Formal C−H Amination of Cyclopropenes

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Supporting Information

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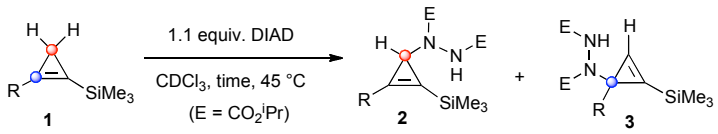
I. General Information: Reactions were carried out in oven or flame-dried glassware unless otherwise noted. Compounds were purchased from Aldrich or Acros or TCI America unless otherwise noted. Flash chromatography was performed using silica gel 60 Å (32–63 mesh) purchased from Silicycle Inc. Analytical thin layer chromatography (TLC) was performed on 0.25 mm E. Merck precoated silica gel 60 (particle size 0.040–0.063 mm). Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), m (multiplet), b (broad), and app (apparent). ^{1}H NMR signals that fall within a ca. 0.3 ppm range are generally reported as a multiplet, with a single chemical shift value corresponding to the center of the peak. Coupling constants, *J*, are reported in Hz (Hertz). Electrospray ionization (ESI) mass spectra were recorded on a Waters Micromass Q-Tof Ultima in the University of Illinois at Urbana-Champaign. Electron impact (EI) mass spectra and Chemical Ionization (CI) mass spectra were obtained using a Micromass 70-VSE in the University of Illinois at Urbana-Champaign.

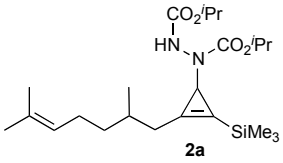
II. Typical procedure for C–H bond amination of cyclopropenes



To silylated cyclopropene **1a**[1] (118 mg, 0.5 mmol) in $CDCl_3$ (1 mL) was added diisopropyl diazocarboxylate (1.1 equiv, 0.55 mmol, 111 mg). The resulting yellow solution was stirred in a 45 ^{o}C sand bath for a certain period of time, at which point ^{1}H NMR indicated the consumption of the starting material. The solution was evaporated or concentrated to afford the crude product, which was purified by column chromatography with a mixture of Hexane : Ethyl Acetate = 8 : 1 to 10 : 1 to give the desired major C−H amination product **2a** (colorless oil, 174 mg) and the minor ene reaction product **3a** (colorless oil, 29 mg), in 93% overall yield (**2a** : **3a** = 6 : 1).

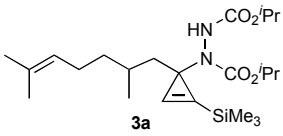
[1] Li, J.; Sun, C.; Lee, D. *J. Am. Chem. Soc.* **2010**, *132*, 6640-6641.

Note on spectroscopic data. *Because of the restricted rotation around the carbamate C–N bonds, the hydrazodicarboxylate products* ***2*** *and* ***3*** *exist as mixtures of rotamers at room temperature. As a result, the NMR spectra are of low quality, especially the* ^{13}*C-NMR, even at a high concentration. In the* ^{13}*C-NMR, only those peaks which are readily evident in the spectrum are listed.*



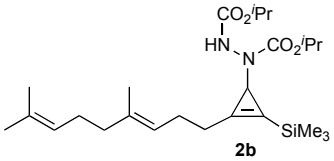
2a

2a: Colorless oil (79% yield, **2a** : **3a** = 6 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.16-6.02 (bm, 1H), 5.12-5.08 (m, 1H), 5.04-4.90 (bm, 2H), 3.70-3.50 (bs, 1H), 2.58-2.52 (m, 1H), 2.47-2.38 (m, 1H), 2.08-1.93 (m, 2H), 1.88-1.79 (m, 1H), 1.72-1.66 (s, 3H), 1.65-1.58 (s, 3H), 1.47-1.36 (m, 2H), 1.23-1.10 (bm, 12H), 0.96 (d, J = 6.7 Hz, 1H), 0.93 (d, J = 6.5 Hz, 2H), 0.18 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.72, 136.89, 131.36, 124.51, 112.80, 69.27, 38.49, 38.32, 37.00, 36.71, 34.20, 34.05, 31.44, 31.24, 25.71, 25.58, 25.51, 22.20, 22.04, 19.82, 19.65, 17.65, 1.18. HRMS (EI) calcd for $C_{23}H_{42}N_2O_4NaSi$ $[M+Na]^+$ 461.2812, found 461.2814.



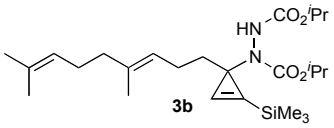
3a

3a: Colorless oil (13% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77-7.70 (bm, 1H), 6.24-6.17 (bm, 1H), 5.11-5.05 (m, 1H), 4.99-4.87 (bm, 2H), 2.04-1.83 (m, 3H), 1.65 (s, 3H), 1.61 (s, J = 1.2, 0.4 Hz, 4H), 1.41-1.17 (bm, 14H), 1.16-1.10 (m, 1H), 1.08-1.00 (m, 1H), 0.89 (d, J = 6.4 Hz, 2H), 0.77 (d, J = 6.3 Hz, 1H), 0.19 (d, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.00, 131.12, 131.02, 125.00, 69.29, 45.12, 43.80, 37.11, 31.60, 30.24, 29.85, 25.70, 25.46, 25.42, 22.67, 22.25, 22.17, 22.01, 19.85, 19.69, 17.64, 14.12,-1.09. HRMS (EI) calcd for $C_{23}H_{42}N_2O_4Si$ 438.2954, found 438.2919.



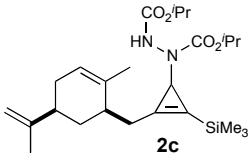
2b

2b: Colorless oil (83% yield, **2b** : **3b** = 12 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.19-6.16 (bm, 1H), 5.14-5.08 (m, 2H), 5.01-4.94 (m, 2H), 3.69 (bs, 1H), 2.64-2.53 (m, 2H), 2.32-2.29 (m, 2H), 2.09-2.02 (m, 3H), 2.02-1.97 (m, 1H), 1.70 (bs, 3H), 1.65-1.59 (m, 6H), 1.37-1.19 (bm, 12H), 0.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.14, 131.62, 131.39, 124.23, 123.24, 113.09, 69.34, 39.62, 38.57, 32.02, 27.30, 27.06, 26.71, 26.53, 25.71, 25.61, 23.36, 22.20, 22.03, 17.68, 16.11, -1.13. HRMS (EI) calcd for $C_{25}H_{44}N_2O_4NaSi$ $[M+Na]^+$ 487.2968, found 487.2961.



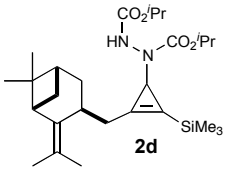
3b

3b: Colorless oil (7% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.79-7.70 (bm, 1H), 6.24-6.17 (bm, 1H), 5.09-5.03 (m, 2H), 4.94-4.87 (bm, 2H), 2.14-2.07 (bm, 1H), 2.08-2.00 (m, 2H), 2.00-1.93 (m, 2H), 1.86-1.70 (bm, 3H), 1.67 (s, 3H), 1.59 (s, 3H), 1.52 (s, 3H), 1.38-1.13 (bm, 12H), 0.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.91, 134.88, 131.30, 128.43, 124.39, 124.27, 63.31, 46.27, 39.73, 35.54, 26.74, 25.71, 25.53, 22.25, 22.02, 17.69, 16.02, -1.06. HRMS (EI) calcd for $C_{25}H_{44}N_2O_4Si$ 464.3070, found 464.3078.



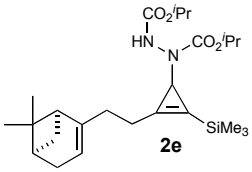
2c

2c: Colorless oil (81% yield, **2c** : **3c** = 8 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.14-6.11 (bm, 1H), 5.47 (s, 1H), 4.94-4.91 (bm, 2H), 4.68 (s, 2H), 3.66 (bs, 1H), 2.88-2.81 (m, 1H), 2.50-2.48 (m, 2H), 2.18-2.14 (m, 1H), 2.07-2.03 (m, 1H), 1.91-1.79 (m, 2H), 1.70 (s, 3H), 1.67 (s, 3H), 1.34-1.14 (m, 13H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.67, 149.84, 136.21, 135.53, 123.47, 113.28, 108.59, 69.29, 41.55, 41.54, 38.87, 38.54, 38.27, 38.13, 35.08, 31.21, 30.83, 22.23, 22.07, 21.20, 21.13, 20.73, 20.69, -1.19. HRMS (EI) calcd for $C_{25}H_{42}N_2O_4Si$ [M] 462.2914, found 462.2903.



2d

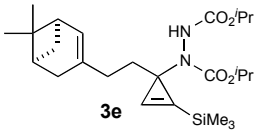
2d: Colorless oil (74% yield, **2d** : **3d** = 6 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.15-6.08 (bm, 1H), 4.96-4.88 (bm, 2H), 3.72-3.69 (m, 1H), 3.47 (qd, J = 7.0, 3.9 Hz, 1H), 2.94-2.61 (m, 3H), 2.29-2.20 (m, 1H), 2.07-2.01 (m, 1H), 1.95-1.94 (m, 1H), 1.64 (s, 3H), 1.57 (s, 3H), 1.34-1.09 (m, 15H), 0.66-0.59 (d, J = 6.5 Hz, 3H), -0.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.75, 137.46, 137.10, 123.13, 113.31, 69.28, 65.85, 45.92, 41.12, 40.96, 39.19, 38.64, 38.32, 32.13, 30.82, 30.57, 26.80, 26.12, 22.23, 22.05, 21.27, 20.48, 19.75, 15.28, -1.03. HRMS (EI) calcd for $C_{27}H_{46}N_2O_4NaSi$ $[M+Na]^+$ 513.3149, found 513.3137.



2e

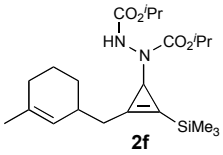
2e: Colorless oil (74% yield, **2e** : **3e** = 4 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.21-6.10 (bm, 1H), 5.19 (s, 1H), 4.92 (bm, 2H), 3.64 (bs, 1H), 2.56 (m, 2H), 2.35-2.28 (m, 1H), 2.28-2.10 (m, 4H), 2.08-2.05 (m, 1H), 2.02-1.96 (m, 1H), 1.34 (bm, 15H), 1.14-1.07 (m, 1H), 0.82-0.76 (s, 3H), -0.16 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.23, 137.79, 116.34, 112.66, 69.25, 45.84, 45.73, 40.84,

38.53, 38.46, 37.96, 34.33, 34.22, 31.61, 31.23, 26.30, 24.87, 24.71, 22.20, 22.03, 21.22, 21.13, 1.15. HRMS (EI) calcd for $C_{25}H_{42}N_2O_4NaSi$ $[M+Na]^+$ 485.2812, found 485.2794.



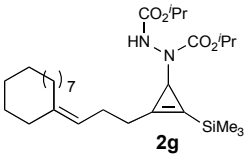
3e

3e: Colorless oil (19% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77-7.71 (bs, 1H), 6.23-6.20 (bm, 1H), 6.23-6.20 (bm, 1H), 5.14-5.14 (s, 1H), 4.98-4.88 (bm, 2H), 2.33-2.29 (m, 1H), 2.24-2.11 (m, 4H), 2.08-2.02 (m, 2H), 1.95-1.90 (m, 1H), 1.87-1.79 (m, 1H), 1.66-1.58 (m, 2H), 1.33-1.16 (bm, 12H), 1.11 (q, *J* = 7.7 Hz, 1H), 0.79 (d, *J* = 4.7 Hz, 3H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.79, 148.09, 128.66, 115.52, 69.31, 45.06, 45.97, 40.89, 37.90, 34.36, 31.65, 31.59, 31.27, 26.35, 22.26, 21.19, 21.16, -1.06. HRMS (EI) calcd for $C_{25}H_{42}N_2O_4NaSi$ $[M+Na]^+$ 485.2812, found 485.2794.



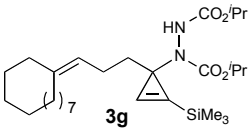
2f

2f: Colorless oil (64% yield, **2f** : **3f** = 3 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.32-6.30 (bm, 1H), 5.24 (d, *J* = 13.2 Hz, 1H), 4.15 (bm, 4H), 3.65 (bs, 1H), 2.50 (d, *J* = 6.8 Hz, 2H), 2.38 (dd, *J* = 1.7, 0.6 Hz, 1H), 1.85 (d, *J* = 11.9 Hz, 2H), 1.71 (ddt, *J* = 16.1, 10.4, 5.3 Hz, 2H), 1.61 (s, 3H), 1.54-1.48 (m, 1H), 1.26-1.09 (bm, 7H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.06, 136.55, 134.83, 125.19, 113.33, 61.67, 38.55, 34.06, 33.50, 30.07, 29.01, 28.68, 23.84, 21.69, 21.52, 14.67, 14.54, -1.24. HRMS (EI) calcd for $C_{20}H_{34}N_2O_4NaSi$ $[M+Na]^+$ 417.2186, found 417.2181.



2g

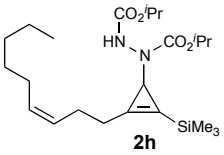
2g: Colorless oil (60% yield, **2g** : **3g** = 2.5 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.17-6.12 (bm, 1H), 5.19-5.16 (m, 1H), 5.01-4.90 (bm, 2H), 3.67-3.65 (bm, 1H), 2.64-2.52 (m, 2H), 2.37-2.30 (m, 2H), 2.10-1.99 (m, 4H), 1.57-1.48 (m, 2H), 1.48-1.40 (m, 2H), 1.26 (bs, 18H), 1.26-1.19 (m, 8H), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.74, 138.59, 137.81, 123.89, 113.10, 69.31, 38.61, 31.76, 28.78, 27.35, 25.75, 25.05, 24.82, 24.29, 24.21, 24.05, 23.96, 23.43, 23.02, 22.32, 22.22, 22.05, -1.11. HRMS (EI) calcd for $C_{29}H_{52}N_2O_4NaSi$ $[M+Na]^+$ 543.3594, found 543.3597.



3g

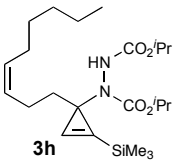
3g: Colorless oil (24% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.80-7.70 (bs, 1H), 6.26-5.98 (bm, 1H), 5.12 (t, *J* = 6.2 Hz, 1H), 4.99-4.86 (bm, 2H), 2.13-2.03 (m, 1H), 2.05-1.94 (m, 5H), 1.87-1.66 (m, 3H), 1.54-1.46 (m,

2H), 1.45-1.36 (m, 2H), 1.36-1.09 (m, 25H), 0.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.98, 137.52, 127.74, 124.86, 69.30, 46.26, 35.80, 31.81, 28.58, 25.56, 24.97,24.73, 24.37, 24.24, 24.06, 23.52, 23.20, 22.33, 22.26, 22.03, -1.06. HRMS (EI) calcd for $C_{29}H_{52}N_2O_4NaSi$ $[M+Na]^+$ 543.3594, found 543.3597.



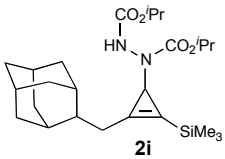
2h

2h: Colorless oil (61% yield, **2h** : **3h** = 2.3 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.18-6.10 (bm, 1H), 5.40-5.33 (m, 2H), 4.94-4.92 (bm, 2H), 3.67 (bs, *J* = 0.3 Hz, 1H), 2.61-2.56 (m, 2H), 2.32 (q, *J* = 6.9 Hz, 2H), 2.01 (q, *J* = 6.9 Hz, 2H), 1.35-1.22 (bm, 18H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.18 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.71, 137.58, 131.03, 128.28, 113.27, 69.29, 38.58, 31.51, 29.31, 27.28, 27.00, 25.03, 22.57, 22.20, 22.05, 22.03, 14.06, -1.13. HRMS (EI) calcd for $C_{23}H_{42}N_2O_4NaSi$ $[M+Na]^+$ 461.2812, found 461.2819.



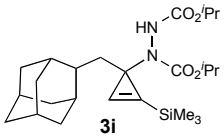
3h

3h: Colorless oil (27% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.79-7.73 (bm, 1H), 6.23-6.20 (bm, 1H), 5.30 (d, *J* = 5.6 Hz, 2H), 4.94-4.92 (bm, *J* = 6.0 Hz, 2H), 2.15-2.09 (m, 1H), 1.96 (q, *J* = 6.7 Hz, 2H), 1.76 (d, *J* = 6.3 Hz, 3H), 1.36-1.14 (m, 18H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 129.98, 129.34, 69.29, 46.18, 31.55, 29.34, 27.25, 24.84, 22.56, 22.22, 22.00, 14.06, -1.10. HRMS (EI) calcd for $C_{23}H_{42}N_2O_4NaSi$ $[M+Na]^+$ 461.2812, found 461.2796



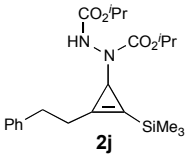
2i

2i: Colorless oil (84% yield, **2i** : **3i** = 7 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.15-6.11 (m, 1H), 4.96-4.90 (m, 2H), 3.63-3.60 (m, 1H), 2.80 (dt, *J* = 12.6, 6.2 Hz, 1H), 2.61-2.56 (m, 1H), 2.08-2.05 (m, 1H), 1.88-1.80 (m, 6H), 1.80-1.68 (m, 5H), 1.67-1.62 (m, 1H), 1.51 (t, *J* = 13.9 Hz, 2H), 1.36-1.16 (bm, 12H), -0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.69, 136.93, 112.50, 69.27, 42.42, 39.09, 39.04, 38.34, 38.19, 32.14, 31.65, 31.38, 30.17, 28.09, 28.00, 22.22, 22.05, -1.17. HRMS (EI) calcd for $C_{25}H_{42}N_2O_4NaSi$ $[M+Na]^+$ 485.2812, found 485.2805.



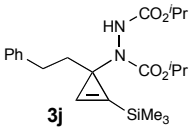
3i

3i: Colorless oil (12% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73-7.65 (bm, 1H), 6.23-6.15 (bm, 1H), 4.98-4.87 (bm, 2H), 2.35-2.26 (bm, 1H), 1.91-1.59 (m, 11H), 1.53-1.38 (m, 5H), 1.37-1.11 (m, 12H), 0.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.86, 127.68, 69.30, 45.66, 41.45, 39.34, 39.22, 38.45, 32.25, 31.94, 31.76, 31.58, 28.18, 22.26, 22.04, -1.04. HRMS (EI) calcd for $C_{25}H_{42}N_2O_4Si$ 462.2914, found 462.2919.



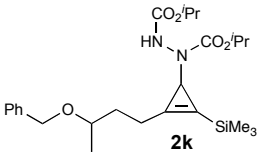
2j

2j: Colorless oil (57% yield, **2j** : **3j** = 2.5 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29-7.26 (m, 2H), 7.19 (m, 3H), 6.14-6.11 (bm, 1H), 5.01-4.93 (bm, 2H), 3.70 (bm, 1H), 2.96-2.83 (m, 4H), 1.37-1.17 (m, 12H), 0.13 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.71, 141.14, 137.08, 128.38, 128.25, 126.07, 113.72, 69.33, 38.54, 33.26, 28.30, 22.24, 22.06, -1.23. HRMS (EI) calcd for $C_{22}H_{34}N_2O_4NaSi$ $[M+Na]^+$ 441.2186, found 441.2177.



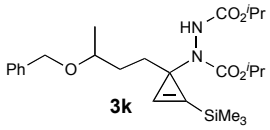
3j

3j: Colorless oil (38% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78-7.64 (bs, 1H), 7.29-7.20 (m, 2H), 7.21-7.15 (m, 3H), 6.26-6.13 (bm, 1H), 5.02-4.87 (bm, 2H), 2.50-2.36 (m, 3H), 2.07-1.98 (m, 1H), 1.41-1.11 (bm, 12H), 0.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.20, 142.20, 128.41, 128.22, 125.61, 69.37, 46.12, 37.84, 33.22, 22.04, -1.06. HRMS (EI) calcd for $C_{22}H_{34}N_2O_4NaSi$ $[M+Na]^+$ 441.2186, found 441.2191.



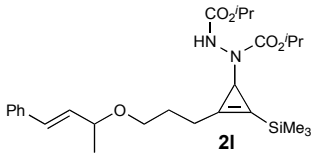
2k

2k: Colorless oil (71% yield, **2k** : **3k** = 3 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (m, 4H), 7.26-7.24 (m, 1H), 6.26-6.16 (bm, 1H), 4.93-4.91 (bm, 2H), 4.55 (d, J = 11.5 Hz, 1H), 4.42 (dd, J = 11.6, 6.7 Hz, 1H), 3.65-3.49 (bm, 2H), 2.74-2.55 (m, 2H), 1.89-1.73 (m, 2H), 1.22 (bm, 15H), -0.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.77, 138.86, 128.33, 128.26, 127.64, 127.46, 112.73, 74.14, 73.96, 70.48, 70.39, 69.26, 38.55, 38.47, 34.33, 34.19, 29.71, 23.00, 22.21, 22.05, 19.57, 19.43, -1.09. HRMS (EI) calcd for $C_{25}H_{40}N_2O_5NaSi$ $[M+Na]^+$ 499.2604, found 499.2599.



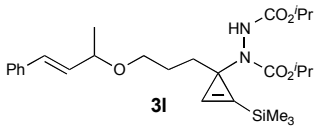
3k

3k: Colorless oil (23% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77-7.72 (bm, 1H), 7.32-7.28 (m, 4H), 7.28-7.23 (m, 1H), 6.23-6.19 (bm, 1H), 4.97-4.88 (bm, 2H), 4.54-4.51 (d, *J* = 11.5 Hz, 1H), 4.43 (dd, *J* = 11.8, 5.6 Hz, 1H), 3.51-3.43 (m, 2H), 2.19-2.08 (bm, 1H), 1.83-1.76 (bm, 1H), 1.40-1.18 (m, 13H), 1.19-1.13 (d, *J* = 9.4 Hz, 3H), -0.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.17, 128.28, 127.65, 127.59, 127.34, 74.85, 70.26, 70.20, 69.34, 65.86, 34.00, 29.72, 22.24, 22.22, 22.04, 19.75, 19.63, 15.30, -1.08. HRMS (EI) calcd for $C_{25}H_{40}N_2O_5Si$ 476.2707, found 476.2711.



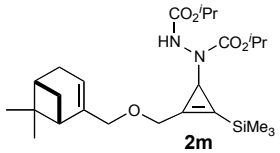
2l

2l: Colorless oil (60% yield, **2l** : **3l** = 2 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40-7.35 (m, 2H), 7.34-7.28 (m, 2H), 7.27-7.20 (m, 1H), 6.52-6.46 (m, 1H), 6.20-6.13 (bm, 1H), 6.12-6.05 (m, 1H), 5.02-4.87 (m, 2H), 4.00-3.93 (m, 1H), 3.70-3.59 (bs, 1H), 3.58-3.50 (m, 1H), 3.40-3.33 (m, 1H), 2.74-2.64 (m, 1H), 2.65-2.53 (m, 1H), 1.94-1.84 (m, 2H), 1.34-1.30 (m, 3H), 1.30-1.18 (bm, 12H), 0.14 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.74, 136.67, 131.97, 130.94, 128.58, 127.64, 126.44, 113.00, 77.25, 76.68, 69.30, 67.56, 38.51, 29.72, 27.68, 27.65, 23.65, 22.20, 22.04, 21.67, -1.13. HRMS (EI) calcd for $C_{27}H_{42}N_2O_4NaSi$ $[M+Na]^+$ 525.2761, found 525.2752.



3l

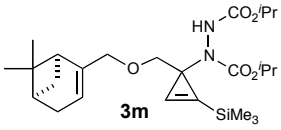
3l: Colorless oil (30% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78-7.69 (bm, 1H), 7.39-7.36 (m, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.24-7.17 (m, 1H), 6.50-6.44 (m, 1H), 6.28-6.24 (bm, 1H), 6.11-6.03 (m, 1H), 4.97-4.84 (bm, 2H), 3.97-3.91 (m, 1H), 3.47-3.37 (m, 1H), 3.33-3.26 (m, 1H), 2.16-2.09 (m, 1H), 1.80-1.68 (m, 1H), 1.41-1.09 (m, 23H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.96, 136.77, 132.19, 130.73, 128.55, 128.24, 127.55, 126.44, 76.45, 69.31, 68.36, 32.55, 27.49, 22.23, 22.01, 21.68, -1.10. HRMS (EI) calcd for $C_{27}H_{42}N_2O_4NaSi$ $[M+Na]^+$ 525.2761, found 525.2768.



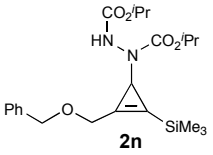
2m

2m: Colorless oil (45% yield, **2m** : **3m** = 1 : 1) ; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.19-6.15 (bm, 1H), 5.51-5.49 (m, 1H), 5.02-4.89 (bm, 2H), 4.59-4.48 (bm, 2H), 3.97-3.88 (m, 1H), 3.81-3.77 (bm, 1H), 2.43-2.36 (m, 1H), 2.35-2.16 (m, 3H), 2.14-2.08 (m, 1H), 1.28 (s, 3H), 1.28-1.18 (bm, 14H), 0.83 (s, 3H), 0.21 (s, 6H), 0.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.99, 120.21, 73.43, 69.39, 65.69,

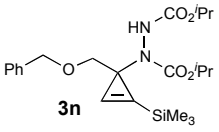
43.39, 40.92, 38.75, 38.01, 31.56, 31.30, 29.72, 26.20, 22.19, 22.03, 21.09, -1.25, -1.86. HRMS (EI) calcd for $C_{25}H_{42}N_2O_5NaSi$ $[M+Na]^+$ 501.2761, found 501.2764.



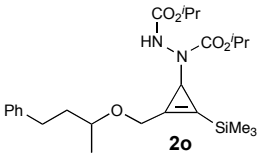
3m: Colorless oil (45% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77-7.64 (bm, 1H), 6.52-6.46 (bm, 1H), 5.41 (s, 1H), 4.99-4.84 (bm, 2H), 3.76 (s, 2H), 3.65-3.49 (bm, 1H), 2.38-2.34 (m, 1H), 2.30-2.18 (m, 2H), 2.08 (s, 2H), 1.35 (s, J = 4.5, 2.0 Hz, 3H), 1.22 (bm, 12H), 1.14-1.09 (m, 2H), 0.81 (s, 3H), -0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.01, 145.55, 126.56, 126.52, 119.44, 119.33, 73.60, 69.17, 43.31, 37.99, 31.52, 31.22, 26.21, 22.03, 21.09, -1.31. HRMS (EI) calcd for $C_{25}H_{42}N_2O_5NaSi$ $[M+Na]^+$ 501.2761, found 501.2752.



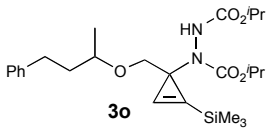
2n: Colorless oil (46% yield, **2n** : **3n** = 1 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39-7.38 (m, 4H), 7.29 (m, 1H), 6.24-6.12 (bm, 1H), 5.05-4.83 (bm, 2H), 4.72-4.53 (m, 3H), 3.85-3.76 (bs, 1H), 1.39-1.13 (bm, 12H), 0.22 (s, 8H), 0.01 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.95, 128.40, 127.86, 127.70, 127.64, 72.51, 69.44, 66.00, 38.71, 22.04, -1.25. HRMS (EI) calcd for $C_{22}H_{34}N_2O_5NaSi$ $[M+Na]^+$ 457.2135, found 457.2135.



3n: Colorless oil (46% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.80-7.68 (bm, 1H), 7.35-7.24 (m, 5H), 6.47-6.19 (bm, 1H), 4.99-4.86 (bm, 2H), 4.51-4.44 (m, 2H), 3.87-3.58 (bm, 2H), 1.29-1.12 (bm, 12H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.02, 138.54, 128.31, 127.51, 127.46, 126.31, 72.66, 69.43, 22.19, 22.02, -1.28. HRMS (EI) calcd for $C_{22}H_{34}N_2O_5NaSi$ $[M+Na]^+$ 457.2135, found 457.2131.

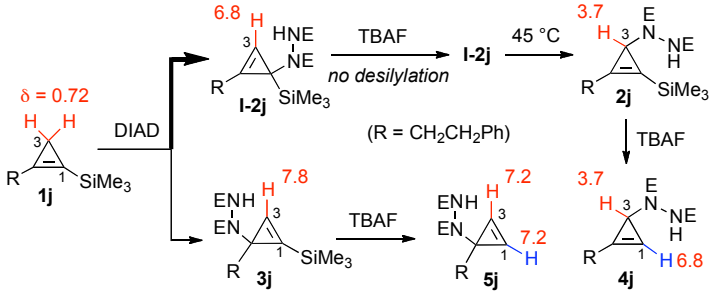


2o: Colorless oil (66% yield, **2o** : **3o** = 1 : 3); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29-7.24 (m, 2H), 7.19-7.15 (m, 3H), 6.18-6.14 (bm, 1H), 5.01-4.88 (b, 2H), 4.66-4.45 (m, 2H), 3.81-3.79 (bm, 1H), 3.58-3.52 (m, 1H), 2.76-2.63 (m, 2H), 1.92-1.85 (m, 1H), 1.78-1.71 (m, 1H), 1.36-1.13 (m, 15H), 0.19 (s, 8H), 0.02 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.70, 142.30, 128.37, 125.75, 115.07, 74.83, 69.39, 64.28, 38.80, 38.43, 38.35, 31.71, 31.66, 29.72, 22.21, 22.04, 21.75, 19.47, 19.32, -1.19, -1.85. HRMS (EI) calcd for $C_{25}H_{40}N_2O_5Si$ 476.2707, found 476.2704.

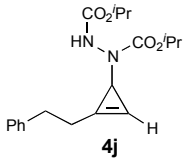


3o: Colorless oil (22% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78-7.68 (bm, 1H), 7.28-7.25 (m, 2H), 7.17 (m, *J* = 6.7 Hz, 3H), 6.47-6.43 (bm, 1H), 5.01-4.87 (bm, 2H), 3.60-3.32 (m, 1H), 2.70-2.63 (bm, 1H), 2.63-2.56 (m, 1H), 1.85-1.73 (m, 1H), 1.73-1.61 (m, 1H), 1.36-1.14 (m, 13H), 1.14-1.10 (m, 3H), 0.88 (t, *J* = 6.9 Hz, 1H), -0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.06, 142.41, 128.38, 128.34, 126.41, 125.71, 74.39, 69.20, 38.55, 31.87, 22.21, 22.19, 19.54, -1.25. HRMS (EI) calcd for $C_{25}H_{40}N_2O_5NaSi$ $[M+Na]^+$ 499.2604, found 499.2605.

III. Procedure for the mechanistic study via desilylation.

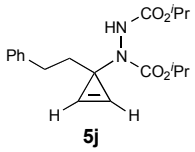


To cyclopropene **1j** (216 mg, 1 mmol) in $CDCl_3$ (2 mL) was added diisopropyl azocarboxylate (1.1 equiv, 1.1 mmol, 222 mg). The resulting yellow solution was stirred at rt for 3.5 h, at which point ^{1}H NMR indicated the complete consumption of the starting material. $CDCl_3$ was removed and the residue was taken up in 2 mL of THF and tetrabutylammonium fluoride (TBAF) (1 M in THF, 1.1 equiv, 1.1 mL) was added. The reaction was stirred at rt for 30 min, the crude NMR showed two major compounds **I-2j** and **5j**. THF was removed and the residue was taken up in $CDCl_3$ and heated at 45 ^{o}C until the crude NMR showed the full consumption of **I-2j**(ca. 20 h). The reaction was concentrated and purified by column chromatography (Hexane : Ethyl Acetate = 8 : 1) to give **2j** (201 mg, 48%) and **5j** (117 mg, 31%). Compound **2j** (201 mg, 0.48 mmol) was dissolved in THF (1 mL) and TBAF (1 M, 0.5 mL) was added and the reaction was kept at rt for 30 min followed by the removal of the solvent, and purified by column chromatography Hexane : Ethyl Acetate = 8 : 1 to afford compound **4j** (157 mg, 95%).



4j

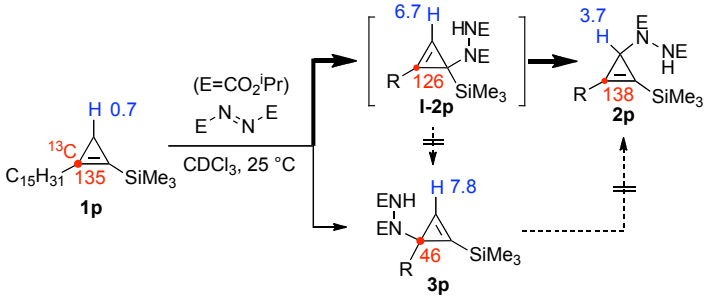
4j: Colorless oil (45% yield in 2 steps); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26 (quintet, J = 6.7 Hz, 2H), 7.23-7.15 (m, 3H), 6.69 (s, 1H), 6.29-6.11 (bm, 1H), 5.00-4.88 (bm, 2H), 3.76-3.71 (bm, 1H), 2.98-2.88 (m, 2H), 2.88-2.76 (m, 2H), 1.36-1.16 (bm, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.07, 141.04, 128.35, 128.21, 126.14, 124.86, 103.63, 69.44, 36.67, 32.98, 26.87, 22.20, 22.00. HRMS (EI) calcd for $C_{19}H_{26}N_2O_4Na$ $[M+Na]^+$ 369.1790, found 369.1780.



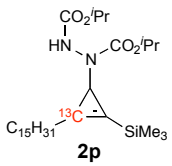
5j

5j: Colorless oil (31 % yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37-7.28 (bm, 1H), 7.29-7.22 (m, 2H), 7.20-7.12 (m, 3H), 6.37-6.02 (bm, 1H), 4.99-4.86 (bm, 2H), 2.45 (t, J = 8.4 Hz, 2H), 2.23 (t, J = 8.0 Hz, 2H), 1.38-1.11 (bm, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 128.43, 128.23, 125.69, 116.56, 69.64, 43.70, 36.41, 32.75 22.20, 21.98. HRMS (EI) calcd for $C_{19}H_{26}N_2O_4Na$ $[M+Na]^+$ 369.1790, found 369.1790.

IV. Procedure for the mechanistic study using ^{13}C–labeled cyclopropene .



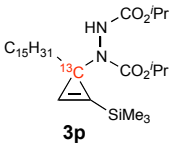
To cyclopropene **1p** (162 mg, 0.5 mmol) in $CDCl_3$ (1 mL) was added diisopropyl azocarboxylate (1.1 equiv, 0.55 mmol, 111 mg) and the reaction was stirred at rt until the crude NMR showed full consumption of **1p**, at which point ^{1}H NMR indicated the ratio of **2p-I** to **3p** was 2.7 to 1. Then the reaction was heated at 45 ^{o}C for 40 hs. The crude NMR showed full conversion of **2p-I.** Solvent was removed and the residue was purified by column chromatography with Hexane : Ethyl Acetate = 10 : 1 to give **2p** (176 mg) and **3p** (65 mg), in 92% overall yield.



2p

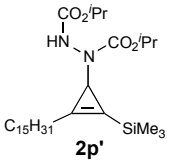
2p: Colorless oil (67% yield, **2p** : **3p** = 2.7 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.17-6.11 (bm, 1H), 4.96-4.91 (bm, 2H), 3.65 (bs, 1H), 2.58-2.46 (m, 2H), 1.61-1.56 (m, 2H), 1.36-1.12 (m, 36H), 0.87 (t, J = 6.9 Hz, 3H), 0.21 (s, 9H); ^{13}C

NMR ($CDCl_3$, 125 MHz) δ 138.75, 138.00, 137.07, 69.26, 38.57, 38.45, 31.94, 29.67, 29.62, 29.43, 29.37, 29.34, 27.21, 22.70, 22.20, 22.05, 14.12, -1.13. HRMS (EI) calcd for $C_{28}{}^{13}CH_{56}N_2O_4NaSi$ $[M+Na]^+$ 548.3941, found 548.3930.



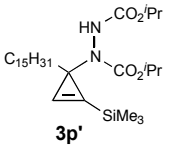
3p

3p: Colorless oil (24% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82-7.70 (bm, 1H), 6.26-5.97 (bm, 1H), 4.99-4.86 (bm, 2H), 2.09-1.99 (m, 1H), 1.82-1.69 (m, 1H), 1.41-1.09 (m, 36H), 1.07-0.92 (m, 2H), 0.92-0.84 (m, 3H), 0.18-0.17 (m, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 69.29, 46.40, 42.80, 31.94, 29.38, 27.11, 22.71, 22.45, 22.03, 14.14, -1.07. HRMS (EI) calcd for $C_{28}{}^{13}CH_{56}N_2O_4NaSi$ $[M+Na]^+$ 548.3941, found 548.3945.



2p'

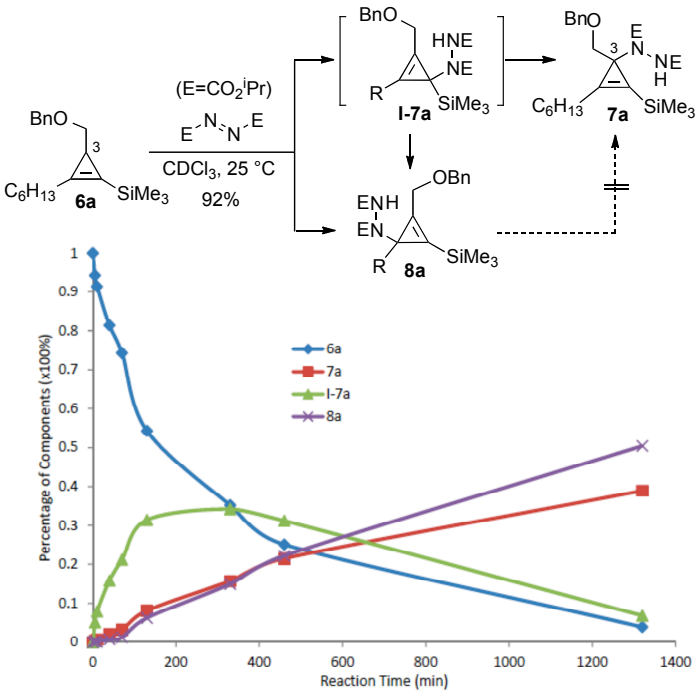
2p': Colorless oil (66% yield, **2p'** : **3p'** = 2.5 : 1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.15-6.10 (bm, 1H), 5.00-4.89 (bm, 2H), 3.67-3.62 (bm, 1H), 2.60-2.46 (m, 2H), 1.60-1.54 (m, 3H), 1.43-1.10 (m, 37H), 0.91-0.83 (m, 3H), 0.18 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 112.48, 69.27, 38.52, 31.94, 29.68, 29.62, 29.43, 29.37, 27.21, 26.74, 22.71, 22.21, 22.04, 14.13, -1.12. HRMS (EI) calcd for $C_{29}H_{56}N_2O_4Si$ 524.4009, found 524.4008.



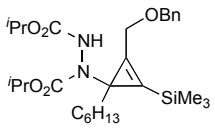
3p'

3p': Colorless oil (26% yield); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.81-7.72 (bm, 1H), 6.24-5.96 (bm, 1H), 5.00-4.88 (bm, 2H), 2.09-2.00 (m, 1H), 1.80-1.68 (m, 1H), 1.36-1.14 (m, 36H), 1.04-0.93 (m, 2H), 0.91-0.84 (m, 3H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 69.26, 46.38, 31.93, 29.69, 29.64, 29.43, 29.36, 27.08, 22.69, 22.19, 22.01, 14.11, -1.09. HRMS (EI) calcd for $C_{29}H_{56}N_2O_4Si$ 524.4009, found 524.4018.

V. Reaction profile of C–H amination with a C3-substituted cyclopropene.

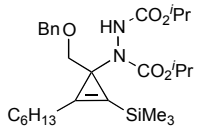


To cyclopropene **6a** (158 mg, 0.5 mmol) in $CDCl_3$ (1 mL) was added diisopropyl azocarboxylate (1.1 equiv, 0.55 mmol, 111 mg) and the reaction was stirred at rt and the reaction was monitored by NMR spectroscopy for 20 h, at which point ^{1}H NMR indicated the ratio of **7a** to **8a** was 1.7 to 1. Solvent was removed and the residue was purified by column chromatography with Hexane : Ethyl Acetate = 10 : 1 to give a inseparable mixture of **7a** and **8a**.



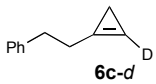
7a

and



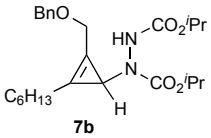
8a

Compounds **7a** and **8a** are inseparable by column chromatography on silica gel. For ^{1}HNMR and ^{13}CNMR, please see the spectrum. HRMS (EI) calcd for $C_{28}H_{46}N_2O_5SiNa$ 541.3074, found 541.3073.



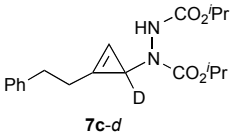
6c-*d*

6c-*d*: purification by column chromatography on silica gel using Hexanes; Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31-7.27 (m, 2H), 7.22-7.19 (m, 3H), 2.91 (q, J = 7.8 Hz, 2H), 2.82-2.79 (m, 2H), 0.93 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.58, 128.41, 128.36, 126.00, 119.67, 98.70, 33.32, 28.63, 5.26. HRMS (EI) calcd for $C_{11}H_{11}D$ 145.1002, found 145.1004.



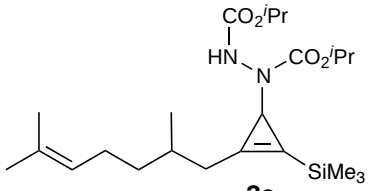
7b

7b: Colorless oil (95%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39-7.34 (m, 3H), 7.34-7.30 (m, 2H), 7.29 (s, 1H), 6.30-6.22 (bm, 1H), 5.06-4.91 (m, 2H), 4.62-4.56 (m, 2H), 4.54-4.47 (m, 2H), 3.89-3.80 (bm, 1H), 2.56-2.43 (m, 2H), 1.69-1.54 (m, 2H), 1.41-1.18 (m, 17H), 0.94-0.85 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.12, 128.41, 127.75, 72.59, 60.39, 39.13, 31.59, 29.08, 27.07, 24.82, 22.57, 22.16, 22.00, 21.97, 21.73, 21.04, 14.21, 14.06. HRMS (EI) calcd for $C_{25}H_{38}N_2O_5Na$ $[M+Na]^+$ 469.2678, found 469.2668.

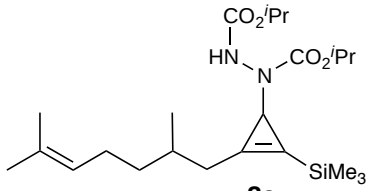


7c-*d*

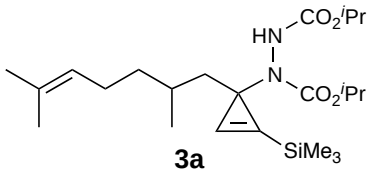
7c-*d*: Colorless oil (95%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30-7.23 (m, 2H), 7.24-7.14 (m, 2H), 6.68 (s, 0.65H), 5.00-4.90 (bm, 2H), 2.96-2.89 (m, 2H), 2.87-2.78 (m, 2H), 1.38-1.19 (bm, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.08, 128.41, 128.37, 126.16, 103.49, 69.50, 33.00, 26.86, 22.20, 22.00. HRMS (EI) calcd for $C_{19}H_{25}N_2O_4DSi$ 347.1996, found 347.1950.



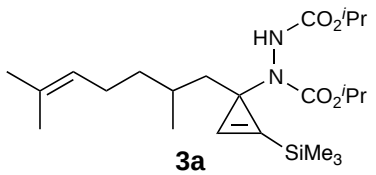
2a



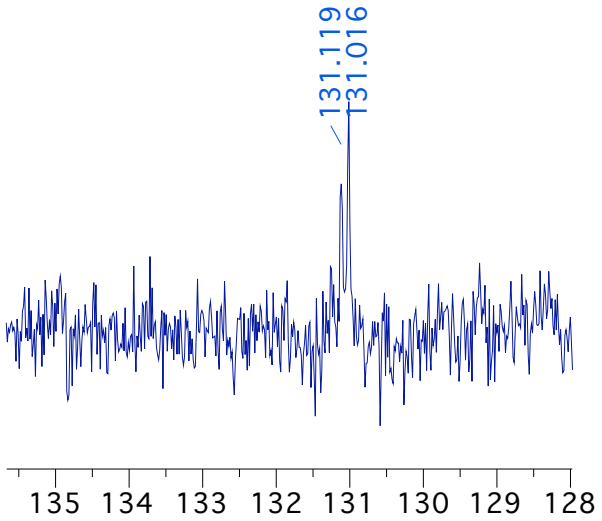
2a

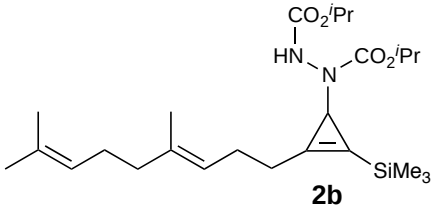


3a

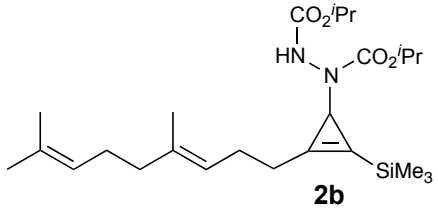


3a



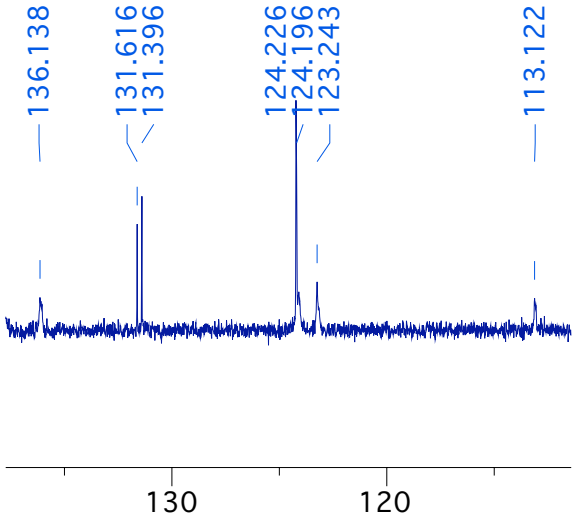


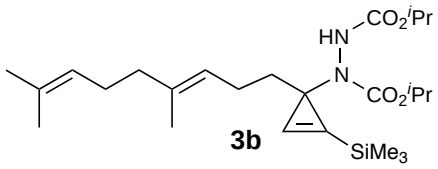
2b



2b

136.138
131.616
131.396
124.226
124.196
123.243
113.122





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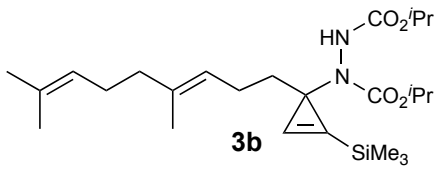
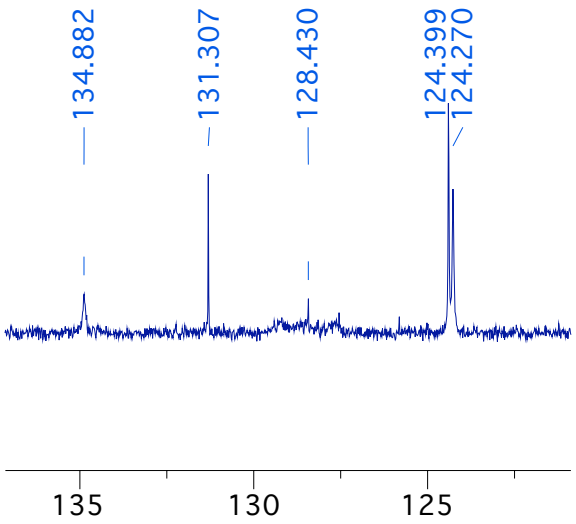
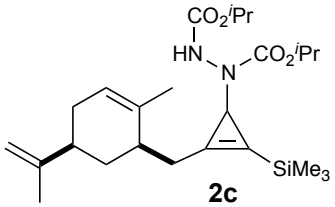


3b

155.915
134.882
131.307
128.430
124.399
124.270





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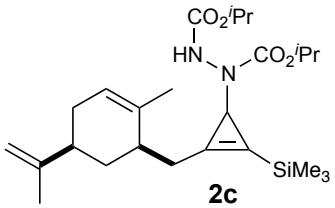
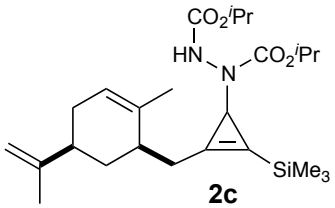


2c



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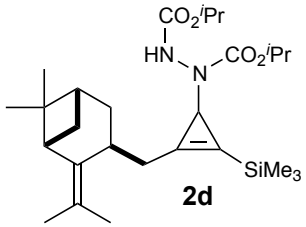

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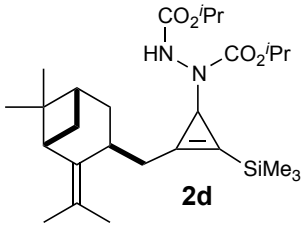
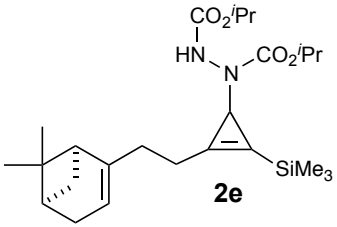


2d



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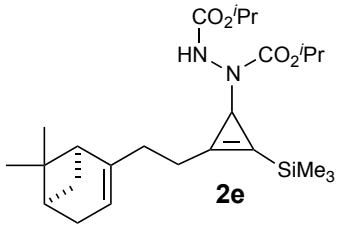
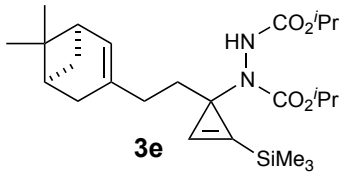


2e

147.227
137.787
116.344
112.662

ppm 220 200 180 160 140 120 100 80 60 40 20 0



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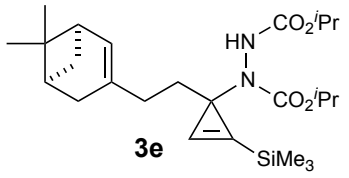

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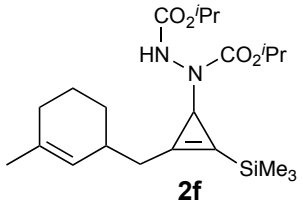

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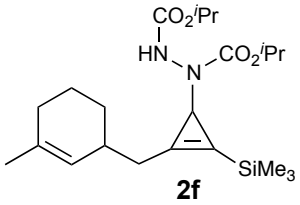
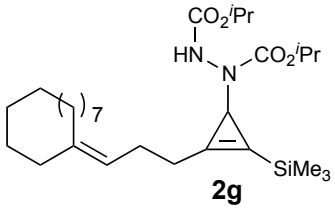
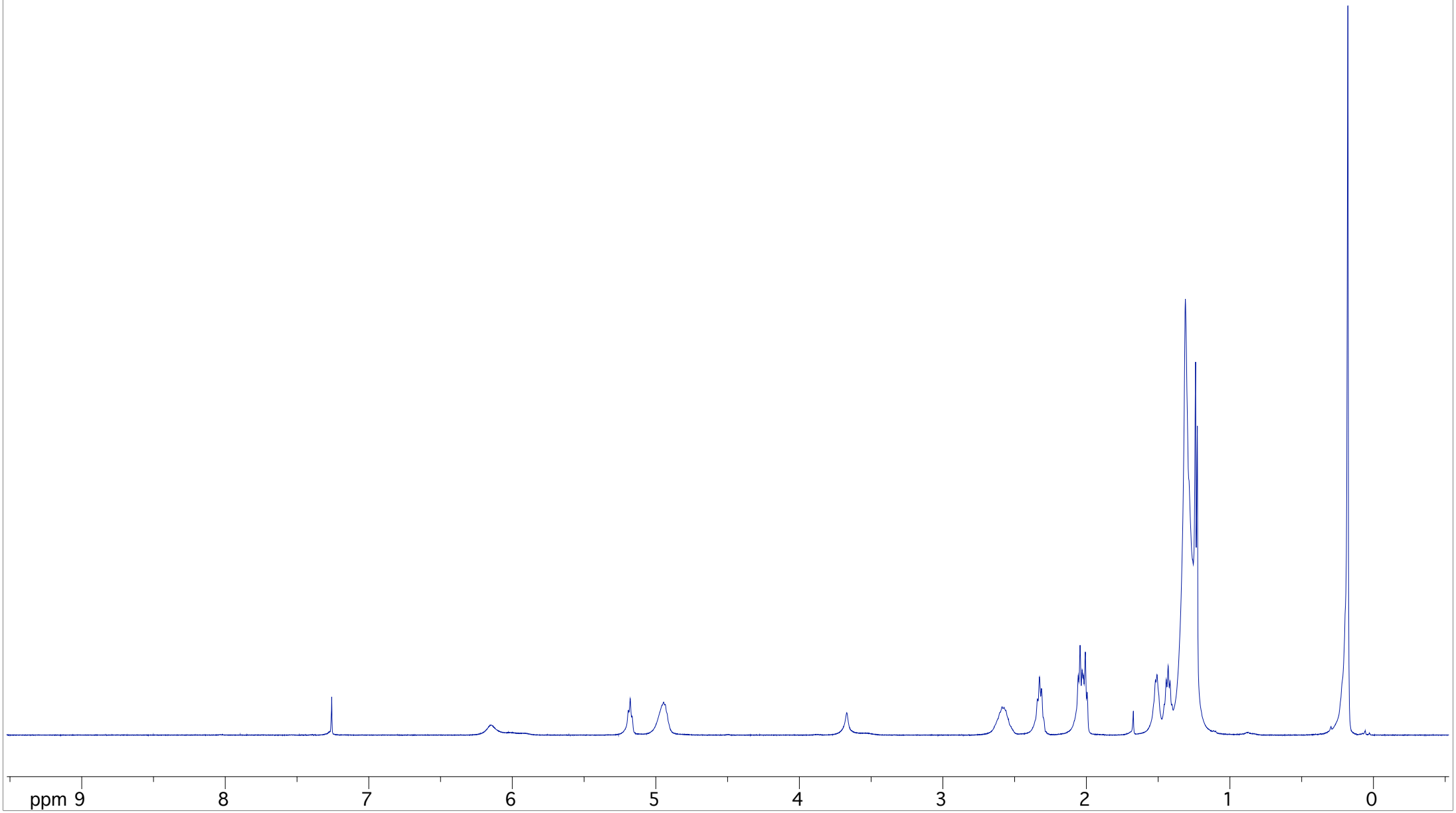
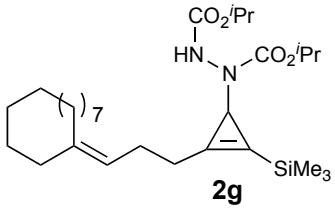


2f



2g





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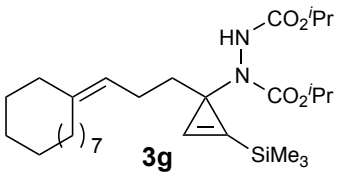
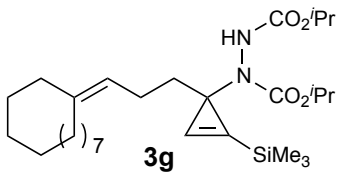


3g



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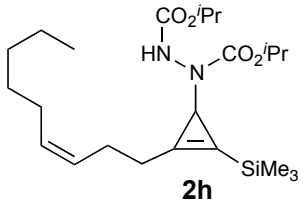

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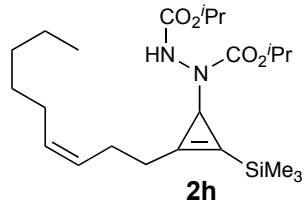
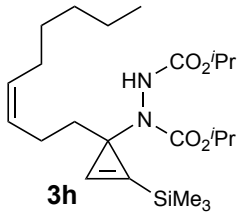
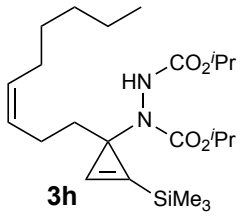


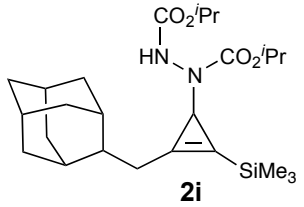
2h



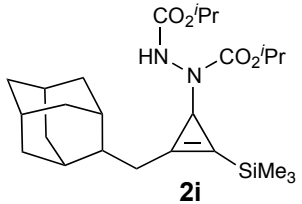
3h



3h



2i



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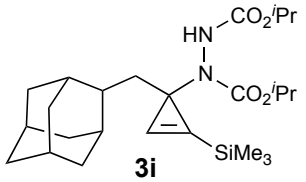
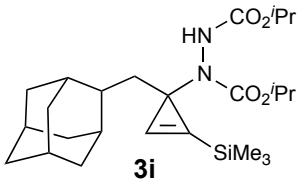


3i



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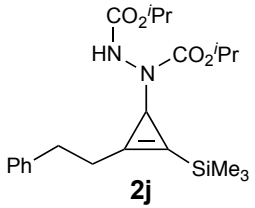
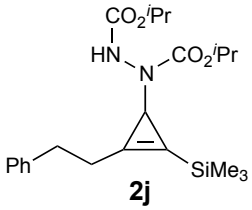
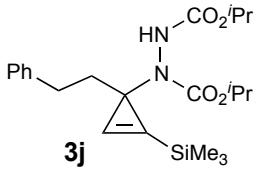


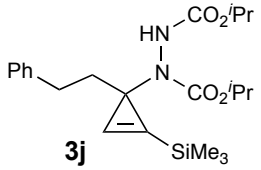
2j



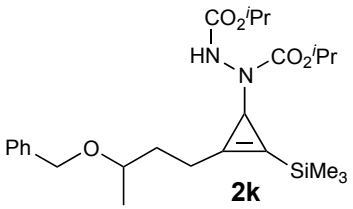
2j



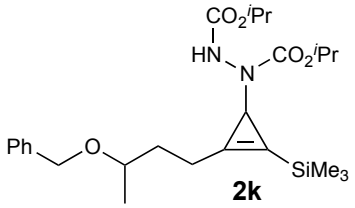
3j



3j

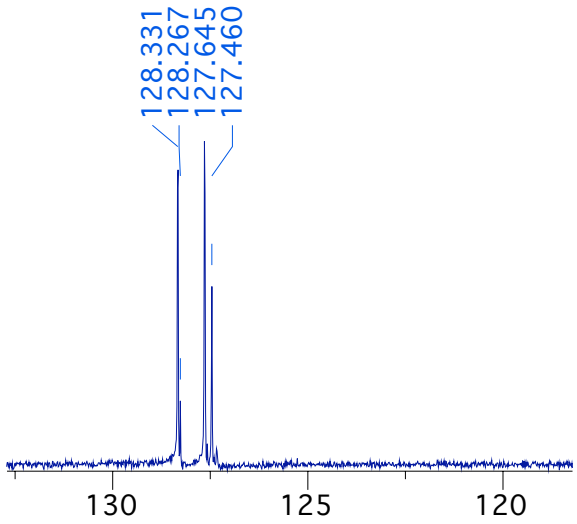


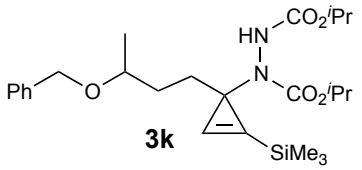
2k



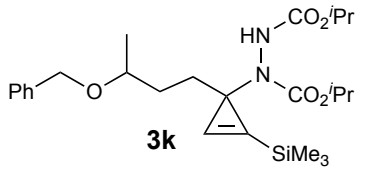
2k

155.772
138.867
128.331
128.267
127.645
127.460
112.731





3k



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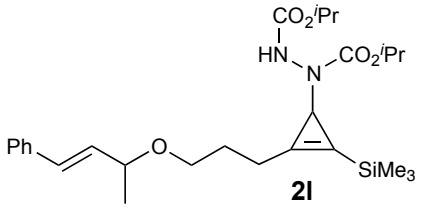

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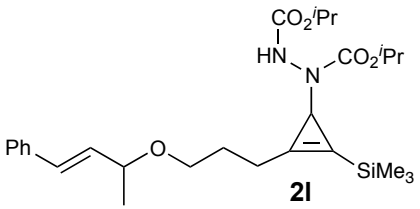

2l

155.737
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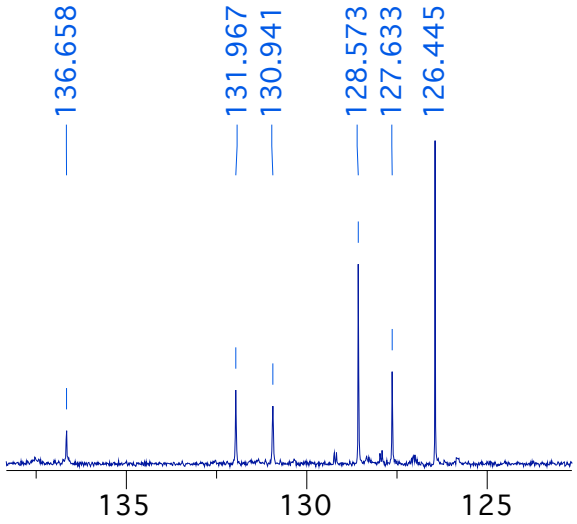
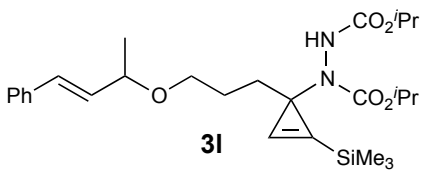
131.967
130.941
128.573
127.633
126.445
113.000





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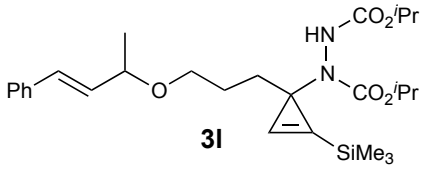

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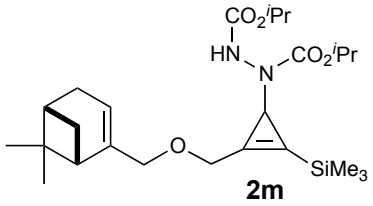

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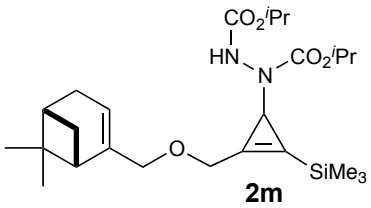

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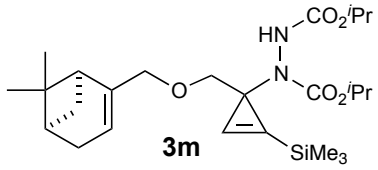
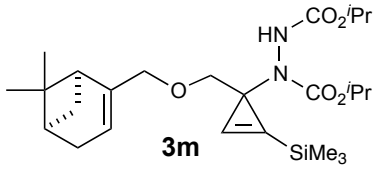
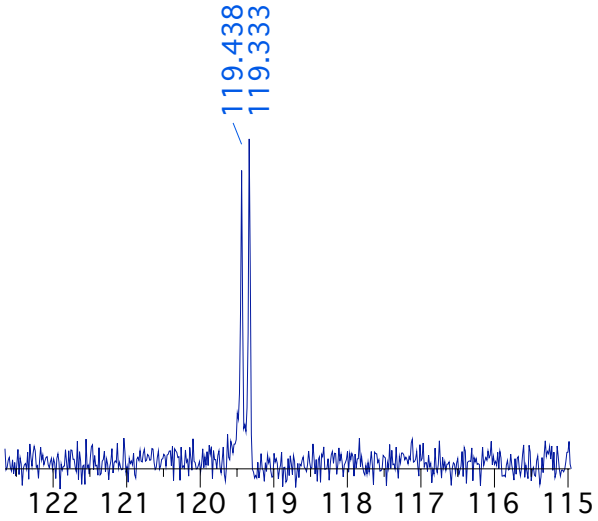


3m



3m

156.013
145.551
126.562
126.518
119.438
119.333



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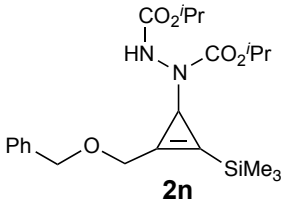

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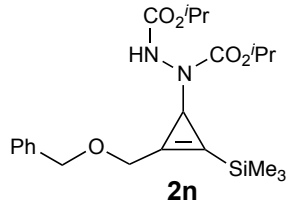

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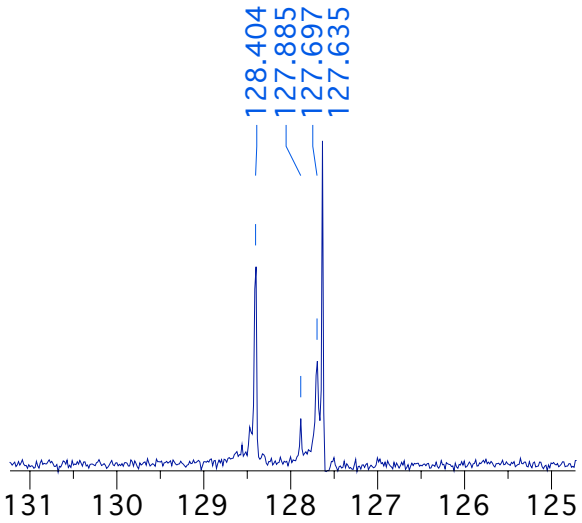

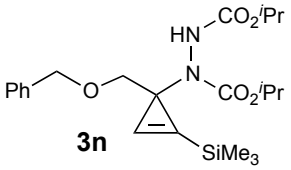

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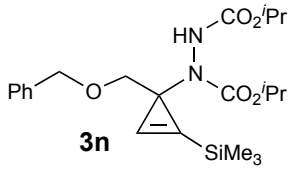
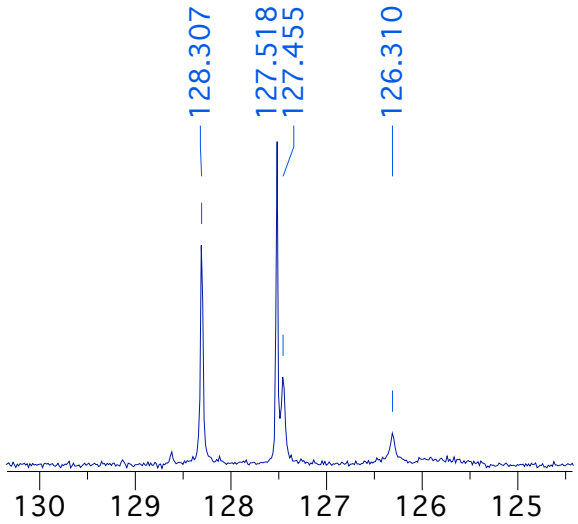


3n

156.017
138.537
128.307
127.518
127.455
126.310



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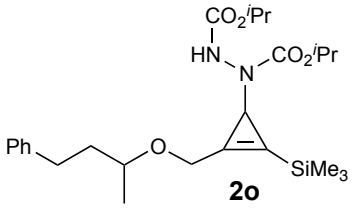

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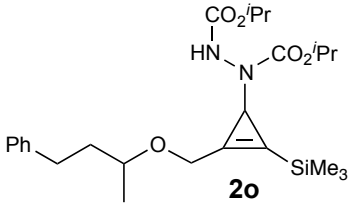

2o

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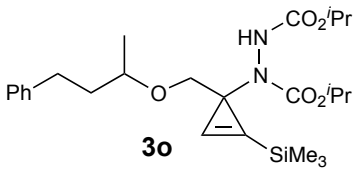
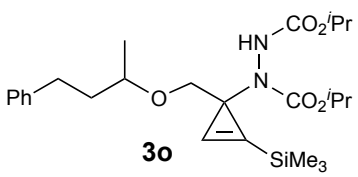
125.754
115.075

20 200 180 160 140 120 100 80 60 40 20 0



3o



3o

156.062
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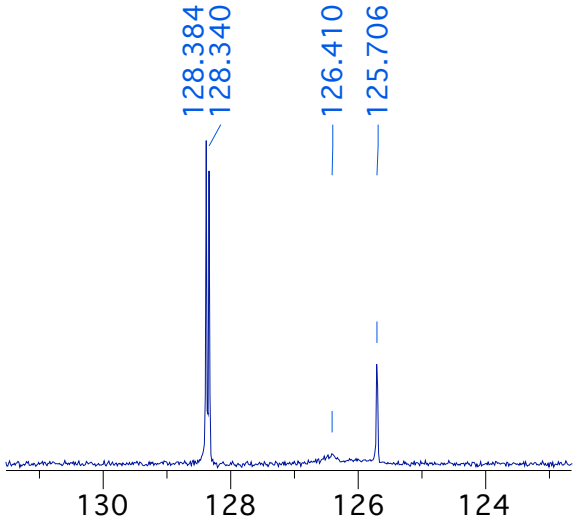
128.340
126.410
125.706



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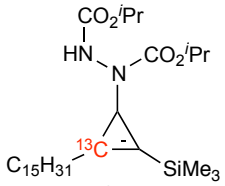

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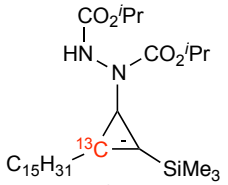

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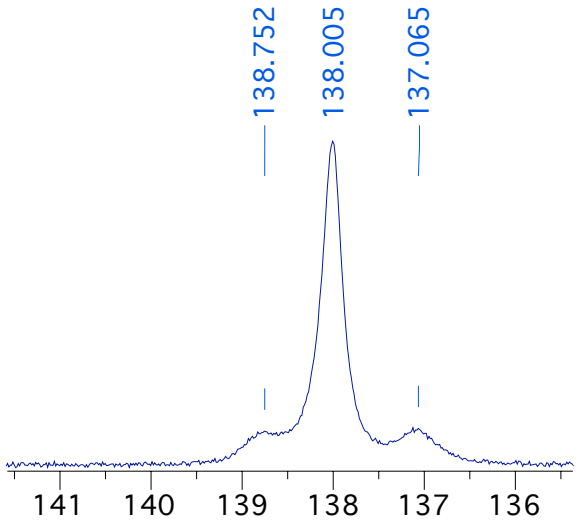

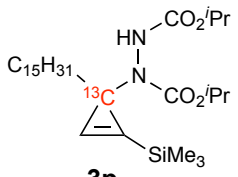

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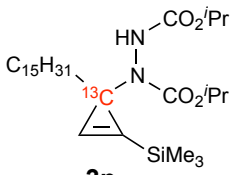

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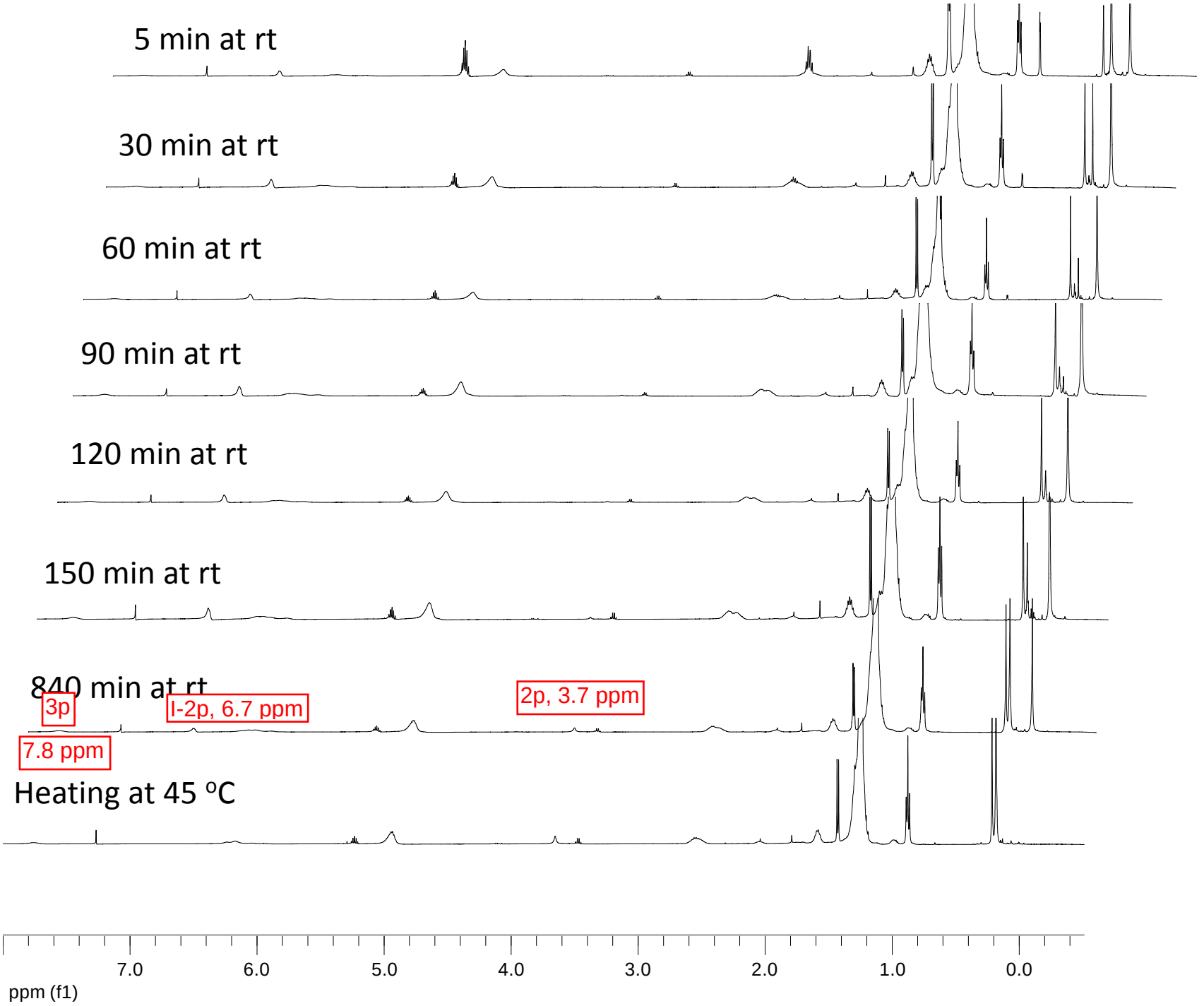

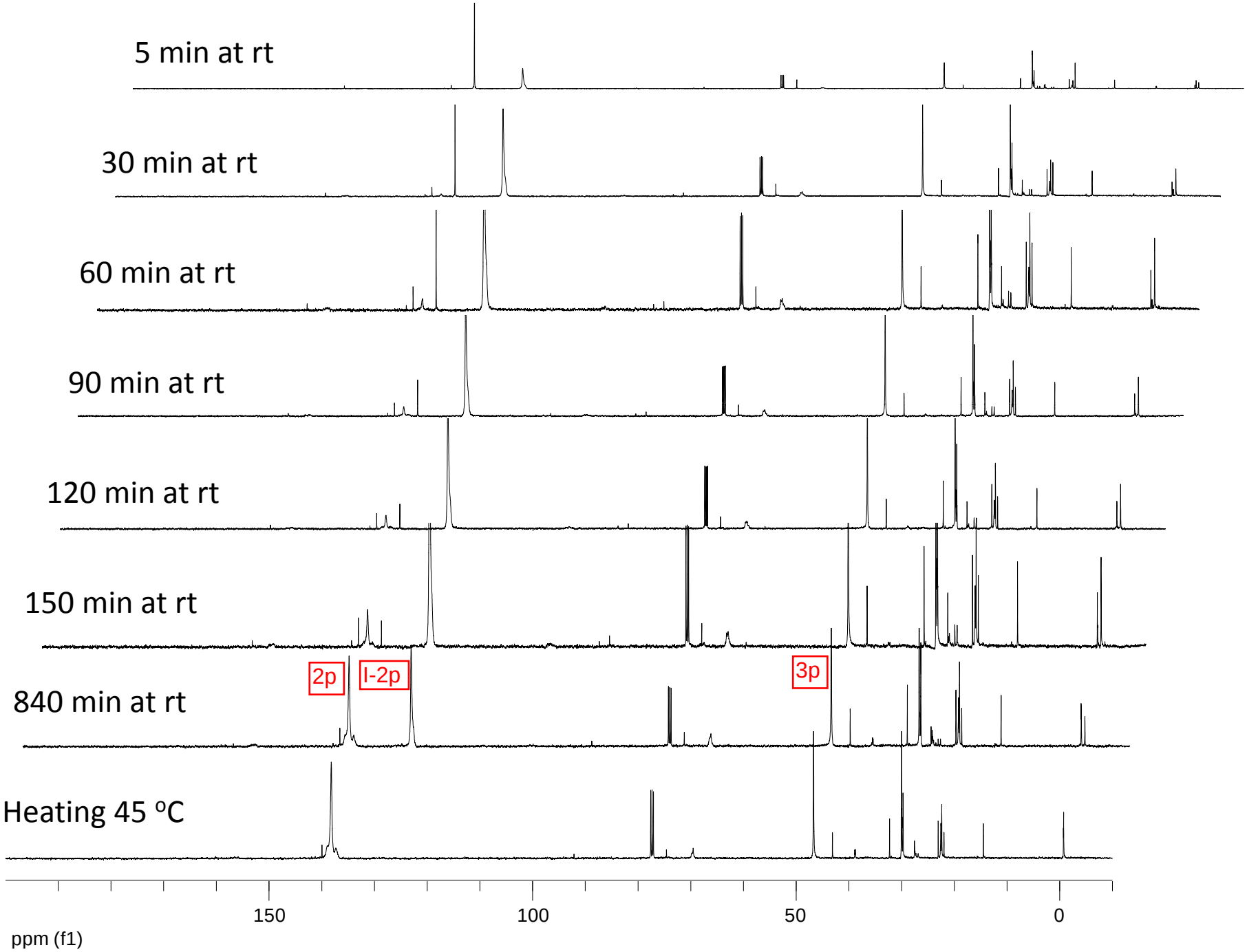

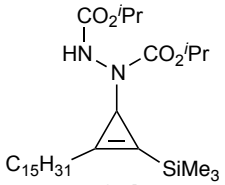

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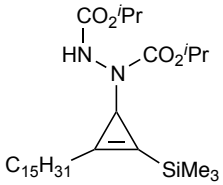

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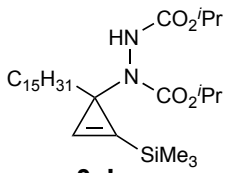

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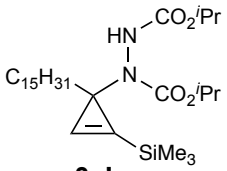

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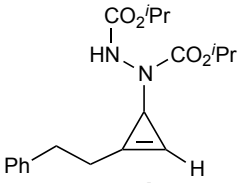
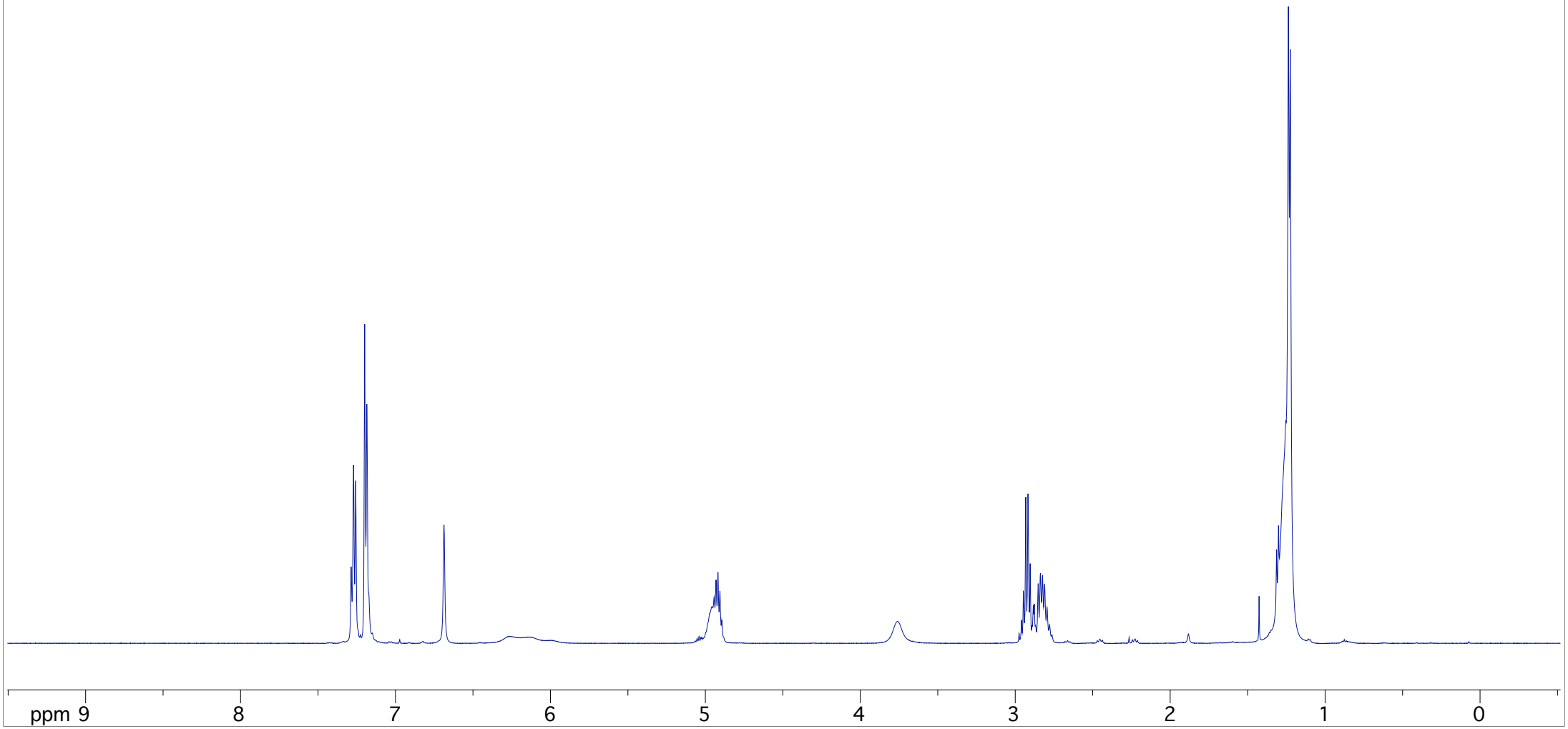
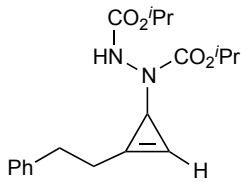


4j





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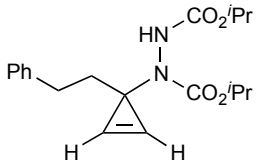
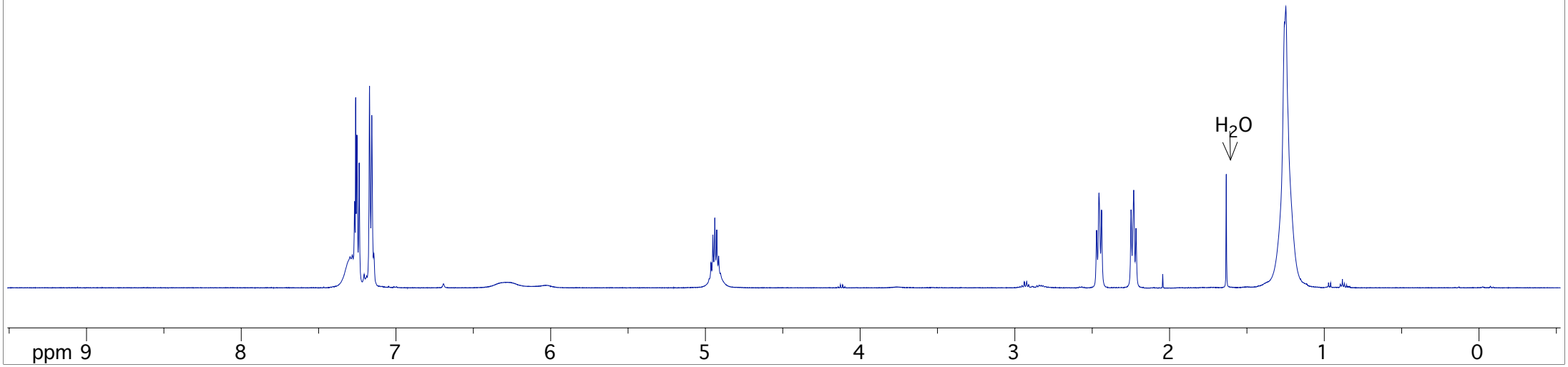
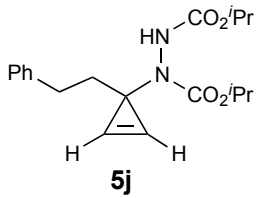
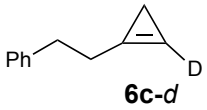


5j

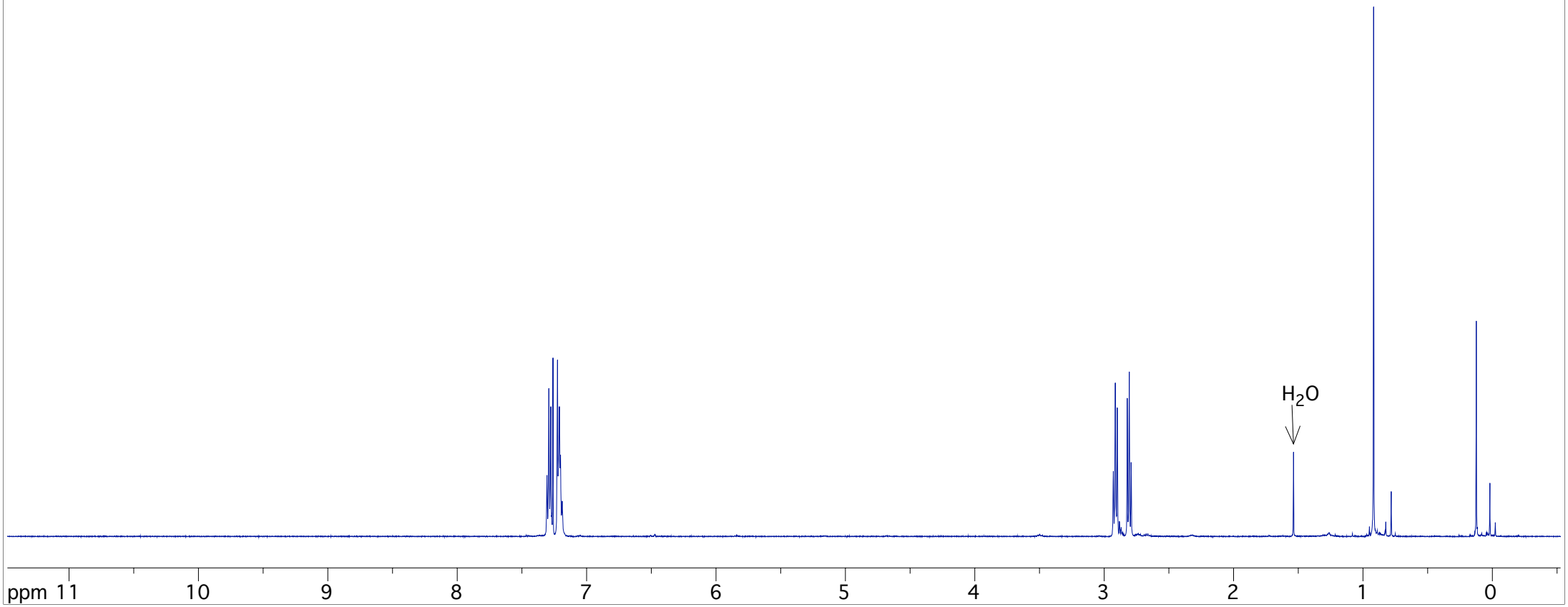


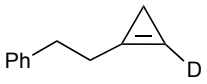


5j



6c-*d*





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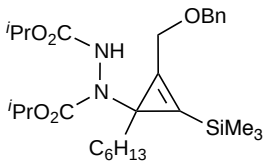
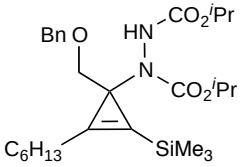
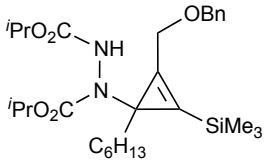


7a

and

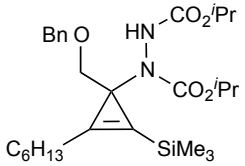


8a



7a

and



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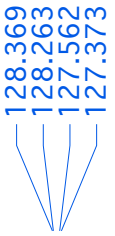
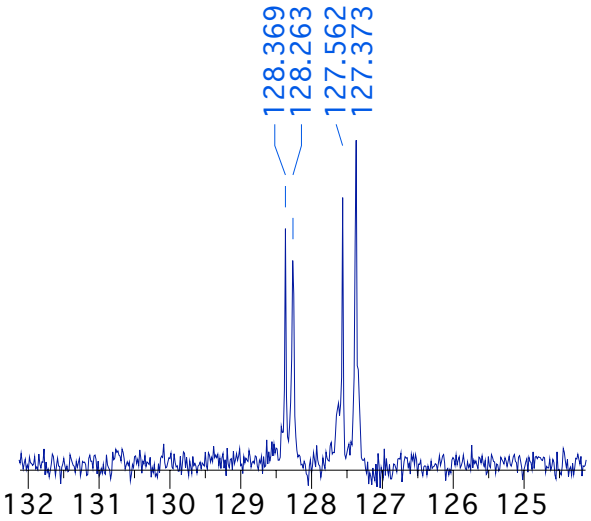
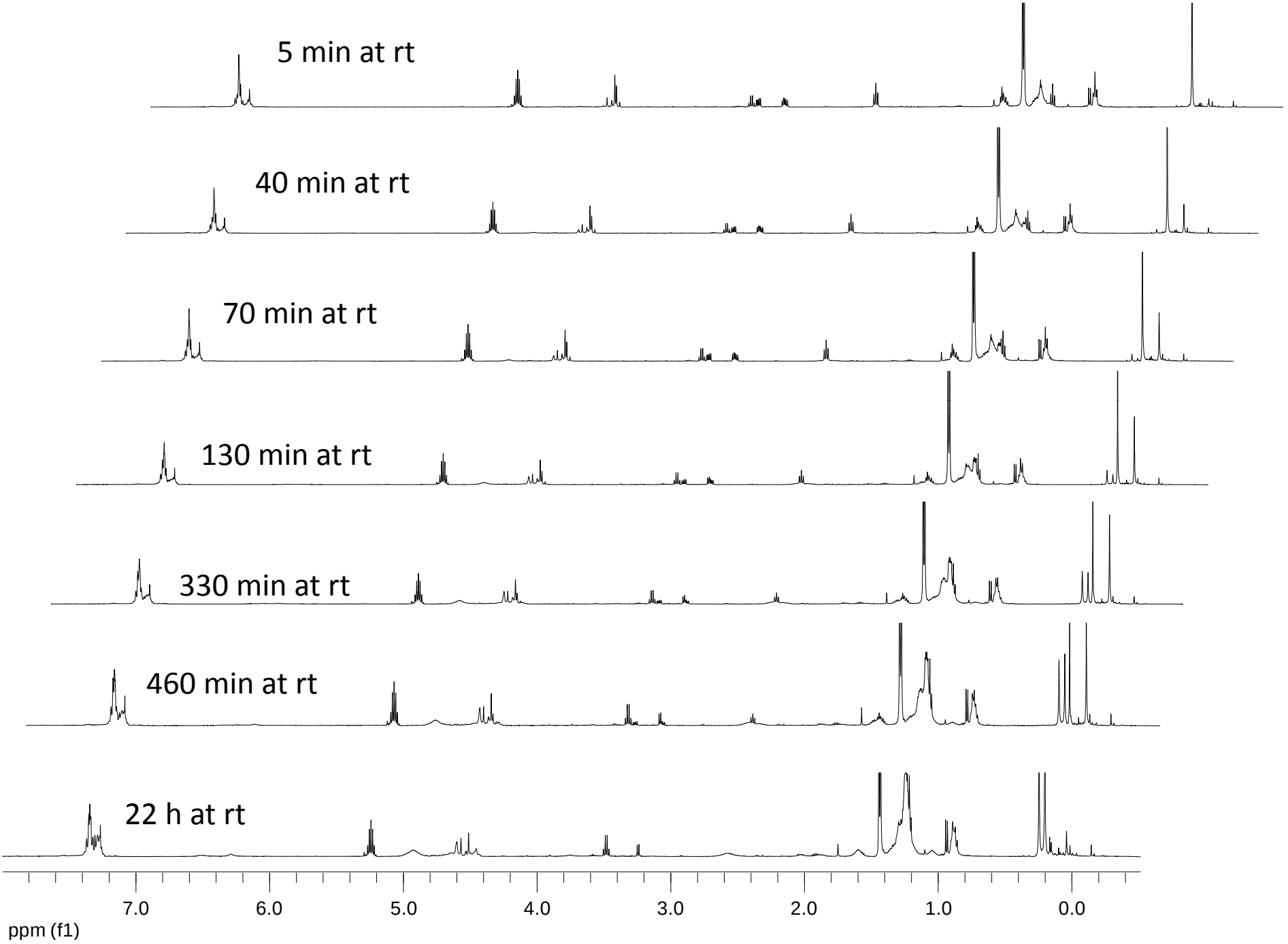
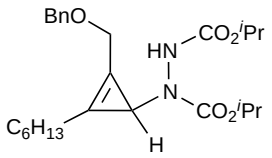
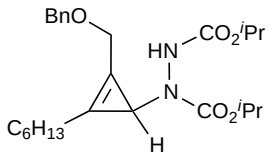




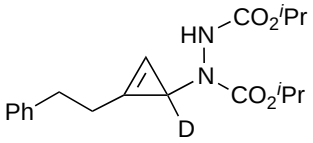




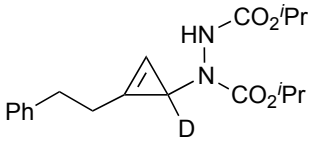
7b



7b



7c-*d*



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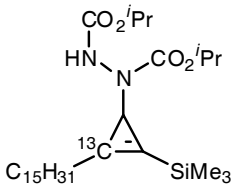
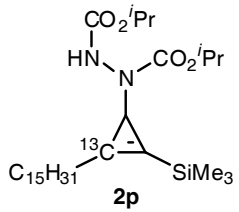


2p @ 370 K in d_6-DMSO



2p