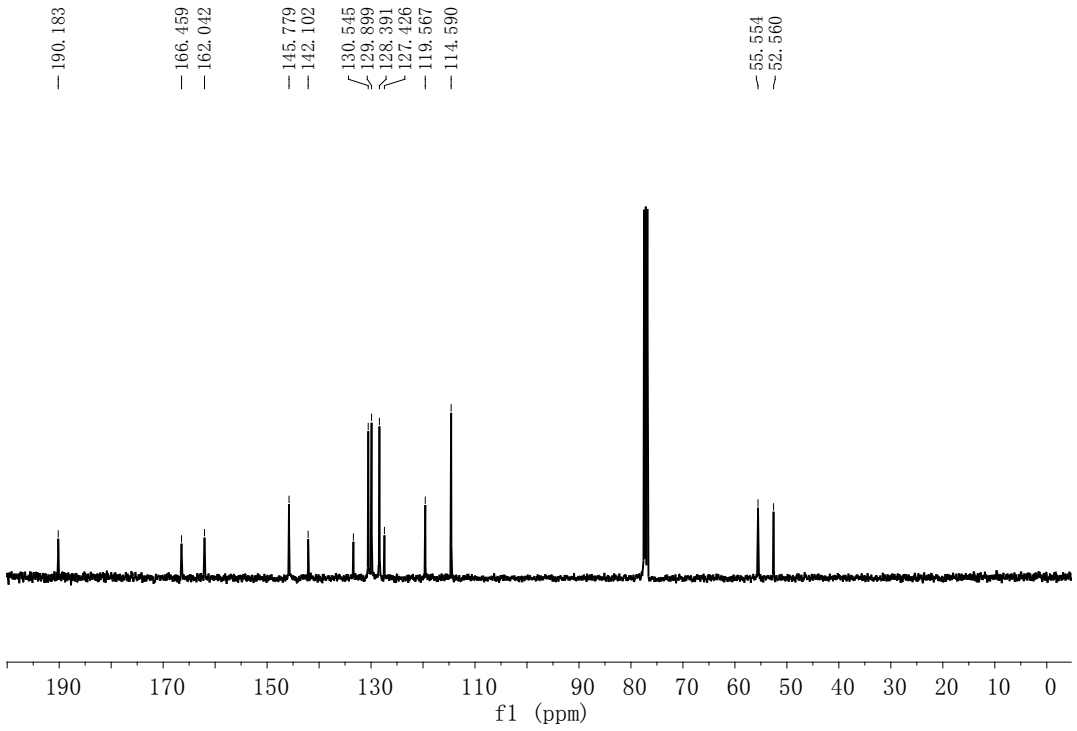

8.100
8.080
7.751
7.606
7.352
6.963
6.941
3.867
0.000
OMe
O
CF3
4d
2.00
3.06
2.05
0.98
2.02
3.10
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

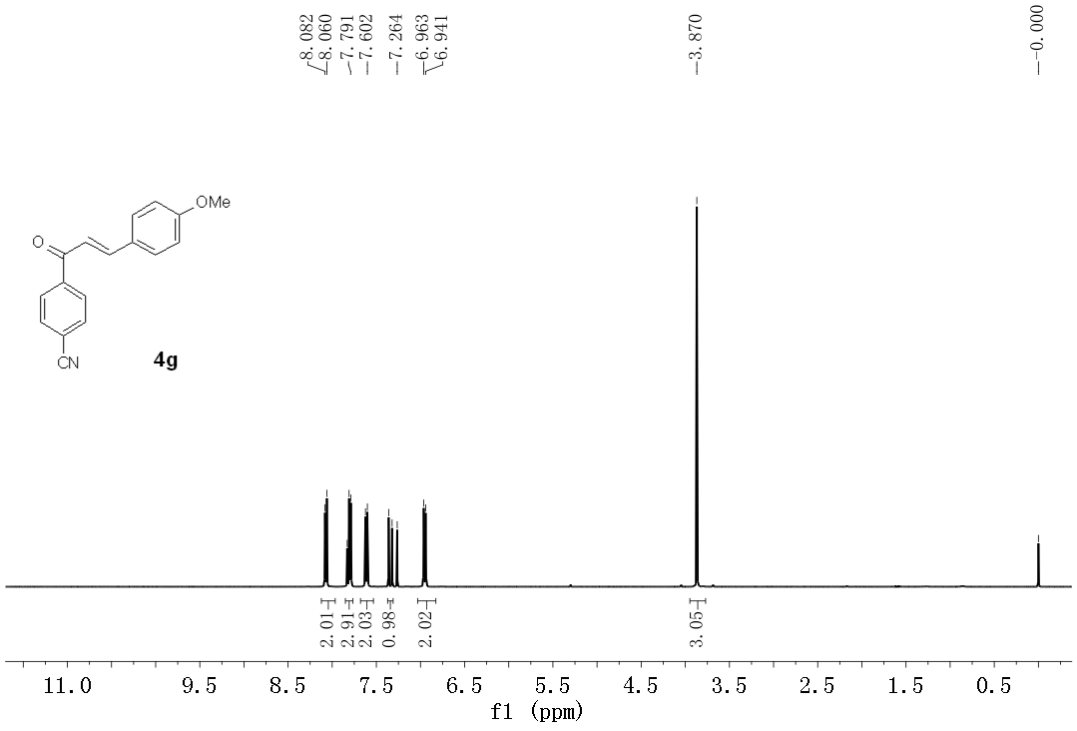

189.658
162.005
145.992
130.469
127.747
125.571
122.330
119.176
114.498
55.446
OMe
O
CF3
4d
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

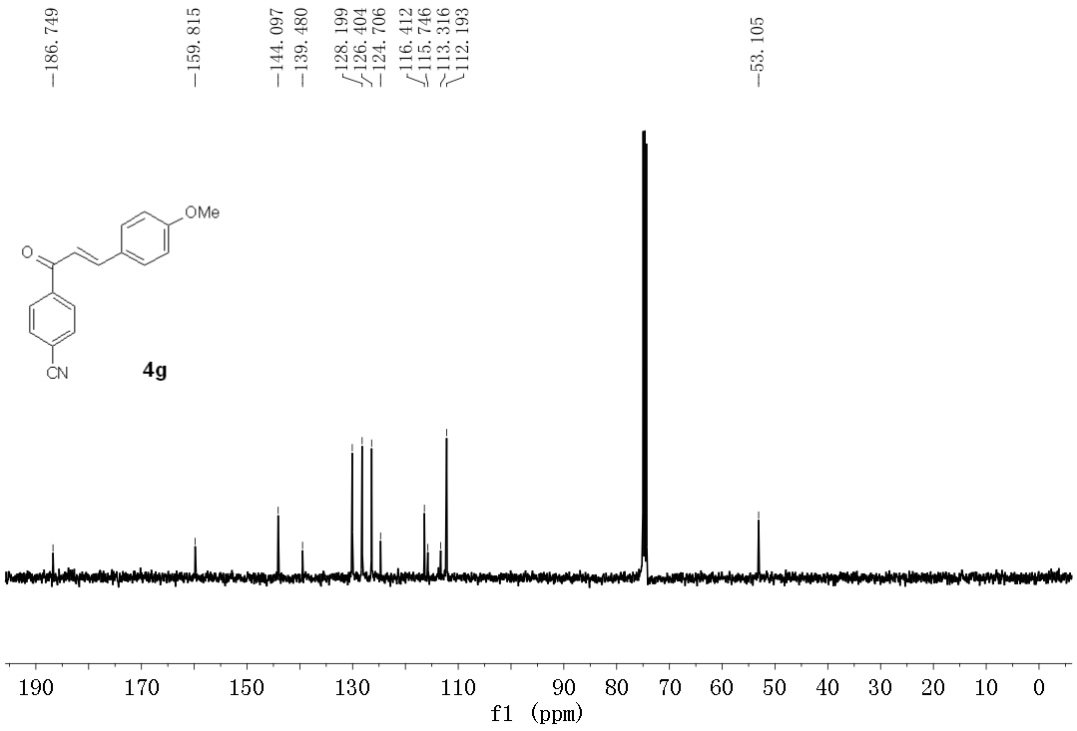

10.113
8.115
8.012
7.992
7.823
7.783
7.624
7.602
7.407
7.367
6.955
6.934
3.858
0.000
OMe
O
CHO
4e
0.92
1.95
1.98
1.00
2.07
1.00
2.13
3.23
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

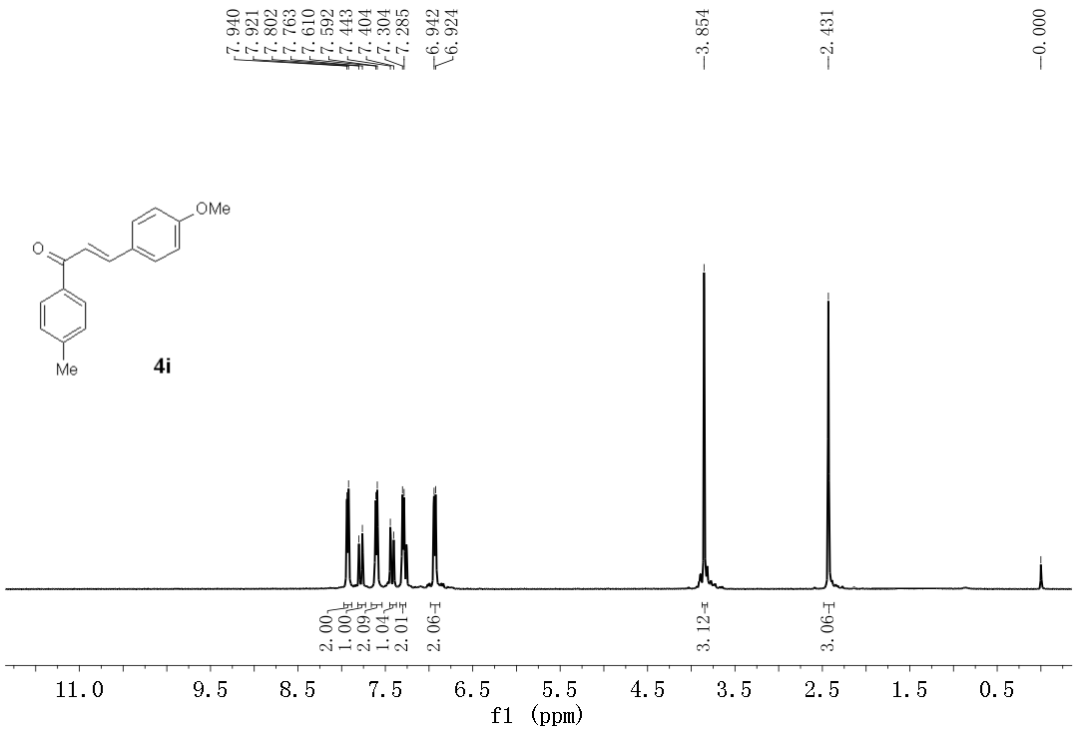

191.728
189.907
162.013
145.987
143.110
138.535
130.503
129.794
128.858
127.174
119.283
114.495
55.437
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

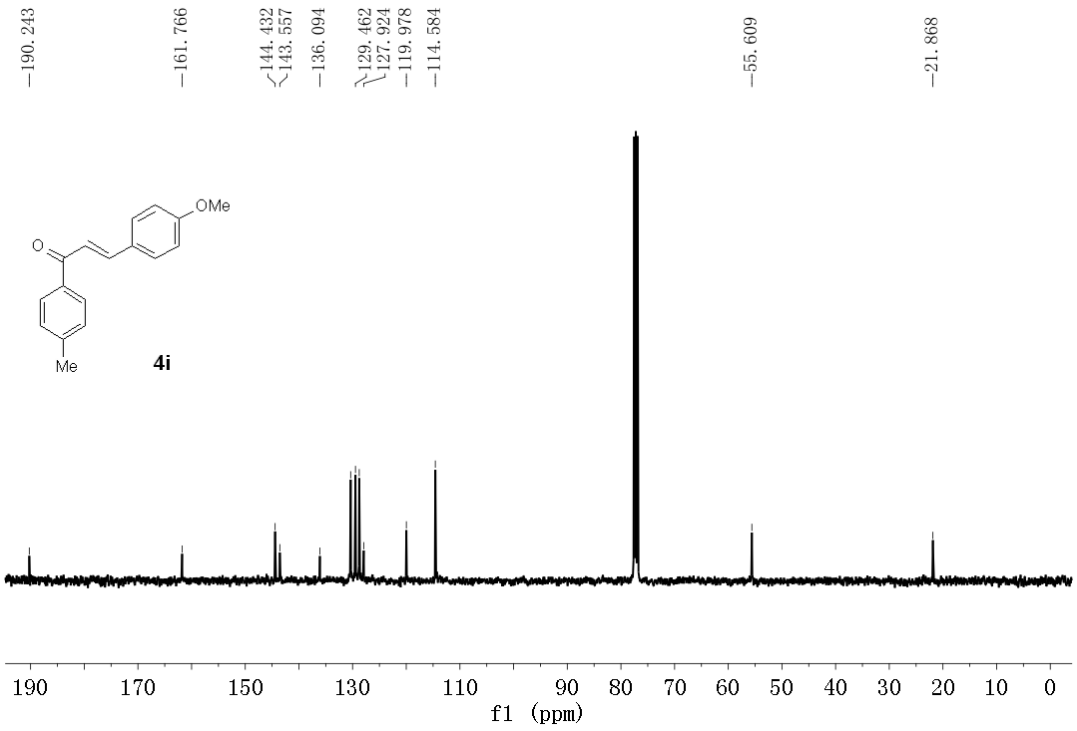

8.167
8.146
8.051
8.030
7.817
7.778
7.624
7.602
7.409
7.370
6.956
6.934
3.961
3.862
0.000
OMe
O
COOMe
4f
2.00
2.03
1.00
2.04
0.99
2.05
3.03
3.15
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

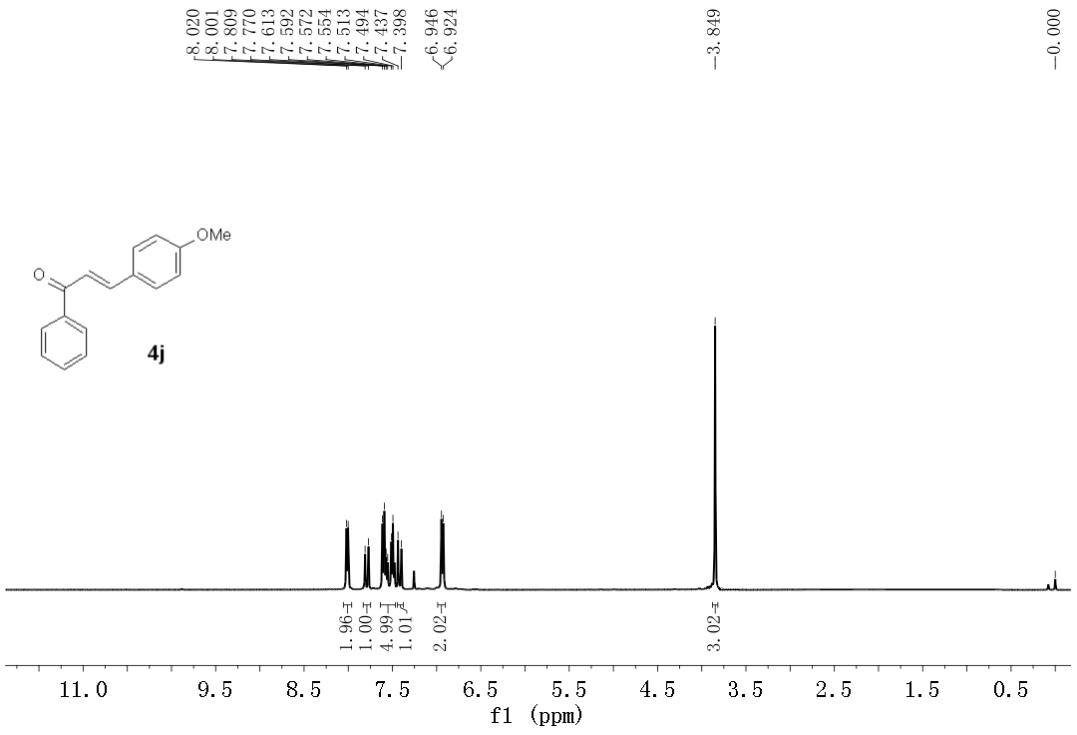

190.183
166.459
162.042
145.779
142.102
130.545
129.899
128.391
127.426
119.567
114.590
55.554
52.560
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

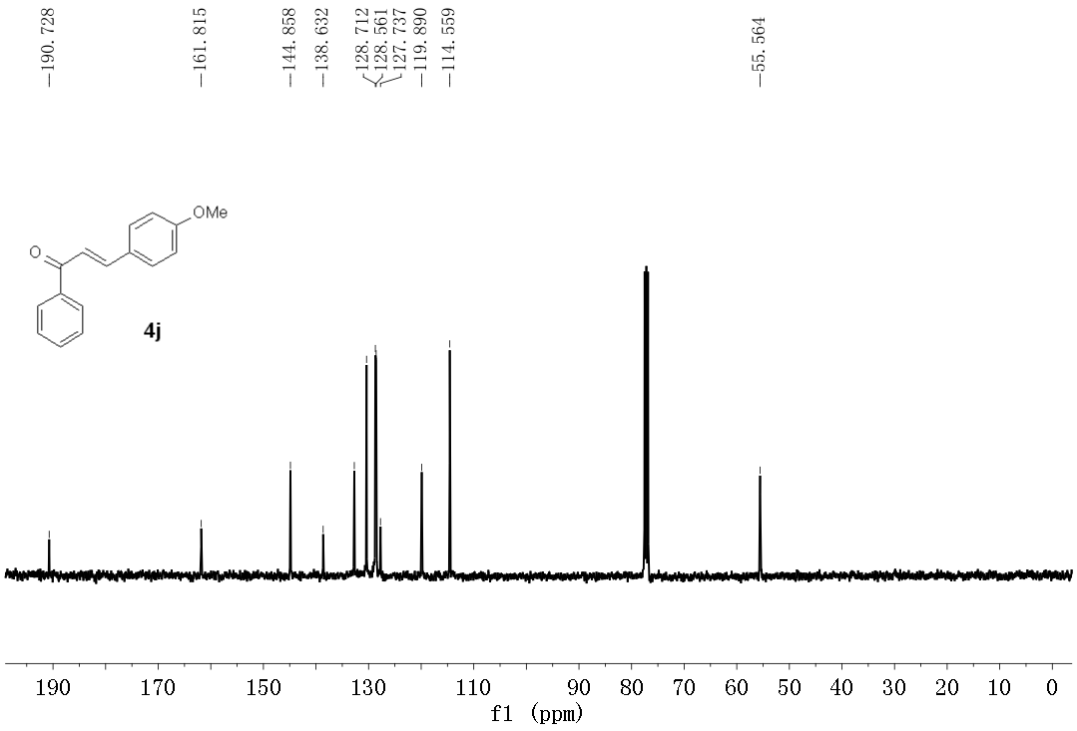

8.082
8.060
7.791
7.602
7.264
6.963
6.941
3.870
0.000
OMe
O
CN
4g
2.01
2.91
2.03
0.98
2.02
3.05
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

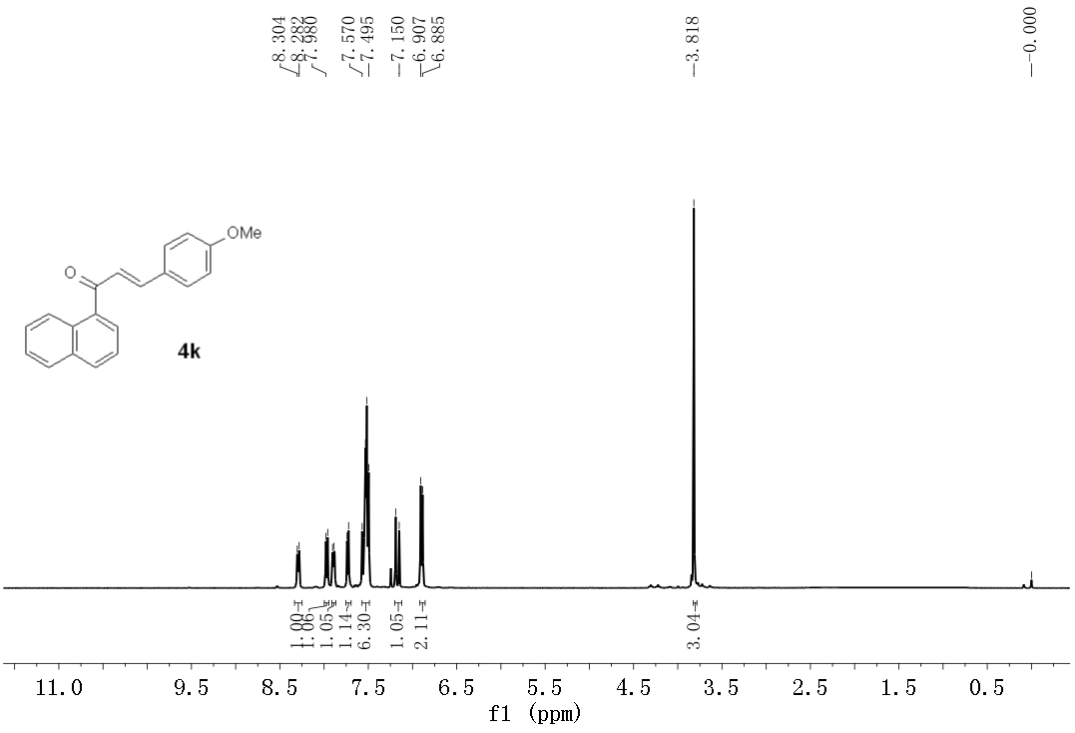

186.749
159.815
144.097
139.480
128.199
126.404
124.706
116.412
115.746
113.316
112.193
53.105
OMe
O
CN
4g
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

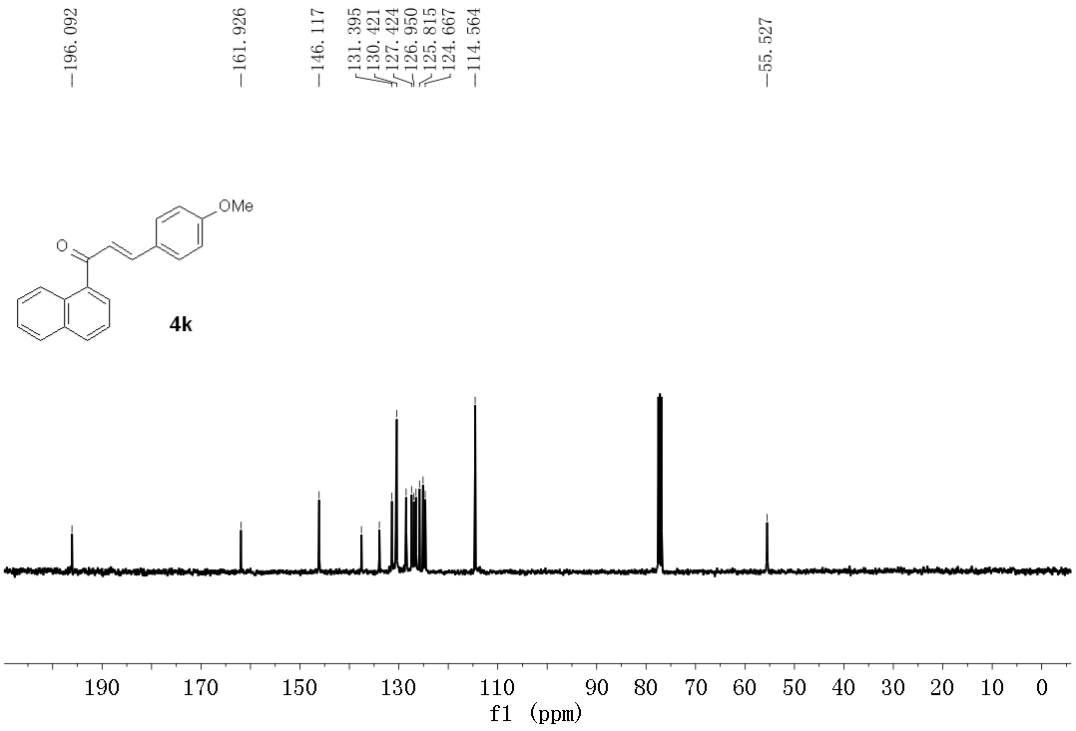

7.940
7.921
7.802
7.763
7.610
7.592
7.443
7.404
7.304
7.285
6.942
6.924
3.854
2.431
0.000
OMe
O
Me
4i
2.00
1.00
2.09
1.04
2.01
2.06
3.12
3.06
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

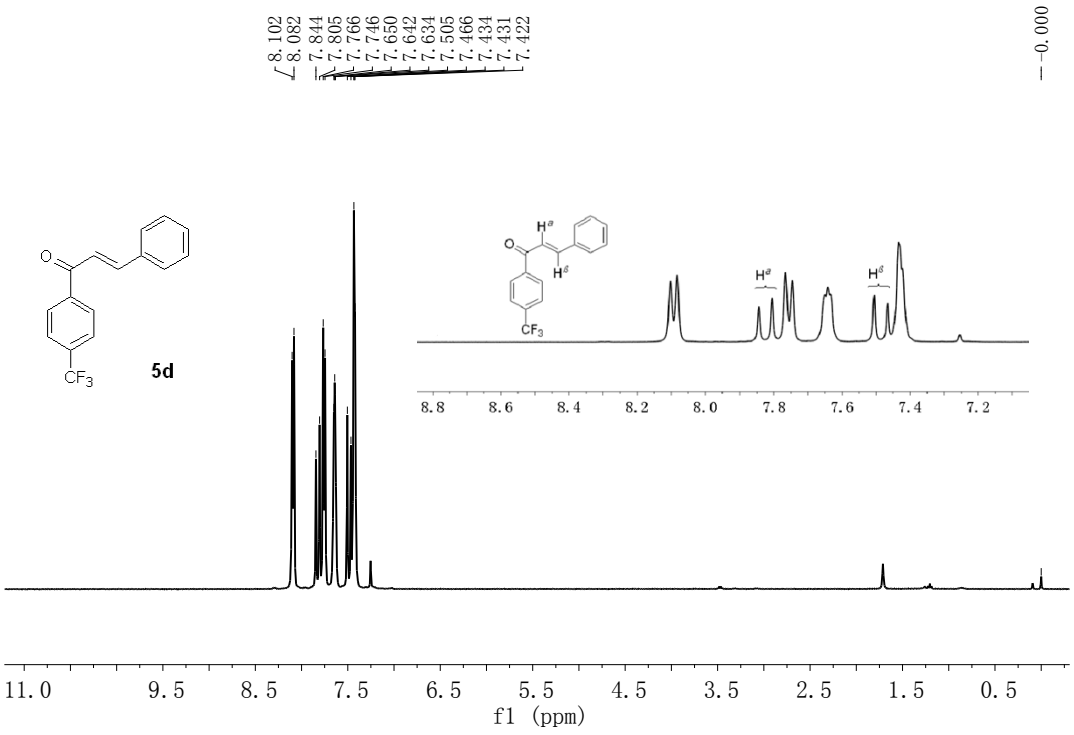

190.243
161.766
144.432
143.557
136.094
129.462
127.924
119.978
114.584
55.609
21.868
OMe
O
Me
4i
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

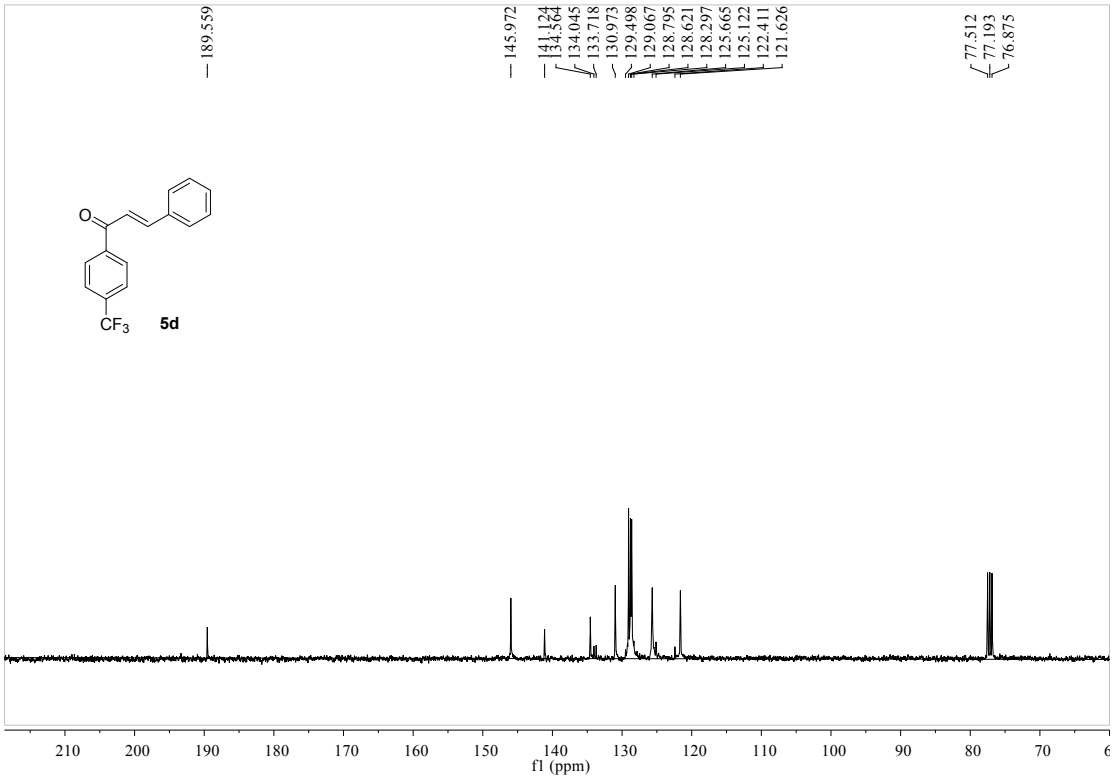

8.020
8.001
7.809
7.770
7.613
7.592
7.572
7.554
7.513
7.494
7.437
7.398
6.946
6.924
3.849
0.000
OMe
O
4j
1.96
1.00
4.99
1.01
2.02
3.02
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

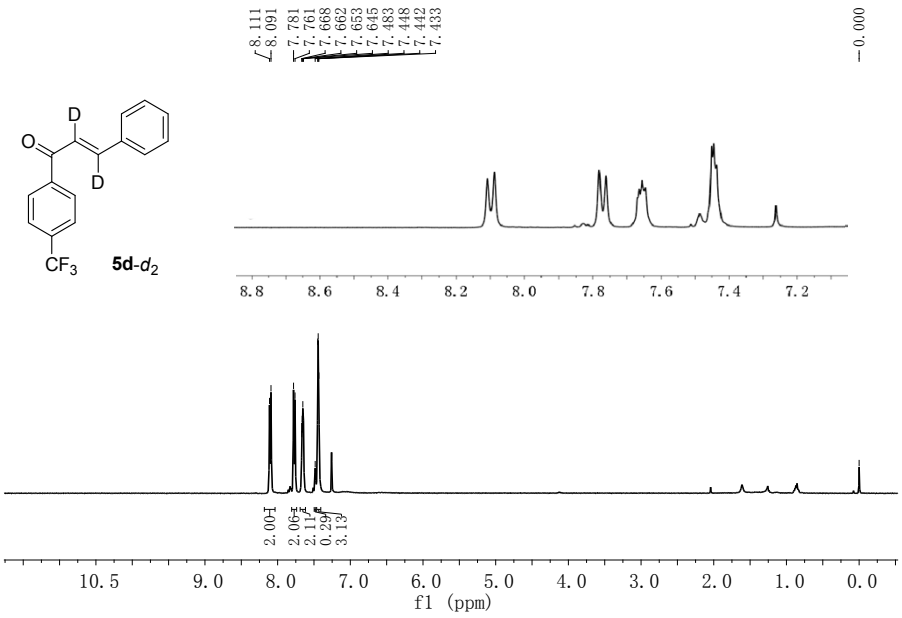

190.728
161.815
144.858
138.632
128.712
128.561
127.737
119.890
114.559
55.564
OMe
O
4j
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.304
8.282
7.980
7.570
7.495
7.150
6.907
6.885
3.818
0.000
OMe
O
4k
1.00
1.06
1.05
1.14
6.30
1.05
2.11
3.04
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


196.092
161.926
146.117
131.395
130.421
127.424
126.950
125.815
124.667
114.564
55.527
OMe
O
4k
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.102
8.082
7.844
7.805
7.766
7.746
7.650
7.642
7.634
7.505
7.466
7.434
7.431
7.422
0.000
5d
H^a
H^β
CF_3
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


189.559
145.972
141.124
134.564
134.045
133.718
130.973
129.498
129.067
128.795
128.621
128.297
125.665
125.122
122.411
121.626
77.512
77.193
76.875
5d
CF_3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
f1 (ppm)


8.111
8.091
7.781
7.761
7.668
7.662
7.653
7.645
7.483
7.448
7.442
7.433
0.000
D
O
D
CF3
5d-d2
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
2.00
2.06
2.11
0.29
3.13
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)