Supporting information for:

The Air-Stable Carbocation Salt $[(MeOC_6H_4)CPh_2][BF_4]$ in Lewis acid Catalyzed Hydrothiolation of Alkenes

Eliar Mosaferi, David Ripsman, Douglas. W. Stephan*

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General remarks.

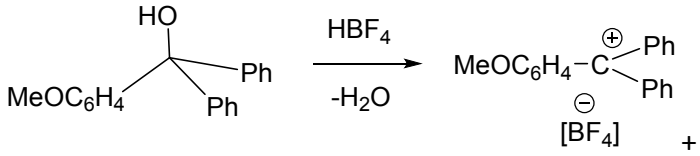
All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing a VAC atmospheres glove box and a Schlenk vacuum-line, unless stated otherwise. Unless stated otherwise, all (pentanes, hexanes, toluene, tetrahydrofuran, dichloromethane, chloroform) and reagents (tetrafluoroboric acid, mercaptans, and alkenes) were purchased from commercial sources and used without further purification. In specific cases requiring air and moisture-free conditions solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass flasks equipped with Teflon-valve stopcocks. Deuterated solvents were dried over the appropriate agents, vacuum-transferred into storage flasks with Young-type Teflon stopcocks and degassed accordingly (CD_2Cl_2 and $CDCl_3$). Where required, reagents were dispensed into thick-walled Schlenk glass flasks equipped with Teflon-valve stopcocks and degassed via repeated cycles of freeze-pump-thaw. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 25 ^oC on a Bruker 500 MHz spectrometer equipped with a cold probe. Chemical shifts are given relative to $SiMe_4$ and referenced to the residual solvent signal (^1H, ^{13}C). $^{11}B\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra were recorded at 25 ^oC on a Bruker 400 MHz spectrometer and chemical shifts are given relative to 15% BF_3-Et_2O and $CFCl_3$, respectively. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. (p-$OMeC_6H_4$)Ph_2COH was purchased from Alfa while $[Ph_3C][B(C_6F_5)_4]$ was purchased from Boulder Scientific and used as received.

General Procedure.

To a mixture of thiol (1 mmol) and alkene (1 mmol) was added the corresponding trityl catalyst in chloroform or dichloromethane (5 mL). Reactions were either carried out at room temperature or at 50 ^oC for a period of time, as indicated in Tables 2 and 3. Reaction was monitored by ^1H NMR spectroscopy and upon completion was evacuated to dryness and residue re-dissolved in hexanes. Suspension was then passed through a short silica plug to remove catalyst as well as hydrolysis by-products. Filtrate was then

concentrated to dryness to afford the product. In most cases no further purification was required. In some instances the isolated yields of the products are lower than their conversion yields due to their volatility and/or solubility in hydrocarbon solvents.

Synthesis of [(OMe-C_6H_4)CPh_2][BF_4] (3)



In a 100 mL round-bottom flask (p-$OMeC_6H_4$)Ph_2COH (0.995 g, 3.43 mmol) was dissolved in diethyl ether (20 mL) and stirred at 0 °C for 15 minutes. Tetrafluoroboric acid (50-55% w/w in diethyl ether, 2.5 mL, 17 mmol) was added dropwise to the solution over a period of 15 minutes. Mixture immediately turned to a bright orange suspension. Upon addition of the tetrafluoroboric acid solution reaction was allowed to continue at 0 °C for 1 hour. Mixture was then evacuated to dryness to afford a orange-red oil and was dissolved in dichloromethane (10 mL). Diethyl ether (100 mL) was added to precipitate the product as a red solid. Product was filtered over a fine-pore frit and washed with ether (3 x 15 mL) and dried under vacuum overnight to afford the desired product as an orange-red solid (1.185g, 96%). **^{1}H NMR ($CDCl_3$):** δ 4.30 (s, 3H, OCH_3), 7.51-7.54 (m, 6H, ArH), 7.73-7.76 (m, 4H, ArH), 7.84-7.86 (m, 2H, ArH), 7.98-8.00 (m, 2H, ArH). **^{13}C NMR ($CDCl_3$):** 58.9 (s, OCH_3), 119.2 (s, *m*-C_6H_4), 129.7 (s, *m*-C_6H_5), 133.4 (s, *ipso*-C_6H_4), 138.6 (s, *ipso*-C_6H_5), 138.9 (s, *o*-C_6H_5), 139.2 (s, *o*-C_6H_4), 147.9 (s, *p*-C_6H_5), 177.0 (s, *C*(OMe)), 203.9 (s, *C*Ph_2(MeO(C_6H_4))). **^{19}F NMR ($CDCl_3$):** δ -153.2 (s, BF_4). **^{11}B NMR ($CDCl_3$):** δ -1.0 (*B*F_4). DART-MS exact mass calculated for $(C_{20}H_{17}O)^+$ require m/z 273.13, found m/z 273.13.

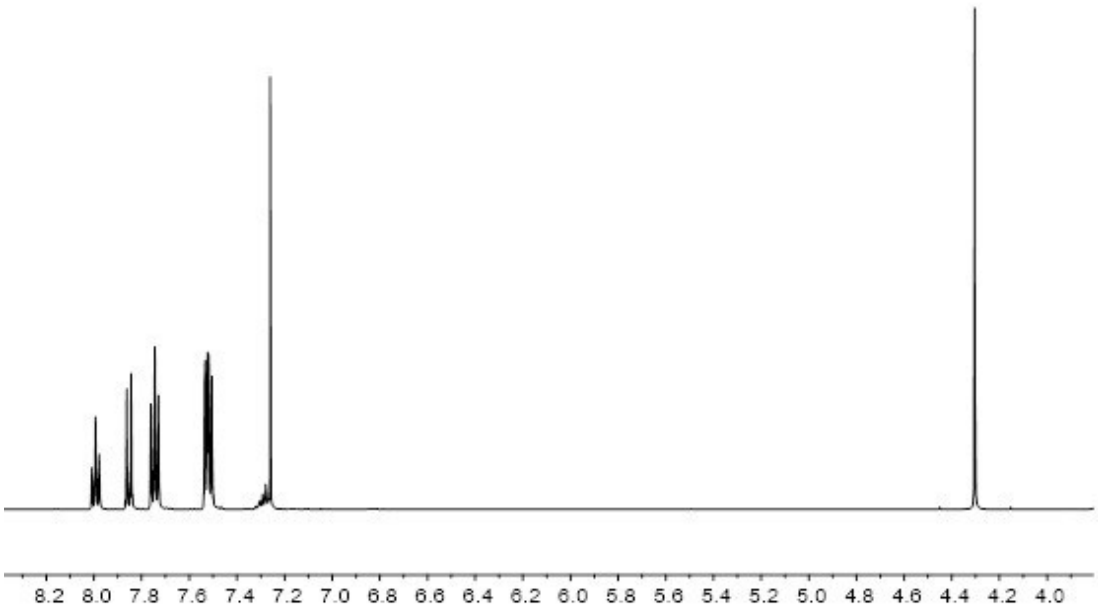


Figure S1: ^{1}H NMR spectrum of [(*p*-MeO(C_6H_4))CPh_2][BF_4] in $CDCl_3$.

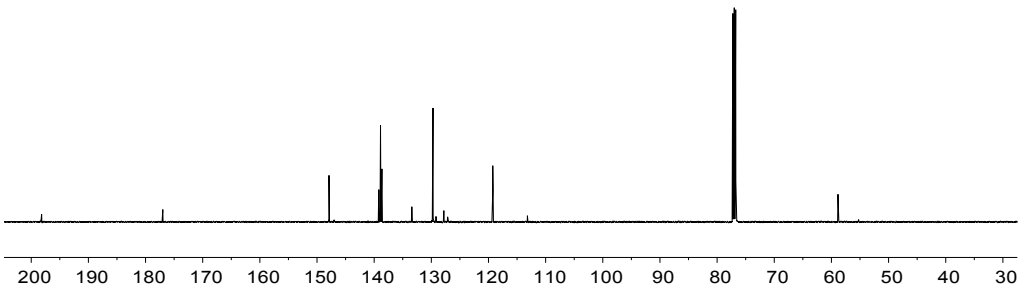


Figure S2: ^{13}C NMR spectrum of [(*p*-MeO(C_6H_4))CPh_2][BF_4] in $CDCl_3$.

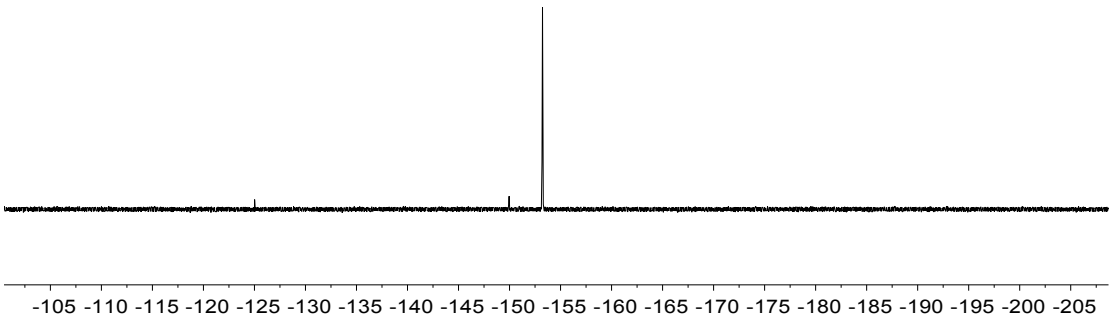


Figure S3: ^{19}F NMR spectrum of [(*p*-MeO(C_6H_4))CPh_2][BF_4] in $CDCl_3$.

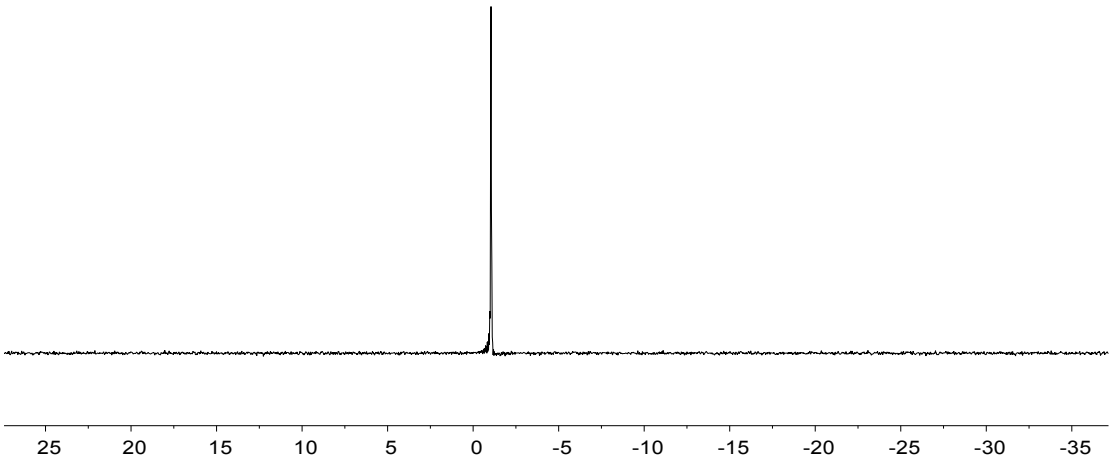
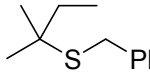


Figure S4: ^{11}B NMR spectrum of [(*p*-MeO(C_6H_4))CPh_2][BF_4] in $CDCl_3$.



(Table 2 entry 1, Table 3, entry 1.)

Pale yellow liquid, 0.1846 g, 95 %. **^{1}H NMR ($CDCl_3$):** δ 1.00 (t, $^{3}J_{HH}$ = 7.43 Hz, 3H, CH_3), 1.32 (s, 6H, CH_3), 1.61 (q, $^{3}J_{HH}$ = 7.41 Hz, 2H, CH_2), 3.72 (s, 2H, CH_2), 7.22-7.38 (m, 5H, Ph). **^{13}C NMR ($CDCl_3$):** δ 9.2 (s, *C*H_3), 28.4 (s, *C*H_3), 32.9 (s, *C*H_2), 34.9 (s, *C*H_2), 46.7 (s, *C*$(CH_3)_2$), 126.8 (s, *p*-C_6H_5), 128.5 (s, *m*-C_6H_5), 129.1 (s, *o*-C_6H_5), 138.7 (s, *ipso*-C_6H_5). DART-MS exact mass calculated for $(C_{12}H_{19}S)^+$ require m/z 195.12, found m/z 195.12.

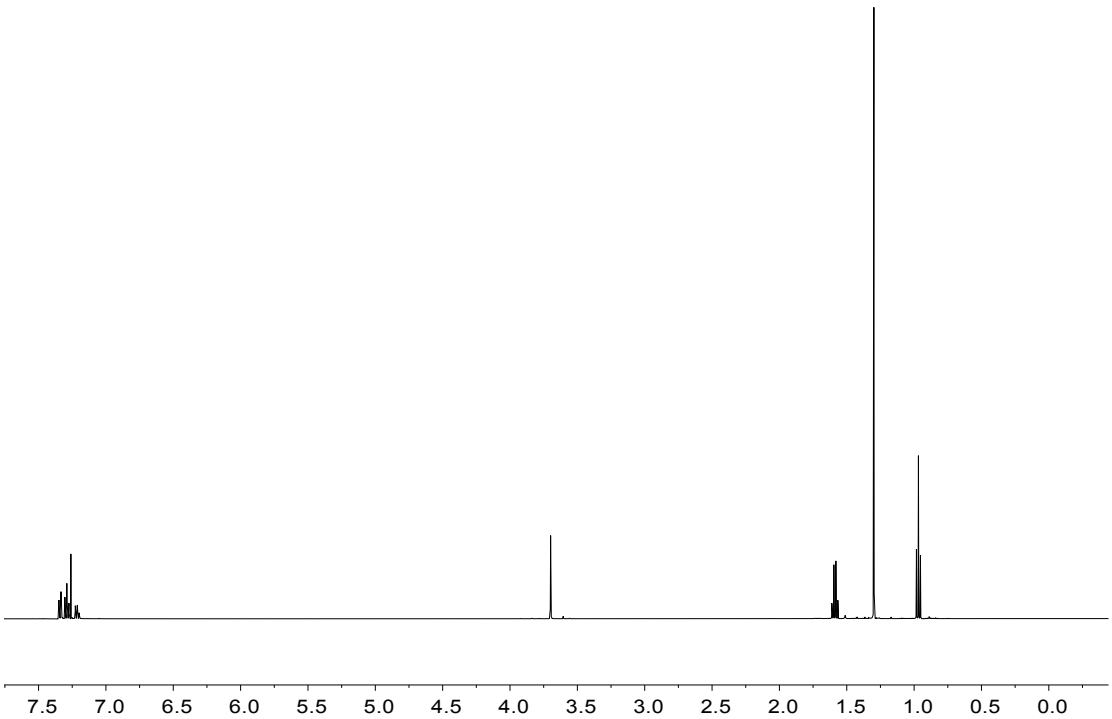


Figure S5: ^{1}H NMR spectrum of entry 1 in $CDCl_3$.

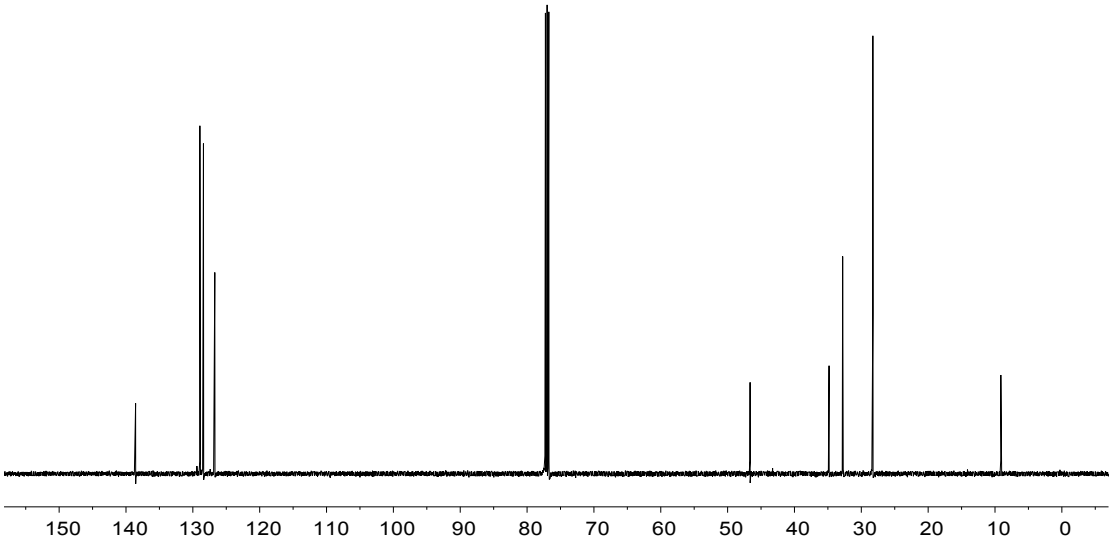
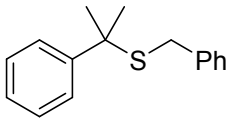


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of entry 1 in $CDCl_3$.



(Table 3 entry 2)

Colourless liquid, 0.240 g, 99 %. . **^{1}H NMR ($CDCl_3$):** δ 1.73 (s, 6H, CH_3), 3.41 (s, 2H, CH_2), 7.13-7.26 (m, 6H, ArH), 7.34-7.38 (m, 2H, ArH), 7.58-7.60 (m, 2H, ArH). **^{13}C NMR ($CDCl_3$):** 30.2 (s, *C*H_3), 34.5 (s, *C*H_2), 48.5 (s, *C*$(CH_3)_2$), 126.5 (s, *p*-C_6H_5, C(CH_2)Ph), 126.6 (s, *o*-C_6H_5, C(CH_2)Ph), 126.7 (s, *p*-C_6H_5, SCH_2Ph), 128.1 (s, *m*-C_6H_5, C(CH_2)Ph), 128.3 (s, *m*-C_6H_5, SCH_2Ph), 128.9 (s, *o*-C_6H_5, SCH_2Ph), 138.1 (s, *ipso*-C_6H_5, SCH_2Ph), 146.3 (s, *ipso*-C_6H_5, C(CH_2)Ph). DART-MS exact mass calculated for $(C_{16}H_{19}S)^+$ require m/z 243.12, found m/z 243.12.

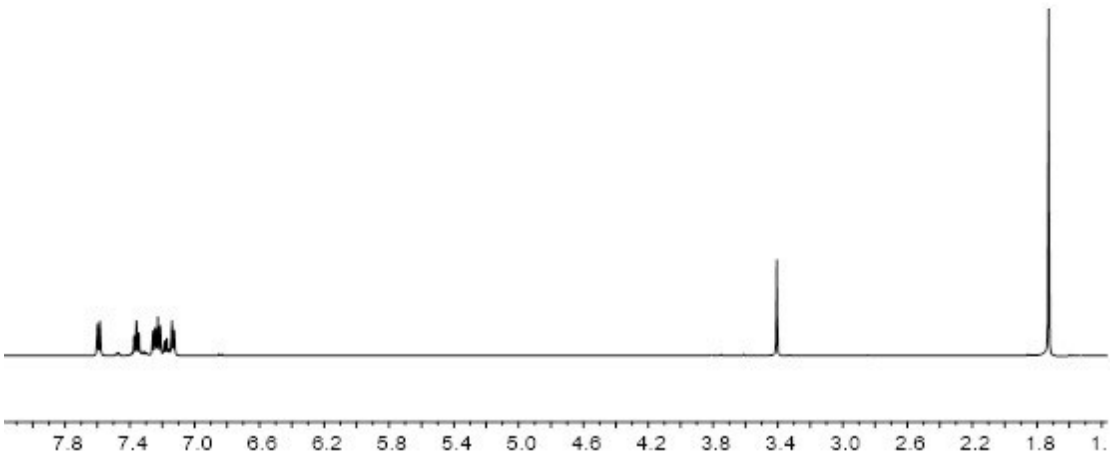


Figure S7: ^{1}H NMR spectrum of entry 2 in $CDCl_3$.

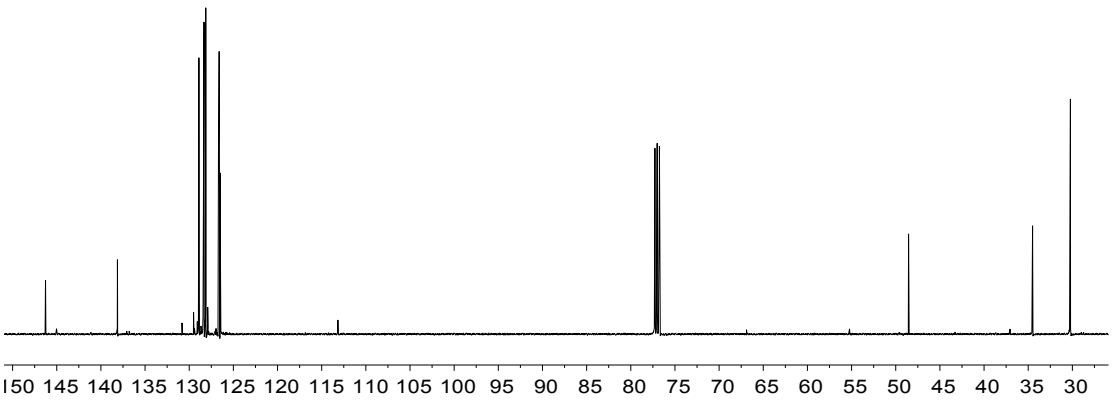
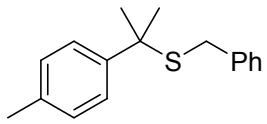


Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of entry 2 in $CDCl_3$.



(Table 3 Entry 3)

Pale-yellow liquid, 0.236 g, 92%. **^{1}H NMR ($CDCl_3$):** δ 1.71 (s, 6H, CH_3), 2.36 (s, 3H, *p*-CH_3), 3.41 (s, 2H, CH_2), 7.14-7.18 (m, 5H, ArH), 7.21-4.24 (m, 2H, ArH), 7.46-7.49 (m, 2H, ArH). **^{13}C{^{1}H} NMR ($CDCl_3$):** δ 20.9 (s, *p*-*C*H_3), 30.3 (s, *C*H_3), 34.5 (s, *C*H_2), 48.4 (s, *C*$(CH_3)_2$), 126.5 (s, *o*-C_6H_4), 126.6 (s, *p*-C_6H_5), 128.3 (s, *m*-C_6H_5), 128.8 (*o*-C_6H_5), 128.9 (*m*-C_6H_4), 136.1 (s, *C*(CH_3), 138.2 (s, *ipso*-C_6H_5), 143.3 (s, *ipso*-C_6H_4). DART-MS exact mass calculated for $(C_{17}H_{21}S)^+$ require m/z 257.14, found m/z 257.14.

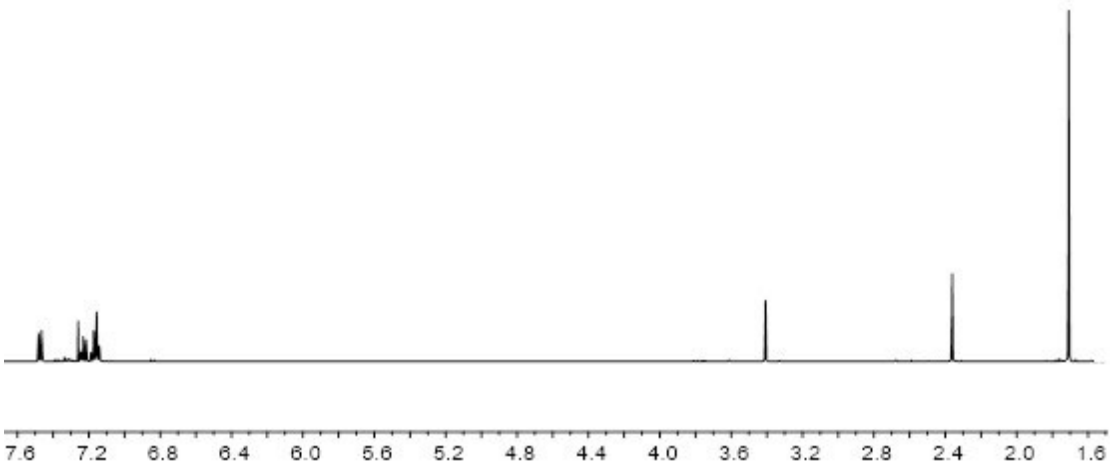


Figure S9: ^{1}H NMR spectrum of entry 3 in $CDCl_3$.

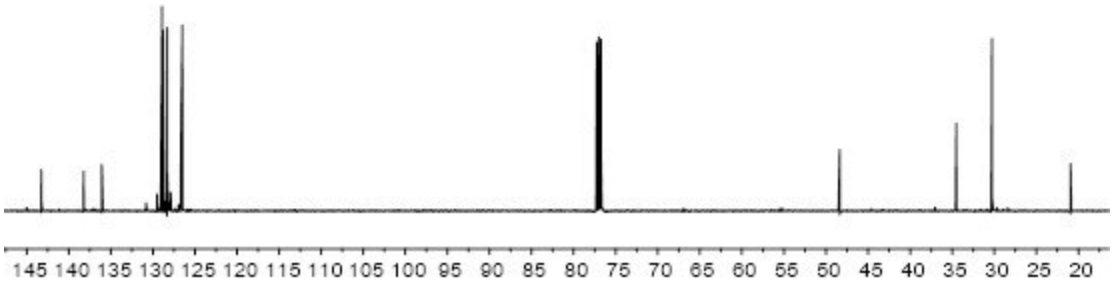
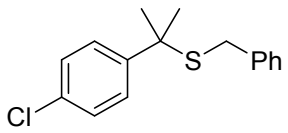


Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum of entry 3 in $CDCl_3$.



(Table 3, Entry 4)

Colourless liquid, 0.182 g, 64 %. **^{1}H NMR ($CDCl_3$):** δ 1.69 (s, 6H, CH_3), 3.40 (s, 2H, CH_2), 7.11-7.16 (m, 2H, ArH), 7.16-7.20 (m, 1H, ArH), 7.21-7.25 (m, 2H, ArH), 7.28-7.32 (m, 2H, ArH), 7.48-7.52 (m, 2H, ArH). **^{13}C NMR ($CDCl_3$):** δ 30.2 (s, CH_3), 34.5 (s, CH_2), 48.1 (s, S$C(CH_3)_2$), 126.8 (s, *p*-C_6H_5), 128.1 (s, *o*-C_6H_5Cl), 128.2 (s, *m*-C_6H_5Cl), 128.4 (s, *m*-C_6H_5), 128.9 (s, *o*-C_6H_5), 132.2 (s, *C*-Cl), 137.8 (s, *ipso*-C_6H_5), 145.0 (s, *ipso*-C_6H_4Cl). DART-MS exact mass calculated for $(C_{18}H_{18}SCl)^+$ require m/z 277.08, found m/z 277.08.

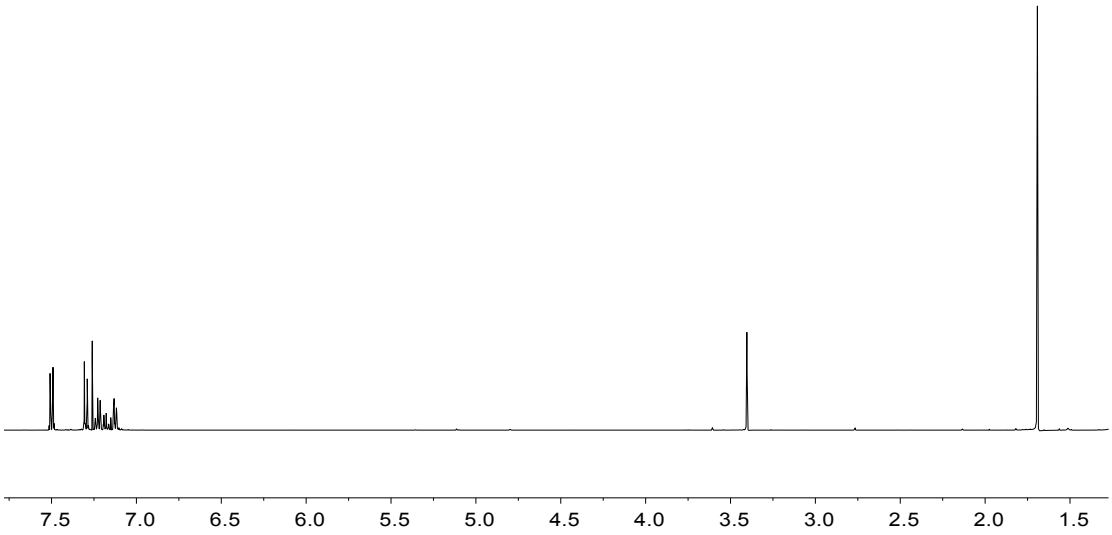


Figure S11: ^{1}H NMR spectrum of entry 4 in $CDCl_3$.

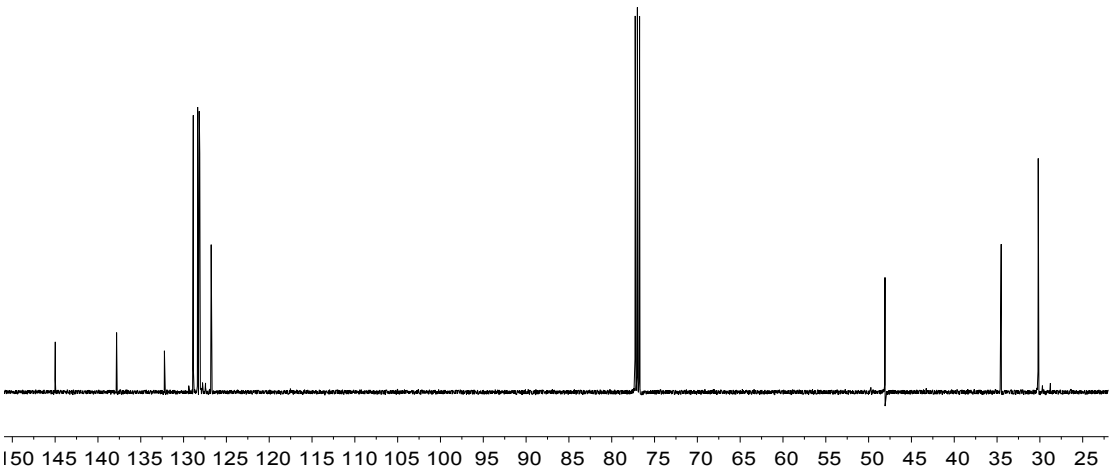
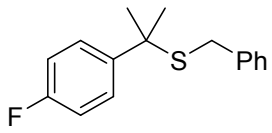


Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum of entry 4 in $CDCl_3$.



(Table 3, Entry 5).

Colourless solid, 0.090 g, 34%. **^{1}H NMR ($CDCl_3$):** δ 1.70 (s, 6H, CH_3), 3.41 (s, 2H, CH_2), 7.00-7.03 (m, 2H, ArH), 7.11-7.15 (m, 2H, ArH), 7.15-7.20 (m, 1H, ArH), 7.20-7.25 (m, 2H, ArH), 7.51-7.56 (m, 2H, ArH). **^{13}C NMR ($CDCl_3$):** δ 30.5 (s, CH$_3$), 34.7 (s, CH$_2$), 48.2 (s, C(CH$_3$)$_2$), 114.9 (d, $^{2}J_{CF}$ = 21 Hz, *m*-C$_6$H$_4$F), 126.9 (s, *ipso*-C$_6$H$_5$), 128.4 (d, $^{2}J_{CF}$ = 8.0 Hz, *o*-C$_6$H$_4$F), 128.5 (s, *m*-C$_6$H$_5$), 129.0 (s, *ipso*-C$_6$H$_4$F), 138.1 (s, *o*-C$_6$H$_5$), 142.3 (s, *p*-C$_6$H$_5$), 161.5 (d, $^{1}J_{CF}$ = 245 Hz, C-F). DART-MS exact mass calculated for $(C_{16}H_{18}SF)^{+}$ require m/z 261.11, found m/z 261.11.

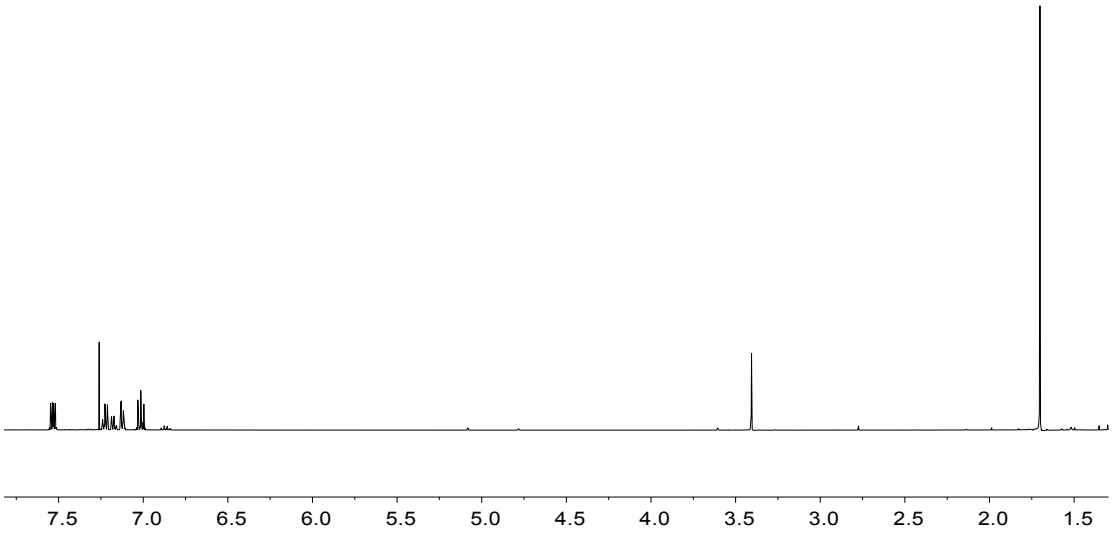


Figure S13: ^{1}H NMR spectrum of entry 5 in $CDCl_3$.

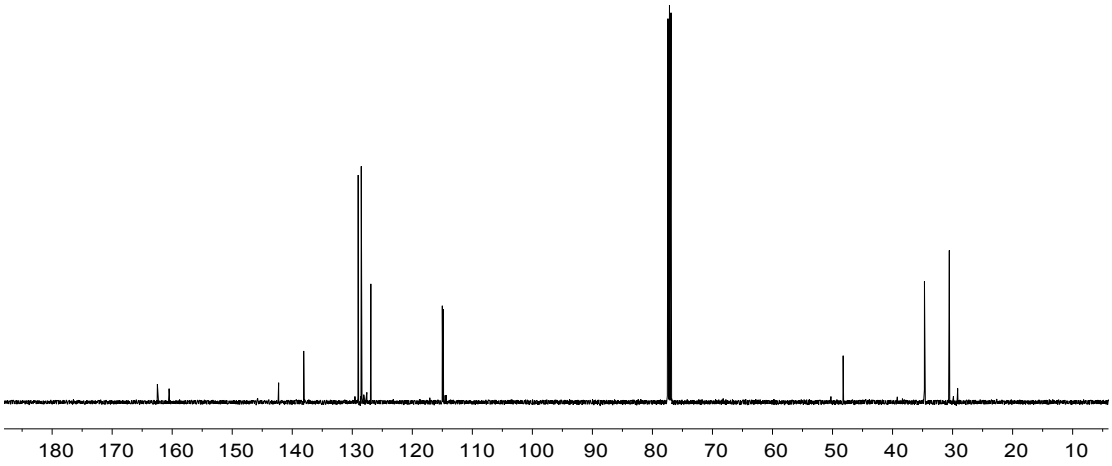
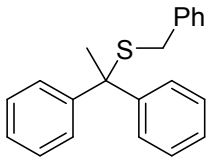


Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum of entry 5 in $CDCl_3$.



(Table 3, Entry 6)

Crude mixture, 70%. **^{1}H NMR ($CDCl_3$):** δ 2.21 (s, 3H, CH_3), 3.56 (s, 2H, CH_2), 7.27-7.39 (m, 3H, ArH), 7.32-7.35 (m, 2H, ArH), 7.40-7.45 (m, 8H, ArH), 7.58-7.60 (m, 2H, ArH).

*Asterisks represent remaining thiol, alkene, catalyst, and triarylmethanol by-products.

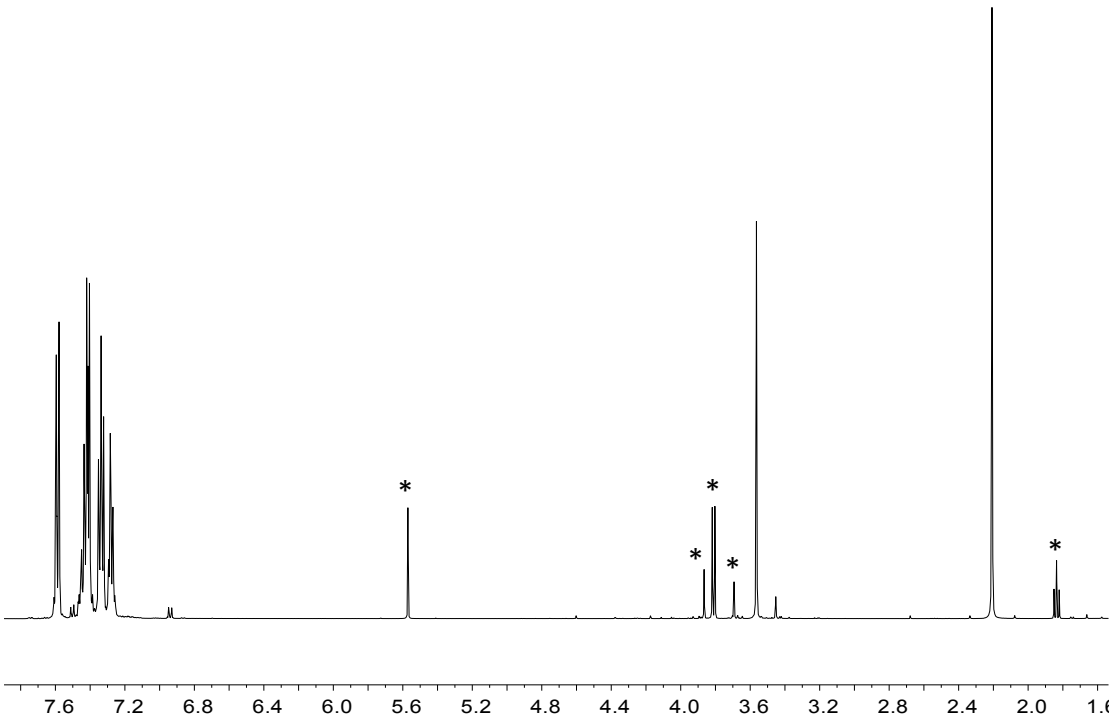


Figure S15: ^{1}H NMR spectrum of entry 6 in $CDCl_3$.

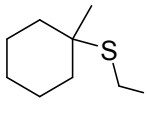


Table 3 Entry 7)

Colourless liquid, 0.223 g, 99 %. **^{1}H NMR ($CDCl_3$):** δ 1.37 (s, 3H CH_3), 1.42-1.54 (m, 5H, CH_2), 1.66-1.77 (m, 5H, CH_2), 3.68 (s, 2H, CH_2), 7.19-7.23 (m, 1H, ArH), 7.27-7.31 (m, 2H, ArH), 7.33-7.68 (m, 2H, ArH). **^{13}C NMR ($CDCl_3$):** δ 22.3 (s, CH$_2$, cyclohexyl), 25.9 (s, CH$_3$), 28.9 (br, s, quaternary carbon), 32.0 (s, SCH$_2$), 38.3 (s, CH$_2$, cyclohexyl), 47.1 (s, CH$_2$, cyclohexyl), 126.7 (s, *p*-C$_6$H$_5$), 128.4 (s, *m*-C$_6$H$_5$), 129.0 (*o*-C$_6$H$_5$), 138.7 (*ipso*-C$_6$H$_5$). DART-MS exact mass calculated for $(C_{14}H_{21}S)^+$ require m/z 221.14, found m/z 221.14.

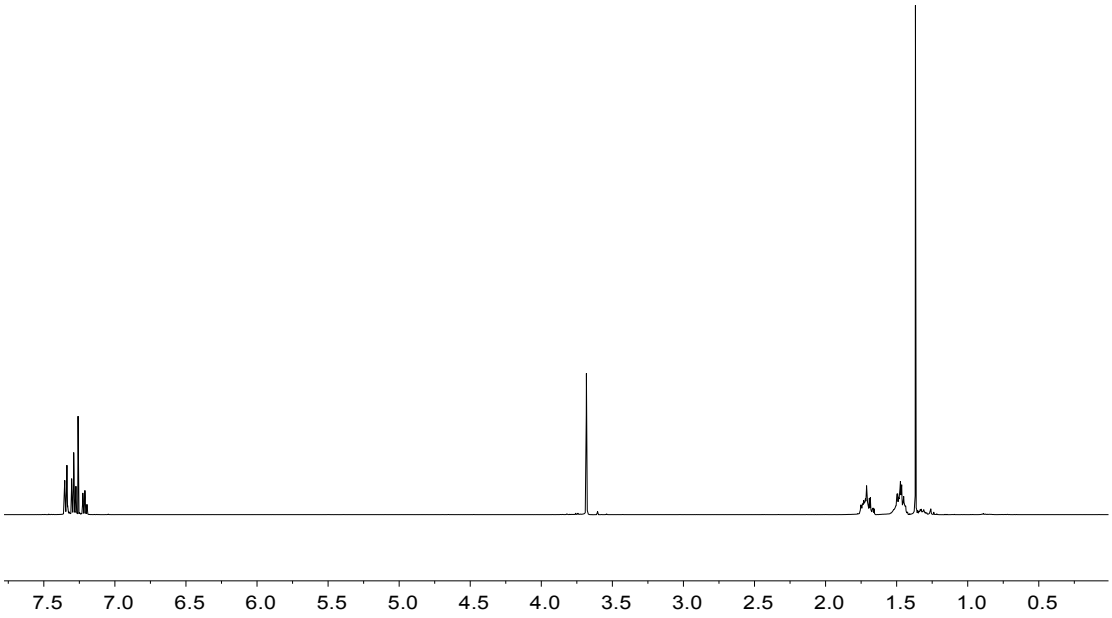


Figure S16: ^{1}H NMR spectrum of entry 7 in $CDCl_3$.

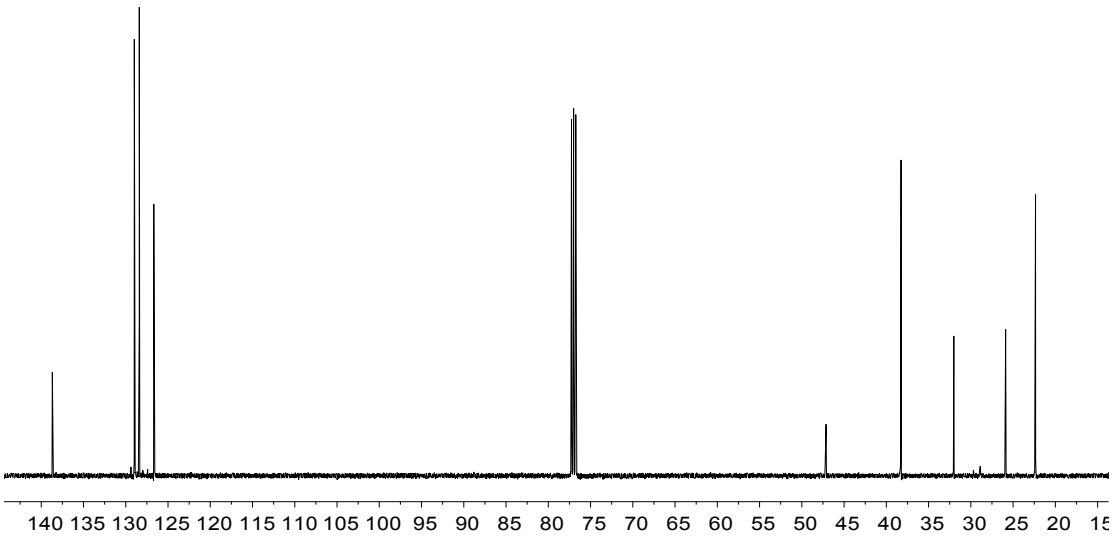
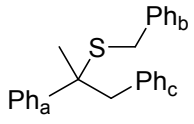


Figure S17: $^{13}C\{^{1}H\}$ NMR spectrum of entry 7 in $CDCl_3$.



(Table 3 Entry 8)

White crystalline solid, 0.124 g, 39%. **^{1}H NMR (CD_2Cl_2):** δ 1.68 (s, 3H, CH_3), 3.20 (m, 2H, CH_2, diastereotopic), 3.38 (m, 2H, SCH_2, diastereotopic), 6.85-6.87 (m, 3H, ArH), 7.10-7.27 (m, 8H, ArH), 7.33-7.36 (m, 2H, ArH), 7.53-7.56 (m, 2H, ArH). **^{13}C{^{1}H} NMR (CD_2Cl_2):** δ 25.3 (s, *C*H_3), 33.9 (s, S*C*H_2), 49.4 (s, *C*(CH_3)$_2$), 53.1 (s, *C*H_2), 126.3 (*p*-Ph_a), 126.6 (*p*-Ph_c), 126.7 (*p*-Ph_b), 127.5 (*o*-Ph_a), 127.7 (*o*-Ph_c), 128.0 (*m*-Ph_a), 128.3 (*m*-Ph_c), 128.9 (*o*-Ph_b), 130.6 (*m*-Ph_c), 136.9 (*ipso*-Ph_c), 138.1 (*ipso*-Ph_b), 144.4 (*ipso*-Ph_a). DART-MS exact mass calculated for $(C_{22}H_{23}S)^+$ require m/z 319.15, found m/z 319.15.

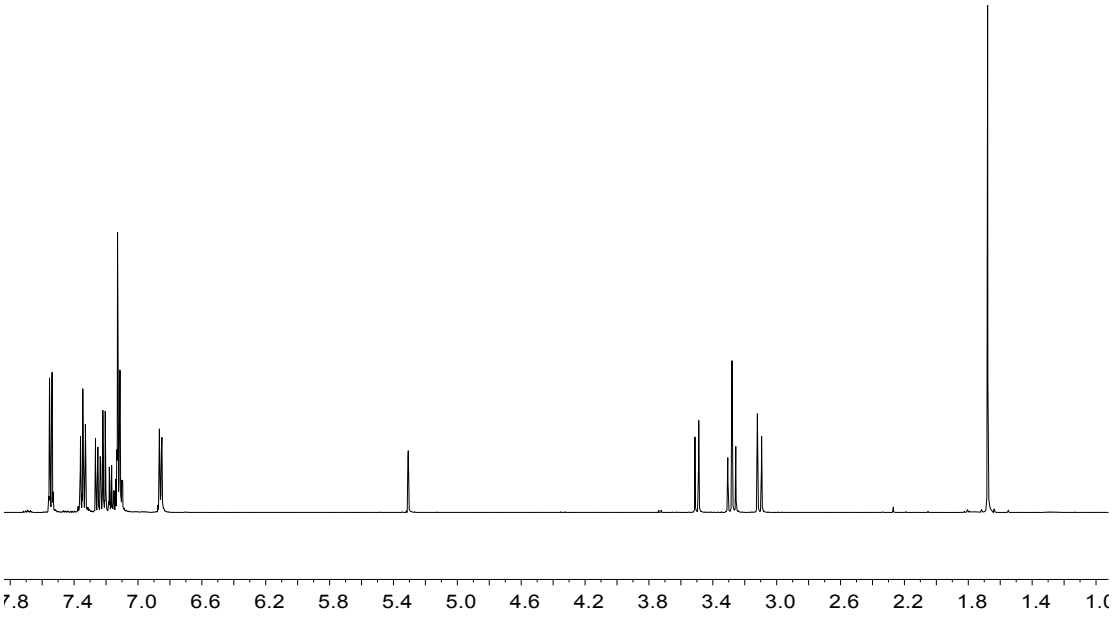


Figure S18: ^{1}H NMR spectrum of entry 8 in CD_2Cl_2.

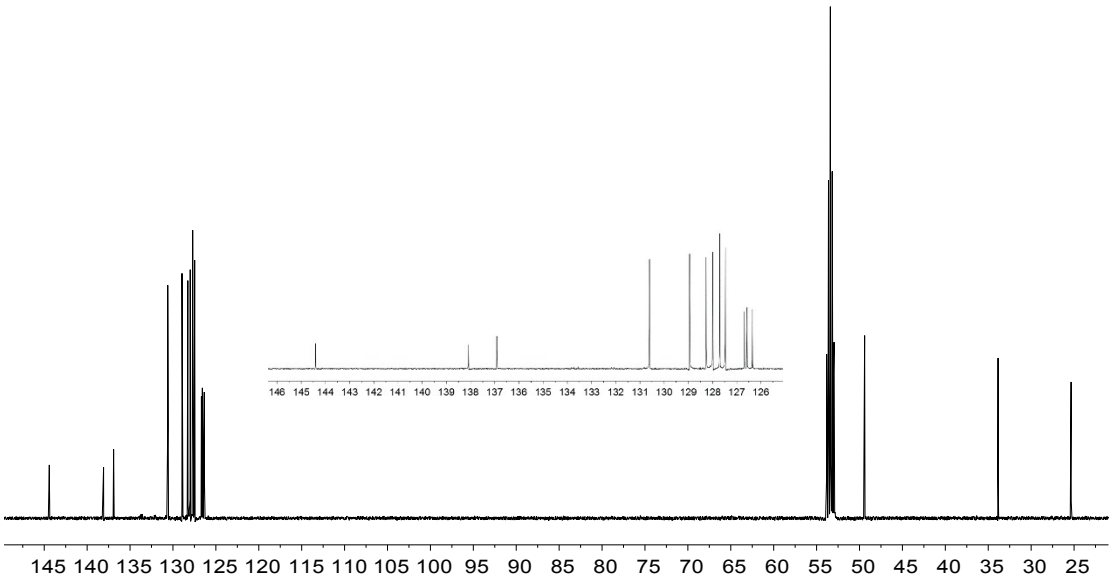
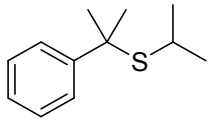


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of entry 8 in CD_2Cl_2.



(Table 3 Entry 12)

Colourless liquid, 0.167 g, 86 %. **^{1}H NMR ($CDCl_3$):** δ 1.04 (d, $^{3}J_{HH}$ = 6.86 Hz, 6H, CH_3), 1.72 (s, 6H, CH_3), 2.56 (sept, $^{3}J_{HH}$ = 6.84 Hz, 1H, CH), 7.20 (m, 1H, ArH), 7.31 (m, 2H, ArH), 7.56 (m, 2H, ArH). **^{13}C NMR ($CDCl_3$):** δ 25.2 (s, CH(CH$_3$)$_2$), 30.9 (s, SC(CH$_3$)$_2$), 34.2 (s, CH(CH$_3$)$_2$), 48.2 (s, SC(CH$_3$)$_2$), 126.3 (s, *p*-C_6H_5), 126.6 (s, *o*-C_6H_5), 127.9 (s, *m*-C_6H_5), 147.1 (s, *ipso*-C_6H_5). DART-MS exact mass calculated for $(C_{12}H_{19}S)^+$ require m/z 195.12, found m/z 195.12.

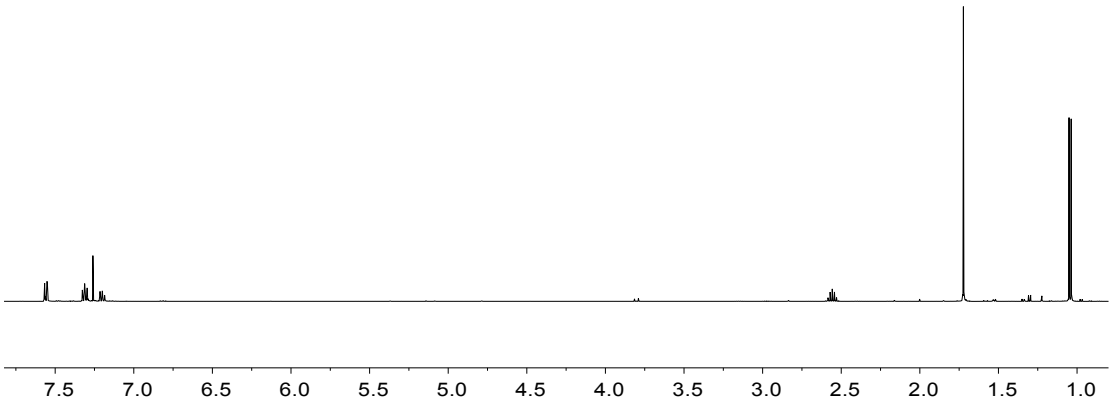


Figure S20: ^{1}H NMR spectrum of entry 12 in $CDCl_3$.

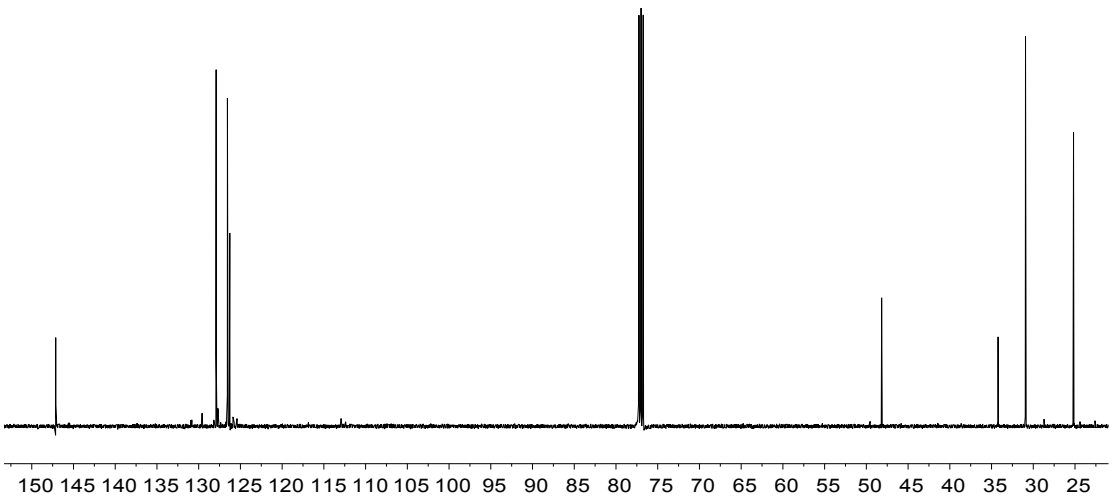
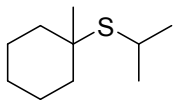


Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum of entry 12 in $CDCl_3$.



(Table 3, Entry 13)

Volatile, colourless liquid, 0.023 g, 12 %. **^{1}H NMR ($CDCl_3$):** δ 1.29 (d, $^3J_{HH}$ = 7 Hz, 6H, CH_3), 1.34 (s, 3H, CH_3), 1.39-1.52 (m, 6H, CH_2), 1.62-1.73 (m, 4H, CH_2), 2.90 (hept, $^3J_{HH}$ = 7 Hz, 1H, C*H*). **^{13}C NMR ($CDCl_3$):** δ 22.5 (s, *C*H_2, cyclohexyl), 25.9 (s, CH(*C*H_3)$_2$), 26.3 (s, *C*H_3), 29.3 (br, s, quaternary carbon), 31.8 (s, *C*H(CH$_3$)$_2$), 39.0 (s, *C*H_2, cyclohexyl), 47.3 (s, *C*H_2, cyclohexyl). DART-MS exact mass calculated for $(C_{10}H_{21}S)^+$ require m/z 173.14, found m/z 173.14

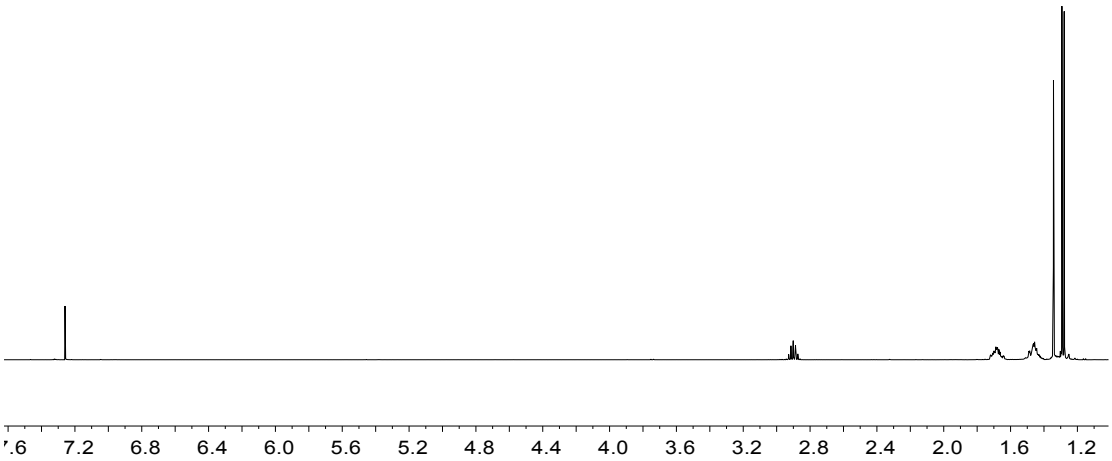


Figure S22: ^{1}H NMR spectrum of entry 13 in $CDCl_3$.

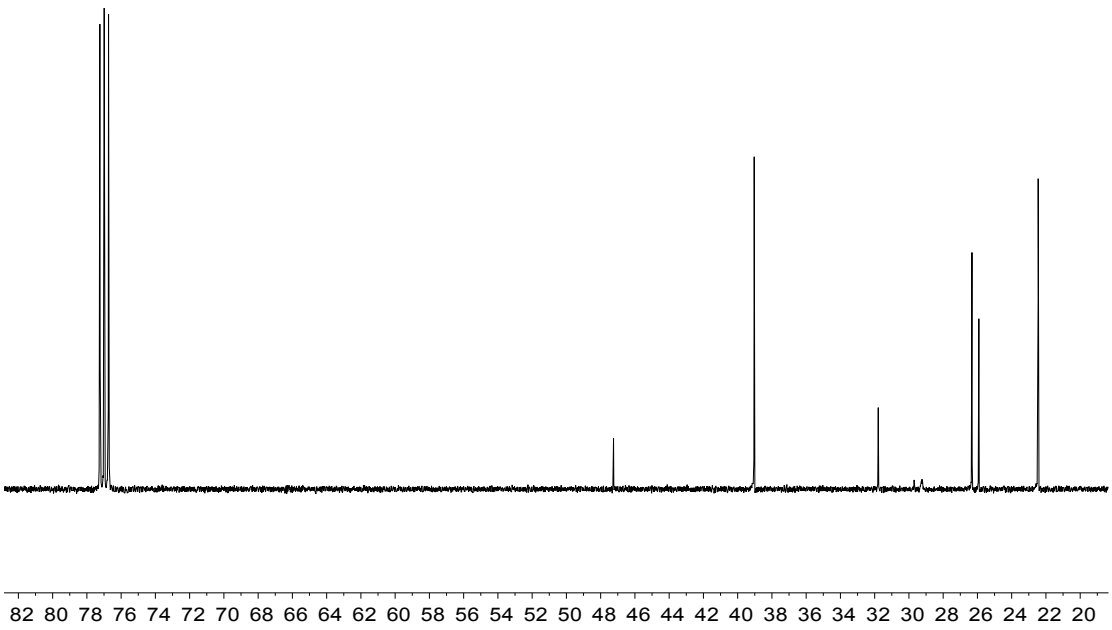
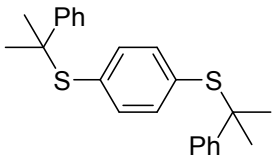


Figure S23: $^{13}C\{^{1}H\}$ NMR spectrum of entry 13 in $CDCl_3$.



(Table 3 Entry 14)

Off-white solid, 0.232 g, 61 %. . **^{1}H NMR ($CDCl_3$):** δ 1.66 (s, 12H, CH_3), 6.90 (s, 4H, phenylene C*H*), 7.18-7.21 (m, 2H, ArH), 7.24-7.26 (m, 4H, ArH), 7.35-7.37 (m, 4H, ArH). **^{13}C NMR ($CDCl_3$):** δ 29.7 (s, *C*H_3), 51.2 (s, *C*$(CH_3)_2$), 126.5 (s, *o*-C_6H_5), 126.6 (s, *p*-C_6H_5), 127.9 (s, *m*-C_6H_5), 133.6 (s, *ipso*-phenylene), 135.9 (s, phenylene *C*H), 146.1 (s, *ipso*-C_6H_5). DART-MS exact mass calculated for $(C_{24}H_{27}S_2)^+$ require m/z 379.15, found m/z 379.15.

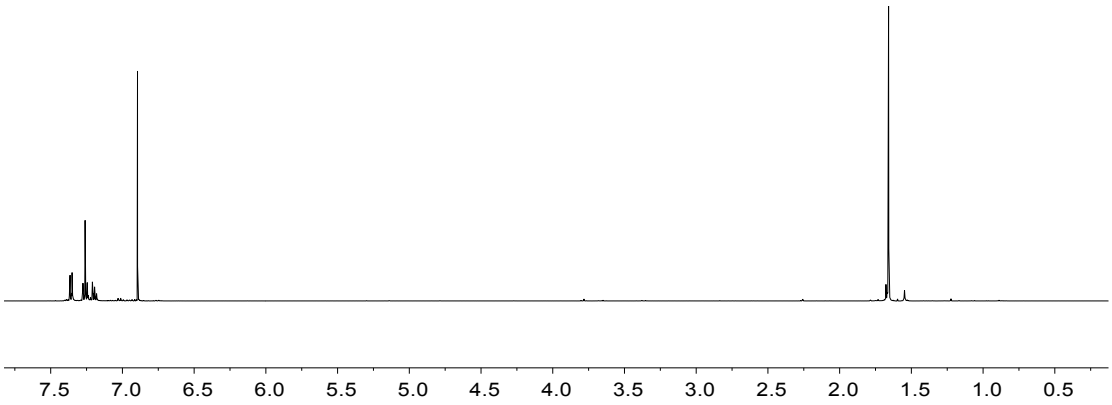


Figure S24: ^{1}H NMR spectrum of entry 14 in $CDCl_3$.

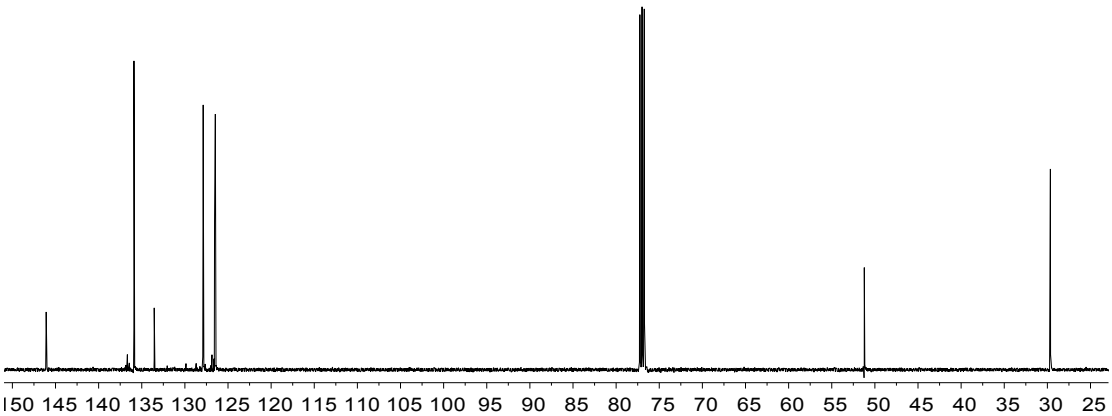
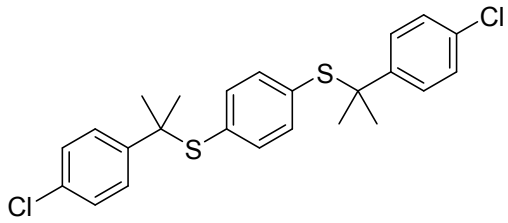


Figure S25: $^{13}C\{^{1}H\}$ NMR spectrum of entry 14 in $CDCl_3$.



(Table 3, Entry 15)

Colourless solid, 0.081 g, 18%. **^{1}H NMR ($CDCl_3$):** δ 1.63 (s, 12H, CH_3), 6.91 (s, 4H, ArH), 7.21-7.22 (m, 2H, ArH), 7.23-7.24 (m, 2H, ArH), 7.26-7.27 (m, 2H, ArH), 7.28-7.29 (m, 2H, ArH). **^{13}C NMR ($CDCl_3$):** δ 29.7 (s, CH_3), 50.8 (s, $C(CH_3)_2$), 127.9 (s, *o*-C_6H_4Cl), 128.0 (s, C_6H_4), 132.3 (s, *C*-Cl), 133.5 (s, *ipso*-C_6H_4), 136.0 (s, *m*-C_6H_4Cl), 144.8 (s, *ipso*-C_6H_4Cl). DART-MS exact mass calculated for $(C_{24}H_{25}S_2Cl_2)^+$ require m/z 447.08, found m/z 447.08.

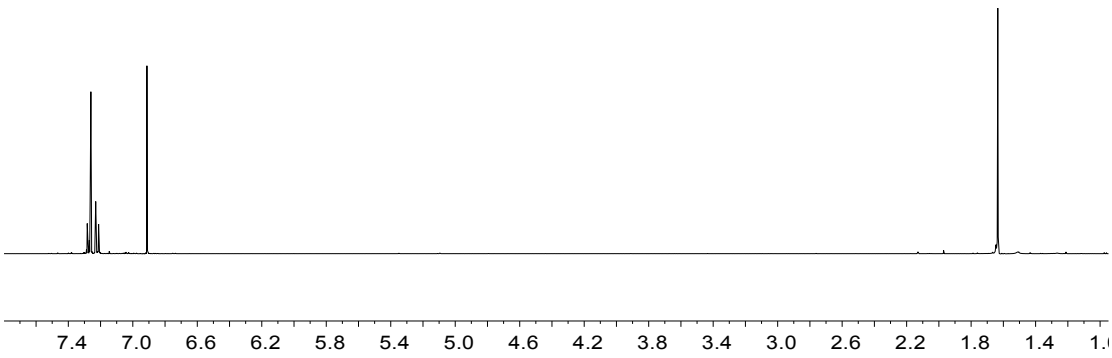


Figure S26: ^{1}H NMR spectrum of entry 15 in $CDCl_3$.

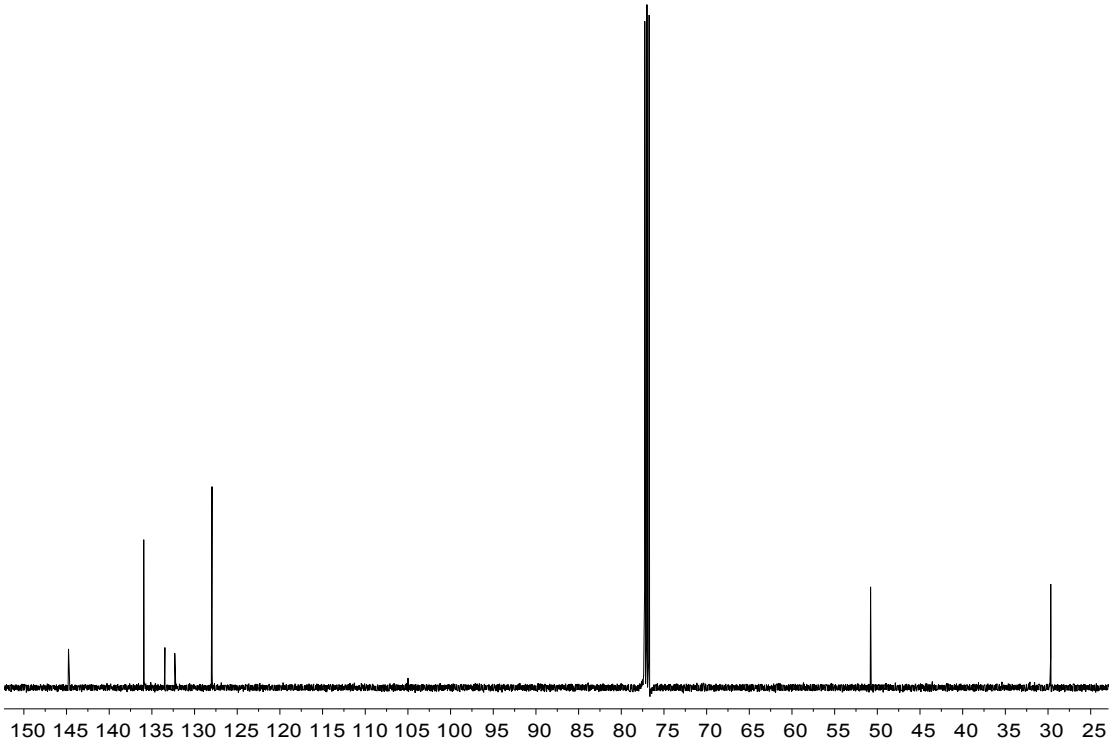


Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum of entry 15 in $CDCl_3$.

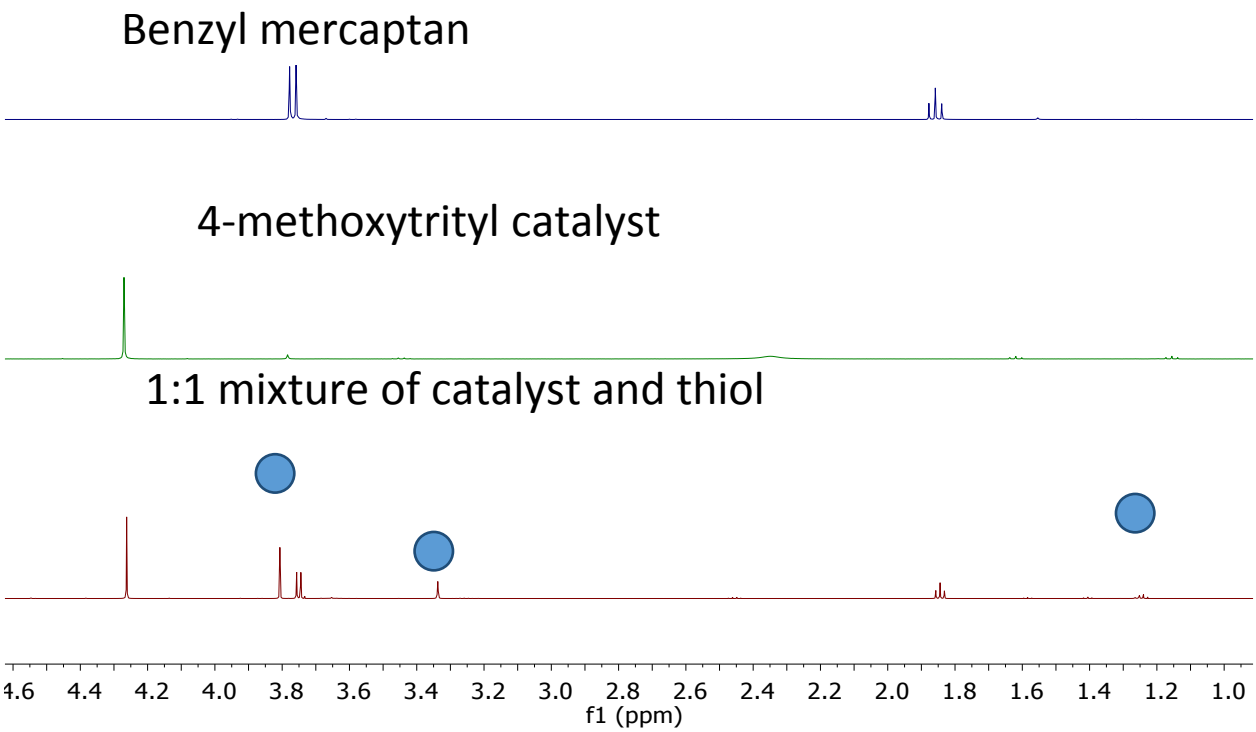


Figure S28 ^{1}H NMR spectra in 1-4.6 ppm range for 4-methoxytrityl with thiol.

At room temperature, equimolar mixture of catalyst and thiol shows complexation of thiol with carbocatioin, as evidenced by the presence of new signals that show a relative integration of 3:2:1, indicative of the methoxy, methylene, and thiol protons, respectively.

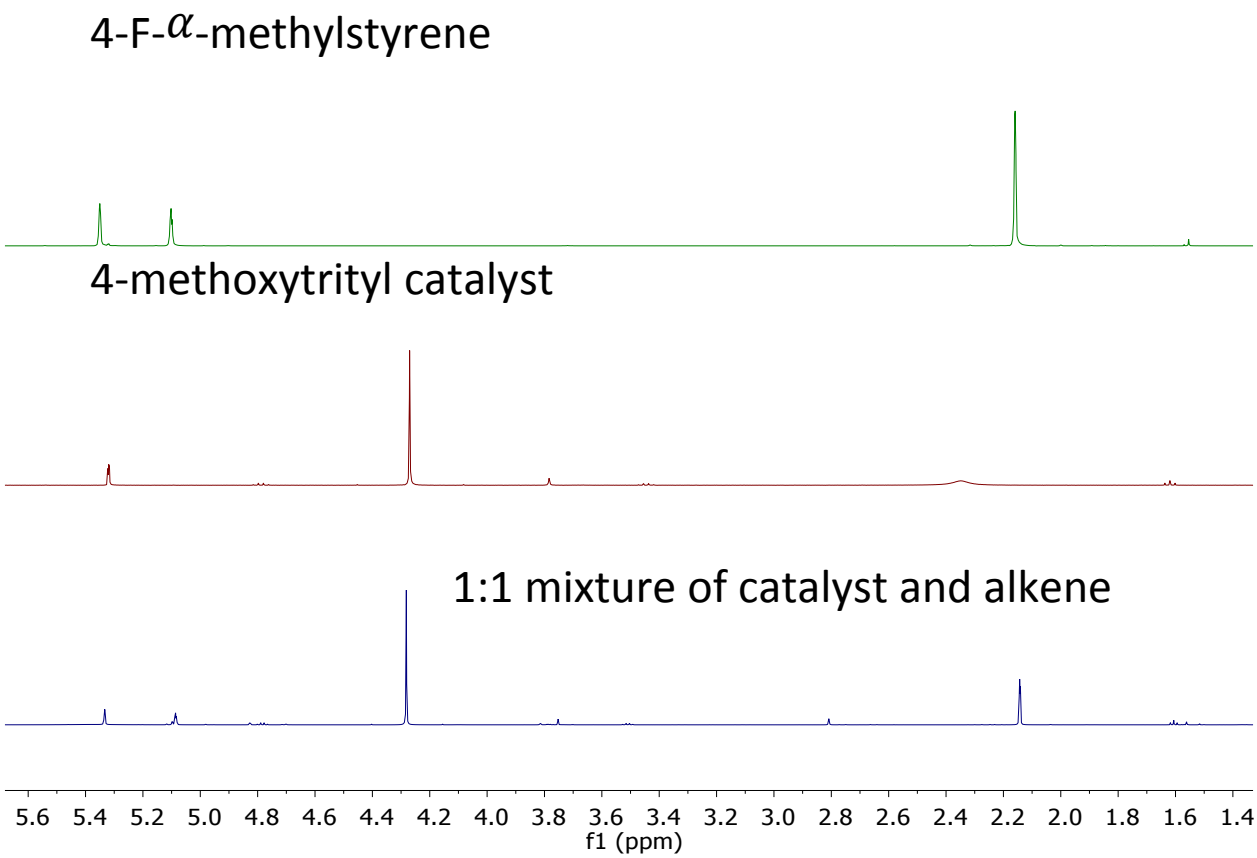


Figure S29 ^{1}H NMR spectra in 1-4.6 ppm range for 4-methoxytrityl with alkyne.

By contrast, there is no such complexation observed using an equimolar mixture of an alkene substrate and the catalyst, even at -80 ^{o}C.