A Second-Generation Ligand for the Enantioselective Rhodium-Catalyzed Addition of Arylboronic Acids to Alkenylazaarenes

Iain D. Roy,[a] Alan R. Burns,[a,b] Graham Pattison,[a] Boris Michel,[a] Alexandra J. Parker,[c] and Hon Wai Lam*[,a,b]

[a]*EaStCHEM, School of Chemistry, University of Edinburgh, Joseph Black Building, The King's Buildings, West Mains Road, Edinburgh, EH9 3JJ, United Kingdom*

[b] *School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom*

[c] *AstraZeneca Process Research and Development, Charter Way, Silk Road Business Park, Macclesfield, Cheshire, SK10 2NA, United Kingdom*

Supplementary Information

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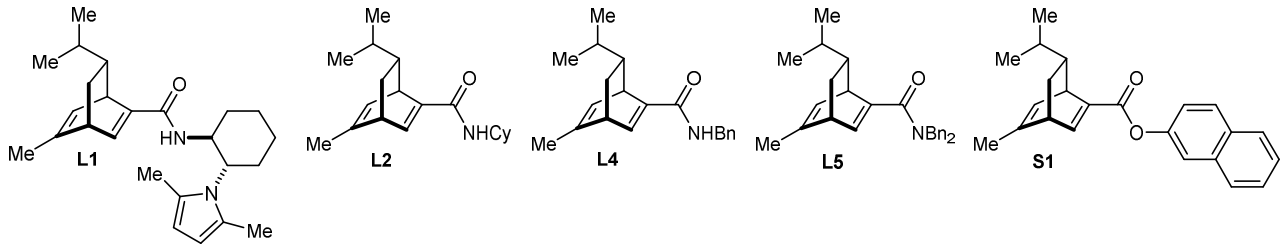
General Information

THF, CH_2Cl_2, MeCN, and toluene were dried and purified by passage through activated alumina columns using a solvent purification system. All commercially available reagents were used as received. Thin layer chromatography (TLC) was performed on Merck DF-Alufoilien $60F_{254}$ 0.2 mm precoated plates. Product spots were visualized by UV light at 254 nm, and subsequently developed using vanillin, potassium permanganate, or ceric ammonium molybdate solution as appropriate. Flash column chromatography was carried out using silica gel (Fisher Scientific 60Å particle size 35-70 micron) employing the method of Still and co-workers.[1] Melting points are uncorrected. Infra-red spectra were recorded on a Shimadzu IRAffinity-1 instrument on the neat compound. For ^{1}H NMR spectra, chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal standard ($CDCl_3$ at 7.27 ppm, d_6-DMSO at 2.50 ppm). Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q, (quartet), app (apparent), br (broad). Coupling constants (*J*) are quoted to the nearest 0.1 Hz. For proton-decoupled ^{13}C NMR spectra, chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using deuterated solvent as internal standard ($CDCl_3$ at 77.0 ppm, d_6-DMSO at 39.52 ppm). Assignments were made using the DEPT sequence with secondary pulses at 90° and 135°. For proton-decoupled ^{19}F NMR spectra, chemical shifts (δ) are quoted in parts per million (ppm) downfield of $CFCl_3$, using residual protonated solvent as internal standard ($CFCl_3$ at 376.38 MHz with respect to tetramethylsilane at 400.00 MHz). For proton-decoupled ^{31}P NMR spectra, chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal standard (aqueous 85% H_3PO_4 at 161.9 MHz with respect to tetramethylsilane at 400.00 MHz). High resolution mass spectra were recorded using electrospray ionization (ESI) or electron impact (EI) techniques. Chiral HPLC analysis was performed using 4.6 x 250 mm columns. Authentic racemic samples of products for chiral HPLC assay determinations were obtained using $[Rh(cod)Cl]_2$.

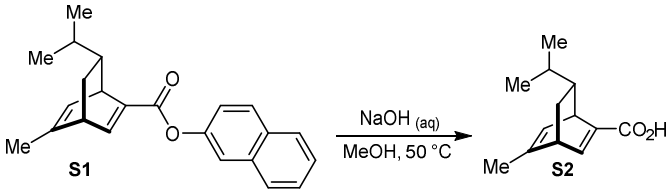
1. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem*. **1978**, *43*, 2923–2925.

Preparation of Chiral Diene Ligands



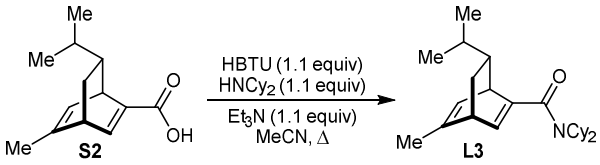
Chiral dienes **L1**,[2] **L2**,[3] **L4**,[3] **L5**,[3] and **S1**,[4] were prepared as described previously.

(1*R*,4*R*,7*R*)-7-Isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid (S2)[2]



To a solution of the naphthyl ester **S1**[4] (4.99 g, 15.0 mmol) in MeOH (150 mL) at room temperature was added 1 M aqueous NaOH solution (70 mL, 70 mmol) over 30 min and the resulting mixture was heated to 50 °C for 16 h. The reaction was cooled to room temperature and 1 M aqueous HCl solution (100 mL, 100 mmol) was carefully added. The mixture was diluted with H_2O (100 mL) and extracted with Et_2O (4 x 100 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (10% *i*-Pr_2O/hexane) gave the acid **S2** as a white solid (2.17 g, 66%). The data were in agreement with those reported previously.[2]

(1*R*,4*R*,7*R*)-7-Isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid dicyclohexylamide (L3)

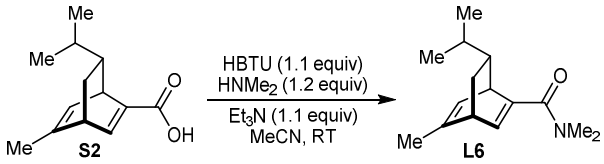


To a solution of the carboxylic acid **S2** (62 mg, 0.30 mmol) and HBTU (125 mg, 0.33 mmol) in MeCN (8 mL) at room temperature was added Et_3N (52 µL, 0.33 mmol) and dicyclohexylamine (66 µL, 0.33 mmol). The reaction was heated at reflux for 16 h, cooled to room temperature, quenched with brine (8 mL), and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with 2 M

2. Pattison, G.; Piraux, G.; Lam, H. W. *J. Am. Chem. Soc*. **2010**, *132*, 14373–14375.
3. Saxena, A.; Lam, H. W. *Chem. Sci.* **2011**, *2*, 2326–2331.
4. Okamoto, K.; Hayashi, T.; Rawal, V. H. *Chem. Commun.* **2009**, 4815–4817.

aqueous HCl solution (30 mL), saturated aqueous $NaHCO_3$ solution (30 mL), and brine (30 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (10% EtOAc/hexane) gave the *chiral diene* **L3** as a white solid (37 mg, 33%). R_f = 0.37 (10% EtOAc/hexane); m.p. 101-102 °C (CH_2Cl_2/hexane); $[\alpha]_D^{20}$ +56.0 (*c* 0.20, $CHCl_3$); IR 2926, 2855, 1628 (C=O), 1466, 1368, 1314, 1292, 1246, 810 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.18 (1H, dd, *J* = 6.1, 1.5 Hz, =C**H**), 5.83-5.79 (1H, m, =C**H**), 3.54 (1H, dt, *J* = 5.9, 1.9 Hz, =CHC**H**), 3.29-3.25 (1H, m, =CHC**H**), 2.94 (1H, br s, NC**H**), 2.48 (1H, br s, NC**H**) 1.83 (3H, d, *J* = 1.5 Hz, =CC**H**$_3$), 1.80-1.75 (4H, m), 1.67-1.39 (11H, m), 1.30-1.00 (8H, m), 0.95 (3H, d, *J* = 6.5 Hz, CH(C**H**$_3$)$_2$), 0.92 (1H, ddd, *J* = 11.4, 4.7, 2.4 Hz, C**H**$_2$), 0.81 (3H, d, *J* = 6.5 Hz, CH(C**H**$_3$)$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 171.1 (C), 146.8 (C), 144.4 (C), 130.3 (CH), 123.5 (CH), 48.0 (CH), 43.1 (CH), 42.8 (CH), 34.0 (CH), 32.1 (CH_2), 30.7 (4 x CH_2), 26.3 (4 x CH_2), 25.4 (2 x CH_2), 21.7 (CH_3), 21.3 (CH_3), 19.1 (CH_3), (2 x CH not observed); HRMS (EI) Exact mass calculated for $C_{25}H_{39}NO$ $[M]^+$: 369.3026, found: 369.3023.

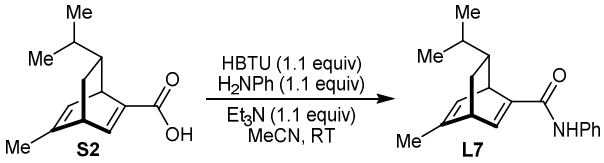
(1*R*,4*R*,7*R*)-7-Isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid dimethylamide (L6)



To a solution of the carboxylic acid **S2** (83 mg, 0.40 mmol) and HBTU (167 mg, 0.44 mmol) in MeCN (8 mL) at room temperature was added Et_3N (70 µL, 0.44 mmol) and dimethylamine (2.0 M in THF, 240 µL, 0.48 mmol). The reaction was stirred at room temperature for 1 h, quenched with brine (8 mL), and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with 2 M aqueous HCl solution (30 mL), saturated aqueous $NaHCO_3$ solution (30 mL), and brine (30 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (20% EtOAc/hexane) gave the *chiral diene* **L6** as a pale yellow oil (75 mg, 68%). R_f = 0.35 (20% EtOAc/hexane); $[\alpha]_D^{20}$ +21.4 (*c* 1.12, $CHCl_3$); IR 2953, 2868, 1648 (C=O), 1391, 1067, 816, 737 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.41 (1H, dd, *J* = 6.1, 1.7 Hz, =C**H**), 5.79 (1H, app dt, *J* = 4.4, 1.5 Hz, =C**H**), 3.70 (1H, dt, *J* = 5.9, 1.9 Hz, =CHC**H**), 3.32-3.27 (1H, m, =CHC**H**), 2.94 (6H, s, N(C**H**$_3$)$_2$), 1.81 (3H, d, *J* = 1.6 Hz, =CC**H**$_3$), 1.61 (1H, ddd, *J* = 11.6, 8.9, 3.0 Hz, C**H**$_2$), 1.40-1.32 (1H, m, C**H**), 1.12-1.00 (1H, m, C**H**), 0.95 (3H, d, *J* = 6.5 Hz, CH(C**H**$_3$)$_2$), 0.91 (1H, ddd, *J* = 11.6, 4.8, 2.4

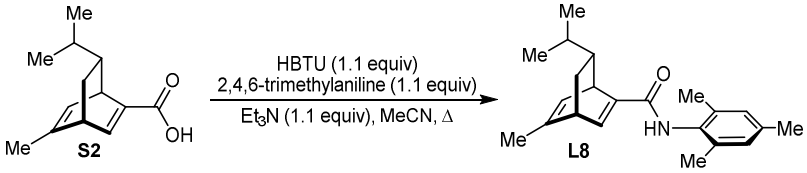
Hz, C**H**$_2$), 0.80 (3H, d, *J* = 6.5 Hz, CH(C**H**$_3$)$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.4 (C), 144.2 (C), 144.1 (C), 135.6 (CH), 123.6 (CH), 48.0 (CH), 43.2 (CH), 42.5 (CH), 38.8 (CH_3), 34.9 (CH_3), 33.9 (CH), 32.0 (CH_2), 21.7 (CH_3), 21.3 (CH_3), 19.0 (CH_3); HRMS (ESI) Exact mass calculated for $C_{15}H_{24}NO$ $[M+H]^+$: 234.1852, found: 234.1854.

(1*R*,4*R*,7*R*)-7-Isopropyl-5-methyl-*N*-phenylbicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid phenylamide (L7)



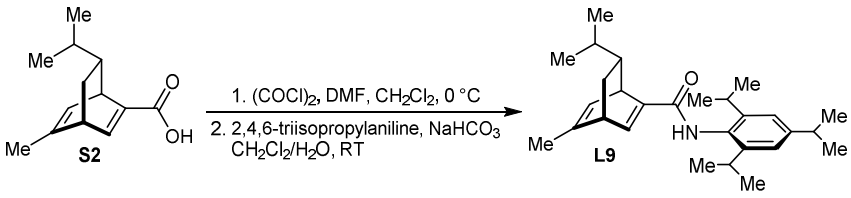
To a solution of the carboxylic acid **S2** (83 mg, 0.40 mmol) and HBTU (167 mg, 0.44 mmol) in MeCN (8 mL) at room temperature was added Et_3N (70 µL, 0.44 mmol) and aniline (40 µL, 0.44 mmol). The reaction was stirred at room temperature for 1 h, quenched with brine (8 mL), and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with 2 M aqueous HCl solution (30 mL), saturated aqueous $NaHCO_3$ solution (30 mL), and brine (30 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (10% EtOAc/hexane) gave the *chiral diene* **L7** as a white solid (73 mg, 89%). R_f = 0.35 (10% EtOAc/hexane); m.p. 83-85 °C (CH_2Cl_2); $[\alpha]_D^{20}$ +18.4 (*c* 1.10, $CHCl_3$); IR 1793, 1668 (C=O), 1597, 1093, 904, 802, 650 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.53 (2H, m, Ar**H**), 7.37 (1H, br s, N**H**), 7.34-7.31 (2H, m, Ar**H**), 7.09 (1H, t, *J* = 7.4 Hz, Ar**H**), 6.96 (1H, dd, *J* = 6.2, 1.8 Hz, =C**H**), 5.86-5.85 (1H, m, =C**H**), 4.16 (1H, dt, *J* = 6.0, 2.0 Hz, =CHC**H**), 3.42 (1H, dt, *J* = 8.5, 2.4 Hz, =CHC**H**), 1.86 (3H, d, *J* = 1.6 Hz, =CC**H**$_3$), 1.63 (1H, ddd, *J* = 11.7, 8.8, 3.0 Hz, C**H**$_2$), 1.31-1.26 (1H, m, C**H**), 1.17-1.10 (1H, m, C**H**), 1.03 (3H, d, *J* = 6.4 Hz, CH(C**H**$_3$)$_2$), 1.03-0.99 (1H, m, C**H**$_2$), 0.85 (3H, d, *J* = 6.5 Hz, CH(C**H**$_3$)$_2$); ^{13}C NMR (125.8 MHz; $CDCl_3$) δ 164.1 (C), 145.6 (C), 143.8 (C), 138.6 (CH), 138.1 (C), 129.0 (2 x CH), 124.2 (CH), 123.9 (CH), 119.6 (2 x CH), 47.8 (CH), 43.8 (CH), 40.0 (CH), 33.8 (CH), 31.8 (CH_2), 21.8 (CH_3), 21.4 (CH_3), 19.0 (CH_3); HRMS (EI) Exact mass calculated for $C_{19}H_{23}NO$ $[M^+]$: 281.1774, found: 281.1772.

(1*R*,4*R*,7*R*)-7-Isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid (2,4,6-trimethylphenyl)amide (L8)



To a solution of the carboxylic acid **S2** (62 mg, 0.30 mmol) and HBTU (125 mg, 0.33 mmol) in MeCN (8 mL) at room temperature was added Et_3N (52 µL, 0.33 mmol) and 2,4,6-trimethylaniline (50 µL, 0.33 mmol). The reaction was heated at reflux for 16 h, cooled to room temperature, quenched with brine (8 mL), and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with 2 M aqueous HCl solution (30 mL), saturated aqueous $NaHCO_3$ solution (30 mL), and brine (30 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (10% EtOAc/hexane) gave the *chiral diene* **L8** as a white solid (73 mg, 75%). R_f = 0.31 (50% Et_2O/hexane); m.p. 158-160 °C (EtOAc/hexane); $[\alpha]_D^{20}$ +30.0 (*c* 0.20, $CHCl_3$); IR 3150 (br, NH), 2899, 2851, 1599 (C=O), 1435, 1215, 1010, 758, 669 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.02 (1H, dd, *J* = 6.1, 1.6 Hz, =C**H**), 6.89 (2H, s, Ar**H**), 6.85 (1H, br s, N**H**), 5.86 (1H, d, *J* = 5.8 Hz, =C**H**), 4.12-4.09 (1H, m, =CHC**H**), 3.43-3.39 (1H, m, =CHC**H**), 2.27 (3H, s, ArC$\mathbf{H}_3$), 2.19 (6H, s, 2 x ArC$\mathbf{H}_3$), 1.87 (3H, d, *J* = 1.2 Hz, =CC$\mathbf{H}_3$), 1.65 (1H, ddd, *J* = 11.6, 8.9, 2.8 Hz, C$\mathbf{H}_2$), 1.32-1.24 (1H, m, C**H**), 1.18-1.09 (1H, m, C**H**), 1.03-0.98 (1H, m, C$\mathbf{H}_2$), 1.01 (3H, d, *J* = 6.5 Hz, CH(C$\mathbf{H}_3$)$_2$), 0.85 (3H, d, *J* = 6.5 Hz, CH(C$\mathbf{H}_3$)$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.2 (C), 145.0 (C), 143.8 (C), 138.6 (CH), 136.7 (C), 135.3 (2 x C), 131.3 (C), 128.8 (2 x CH), 124.1 (CH), 48.0 (CH), 43.7 (CH), 40.2 (CH), 33.8 (CH), 31.8 (CH_2), 21.8 (CH_3), 21.4 (CH_3), 20.9 (CH_3), 19.0 (CH_3), 18.4 (2 x CH_3); HRMS (EI) Exact mass calculated for $C_{22}H_{29}NO$ $[M]^+$: 323.2244, found: 323.2245.

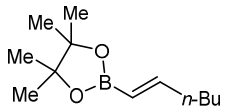
(1*R*,4*R*,7*R*)-7-Isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid (2,4,6-triisopropylphenyl)amide (L9)



To a solution of the carboxylic acid **S2** (62 mg, 0.30 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added oxalyl chloride (31 µL, 0.36 mmol) dropwise over 1 min, and the solution was stirred at 0 °C for 5 min.

DMF (30 μL) was added and the solution was stirred at room temperature for 1.5 h to generate the acid chloride. This solution was then transferred *via* cannula to a biphasic mixture of 2,4,6-triisopropylaniline[5] (263 mg, 1.20 mmol) in CH_2Cl_2 (20 mL) and saturated aqueous $NaHCO_3$ solution (20 mL) at 0 °C. Once the addition was complete, the mixture was stirred at room temperature for 16 h, before being extracted with CH_2Cl_2 (3 x 20 mL). The combined orgnic extracts were washed with saturated aqueous NH_4Cl solution (20 mL), dried $(MgSO)_4$, filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (10% Et_2O/hexane) gave the *chiral diene* **L9** as a peach solid (86 mg, 70%). R_f = 0.32 (10% EtOAc/hexane); m.p. 238-240 °C (EtOAc/hexane); $[\alpha]_D^{20}$ +14.2 (*c* 0.40, $CHCl_3$); IR 3296 (br, NH), 2955, 2926, 1638 (C=O), 1589, 1460, 1362, 1265, 1229, 910, 874, 828, 737, 689 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.03 (1H, dd, *J* = 6.3, 1.9 Hz, =C**H**), 7.02 (2H, s, Ar**H**), 6.82 (1H, br s, N**H**), 5.88-5.86 (1H, m, =C**H**), 4.08 (1H, dt, *J* = 6.0, 1.9 Hz, =CHC**H**), 3.43-3.40 (1H, m, =CHC**H**), 3.04 (2H, sept, *J* = 6.9 Hz, 2 x C**H**$(CH_3)_2$), 2.90 (1H, sept, *J* = 6.9 Hz, C**H** C**H**$(CH_3)_2$), 1.88 (3H, d, *J* = 1.6 Hz, =CC**H**$_3$), 1.67 (1H, ddd, *J* = 11.6, 8.8, 3.0 Hz, C**H**$_2$), 1.30-1.22 (1H, m, C**H**), 1.26 (6H, d, *J* = 6.9 Hz, CH(C**H**$_3)_2$), 1.22 (6H, d, *J* = 6.9 Hz, CH(C**H**$_3)_2$), 1.19 (6H, d, *J* = 6.9 Hz, CH(C**H**$_3)_2$), 1.16-1.07 (1H, m, C**H**), 1.03-1.00 (1H, m, C**H**$_2$), 1.01 (3H, d, *J* = 6.5 Hz, CH(C**H**$_3)_2$), 0.87 (3H, d, *J* = 6.4 Hz, CH(C**H**$_3)_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.0 (C), 148.3 (C), 145.9 (2 x C), 144.9 (C), 143.9 (C), 138.6 (CH), 129.0 (C), 123.9 (CH), 121.4 (2 x CH), 48.2 (CH), 43.7 (CH), 40.3 (CH), 34.3 (CH), 33.7 (CH), 31.7 (CH_2), 28.9 (2 x CH), 24.1 (2 x CH_3), 23.7 (2 x CH_3), 23.6 (2 x CH_3), 21.8 (CH_3), 21.4 (CH_3), 19.0 (CH_3); HRMS (EI) Exact mass calculated for $C_{28}H_{41}NO$ $[M]^+$: 407.3183, found: 407.3187.

Preparation of Alkenylboronic Esters

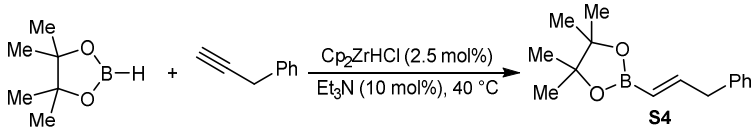


S3

Alkenylboronic ester **S3**[6] was prepared according to a previously reported procedure.

5. Prepared as in: Liu, J.-Y.; Zheng, Y.; Li, Y.-G.; Pan, L.; Li, Y.-S.; Hu, N.-H. *J. Organomet. Chem*. **2005**, *690*, 1233–1239.
6. Wang, Y. D.; Kimball, G.; Prashad, A. S.; Wang, Y. *Tetrahedron Lett.* **2005**, *46*, 8777–8780.

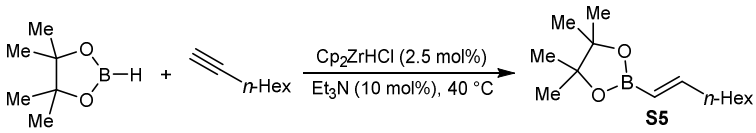
4,4,5,5-Tetramethyl-2-[(*E*)-3-phenylpropenyl]-[1,3,2]dioxaborolane (S4)[7]



S4

A mixture of pinacolborane (5.8 mL, 40.0 mmol), prop-2-ynylbenzene (4.98 g, 40.0 mmol), Cp_2ZrHCl (292 mg, 1.00 mmol), and Et_3N (0.56 mL, 4.00 mmol) was heated at 40 °C for 15 h and cooled to room temperature. The reaction was quenched with H_2O (60 mL) and extracted with CH_2Cl_2 (5 x 30 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (10% EtOAc/hexane) gave the alkenylboronic ester **S4** as a colorless oil (8.36 g, 86%) that displayed spectroscopic data consistent with those reported previously.[7]

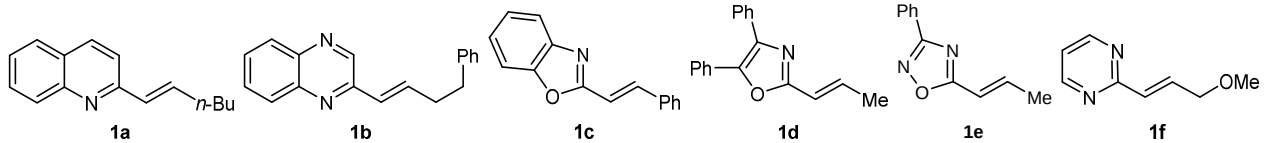
4,4,5,5-Tetramethyl-2-[(*E*)-oct-1-en-1-yl]-[1,3,2]-dioxaborolane (S5)[8]



S5

A mixture of pinacolborane (6.91 mL, 47.6 mmol), 1-octyne (5.00 g, 45.4 mmol), Cp_2ZrHCl (1.17 g, 4.54 mmol), and Et_3N (0.63 mL, 4.54 mmol) was heated at 40 °C for 17 h and cooled to room temperature. The reaction was quenched with H_2O (60 mL) and extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine (150 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (98:2→95:5→90:10 petroleum ether/EtOAc) gave the alkenylboronic ester **S5** as a colorless oil (9.95 g, 92%) that displayed spectroscopic data consistent with those reported previously.[8]

Preparation of Alkenylazaarenes

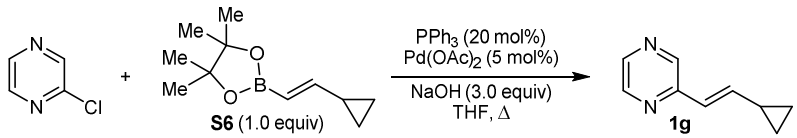


1a **1b** **1c** **1d** **1e** **1f**

Alkenylazaarenes **1a**,[2] **1b**,[2] **1c**,[9] **1d**,[10] **1e**,[2] and **1f**[11] were prepared according to previously reported procedures.

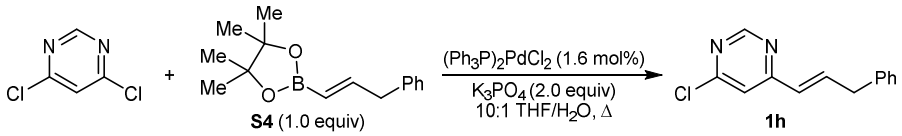
7. Shimizu, H.; Igarashi, T.; Miura, T.; Murakami, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 11465–11469.
8. Morrill, C.; Grubbs, R. H. *J. Org. Chem.* **2003**, *68*, 6031–6034.
9. Evindar, G.; Batey, R. A. *J. Org. Chem.* **2006**, *71*, 1802–1808.
10. Evans, D. A.; Nagorny, P.; Xu, R. *Org. Lett.* **2006**, *8*, 5669–5672.
11. Saxena, A.; Choi, B.; Lam, H. W. *J. Am. Chem. Soc.* **2012**, *134*, 8428–8431.

2-[(*E*)-2-Cyclopropylvinyl]pyrazine (1g)



To a solution of 2-chloropyrazine (2.30 g, 20.0 mmol), $Pd(OAc)_2$ (225 mg, 1.00 mmol), PPh_3 (1.05 g, 4.00 mmol), and NaOH (2.40 g, 60.0 mmol) in THF (25 mL) at room temperature was added a solution of alkenylboronic ester **S6**[12] (3.90 g, 20.1 mmol) in THF (15 mL) *via* cannula over 5 min. The resulting mixture was heated at reflux for 15 h, cooled to room temperature, and diluted with H_2O (20 mL) and Et_2O (30 mL). The aqueous layer was separated and extracted with Et_2O (5 x 30 mL). The combined organic layers were dried $(MgSO)_4$, filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (10% EtOAc/hexane) gave the *alkenylpyrazine* **1g** as an orange oil (2.32 g, 79%). R_f = 0.38 (20% EtOAc/hexane); IR 3005, 1647, 1518, 1404, 1125, 1013, 956, 853, 756 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.38 (1H, app d, *J* = 1.5 Hz, Ar**H**), 8.37-8.36 (1H, m, Ar**H**), 8.26 (1H, d, *J* = 2.5 Hz, Ar**H**), 6.50 (1H, d, *J* = 15.5 Hz, ArC**H**=CH), 6.33 (1H, dd, *J* = 15.5, 5.5 Hz, ArCH=C**H**), 1.65-1.56 (1H, m, =CHC**H**), 0.89-0.84 (2H, m, C**H**$_2$C**H**$_2$), 0.60-0.56 (2H, m, C**H**$_2$C**H**$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 151.2 (C), 143.8 (CH), 143.0 (CH), 142.5 (CH), 141.8 (CH), 123.3 (CH), 14.9 (CH), 8.0 (2 x CH_2); HRMS (EI) Exact mass calculated for $C_9H_{10}N_2$ $[M]^+$: 146.0838, found: 146.0836.

4-Chloro-6-[(*E*)-3-phenylprop-1-en-1-yl]pyrimidine (1h)

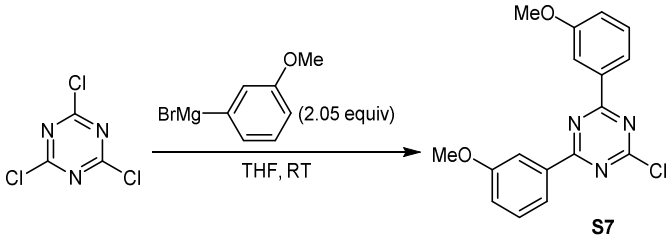


To a solution of 4,6-dichloropyrimidine (745 mg, 5.00 mmol), $Pd(PPh_3)_2Cl_2$ (53 mg, 0.08 mmol), and K_3PO_4 (2.10 g, 10.0 mmol) in THF (40 mL) and H_2O (5 mL) at room temperature was added a solution of alkenylboronic ester **S4**[7] (1.22 g, 5.00 mmol) in THF (10 mL) *via* cannula over 5 min. The resulting mixture was heated at reflux for 16 h, cooled to room temperature, and diluted with H_2O (50 mL) and EtOAc (50 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were dried $(MgSO)_4$, filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (30% EtOAc/hexane) gave the *alkenylpyrimidine* **1h** as a pale yellow oil (525 mg, 47%). R_f = 0.33 (20% EtOAc/hexane); IR 1653, 1514, 1451, 1277, 1103, 982, 872, 737, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.85 (1H, d, *J* = 0.7

12. Commercially available from Sigma–Aldrich.

Hz, Ar**H**), 7.35-7.31 (2H, m, Ar**H**), 7.29-7.20 (5H, m, Ar**H** and =C**H**CH_2), 6.36 (1H, dt, *J* = 15.5, 1.6 Hz, ArC**H**=CH), 3.62 (2H, dd, *J* = 6.9, 1.2 Hz, C$\mathbf{H}_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.0 (C), 161.5 (C), 158.6 (CH), 141.4 (CH), 138.0 (C), 128.8 (2 x CH), 128.7 (2 x CH), 127.8 (CH), 126.6 (CH), 118.1 (CH), 39.1 (CH_2); HRMS (ESI) Exact mass calculated for $C_{13}H_{12}N_2Cl$ $[M+H]^+$: 231.0684, found: 231.0686.

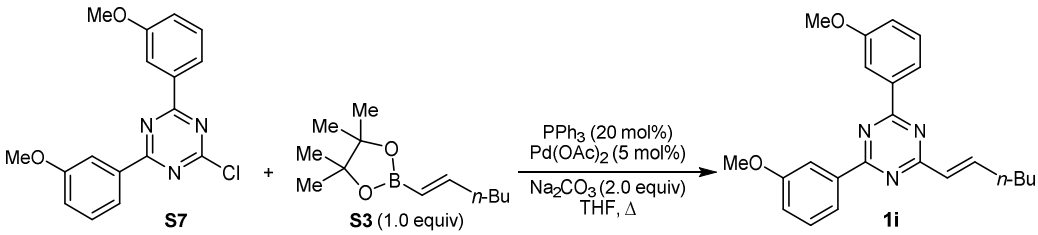
2-Chloro-4,6-bis-(3-methoxyphenyl)-[1,3,5]triazine (S7)



S7

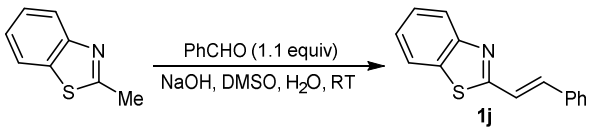
A solution of 3-bromoanisole (7.96 mL, 62.9 mmol) in THF (20 mL) was slowly added to a mixture of magnesium turnings (1.62 g, 61.6 mmol) in THF (40 mL). The resulting mixture was allowed to stir until it cooled to room temperature, before being slowly added to a solution of cyanuric chloride (5.53 g, 30.0 mmol) in THF (100 mL) at room temperature. The reaction stirred at room temperature for 16 h, and quenched carefully with saturated aqueous NH_4Cl solution (75 mL). The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 75 mL). The combined organic layers were dried $(MgSO)_4$, filtered, and concentrate *in vacuo*. Purification of the residue by column chromatography (20-40% toluene/hexane) gave the *triazine* **S7** as a white solid (7.77 g, 79%). R_f = 0.33 (10% EtOAc/hexane); m.p. 94-96 °C (EtOAc/hexane); IR 2926, 2832, 1531, 1501, 1454, 1369, 1323, 1296, 1283, 1246, 1034, 891, 870, 777, 764, 692, 665 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (2H, dd, *J* = 8.0, 0.8 Hz, Ar**H**), 8.13-8.11 (2H, m, Ar**H**), 7.45 (2H, t, *J* = 8.0 Hz, Ar**H**), 7.17 (2H, dd, *J* = 8.0, 2.7 Hz, Ar**H**), 3.94 (6H, s, 2 x OC$\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 173.1 (2 x C), 172.1 (C), 160.0 (2 x C), 135.7 (2 x C), 129.8 (2 x CH), 121.9 (2 x CH), 119.8 (2 x CH), 113.8 (2 x CH), 55.5 (2 x CH_3); HRMS (EI) Exact mass calculated for $C_{17}H_{14}N_3O_2Cl$ $[M]^+$: 327.0769, found: 327.0771.

2-[(*E*)-Hex-1-en-1-yl]-4,6-bis-(3-methoxyphenyl)-[1,3,5]triazine (1i)



To a solution of 2-chlorotriazine **S7** (1.64 g, 5.00 mmol), $Pd(OAc)_2$ (56 mg, 0.25 mmol), PPh_3 (262 mg, 1.00 mmol) and Na_2CO_3 (1.06 g, 10.0 mmol) in THF (15 mL) at room temperature was added a solution of alkenylboronic ester **S3** (1.05 g, 5.00 mmol) in THF (10 mL) *via* cannula over 5 min. The resulting mixture was heated at reflux for 16 h, cooled to room temperature, and diluted with H_2O (15 mL) and Et_2O (15 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic layers were dried $(MgSO)_4$, filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (5% EtOAc/hexane) gave the *alkenyltriazine* **1i** as a colorless amorphous solid (1.68 g, 89%). R_f = 0.46 (10% EtOAc/hexane); IR 2959, 2924, 1653, 1601, 1518, 1454, 1360, 1316, 1281, 1227, 1182, 1086, 1047, 974, 883, 858, 831, 783, 766, 731, 698, 675, 554 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.28 (2H, dt, *J* = 7.9, 1.4 Hz, Ar**H**), 8.21 (2H, dd, *J* = 2.7, 1.4 Hz, Ar**H**), 7.67 (1H, dt, *J* = 15.5, 7.0 Hz, =C**H**CH_2), 7.46 (2H, t, *J* = 7.9 Hz, Ar**H**), 7.14 (2H, ddd, *J* = 7.9, 2.7, 0.9 Hz, Ar**H**), 6.65 (1H, dt, *J* = 15.5, 1.5 Hz, ArC**H**=CH), 3.95 (6H, s, 2 x OC**H**$_3$), 2.44-2.39 (2H, m, C**H**$_2CH_2CH_2CH_3$), 1.63-1.57 (2H, m, C**H**$_2CH_2CH_3$), 1.49-1.42 (2H, m, C**H**$_2CH_3$), 0.98 (3H, t, *J* = 7.3 Hz, CH_2C**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 171.7 (C), 171.1 (2 x C), 159.9 (2 x C), 146.9 (CH), 137.6 (2 x C), 129.6 (2 x CH), 128.9 (CH), 121.4 (2 x CH), 118.4 (2 x CH), 113.6 (2 x CH), 55.4 (2 x CH_3), 32.6 (CH_2), 30.5 (CH_2), 22.4 (CH_2), 13.9 (CH_3); HRMS (EI) Exact mass calculated for $C_{23}H_{25}N_3O_2$ $[M]^+$: 375.1941, found: 375.1943.

2-[(*E*)-Styryl]benzothiazole (1j)[13]

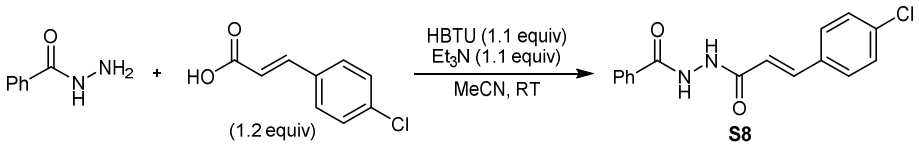


To a solution of 2-methylbenzothiazole (2.98 g, 20.0 mmol) and benzaldehyde (2.24 mL, 22.0 mmol) in DMSO (20 mL) at room temperature was added 17.6 M aqueous NaOH solution (21.0 mL, 370 mmol). The solution was stirred for 16 h, diluted with H_2O water (1.0 L), and the resulting precipitate

13. Besselièvre, F.; Piguel, S.; Mahuteau-Betzer, F.; Grierson, D. S. *Org. Lett.* **2008**, *10*, 4029–4032.

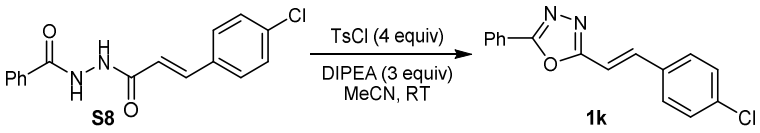
was collected by vacuum filtration and dried to leave the alkenylbenzothiazole **1j** as a yellow solid (3.85 g, 81%) that displayed spectroscopic data consistent with those reported previously.[13]

Benzoic acid *N*'-[(*E*)-3-(4-chlorophenyl)acryloyl] hydrazide (S8)



To a solution of 4-chlorocinnamic acid (8.80 g, 48.0 mmol) and HBTU (16.7 g, 44.0 mmol) in MeCN (450 mL) at room temperature was added Et_3N (6.1 mL, 44.0 mmol) and benzoic acid hydrazide (5.50 g, 40.0 mmol). The reaction was stirred at room temperature for 48 h and the precipitate formed was collected by filtration and washed with MeCN (2 x 150 mL) to leave the *hydrazide* **S8** as a white solid which required no further purification (11.8 g, 98%). R_f = 0.38 (10% EtOAc/hexane); m.p. 224-225 °C (MeCN); IR 3276 (br, NH), 1635 (C=O), 1496, 1325, 1112, 984, 687 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 9.62 (1H, s, N**H**), 9.34 (1H, s, N**H**), 6.99 (2H, app d, *J* = 7.3 Hz, Ar**H**), 6.74 (2H, app d, *J* = 8.4 Hz, Ar**H**), 6.68-6.63 (2H, m, Ar**H** and =C**H**), 6.60-6.56 (4H, m, Ar**H**), 5.85 (1H, d, *J* = 15.9 Hz, =C**H**); ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 165.5 (C), 164.2 (C), 138.9 (CH), 134.3 (C), 133.5 (C), 132.4 (C), 131.9 (CH), 129.4 (2 x CH), 129.0 (2 x CH), 128.5 (2 x CH), 127.5 (2 x CH), 120.3 (CH); HRMS (ESI) Exact mass calculated for $C_{16}H_{14}O_2N_2Cl$ $[M+H]^+$: 301.0738, found: 301.0743.

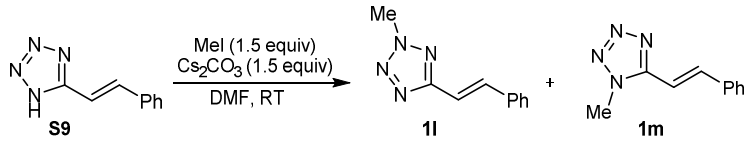
2-[(*E*)-2-(4-Chlorophenyl)vinyl]-5-phenyl-[1,3,4]oxadiazole (1k)



A suspension of the hydrazide **S8** (10.5 g, 35.0 mmol), *p*-toluenesulfonyl chloride (26.7 g, 140.0 mmol), and diisopropylethylamine (18.3 mL, 105 mmol) in MeCN (500 mL) was stirred at room temperature for 24 h. The precipitate formed was collected by filtration and washed with H_2O (2 x 150 mL) and MeCN (2 x 75 mL) to leave the *oxadiazole* **1k** as an off-white solid which required no further purification (6.52 g, 66%). R_f = 0.25 (20% EtOAc/hexane); m.p. 152-153 °C (EtOAc/hexane); IR 1645, 1516, 1449, 1084, 1009, 691, 808, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (2H, d, *J* = 6.9 Hz, Ar**H**), 7.61-7.52 (6H, m, Ar**H** and =C**H**), 7.41 (2H, app d, *J* = 7.1 Hz, Ar**H**), 7.08 (1H, d, *J* = 16.4 Hz, =C**H**); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.1 (C), 164.0 (C), 137.5 (CH), 135.8 (C), 133.3 (C), 131.8

(CH), 129.3 (2 x CH), 129.1 (2 x CH), 128.6 (2 x CH), 127.0 (2 x CH), 123.8 (C), 110.5 (CH); HRMS (ESI) Exact mass calculated for $C_{16}H_{12}ON_2Cl$ $[M+H]^+$: 283.0633, found: 283.0635.

2-Methyl-5-[(*E*)-styryl]tetrazole and 1-methyl-5-[(*E*)-styryl]tetrazole (1l and 1m)



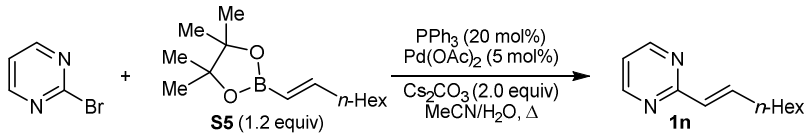
To a mixture of cinnamyltetrazole **S9**[14] (344 mg, 2.00 mmol) and Cs_2CO_3 (978 mg, 3.00 mmol) in DMF (50 mL) at room temperature was added MeI (0.19 mL, 3.00 mmol) in one portion and the resulting slurry was stirred for 16 h. The mixture was diluted with brine (100 mL) and extracted with EtOAc (3 x 100 mL). The combined organic layers were dried $(MgSO)_4$, filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (20-50% EtOAc/hexane) gave the *alkenyltetrazole* **1l** as a white solid (145 mg, 39%) followed by the isomeric *alkenyltetrazole* **1m** as an off-white solid (161 mg, 0.87 mmol, 43%). Recrystallization of **1m** from EtOAc/hexane gave colorless crystals that were suitable for X-ray diffraction.

Data for **1l**: R_f = 0.20 (10% EtOAc/hexane); m.p. 90-91 °C (EtOAc/hexane); IR 1649, 1495, 1476, 1443, 1389, 1080, 1024, 970, 799, 766, 729, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (1H, d, *J* = 16.5 Hz, =C**H**), 7.58-7.56 (2H, m, Ar**H**), 7.42-7.39 (2H, m, Ar**H**), 7.36-7.33 (1H, m, Ar**H**), 7.15 (1H, d, *J* = 16.5 Hz, =C**H**), 4.36 (3H, s, C$\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.4 (C), 136.3 (CH), 135.7 (C), 129.0 (CH), 128.8 (2 x CH), 127.1 (2 x CH), 113.4 (CH), 39.3 (CH_3); HRMS (EI) Exact mass calculated for $C_{10}H_{10}N_4$ $[M]^+$: 186.0900, found: 186.0901.

Data for **1m**: R_f = 0.30 (40% EtOAc/hexane); m.p. 118-120 °C (EtOAc/hexane); IR 1641, 1518, 1147, 1406, 1277, 1204, 1184, 1105, 972, 766, 729, 702, 679 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (1H, d, *J* = 16.1 Hz, =C**H**), 7.59-7.57 (2H, m, Ar**H**), 7.45-7.38 (3H, m, Ar**H**), 6.87 (1H, d, *J* = 16.1 Hz, =C**H**), 4.12 (3H, s, C$\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 152.6 (C), 140.8 (CH), 134.6 (C), 130.1 (CH), 129.0 (2 x CH), 127.5 (2 x CH), 106.7 (CH), 33.5 (CH_3); HRMS (EI) Exact mass calculated for $C_{10}H_{10}N_4$ $[M]^+$: 186.0900, found: 186.0895.

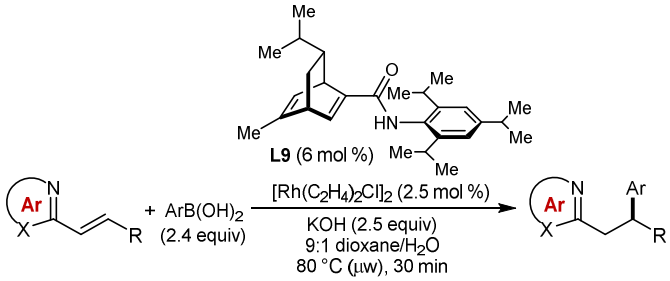
14. Prepared as in: Demko, Z. P.; Sharpless, K. B. *J. Org. Chem.* **2001**, *66*, 7945–7650.

(*E*)-2-(Oct-1-en-1-yl)pyrimidine (1n)



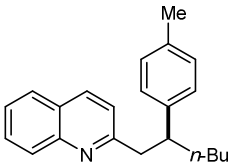
A solution of 2-bromopyrimidine (1.11 g, 7.00 mmol), alkenylboronic ester **S5** (2.00 g, 8.40 mmol), $Pd(OAc)_2$ (79 mg, 0.35 mmol), PPh_3 (367 mg, 1.40 mmol) and Cs_2CO_3 (4.56 g, 14.0 mmol) in MeCN (93 mL) and H_2O (24 mL) was heated at reflux for 20 h, cooled to room temperature, and diluted with H_2O (100 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (3 x 100 mL) and the combined organic layers were washed with saturated aqueous NH_4Cl solution (200 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (9:1→4:1 petroleum ether/EtOAc) gave the *alkenylpyrimidine* **1n** as a pale yellow oil (1.10 g, 83%). R_f = 0.24 (4:1 petroleum ether/EtOAc); IR 2927, 2856, 1647, 1591, 1573, 1517, 1111, 908, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.66 (2H, d, *J* = 4.9 Hz, Ar**H**), 7.19 (1H, dt, *J* = 15.6, 7.1 Hz, ArCH=C**H**), 7.06 (1H, t, *J* = 4.9 Hz, Ar**H**), 6.57 (1H, dt, *J* = 15.6, 1.5 Hz, ArC**H**=CH), 2.32 (2H, qd, *J* = 7.3, 1.5 Hz, =CHC$\mathbf{H}_2$), 1.57-1.49 (2H, m, =CHCH$_2$C$\mathbf{H}_2$), 1.42-1.25 (6H, m, C$\mathbf{H}_2$C$\mathbf{H}_2$C$\mathbf{H}_2$CH$_3$), 0.89 (3H, t, *J* = 7.0 Hz, C$\mathbf{H}_3$); ^{13}C NMR (125.8 MHz; $CDCl_3$) δ 164.8 (C), 156.9 (2 x CH), 142.5 (CH), 129.4 (CH), 118.3 (CH), 32.7 (CH_2), 31.7 (CH_2), 28.9 (CH_2), 28.6 (CH_2), 22.6 (CH_2), 14.1 (CH_3); HRMS (EI) Exact mass calcd for $C_{12}H_{18}N_2$ $[M]^+$: 190.1466, found: 190.1466.

Enantioselective Rhodium-Catalyzed Arylation of Alkenylazaarenes: General Procedure A

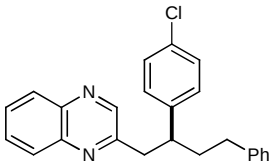


A solution of $[Rh(C_2H_4)_2Cl]_2$ (2.5 mol%) and chiral diene **L9** (6 mol%) in dioxane (2.5 mL/mmol of alkenylazaarene) was flushed with nitrogen and stirred at room temperature for 15 min. This solution was added to a mixture of the appropriate alkenylazaarene (1.0 equiv) and arylboronic acid (2.4 equiv) in a microwave vial *via* cannula, using further dioxane (2 mL/mmol of alkenylazaarene) as a rinse. 5 M Aqueous KOH solution (0.5 mL/mmol of alkenylazaarene, 2.5 equiv) was then added, and the resulting mixture was heated to 80 °C in a microwave reactor for 30 min. After cooling to room temperature, the

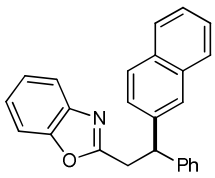
mixture was filtered through a short plug of SiO_2 using $CHCl_3$ as eluent and concentrated in *vacuo*. Purification of the residue by column chromatography gave the arylated product.



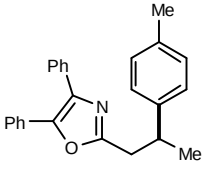
2-[(*S*)-2-(4-Methylphenyl)hexyl]quinoline (2a). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (4.9 mg, 0.0125 mmol), chiral diene **L9** (12.2 mg, 0.03 mmol), alkenylazaarene **1a** (105 mg, 0.50 mmol), and 4-methylphenylboronic acid (163 mg, 1.20 mmol) and purified by column chromatography (5% EtOAc/hexane) to give a yellow oil (115 mg, 76%). Data as described previously.[2] Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (major) = 7.8 min, t_r (minor) 12.1 min; 98% ee.



2-[(*S*)-2-(4-Chlorophenyl)-4-phenylbutyl]quinoxaline (2b). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (4.9 mg, 0.0125 mmol), chiral diene **L9** (12.2 mg, 0.03 mmol), alkenylazaarene **1b** (130 mg, 0.50 mmol), and 4-chlorophenylboronic acid (188 mg, 1.20 mmol) and purified by column chromatography (10% EtOAc/hexane) to give a yellow oil (136 mg, 73%). Data as described previously.[2] Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (major) = 31.5 min, t_r (minor) = 41.8 min; 97% ee.



2-[(*R*)-2-Naphthalen-2-yl-2-phenylethyl]benzoxazole (2c). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (4.9 mg, 0.0125 mmol), chiral diene **L9** (12.2 mg, 0.03 mmol), alkenylazaarene **1c** (111 mg, 0.50 mmol), and 2-naphthylboronic acid (206 mg, 1.20 mmol) and purified by column chromatography (10% EtOAc/hexane) to give a white solid (141 mg, 81%). Data as described previously.[2] Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (minor) = 24.0 min, t_r (major) = 35.1 min; 99% ee.

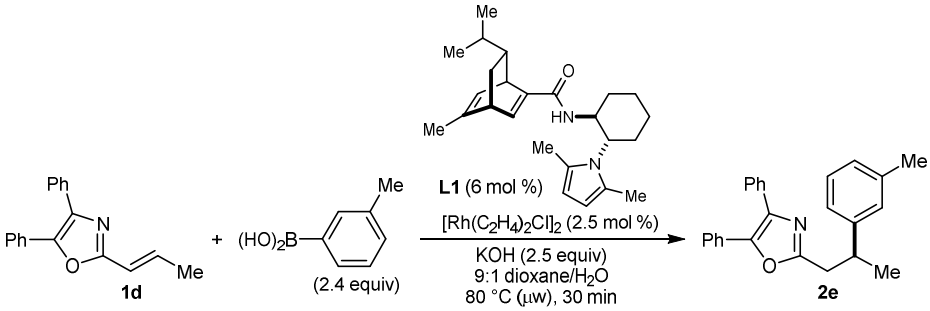


4,5-Diphenyl-2-[(*S*)-2-(4-methylphenyl)propyl]oxazole (2d). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (4.9 mg, 0.0125 mmol), chiral diene **L9** (12.2 mg, 0.03 mmol), alkenylazaarene **1d** (131 mg, 0.50 mmol), and 4-methylphenylboronic acid (163 mg, 1.20 mmol) and purified by column chromatography (5% EtOAc/hexane) to give a colorless oil (126 mg, 71%). Data as described

previously.[2] Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (minor) = 8.8 min, t_r (major) = 9.6 min; 77% ee.

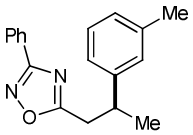
4,5-Diphenyl-2-[(S)-2-(3-methylphenyl)propyl]oxazole (2e)

*Using **L1**:*

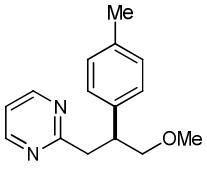


A solution of $[Rh(C_2H_4)_2Cl]_2$ (4.9 mg, 12.5 μmol) and chiral diene **L1** (11.4 mg, 0.03 mmol) in dioxane (1.25 mL) was flushed with nitrogen and stirred at room temperature for 15 min. This solution was added to a mixture of the alkenylazaarene **1d** (131 mg, 0.50 mmol) and 3-methylphenylboronic acid (163 mg, 1.20 mmol) in a microwave vial *via* cannula, using further dioxane (1 mL) as a rinse. 5 M Aqueous KOH solution (0.25 mL, 1.25 mmol) was then added, and the resulting mixture was heated to 80 °C in a microwave reactor for 30 min. After cooling to room temperature, the mixture was filtered through a short plug of SiO_2 using $CHCl_3$ as eluent and concentrated in *vacuo*. Purification of the residue by column chromatography (95:5→90:10 hexane/EtOAc) gave the *arylation product* **2e** as a white solid (169 mg, 95%). R_f = 0.29 (10% EtOAc/hexane); $[\alpha]_D^{24}$ +29.1 (*c* 1.75, $CHCl_3$); m.p. 98-99 °C (CH_2Cl_2/hexane); IR 3131, 1632, 1445, 1224, 1171, 1132, 1015, 954, 832, 754, 701, 661 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69-7.61 (2H, m, Ar**H**), 7.54 (2H, d, *J* = 7.0 Hz, Ar**H**), 7.41-7.30 (6H, m, Ar**H**), 7.24 (1H, t, *J* = 7.8 Hz, Ar**H**), 7.13-7.10 (2H, m, Ar**H**), 7.06 (1H, d, *J* = 7.6 Hz, Ar**H**), 3.46-3.37 (1H, m, CH_2C**H**), 3.16 (1H, dd, *J* = 14.8, 6.3 Hz, ArC**H**$_2$), 3.09 (1H, dd, *J* = 14.8, 8.9 Hz, ArC**H**$_2$), 2.36 (3H, s, ArC**H**$_3$), 1.41 (3H, d, *J* = 7.0 Hz, CHC**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 162.4 (C), 145.7 (C), 145.1 (C), 138.0 (C), 135.0 (C), 132.6 (C), 129.1 (C), 128.6 (2 x CH), 128.5 (2 x CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.9 (2 x CH), 127.7 (CH), 127.2 (CH), 126.4 (2 x CH), 123.8 (CH), 38.4 (CH), 36.9 (CH_2), 21.5 (CH_3), 21.4 (CH_3); HRMS (ESI) Exact mass calculated for $C_{25}H_{23}NO$ $[M]^+$: 353.1744, found: 353.1773. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (minor) = 8.3 min, t_r (major) = 8.8 min; 87% ee.

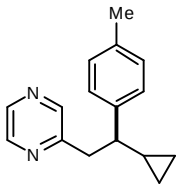
*Using **L9**:*
The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1d** (78 mg, 0.30 mmol), and 3-methylphenylboronic acid (98 mg, 0.72 mmol) and purified by column chromatography (2.5% EtOAc/hexane) to give a colorless film (81 mg, 76%). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (minor) = 8.1 min, t_r (major) = 8.5 min; 92% ee.



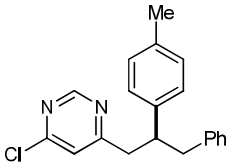
3-Phenyl-5-[(*S*)-2-(3-methylphenyl)propyl]-[1,2,4]oxadiazole (2f). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (4.9 mg, 0.0125 mmol), chiral diene **L9** (12.2 mg, 0.03 mmol), alkenylazaarene **1e** (93 mg, 0.50 mmol), and 3-methylphenylboronic acid (163 mg, 1.20 mmol) and purified by column chromatography (1% CH_2Cl_2/toluene) to give a colorless oil (96 mg, 69%). Data as described previously.[2] Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (minor) 10.9 min, t_r (major) = 11.6 min; 97% ee.



2-(*R*)-[3-Methoxy-2-(4-methylphenyl)propyl]pyrimidine (2g). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1f** (45 mg, 0.30 mmol), and 4-methylphenylboronic acid (98 mg, 0.72 mmol) and purified by column chromatography (60% EtOAc/hexane) to give a pale yellow oil (56 mg, 77%). R_f = 0.23 (60% EtOAc/hexane); $[\alpha]_D^{20}$ +56.0 (*c* 0.20, $CHCl_3$); IR 3036, 2978, 2924, 2868, 2824, 1638, 1560, 1514, 1439, 1398, 1381, 1346, 1192, 1115, 939, 814, 729, 635, 588 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.61 (2H, d, *J* = 4.9 Hz, Ar**H**), 7.15 (2H, app d, *J* = 8.0 Hz, Ar**H**), 7.07-7.05 (3H, m, Ar**H**), 3.71-3.65 (1H, m, C**H**), 3.60 (1H, dd, *J* = 9.5, 6.3 Hz, C**H**$_2$O), 3.56 (1H, dd, *J* = 9.5, 7.2 Hz, C**H**$_2$O), 3.44 (1H, dd, *J* = 14.1, 7.0 Hz, ArC**H**$_2$), 3.29 (3H, s, OC**H**$_3$), 3.24 (1H, dd, *J* = 14.1, 8.1 Hz, ArC**H**$_2$), 2.28 (3H, s, ArC**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.0 (C), 156.8 (2 x CH), 139.0 (C), 135.9 (C), 129.0 (2 x CH), 127.7 (2 x CH), 118.3 (CH), 76.7 (CH_2), 58.8 (CH_3), 44.5 (CH), 42.8 (CH_2), 21.0 (CH_3); HRMS (EI) Exact mass calculated for $C_{15}H_{18}N_2O$ $[M]^+$: 242.1414, found: 242.1415. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 210 nm, 25 °C); t_r (major) = 24.3 min, t_r (minor) *ca.* 27.0 min; 99% ee.

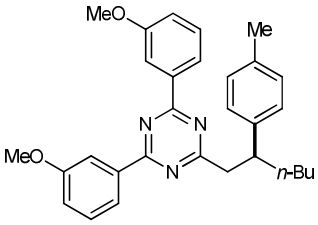


2-[(*R*)-2-Cyclopropyl-2-(4-methylphenyl)ethyl]pyrazine (2h). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1g** (44 mg, 0.30 mmol), and 4-methylphenylboronic acid (98 mg, 0.72 mmol) and purified by column chromatography (10% EtOAc/hexane) to give a pale yellow oil (34 mg, 48%). R_f = 0.09 (10% EtOAc/hexane); $[\alpha]_D^{20}$ +85.1 (*c* 0.09, $CHCl_3$); IR 2999, 1514, 1474, 1431, 1402, 1344, 1117, 1057, 1011, 839, 808 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.47 (1H, dd, *J* = 2.3, 1.6 Hz, Ar**H**), 8.34 (1H, d, *J* = 2.3 Hz, Ar**H**), 8.22 (1H, s, Ar**H**), 7.09-7.05 (4H, m, Ar**H**), 3.27 (1H, dd, *J* = 13.4, 7.0 Hz, ArC**H**$_2$), 3.19 (1H, dd, *J* = 13.4, 8.2 Hz, ArC**H**$_2$), 2.34-2.28 (1H, m, ArCH$_2$C**H**), 2.30 (3H, s, ArC**H**$_3$), 1.09 (1H, dtt, *J* = 9.8, 8.1, 5.0 Hz, C**H**CH$_2$CH$_2$), 0.51-0.46 (1H, m, C**H**$_2$CH$_2$), 0.43-0.38 (1H, m, C**H**$_2$CH$_2$), 0.12-0.07 (1H, m, C**H**$_2$CH$_2$), 0.03-0.00 (1H, m, C**H**$_2$CH$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 156.3 (C), 145.3 (CH), 143.9 (CH), 142.0 (CH), 141.1 (C), 135.9 (C), 129.1 (2 x CH), 127.3 (2 x CH), 50.9 (CH), 43.0 (CH_2), 21.0 (CH_3), 17.0 (CH), 5.7 (CH_2), 3.9 (CH_2); HRMS (EI) Exact mass calculated for $C_{16}H_{18}N_2$ $[M]^+$: 238.1465, found: 238.1463. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (minor) *ca.* 8.8 min, t_r (major) = 9.9 min; 99% ee.

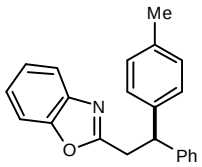


4-Chloro-6-[(*S*)-2-(4-methylphenyl)-3-phenylpropyl]pyrimidine (2i). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1h** (69 mg, 0.30 mmol), and 4-methylphenylboronic acid (98 mg, 0.72 mmol) and purified by column chromatography (5% Et_2O/hexane) to give a colorless oil (76 mg, 78%). R_f = 0.34 (20% EtOAc/hexane); $[\alpha]_D^{20}$ +53.1 (*c* 0.50, $CHCl_3$); IR 3057, 3026, 1630, 1573, 1493, 1477, 1437, 1414, 1194, 1103, 957, 897, 866, 814, 748, 698, 662, 608, 592 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.83 (1H, d, *J* = 0.8 Hz, Ar**H**), 7.24-7.21 (2H, m, Ar**H**), 7.16 (1H, app tt, *J* = 7.3, 1.3 Hz, Ar**H**), 7.10-7.08 (2H, m, Ar**H**), 7.03 (2H, app d, *J* = 8.0 Hz, Ar**H**), 6.97 (2H, app d, *J* = 8.0 Hz, Ar**H**), 6.88 (1H, d, *J* = 0.8 Hz, Ar**H**), 3.50-3.44 (1H, m, CH$_2$C**H**CH$_2$), 3.11 (1H, dd, *J* = 13.9, 5.8 Hz, C**H**$_2$CHCH$_2$Ph), 3.04-2.98 (2H, m, C**H**$_2$Ph), 2.94 (1H, dd, *J* = 13.9, 7.8 Hz, C**H**$_2$CHCH$_2$Ph), 2.29 (3H, s, ArC**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 171.1 (C), 160.8 (C), 158.4 (CH), 139.7 (C), 139.6 (C), 136.2 (C), 129.1 (4 x CH), 128.2 (2 x CH), 127.4 (2 x CH), 126.2 (CH), 121.4 (CH), 46.5 (CH), 43.5 (CH_2), 43.2 (CH_2), 21.0 (CH_3); HRMS (EI) Exact mass calculated for $C_{20}H_{19}N_2Cl$ $[M]^+$: 322.1231, found: 322.1233.

Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 210 nm, 25 °C); t_r (major) = 8.2 min, t_r (minor) = 9.6 min; 99% ee.



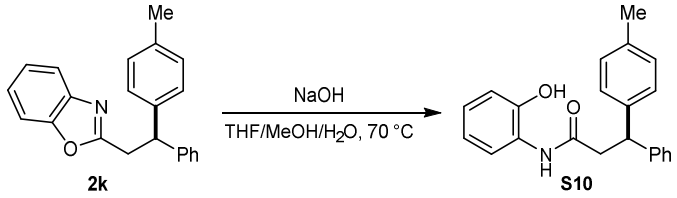
2,4-Bis-(3-methoxyphenyl)-6-[(*S*)-2-(4-methyphenyl)hexyl]-[1,3,5]triazine (2j). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1i** (113 mg, 0.30 mmol), and 4-methylphenylboronic acid (98 mg, 0.72 mmol) and purified by column chromatography (10% EtOAc/hexane) to give a colorless oil (125 mg, 89%). R_f = 0.24 (10% EtOAc/hexane); $[\alpha]_D^{20}$ +70.0 (*c* 1.40, $CHCl_3$); IR 3005, 2955, 2928, 2857, 1601, 1524, 1454, 1429, 1371, 1316, 1281, 1240, 1045, 818, 783, 766, 737, 689 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.24 (2H, br d, *J* = 7.9 Hz, Ar**H**), 8.18-8.16 (2H, m, Ar**H**), 7.47 (2H, t, *J* = 7.9 Hz, Ar**H**), 7.21 (2H, app d, *J* = 8.0 Hz, Ar**H**), 7.16 (2H, ddd, *J* = 7.9, 2.7, 0.8 Hz, Ar**H**), 7.11 (2H, app d, *J* = 8.0 Hz, Ar**H**), 3.96 (6H, s, 2 x OC**H**$_3$), 3.56-3.50 (1H, m, CH_2C**H**CH_2), 3.38 (1H, dd, *J* = 14.5, 6.9 Hz, ArC**H**$_2$), 3.32 (1H, dd, *J* = 14.5, 8.2 Hz, ArC**H**$_2$), 2.31 (3H, s, ArC**H**$_3$), 1.86-1.73 (2H, m, C**H**$_2CH_2CH_2CH_3$), 1.41-1.21 (4H, m, C**H**$_2$C**H**$_2CH_3$), 0.88 (3H, t, *J* = 7.0 Hz, C**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 178.6 (C), 170.7 (2 x C), 159.8 (2 x C), 141.6 (C), 137.5 (2 x C), 135.4 (C), 129.5 (2 x CH), 128.9 (2 x CH), 127.6 (2 x CH), 121.4 (2 x CH), 118.4 (2 x CH), 113.5 (2 x CH), 55.3 (2 x CH_3), 46.1 (CH_2), 43.6 (CH), 36.1 (CH_2), 29.6 (CH_2), 22.7 (CH_2), 20.9 (CH_3), 14.0 (CH_3); HRMS (EI) Exact mass calculated for $C_{30}H_{33}N_3O_2$ $[M]^+$: 467.2567, found: 467.2562. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (100% hexane, 0.4 mL/min, 250 nm, 25 °C); t_r (major) = 51.5 min, t_r (minor) = 55.6 min; 90% ee.



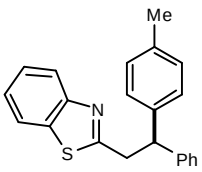
2-[(*R*)-2-(4-Methylphenyl)-2-phenylethyl]benzooxazole (2k). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1c** (66 mg, 0.30 mmol), and 4-methylphenylboronic acid (98 mg, 0.72 mmol) and purified by column chromatography (10% EtOAc/hexane) to give a colorless film (68 mg, 72%). R_f = 0.30 (10% EtOAc/hexane); $[\alpha]_D^{20}$ +30.1 (*c* 0.46, $CHCl_3$); IR 3031, 1619, 1425, 1208, 1191, 1109, 1034, 956, 832, 721, 702, 654 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.68-7.63 (1H, m, Ar**H**), 7.49-7.44 (1H, m, Ar**H**), 7.35-7.27 (6H, m, Ar**H**), 7.25-7.18 (3H, m, Ar**H**), 7.11 (2H, d, *J* = 4.9 Hz, Ar**H**), 4.83 (1H, t, *J* = 8.1 Hz, CH_2C**H**), 3.70 (2H, d, *J* = 8.1 Hz, C**H**$_2$), 2.31 (3H, s, ArC**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ

165.2 (C), 150.6 (C), 143.3 (C), 141.2 (C), 140.1 (C), 136.2 (C), 129.3 (2 x CH), 128.6 (2 x CH), 127.6 (2 x CH), 127.5 (2 x CH), 126.6 (CH), 124.4 (CH), 124.0 (CH), 119.6 (CH), 110.3 (CH), 48.2 (CH), 35.1 (CH_2), 20.9 (CH_3); HRMS (EI) Exact mass calculated for $C_{22}H_{19}NO$ $[M]^+$: 313.1461, found: 313.1459. To facilitate determination of enantiomeric excess, **2k** was converted into the amide **S10** using the following procedure:

(3*R*)-*N*-(2-Hydroxyphenyl)-3-(4-methylphenyl)-3-phenylpropanamide (S10)

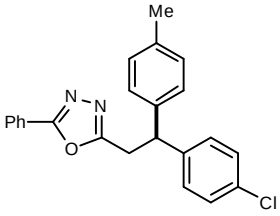


To a solution of benzoxazole **2k** (45 mg, 0.14 mmol) in THF (1.5 mL) and MeOH (1.5 mL) was added 2 M aqueous NaOH solution (1.0 mL) and the reaction was heated at 70 °C for 18 h. After cooling to room temperature, the mixture was acidified with 10% aqueous HCl solution (10 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (9:1→4:1 hexane/EtOAc) gave the *amide* **S10** as a white solid (29 mg, 61%). R_f = 0.17 (4:1 hexane/EtOAc); R_f = 0.17 (4:1 hexane/EtOAc); $[\alpha]_D^{20}$ +5.0 (*c* 0.20, $CHCl_3$); m.p. 147-149 °C (CH_2Cl_2/hexane); IR 3312 (OH), 3055, 3026, 1645 (C=O), 1603, 1537, 1497, 1452, 1447, 1396, 1366, 1312, 1265, 1242, 1159, 746, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.53 (1H, s, O**H** or N**H**), 7.35-7.30 (2H, m, Ar**H**), 7.29-7.21 (3H, m, Ar**H** and O**H** or N**H**), 7.20-7.12 (5H, m, Ar**H**), 7.11-7.07 (1H, m, Ar**H**), 6.97 (1H, dd, *J* = 8.1, 1.2 Hz, Ar**H**), 6.80-6.74 (1H, m, Ar**H**), 6.53 (1H, dd, *J* = 7.9, 1.2 Hz, Ar**H**), 4.57 (1H, t, *J* = 7.8 Hz, CH_2C**H**), 3.16 (2H, d, *J* = 7.8 Hz, C$\mathbf{H}_2$), 2.32 (3H, s, C$\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 171.7 (C), 148.9 (C), 143.1 (C), 139.8 (C), 136.6 (C), 129.6 (2 x CH), 128.9 (2 x CH), 127.6 (2 x CH), 127.5 (2 x CH), 127.3 (CH), 126.9 (CH), 125.2 (C), 122.1 (CH), 120.3 (CH), 119.9 (CH), 47.3 (CH), 43.7 (CH_2), 21.0 (CH_3); HRMS (ESI) Exact mass calculated for $C_{22}H_{22}NO_2$ $[M+H]^+$: 332.1645, found: 332.1647; Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 hexane/*i*-PrOH, 0.8 mL/min, 210 nm, 25 °C); t_r (major) = 23.5 min, t_r (minor) *ca.* 27.2 min; 99% ee.



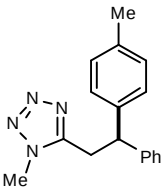
2-[(*R*)-2-(4-Methylphenyl)-2-phenylethyl]benzothiazole (2l). The title compound was prepared according to a modification of General Procedure A (in that a different workup was used) from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg,

0.018 mmol), alkenylazaarene **1j** (71 mg, 0.30 mmol), and 4-methylphenylboronic acid (98 mg, 0.72 mmol). After cooling to room temperature, the mixture was filtered through a short plug of SiO_2 using $CHCl_3$ as eluent and concentrated in *vacuo*. To the residue was added a solution of $K_2[OsO_2(OH)_4]$ (6 mg, 15 μmol) and NMO (53 mg, 0.45 mmol) in acetone (4.5 mL) and H_2O (1.5 mL). The resulting solution was stirred for 16 h at room temperature, filtered through a short plug of SiO_2 using $CHCl_3$ as eluent, and concentrated in *vacuo*. Purification of the residue by column chromatography (10% EtOAc/hexane) gave the *arylation product* **2l** as a pale yellow oil (69 mg, 70%). R_f = 0.17 (10% EtOAc/hexane); $[\alpha]_D^{20}$ +63.0 (*c* 0.50, $CHCl_3$); IR 3057, 3028, 1630, 1435, 1308, 1192, 1105, 1076, 1013, 957, 866, 818, 756, 727, 710, 687, 662, 621, 594 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (1H, br d, *J* = 8.0 Hz, Ar**H**), 7.76 (1H, br d, *J* = 8.0 Hz, Ar**H**), 7.43 (1H, ddd, *J* = 8.3, 7.2, 1.2 Hz, Ar**H**), 7.35-7.28 (5H, m, Ar**H**), 7.22 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.19 (1H, tt, *J* = 7.1, 1.5 Hz, Ar**H**), 7.10 (2H, d, *J* = 8.0 Hz, Ar**H**), 4.66 (1H, t, *J* = 8.0 Hz, CH_2C**H**), 3.88 (2H, d, *J* = 8.0 Hz, C**H**$_2$), 2.30 (3H, s, ArC**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.0 (C), 152.9 (C), 143.4 (C), 140.1 (C), 136.2 (C), 135.2 (C), 129.3 (2 x CH), 128.6 (2 x CH), 127.80 (2 x CH), 127.70 (2 x CH), 126.6 (CH), 125.8 (CH), 124.6 (CH), 122.5 (CH), 121.4 (CH), 50.7 (CH), 40.5 (CH_2), 21.0 (CH_3); HRMS (EI) Exact mass calculated for $C_{22}H_{19}NS$ $[M]^+$: 329.1233, found: 329.1234. Enantiomeric excess was determined by HPLC with a Chiralpak IA-3 column (99.5:0.5 hexane:*i*-PrOH, 0.3 mL/min, 210 nm, 25 °C); t_r (major) = 51.2 min, t_r (minor) *ca*. 55 min; 99% ee.

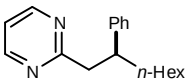


2-[(*S*)-2-(4-Chlorophenyl)-2-(4-methylphenyl)ethyl]-5-phenyl-[1,3,4]oxadiazole (2m). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1k** (85 mg, 0.30 mmol) and 4-methylphenylboronic acid (98 mg, 0.72 mmol) and purified by column chromatography (5-10% EtOAc/hexane) to give a white solid (93 mg, 83%). Vapor diffusion of hexane into a solution of **2m** in EtOAc provided colorless crystals suitable for X-ray diffraction. R_f = 0.25 (10% EtOAc/hexane); m.p. 138-139 °C (EtOAc/hexane); $[\alpha]_D^{20}$ +32.1 (*c* 0.20, $CHCl_3$); IR 2940, 2868, 1762, 1553, 1514, 1487, 1445, 961, 912, 775, 710, 687, 561 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.93-7.91 (2H, m, Ar**H**), 7.54-7.46 (3H, m, Ar**H**), 7.26 (2H, app d, *J* = 8.6 Hz, Ar**H**), 7.23 (2H, app d, *J* = 8.6 Hz, Ar**H**), 7.16 (2H, app d, *J* = 8.1 Hz, Ar**H**), 7.12 (2H, app d, *J* = 8.1 Hz, Ar**H**), 4.63 (1H, t, *J* = 8.1 Hz, CH_2C**H**), 3.64 (2H, d, *J* = 8.1 Hz, C**H**$_2$), 2.31 (3H, s, C**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.0 (C), 164.7 (C), 141.3 (C), 139.1 (C), 136.8 (C), 132.6 (C), 131.6 (CH), 129.5 (2 x CH), 128.99

(CH), 128.97 (CH), 129.0 (2 x CH), 128.8 (2 x CH), 127.4 (2 x CH), 126.7 (2 x CH), 123.8 (C), 47.6 (CH), 31.8 (CH_2), 21.0 (CH_3); HRMS (EI) Exact mass calculated for $C_{23}H_{19}ClN_2O$ $[M]^+$: 374.1180, found: 374.1181. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 254 nm, 25 °C); t_r (major) = 24.2 min, t_r (minor) = 27.6 min; 99% ee.

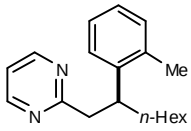


1-Methyl-5-[(*R*)-2-(4-methylphenyl)-2-phenylethyl)]tetrazole (2o). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1m** (56 mg, 0.30 mmol), and 4-methylphenylboronic acid (98 mg, 0.72 mmol) and purified by column chromatography (40% Et_2O/hexane) to give a colorless film (53 mg, 64%). R_f = 0.28 (40% EtOAc/hexane); $[\alpha]_D^{20}$ +43.1 (*c* 0.50, $CHCl_3$); IR 2952, 2835, 1638, 1528, 1144, 1398, 1235, 1204, 1185, 1109, 973, 766, 729, 709, 679 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.26 (2H, m, Ar**H**), 7.22 (1H, tt, *J* = 7.3, 1.2 Hz, Ar**H**), 7.18-7.15 (2H, m, Ar**H**), 7.10 (2H, app d, *J* = 8.0 Hz, Ar**H**), 7.06 (2H, app d, *J* = 8.0 Hz, Ar**H**), 4.54 (1H, t, *J* = 7.9 Hz, CH_2C**H**), 3.55 (2H, d, *J* = 7.9 Hz, C$\mathbf{H}_2$), 3.40 (3H, s, NC$\mathbf{H}_3$), 2.31 (3H, s, ArC$\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 154.1 (C), 142.5 (C), 139.3 (C), 136.8 (C), 129.5 (2 x CH), 128.8 (2 x CH), 127.6 (2 x CH), 127.5 (2 x CH), 127.0 (CH), 49.6 (CH), 32.8 (CH_3), 29.9 (CH_2), 21.0 (CH_3); HRMS (EI) Exact mass calculated for $C_{17}H_{18}N_4$ $[M]^+$: 278.1526, found: 278.1528. Enanti omeric excess was determined by HPLC with a Chiralpak AD-H column (92:8 hexane:*i*-PrOH, 0.8 mL/min, 254 nm, 25 °C); t_r (minor) = 27.0 min, t_r (major) = 30.5 min; 95% ee.

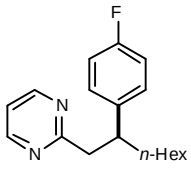


2-[(*S*)-2-Phenyloctyl]pyrimidine (2p). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1n** (57 mg, 0.30 mmol), and phenylboronic acid (88 mg, 0.72 mmol) and purified by column chromatography (20% EtOAc/hexane) to give a pale yellow oil (72 mg, 89%). R_f = 0.15 (20% EtOAc/hexane); $[\alpha]_D^{20}$ +30.3 (*c* 1.45, $CHCl_3$); IR 2926, 2854, 1606, 1560, 1490, 1452, 1421, 908, 761, 732, 695, 634 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.61 (2H, br s, Ar**H**), 7.25-7.22 (2H, m, Ar**H**), 7.20-7.18 (2H, m, Ar**H**), 7.16-7.12 (1H, m, Ar**H**), 7.07 (1H, br s, Ar**H**), 3.34-3.27 (2H, m, ArC$\mathbf{H}_2$C**H**), 3.21 (1H, dd, *J* = 12.3, 7.4 Hz, ArC$\mathbf{H}_2$), 1.73-1.61 (2H, m, C$\mathbf{H}_2(CH_2)_4CH_3$), 1.26-1.13 (8H, m, $(C\mathbf{H}_2)_4CH_3$), 0.83 (3H, d, *J* = 7.1 Hz, C$\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.2 (C), 156.8 (2 x CH), 144.7 (C), 128.2 (2 x CH), 127.6 (2 x CH), 126.0 (CH), 118.4 (CH), 46.8 (CH_2), 45.4 (CH), 36.0 (CH_2), 31.7 (CH_2), 29.3 (CH_2), 27.4 (CH_2), 22.6 (CH_2), 14.0 (CH_3); HRMS (EI) Exact mass calcd for $C_{18}H_{24}N_2$ $[M]^+$: 268.1934, found: 268.1935. Enantiomeric excess was determined by HPLC

with a Chiralpak IA-3 column (99:1 hexane:*i*-PrOH, 0.3 mL/min, 230 nm, 25 °C); t_r (minor) = 31.9 min, t_r (major) = 34.9 min; 99% ee.

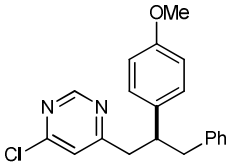


2-[(*S*)-2-(2-Methylphenyl)octyl]pyrimidine (2q). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1n** (57 mg, 0.30 mmol), and 2-methylphenylboronic acid (98 mg, 0.72 mmol) and purified by column chromatography (10%→20% EtOAc/hexane) to give a pale yellow oil (82 mg, >95%). R_f = 0.24 (20% EtOAc/hexane); $[\alpha]_D^{20}$ +19.4 (*c* 1.75, $CHCl_3$); IR 2926, 2854, 1606, 1560, 1490, 1421, 783, 634 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.60 (2H, d, *J* = 4.7 Hz, Ar**H**), 7.30 (1H, d, *J* = 7.9 Hz, Ar**H**), 7.19-7.15 (1H, m, Ar**H**), 7.06-7.02 (3H, m, Ar**H**), 3.70-3.64 (1H, m, $ArCH_2C\mathbf{H}$), 3.26 (1H, dd, *J* = 13.6, 7.4 Hz, $ArC\mathbf{H}_2$), 3.20 (1H, dd, *J* = 13.6, 7.9 Hz, $ArC\mathbf{H}_2$) 2.29 (3H, s, $ArC\mathbf{H}_3$), 1.74-1.61 (2H, m, $C\mathbf{H}_2(CH_2)_4CH_3$), 1.26-1.15 (8H, m, $(C\mathbf{H}_2)_4CH_3$), 0.83 (3H, d, *J* = 7.0 Hz, $CH_2C\mathbf{H}_3$); ^{13}C NMR (125.8 MHz; $CDCl_3$) δ 170.4 (C), 156.7 (2 x CH), 143.1 (C), 136.0 (C), 130.0 (CH), 126.1 (CH), 126.0 (CH), 125.5 (CH), 118.3 (CH), 46.5 (CH_2) 39.7 (CH), 36.0 (CH_2), 31.7 (CH_2), 29.4 (CH_2), 27.3 (CH_2), 22.6 (CH_2), 19.8 (CH_3), 14.0 (CH_3); HRMS (EI) Exact mass calcd for $C_{19}H_{26}N_2$ $[M]^+$: 282.2091, found: 282.2092. Enantiomeric excess was determined by HPLC with a Chiralpak IA-3 column (98:2 hexane/*i*-PrOH, 1.5 mL/min, 230 nm, 25 °C); t_r (minor) = 4.0 min; t_r (major) = 4.9 min; 97% ee.



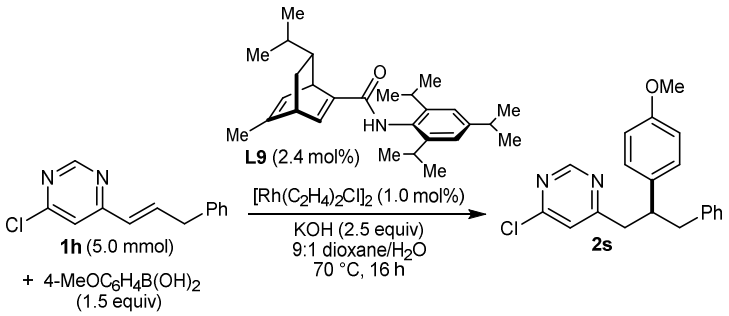
2-[(*S*)-2-(4-Fluorophenyl)octyl]pyrimidine (2r). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1n** (57 mg, 0.30 mmol), and 4-fluorophenylboronic acid (101 mg, 0.72 mmol) and purified by column chromatography (10%→20% EtOAc/hexane) to give a colorless oil (67 mg, 78%). R_f = 0.15 (20% EtOAc/hexane); $[\alpha]_D^{20}$ +34.0 (*c* 1.50, $CHCl_3$); IR 2954, 2924, 2854, 1560, 1514, 1422, 813, 723, 634, 563 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.59 (2H, d, *J* = 4.9 Hz, Ar**H**), 7.15-7.08 (2H, m, Ar**H**), 7.05 (1H, t, *J* = 4.9 Hz, Ar**H**), 6.93-6.87 (2H, m, Ar**H**), 3.35-3.24 (2H, m, $ArC\mathbf{H}_2$), 3.21-3.10 (1H, m, ArC**H**), 1.71-1.58 (2H, m, $C\mathbf{H}_2(CH_2)_4CH_3$), 1.31-1.04 (8H, m, $(C\mathbf{H}_2)_4CH_3$), 0.83 (3H, t, *J* = 7.1 Hz, $C\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.9 (C), 161.2 (C, d, J_{CF} = 243.4 Hz), 156.8 (2 x CH), 140.2 (C, d, J_{CF} = 3.1 Hz), 128.9 (2 x CH, d, J_{CF} = 7.7 Hz), 118.3 (CH), 114.9 (2 x CH, d, J_{CF} = 21.0 Hz), 46.8 (CH_2), 44.6 (CH), 36.2 (CH_2), 31.6 (CH_2), 29.2 (CH_2), 27.3 (CH_2), 22.5 (CH_2), 14.0 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –117.4 (1F, s); HRMS (EI) Exact mass calcd for $C_{18}H_{23}FN_2$ $[M]^+$:

286.1840, found: 286.1841. Enantiomeric excess was determined by HPLC with a Chiralpak IA-3 column (98:2 hexane/*i*-PrOH, 1.5 mL/min, 230 nm, 25 °C); t_r (minor) = 4.9 min, t_r (major) = 5.7 min; 99% ee.



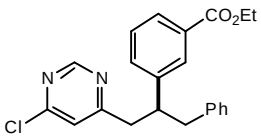
4-Chloro-6-[(S)-2-(4-methoxyphenyl)-3-phenylpropyl]pyrimidine (2s). *On a 0.30 mmol scale*: The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1h** (69 mg, 0.30 mmol), and 4-methoxyphenylboronic acid (109 mg, 0.72 mmol) and purified by column chromatography (5% Et_2O/hexane) to give a colorless oil (83 mg, 82%). R_f = 0.19 (10% EtOAc/hexane); $[\alpha]_D^{20}$ +16.0 (*c* 0.40, $CHCl_3$); IR 2957, 2924, 2855, 1734, 1611, 1566, 1530, 1512, 1454, 1304, 1248, 1179, 1103, 1036, 989, 901, 828, 747, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.84 (1H, br s, Ar**H**), 7.24-7.19 (2H, m, Ar**H**), 7.16-7.15 (1H, m, Ar**H**), 7.07 (2H, app d, *J* = 7.0 Hz, Ar**H**), 6.99 (2H, app d, *J* = 8.6 Hz, Ar**H**), 6.89 (1H, s, Ar**H**), 6.77 (2H, app d, *J* = 8.6 Hz, Ar**H**), 3.76 (3H, s, OC**H**$_3$), 3.49-3.43 (1H, m, $CH_2C\mathbf{H}CH_2$), 3.12 (1H, dd, *J* = 13.9, 5.7 Hz, C**H**$_2$CHCH$_2$Ph), 3.02-2.93 (3H, m, C**H**$_2$CHC**H**$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 171.0 (C), 160.7 (C), 158.3 (CH), 158.1 (C), 139.5 (C), 134.6 (C), 129.1 (2 x CH), 128.4 (2 x CH), 128.2 (2 x CH), 126.1 (CH), 121.3 (CH), 113.8 (2 x CH), 55.1 (CH_3), 46.1 (CH), 43.6 (CH_2), 43.3 (CH_2); HRMS (EI) Exact mass calculated for $C_{20}H_{19}ON_2Cl$ $[M]^+$: 338.1180, found: 338.1183. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (95:5 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (major) = 12.8 min, t_r (minor) = 14.2 min; 98% ee.

On a 5.00 mmol scale:



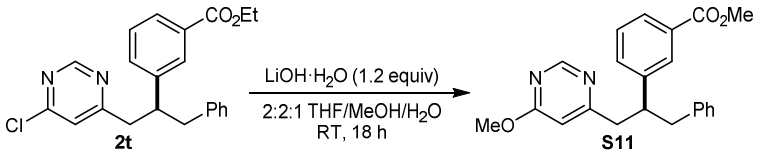
A solution of $[Rh(C_2H_4)_2Cl]_2$ (20 mg, 0.05 mmol) and chiral diene **L9** (50 mg, 0.12 mmol) in dioxane (15 mL) was flushed with nitrogen and stirred at room temperature for 15 min. This solution was added to a mixture of alkenylazaarene **1h** (1.15 g, 5.00 mmol) and 4-methoxyphenylboronic acid (1.14 g, 7.50 mmol) in a separate flask *via* cannula, using further dioxane (7.5 mL) as a rinse. 5 M Aqueous KOH solution (2.5 mL, 12.5 mmol) was then added, and the resulting mixture was heated to 70 °C in an oil

bath for 16 h. After cooling to room temperature, the mixture was filtered through a short plug of SiO_2 using $CHCl_3$ as eluent and concentrated in *vacuo*. Purification of the residue by column chromatography (5% Et_2O/hexane) gave the arylation product **2s** as a colorless oil (1.27 g, 75%). Enantiomeric excess was determined by HPLC with a Chiralpak IC column (95:5 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (major) = 11.8 min, t_r (minor) = 12.8 min; 96% ee.



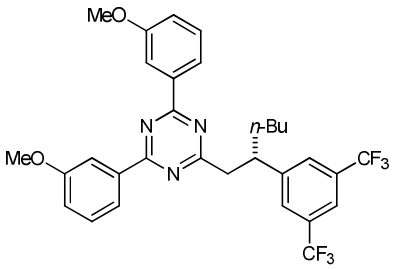
3-[(*S*)-1-Benzyl-2-(6-chloropyrimidin-4-yl)ethyl]benzoic acid ethyl ester (2t). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1h** (69 mg, 0.30 mmol), and 3-ethoxycarbonylphenylboronic acid (140 mg, 0.72 mmol) and purified by column chromatography (5% EtOAc/hexane) to give a colorless oil (71 mg, 62%). R_f 0.14 (10% EtOAc/hexane); $[\alpha]_D^{20}$ –5.0 (*c* 0.40, $CHCl_3$); IR 3112, 3021, 1638 (C=O), 1402, 1238, 1106, 1021, 926, 833, 812, 622 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.84 (1H, d, *J* = 0.7 Hz, Ar**H**), 7.86-7.84 (2H, m, Ar**H**), 7.29-7.14 (5H, m, Ar**H**), 7.08-7.04 (2H, m, Ar**H**), 6.92 (1H, d, *J* = 0.7 Hz, Ar**H**), 4.38 (2H, q, OC**H**$_2$), 3.66-3.58 (1H, m, $CH_2C\mathbf{H}CH_2$), 3.17 (1H, dd, *J* = 14.1, 6.0 Hz, C**H**$_2$CHCH$_2$Ph), 3.07-2.97 (3H, m, C**H**$_2$CHC**H**$_2$Ph), 1.41 (3H, t, *J* = 7.1 Hz, C**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.5 (C), 166.5 (C), 161.0 (C), 158.5 (CH), 143.2 (C), 139.0 (C), 132.4 (CH), 130.7 (C), 129.1 (2 x CH), 128.43 (CH), 128.37 (CH), 128.31 (2 x CH), 127.9 (CH), 126.4 (CH), 121.4 (CH), 61.0 (CH_2), 46.6 (CH), 43.2 (CH_2), 42.9 (CH_2), 14.3 (CH_3); HRMS (EI) Exact mass calculated for $C_{22}H_{21}ClN_2O_2$ $[M]^+$: 380.1327, found: 380.1331. To facilitate determination of enantiomeric excess, **2t** was converted into the derivative **S11** using the following procedure:

Methyl-3-[(2*S*)-1-(6-methoxypyrimidin-4-yl)-3-phenylpropan-2-yl]benzoate (S11)



To a solution of ester **2t** (19 mg, 0.05 mmol) in 2:2:1 THF/MeOH/H_2O (2.5 mL) at room temperature was added LiOH·H_2O (2.5 mg, 0.06 mmol) and the mixture was stirred for 18 h. The reaction was acidified with 10% aqueous HCl solution (10 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (9:1→2:1 hexane/EtOAc) gave the *methyl ester* **S11** as a colorless film (5 mg, 28%). R_f = 0.24 (2:1 hexane/EtOAc); IR 3022, 2953, 2928, 1719 (C=O), 1593, 1549, 1476,

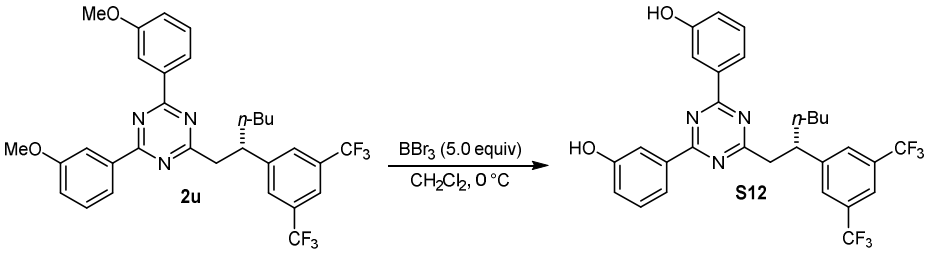
1379, 1285, 1215, 1034, 754 cm^{-1}; $[\alpha]_D^{20}$ −8.0 (*c* 0.25, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.66 (1H, d, *J* = 0.6 Hz, Ar**H**), 7.86 (1H, t, *J* = 1.5 Hz, Ar**H**), 7.81 (1H, dt, *J* = 7.6, 1.5 Hz, Ar**H**), 7.24 (1H, t, *J* = 7.6 Hz, Ar**H**), 7.20-7.17 (3H, m, Ar**H**), 7.14-7.11 (1H, m, Ar**H**), 7.03-7.02 (2H, m, Ar**H**), 6.32 (1H, s, Ar**H**), 3.91 (3H, s, OC$\mathbf{H}_3$), 3.89 (3H, s, OC$\mathbf{H}_3$), 3.60 (1H, ddd, *J* = 15.1, 8.3, 6.8 Hz, ArC**H**), 3.10 (1H, dd, *J* = 13.9, 6.2 Hz, C$\mathbf{H}_2$CHCH_2Ph), 3.05-2.92 (3H, m, C$\mathbf{H}_2$CHCH_2Ph and C$\mathbf{H}_2$Ph); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.6 (C), 168.5 (C), 167.1 (C), 157.9 (CH), 143.7 (C), 139.3 (C), 132.8 (CH), 130.2 (C), 129.1 (CH), 128.5 (CH), 128.3 (2 x CH), 128.2 (CH), 127.7 (2 x CH), 126.1 (CH), 107.4 (CH), 53.6 (CH_3), 52.1 (CH_3), 46.6 (CH), 43.3 (CH_2), 42.9 (CH_2); HRMS (ESI) Exact mass calculated for $C_{22}H_{23}N_2O_3$ $[M+H]^+$: 363.1703, found: 363.1705; Enantiomeric excess was determined by HPLC with a Chiralpak IA-3 column (98:2 hexane/*i*-PrOH, 1.0 mL/min, 210 nm, 25 °C); t_r (major) = 20.6 min, t_r (minor) = 22.4 min; 93% ee.



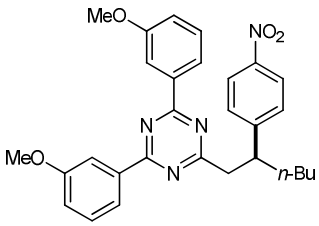
2-[(*S*)-2-(3,5-Bistrifluoromethylphenyl)hexyl]-4,6-bis-(3-methoxyphenyl)-[1,3,5]triazine (2u). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1i** (113 mg, 0.30 mmol), and 3,5-bistrifluromethylphenylboronic acid (186 mg, 0.72 mmol) and purified by column chromatography (50% EtOAc/hexane) to give a pale yellow oil (162 mg, 92%). R_f = 0.31 (10% EtOAc/hexane); $[\alpha]_D^{20}$ +48.0 (*c* 0.50, $CHCl_3$); IR 1601, 1587, 1526, 1464, 1456, 1369, 1362, 1276, 1244, 1171, 1130, 1098, 908, 893, 845, 781, 683 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.17 (2H, app dt, *J* = 7.8, 1.2 Hz, Ar**H**), 8.13 (2H, dd, *J* = 2.6, 1.5 Hz, Ar**H**), 7.77 (2H, s, Ar**H**), 7.69 (1H, s, Ar**H**), 7.45 (2H, t *J* = 8.0 Hz, Ar**H**), 7.15 (2H, ddd, *J* = 8.2, 2.7, 0.9 Hz, Ar**H**), 3.94 (6H, s, 2 x OC$\mathbf{H}_3$), 3.73-3.67 (1H, m, CH_2C**H**CH_2), 3.44 (1H, dd, *J* = 15.1, 6.5 Hz, ArC$\mathbf{H}_2$), 3.34 (1H, dd, *J* = 15.1, 8.7 Hz, ArC$\mathbf{H}_2$), 1.92-1.85 (1H, m, C$\mathbf{H}_2$$CH_2CH_2CH_3$), 1.82-1.74 (1H, m, C$\mathbf{H}_2$$CH_2CH_2CH_3$), 1.39-1.18 (4H, m, C$\mathbf{H}_2C\mathbf{H}_2$$CH_2CH_3$), 0.88 (3H, t, *J* = 7.2 Hz, C$\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 177.4 (C), 171.0 (2 x C), 159.9 (2 x C), 147.5 (C), 137.1 (2 x C), 131.5 (2 x C, q, J_{CF} = 33.0 Hz), 129.6 (2 x CH), 128.0 (2 x CH, app d, J_{CF} = 2.6 Hz), 123.4 (2 x C, q, J_{CF} = 272.7 Hz), 121.4 (2 x CH), 120.3 (CH, sept, J_{CF} = 7.6 Hz), 118.5 (2 x CH), 113.6 (2 x CH), 55.4 (2 x CH_3), 45.1 (CH_2), 43.7 (CH), 36.1 (CH_2), 29.4 (CH_2), 22.5 (CH_2), 13.9 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7 (6F, s); HRMS (ESI) Exact mass calculated for $C_{31}H_{30}F_6N_3O_2$ $[M+H]^+$: 590.2237, found: 590.2229. To facilitate determination of

enantiomeric excess, **2u** was demthylated into the corresponding bisphenol **S12** using the following procedure:

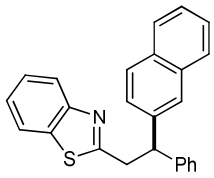
2-[(*S*)-2-(3,5-Bistrifluoromethylphenyl)hexyl]-4,6-bis-(3-hydroxyphenyl)-[1,3,5]triazine (S12)



To a solution of bismethyl ether **2u** (177 mg, 0.30 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added BBr_3 (0.14 mL, 1.50 mmol) dropwise over 1 min. The solution was stirred at 0 °C for 3 h and quenched carefully with saturated aqueous $NaHCO_3$ solution (10 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (2 x 50mL). The combined organic layers were dried $(MgSO)_4$, filtered, and concentrated *in vacuo*. Purification of the resiude by column chromatography (30% EtOAc/hexane) gave the *bisphenol* **S12** as a yellow solid (153 mg, 91%). R_f = 0.34 (30% EtOAc/hexane); $[\alpha]_D^{20}$ +41.7 (*c* 0.50, $CHCl_3$); m.p. decomposes at ~120 °C; IR 3370 (br, OH), 2957, 2930, 1530, 1505, 1456, 1375, 1350, 1275, 1171, 1130, 1078, 895, 849, 789, 779, 735, 706, 683, 648, 573 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.17-8.09 (2H, m, Ar**H**), 8.03 (2H, app dd, *J* = 2.6, 1.5 Hz, Ar**H**), 7.75 (2H, s, Ar**H**), 7.68 (1H, s, Ar**H**), 7.41 (2H, t, *J* = 7.9 Hz, Ar**H**), 7.08 (2H, ddd, *J* = 8.0, 2.6, 0.9 Hz, Ar**H**), 5.06 (2H, br s, O**H**), 3.68-3.63 (1H, m, $CH_2C\mathbf{H}CH_2$), 3.42 (1H, dd, *J* = 15.0, 6.3 Hz, Ar$C\mathbf{H}_2$), 3.29 (1H, dd, *J* = 15.0, 9.0 Hz, Ar$C\mathbf{H}_2$), 1.90-1.81 (1H, m, $C\mathbf{H}_2CH_2CH_2CH_3$), 1.81-1.71 (1H, m, $C\mathbf{H}_2CH_2CH_2CH_3$), 1.38-1.13 (4H, m, $C\mathbf{H}_2C\mathbf{H}_2CH_3$), 0.87 (3H, t, *J* = 7.1 Hz, $C\mathbf{H}_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 177.5 (C), 170.8 (2 x C), 155.9 (2 x C), 147.4 (C), 137.3 (2 x C), 131.4 (2 x C, q, J_{CF} = 33.0 Hz), 130.0 (2 x CH), 128.1 (2 x CH, app d, J_{CF} = 2.7 Hz), 123.4 (2 x C, q, J_{CF} = 272.7 Hz), 121.5 (2 x CH), 120.4 (CH, sept, J_{CF} = 7.5 Hz), 119.8 (2 x CH), 115.3 (2 x CH), 45.1 (CH_2), 43.8 (CH), 36.2 (CH_2), 29.4 (CH_2), 22.5 (CH_2), 13.9 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7 (6F, s); HRMS (EI) Exact mass calculated for $C_{29}H_{25}F_6N_3O_2$ $[M]^+$: 561.1846, found: 561.1854. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (95:5 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (major) = 14.3 min, t_r (minor) = 21.9 min; 96% ee.

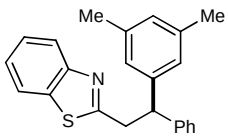


2,4-Bis-(3-methoxyphenyl)-6-[(*S*)-2-(4-nitrophenyl)hexyl]-[1,3,5]triazine (2v). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1i** (113 mg, 0.30 mmol), and 4-nitrophenylboronic acid (120 mg, 0.72 mmol) and purified by column chromatography (5% EtOAc/hexane) to give a yellow oil (128 mg, 85%). R_f = 0.32 (10% EtOAc/hexane); $[\alpha]_D^{20}$ +61.8 (*c* 0.50, $CHCl_3$); IR 2955, 2928, 1599, 1520 (NO_2), 1454, 1429, 1371 (NO_2), 1344, 1317, 1281, 1240, 1182, 1107, 1045, 908, 854, 783, 766, 735, 700, 687, 644 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (2H, app dt, *J* = 7.9, 1.2 Hz, Ar**H**), 8.13 (2H, app d, *J* = 8.8 Hz, Ar**H**), 8.08 (2H, dd, *J* = 2.7, 1.5 Hz, Ar**H**), 7.47-7.42 (4H, m, Ar**H**), 7.14 (2H, ddd, *J* = 8.2, 2.7, 0.9 Hz, Ar**H**), 3.93 (6H, s, 2 x OC**H**$_3$), 3.70-3.60 (1H, m, CH_2C**H**CH_2), 3.42 (1H, dd, *J* = 14.8, 6.1 Hz, ArC**H**$_2$), 3.31 (1H, dd, *J* = 14.8, 9.1 Hz, ArC**H**$_2$), 1.93-1.82 (1H, m, C**H**$_2CH_2CH_2CH_3$), 1.81-1.73 (1H, m, C**H**$_2CH_2CH_2CH_3$), 1.40-1.14 (4H, m, C**H**$_2CH_3$), 0.86 (3H, t, *J* = 7.1 Hz, C**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 177.6 (C), 170.9 (2 x C), 159.9 (2 x C), 152.7 (C), 146.5 (C), 137.2 (2 x C), 129.7 (2 x CH), 128.7 (2 x CH), 123.6 (2 x CH), 121.3 (2 x CH), 118.5 (2 x CH), 113.8 (2 x CH), 55.4 (2 x CH_3), 45.3 (CH_2), 44.0 (CH), 36.1 (CH_2), 29.5 (CH_2), 22.6 (CH_2), 13.9 (CH_3); HRMS (ESI) Exact mass calculated for $C_{29}H_{31}N_4O_4$ $[M+H]^+$: 499.2340, found: 499.2348. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (hexane, 0.15 mL/min, 230 nm, 25 °C); t_r (major) = 68.7 min, t_r (minor) = 75.3 min; 94% ee.

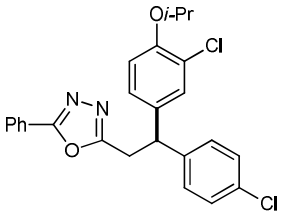


2-[(*S*)-2-Naphthalen-1-yl-2-phenylethyl]benzothiazole (2w). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1j** (71 mg, 0.30 mmol), and 2-naphthylboronic acid (123 mg, 0.72 mmol) and purified by column chromatography (5% EtOAc/hexane) to give a light brown solid (68 mg, 62%). R_f = 0.30 (10% EtOAc/hexane); m.p. 108-112 °C (EtOAc/hexane); $[\alpha]_D^{20}$ +19.4 (*c* 1.00, $CHCl_3$); IR 3943, 3054, 2986, 2305, 1421, 1266, 911, 742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (1H, br d, *J* = 8.1 Hz, Ar**H**), 7.85-7.76 (4H, m, Ar**H**), 7.76-7.71 (1H, m, Ar**H**), 7.50-7.41 (4H, m, Ar**H**), 7.40-7.37 (2H, m, Ar**H**), 7.36-7.28 (3H, m, Ar**H**), 7.22 (1H, tt, *J* = 7.3, 1.2 Hz, Ar**H**), 4.90 (1H, t, *J* = 8.0 Hz, CH_2C**H**), 4.05 (1H, dd, *J* = 15.0, 8.0 Hz, C**H**$_2$), 3.99 (1H, dd, *J* = 15.0, 8.0 Hz, C**H**$_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.7 (C), 152.9 (C), 143.0 (C), 140.5 (C), 135.1 (C), 133.4 (C), 132.3 (C), 128.6 (2 x CH), 128.3 (CH), 128.0 (2 x CH), 127.8 (CH), 127.5 (CH), 126.7 (CH), 126.5 (CH), 126.10 (CH), 126.05 (CH), 125.8

(CH), 125.6 (CH), 124.7 (CH), 122.5 (CH), 121.4 (CH), 51.0 (CH), 40.3 (CH_2); HRMS (ESI) Exact mass calculated for $C_{25}H_{20}NS$ $[M+H]^+$: 366.1311, found: 366.1317. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (minor) = 13.2 min, t_r (major) = 15.0 min; 98% ee.



2-[(*R*)-2-(3,5-Dimethylphenyl)-2-phenylethyl]benzothiazole (2x). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1j** (71 mg, 0.30 mmol), and 3,5-dimethylphenylboronic acid (108 mg, 0.72 mmol) and purified by column chromatography (5% EtOAc/hexane) to give a pale yellow oil (88 mg, 85%). R_f = 0.43 (10% EtOAc/hexane); $[\alpha]_D^{20}$ +32.0 (*c* 0.80, $CHCl_3$); IR 2918, 2868, 1595, 1502, 1472, 1454, 1312, 1240, 1132, 1123, 872, 854, 789, 723, 714 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (1H, app d, *J* = 8.1 Hz, Ar**H**), 7.76 (1H, ddd, *J* = 8.1, 1.1, 0.6 Hz, Ar**H**), 7.44 (1H, ddd, *J* = 8.3, 7.3, 1.2 Hz, Ar**H**), 7.37-7.33 (2H, m, Ar**H**), 7.33-7.28 (3H, m, Ar**H**), 7.22-7.19 (1H, m, Ar**H**), 6.98 (2H, s, Ar**H**), 6.86 (1H, s, Ar**H**), 4.63 (1H, t, *J* = 8.0 Hz, CH_2C**H**), 3.89 (2H, d, *J* = 8.0 Hz, C**H**$_2$CH), 2.29 (6H, s, 2 x ArC**H**$_3$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.0 (C), 152.9 (C), 143.3 (C), 143.0 (C), 138.0 (2 x C), 135.2 (C), 128.5 (2 x CH), 128.3 (CH), 127.8 (2 x CH), 126.5 (CH), 125.7 (CH), 125.6 (2 x CH), 124.6 (CH), 122.5 (CH), 121.4 (CH), 51.0 (CH), 40.4 (CH_2), 21.3 (2 x CH_3); HRMS (EI) Exact mass calculated for $C_{23}H_{21}NS$ $[M]^+$: 343.1389, found: 343.1390. Enantiomeric excess was determined by HPLC with a Chiralpak IA-3 column (99.5:0.5 hexane:*i*-PrOH, 0.3 mL/min, 210 nm, 25 °C); t_r (major) = 30.9 min, t_r *ca* 33 min; 99% ee.

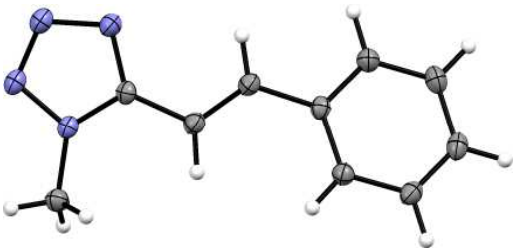


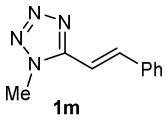
2-[(*R*)-2-(3-Chloro-4-isopropoxyphenyl)-2-(4-chlorophenyl)ethyl]-5-phenyl-[1,3,4]oxadiazole (2y). The title compound was prepared according to General Procedure A from $[Rh(C_2H_4)_2Cl]_2$ (2.9 mg, 7.5 μmol), chiral diene **L9** (7.3 mg, 0.018 mmol), alkenylazaarene **1k** (85 mg, 0.30 mmol), and 3-chloro-4-isopropoxyphenylboronic acid (154 mg, 0.72 mmol) and purified by column chromatography (30% EtOAc/hexane) to give a pale yellow oil (86 mg, 63%). R_f = 0.19 (20% EtOAc/hexane); $[\alpha]_D^{20}$ +28.0 (*c* 1.20, $CHCl_3$); IR 2978, 2932, 1736, 1605, 1570, 1553, 1512, 1451, 1385, 1373, 1285, 1252, 1179, 1138, 1109, 1090, 1059, 1015, 955, 910, 818, 777, 731, 710 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (2H, d, *J* = 6.9 Hz, Ar**H**), 7.54-7.46 (3H, m, Ar**H**), 7.30-7.27 (3H, m, Ar**H**), 7.23-7.21 (2H, m, Ar**H**), 7.09 (1H, app d, *J* = 7.6 Hz, Ar**H**), 6.87 (1H, d, *J* = 8.5 Hz, Ar**H**), 4.59 (1H, br s, CH_2C**H**), 4.50 (1H, sept, *J* = 6.1

Hz, C**H**$(CH_3)_2$), 3.62 (2H, br s, C**H**$_2$CH), 1.35 (3H, d, *J* = 6.1 Hz, CH(C**H**$_3)_2$), 1.34 (3H, d, *J* = 6.1 Hz, CH(C**H**$_3)_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.72 (C), 164.69 (C), 164.66 (C), 152.7 (C), 140.7 (C), 135.2 (C), 132.9 (C), 131.7 (CH), 129.5 (CH), 129.02 (2 x CH), 128.97 (3 x CH), 128.95 (CH), 126.7 (2 x CH), 126.6 (CH), 124.4 (C), 115.9 (CH), 72.1 (CH), 47.0 (CH), 31.9 (CH_2), 22.0 (2 x CH_3); HRMS (ESI) Exact mass calculated for $C_{25}H_{23}N_2O_2Cl_2$ $[M+H]^+$: 453.1131, found: 453.1131. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (major) = 38.9 min, t_r (minor) = 44.5 min; 99% ee.

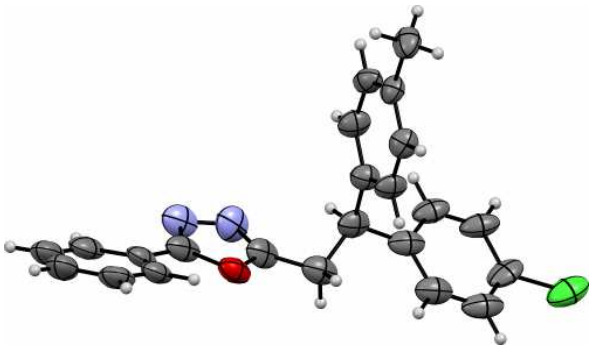
Structural Determinations

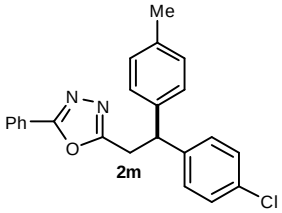
The structures of **1m** and **2m** were determined by X-ray crystallography:





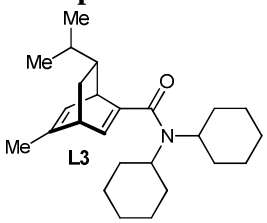
1m



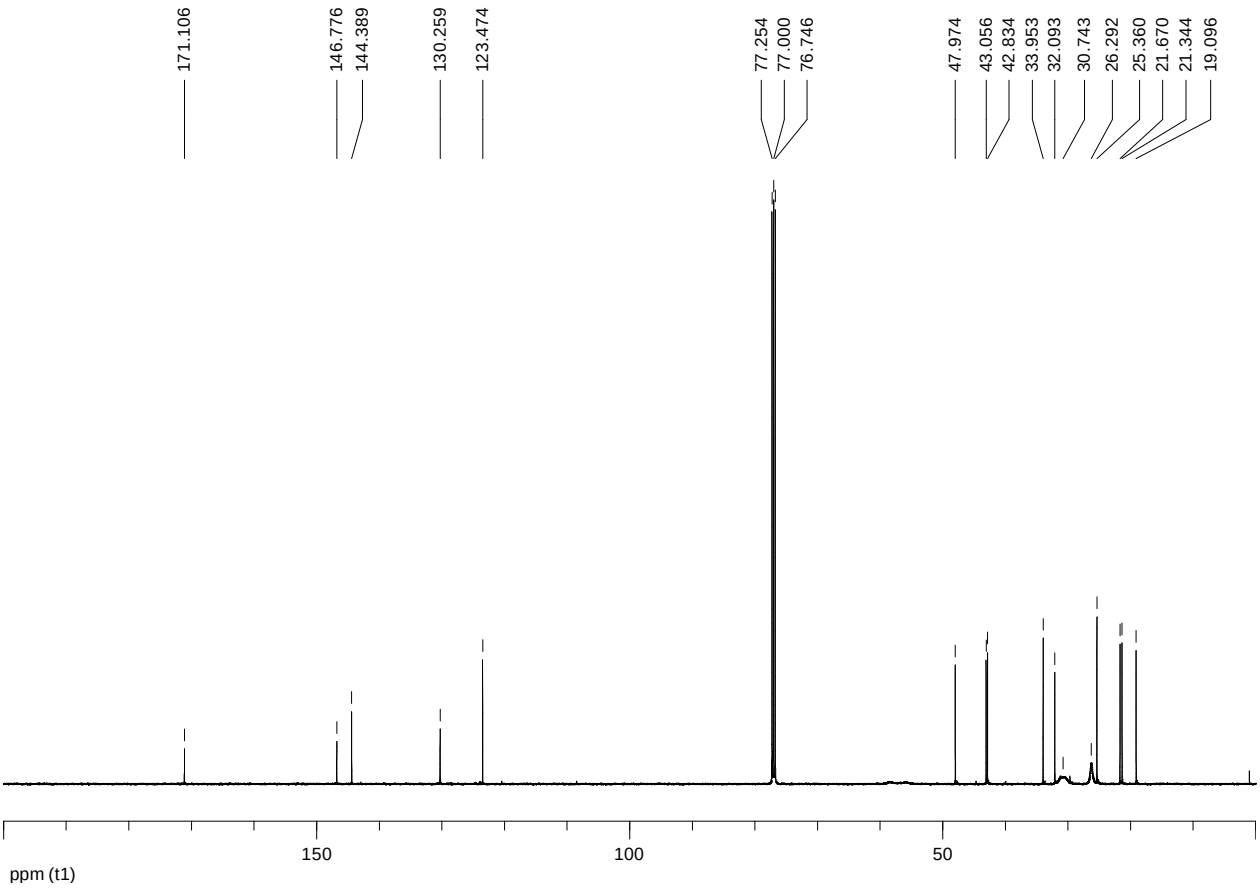


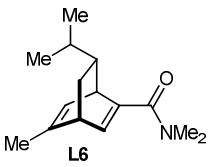
2m

NMR Spectra



L3





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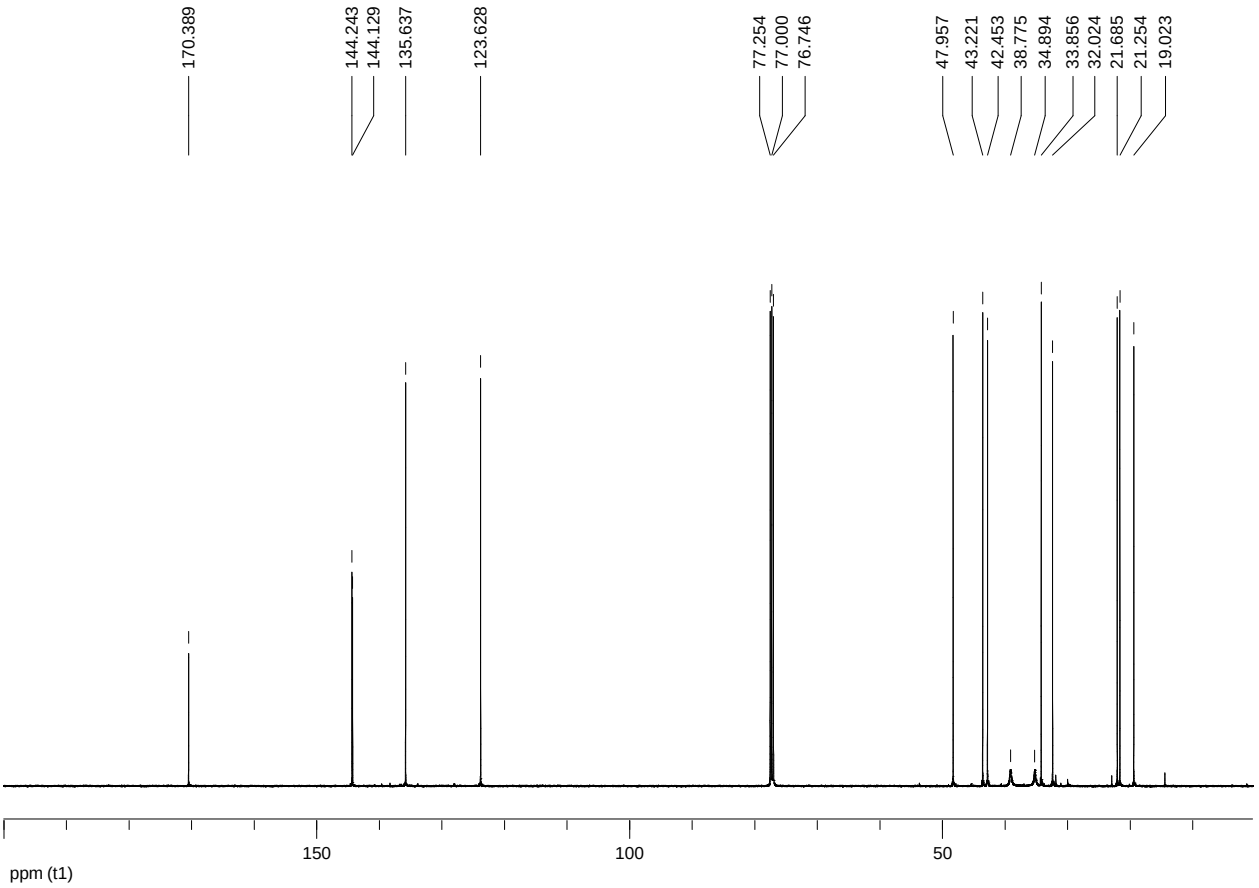
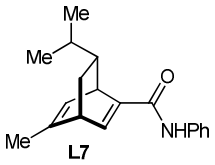
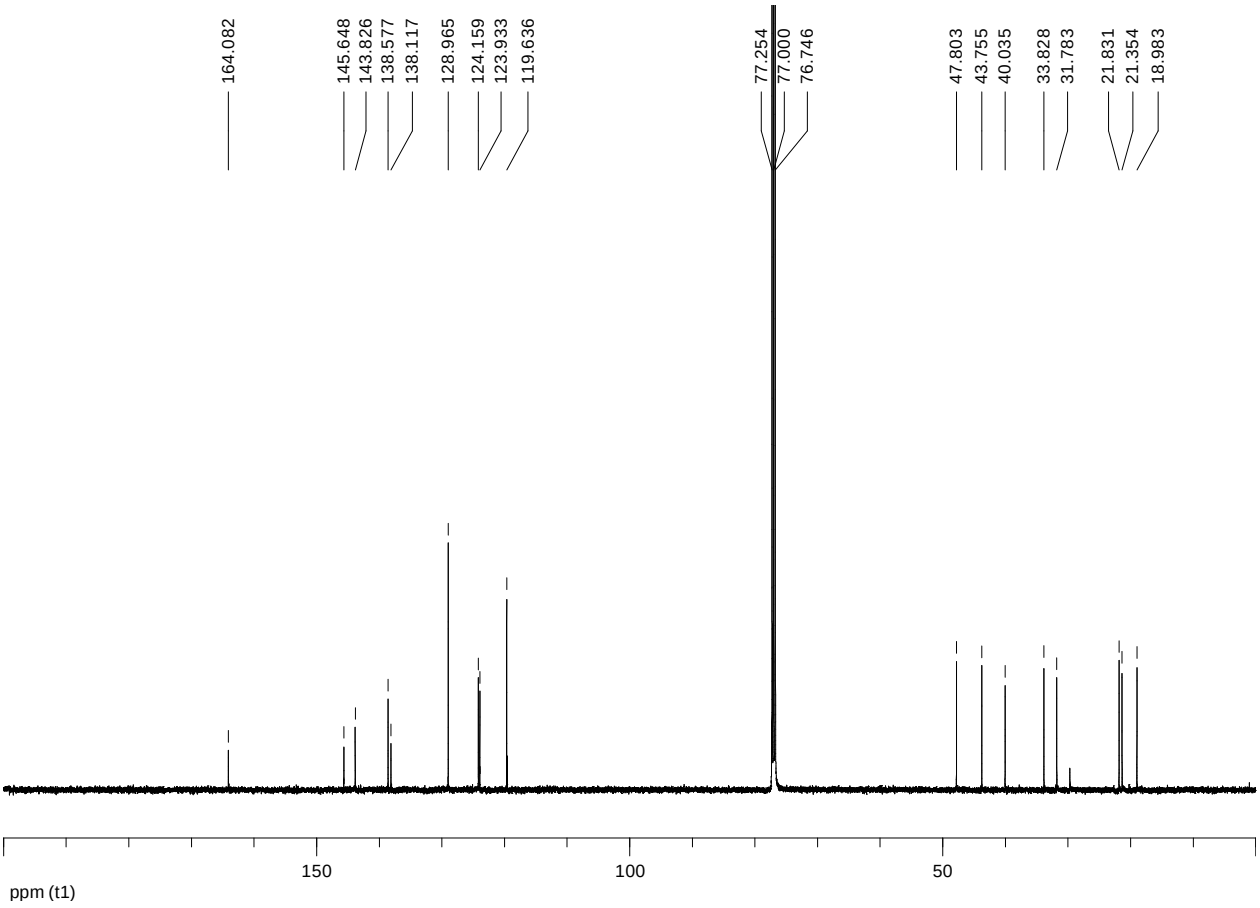
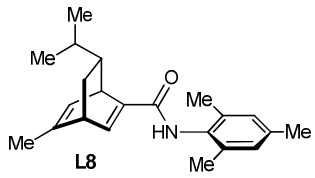




L7





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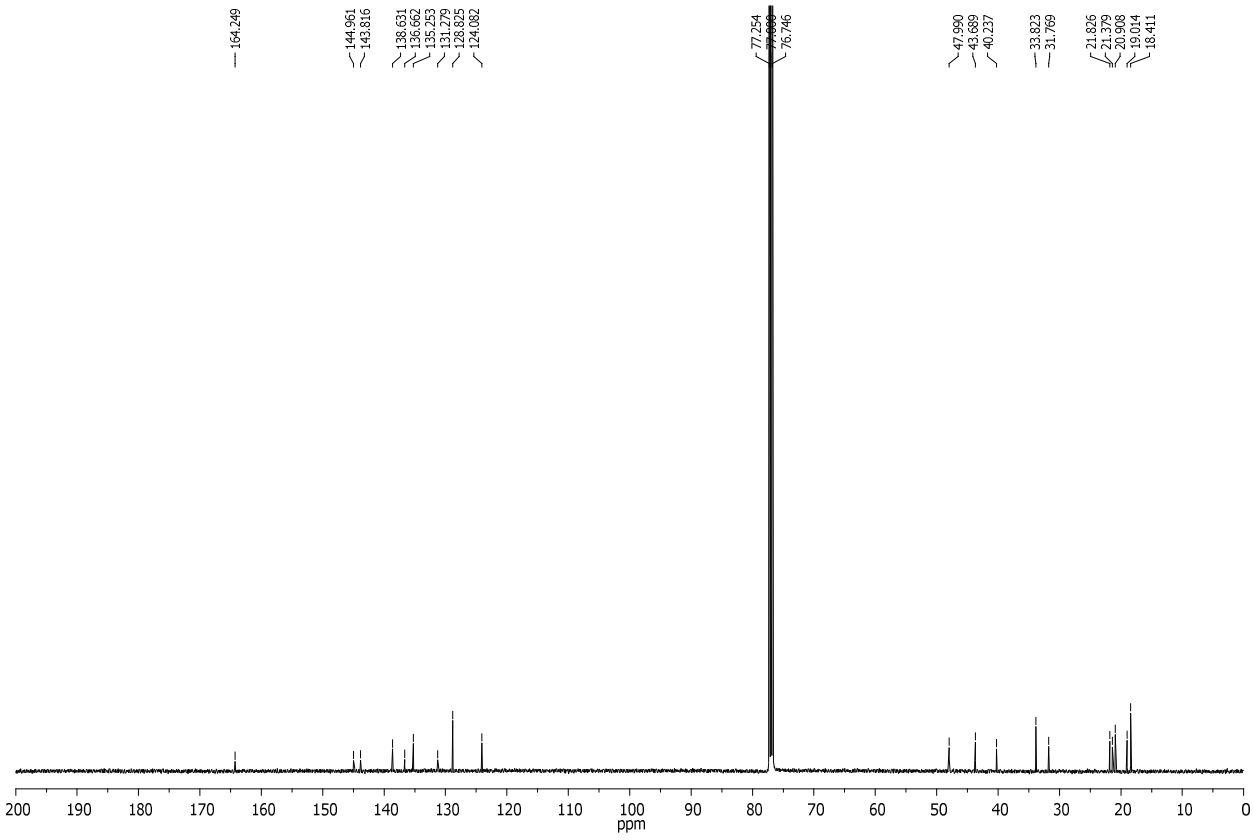

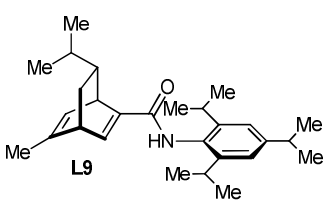

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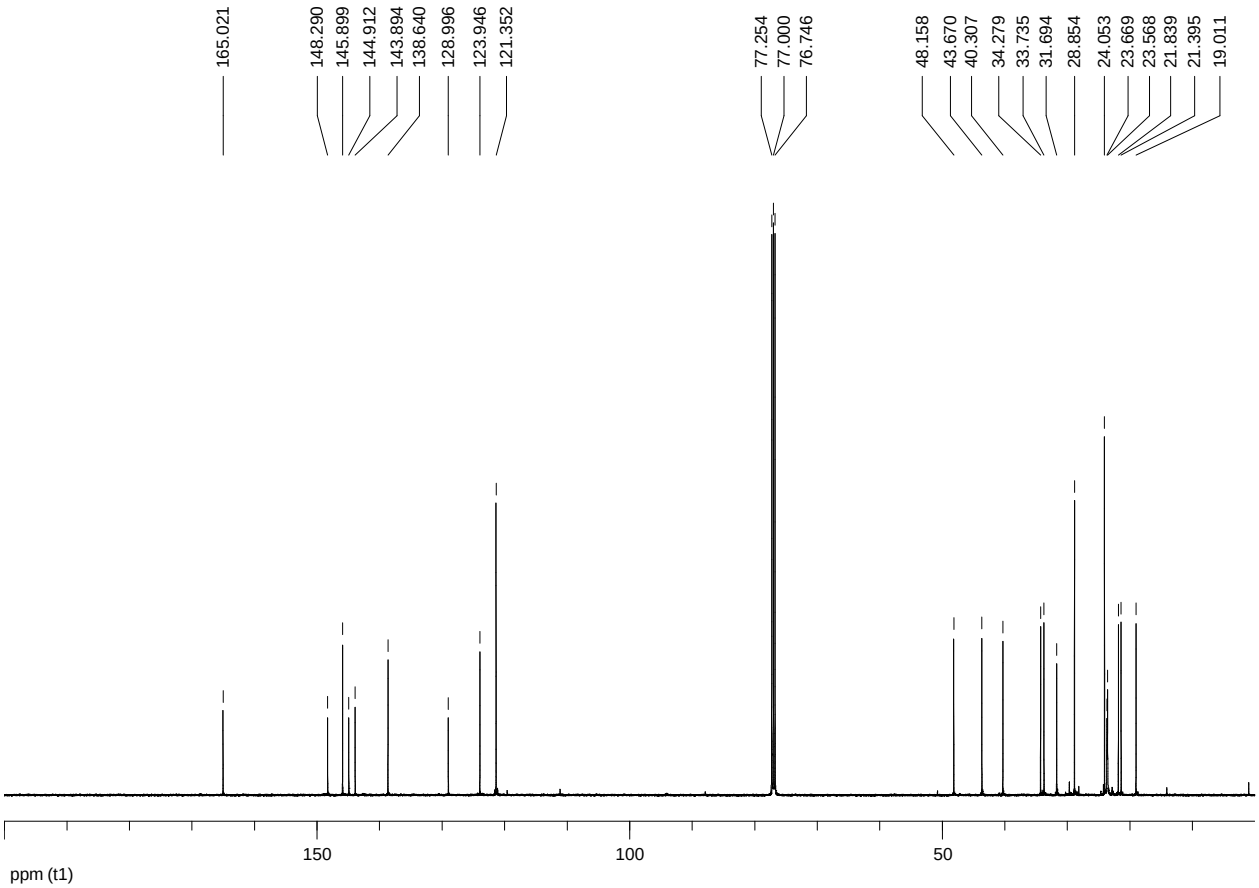
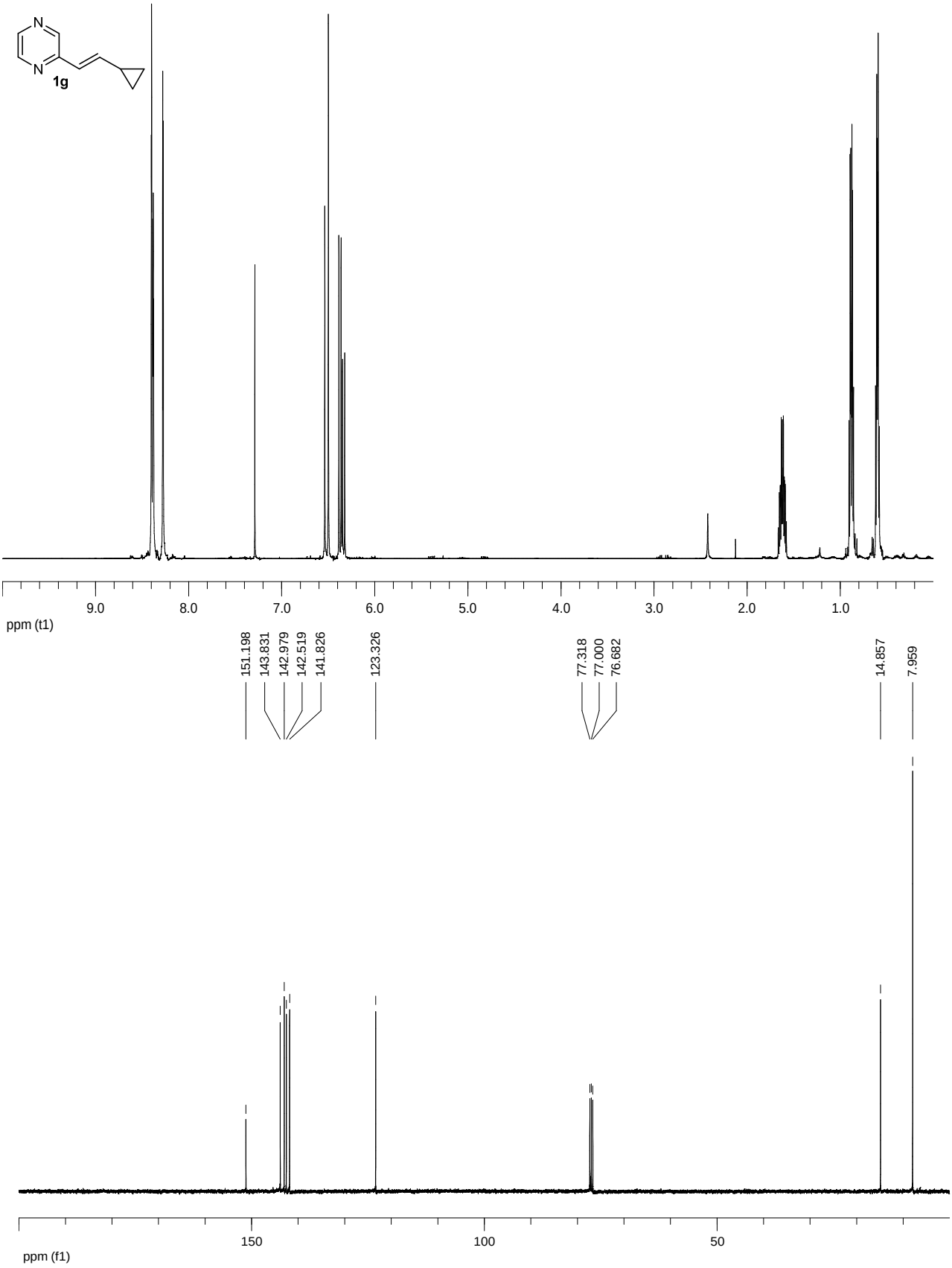
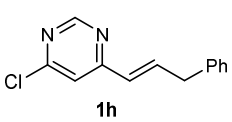
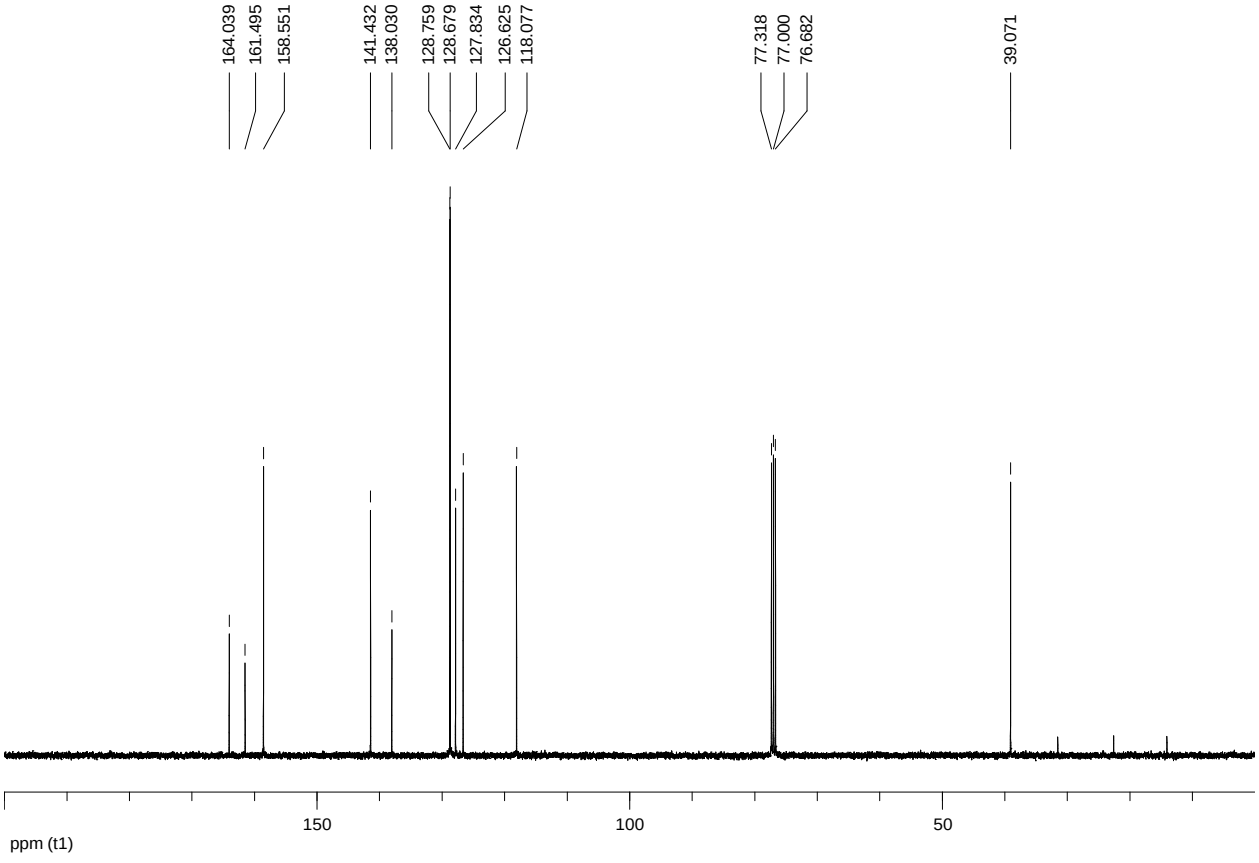
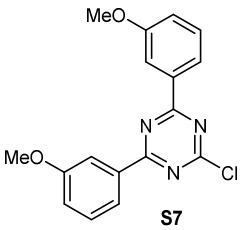




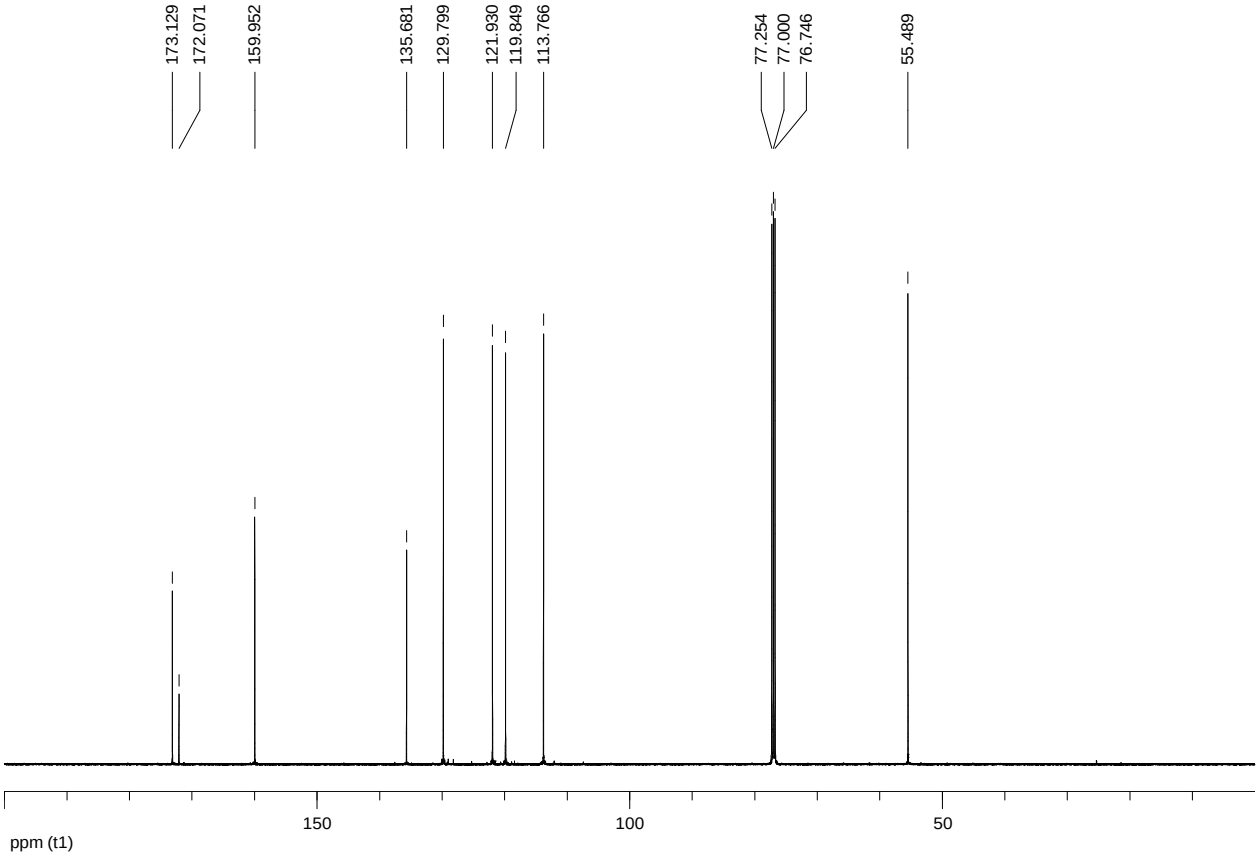


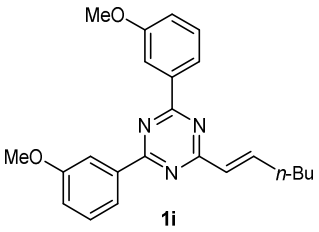
1h



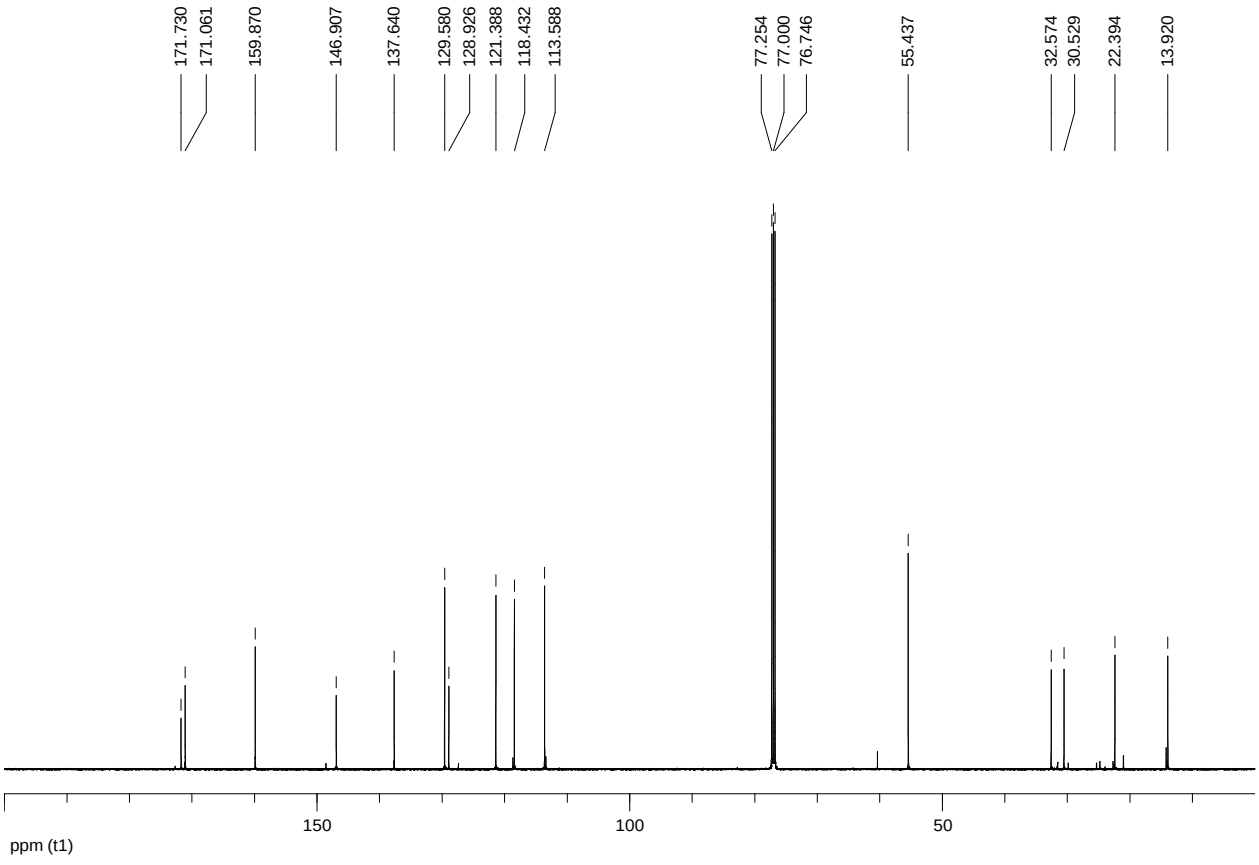


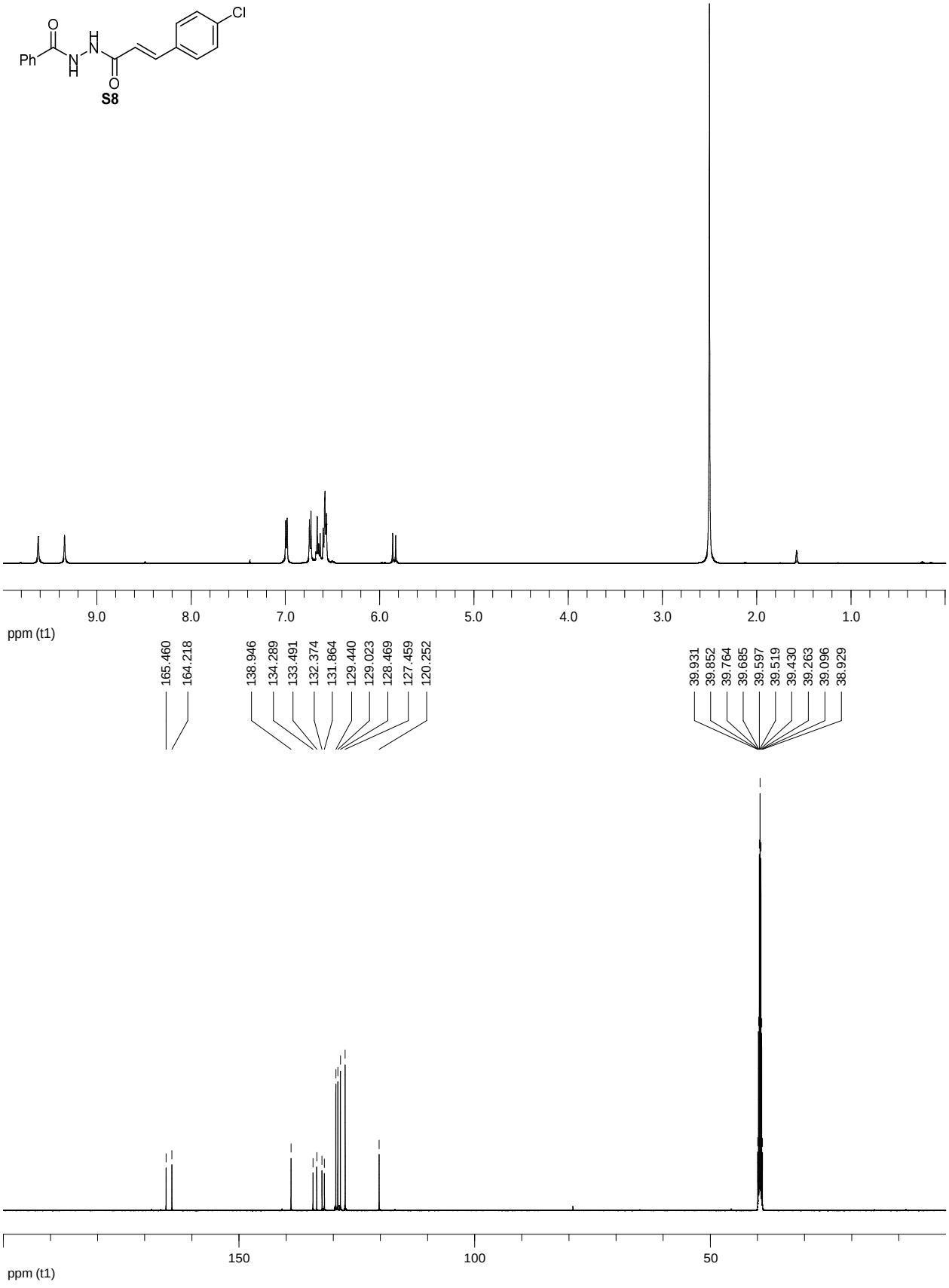
S7

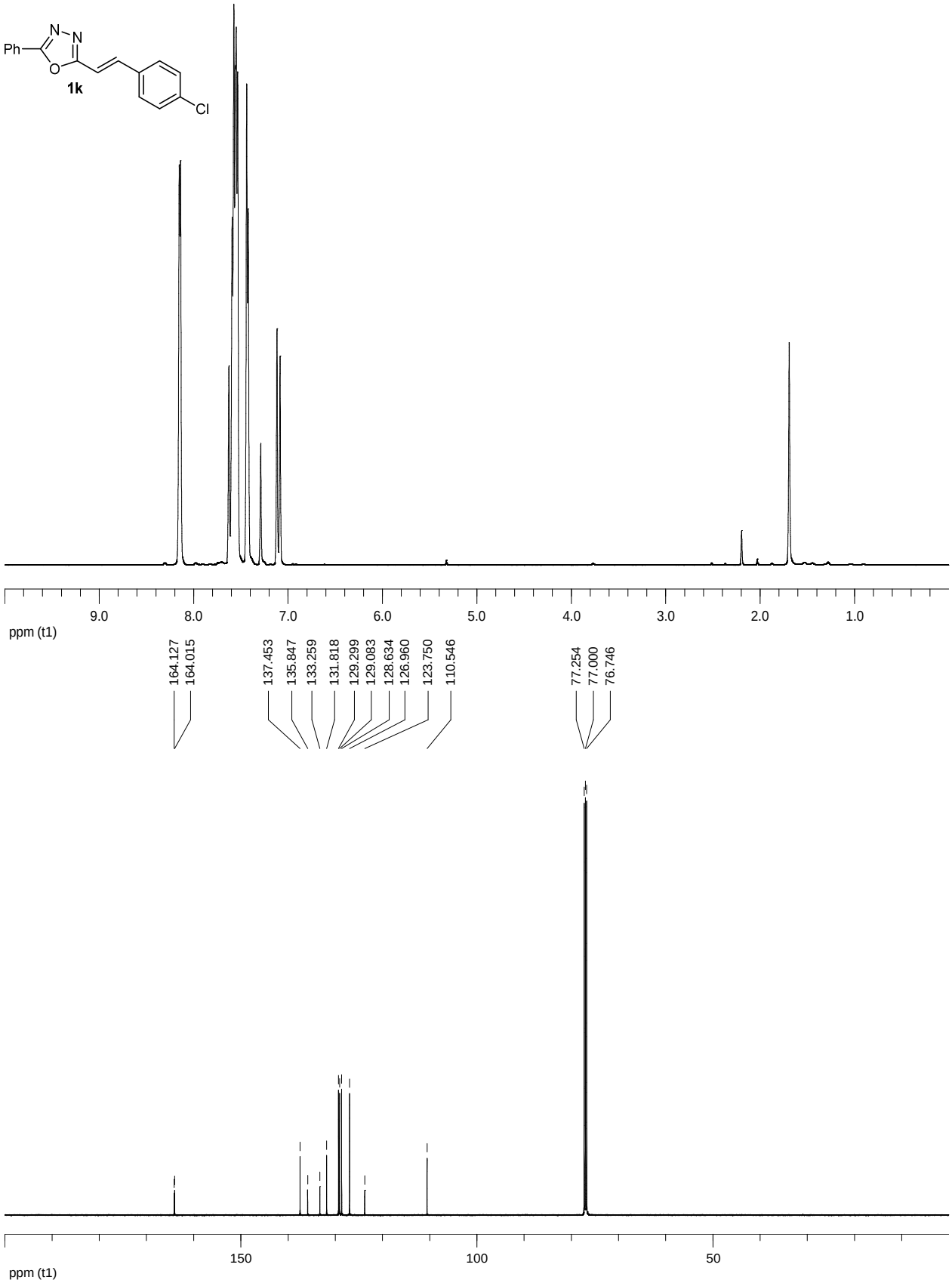


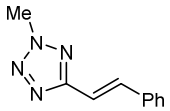


1i

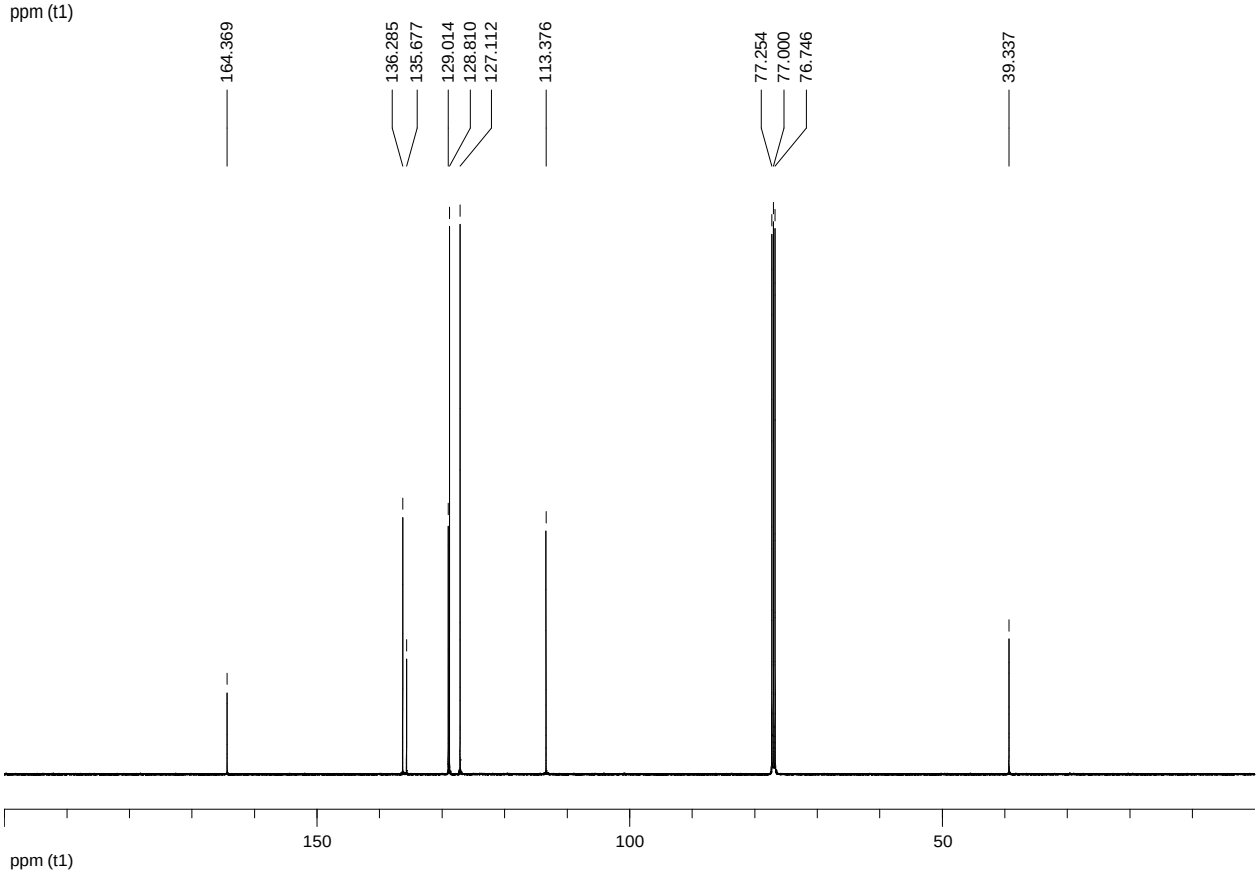


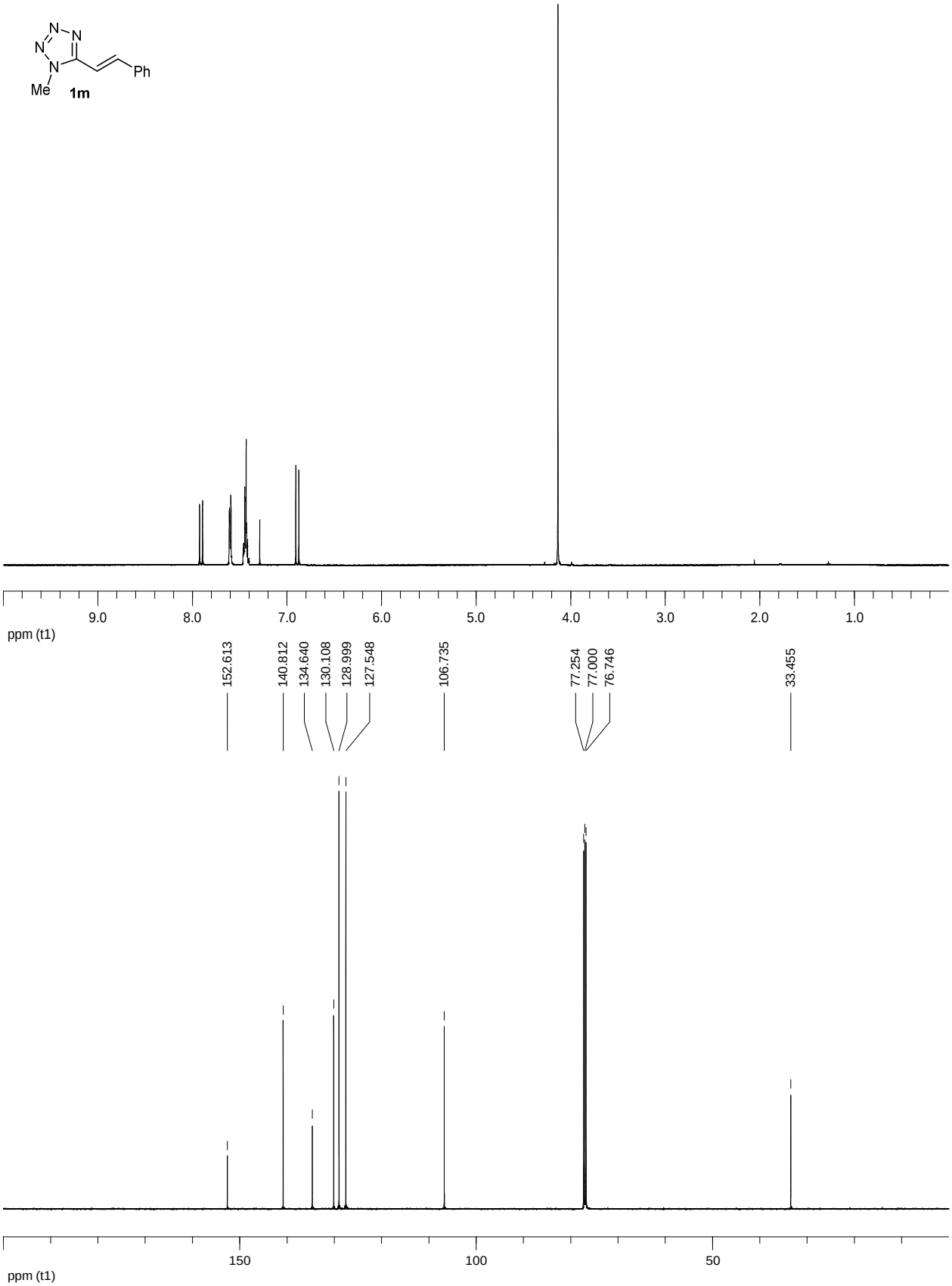


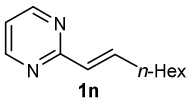




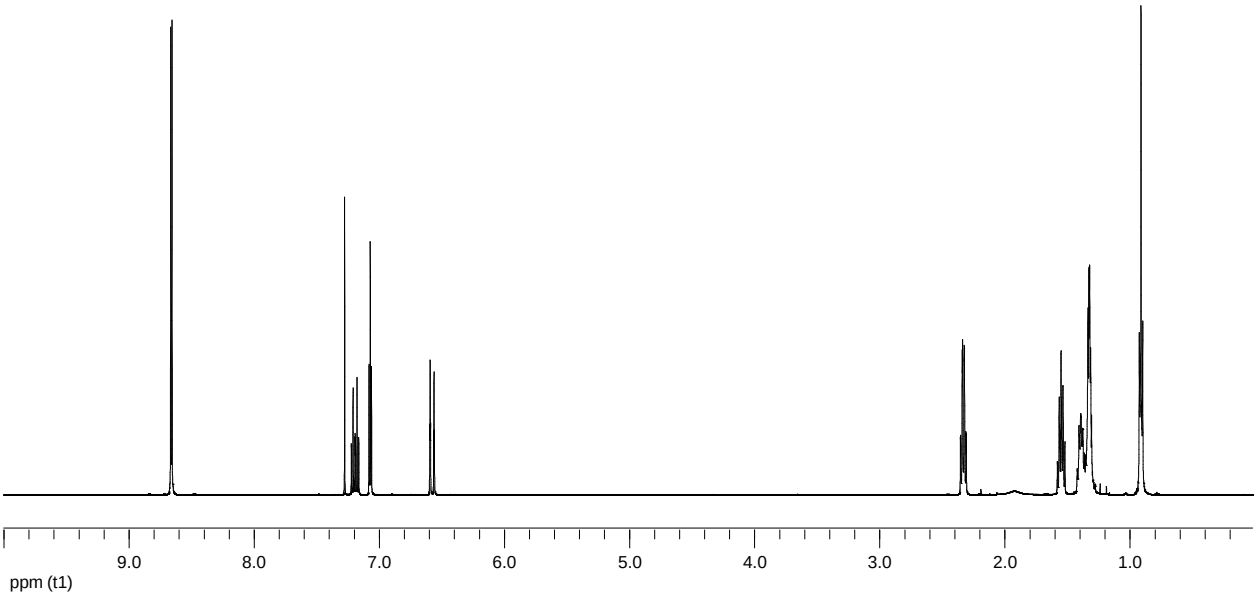
1l



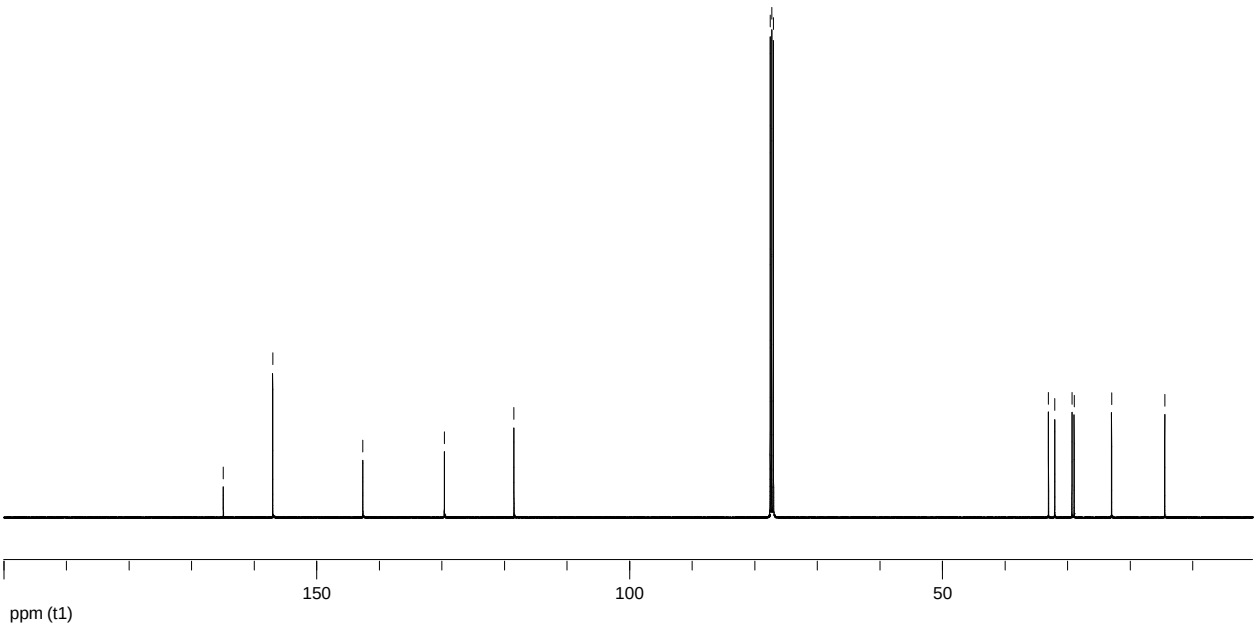


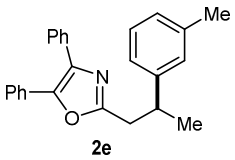

N
N
n-Hex

1n

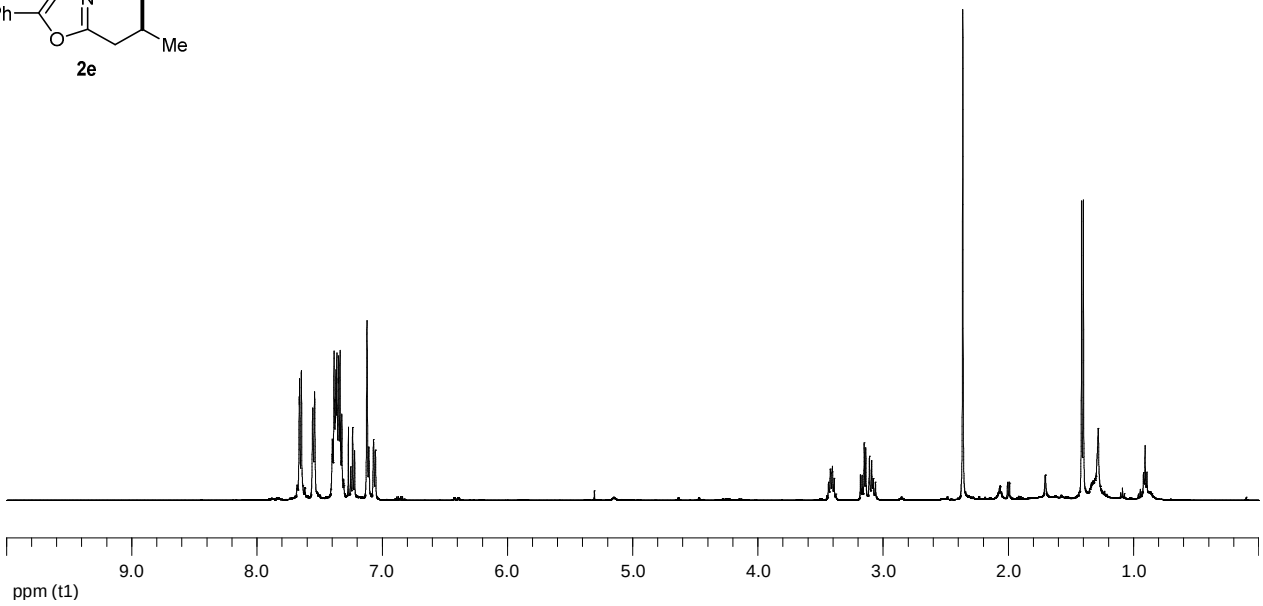

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


164.837
156.924
142.493
129.431
118.297
77.254
77.000
76.746
32.686
31.688
28.927
28.585
22.586
14.077


150
100
50
ppm (t1)


Ph
N
Ph
O
Me
Me

2e


9.0
8.0
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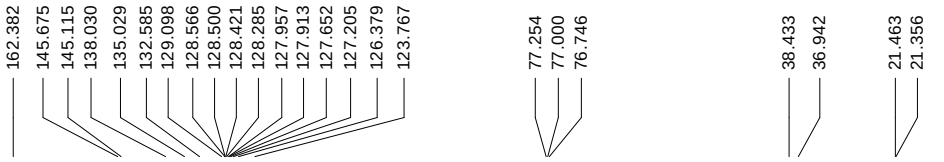
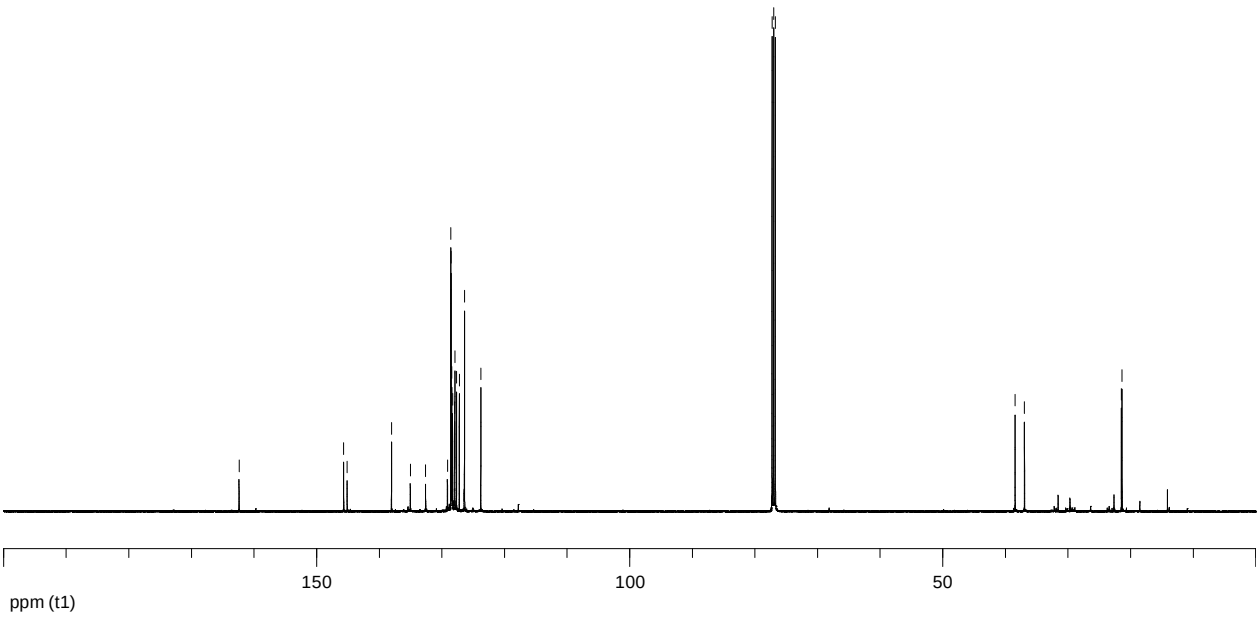
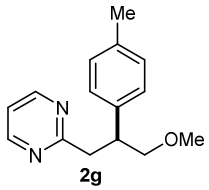
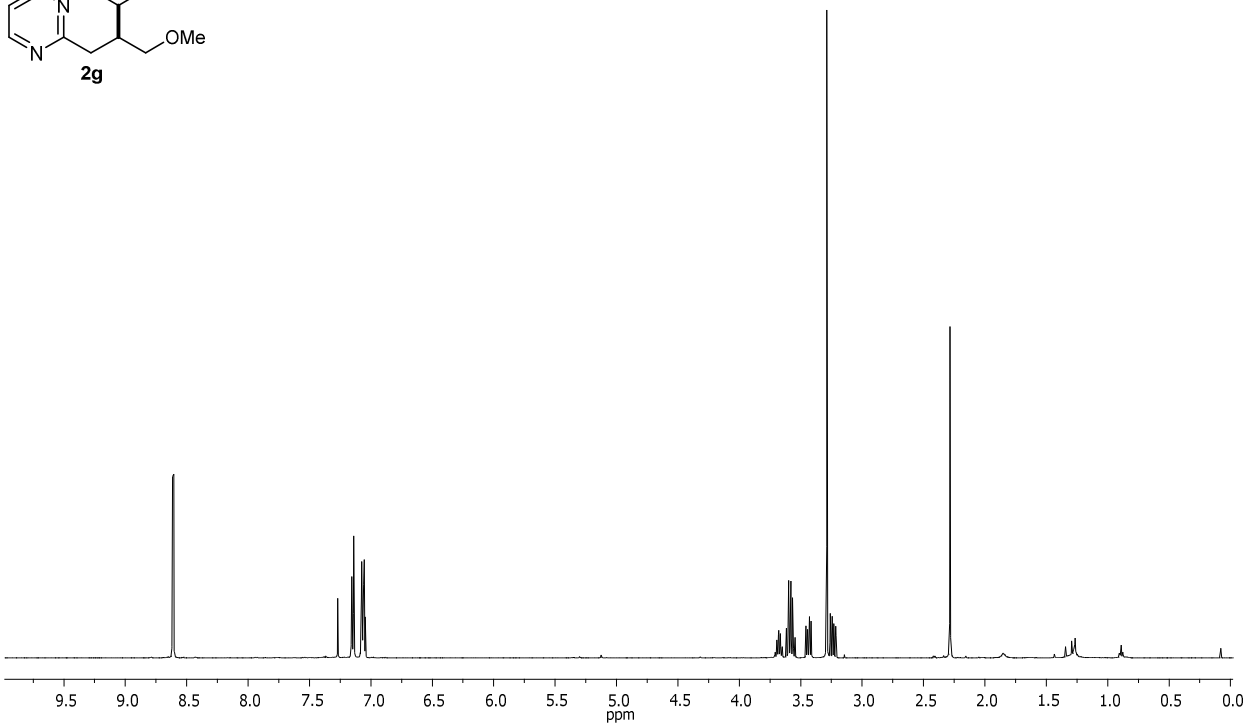
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

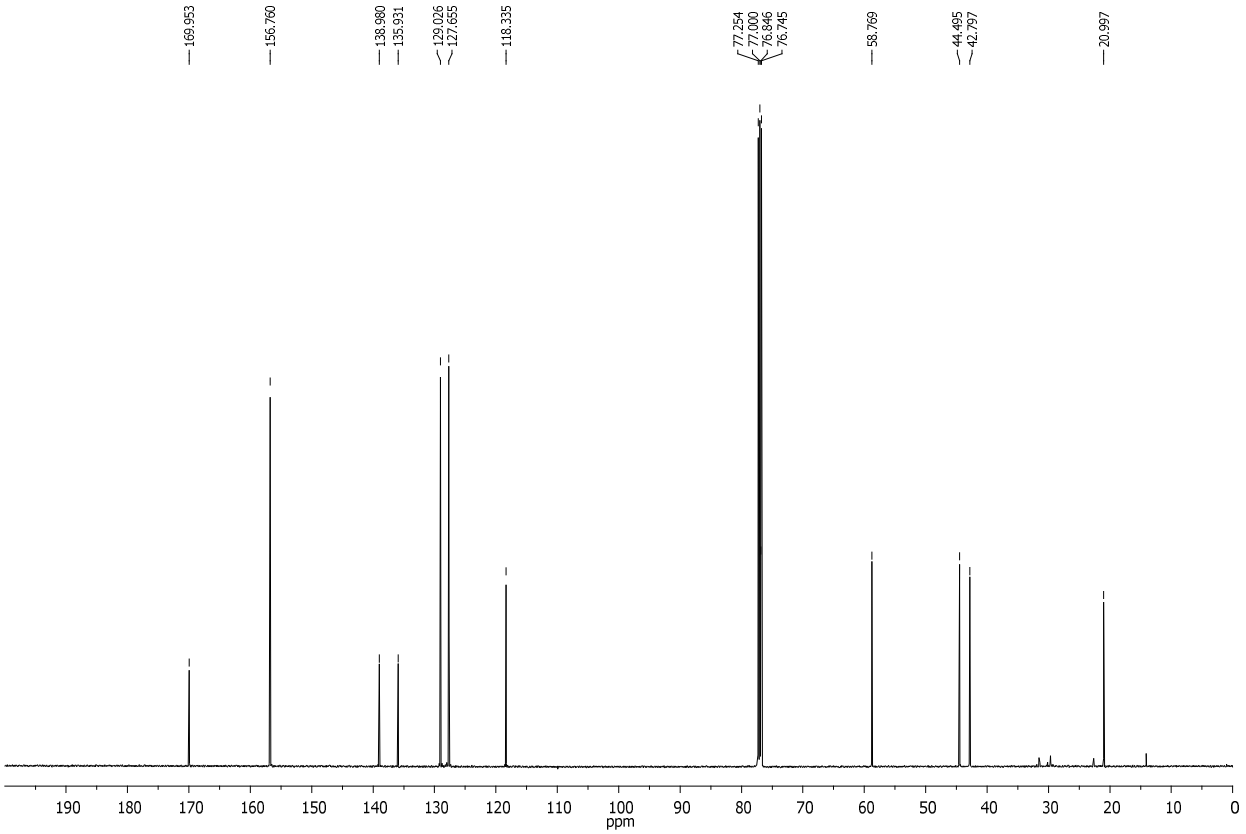

162.382
145.675
145.115
138.030
135.029
132.585
129.098
128.566
128.500
128.421
128.285
127.957
127.913
127.652
127.205
126.379
123.767
77.254
77.000
76.746
38.433
36.942
21.463
21.356

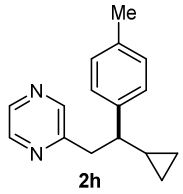

150
100
50
ppm (t1)



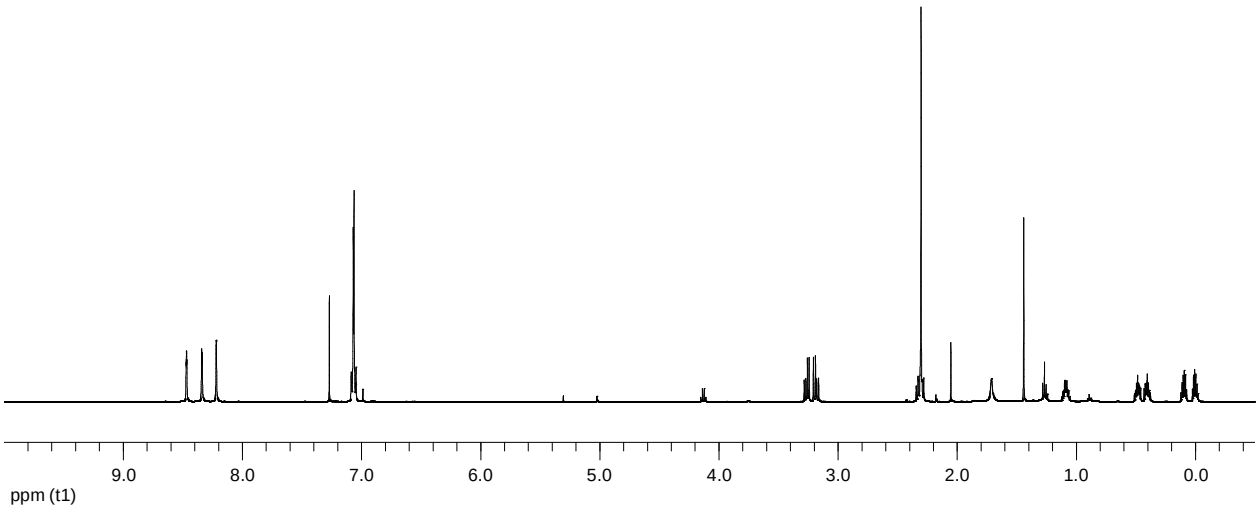
2g

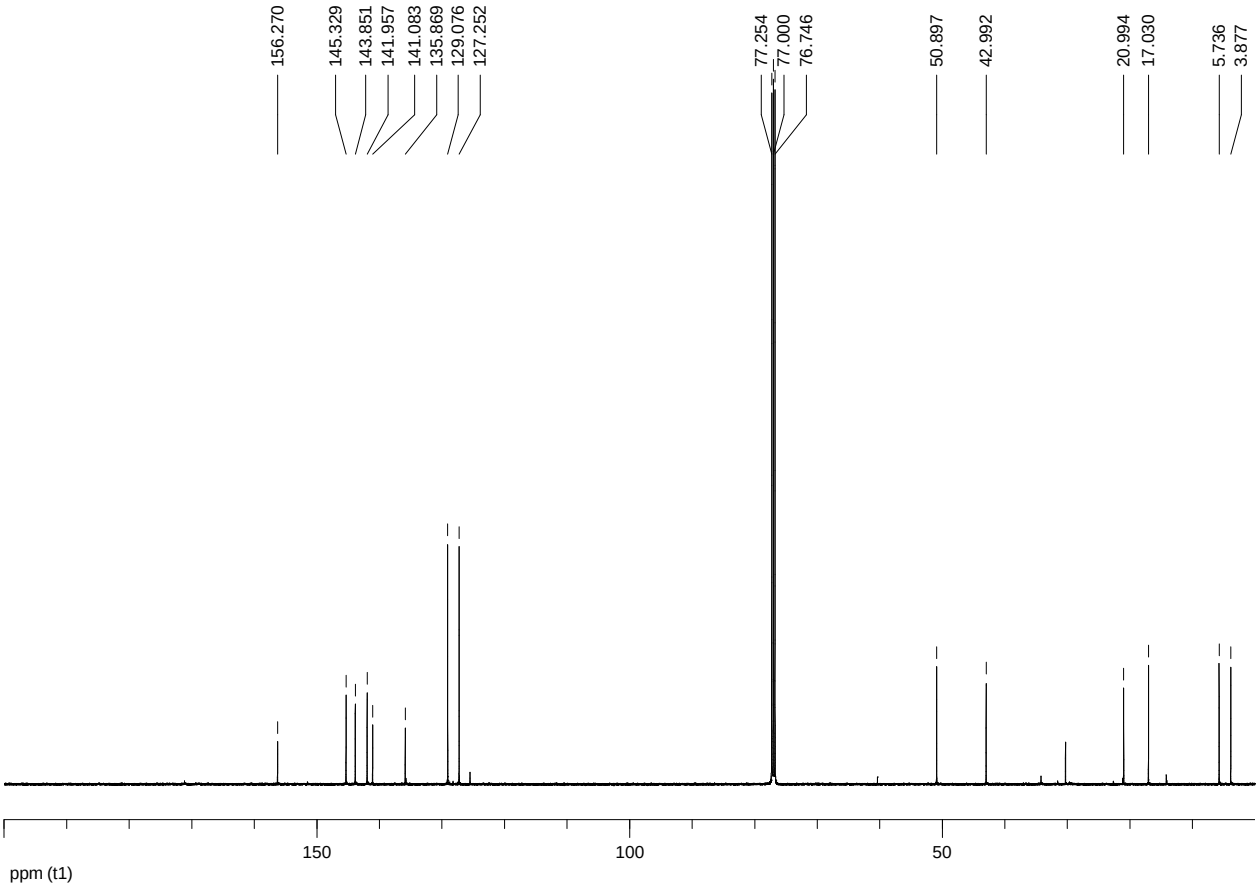


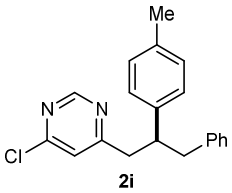




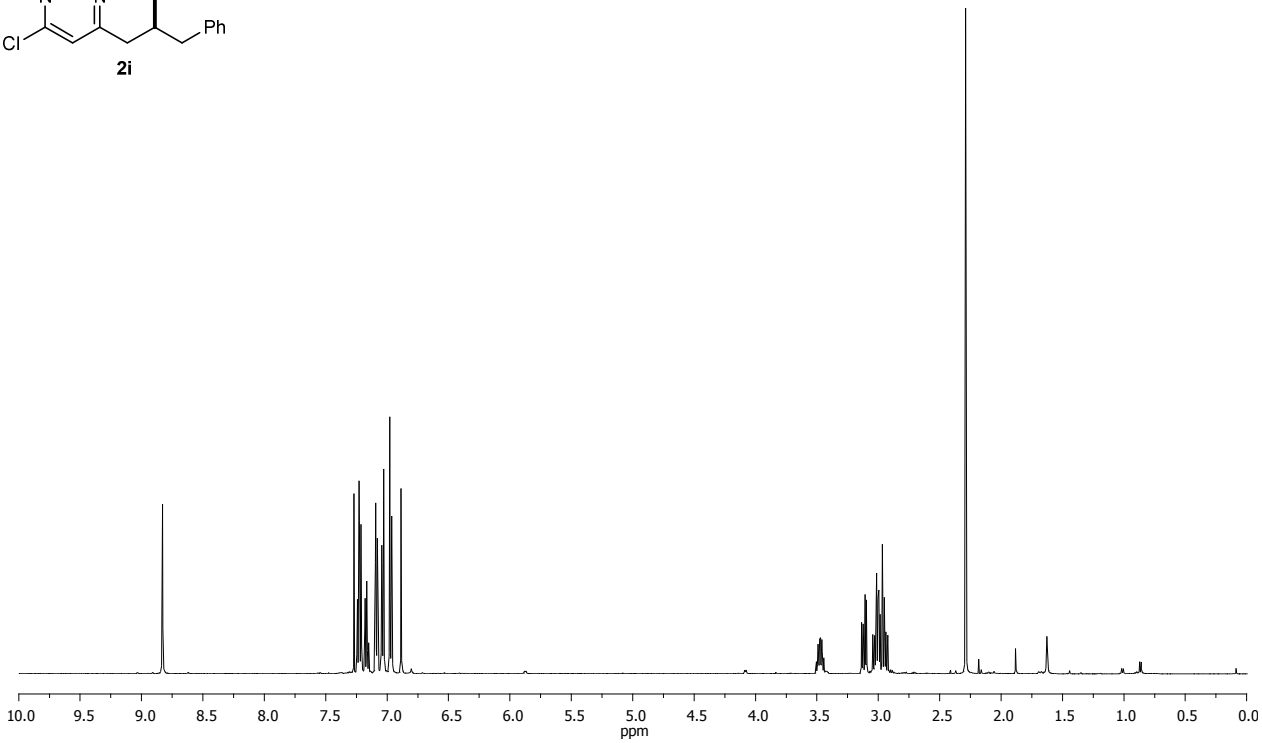
2h

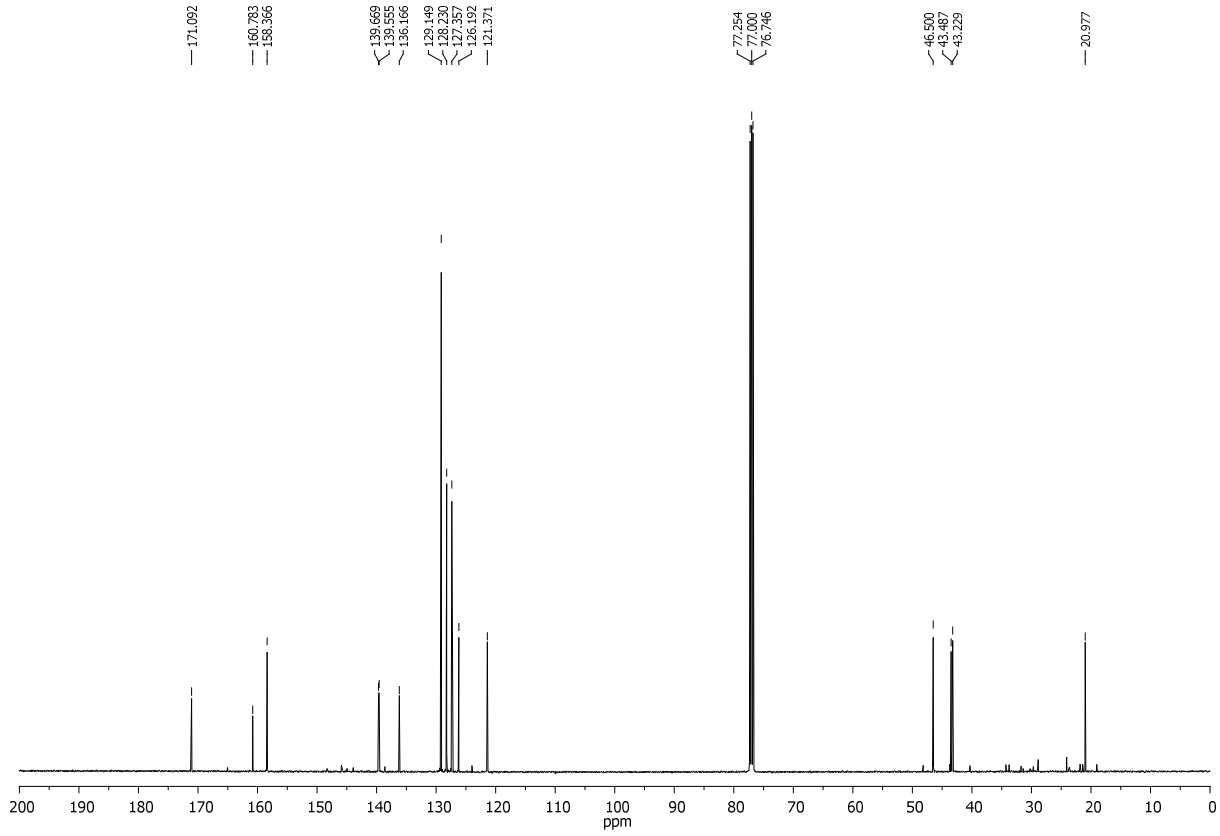


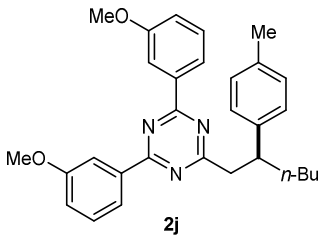




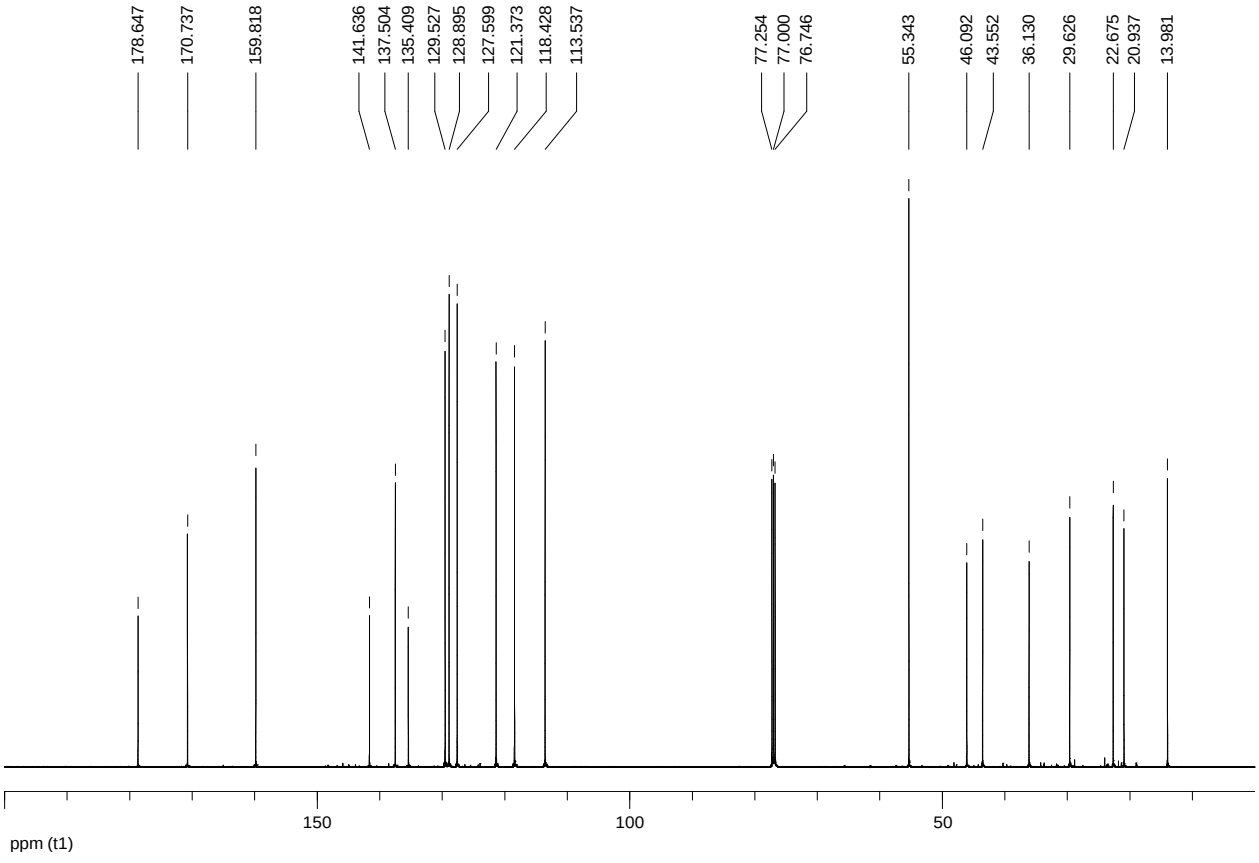
2i

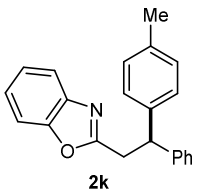






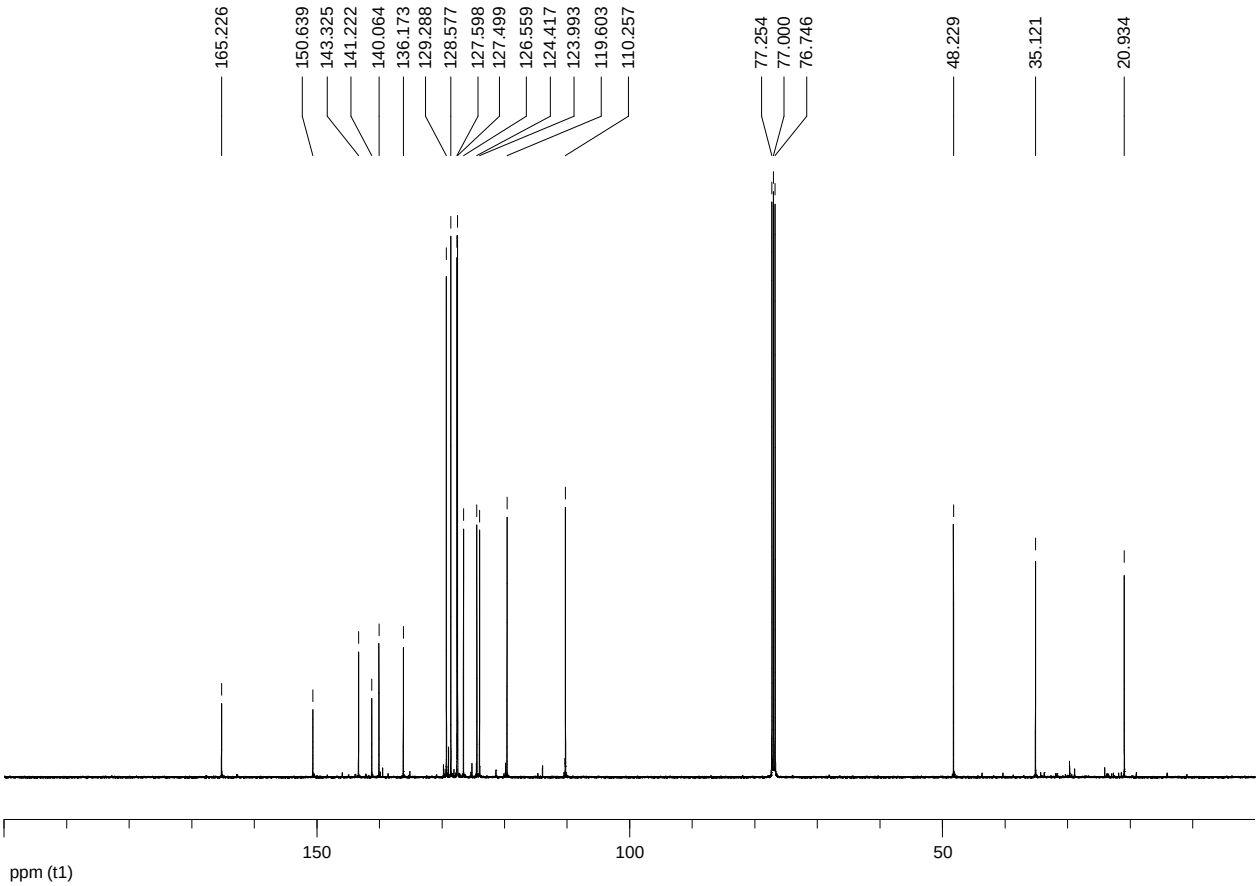
2j




Me
N
O
Ph

2k

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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136.173
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128.577
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127.499
126.559
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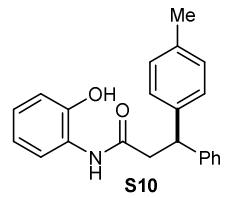
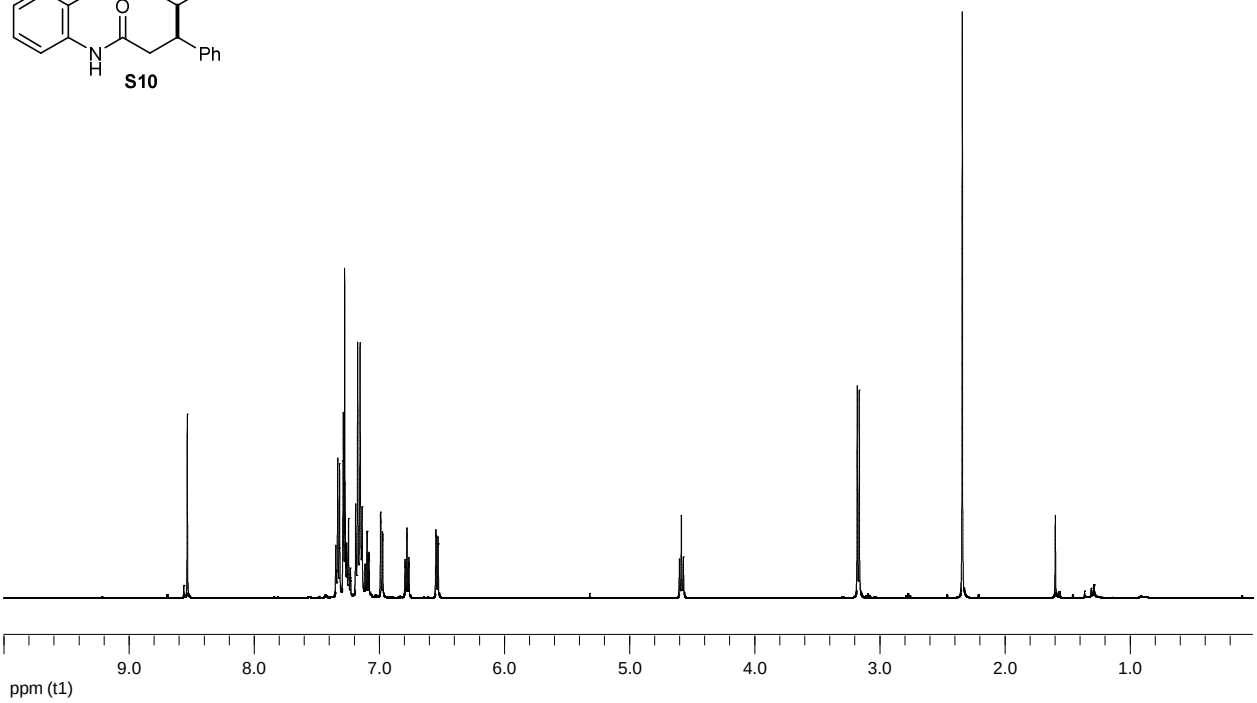
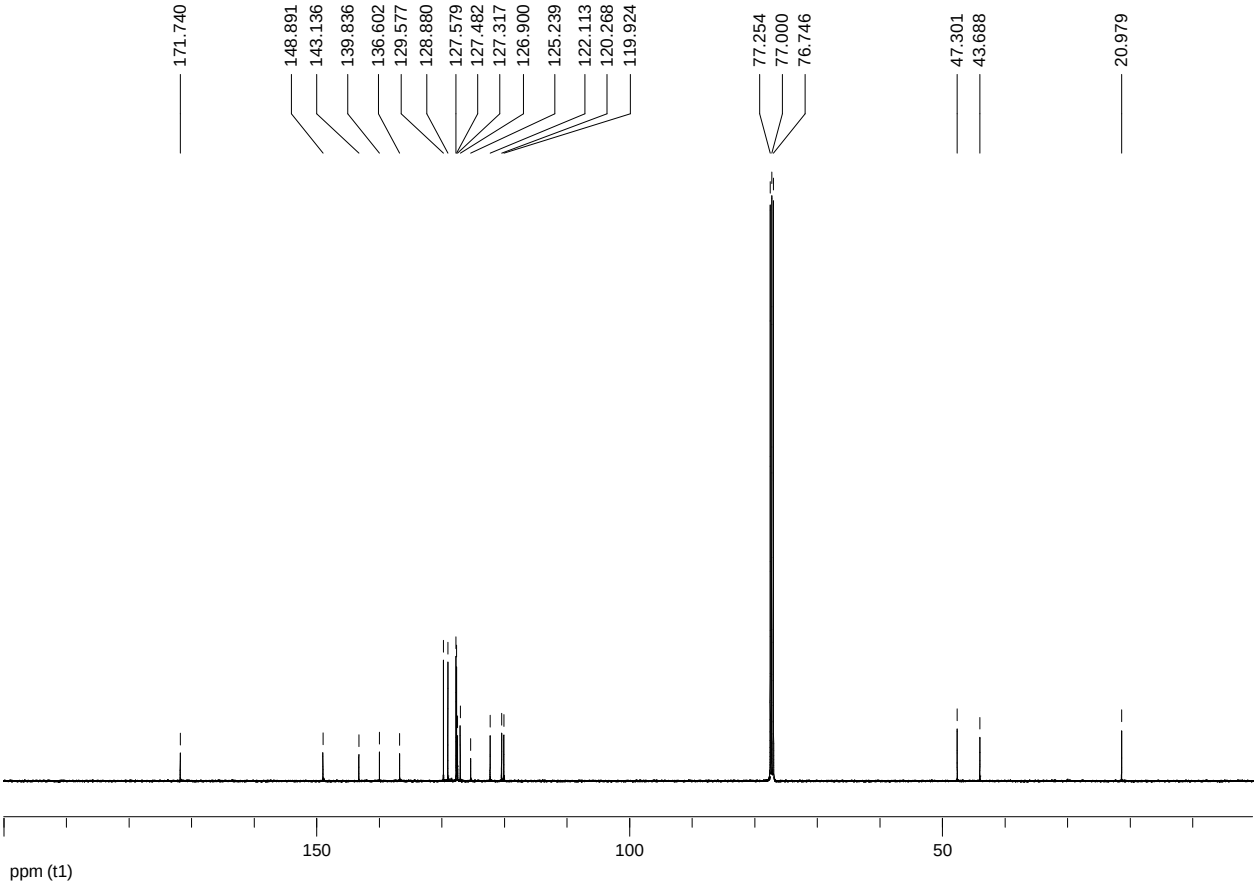
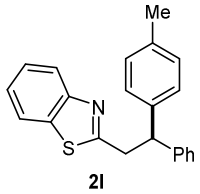
35.121
20.934
150
100
50
ppm (t1)



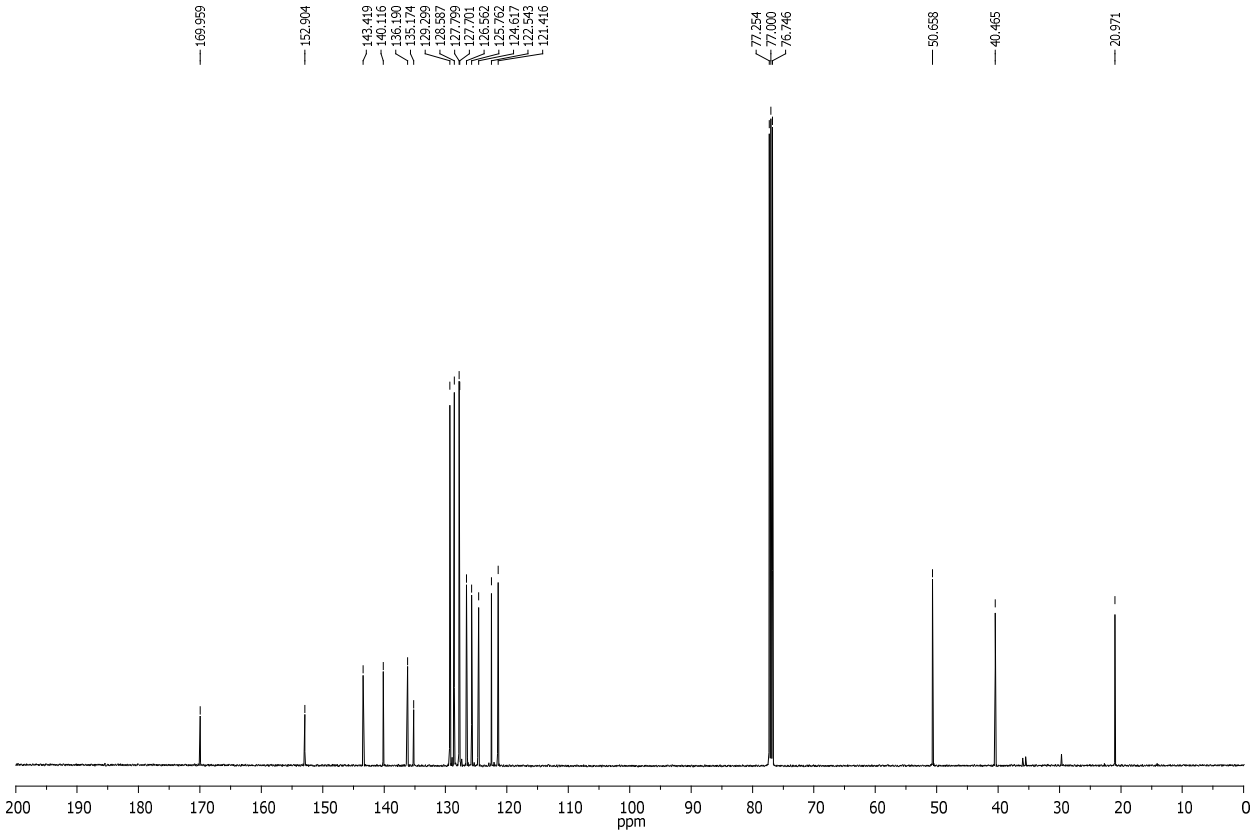
S10

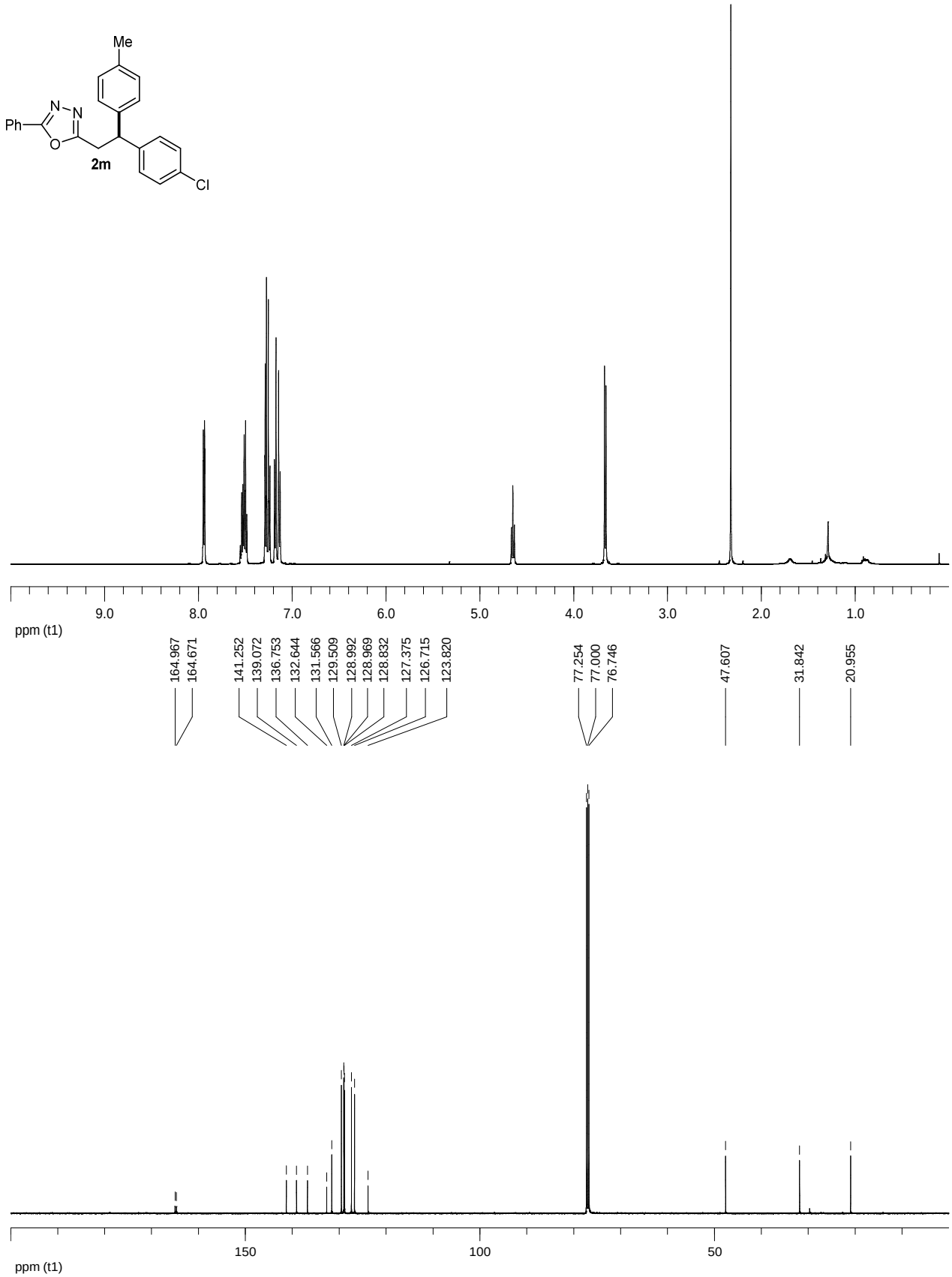


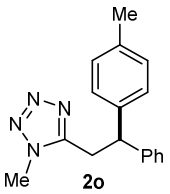




2l







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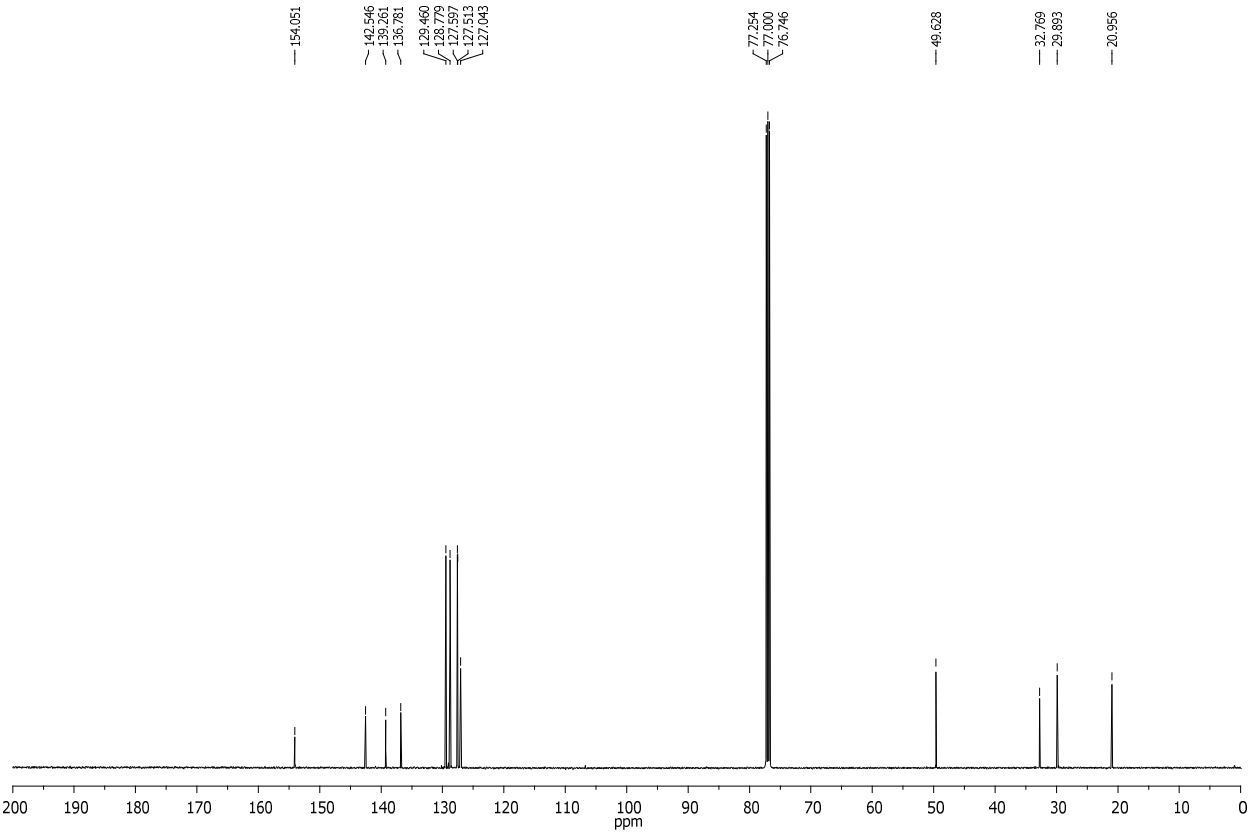

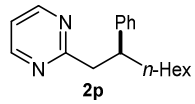

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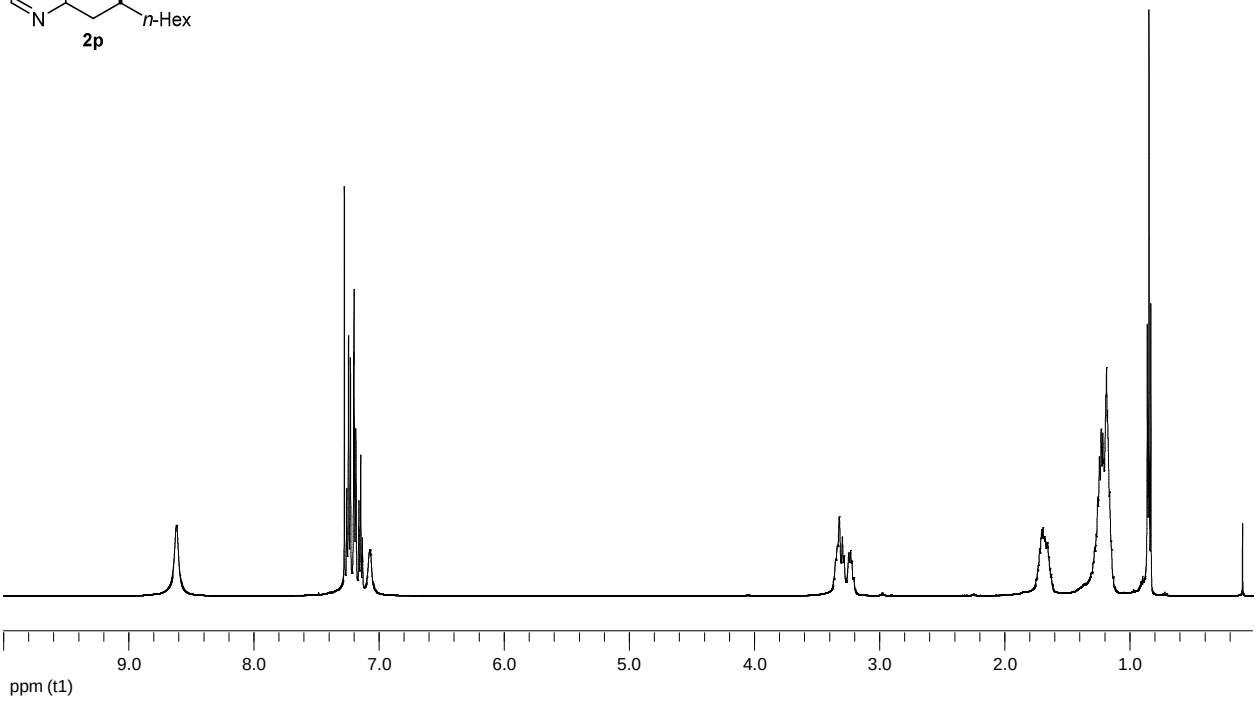
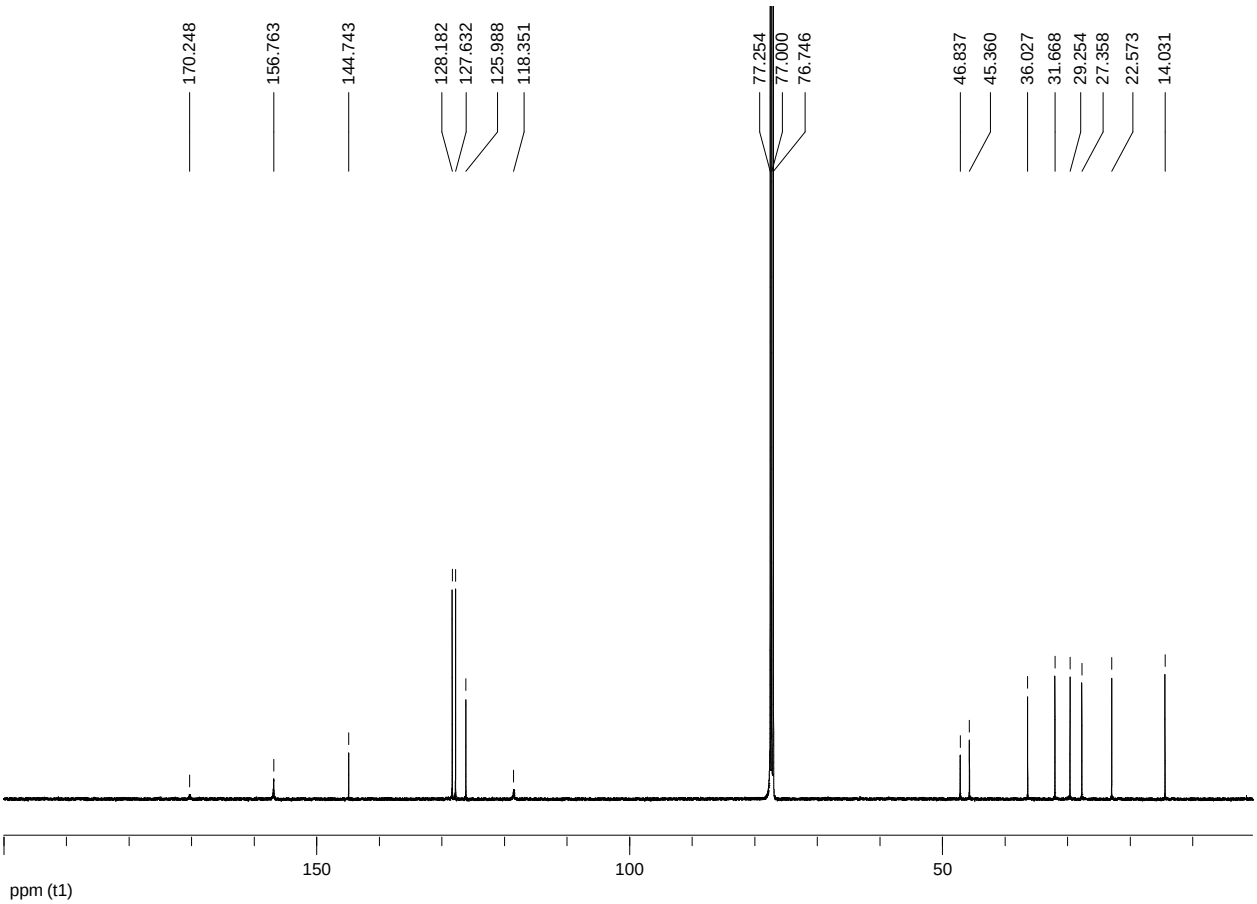
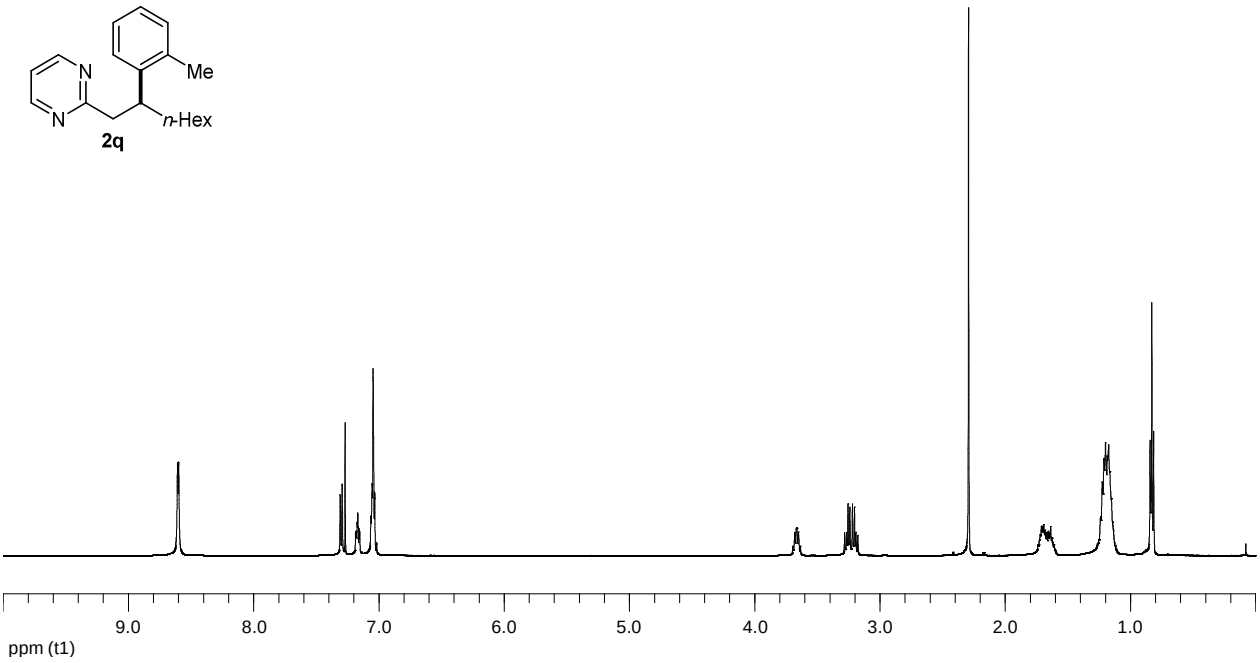
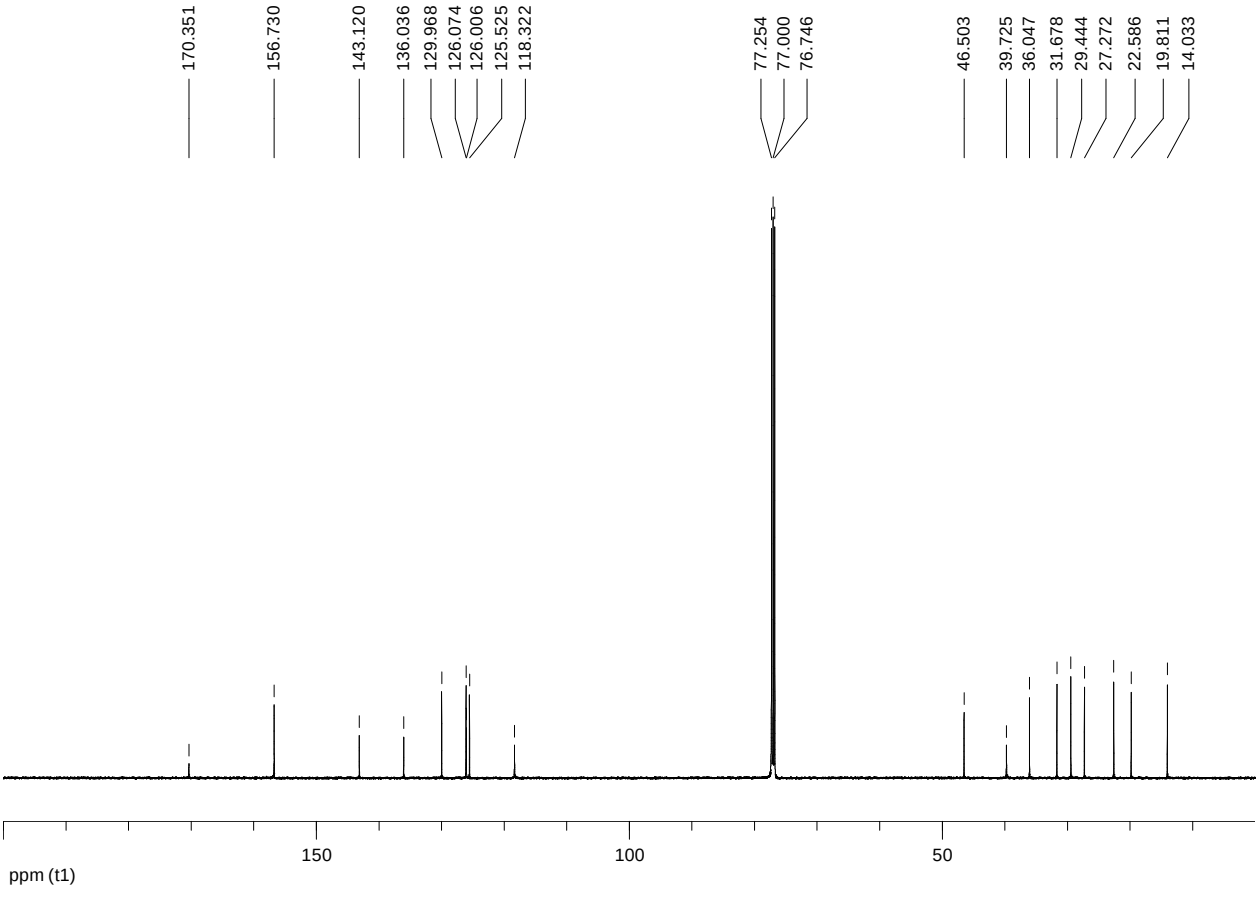
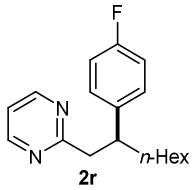




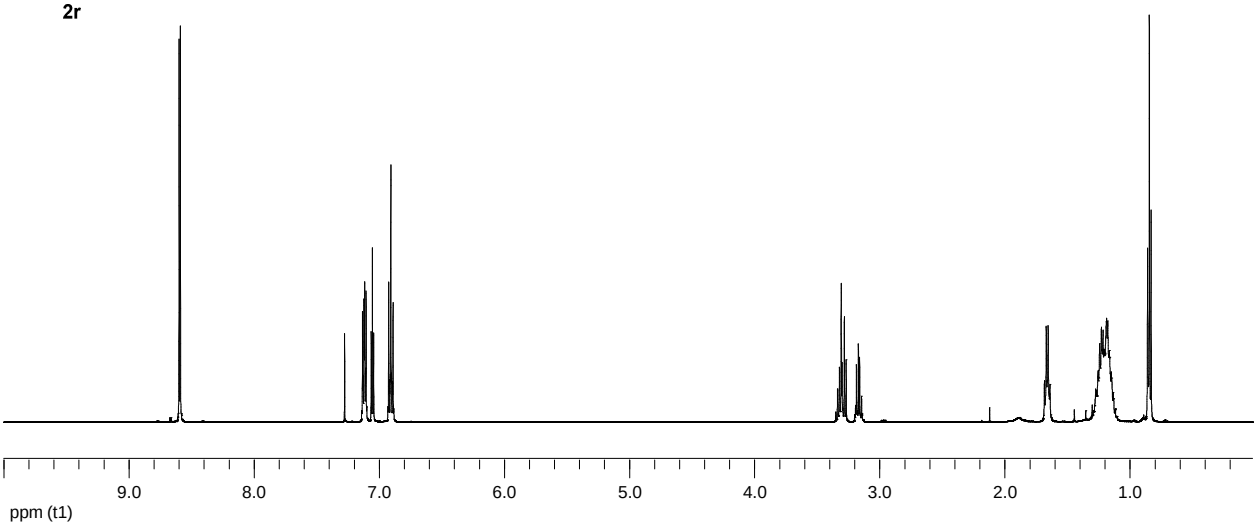


2q




F
N
N
n-Hex

2r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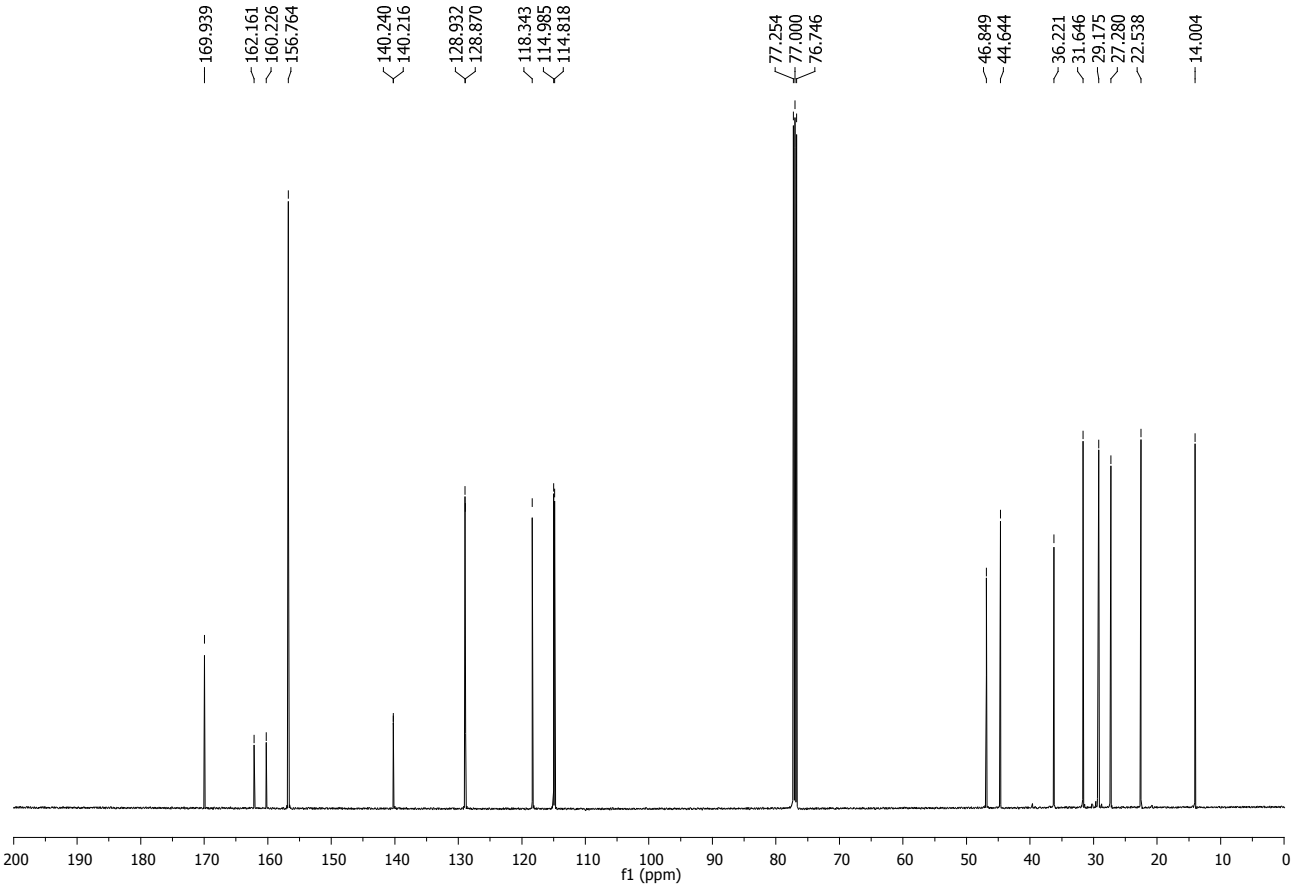
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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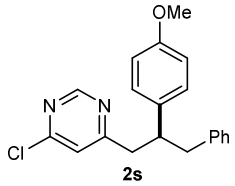
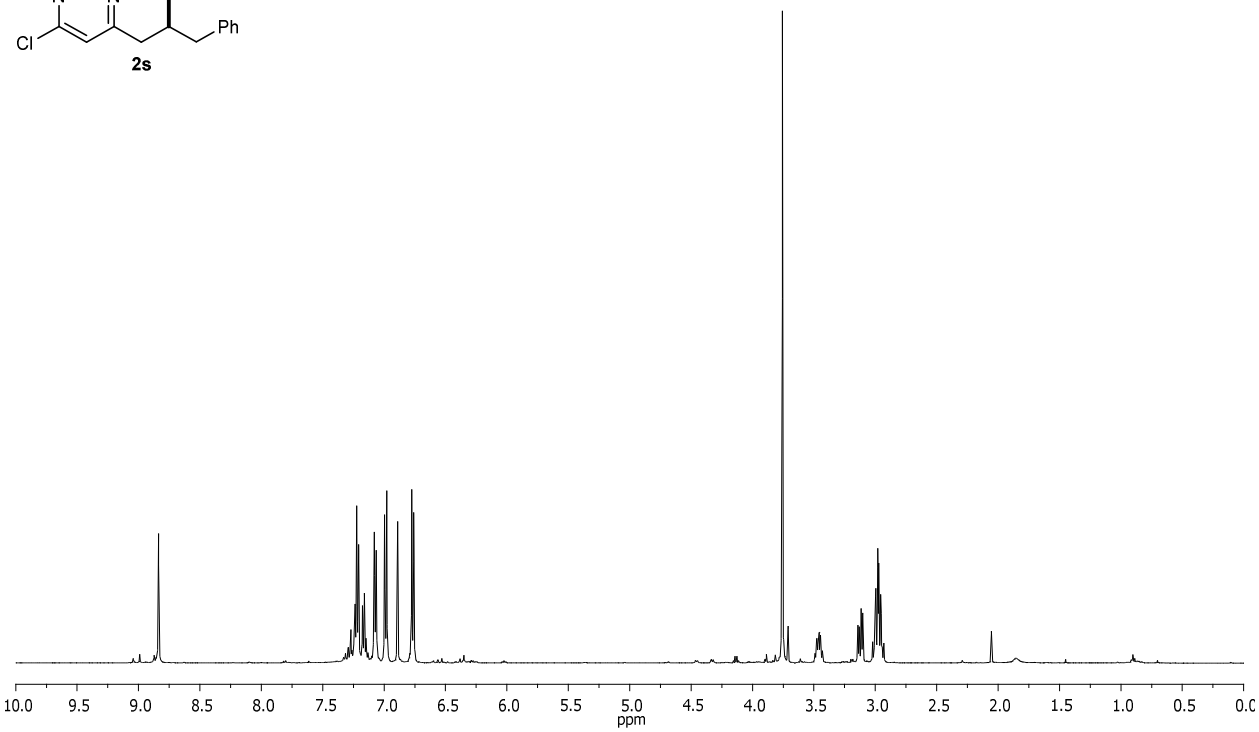
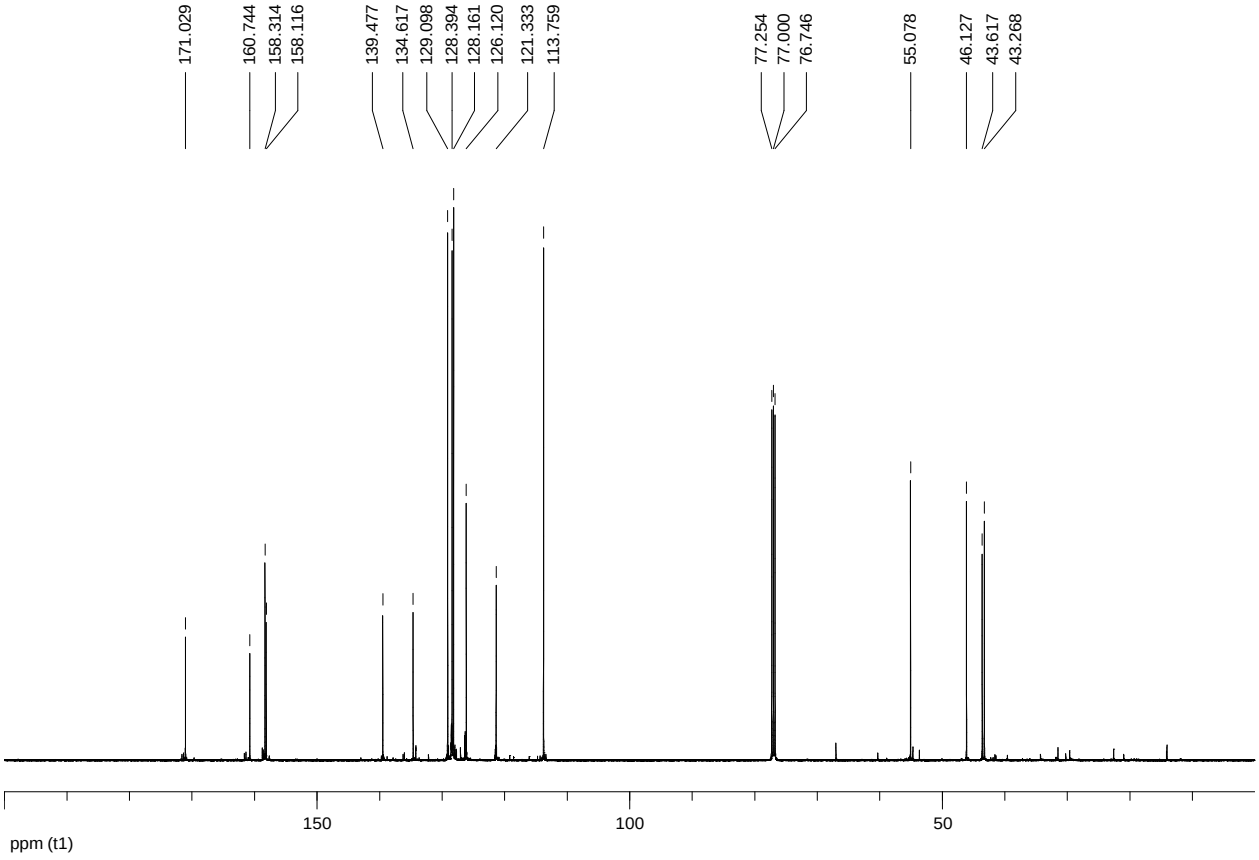
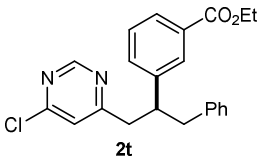
162.161
160.226
156.764
140.240
140.216
128.932
128.870
118.343
114.985
114.818
77.254
77.000
76.746
46.849
44.644
36.221
31.646
29.175
27.280
22.538
14.004
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



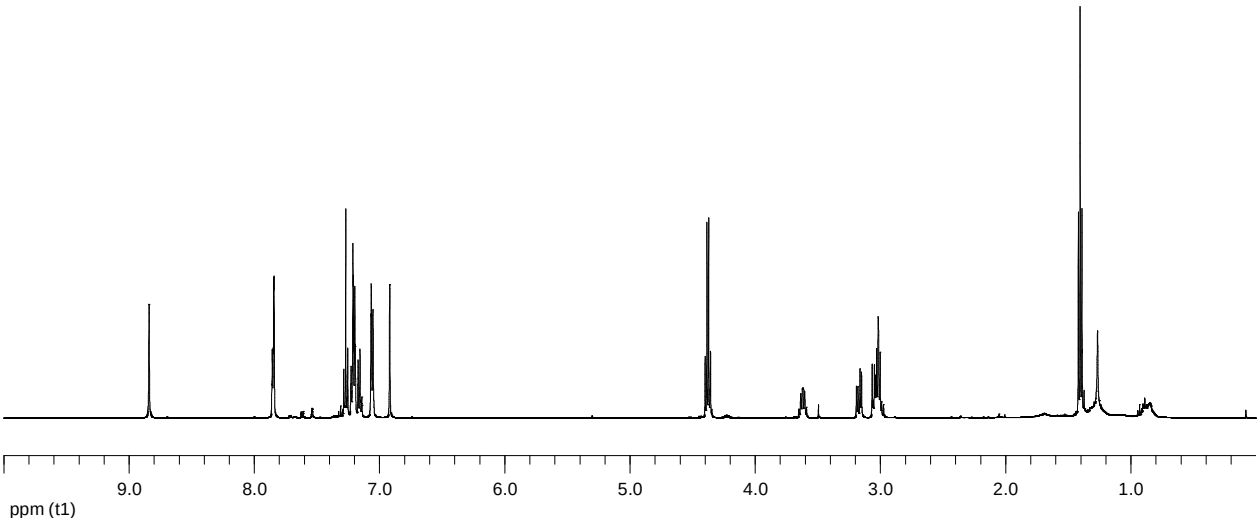
2s

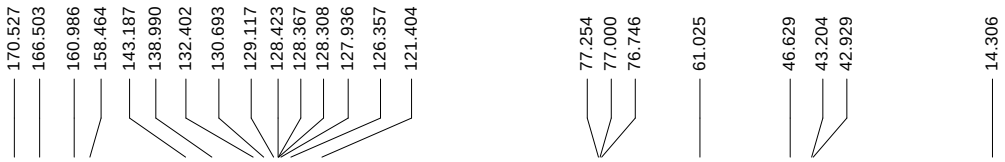


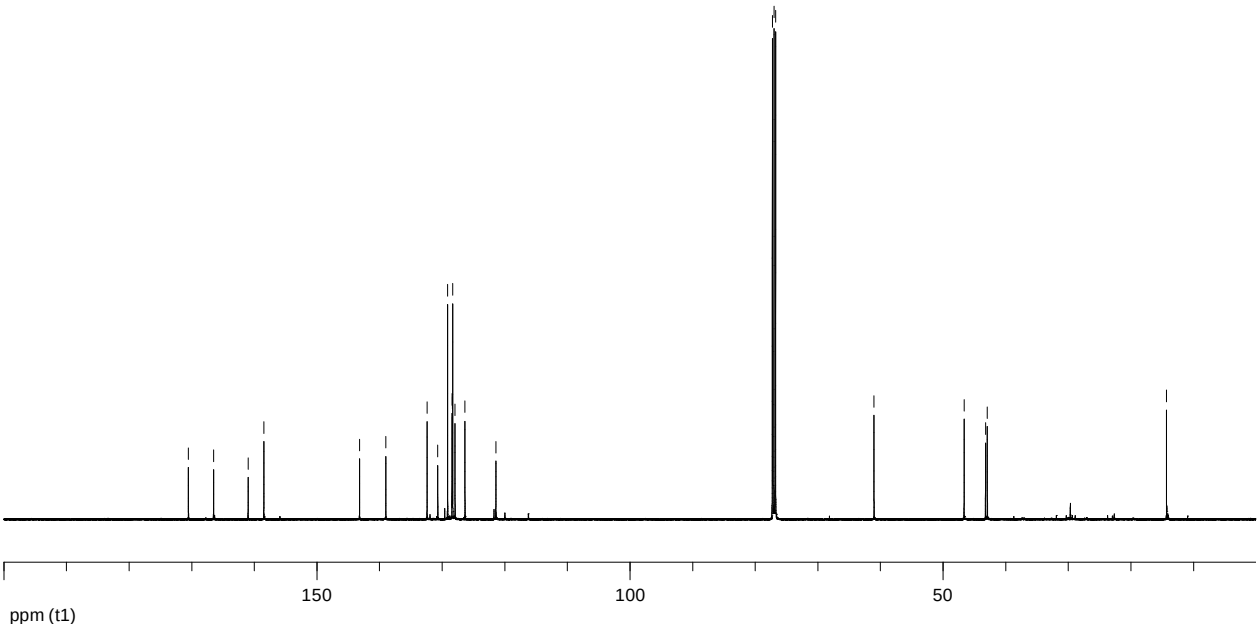


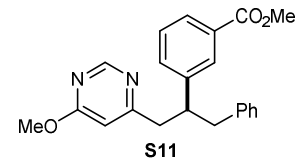


2t

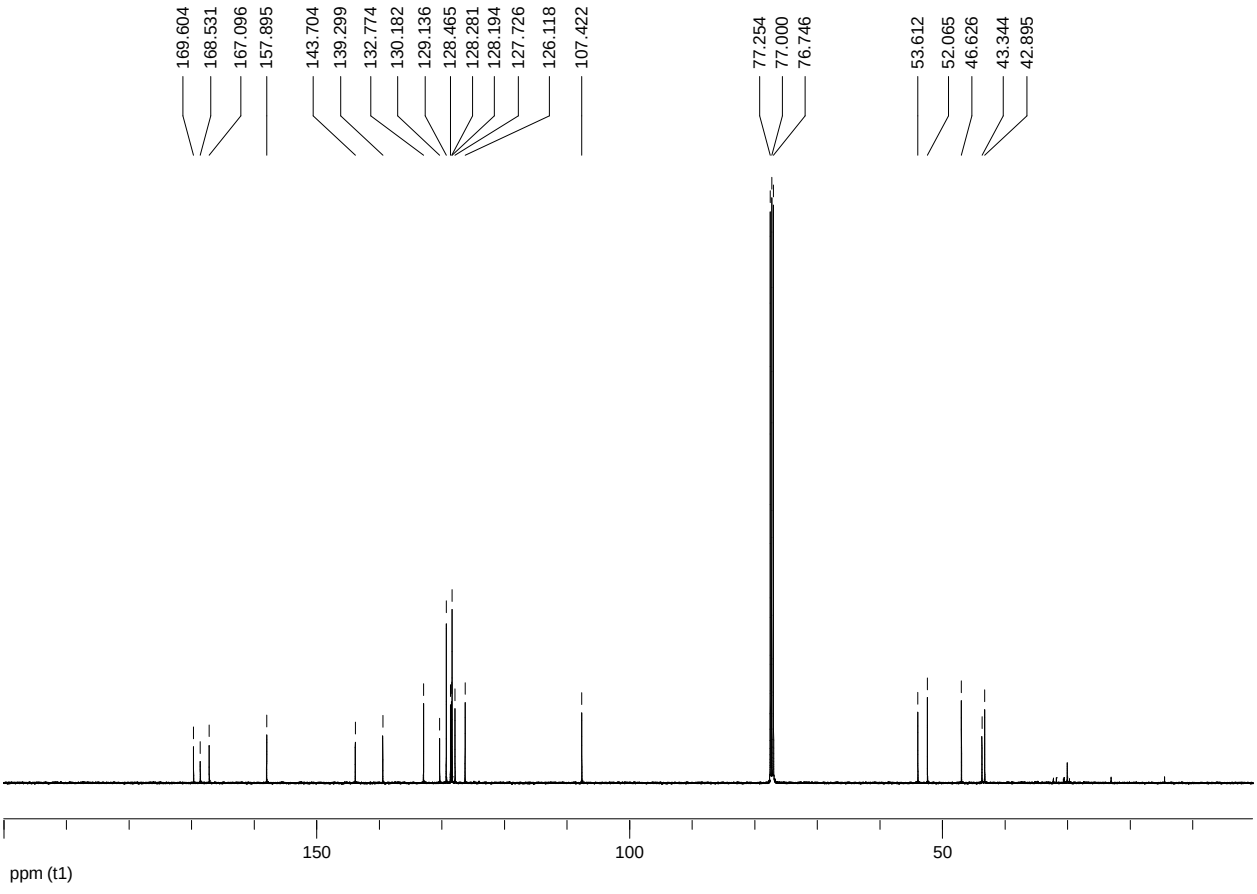


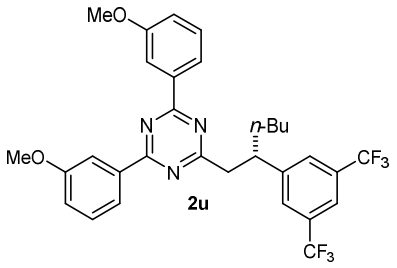






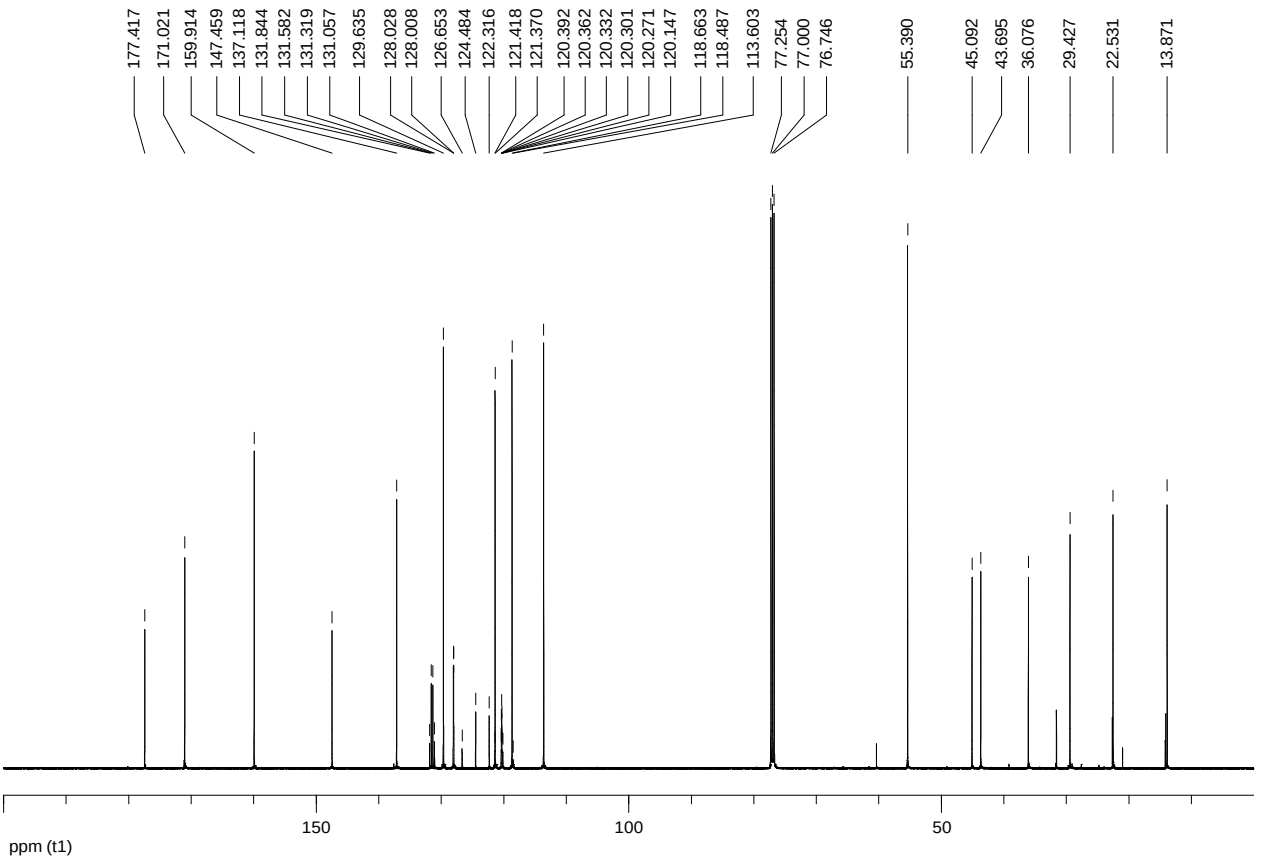
S11

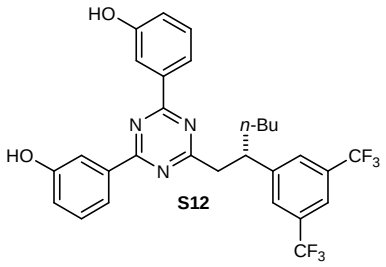



MeO
N
N
N
n-Bu
MeO
CF3
CF3

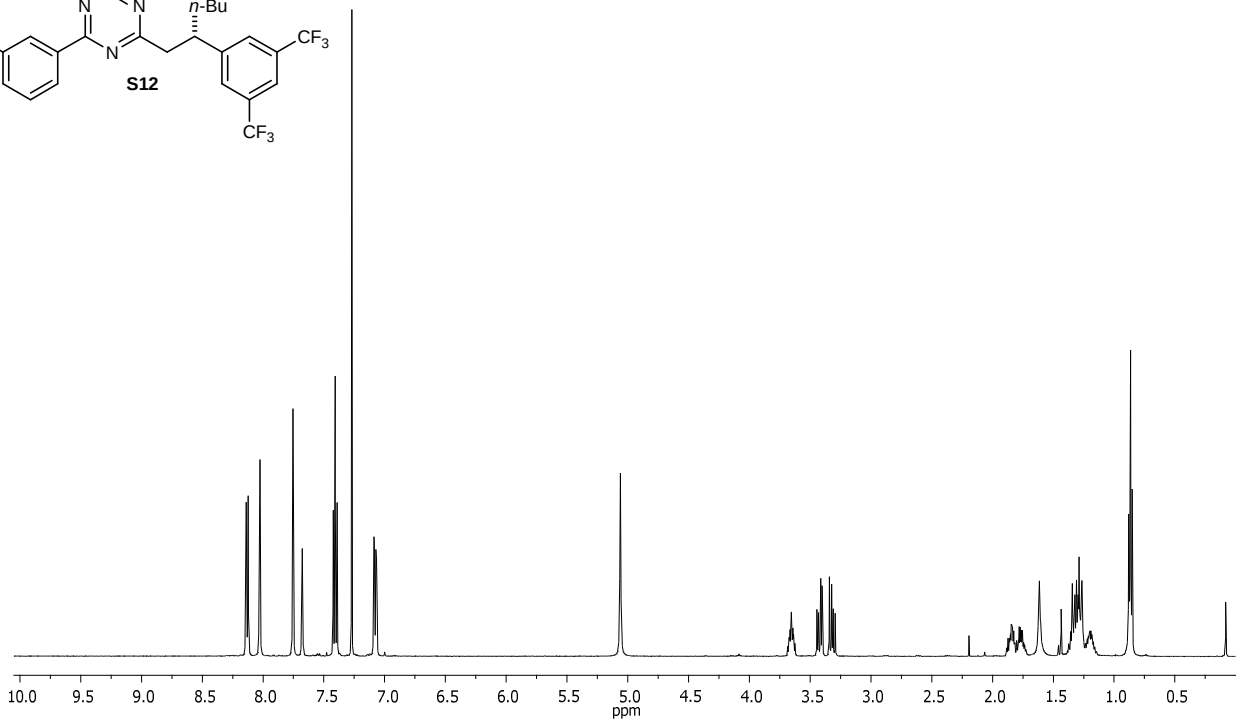
2u

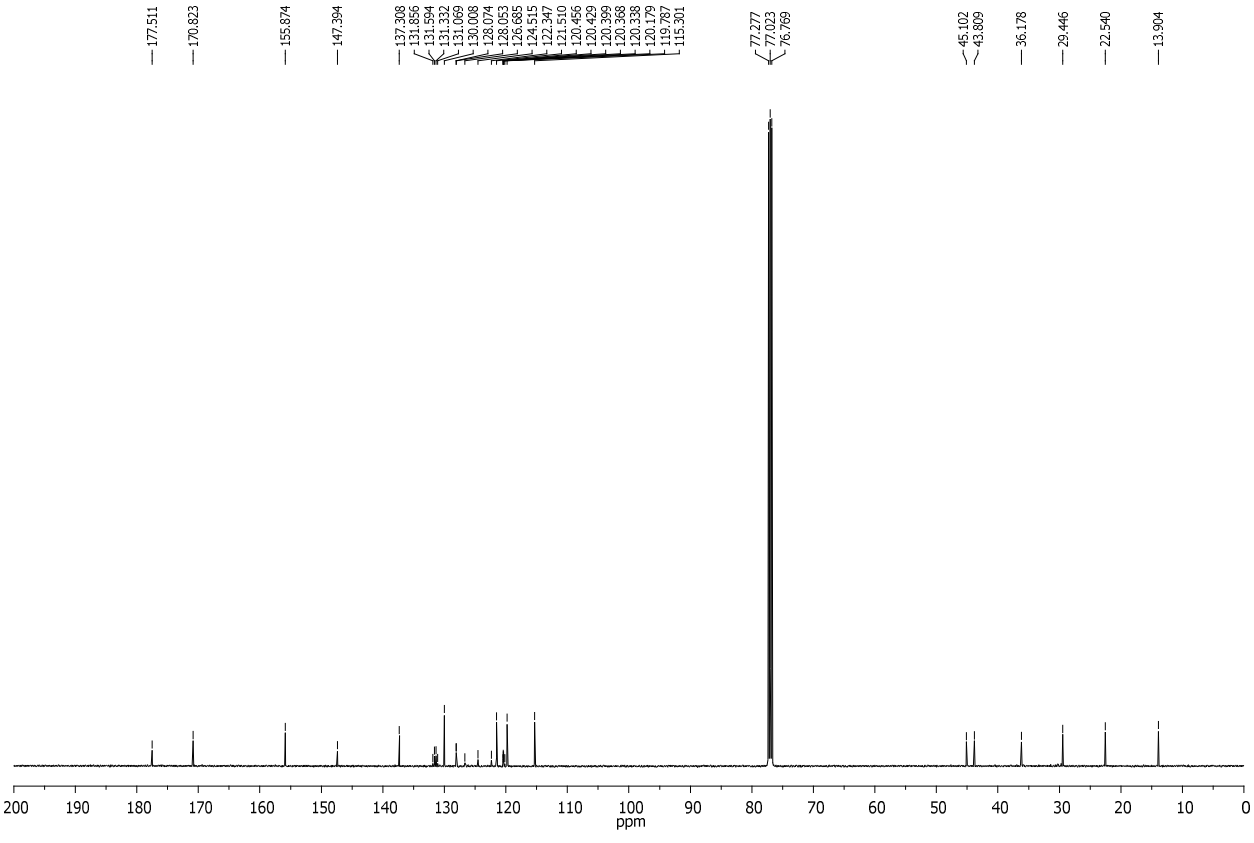
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

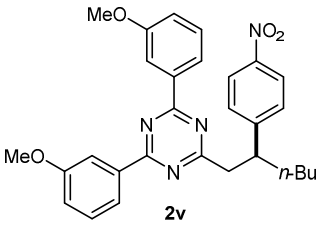

177.417
171.021
159.914
147.459
137.118
131.844
131.582
131.319
131.057
129.635
128.028
128.008
126.653
124.484
122.316
121.418
121.370
120.392
120.362
120.332
120.301
120.271
120.147
118.663
118.487
113.603
77.254
77.000
76.746
55.390
45.092
43.695
36.076
29.427
22.531
13.871
150
100
50
ppm (t1)



S12

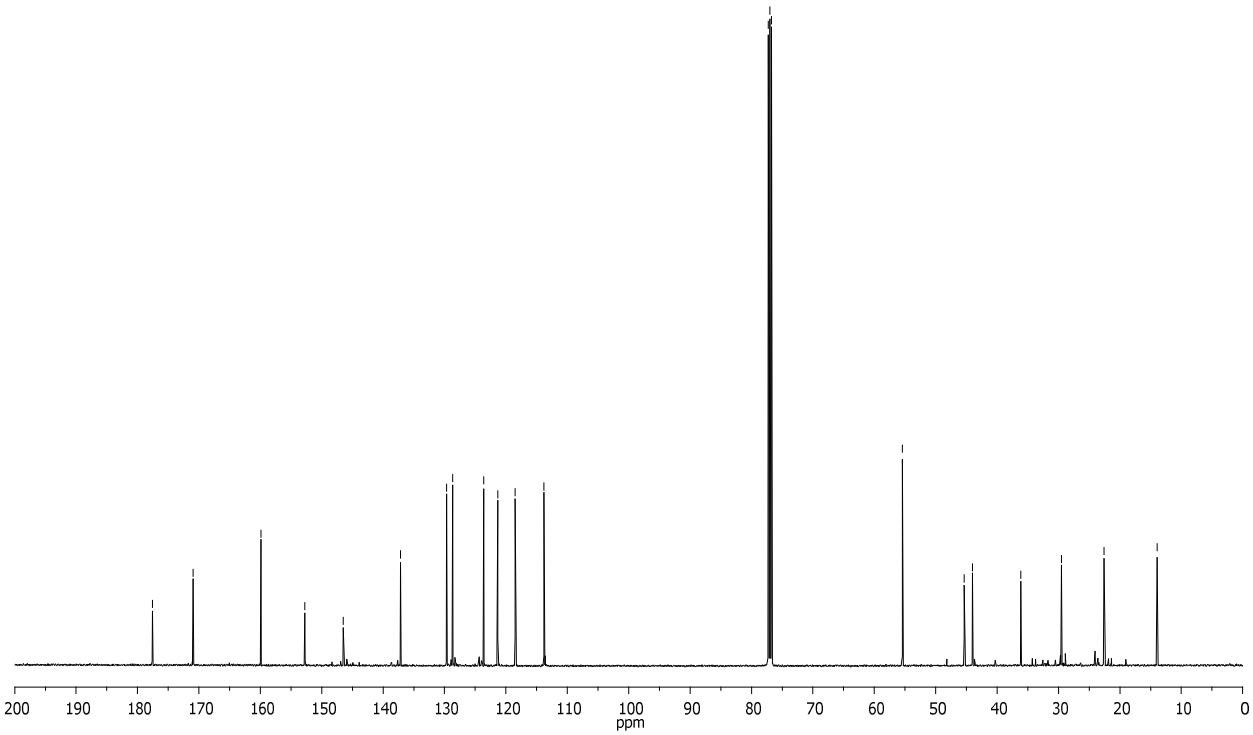


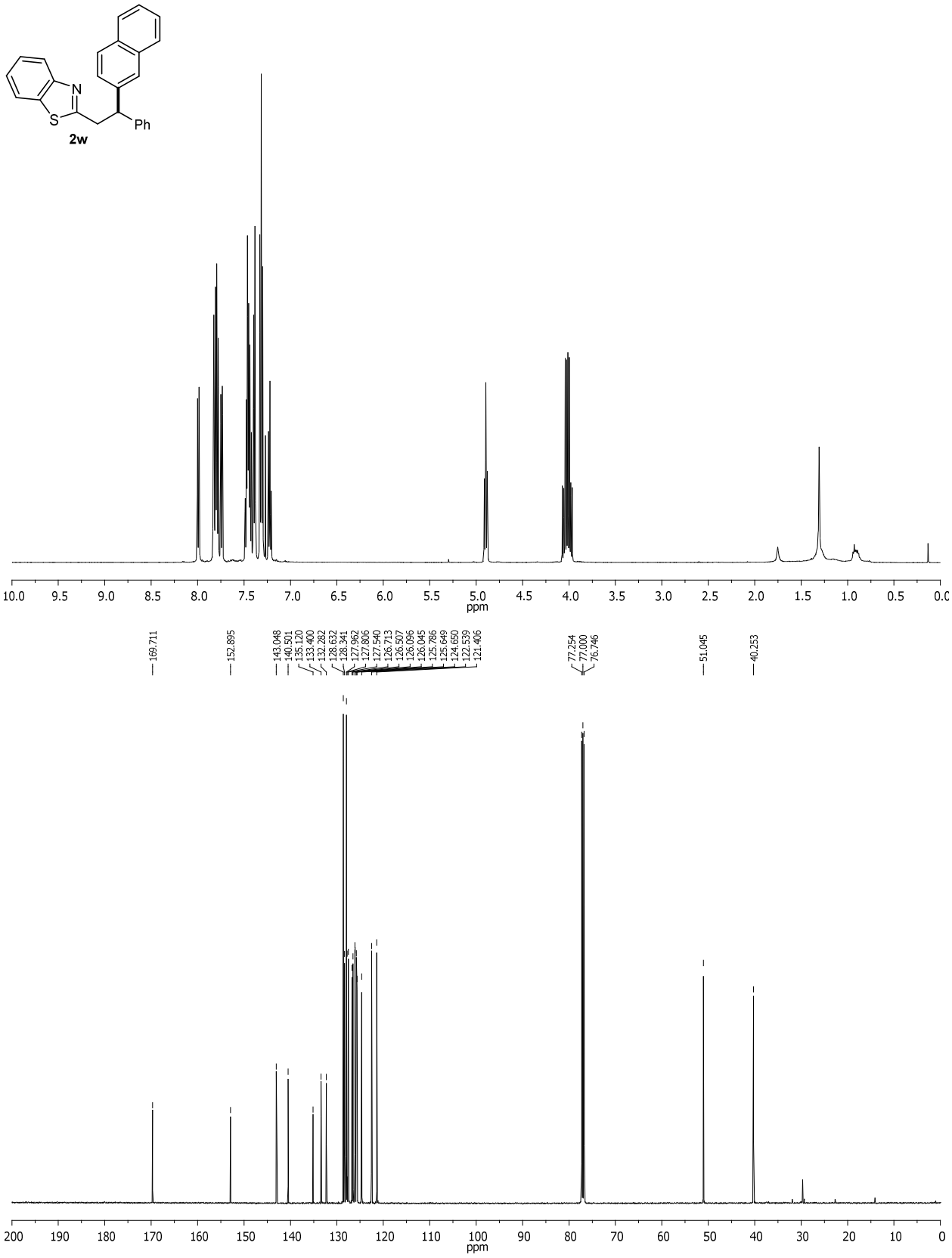


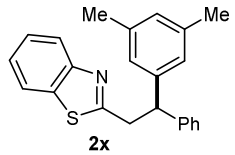


2v

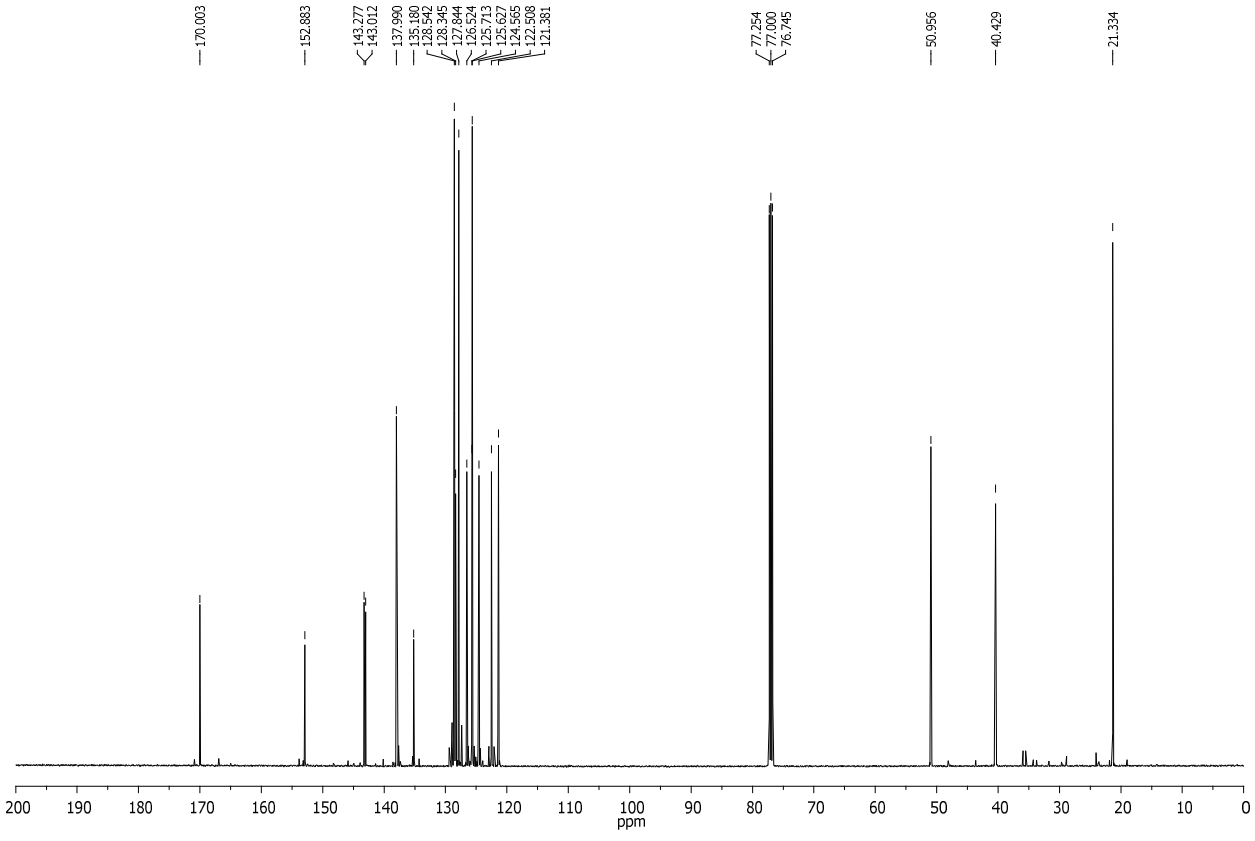
177.583, 170.938, 159.903, 152.740, 146.482, 137.176, 129.667, 128.651, 123.591, 121.312, 118.477, 113.790, 77.254, 77.000, 76.746, 55.423, 45.341, 43.992, 36.136, 29.527, 22.590, 13.925

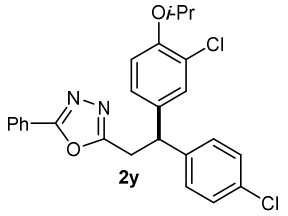




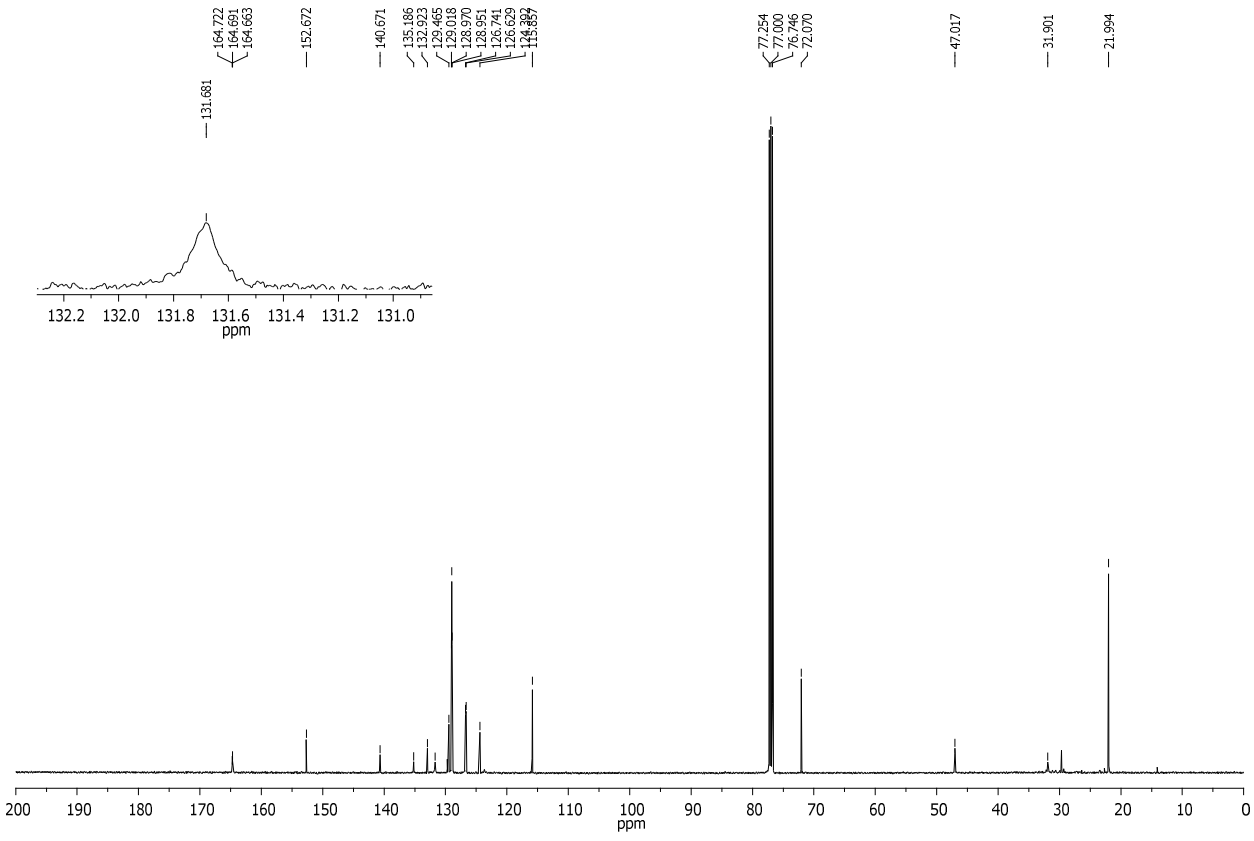


2x

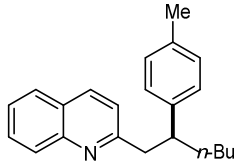




2y

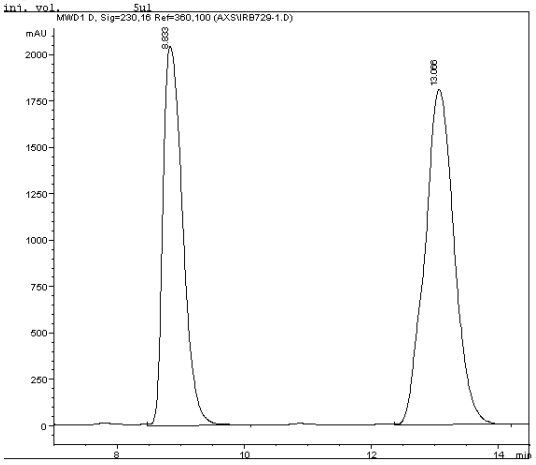


HPLC Traces



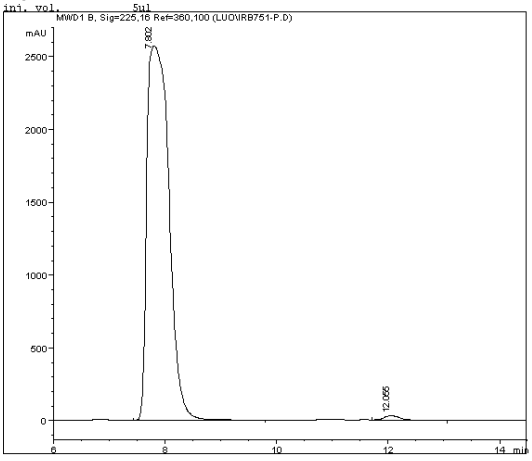
2a

```
Data File name:                 C:\HPCHEM\1\DATA\AXS\IRB729-1.D
Method name:                    ODH9802.M
data acquired by:   Hon Wai Lam
on:                 07/12/2012
location:           Vial 72
Sample:             IRB729
inj. vol.           5ul
```

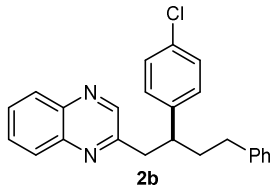


Meas.	R Area %	Width	Symmetr
8.833	43.004	0.338	0.548
13.066	56.996	0.481	0.924

```
Data File name:                 C:\HPCHEM\1\DATA\LUO\IRB751-P.D
Method name:                    ODH9802.M
data acquired by:   Alan
on:                 17/01/2013
location:           Vial 41
Sample:             IRB751P
inj. vol.           5ul
```

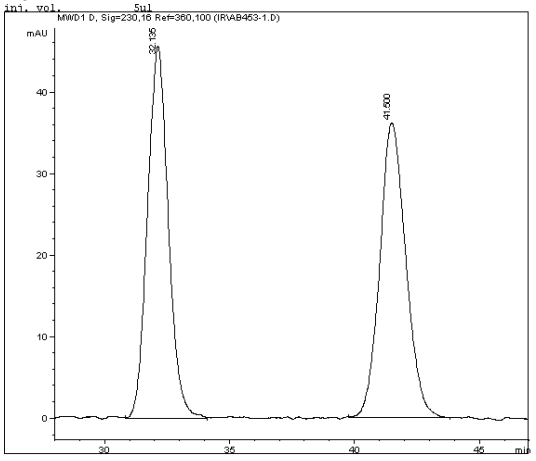


Meas.	R Area %	Width	Symmetr
7.802	98.913	0.386	0.444
12.055	1.087	0.322	0.784



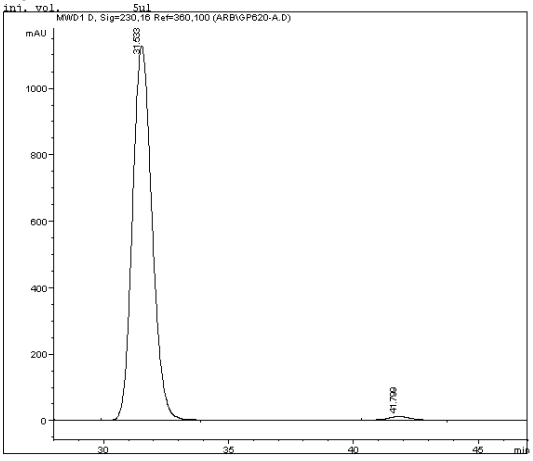
2b

```
Data File name:                 C:\HPCHEM\1\DATA\IR\AB453-1.D
Method name:                    ODH9802.M
data acquired by:   Hon Wai Lam
on:                 04/04/2013
location:           Vial 47
Sample:             ARB-4-53-1
inj. vol.           5ul
```

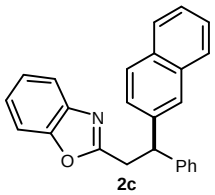


Meas.	R Area %	Width	Symmetr
32.135	50.169	0.962	0.950
41.500	49.831	1.207	0.845

```
Data File name:                 C:\HPCHEM\1\DATA\ARB\GP620-A.D
Method name:                    ODH9802.M
data acquired by:   Hon Wai Lam
on:                 04/04/2013
location:           Vial 48
Sample:             GP620-A
inj. vol.           5ul
```

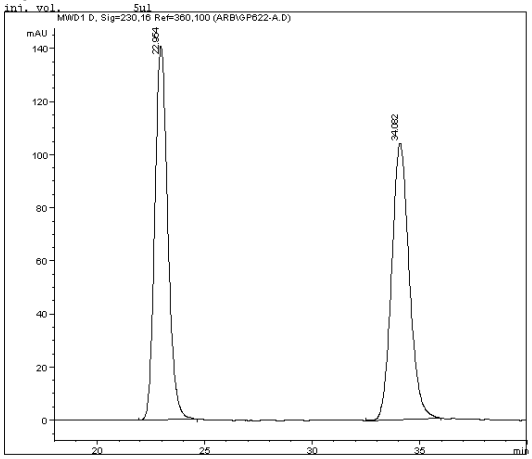


Meas.	R Area %	Width	Symmetr
31.533	98.712	0.852	0.856
41.799	1.288	0.879	0.836



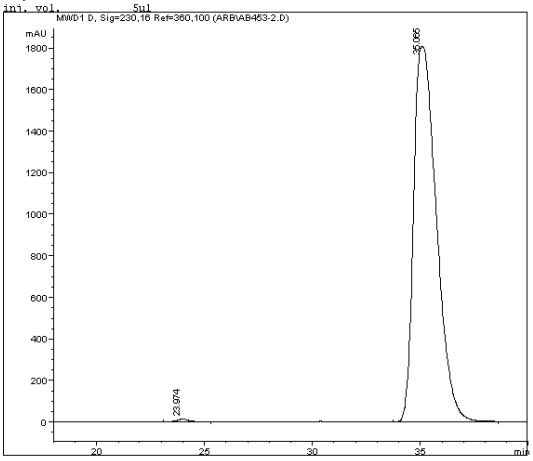
2c

Data File name: C:\HPCHEM\1\DATA\ARB\GP622-A.D
Method name: ODH9802.M
data acquired by: Hon Wai Lam
on: 04/04/2013
location: Vial 58
Sample: GP622-A
inj. vol. 5ul

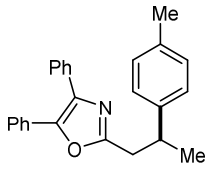


Meas.	R Area %	Width	Symmetr
22.954	49.921	0.644	0.838
34.082	50.079	0.836	0.879

Data File name: C:\HPCHEM\1\DATA\ARB\AB453-2.D
Method name: ODH9802.M
data acquired by: Hon Wai Lam
on: 04/04/2013
location: Vial 57
Sample: ARB-4-53-2
inj. vol. 5ul

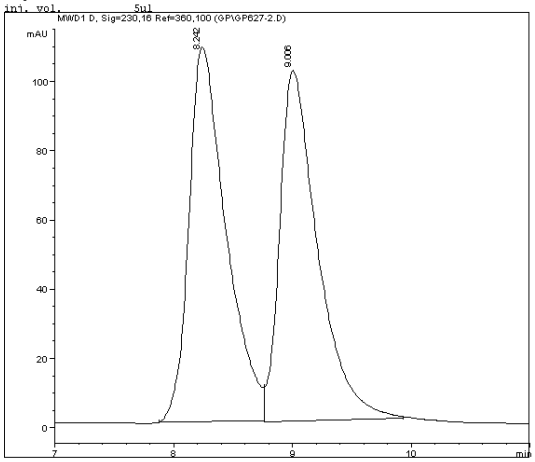


Meas.	R Area %	Width	Symmetr
23.974	0.441	0.619	0.842
35.065	99.559	0.975	0.515



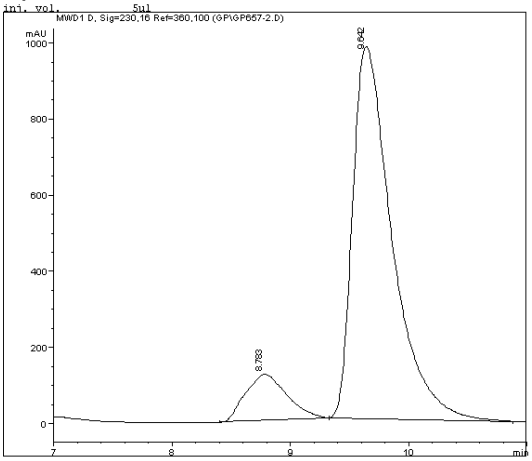
2d

Data File name: C:\HPCHEM\1\DATA\GP\GP627-2.D
Method name: ADH9802.M
data acquired by: Hon Wai Lam
on: 11/07/2012
location: Vial 32
Sample: GP627
inj. vol. 5ul

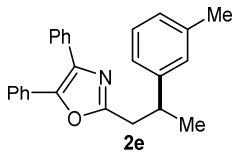


Meas.	R Area %	Width	Symmetr
8.242	51.083	0.362	0.551
9.006	48.917	0.370	0.517

Data File name: C:\HPCHEM\1\DATA\GP\GP657-2.D
Method name: ADH9802.M
data acquired by: Hon Wai Lam
on: 14/09/2012
location: Vial 27
Sample: GP657
inj. vol. 5ul

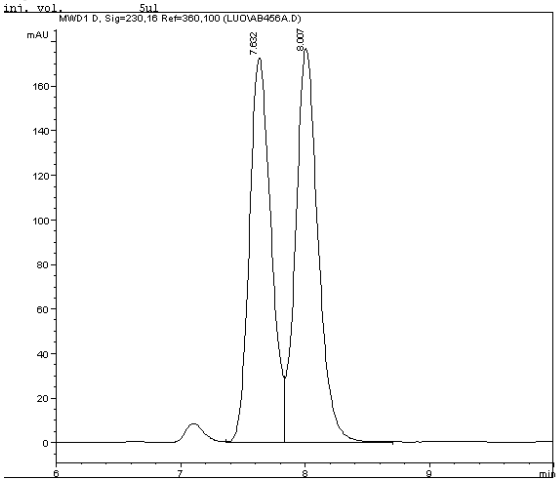


Meas.	R Area %	Width	Symmetr
8.783	11.502	0.403	0.840
9.642	88.498	0.384	0.510



2e

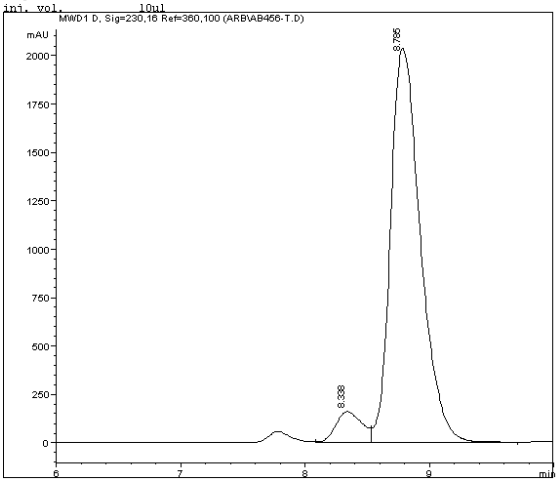
```
Data File name:                 C:\HPCHEM\1\DATA\LUO\AB456A.D
Method name:                    09802AB2.M
data acquired by:   Hon Wai Lam
on:                 03/05/2013
location:           Vial 4
Sample:             ARB-4-56-RACA
inj. vol.           5ul
```




```
Meas. R Area %   Width  Symmetr
-------------------------------
  7.632  48.477  0.184  0.793
  8.007  51.523  0.187  0.790
-------------------------------
```

*Using **L1**:*

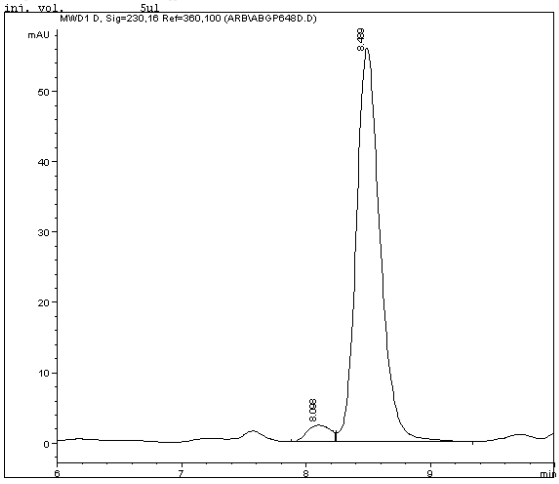
```
Data File name:                 C:\HPCHEM\1\DATA\ARB\AB456-T.D
Method name:                    0D9802AB.M
data acquired by:   Hon Wai Lam
on:                 01/05/2013
location:           Vial 11
Sample:             arb-4-56-rest
inj. vol.           10ul
```



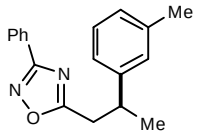

```
Meas. R Area %   Width  Symmetr
-------------------------------
  8.338   6.496  0.219  0.766
  8.785  93.504  0.255  0.648
-------------------------------
```

*Using **L9**:*

```
Data File name:                 C:\HPCHEM\1\DATA\ARB\ABGP648D.D
Method name:                    09802AB2.M
data acquired by:   Hon Wai Lam
on:                 02/05/2013
location:           Vial 1
Sample:             arb-gp648d
inj. vol.           5ul
```

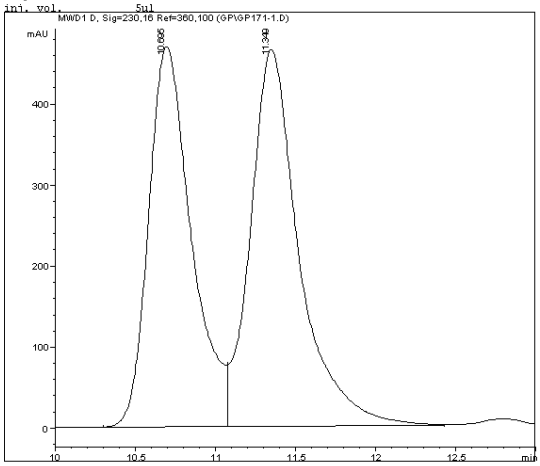



```
Meas. R Area %   Width  Symmetr
-------------------------------
  8.098   4.007  0.219  0.930
  8.489  95.993  0.221  0.775
-------------------------------
```



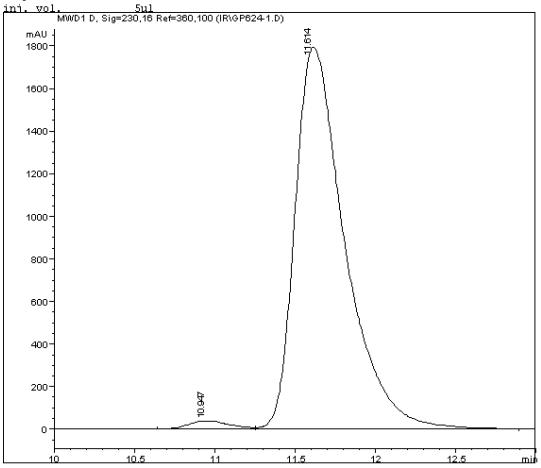
2f

Data File name: C:\HPCHEM\1\DATA\GP\GP171-1.D
Method name: ODH9802.M
data acquired by: Darryl
on: 21/07/2010
location: Vial 2
Sample: GP171
inj. vol. 5ul

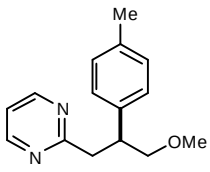


Meas. R Area %		Width	Symmetr
10.695	47.147	0.310	0.000
11.349	52.853	0.351	0.716

Data File name: C:\HPCHEM\1\DATA\IR\GP624-1.D
Method name: ODH9802.M
data acquired by: Hon Wai Lam
on: 06/07/2012
location: Vial 35
Sample: GP624
inj. vol. 5ul

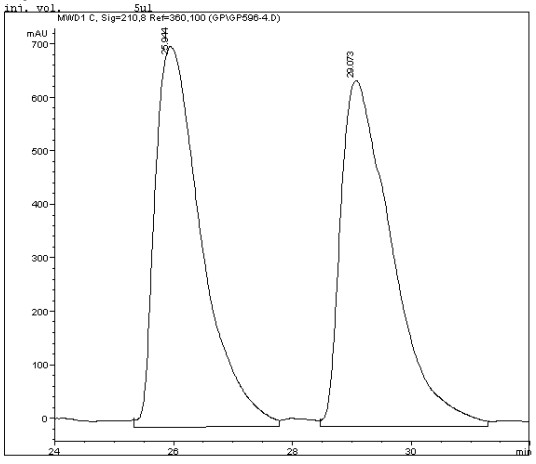


Meas. R Area %		Width	Symmetr
10.947	1.742	0.291	0.746
11.614	98.258	0.359	0.568



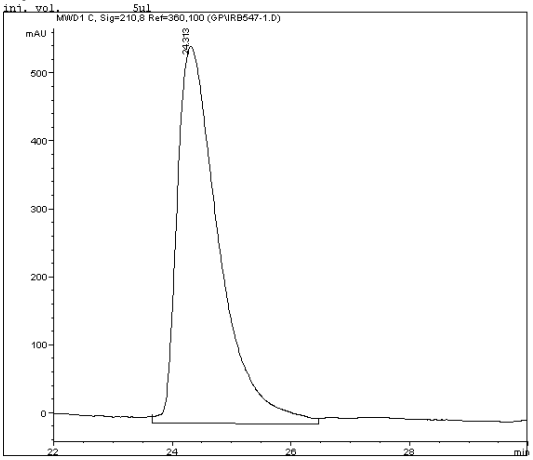
2g

Data File name: C:\HPCHEM\1\DATA\GP\GP596-4.D
Method name: ADH9802.M
data acquired by: Hon Wai Lam
on: 20/06/2012
location: Vial 92
Sample: GP596
inj. vol. 5ul

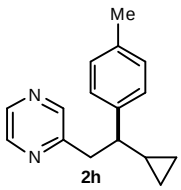


Meas. R Area %		Width	Symmetr
25.944	49.878	0.657	0.453
29.073	50.122	0.796	0.404

Data File name: C:\HPCHEM\1\DATA\GP\IRB547-1.D
Method name: ADH9802.M
data acquired by: Hon Wai Lam
on: 20/06/2012
location: Vial 91
Sample: IRB547P
inj. vol. 5ul

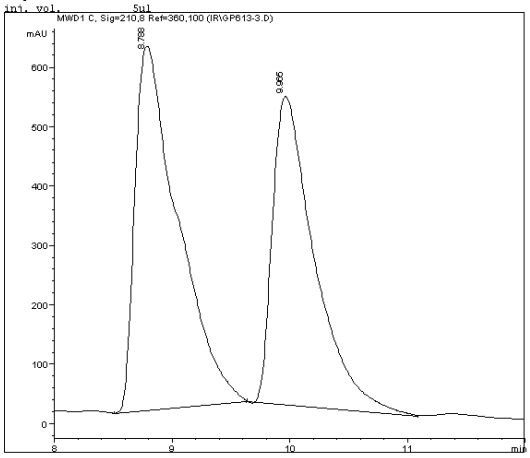


Meas. R Area %		Width	Symmetr
24.313	100.000	0.672	0.451



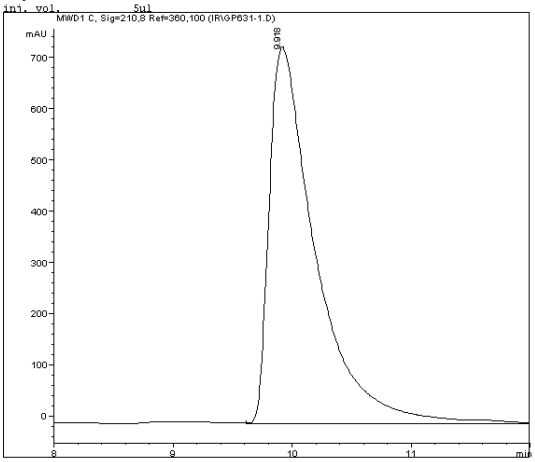
2h

```
Data File name:                 C:\HPCHEM\1\DATA\IR\GP613-3.D
Method name:                    ADH9802.M
data acquired by:   Hon Wai Lam
on:                 04/08/2012
location:           Vial 7
Sample:             GP613
inj. vol.           5ul
```

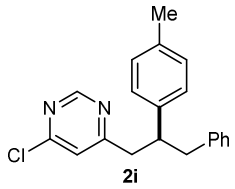


Meas. R	Area %	Width	Symmetr
8.788	54.720	0.424	0.378
9.965	45.280	0.414	0.436

```
Data File name:                 C:\HPCHEM\1\DATA\IR\GP631-1.D
Method name:                    ADH9802.M
data acquired by:   Hon Wai Lam
on:                 03/08/2012
location:           Vial 8
Sample:             GP631
inj. vol.           5ul
```

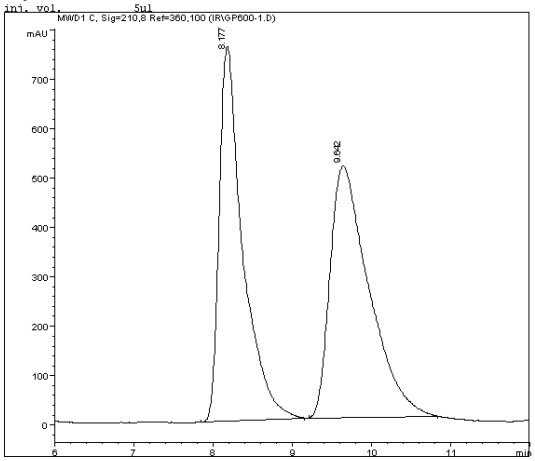


Meas. R	Area %	Width	Symmetr
9.918	100.000	0.451	0.376



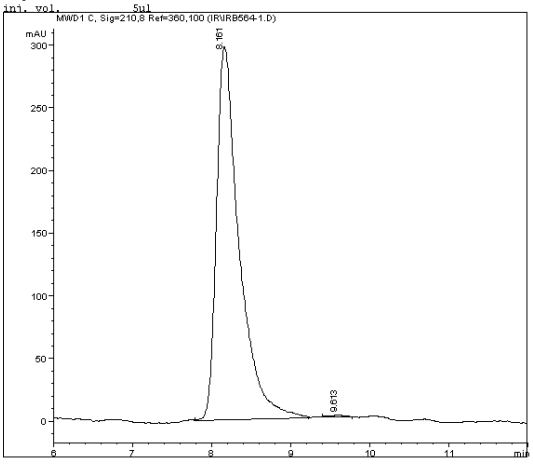
2i

```
Data File name:                 C:\HPCHEM\1\DATA\IR\GP600-1.D
Method name:                    ASH9802.M
data acquired by:   Hon Wai Lam
on:                 09/07/2012
location:           Vial 91
Sample:             GP600-1
inj. vol.           5ul
```

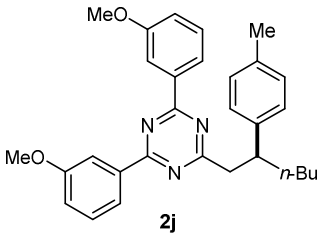


Meas. R	Area %	Width	Symmetr
8.177	47.498	0.345	0.497
9.642	52.502	0.569	0.497

```
Data File name:                 C:\HPCHEM\1\DATA\IR\IRB564-1.D
Method name:                    ASH9802.M
data acquired by:   Hon Wai Lam
on:                 09/07/2012
location:           Vial 92
Sample:             IRB564P
inj. vol.           5ul
```

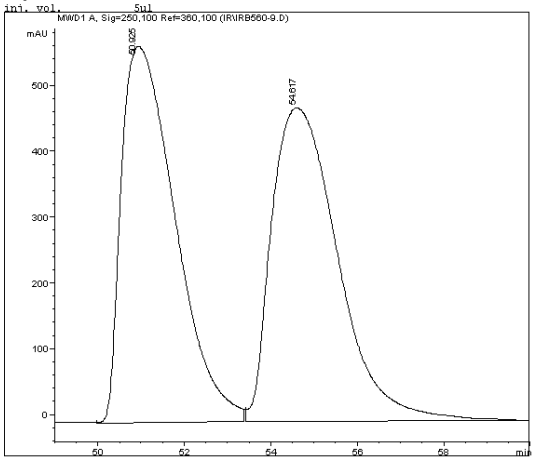


Meas. R	Area %	Width	Symmetr
8.161	99.691	0.331	0.519
9.613	0.309	0.191	1.436



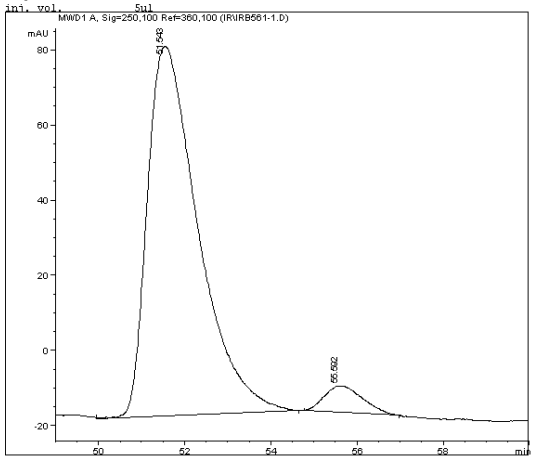
2j

```
Data File name:                 C:\HPCHEM\1\DATA\IR\IRB560-9.D
Method name:                    ADH100.M
data acquired by:   Hon Wai Lam
on:                 06/07/2012
location:           Vial 91
Sample:             IRB560CD
inj. vol.           5ul
```

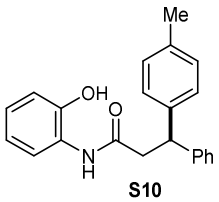



```
Meas. R Area %   Width  Symmetr
-------------------------------
 50.925  49.306  1.440   0.435
 54.617  50.694  1.779   0.613
-------------------------------
```

```
Data File name:                 C:\HPCHEM\1\DATA\IR\IRB561-1.D
Method name:                    ADH100.M
data acquired by:   Hon Wai Lam
on:                 09/07/2012
location:           Vial 92
Sample:             IRB561P
inj. vol.           5ul
```

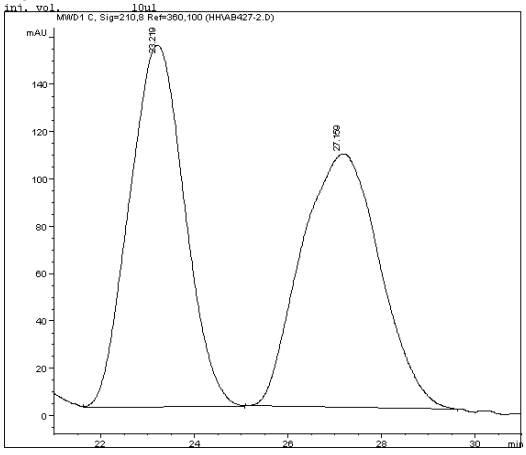



```
Meas. R Area %   Width  Symmetr
-------------------------------
 51.543  94.847  1.363   0.521
 55.592   5.153  1.042   0.627
-------------------------------
```



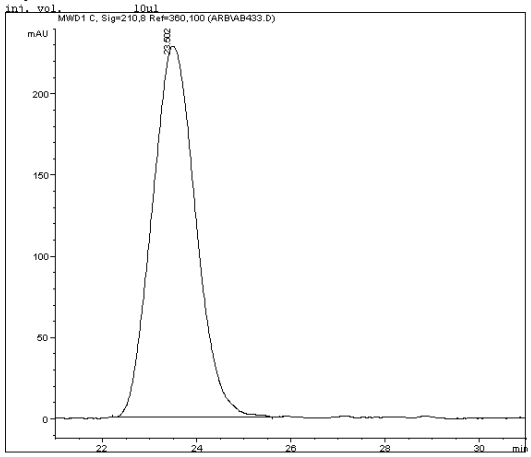
S10

```
Data File name:                 C:\HPCHEM\1\DATA\HH\AB427-2.D
Method name:                    AD9010AB.M
data acquired by:   Hon Wai Lam
on:                 18/02/2013
location:           Vial 51
Sample:             arb-4-27-rac2
inj. vol.           10ul
```

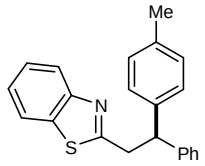



```
Meas. R Area %   Width  Symmetr
-------------------------------
 23.219  49.995  1.360   1.017
 27.159  50.005  1.943   1.038
-------------------------------
```

```
Data File name:                 C:\HPCHEM\1\DATA\ARB\AB433.D
Method name:                    AD9010AB.M
data acquired by:   Hon Wai Lam
on:                 20/02/2013
location:           Vial 6
Sample:             arb-4-33
inj. vol.           10ul
```

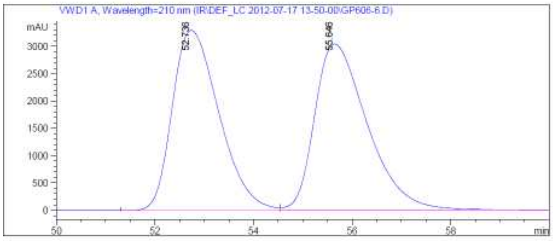



```
Meas. R Area %   Width  Symmetr
-------------------------------
 23.502 100.000  1.068   0.904
-------------------------------
```



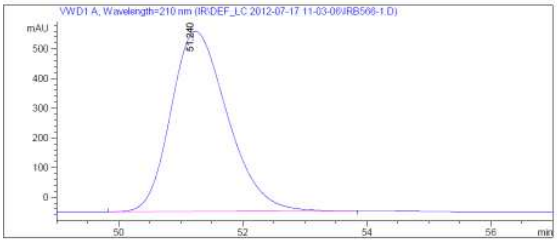
2l

data acquired by: Hamish
on: 7/17/2012
location: Vial 94

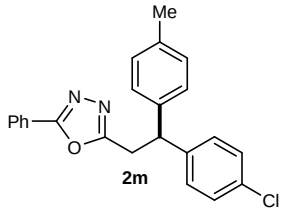


Meas. R	Area %	Width	Symmetr.
52.736	48.975	1.023	0.649
55.646	51.025	1.142	0.575

data acquired by: Hamish
on: 7/17/2012
location: Vial 95

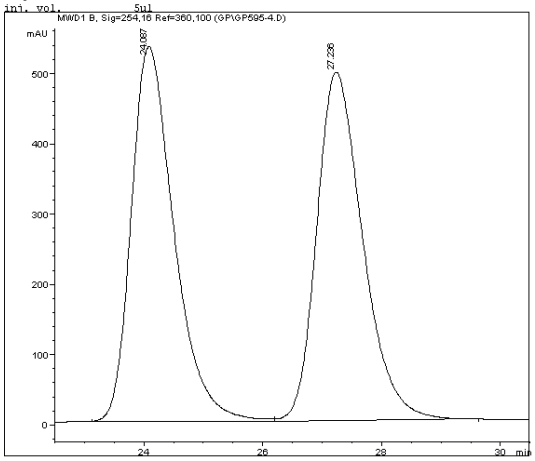


Meas. R	Area %	Width	Symmetr.
51.240	100.000	0.984	0.737



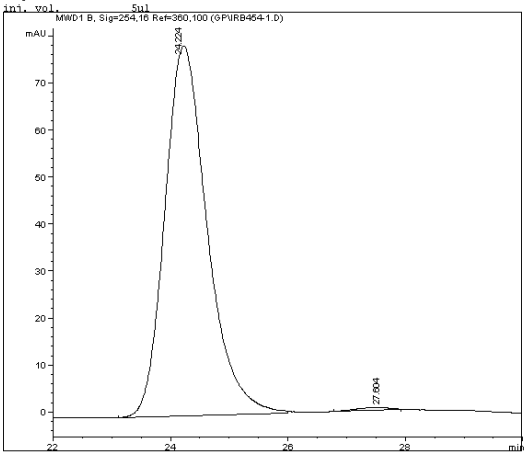
2m

Data File name: C:\HPCHEM\1\DATA\GP\GP595-4.D
Method name: ODH9010.M
data acquired by: Hon Wai Lam
on: 18/06/2012
location: Vial 33
Sample: GP595
inj. vol. 5ul

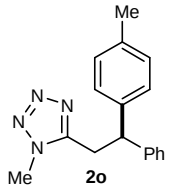


Meas. R	Area %	Width	Symmetr
24.087	49.917	0.830	0.679
27.236	50.083	0.896	0.711

Data File name: C:\HPCHEM\1\DATA\GP\IRB454-1.D
Method name: ODH9010.M
data acquired by: Hon Wai Lam
on: 18/06/2012
location: Vial 37
Sample: IRB545
inj. vol. 5ul

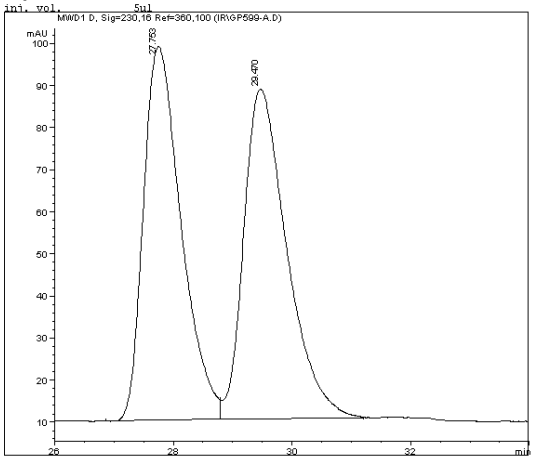


Meas. R	Area %	Width	Symmetr
24.224	99.463	0.754	0.758
27.604	0.537	0.692	3.479



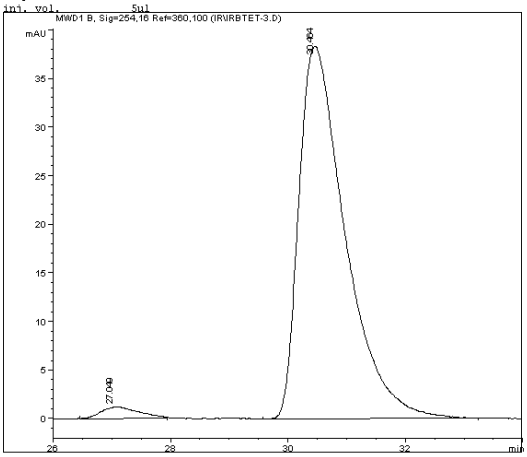
2o

```
Data File name:                 C:\HPCHEM\1\DATA\IR\GP599-A.D
Method name:                    ADH9208.M
data acquired by:   Hon Wai Lam
on:                 06/07/2012
location:           Vial 93
Sample:             GP599
inj. vol.           5ul
```

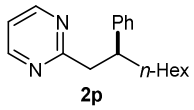


Meas. R	Area %	Width	Symmetr
27.753	49.845	0.734	0.650
29.470	50.155	0.840	0.615

```
Data File name:                 C:\HPCHEM\1\DATA\IR\IRBTET-3.D
Method name:                    ADH9208.M
data acquired by:   Hon Wai Lam
on:                 06/07/2012
location:           Vial 94
Sample:             IRBTET
inj. vol.           5ul
```

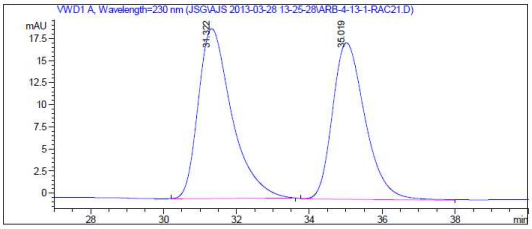


Meas. R	Area %	Width	Symmetr
27.049	2.428	0.725	0.579
30.464	97.572	0.912	0.521



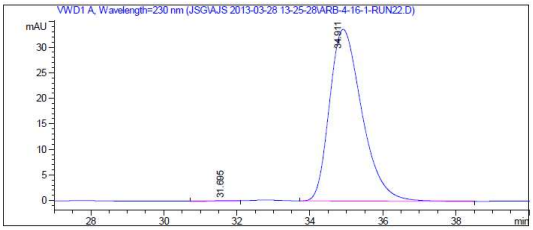
2p

```
data acquired by:   Jorge
on:                 3/28/2013
location:           Vial 95
```

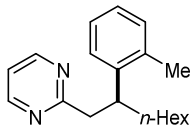


Meas. R	Area %	Width	Symmetr.
31.322	52.757	1.067	0.649
35.019	47.243	1.036	0.720

```
data acquired by:   Jorge
on:                 3/28/2013
location:           Vial 96
```

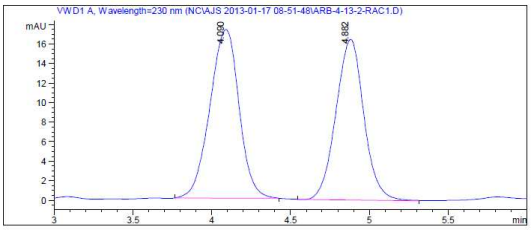


Meas. R	Area %	Width	Symmetr.
31.695	0.326	0.897	1.458
34.911	99.674	0.926	0.686



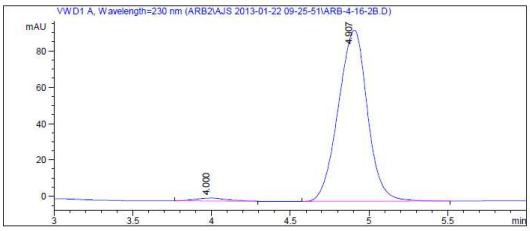
2q

data acquired by: Nawasit
on: 1/18/2013
location: Vial 3

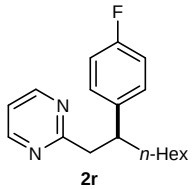


Meas. R	Area %	Width	Symmetr.
4.090	52.228	0.215	1.182
4.882	47.772	0.206	1.061

data acquired by: Alan
on: 1/22/2013
location: Vial 2

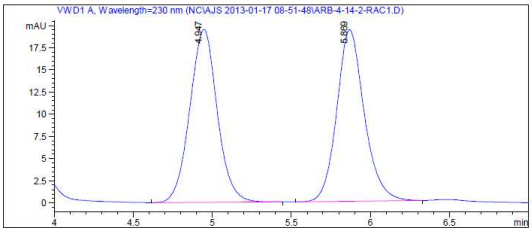


Meas. R	Area %	Width	Symmetr.
4.000	1.711	0.223	0.945
4.907	98.289	0.214	1.150



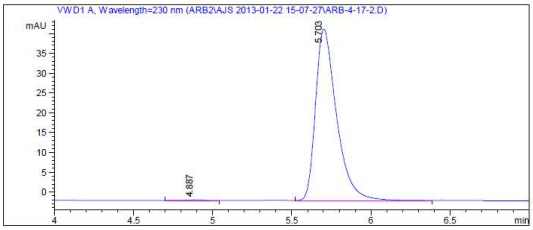
2r

data acquired by: Nawasit
on: 1/18/2013
location: Vial 18

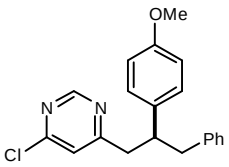


Meas. R	Area %	Width	Symmetr.
4.947	50.196	0.187	1.009
5.869	49.804	0.181	0.833

data acquired by: Alan
on: 1/22/2013
location: Vial 36



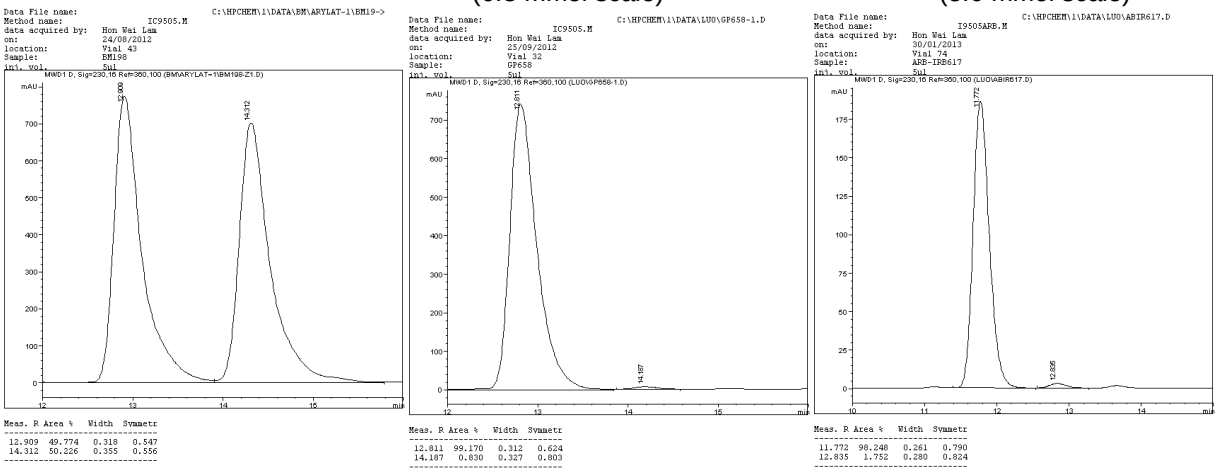
Meas. R	Area %	Width	Symmetr.
4.887	0.490	0.172	1.282
5.703	99.510	0.138	0.600

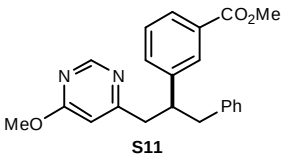


2s

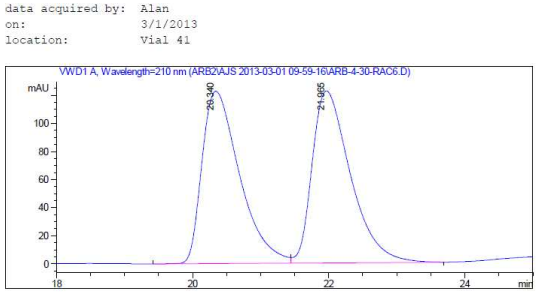
(0.3 mmol scale)

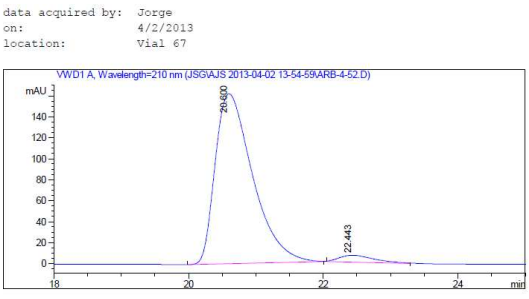
(5.0 mmol scale)

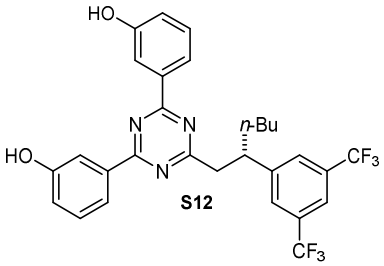




S11

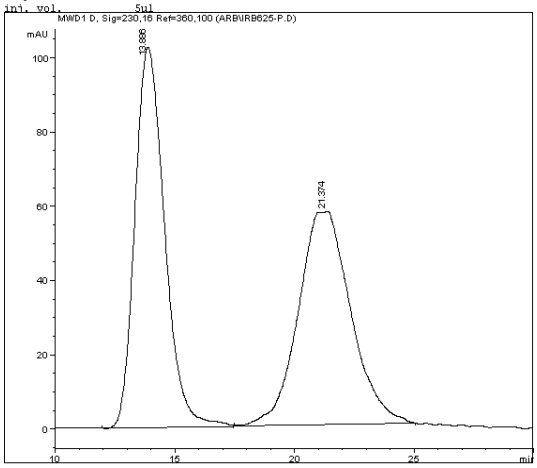






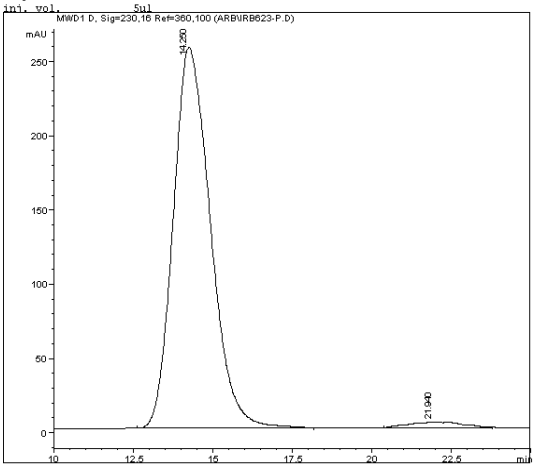
S12

Data File name: C:\HPCHEM\1\DATA\ARB\IRB625-P.D
Method name: ASH9505.M
data acquired by: Hon Wai Lam
on: 23/08/2012
location: Vial 71
Sample: IRB625P
inj. vol. 5ul

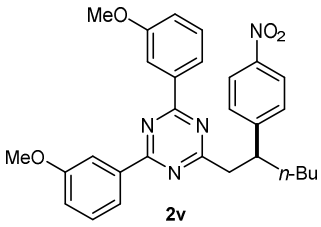


Meas. R	Area %	Width	Symmetr
13.886	50.341	1.436	0.761
21.374	49.659	2.531	1.166

Data File name: C:\HPCHEM\1\DATA\ARB\IRB623-P.D
Method name: ASH9505.M
data acquired by: Hon Wai Lam
on: 23/08/2012
location: Vial 72
Sample: IRB623P
inj. vol. 5ul

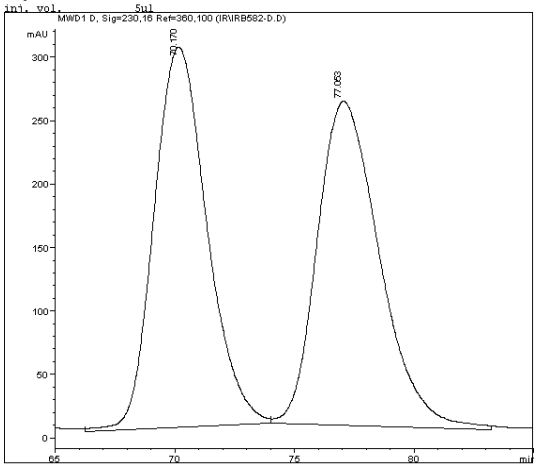


Meas. R	Area %	Width	Symmetr
14.250	98.069	1.353	0.717
21.940	1.931	1.957	0.840



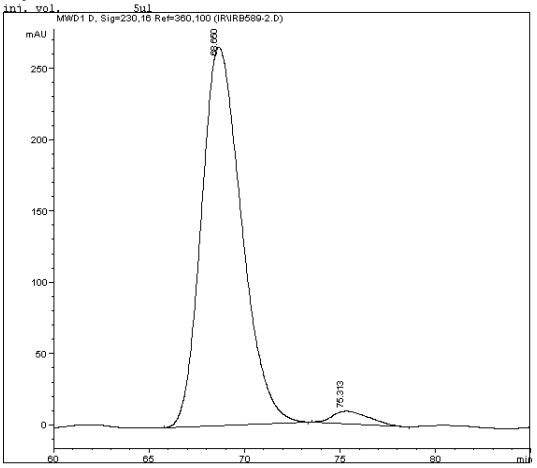
2v

Data File name: C:\HPCHEM\1\DATA\IR\IRB582-D.D
Method name: ASH9802.M
data acquired by: Hon Wai Lam
on: 06/08/2012
location: Vial 93
Sample: IRB582P
inj. vol. 5ul

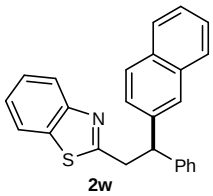


Meas. R	Area %	Width	Symmetr
70.170	49.863	2.554	0.855
77.053	50.137	3.013	0.707

Data File name: C:\HPCHEM\1\DATA\IR\IRB589-2.D
Method name: ASH9802.M
data acquired by: Hon Wai Lam
on: 06/08/2012
location: Vial 92
Sample: IRB589P
inj. vol. 5ul

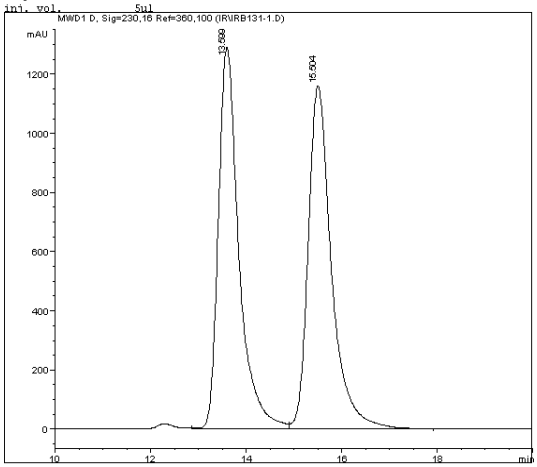


Meas. R	Area %	Width	Symmetr
68.650	97.073	2.122	0.733
75.313	2.927	1.579	0.608



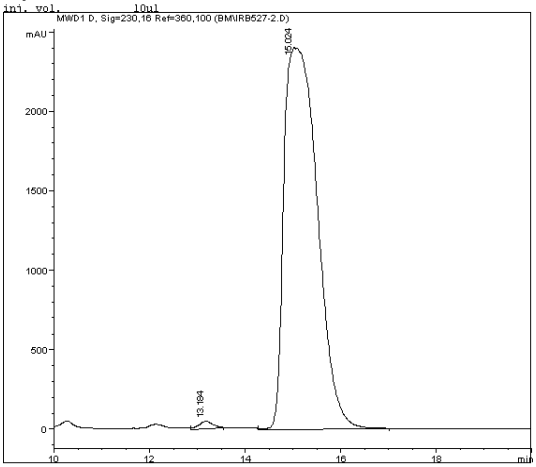
2w

Data File name: C:\HPCHEM\1\DATA\IR\IRB131-1.D
Method name: ODH9010.M
data acquired by: Jorge
on: 24/05/2011
location: Vial 1
Sample: IRB131P
inj. vol. 5ul

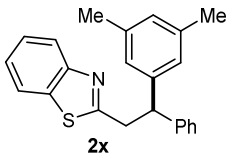


Meas. R	Area %	Width	Symmetr
13.599	49.561	0.448	0.652
15.504	50.439	0.506	0.666

Data File name: C:\HPCHEM\1\DATA\BM\IRB527-2.D
Method name: ODH9010.M
data acquired by: Hon Wai Lam
on: 29/05/2012
location: Vial 2
Sample: IRB527CD
inj. vol. 10ul

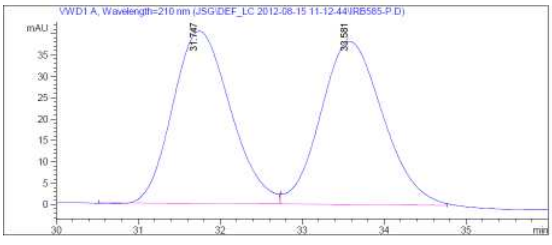


Meas. R	Area %	Width	Symmetr
13.184	0.876	0.370	1.054
15.024	99.124	0.809	0.434



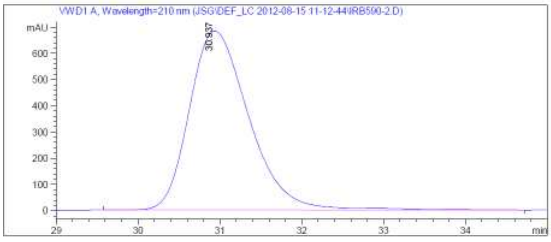
2x

data acquired by: Jorge
on: 8/15/2012
location: Vial 95

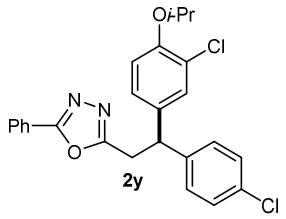


Meas. R	Area %	Width	Symmetr.
31.747	49.489	0.816	0.831
33.581	50.511	0.880	0.856

data acquired by: Jorge
on: 8/15/2012
location: Vial 96

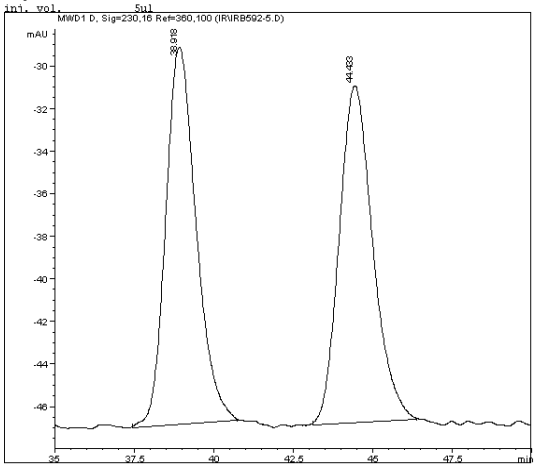


Meas. R	Area %	Width	Symmetr.
30.937	100.000	0.772	0.688



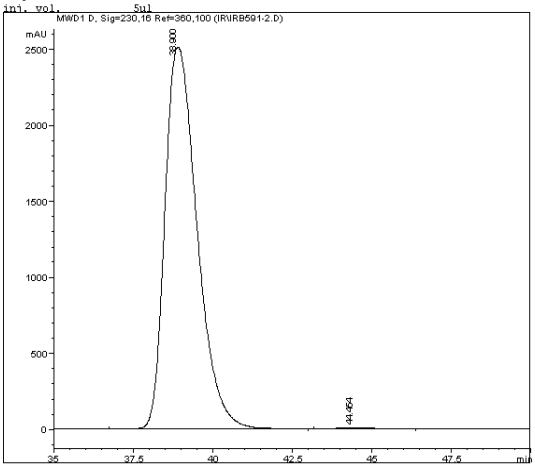
2y

```
Data File name:                 C:\HPCHEM\1\DATA\IR\IRB592-5.D
Method name:                    ADH9010Q.M
data acquired by:   Hon Wai Lam
on:                 30/07/2012
location:           Vial 82
Sample:             IRB592P
inj. vol.           5ul
```




```
Meas. R Area %   Width  Symmetr
---------------------------------
 38.918  50.397   0.965   0.791
 44.433  49.603   1.063   0.823
---------------------------------
```

```
Data File name:                 C:\HPCHEM\1\DATA\IR\IRB591-2.D
Method name:                    ADH9010Q.M
data acquired by:   Hon Wai Lam
on:                 30/07/2012
location:           Vial 41
Sample:             IRB591P
inj. vol.           5ul
```




```
Meas. R Area %   Width  Symmetr
---------------------------------
 38.900  99.672   1.089   0.633
 44.454   0.328   0.905   0.816
---------------------------------
```