Supporting Information

Controlled Ni-catalyzed mono-and double-decarbonylations of α-ketothioesters

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1. General information

Commercially available reagents were used without further purification. All reactions were carried out under an atmosphere of nitrogen. Column chromatography was carried out on silica gel (200–300 mesh) using a forced flow of eluent at 0.3–0.5 bar pressure. ^{1}H NMR, ^{13}C NMR spectra were recorded on a WNMR-I spectrometer (400 MHz ^{1}H, 101 MHz ^{13}C). The spectra were recorded in $CDCl_3$ as the solvent at room temperature. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to either the residual solvent peak (^{13}C) or TMS (^{1}H) as an internal standard. HRMS were performed on Bruker Daltonics MicroTof-Q II mass spectrometer.

2. Experimental procedures

2.1 Typical Procedure for the Ni -Catalyzed Mono-Decarbonylation.

$Ni(cod)_2$ (2.75 mg, 0.01 mmol), PPh_3 (5.3 mg, 0.02 mmol) and toluene (1 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen, and the resulting mixture was stirred at room temperature for 3 min. A α-ketothioester (0.1 mmol) in toluene (1.0 mL) was then added to the vial and the cap was closed. The contents of the vial were then stirred at 150 °C for 15 h. The reaction was cooled to room temperature, and the crude mixture was filtered through a pad of silica gel. The filtrate was then concentrated *in vacuo* to give a residue, which was purified by flash column chromatography over silica gel.

2.2 Typical Procedure for the Ni -Catalyzed Double-Decarbonylation.

$Ni(cod)_2$ (2.75 mg, 0.01 mmol), IPr^{Me}•HCl (8.3 mg, 0.02 mmol), Cs_2CO_3 (6 mg, 0.02 mmol) and dioxane (1 mL) were added to a 10 mL-sample vial with a Teflon-sealed screwcap in a glovebox filled with nitrogen, and the resulting mixture was stirred at room temperature for 3 min. A α-ketothioester (0.1 mmol) in dioxane (1.0 mL) was then added to the vial and the cap was closed. The contents of the vial were then stirred at 150 °C for 12 h. The reaction was cooled to room temperature, and the crude mixture was filtered through a pad of silica gel. The filtrate was then concentrated *in vacuo* to give a residue, which was purified by flash column chromatography over silica gel.

3. Spectral data

S-Phenyl benzothioate (**2a**).[1] White solid; mp 52-53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.0 Hz, 2H), 7.62–7.61 (m, 1H), 7.59–7.46 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 136.6, 135.1, 133.6, 129.5, 129.2, 128.7, 128.5, 127.3; HRMS *m/z* calcd for $C_{13}H_{10}OSNa$ $[M + Na]^+$ 237.0345, found 237.0341.

***S*-*p*-Tolyl benzothioate** (**2b**).[1] White solid; mp 78-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.38 (d, J = 12.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 139.8, 136.7, 135.0, 133.6, 130.1, 128.7, 127.5, 123.8, 21.4; HRMS *m/z* calcd for $C_{14}H_{12}OSNa$ $[M + Na]^+$ 251.0501, found 251.0526.

***S*-(4-(tert-butyl)phenyl) benzothioate** (**2c**). White solid; mp 73-75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 4.0 Hz, 1H), 7.57–7.46 (m, 6H), 1.35 (s, 9H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 190.6, 152.8, 136.8, 134.7, 133.6, 128.7, 127.5, 126.5, 123.9, 34.8, 31.3; HRMS *m/z* calcd for $C_{17}H_{18}OS$ $[M + Na]^+$ 293.0971, found: 293.1007.

***S*-(4-Methoxyphenyl) benzothioate (2d).**[2] White solid; mp 97-99 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 4.0 Hz, 1H), 7.48 (dd, J = 16.0, 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 160.8, 136.6, 134.5, 133.6, 128.7, 127.5, 117.8, 115.0, 55.4; HRMS *m/z* calcd for $C_{14}H_{12}O_2SNa$ $[M + Na]^+$ 267.0450, found: 267.0475.

***S*-(4-Fluorophenyl) benzothioate (2e).**[2] White solid; mp 51-52 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02–8.01 (m, 2H), 7.61 (t, J = 8.0 Hz, 1H), 7.50–7.43 (m, 2H), 7.18–7.11 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 163.6 (d, $J_{C\text{-}F}$ = 249.0 Hz), 137.2 (d, $J_{C\text{-}F}$ = 9.0 Hz), 136.4, 133.8, 128.8, 127.5, 122.6 (d, $J_{C\text{-}F}$ = 4.0 Hz), 116.6 (d, $J_{C\text{-}F}$ = 22.0 Hz); HRMS *m/z* calcd for $C_{13}H_9OFSNa$ $[M + Na]^+$ 255.0250, found: 255.0258.

***S*-(4-Chlorophenyl) benzothioate (2f).**[1] White solid; mp 64-66 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05–7.96 (m, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.48–7.39 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 136.3, 136.0, 133.9, 129.5, 128.8, 127.5, 125.8; HRMS *m/z* calcd for $C_{13}H_9OClSNa$ $[M + Na]^+$ 270.9955, found 270.9981.

***S*-4-Bromophenyl benzothioate (2g).**[1] White solid. mp 68-70 ℃; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, J = 8.0 Hz, 2H), 7.62–7.56 (m, 3H), 7.48 (t, J = 8.0 Hz, 2H), 7.46–7.35 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 189.5, 136.5, 136.4, 133.9, 132.5, 128.8, 127.5, 126.5, 124.3. HRMS *m/z* calcd for $C_{13}H_9OBrSNa$ $[M + Na]^+$ 314.9450, found 314.9447.

***S*-Phenyl 2-methylbenzothioate (2h)**[1] yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, J = 8.0 Hz, 2H), 7.54–7.52 (m, 2H), 7.52–7.46 (m, 3H), 7.37–7.31 (m, 3H), 2.50 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.1, 137.4, 136.7, 134.9, 132.0, 131.7, 129.5, 129.2, 128.6, 128.2, 125.8, 20.8. HRMS *m/z* calcd for $C_{14}H_{12}OSNa$ $[M + Na]^+$ 251.0501, found 251.0527.

***S*-phenyl 4-isopropylbenzothioate (2i)** yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.52–7.46 (m, 3H), 7.33 (d, J = 8.0 Hz, 2H), 3.01–2.94 (m, 1H), 1.29 (d, J = 8.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.7, 155.3, 135.1, 134.2, 129.2, 127.7, 127.6, 126.8, 34.3, 24.6. HRMS m/z calcd for $C_{16}H_{16}NaOS$ $[M + Na]^+$ 279.0814, found 279.0841.

Methyl 4-((phenylthio)carbonyl)benzoate (2j)[2] White solid. mp 109-111 ℃; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.15–8.13 (m, 2H), 8.09–8.07 (m, 2H), 7.53–7.52 (m, 2H), 7.51- 7.46 (m, 3H), 3.96 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.7, 166.0, 139.9, 135.0, 134.3, 129.9, 129.3, 127.3, 126.8, 52.4. HRMS m/z calcd for $C_{15}H_{12}NaO_3S$ $[M + Na]^+$ 295.0399, found 295.0403.

***S*-Phenyl 4-methoxybenzothioate (2k).**[2] Yellow solid. mp 90-92 ℃; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, J = 8.0 Hz, 2H), 7.50–7.43 (m, 2H), 7.45–7.40 (m, 3H), 6.95 (d, J = 8.0 Hz, 2H), 3.90 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 188.5, 164.0, 135.2, 129.7, 129.4, 129.3, 129.1, 127.7, 114.0, 55.5. HRMS *m/z* calcd for $C_{14}H_{12}O_2SNa$ $[M + Na]^+$ 267.0450, found: 267.0462.

***S*-Phenyl 3,4-dimethoxybenzothioate (2l).** Yellow solid. mp 101-103 ℃; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, J = 8.0 Hz, 2H), 7.53–7.50 (m, 2H), 7.45–7.43 (m, 2H), 6.92 (d, J = 8.0 Hz, 2 H), 3.95 (s, 3H), 3.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 188.7, 153.7, 149.0, 135.1, 129.5, 129.4, 129.2, 127.6, 122.0, 110.3, 109.7, 56.1, 56.0. HRMS *m/z* calcd for $C_{15}H_{14}O_3SNa$ $[M + Na]^+$ 297.0556, found: 297.0559.

***S*-Phenyl naphthalene-2-carbothioate (2m).**[2] White solid. mp 118-120 ℃;^1H NMR ($CDCl_3$, 400 MHz) δ 8.61 (s, 1 H), 8.04–8.00 (m, 2H), 7.92–7.87 (m, 2H), 7.67–7.59 (m, 4H), 7.49–7.46 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.1, 135.9, 135.1, 133.9, 133.8, 132.5, 129.6, 129.5, 129.3,

129.0, 128.6, 127.8, 127.4, 127.0, 123.2. HRMS *m/z* calcd for $C_{17}H_{12}OSNa$ $[M + Na]^+$ 287.0501, found: 287.0500.

***S*-Pentyl benzothioate** (**2n**). Brown oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 8.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 3.07 (t, J = 8.0 Hz, 2H), 1.68 (t, J = 8.0 Hz, 2H), 1.45–1.43 (m, 4H), 0.91 (t, J = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.2, 137.3, 133.2, 128.6, 127.2, 31.1, 29.3, 29.1, 22.3, 13.9. HRMS m/z calcd for $C_{12}H_{16}OSNa$ $[M + Na]^+$ 231.0814, found 231.0802.

***S*-Phenyl 4-(dibenzo[*b,d*]thiophen-4-yl)benzothioate (2o)**.[2] White solid. mp 141-143 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.58–7.56 (m, 2H), 7.53–7.50 (m, 5H), 7.41–7.40 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.6, 146.4, 139.7, 135.3, 135.1, 129.5, 129.2, 129.0, 128.3, 128.0, 127.40, 127.3, 127.2. HRMS *m/z* calcd for $C_{19}H_{14}OSNa$ $[M + Na]^+$ 313.0658, found: 313.0651.

Diphenylsulfide (**3a**).[2] Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.30 (m, 5H), 7.28–7.21 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 129.0, 127.5, 127.2.

Phenyl(p-tolyl)sulfide (3b).[2] Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.29 (m, 6H), 7.25–7.12 (m, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 137.1, 132.3, 131.2, 130.1, 129.9, 129.1, 126.4, 21.2.

(4-tert-Butylphenyl)phenylsulfane (3c).[3] Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.35–7.08 (m, 9H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 131.4, 130.4, 130.2, 129.0, 127.8, 126.7, 126.2, 34.6, 31.2.

(4-Methoxyphenyl)phenylsulfane (**3d**).[3] Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.42 (dd, J = 8.0, 4.0 Hz, 2H), 7.25–7.21 (m, 2H), 7.17–7.13 (m, 3H), 6.82 (d, J = 8.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 138.5, 135.3, 128.8, 128.1, 125.7, 124.2, 114.9, 55.3.

(4-Fluorophenyl)phenylsulfane (3e).[3] Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.36–7.30 (m, 2H), 7.26–7.19 (m, 5H), 7.02 (t, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, $J_{C\text{-}F}$ = 246 Hz), 136.6, 134.10 (d, $J_{C\text{-}F}$ = 8.0 Hz), 130.2 , 129.9, 126.7, 116.4 (d, $J_{C\text{-}F}$ = 22.0 Hz).

(4-Chlorophenyl)phenylsulfane (3f).[2] Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.22 (m, 7H), 7.16 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 134.7, 132.1, 132.0, 131.4, 129.5, 129.3, 127.5.

(4-Bromophenyl)phenylsulfane (3g).[2] Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.44–7.22 (m, 7H), 7.16 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 132.6, 132.2, 132.0, 131.4, 129.3, 127.5.

Phenyl(o-tolyl)sulfide (3h).[2] Colorless oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.33–7.28 (m, 3H), 7.26–7.11 (m, 6H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 136.1, 133.7, 133.0, 130.5, 129.6, 129.1, 127.9, 126.7, 126.3, 20.6.

(4-Isopropylphenyl)phenylsulfane (3i).[3] Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.33–7.16 (m, 9H), 2.92–2.85 (m, 1H), 1.25 (d, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 136.8, 131.9, 130.0, 129.2, 129.0, 127.4, 126.4, 33.7, 23.8.

Methyl 4-(phenylthio)benzoate (3j).[2] Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, J = 8.0 Hz, 2H), 7.50–7.47 (m, 2H), 7.40–7.37 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 144.3, 133.7, 132.4, 130.1, 129.6, 128.6, 127.6, 125.8, 52.1;

(3,4-Dimethoxyphenyl)(phenyl)sulfane (3l). Colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.26–7.14 (m, 6H), 7.17–7.12 (m, 1H), 6.85 (d, J = 8.0 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 149.3, 138.3, 128.9, 128.2, 126.6, 125.8, 124.5, 116.5, 11.7, 55.9,

55.9.

(Naphthalen-2-yl)phenylsulfane (**3m**).[2] White solid. mp 49-51; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (s, 1H), 7.79–7.70 (m, 3H), 7.45–7.36 (m, 5H), 7.31–7.21 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 133.839, 133.059, 132.339, 131.009, 129.9, 129.1, 128.9, 128.8, 127.7, 127.4, 127.0, 126.6, 126.2.

[1,1'-biphenyl]-4-yl(phenyl)sulfane (3o).[2] White solid. mp 70-71 ℃;^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57–7.55 (d, J = 8.0 Hz, 2H), 7.52–7.50 (d, J = 8.0 Hz, 2H), 7.44–7.38 (m, 6H), 7.31–7.24 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 139.9, 135.6, 134.8, 131.3, 131.1, 129.2, 128.8, 127.8, 127.5, 127.1, 126.9.

Characterization Data for Starting Materials

Note: All starting materials have been prepared according to the previously published procedures.[4]

***S*-Phenyl 2-oxo-2-phenylethanethioate** (**1a**). Yellow solid. mp 47-49 ℃;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 4.0 Hz, 2H), 7.67–7.63 (m, 1H), 7.51–7.47 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 186.0, 135.5, 134.7, 131.5, 120.9, 129.5, 128.9. HRMS *m/z* calcd for $C_{14}H_{10}O_2SNa$ $[M + Na]^+$ 265.0294, found 265.0316.

***S*-(p-Tolyl) 2-oxo-2-phenylethanethioate** (**1b**). Yellow solid. mp 65-67 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 8.0 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.37 (d, J = 4.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 186.2, 140.4, 135.8, 134.6, 131.6, 130.9, 130.4, 128.9, 122.7, 21.4. HRMS *m/z* calcd for $C_{15}H_{12}O_2SNa$ $[M + Na]^+$ 279.0450, found 279.0482.

***S*-(4-(Tert-butyl)phenyl) 2-oxo-2-phenylethanethioate** (**1c**). Yellow solid. mp 74-76 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 2H), 7.58 (dd, J = 12.0, 4.0 Hz, 1H), 7.41–7.33 (m, 6H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 186.2, 153.3, 135.1, 134.4, 131.6, 130.8, 129.0, 126.7, 123.0, 34.9, 31.3. HRMS *m/z* calcd for $C_{18}H_{18}O_2S$ $[M + Na]^+$ 321.0920, found: 321.0918.

***S*-(4-Methoxyphenyl) 2-oxo-2-phenylethanethioate (1d).** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 4.0 Hz, 1H), 7.47 (t, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 186.4, 161.2, 136.6, 135.1, 131.5, 130.1, 128.9, 116.6, 115.2, 55.4. HRMS *m/z* calcd for $C_{15}H_{12}O_3SNa$ $[M + Na]^+$ 295.0399, found: 295.0408.

***S*-(4-Fluorophenyl) 2-oxo-2-phenylethanethioate (1e).** Yellow solid. mp 95-97 ℃;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.13 (d, J = 8.0 Hz, 2H), 7.63 (t, J = 8.0 Hz, 1H), 7.48–7.46 (m, 4H), 7.18–7.15 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 185.6, 165.1 (d, $J_{C\text{-}F}$ = 250.0 Hz), 136.7 (d, $J_{C\text{-}F}$ = 9.0 Hz), 135.1, 131.1, 130.9, 128.8, 121.6 (d, $J_{C\text{-}F}$ = 3.0 Hz), 116.9 (d, $J_{C\text{-}F}$ = 22.0 Hz); HRMS *m/z* calcd for $C_{14}H_9O_2FSNa$ $[M + Na]^+$ 283.0199, found: 283.0229.

***S*-(4-Chlorophenyl) 2-oxo-2-phenylethanethioate (1f).** Yellow solid. mp 71-73 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.52–7.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 185.5, 136.5, 135.9, 135.2, 131.4, 130.9, 129.8, 129.0, 125.0. HRMS *m/z* calcd for $C_{14}H_9O_2ClSNa$ $[M + Na]^+$ 298.9904, found 298.9913.

***S*-(4-Bromophenyl) 2-oxo-2-phenylethanethioate (1g).** Yellow solid. mp 72-74 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.7.81 (d, J = 8.0 Hz, 2H), 7.50–7.44 (m, 6H), 7.30–7.25 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 190.3, 189.5, 136.1, 135.2, 132.8, 131.3, 130.9, 128.9, 125.6, 124.8. HRMS *m/z* calcd for $C_{14}H_9O_3BrSNa$ $[M + Na]^+$ 342.9399, found 342.9924.

***S*-Phenyl 2-oxo-2-(o-tolyl)ethanethioate (1h)** Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, J = 8.0 Hz, 2H), 7.54–7.52 (m, 2H), 7.52–7.46 (m, 3H), 7.37–7.31 (m, 3H), 2.50 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.5, 188.8, 141.3, 134.6, 133.6, 132.3, 132.2, 130.5, 129.9, 129.4, 126.4, 125.6, 21.4. HRMS *m/z* calcd for $C_{15}H_{12}O_2SNa$ $[M + Na]^+$ 279.0450, found 279.0458.

***S*-Phenyl 2-(3-isopropylphenyl)-2-oxoethanethioate (1i)**. Yellow solid. mp 44-46 ℃;^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.14 (d, J = 8.0 Hz, 2H), 7.52–7.46 (m, 5H), 7.33 (d, J = 8.0 Hz, 2H), 3.01–2.94 (m, 1H), 1.26 (d, J = 4.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.1, 185.5, 157.1, 134.6, 131.1, 129.9, 129.4, 129.2, 127.1, 126.5, 34.5, 23.5. HRMS m/z calcd for $C_{17}H_{16}NaO_2S$ $[M + Na]^+$ 307.0763, found 307.0761.

Methyl 3-(2-oxo-2-(phenylthio)acetyl)benzoate (**1j**) Yellow solid. mp 50-52 ℃;^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.22 (t, J = 4.0 Hz, 2H), 8.13 (t, J = 4.0 Hz, 2H), 7.50 (m, 5 H), 3.96 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.5, 185.3, 165.9, 135.4, 134.8, 134.6, 130.8, 129.9, 129.8, 129.5, 52.6. HRMS m/z calcd for $C_{16}H_{12}NaO_4S$ $[M + Na]^+$ 323.0349, found 323.0345.

***S*-phenyl 2-(3-methoxyphenyl)-2-oxoethanethioate (1k).** Yellow solid. mp 74-76 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, J = 8.0 Hz, 2 H), 7.50–7.45 (m, 5 H), 6.95 (d, J = 20.0 Hz, 2 H), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.5, 183.9, 165.2, 134.6, 133.4, 129.8, 129.3, 126.7, 124.2, 114.3, 55.6. HRMS *m/z* calcd for $C_{15}H_{12}O_3SNa$ $[M + Na]^+$ 295.0399, found: 295.0392.

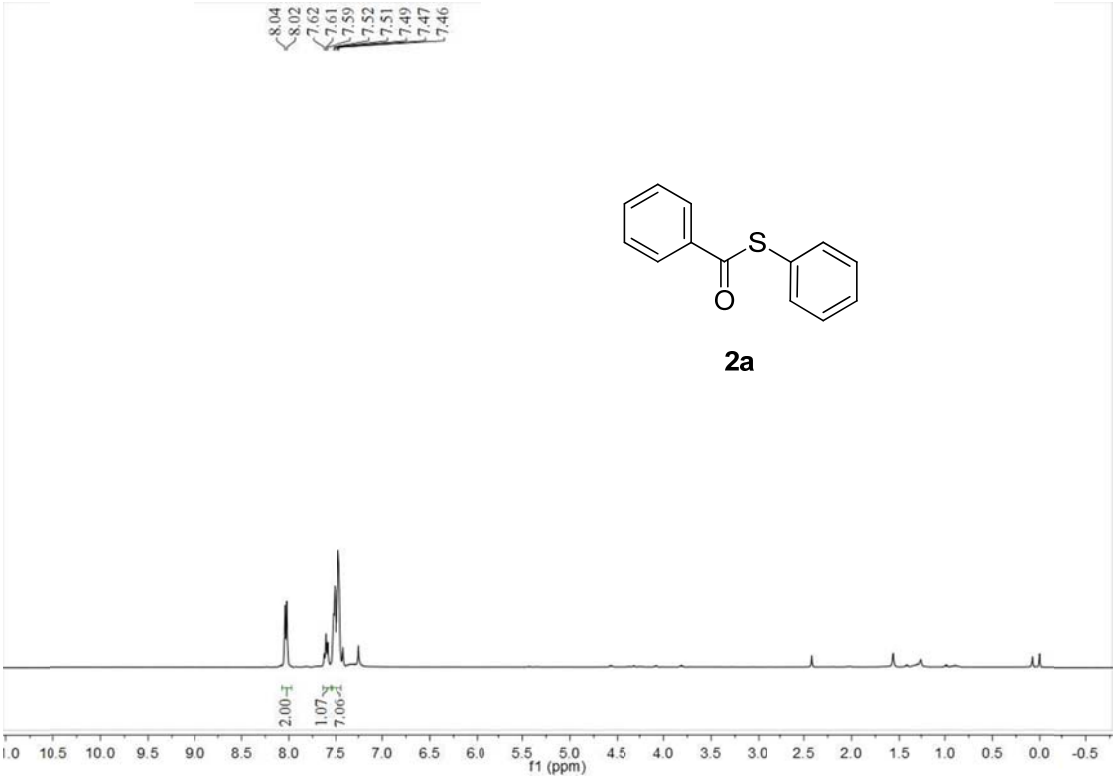
***S*-phenyl 2-(3,4-dimethoxyphenyl)-2-oxoethanethioate (1l).** Yellow solid. mp 82-84 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 4.0 Hz, 1H), 7.51–7.47 (m, 5H), 6.90 (d, J = 12.0 Hz, 2H), 3.97 (s, 3 H), 3.93 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.4, 183.9, 155.2, 149.3, 134.7, 129.8, 129.4, 127.1, 126.7, 124.3, 110.8, 110.3, 56.2, 56.0. HRMS *m/z* calcd for $C_{16}H_{14}O_4SNa$ $[M + Na]^+$ 325.0505, found: 325.0502.

***S*-phenyl 2-(naphthalen-2-yl)-2-oxoethanethioate** (**1m**). Yellow solid. mp 70-71 ℃;^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.82 (s, 1 H), 8.12 (d, J = 8.0 Hz, 1H), 7.95–7.86 (m, 3H), 7.64–7.49 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.2, 185.5, 136.3, 134.8, 134.5, 132.3, 130.2, 129.9, 129.7, 129.5, 129.0, 128.6, 127.8, 127.1, 126.6, 124.7. HRMS *m/z* calcd for $C_{18}H_{12}O_2SNa$ $[M + Na]^+$ 315.0405, found: 315.0402.

***S*-pentyl 2-oxo-2-phenylethanethioate** (**1n**). Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.12 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 8.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 2H), 3.05 (t, J = 8.0 Hz, 2H), 1.69 (t, J = 8.0 Hz, 2H), 1.38–1.33 (m, 4H), 0.92 (t, J = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.0, 186.4, 134.8, 131.7, 130.7, 128.8, 31.0, 28.9, 22.2, 22.1, 13.9. HRMS m/z calcd for $C_{20}H_{14}O_2SNa$ $[M + Na]^+$ 259.0763, found 259.0755.

***S*-phenyl 2-([1,1'-biphenyl]-4-yl)-2-oxoethanethioate (1o)**. Yellow solid. mp 68-70 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.23 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.52–7.40 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.0, 185.2, 147.6, 139.3, 134.6, 131.4, 130.0, 129.8, 129.4, 129.0, 128.6, 127.4, 127.3, 126.4. HRMS *m/z* calcd for $C_{20}H_{14}O_2SNa$ $[M + Na]^+$ 341.0607, found: 341.0602.

4. ^{1}H and ^{13}C NMR spectra



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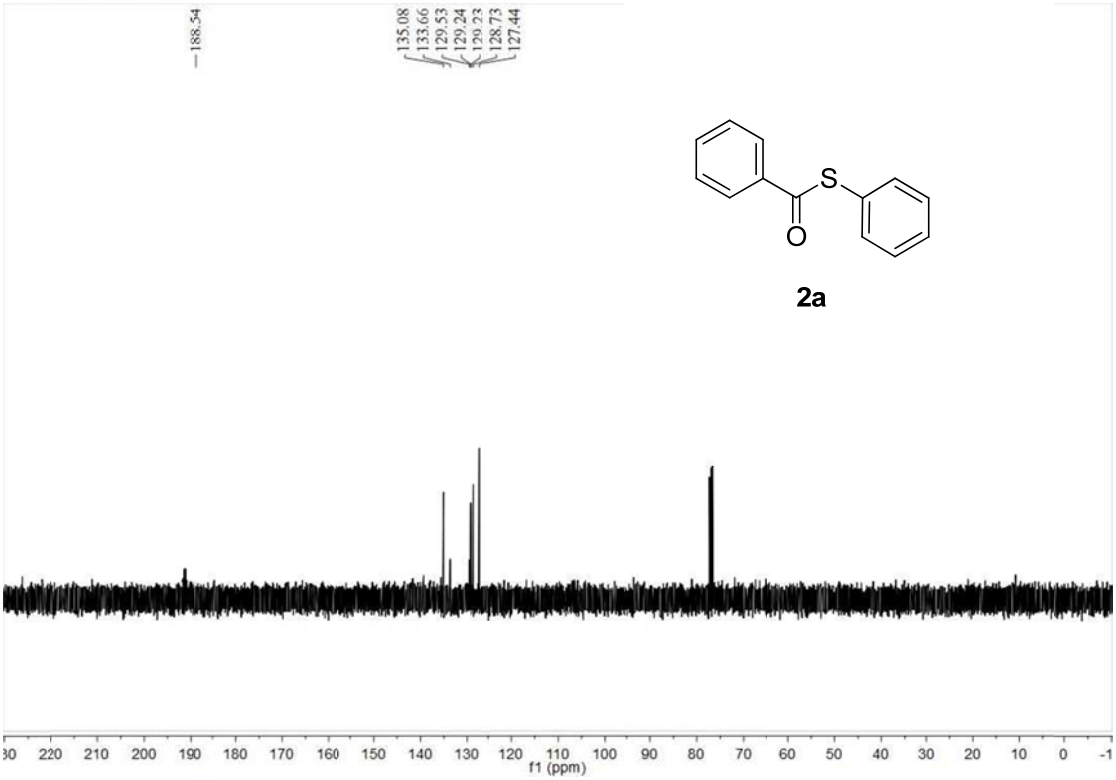

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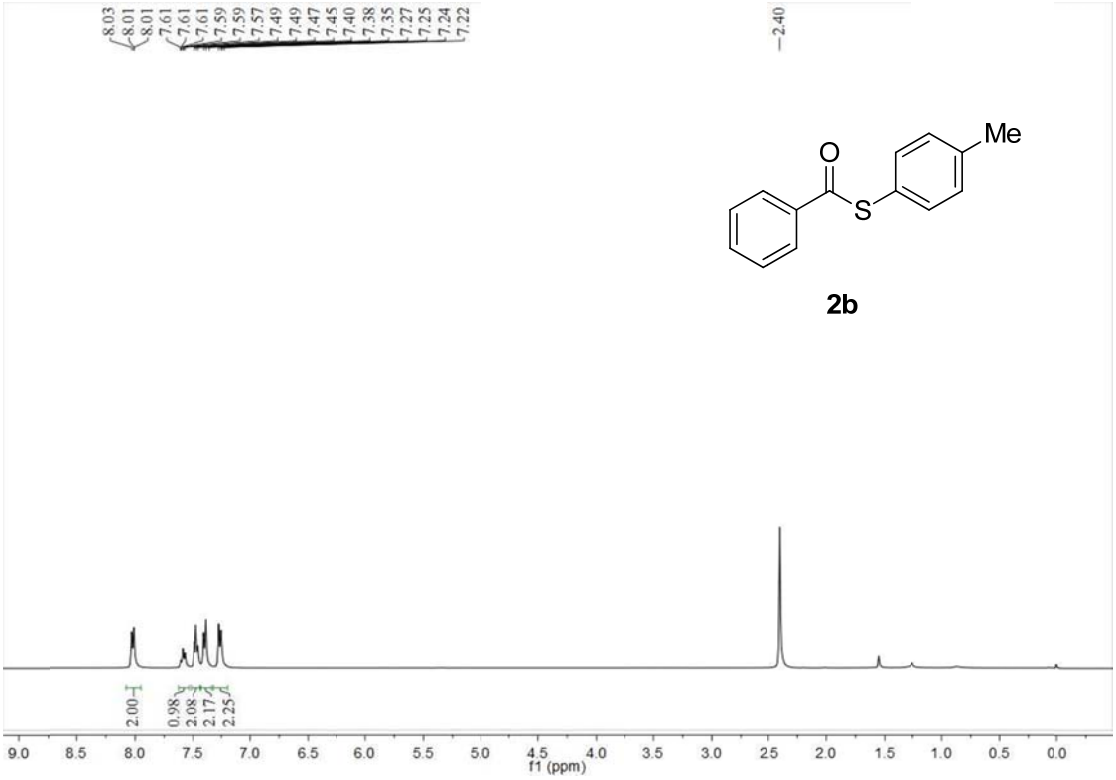
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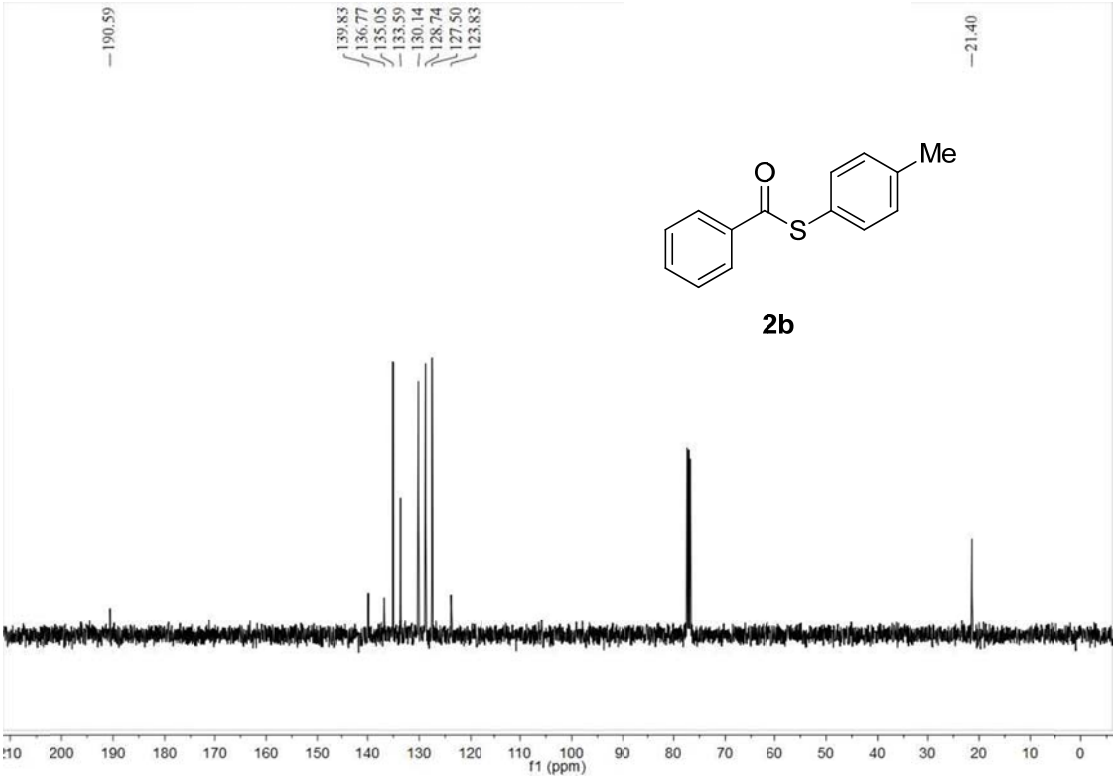
7.40
7.38
7.35
7.27
7.25
7.24
7.22
2.40
O
S
Me
2.00
0.98
2.08
2.17
2.25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2b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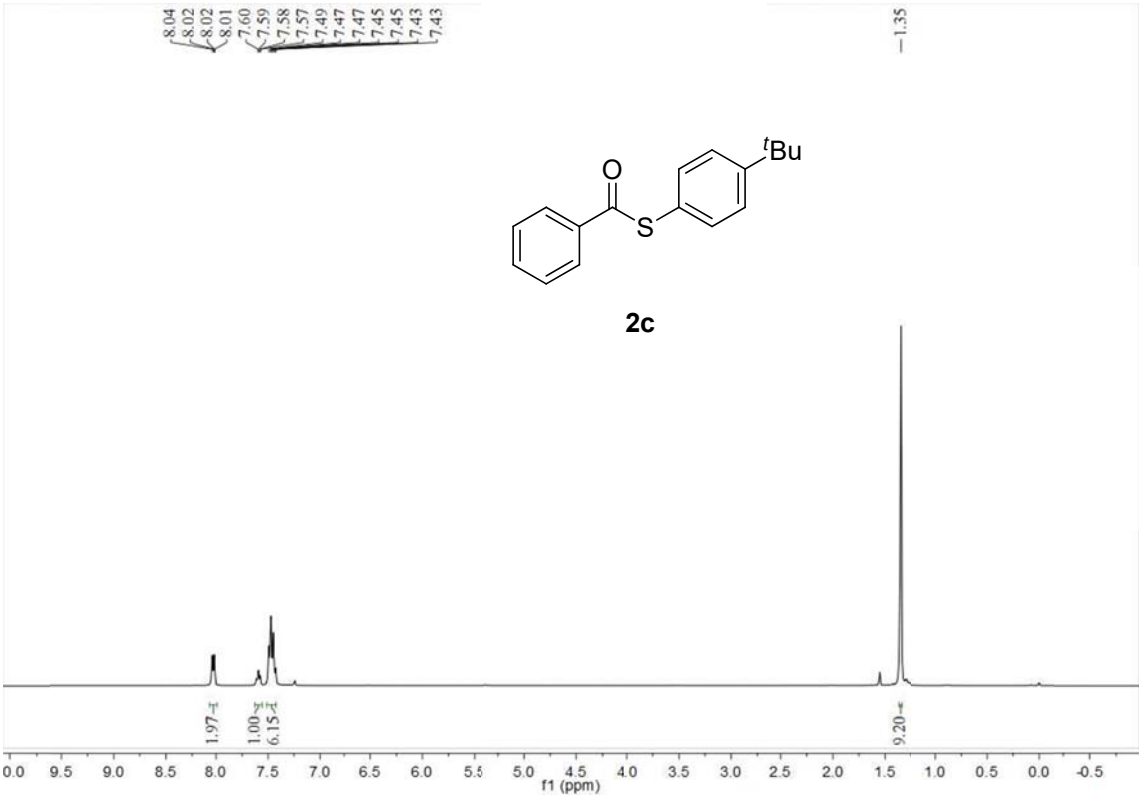
S
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2b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1.35
O
S
tBu
2c
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1.00
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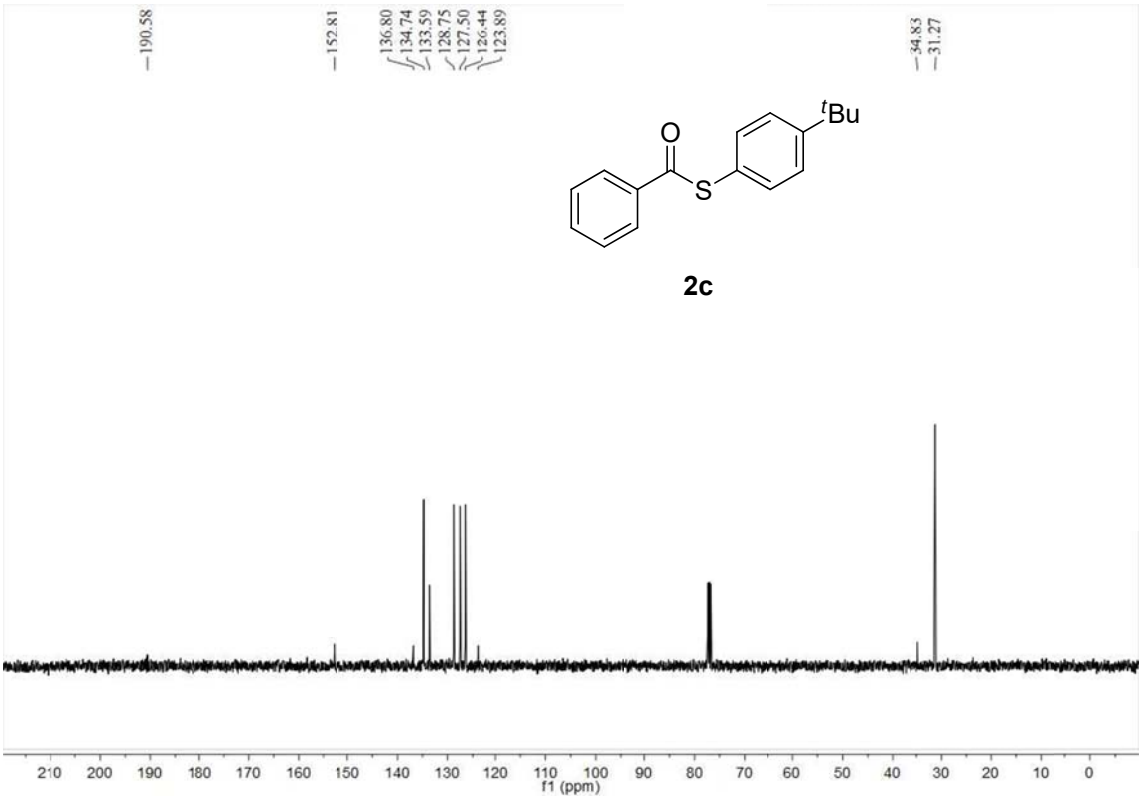
9.20
f1 (ppm)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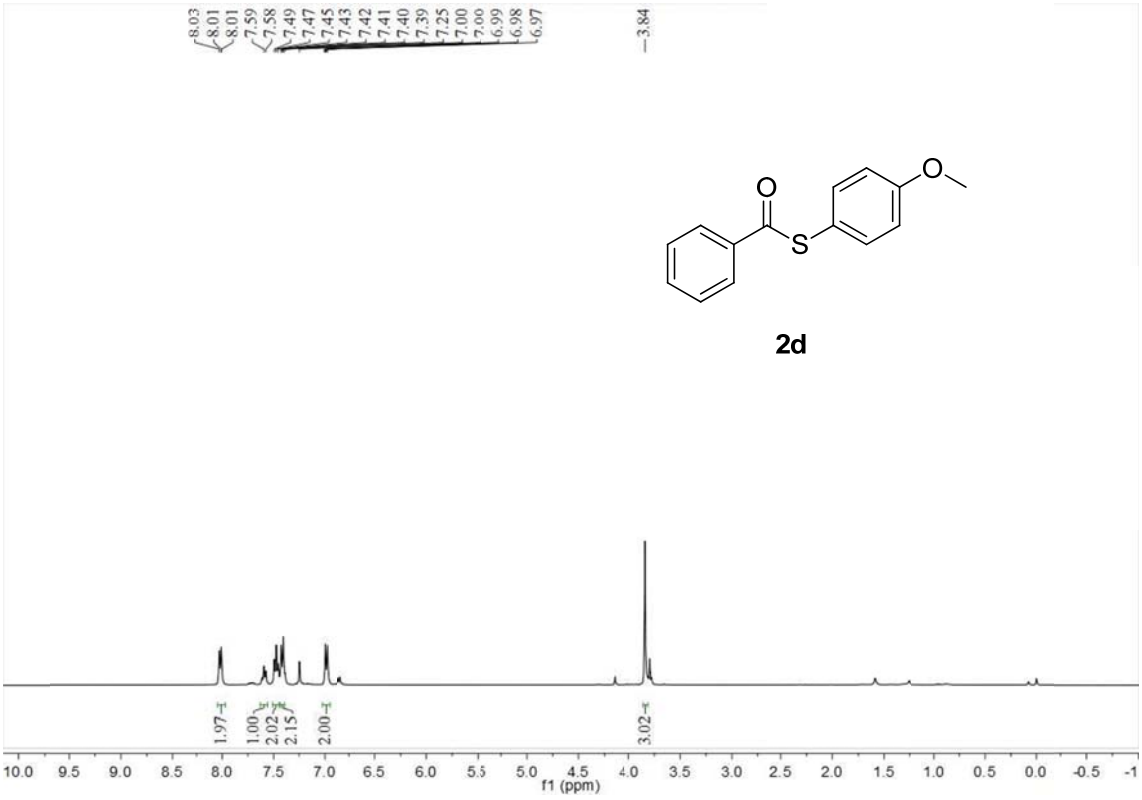
O
S
tBu
2c
f1 (ppm)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8.01
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7.39
7.25
7.00
7.00
6.99
6.98
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O
O
S
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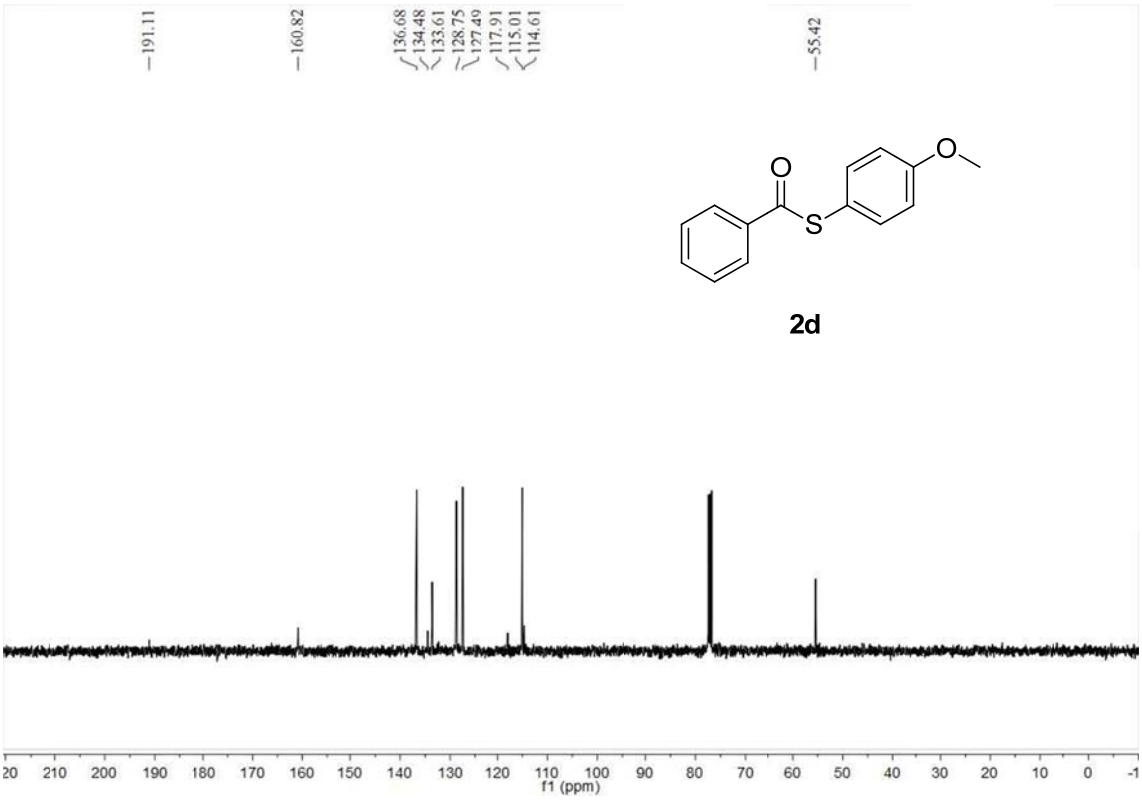
3.02
f1 (ppm)

2d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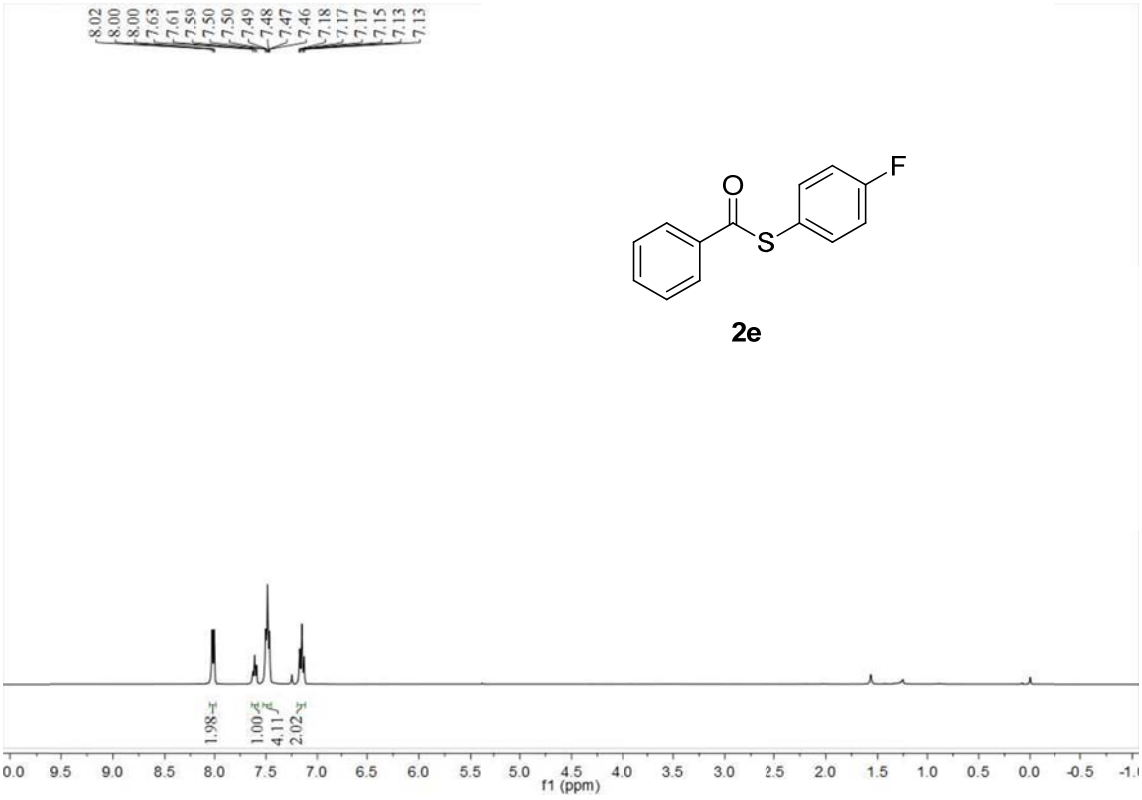
O
S
f1 (ppm)

2d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7.50
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7.47
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S
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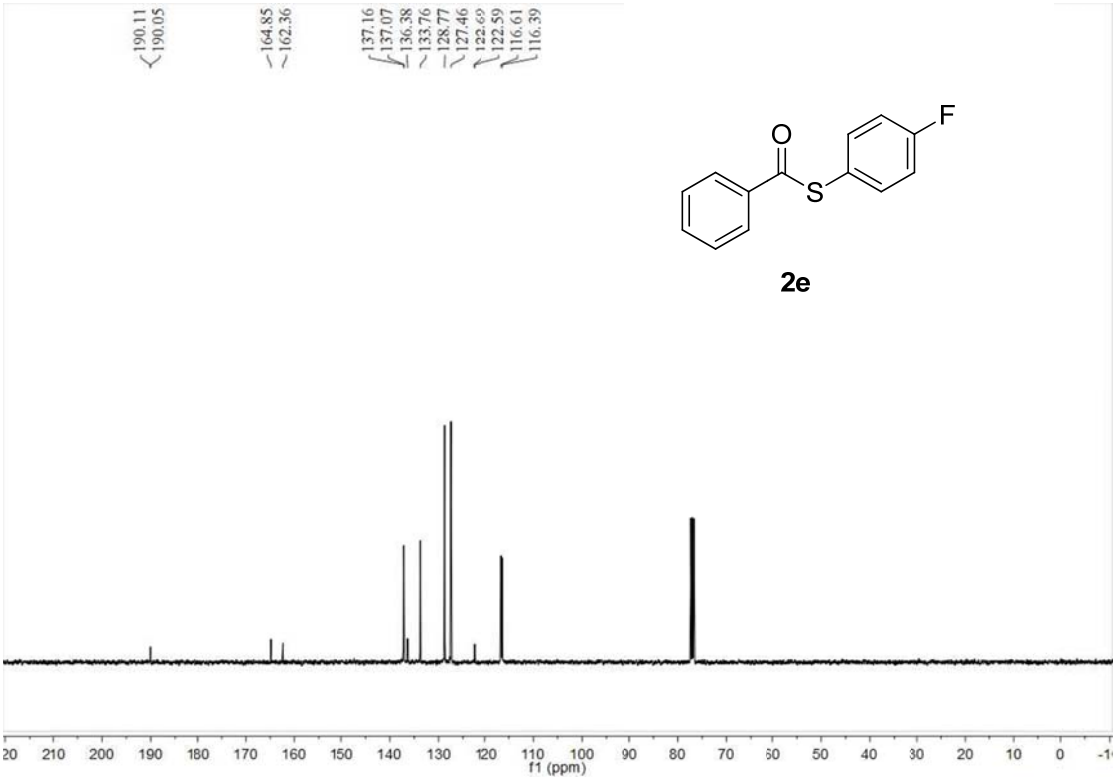
2e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116.39
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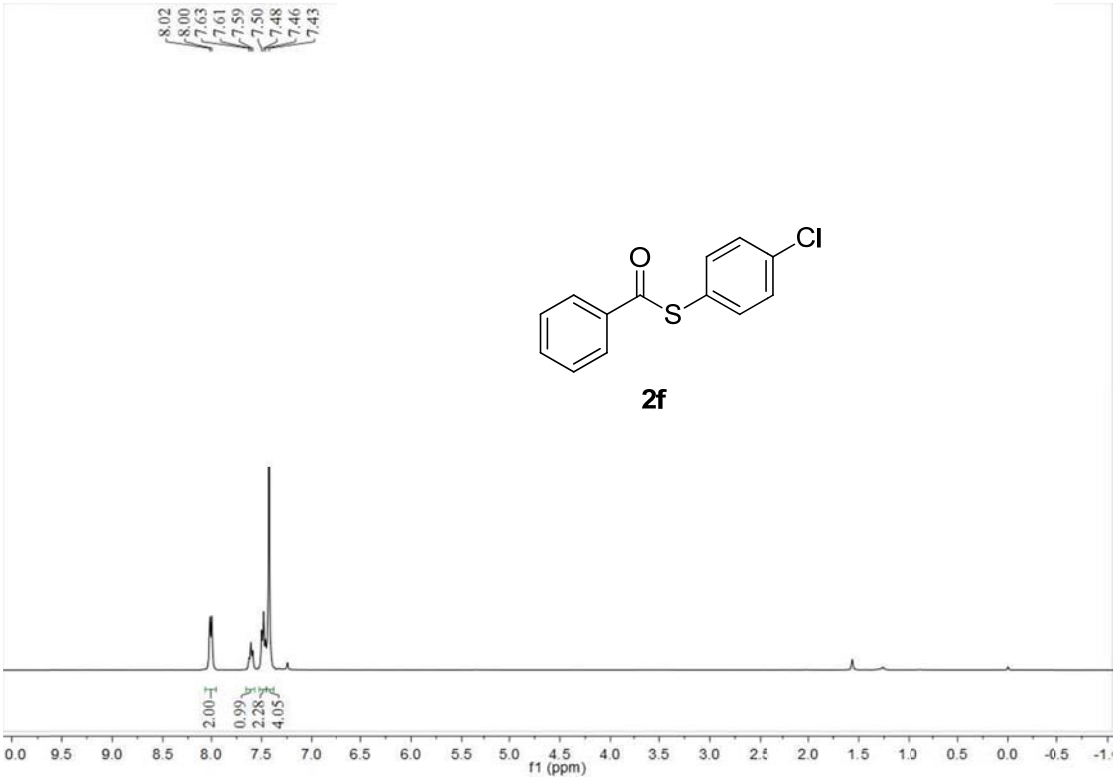
S
F
f1 (ppm)

2e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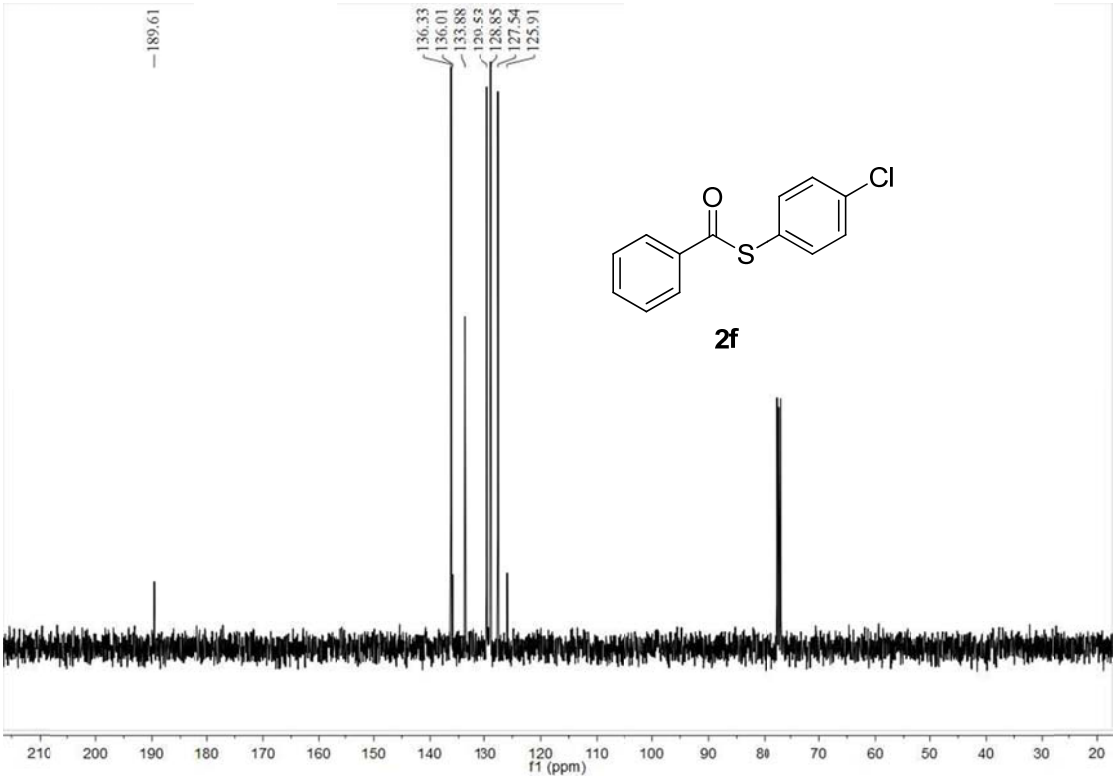
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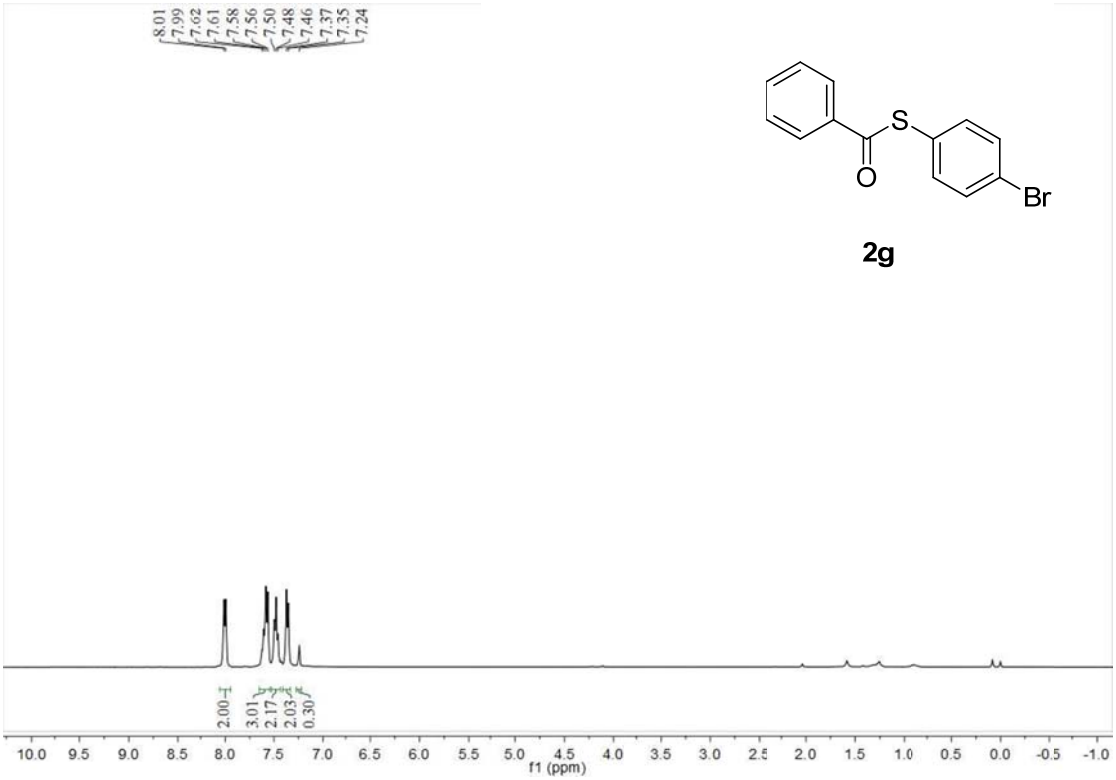
Cl
2f
f1 (ppm)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7.24
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O
Br
2g
2.00
3.01
2.17
2.03
0.30
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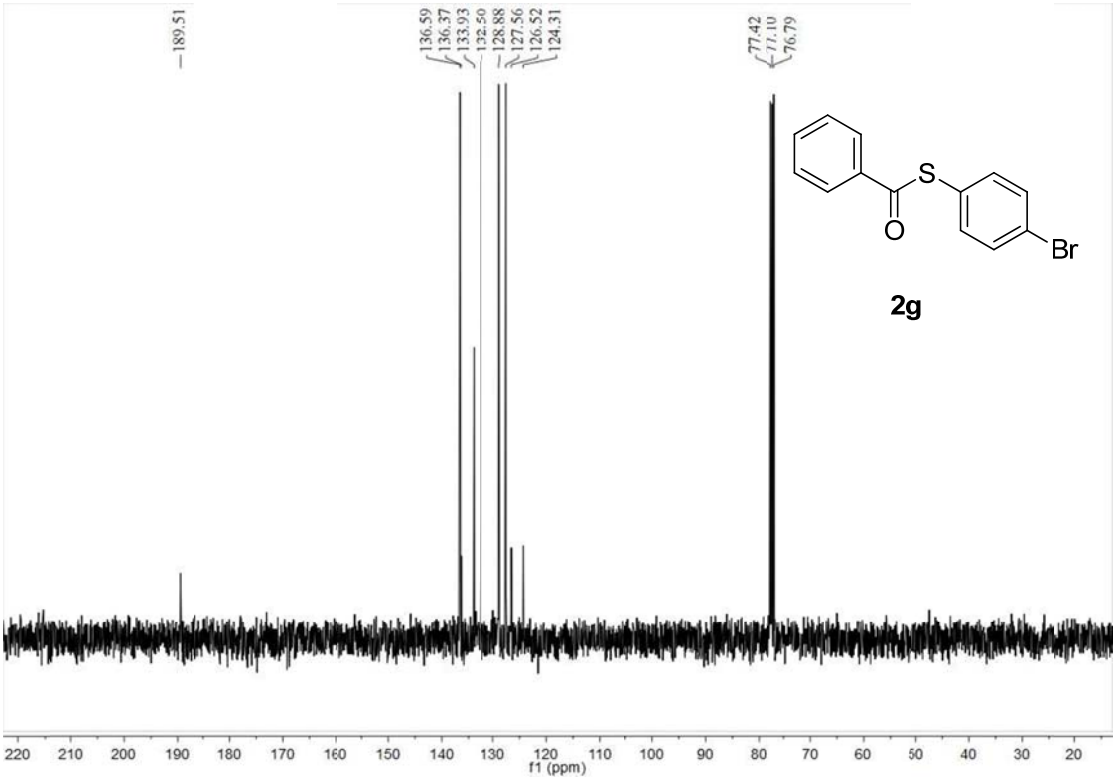
f1 (ppm)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S
O
Br
2g
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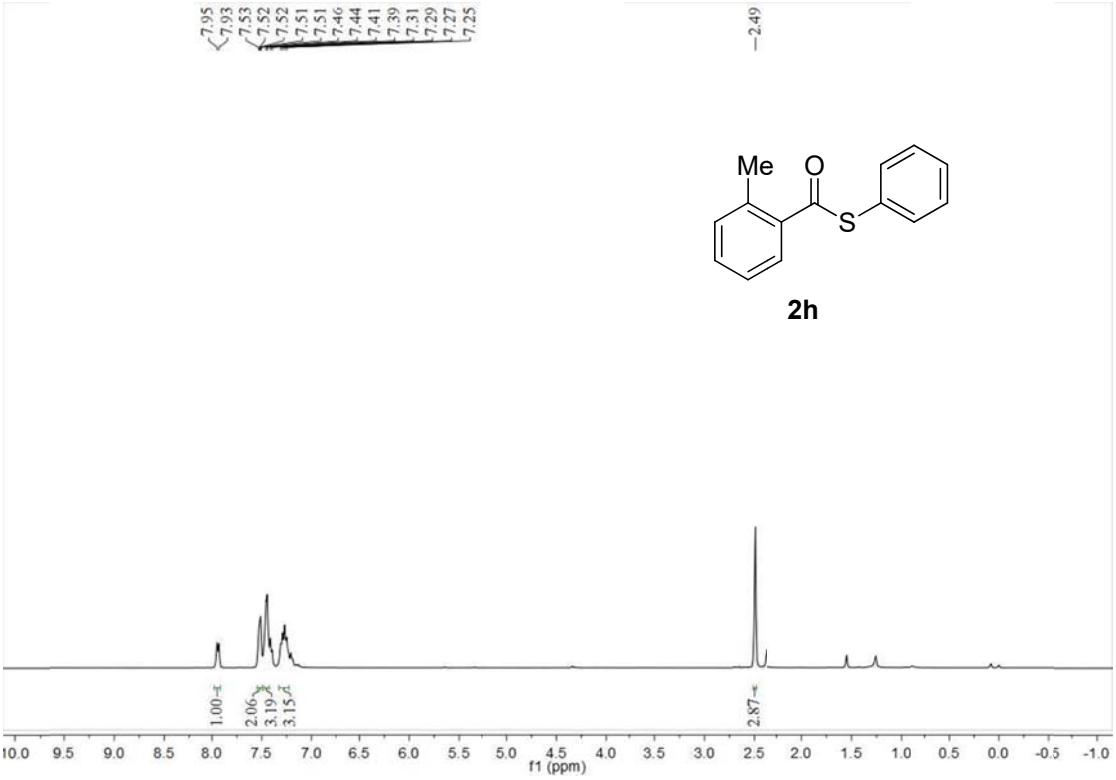
f1 (ppm)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O
S
2h
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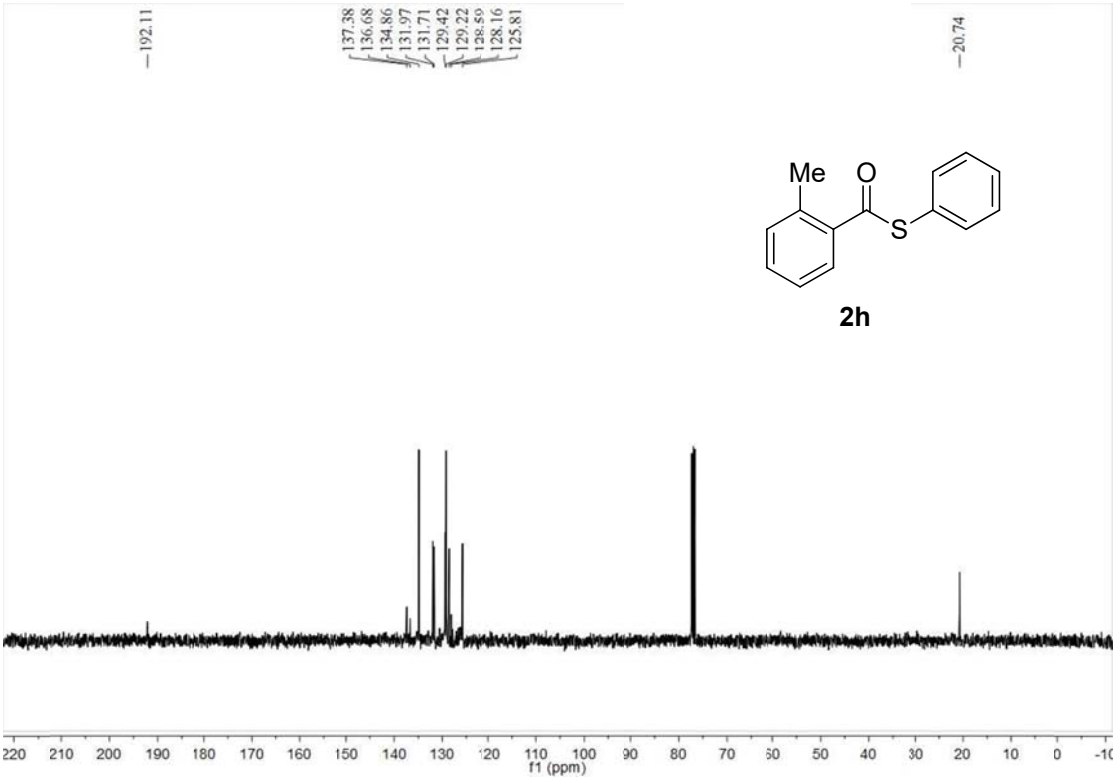
3.19
3.15
2.87
f1 (ppm)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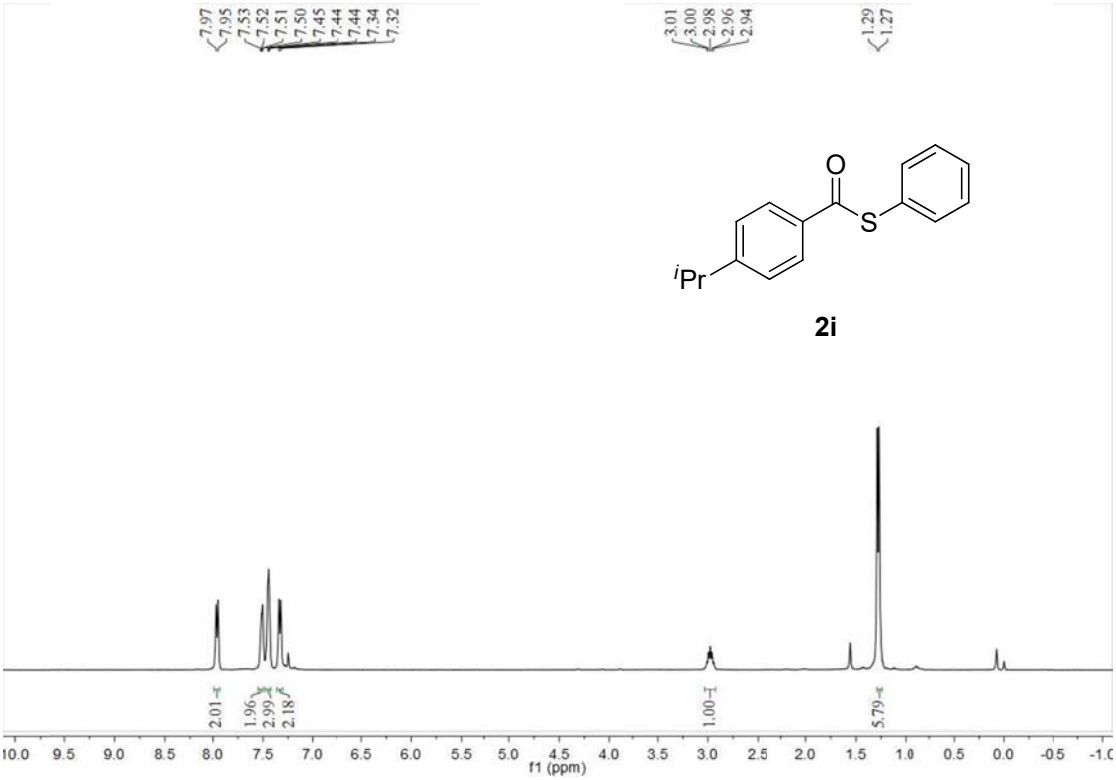
O
S
2h
f1 (ppm)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3.00
2.98
2.96
2.94
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S
iPr
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2.18
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5.79
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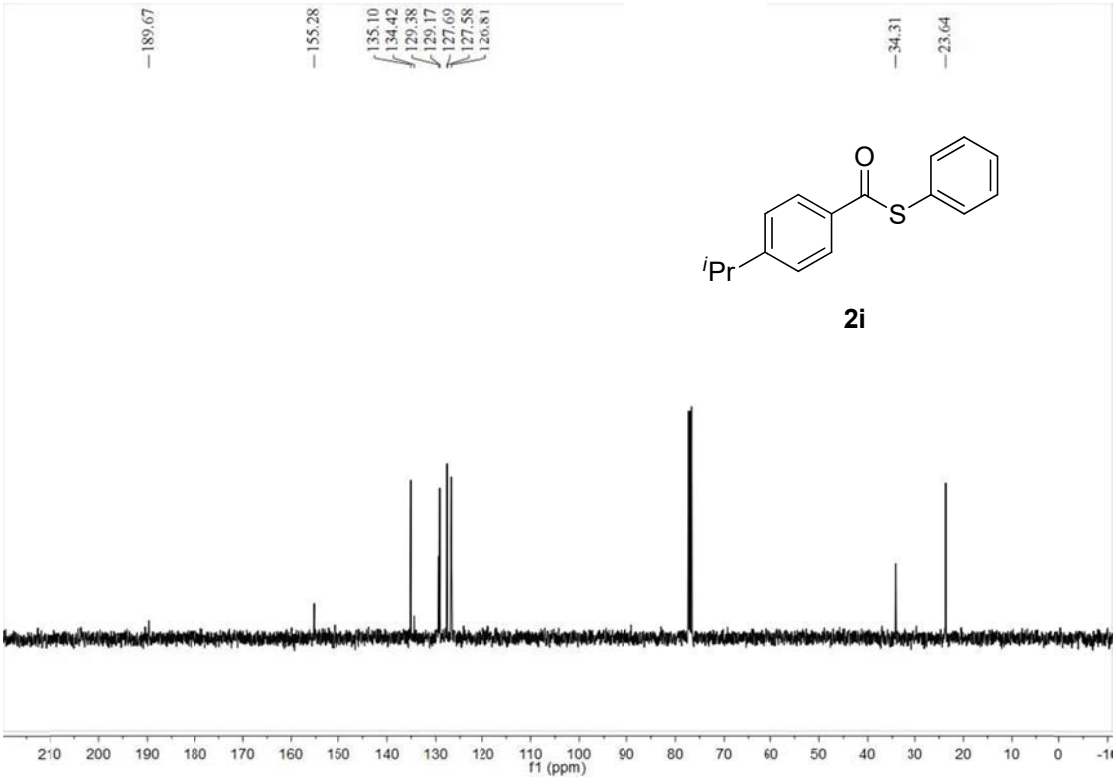
2i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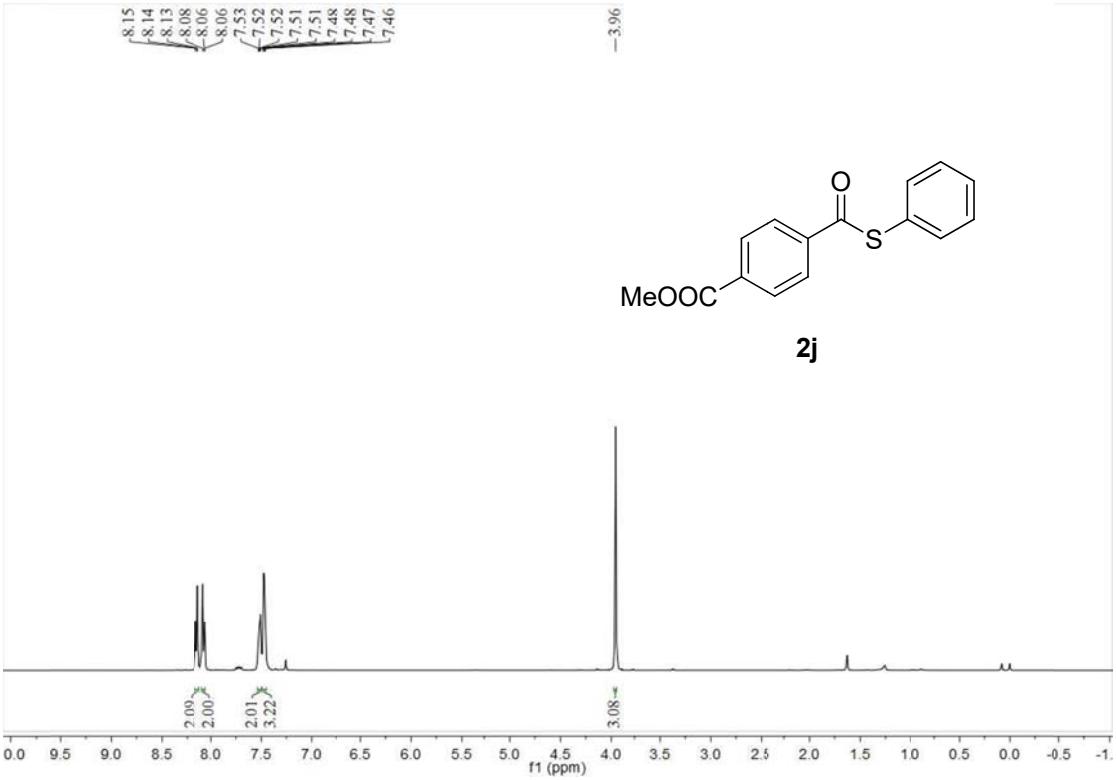
iPr
f1 (ppm)

2i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7.48
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S
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2j
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2.01
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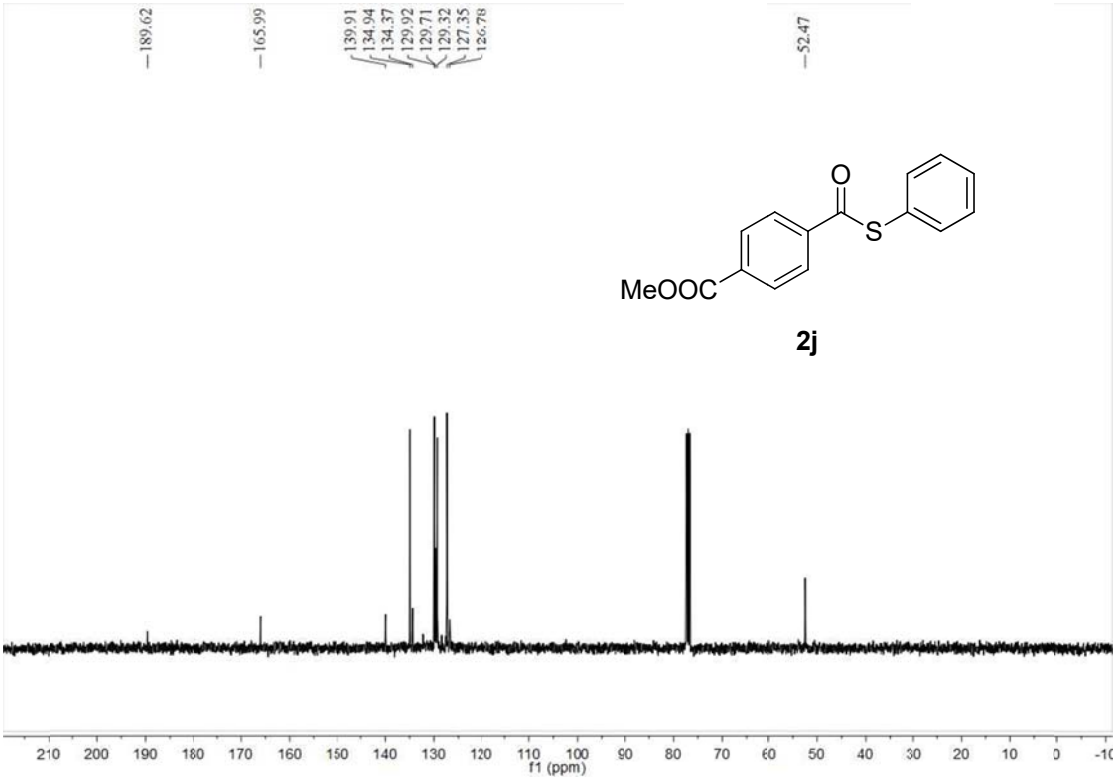
f1 (ppm)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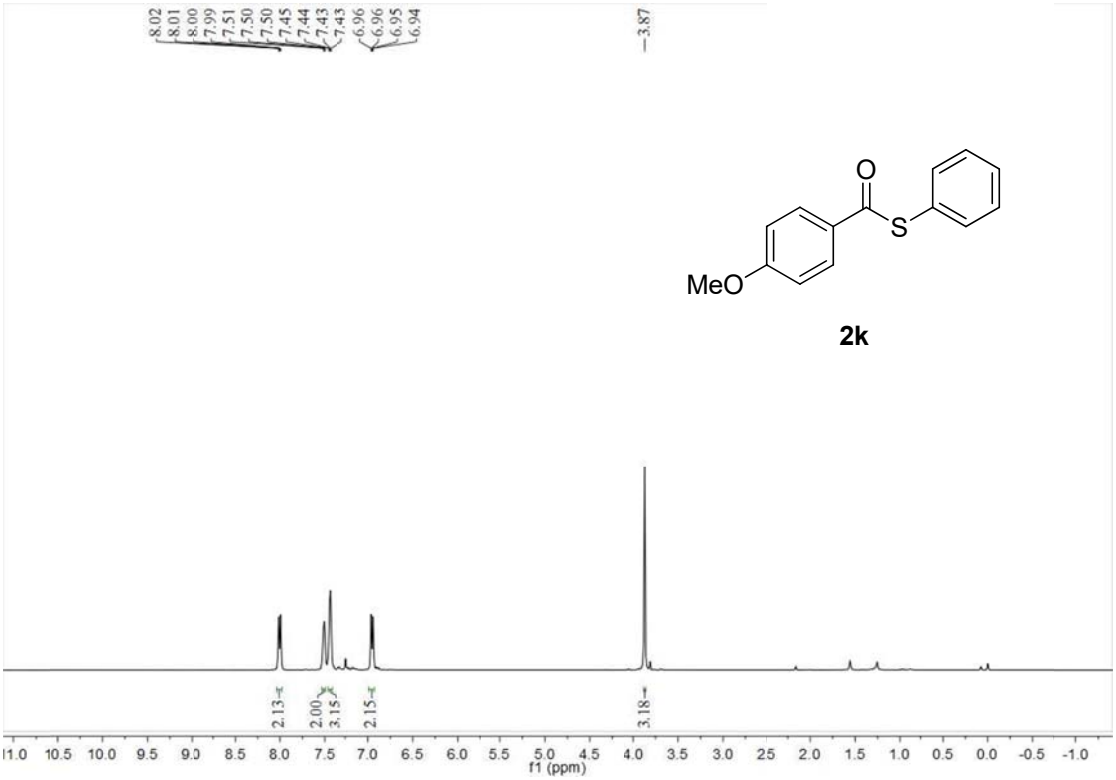
f1 (ppm)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S
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2k
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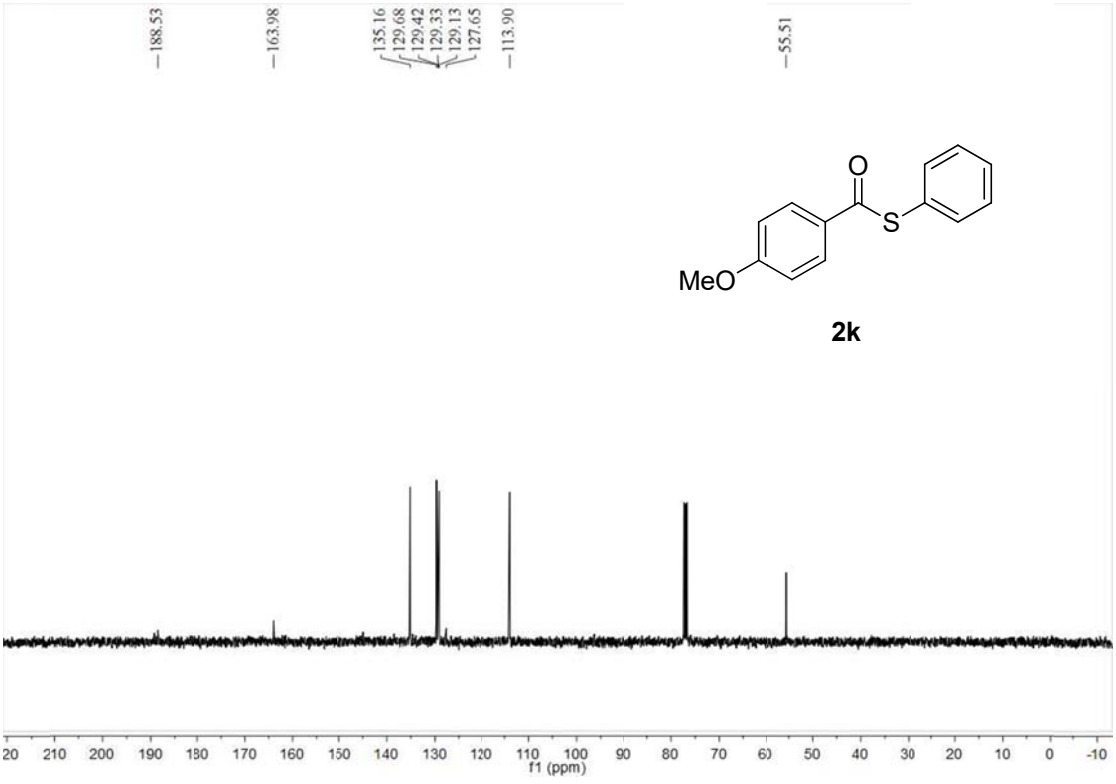
f1 (ppm)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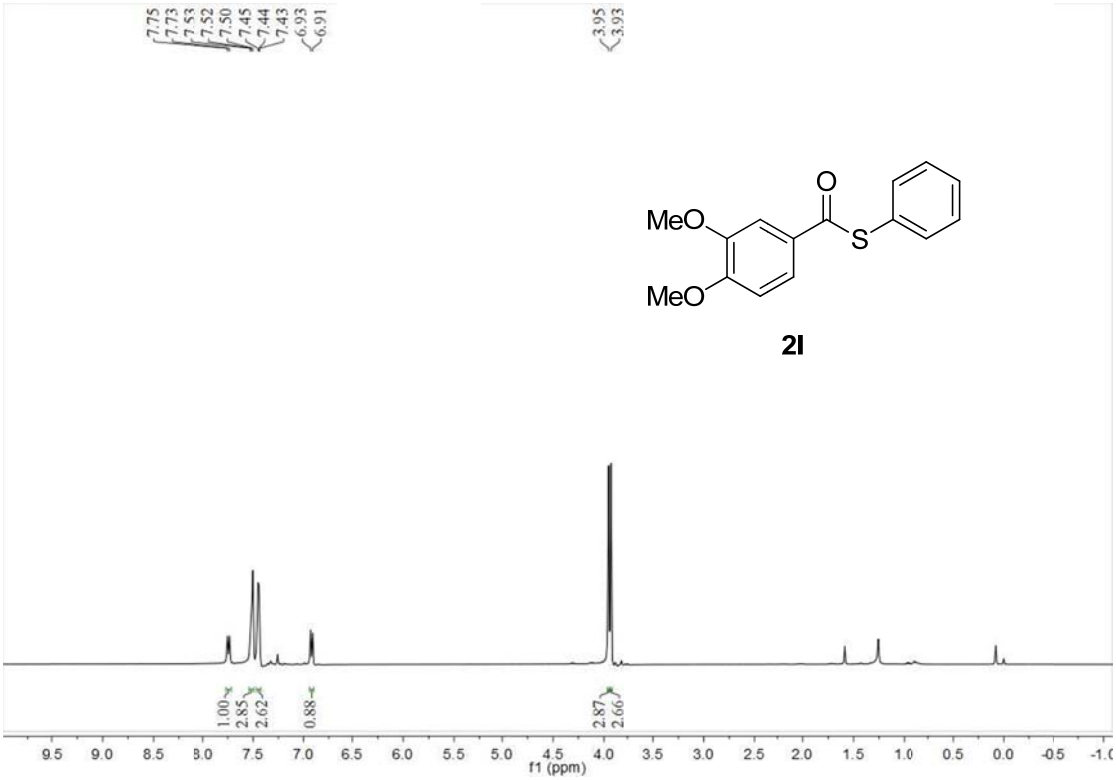
f1 (ppm)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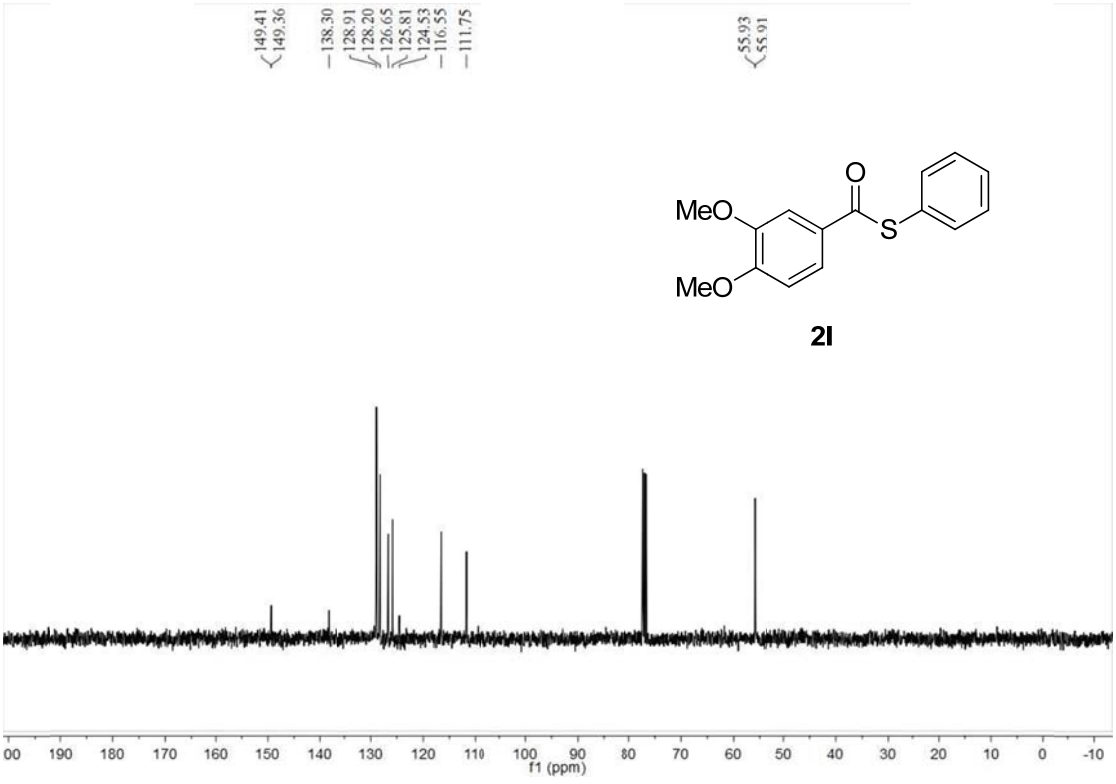
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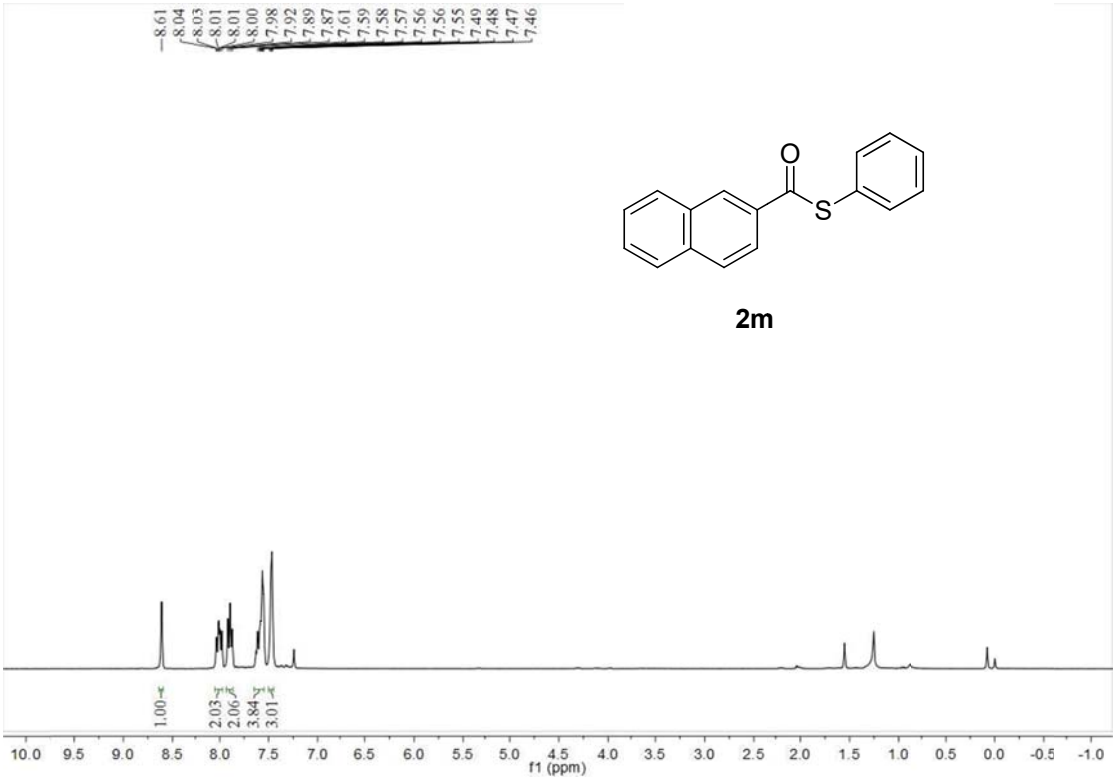
MeO
O
S
2l
f1 (ppm)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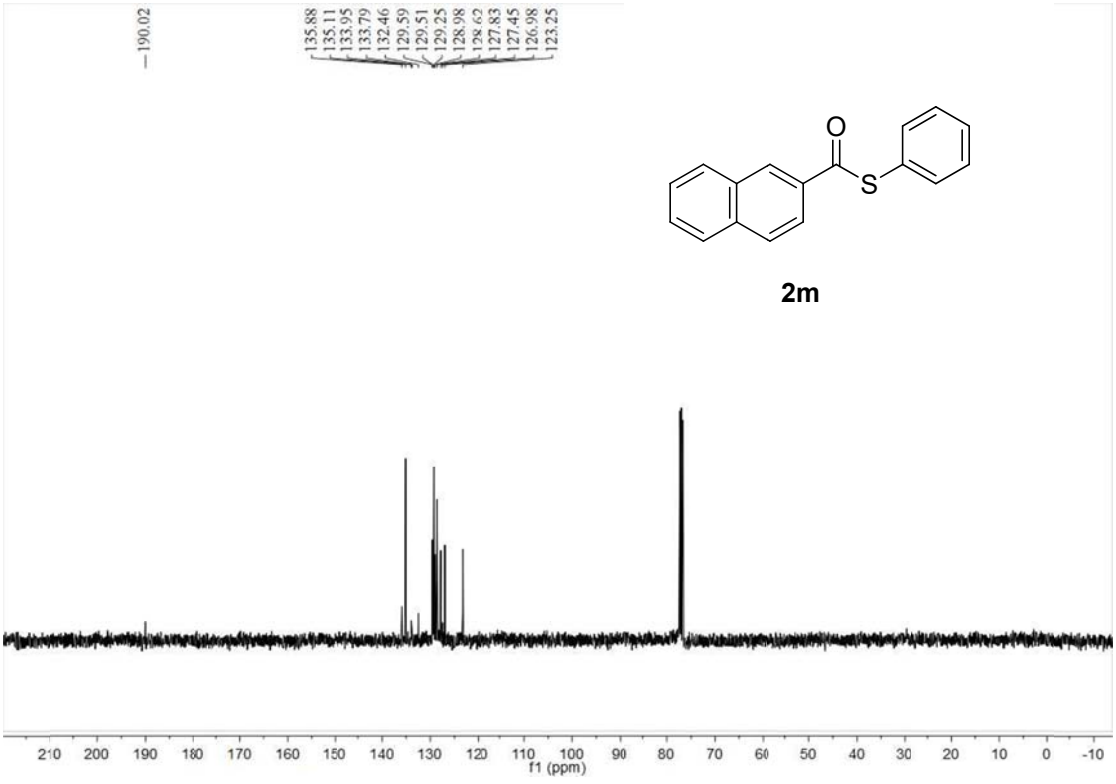
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

2m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123.25
O
S
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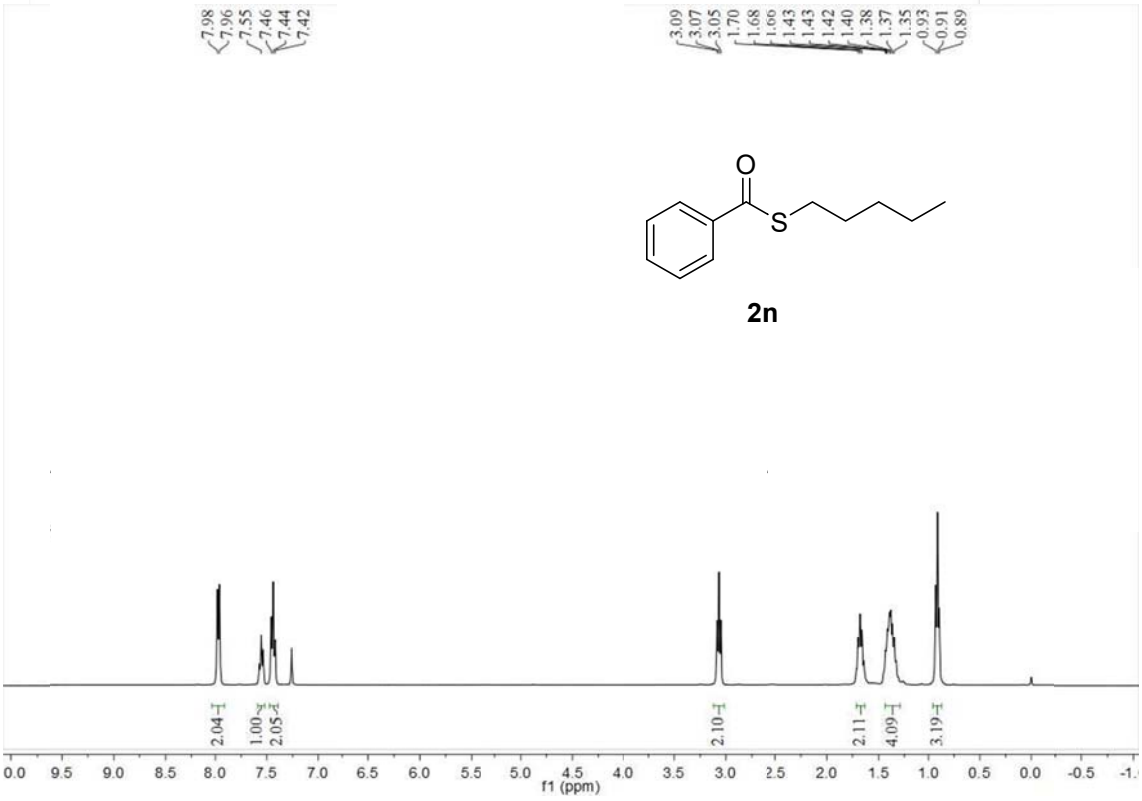
f1 (ppm)

2m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1.43
1.42
1.40
1.38
1.37
1.35
0.93
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S
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4.09
3.19
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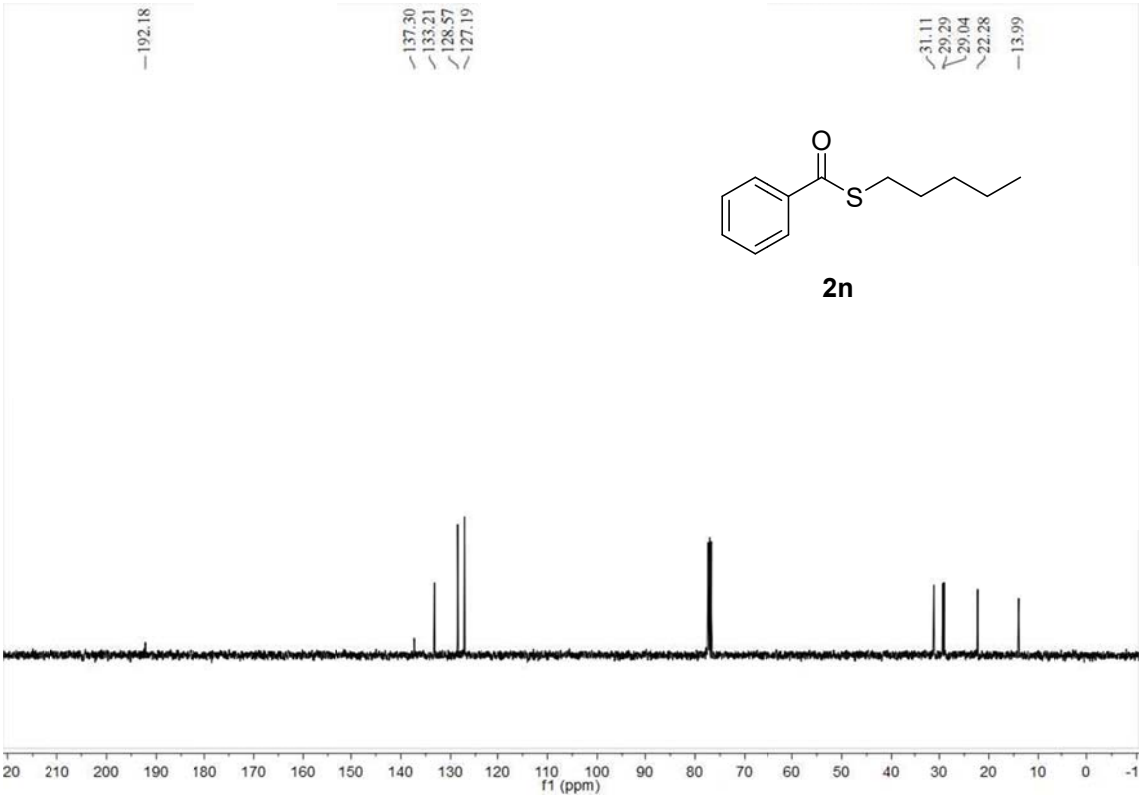
2n


192.18
137.30
133.21
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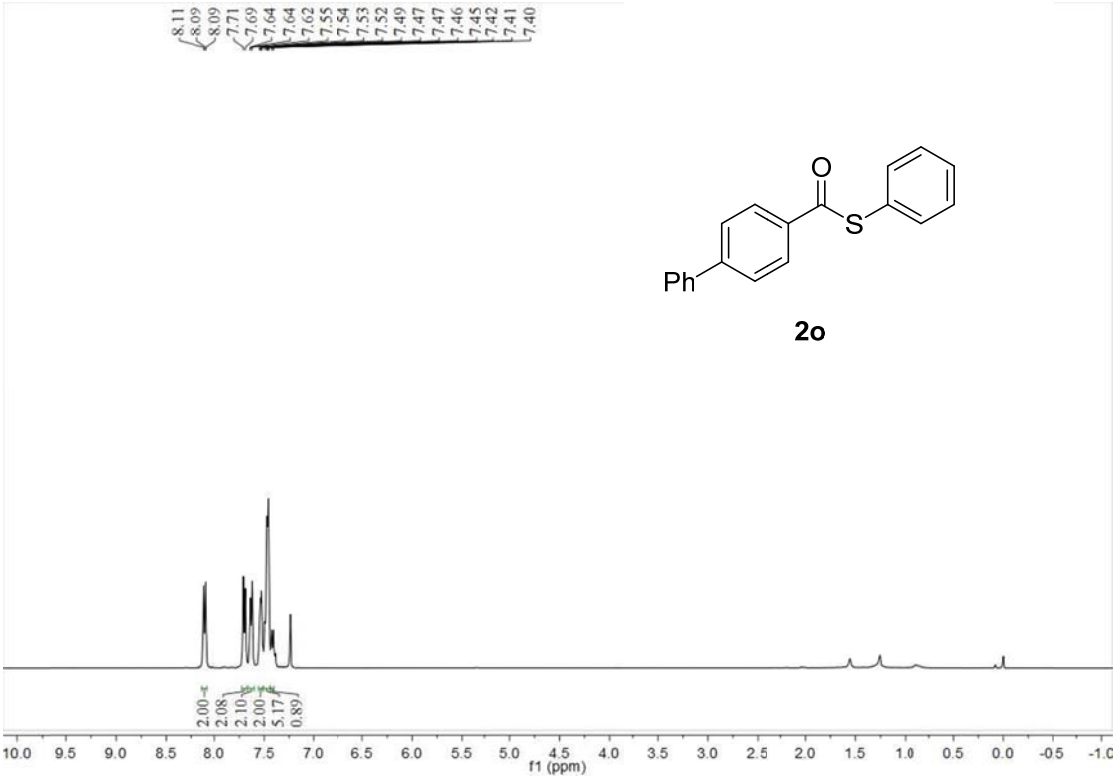
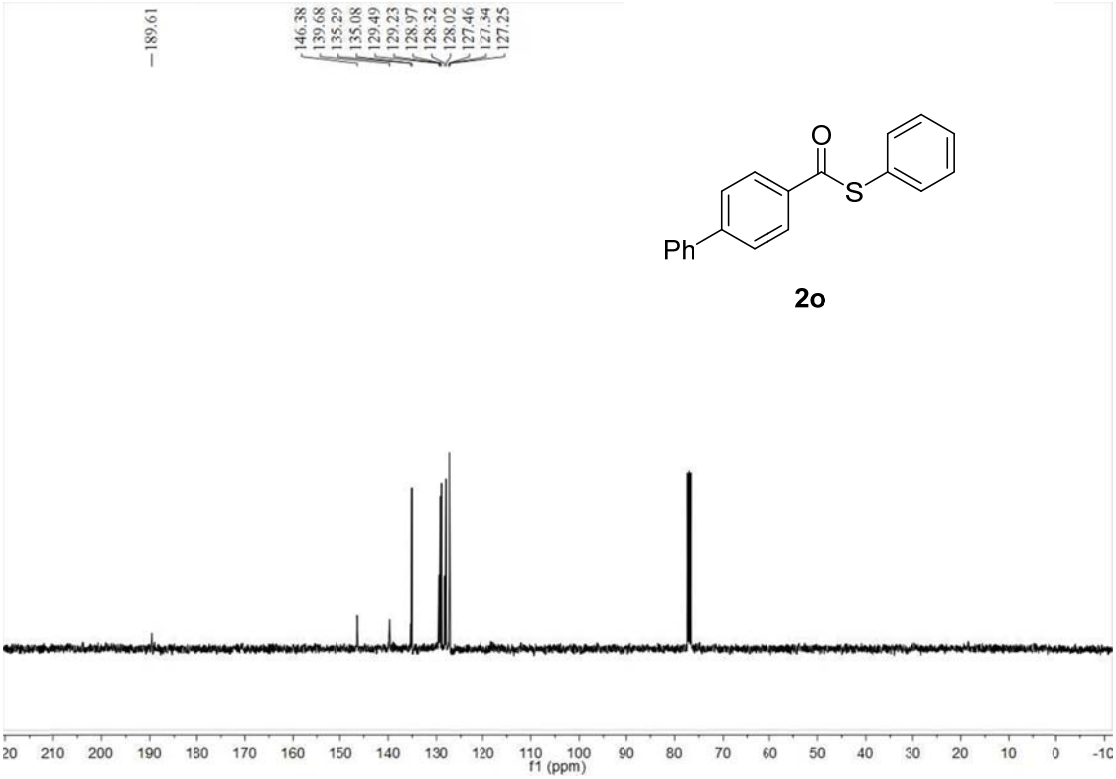
127.19
31.11
29.29
29.04
22.28
13.99
O
S
f1 (ppm)

2n


8.11
8.09
8.09
7.71
7.69
7.64
7.64
7.62
7.55
7.54
7.53
7.52
7.49
7.47
7.47
7.46
7.45
7.42
7.41
7.40
O
S
Ph
2.00
2.08
2.10
2.00
5.17
0.89
f1 (ppm)

2o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139.68
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135.08
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129.23
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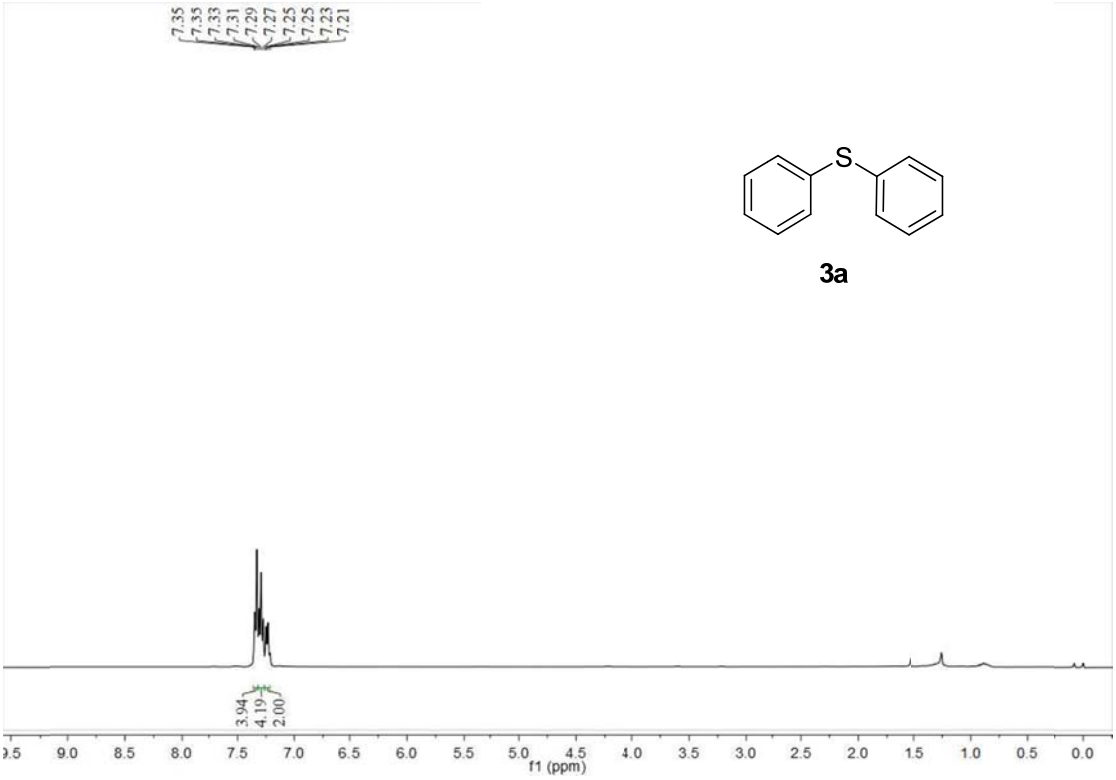
128.02
127.46
127.34
127.25
O
S
Ph
f1 (ppm)

2o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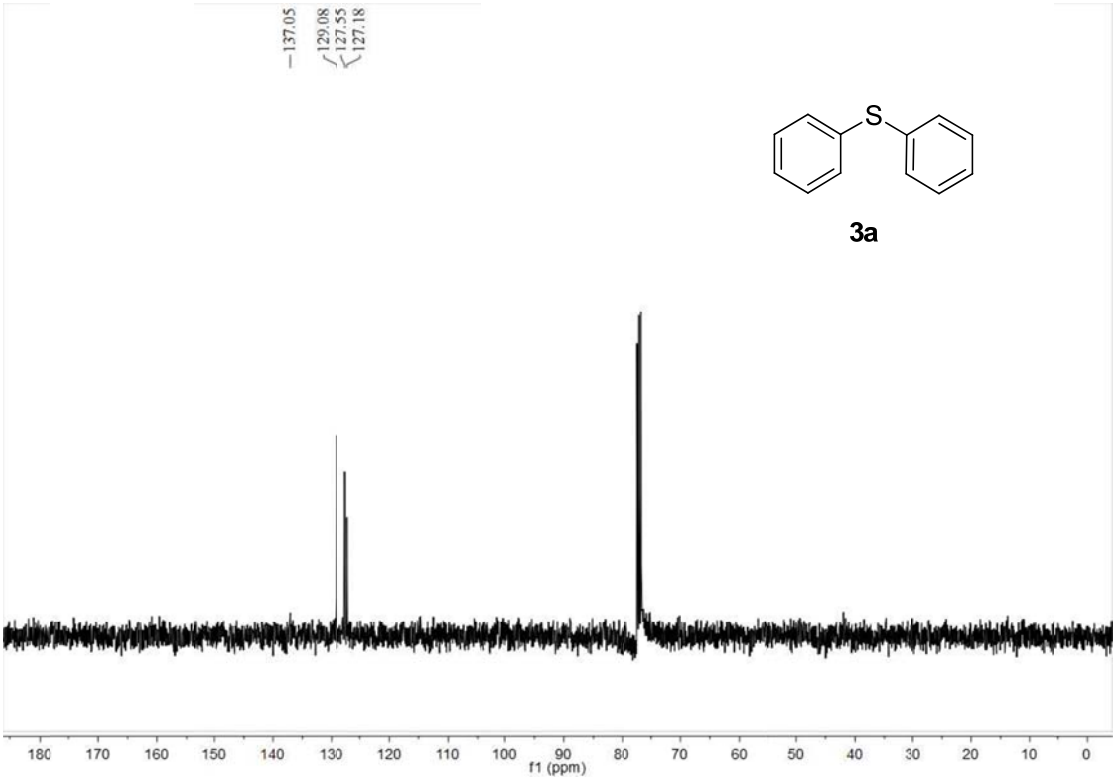
7.35
7.33
7.31
7.29
7.27
7.25
7.25
7.23
7.21
S
3a
3.94
4.19
2.00
f1 (ppm)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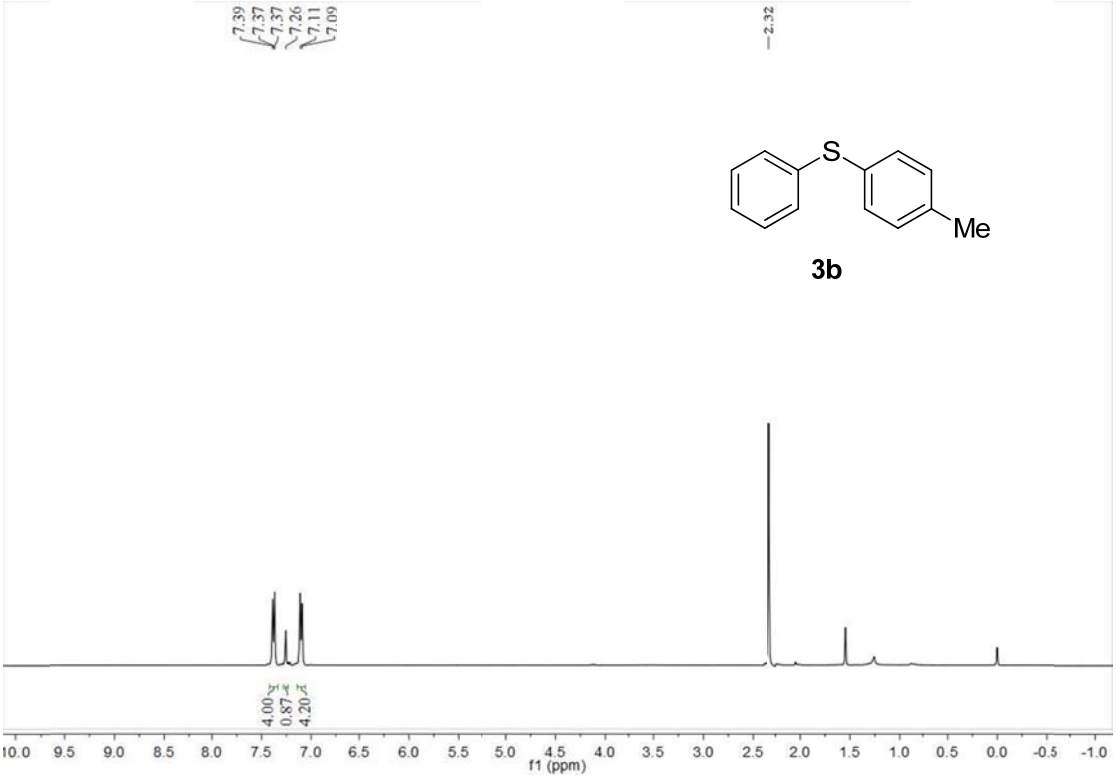
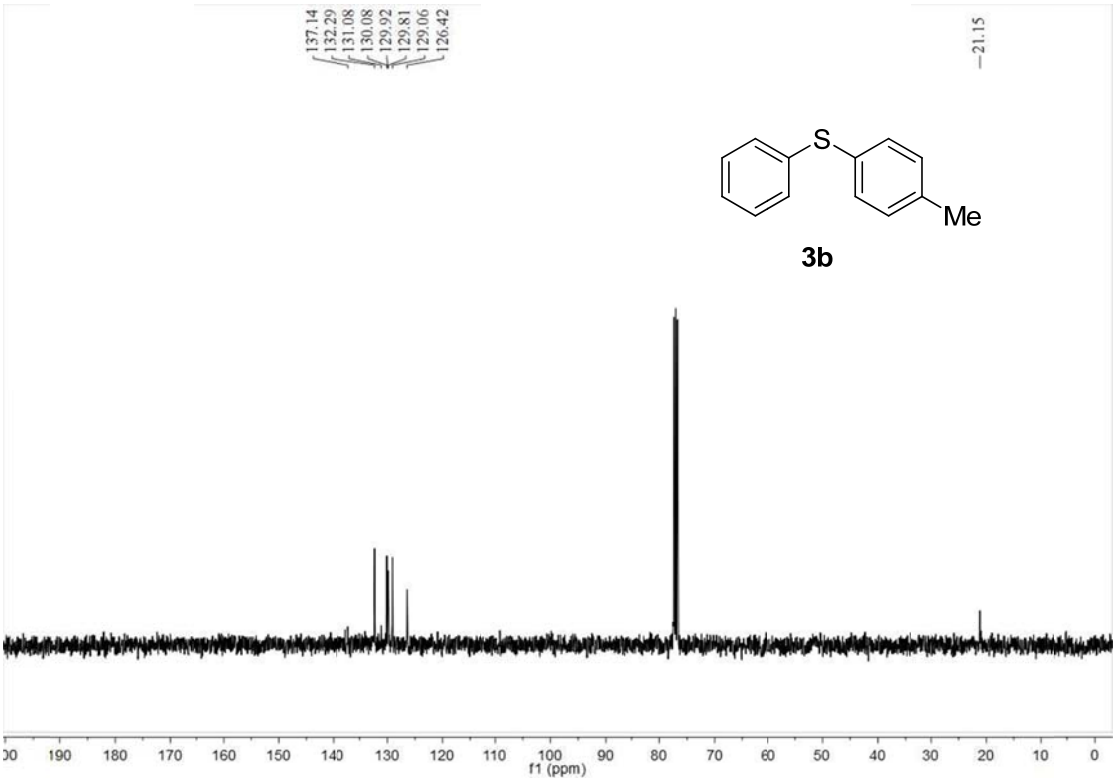
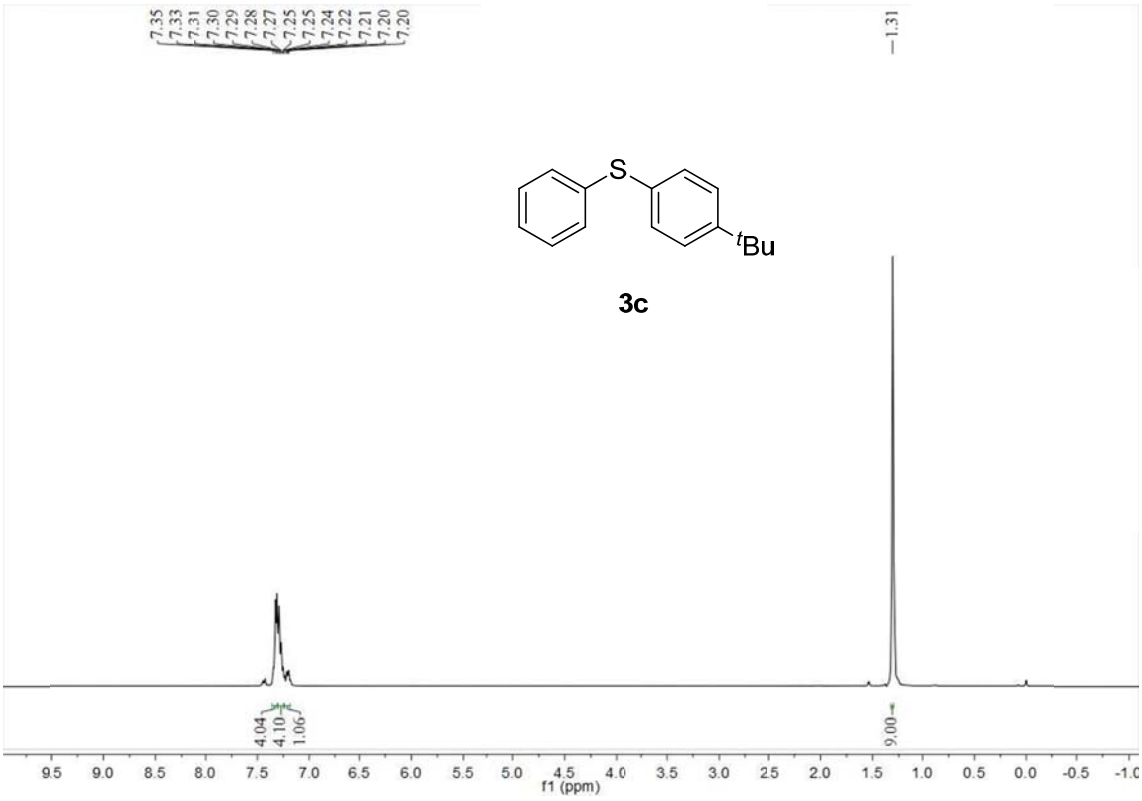
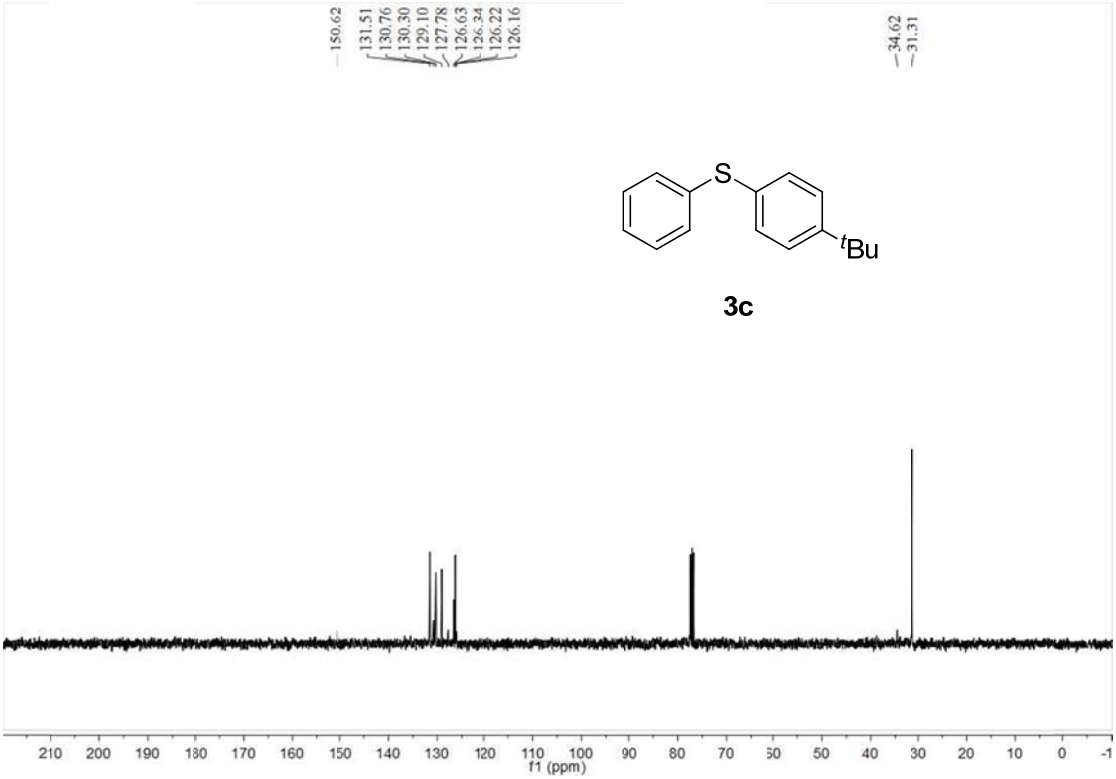
127.55
127.18
S
3a
f1 (ppm)


7.39
7.37
7.37
7.26
7.11
7.09
2.32
S
Me
3b
4.00
0.87
4.20
f1 (ppm)

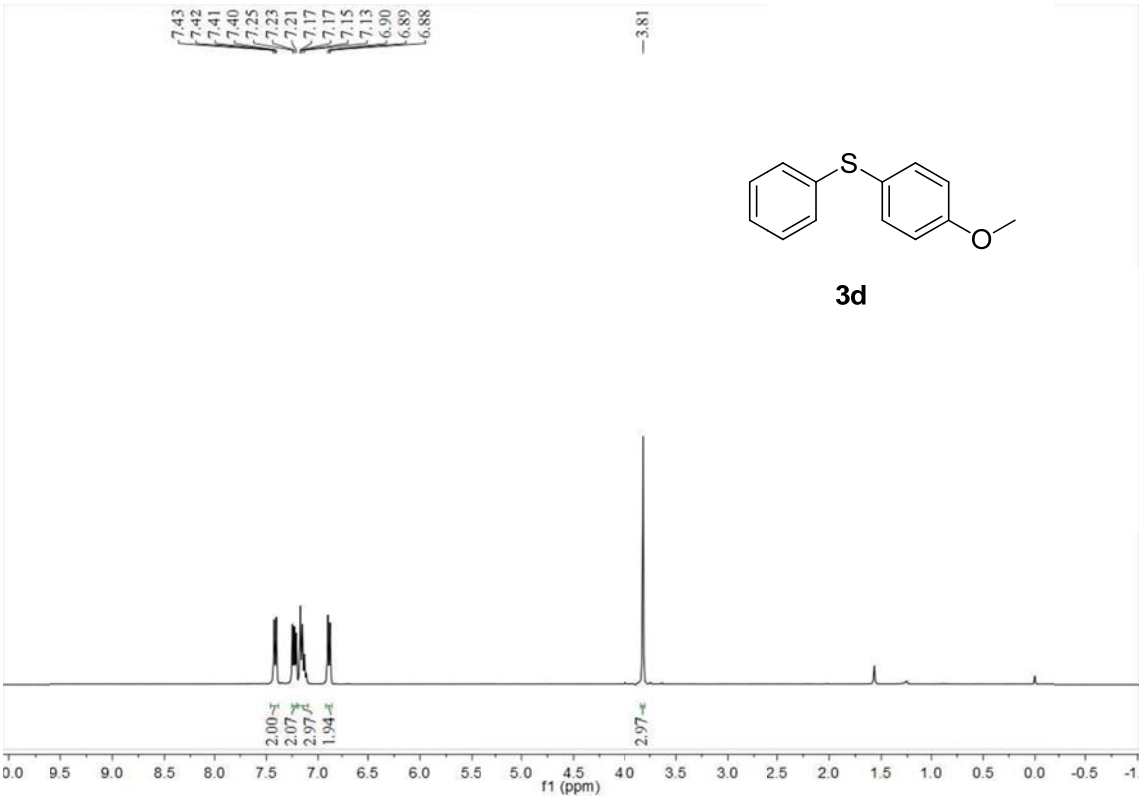

137.14
132.29
131.08
130.08
129.92
129.81
129.06
126.42
21.15
S
Me
3b
f1 (ppm)


7.35
7.33
7.31
7.30
7.29
7.28
7.27
7.25
7.25
7.24
7.22
7.21
7.20
7.20
1.31
S
tBu
4.04
4.10
1.06
9.00
f1 (ppm)

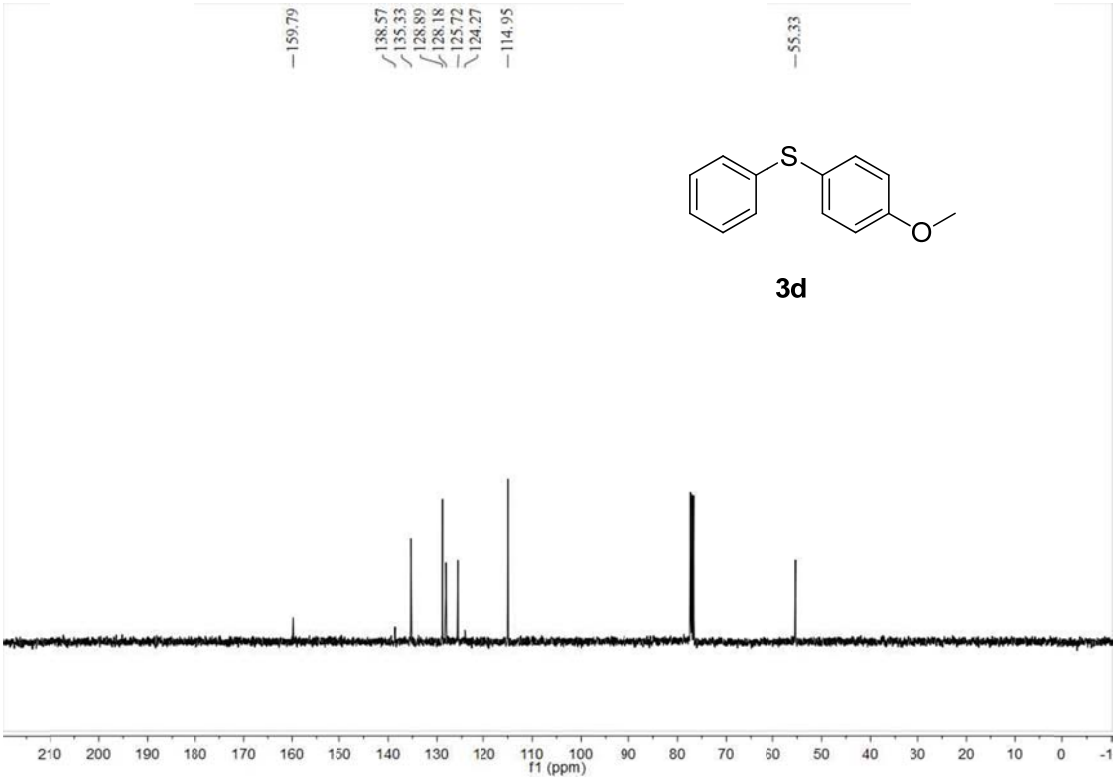
3c


150.62
131.51
130.76
130.30
129.10
127.78
126.63
126.34
126.22
126.16
34.62
31.31
S
tBu
f1 (ppm)

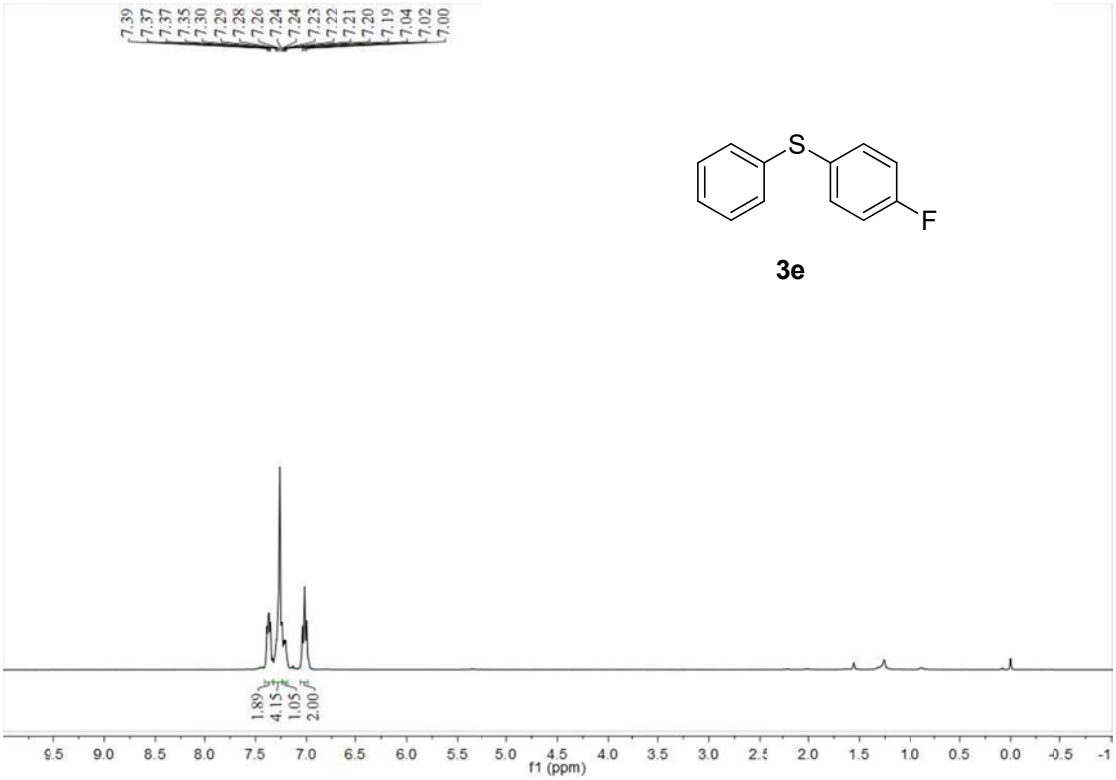
3c


7.43
7.42
7.41
7.40
7.25
7.23
7.21
7.17
7.17
7.15
7.13
6.90
6.89
6.88
3.81
S
O
2.00
2.07
2.97
1.94
2.97
f1 (ppm)

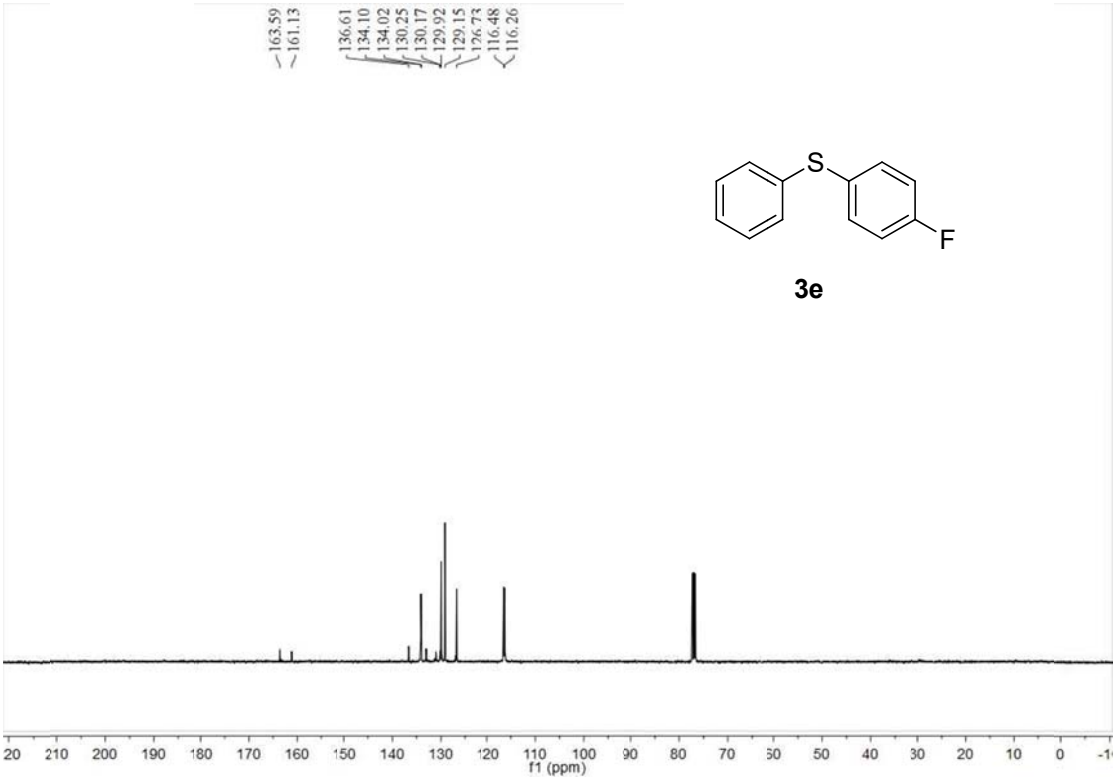
3d


159.79
138.57
135.33
128.89
128.18
125.72
124.27
114.95
55.33
S
O
f1 (ppm)

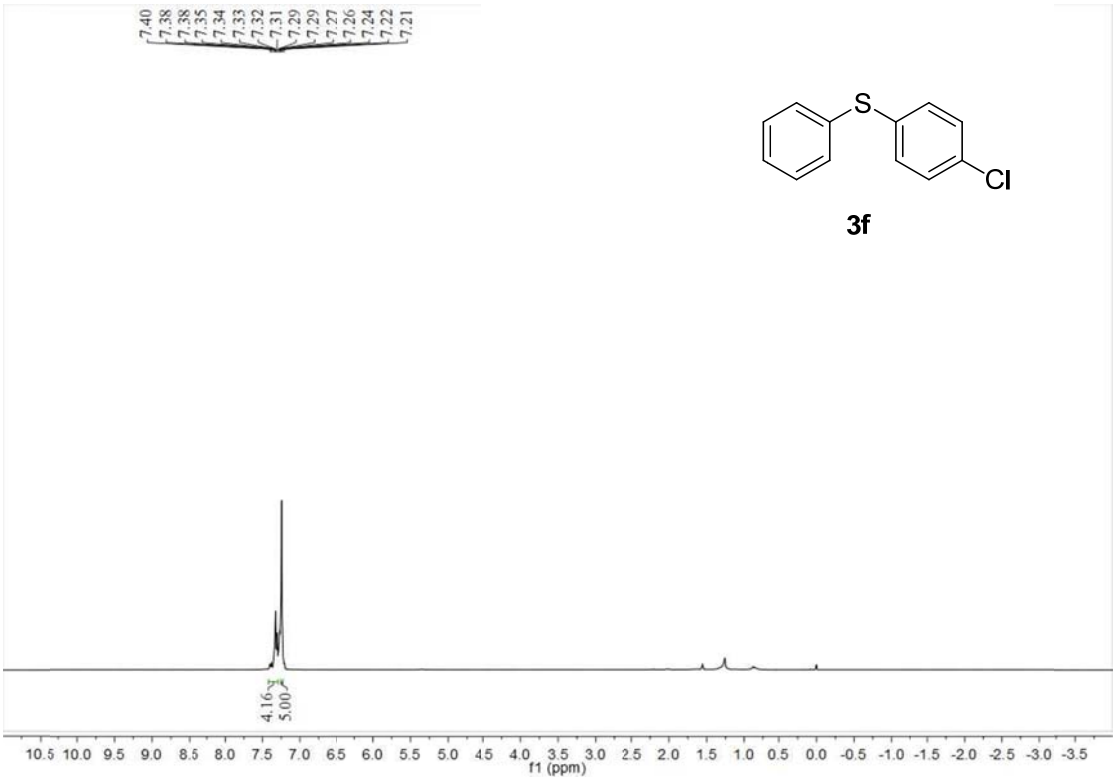
3d


7.39
7.37
7.37
7.35
7.30
7.29
7.28
7.26
7.24
7.24
7.23
7.22
7.21
7.20
7.19
7.04
7.02
7.00
S
F
1.89
4.15
1.05
2.00
f1 (ppm)

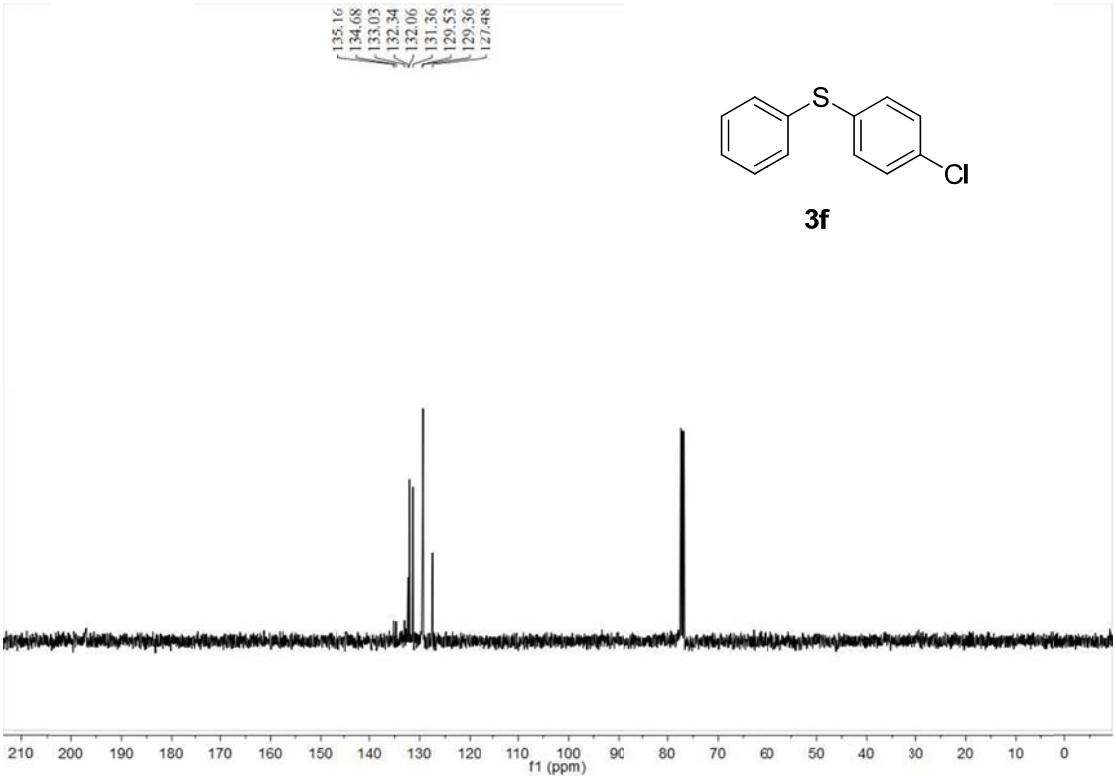
3e


163.59
161.13
136.61
134.10
134.02
130.25
130.17
129.92
129.15
126.73
116.48
116.26
S
F
f1 (ppm)

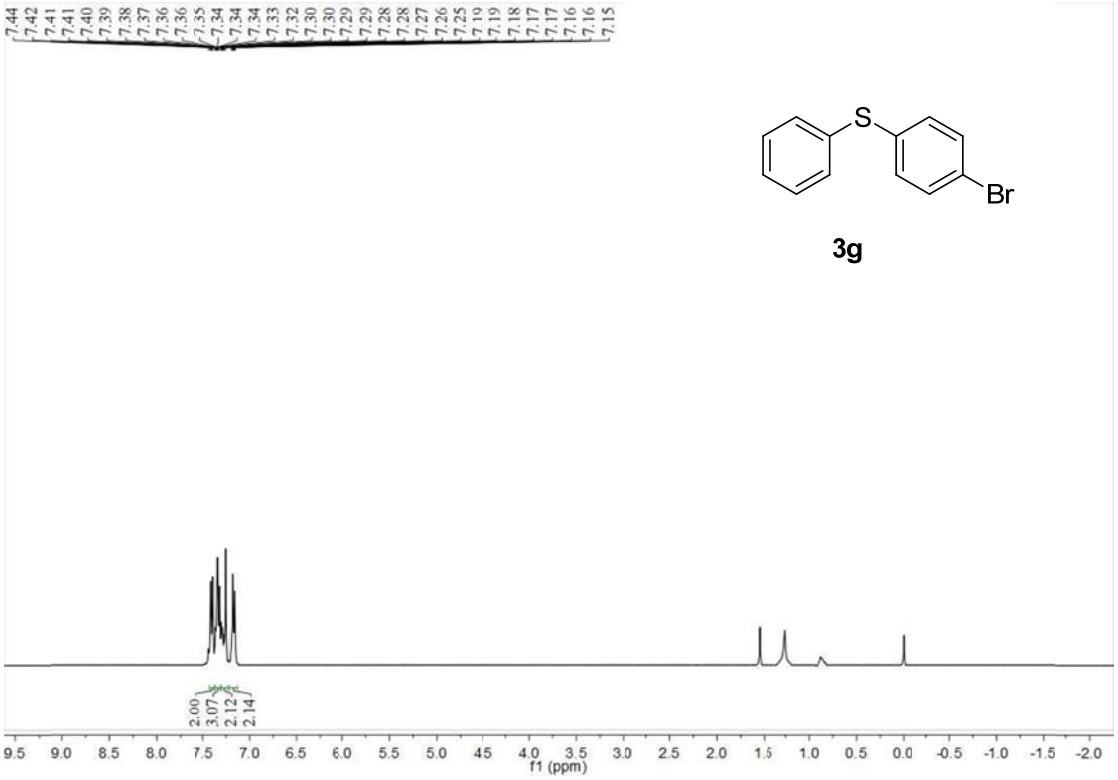
3e

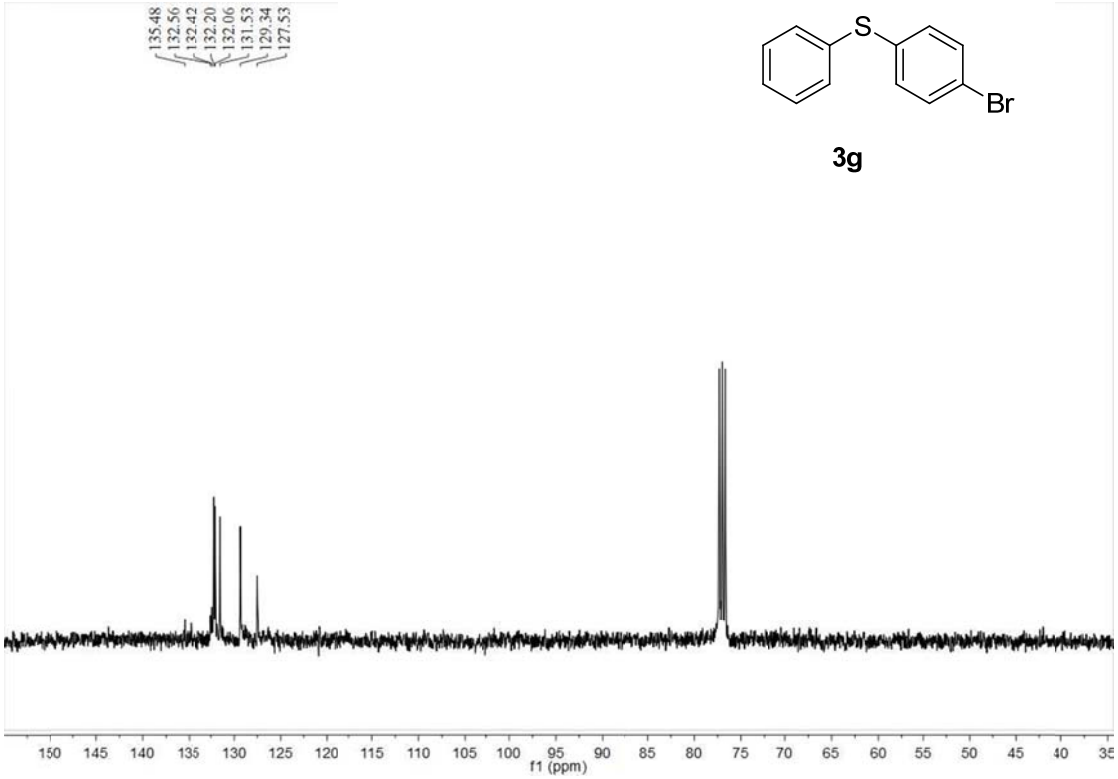

7.40
7.38
7.38
7.35
7.34
7.33
7.32
7.31
7.29
7.29
7.27
7.26
7.24
7.22
7.21
S
Cl
4.16
5.00
f1 (ppm)

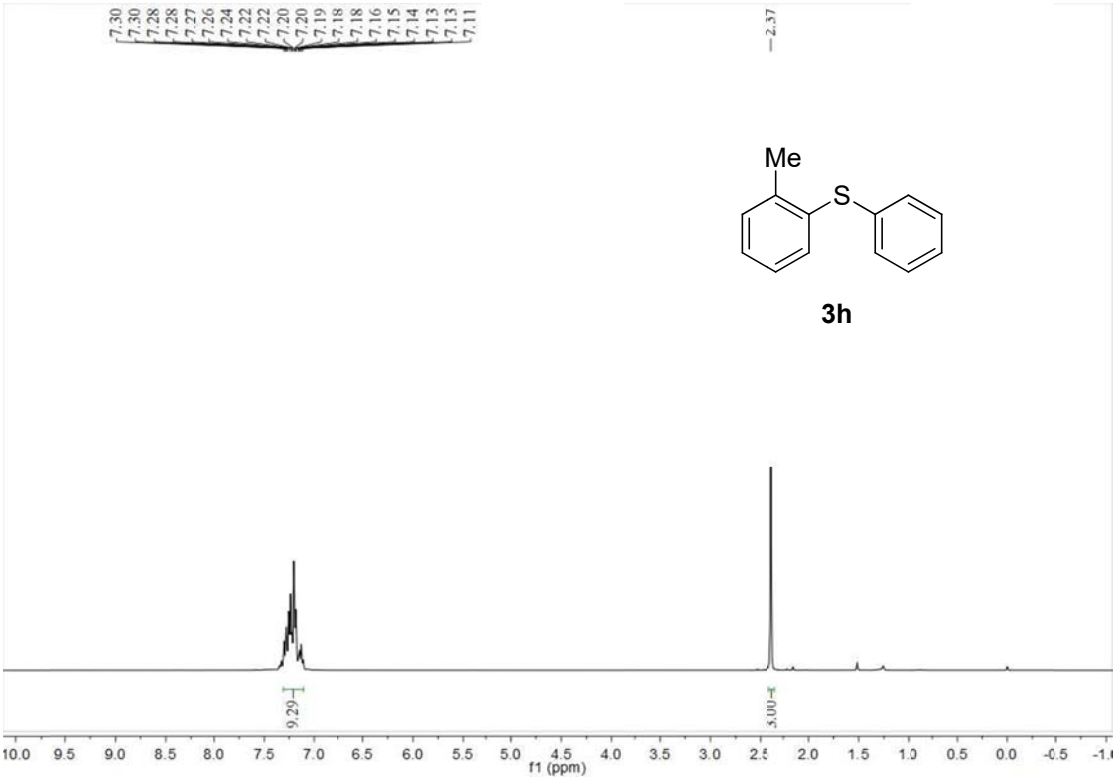
3f


135.16
134.68
133.03
132.34
132.06
131.36
129.53
129.36
127.48
S
Cl
f1 (ppm)

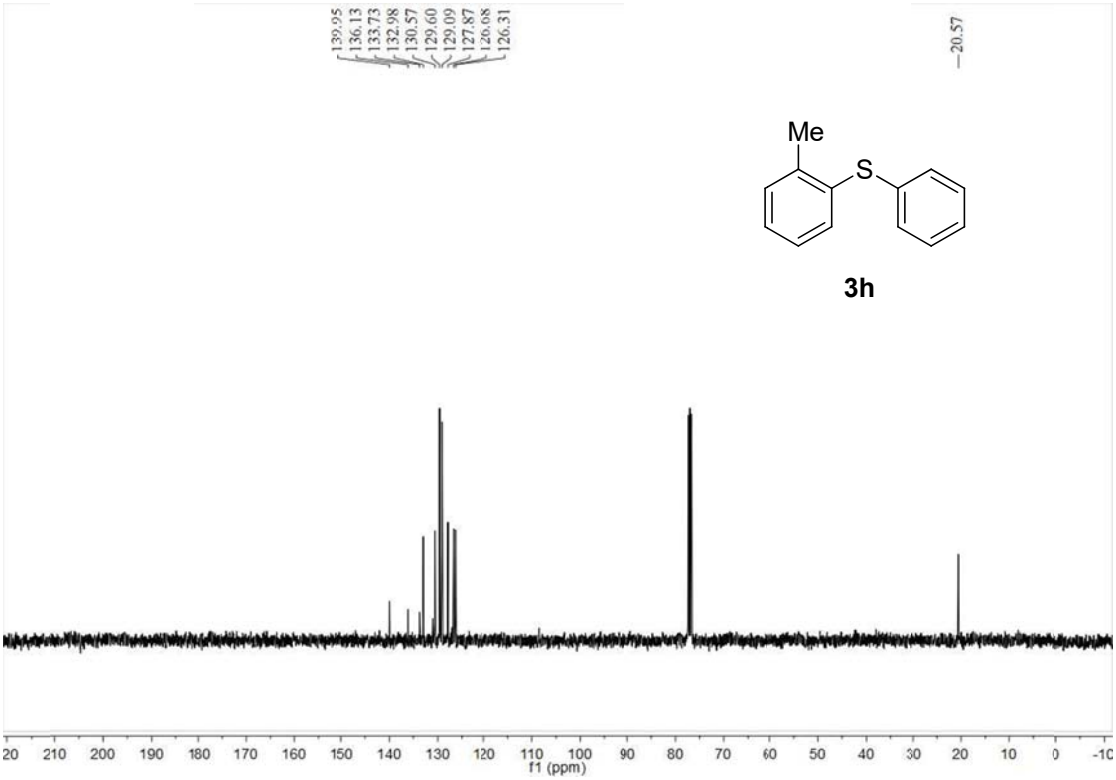
3f


7.44
7.42
7.41
7.41
7.40
7.39
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.25
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.15
S
Br
3g
2.00
3.07
2.12
2.14
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 -1.5 -2.0
f1 (ppm)

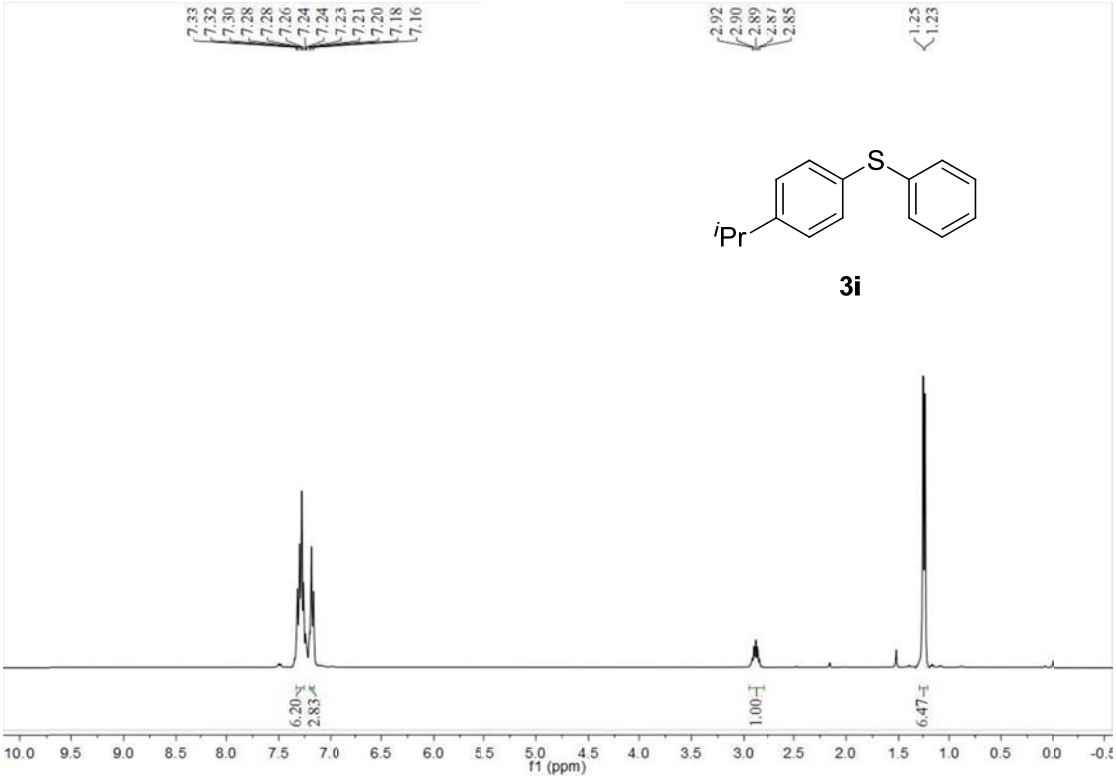

135.48
132.56
132.42
132.20
132.06
131.53
129.34
127.53
S
Br
3g
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
f1 (ppm)

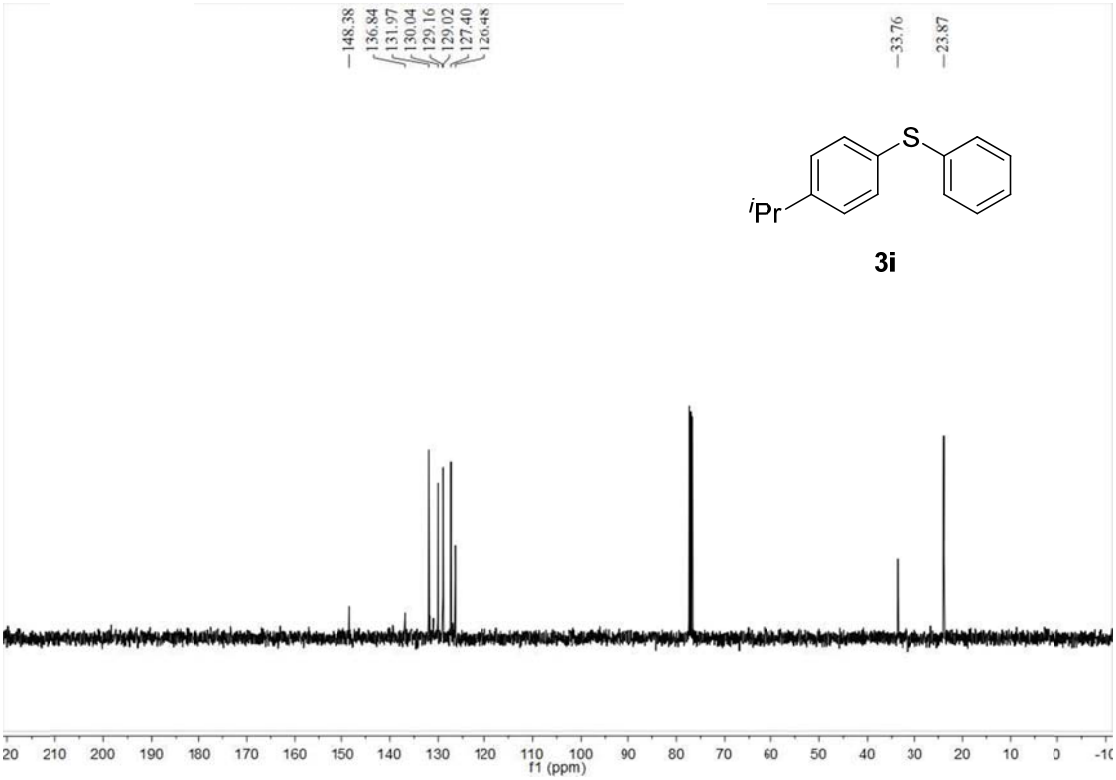

7.30
7.30
7.28
7.28
7.27
7.26
7.24
7.22
7.22
7.20
7.20
7.19
7.18
7.18
7.16
7.15
7.14
7.13
7.13
7.11
2.37
Me
S
9.29
5.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

3h


139.95
136.13
133.73
132.98
130.57
129.60
129.09
127.87
126.68
126.31
20.57
Me
S
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3h


7.33
7.32
7.30
7.28
7.28
7.26
7.24
7.24
7.23
7.21
7.20
7.18
7.16
2.92
2.90
2.89
2.87
2.85
1.25
1.23
S
iPr
3i
6.20
2.83
1.00
6.47
f1 (ppm)


148.38
136.84
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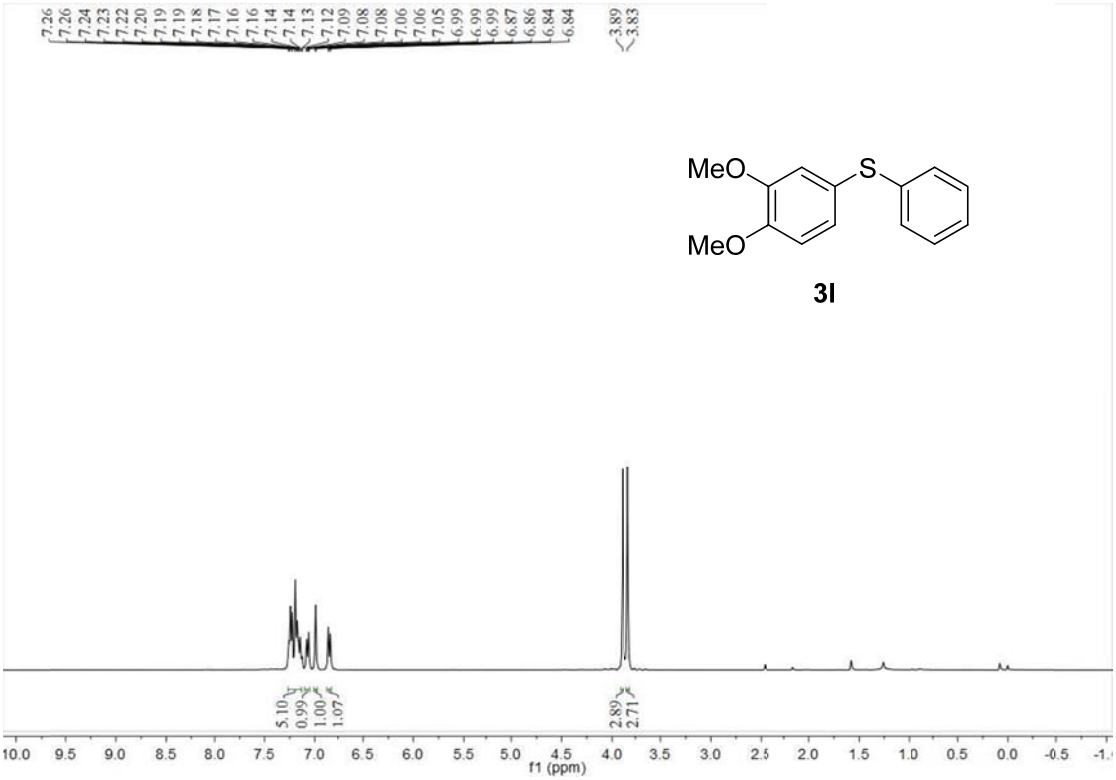
129.16
129.02
127.40
126.48
33.76
23.87
S
iPr
3i
f1 (ppm)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7.26
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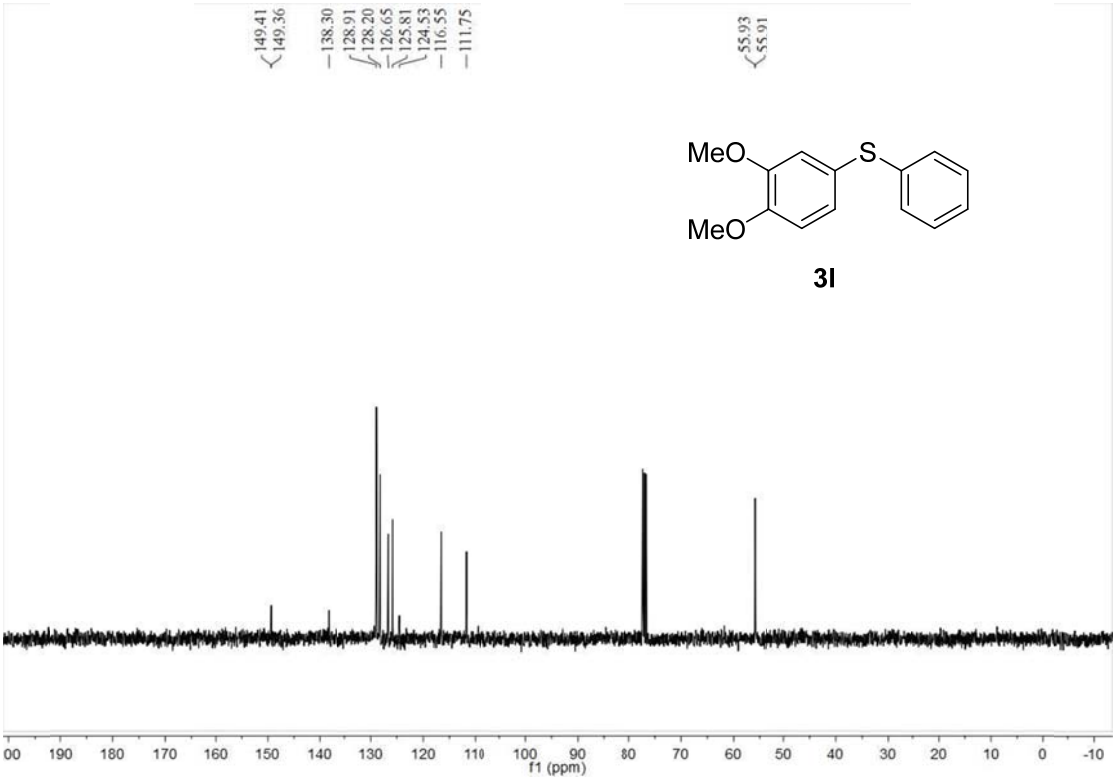
7.23
7.22
7.20
7.19
7.19
7.18
7.17
7.16
7.16
7.14
7.14
7.13
7.12
7.09
7.08
7.08
7.06
7.06
7.05
6.99
6.99
6.99
6.87
6.86
6.84
6.84
3.89
3.83
MeO
MeO
S
3l
5.10
0.99
1.00
1.07
2.89
2.71
f1 (ppm)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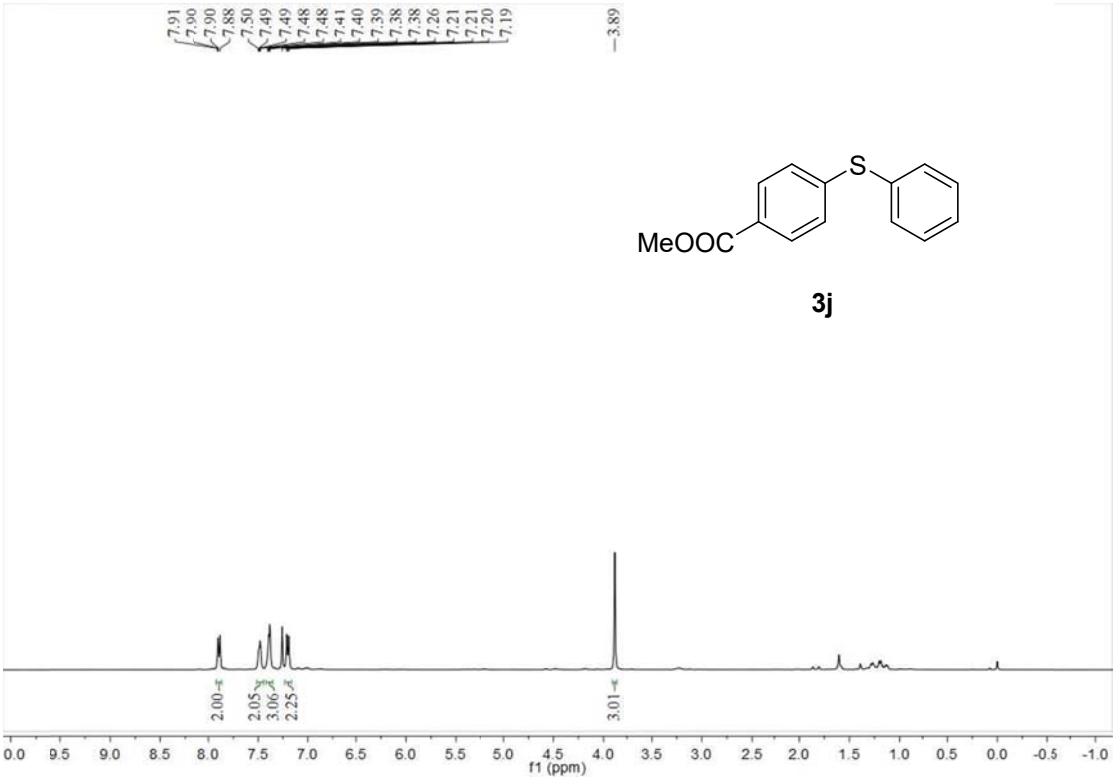
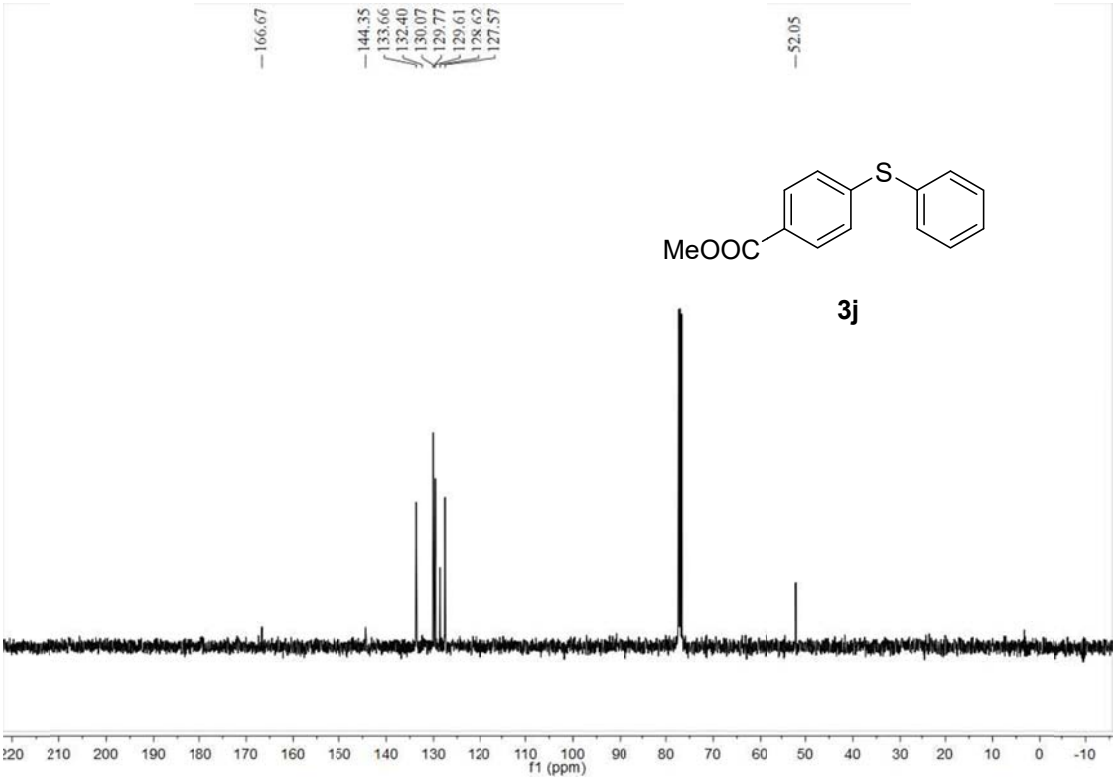
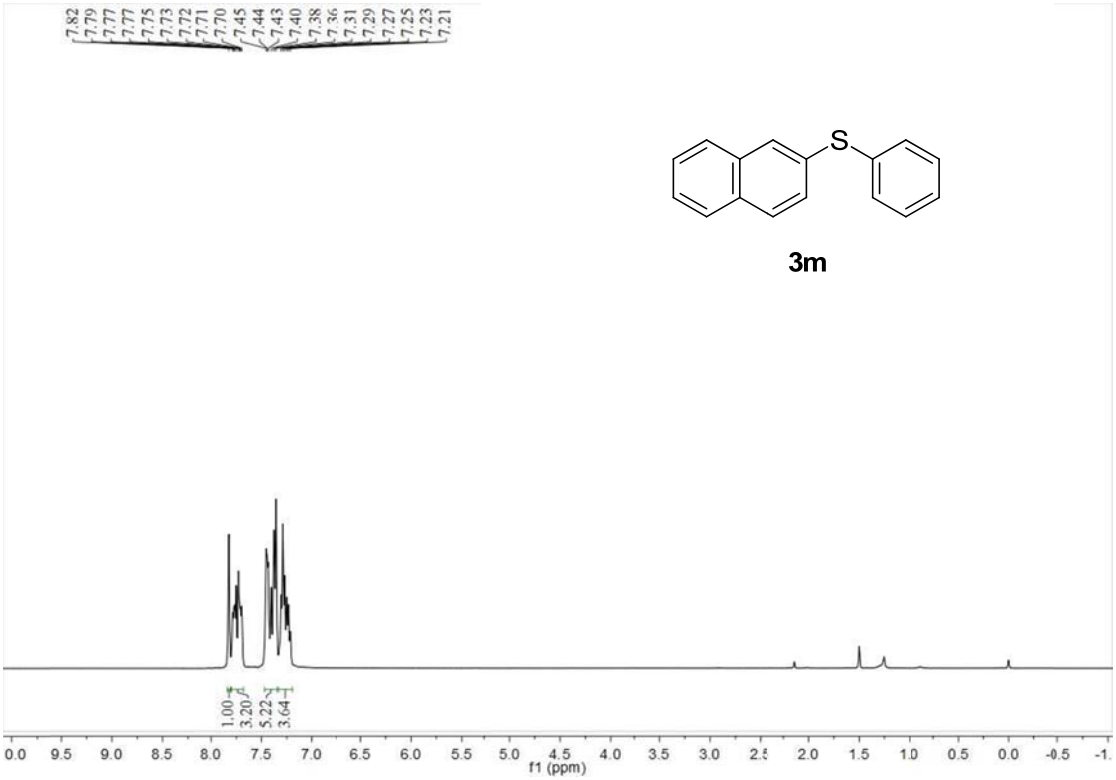
149.36
138.30
128.91
128.20
126.65
125.81
124.53
116.55
111.75
55.93
55.91
MeO
MeO
S
3l
f1 (ppm)

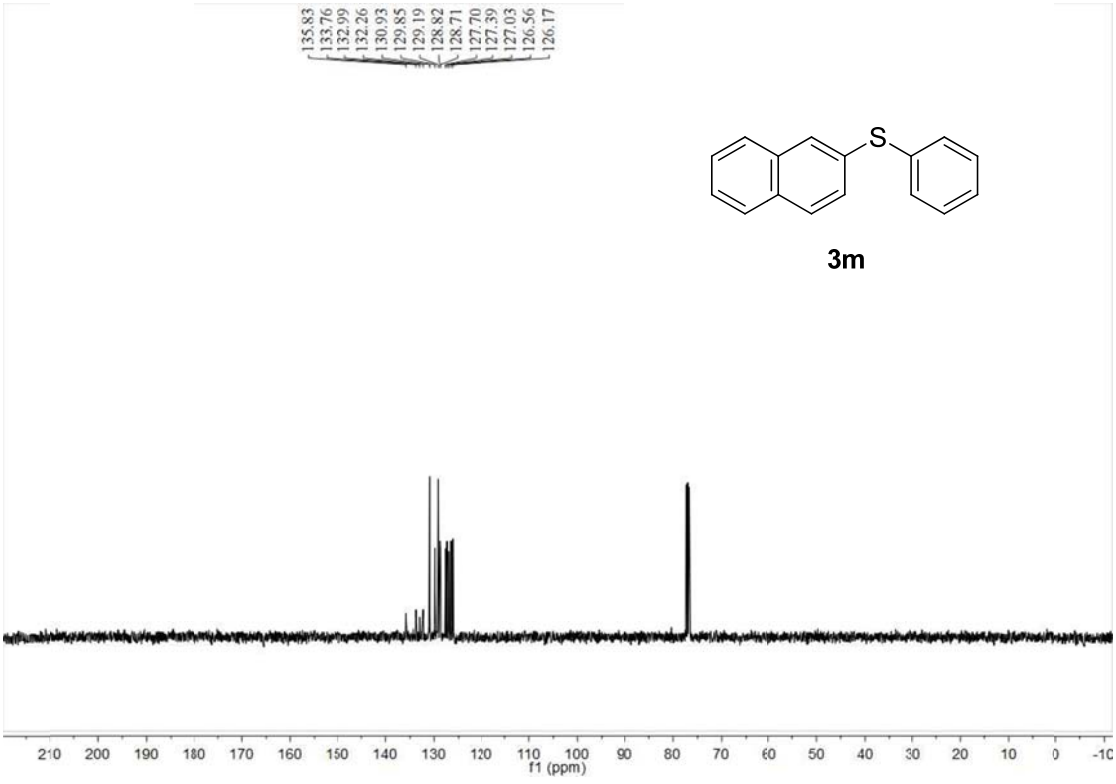

7.91
7.90
7.90
7.88
7.50
7.49
7.49
7.48
7.48
7.41
7.40
7.39
7.38
7.38
7.26
7.21
7.21
7.20
7.19
3.89
S
MeOOC
2.00
2.05
3.06
2.25
3.01
f1 (ppm)

3j


166.67
144.35
133.66
132.40
130.07
129.77
129.61
128.62
127.57
52.05
S
MeOOC
f1 (ppm)

3j


7.82
7.79
7.77
7.77
7.75
7.73
7.72
7.71
7.70
7.45
7.44
7.43
7.40
7.38
7.31
7.29
7.27
7.25
7.23
7.21
S
3m
1.00
3.20
5.22
3.64
f1 (ppm)


135.83
133.76
132.99
132.26
130.93
129.85
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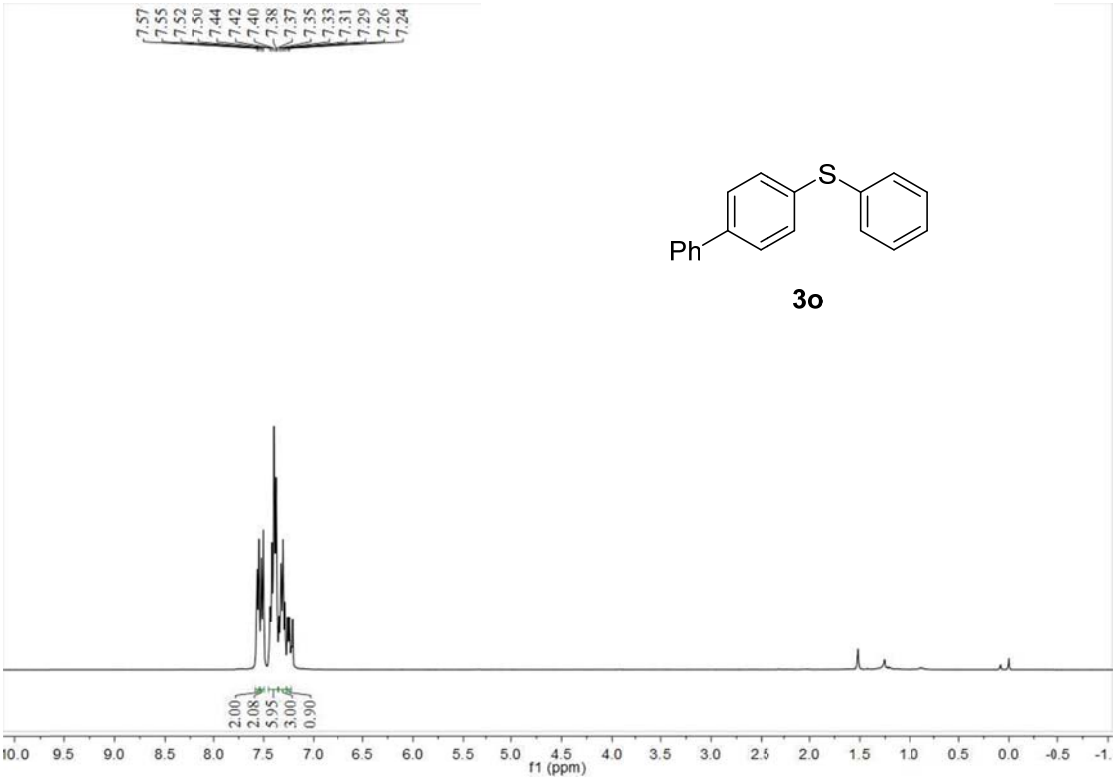
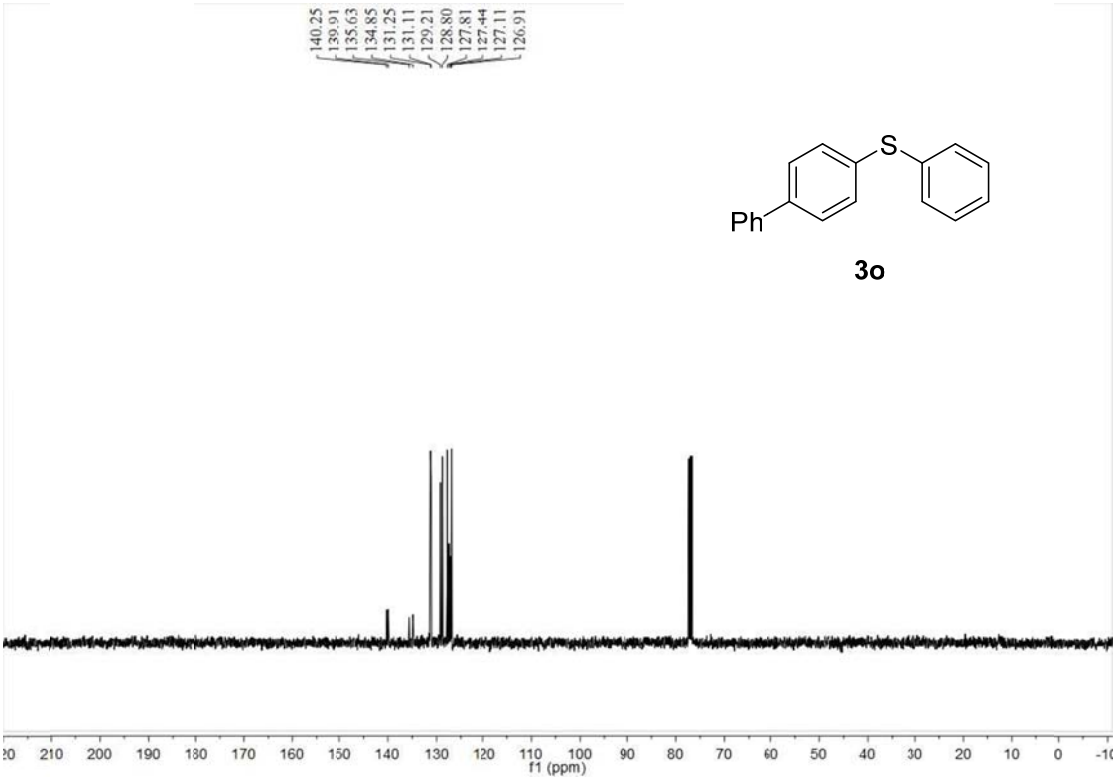
128.82
128.71
127.70
127.39
127.03
126.56
126.17
S
3m
f1 (ppm)


7.57
7.55
7.52
7.50
7.44
7.42
7.40
7.38
7.37
7.35
7.33
7.31
7.29
7.26
7.24
S
Ph
2.00
2.08
5.95
3.00
0.90
f1 (ppm)

3o


140.25
139.91
135.63
134.85
131.25
131.11
129.21
128.80
127.81
127.44
127.11
126.91
S
Ph
f1 (ppm)

3o

5. References

1. K. Yan, D. Yang, W. Wei, J. Zhao, Y. Shuai, L. Tian and H. Wang, *Org. Biomol. Chem*., 2015, 13, 7323–7330
2. C. Liu and M. Szostak, *Chem. Commun.,* 2018, **54**, 2130–2133.
3. V. K. Akkilagunta and R. R. Kakulapati, *J. Org. Chem*., 2011, **76**, 6819–6824.
4. K, Mal, S. Naskar, S. K. Sen, R. Natarajun and I. Das, *Adv. Synth. Catal.,* 2016, **358**, 3212–3230.