Supporting Information for

A Mismatch-Free Strategy for the Diastereoselective α,α-Bisalkylation of Chiral Nonracemic Methyl Ketones

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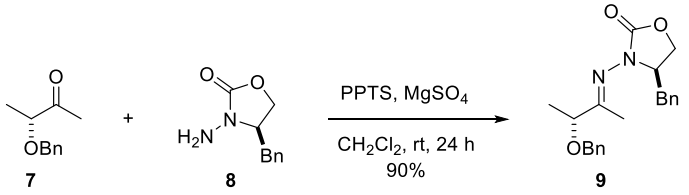
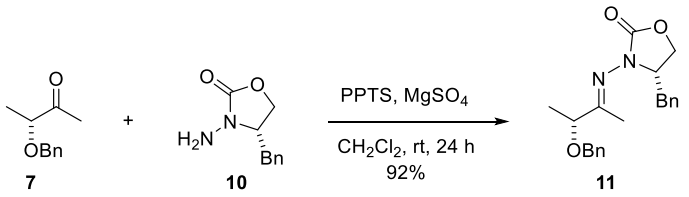
I. Experimental

General consideration: Unless stated to the contrary, where applicable, the following conditions apply: Reactions were carried out using dried solvents (see below) and under a slight static pressure of Argon (pre-purified quality) that had been passed through a column (5 x 20 cm) of Drierite. Glassware was dried in an oven at 120 °C for at least 12 h prior to use and then either cooled in a desiccator cabinet over Drierite or assembled quickly while hot, sealed with rubber septa, and allowed to cool under a stream of Ar. Reactions were stirred magnetically using Teflon-coated magnetic stirring bars. Teflon-coated magnetic stirring bars and syringe needles were dried in an oven at 120 °C for at least 12 h prior to use then cooled in a desiccator cabinet over Drierite. Hamilton micro-syringes were dried in an oven at 60 °C for at least 24 h prior to use and cooled in the same manner. Commercially available Norm-Ject disposable syringes were used. Dry CH_2Cl_2, THF were obtained using an Innovative Technologies solvent purification system. All other dry solvents were purchased from Aldrich and of anhydrous quality. Commercial grade solvents were used for routine purposes without further purification. *i*-Pr_2NH was distilled from CaH_2 under a N_2 atmosphere prior to use. Flash column chromatography was performed on silica gel 60 (230–400 mesh). ^1H and ^{13}C NMR spectra were recorded on a JEOL ECA-600II, ECA-500 or ECX-400P spectrometer at ambient temperature. All ^1H and ^{13}C chemical shifts are reported in ppm (δ) using residual solvent peak as an internal reference ($CDCl_3$: 7.25 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR). The diastereomeric ratios for the α,α-bisalkylated hydrazones and the hydrolyzed ketones were computed from the ^1H NMR spectrum of the crude material. HRMS analyses were performed using UT Austin's mass spectrometric facility on Micromass Autospec Ultima instrument via positive mode CI method.

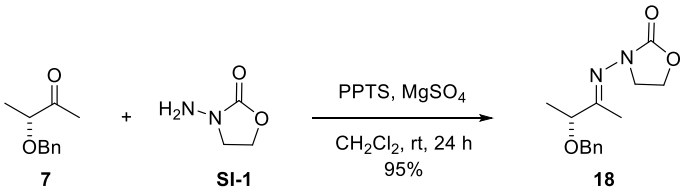


General procedure for hydrazone formation: To a stirred solution of ketone **7**[1] (0.965 g, 5.414 mmol) in 10 mL of CH_2Cl_2 were added *N*-Amino Cyclic Carbamate auxiliary **8**[2] (1.145 g, 5.956 mmol), pyridinium *p*-toluenesulfonate (0.068 g, 0.271 mmol) and anhydrous $MgSO_4$ (3.285 g, 27.0 mmol). The reaction mixture was stirred 24 h at room temperature. Then the solution was

filtered through a pad of celite, partitioned between Et_2O (30 mL) and aqueous saturated $NaHCO_3$ solution (10 mL). The aqueous phase was extracted with Et_2O (3 x 20 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided hydrazone **9** as a colorless liquid (1.717 g, 90%). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.37-7.24 (m, 8 H), 7.15-7.13 (m, 2 H), 4.61, 4.41(ABq, 2 H, *J* = 11.5 Hz), 4.39-4.34 (m, 1 H), 4.32-4.29 (m, 1 H), 4.18 (q, 1 H, *J* = 6.3Hz), 4.10-4.06 (m, 1 H), 3.12 (dd, 1 H, *J* = 4.3, 13.5 Hz), 2.77 (dd, 1 H, *J* = 8.6, 13.8 Hz), 2.03 (s, 3 H), 1.38 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 177.1, 154.4, 138.0, 135.6, 129.3, 128.9, 128.5, 128.1, 127.8, 127.2, 78.2, 71.0, 66.8, 60.9, 38.5, 19.3, 14.4. **HRMS**(**ESI**): *m/z* calculated for $C_{21}H_{24}N_2O_3$ $[M+Na]^+$: 375.1679, found: 375.1680.

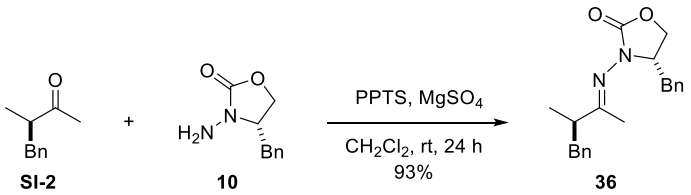


Hydrazone 11: The title compound was prepared from ketone **7**[1] (0.850 g, 4.769 mmol) and auxiliary **10**[2] following general procedure for hydrazone formation. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided hydrazone **11** as a colorless solid (1.546 g, 92%). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.37-7.24 (m, 8 H), 7.18-7.16 (m, 2 H) 4.47, 4.41 (ABq, 2 H, *J* = 11.5 Hz), 4.40-4.36 (m, 1 H), 4.30-4.26 (m, 1 H), 4.21 (q, 1 H, *J* = 6.9 Hz), 4.08-4.04 (m, 1 H), 3.15 (dd, 1 H, *J* = 4.0, 13.8 Hz), 2.77 (dd, 1 H, *J* = 9.2, 13.8 Hz), 2.05 (s, 3 H), 1.42 (d, 3 H, *J*= 6.5 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 176.9, 154.1, 137.9, 135.4, 129.2, 129.0, 128.6, 127.9, 127.3, 78.4, 71.1, 66.8, 60.8, 38.6, 19.5, 14.2. **HRMS**(**ESI**): *m/z* calculated for $C_{21}H_{24}N_2O_3$ $[M+Na]^+$: 375.1679, found: 375.1680.

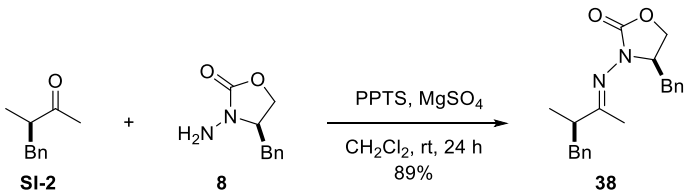


Hydrazone 18: Hydrazone **18** was prepared from ketone **7**[1] (0.168 g, 0.943 mmol) and auxiliary **SI-1**[2] following general procedure for hydrazone formation. Flash chromatography over silica gel (30:70, EtOAc-hexanes) provided hydrazone **18** as a colorless liquid (0.235 g, 95%). **^{1}H NMR**

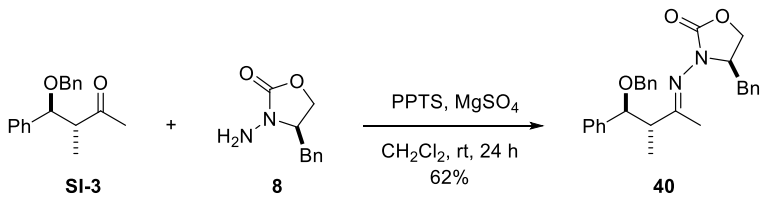
($CDCl_3$, 400 MHz): δ 7.36-7.27 (m, 5 H), 4.52 (A of AB_q, 1 H, J_{AB} = 11.5 Hz), 4.44-4.40 (m, 3 H, including B of AB_q), 4.17 (q, 1 H, *J* = 6.9 Hz), 3.90-3.80 (m, 2 H), 2.03 (s, 3 H), 1.39 (d, 3 H, *J* = 6.4 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 176.2, 155.1, 138.0, 128.5, 128.0, 127.8, 78.3, 71.1, 62.0, 49.0, 19.4, 14.0. **HRMS**(**ESI**): *m/z* calculated for $C_{14}H_{18}N_2O_3$ $[M+Na]^+$: 285.1210, found: 285.1215.



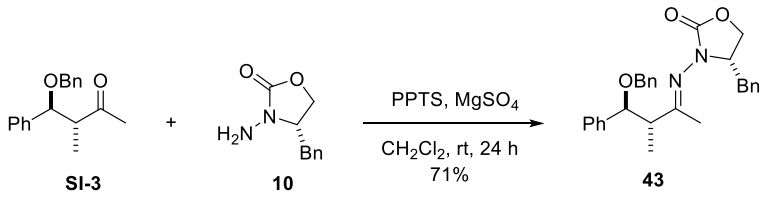
Hydrazone 36: Hydrazone **36** was prepared from ketone **SI-2**[3] (0.187 g, 1.153 mmol) and auxiliary **10** following general procedure for hydrazone formation. Flash chromatography over silica gel (15:85, EtOAc-hexanes) provided hydrazone **36** as a colorless liquid (0.361 g, 93%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.32-7.15 (m, 8 H), 7.09-7.06 (m, 2 H), 4.32-4.22 (m, 2 H), 4.04-3.98 (m, 1 H), 3.04-2.94 (m, 2 H), 2.86-2.77 (m, 1 H), 2.69-2.62 (m, 2 H), 1.98 (s, 3 H), 1.16 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 179.3, 154.5, 140.2, 135.7, 129.3, 129.2, 128.8, 128.4, 127.1, 126.2, 66.6, 60.8, 44.4, 40.2, 38.3, 18.3, 18.1. **HRMS**(**ESI**): *m/z* calculated for $C_{21}H_{24}N_2O_2$ $[M+H]^+$: 337.19110, found: 337.19090.



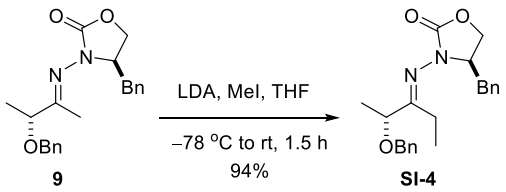
Hydrazone 38: This hydrazone was prepared from ketone **SI-2** (0.160 g, 0.986 mmol) and auxiliary **8** following general procedure for hydrazone formation. Flash chromatography over silica gel (15:85, EtOAc-hexanes) provided hydrazone **38** as a colorless liquid (0.295 g, 89%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.31-7.18 (m, 7 H), 7.15-7.10 (m, 1 H), 7.05-6.95 (m, 2H), 4.25-4.17 (m, 2H), 4.00-3.94 (m, 1 H), 2.95-2.86 (m, 2 H), 2.83-2.76 (m, 1 H), 2.67 (dd, 1 H, *J* = 3.4, 14 Hz), 2.46 (dd, 1 H, *J* = 8.2, 14.2 Hz), 1.96 (s, 3 H), 1.19 (d, 3 H, *J* = 6.4); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 179.4, 154.5, 139.8, 135.6, 129.3, 129.1, 128.8, 128.5, 127.1, 126.4, 66.8, 60.9, 44.5, 40.7, 38.2, 18.2, 16.5. **HRMS**(**ESI**): *m/z* calculated for $C_{21}H_{24}N_2O_2$ $[M+H]^+$: 337.19110, found: 337.19090.



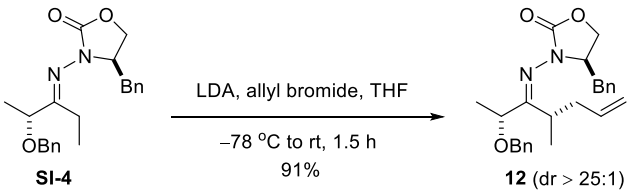
Hydrazone 40: The title hydrazone was prepared from ketone **SI-3**[4] (0.155 g, 0.578 mmol) and auxiliary **8** following general procedure for hydrazone formation. Flash chromatography over silica gel (15:85, EtOAc-hexanes) provided hydrazone **40** as a colorless solid (0.158 g, 62%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.45-7.14 (m, 13 H), 7.11-7.09 (m, 2 H), 4.39, 4.37 (ABq, 2 H, *J* = 11.5 Hz), 4.34-4.17 (m, 3 H), 4.04-3.99 (m, 1 H), 3.07-2.94 (m, 2 H), 2.59 (dd, 1 H, *J* = 9.2, 13.7 Hz), 2.02 (s, 3 H), 0.94 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 179.3, 154.5, 139.9, 138.2, 135.7, 129.3, 128.8, 128.6, 128.3, 128.0, 127.9, 127.6, 127.1, 83.9, 70.7, 66.8, 60.9, 49.8, 38.5, 16.7, 15.5. **HRMS(ESI)**: *m/z* calculated for $C_{28}H_{30}N_2O_3$ $[M+Na]^+$: 465.21490, found: 465.21560.



Hydrazone 43: The title hydrazone was prepared from ketone **SI-3** (0.129 g, 0.481 mmol) and auxiliary **8** following general procedure for hydrazone formation. Flash chromatography over silica gel (15:85, EtOAc-hexanes) provided hydrazone **43** as a colorless solid (0.151 g, 71%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.41-7.19 (m, 13 H), 7.05-7.02 (m, 2 H), 4.44, 4.41 (ABq, 2 H, *J* = 10.6 Hz), 4.40-4.33 (m, 1 H), 4.28-4.23 (m, 1 H), 4.20-4.17 (m, 1 H), 4.06-4.02 (m, 1 H), 3.08 (dd, 1 H, *J* = 3.7, 13.7 Hz), 3.00-2.93 (m, 1 H), 2.69 (dd, 1 H, *J* = 9.0, 13.8 Hz), 1.99 (s, 3 H), 0.87 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 179.0, 154.5, 139.9, 138.0, 135.6, 129.4, 128.8, 128.6, 128.4, 128.3, 128.0, 127.9, 127.6, 127.1, 83.5, 70.4, 66.5, 60.7, 49.5, 38.2, 18.0, 15.9. **HRMS(ESI)**: **HRMS(ESI)**: *m/z* calculated for $C_{28}H_{30}N_2O_3$ $[M+Na]^+$: 465.21490, found: 465.21560.

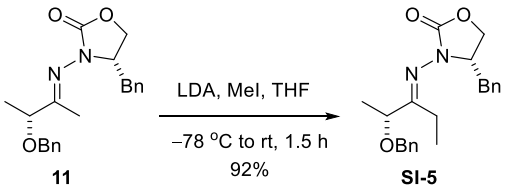


General procedure for hydrazone alkylation: *n*-BuLi (2.5 M in hexanes, 0.354 mL, 0.885 mmol) was added drop wise (ca. 2 min) to a stirred and cold (ice-H_2O bath) solution of *i*-Pr_2NH (0.132 mL, 0.944 mmol) in THF (2 mL) under Argon atmosphere. The mixture was stirred for 30 min, and then cooled to –78 °C. A solution of hydrazone **9** (0.104 g, 0.295 mmol) in THF (1.0 mL) was added to the above made LDA solution by cannula, with additional THF (2 x 0.5 mL) as a rinse, and the mixture was stirred at –78 °C for 1 h. Then MeI (0.073 mL, 1.180 mmol) was added drop wise at –78 °C and stirred another 5 min at this temperature. Then the solution was removed from the cold bath and allowed to warm to room temperature over 1.5 h. The mixture was then partitioned between Et_2O (20 mL) and H_2O (10 mL). The aqueous phase was extracted with Et_2O (3 x 15 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a yellow oil. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided **SI-4** (0.102 g, 94%) as a colorless viscous oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.39-7.23 (m, 8 H), 7.18-7.14 (m, 2 H), 4.64, 4.43 (AB_q, 2 H, J_{AB} = 11.7 Hz), 4.40-4.33 (m, 1 H), 4.31-4.27 (m, 1 H), 4.23 (q, 1 H, *J*= 6.8 Hz), 4.09-4.05 (m, 1 H), 3.14 (dd, 1 H, *J* = 4.4, 13.5 Hz), 2.73 (dd, 1 H, *J* = 9.4, 13.5 Hz), 2.66-2.56 (m, 1 H), 2.51-2.42 (m, 1 H), 1.42 (d, 3 H, *J*= 6.9 Hz), 1.19 (t, 3 H, *J*= 7.8 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 181.2, 154.8, 138.1, 135.6, 129.1, 129.0, 128.5, 128.0, 127.3, 127.3, 77.6, 71.0, 67.2, 61.2, 38.9, 22.3, 19.4, 11.0. **HRMS**(**ESI**): *m/z* calculated for $C_{22}H_{26}N_2O_3$ $[M+Na]^+$: 389.1836, found: 389.1841.

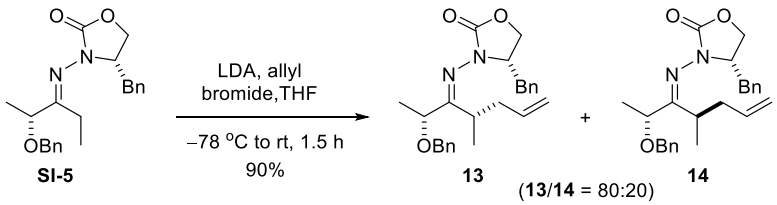


***α,α*-Bisalkylated hydrazone 12**: Allylation of hydrazone **SI-4** (0.091 g, 0.248 mmol) following the general procedure for hydrazone alkylation provided the title compound **12** as a yellow liquid. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided **12** as a single diastereomer

(0.092 g, 91%, dr = >25:1) and colorless oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.38-7.23 (m, 8 H), 7.17-7.15 (m, 2 H), 5.78-5.67 (m, 1 H), 5.08-5.02 (m, 2 H), 4.63, 4.50 (AB_q, 2 H, J_{AB} = 11.7 Hz), 4.46-4.41 (m, 1 H), 4.39 (q, 1 H, *J* = 6.4 Hz), 4.26-4.22 (m, 1 H), 4.04 (dd, 1 H, *J* = 8.6, 10.0 Hz), 3.24-3.15 (m, 2 H), 2.64 (dd, 1 H, *J* = 10.5, 13.3 Hz), 2.33-2.26 (m, 1 H), 2.17-2.07 (m, 1 H), 1.52 (d, 3 H, *J* = 6.4 Hz), 1.20 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 182.0, 155.0, 138.2, 136.1, 135.7, 129.0, 128.99, 128.5, 127.8, 127.3, 117.1, 73.6, 70.9, 67.4, 61.5, 39.6, 38.8, 30.1, 21.2, 16.7. **HRMS**(**ESI**): *m/z* calculated for $C_{25}H_{30}N_2O_3$ $[M+Na]^+$: 429.2149, found: 429.2154.

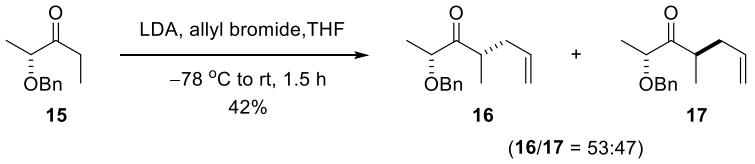


SI-5: Methylation of hydrazone **11** (0.115 g, 0.326 mmol) following the general procedure for hydrazone alkylation gave **SI-5** as a yellow liquid. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided **SI-5** (0.110 g, 92%) as a colorless oil. ($CDCl_3$, 400 MHz): δ 7.39-7.24 (m, 8 H), 7.20-7.16 (m, 2 H), 4.56, 4.46 (AB_q, 2 H, J_{AB} = 11.7 Hz), 4.46-4.41 (m, 1 H), 4.39-4.24 (m, 3 H), 4.09-4.05 (m, 1 H), 3.19 (dd, 1 H, *J* = 4.4, 13.5 Hz), 2.75 (dd, 1 H, *J* = 9.2, 13.7 Hz), 2.61-2.46 (m, 2 H), 1.44 (d, 3 H, *J* = 6.9 Hz), 1.19 (t, 3 H, *J* = 7.8 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 181.2, 154.5, 138.1, 135.6, 129.1, 128.97, 128.5, 127.9, 127.8, 127.3, 77.7, 71.0, 67.0, 61.0, 38.6, 22.6, 19.5, 10.7. **HRMS**(**ESI**): *m/z* calculated for $C_{22}H_{26}N_2O_3$ $[M+Na]^+$: 389.1836, found: 389.1841.

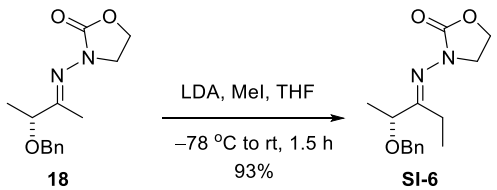


α,α-Bisalkylated hydrazones 13 and 14: Allylation of **SI-5** (0.085 g, 0.232 mmol) following the general procedure for hydrazone alkylation provided mixture of compounds **13** and **14** as a yellow liquid. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided 80:20 diastereomeric mixture of **13** and **14** as a colorless oil (0.085 g, 90%, dr = 80:20). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.37-7.23 [m, 8 H (both diastereomers)], 7.18-7.15 [m, 2.46 H (both)], 5.77-5.61[m, 1.18 H (both)], 5.06-5.02 [m, 2.53 H (both)], 4.63 [A of AB_q, 1.25 H, *J* = 12.0 Hz (both)], 4.54-

4.36 [m, 3.76 H, including the B of AB_q (both)], 4.30-4.24 [m, 1.25 H (both)], 4.09-4.02 [m, 1.27 H (both)], 3.23-3.07 [m, 2.52 H (both)], 2.76-2.62 [m, 2.33 H (both)], 2.21-1.99 [m, 1.55 H (both)], 1.58-1.50 [m, 3.76 H (both)], 1.28 [d, 0.76 H, J = 6.9 Hz (minor)], 1.04 [d, 3 H, J = 7.4 Hz (major)]. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 182.8, 182.0, 155.1, 154.9, 138.3, 138.2, 136.4, 135.9, 135.7, 129.2, 129.0, 128.9, 128.4, 128.0, 127.7, 127.3, 127.2, 117.1, 117.0, 73.0, 72.4, 70.6, 70.2, 67.4, 66.9, 61.4, 61.1, 39.5, 38.7, 37.4, 36.4, 35.7, 20.8, 20.3, 16.7, 16.6. **HRMS**(**ESI**): *m/z* calculated for $C_{25}H_{30}N_2O_3$ $[M+Na]^+$: 429.2149, found: 429.2154.

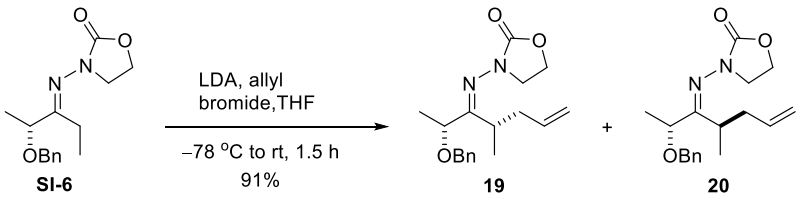


Procedure for the allylation of ketone 15: *n*-BuLi (2.5 M in hexanes, 0.243 mL, 0.606 mmol) was added drop wise (ca. 2 min) to a stirred and cold (ice-H_2O bath) solution of *i*-Pr_2NH (0.093 mL, 0.661 mmol) in THF (2.5 mL) under Argon atmosphere. The mixture was stirred for 30 min, and then cooled to –78 °C. A solution of ketone **15** (0.106 g, 0.551 mmol) in THF (1.5 mL) was added to the above made LDA solution by cannula, with additional THF (2 x 0.5 mL) as a rinse, and the mixture was stirred at –78 °C for 1 h. Then allylbromide (0.095 mL, 1.102 mmol) was added drop wise at –78 °C and stirred another 5 min at this temperature. Then the solution was removed from the cold bath and allowed to warm to room temperature over 1.5 h. The mixture was then partitioned between Et_2O (25 mL) and H_2O (10 mL). The aqueous phase was extracted with Et_2O (3 x 20 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a yellow liquid. ^{1}HNMR of the crude material showed a 53:47 diastereomeric mixture of **16** and **17** as a yellow liquid. Flash chromatography over silica gel (2:98, EtOAc-hexanes) provided a mixture of **16** and **17** (0.054 g, 42%) as a colorless liquid.

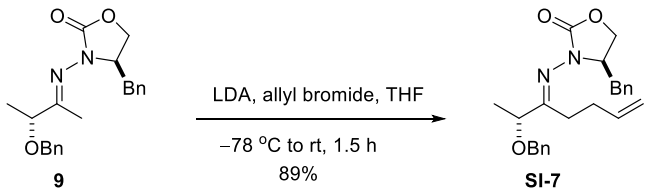


SI-6: Methylation of hydrazone **18** (0.130 g, 0.496 mmol) following the general procedure for hydrazone alkylation gave **SI-6** as a yellow liquid. Flash chromatography over silica gel (30:70,

EtOAc-hexanes) provided **SI-6** (0.127 g, 93%) as a colorless oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.38-7.24 (m, 5 H), 4.59 (A of AB_q, 1 H, J_{AB} = 11.9 Hz), 4.48-4.44 (m, 3 H, including B of AB_q), 4.23 (q, 1 H, *J* = 6.9 Hz), 3.88-3.78 (m, 2 H), 2.57-2.43 (m, 2 H), 1.43 (d, 3 H, *J* = 6.9 Hz), 1.15 (t, 3 H, *J* = 7.8 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 180.9, 155.5, 138.1, 128.5, 128.0, 127.8, 77.8, 71.1, 62.0, 49.0, 22.1, 19.3, 10.9. **HRMS**(**ESI**): *m/z* calculated for $C_{15}H_{20}N_2O_3$ $[M+H]^+$: 277.1547, found: 277.1547.

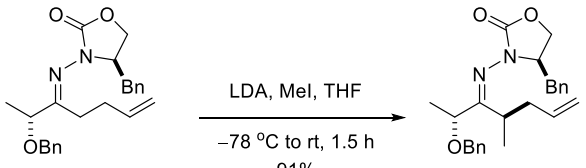


α,α-Bisalkylated hydrazones 19 and 20: Allylation of **SI-6** (0.070 g, 0.253 mmol) following the general procedure for hydrazone alkylation provided compounds **19** and **20** as a yellow liquid. Flash chromatography over silica gel (30:70, EtOAc-hexanes) provided 88:12 diastereomeric mixture of **19** and **20** as a colorless oil (0.073 g, 91%, dr = 88:12). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.37-7.27 [m, 5.82 H (both diastereomers)], 5.89-5.60 [m, 1.14 H (both)], 5.04-4.99 [m, 2.45 H (both)], 4.61-4.48 [m, 2.31 H (both)], 4.46-4.38 [m, 2.44 H (both)], 4.36-4.30 [m, 1.12 H (both)], 3.93-3.86 [m, 1.12 H (both)], 3.80-3.72 [m, 1.12 H (both)], 3.17-3.08 [m, 1.08 H (both)], 2.42-2.35 [m, 1.16 H (both)], 2.13-2.04 [m, 1.12 H (both)], 1.48-1.43 [m, 3.40 H (both)], 1.19 [d, 0.40 H, *J* = 7.3 Hz (minor)], 1.12 [d, 3.0 H, *J* = 7.3 Hz (major)]; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 182.5, 182.4, 155.7, 138.2, 136.2, 136.1, 128.4, 128.0, 127.7, 127.7, 127.6, 127.4, 116.8, 73.8, 73.6, 70.8, 70.6, 61.9, 49.3, 38.2, 38.1, 35.9, 35.8, 20.3, 20.0, 16.9, 16.8. **HRMS**(**ESI**): *m/z* calculated for $C_{18}H_{24}N_2O_3$ $[M+H]^+$: 317.1860, found: 317.1852.



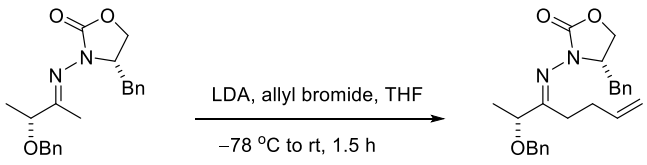
SI-7: Allylation of hydrazone **9** (0.115 g, 0.326 mmol) following the general procedure for hydrazone alkylation provided **SI-7** as a yellow liquid. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided **SI-7** as a colorless oil (0.114 g, 89%). **^{1}H NMR** ($CDCl_3$, 400

MHz): δ 7.38-7.24 (m, 8 H), 7.17-7.15 (m, 2 H), 5.85-5.75 (m, 1 H), 5.08-4.99 (m, 2 H), 4.65, 4.44 (AB_q, 2 H, J_{AB} = 11.7 Hz), 4.41-4.33 (m, 1 H), 4. 30-4.22 (m, 2 H), 4.10-4.06 (m, 1 H), 3.16 (dd, 1 H, *J* = 4.4, 13.5 Hz), 2.75-2.66 (m, 2 H), 2.55-2.29 (m, 3 H), 1.42 (d, 3 H, *J* = 6.4 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 179.1, 154.7, 138.1, 137.4, 135.6, 129.1, 129.0, 128.5, 128.0, 127.8, 127.3, 115.5, 77.5, 71.1, 67.2, 61.4, 38.9, 30.0, 28.9, 19.4. **HRMS(ESI)**: *m/z* calculated for $C_{24}H_{28}N_2O_3$ $[M+Na]^+$: 415.1992, found: 415.1990.



SI-7 **21** (dr > 25:1)

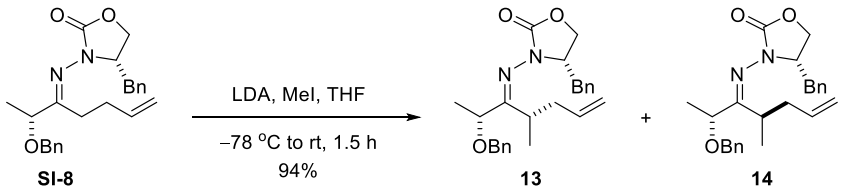
α,α-Bisalkylated Hydrazone 21: Methylation of **SI-7** (0.096 g, 0.245 mmol) following the general procedure for hydrazone alkylation gave compound **21** as a yellow liquid. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided **21** (0.091 g, 91%, dr >25:1) as a colorless oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.38-7.23 (m, 8 H), 7.17-7.15 (m, 2 H), 5.76-5.68 (m, 1 H), 5.07-5.03 (m, 2 H), 4.62, 4.48 (AB_q, 2 H, J_{AB} = 11.5 Hz), 4.42-4.34 (m, 2 H), 4.27-4.23 (m, 1 H), 4.10-4.05 (m, 1 H), 3.21 (dd, 1 H, *J* = 4.0, 13.8 Hz), 3.17-3.10 (m, 1 H), 2.72 (dd, 1 H, *J* = 9.7, 13.8 Hz), 2.57-2.52 (m, 1 H), 2.08-2.02 (m, 1 H), 1.50 (d, 3 H, *J* = 6.9 Hz), 1.12 (d, 3 H, *J* = 6.8 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 182.4, 154.8, 138.3, 136.3, 135.6, 129.1, 129.0, 128.5, 127.8, 127.3, 117.0, 73.8, 70.6, 67.0, 61.2, 38.8, 37.3, 35.8, 20.7, 16.7. **HRMS(ESI)**: *m/z* calculated for $C_{25}H_{30}N_2O_3$ $[M+Na]^+$: 429.2149, found: 429.2154.



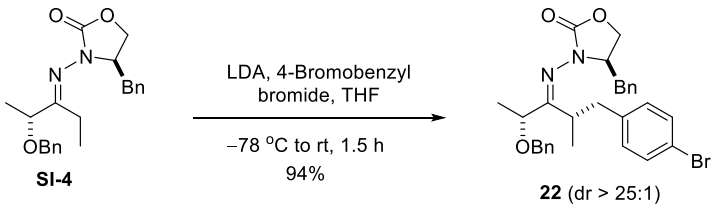
11 **SI-8**

SI-8: Allylation of hydrazone **11** (0.105 g, 0.298 mmol) following the general procedure for hydrazone alkylation provided **SI-8** as a yellow liquid. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided **SI-8** as a colorless oil (0.108 g, 92%). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.38-7.24 (m, 8 H), 7.19-7.17 (m, 2 H), 5.84-5.76 (m, 1 H), 5.06-4.98 (m, 2 H), 4.56, 4.47 (AB_q, 2 H, J_{AB} = 12.0 Hz), 4.37-4.31 (m, 1 H), 4. 29-4.26 (m, 2 H), 4.09-4.06 (m, 1 H), 3.20 (dd, 1 H, *J* = 4.0, 13.8 Hz), 2.75 (dd, 1 H, *J* = 9.5, 13.5 Hz), 2.67-2.52 (m, 2 H), 2.40-2.36 (m, 2 H),

1.44 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 179.1, 154.5, 138.1, 137.6, 135.6, 129.1, 129.0, 128.5, 127.9, 127.8, 127.3, 115.4, 77.7, 71.0, 67.0, 61.2, 38.6, 29.9, 28.9, 19.3. **HRMS**(**ESI**): *m/z* calculated for $C_{24}H_{28}N_2O_3$ $[M+Na]^+$: 415.1992, found: 415.1990.

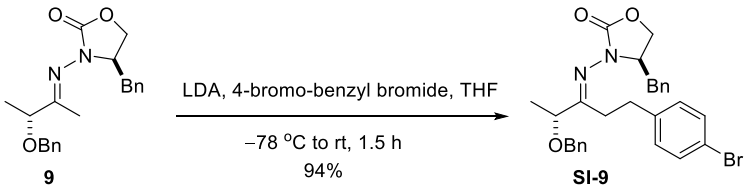


α,α-Bisalkylated hydrazones 13 and 14 from reverse alkylation sequence: Methylation of **SI-8** (0.092 g, 0.234 mmol) following the general procedure for hydrazone alkylation provided mixture of compounds **13** and **14** as a yellow liquid. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided 27:73 diastereomeric mixture of **13** and **14** as a colorless oil (0.089 g, 94%). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.37-7.23 [m, 8 H (both diastereomers)], 7.18-7.14 [m, 2.7 H (both)], 5.77-5.61[m, 1.3 H (both)], 5.06-5.00 [m, 2.8 H (both)], 4.63, 4.52 [AB_q, 2.6 H (both), *J* = 12.0 Hz], 4.49-4.36 [m, 3.6 H (both)], 4.30-4.24 [m, 1.4 H (both)], 4.09-4.03 [m, 1.4 H (both)], 3.25-3.08 [m, 2.7 H (both)], 2.76-2.62 [m, 2.3 H (both)], 2.21-2.00 [m, 2.4 H (both)], 1.48-1.45 [m, 4.1 H, (both)], 1.28 [d, 3 H, *J* = 6.9 Hz (major)], 1.04 [d, 1.1 H, *J* = 7.5 Hz (minor)] . **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 182.8, 182.0, 155.1, 154.9, 138.3, 138.2, 136.4, 135.9, 135.8, 135.7, 129.2, 129.0, 128.97, 128.94, 128.4, 128.0, 127.72, 127.68, 127.3, 127.2, 117.1, 117.0, 73.0, 72.4, 70.6, 70.2, 67.4, 66.9, 61.4, 61.1, 39.5, 38.7, 37.4, 36.4, 35.7, 20.8, 20.3, 16.7, 16.6. **HRMS**(**ESI**): *m/z* calculated for $C_{25}H_{30}N_2O_3$ $[M+Na]^+$: 429.2149, found: 429.2154.



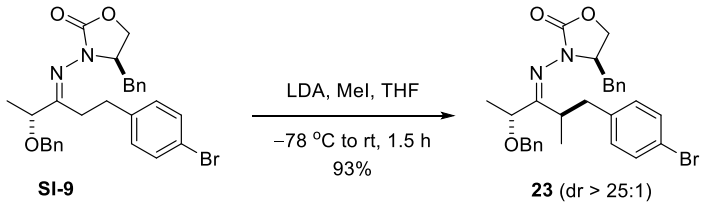
α,α-Bisalkylated hydrazone 22: Compound **22** was obtained from hydrazone **SI-4** (0.087 g, 0.237 mmol) following the general procedure for hydrazone alkylation as a yellow liquid. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided **22** as a colorless foam (0.120 g, 94%, dr >25:1). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.41-7.21 (m, 8 H), 7.11(d, 2 H, *J* = 7.6 Hz), 7.02 (d, 2 H, *J* = 8.3 Hz), 4.63, 4.59 (AB_q, 2 H, J_{AB} = 11.7 Hz), 4.49 (q, 1 H, *J* = 6.2 Hz), 4.34-

4.29 (m, 1 H), 4.18-4.16 (m, 1 H), 3.94-3.91 (m, 1 H), 3.33-3.29 (m, 1 H), 2.93 (dd, 1 H, *J* = 4.1, 13.8 Hz), 2.87 (dd, 1 H, *J* = 6.5, 13.4 Hz), 2.53 (dd, 1 H, *J* = 7.9, 13.4 Hz), 2.10 (dd, 1 H, *J* = 10.3, 13.8 Hz), 1.54 (d, 3 H, *J* = 6.2 Hz), 1.16 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 180.5, 154.9, 138.8, 138.0, 135.6, 131.5, 131.2, 128.96, 128.94, 128.6, 128.0, 127.9, 127.2, 120.3, 73.7, 70.8, 67.2, 61.3, 39.7, 38.4, 38.3, 20.1, 16.7. **HRMS**(**ESI**): *m/z* calculated for $C_{29}H_{31}BrN_2O_3$ $[M+H]^+$: 535.1591, found: 535.1597.



9 **SI-9**

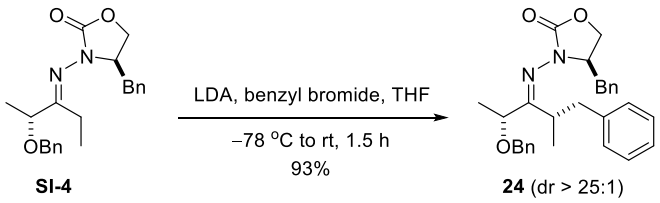
SI-9: The title compound **SI-9** was obtained from hydrazone **9** (0.105 g, 0.297 mmol) following the general procedure for hydrazone alkylation as a yellow liquid. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided **SI-9** as a colorless viscous oil (0.146 g, 94%). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.40-7.24 (m, 8 H), 7.14 (d, 2 H, *J* = 7.6 Hz), 7.04 (d, 2 H, *J* = 8.3 Hz), 4.61, 4.46 (AB_q, 2 H, J_{AB} = 11.7 Hz), 4.35-4.22 (m, 3 H), 4.07-4.04 (m, 1 H), 3.12 (dd, 1 H, *J* = 4.5, 13.4 Hz), 2.96-2.86 (m, 2H), 2.82-2.77 (m, 1H), 2.71-2.64 (m, 2 H), 1.44 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 178.0, 154.8, 140.3, 138.0, 135.5, 131.7, 130.2, 129.1, 129.0, 128.6, 128.0, 127.9, 127.3, 120.1, 77.7, 71.1, 67.2, 61.3, 38.7, 31.4, 31.2, 19.1. **HRMS**(**ESI**): *m/z* calculated for $C_{28}H_{29}BrN_2O_3$ $[M+H]^+$: 521.1434, found: 521.1443.



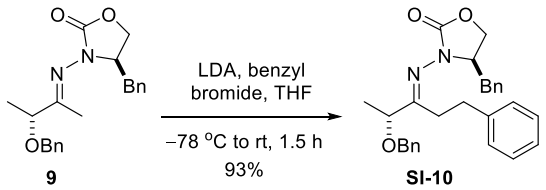
SI-9 **23** (dr > 25:1)

***α,α*-Bisalkylated hydrazone 23**: Methylation of **SI-9** (0.074 g, 0.142 mmol) utilizing the exact same general procedure for hydrazone alkylation provided **23** as a yellow liquid. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided **23** as a colorless foam (0.071 g, 93%, dr >25:1). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.40-7.22 (m, 11 H), 7.12 (d, 2 H, *J* = 7.6 Hz), 7.07 (d, 2 H, *J* = 8.2 Hz), 4.63(A of the AB_q, 1 H, J_{AB} = 11.9 Hz), 4.54-4.44 (m, 2 H, including B of the AB_q), 4.32-4.21 (m, 2 H), 4.07-4.03 (m, 1 H), 3.28-3.12 (m, 3 H), 2.64 (dd, 1 H, *J* = 9.8, 13.5 Hz), 2.48-2.42 (m, 1 H), 1.55 (d, 3 H, *J* = 6.4 Hz), 1.02 (d, 3 H, *J* = 7.3 Hz); **^{13}C NMR** ($CDCl_3$,

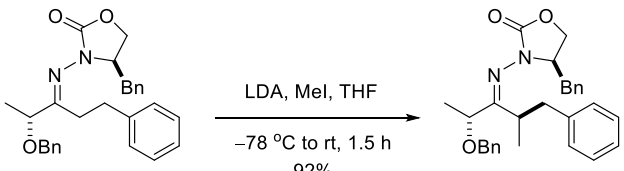
150 MHz): δ 181.5, 154.8, 138.9, 138.2, 135.5, 131.4, 131.3, 120.0, 128.97, 128.6, 128.0, 127.8, 127.7, 127.3, 120.2, 74.2, 70.6, 67.1, 61.1, 38.9, 38.4, 38.3, 20.8, 16.3. **HRMS**(**ESI**): *m/z* calculated for $C_{29}H_{31}BrN_2O_3$ [M+H]$^+$: 535.1591, found: 535.1597.



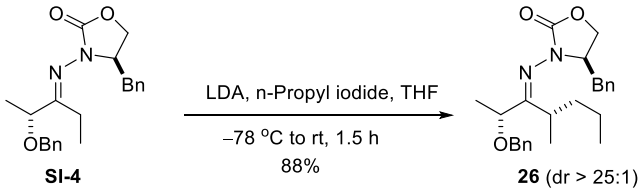
α,α-Bisalkylated hydrazone 24: Benzylation of hydrazone **SI-4** (0.103 g, 0.281 mmol) utilizing the general procedure for hydrazone alkylation gave compound **24** as a yellow liquid. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided **24** as a colorless solid (0.172 g, 93%, dr >25:1). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.42-7.16 (m, 13 H), 7.10-7.08 (m, 2 H), 4.62, 4.58 (AB_q, 2 H, J_{AB} = 12.1 Hz), 4.51 (q, 1 H, J = 6.4 Hz), 4.37-4.29 (m, 1 H), 4.19-4.15 (m, 1 H), 3.94 (dd, 1 H, J = 8.7, 10.0 Hz), 3.45-3.36 (m, 1 H), 2.93 (dd, 2 H, J = 6.0, 13.7 Hz), 2.60 (dd, 1 H, J = 8.2, 13.7 Hz), 2.11 (dd, 1 H, J = 10.5, 13.7 Hz), 1.56 (d, 3 H, J = 6.2 Hz), 1.19 (d, 3 H, J = 7.1 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 181.4, 154.9, 139.6, 138.2, 135.8, 129.4, 128.95, 128.90, 128.53, 128.50, 127.9, 127.8, 127.2, 126.5, 73.7, 70.8, 67.4, 61.3, 40.5, 38.5, 38.4, 20.6, 16.7. **HRMS**(**ESI**): *m/z* calculated for $C_{29}H_{32}N_2O_3$ [M+Na]$^+$: 479.2313, found: 479.2305.



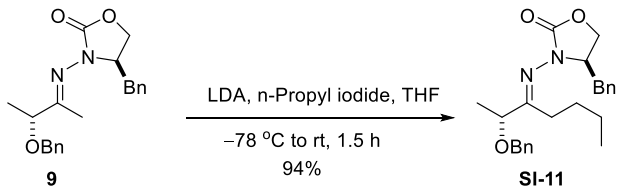
SI-10: Benzylation of hydrazone **9** (0.112 g, 0.318 mmol) following the exact same general procedure for hydrazone alkylation provided **SI-10** as a yellow liquid. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided **SI-10** as a colorless viscous oil (0.131 g, 93%). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.38-7.14 (m, 15 H), 4.63, 4.44 (AB_q, 2 H, J_{AB} = 11.5 Hz), 4.36-4.25 (m, 3 H), 4.08-4.04 (m, 1 H), 3.14 (dd, 1 H, J = 4.3, 13.5 Hz), 3.04-2.85 (m, 3 H), 2.78-2.63 (m, 2 H), 1.45 (d, 3 H, J = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 178.6, 154.8, 141.2, 138.1, 135.6, 129.1, 129.0, 128.7, 128.5, 128.4, 128.0, 127.8, 127.3, 126.4, 77.7, 71.1, 67.2, 61.3, 38.8, 32.1, 31.3, 19.3. **HRMS**(**ESI**): *m/z* calculated for $C_{28}H_{30}N_2O_3$ [M+Na]$^+$: 465.2149, found: 465.2154.



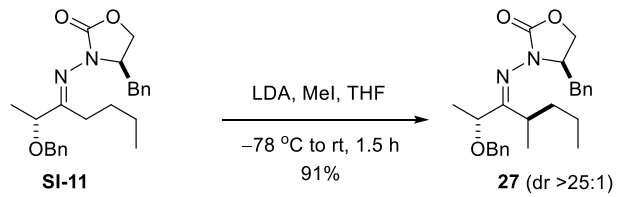
α,α-Bisalkylated hydrazone 25: Methylation of **SI-10** (0.090 g, 0.204 mmol) utilizing the exact same general procedure for hydrazone alkylation provided **25** as a yellow liquid. Flash chromatography over silica gel (10:90, EtOAc-hexanes) provided **25** as a colorless viscous oil (0.086 g, 92%, dr >25:1). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.41-7.10 (m, 15 H), 4.64 (A of the AB_q, 1 H, J_{AB} = 11.5 Hz), 4.53-4.48 (m, 2 H, including B of the AB_q), 4.23-4.15 (m, 2 H), 4.06-4.00 (m, 1 H), 3.33-3.26 (m, 1 H), 3.19-3.14 (m, 2 H), 2.63 (dd, 1 H, *J* = 9.4, 13.5 Hz), 2.50 (dd, 1 H, *J* = 10.8, 12.6 Hz), 1.57 (d, 3 H, *J* = 6.4 Hz), 1.06 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 182.0, 154.7, 139.8, 138.3, 135.6, 129.6, 129.1, 129.0, 128.6, 128.4, 127.8, 127.2, 126.3, 74.0, 70.5, 67.0, 61.0, 39.0, 38.8, 38.6, 20.8, 16.4. **HRMS(ESI)**: *m/z* calculated for $C_{29}H_{32}N_2O_3$ $[M+Na]^+$: 479.2313, found: 479.2305.



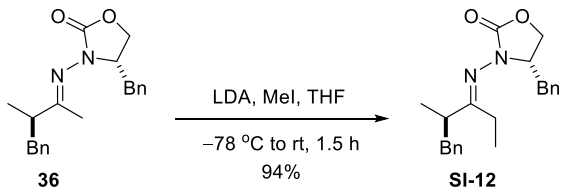
α,α-Bisalkylated hydrazone 26: *n*-Propylation of hydrazone **SI-4** (0.059 g, 0.161 mmol) utilizing the general procedure for hydrazone alkylation gave compound **26** as a yellow liquid. Flash chromatography over silica gel (15:85, EtOAc-hexanes) provided **26** as a colorless solid (0.058 g, 88%, dr >25:1). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.39-7.23 (m, 8 H), 7.19-7.14 (m, 2 H), 4.63 (A of the AB_q, J_{AB} = 11.9 Hz), 4.51-4.42 (m, 2 H, that includes B of the AB_q) 4.36 (q, 1 H, *J* = 6.4 Hz), 4.23 (dd, 1 H, *J* = 7.8, 8.7 Hz), 4.03 (dd, 1 H, *J* = 8.7, 10.5 Hz), 3.23 (dd, 1 H, *J* = 4.1, 13.3 Hz), 3.16-3.07 (m, 1 H), 2.61 (dd, 1 H, *J* = 10.5, 13.3 Hz), 1.51 (d, 3 H, *J* = 6.4 Hz), 1.46-1.25 (m, 4 H), 1.18 (d, 3 H, *J* = 6.9 Hz), 0.91 (t, 3 H, *J* = 6.4 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 182.9, 155.1, 138.3, 135.6, 129.0, 128.9, 128.5, 127.8, 127.3, 73.1, 70.7, 67.5, 61.5, 39.6, 36.8, 36.0, 21.5, 21.1, 17.0, 14.4. **HRMS(ESI)**: *m/z* calculated for $C_{25}H_{32}N_2O_3$ $[M+H]^+$: 409.2486, found: 409.2495.



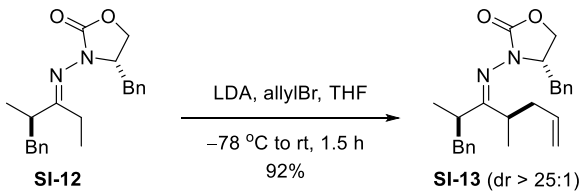
SI-11: *n*-Propylation of hydrazone **9** (0.090 g, 0.255 mmol) utilizing the exact same general procedure for hydrazone alkylation provided **SI-11** as a yellow liquid. Flash chromatography over silica gel (15:85, EtOAc-hexanes) provided **SI-11** as a colorless liquid (0.095 g, 94%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.38-7.23 (m, 8 H), 7.18-7.14 (m, 2 H), 4.65, 4.43 (AB_q, 2 H, J_{AB} = 11.9 Hz), 4.39-4.33 (m, 1 H), 4.30-4.26 (m, 1 H), 4.22 (q, 1 H, *J* = 6.9 Hz), 4.09-4.04 (m, 1 H), 3.15 (dd, 1 H, *J* = 4.4, 13.5 Hz), 2.70 (dd, 1 H, *J* = 9.6, 13.3 Hz), 2.62-2.55 (m, 1 H), 2.43-2.35 (m, 1 H), 1.67-1.48 (m, 2 H), 1.42 (d, 3 H, *J* = 6.9 Hz), 1.39-1.31 (m, 2 H), 0.92 (t, 3 H, *J* = 7.3 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 180.2, 154.7, 138.2, 135.6, 129.1, 129.0, 128.5, 128.0, 127.8, 127.3, 77.5, 71.0, 67.2, 61.3, 38.9, 29.1, 28.3, 23.5, 19.5, 13.9. **HRMS**(**ESI**): *m/z* calculated for $C_{24}H_{30}N_2O_3$ $[M+Na]^+$: 417.2149, found: 417.2155.



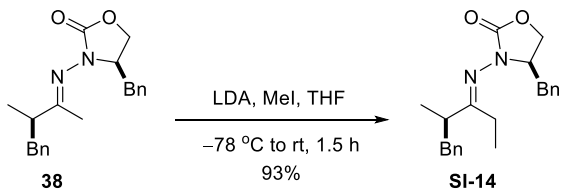
***α,α*-Bisalkylated hydrazone 27**: Methylation of hydrazone **SI-11** (0.068 g, 0.172 mmol) utilizing the exact same general procedure for hydrazone alkylation provided **27** as a yellow liquid. Flash chromatography over silica gel (15:85, EtOAc-hexanes) provided **27** as a colorless liquid (0.064 g, 91%, dr >25:1). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.39-7.23 (m, 8 H), 7.19-7.14 (m, 2 H), 4.63, 4.47 (AB_q, J_{AB} = 11.9 Hz), 4.40-4.29 (m, 2 H), 4.23 (dd, 1 H, *J* = 7.6, 8.5 Hz), 4.1-4.06 (m, 1 H), 3.23 (dd, 1 H, *J* = 3.9, 13.5 Hz), 3.12-3.03 (m, 1 H), 2.72 (dd, 1 H, *J* = 10.1, 13.3 Hz), 1.68-1.61 (m, 1 H), 1.50 (d, 3 H, *J* = 6.4 Hz), 1.46-1.17 (m, 3 H), 1.12 (d, 3 H, *J* = 6.9 Hz), 0.89 (t, 3 H, *J* = 7.3 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 183.5, 154.7, 138.3, 135.7, 129.1, 129.0, 128.5, 127.8, 127.7, 127.2, 73.4, 70.5, 66.8, 61.1, 38.6, 35.8, 35.0, 21.0, 20.9, 17.1, 14.2. **HRMS**(**ESI**): *m/z* calculated for $C_{25}H_{32}N_2O_3$ $[M+H]^+$: 409.2486, found: 409.2495.



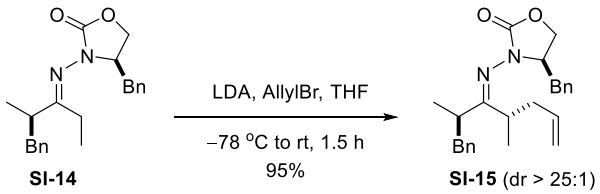
SI-12: Methylation of hydrazone **36** (0.105 g, 0.312 mmol) followed by flash chromatography over silica gel (15:85, EtOAc-hexanes) provided **SI-12** as a colorless viscous oil (0.103 g, 94%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.33-7.23 (m, 7 H), 7.17-7.13 (m, 1 H), 7.10-7.08 (m, 2 H), 4.35-4.22 (m, 2 H), 4.03-3.98 (m, 1 H), 3.09-3.04 (m, 1 H), 2.95-2.86 (m, 2 H), 2.73-2.67 (m, 1 H), 2.60-2.55 (m, 1 H), 2.51-2.42 (m, 1 H), 2.35-2.25 (m, 1 H), 1.21 (d, 3 H, *J* = 6.9 Hz), 1.02 (t, 3 H, *J* = 7.3 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 183.8, 154.8, 140.8, 135.8, 129.2, 129.1, 128.8, 128.3, 127.1, 126.1, 66.8, 61.0, 41.0, 40.1, 38.5, 25.5, 19.6, 10.4. **HRMS**(**ESI**): *m/z* calculated for $C_{22}H_{26}N_2O_2$ $[M+Na]^+$: 373.1892, found: 373.1893.



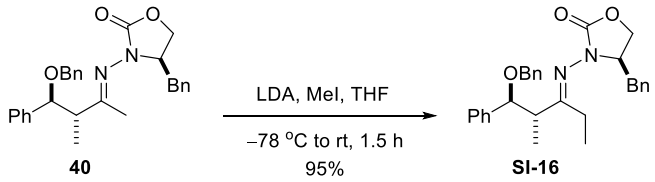
***α,α*-Bisalkylated hydrazone SI-13**: Allylation of hydrazone **SI-12** (0.075 g, 0.214 mmol) followed by flash chromatography over silica gel (10:90, EtOAc-hexanes) provided hydrazone **SI-13** as a colorless oil (0.077 g, 92%, dr > 25:1). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.36-7.32 (m, 2 H), 7.30-7.24 (m, 5 H), 7.20-7.16 (m, 3 H), 5.49-5.39 (m, 1 H), 4.99-4.91 (m, 2 H), 4.42-4.34 (m, 1 H), 4.27-4.23 (m, 1 H), 4.04-3.99 (m, 1 H), 3.19-3.10 (m, 2 H), 3.05-2.98 (m, 1 H), 2.87-2.77 (m, 2 H), 2.56 (dd, 1 H, *J* = 10, 13.3 Hz), 1.97-1.94 (m, 2 H), 1.22-1.19 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 186.3, 155.2, 140.8, 136.1, 135.9, 129.5, 129.0, 128.9, 128.4, 127.3, 126.3, 116.8, 67.4, 61.4, 41.2, 39.6, 38.4, 37.7, 37.1, 22.0, 16.9. **HRMS**(**ESI**): *m/z* calculated for $C_{25}H_{30}N_2O_2$ $[M+Na]^+$: 413.2205, found: 413.2201.



SI-14: Methylation of hydrazone **38** (0.096 g, 0.285 mmol) followed by flash chromatography over silica gel (15:85, EtOAc-hexanes) provided **SI-14** as a colorless viscous oil (0.093 g, 93%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.34-7.17 (m, 8 H), 7.15-7.13 (m, 2 H), 4.31-4.24 (m, 2 H), 4.07-4.00 (m, 1 H), 3.10 -3.04 (m, 2 H), 2.90-2.82 (m, 1 H), 2.73-2.61 (m, 2 H), 2.53-2.44 (m, 1 H), 2.38-2.29 (m, 1 H), 1.13-1.07 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 184.2, 154.8, 140.4, 135.9, 129.5, 129.3, 129.2, 128.9, 128.4, 127.1, 126.2, 66.7, 61.1, 41.5, 41.3, 38.4, 25.4, 18.2, 10.6. **HRMS**(**ESI**): *m/z* calculated for $C_{22}H_{26}N_2O_2$ $[M+Na]^+$: 373.1892, found: 373.1893.

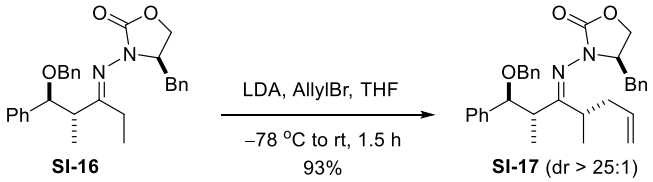


α,α-Bisalkylated hydrazone SI-15: Allylation of hydrazone **SI-14** (0.072 g, 0.205 mmol) followed by flash chromatography over silica gel (10:90, EtOAc-hexanes) provided hydrazone **SI-SI-15** as a colorless oil (0.076 g, 95%, dr > 25:1). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.35-7.24 (m, 5 H), 7.23-7.17 (m, 5 H), 5.72-5.62 (m, 1 H), 5.07-4.99 (m, 2 H), 4.40-4.32 (m, 1 H), 4.28-4.23 (m, 1 H), 4.07-4.02 (m, 1 H), 3.201-3.14 (m, 2 H), 3.09 (dd, 1 H, *J* = 4.8, 13.5 Hz), 2.82-2.71 (m, 1 H), 2.66-2.56 (m, 2 H), 2.27-2.20 (m, 1 H), 2.13-2.06 (m, 1 H), 1.15-1.11 (m, 6 H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 185.9, 155.1, 140.7, 136.1, 135.9, 129.7, 129.4, 129.0, 128.4, 127.2, 126.3, 117.0, 67.2, 61.4, 43.8, 39.4, 38.6, 37.4, 37.3, 19.2, 16.4. **HRMS**(**ESI**): *m/z* calculated for $C_{25}H_{30}N_2O_2$ $[M+Na]^+$: 413.2205, found: 413.2201.

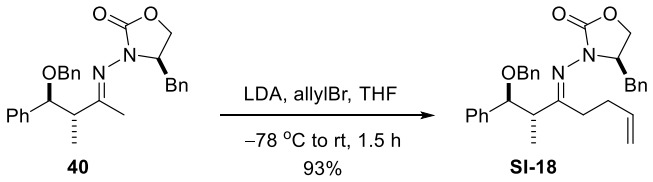


SI-16: Methylation of hydrazone **40** followed by flash chromatography over silica gel (15:85, EtOAc-hexanes) provided hydrazone **SI-16** as a colorless oil in 95% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.45-7.14 (m, 13 H), 7.11-7.08 (m, 2 H), 4.49 (d, 1 H, *J* = 9.6 Hz), 4.32-4.20 (m, 4 H), 4.048-4.01 (m, 1 H)), 3.12 (dd, 1 H, *J* = 3.7, 13.3 Hz), 3.01-2.93 (m, 1 H), 2.72-2.46 (m, 3 H), 1.17 (t, 3 H, *J* = 7.3 Hz), 0.86 (d, 3 H, *J* = 7.3 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 184.3, 154.7, 140.4, 138.5, 135.9, 129.2, 128.8, 128.5, 128.2, 128.1, 128.0, 127.9, 127.4, 127.1, 85.5, 70.9, 66.7, 61.0,

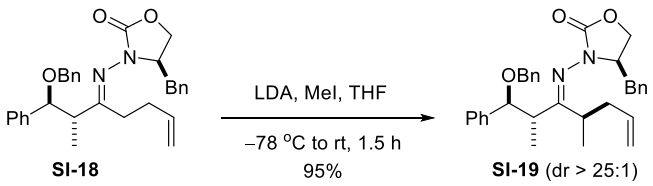
46.6, 38.3, 26.5, 16.2, 10.5. **HRMS**(**ESI**): *m/z* calculated for $C_{29}H_{32}N_2O_3$ $[M+Na]^+$: 479.2311, found: 479.2317.



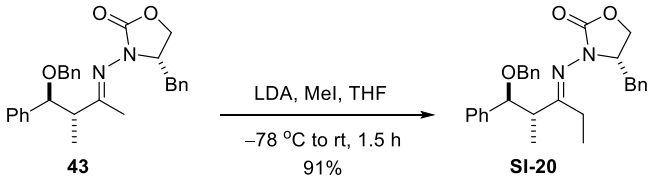
α,α-Bisalkylated hydrazone SI-17: Allylation of **SI-16** followed by flash chromatography over silica gel (15:85, EtOAc-hexanes) provided hydrazone **SI-17** as a colorless oil in 93% yield and dr >25:1. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.44-7.37 (m, 4 H), 7.35-7.18 (m, 9 H), 7.14-7.10 (m, 2 H), 5.76-5.66 (m, 1 H), 5.08-5.00 (m, 2 H), 4.54 (d, 1 H, *J* = 9.6 Hz), 4.28-4.18 (m, 4 H), 4.10-4.02 (m, 1 H), 3.28-3.19 (m, 1 H), 3.15 (dd, 1 H, *J* =3.8, 13.5 Hz), 2.94-2.87 (m, 1 H), 2.67 (dd, 1 H, *J* = 9.6, 13.3 Hz), 2.32-2.20 (m, 1 H), 2.11-2.03 (m, 1 H), 1.28 (d, 3 H, *J* = 6.9 Hz), 0.87 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 185.4, 154.9, 141.0, 138.6, 136.3, 136.0, 129.1, 128.9, 128.4, 128.3, 128.1, 128.0, 127.3, 127.1, 116.9, 86.3, 71.1, 66.7, 61.3, 40.1, 38.6, 38.4, 37.3, 18.2, 16.5. **HRMS**(**ESI**): *m/z* calculated for $C_{32}H_{36}N_2O_3$ $[M+Na]^+$: 519.2624, found: 519.2615.



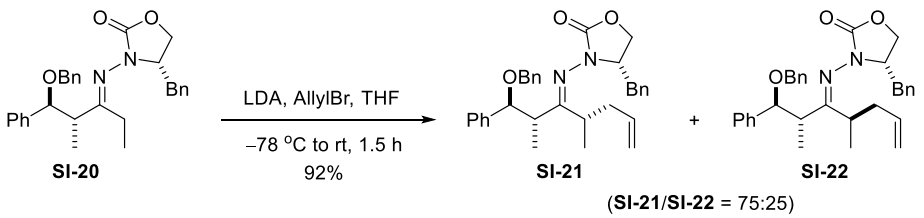
SI-18: Allylation of hydrazone **40** followed by flash chromatography over silica gel (15:85, EtOAc-hexanes) provided hydrazone **SI-18** as a colorless oil in 93% yield. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.42-7.18 (m, 13 H), 7.11-7.10 (m, 2 H), 5.85-5.77 (m, 1 H), 5.05-4.97 (m, 2 H), 4.46 (d, 1 H, *J* = 9.2 Hz), 4.31-4.22 (m, 4 H), 4.08-4.03 (m, 1 H)), 3.13 (dd, 1 H, *J* = 3.4, 13.8 Hz), 2.98-2.92 (m, 1 H), 2.74-2.56 (m, 3 H), 2.41-2.32 (m, 2 H), 0.85 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 182.6, 154.7, 140.4, 138.5, 137.7, 135.9, 129.2, 128.9, 128.5, 128.3, 128.2, 127.9, 127.5, 127.1, 115.3, 86.2, 71.0, 66.8, 61.2, 46.7, 38.5, 33.0, 30.0, 26.5, 16.1. **HRMS**(**ESI**): *m/z* calculated for $C_{31}H_{34}N_2O_3$ $[M+H]^+$: 483.2649, found: 483.2642.



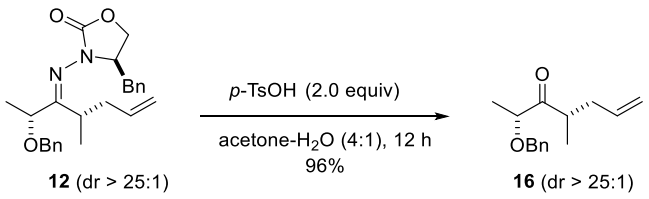
***α,α*-Bisalkylated hydrazone SI-19**: Allylation of **SI-18** followed by flash chromatography over silica gel (15:85, EtOAc-hexanes) provided hydrazone **SI-19** as a colorless oil in 95% yield and dr >25:1. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.43-7.38 (m, 4 H), 7.35-7.19 (m, 9 H), 7.13-7.10 (m, 2 H), 5.81-5.73 (m, 1 H), 5.03-4.94 (m, 2 H), 4.61 (d, 1 H, *J* = 9.7 Hz), 4.30-4.22 (m, 3 H), 4.18-4.13 (m, 1 H), 4.10-4.03 (m, 1 H), 3.17-3.10 (m, 2 H), 2.92-2.86 (m, 1 H), 2.78-2.71 (m, 2 H), 2.12-2.04 (m, 1 H), 1.08 (d, 3 H, *J* = 6.9 Hz), 0.86 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 186.1, 154.7, 141.0, 138.5, 137.0, 136.0, 129.3, 128.9, 128.5, 128.4, 128.1, 128.0, 127.4, 127.1, 116.4, 85.7, 71.1, 66.2, 61.0, 42.6, 37.7, 37.3, 36.8, 19.0, 16.5. **HRMS**(**ESI**): *m/z* calculated for $C_{32}H_{36}N_2O_3$ $[M+H]^+$: 497.2803, found: 497.2799.



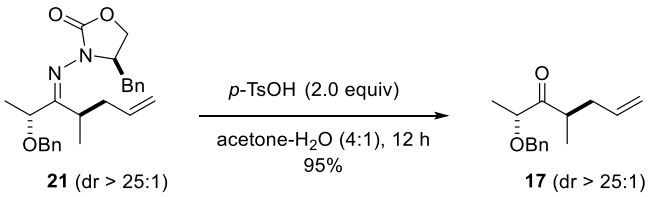
SI-20: Methylation of **43** followed by flash chromatography over silica gel (15:85, EtOAc-hexanes) provided hydrazone **SI-20** as a colorless oil in 91% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.45-7.31 (m, 5 H), 7.27-7.11 (m, 8 H), 7.05-7.02 (m, 2 H), 4.68 (d 1 H, *J* = 10.0 Hz), 4.38-4.31 (m, 2 H), 4.28-4.23 (m, 2 H), 4.04-4.00 (m, 1 H), 3.03 (dd, 1 H, *J* = 3.6, 13.8 Hz),) 2.96 (dd, 1 H, *J* = 6.8, 10.8 Hz), 2.64-2.40 (m, 3 H), 1.20 (t, 3 H, *J* = 7.8 Hz), 0.89 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 184.7, 154.9, 140.5, 138.5, 135.6, 129.2, 128.8, 128.6, 128.2, 127.9, 127.4, 127.3, 127.0, 85.4, 70.8, 66.8, 60.9, 46.3, 38.4, 27.2, 17.2, 10.3. **HRMS**(**ESI**): *m/z* calculated for $C_{29}H_{32}N_2O_3$ $[M+Na]^+$: 479.2311, found: 479.2317.



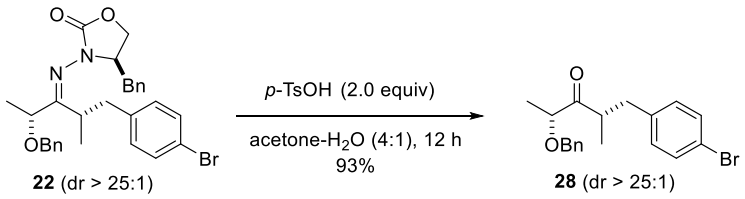
α,α-Bisalkylated hydrazones SI-21 and **SI-22**: Allylation of **SI-20** followed by flash chromatography over silica gel (15:85, EtOAc-hexanes) provided hydrazones **SI-21** and **SI-22** as a 75:25 diastereomeric mixture in 92% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.48-7.20 (m, 9 H), 7.15-7.04 (m, 6 H), 5.80-5.68 (m, 1 H), 5.09-4.74 (m, 3 H), 4.34-4.21 (m, 4 H), 4.04-4.01 (m, 1 H), 3.18-23.11 (m, 1 H), 3.05-3.00 (m, 1 H), 2.93-2.89 (m, 1 H), 2.64-2.42 (m, 4 H), 2.15-1.96 (m, 2 H), 1.20 {d, 0.75 H (one of the -CH_3 for the minor diastereomer), J = 6.9 Hz}, 1.14 {d, 2.23 H (one of the -CH_3 for the major diastereomer), J = 6.4 Hz}, 0.911 (d, 3 H, the other -CH_3 for both diastereomers, J = 7.33 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 186.9, 186.5, 155.2, 155.1, 140.8, 138.5, 138.3, 136.9, 136.4, 135.8, 135.7, 129.0, 128.9, 128.8, 128.6, 128.2, 128.1, 128.0, 127.6, 127.3, 127.2, 127.1, 116.9, 116.2, 85.9, 85.4, 71.1, 71.0, 67.2, 67.0, 61.2, 61.1, 42.6, 42.4, 39.2, 38.6, 38.1, 37.5, 37.1, 36.8, 19.5, 18.9, 16.7, 16.0. **HRMS**(**ESI**): *m/z* calculated for $C_{32}H_{36}N_2O_3$ $[M+Na]^+$: 519.2624, found: 519.2615.



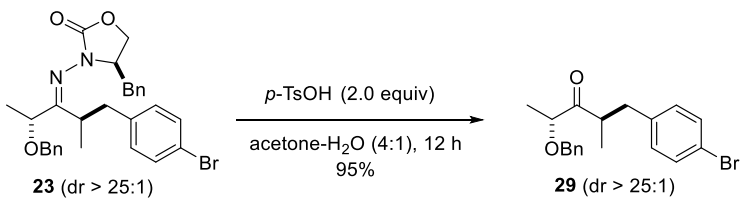
General procedure for hydrazone hydrolysis: Hydrazone **12** (0.076 g, 0.187 mmol) was dissolved in acetone- H_2O (4:1 v/v, 2.0 mL) followed by the addition of *p*-TsOH·H_2O (0.071 g, 0.374 mmol). The reaction mixture was stirred for 12 h at room temperature and then partitioned between Et_2O and saturated aqueous $NaHCO_3$. The aqueous phase was extracted with Et_2O (3 x 10 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a yellow liquid. Flash chromatography over silica gel (5:95, EtOAc-hexanes) provided **16** (0.042 g, 96%) as a colorless liquid. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.36-7.27 (m, 5 H), 5.74-5.64 (m, 1 H), 5.05-4.98 (m, 2 H), 4.57, 4.48 (AB_q, 2 H, J_{AB} = 11.7 Hz), 4.03 (q, 1 H, J = 6.9 Hz), 3.05-2.97 (m, 1 H), 2.44-2.37 (m, 1 H), 2.10-2.03(m, 1 H) 1.35 (d, 3 H, J = 6.9 Hz), 1.07 (d, 3 H, J = 6.6 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 214.9, 137.8, 135.9, 128.6, 127.9, 127.8, 117.0, 79.5, 71.7, 41.2, 36.9, 17.2,16.8. **HRMS**(**ESI**): *m/z* calculated for $C_{15}H_{20}O_2$ $[M+Na]^+$: 255.1356, found: 255.1360.



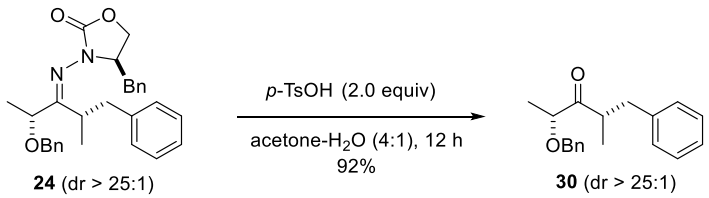
α,α-Bisalkylated ketone 17: The title ketone **17** was obtained by the hydrolysis of hydrazone **21** (0.072 g, 0.177 mmol) following the general procedure for hydrazone hydrolysis. Flash chromatography over silica gel (5:95, EtOAc-hexanes) provided **17** (0.039 g, 95%, dr >25:1) as a colorless liquid. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.37-7.28 (m, 5 H), 5.74-5.66 (m, 1 H), 5.06-4.99 (m, 2 H), 4.58, 4.48 (AB_q, 2 H, J_{AB} = 11.5 Hz), 4.03 (q, 1 H, J = 6.9 Hz), 3.05-2.98 (m, 1 H), 2.42-2.36 (m, 1 H), 2.10-2.05 (m, 1 H), 1.35 (d, 3 H, J = 6.9 Hz), 1.07 (d, 3 H, J = 6.6 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 215.0, 137.9, 135.7, 128.6, 127.9, 127.8, 117.2, 79.9, 71.8, 40.9, 37.6, 17.1,16.3. **HRMS(ESI)**: *m/z* calculated for $C_{15}H_{20}O_2$ $[M+Na]^+$: 255.1356, found: 255.1360.



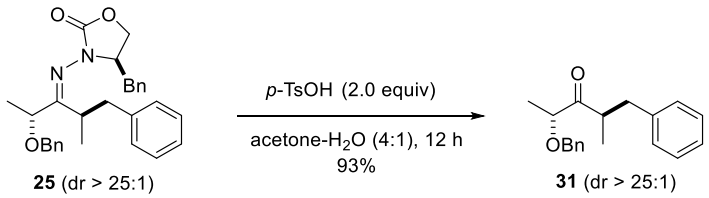
α,α-Bisalkylated ketone 28: The title ketone **28** was obtained by the hydrolysis of hydrazone **22** (0.087 g, 0.162 mmol) following the general procedure for hydrazone hydrolysis. Flash chromatography over silica gel (8:92, EtOAc-hexanes) provided ketone **28** (0.055 g, 93%, dr >25:1) as a colorless liquid. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.36-7.27 (m, 6 H), 7.98-7.96 (m, 2 H), 4.40, 4.37 (AB_q, 2 H, J_{AB} = 12.0 Hz), 3.88 (q, 1 H, J = 6.9 Hz), 3.23-3.16 (m, 1 H), 2.95 (dd, 1 H, J = 8.0, 13.8 Hz), 2.49 (dd, 1 H, J = 6.5, 13.5 Hz), 1.18 (d, 3 H, J = 6.9 Hz), 1.08 (d, 3 H, J = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 214.9, 139.0, 137.7, 131.5, 131.0, 128.6, 128.0, 127.8, 120.2, , 79.7, 71.6, 43.5, 38.2, 17.5, 17.0. **HRMS(ESI)**: *m/z* calculated for $C_{19}H_{21}BrO_2$ $[M+Na]^+$: 383.0617, found: 383.0621.



α,α-Bisalkylated ketone 29: Hydrolysis of hydrazone **23** (0.100 g, 0.186 mmol) following the general procedure for hydrazone hydrolysis. Flash chromatography over silica gel (8:92, EtOAc-hexanes) provided ketone **29** (0.064 g, 95%, dr >25:1) as a colorless liquid. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.38-7.26 (m, 6 H), 7.00 (d, 2 H, J = 8.2 Hz), 4.48, 4.32 (AB_q, 2 H, J_{AB} = 11.9 Hz), 3.85 (q, 1 H, J = 6.9 Hz), 3.27-3.18 (m, 1 H), 2.94 (dd, 1 H, J = 8.0, 13.5 Hz), 2.50 (dd, 1 H, J = 6.9, 13.3 Hz), 1.18 (d, 3 H, J = 7.3 Hz), 1.08 (d, 3 H, J = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 214.9, 138.8, 137.7, 131.5, 131.0, 128.6, 128.0, 127.8, 120.2, 80.3, 71.7, 43.1, 39.0, 17.0, 16.7. **HRMS**(**ESI**): *m/z* calculated for $C_{19}H_{21}BrO_2$ $[M+Na]^+$: 383.0617, found: 383.0621.

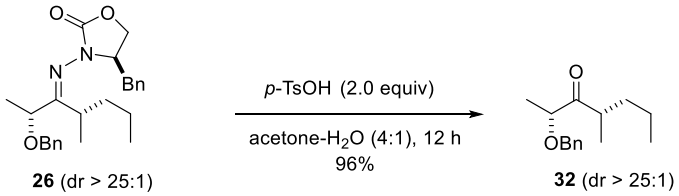


α,α-Bisalkylated ketone 30: Hydrolysis of hydrazone **24** (0.070 g, 0.153 mmol) following the general procedure for hydrazone hydrolysis. Flash chromatography over silica gel (8:92, EtOAc-hexanes) provided ketone **30** (0.040 g, 95%, dr >25:1) as a colorless liquid. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.37-7.09 (m, 10 H), 4.41, 4.32 (AB_q, 2 H, J_{AB} = 11.9 Hz), 3.89 (q, 1 H, J = 6.9 Hz), 3.27-3.18 (m, 1 H), 3.01 (dd, 1 H, J = 8.2, 13.3 Hz), 2.55 (dd, 1 H, J = 6.4, 13.3 Hz), 1.15 (d, 3 H, J = 6.9 Hz), 1.09 (d, 3 H, J = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 215.2, 140.0, 137.8, 129.3, 128.5, 128.4, 127.9, 127.8, 126.3, 79.7, 71.6, 43.7, 39.0, 17.5, 16.9. **HRMS**(**ESI**): *m/z* calculated for $C_{19}H_{22}O_2$ $[M+Na]^+$: 305.1512, found: 305.1517.

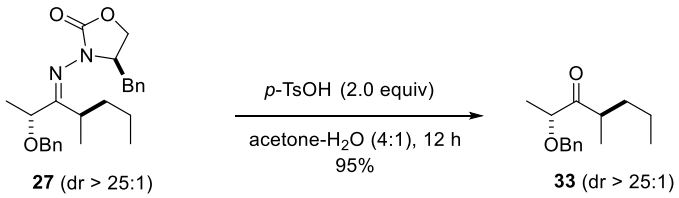


α,α-Bisalkylated ketone 31: Hydrolysis of hydrazone **25** (0.075 g, 0.164 mmol) following the general procedure for hydrazone hydrolysis. Flash chromatography over silica gel (8:92, EtOAc-hexanes) provided ketone **31** (0.043 g, 95%, dr >25:1) as a colorless liquid.**^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.35-7.10 (m, 10 H), 4.47, 4.23 (AB_q, 2 H, J_{AB} = 11.7 Hz), 3.83 (q, 1 H, J = 6.9 Hz), 3.29-3.20 (m, 1 H), 2.97 (dd, 1 H, J = 7.8, 13.3 Hz), 2.57 (dd, 1 H, J = 7.3, 13.3 Hz), 1.18 (d, 3 H, J = 7.3 Hz), 1.10 (d, 3 H, J = 7.1 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 215.3, 139.7, 137.9, 129.3,

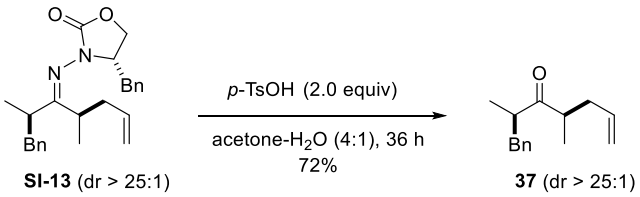
128.5, 127.9, 127.8, 126.4, 80.6, 71.7, 43.3, 39.8, 17.0, 16.7. **HRMS**(**ESI**): *m/z* calculated for $C_{19}H_{22}O_2$ [M+Na]$^+$: 305.1512, found: 305.1517.



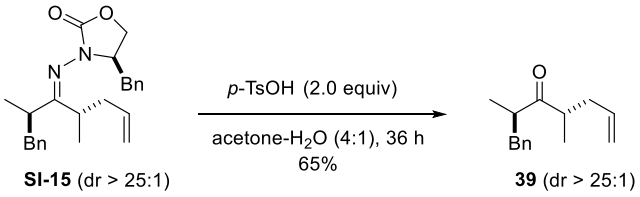
***α,α*-Bisalkylated ketone 32**: Hydrolysis of hydrazone **26** (0.052 g, 0.127 mmol) following the general procedure for hydrazone hydrolysis. Flash chromatography over silica gel (8:92, EtOAc-hexanes) provided ketone **32** (0.029 g, 96%, dr >25:1) as a colorless liquid.**^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.35 (d, 4 H, *J* = 4.1 Hz), 7.33-7.27 (m, 1 H), 4.58, 4.46 (AB_q, 2 H, J_{AB} = 11.9 Hz), 4.04 (q, 1 H, *J* = 6.9 Hz), 2.95-2.86 (m, 1 H), 1.70-1.60 (m, 1 H), 1.35 (d, *J* = 6.9 Hz), 1.32-1.18 (m, 3 H), 1.05 (d, *J* = 6.9 Hz), 0.87 (t, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 215.6, 137.9, 128.5, 127.9, 127.8, 79.3, 71.7, 41.3, 34.8, 20.7, 17.2, 17.1, 14.2. **HRMS**(**ESI**): *m/z* calculated for $C_{15}H_{22}O_2$ [M+Na]$^+$: 257.1512, found: 257.1506.



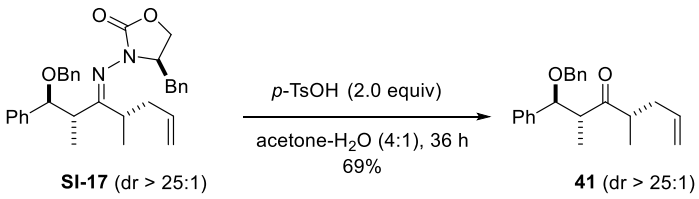
***α,α*-Bisalkylated ketone 33:** Hydrolysis of hydrazone **27** (0.060 g, 0.147 mmol) following the general procedure for hydrazone hydrolysis. Flash chromatography over silica gel (8:92, EtOAc-hexanes) provided ketone **33** (0.032 g, 95%, dr >25:1) as a colorless liquid. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.35 (d, 4 H, *J* = 4.1 Hz), 7.33-7.27 (m, 1 H), 4.59, 4.47 (AB_q, 2 H, J_{AB} = 11.9 Hz), 4.03 (q, 1 H, *J* = 6.9 Hz), 2.97-2.88 (m, 1 H), 1.67-1.56 (m, 1 H), 1.35 (d, *J* = 6.9 Hz), 1.32-1.18 (m, 3 H), 1.05 (d, *J* = 6.9 Hz), 0.88 (t, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 215.9, 137.9, 128.5, 127.9, 127.8, 79.8, 71.7, 40.9, 35.6, 20.6, 17.3, 16.4, 14.2. **HRMS**(**ESI**): *m/z* calculated for $C_{15}H_{22}O_2$ [M+Na]$^+$: 257.1512, found: 257.1506.



α,α-Bisalkylated ketone 37: Hydrolysis of hydrazone **SI-13** (0.063 g, 0.161 mmol) following the general procedure for hydrazone hydrolysis. Flash chromatography over silica gel (5:95, EtOAc-hexanes) provided ketone **37** (0.025 g, 72%, dr >25:1) as a colorless liquid. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.28-7.24 (m, 2 H), 7.20-7.13 (m, 3 H), 5.71-5.61 (m, 1 H), 5.03-4.96 (m, 2 H), 2.98-2.89 (m, 2 H), 2.57-2.49 (m, 2 H), 2.37-2.30 (m, 1 H), 2.03-1.96 (m, 1 H), 1.06 (d, 3 H, *J* = 6.9 Hz), 0.82 (d, 3 H, *J* = 6.9 Hz); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 216.8, 140.1, 136.0, 129.1, 128.4, 126.3, 116.8, 47.5, 45.7, 39.3, 36.9, 16.8, 15.7. **HRMS**(**ESI**): *m/z* calculated for $C_{15}H_{20}O$ $[M+Na]^+$: 239.14060, found: 239.14130.

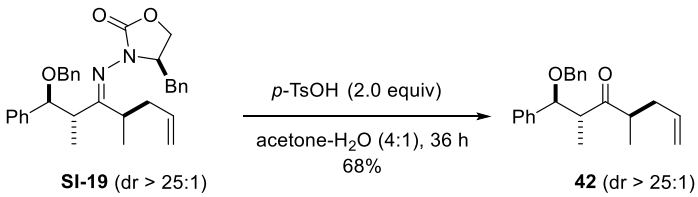


α,α-Bisalkylated ketone 39: Hydrolysis of hydrazone **SI-15** (0.057 g, 0.146 mmol) following the general procedure for hydrazone hydrolysis. Flash chromatography over silica gel (5:95, EtOAc-hexanes) provided ketone **39** (0.021 g, 65%, dr >25:1) as a colorless liquid. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.29-7.11 (m, 5 H), 5.58-5.48 (m, 1 H), 4.96-4.89 (m, 2 H), 2.98-2.89 (m, 2 H), 2.57-2.48 (m, 2 H), 2.22-2.16 (m, 1 H), 1.94-1.86 (m, 1 H), 1.07 (d, 3 H, *J* = 6.0 Hz), 1.01 (d, 3 H, *J* = 6.9 Hz)**^{13}C NMR** ($CDCl_3$, 100 MHz): δ 217.1, 140.0, 135.8, 129.2, 128.4, 126.3, 116.8, 47.4, 45.5, 39.1, 36.8, 16.9, 15.9. **HRMS**(**ESI**): *m/z* calculated for $C_{15}H_{20}O$ $[M+Na]^+$: 239.14060, found: 239.14130.



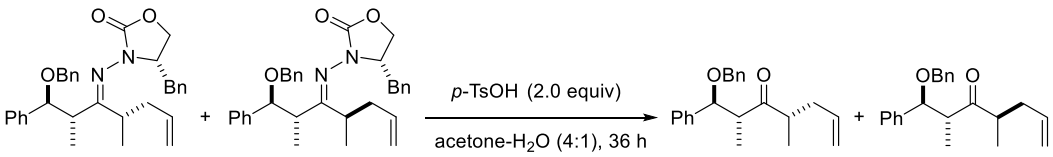
α,α-Bisalkylated ketone 41: Hydrolysis of hydrazone **SI-17** (0.065 g, 0.131 mmol) following the general procedure for hydrazone hydrolysis. Flash chromatography over silica gel (5:95,

EtOAc-hexanes) provided ketone **41** (0.029 g, 69%, dr >25:1) as a colorless liquid.**^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.41-7.21 (m, 8 H), 7.18-7.14 (m, 2 H), 5.77- 5.67 (m, 1 H), 5.04-4.94 (m, 2 H), 4.44 (d, 1 H, *J* = 9.6 Hz), 4.25, 4.17 (ABq, 2 H, *J* = 11.5 Hz), 3.14-3.06 (m, 1 H), 2.82-2.74 (m, 1 H), 2.56-2.49 (m, 1 H), 2.09-1.98 (m, 1 H), 1.10 (d, 3 H, J = 7.3 Hz),0.74 (d, 3 H, J = 6.9 Hz), **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 216.6, 139.8, 138.2, 136.5, 128.6, 128.3, 128.2, 127.8, 127.5, 116.5, 85.1, 70.8, 51.0, 47.3, 36.1, 15.4, 14.4. **HRMS**(**ESI**): *m/z* calculated for $C_{22}H_{26}O_2$ $[M+Na]^+$: 345.18250, found: 345.18310.



SI-19 (dr > 25:1) → **42** (dr > 25:1)

α,α-Bisalkylated ketone 42: Hydrolysis of hydrazone **SI-22** (0.055 g, 0.111 mmol) following the general procedure for hydrazone hydrolysis. Flash chromatography over silica gel (5:95, EtOAc-hexanes) provided ketone **42** (0.024 g, 68%, dr>25:1) as a colorless liquid. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.40-7.20 (m, 8 H), 7.16-7.15 (m, 2 H), 5.77- 5.67 (m, 1 H), 5.06-4.99 (m, 2 H), 4.44 (d, 1 H, *J* = 10.1 Hz), 4.26, 4.17 (ABq, 2 H, *J* = 11.5 Hz), 3.11-3.03 (m, 1 H), 2.84-2.76 (m, 1 H), 2.48-2.41 (m, 1 H), 2.12-2.05 (m, 1 H), 1.11 (d, 3 H, J = 6.9 Hz), 0.71 (d, 3 H, J = 6.9 Hz), **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 216.5, 139.9, 138.3, 136.0, 128.6, 128.3, 127.8, 127.5, 116.9, 84.9, 70.9, 51.4, 47.5, 36.8, 15.3, 13.9. **HRMS**(**ESI**): *m/z* calculated for $C_{22}H_{26}O_2$ $[M+Na]^+$: 345.1825, found: 345.1828.



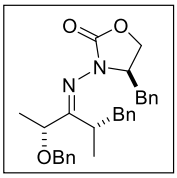
SI-21 + **SI-22** (**SI-21**/**SI-22** = 75:25) → **41** + **42** (**41**/**42** = 75:25)

α,α-Bisalkylated ketones 41 and 42: Hydrolysis of hydrazones **SI-21** and **SI-22** (0.071 g, 0.143 mmol) following the general procedure for hydrazone hydrolysis followed by flash chromatography over silica gel (5:95, EtOAc-hexanes) provided mixture of ketone**s 41** and **42** (0.030 g, 66%, dr = 75:25) as a colorless liquid.**^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.41-7.21 (m, 8 H), 7.18-7.14 (m, 2 H), 5.78-5.77 (m, 1 H), 5.07-4.94 (m, 2 H), 4.44 (d, 1 H, *J* = 9.6 Hz), 4.25,

4.17 (ABq, 2 H, *J* = 11.5 Hz), 3.14-3.00 (m, 1 H), 2.85-2.73 (m, 1 H), 2.56-2.42 (m, 1 H), 2.12-12.01 (m, 1 H), , 1.10 (d, 3 H, the -CH_3 for both diastereomers, *J* = 7.33 Hz) 0.74{d, 2.26 H (one of the -CH_3 for the major diastereomer), *J* = 6.9 Hz}, 10.71 {d, 0.75 H (one of the -CH_3 for the minor diastereomer), *J* = 7.3 Hz}; **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 216.7, 216.5, 139.9, 139.8, 138.3, 138.2, 136.5, 136.0, 128.6, 128.3, 128.2, 127.8, 127.7, 127.6, 127.5, 116.9, 116.5, 85.1, 84.9, 77.3, 70.8, 51.4, 51.0, 47.5, 47.4, 36.7, 36.2, 15.5, 15.3, 14.4, 14.0. **HRMS**(**ESI**): *m/z* calculated for $C_{22}H_{26}O_2$ $[M+Na]^+$: 345.1825, found: 345.1831.

II. X-Ray Crystallographic Information

Crystal structure for Hydrazone **24**



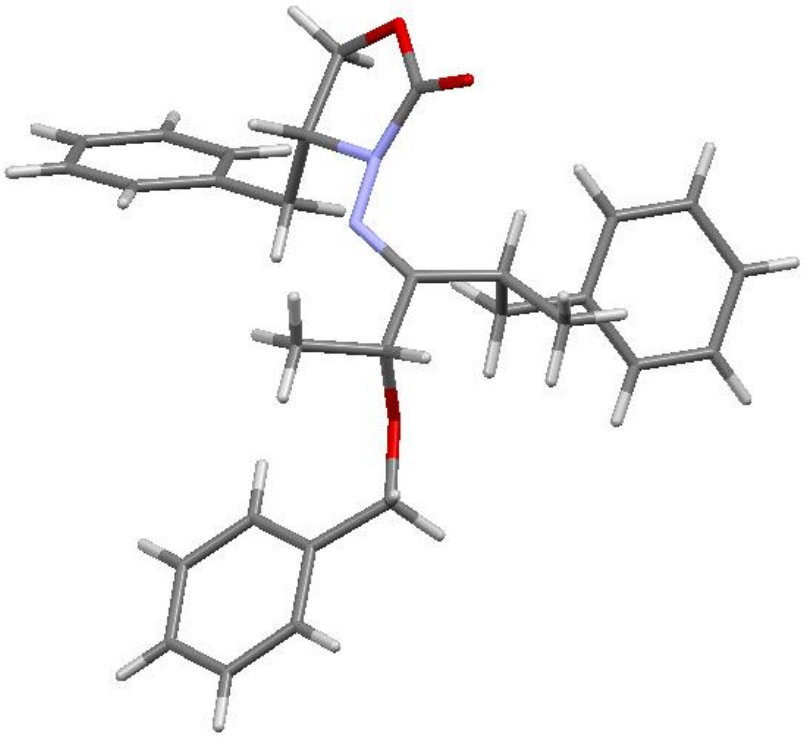


Table 1. Crystal data and structure refinement for **24**.

Empirical formula	$C_{29}H_{32}N_2O_3$
Formula weight	456.57
Temperature	123(2) K
Wavelength	1.54178 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 9.9516(2) Å alpha = 90 deg.
	b = 10.5201(2) Å beta = 90 deg.
	c = 23.8875(4) Å gamma = 90 deg.
Volume	2500.83(8) $Å^3$
Z, Calculated density	4, 1.213 Mg/m^3
Absorption coefficient	0.622 mm^{-1}
F(000)	976
Crystal color and shape	Colorless thick plate
Crystal size	0.40 x 0.40 x 0.25 mm
Theta range for data collection	3.70 to 66.56 deg.
Limiting indices	-11<=h<=11, 0<=k<=11, 0<=l<=28
Reflections collected / unique	17163 / 4290 [R(int) = 0.0234]
Completeness to theta = 66.56	97.5 %
Absorption correction	Empirical
Max. and min. transmission	0.7528 and 0.6518
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4239 / 0 / 310
Goodness-of-fit on F^2	1.081
Final R indices [I>4sigma(I)]	R1 = 0.0227, wR2 = 0.0587
R indices (all data)	R1 = 0.0229, wR2 = 0.0590
Absolute structure parameter	-0.03(12)
Extinction coefficient	0.00502(18)
Largest diff. peak and hole	0.165 and -0.134 e. $Å^{-3}$

III. Cartesian coordinates and Total Energies

Cartesian coordinates (in Å) for optimized geometries at B3LYP/6-31+G(d) and computed energies [in Hartree, computed at B3LYP/6-31+G(d) and mPW2PLYP/6-311+G(d,p)]

High Selectivity (**34**)				Low Selectivity (**35**)			
Atom	X	Y	Z	Atom	X	Y	Z
C	0.90090	-1.20907	-1.84538	C	1.01376	-2.46924	-0.94136
O	1.65684	-0.14006	-1.22727	O	1.60561	-1.95086	0.26913
C	3.02772	-0.56780	-0.99992	C	1.86050	-3.03222	1.20767
C	3.15223	-1.95273	-1.64698	C	1.43799	-4.32253	0.49037
C	1.70846	-2.47935	-1.58364	C	0.41725	-3.81877	-0.54485
Li	0.69249	0.81473	0.23661	Li	1.21440	-0.13477	0.87182
O	1.28418	-0.49405	1.70999	O	0.00367	-0.69866	2.59935
C	0.29038	-0.67424	2.42237	C	-1.09382	-0.22598	2.30266
O	0.30783	-1.44281	3.54155	O	-2.26713	-0.72723	2.78214
C	-1.03170	-1.46437	4.09675	C	-3.34553	0.05900	2.21435
C	-1.80789	-0.33743	3.37833	C	-2.73058	0.71213	0.96803
N	-0.93697	-0.15035	2.20928	N	-1.32763	0.79242	1.42622
H	-1.46104	-2.45084	3.89401	H	-4.17716	-0.61518	2.00255
N	-1.00540	0.92376	1.30400	C	-2.86262	-0.10918	-0.33624
C	-1.94542	0.77056	0.30203	N	-0.21831	1.08677	0.61419
C	-1.84483	1.96903	-0.63570	C	-0.01711	2.40486	0.29579
O	-0.42253	2.15523	-0.92031	C	1.44389	2.63800	-0.12368
C	-0.14202	2.80201	-2.16024	O	2.13523	1.36241	-0.27253
H	-0.94159	-1.31505	5.17461	C	3.18461	1.39377	-1.24334
H	1.48607	-2.86924	-0.58410	H	-3.65055	0.80639	2.95462
H	-0.10127	-1.21515	-1.40554	H	-0.56587	-3.67863	-0.08011
H	0.81460	-1.00045	-2.92179	H	0.27985	-1.73731	-1.29125
H	1.50228	-3.26492	-2.31817	H	1.79913	-2.57990	-1.70198
H	3.48250	-1.86708	-2.68979	H	0.30085	-4.49328	-1.39954
H	3.86620	-2.59070	-1.11674	H	2.29476	-4.78392	-0.01533
H	3.69118	0.18188	-1.44302	H	1.01843	-5.05843	1.18336
H	3.18706	-0.60858	0.08240	H	2.92462	-3.01339	1.46498
H	-0.81400	3.66456	-2.28035	H	1.26409	-2.83203	2.10298
C	1.29565	3.26846	-2.18726	H	3.74196	2.33694	-1.14565
H	-0.33631	2.11329	-2.99658	C	4.12642	0.22927	-1.04722
C	1.83346	3.98411	-1.10710	H	2.74950	1.36907	-2.25346
C	3.15098	4.44560	-1.14732	C	4.80988	0.06526	0.16736
C	3.94714	4.20535	-2.27232	C	5.70774	-0.98874	0.34117
C	2.10166	3.02687	-3.30600	C	5.94270	-1.89113	-0.70279
C	3.41788	3.49648	-3.35357	C	4.36568	-0.67988	-2.08399
H	1.21612	4.17282	-0.23259	C	5.27149	-1.73294	-1.91716
H	3.55547	4.99680	-0.30187	H	4.63447	0.76818	0.97844
H	4.97172	4.56726	-2.30414	H	6.23151	-1.10218	1.28722

H	1.69966	2.46312	-4.14541	H	6.64793	-2.70781	-0.57000
H	4.02982	3.30167	-4.23096	H	3.84249	-0.56255	-3.03094
H	-2.33703	1.73923	-1.58652	H	5.45052	-2.42725	-2.73456
C	-2.43814	3.24696	-0.03776	H	1.48360	3.14754	-1.09601
H	-2.32462	4.10464	-0.71222	C	2.19983	3.45492	0.93232
H	-3.50966	3.10506	0.14527	H	3.26253	3.55108	0.67453
H	-1.94941	3.47313	0.91385	H	1.78400	4.46085	1.02936
C	-2.83233	-0.24704	0.09623	H	2.11913	2.95770	1.90527
C	-3.87172	-0.38102	-0.98951	C	-0.88072	3.46113	0.36300
H	-2.82208	-1.06109	0.81970	C	-0.60525	4.88847	-0.04606
H	-3.84477	-1.38261	-1.44411	H	-1.86574	3.28891	0.78730
H	-4.89722	-0.24628	-0.60787	H	-1.49745	5.33459	-0.50741
H	-3.74714	0.33938	-1.80634	H	-0.33582	5.54768	0.79738
C	-2.05042	0.95571	4.19535	H	0.20158	4.97617	-0.78538
H	-2.83668	0.72886	4.92777	H	-2.13411	0.30415	-1.04364
C	-0.84737	1.53754	4.90651	H	-2.56180	-1.14582	-0.13536
H	-2.46730	1.69075	3.49699	C	-4.25648	-0.07391	-0.91998
C	0.15590	2.20859	4.18774	C	-4.71705	1.06799	-1.59739
C	-0.70897	1.42384	6.29821	C	-6.01136	1.12113	-2.11887
C	0.40314	1.95553	6.95819	C	-6.87318	0.02865	-1.97588
H	-1.48509	0.92316	6.87517	C	-5.13140	-1.16283	-0.78678
C	1.26844	2.73897	4.84461	C	-6.42757	-1.11541	-1.30953
H	0.05060	2.30664	3.10963	H	-4.04951	1.91849	-1.72330
H	0.48897	1.85769	8.03786	H	-6.34553	2.01363	-2.64248
C	1.39800	2.61388	6.23134	H	-7.87978	0.06778	-2.38443
H	2.26456	3.02812	6.74085	H	-4.79126	-2.06234	-0.27662
H	2.03719	3.25222	4.27145	H	-7.08626	-1.97340	-1.19786
H	-2.78905	-0.69678	3.04851	H	-3.14183	1.71077	0.80740

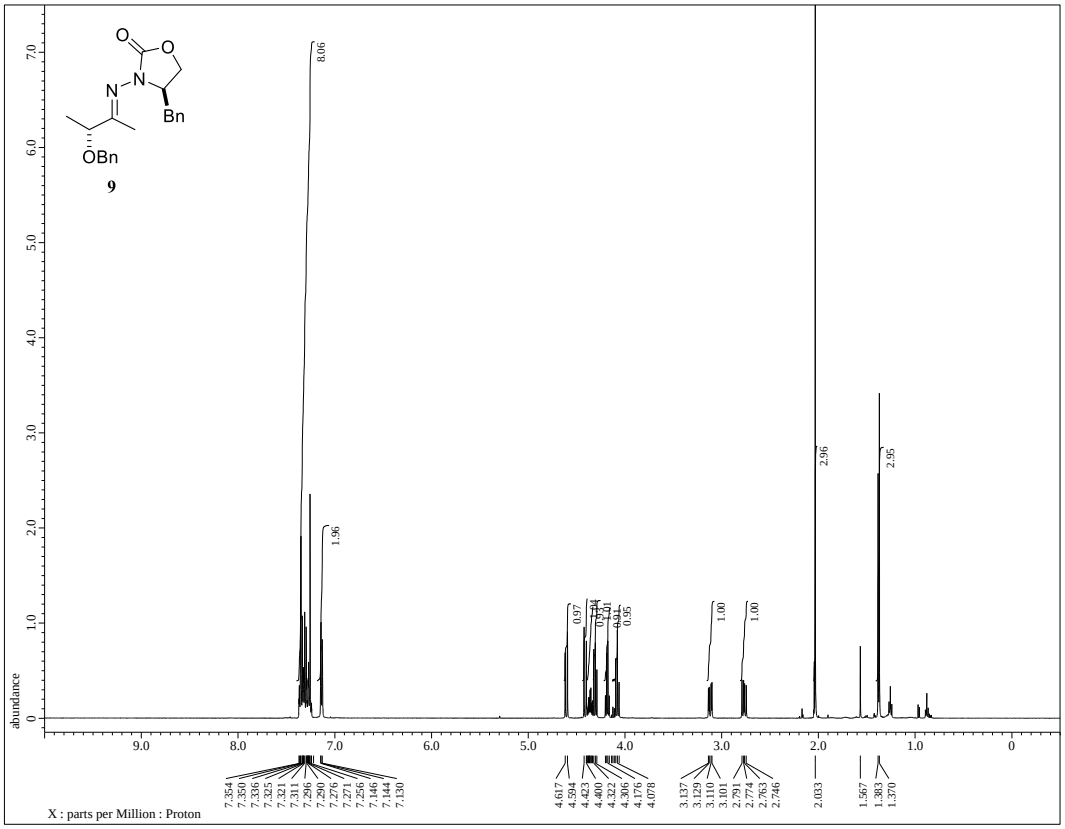
Electronic energies:
B3LYP/6-31+G(d) energy –1428.6493894
mPW2PLYP/6-311+G(d,p) energy –1427.5639231

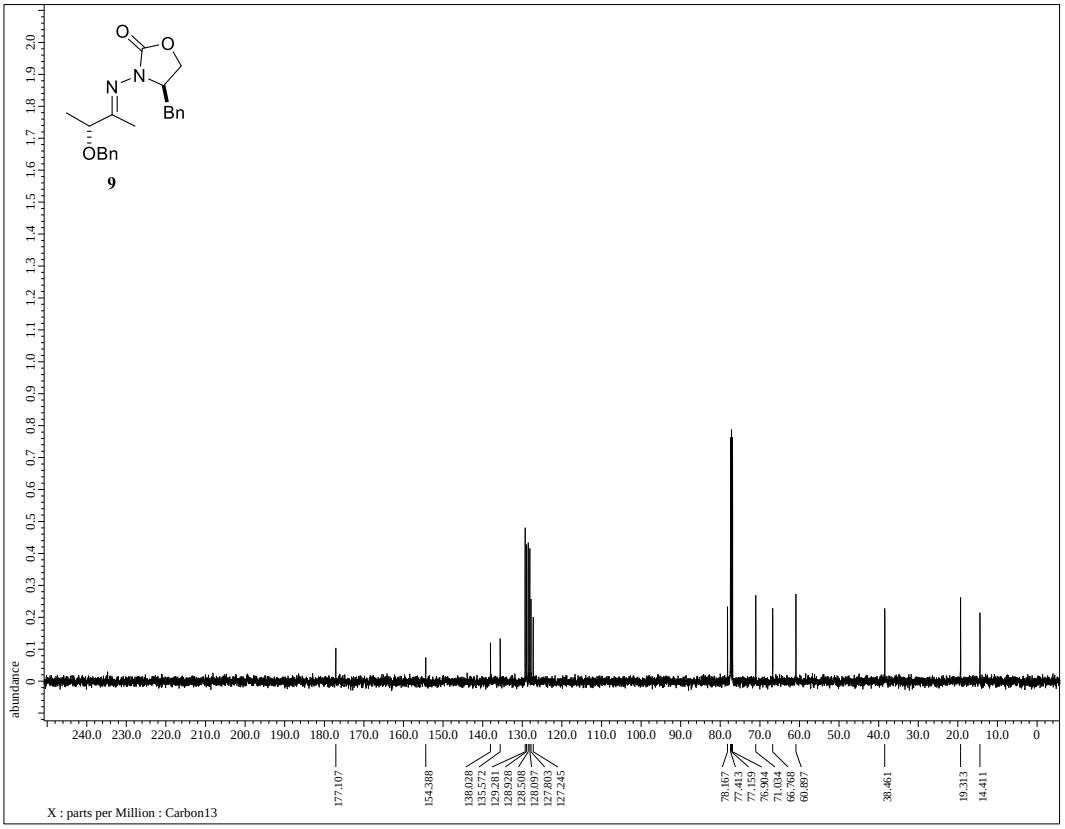
Zero-point correction energy: 0.553406
Thermal correction (298K) to Gibbs Free Energy: 0.482746

Electronic energies:
B3LYP/6-31+G(d) energy –1428.6430618
mPW2PLYP/6-311+G(d,p) energy –1426.0666257

Zero-point correction energy: 0.553401
Thermal correction (298K) to Gibbs Free Energy: 0.482717

IV. NMR Spectra


9
abundance
X : parts per Million : Proton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abundance
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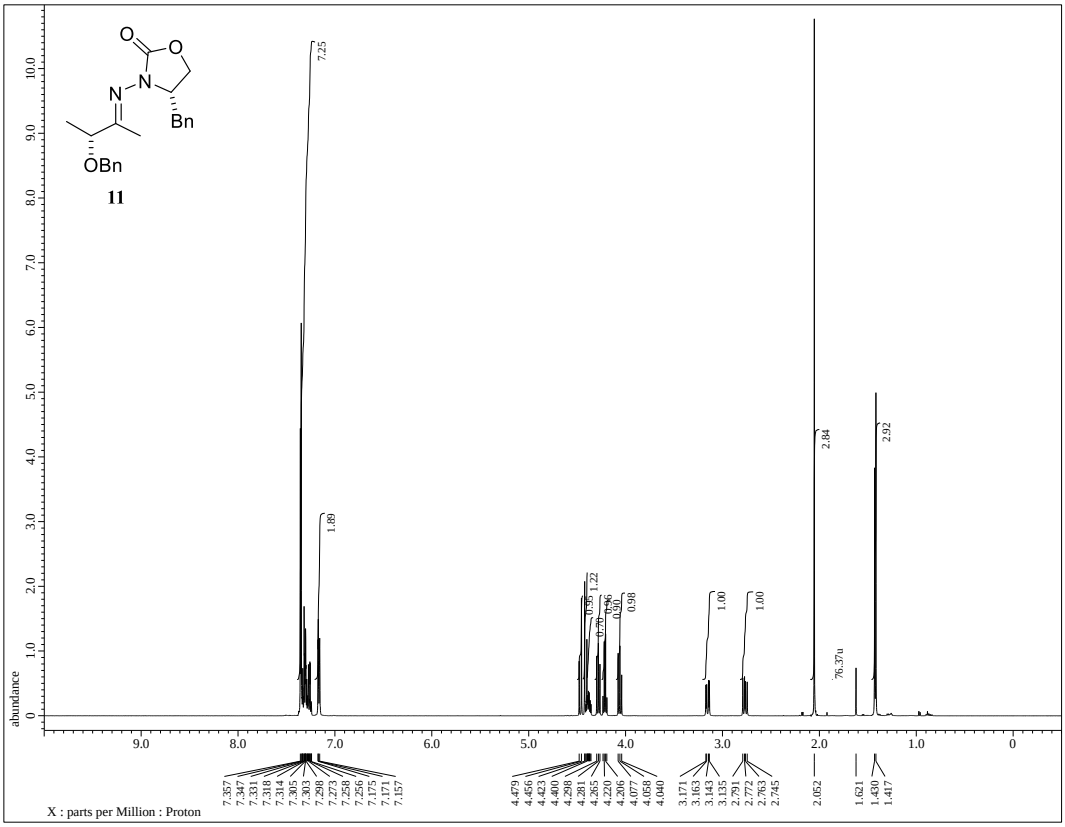
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abundance
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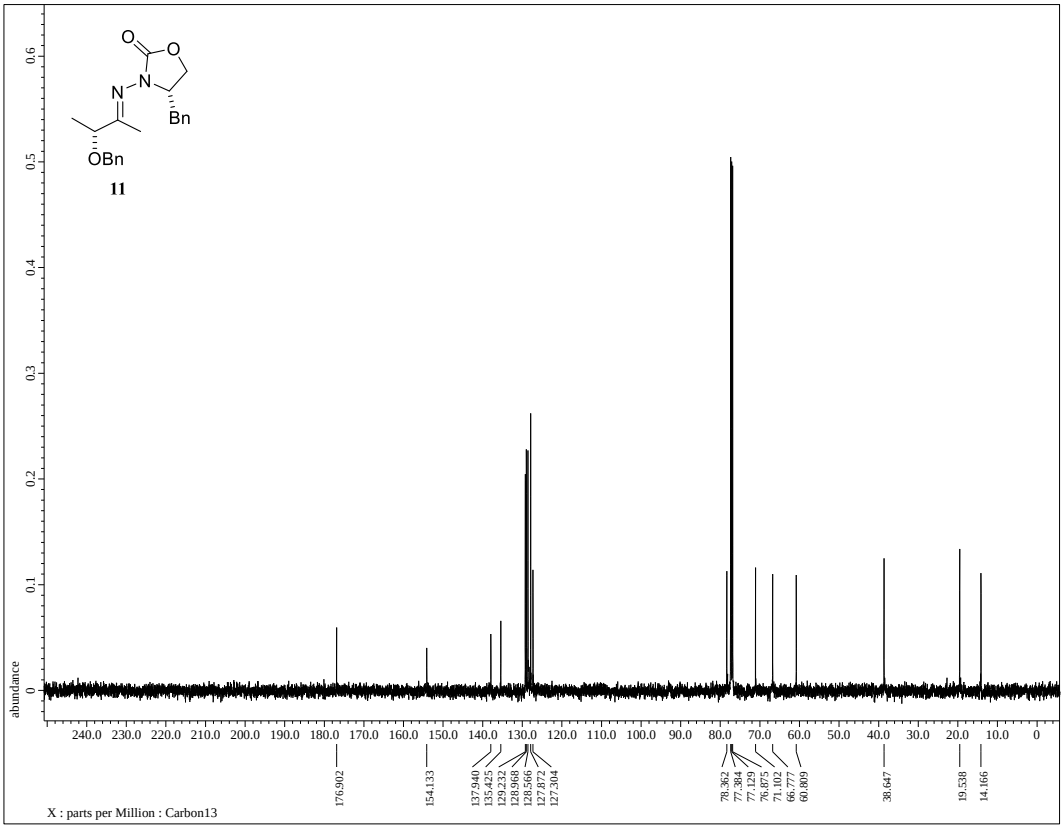
11
abundance
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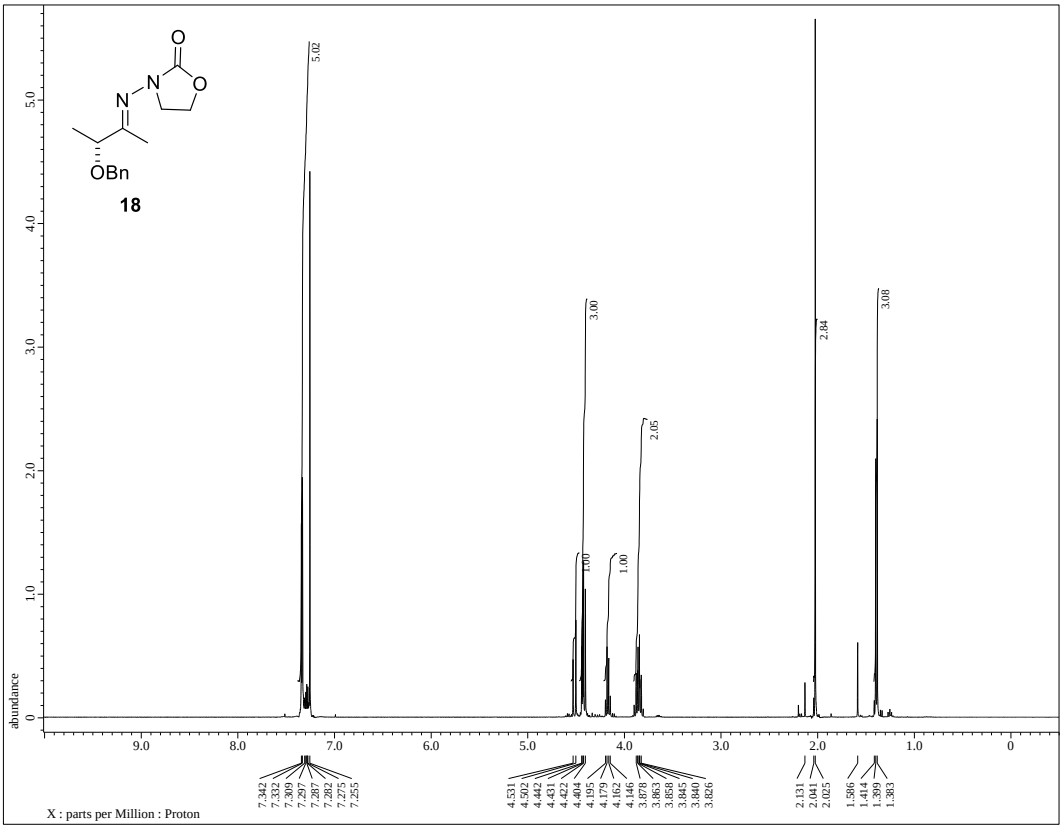
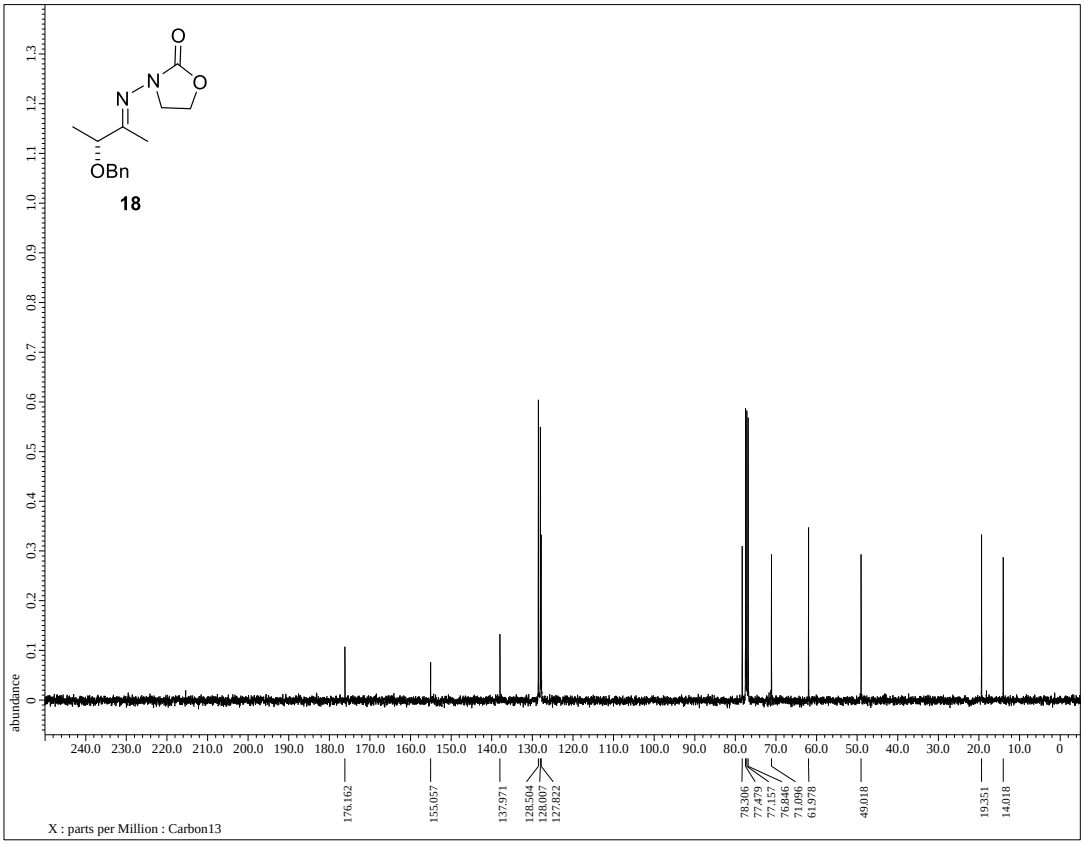
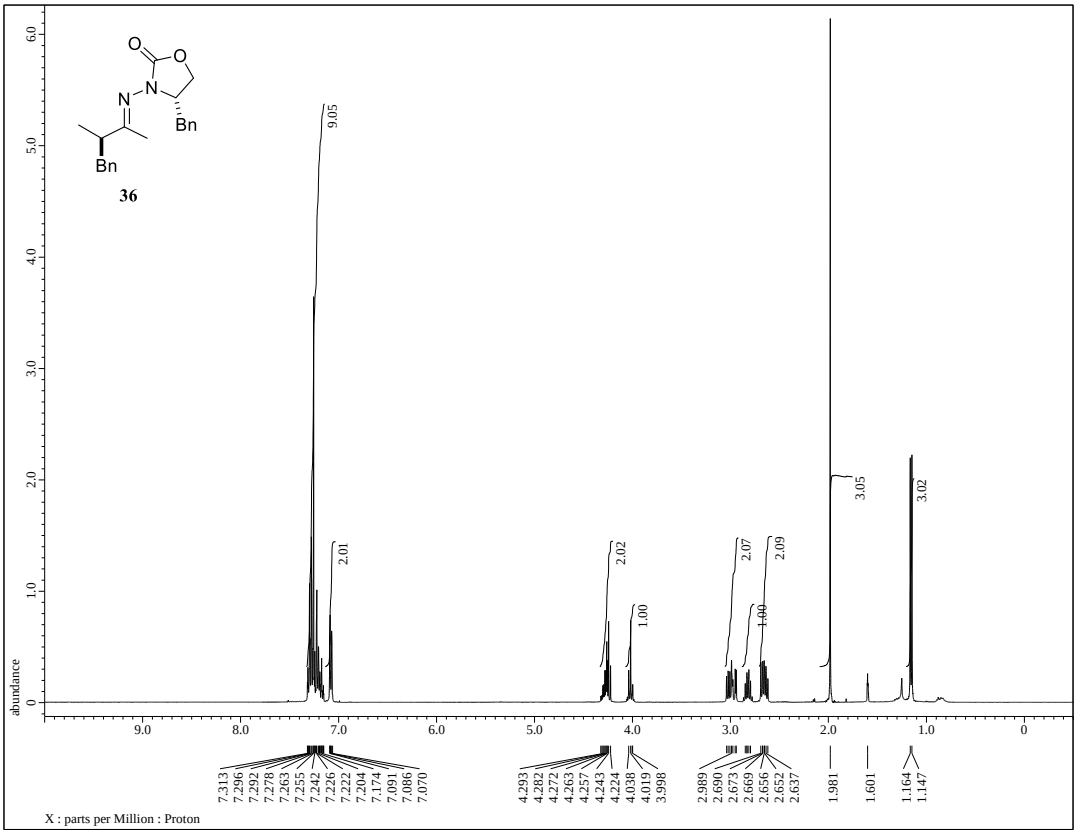
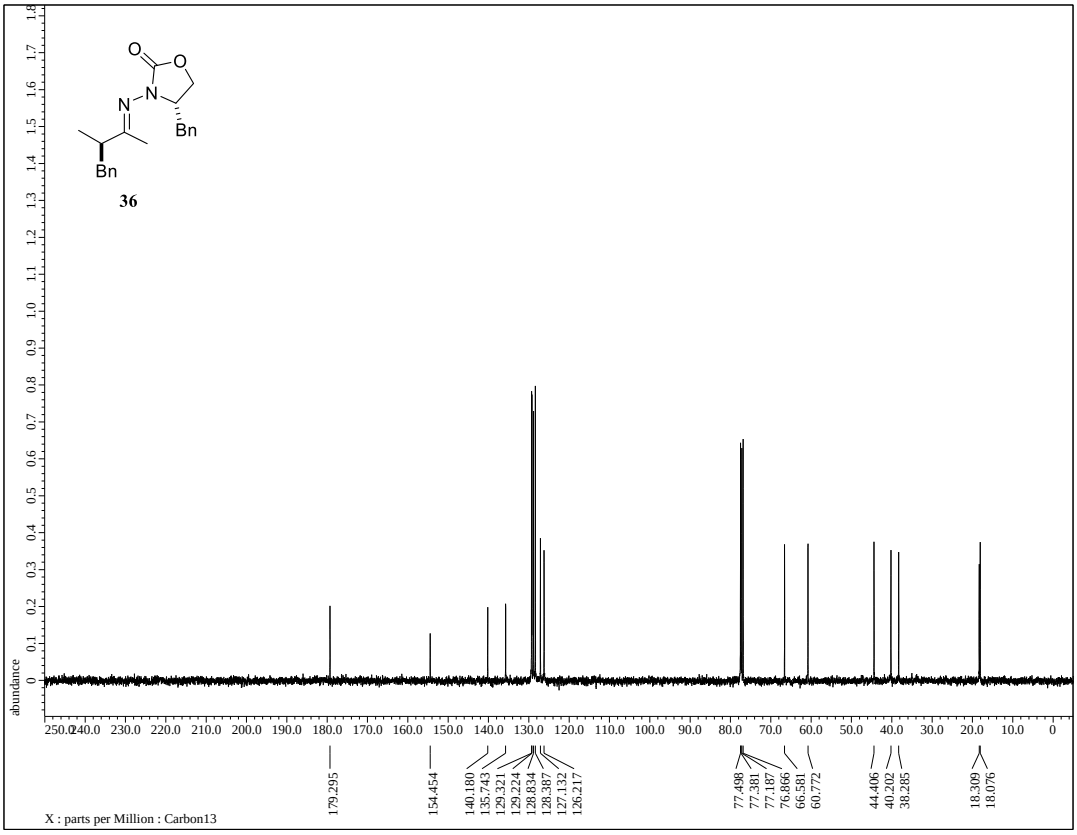

18
5.02
3.00
2.84
3.08
2.05
1.00
1.00
abundance
X : parts per Million : Proton


18
176.162
155.057
137.971
128.504
128.007
127.622
78.306
77.479
77.157
76.846
71.096
61.978
49.018
19.351
14.018
abundance
X : parts per Million : Carbon13


36
9.05
2.01
2.02
1.00
2.07
1.09
2.09
3.05
3.02
abundance
X : parts per Million : Proton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abundance
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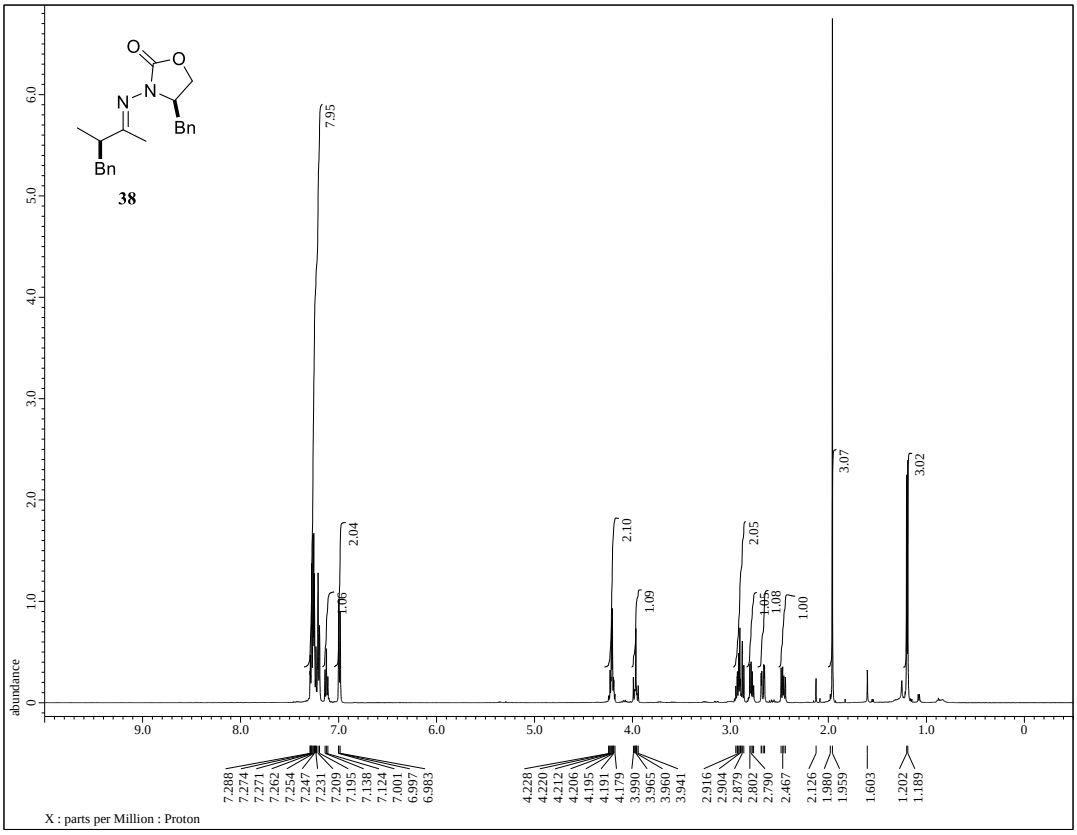
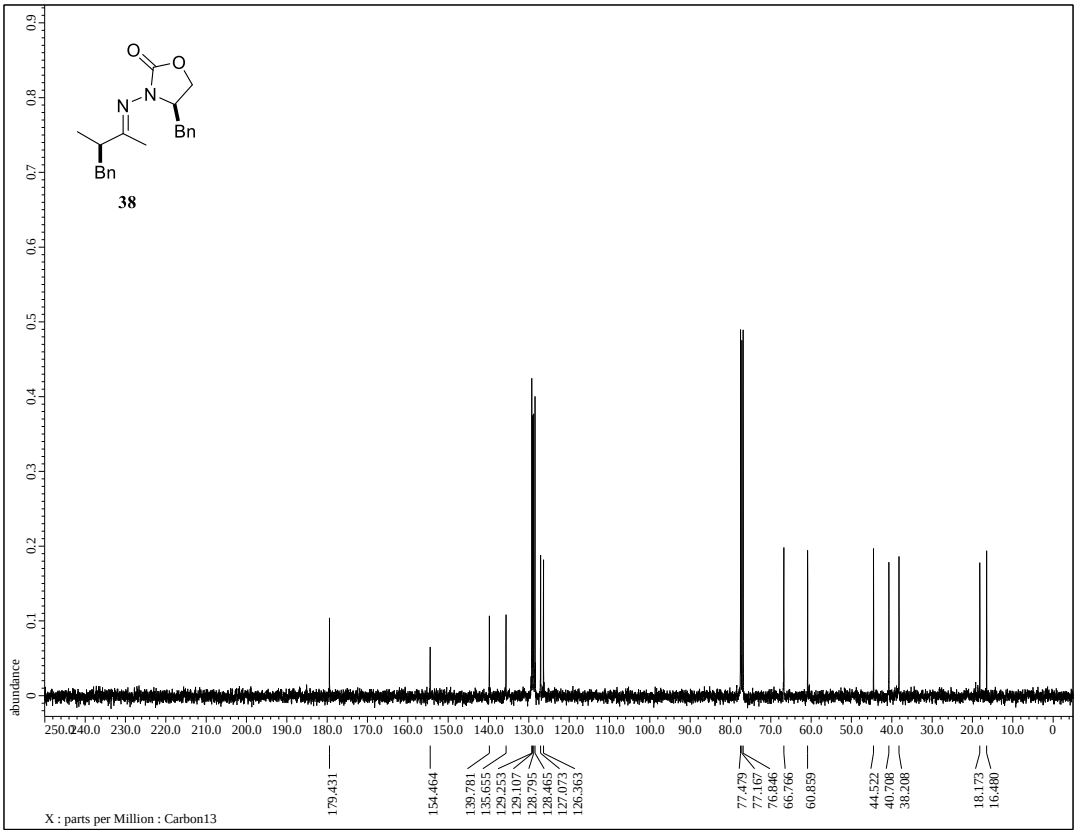
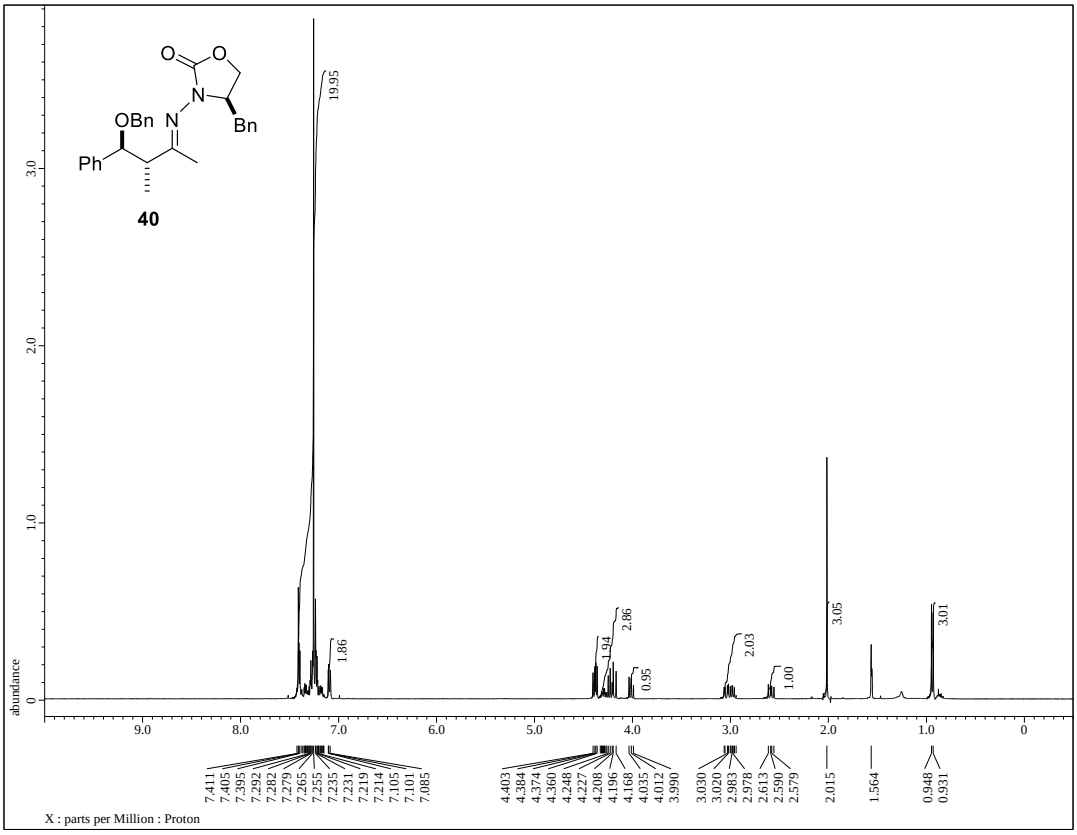
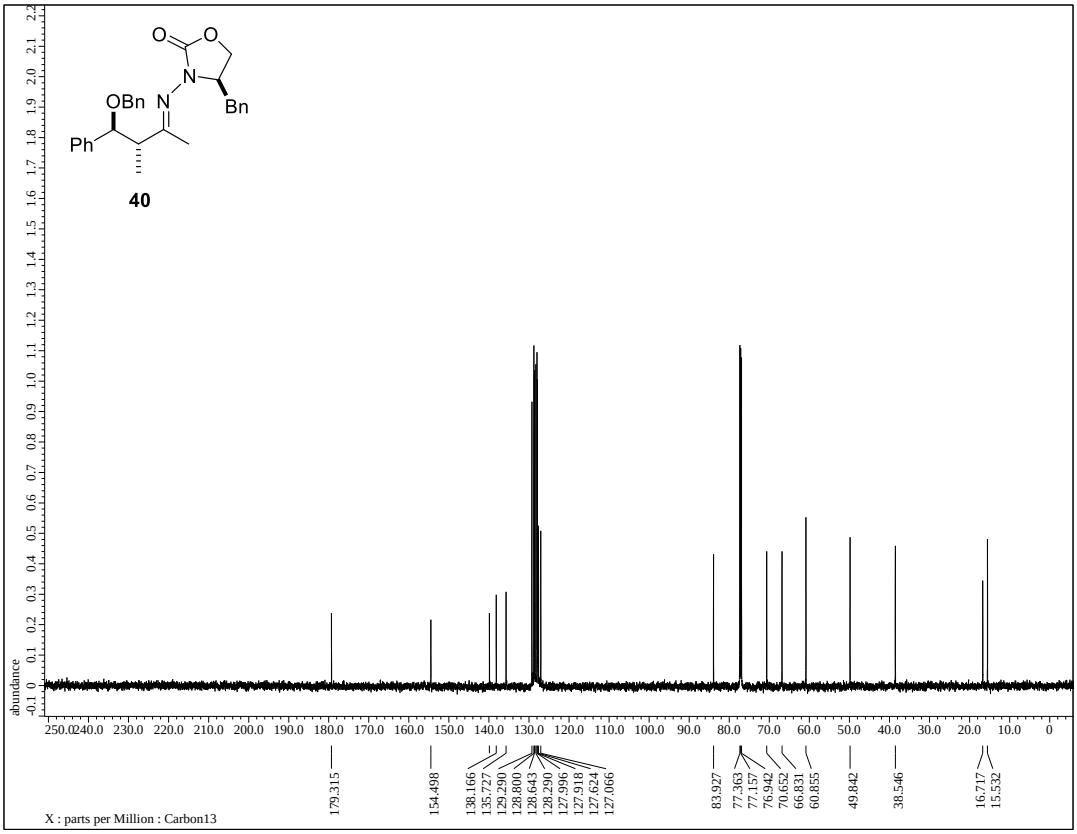
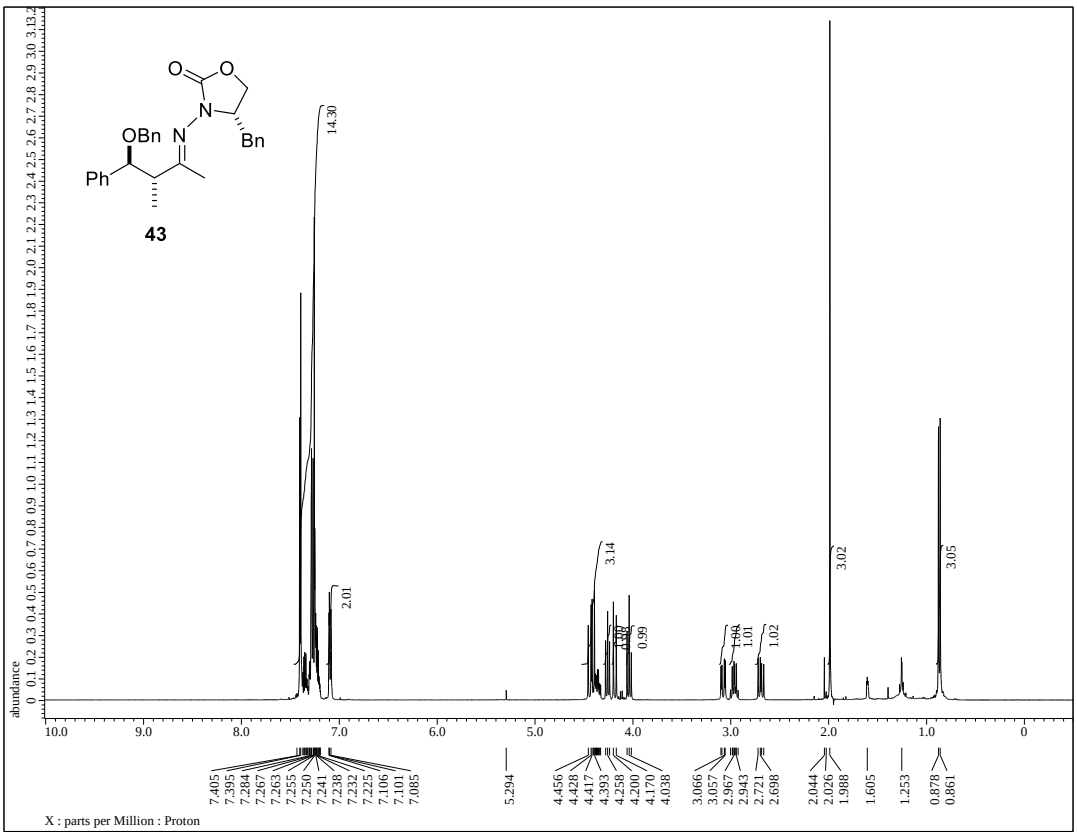
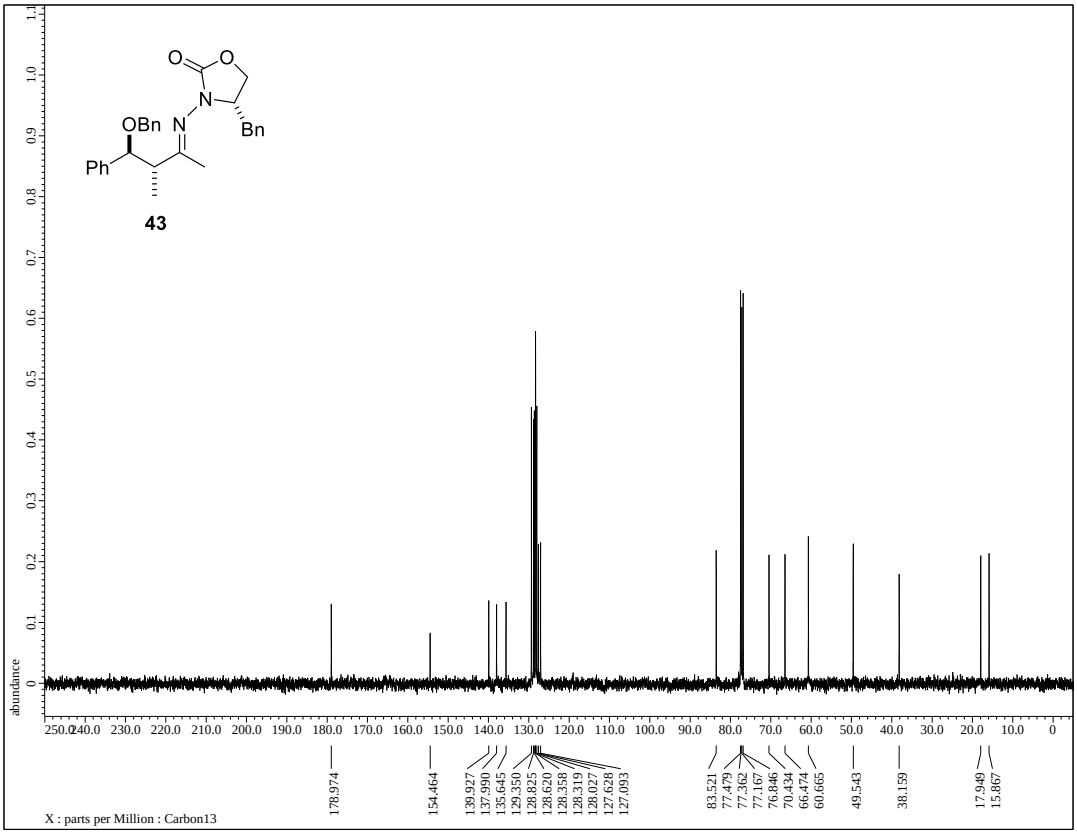

38
abundance
7.95
2.04
1.06
2.10
1.09
2.05
1.65
1.08
1.00
3.07
3.02
7.288
7.274
7.271
7.262
7.254
7.247
7.231
7.209
7.195
7.138
7.124
7.001
6.997
6.983
4.228
4.220
4.212
4.206
4.195
4.191
4.179
3.990
3.965
3.960
3.941
2.916
2.904
2.879
2.802
2.790
2.467
2.126
1.980
1.959
1.603
1.202
1.189
X : parts per Million : Proton

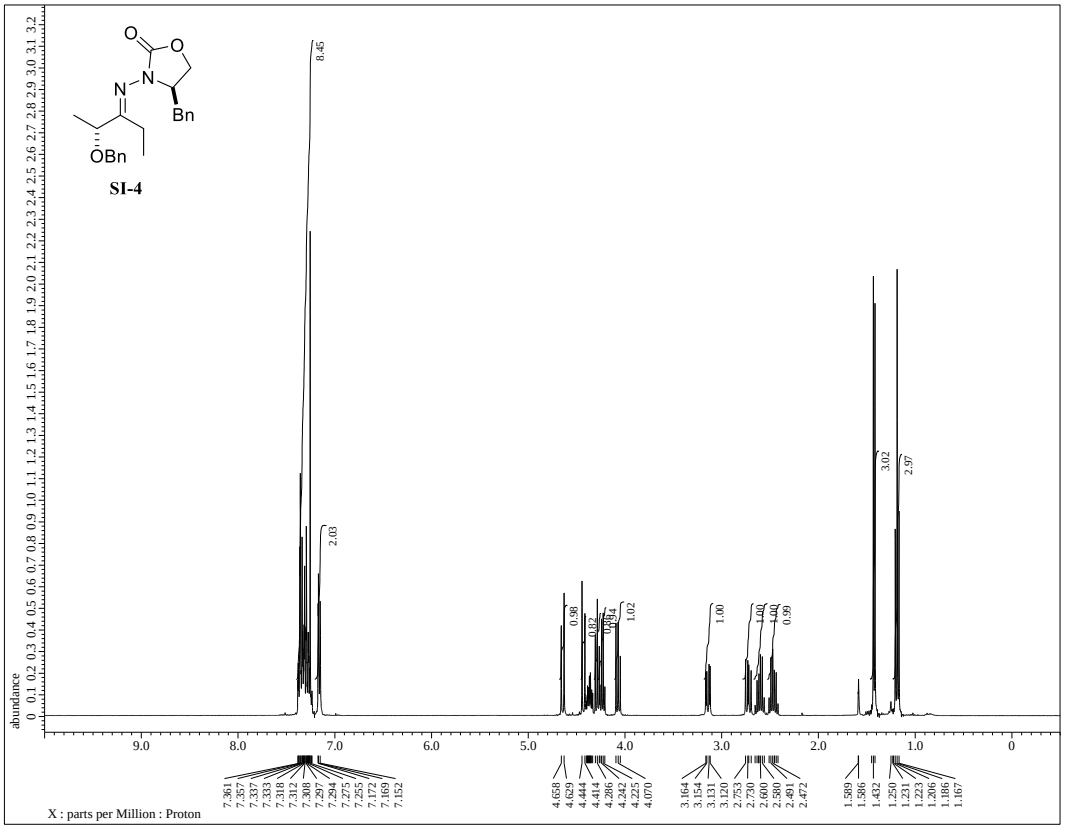

38
abundance
179.431
154.464
139.781
135.655
129.253
129.107
128.795
128.465
127.073
126.363
77.479
77.167
76.846
66.766
60.859
44.522
40.708
38.208
18.173
16.480
X : parts per Million : Carbon13

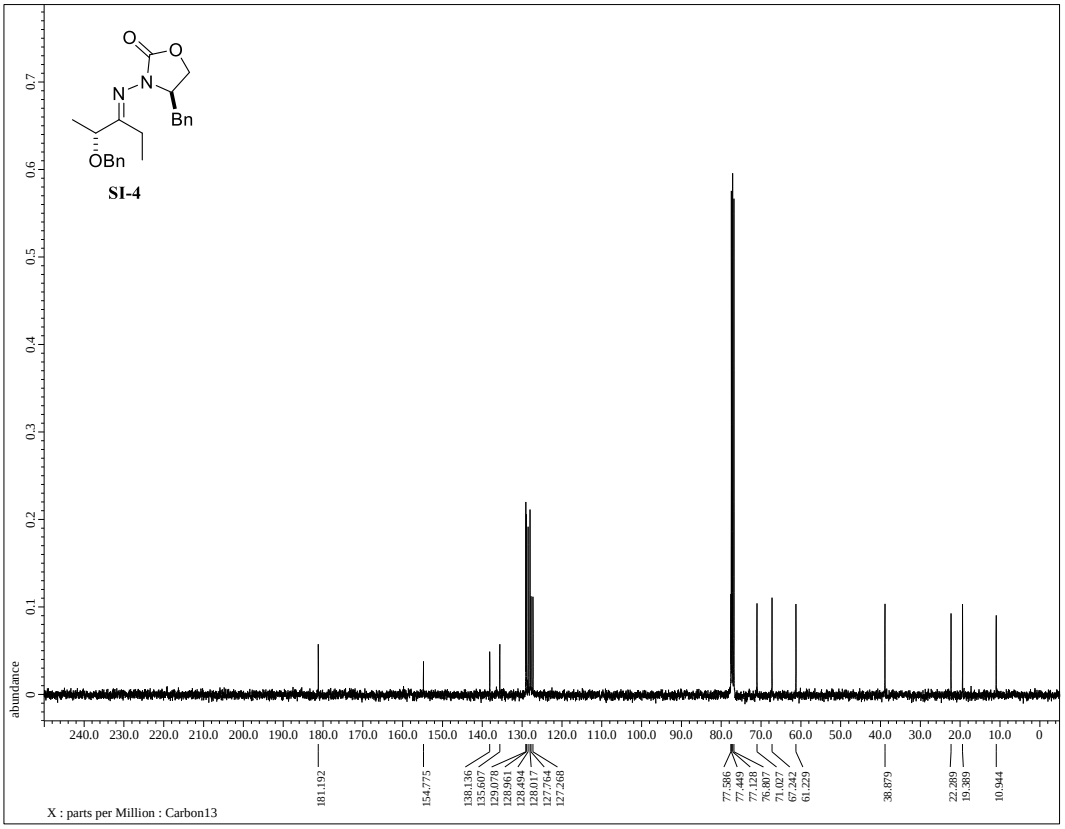

40
19.95
1.86
2.86
1.94
0.95
2.03
1.00
3.05
3.01
abundance
X : parts per Million : Proton

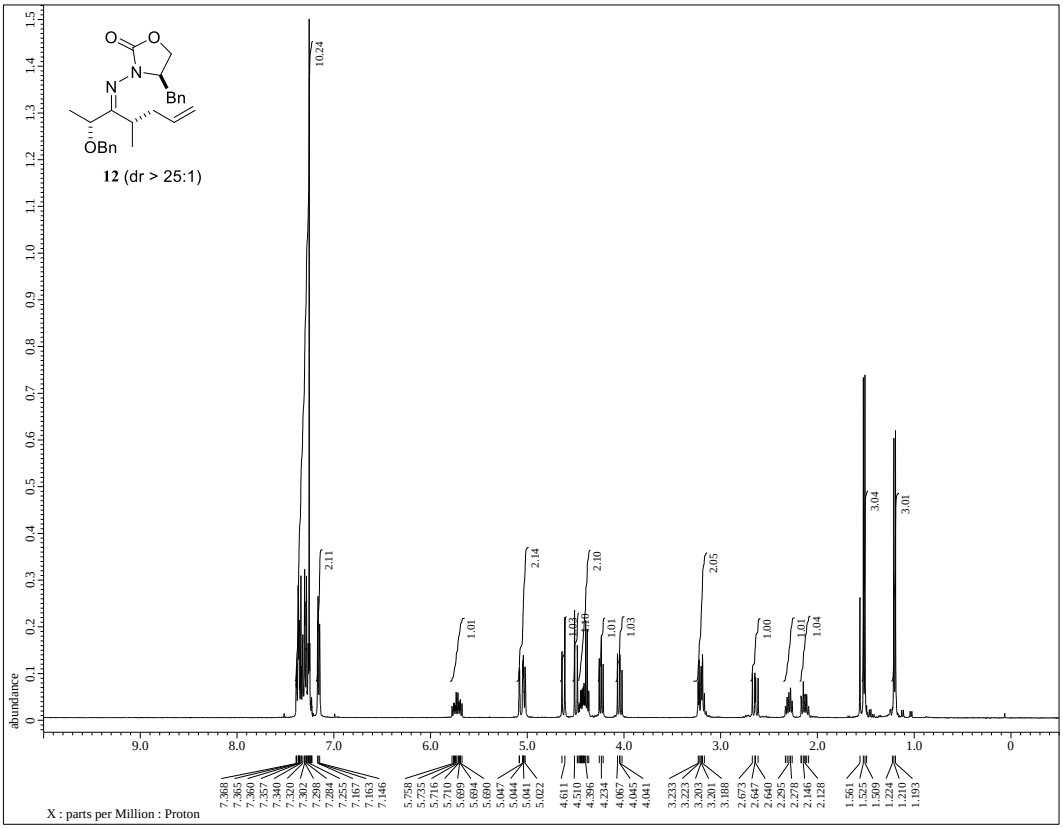

40
179.315
154.498
138.166
135.727
129.290
128.800
128.643
128.290
127.996
127.918
127.624
127.066
83.927
77.363
77.157
76.942
70.652
66.831
60.855
49.842
38.546
16.717
15.532
abundance
X : parts per Million : Carbon13

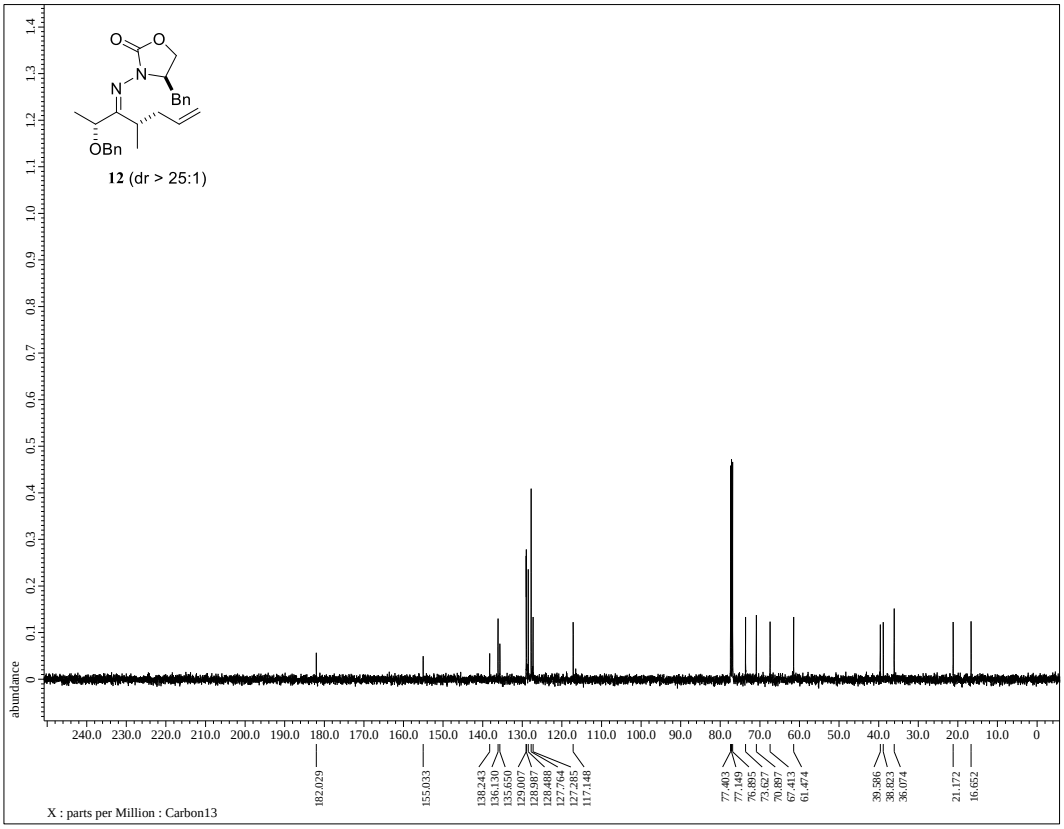

43
14.30
3.14
2.01
0.99
1.00
1.00
1.01
1.02
3.02
3.05
abundance
X : parts per Million : Proton

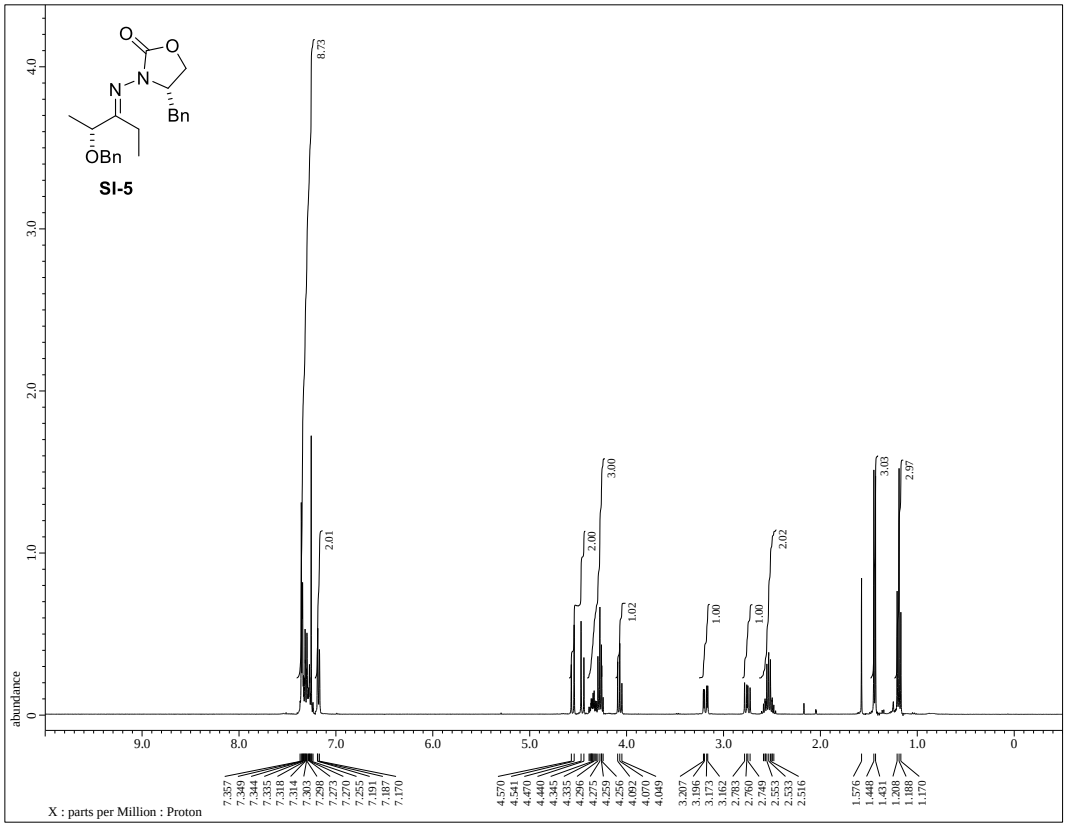

43
abundance
X : parts per Million : Carbon13


SI-4
abundance
X : parts per Million : Proton


SI-4
abundance
X : parts per Million : Carbon13


12 (dr > 25:1)
abundance
X : parts per Million : Proton


12 (dr > 25:1)
abundance
X : parts per Million : Carbon13


SI-5
abundance
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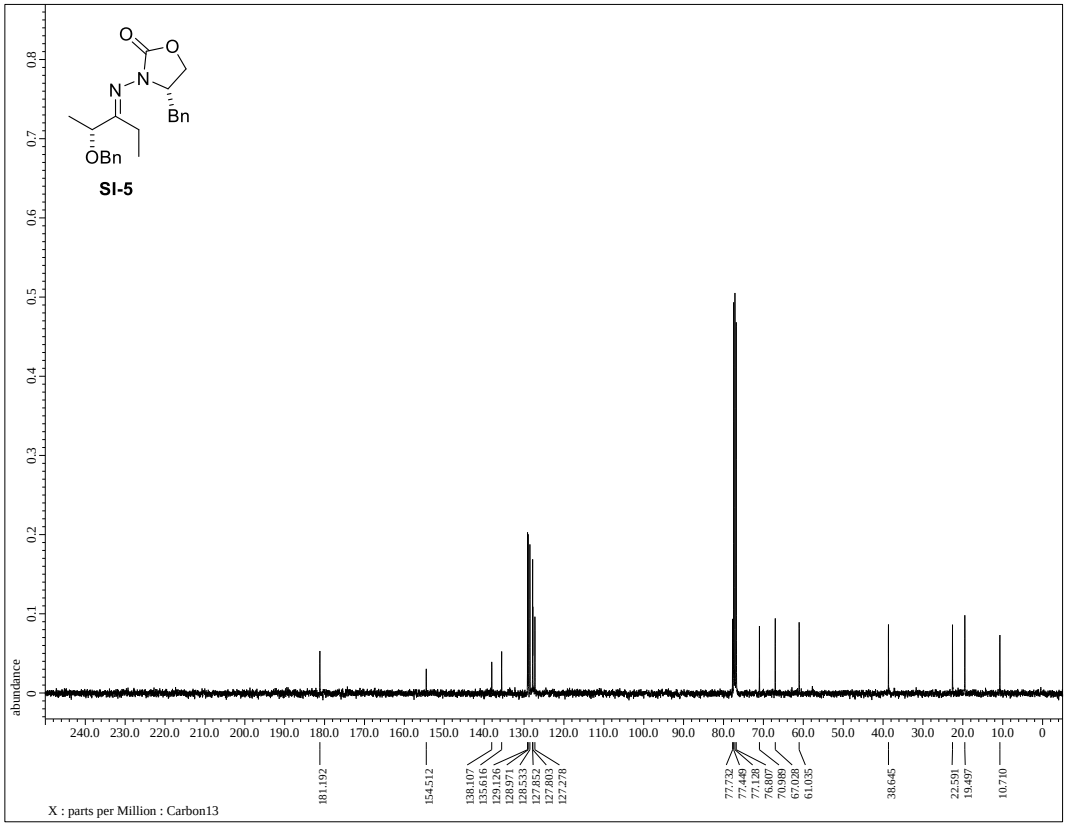
SI-5
abundance
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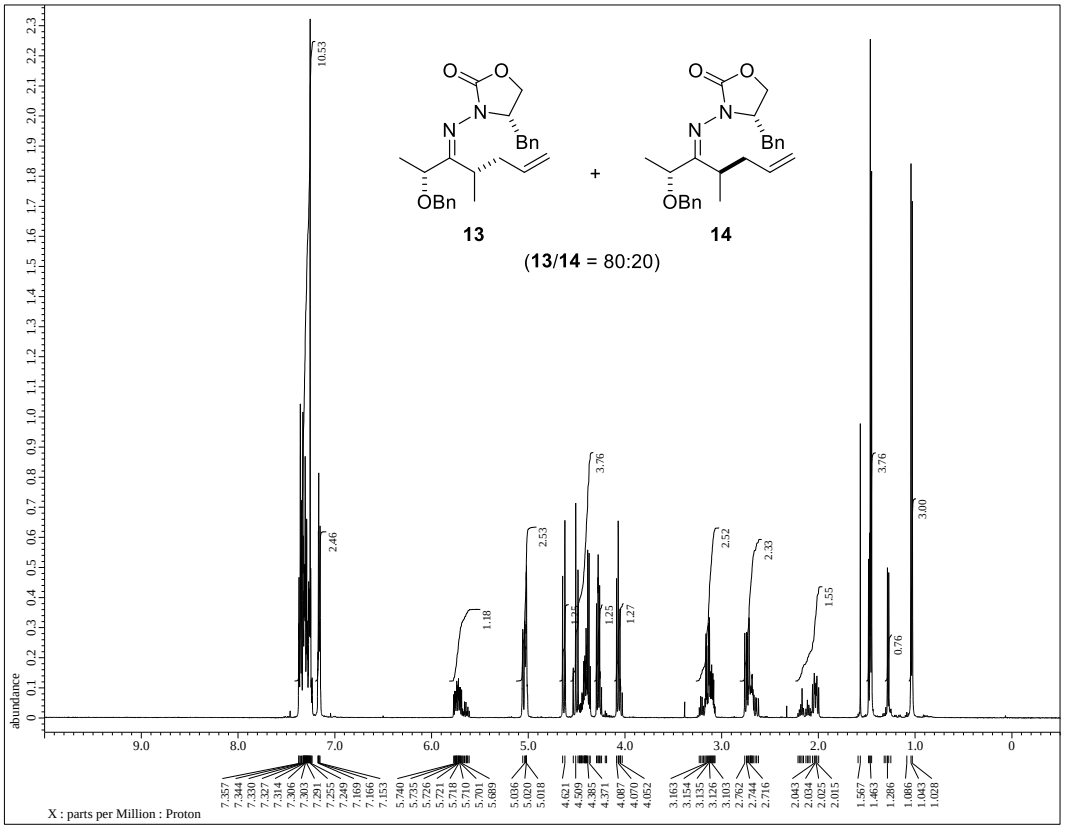
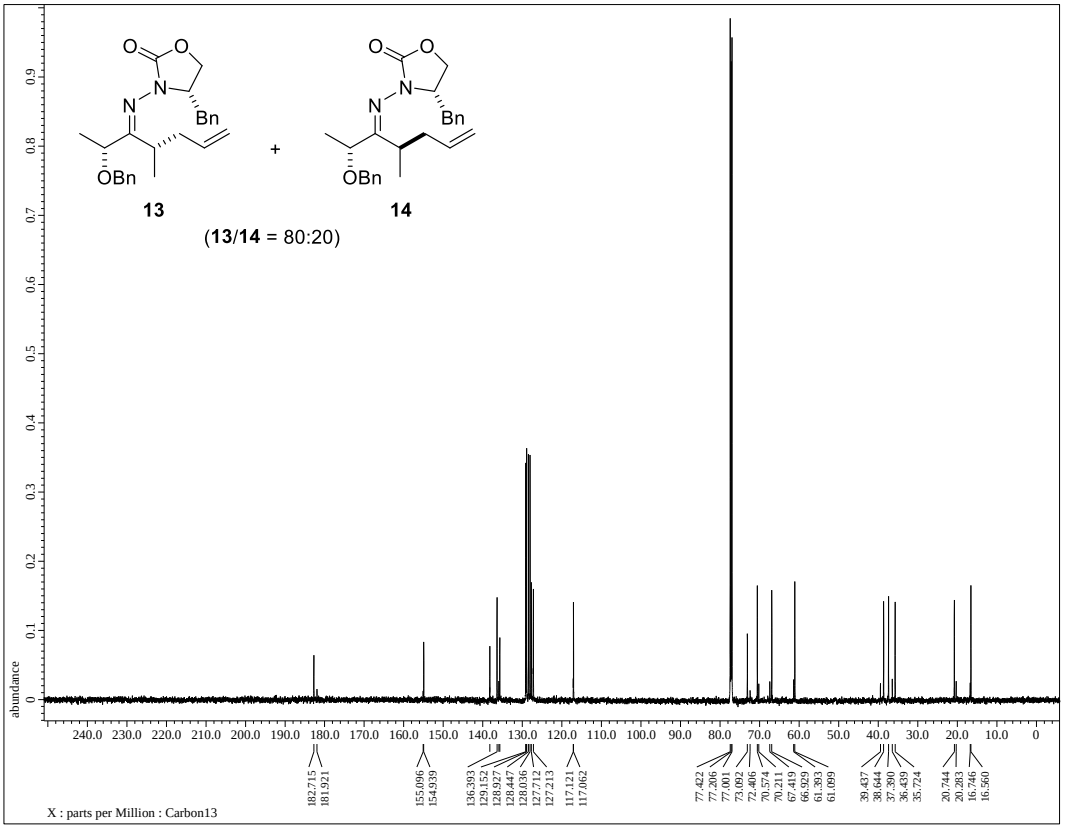
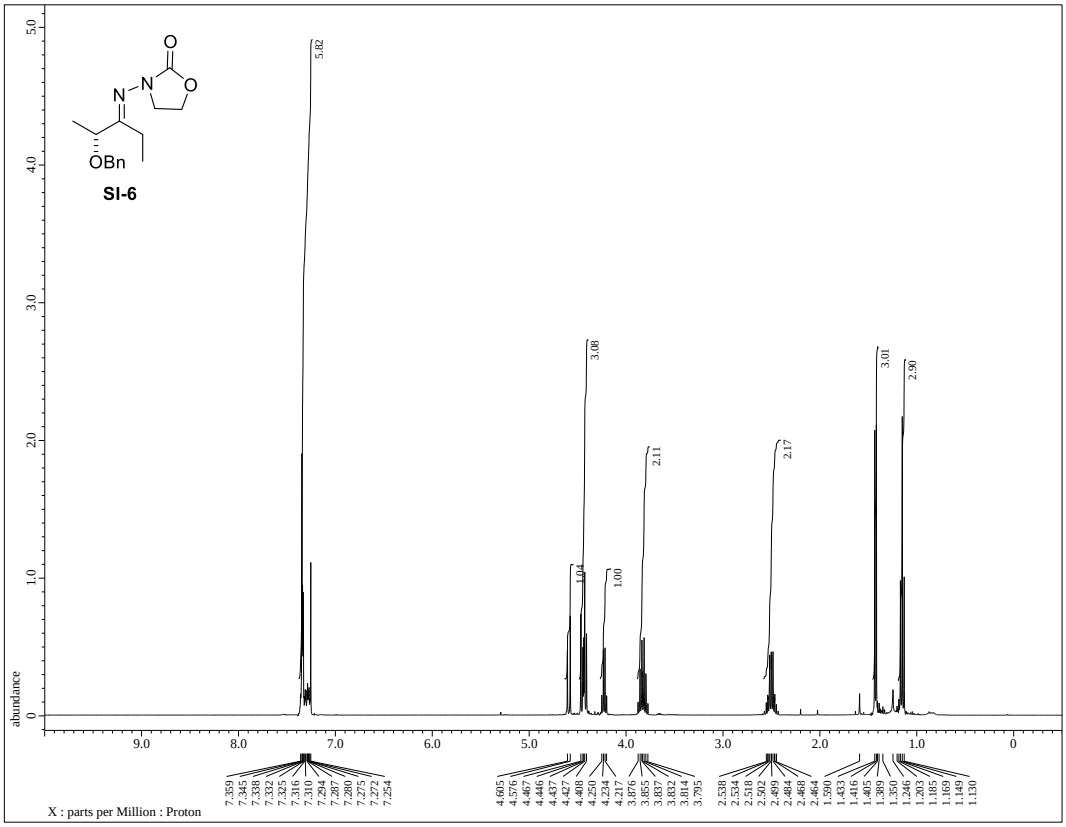
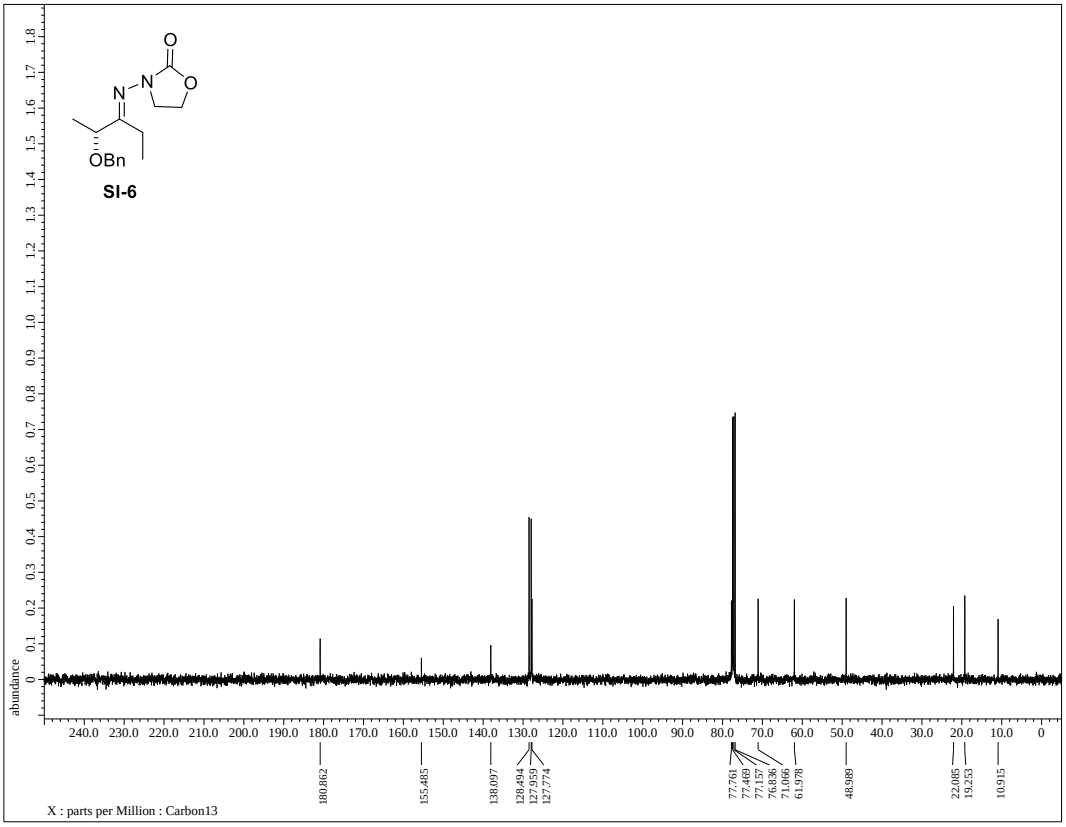
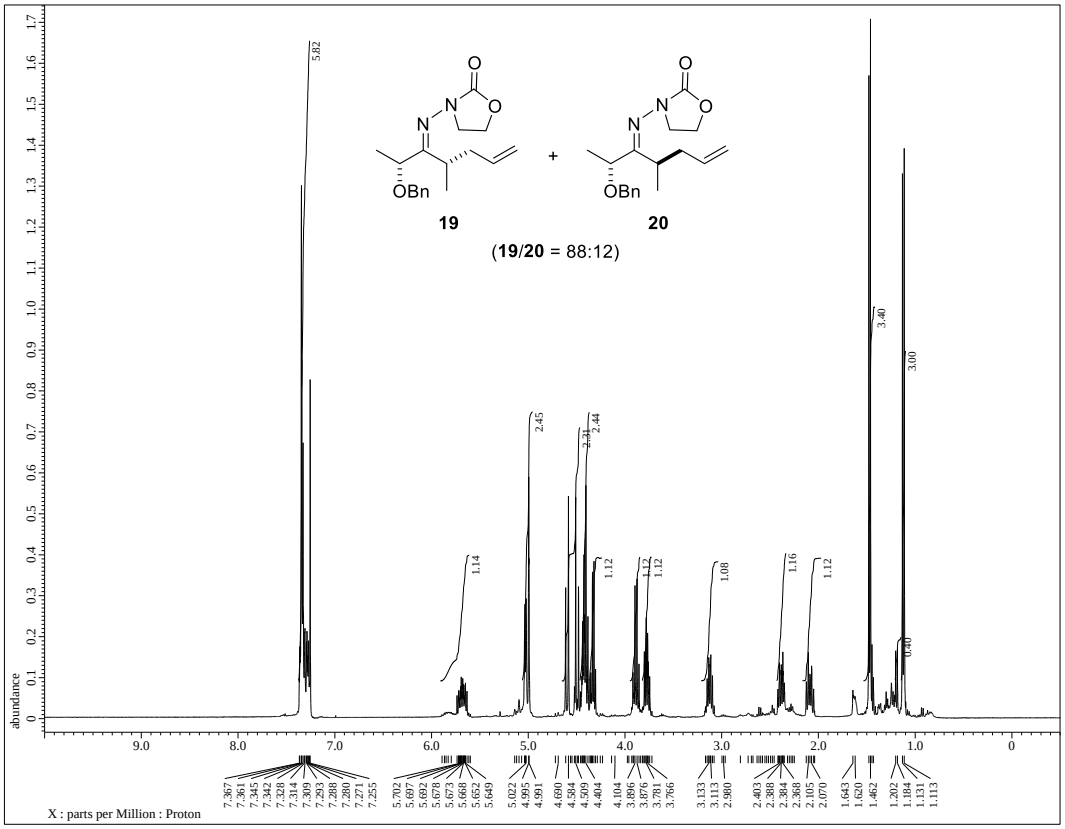
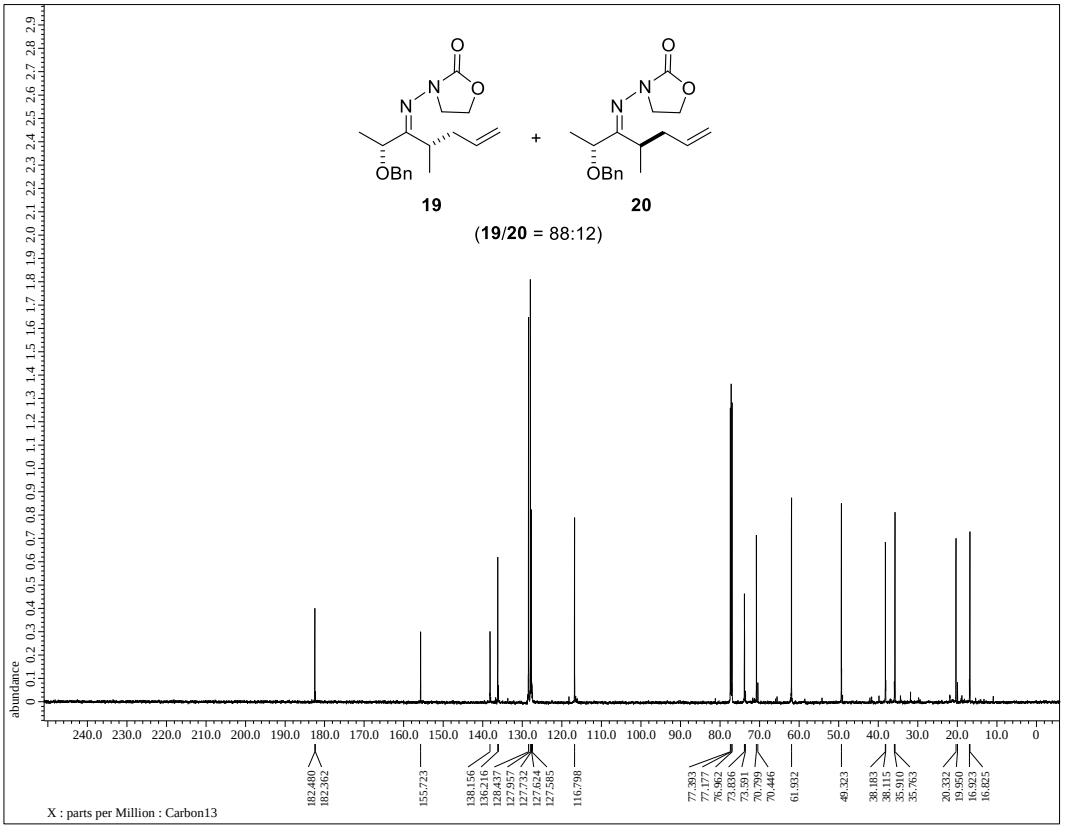

13
14
(13/14 = 80:20)
abundance
X : parts per Million : Proton

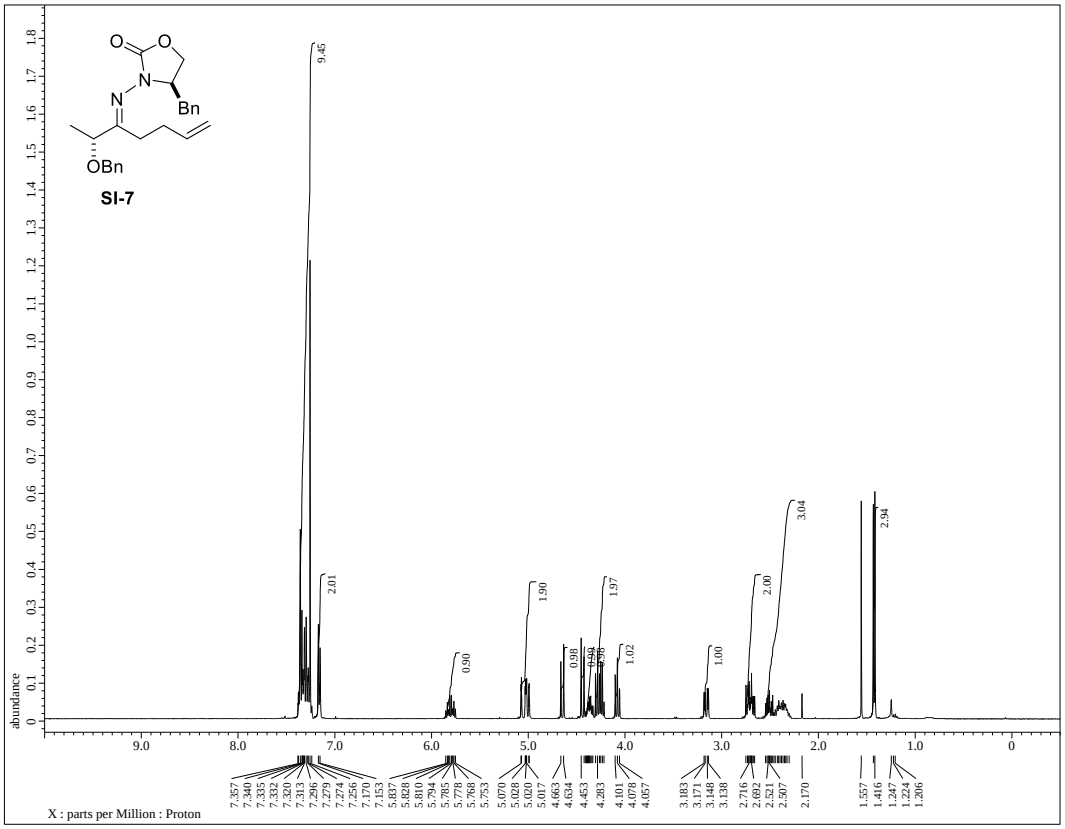

13
14
(13/14 = 80:20)
abundance
X : parts per Million : Carbon13

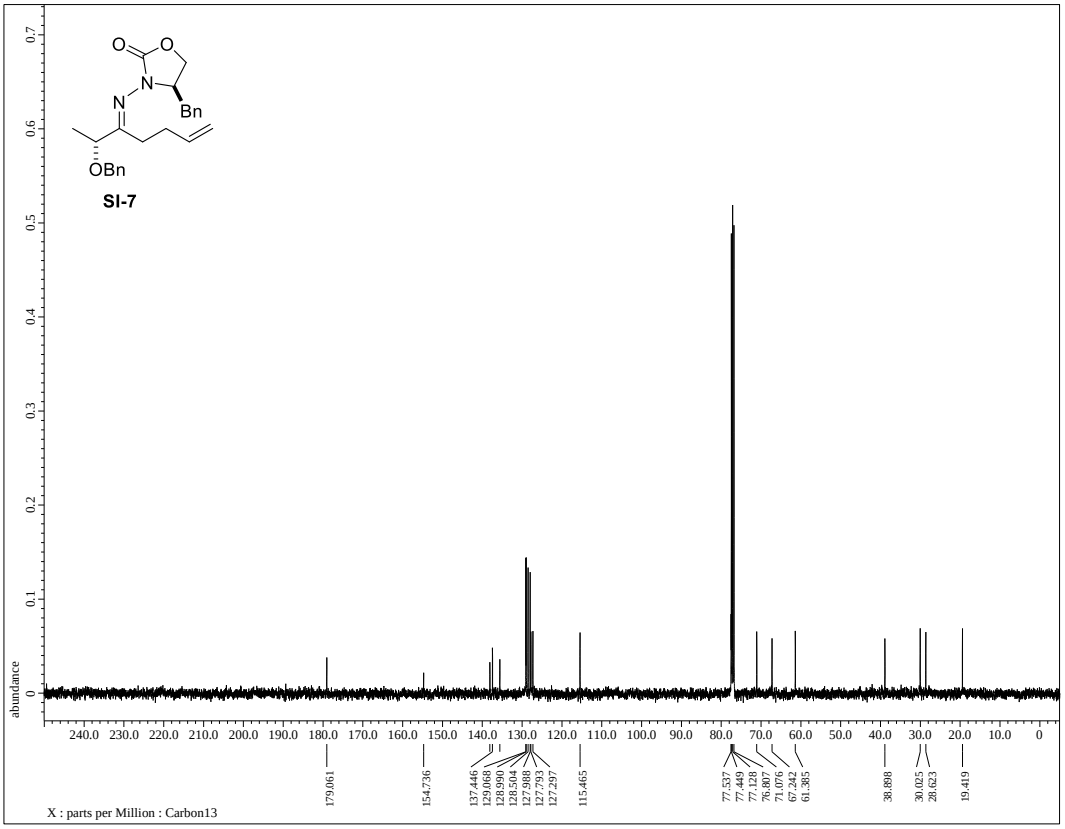

SI-6
abundance
X : parts per Million : Proton

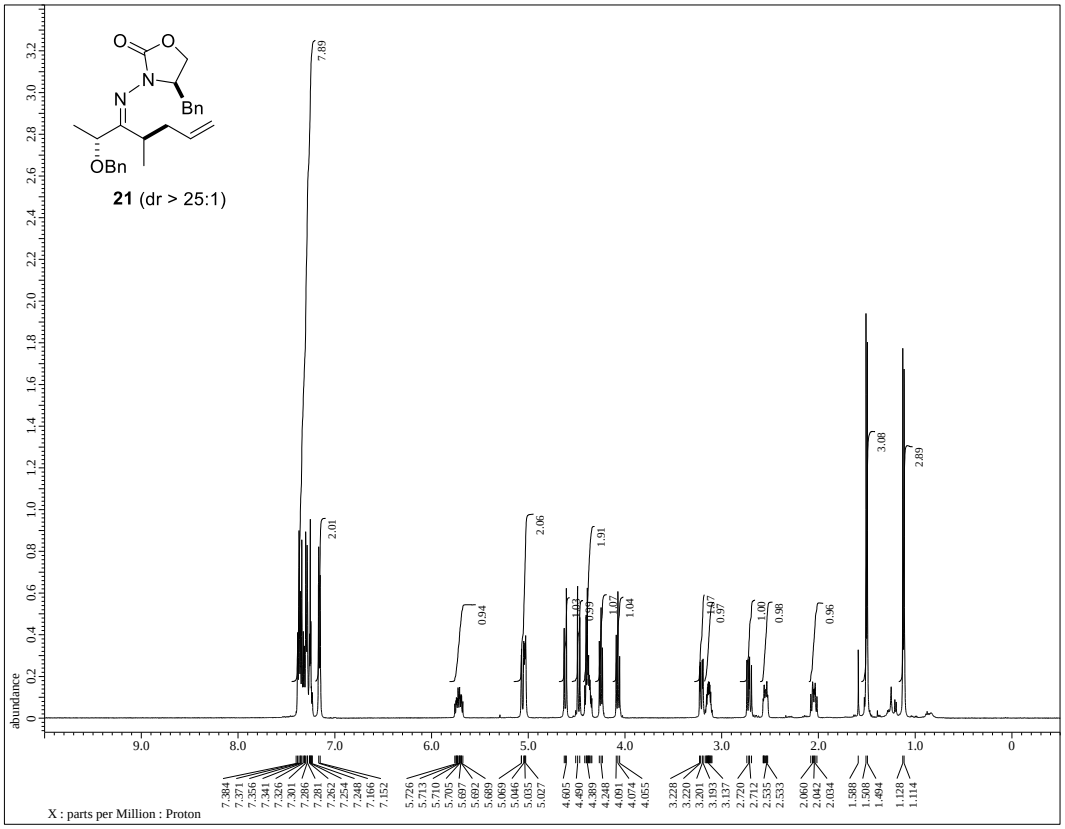

SI-6
abundance
X : parts per Million : Carbon13

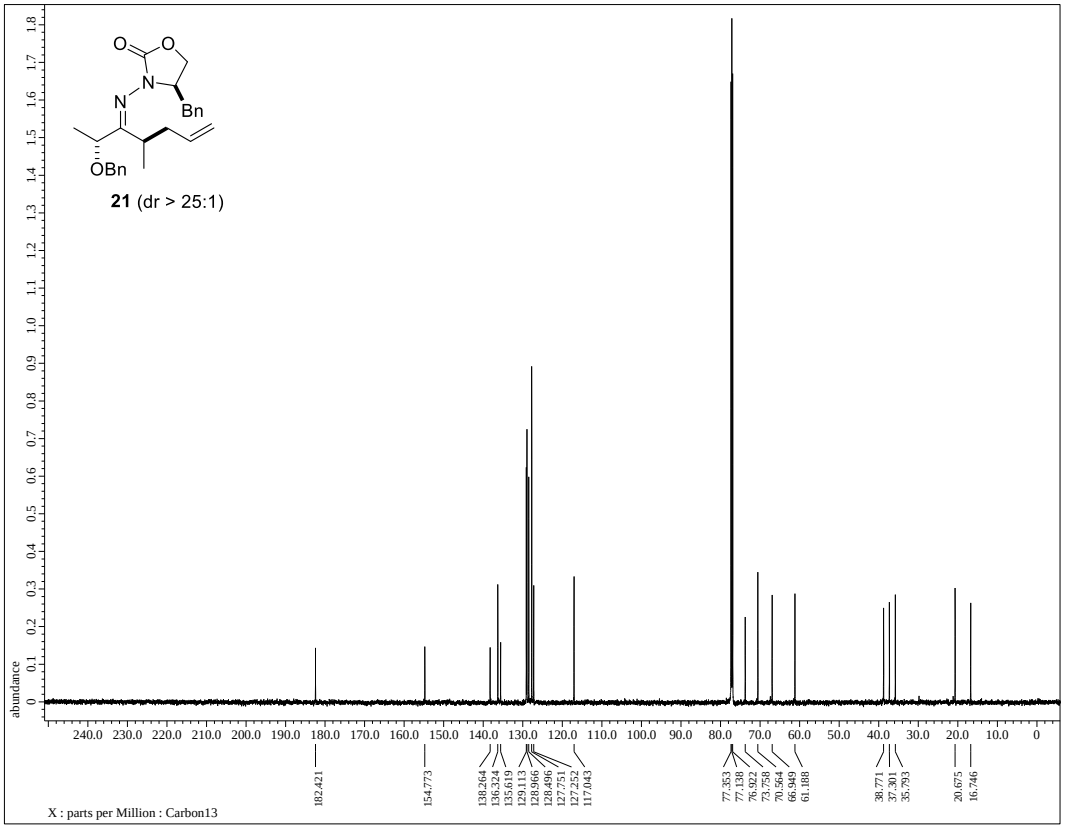

19
20
(19/20 = 88:12)
abundance
X : parts per Million : Proton


19
20
(19/20 = 88:12)
abundance
X : parts per Million : Carbon13


SI-7
abundance
X : parts per Million : Proton


SI-7
abundance
X : parts per Million : Carbon13


Bn
OBn
21 (dr > 25:1)
abundance
X : parts per Million : Proton


Bn
OBn
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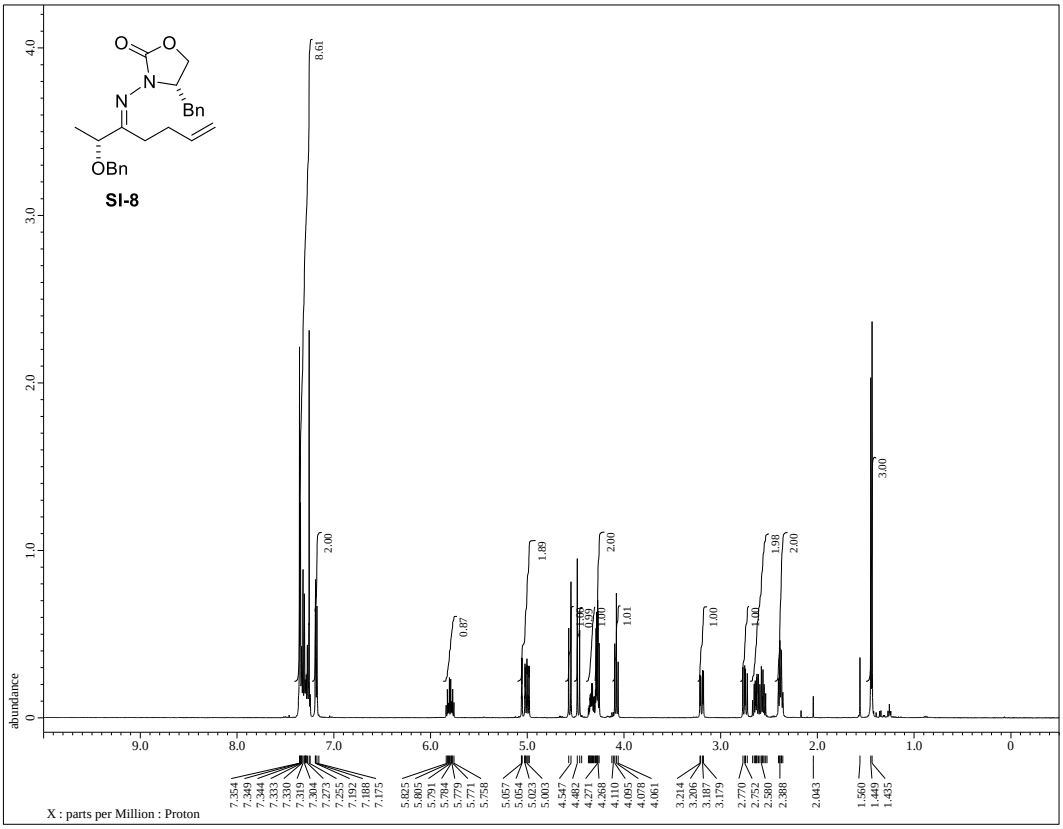
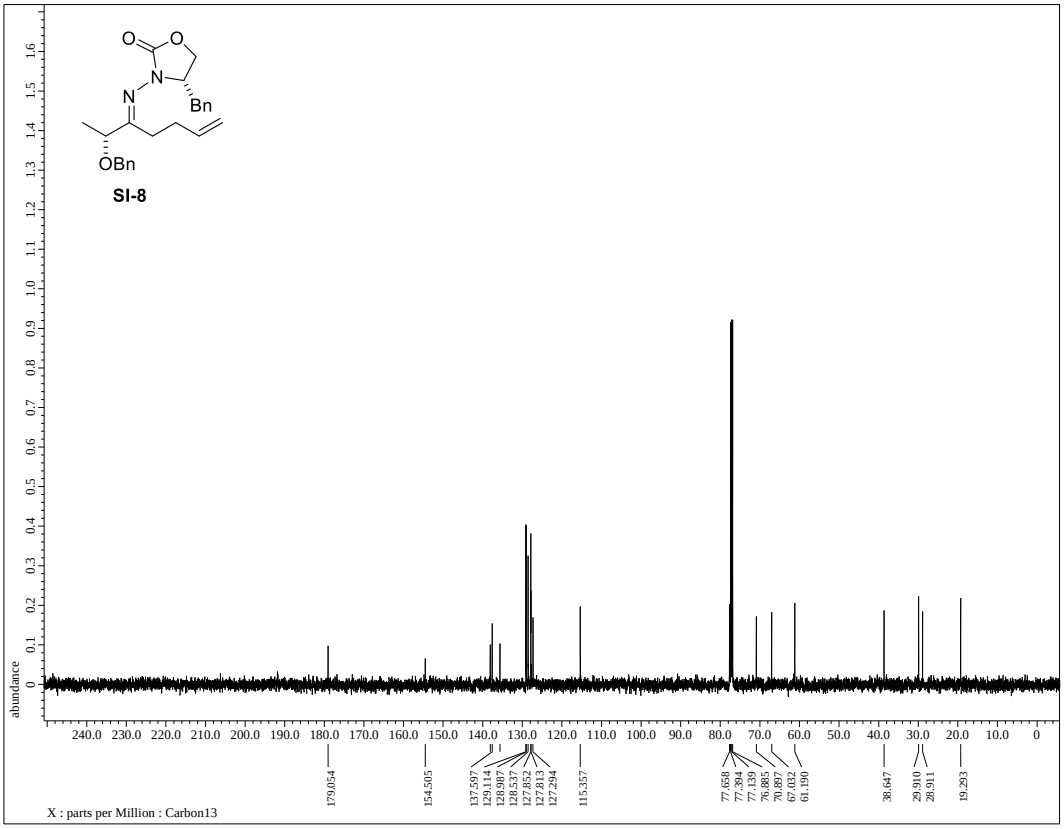
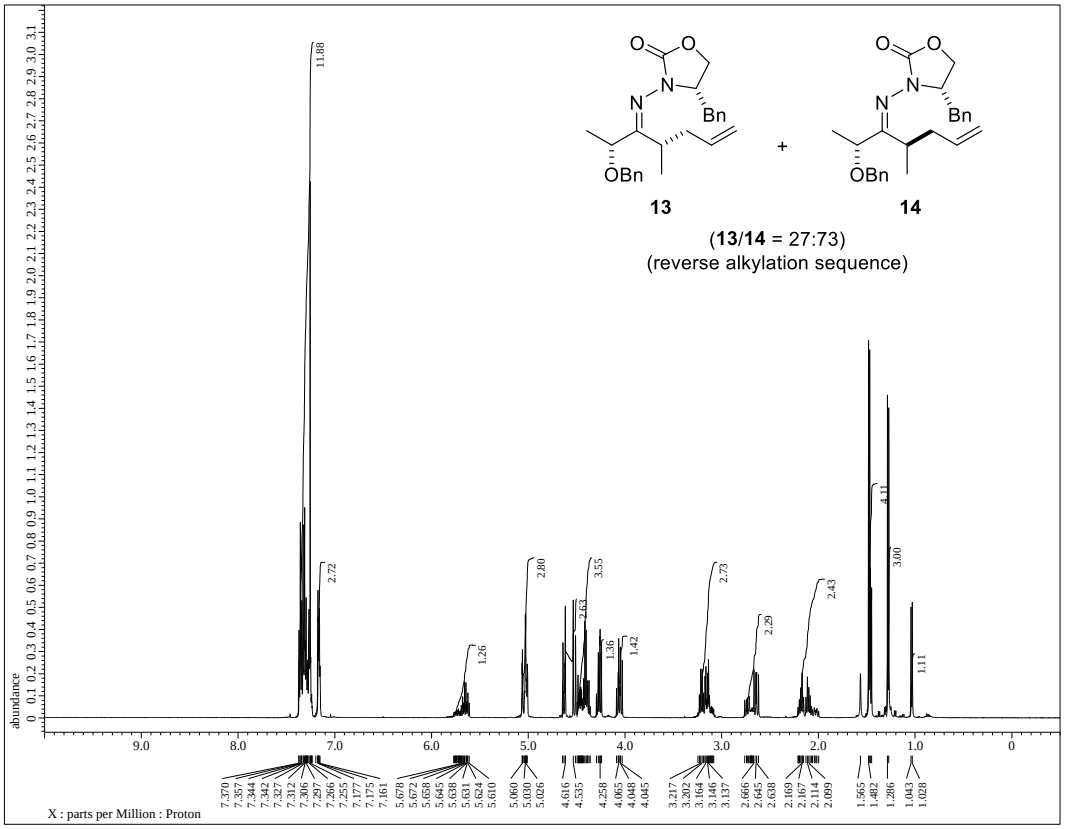
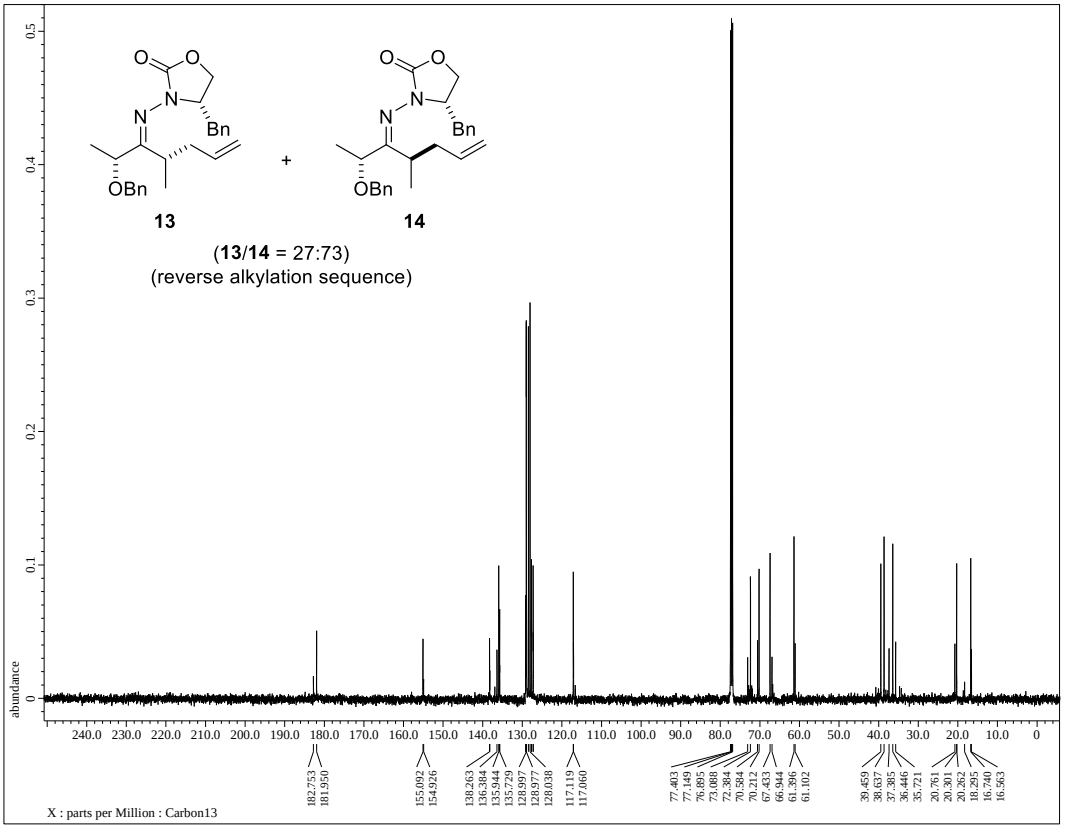
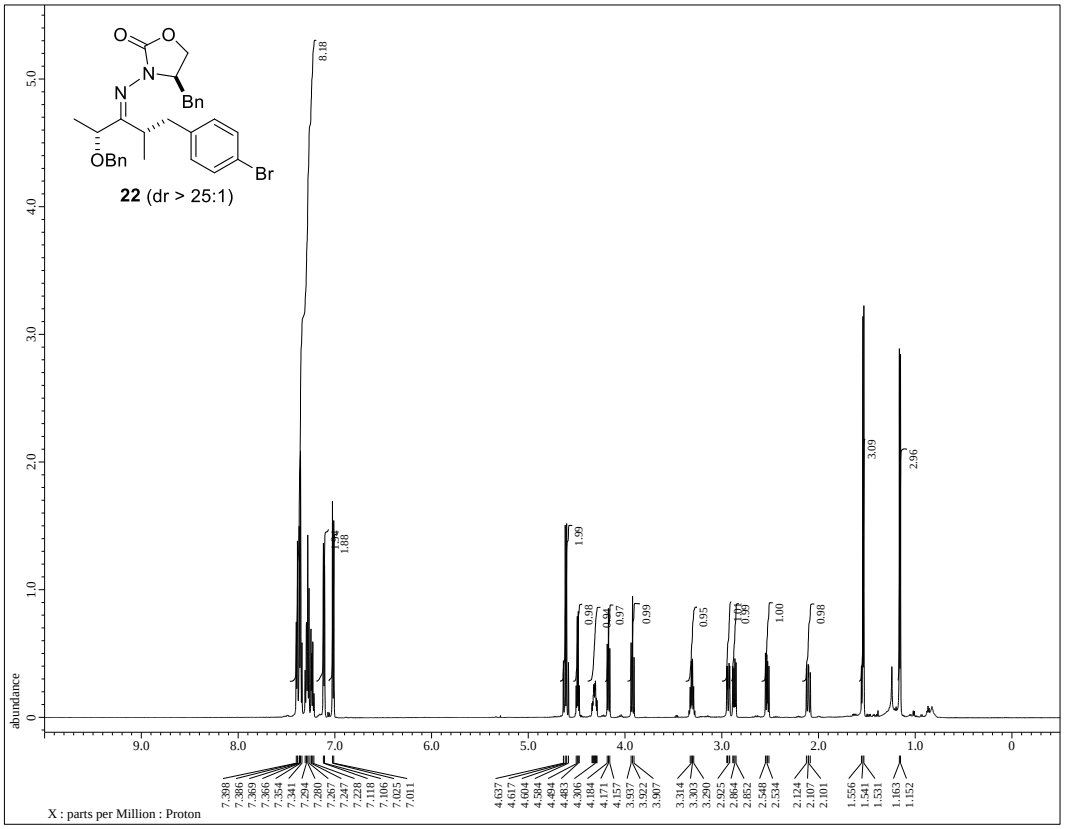
abundance
X : parts per Million : Carbon13

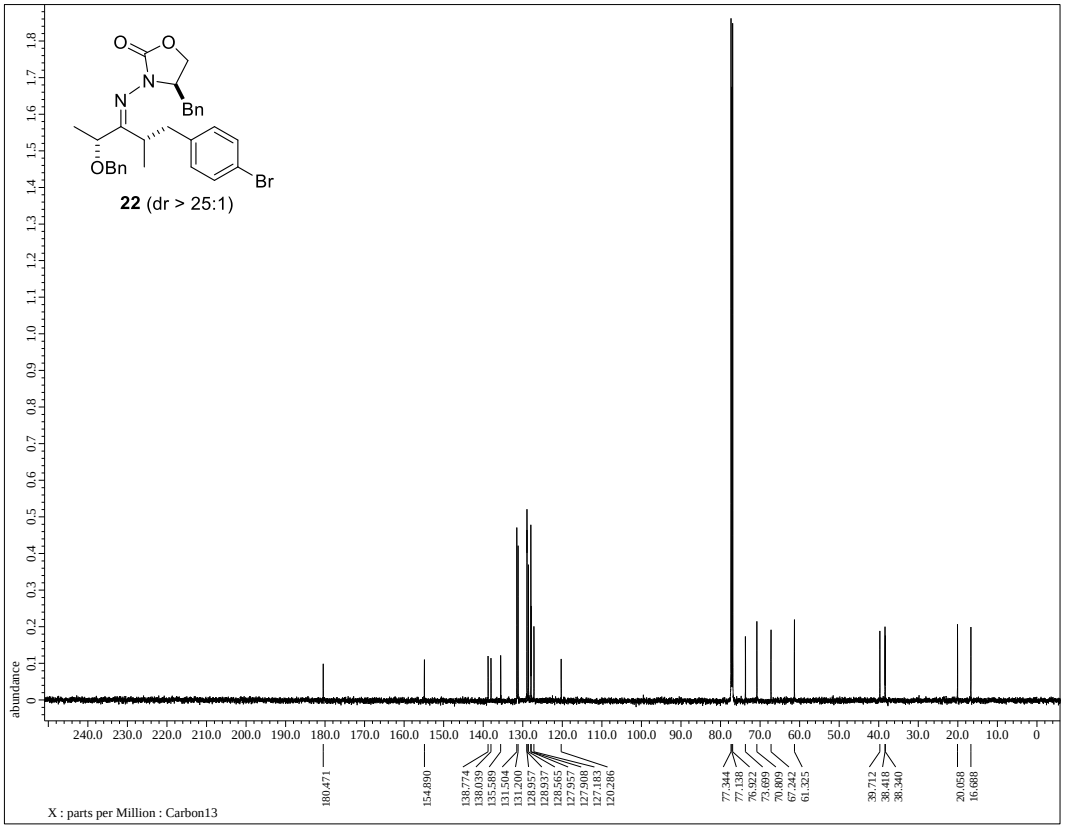

SI-8
abundance
X : parts per Million : Proton

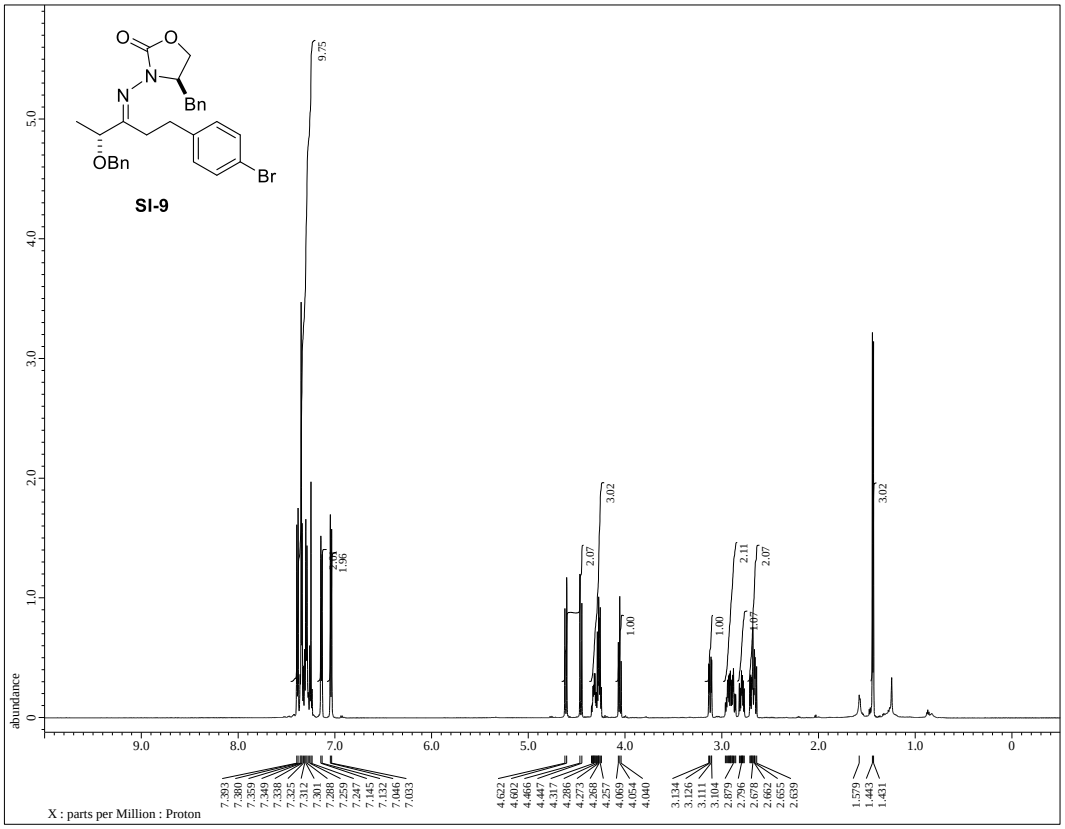

SI-8
abundance
X : parts per Million : Carbon13

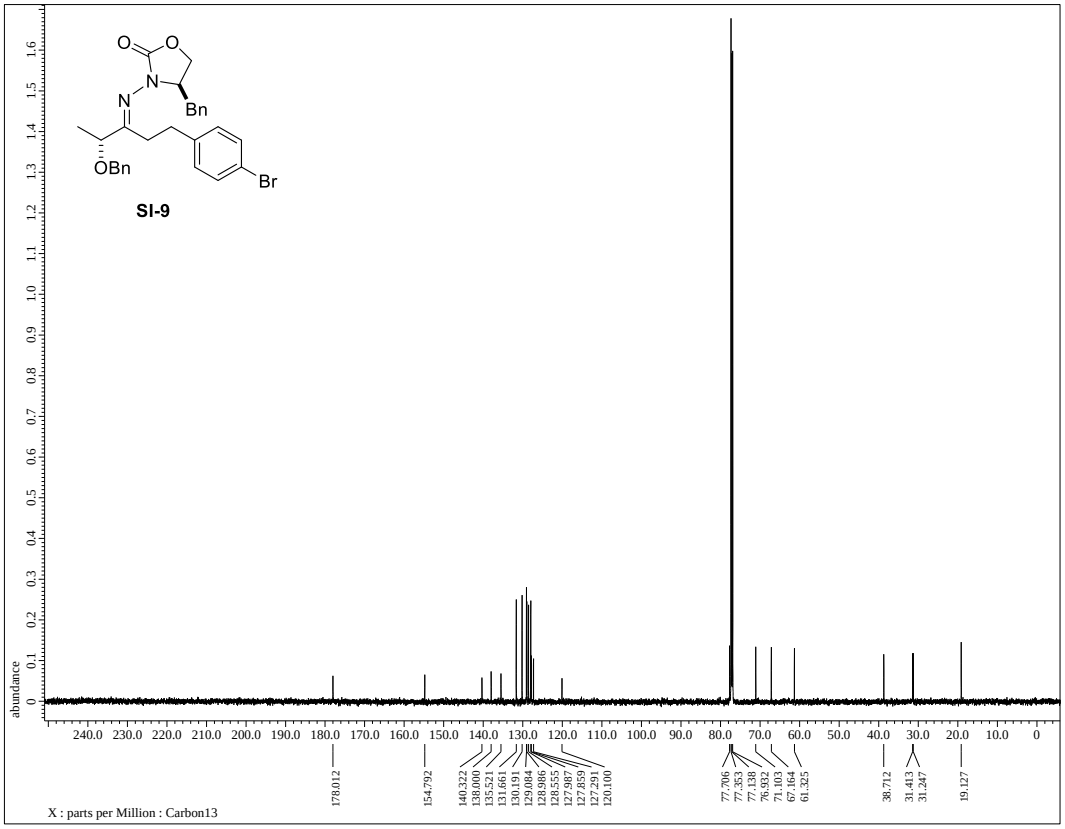

13
14
(13/14 = 27:73)
(reverse alkylation sequence)
X : parts per Million : Proton

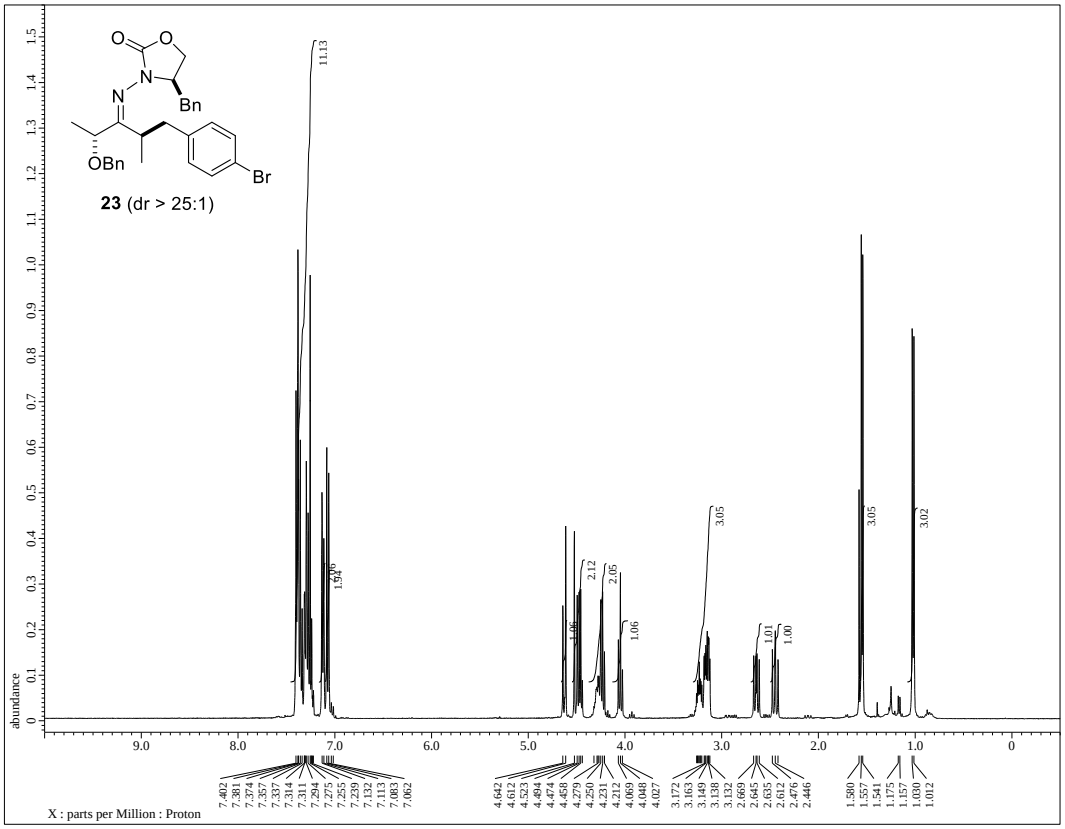

13
14
(13/14 = 27:73)
(reverse alkylation sequence)
X : parts per Million : Carbon13

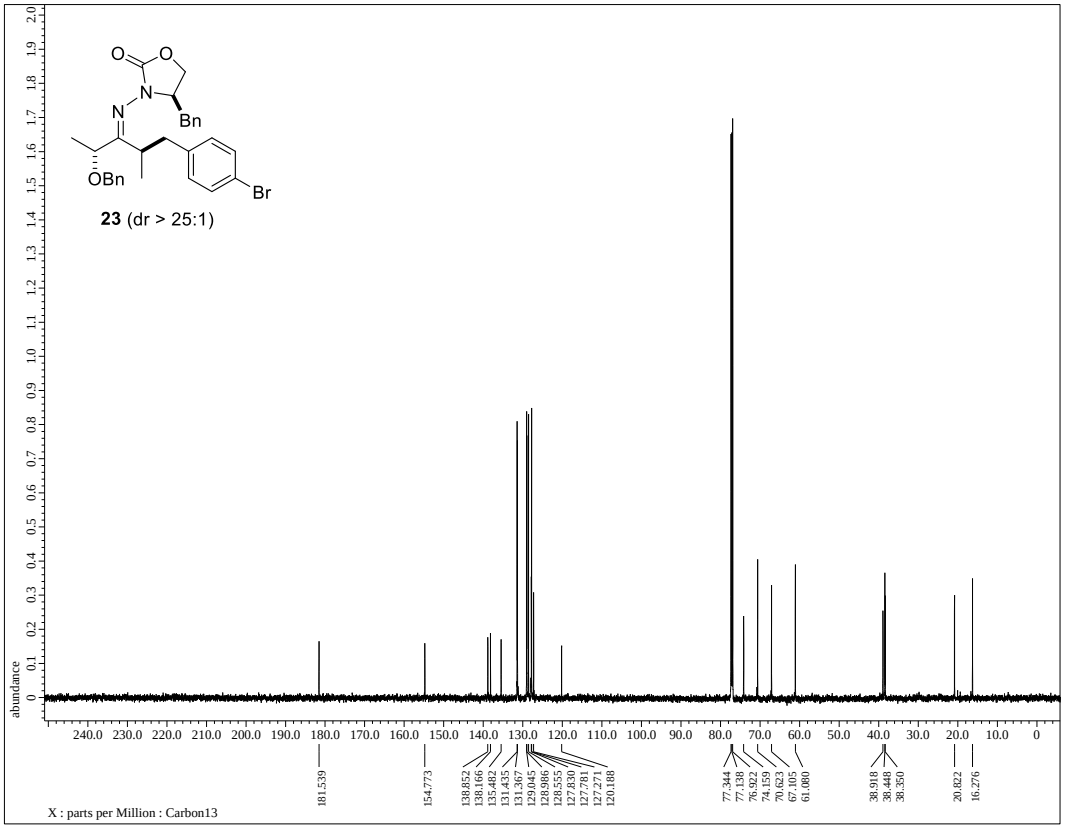

22 (dr > 25:1)
abundance
X : parts per Million : Proton

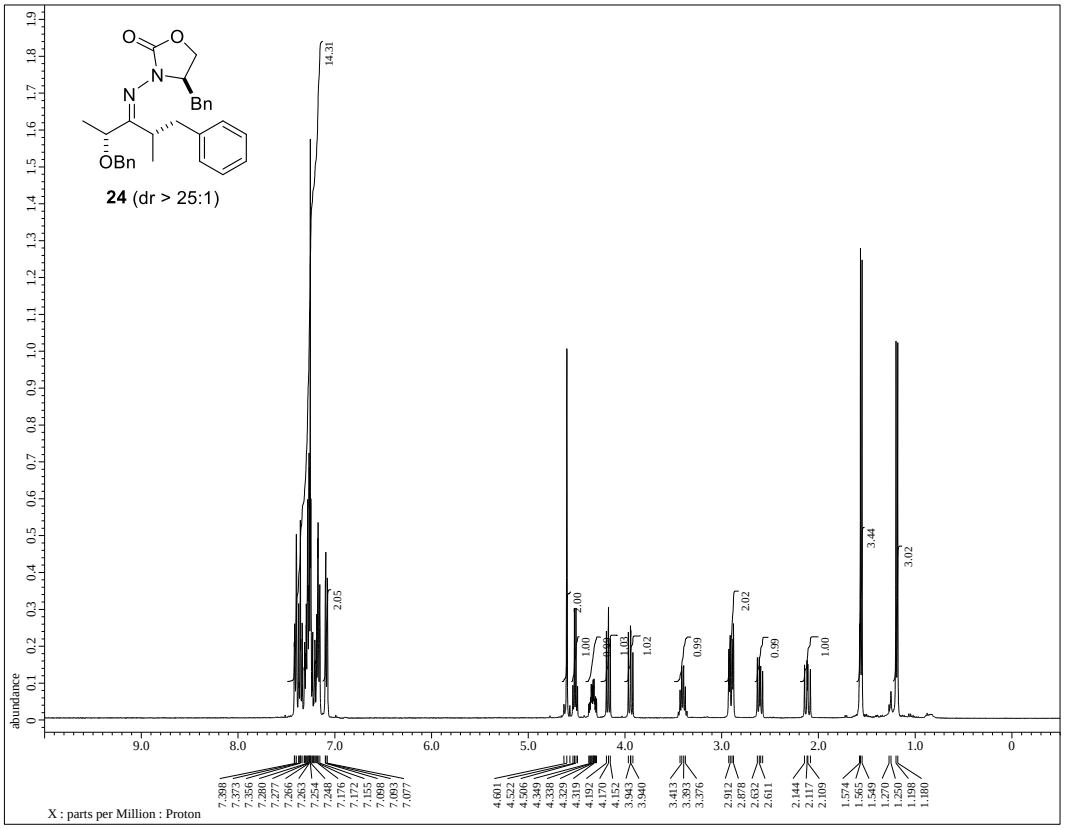

22 (dr > 25:1)
abundance
X : parts per Million : Carbon13

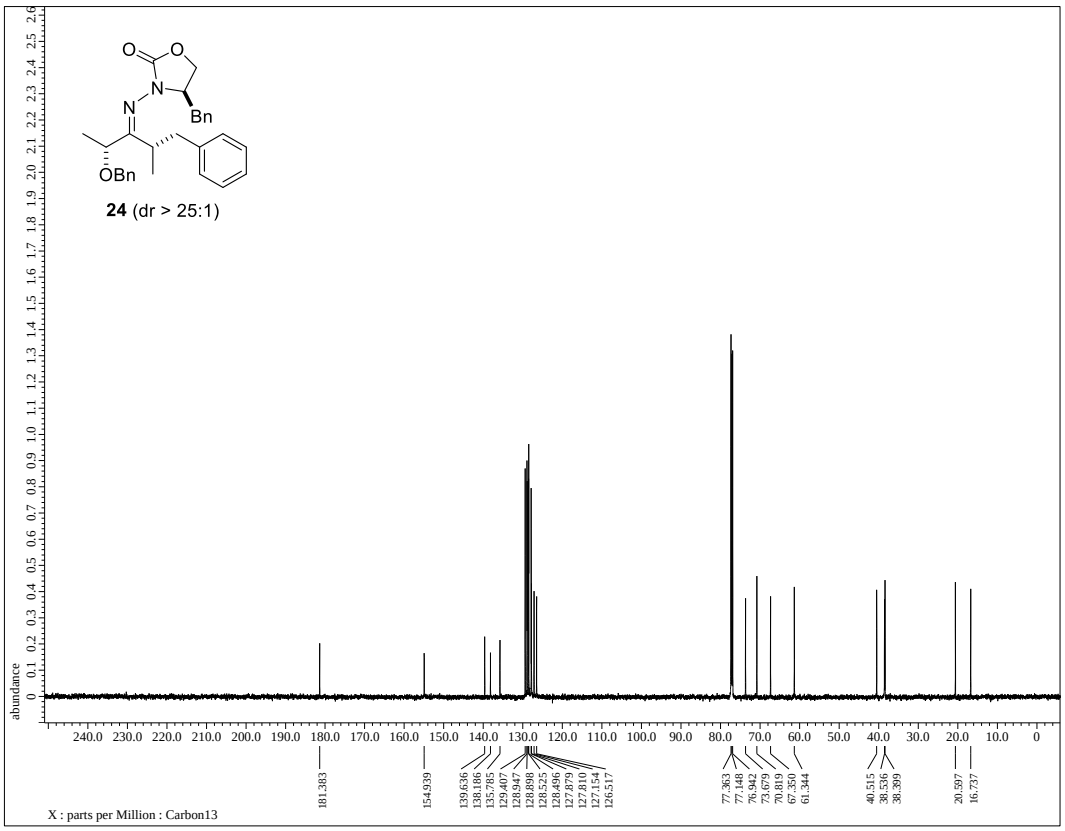

SI-9
abundance
X : parts per Million : Proton

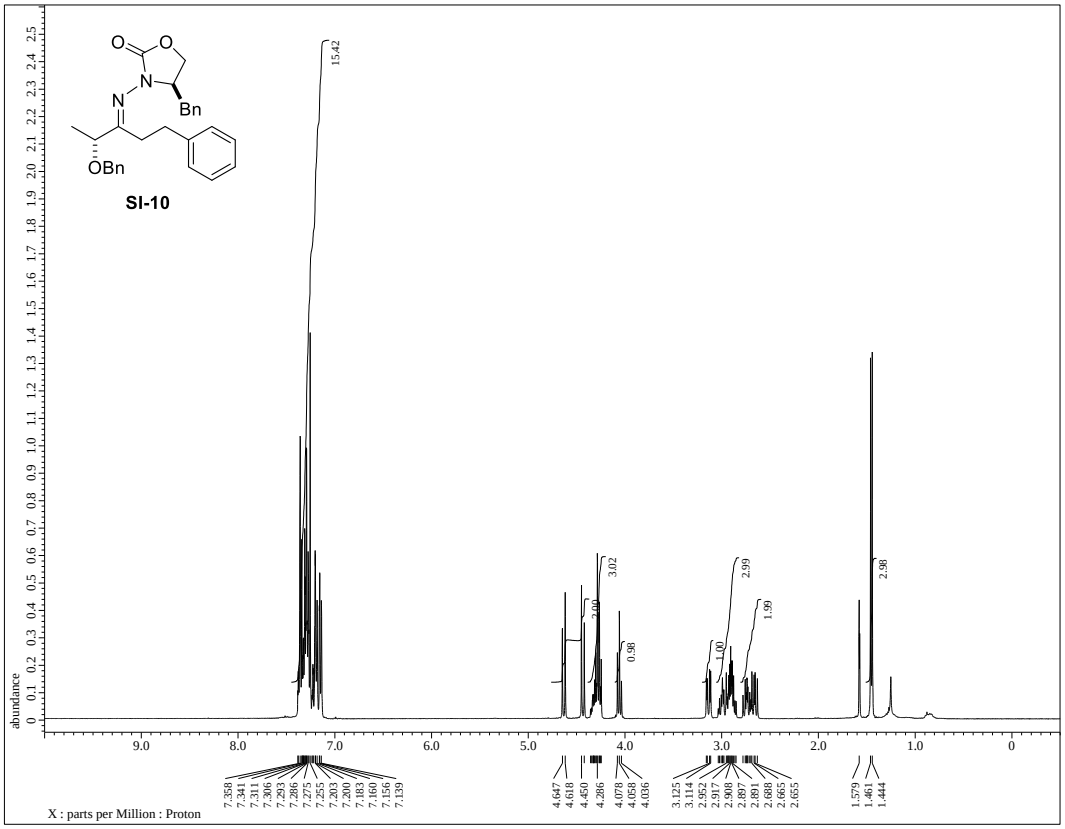

SI-9
abundance
X : parts per Million : Carbon13

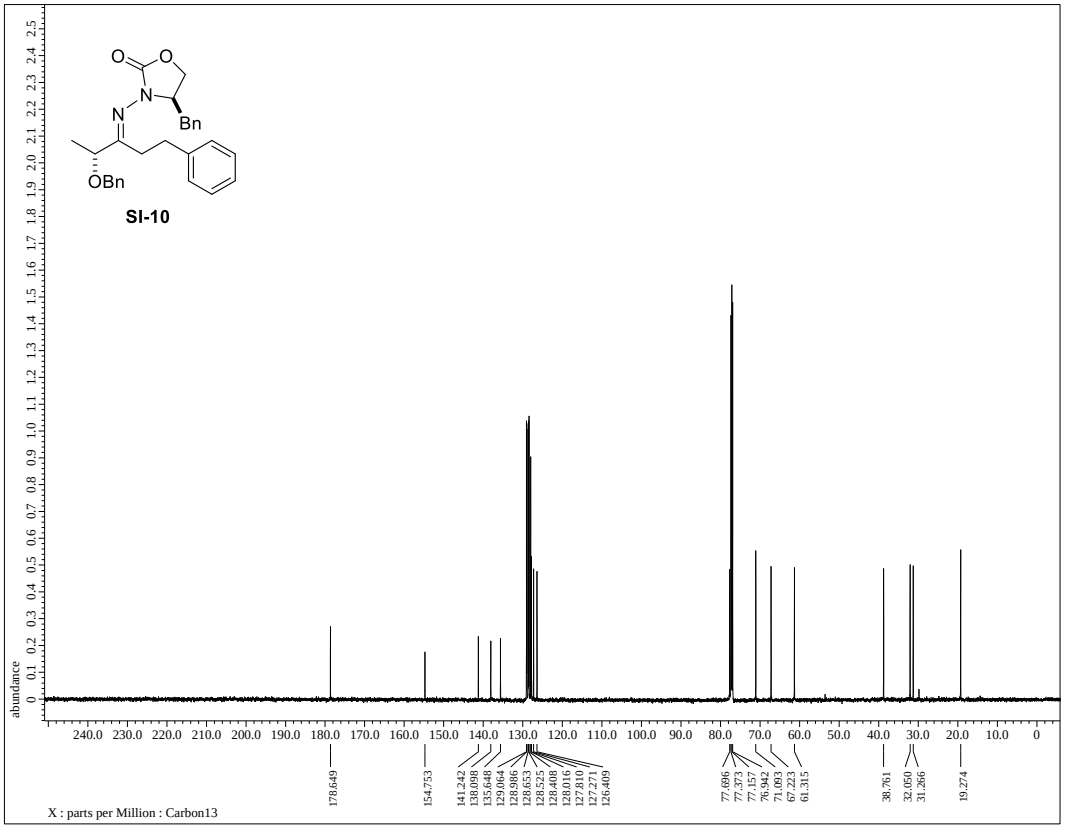

23 (dr > 25:1)
X : parts per Million : Proton

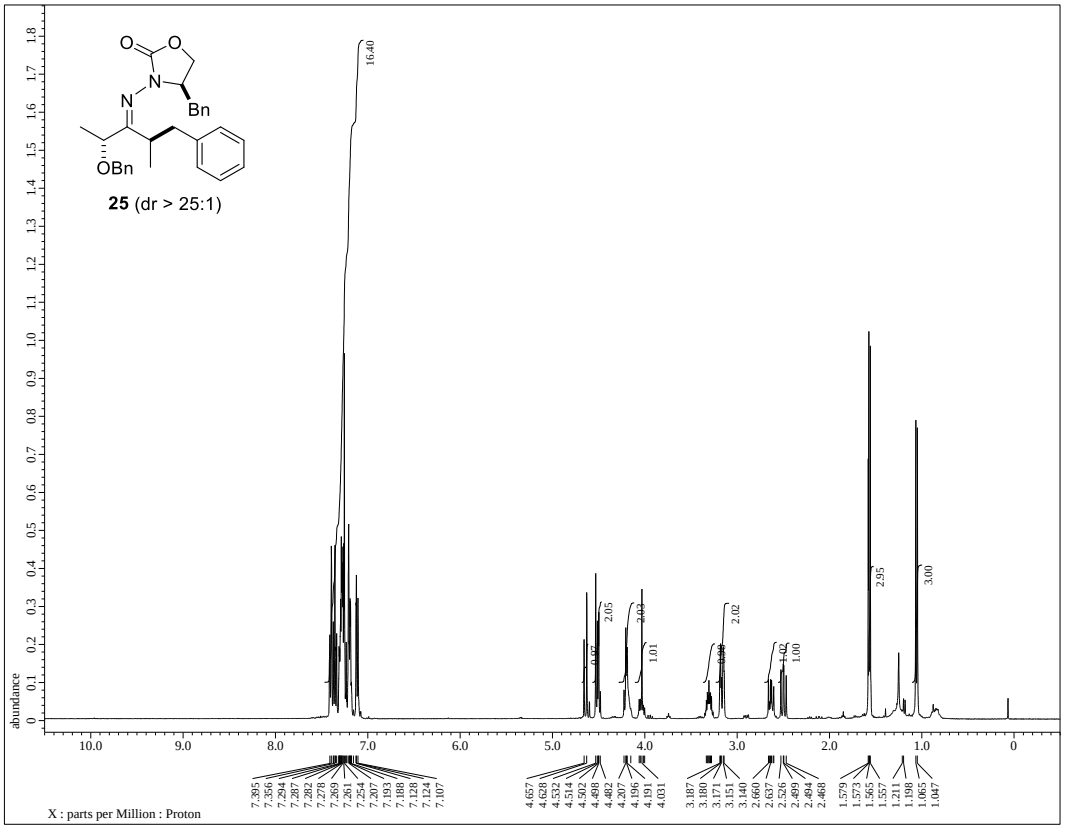

23 (dr > 25:1)
X : parts per Million : Carbon13

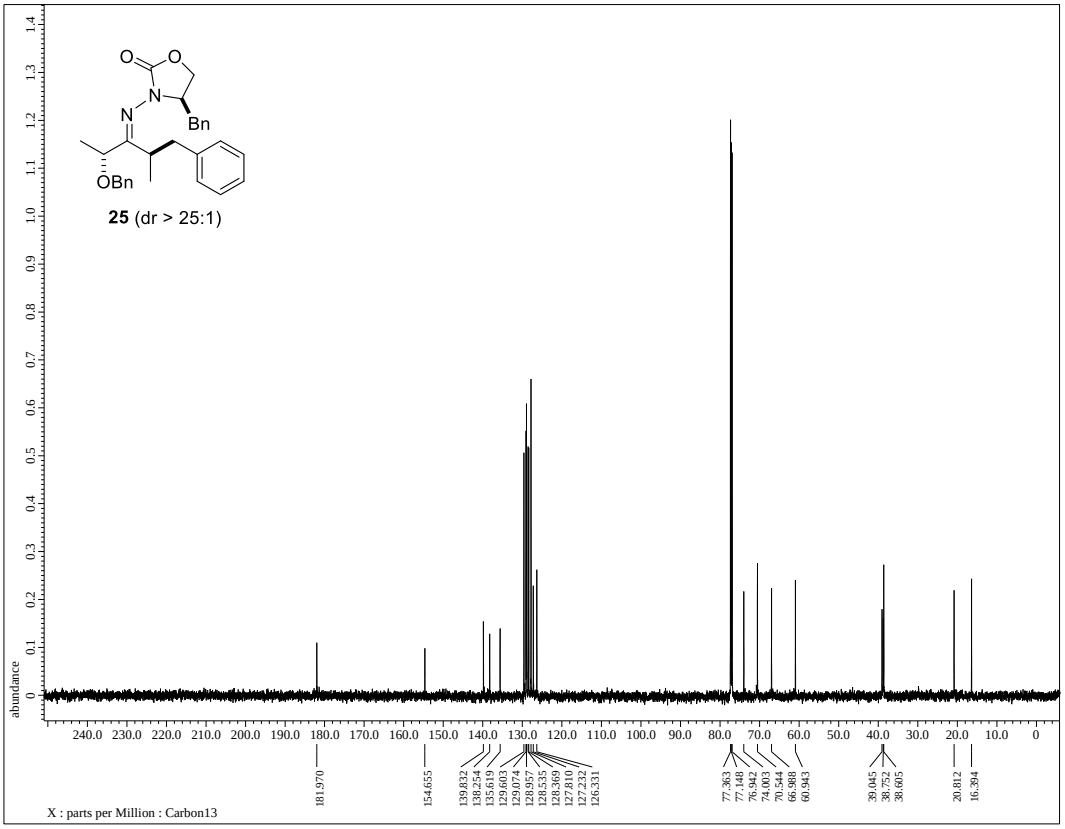

24 (dr > 25:1)
X : parts per Million : Proton

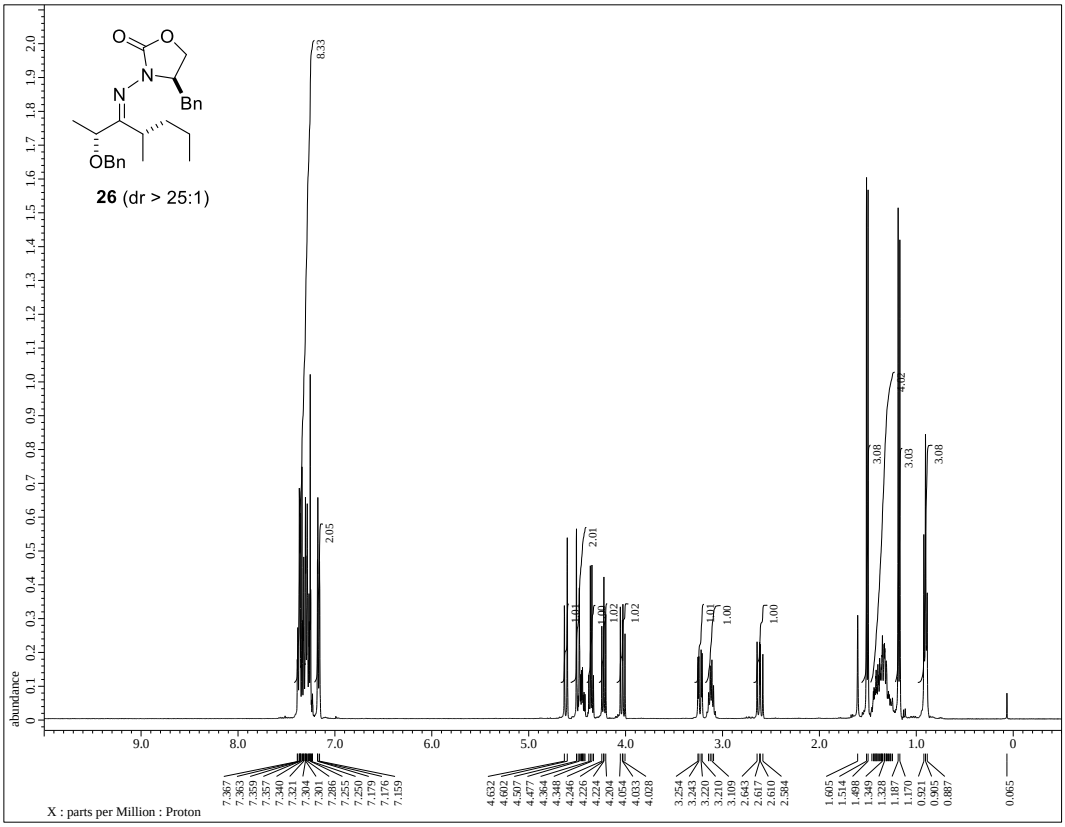

24 (dr > 25:1)
X : parts per Million : Carbon13

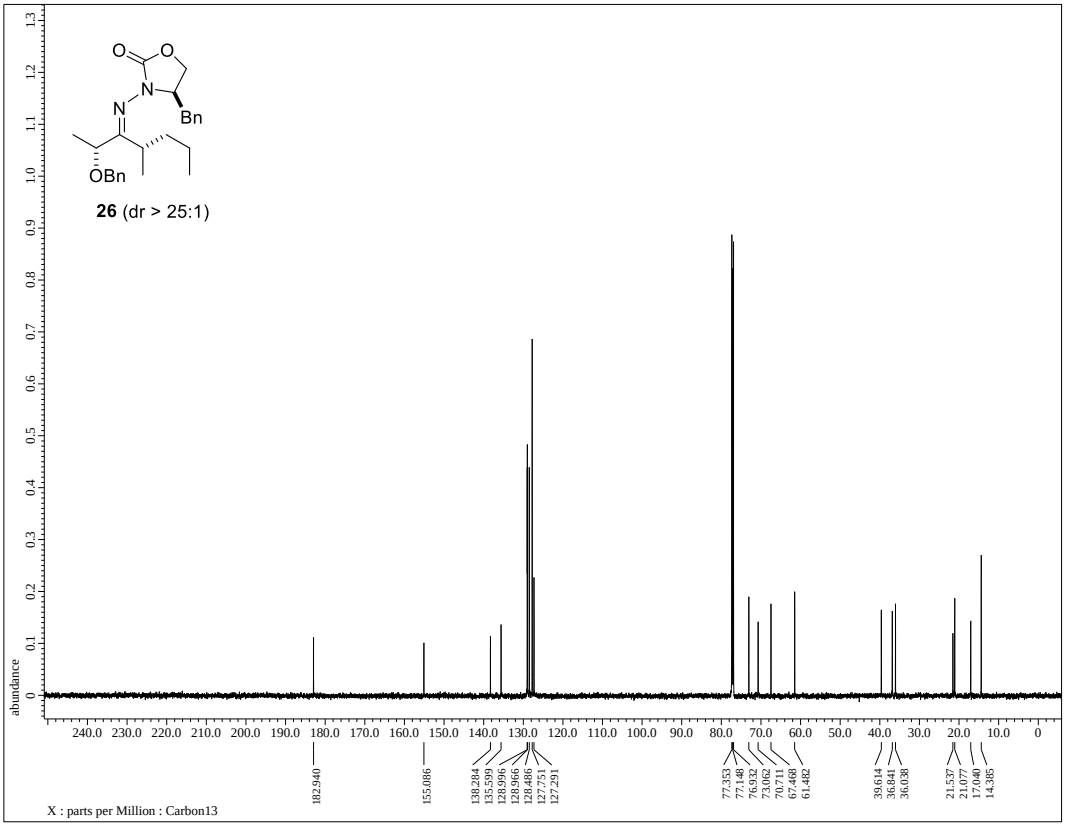

SI-10
abundance
X : parts per Million : Proton

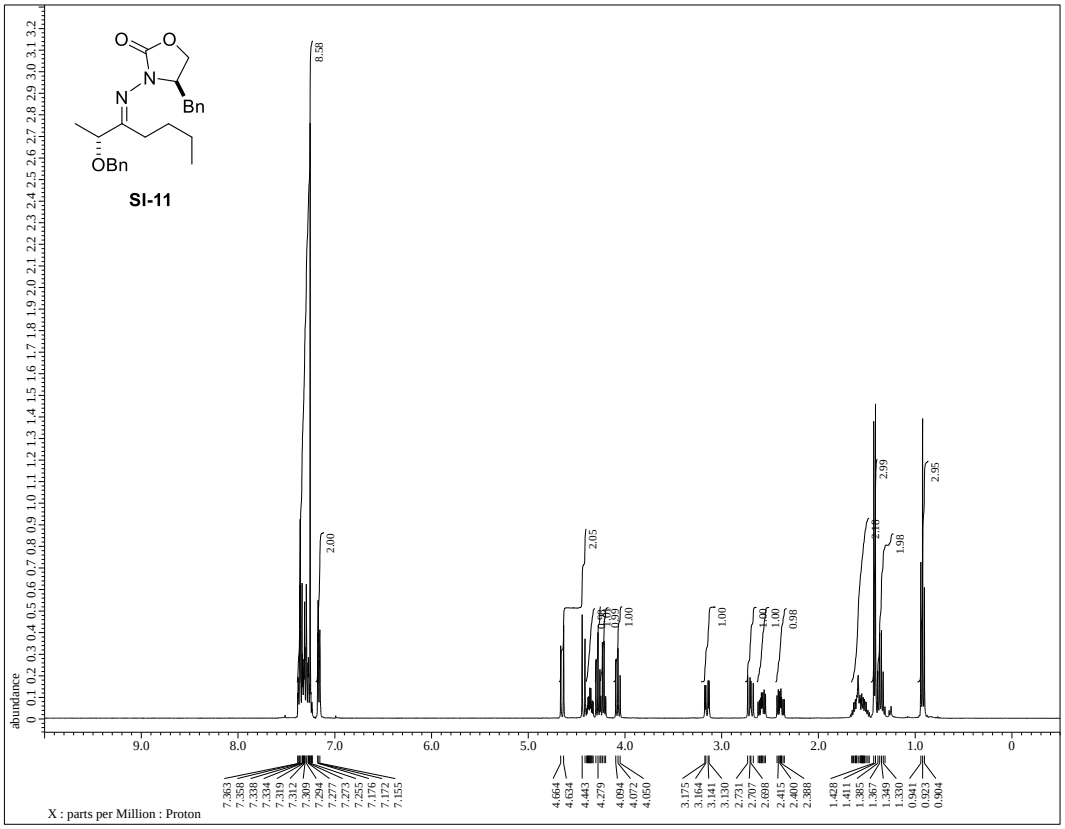

SI-10
abundance
X : parts per Million : Carbon13

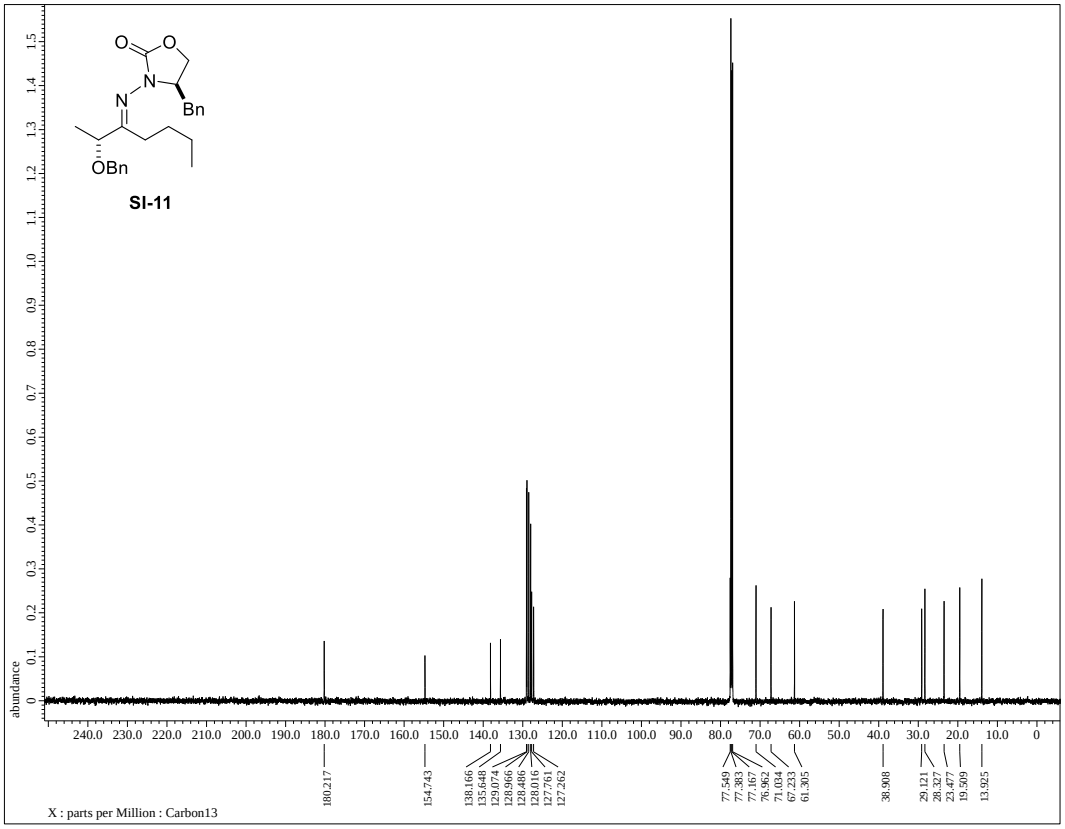

Bn
OBn
25 (dr > 25:1)
abundance
X : parts per Million : Proton

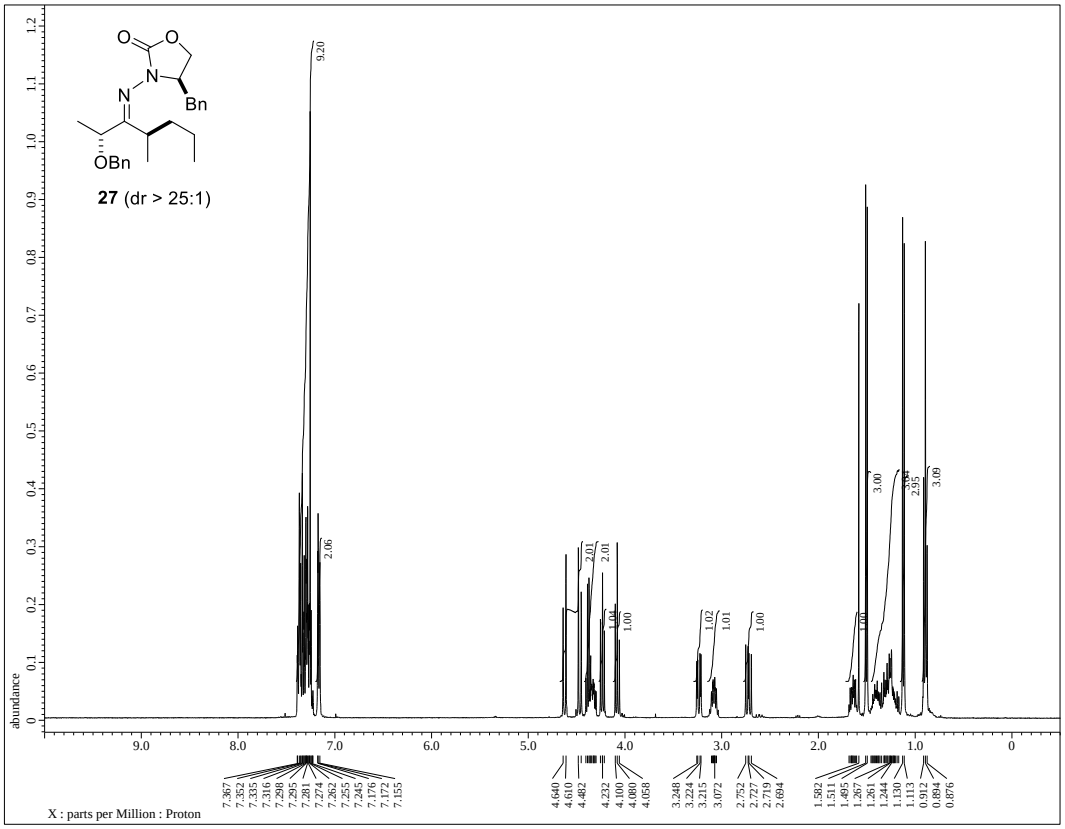

Bn
OBn
25 (dr > 25:1)
abundance
X : parts per Million : Carbon13

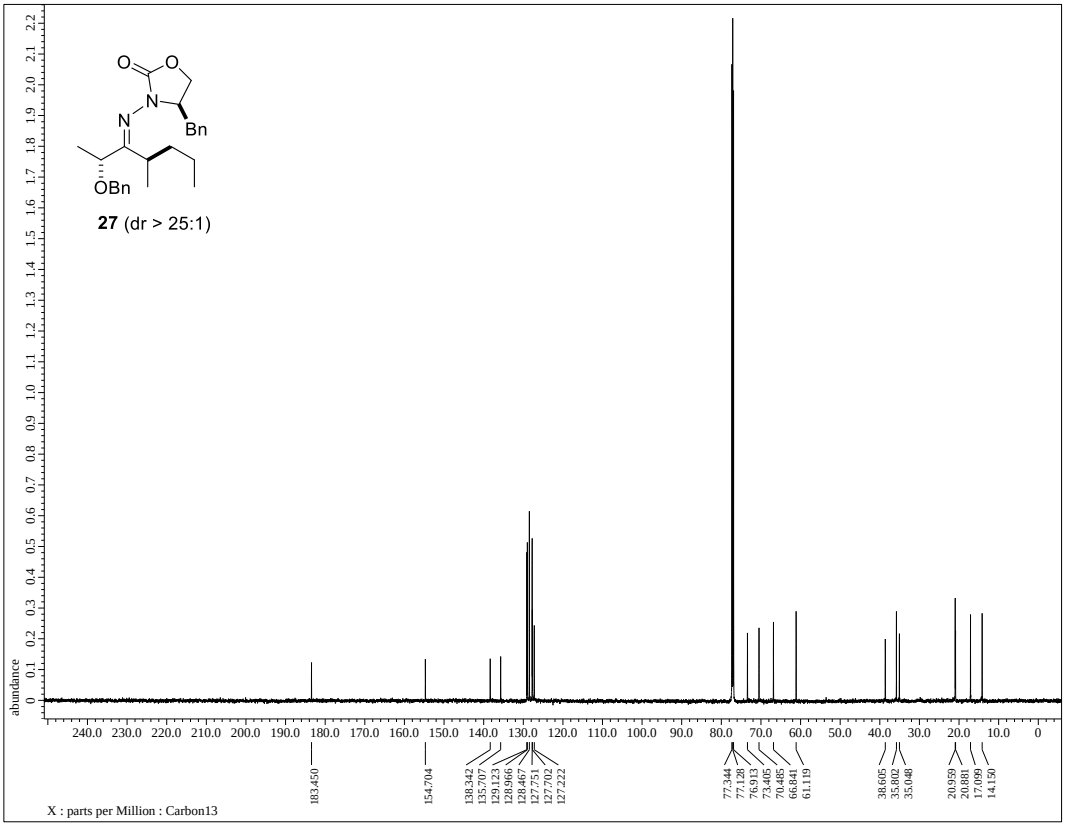

26 (dr > 25:1)
X : parts per Million : Proton

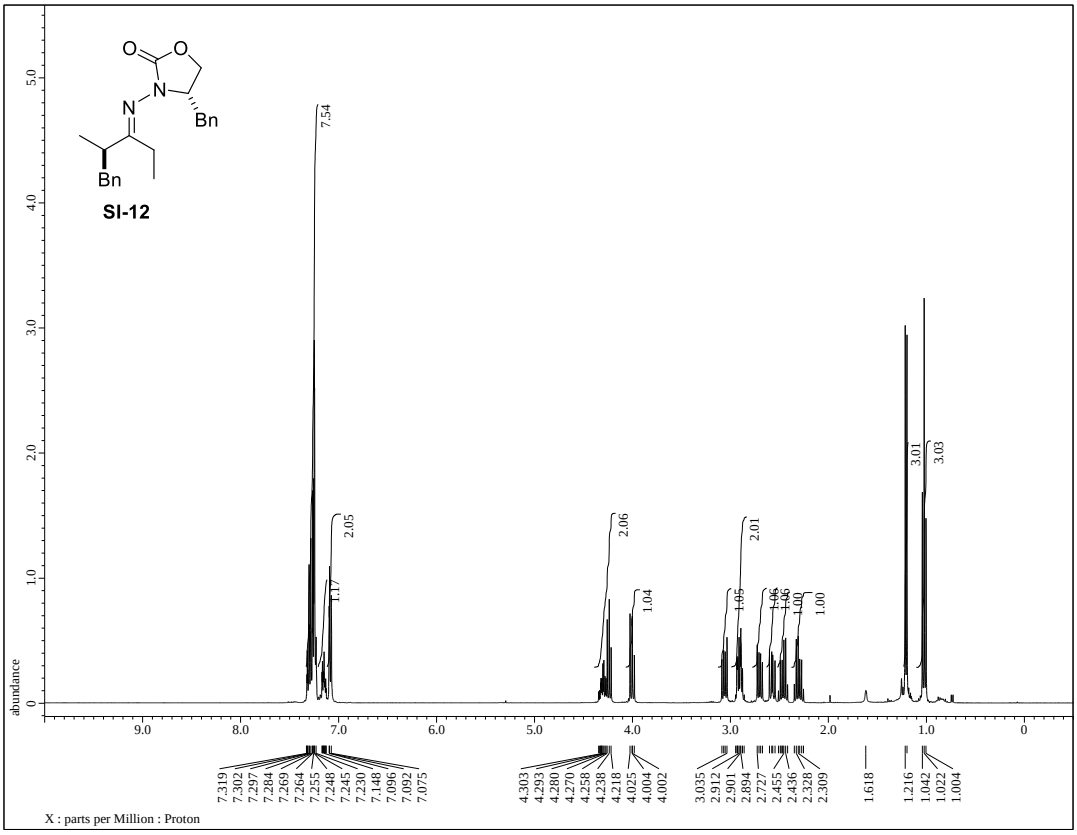

26 (dr > 25:1)
X : parts per Million : Carbon13

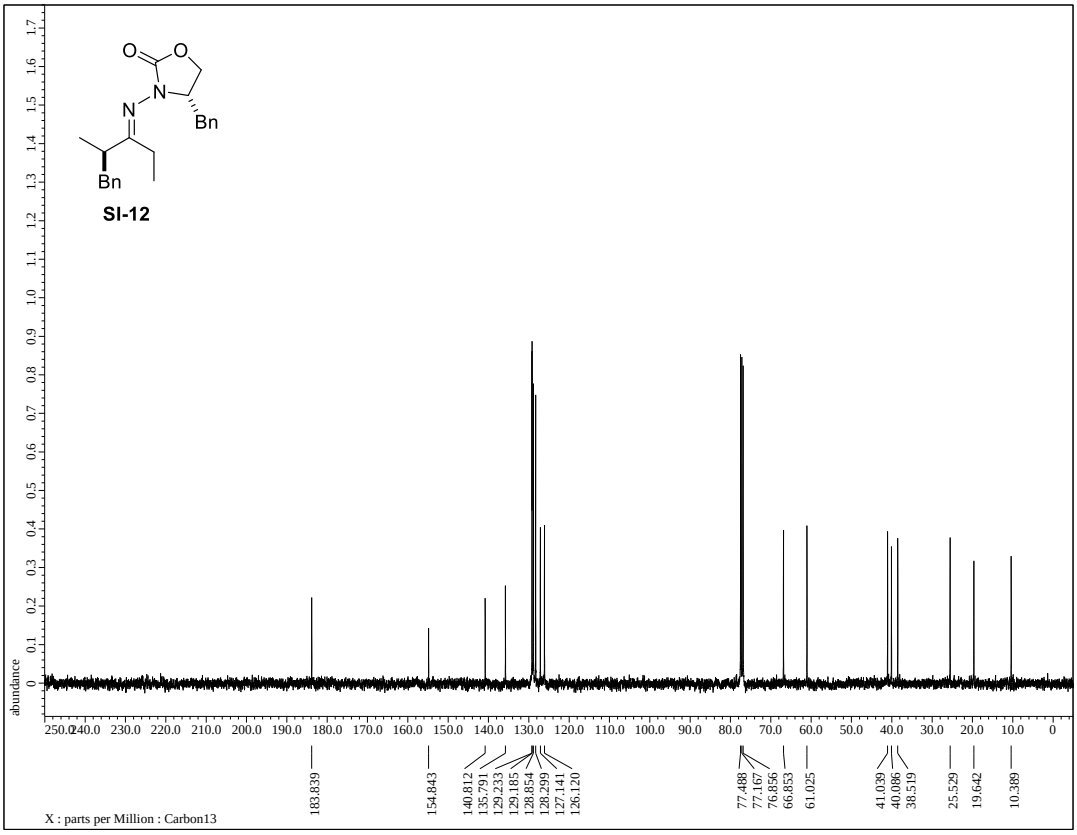

SI-11
X : parts per Million : Proton

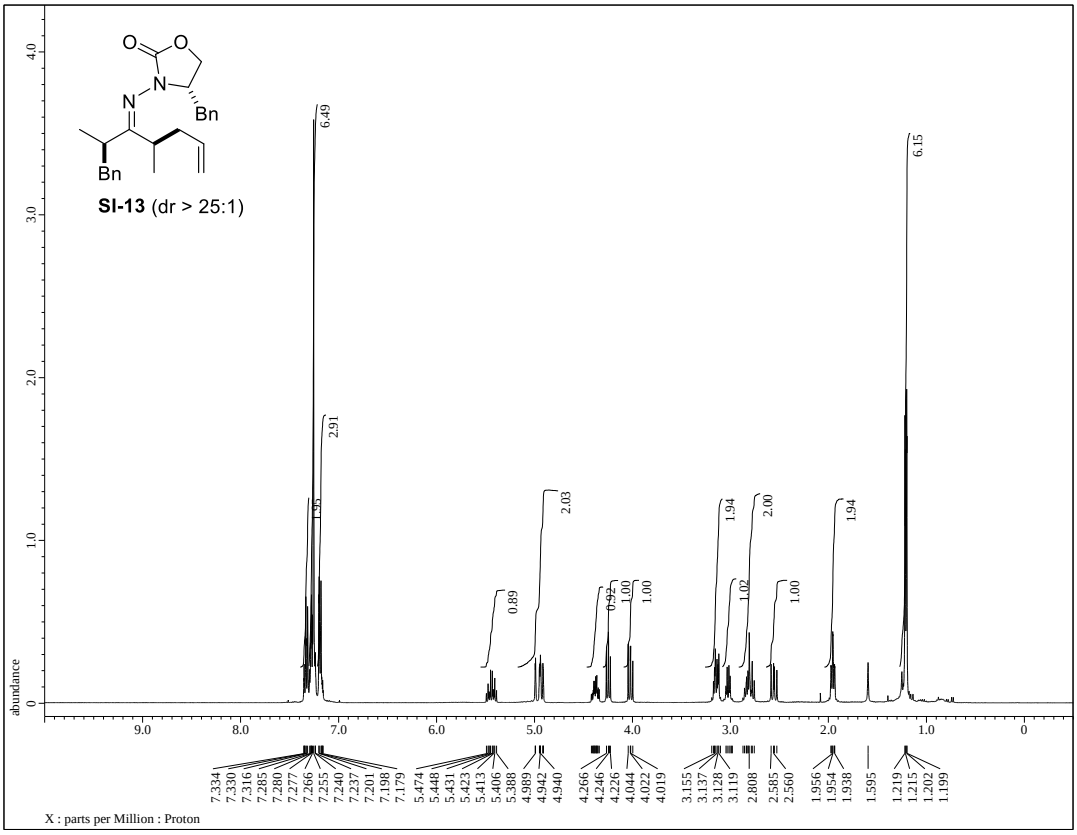

SI-11
X : parts per Million : Carbon13

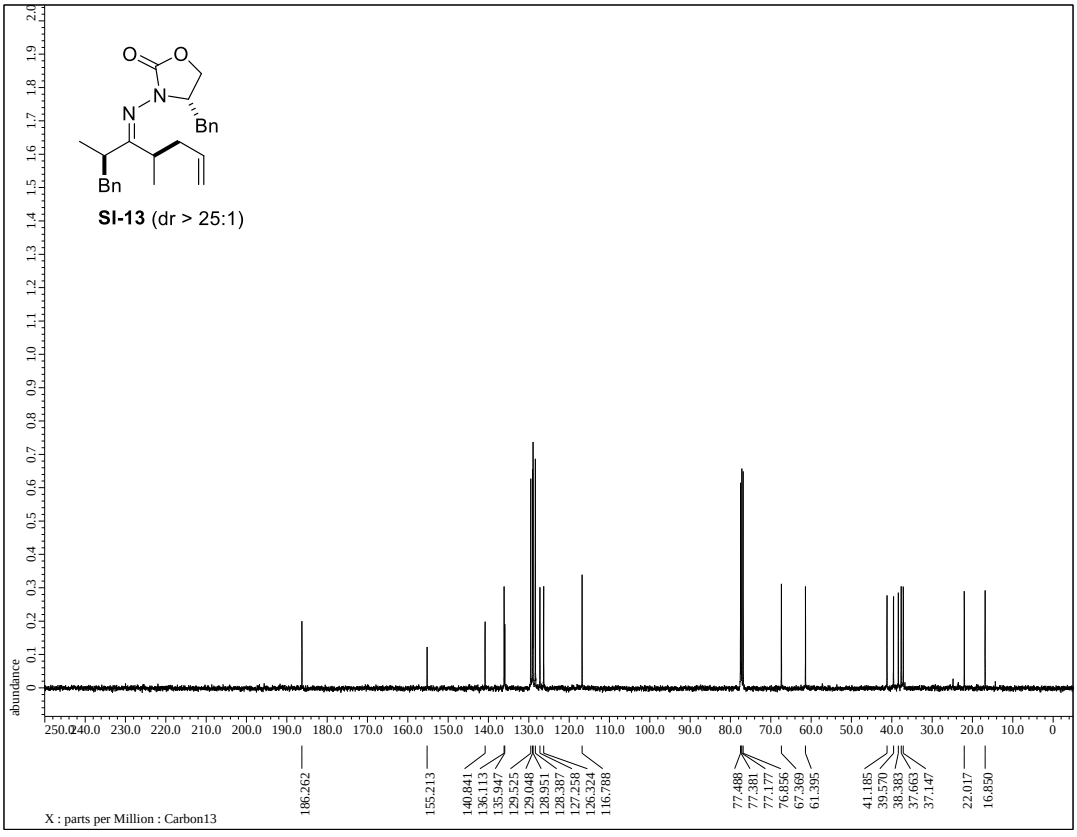

27 (dr > 25:1)
X : parts per Million : Proton

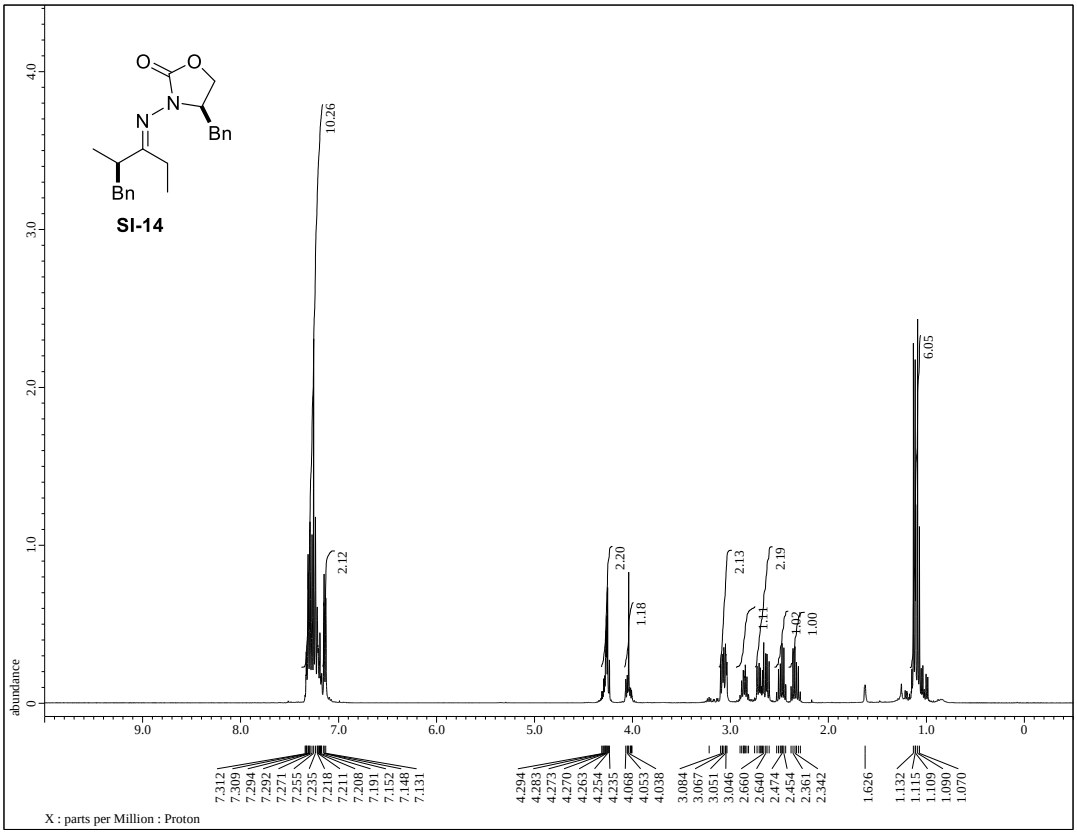

27 (dr > 25:1)
X : parts per Million : Carbon13

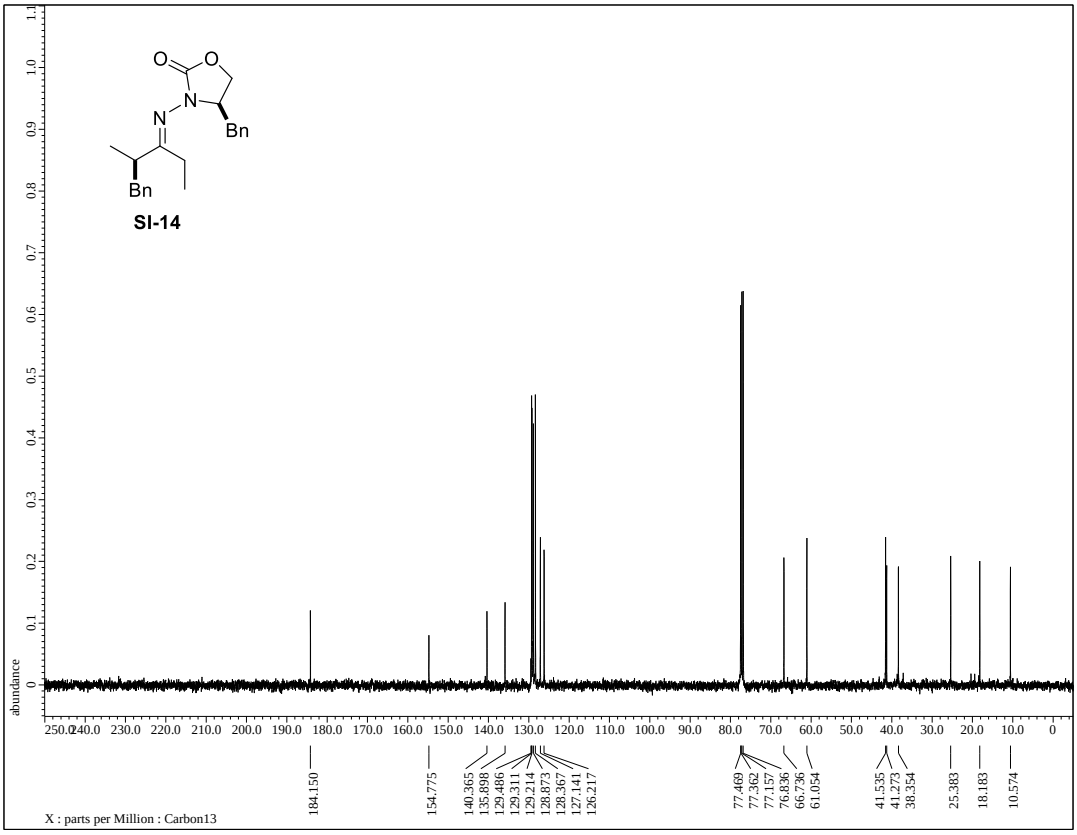

SI-12
abundance
X : parts per Million : Proton

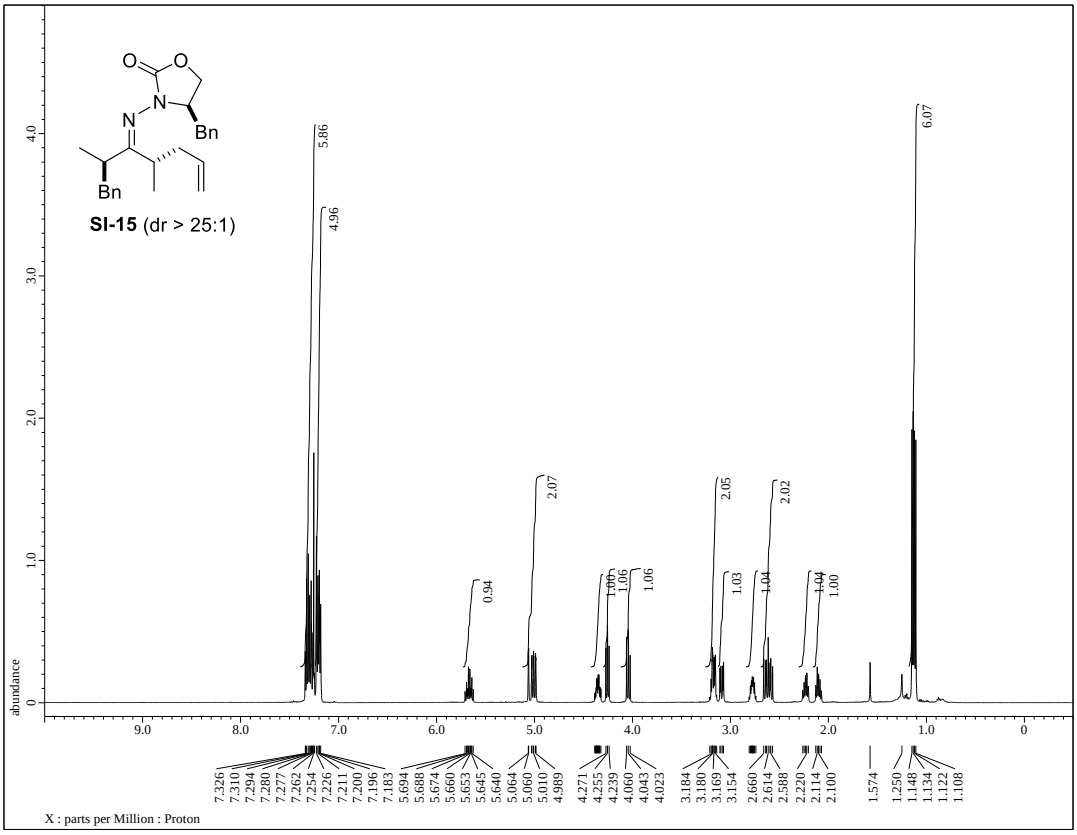

SI-12
abundance
X : parts per Million : Carbon13

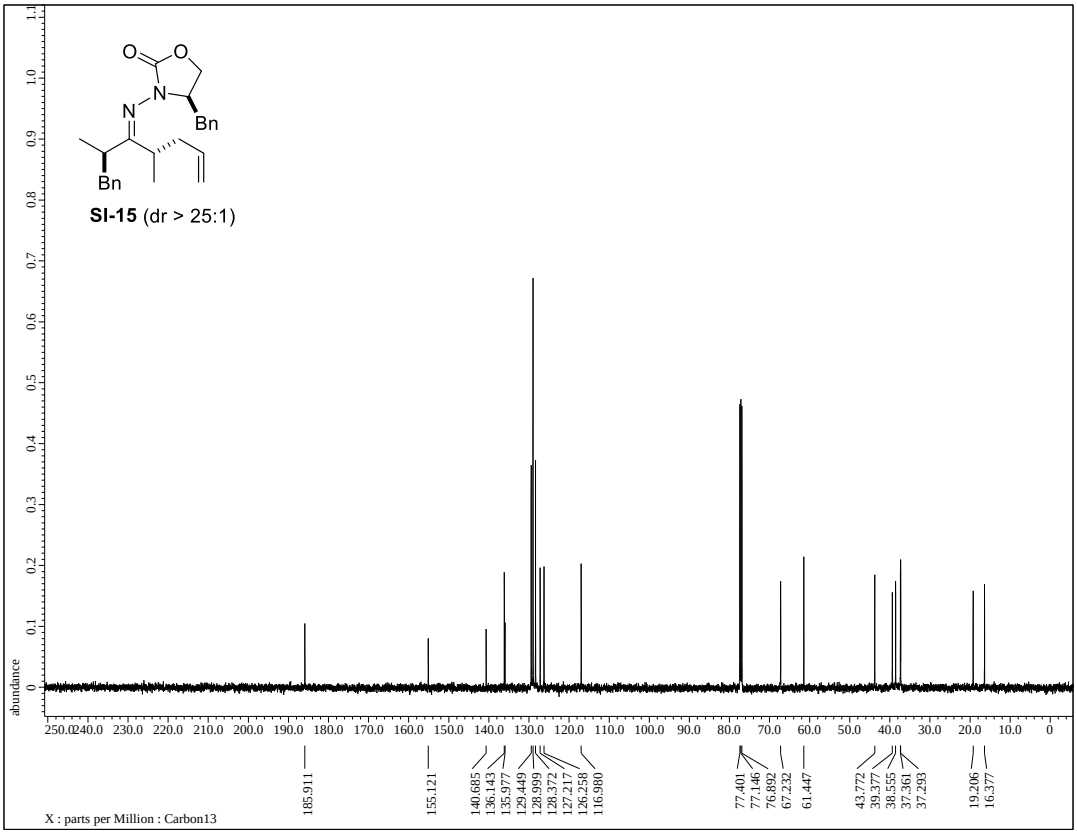

Bn
Bn
SI-13 (dr > 25:1)
6.49
2.91
1.95
2.03
0.89
0.92
1.00
1.00
1.94
1.02
2.00
1.00
1.94
6.15
abundance
X : parts per Million : Proton

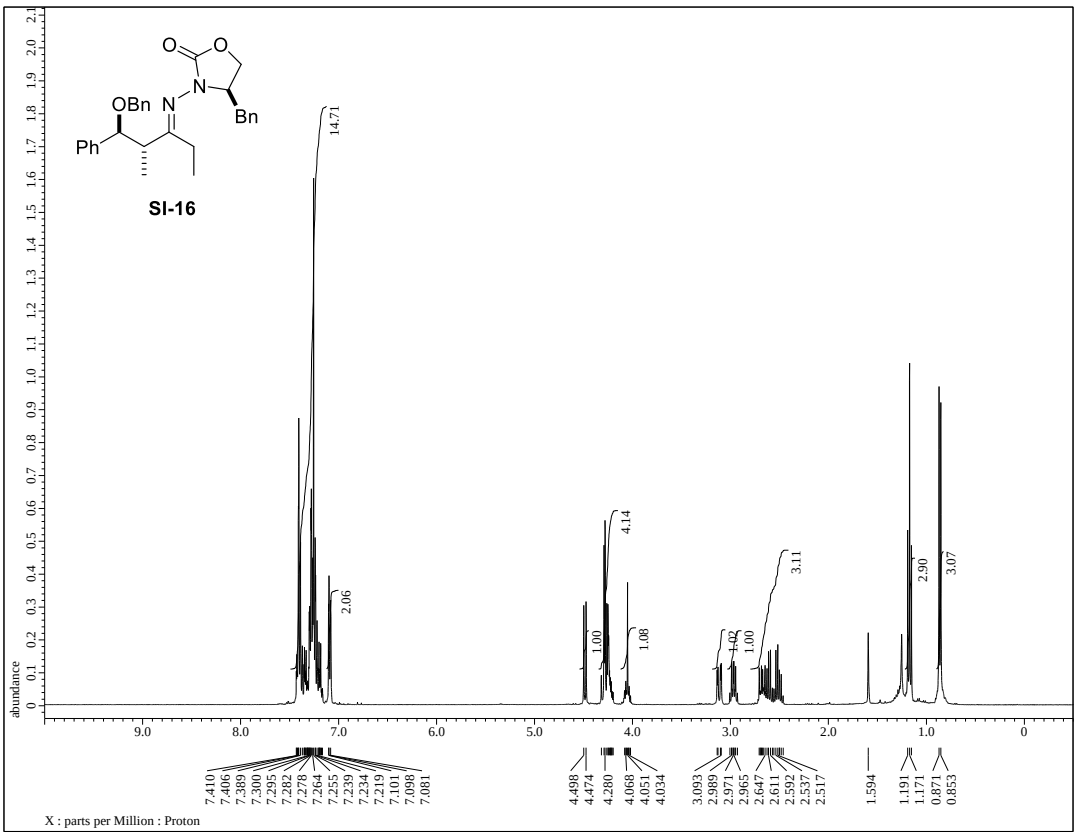

Bn
Bn
SI-13 (dr > 25:1)
abundance
X : parts per Million : Carbon13

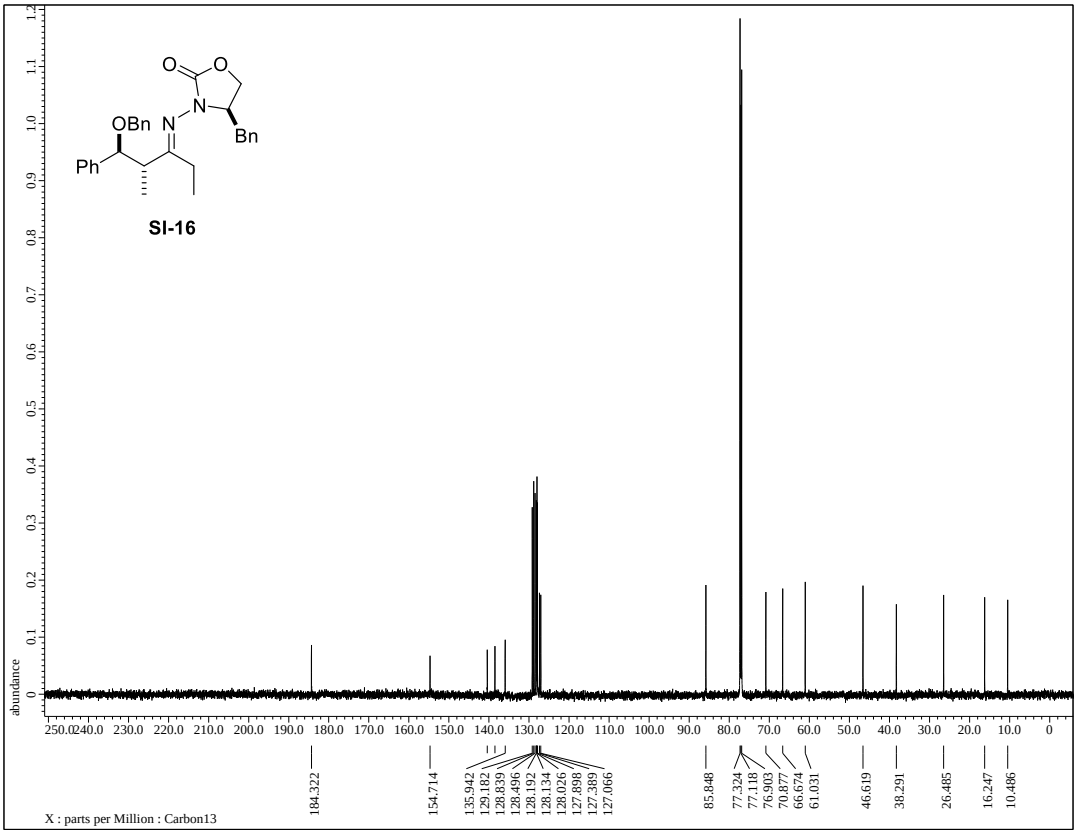

SI-14
10.26
2.12
2.20
1.18
2.13
2.19
1.11
1.02
1.00
6.05
abundance
X : parts per Million : Proton

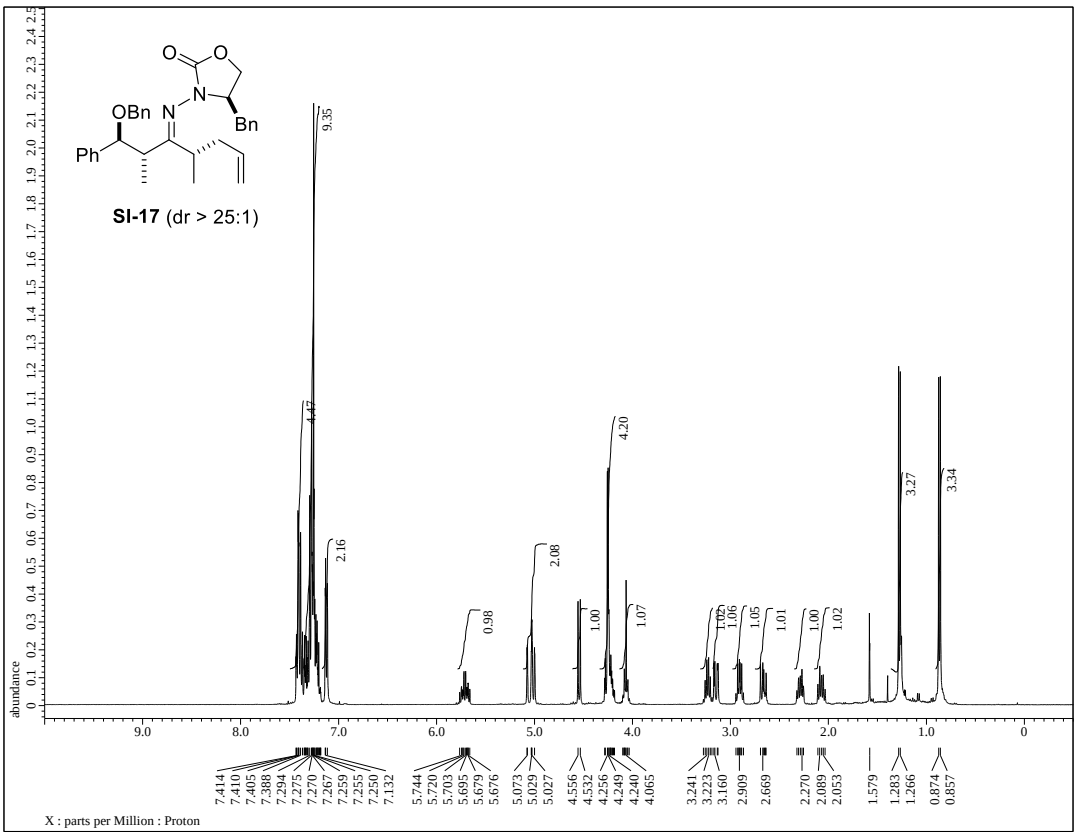

SI-14
abundance
X : parts per Million : Carbon13

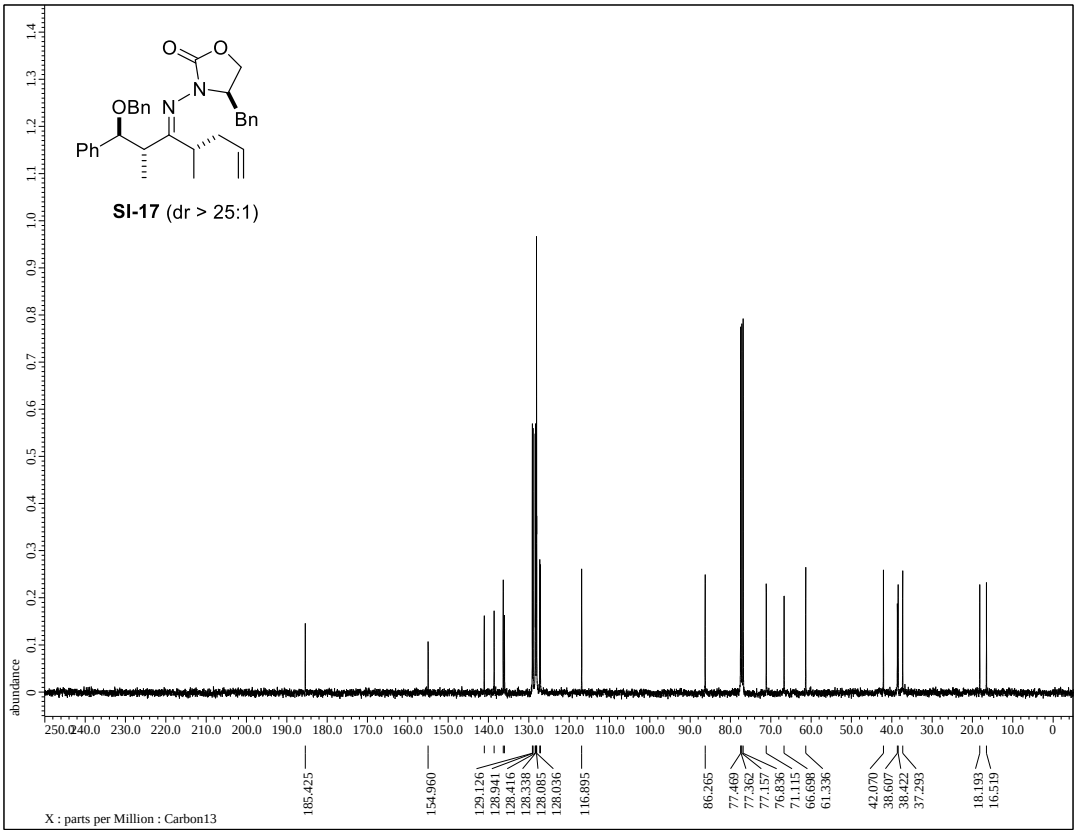

SI-15 (dr > 25:1)
X : parts per Million : Proton

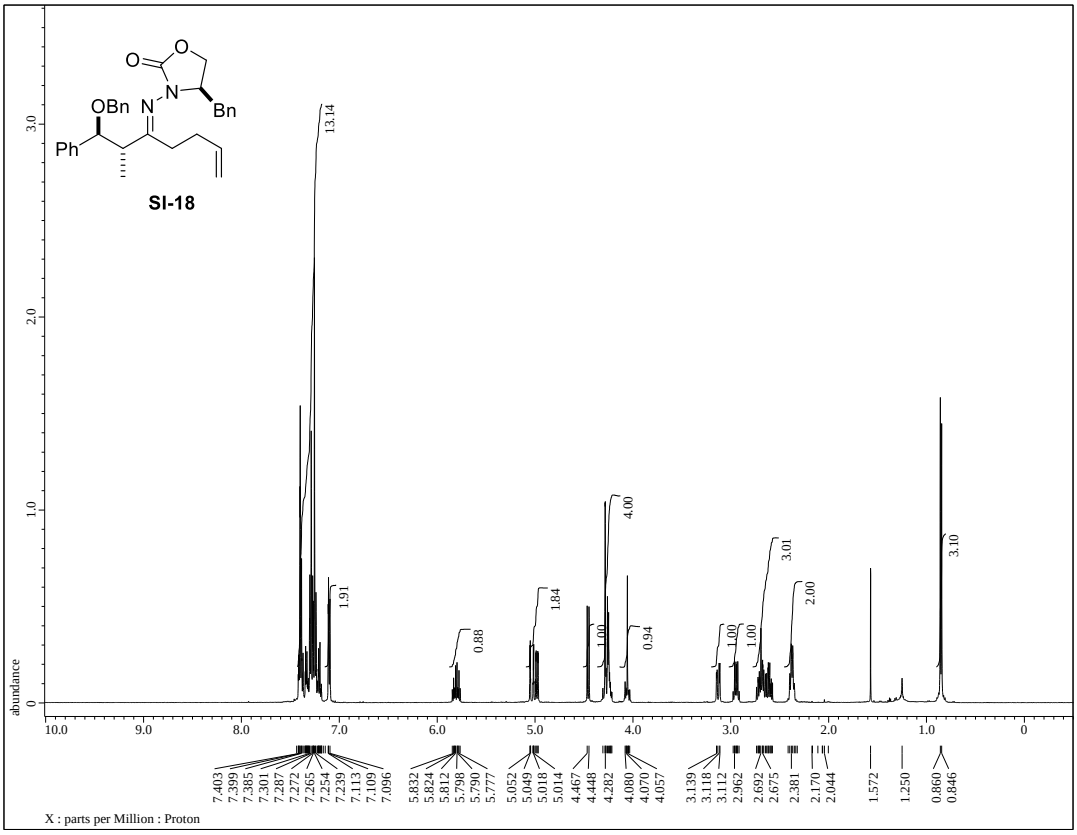

SI-15 (dr > 25:1)
X : parts per Million : Carbon13

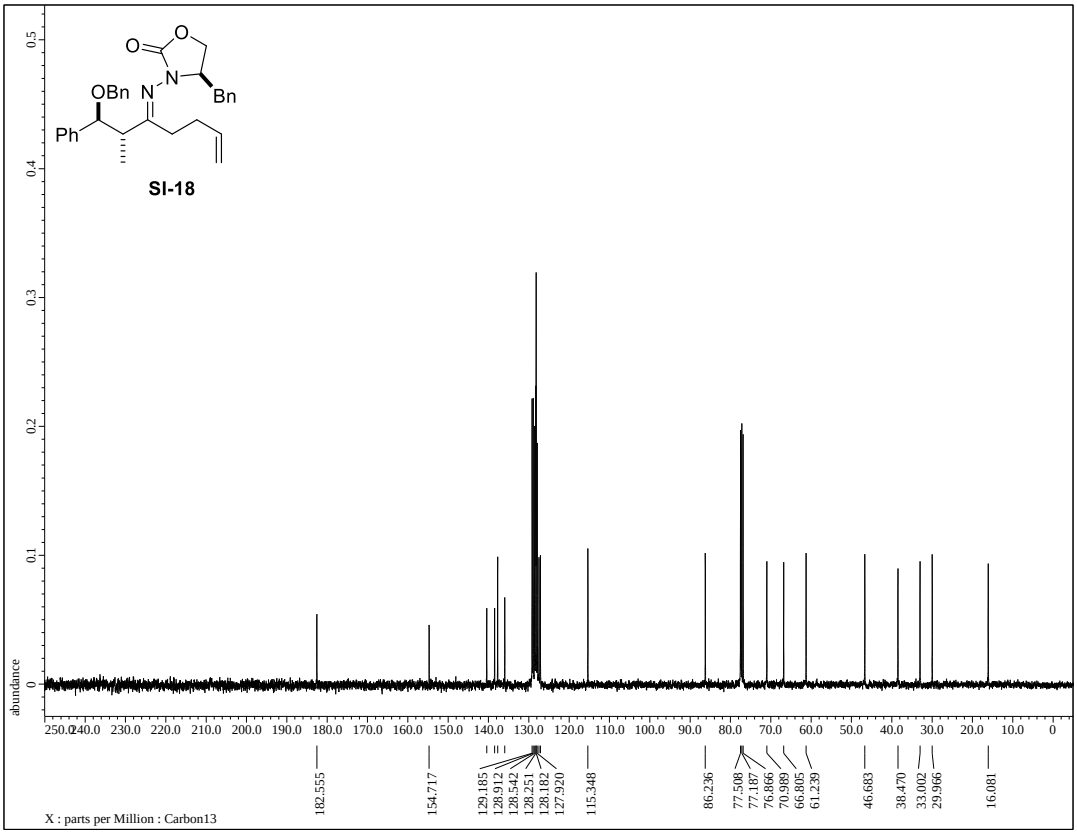

SI-16
14.71
2.06
4.14
1.00
1.08
1.02
1.00
3.11
2.90
3.07
abundance
X : parts per Million : Proton

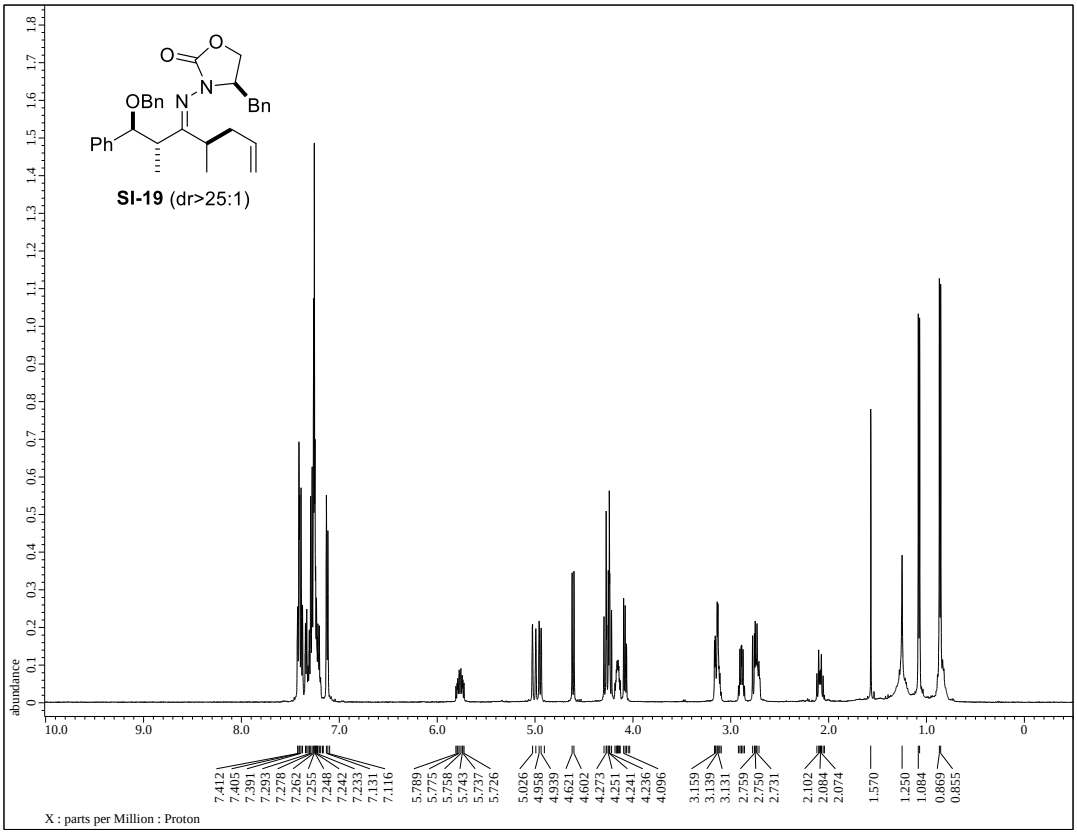

SI-16
abundance
X : parts per Million : Carbon13

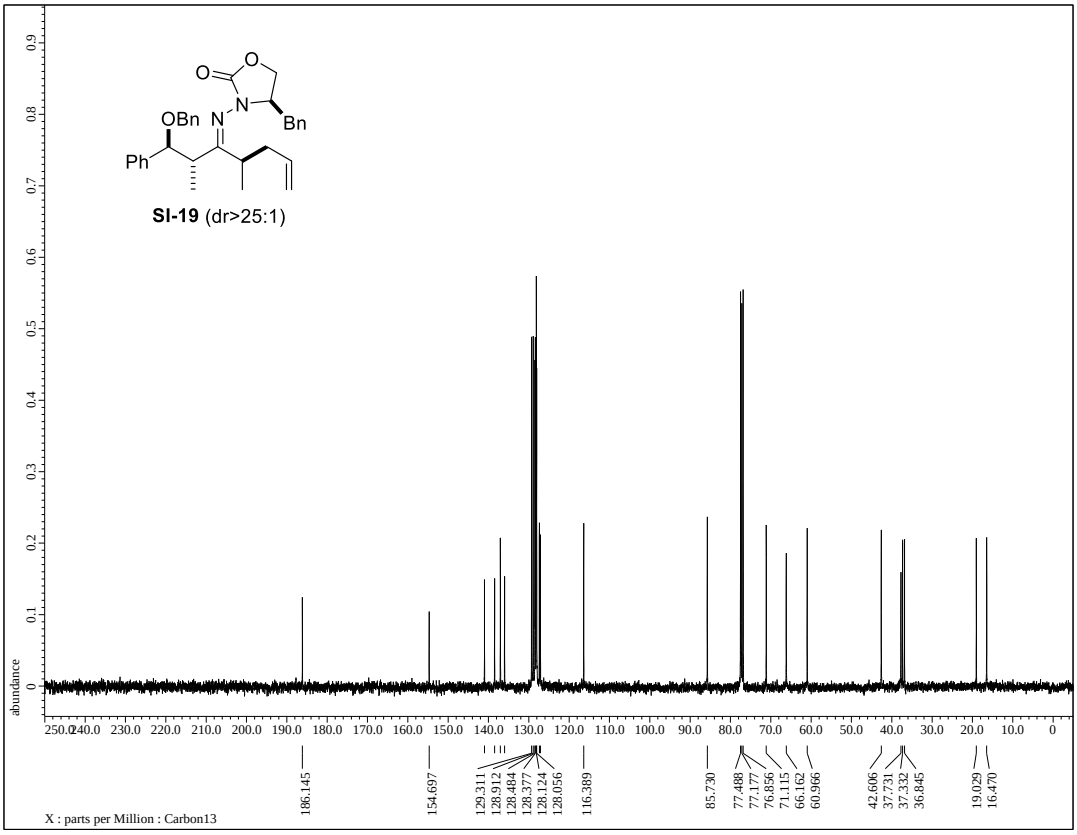

SI-17 (dr > 25:1)
abundance
X : parts per Million : Proton

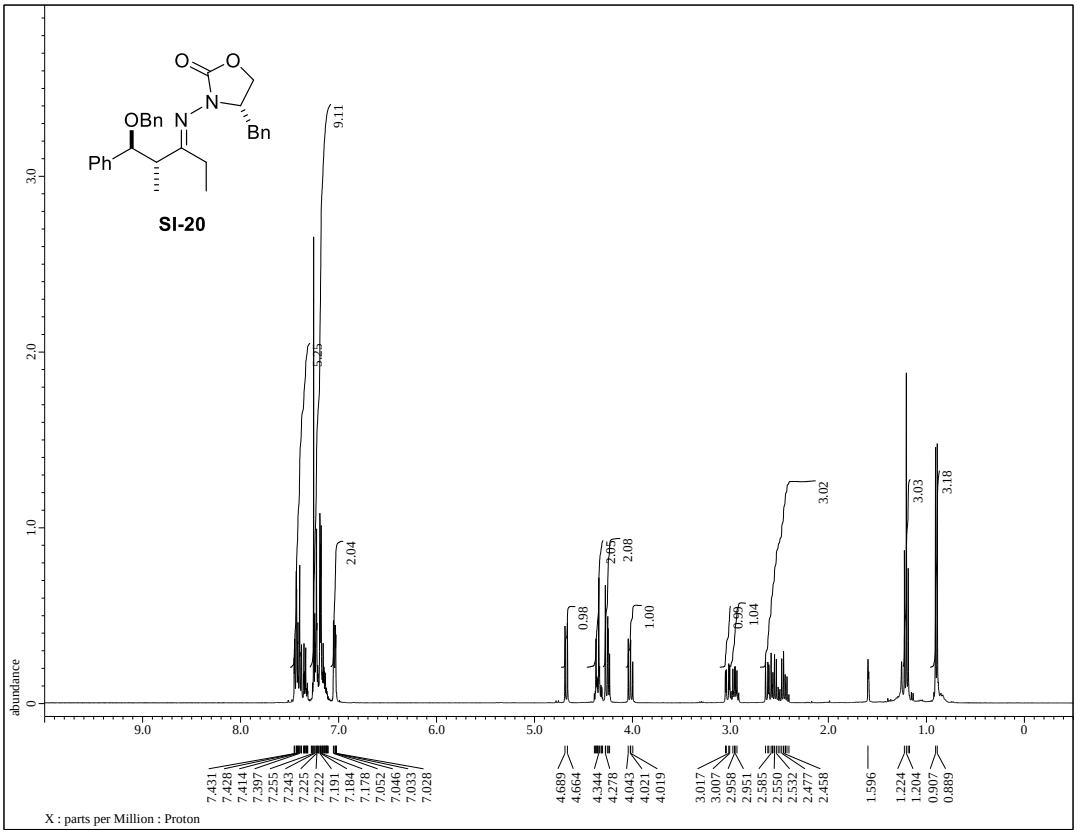

SI-17 (dr > 25:1)
abundance
X : parts per Million : Carbon13

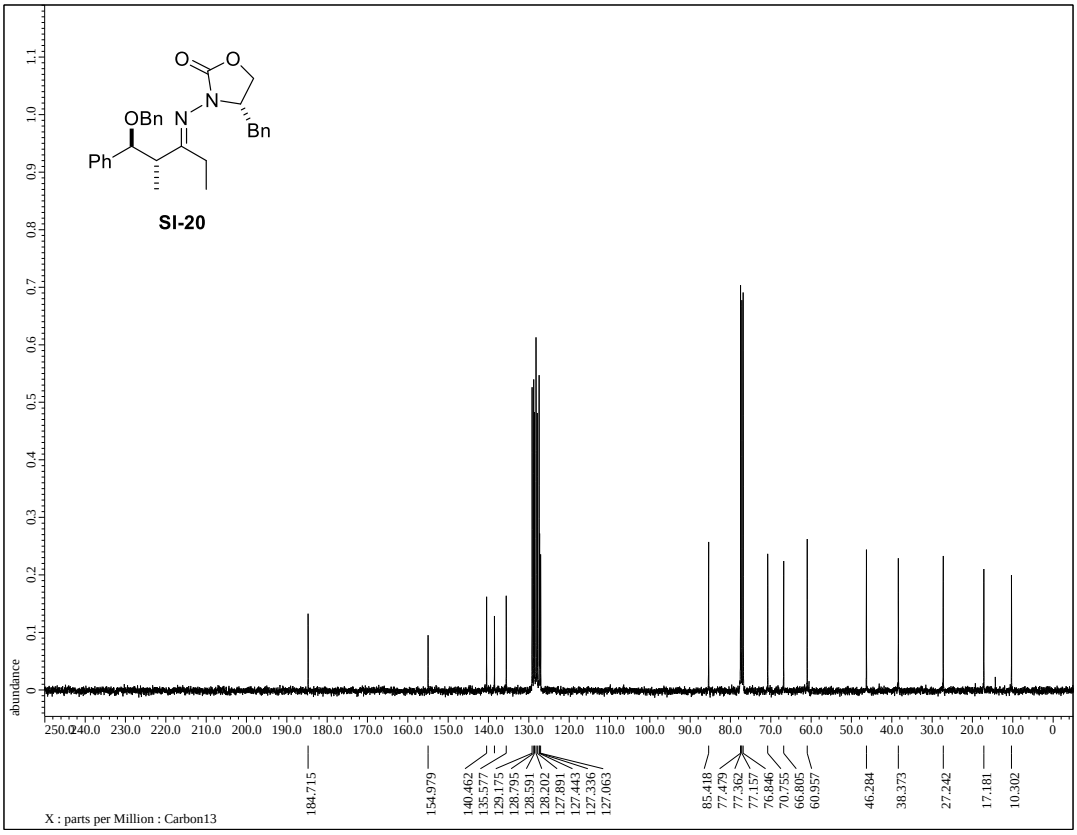

SI-18
abundance
X : parts per Million : Proton

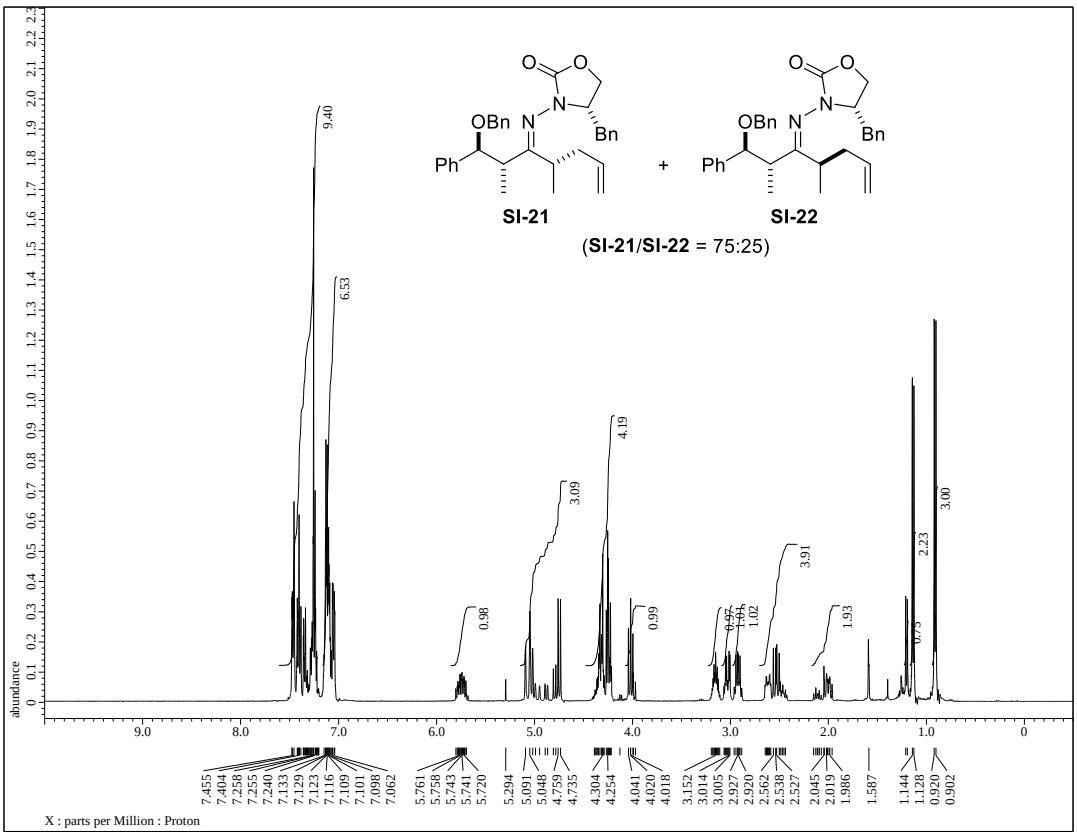

SI-18
abundance
X : parts per Million : Carbon13

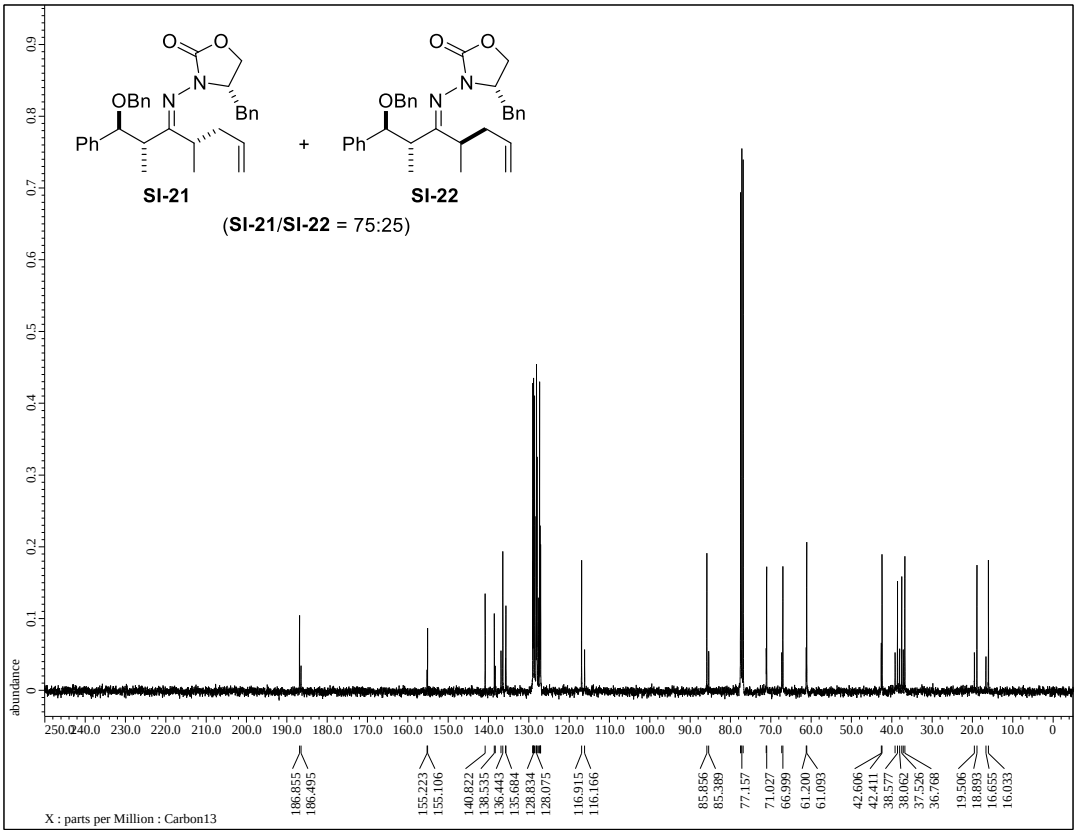

SI-19 (dr>25:1)
abundance
X : parts per Million : Proton

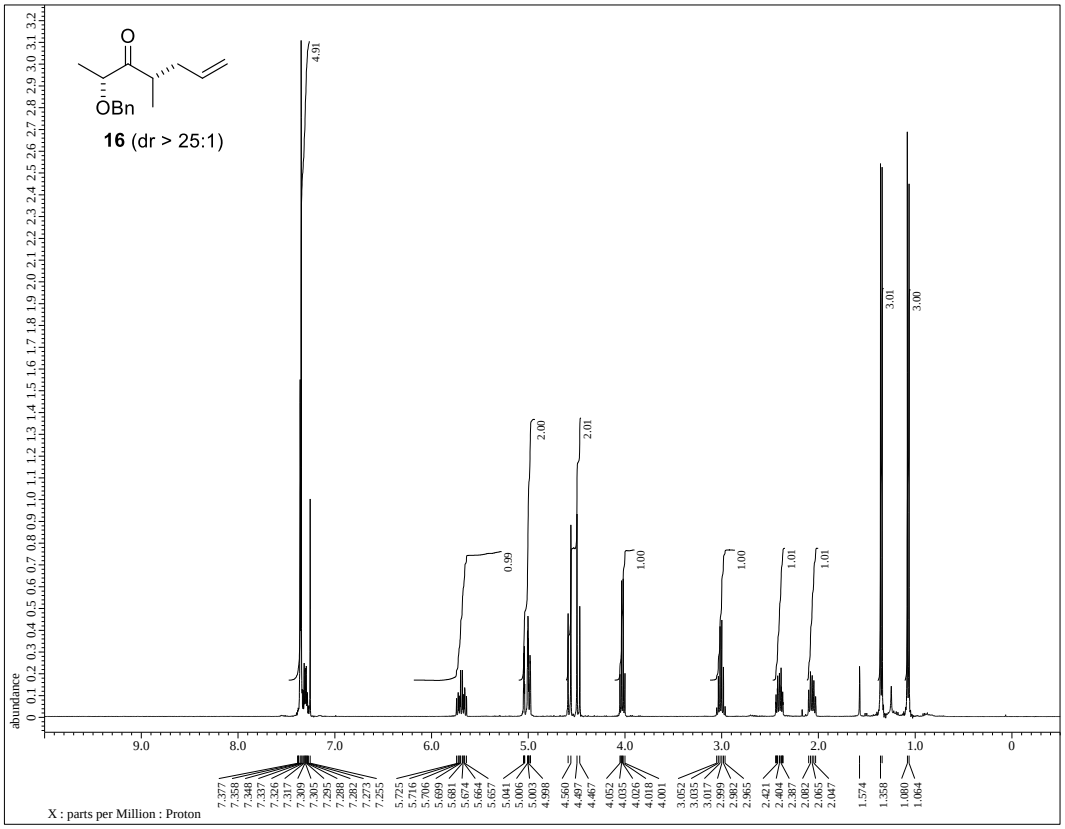

SI-19 (dr>25:1)
abundance
X : parts per Million : Carbon13

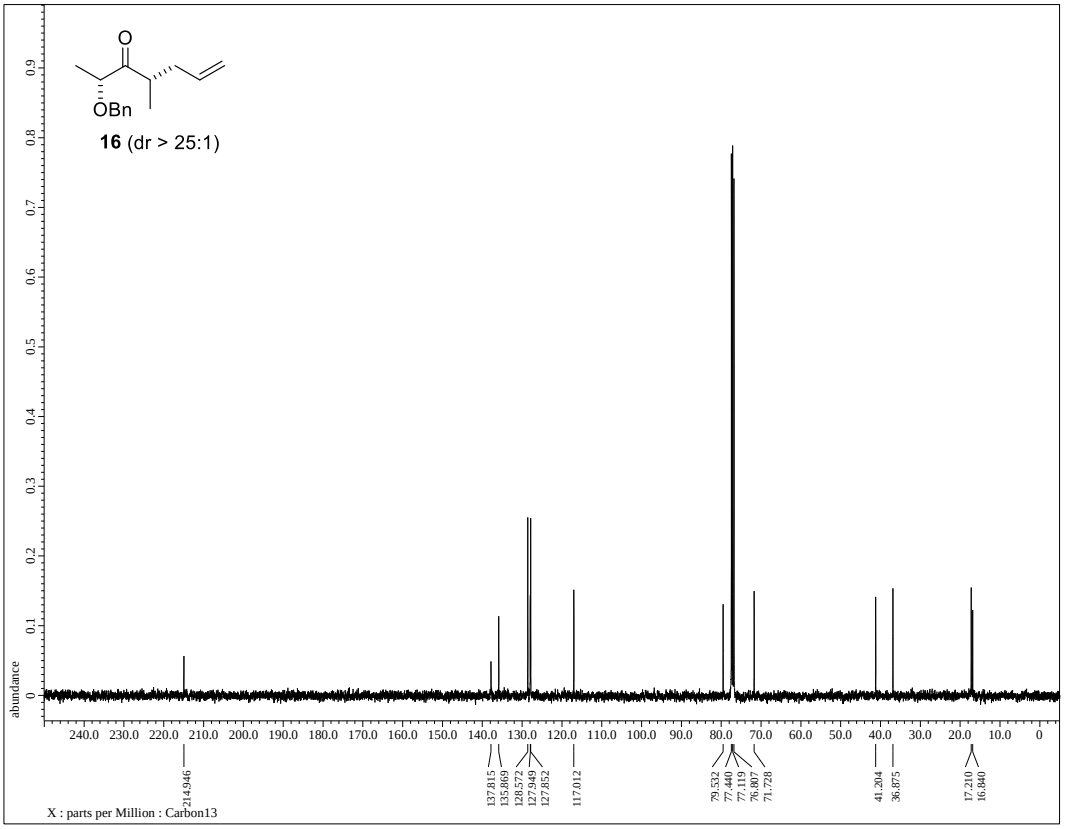

SI-20
abundance
X : parts per Million : Proton

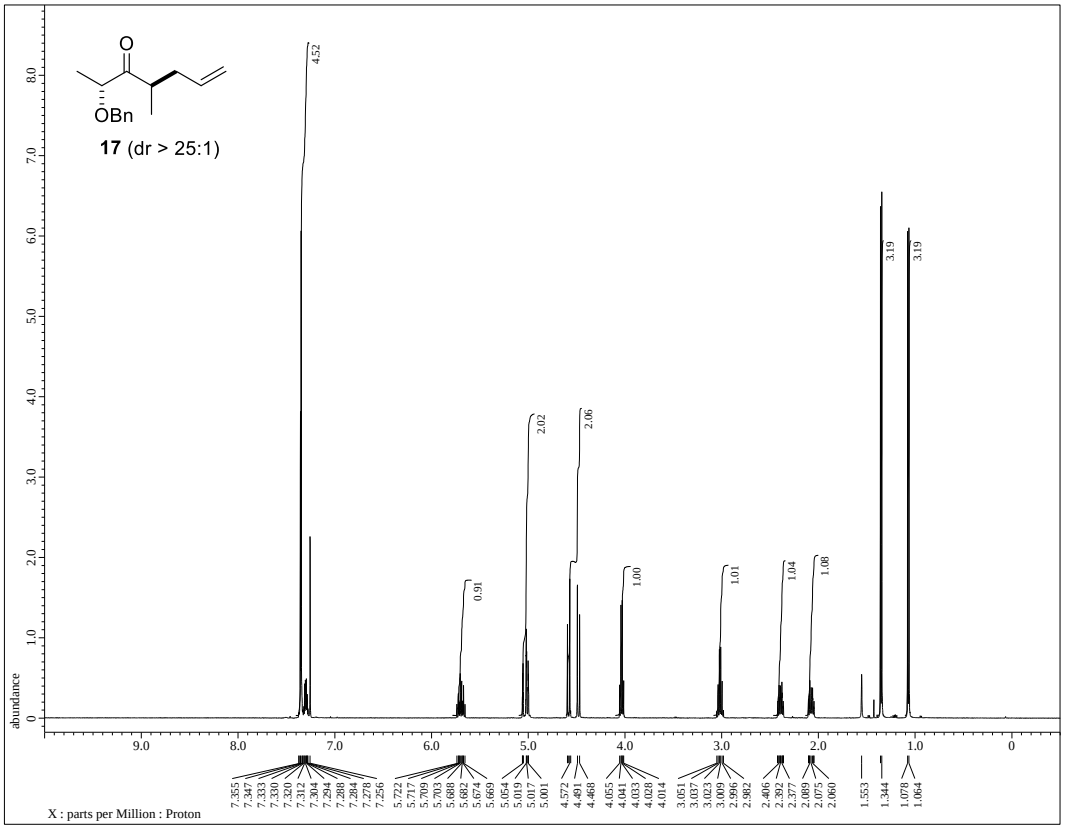

SI-20
abundance
X : parts per Million : Carbon13

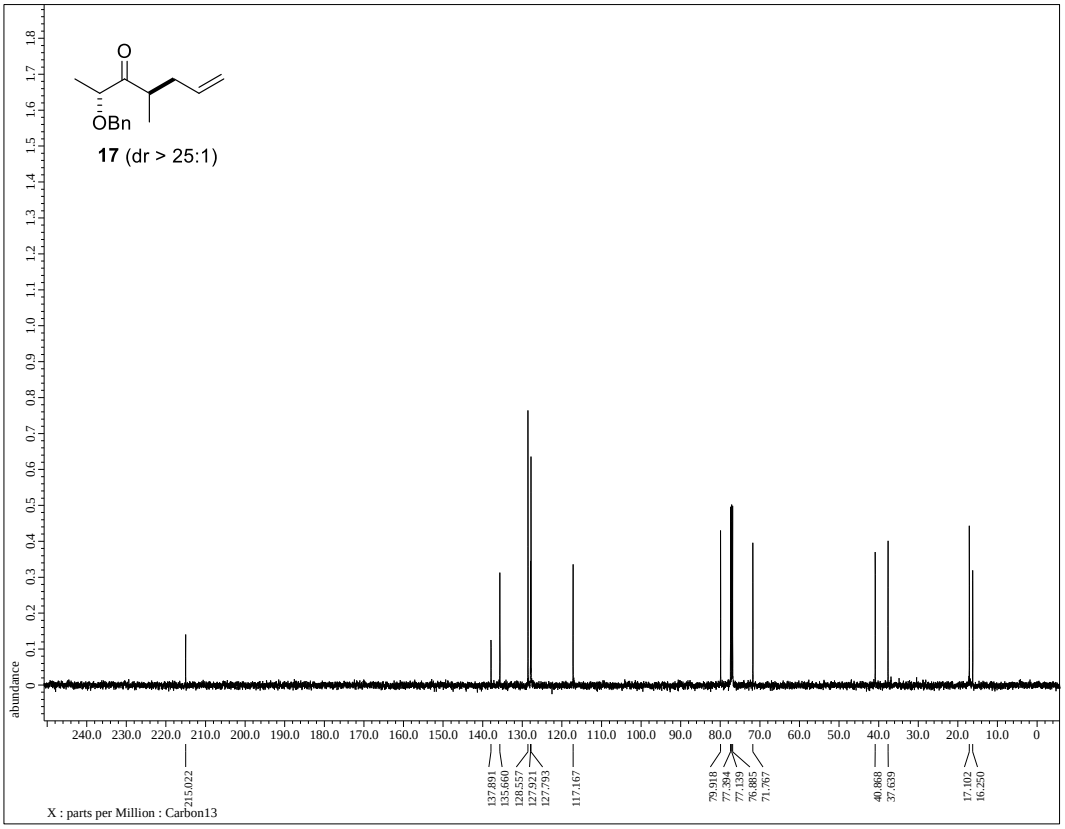

SI-21
SI-22
(SI-21/SI-22 = 75:25)
abundance
X : parts per Million : Proton

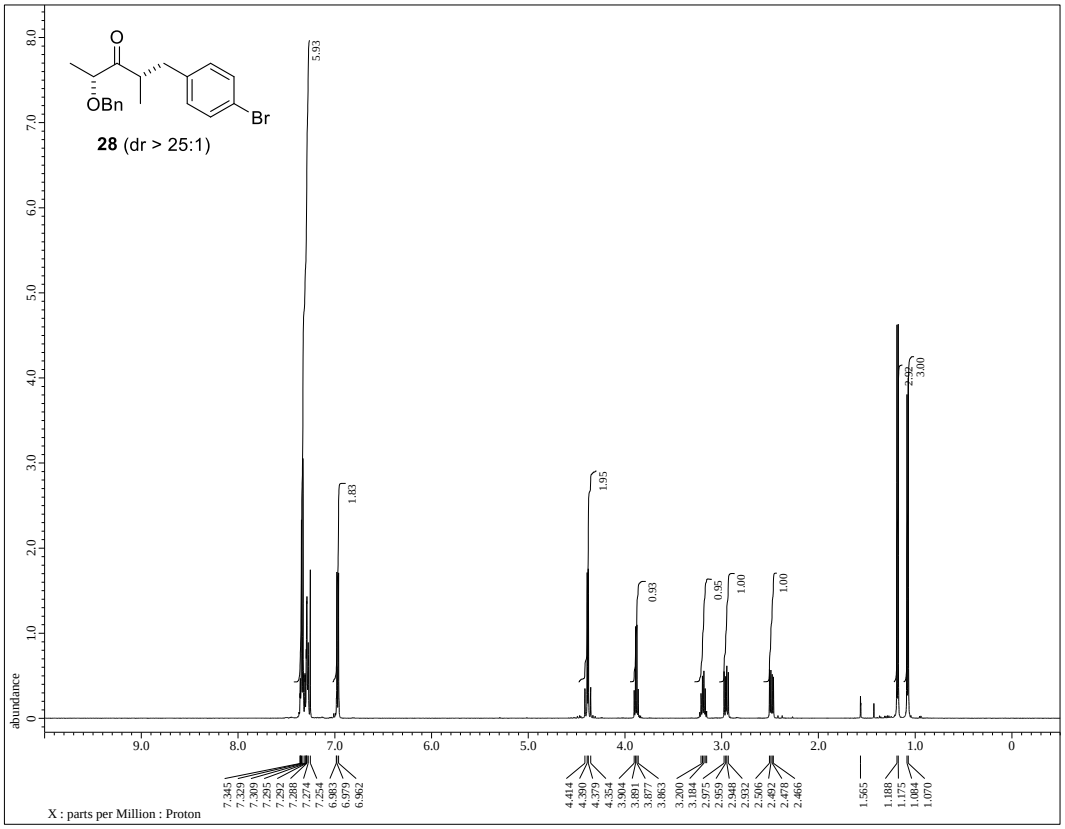

SI-21
SI-22
(SI-21/SI-22 = 75:25)
abundance
X : parts per Million : Carbon13

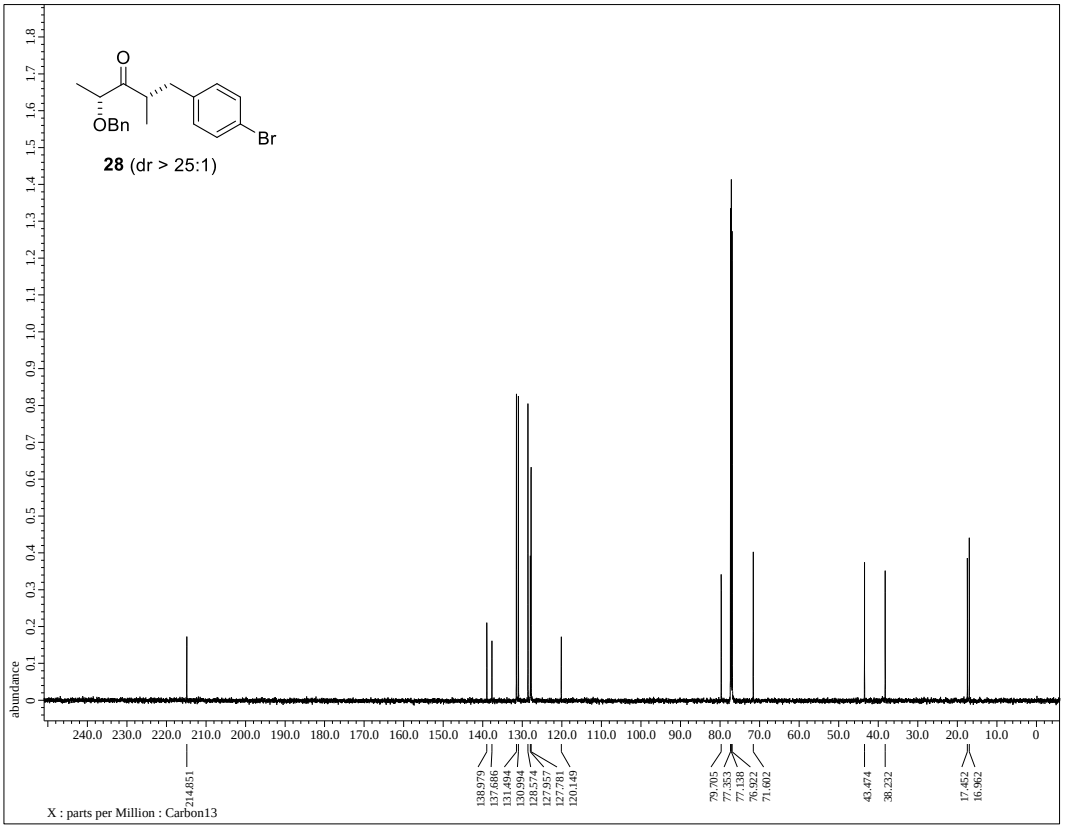

O
OBn
16 (dr > 25:1)
abundance
X : parts per Million : Proton

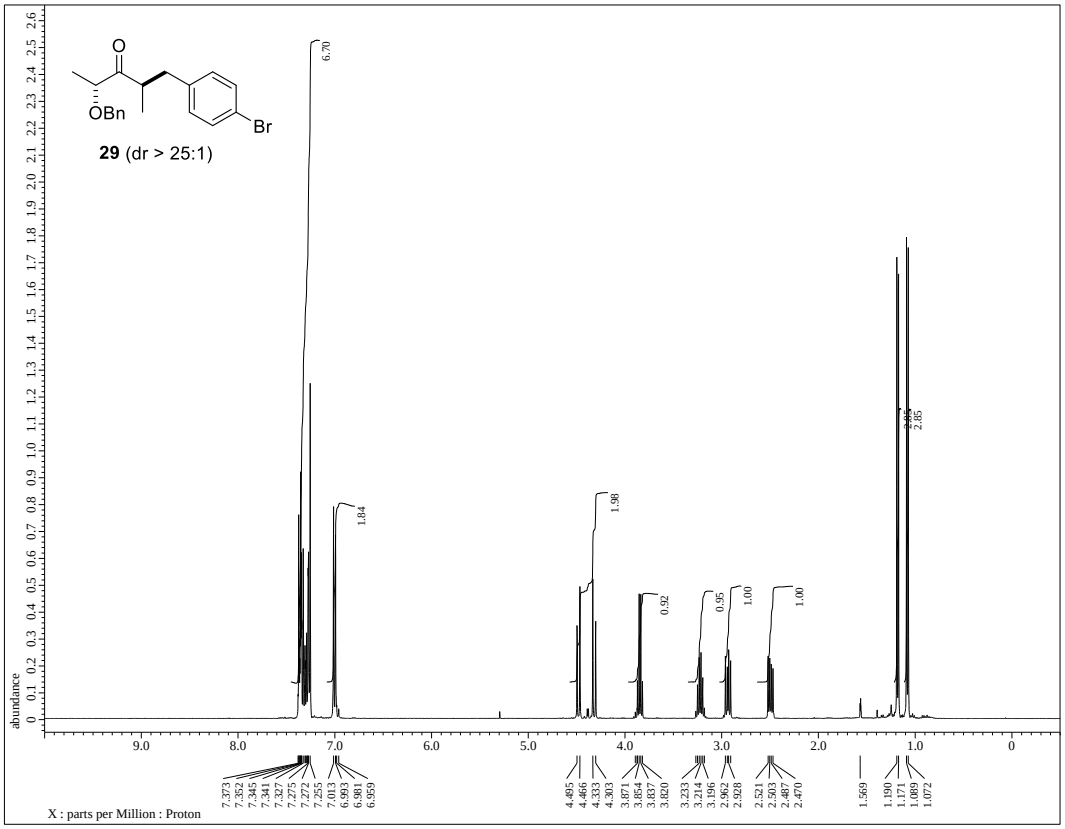

O
OBn
16 (dr > 25:1)
abundance
X : parts per Million : Carbon13

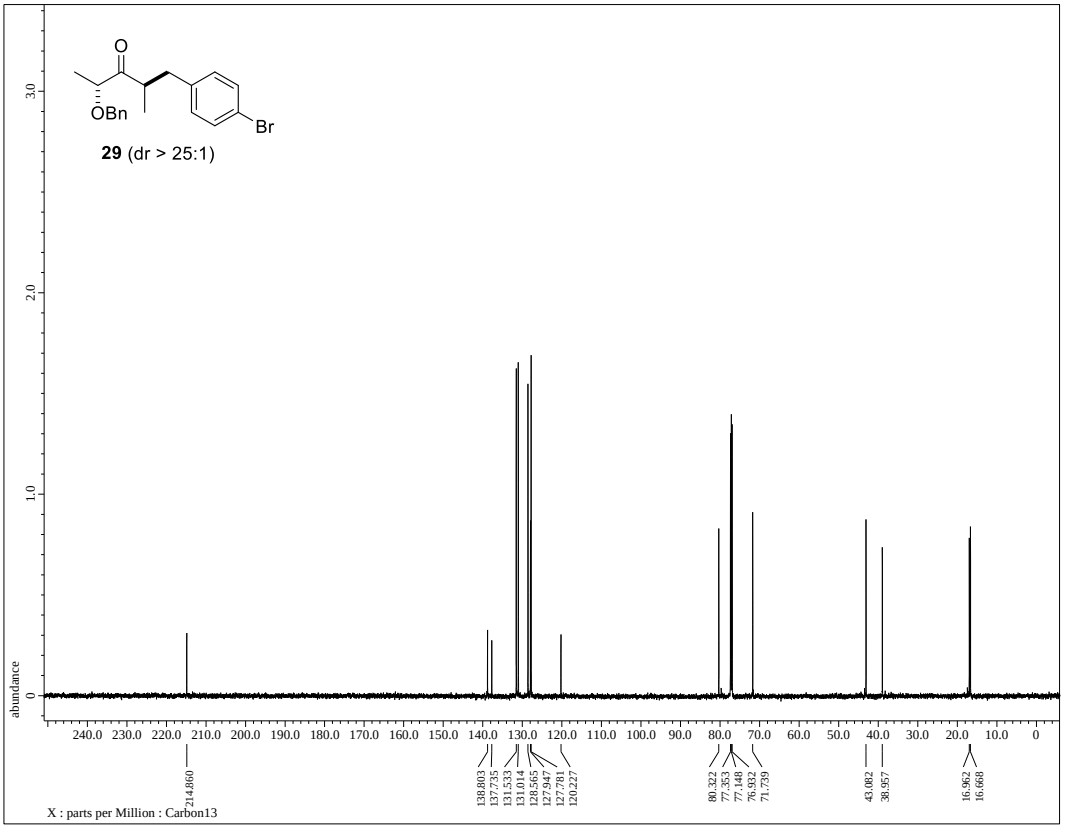

O
OBn
17 (dr > 25:1)
4.52
2.02
2.06
3.19
3.19
0.91
1.00
1.01
1.04
1.08
abundance
X : parts per Million : Proton

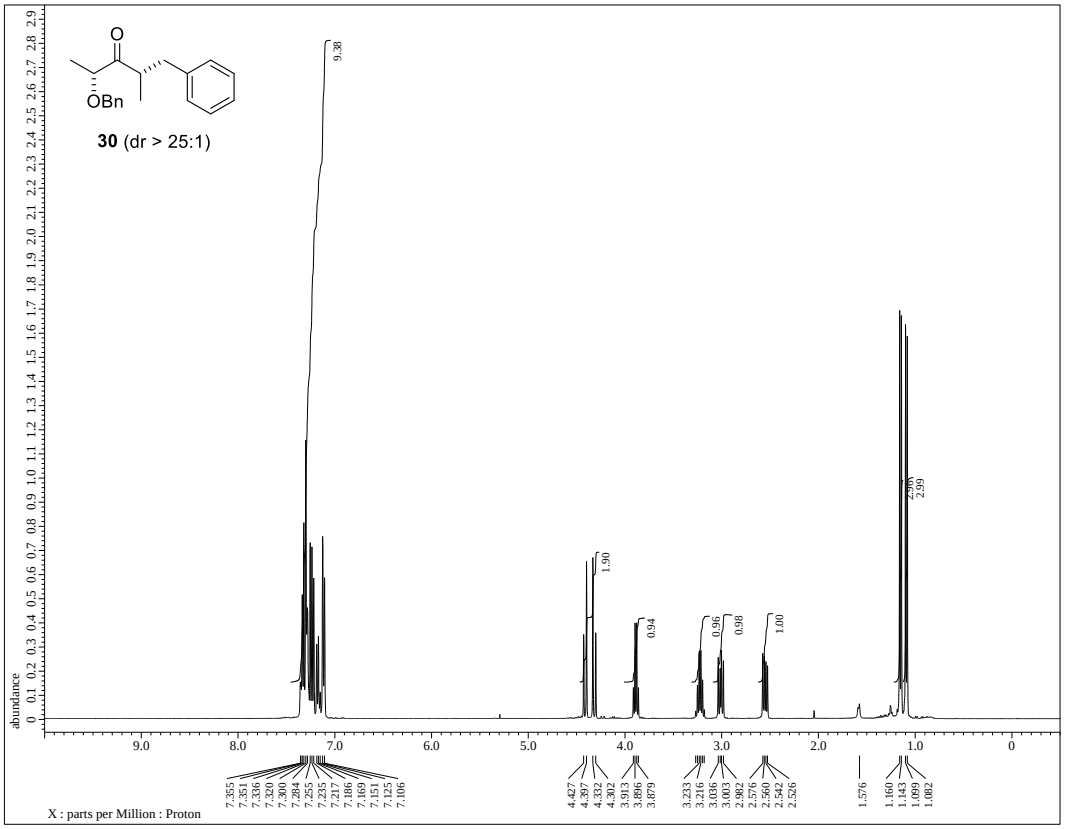

O
OBn
17 (dr > 25:1)
abundance
215.022
137.891
135.660
128.557
127.921
127.793
117.167
79.918
77.304
77.139
76.885
71.767
40.868
37.639
17.102
16.250
X : parts per Million : Carbon13

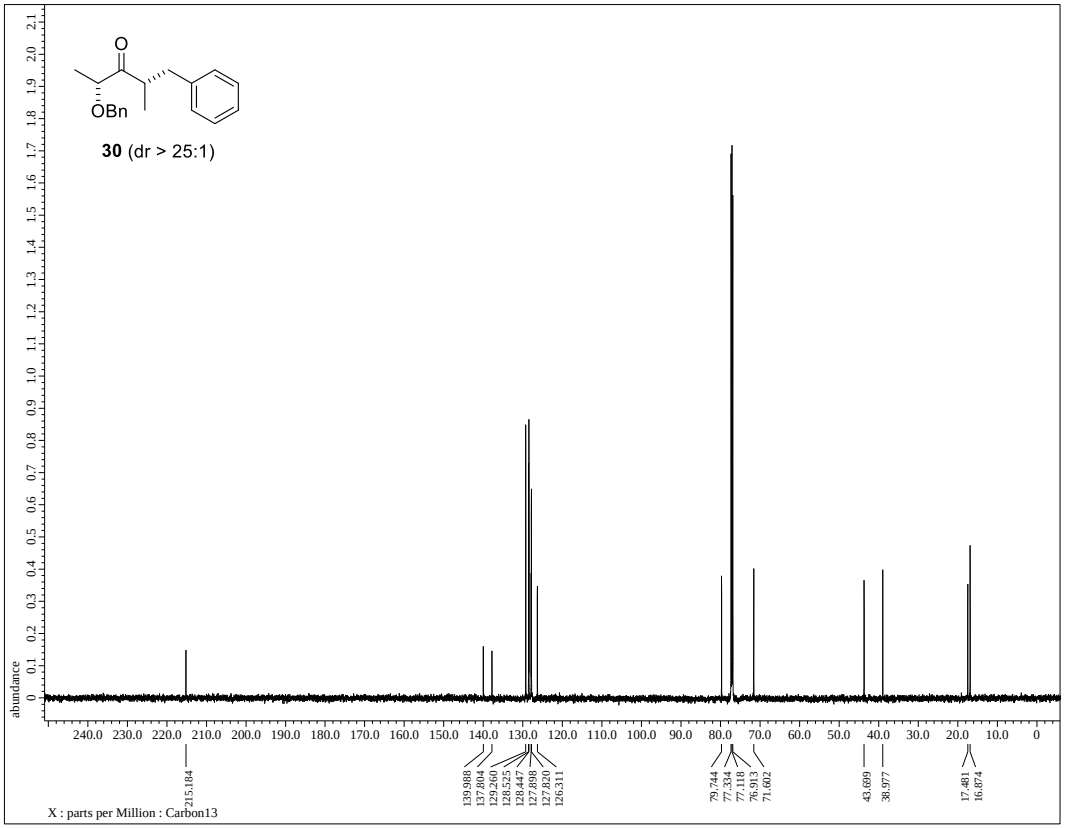

O
OBn
Br
28 (dr > 25:1)
abundance
X : parts per Million : Proton

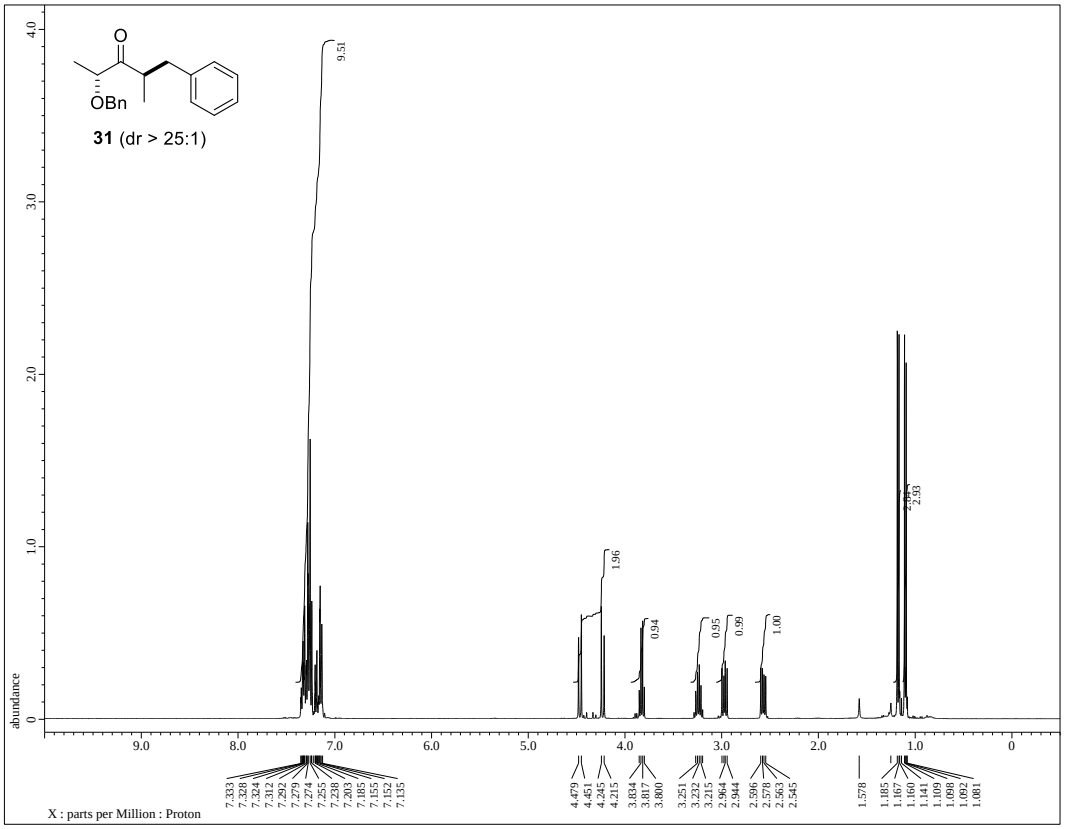

O
OBn
Br
28 (dr > 25:1)
abundance
X : parts per Million : Carbon13

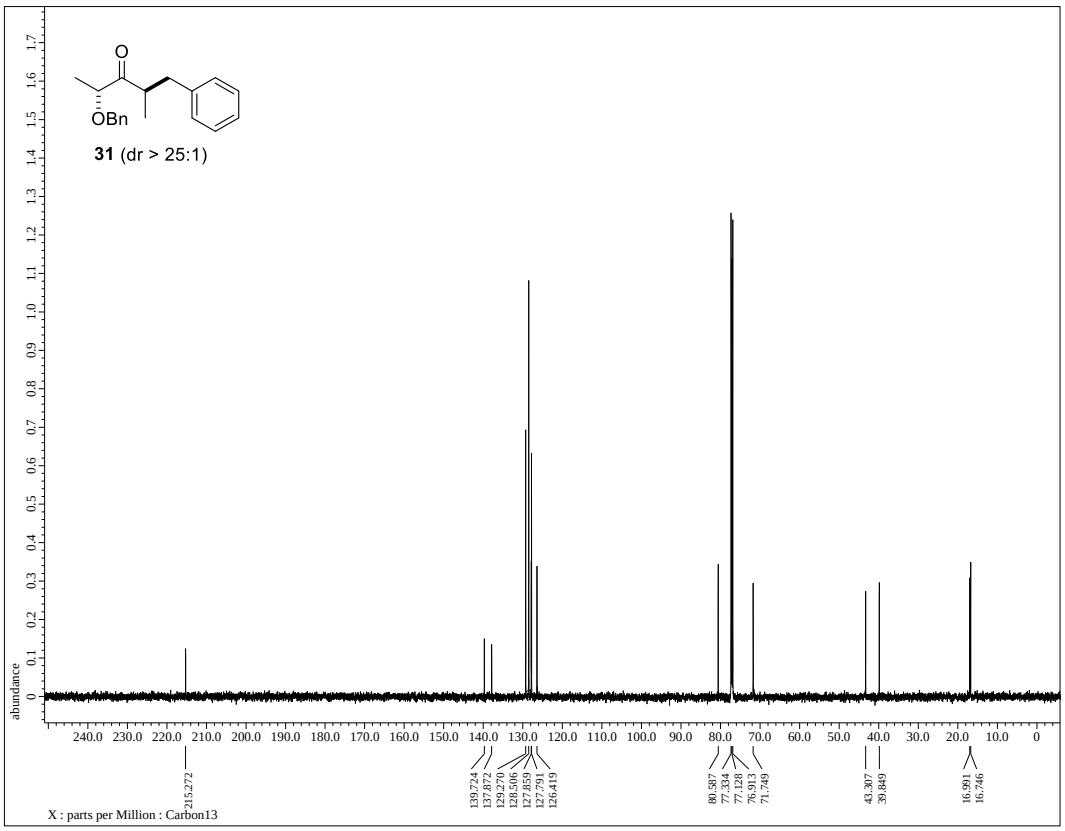

O
OBn
Br
29 (dr > 25:1)
abundance
X : parts per Million : Proton

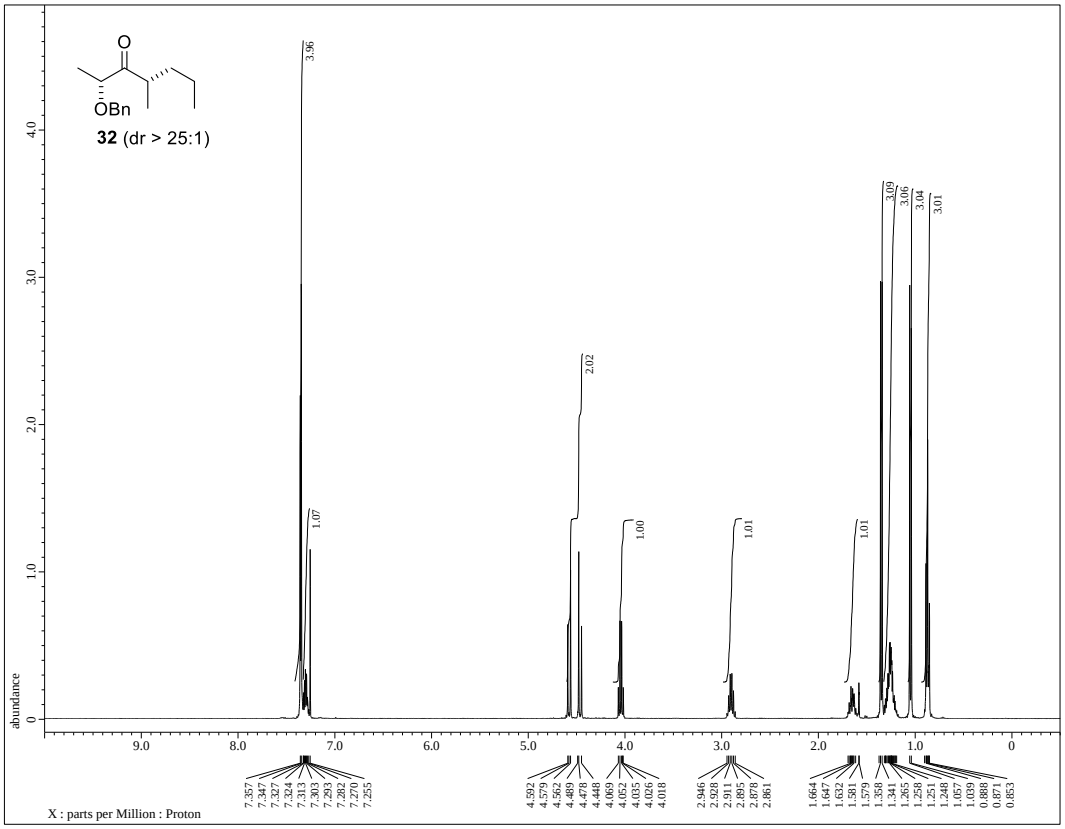

O
OBn
Br
29 (dr > 25:1)
abundance
X : parts per Million : Carbon13

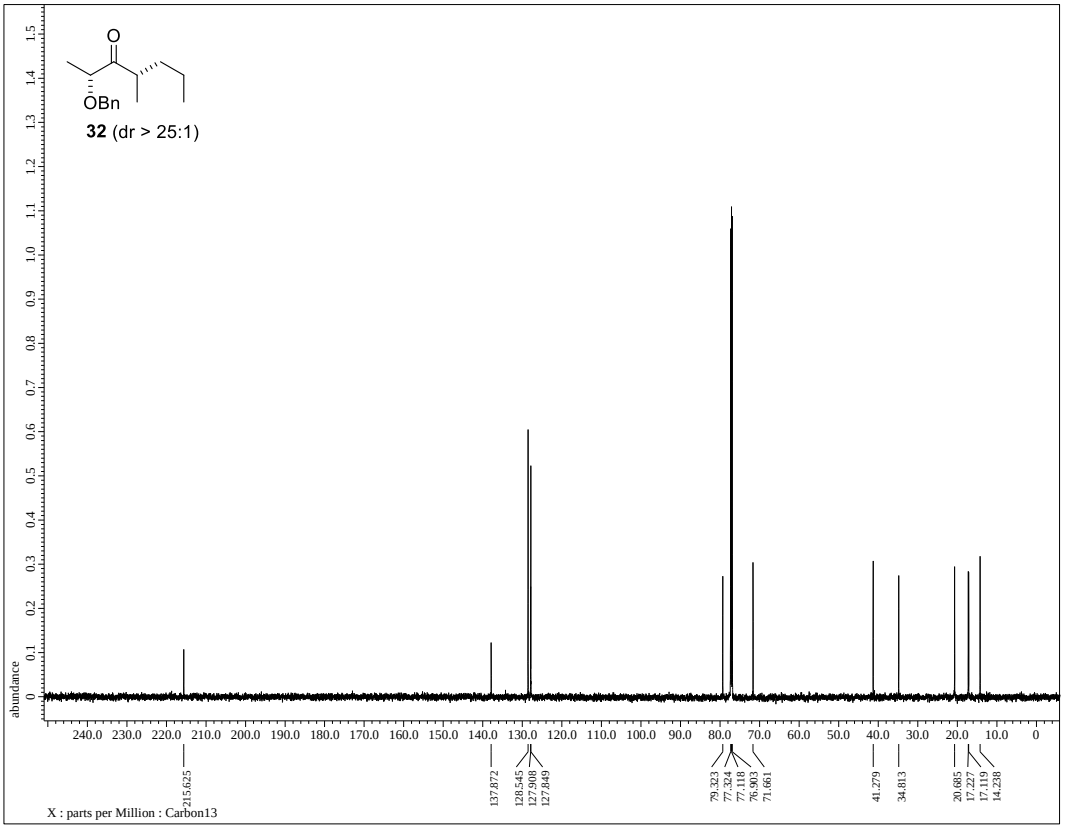

OBn
30 (dr > 25:1)
9.38
1.90
0.94
0.96
0.98
1.00
2.98
2.99
abundance
X : parts per Million : Proton

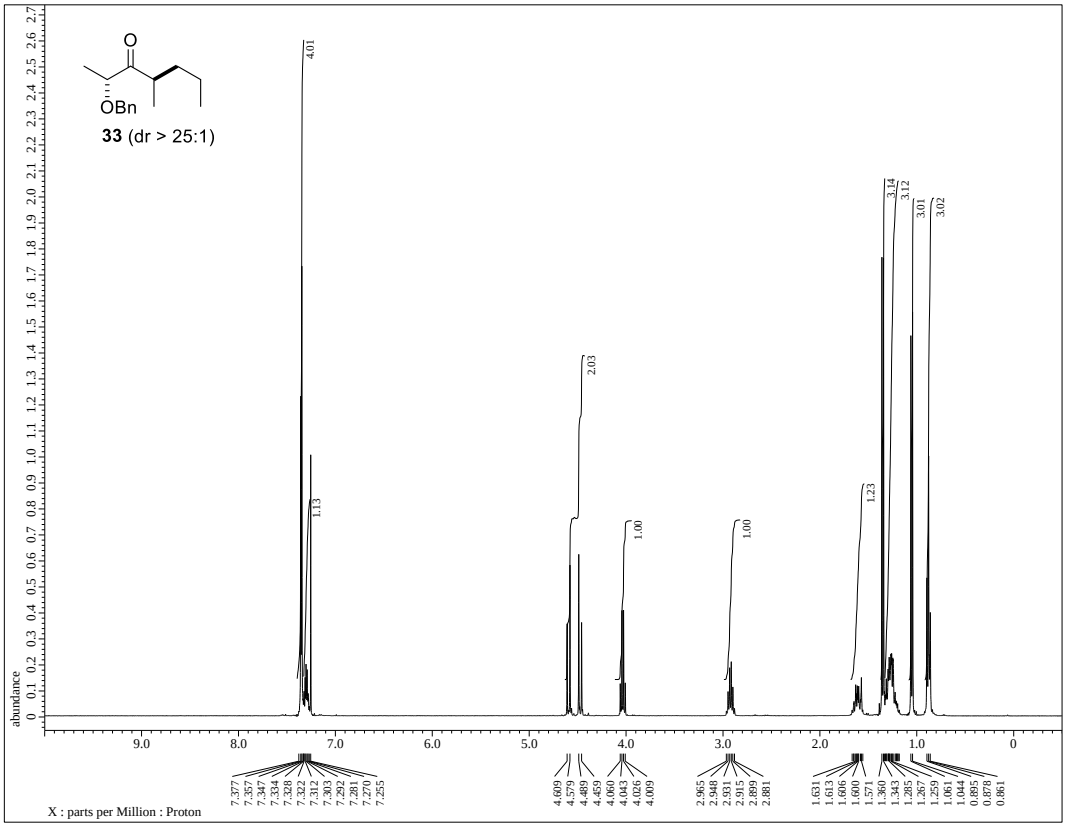

OBn
30 (dr > 25:1)
abundance
X : parts per Million : Carbon13

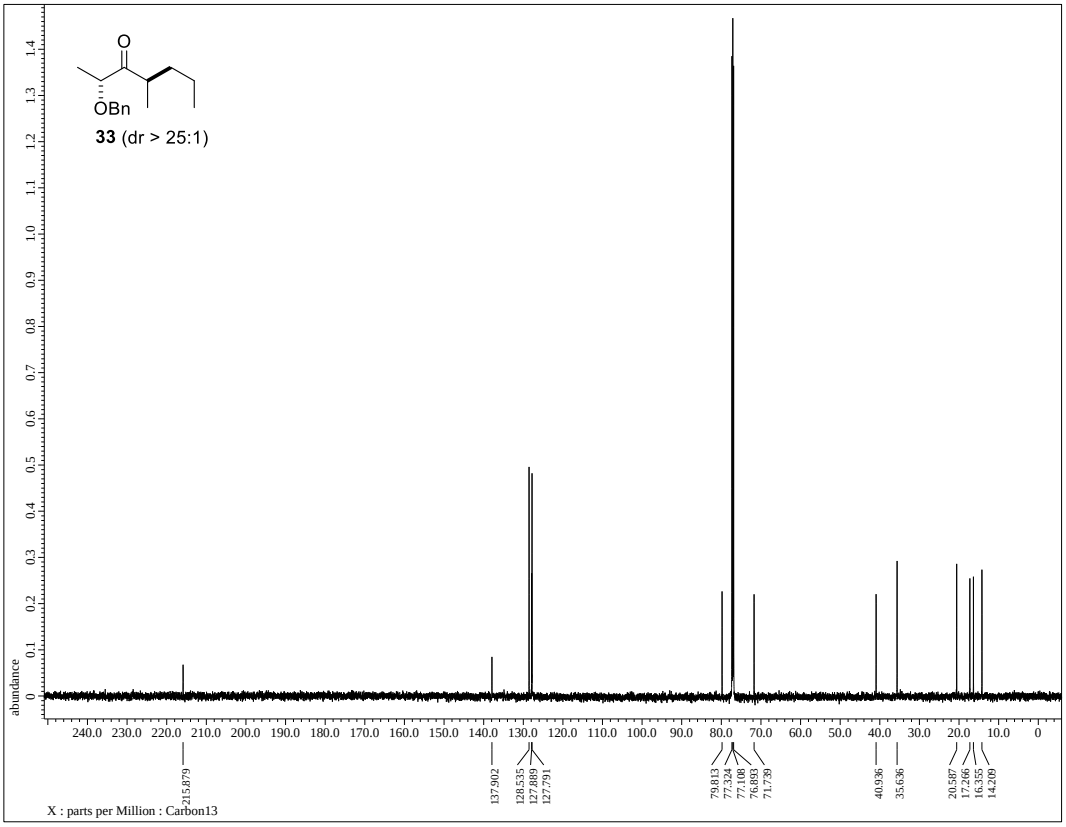

O
OBn
31 (dr > 25:1)
9.51
1.96
0.94
0.95
0.99
1.00
2.94
2.93
abundance
X : parts per Million : Proton

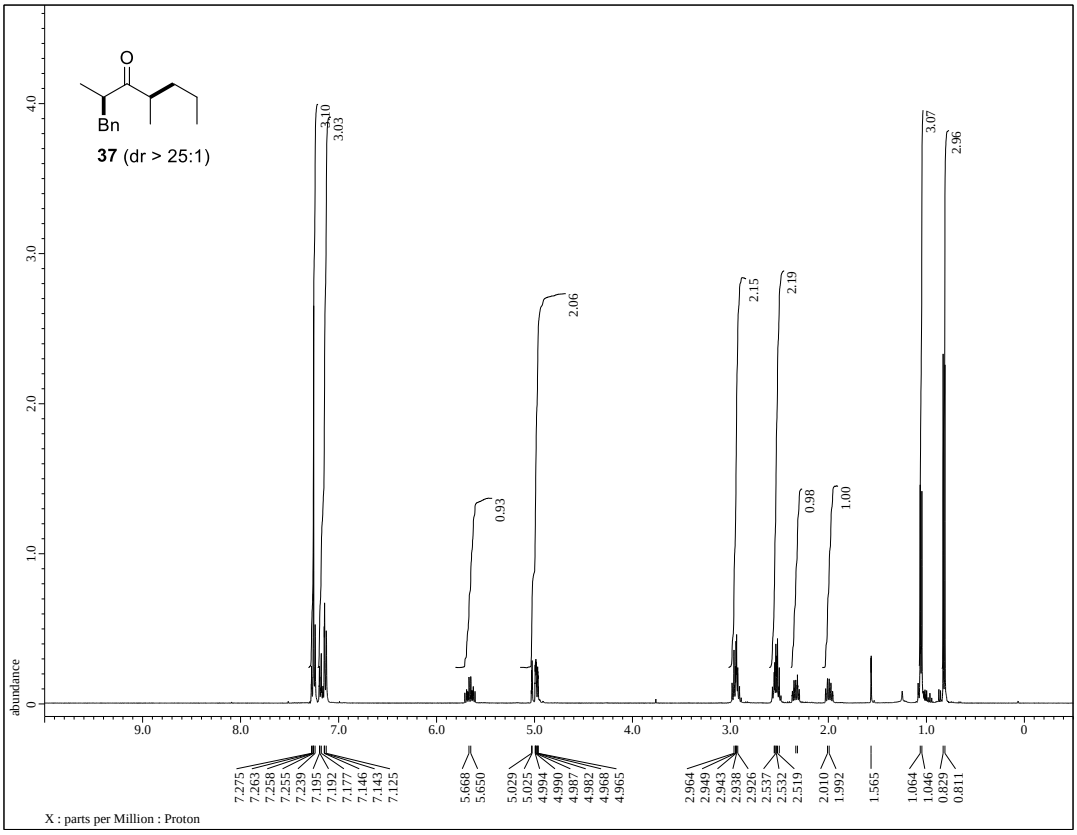

O
OBn
31 (dr > 25:1)
abundance
X : parts per Million : Carbon13

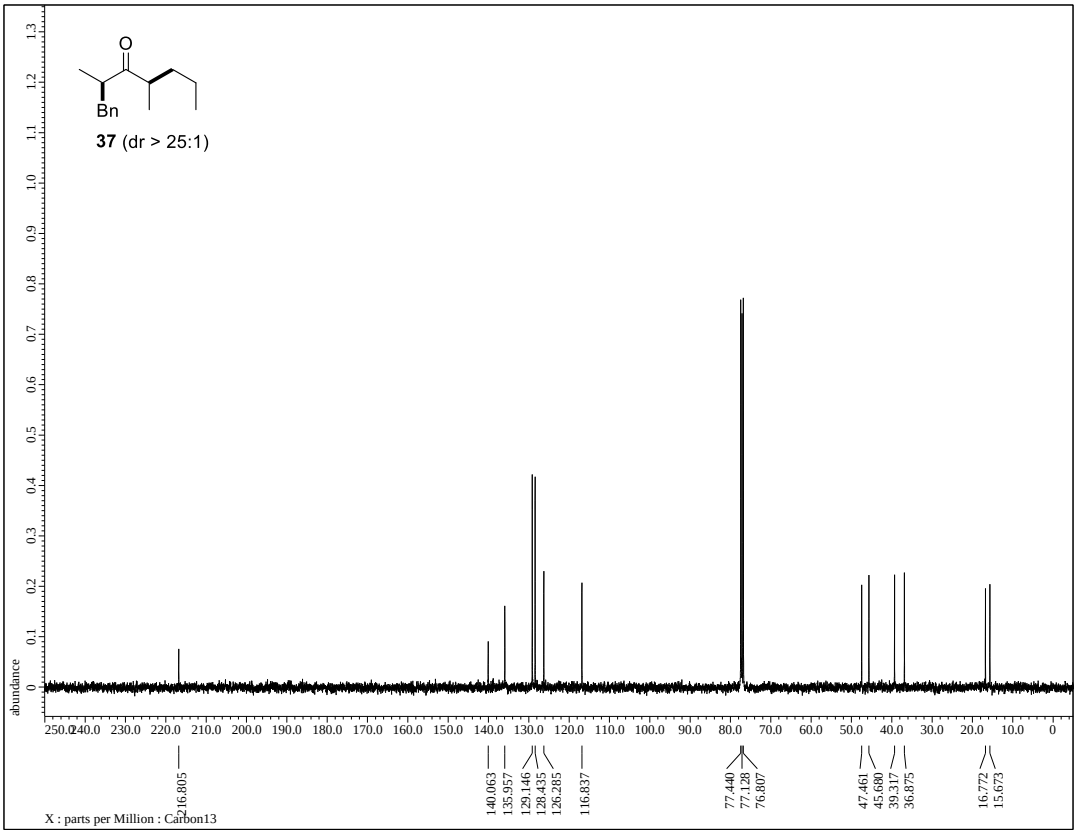

O
OBn
32 (dr > 25:1)
3.96
2.02
1.07
1.00
1.01
1.01
3.09
3.06
3.04
3.01
abundance
X : parts per Million : Proton

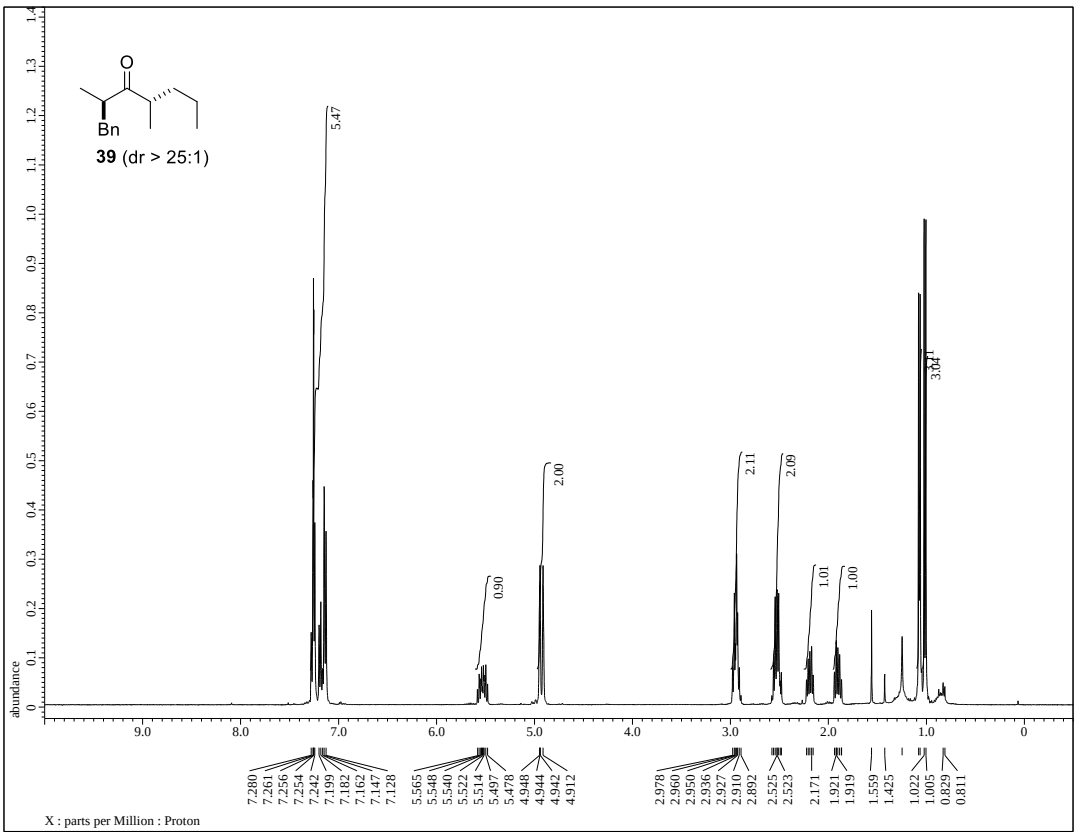

O
OBn
32 (dr > 25:1)
abundance
215.625
137.872
128.545
127.908
127.049
79.323
77.214
77.118
76.903
71.661
41.279
34.813
20.685
17.227
17.119
14.238
X : parts per Million : Carbon13

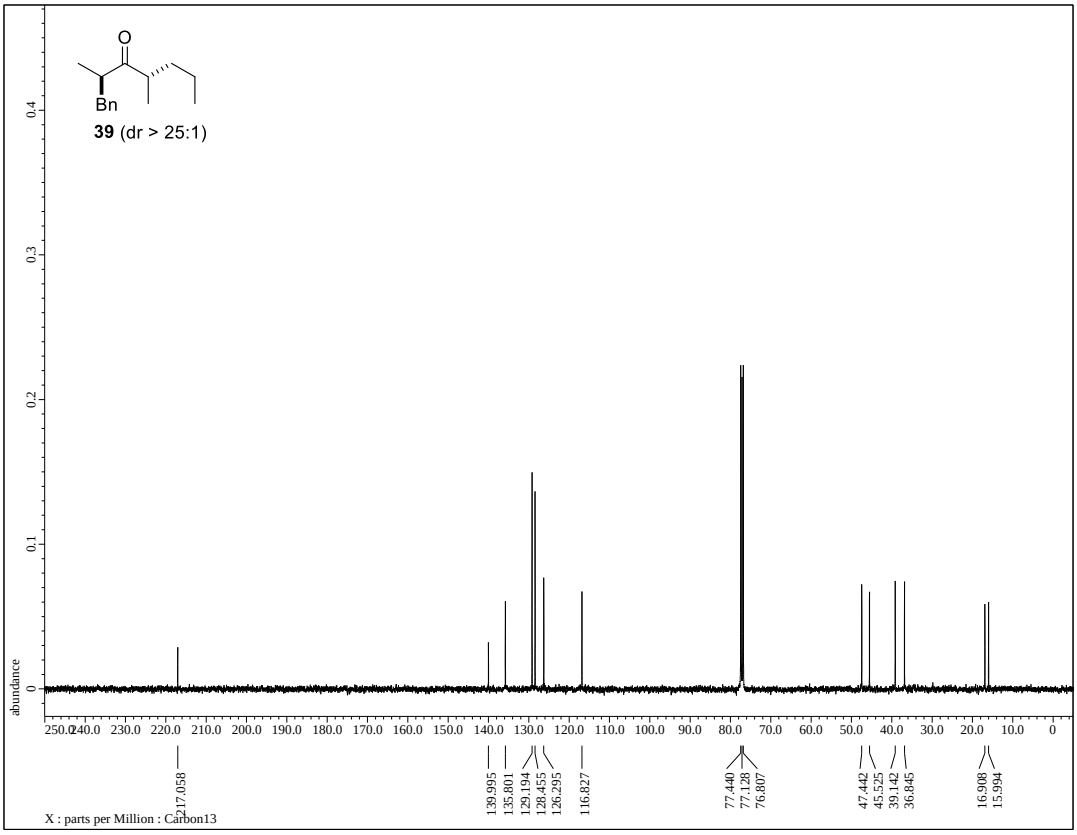

O
OBn
33 (dr > 25:1)
abundance
X : parts per Million : Proton

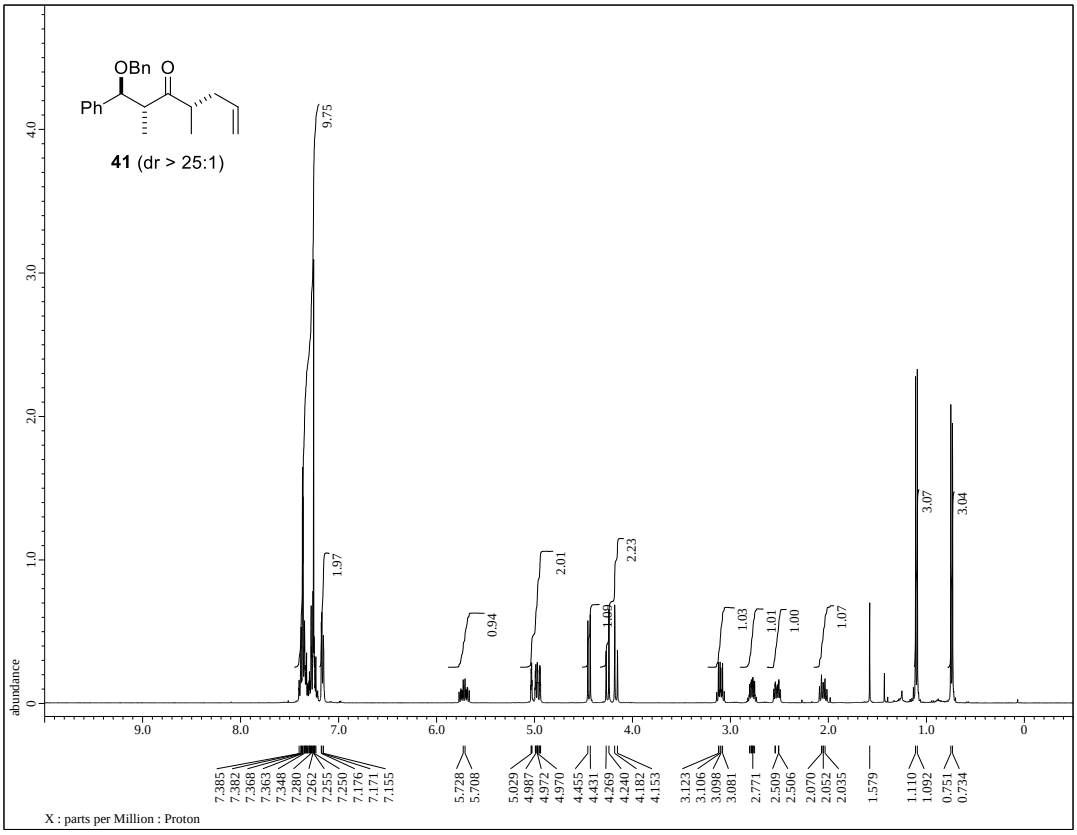

O
OBn
33 (dr > 25:1)
abundance
X : parts per Million : Carbon13

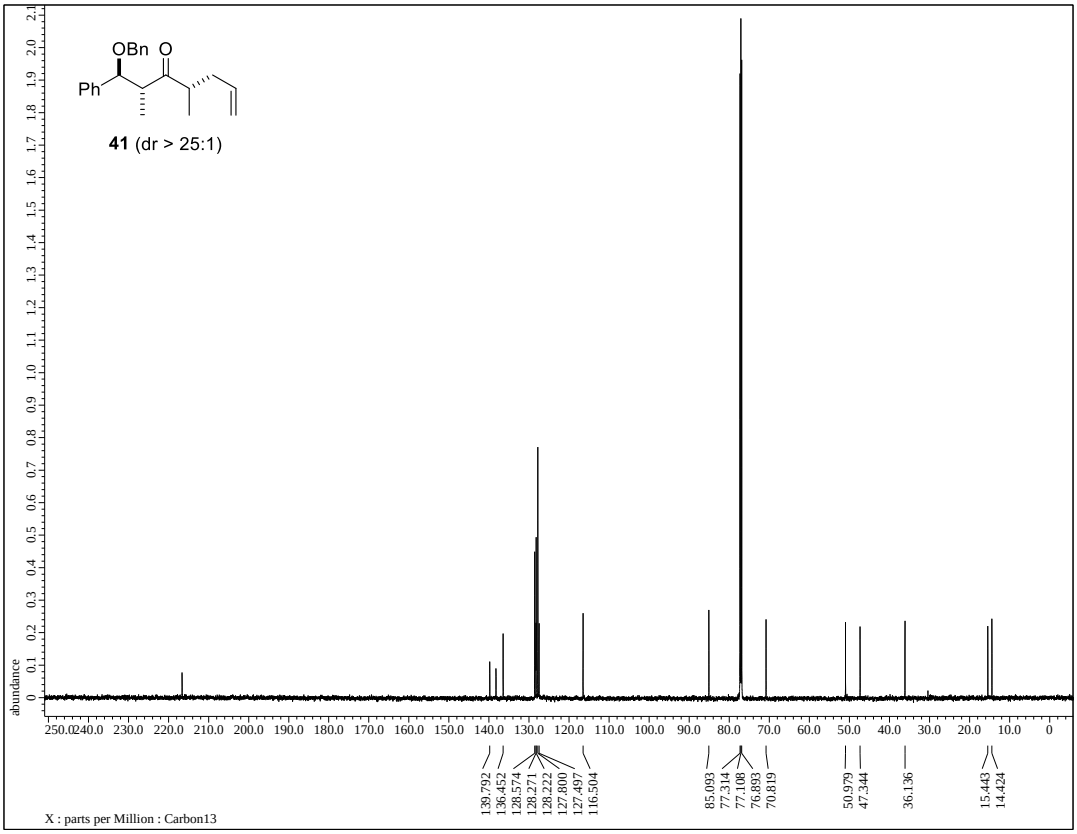

O
Bn
37 (dr > 25:1)
3.10
3.03
3.07
2.96
2.15
2.19
2.06
0.93
0.98
1.00
abundance
7.275
7.263
7.258
7.255
7.239
7.195
7.192
7.177
7.146
7.143
7.125
5.668
5.650
5.029
5.025
4.994
4.990
4.987
4.982
4.968
4.965
2.964
2.949
2.943
2.938
2.926
2.537
2.532
2.519
2.010
1.992
1.565
1.064
1.046
0.829
0.811
X : parts per Million : Proton

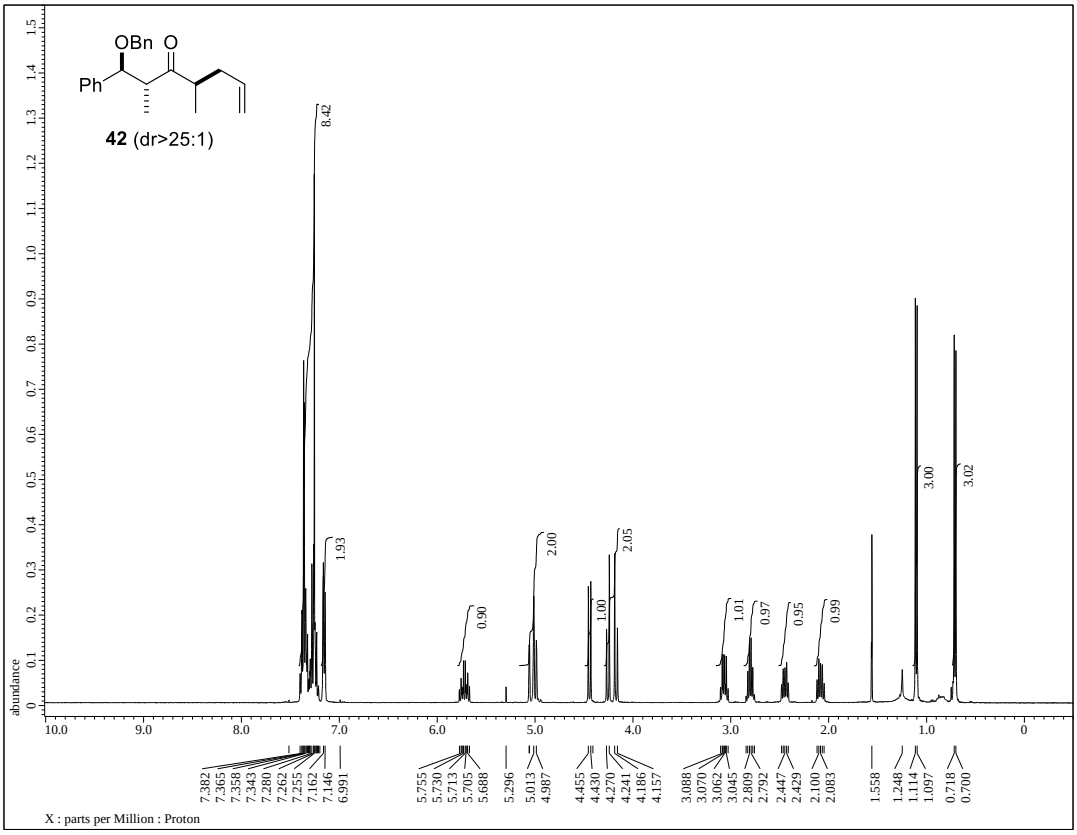

O
Bn
37 (dr > 25:1)
abundance
216.805
140.063
135.957
129.146
128.435
126.285
116.837
77.440
77.128
76.807
47.461
45.680
39.317
36.875
16.772
15.673
X : parts per Million : Carbon13

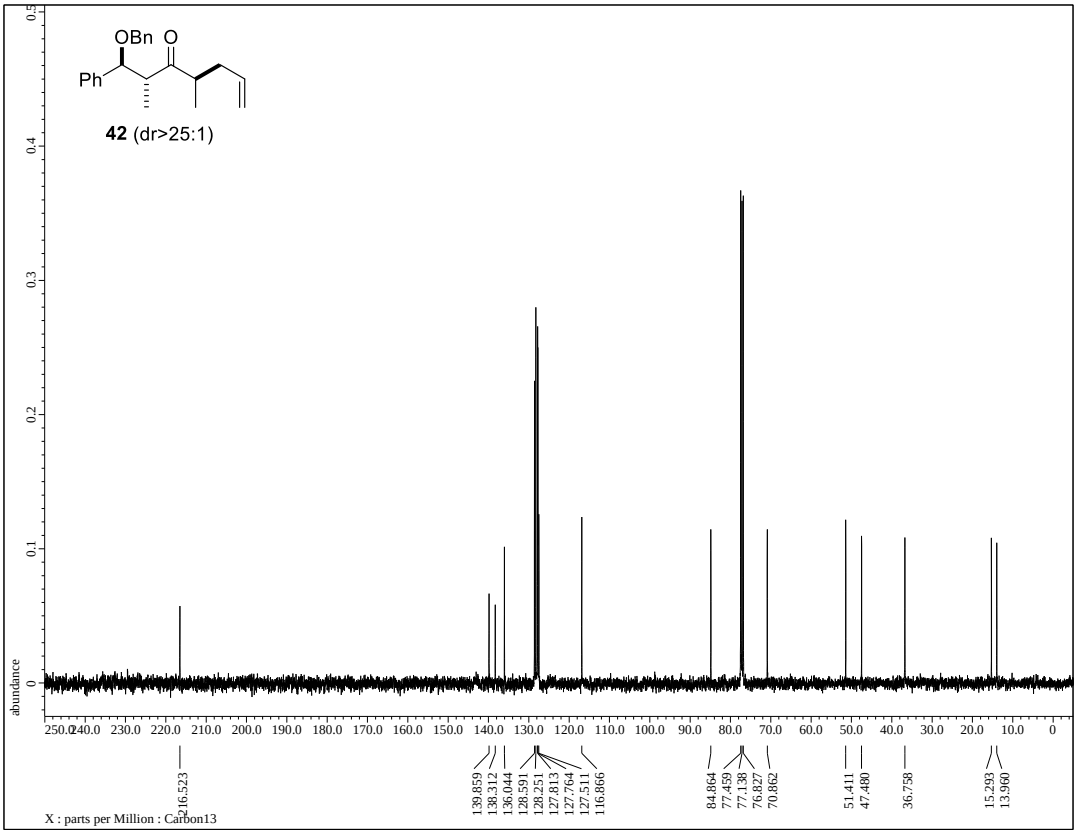

O
Bn
39 (dr > 25:1)
5.47
0.90
2.00
2.11
2.09
1.01
1.00
3.11
3.04
abundance
X : parts per Million : Proton

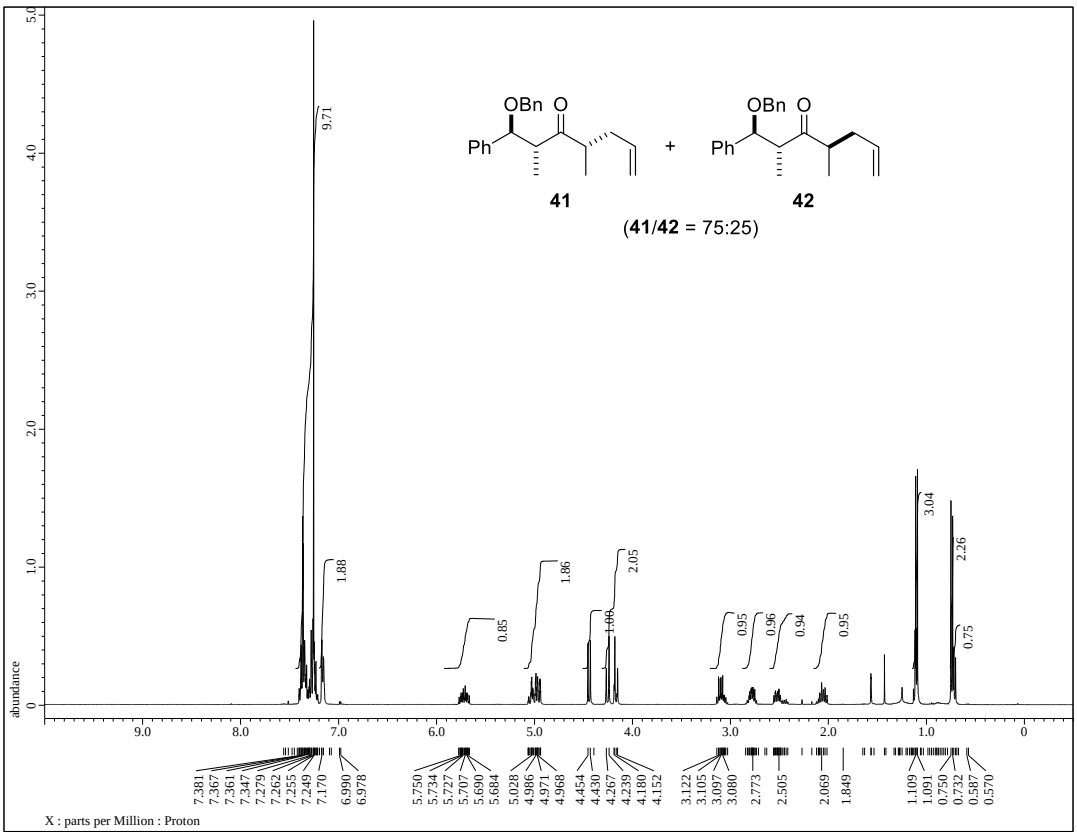

O
Bn
39 (dr > 25:1)
217.058
139.995
135.801
129.194
128.455
126.295
116.827
77.440
77.128
76.807
47.442
45.525
39.142
36.845
16.908
15.994
abundance
X : parts per Million : Carbon13

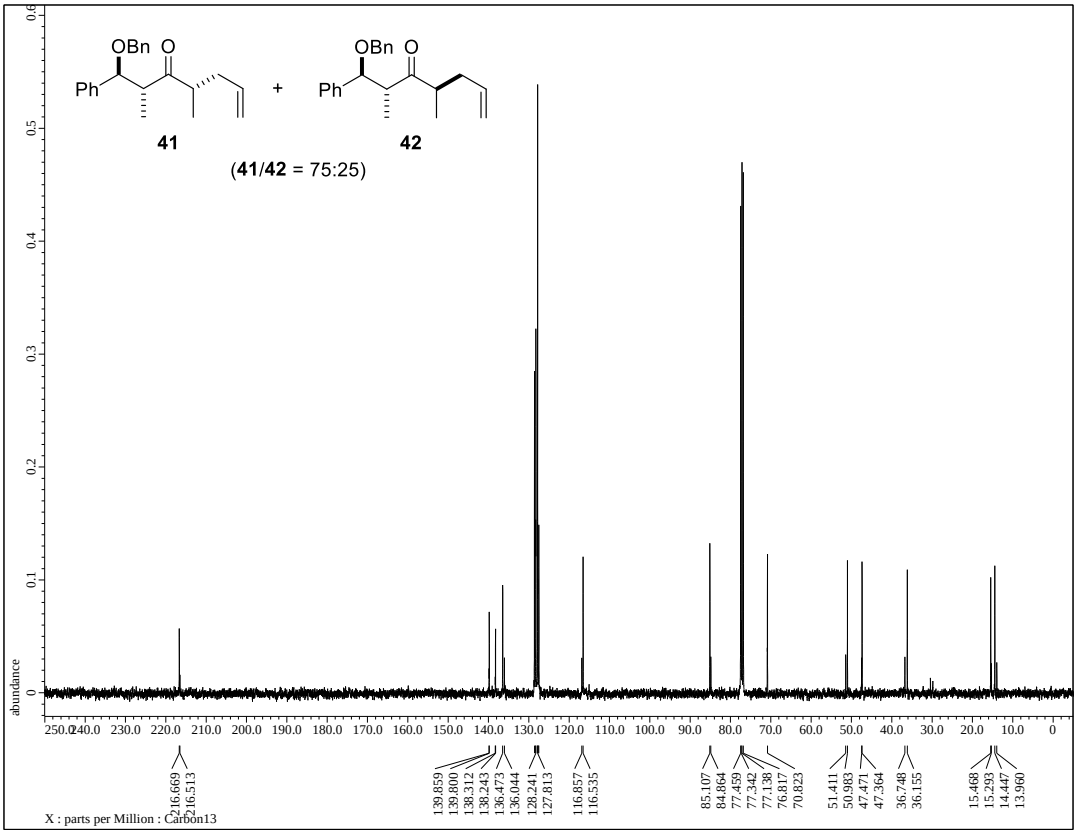

OBn O
Ph
41 (dr > 25:1)
abundance
X : parts per Million : Proton


OBn O
Ph
41 (dr > 25:1)
abundance
X : parts per Million : Carbon13


OBn O
Ph
42 (dr>25:1)
abundance
X : parts per Million : Proton


OBn O
Ph
42 (dr>25:1)
abundance
X : parts per Million : Carbon13


OBn O
Ph
41
+
OBn O
Ph
42
(41/42 = 75:25)
abundance
X : parts per Million : Proton


OBn O
Ph
41
+
OBn O
Ph
42
(41/42 = 75:25)
abundance
X : parts per Million : Carbon13

V. References

1) Ferreró, M.; Galobardes, M.; Martín, R.; Montes, T.; Romeo, P.; Rovira, R.; Urpí, F.; Vilarrasa, J. *Synthesis*, **2000**, *11*, 1608–1614.

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3) Wengryniuk, S. E.; Lim, D.; Coltart, D. M. *J. Am. Chem. Soc*. **2011**, *133*, 8714–8720.

4) Knight, J. D.; Coltart, D. M. *Tetrahedron. Lett.* **2013**, *54*, 5470–5472.