SUPPORTING INFORMATION

Gold(I)-catalyzed Intermolecular Cycloaddition of Allenamides with α,β-Unsaturated Hydrazones: Efficient Access to Highly Substituted Cyclobutanes

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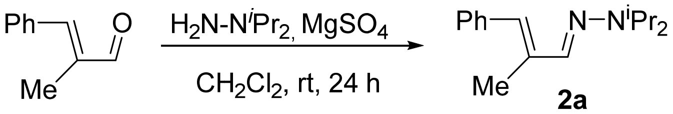
General Procedures

Dry solvents were freshly distilled under argon from an appropriate drying agent before use. Dry THF was obtained using Solvent Purification System (SPS). Toluene and CH_2Cl_2 was purchased from Aldrich. Gold complex **Au1** was purchased from Aldrich. All other chemicals were purchased from Aldrich, TCI or Alfa Aesar and used without further purification, unless otherwise noted. Reactions were conducted in dry solvents under argon atmosphere unless otherwise stated. The abbreviation "rt" refers to reactions carried out approximately at 23ºC. Reaction mixtures were stirred using Teflon-coated magnetic stirring bars. Reaction temperatures were maintained using Thermowatch-controlled silicone oil baths. Thin-layer chromatography (TLC) was performed on silica gel plates and components were visualized by observation under UV light, and / or by treating the plates with *p*-anisaldehyde or cerium nitrate solutions, followed by heating. Flash chromatography was carried out on silica gel unless otherwise stated. Dryings were performed with anhydrous Na_2SO_4 or $MgSO_4$. Concentration refers to the removal of volatile solvents via distillation using a Büchi rotary evaporator followed by residual solvent removal under high vacuum. NMR spectra were recorded in $CDCl_3$, at 250 MHz (Bruker), 300 MHz (Varian), 400 MHz (Varian) or 500 MHz (Varian) for cycloadducts. Carbon types and structure assignments were determined from DEPT-NMR and two-dimensional experiments (HMQC and HMBC, COSY and NOESY). NMR spectra were analyzed using MestreNova© NMR data processing software (www.mestrelab.com). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; dd, double doublet; td, triple doublet; m, multiplet; br, broad. Mass spectra were acquired using chemical ionization (CI) electron impact (EI), or electrospray ionization (ESI) and were recorded at the CACTUS facility of the University of Santiago de Compostela. The reactions were monitored by TLC or GC-MS using the Agilent Technologies 6890N, Network GC System, equipped with the Agilent 190915-433 column and the Agilent 5973 Inert Mass Selective Detector in Electron Impact or Chemical Ionization Mode (with Methane).

Experimental data

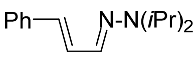
Experimental procedures for the synthesis of α,β-Unsaturated Hydrazones (2). Exemplified for the synthesis of **2a**



2a

$MgSO_4$ (0.99 mg, 8.21 mmol) and *N,N*-diisorpropylhidrazine (20.5 mmol, 2.4 g) were added to a solution of (*E*)-2-methyl-3-phenylacrylaldehyde (0.96 ml, 6.84 mmol) in CH_2Cl_2 (3.4 ml). After stirring at rt for 24h, the mixture was filtered, washed with brine (5 ml) and extracted (CH_2Cl_2, 2 x 10 ml). The combined organic phases were dried, filtered and evaporated to yield a crude oil that was purified by column chromatography (hexanes: EtOAc 8:2) to afford the hydrazone **2a** (1.48 g) in 89% yield. Yellow solid. (1*E*,2*E*)-2-Methyl-3-phenylacrylaldehyde diisopropylhydrazone. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.61 – 7.41 (m, 4H), 7.40 – 7.22 (m, 2H), 6.59 (s, 1H), 4.06 – 3.96 (m,2H), 2.37 (d, *J* = 1.2 Hz, 3H), 1.36 (d, *J* = 6.5 Hz, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.60 (C), 138.01 (C), 132.34 (CH), 128.96 (CH), 128.12 (CH), 127.44 (CH), 125.83 (CH), 47.47 (CH), 20.97 (CH_3), 13.59 (CH_3). **LRMS** (ESI): 245 (M^+ +1), 203, 161, 144, 118, 86; **HRMS** calculated for $C_{16}H_{25}N_2$ 245.2012, found 245.2010.

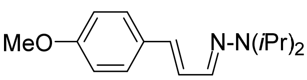
(1*E*,2*E*)-3-Phenylacrylaldehyde diisopropylhydrazone (**2b**)



2b

Yellow oil, 83% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.7 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.15 (m, 2H), 7.04 (dd, *J* = 15.9, 8.7 Hz, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 3.88 (hept, *J* = 6.6 Hz, 2H), 1.22 (d, *J* = 6.6 Hz 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.05 (C), 129.43 (CH), 129.40 (CH), 128.43 (CH), 127.82 (CH), 126.46 (CH), 125.78 (CH), 47.49 (CH), 20.81 (CH_3). **LRMS** (ESI): 231 (M^+ +1), 203. 189, 173, 147, 132, 100, 86; **HRMS** calculated for $C_{15}H_{23}N_2$ 231.1856, found 231.1855.

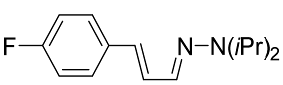
(1*E*,2*E*)-3-(4-Methoxyphenyl)acrylaldehyde diisopropylhydrazone (**2c**)



2c

Yellow solid, 87% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 1H), 6.93 – 6.82 (m, 3H), 6.44 (d, *J* = 15.9 Hz, 1H), 3.89 – 3.81 (m, 2H), 3.81 (s, 3H), 1.19 (d, *J* = 6.6 Hz, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.71 (C), 131.07 (C), 130.48 (CH), 128.02 (CH), 127.62 (CH), 127.16 (CH), 114.15 (CH), 55.38 (CH_3), 47.64 (CH), 20.99 (CH_3). **LRMS** (ESI): 261 (M^+ + 1), 235, 219, 203, 177, 162, 135, 86; **HRMS** calculated for $C_{16}H_{25}N_2O$ 261.1961, found 261.1957.

(1*E*,2*E*)-3-(4-Fluorophenyl)acrylaldehyde diisopropylhydrazone (**2d**)

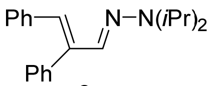


2d

White solid, 93% yield **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.4, 5.7 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 1H), 7.02 – 6.83 (m, 3H), 6.42 (d, *J* = 15.9 Hz, 1H), 3.85 (hept, *J* = 6.5 Hz, 2H), 1.19 (d, *J* = 6.5 Hz, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.84 (d, *J* = 245.9 Hz, C), 134.47 (d, *J* = 3.0 Hz, C), 129.44 (d, *J* = 2.0 Hz, CH), 129.34 (CH), 127.32 (d, *J* = 7.7 Hz, CH), 126.71 (CH), 115.55 (d, *J* = 21.5 Hz,

CH), 47.73 (CH), 21.01 (CH_3). **LRMS** (ESI): 249 (M^+ + 1), 165, 150, 123, 100, 86; **HRMS** calculated for $C_{15}H_{22}N_2F$ 249.1762, found 249.1761.

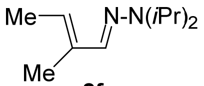
(1*E*,2*E*)-2,3-Diphenylacrylaldehyde diisopropylhydrazone (**2e**).[1]



2e

Yellow oil, 43% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 7H), 7.12 – 7.01 (m, 2H), 6.99 – 6.93 (m, 2H), 6.55 (s, 1H), 3.81 (hept, *J* = 6.5 Hz, 2H), 1.06 (d, *J* = 6.5 Hz, 12H). **LRMS** (ESI): 307 (M^+ + 1), 282, 265, 206, 179, 163, 86; **HRMS** calculated for $C_{21}H_{27}N_2$ 307.2169, found 307.2178.

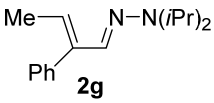
(1*E*,2*E*)-2-Methylbut-2-enal diisopropylhydrazone (**2f**)



2f

Yellow oil, 72% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.04 (s, 1H), 5.45 (q, *J* = 6.7 Hz, 1H), 3.73 (hept, *J* = 6.5 Hz, 2H), 1.84 (s, 3H), 1.74 (d, *J* = 7.0 Hz, 3H), 1.11 (d, *J* = 6.6 Hz, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 136.56 (C), 134.39 (CH), 123.53 (CH), 47.14 (CH), 20.74 (CH_3), 13.65 (CH_3), 11.48 (CH_3). **LRMS** (ESI): 183 (M^+ + 1), 141, 125, 86; **HRMS** calculated for $C_{11}H_{23}N_2$ 183.1856, found 183.1853.

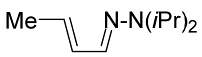
(1*E*,2*E*)-2-Phenylbut-2-enal diisopropylhydrazone (**2g**)



2g

Yellow oil, 37% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47 – 7.20 (m, 6H), 5.82 (q, *J* = 7.2 Hz, 1H), 3.85 – 3.71 (m, 2H), 1.76 (d, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 6.5 Hz, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 130.45 (C), 130.41 (CH), 130.21 (CH), 128.30 (CH), 127.27 (CH), 126.26 (C), 125.93 (CH), 52.25 (CH), 20.86 (CH_3), 19.48 (CH_3). **LRMS** (ESI): 245 (M^+ + 1), 203, 177, 161, 144, 118, 100, 86; **HRMS** calculated for $C_{16}H_{25}N_2$ 245.2012, found 245.2010.

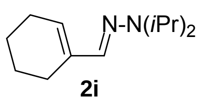
(1*E*,2*E*)-But-2-enal diisopropylhydrazone (**2h**)



2h

Yellow oil, 77% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.7 Hz, 1H), 6.30 – 6.18 (m, 1H), 5.71 – 5.56 (m, 1H), 3.80 – 3.66 (m, 2H), 1.79 (dd, *J* = 6.8, 1.4 Hz, 3H), 1.12 (d, *J* = 6.6 Hz, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 131.90 (CH), 131.62 (CH), 126.25 (CH), 47.33 (CH), 20.83 (CH_3), 18.19 (CH_3). **LRMS** (ESI): 169 (M^+ + 1), 127, 111, 100, 86; **HRMS** calculated for $C_{10}H_{21}N_2$ 169.1699, found 169.1697.

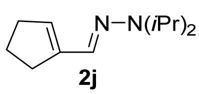
Cyclohex-1-ene-1-carbaldehyde diisopropylhydrazone (**2i**)



2i

Yellow oil, 83% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.03 (s, 1H), 5.71 – 5.64 (m, 1H), 3.75 (hept, *J* = 6.5 Hz, 2H), 2.37 – 2.30 (m, 2H), 2.20 – 2.10 (m, 2H), 1.70 – 1.60 (m, 4H), 1.13 (d, *J* = 6.6 Hz, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 137.80 (C), 132.76 (CH), 126.13 (CH), 47.09 (CH), 25.85 (CH_2), 24.22 (CH_2), 23.17 (CH_2), 22.67 (CH_2), 20.80 (CH_3). **LRMS** (ESI): 209 (M^+ + 1), 167, 141, 125, 86. **HRMS** calculated for $C_{13}H_{25}N_2$ 209.2012, found 209.2007.

Cyclopent-1-ene-1-carbaldehyde diisopropylhydrazone (**2j**)



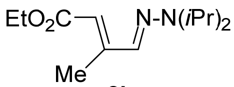
2j

Yellow oil, 69% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.26 (s, 1H), 5.65 – 5.59 (m, 1H), 3.79 (hept, *J* = 6.5 Hz, 2H), 2.61 (td, *J* = 7.7, 1.9 Hz, 2H), 2.51 – 2.39 (m, 2H), 1.95 – 1.84 (m, 2H), 1.15 (d, *J* = 6.5 Hz, 12H). **^{13}C NMR** (126

[1] This product turned out to be unstable. It was immediately used after purification.

MHz, $CDCl_3$) δ 137.78 (C), 126.26, (CH), 125.80, (CH), 47.62 (CH), 32.85 (CH_2), 31.28 (CH_2), 22.98 (CH_2), 20.72 (CH_3). **LRMS** (ESI): 217 (M^+ + Na), 209, 172, 115, 86; **HRMS** calculated for $C_{12}H_{22}N_2Na$ 217.1675 found 217.1682.

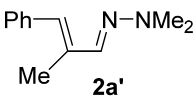
Ethyl (*2E*, *4E*)-4-(2,2-diisopropylhydrazono)-3-methylbut-2-enoate (**2k**)



2k

Yellow oil, 74% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.95 (s, 1H), 5.65 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.93 – 3.80 (m, 2H), 2.39 (d, *J* = 1.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.19 (d, *J* = 6.5 Hz, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.02 (C), 155.32 (C), 128.13 (CH), 113.88 (CH), 59.39 (CH), 48.34 (CH_2), 21.09 (CH_3), 14.60 (CH_3), 13.56 (CH_3). **LRMS** (ESI): 241 (M^+ + 1), 199, 153, 112, 100; **HRMS** calculated for $C_{13}H_{25}N_2O_2$ 241.1911, found 241.1910.

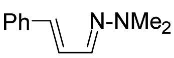
(1*E*,2*E*)-2-Methyl-3-phenylacrylaldehyde dimethyldrazone (**2a'**)



2a'

White solid, 74% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 4H), 7.29 – 7.24 (m, 1H), 7.19 (s, 1H), 6.58 (s, 1H), 2.95 (s, 6H), 2.20 (s, *J* = 1.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.17 (CH), 137.94 (C), 136.41 (C), 130.66 (CH), 129.14 (CH), 128.24 (CH), 126.49 (CH), 43.09 (CH_3), 13.50 (CH_3). **LRMS** (ESI): 189 (M^+ + 1), 173, 146, 117, 91; **HRMS** calculated for $C_{12}H_{17}N_2$ 189.1386, found 189.1381.

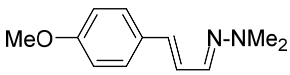
(1*E*,2*E*)-3-Phenylacrylaldehyde dimethylhydrazone (**2b'**)



2b'

Yellow solid, 99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 9.0 Hz, 1H), 7.04 – 6.97 (m, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 2.94 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.31 (C), 135.07 (CH), 131.57 (CH), 128.62 (CH), 127.56 (CH), 127.33 (CH), 126.18 (CH), 42.70 (CH_3). **LRMS** (ESI): 175 (M^+ + 1), 148, 132, 115; **HRMS** calculated for $C_{11}H_{15}N_2$ 175.1230, found 175.1228.

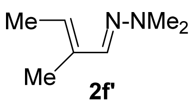
(1E,2E)-3-(4-Methoxyphenyl)acrylaldehyde dimethylhydrazone (**2c'**)



2c'

Yellow solid, 93% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.33 δ 7.34 (d, *J* = 8.9 Hz, 2H), 7.14 (d, *J* = 8.9 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.81 (dd, *J* = 16.0, 8.9 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 3.79 (s, 3H), 2.89 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.24 (C), 136.22 (CH), 131.76 (CH), 130.16 (C), 127.54 (CH), 125.57 (CH), 114.20 (CH), 55.35 (CH_3), 42.94 (CH_3). **LRMS** (ESI): 205 (M^+ + 1), 178, 160, 133,117, 90; **HRMS** calculated for $C_{12}H_{17}N_2O$ 205.1335, found 205.1335.

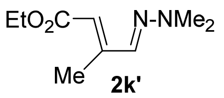
(1E,2E)-2-Methylbut-2-enal dimethylhydrazone (**2f'**)



2f'

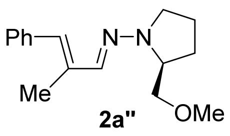
Yellow oil, 72% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.95 (s, 1H), 5.54 (q, *J* = 6.7 Hz, 1H), 2.72 (s, 6H), 1.77 – 1.75 (m, 3H), 1.70 (dd, *J* = 7.0, 0.9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 140.24 (CH), 135.24 (C), 126.99 (CH), 43.06 (CH_3), 13.67 (CH_3), 11.27 (CH_3). **LRMS** (ESI): 127 (M^+ + 1), 111, 84; **HRMS** calculated for $C_7H_{15}N_2$ 127.1230, found 127.1235.

Ethyl (2E,4Z)-4-(2,2-dimethylhydrazono)-3-methylbut-2-enoate (**2k’**)



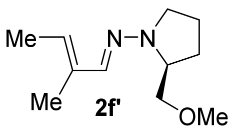
Yellow oil, 74% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.74 (d, *J* = 6.1 Hz, 1H), 5.66 (d, *J* = 5.8 Hz, 1H), 4.13 – 4.04 (m, 2H), 2.94 – 2.88 (m, 6H), 2.29 – 2.24 (m, 3H), 1.23 – 1.17 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.29 (C), 153.16 (C), 132.66 (CH), 116.25 (CH), 59.32 (CH_2), 42.30 (CH_3), 14.31 (CH_3), 13.19 (CH_3). **LRMS** (ESI): 185 (M^+ + 1), 139, 111, 96; **HRMS** calculated for $C_9H_{16}N_2O_2$185.1285, found 185.1286.

(*2S*)-2-(Methoxymethyl)-*N*-[(1*E*,2*E*)-2-methyl-3-phenylprop-2-en-1-ylidene]pyrrolidin-1-amine (**2a’’**)



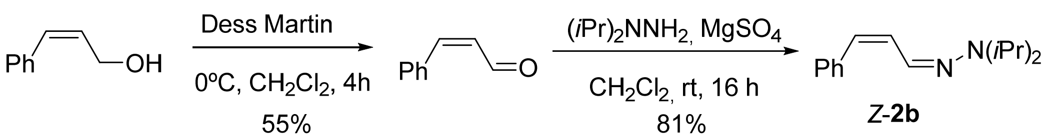
Yellow oil, 67 % yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 4H), 7.26 – 7.18 (m, 1H), 7.15 (s, 1H), 6.50 (s, 1H), 3.70 – 3.58 (m, 2H), 3.54 – 3.45 (m, 2H), 3.42 (s, 3H), 3.01 (dd, *J* = 16.8, 7.9 Hz, 1H), 2.16 (d, *J* = 1.2 Hz, 3H), 2.12 – 1.84 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.61 (CH), 138.11 (C), 136.74 (C), 129.64 (CH), 129.05 (CH), 128.18 (CH), 126.27 (CH), 74.62 (CH_2), 63.19 (CH_3), 59.27 (CH), 49.12 (CH_2), 26.87 (CH_2), 22.28 (CH_2), 13.45 (CH_3). **LRMS** (ESI): 259 (M^+ + 1), 227, 146, 114, 91; **HRMS** calculated for $C_{16}H_{23}N_2O$ 259.1805, found 259.1803.

(2S)-2-(Methoxymethyl)-N-[(1E,2E)-2-methylbut-2-en-1-ylidene]pyrrolidin-1-amine (**2f’’**)



Yellow oil, 65 % yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.02 (s, 1H), 5.57 (q, *J* = 6.9 Hz, 1H), 3.65 – 3.59 (m, 1H), 3.49 – 3.42 (m, 2H), 3.40 – 3.37 (m, 4H), 2.90 – 2.79 (m, 1H), 2.00 – 1.84 (m, 4H), 1.83 – 1.81 (m, 3H), 1.76 (dd, *J* = 7.0, 0.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.25 (CH), 135.70 (C), 126.33 (CH), 74.85 (CH_2), 63.44 (CH), 59.37 (CH_3), 49.65 (CH_2), 26.90 (CH_2), 22.27 (CH_2), 13.90 (CH_3), 11.46 (CH_3).

Synthesis of (1*E*,2Z)-3-phenylacrylaldehyde diisopropylhydrazone (Z-2b*)*

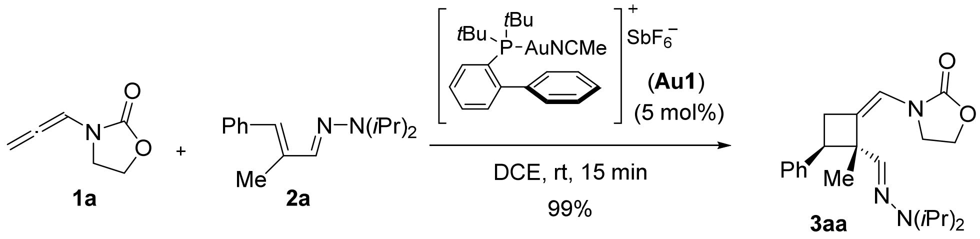


Dess-Martin periodinane (1.04 g, 2.46 mmol) was added to a solution of (Z)-3-fenilprop-2-en-1-ol[2] (300 mg, 2.24 mmol) in CH_2Cl_2 (2.5 ml) and the resulting mixture was stirred for 4h at rt. Then, solutions of $NaHCO_3$ (1 ml) and $H_2S_2O_3$ (1 ml) were subsequently added and the resulting mixture was stirred for 15 min. After extraction with CH_2Cl_2 (2 x 5 ml), the combined organic phases were washed with $NaCl_{sat}$ (10 ml), dried and concentrated to provide a crude residue containing the (Z)-3-phenylacrylaldehyde,[3] which was subsequently treated with diisopropyl hydrazine and $MgSO_4$ (16h at rt) to provide the hydrazone *Z*-**2b**, which was obtained in 81% yield after column chromatography. (1*E*,2*E*)-3-Phenylacrylaldehyde diisopropylhydrazone (***Z*-2b**). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 9.0 Hz, 1H), 7.40 – 7.30 (m, 4H), 7.27 – 7.17 (m, 1H), 6.48 – 6.31 (m, 2H), 3.82 (hept, *J* = 6.6 Hz, 2H), 1.19 (d, *J* = 6.6 Hz, 12H). **^{13}C NMR** (75

[2] Pavlakos E., Georgiou T., Tofi M., Montagnon T.,Vassilikogiannakis G. *Org. Lett.***2009**, *11*, 4556-4559.
[3] Fehr C., Magpantay I., Vuagnoux M., Dupau P. *Chem. Eur. J.* **2011**, *17*, 1257-1260

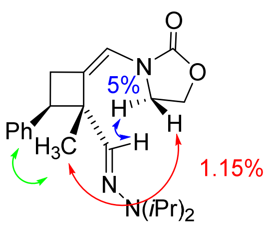
MHz, $CDCl_3$) δ 138.64 (C), 130.57 (CH), 128.77 (CH), 128.35 (CH), 126.33 (CH), 126.18 (CH), 124.96 (CH), 47.87 (CH), 21.02 (CH_3). **LRMS** (ESI): 231 (M^+ + 1), 189, 132, 86. **HRMS** calculated for $C_{15}H_{23}N_2$ 231.1856, found 231.1847.

Experimental procedure for the Au1-catalyzed [2+2] cycloaddition. Exemplified for the cycloaddition of **1a** and **2a**



The gold complex **Au1** (12.3 mg, 0.016 mmol) was added to a solution of **1a** (40 mg, 0.32 mmol) and **2a** (156 mg, 0.64 mmol) in $(CH_2)_2Cl_2$ (1.3 ml) at rt. The resulting mixture was stirred for 10 min, filtered through florisil (eluting with CH_2Cl_2) and concentrated. The crude residue was purified on column chromatography (hexanes: EtOAc 7:3) to afford 117 mg of the [2+2] cycloadduct **3aa** (0.32 mmol, 99% yield). (1*R*,2*Z*,4*R*)-1-methyl-2-[(2-oxo-1,3-oxazolidin-3-yl)methylene]-4-phenylcyclobutanecarbaldehyde diisopropylhydrazone (**3aa**). Yellow solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.32 (t, J = 7.6 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.14 (d, J = 7.9 Hz, 2H), 6.81 (s, 1H), 6.38 (d, J = 0.7 Hz, 1H), 4.35 – 4.26 (m, 1H), 4.19 (dd, J = 17.2, 8.5 Hz, 1H), 3.91 (td, J = 9.0, 5.4 Hz, 1H), 3.82 – 3.73 (m, 2H), 3.68 (t, J = 9.4 Hz, 1H), 3.63 – 3.56 (m, 1H), 3.14 (ddd,J = 14.3, 10.0, 2.5 Hz, 1H), 2.86 (ddd, J = 14.3, 8.6, 1.3 Hz, 1H), 1.14 (d, J = 6.5 Hz, 12H), 1.08 (s, 3H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 156.90 (C), 139.73 (C), 133.91 (CH), 129.06 (C), 128.12 (CH), 127.54 (CH), 126.25 (CH), 116.58 (CH), 62.42 (CH_2), 54.47 (C), 47.26 (CH), 46.87 (CH_2), 45.68 (CH), 29.27 (CH_2), 21.31 (CH_3), 20.38 (CH_3), 18.64 (CH_3). **LRMS** (ESI): 370 (M^+ + 1), 270, 242, 181, 155, 126; **HRMS** calculated for $C_{22}H_{32}N_3O_2$ 370.2489, found 370.2481.

In addition to nOe experiments (Figure S1), the structure and stereochemical identity of this adduct could be further corroborated by X-ray analysis (Figure S2).[4]



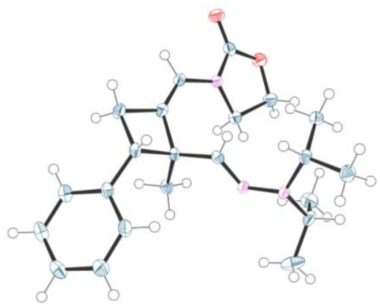
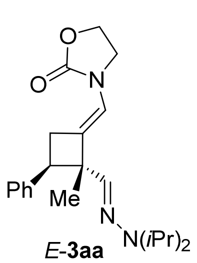


Figure S1. nOe signals observed for *Z*-**3aa.** **Figure S2.** X-ray crystal structure of **3aa**

Other products isolated on the preliminary screening of Table 1 (manuscript)

(1*R*,2*Z*,4*R*)-1-Methyl-2-[(2-oxo-1,3-oxazolidin-3-yl)methylene]-4-phenylcyclobutanecarbal dehyde diisopropylhydrazone (***E*-3aa**).[5]

[4] CCDC 1029359 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



E-**3aa**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.19 (m, 5H), 6.58 (s, 1H), 6.01 (dd, *J* = 3.0, 2.2 Hz, 1H), 4.33 – 4.24 (m, 2H), 3.86 – 3.67 (m, 5H), 2.94 – 2.82 (m, 1H), 2.69 (ddd, *J* = 15.8, 7.9, 3.1 Hz, 1H), 1.16 (d, *J* = 6.5 Hz, 6H), 1.11 (d, *J* = 6.5 Hz, 6H), 0.97 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.49 (C), 142.59 (C), 140.02 (C), 132.78 (CH), 128.78 (CH), 127.85 (CH), 126.44 (CH), 116.99 (CH), 61.92 (CH_2), 55.17 (C), 54.70 (CH), 47.22 (CH), 45.86 (CH_2), 32.27 (CH_2), 21.36 (CH_3), 20.65 (CH_3), 17.94 (CH_3). **LRMS** (ESI): 370 (M^+ + 1), 263, 242, 198, 155, 129, 100; **HRMS** calculated for $C_{22}H_{32}N_3O_2$ 370.2489, found 370.2492.

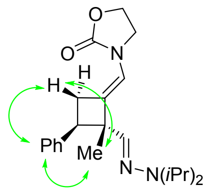
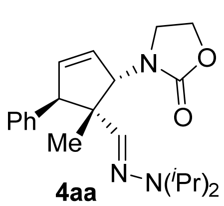


Figure S3. nOe signals observed for *E*-**3aa**

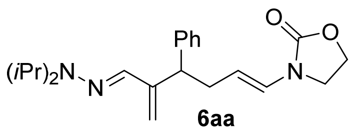
3-((1S,4R,5R)-5-((E)-(2,2-Diisopropylhydrazono)methyl)-5-methyl-4-phenylcyclopent-2-en-1-yl)oxazolidin-2-one (**4aa**).[6]



4aa

NMR H (500 MHz, $CDCl_3$) δ 6.45 (s, 1H), 6.28 (d, *J* = 5.9 Hz, 1H), 5.78 (dt, *J* = 5.8, 2.8 Hz, 1H), 5.10 (dd, *J* = 4.2, 1.9 Hz, 1H), 4.25 – 4.21 (m, 1H), 4.17 – 4.11 (m, 1H), 3.59 (ddd, *J* = 9.5, 8.5, 6.7 Hz, 2H), 3.49 – 3.39 (m, 2H) 1.22 (d, *J* = 6.5 Hz, 6H), 1.19 (d, *J* = 6.5 Hz, 6H), 0.80 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.08 (C), 130.32 (CH), 128.78 (CH), 128.72 (CH), 127.80 (CH), 126.60 (CH), 126.39 (CH), 68.86 (CH), 62.17 (CH_2), 52.98 (C), 52.78 (CH), 46.90 (CH), 41.71 (CH_2), 24.42 (CH_3), 21.03 (CH_3). **LRMS** (ESI): 370 (M^+ + 1), 328, 269, 225, 202, 182, 155, 100; **HRMS** calculated for $C_{22}H_{32}N_3O_2$ 370.2489, found 370.2486.

(1*E*,5*E*)-2-Methylene-6-(2-oxo-1,3-oxazolidin-3-yl)-3-phenylhex-5-enal diisopropylhydrazone (**6aa**).[7]



6aa

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.2 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.99 (s, 1H), 6.65 (d, *J* = 14.3 Hz, 1H), 5.06 (d, *J* = 8.8 Hz, 2H), 4.73 (dt, *J* = 14.4, 7.2 Hz, 1H), 4.36 (t, *J* = 8.3 Hz, 2H), 4.18 (t, *J* = 7.8 Hz, 1H), 3.76 (p, *J* = 6.5 Hz, 2H), 3.63 – 3.52 (m, 2H), 2.73 (dt, *J* = 14.3, 7.3 Hz, 1H), 2.58 (dt, *J* = 14.4, 7.3 Hz, 1H), 1.15 (d, *J* = 6.6 Hz, 6H), 1.03 (d, *J* = 6.5 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.4 (C), 150.0 (C), 144.3 (C), 129.5 (CH), 128.3 (CH), 128.0 (CH), 125.9 (CH), 124.6 (CH), 111.9 (CH_2), 110.1 (CH), 62.0 (CH_2), 47.1 (CH), 46.1 (CH), 42.5 (CH_2), 35.0 (CH_2), 20.9 (CH_3), 20.7 (CH_3). **LRMS** (*m/z, ESI*): 370.25, $(M+H)^+$, 283.21, 241.17, 199.12, 182.10, 155.09, 126.06. **HRMS** Calculated for $C_{22}H_{32}N_3O_2$: 370.2489, found 370.2495.

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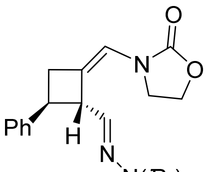
[5] a) Isolated from the reactions catalyzed by $PtCl_2$, $PtBr_2$, AuCl or $PicAuCl_2$, Table 1 (main manuscript), entries 1-5). b) As a general trend, besides nOe experiments and X-ray analysis, the assignment of the *Z* / *E* geometry of the exo-enamide moiety could also be carried out on the bases of the ^{1}H NMR chemical shifts of the enamide and hydrazone signals. We found that *Z* isomers have the enamide and hydrazone signals more deshielded than the corresponding *E* counterparts. In this particular case, chemical shifts for *Z*-**3aa** are δ= 6.81ppm (hydrazone) and 6.38 ppm (enamide), whereas for *E*-**3aa** are 6.58 ppm (hydrazone) and 6.01 ppm (enamide).

[6] Data deduced from a sample of **4aa** slightly contaminated with *E*-**3aa** and **5aa** (Table 1, entries 1-3).

[7] Obtained from the reaction catalyzed by $PhPAuNTf_2$ (Table 1, entry 6)

Cycloadducts obtained following the general procedure with the catalyst Au1 (Table 2, manuscript)

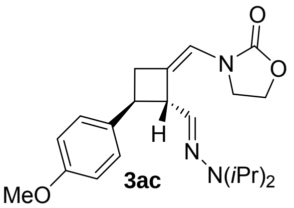
(1*R*,2*Z*,4*S*)-2-[(2-Oxo-1,3-oxazolidin-3-yl)methylene]-4-phenylcyclobutanecarbaldehyde diisopropylhydrazone (*Z*-**3ab**)



3ab

Yellow solid, 62% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 4H), 7.24 – 7.19 (m, 1H), 6.71 (d, *J* = 6.7 Hz, 1H), 6.40 (q, *J* = 2.2 Hz, 1H), 4.34 – 4.28 (m, 1H), 4.23 – 4.17 (m, 1H), 4.06 (td, *J* = 9.1, 5.4 Hz, 1H), 3.94 (ddd, *J* = 9.4, 6.4, 2.8 Hz, 1H), 3.73 (hept, *J* = 6.5 Hz, 2H), 3.66 (q, *J* = 9.1 Hz, 1H), 3.51 (dt, *J* = 9.3, 7.1 Hz, 1H), 3.19 – 3.12 (m, 1H), 2.81 (ddd, *J* = 15.4, 7.4, 2.4 Hz, 1H), 1.11 (d, *J* = 6.7 Hz, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.71 (C), 144.53 (C), 131.12 (CH), 128.49 (CH), 126.52 (CH), 126.30 (CH), 123.51 (C), 118.03 (CH), 62.56 (CH_2), 54.14 (CH), 47.14 (CH), 45.60 (CH_2), 41.84 (CH), 33.73 (CH_2), 20.97 (CH_3), 20.61 (CH_3). **LRMS** (ESI): 356 (M^+ + 1), 314, 256, 228, 167, 126, 100; **HRMS** calculated for $C_{21}H_{30}N_3O_2$ 356.2333, found 356.2335.

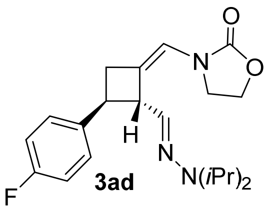
(1*R*,2*S*,4*Z*)-2-(4-Methoxyphenyl)-4-[(2-oxo-1,3-oxazolidin-3-yl)methylene]cyclobutanecarbalde hyde diisopropylhydrazone (**3ac**)



3ac

Yellow solid, 88% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ, 7.21 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H) , 6.70 (d, *J* = 6.8 Hz, 1H), 6.38 (d, *J* = 2.1 Hz, 1H), 4.30 (td, *J* = 8.9, 5.5 Hz, 1H), 4.19 (q, *J* = 8.5 Hz, 1H), 4.05 (td, *J* = 9.1, 5.4 Hz, 1H), 3.90 – 3.85 (m, 1H), 3.79 (s, 3H), 3.68 (hept, *J* = 6.5 Hz, 2H), 3.65 (q, *J* = 9.0 Hz, 1H), 3.44 (dd, *J* = 16.2, 7.1 Hz, 1H), 3.15 – 3.08 (m, 1H), 2.76 (ddd, *J* = 15.3, 7.4, 2.3 Hz, 1H), 1.12 – 1.07 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.12 (C), 156.68 (C), 136.62 (C), 131.33 (CH), 127.48 (CH), 123.60 (C), 117.95 (CH), 113.86 (CH), 62.54 (CH_2), 55.36 (CH_3), 54.35 (CH), 47.12 (CH), 45.59 (CH_2), 41.20 (CH), 33.96 (CH_2), 20.92 (CH_3), 20.58 (CH_3). **LRMS** (ESI): 386 (M^+ + 1), 286, 257, 199, 167, 125, 100; **HRMS** calculated for $C_{22}H_{32}N_3O_3$ 386.2438, found 386.2437.

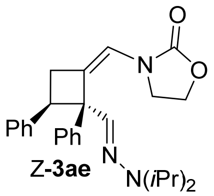
(1*R*,2*S*,4*Z*)-2-(4-Fluorophenyl)-4-[(2-oxo-1,3-oxazolidin-3-yl)methylene]cyclobutanecarbaldehy-de diisopropylhydrazone (**3ad**)



3ad

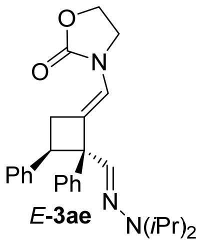
White solid, 55% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.05 – 6.99 (m, 2H), 6.71 (d, *J* = 6.7 Hz, 1H), 6.42 (q, *J* = 2.2 Hz, 1H), 4.37 – 4.31 (m, 1H), 4.22 (dd, *J* = 17.2, 8.5 Hz, 1H), 4.06 (td, *J* = 9.1, 5.4 Hz, 1H), 3.94 – 3.88 (m, 1H), 3.76 (hept, *J* = 6.5 Hz, 2H), 3.69 (q, *J* = 9.2 Hz, 1H), 3.50 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.20 – 3.13 (m, 1H), 2.79 (ddd, *J* = 15.4, 7.5, 2.4 Hz, 1H), 1.13 (dd, *J* = 7.9, 6.6 Hz, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ161.50 (d, *J* = 244.2 Hz, C), 156.70 (C), 140.21 (C), 130.69 (CH), 127.96 (d, *J* = 7.8 Hz, CH), 123.25 (C), 118.17 (CH), 115.22 (d, *J* = 21.2 Hz, CH), 62.57 (CH2), 54.42 (CH), 47.16 (CH), 45.65 (CH_2), 41.25 (CH), 33.90 (CH_2), 20.96 (CH_3), 20.63 (CH_3). **LRMS** (ESI): 374 (M^+ + 1), 274, 249, 207, 167, 126; **HRMS** calculated for $C_{21}H_{29}FN_3O_2$ 374.2238, found 374.2242.

(1*S*,2*Z*,4*R*)-2-[(2-Oxo-1,3-oxazolidin-3-yl)methylene]-1,4-diphenylcyclobutanecarbaldehyde diisopropylhydrazone (*Z*-**3ae**)[8]



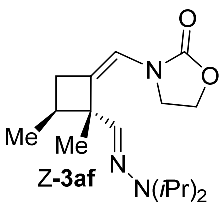
Yellow oil. **^{1}H NMR** (500 MHz, C_6D_6) δ 7.39 (dd, *J* = 8.0, 0.9 Hz, 2H), 7.18 (t, *J* = 7.7 Hz, 2H), 7.12 (s, 1H), 7.09 – 7.03 (m, 2H), 7.02 – 6.95 (m, 4H), 6.31 (s, 1H), 3.67 (t, *J*= 9.0 Hz, 1H), 3.35 – 3.22 (m, 4H), 3.04 – 2.95 (m, 2H), 2.74 (ddd, *J* = 14.9, 9.1, 1.6 Hz, 1H), 2.58 (td, *J* = 9.0, 6.4 Hz, 1H), 0.82 (d, *J* = 6.6 Hz, 6H), 0.77 (d, *J* = 6.4 Hz, 6H). **^{13}C NMR** (126 MHz, C_6D_6) δ 156.24 (C), 147.34 (C), 140.12 (C), 128.83 (CH), 128.69 (CH), 128.49 (CH), 128.43 (CH), 128.35 (CH), 127.14 (CH), 126.71 (CH), 120.66 (C), 119.36 (CH), 62.22 (C), 61.74 (CH_2), 53.61 (CH), 47.28 (CH), 45.03 (CH_2), 29.76 (CH_2), 21.22 (CH_3), 20.52 (CH_3). **LRMS** (ESI): 432 (M^+ + 1), 361, 345, 331; **HRMS** calculated for $C_{27}H_{34}N_3O_2$ 432.2646, found 432.2655.

(1*S*,2*E*,4*R*)-2-[(2-Oxo-1,3-oxazolidin-3-yl)methylene]-1,4-diphenylcyclobutanecarbaldehyde diisopropylhydrazone (*E*-**3ae**)



Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.16 – 7.01 (m, 8H), 6.93 (s, 1H), 6.84 (dd, *J* = 7.0, 2.5 Hz, 2H), 6.75 – 6.70 (m, 1H), 4.45 (t, *J* = 9.2 Hz, 1H), 4.20 – 4.07 (m, 2H), 3.82 (dq, *J* = 12.8, 6.4 Hz, 2H), 3.64 (td, *J* = 8.6, 6.8 Hz, 1H), 3.42 (td, *J* = 9.0, 5.5 Hz, 1H), 3.15 – 2.96 (m, 2H), 1.23 – 1.16 (m, 12H). **LRMS** (ESI): 432 (M^+ + 1), 381, 353, 345, 331; **HRMS** calculated for $C_{27}H_{34}N_3O_2$ 432.2646, found 432.2632.

(1*R*,2*S*,4*Z*)-1,2-Dimethyl-4-[(2-oxo-1,3-oxazolidin-3-yl)methylene]cyclobutanecarbaldehyde diiso propylhydrazone (*Z*-**3af**)[9]



Yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.59 (s, 1H), 6.18 – 6.16 (m, 1H), 4.26 (ddd, *J* = 9.0, 7.3, 3.7 Hz, 1H), 4.17 – 4.08 (m, 1H), 3.86 (td, *J* = 9.1, 5.5 Hz, 1H), 3.68 (dt, *J* = 13.0, 6.5 Hz, 2H), 3.61 – 3.55 (m, 1H), 2.70 – 2.63 (m, 1H), 2.40 – 2.26 (m, 2H), 1.31 (s, 3H), 1.09 (d, *J* = 6.5 Hz, 6H), 1.05 (d, *J* = 6.5 Hz, 6H) , 0.99 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.96 (C), 135.44 (CH), 130.41 (C), 116.16 (CH), 62.39 (CH_2), 51.96 (C), 47.15 (CH), 46.90 (CH_2), 36.06 (CH), 33.79 (CH_2), 21.00 (CH_3), 20.62 (CH_3), 17.07 (CH_3), 15.04 (CH_3). **LRMS** (ESI): 308 (M^+ + 1), 266, 221, 180, 126, 100;; **HRMS** calculated for $C_{17}H_{30}N_3O_2$ 308.2333, found 308.2332.

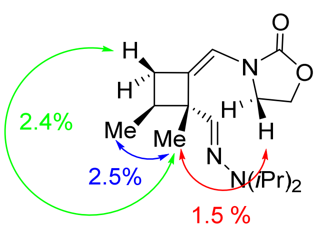
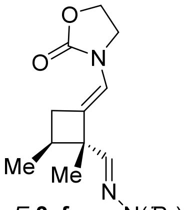


Figure S4. nOe signals observed for *Z*-**3af**

[8] The combined yield for the mixture of *Z*-**3ae** and *E*-**3ae** is 95% (Z/E ratio = 6:4). We could separate a small amount of the Z isomer that allowed its independent characterization.

[9] The combined yield for the mixture of *Z*-**3af** and *E*-**3af** is 87% (Z/E ratio = 8:2). We could separate a small amount of both isomers that allowed their independent characterization.

(1*R*,2*S*,4*E*)-1,2-Dimethyl-4-[(2-oxo-1,3-oxazolidin-3-yl)methylene]cyclobutanecarbaldehyde diisopropylhydrazone (*E*-**3af**)



E-**3af**

Yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.47 (s, 1H), 5.83 (s, 1H), 4.30 – 4.19 (m, 2H), 3.81 – 3.75 (m, 1H), 3.74 – 3.64 (m, 3H), 2.46 (ddd, *J* = 15.5, 7.6, 3.2 Hz, 1H), 2.38 – 2.29 (m, 1H), 2.07 – 1.99 (m, 1H), 1.15 (s, 3H), 1.09 (dd, *J* = 8.4, 6.7 Hz, 12H), 0.93 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.5 (C), 143.30 (C), 135.21 (CH), 117.68 (CH), 61.94 (CH_2), 53.96 (C), 47.34 (CH), 45.78 (CH_2), 43.53 (CH), 35.90 (CH_2), 21.19 (CH_3), 20.44 (CH_3), 15.91 (CH_3), 13.72 (CH_3). **LRMS** (ESI): 308 (M^+ + 1), 266, 221, 180, 126, 100, 86; **HRMS** calculated for $C_{17}H_{30}N_3O_2$ 308.2333, found 308.2330.

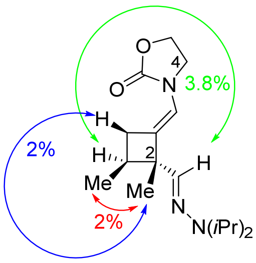
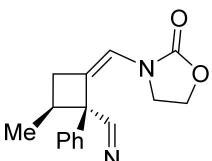


Figure S5. nOe signals observed for *E*-**3af.**

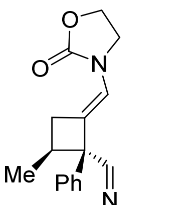
(1*S*,2*S*,4*Z*)-2-Methyl-4-[(2-oxo-1,3-oxazolidin-3-yl)methylene]-1-phenylcyclobutanecarbaldehyde diisopropylhydrazone (*Z*-**3ag**).[10]



Z-**3ag**

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.36 – 7.29 (m, 2H), 7.24 – 7.17 (m, 1H), 6.96 (s, 1H), 6.53 (t, *J* = 2.0 Hz, 1H), 4.06 – 3.84 (m, 2H), 3.76 (dq, *J* = 12.9, 6.5 Hz, 2H), 3.60 (hept, *J* = 9.4, 1H), 2.99 – 2.80 (m, 2H), 2.65 – 2.51 (m, 1H), 2.30 (ddd, *J* = 14.5, 7.8, 2.4 Hz, 1H), 1.15 (d, *J* = 6.5 Hz, 3H), 1.10 (d, *J* = 6.6 Hz, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.72 (C), 147.00 (C), 128.79 (CH), 128.47 (CH), 126.65 (CH), 126.31 (CH), 123.81 (C), 117.45 (CH), 62.56 (CH_2), 59.64 (C), 47.39 (CH), 45.18 (CH_2), 43.73 (CH), 33.46 (CH_2), 21.53 (CH_3), 20.63 (CH_3), 17.00 (CH_3). **LRMS** (ESI): 370 (M^+ + 1), 270, 242, 182, 155, 126, 100; **HRMS** calculated for $C_{22}H_{32}N_3O_2$ 370.2489, found 370.2485.

(1*S*,2*S*,4*E*)-2-Methyl-4-[(2-oxo-1,3-oxazolidin-3-yl)methylene]-1-phenylcyclobutanecarbaldehy-de diisopropylhydrazone (*E*-**3ag**)



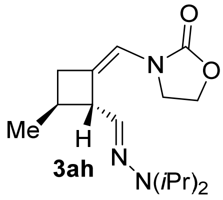
E-**3ag**

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 5H), 6.92 (s, 1H), 6.08 – 6.05 (m, 1H), 4.12 (t, *J* = 8.0 Hz, 2H), 3.77 (dt, *J* = 13.0, 6.5 Hz, 2H), 3.61 (dd, *J* = 16.4, 8.5 Hz, 1H), 3.26 (dd, *J* = 17.0, 8.2 Hz, 1H), 3.13 (dd, *J* = 16.1, 7.5 Hz, 1H), 2.55 (ddd, *J* = 15.8, 7.7, 3.1 Hz, 1H), 1.95 (ddd, *J* = 15.8, 9.0, 2.1 Hz, 1H), 1.18 – 1.10 (m, 12H), 0.55 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.27 (C), 140.32 (C), 132.97 (CH), 128.13 (CH),

[10] The combined yield for the mixture of *Z*-**3ag** and *E*-**3ag** is 94% (Z/E ratio = 6:4). We could separate a small amount of both isomers that allowed their independent characterization.

126.51 (CH), 119.31 (CH), 62.34 (CH_2), 61.97 (C), 47.41 (CH), 46.03 (CH_2), 44.20 (CH), 36.18 (CH_2), 21.10 (CH_3), 20.94 (CH_3), 16.63 (CH_3). **LRMS** (ESI): 370 (M^+ + 1), 328, 283, 242, 198, 155, 126, 100; **HRMS** calculated for $C_{22}H_{32}N_3O_2$ 370.2489, found 370.2487.

(1*R*,2*S*,4*Z*)-2-Methyl-4-[(2-oxo-1,3-oxazolidin-3-yl)methylene]cyclobutanecarbaldehyde diisopropylhydrazone (*Z*-**3ah**)



3ah

Yellow oil, 95% yield. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 6.62 (d, *J* = 6.9 Hz, 1H), 6.27 (t, *J* = 3.7 Hz, 1H), 4.28 (td, *J* = 8.9, 5.5 Hz, 1H), 4.16 (q, *J* = 8.7 Hz, 1H), 4.04 – 3.99 (m, 1H), 3.70 – 3.62 (m, 3H), 3.37 – 3.31 (m, 1H), 2.88 – 2.81 (m, 1H), 2.33 – 2.26 (m, 1H), 2.18 – 2.12 (m, 1H), 1.18 (dd, *J* = 6.8, 2.4 Hz, 3H), 1.07 (d, *J* = 6.6 Hz, 6H), 1.03 (d, *J* = 6.6 Hz, 6H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 156.53 (C), 133.25 (CH), 123.40 (C), 118.05 (CH), 62.45 (CH_2), 53.35 (CH), 47.07 (CH), 45.28 (CH_2), 34.16 (CH_2), 32.50 (CH), 20.66 (CH_3), 20.65 (CH_3), 20.63 (CH_3). **LRMS** (ESI): 294 (M^+ + 1), 252, 207, 166, 126; **HRMS** calculated for $C_{16}H_{28}N_3O_2$ 294.2176, found 294.2179.

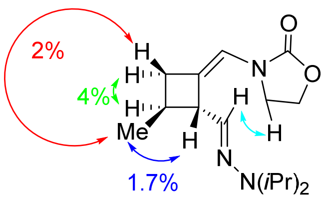
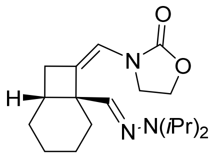


Figure S6. nOe signals observed for *E*-**3ah**

(1*R*,6*S*,8*Z*)-8-[(2-Oxo-1,3-oxazolidin-3-yl)methylene]bicyclo[4.2.0]octane-1-carbaldehyde diisopropylhydrazone (*Z*-**3ai**)[11]



Z-**3ai**

Yellow oil. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 6.50 (s, 1H), 6.14 (s, 1H), 4.26 (td, *J* = 8.9, 5.3 Hz, 1H), 4.13 (q, *J* = 8.6 Hz, 1H), 3.85 (td, *J* = 9.1, 5.3 Hz, 1H), 3.70 (hept,*J* = 6.5 Hz, 2H), 3.50 (q, *J* = 9.1 Hz, 1H), 2.65 – 2.54 (m, 2H), 2.47 (ddd, *J* = 14.0, 8.8, 0.7 Hz, 1H), 2.42 – 2.34 (m, 1H), 1.64 – 1.39 (m, 6H), 1.28 – 1.18 (m, 1H), 1.09 (d, *J* = 6.6 Hz, 6H), 1.08 (d, *J* = 6.5 Hz, 6H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 157.03 (C), 133.41 (CH), 131.89 (C), 115.15 (CH), 62.47 (CH_2), 50.93 (C), 47.19 (CH), 47.11 (CH_2), 36.70 (CH), 29.93 (CH_2), 29.24 (CH_2), 25.33 (CH_2), 21.56 (CH_2), 21.16 (CH_3), 21.08 (CH_2), 20.64 (CH_3). **LRMS** (ESI): 334 (M^+ + 1), 292, 247, 206, 162, 119, 100; **HRMS** calculated for $C_{19}H_{32}N_3O_2$ 334.2489, found 334.2493.

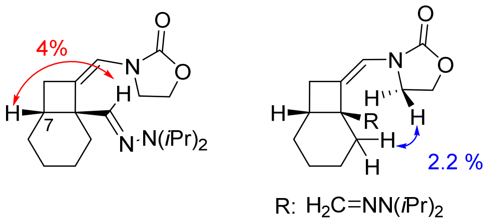
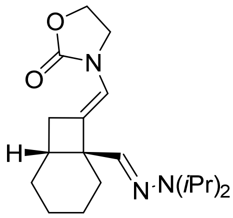


Figure S7. nOe signals observed for Z-**3ai**

[11] The combined yield for the mixture of *Z*-**3ai** and *E*-**3ai** is 90% (Z/E ratio = 7:3). We could separate a small amount of both isomers that allowed their independent characterization.

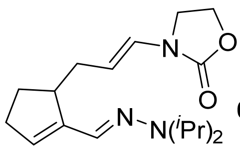
(1*R*,6*S*,8*E*)-8-[(2-Oxo-1,3-oxazolidin-3-yl)methylene]bicyclo[4.2.0]octane-1-carbaldehyde diisopropylhydrazone (*E*-**3ai**)



E-**3ai**

Yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.42 (s, 1H), 5.75 (s, 1H), 4.28 – 4.16 (m, 2H), 3.85 (ddd, *J* = 9.0, 7.9, 4.7 Hz, 1H), 3.74 – 3.59 (m, 3H), 2.45 – 2.37 (m, 2H), 2.33 – 2.27 (m, 2H), 1.61 – 1.56 (m, 1H), 1.54 – 1.33 (m, 6H),1.11 – 1.07 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.40 (C), 144.85 (C), 133.64 (CH), 117.41 (CH), 61.92 (CH_2), 52.85 (C), 47.23 (CH), 45.85 (CH_2), 44.63 (CH), 32.21 (CH_2), 30.92 (CH_2), 25.96 (CH_2), 21.64 (CH_2), 21.48 (CH_2), 21.13 (CH_3), 20.74 (CH_3). **LRMS** (ESI): 334 (M^+ + 1), 292, 247, 206, 162, 119, 100; **HRMS** calculated for $C_{19}H_{32}N_3O_2$ 334.2489, found 334.2491.

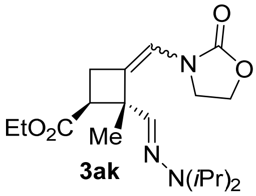
5-[(2*E*)-3-(2-Oxo-1,3-oxazolidin-3-yl)prop-2-en-1-yl]cyclopent-1-ene-1-carbaldehyde diisopropyl hydrazone (**6aj**)



6aj

Yellow oil, 65% yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (s, 1H), 6.65 (d, *J* = 14.6 Hz, 1H), 5.59 (s, 1H), 4.80 (dt,*J* = 14.6, 7.5 Hz, 1H), 4.43 – 4.38 (m, 2H), 3.83 – 3.75 (m, 2H), 3.69 (dd, *J* = 8.8, 7.4 Hz, 2H), 3.14 – 3.07 (m, 1H), 2.56 (dddd, *J* = 13.7, 7.3, 3.3, 1.1 Hz, 1H), 2.41 – 2.26 (m, 2H), 2.24 – 2.17 (m, 1H), 1.97 (ddd, *J* = 17.1, 12.9, 9.1 Hz, 1H), 1.75 – 1.67 (m, 1H), 1.14 (d, *J* = 6.5 Hz, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.53 (C), 146.10 (C), 127.09 (CH), 125.67 (CH), 124.38 (CH), 110.45 (CH), 62.18 (CH_2), 47.12 (CH), 44.25 (CH), 42.84 (CH_2), 33.64 (CH_2), 31.46 (CH_2), 28.75 (CH_2), 21.22 (CH_3), 20.96 (CH_3). **LRMS** (ESI): 320 (M^+ + 1), 278, 233, 191, 126; **HRMS** calculated for $C_{18}H_{30}N_3O_2$ 320.2333, found 320.2332.

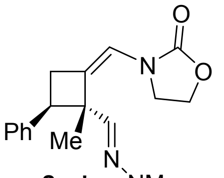
Ethyl (1*S*,2*R*,3*Z/E*)-2-[(*E*)-(diisopropylhydrazono)methyl]-2-methyl-3-[(2-oxo-1,3-oxazolidin-3-yl)methylene]cyclobutanecarboxylate (**3ak**).[12]



Yellow oil, 83% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.60 (s, 0.62H), 6.50 (s, 0.38H), 6.26 (d, *J* = 2.0 Hz, 0.62H), 5.76 (dd, *J* = 2.8, 2.2 Hz, 0.38H), 4.32 – 4.03 (m, 4H), 3.82 (td, *J* = 9.1, 5.6 Hz, 0.62H), 3.78 – 3.66 (m, 2.8H), 3.56 (dd, *J* = 17.3, 9.1 Hz, 0.62H), 3.32 (dd, *J* = 9.3, 8.6 Hz, 0.38H), 3.18 – 3.07 (m, 1.24H), 2.83 (ddd, *J* = 16.3, 9.6, 2.0 Hz, 0.38H), 2.60 (ddd, *J* = 14.5, 7.9, 1.4 Hz, 0.62H), 2.48 (ddd, *J* = 16.2, 8.3, 3.1 Hz, 0.38H), 1.39 (s, 2H), 1.26 (s, 1H), 1.24 – 1.18 (m, 3H), 1.13 – 1.06 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.56 (C), 172.00 (C), 156.58 (C), 156.55 (C), 132.74 (CH), 132.03 (CH), 126.85 (C), 117.15 (CH), 115.94 (CH), 62.24 (CH_2), 61.84 (CH_2), 60.31 (CH_2), 60.23 (CH_2), 54.03 (CH), 53.72 (C), 47.20 (CH_2), 47.17 (CH_2), 45.77 (CH_2), 44.73 (CH), 29.61 (CH_2), 27.17 (CH_2), 21.21 (CH_3), 21.13 (CH_3), 20.36 (CH_3), 20.22 (CH_3), 18.69 (CH), 17.73 (CH), 14.38 (CH_3), 14.26 (CH_3). **LRMS** (ESI): 366, 324, 279, 238, 181, 164, 126; **HRMS** calculated for $C_{19}H_{32}N_3O_4$ 366.2386, found 366.2387.

[12] *Z* and *E* isomers of **3ak** could not be separated by standard column chromatography techniques.

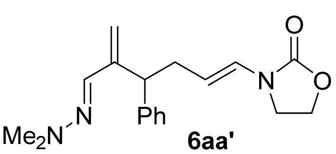
(1*R*,2*Z*,4*R*)-1-Methyl-2-[(2-oxo-1,3-oxazolidin-3-yl)methylene]-4-phenylcyclobutanecarbaldehyde dimethylhydrazone (**3aa'**)



3aa'

Yellow solid, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (q, *J* = 7.3 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.85 (s, 1H), 6.36 (s, 1H), 4.33 – 4.20 (m, 2H), 3.86 – 3.78 (m, 1H), 3.68 (t, *J* = 9.4 Hz, 1H), 3.57 (dd, *J* = 16.9, 9.0 Hz, 1H), 3.13 – 3.10 (m, 1H), 2.87 (dd, *J* = 14.6, 8.8 Hz, 1H), 2.79 (s, 6H), 1.05 (s, 3H). **^{13}C NMR**(101 MHz, $CDCl_3$) δ 156.78 (C), 141.58 (CH), 139.19 (C), 128.16 (CH), 127.93 (C), 127.60 (CH), 126.45 (CH), 117.07 (CH), 62.19 (CH_2), 53.42 (C), 46.74 (CH_2), 45.29 (CH), 43.37 (CH_3), 29.35 (CH_2), 18.58 (CH_3). **LRMS** (CI): 314.1 (M^+ + 1), 227, 182, 126. **HRMS** calculated for $C_{18}H_{24}N_3O_2$ 314.1869, found 314.1860.

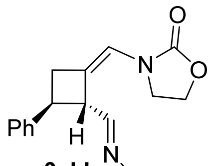
(1*E*,5*E*)-2-Methylene-6-(2-oxo-1,3-oxazolidin-3-yl)-3-phenylhex-5-enal dimethylhydrazone (**6aa'**)



6aa'

6% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 4H), 7.23 – 7.16 (m, 1H), 6.94 (s, 1H), 6.68 (d, *J* = 14.3 Hz, 1H), 5.22 (s, 1H), 5.21 (s, 1H), 4.75 (dt, *J* = 14.3, 7.2 Hz, 1H), 4.36 (t, *J* = 8.1 Hz, 2H), 4.17 (t, *J* = 7.8 Hz, 1H), 3.61 – 3.54 (m, 2H), 2.85 (s, 6H), 2.81 – 2.70 (m, 1H), 2.67 – 2.57 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.39 (C), 148.79 (C), 143.79 (C), 134.93 (CH), 128.30 (CH), 128.06 (CH), 126.01 (CH), 124.71 (CH), 114.29 (CH_2), 109.74 (CH), 62.10 (CH_2), 45.95 (CH), 42.69 (CH_3), 42.58 (CH_2), 34.75 (CH_2). **LRMS** (ESI): 314 (M^+ + 1), 182, 111. **HRMS** calculated for $C_{18}H_{24}N_3O_2$ 314.1869, found 314.1875.

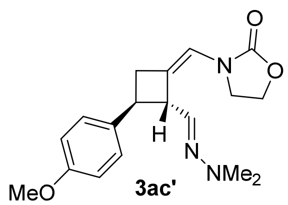
(1*R*,2*Z*,4*S*)-2-[(2-Oxo-1,3-oxazolidin-3-yl)methylene]-4-phenylcyclobutanecarbaldehyde dimethylhydrazone (**3ab'**)



3ab'

Yellow oil, 53% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 4H), 7.16 – 7.11 (m, 1H), 6.66 (d, *J* = 7.2 Hz, 1H), 6.33 (q, *J* = 2.3 Hz, 1H), 4.27 – 4.16 (m, 2H), 3.91 – 3.83 (m, 2H), 3.59 (dd, *J* = 16.9, 9.2 Hz, 1H), 3.45 – 3.40 (m, 1H), 3.13 – 3.06 (m, 1H), 2.80 – 2.73 (m, 1H), 2.69 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.61 (C), 143.77 (C), 137.81 (CH), 128.53 (CH), 126.58 (CH), 126.52 (CH), 122.12 (C), 118.60 (CH), 62.43 (CH_2), 53.30 (CH), 45.57 (CH_2), 43.18 (CH_3), 41.81 (CH), 34.13 (CH_2). **LRMS** (CI): 300.1 (M^+ + 1), 255, 213, 126, 111. **HRMS** calculated for $C_{17}H_{22}N_3O_2$ 300.1712, found 300.1714.

(1*R*,2*S*,4*Z*)-2-(4-Methoxyphenyl)-4-[(2-oxo-1,3-oxazolidin-3-yl)methylene]cyclobutanecarbaldehyde dimethylhydrazone (**3ac'**)



3ac'

Yellow solid, 41% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 6.90 – 6.87 (m, 2H), 6.75 (d, *J* = 7.3 Hz, 1H), 6.44 – 6.41 (m, 1H), 4.38 – 4.26 (m, 2H), 3.99 – 3.94 (m, 1H), 3.93 – 3.88 (m, 1H), 3.81 (s, 3H), 3.69 (dd, *J* = 17.0, 9.2 Hz, 1H), 3.49 – 3.43 (m, 1H), 3.20 – 3.13 (m, 1H), 2.85 – 2.80 (m, 1H), 2.79 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.35 (C), 156.68 (C), 138.23 (CH), 135.94 (C), 127.64 (CH), 122.36 (C), 118.58 (CH), 113.99 (CH), 62.48 (CH_2), 55.43 (CH), 53.61 (CH), 45.66 (CH_2), 43.26 (CH_3), 41.28 (CH_3), 34.46 (CH_2). **LRMS** (CI): 330.1 (M^+ + 1), 286, 243, 198, 111, 88. **HRMS** calculated for $C_{18}H_{24}N_3O_3$ 329.1818, found 330.1819. In addition to nOe experiments, the structure and stereochemical identity of this adduct could be further corroborated by X-ray analysis (Figure S8).[13]

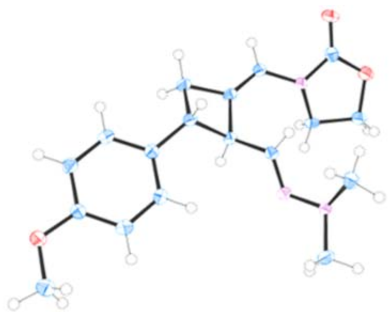
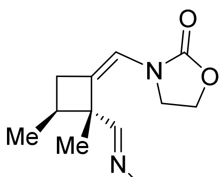


Figure S8. X-ray structure of **3ac'**

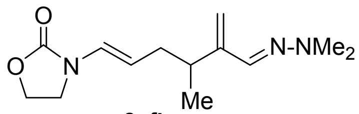
(1*R*,2*S*,4*Z*/*E*)-1,2-Dimethyl-4-[(2-oxo-1,3-oxazolidin-3-yl)methylene]cyclobutanecarbaldehyde dimethylhydrazone (**3af'**)



3af'

White solid, 47% yield.[14] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.70 (s, 0.18H), 6.65 (s, 0.82H), 6.25 (t, *J* = 2.0 Hz, 0.18H), 6.19 (t, *J* = 1.9 Hz, 0.82H), 4.32 – 4.19 (m, 2H), 3.81 – 3.63 (m, 2H), 3.61 – 3.55 (m, 2H), 2.74 (s, 1.08H), 2.72 (s, 4.92H), 2.42 – 2.29 (m, 2H), 1.43 (s, 0.54H), 1.31 (s, 2.46H), 1.03 (d, *J* = 7.0 Hz, 0.54H), 1.00 (d, *J* = 6.8 Hz, 2.46H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.90, 142.47, 129.35, 117.79, 116.60, 62.24, 50.90, 46.80, 43.54, 43.39, 35.74, 33.80, 33.16, 24.53, 17.03, 16.86, 14.94, 13.61. **LRMS** (CI): 252.1 (M^+ + 1), 207, 165, 126, 116, 88. **HRMS** calculated for $C_{13}H_{22}N_3O_2$ 252.1712, found 251.1710.

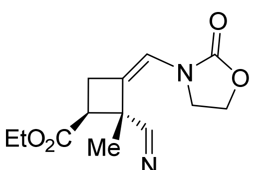
3-((E)-5-((E)-(2,2-dimethylhydrazono)methyl)-4-methylhexa-1,5-dien-1-yl)oxazolidin-2-one (**6af'**)



6af'

White solid. 21% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.95 (s, 1H), 6.61 (d, *J* = 14.3 Hz, 1H), 5.08 – 5.04 (m, 2H), 4.80 – 4.73 (m, 1H), 4.43 – 4.37 (m, 2H), 3.67 (dd, *J* = 14.7, 6.1 Hz, 2H), 2.95 – 2.87 (m, 1H), 2.84 (s, 6H), 2.38 – 2.29 (m, 1H), 2.19 – 2.09 (m, 1H), 1.07 (dd, *J* = 7.0, 0.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.53 (C), 150.89 (C), 136.17 (CH), 124.58 (CH), 113.52 (CH_2), 110.05 (CH), 62.19 (CH_2), 42.93 (CH_3), 42.80 (CH_2), 36.32 (CH_2), 34.04 (CH), 19.43 (CH_3). **LRMS** (CI): 252.1 (M^+ + 1), 207, 180, 165, 126, 59. **HRMS** calculated for $C_{13}H_{22}N_3O_2$ 252.1712, found 251.1711.

Ethyl (1S,2R,*Z*)-2-((E)-(2,2-dimethylhydrazono)methyl)-2-methyl-3-((2-oxooxazolidin-3-yl)methylene)cyclobutane-1-carboxylate (**3ak'**)



3ak´

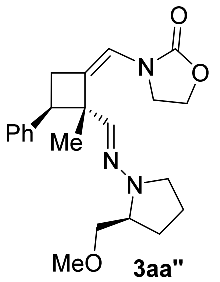
Yellow oil, 63% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.66 (s, 1H), 6.29 – 6.27 (m, 1H), 4.34 – 4.22 (m, 2H), 4.20 – 4.11 (m, 2H), 3.83 – 3.77 (m, 1H), 3.60 – 3.54 (m, 1H), 3.21 – 3.10 (m, 3H), 2.77 (s, 6H), 2.69 – 2.63 (m, 1H), 1.39 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.92 (C), 156.72 (C), 139.48 (CH), 126.33 (C), 117.88 (CH),

[13] CCDC 1029358 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] Z : E ratio = 0.93: 0.07, (1H NMR of the crude mixture) *Z : E* ratio = 0.82 : 0.18 after column chromatography. The isomers could not be separated.

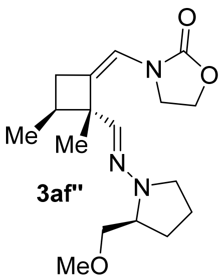
62.24 (CH_2), 60.70 (CH_2), 52.73 (C), 46.64 (CH_2), 44.45 (CH), 43.24 (CH_3), 27.42 (CH_2), 18.89 (CH_3), 14.56 (CH_3). **LRMS** (CI): 310 (M^+ + 1), 299.1, 223.1, 126.1, 88.0. **HRMS** calculated for $C_{15}H_{24}N_3O_4$ 310.1767 found 310.1768.

3-((Z)-((2R,3R)-2-((E)-(((S)-2-(methoxymethyl)pyrrolidin-1-yl)imino)methyl)-2-methyl-3-phenylcyclobutylidene)methyl)oxazolidin-2-one (**3aa''**)


3aa''

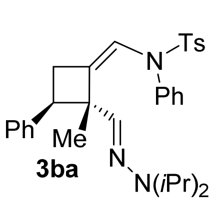
Yellow oil, 85% yield, *dr* = 7: 3. **^{1}H NMR** (500 MHz, $CDCl_3$) δ7.38 – 7.28 (m, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.18 – 7.14 (m, 2H), 6.87 (s, 0.7H), 6.83 (s, 0.3H), 6.39 (s, 0.7H), 6.38 (s, 0.3H), 4.38 – 4.22 (m, 3H), 4.01 – 3.87 (m, 2H), 3.75 – 3.66 (m, 1H), 3.64 – 3.54 (m, 2H), 3.53 – 3.45 (m, 2H), 3.44 – 3.40 (m, 1H), 3.39 (s, 2.1H), 3.36 (s, 0.9H), 3.19 – 3.11 (m, 0.3H), 2.91 – 2.82 (m, 0.7H), 2.08 – 1.92 (m, 2.8H), 1.90 – 1.80 (m, 1.2H), 1.07 (s, 2.1H), 1.04 (s, 0.9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.36 (CH), 141.00 (CH), 139.37 (C), 128.57 (C), 128.14 (CH), 128.02 (C), 127.90 (C), 127.72 (C), 127.66 (CH), 126.43 (CH), 116.99 (CH), 74.78 (CH_2), 74.55 (CH_2), 63.35 (CH_3), 62.35 (CH_2), 62.21 (CH_2), 59.69 (CH), 59.53 (CH), 53.60 (C), 46.82 (CH_2), 46.79 (CH_2), 45.66, 45.28, 29.33 (CH_2), 29.25 (CH_2), 26.72 (CH_2), 26.55 (CH_2), 22.23 (CH_2), 22.12 (CH_2), 18.88 (CH_3), 18.75 (CH_3). **LRMS** (ESI): 384 (M^+ + 1), 297, 270, 242, 195, 155, 129; **HRMS** calculated for $C_{22}H_{30}N_3O_3$ 384.2282, found 384.2270.

3-((Z)-((2R,3S)-2-((E)-(((S)-2-(methoxymethyl)pyrrolidin-1-yl)imino)methyl)-2,3-dimethylcyclobutylidene)methyl)oxazolidin-2-one (**3af''**)


3af''

Yellow oil, 63% yield, *dr* = 6 : 4. **^{1}H NMR** (500 MHz, $CDCl_3$) δ6.66 (s, 0.6H), 6.60 (s, 0.4H), 6.20 – 6.18 (m, 1H), 4.33 – 4.09 (m, 2H), 3.92 – 3.81 (m, 2H), 3.62 – 3.53 (m, 3H), 3.45 – 3.39 (m, 1H), 3.36 (s, 1.8H), 3.34 (s, 1.2H), 2.77 – 2.66 (m, 2H), 2.43 – 2.27 (m, 2H), 2.00 – 1.85 (m, 3H), 1.83 – 1.74 (m, 1H), 1.30 (s, 1.8H), 1.30 (s, 1.2H), 1.00 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.85 (C), 142.44 (CH), 141.61 (CH), 129.64 (C), 129.06 (C), 116.48 (CH), 74.87 (CH_2), 74.59 (CH_2), 63.49 (CH_3), 63.35 (CH_3), 62.31 (CH_2), 62.15 (CH_2), 59.32 (CH), 59.21 (CH), 51.07 (C), 50.06 (C), 49.83 (CH_2), 46.88 (CH_2), 46.73 (CH_2), 35.84 (CH), 35.70 (CH), 33.68 (CH_2), 26.71 (CH_2), 26.58 (CH_2), 22.24 (CH_2), 22.19 (CH_2), 17.11 (CH_3), 14.99 (CH_3), 14.92 (CH_3). **LRMS** (ESI): 321 (M^+ + 1), 235, 180, 126; **HRMS** calculated for $C_{17}H_{27}N_3O_3$ 321.2125, found 321.2131.

N-((*Z*)-((2R,3R)-2-((E)-(2,2-diisopropylhydrazono)methyl)-2-methyl-3-phenylcyclobutylidene) methyl)-4- methyl-N-phenylbenzenesulfonamide (**3ba**)


3ba

95% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.15 (m, 10H), 7.12 – 7.04 (m, 2H), 6.78 (s, 1H), 6.19 – 6.16 (m, 1H), 3.98 (t, *J* = 9.1 Hz, 1H), 3.81 – 3.68 (m, 2H), 3.03 (ddd, *J* = 14.6, 9.6, 2.3 Hz, 1H), 2.95 – 2.83 (m, 1H), 2.44 (s, *J* = 8.1 Hz, 3H), 1.23 (d, *J* = 6.5 Hz, 6H), 1.13 (d, *J* = 6.4 Hz, 6H), 0.51 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.40 (C), 143.69 (C), 142.61 (C), 140.32 (C), 134.34 (C), 133.04 (CH), 129.44 (CH), 128.60 (CH), 127.92 (CH), 127.81 (CH), 127.66 (CH), 126.85 (CH), 125.94 (CH), 119.32 (CH), 55.19 (C), 47.01 (CH), 43.19 (CH), 29.30 (CH_2), 21.68 (CH_3), 21.41 (CH_3), 20.43 (CH_3), 17.01 (CH_3).

LRMS (ESI): 530, 457, 381, 353; **HRMS** calculated for $C_{32}H_{40}N_3O_2S_2$ 530.2836, found 530.2835.

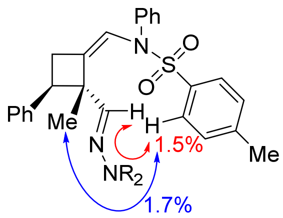
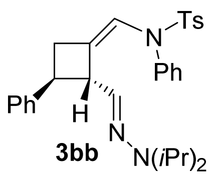


Figure S9. nOe signals observed for **3ba**

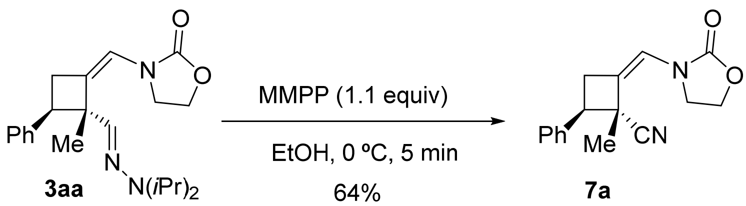
N-((*Z*)-{(2*R*,3*S*)-2-[(*E*)-(diisopropylhydrazono)methyl]-3-phenylcyclobutylidene}methyl)-4-methyl-*N*-phenylbenzenesulfonamide (**3bb**)



3bb

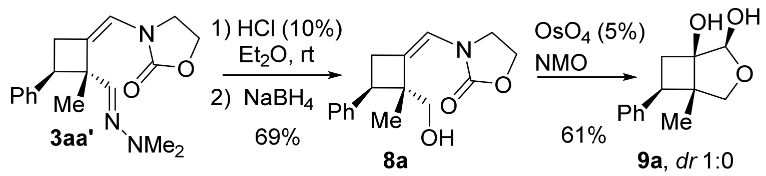
97% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.14 (m, 10H), 7.09 (d, *J* = 9.1 Hz, 2H), 6.37 – 6.32 (m, 1H), 3.79 (q, *J* = 8.4 Hz, 1H), 3.69 – 3.60 (m, 2H), 3.32 – 3.24 (m, 1H), 3.12 – 3.00 (m, 1H), 2.77 (ddd, *J* = 15.0, 8.5, 2.3 Hz, 1H), 2.44 (d, *J* = 5.2 Hz, 3H), 1.11 (dd, *J* = 8.8, 6.6 Hz, 12H), 0.10 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.93 (C), 143.76 (C), 140.25 (C), 135.20 (C), 134.12 (C), 129.56 (CH), 128.74 (CH), 128.42 (CH), 128.24 (CH), 128.09 (CH), 127.8 1(CH), 127.25 (CH), 126.69 (CH), 125.95 (CH), 119.90 (CH), 54.21 (CH), 46.99 (CH), 39.91 (CH), 33.30 (CH_2), 21.73 (CH_3), 21.20 (CH_3), 20.63 (CH_3). **LRMS** (ESI): 516, 457, 381, 353; **HRMS** calculated for $C_{31}H_{38}N_3O_2S_2$ 516.2679, found 516.2669.

(1R,4R,Z)-1-Methyl-2-((2-oxooxazolidin-3-yl)methylene)-4-phenylcyclobutane-1-carbo nitrile **(7a).**



Magnesium monoperoxiphthalate (MMPP, 73.6 mg, 1.49 mmol) was added to a solution of **3aa** (50 mg, 0.14 mmol) in EtOH (2 ml) at 0ºC. After stirring for 5 min, a solution of Na_2SO_3 (sat) (2 ml) was added and the mixture was extracted with CH_2Cl_2 (2 x 5 ml). The combined organic phases were subsequently washed with $NaHCO_3$ (5 ml) and NaCl (5 ml), dried and concentrated to afford a crude residue that was purified on column chromatography (hexanes:Et_2O = 9:1), to yield 23.3 mg of **7a** (64 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47 – 7.31 (m, 3H), 7.30 – 7.24 (m, 2H), 6.54 (dd, *J* = 5.7, 3.6 Hz, 1H), 4.52 – 4.43 (m, 2H), 4.39 – 4.29 (m, 1H), 4.21 (t, *J* = 9.6 Hz, 1H), 3.96 – 3.86 (m, 1H), 3.27 (ddd, *J* = 15.1, 10.0, 2.5 Hz, 1H), 3.02 (ddd, *J* = 15.1, 9.3, 1.6 Hz, 1H), 1.25 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.28 (C), 136.11 (C), 128.81 (CH), 127.94 (CH), 127.88 (CH), 123.97 (C), 119.73 (CH), 117.49 (C), 62.32 (CH_2), 45.61 (CH_2), 45.33 (CH), 40.33 (C), 29.59 (CH_2), 21.42 (CH_3). **LRMS** (CI): 268 (M^+). **HRMS** calculated for $C_{16}H_{17}N_2O_2$ 268.1212, found 268.1205.

(1R,2S,5S,6R)-5-Methyl-6-phenyl-3-oxabicyclo[3.2.0]heptane-1,2-diol (**9a**)



HCl 1M (0.16 ml, 1.37 mmol) was added to a solution of **3aa'** (50 mg, 1.37 mmol) in Et_2O (2.3 ml) and the mixture was stirred for 5 min at rt. The mixture was poured into brine (10 ml), extracted with Et_2O and dried. The solvent was removed under reduced pressure and the crude residue was chromatographed on silica gel (hexanes:Et_2O 8:2), to yield 39 mg of the corresponding aldehyde (90 % yield). (1R,4R,Z)-1-methyl-2-((2-oxooxazolidin-3-yl)methylene)-4-phenylcyclobutane-1-carbal dehyde. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.12 (d, *J* = 7.4 Hz, 2H), 6.57 (t, *J* = 2.0 Hz, 1H), 4.35 (t, *J* = 8.0 Hz, 2H), 3.98 (t, *J* = 9.1 Hz, 1H), 3.65 – 3.54 (m, 2H), 3.32 (ddd, *J* = 15.1, 9.1, 2.4 Hz, 1H), 3.06 (ddd, *J* = 15.2, 9.2, 1.6 Hz, 1H), 1.04 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 200.78 (CH), 156.33 (C), 137.49 (C), 128.49 (CH), 127.94 (CH), 127.14 (CH), 119.88 (CH), 119.29 (C), 62.08 (CH_2), 60.65 (C), 45.28 (CH_2), 39.96 (CH), 30.46 (CH_2), 15.81 (CH_3). **LRMS** (ESI): 271 (M^+ + 1); **HRMS** calculated for $C_{16}H_{17}NO_3$ 271.1208, found 271.1204.

$NaBH_4$ (0.013 g, 0.350 mmol) was added to a solution of (*Z*)-1-methyl-2-((2-oxooxazolidin-3-yl)methylene)-4-phenylcyclobutanecarbaldehyde (38 mg, 0.140 mmol) in MeOH (2 ml). After stirring at rt for 5 min, acetone and water were successively added to the reaction mixture. After extraction with Et_2O (3 x 5 ml) the combined organic phases were dried and evaporated to afford a crude residue that was chromatographed (hexanes/EtOAc, 1:1) to give **8a** (29.2 mg, 0.107 mmol, 76 % yield). 3-((Z)-((2R,3R)-2-(hydroxymethyl)-2-methyl-3-phenylcyclobutylidene) methyl)oxazolidin-2-one (**8a**). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.25 – 7.14 (m, 3H), 5.99 (t, *J* = 2.1 Hz, 1H), 4.45 – 4.30 (m, 2H), 3.86 – 3.65 (m, 4H), 3.63 – 3.54 (m, 1H), 3.15 (t, *J* = 6.4 Hz, 1H), 3.09 – 2.85 (m, 2H), 0.78 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.08 (C), 139.99 (C), 139.21 (C), 128.11 (CH), 127.97 (CH), 126.31 (CH), 116.94 (CH), 68.57 (CH_2), 62.24 (CH_2), 53.90 (C), 46.83 (CH_2), 40.36 (CH), 29.03 (CH_2), 18.16 (CH_3). **LRMS** (*m/z, ESI*): 269.13 $(M+Na)^+$, 256.13, 212.14, 169.10, 154.08, 105.05. **HRMS** Calculated for $C_{16}H_{19}NNaO_3$: 296.1257, found 296.1258.

H_2O (141 µl), NMO (21.43 mg, 0.183 mmol) and OsO_4 (4%wt solution in H_2O, 29.1 µl, 4.57 µmol) were added successively to a stirred solution of (Z)-3-((2-(hydroxymethyl)-2-methyl-3-phenylcyclobutylidene) methyl)oxazolidin-2-one (25 mg, 0.091 mmol) in acetone:acetonitrile 1:1 (0.3mL). After being stirred at rt for 3h, the reaction mixture was quenched with $Na_2S_2O_3$ $_{sat}$ (2 ml) and further stirred for 30 min. After extraction with CH_2Cl_2, the organic phases were dried and evaporated to afford a crude residue that was chromatographed (hexanes/EtOAc 10-50%) to give **9a** (12.2 mg 61% yield). (1R,2S,5S,6R)-5-methyl-6-phenyl-3-oxabicyclo[3.2.0]heptane-1,2-diol (**9a**). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.17 (m, 3H), 5.39 (s, 1H), 3.93 (d, *J* = 8.9 Hz, 1H), 3.84 (d, *J* = 8.9 Hz, 1H), 3.48 (s, 1H), 3.17 (t, *J* = 9.2 Hz, 1H), 3.12 (s, 1H), 2.60 (dd, *J* = 12.9, 9.6 Hz, 1H), 2.45 (dd, *J* = 12.9, 8.9 Hz, 1H), 1.67 (s, 1H), 0.72 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.09 (C), 128.12 (CH), 127.87 (CH), 126.30 (CH), 100.35

(CH), 78.90 (C), 77.47 (CH_2), 51.94 (C), 39.41 (CH), 32.05 (CH_2), 11.68 (CH_3). (ESI): 243.1 (M+ Na), 173.1, 131.1, 105.1. **HRMS** Calculated for $C_{13}H_{16}NaO_3$: 243.0992, found 243.0986.

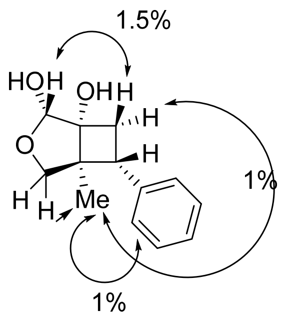
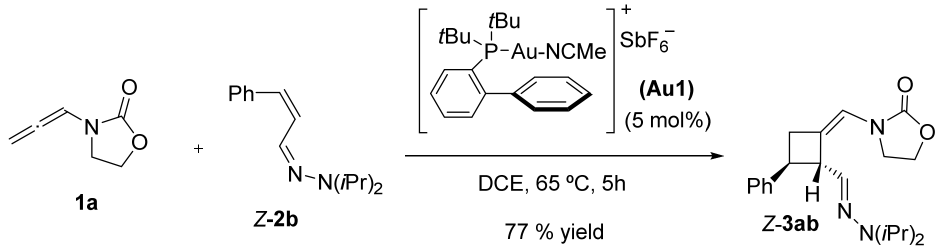


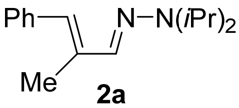
Figure S10. nOe signals observed for **9a**

Studies on the stereospecificity of the process. Cycloaddition between 1a and *Z*-2b

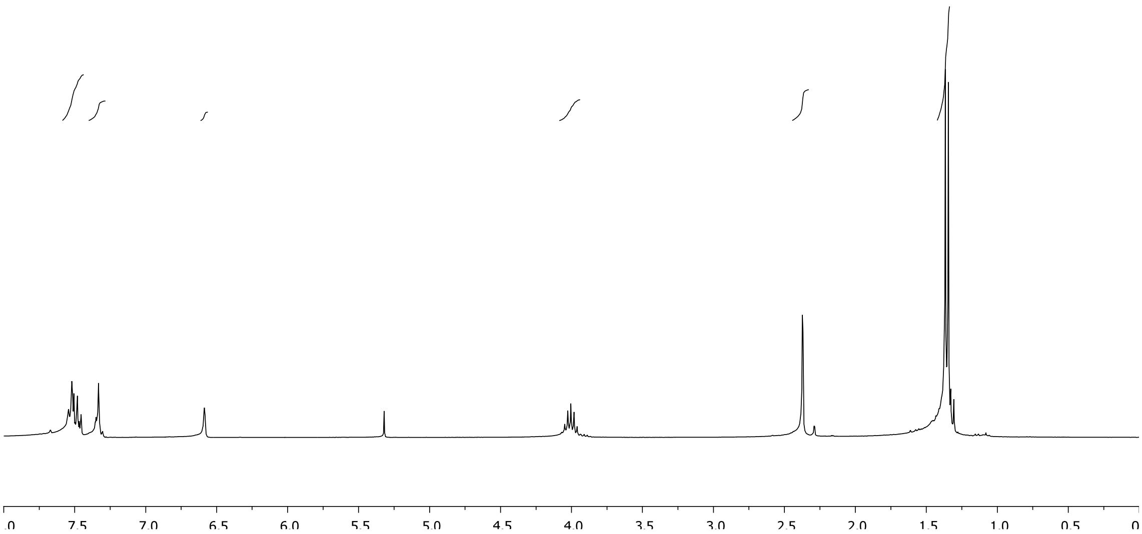


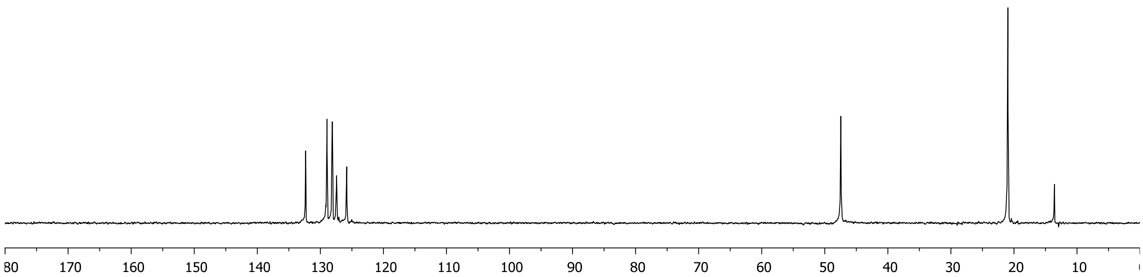
The cycloaddition of the *Z*-**2b** provided the same cycloadduct (*Z*-**3ab**) than that obtained from *E*-**2b**. A potential isomerization of the hydrazone (Z-**2a**) to the more stable *E*-counterpart during the reaction could be ruled out by submitting the hydrazone *Z*-**2b** to the reaction conditions, in the absence of the allenamide: after 5h, Z-**2b** had not been converted to the E-counterpart (*E*-**3ab**) and could be recovered or, alternatively, if allenamide **1a** was added, the cycloadduct Z-**3ab** was obtained in good yield. Moreover, analysis of this reaction by ^{1}H-NMR at different conversions did not show the presence of *E*-**2b** in the reaction media.

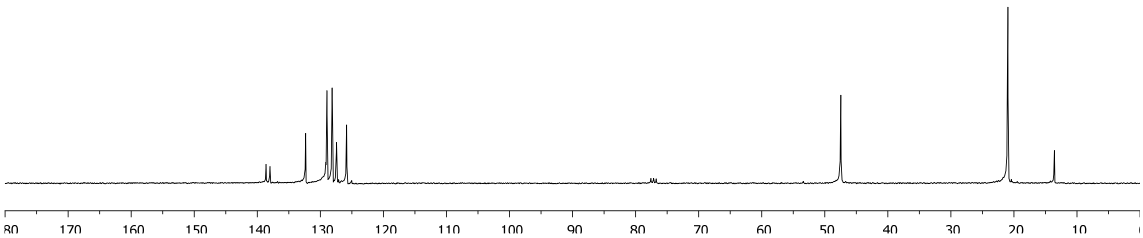
NMR SPECTRA

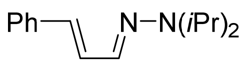


2a

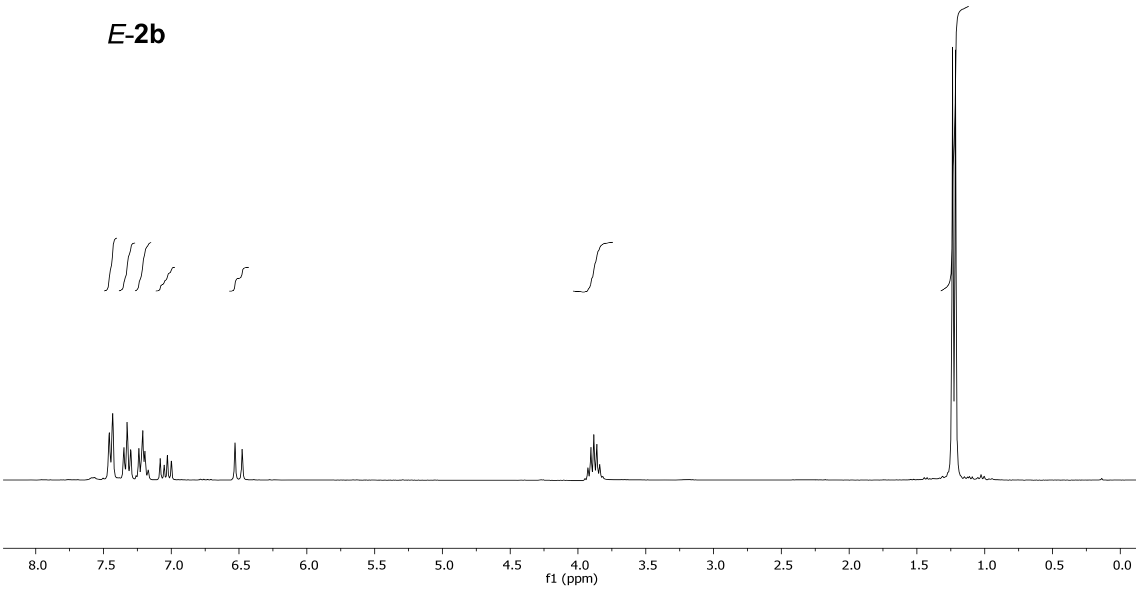


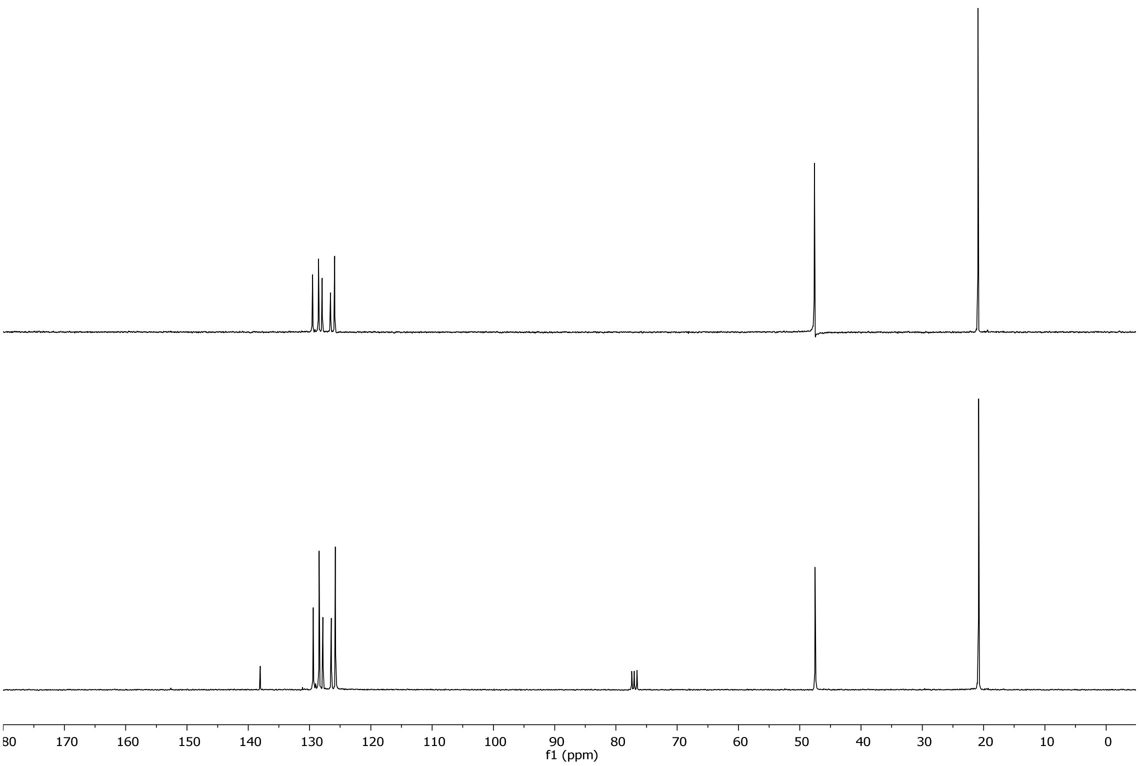




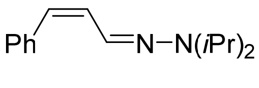

Ph
N−N(iPr)2

E-**2b**

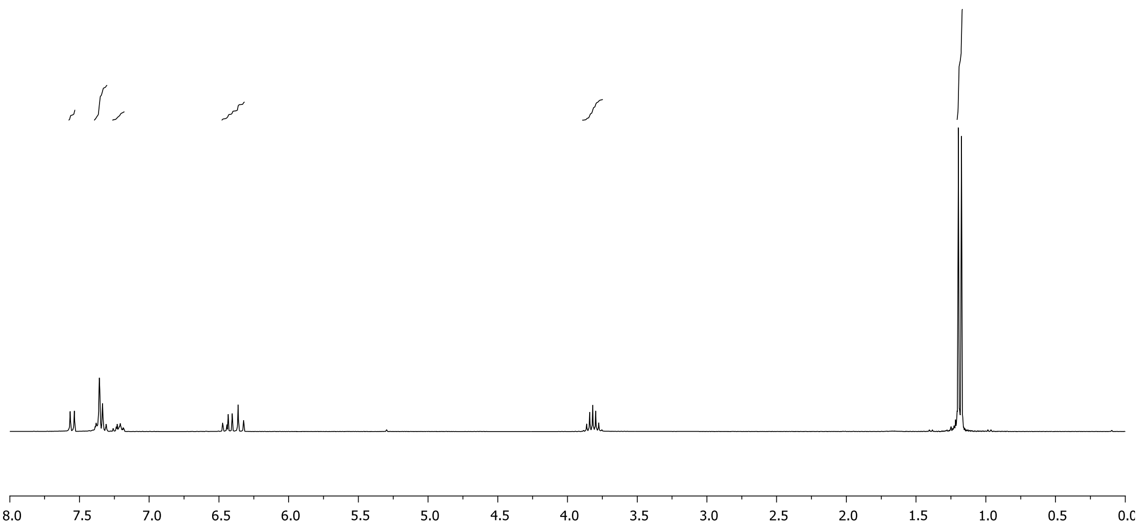

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

r


Ph
=N−N(iPr)2

Z-**2b**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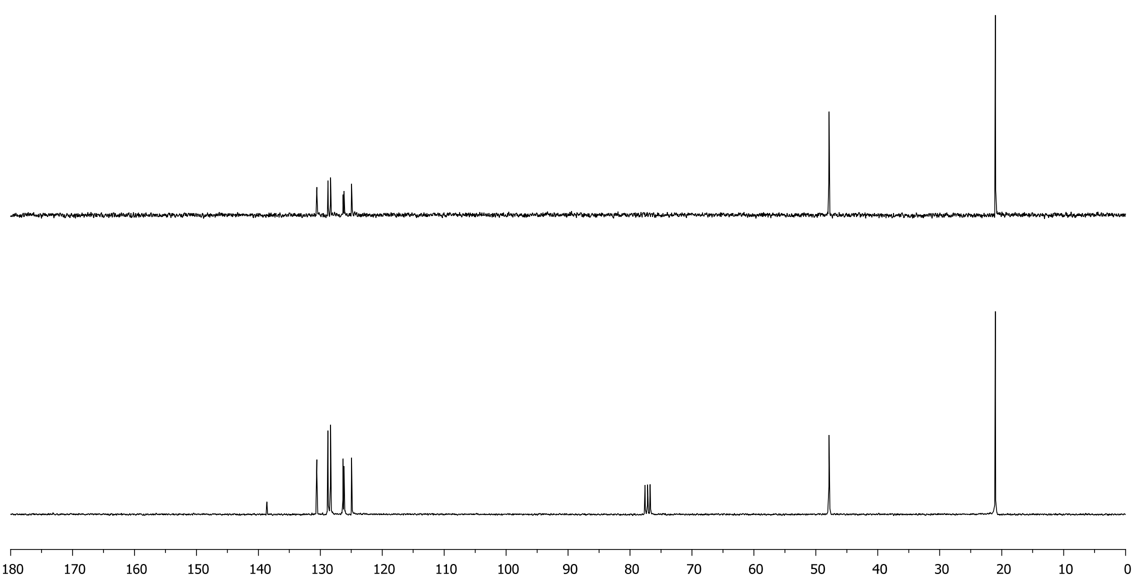
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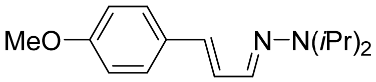
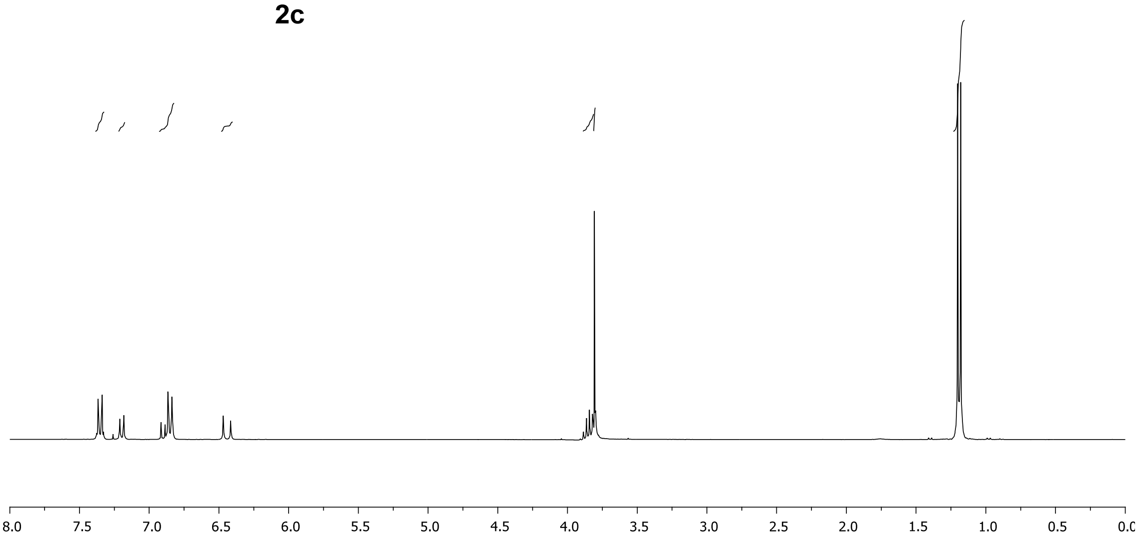

MeO
N−N(*i*Pr)$_2$

2c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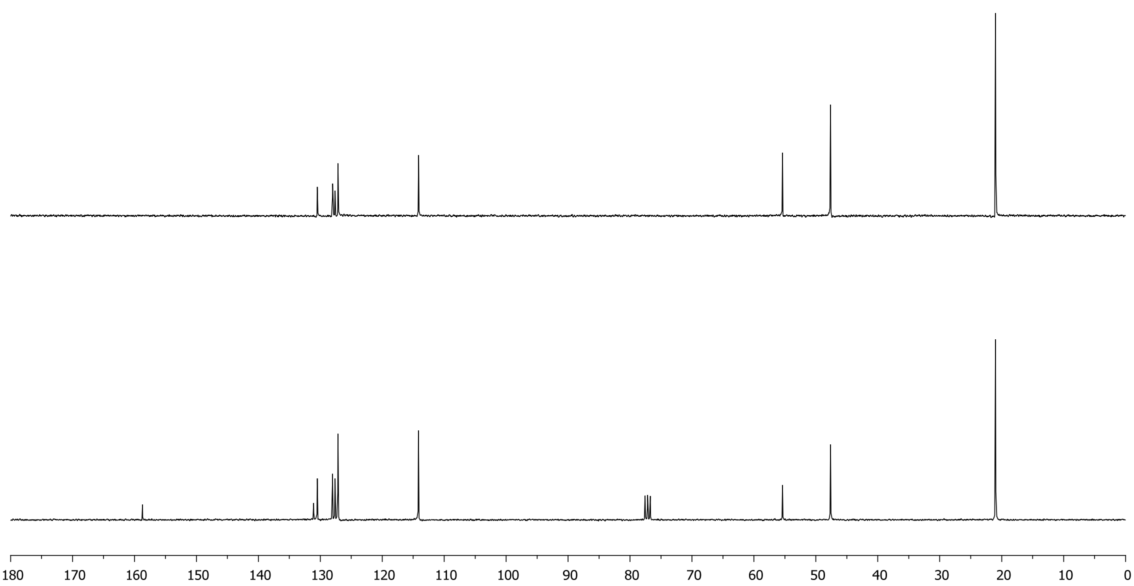
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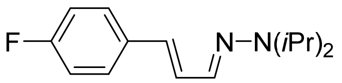
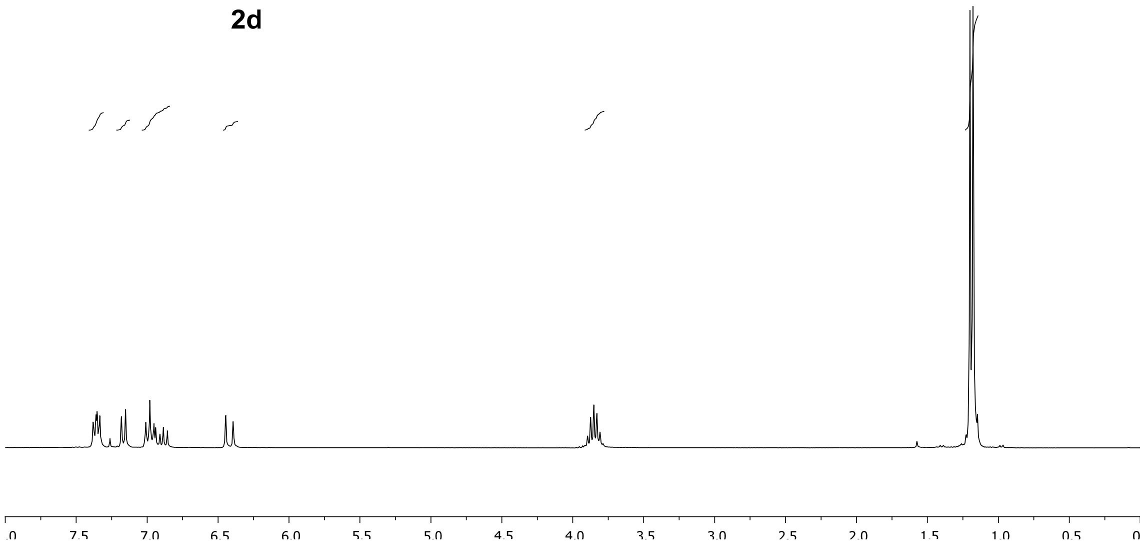

F
N−N(iPr)2

2d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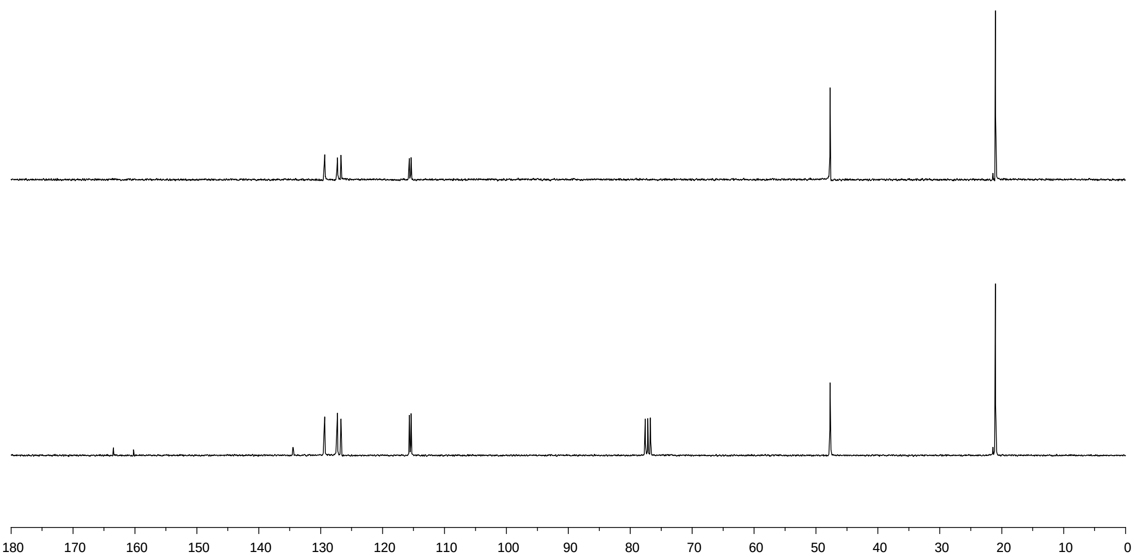
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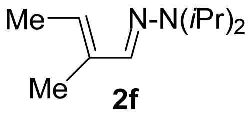
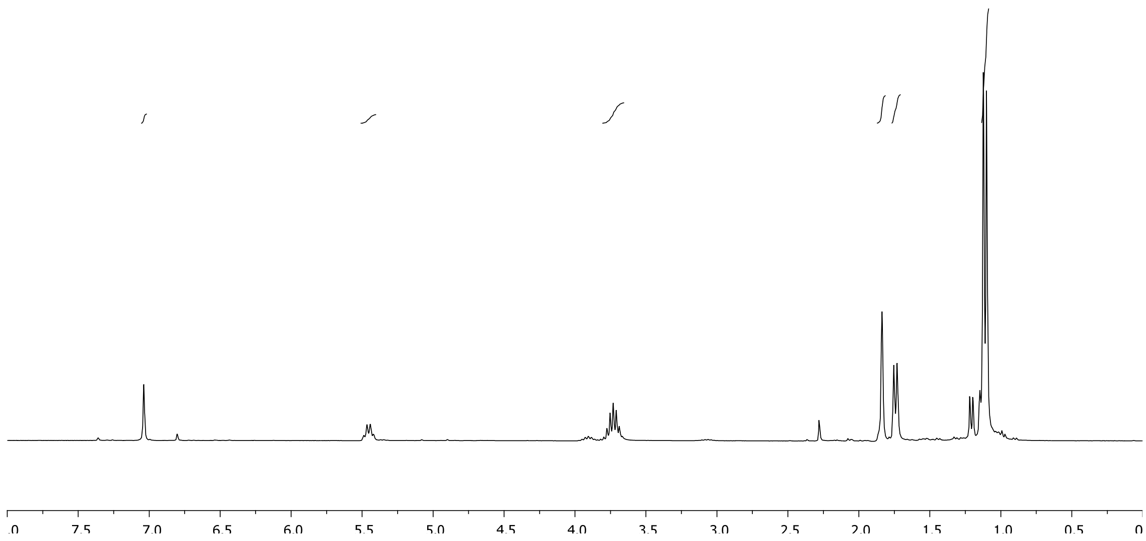

Me
N-N(iPr)2
Me

2f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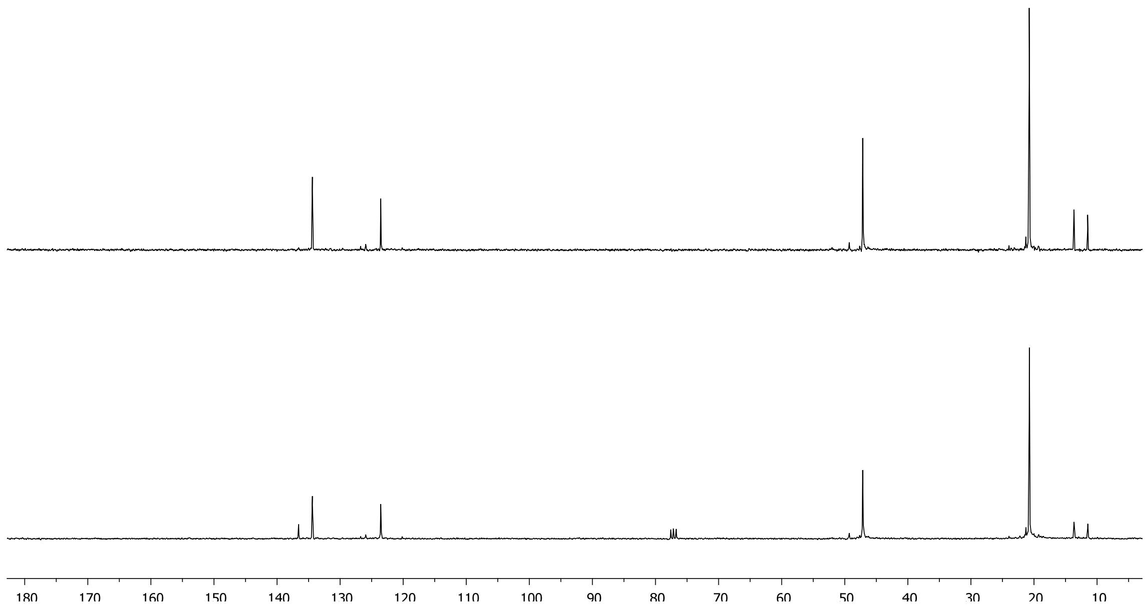
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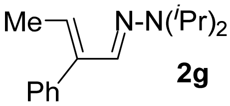
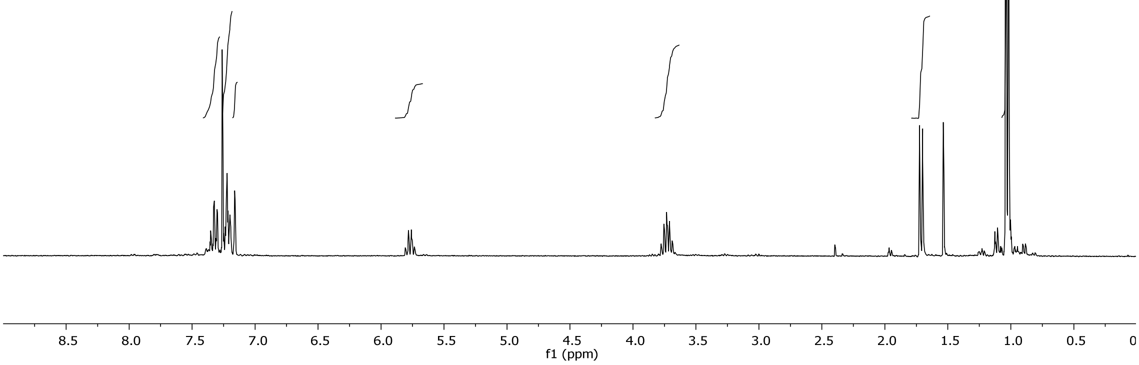


2g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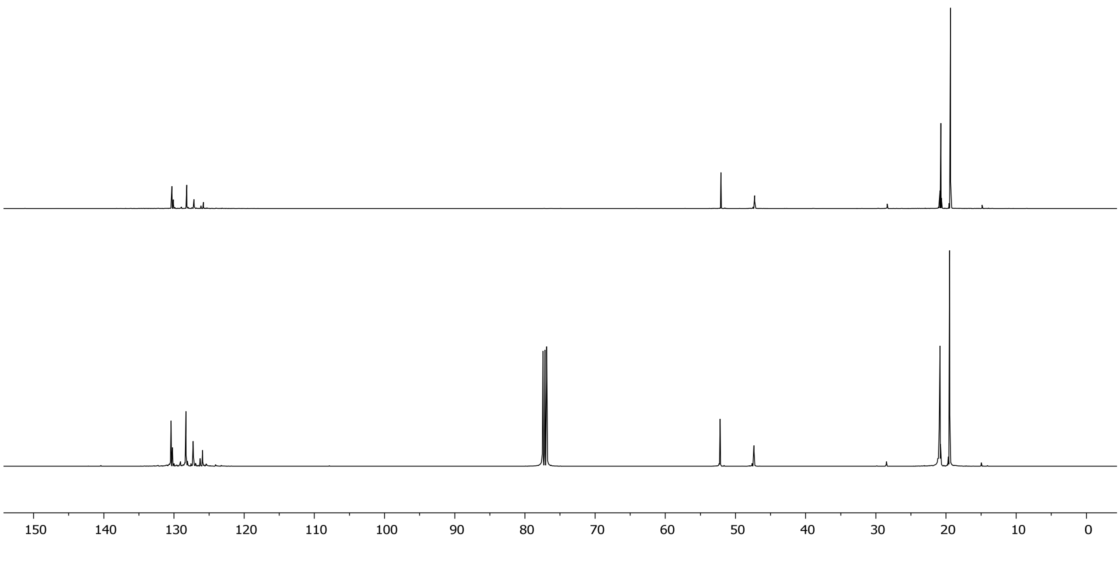
f1 (ppm)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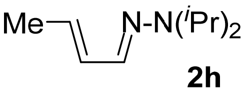
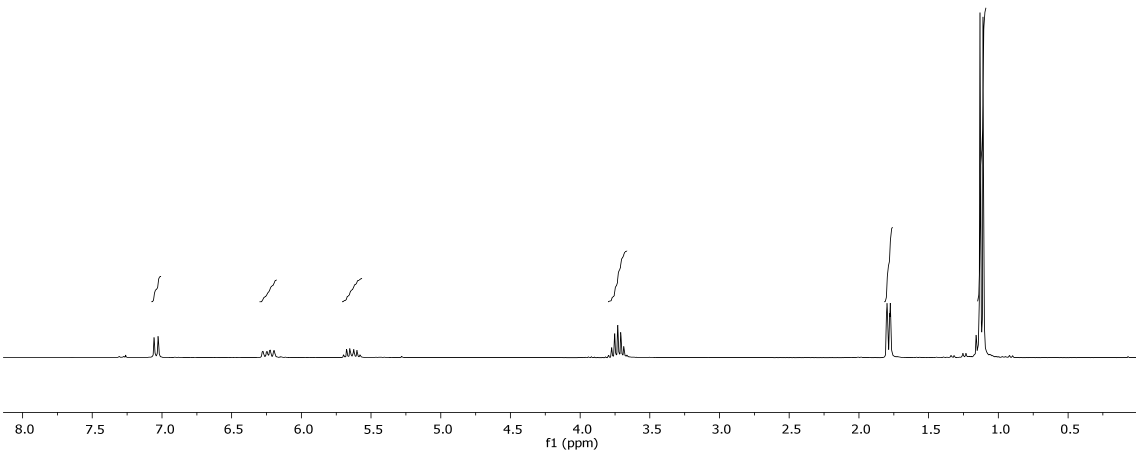
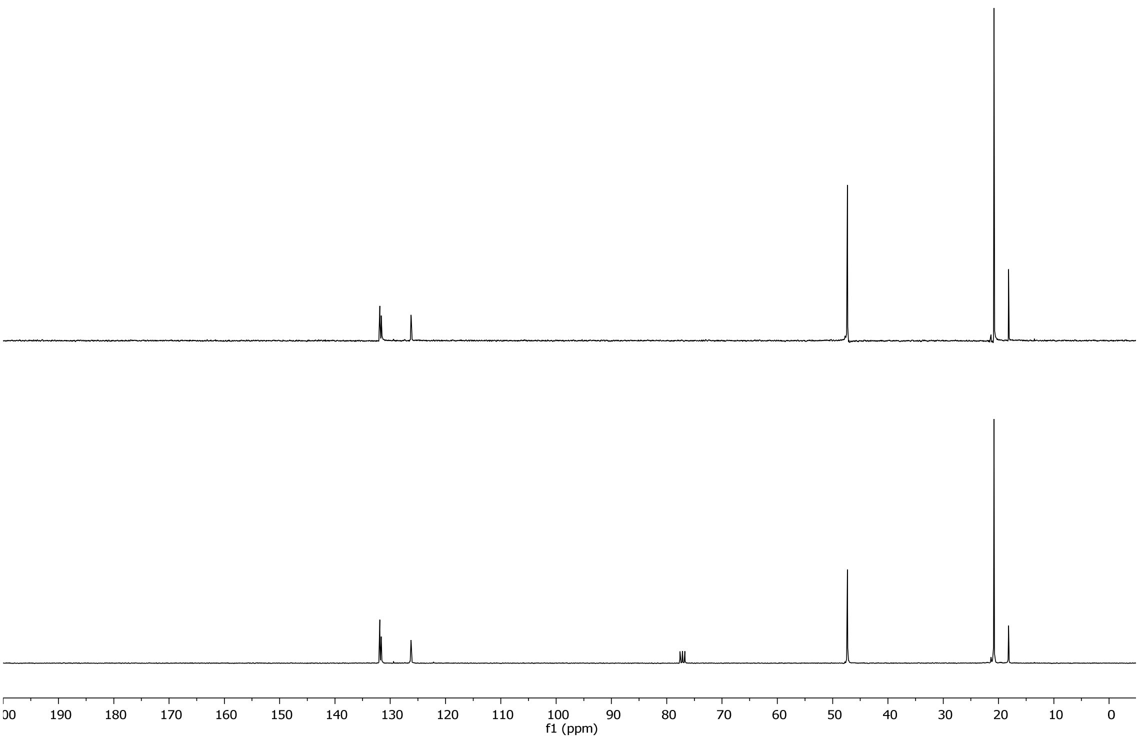
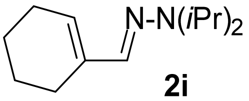


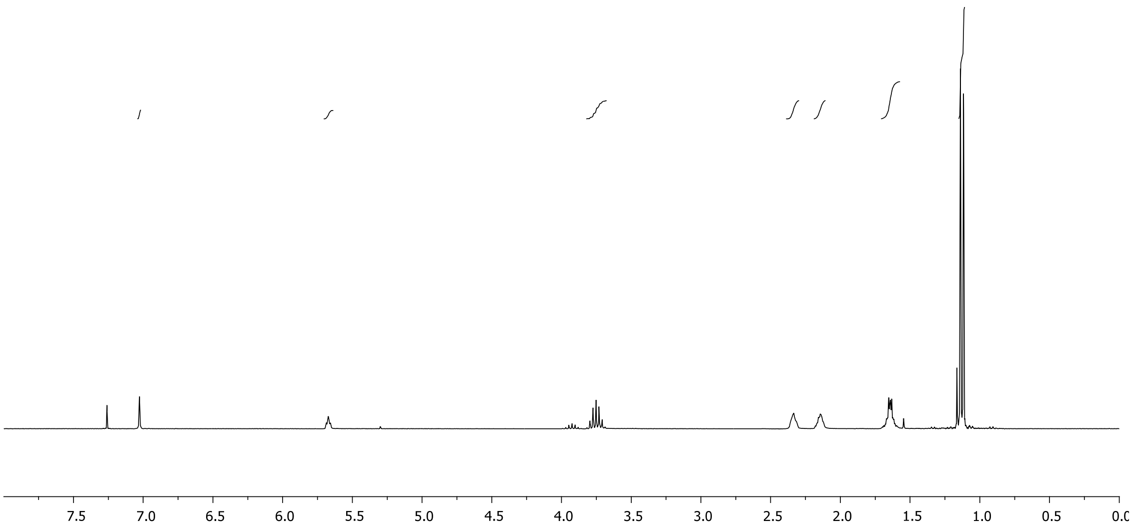
2h

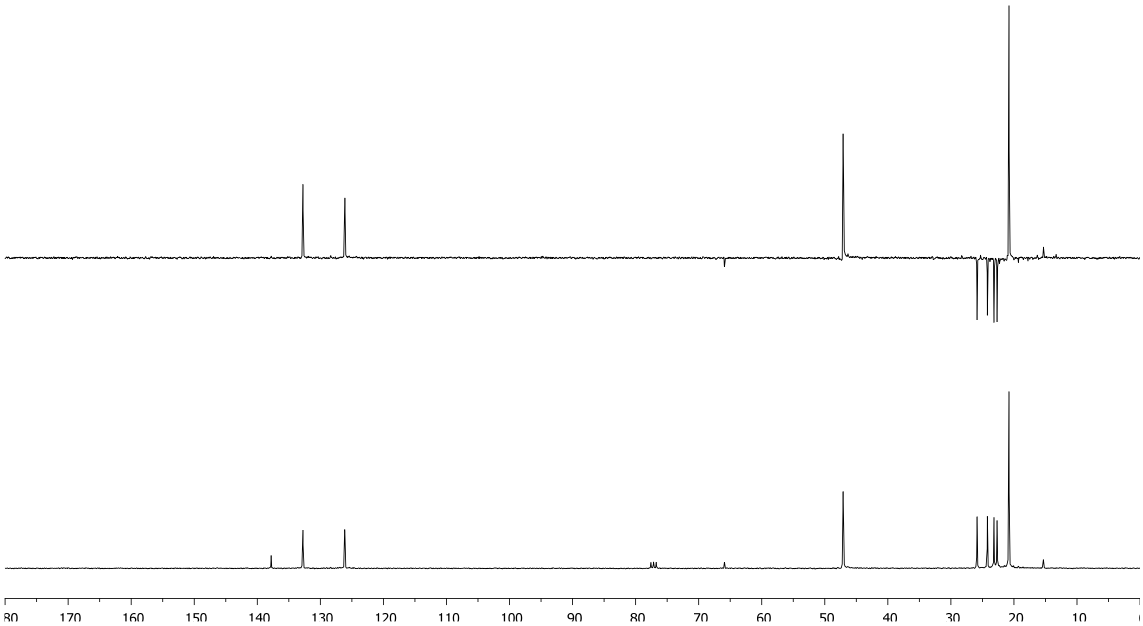





N-N(iPr)2

2i


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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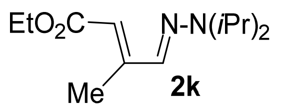
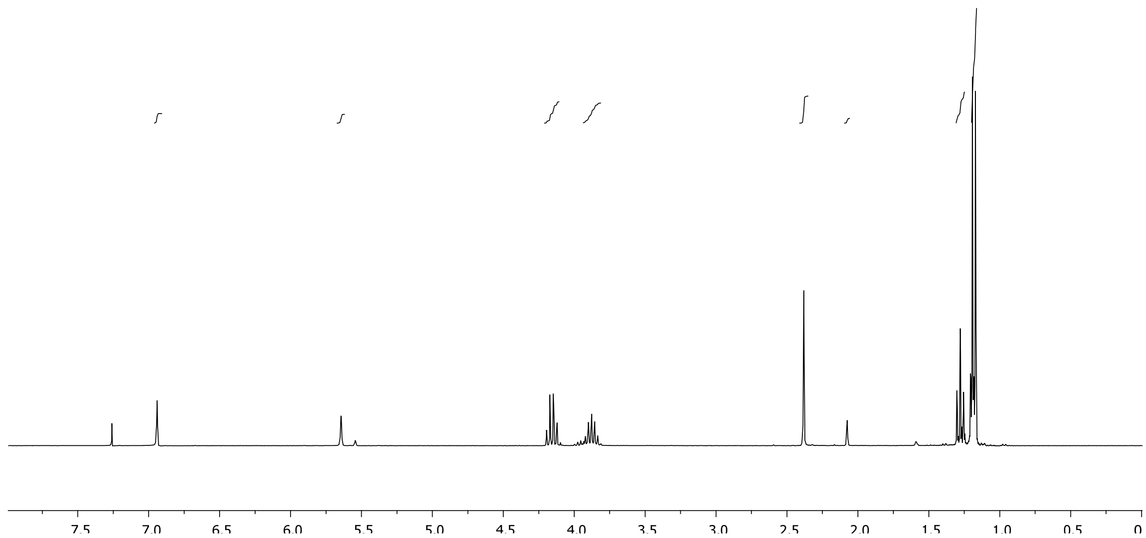
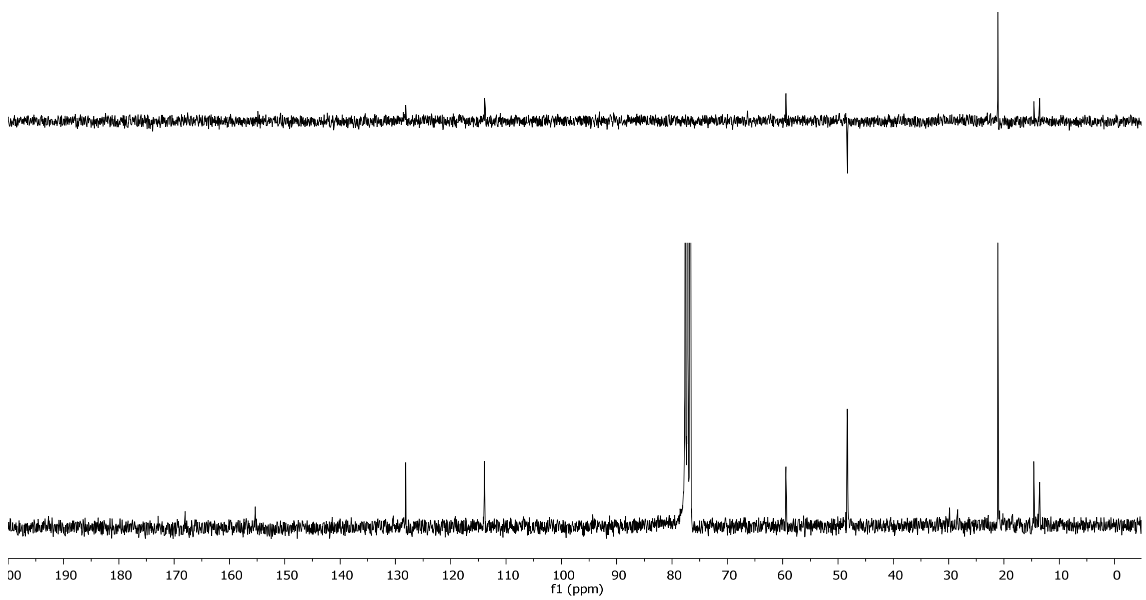
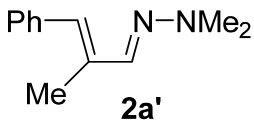
40
30
20
10


EtO2C
N-N(iPr)2
Me

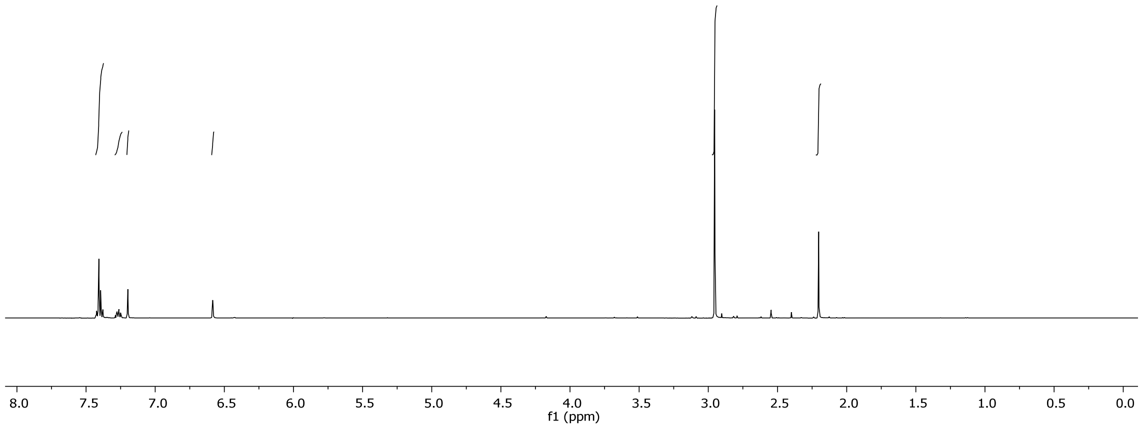
2k

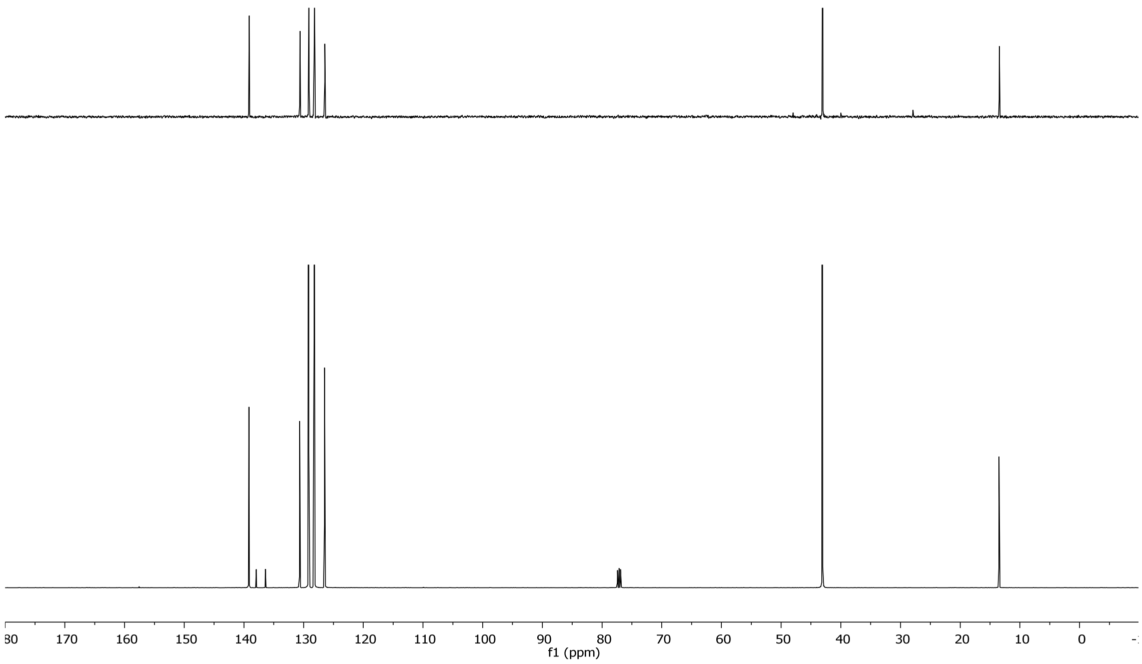

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0

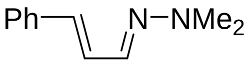

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
N−NMe2
Me

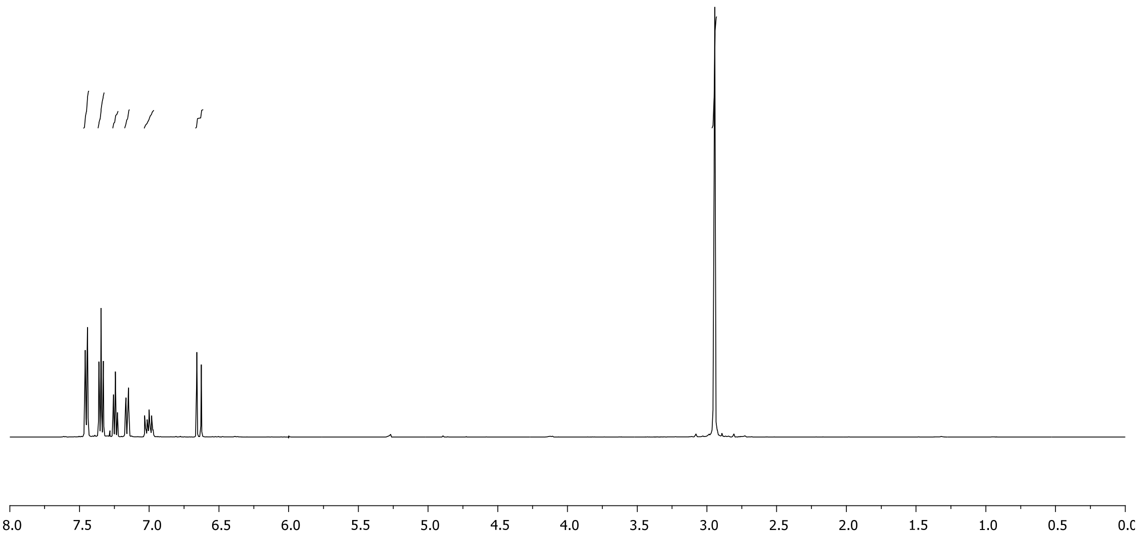
2a'

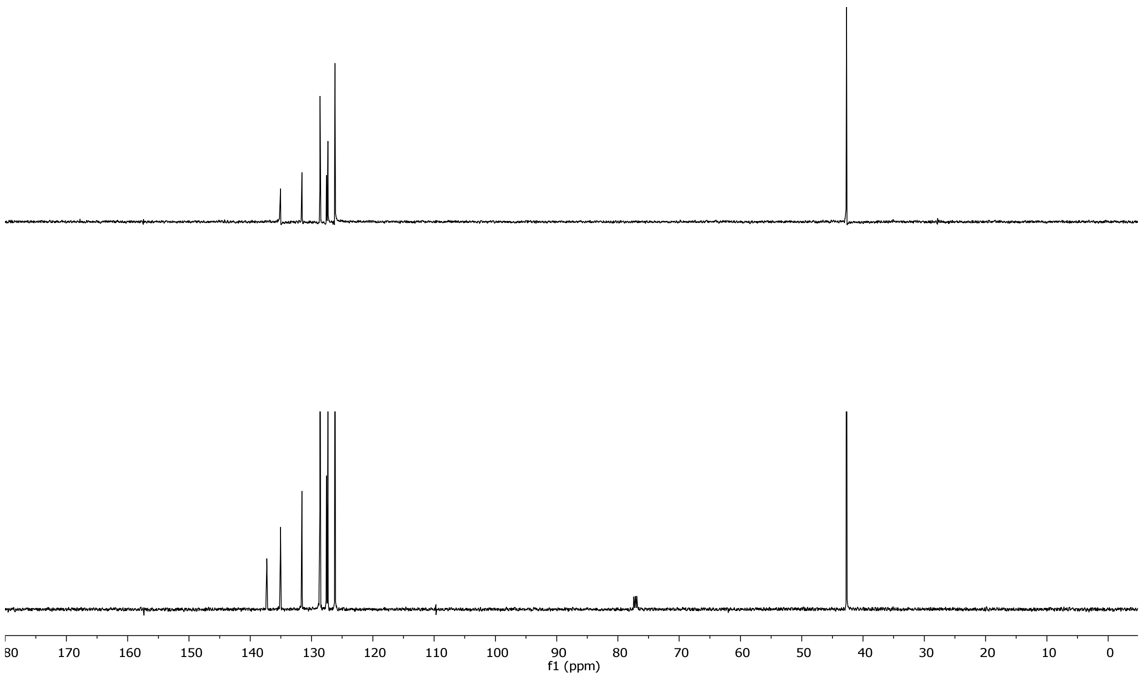

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

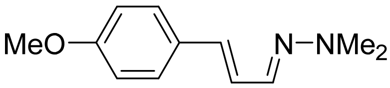

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



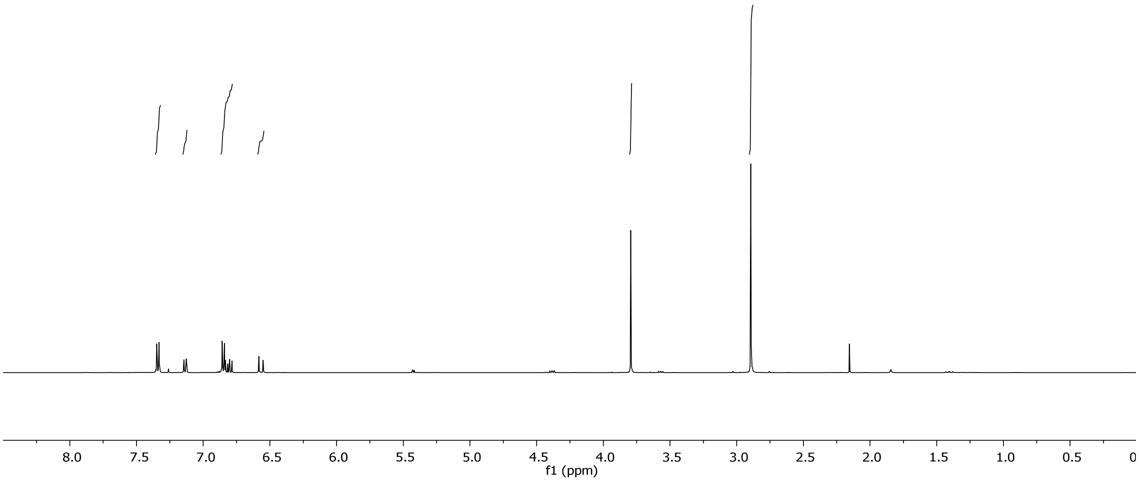
2b'

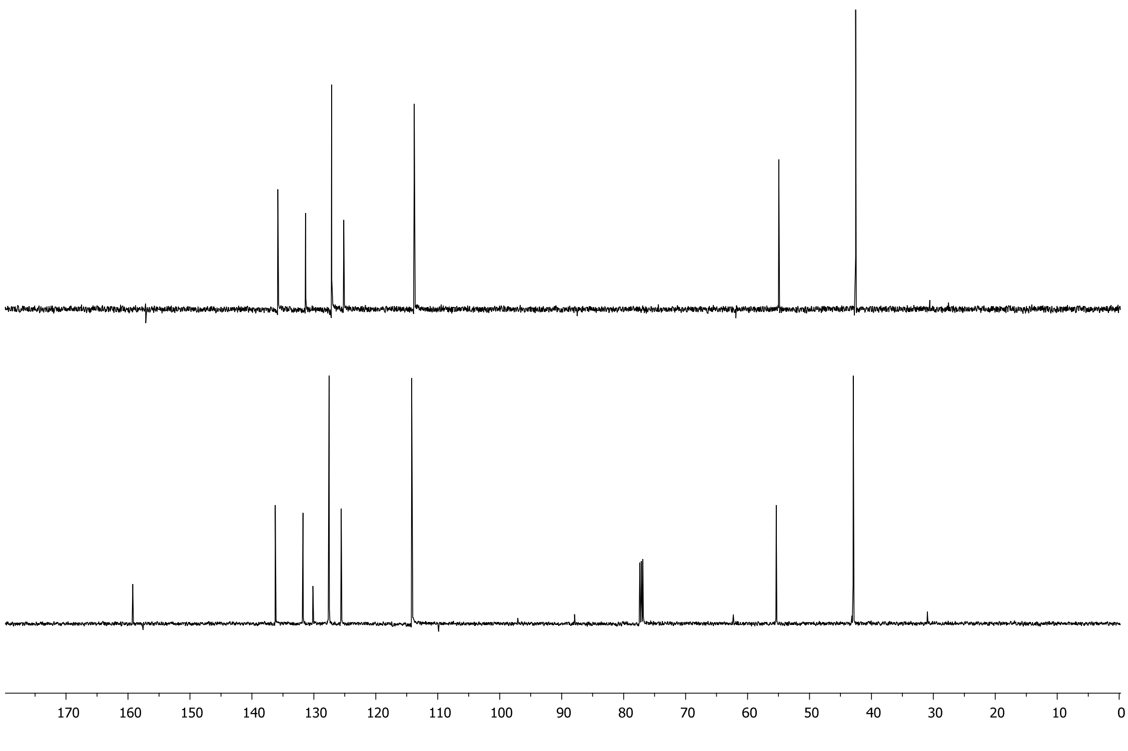





MeO
N
NMe2

2c'


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)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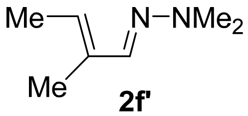
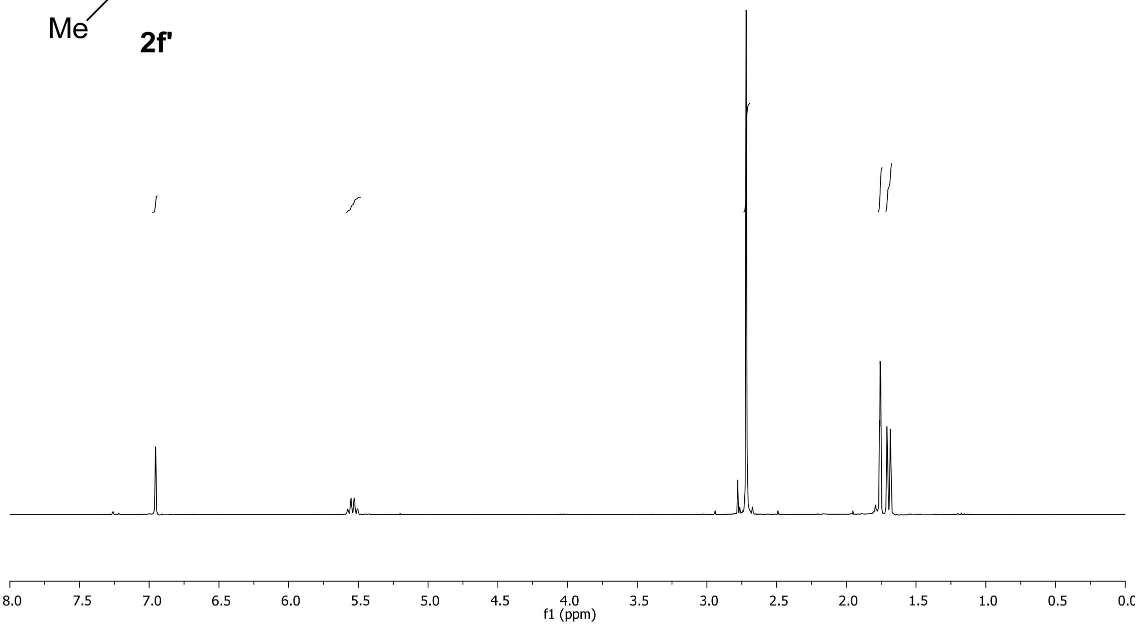
10
0

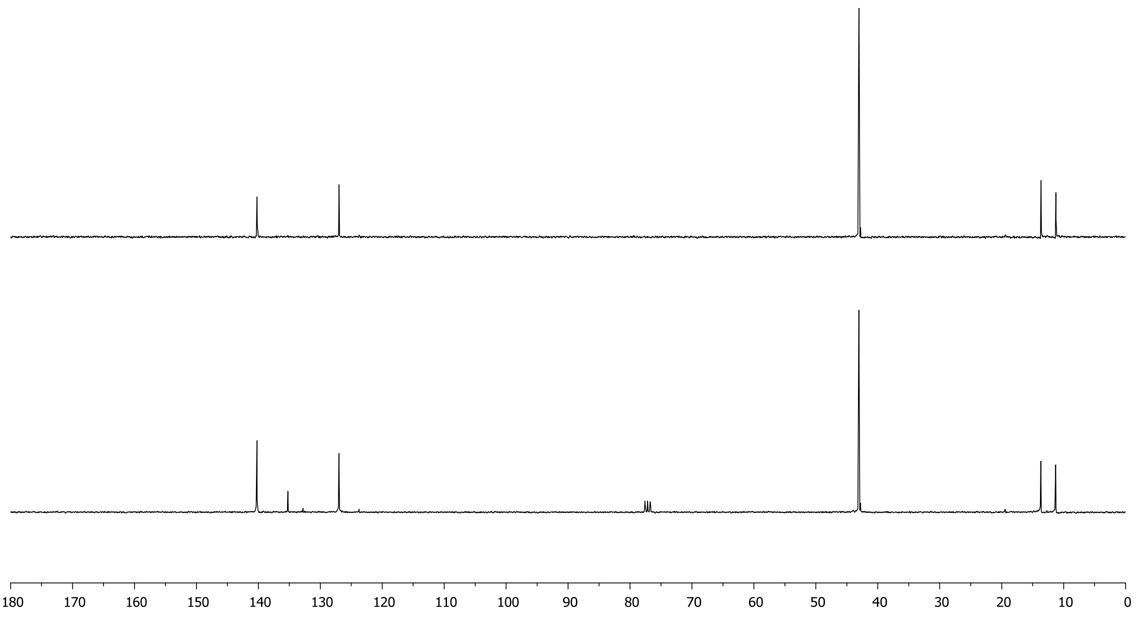


Me
N−NMe2
Me

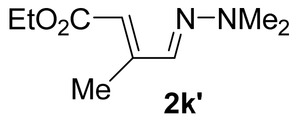
2f'



8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

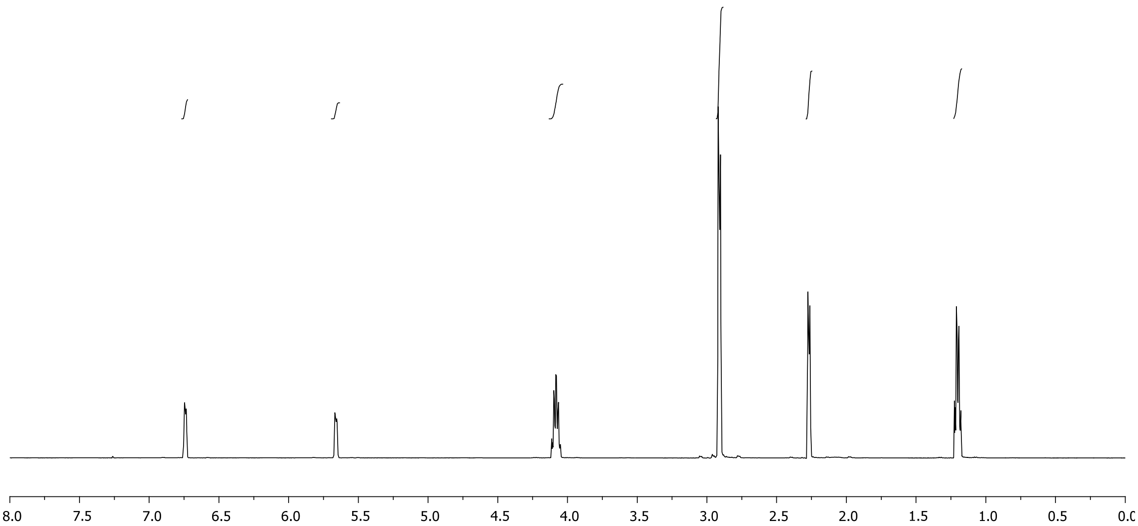


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

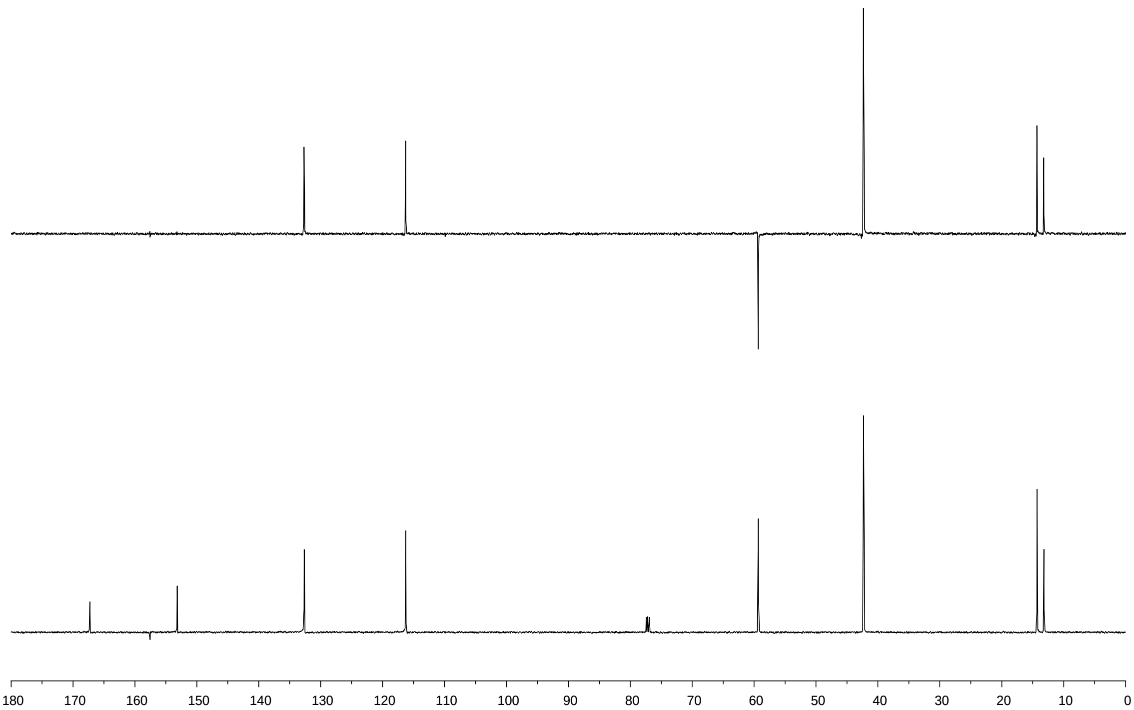


EtO2C
N−NMe2
Me

2k'



8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



180
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130
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100
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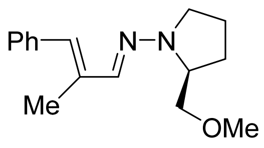
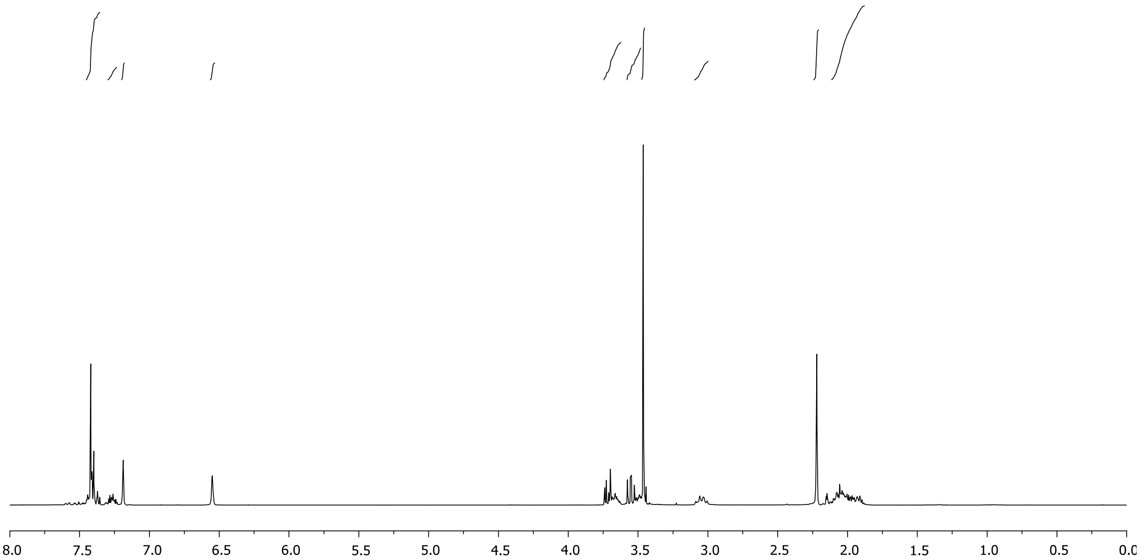
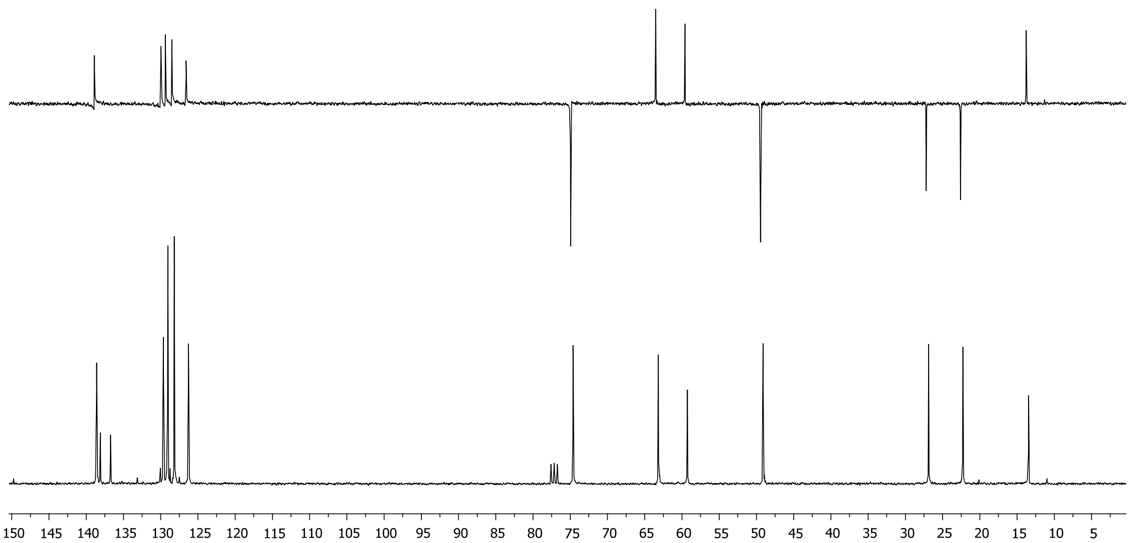
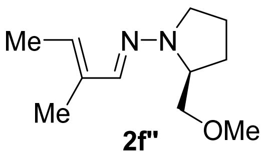
80
70
60
50
40
30
20
10
0



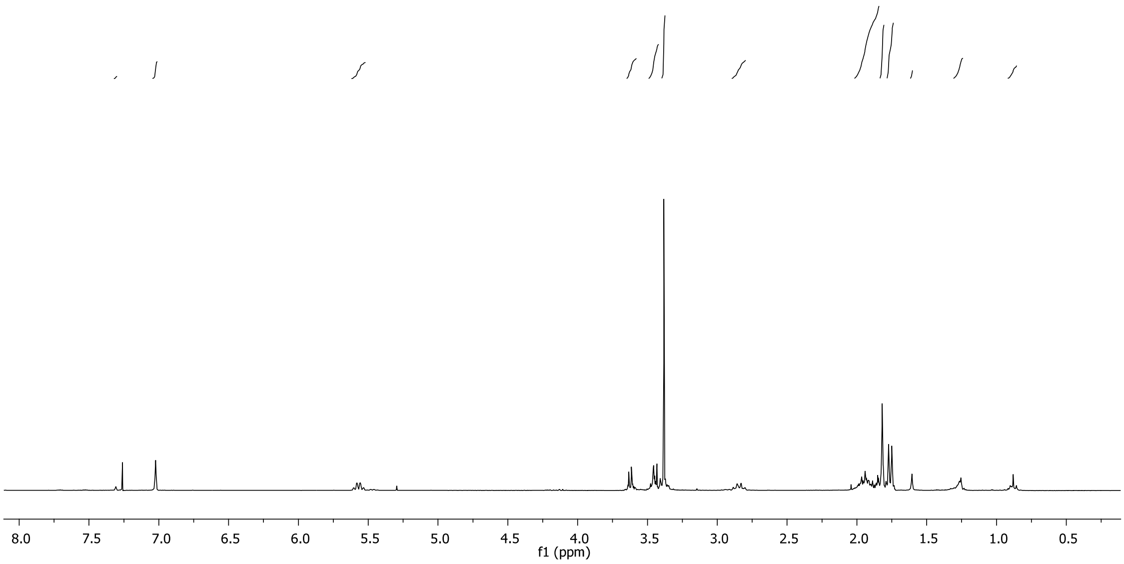
2a''

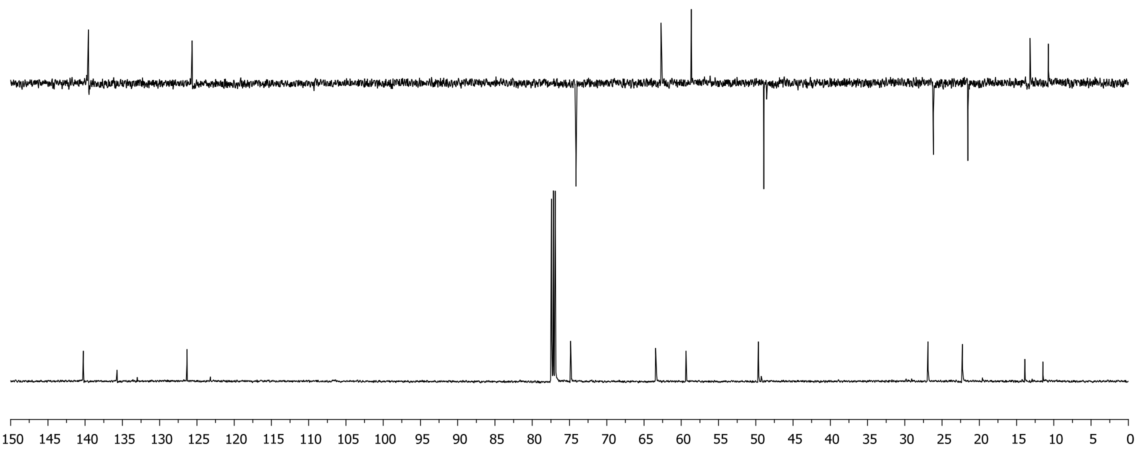


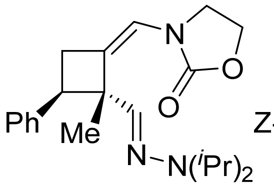



Me
N
N
Me
OMe

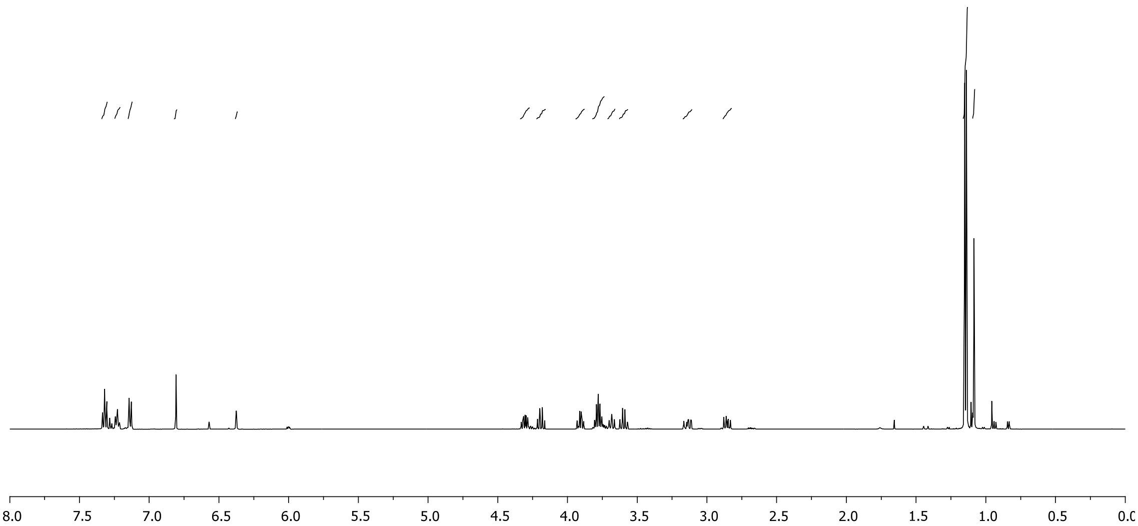
2f''


8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0


Ph
Me
N
O
O
N
N(iPr)2

Z-**3aa**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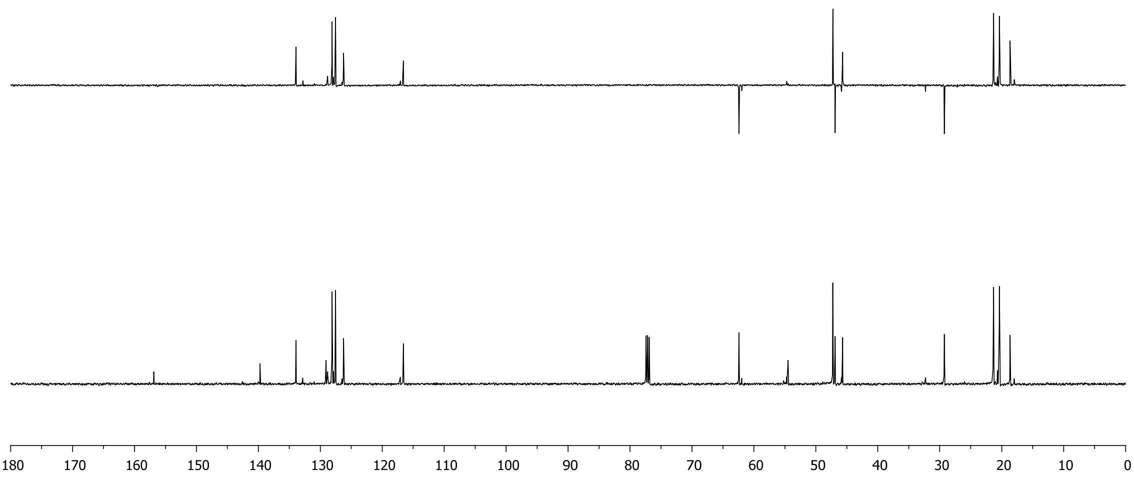
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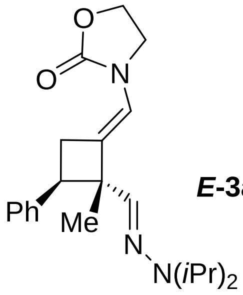
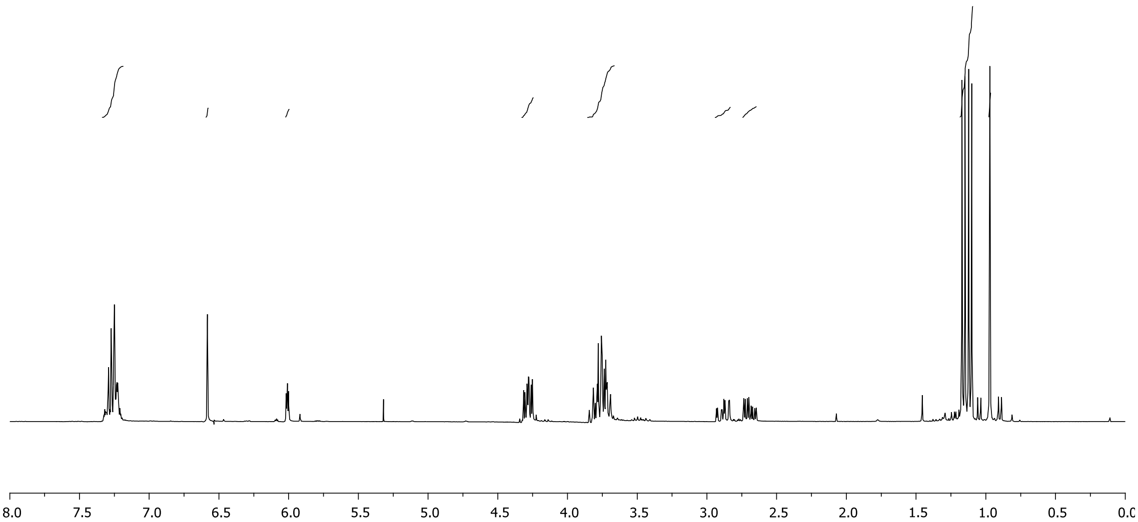
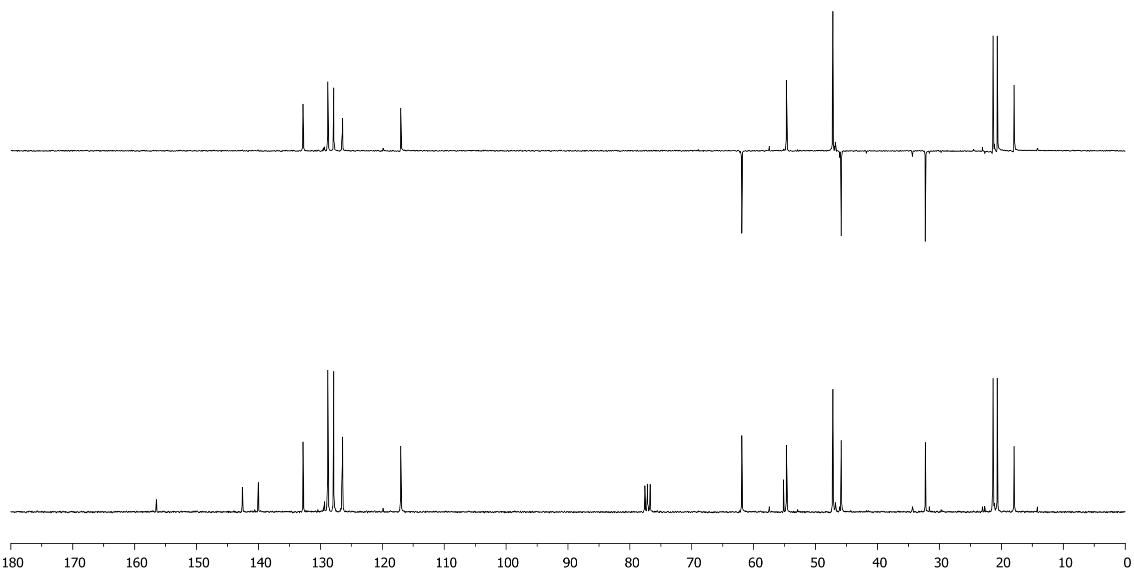


O
O
N
Ph
Me
N
N(iPr)2

***E*-3aa**



8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



180
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140
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70
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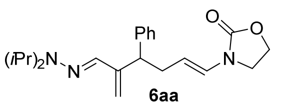
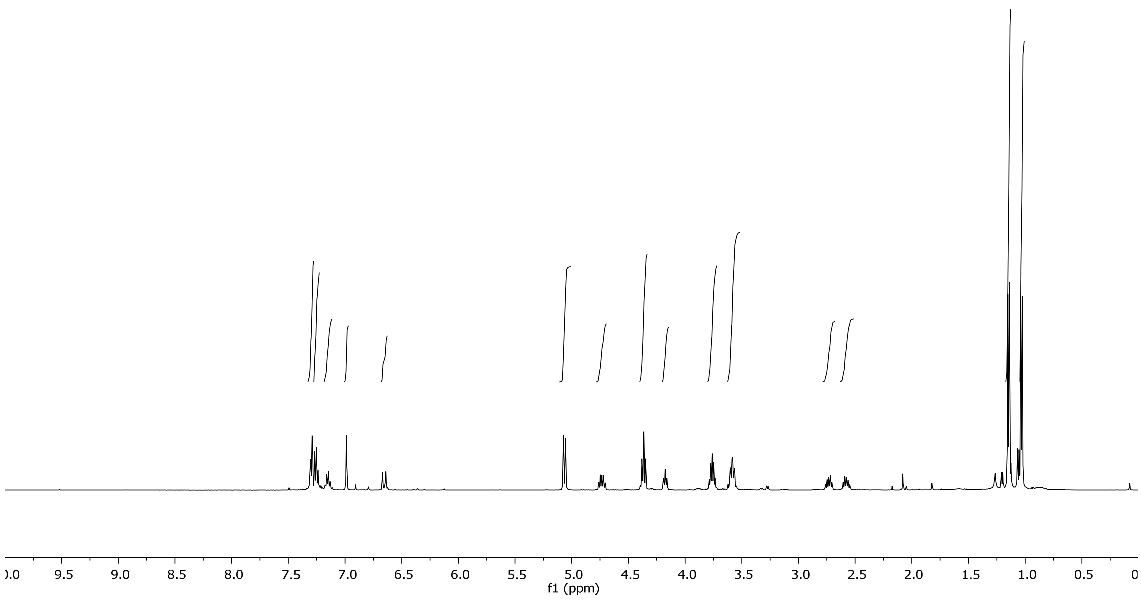
0

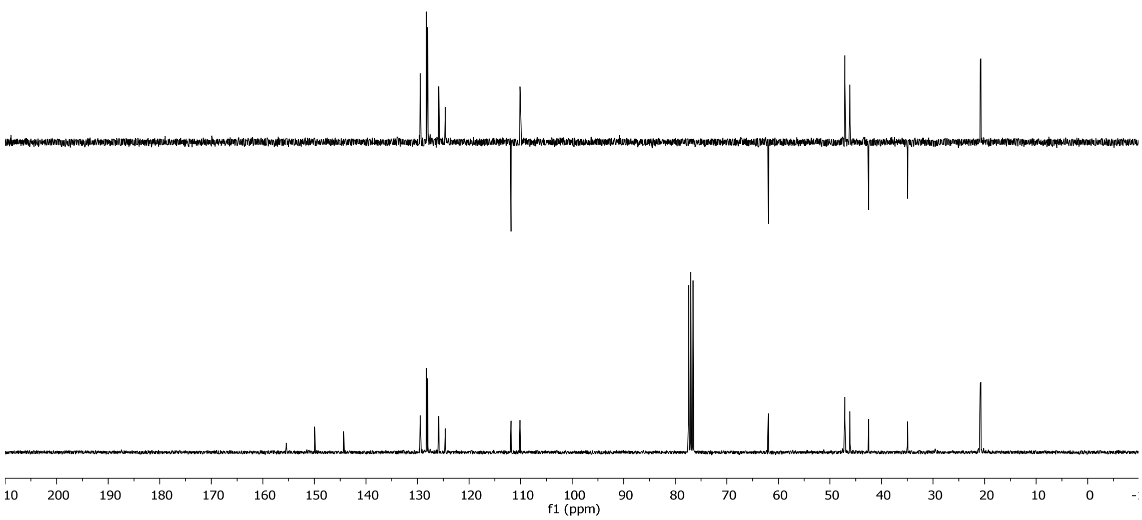


(iPr)2N
N
Ph
O
O
N

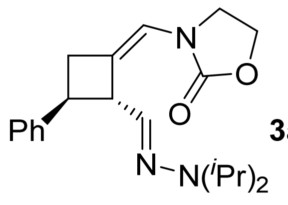
6aa



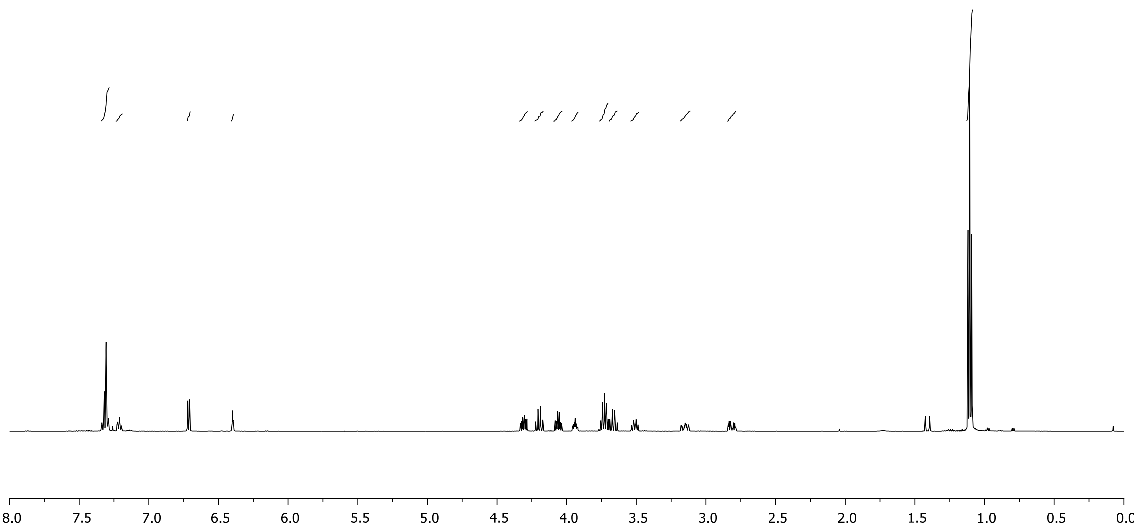
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



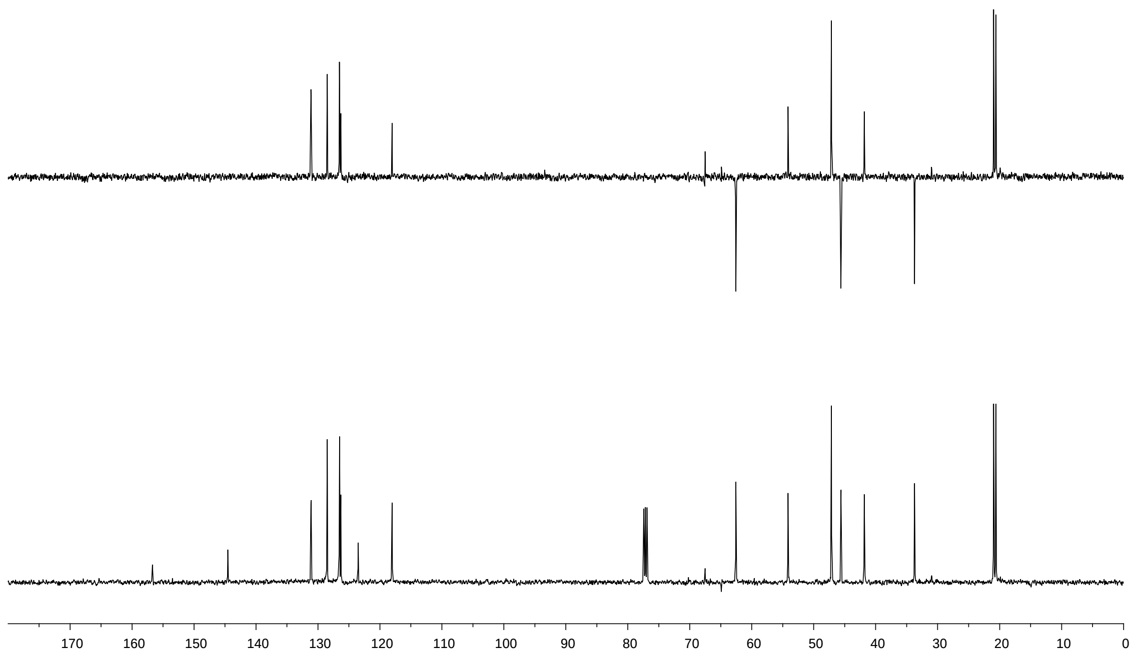
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3ab



8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



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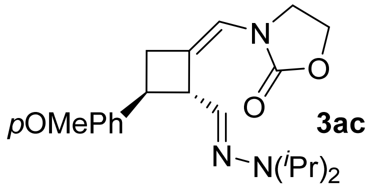
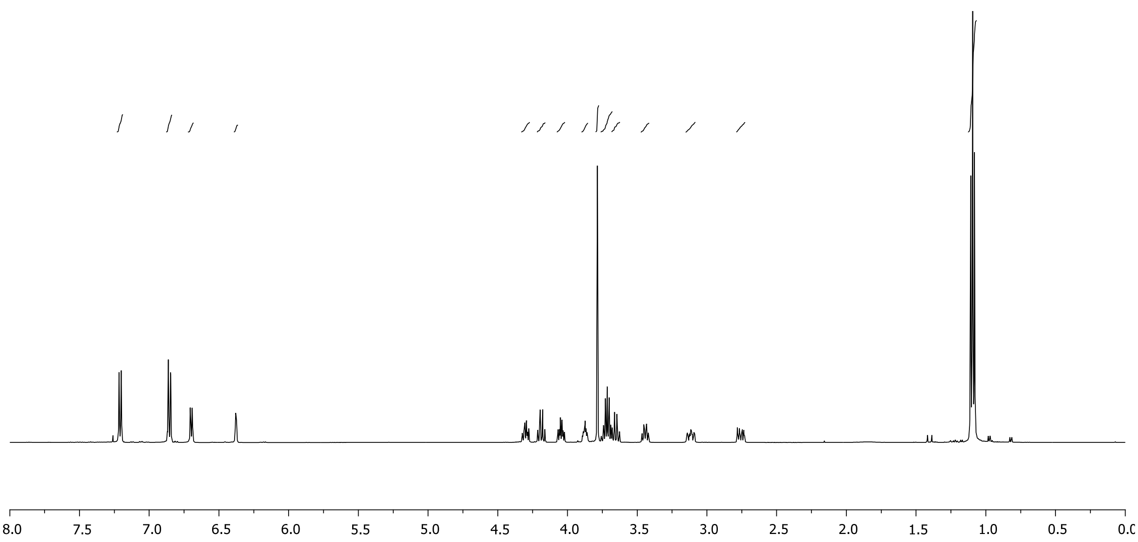
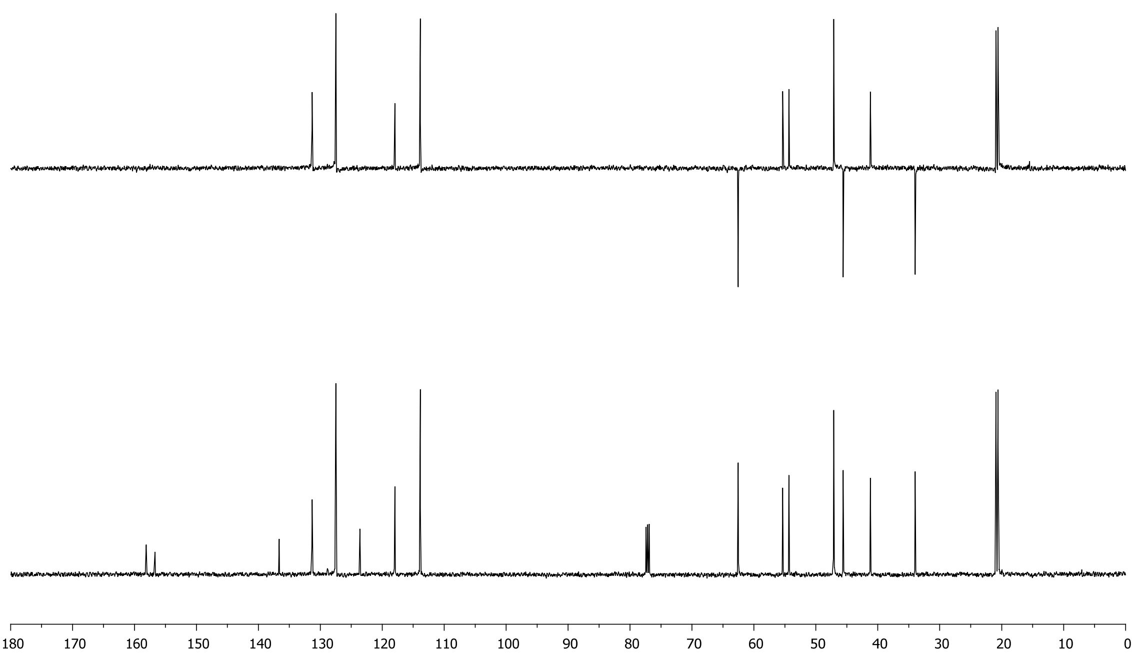
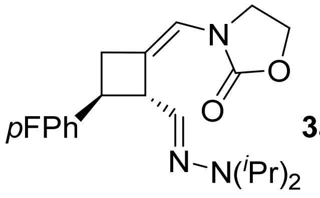


3ac

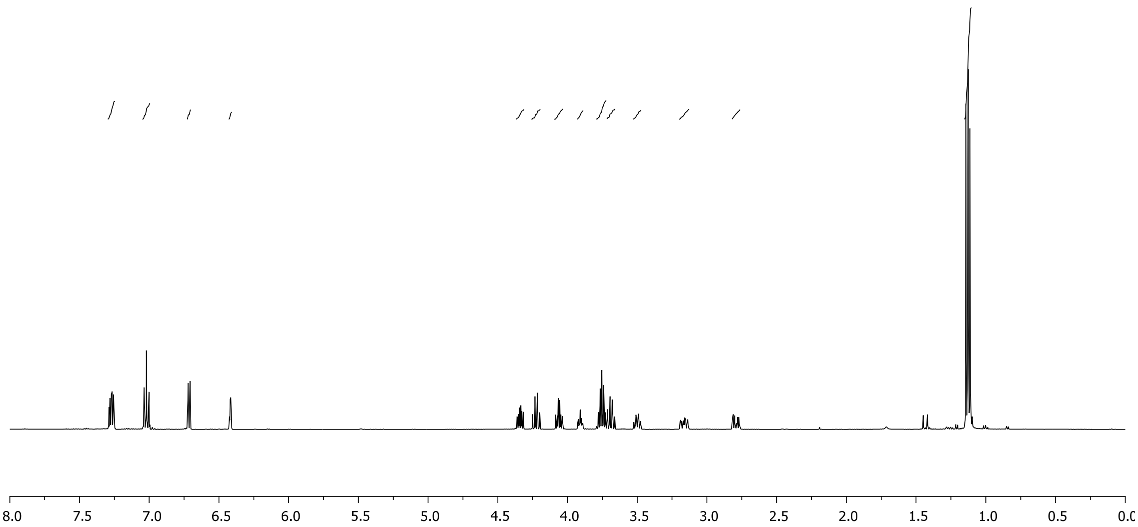






pFPh
N
O
O
N
N(iPr)2

3ad



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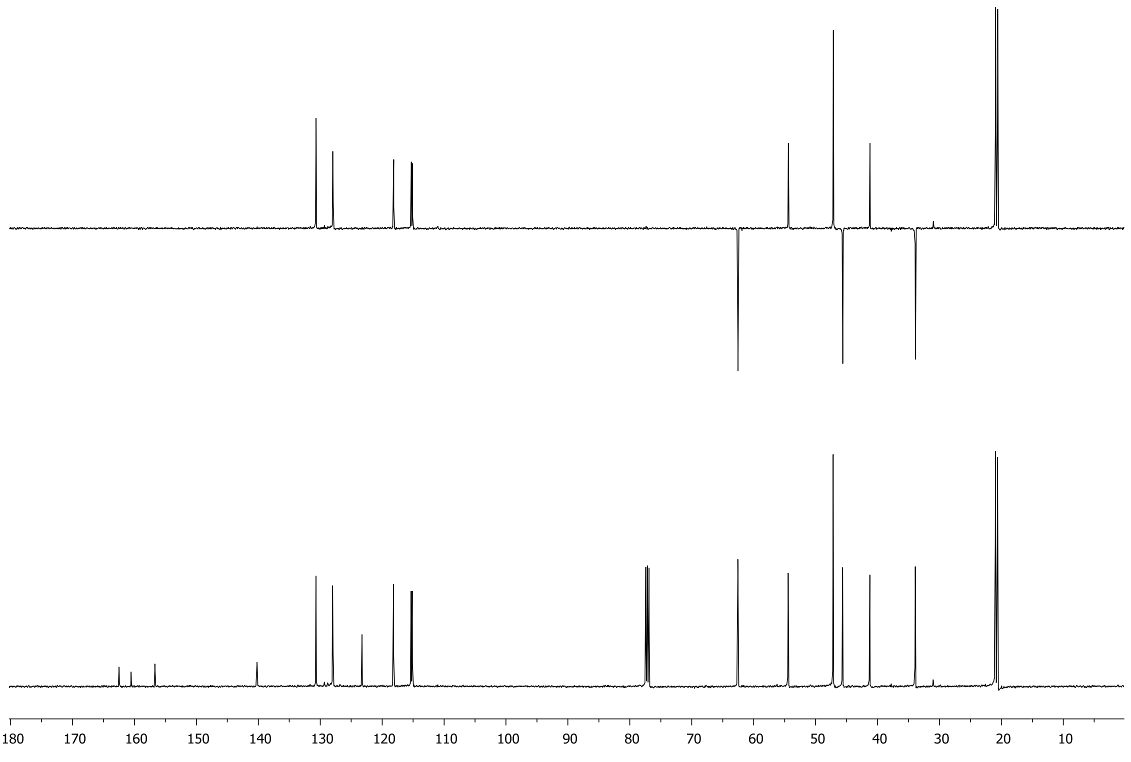

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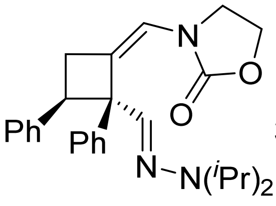
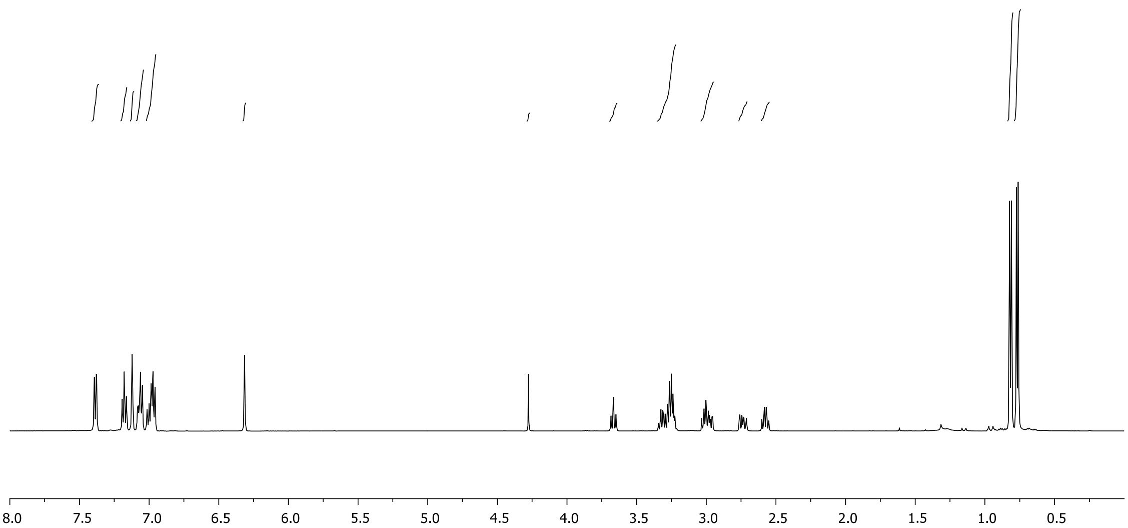
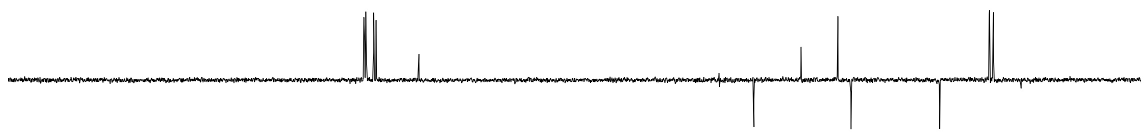
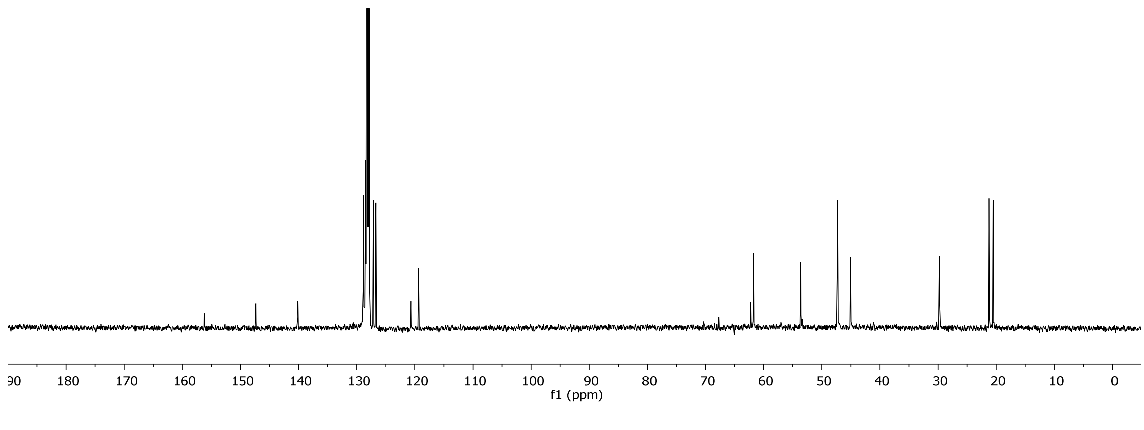
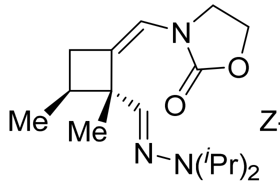


3ae (C_6D_6)

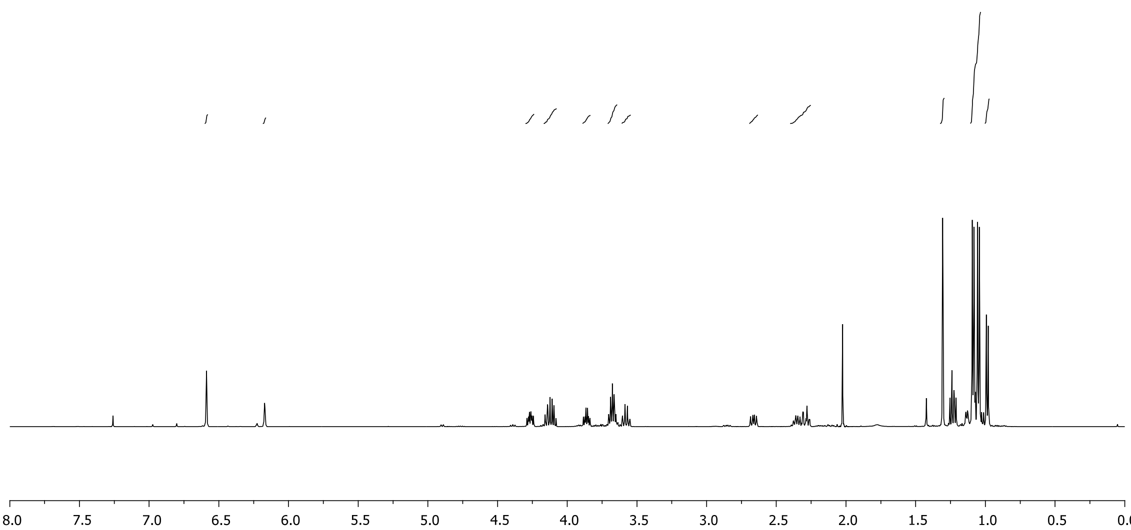








Z-**3af**



8.0
7.5
7.0
6.5
6.0
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4.5
4.0
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3.0
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2.0
1.5
1.0
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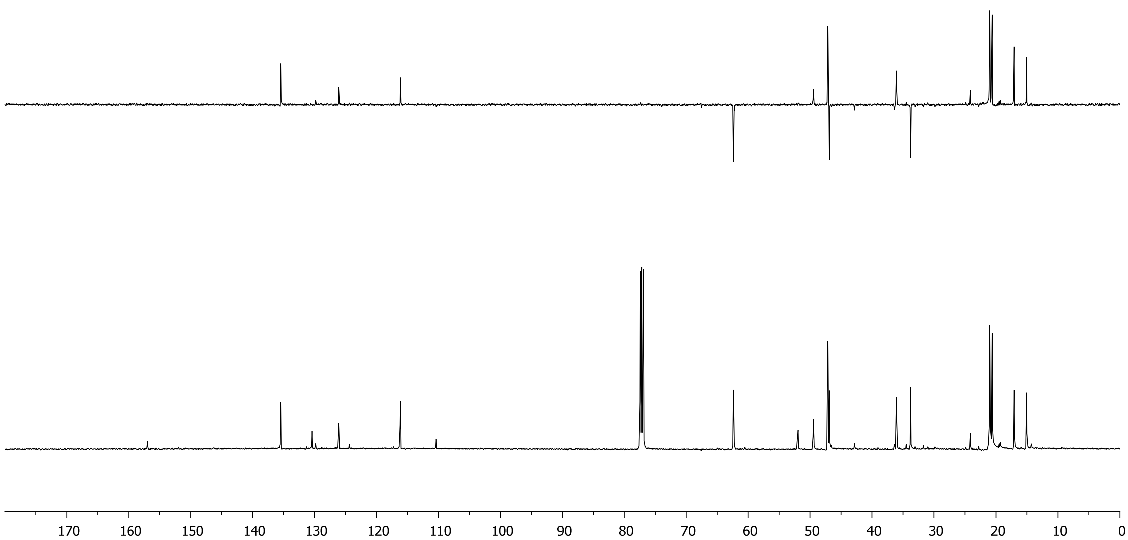
0.0



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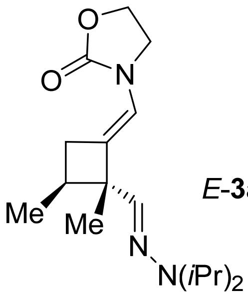
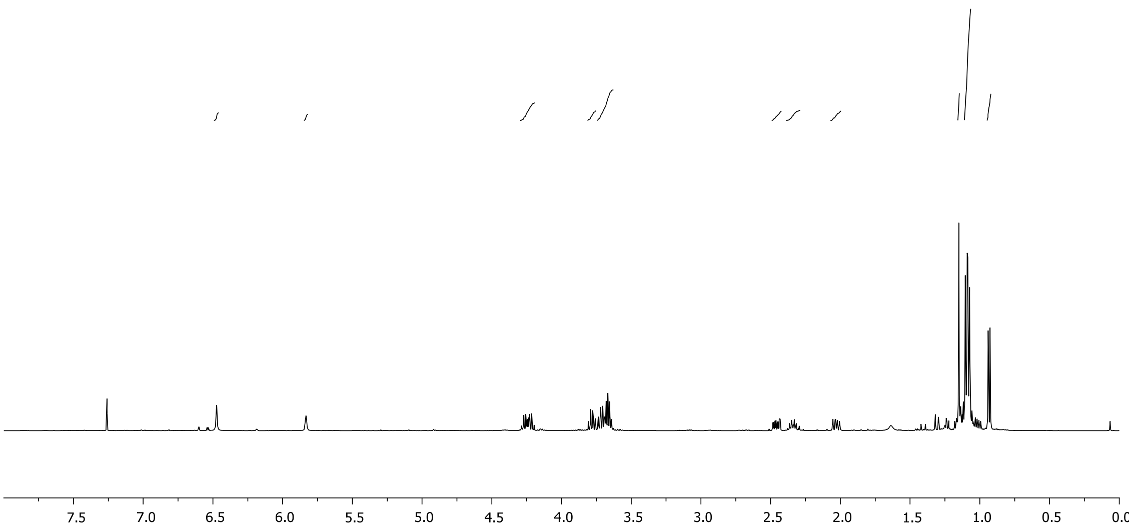

O
O
N
Me
Me
N
N(iPr)2

E-**3af**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4.0
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2.0
1.5
1.0
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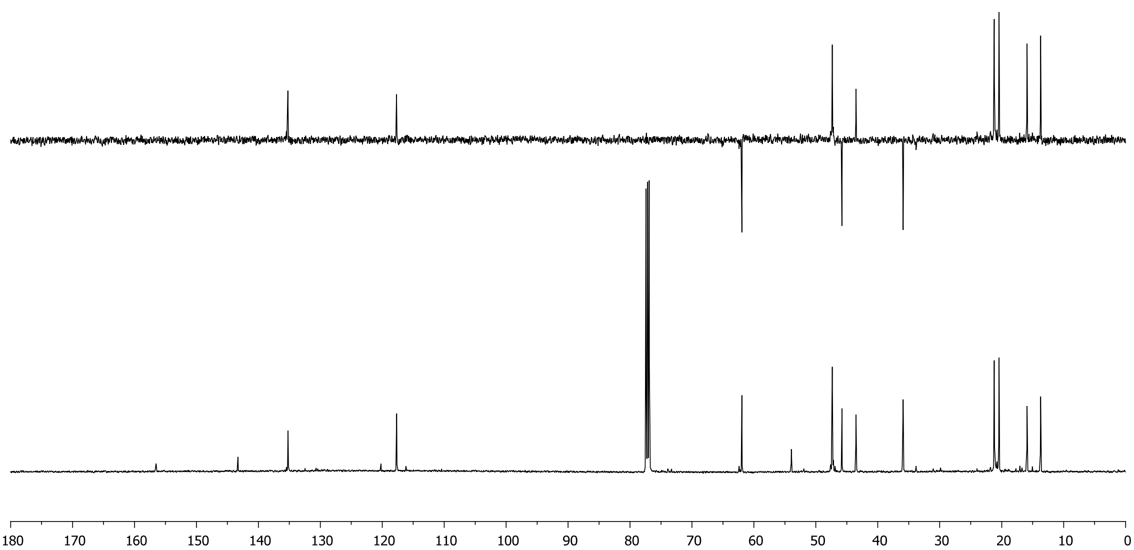
0.0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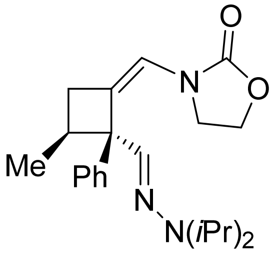
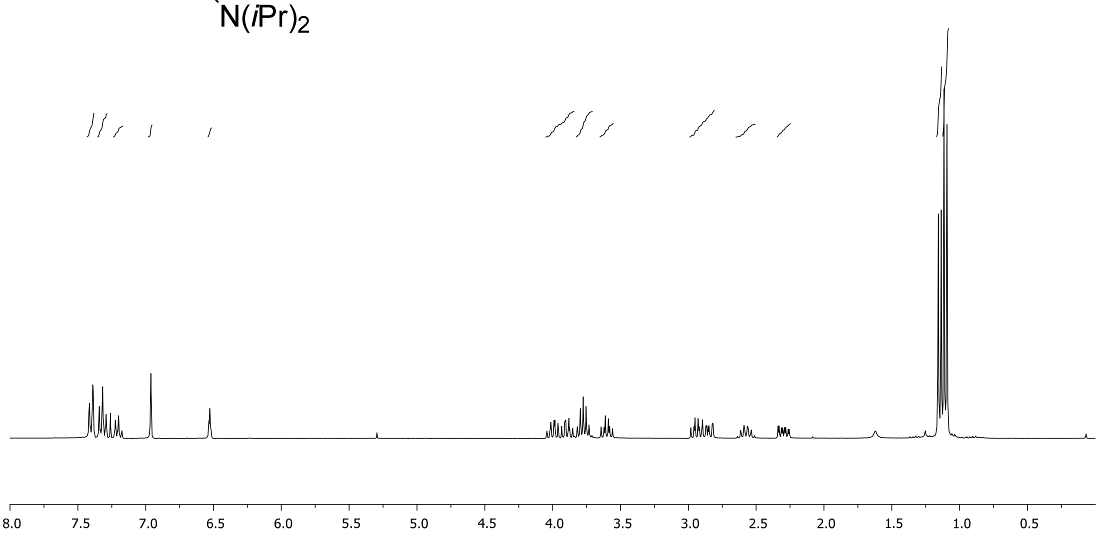

O
N
O
Me
Ph
N
N(iPr)2

Z-**3ag**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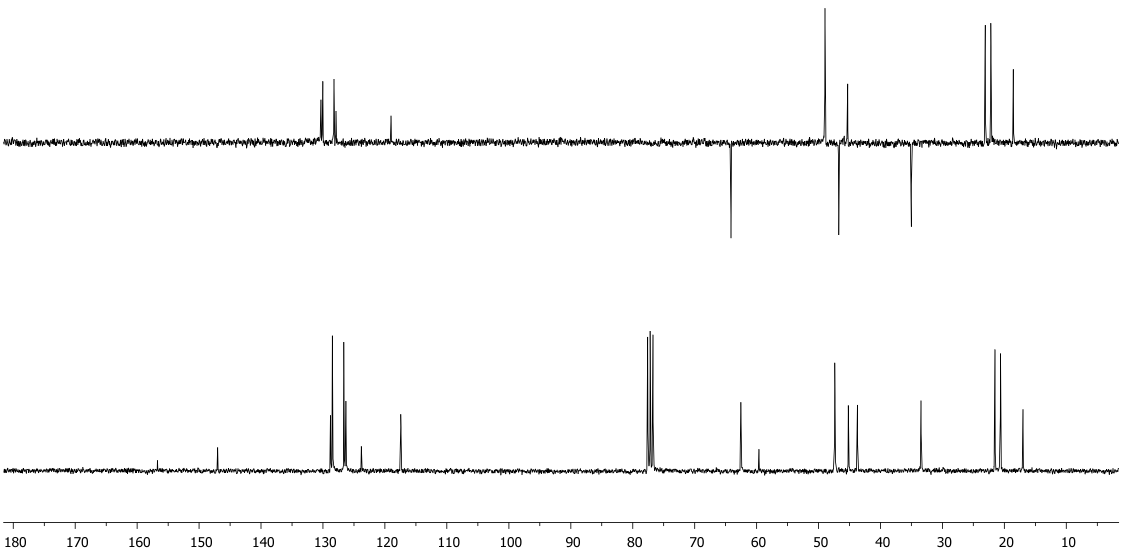
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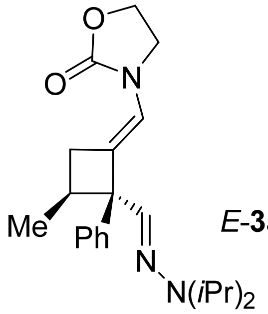

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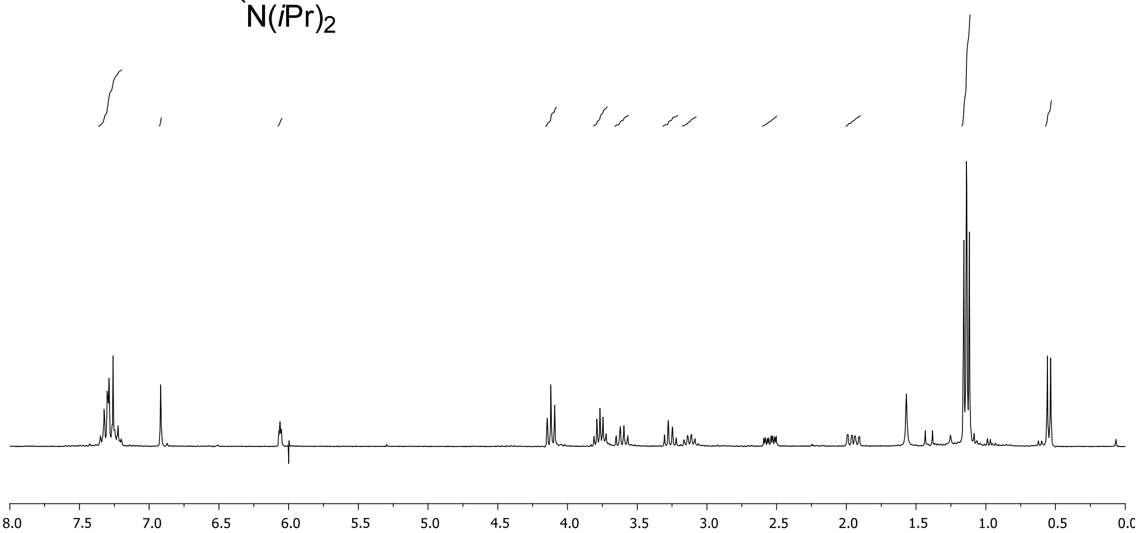

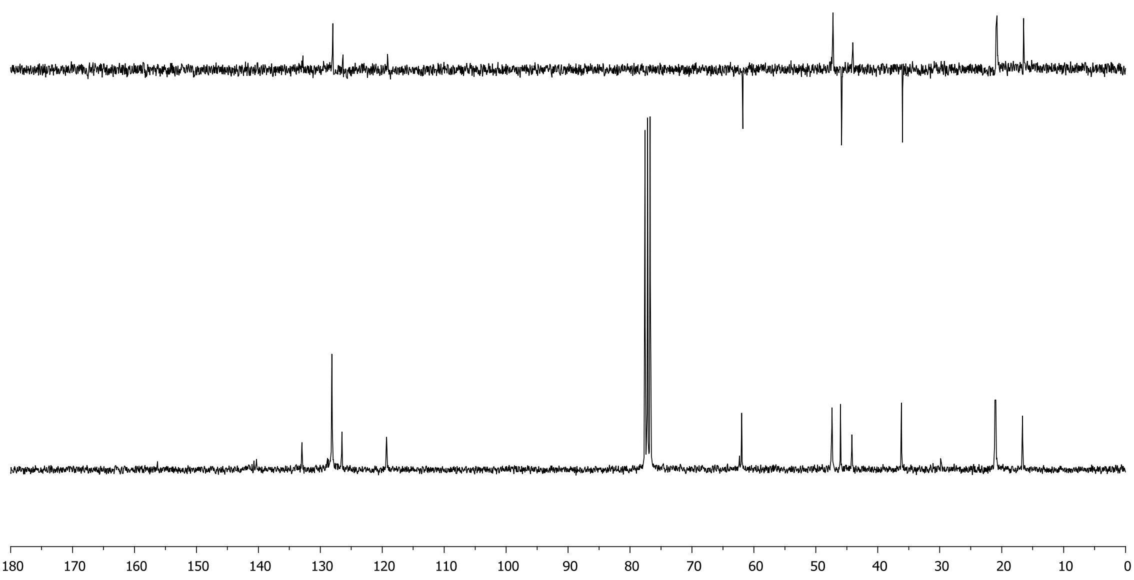

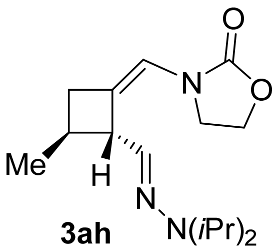

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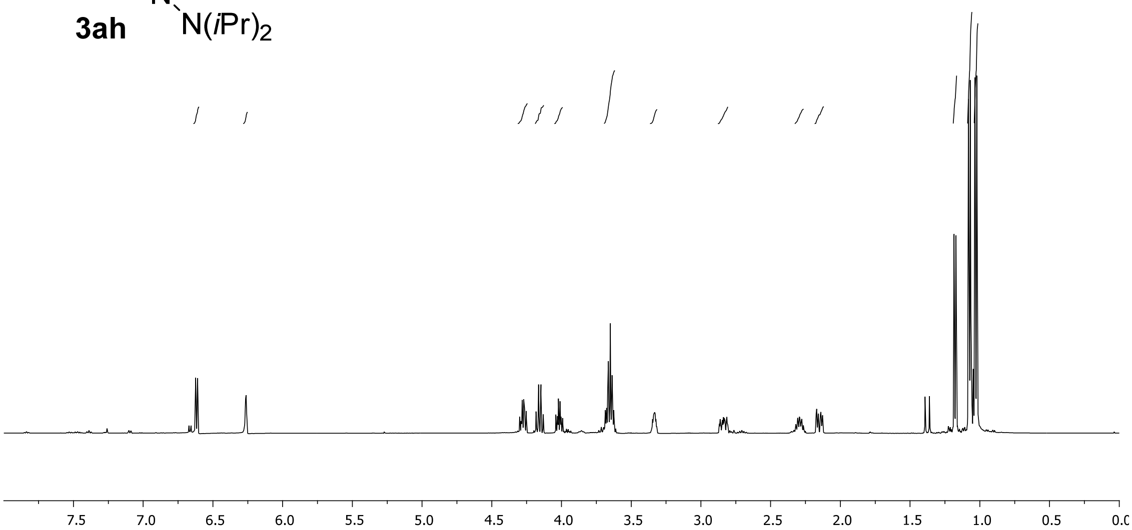
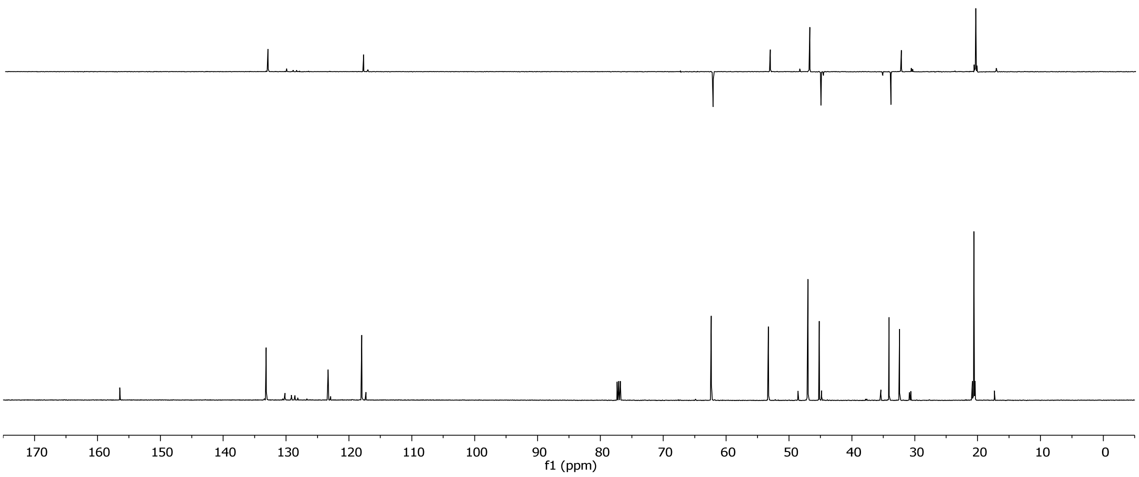
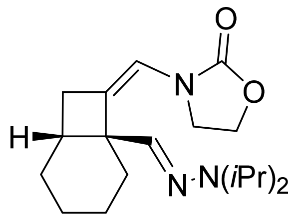
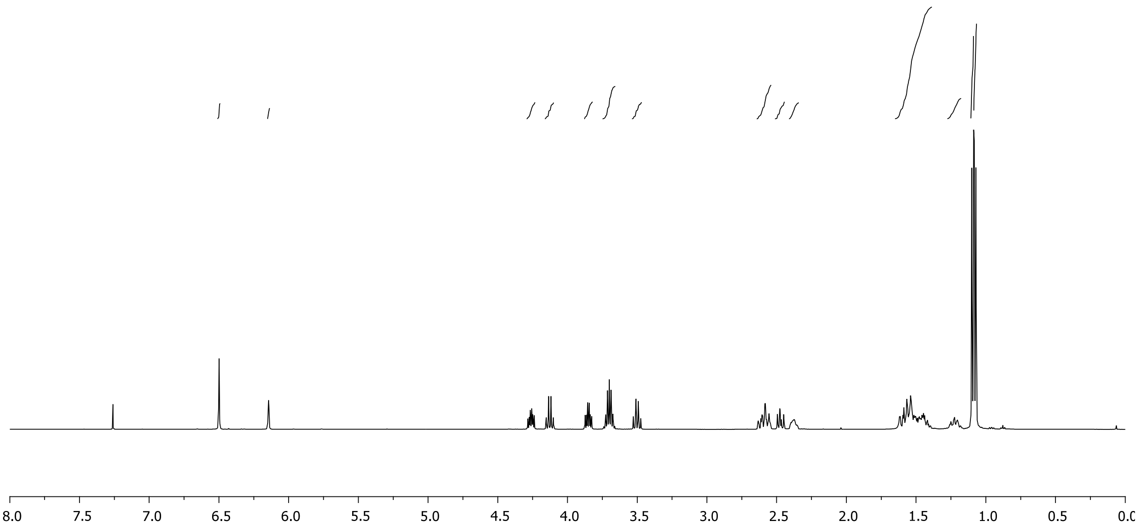





O
N
O
H
N
N(iPr)2

Z-**3ai**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4.5
4.0
3.5
3.0
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2.0
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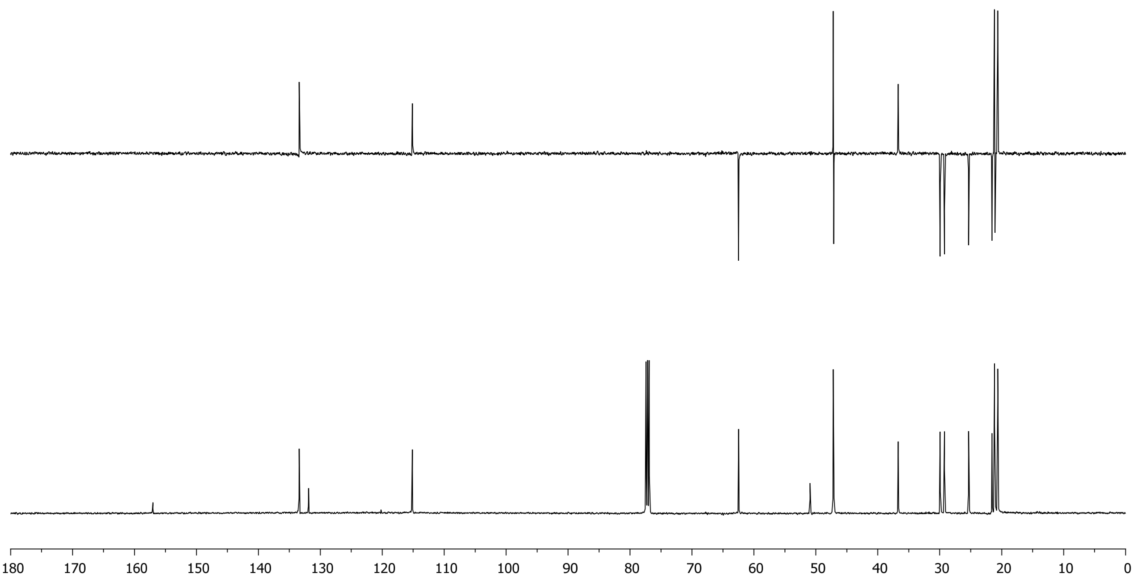
1.0
0.5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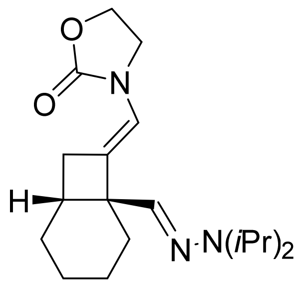
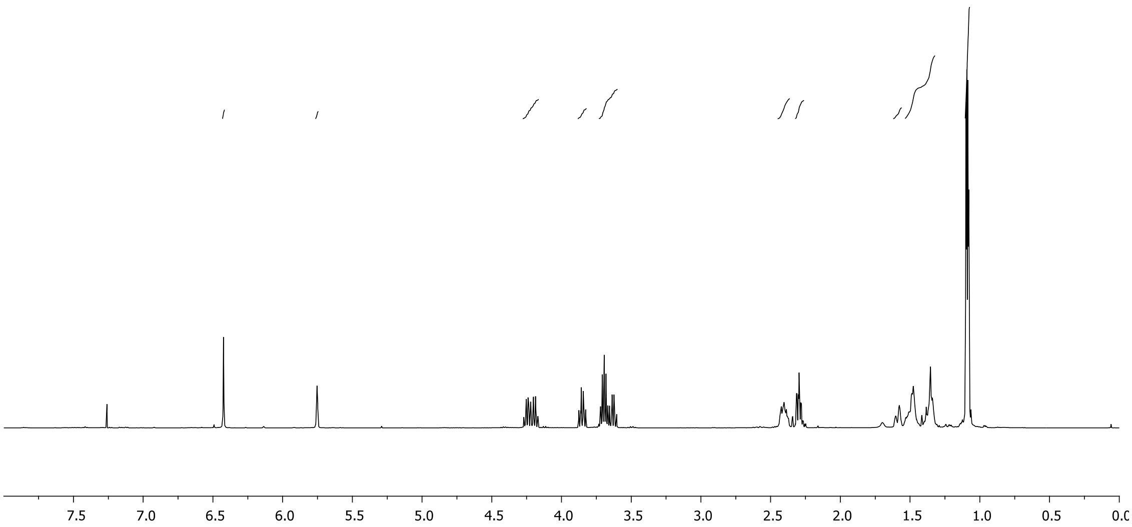


E-**3ai**



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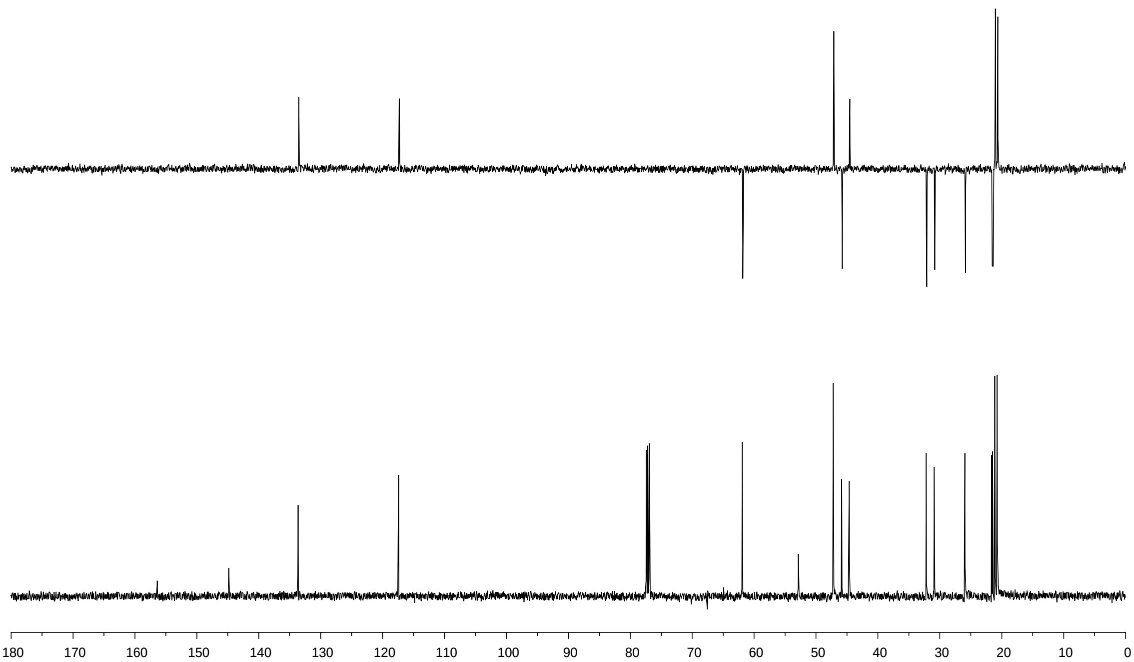
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



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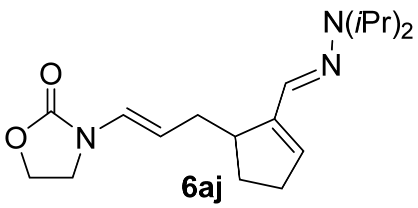
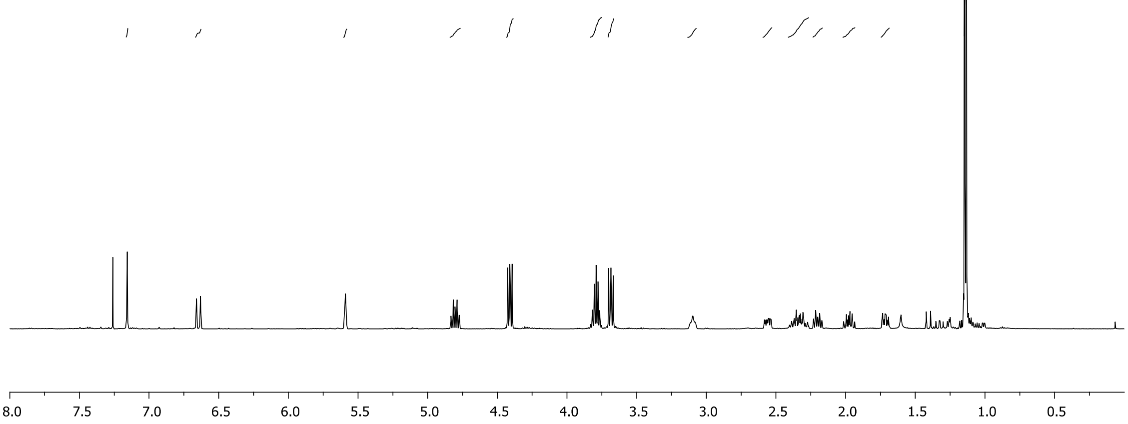

N(iPr)2
N
O
O
N

6aj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7.0
6.5
6.0
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4.5
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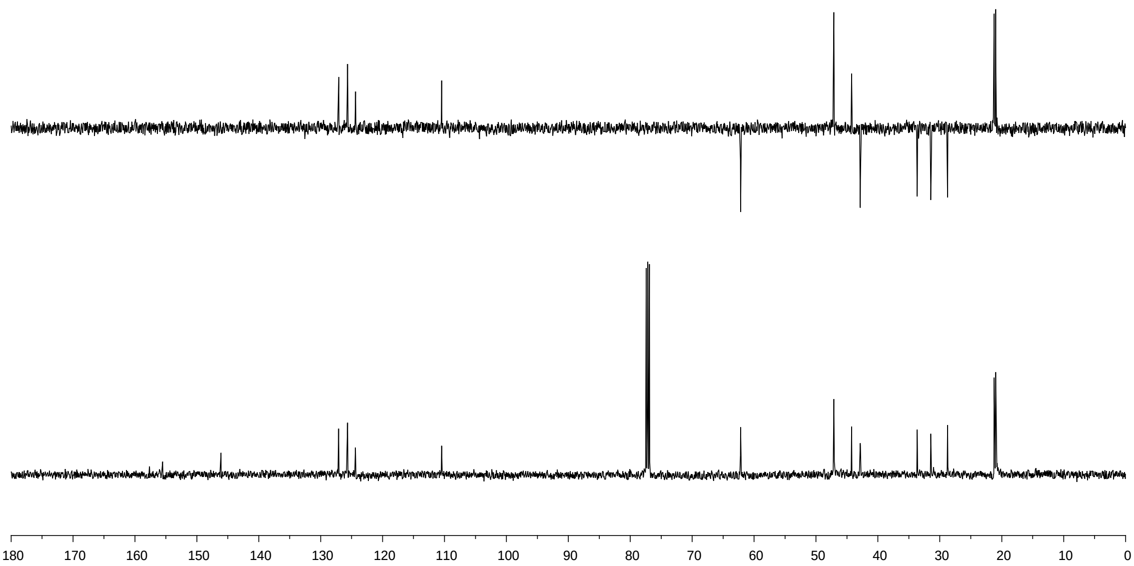
0.5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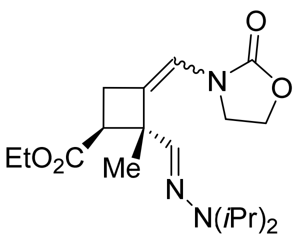
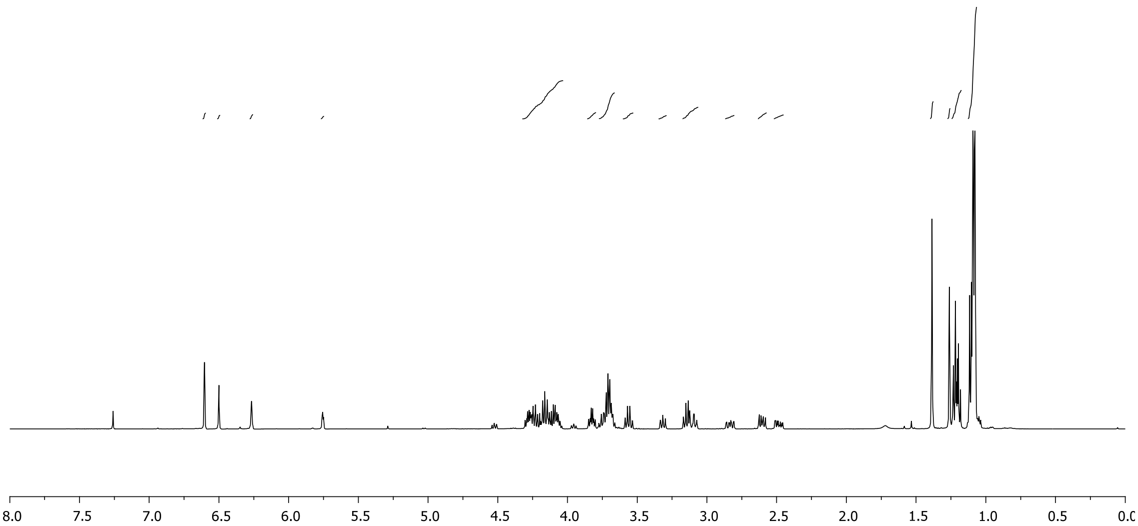
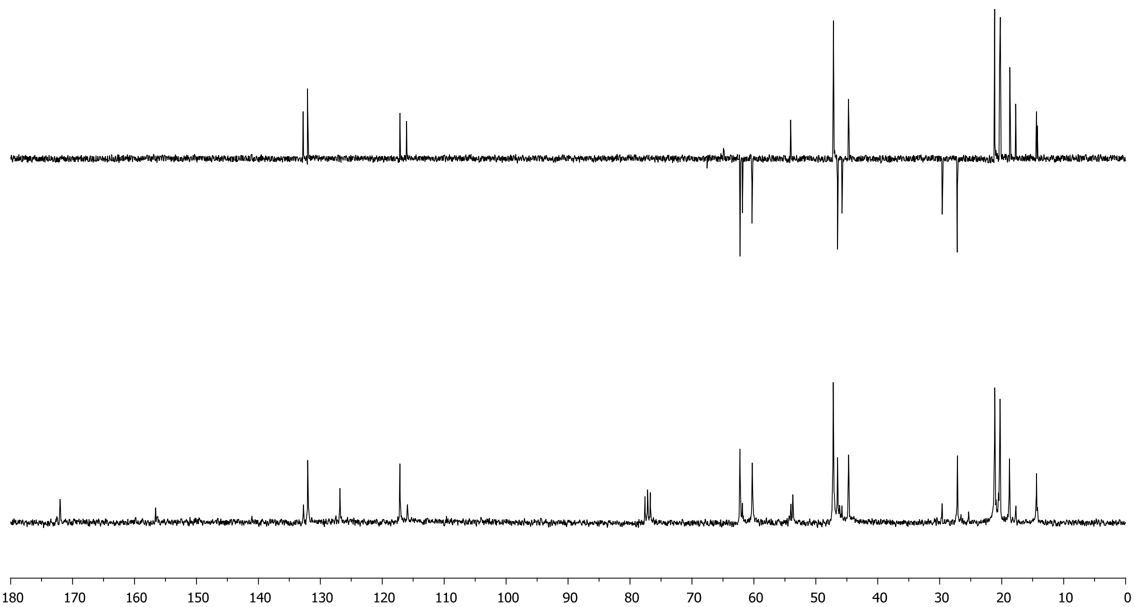
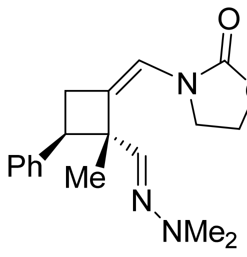


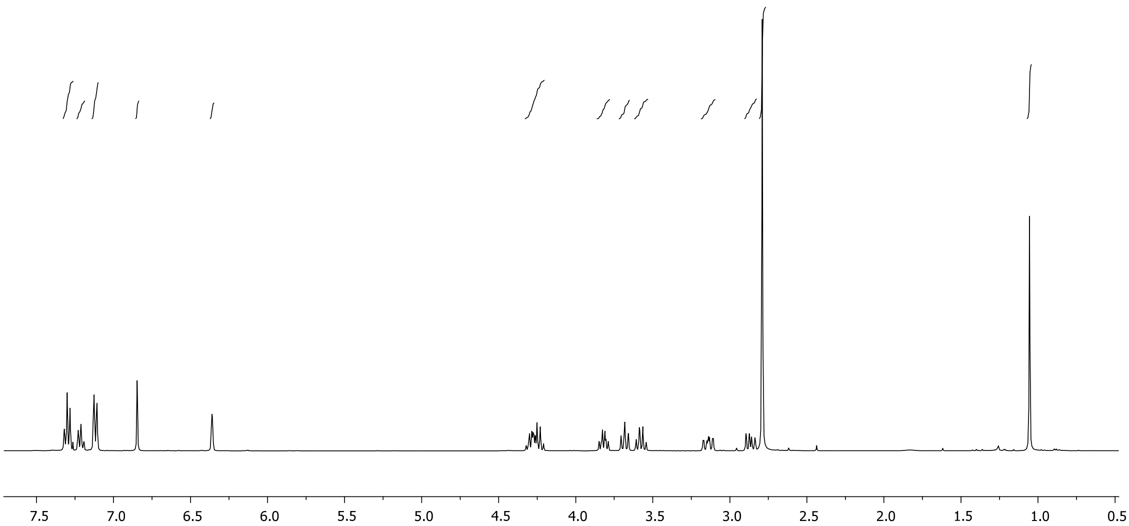
Z-**3ak** + *E*-**3ak**






O
N
O
Ph
Me
N
NMe_2

3aa'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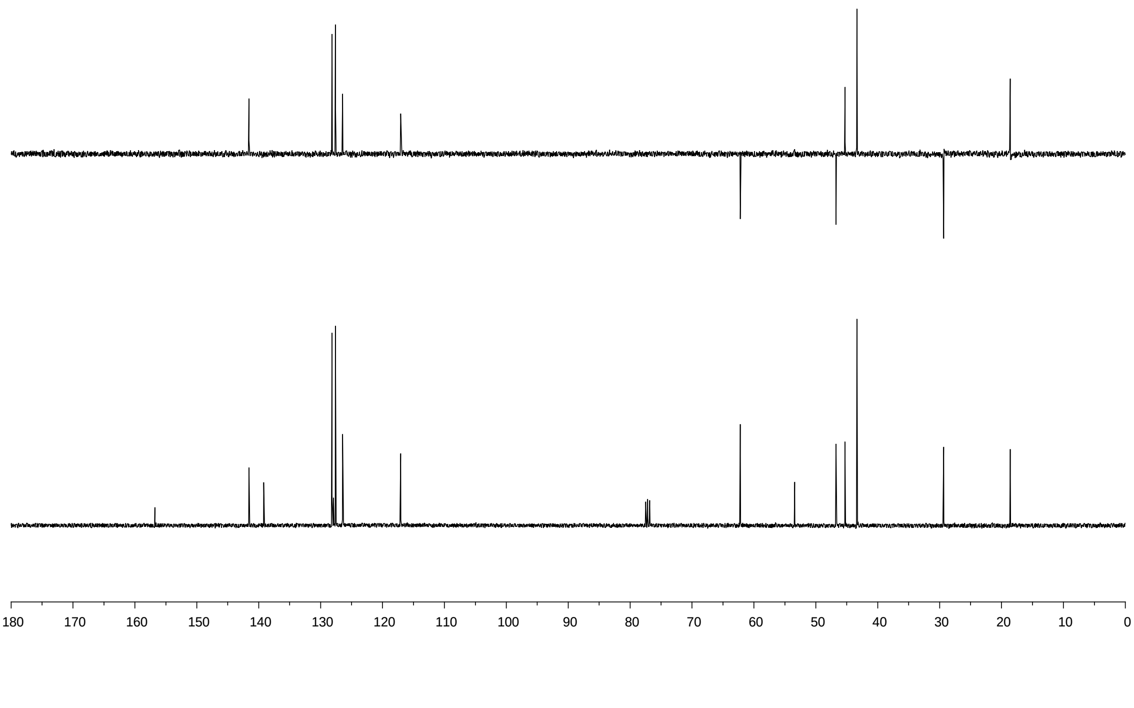
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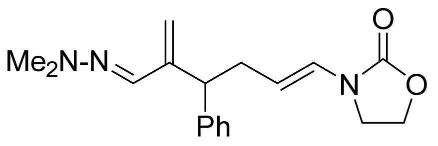
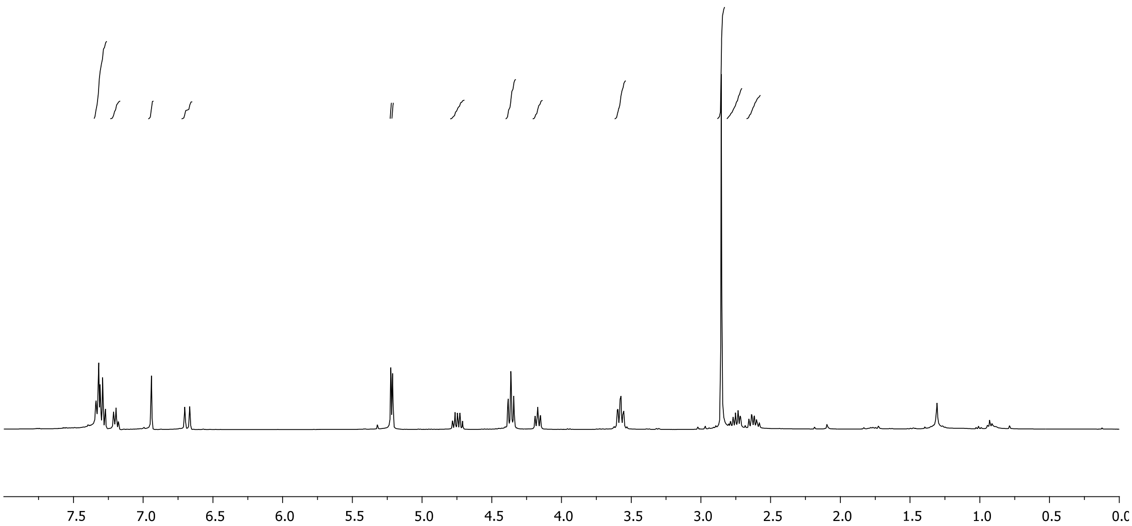


6aa'



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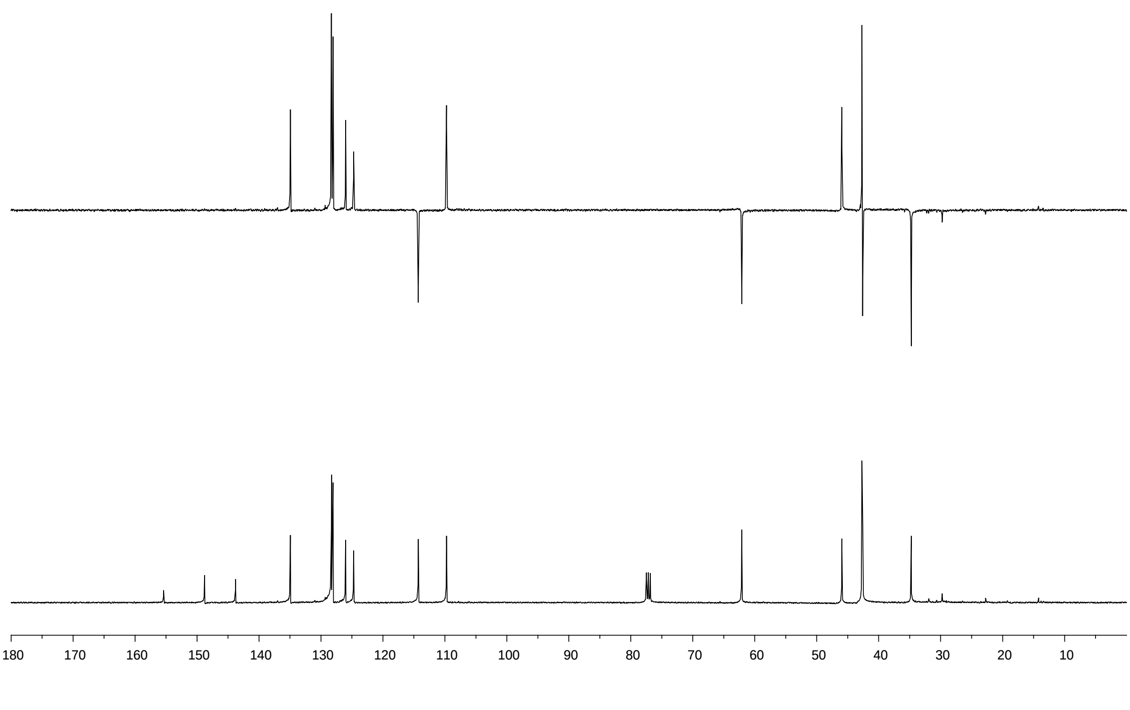

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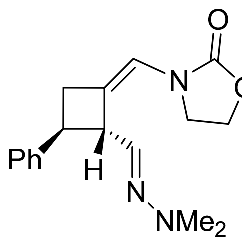

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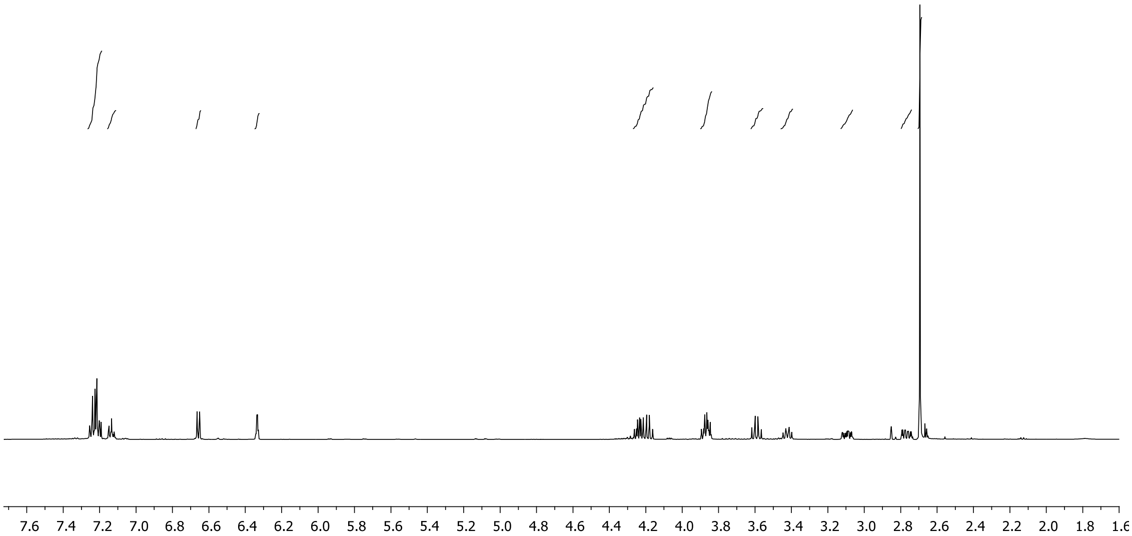
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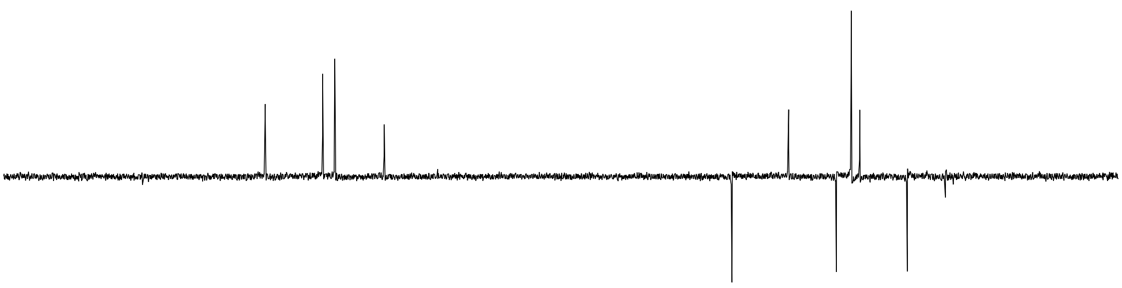

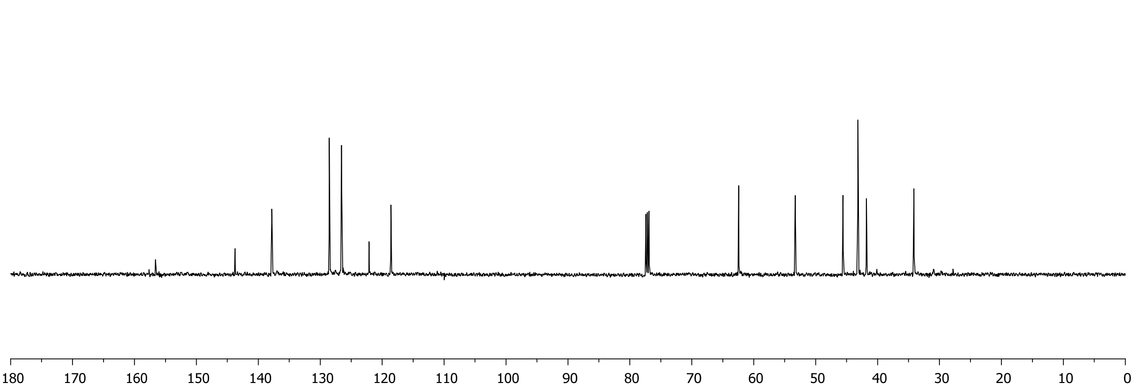
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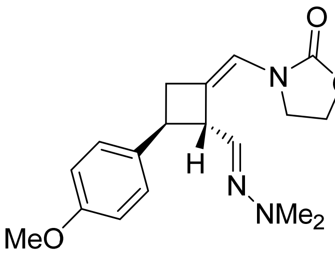
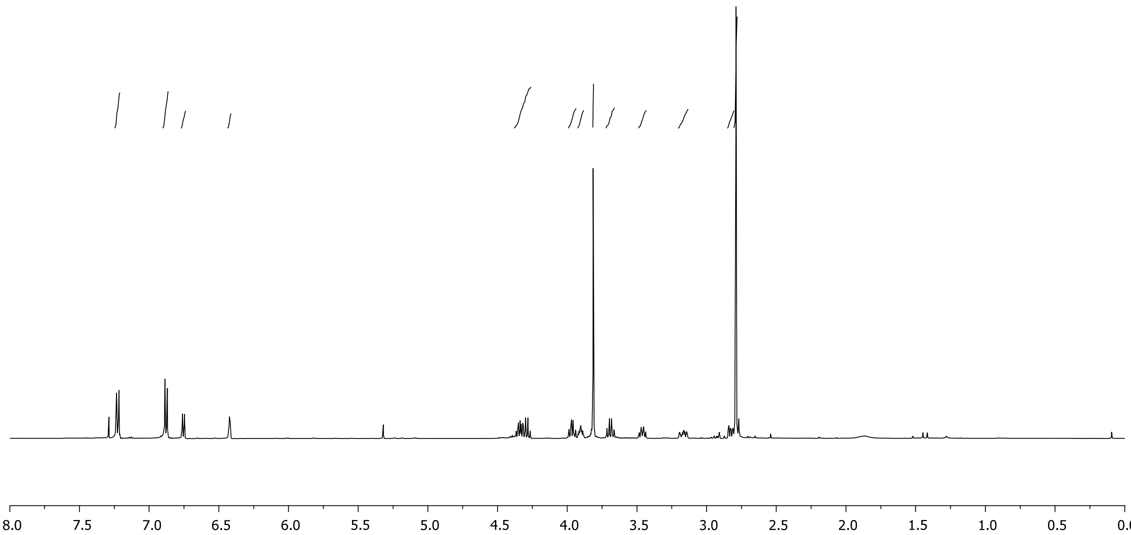

O
N
O
H
N
NMe2
MeO

3ac'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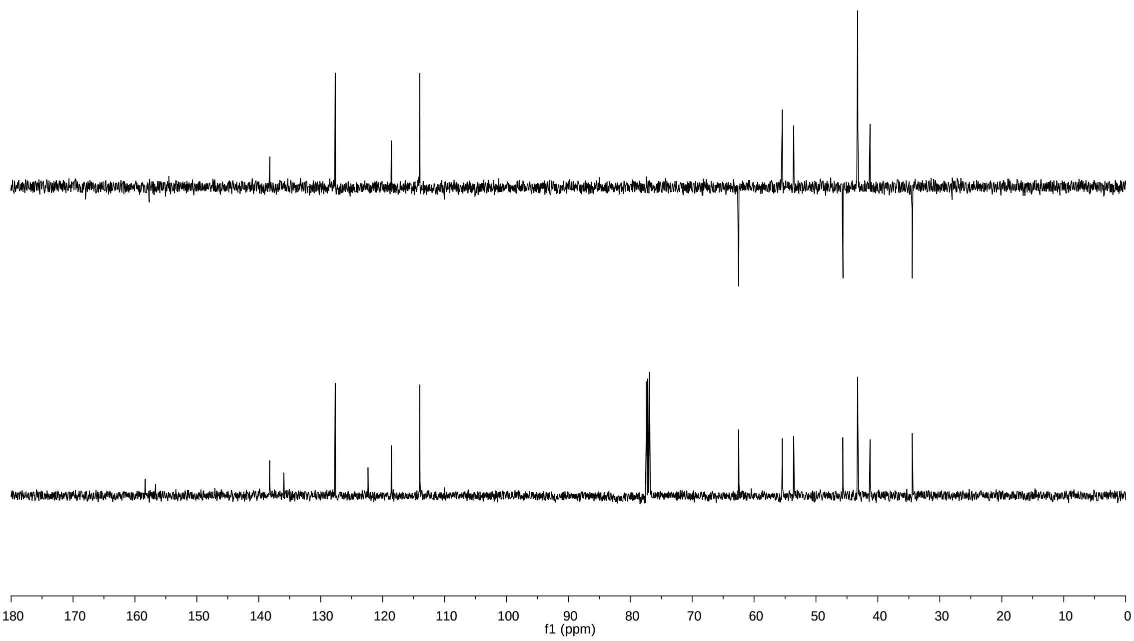
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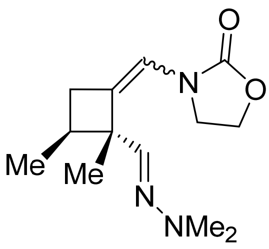
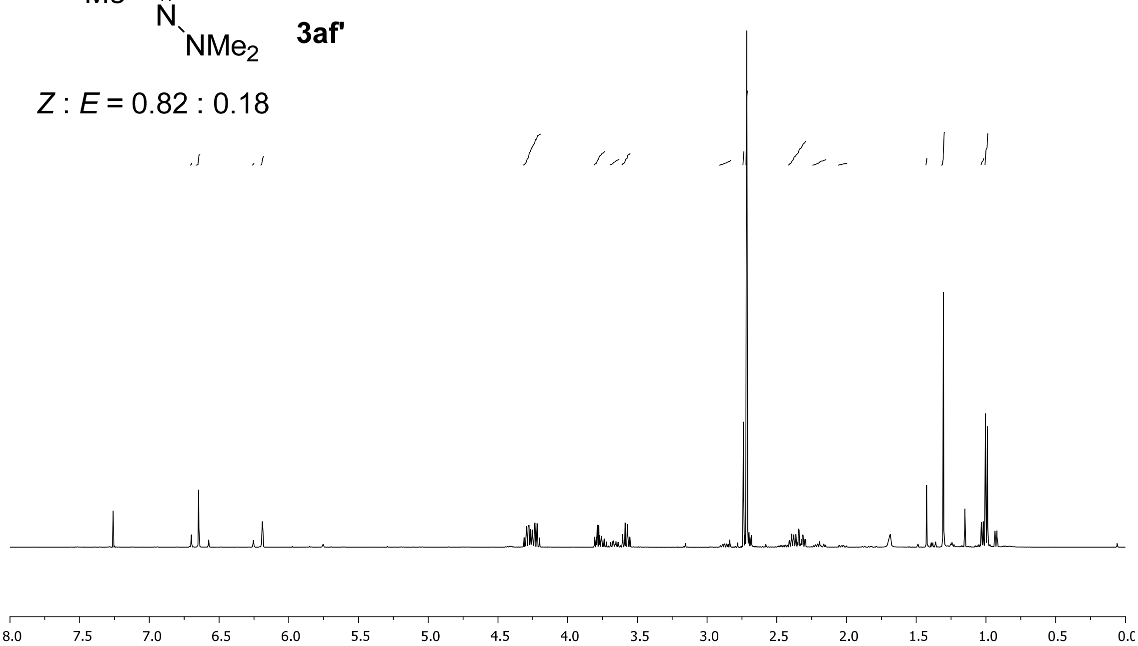
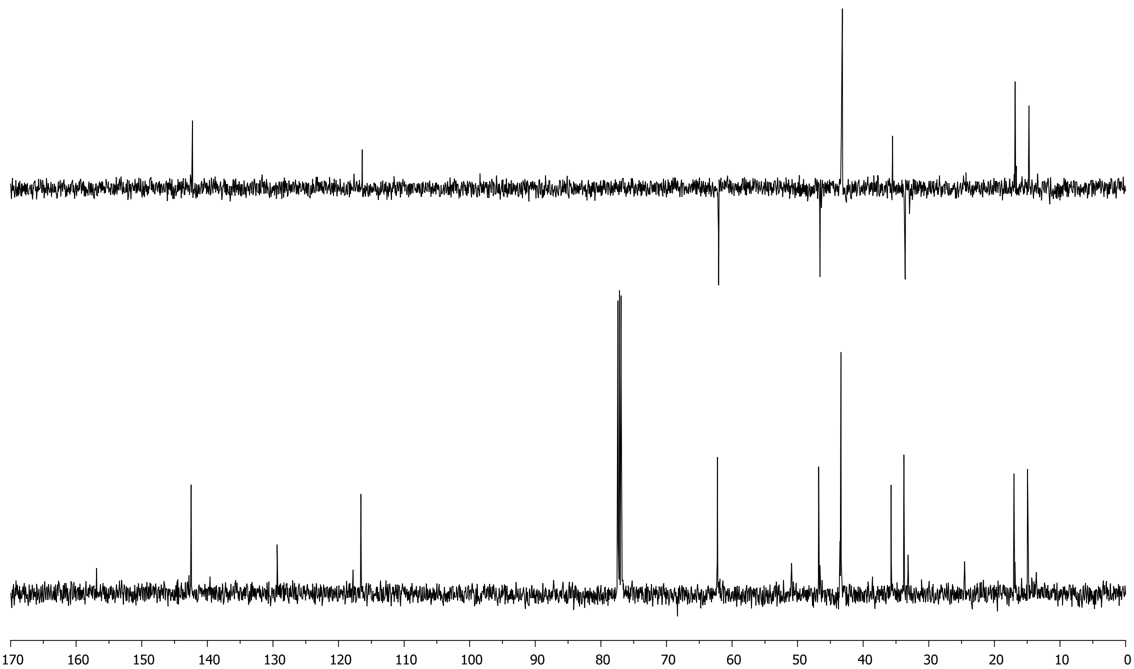
f1 (ppm)

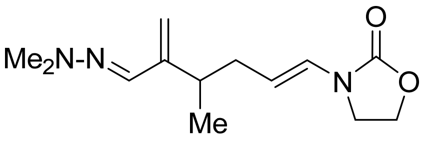


3af'

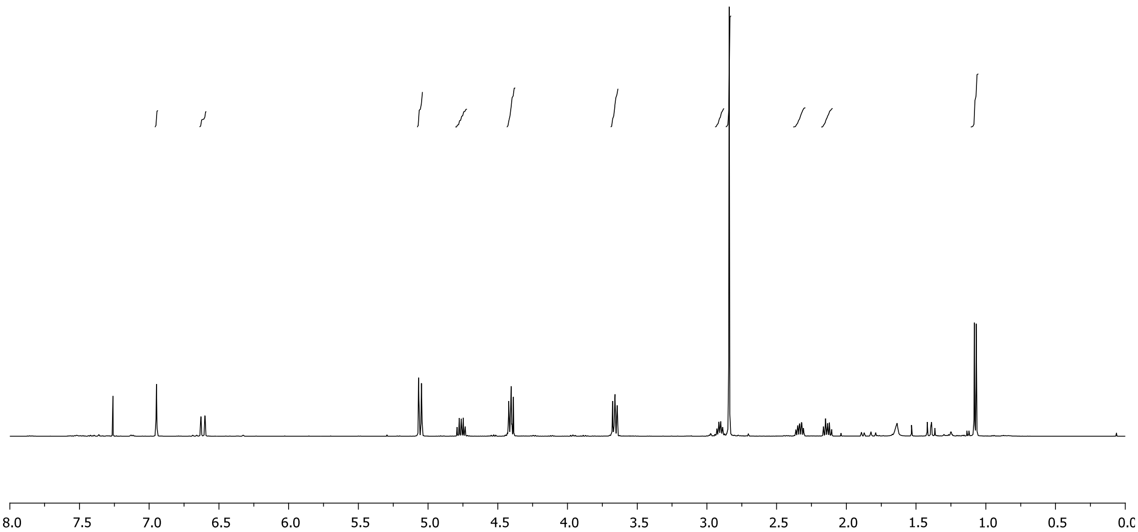
Z : *E* = 0.82 : 0.18






Me2N-N
O
N
O
Me

6af'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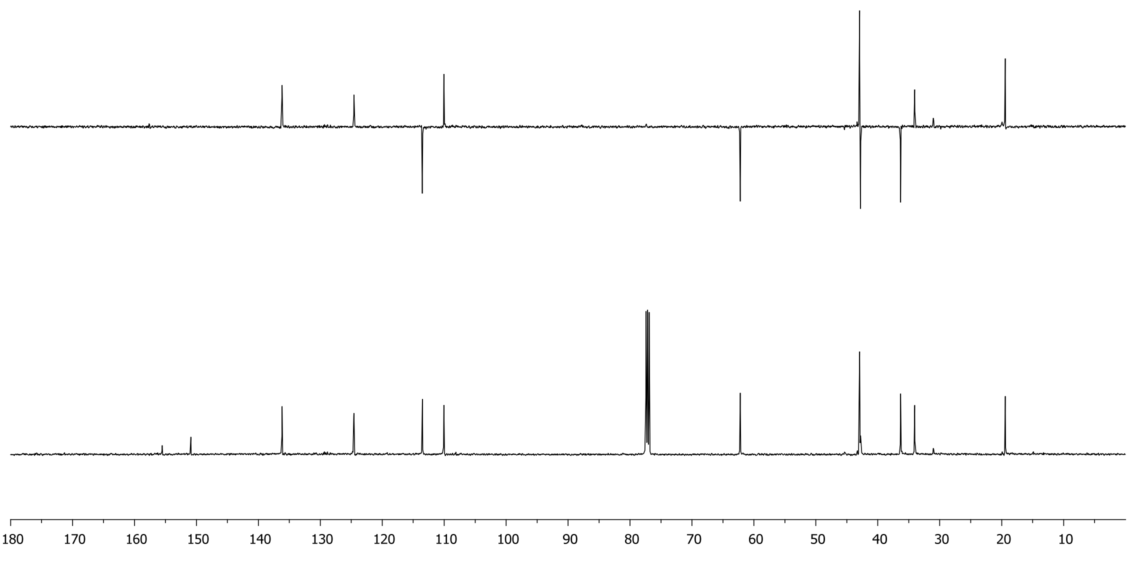
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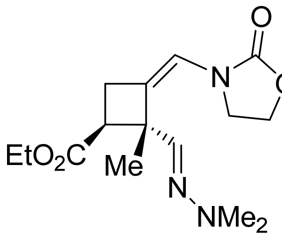
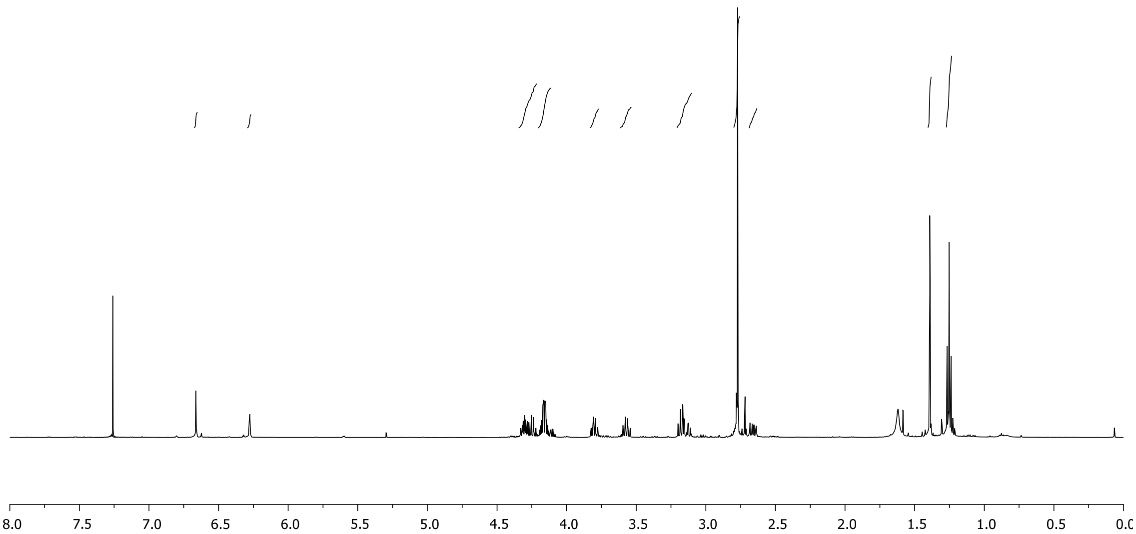

O
N
O
EtO_2C
Me
N
NMe_2

3ak'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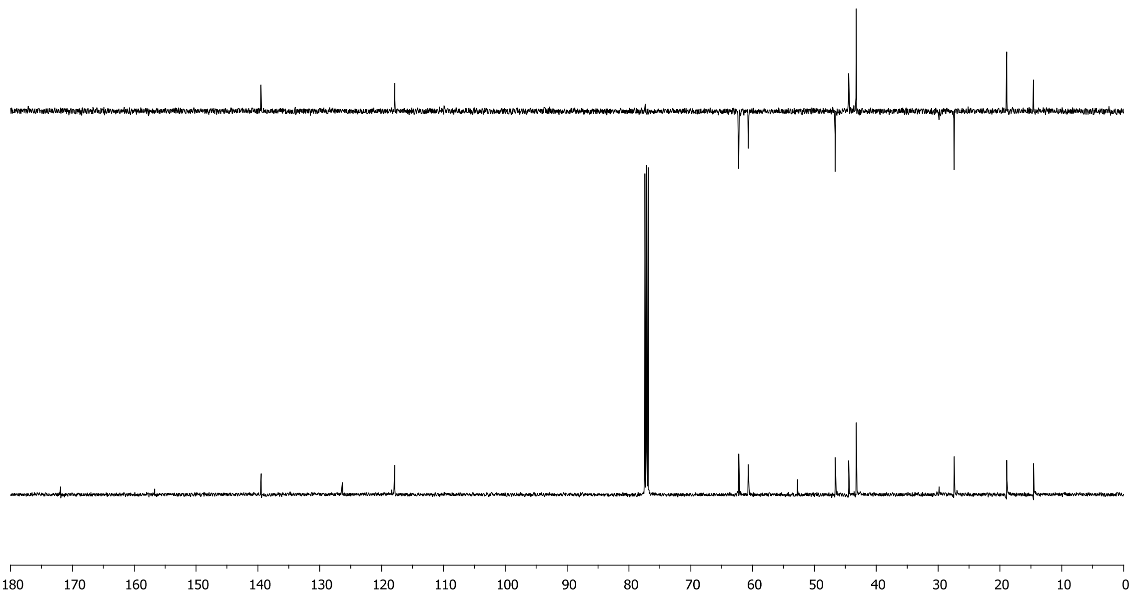
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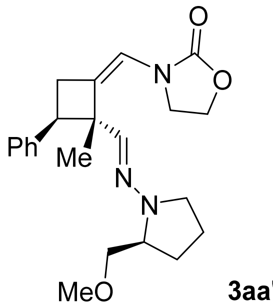
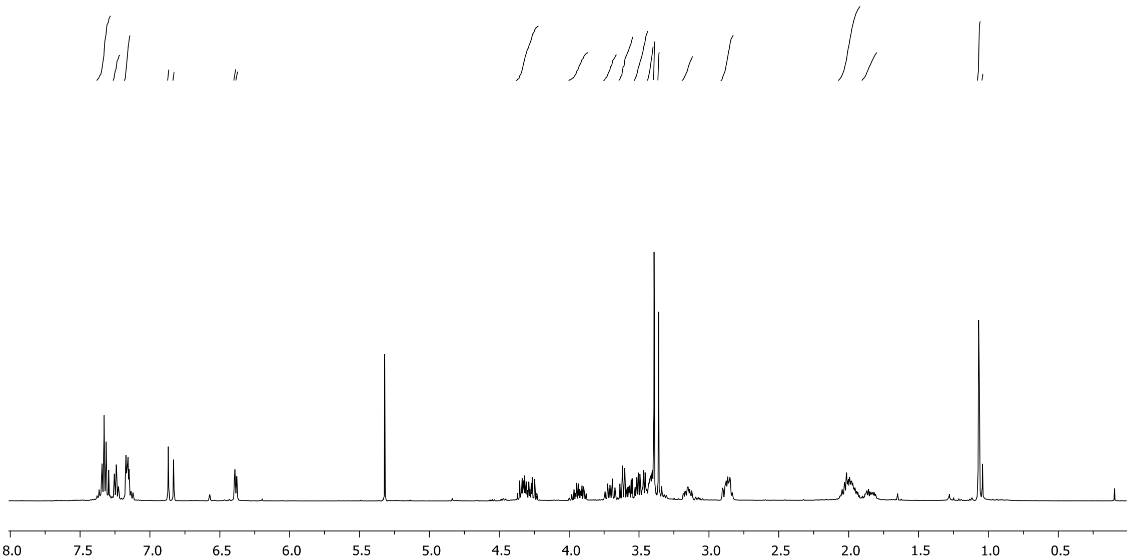
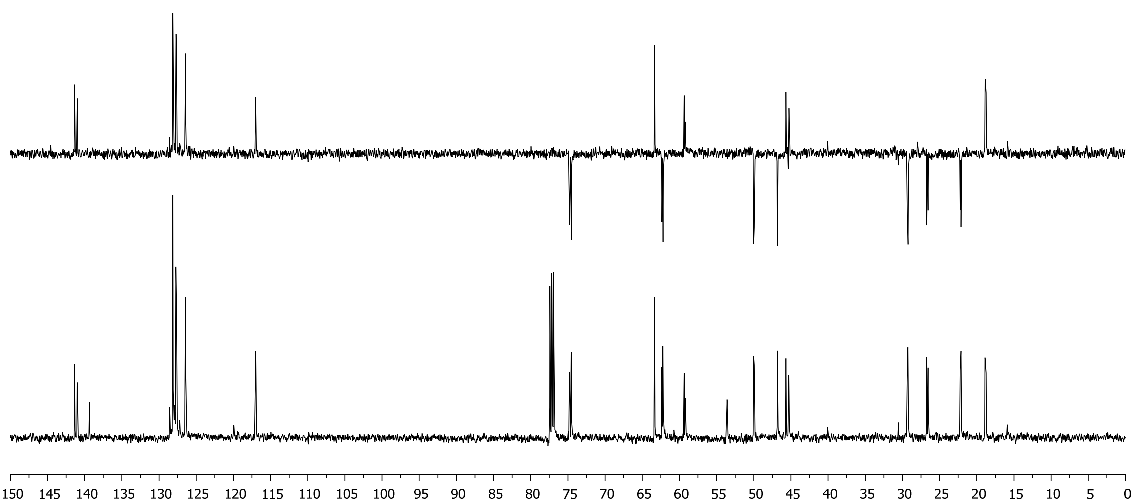
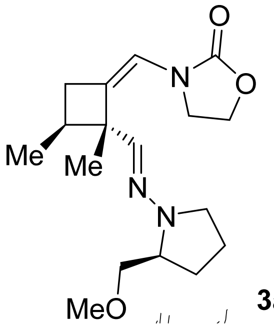


3aa''







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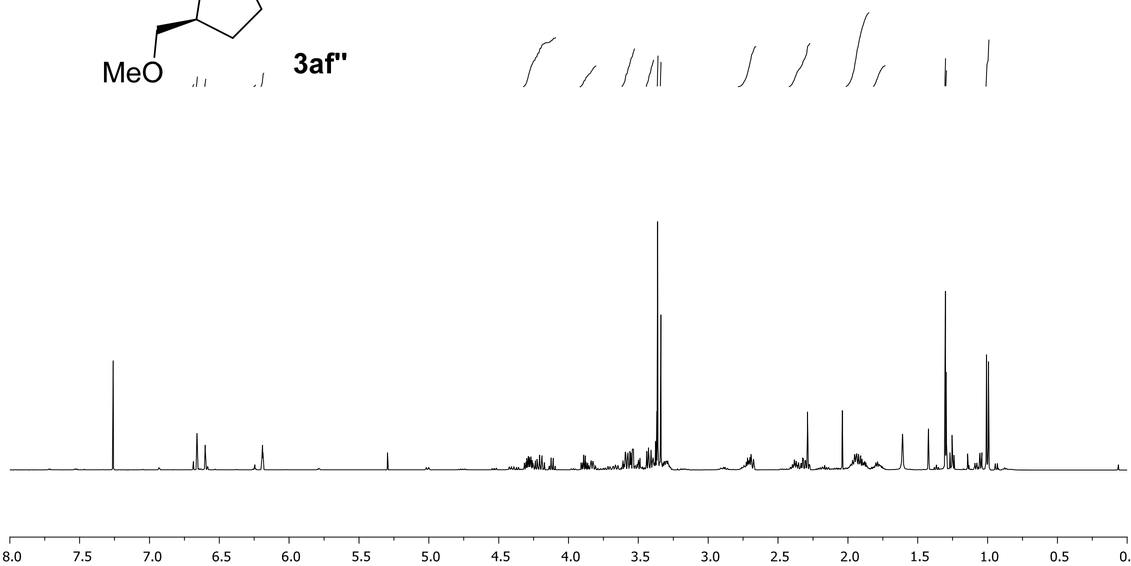

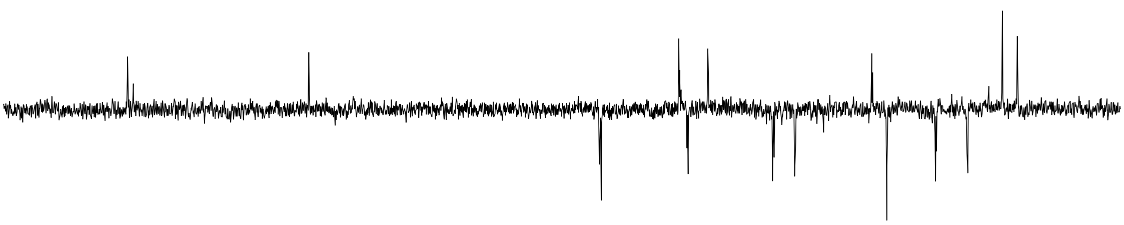

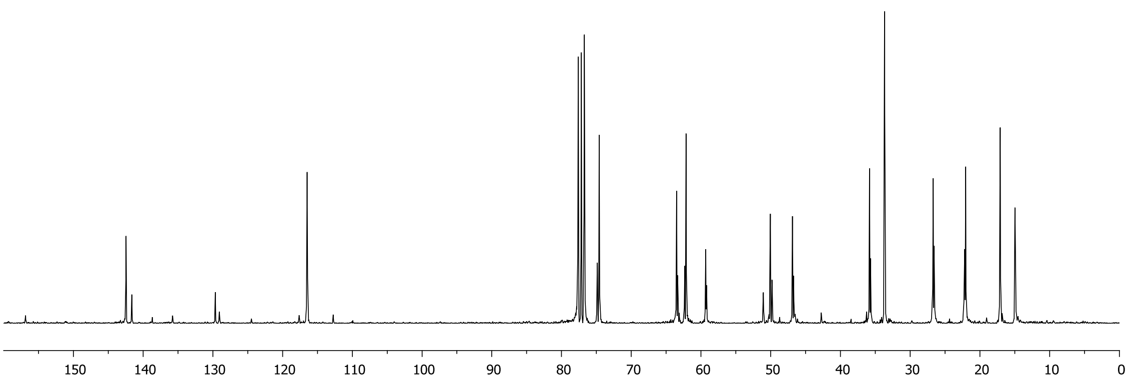

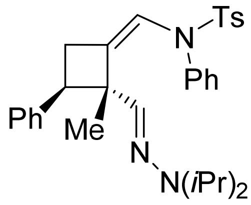

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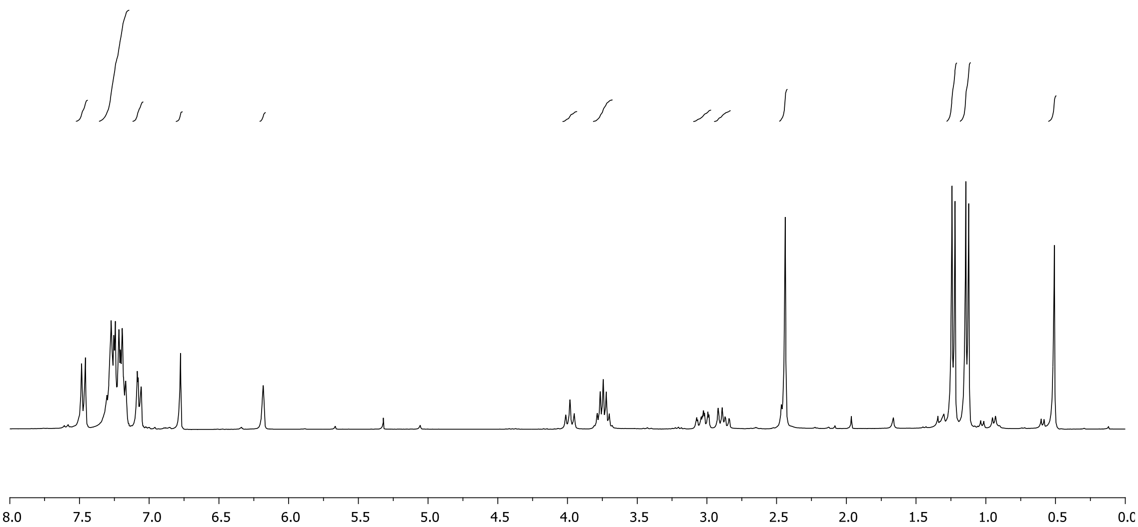

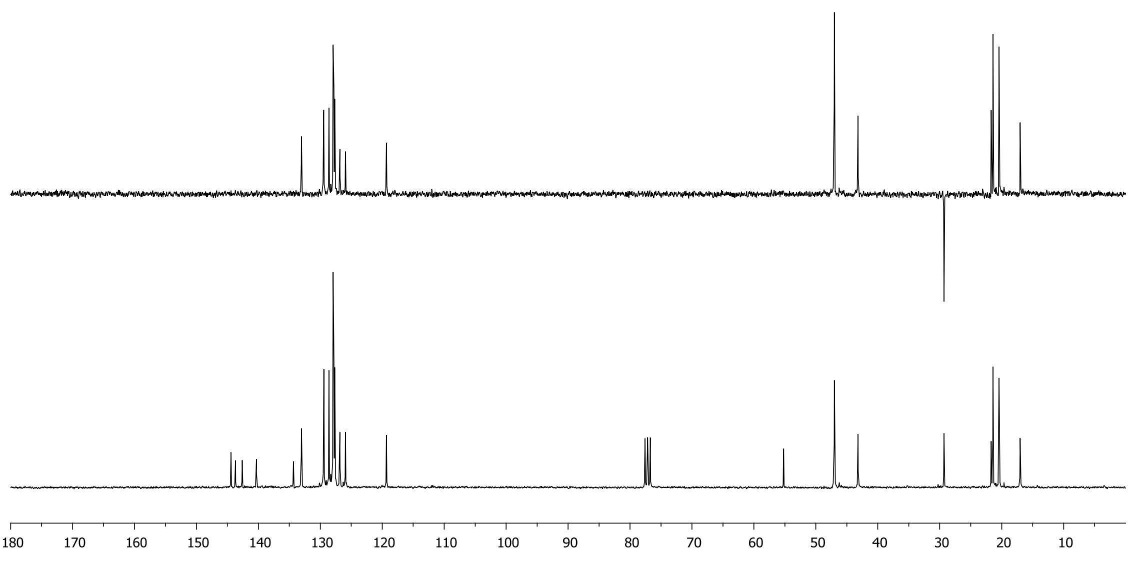

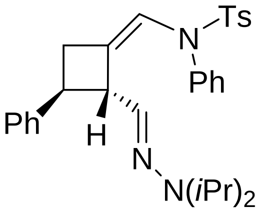
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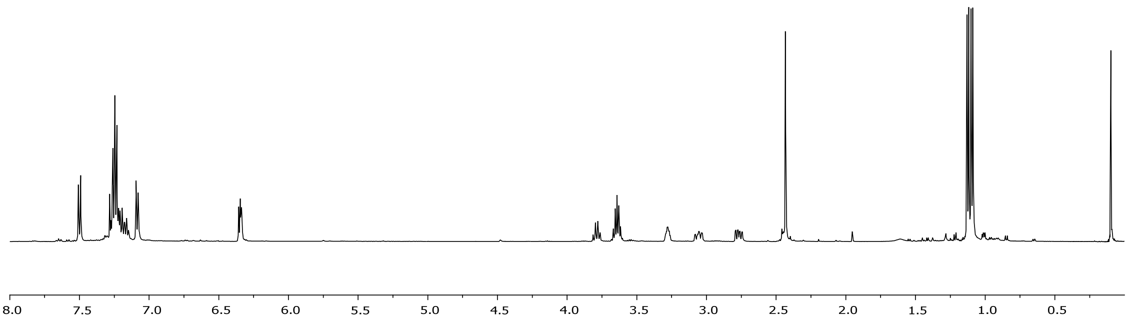
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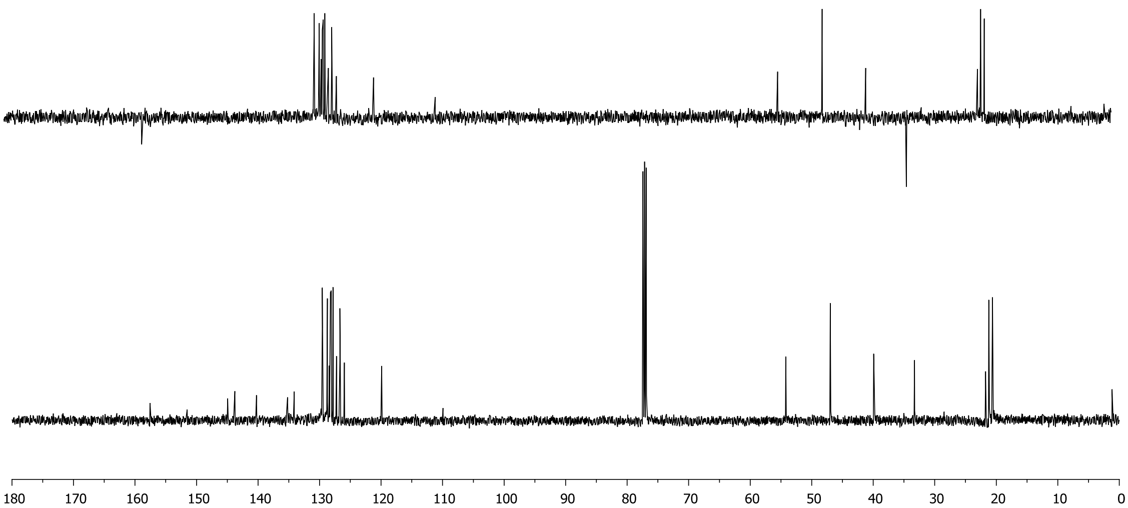
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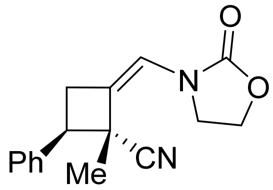
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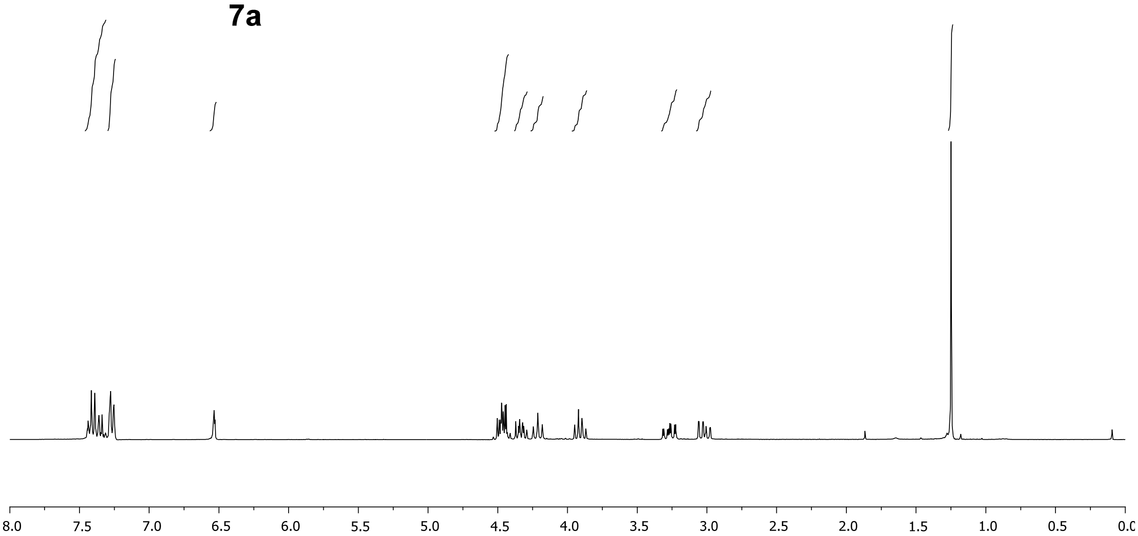
7a


8.0
7.5
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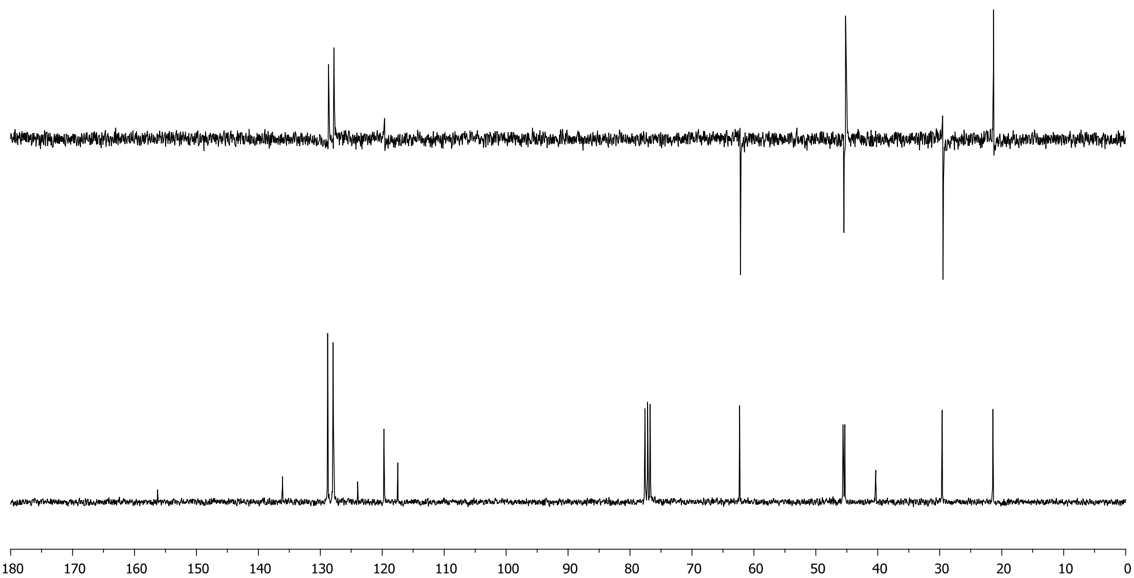
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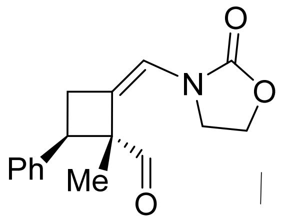
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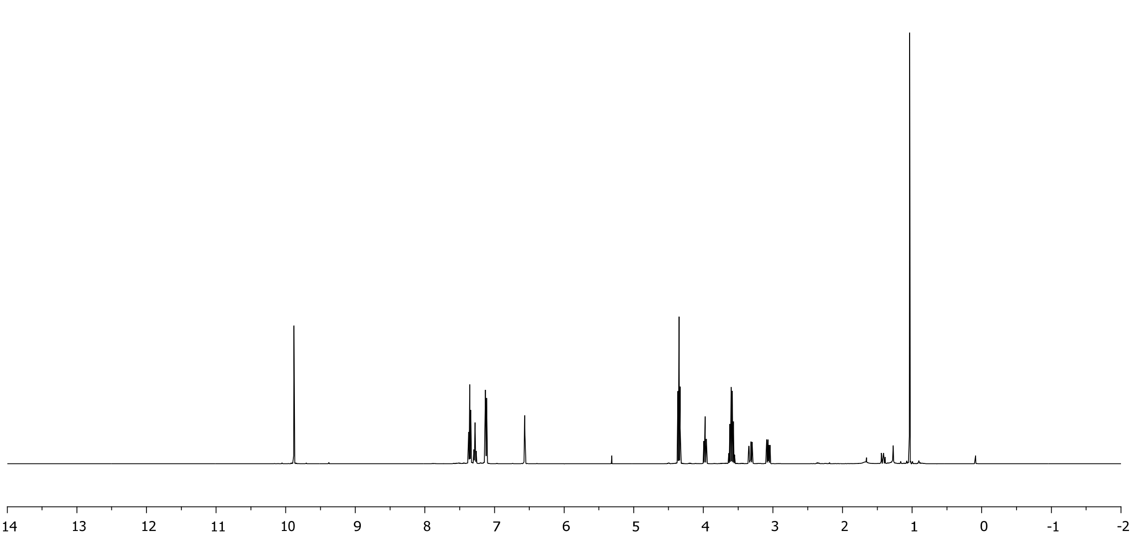

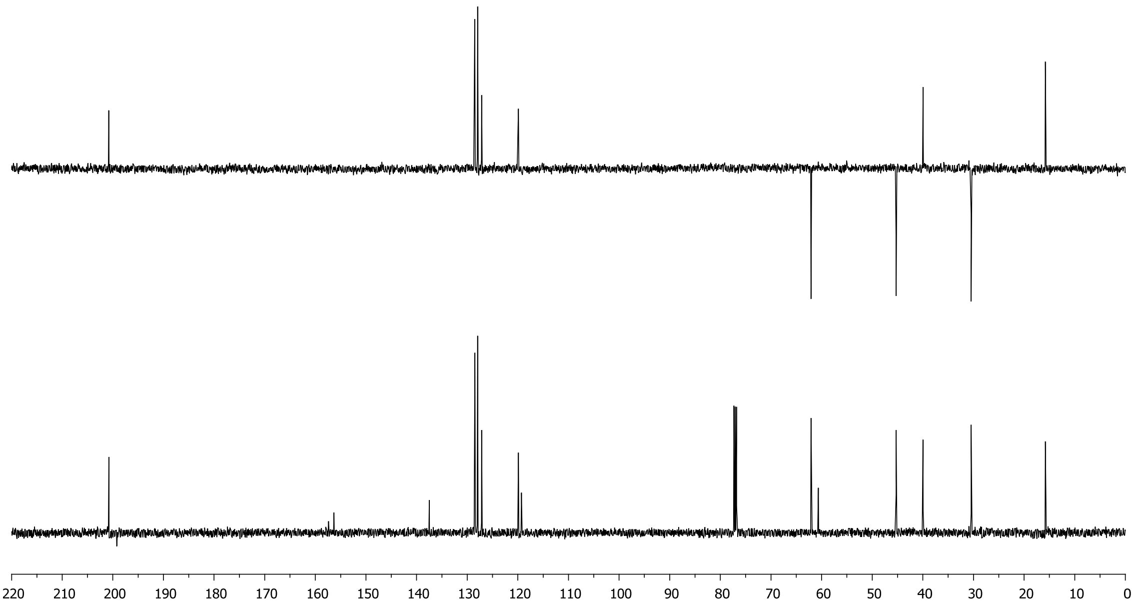

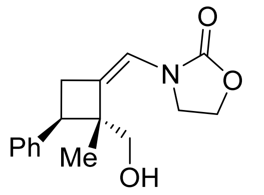

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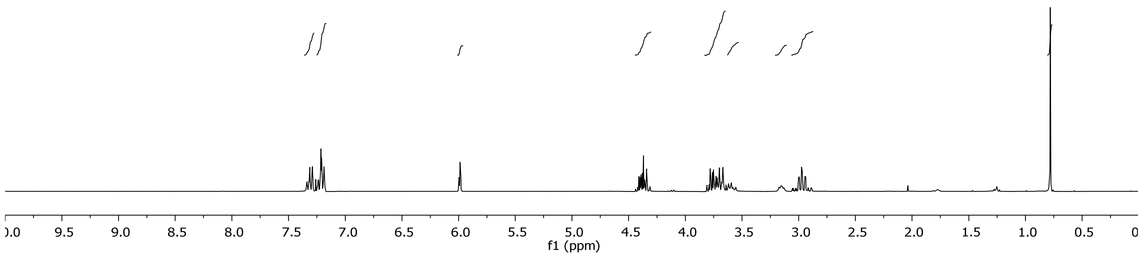

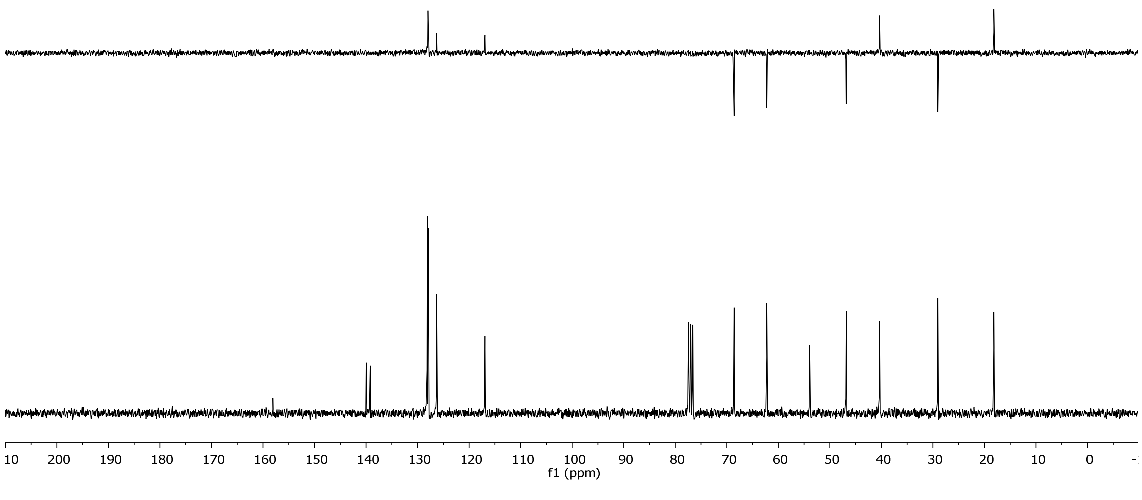

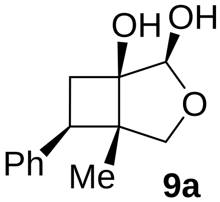

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