

SUPPORTING INFORMATION

o-Nitrophenyl Sulfoxides: Efficient Precursors for the Mild Preparation of Alkenes

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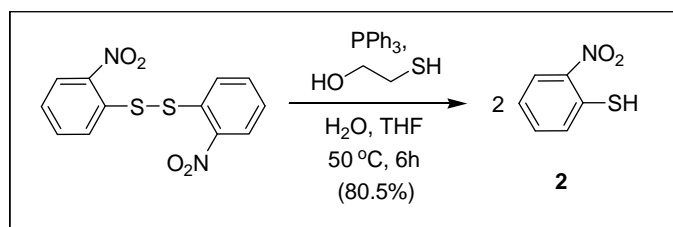
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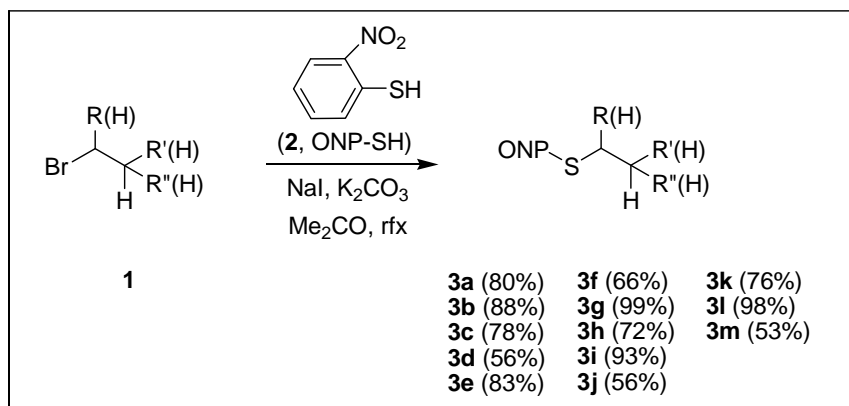
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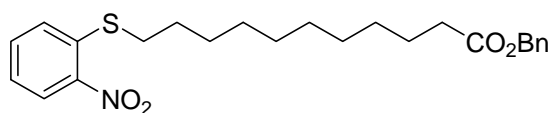
General Methods. Chemicals were purchased from commercial sources and used as received. Products were purified by flash chromatography on 60-100 mesh silica and visualized by UV on TLC plates (silica gel 60 F₂₅₄). Melting points were determined on a melting point apparatus and are uncorrected. High resolution mass spectrometry (HRMS) was performed by electrospray ionization (ESI). ¹H and ¹³C NMRs were recorded on a 500 MHz NMR and referenced to residual CDCl₃. Abbreviations used in the description of resonances are as follow: s (singlet); d (doublet); t (triplet); q (quartet); qnt (quintet); sxt (sextet); spt (septet); oct (octet), m (multiplet); app (apparent); bs (broad singlet). The designation “ABq” for a ¹H NMR peak indicates that a peak was one partner of an AB quartet; if additional splitting was observed, they are noted after the ABq designation (e.g., ABqd).



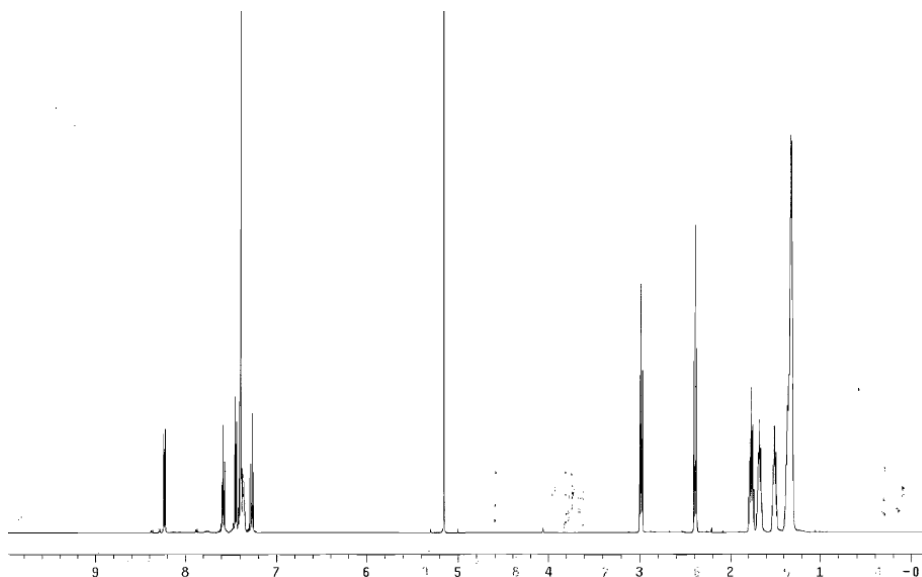
Preparation of *o*-Nitrothiophenol (2**):** To a suspension of *o*-nitrophenyl disulfide (0.805 g, 2.61 mmol) in 20 mL of degassed THF was added PPh₃ (1.03 g, 3.92 mmol), 2-mercaptoethanol (184 μL, 2.61 mmol), and 470 μL of H₂O (26.1 mmol). The solution was stirred at 50 °C for 6 h then cooled to RT, concd, redissolved in DCM, washed with brine, dried over Na₂SO₄, and evaporated. The resulting orange oil was subject to flash chromatography (9:1 hexanes:EtOAc) and pure *o*-nitrothiophenol¹⁶ (653 mg, 4.21 mmol) was isolated in 80.5% yield from the bright yellow band fractions. mp 40-42 °C.

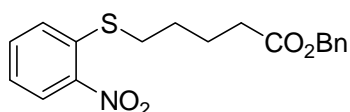
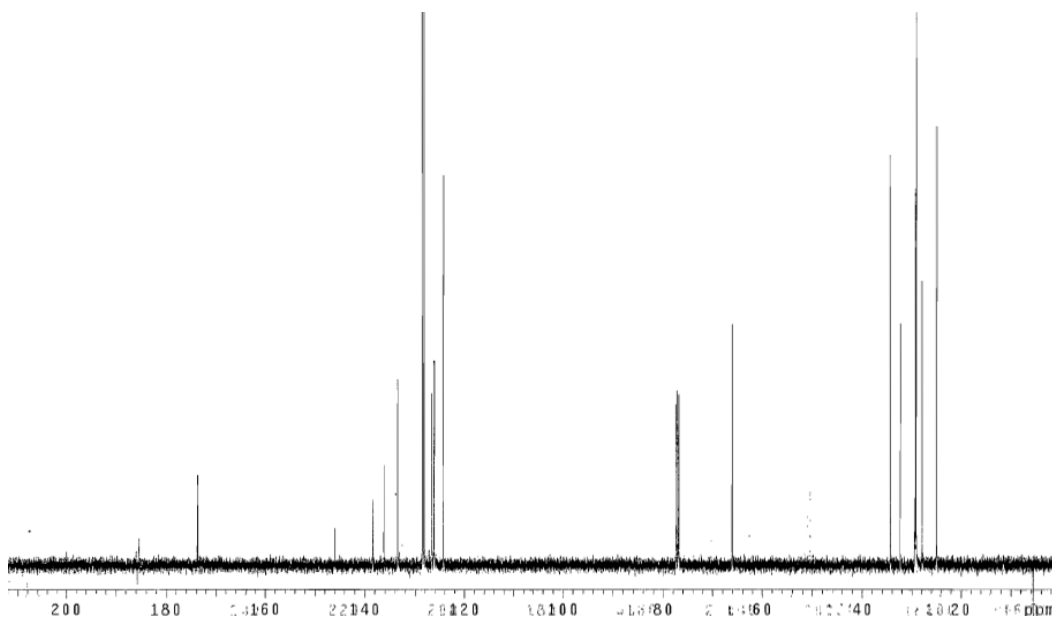


Preparation of Sulfides 3; General Procedure: To a suspension of NaI (0.4 mmol), K₂CO₃ (1 mmol), and bromide **1** (1 mmol) in dry acetone (10 mL) was added 1.05 mmol equiv of *o*-nitrothiophenol (**2**). The mixture was refluxed with stirring until the reaction was complete. The solution was then filtered, evaporated, redissolved in DCM, washed with brine, dried over Na₂SO₄, and concd. The sulfides were purified by flash chromatography in accordance to product R_f values.

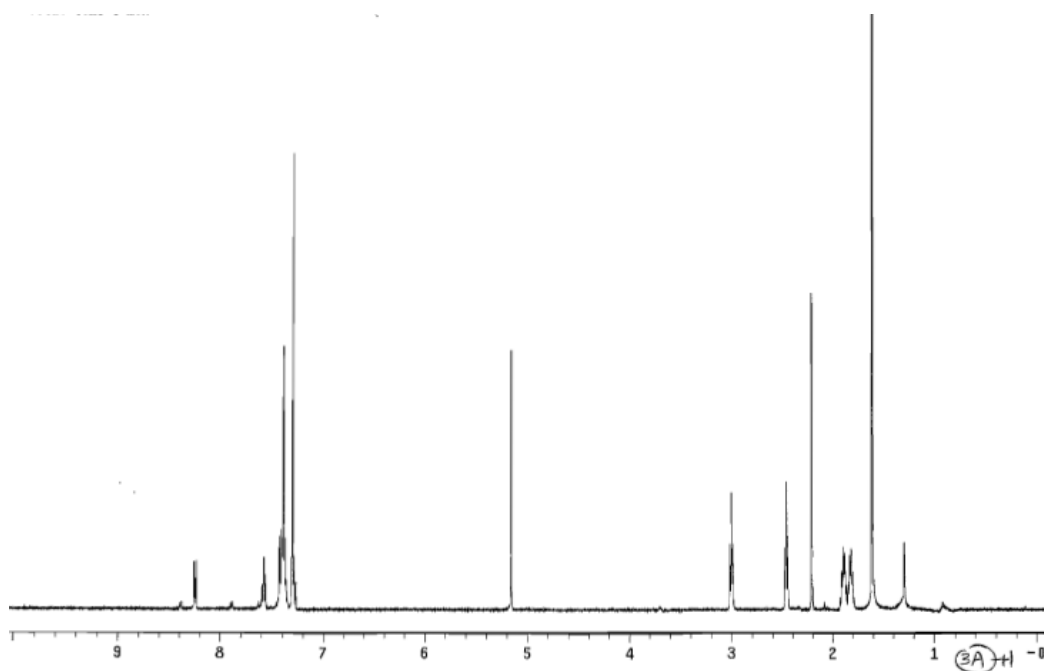


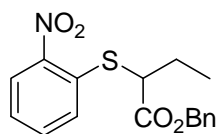
benzyl 11-(2-nitrophenylthio)undecanoate (3a): yellow oil (670 mg, 88%); TLC (SiO₂) R_f 0.48 (6:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.17 (dd, 1H, *J* = 7.0, 1.5 Hz), 7.52 (dt, 1H, *J* = 8.0, 1.5 Hz), 7.38 (d, 1H, *J* = 8.0 Hz), 7.34-7.29 (m, 5H), 7.21 (dt, 1H, *J* = 8.0, 1.0 Hz), 5.09 (s, 2H), 2.92 (t, 2H, *J* = 7.5 Hz), 2.33 (t, 2H, *J* = 7.5 Hz), 1.71 (qnt, 2H, *J* = 7.5 Hz), 1.62 (qnt, 2H, *J* = 7.5 Hz), 1.45 (qnt, 2H, *J* = 7.5 Hz), 1.30-1.26 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 173.7, 146.0, 138.4, 136.2, 133.5, 128.6, 128.2, 126.7, 126.2, 124.3, 66.1, 34.4, 32.4, 29.4, 29.3, 29.2, 27.9, 25.0; ESI-HRMS calcd for C₂₄H₃₁NO₄S [M+H]⁺ 430.2052, found 430.2041.



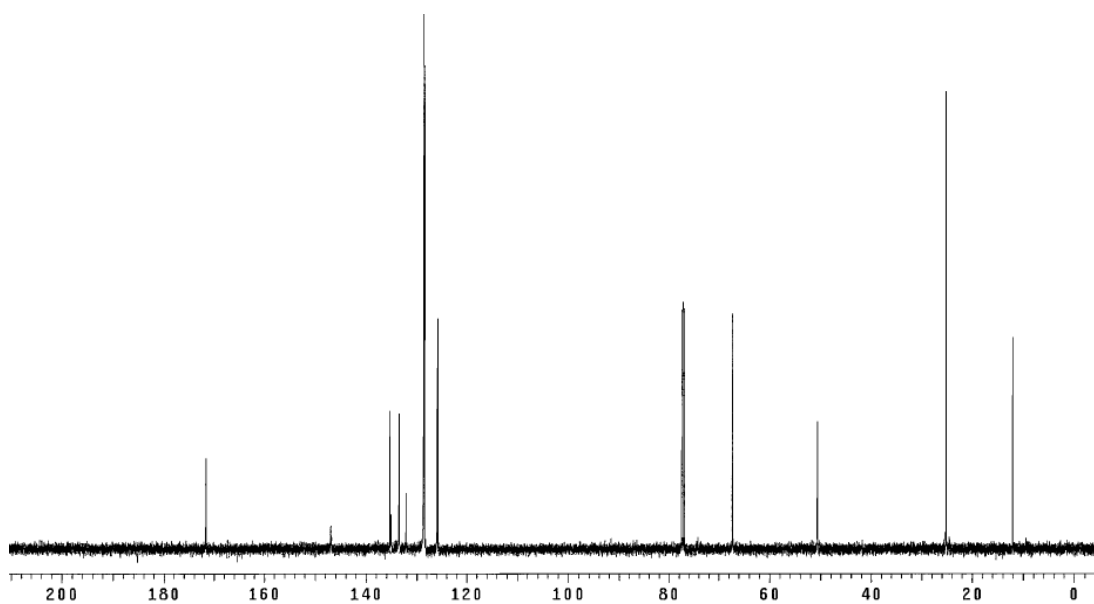
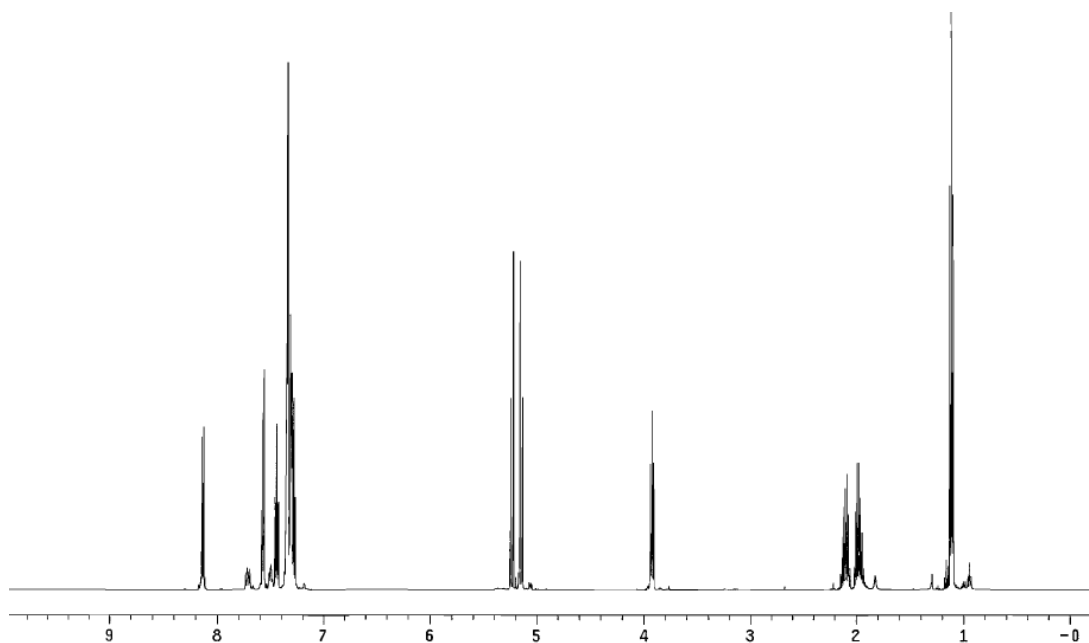


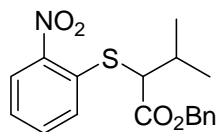
benzyl 5-(2-nitrophenylthio)pentanoate (3b): yellow oil (74 mg, 80%); TLC (SiO₂) R_f 0.23 (6:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, 1H, *J* = 8.5 Hz), 7.52 (t, 1H, *J* = 7.5 Hz), 7.37-7.31 (m, 4H), 7.25-7.20 (m, 3H), 5.10 (s, 2H), 2.94 (t, 2H, *J* = 7.0 Hz), 1.82 (qnt, 2H, *J* = 7.5 Hz), 1.76 (qnt, 2H, *J* = 7.5 Hz); ESI-HRMS calcd for C₁₈H₂₀NO₄S [M+H]⁺ 346.1180, found 346.1112.



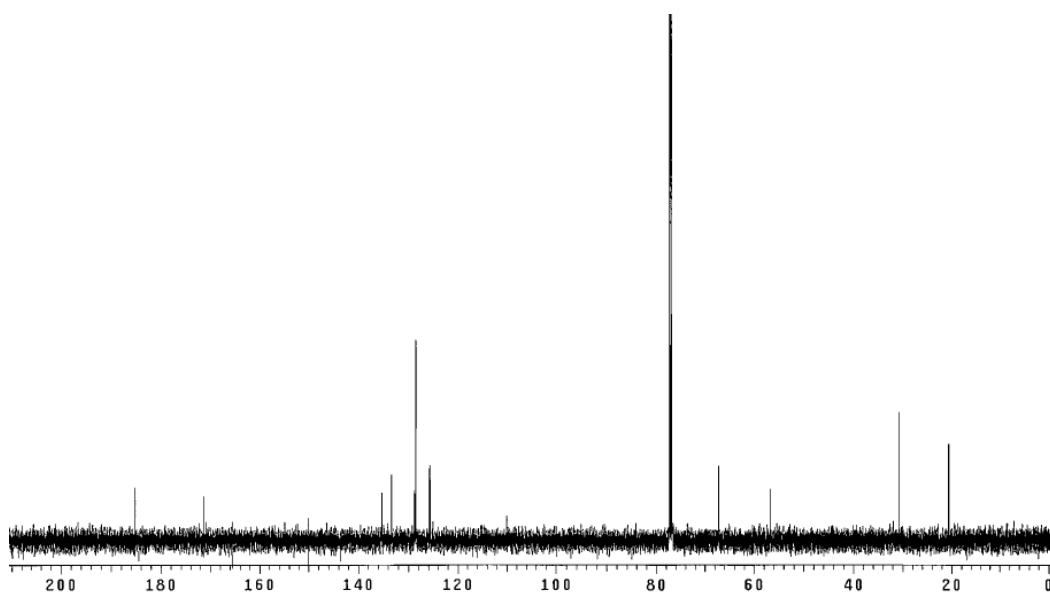
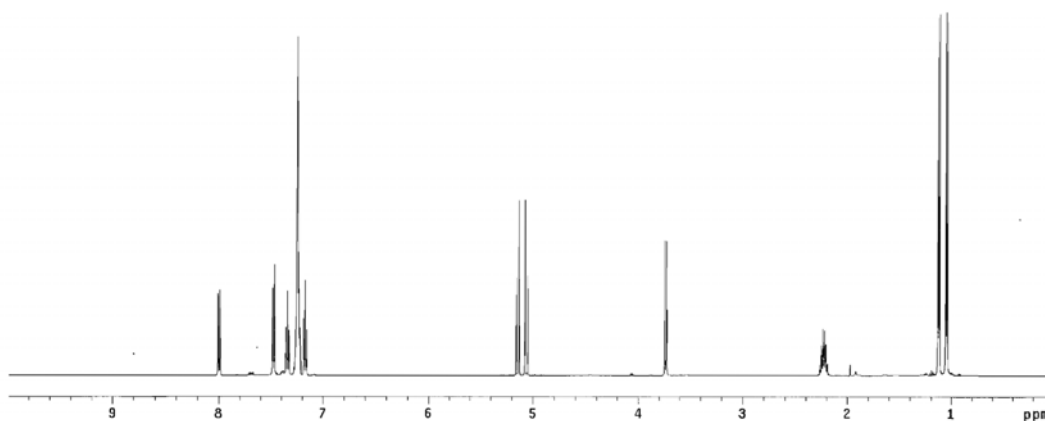


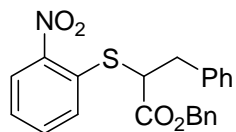
benzyl 2-(2-nitrophenylthio)butanoate (3c): yellow oil (166 mg, 78%); TLC (SiO₂) R_f 0.34 (9:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.07 (dd, 1H, *J* = 8.0, 1.0 Hz), 7.51 (d, 1H, *J* = 8.0 Hz), 7.39 (dt, 1H, *J* = 8.0, 1.0 Hz), 7.31-7.21 (m, 6H), 5.17 and 5.09 (ABq, 2H, Δ*v* = 40.0 Hz, *J* = 12.0 Hz), 3.87 (t, 1H, *J* = 7.5 Hz), 2.09-2.00 (m, 1H), 1.96-1.87 (m, 1H), 1.06 (t, 3H, *J* = 7.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 171.7, 147.0, 135.4, 135.1, 133.5, 132.2, 132.1, 128.8, 128.7, 128.5, 125.9, 125.8, 67.3, 50.6, 25.2, 12.1.



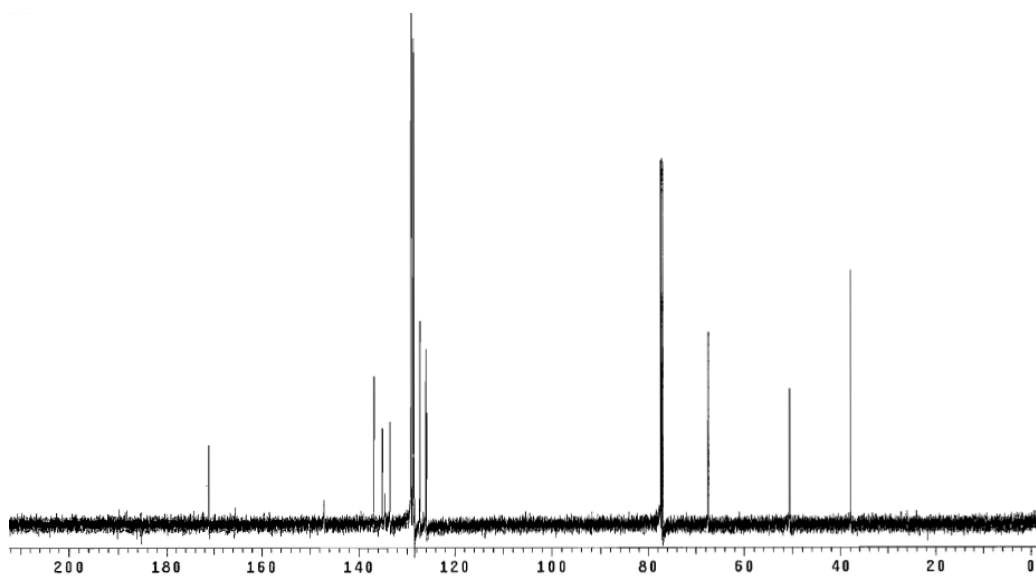
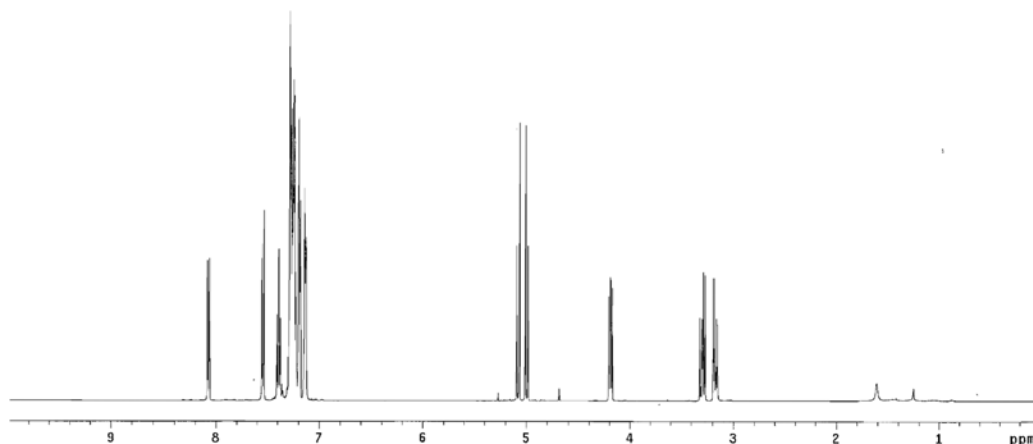


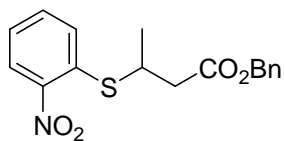
benzyl 2-(2-nitrophenylthio)-3-methylbutanoate (3d): yellow solid (489 mg, 56%); mp 54-55 °C; TLC (SiO₂) R_f 0.50 (9:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 7.99 (dd, 1H, *J* = 8.0, 1.0 Hz), 7.46 (d, 1H, *J* = 8.0 Hz), 7.33 (dt, 1H, *J* = 8.0, 1.0 Hz), 7.26-7.21 (m, 5H), 7.16 (t, 1H, *J* = 7.5 Hz), 5.13 and 5.05 (ABq, 2H, Δ*ν* = 40.0 Hz, *J* = 12.0 Hz), 3.72 (d, 1H, *J* = 8.5 Hz), 2.24 (oct, 1H, *J* = 7.0 Hz), 1.12 (d, 3H, *J* = 7.0 Hz), 1.04 (d, 3H, *J* = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 185.4, 135.5, 133.5, 129.0, 128.8, 128.7, 126.0, 125.8, 67.4, 56.9, 31.0, 20.8.



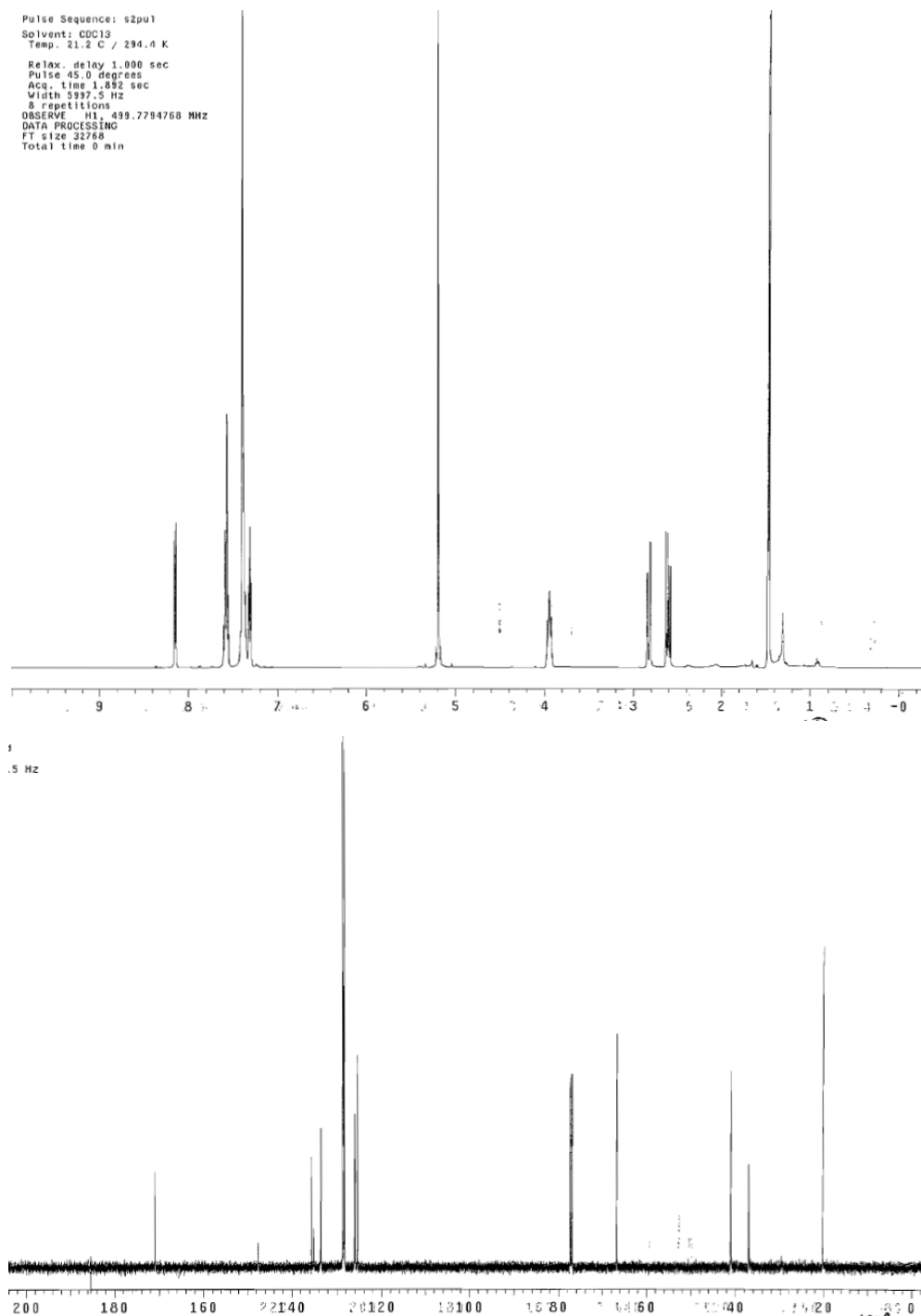


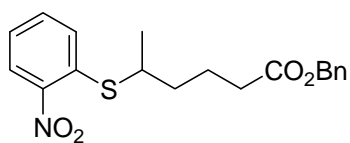
benzyl 2-(2-nitrophenylthio)-3-phenylpropanoate (3e): yellow oil (199 mg, 83%); TLC (SiO₂) R_f 0.50 (7:1 hexanes:EtOAc); 8.06 (d, 1H, $J = 8.5$ Hz), 7.53 (d, 1H, $J = 8.0$ Hz), 7.38 (dt, 1H, $J = 7.5, 1.5$ Hz), 7.27-7.21 (m, 7H), 7.18-7.17 (m, 2H), 7.13-7.11 (m, 2H), 5.07 and 4.98 (ABq, 2H, $\Delta\nu = 45.0$ Hz, $J = 12.0$ Hz), 4.18 (dd, 1H, ABX, $J_{AX} = 9.0$ Hz, $J_{BX} = 6.0$ Hz), 3.29 (ABdq, 1H, ABX, $J_{AB} = 14.0$ Hz, $J_{BX} = 6.0$ Hz), 3.13 (ABdq, 1H, ABX, $J_{AB} = 14.0$ Hz, $J_{AX} = 9.0$ Hz); ¹³C NMR (125 MHz, CDCl₃) δ 171.2, 136.9, 135.2, 133.6, 129.2, 128.9, 128.7, 128.6, 128.5, 127.4, 126.2, 126, 67.5, 50.7, 37.9. ESI-HRMS calcd for C₂₂H₁₉NO₄S [M+Na]⁺ 416.0932, found 416.0920.



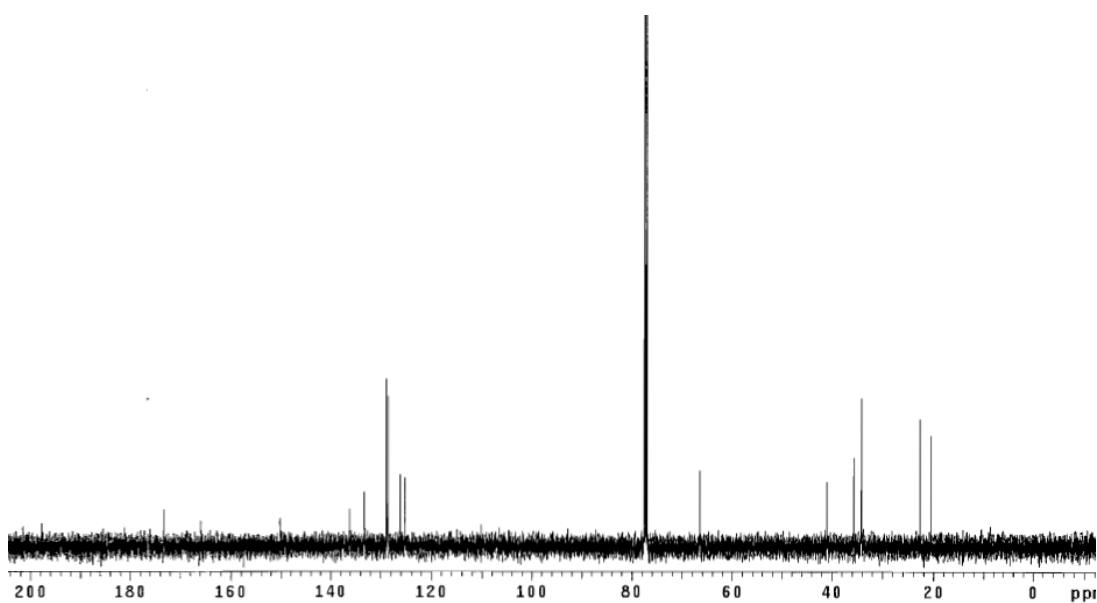
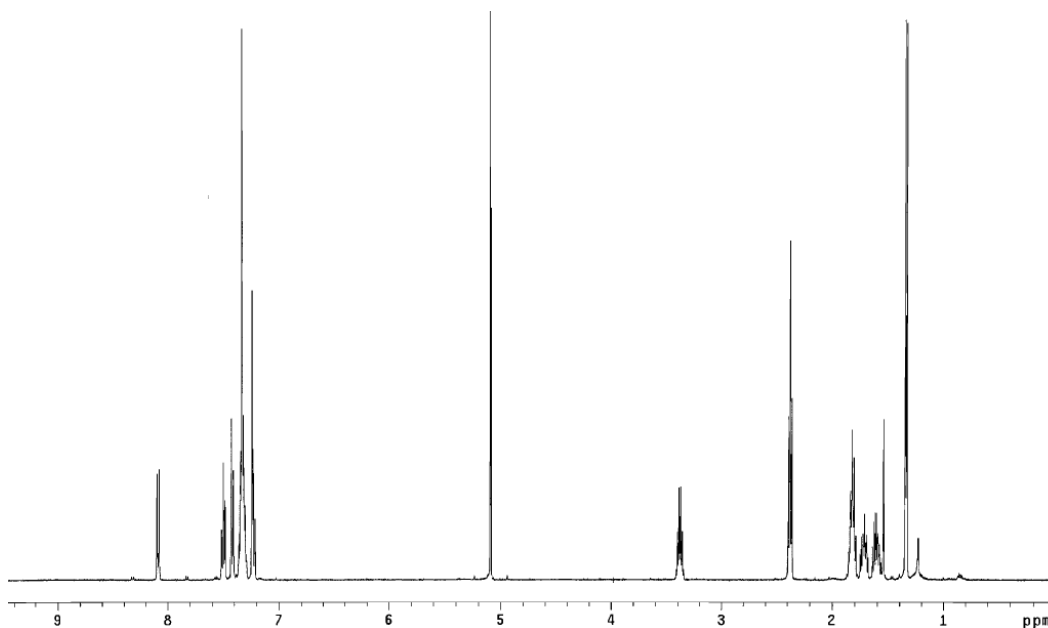


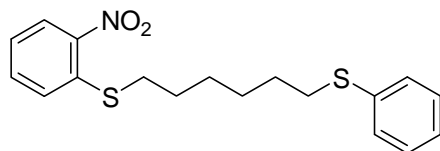
benzyl 3-(2-nitrophenylthio)butanoate (3f): yellow oil (179 mg, 66%); TLC (SiO₂) R_f 0.52 (25:1 hexanes:EtOAc); δ 8.08 (d, 1H, $J = 8.0$ Hz), 7.54-7.49 (m, 2H), 7.36-7.29 (m, 5H), 7.26 (t, 1H, $J = 6.5$ Hz), 5.13 (s, 2H), 3.88 (m, 1H), 2.76 (ABdq, 1H, $J_{AB} = 16.0$ Hz, $J = 5.0$ Hz), 2.54 (ABdq, 1H, $J_{AB} = 16.0$ Hz, $J = 8.5$ Hz), 1.41 (d, 3H, $J = 6.5$ Hz); ¹³C NMR (125 MHz, CDCl₃) δ 170.9, 147.5, 135.6, 135.1, 133.5, 128.7, 128.5, 128.4, 126.1, 125.5, 66.8, 41.1, 37.1, 20.4.



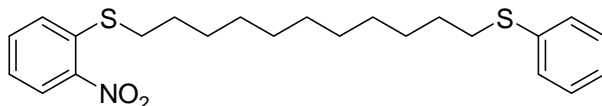


Benzyl 5-(2-nitrophenylthio)hexanoate (3g): yellow oil (250 mg, 99%); TLC (SiO₂) R_f 0.62 (3:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, 1H, *J* = 8.5 Hz), (7.50 (dt, 1H, *J* = 7.0, 1.0 Hz), 7.41 (d, 1H, *J* = 8.0 Hz), 7.33-7.29 (m, 5H), 5.09 (s, 2H), 3.38 (m, 1H), 2.37 (t, 2H, *J* = 7.0 Hz), 1.85-1.79 (m, 2H), 1.75-1.68 (m, 1H), 1.64-1.56 (m, 1H), 1.35 (d, 3H, *J* = 6.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 173.2, 136.1, 133.2, 128.8, 128.5, 126.1, 125.2, 66.5, 40.9, 25.7, 34.1, 22.7, 20.5; ESI-HRMS calcd for C₁₉H₂₁NO₄S [M+Na]⁺ 382.1083, found 382.1082.

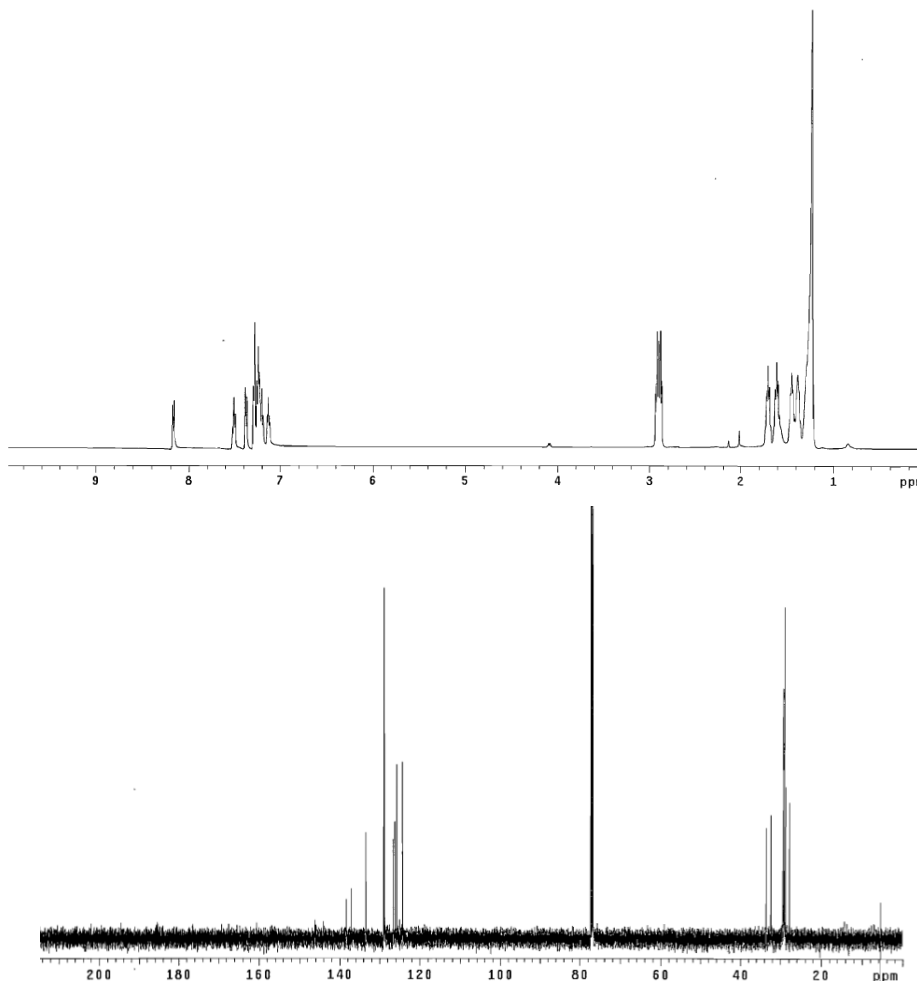


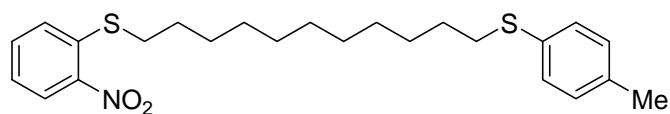


1-(6-(phenylthio)hexylthio)-2-nitrobenzene (3h): yellow solid (253 mg, 72%); mp 39-40 °C; R_f 0.49 (9:1 hexanes:EtOAc); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.21 (dd, 1H, $J = 10.0, 2.0$ Hz), 7.54 (dt, 1H, $J = 10.5, 2.0$ Hz), 7.40-7.15 (m, 7H), 2.96-2.91 (m, 4H), 1.76-1.65 (m, 4H), 1.51-1.48 (m, 4H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 133.6, 129.2, 129, 126.7, 126.4, 125.9, 124.5, 33.7, 32.4, 29.1, 28.8, 28.5, 27.9; ESI-HRMS calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2\text{S}_2$ $[\text{M}+\text{H}]^+$ 348.1086, found 348.1095.

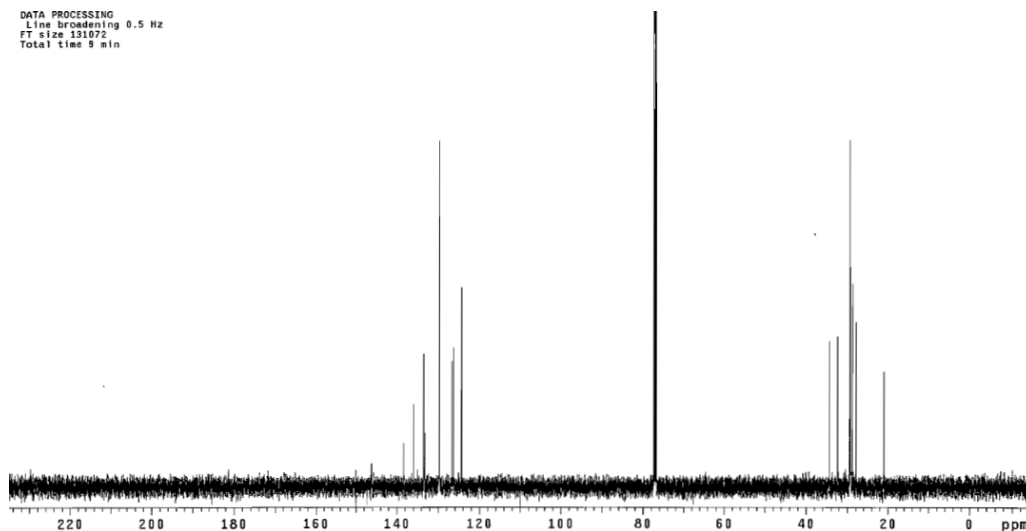
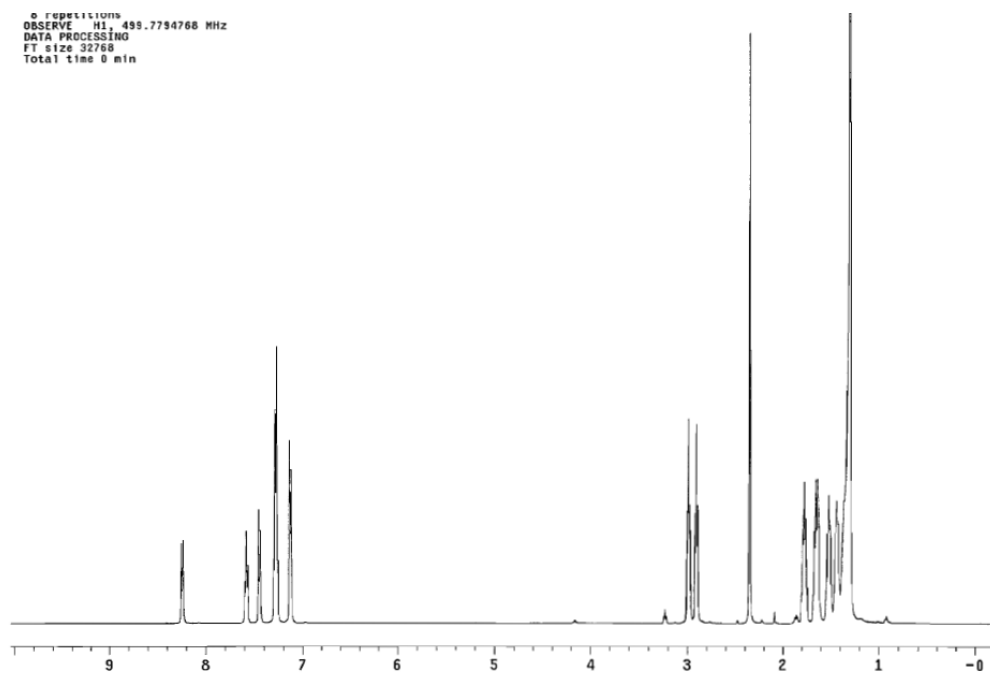


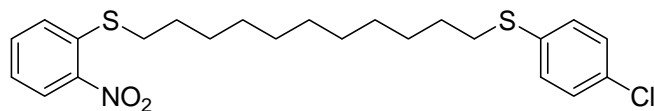
1-(11-(2-nitrophenylthio)undecylthio)benzene (3i): yellow solid (664 mg, 93%); mp 38-39 °C; TLC (SiO_2) R_f 0.47 (9:1 hexanes:EtOAc); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.16 (d, 1H, $J = 8.5$ Hz), 7.51 (t, 1H, $J = 7.5$ Hz), 7.37 (d, 1H, $J = 8.0$ Hz), 7.29-7.19 (m, 5H), 7.13 (t, 1H, $J = 7.5$ Hz), 2.91 (t, 2H, $J = 7.5$ Hz), 2.88 (t, 2H, $J = 7.5$ Hz), 1.71 (qnt, 2H, $J = 7.5$ Hz), 1.61 (qnt, 2H, $J = 7.5$ Hz), 1.48-1.42 (m, 2H), 1.41-1.36 (m, 2H), 1.32-1.24 (m, 10H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 137.3, 133.5, 129.1, 129, 126.8, 126.4, 125.8, 124.4, 33.8, 32.6, 29.6, 29.4, 29.3, 29, 28.1.



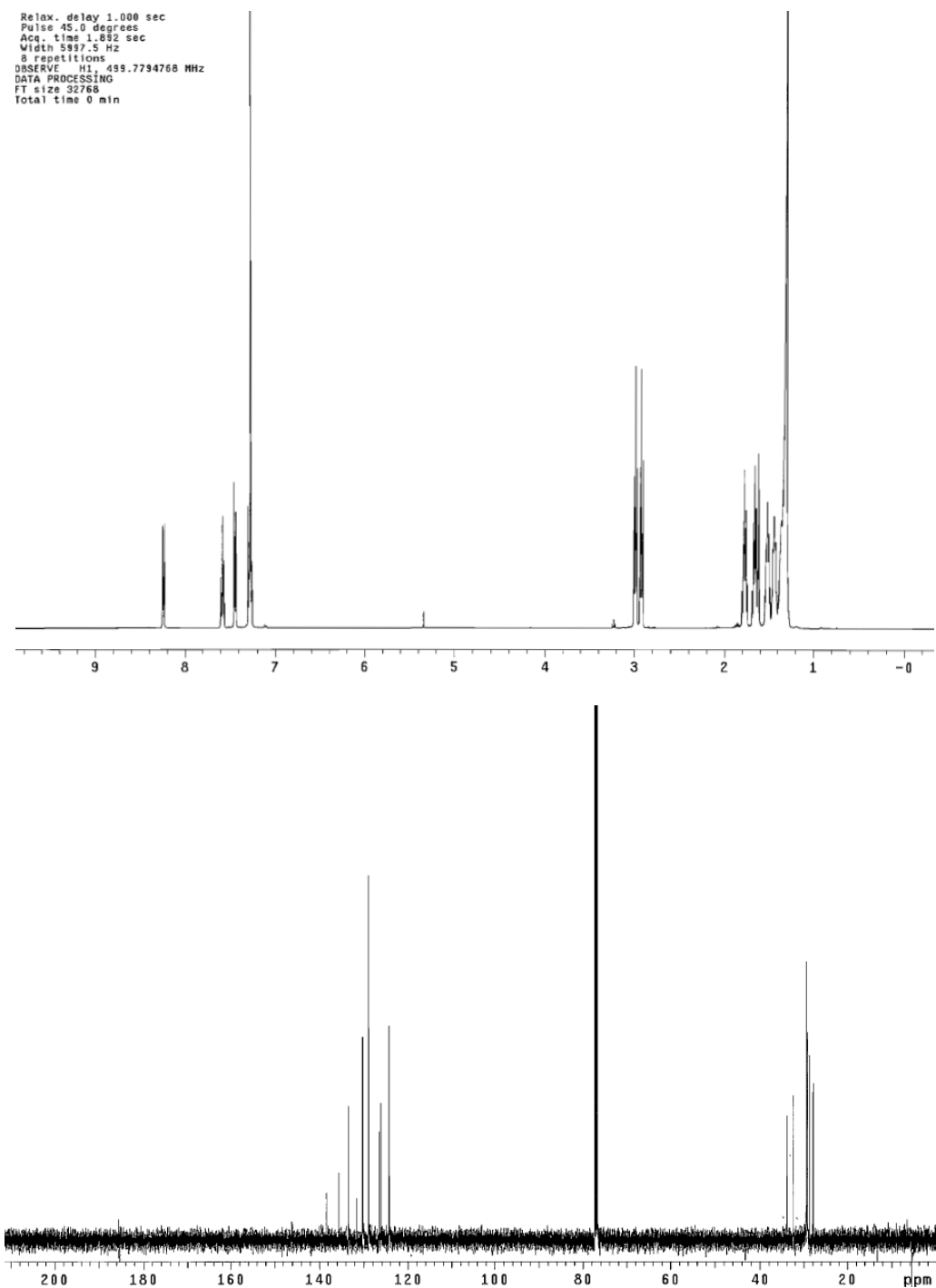


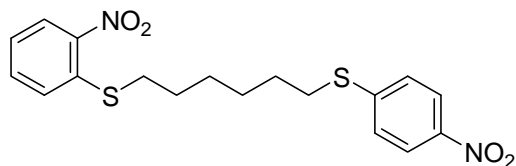
1-(11-(2-nitrophenylthio)undecylthio)-4-methylbenzene (3j): yellow solid (96.5 mg, 56%); mp 66-67 °C; TLC (SiO₂) R_f 0.51 (9:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, 1H, *J* = 8.0 Hz), 7.53 (t, 1H, *J* = 7.0 Hz), 7.39 (d, 1H, *J* = 8.5 Hz), 7.25-7.20 (m, 3H), 7.08-7.07 (m, 2H), 2.94 (t, 2H, *J* = 7.5 Hz), 2.86 (t, 2H, *J* = 7.5 Hz), 2.30 (s, 3H), 1.72 (qnt, 2H, *J* = 7.5 Hz), 1.60 (qnt, 2H, *J* = 7.5 Hz), 1.50-1.42 (m, 2H), 1.41-1.36 (m, 2H), 1.36-1.22 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 138.5, 136.0, 133.5, 133.3, 129.9, 129.8, 126.8, 126.3, 124.4, 34.5, 32.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 29.0, 28.0, 21.2.



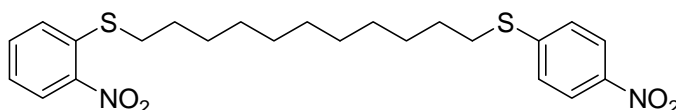


1-(11-(2-nitrophenylthio)undecylthio)-4-chlorobenzene (3k): yellow solid (343 mg, 76%; 2 steps); mp 83-84 °C; TLC (SiO₂) R_f 0.5 (9:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.20 (d, 1H, *J* = 8.5 Hz), 7.54 (t, 1H, *J* = 7.5 Hz), 7.40 (d, 1H, *J* = 8.5 Hz), 7.26-7.22 (m, 5H), 2.95 (t, 2H, *J* = 7.5 Hz), 2.88 (t, 2H, *J* = 7.5 Hz), 1.74 (qnt, 2H, *J* = 7.5 Hz), 1.63 (qnt, 2H, *J* = 7.5 Hz), 1.48 (qnt, 2H, *J* = 7.5 Hz), 1.41 (qnt, 2H, *J* = 7.5 Hz), 1.36-1.26 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 138.5, 135.8, 133.5, 131.8, 130.4, 129.1, 126.8, 126.3, 124.5, 34.1, 32.6, 29.6, 29.4, 29.3, 29.2, 28.9, 28.1.

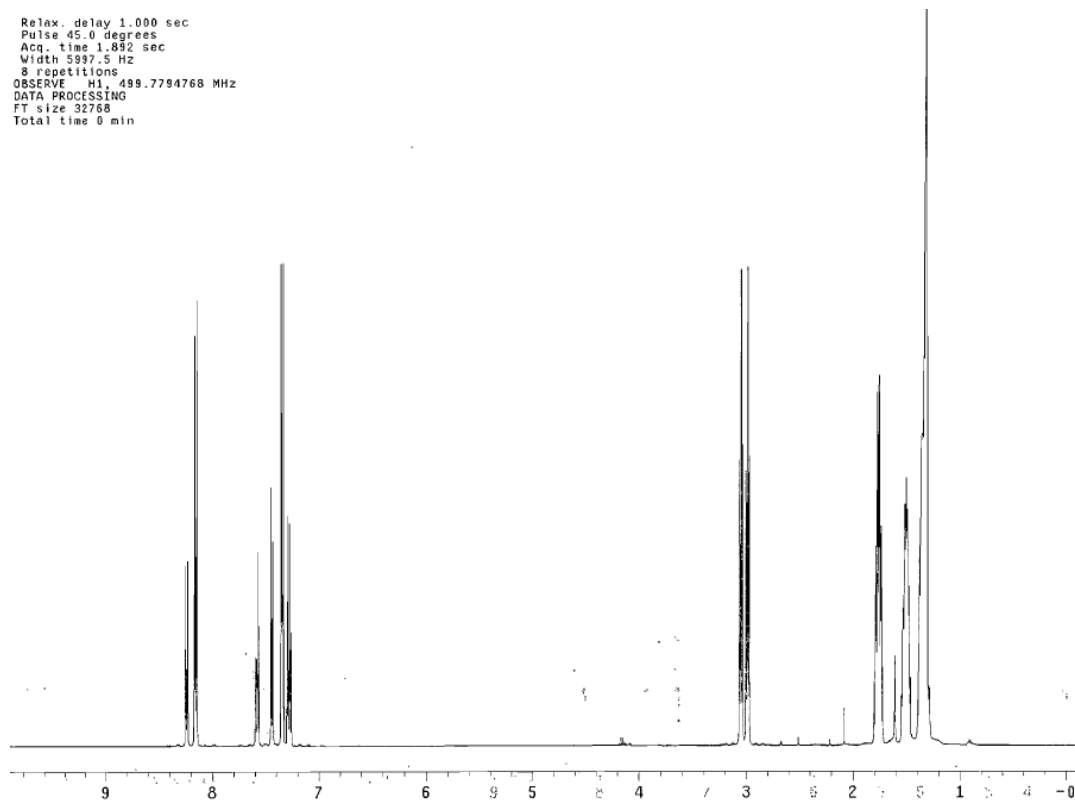




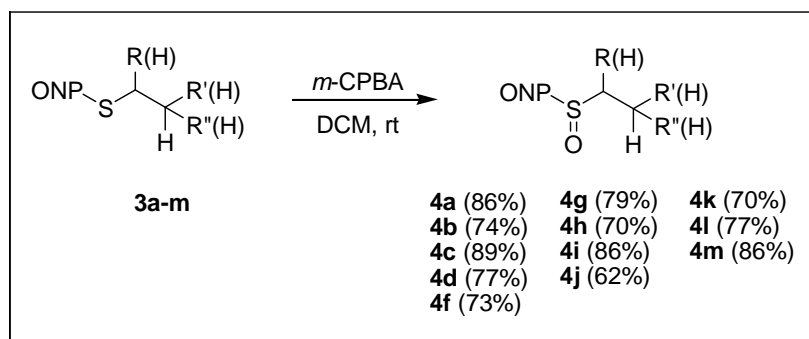
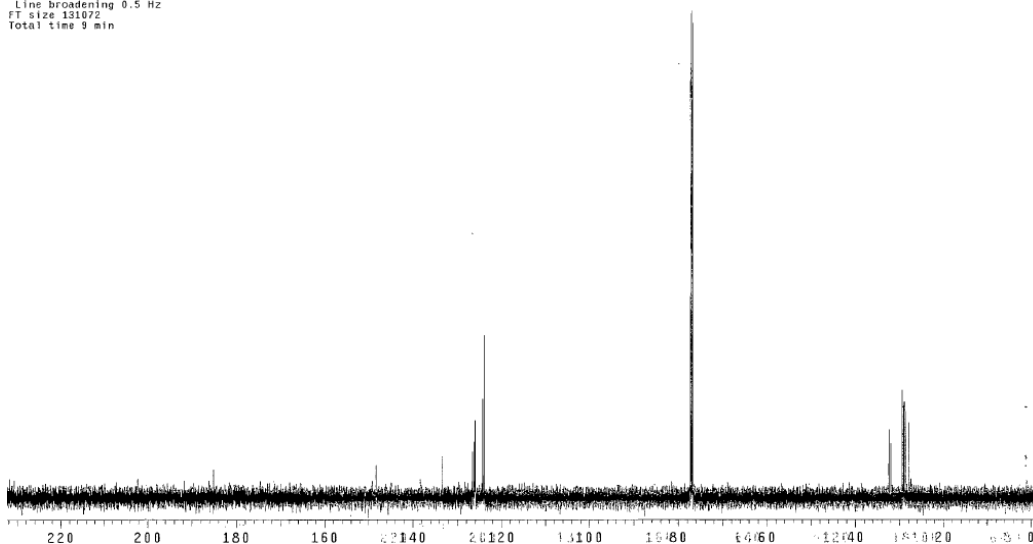
1-(6-(4-nitrophenylthio)hexylthio)-2-nitrobenzene (3l): yellow solid (156.7 mg, 98%); mp 83-84 °C; TLC (SiO₂) R_f 0.68 (1:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, 1H, *J* = 8.0 Hz), 8.10 (d, 2H, *J* = 8.5 Hz), 7.52 (t, 1H, *J* = 7.5 Hz), 7.37 (d, 1H, *J* = 8.5 Hz), 7.29 (d, 2H, *J* = 8.0 Hz), 7.21 (m, 1H), 2.99 (t, 2H, *J* = 7.0 Hz), 2.95 (t, 2H, *J* = 7.0 Hz), 1.76-1.72 (m, 4H), 1.54 (m, 4H); ESI-HRMS calcd for C₁₈H₂₀N₂O₄S₂ [M+H]⁺ 393.0937, found 393.0943.



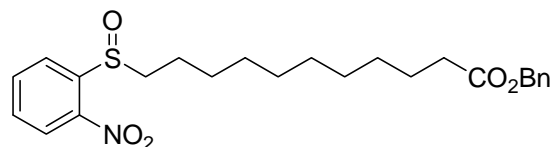
1-(11-(2-nitrophenylsulfinyl)undecylsulfinyl)-4-nitrobenzene (3m): yellow solid (96.5 mg, 53%; 2 steps); mp 66-67 °C; TLC (SiO₂) R_f 0.26 (9:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, 1H, *J* = 8.0 Hz), 8.09 (d, 2H, *J* = 9.0 Hz), 7.52 (t, 1H, *J* = 8.0 Hz), 7.38 (d, 1H, *J* = 8.5 Hz), 7.28 (d, 1H, *J* = 9.0 Hz), 7.22 (t, 1H, *J* = 8.0 Hz), 7.18, (t, 1H, *J* = 8.0 Hz) 2.95 (t, 2H, *J* = 7.5 Hz), 2.89 (t, 2H, *J* = 7.5 Hz), 1.71-1.63 (m, 4H), 1.45-1.37 (m, 4H), 1.26-1.19 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 148.4, 133.6, 126.9, 126.8, 126.3, 126.2, 124.5, 124.1, 32.6, 32.1, 29.6, 29.3, 29.2, 29, 28.7, 28.0.



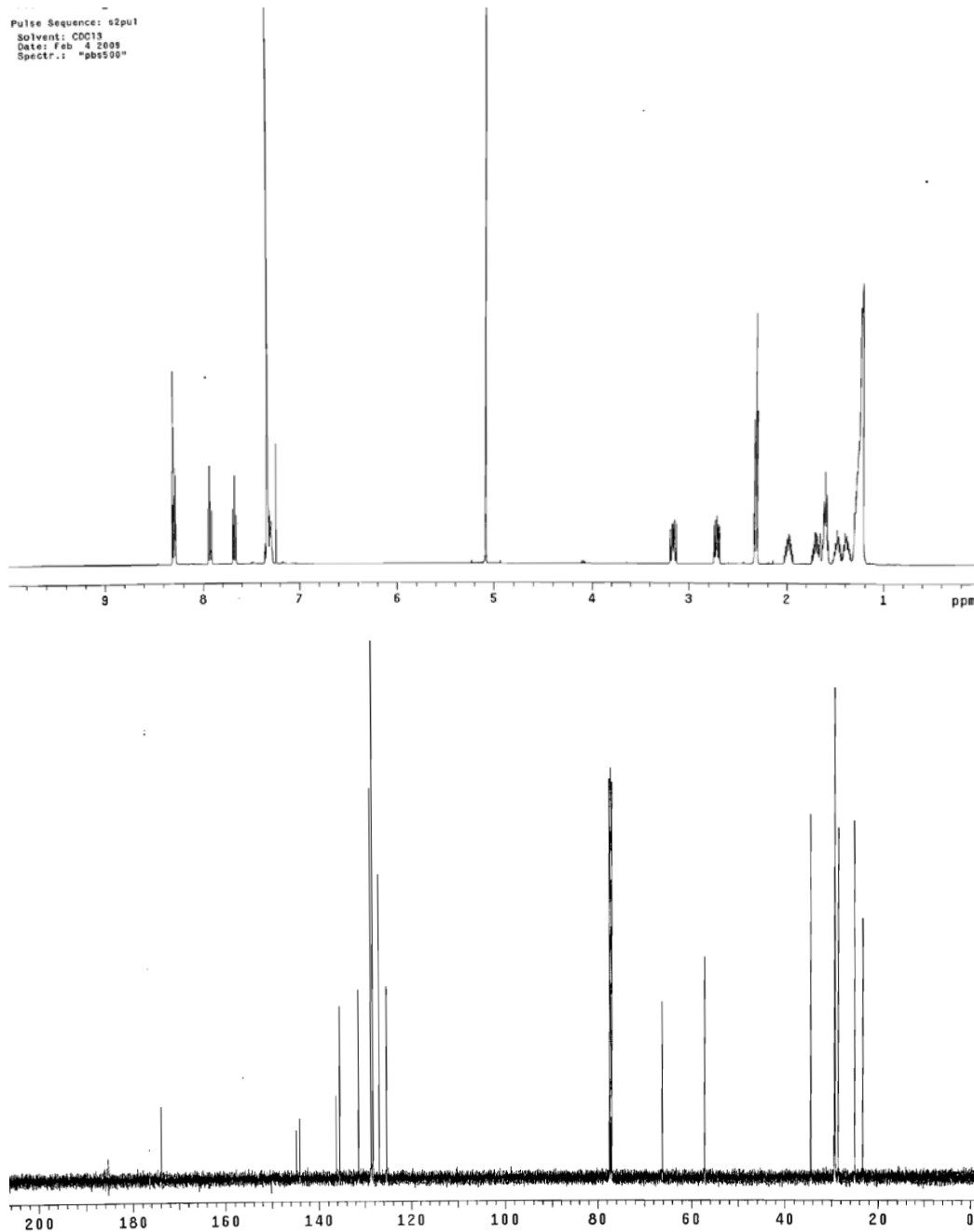
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 Line broadening 0.5 Hz
 FT size 131072
 Total time 9 min

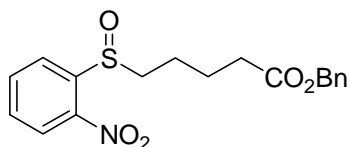


S-Oxidation of Sulfides 3; General Procedure: To a stirring solution of sulfides **3a-g** (1 mmol) in DCM (10 mL) was added *m*-CPBA (1.25 mmol equiv) in 5 mL of DCM or in the case of disulfides **4h-m**, 2.50 equiv of peroxide was used. After 2.5 hrs, the reactions were quenched with 5% NaHCO₃ (20 mL) and extracted twice with DCM. The combined organic extracts were dried over Na₂SO₄, filtered, and concd. The crude sulfoxides were purified by flash chromatography in accordance to product R_f values.

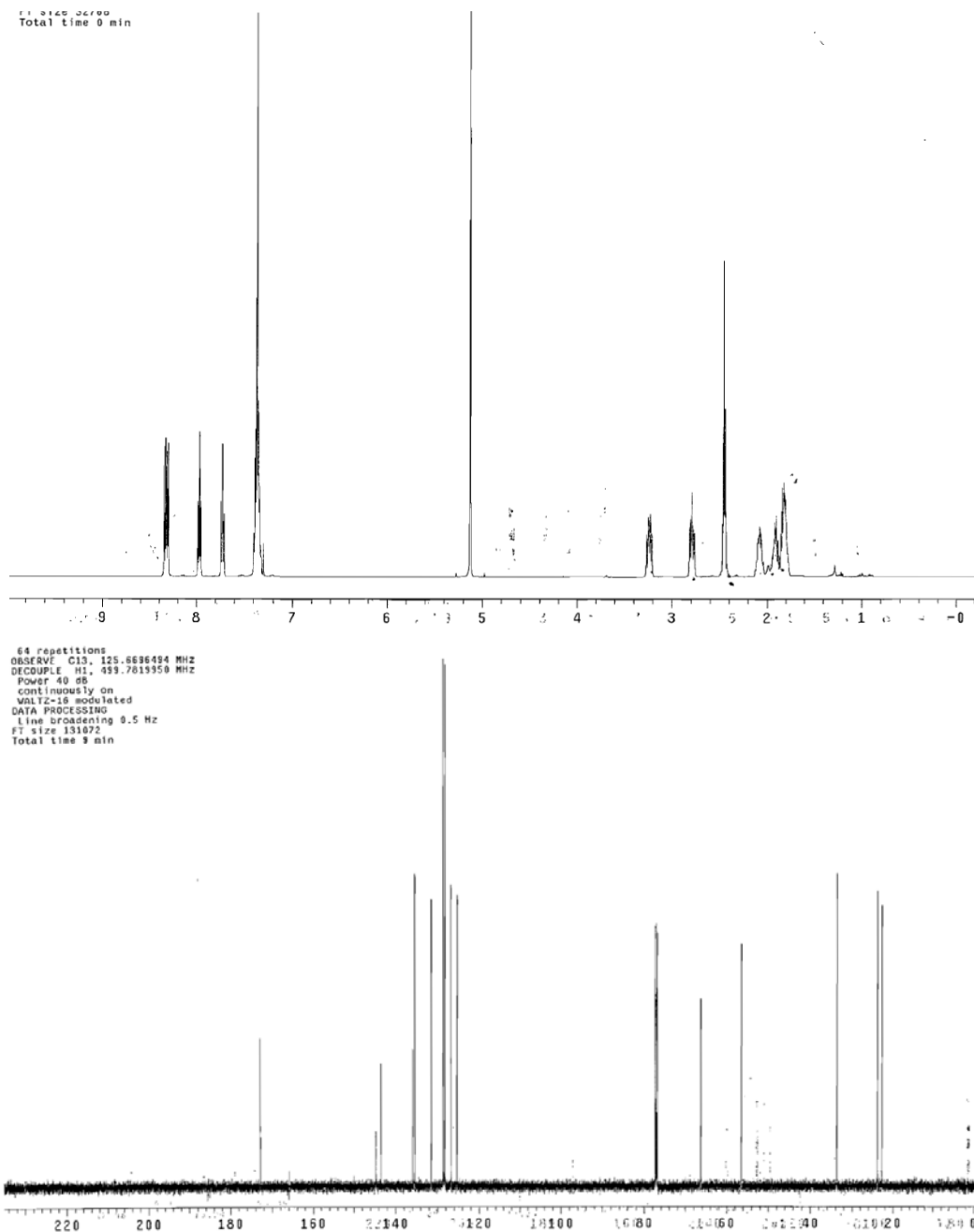


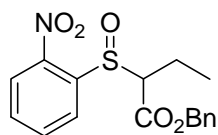
benzyl 11-(2-nitrophenylsulfinyl)undecanoate (4a): yellow solid (532 mg, 74%); mp 37-38 °C; TLC (SiO₂) R_f 0.43 (3:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.31-8.28 (m, 2H), 7.93 (t, 1H, *J* = 7.5 Hz), 7.68 (t, 1H, *J* = 7.5 Hz), 7.32-7.28 (m, 5H), 5.09 (s, 2H), 3.15 (ddd, 1H, *J* = 13.0, 9.5, 7.0 Hz), 2.72 (ddd, 1H, *J* = 13.0, 9.5, 4.5 Hz), 2.32 (t, 2H, *J* = 7.5 Hz), 2.02-1.95 (m, 1H), 1.73-1.66 (m, 1H), 1.63-1.58 (qnt, 2H, *J* = 7.5 Hz), 1.51-1.46 (m, 1H), 1.41-1.35 (m, 1H), 1.30-1.24 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 173.8, 144.8, 144.0, 136.3, 135.5, 131.4, 128.7, 128.3, 126.9, 125.3, 66.2, 57.2, 34.4, 29.4, 29.4, 29.3, 29.2, 28.6, 25.2, 23.3; ESI-HRMS calcd for C₂₄H₃₂NO₅S [M+H]⁺ 446.1996, found 446.2004.



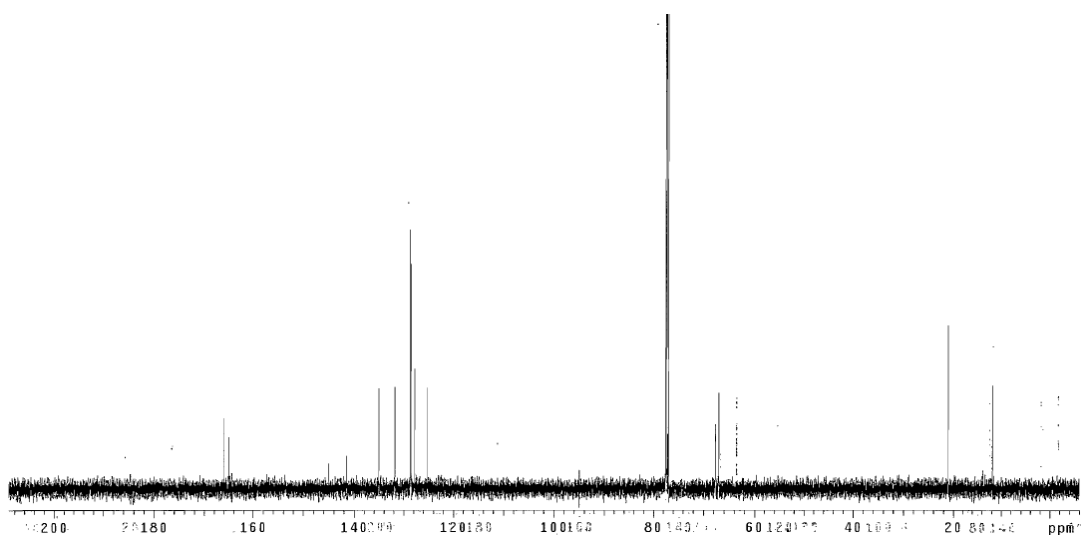
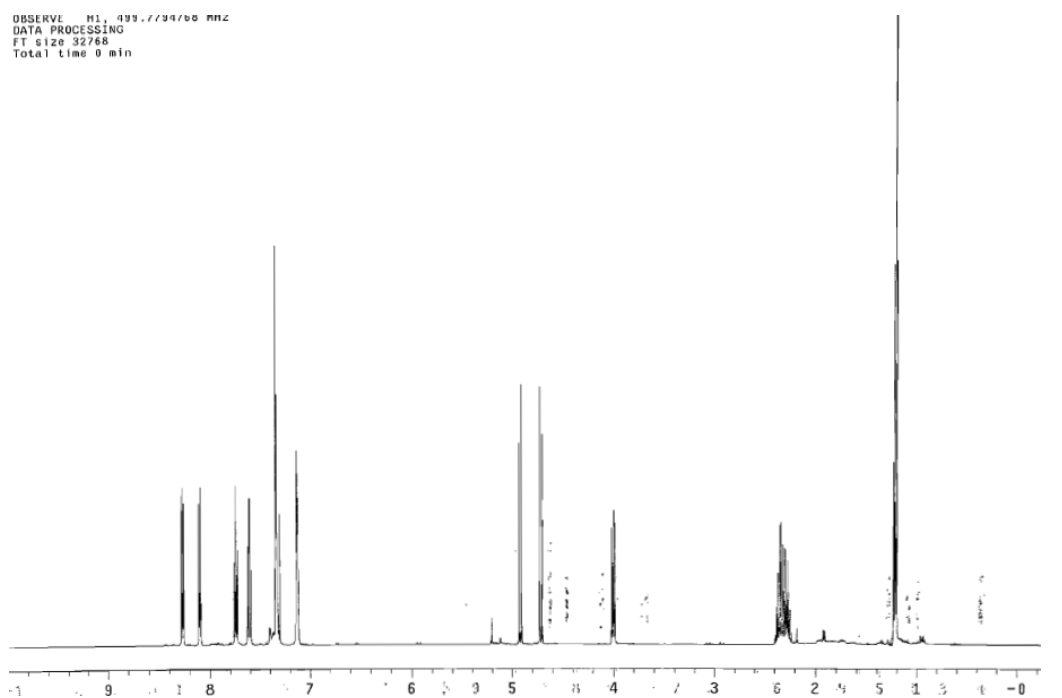


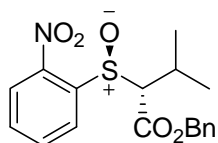
benzyl 5-(2-nitrophenylsulfinyl)pentanoate (4b): yellow solid (85.5 mg, 86%); mp 60-61 °C; TLC (SiO₂) R_f 0.25 (1:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.28 (d, 1H, *J* = 8.0 Hz), 8.25 (d, 1H, *J* = 8.0 Hz), 7.91 (t, 1H, *J* = 7.5 Hz), 7.67 (t, 1H, *J* = 7.5 Hz), 7.34-7.27 (m, 5H), 5.07 (s, 2H), 3.17 (ddd, 1H, AA'MX, *J*_{MX} = 13.5 Hz, *J*_{AX} = 9.0 Hz, *J*_{A'X} = 7.0 Hz), 2.73 (ddd, 1H, AA'MX, *J*_{MX} = 13.5, *J*_{AM} = 9.0 Hz, *J*_{A'M} = 4.5 Hz), 2.38 (t, 2H, *J* = 7.0 Hz), 2.02 (m, 1H, AA'MX), 1.86 (m, 1H, AA'MX), 1.75 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 172.9, 144.7, 143.6, 136, 135.5, 131.5, 128.7, 128.4, 128.3, 126.9, 125.4, 66.4, 56.5, 33.8, 23.8, 22.7; ESI-HRMS calcd for C₁₈H₂₀NO₅S [M+H]⁺ 362.1057, found 362.1067.





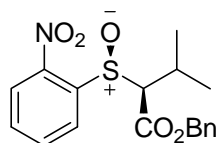
benzyl 2-(2-nitrophenylsulfinyl)butanoate (4c): yellow oil (140 mg, 89%); TLC (SiO₂) R_f 0.29 (3:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.26 (dd, 1H, *J* = 8.0, 1.0 Hz), 8.04 (dd, 1H, *J* = 8.0, 1.5 Hz), 7.69 (dt, 1H, *J* = 8.0, 1.0 Hz), 7.55 (dt, 1H, *J* = 8.0, 1.5 Hz), 7.28-7.26 (m, 3H), 7.08-7.06 (m, 2H), 4.86 and 4.65 (ABq, 2H, Δ*v* = 105.0 Hz, *J* = 12.5 Hz), 3.94 (dd, 1H, *J* = 9.0, 7.0 Hz), 2.34-2.17 (m, 2H), 1.22 (t, 3H, *J* = 7.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 166.1, 164.9, 145.1, 141.4, 135.1, 131.8, 128.7, 128.6, 128.5, 127.8, 125.2, 67.7, 67.0, 21.1, 11.8; ESI-HRMS calcd for C₁₇H₁₈NO₅S [M+H]⁺ 348.0900, found 348.0893.





(+/-) anti-4d

(major)



(+/-) syn-4d

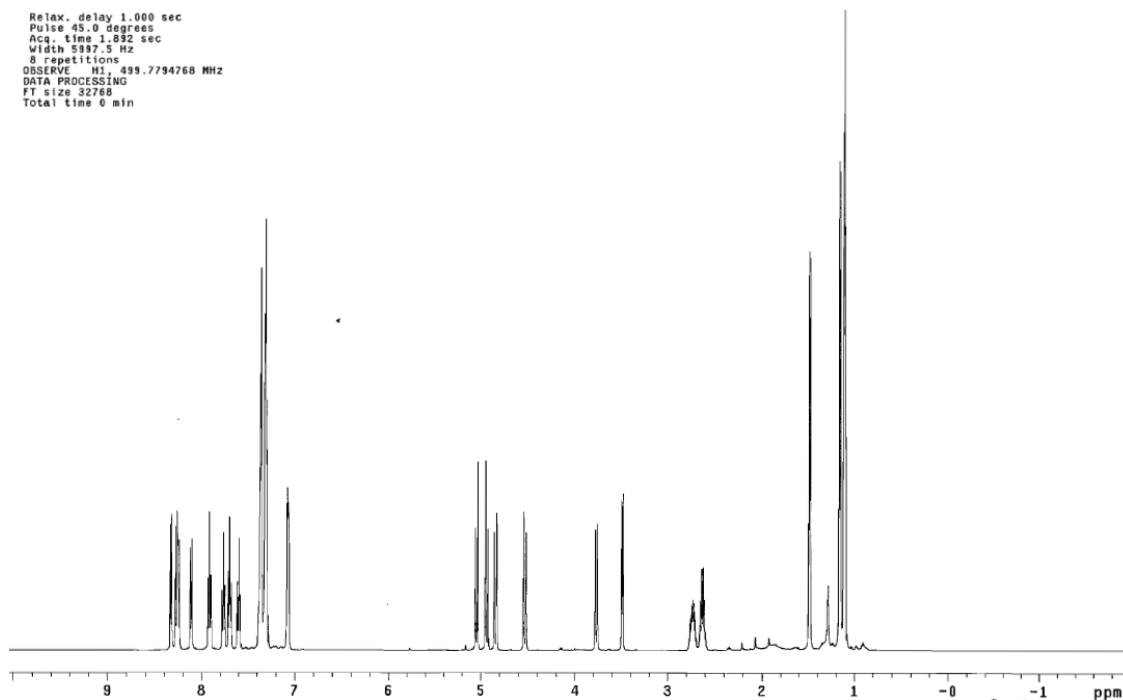
(minor)

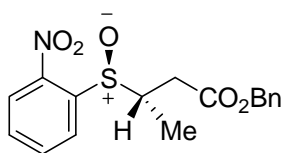
benzyl 2-(2-nitrophenylsulfinyl)-3-methylbutanoate (4d): yellow solid (68.4 mg, 77%; inseparable mixture of diastereomers); mp 101-102 °C; TLC (SiO₂) R_f 0.33 (3:1 hexanes:EtOAc); ESI-HRMS calcd for C₁₈H₂₀NO₅S [M+H]⁺ 362.1057, found 362.1050;

(±) **anti-4d** (major) ¹H NMR (500 MHz, CDCl₃) δ 8.27 (d, 1H, *J* = 8.0 Hz), 8.20 (d, 1H, *J* = 8.0 Hz), 7.85 (t, 1H, *J* = 7.5 Hz), 7.63 (t, 1H, *J* = 7.5 Hz), 7.30-7.23 (m, 4H), 7.01 (m, 1H), 4.98 and 4.87 (ABq, 2H, Δ*v* = 55.0 Hz, *J* = 12.0 Hz), 3.42 (d, 1H, AA'BC, *J*_{BC} = 7.0 Hz), 2.56 (app sxt, 1H, AA'BC, *J* = 7.0 Hz), 1.09 (d, 3H, AA'BC, *J*_{A'B} = 7.0 Hz), 1.05 (d, 3H, AA'BC, *J*_{AB} = 7.0 Hz);

(±) **syn-4d** (minor) ¹H NMR (500 MHz, CDCl₃) 8.23 (d, 1H, *J* = 8.0 Hz), 8.10 (d, 1H, *J* = 8.0 Hz), 7.76 (t, 1H, *J* = 7.5 Hz), 7.60 (t, 1H, *J* = 7.5 Hz), 7.30-7.23 (m, 4H), 7.01 (m, 1H), 4.77 and 4.46 (ABq, 2H, Δ*v* = 155.0 Hz, *J* = 12.0 Hz), 3.70 (d, 1H, *J* = 11.5 Hz), 2.66 (app spt, 1H, AA'B, *J* = 6.5 Hz), 1.41 (d, 3H, AA'B, *J*_{A'B} = 6.5 Hz), 1.03 (d, 3H, AA'B, *J*_{AB} = 6.5 Hz);

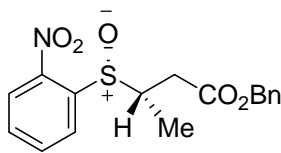
Mixture of **4d**: ¹³C NMR (125 MHz, CDCl₃) δ 168.1, 165.7, 144.9, 143.1, 141.5, 135.1, 135.0, 134.9, 131.9, 131.8, 128.7, 128.6, 128.5, 128.4, 127.8, 127.4, 125.2, 79.5, 76.7, 72.2, 67.4, 66.6, 27.3, 26.9, 21.6, 21.3, 21.2, 20.1, 19.7.





(+/-) **anti-4f**

(major)



(+/-) **syn-4f**

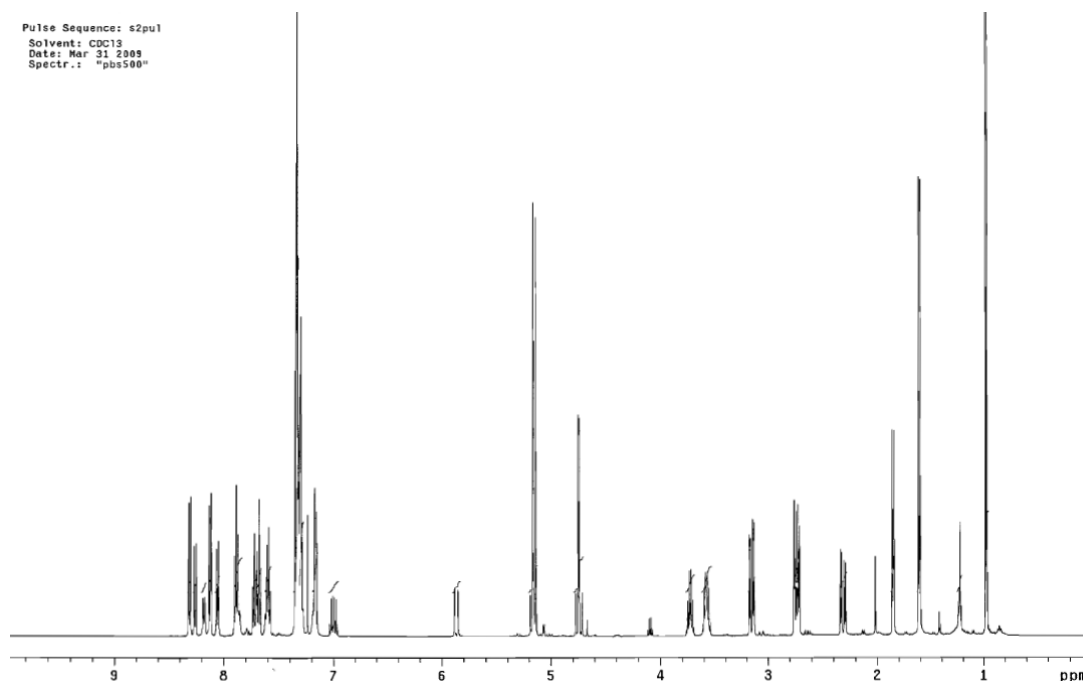
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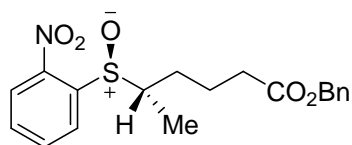
benzyl 3-(2-nitrophenylsulfinyl)butanoate (4f): orange solid (75 mg, 73%; mixture of diastereomers); mp 108-109 °C; ESI-HRMS calcd for C₁₇H₁₇NO₅S [M+H]⁺ 348.0900, found 348.0910;

(±) **anti-4f** (major): yellow oil; TLC (SiO₂) R_f 0.30 (5:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.31 (d, 1H, *J* = 8.5 Hz), 8.12 (dd, 1H, *J* = 8.0, 1.5 Hz), 7.89 (dt, 1H, *J* = 8.0, 1.0 Hz), 7.68 (dt, 1H, *J* = 8.0, 1.0 Hz), 7.43-7.31 (m, 5H), 5.17 and 5.13 (ABq, 2H, Δ*v* = 20.0 Hz, *J* = 12.5 Hz), 3.58 (m, 1H), 3.15 (dd, 1H, *J* = 16.0, 6.0 Hz), 2.73 (dd, 1H, *J* = 16.0, 9.5 Hz), 0.97 (d, 3H, *J* = 7.0 Hz);

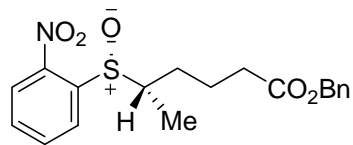
(±) **syn-4f** (minor): yellow oil; TLC (SiO₂) R_f 0.44 (5:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.26 (d, 1H, *J* = 8.0 Hz), 8.06 (dd, 1H, *J* = 8.0, 1.0 Hz), 7.72 (dt, 1H, *J* = 8.0, 1.0 Hz), 7.60 (dt, 1H, *J* = 8.0, 1.0 Hz), 7.43-7.31 (m, 5H), 4.77 and 4.73 (ABq, 2H, Δ*v* = 20.0 Hz, *J* = 12.5 Hz), 3.72 (m, 1H), 2.73 (dd, 1H, *J* = 17.5, 7.0 Hz), 2.31 (dd, 1H, *J* = 17.5, 6.0 Hz), 1.61 (d, 3H, *J* = 7.5 Hz);

Mixture of **4f**: ¹³C NMR (125 MHz, CDCl₃) δ 170.8, 170.4, 145.5, 145.0, 141.0, 140.9, 135.0, 128.8, 128.7, 128.6, 128.3, 128.1, 127.3, 125.7, 125.6, 76.2, 66.7, 66.2, 54.1, 53.1, 37.8, 31.4, 18.8, 17.9, 10.3.





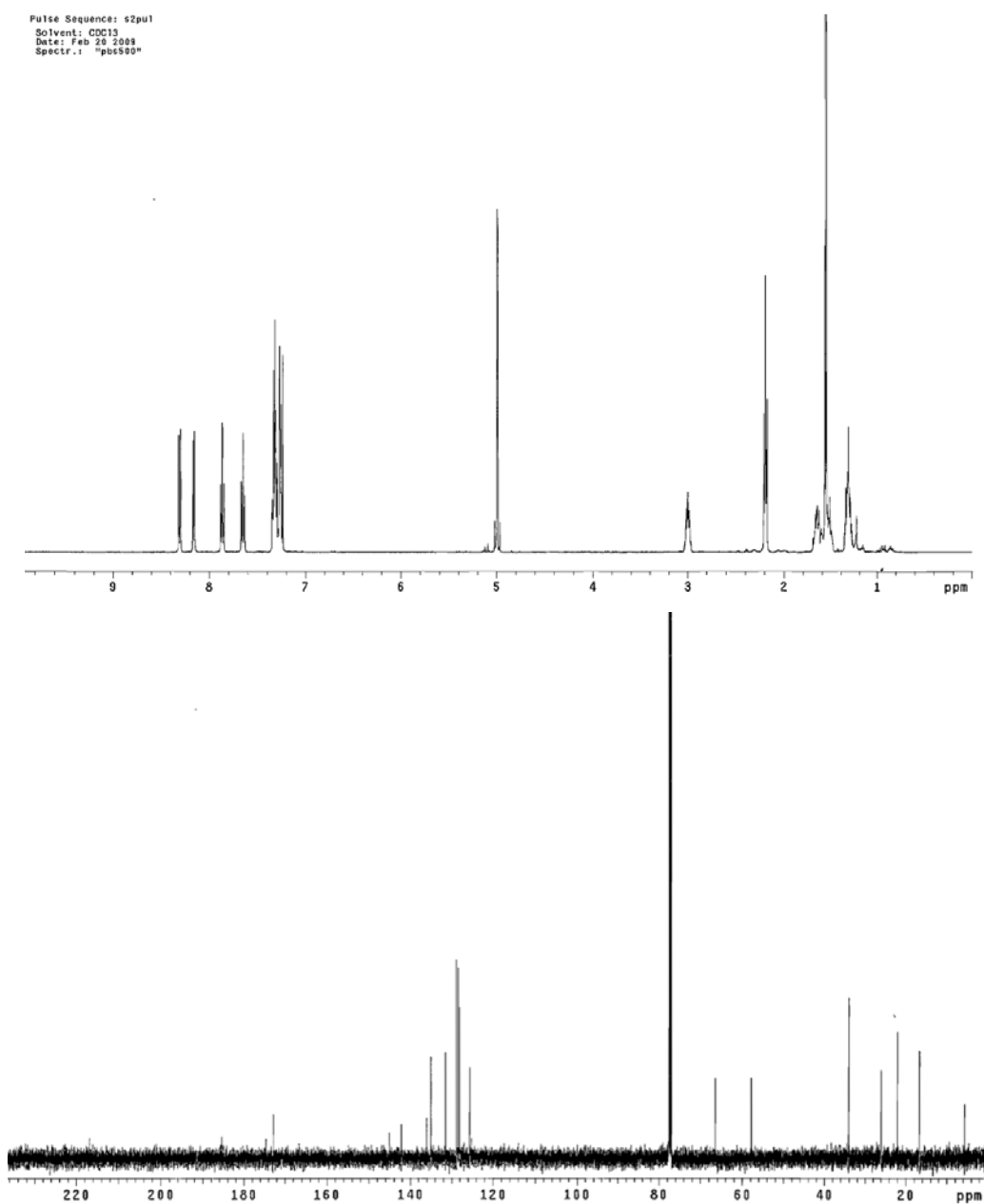
(+/-) **anti-4g**



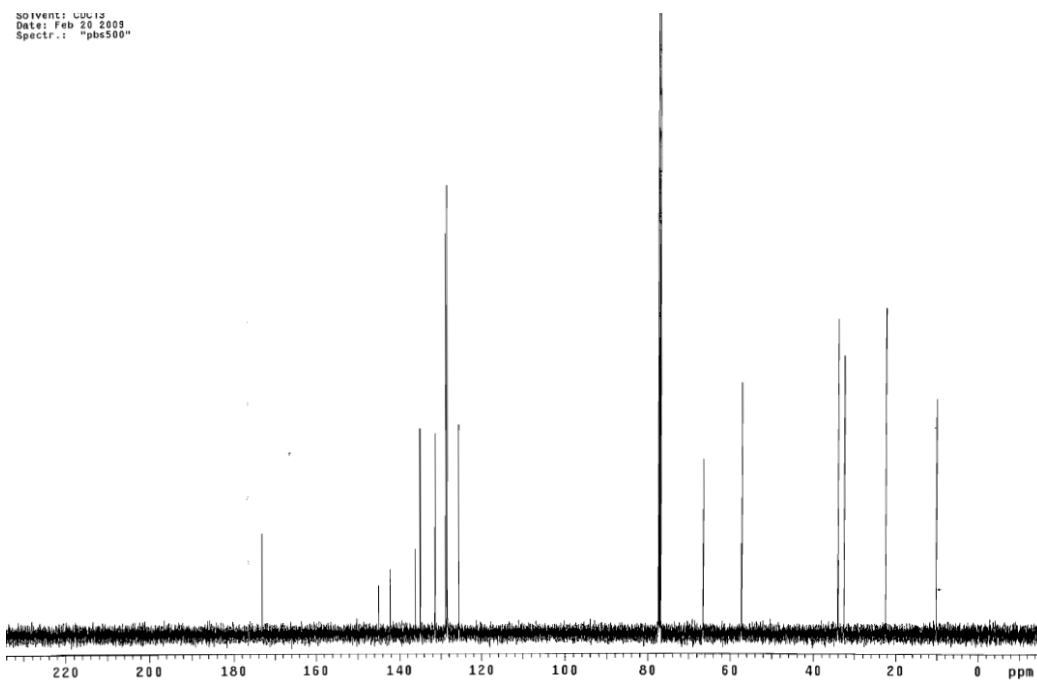
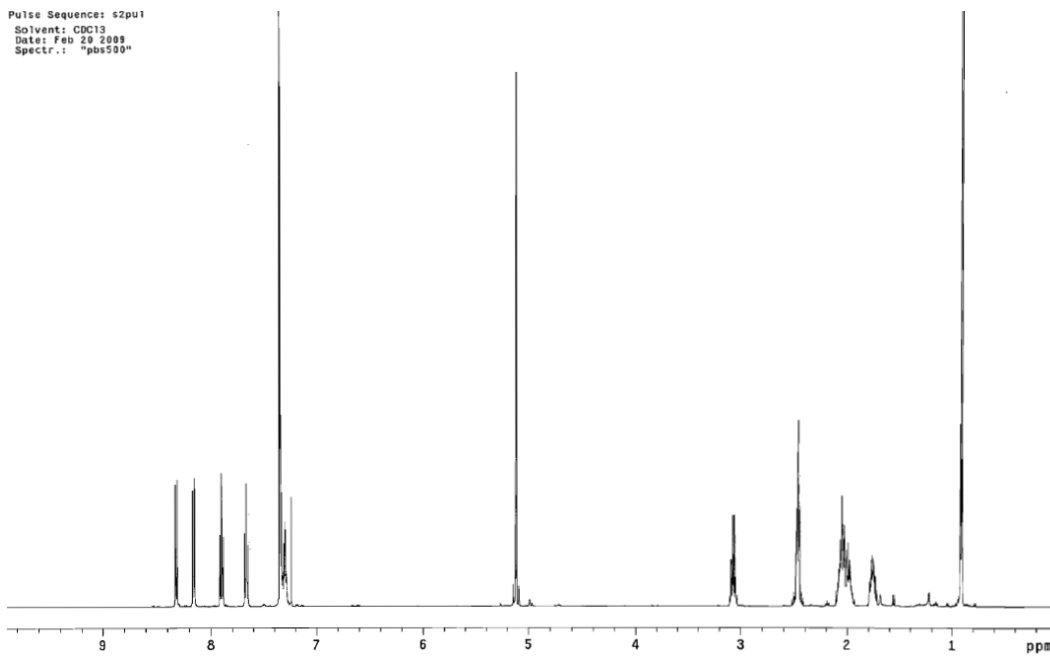
(+/-) **syn-4g**

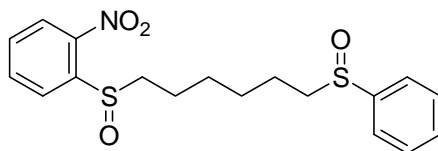
Benzyl 5-(2-nitrophenylsulfinyl)hexanoate (4g): yellow oil (320 mg, 79%; mixture of diastereomers); ESI-HRMS calcd for $C_{19}H_{21}NO_5S$ $[M+H]^+$ 376.1213, found 376.1218;

(±) **anti-4g**: yellow oil; TLC (SiO_2) R_f 0.16 (3:1 hexanes:EtOAc); 1H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, 1H, $J = 8.0$ Hz), 8.16 (dd, 1H, $J = 7.5$ Hz), 7.86 (t, 1H, $J = 7.5$ Hz), 7.65 (td, 1H, $J = 8.0$ Hz), 7.35-7.26 (m, 5H), 4.99 (s, 2H), 3.00 (m, 1H), 2.19 (t, 2H, $J = 7.5$ Hz), 1.69-1.63 (m, 1H), 1.56 (d, 3H, $J = 7.5$ Hz), 1.54-1.50 (m, 1H), 1.36-1.27 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 145.1, 142.2, 136.0, 135.0, 131.5, 128.8, 128.5, 128.4, 128.0, 125.6, 66.4, 57.8, 34.1, 26.0, 22.0, 16.6;

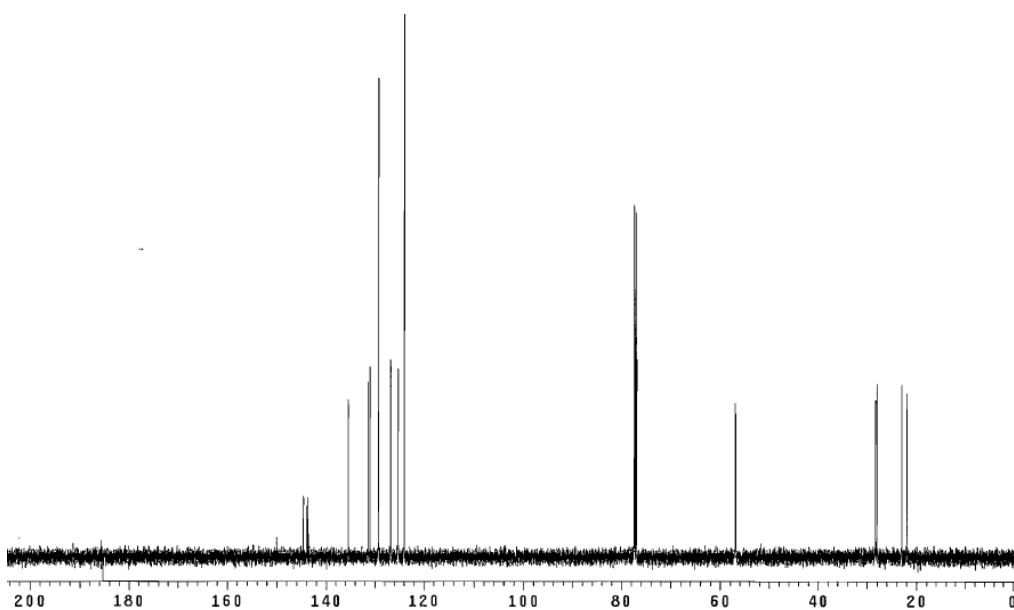
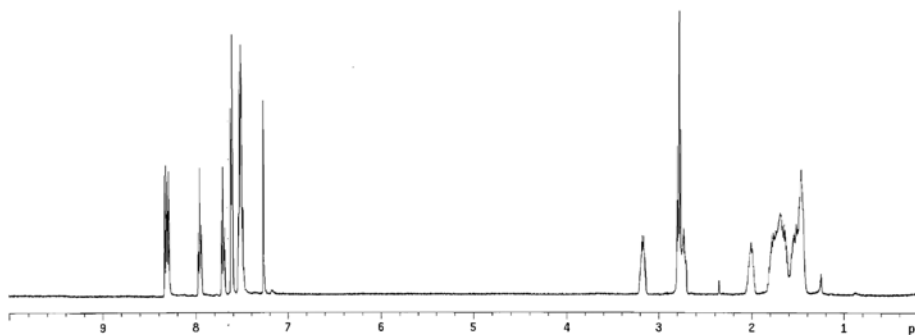


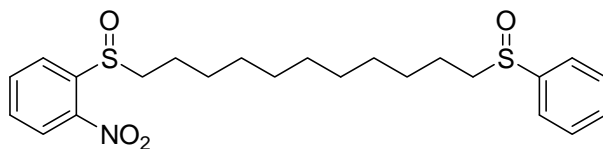
(±) *syn-4g*: yellow oil; TLC (SiO₂) R_f 0.11 (3:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.31 (dd, 1H, *J* = 8.0, 0.5 Hz), 8.16 (dd, 1H, *J* = 7.5, 1.5 Hz), 7.90 (td, 1H, *J* = 8.0, 1.0 Hz), 7.67 (td, 1H, *J* = 7.5, 1.5 Hz), 7.35-7.28 (m, 5H), 5.12 (s, 2H), 3.07 (sxt, 1H, *J* = 7.0 Hz), 2.47 (td, 2H, *J* = 7.0, 3.0 Hz), 2.10-1.93 (m, 3H), 1.79-1.72 (m, 1H), 0.91 (d, 3H, *J* = 6.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 173.1, 145.0, 142.2, 136.2, 134.9, 131.4, 128.8, 128.4, 125.6, 66.5, 57.3, 34.1, 32.6, 22.5, 10.2.





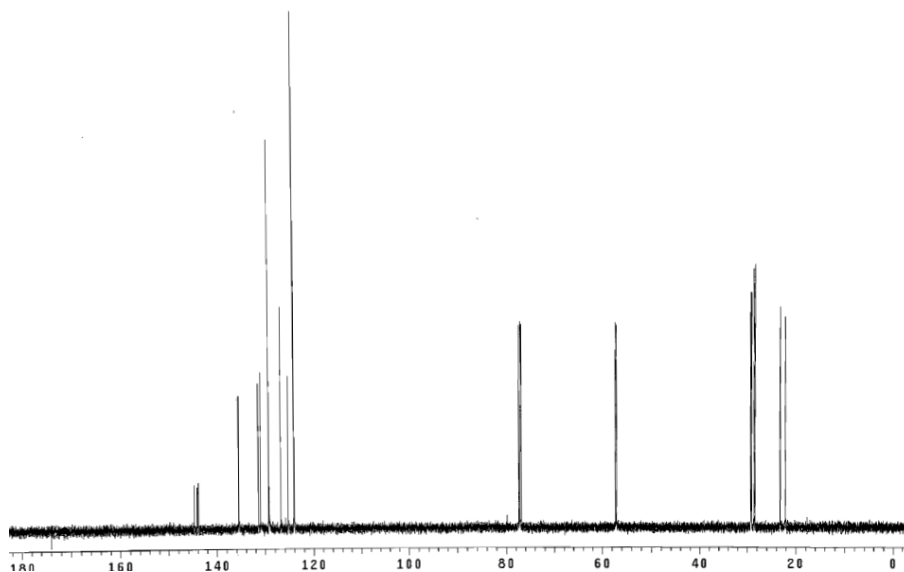
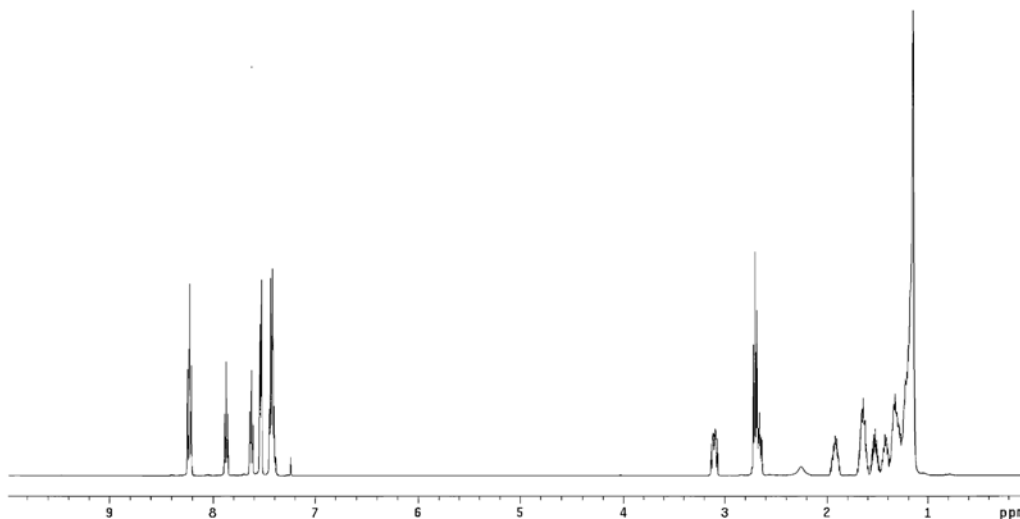
1-(6-(phenylsulfinyl)hexylsulfinyl)-2-nitrobenzene (4h): yellow solid (92.7 mg, 70%); mp 104-105 °C; TLC (SiO₂) R_f 0.26 (1:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.26 (d, 1H, *J* = 8.0 Hz), 8.22 (d, 1H, *J* = 8 Hz), 7.89 (t, 1H, *J* = 7.5 Hz), 7.65 (t, 1H, *J* = 7.5 Hz), 7.56-7.54 (m, 2H), 7.47-7.41 (m, 3H), 3.14-3.07 (m, 1H), 2.72 (t, 2H, *J* = 7.5 Hz), 2.69-2.64 (m, 1H), 1.99-1.90 (m, 1H), 1.76-1.62 (m, 2H), 1.60-1.54 (m, 1H), 1.52-1.37 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 144.7, 144.0, 143.7, 135.5, 131.5, 131.1, 129.3, 126.8, 125.3, 124.1, 57.0, 56.9, 28.4, 28.1, 23.1, 22.0; ESI-HRMS calcd for C₁₈H₂₁NO₄S₂ [M+H]⁺ 380.0985, found 380.0990.

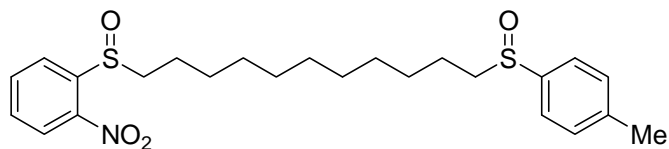




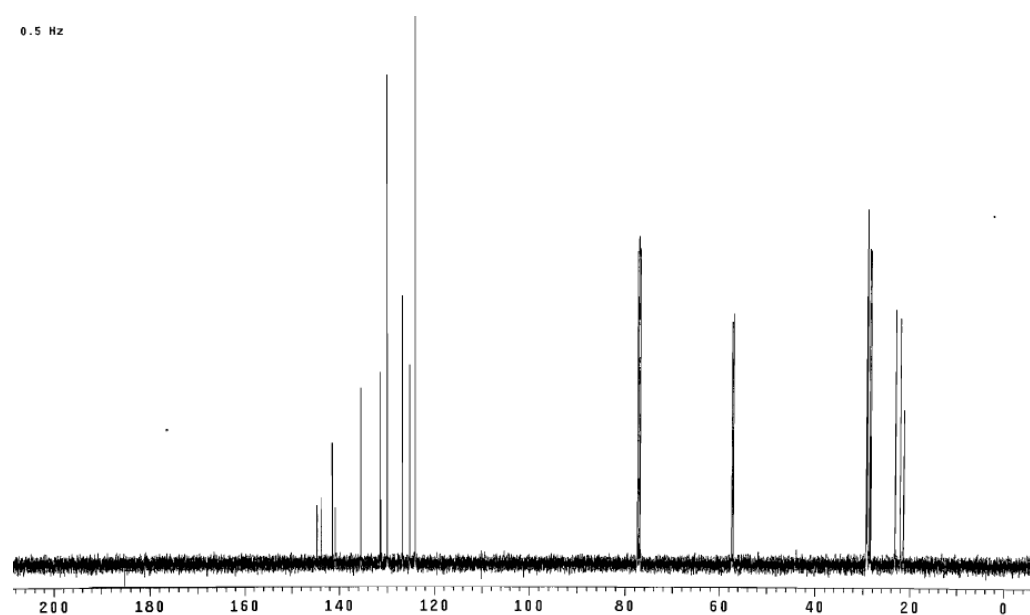
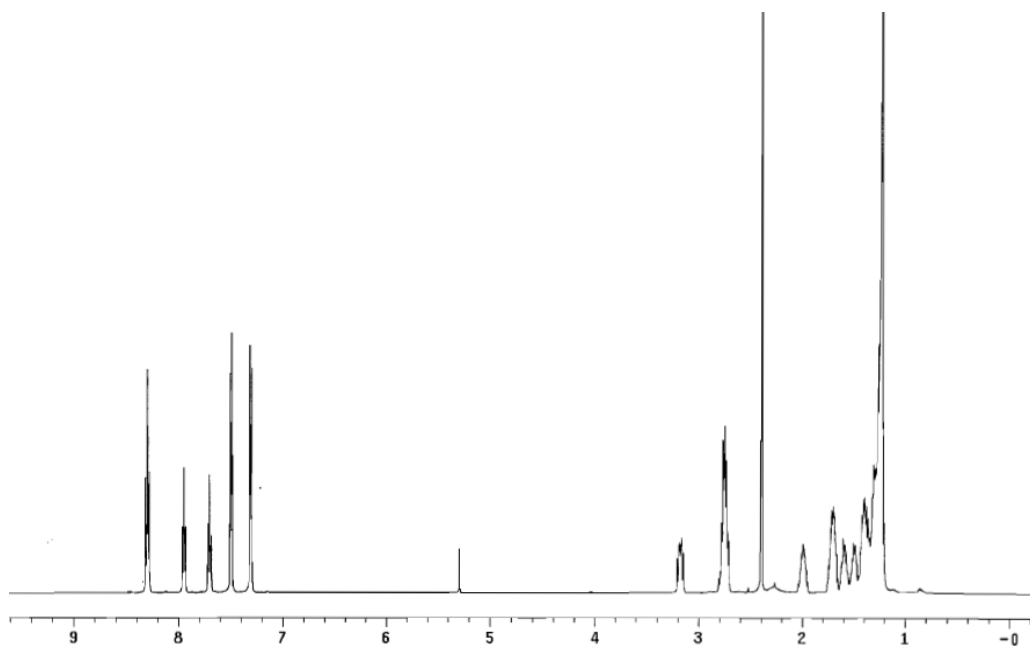
1-(11-(2-nitrophenylsulfinyl)undecylsulfinyl)benzene (4i): yellow solid (128 mg, 86%); mp 65-66 °C; TLC (SiO₂) R_f 0.05 (1:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.23 (t, 2H, *J* = 9.0 Hz), 7.88 (t, 1H, *J* = 7.5 Hz), 7.63 (t, 1H, *J* = 7.5 Hz), 7.55-7.53 (m, 2H), 7.45-7.39 (m, 3H), 3.10 (ddd, 1H, *J* = 13.0, 10.0, 7.0 Hz), 2.71 (t, 2H, *J* = 8.0 Hz), 2.66 (ddd, 1H, *J* = 13.0, 9.5, 5.0 Hz), 1.99-1.87 (m, 1H), 1.70-1.59 (m, 2H), 1.57-1.49 (m, 1H), 1.47-1.38 (m, 1H), 1.36-1.26 (m, 3H), 1.26-1.16 (m 10H); ¹³C NMR (125 MHz, CDCl₃) δ 144.6, 144.0, 143.8, 135.4, 131.4, 130.9, 129.2, 126.8, 125.2, 124.0, 57.3, 57.1, 29.3, 29.2, 29.1, 28.6, 28.4, 23.2; ESI-HRMS calcd for C₂₃H₃₁NO₄S₂ 450.1773 [M+H]⁺, found 450.1773.

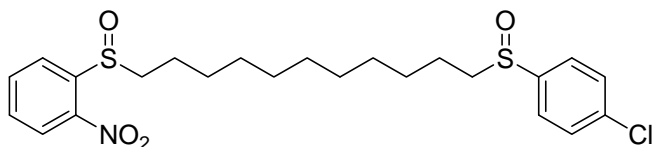
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Date: May 15 2009
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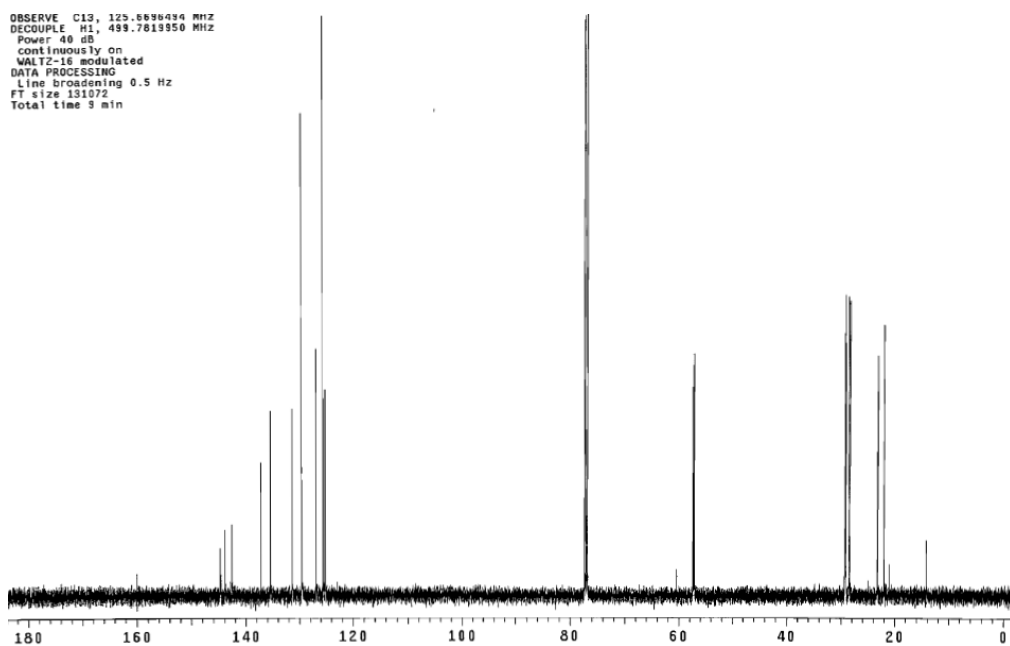
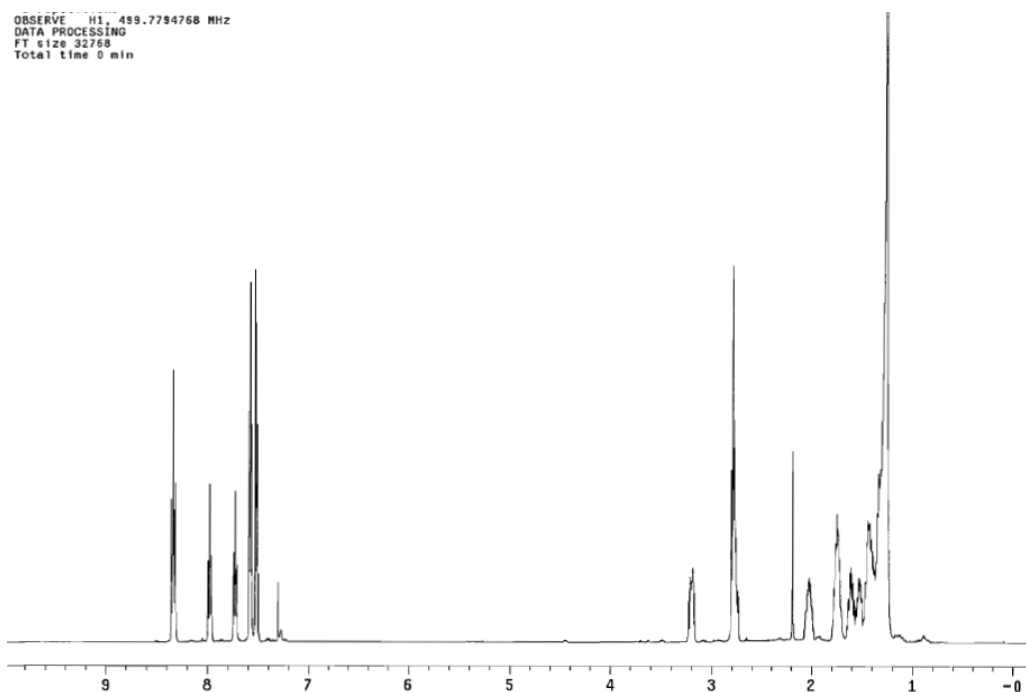


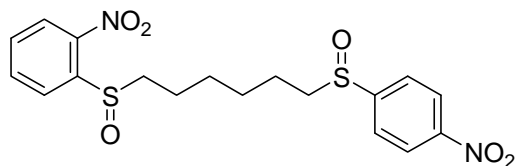
1-(11-(2-nitrophenylsulfinyl)undecylsulfinyl)-4-methylbenzene (4j): yellow oil (61 mg, 62%); TLC (SiO₂) R_f 0.20 (1:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.24 (t, 2H, *J* = 8.5 Hz), 7.89 (t, 1H, *J* = 7.5 Hz), 7.64 (t, 1H, *J* = 7.5 Hz), 7.43 (d, 2H, *J* = 7.5 Hz), 7.25 (d, 2H, *J* = 7.5 Hz), 3.12 (ddd, 1H, *J* = 12.5, 9.5, 7.0 Hz), 2.74-2.65 (m, 3H), 1.98-1.89 (m, 1H), 1.69-1.59 (m, 2H), 1.57-1.50 (m, 1H), 1.49-1.39 (m, 1H), 1.37-1.28 (m, 3H), 1.25-1.17 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 144.7, 143.8, 141.4, 140.8, 135.4, 131.4, 129.9, 126.8, 125.2, 124.1, 57.4, 57.1, 29.4, 29.3, 29.1, 28.7, 28.5, 23.2, 22.2, 21.5; ESI-HRMS calcd for C₂₄H₃₄NO₄S₂ 464.1924 [M+H]⁺, found 464.1910.





1-(11-(2-nitrophenylsulfinyl)undecylsulfinyl)-4-chlorobenzene (4k): yellow oil (130.1 mg, 70%); TLC (SiO₂) R_f 0.2 (1:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.27 (t, 2H, *J* = 8.5 Hz), 7.92 (t, 1H, *J* = 7.5 Hz), 7.67 (t, 1H, *J* = 7.5 Hz), 7.52 (d, 2H, *J* = 8.5 Hz), 7.46 (d, 2H, *J* = 8.0 Hz), 3.17-3.11 (m, 1H), 2.74-2.67 (m, 3H), 1.99-1.92 (m, 1H), 1.71-1.64 (m, 2H), 1.59-1.51 (m, 1H), 1.50-1.43 (m, 1H), 1.40-1.31 (m, 2H), 1.29-1.20 (m, 11H); ¹³C NMR (125 MHz, CDCl₃) δ 144.8, 144.0, 142.7, 137.2, 135.5, 131.4, 129.6, 126.9, 125.6, 125.3, 57.5, 57.3, 29.5, 29.4, 29.3, 29.2, 28.8, 28.5, 23.4, 22.2; ESI-HRMS calcd for C₂₃H₃₀ClNO₄S₂ 484.1383 [M+H]⁺ found 484.1383.



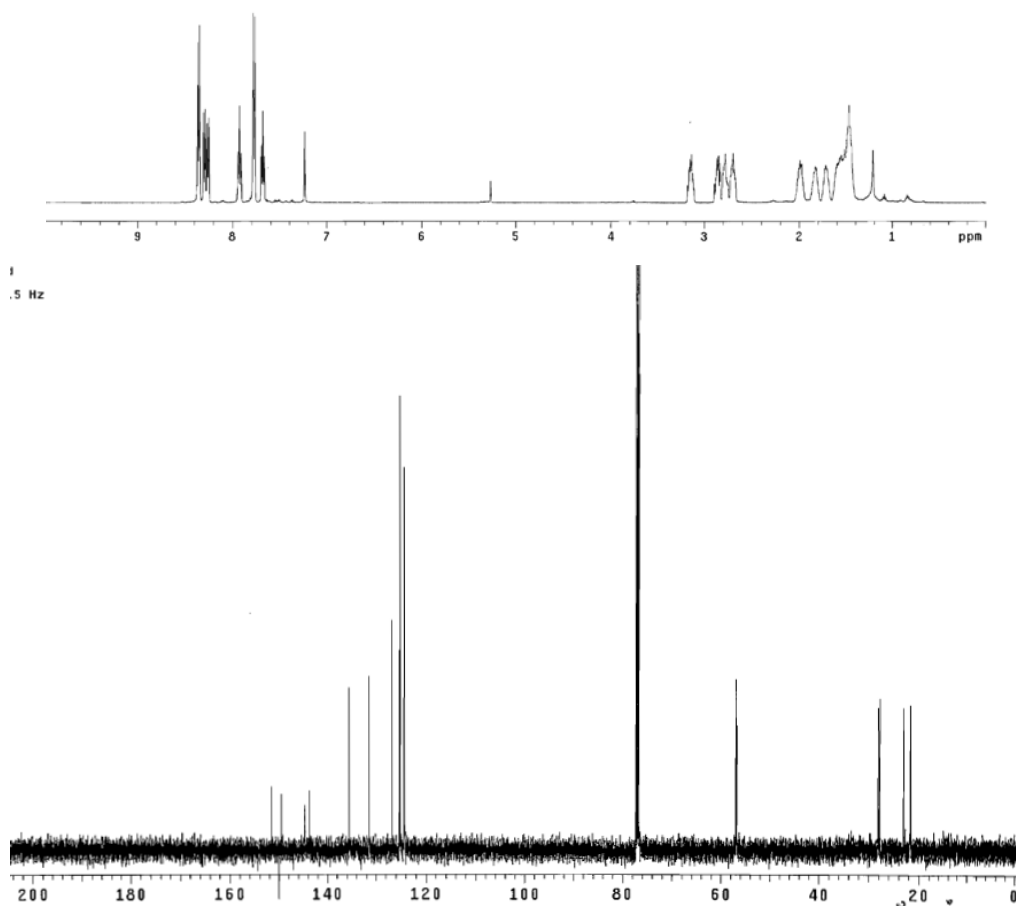


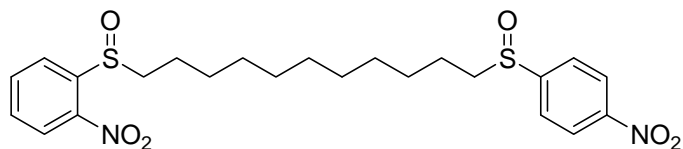
1-(6-(4-nitrophenylsulfinyl)hexylsulfinyl)-2-nitrobenzene (4I): yellow solid (89 mg, 77%); mp 86-88 °C; TLC (SiO₂) R_f 0.26 (1:1 hexanes:EtOAc); 8.37 (d, 2H, *J* = 8.5 Hz), 8.30 (d, 1H, *J* = 8.0 Hz), 8.27 (d, 1H, *J* = 8.5 Hz), 7.94 (t, 1H, *J* = 7.5 Hz), 7.78 (d, 2H, *J* = 8.5 Hz), 7.69 (t, 1H, *J* = 7.5 Hz), 3.19-3.12 (m, 1H), 2.89-2.83 (m, 1H), 2.80-2.77 (m, 1H), 2.74-2.69 (m, 1H), 2.06-1.98 (m, 1H), 1.90-1.81 (m, 1H), 1.77-1.69 (m, 1H), 1.65-1.44 (m, 5H); ¹³C NMR (125 MHz, CDCl₃) δ 151.7, 149.7, 144.8, 143.8, 135.7, 131.6, 126.9, 125.4, 125.3, 124.5, 57.1, 56.9, 28.4, 28, 23.2, 21.9; ESI-HRMS calcd for C₁₈H₂₁N₂O₆S₂ 450.1773 [M+H]⁺ 425.0836, found 425.0837.

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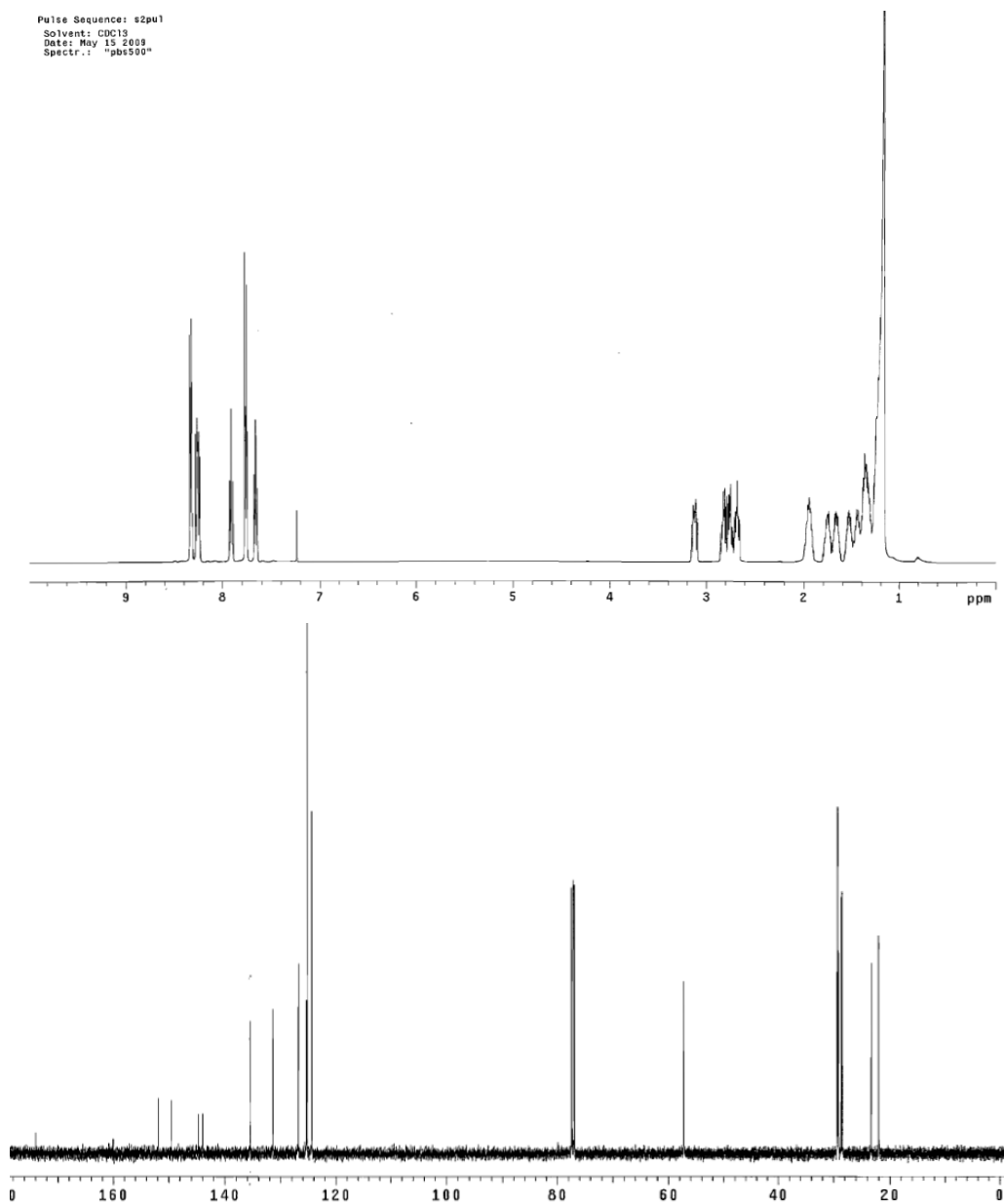
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Sample directory:
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Solvent: CDCl3
Date: Jul 16 2009
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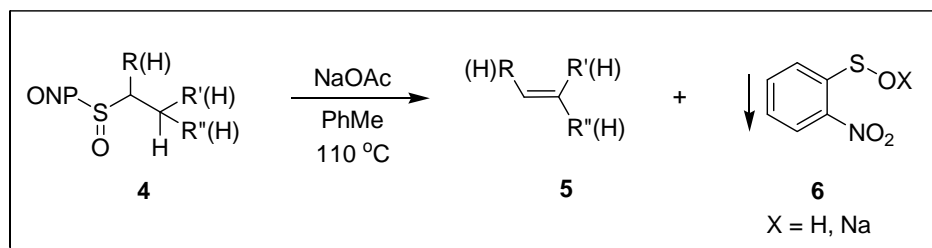
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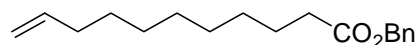


1-(11-(2-nitrophenylsulfinyl)undecylsulfinyl)-4-nitrobenzene (4m): yellow solid (87.5 mg, 86%); mp 82-83 °C; TLC (SiO₂) R_f 0.12 (1:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ (8.32 (d, 2H, *J* = 7.5 Hz), 8.27 (d, 1H, *J* = 8.0 Hz), 8.24 (d, 1H, *J* = 8.0 Hz), 7.91 (t, 1H, *J* = 7.5 Hz), 7.76 (d, 2H, *J* = 8.5 Hz), 7.66 (t, 1H, *J* = 7.5 Hz), 3.12 (dt, 1H, *J* = 13.0, 6.5 Hz), 2.86-2.80 (m, 1H), 2.78-2.73 (m, 1H), 2.71-2.67 (m, 1H), 1.99-1.90 (m, 1H), 1.80-1.73 (m, 1H), 1.70-1.63 (m, 1H), 1.58-1.51 (m, 1H), 1.48-1.43 (m, 1H), 1.40-1.31 (m, 3H), 1.29-1.19 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 151.9, 149.5, 144.7, 143.9, 135.5, 131.4, 126.9, 125.3, 125.2, 124.3, 57.3, 57.2, 29.4, 29.3, 29.2, 28.7, 28.5, 23.3, 22.0; ESI-HRMS calcd for C₂₃H₃₀N₂O₆S₂ 495.1624 [M+H]⁺ found 495.1624.



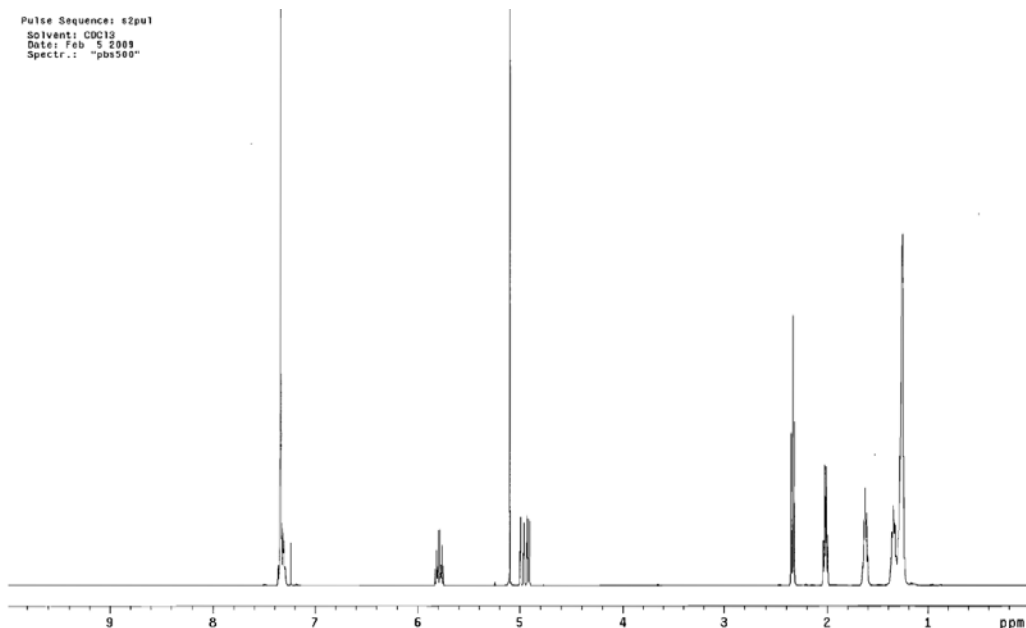


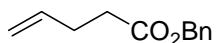
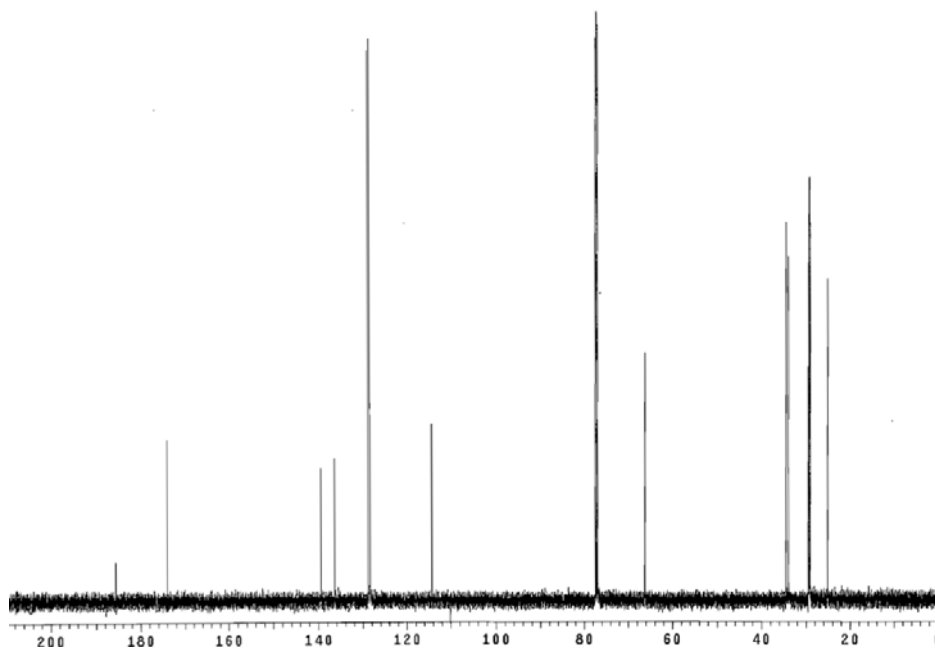
Elimination of ONP Sulfoxides (4); General Procedure: Sulfoxide **4** (1 mmol equiv) and NaOAc (10 mmol equiv) were heated with stirring in PhMe (10 mL) at 110 °C for 1-18 hrs. The solution was then cooled to RT and the precipitate removed by vacuum filtration through Celite. The flask was rinsed with toluene, filtered, and the solvent was evaporated to provide alkene **5**. Decolorization of the concd product can be achieved by vacuum filtration of the oil through a plug of silica with 3:1 hexanes:EtOAc or for instances when starting material is still present, the mixture can be reheated in toluene with a fresh 10 equiv NaOAc until the reaction is complete.



Flippin, L. A.; Gallagher, D. W.; Jalali-Araghi, K. *J. Org. Chem.* **1989**, *54*, 1430-2.

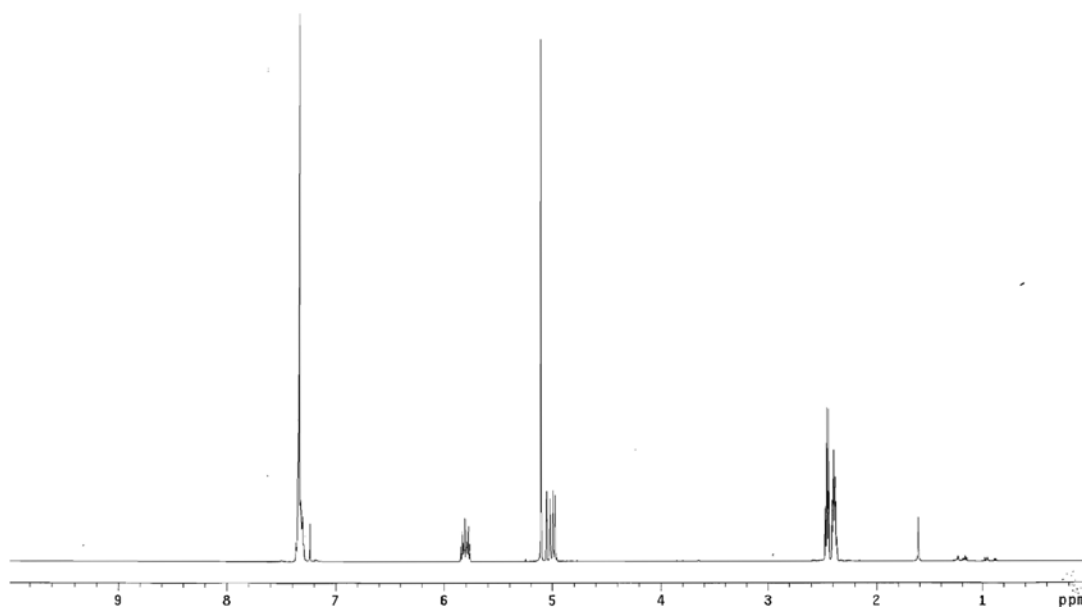
benzyl undec-10-enoate (5a): colorless oil (28.2 mg, 86%); TLC (SiO₂) R_f 0.40 (20:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 7.34-7.30 (m, 5H), 5.79 (ddt, 1H, ABM, J_{BM} = 16.5 Hz, J_{AM} = 10.5, 6.5 Hz), 5.10 (s, 2H), 4.98 (dd, 1H, ABM, J_{BM} = 16.5 Hz, J_{AB} = 1.5 Hz), 4.92 (dd, 1H, ABM, J_{AM} = 10.5 Hz, J_{AB} = 1.5 Hz), 2.34 (t, 2H, J = 7.5 Hz), 2.02 (m, 2H), 1.63 (qnt, 2H, J = 7.0 Hz), 1.36 (qnt, 2H, J = 7.0 Hz), 1.28-1.25 (m, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 173.7, 139.2, 136.2, 128.6, 128.2, 128.2, 114.2, 66.1, 34.4, 33.8, 29.3, 29.2, 29.1, 28.9, 24.0; ESI-HRMS calcd for C₁₈H₂₆O₂ [M+Na]⁺ 297.1825, found 297.1826.

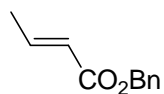
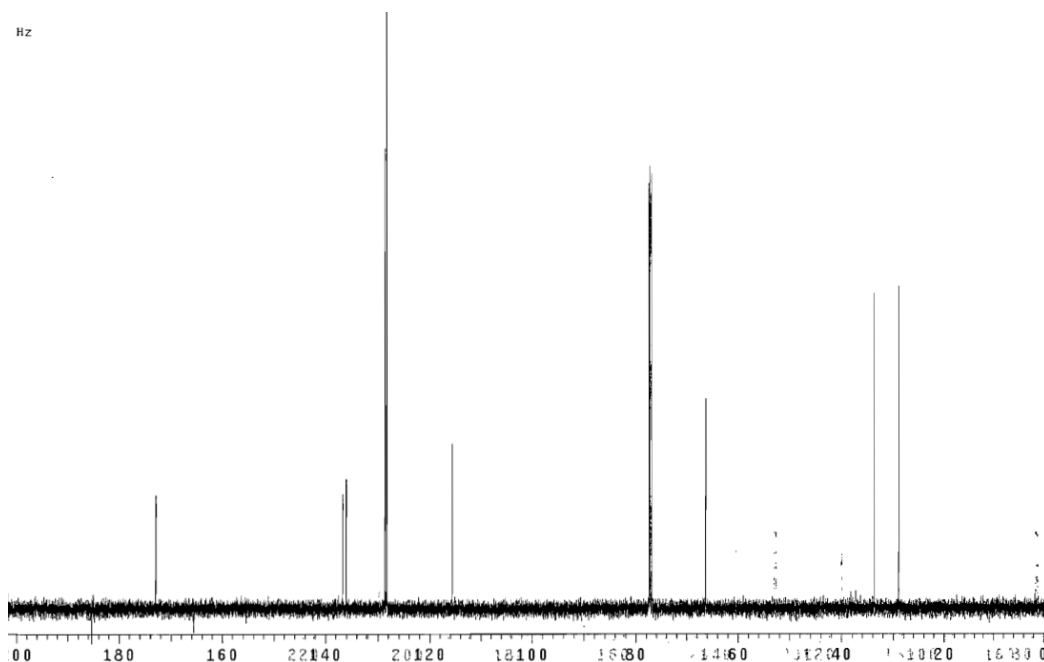




Waser, J.; Gasper, B.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc.*, **2006**, *128*, 11693–11712

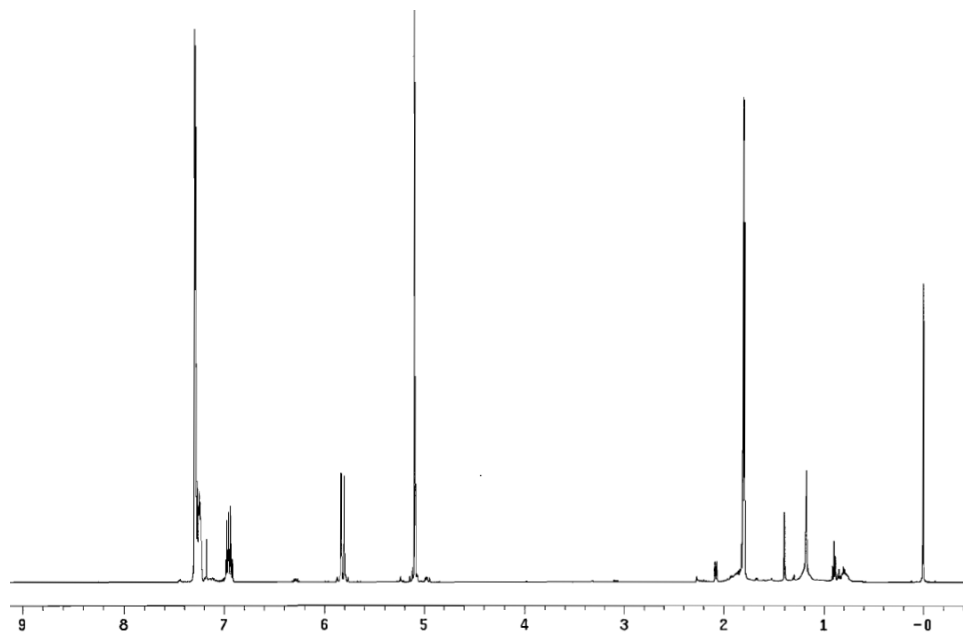
benzyl pent-4-enoate (5b): colorless oil (19 mg, 75%); TLC (SiO₂) R_f 0.48 (20:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.30 (m, 5H), 5.81 (ddt, 1H, ABM, J_{BM} = 17.0 Hz, J_{AM} = 10.5 Hz, J = 7.5 Hz), 5.11 (s, 2H), 5.03 (dd, 1H, ABM, J_{BM} = 17.0 Hz, J_{AB} = 1.5 Hz), 4.98 (dd, 1H, ABM, J_{AM} = 10.5 Hz, J_{AB} = 1.5 Hz), 2.47-2.44 (m, 2H), 2.41-2.36 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 173.1, 136.8, 136.2, 128.7, 128.4, 115.8, 66.4, 33.7, 29.0.

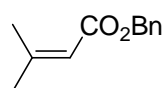
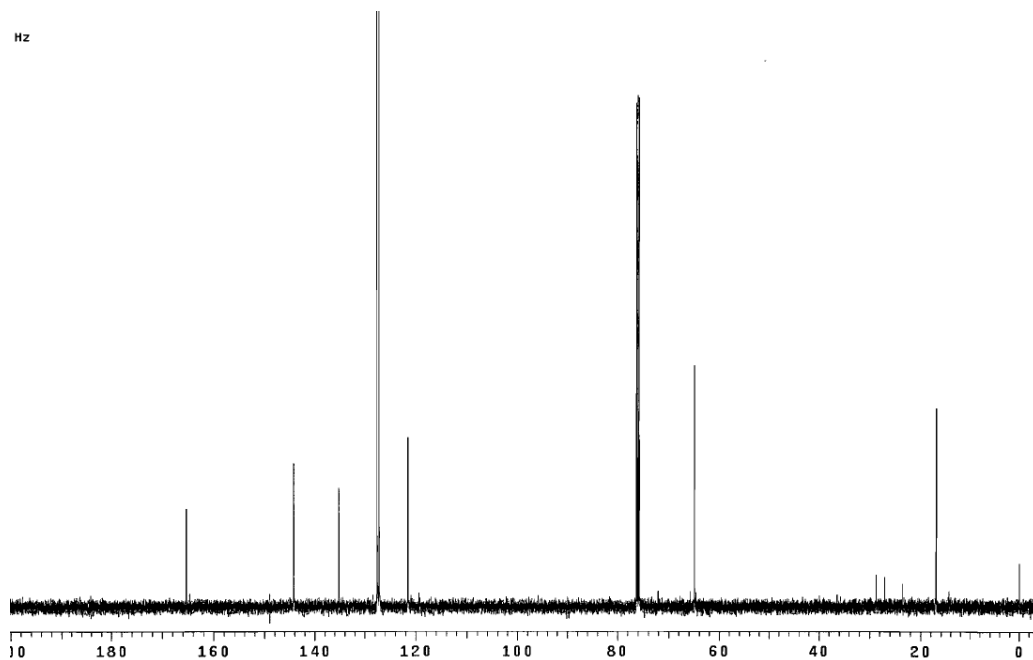




Grobelny, Z.; Stolarzewicz, A.; Morejko, B.a; Pisarski, W.h; Maercker, A.; Skibinski, A.; Krompiec, S.; Rzepa, J. *Macromolecules* **2006**, *39*, 6832-6837.

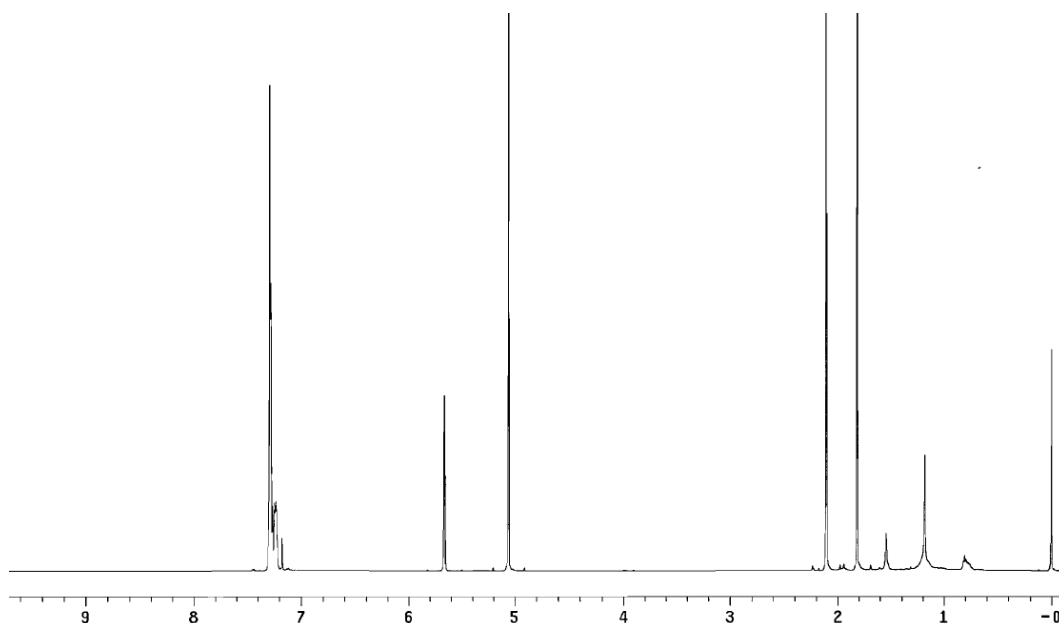
(E)-benzyl but-2-enoate ((E)-5c): colorless oil (24.7 mg, 88%); TLC (SiO₂) R_f 0.55 (9:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.29 (m, 5H), 7.06 (dq, 1H, AMX, J_{MX} = 16.0 Hz, J_{AX} = 7.0 Hz), 5.87 (d, 1H, AMX, J_{MX} = 16.0 Hz), 5.16 (s, 2H), 1.86 (d, 3H, AMX, J_{AX} = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 166.5, 145.3, 136.4, 128.7, 122.7, 66.1, 18.2; MS (*m/z*): 176(25), 158(48), 147(5), 131(96), 117(8), 107(50).

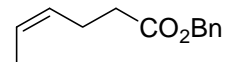
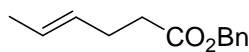
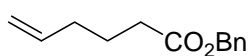
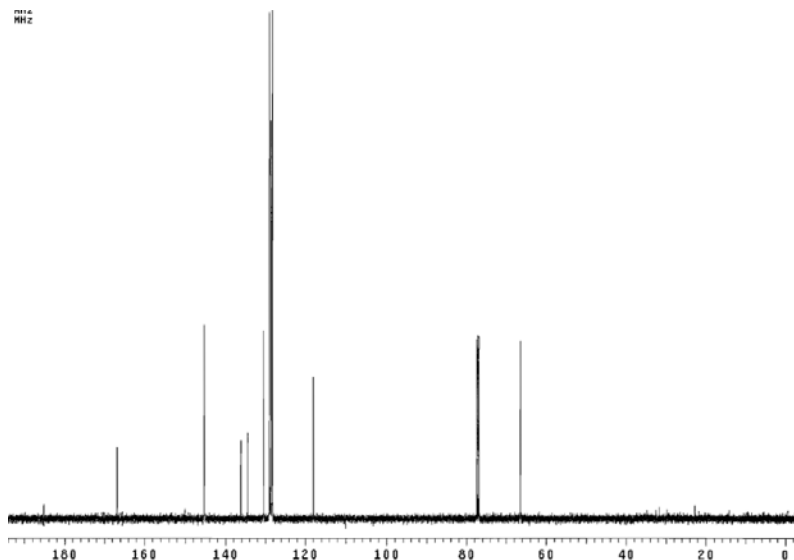




Chen, C-Tien; Munot, Y. S. *J. Org. Chem.* **2005**, *70*, 8625-8627.

benzyl 3-methylbut-2-enoate (5d): colorless oil (20 mg, 93%); TLC (SiO₂) R_f 0.60 (9:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 7.38-7.29 (m, 5H), 5.72 (s, 1H), 5.12 (s, 2H), 2.17 (s, 3H), 1.88 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.6, 157.5, 136.7, 128.7, 128.3, 128.2, 116.0, 65.6, 27.6, 20.5; MS (*m/z*): 190(48), 175(27), 145(95), 144(42), 131(10), 117(5), 107(33).

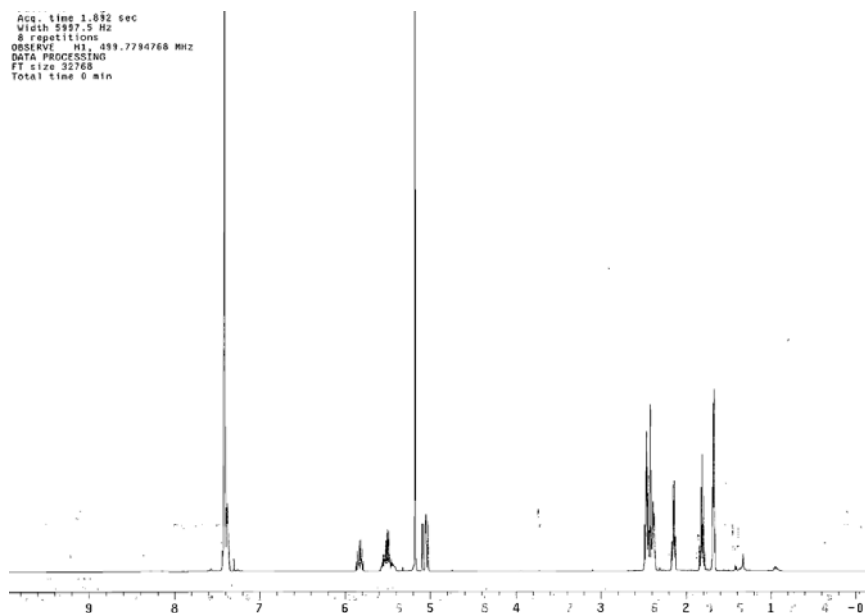


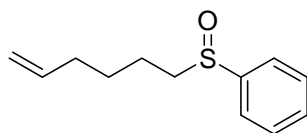


Chan, A.; Scheidt, K. A. *Org. Lett.*, **2005**, *7*, 905–908.
 Fujimura, O.; Fu, Gregory C.; Grubbs, R. H. *J. Org. Chem.* **1994**, *59*, 4029-4031.

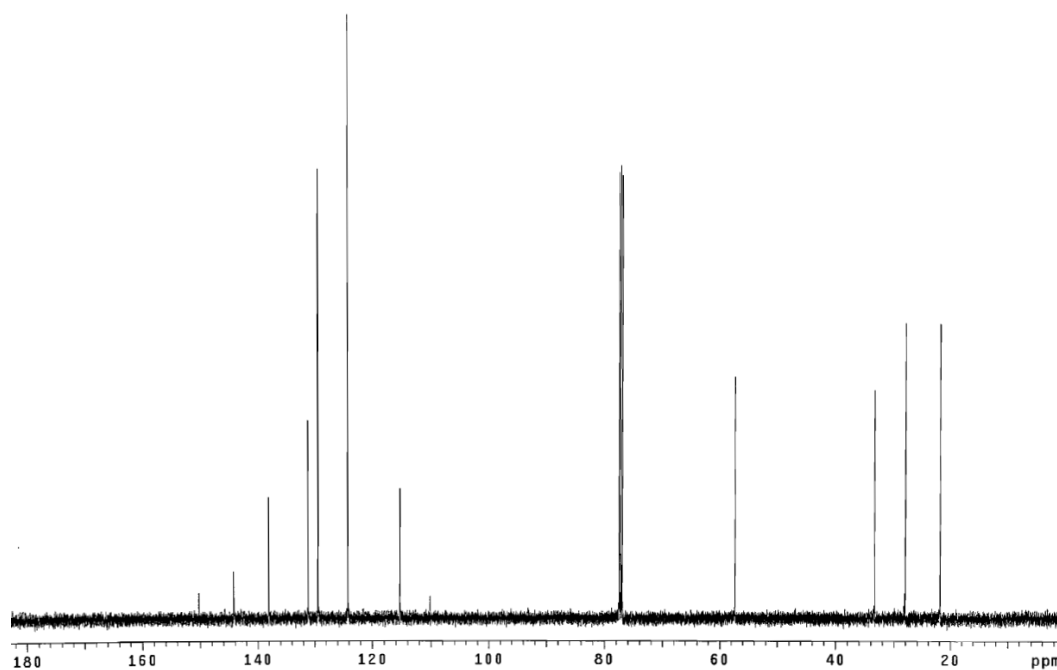
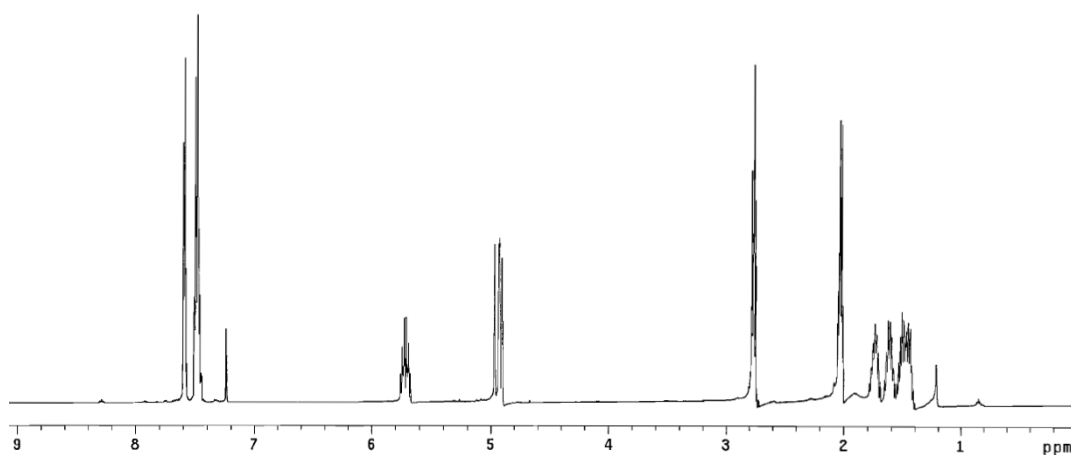
benzyl hexenoate: colorless oil (71 mg, 75%); TLC (SiO₂) R_f 0.52 (25:1 hexanes:EtOAc; inseparable mixture of isomers); Ratio of isomers was determine by GC/MS.

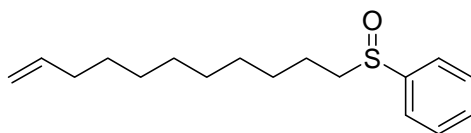
benzyl hex-5-enoate: ¹H NMR (500 MHz, CDCl₃) δ 7.38-7.29 (m, 5H), 5.77(ddt, 1H, ABM, J_{BM} = 17.0 Hz, J_{AM} = 10.5 Hz, J = 7.0 Hz), 5.11 (s, 2H), 5.02 (dd, 1H, ABM, J_{BM} = 17.0 Hz, J_{AB} = 1.0 Hz), 4.98 (dd, 1H, ABM, J_{AM} = 10.5 Hz, J_{AB} = 1.0 Hz), 2.37 (t, 2H, J = 7.5 Hz), 2.09 (q, 2H, J = 7.5 Hz), 1.75 (qnt, 2H, J = 7.5 Hz); (*E*)-**benzyl hexenoate ((E)-5g):** δ 7.38-7.29 (m, 5H), 5.52-5.35 (m, 2H), 5.11 (s, 2H), 2.41 (t, 2H, J = 7.5 Hz), 2.32 (q, 2H, J = 7.0 Hz), 2.32 (q, 2H, J = 7.0 Hz), 1.62 (t, 3H, J = 7.5 Hz).



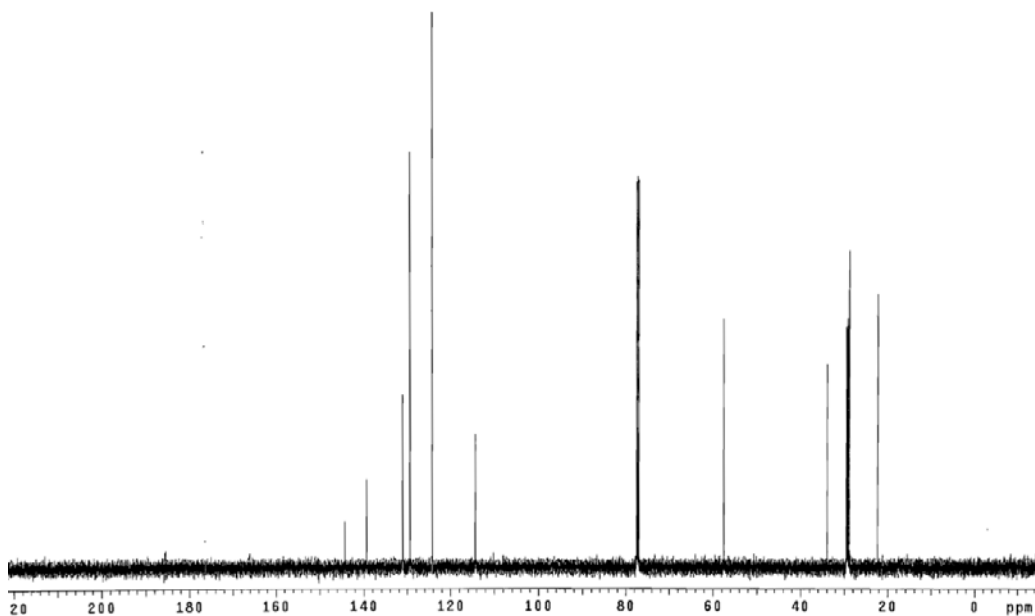
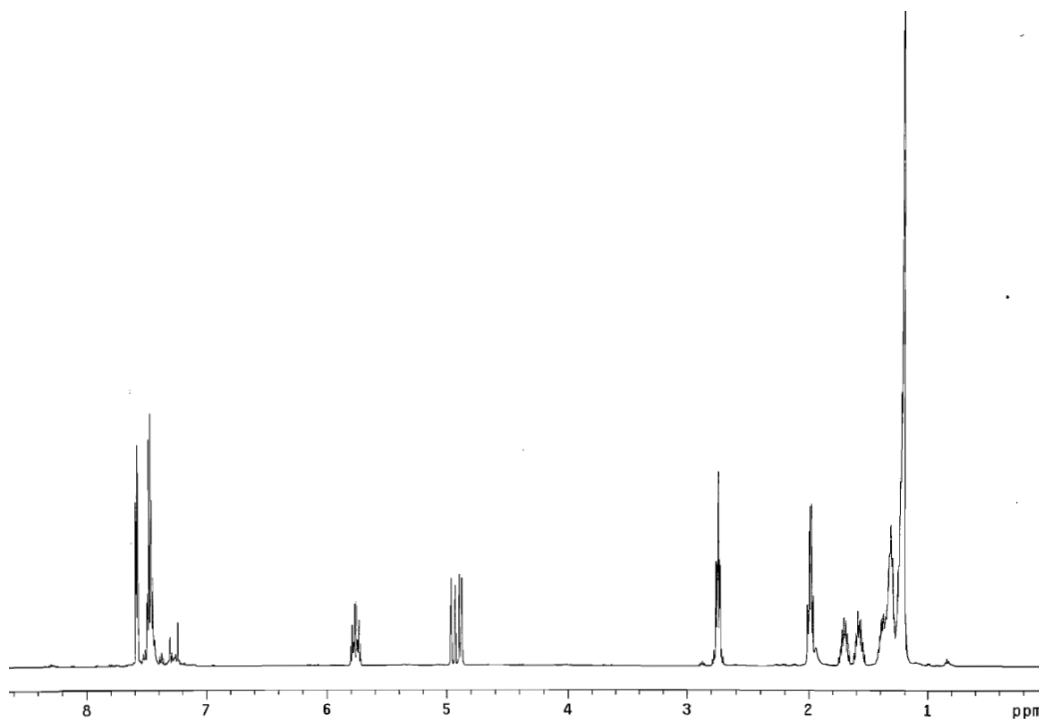


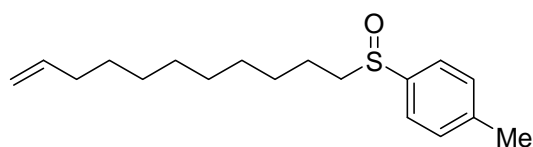
1-(hex-5-enylsulfinyl)benzene (5h): colorless oil (22 mg, 62%); TLC (SiO₂) R_f 0.32 (3:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 7.59-7.58 (m, 2H), 7.50-7.45 (m, 3H), 5.71 (ddt, 1H, ABM, J_{BM} = 17.0 Hz, J_{AM} = 10.0 Hz, J = 6.5 Hz), 4.95 (dd, 1H, ABM, J_{BM} = 17.0 Hz, J_{AB} = 1.5 Hz), 4.91 (dd, 1H, ABM, J_{AM} = 10.0 Hz, J_{AB} = 1.5 Hz), 2.76 (t, 2H, J = 8.0 Hz), 2.02 (m, 2H), 1.76-1.71 (m, 1H), 1.64-1.58 (m, 1H), 1.54-1.48 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 150.2, 144.2, 138, 131.1, 124.2, 115.3, 110.2, 57.4, 33.4, 28.1, 21.9.



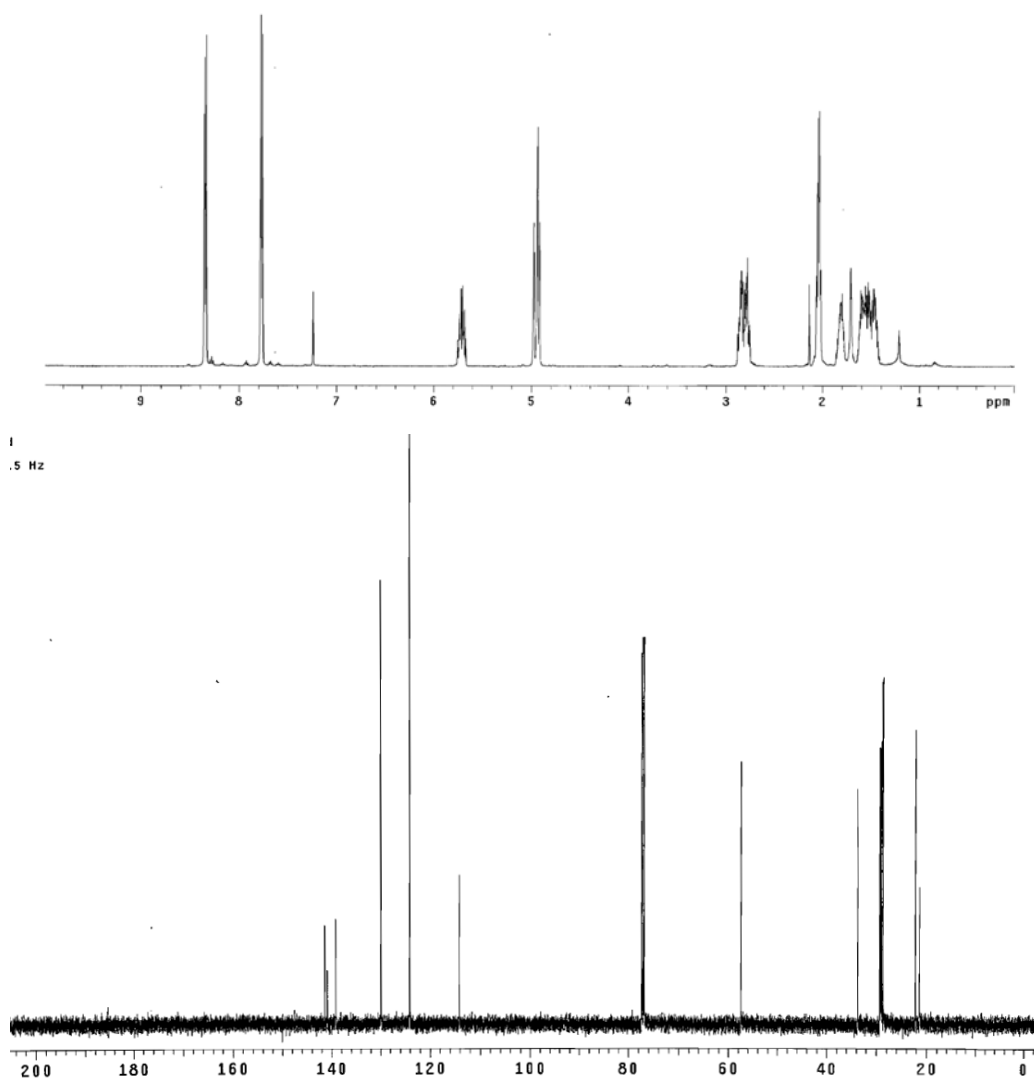


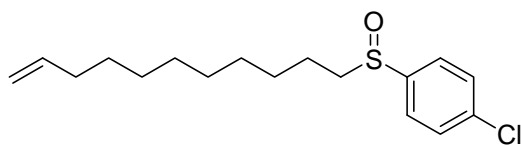
1-(undec-10-enylsulfinyl)benzene (5i): colorless oil (28.5 mg, 86%); TLC (SiO₂) R_f 0.18 (7:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 7.59-7.57 (m, 2H), 7.49-7.43 (m, 3H), 5.75 (ddt, 1H, ABM, J_{BM} = 17.0 Hz, J_{AM} = 10.5, J = 6.5 Hz), 4.95 (dd, 1H, ABM, J_{BM} = 17.0 Hz, J_{AB} = 1.5 Hz), 4.88 (dd, 1H, ABM, J_{AM} = 10.5 Hz, J_{AB} = 1.5 Hz), 2.76 (app t, 2H, J = 7.0 Hz), 2.00 (m, 2H), 1.75-1.66 (m, 1H), 1.64-1.54 (m, 1H), 1.41-1.30 (m, 2H), 1.29-1.21 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 144.3, 139.3, 131.1, 129.4, 124.2, 114.3, 57.6, 33.9, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 22.3.



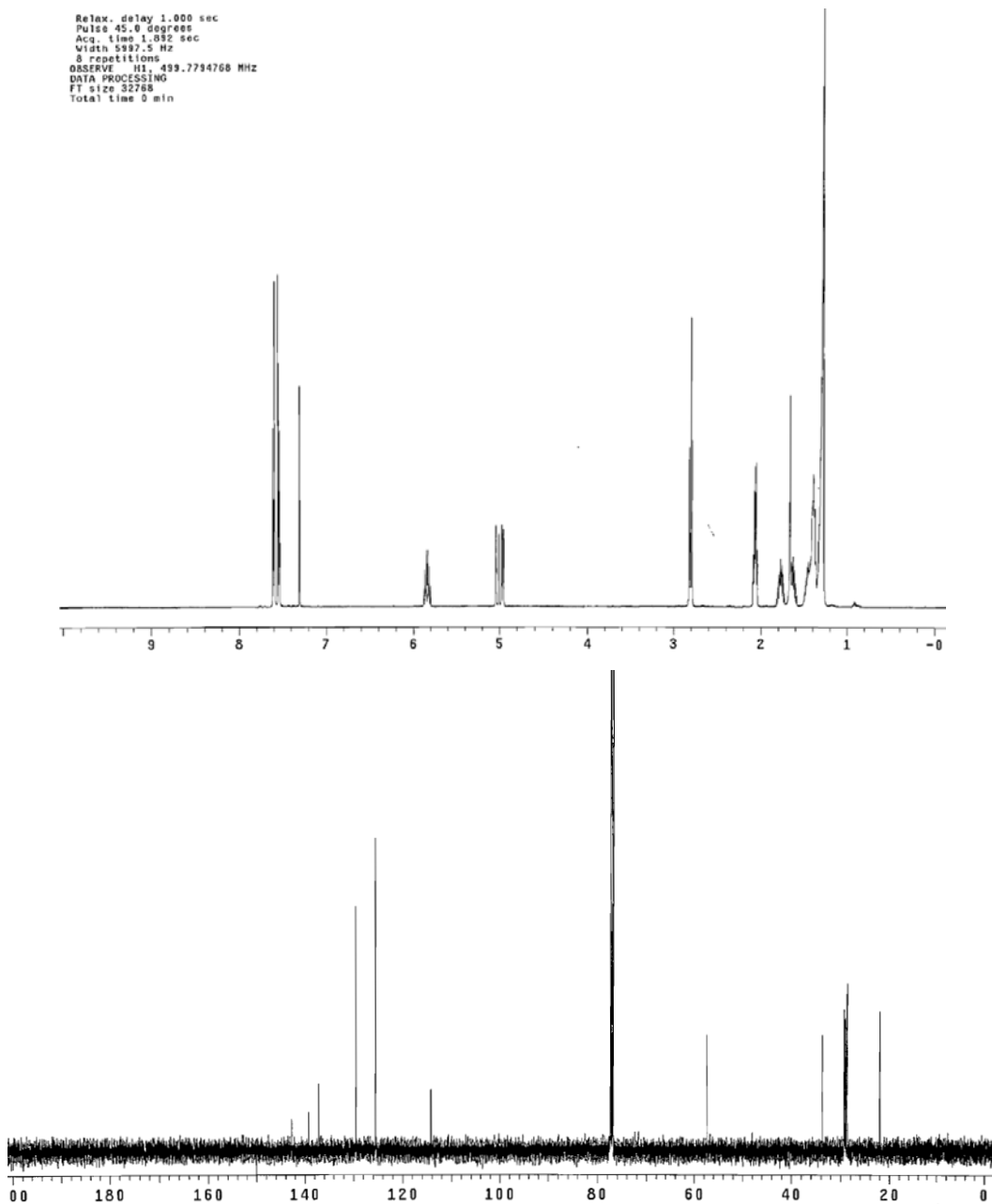


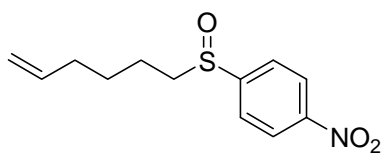
1-methyl-4-(undec-10-enylsulfinyl)benzene (5j): colorless oil (33.8 mg, 87%); TLC (SiO₂) R_f 0.3 (4:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, 2H, *J* = 8.5 Hz), 7.28 (d, 2H, *J* = 8.0 Hz), 5.77 (ddt, 1H, ABM, *J*_{BM} = 17.0 Hz, *J*_{AM} = 10.0 Hz, *J* = 7.0 Hz), 4.95 (d, 1H, ABM, *J*_{BM} = 17.0 Hz), 4.89 (d, 1H, ABM, *J*_{AM} = 10.0 Hz), 2.78-2.67 (m, 2H), 2.38 (s, 3H), 1.98 (q, 2H, *J* = 7.0 Hz), 1.72-1.63 (m, 1H), 1.60-1.53 (m, 1H), 1.41-1.31 (m, 4H), 1.22 (m, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 141.5, 141.0, 139.3, 130.0, 124.2, 114.3, 57.6, 33.9, 29.5, 29.4, 29.3, 29.2, 29.0, 28.8, 22.4, 21.6; ESI-HRMS calcd for C₁₈H₂₈O [M+H]⁺ 293.1934, found 293.1933.



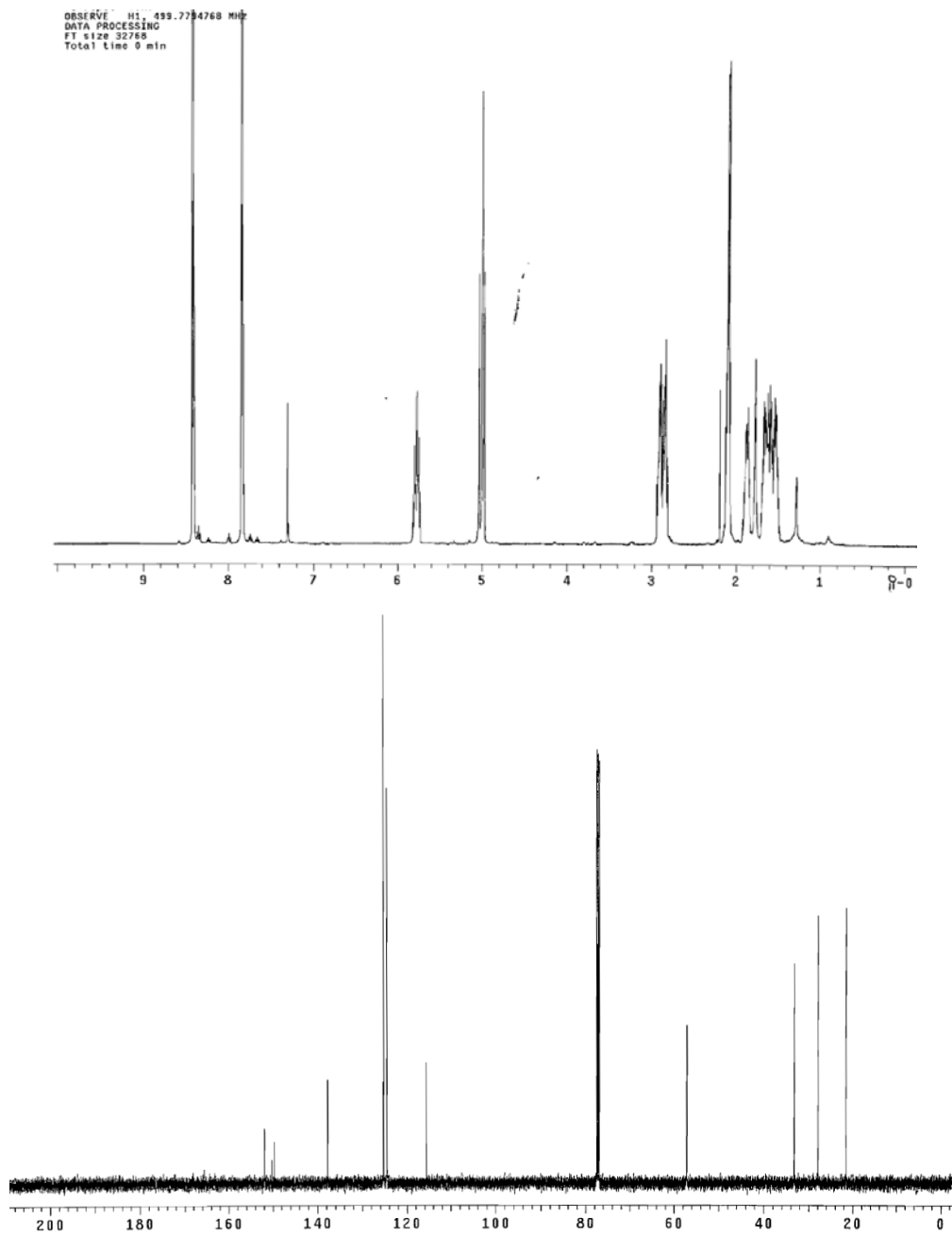


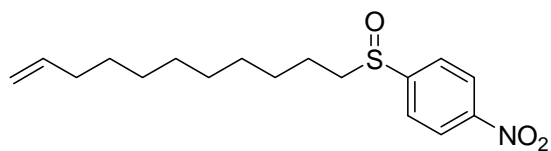
1-chloro-4-(undec-10-enylsulfinyl)benzene (5k): colorless oil (12.9 mg, 74%); TLC (SiO₂) R_f 0.23 (7:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 7.54 (m, 2H), 7.49-7.47 (m, 2H), 5.78 (ddt, 1H, ABM, J_{BM} = 17.0 Hz, J_{AM} = 10.5 Hz, J = 6.5 Hz), 4.95 (dd, 1H, ABM, J_{BM} = 17.0 Hz, J_{AB} = 1.5 Hz), 4.90 (dd, 1H, ABM, J_{AM} = 10.5 Hz, J_{AB} = 1.5 Hz), 2.74 (t, 2H, J = 8.0 Hz), 2.00 (m, 2H), 1.75-1.65 (m, 1H), 1.61-1.52 (m, 1H), 1.43-1.31 (m, 3H), 1.23 (m, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 142.8, 139.4, 137.3, 129.7, 125.7, 114.4, 57.6, 34.0, 29.5, 29.3, 29.2, 29.1, 28.8, 22.2; ESI-HRMS calcd for C₁₇H₂₅ClO [M+H]⁺ 313.1387, found 313.1387.





1-(hex-5-enylsulfinyl)-4-nitrobenzene (5l): yellow oil (13.4 mg, 61%); TLC (SiO₂) R_f 0.27 (3:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.35 (d, 2H, *J* = 8.5 Hz), 7.77 (d, 2H, *J* = 8.5 Hz), 5.71 (ddt, 1H, ABM, *J*_{AM} = 17.0 Hz, *J*_{BM} = 10.5 Hz, *J* = 7.0 Hz), 4.97-4.91 (m, ABM, 2H), 2.84 (m, 1H), 2.78 (m, 1H), 2.04 (m, 2H), 1.86-1.79 (m, 1H), 1.64-1.44 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 151.9, 150.2, 149.6, 137.7, 125.3, 124.4, 115.6, 57.1, 33.3, 27.9, 21.6; ESI-HRMS calcd for C₁₂H₁₅NNaO₃S 276.0665 [M+Na]⁺, found 276.0673.





1-nitro-4-(undec-10-enylsulfinyl)benzene (5m): colorless oil (15.3 mg, 64%); TLC (SiO₂) R_f 0.47 (3:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.35 (d, 2H, *J* = 8.0 Hz), 7.78 (d, 2H, *J* = 8.0 Hz), 5.76 (ddt, 1H, ABM, *J*_{BM} = 17.5 Hz, *J*_{AM} = 10.0 Hz, *J* = 6.5 Hz), 4.95 (dd, 1H, ABM, *J*_{BM} = 17.5 Hz, *J*_{AB} = 1.5 Hz), 4.90 (dd, 1H, ABM, *J*_{AM} = 10.0 Hz, *J*_{AB} = 1.5 Hz), 2.88-2.75 (m, 2H), 2.00 (m, 2H), 1.84-1.75 (m, 1H), 1.60-1.52 (m, 1H), 1.45-1.38 (m, 1H), 1.37-1.30 (m, 3H), 1.27-1.22 (m, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 152.0, 139.3, 125.3, 124.4, 114.4, 57.4, 34.0, 29.5, 29.4, 29.3, 29.2, 29.1, 28.8, 22.1; ESI-HRMS calcd for C₁₇H₂₆NO₃S [M+H]⁺ 324.1628, found 324.1622.

