SUPPORTING INFORMATION

Convenient One-Pot Synthesis of (*E*)-β-Aryl Vinyl Halides from Benzyl Bromides and Dihalomethanes

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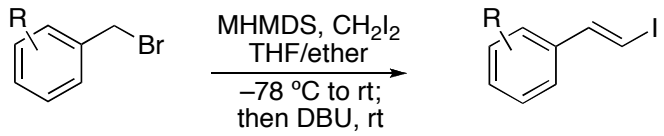
General Conditions: All non-aqueous reactions were run under an inert atmosphere (argon) with flame-dried glassware using standard techniques for manipulating air-sensitive compounds. Anhydrous solvents were obtained by filtration through drying columns (THF, diethyl ether).
Flash column chromatography was performed using 230-400 mesh silica with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) and/or aqueous potassium permanganate.
Nuclear magnetic resonance spectra were recorded either on 300 MHz or 400 MHz spectrometers. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ = 7.26 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (77.0 ppm) as the internal standard. Only the NMR signals from the major *E*-isomers are recorded.
Infrared spectra (FTIR) are reported in reciprocal centimeters (cm^{-1}).

Reagents: Commercial reagents were used as supplied or purified by standard techniques where necessary.

Compound Handling/Storage: Some of the vinyl iodides underwent decomposition upon prolongued exposure to light. However, the vinyl halide products may be stored for prolonged periods (>1 month) under argon at –20 ºC without noticeable decomposition.

Experimental Procedures

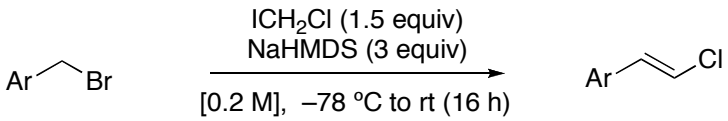
Synthesis of (*E*)-β-Aryl Vinyl Iodides from Benzyl Bromides and CH_2I_2



Method A:
A solution of CH_2I_2 (483 μL, 6.0 mmol) in THF (1.5 mL) was added dropwise to a solution of NaHMDS (2.20 g, 12.0 mmol) in THF (8 mL) and ether (8 mL) at –78 °C (dry ice/acetone bath) in the dark. After 20 min, a solution of the benzyl bromide substrate (4.0 mmol) in THF (3 mL) was added dropwise. The reaction mixture was stirred for 90 min then removed from the cold bath to warm to rt. After 30 min, DBU (597 μL, 4.0 mmol) was added dropwise and the solution stirred for 1 h before ether (50 mL) was added. The mixture was filtered through a plug of celite/silica (approximately 3 cm celite over 3 cm silica) and the solvent removed under reduced pressure. The residue was purified by flash chromatography to provide the pure vinyl iodide.

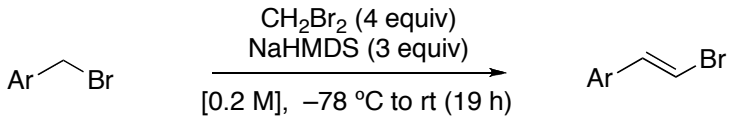
Method B:
A solution of CH_2I_2 (644 μL, 8.0 mmol) in THF (1.9 mL) was added dropwise to a solution of LiHMDS (1.34 g, 8.0 mmol) in THF (8 mL) and ether (8 mL) at –78 °C (dry ice/acetone bath) in the dark. After 20 min, a solution of the benzyl bromide substrate (4.0 mmol) in THF (3 mL) was added dropwise. The reaction mixture was stirred at –78 ºC allowing to warm to rt slowly over 16 h. After this time DBU (1.19 mL, 8.0 mmol) was added dropwise and the solution stirred for 1 h before ether (50 mL) was added. The mixture was filtered through a plug of celite/silica (approximately 3 cm celite over 3 cm silica) and the solvent removed under reduced pressure. The residue was purified by flash chromatography to provide the vinyl iodide. Where necessary, residual CH_2I_2 following flash chromatography was removed under high vacuum.

Synthesis of (*E*)-β-Aryl Vinyl Chlorides from Benzyl Bromides and ICH_2Cl



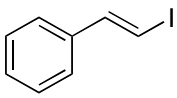
Chloroiodomethane (109 μL, 1.5 mmol) was added dropwise to a solution of NaHMDS (550 mg, 3.0 mmol) in THF (2 mL) and ether (2 mL) at –78 °C (dry ice/acetone bath) in the dark. After 20 min, a solution of the benzyl bromide substrate (1.0 mmol) in THF (1 mL) was added dropwise. The reaction mixture was stirred at –78 ºC allowing to warm to rt slowly over 16 h. Ether (50 mL) was added then the mixture was filtered through a plug of celite/silica (approximately 3 cm celite over 3 cm silica) and the solvent removed under reduced pressure. The residue was purified by flash chromatography to provide the pure vinyl chloride.

Synthesis of (*E*)-β-Aryl Vinyl Bromides from Benzyl Bromides and CH_2Br_2



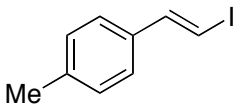
Dibromomethane (281 μL, 4 mmol) was added dropwise to a solution of NaHMDS (550 mg, 3.0 mmol) in THF (2 mL) and ether (2 mL) at –78 °C (dry ice/acetone bath) in the dark. After 20 min, a solution of the benzyl bromide substrate (1.0 mmol) in THF (1 mL) was added dropwise. The reaction mixture was maintained at –78 ºC for at least 3 h then continued stirred at –78 ºC allowing to warm to rt slowly over 16 h. Ether (50 mL) was added then the mixture was filtered through a plug of celite/silica (approximately 3 cm celite over 3 cm silica) and the solvent removed under reduced pressure. The residue was purified by flash chromatography to provide the vinyl bromide.

Characterisation Data: (*E*)-β-Aryl Vinyl Iodides



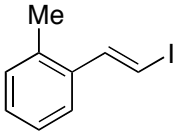
(*E*)-(2-Iodovinyl)benzene (3a)

Prepared according to the general procedure (Method A) starting from benzyl bromide **1a** (684 mg, 4.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl iodide **3a** as a yellow oil (849 mg, 92%, 98:2 *E*:*Z*). The observed characterization data (^{1}H, ^{13}C) was consistent with that previously reported in the literature.[1] R*f* 0.65 (100% hexane). IR (film)/cm^{-1} 3059, 3021, 1595, 1494, 1444, 1210, 1169, 1070, 945, 726, 688. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.44 (d, *J* = 14.9 Hz, 1H), 7.38-7.27 (m, 5H), 6.84 (dd, *J* = 14.9, 1.8 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 145.0, 137.6, 128.7, 128.4, 126.0, 76.7.



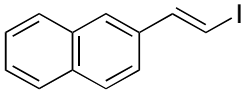
(*E*)-1-(2-Iodovinyl)-4-methylbenzene (3b)

Prepared according to the general procedure (Method A) starting from 4-methylbenzyl bromide **1b** (740 mg, 4.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl iodide **3b** as an off-white solid (906 mg, 93%, 99:1 *E*:*Z*). The observed characterization data (^{1}H) was consistent with that previously reported in the literature.[2] R*f* 0.54 (100% hexane). IR (film)/cm^{-1} 3053, 3029, 2915, 2859, 1608, 1591, 1561, 1509, 1379, 1280, 1189, 1172, 958, 939, 827, 765. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.40 (d, *J* = 14.9 Hz, 1H), 7.21-7.13 (m, 4H), 6.75 (d, *J* = 14.9 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 144.7, 138.2, 134.9, 129.3, 125.8, 75.4, 21.3.



(*E*)-1-(2-Iodovinyl)-2-methylbenzene (3c)

Prepared according to the general procedure (Method A) starting from 2-methylbenzyl bromide **1c** (740 mg, 4.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl iodide **3c** as an off-white solid (879 mg, 90%, 99:1 *E*:*Z*). The observed characterization data (^{1}H) was consistent with that previously reported in the literature.[1] R*f* 0.63 (100% hexane). IR (film)/cm^{-1} 3055, 3017, 2921, 1587, 1562, 1479, 1457, 1379, 1280, 1190, 1176, 947, 740. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.63 (d, *J* = 14.7 Hz, 1H), 7.32-7.11 (m, 4H), 6.68 (d, *J* = 14.7 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 143.3, 136.9, 134.7, 130.3, 128.2, 126.2, 125.6, 77.7, 19.7.



(*E*)-2-(2-Iodovinyl)naphthalene (3d)

Prepared according to the general procedure (Method A) starting from 2-(bromomethyl)napthylene **1d** (884 mg, 4.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl iodide **3d** as a yellow solid (782 mg, 70%, 98:2 *E*:*Z*). The observed characterization data (^{1}H, ^{13}C) was consistent with that previously reported in the literature.[1] R*f* 0.53 (100% hexane). IR (film)/cm^{-1} 3049, 1599, 1585, 1507, 1433, 1293, 1274, 1216, 1181, 1152, 952, 828, 781, 765, 735. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.81-7.75 (m, 3H), 7.65 (s, 1H), 7.56 (d, *J* = 14.9 Hz, 1H), 7.46 (m, 3H), 6.94 (d, *J* = 14.9 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 145.0, 135.0, 133.3, 133.1, 128.4, 128.2, 127.7, 126.6, 126.4, 126.2, 122.7, 77.0.

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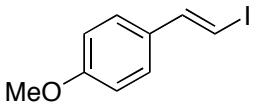
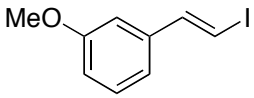
[1] Lee, G. C. M.; Tobias, B.; Holmes, J. M.; Harcourt, D. A.; Garst, M. E. *J. Am. Chem. Soc.* **1990**, *112*, 9330-9336.

[2] Shastin, A. V.; Korotchenko, V. N.; Varseev, G. N.; Nenaidenko, V. G.; Balenkova, E. S. *Russ. J. Org. Chem.* **2003**, *39*, 403-407.



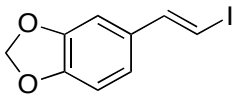
(*E*)-1-(2-Iodovinyl)-4-methoxybenzene (3e)

Prepared according to a modification of the general procedure (Method A) on a 1 mmol scale starting from 4-methoxybenzyl bromide **1e** (220 mg, 1.1 mmol) and employing excess DBU (240 μL, 1.5 mmol). Purification by flash chromatography (5% ether/hexane) afforded vinyl iodide **3e** as a white solid (265 mg, 92%, 97:3 *E*:*Z*). The observed characterization data (^{1}H) was consistent with that previously reported in the literature.[1] R*f* 0.71 (5% ether/hexane). IR (film)/cm^{-1} 3055, 3005, 2965, 2933, 2838, 1602, 1509, 1460, 1250, 1177, 1028, 948, 840, 770. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.37 (d, *J* = 14.9 Hz, 1H), 7.26-7.23 (m, 2H), 6.88-6.85 (m, 2H), 6.64 (d, *J* = 14.9 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 159.7, 144.3, 130.7, 127.2, 114.0, 73.6, 55.3.



(*E*)-1-(2-Iodovinyl)-3-methoxybenzene (3f)

Prepared according to a modification of the general procedure (Method A) starting from 3-methoxybenzyl bromide **1f** (834 mg, 4.1 mmol) and employing excess DBU (900 μL, 6.0 mmol). Purification by flash chromatography (5% ether/hexane) afforded vinyl iodide **3f** as a yellow oil (1.038 g, 95%, 99:1 *E*:*Z*). R*f* 0.70 (5% ether/hexane). IR (film)/cm^{-1} 3057, 2999, 2936, 2832, 1596, 1572, 1490, 1463, 1428, 1313, 1284, 1261, 1152, 1048, 944, 757, 684. ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.43 (d, *J* = 14.9 Hz, 1H), 7.27 (t, *J* = 7.9 Hz, 1H), 6.93-6.85 (m, 4H), 3.84 (s, 3H).^{13}C NMR (100 MHz; $CDCl_3$): δ 159.6, 144.7, 138.8, 129.6, 118.5, 113.9, 111.2, 77.1, 55.2. HRMS Calcd for C_9H_9IO $[M]^+$: 259.9693 Found: 259.9691.[3]



(*E*)-5-(2-Iodovinyl)benzo[d][1,3]dioxole (3g)

Prepared according to a modification of the general procedure (Method A) starting from 3,4-(methylenedioxy)benzyl bromide **1g**[4] (860 mg, 4.0 mmol) and employing excess DBU (896 μL, 6.0 mmol). Purification by flash chromatography (5% ether/hexane) afforded vinyl iodide **3g** as a white solid (1.02 g, 93%, 99:1 *E*:*Z*). R*f* 0.42 (5% ether/hexane). IR (film)/cm^{-1} 3058, 2890, 2777, 1499, 1487, 1444, 1350, 1247, 1171, 1037, 943, 928, 762. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.31 (d, *J* = 14.9 Hz, 1H), 6.81 (m, 1H), 6.74 (m, 2H), 6.62 (dd, *J* = 14.8, 0.1 Hz, 1H), 5.96 (d, *J* = 0.2 Hz, 2H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 148.0, 147.8, 144.3, 132.2, 120.9, 108.3, 105.2, 101.3, 74.1. HRMS Calcd for $C_9H_7IO_2$ $[M]^+$: 273.9485 Found: 273.9491.[5]

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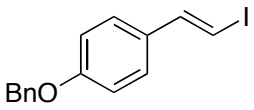
[3] Compound previously reported: Furstner, A.; Dierkes, T.; Thiel, O. R.; Blanda, G. *Chem. Eur. J.* **2001**, *7*, 5286-5298.

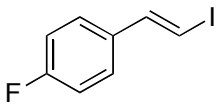
[4] Prepared according to previously reported procedure: Imperio, D.; Pirali, T.; Galli, U.; Pagliai, F.; Cafici, L.; Luigi Canonico, P.; Sorba, G.; Genazzani, A. A.; Cesare Tron, G. *Bioorg. Med. Chem.* **2007**, *15*, 6748-6757.

[5] Compound previously reported: Naskar, D.; Roy, S. *Tetrahedron* **2000**, *56*, 1369-1377.



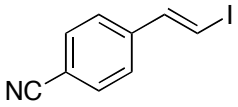
(*E*)-1-(2-Iodovinyl)-4-benzyloxybenzene (3h)

Prepared according to a modification of the general procedure (Method B) starting from 1-(benzyloxy)-4-(bromomethyl)benzene **1h**[6] (1.11g mg, 4.0 mmol) and employing excess DBU (1.8 mL, 12.0 mmol). Purification by flash chromatography (1% ether/hexane) afforded vinyl iodide **3h** as an off-white solid (1.02 g, 76%, 99:1 *E*:*Z*). R*f* 0.18 (1% ether/hexane). IR (film)/cm^{-1} 3054, 2932, 2868, 1600, 1508, 1467, 1454, 1377, 1281, 1250, 1181, 999, 947, 836, 768, 747, 735, 701. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.44-7.32 (m, 6H), 7.24-7.19 (m, 2H), 6.94-6.90 (m, 2H), 6.62 (d, *J* = 14.9 Hz, 1H), 5.05 (s, 2H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 158.9, 144.2, 136.6, 130.9, 128.6, 128.0, 127.44, 127.26, 115.0, 73.8, 70.0. HRMS Calcd for $C_{15}H_{13}IOAg$ $[M + Ag]^+$: 442.9057 Found: 442.9063.



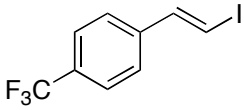
(*E*)-1-Fluoro-4-(2-iodovinyl)benzene (3i)

Prepared according to the general procedure (Method A) starting from 4-fluorobenzyl bromide **1i** (756 mg, 4.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl iodide **3i** as a yellow solid (843 mg, 85%, 98:2 *E*:*Z*).R*f* 0.66 (100% hexane). IR (film)/cm^{-1} 3056, 1598, 1578, 1505, 1230, 1172, 1157, 949, 837, 769. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.36 (d, *J* = 14.9 Hz, 1H), 7.27-7.22 (m, 2H), 7.02-6.95 (m, 2H), 6.73 (dd, *J* = 14.9, 0.6 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 162.5 (d, *J* = 249 Hz), 143.7, 133.9 (d, *J* = 3 Hz), 127.6 (d, *J* = 8 Hz), 115.7 (d, *J* = 22 Hz), 76.1 (d, 2.5 Hz). HRMS Calcd for C_8H_6FI $[M]^+$: 247.9493 Found: 247.9493.



(*E*)-4-(2-Iodovinyl)benzonitrile (3j)

Prepared according to the general procedure (Method B) starting from 4-(bromomethyl)benzonitrile **1j** (756 mg, 4.0 mmol). Purification by flash chromatography (10% ether/hexane) afforded vinyl iodide **3j** as a pale yellow solid (843 mg, 51%, 99:1 *E*:*Z*). R*f* 0.34 (10% ether/hexane). IR (film)/cm^{-1} 3242, 3048, 2221, 1601, 1407, 1173, 937, 840, 771. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.59-7.56 (m, 2H), 7.40 (d, *J* = 15.0 Hz, 1H), 7.35-7.33 (m, 2H), 7.06 (d, *J* = 15.0 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 143.2, 141.4, 132.5, 126.3, 118.5, 111.5, 81.7. HRMS Calcd for C_9H_6INAg $[M + Ag]^+$: 361.8590 Found: 361.8596.[7]



(*E*)-1-(2-Iodovinyl)-4-(trifluoromethyl)benzene (3k)

Prepared according to the general procedure (Method B) starting from 4-(trifluoromethyl)benzyl bromide **1k** (956 mg, 4.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl iodide **3k** as a yellow solid (750 mg, 63%, 99:1 *E*:*Z*). R*f* 0.39 (100% hexane). IR (film)/cm^{-1} 3055, 1614, 1409, 1322, 1160, 1106, 1066, 940, 844, 776. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 15.0 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 15.0 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 143.6, 140.7 (q, *J* = 1 Hz), 130.1 (q, *J* = 33 Hz), 126.1, 125.7 (q, *J* = 4 Hz), 124.0 (q, *J* = 274 Hz), 118.6.[8]

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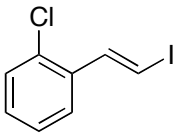
[6] Prepared from 4-benzyloxybenzyl alcohol by a previously reported procedure: Albert, S.; Soret, A.; Blanco, L.; Deloisy, S. *Tetrahedron* **2007**, *63*, 2888-2900.

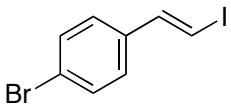
[7] Compound previously reported: Furstner, A.; Brunner, H. *Tetrahedron Lett.* **1996**, *37*, 7009-7012

[8] Compound previously reported: Shimizu, M.; Shimono, K.; Schelper, M.; Hiyama, T. *Synlett* **2007**, 1969-1971.



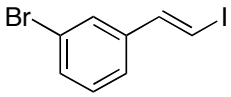
(*E*)-1-Chloro-2-(2-iodovinyl)benzene (3l)

Prepared according to the general procedure (Method A) starting from 2-chlorobenzyl bromide **1l** (823 mg, 4.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl iodide **3l** as a yellow oil (816 mg, 78%, 98:2 *E*:*Z*). R*f* 0.75 (100% hexane). IR (film)/cm^{-1} 3057, 1590, 1466, 1438, 1274, 1180, 1121, 1051, 946, 747. ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.80 (d, *J* = 14.9 Hz, 1H), 7.42-7.33 (m, 2H), 7.26-7.21 (m, 2H), 6.90 (d, *J* = 14.9 Hz, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ 141.2, 135.6, 132.0, 129.9, 129.2, 126.9, 126.7, 79.6. HRMS Calcd for $C_8H_6ClI_2$ $[M]^+$: 263.9197 Found: 263.9200.



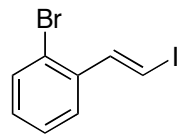
(*E*)-1-Bromo-4-(2-iodovinyl)benzene (3m)

Prepared according to the general procedure, (Method B) starting from 4-bromobenzyl bromide **1m** (1.0 g, 4.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl iodide **3m** as an off-white solid (1.07 g, 87%, 99:1 *E*:*Z*). R*f* 0.74 (100% hexane). IR (film)/cm^{-1} 3044, 1582, 1483, 1394, 1169, 1072, 1007, 959, 941, 832, 766, 708. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.44-7.40 (m, 2H), 7.34 (d, *J* = 14.9 Hz, 1H), 7.15-7.12 (m, 2H), 6.84 (d, *J* = 14.9 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 143.7, 136.5, 131.8, 127.4, 122.3, 77.6. HRMS Calcd for C_8H_6BrI $[M]^+$: 307.8692 Found: 307.8700.



(*E*)-1-Bromo-3-(2-iodovinyl)benzene (3n)

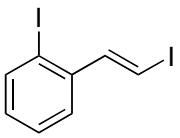
Prepared according to the general procedure, (Method B) starting from 3-bromobenzyl bromide **1n** (1.0 g, 4.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl iodide **3n** as a yellow oil (1.08 g, 87%, 98:2 *E*:*Z*). The observed characterization data (^{1}H) was consistent with that previously reported in the literature.[9] R*f* 0.56 (100% hexane). IR (film)/cm^{-1} 3056, 1590, 1557, 1474, 1209, 1071, 942, 755. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.42-7.37 (m, 2H), 7.33 (d, *J* = 14.9 Hz, 1H), 7.20-7.14 (m, 2H), 6.87 (d, *J* = 14.9 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 143.3, 139.4, 131.1, 130.1, 128.8, 124.5, 122.8, 78.7.



(*E*)-1-Bromo-2-(2-iodovinyl)benzene (3o)

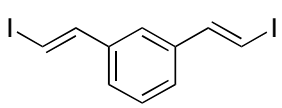
Prepared according to the general procedure, (Method B) starting from 2-bromobenzyl bromide **1o** (1.0 g, 4.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl iodide **3o** as a yellow oil (1.09 g, 87%, 98:2 *E*:*Z*). The observed characterization data (^{1}H, ^{13}C) was consistent with that previously reported in the literature.[2] R*f* 0.48 (100% hexane). IR (film)/cm^{-1} 3056, 1587, 1461, 1434, 1180, 1027, 945, 938, 743. ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.76 (d, *J* = 14.8 Hz, 1H), 7.55 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.40 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.30-7.26 (m, 1H), 7.16 (td, *J* = 7.7, 1.7 Hz, 1H), 6.86 (d, *J* = 14.8 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 143.7, 137.5, 132.9, 129.5, 127.6, 127.0, 122.3, 79.9.

[9] Allred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1996**, *118*, 2748-2749.



(*E*)-1-Iodo-2-(2-iodovinyl)benzene (3p)

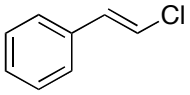
Prepared according to the general procedure (Method B) on a 1 mmol scale, starting from 2-iodobenzyl bromide **1p** (297 mg, 1.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl iodide **3p** as a yellow oil (260 g, 73%, 99:1 *E*:*Z*).R*f* 0.57 (100% hexane). IR (film)/cm^{-1} 3053, 1584, 1456, 1429, 1323, 1177, 1015, 1007, 935, 742. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.82 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.60 (d, *J* = 14.7 Hz, 1H), 7.37-7.28 (m, 2H), 7.01-6.95 (m, 1H), 6.78 (d, *J* = 14.7 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 148.4, 141.1, 139.5, 129.7, 128.5, 126.7, 98.0, 80.0. HRMS Calcd for $C_8H_7I_2$ [M]$^+$: 356.8632 Found: 356.8647.



1,3-bis((*E*)-2-Iodovinyl)benzene (5)

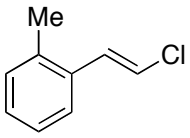
A solution of CH_2I_2 (483 μL, 6.0 mmol) in THF (1.5 mL) was added dropwise to a solution of NaHMDS (2.20 g, 12.0 mmol) in THF (8 mL) and ether (8 mL) at –78 °C (dry ice/acetone bath) in the dark. After 20 min, a solution of α,α'-dibromo-m-xylene **5** (528 mg, 2.0 mmol) in THF (3 mL) was added dropwise. The reaction mixture was stirred for 90 min then removed from the cold bath to warm to rt. After 30 min, DBU (597 μL, 4.0 mmol) was added dropwise and the solution stirred for 1 h before ether (50 mL) was added. The mixture was filtered through a plug of celite/silica (approximately 3 cm celite over 3 cm silica) and the solvent removed under reduced pressure. Purification by flash chromatography (100% hexane) afforded vinyl iodide **6** as a pale yellow solid (560 mg, 73%, 97:3 *EE*:*EZ*). R*f* 0.44 (100% hexane). IR (film)/cm^{-1} 3046, 1598, 1584, 1569, 1481, 1172, 945, 752. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.39 (d, *J* = 14.9 Hz, 2H), 7.26-7.17 (m, 4H), 6.84 (d, *J* = 14.9 Hz, 2H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 144.4, 138.1, 129.1, 125.8, 123.6, 77.6. HRMS Calcd for $C_{10}H_8I_2$ [M]$^+$: 381.8710 Found: 381.8707.

Characterisation Data: (*E*)-β-Aryl Vinyl Chlorides



(*E*)-(2-Chlorovinyl)benzene (6a)

Prepared according to the general procedure for vinyl chlorides starting from benzyl bromide **1a** (171 mg, 1.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl chloride **6a** as a colourless oil (123 mg, 89%, 97:3 *E*:*Z*). The observed characterization data (^{1}H) was consistent with that previously reported in the literature.[10] R*f* 0.60 (100% hexane). IR (film)/cm^{-1} 3076, 3025, 1607, 1573, 1497, 1446, 1245, 1073, 936, 737, 691. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.38-7.26 (m, 5H), 6.86 (d, *J* = 13.7 Hz, 1H), 6.66 (dd, *J* = 13.7, 0.5 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 134.8, 133.2, 128.7, 128.1, 126.1, 118.7.

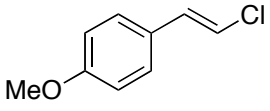


(*E*)-1-(2-Chlorovinyl)-2-methylbenzene (6c)

Prepared according to the general procedure for vinyl chlorides starting from 4-methylbenzyl bromide **1c** (185 mg, 1.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl chloride **6c** as a colourless oil (129 mg, 85%, 97:3 *E*:*Z*). The observed characterization data (^{1}H, ^{13}C) was consistent with that

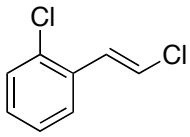
[10] Rajanna, K. C.; Maasi Reddy, N.; Rajender Reddy, M.; Saiprakash, P. K. *J. Disp. Sci. Technol.* **2007**, 613-616.

previously reported in the literature.[11] R*f* 0.58 (100% hexane). IR (film)/cm^{-1} 3068, 3019, 1611, 1481, 1459, 1239, 931, 832, 743, 605. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.36-7.32 (m, 1H), 7.24-7.18 (m, 3H), 7.07 (d, *J* = 13.5 Hz, 1H), 6.54 (d, *J* = 13.5 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 135.3, 133.9, 131.5, 130.4, 128.1, 126.2, 125.7, 119.3, 19.7.



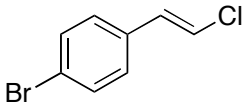
(*E*)-1-(2-Chlorovinyl)-4-methoxybenzene (6e)

Prepared according to the general procedure for vinyl chlorides starting from 4-methoxybenzyl bromide **1e** (201 mg, 1.0 mmol). Purification by flash chromatography (5% ether/hexane) afforded vinyl chloride **6e** as a colourless oil (149 mg, 88%, 96:4 *E*:*Z*). The observed characterization data (^{1}H, ^{13}C) was consistent with that previously reported in the literature.[11] R*f* 0.41 (5% ether/hexane). IR (film)/cm^{-1} 3073, 2956, 2935, 2836, 1606, 1510, 1465, 1302, 1240, 1175, 1032, 832. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.23-7.20 (m, 2H), 6.85-6.83 (m, 2H), 6.76 (d, *J* = 13.7 Hz, 1H), 6.49 (d, *J* = 13.6 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 159.5, 132.6, 127.6, 127.3, 116.3, 114.2, 55.3.



(*E*)-1-Chloro-2-(2-chlorovinyl)benzene (6l)

Prepared according to the general procedure for vinyl chlorides starting from 2-chlorobenzyl bromide **1l** (205 mg, 1.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl chloride **6l** as a colourless oil (96 mg, 55%, >99:1 *E*:*Z*). The observed characterization data (^{1}H, ^{13}C) was consistent with that previously reported in the literature.[12] R*f* 0.45 (100% hexane). IR (film)/cm^{-1} 3070, 1607, 1469, 1439, 1125, 1050, 930, 745. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.40-7.33 (m, 2H), 7.24-7.16 (m, 3H), 6.64 (d, *J* = 13.7 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 133.1, 132.6, 129.92, 129.90, 129.2, 126.99, 126.84, 121.2.

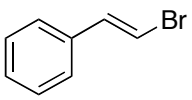


(*E*)-1-Bromo-4-(2-chlorovinyl)benzene (6m)

Prepared according to the general procedure for vinyl chlorides starting from 4-bromobenzyl bromide **1m** (205 mg, 1.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl chloride **6m** as a colourless oil (96 mg, 55%, >99:1 *E*:*Z*). The observed characterization data (^{1}H) was consistent with that previously reported in the literature.[13] R*f* 0.62 (100% hexane). IR (film)/cm^{-1} 3071, 1607, 1487, 1397, 1074, 927, 780. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.45-7.40 (m, 2H), 7.16-7.12 (m, 2H), 6.75 (dd, *J* = 13.7, 0.2 Hz, 1H), 6.63 (d, *J* = 13.7 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 133.6, 132.1, 131.8, 127.5, 121.9, 119.4

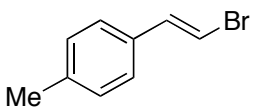
[11] Barluenga, J.; Moriel, P.; Aznar, F.; Valdés, C. *Adv. Synth. Catal.* **2006**, *348*, 347-353.
[12] Miyano, S.; Izumi, Y.; Fujii, K.; Ohno, Y.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1197-1202.
[13] Kauffmann, T.; Salker R.; Vo, K.-U. *Chem. Ber.* **1993**, *126*, 1447- 1452

Characterisation Data: (*E*)-β-Aryl Vinyl Bromides



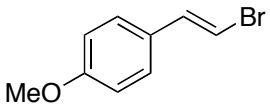
(*E*)-(2-Bromovinyl)benzene (7a)

Prepared according to the general procedure for vinyl bromides starting from benzyl bromide **1a** (171 mg, 1.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl bromide **7a** as a colourless oil (127 mg, 69%, 99:1 *E*:*Z*). The observed characterization data (^{1}H, ^{13}C) was consistent with that previously reported in the literature.[14] R*f* 0.60 (100% hexane). IR (film)/cm^{-1} 3074, 3024, 1607, 1496, 1445, 1221, 939, 730. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.37-7.29 (m, 5H), 7.12 (d, *J* = 14.0 Hz, 1H), 6.78 (d, *J* = 14.0 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 137.1, 135.9, 128.8, 128.2, 126.1, 106.5



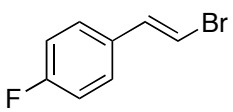
(*E*)-1-(2-Bromovinyl)-4-methylbenzene (7b)

Prepared according to the general procedure for vinyl bromides starting from 4-methylbenzyl bromide **1b** (186 mg, 1.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl bromide **7b** as a white solid (179 mg, 91%, >99:1 *E*:*Z*). The observed characterization data (^{1}H, ^{13}C) was consistent with that previously reported in the literature.[14] R*f* 0.59 (100% hexane). IR (film)/cm^{-1} 3070, 2914, 1602, 1509, 1226, 1194, 949, 936, 907, 825, 769, 725. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.24-7.12 (m, 4H), 7.08 (d, *J* = 14.0 Hz, 1H), 6.71 (d, *J* = 14.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 138.1, 136.9, 133.1, 129.4, 125.9, 105.4, 21.2



(*E*)-1-(2-Bromovinyl)-4-methoxybenzene (7e)

Prepared according to the general procedure for vinyl bromides starting from 4-methoxybenzyl bromide **1e** (201 mg, 1.0 mmol). Purification by flash chromatography (5% ether/hexane) afforded vinyl bromide **7e** as a white solid (153 mg, 72%, >99:1 *E*:*Z*). The observed characterization data (^{1}H, ^{13}C) was consistent with that previously reported in the literature.[14] R*f* 0.46 (5% ether/hexane). IR (film)/cm^{-1} 3067, 2956, 2932, 2837, 1605, 1510, 1460, 1304, 1254, 1177, 1028, 950, 836, 776. ^{1}H-NMR (300 MHz; $CDCl_3$): δ 7.24-7.20 (m, 2H), 7.02 (d, *J* = 13.9 Hz, 1H), 6.85-6.82 (m, 2H), 6.59 (d, *J* = 13.9 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 159.5, 136.4, 128.6, 127.2, 114.1, 103.9, 55.2.

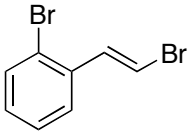


(*E*)-1-Fluoro-4-(2-bromovinyl)benzene (7i)

Prepared according to the general procedure for vinyl bromides starting from 4-fluorobenzyl bromide **1i** (189 mg, 1.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl bromide **7i** as a colourless oil (159 mg, 79%, >99:1 *E*:*Z*). The observed characterization data (^{1}H, ^{13}C) was consistent with that previously reported in the literature.[15] R*f* 0.53 (100% hexane). IR (film)/cm^{-1} 3056, 1590, 1557, 1474, 1421, 1209, 1071, 942, 755. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.27-7.22 (m, 2H), 7.07-6.97 (m, 3H), 6.67 (dd, *J* = 14.0, 0.4 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 162.6 (d, *J* = 248 Hz), 136.0, 132.1 (d, *J* = 3 Hz), 127.7 (d, *J* = 8 Hz), 115.8 (d, *J* = 22 Hz), 106.9 (d, 2.5 Hz).

[14] Kuang, C.; Senboku, H.; Tokuda, M. *Tetrahedron*, **2002**, *58*, 1491-1496

[15] Kuang, C.; Yang, Q.; Senboku, H.; Tokuda, M. *Synthesis*, **2005**, 1319-1325.

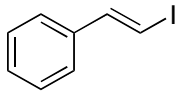


(*E*)-1-Bromo-2-(2-bromovinyl)benzene (7o)

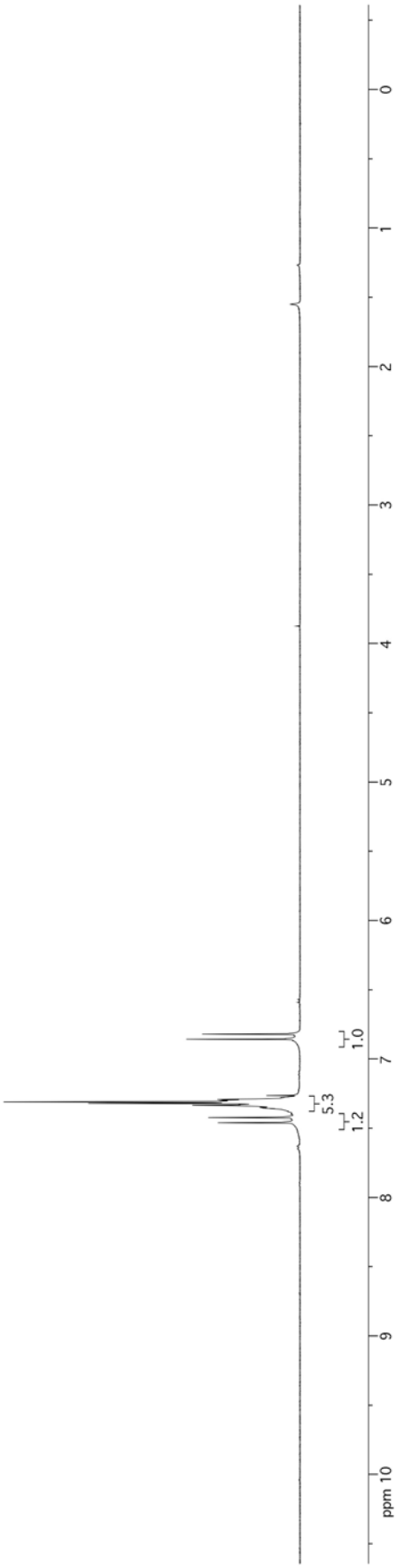
Prepared according to the general procedure for vinyl bromides starting from 2-bromobenzyl bromide **1o** (250 mg, 1.0 mmol). Purification by flash chromatography (100% hexane) afforded vinyl bromide **7o** as a colourless oil (175 mg, 67%, >99:1 *E*:*Z*). The observed characterization data (^{1}H, ^{13}C) was consistent with that previously reported in the literature.[16] R*f* 0.56 (100% hexane). IR (film)/cm^{-1} 3069, 1603, 1463, 1435, 1219, 1020, 931, 740. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.55-7.52 (m, 1H), 7.42 (d, *J* = 13.9 Hz, 1H), 7.38-7.35 (m, 1H), 7.28-7.23 (m, 1H), 7.16-7.11 (m, 1H), 6.74 (d, *J* = 13.9 Hz, 1H). ^{13}C NMR (75 MHz; $CDCl_3$): δ 136.2, 135.9, 133.1, 129.6, 127.6, 127.1, 122.7, 109.2.

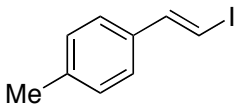
[16] Horibe, H.; Fukuda, Y.; Kondo, K.; Okuno, H.; Murakamia, Y.; Aoyama, T. *Tetrahedron* **2004**, *60*, 10701–10709.

^{1}H and ^{13}C NMR spectra of selected compounds

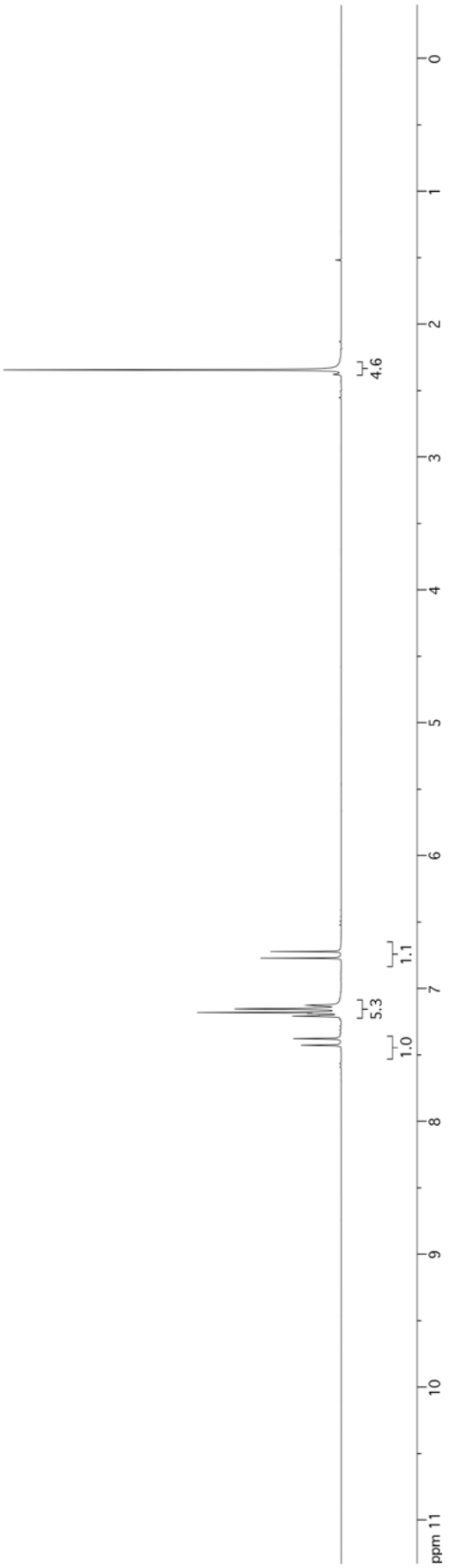


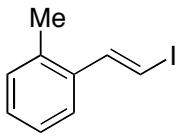
3a
^{1}H NMR (300 MHz, $CDCl_3$)



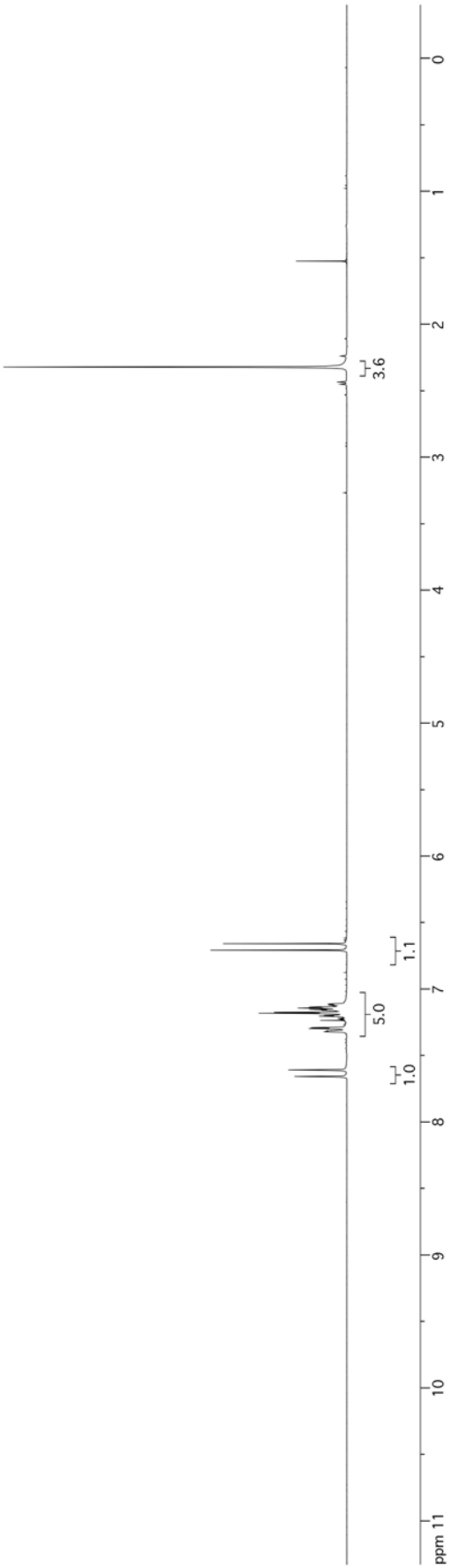


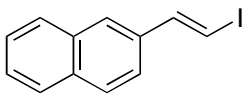
3b
^{1}H NMR (300 MHz, $CDCl_3$)



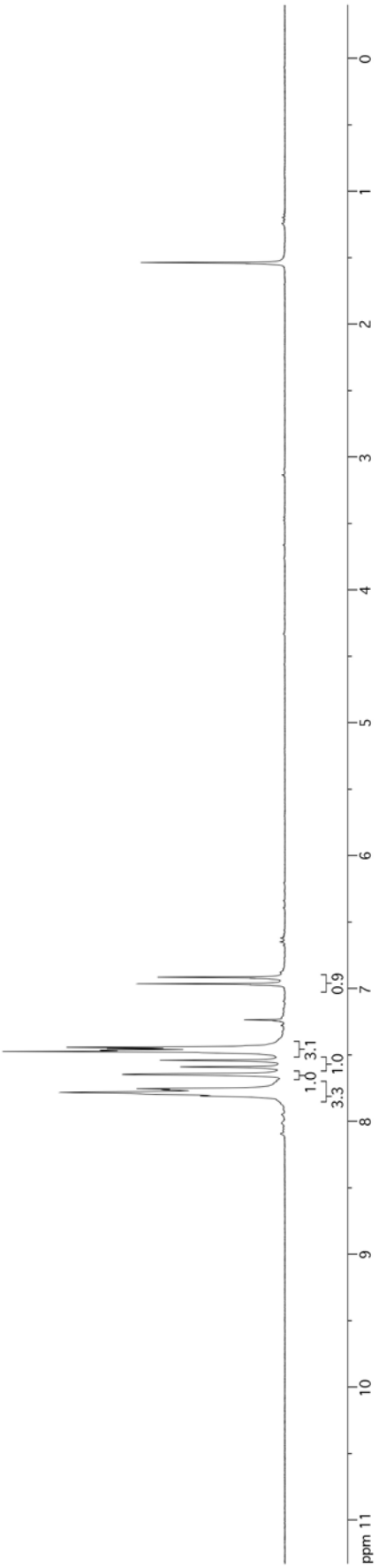


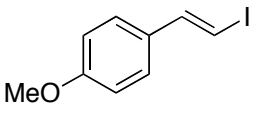
3c
^{1}H NMR (300 MHz, $CDCl_3$)



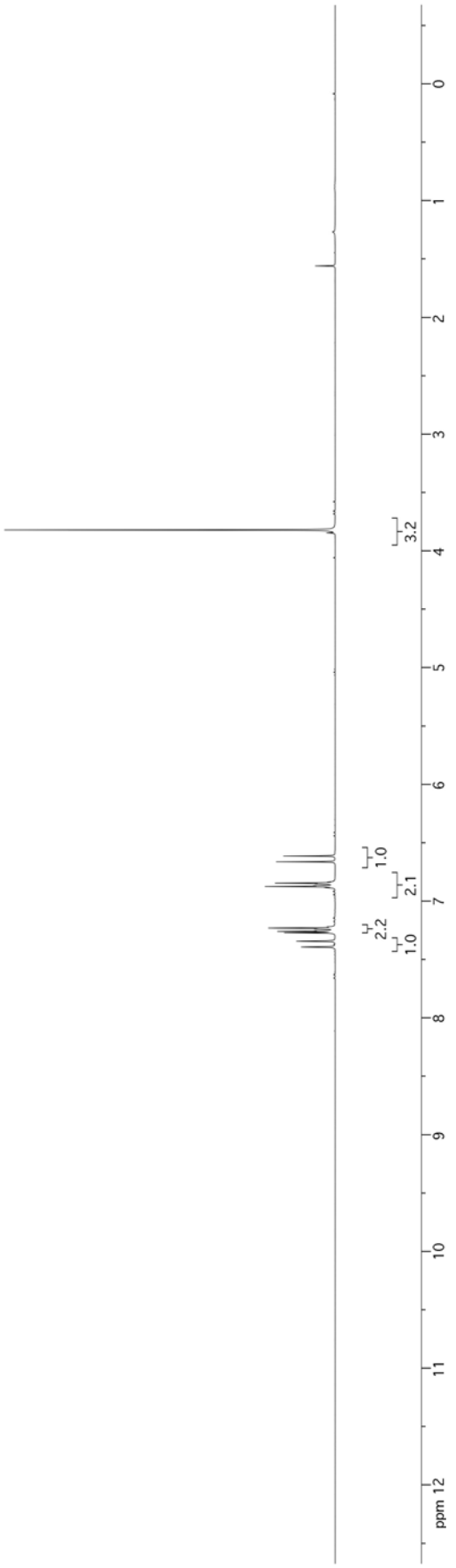


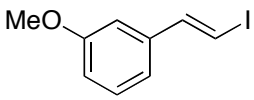
3d
^{1}H NMR (300 MHz, $CDCl_3$)



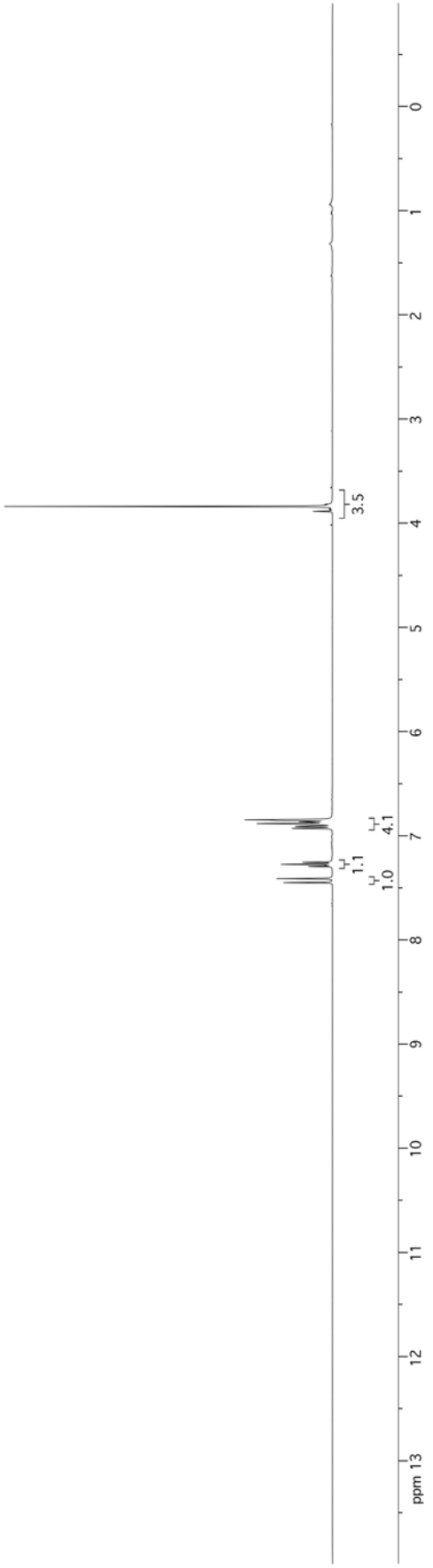


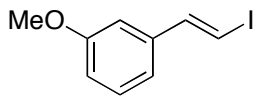
3e
^{1}H NMR (300 MHz, $CDCl_3$)



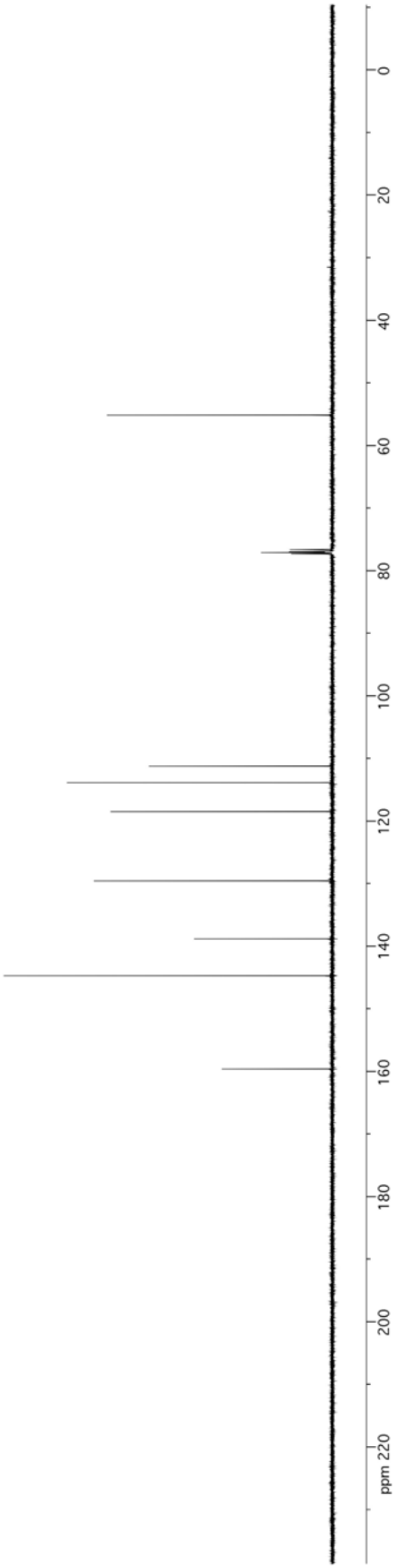


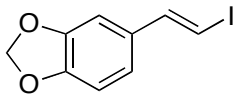
3f
^{1}H NMR (400 MHz, $CDCl_3$)



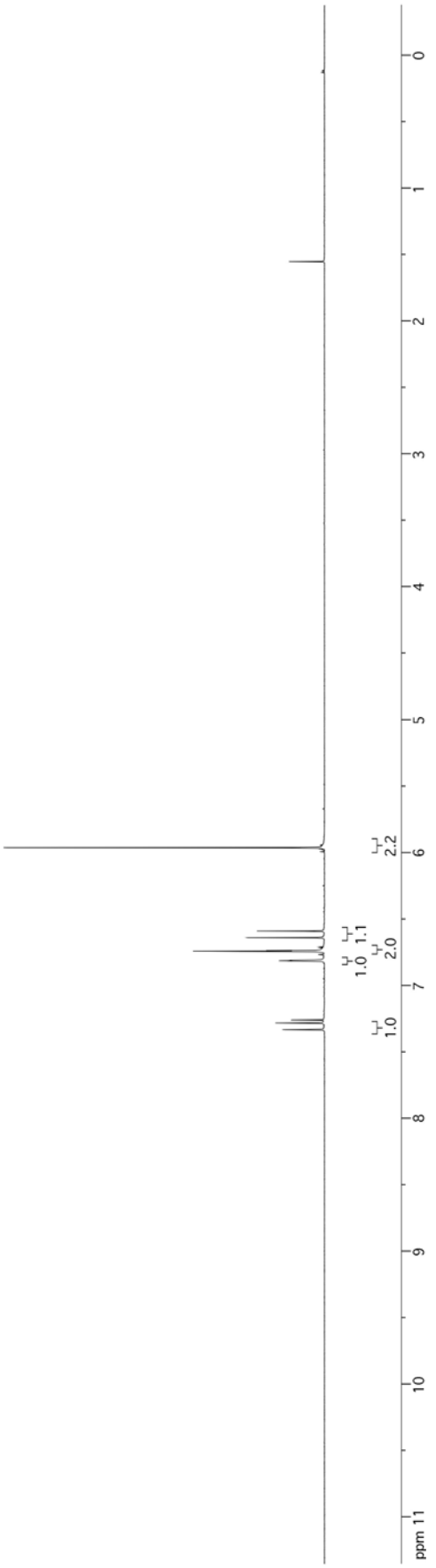


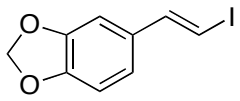
3f
^{13}C NMR (100 MHz, $CDCl_3$)



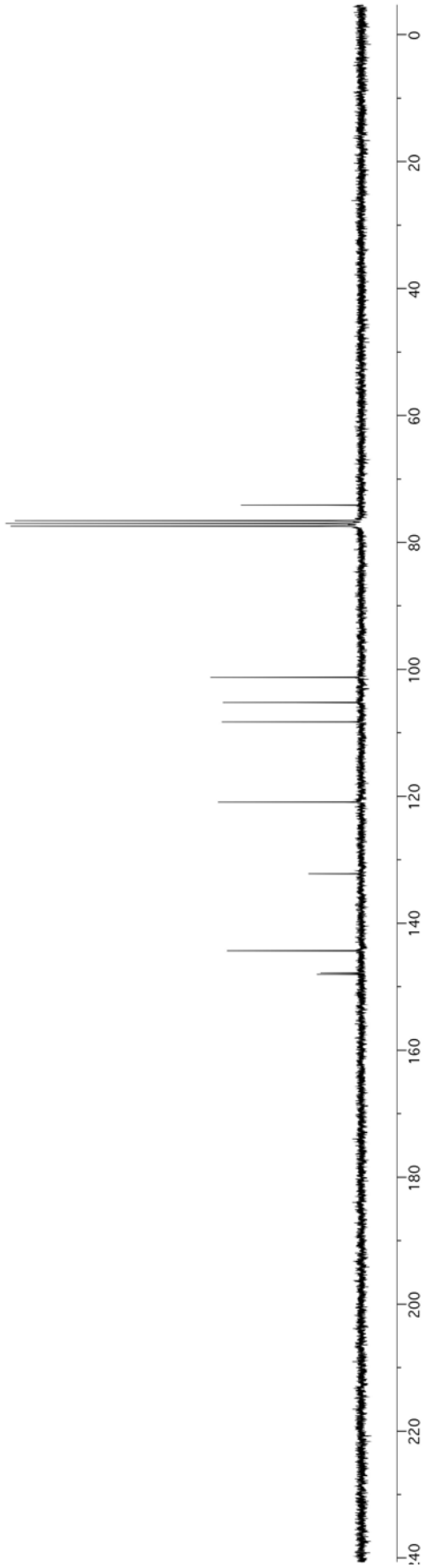


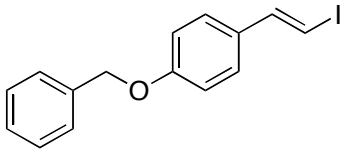
3g
^{1}H NMR (300 MHz, $CDCl_3$)



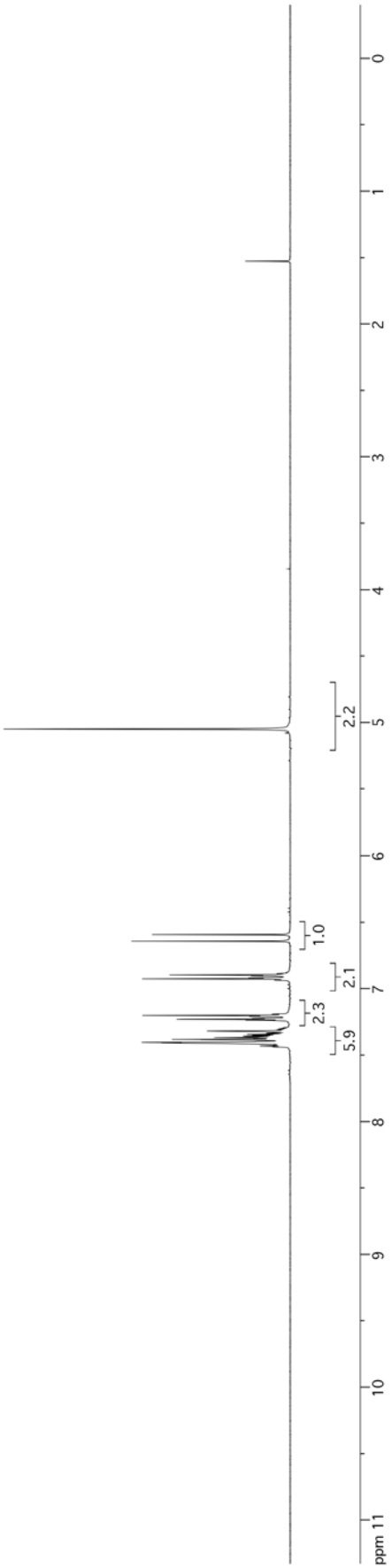


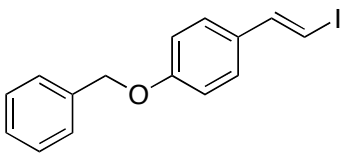
3g
^{13}C NMR (75 MHz, $CDCl_3$)



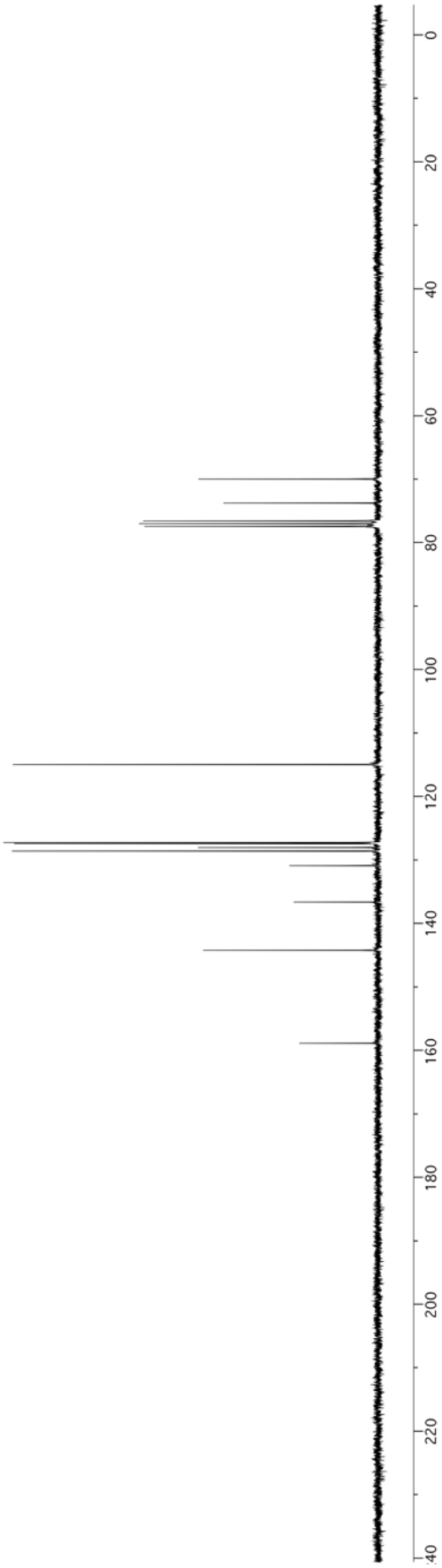


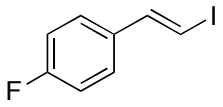
3h
^{1}H NMR (300 MHz, $CDCl_3$)



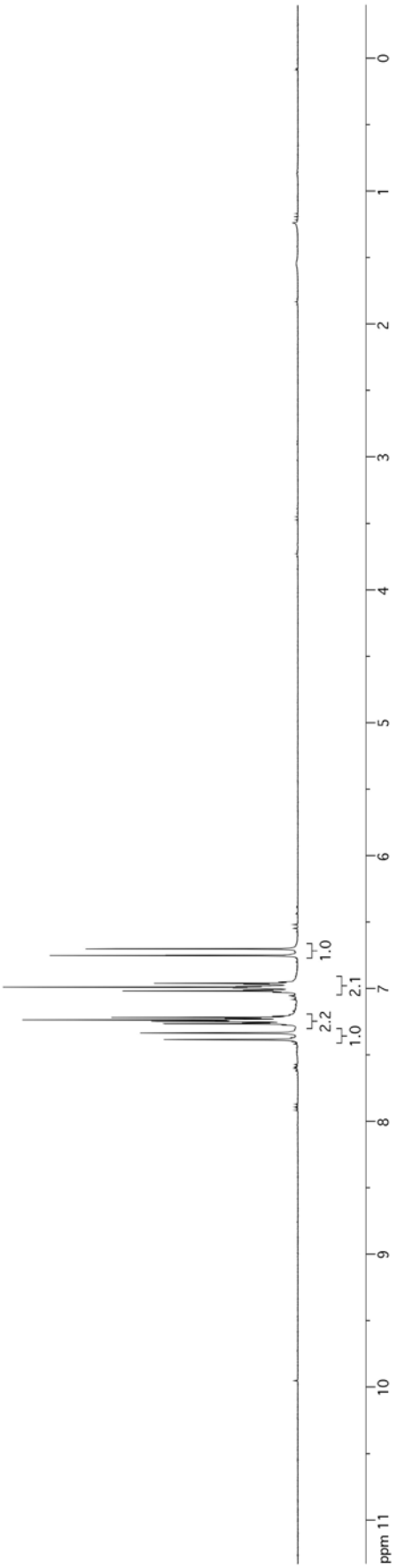


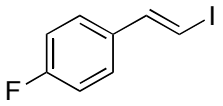
3h
^{13}C NMR (75 MHz, $CDCl_3$)



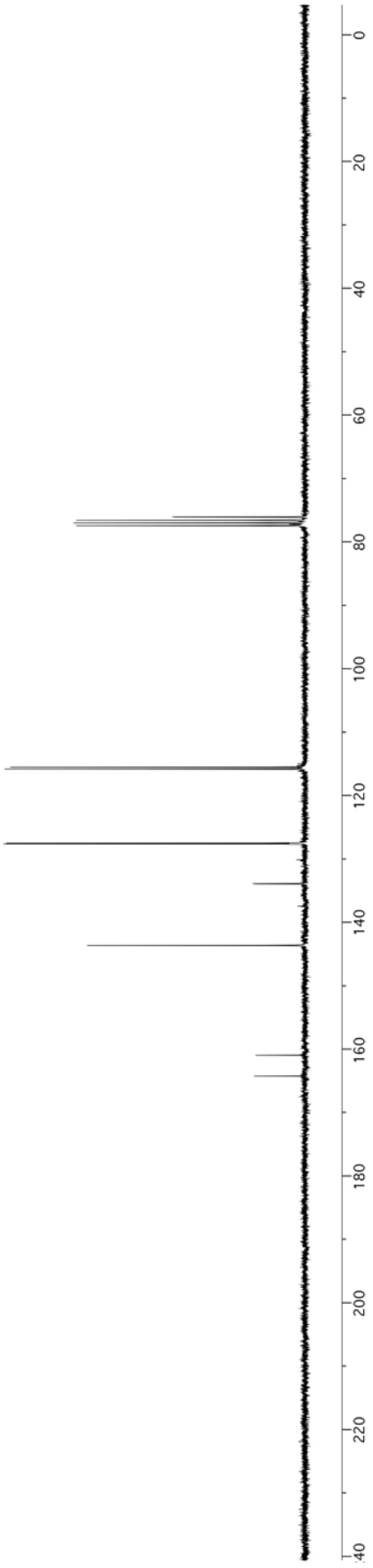


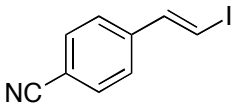
3i
^{1}H NMR (300 MHz, $CDCl_3$)



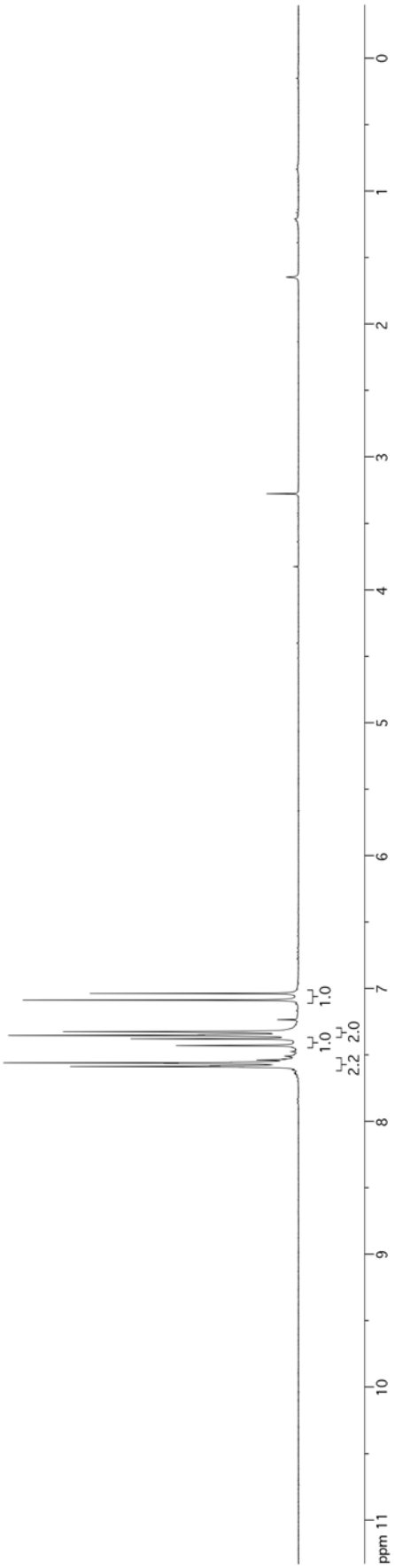


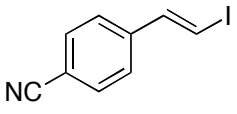
3i
^{13}C NMR (75 MHz, $CDCl_3$)





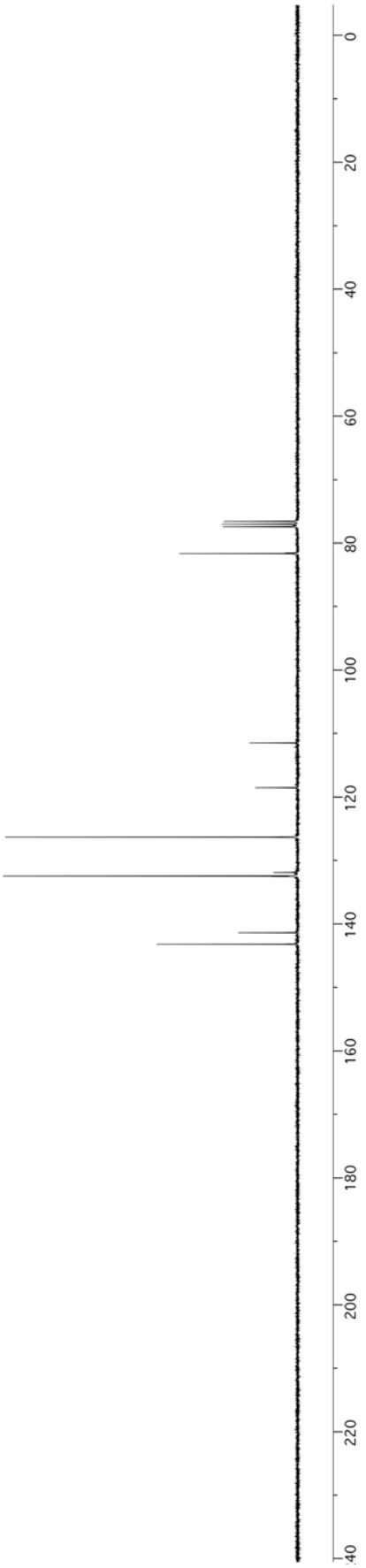
3j
^{1}H NMR (300 MHz, $CDCl_3$)

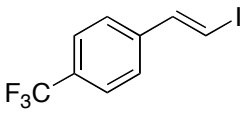




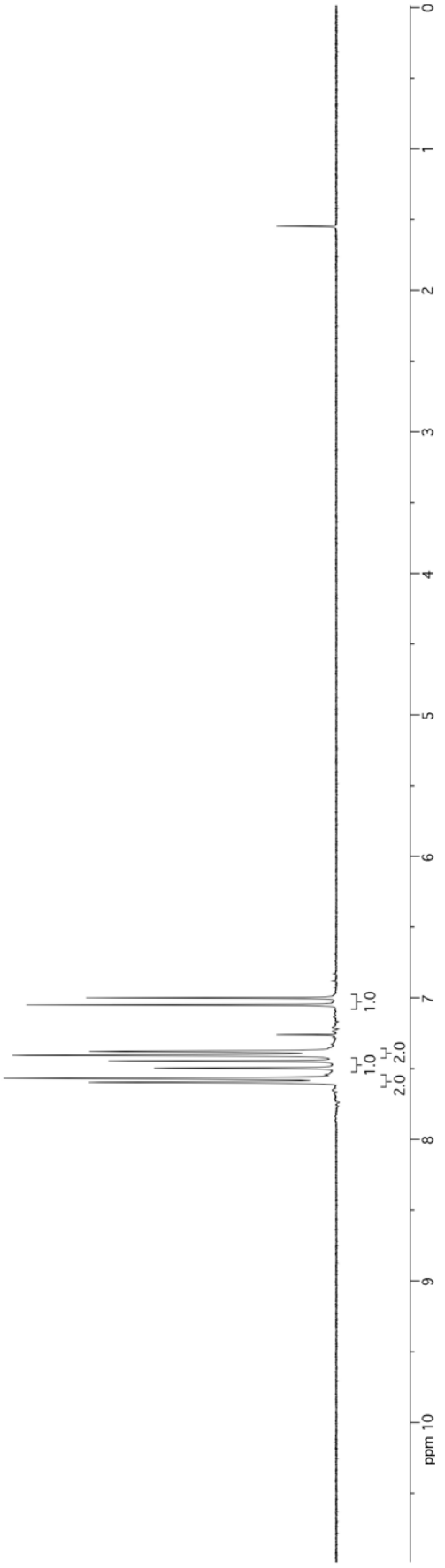
3j

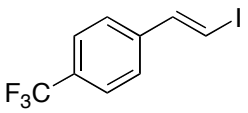
^{13}C NMR (75 MHz, $CDCl_3$)



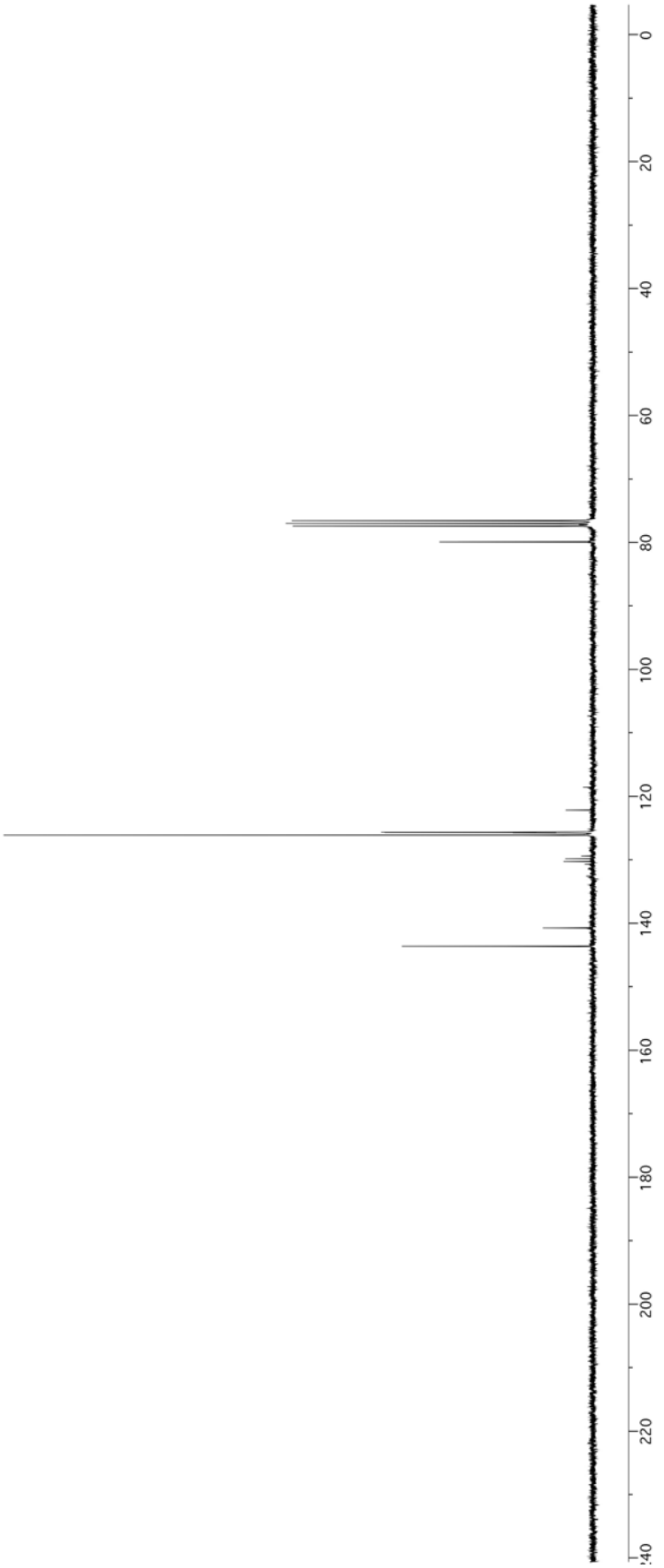


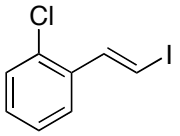
3k
^{1}H NMR (300 MHz, $CDCl_3$)



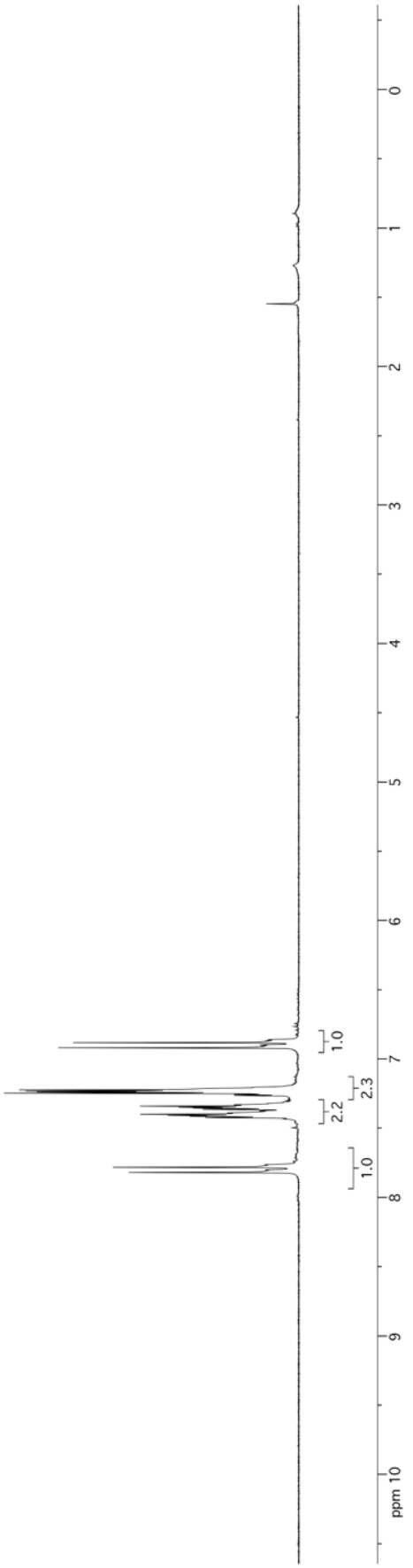


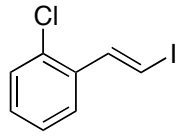
3k
^{13}C NMR (75 MHz, $CDCl_3$)





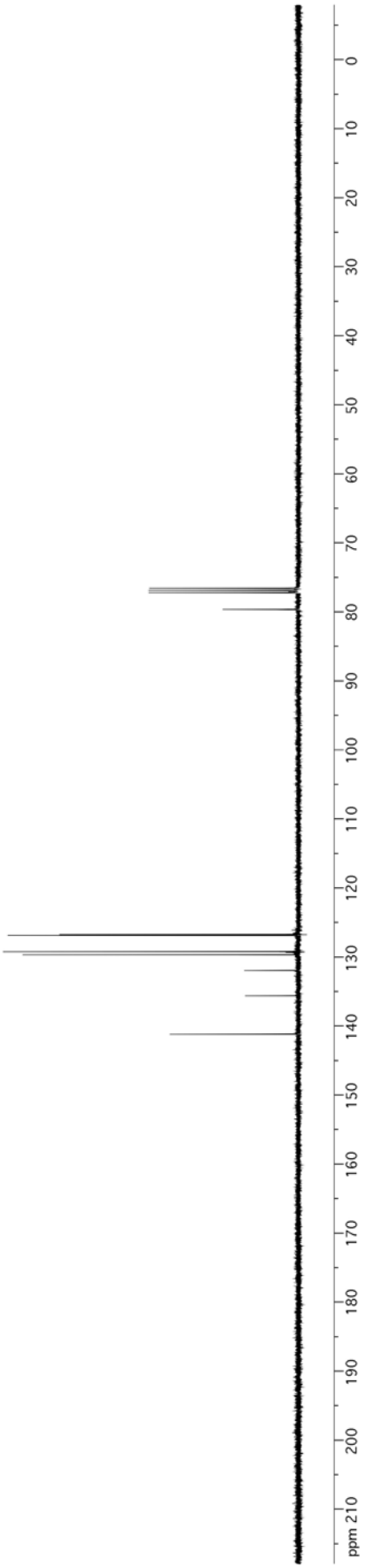
3l
^{1}H NMR (400 MHz, $CDCl_3$)

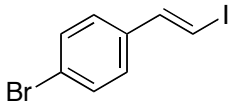




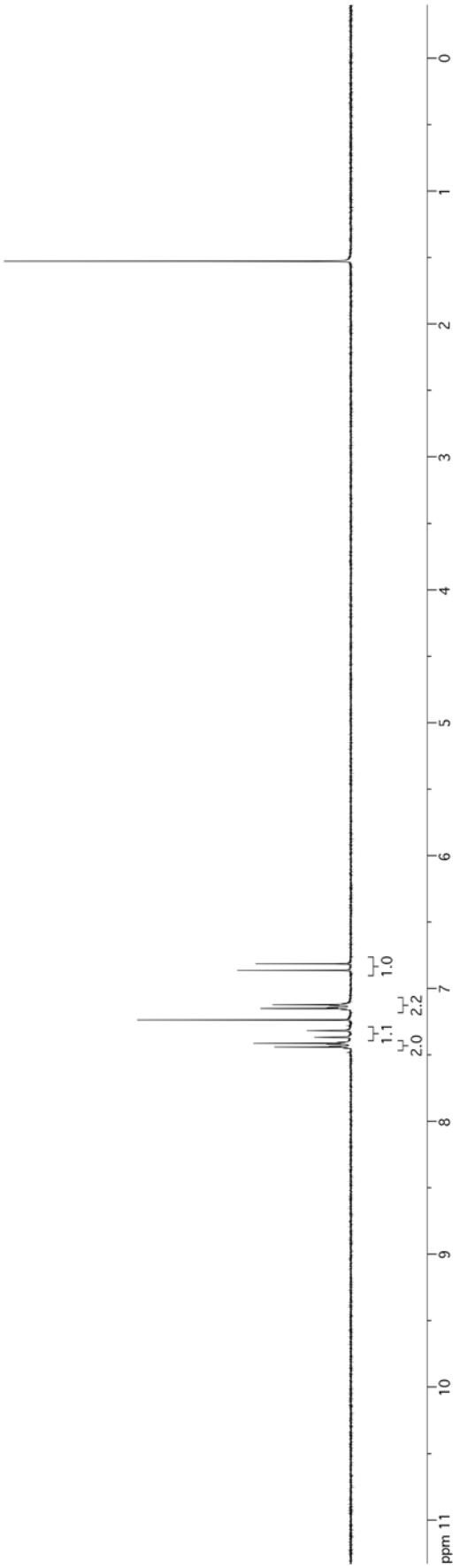
3l

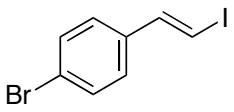
^{13}C NMR (100 MHz, $CDCl_3$)



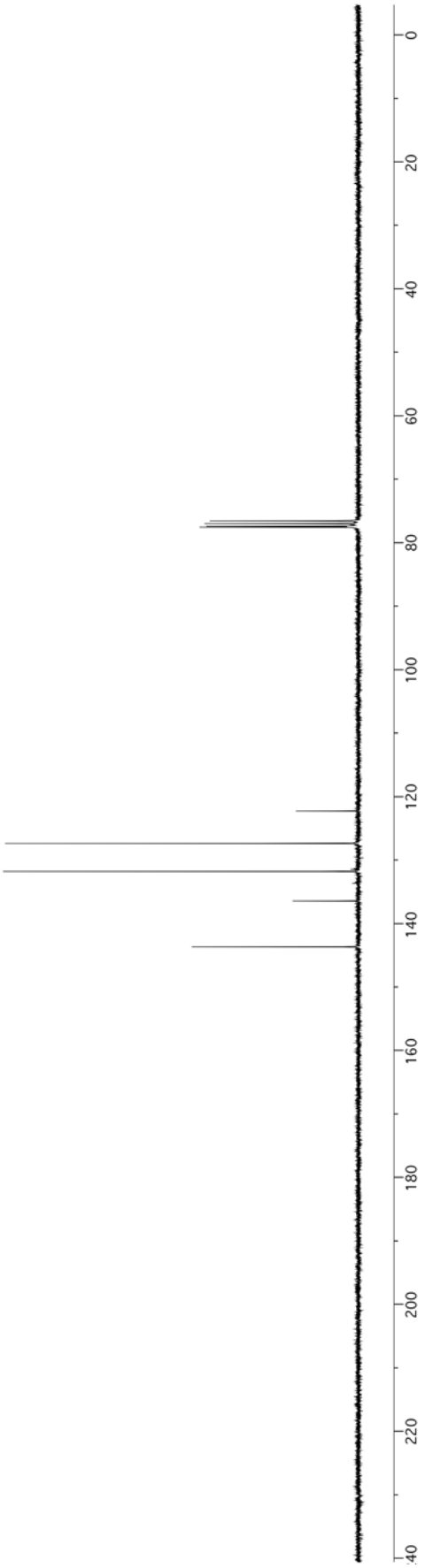


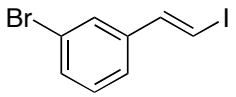
3m
^{1}H NMR (300 MHz, $CDCl_3$)



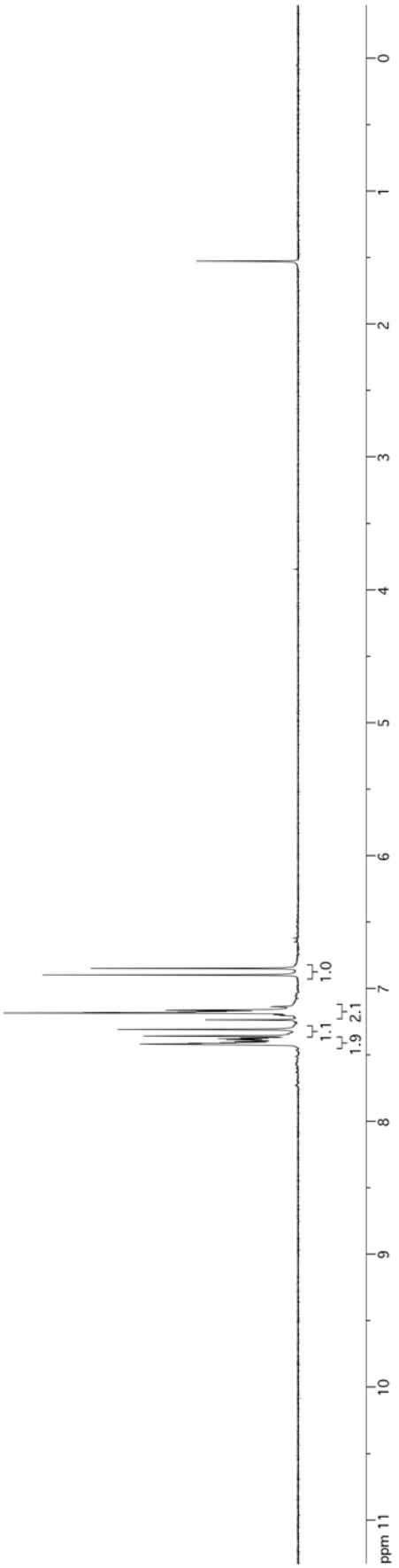


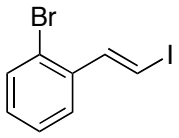
3m
^{13}C NMR (75 MHz, $CDCl_3$)



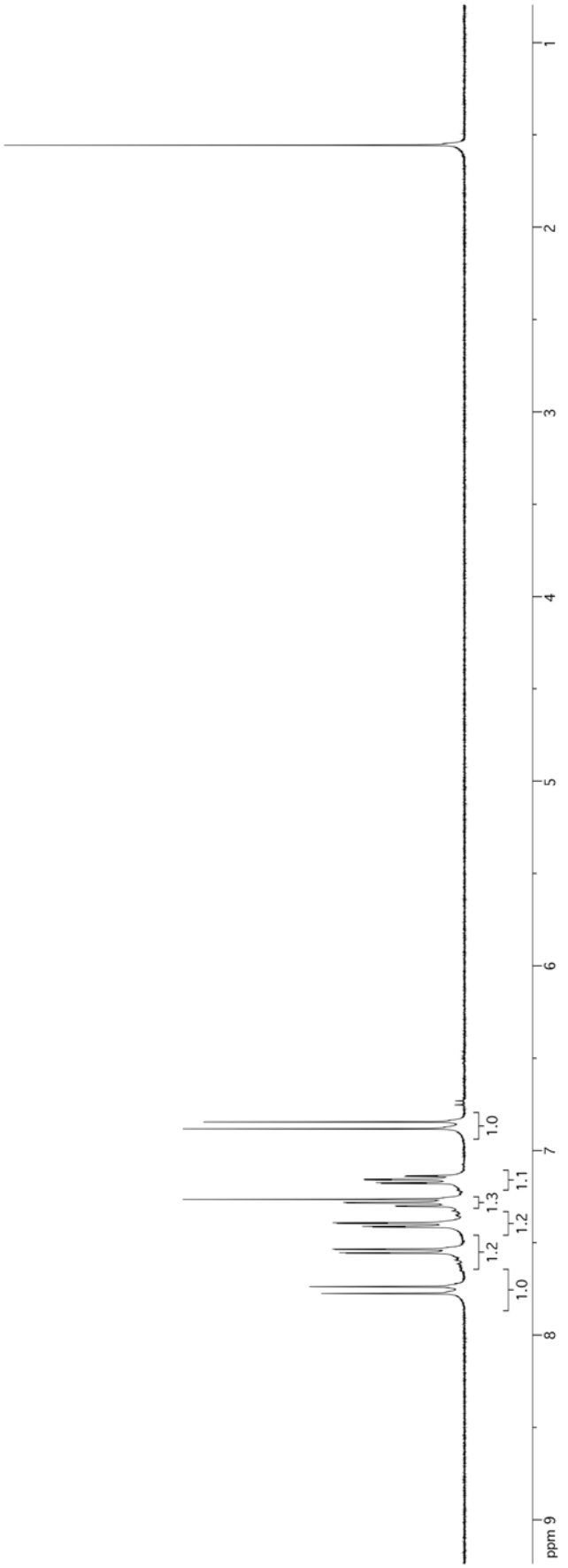


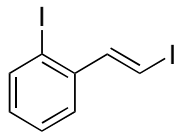
3n
^{1}H NMR (300 MHz, $CDCl_3$)



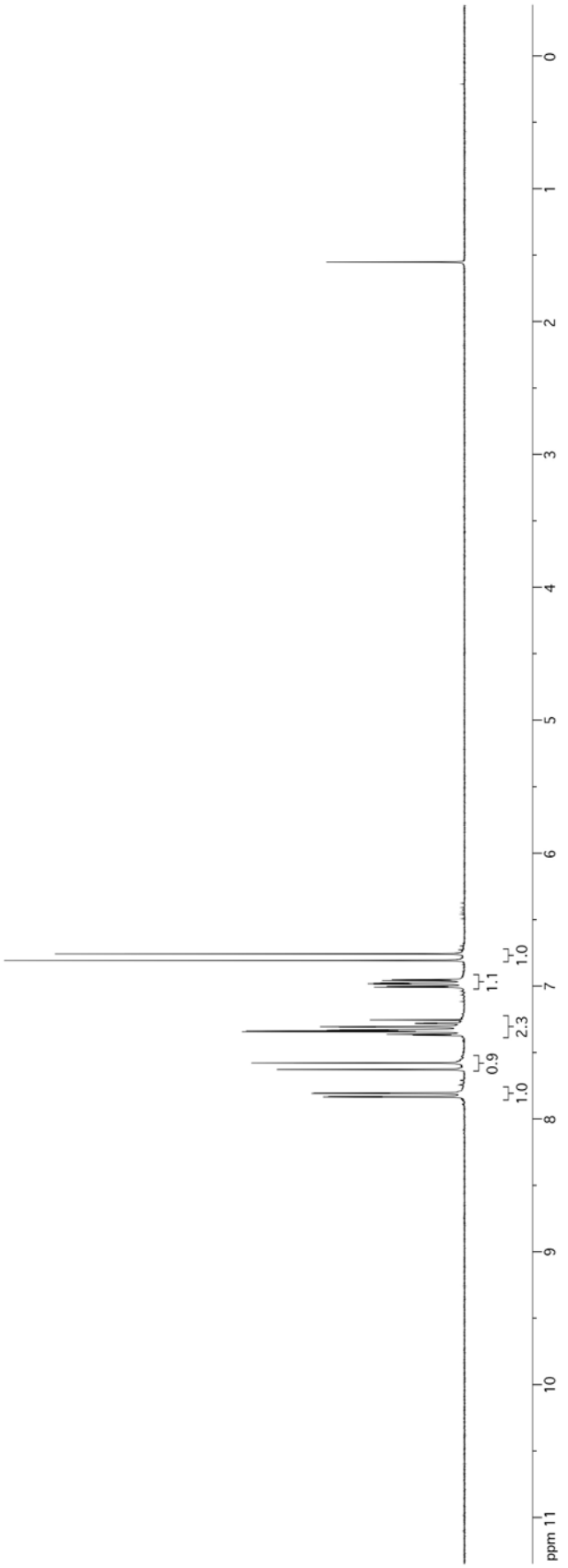


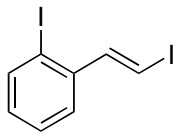
3o
^{1}H NMR (400 MHz, $CDCl_3$)



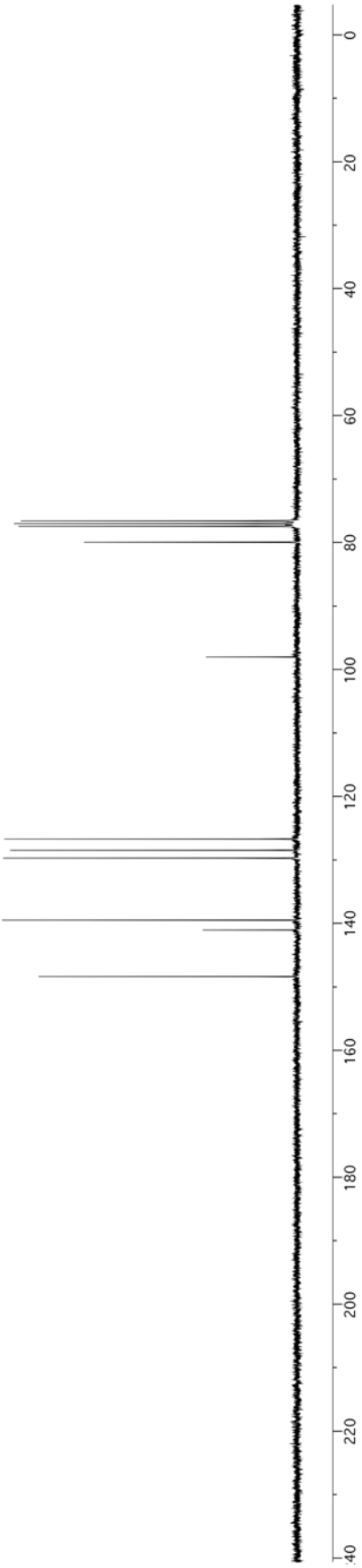


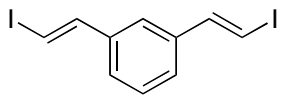
3p
^{1}H NMR (300 MHz, $CDCl_3$)





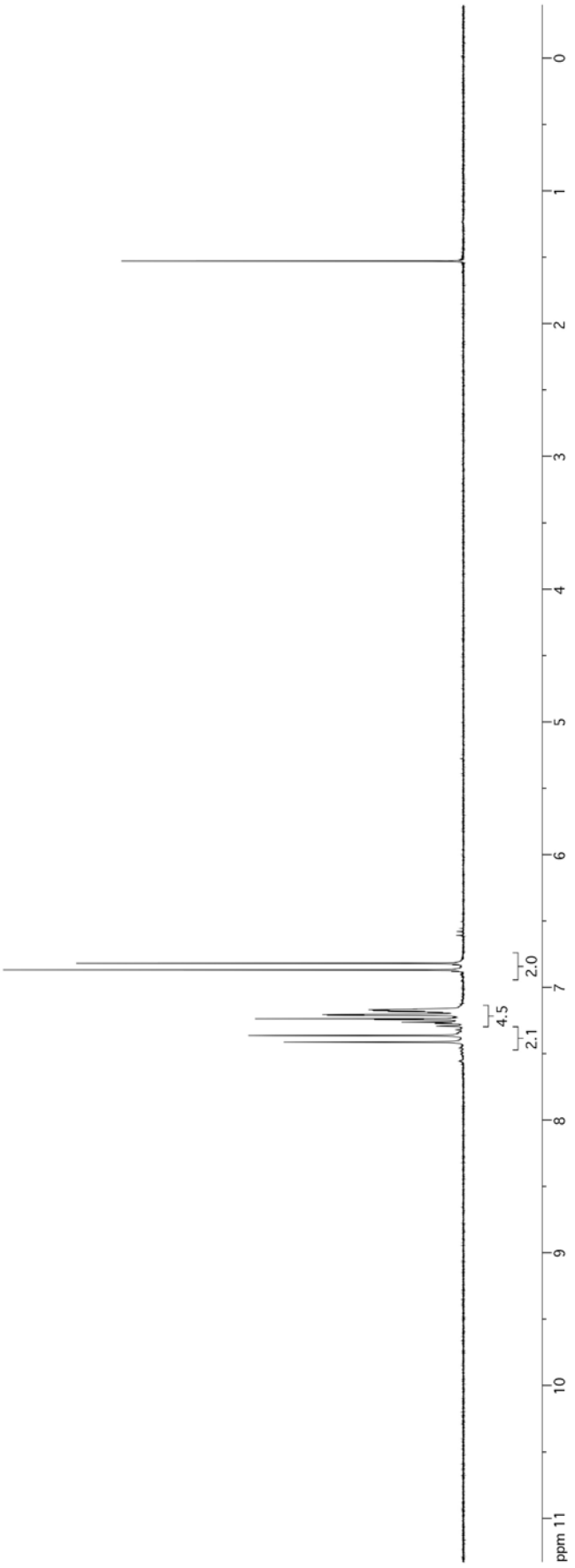
3p
^{13}C NMR (75 MHz, $CDCl_3$)

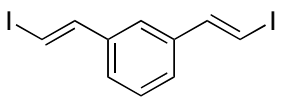




5

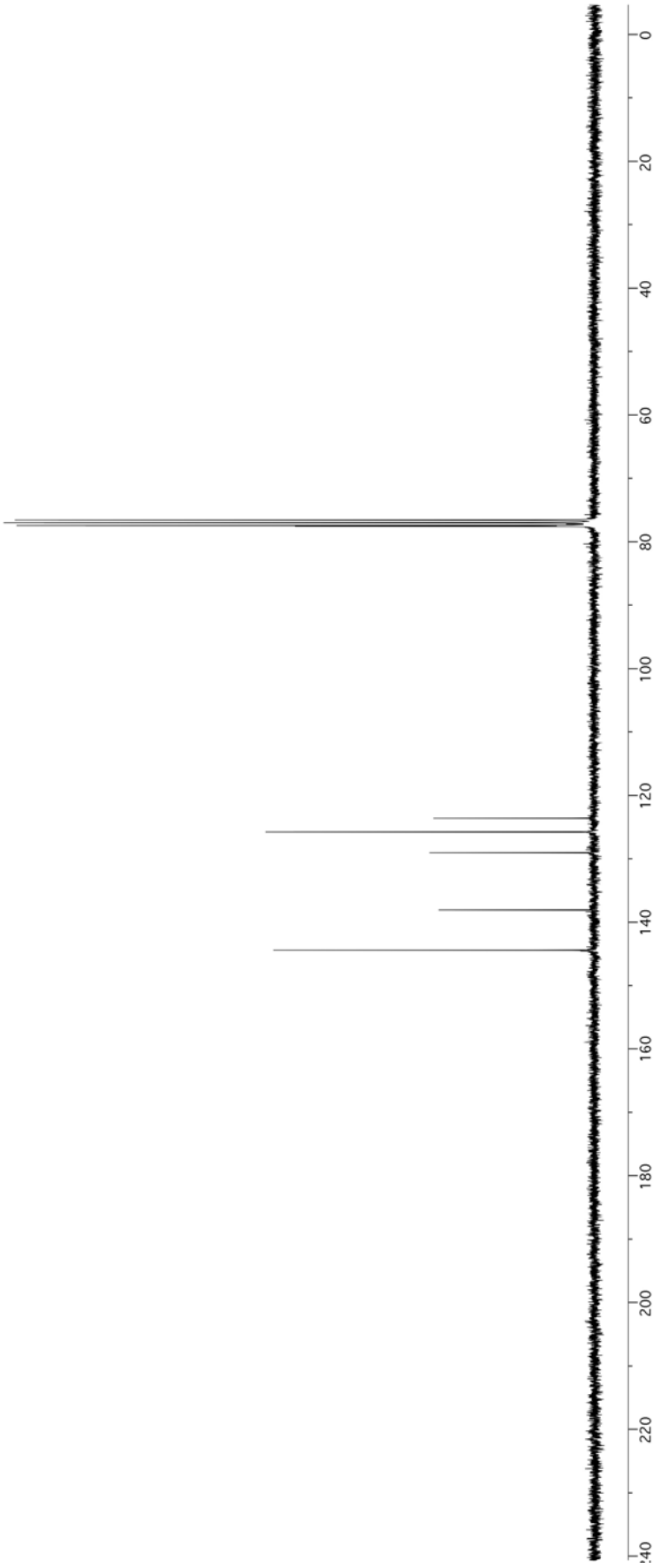
^{1}H NMR (300 MHz, $CDCl_3$)

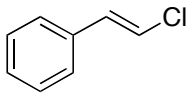




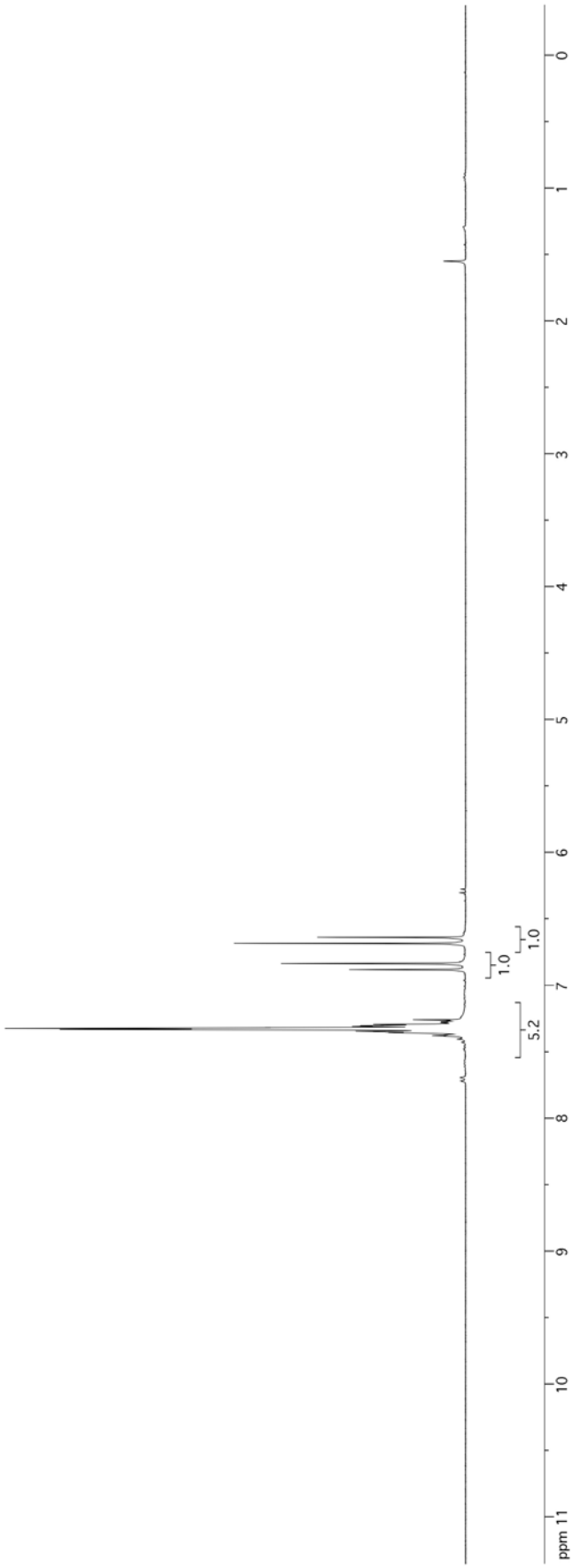
5

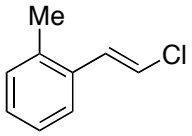
^{13}C NMR (75 MHz, $CDCl_3$)



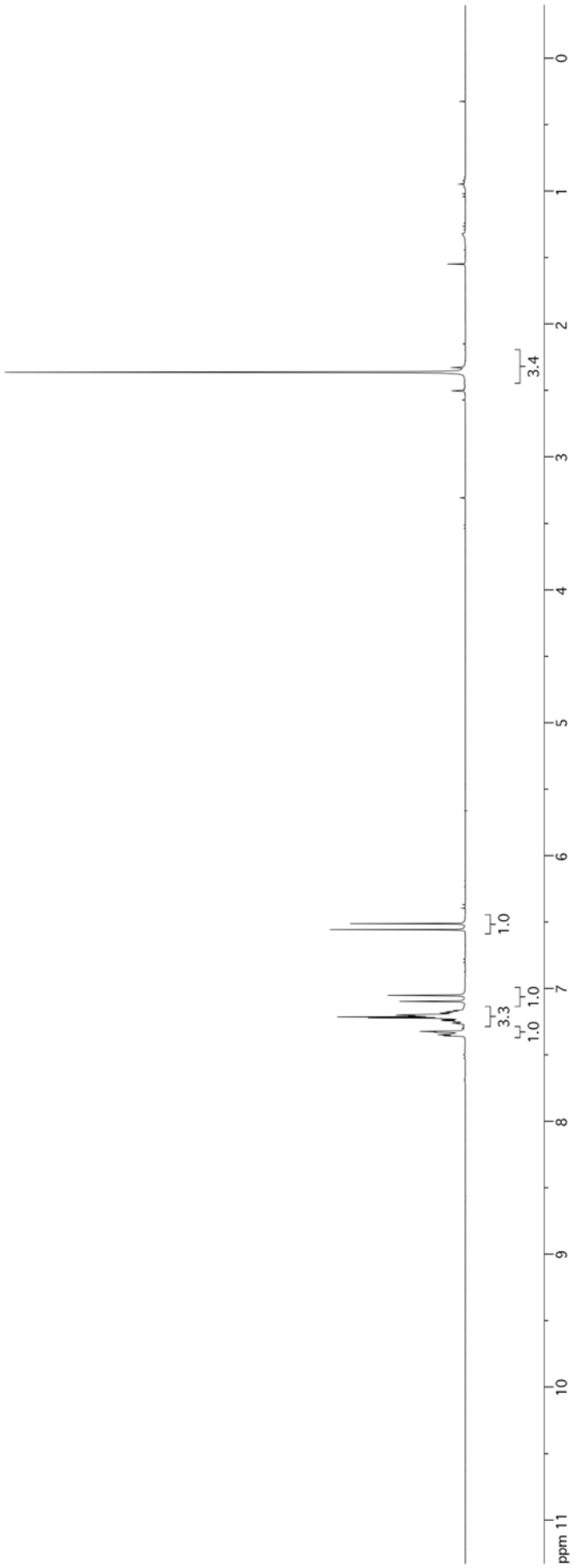


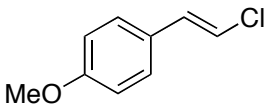
6a
^{1}H NMR (300 MHz, $CDCl_3$)



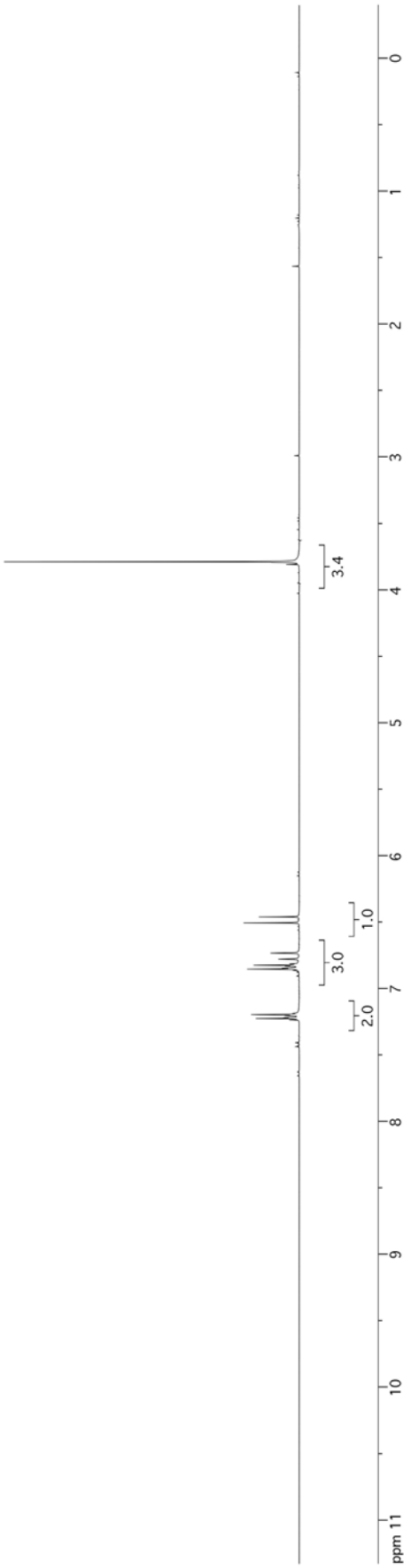


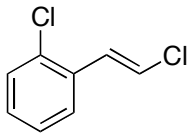
6c
^{1}H NMR (300 MHz, $CDCl_3$)



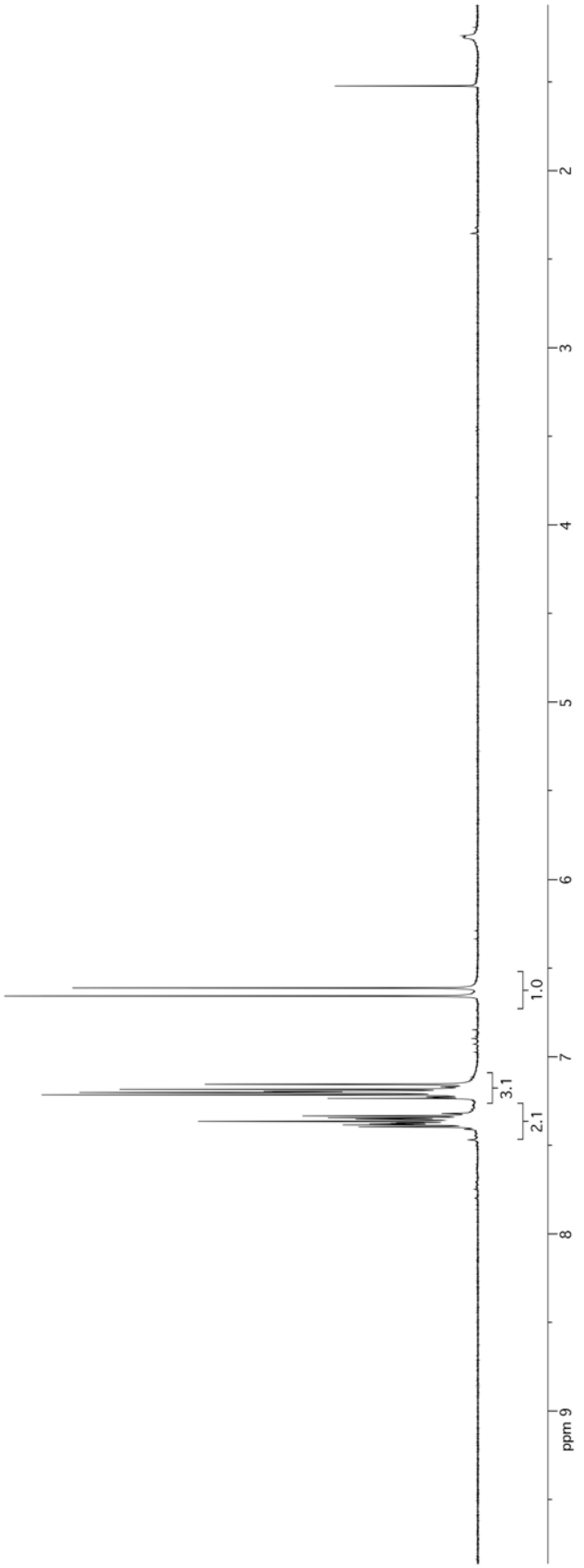


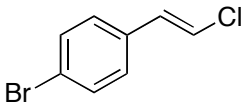
6e
^{1}H NMR (300 MHz, $CDCl_3$)



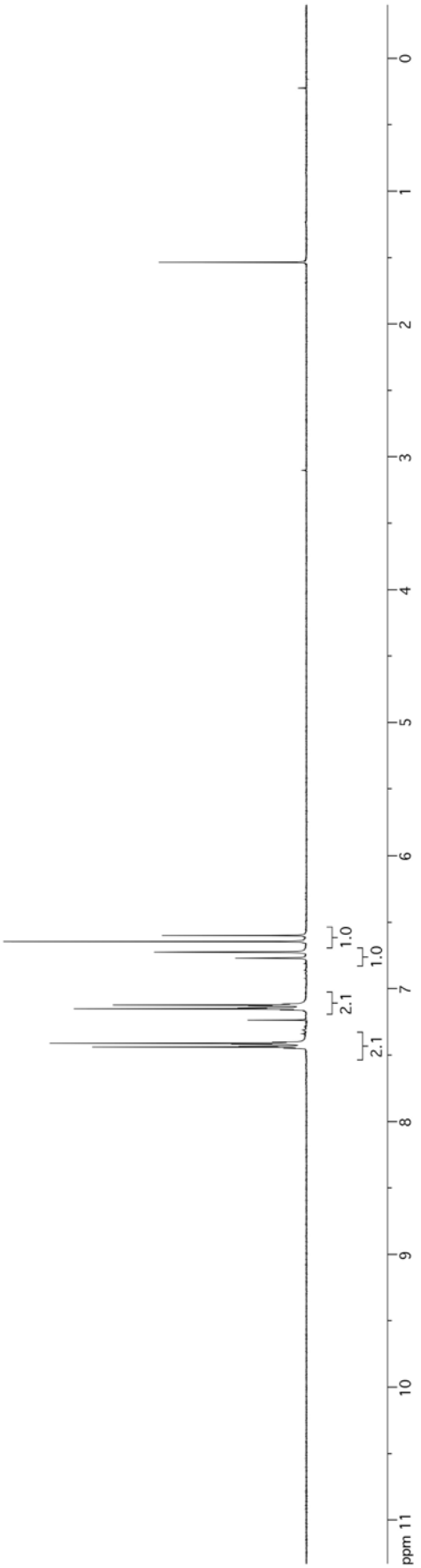


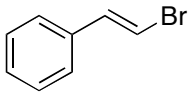
6l
^{1}H NMR (300 MHz, $CDCl_3$)



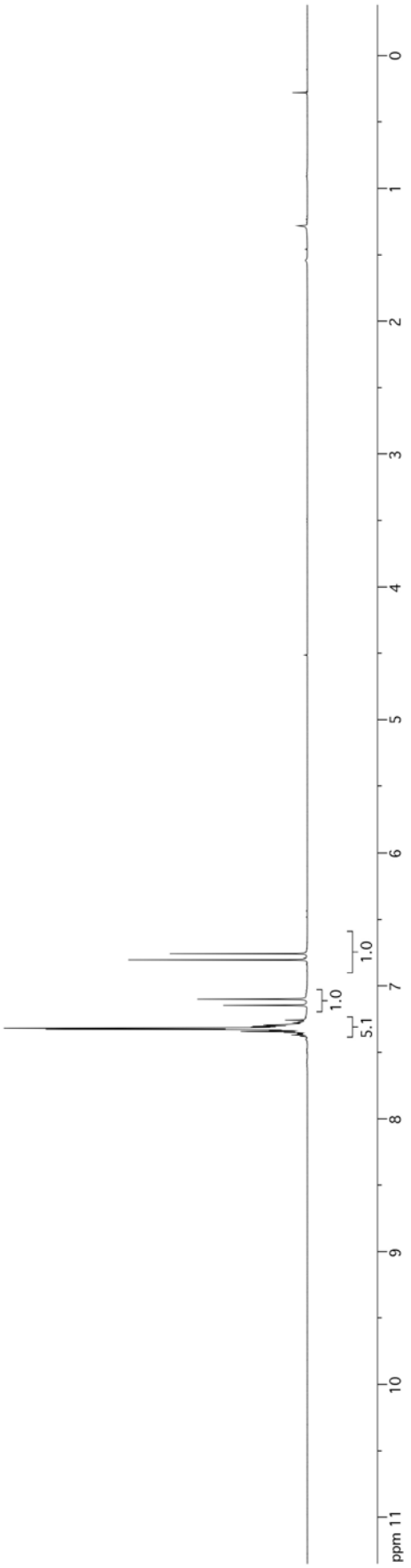


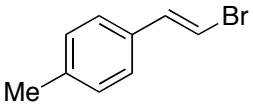
6m
^{1}H NMR (300 MHz, $CDCl_3$)



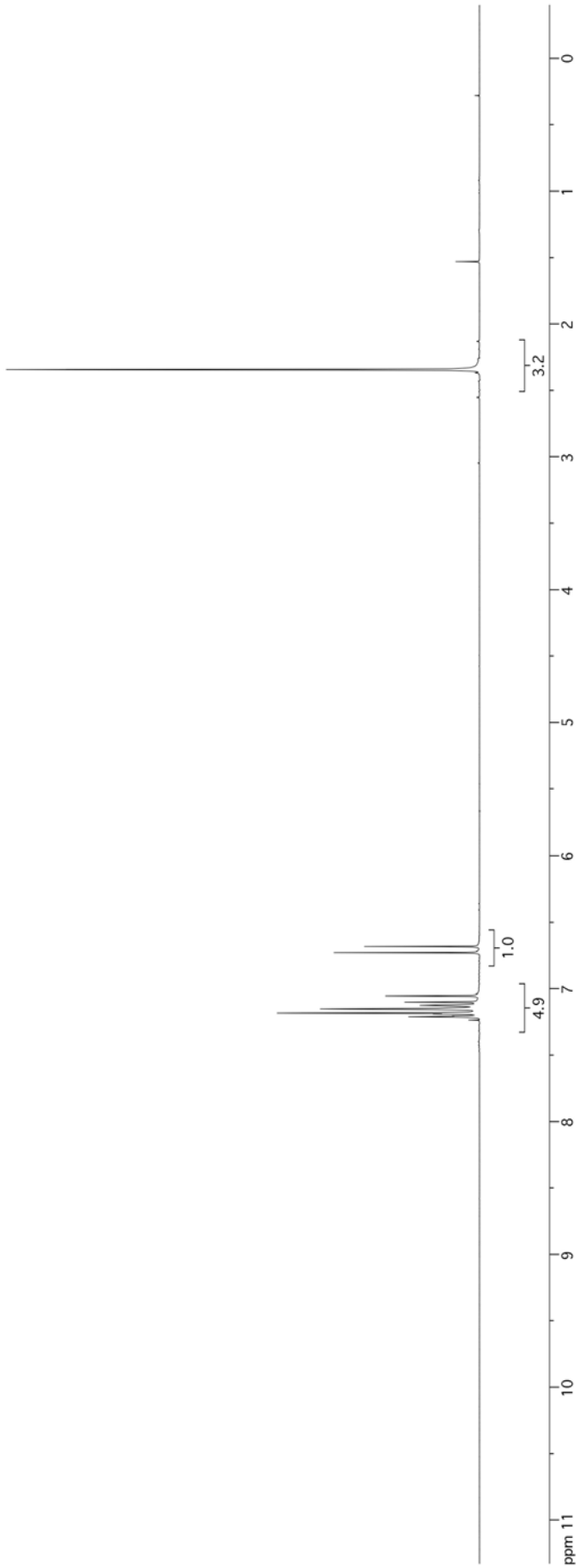


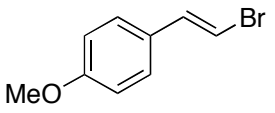
7a
^{1}H NMR (300 MHz, $CDCl_3$)





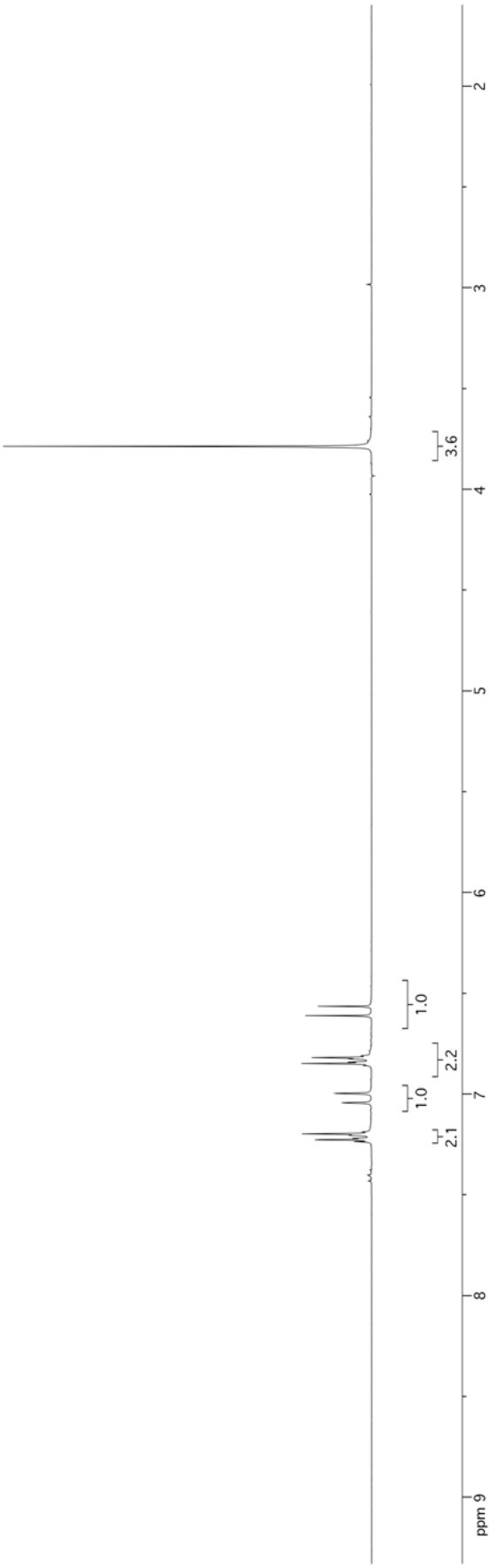
7b
^{1}H NMR (300 MHz, $CDCl_3$)

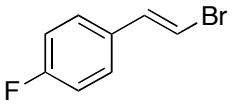




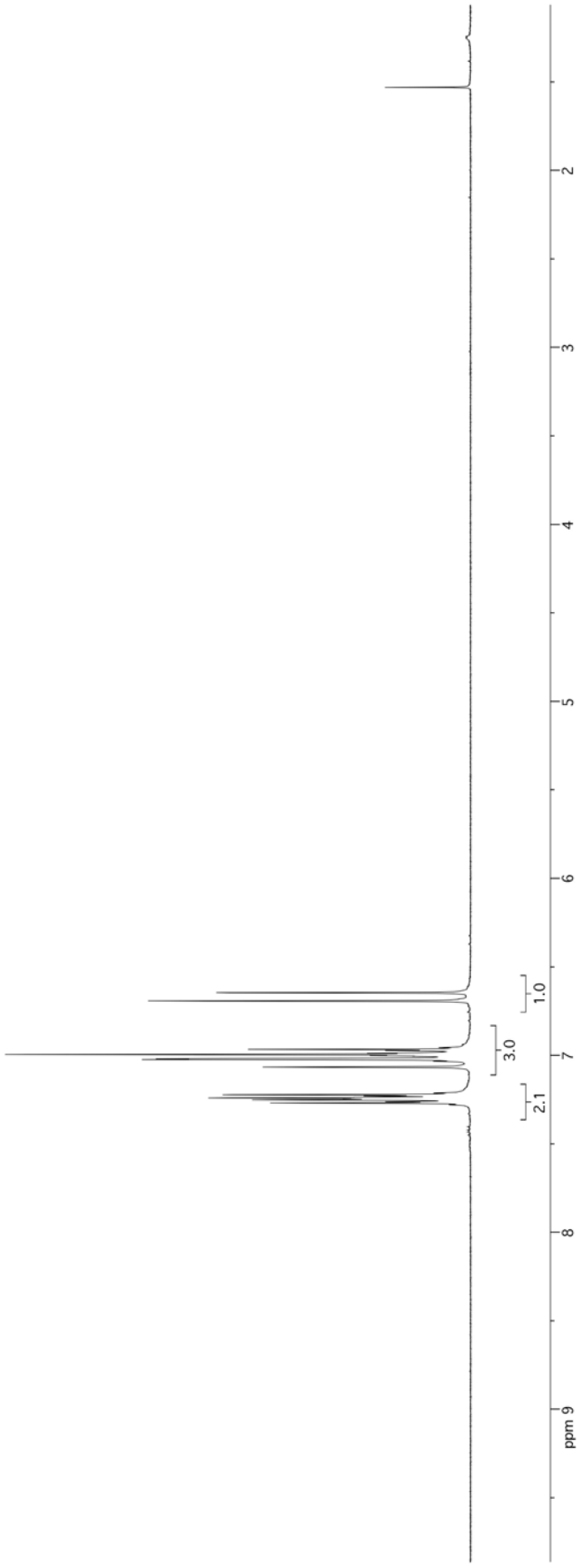
7e

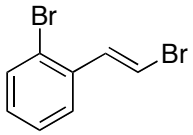
^{1}H NMR (300 MHz, $CDCl_3$)





7i
^{1}H NMR (300 MHz, $CDCl_3$)





7o
^{1}H NMR (300 MHz, $CDCl_3$)