Electronic Supplementary Material (ESI) for Chemical Communications

Donor-acceptor cyclopropanes with Lawesson's and Woollins' reagent: Formation of bisthiophenes and unprecedented cage-like molecules

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Supplementary information

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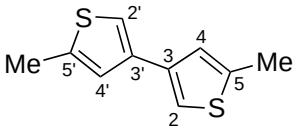
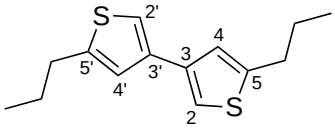
General Experimental

All reactions were performed in flame-dried glassware under an argon atmosphere. The solvents were dried by standard procedures and distilled prior to use. Commercially available compounds were used without further purification unless otherwise stated. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a 300, 500 or 600 MHz instrument using the residual signals from $CHCl_3$, δ = 7.26 ppm and δ = 77.0 ppm, DMSO, δ = 2.54 ppm and δ = 40.45 ppm, acetone, = δ 2.09 ppm and δ = 30.92 ppm, δ = 207.07 ppm, and methanol, δ = 4.87 ppm and δ = 49.2 ppm, as internal references for ^{1}H and ^{13}C chemical shifts, respectively. Assignments of the respective signals were made by the combination of H,H-COSY, HSQC and HMBC experiments. Unclear assignments were marked with *. ESI-HRMS spectrometry was carried out on a FTICR instrument. IR spectra were measured with an ATR spectrometer. UV spectra were measured with a common photometer.

Syntheses and analytical data of the compounds

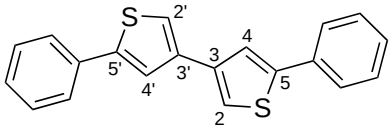


Bisthiophene 5a. A solution of diketone **6a**[1] (25 mg, 0.14 mmol, 1.0 equiv) in benzene (5 mL) was heated to 80 °C. After the addition of Lawesson's reagent (74 mg, 0.18 mmol, 1.3 equiv) the mixture was stirred for 2 h at 80 °C. The crude product was purified by flash column chromatography (SiO_2, pentane) to yield 9 mg (0.05 mmol, 33 %) of a white solid. R_f: 0.74 (hexane/EtOAc = 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.50 (s, 6H, Me), 6.96 (s, 2H, 4,4'-H), 7.06 (s, 2H, 2,2'-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 15.3 (Me), 117.2 (C-2,2'), 124.5 (C-4,4'), 137.3 (C-3,3'), 140.2 (C-5,5'). IR (ATR): $\widetilde{\nu}$ (cm^{-1}) = 2919, 2851, 1446, 1198. UV (CH_3CN): λ_{max} [nm] (lg ϵ) = 219 (3.94), 264 (3.64). MS (EI+, 70 eV): m/z (%) = 194.0 (100) $[M]^+$. HRMS (EI+): m/z calculated for $C_{10}H_{10}S_2$ $[M]^+$ 194.0224; observed: 194.0231.

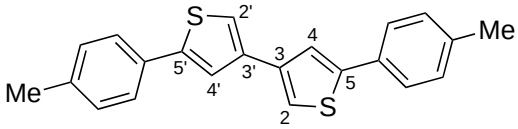


Bisthiophene 5b. A solution of diketone **6b**[1] (40 mg, 0.17 mmol, 1.0 equiv) in benzene (5 mL) was heated to 80 °C. After the addition of Lawesson's reagent (89 mg, 0.22 mmol,

1.3 equiv) the mixture was stirred for 2 h at 80 °C. The crude product was purified by flash column chromatography (SiO_2, pentane/EtOAc 50:1) to yield 8 mg (0.03 mmol, 19 %) of a pale yellow solid. R_f: 0.73 (hexane/EtOAc = 5:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.99 (t, J = 7.3 Hz, 6H, $CH_2CH_2CH_3$), 1.51–1.96 (m, 4H, $CH_2CH_2CH_3$), 2.79 (t, J = 7.5 Hz, 4H, $CH_2CH_2CH_3$), 6.99 (s, 2H, 4,4'-H), 7.10 (s, 2H, 2,2'-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 13.7 ($CH_2CH_2CH_3$), 24.8 ($CH_2CH_2CH_3$), 32.2 ($CH_2CH_2CH_3$), 117.0 (C-2,2'), 123.4 (C-4,4'), 137.1 (C-3,3'), 140.2 (C-5,5'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2957, 2927, 1766, 1540, 1455, 1189, UV (CH_3CN): λ_{max} [nm] (lg ϵ) = 220 (4.28), 264 (3.98). MS (EI+, 70 eV): m/z (%) = 250.1 (58) $[M]^+$. HRMS (EI+): m/z calculated for $C_{14}H_{18}S_2$ $[M]^+$ 250.0850; observed: 250.0853.

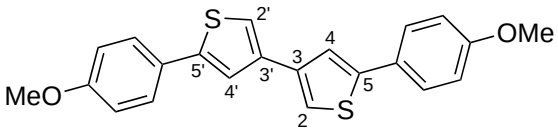


Bisthiophene 5c. A solution of diketone **6c**[1] (30 mg, 0.10 mmol, 1.0 equiv) in toluene (5 mL) was heated to 100 °C. After the addition of Lawesson's reagent (90 mg, 0.22 mmol, 2.2 equiv) the mixture was stirred for 16 h at 100 °C. The crude product was purified by flash column chromatography (SiO_2, pentane/EtOAc 30:1→25:1) to yield 16 mg (0.05 mmol, 51 %) of a pale yellow solid. R_f: 0.49 (hexane/EtOAc = 5:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.22–7.71 (m, 14H, 2,2', 4,4'-H, Ph). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 119.3 (C-4,4'), 122.2 (C-2,2'), 125.9 (Ph_{tert}), 127.8 (Ph_{tert}), 128.9 (Ph_{tert}), 134.2 (Ph_{quart}), 138.1 (C-3,3'), 145.0 (C-5,5'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2921, 1486, 1444, 1029. UV (CH_3CN): λ_{max} [nm] (lg ϵ) = 199 (4.54), 225 (4.26), 264 (4.37). MS (EI+, 70 eV): m/z (%) = 318.1 (100) $[M]^+$. HRMS (EI+): m/z calculated for $C_{20}H_{14}S_2$ $[M]^+$ 318.0537; observed: 318.0538.

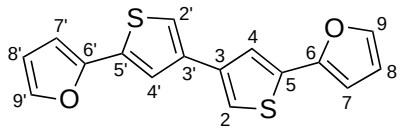


Bisthiophene 5d. A solution of diketone **6d** (32 mg, 0.10 mmol, 1.0 equiv) in toluene (5 mL) was heated to 100 °C. After the addition of Lawesson's reagent (86 mg, 0.21 mmol, 2.2 equiv) the mixture was stirred for 16 h at 100 °C. The crude product was purified by flash column chromatography (SiO_2, pentane/EtOAc 25:1) to yield 15 mg (0.04 mmol, 45 %) of a white solid. R_f: 0.59 (hexane/EtOAc = 5:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.39 (s, 6H, Me), 7.18–7.25 (m, 4H, Ph), 7.31 (d, J = 1.3 Hz, 2H, 4,4'-H), 7.51 (d, J = 1.3 Hz, 2H, 2,2'-H), 7.52–7.59 (m, 4H, Ph). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 21.2 (Me), 118.7 (C-4,4'), 121.7 (C-2,2'), 125.7 (Ph_{tert}), 129.4 (Ph_{quart}), 129.6 (Ph_{tert}), 131.4 (Ph_{quart}), 137.6 (C-3,3'), 145.1 (C-5,5'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1497, 1309, 1186, 1123, 1110. UV (CH_3CN): λ_{max} [nm] (lg ϵ) = 267 (4.57).

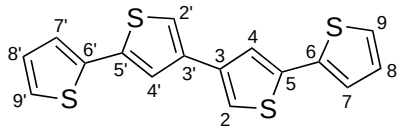
MS (EI+, 70 eV): m/z (%) = 346.1 (100) $[M]^+$. HRMS (EI+): m/z calculated for $C_{22}H_{18}S_2$ $[M]^+$ 346.0850; observed: 346.0849.



Bisthiophene 5f. A solution of diketone **6f** (19 mg, 0.05 mmol, 1.0 equiv) in toluene (5 mL) was heated to 100 °C. After the addition of Lawesson's reagent (46 mg, 0.12 mmol, 2.2 equiv) the mixture was stirred for 16 h at 100 °C. After flash column chromatography (SiO_2, pentane/EtOAc 15:1) 2 mg of a still crude reaction product was obtained. Mass spectrometry showed presence of **5f**. MS (EI+, 70 eV): m/z (%) = 378.1 (100) $[M]^+$. HRMS (EI+): m/z calculated for $C_{22}H_{18}O_2S_2$ $[M]^+$ 378.0748; observed: 378.0746.

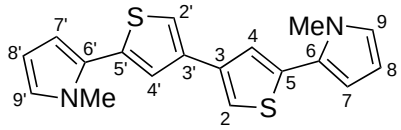


Bisthiophene 5g. A solution of diketone **6g** (33 mg, 0.12 mmol, 1.0 equiv) in toluene (5 mL) was heated to 100 °C. After the addition of Lawesson's reagent (103 mg, 0.26 mmol, 2.2 equiv) the mixture was stirred for 16 h at 100 °C. The crude product was purified by flash column chromatography (SiO_2, pentane/EtOAc 12:1) to yield 14 mg (0.05 mmol, 41 %) of a pale orange solid. R_f: 0.48 (hexane/EtOAc = 10:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.45 (dd, J = 1.8, 3.4 Hz, 2H, 8,8'-H), 6.53 (d, J = 3.4 Hz, 2H, 7,7'-H), 7.25 (d, J = 1.4 Hz 2H, 4,4'-H), 7.39–7.43 (m, 2H, 9,9'-H), 7.45 (d, J = 1.4 Hz, 2H, 2,2'-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 105.3 (C-7,7'), 111.7 (C-8,8'), 118.6 (C-4,4'), 121.4 (C-2,2'), 134.3 (C-5,5'), 137.3 (C-3,3'), 141.8 (C-9,9'), 149.1 (C-6,6'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3090, 1520, 1314, 1193, 1147, 1012. UV (CH_3CN): λ_{max} [nm] (lg ϵ) = 270 (4.60), 299 (4.47). MS (EI+, 70 eV): m/z (%) = 298.0 (100) $[M]^+$. HRMS (EI+): m/z calculated for $C_{16}H_{10}O_2S_2$ $[M]^+$ 298.0106; observed: 298.0122.

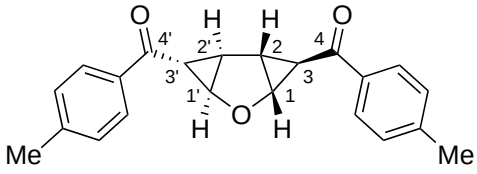


Bisthiophene 5h. A solution of diketone **6h** (29 mg, 0.09 mmol, 1.0 equiv) in toluene (5 mL) was heated to 100 °C. After the addition of Lawesson's reagent (82 mg, 0.20 mmol, 2.2 equiv) the mixture was stirred for 16 h at 100 °C. The crude product was purified by flash column chromatography (SiO_2, pentane/EtOAc 15:1) to yield 17 mg (0.05 mmol, 56 %) of an orange solid.

R_f: 0.51 (hexane/EtOAc = 10:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.02 (dd, J = 3.6, 5.1 Hz, 2H, Ar), 7.13–7.28 (m, 6H, Ar), 7.36 (d, J = 1.4 Hz, 2H, Ar). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 118.9 (Ar_{tert}), 122.6 (Ar_{tert}), 124.0 (Ar_{tert}), 124.6 (Ar_{tert}), 127.8 (Ar_{tert}), 137.1 (Ar_{quart}), 137.5 (Ar_{quart}), 138.0 (Ar_{quart}). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3092, 2922, 1498, 1190, 1049. UV (CH_3CN): λ_{max} [nm] (lg ε) = 212 (4.34), 275 (4.43), 307 (4.36). MS (EI+, 70 eV): m/z (%) = 330.0 (100) $[M]^+$. HRMS (EI+): m/z calculated for $C_{16}H_{10}S_4$ $[M]^+$ 329.9665; observed: 329.9661.

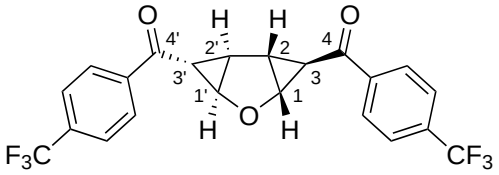


Bisthiophene 5i. A solution of diketone **6i** (36 mg, 0.12 mmol, 1.0 equiv) in toluene (5 mL) was heated to 100 °C. After the addition of Lawesson's reagent (103 mg, 0.26 mmol, 2.2 equiv) the mixture was stirred for 16 h at 100 °C. The crude product was purified by flash column chromatography (SiO_2, pentane/EtOAc 12:1→10:1) to yield 11 mg (0.03 mmol, 29 %) of a pale yellow solid. R_f: 0.37 (hexane/EtOAc = 10:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.76 (s, 6H, Me), 6.10–6.24 (m, 2H, 8,8'-H)), 6.37 (dd, J = 1.8, 6.3 Hz, 2H, 7.7'-H), 6.59–6.83 (m, 2H, 9,9'-H), 7.23 (d, J = 1.2 Hz, 2H, 4,4'-H), 7.29 (d, J = 1.2 Hz, 2H, 2,2'-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 35.2 (Me), 107.9 (C-8,8'), 110.1 (C-7,7'), 119.0 (C-4,4'), 124.0 (C-2,2'), 124.2 (C-9,9'), 126.9 (C-6,6'), 135.7, 137.3 (C-3,3',5,5'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3086, 1464, 1315, 1289, 1092. UV (CH_3CN): λ_{max} [nm] (lg ε) = 236 (4.30), 269 (4.44), 299 (4.24). MS (ESI): m/z (%) = 325.1 (38) $[M+H]^+$, 347.1 (11) $[M+Na]^+$. HRMS (ESI): m/z calculated for $C_{18}H_{17}N_2S_2$ $[M+H]^+$ 325.0828; observed: 325.0815.

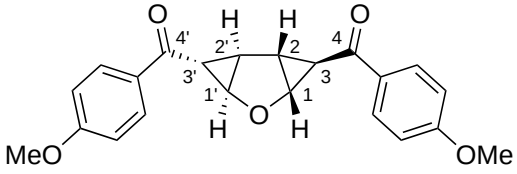


Diketone 6d. *p*-Tolylmagnesium bromide solution (5.18 mL, 0.5 M in Et_2O, 2.59 mmol, 3.5 equiv) was slowly given to a stirred solution of Weinreb amide **6WA**[1] (200 mg, 0.74 mmol, 1.0 equiv) in THF (20 mL) at 0 °C. The mixture was stirred for 3 h at 0 °C, stopped by the addition of sat. ammonium chloride solution, extracted with ethyl acetate (3 × 20 mL) and dried over sodium sulfate. After purification by flash column chromatography (SiO_2, pentane/EtOAc 5:1→4:1) the product was obtained as a white solid (198 mg, 0.60 mmol, 81 %). R_f: 0.44 (hexane/EtOAc = 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.43 (s, 6H, Me), 2.75–2.83 (m, 2H, 3,3'-H), 2.93 (d, J = 3.2 Hz, 2H, 2,2'-H), 4.07 (d, J = 5.2 Hz, 2H, 1,1'-H), 7.24–7.35 (m, 4H, Ph), 7.84–7.95 (m, 4H, Ph). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] =

21.7 (Me), 32.7, 33.0 (C-2,2',3,3'), 67.6 (C-1,1'), 128.1 (Ph_{tert}), 129.2 (Ph_{tert}), 134.5 (Ph_{quart}), 143.9 (Ph_{quart}), 195.5 (C-4,4'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1643, 1604, 1377, 1284, 1159, 1030. UV (CH_3CN): λ_{max} [nm] (lg ϵ) = 203 (4.63), 260 (4.59). MS (ESI): *m/z* (%) = 333.2 (42) $[M+H]^+$. HRMS (ESI): *m/z* calculated for $C_{22}H_{21}O_3$ $[M+H]^+$ 333.1485; observed: 333.1472.

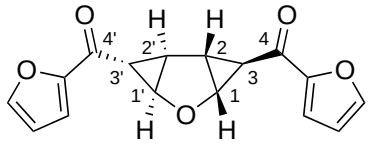


Diketone 6e. To a solution of 4-bromobenzotrifluoride (3.04 g, 13.5 mmol, 10.2 equiv) in THF (5 mL) was given *i*-propylmagnesium chloride solution (7.09 mL, 2 M in THF, 14.2 mmol, 10.8 equiv) and the mixture was stirred for 3.5 h at room temperature. The resulting solution was directly given to a solution of Weinreb amide **6WA**[1] (358 mmol, 1.32 mmol, 1.0 equiv) in THF (30 mL) at 0 °C. The mixture was stirred for 3 h at 0 °C, stopped by the addition of sat. ammonium chloride solution, extracted with ethyl acetate (3 × 30 mL) and dried over sodium sulfate. After purification by flash column chromatography (SiO_2, pentane/EtOAc 6:1→4:1→2:1) the product was obtained as a yellow solid (391 mg, 0.89 mmol, 67 %). R_f: 0.14 (hexane/EtOAc = 3:1). R_f: 0.81 (hexane/EtOAc = 0:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.87 (dd, J = 5.4, 3.6 Hz, 2H, 3,3'-H), 2.93 (d, J = 3.6 Hz, 2H, 2,2'-H), 4.11 (d, J = 5.4 Hz, 2H, 1,1'-H), 7.73–7.78 (m, 4H, Ph), 8.06–8.12 (m, 4H, Ph). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 33.1 (C-2,2'), 33.3 (C-3,3'), 68.0 (C-1,1'), 123.5 (q, $^1J_{C\text{-}F}$ = 272.7 Hz, CF_3), 125.8 (Ph_{tert}), 128.4 (Ph_{tert}), 134.6 (q, $^2J_{C\text{-}F}$ = 33.0 Hz, Ph_{quart}), 139.6 (Ph_{tert}), 195.0 (C-4,4'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1651, 1328, 1132, 1068. UV (CH_3CN): λ_{max} [nm] (lg ϵ) = 196 (4.76), 238 (4.41). MS (ESI): *m/z* (%) = 463.1 (100) $[M+Na]^+$. HRMS (ESI): *m/z* calculated for $C_{22}H_{14}F_6O_3Na$ $[M+Na]^+$ 463.0739; observed: 463.0734.

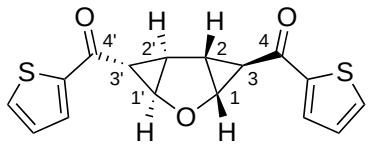


Diketone 6f. *p*-Methoxyphenylmagnesium bromide solution (5.32 mL, 1.0 M in THF, 5.32 mmol, 12.5 equiv) was slowly given to a stirred solution of Weinreb amide **6WA**[1] (115 mg, 0.43 mmol, 1.0 equiv) in THF (15 mL) at 0 °C. The mixture was stirred for 3 h at 0 °C, stopped by the addition of sat. ammonium chloride solution, extracted with ethyl acetate (3 × 20 mL) and dried over sodium sulfate. After purification by flash column chromatography (SiO_2, pentane/EtOAc 6:1) the product was obtained as a pale yellow solid (138 mg, 0.38 mmol, 89 %). R_f:

0.14 (hexane/EtOAc = 3:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.76 (dd, J = 5.4, 3.6 Hz, 2H, 3,3'-H), 2.88 (dd, J = 3.6, 0.6 Hz, 2H, 2,2'-H), 3.87 (s, 6H, OMe), 4.05 (d, J = 5.4 Hz, 2H, 1,1'-H), 6.93–7.00 (m, 4H, Ph), 7.94–8.04 (m, 4H, Ph). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 32.4 (C-2,2'), 32.8 (C-3,3'), 55.5 (OMe), 67.5 (C-1,1'), 113.8 (Ph_{tert}), 130.1 (Ph_{quart}), 130.4 (Ph_{tert}), 163.7 (Ph_{quart}), 194.6 (C-4,4'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1638, 1600, 1421, 1379, 1250, 1216, 1175, 1023, 1003. UV (CH_3CN): λ_{max} [nm] (lg ε) = 197 (4.55), 217 (4.39), 281 (4.53). MS (ESI): m/z (%) = 365.2 (30) $[M+H]^+$, 387.2 (100) $[M+Na]^+$. HRMS (ESI): m/z calculated for $C_{22}H_{20}O_5Na$ $[M+Na]^+$ 387.1203; observed: 387.1204.

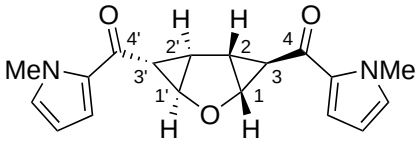


Diketone 6g. To a solution of furan (153 mg, 2.24 mmol, 3.0 equiv) in THF (5 mL) at -78 °C was given tBuLi solution (1.40 mL, 1.6 M in pentane, 2.24 mmol, 3.0 equiv). The mixture was stirred for 10 min at -78 °C, for 30 min at rt and then was cooled to 0 °C. A solution of Weinreb amide **6WA**[1] (202 mg, 0.75 mmol, 1.0 equiv) in THF (10 mL) was added and the mixture was stirred for 90 min at rt. The reaction was stopped by the addition of water, the mixture was extracted with ethyl acetate (3 × 20 mL), washed with brine and dried over sodium sulfate. After purification by flash column chromatography (SiO_2, pentane/EtOAc 2:1) the product was obtained as a pale yellow solid (168 mg, 0.59 mmol, 79 %). R_f: 0.51 (hexane/EtOAc = 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.64–2.94 (m, 4H, 2,2',3,3'-H), 3.87–4.19 (m, 2H, 1,1'-H), 6.55 (dd, J = 1.7, 3.6 Hz, 2H, Ar), 7.21 (dd, J = 0.8, 3.6 Hz, 2H, Ar), 7.60 (dd, J = 0.8, 1.7 Hz, 2H, Ar). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 32.4, 32.6 (C-2,2',3,3'), 67.0 (C-1,1'), 112.4 (Ar_{tert}), 116.9 (Ar_{tert}), 146.6 (Ar_{tert}), 152.6 (Ar_{quart}), 184.6 (C-4,4'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3126, 1639, 1560, 1465, 1402, 1305, 1165, 1019. UV (CH_3CN): λ_{max} [nm] (lg ε) = 220 (3.95), 278 (4.56). MS (ESI): m/z (%) = 285.1 (19) $[M+H]^+$, 307.1 (44) $[M+Na]^+$. HRMS (ESI): m/z calculated for $C_{16}H_{12}O_5Na$ $[M+Na]^+$ 307.0577; observed: 307.0573.

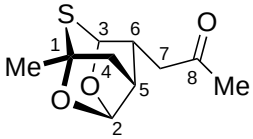


Diketone 6h. 2-Thienylmagnesium bromide solution (2.85 mL, 1.0 M in THF, 3.5 equiv) was slowly given to a stirred solution of Weinreb amide **6WA**[1] (220 mg, 0.81 mmol, 1.0 equiv) in THF (25 mL) at 0 °C. The mixture was stirred for 3 h at rt, the reaction was stopped by the addition of sat. ammonium chloride solution, extracted with ethyl acetate (3 × 20 mL) and dried over sodium sulfate. After purification by flash column chromatography (SiO_2,

pentane/EtOAc 3:1→2:1→3:2) the product was obtained as a white solid (207 mg, 0.65 mmol, 80 %). R_f: 0.57 (hexane/EtOAc = 2:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.91–2.67 (m, 4H, 2,2',3,3'-H), 4.08 (dd, J = 1.7, 4.7 Hz, 2H, 1,1'-H), 7.16 (dd, J = 3.8, 4.9 Hz, 2H, Ar), 7.65 (dd, J = 1.1, 4.9 Hz, 2H, Ar), 7.82 (dd, J = 1.1, 3.8 Hz, 2H, Ar). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 32.7, 33.4 (C-2,2',3,3'), 67.1 (C-1,1'), 128.3 (Ar_{tert}), 132.1 (Ar_{tert}), 133.9 (Ar_{tert}), 144.2 (Ar_{quart}), 188.4 (C-4,4'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1625, 1412, 1381, 1295, 1211, 1010. UV (CH_3CN): λ_{max} [nm] (lg ε) = 267 (4.33), 287 (4.40). MS (ESI): m/z (%) = 317.0 (16), $[M+H]^+$, 339.0 (40) $[M+Na]^+$. HRMS (ESI): m/z calculated for $C_{16}H_{12}O_3S_2Na$ $[M+Na]^+$ 339.0120; observed: 339.0120.

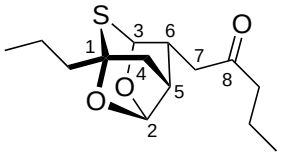


Diketone 6i. To a solution of N-methylpyrrole (208 mg, 2.31 mmol, 3.0 equiv) in THF (5 mL) at -78 °C was given *t*BuLi solution (1.44 mL, 1.6 M in pentane, 2.31 mmol, 3.0 equiv). The mixture was stirred for 10 min at -78 °C, for 30 min at rt and then was cooled to 0 °C. A solution of Weinreb amide **6WA**[1] (208 mg, 0.77 mmol, 1.0 equiv) in THF (10 mL) was added and the mixture was stirred for 90 min at rt. The reaction was stopped by the addition of water, the mixture was extracted with ethyl acetate (3 × 20 mL), washed with brine and dried over sodium sulfate. After purification by flash column chromatography (SiO_2, pentane/EtOAc 5:1→3:1) the product was obtained as a white solid (156 mg, 0.50 mmol, 65 %). R_f: 0.64 (hexane/EtOAc = 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.46–2.84 (m, 4H, 2,2',3,3'-H), 3.87 (s, 6H, Me), 3.96 (d, J = 5.4 Hz, 2H, 1,1'-H), 6.15 (dd, J = 2.5, 4.1 Hz, 2H, Ar), 6.72–6.84 (m, 2H, Ar), 7.11 (dd, J = 1.7, 4.1 Hz, 2H, Ar). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 31.6, 33.3 (C-2,2',3,3'), 37.5 (Me), 66.3 (C-1,1'), 108.3 (Ar_{tert}), 119.7 (Ar_{tert}), 130.8 (Ar_{quart}), 131.2 (Ar_{tert}), 186.1 (C-4,4'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1625, 1407, 1387, 1159, 1044. UV (CH_3CN): λ_{max} [nm] (lg ε) = 243 (4.08), 292 (4.70), 335 (3.10). MS (ESI): m/z (%) = 311.2 (71) $[M+H]^+$, 333.1 (50) $[M+Na]^+$, 643.3 (100) $[2M+Na]^+$, 953.4 (95) $[3M+Na]^+$. HRMS (ESI): m/z calculated for $C_{18}H_{18}N_2O_3Na$ $[M+Na]^+$ 333.1210; observed: 333.1207.

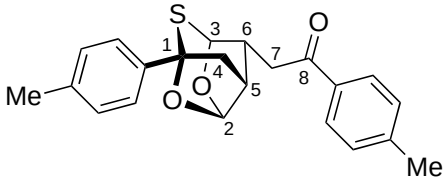


Compound 8a. To a solution of diketone **6a**[1] (25 mg, 0.14 mmol, 1.0 equiv) in dichloromethane (5 mL) was given Lawesson's reagent (85 mg, 0.21 mmol, 1.5 equiv) and the mixture

was stirred for 3.5 h at room temperature. After purification by flash column chromatography (SiO_2, pentane/EtOAc 2:1→1:1) the product was obtained as a pale yellow solid (18 mg, 0.08 mmol, 60 %). R_f: 0.23 (hexane/EtOAc = 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.52 (s, 3H, Me), 1.89–2.22 (m, 4H, 4-H_a,Me), 2.32–2.64 (m, 3H, 7-$H_{a,b}$,4-H_b), 2.85 (ddd, J = 1.4, 4.3, 7.8 Hz, 1H, 5-H), 3.06 (t, J = 7.1 Hz, 1H, 6-H), 5.11 (s, 1H, 3-H), 5.93 (d, J = 4.3 Hz, 1H, 2-H) . ^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 24.9 (Me), 30.2 (Me), 46.7 (C-7), 48.0 (C-5), 49.8 (C-6), 49.9 (C-4), 85.7 (C-3), 91.4 (C-1), 107.5 (C-2), 206.6 (C-8). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1713, 1595, 1444, 1377, 1266, 1161, 1043. UV (CH_3CN): λ_{max} [nm] (lg ϵ) = 197 (4.21), 223 (3.55). MS (ESI): m/z (%) = 237.1 (40) $[M+Na]^+$. HRMS (ESI): m/z calculated for $C_{10}H_{14}O_3SNa$ 237.0556; observed: 237.0559.

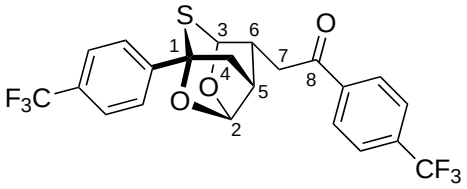


Compound 8b. To a solution of diketone **6b**[1] (25 mg, 0.11 mmol, 1.0 equiv) in dichloromethane (5 mL) was given Lawesson's reagent (64 mg, 0.16 mmol, 1.5 equiv) and the mixture was stirred for 3.5 h at room temperature. After purification by flash column chromatography (SiO_2, pentane/EtOAc 3:1) the product was obtained as a pale yellow oil (16 mg, 0.06 mmol, 56 %). R_f: 0.56 (hexane/EtOAc = 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.68–1.02 (m, 6H, $CH_2CH_2CH_3$), 1.28–1.87 (m, 6H, $CH_2CH_2CH_3$), 2.08 (dd, J = 8.0, 11.6 Hz, 1H, 4-H_a), 2.21–2.67 (m, 5H, 7-$H_{a,b}$,4-H_b,$CH_2CH_2CH_3$), 2.83 (ddd, J = 1.5, 4.3, 8.0 Hz, 1H, 5-H), 3.08 (t, J = 7.1 Hz, 1H, 6-H), 5.11 (s, 1H, 3-H), 5.91 (d, J = 4.3 Hz, 1H, 2-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 13.7 ($CH_2CH_2CH_3$), 14.3 ($CH_2CH_2CH_3$), 17.2 ($CH_2CH_2CH_3$), 17.3 ($CH_2CH_2CH_3$), 40.8 ($CH_2CH_2CH_3$), 45.1 ($CH_2CH_2CH_3$), 45.9 (C-7), 47.8 (C-5), 48.3 (C-6), 50.4 (C-4), 85.8 (C-3), 95.1 (C-1), 107.2 (C-2), 208.8 (C-8). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2959, 1709, 1457, 1373, 1263, 1127, 1034. UV (CH_3CN): λ_{max} [nm] (lg ϵ) = 193 (3.64). MS (ESI): m/z (%) = 293.1 (15) $[M+Na]^+$, 563.3 (100) $[2M+Na]^+$. HRMS (ESI): m/z calculated for $C_{14}H_{22}O_3SNa$ $[M+Na]^+$ 293.1182; observed: 293.1181.

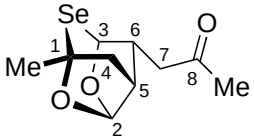


Compound 8d. To a solution of diketone **6d** (38 mg, 0.11 mmol, 1.0 equiv) in dichloromethane (5 mL) was given Lawesson's reagent (69 mg, 0.17 mmol, 1.5 equiv) and the mixture was stirred for 3.5 h at room temperature. After purification by flash column chromatography (SiO_2,

pentane/EtOAc 5:1→4:1) the product was obtained as a white solid (16 mg, 0.04 mmol, 38 %). R_f: 0.35 (hexane/EtOAc = 5:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.34 (s, 3H, Me), 2.37–2.55 (m, 4H, 4-H_a,Me), 2.88–3.23 (m, 4H, 4-H_b,7-$H_{a,b}$,5-H), 3.46 (t, J = 7.1 Hz, 1H, 6-H), 5.30 (s, 1H, 3-H), 6.20 (d, J = 4.3 Hz, 1H, 2-H), 6.78–8.12 (m, 8H, Ph). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 21.2 (Me), 21.7 (Me), 41.8 (C-7), 48.2 (C-5), 49.5 (C-6), 50.6 (C-4), 86.9 (C-3), 94.2 (C-1), 107.7 (C-2), 125.0 (Ph_{tert}), 128.1 (Ph_{tert}), 129.1 (Ph_{tert}), 129.4 (Ph_{tert}), 134.2 (Ph_{quart}), 136.9 (Ph_{quart}), 138.5 (Ph_{quart}), 144.3 (Ph_{quart}), 197.7 (C-8). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1682, 1604, 1404, 1178, 1073. UV (CH_3CN): λ_{max} [nm] (lg ϵ) = 252 (4.28), 196 (4.81). MS (ESI): m/z (%) = 367.1 (38) $[M+H]^+$, 389.1 (100) $[M+Na]^+$, 755.3 (85) $[2M+Na]^+$. HRMS (ESI): m/z calculated for $C_{22}H_{22}O_3SNa$ $[M+Na]^+$ 389.1182; observed: 389.1182.

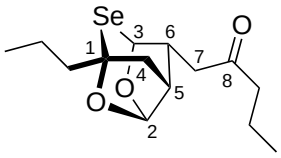


Compound 8e. To a solution of diketone **6e** (38 mg, 0.09 mmol, 1.0 equiv) in dichloromethane (5 mL) was given Lawesson's reagent (52 mg, 0.13 mmol, 1.5 equiv) and the mixture was stirred for 3.5 h at room temperature. After purification by flash column chromatography (SiO_2, pentane/EtOAc 4:1) the product was obtained as a white solid (20 mg, 0.04 mmol, 49 %). R_f: 0.18 (hexane/EtOAc = 5:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.45 (dd, J = 8.0, 11.8 Hz, 1H, 4-H_a, 2.94–3.30 (m, 4H, 4-H_b,5-H,7-$H_{a,b}$), 3.51 (t, J = 7.0 Hz, 1H, 6-H), 5.34 (s, 1H, 3-H), 6.24 (d, J = 4.3 Hz, 1H, 2-H), 7.50–8.18 (m, 8H, Ph). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 42.2 (C-7), 48.2 (C-5), 49.6 (C-6), 50.3 (C-4), 86.9 (C-3), 93.5 (C-1), 107.6 (C-2), 123.5 (q, $^1J_{C\text{-}F}$ = 273.5 Hz, CF_3), 123.8 (q, $^1J_{C\text{-}F}$ = 273.5 Hz, CF_3), 125.4 (Ph_{tert}), 125.6 (Ph_{tert}), 125.9 (Ph_{tert}), 128.3 (Ph_{tert}), 130.8 (q, $^2J_{C\text{-}F}$ = 32.5 Hz, Ph_{quart}), 134.8 (q, $^2J_{C\text{-}F}$ = 32.7 Hz, Ph_{quart}), 139.1 (Ph_{quart}), 143.2 (Ph_{quart}), 196.9 (C-8). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1688, 1412, 1321, 1127, 1064. UV (CH_3CN): λ_{max} [nm] (lg ϵ) = 234 (4.27), 193 (4.79). MS (ESI): m/z (%) = 475.1 (36) $[M+H]^+$, 497.1 (42) $[M+Na]^+$, 971.1 (49) $[2M+Na]^+$. HRMS (ESI): m/z calculated for $C_{22}H_{16}O_3F_6SNa$ $[M+Na]^+$ 497.0617; observed: 497.0614.

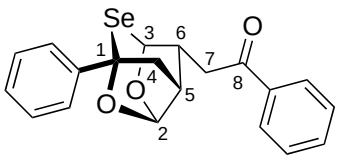


Compound 9a. To a solution of diketone **6a**[1] (20 mg, 0.11 mmol, 1.0 equiv) in dichloromethane (5 mL) was given Woollins' reagent (30 mg, 0.06 mmol, 0.5 equiv) and the mixture

was stirred for 3.5 h at room temperature. After purification by flash column chromatography (SiO_2, pentane/EtOAc 4:1→2:1) the product was obtained as a pale yellow solid (25 mg, 0.10 mmol, 87 %). R_f: 0.21 (hexane/EtOAc = 5:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.68 (s, 3H, Me), 2.14 (s, 3H, Me), 2.16–2.23 (m, 1H, 4-H_a), 2.39–2.65 (m, 2H, 7-H), 2.79 (d, J = 12.1 Hz, 1H, 4-H_b), 2.90 (ddd, J = 1.4, 4.5, 8.3 Hz, 1H, 5-H), 3.29 (t, J = 7.2 Hz, 1H, 6-H), 5.39 (s, 1H, 3-H), 6.05 (d, J = 4.5 Hz, 1H, 2-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 26.8 (Me), 30.3 (Me), 47.4 (C-7), 48.7 (C-5), 50.5 (C-6), 51.1 (C-4), 80.3 (C-3), 88.1 (C-1), 109.2 (C-2), 206.5 (C-8). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1723, 1444, 1398, 1269, 1160, 1100, 1024, UV (MeOH): λ_{max} [nm] (lg ε) = 203 (3.65). MS (ESI): m/z (%) = 285.0 (49) $[M+Na]^+$, 547.0 (100) $[2M+Na]^+$. HRMS (ESI): m/z calculated for $C_{10}H_{14}O_3SeNa$ $[M+Na]^+$ 285.0001; observed: 285.0000.

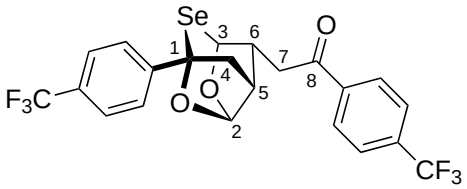


Compound 9b. To a solution of diketone **6b**[1] (20 mg, 0.09 mmol, 1.0 equiv) in dichloromethane (5 mL) was given Woollins' reagent (23 mg, 0.04 mmol, 0.5 equiv) and the mixture was stirred for 3.5 h at room temperature. After purification by flash column chromatography (SiO_2, pentane/EtOAc 4:1→2:1) the product was obtained as a colourless oil (19 mg, 0.06 mmol, 70 %). R_f: 0.38 (hexane/EtOAc = 4:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.77–1.03 (m, 6H, $CH_2CH_2CH_3$), 1.31–1.65 (m, 4H, $CH_2CH_2CH_3$), 1.68–1.93 (m, 2H, $CH_2CH_2CH_3$), 2.15 (dd, J = 8.4, 12.0 Hz, 1H, 4-H_a), 2.27–2.59 (m, 4H, 7-H,$CH_2CH_2CH_3$), 2.76 (d, J = 12.1 Hz, 1H, 4-H_b), 2.85 (ddd, J = 1.5, 4.5, 8.3 Hz, 1H, 5-H), 3.28 (t, J = 7.2 Hz, 1H, 6-H), 5.36 (s, 1H, 3-H), 5.99 (d, J = 4.5 Hz, 1H, 2-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 13.6 ($CH_2CH_2CH_3$), 14.1 ($CH_2CH_2CH_3$), 17.2 ($CH_2CH_2CH_3$), 18.0 ($CH_2CH_2CH_3$), 42.3 ($CH_2CH_2CH_3$), 45.0 ($CH_2CH_2CH_3$), 46.4 (C-7), 48.4 (C-5), 49.3 (C-6), 51.0 (C-4), 80.4 (C-3), 93.0 (C-1), 108.9 (C-2), 209.0 (C-8). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2958, 1708, 1464, 1371, 1254, 1127, 1034. UV (MeOH): λ_{max} [nm] (lg ε) = 203 (3.69). MS (ESI): m/z (%) = 341.1 (20) $[M+Na]^+$, 659.2 (100) $[2M+Na]^+$. HRMS (ESI): m/z calculated for $C_{14}H_{22}O_3SeNa$ $[M+Na]^+$ 341.0627; observed: 341.0627.

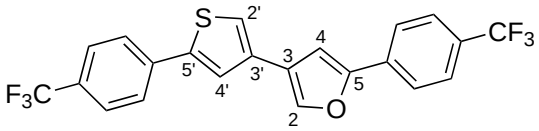


Compound 9c. To a solution of diketone **6c**[1] (13 mg, 0.04 mmol, 1.0 equiv) in dichloromethane (4 mL) was given Woollins' reagent (11 mg, 0.02 mmol, 0.5 equiv) and the mixture

was stirred for 3.5 h at room temperature. After purification by flash column chromatography (SiO_2, pentane/EtOAc 5:1) the product was obtained as a pale orange solid (14 mg, 0.04 mmol, 84 %). R_f: 0.18 (hexane/EtOAc = 4:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.55 (dd, J = 12.3 Hz, 1H, 4-H_a), 2.97–3.29 (m, 3H, 5,7-H), 3.37 (d, J = 12.3 Hz, 1H, 4-H_b), 3.68 (t, J = 7.1 Hz, 1H, 6-H), 5.57 (s, 1H, 3-H), 6.30 (d, J = 4.3 Hz, 1H, 2-H), 7.15–8.17 (m, 10H, Ph). ^{13}C-NMR (125 MHz, DMSO): δ [ppm] = 42.1 (C-7), 47.9 (C-5), 49.5 (C-6), 50.7 (C-4), 81.9 (C-3), 90.3 (C-1), 109.1 (C-2), 124.6 (Ph_{tert}), 127.9 (Ph_{tert}), 128.1 (Ph_{tert}), 128.4 (Ph_{tert}), 128.7 (Ph_{tert}), 133.3 (Ph_{tert}), 136.5 (Ph_{quart}), 141.4 (Ph_{quart}), 198.5 (C-8). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2922, 1676, 1595, 1446, 1312, 1060. UV (MeOH): λ_{max} [nm] (lg ε) = 204 (3.87), 240 (3.62). MS (ESI): m/z (%) = 409.0 (100) $[M+Na]^+$, 795.1 (78) $[2M+Na]^+$. HRMS (ESI): m/z calculated for $C_{20}H_{18}O_3SeNa$ $[M+Na]^+$ 409.0314; observed: 409.0307.



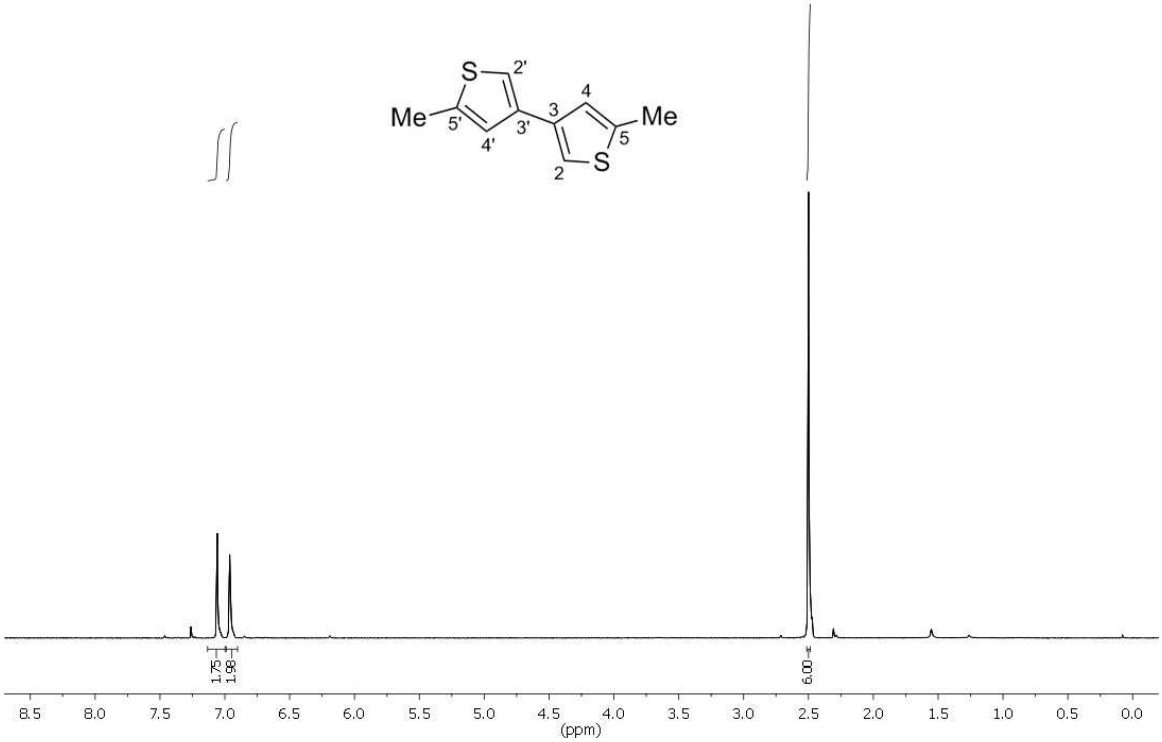
Compound 9e. To a solution of diketone **6e** (42 mg, 0.10 mmol, 1.0 equiv) in dichloromethane (5 mL) was given Woollins' reagent (25 mg, 0.05 mmol, 0.5 equiv) and the mixture was stirred for 14 h at room temperature. After purification by flash column chromatography (SiO_2, pentane/EtOAc 5:1→3:1) the product was obtained as a pale yellow solid (16 mg, 0.03 mmol, 32 %). R_f: 0.15 (hexane/EtOAc = 5:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.53 (dd, J = 8.3, 12.1 Hz, 1H, 4-H_a), 2.97–3.48 (m, 4H, 4-H_b,5-H,7-$H_{a,b}$), 3.70 (t, J = 7.1 Hz, 1H, 6-H), 5.58 (s, 1H, 3-H), 6.31 (d, J = 4.5 Hz, 1H, 2-H), 7.53–8.15 (m, 10H, Ph). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 42.8 (C-7), 48.8 (C-5), 49.9 (C-6), 50.8 (C-4), 81.8 (C-3), 89.5 (C-1), 109.2 (C-2), 121.3 (q, $^1J_{C\text{-}F}$ = 272.6 Hz, CF_3), 121.7 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, CF_3), 125.1 (Ph_{tert}), 125.6 (Ph_{tert}), 125.9 (Ph_{tert}), 128.3 (Ph_{tert}), 130.4 (q, $^2J_{C\text{-}F}$ = 32.8 Hz, Ph_{quart}), 134.9 (q, $^2J_{C\text{-}F}$ = 32.8 Hz, Ph_{quart}), 139.1 (Ph_{quart}), 144.5 (Ph_{quart}), 196.9 (C-8). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1687, 1409, 1318, 1125, 1064. UV (CH_3CN): λ_{max} [nm] (lg ε) = 274 (3.40), 233 (4.38), 194 (4.77). MS (ESI): m/z (%) = 521.0 (100) $[M-H]^-$. HRMS (ESI): m/z calculated for $C_{22}H_{15}O_3F_6$ $[M-H]^-$ 521.0097; observed: 521.0073.

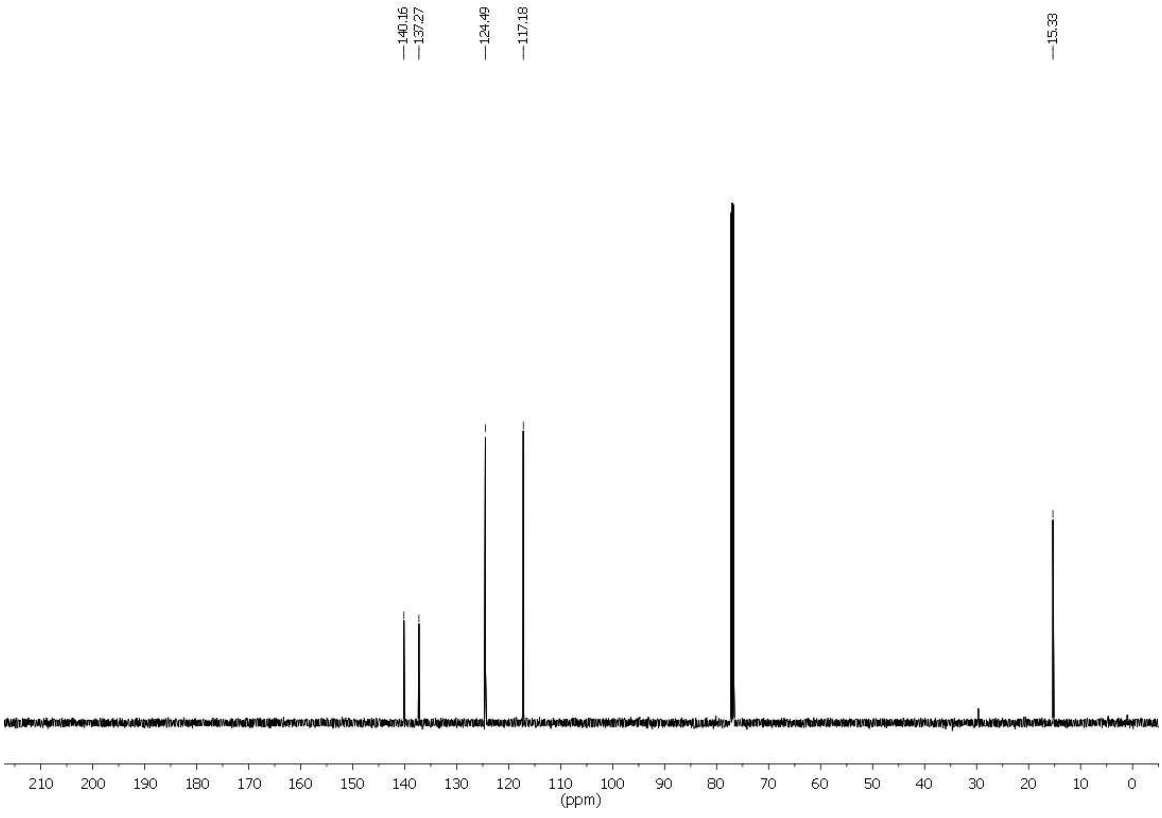


Thiophen-3-yl-furan 14. A solution of diketone **6e** (41 mg, 0.09 mmol, 1.0 equiv) in toluene (5 mL) was heated to 100 °C. After the addition of Lawesson's reagent (83 mg, 0.21 mmol,

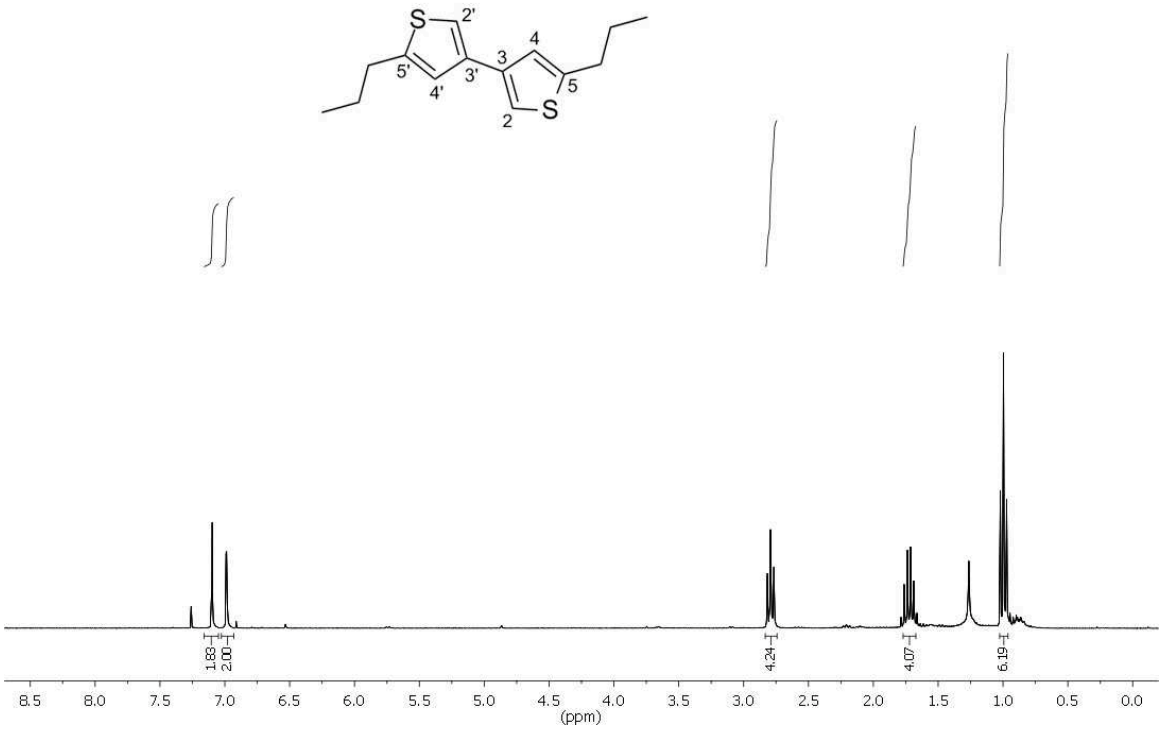
2.2 equiv) the mixture was stirred for 16 h at 100 °C. The crude product was purified by flash column chromatography (SiO_2, pentane/EtOAc 10:1) to yield 26 mg (0.06 mmol, 64 %) of **14** with small impurities of **5e** as a pale orange solid. R_f: 0.62 (hexane/EtOAc = 5:1). ^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.99 (s, 1H, 4-H), 7.34 (d, J = 1.3 Hz, 1H , 4'-H), 7.42 (d, J = 1.3 Hz, 1H, 2'-H), 7.50 (d, J = 1.3 Hz, 1H, 2-H), 7.56–7.84 (m, 8H, Ph). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 106.0 (C-4), 120.5, 120.8, 123.3 (C-4',2,2'), 123.8 (C-3), 123.9 (Ph_{tert}), 124.1 (q, $^1J_{C\text{-}F}$ = 272.1 Hz, CF_3), 124.2 (q, $^1J_{C\text{-}F}$ = 272.1 Hz, CF_3), 125.8 (Ph_{tert}), 125.9 (Ph_{tert}), 126.0 (Ph_{tert}), 129.6 (q, $^2J_{C\text{-}F}$ = 32.6 Hz, Ph_{quart}), 129.6 (q, $^2J_{C\text{-}F}$ = 32.6 Hz, Ph_{quart}), 134.0, 138.0 (C-3',5'), 138.9 (C-2), 143.3 (Ph_{quart}), 143.5 (Ph_{quart}), 153.3 (C-5). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1612, 1410, 1320, 1160, 1108, 1067. UV (CH_3CN): λ_{max} [nm] (lg ε) = 297 (4.46), 270 (4.44), 224 (4.39). MS (EI+, 70 eV): m/z (%) = 438.0 (98) [M(**14**)]$^+$, 454.0 (100) [M(**5e**)]$^+$. HRMS (EI+): m/z calculated for $C_{22}H_{12}F_6SO$ [M(**14**)]$^+$ 438.0513; observed: 438.0526. HRMS (EI+): m/z calculated for $C_{22}H_{12}F_6S_2$ [M(**5e**)]$^+$ 454.0285; observed: 454.0280.

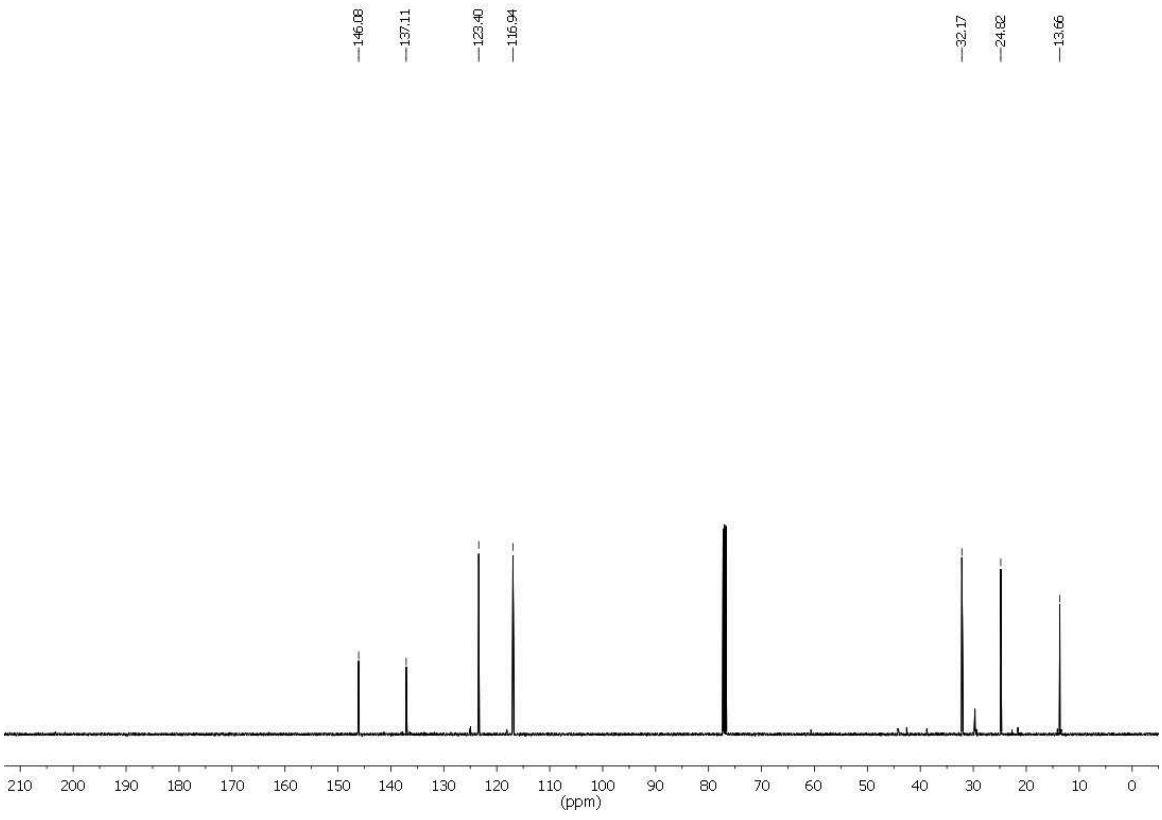
Compound 5a (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))



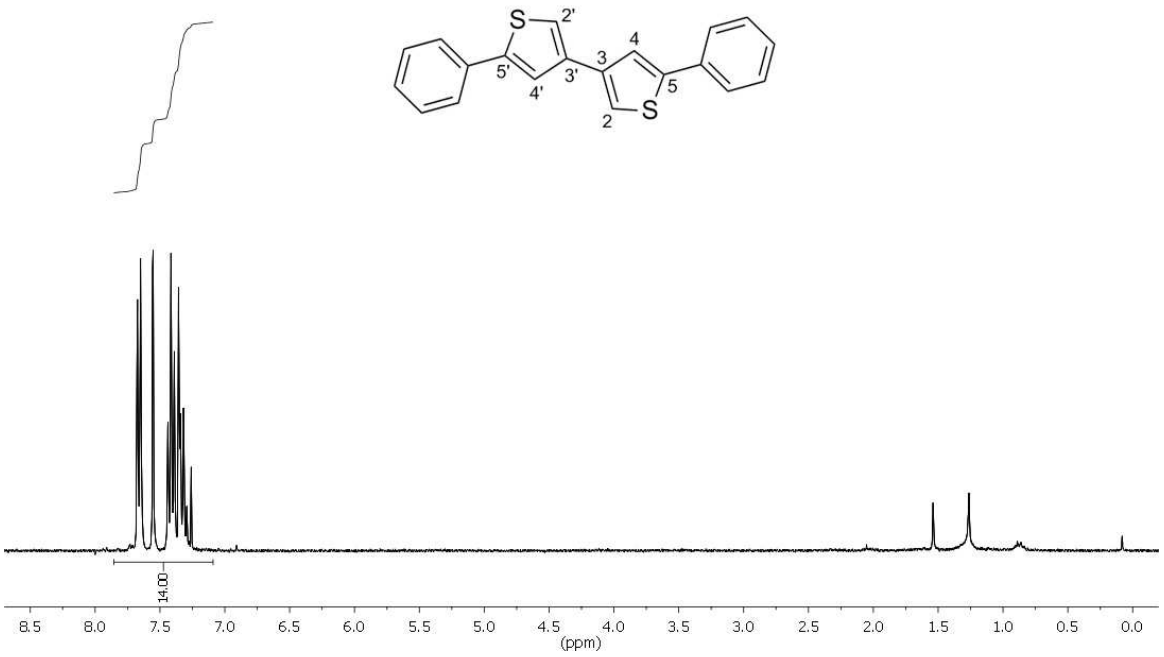


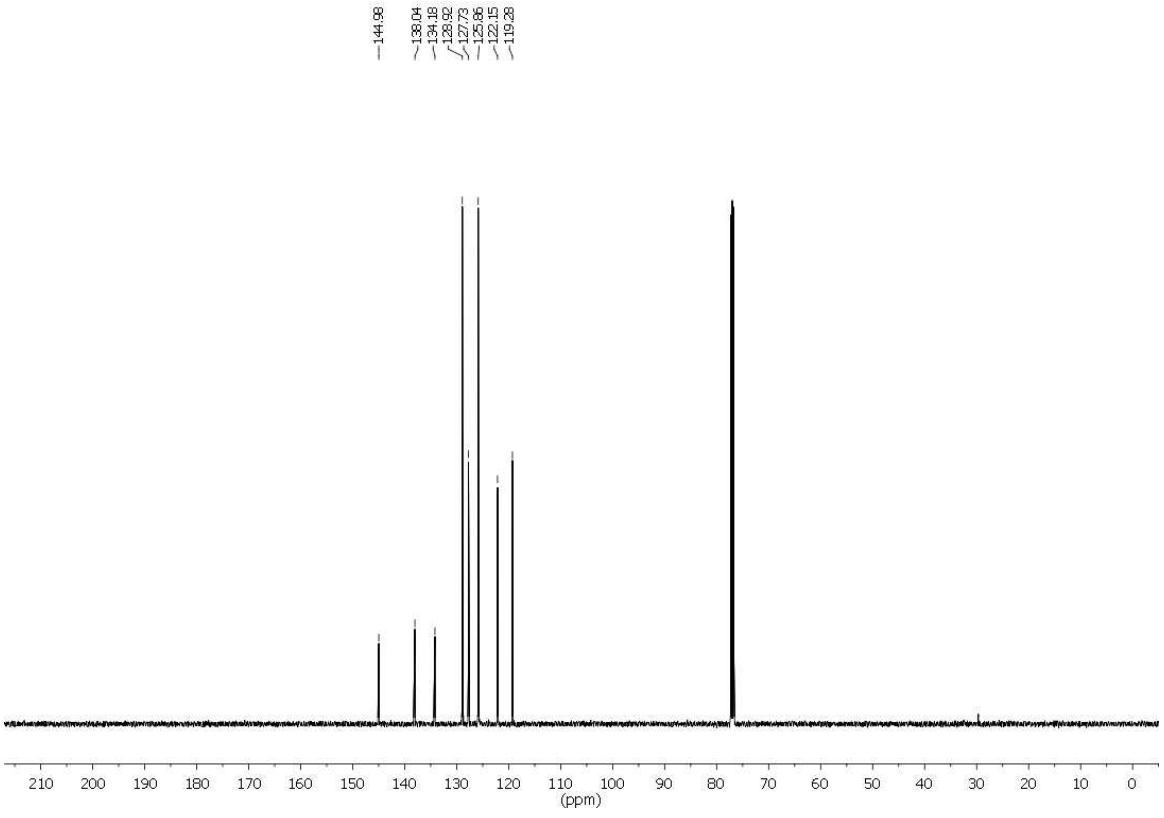
Compound 5b (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))



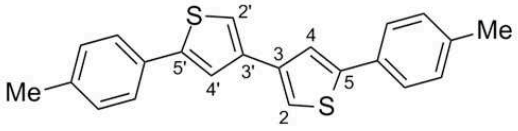


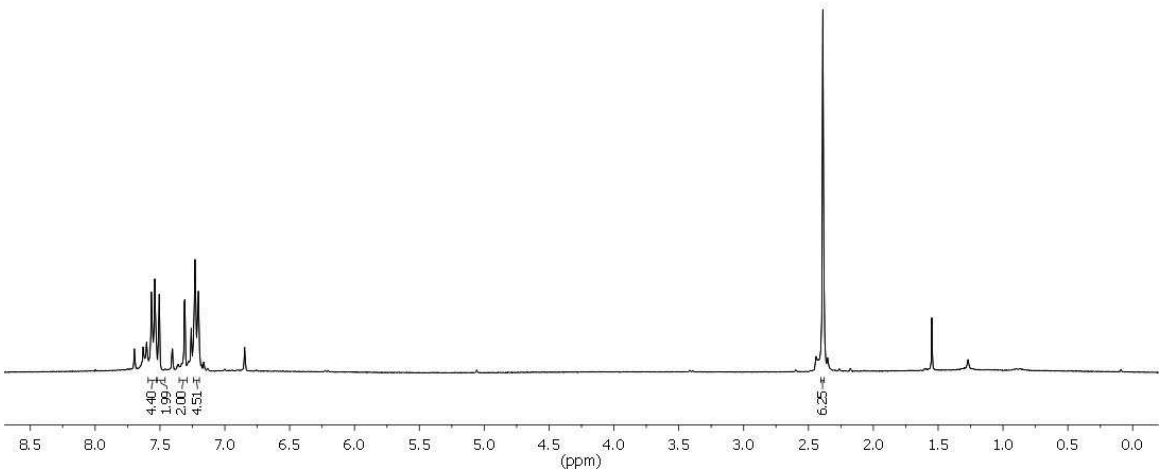
Compound 5c (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))

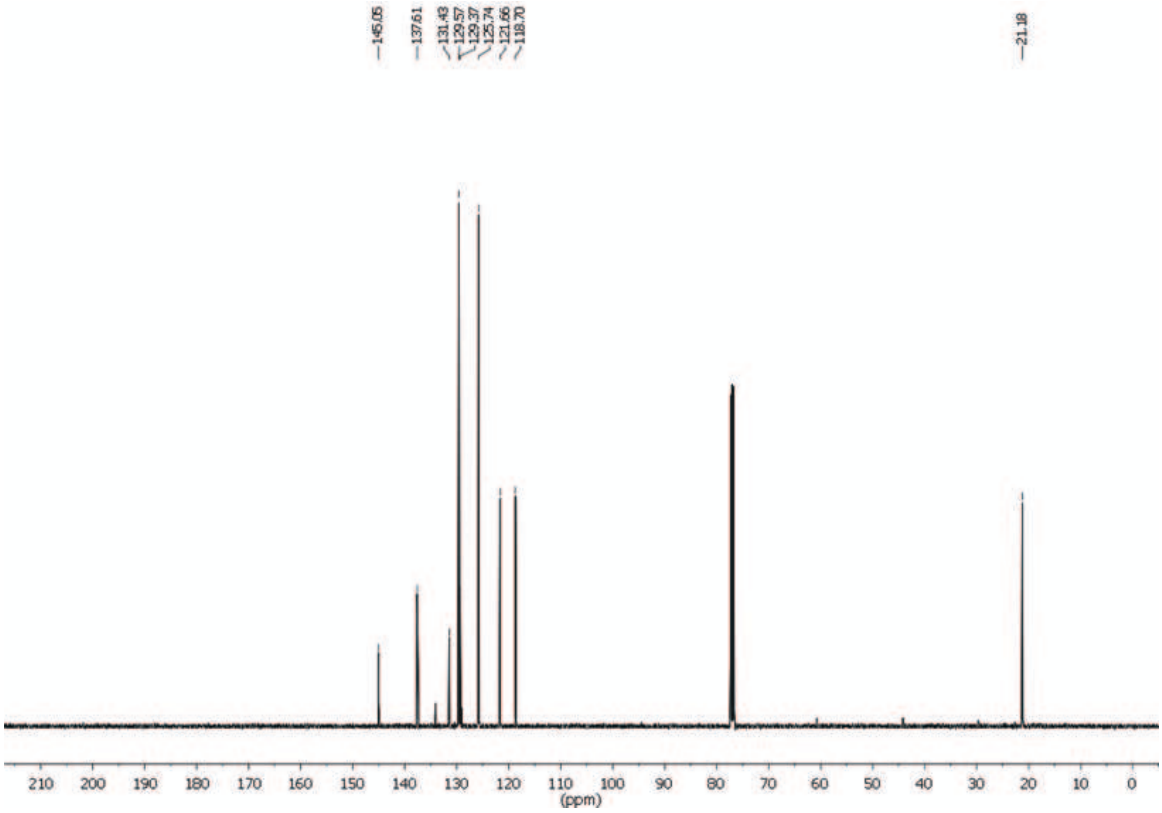




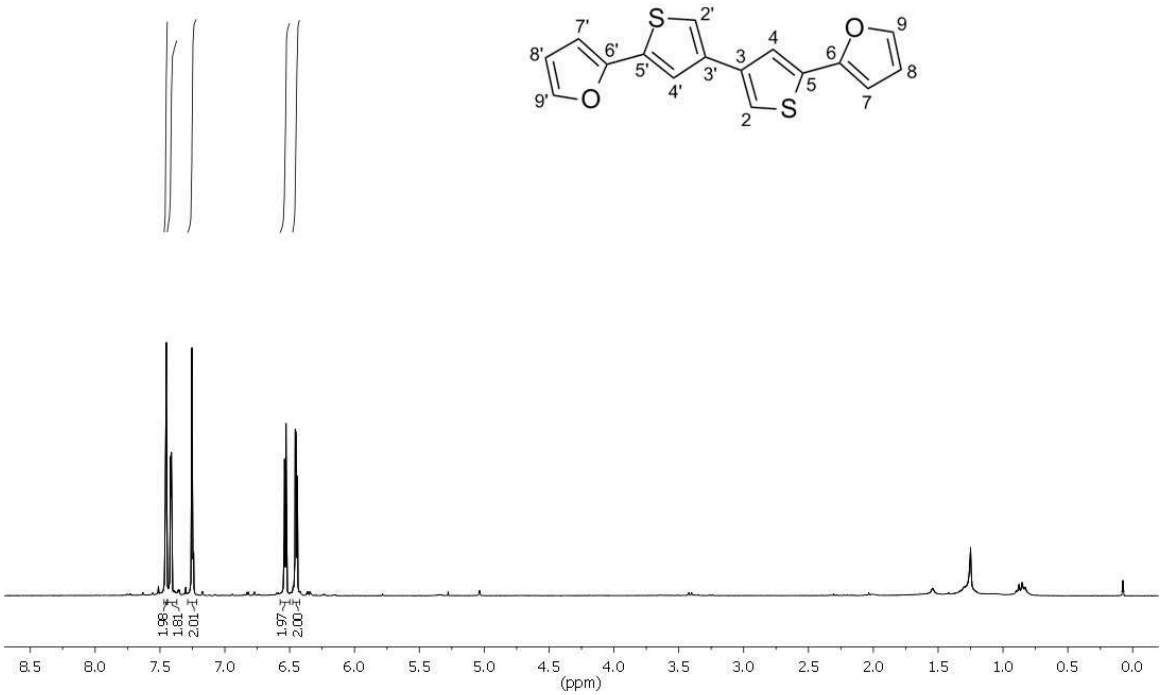
Compound 5d (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))

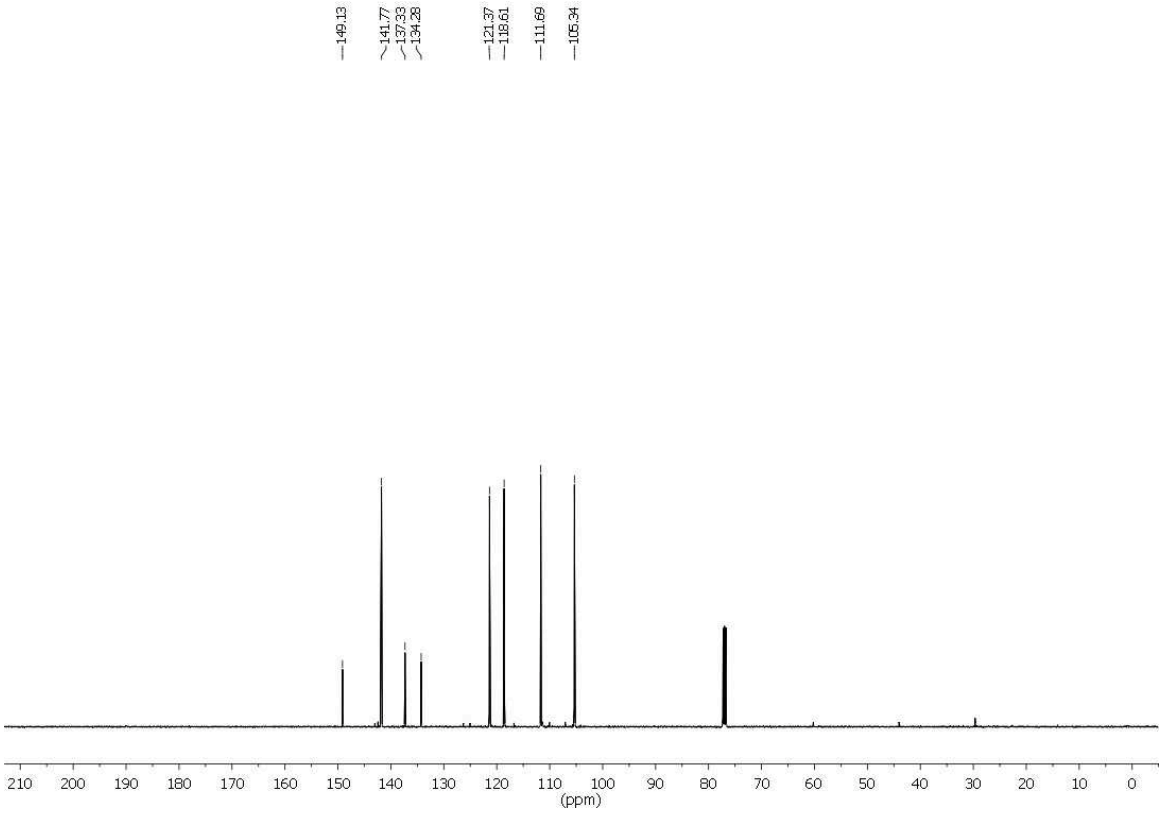




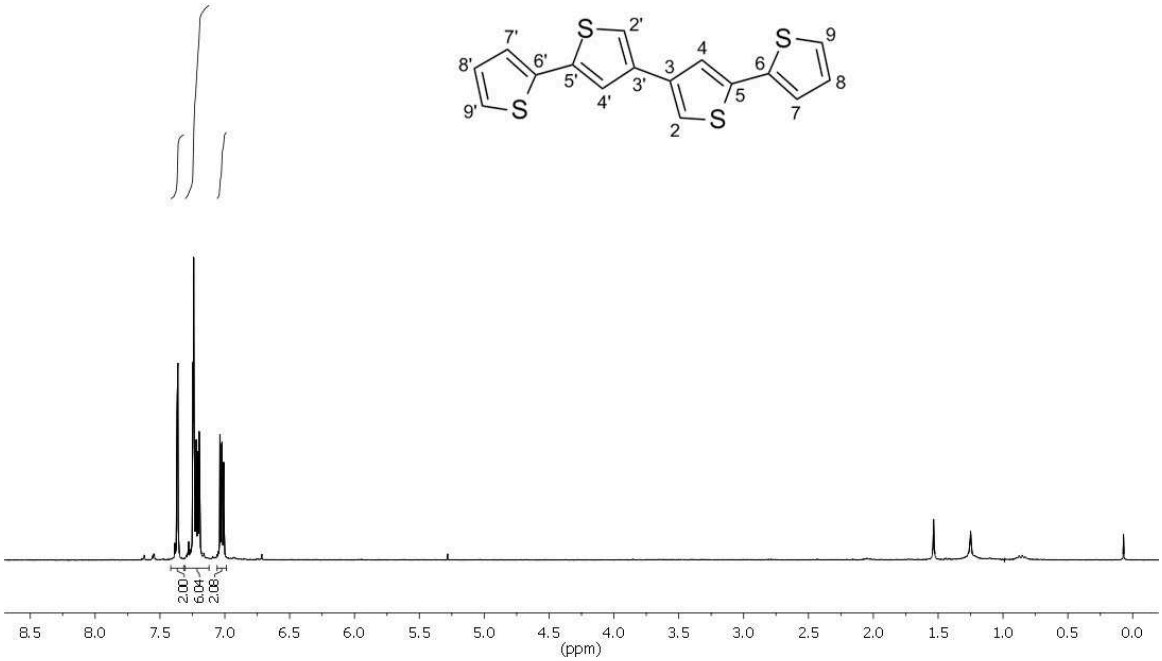


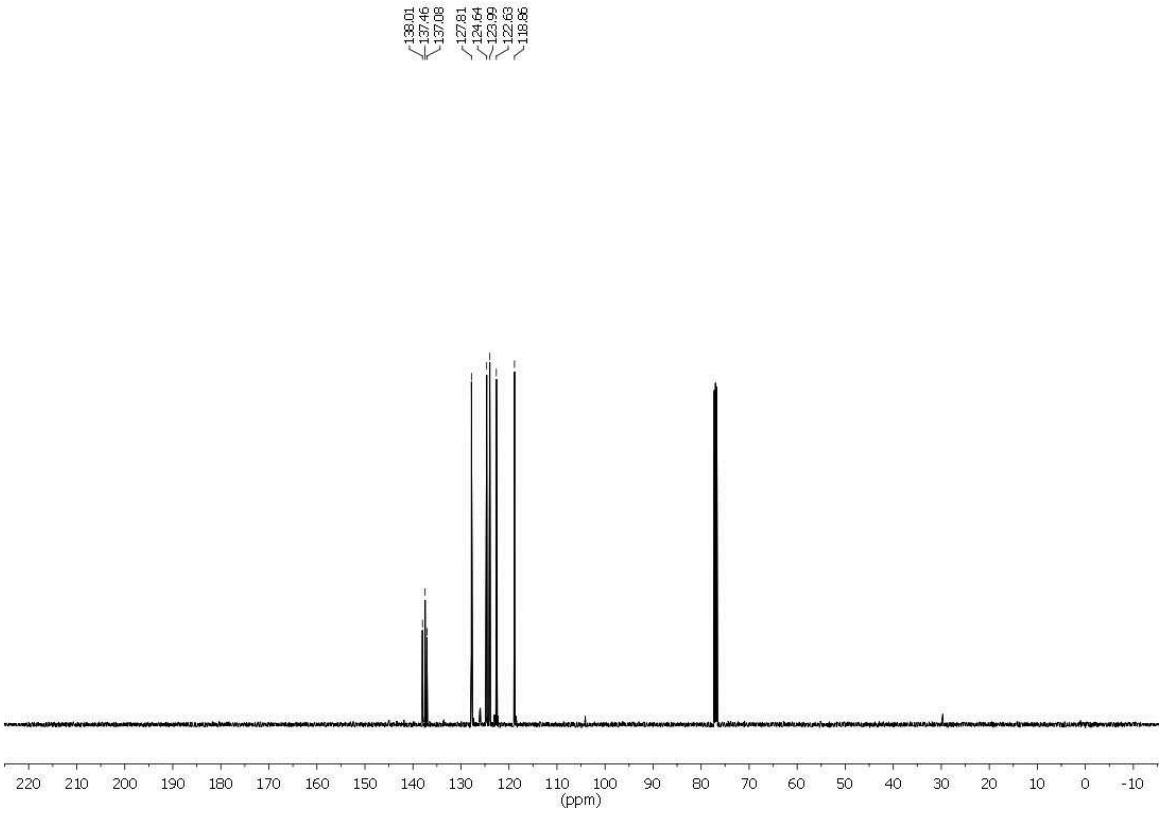
Compound 5g (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))



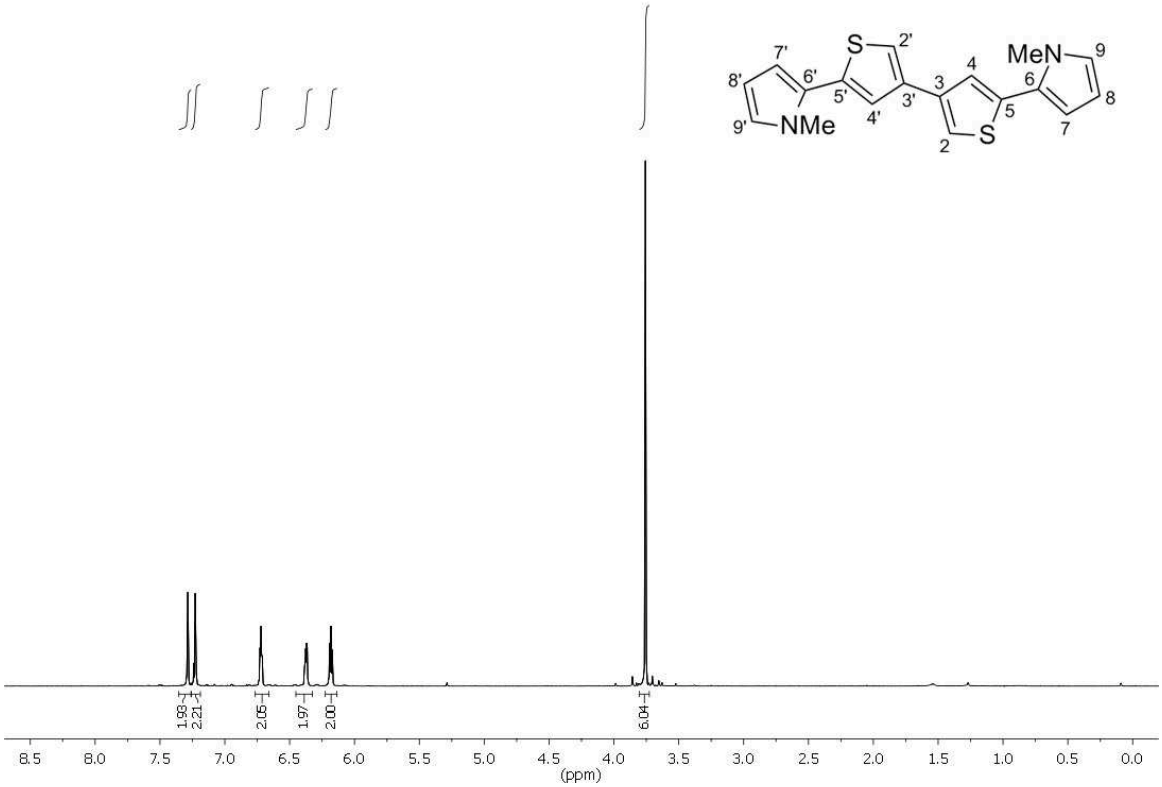


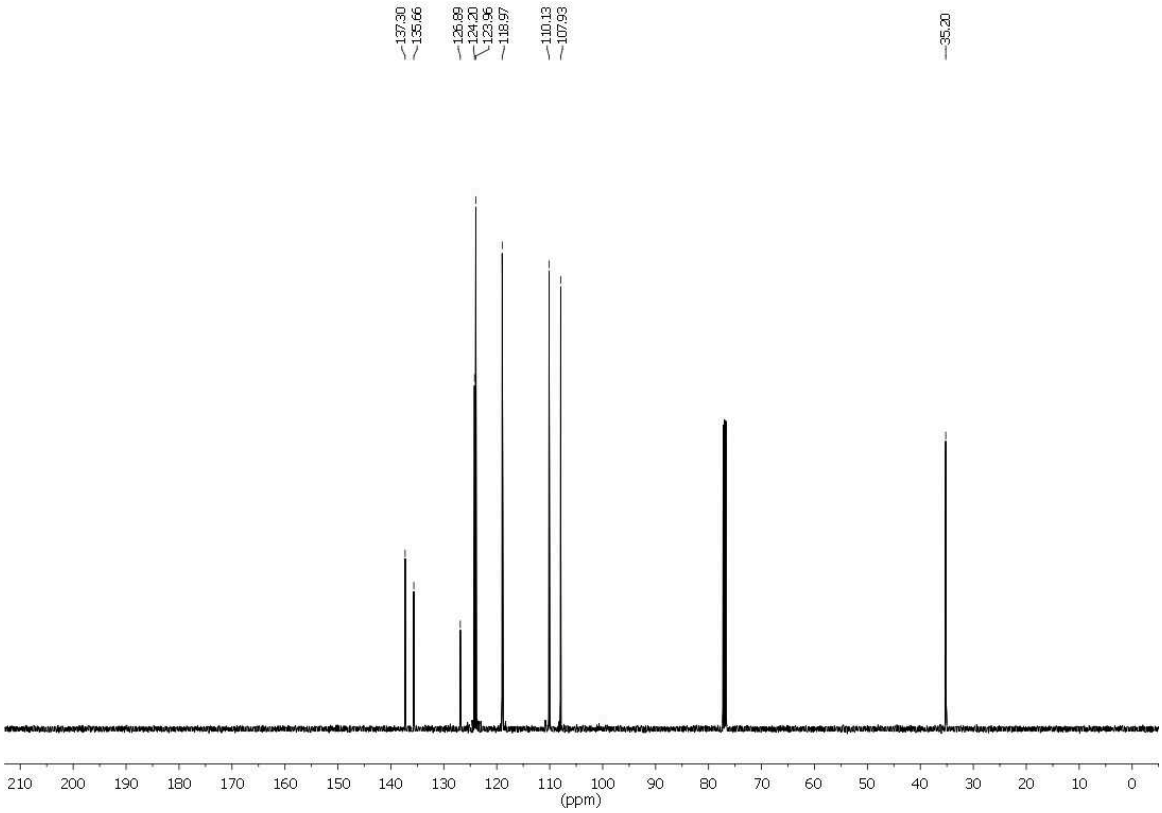
Compound 5h (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))



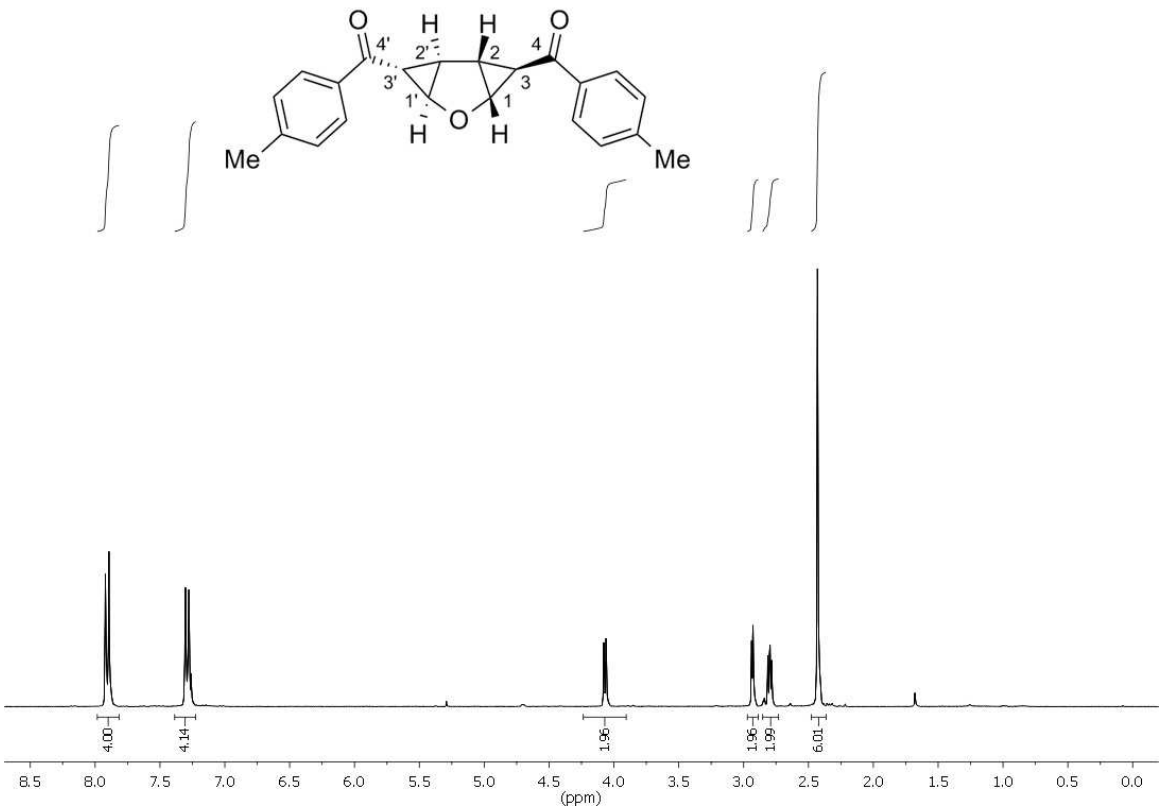


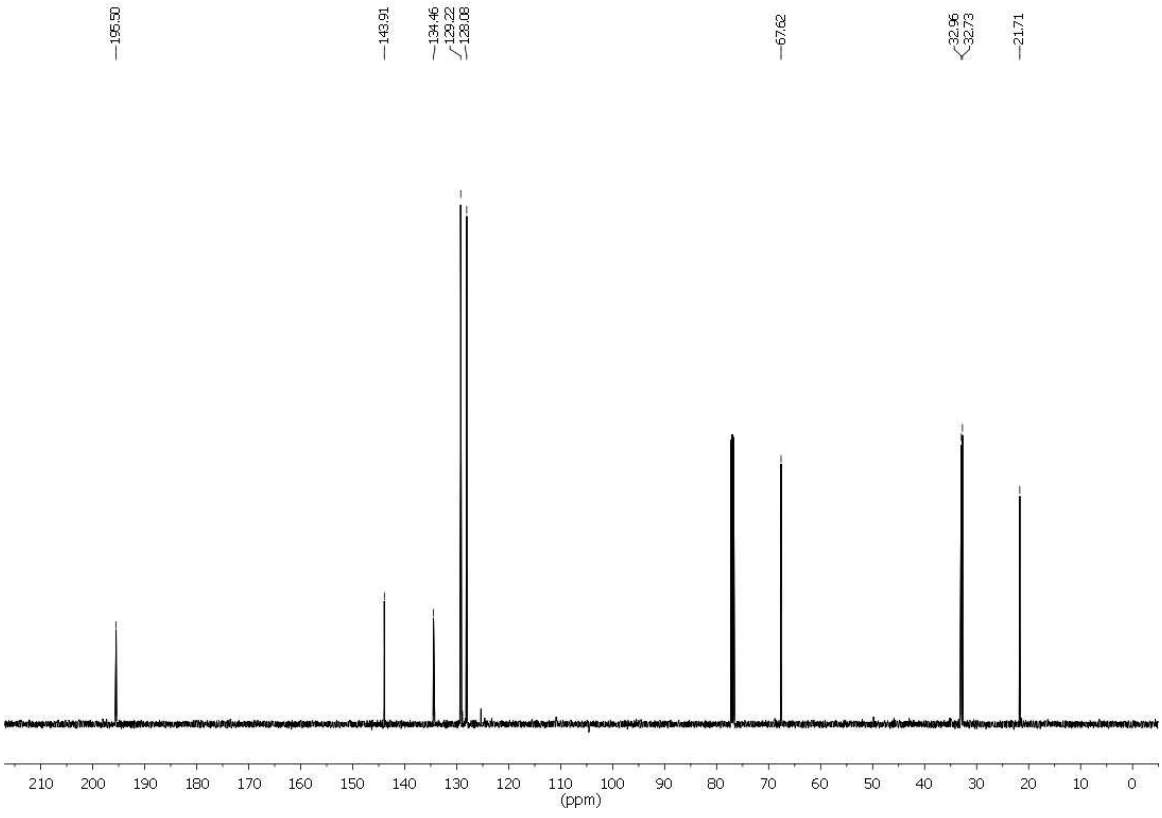
Compound 5i (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))



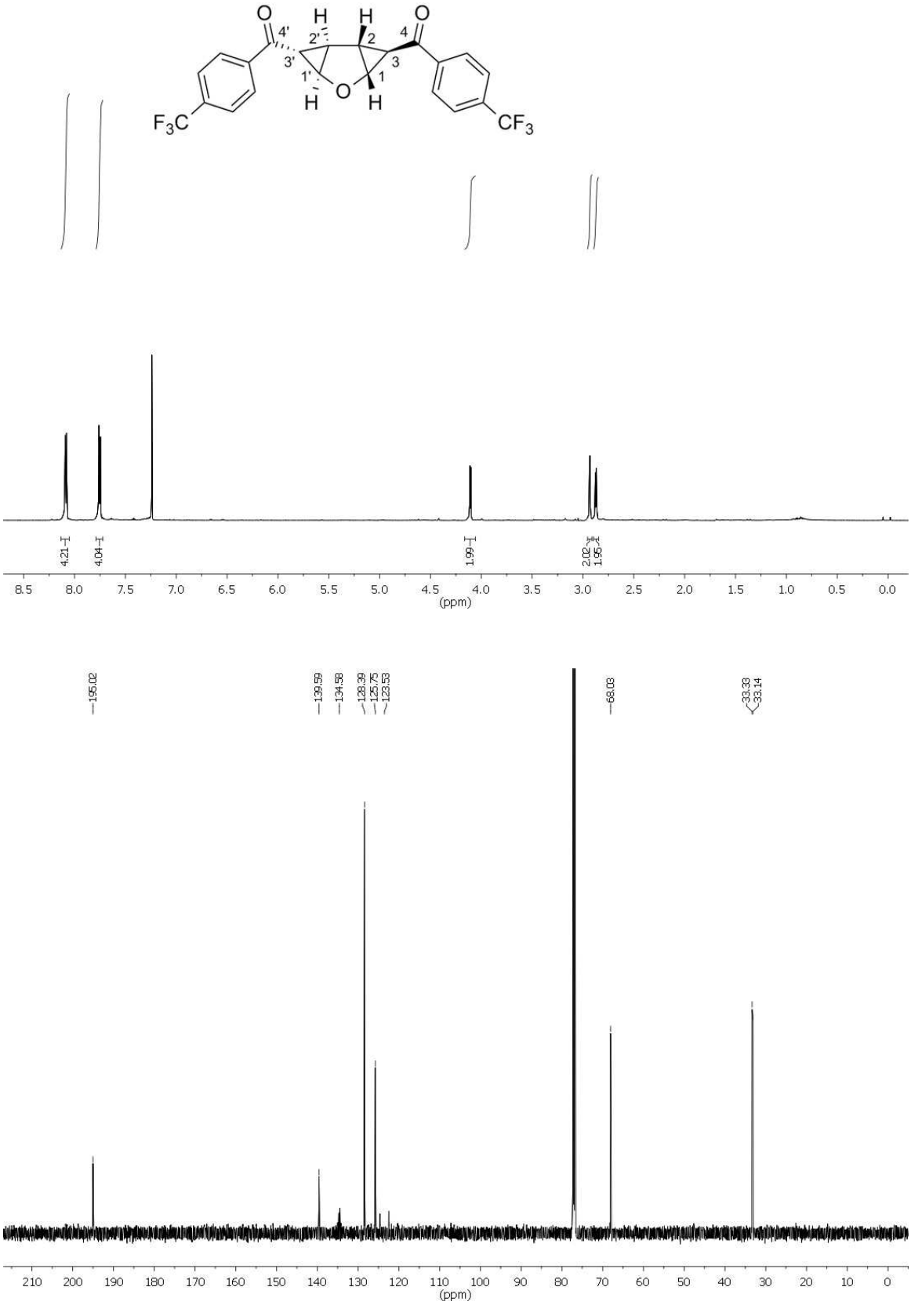


Compound 6d (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))

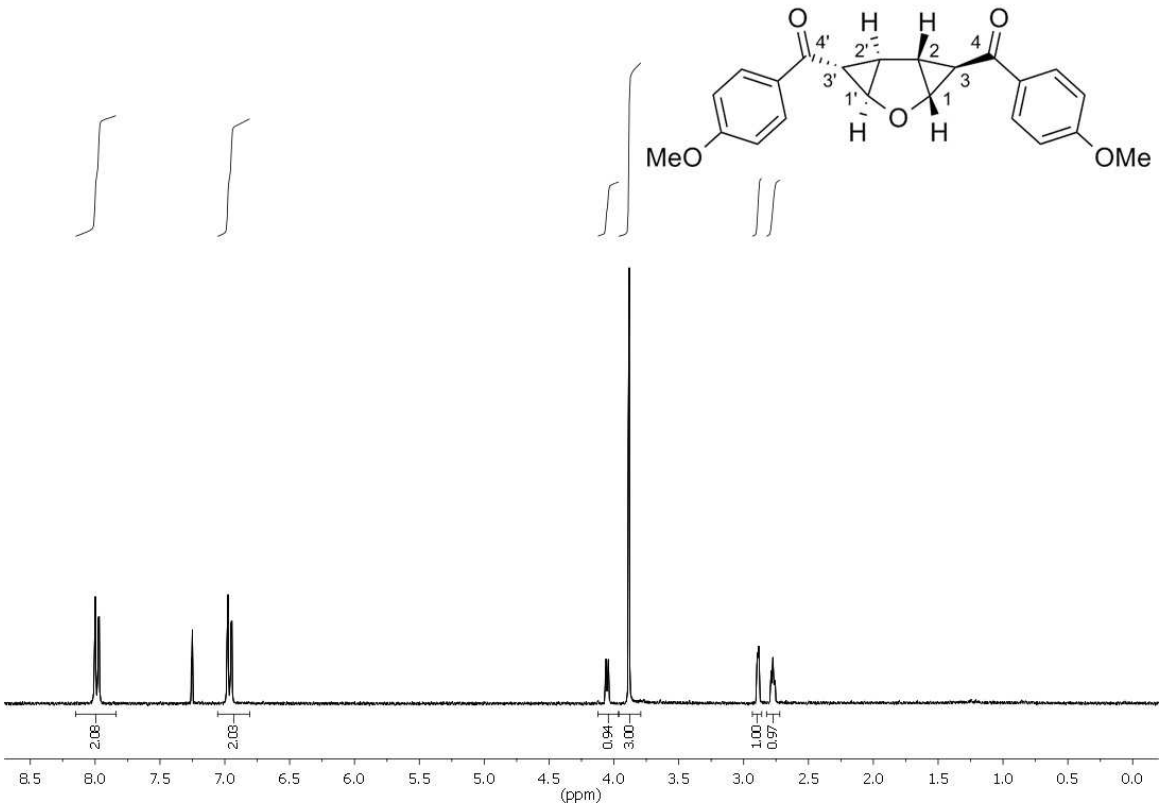


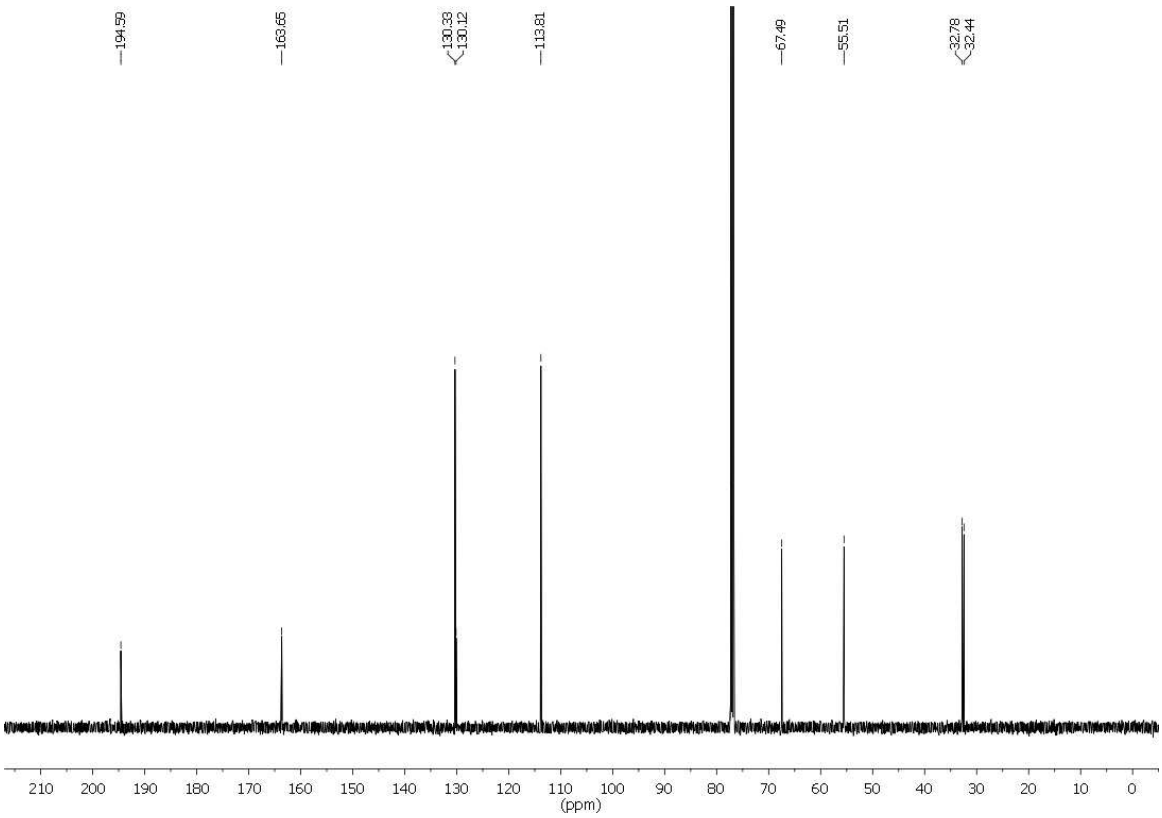


Compound 6e (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))

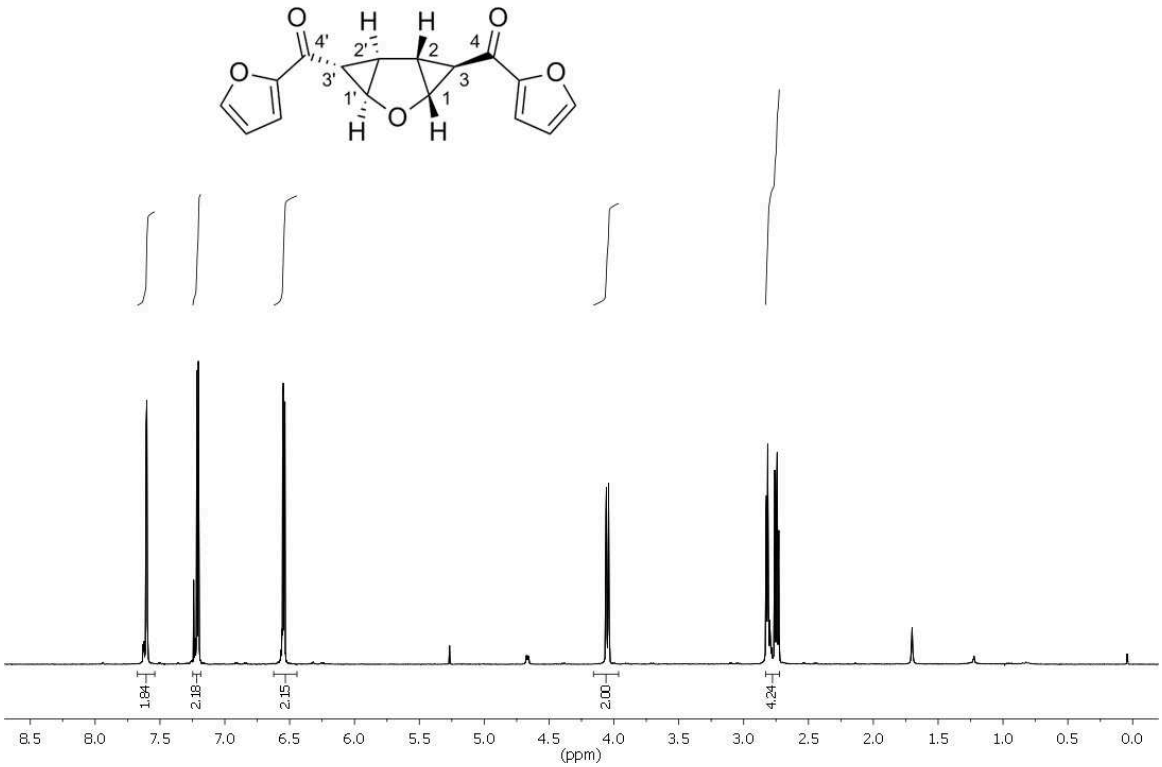


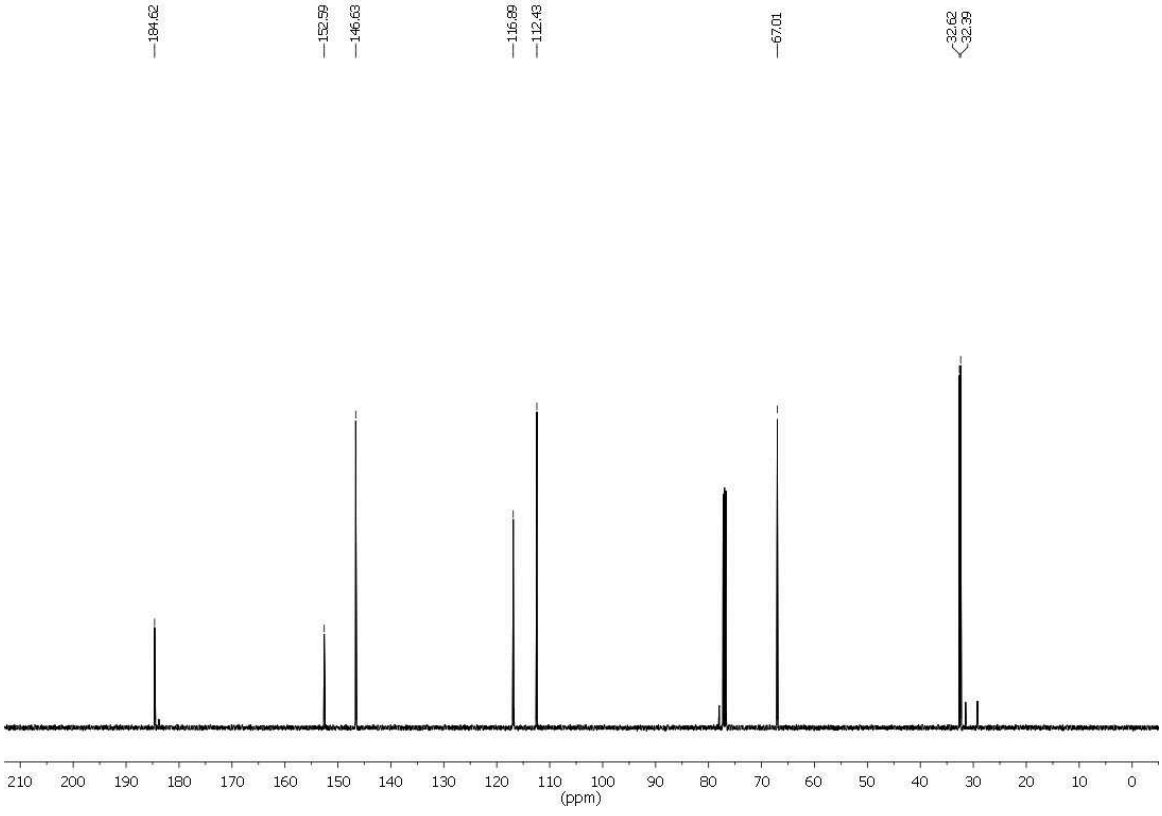
Compound 6f (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))



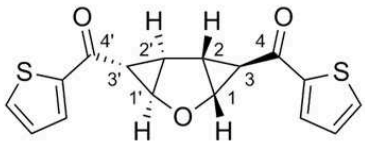


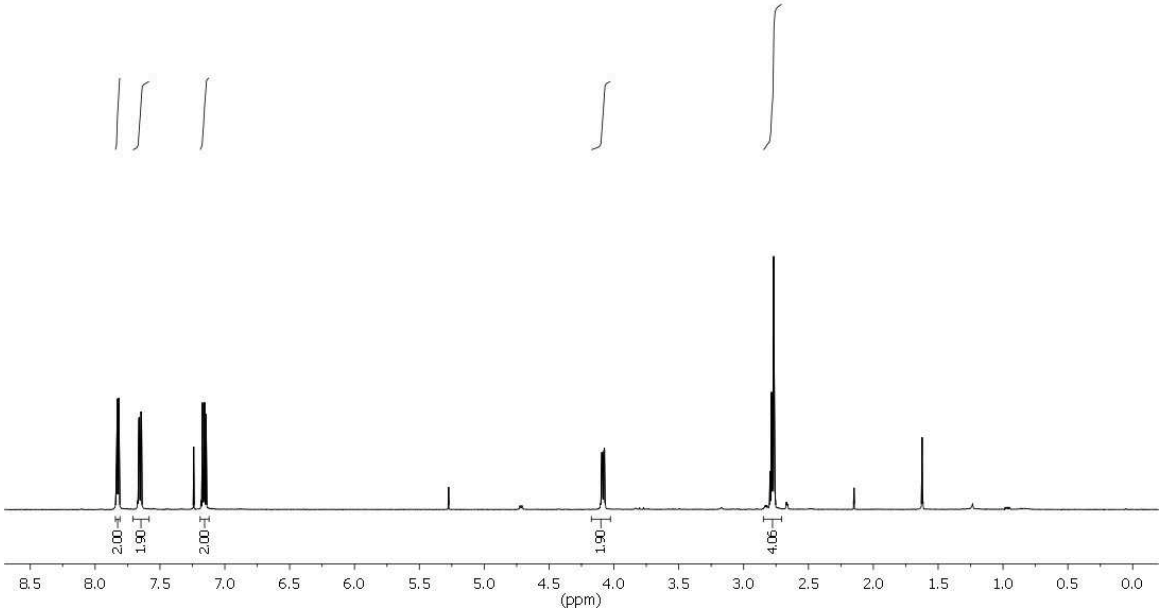
Compound 6g (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))

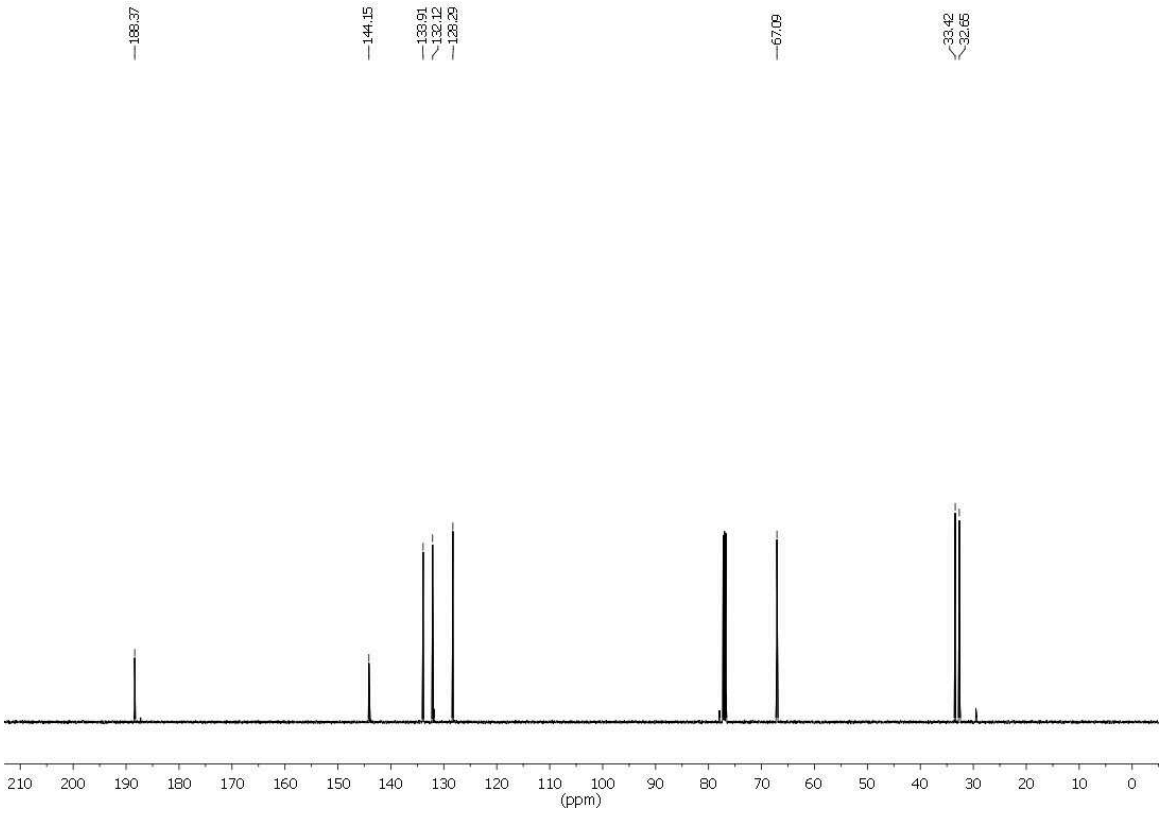




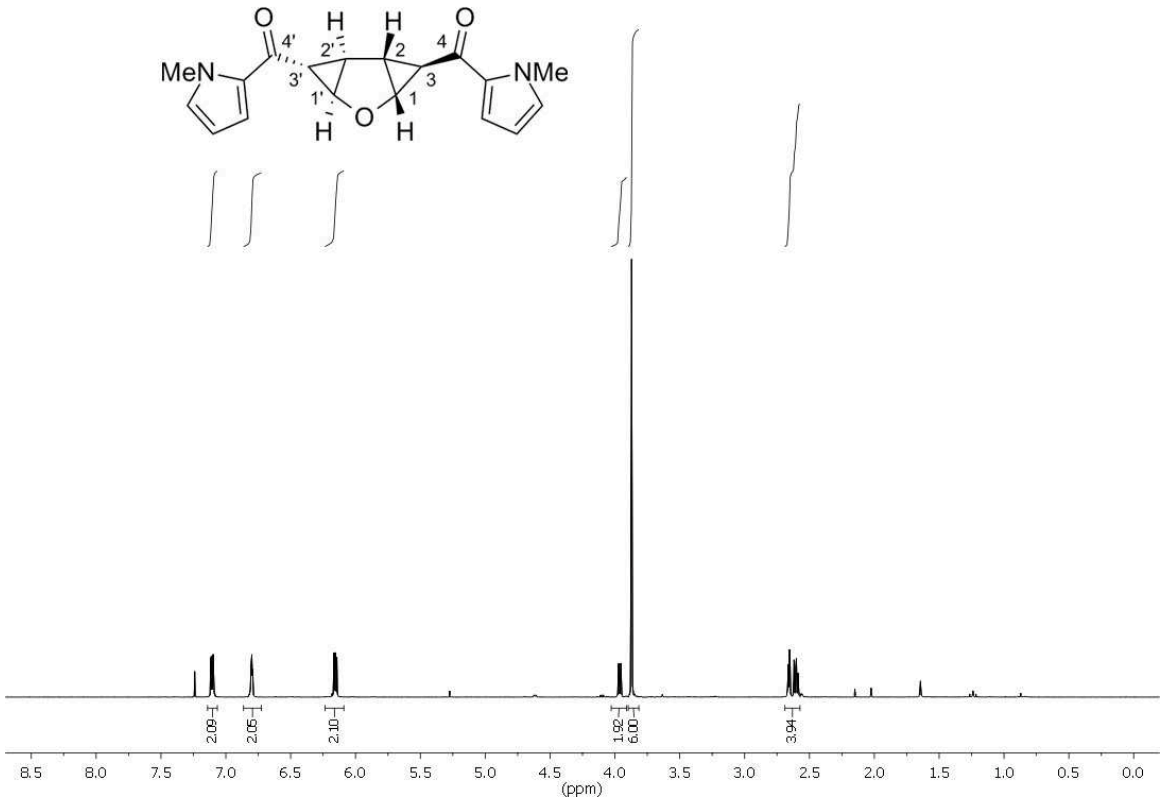
Compound 6h (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))

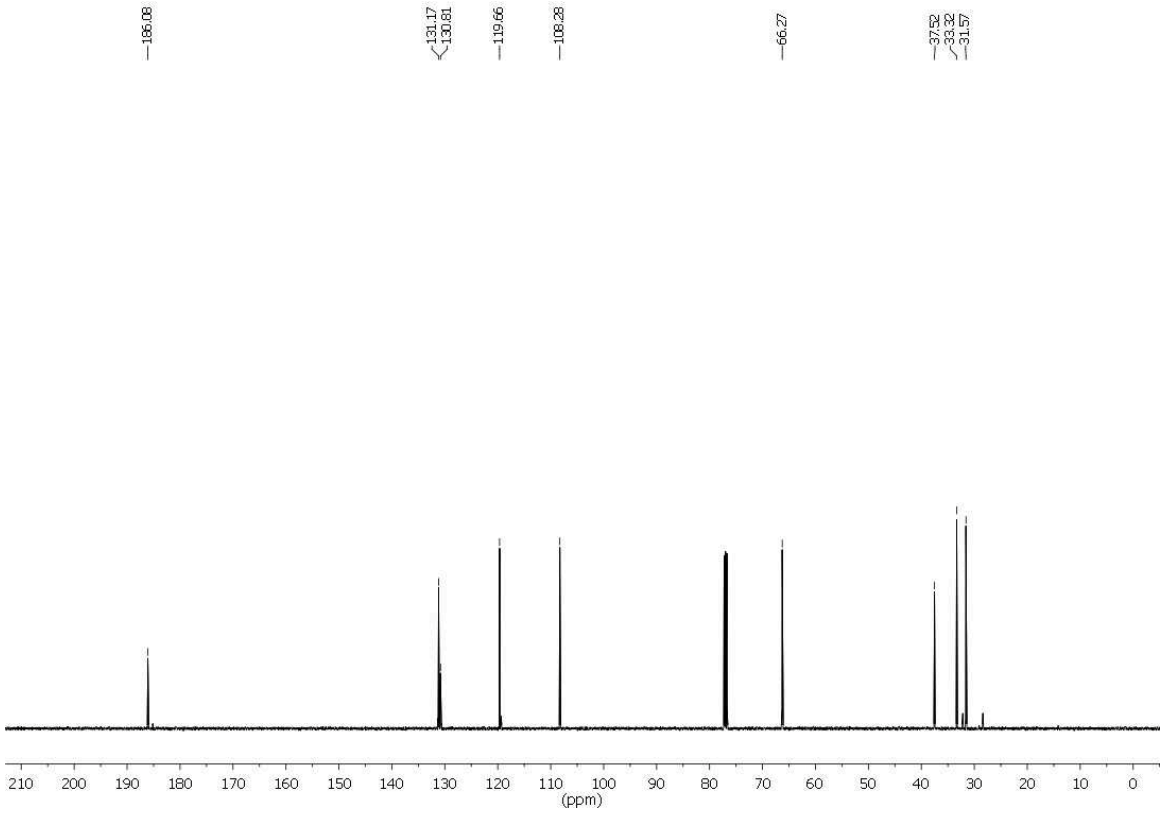




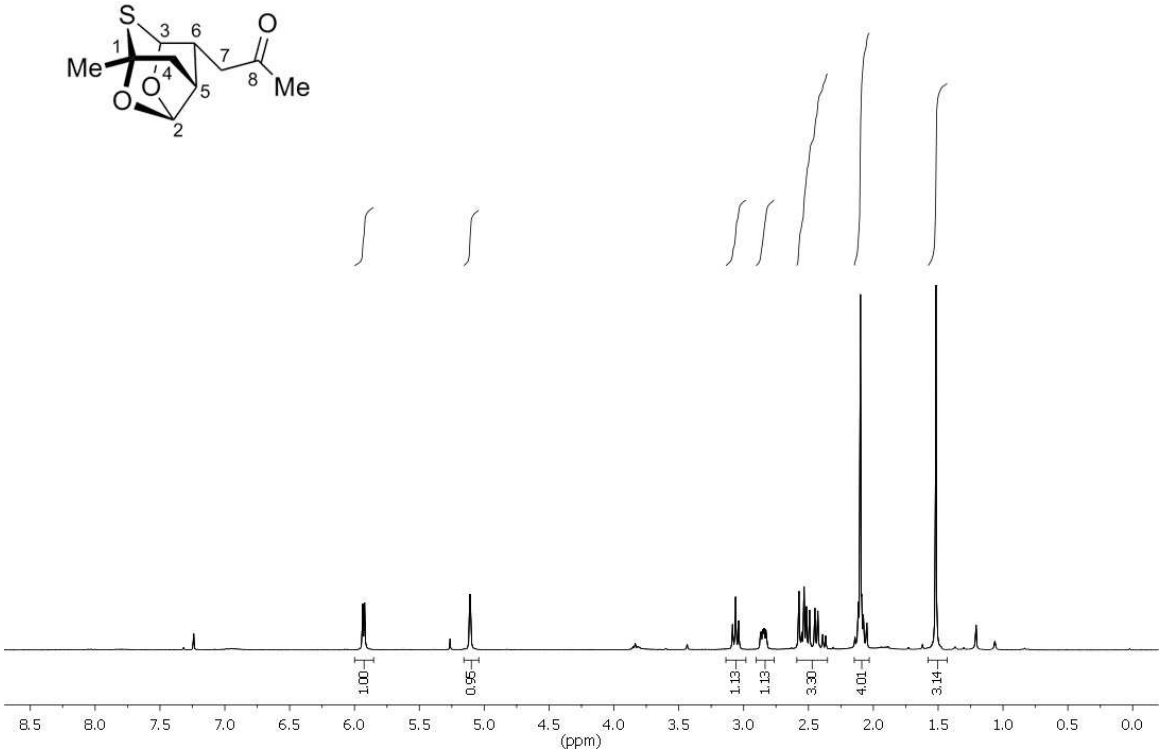


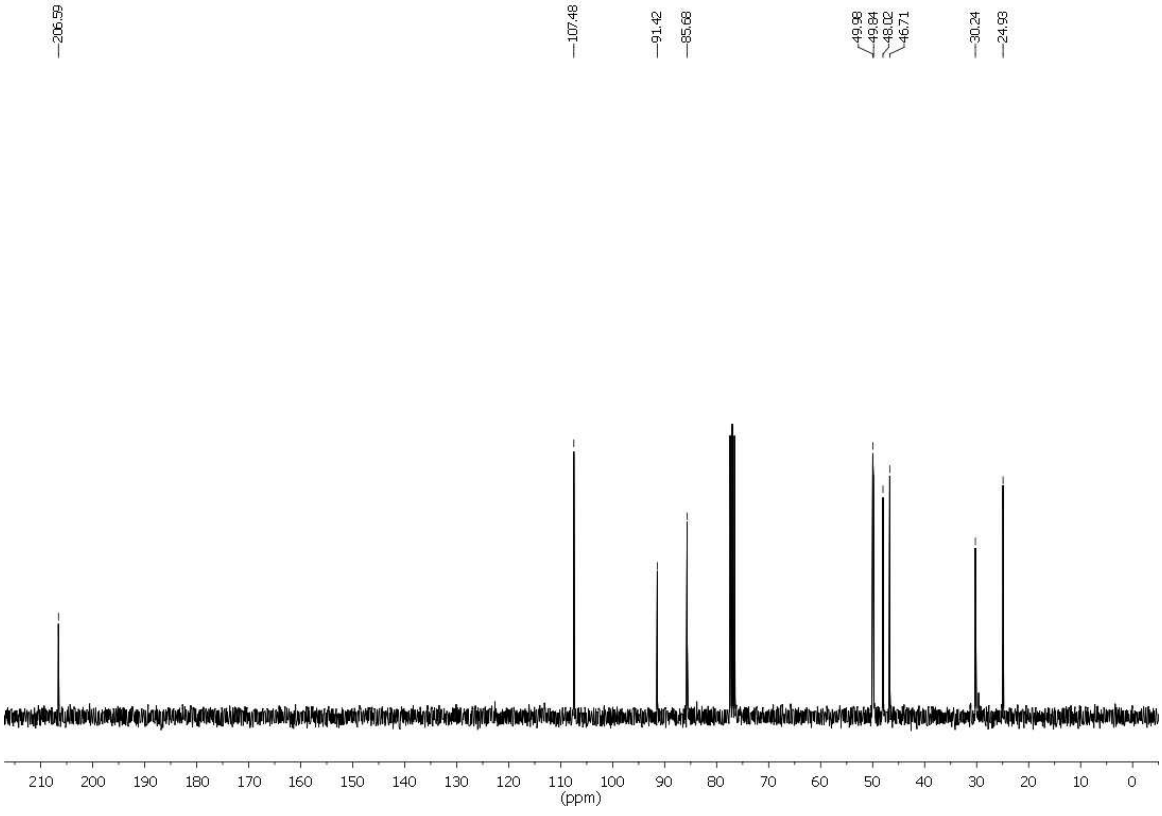
Compound 6i (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))



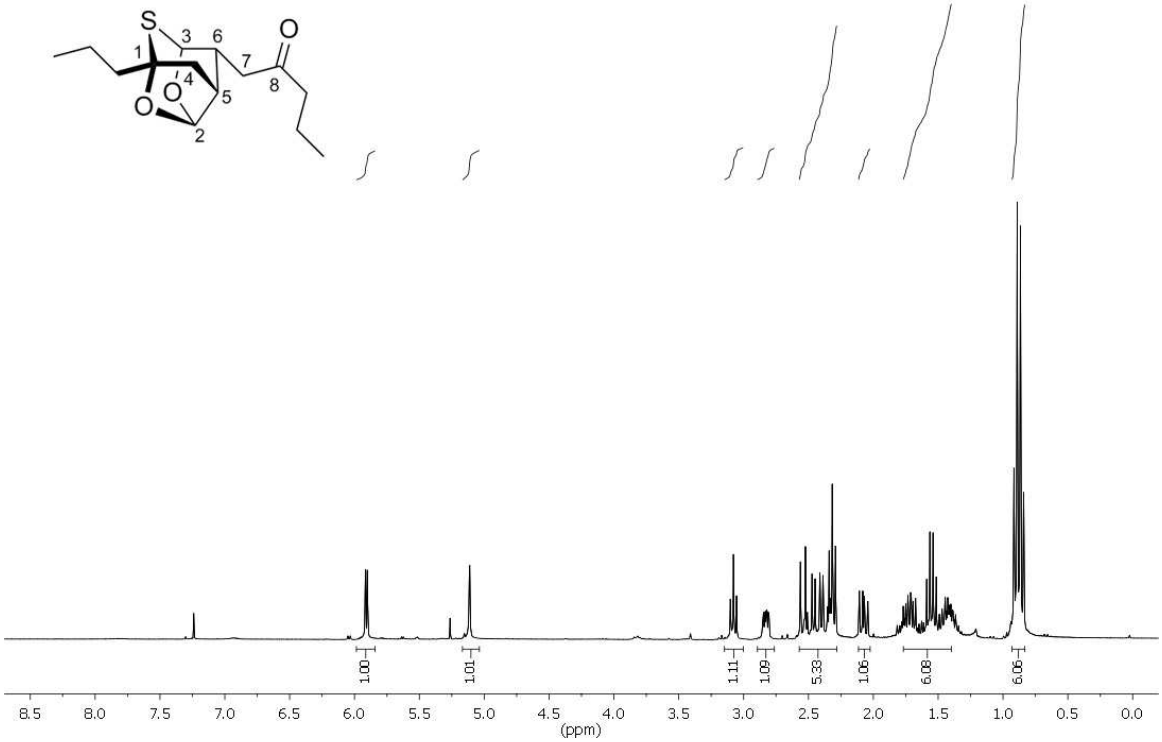


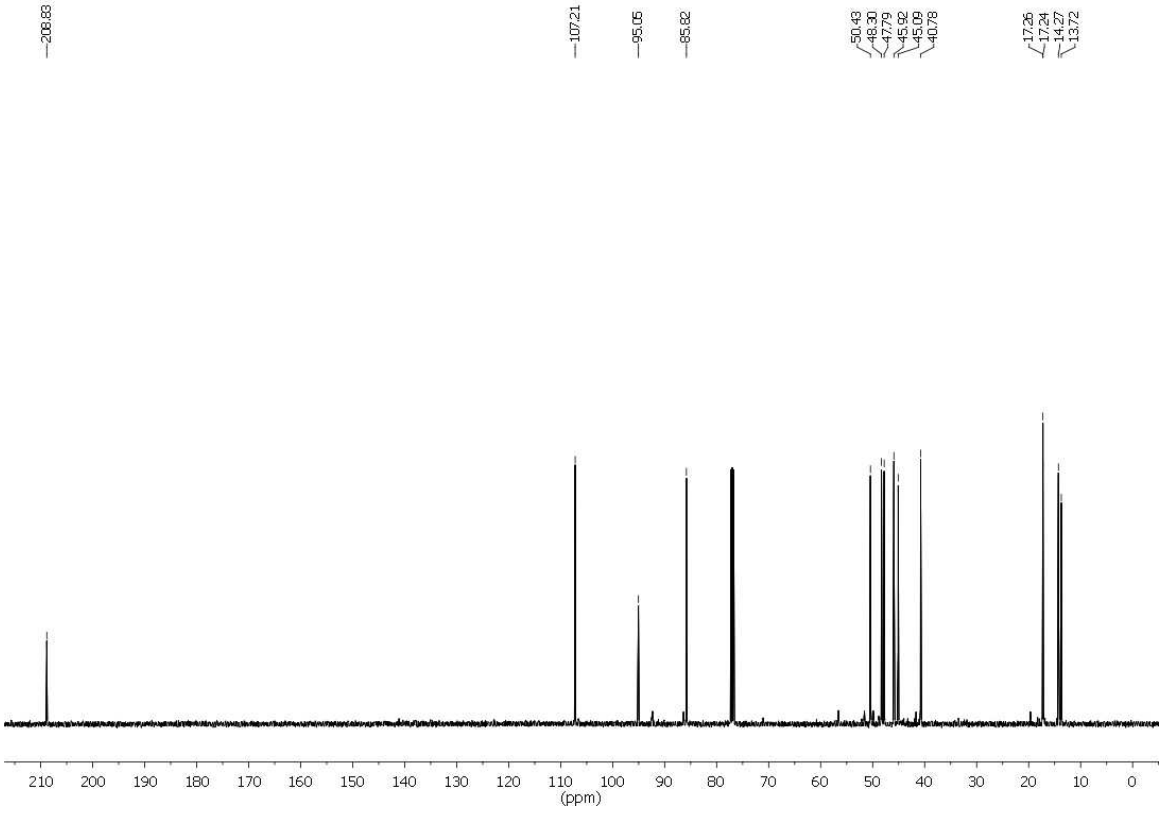
Compound 8a (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (75 MHz, $CDCl_3$))



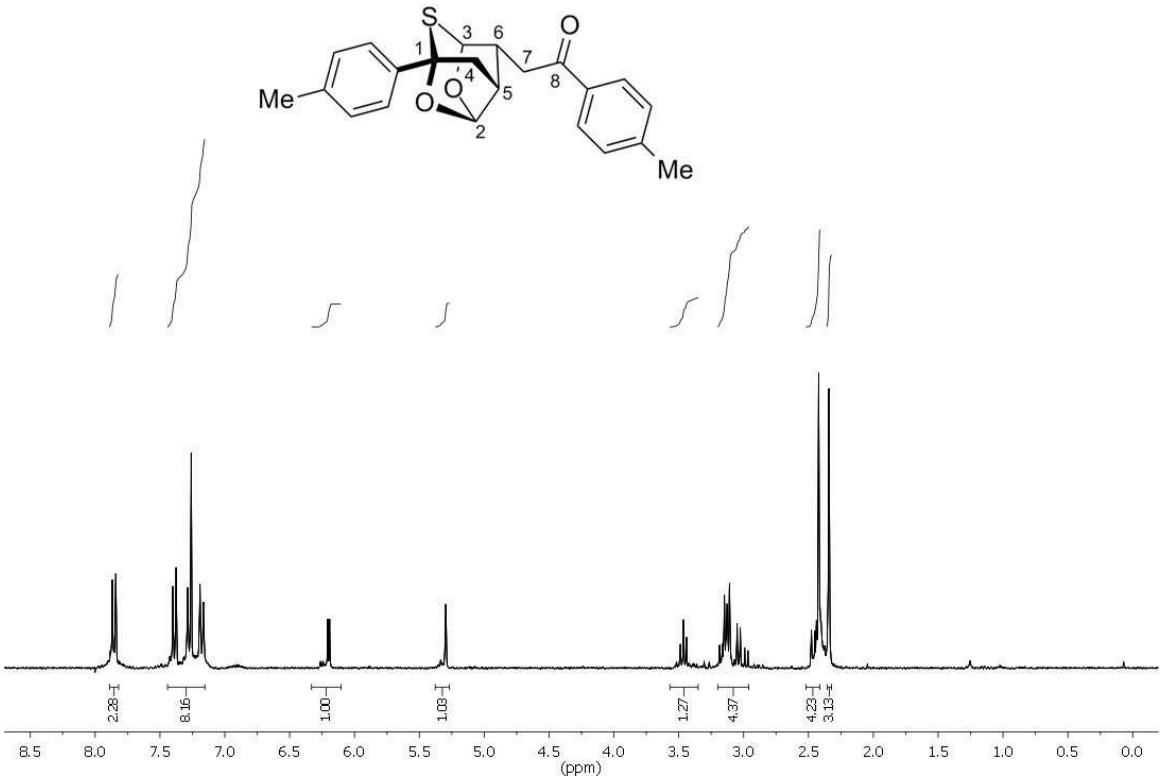


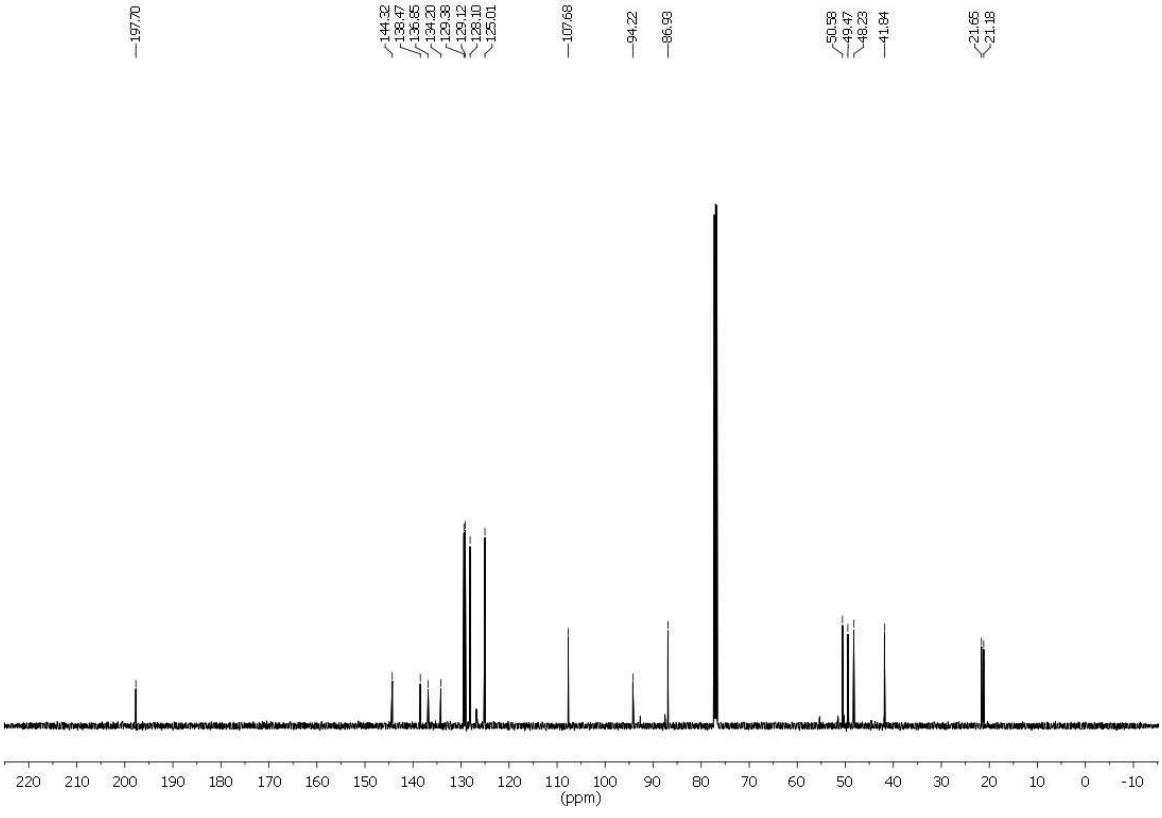
Compound 8b (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))



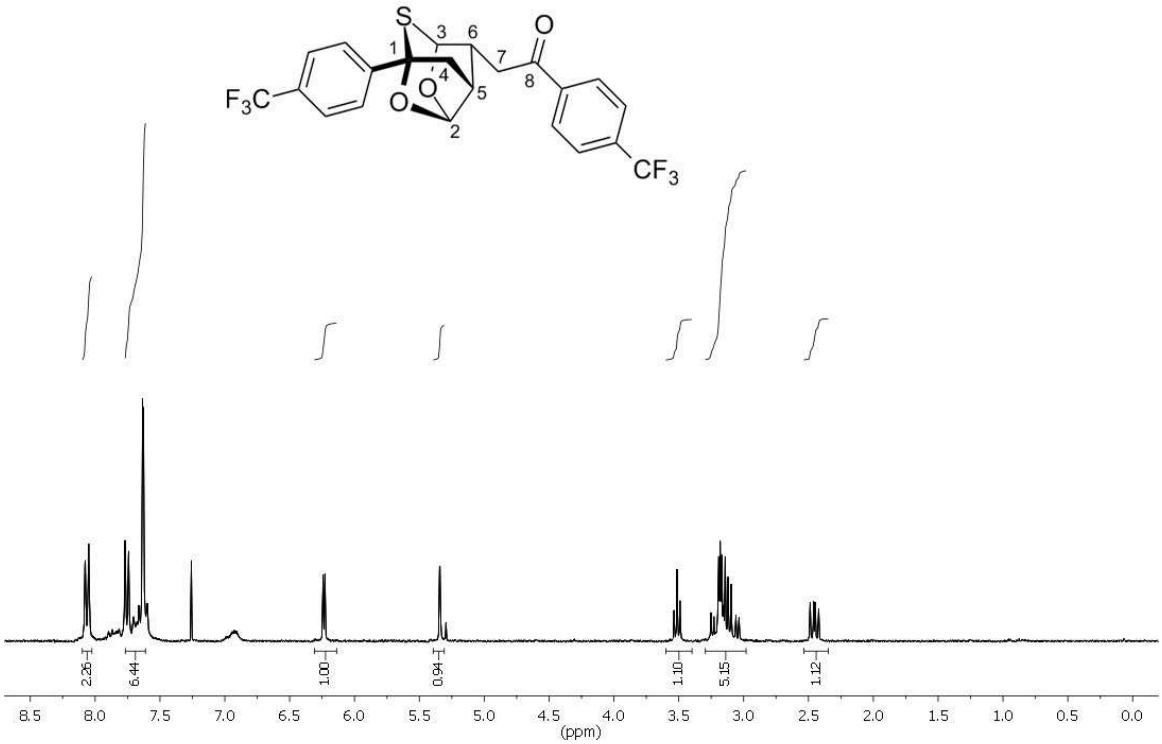


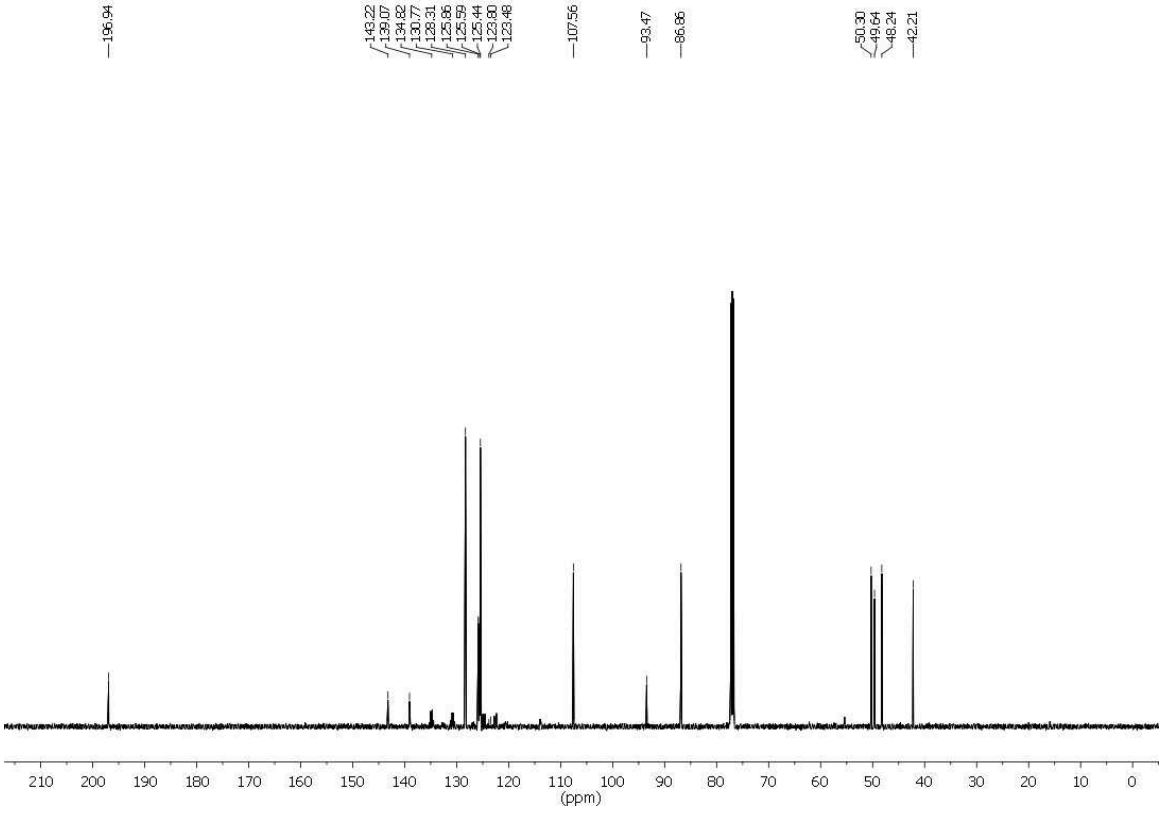
Compound 8d (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (75 MHz, $CDCl_3$))



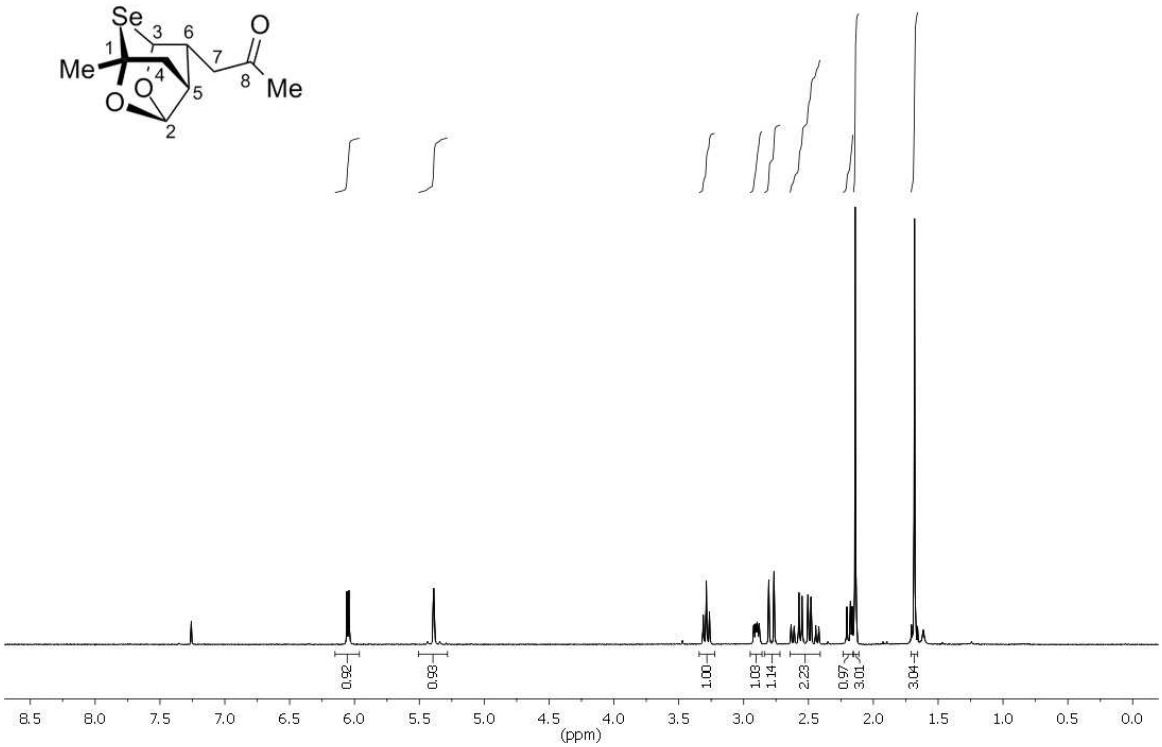


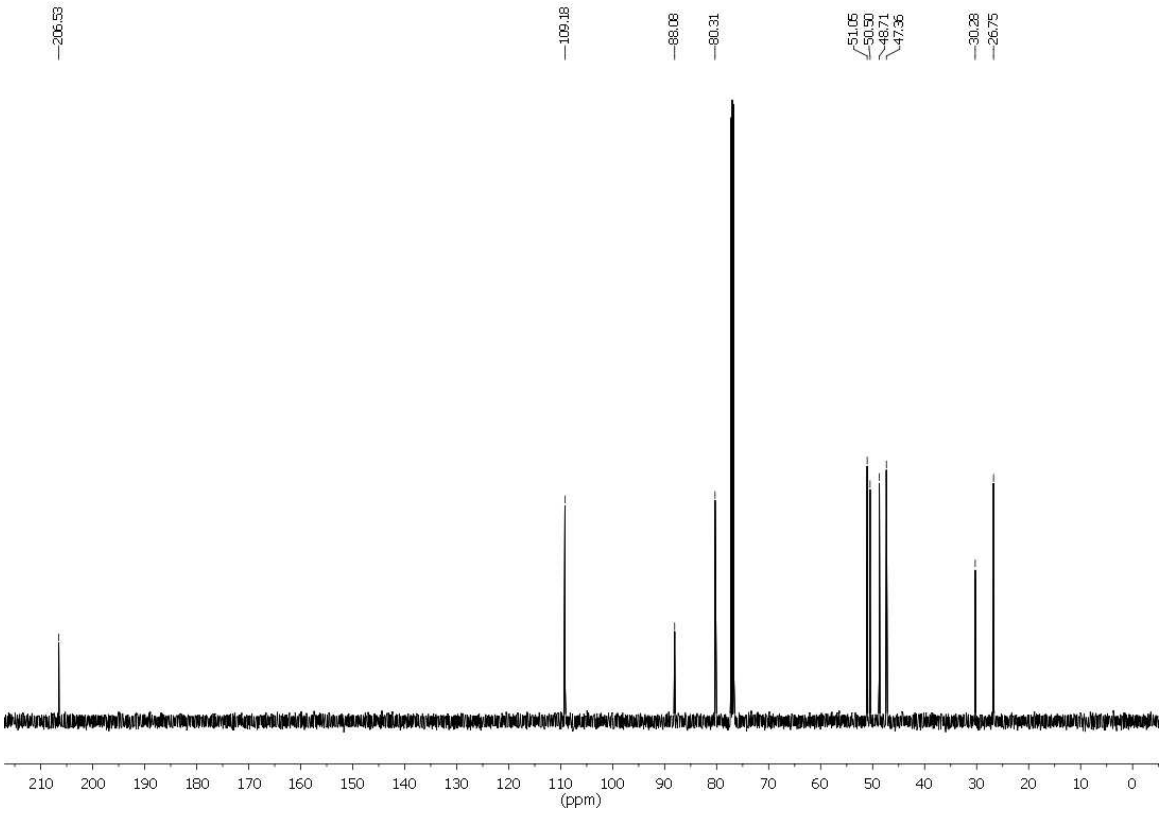
Compound 8e (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))



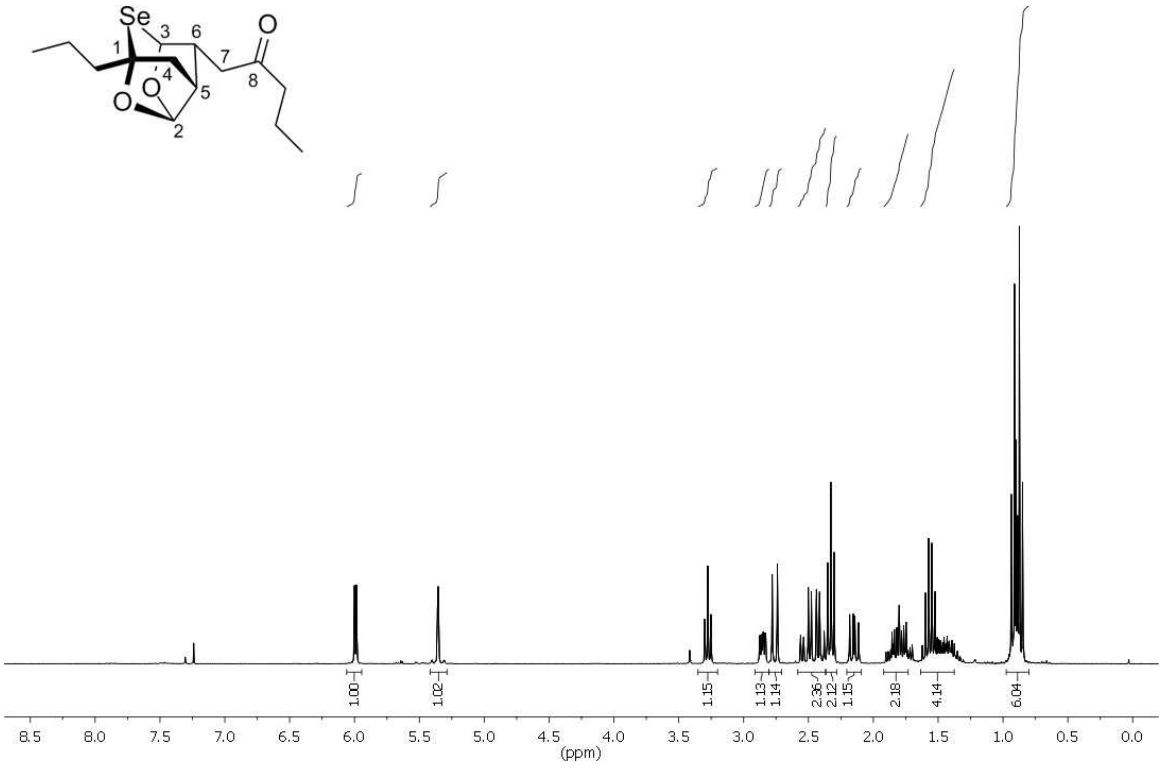


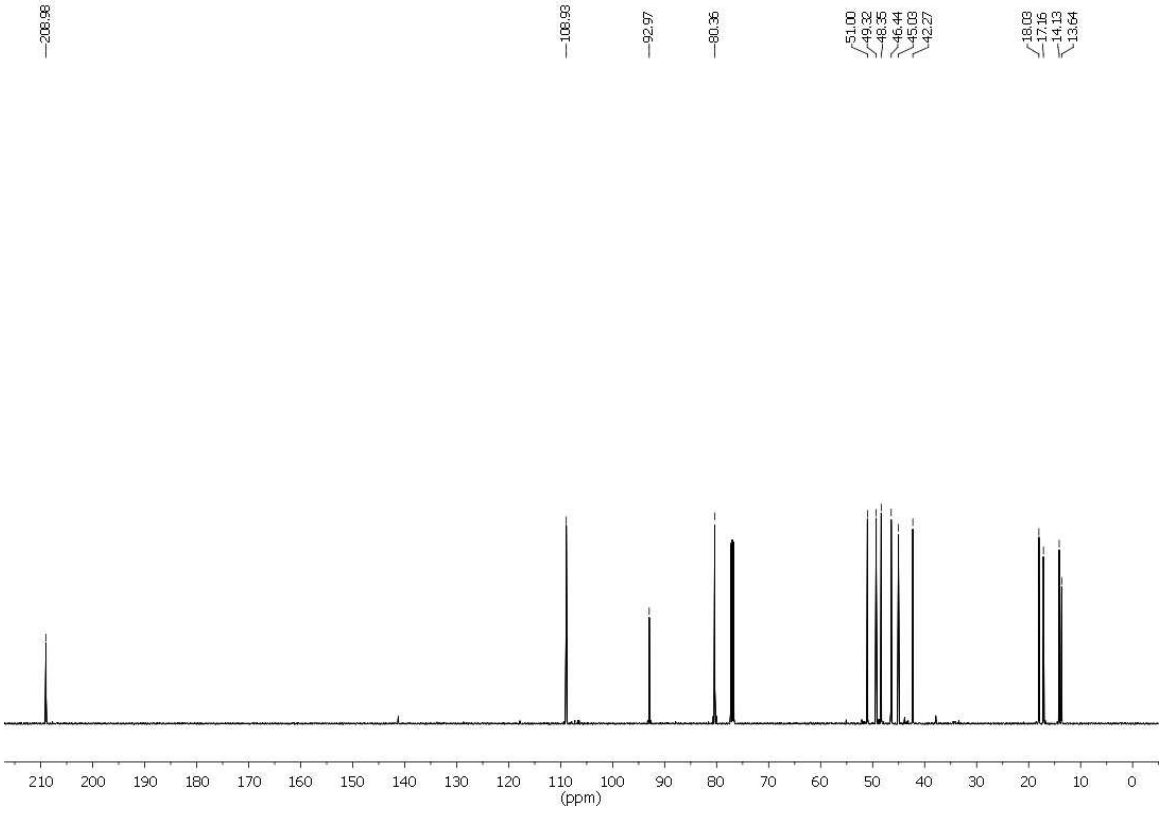
Compound 9a (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))



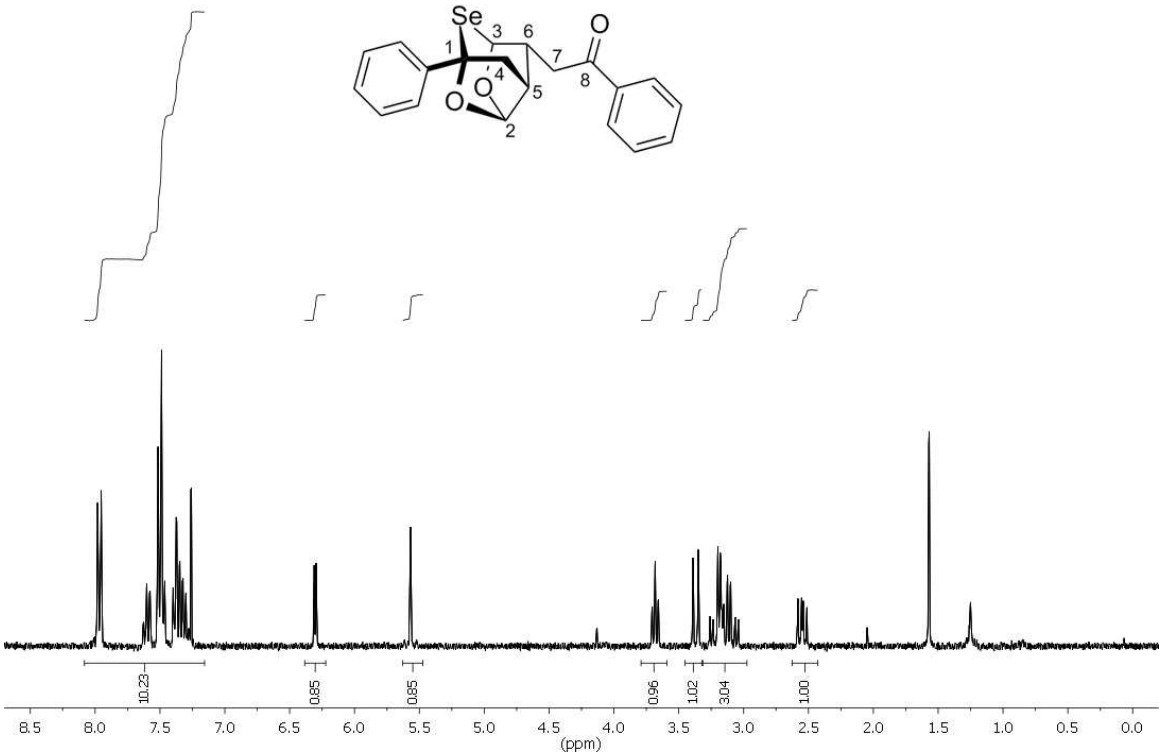


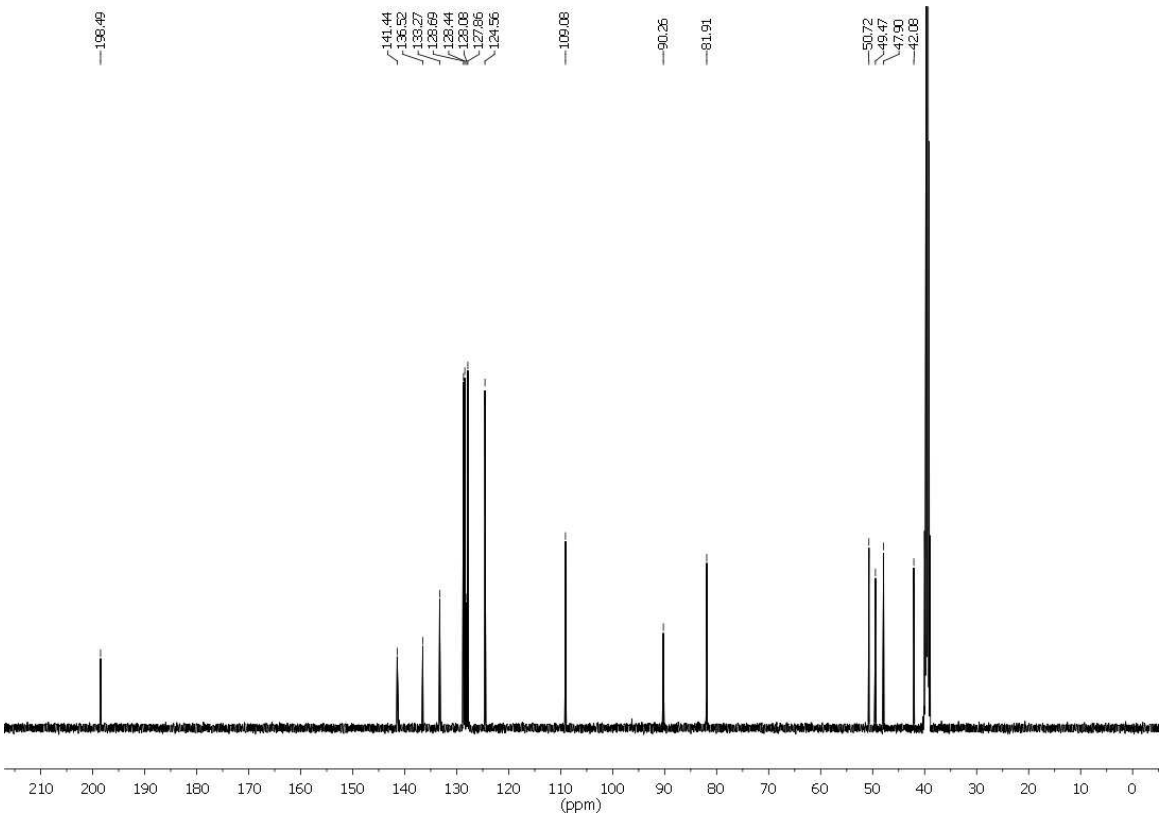
Compound 9b (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))



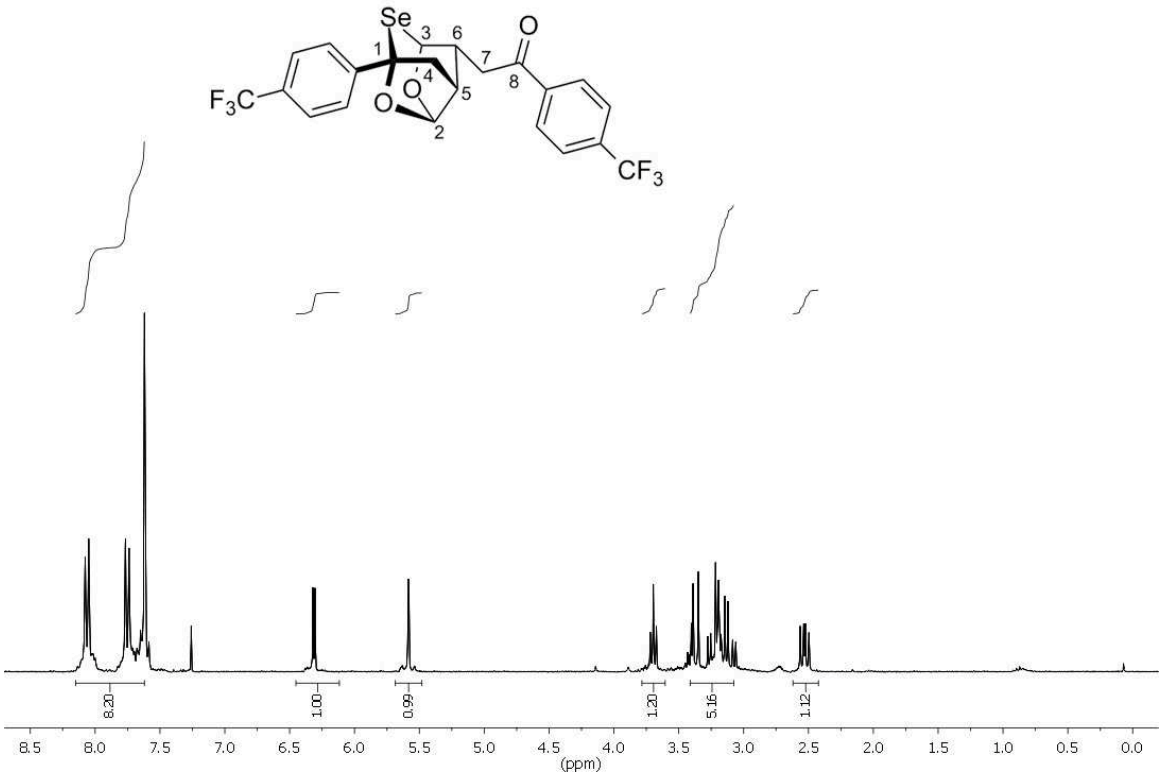


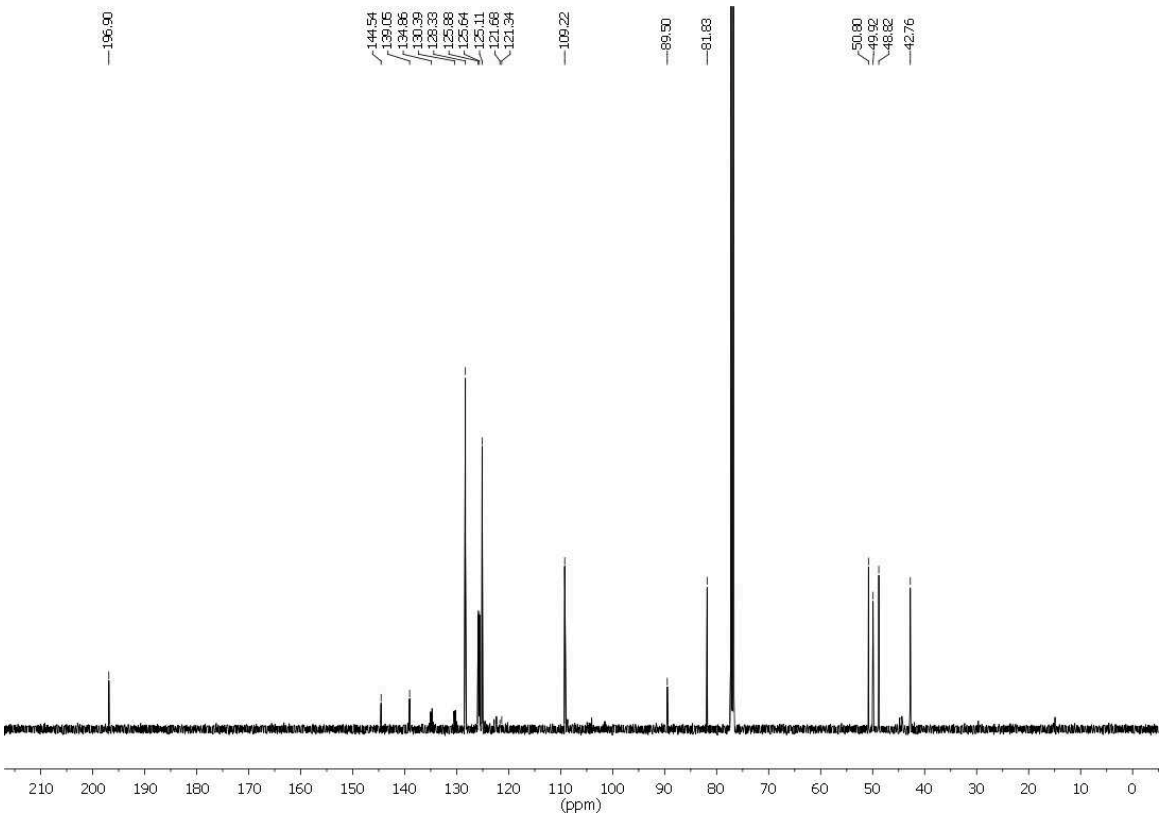
Compound 9c (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, DMSO))



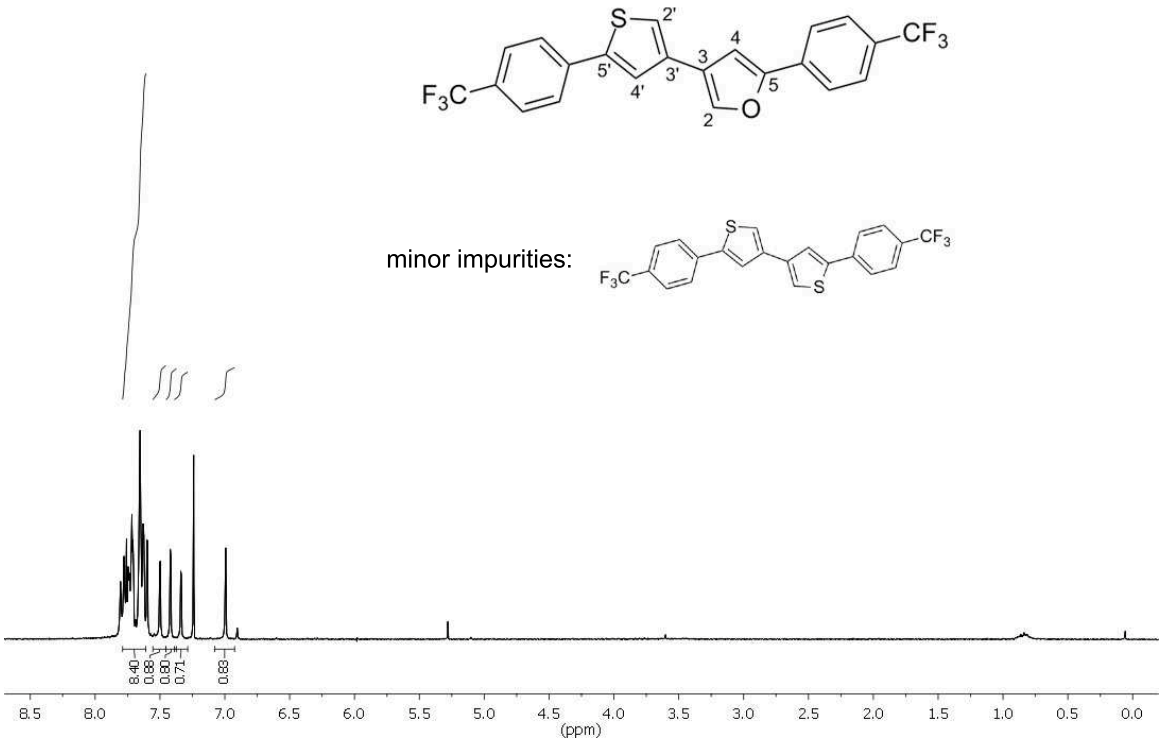


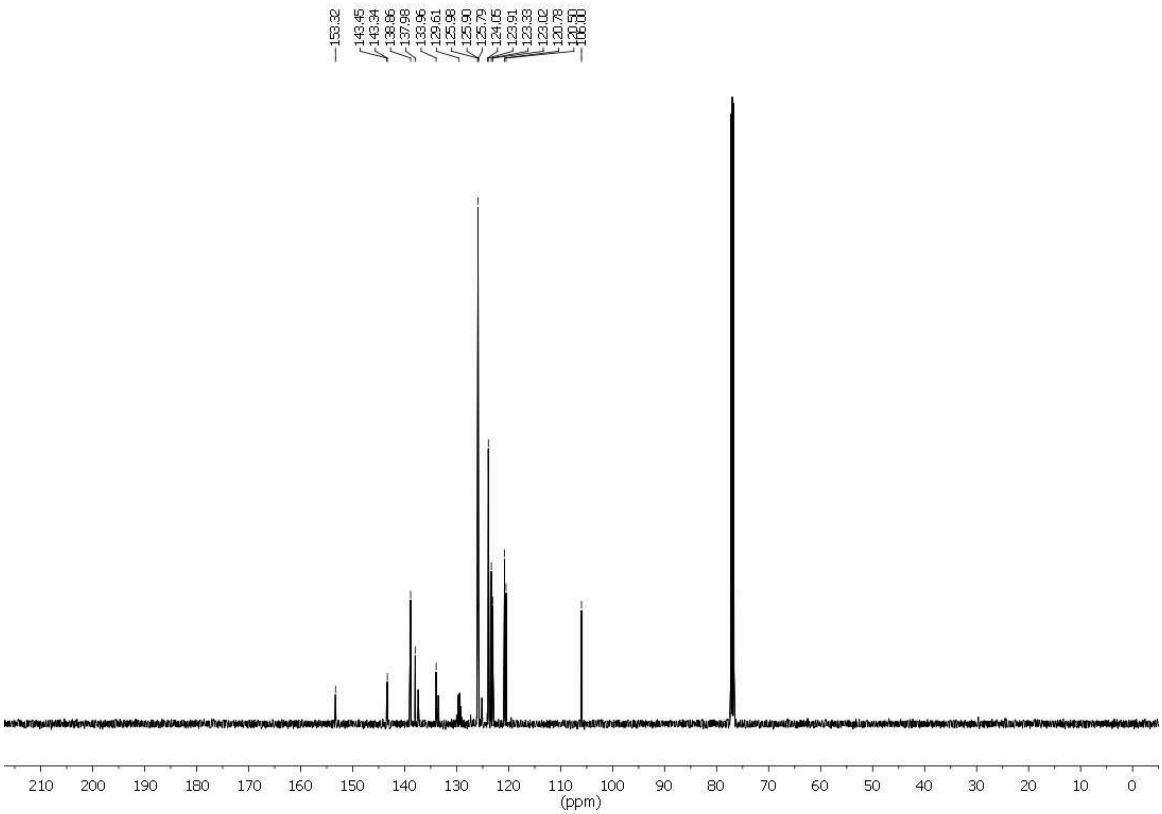
Compound 9e (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, DMSO))





Compound 14 (^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (125 MHz, $CDCl_3$))





X-ray diffraction

For the X-ray crystal structures of **5a**, **5c**, **8e** and **9a** a single crystal was mounted with inert oil on a MiTeGen-Loop. The data was collected from the shock-cooled crystals at 100 K. The data for **5a**, **5c** and **9a** was collected on a Bruker TXS-Mo rotating anode source with mirror optics and MoK_α radiation, $\lambda = 0.71073$ Å. The data for **8e** was collected on a Bruker Smart APEX II Quazar with INCOATEC Mo-Microsource and mirror optics. Data reduction was done with SAINT,[2] and an empirical absorption correction with SADABS[3] was applied. The structures were solved by direct methods (SHELXS-97)[4] and refined by full-matrix least-squares methods against F^3 (SHELXL-97 and ShelXle).[3,4] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^4 carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers, crystal data and experimental details for the X-ray measurements are listed in the supporting information. CCDC 904646 (**5a**), 904644 (**5c**), 904645 (**8e**), 904647 (**9a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via `www.ccdc.cam.ac.uk/data_request/cif`.

Compound 5a

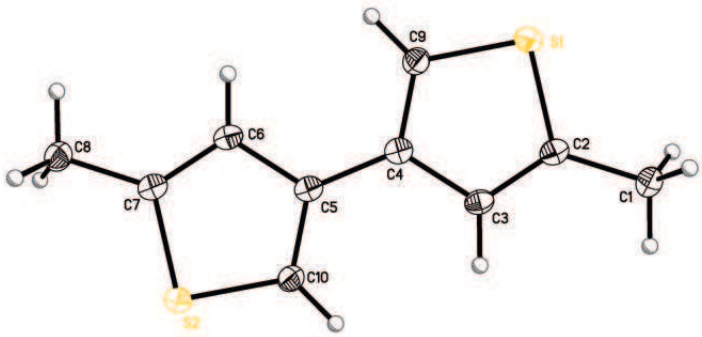


Table 0.1: Crystal data and structure refinement of **5a**

CCDC number	904646
Empirical formula	$C_{10}H_{10}S_2$
Formula weight	194.30

Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.955(2) Å	α= 90°.
	b = 7.649(3) Å	β= 95.301(9)°.
	c = 20.480(7) Å	γ = 90°.
Volume	928.9(6) $Å^3$	
Z	4	
Density (calculated)	1.389 Mg/m^3	
Absorption coefficient	0.510 mm^{-1}	
$F(000)$	408	
Crystal size	0.16 x 0.09 x 0.06 mm^3	
Theta range for data collection	2.00 to 26.95°.	
Index ranges	-7<=h<=7, -9<=k<=9, -26<=l<=26	
Reflections collected	18476	
Independent reflections	2006 [R_{int} = 0.0410]	
Completeness to theta = 26.95°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8620 and 0.7510	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2006 / 0 / 111	
Goodness-of-fit on F2	1.132	
Final R indices [I>2sigma(I)]	R_1 = 0.0341, wR_2 = 0.0813	
R indices (all data)	R_1 = 0.0405, wR_2 = 0.0846	
Largest diff. peak and hole	0.413 and -0.246 $eÅ^{-3}$	

Table 0.2: Bond lengths [Å] of **5a**

Atoms	Bond length [Å]	Atoms	Bond length [Å]
S(1)-C(9)	1.716(2)	C(4)-C(5)	1.465(3)
S(1)-C(2)	1.7307(19)	C(5)-C(10)	1.370(3)
S(2)-C(10)	1.7179(19)	C(5)-C(6)	1.433(3)
S(2)-C(7)	1.7322(19)	C(6)-C(7)	1.358(3)
C(1)-C(2)	1.494(3)	C(6)-H(6)	0.9500

C(1)-H(1A)	0.9800	C(7)-C(8)	1.492(3)
C(1)-H(1B)	0.9800	C(8)-H(8C)	0.9800
C(1)-H(1C)	0.9800	C(8)-H(8A)	0.9800
C(2)-C(3)	1.356(3)	C(8)-H(8B)	0.9800
C(3)-C(4)	1.434(3)	C(9)-H(9)	0.9500
C(3)-H(3)	0.9500	C(10)-H(10)	0.9500
C(4)-C(9)	1.368(3)		

Table 0.3: Bond angles [°] of **5a**

Atoms	Bond angle [°]	Atoms	Bond angle [°]
C(9)-S(1)-C(2)	92.15(9)	C(6)-C(5)-C(4)	124.54(16)
C(10)-S(2)-C(7)	92.27(9)	C(7)-C(6)-C(5)	114.11(17)
C(2)-C(1)-H(1A)	109.5	C(7)-C(6)-H(6)	122.9
C(2)-C(1)-H(1B)	109.5	C(5)-C(6)-H(6)	122.9
H(1A)-C(1)-H(1B)	109.5	C(6)-C(7)-C(8)	128.84(18)
C(2)-C(1)-H(1C)	109.5	C(6)-C(7)-S(2)	110.37(14)
H(1A)-C(1)-H(1C)	109.5	C(8)-C(7)-S(2)	120.79(14)
H(1B)-C(1)-H(1C)	109.5	C(7)-C(8)-H(8C)	109.5
C(3)-C(2)-C(1)	128.78(17)	C(7)-C(8)-H(8A)	109.5
C(3)-C(2)-S(1)	110.56(14)	H(8C)-C(8)-H(8A)	109.5
C(1)-C(2)-S(1)	120.64(14)	C(7)-C(8)-H(8B)	109.5
C(2)-C(3)-C(4)	113.93(17)	H(8C)-C(8)-H(8B)	109.5
C(2)-C(3)-H(3)	123.0	H(8A)-C(8)-H(8B)	109.5
C(4)-C(3)-H(3)	123.0	C(4)-C(9)-S(1)	111.99(14)
C(9)-C(4)-C(3)	111.36(16)	C(4)-C(9)-H(9)	124.0
C(9)-C(4)-C(5)	123.90(17)	S(1)-C(9)-H(9)	124.0
C(3)-C(4)-C(5)	124.74(16)	C(5)-C(10)-S(2)	111.85(14)
C(10)-C(5)-C(6)	111.40(17)	C(5)-C(10)-H(10)	124.1
C(10)-C(5)-C(4)	124.06(17)	S(2)-C(10)-H(10)	124.1

Table 0.4: Torsion angles [°] of **5a**

Atoms	Torsion angle [°]	Atoms	Torsion angle [°]
C(9)-S(1)-C(2)-C(3)	0.01(15)	C(4)-C(5)-C(6)-C(7)	179.51(17)
C(9)-S(1)-C(2)-C(1)	-178.53(16)	C(5)-C(6)-C(7)-C(8)	-179.22(18)
C(1)-C(2)-C(3)-C(4)	178.36(18)	C(5)-C(6)-C(7)-S(2)	0.0(2)
S(1)-C(2)-C(3)-C(4)	0.0(2)	C(10)-S(2)-C(7)-C(6)	-0.03(15)
C(2)-C(3)-C(4)-C(9)	0.0(2)	C(10)-S(2)-C(7)-C(8)	179.28(16)
C(2)-C(3)-C(4)-C(5)	-179.84(17)	C(3)-C(4)-C(9)-S(1)	0.0(2)
C(9)-C(4)-C(5)-C(10)	-179.59(18)	C(5)-C(4)-C(9)-S(1)	179.85(14)
C(3)-C(4)-C(5)-C(10)	0.3(3)	C(2)-S(1)-C(9)-C(4)	0.02(15)
C(9)-C(4)-C(5)-C(6)	0.9(3)	C(6)-C(5)-C(10)-S(2)	0.0(2)
C(3)-C(4)-C(5)-C(6)	-179.18(18)	C(4)-C(5)-C(10)-S(2)	-179.54(14)
C(10)-C(5)-C(6)-C(7)	0.0(2)	C(7)-S(2)-C(10)-C(5)	0.03(15)

Compound 5c

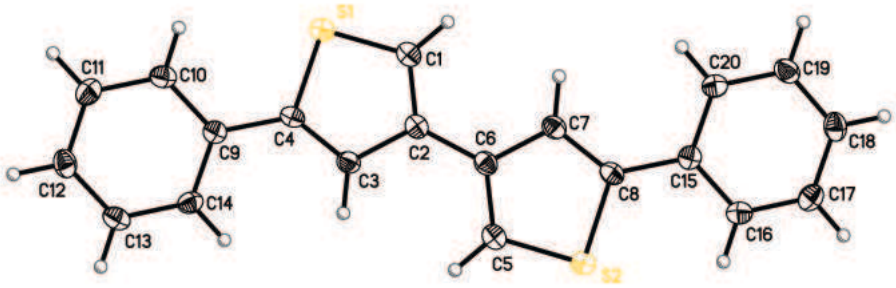


Table 0.5: Crystal data and structure refinement of **5c**

CCDC number	904644
Empirical formula	$C_{20}H_{14}S_2$
Formula weight	318.43
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$

Unit cell dimensions	a = 5.968(2) Å	
	b = 7.465(3) Å	β= 94.026(8)°.
	c = 33.815(13) Å	
Volume	1502.6(10) Å^3	
Z	4	
Density (calculated)	1.408 Mg/m^3	
Absorption coefficient	0.347 mm^{-1}	
F(000)	664	
Crystal size	0.300 x 0.200 x 0.001 mm^3	
Theta range for data collection	1.207 to 25.770°.	
Index ranges	-7<=h<=7, -9<=k<=9, -41<=l<=41	
Reflections collected	30910	
Independent reflections	2873 [R_{int} = 0.0433]	
Completeness to theta = 25.77°	100 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9422 and 0.8787	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2873 / 0 / 199	
Goodness-of-fit on F^2	1.139	
Final R indices [I>2sigma(I)]	R_1 = 0.0508, wR_2 = 0.1156	
R indices (all data)	R_1 = 0.0652, wR_2 = 0.1221	
Extinction coefficient	0	
Largest diff. peak and hole	0.463 and -0.448 eÅ^{-3}	

Table 0.6: Atomic coordinates (×10^5) and equivalent isotropic displacement parameters (Å^2×10^3) for **5c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	7114(1)	5173(1)	3255(1)	26(1)
S(2)	12765(1)	3414(1)	1711(1)	26(1)
C(1)	7478(4)	5059(4)	2761(1)	24(1)
C(2)	9544(4)	4402(3)	2682(1)	19(1)
C(3)	10855(4)	3970(3)	3042(1)	19(1)
C(4)	9799(4)	4348(3)	3377(1)	18(1)
C(5)	12380(4)	3496(4)	2205(1)	24(1)

C(6)	10340(4)	4214(3)	2284(1)	19(1)
C(7)	9075(4)	4704(3)	1926(1)	20(1)
C(8)	10127(4)	4323(3)	1591(1)	18(1)
C(9)	10704(4)	4319(3)	3792(1)	18(1)
C(10)	9616(4)	5213(4)	4088(1)	22(1)
C(11)	10533(5)	5236(4)	4475(1)	24(1)
C(12)	12557(4)	4367(4)	4575(1)	23(1)
C(13)	13648(4)	3481(4)	4286(1)	23(1)
C(14)	12732(4)	3451(3)	3898(1)	20(1)
C(15)	9261(4)	4428(3)	1173(1)	18(1)
C(16)	10422(4)	3640(4)	872(1)	21(1)
C(17)	9569(4)	3704(4)	482(1)	24(1)
C(18)	7525(4)	4544(4)	382(1)	24(1)
C(19)	6353(4)	5325(4)	678(1)	23(1)
C(20)	7211(4)	5273(3)	1070(1)	20(1)

Table 0.7: Bond lengths [Å] of **5c**

Atoms	Bond length [Å]	Atoms	Bond length [Å]
S(1)-C(1)	1.702(3)	C(10)-H(10)	0.9500
S(1)-C(4)	1.738(3)	C(11)-C(12)	1.392(4)
S(2)-C(5)	1.703(3)	C(11)-H(11)	0.9500
S(2)-C(8)	1.735(3)	C(12)-C(13)	1.381(4)
C(1)-C(2)	1.370(4)	C(12)-H(12)	0.9500
C(1)-H(1)	0.9500	C(13)-C(14)	1.386(4)
C(2)-C(3)	1.435(3)	C(13)-H(13)	0.9500
C(2)-C(6)	1.466(4)	C(14)-H(14)	0.9500
C(3)-C(4)	1.364(4)	C(15)-C(20)	1.399(4)
C(3)-H(3)	0.9500	C(15)-C(16)	1.401(4)
C(4)-C(9)	1.469(3)	C(16)-C(17)	1.380(4)
C(5)-C(6)	1.374(4)	C(16)-H(16)	0.9500
C(5)-H(5)	0.9500	C(17)-C(18)	1.392(4)
C(6)-C(7)	1.428(3)	C(17)-H(17)	0.9500
C(7)-C(8)	1.363(4)	C(18)-C(19)	1.388(4)
C(7)-H(7)	0.9500	C(18)-H(18)	0.9500

C(8)-C(15)	1.473(3)	C(19)-C(20)	1.388(4)
C(9)-C(14)	1.397(4)	C(19)-H(19)	0.9500
C(9)-C(10)	1.399(4)	C(20)-H(20)	0.9500
C(10)-C(11)	1.384(4)		

Table 0.8: Bond angles [°] of **5c**

Atoms	Bond angle [°]	Atoms	Bond angle [°]
C(1)-S(1)-C(4)	92.00(13)	C(9)-C(10)-H(10)	119.7
C(5)-S(2)-C(8)	91.85(13)	C(10)-C(11)-C(12)	120.3(2)
C(2)-C(1)-S(1)	112.8(2)	C(10)-C(11)-H(11)	119.9
C(2)-C(1)-H(1)	123.6	C(12)-C(11)-H(11)	119.9
S(1)-C(1)-H(1)	123.6	C(13)-C(12)-C(11)	119.7(2)
C(1)-C(2)-C(3)	111.1(2)	C(13)-C(12)-H(12)	120.2
C(1)-C(2)-C(6)	124.5(2)	C(11)-C(12)-H(12)	120.2
C(3)-C(2)-C(6)	124.3(2)	C(12)-C(13)-C(14)	120.3(2)
C(4)-C(3)-C(2)	113.6(2)	C(12)-C(13)-H(13)	119.9
C(4)-C(3)-H(3)	123.2	C(14)-C(13)-H(13)	119.9
C(2)-C(3)-H(3)	123.2	C(13)-C(14)-C(9)	120.8(2)
C(3)-C(4)-C(9)	129.1(2)	C(13)-C(14)-H(14)	119.6
C(3)-C(4)-S(1)	110.45(19)	C(9)-C(14)-H(14)	119.6
C(9)-C(4)-S(1)	120.10(19)	C(20)-C(15)-C(16)	118.4(2)
C(6)-C(5)-S(2)	112.81(19)	C(20)-C(15)-C(8)	120.4(2)
C(6)-C(5)-H(5)	123.6	C(16)-C(15)-C(8)	121.2(2)
S(2)-C(5)-H(5)	123.6	C(17)-C(16)-C(15)	120.8(2)
C(5)-C(6)-C(7)	110.9(2)	C(17)-C(16)-H(16)	119.6
C(5)-C(6)-C(2)	124.4(2)	C(15)-C(16)-H(16)	119.6
C(7)-C(6)-C(2)	124.6(2)	C(16)-C(17)-C(18)	120.4(2)
C(8)-C(7)-C(6)	113.8(2)	C(16)-C(17)-H(17)	119.8
C(8)-C(7)-H(7)	123.1	C(18)-C(17)-H(17)	119.8
C(6)-C(7)-H(7)	123.1	C(19)-C(18)-C(17)	119.4(2)
C(7)-C(8)-C(15)	129.4(2)	C(19)-C(18)-H(18)	120.3
C(7)-C(8)-S(2)	110.54(18)	C(17)-C(18)-H(18)	120.3
C(15)-C(8)-S(2)	119.75(19)	C(20)-C(19)-C(18)	120.4(2)
C(14)-C(9)-C(10)	118.3(2)	C(20)-C(19)-H(19)	119.8

C(14)-C(9)-C(4)	120.4(2)	C(18)-C(19)-H(19)	119.8
C(10)-C(9)-C(4)	121.2(2)	C(19)-C(20)-C(15)	120.6(2)
C(11)-C(10)-C(9)	120.6(2)	C(19)-C(20)-H(20)	119.7
C(11)-C(10)-H(10)	119.7	C(15)-C(20)-H(20)	119.7

Table 0.9: Anisotropic displacement parameters ($Å^2 \times 10^3$) for **5c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	20(1)	34(1)	23(1)	0(1)	1(1)	8(1)
S(2)	20(1)	34(1)	22(1)	0(1)	1(1)	7(1)
C(1)	23(1)	26(2)	22(1)	2(1)	-1(1)	5(1)
C(2)	19(1)	17(1)	20(1)	1(1)	-1(1)	-1(1)
C(3)	16(1)	21(1)	21(1)	1(1)	0(1)	1(1)
C(4)	16(1)	17(1)	22(1)	2(1)	-1(1)	1(1)
C(5)	23(1)	28(2)	21(1)	2(1)	-2(1)	4(1)
C(6)	19(1)	18(1)	20(1)	-1(1)	-2(1)	-1(1)
C(7)	16(1)	21(1)	21(1)	1(1)	-1(1)	-1(1)
C(8)	16(1)	16(1)	21(1)	1(1)	-2(1)	-1(1)
C(9)	17(1)	17(1)	20(1)	2(1)	2(1)	-2(1)
C(10)	19(1)	22(1)	24(1)	4(1)	3(1)	3(1)
C(11)	28(1)	23(1)	21(1)	-0(1)	6(1)	1(1)
C(12)	25(1)	27(2)	17(1)	4(1)	-0(1)	-3(1)
C(13)	18(1)	24(1)	26(1)	6(1)	0(1)	2(1)
C(14)	19(1)	20(1)	22(1)	2(1)	6(1)	2(1)
C(15)	17(1)	16(1)	20(1)	1(1)	2(1)	-4(1)
C(16)	18(1)	22(1)	24(1)	-1(1)	2(1)	1(1)
C(17)	25(1)	24(1)	22(1)	-4(1)	5(1)	-2(1)
C(18)	25(1)	28(2)	18(1)	-0(1)	-3(1)	-4(1)
C(19)	17(1)	26(2)	25(1)	4(1)	-2(1)	0(1)
C(20)	18(1)	19(1)	23(1)	-1(1)	3(1)	0(1)

Table 0.10: Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **5c**.

	x	y	z	U(eq)
H(1)	6367	5413	2561	29
H(3)	12320	3468	3046	23
H(5)	13462	3089	2404	29
H(7)	7633	5245	1922	23
H(10)	8234	5810	4022	26
H(11)	9779	5847	4673	29
H(12)	13184	4383	4841	28
H(13)	15032	2890	4354	27
H(14)	13494	2833	3702	24
H(16)	11813	3055	937	25
H(17)	10381	3172	281	28
H(18)	6938	4583	114	29
H(19)	4956	5898	611	27
H(20)	6399	5817	1270	24

Table 0.11: Torsion angles [°] of **5c**

Atoms	Torsion angle [°]	Atoms	Torsion angle [°]
C(4)-S(1)-C(1)-C(2)	0.7(2)	S(1)-C(4)-C(9)-C(14)	171.7(2)
S(1)-C(1)-C(2)-C(3)	0.4(3)	C(3)-C(4)-C(9)-C(10)	161.7(3)
S(1)-C(1)-C(2)-C(6)	-177.9(2)	S(1)-C(4)-C(9)-C(10)	-10.9(3)
C(1)-C(2)-C(3)-C(4)	-1.7(3)	C(14)-C(9)-C(10)-C(11)	0.1(4)
C(6)-C(2)-C(3)-C(4)	176.7(2)	C(4)-C(9)-C(10)-C(11)	-177.4(2)
C(2)-C(3)-C(4)-C(9)	-170.9(2)	C(9)-C(10)-C(11)-C(12)	0.0(4)
C(2)-C(3)-C(4)-S(1)	2.2(3)	C(10)-C(11)-C(12)-C(13)	0.0(4)
C(1)-S(1)-C(4)-C(3)	-1.6(2)	C(11)-C(12)-C(13)-C(14)	-0.2(4)
C(1)-S(1)-C(4)-C(9)	172.2(2)	C(12)-C(13)-C(14)-C(9)	0.3(4)
C(8)-S(2)-C(5)-C(6)	-1.0(2)	C(10)-C(9)-C(14)-C(13)	-0.2(4)
S(2)-C(5)-C(6)-C(7)	0.0(3)	C(4)-C(9)-C(14)-C(13)	177.3(2)
S(2)-C(5)-C(6)-C(2)	178.4(2)	C(7)-C(8)-C(15)-C(20)	11.2(4)
C(1)-C(2)-C(6)-C(5)	-177.6(3)	S(2)-C(8)-C(15)-C(20)	-175.35(19)
C(3)-C(2)-C(6)-C(5)	4.3(4)	C(7)-C(8)-C(15)-C(16)	-166.8(3)

C(1)-C(2)-C(6)-C(7)	0.6(4)	S(2)-C(8)-C(15)-C(16)	6.7(3)
C(3)-C(2)-C(6)-C(7)	-177.6(2)	C(20)-C(15)-C(16)-C(17)	0.3(4)
C(5)-C(6)-C(7)-C(8)	1.4(3)	C(8)-C(15)-C(16)-C(17)	178.3(2)
C(2)-C(6)-C(7)-C(8)	-177.0(2)	C(15)-C(16)-C(17)-C(18)	-0.5(4)
C(6)-C(7)-C(8)-C(15)	171.9(2)	C(16)-C(17)-C(18)-C(19)	0.2(4)
C(6)-C(7)-C(8)-S(2)	-2.1(3)	C(17)-C(18)-C(19)-C(20)	0.1(4)
C(5)-S(2)-C(8)-C(7)	1.7(2)	C(18)-C(19)-C(20)-C(15)	-0.3(4)
C(5)-S(2)-C(8)-C(15)	-172.9(2)	C(16)-C(15)-C(20)-C(19)	0.1(4)
C(3)-C(4)-C(9)-C(14)	-15.8(4)	C(8)-C(15)-C(20)-C(19)	-177.9(2)

Compound 8e

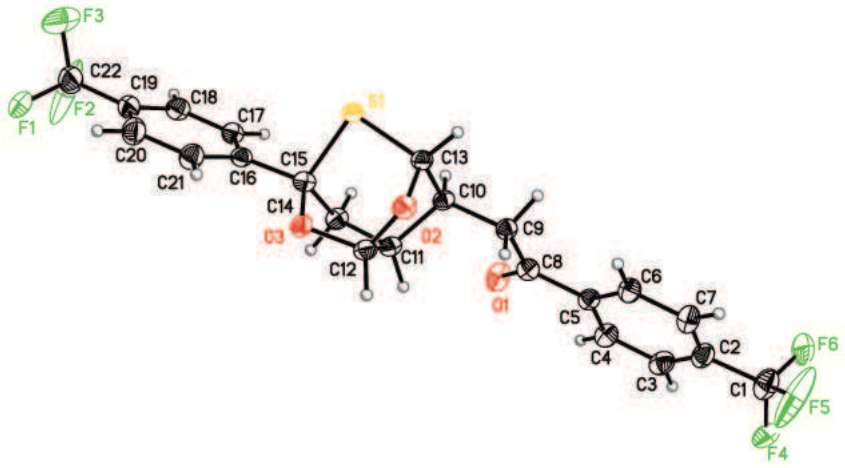


Table 0.12: Crystal data and structure refinement of **8e**

CCDC number	904645	
Empirical formula	$C_{22}H_{16}F_6O_3S$	
Formula weight	474.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 17.201(6) Å	
	b = 6.588(3) Å	β = 98.49(2)°.
	c = 17.859(6) Å	

Volume	2001.6(13) Å^3
Z	4
Density (calculated)	1.574 Mg/m^3
Absorption coefficient	0.240 mm^{-1}
F(000)	968
Crystal size	0.146 x 0.122 x 0.037 mm^3
Theta range for data collection	1.534 to 26.728°.
Index ranges	-21<=h<=21, -8<=k<=8, -22<=l<=22
Reflections collected	41361
Independent reflections	4254 [R_{int} = 0.0423]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8621 and 0.8007
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4254 / 464 / 331
Goodness-of-fit on F^2	1.095
Final R indices [I>2sigma(I)]	R_1 = 0.0643, wR_2 = 0.1591
R indices (all data)	R_1 = 0.0751, wR_2 = 0.1659
Extinction coefficient	0
Largest diff. peak and hole	1.120 and -0.883 eÅ^{-3}

Table 0.13: Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for **8e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	3584(1)	10258(1)	3102(1)	22(1)
C(22)	6730(2)	15325(4)	2694(2)	41(1)
F(1)	7144(5)	14954(14)	2142(4)	47(1)
F(2)	7266(5)	15493(19)	3305(3)	120(3)
F(3)	6458(5)	17177(8)	2565(7)	92(2)
F(1')	6503(3)	17053(5)	2967(3)	47(1)
F(2')	6844(5)	15701(9)	2005(2)	120(3)
F(3')	7432(2)	15011(7)	3090(4)	92(2)
F(1")	7007(6)	16488(14)	3265(3)	120(3)
F(2")	6338(4)	16593(12)	2188(5)	92(2)

F(3")	7343(4)	14790(11)	2374(5)	47(1)
C(1)	912(2)	-3053(4)	5144(1)	40(1)
F(4)	1284(2)	-4674(4)	5451(2)	51(1)
F(5)	450(3)	-3701(7)	4543(2)	93(2)
F(6)	455(2)	-2499(6)	5637(2)	59(1)
F(4')	216(5)	-2740(20)	4730(9)	51(1)
F(5')	770(10)	-2860(30)	5849(4)	93(2)
F(6')	1116(8)	-4882(11)	4951(12)	59(1)
F(4")	241(4)	-2510(20)	5349(8)	59(1)
F(5")	723(7)	-4214(18)	4541(5)	51(1)
F(6")	1237(8)	-4307(19)	5676(7)	93(2)
O(1)	3561(1)	3818(3)	5026(1)	32(1)
O(2)	3174(1)	6566(3)	2552(1)	23(1)
O(3)	4486(1)	7440(3)	2556(1)	23(1)
C(2)	1449(2)	-1371(4)	4981(2)	30(1)
C(3)	2157(2)	-1099(5)	5448(2)	31(1)
C(4)	2641(2)	507(5)	5313(2)	27(1)
C(5)	2417(2)	1823(4)	4709(2)	22(1)
C(6)	1703(2)	1523(5)	4238(2)	26(1)
C(7)	1217(2)	-77(5)	4372(2)	30(1)
C(8)	2953(2)	3554(4)	4590(2)	23(1)
C(9)	2715(2)	4940(4)	3926(2)	22(1)
C(10)	3293(2)	6667(4)	3855(2)	21(1)
C(11)	4096(2)	5958(4)	3669(2)	22(1)
C(12)	3965(2)	5940(4)	2787(2)	23(1)
C(13)	3016(2)	7903(4)	3142(2)	22(1)
C(14)	4719(2)	7633(4)	3854(2)	23(1)
C(15)	4548(2)	8945(4)	3140(2)	21(1)
C(16)	5138(2)	10544(4)	3013(2)	21(1)
C(17)	5473(2)	11739(4)	3621(2)	24(1)
C(18)	5992(2)	13288(4)	3511(2)	27(1)
C(19)	6179(2)	13641(4)	2794(2)	30(1)
C(20)	5856(2)	12438(5)	2188(2)	34(1)
C(21)	5333(2)	10898(5)	2295(2)	29(1)

Table 0.14: Bond lengths [Å] of **8e**

Atoms	Bond length [Å]	Atoms	Bond length [Å]
S(1)-C(13)	1.840(3)	C(4)-H(4)	0.9500
S(1)-C(15)	1.861(3)	C(5)-C(6)	1.397(4)
C(22)-F(2')	1.298(3)	C(5)-C(8)	1.502(4)
C(22)-F(1")	1.308(3)	C(6)-C(7)	1.388(4)
C(22)-F(3)	1.315(3)	C(6)-H(6)	0.9500
C(22)-F(3")	1.319(3)	C(7)-H(7)	0.9500
C(22)-F(1')	1.320(3)	C(8)-C(9)	1.505(4)
C(22)-F(1)	1.322(3)	C(9)-C(10)	1.528(4)
C(22)-F(3')	1.322(3)	C(9)-H(9A)	0.9900
C(22)-F(2)	1.326(3)	C(9)-H(9B)	0.9900
C(22)-F(2")	1.338(3)	C(10)-C(13)	1.528(4)
C(22)-C(19)	1.487(4)	C(10)-C(11)	1.541(4)
C(1)-F(5)	1.310(3)	C(10)-H(10)	1.0000
C(1)-F(4")	1.311(3)	C(11)-C(14)	1.540(4)
C(1)-F(6)	1.315(3)	C(11)-C(12)	1.558(4)
C(1)-F(6')	1.316(3)	C(11)-H(11)	1.0000
C(1)-F(6")	1.319(3)	C(12)-H(12)	1.0000
C(1)-F(4)	1.321(3)	C(13)-H(13)	1.0000
C(1)-F(5")	1.322(3)	C(14)-C(15)	1.533(4)
C(1)-F(5')	1.324(3)	C(14)-H(14A)	0.9900
C(1)-F(4')	1.329(3)	C(14)-H(14B)	0.9900
C(1)-C(2)	1.499(4)	C(15)-C(16)	1.502(4)
O(1)-C(8)	1.221(3)	C(16)-C(21)	1.393(4)
O(2)-C(12)	1.426(3)	C(16)-C(17)	1.395(4)
O(2)-C(13)	1.429(3)	C(17)-C(18)	1.389(4)
O(3)-C(15)	1.432(3)	C(17)-H(17)	0.9500
O(3)-C(12)	1.434(3)	C(18)-C(19)	1.385(4)
C(2)-C(3)	1.382(4)	C(18)-H(18)	0.9500
C(2)-C(7)	1.393(4)	C(19)-C(20)	1.389(4)
C(3)-C(4)	1.390(4)	C(20)-C(21)	1.388(4)
C(3)-H(3)	0.9500	C(20)-H(20)	0.9500
C(4)-C(5)	1.393(4)	C(21)-H(21)	0.9500

Table 0.15: Bond angles [°] of **8e**

Atoms	Bond angle [°]	Atoms	Bond angle [°]
C(13)-S(1)-C(15)	94.73(12)	C(8)-C(9)-C(10)	114.3(2)
F(1")-C(22)-F(3")	105.7(3)	C(8)-C(9)-H(9A)	108.7
F(2')-C(22)-F(1')	106.2(3)	C(10)-C(9)-H(9A)	108.7
F(3)-C(22)-F(1)	104.9(3)	C(8)-C(9)-H(9B)	108.7
F(2')-C(22)-F(3')	106.5(3)	C(10)-C(9)-H(9B)	108.7
F(1')-C(22)-F(3')	103.5(3)	H(9A)-C(9)-H(9B)	107.6
F(3)-C(22)-F(2)	104.6(3)	C(9)-C(10)-C(13)	109.8(2)
F(1)-C(22)-F(2)	104.1(3)	C(9)-C(10)-C(11)	114.0(2)
F(1")-C(22)-F(2")	104.5(3)	C(13)-C(10)-C(11)	99.2(2)
F(3")-C(22)-F(2")	103.3(3)	C(9)-C(10)-H(10)	111.1
F(2')-C(22)-C(19)	116.4(3)	C(13)-C(10)-H(10)	111.1
F(1")-C(22)-C(19)	120.6(4)	C(11)-C(10)-H(10)	111.1
F(3)-C(22)-C(19)	119.8(4)	C(14)-C(11)-C(10)	110.7(2)
F(3")-C(22)-C(19)	114.7(4)	C(14)-C(11)-C(12)	102.4(2)
F(1')-C(22)-C(19)	111.8(3)	C(10)-C(11)-C(12)	102.7(2)
F(1)-C(22)-C(19)	112.0(5)	C(14)-C(11)-H(11)	113.3
F(3')-C(22)-C(19)	111.5(3)	C(10)-C(11)-H(11)	113.3
F(2)-C(22)-C(19)	110.0(5)	C(12)-C(11)-H(11)	113.3
F(2")-C(22)-C(19)	106.3(4)	O(2)-C(12)-O(3)	109.0(2)
F(5)-C(1)-F(6)	106.8(3)	O(2)-C(12)-C(11)	106.5(2)
F(4")-C(1)-F(6")	105.5(3)	O(3)-C(12)-C(11)	106.4(2)
F(5)-C(1)-F(4)	105.9(2)	O(2)-C(12)-H(12)	111.5
F(6)-C(1)-F(4)	104.4(2)	O(3)-C(12)-H(12)	111.5
F(4")-C(1)-F(5")	105.4(3)	C(11)-C(12)-H(12)	111.5
F(6")-C(1)-F(5")	104.6(9)	O(2)-C(13)-C(10)	102.5(2)
F(6')-C(1)-F(5')	115.6(12)	O(2)-C(13)-S(1)	109.34(18)
F(6')-C(1)-F(4')	104.5(3)	C(10)-C(13)-S(1)	112.32(19)
F(5')-C(1)-F(4')	103.7(3)	O(2)-C(13)-H(13)	110.8
F(5)-C(1)-C(2)	113.4(3)	C(10)-C(13)-H(13)	110.8
F(4")-C(1)-C(2)	116.4(6)	S(1)-C(13)-H(13)	110.8
F(6)-C(1)-C(2)	111.8(3)	C(15)-C(14)-C(11)	100.6(2)
F(6')-C(1)-C(2)	115.5(6)	C(15)-C(14)-H(14A)	111.7
F(6")-C(1)-C(2)	113.3(6)	C(11)-C(14)-H(14A)	111.7

F(4)-C(1)-C(2)	113.8(3)	C(15)-C(14)-H(14B)	111.7
F(5")-C(1)-C(2)	110.7(6)	C(11)-C(14)-H(14B)	111.7
F(5')-C(1)-C(2)	108.6(8)	H(14A)-C(14)-H(14B)	109.4
F(4')-C(1)-C(2)	107.8(6)	O(3)-C(15)-C(16)	110.8(2)
C(12)-O(2)-C(13)	103.80(19)	O(3)-C(15)-C(14)	101.5(2)
C(15)-O(3)-C(12)	104.5(2)	C(16)-C(15)-C(14)	118.0(2)
C(3)-C(2)-C(7)	121.2(3)	O(3)-C(15)-S(1)	108.98(17)
C(3)-C(2)-C(1)	119.4(3)	C(16)-C(15)-S(1)	106.64(18)
C(7)-C(2)-C(1)	119.4(3)	C(14)-C(15)-S(1)	110.70(19)
C(2)-C(3)-C(4)	119.4(3)	C(21)-C(16)-C(17)	119.6(3)
C(2)-C(3)-H(3)	120.3	C(21)-C(16)-C(15)	121.1(2)
C(4)-C(3)-H(3)	120.3	C(17)-C(16)-C(15)	119.3(2)
C(3)-C(4)-C(5)	120.2(3)	C(18)-C(17)-C(16)	120.3(3)
C(3)-C(4)-H(4)	119.9	C(18)-C(17)-H(17)	119.9
C(5)-C(4)-H(4)	119.9	C(16)-C(17)-H(17)	119.9
C(4)-C(5)-C(6)	119.8(3)	C(19)-C(18)-C(17)	119.8(3)
C(4)-C(5)-C(8)	118.5(3)	C(19)-C(18)-H(18)	120.1
C(6)-C(5)-C(8)	121.7(2)	C(17)-C(18)-H(18)	120.1
C(7)-C(6)-C(5)	120.1(3)	C(18)-C(19)-C(20)	120.2(3)
C(7)-C(6)-H(6)	119.9	C(18)-C(19)-C(22)	118.4(3)
C(5)-C(6)-H(6)	119.9	C(20)-C(19)-C(22)	121.4(3)
C(6)-C(7)-C(2)	119.3(3)	C(21)-C(20)-C(19)	120.1(3)
C(6)-C(7)-H(7)	120.4	C(21)-C(20)-H(20)	119.9
C(2)-C(7)-H(7)	120.4	C(19)-C(20)-H(20)	119.9
O(1)-C(8)-C(5)	120.3(3)	C(20)-C(21)-C(16)	120.0(3)
O(1)-C(8)-C(9)	121.6(3)	C(20)-C(21)-H(21)	120
C(5)-C(8)-C(9)	118.1(2)	C(16)-C(21)-H(21)	120

Table 0.16: Anisotropic displacement parameters ($Å^2 \times 10^3$) for **8e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	20(1)	17(1)	29(1)	2(1)	1(1)	1(1)
C(22)	41(2)	30(2)	56(2)	-8(2)	21(2)	-8(1)
F(1)	51(2)	24(2)	70(3)	10(2)	28(2)	-5(2)

F(2)	224(7)	103(5)	41(2)	-25(2)	50(3)	-131(5)
F(3)	21(2)	30(2)	224(7)	29(3)	11(3)	-9(2)
F(1')	51(2)	24(2)	70(3)	10(2)	28(2)	-5(2)
F(2')	224(7)	103(5)	41(2)	-25(2)	50(3)	-131(5)
F(3')	21(2)	30(2)	224(7)	29(3)	11(3)	-9(2)
F(1")	224(7)	103(5)	41(2)	-25(2)	50(3)	-131(5)
F(2")	21(2)	30(2)	224(7)	29(3)	11(3)	-9(2)
F(3")	51(2)	24(2)	70(3)	10(2)	28(2)	-5(2)
C(1)	47(2)	38(2)	37(2)	1(1)	13(2)	-13(2)
F(4)	56(2)	21(1)	82(3)	9(2)	27(2)	-3(1)
F(5)	143(5)	89(4)	36(2)	18(2)	-26(2)	-90(3)
F(6)	50(2)	47(2)	92(3)	0(2)	45(2)	-12(2)
F(4')	56(2)	21(1)	82(3)	9(2)	27(2)	-3(1)
F(5')	143(5)	89(4)	36(2)	18(2)	-26(2)	-90(3)
F(6')	50(2)	47(2)	92(3)	0(2)	45(2)	-12(2)
F(4")	50(2)	47(2)	92(3)	0(2)	45(2)	-12(2)
F(5")	56(2)	21(1)	82(3)	9(2)	27(2)	-3(1)
F(6")	143(5)	89(4)	36(2)	18(2)	-26(2)	-90(3)
O(1)	34(1)	37(1)	23(1)	4(1)	-4(1)	-11(1)
O(2)	23(1)	23(1)	22(1)	-1(1)	-1(1)	-3(1)
O(3)	27(1)	18(1)	25(1)	-5(1)	6(1)	-4(1)
C(2)	37(2)	25(2)	29(2)	-2(1)	14(1)	-6(1)
C(3)	42(2)	26(2)	26(2)	4(1)	8(1)	-1(1)
C(4)	31(2)	28(2)	23(1)	2(1)	2(1)	-2(1)
C(5)	26(1)	21(1)	20(1)	-2(1)	5(1)	-1(1)
C(6)	28(1)	27(1)	23(1)	2(1)	4(1)	-2(1)
C(7)	31(2)	32(2)	27(2)	-2(1)	6(1)	-8(1)
C(8)	27(1)	25(1)	17(1)	-3(1)	3(1)	-1(1)
C(9)	22(1)	21(1)	22(1)	-1(1)	2(1)	-1(1)
C(10)	22(1)	18(1)	21(1)	-2(1)	1(1)	-1(1)
C(11)	23(1)	18(1)	23(1)	1(1)	-0(1)	1(1)
C(12)	25(1)	18(1)	26(1)	-1(1)	4(1)	1(1)
C(13)	19(1)	18(1)	27(1)	1(1)	1(1)	1(1)
C(14)	20(1)	23(1)	24(1)	2(1)	-3(1)	0(1)
C(15)	20(1)	21(1)	21(1)	-3(1)	-1(1)	1(1)
C(16)	19(1)	19(1)	24(1)	-0(1)	2(1)	2(1)

C(17)	24(1)	24(1)	25(1)	-1(1)	4(1)	1(1)
C(18)	26(1)	24(1)	31(2)	-6(1)	1(1)	-2(1)
C(19)	29(2)	24(2)	38(2)	-3(1)	11(1)	-2(1)
C(20)	39(2)	31(2)	34(2)	-2(1)	14(1)	-5(1)
C(21)	33(2)	27(2)	27(2)	-2(1)	5(1)	-4(1)

Table 0.17: Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **8e**.

	x	y	z	U(eq)
H(3)	2310	-2003	5858	37
H(4)	3127	709	5634	33
H(6)	1549	2417	3826	31
H(7)	731	-288	4052	36
H(9A)	2194	5531	3969	26
H(9B)	2657	4123	3455	26
H(10)	3357	7549	4316	25
H(11)	4265	4614	3898	26
H(12)	4068	4567	2584	28
H(13)	2441	8203	3096	26
H(14A)	4641	8401	4314	28
H(14B)	5259	7074	3919	28
H(17)	5345	11494	4113	29
H(18)	6218	14102	3925	33
H(20)	5993	12670	1699	40
H(21)	5109	10085	1879	34

Table 0.18: Torsion angles [°] of **8e**

Atoms	Torsion angle [°]	Atoms	Torsion angle [°]
F(5)-C(1)-C(2)-C(3)	-153.6(4)	C(11)-C(10)-C(13)-O(2)	47.2(2)
F(4")-C(1)-C(2)-C(3)	113.5(7)	C(9)-C(10)-C(13)-S(1)	170.22(18)
F(6)-C(1)-C(2)-C(3)	85.6(4)	C(11)-C(10)-C(13)-S(1)	-70.0(2)
F(6')-C(1)-C(2)-C(3)	-76.8(10)	C(15)-S(1)-C(13)-O(2)	-54.11(19)

F(6")-C(1)-C(2)-C(3)	-9.1(9)	C(15)-S(1)-C(13)-C(10)	59.0(2)
F(4)-C(1)-C(2)-C(3)	-32.4(4)	C(10)-C(11)-C(14)-C(15)	-82.2(3)
F(5")-C(1)-C(2)-C(3)	-126.3(7)	C(12)-C(11)-C(14)-C(15)	26.7(3)
F(5')-C(1)-C(2)-C(3)	54.9(11)	C(12)-O(3)-C(15)-C(16)	174.8(2)
F(4')-C(1)-C(2)-C(3)	166.7(8)	C(12)-O(3)-C(15)-C(14)	48.7(2)
F(5)-C(1)-C(2)-C(7)	28.1(4)	C(12)-O(3)-C(15)-S(1)	-68.1(2)
F(4")-C(1)-C(2)-C(7)	-64.9(7)	C(11)-C(14)-C(15)-O(3)	-46.4(2)
F(6)-C(1)-C(2)-C(7)	-92.8(4)	C(11)-C(14)-C(15)-C(16)	-167.7(2)
F(6')-C(1)-C(2)-C(7)	104.8(10)	C(11)-C(14)-C(15)-S(1)	69.2(2)
F(6")-C(1)-C(2)-C(7)	172.5(9)	C(13)-S(1)-C(15)-O(3)	53.2(2)
F(4)-C(1)-C(2)-C(7)	149.3(3)	C(13)-S(1)-C(15)-C(16)	172.81(18)
F(5")-C(1)-C(2)-C(7)	55.4(7)	C(13)-S(1)-C(15)-C(14)	-57.7(2)
F(5')-C(1)-C(2)-C(7)	-123.4(11)	O(3)-C(15)-C(16)-C(21)	23.2(3)
F(4')-C(1)-C(2)-C(7)	-11.6(9)	C(14)-C(15)-C(16)-C(21)	139.5(3)
C(7)-C(2)-C(3)-C(4)	0.7(5)	S(1)-C(15)-C(16)-C(21)	-95.3(3)
C(1)-C(2)-C(3)-C(4)	-177.6(3)	O(3)-C(15)-C(16)-C(17)	-159.1(2)
C(2)-C(3)-C(4)-C(5)	-0.4(5)	C(14)-C(15)-C(16)-C(17)	-42.8(4)
C(3)-C(4)-C(5)-C(6)	0.0(4)	S(1)-C(15)-C(16)-C(17)	82.4(3)
C(3)-C(4)-C(5)-C(8)	179.2(3)	C(21)-C(16)-C(17)-C(18)	0.7(4)
C(4)-C(5)-C(6)-C(7)	0.1(4)	C(15)-C(16)-C(17)-C(18)	-177.0(3)
C(8)-C(5)-C(6)-C(7)	-179.1(3)	C(16)-C(17)-C(18)-C(19)	-0.2(4)
C(5)-C(6)-C(7)-C(2)	0.2(4)	C(17)-C(18)-C(19)-C(20)	-0.7(5)
C(3)-C(2)-C(7)-C(6)	-0.6(5)	C(17)-C(18)-C(19)-C(22)	179.3(2)
C(1)-C(2)-C(7)-C(6)	177.7(3)	F(2')-C(22)-C(19)-C(18)	-175.0(5)
C(4)-C(5)-C(8)-O(1)	-1.7(4)	F(1")-C(22)-C(19)-C(18)	-2.5(7)
C(6)-C(5)-C(8)-O(1)	177.6(3)	F(3)-C(22)-C(19)-C(18)	-86.7(7)
C(4)-C(5)-C(8)-C(9)	178.6(3)	F(3")-C(22)-C(19)-C(18)	125.7(5)
C(6)-C(5)-C(8)-C(9)	-2.2(4)	F(1')-C(22)-C(19)-C(18)	-52.8(4)
O(1)-C(8)-C(9)-C(10)	-0.3(4)	F(1)-C(22)-C(19)-C(18)	149.8(5)
C(5)-C(8)-C(9)-C(10)	179.4(2)	F(3')-C(22)-C(19)-C(18)	62.6(4)
C(8)-C(9)-C(10)-C(13)	177.0(2)	F(2)-C(22)-C(19)-C(18)	34.5(6)
C(8)-C(9)-C(10)-C(11)	66.7(3)	F(2")-C(22)-C(19)-C(18)	-120.8(6)
C(9)-C(10)-C(11)-C(14)	-162.0(2)	F(2')-C(22)-C(19)-C(20)	5.0(5)
C(13)-C(10)-C(11)-C(14)	81.3(2)	F(1")-C(22)-C(19)-C(20)	177.6(7)
C(9)-C(10)-C(11)-C(12)	89.3(3)	F(3)-C(22)-C(19)-C(20)	93.3(7)
C(13)-C(10)-C(11)-C(12)	-27.3(2)	F(3")-C(22)-C(19)-C(20)	-54.3(6)

C(13)-O(2)-C(12)-O(3)	-84.0(2)	F(1')-C(22)-C(19)-C(20)	127.3(4)
C(13)-O(2)-C(12)-C(11)	30.5(3)	F(1)-C(22)-C(19)-C(20)	-30.2(6)
C(15)-O(3)-C(12)-O(2)	83.5(2)	F(3')-C(22)-C(19)-C(20)	-117.4(4)
C(15)-O(3)-C(12)-C(11)	-31.0(3)	F(2)-C(22)-C(19)-C(20)	-145.4(6)
C(14)-C(11)-C(12)-O(2)	-115.2(2)	F(2")-C(22)-C(19)-C(20)	59.2(6)
C(10)-C(11)-C(12)-O(2)	-0.3(3)	C(18)-C(19)-C(20)-C(21)	1.1(5)
C(14)-C(11)-C(12)-O(3)	1.0(3)	C(22)-C(19)-C(20)-C(21)	-179.0(3)
C(10)-C(11)-C(12)-O(3)	115.9(2)	C(19)-C(20)-C(21)-C(16)	-0.6(5)
C(12)-O(2)-C(13)-C(10)	-49.4(2)	C(17)-C(16)-C(21)-C(20)	-0.3(4)
C(12)-O(2)-C(13)-S(1)	70.0(2)	C(15)-C(16)-C(21)-C(20)	177.4(3)
C(9)-C(10)-C(13)-O(2)	-72.5(3)		

Compound 9a

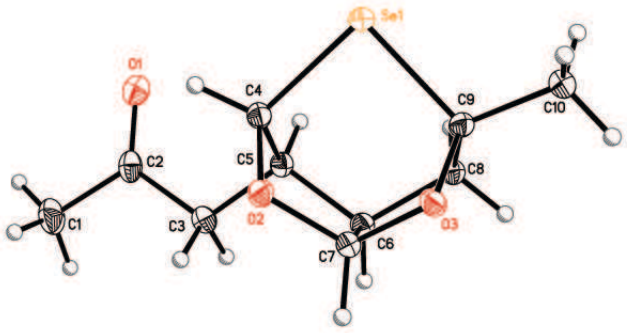


Table 0.19: Crystal data and structure refinement of **9a**

CCDC number	904647	
Empirical formula	$C_{10}H_{14}O_3Se$	
Formula weight	261.17	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 6.388(3) Å	α = 73.414(2)°.
	b = 9.236(5) Å	β = 74.033(3)°.
	c = 9.469(5) Å	γ = 81.773(3)°.
Volume	513.6(5) Å^3	

Z	2
Density (calculated)	1.689 Mg/m^3
Absorption coefficient	3.634 mm^{-1}
$F(000)$	264
Crystal size	0.18 x 0.17 x 0.09 mm^3
Theta range for data collection	2.31 to 26.75°.
Index ranges	-8<=h<=8, -11<=k<=11, -11<=l<=11
Reflections collected	26279
Independent reflections	2185 [R_{int} = 0.0312]
Completeness to theta = 26.75°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7357 and 0.5608
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2185 / 0 / 130
Goodness-of-fit on F^2	1.158
Final R indices [I>2sigma(I)]	R_1 = 0.0160, wR_2 = 0.0427
R indices (all data)	R_1 = 0.0162, wR_2 = 0.0428
Extinction coefficient	0.043(2)
Largest diff. peak and hole	0.437 and -0.271 $eÅ^{-3}$

Table 0.20: Bond lengths [Å] of **9a**

Atoms	Bond length [Å]	Atoms	Bond length [Å]
Se(1)-C(4)	1.9977(13)	C(4)-C(5)	1.5268(18)
Se(1)-C(9)	2.0092(13)	C(4)-H(4)	1.0000
O(1)-C(2)	1.2134(19)	C(5)-C(6)	1.5380(18)
O(2)-C(7)	1.4245(16)	C(5)-H(5)	1.0000
O(2)-C(4)	1.4324(16)	C(6)-C(8)	1.5362(18)
O(3)-C(7)	1.4251(16)	C(6)-C(7)	1.5635(18)
O(3)-C(9)	1.4388(16)	C(6)-H(6)	1.0000
C(1)-C(2)	1.508(2)	C(7)-H(7)	1.0000
C(1)-H(1A)	0.9800	C(8)-C(9)	1.5191(19)
C(1)-H(1B)	0.9800	C(8)-H(8A)	0.9900
C(1)-H(1C)	0.9800	C(8)-H(8B)	0.9900
C(2)-C(3)	1.5122(19)	C(9)-C(10)	1.5041(19)

C(3)-C(5)	1.5246(19)	C(10)-H(10A)	0.9800
C(3)-H(3A)	0.9900	C(10)-H(10B)	0.9800
C(3)-H(3B)	0.9900	C(10)-H(10C)	0.9800

Table 0.21: Bond angles [°] of **9a**

Atoms	Bond angle [°]	Atoms	Bond angle [°]
C(4)-Se(1)-C(9)	90.58(6)	C(8)-C(6)-C(5)	112.30(11)
C(7)-O(2)-C(4)	104.94(10)	C(8)-C(6)-C(7)	102.56(10)
C(7)-O(3)-C(9)	105.66(10)	C(5)-C(6)-C(7)	102.93(10)
C(2)-C(1)-H(1A)	109.5	C(8)-C(6)-H(6)	112.7
C(2)-C(1)-H(1B)	109.5	C(5)-C(6)-H(6)	112.7
H(1A)-C(1)-H(1B)	109.5	C(7)-C(6)-H(6)	112.7
C(2)-C(1)-H(1C)	109.5	O(2)-C(7)-O(3)	109.53(10)
H(1A)-C(1)-H(1C)	109.5	O(2)-C(7)-C(6)	106.50(10)
H(1B)-C(1)-H(1C)	109.5	O(3)-C(7)-C(6)	106.54(10)
O(1)-C(2)-C(1)	122.01(14)	O(2)-C(7)-H(7)	111.3
O(1)-C(2)-C(3)	122.51(13)	O(3)-C(7)-H(7)	111.3
C(1)-C(2)-C(3)	115.48(13)	C(6)-C(7)-H(7)	111.3
C(2)-C(3)-C(5)	114.26(12)	C(9)-C(8)-C(6)	101.69(10)
C(2)-C(3)-H(3A)	108.7	C(9)-C(8)-H(8A)	111.4
C(5)-C(3)-H(3A)	108.7	C(6)-C(8)-H(8A)	111.4
C(2)-C(3)-H(3B)	108.7	C(9)-C(8)-H(8B)	111.4
C(5)-C(3)-H(3B)	108.7	C(6)-C(8)-H(8B)	111.4
H(3A)-C(3)-H(3B)	107.6	H(8A)-C(8)-H(8B)	109.3
O(2)-C(4)-C(5)	102.96(10)	O(3)-C(9)-C(10)	109.95(11)
O(2)-C(4)-Se(1)	108.51(8)	O(3)-C(9)-C(8)	102.48(10)
C(5)-C(4)-Se(1)	111.06(9)	C(10)-C(9)-C(8)	117.12(12)
O(2)-C(4)-H(4)	111.3	O(3)-C(9)-Se(1)	107.97(8)
C(5)-C(4)-H(4)	111.3	C(10)-C(9)-Se(1)	109.49(9)
Se(1)-C(4)-H(4)	111.3	C(8)-C(9)-Se(1)	109.35(9)
C(3)-C(5)-C(4)	110.98(11)	C(9)-C(10)-H(10A)	109.5
C(3)-C(5)-C(6)	111.53(11)	C(9)-C(10)-H(10B)	109.5
C(4)-C(5)-C(6)	100.08(10)	H(10A)-C(10)-H(10B)	109.5
C(3)-C(5)-H(5)	111.3	C(9)-C(10)-H(10C)	109.5

C(4)-C(5)-H(5)	111.3	H(10A)-C(10)-H(10C)	109.5
C(6)-C(5)-H(5)	111.3	H(10B)-C(10)-H(10C)	109.5

Table 0.22: Torsion angles [°] of **9a**

Atoms	Torsion angle [°]	Atoms	Torsion angle [°]
O(1)-C(2)-C(3)-C(5)	10.30(19)	C(9)-O(3)-C(7)-O(2)	-86.42(12)
C(1)-C(2)-C(3)-C(5)	-170.69(12)	C(9)-O(3)-C(7)-C(6)	28.40(13)
C(7)-O(2)-C(4)-C(5)	46.66(12)	C(8)-C(6)-C(7)-O(2)	116.24(11)
C(7)-O(2)-C(4)-Se(1)	-71.11(10)	C(5)-C(6)-C(7)-O(2)	-0.50(13)
C(9)-Se(1)-C(4)-O(2)	53.27(9)	C(8)-C(6)-C(7)-O(3)	-0.61(13)
C(9)-Se(1)-C(4)-C(5)	-59.22(10)	C(5)-C(6)-C(7)-O(3)	-117.35(11)
C(2)-C(3)-C(5)-C(4)	72.71(15)	C(5)-C(6)-C(8)-C(9)	84.49(12)
C(2)-C(3)-C(5)-C(6)	-176.63(11)	C(7)-C(6)-C(8)-C(9)	-25.33(12)
O(2)-C(4)-C(5)-C(3)	72.80(13)	C(7)-O(3)-C(9)-C(10)	-170.52(11)
Se(1)-C(4)-C(5)-C(3)	-171.24(9)	C(7)-O(3)-C(9)-C(8)	-45.29(12)
O(2)-C(4)-C(5)-C(6)	-45.06(12)	C(7)-O(3)-C(9)-Se(1)	70.09(10)
Se(1)-C(4)-C(5)-C(6)	70.90(11)	C(6)-C(8)-C(9)-O(3)	43.26(12)
C(3)-C(5)-C(6)-C(8)	159.64(11)	C(6)-C(8)-C(9)-C(10)	163.65(11)
C(4)-C(5)-C(6)-C(8)	-82.90(12)	C(6)-C(8)-C(9)-Se(1)	-71.10(11)
C(3)-C(5)-C(6)-C(7)	-90.77(12)	C(4)-Se(1)-C(9)-O(3)	-52.42(9)
C(4)-C(5)-C(6)-C(7)	26.69(12)	C(4)-Se(1)-C(9)-C(10)	-172.11(10)
C(4)-O(2)-C(7)-O(3)	86.49(12)	C(4)-Se(1)-C(9)-C(8)	58.35(9)
C(4)-O(2)-C(7)-C(6)	-28.35(13)		

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