Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Mild Ti-catalyzed transformation of *t*-butyl thio-ethers into thio-acetates

T. C. Pijper,[a] J. Robertus,[b] W. R. Browne,[a,b] B. L. Feringa[a,b]

a) Zernike Institute for Advanced Materials University of Groningen, Nijenborgh 4, 9747 Groningen.
b) Stratingh Institute of Chemistry, University of Groningen, Nijenborgh 4, 9747 Groningen.

Electronic Supplementary Information

Contents

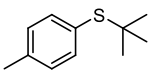
Experimental details

For synthesis all chemicals were obtained from commercial sources and used as received unless stated otherwise. Solvents were reagent grade. For column chromatography, silica gel (Silicycle Siliaflash P60, 40-63m, 230-400 mesh) was used in all cases. Separation and purity were determined on Merck TLC silica gel 60, kieselguhr F254. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 (operating at 200 and 50 MHz), a Varian VXR-300 (operating at 300 and 75 MHz) and a Varian AMX400 (operating at 400 and 100 MHz) spectrometer in $CDCl_3$ and CD_2Cl_2 Chemical shifts are reported in values (ppm) relative to $CDCl_3$ (^{1}H = 7.24, ^{13}C = 77.2), CD_2Cl_2 (^{1}H = 5.32, ^{13}C = 54.0), For ^{1}H-NMR the signals were assigned as following: singlet (s), doublet (d), double doublet (dd), triplet (t), quartet (q), and multiplet (m). For ^{13}C-NMR, the signals were designated as: primary carbon (CH_3), secondary carbon (CH_2), tertiary carbon (CH), quaternary carbon (C). MS spectra were obtained on a Hewlett-Packard HP 6890 GC with HP 5973 mass selective detector, containing a Agilent 5% - 25(phenyl)methylpolysiloxane column (25 m × 0.25 mm × 0.25 m. HRMS (ESI, APCI) spectra were obtained on a Thermo scientific LTQ Orbitrap XL. Melting points were recorded using a Buchi melting point B-545 apparatus.

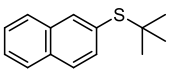
General procedure for the preparation of *t*-butyl substrates

General synthetic procedure:[i] Over the course of 15 min $AlCl_3$ (121 mg, 0.9 mmol) was added in portions to a solution of thiol (18.1 mmol) in DCM (17 mL) at rt. The resulting mixture was stirred at 35°C for 30 min and was subsequently poured onto water (50 mL) and extracted with pentane (3 × 50 mL). The organic layers were combined and washed with brine and dried over Na_2SO_4. The organic solvent was removed in vacuo and the thioether was further purified by flash column chromatography.

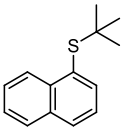
tert-butyl(p-tolyl)sulfane (1a) TLC (SiO_2: heptane/ethyl acetate, 4:1, R_f = 0.75) (yield: 58%) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 2.35 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 138.8 (C), 137.6 (CH), 129.4 (C), 129.4 (CH), 45.7 (C), 31.1 (CH_3), 21.4 (CH_3). *m/z* (EI) 180. HRMS (APCI): calcd. for $C_{11}H_{16}OS$: 181.1046, found 181.1043.



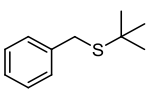
tert-butyl(naphthalen-2-yl)sulfane (2a) TLC (SiO_2: heptane/ethyl acetate, 4:1, R_f = 0.70) (85%) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (s, 1H), 7.83 (dd, *J* = 9.2, 3.1 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.49 (dd, *J* = 6.1, 3.3 Hz, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 137.3 (CH), 134.5 (CH), 133.6 (C), 133.3 (C), 130.4 (C), 128.1 (CH), 128.0 (CH), 127.8 (CH), 126.9 (CH), 126.5 (CH), 46.5 (C), 31.3 (CH_3). *m/z* (EI) 216. HRMS (APCI): calcd. for $C_{14}H_{16}S$: 217.1046, found 217.1045.



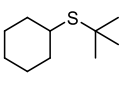
tert-butyl(naphthalen-1-yl)sulfane (3a) Obtained as a white solid TLC (SiO_2: heptane/ethyl acetate, 4:1, R_f = 0.70) (80%) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.74 (d, *J* = 8.3 Hz, 1H), 7.90-7.78 (m, 3H), 7.58-7.39 (m, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 137.6 (CH), 137.0 (C), 134.3 (C), 130.9 (C), 130.0 (CH), 128.4 (CH) , 127.6 (CH), 126.6 (CH), 126.2 (CH), 125.4 (CH), 47.7 (C), 31.5 (CH_3). *m/z* (EI) 216. HRMS (APCI): calcd. for $C_{14}H_{16}S$: 217.1046, found 217.1044.



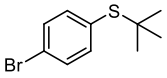
benzyl(tert-butyl)sulfane (4a) TLC (SiO_2: heptane/ethyl acetate, 4:1, R_f = 0.80) (87%) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 3.75 (s, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 138.8 (C), 129.1 (CH), 128.6 (CH), 126.9 (CH), 43.0 (C), 33.6 (CH_2), 31.1 (CH_3). HRMS (APCI): calcd. for $C_{11}H_{16}S$: 181.046, found 181.1044.



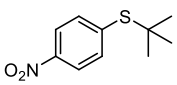
tert-butyl(cyclohexyl)sulfane (5a) TLC (SiO_2: heptane/ethyl acetate, 4:1, R_f = 0.84). Colorless liquid (70%) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.62-2.56 (m, 1H), 1.98-1.91 (m, 2H), 1.74-1.66 (m, 2H), 1.58-1.50 (m, 1H), 1.40-1.32 (m, 4H), 1.31 (s, 9H), 1.25-1.14 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ: 42.9 (C), 41.2 (CH), 36.2 (CH_2), 31.6 (CH_3), 26.4 (CH_2), 25.5 (CH_2). *m/z* (EI) 172. HRMS (APCI): calcd. for $C_{10}H_{20}S$: 173.1359, found 173.1358.



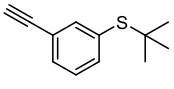
(4-bromophenyl)(tert-butyl)sulfane (6a) distilled under reduced pressure 1.7×10^{-2} mbar at 90°C colorless liquid (89%). TLC (SiO_2: heptanes/ethyl acetate, 4:1, R_f = 0.85). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (dd, *J* = 26.1, 7.1 Hz, 4H), 1.53 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 139.0 (CH), 132.0 (C), 131.8 (CH), 123.6 (C), 46.2 (C), 31.0 (CH_3). *m/z* (EI) 246. HRMS (APCI): calcd. for C_8H_8BrS: 244.9817, found 244.9816.



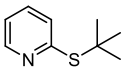
tert-butyl(4-nitrophenyl)sulfane (7a) TLC (SiO_2: heptane/ethyl acetate, 4:1, R_f = 0.64) (73%) ^{1}H NMR (400 MHz, $CDCl_3$) δ: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.13 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.9 (C), 142.5 (C), 137.0 (CH), 123.5 (CH), 47.7 (C), 31.3 (CH_3). *m/z* (EI) 211. HRMS (APCI): calcd. for $C_{10}H_{13}NO_2S$: 212.0740, found 212.0739.



tert-butyl(3-ethynylphenyl)sulfane (8a) TLC (SiO_2: heptane/ethyl acetate, 4:1, R_f = 0.81) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (s, 1H), 7.50 (dd, *J* = 13.5, 7.7 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 1H), 3.10 (s, 1H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 140.9 (CH), 138.1 (CH), 133.3 (C), 132.5 (CH), 128.6 (CH), 122.7 (C), 83.2 (C), 78.0 (CH), 46.4 (C), 31.2 (CH_3). *m/z* (EI) 190. HRMS (APCI): calcd. for $C_{12}H_{14}S$: 191.0887, found 191.0887.



2-(tert-butylthio)pyridine (10a) TLC (SiO_2: heptane/ethyl acetate, 4:1, R_f = 0.19) (4%) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.47 (td, *J* = 7.7, 1.9 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.03 (ddd, *J* = 7.2, 4.9, 0.8 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.7 (C), 149.6 (CH), 136.0 (CH), 127.4 (CH), 120.8 (CH), 47.6 (C), 31.2 (CH_3). *m/z* (EI) 167. HRMS (APCI): calcd. for $C_9H_{13}NS$: 168.0842, found 168.0840.

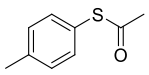


5-(4-((11-(tert-butylthio)undecyl)oxy)phenyl)-3-(2-(5-chloro-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-2-methylthiophene (11a). To a solution of 1,2-bis(5-chloro-2-methylthiophen-3-yl)cyclopent-1-ene (2.98 g, 9.04 mmol) in THF (40 mL) n-BuLi (1.6 M, 6.8 ml, 10.85 mmol) was added dropwise at 0°C under an atmosphere of argon. The temperature was allowed to reach rt, while stirring was continued for 1 h. Subsequently, the reaction mixture was cooled to 0°C and tributyl borate (2.50 g, 10.85 mmol) was added dropwise. The mixture was allowed to reach rt and was stirred for 1.5 h. The resulting solution of boronic ester was added without further purification to a solution of (11-(4-bromophenoxy)undecyl)(tert-butyl)sulfane (3.87 g, 9.33 mmol), Na_2CO_3 in H_2O (40 ml, 2M) and ethylene glycol (1 mL) in THF (20 mL) under an argon atmosphere. The reaction mixture was heated to reflux and stirred for 48 h. Upon completion the mixture was allowed to attain room temperature and DCM (200 mL) was added. The organic layer was washed with H_2O (3 × 100 mL) and brine (100 mL), dried over $MgSO_4$ and subsequently concentrated under reduced pressure. **11a** was further purified using flash chromatography and was obtained as a brown oil (4.03 g, 6.41 mmol, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 8.7 Hz, 2H), 6.86 (t, *J* = 4.3 Hz, 3H), 6.62 (s, 1H), 3.94 (t, *J* = 6.5 Hz, 2H), 2.77 (dt, *J* = 17.1, 7.2 Hz, 4H), 2.52 (t, *J* = 7.4 Hz, 2H), 2.02 (dd, *J* = 13.4, 5.8 Hz, 3H), 1.97 (s, 3H), 1.89 (d, *J* = 6.9 Hz, 3H), 1.81-1.71 (m, 3H), 1.56 (dd, *J* = 14.8, 7.5 Hz, 3H), 1.35 (m, 28H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.5 (C), 140.0 (C), 136.2 (C), 135.5 (C), 135.3 (C), 133.6 (C), 133.3 (C), 133.3 (C), 127.2 (C), 126.9 (CH), 126.6 (CH), 125.0 (C), 122.7 (CH), 114.9 (CH), 68.1 (CH_2), 41.8 (C), 38.6 (CH_2), 38.5 (CH_2), 31.1 (CH_3), 30.0 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 28.4 (CH_2), 26.2 (CH_2), 23.0 (CH_2), 14.4 (CH_3), 14.3 (CH_3). HRMS (ESI): calcd. for $C_{36}H_{50}ClOS_3$: 629.2707 found 629.2673

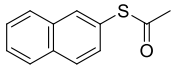
General procedure for *S*-*t*-butyl to *S*-acetyl exchange reaction

$TiCl_4$ (0.13 mL, 1.22 mmol) or BBr_3 (1 M in DCM, 1.22 mL, 1.22 mmol) was added in a dropwise fashion to a solution of *t*-butyl thioether (1.11 mmol) and acetyl chloride (0.09 ml, 1.22 mmol) in DCM at 0°C. The resulting mixture was stirred at rt and the conversion was verified by TLC (heptane/ethyl acetate, 4:1). Typically, reaction times with $TiCl_4$ were between 5 s and 1 h, while reactions with BBr_3 took 2.5 to 7 h. Upon completion water (10 ml) was added and the aqueous layer was extracted with DCM (3 × 15 mL). The organic layers were combined and washed with brine (20 mL), dried over $MgSO_4$ and the organic solvent was removed in vacuo. Where necessary the product was further purified by flash column chromatography (heptane/ethyl acetate, 4:1).

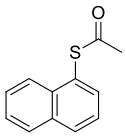
S-(*p*-tolyl) ethanethioate (1b) $TiCl_4$: 90%, BBr_3: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 194.7 (C), 139.8 (C), 134.6 (CH), 130.2 (CH), 124.6 (C), 30.3 (CH_3), 21.5 (CH_3). *m/z* (EI) 166. HRMS (ESI): calcd. for $C_9H_{11}OS$: 167.0525, found 167.0522.



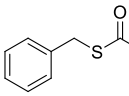
S-naphthalen-2-yl ethanethioate (2b) TLC (SiO_2: heptane/ethyl acetate, 4:1, R_f = 0.63). $TiCl_4$: 94%, BBr_3: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (s, 1H), 7.90-7.82 (m, 3H), 7.56-7.48 (m, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 194.3 (C), 134.4 (CH), 133.6 (C), 133.4 (C), 131.0 (CH), 128.9 (CH), 128.1 (CH), 127.9 (CH), 127.3 (CH), 126.7 (CH), 125.4 (C), 31.3 (C), 30.3 (CH_3). HRMS (ESI): calcd. for $C_{12}H_{11}OS$: 203.0525, found 203.0523.



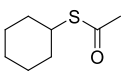
S-naphthalen-1-yl ethanethioate (3b) $TiCl_4$: 88%, BBr_3: 76%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.23 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.0 Hz, 1H), 7.55 (ddd, *J* = 30.3, 15.1, 7.3 Hz, 3H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.2 (C), 135.1 (CH), 134.3 (2 × C), 131.1 (CH), 128.8 (CH), 127.3 (CH), 126.6 (CH), 125.7 (CH), 125.6 (C), 125.4 (CH), 30.4 (CH_3). *m/z* (EI) 202. HRMS (ESI): calcd. for $C_{12}H_{11}OS$: 203.0525, found 203.0521.



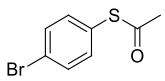
S-benzyl ethanethioate (4b) TLC (SiO_2: heptane/ethyl acetate, 4:1, R_f = 0.66) $TiCl_4$: >99% $TiCl_4$ (10% mol): full conversion, BBr_3: >99%. $CDCl_3$) δ: 7.33-7.26 (m, 4H), 7.90-7.82 (m, 1H), 4.13 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.1 (C), 137.7 (C), 128.9 (CH), 128.7 (C), 127.4 (CH), 33.5 (C), 30.4 (CH_3). *m/z* (EI) 166. HRMS (ESI): calcd. for $C_9H_{11}OS$: 167.0525, found 167.0521.



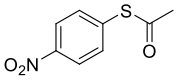
S-cyclohexyl ethanethioate (5b) TLC (SiO_2: heptane/ethyl acetate, 4:1, R_f = 0.57). $TiCl_4$: >99%, BBr_3: 92%. $CDCl_3$) δ: 3.47-3.41 (m, 1H), 2.23 (s, 3H), 1.85-1.81 (m, 2H), 1.60-1.63 (m, 2H), 1.54-1.51 (m, 1H), 1.42-1.29 (m, 4H), 1.25-1.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.8 (C), 42.5 (CH), 33.1 (CH_3), 30.9 (CH_2), 26,0 (CH_2), 25.7 (CH_2). *m/z* (EI) 158. HRMS (ESI): calcd. for $C_8H_{15}OS$: 159.0838, found 159.0836.



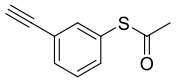
S-(4-bromophenyl) ethanethioate (6b) TLC (SiO_2: heptane/ethyl acetate, 4:1, R_f = 0.58) $TiCl_4$ 89%, BBr_3: 65% ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 193.21 (C), 135.94 (CH), 132.45 (CH), 127.05 (C), 124.14 (C), 30.31 (CH_3). HRMS (ESI): calcd. for $C_9H_{11}OS$: 230.9474, found 230.9470.



S-4-nitrophenyl ethanethioate (7b) $TiCl_4$: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.21 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 191.7 (C), 148.3 (C), 136.5 (C), 134.8 (CH), 124.1 (CH), 30.7 (CH_3). *m/z* (EI) 197. HRMS (APCI): calcd. for $C_8H_8NO_3S$: 198.0219, found 198.0215.



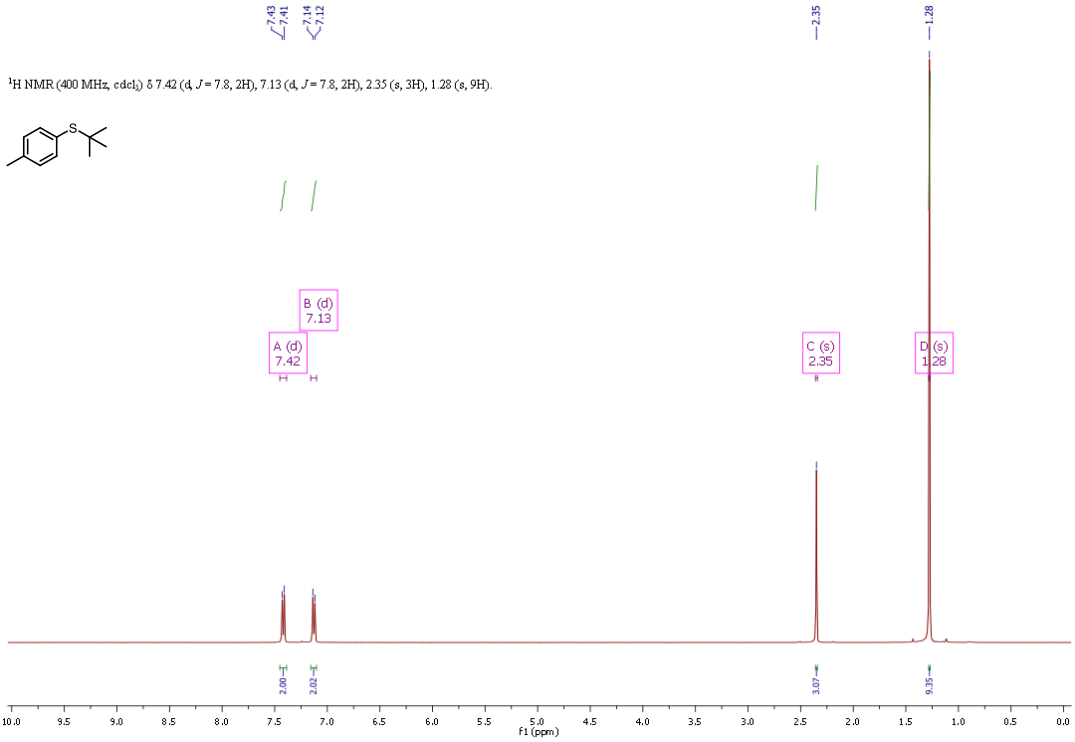
S-3-ethynylphenyl ethanethioate (8b) TLC (SiO_2: heptanes/ethyl acetate, 4:1, R_f = 0.54) $TiCl_4$: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.51 (m, 2H), 7.42-7.35 (m, 2H), 3.11 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 193.2 (C), 137.8 (CH), 134.9 (CH), 133.0 (CH), 129.2 (CH), 128.4 (C), 123.4 (C), 82.6 (C), 78.6 (CH), 30.3 (CH_3). *m/z* (EI, %): 176 (M+, 14), 134 (100); HRMS (APPI): calcd. for $C_{10}H_9OS$ ([M + H]+): 177.0369, found 177.0364.

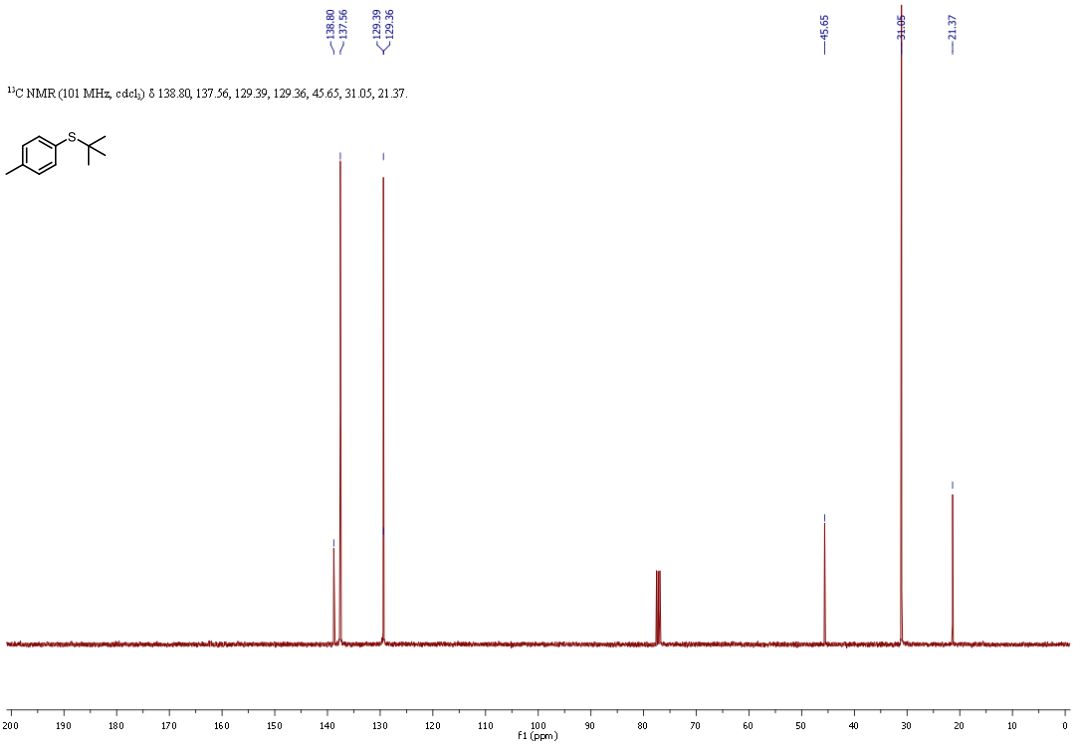


S-(11-(4-(4-(2-(5-chloro-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)phenoxy)undecyl) ethanethioate (11b) $TiCl_4$: 87 %. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 8.6 Hz, 2H), 6.88-6.82 (m, 3H), 6.61 (s, 1H), 3.94 (t, *J* = 6.5 Hz, 2H), 2.85 (t, *J* = 7.3 Hz, 2H), 2.76 (dt, *J* = 25.3, 7.3 Hz, 4H), 2.31 (s, 3H), 2.09-1.99 (m, 2H), 1.97 (s, 3H), 1.87 (s, 3H), 1.82-1.71 (m, 2H), 1.60-1.50 (m, 2H), 1.43 (dd, *J* = 14.6, 6.9 Hz, 2H), 1.36-1.26 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.1 (C), 158.6 (C), 140.0 (C), 136.3 (C), 135.6 (C), 135.4 (C), 133.7 (C), 133.5 (C),133.4 (C), 127.3 (C), 127.0 (CH), 126.7 (CH), 125.1 (C), 122.8 (CH), 115.0 (CH), 68.3 (CH_2), 38.6 (CH_2) 38.5 (CH_2), 30.8 (CH_3), 29.7 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 29.0 (CH_3), 26.2 (CH_3), 23.1 (CH_2), 14.5 (CH_2), 14.4 (CH_2). HRMS (ESI): calcd. for $C_{34}H_{44}ClO_2S_3$: 615.2187, found 615.2159.

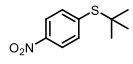
1-(4-(methylthio)phenyl)ethan-1-one (12b) TLC (SiO_2: heptane/ethyl acetate, 4:1, R_f = 0.41) $TiCl_4$ 94% ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 2.46 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.89 (C), 145.77 (C), 133.23 (C), 128.54 (CH), 124.71 (CH), 26.28 (CH_3), 14.54 (CH_3). *m/z* (EI) 166. HRMS (ESI): calcd. for $C_9H_{11}OS$: 167.0525, found 167.0521.

NMR Spectra *t*-butyl substrates

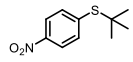




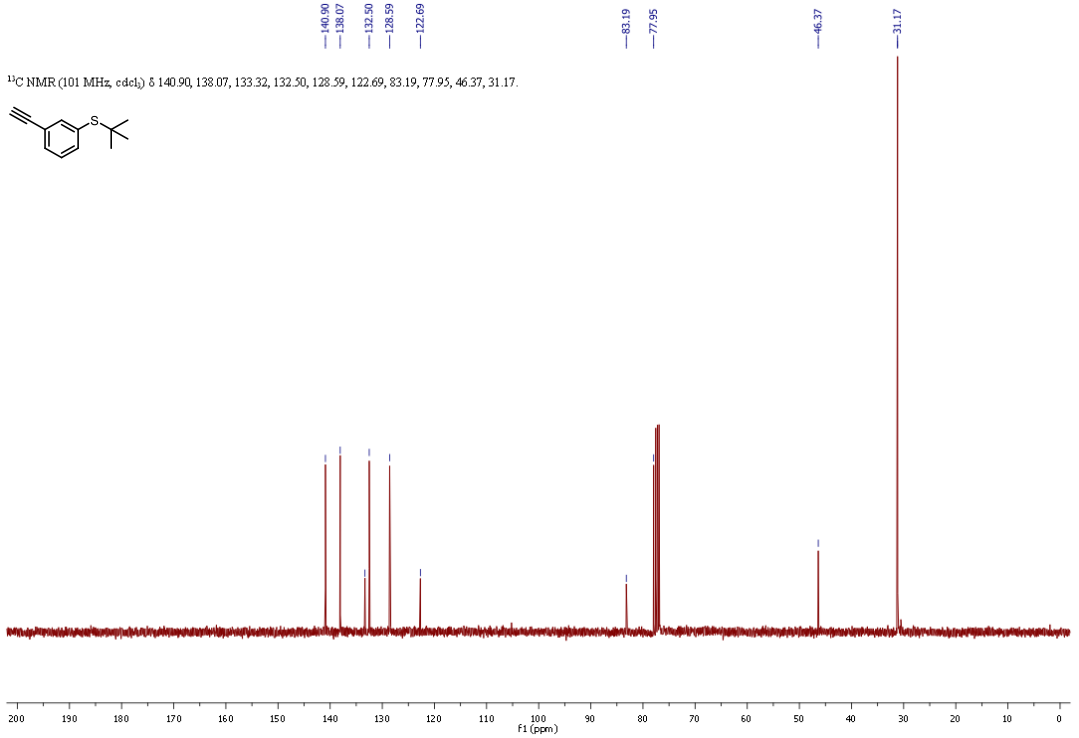
^{1}H NMR (400 MHz, cdcl$_3$) δ 8.13 (d, J = 8.7, 2H), 7.64 (d, J = 8.7, 2H), 1.32 (s, 9H).



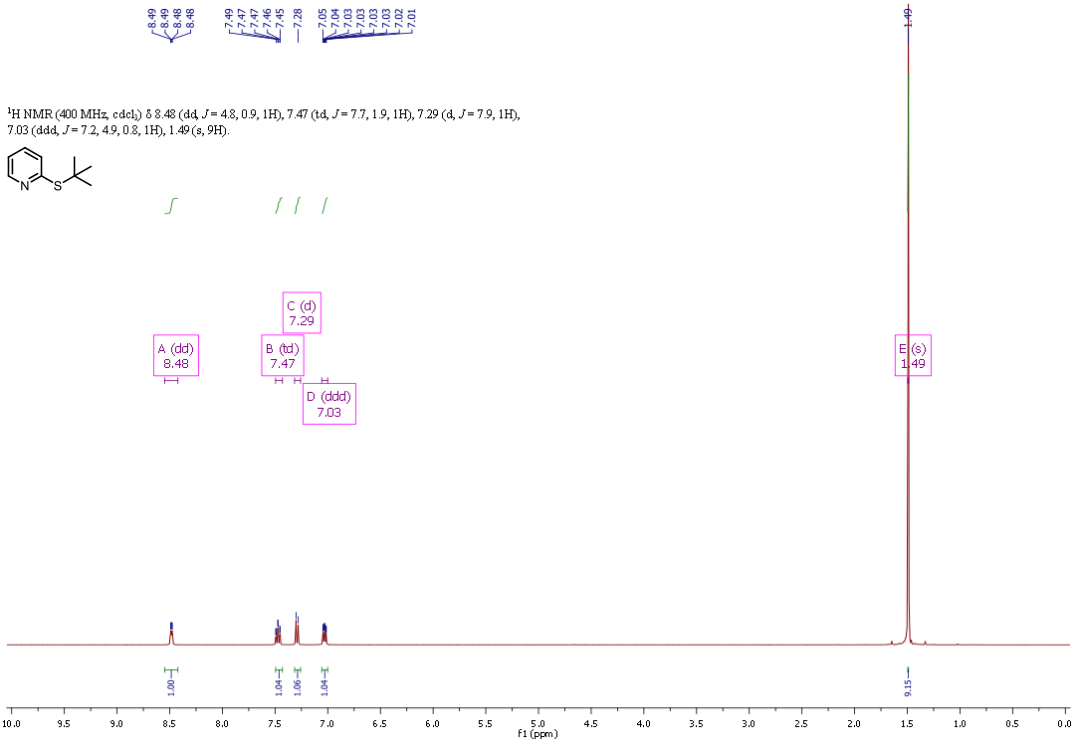
^{13}C NMR (101 MHz, cdcl$_3$) δ 147.90, 142.52, 137.03, 123.50, 47.73, 31.29.



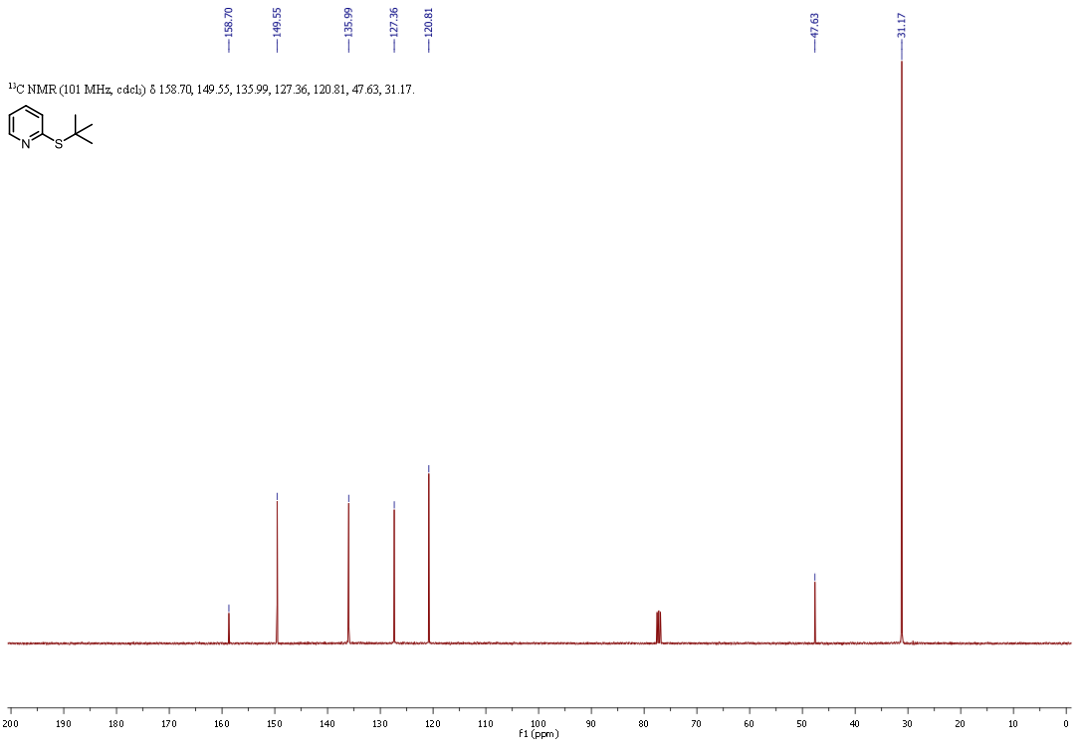
^{1}H NMR (400 MHz, cdcl$_3$) δ 7.67 (s, 1H), 7.50 (dd, *J* = 13.5, 7.7, 2H), 7.28 (t, *J* = 7.8, 1H), 3.10 (s, 1H), 1.29 (s, 9H).



^{13}C NMR (101 MHz, cdcl$_3$) δ 140.90, 138.07, 133.32, 132.50, 128.59, 122.69, 83.19, 77.95, 46.37, 31.17.

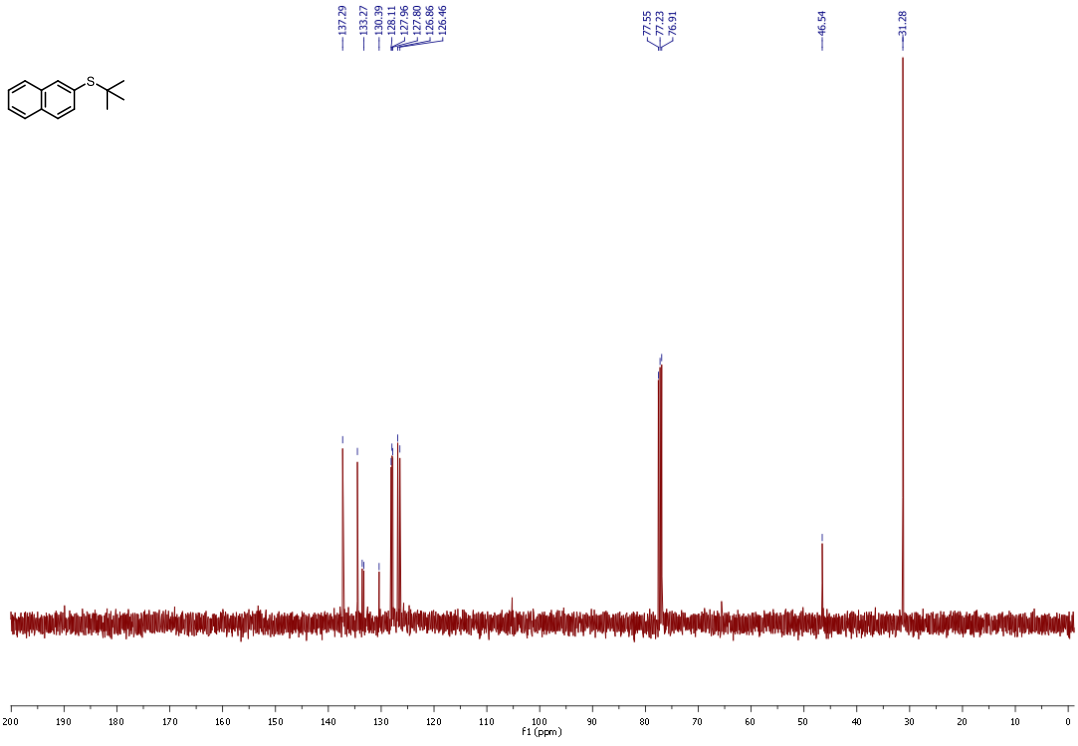


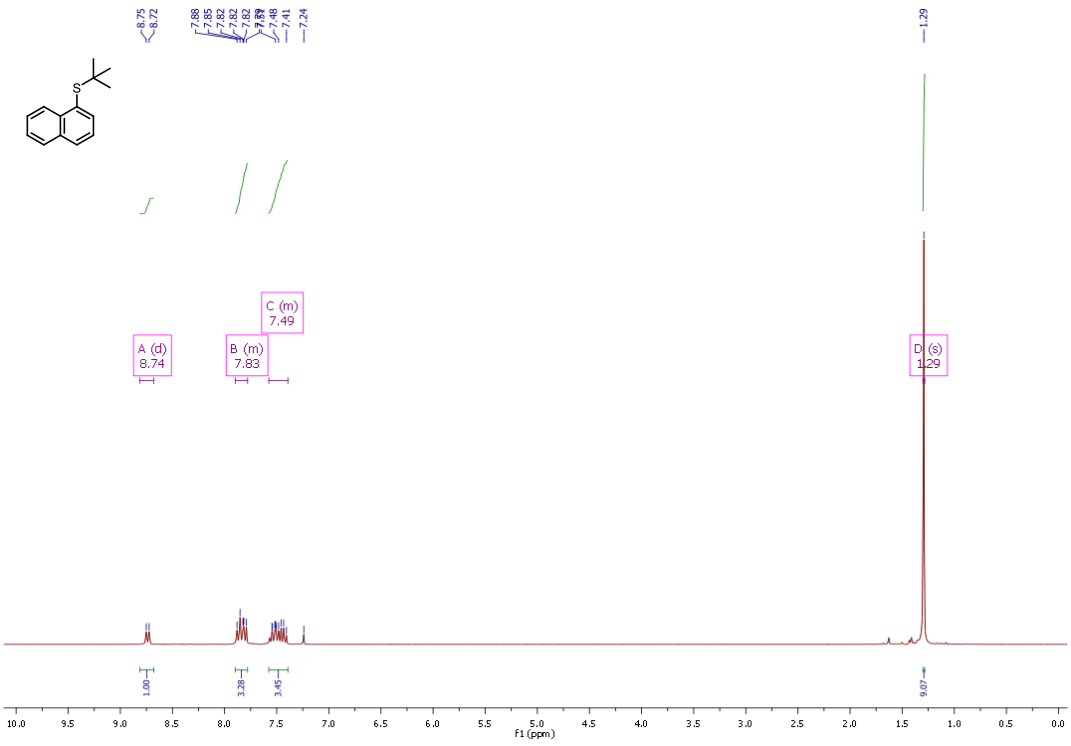
^{1}H NMR (400 MHz, cdcl$_3$) δ 8.48 (dd, *J* = 4.8, 0.9, 1H), 7.47 (td, *J* = 7.7, 1.9, 1H), 7.29 (d, *J* = 7.9, 1H), 7.03 (ddd, *J* = 7.2, 4.9, 0.8, 1H), 1.49 (s, 9H).

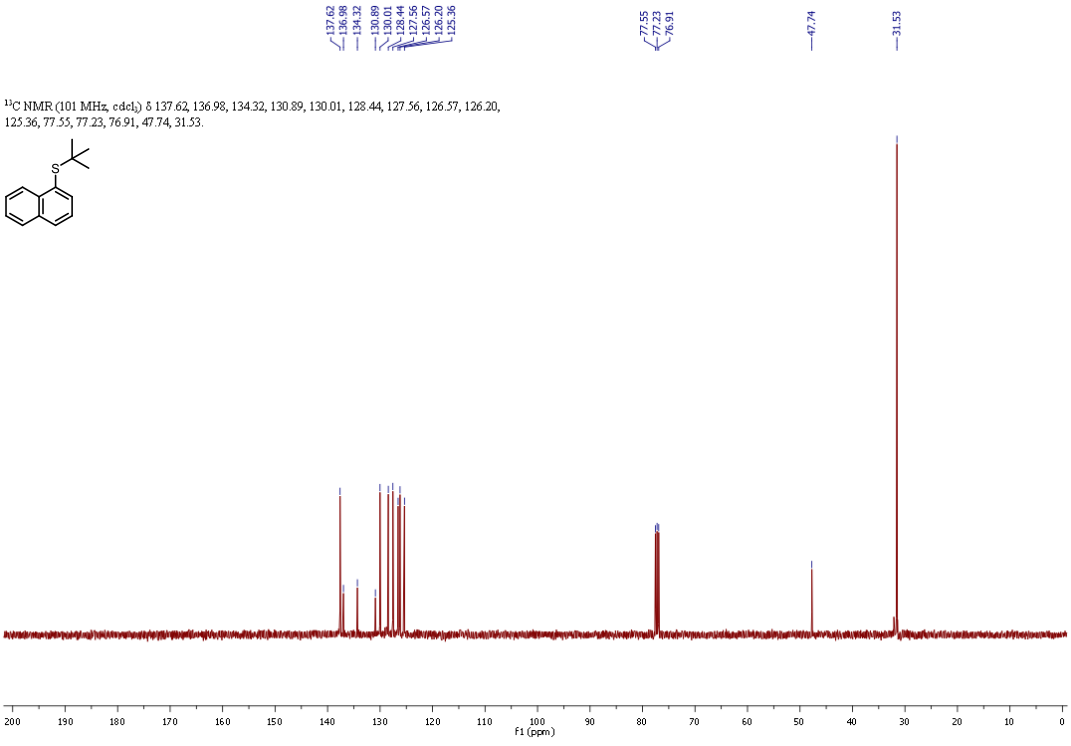


^{13}C NMR (101 MHz, cdcl$_3$) δ 158.70, 149.55, 135.99, 127.36, 120.81, 47.63, 31.17.


8.06
7.76
7.60
7.59
7.58
7.57
7.50
7.50
7.49
7.49
7.48
1.41
1.33
1.31
E (dd)
7.49
B (dd)
7.83
A (s)
8.06
D (dd)
7.58
C (d)
7.77
F (s)
1.33
1.00
2.10
1.20
1.03
2.06
9.54
f1 (ppm)

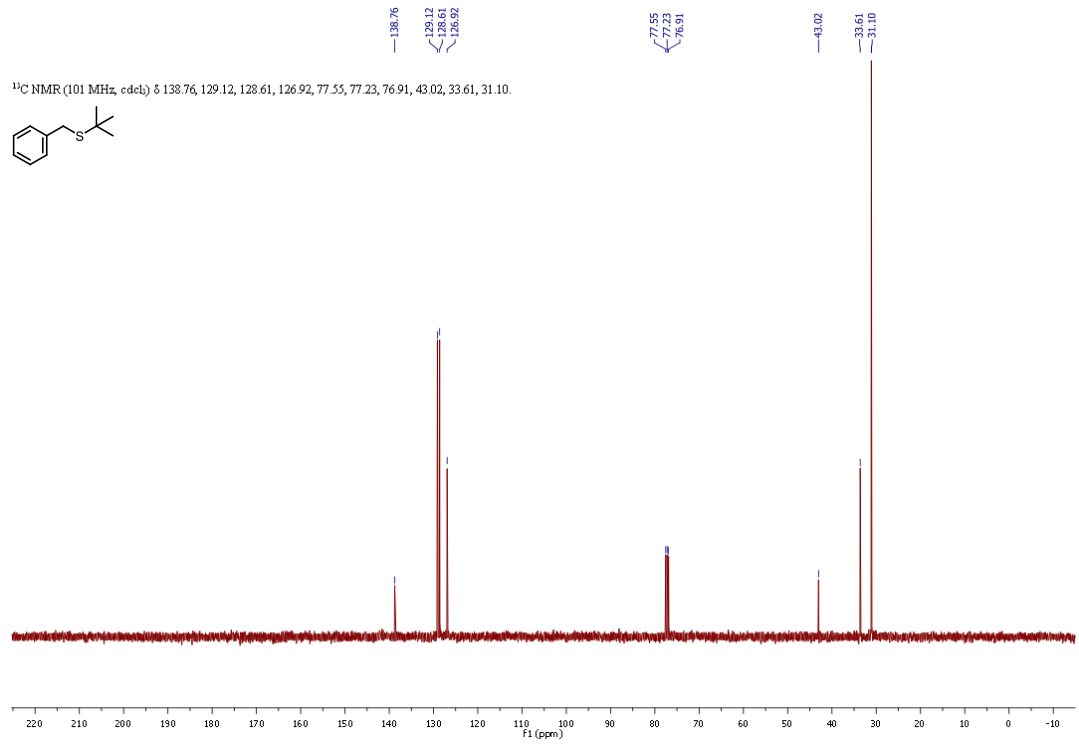

137.29
133.27
130.39
128.11
127.96
127.80
126.86
126.46
77.55
77.23
76.91
46.54
31.28
f1 (ppm)

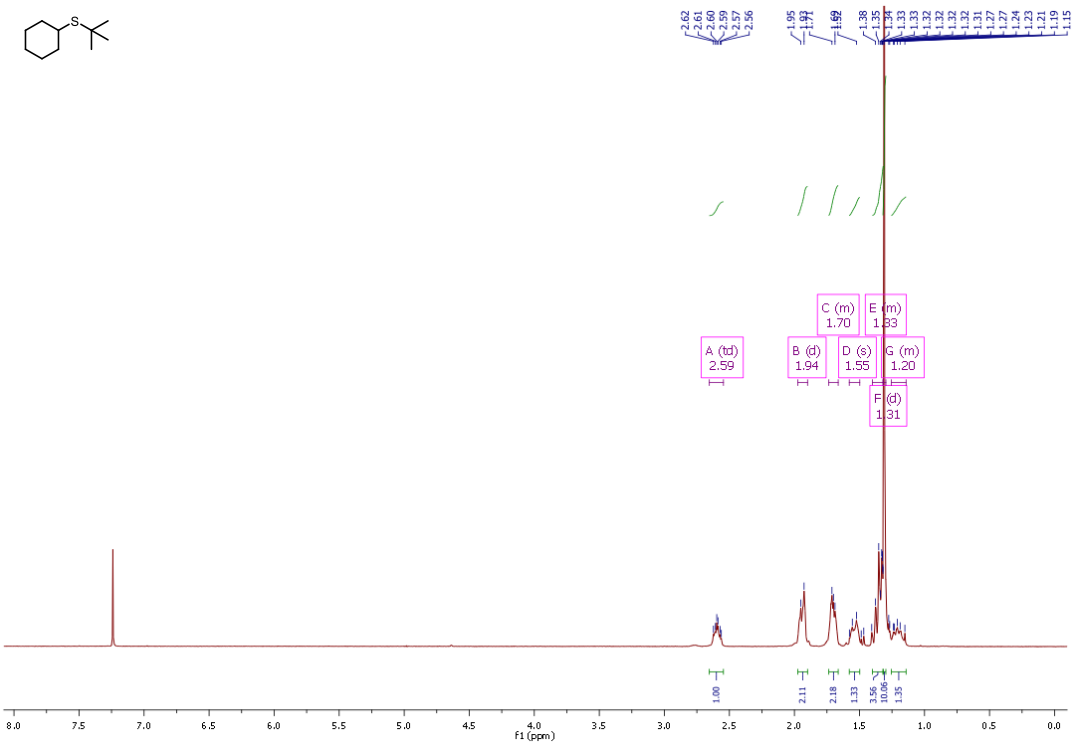


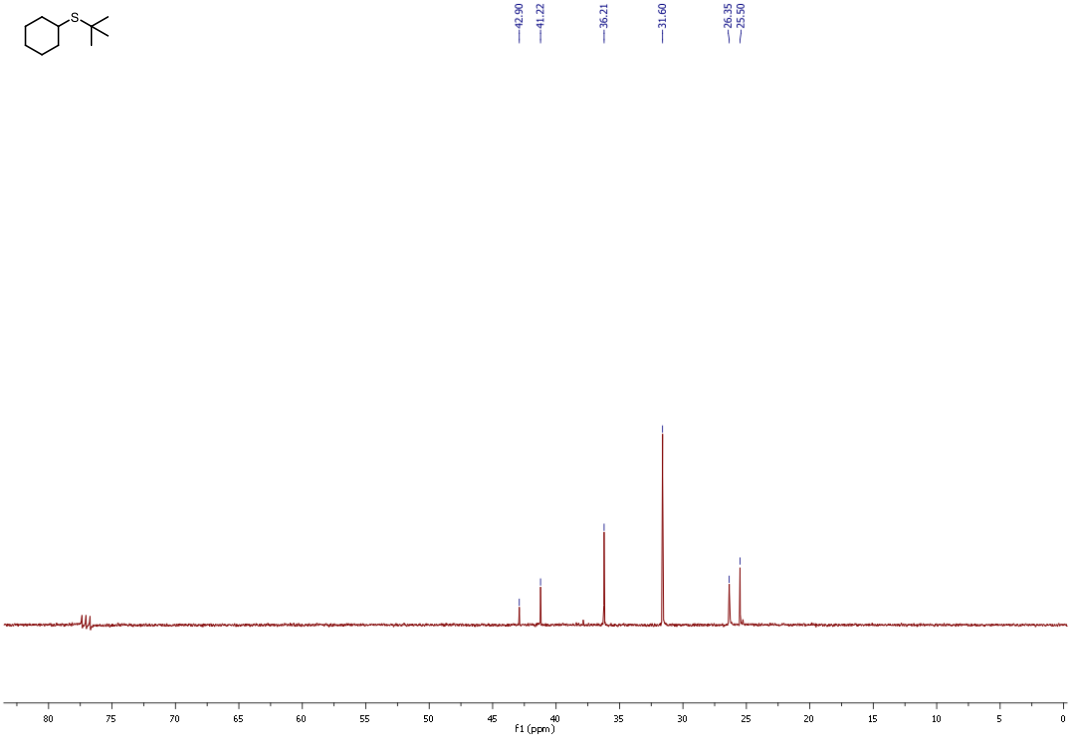


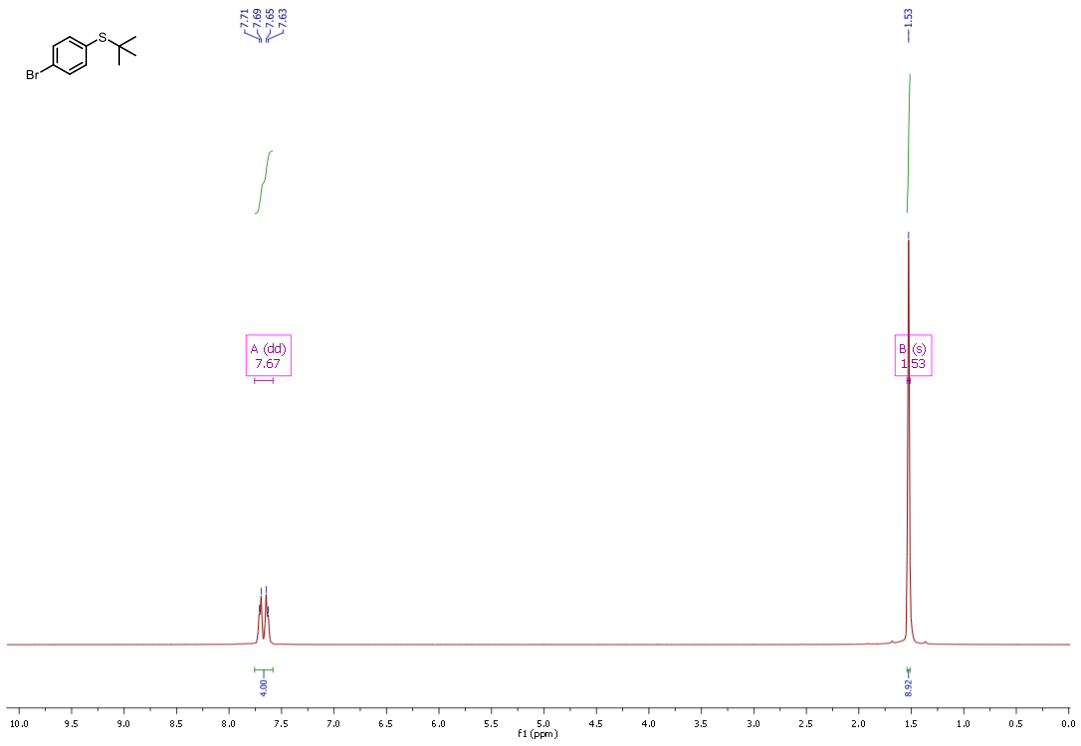
^{13}C NMR (101 MHz, cdcl$_3$) δ 137.62, 136.98, 134.32, 130.89, 130.01, 128.44, 127.56, 126.57, 126.20, 125.36, 77.55, 77.23, 76.91, 47.74, 31.53.

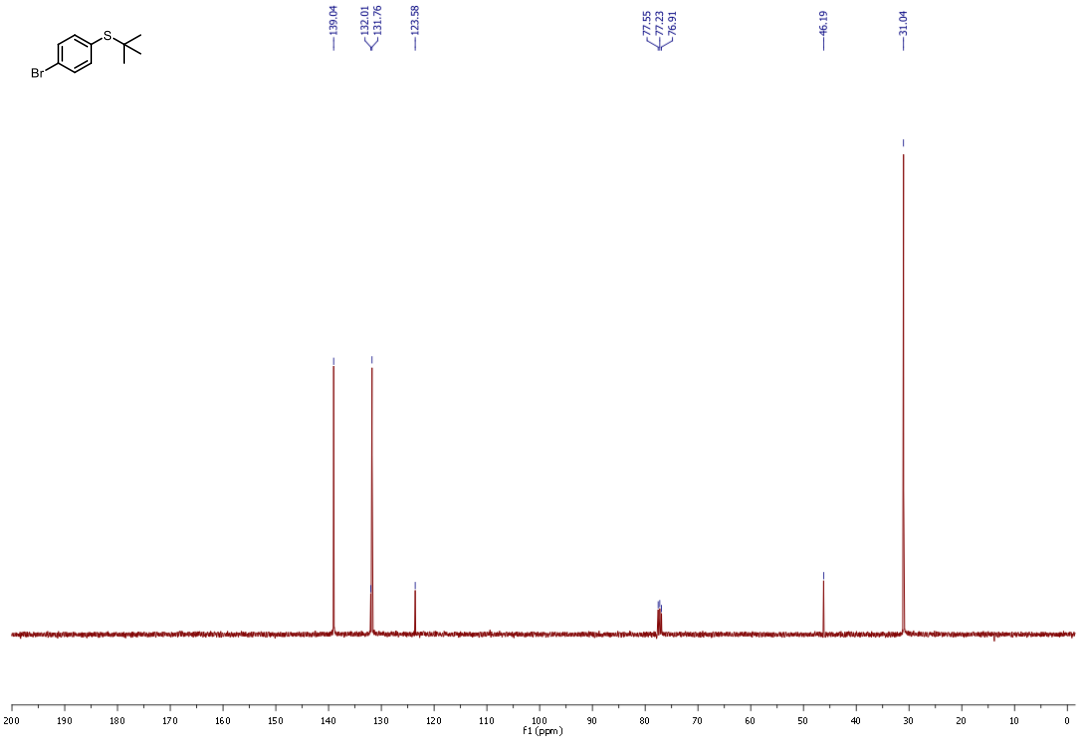
^{13}C NMR (101 MHz, cdcl$_3$) δ 138.76, 129.12, 128.61, 126.92, 77.55, 77.23, 76.91, 43.02, 33.61, 31.10.

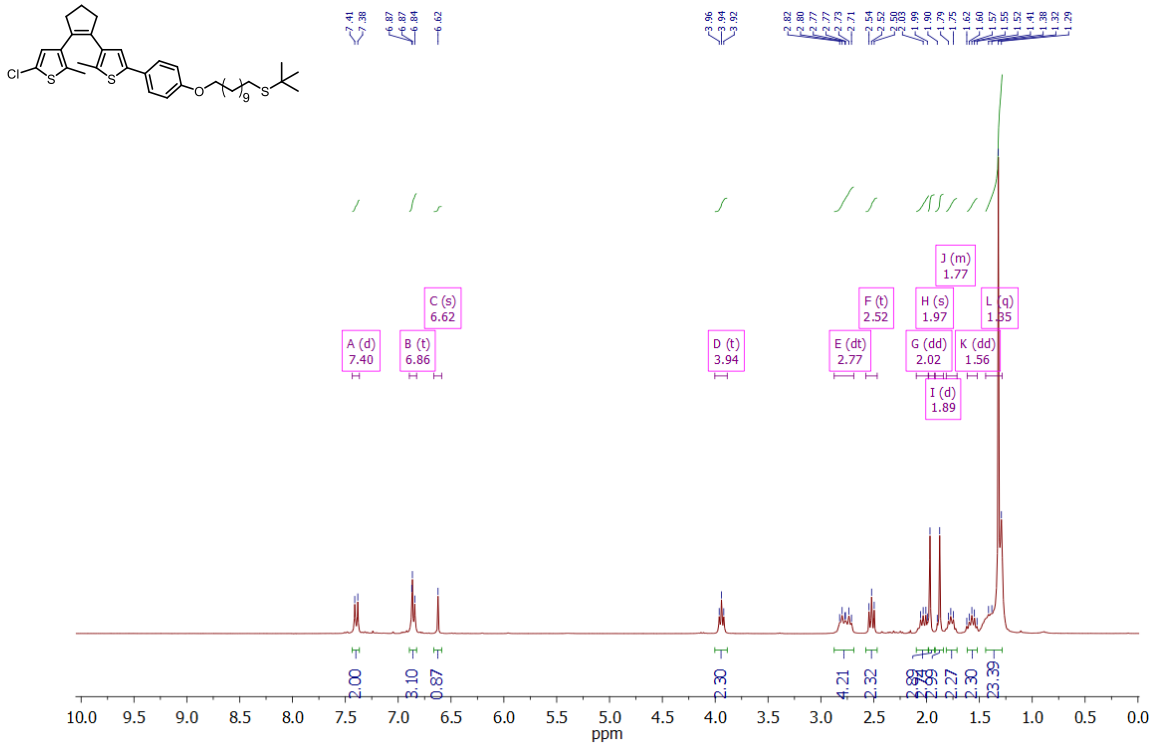


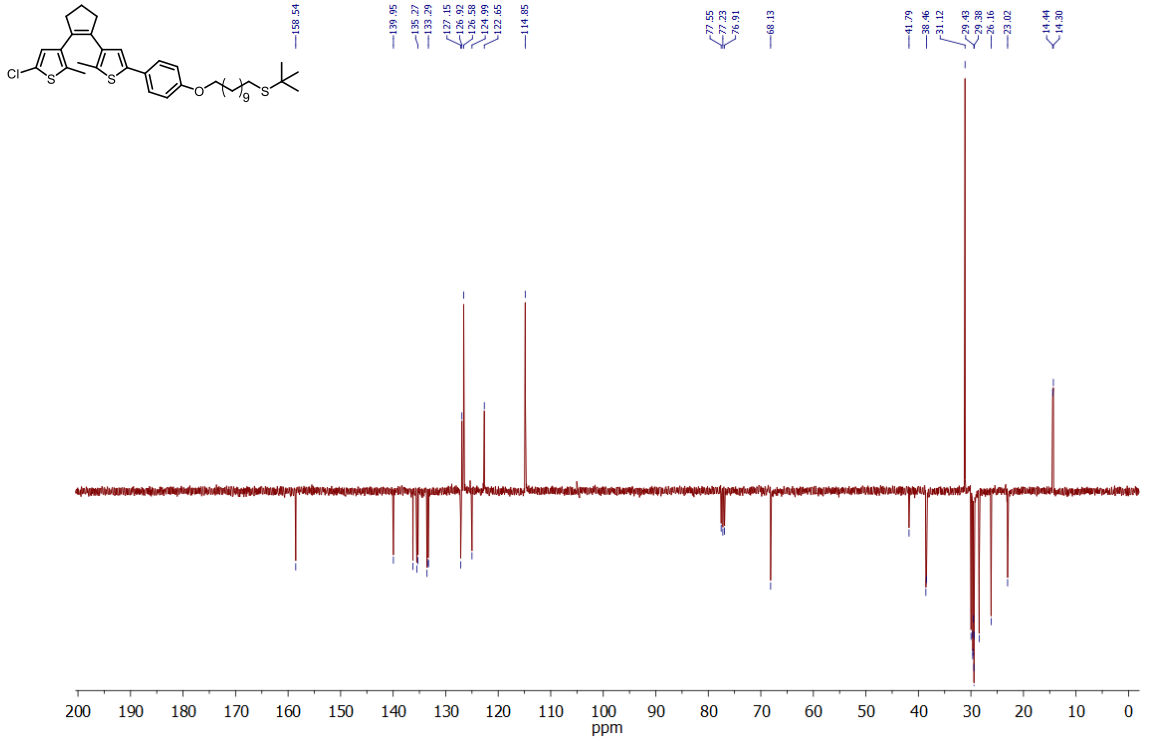

A (td)
2.59
B (d)
1.94
C (m)
1.70
D (s)
1.55
E (m)
1.33
F (d)
1.31
G (m)
1.20
f1 (ppm)


42.90
41.22
36.21
31.60
26.35
25.50
f1 (ppm)

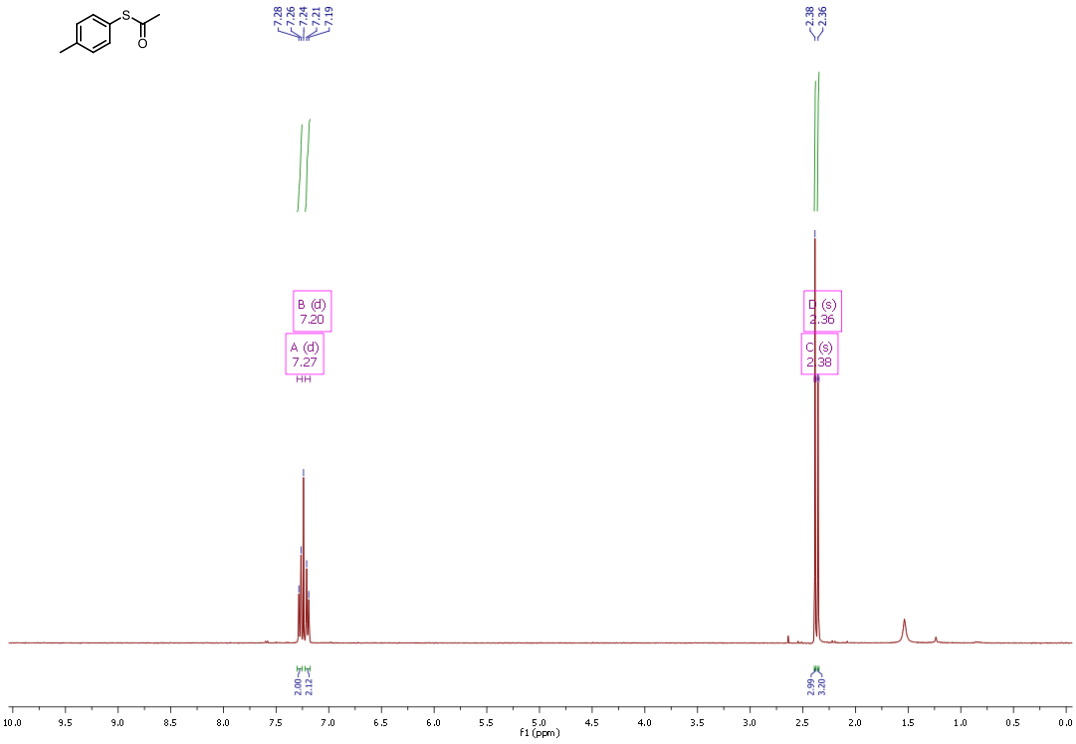

Br
S
7.71
7.69
7.65
7.63
1.53
A (dd)
7.67
B (s)
1.53
4.00
8.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

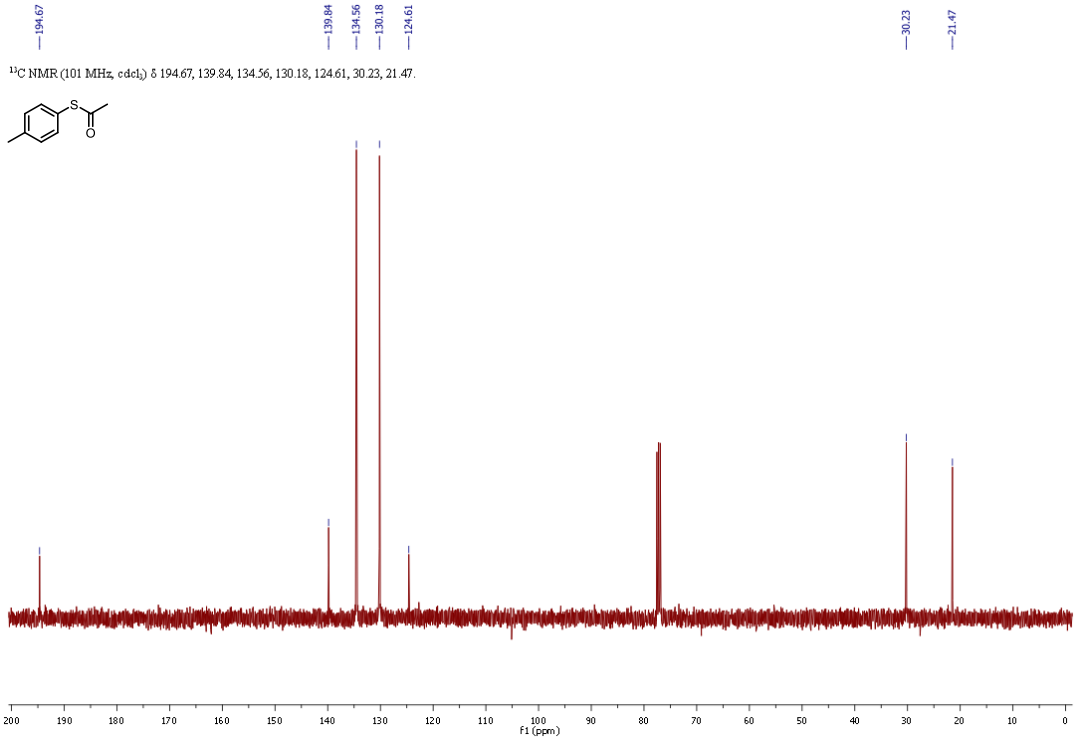

Br
S
139.04
132.01
131.76
123.58
77.55
77.23
76.91
46.19
31.04
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


A (d) 7.40
B (t) 6.86
C (s) 6.62
D (t) 3.94
E (dt) 2.77
F (t) 2.52
G (dd) 2.02
H (s) 1.97
I (d) 1.89
J (m) 1.77
K (dd) 1.56
L (q) 1.35
ppm

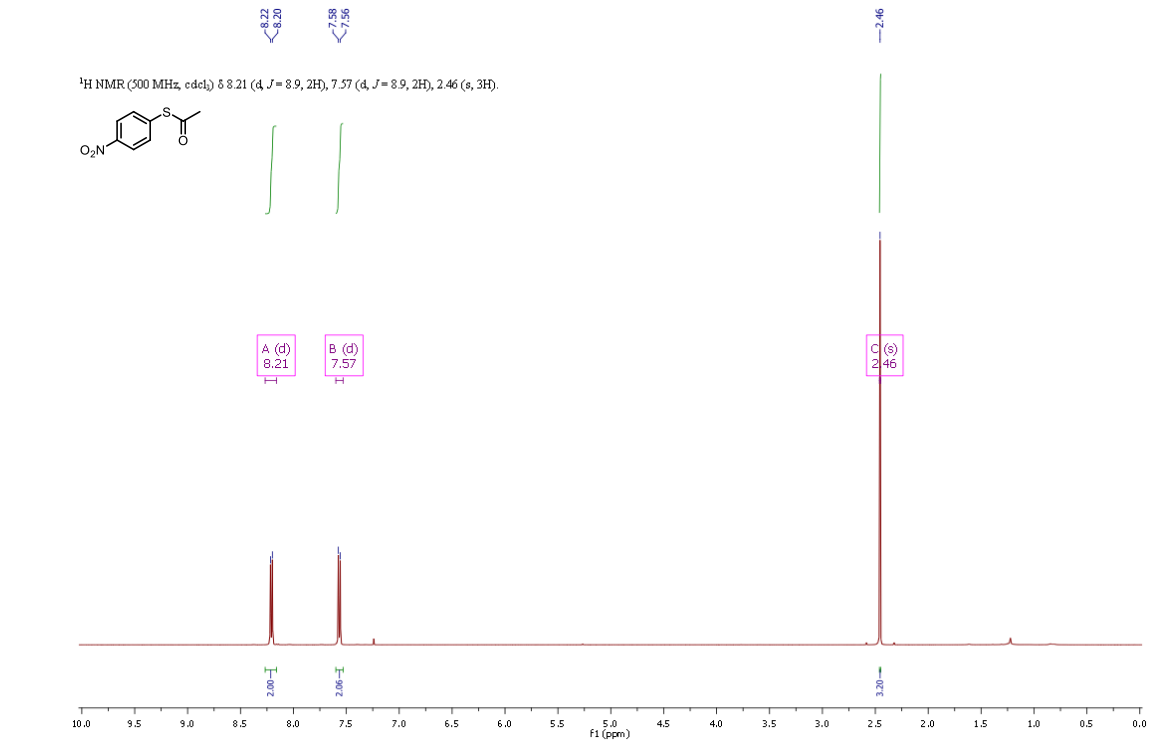

ppm

NMR Spectra of acetyl substrates

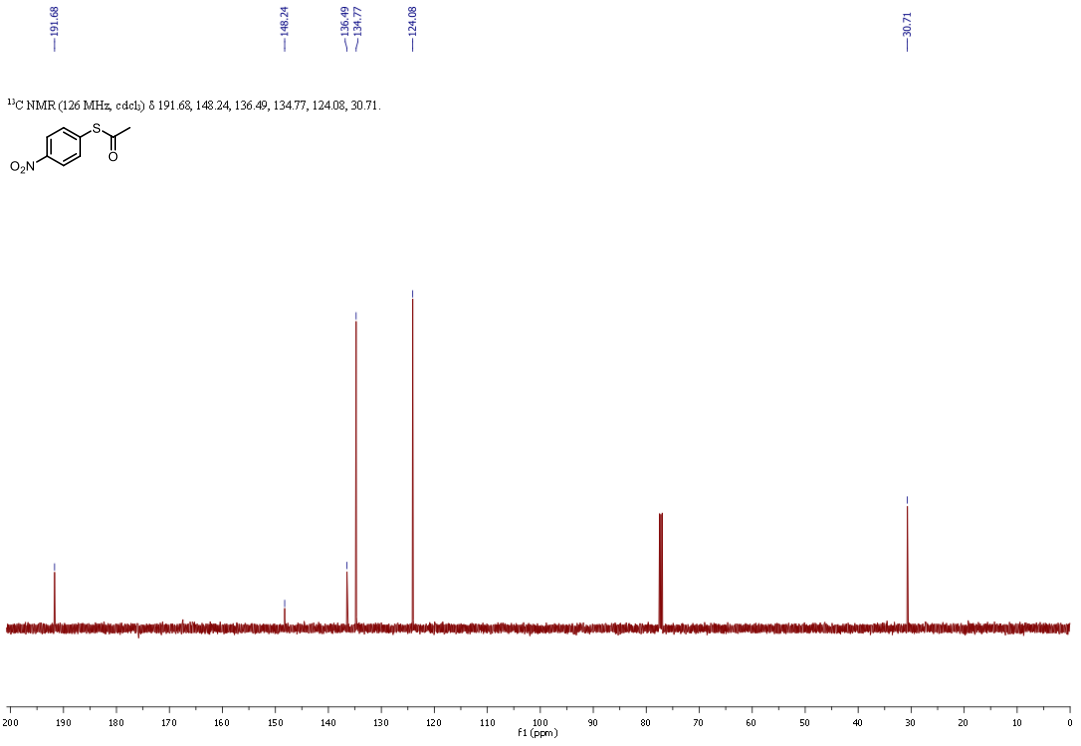




^{13}C NMR (101 MHz, cdcl$_3$) δ 194.67, 139.84, 134.56, 130.18, 124.61, 30.23, 21.47.

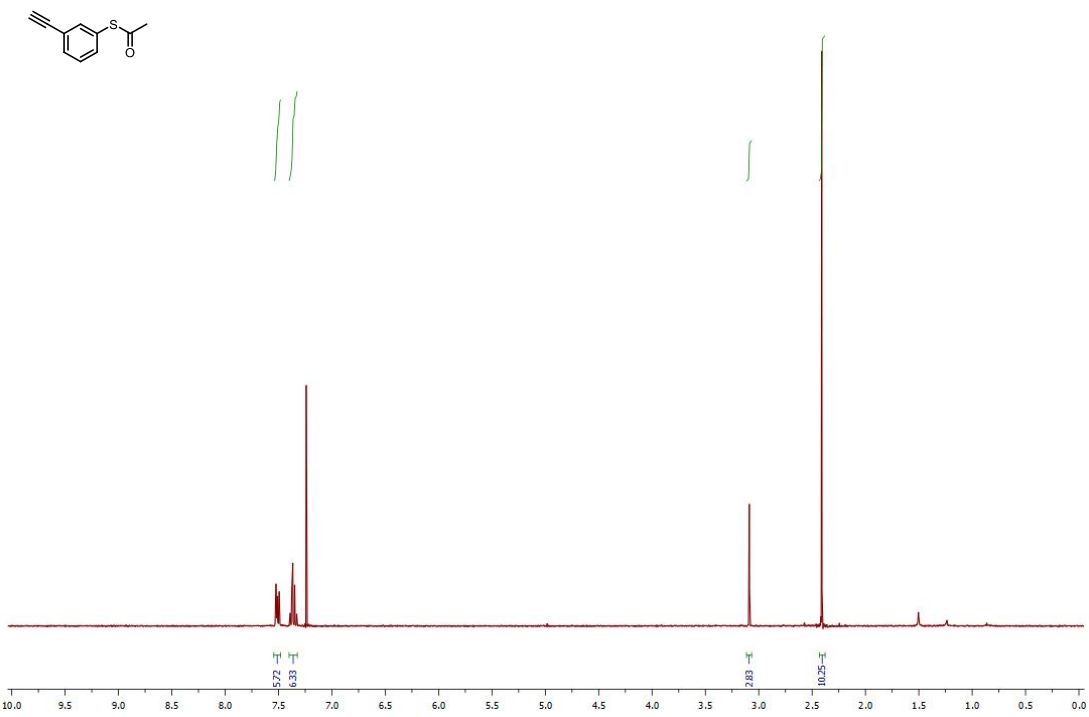


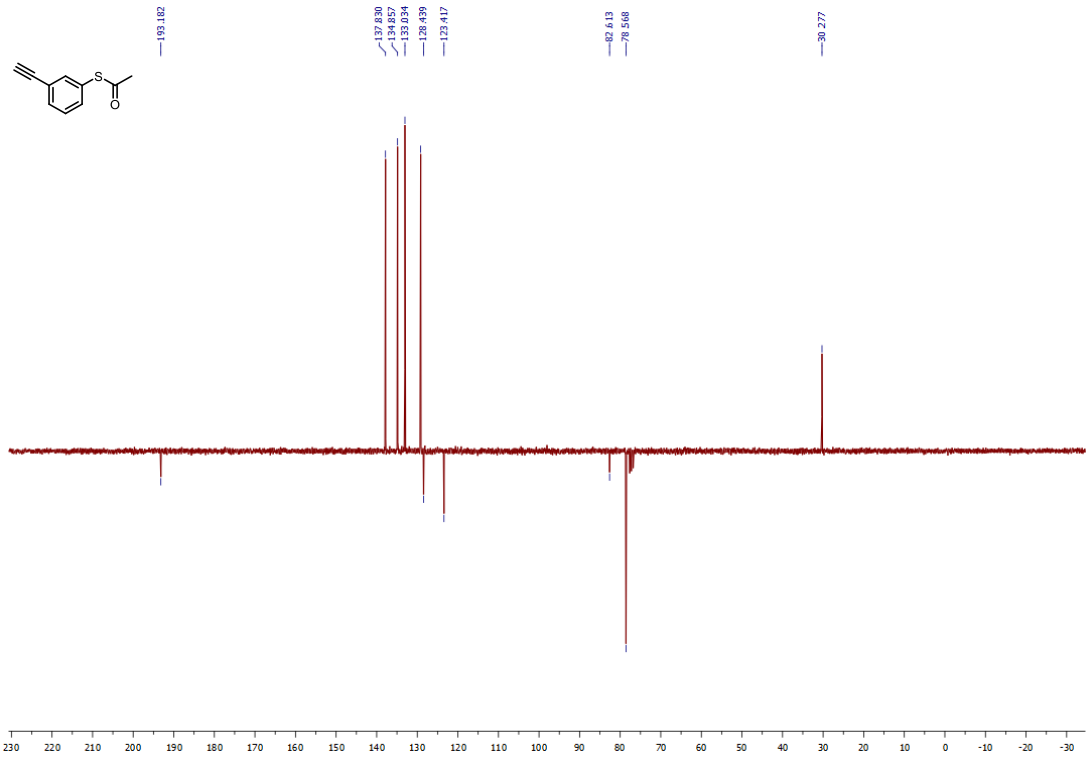
^{1}H NMR (500 MHz, cdcl$_3$) δ 8.21 (d, *J* = 8.9, 2H), 7.57 (d, *J* = 8.9, 2H), 2.46 (s, 3H).

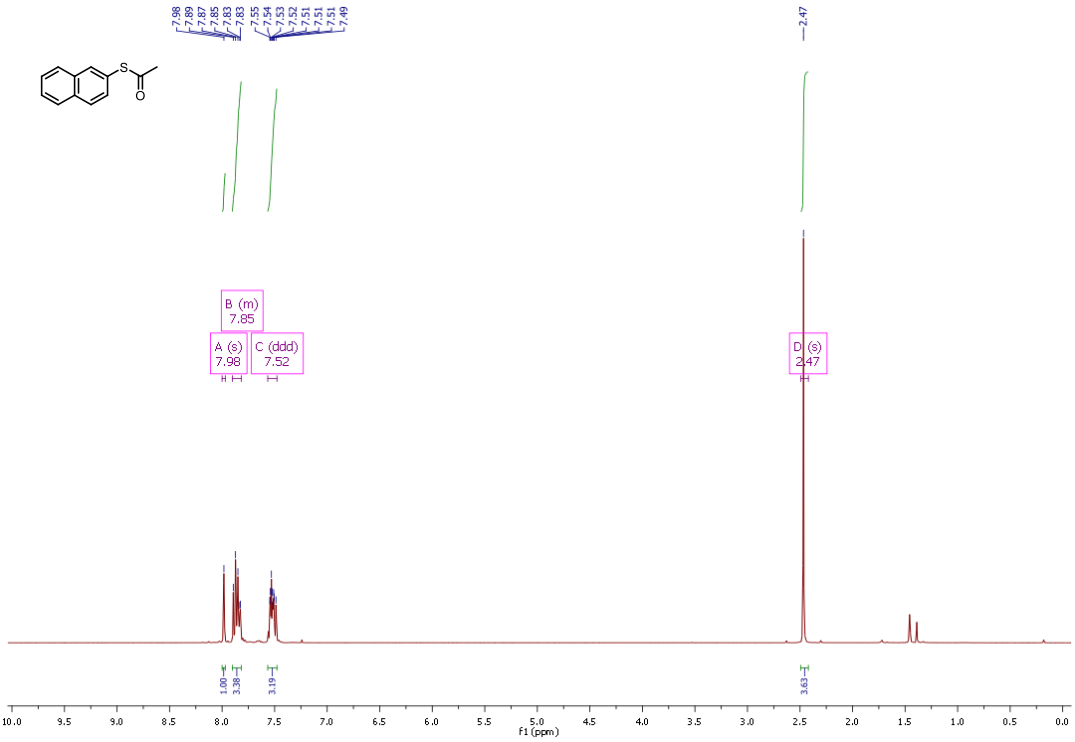


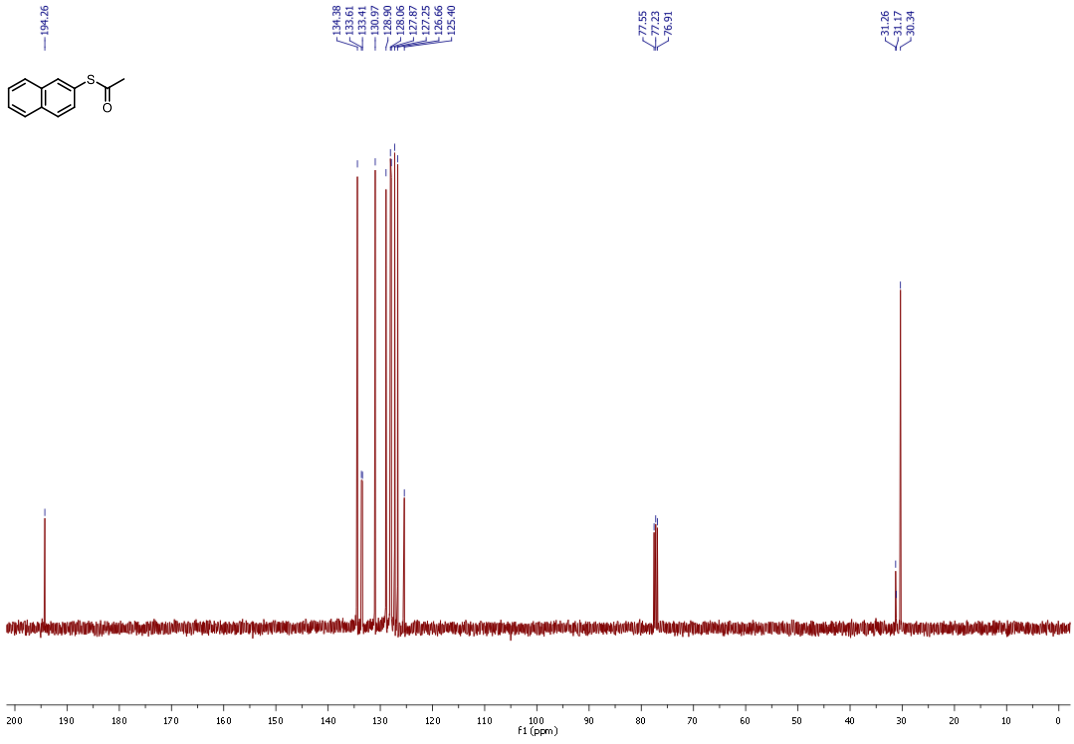
^{13}C NMR (126 MHz, cdcl$_3$) δ 191.68, 148.24, 136.49, 134.77, 124.08, 30.71.

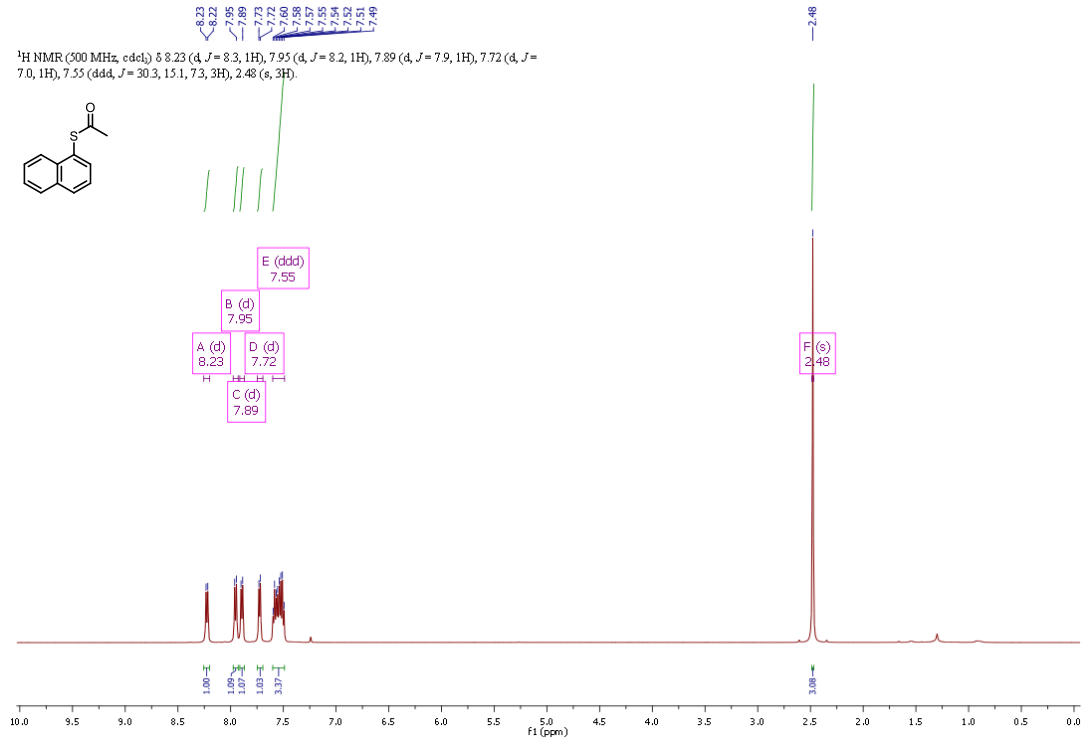
^{1}H NMR (400 MHz, cdcl$_3$) δ 7.55 – 7.51 (m, 2H), 7.42 – 7.35 (m, 2H), 3.11 (s, 1H), 2.43 (s, 3H).

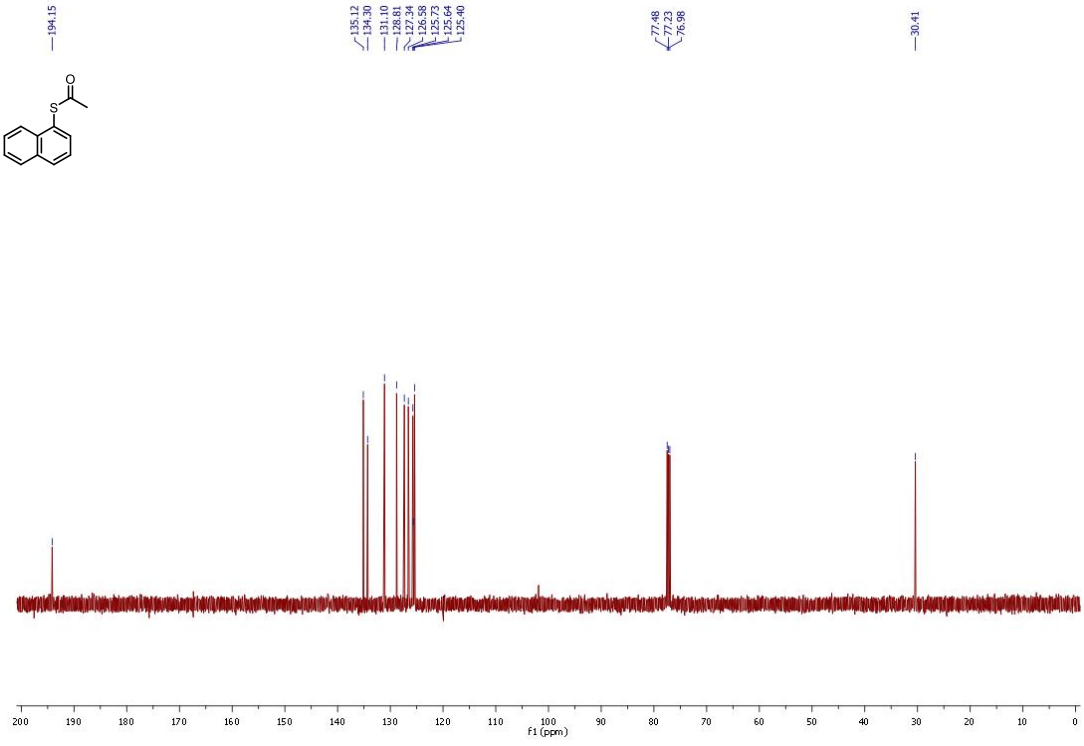


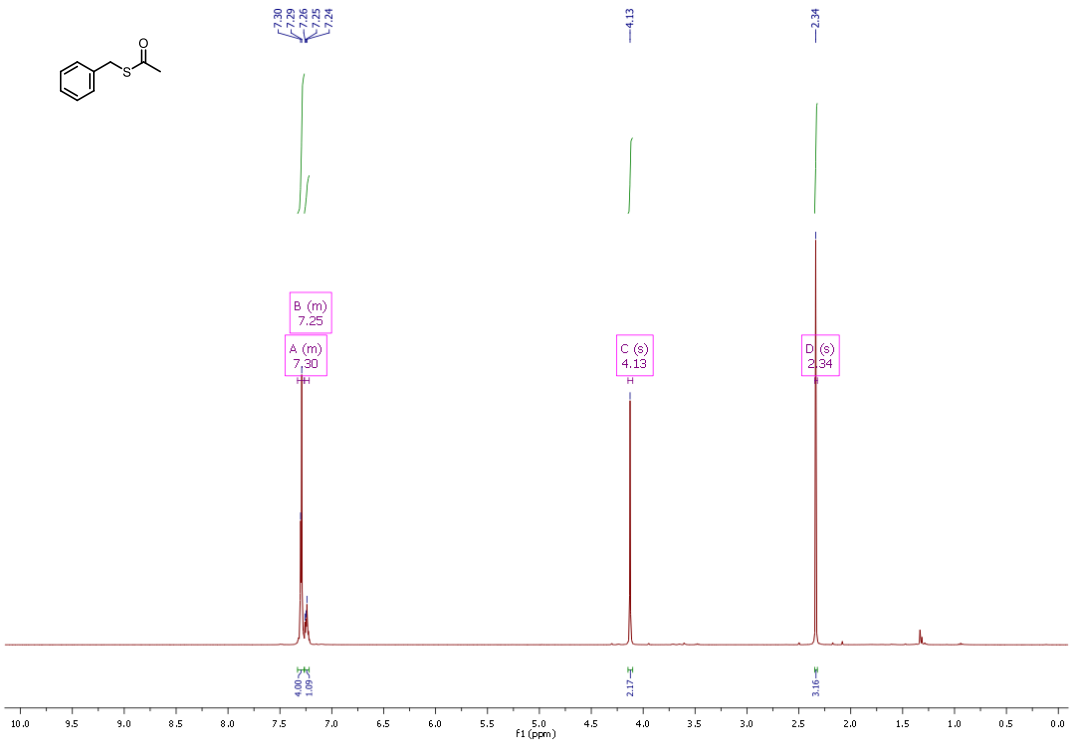


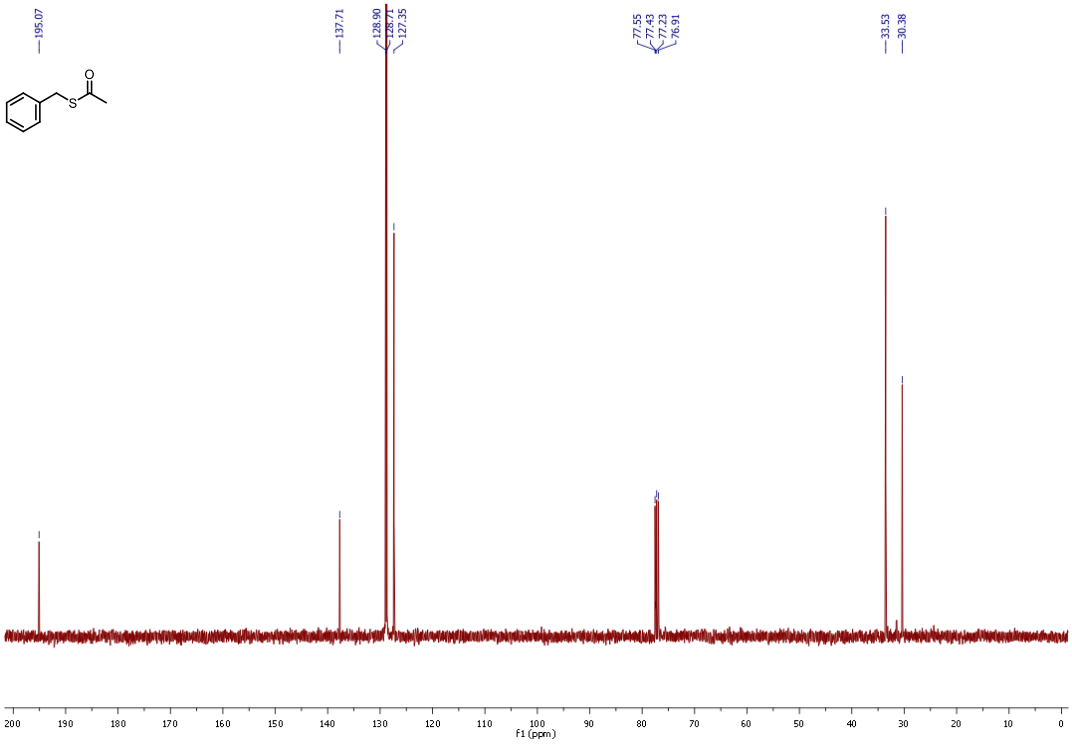

7.98
7.89
7.87
7.85
7.83
7.55
7.54
7.53
7.52
7.51
7.51
7.51
7.49
2.47
B (m)
7.85
A (s)
7.98
C (ddd)
7.52
D (s)
2.47
1.00
3.38
3.19
3.63
f1 (ppm)

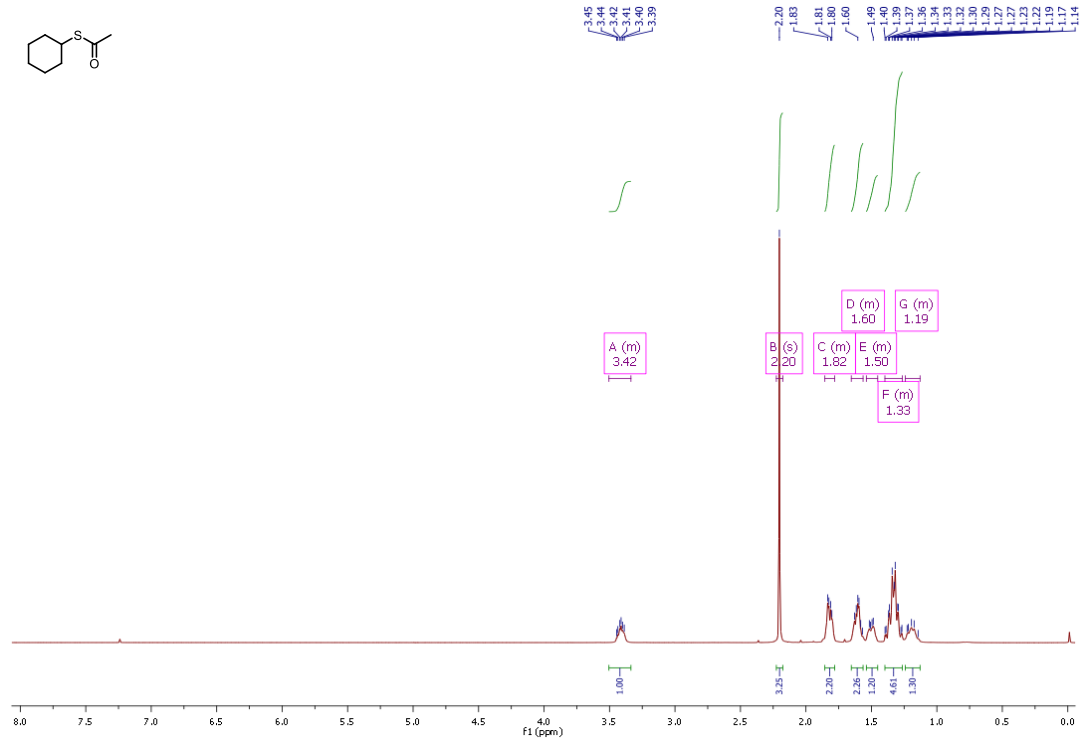

194.26
134.38
133.61
133.41
130.97
128.90
128.06
127.87
127.25
126.66
125.40
77.55
77.23
76.91
31.26
31.17
30.34
f1 (ppm)

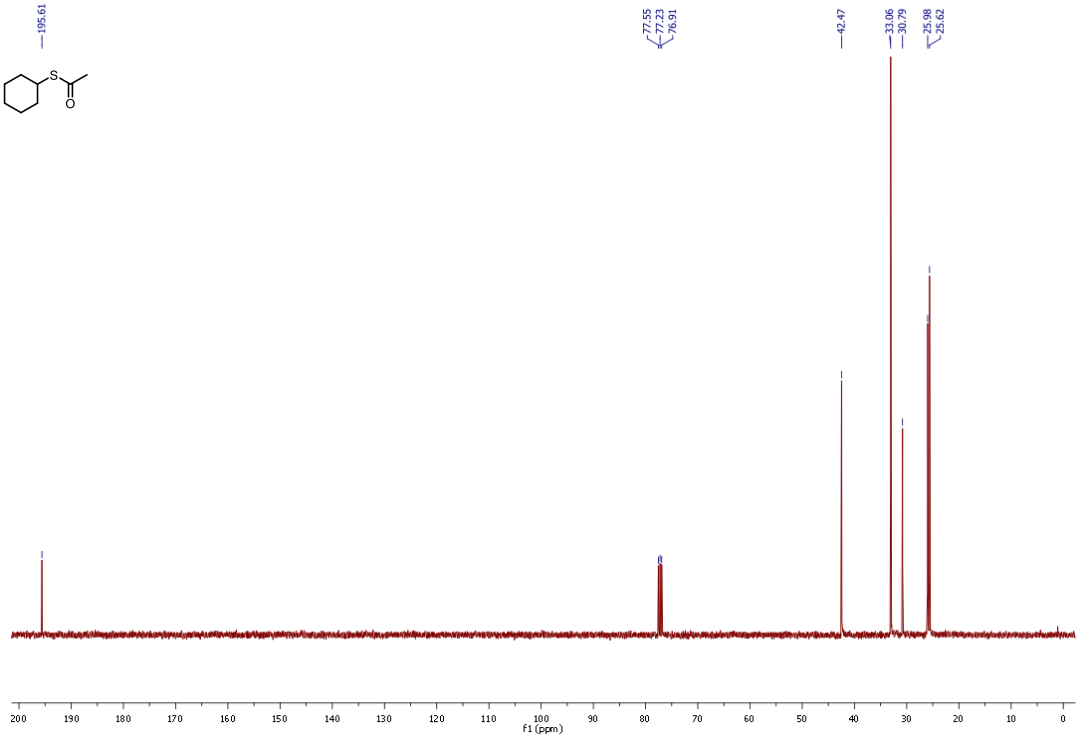

8.23
8.22
7.95
7.89
7.73
7.72
7.60
7.58
7.57
7.55
7.54
7.52
7.51
7.49
2.48
^{1}H NMR (500 MHz, cdcl$_3$) δ 8.23 (d, J = 8.3, 1H), 7.95 (d, J = 8.2, 1H), 7.89 (d, J = 7.9, 1H), 7.72 (d, J = 7.0, 1H), 7.55 (ddd, J = 30.3, 15.1, 7.3, 3H), 2.48 (s, 3H).
O
S
E (ddd) 7.55
B (d) 7.95
A (d) 8.23
D (d) 7.72
C (d) 7.89
F (s) 2.48
1.00
1.09
1.07
1.03
3.37
3.08
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)

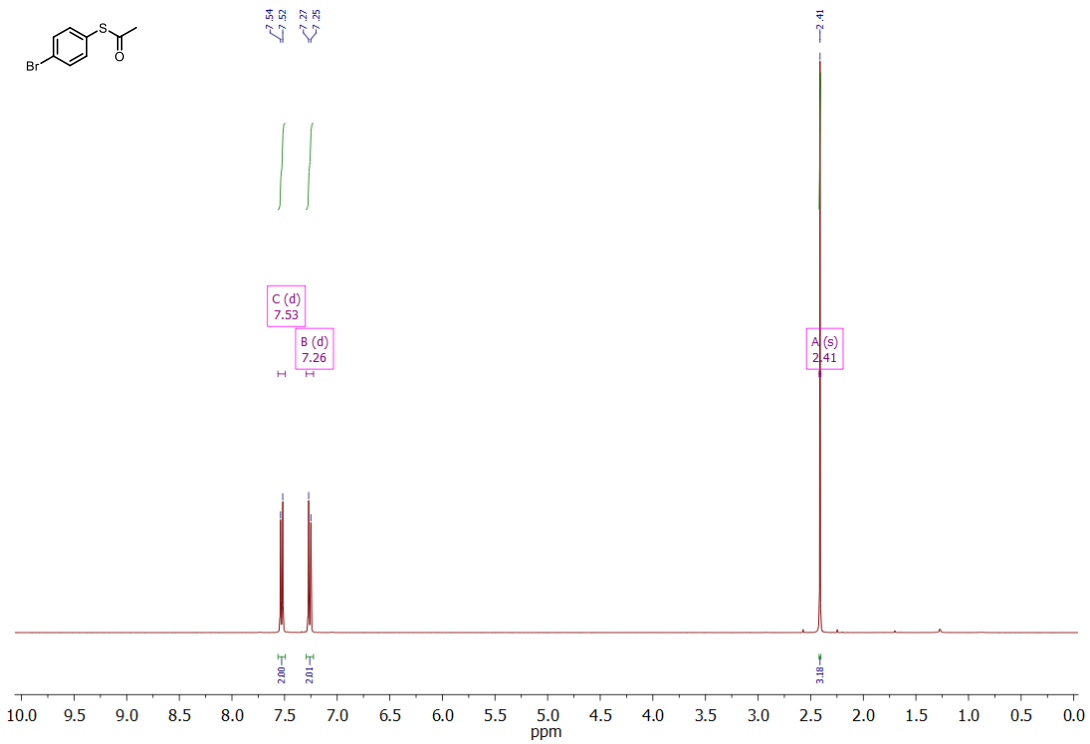

194.15
135.12
134.30
131.10
128.81
127.34
126.58
125.73
125.64
125.40
77.48
77.23
76.98
30.41
O
S
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

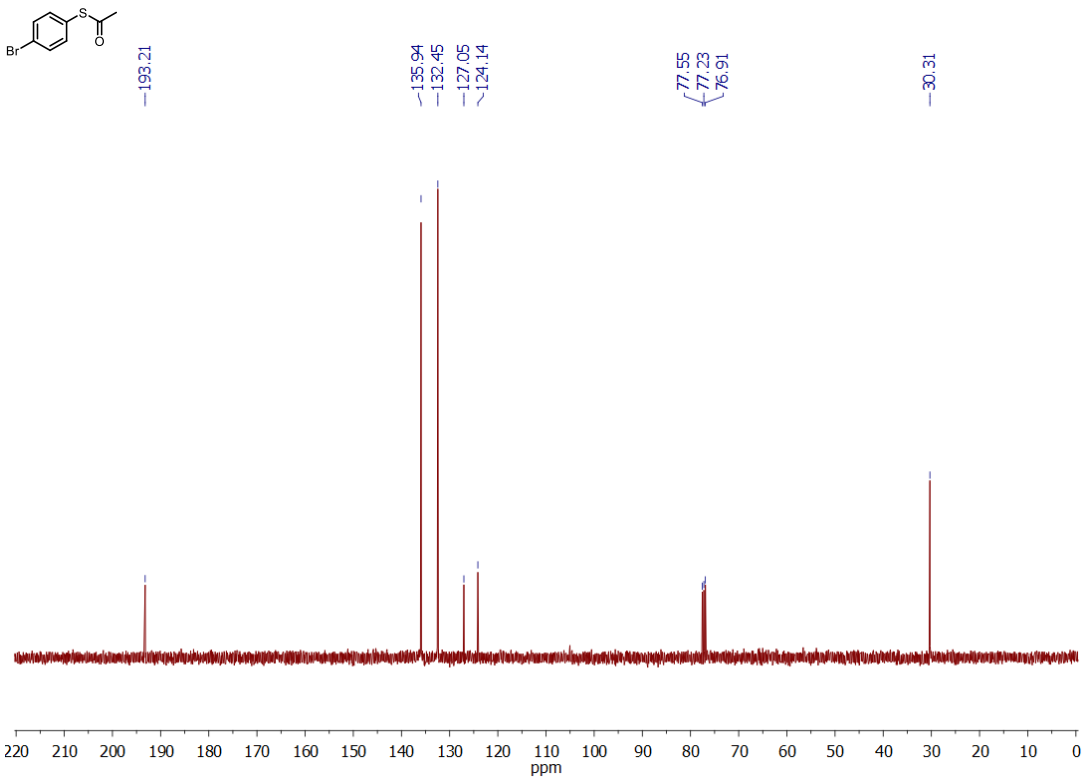

7.30
7.29
7.26
7.25
7.24
4.13
2.34
B (m)
7.25
A (m)
7.30
C (s)
4.13
D (s)
2.34
4.00
1.09
2.17
3.16
f1 (ppm)

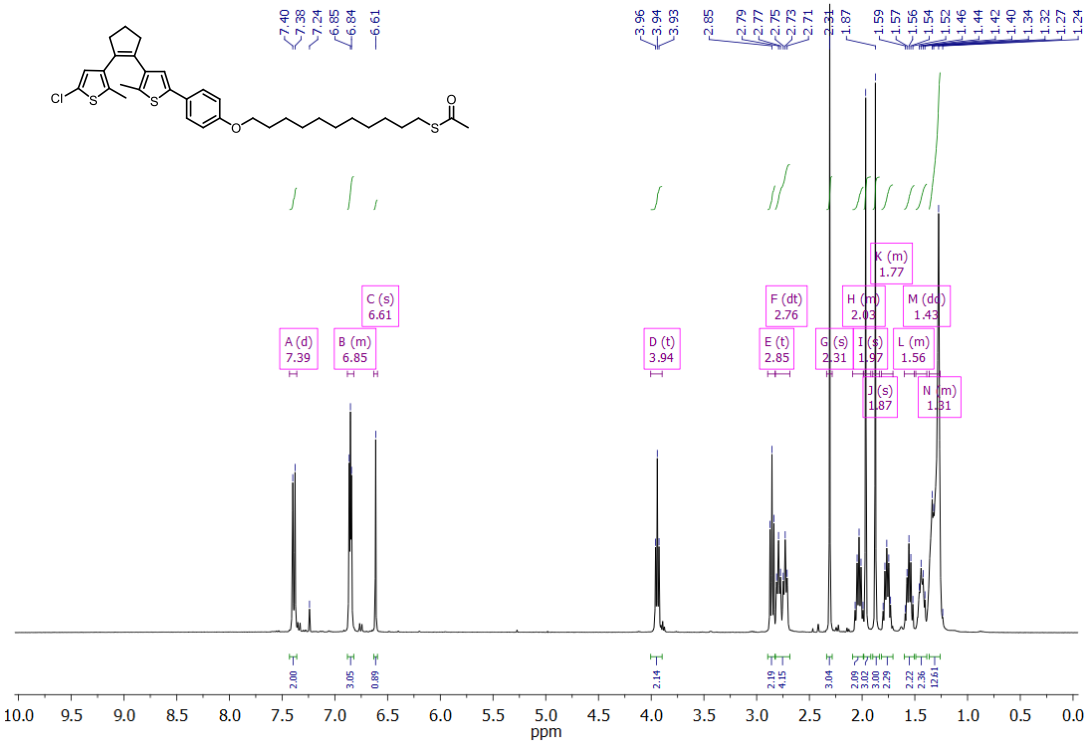

195.07
137.71
128.90
128.71
127.35
77.55
77.43
77.23
76.91
33.53
30.38
f1 (ppm)

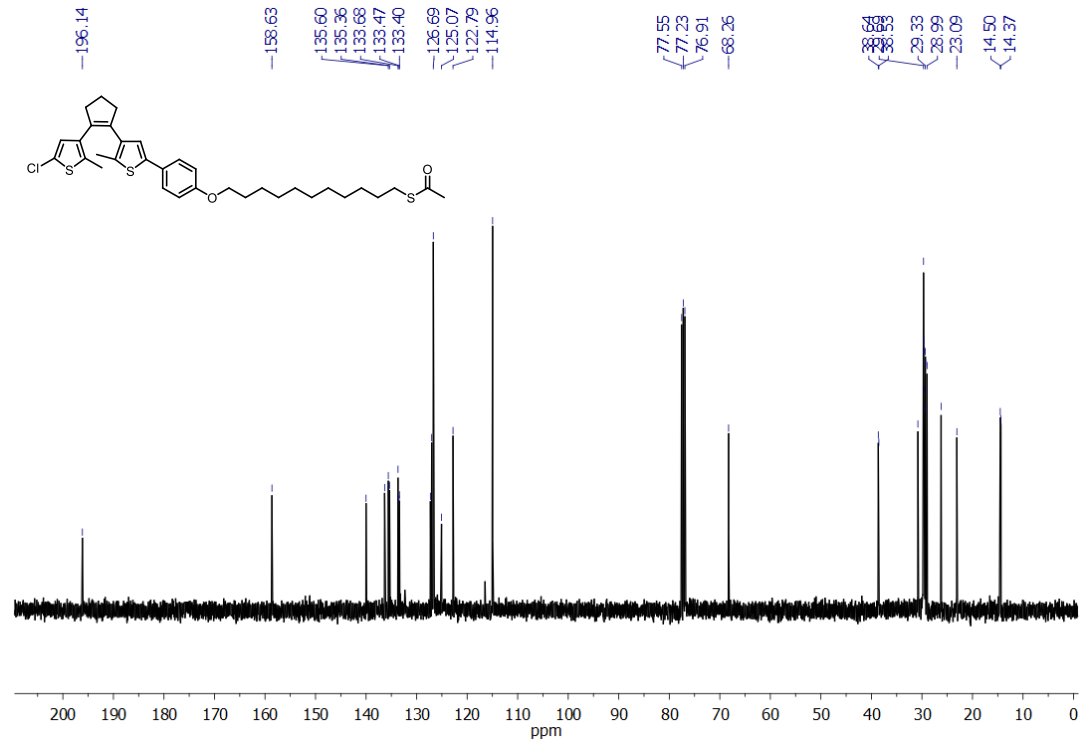

A (m) 3.42
B (s) 2.20
C (m) 1.82
D (m) 1.60
E (m) 1.50
F (m) 1.33
G (m) 1.19
f1 (ppm)

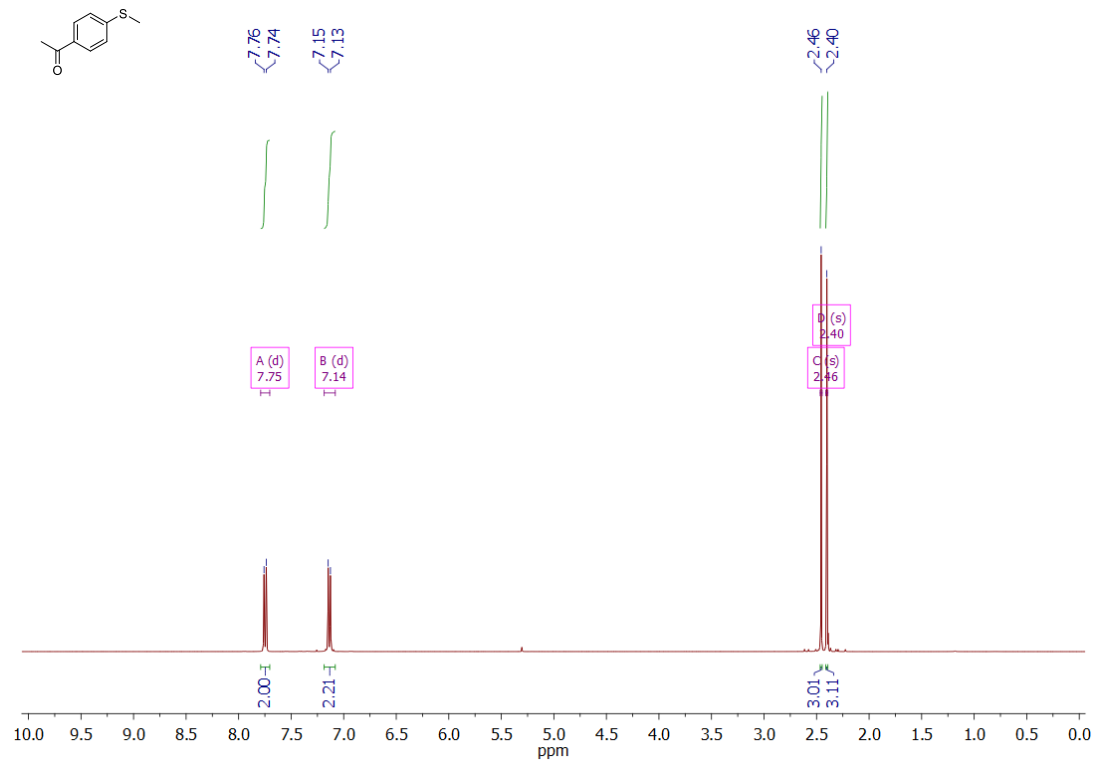

195.61
77.55
77.23
76.91
42.47
33.06
30.79
25.98
25.62
f1 (ppm)

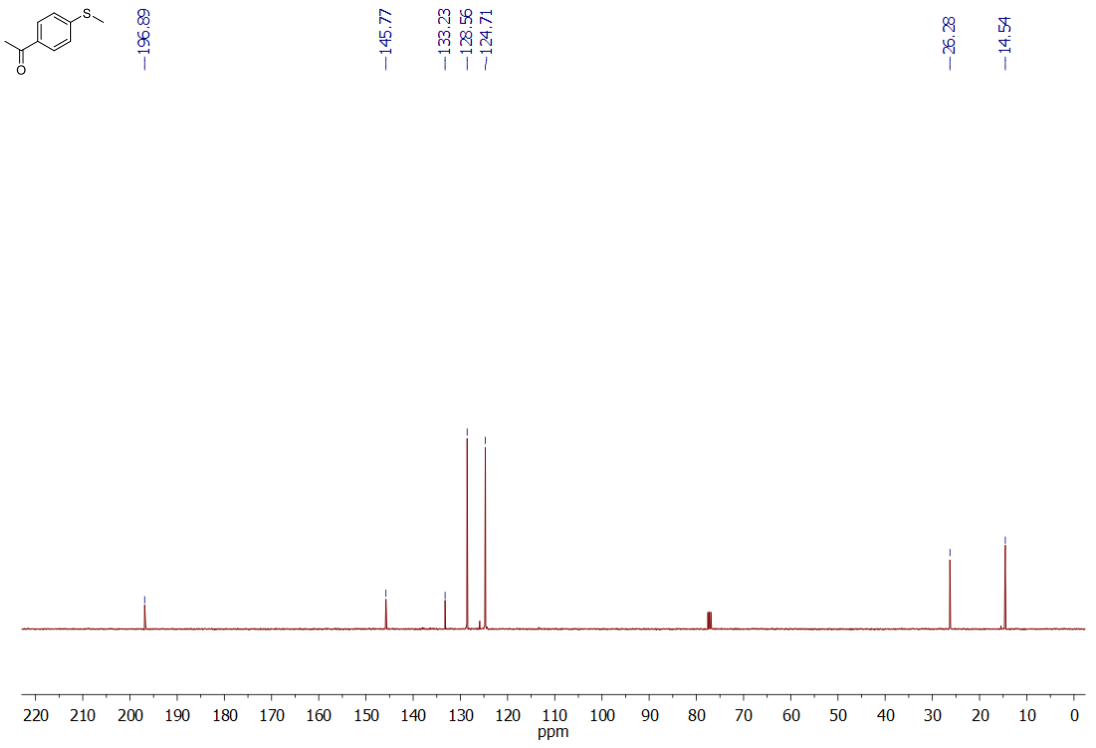

Br
S
O
7.54
7.52
7.27
7.26
2.41
C (d)
7.53
B (d)
7.26
A (s)
2.41
2.00
2.01
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


Br
S
O
193.21
135.94
132.45
127.05
124.14
77.55
77.23
76.91
30.31
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


A (d) 7.39
B (m) 6.85
C (s) 6.61
D (t) 3.94
E (t) 2.85
F (dt) 2.76
G (s) 2.31
H (m) 2.03
I (s) 1.97
J (s) 1.87
K (m) 1.77
L (m) 1.56
M (dd) 1.43
N (m) 1.31
ppm


196.14
158.63
135.60
135.36
133.68
133.47
133.40
126.69
125.07
122.79
114.96
77.55
77.23
76.91
68.26
29.33
28.99
23.09
14.50
14.37
ppm


7.76
7.74
7.15
7.13
2.46
2.40
A (d)
7.75
B (d)
7.14
D (s)
2.40
C (s)
2.46
2.00
2.21
3.01
3.11
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
ppm


196.89
145.77
133.23
128.56
124.71
26.28
14.54
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

^{1}H-NMR spectral analysis showing conversion of 4a to 4b

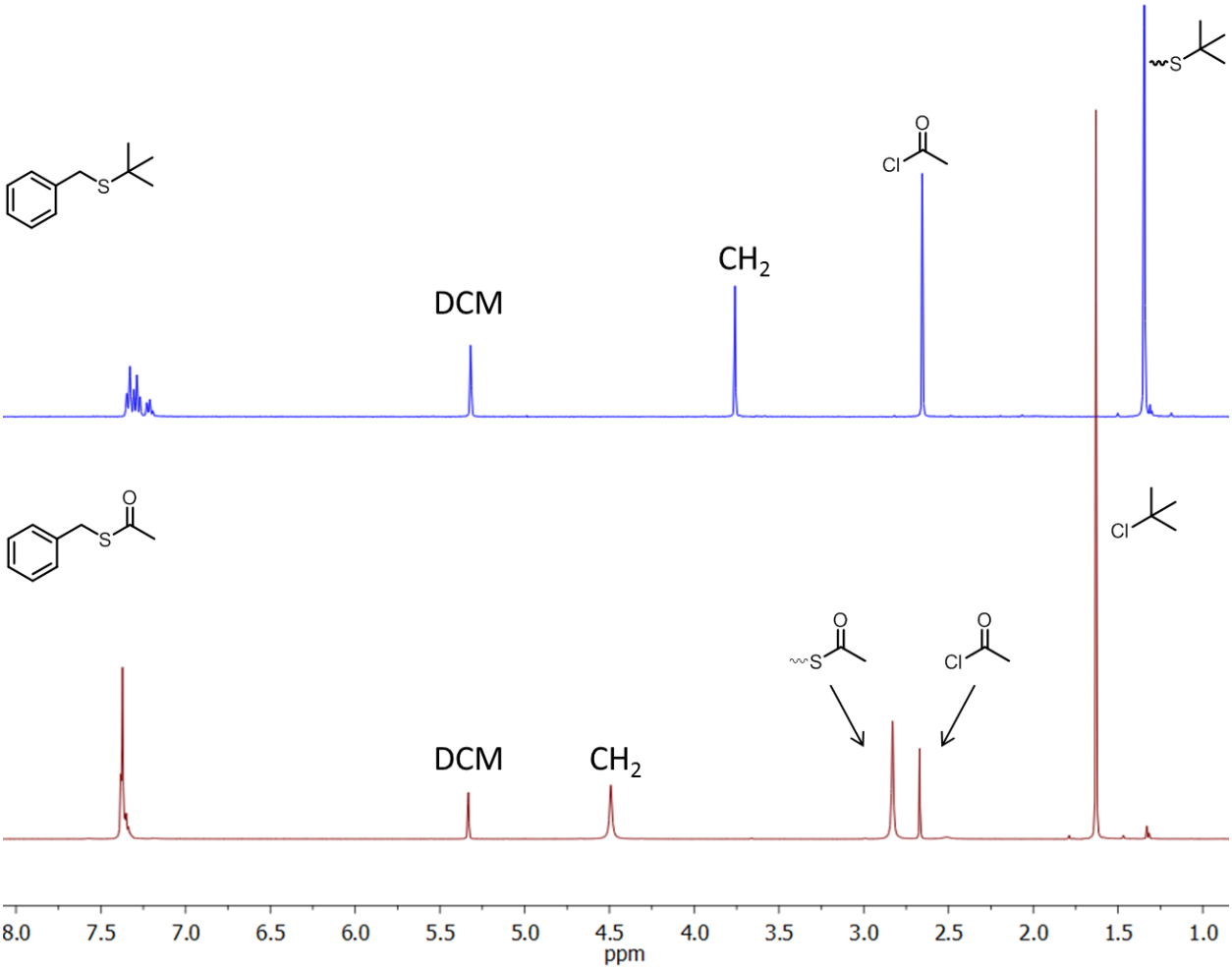


Figure S1: Temporal arrayed ^{1}H-NMR spectra of conversion of **4a** ━ (at t_0: no $TiCl_4$ added) to **4b** ━ using $TiCl_4$ (after 30 min) in CD_2Cl_2.

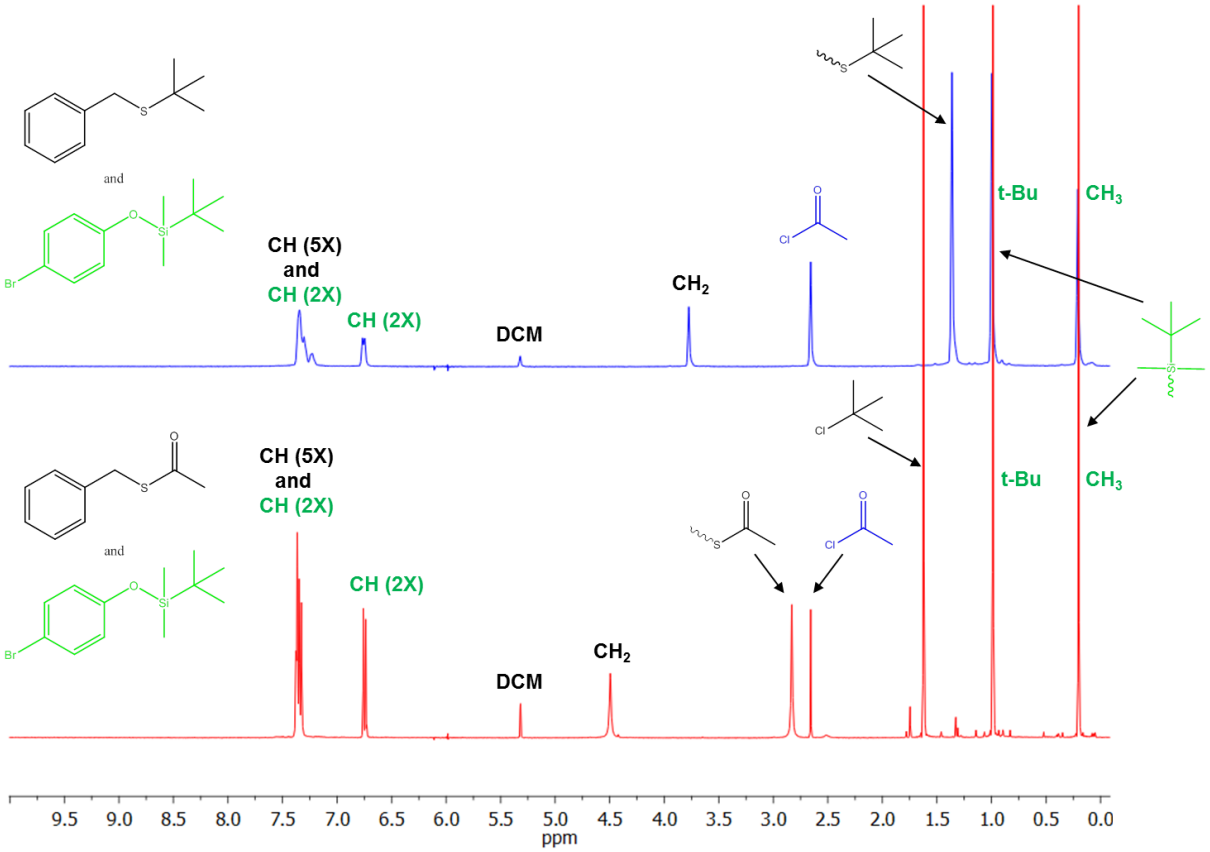


Figure S2: ^{1}H-NMR spectra before (upper spectrum) and 10 min after (lower spectrum) a reaction of 1.1 eq of $TiCl_4$ and acetyl chloride (1.1 eq) in d_2-DCM with phenyl tbutyl thioether (**4a**) in the presence of a TBDMS protected alcohol.

References

i N. Stuhr-Hansen, *Synth. Commun.* 2003, **33**, 641.