# Supporting Information

## *N*-Heterocyclic Carbene Catalyzed Sulfenylation of *α,β*-Unsaturated Aldehydes

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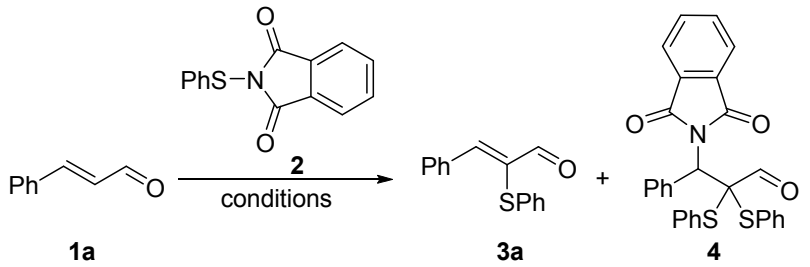
**General.** All reactions that required anhydrous conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents were used as received. The solvents were dried by distillation over the appropriate drying reagents. Infrared spectra were recorded on a TENSOR 27 FT-IR spectrophotometer and reported in wave numbers ($cm^{-1}$). $^{1}H$ and $^{13}C$ NMR spectra were recorded on Varian (400 MHz) spectrometer. Chemical shifts (δ) are reported in ppm relative to TMS (δ 0.00) for the $^{1}H$ NMR and to chloroform (δ 77.0) for the $^{13}C$ NMR measurements. High resolution mass spectra were obtained on a UltiMate 3000 spectrometer. Reactions were followed with TLC (0.254mm silica gel 60-F plates). Visualization was accomplished with UV light. Flash chromatography separations were performed on 200-300 mesh silica gel.

**Table S1 Sulfenylation of 1a**[a]

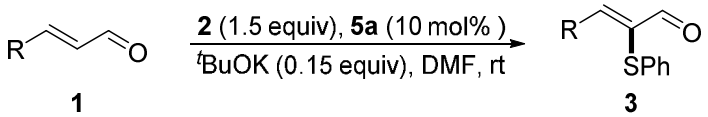



**1a** **3a** **4**

| entry | Catalyst (0.1 equiv) | base | additive | Time | **3a** yield (%)[b] | **4a** yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 | potassium phthalimide | -- | -- | 22 h | 14 | 15 |
| 2 | $^{t}$BuOK | -- | -- | 22 h | 12 | 13 |
| 3 | **5a** | $^{t}$BuOK | BHT | 36 h | 78 | -- |
| 4 | **5a** | $^{t}$BuOK | TEMPO | 36 h | 81 | -- |

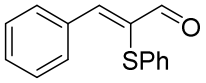
[a] Reactions were carried out with compound **1a** (0.20 mmol), **2** (0.30 mmol), catalyst (0.02 mmol), base (0.30 mmol), additive (0.02 mmol) in DMF (1.0 mL) at room temperature under $N_2$. [b] isolated yield. BHT = butylated hydroxytoluene, TEMPO = 2,2,6,6-tetramethylpiperidinooxy.

**Genera procedure for *N*-Heterocyclic Carbene Catalyzed Sulfenylation of α,β-Unsaturated Aldehydes**



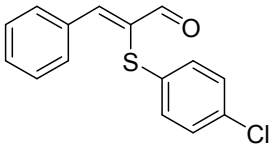

**1** **3**

A suspension of potassium $^{t}$BuOK (3.4 mg, 0.03 mmol) and IMes·HCl (**3**, 6.9 mg, 0.02 mmol) in dry DMF (1.0 mL) was stirred at ambient temperature for 0.5 h. *N*-(Phenylthio)phthalimide (**2**, 76.6 mg, 0.30 mmol) and aldehyde **1** (0.2 mmol) were added subsequently and the solution was stirred at room temperature for 36 h. TLC revealed the absence of starting material, the reaction mixture was diluted with water (5 mL) and extracted with $CH_2Cl_2$ (3 × 5 mL). The organic layers were washed with brine (10 mL), dried over anhydrous $Na_2SO_4$, filtrated and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (petroleum ether : EtOAc = 50 : 1) to yield the corresponding product.



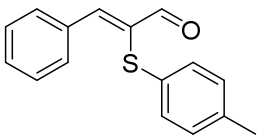

**(*Z*)-3-Phenyl-2-(phenylthio)acrylaldehyde (3a)[1]**

Light yellow oil, 41.3 mg, 86% yield. IR (KBr): 3058, 2825, 1693, 1444, 1116, 688 cm$^{-1}$. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.98–7.96 (m, 2H), 7.88 (s, 1H), 7.46–7.43 (m, 3H), 7.29–7.15 (m, 5H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.9, 151.1, 133.7, 133.6, 133.1, 131.3, 131.1, 129.1, 128.9, 128.6, 126.7. HRMS (ESI) calcd for $C_{15}H_{12}OSNa$ *m/z* $[M + Na]^+$: 263.0501; found: 263.0505.



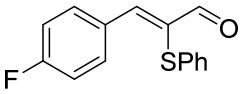

**(*Z*)-2-((4-Chlorophenyl)thio)-3-phenylacrylaldehyde (3ab)**

Light yellow oil, 44.5 mg, 81% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.96 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.88 (s, 1H), 7.45-7.47 (m, 3H), 7.21 (s, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.5, 152.4, 133.4, 133.0, 132.8, 132.2, 131.4, 131.3, 130.4, 129.2, 128.7. HRMS (ESI) calcd for $C_{11}H_{11}ClOSNa$ *m/z* $[M + Na]^+$: 297.0111; found: 297.0120.



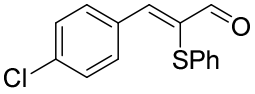

**(*Z*)-3-Phenyl-2-(*p*-tolylthio)acrylaldehyde (3ac)**

Light yellow oil, 41.7 mg, 82% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.95–7.98 (m, 2H), 7.82 (s, 1H), 7.45–7.43 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 190.9, 149.9, 136.9, 133.8, 133.6, 131.3, 131.0, 130.2, 129.9, 129.6, 128.6, 21.0. HRMS (ESI) calcd for $C_{16}H_{14}OSNa$ *m/z* $[M + Na]^+$: 277.0658; found: 277.0663.



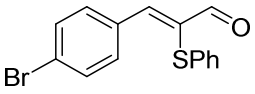

**(*Z*)-3-(4-Fluorophenyl)-2-(phenylthio)acrylaldehyde (3b)**

Light yellow oil, 42.4 mg, 82% yield. IR (KBr): 3058, 2858, 1693, 1504, 1234, 742 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.03-8.00 (m, 2H), 7.84 (s, 1H), 7.26–7.10 (m, 7H). $^{13}$CNMR (100 MHz, $CDCl_3$) δ 190.8, 164.1 (d, *J* = 252.0 Hz), 149.6, 133.6 (d, *J* = 12.0 Hz), 133.0 (d, *J* = 92.0 Hz), 129.9, 129.2, 128.9, 126.8, 115.9 (d, *J* = 21.0 Hz). HRMS (ESI) calcd. for $C_{15}H_{11}FOSNa$ *m/z* $[M + Na]^+$: 281.0407, found: 281.0405.



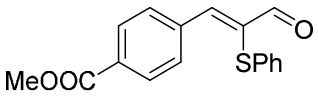

**(*Z*)-3-(4-Chlorophenyl)-2-(phenylthio)acrylaldehyde (3c)[1b]**

Light yellow oil, 46.7 mg, 85% yield. IR (KBr): 3062, 2824, 1693, 1456, 843 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.81 (s, 1H), 7.41–7.39 (m, 2H), 7.28–7.18 (m, 5H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.6, 148.8, 137.1, 133.5, 133.3, 132.5, 132.1, 129.2, 129.1, 128.9, 126.9. HRMS (ESI) calcd. for $C_{15}H_{11}ClOSNa$ *m/z* $[M + Na]^+$: 297.0111, found: 297.0106.



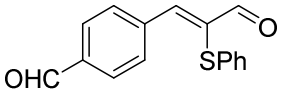

**(*Z*)-3-(4-Bromophenyl)-2-(phenylthio)acrylaldehyde (3d)**

Light yellow oil, 55.5 mg, 87% yield. IR (KBr): 3059, 2831, 1695, 1481, 1008, 746, 536 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.85–7.80 (m, 3H), 7.58–7.56 (m,2H), 7.26–7.07 (m, 5H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.6, 148.7, 133.7, 133.2, 132.6, 132.5, 131.9, 129.24, 129.18, 127.0, 125.6. HRMS (ESI) calcd. for $C_{15}H_{11}BrOSNa$ *m/z* $[M + Na]^+$: 340.9606, found: 340.9595.



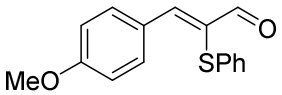

**Methyl (*Z*)-4-(3-oxo-2-(phenylthio)prop-1-en-1-yl)benzoate (3e)**

Light yellow solid: mp 94-96 °C, 48.3 mg, 81% yield. IR (KBr): 3058, 2825, 1720, 1693, 1504, 1231, 747 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.86 (s, 1H), 7.30–7.24 (m, 5H), 3.94 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 190.4, 166.3, 147.5, 137.8, 135.4, 133.0, 131.6, 130.9, 129.64, 129.56, 129.3, 127.2, 52.4. HRMS (ESI) calcd. for $C_{17}H_{14}O_3SNa$ *m/z* $[M + Na]^+$: 321.0556, found: 321.0552.



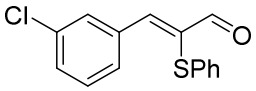

**(*Z*)-4-(3-Oxo-2-(phenylthio)prop-1-en-1-yl)benzaldehyde (3f)**

Light yellow oil, 45.1 mg, 84% yield. IR (KBr): 3058, 2835, 1693, 1604, 1305, 1211, 744 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 9.53 (s, 1H), 8.05 (d, *J* = 8.1 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.86 (s, 1H), 7.31-7.22 (m, 5H).$^{13}C$ NMR (100 MHz, $CDCl_3$) δ 191.4, 190.2, 146.3, 139.2, 137.0, 136.2, 132.6, 131.4, 129.7, 129.6, 129.3, 127.3. HRMS (ESI) calcd. for $C_{16}H_{12}O_2SNa$ *m/z* $[M + Na]^+$: 291.0450, found: 291.0446.



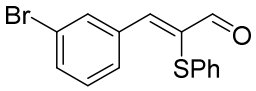

**(*Z*)-3-(4-Methoxyphenyl)-2-(phenylthio)acrylaldehyde (3g)[2]**

Light Light yellow solid: mp 76-78 °C, 31.4 mg, 58% yield. IR (KBr): 3147, 2839, 1585, 1259, 1024, 740 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.05–8.03 (m, 2H), 7.86 (s, 1H), 7.25 – 7.15 (m, 5H), 6.96–6.93 (m, 2H), 3.85 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 191.1, 162.2, 152.7, 134.2, 133.8, 129.7, 129.1, 128.3, 126.4, 126.3, 114.2, 55.4. HRMS (ESI) calcd. for $C_{16}H_{14}O_2SNa$ *m/z* $[M + Na]^+$:293.0607, found: 293.0609.



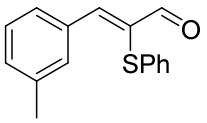

**(*Z*)-3-(3-Chlorophenyl)-2-(phenylthio)acrylaldehyde (3h)**

Light Light yellow oil, 46.7 mg, 85% yield. IR (KBr): 3000, 2832, 1695, 1475, 1112, 742 $cm^{-1}$. $^1H$ NMR (400 MHz, CDCl3) δ 9.51 (s, 1H), 7.95 (s, 1H), 7.84-7.73 (m, 2H), 7.41-7.34 (m, 2H), 7.31–7.13 (m, 5H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 190.4, 147.7, 135.3, 134.7, 134.5, 133.0, 132.3, 130.72, 130.70, 129.8, 129.5, 129.2, 127.1. HRMS (ESI) calcd. for $C_{15}H_{11}ClOSNa$ *m/z* $[M + Na]^+$: 297.0111, found: 297.0120.



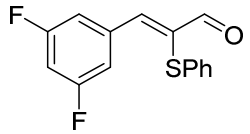

**(*Z*)-3-(3-Bromophenyl)-2-(phenylthio)acrylaldehyde (3i)**

Light yellow oil, 56.2 mg, 88% yield. IR (KBr): 3006, 2842, 1695, 1432, 1212, 732 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 8.08 (t, *J* = 1.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.75 (s, 1H), 7.54 (ddd, *J* = 8.0, 1.8, 0.9 Hz, 1H), 7.35–7.15 (m, 6H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 190.4, 147.5, 135.5, 134.8, 133.62, 133.59, 133.0, 130.0, 129.6, 129.5, 129.2, 127.1, 122.6. HRMS (ESI) calcd. for $C_{15}H_{11}BrOSNa$ *m/z* $[M + Na]^+$: 340.9606, found: 340.9608.



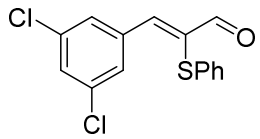

**(*Z*)-2-(Phenylthio)-3-(m-tolyl)acrylaldehyde (3j)**

Light yellow oil, 40.2 mg, 79% yield. IR (KBr): 3058, 2922, 1693, 1475, 1114, 688 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.85-7.76 (m, 3H), 7.40 – 7.08 (m, 7H), 2.39 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 191.0, 151.5, 138.4, 133.9, 133.6, 132.9, 132.1, 132.0, 129.6, 129.1, 129.0, 128.6, 126.7, 21.43. HRMS (ESI) calcd. for $C_{16}H_{14}OSNa$ *m/z* $[M + Na]^+$: 277.0658, found: 277.0660.



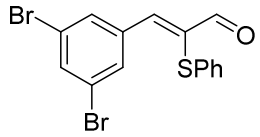

**(*Z*)-3-(3,5-Difluorophenyl)-2-(phenylthio)acrylaldehyde (3k)**

Light yellow oil, 50.3 mg, 91% yield. IR (KBr): 3082, 2804, 1697, 1323, 1122, 742 $cm^{-1}$. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.70 (s, 1H), 7.48-7.45 (m, 2H), 7.29–7.25 (m, 5H), 6.90–6.86 (m, 1H). $^{13}CNMR$ (100 MHz, $CDCl_3$) δ 190.1, 162.7 (dd, *J* = 248.0, 13.0 Hz), 145.3, 136.4 (t, *J* = 10.0 Hz), 135.9, 132.5, 129.7, 129.3, 127.4, 113.7 (dd, *J* = 20.0, 7.0 Hz), 106.0 (t, *J* = 15.0 Hz). HRMS (ESI) calcd. for $C_{15}H_{10}F_2OSNa$ *m/z* $[M + Na]^+$: 299.0313, found: *m/z* 299.0320.



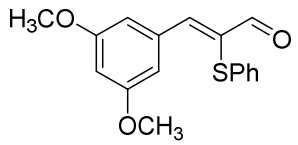

**(*Z*)-3-(3,5-Dichlorophenyl)-2-(phenylthio)acrylaldehyde (3l)**

Light yellow oil, 57.5 mg, 93% yield. IR (KBr): 3058, 2860, 1697, 1101, 736 $cm^{-1}$. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 9.48 (d, *J* = 1.5 Hz, 1H), 7.77 (s, 2H), 7.65 (s, 1H), 7.39 (d, *J* = 1.7 Hz, 1H), 7.33–7.15 (m, 5H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 190.1, 144.5, 136.3, 135.2, 132.3, 130.2, 130.0, 129.4, 128.9, 127.5. HRMS (ESI) calcd. for $C_{15}H_{10}Cl_2OSNa$ *m/z* $[M + Na]^+$: 330.9722, found: 330.9728.



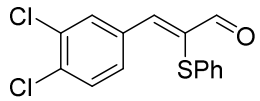

**(*Z*)-3-(3,5-Dibromophenyl)-2-(phenylthio)acrylaldehyde (3m)**

Light yellow oil, 74.8 mg, 94% yield. IR (KBr): 3057, 2860, 1698, 1433, 1101, 744 $cm^{-1}$. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.95 (d, *J* = 1.6 Hz, 2H), 7.68 (t, *J* = 1.6 Hz, 1H), 7.62 (s, 1H), 7.32–7.13 (m, 5H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 190.0, 144.2, 136.9, 136.4, 135.6, 132.3, 132.1, 130.0, 129.3, 127.5, 122.9. HRMS (ESI) calcd. for $C_{15}H_{10}Br_2OSNa$ *m/z* $[M + Na]^+$: 418.8711, found: 418.8715.



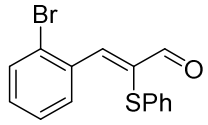

**(*Z*)-3-(3,5-Dimethoxyphenyl)-2-(phenylthio)acrylaldehyde (3n)**

Light yellow solid: 55-57 °C, 52.3 mg, 87% yield IR (KBr): 2945, 2837, 1691, 1155, 1058, 742 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.80 (s, 1H), 7.36–7.06 (m, 7H), 6.56 (t, *J* = 2.2 Hz, 1H), 3.80 (s, 6H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 190.9, 160.6, 150.8, 135.2, 133.7, 133.4, 129.2, 129.1, 126.8, 109.1, 103.7, 55.5. HRMS (ESI) calcd. for $C_{17}H_{16}O_3SNa$ *m/z* $[M + Na]^+$: 323.0712, found: 323.0718.



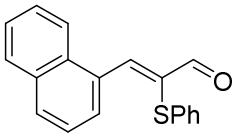

**(*Z*)-3-(3,4-Dichlorophenyl)-2-(phenylthio)acrylaldehyde (3o)**

Light yellow solid: 72-74 °C, 53.2 mg, 86% yield. IR (KBr): 2933, 2856, 1695, 1192, 738 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.05 (s, 1H), 7.77–7.74 (m, 1H), 7.71 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.33–7.10 (m, 5H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 190.2, 146.0, 135.0, 134.9, 133.5, 132.9, 132.7, 132.5, 130.5, 130.1, 129.6, 129.3, 127.3. HRMS (ESI) calcd. for $C_{15}H_{10}Cl_2OSNa$ *m/z* $[M + Na]^+$: 330.9722, found: 330.9723.



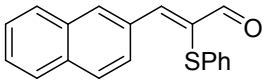

**(*Z*)-3-(2-Bromophenyl)-2-(phenylthio)acrylaldehyde (3p)**

Light yellow oil, 56.2 mg, 88% yield. IR (KBr): 3049, 2848, 1697, 1101, 742 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.06 (s, 1H), 7.84 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.38–7.07 (m, 7H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 190.3, 148.9, 136.4, 133.8, 133.0, 132.8, 131.4, 131.2, 129.5, 129.1, 127.0, 126.9, 125.1. HRMS (ESI) calcd. for $C_{15}H_{11}BrOSNa$ *m/z* $[M + Na]^+$: 340.9606, found: 340.9609.



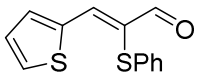

**(*Z*)-3-(Naphthalen-1-yl)-2-(phenylthio)acrylaldehyde (3q)**

Light yellow solid: 86-88 °C, 45.3 mg, 78% yield. IR (KBr): 2931, 2856, 1691, 1124, 773 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.57 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.96–7.80 (m, 3H), 7.68–7.43 (m, 3H), 7.36–7.04 (m, 5H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 190.4, 147.0, 136.4, 133.4, 133.3, 131.5, 130.9, 130.4, 129.7, 129.1, 128.9, 128.5, 127.1, 126.9, 126.4, 125.0, 123.6. HRMS (ESI) calcd. for $C_{19}H_{14}OSNa$ *m/z* $[M + Na]^+$: 313.0658, found: 313.0661.



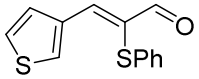

**(*Z*)-3-(Naphthalen-2-yl)-2-(phenylthio)acrylaldehyde (3r)**

Light yellow solid: 107-109 °C, 47.0 mg, 81% yield. IR (KBr): 3057, 2844, 1691, 1110, 779 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.40 (s, 1H), 8.15 (dd, *J* = 8.7, 1.7 Hz, 1H), 8.03 (s, 1H), 7.97–7.75 (m, 3H), 7.54 (m, 2H), 7.39–7.10 (m, 5H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 190.9, 151.1, 134.3, 133.8, 133.0, 132.9, 132.8, 131.2,131.0, 129.1, 129.0,128.9, 128.2, 128.0, 127.7, 127.2, 126.7. HRMS (ESI) calcd. for $C_{19}H_{14}OSNa$ *m/z* $[M + Na]^+$: 313.0658, found: 313.0656.



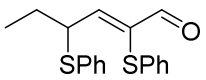

**(*Z*)-2-(Phenylthio)-3-(thiophen-2-yl)acrylaldehyde (3s)**

Light yellow oil, 31.0 mg, 63% yield. IR (KBr): 3068, 2837, 1679, 1579, 1411, 1109, 740 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.15 (s, 1H), 7.66–7.62 (m, 2H), 7.30–7.16 (m, 6H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 190.2, 146.0, 137.7, 137.0, 134.5, 133.8, 129.2, 128.9, 128.5, 127.4, 126.7. HRMS (ESI) calcd. for $C_{13}H_{10}OS_2Na$ *m/z* $[M + Na]^+$: 269.0065, found: 269.0067.



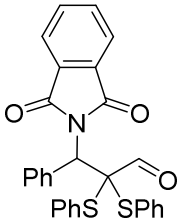

**(*Z*)-2-(Phenylthio)-3-(thiophen-3-yl)acrylaldehyde (3t)**

Light yellow oil, 44.8 mg, 91% yield. IR (KBr): 3089, 2825, 1687, 1477, 1112, 740 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.20 (d, *J* = 1.9 Hz, 1H), 7.91 (s, 1H), 7.81 (d, *J* = 4 Hz, 1H), 7.45–7.09 (m, 6H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 190.9, 145.4, 135.9, 133.8, 132.9, 130.9, 129.4, 129.1, 128.6, 126.6, 126.2. HRMS (ESI) calcd. for $C_{13}H_{10}OS_2Na$ *m/z* $[M + Na]^+$: 269.0065, found: 269.0066.




**(*Z*)-2,4-Bis(phenylthio)hex-2-enal (3u)**

Light yellow oil, 26.4 mg, 42% yield. IR (KBr): 3197, 2966, 2823, 1699, 1477, 1070, 720 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.46–7.44 (m, 2H), 7.26–7.22 (m, 3H), 7.17-7.13 (m, 3H), 6.98 (d, *J* = 10.4 Hz, 1H), 6.93-6.90 (m, 2H), 4.57-4.51 (m, 1H), 2.03–1.83 (m, 1H), 1.83 – 1.65 (m, 1H), 1.05 (t, *J* = 7.4 Hz, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 189.4, 157.3, 136.1, 133.8, 133.6, 132.5, 129.1, 128.97, 128.89, 128.1, 126.5, 49.9, 27.1, 11.9. HRMS (ESI) calcd. for $C_{18}H_{18}OS_2Na$ *m/z* $[M + Na]^+$: 337.0691, found: 337.0695.



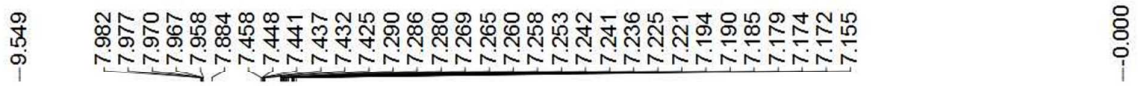

**3-(1,3-Dioxoisoindolin-2-yl)-3-phenyl-2,2-bis(phenylthio)propanal (4)**

White solid: 73-75 °C. $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.77-7.74 (m, 2H), 7.69-7.67 (m, 2H), 7.61-7.59 (m, 2H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.47 (d, *J* = 7.3 Hz, 2H), 7.41-7.17 (m, 9H), 5.81 (s, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ184.9, 167.5, 137.1, 134.6, 134.3, 134.2, 131.3, 130.2, 130.11, 130.06, 129.0, 128.9, 128.81, 128.77, 128.4, 123.5, 75.9, 58.0. HRMS (ESI) calcd. for $C_{29}H_{21}NO_3S_2Na$ *m/z* $[M + Na]^+$: 518.0855, found: 518.0860.

**References:**

(1) (a) He, L.; Guo, H.; Li, Y. Z.; Du, G. F.; Dai, B. *Chem. Commun.*, **2014**, *50*, 3719. (b) Silveira1,C.; Perin1, G.; Braga,A.; Dabdoub,M.; Jacob , R. *Tetrahedron*, **1999**, *55*, 7421. (c) Vlattas.; Isidoros. *J. Am. Chem. Soc.*,**1976**, *98*, 2008.

(2) (a) Yoshimatsu, M,; Hatanaka, F. *Chem. & Pharm. Bull.*, **2004**, *52*, 248. (b) Yoshimatsu, M,; Hatanaka, F. *Phosphorus, Sulfur and Silicon and the Related Elements*, **2005**, *180*, 1007.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7.967
7.958
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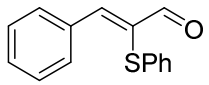
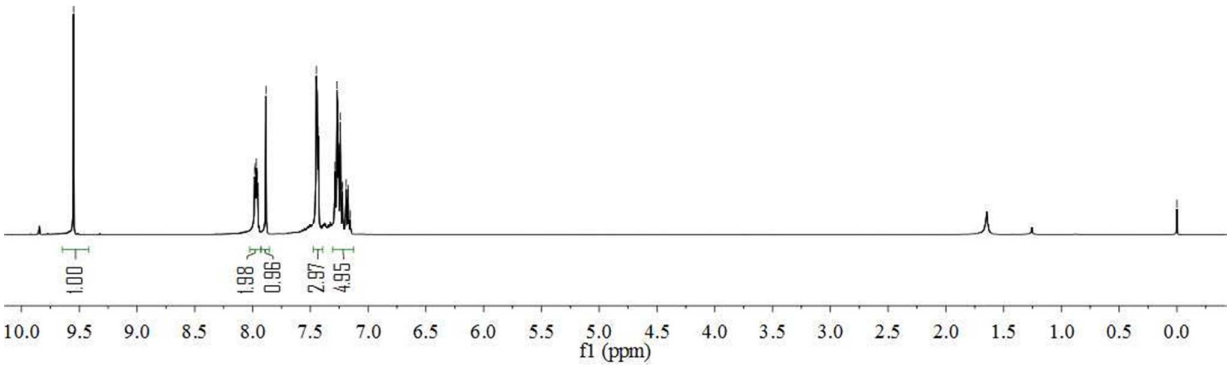
7.448
7.441
7.437
7.432
7.425
7.290
7.286
7.280
7.269
7.265
7.260
7.258
7.253
7.242
7.241
7.236
7.225
7.221
7.194
7.190
7.185
7.179
7.174
7.172
7.155
0.000


O
SPh

**3a**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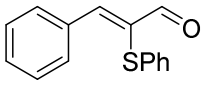
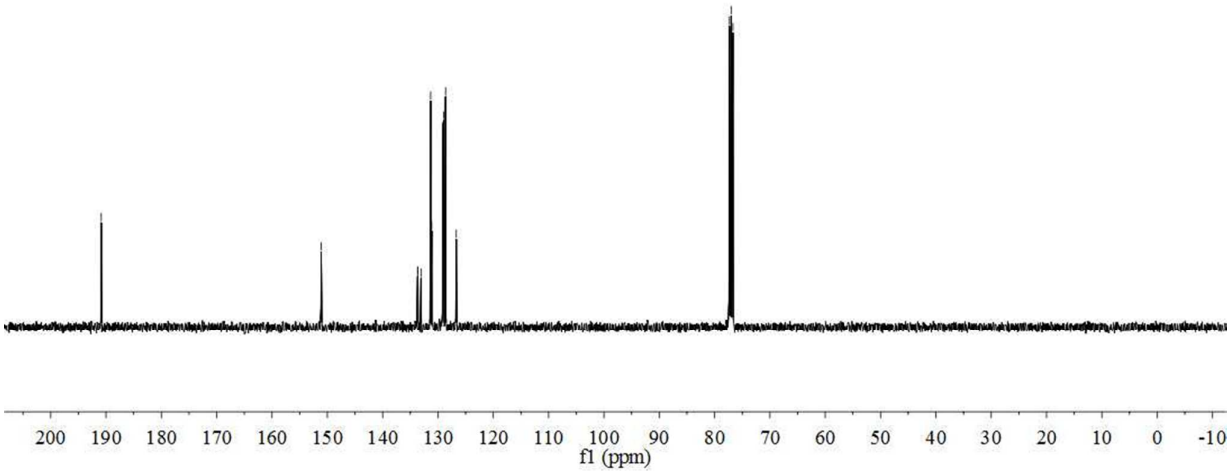
1.98
0.98
2.97
4.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.864
151.111
133.698
133.626
133.063
131.328
131.131
129.122
128.972
128.624
126.688
77.319
77.000
76.683


O
SPh

**3a**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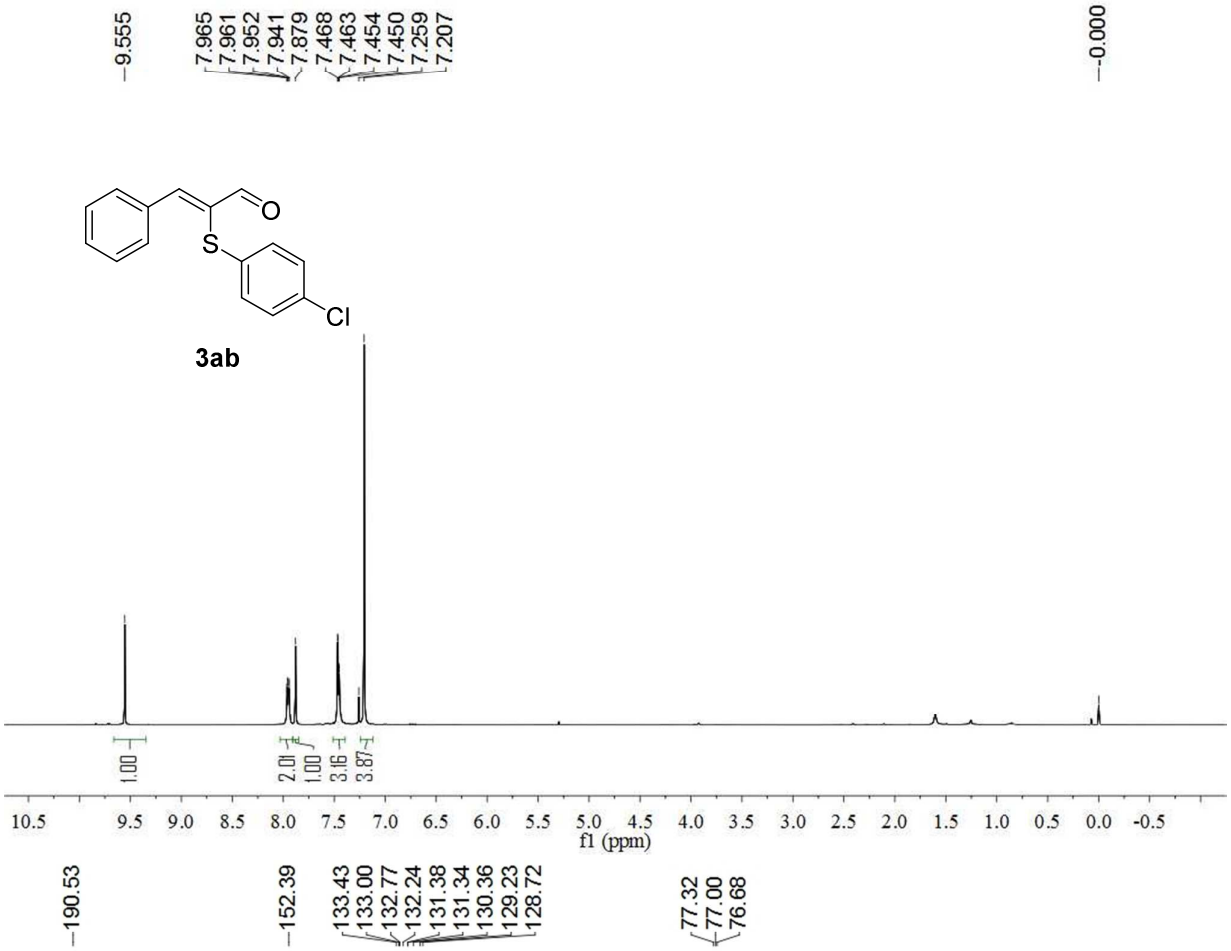
f1 (ppm)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7.941
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7.468
7.463
7.454
7.450
7.259
7.207
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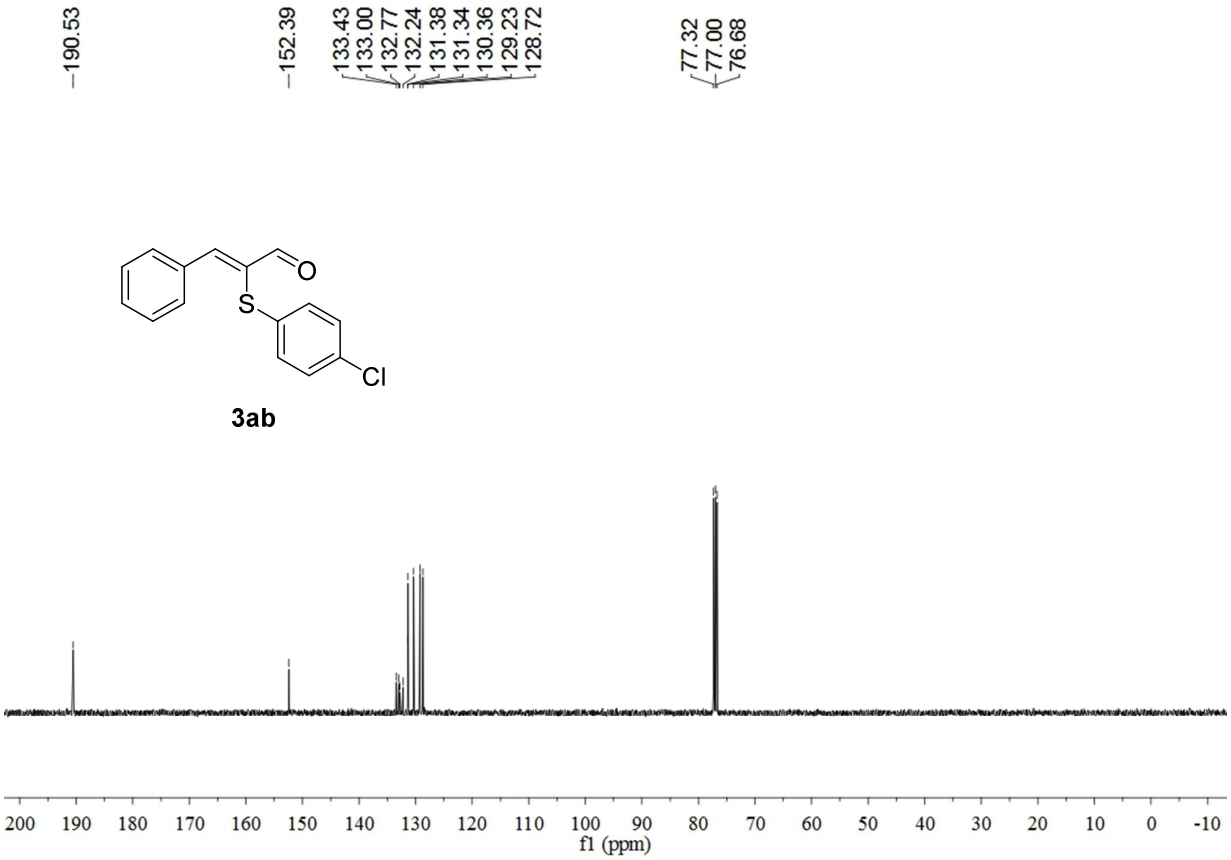
O
S
Cl
1.00
2.01
1.00
3.16
3.87
f1 (ppm)

**3ab**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152.39
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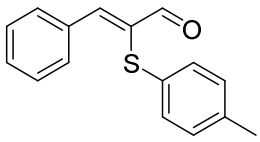
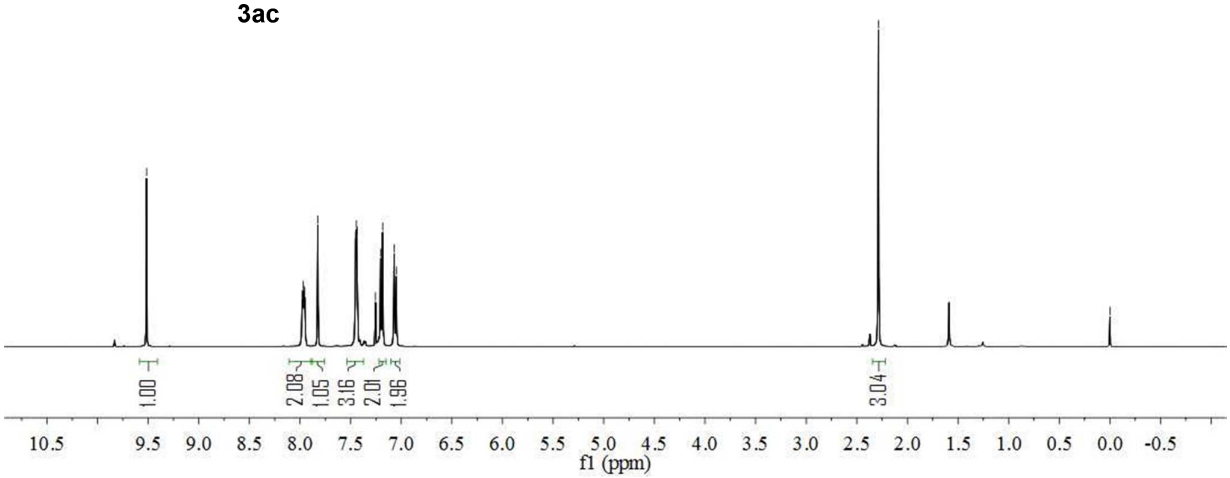
133.00
132.77
132.24
131.38
131.34
130.36
129.23
128.72
77.32
77.00
76.68
O
S
Cl
f1 (ppm)

**3ab**


9.516
7.978
7.969
7.965
7.960
7.954
7.824
7.451
7.443
7.435
7.254
7.204
7.184
7.070
7.050
2.286
0.000


O
S

**3ac**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1.05
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2.01
1.96
3.04
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
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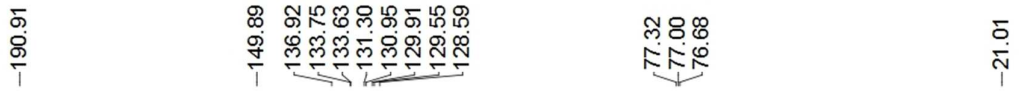
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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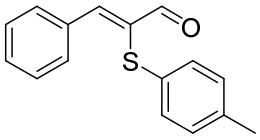
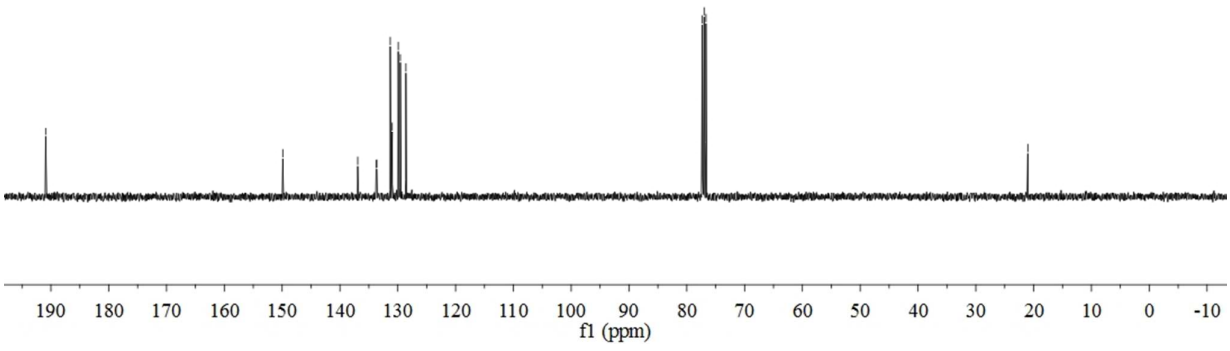
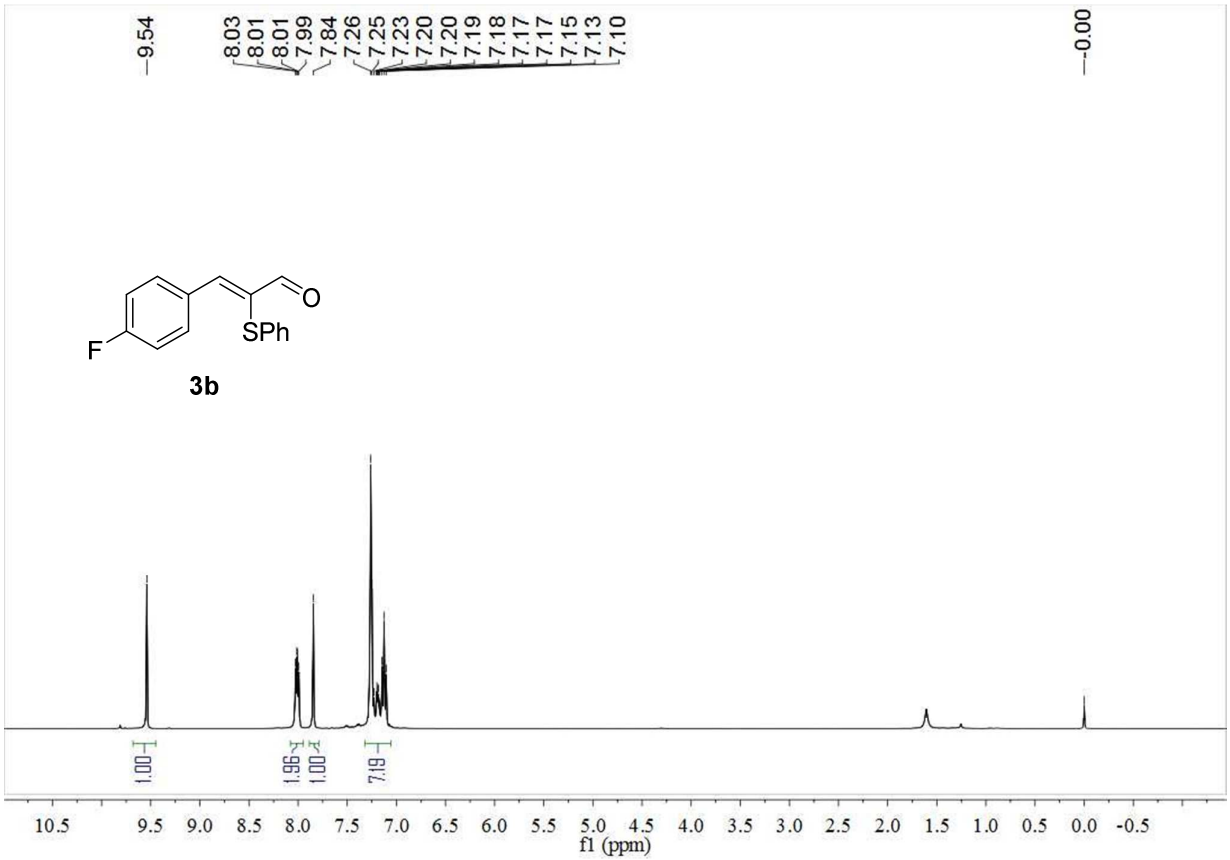
129.91
129.55
128.59
77.32
77.00
76.68
21.01


O
S

**3ac**


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.01
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7.84
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7.25
7.23
7.20
7.20
7.19
7.18
7.17
7.17
7.15
7.13
7.10
0.00
O
SPh
F
1.00
1.96
1.00
7.19
f1 (ppm)

**3b**


190.76
165.36
162.84
149.60
133.65
133.57
133.45
129.20
128.91
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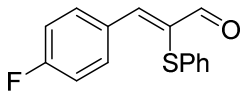
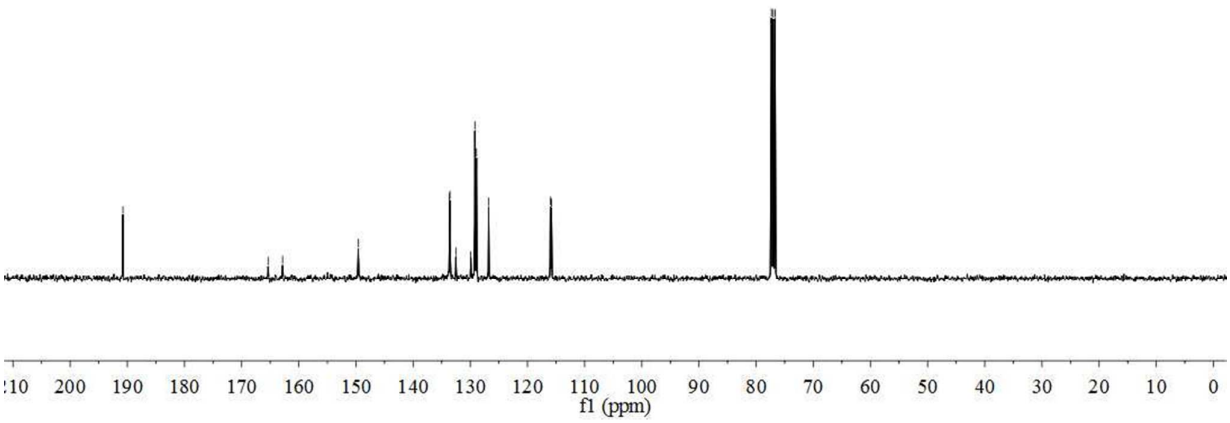
77.32
77.00
76.68
f1 (ppm)


O
SPh
F

**3b**


f1 (ppm)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7.811
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7.397
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7.278
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7.197
7.189
7.180
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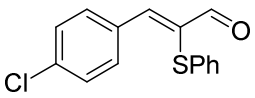
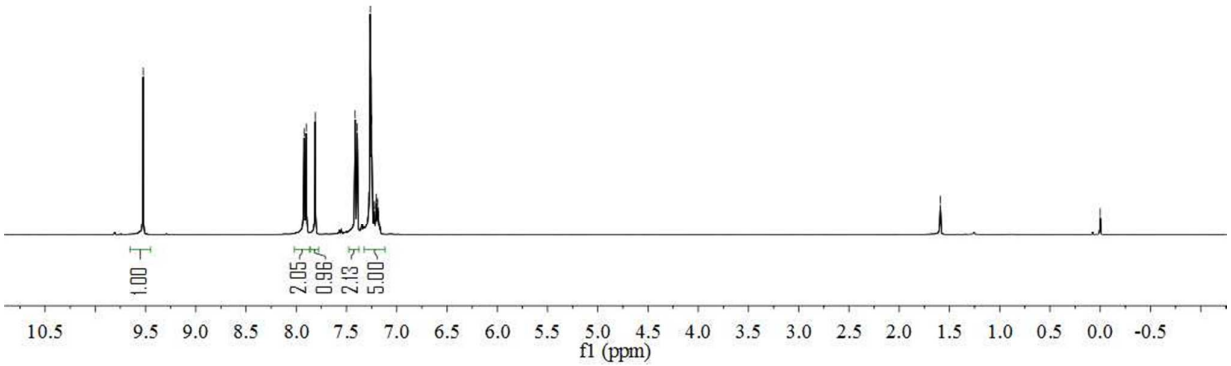
0.000


Cl
SPh
O

**3c**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8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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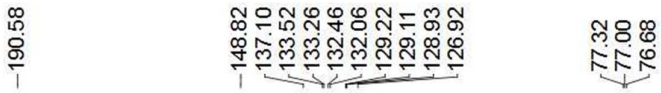
0.5
0.0
-0.5
f1 (ppm)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133.52
133.26
132.46
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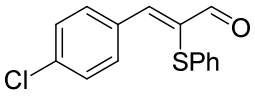
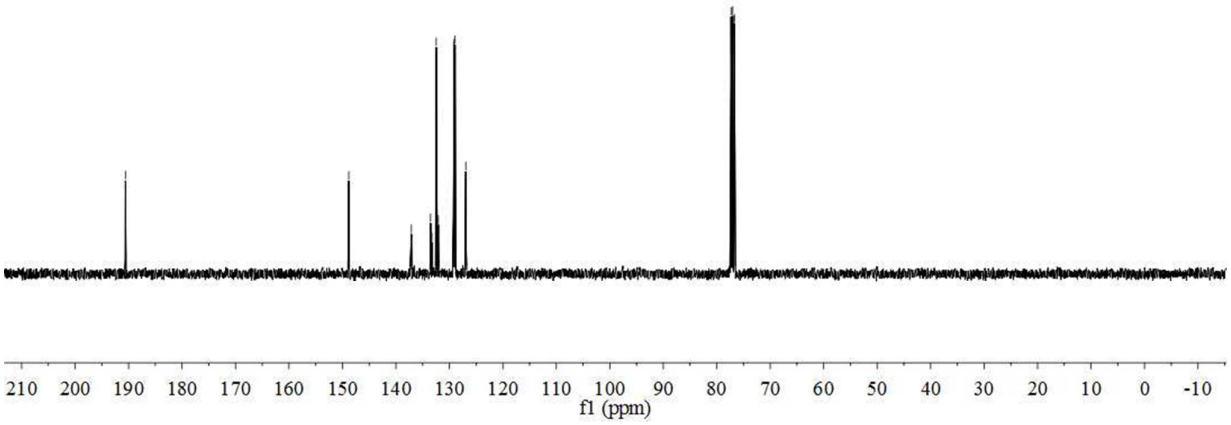
128.93
126.92
77.32
77.00
76.68


Cl
SPh
O

**3c**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200
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180
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150
140
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120
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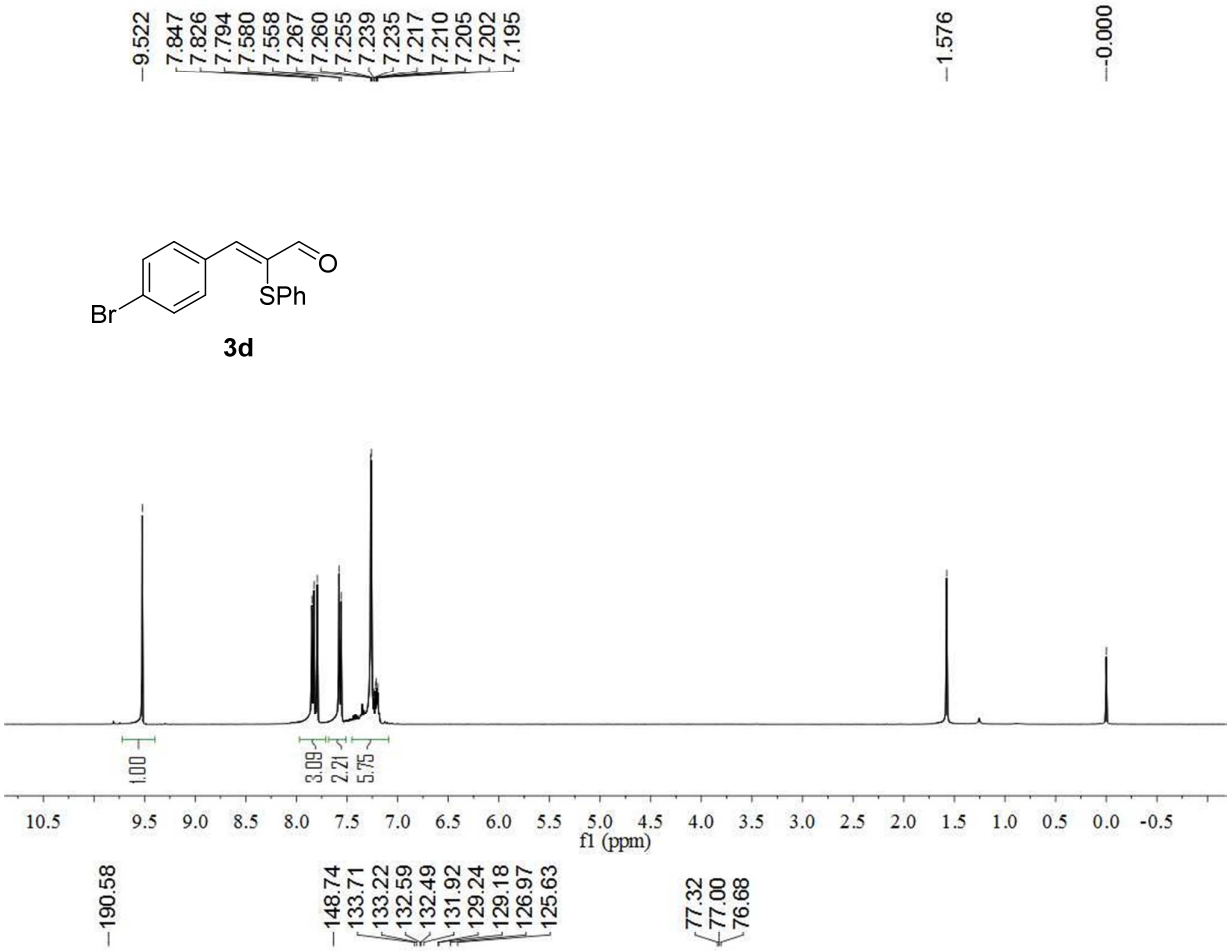
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.580
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7.267
7.260
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7.239
7.235
7.217
7.210
7.205
7.202
7.195
1.576
0.000
O
SPh
Br
3d
1.00
3.09
2.21
5.75
f1 (ppm)
190.58
148.74
133.71
133.22
132.59
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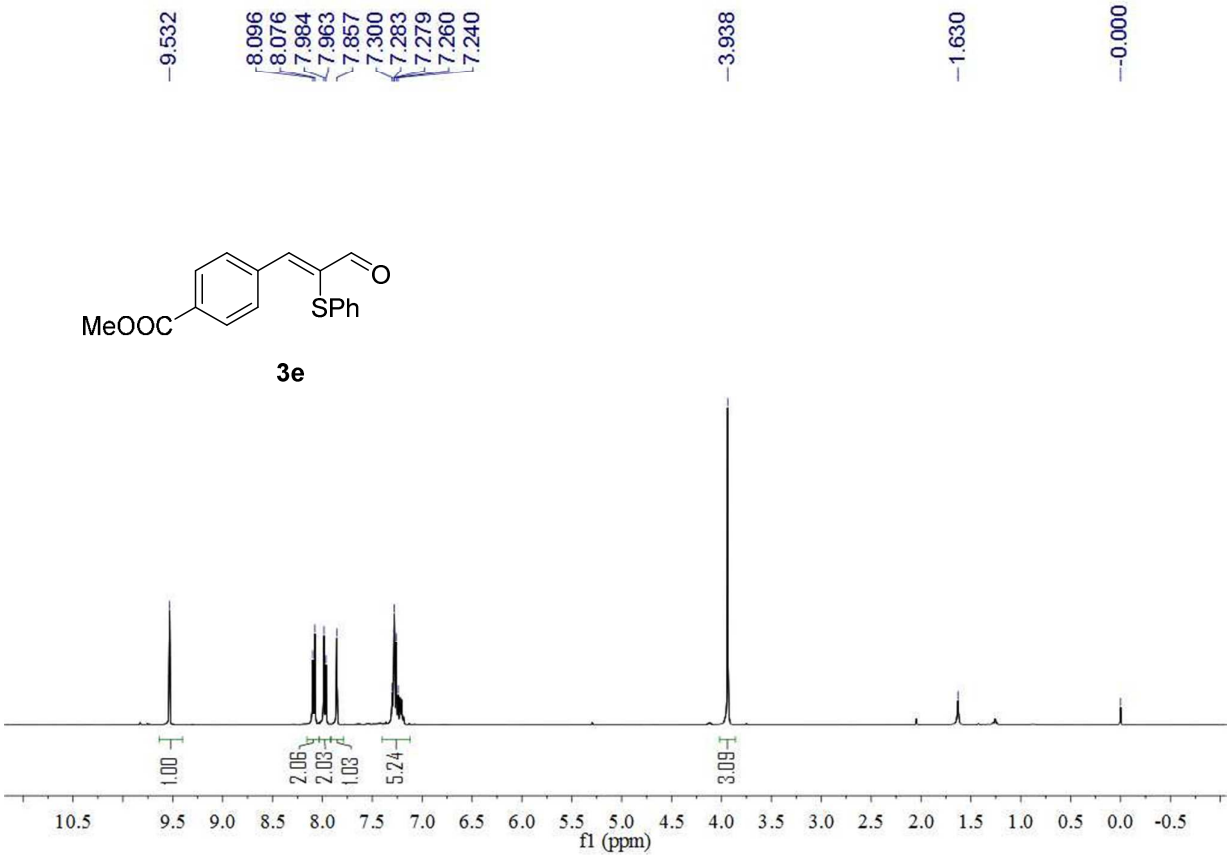
76.68
O
SPh
Br
3d
f1 (ppm)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7.260
7.240
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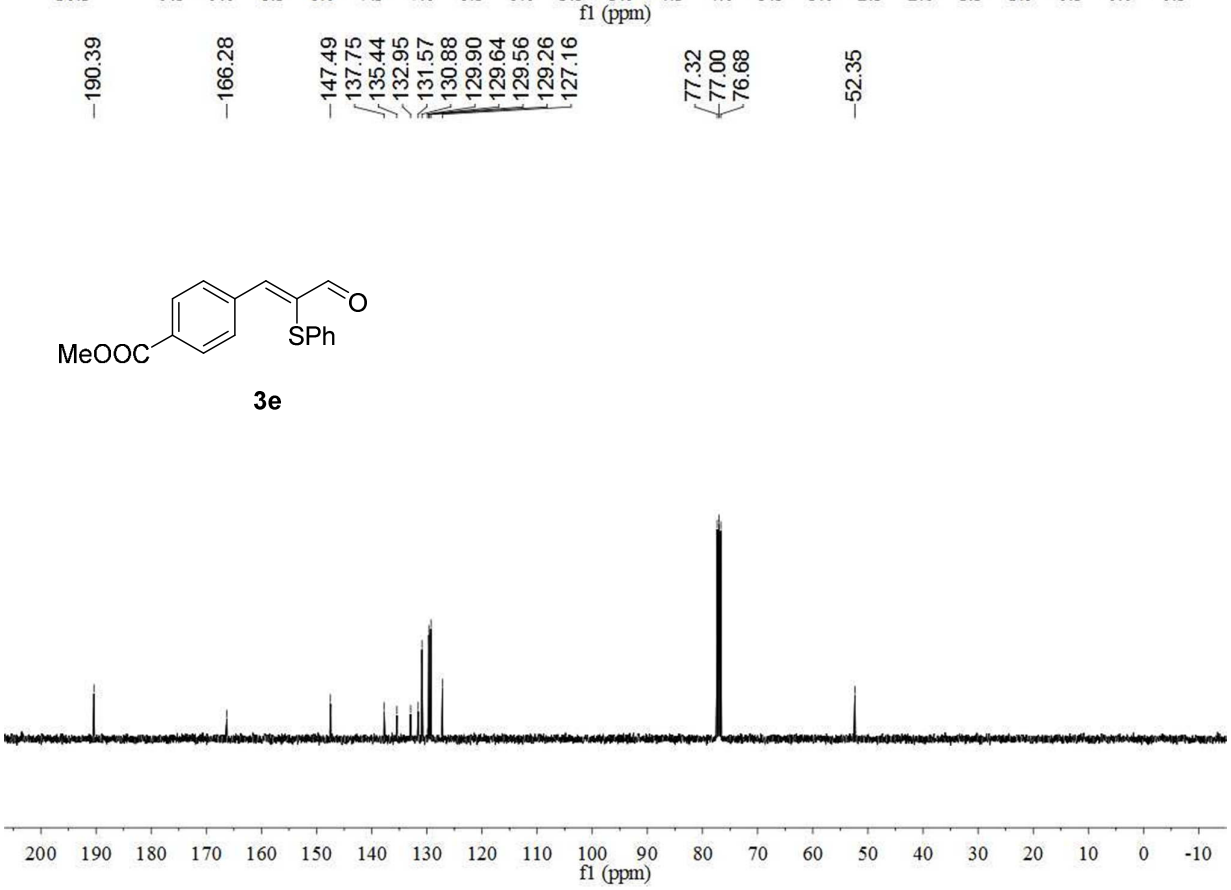
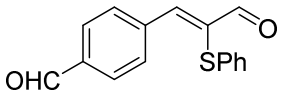
1.630
0.000
O
SPh
MeOOC
1.00
2.06
2.03
1.03
5.24
3.09
f1 (ppm)

**3e**

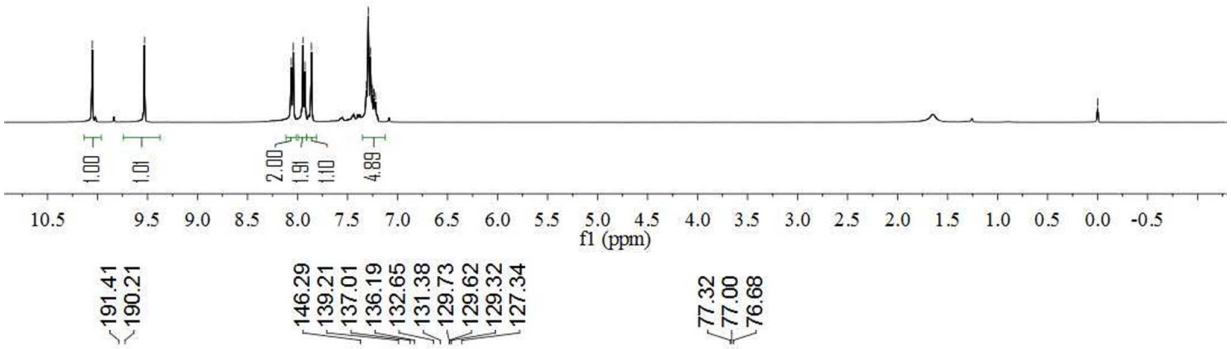

190.39
166.28
147.49
137.75
135.44
132.95
131.57
130.88
129.90
129.64
129.56
129.26
127.16
77.32
77.00
76.68
52.35
O
SPh
MeOOC
f1 (ppm)

**3e**

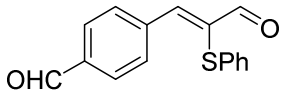

10.051
9.531
8.062
8.042
7.946
7.926
7.860
7.310
7.293
7.272
7.255
7.253
7.240
7.235
7.220
0.000


O
SPh
OHC

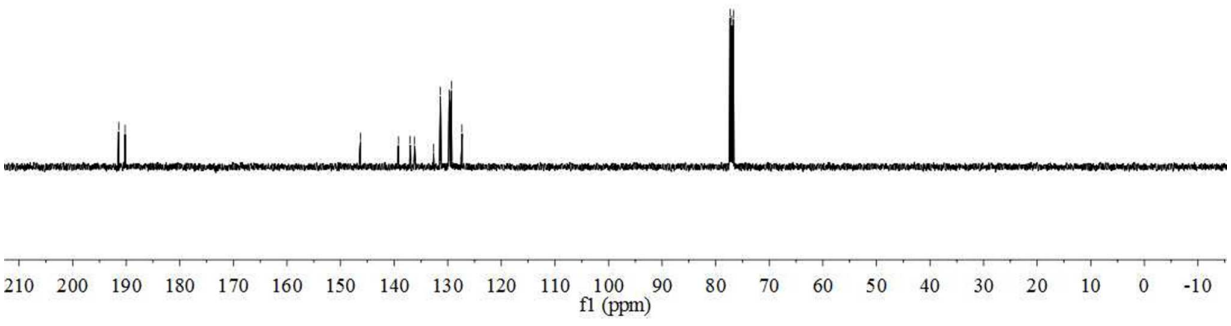
**3f**

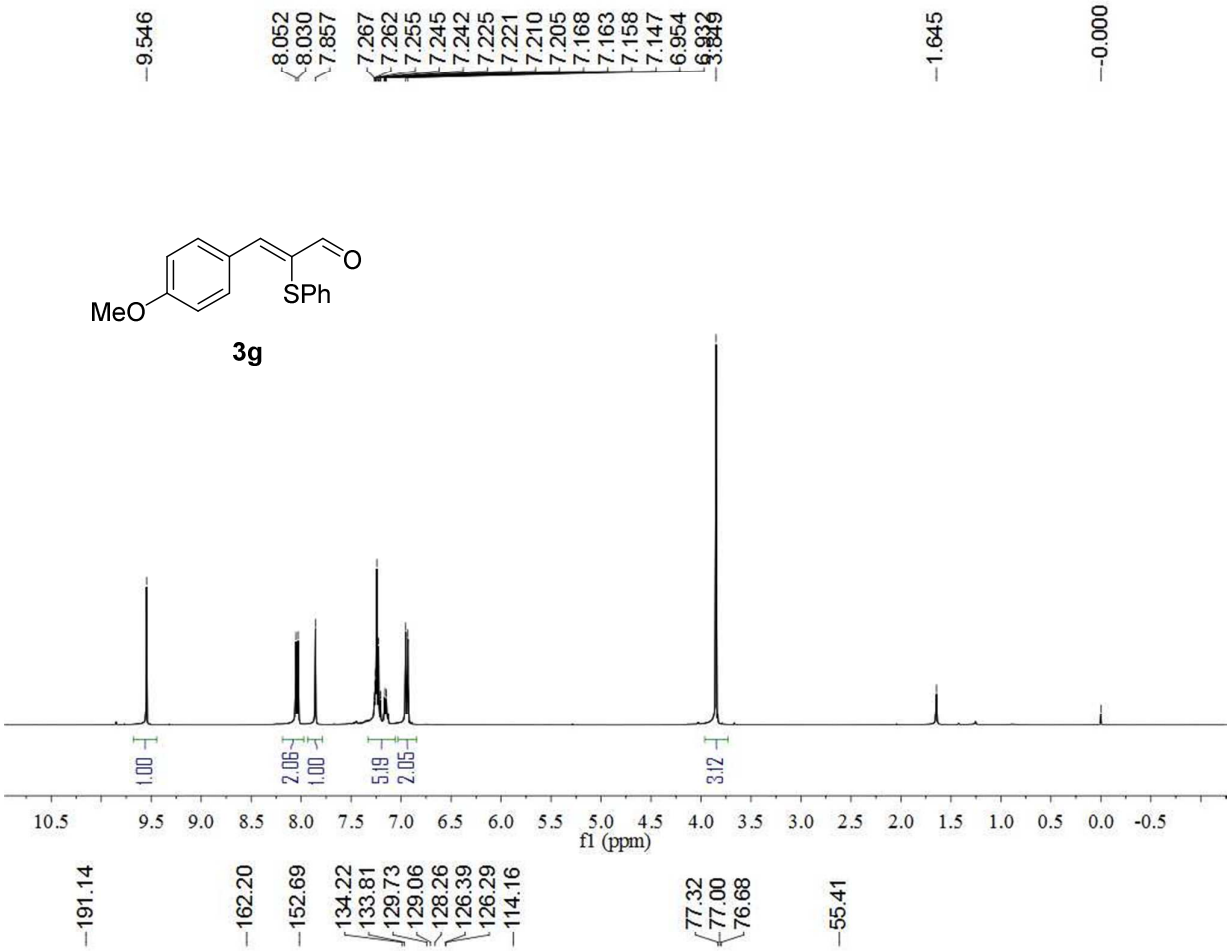

1.00
1.01
2.00
1.91
1.10
4.89
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


191.41
190.21
146.29
139.21
137.01
136.19
132.65
131.38
129.73
129.62
129.32
127.34
77.32
77.00
76.68

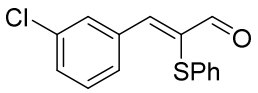

O
SPh
OHC

**3f**

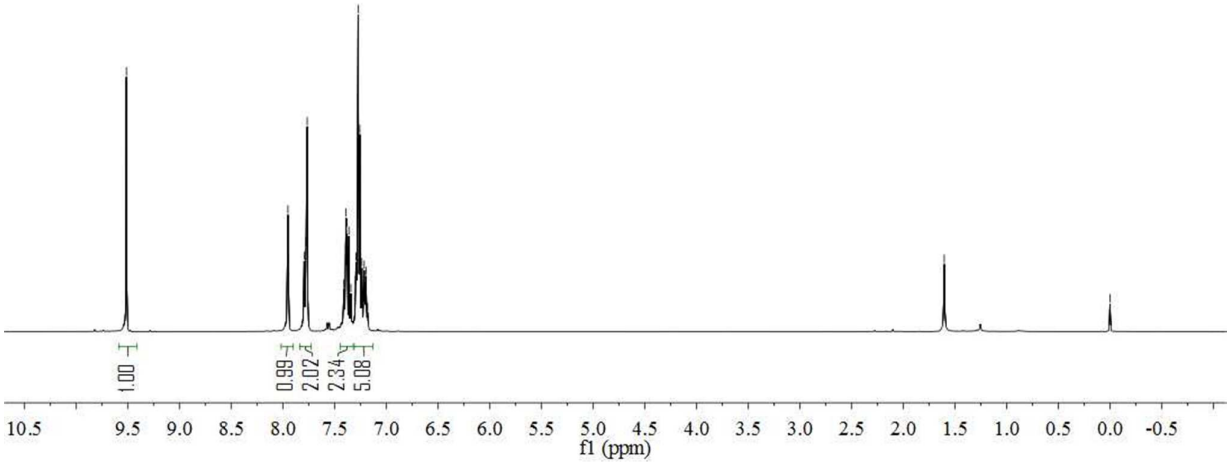

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

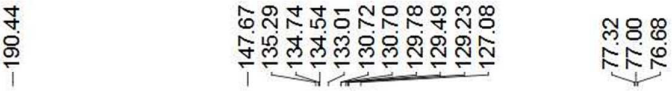

9.546
8.052
8.030
7.857
7.267
7.262
7.255
7.245
7.242
7.225
7.221
7.210
7.205
7.168
7.163
7.158
7.147
6.954
3.849
1.645
0.000
MeO
SPh
O
3g
1.00
2.06
1.00
5.19
2.05
3.12
f1 (ppm)
191.14
162.20
152.69
134.22
133.81
129.73
129.06
128.26
126.39
126.29
114.16
77.32
77.00
76.68
55.41
MeO
SPh
O
3g
f1 (ppm)

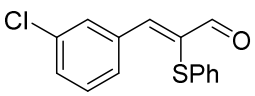

9.512
7.950
7.793
7.775
7.764
7.409
7.405
7.393
7.389
7.385
7.379
7.361
7.341
7.297
7.291
7.271
7.255
7.235
7.217
7.213
7.207
7.204
7.196
7.188
7.180
1.603
0.000


Cl
O
SPh

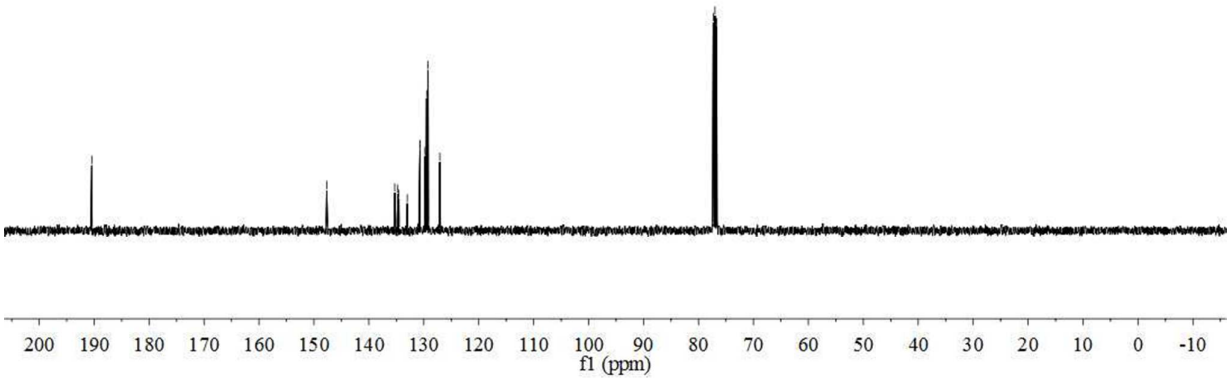
**3h**


1.00
0.99
2.02
2.34
5.08
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)

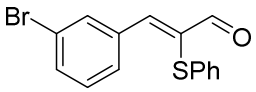

190.44
147.67
135.29
134.74
134.54
133.01
130.72
130.70
129.78
129.49
129.23
127.08
77.32
77.00
76.68


Cl
O
SPh

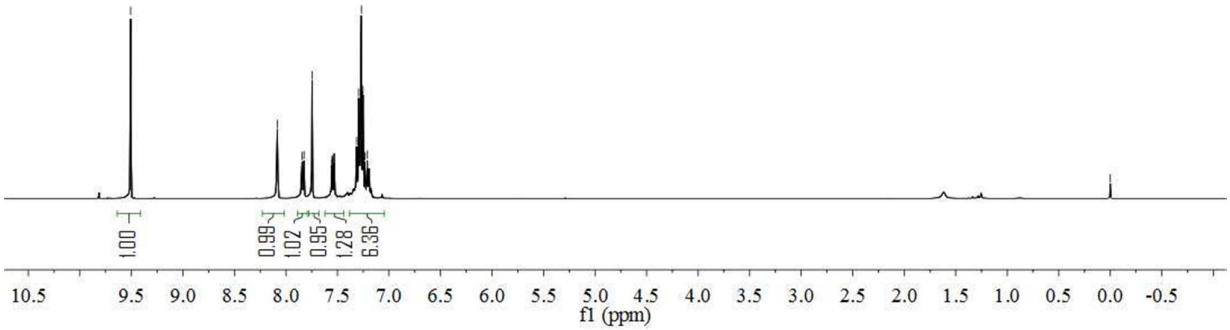
**3h**


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

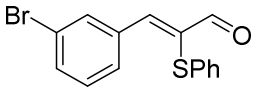

9.507
8.084
7.845
7.825
7.746
7.555
7.553
7.551
7.548
7.535
7.533
7.531
7.528
7.314
7.294
7.289
7.283
7.272
7.268
7.264
7.254
7.252
7.247
7.233
7.210
0.000


Br
O
SPh

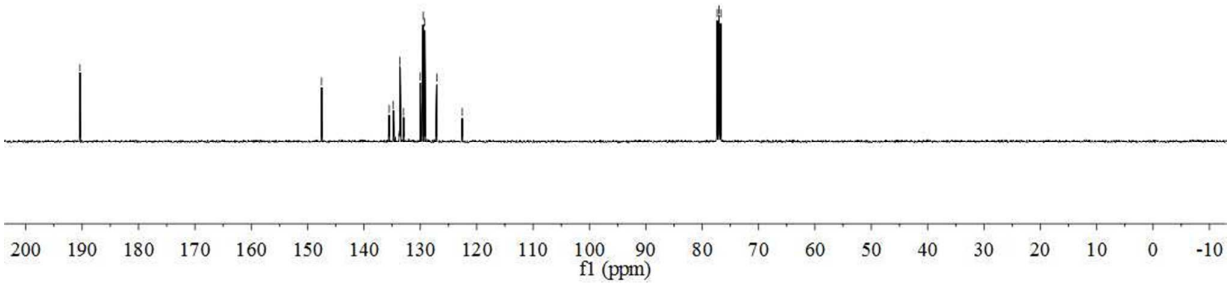
**3i**


1.00
0.99
1.02
0.95
1.28
6.38
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)

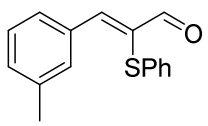

190.40
147.52
135.54
134.79
133.62
133.59
132.98
130.01
129.61
129.52
129.22
127.09
122.57
77.32
77.00
76.68


Br
O
SPh

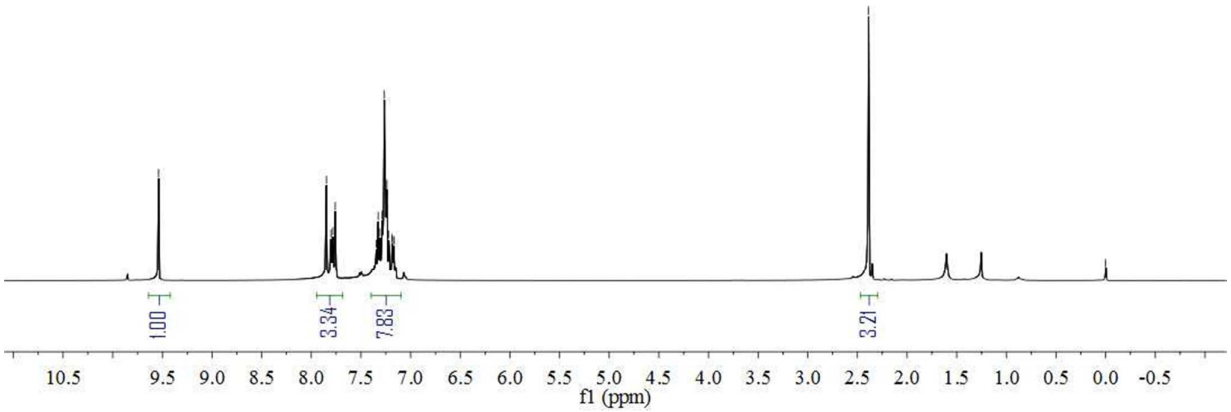
**3i**

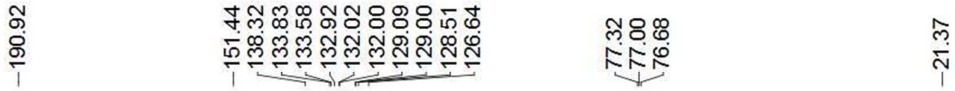

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

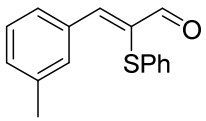

9.538
7.848
7.802
7.783
7.759
7.346
7.327
7.308
7.286
7.282
7.264
7.256
7.247
7.239
7.220
7.187
7.183
7.167
2.388
0.000


O
SPh

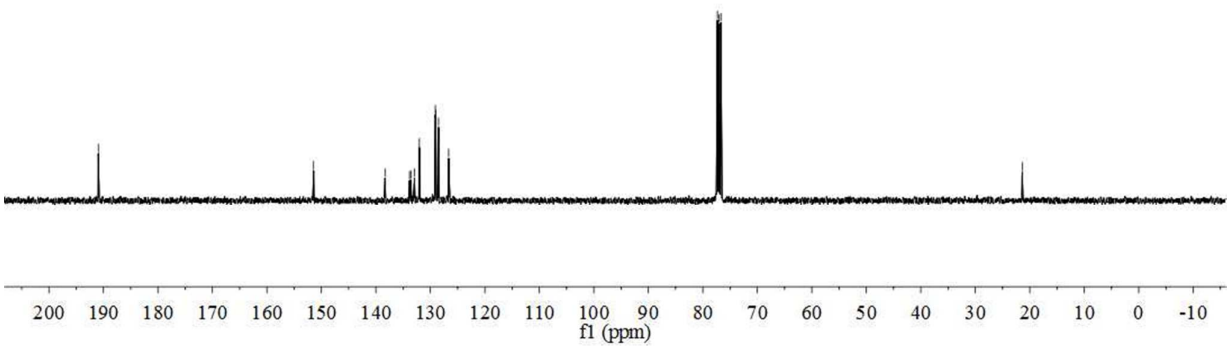
**3j**


1.00
3.34
7.83
3.21
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)

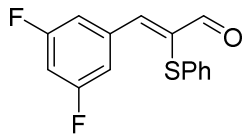

190.92
151.44
138.32
133.83
133.58
132.92
132.02
132.00
129.09
129.00
128.51
126.64
77.32
77.00
76.68
21.37


O
SPh

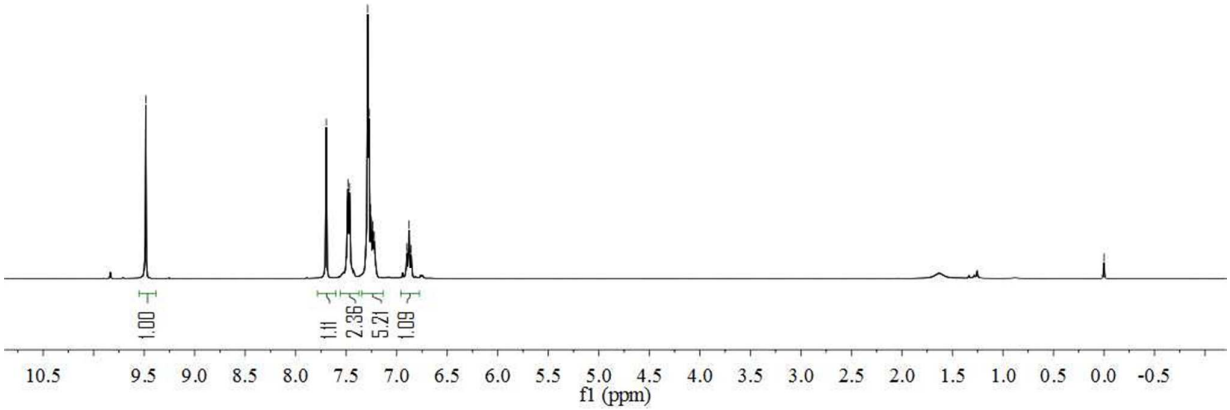
**3j**

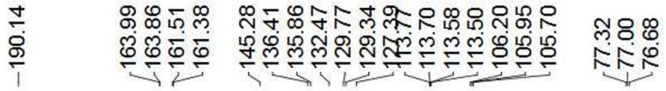

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

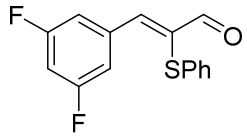

9.484
7.697
7.483
7.467
7.288
7.282
7.273
7.258
7.253
7.243
7.237
7.230
7.222
7.212
6.900
6.883
6.878
6.857
0.000


F
O
SPh
F

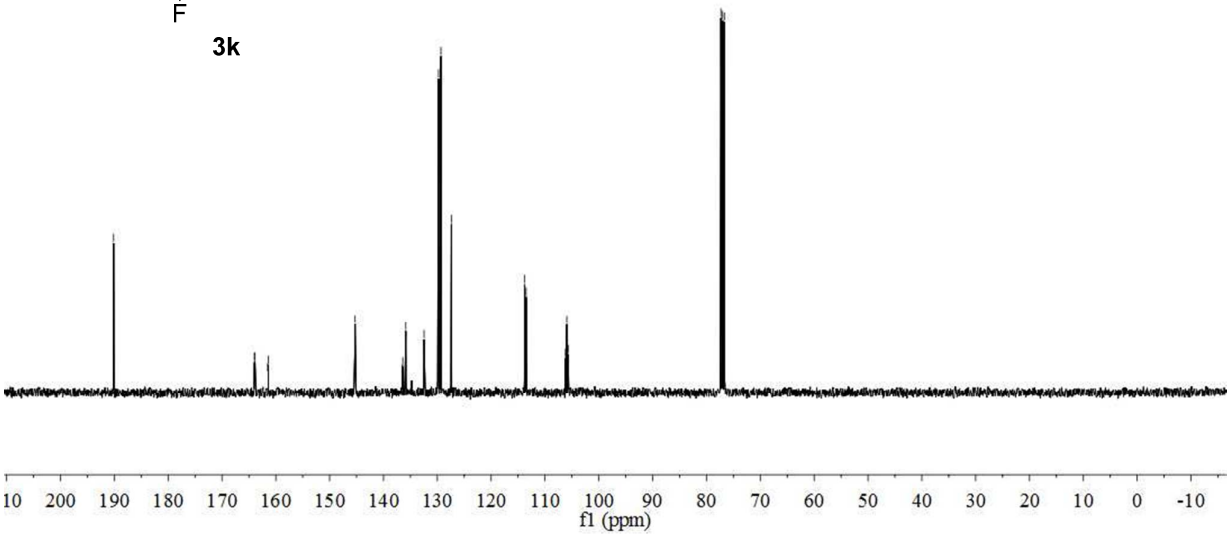
**3k**

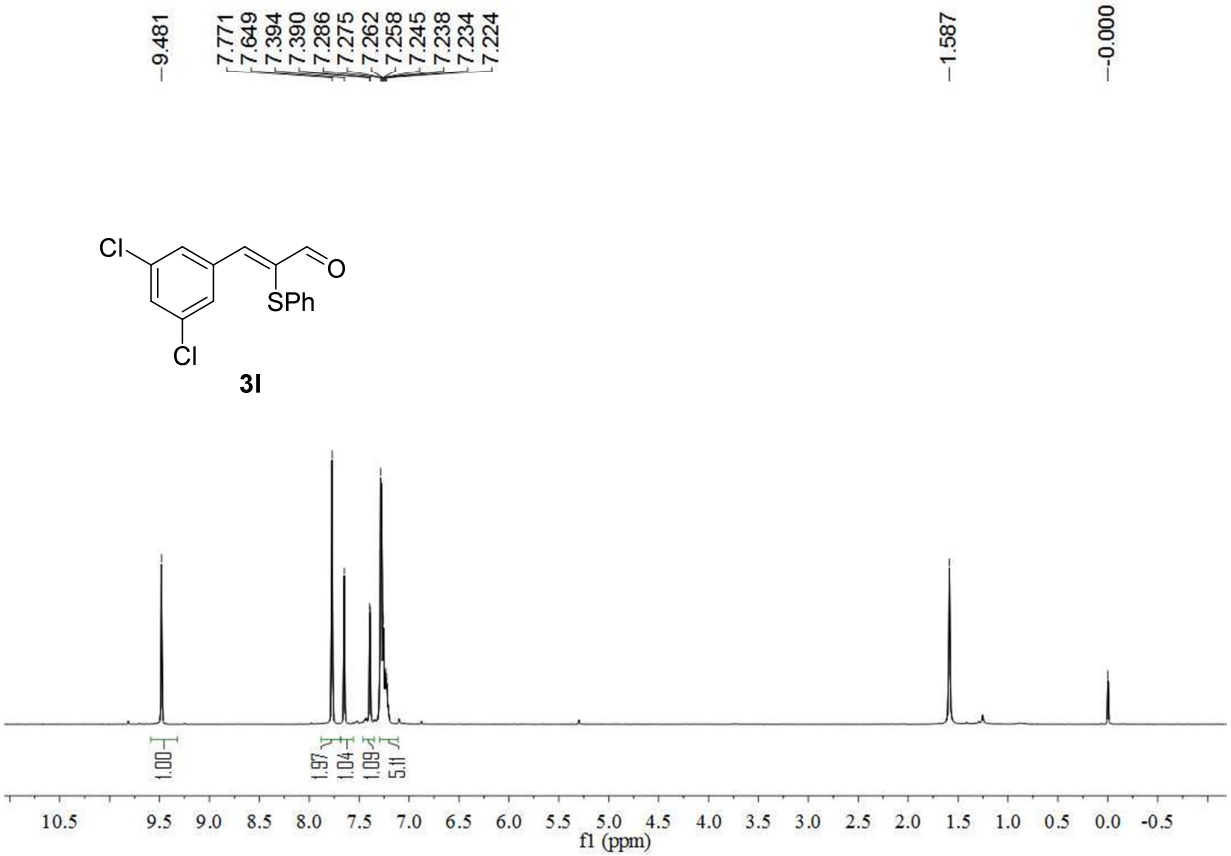

1.00
1.11
2.36
5.21
1.09
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


190.14
163.99
163.86
161.51
161.38
145.28
136.41
135.86
132.47
129.77
129.34
127.39
113.70
113.58
113.50
106.20
105.95
105.70
77.32
77.00
76.68

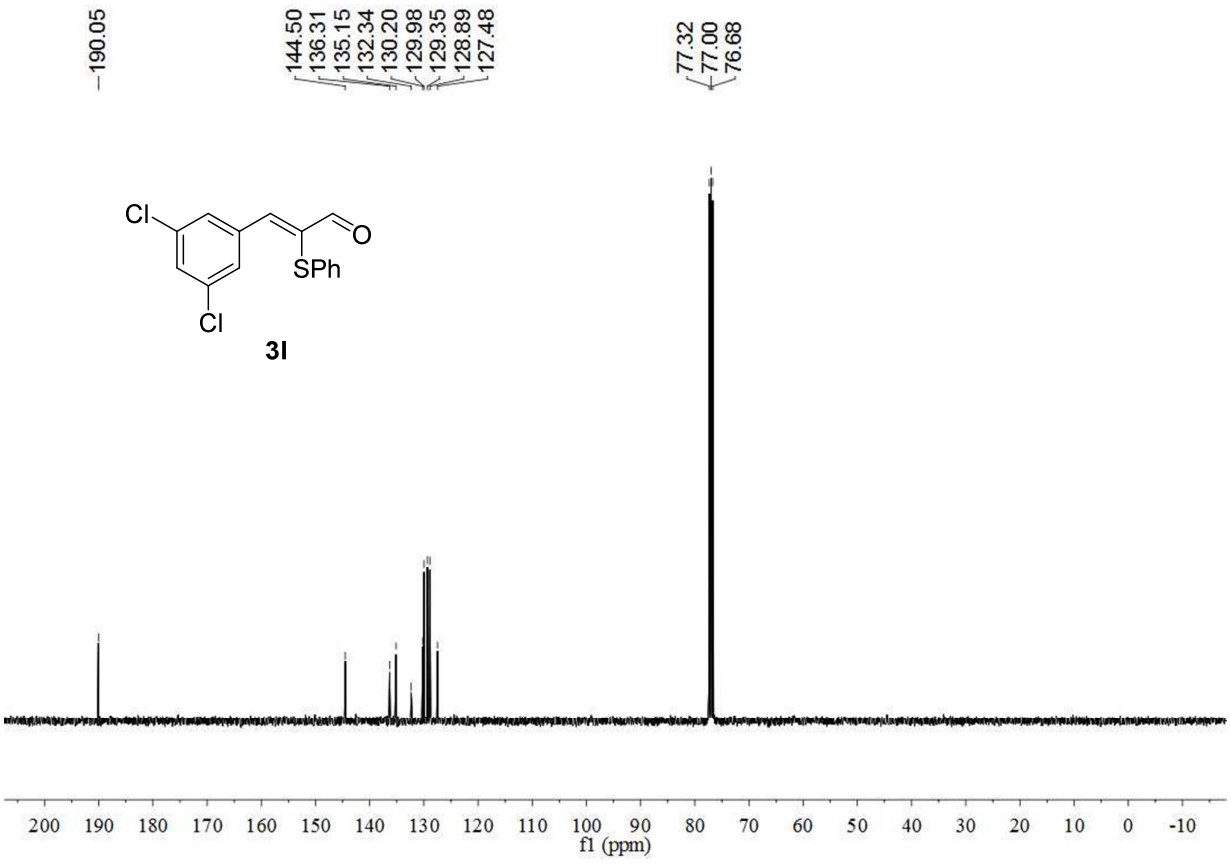

F
O
SPh
F

**3k**


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

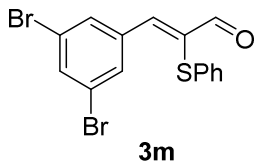

9.481
7.771
7.649
7.394
7.390
7.286
7.275
7.262
7.258
7.245
7.238
7.234
7.224
1.587
0.000
Cl
O
SPh
Cl
1.00
1.97
1.04
1.09
5.11
f1 (ppm)

**3l**

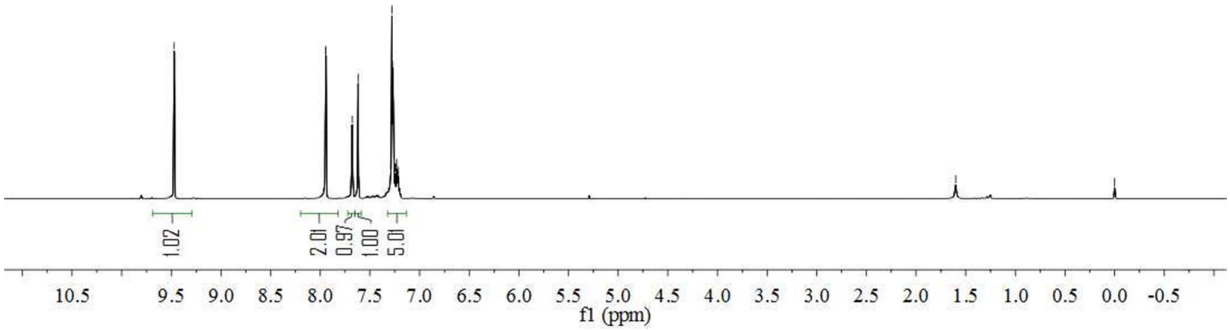

190.05
144.50
136.31
135.15
132.34
130.20
129.98
129.35
128.89
127.48
77.32
77.00
76.68
Cl
O
SPh
Cl
f1 (ppm)

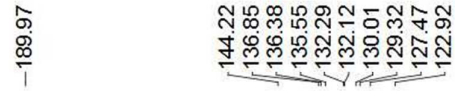
**3l**

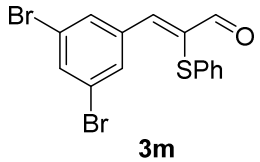

9.471
7.948
7.944
7.683
7.678
7.675
7.619
7.292
7.279
7.273
7.266
7.257
7.245
7.237
7.230
7.225
7.223
7.220
7.219
7.216
1.601
0.000


Br
O
SPh
Br

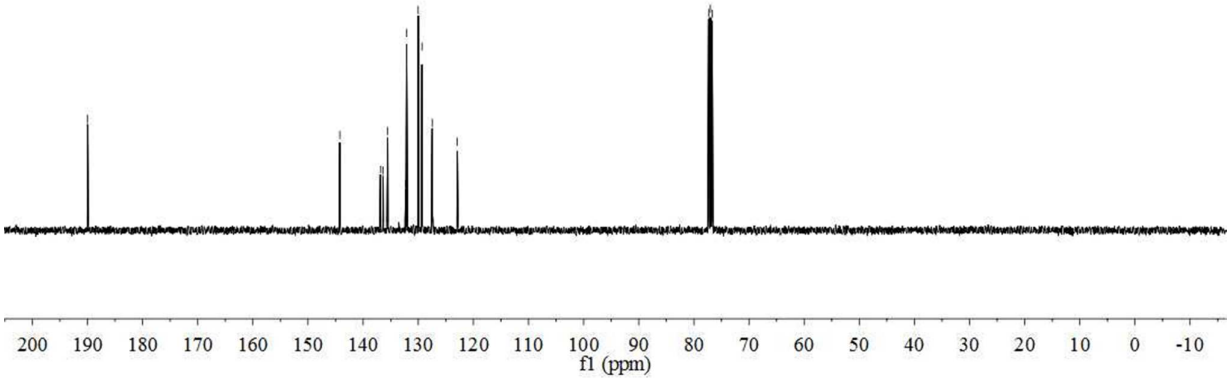
**3m**

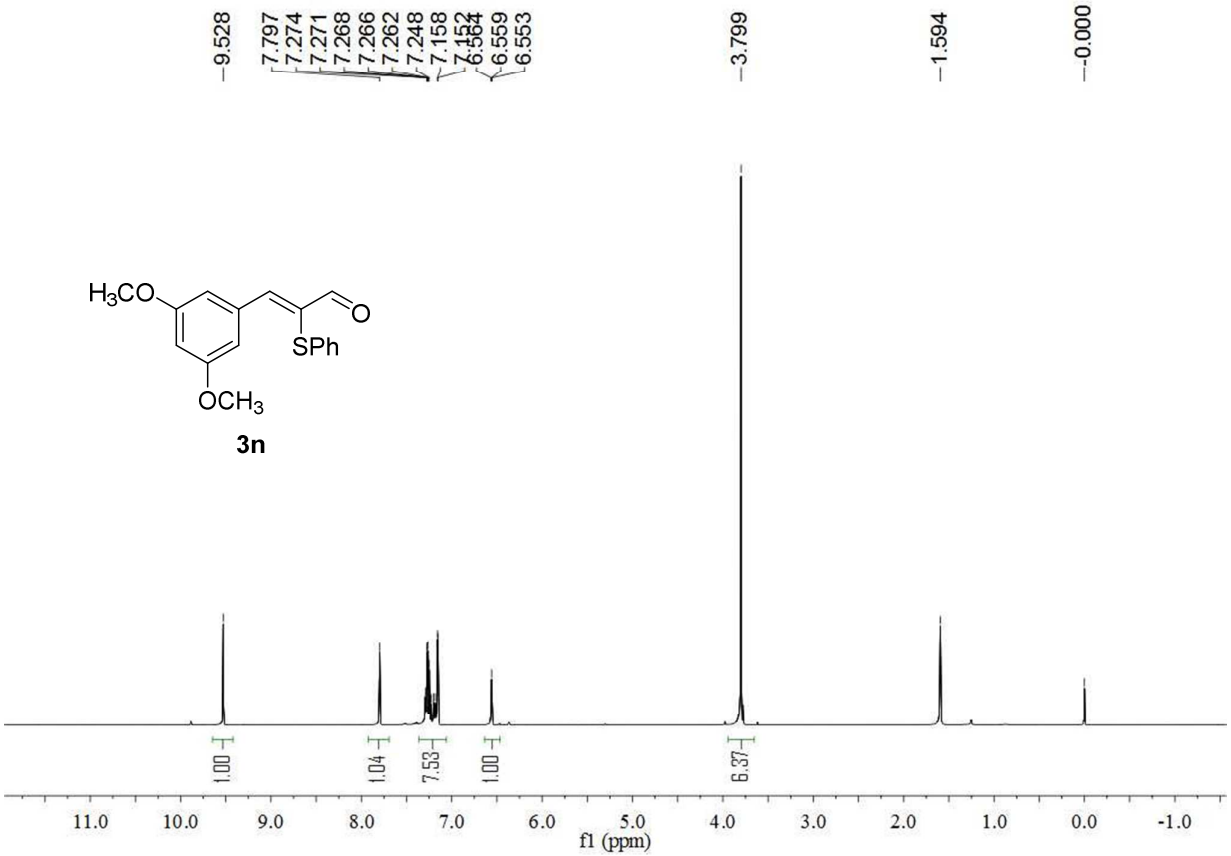

1.02
2.01
0.97
1.00
5.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


189.97
144.22
136.85
136.38
135.55
132.29
132.12
130.01
129.32
127.47
122.92
77.32
77.00
76.68

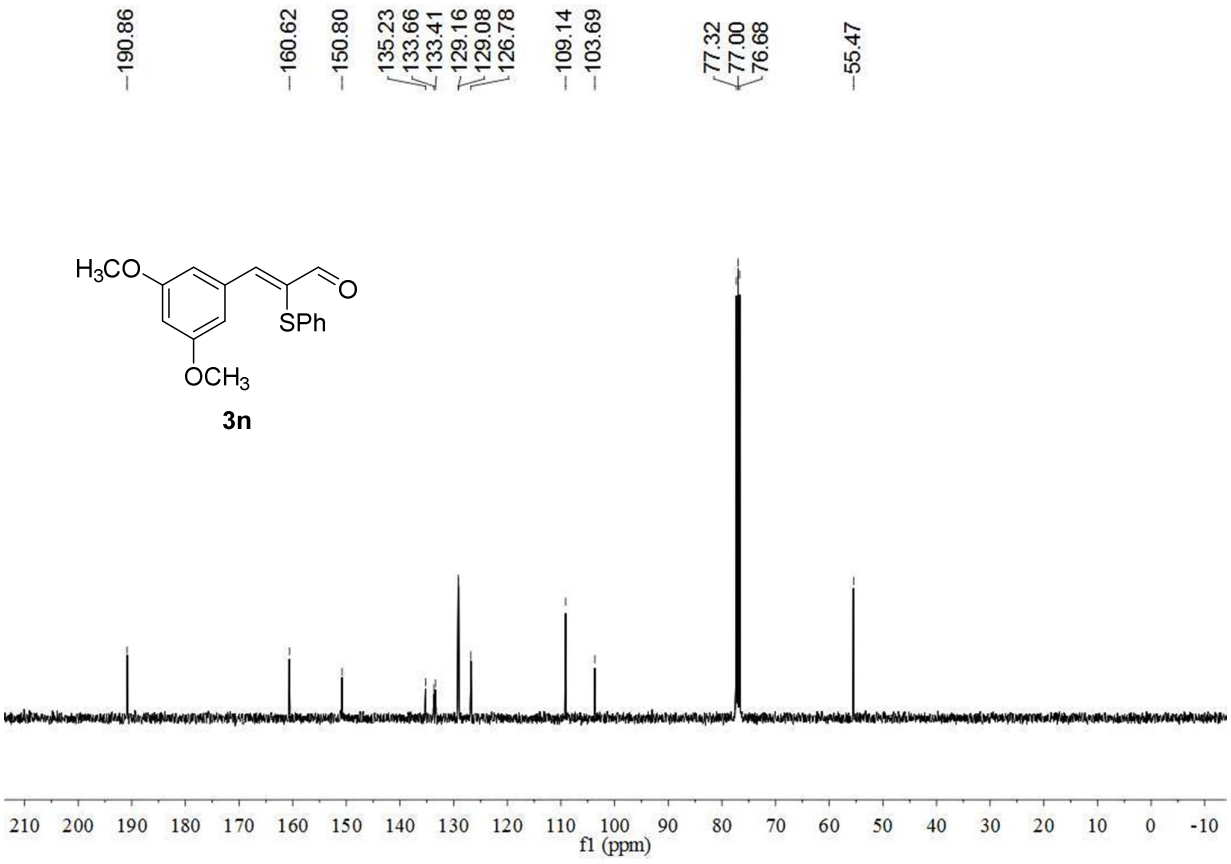

Br
O
SPh
Br

**3m**

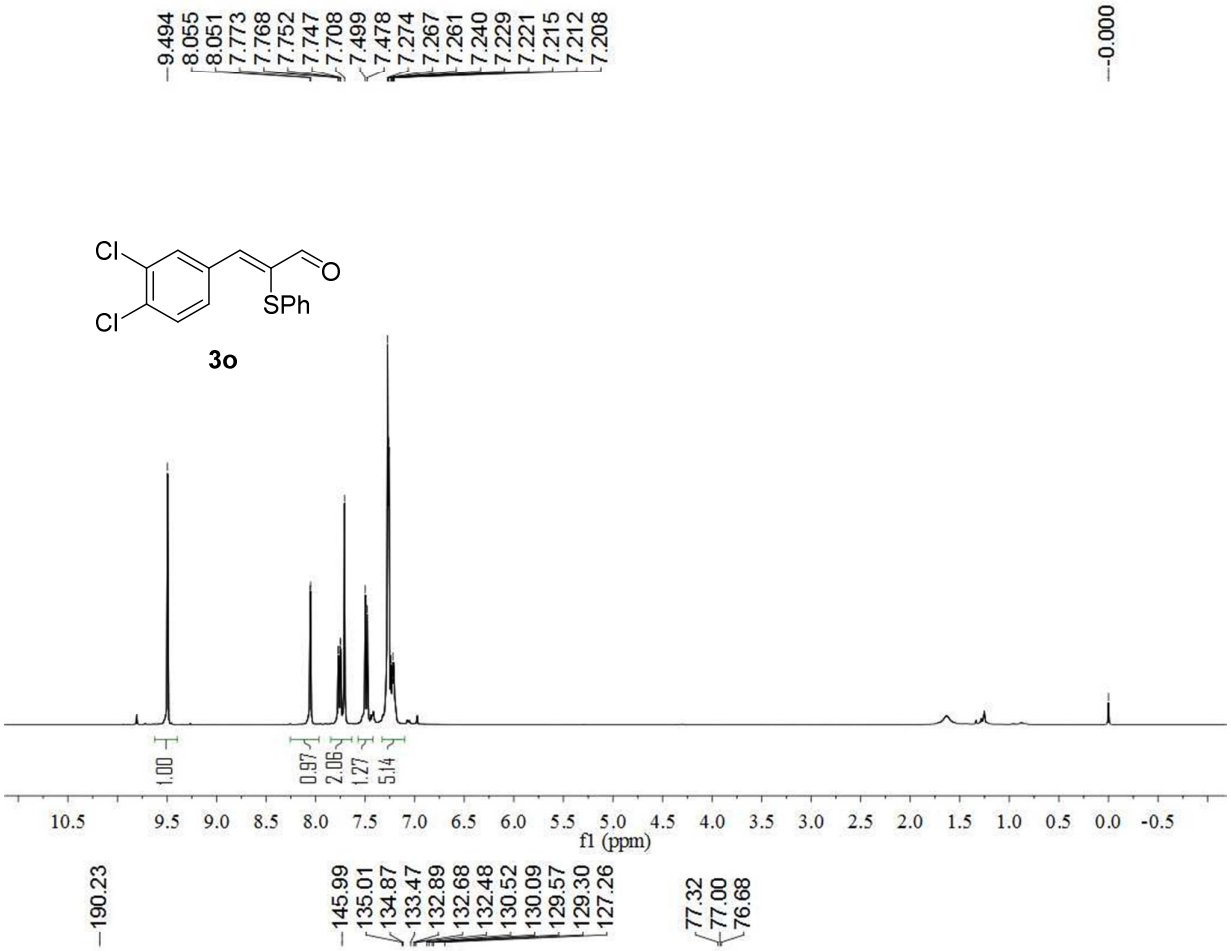

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.528
7.797
7.274
7.271
7.268
7.266
7.262
7.248
7.158
7.152
6.564
6.559
6.553
3.799
1.594
0.000
H3CO
O
SPh
OCH3
1.00
1.04
7.53
1.00
6.37
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

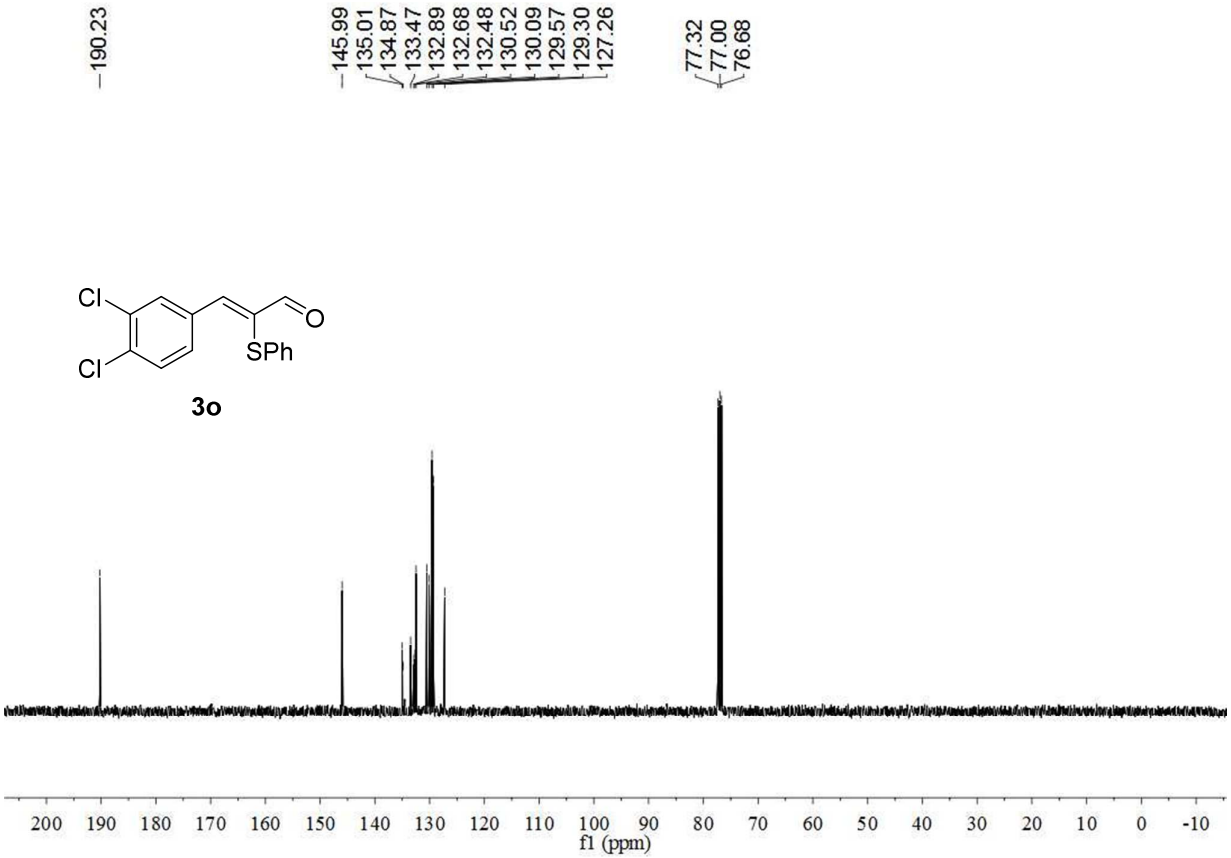
**3n**


190.86
160.62
150.80
135.23
133.66
133.41
129.16
129.08
126.78
109.14
103.69
77.32
77.00
76.68
55.47
H3CO
O
SPh
OCH3
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)

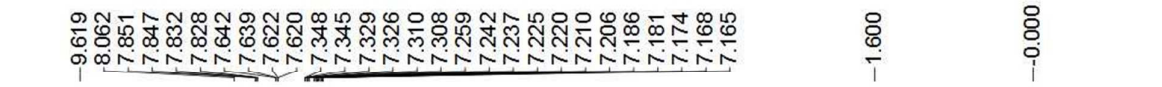
**3n**

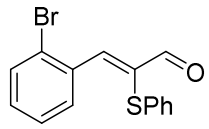

9.494
8.055
8.051
7.773
7.768
7.752
7.747
7.708
7.499
7.478
7.274
7.267
7.261
7.240
7.229
7.221
7.215
7.212
7.208
0.000
Cl
Cl
O
SPh
1.00
0.97
2.06
1.27
5.14
f1 (ppm)

**3o**

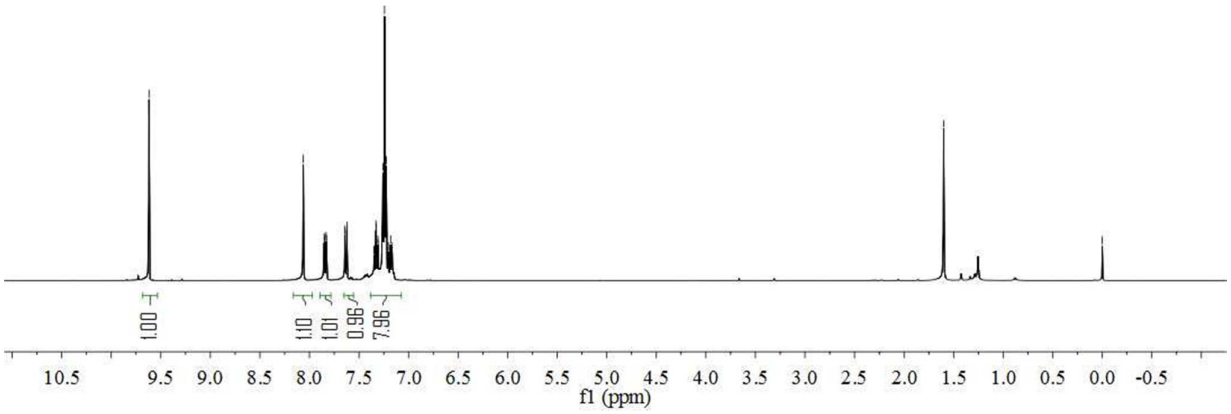

190.23
145.99
135.01
134.87
133.47
132.89
132.68
132.48
130.52
130.09
129.57
129.30
127.26
77.32
77.00
76.68
Cl
Cl
O
SPh
f1 (ppm)

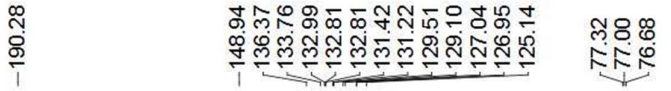
**3o**

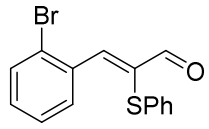

9.619
8.062
7.851
7.847
7.832
7.828
7.642
7.639
7.622
7.620
7.348
7.345
7.329
7.326
7.310
7.308
7.259
7.242
7.237
7.225
7.220
7.210
7.206
7.186
7.181
7.174
7.168
7.165
1.600
0.000


Br
O
SPh

**3p**


1.00
1.10
1.01
0.98
7.96
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)

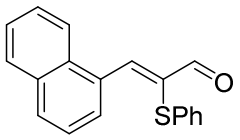

190.28
148.94
136.37
133.76
132.99
132.81
132.81
131.42
131.22
129.51
129.10
127.04
126.95
125.14
77.32
77.00
76.68


Br
O
SPh

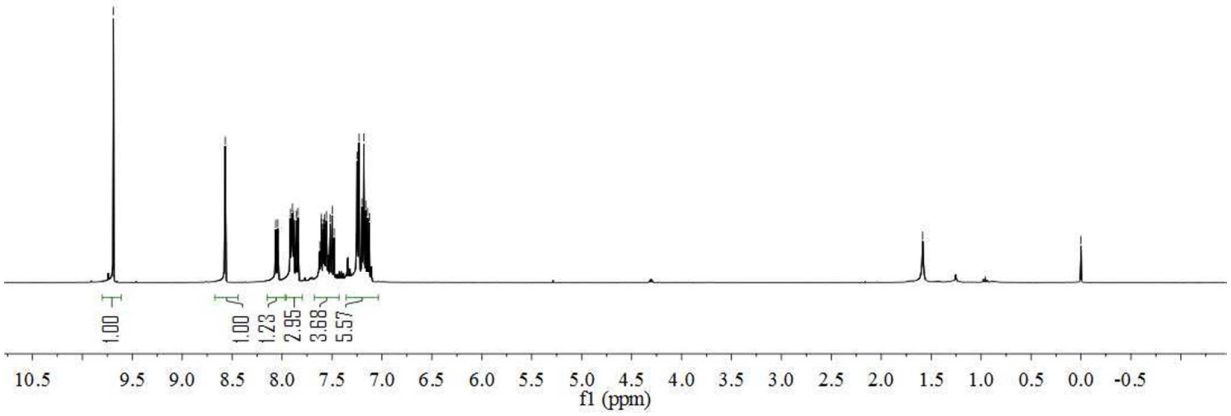
**3p**

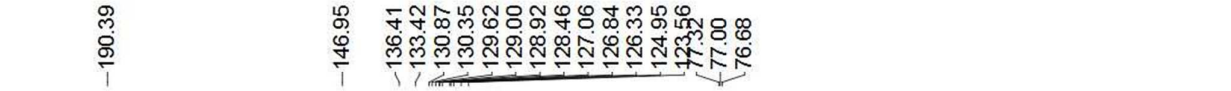

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

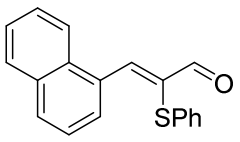

9.689
8.569
8.043
7.917
7.905
7.896
7.887
7.883
7.858
7.840
7.609
7.605
7.589
7.576
7.573
7.556
7.517
7.498
7.250
7.247
7.230
7.227
7.202
7.199
7.181
7.177
7.163
7.143
0.000


O
SPh

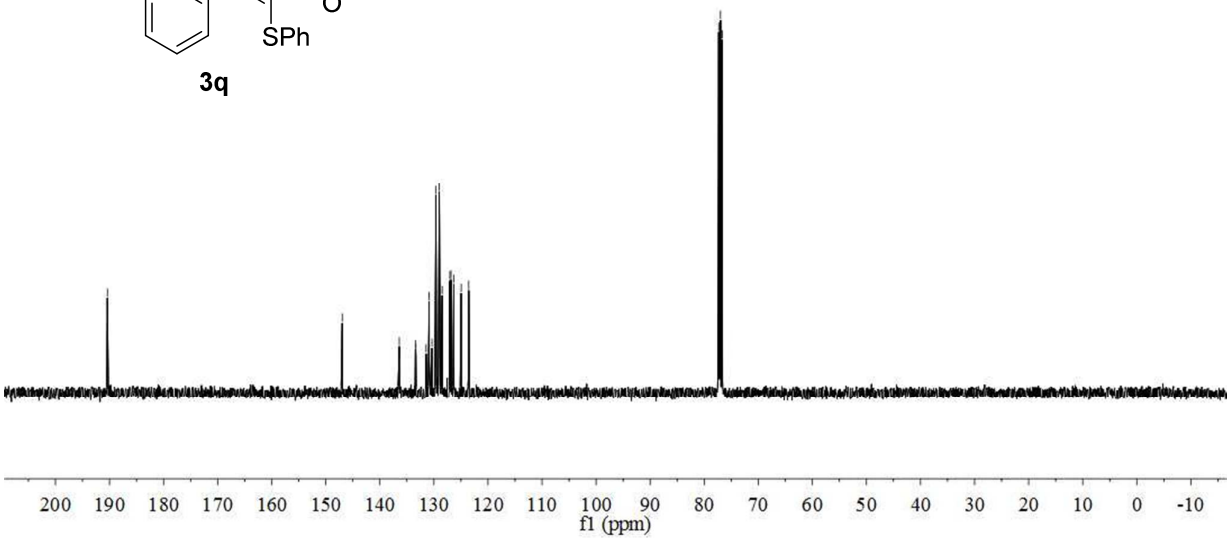
**3q**

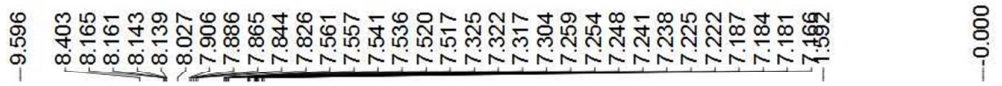

1.00
1.00
1.23
2.95
3.68
5.57
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

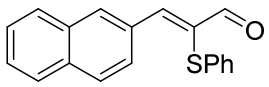

190.39
146.95
136.41
133.42
130.87
130.35
129.62
129.00
128.92
128.46
127.06
126.84
126.33
124.95
123.56
77.32
77.00
76.68


O
SPh

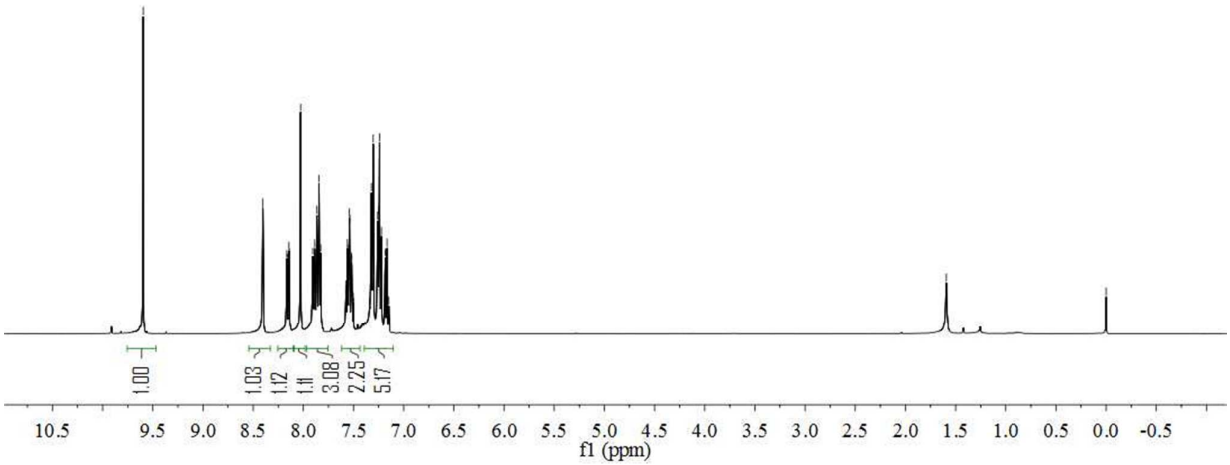
**3q**

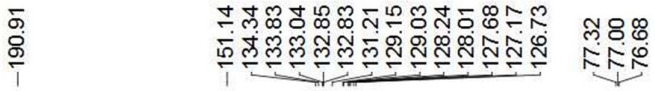

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

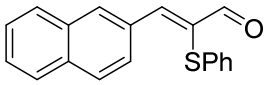

9.596
8.403
8.165
8.161
8.143
8.139
8.027
7.906
7.886
7.865
7.844
7.826
7.561
7.557
7.541
7.536
7.520
7.517
7.325
7.322
7.317
7.304
7.259
7.254
7.248
7.241
7.238
7.225
7.222
7.187
7.184
7.181
0.000


O
SPh

**3r**

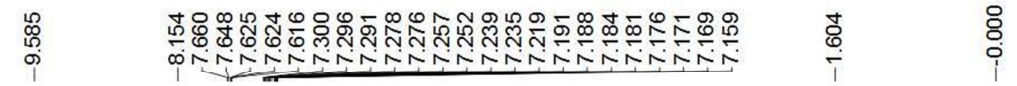

1.00
1.03
1.12
1.11
3.08
2.25
5.17
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

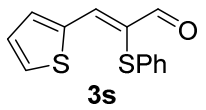

190.91
151.14
134.34
133.83
133.04
132.85
132.83
131.21
129.15
129.03
128.24
128.01
127.68
127.17
126.73
77.32
77.00
76.68


O
SPh

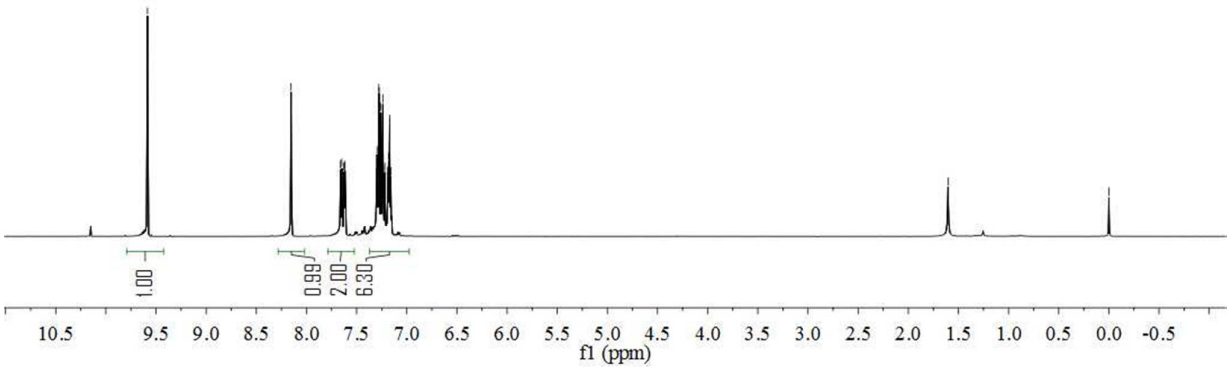
**3r**

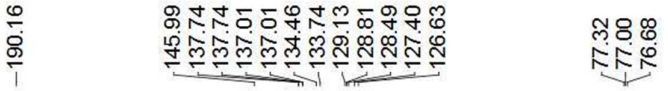

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

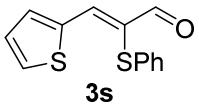

9.585
8.154
7.660
7.648
7.625
7.624
7.616
7.300
7.296
7.291
7.278
7.276
7.257
7.252
7.239
7.235
7.219
7.191
7.188
7.184
7.181
7.176
7.171
7.169
7.159
1.604
0.000


O
S
SPh

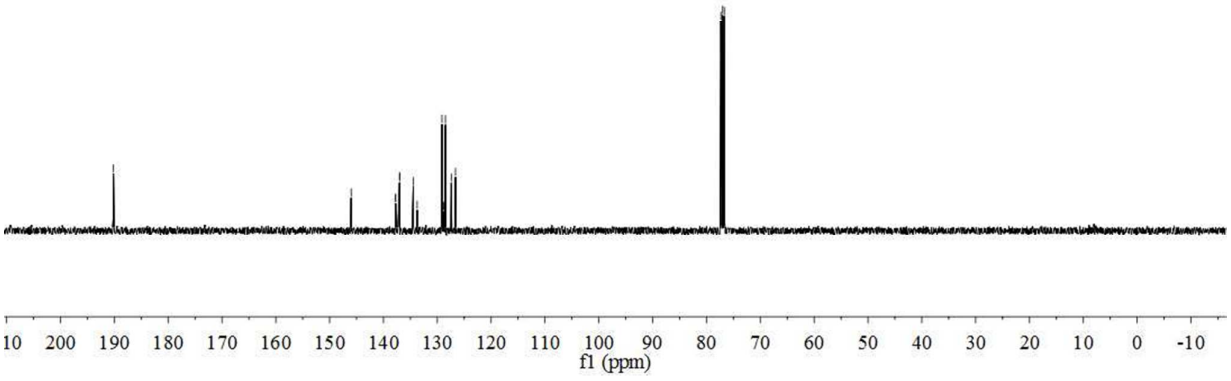
**3s**

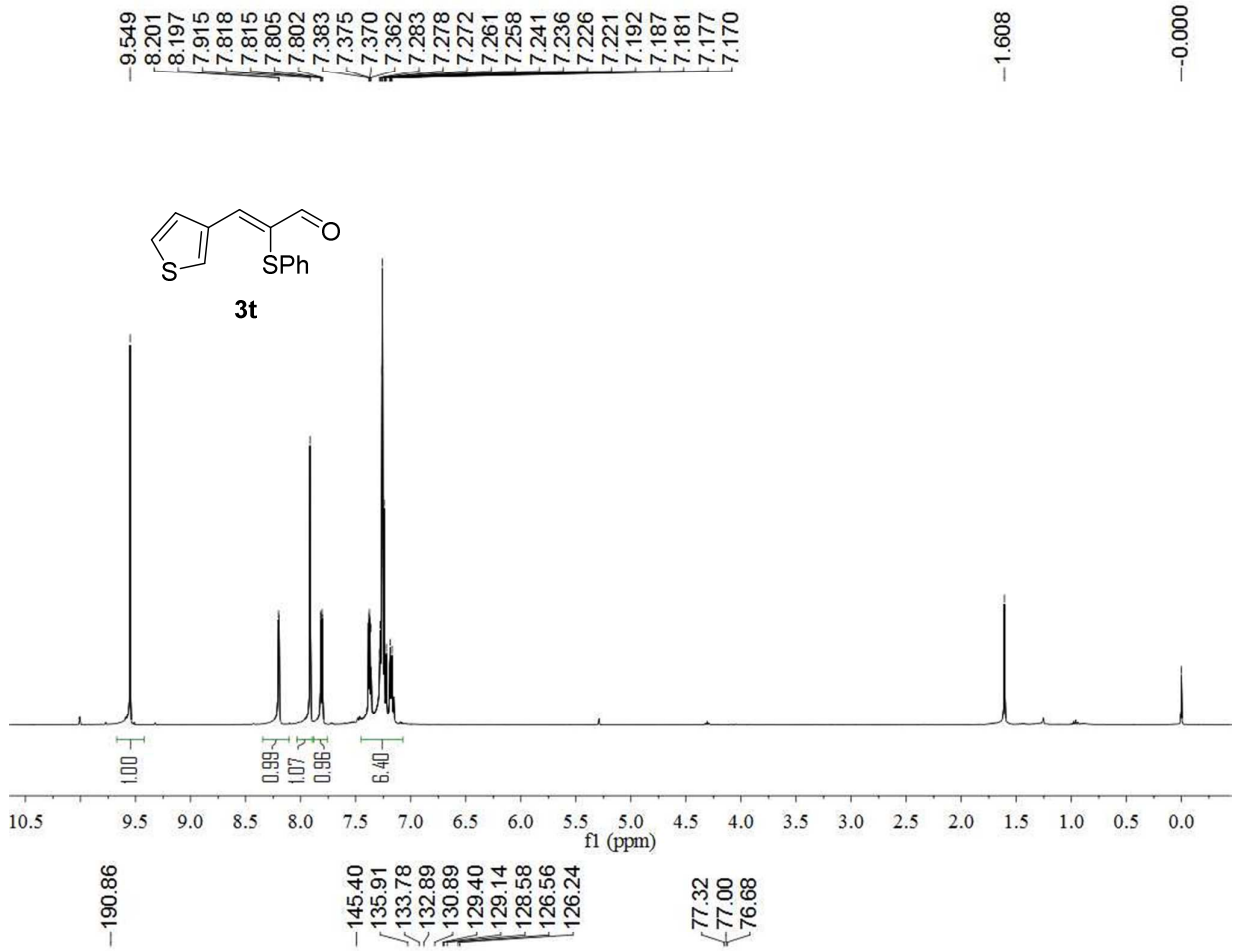

1.00
0.99
2.00
6.30
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

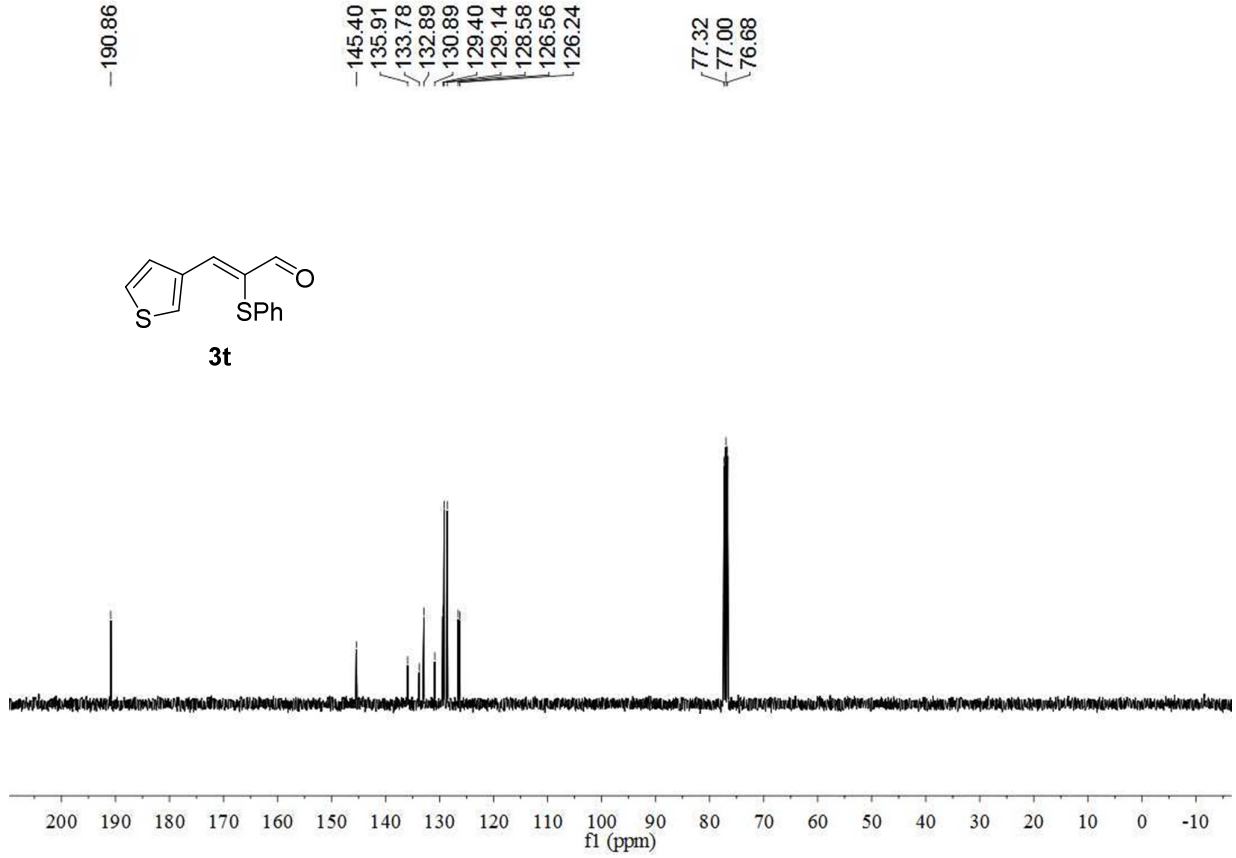

190.16
145.99
137.74
137.74
137.01
137.01
134.46
133.74
129.13
128.81
128.49
127.40
126.63
77.32
77.00
76.68

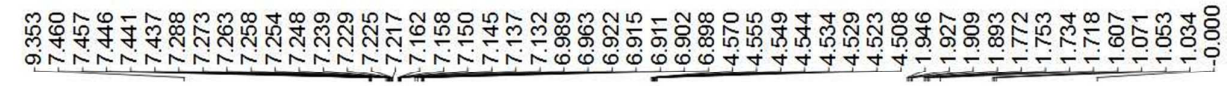

O
S
SPh

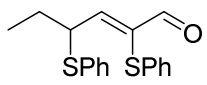
**3s**


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

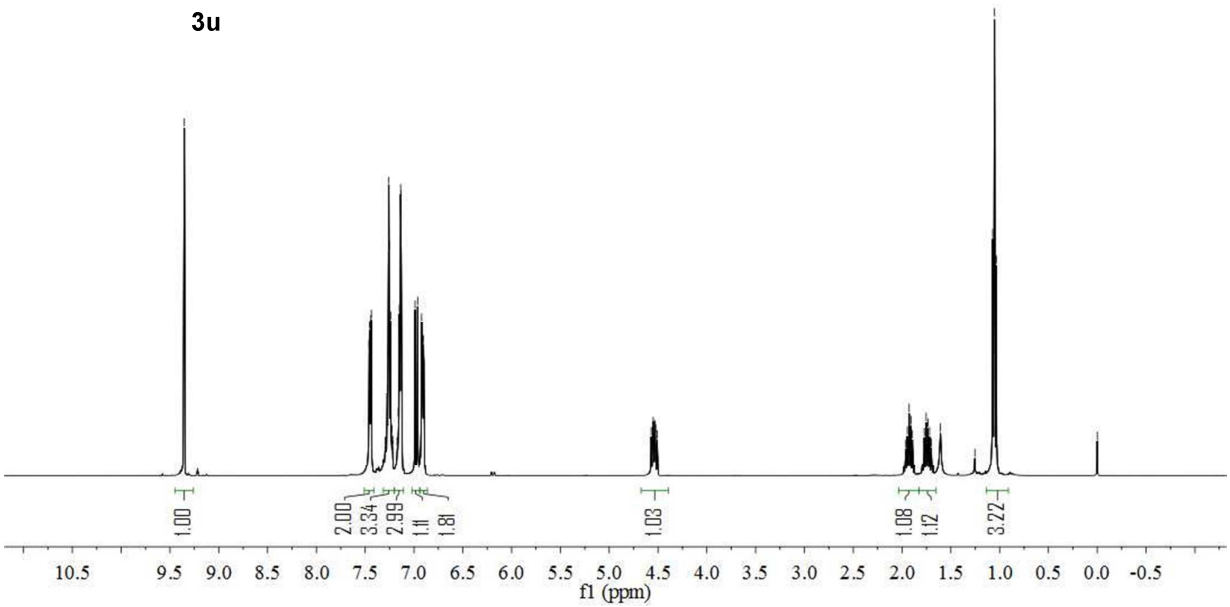

9.549
8.201
8.197
7.915
7.818
7.815
7.805
7.802
7.383
7.375
7.370
7.362
7.283
7.278
7.272
7.261
7.258
7.241
7.236
7.226
7.221
7.192
7.187
7.181
7.177
7.170
1.608
0.000
O
SPh
S
3t
1.00
0.99
1.07
0.96
6.40
f1 (ppm)


190.86
145.40
135.91
133.78
132.89
130.89
129.40
129.14
128.58
126.56
126.24
77.32
77.00
76.68
O
SPh
S
3t
f1 (ppm)

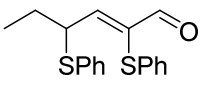

9.353
7.460
7.457
7.446
7.441
7.437
7.288
7.273
7.263
7.258
7.254
7.248
7.239
7.229
7.225
7.217
7.162
7.158
7.150
7.145
7.137
7.132
6.989
6.963
6.922
6.915
6.911
6.902
6.898
4.570
4.555
4.549
4.544
4.534
4.529
4.523
4.508
1.946
1.927
1.909
1.893
1.772
1.753
1.734
1.718
1.607
1.071
1.053
1.034
-0.000


O
SPh SPh

**3u**

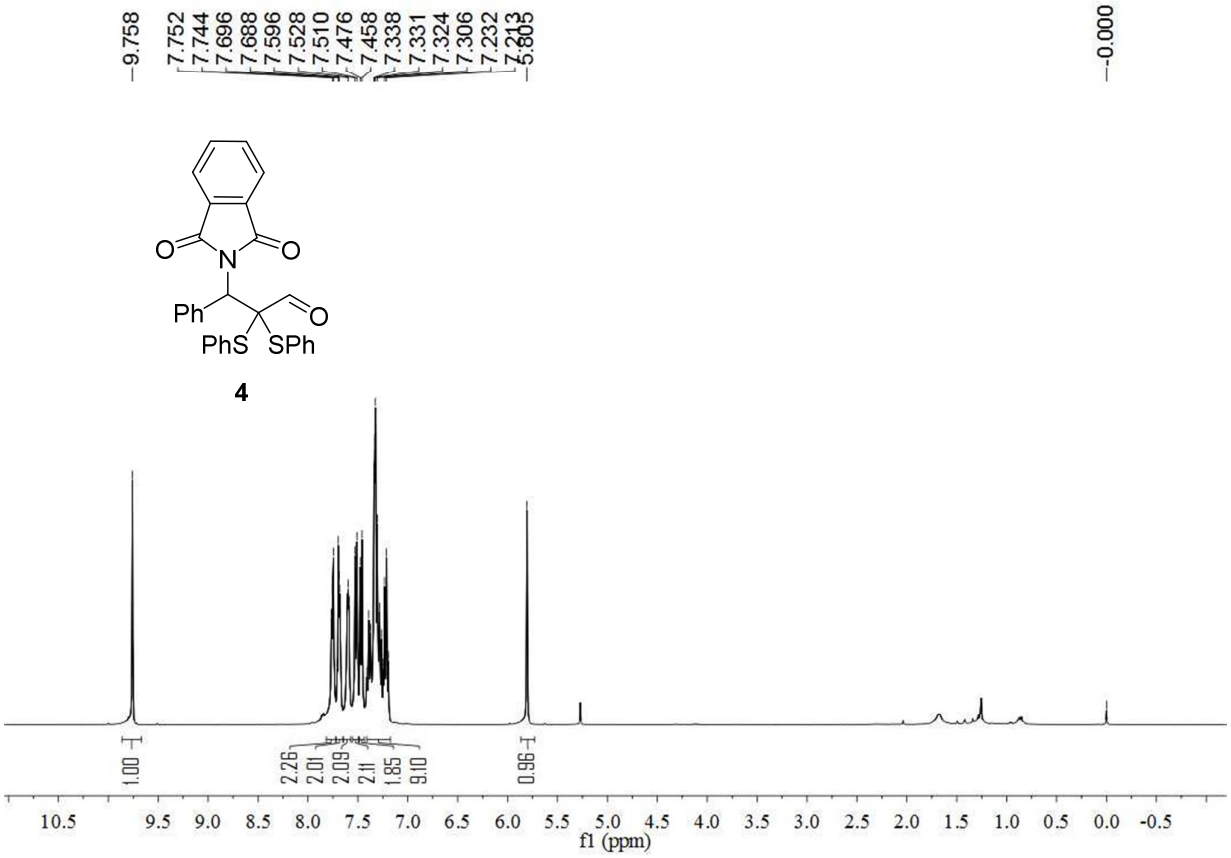

1.00
2.00
3.34
2.99
1.11
1.81
1.03
1.08
1.12
3.22
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


189.43
157.28
136.14
133.77
133.59
132.52
129.10
128.97
128.89
128.14
126.52
77.32
77.00
76.68
49.86
27.11
11.93


O
SPh SPh

**3u**


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


9.758
7.752
7.744
7.696
7.688
7.596
7.528
7.510
7.476
7.458
7.338
7.331
7.324
7.306
7.232
7.213
5.805
0.000
O
N
O
Ph
O
PhS
SPh
4
1.00
2.26
2.01
2.09
2.11
1.85
9.10
0.96
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)

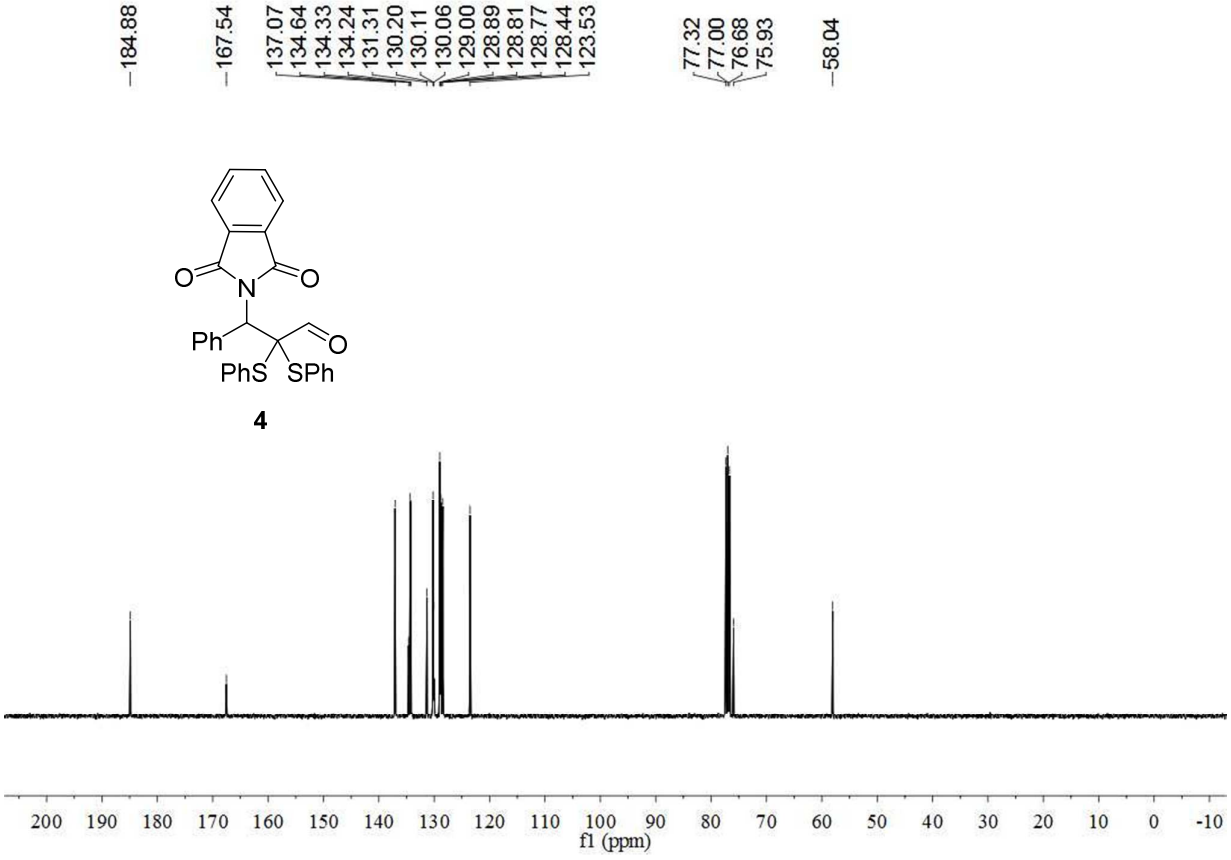

184.88
167.54
137.07
134.64
134.33
134.24
131.31
130.20
130.11
130.06
129.00
128.89
128.81
128.77
128.44
123.53
77.32
77.00
76.68
75.93
58.04
O
N
O
Ph
O
PhS
SPh
4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

**Figure S1. X-ray structure of 4**