Supplementary Information for Catalyric Asymmetric Mannich-Type Reactions of α-Cyano α-Sulfonyl Carbanions

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General Information: Infrared spectra were recorded on a Shimadzu IRAffinity-1 spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane (0.0 ppm) resonance as the internal standard ($CDCl_3$). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$; 77.16 ppm). Optical rotations were measured on a HORIBA SEPA-500 polarimeter. The high resolution mass spectra were conducted on Thermo Fisher Scientific Exactive. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Flash column chromatography was performed on PSQ60AB (spherical, av. 55 μm; Fuji Silysia Chemical ltd.). Enantiomeric excesses were determined by HPLC analysis using chiral columns (φ 4.6 mm x 250 mm, DAICEL CHIRALCEL OD-H (ODH), CHIRALCEL OD-3 (OD3), CHIRALPAK AD-H (ADH), CHIRALPAK AD-3 (AD3), CHIRALPAK AY-3 (AY3), CHIRALPAK IC (IC), CHIRALPAK IA (IA), and CHIRALPAK AS-H (ASH)) with hexane (H) isopropyl alcohol (IPA) and ethanol (EtOH), as eluent.

Toluene was supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by both A2 alumina and Q5 reactant using a GlassContour solvent dispensing system. *N*-Boc imines[1], and 1,2,3-triazolium salts **1**·X[2] were synthesized by following the literature methods. α-Cyano-α-sulfones were prepared via monoalkylation reactions of aryl- or alkylsulfonyl acetonitriles.[3]

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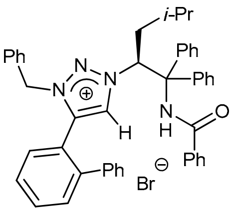
[1] (a) Wenzel, A. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 12964. (b) Song, J.; Wang, Y.; Deng, L. *J. Am. Chem. Soc.* **2006**, *128*, 6048.

[2] Ohmatsu, K.; Kiyokawa, M.; Ooi, T. *J. Am. Chem. Soc.* **2011**, *133*, 1307.

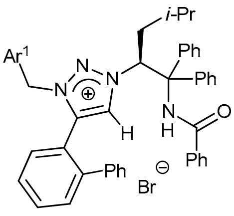
[3] Ono, N.; Tamura, R.; Tanikaga, R.; Kaji, A. *Synthesis* **1977**, 690.

Experimental Section:

Characterization of 1,2,3-Triazolium Bromide:

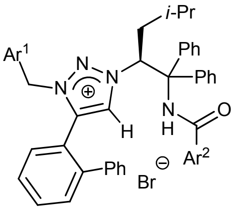


1a·Br: ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.25 (1H, brs), 8.71 (1H, brs), 8.25 (2H, brs), 7.83 (2H, brs), 7.67 (2H, m), 7.52-7.36 (8H, m), 7.29-7.05 (12H, m), 6.89 (2H, brs), 6.64 (2H, d, J = 7.3 Hz), 5.04 (2H, brs), 1.86 (2H, brm), 1.07 (3H, d, J = 6.4Hz), 0.91 (1H, m), 0.63 (3H, d, J = 6.9 Hz); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.9, 142.7, 140.4, 138.5, 133.5, 132.3, 132.1, 131.8, 130.8, 130.5, 129.7, 129.3, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.7, 127.6, 127.1, 69.1, 68.7, 55.6, 38.4, 25.5, 23.2, 22.0, five peaks for aromatic carbons were not found probably due to overlapping; IR 3030, 2957, 1674, 1519, 1485, 1287, 1146 cm^{-1}; HRMS (ESI) Calcd for $C_{46}H_{43}N_4O^+$ ([M–Br]$^+$) 667.3431. Found 667.3429.; $[\alpha]_D^{19}$ = +35.4 (c = 1.0, CHCl$_3$).



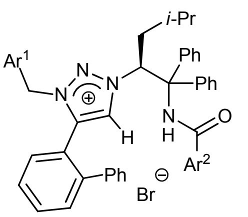
(Ar^1 = p-CF$_3$-C$_6$H$_4$)

1b·Br: ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.74 (1H, brs), 8.52 (1H, brs), 8.19 (2H, brd, J = 6.0 Hz), 7.83 (1H, br), 7.73 (1H, br), 7.68 (1H, t, J = 7.8 Hz), 7.53 (1H, t, J = 7.8 Hz), 7.48 (1H, d, J = 7.8 Hz), 7.43-7.35 (8H, m), 7.30-7.25 (5H, m), 7.20 (3H, br), 7.11 (2H, t, J = 7.8 Hz), 6.90 (2H, d, J = 7.3 Hz), 6.81 (2H, d, J = 8.2 Hz), 5.45-5.15 (2H, brm), 1.87 (1H, dd, J = 14.6, 9.6 Hz), 1.73 (1H, brm), 1.06 (3H, d, J = 6.4 Hz), 0.88 (1H, m), 0.60 (3H, d, J = 6.4 Hz); ^{13}C NMR (101 MHz, CDCl$_3$) δ 168.0, 142.6, 141.0, 140.9, 138.4, 136.1, 134.2, 133.6, 132.8, 132.6, 132.2, 131.9, 131.8 (q, $J_{C\text{-}F}$ = 33.5 Hz), 130.9, 129.4, 129.3, 129.0, 128.8, 128.7, 128.5, 128.3, 128.2, 127.8, 127.4, 125.9 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.5 (q, $J_{C\text{-}F}$ = 274.0 Hz), 119.9, 69.1, 68.8, 55.0, 38.6, 25.6, 23.2, 21.9, three peaks for aromatic carbons were not found probably due to overlapping; IR 3059, 3003, 1672, 1568, 1531, 1325, 1128 cm^{-1}; HRMS (ESI) Calcd for $C_{47}H_{42}F_3N_4O^+$ ([M–Br]$^+$) 735.3305. Found 735.3302.; $[\alpha]_D^{19}$ = +40.6 (c = 0.7, CHCl$_3$).



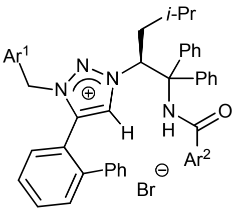
(Ar^1 = p-CF$_3$-C$_6$H$_4$)
(Ar^2 = p-CF$_3$-C$_6$H$_4$)

1c·Br: ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.12 (1H, brs), 8.39 (1H, brs), 7.79 (2H, brs), 7.72-7.69 (4H, m), 7.56-7.50 (3H, m), 7.44 (2H, d, J = 8.4 Hz), 7.39 (2H, t, J = 8.4 Hz), 7.32-7.26 (3H, m), 7.16-7.12 (6H, brm), 6.93 (2H, brd, J = 6.4 Hz), 6.78 (2H, d, J = 7.6 Hz), 5.11 (2H, brs), 1.89-1.74 (2H, m), 1.07 (3H, d, J = 6.8 Hz), 0.80-0.81 (1H, brm), 0.61 (3H, d, J = 6.8 Hz); ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.8, 142.6, 141.0, 140.4, 138.3, 136.6, 135.5, 134.0, 133.3 (q, $J_{C\text{-}F}$ = 32.6 Hz), 132.9, 132.7, 132.0, 132.0 (q, $J_{C\text{-}F}$ = 33.5 Hz), 131.0, 129.3, 129.1, 129.0, 129.0, 128.7, 128.5, 128.2, 127.9, 127.8, 127.2, 126.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.8 (q, $J_{C\text{-}F}$ = 274.0 Hz), 123.3 (q, $J_{C\text{-}F}$ = 274.0 Hz), 119.8, 69.4, 68.8, 54.8, 38.4, 25.5, 23.1, 21.8, two peaks for aromatic carbons were not found probably due to overlapping; IR 3024, 2959, 1682, 1530, 1476, 1288, 1128 cm^{-1}; HRMS (ESI) Calcd for $C_{48}H_{41}F_6N_4O^+$ ([M–Br]$^+$) 803.3179. Found 803.3169.; $[\alpha]_D^{19}$ = +18.6 (c = 1.0, CHCl$_3$).



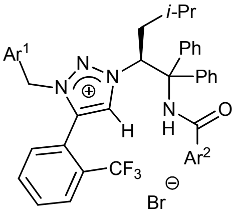
(Ar^1 = *p*-CF$_3$-C$_6$H$_4$)
(Ar^2 = 3,5-(CF$_3$)$_2$-C$_6$H$_3$)

1d·Br: ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.34 (1H, brs), 9.78 (1H, brs), 8.61 (2H, s), 7.93 (1H, s), 7.88 (2H, d, J = 7.8 Hz), 7.74-7.70 (1H, m), 7.55-7.51 (4H, brm), 7.45 (2H, d, J = 8.2 Hz), 7.40 (2H, t, J = 7.8 Hz), 7.33-7.24 (4H, m), 7.18-7.14 (5H, brm), 7.01 (2H, d, J = 7.8 Hz), 6.73 (2H, d, J = 7.8 Hz), 5.00 (1H, brd, J = 14.6 Hz), 4.96 (1H, brd, J = 14.6 Hz), 1.90-1.77 (2H, m), 1.09 (3H, d, J = 6.4 Hz), 0.87 (1H, m), 0.63 (3H, d, J = 6.9 Hz); ^{13}C NMR (101 MHz, CDCl$_3$) δ 165.6, 142.4, 141.2, 140.1, 138.4, 135.9, 135.3, 133.8, 133.0, 132.8, 132.0 (q, $J_{\text{C-F}}$ = 33.5 Hz), 132.0, 131.4 (q, $J_{\text{C-F}}$ = 33.5 Hz), 131.1, 129.2, 129.0, 128.7, 128.7, 128.5, 128.2, 128.0, 127.8, 127.2, 126.0 (q, $J_{\text{C-F}}$ = 3.8 Hz), 125.2 (q, $J_{\text{C-F}}$ = 3.8 Hz), 123.3 (q, $J_{\text{C-F}}$ = 274.0 Hz), 123.1 (q, $J_{\text{C-F}}$ = 274.0 Hz), 119.7, 69.8, 69.0, 54.6, 38.2, 25.6, 23.1, 21.8, four peaks for aromatic carbons were not found probably due to overlapping; IR 3022, 2961, 1684, 1522, 1279, 1134 cm^{-1}; HRMS (ESI) Calcd for $C_{49}H_{40}F_9N_4O^+$ ([M–Br]$^+$) 871.3053. Found 871.3044.; $[\alpha]_D^{19}$ = +10.3 (c = 1.0, CHCl$_3$).



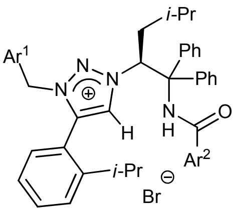
(Ar^1 = *p*-CF$_3$-C$_6$H$_4$)
(Ar^2 = 3,5-Me$_2$-C$_6$H$_3$)

1e·Br: ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.43 (1H, brs), 8.12 (1H, brs), 8.02 (1H, brs), 7.73 (2H, brs), 7.67 (1H, t, J = 7.8 Hz), 7.67-7.59 (2H, m), 7.55 (1H, t, J = 7.8 Hz), 7.46 (1H, d, J = 7.3 Hz), 7.41 (2H, d, J = 8.2 Hz), 7.35 (2H, d, J = 7.8 Hz), 7.33-7.25 (8H, brm), 7.13 (2H, d, J = 7.8 Hz), 7.07 (1H, s), 6.88-6.81 (4H, brm), 5.50 (1H, br), 5.32 (1H, brd, J = 14.2 Hz), 2.34 (6H, s), 1.88 (1H, dd, J = 14.6, 9.6 Hz), 1.69 (1H, br), 1.02 (3H, d, J = 6.4 Hz), 0.90-0.83 (1H, brm), 0.59 (3H, d, J = 6.4 Hz); ^{13}C NMR (101 MHz, CDCl$_3$) δ 168.5, 142.5, 141.0, 138.3, 138.2, 136.3, 134.2, 133.6, 133.6, 132.6, 132.2, 131.7 (q, $J_{\text{C-F}}$ = 33.5 Hz), 130.8, 129.5, 129.1, 128.9, 128.7, 128.7, 128.4, 128.1, 127.9, 127.7, 127.5, 125.8 (q, $J_{\text{C-F}}$ = 3.8 Hz), 125.6, 123.4 (q, $J_{\text{C-F}}$ = 273.5 Hz), 119.8, 69.0, 68.6, 55.1, 38.6, 25.5, 23.1, 21.8, 21.1, three peaks for aromatic carbons were not found probably due to overlapping; IR 3021, 2959, 1674, 1516, 1474, 1325, 1128 cm^{-1}; HRMS (ESI) Calcd for $C_{49}H_{46}F_3N_4O^+$ ([M–Br]$^+$) 763.3618. Found 763.3613.; $[\alpha]_D^{19}$ = +14.0 (c = 1.0, CHCl$_3$).



(Ar^1 = *p*-CF$_3$-C$_6$H$_4$)
(Ar^2 = 3,5-Me$_2$-C$_6$H$_3$)

1f·Br: ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.11 (1H, brs), 8.40 (1H, brs), 7.86 (1H, d, J = 7.8 Hz), 7.78-7.73 (2H, m), 7.64-7.30 (16H, brm), 7.16 (2H, d, J = 7.8 Hz), 7.07 (1H, s), 5.68 (2H, br), 2.35 (6H, s), 2.06-1.99 (2H, m), 1.11 (3H, br), 0.87 (1H, m), 0.65 (3H, br); ^{13}C NMR (101 MHz, CDCl$_3$) δ 169.7, 142.2, 138.7, 138.3, 137.5, 135.3, 134.0, 133.6, 132.5, 131.8 (q, $J_{\text{C-F}}$ = 32.6 Hz), 131.4, 130.4, 130.0, 129.7, 129.3 (q, $J_{\text{C-F}}$ = 37.4 Hz), 128.8, 128.4, 128.3, 128.1, 128.0, 126.6, 125.8, 125.3, 123.6 (q, $J_{\text{C-F}}$ = 273.0 Hz), 123.1 (q, $J_{\text{C-F}}$ = 275.0 Hz), 125.6, 119.4, 68.6, 67.6, 57.0, 39.9, 25.8, 23.0, 21.7, 21.2, one peak for aromatic carbon was not found probably due to overlapping; IR 3013, 2959, 1670, 1497, 1491, 1319, 1128 cm^{-1}; HRMS (ESI) Calcd for $C_{44}H_{41}F_3N_4O^+$ ([M–Br]$^+$) 755.3179. Found 755.3164.; $[\alpha]_D^{19}$ = +12.8 (c = 1.0, CHCl$_3$).

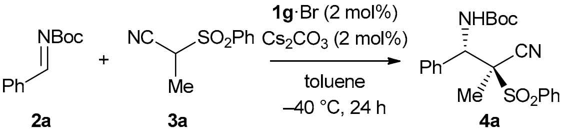


(Ar^1 = *p*-CF$_3$-C$_6$H$_4$)
(Ar^2 = 3,5-Me$_2$-C$_6$H$_3$)

1g·Br: ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.83 (1H, brs), 8.49 (1H, brs), 7.75 (4H, br), 7.58 (2H, t, J = 8.0 Hz), 7.58-7.49 (1H, m), 7.49 (2H, d, J = 8.2 Hz), 7.41-7.34 (9H, m), 7.31 (1H, t, J = 7.3 Hz), 7.05 (1H, s), 6.99 (2H, d, J = 8.2 Hz), 5.60 (1H, br), 5,42 (1H, brd, J = 15.6 Hz), 2.34-2.27 (1H, m), 2.32 (6H, s), 2.07-1.95 (2H, m), 1.32-1.26 (1H, m), 1.16 (3H, d, J = 6.9 Hz), 1.02 (3H, d, J = 6.9 Hz), 0.79 (3H, d, J = 6.9 Hz), 0.74

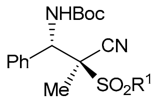
(3H, d, *J* = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 148.6, 140.4, 138.3, 136.8, 134.6, 133.6, 133.3, 132.8, 132.3, 131.8 (q, $J_{C\text{-}F}$ = 33.5 Hz), 131.2, 129.2, 128.9, 128.8, 128.2, 127.9, 127.8, 127.7, 127.0, 126.5, 126.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.6, 123.4 (q, $J_{C\text{-}F}$ = 273.5 Hz), 119.2, 69.3, 69.2, 54.9, 38.4, 30.8, 25.6, 23.1, 22.0, 21.5, 21.1, one peak for aromatic carbon was not found probably due to overlapping; IR 3021, 2963, 1670, 1508, 1489, 1325, 1128 cm^{-1}; HRMS (ESI) Calcd for $C_{46}H_{48}F_3N_4O^+$ ([M–Br]$^+$) 729.3775. Found 729.3763.; $[\alpha]_D^{19}$ = +15.3 (c = 1.0, $CHCl_3$).

General Procedure for 1g·Br-Catalyzed Asymmetric Mannich-Type Reaction, and Characterization of 4:



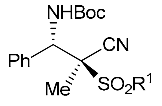
To a test tube was added **1g**·Br (1.62 mg, 0.002 mmol), Cs_2CO_3 (0.65 mg, 0.002 mmol), α-cyanosulfone **3a** (19.5 mg, 0.1 mmol) and the tube was degassed by alternating vaccum evacuation/Ar backfill. Then toluene (500 μL) was added, and the resulting mixture was cooled to –40 ºC. To this solution was added *N*-Boc imine **2a** (24.6 mg, 0.12 mmol) and stirred for 24 h. The reaction mixture was quenched by NH_4Cl, and the extractive workup was performed with EtOAc. After drying over Na_2SO_4, filtration, and removal of solvent, the resulting crude residue was purified by column chromatography (H/EtOAc = 10:1 as eluent) to afford **4a** (40.0 mg, 0.099 mmol, 99% yield) as a white solid.

4a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (2H, d, *J* = 8.0 Hz), 7.75 (1H, t, *J* = 7.4 Hz), 7.62 (2H, dd, *J* = 8.0, 7.4 Hz), 7.41-7.32 (5H, m), 5.46 (1H, br), 5.29 (1H, brd, *J* = 8.7 Hz), 1.38 (3H, s), 1.37 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 137.0, 135.6, 135.1, 130.5, 129.4, 129.0, 129.0, 116.3, 80.7, 65.4, 57.2, 28.2, 19.9; IR 2978, 1717, 1499, 1449, 1368, 1331, 1246, 1152 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{24}N_2NaO_4S^+$ ([M+Na]$^+$) 423.1349. Found 423.1346.; HPLC ASH, H/IPA/EtOH = 97:1.5:1.5, flow rate = 0.5 mL/min, λ = 210 nm, 36.7 min (major *anti* isomer), 41.3 min (major *syn* isomer), 71.2 min (minor *anti* isomer), 81.1 min (minor *syn* isomer).



(R^1 = *p*-*t*-Bu-C_6H_4)

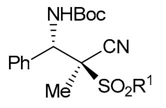
4b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (2H, d, *J* = 8.7 Hz), 7.61 (2H, d, *J* = 8.7 Hz), 7.38-7.34 (5H, m), 5.53 (1H, br), 5.30 (1H, brd, *J* = 7.8 Hz), 1.38 (12H, s), 1.37 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 154.0, 137.0, 132.4, 128.9, 128.9, 127.6, 126.4, 116.4, 80.6, 65.2, 57.3, 35.5, 31.0, 28.2, 20.0; IR 2968, 1717, 1497, 1456, 1366, 1329, 1267, 1153 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{32}N_2KO_4S^+$ ([M+K]$^+$) 495.1714. Found 495.1709.; HPLC OD3, H/IPA/EtOH = 97:1.5:1.5, flow rate = 0.5 mL/min, λ = 210 nm, 17.9 min (major *anti* isomer), 20.5 min (major *syn* isomer), 24.4 min (minor *anti* isomer), 25.7 min (minor *syn* isomer).



(R^1 = *p*-MeO-C_6H_4)

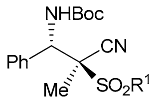
4c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (2H, d, *J* = 9.2 Hz), 7.41-7.33 (5H, m), 7.06 (2H, d, *J* = 9.2 Hz), 5.53 (1H, br), 5.23 (1H, d, *J* = 8.9 Hz), 3.92 (3H, s), 1.38 (9H, s), 1.37 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 154.0, 137.1, 132.8, 128.9, 127.6, 126.4, 116.5, 114.6, 80.6, 65.3, 57.3, 55.8, 28.2, 20.0, one peak for aromatic carbon was not found probably due to overlapping; IR 2978, 1716, 1593, 1497, 1456, 1331, 1314, 1267, 1148 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{26}N_2KO_5S^+$ ([M+K]$^+$) 469.1194. Found 469.1192.; HPLC ADH, H/IPA = 5:1, flow rate

= 0.5 mL/min, λ = 210 nm, 32.6 min (minor *anti* isomer), 39.2 min (minor *syn* isomer), 45.8 min (major *anti* isomer), 67.7 min (major *syn* isomer).



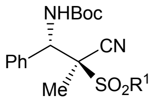
(R^1 = *p*-CF$_3$-C$_6$H$_4$)

4d: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.19 (2H, d, J = 8.5 Hz), 7.88 (2H, d, J = 8.5 Hz), 7.40-7.33 (5H, m), 5.34 (1H, brd, J = 10.1 Hz), 5.24 (1H, brd, J = 10.1 Hz), 1.47 (3H, s), 1.35 (9H, s); ^{13}C NMR (101 MHz, CDCl$_3$) δ 153.8, 139.5, 136.6, 136.4 (q, $J_{C\text{-}F}$ = 33.5 Hz), 131.1, 129.3, 129.2, 127.4, 126.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 122.9 (q, $J_{C\text{-}F}$ = 275 Hz), 116.3, 81.0, 66.0, 56.9, 28.2, 19.2; IR 2980, 1717, 1506, 1489, 1456, 1368, 1321, 1246, 1155 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{23}F_3KN_2O_4S^+$ ([M+K]$^+$) 507.0962. Found 507.0961.; HPLC ASH, H/IPA/EtOH = 97:1.5:1.5, flow rate = 0.5 mL/min, λ = 250 nm, 17.0 min (major *anti* isomer), 19.6 min (major *syn* isomer), 26.9 min (minor *anti* isomer), 26.8 min (minor *syn* isomer).



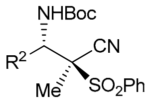
(R^1 = *p*-NO$_2$-C$_6$H$_4$)

4e: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.43 (2H, d, J = 8.9 Hz), 8.25 (2H, d, J = 8.9 Hz), 7.40-7.33 (5H, m), 5.35 (1H, brd, J = 9.8 Hz), 5.18 (1H, brd, J = 9.8 Hz), 1.49 (3H, s), 1.35 (9H, s); ^{13}C NMR (101 MHz, CDCl$_3$) δ 153.8, 151.3, 141.5, 136.4, 131.9, 129.4, 129.3, 127.3, 124.3, 116.2, 81.2, 66.5, 56.9, 28.2, 19.0; IR 2980, 1717, 1533, 1499, 1367, 1348, 1244, 1155 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{23}N_3NaO_6S^+$ ([M+Na]$^+$) 468.1200. Found 468.1199.; HPLC IC, H/IPA = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, 12.6 min (minor *anti* isomer), 14.6 min (minor *syn* isomer), 16.0 min (major *syn* isomer), 17.2 min (major *anti* isomer).



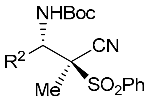
(R^1 = *i*-Pr)

4f: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46-7.39 (5H, m), 5.83 (1H, br), 5.35 (1H, brd, J = 7.8 Hz), 3.33 (1H, m), 1.59 (3H, s), 1.54 (3H, d, J = 6.4 Hz), 1.45 (3H, d, J = 6.4 Hz), 1.41 (9H, s); ^{13}C NMR (101 MHz, CDCl$_3$) δ 154.6, 136.5, 129.3, 129.2, 127.7, 117.3, 81.2, 63.9, 57.6, 56.4, 28.3, 19.0, 17.8, 16.6; IR 2980, 1699, 1506, 1489, 1456, 1364, 1315, 1246, 1163 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{26}N_2NaO_4S^+$ ([M+Na]$^+$) 389.1505. Found 389.1506.; HPLC IC, H/EtOH = 95:5, flow rate = 1.0 mL/min, λ = 210 nm, 8.6 min (major *syn* isomer), 9.0 min (minor *anti* isomer), 11.6 min (minor *syn* isomer), 12.6 min (major *anti* isomer).



(R^2 = *o*-Me-C$_6$H$_4$)

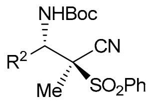
4g: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.10 (2H, d, J = 7.8 Hz), 7.76 (1H, t, J = 7.8 Hz), 7.64 (2H, t, J = 7.8 Hz), 7.40 (1H, d, J = 7.8 Hz), 7.26-7.22 (2H, m), 7.18 (1H, d, J = 8.2 Hz), 5.77 (1H, d, J = 9.2 Hz), 5.26 (1H, br), 2.46 (3H, s), 1.36 (9H, s), 1.34 (3H, s); ^{13}C NMR (101 MHz, CDCl$_3$) δ 154.0, 136.5, 135.7, 135.2, 131.1, 130.8, 129.5, 128.7, 127.3, 125.8, 116.7, 80.7, 66.4, 51.2, 28.4, 19.9, 18.4, one peak for aromatic carbon was not found probably due to overlapping; IR 2978, 1717, 1506, 1489, 1449, 1368, 1331, 1246, 1153 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{26}N_2KO_4S^+$ ([M+K]$^+$) 453.1245. Found 453.1241.; HPLC AY3, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 210 nm, 12.1 min (minor *syn* isomer), 16.5 min (minor *anti* isomer), 26.7 min (major *syn* isomer), 62.8 min (major *anti* isomer).



(R^2 = *o*-MeO-C$_6$H$_4$)

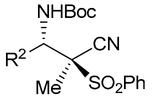
4h: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.11 (2H, d, J = 7.8 Hz), 7.73 (1H, t, J = 7.8 Hz), 7.61 (2H, t, J = 7.8 Hz), 7.34-7.26 (2H, m), 6.96 (1H, t, J = 7.8 Hz), 6.89 (1H, d, J = 8.2 Hz), 5.75-5.52 (2H, brm), 3.85 (3H, s), 1.38 (3H, s), 1.35 (9H, s); ^{13}C NMR (101

MHz, $CDCl_3$) δ 156.7, 154.1, 135.6, 134.8, 130.8, 130.1, 129.2, 125.2, 121.1, 116.8, 110.9, 80.2, 66.3, 55.0, 28.3, 18.8, one peak for aromatic carbon was not found probably due to overlapping; IR 2978, 1717, 1495, 1449, 1368, 1331, 1248, 1153 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{26}N_2KO_5S^+$ ($[M+K]^+$) 469.1194. Found 469.1192.; HPLC IA, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 16.2 min (major *syn* isomer), 17.4 min (minor *syn* isomer), 20.0 min (major *anti* isomer), 34.0 min (minor *anti* isomer).



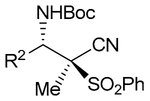
(R^2 = *o*-Cl-C_6H_4)

4i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (2H, d, J = 7.8 Hz), 7.78 (1H, t, J = 7.8 Hz), 7.66 (2H, t, J = 7.8 Hz), 7.53 (1H, d, J = 7.8 Hz), 7.40-7.25 (3H, m), 5.99 (1H, d, J = 8.2 Hz), 5.53 (1H, br), 1.43 (3H, s), 1.37 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 135.3, 135.3, 133.8, 130.7, 130.0, 129.5, 129.3, 127.9, 127.1, 115.9, 81.1, 65.9, 52.3, 28.2, 18.3, one peak for aromatic carbon was not found probably due to overlapping; IR 2978, 1705, 1506, 1449, 1368, 1333, 1246, 1155 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{23}ClN_2KO_4S^+$ ($[M+K]^+$) 473.0699. Found 473.0698.; HPLC ADH, H/IPA = 4:1, flow rate = 1.0 mL/min, λ = 254 nm, 9.0 min (major *syn* isomer), 10.4 min (minor *syn* isomer), 11.8 min (major *anti* isomer), 38.1 min (minor *anti* isomer).



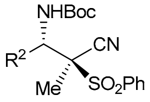
(R^2 = *o*-Br-C_6H_4)

4j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (2H, d, J = 7.8 Hz), 7.78 (1H, t, J = 7.8 Hz), 7.66 (2H, t, J = 7.8 Hz), 7.57 (1H, d, J = 7.8 Hz), 7.52 (1H, d, J = 7.8 Hz), 7.39 (1H, t, J = 7.8 Hz), 7.20 (1H, t, J = 7.8 Hz), 5.97 (1H, d, J = 7.8 Hz), 5.51 (1H, brs), 1.45 (3H, s), 1.38 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 137.1, 135.3, 134.9, 133.3, 130.7, 130.3, 129.5, 128.6, 128.1, 124.5, 115.8, 81.0, 66.1, 55.3, 28.2, 18.5; IR 2978, 1705, 1506, 1491, 1449, 1368, 1333, 1246, 1155 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{23}BrN_2KO_4S^+$ ($[M+K]^+$) 517.0193. Found 517.0193.; HPLC IA, H/IPA = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, 11.6 min (major *syn* isomer), 13.9 min (minor *syn* isomer), 16.6 min (major *anti* isomer), 39.8 min (minor *anti* isomer).



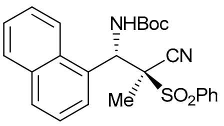
(R^2 = *p*-MeO-C_6H_4)

4k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (2H, d, J = 7.8 Hz), 7.75 (1H, t, J = 7.8 Hz), 7.62 (2H, t, J = 7.8 Hz), 7.30 (2H, d, J = 8.7 Hz), 6.89 (2H, d, J = 8.7 Hz), 5.42 (1H, br), 5.23 (1H, d, J = 8.7 Hz), 3.80 (3H, s), 1.38 (3H, s), 1.38 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 157.2, 139.0, 138.4, 133.8, 132.7, 132.0, 119.7, 117.6, 83.9, 68.9, 60.1, 58.6, 31.6, 23.2, one peak for aromatic carbon was not found probably due to overlapping; IR 2978, 1717, 1512, 1448, 1368, 1329, 1246, 1153 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{26}N_2KO_5S^+$ ($[M+K]^+$) 469.1194. Found 469.1189.; HPLC IC, H/IPA = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, 12.3 min (minor *anti* isomer), 16.9 min (major *syn* isomer), 22.4 min (major *anti* isomer), 34.8 min (minor *syn* isomer).

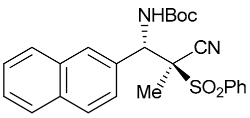


(R^2 = *p*-Br-C_6H_4)

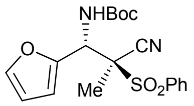
4l: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (2H, d, J = 7.8 Hz), 7.77 (1H, t, J = 7.8 Hz), 7.63 (2H, t, J = 7.8 Hz), 7.51 (1H, d, J = 8.2 Hz), 7.27 (1H, d, J = 8.2 Hz), 5.55 (1H, br), 5.23 (1H, brd, J = 8.2 Hz), 1.39 (3H, s), 1.38 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 135.3, 134.5, 132.1, 131.8, 130.4, 129.9, 129.5, 129.3, 123.2, 116.1, 80.9, 64.9, 56.9, 28.2, 19.9; IR 2978, 1717, 1506, 1489, 1449, 1368, 1331, 1246, 1153 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{23}BrN_2KO_4S^+$ ($[M+K]^+$) 517.0193. Found 517.0194.; HPLC IC, H/IPA = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, 6.9 min (minor *anti* isomer), 10.2 min (major *syn* isomer), 13.4 min (major *anti* isomer), 17.4 min (minor *syn* isomer).



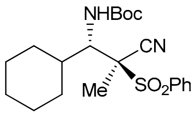
4m: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.22 (1H, d, *J* = 8.2 Hz), 8.14 (2H, d, *J* = 7.8 Hz), 7.87 (2H, t, *J* = 7.8 Hz), 7.78 (1H, t, *J* = 7.8 Hz), 7.67-7.63 (3H, m), 7.58 (1H, t, *J* = 7.8 Hz), 7.52 (2H, t, *J* = 7.8 Hz), 6.46 (1H, brd, *J* = 7.8 Hz), 5.50 (1H, br), 1.32 (9H, s), 1.25 (3H, s); ^{13}C NMR (101 MHz, CDCl$_3$) δ 153.9, 135.5, 135.1, 134.2, 133.6, 131.3, 130.6, 129.5, 129.4, 129.1, 127.3, 126.2, 125.6, 124.2, 122.5, 116.4, 80.7, 66.6, 49.8, 28.2, 19.0; IR 2979, 1717, 1506, 1491, 1449, 1368, 1331, 1246, 1153 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{26}N_2KO_4S^+$ ([M+K]$^+$) 489.1245. Found 489.1247.; HPLC IA, H/IPA = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, 10.5 min (major *syn* isomer), 13.8 min (major *anti* isomer).



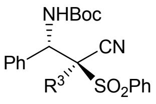
4n: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.07 (2H, d, *J* = 7.8 Hz), 7.87-7.73 (4H, m), 7.75 (1H, d, *J* = 7.8 Hz), 7.62 (2H, d, *J* = 7.8 Hz), 7.53 (3H, m), 5.57 (1H, br), 5.46 (1H, brd, *J* = 8.7 Hz), 1.42 (3H, s), 1.36 (9H, s); ^{13}C NMR (101 MHz, CDCl$_3$) δ 153.9, 135.5, 135.1, 134.2, 133.3, 133.0, 130.5, 129.4, 129.1, 128.2, 127.7, 127.4, 126.8, 126.7, 124.3, 116.5, 80.7, 65.4, 57.3, 28.2, 19.9; IR 2978, 1716, 1506, 1491, 1449, 1368, 1329, 1246, 1153 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{26}N_2KO_4S^+$ ([M+K]$^+$) 489.1245. Found 489.1246.; HPLC IC, H/IPA = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, 10.3 min (minor *anti* isomer), 13.9 min (major *syn* isomer), 17.2 min (major *anti* isomer), 24.5 min (minor *syn* isomer).



4o: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (2H, d, *J* = 7.8 Hz), 7.73 (1H, t, *J* = 7.8 Hz), 7.59 (2H, t, *J* = 7.8 Hz), 7.49 (1H, s), 7.37 (1H, s), 6.49 (1H, br), 5.39 (1H, brd, *J* = 9.4 Hz), 5.33 (1H, brd, *J* = 9.4 Hz), 1.58 (3H, s), 1.42 (9H, s); ^{13}C NMR (101 MHz, CDCl$_3$) δ 154.1, 144.0, 140.9, 135.0, 130.4, 129.3, 129.2, 121.8, 116.8, 108.6, 80.9, 64.9, 50.5, 28.3, 19.6; IR 2980, 1717, 1499, 1491, 1449, 1368, 1329, 1246, 1155 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{22}N_2KO_5S^+$ ([M+K]$^+$) 429.0881. Found 429.0881.; HPLC IA, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 24.7 min (minor *syn* isomer), 28.2 min (minor *anti* isomer), 34.0 min (major *syn* isomer), 37.2 min (major *anti* isomer).



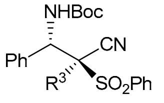
4p: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (2H, d, *J* = 7.8 Hz), 7.74 (1H, t, *J* = 7.8 Hz), 7.64 (2H, t, *J* = 7.8 Hz), 4.92 (1H, d, *J* = 11.0 Hz), 4.32-4.24 (1H, m), 2.34-2.22 (1H, m), 1.98-1.65 (4H, m), 1.55 (3H, s), 1.46 (9H, s), 1.37-1.01 (6H, m); ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.3, 135.5, 135.1, 130.6, 129.4, 117.5, 80.2, 63.9, 58.1, 40.7, 31.7, 28.3, 26.1, 25.8, 21.2; IR 2978, 1701, 1506, 1491, 1449, 1368, 1329, 1244, 1155 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{30}N_2KO_4S^+$ ([M+K]$^+$) 445.1558. Found 445.1560.; HPLC IC, H/IPA = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, 6.0 min (major *syn* isomer), 10.1 min (major *anti* isomer), 13.7 min (minor *anti* isomer), 39.6 min (minor *syn* isomer).



(R^3 = *n*-Hep)

4q: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (2H, d, *J* = 7.8 Hz), 7.69 (1H, t, *J* = 7.8 Hz), 7.54 (2H, t, *J* = 7.8 Hz), 7.46-7.43 (2H, brm), 7.37-7.31 (3H, m), 5.82 (1H, br), 5.41 (1H, brd, *J* = 8.2 Hz), 1.97 (1H, td, *J* = 13.0, 4.8 Hz), 1.83 (1H, td, *J* = 13.0, 4.8 Hz), 1.39 (9H, s), 1.28-1.19 (4H, m), 1.15-1.06 (6H, brs), 0.84 (3H, t, *J* = 7.3 Hz); ^{13}C NMR (101 MHz, CDCl$_3$) δ 154.1, 136.4, 134.8, 130.3, 129.1, 128.8, 128.6, 128.5, 127.9, 116.2, 80.7, 69.9, 56.2, 32.4, 31.4, 29.2, 28.5, 28.2, 24.6, 22.5, 14.0; IR 2928, 1719, 1497, 1449, 1329, 1242, 1153 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{36}N_2KO_4S^+$

([M+K]$^+$) 523.2027. Found 523.2026.; HPLC AD3, H/IPA = 5:1, flow rate = 1.0 mL/min, λ = 210 nm, 7.2 min (minor *syn* isomer), 10.1 min (major *anti* isomer), 13.7 min (major *syn* isomer), 49.6 min (major *anti* isomer).



(R^3 = CH$_2$*i*-Pr)

4r: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (2H, d, *J* = 7.8 Hz), 7.70 (1H, t, *J* = 7.8 Hz), 7.57 (2H, t, *J* = 7.8 Hz), 7.49-7.44 (2H, m), 7.36-7.33 (3H, m), 5.90 (1H, br), 5.32 (1H, brd, *J* = 5.0 Hz), 1.80 (2H, br), 1.38 (9H, s), 0.92 (1H, d, *J* = 6.4 Hz), 0.82 (3H, d, *J* = 6.4 Hz), 0.65 (3H, d, *J* = 6.4 Hz); ^{13}C NMR (101 MHz, CDCl$_3$) δ 154.1, 136.1, 135.2, 135.0, 130.6, 129.2, 129.0, 128.6, 128.3, 116.5, 80.7, 68.8, 57.3, 39.9, 28.3, 25.5, 23.5, 22.7; IR 2968, 1717, 1497, 1449, 1393, 1327, 1244, 1153 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{30}N_2KO_4S^+$ ([M+K]$^+$) 481.1558. Found 481.1559.; HPLC IC, H/IPA = 95:5, flow rate = 1.0 mL/min, λ = 210 nm, 14.6 min (minor *anti* isomer), 30.9 min (major *anti* isomer), 35.0 min (major *syn* isomer), 135.6 min (minor *syn* isomer).

Crystallographic Structure Determination:

Recrystallization of major diastereomer of 4a (CCDC 867728) and minor diastereomer of 4i (CCDC 867729): 4a·was recrystallized from EtOAc/hexane solvent system at –5 °C, and minor isomer of **4i** was recrystallized from MeOH/hexane solvent system at –5 °C.

The single crystals thus obtained were mounted on CryoLoop. Data of X-ray diffraction were collected at 153 K on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An absorption correction was made using SADABS. The structures were solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXTL.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to nitrogen atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined. The crystallographic data were summarized in the following table.

Table S1. Crystal data and structure refinement for **4a**.

Empirical formula	C21 H24 N2 O4 S	
Formula weight	400.48	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 13.817(2) Å	α= 90°.
	b = 10.8098(16) Å	β= 99.403(3)°.
	c = 14.445(2) Å	γ = 90°.
Volume	2128.4(5) $Å^3$	
Z	4	
Density (calculated)	1.250 Mg/m^3	
Absorption coefficient	0.180 mm^{-1}	
F(000)	848	
Crystal size	0.40 x 0.10 x 0.05 mm^3	
Theta range for data collection	1.43 to 28.30°.	
Index ranges	-16<=h<=18, -12<=k<=14, -19<=l<=19	
Reflections collected	15602	
Independent reflections	8724 [R(int) = 0.0283]	
Completeness to theta = 28.30°	99.4 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9911 and 0.9315	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8724 / 1 / 513	
Goodness-of-fit on F^2	1.161	
Final R indices [I>2sigma(I)]	R1 = 0.0584, wR2 = 0.1356	
R indices (all data)	R1 = 0.0648, wR2 = 0.1385	
Absolute structure parameter	0.01(7)	
Largest diff. peak and hole	0.563 and -0.305 e.$Å^{-3}$	

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[4] Sheldrick, G. M. SHELXTL 5.1, Bruker AXS Inc., Madison, Wisconsin, 1997.

Table S2. Crystal data and structure refinement for **4j**.

Empirical formula	C21 H23 Cl N2 O4 S	
Formula weight	434.92	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.911(4) Å	α= 90°.
	b = 9.919(4) Å	β= 90°.
	c = 24.452(11) Å	γ = 90°.
Volume	2161.1(16) $Å^3$	
Z	4	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	0.303 mm^{-1}	
F(000)	912	
Crystal size	0.30 x 0.20 x 0.10 mm^3	
Theta range for data collection	1.67 to 28.24°.	
Index ranges	-8<=h<=11, -12<=k<=13, -32<=l<=32	
Reflections collected	15486	
Independent reflections	5319 [R(int) = 0.0395]	
Completeness to theta = 28.24°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9704 and 0.9147	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5319 / 0 / 266	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0329, wR2 = 0.0842	
R indices (all data)	R1 = 0.0339, wR2 = 0.0850	
Absolute structure parameter	0.05(4)	
Largest diff. peak and hole	0.319 and -0.326 e.$Å^{-3}$	

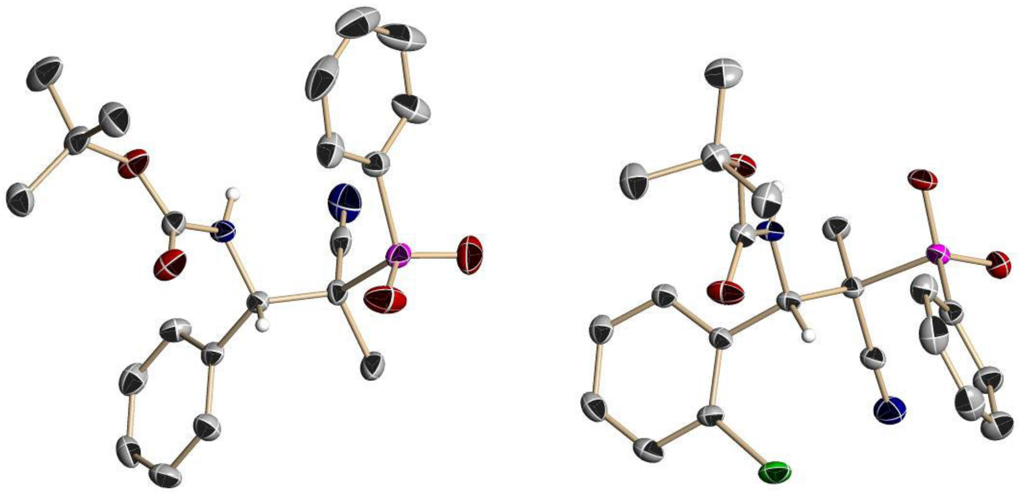
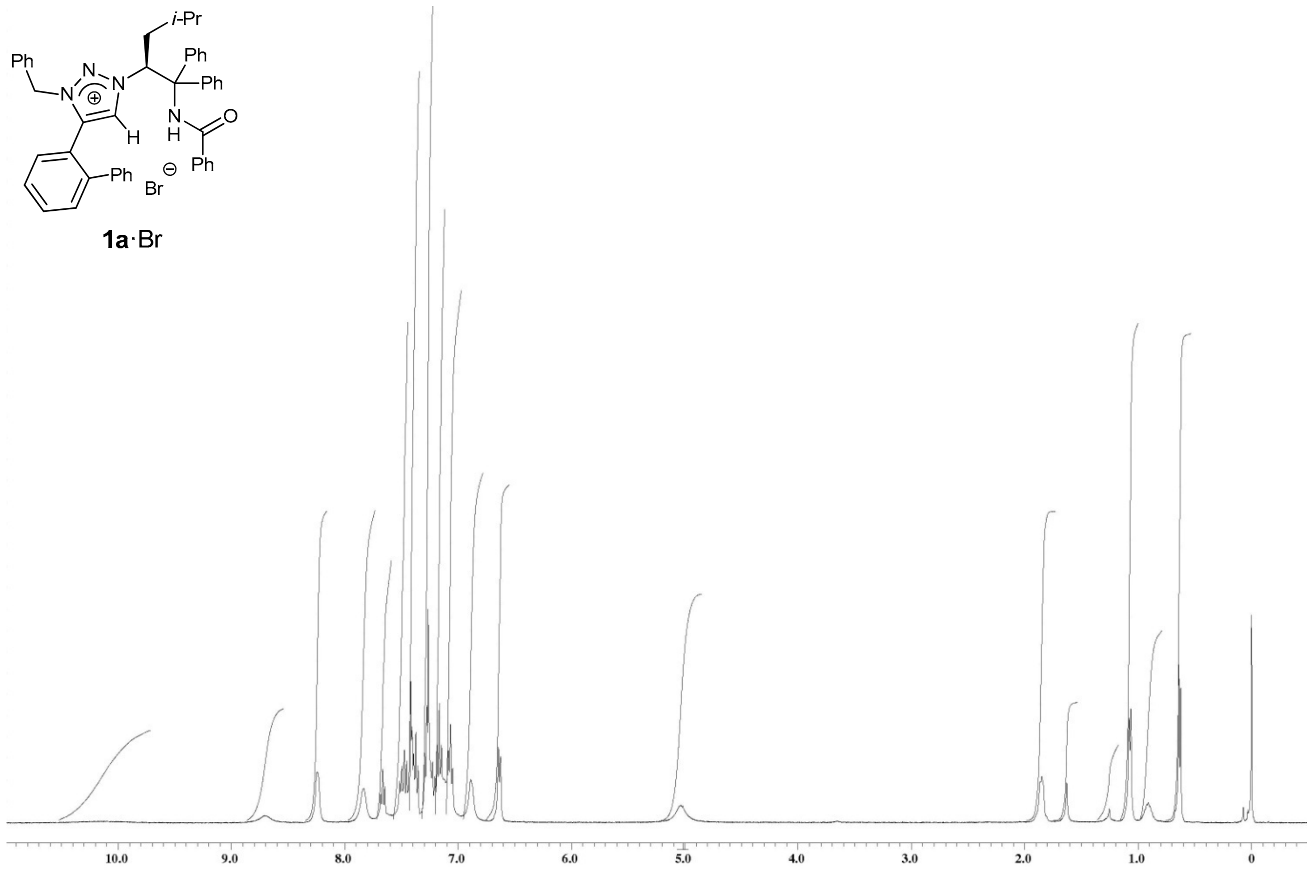
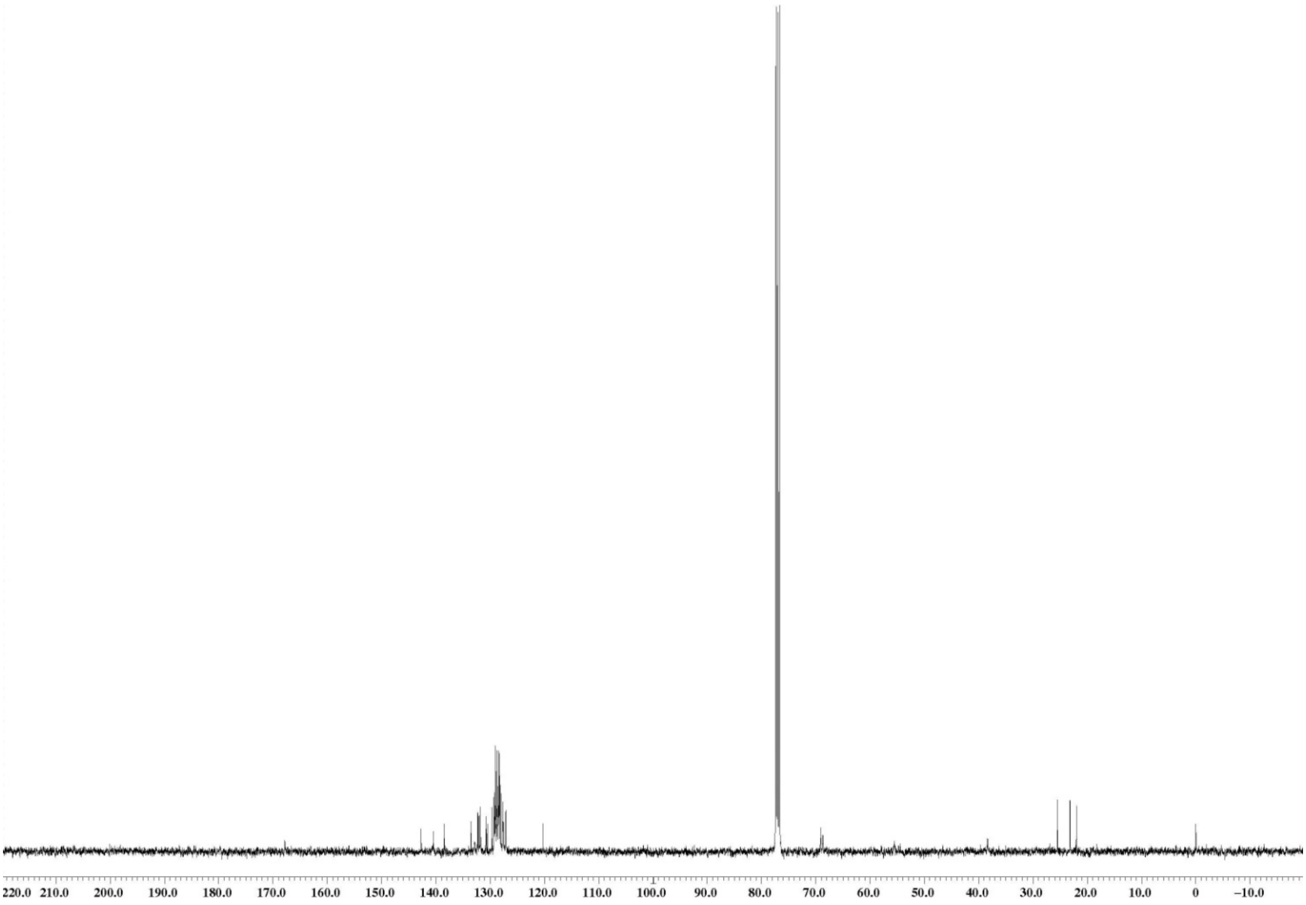


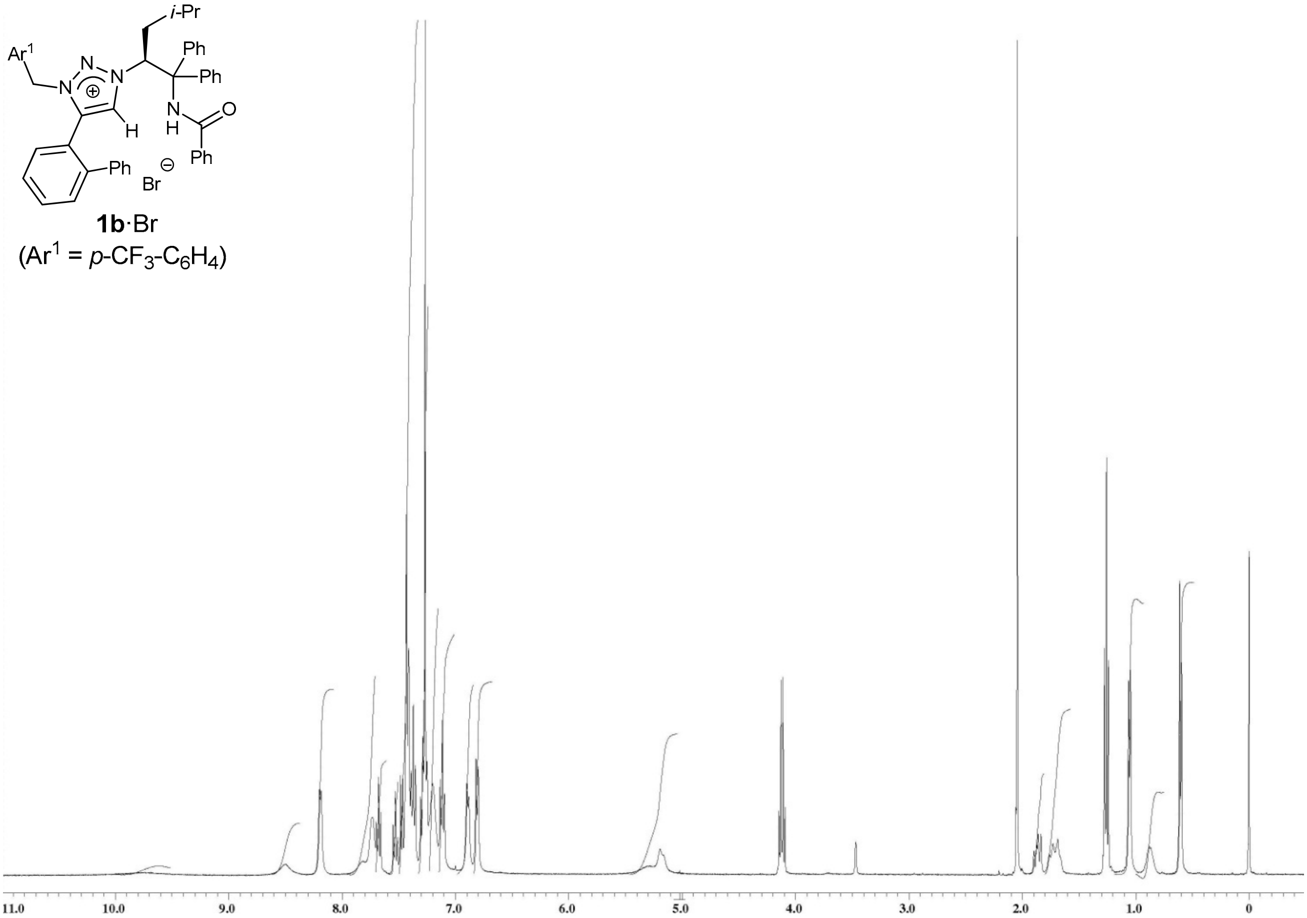
Figure S1. ORTEP diagrams of *anti*-**4a** (left) and *syn*-**4j** (right). Calculated hydrogen atoms and solvent molecules are omitted for clarity. Purple = sulfur, blue = nitrogen, red = oxygen, green = chlorine, and gray = carbon. Only one of the two independent molecules of **4a** is shown. The thermal ellipsoids are at the 50% probability level.

Copies of ^{1}H and ^{13}C NMR Spectra:

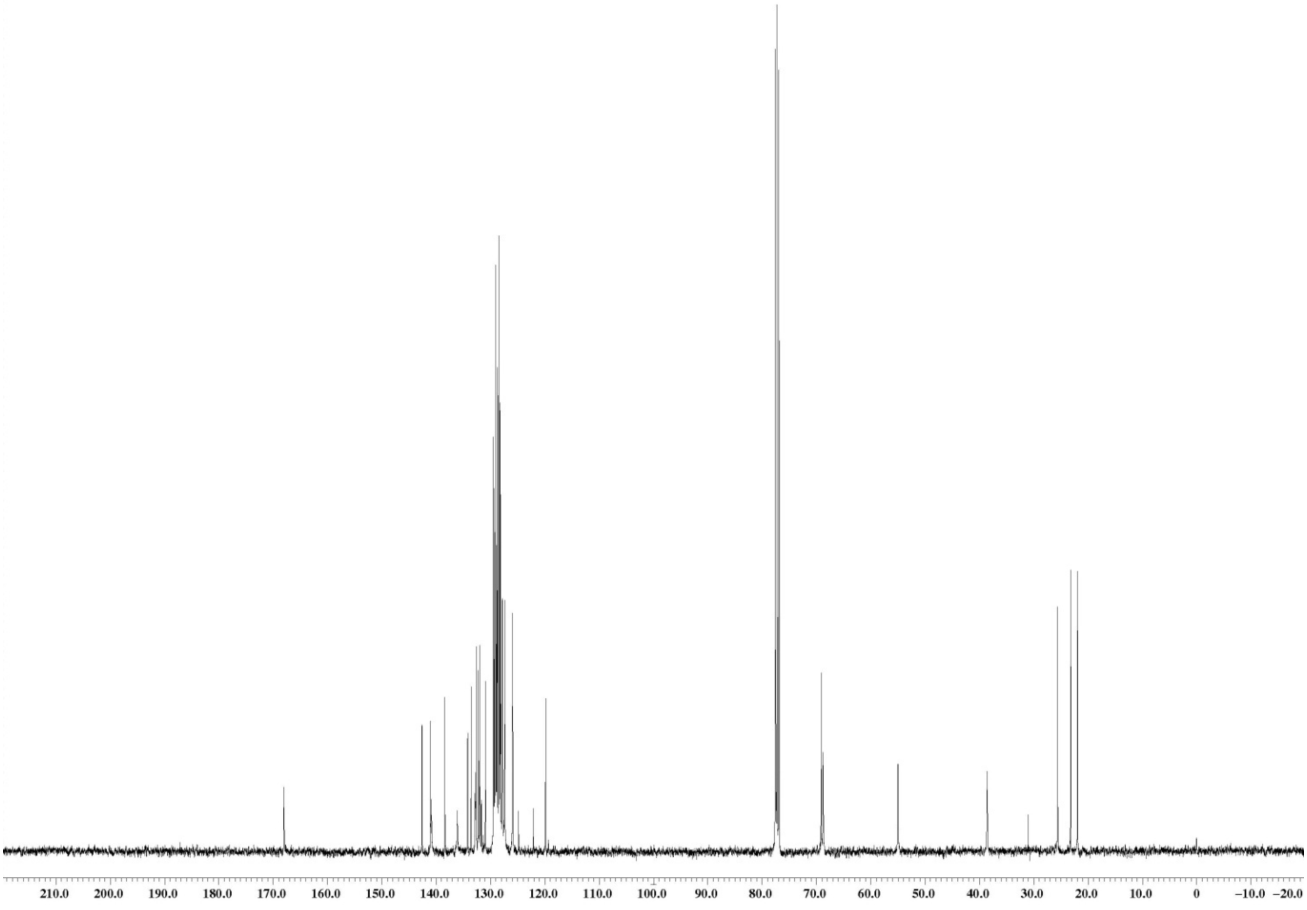


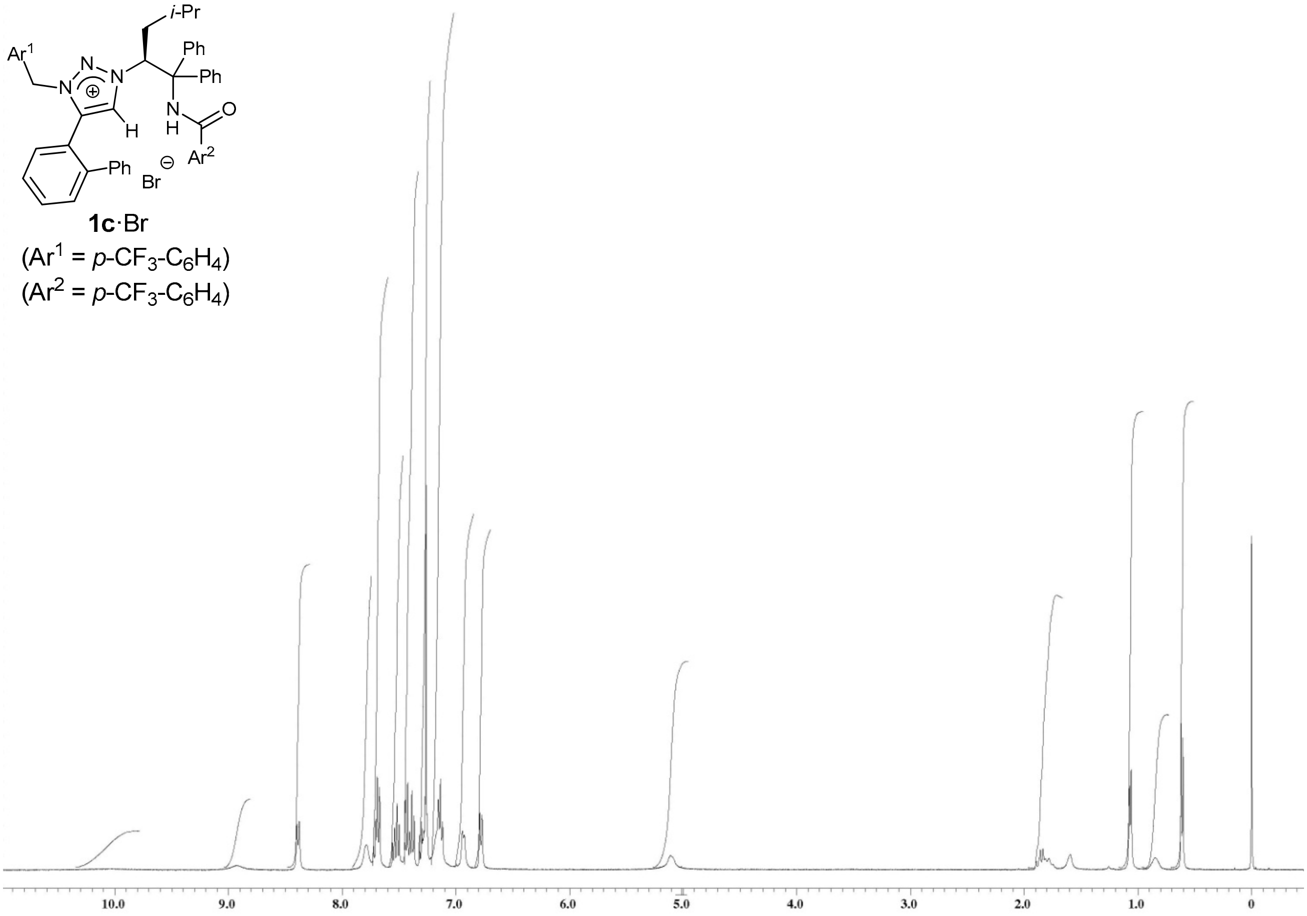
1a·Br



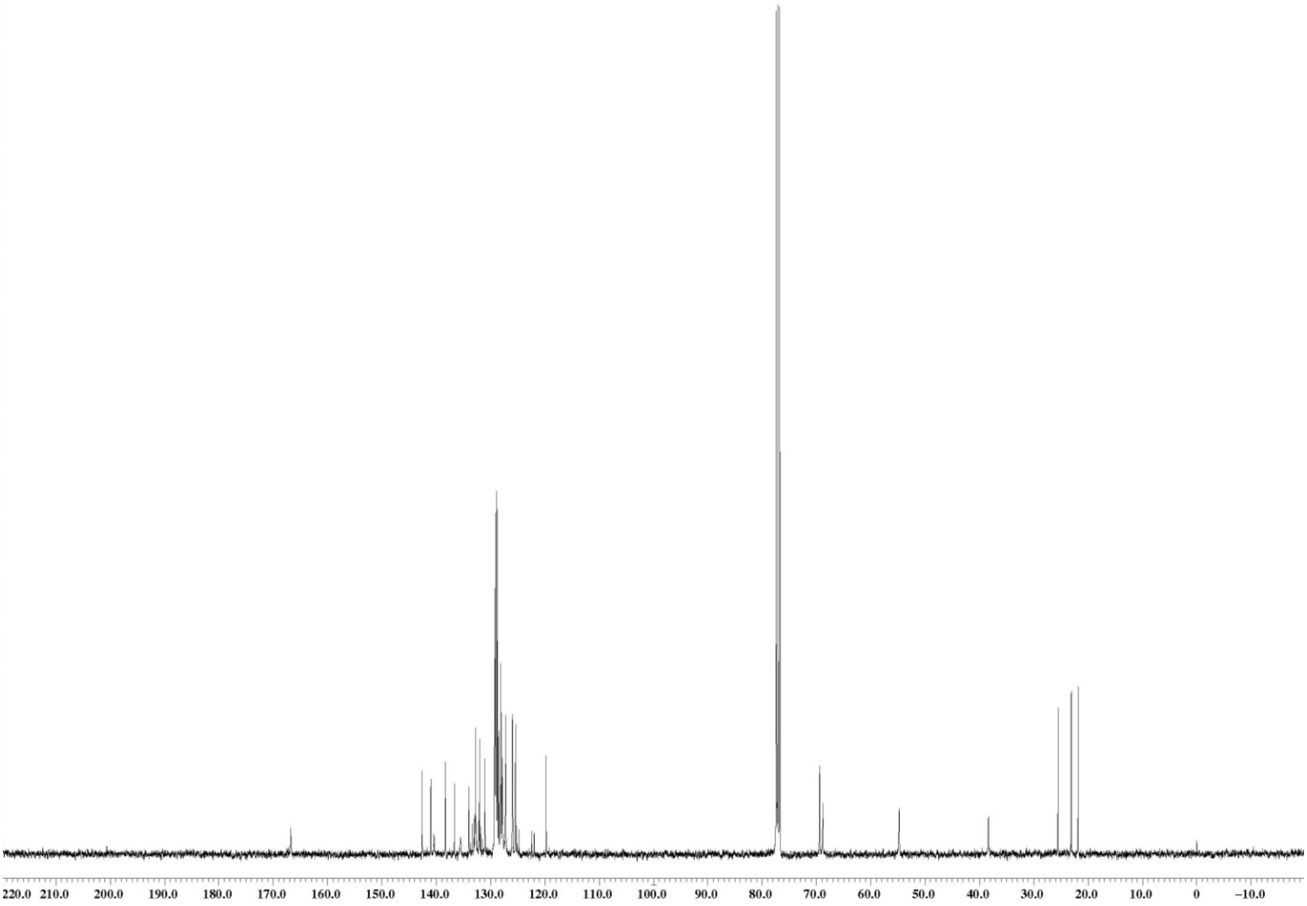


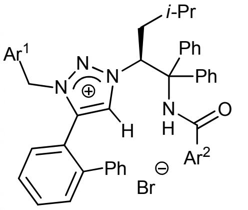
1b·Br
(Ar^1 = *p*-CF_3-C_6H_4)



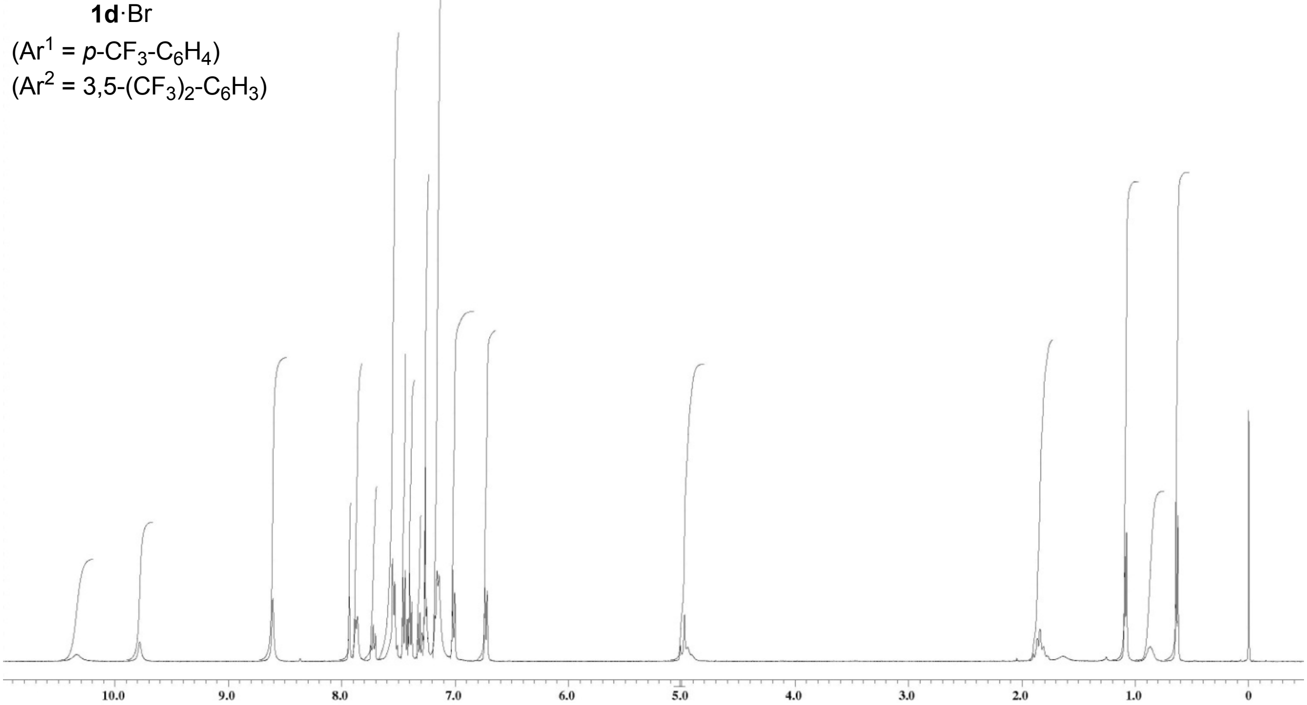


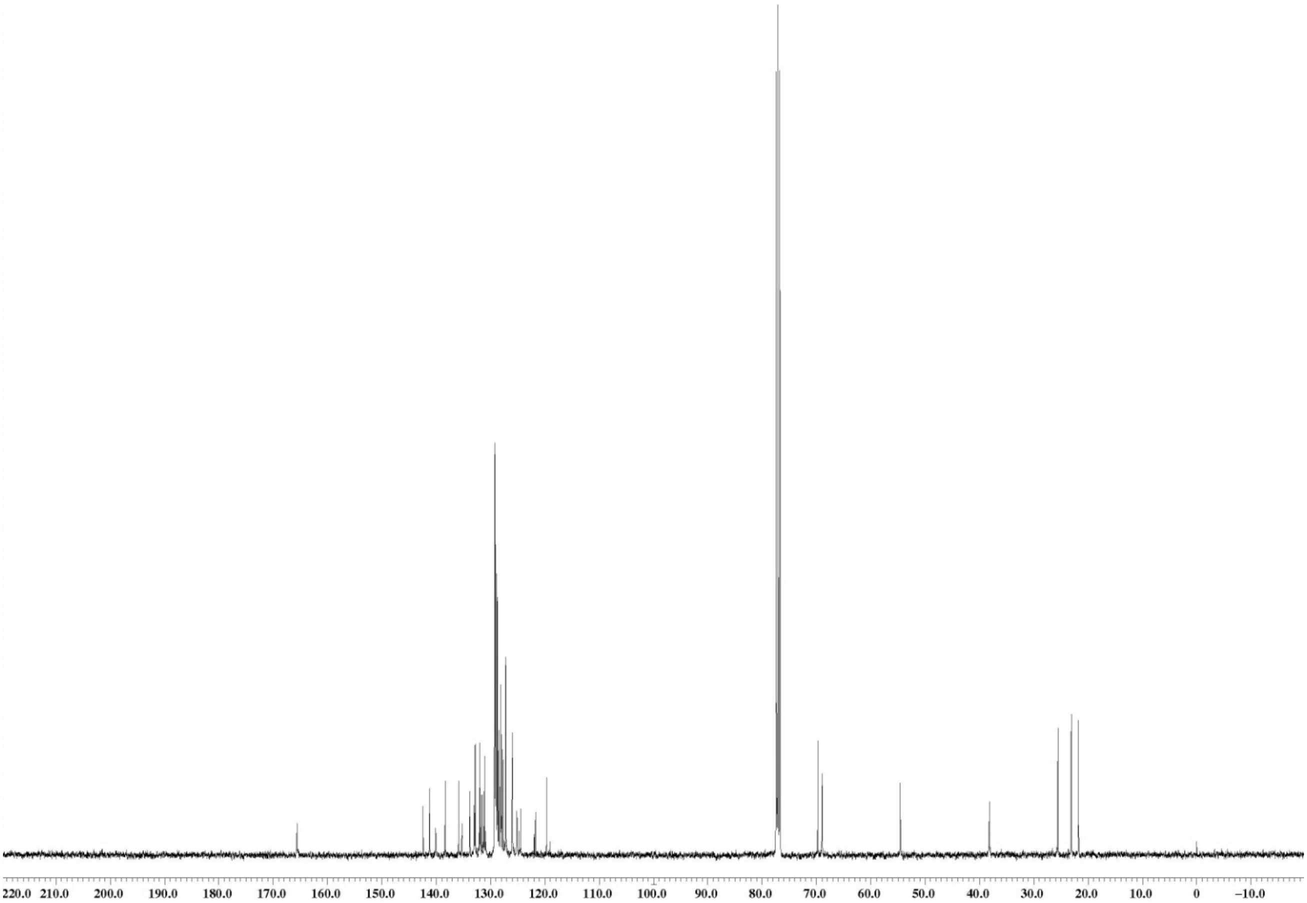
1c·Br
(Ar^1 = p-CF$_3$-C$_6$H$_4$)
(Ar^2 = p-CF$_3$-C$_6$H$_4$)

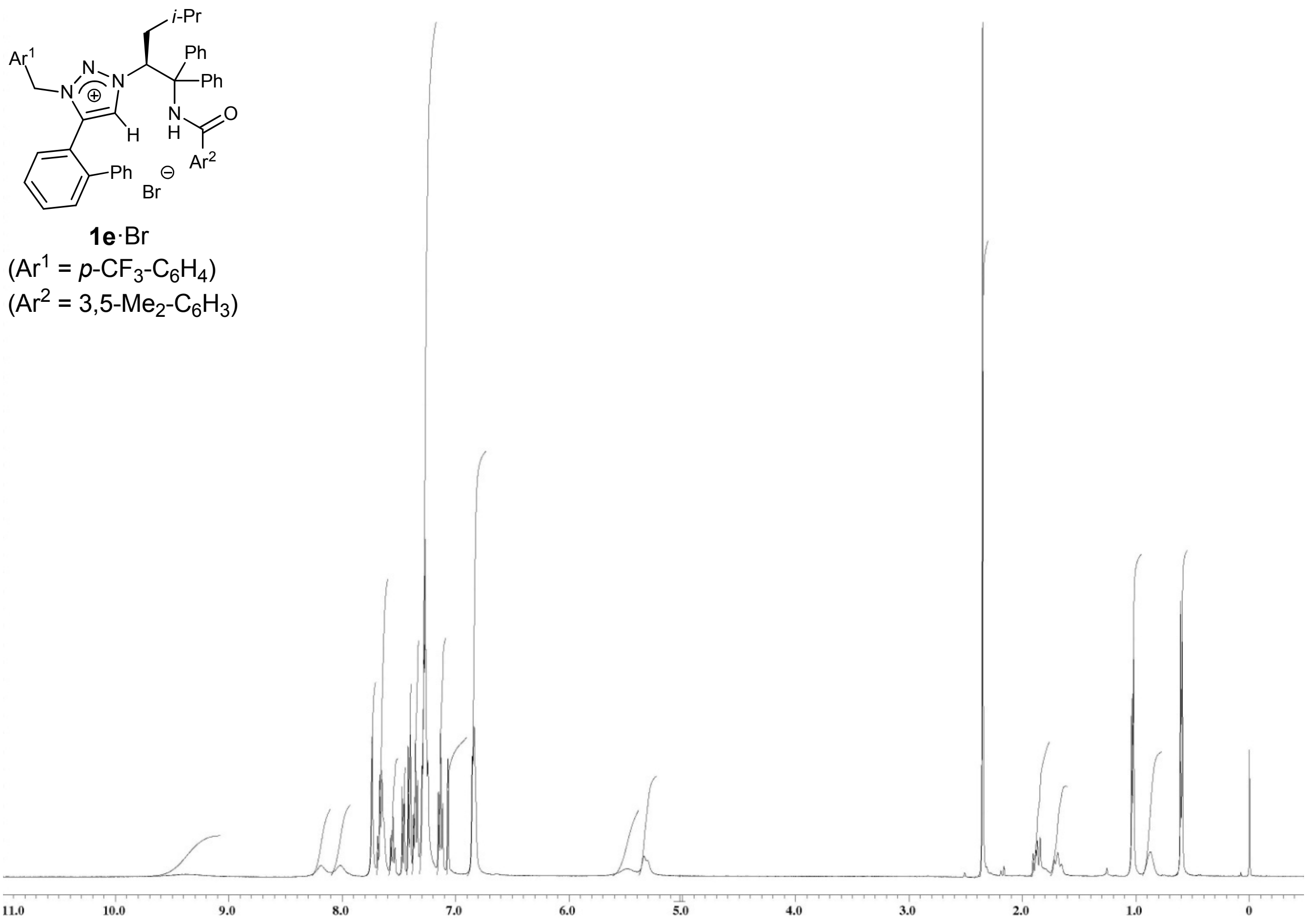




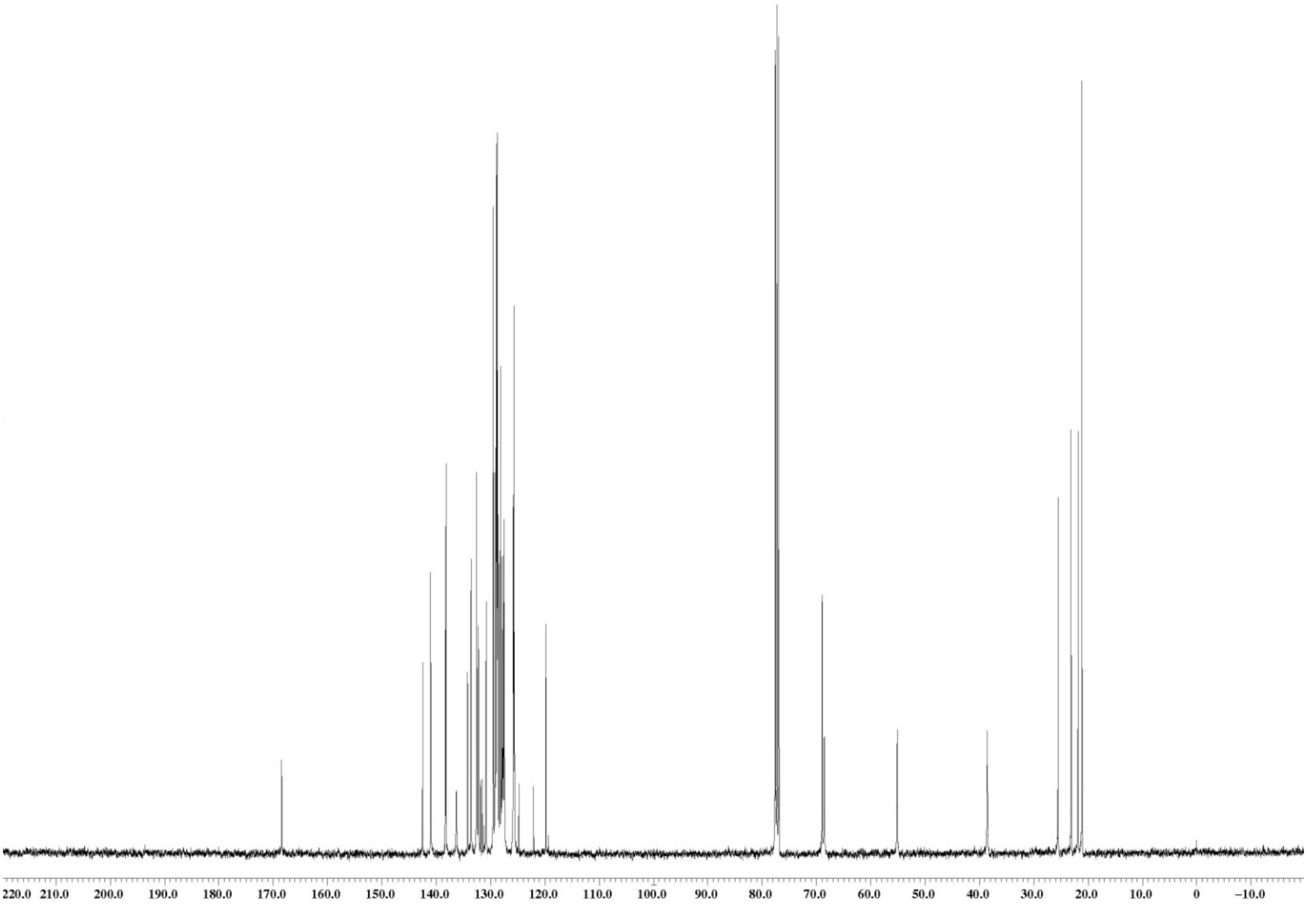
1d·Br
(Ar^1 = p-CF_3-C_6H_4)
(Ar^2 = 3,5-$(CF_3)_2$-C_6H_3)

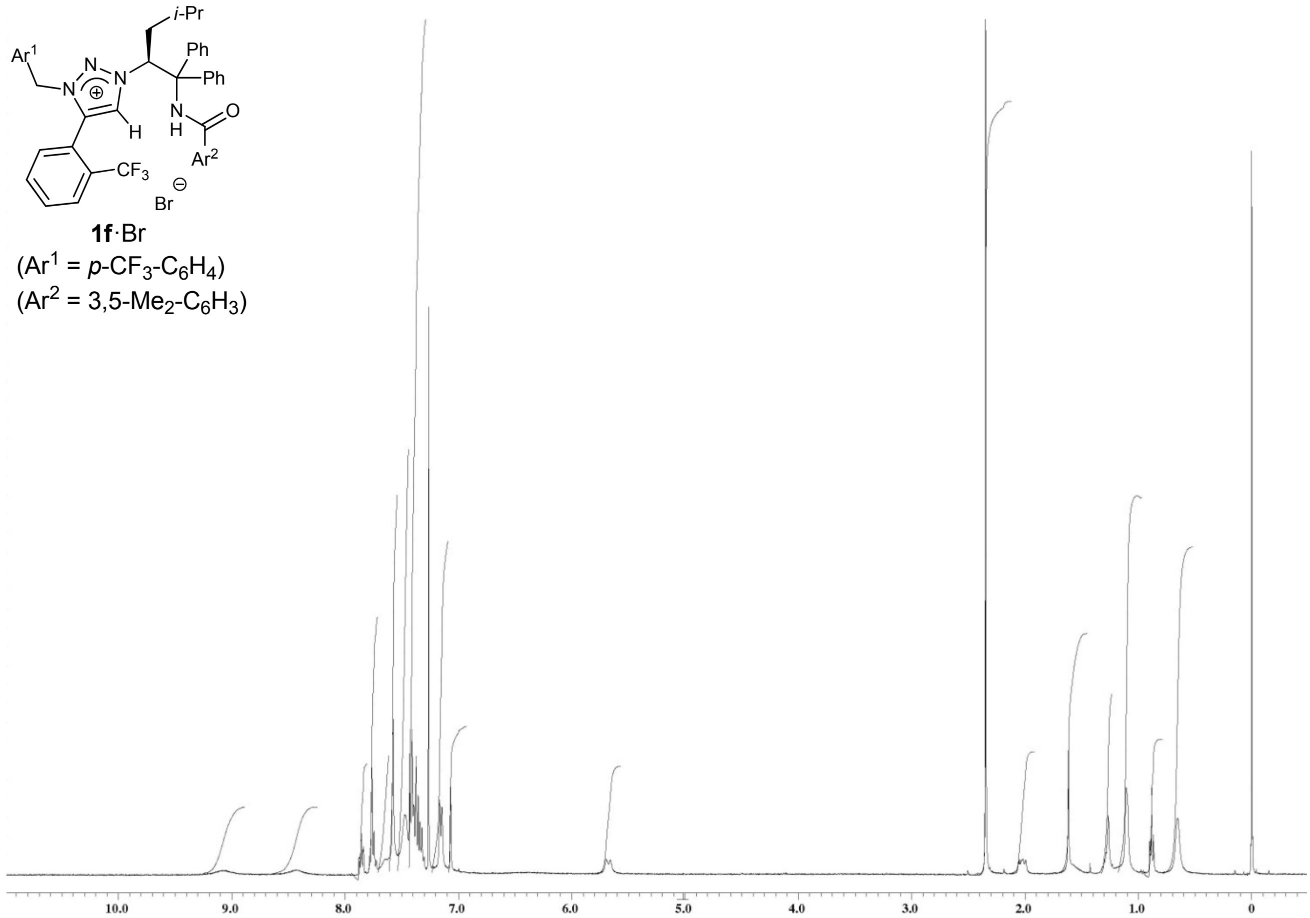




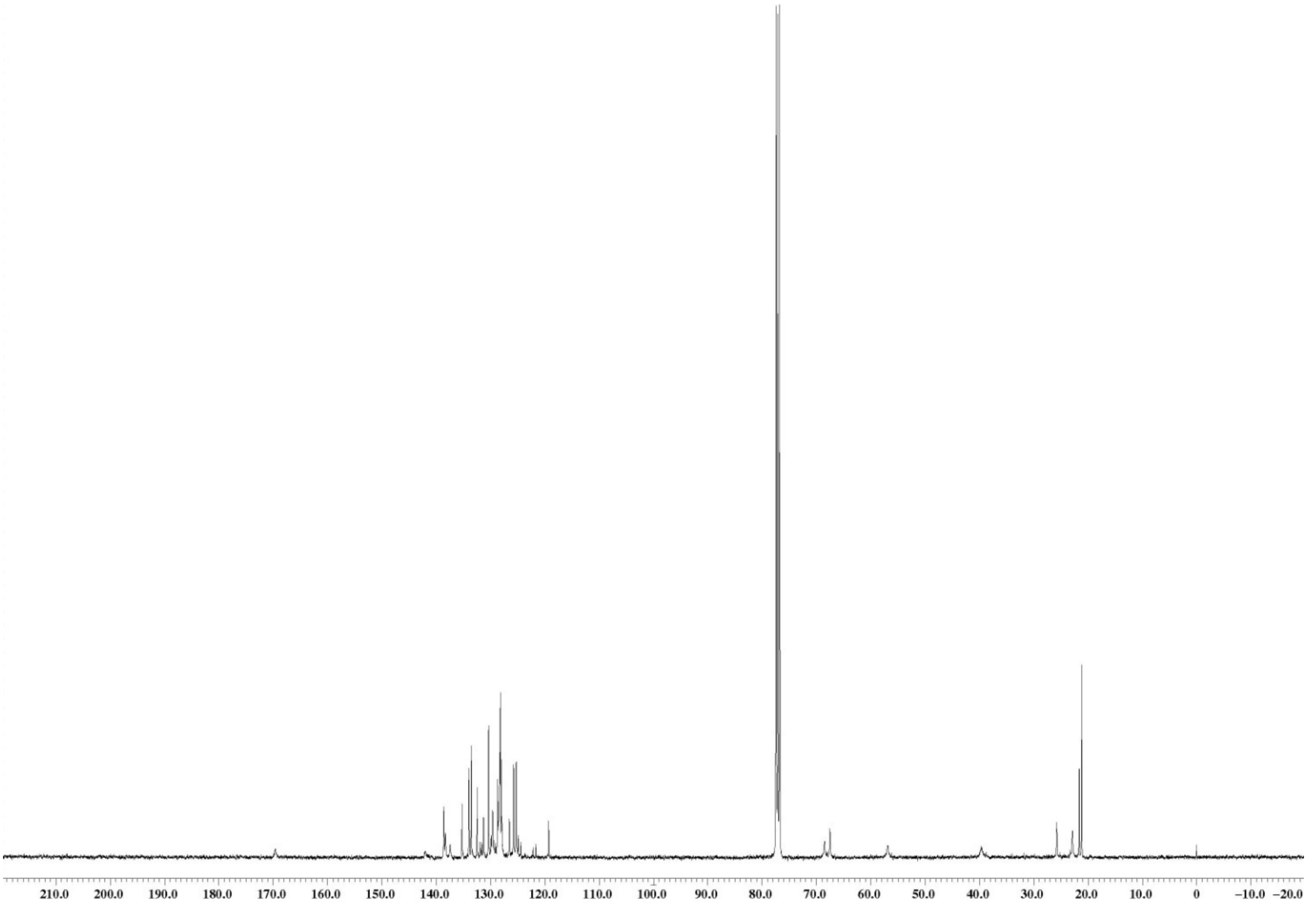


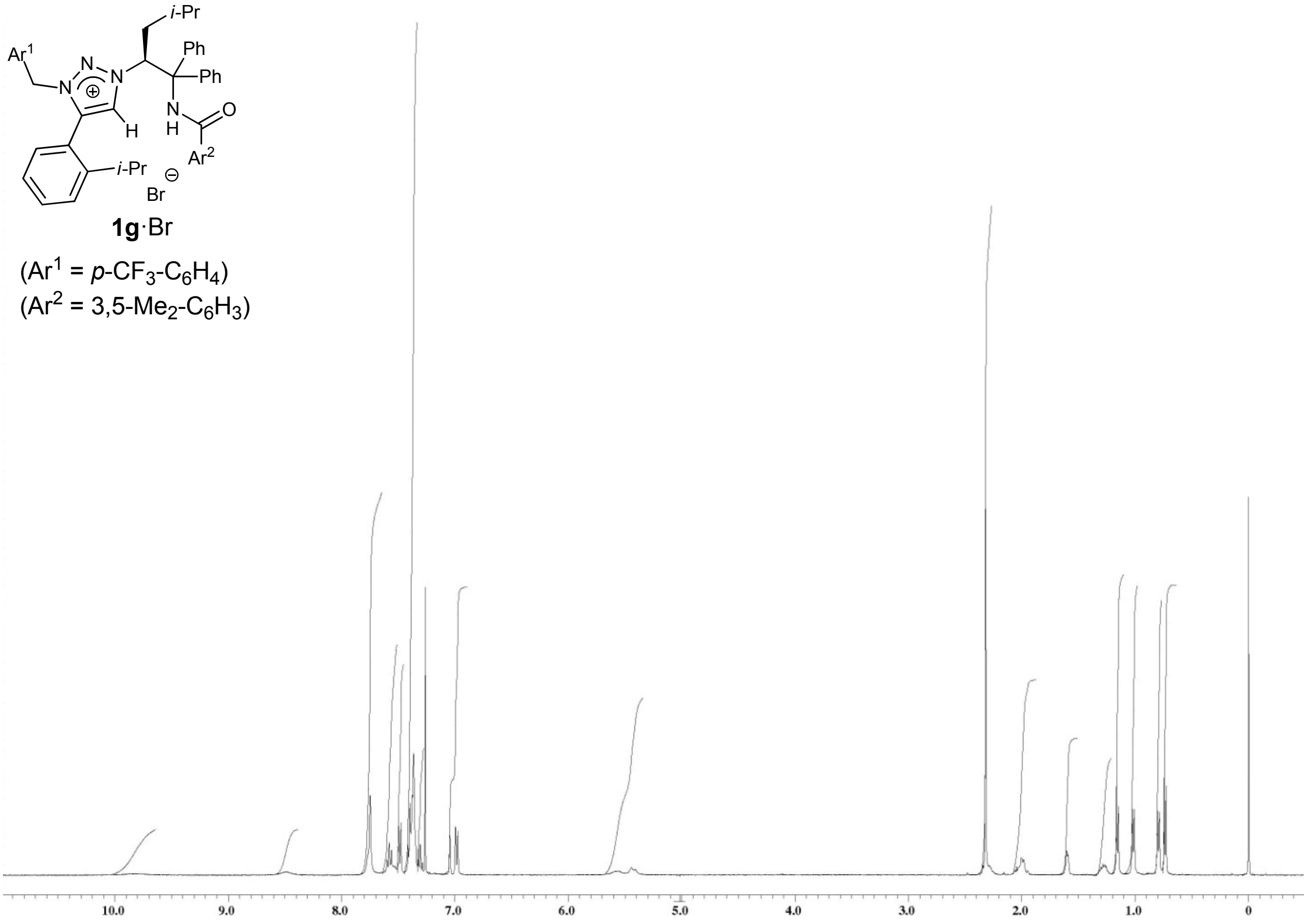
1e·Br
(Ar^1 = *p*-CF_3-C_6H_4)
(Ar^2 = 3,5-Me_2-C_6H_3)





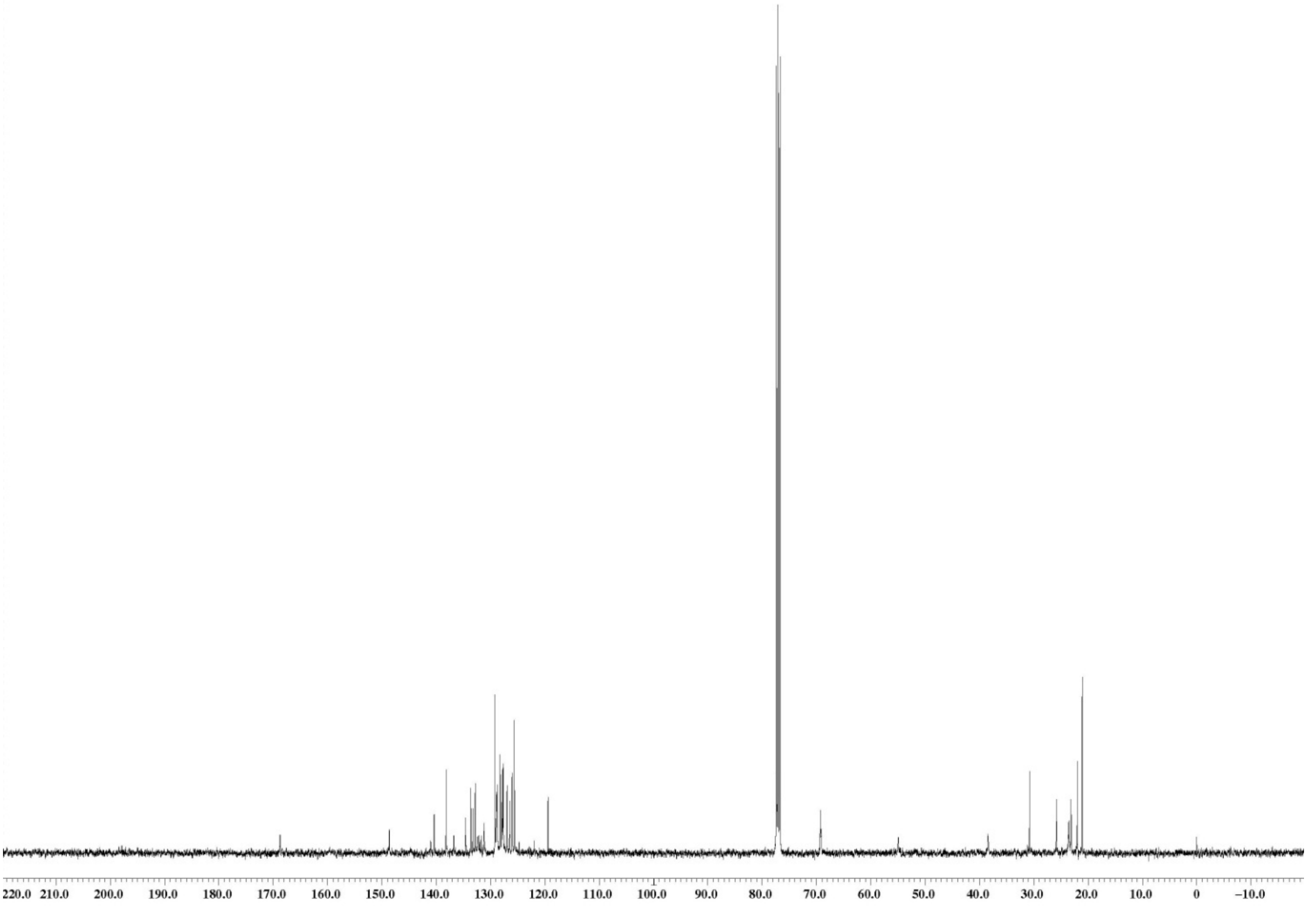
1f·Br
(Ar^1 = *p*-CF_3-C_6H_4)
(Ar^2 = 3,5-Me_2-C_6H_3)

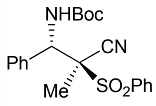




1g·Br

(Ar^1 = *p*-CF$_3$-C$_6$H$_4$)
(Ar^2 = 3,5-Me$_2$-C$_6$H$_3$)

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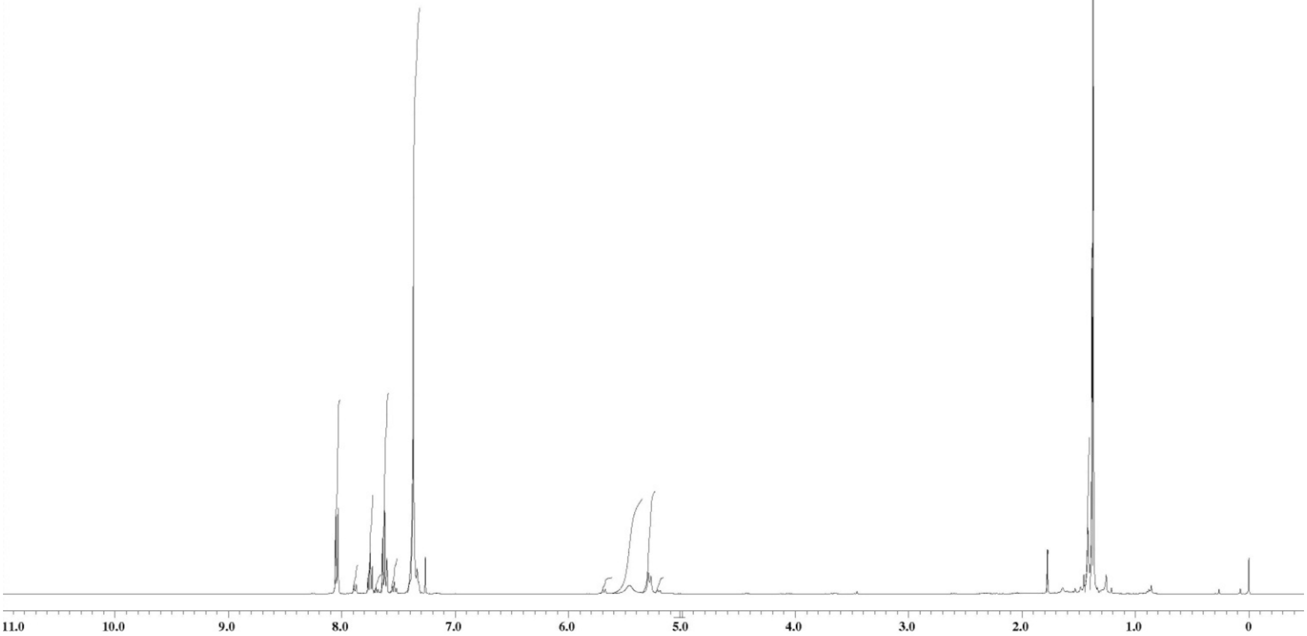
Ph
Me
SO2Ph

4a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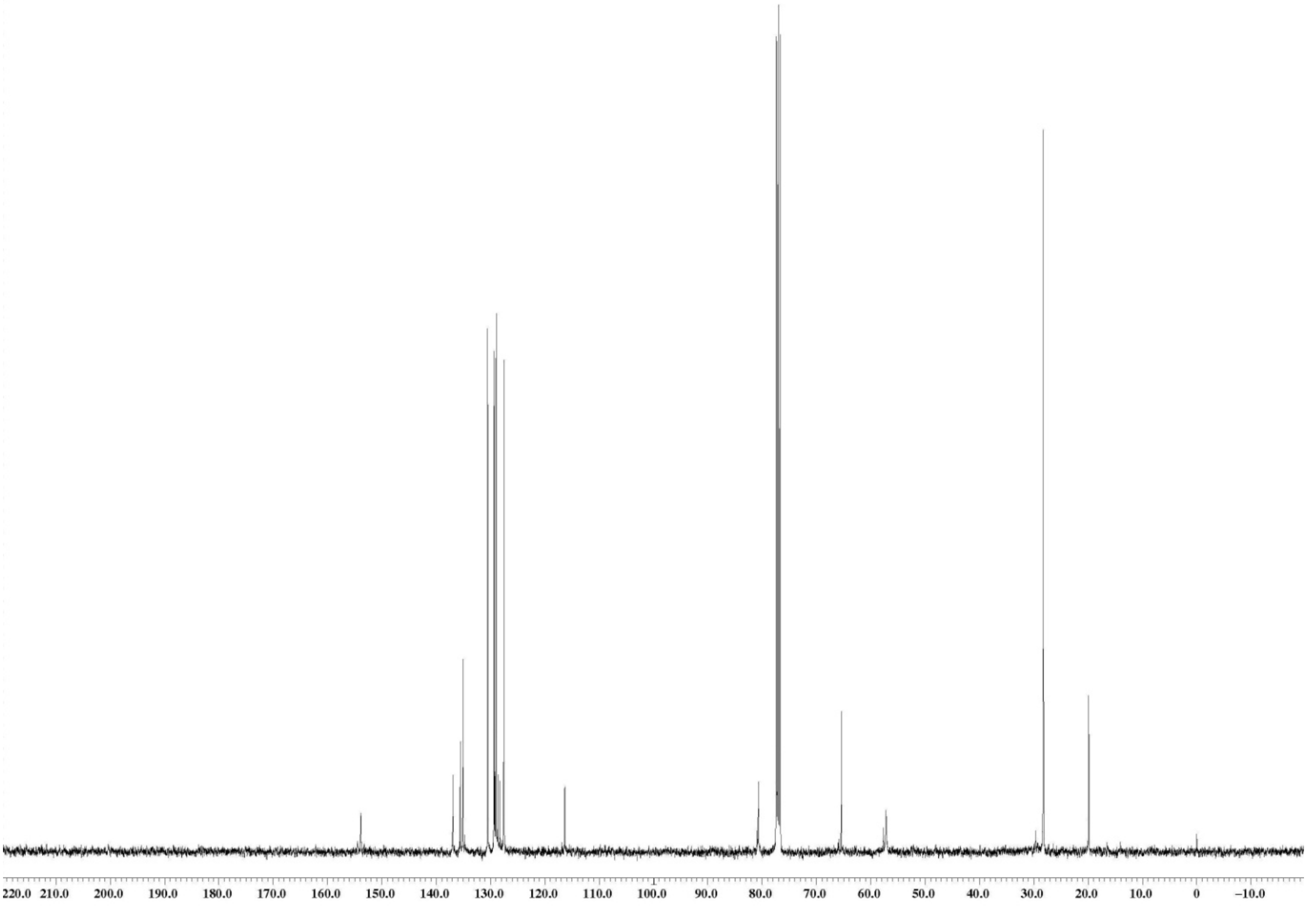
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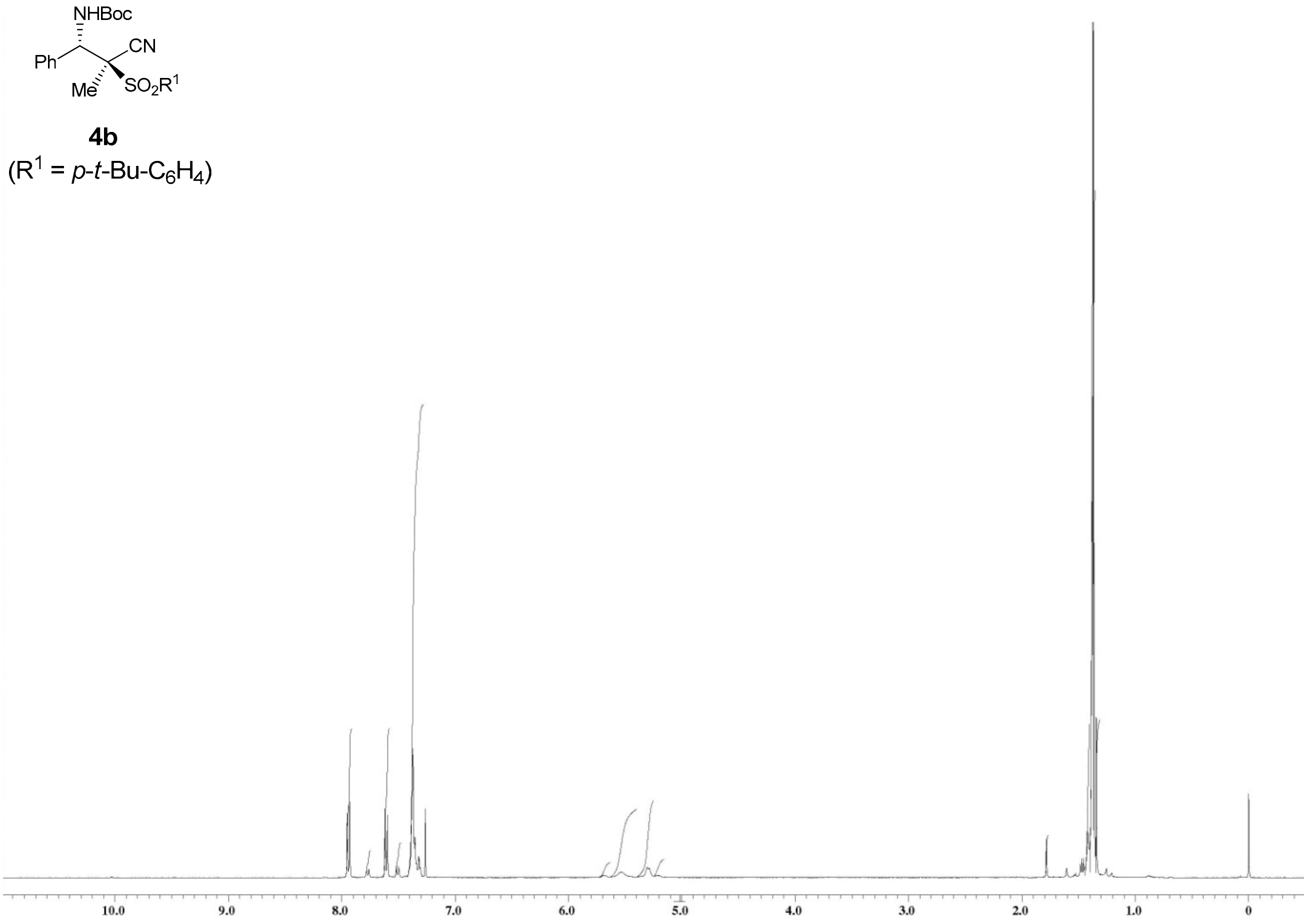
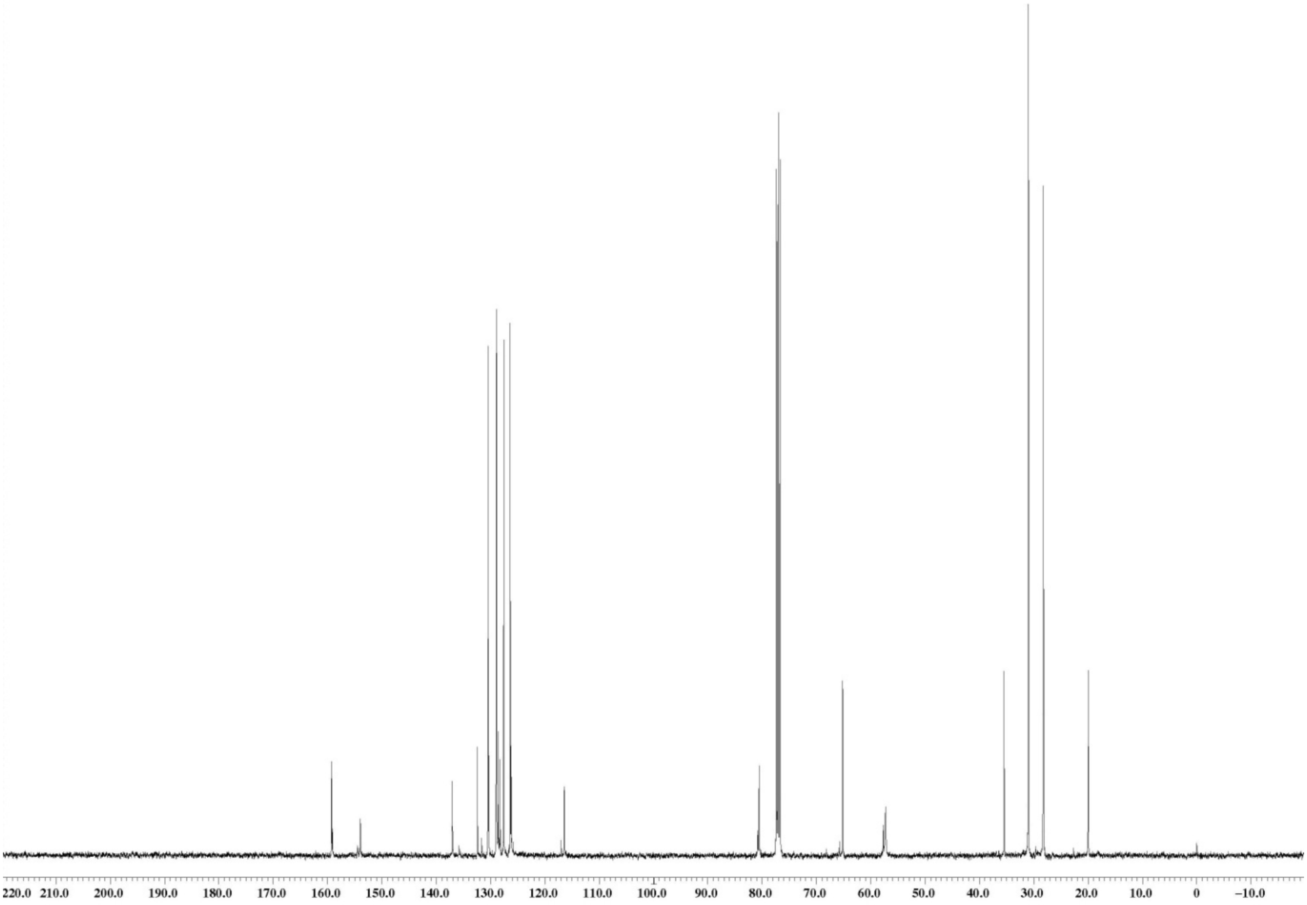
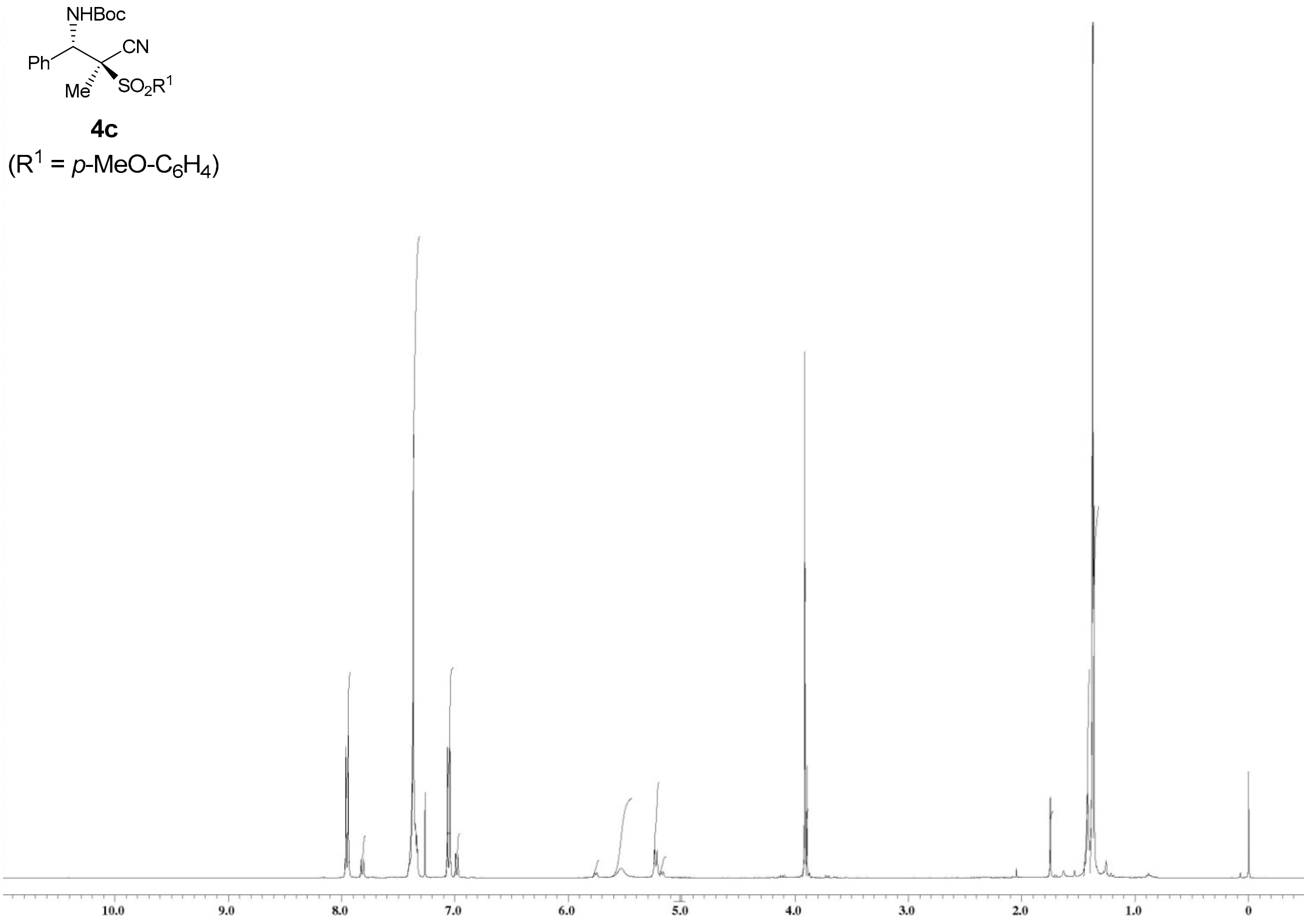


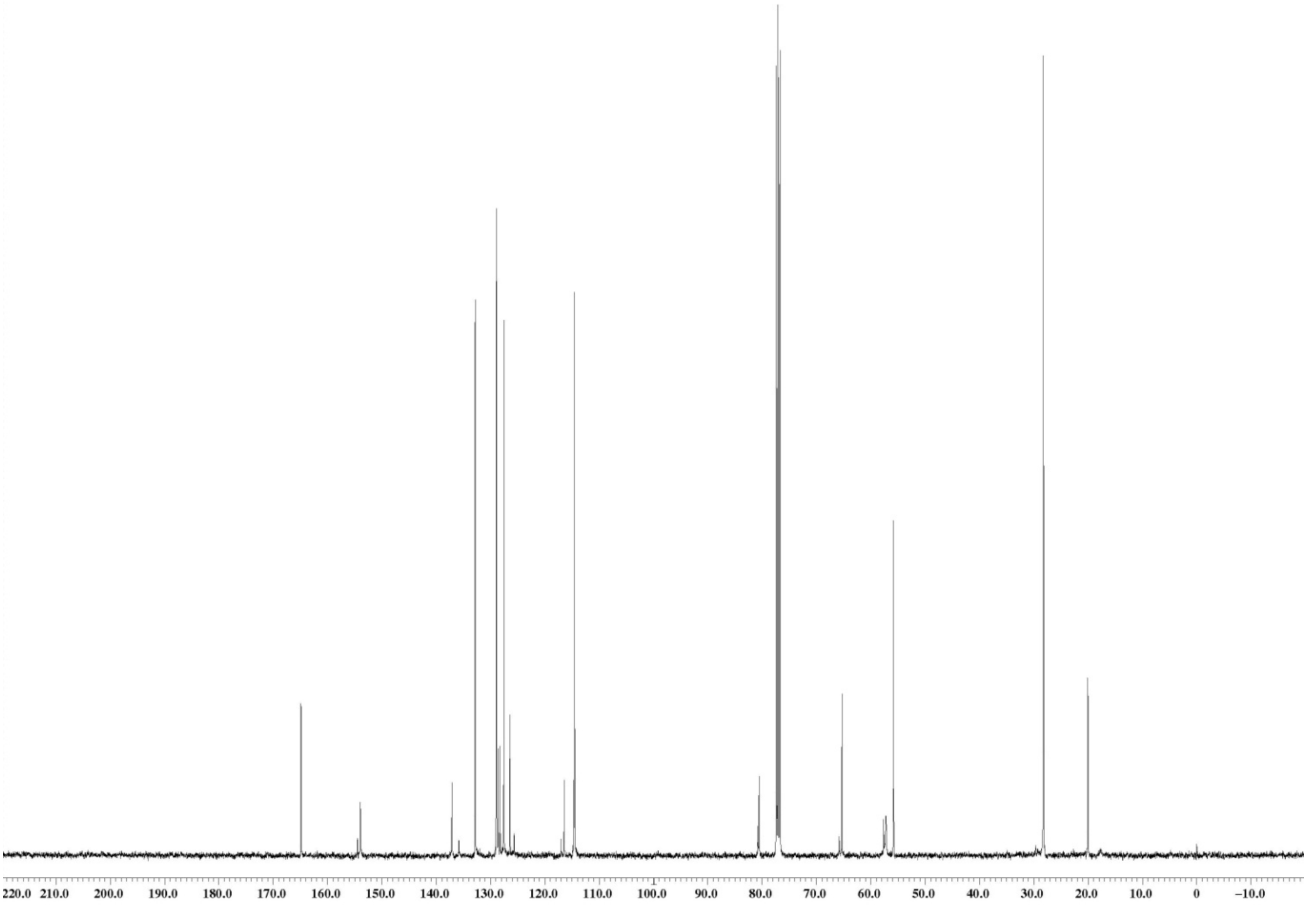
4b
(R^1 = *p*-*t*-Bu-C_6H_4)

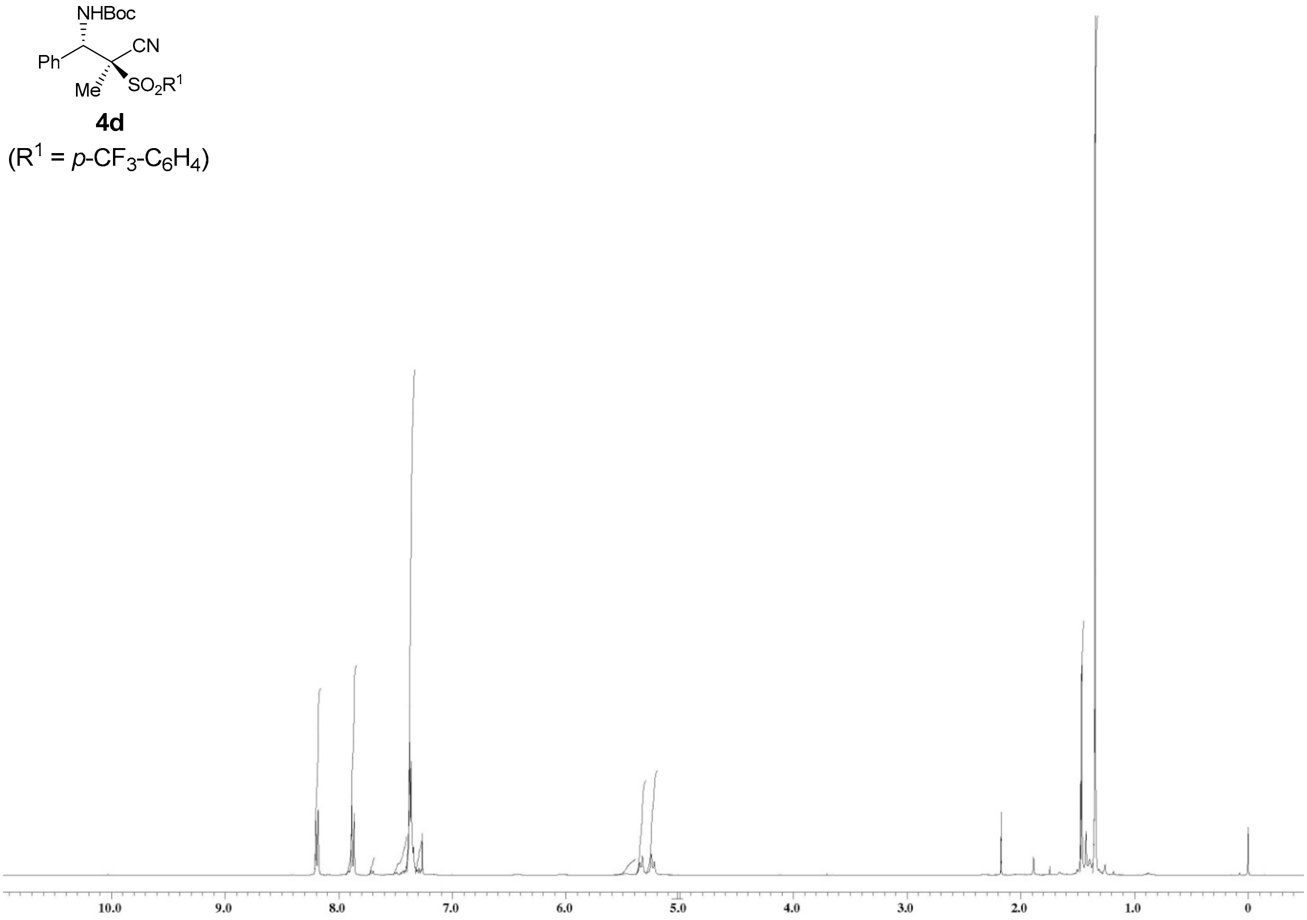




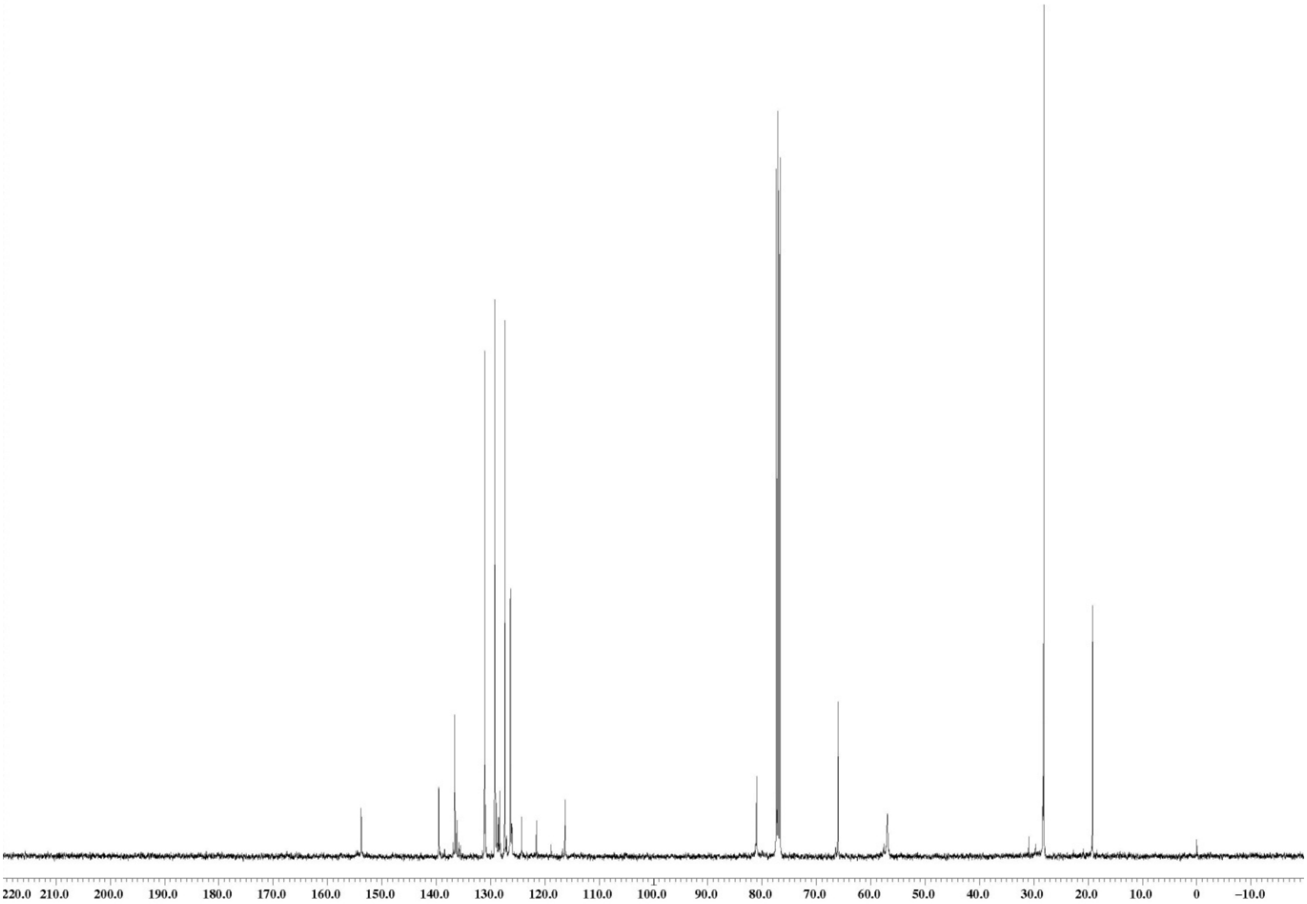
4c

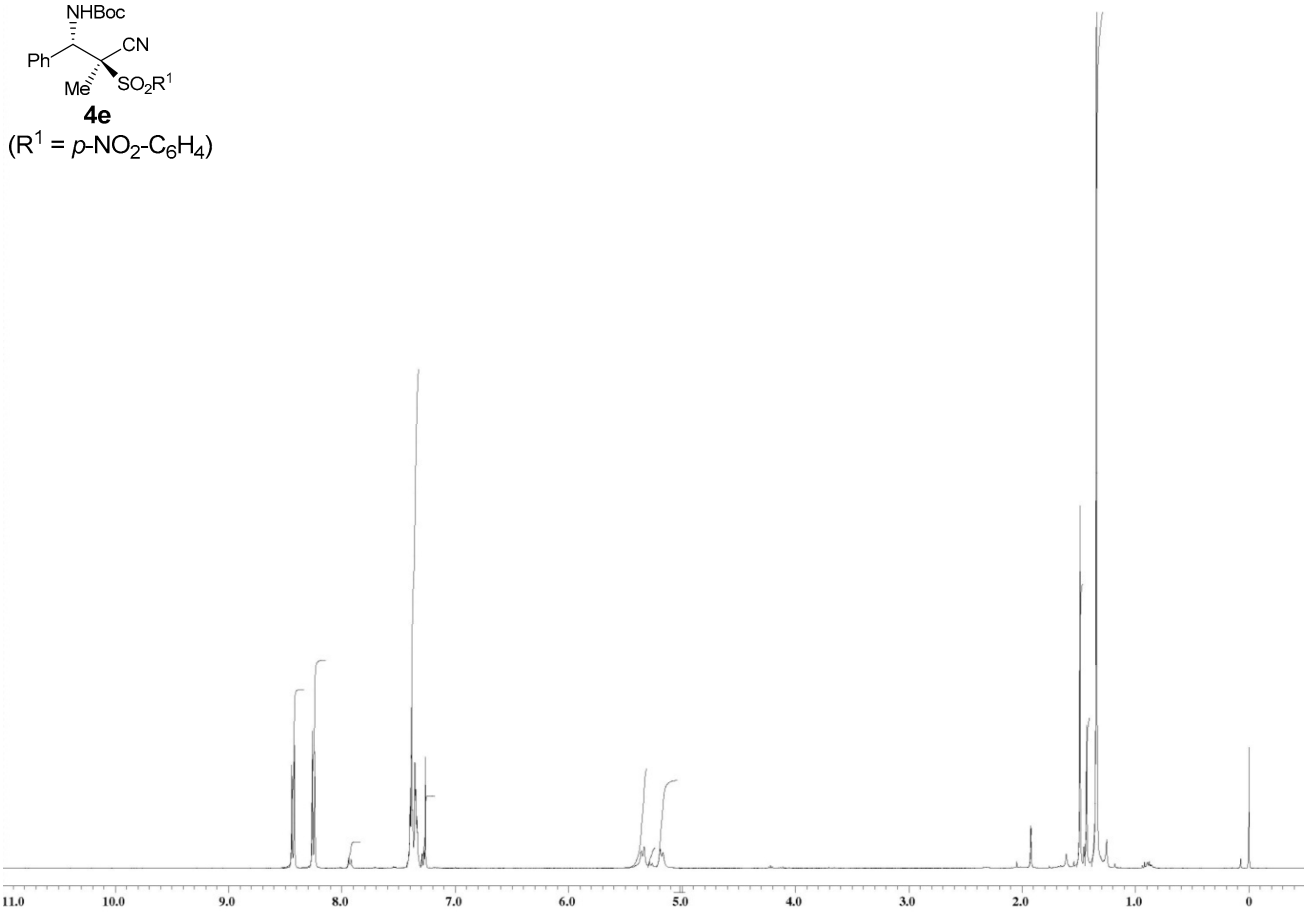
(R^1 = *p*-MeO-C_6H_4)





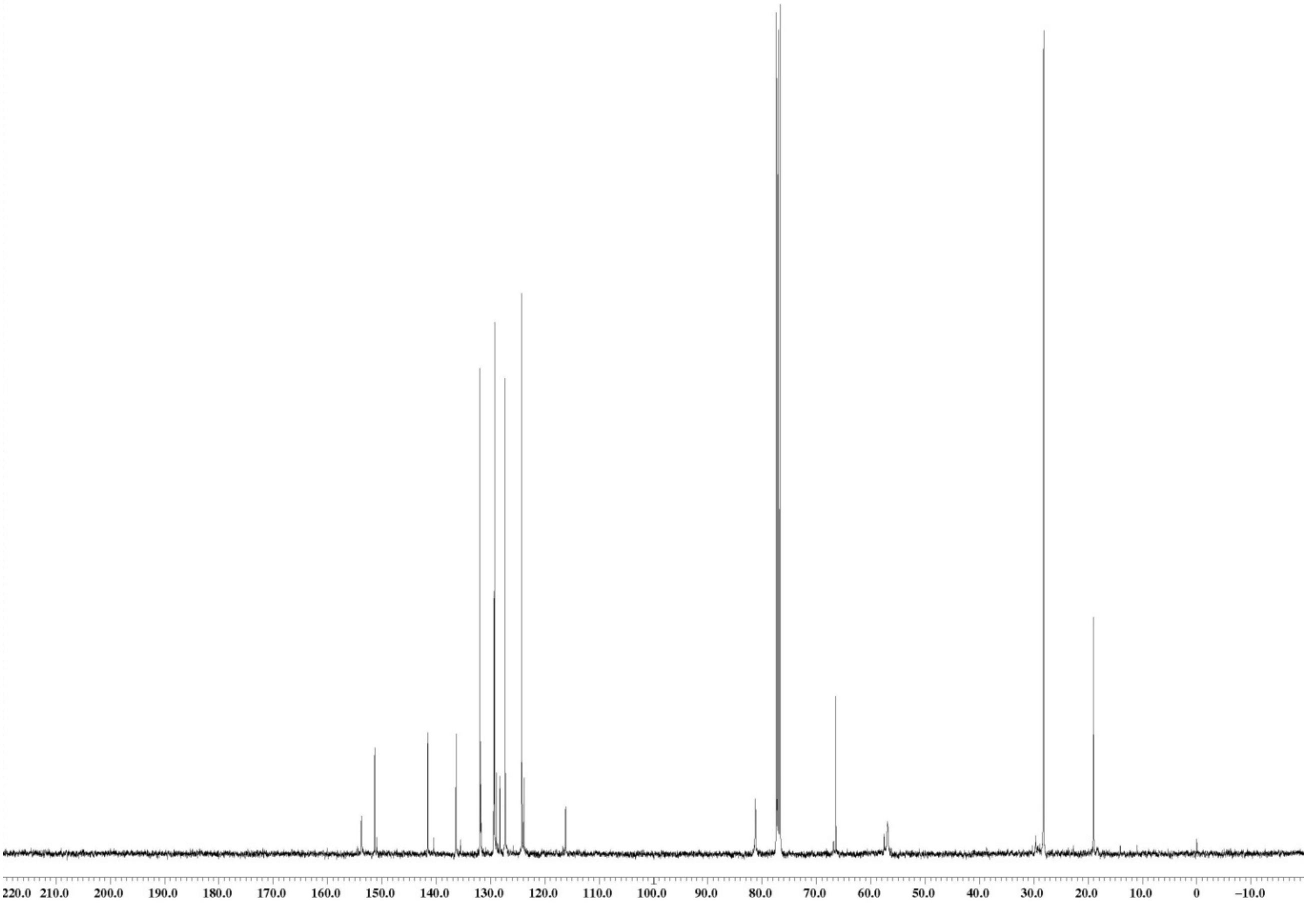
4d
(R^1 = *p*-CF_3-C_6H_4)

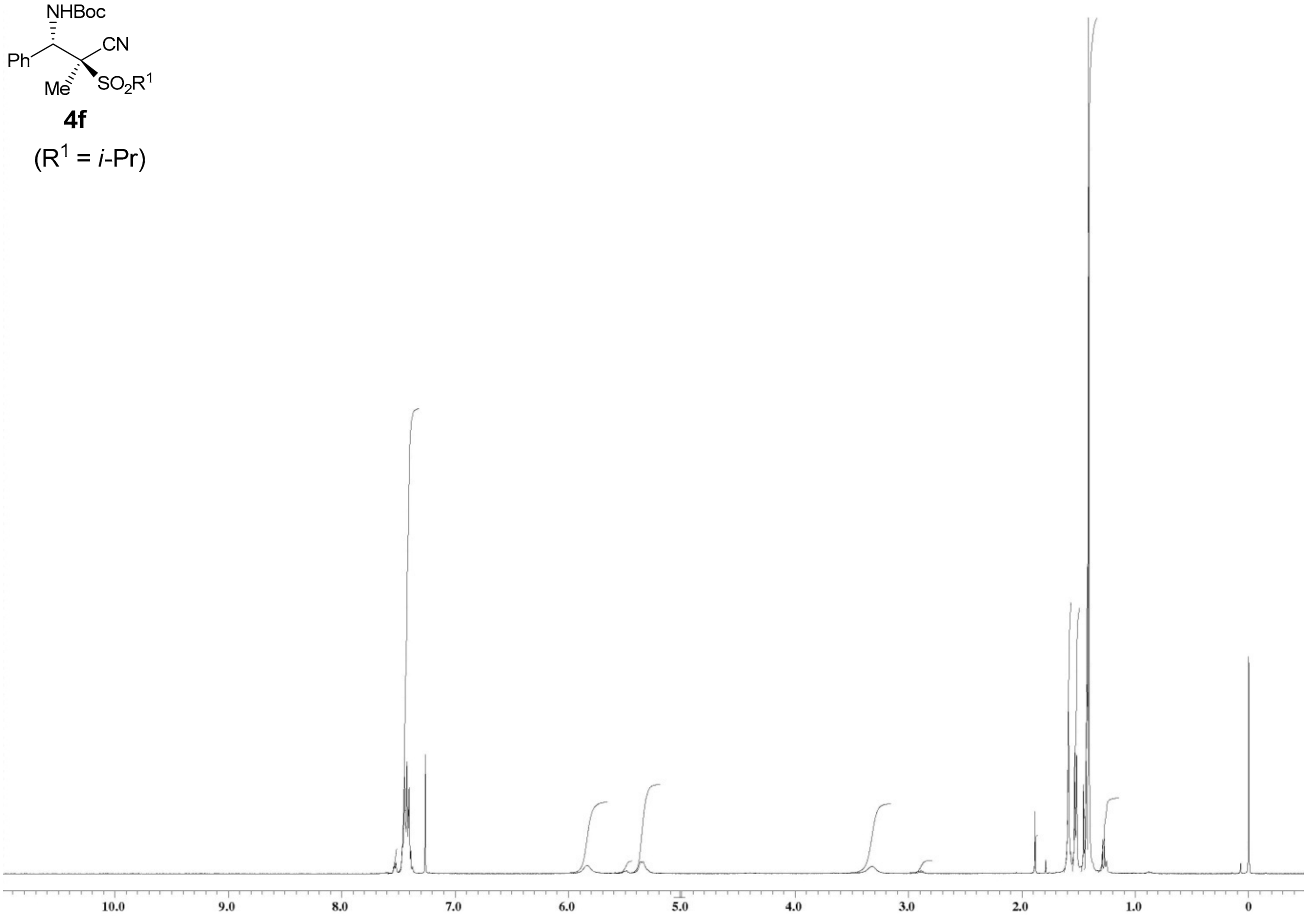




4e

(R^1 = *p*-NO_2-C_6H_4)

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CN
Ph
Me
SO2R1
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7.0
6.0
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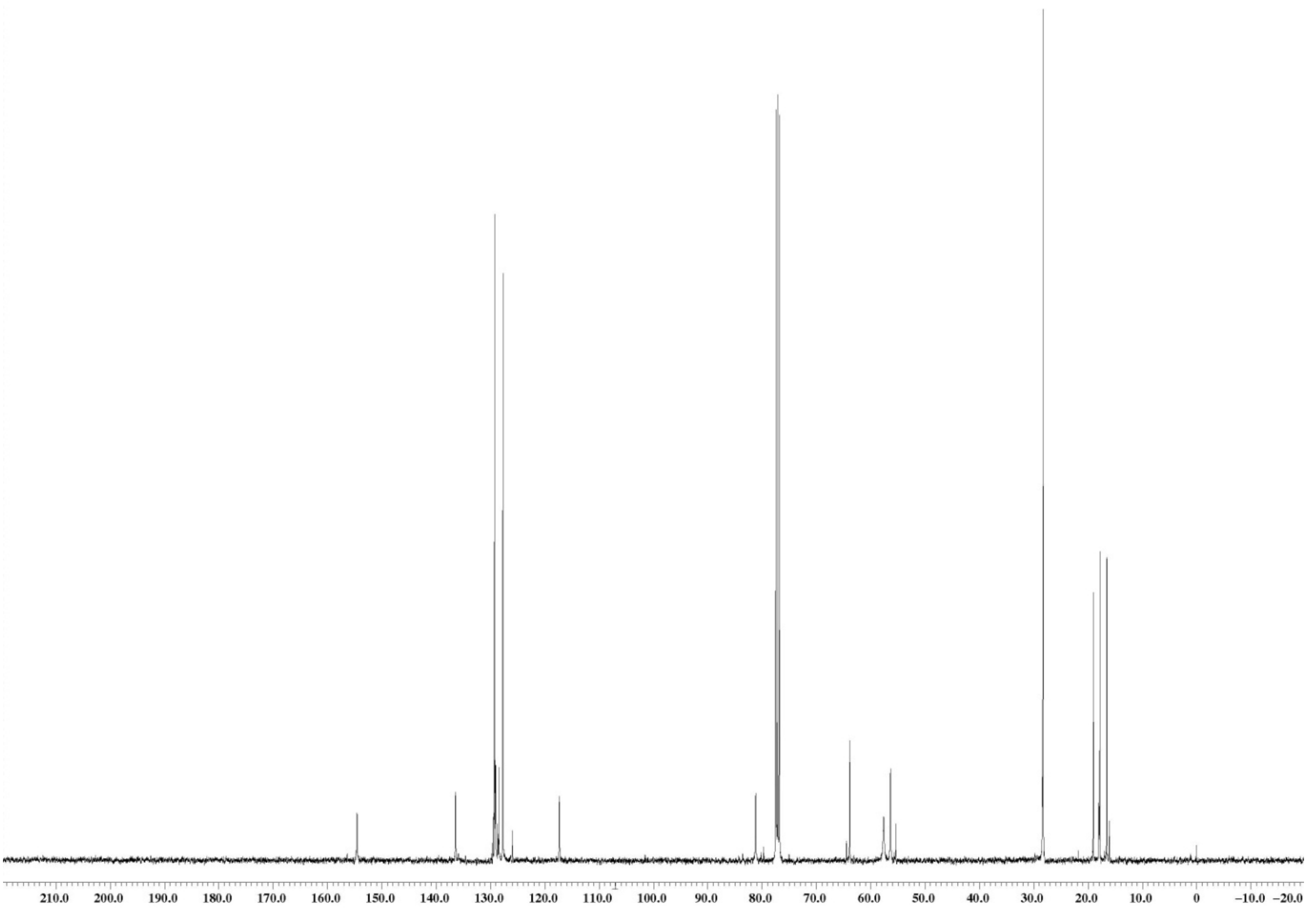
2.0
1.0
0

4f

(R^1 = *i*-Pr)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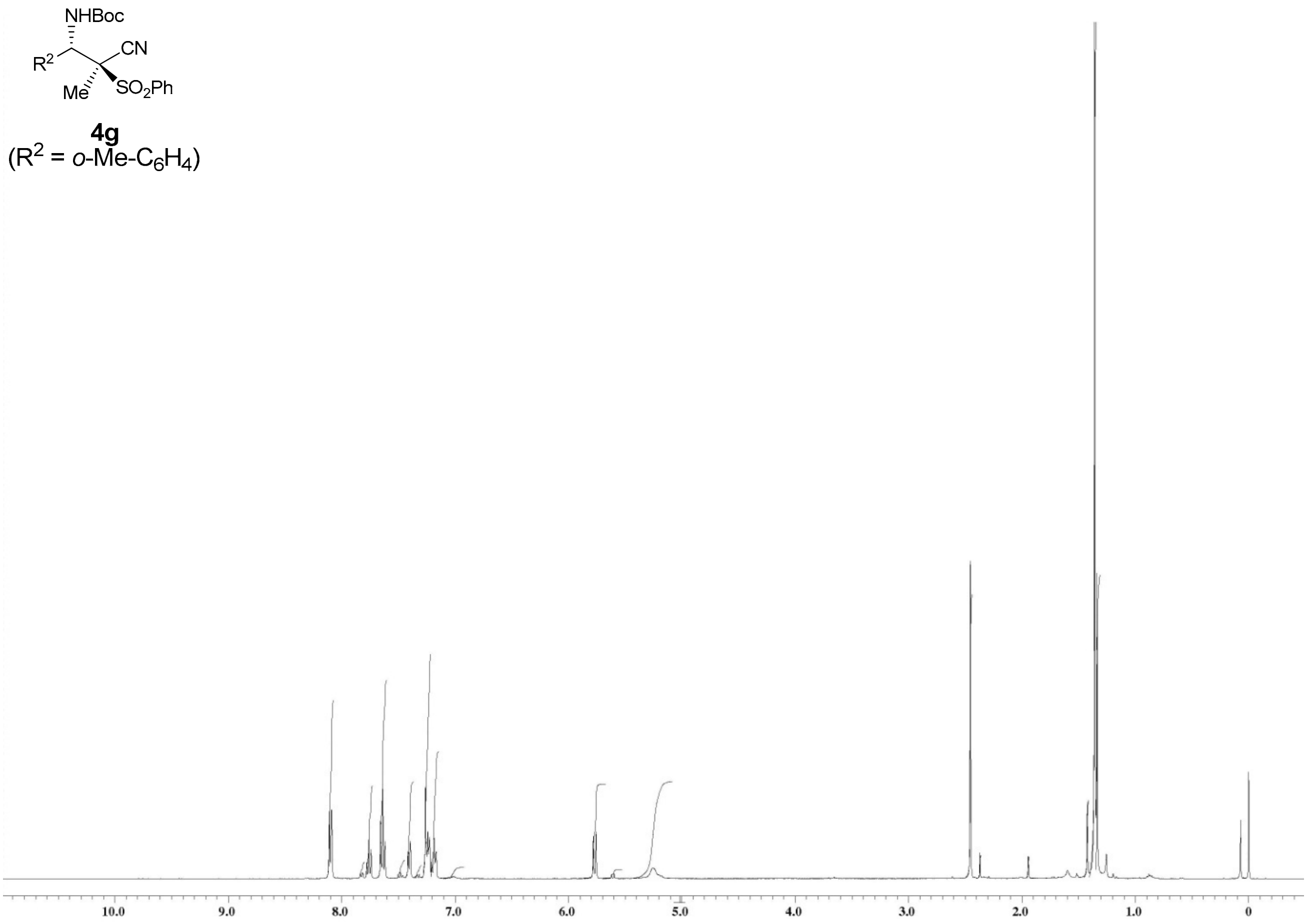
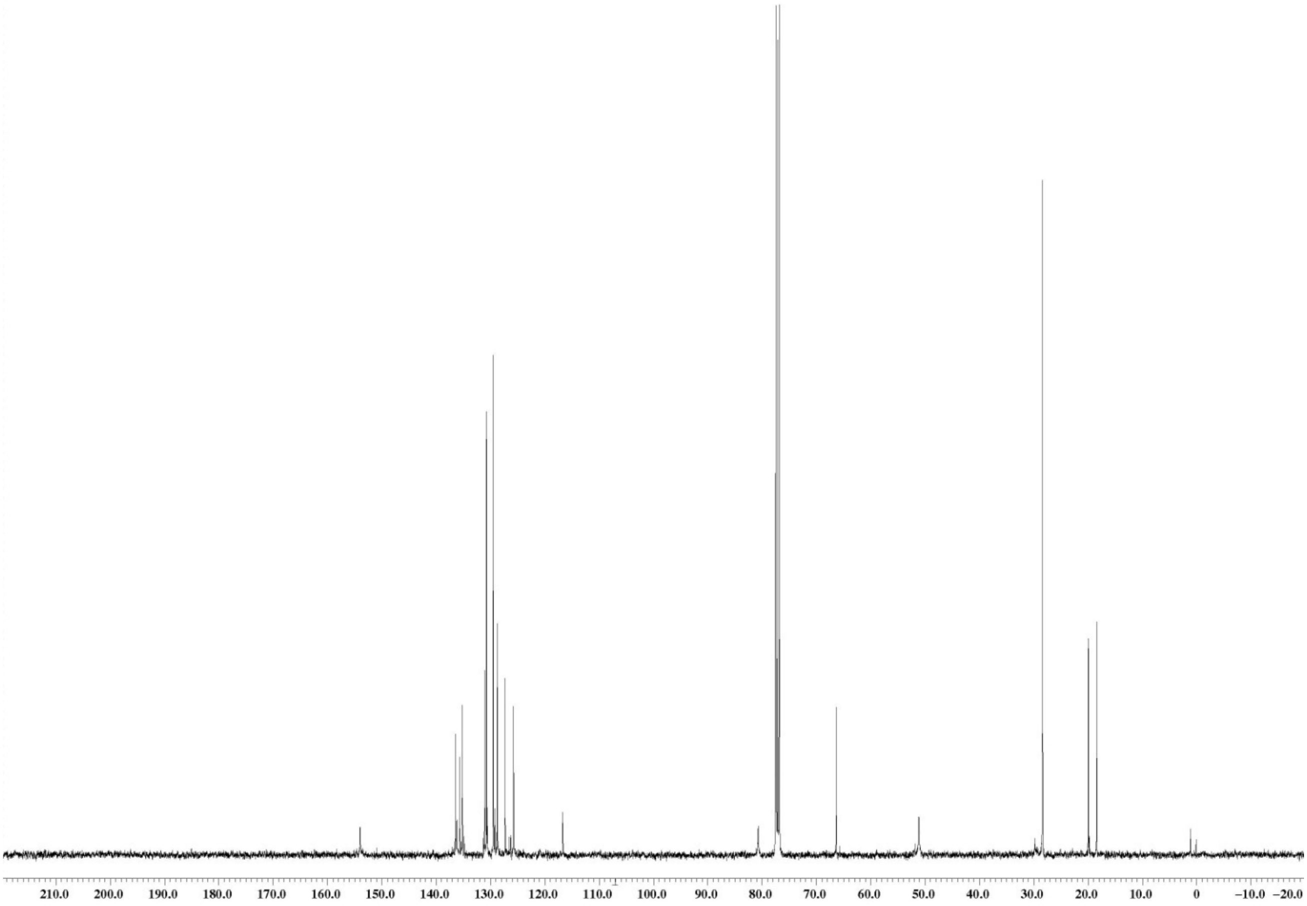
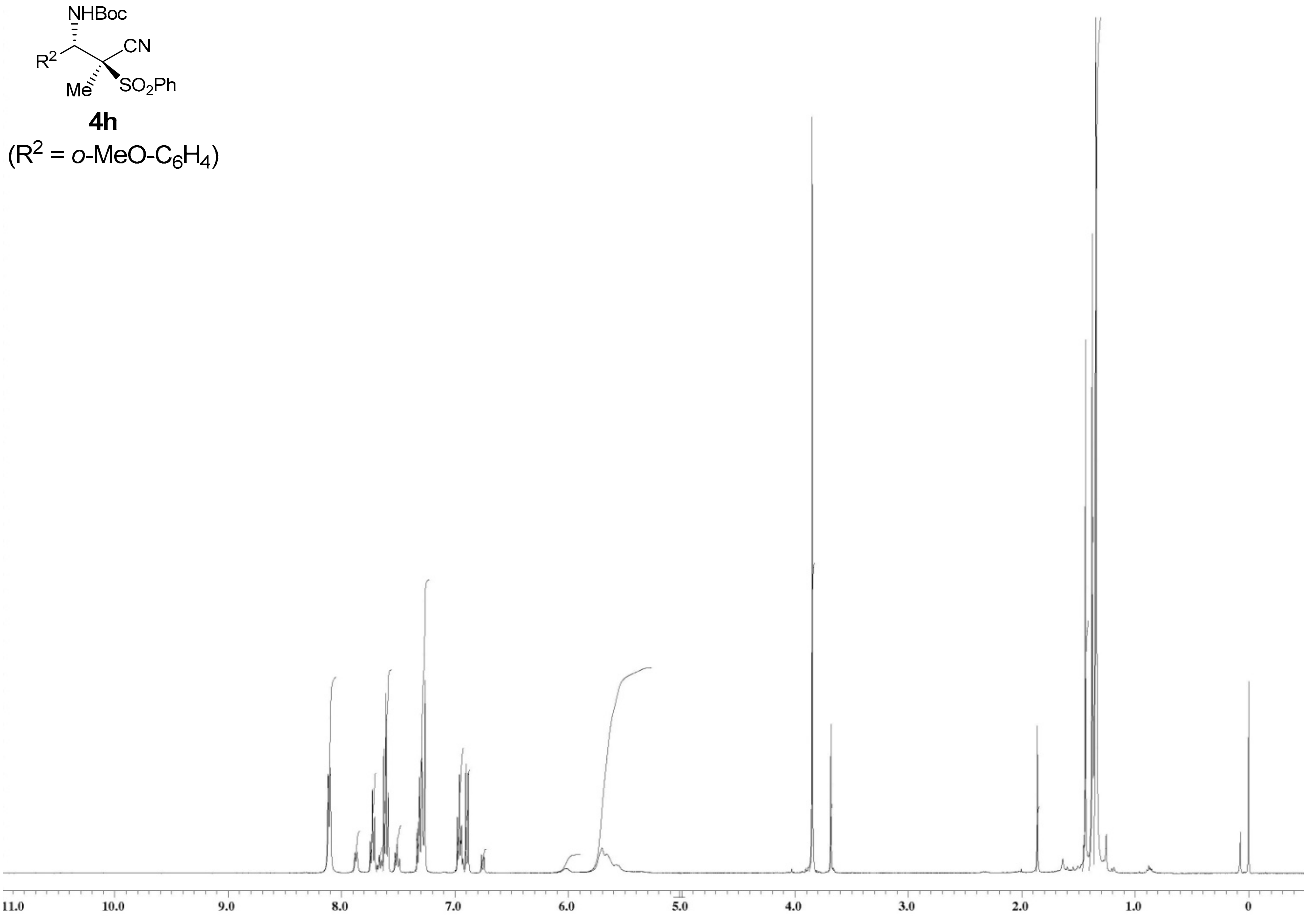
−20.0

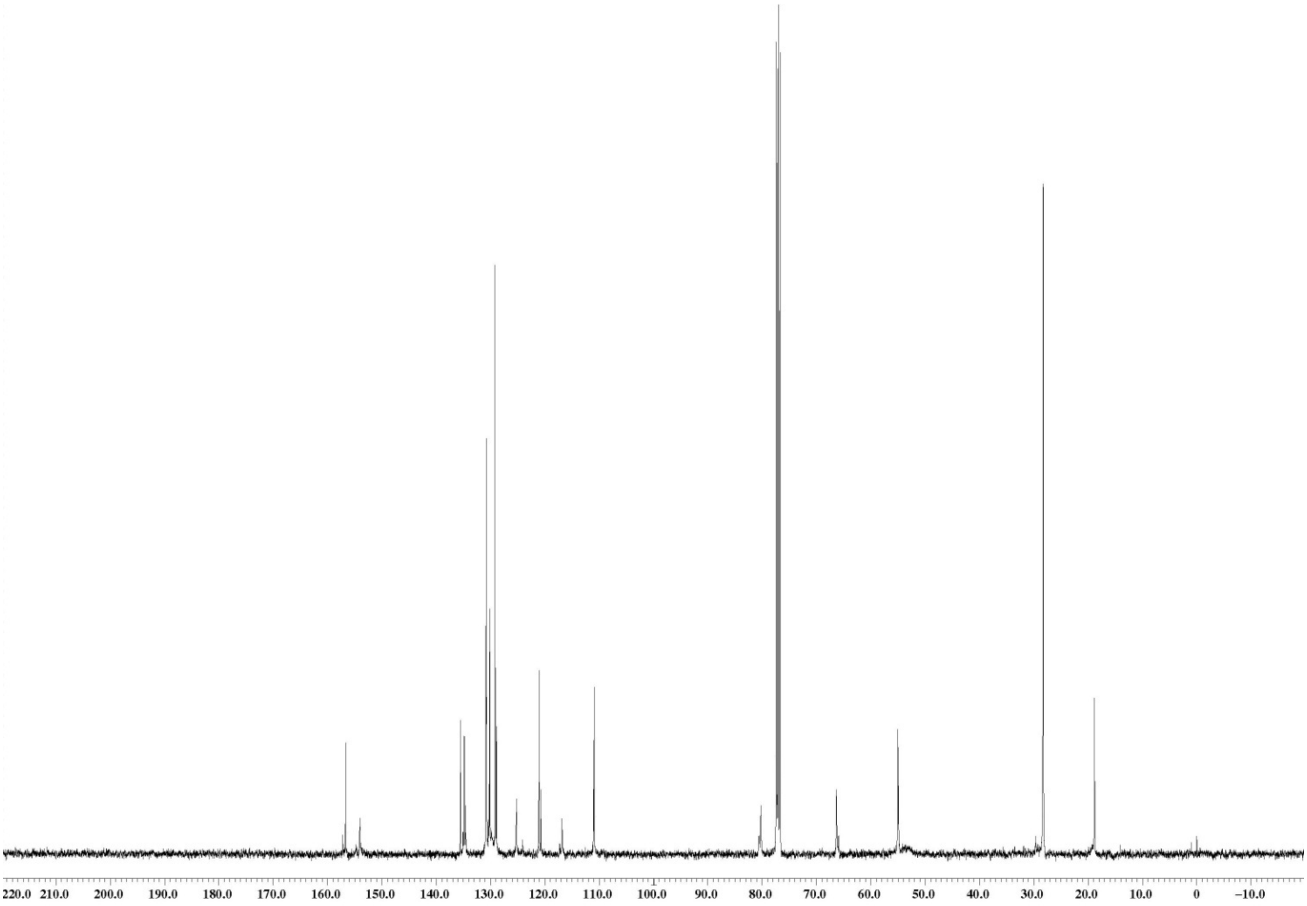


4g
(R^2 = *o*-Me-C_6H_4)



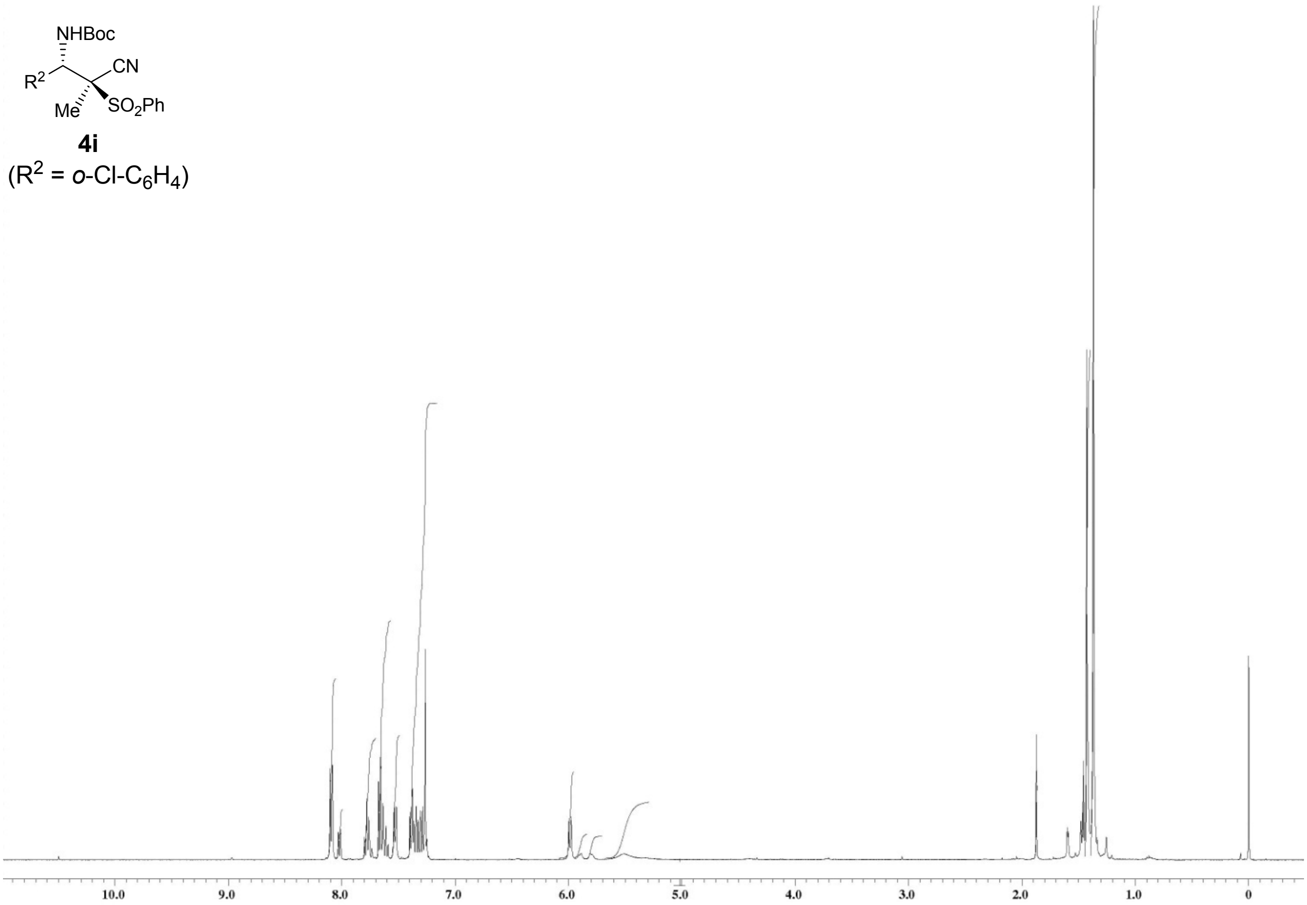


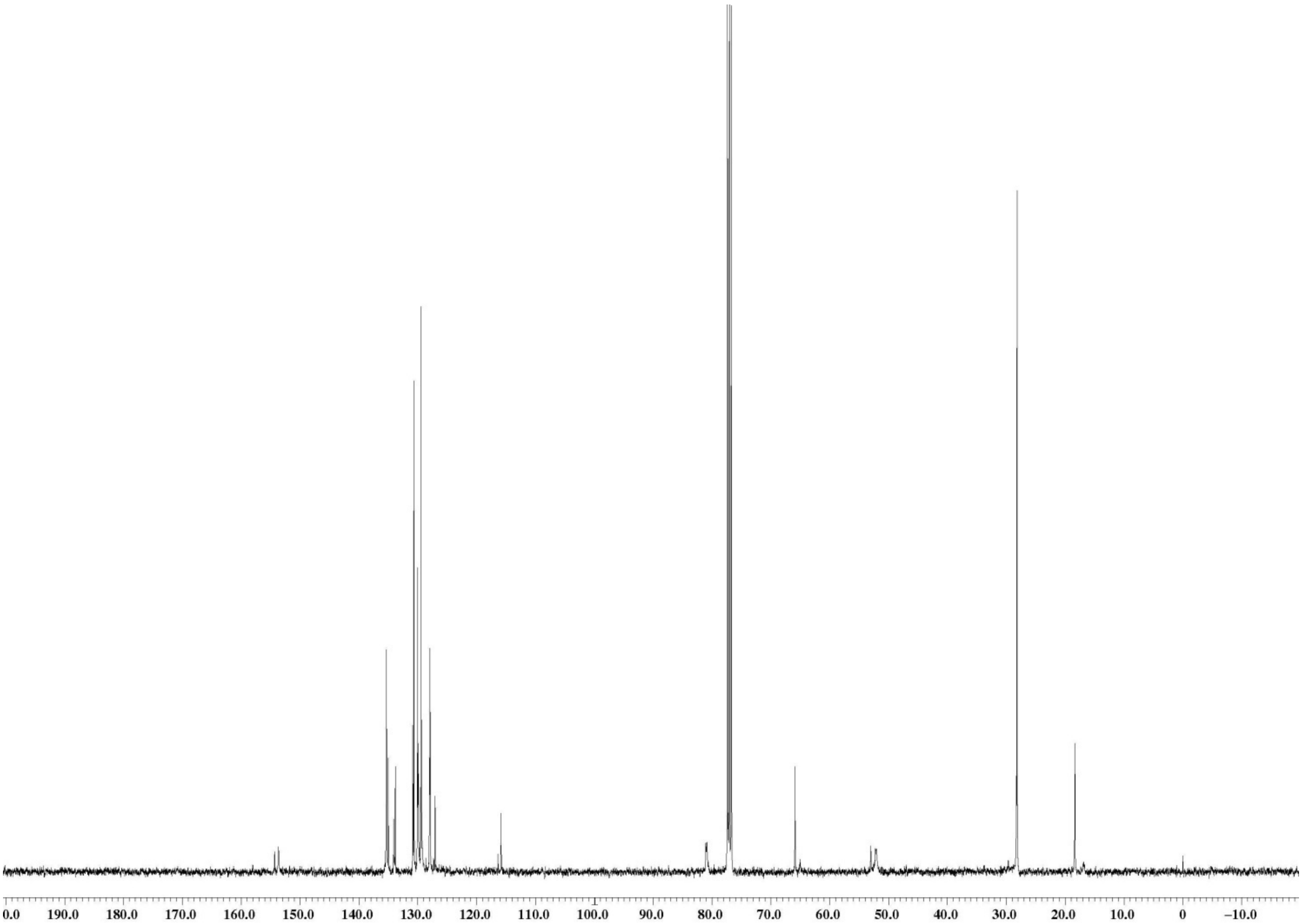
4h
(R^2 = *o*-MeO-C_6H_4)

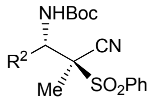


4i

(R^2 = *o*-Cl-C_6H_4)

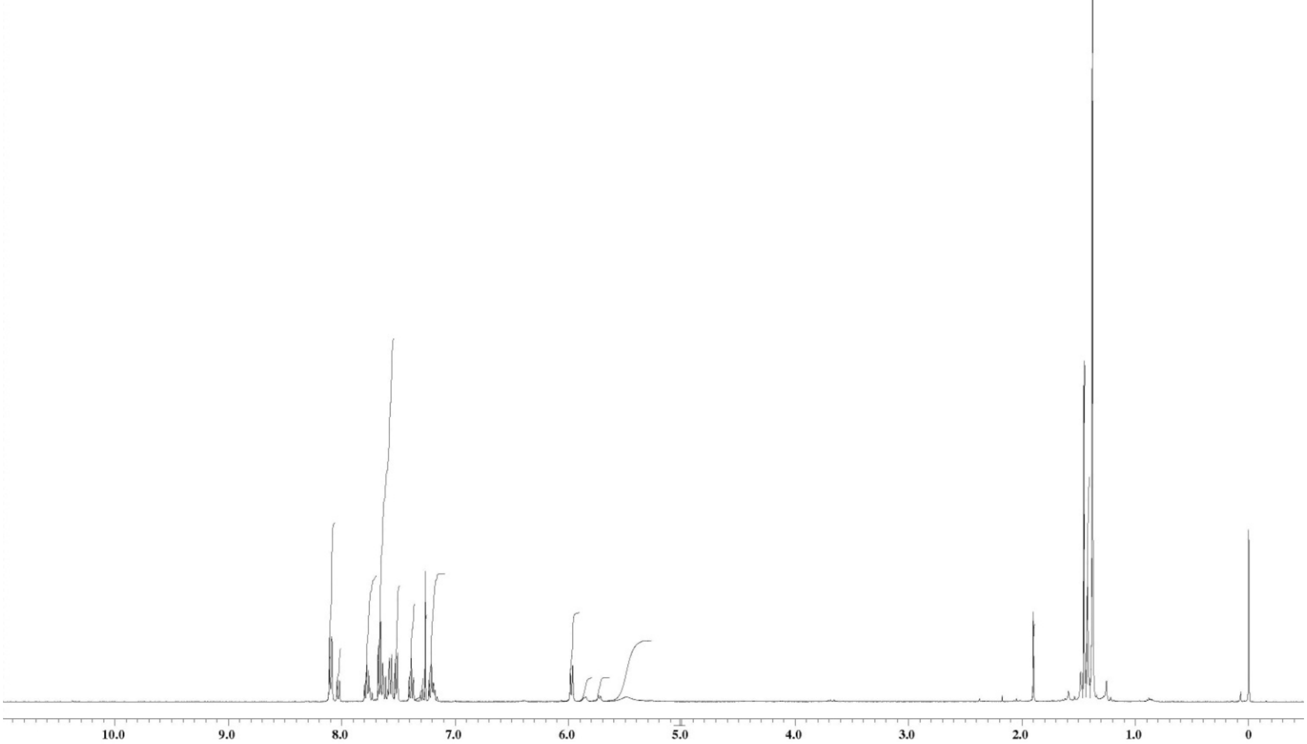


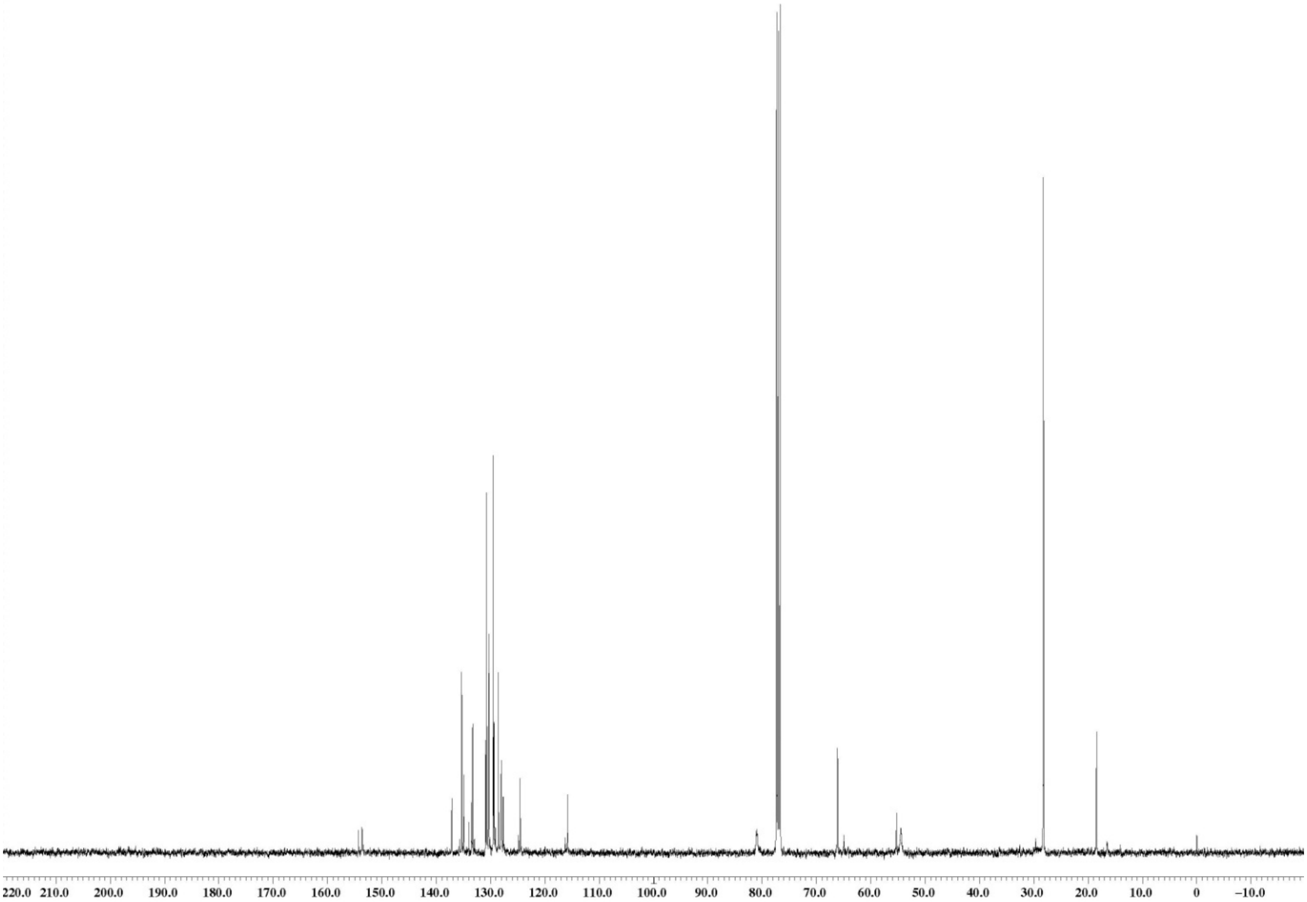


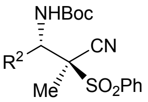


4j

(R^2 = *o*-Br-C_6H_4)

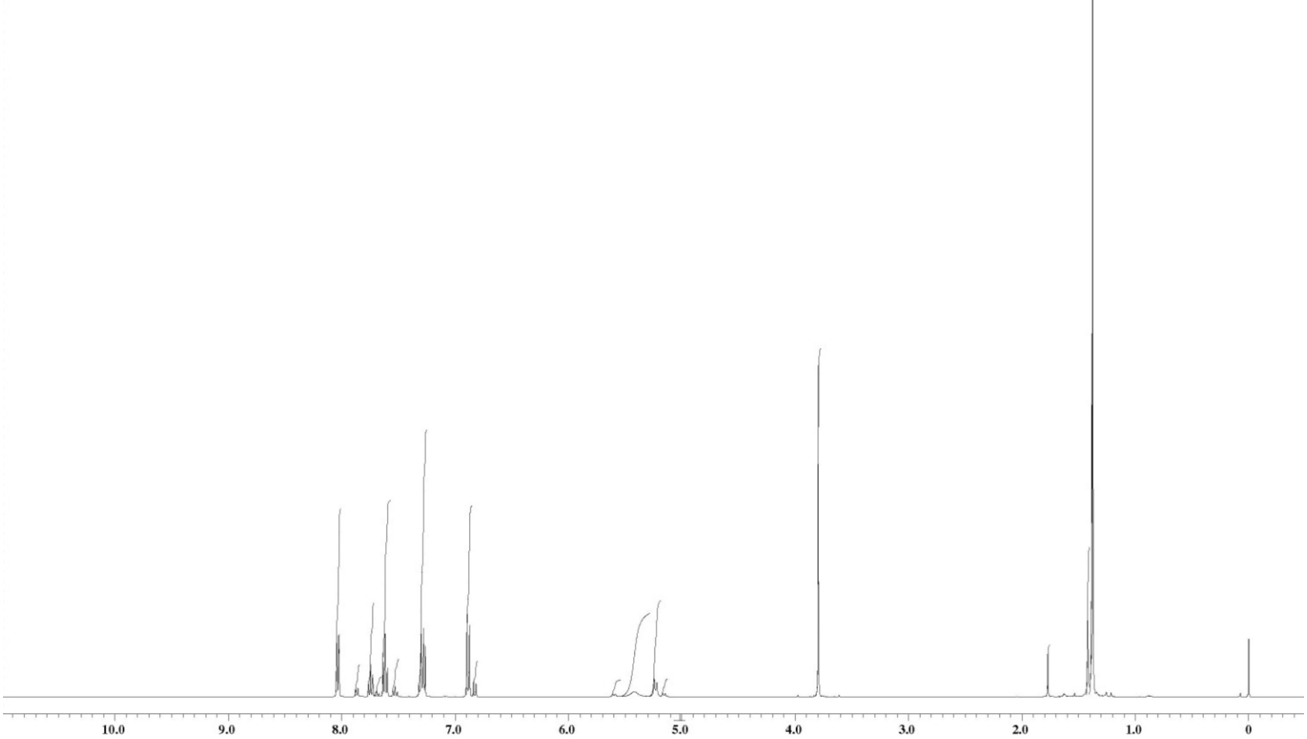


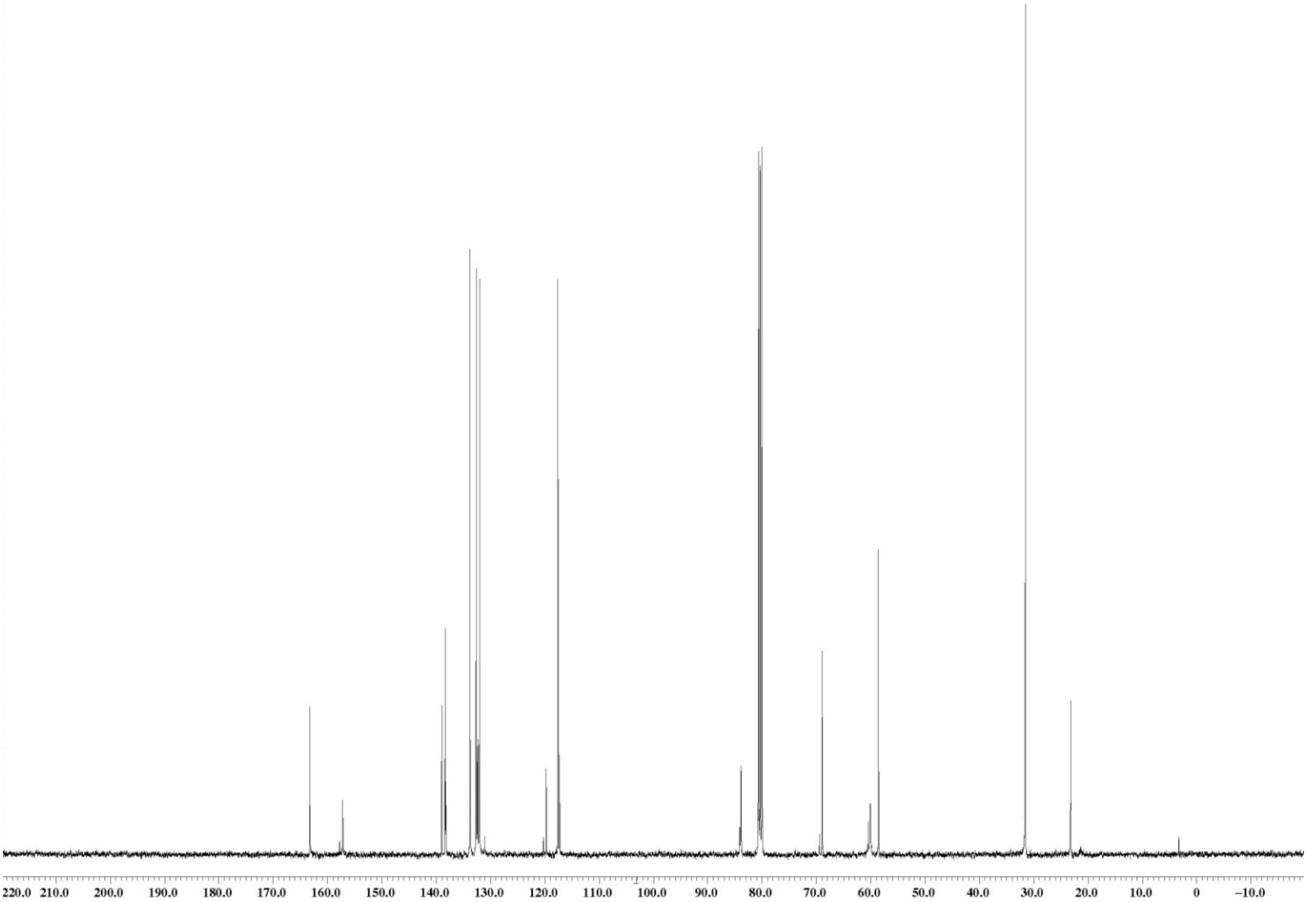


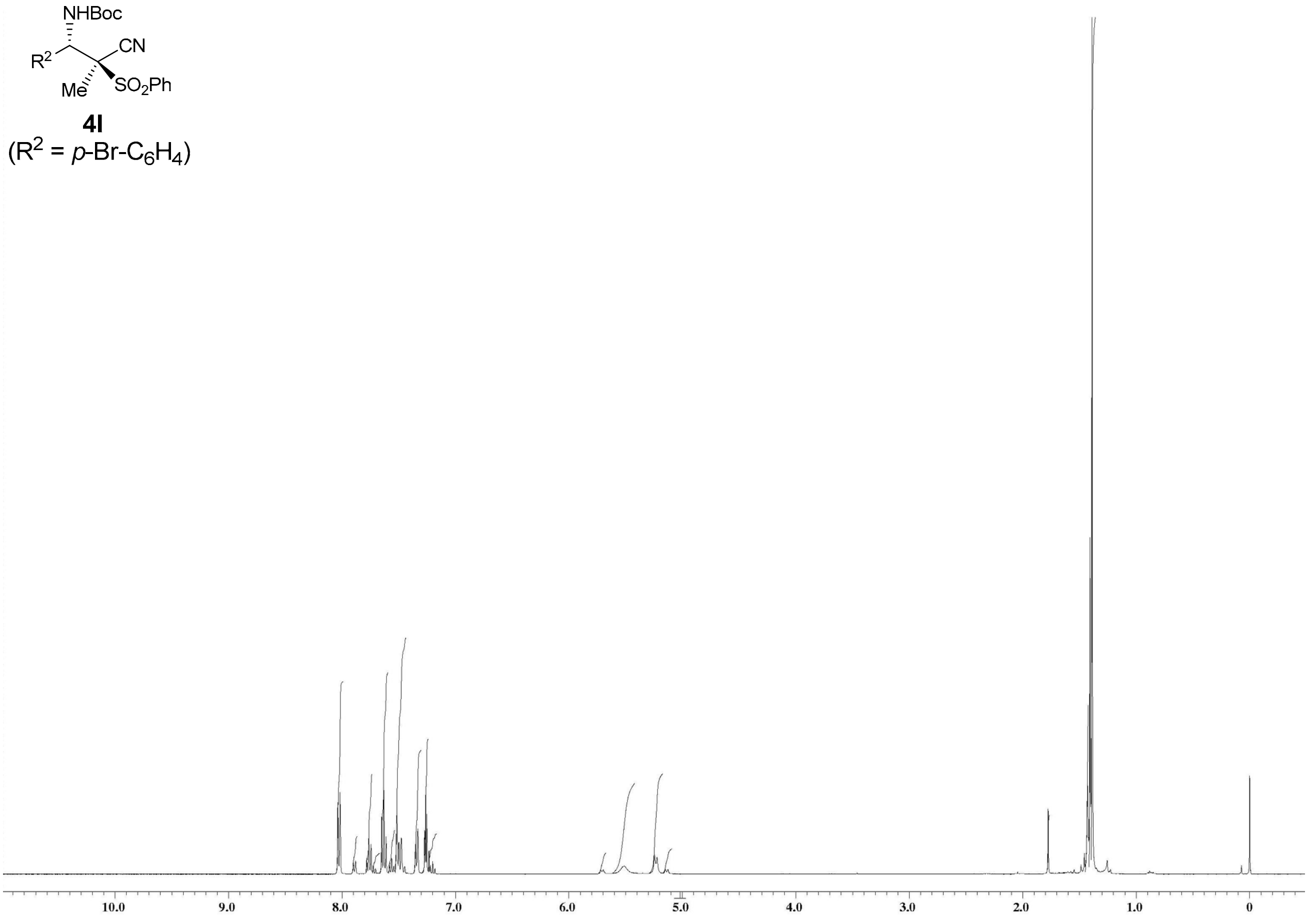


4k

(R^2 = *p*-MeO-C_6H_4)

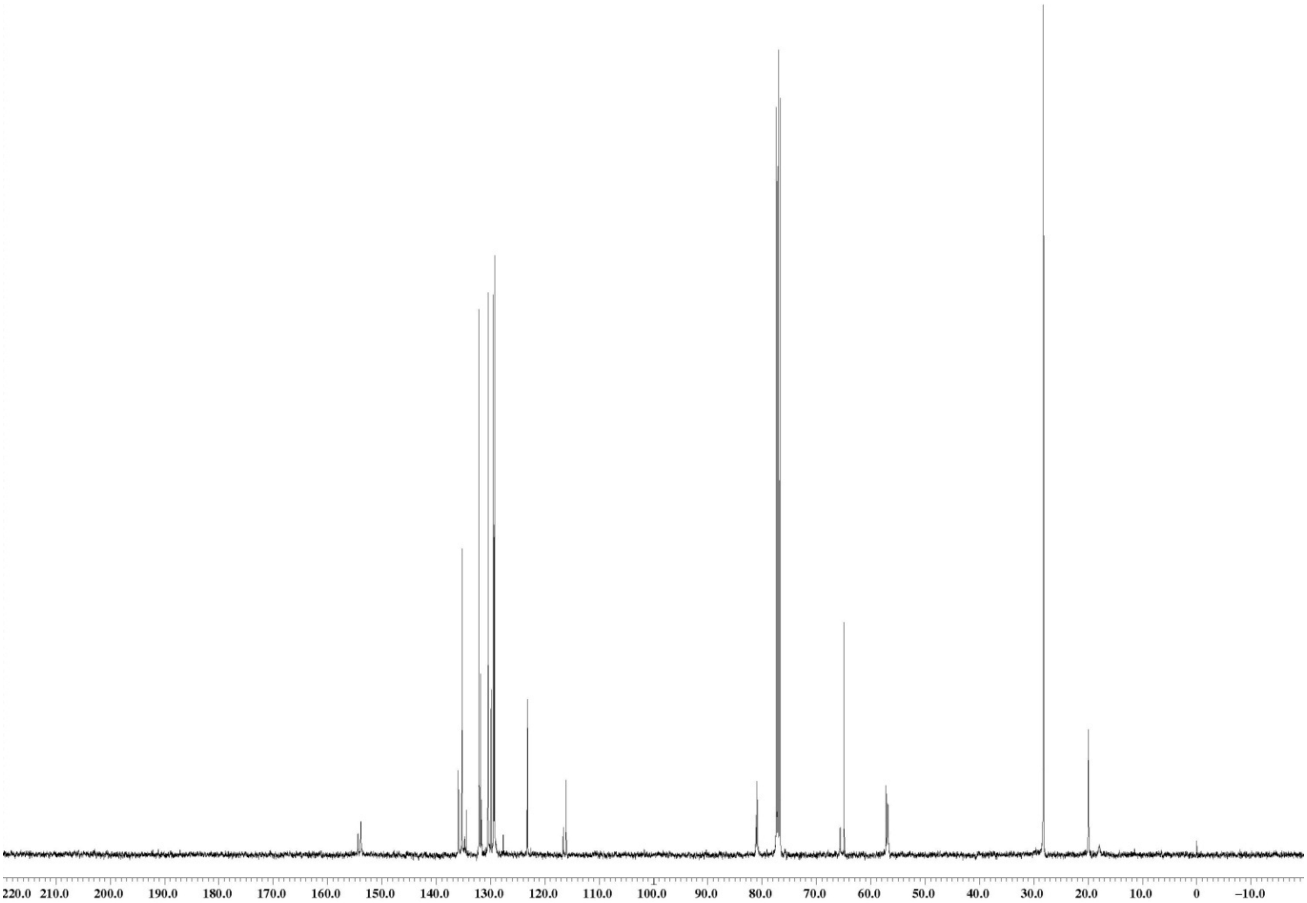


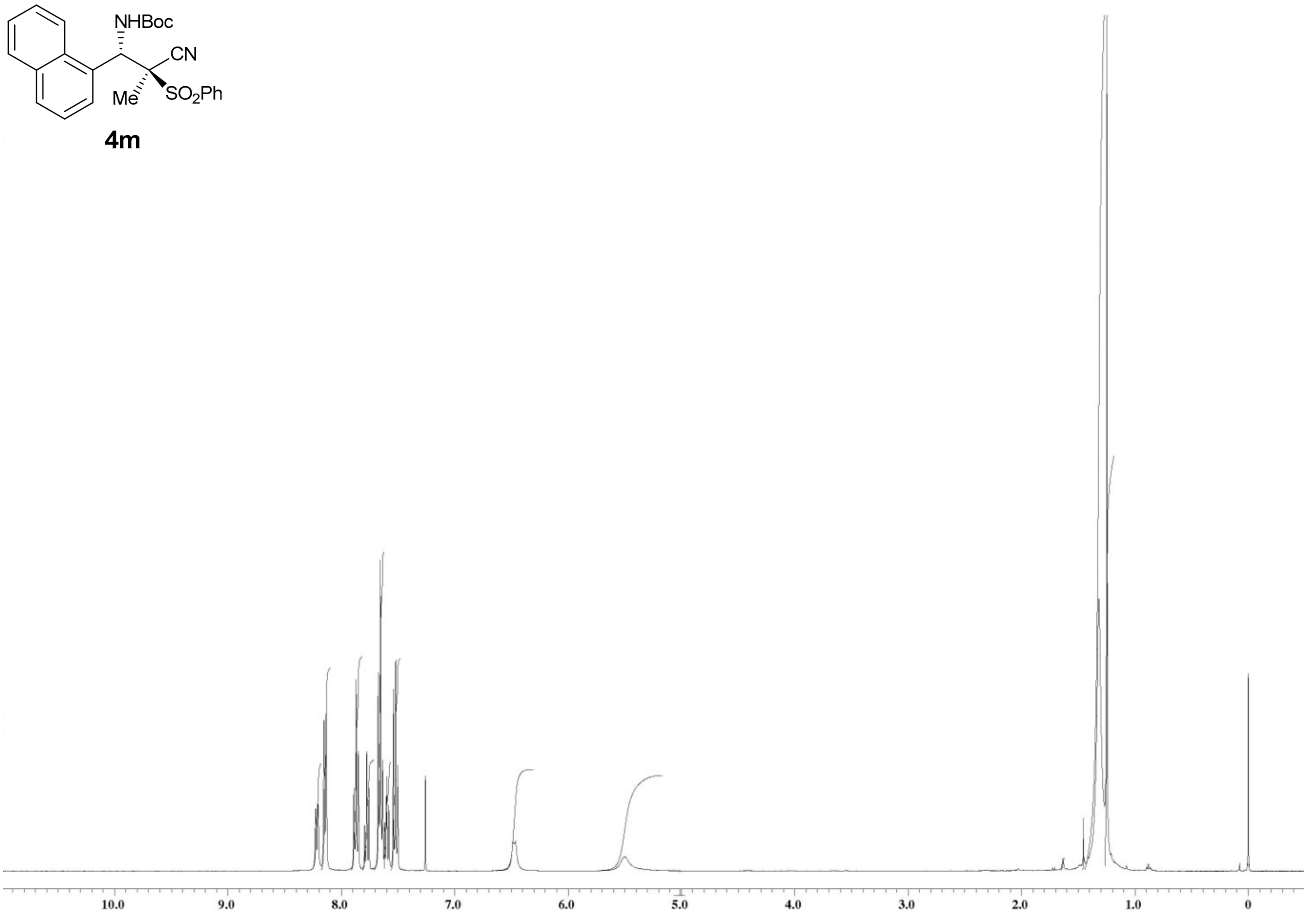




4l

(R^2 = *p*-Br-C_6H_4)

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SO2Ph

4m

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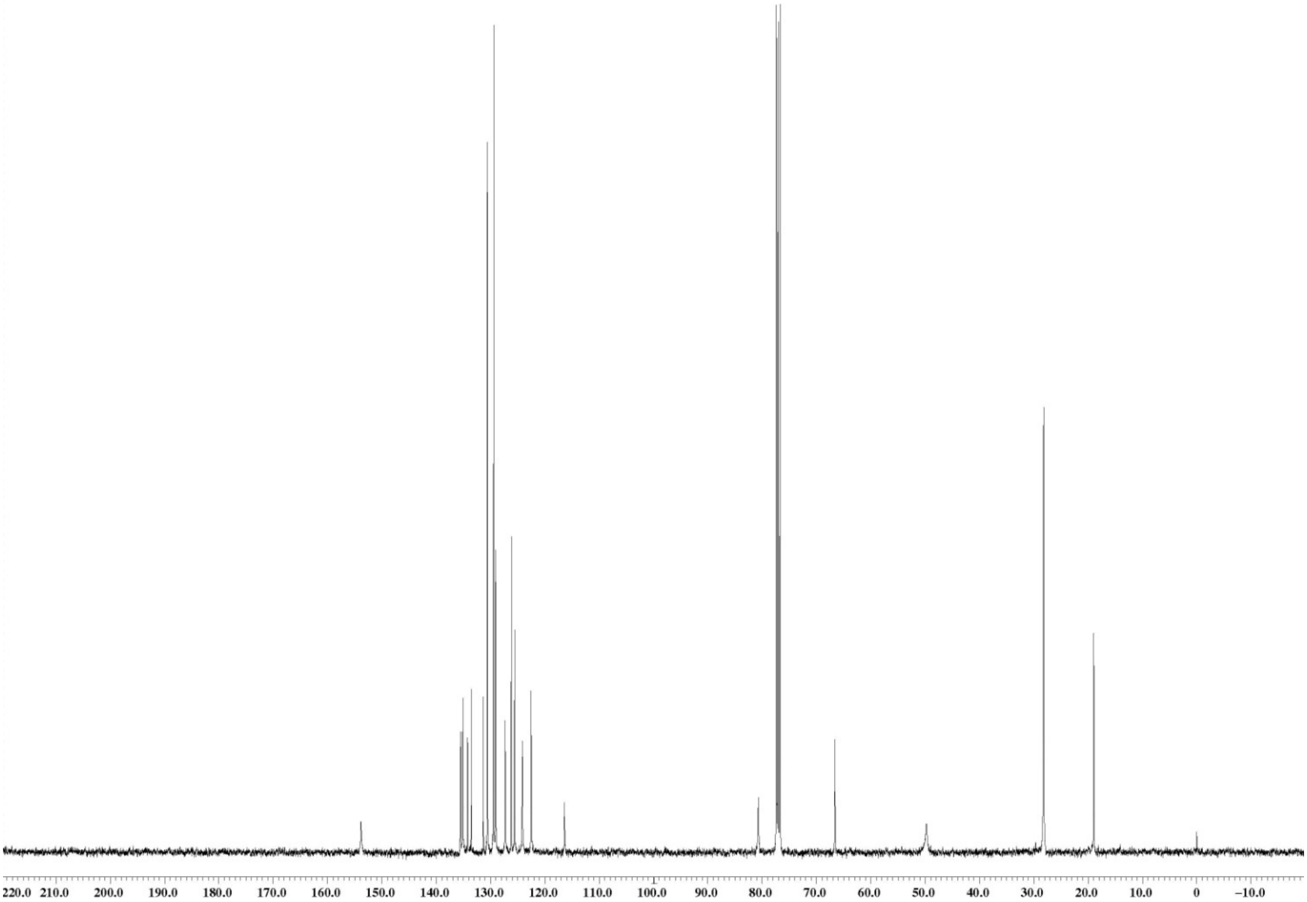
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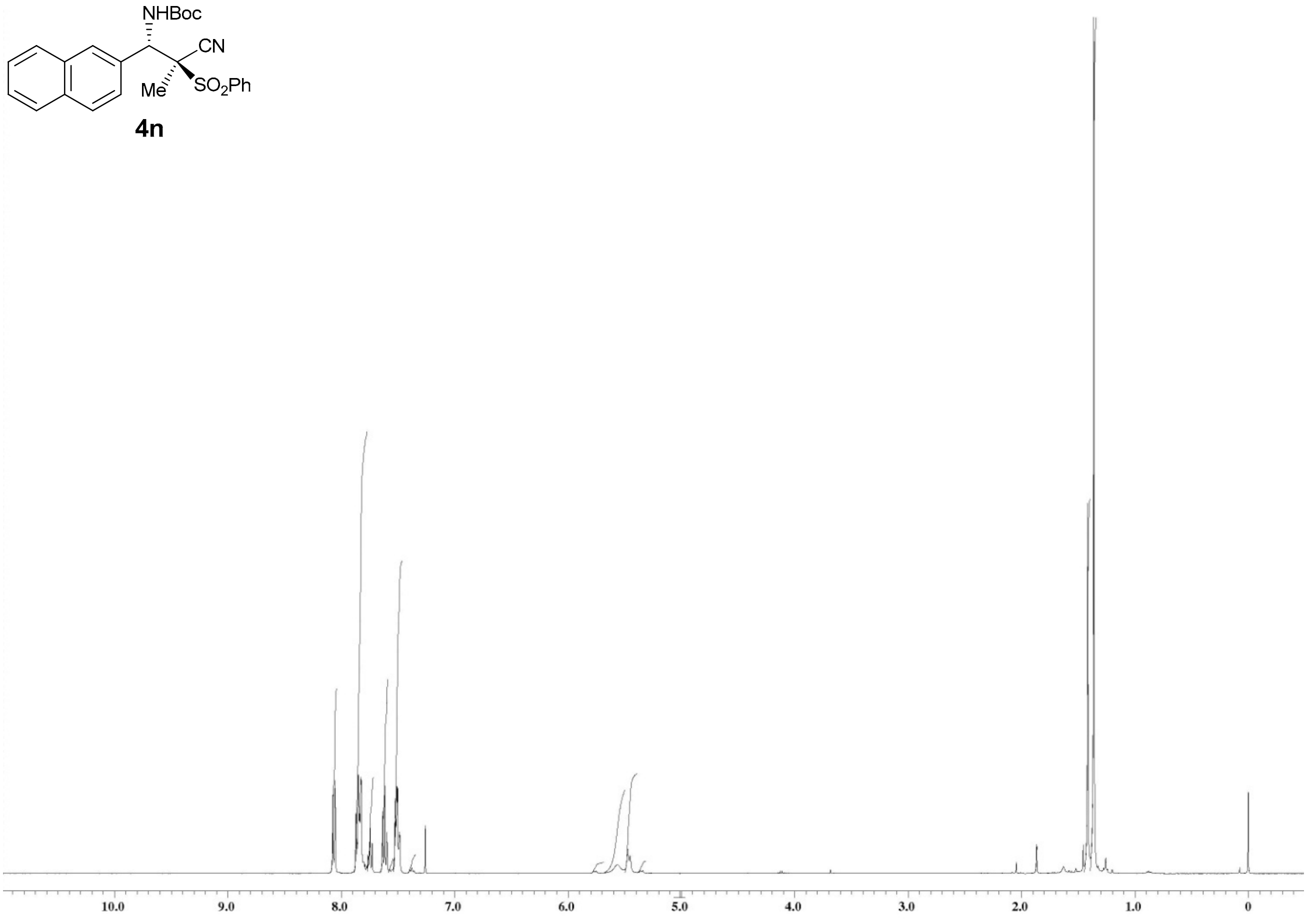
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SO_2Ph
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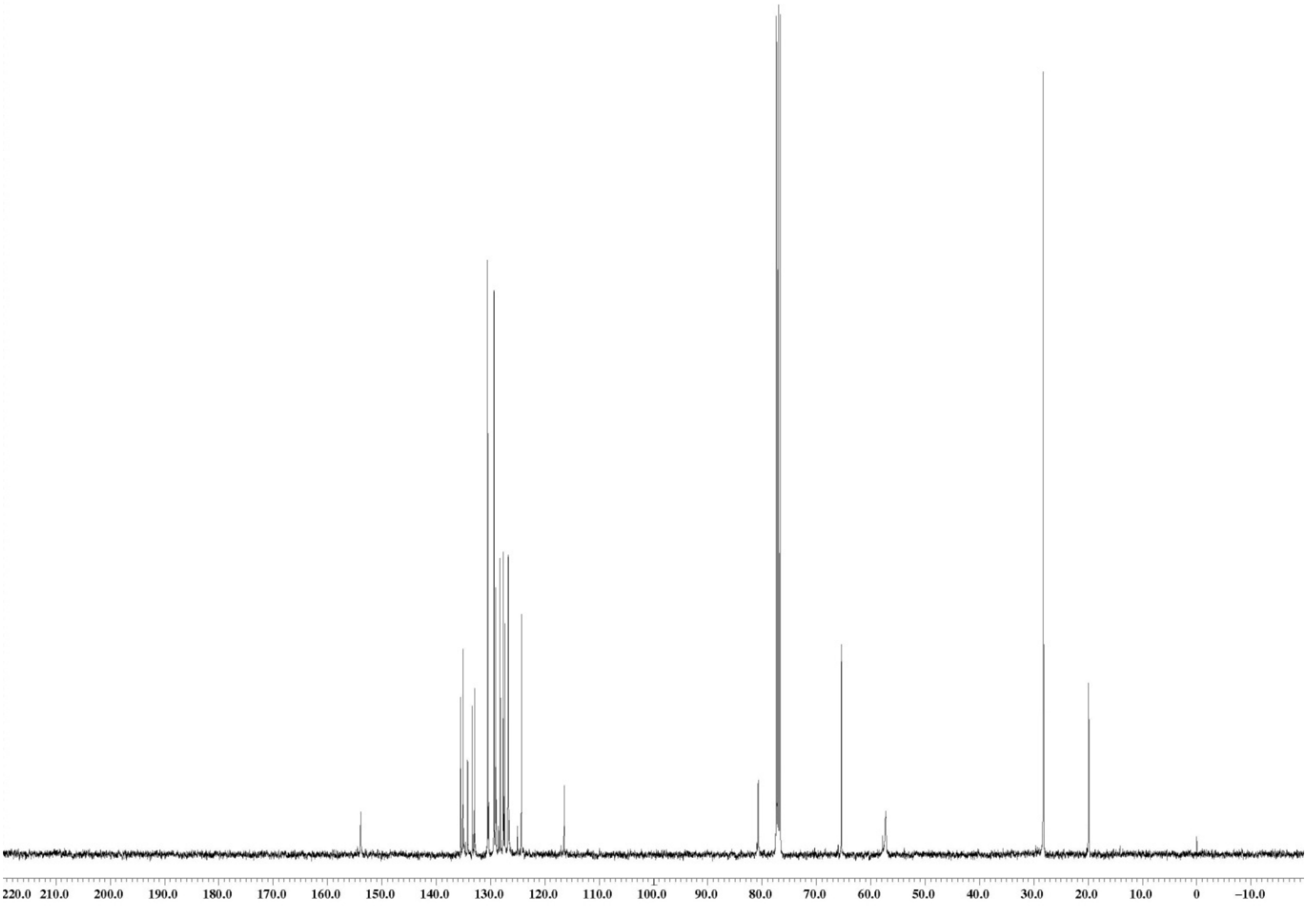
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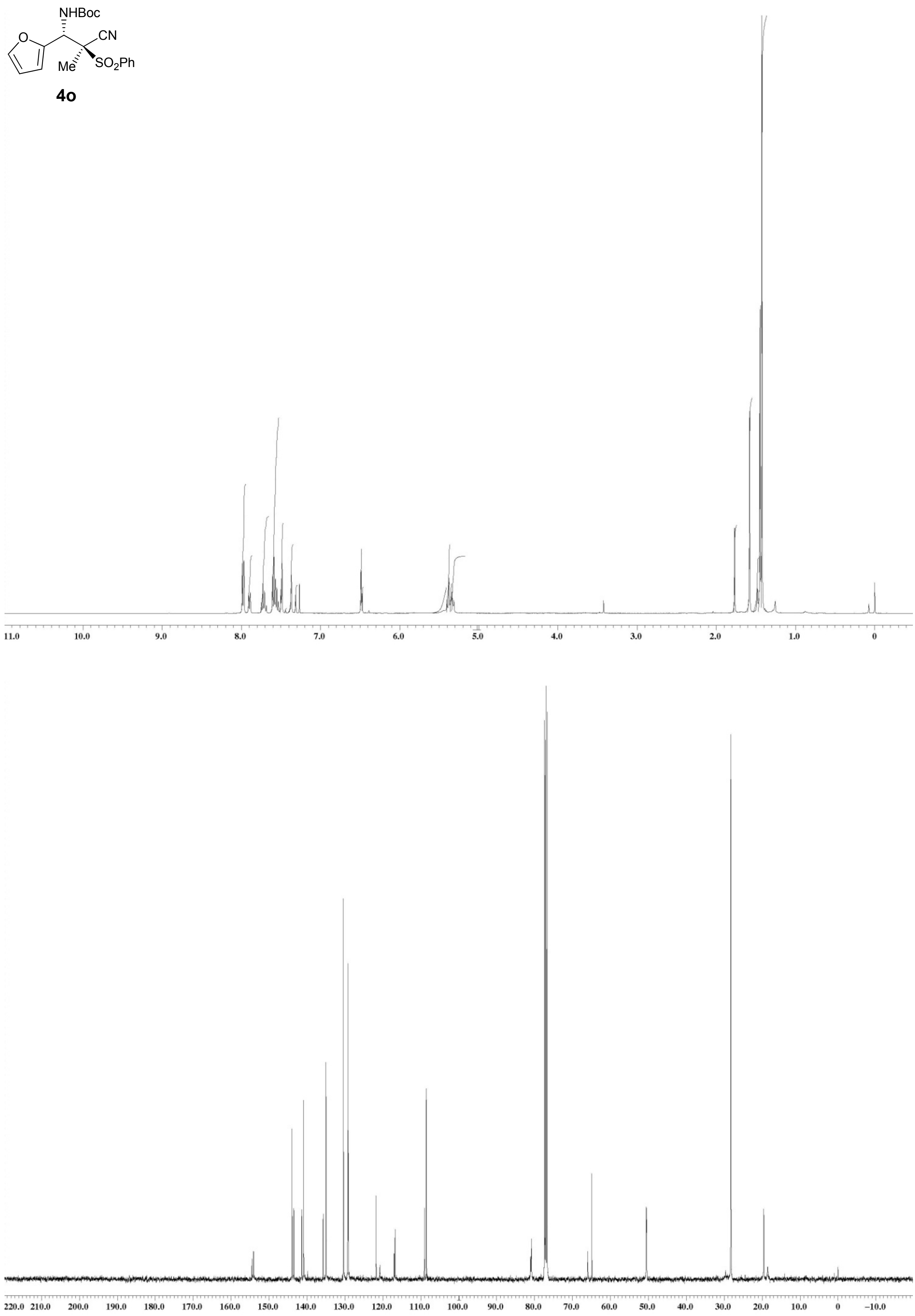
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O
Me
SO_2Ph
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2.0
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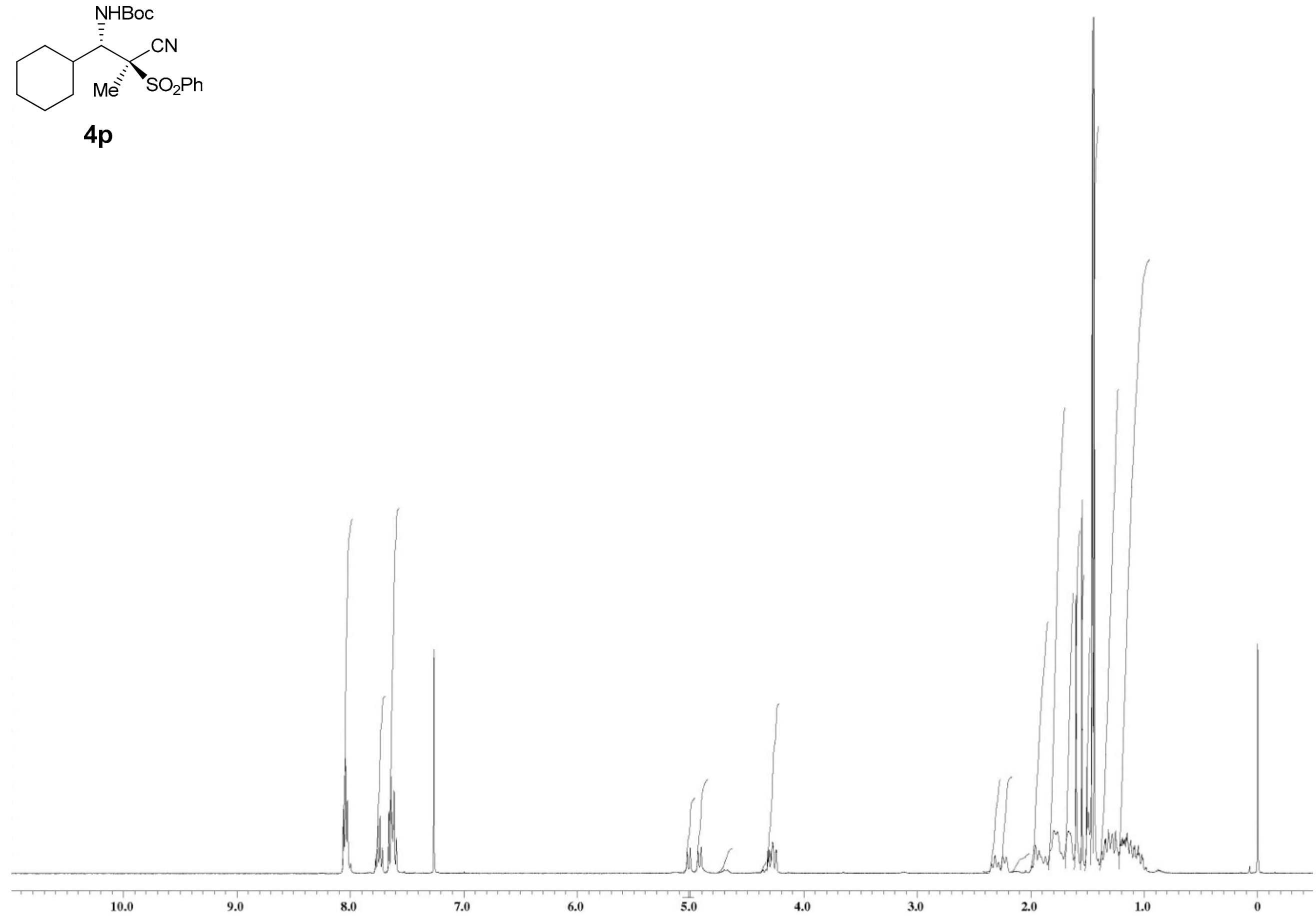
−10.0

4o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Me
SO$_2$Ph
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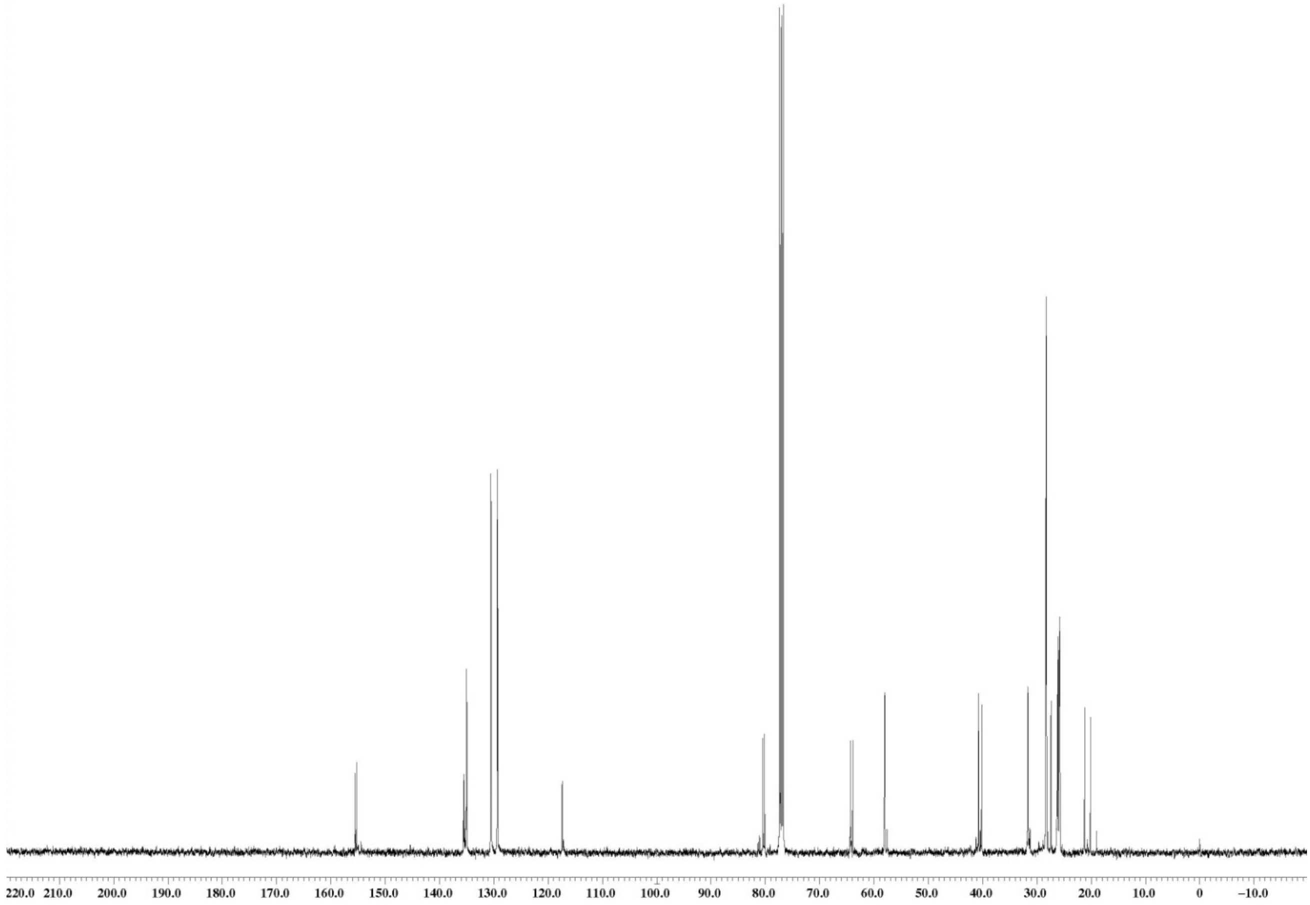
4p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20.0
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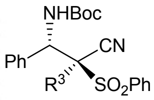
0
−10.0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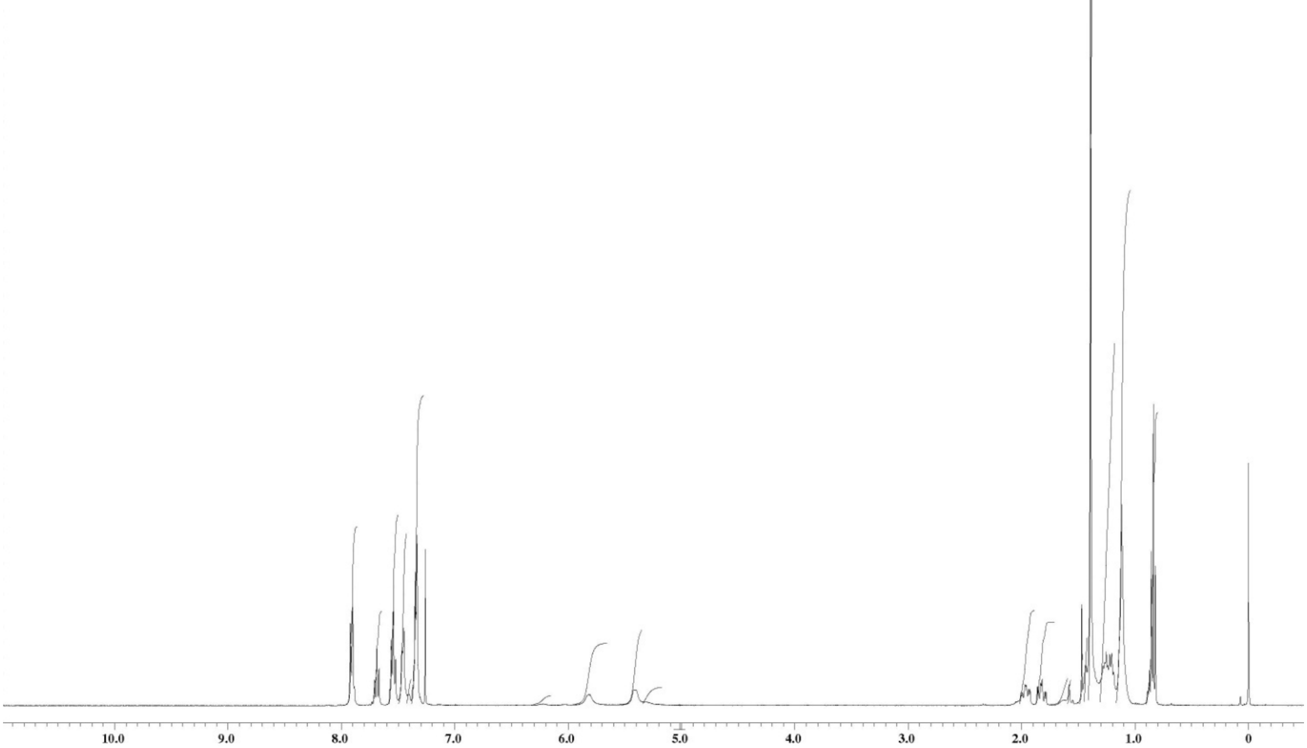
Ph
CN
R3
SO2Ph

4q
(R^3 = *n*-Hep)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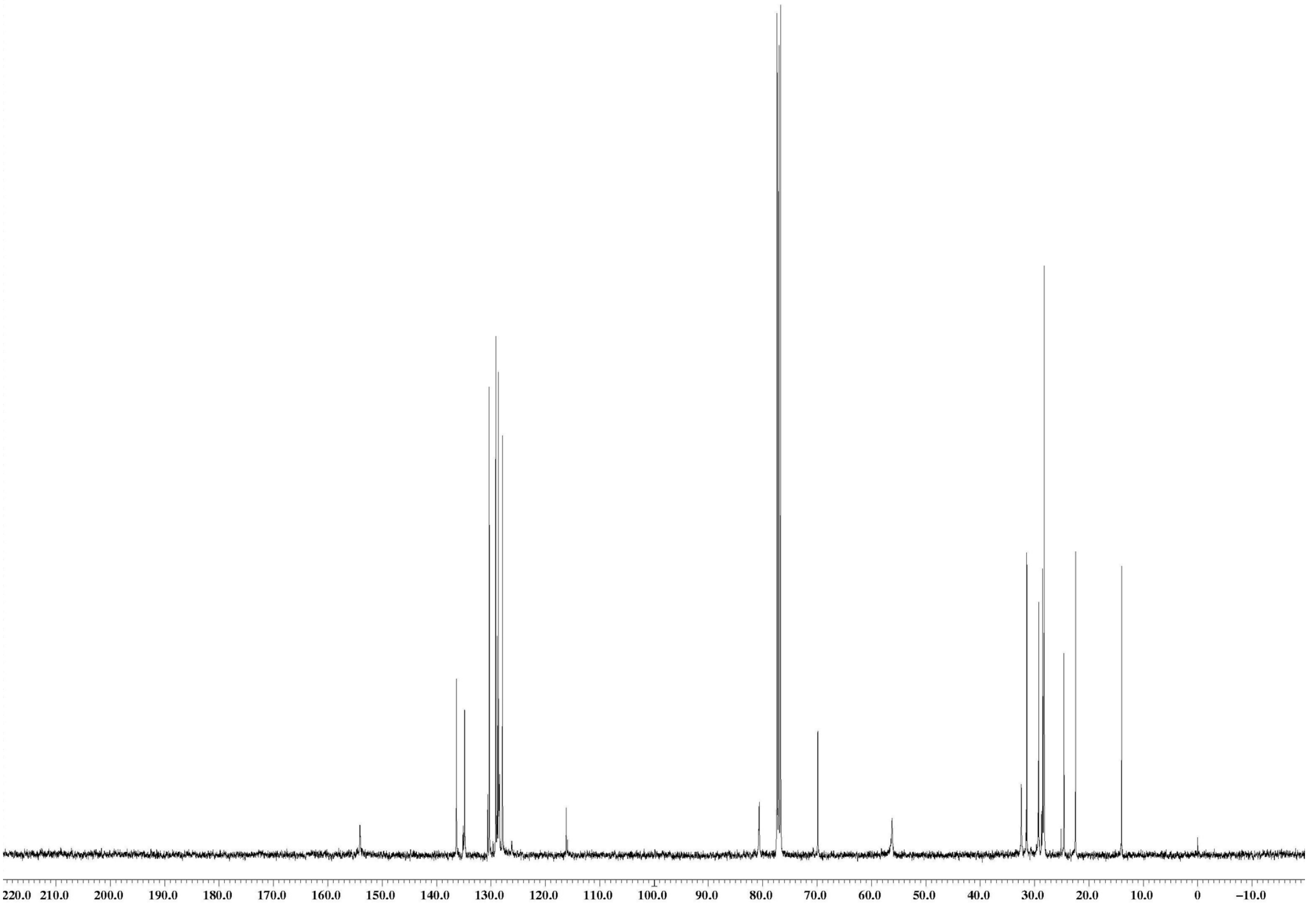
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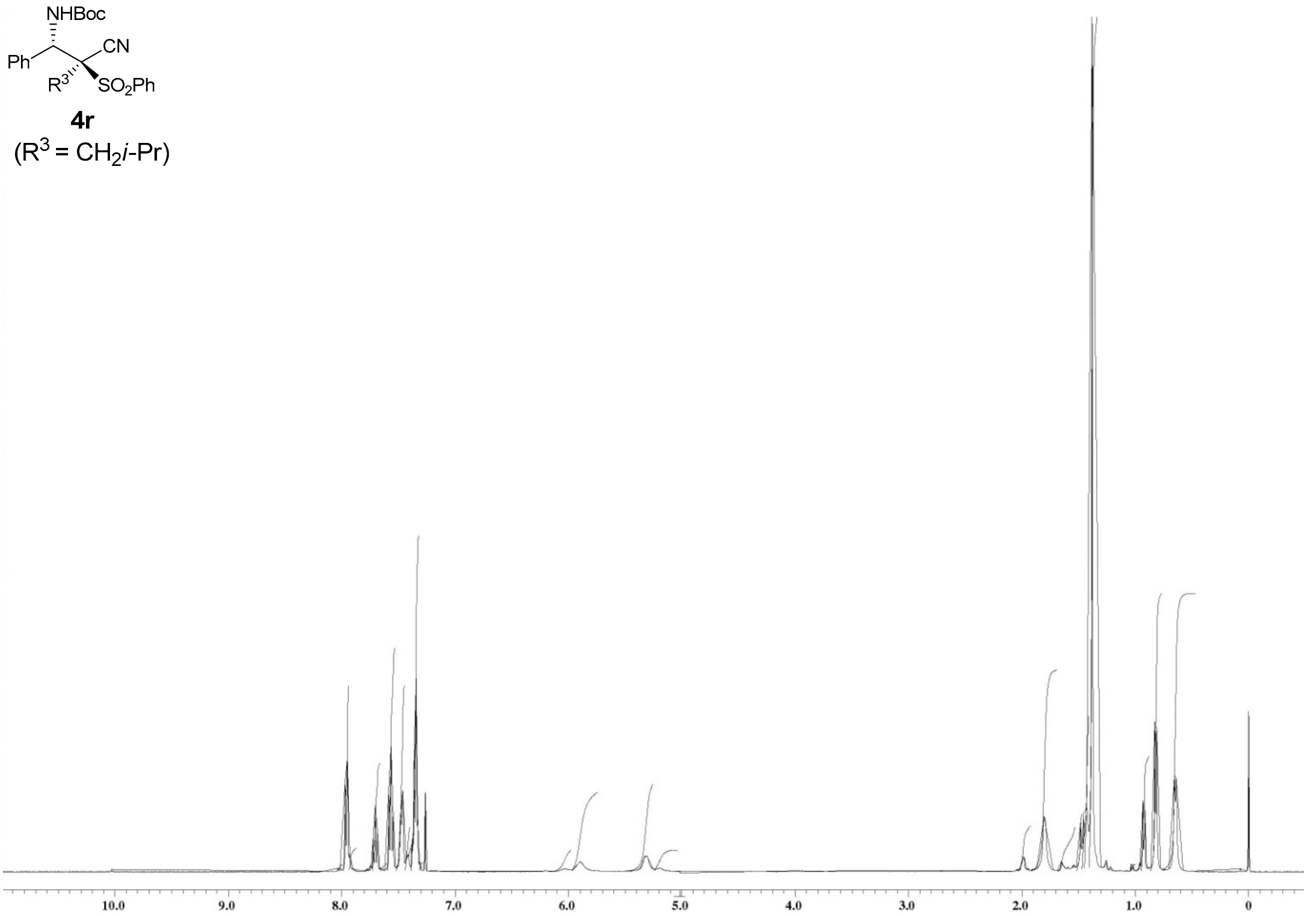
–10.0


NHBoc
CN
Ph
R3
SO2Ph

4r
(R^3 = CH_2*i*-Pr)

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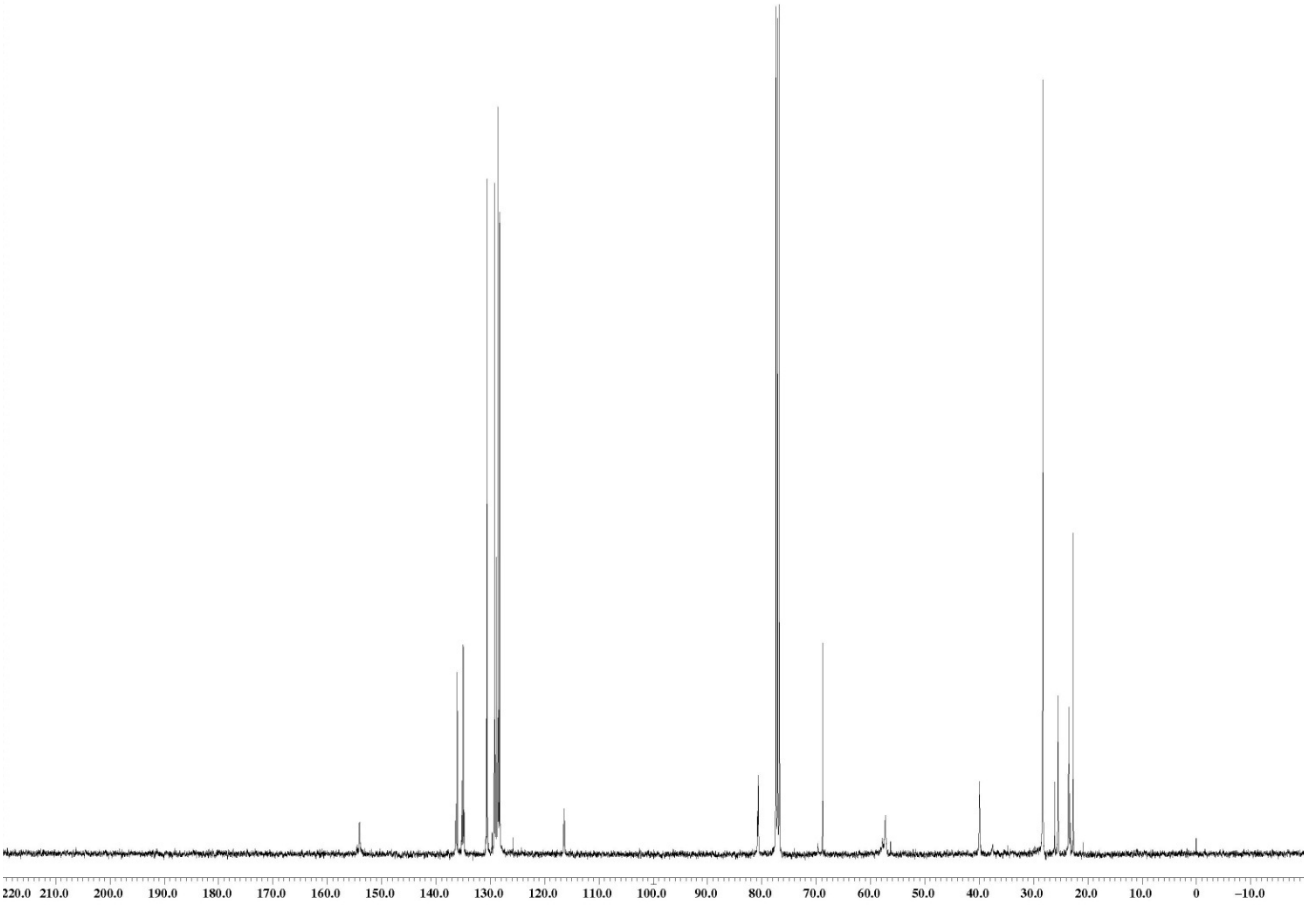
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


220.0
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190.0
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90.0
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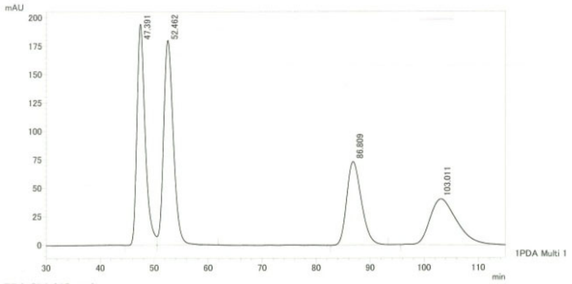
40.0
30.0
20.0
10.0
0
−10.0

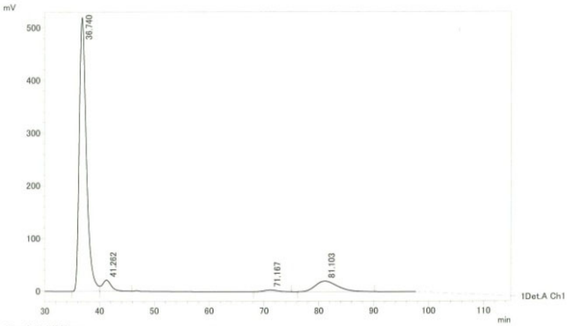
HPLC Chromatograms:

4a



PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	47.391	29.480
2	52.462	31.579
3	86.809	19.425
4	103.011	19.516
合計		100.000

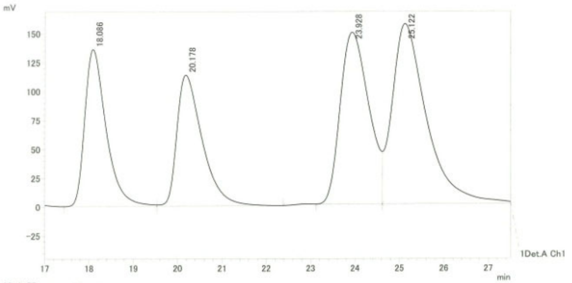


1 Det.A Ch1/210nm

検出器A Ch1 210nm

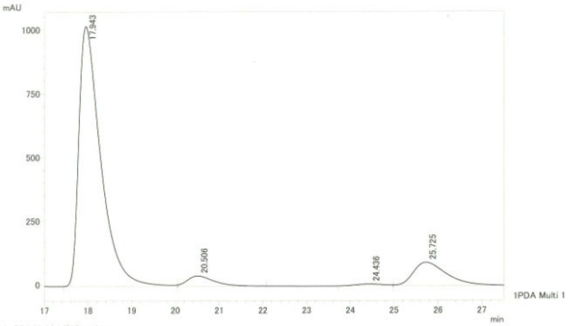
ピーク#	保持時間	面積%
1	36.740	84.615
2	41.262	4.337
3	71.167	0.955
4	81.103	10.093
合計		100.000

4b



検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	18.086	18.956
2	20.178	18.681
3	23.928	27.651
4	25.122	34.712
合計		100.000

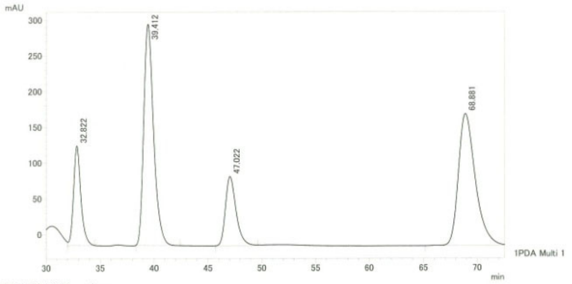


1 PDA Multi 1/210nm 4nm

PDA Ch1 210nm 4nm

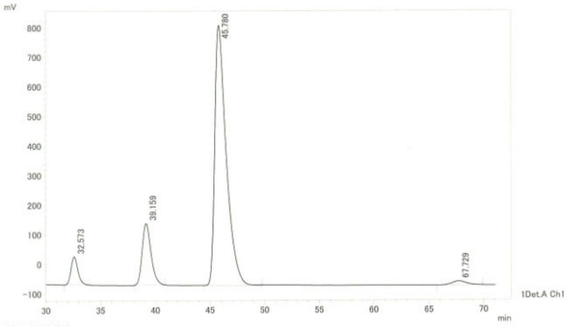
ピーク#	保持時間	面積%
1	17.943	83.838
2	20.506	3.995
3	24.436	0.767
4	25.725	11.400
合計		100.000

4c



PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	32.822	12.311
2	39.412	36.879
3	47.022	12.515
4	68.881	38.295
合計		100.000

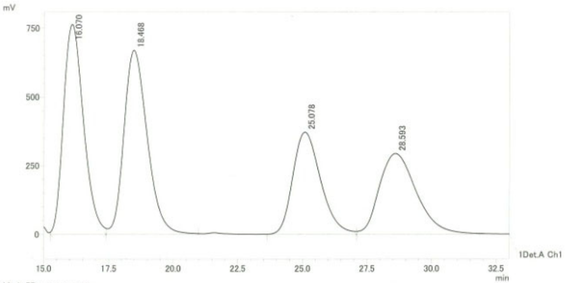


1 Det.A Ch1/210nm

検出器A Ch1 210nm

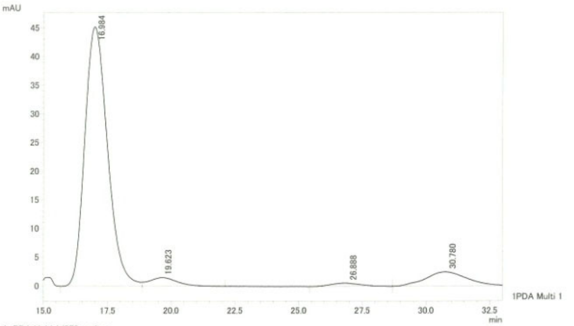
ピーク#	保持時間	面積%
1	32.573	5.035
2	39.159	14.426
3	45.780	79.049
4	67.729	1.490
合計		100.000

4d



検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	16.070	29.155
2	18.468	30.001
3	25.078	19.930
4	28.593	20.914
合計		100.000

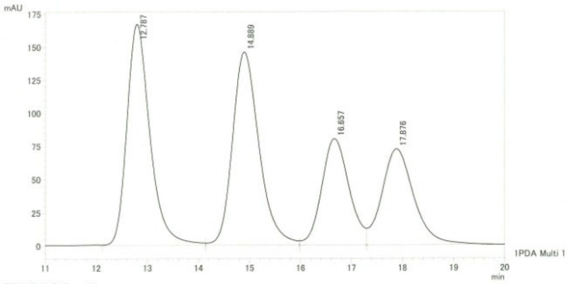


1 PDA Multi 1/250nm 4nm

PDA Ch1 250nm 4nm

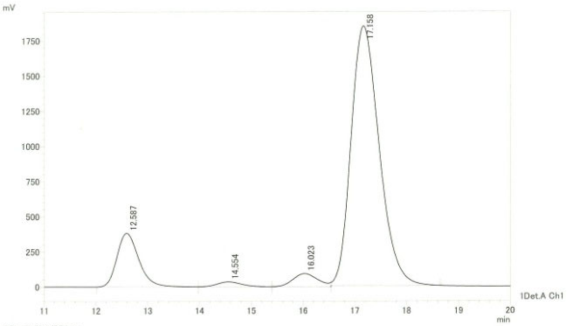
ピーク#	保持時間	面積%
1	16.984	86.734
2	19.623	3.456
3	26.888	1.289
4	30.780	8.521
合計		100.000

4e



PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	12.787	31.472
2	14.889	31.670
3	16.657	17.990
4	17.876	18.869
合計		100.000

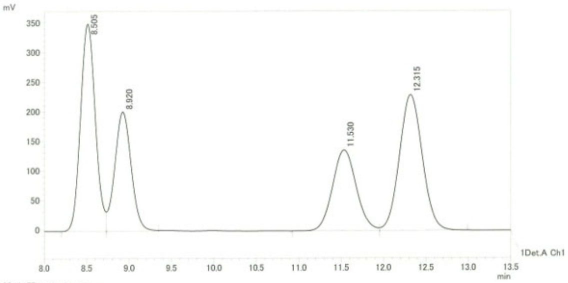


1Det.A Ch1/254nm

検出器A Ch1 254nm

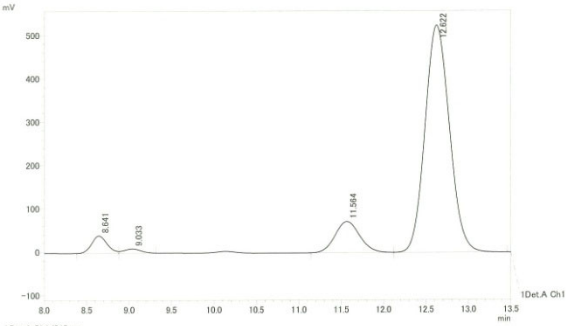
ピーク#	保持時間	面積%
1	12.587	13.052
2	14.554	1.489
3	16.023	3.776
4	17.158	81.683
合計		100.000

4f



検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	8.505	30.548
2	8.920	19.468
3	11.530	19.161
4	12.315	30.824
合計		100.000

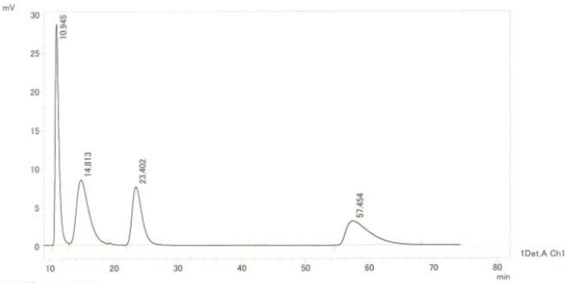


1Det.A Ch1/210nm

検出器A Ch1 210nm

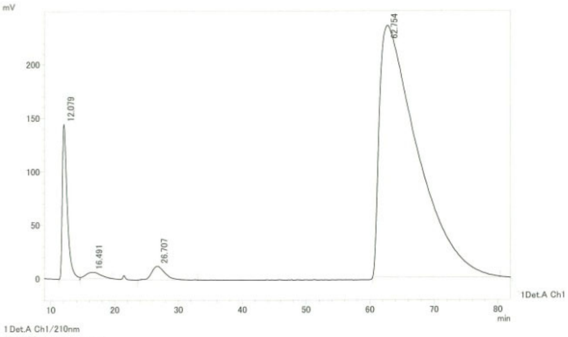
ピーク#	保持時間	面積%
1	8.641	4.055
2	9.033	1.079
3	11.564	11.638
4	12.622	83.229
合計		100.000

4g



検出器A Ch1 254nm

ピーク#	保持時間	面積%
1	10.945	29.335
2	14.813	29.353
3	23.402	20.525
4	57.454	20.787
合計		100.000

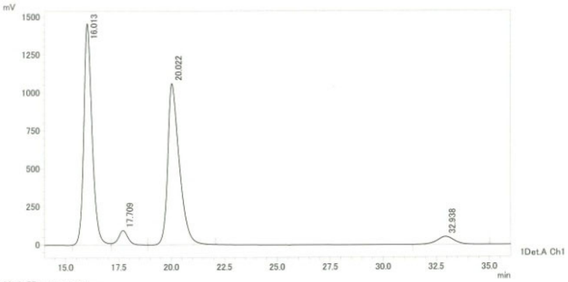


1Det.A Ch1/210nm

検出器A Ch1 210nm

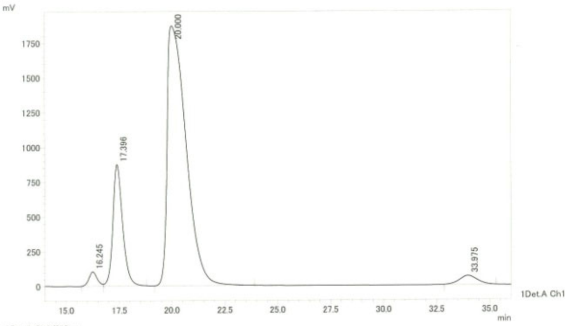
ピーク#	保持時間	面積%
1	12.079	7.250
2	16.491	0.887
3	26.707	1.727
4	62.754	90.136
合計		100.000

4h



検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	16.013	46.335
2	17.709	3.484
3	20.022	46.791
4	32.938	3.390
合計		100.000

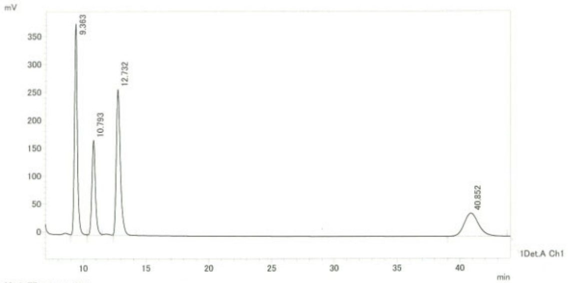


1Det.A Ch1/210nm

検出器A Ch1 210nm

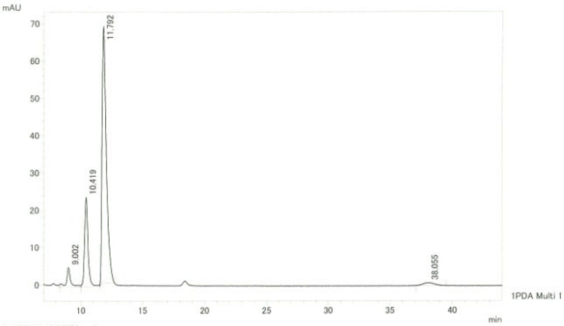
ピーク#	保持時間	面積%
1	16.245	1.865
2	17.396	18.536
3	20.000	77.100
4	33.975	2.499
合計		100.000

4i



検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	9.363	32.093
2	10.793	17.917
3	12.732	31.967
4	40.852	18.023
合計		100.000

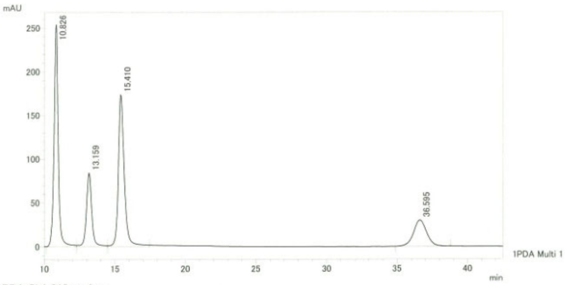


1 PDA Multi 1/254nm 4nm

PDA Ch1 254nm 4nm

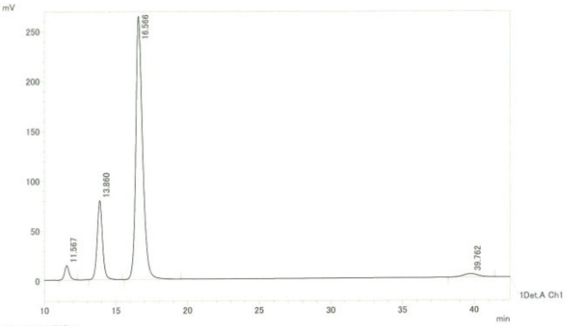
ピーク#	保持時間	面積%
1	9.002	4.864
2	10.419	20.439
3	11.792	72.454
4	38.055	2.243
合計		100.000

4j



PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	10.826	36.302
2	13.159	14.845
3	15.410	35.230
4	36.595	13.623
合計		100.000

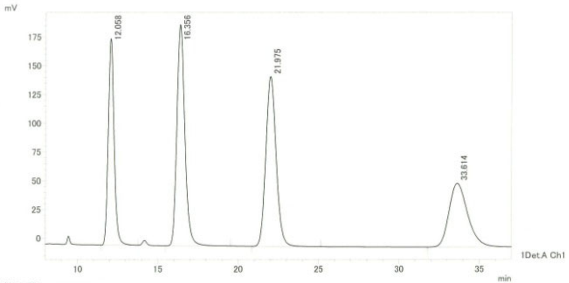


1 Det.A Ch1/210nm

検出器A Ch1 210nm

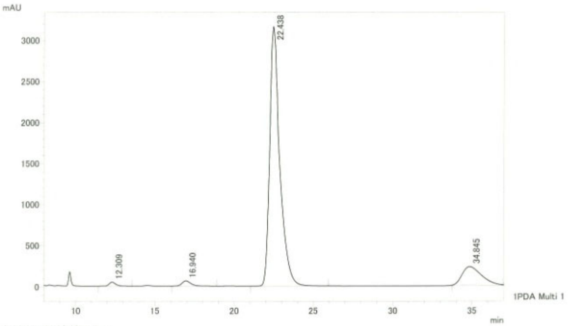
ピーク#	保持時間	面積%
1	11.567	2.899
2	13.860	18.529
3	16.566	76.516
4	39.762	2.056
合計		100.000

4k



検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	12.058	20.255
2	16.356	29.803
3	21.975	29.776
4	33.614	20.167
合計		100.000

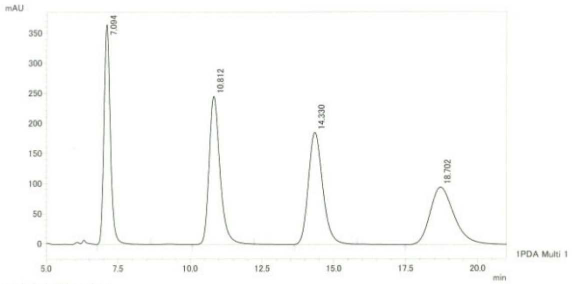


1 PDA Multi 1/210nm 4nm

PDA Ch1 210nm 4nm

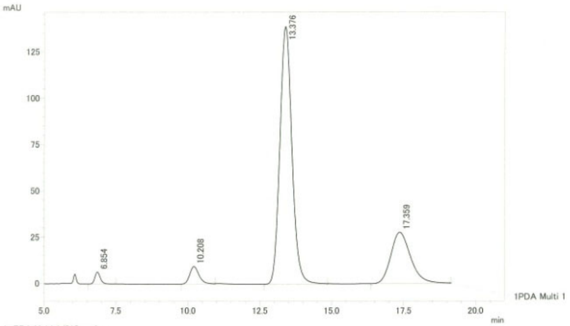
ピーク#	保持時間	面積%
1	12.309	1.046
2	16.940	1.502
3	22.438	85.781
4	34.845	11.672
合計		100.000

4l



PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	7.094	23.097
2	10.812	27.181
3	14.330	26.956
4	18.702	22.766
合計		100.000

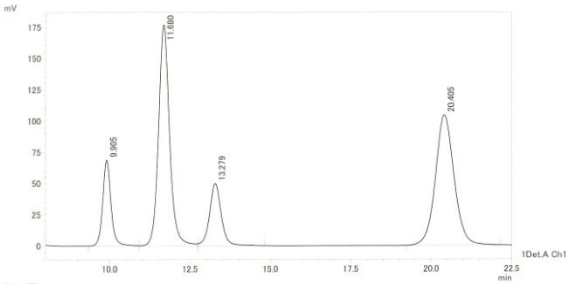


1 PDA Multi 1/210nm 4nm

PDA Ch1 210nm 4nm

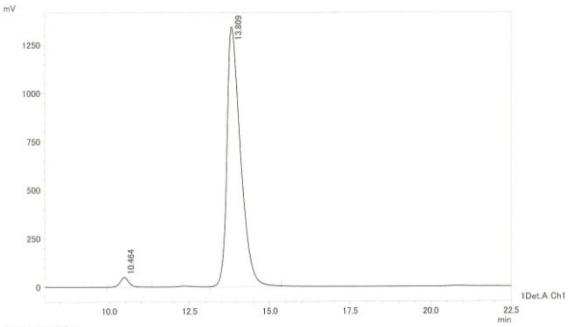
ピーク#	保持時間	面積%
1	6.854	1.503
2	10.208	3.834
3	13.376	71.321
4	17.359	23.342
合計		100.000

4m



検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	9.905	11.264
2	11.680	38.644
3	13.279	11.444
4	20.405	38.649
合計		100.000

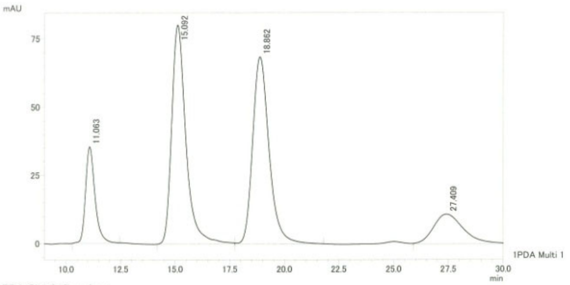


1Det.A Ch1/210nm

検出器A Ch1 210nm

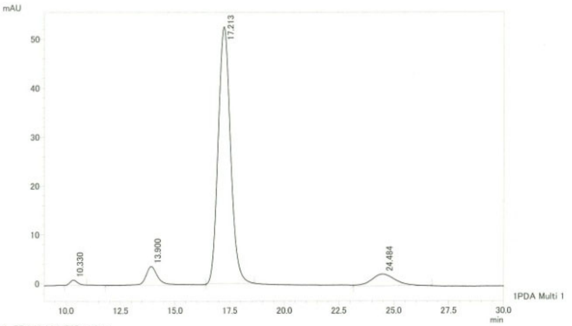
ピーク#	保持時間	面積%
1	10.464	2.399
2	13.809	97.601
合計		100.000

4n



PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	11.063	11.611
2	15.092	38.847
3	18.862	38.426
4	27.409	11.116
合計		100.000

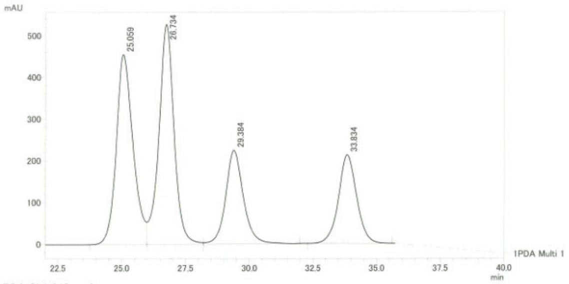


1 PDA Multi 1/210nm 4nm

PDA Ch1 210nm 4nm

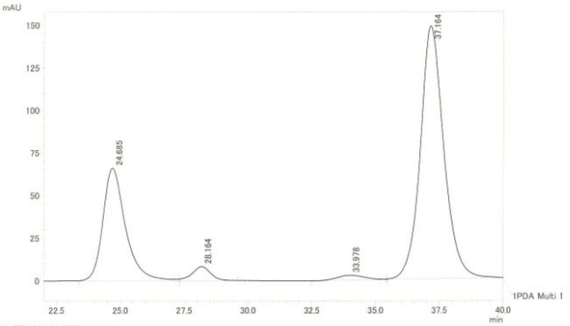
ピーク#	保持時間	面積%
1	10.330	0.995
2	13.900	7.189
3	17.213	84.444
4	24.484	7.372
合計		100.000

4o



PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	25.059	32.553
2	26.734	34.135
3	29.384	16.852
4	33.834	16.460
合計		100.000

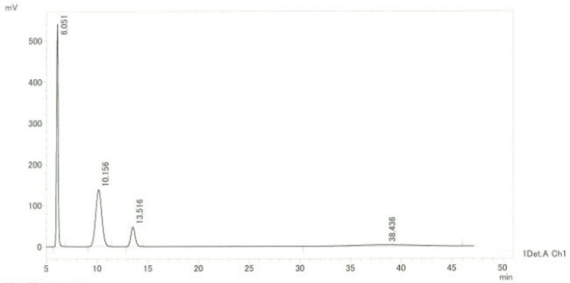


1 PDA Multi 1/210nm 4nm

PDA Ch1 210nm 4nm

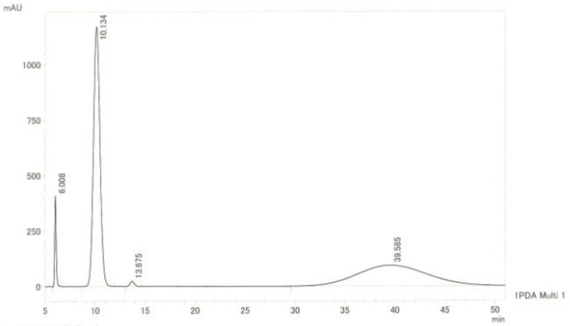
ピーク#	保持時間	面積%
1	24.685	28.544
2	28.164	2.865
3	33.978	1.433
4	37.164	67.158
合計		100.000

4p



検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	6.051	40.275
2	10.156	40.574
3	13.516	9.682
4	38.436	9.469
合計		100.000

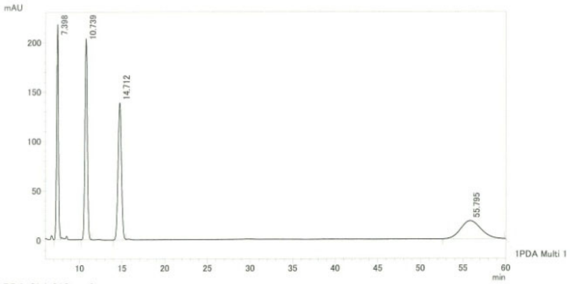


1 PDA Multi 1/210nm 4nm

PDA Ch1 210nm 4nm

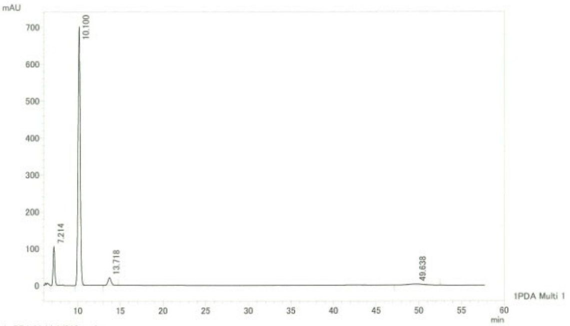
ピーク#	保持時間	面積%
1	6.008	4.218
2	10.134	51.331
3	13.675	0.652
4	39.585	43.799
合計		100.000

4q



PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	7.398	22.300
2	10.739	28.207
3	14.712	28.221
4	55.795	21.272
合計		100.000

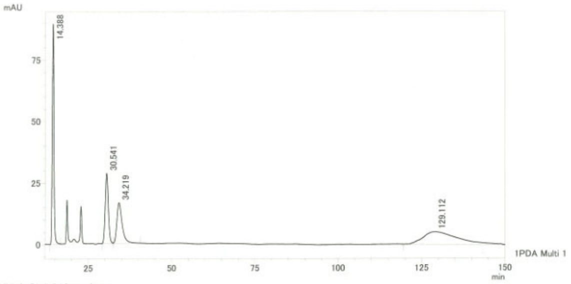


1 PDA Multi 1/210nm 4nm

PDA Ch1 210nm 4nm

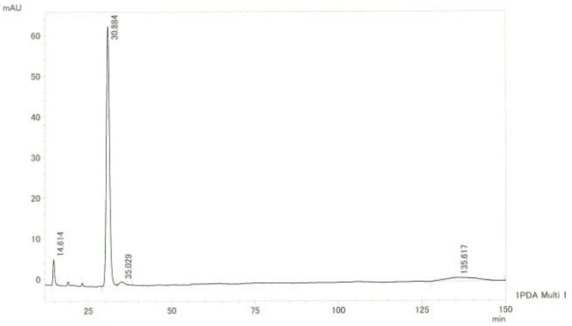
ピーク#	保持時間	面積%
1	7.214	9.500
2	10.100	84.405
3	13.718	3.465
4	49.638	2.630
合計		100.000

4r



PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	14.388	28.682
2	30.541	17.693
3	34.219	17.539
4	129.112	36.086
合計		100.000



1 PDA Multi 1/210nm 4nm

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	14.614	4.117
2	30.884	81.956
3	35.029	1.971
4	135.617	11.956
合計		100.000