Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for:

α-Keto Hydrazones in Asymmetric Aminocatalysis: Reactivity through β-Aza-dienamine Intermediates

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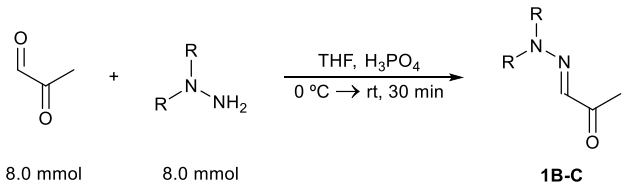
1. General Information

^{1}H NMR spectra were recorded at 300 MHz or 500 MHz (internal reference; $CDCl_3$ = 7.26; CD_2Cl_2 = 5.32; CD_3OD = 4.87; toluene-d_8 = 2.09). ^{13}C NMR spectra were recorded at 75.5 or 126 MHz (internal reference; $CDCl_3$ = 77.0; CD_2Cl_2 = 54.0; CD_3OD = 49.0; toluene-d_8 = 20.4); ^{19}F NMR spectra were recorded at 471 MHz. ^{1}H NMR DOSY spectra were recorded on a Bruker Avance III 500 MHz spectrometer equipped with a 5 mm TCI Z gradient cryoprobe (maximum gradient strength 57.1 G/cm). All diffusion experiments were performed with convection compensated double stimulated echo pulse sequence (dstebpgp3s). The temperature was set and controlled at 298 K with an air flow of 535 l h^{-1}. For each experiment, 16 scans were used, with a relaxation delay of 10 s and a diffusion delay of 120 ms. The shape of the gradients was smoothed square, with lengths between 0.55 and 1 ms, and the strength was varied in 24 increments (2-95%) in a linear ramp. Column chromatography was performed on silica gel (Merck Kieselgel 60). Analytical TLC was performed on aluminum backed plates (1.5 × 5 cm) pre-coated (0.25 mm) with silica gel (Merck, Silica Gel 60 F254). Compounds were visualized by exposure to UV light or by dipping the plates in solutions of $KMnO_4$, vainilline or phosphomolibdic acid stains followed by heating. Melting points were recorded in a metal block and are uncorrected. Optical rotations were measured on a JASCO *P-2000* polarimeter. The enantiomeric excess (*ee*) of the products was determined by chiral stationary phase HPLC (Daicel Chiralpak IA/IB/IC/ID/OD columns). Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. Not commercially available nitroalkenes **2h**,[1] **2g**,[2] **2j**,[3] **2k**[4] and organocatalysts **O2**[5], **O5**,[6] **Ia**[7] were synthesized according to literature procedures. Crystals of suitable size were covered with FOMBLIN oil and mounted on a glass fiber. Data collection has been performed with Bruker SMART APEX II CCD area detector on a D8 goniometer at 100 K, using a graphite monochromator Cu Kα1 (λ=1.54178 Å) and a Bruker Cryo-Flex low-temperature device. Data collection was processed with APEX-W2D-NT,[8] cell refinement and data reduction with SAINT-Plus1 and the absorption was corrected by multiscan method applied by SADABS.[9] The structure was solved by direct method and refined on F^2 (SHELXTL).[10] Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms attached to refined atoms were placed in geometrically idealized positions and refined by using a riding model.

[1] H. Chen, X. Han, N. Qin, L. Wei, Y. Yang, L. Rao, B. Chi, L. Feng, Y. Ren and J. Wan, *Bioorg. Med. Chem.*, 2016, **24**, 1225.
[2] N. S. Kondratyev, A. A. Zemtsov, V. V. Levin, A. D. Dilman and M. I. Struchkova, *Synthesis*, 2012, **44**, 2436.
[3] S. Belot, A. Massaro, A. Tenti, A. Mordini and A. Alexakis, *Org. Lett.*, 2008, **10**, 4557.
[4] O. Bassas, J. Huuskonen, K. Rissanen and A. M. P. Koskinen, *Eur. J. Org. Chem.*, 2009, 1340.
[5] (a) O. Lifchits, M. Mahlau, C. M. Reisinger, A. Lee, C. Farès, I. Polyak, G. Gopakumar, W. Thiel and B. List, *J. Am. Chem. Soc.*, 2013, **135**, 6677; (b) C. Cassani, R. Martín-Rapún, E. Arceo, F. Bravo and P. Melchiorre, *Nature Protocols*, 2013, **8**, 325.
[6] D. R. Li, A. He and J. R. Falck, *Org. Lett.*, 2010, **12**, 1756.
[7] A. G. Wenzel and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2002, **124**, 12964.
[8] APEX2 (version 2009.11_0). Program for Bruker CCD X-ray Difractometer Control, Bruker AXS Inc., Madison, WI, 2009.
[9] SADABS, Bruker (2006). APEX 2. Version 2.1. Bruker Analytical X-ray Solutions, Madison, Wisconsin, USA.
[10] G. M. Sheldrick, SHELXTL, version 6.14. Program for solution and refinement of crystal structures, Universität Göttingen, Germany, 2000.

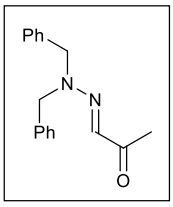
2. General procedure for the synthesis of ketones 1A-D, 4

Procedure A: Starting from free hydrazines

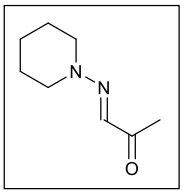


Free hydrazine (8.0 mmol) was dropwise added to a solution of pyruvaldehyde (40% in water, 1.25 mL, 8.0 mmol) and H_3PO_4 (0.39 g, 4.0 mmol) in THF (5 mL) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred until the consumption of the starting material (15-30 minutes, TLC monitoring). After this time, the solvent was eliminated under reduced pressure. The mixture was then neutralized with a saturated solution of $NaHCO_3$ and extracted with Et_2O (3 x 25 mL). The combined organic layers were washed with brine (1 x 50 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (pure *n*-hexanes to *n*-hexanes/EtOAc 3/1) to afford pure product **1B-C**.

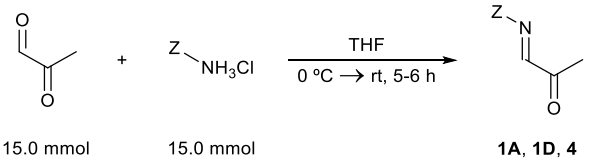
(*E*)-1-(2,2-Dibenzylhydrazineylidene)propan-2-one, 1B. Following the general procedure **2.A**, starting from 1,1-dibenzylhydrazine (1.80 g, 8.0 mmol), compound **1B** was obtained as a light yellow oil (0.81 g, 38%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.37 – 7.29 (m, 6H), 7.19 – 7.16 (m, 4H), 6.69 (s, 1H), 4.63 (s, 4H), 2.34 (s, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 197.7, 135.2, 129.3, 128.8, 127.8, 127.3, 57.7, 24.2. **HRMS** (ESI): m/z calcd for $C_{17}H_{18}ON_2Na$ [M^++Na] 289.1311, found 289.1311.



(*E*)-1-(Piperidin-1-ylimino)propan-2-one, 1C. Following the general procedure **2.A**, starting from piperidin-1-amine (0.89 mL, 8.0 mmol), compound **1C** was obtained as a light yellow oil (0.76 g, 82%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.83 (s, 1H), 3.35 – 3.25 (m, 4H), 2.27 (s, 3H), 1.75 – 1.54 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 198.1, 129.7, 51.0, 24.8, 24.1, 23.5. **HRMS** (ESI): m/z calcd for $C_8H_{14}ON_2Na$ [M^++Na] 177.0998, found 177.0996.



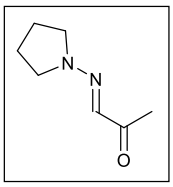
Procedure B: Starting from hydrochloride *N*-nucleophiles



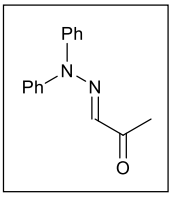
Pyruvaldehyde (40% in water, 2.3 mL, 15.0 mmol) was added to a suspension of hydrochloride *N*-nucleophile (15.0 mmol) in dry THF (30 mL) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred until the consumption of the starting material (5-6 hours, TLC monitoring). After this time, the solvent was eliminated under reduced pressure. The mixture was then diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with a saturated solution of $NaHCO_3$ (1 x 100 mL) and brine (1 x 100 mL), dried over anhydrous $MgSO_4$ and

concentrated under reduced pressure. The resulting residue was purified by flash chromatography (pure *n*-hexanes to *n*-hexanes/EtOAc 6/1) to afford pure product **1A**, **1D**, **4**.

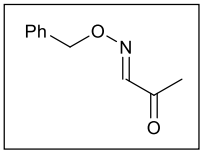
(*E*)-1-(Pyrrolidin-1-ylimino)propan-2-one, 1A. Following the general procedure **2.B**, starting from pyrrolidin-1-amine hydrochloride (2.04 g, 15.0 mmol), compound **1A** was obtained as a pale brown viscous oil (1.72 g, 82%) after liquid-liquid extractions (no flash chromatography was required). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.47 (s, 1H), 3.57 – 3.10 (m, 4H), 2.21 (s, 3H), 2.09 – 1.75 (m, 4H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 197.2, 128.5, 50.4, 23.8, 23.7. **HRMS** (ESI): m/z calcd for $C_7H_{13}ON_2$ [M^++H] 141.1022, found 141.1022.



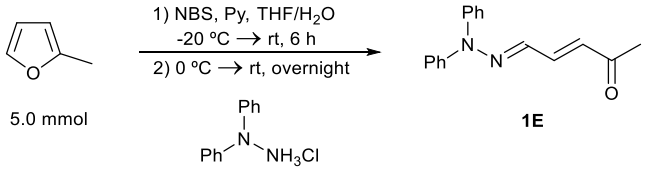
(*E*)-1-(2,2-Diphenylhydrazineylidene)propan-2-one, 1D. Following the general procedure **2.B**, starting from 1,1-diphenylhydrazine hydrochloride (3.41 g, 15.0 mmol), compound **1D** was obtained as a light yellow solid (2.00 g, 57%); mp. = 70-72 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.44 (t, *J* = 7.8 Hz, 4H), 7.33 – 7.23 (m, 2H), 7.21 – 7.14 (m, 4H), 6.63 (s, 1H), 2.50 (s, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 197.9, 142.0, 133.8, 129.9, 126.1, 122.1, 24.7. **HRMS** (ESI): m/z calcd for $C_{15}H_{14}ON_2Na$ [M^++Na] 261.0998, found 261.1001.



(*E*)-2-Oxopropanal *O*-benzyl oxime, 4. Following the general procedure **2.B**, starting from *O*-benzylhydroxylamine hydrochloride (2.42 g, 15.0 mmol), compound **4** was obtained as a white solid (1.12 g, 42%); mp. = 41-43 °C. **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 7.48 (s, 1H), 7.41 – 7.33 (m, 5H), 5.26 (s, 2H), 2.33 (s, 3H). **^{13}C NMR** (75.5 MHz, CD_2Cl_2): δ 196.4, 148.9, 137.0, 129.1, 129.1, 129.0, 78.4, 25.8. **HRMS** (ESI): m/z calcd for $C_{10}H_{12}O_2N$ [M^++H] 178.0863, found 178.0863.

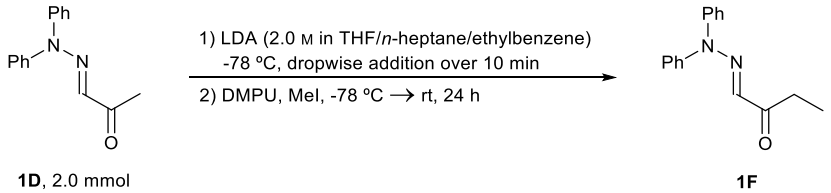


3. Synthesis of (3*E*,5*E*)-5-(2,2-diphenylhydrazineylidene)pent-3-en-2-one (1E)



N-Bromosuccinimide (1.35 g, 7.5 mmol) and pyridine (809 µL, 10 mmol) were subsequently added to a solution of 2-methylfuran (456 µL, 5 mmol) in THF/H_2O (25 mL, 9/1) at −20 °C. The mixture was allowed to warm slowly to room temperature and stirred for 6 hours. After this time, the reaction was cooled to 0 °C and 1,1-diphenylhydrazine hydrochloride (1.14 g, 5.0 mmol) was added in one portion. The resulting mixture was allowed to warm to room temperature and stirred overnight. After this time, the solvent was eliminated under reduced pressure and the mixture was then diluted with CH_2Cl_2 (50 mL), washed with aq. $Na_2S_2O_3$ (3 x 50 mL, 10% w/w) and brine (1 x 50 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (*n*-hexanes/EtOAc 3/1) to afford **1E** as a light yellow solid (0.70 g, 53%); mp. = 130-132 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.49 – 7.34 (m, 5H), 7.30 – 7.20 (m, 2H), 7.20 – 7.11 (m, 4H), 6.92 (d, *J* = 9.3 Hz, 1H), 6.04 (d, *J* = 16.0 Hz, 1H), 2.30 (s, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 198.1, 142.5, 141.4, 134.2, 130.5, 129.8, 125.5, 122.3, 26.8. **HRMS** (ESI): m/z calcd for $C_{17}H_{16}ON_2Na$ [M^++Na] 287.1155, found 287.1154.

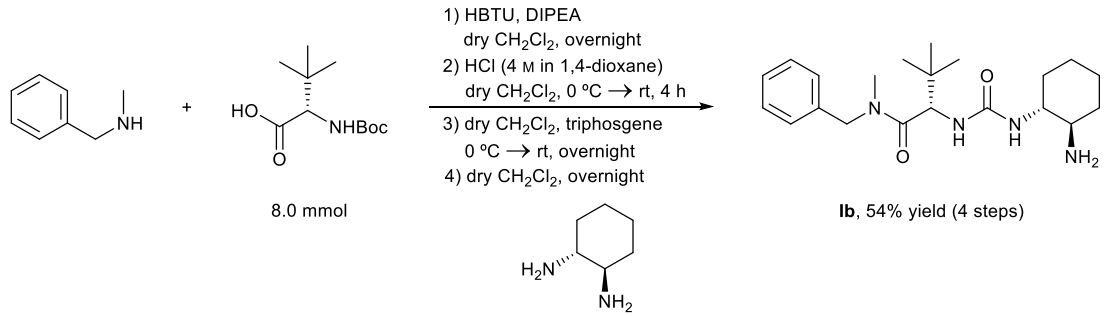
4. Synthesis of (*E*)-1-(2,2-diphenylhydrazineylidene)butan-2-one (1F)



1D, 2.0 mmol **1F**

Lithium diisopropylamide (1.5 mL, 3.0 mmol, 2.0 M in THF/*n*-heptane/ethylbenzene) was dropwise added to a solution of **1D** (476 mg, 2.0 mmol) in dry THF (4.0 mL) at −78 °C. The mixture was stirred at the same temperature over 30 min and then, DMPU (617 µL, 5.0 mmol) and MeI (349 µL, 5.6 mmol) were subsequently added. The resulting mixture was allowed to warm to room temperature and stirred for 48 hours. After this time, aq. HCl (2.0 M, 0.5 mL) and H_2O (15 mL) were subsequently added and the mixture was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with H_2O (50 mL), a saturated solution of $NaHCO_3$ (1 x 50 mL), a saturated solution of $CuSO_4$ (1 x 50 mL) and brine (1 x 50 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (*n*-hexanes to *n*-hexanes/EtOAc 6/1) to afford **1F** as a yellow solid (260 mg, 52%); mp. = 68-70 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.31 (t, *J* = 7.7 Hz, 4H), 7.19 – 7.08 (m, 2H), 7.07 – 7.01 (m, 4H), 6.50 (s, 1H), 2.85 (q, *J* = 7.4 Hz, 1H), 1.06 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 200.9, 142.2, 133.3, 130.0, 126.2, 122.5, 30.2, 8.5. **HRMS** (ESI): m/z calcd for $C_{16}H_{16}ON_2Na$ [M^++Na] 275.1155, found 275.1158.

5. Synthesis of organocatalyst Ib



8.0 mmol **Ib**, 54% yield (4 steps)

Step 1: DIPEA (1.68 mL, 9.6 mmol) and *N*-methyl-1-phenylmethanamine (1.18 mL, 8.8 mmol) were subsequently added to a suspension of HBTU (3.35 g, 8.8 mmol) and (*S*)-2-[(*tert*-butoxycarbonyl)amino]-3,3-dimethylbutanoic acid (1.89 g, 8.0 mmol) in dry CH_2Cl_2 (120 mL) at room temperature. The reaction was stirred overnight. After this time, the reaction was diluted with Et_2O (180 mL) and washed with aq. HCl (2 x 150 mL, 1.0 M), a saturated solution of $NaHCO_3$ (2 x 150 mL) and brine (2 x 150 mL), and the organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to afford *tert*-butyl (*S*)-{1-[benzyl(methyl)amino]-3,3-dimethyl-1-oxobutan-2-yl}carbamate as a yellow oil, which was used in the next step without further purification.

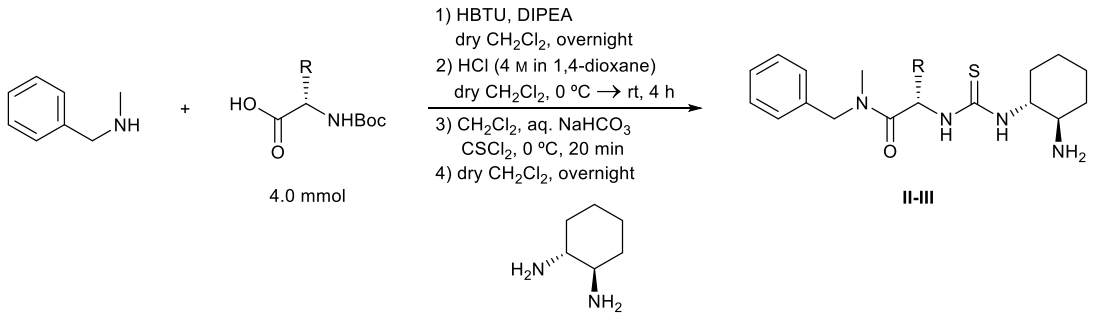
Step 2: HCl (20 mL, 80 mmol, 4.0 M in 1,4-dioxane) was dropwise added to a solution of *tert*-butyl (*S*)-{1-[benzyl(methyl)amino]-3,3-dimethyl-1-oxobutan-2-yl}carbamate (~8 mmol) in dry CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 4 hours. After this time, the reaction was concentrated under reduced pressure to afford (*S*)-2-amino-*N*-benzyl-*N*,3,3-trimethylbutanamide hydrochloride as a pale yellow solid, which was used in the next step without further purification.

Step 3: Triphosgene (3.09 g, 10.4 mmol) was added to a solution of (*S*)-2-amino-*N*-benzyl-*N*,3,3-trimethylbutanamide hydrochloride (~8 mmol) in dry CH_2Cl_2 (40 mL) at room temperature. The reaction

mixture was allowed to warm to room temperature and stirred overnight. After this time, the mixture was diluted with a saturated solution of $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with brine (1 x 100 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to afford (*S*)-*N*-benzyl-2-isocyanato-*N*,3,3-trimethylbutanamide as a yellow oil, which was used in the next step without further purification.

Step 4: (1*R*,2*R*)-Cyclohexane-1,2-diamine (1.39 g, 12.0 mmol) was added to a solution of (*S*)-*N*-benzyl-2-isocyanato-*N*,3,3-trimethylbutanamide (~8 mmol) in dry CH_2Cl_2 (90 mL) at room temperature. The reaction mixture was stirred overnight and then was concentrated under reduced pressure. The resulting residue was purified by flash chromatography (CH_2Cl_2 saturated with ammonia/MeOH 98/2) to afford (*S*)-2-{3-[(1*R*,2*R*)-2-aminocyclohexyl]ureido}-*N*-benzyl-*N*,3,3-trimethylbutanamide (**Ib**) as an off-white solid (1.62 g, 54% in 4 steps). The experimental data is in accordance with those reported in the literature.[11] **^{1}H NMR** (300 MHz, $CDCl_3$): the compound exists as a ~2.9:1 mixture of carbamate rotamers. *Signals corresponding to the major rotamer*: δ 7.35 – 7.26 (m, 3H), 7.24 – 7.16 (m, 2H), 6.02 (d, *J* = 9.6 Hz, 1H), 5.35 (d, *J* = 8.8 Hz, 1H), 5.03 – 4.75 (m, 2H), 4.35 (d, *J* = 15.7 Hz, 1H), 3.28 – 3.11 (m, 1H), 3.08 (s, 3H), 2.25 – 2.11 (m, 1H), 1.95 – 1.74 (m, 4H), 1.69 – 1.54 (m, 2H), 1.34 – 1.05 (m, 4H), 1.01 (s, 9H), 0.98 (s, 9H). *Representative signals corresponding to the minor rotamer*: δ 6.06 (d, *J* = 9.6 Hz, 1H), 5.40 (d, *J* = 8.8 Hz, 1H), 4.37 (d, *J* = 15.7 Hz, 1H), 2.87 (s, 3H).

6. General procedure for the synthesis of organocatalysts II-III



Step 1: DIPEA (0.84 mL, 4.8 mmol) and *N*-methyl-1-phenylmethanamine (0.59 mL, 4.4 mmol) were subsequently added to a suspension of HBTU (1.70 g, 4.4 mmol) and the corresponding *N*-Boc amino acid (4.0 mmol) in dry CH_2Cl_2 (60 mL) at room temperature. The reaction was stirred overnight. After this time, the reaction was diluted with Et_2O (90 mL) and washed with aq. HCl (2 x 75 mL, 1.0 M), a saturated solution of $NaHCO_3$ (2 x 75 mL) and brine (2 x 75 mL), and the organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to afford the corresponding carbamate, which was used in the next step without further purification.

Step 2: HCl (10 mL, 40 mmol, 4.0 M in 1,4-dioxane) was dropwise added to a solution of the corresponding amide (~4 mmol) in dry CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 4 hours. After this time, the reaction was concentrated under reduced pressure to afford the corresponding amine hydrochloride, which was used in the next step without further purification.

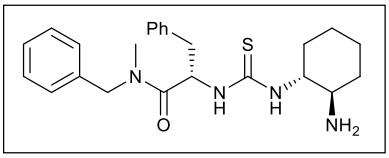
Step 3: A saturated solution of $NaHCO_3$ (40 mL) was added to a solution of the corresponding amine hydrochloride (~4 mmol) in CH_2Cl_2 (40 mL) at 0 °C. The biphasic mixture was stirred for 15 minutes and thiophosgene (336 µL, 4.4 mmol) was added to the organic layer. The resulting mixture was stirred at 0 °C for 20 minutes. After this time, the mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 60 mL). The combined organic layers were washed with H_2O (1 x 100 mL) and brine (1 x 100 mL),

[11] M. P. Lalonde, M. A. McGowan, N. S. Rajapaksa and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2013, **135**, 1891.

dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to afford the corresponding isothiocyanate, which was used in the next step without further purification.

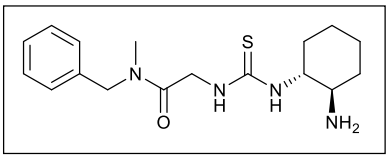
Step 4: (1*R*,2*R*)-Cyclohexane-1,2-diamine (0.70 g, 6.0 mmol) was added to a solution of the corresponding isothiocyanate (~4 mmol) in dry CH_2Cl_2 (45 mL) at room temperature. The reaction mixture was stirred overnight and then was concentrated under reduced pressure. The resulting residue was purified by flash chromatography (CH_2Cl_2 saturated with ammonia/MeOH 95/5) to afford the organocatalysts **II-III**.

(*S*)-2-{3-[(1*R*,2*R*)-2-Aminocyclohexyl]thioureido}-*N*-benzyl-*N*-methyl-3-phenylpropanamide (II).

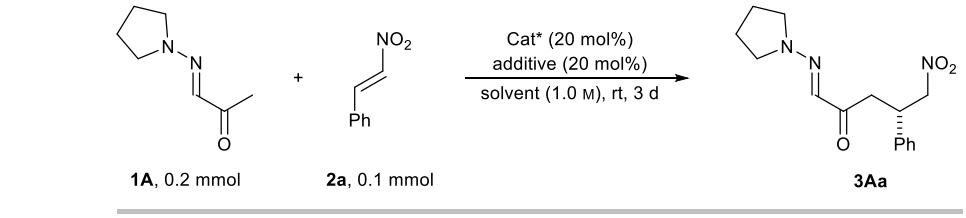


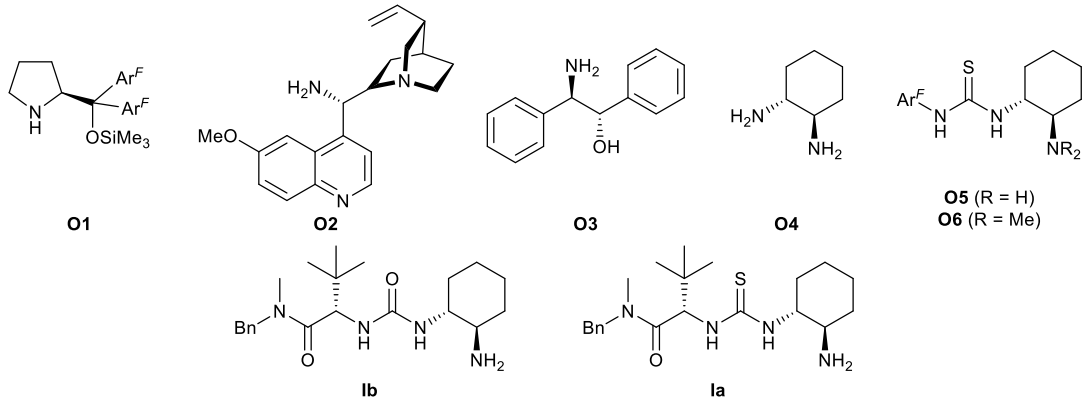
Following the general procedure **6**, starting from (*tert*-butoxycarbonyl)-L-phenylalanine (1.06 g, 4.0 mmol), compound **II** was obtained as a white solid (1.02 g, 60% in 4 steps); mp. = 66-68 °C. **^{1}H NMR** (500 MHz, CD_3OD): the compound exists as a ~2.6:1 mixture of carbamate rotamers. *Signals corresponding to the major rotamer*: δ 7.33 – 7.21 (m, 8H), 7.20 – 7.10 (m, 3H), 5.60 (t, *J* = 7.0 Hz, 1H), 4.61 (d, *J* = 15.0 Hz, 1H), 4.41 (d, *J* = 15.0 Hz, 1H), 4.07 (br s, 1H), 3.06 (d, *J* = 7.1 Hz, 2H), 2.80 (s, 3H), 2.51 – 2.39 (m, 1H), 2.06 – 1.88 (m, 2H), 1.80 – 1.64 (m, 2H), 1.39 – 1.08 (m, 4H), 0.93 – 0.83 (m, 1H). *Representative signals corresponding to the minor rotamer*: δ 5.75 (t, *J* = 7.0 Hz, 1H), 4.57 (d, *J* = 15.0 Hz, 1H), 4.47 (d, *J* = 15.0 Hz, 1H), 2.98 (d, *J* = 7.1 Hz, 2H), 2.83 (s, 3H). **^{13}C NMR** (126 MHz, CD_3OD): *signals corresponding to both rotamers*: δ 174.6, 174.4, 138.1, 137.8, 137.7, 130.5, 129.8, 129.6, 129.6, 129.5, 129.0, 128.7, 128.4, 128.1, 127.9, 61.2, 61.1, 56.7, 56.3, 56.3, 54.3, 52.3, 40.0, 39.6, 35.4, 34.8, 34.7, 34.4, 33.0, 26.1, 25.9. **HRMS** (ESI): m/z calcd for $C_{24}H_{33}ON_4S$ [M^++H] 425.2370, found 425.2362. $[\alpha]_D^{20}$ = +38.2 (c 0.5, $CHCl_3$).

2-{3-[(1*R*,2*R*)-2-Aminocyclohexyl]thioureido}-*N*-benzyl-*N*-methylacetamide (III). Following the general procedure **6**, starting from (*tert*-butoxycarbonyl)glycine (0.70 g, 4.0 mmol), compound **III** was obtained as a white solid (0.73 g, 55% in 4 steps); mp. = 51-53 °C. **^{1}H NMR** (500 MHz, CD_3OD): the compound exists as a ~1.7:1 mixture of carbamate rotamers. *Signals corresponding to the major rotamer*: δ 7.42 – 7.22 (m, 5H), 4.70 – 4.32 (m, 4H), 4.11 (s, 1H), 2.99 (s, 3H), 2.60 – 2.45 (m, 1H), 2.08 – 1.92 (m, 2H), 1.82 – 1.66 (m, 2H), 1.41 – 1.12 (m, 5H). *Representative signals corresponding to the minor rotamer*: δ 2.93 (s, 3H). **^{13}C NMR** (126 MHz, CD_3OD): *signals corresponding to both rotamers*: δ 171.1, 138.1, 137.6, 130.0, 129.7, 128.8, 128.8, 128.5, 128.0, 61.2, 56.2, 53.4, 52.1, 46.9, 34.8, 34.3, 34.3, 33.0, 26.1, 26.0. **HRMS** (ESI): m/z calcd for $C_{17}H_{27}ON_4S$ [M^++H] 335.1880, found 335.1875. $[\alpha]_D^{20}$ = +31.7 (c 0.5, $CHCl_3$).



7. Screening of chiral organocatalysts and preliminary optimization of the reaction parameters





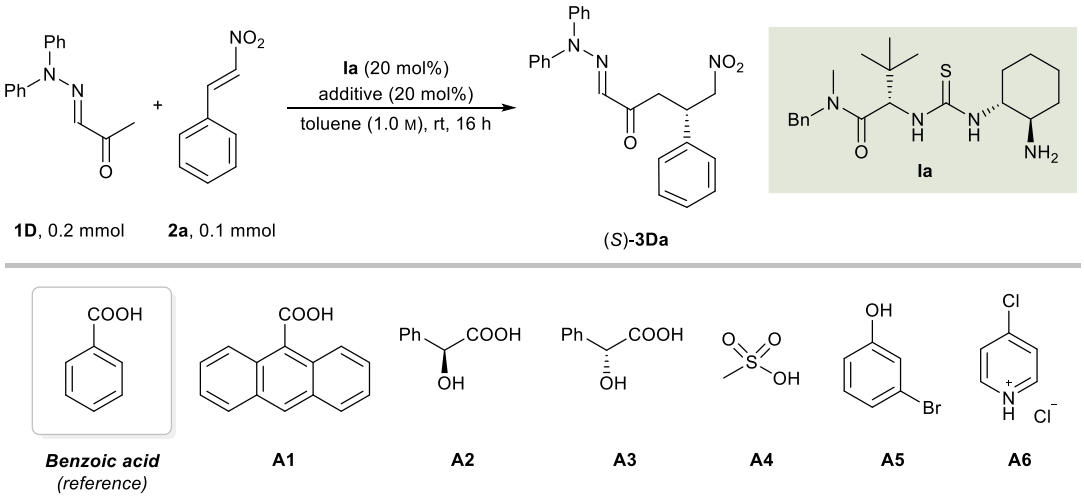
The corresponding solvent (1.0 M, 100 µL) was added to mixture of ketone **1A** (28 mg, 0.2 mmol), nitroalkene **2a** (15 mg, 0.1 mmol), the corresponding organocatalyst (0.04 mmol) and additive (0.04 mmol) at room temperature. The resulting mixture was stirred at this temperature for 3 days. Conversions were determined by ^{1}H-NMR and enantiomeric ratios were determined by HPLC analysis.

Table S1

Entry	Catalyst	Additive	Solvent	Conv. (%)[a]	ee (%)[b]
1[c]	**Pyrrolidine**	$PhCO_2H$	Toluene	17 (29)	-
2	**O1**	$PhCO_2H$	Toluene	nr	nd
3	**O2**	$PhCO_2H$	Toluene	25	50
4	**O3**	$PhCO_2H$	Toluene	<5	nd
5	**O4**	$PhCO_2H$	Toluene	10	29
6	**O5**	$PhCO_2H$	Toluene	nr	nd
7	**O6**	-	Toluene	nr	nd
8	**Ib**	$PhCO_2H$	Toluene	8	90
9	**Ia**	$PhCO_2H$	Toluene	**47**	**95**
10	**Ia**	$PhCO_2H$	$CF_3C_6H_5$	37	95
11	**Ia**	$PhCO_2H$	1,3-$(CF_3)_2C_6H_4$	22	95
12	**Ia**	$PhCO_2H$	THF	18	94
13	**Ia**	$PhCO_2H$	CH_3CN	12	96
14	**Ia**	$PhCO_2H$	^{i}PrOH	<5	nd
15	**Ia**	$PhCO_2H$	$CHCl_3$	34	95
16	**Ia**	$PhCO_2H$	$ClCH_2CH_2Cl$	36	95
17	**Ia**	*m*-OMe-C_6H_4-CO_2H	Toluene	37	94
18	**Ia**	*m*-Cl-C_6H_4-CO_2H	Toluene	28	94
19	**Ia**	*p*-NO_2-C_6H_4-CO_2H	Toluene	21	95
20	**Ia**	C_6F_5-CO_2H	Toluene	nr	nd
21	**Ia**	Phenol	Toluene	<5	nd
22	**Ia**	Et_3N	Toluene	15	94
23	**Ia**	-	Toluene	nr	nd

[a] Determined by ^{1}H NMR in the crude mixture. [b] Determined by HPLC analysis after isolation of the product by semipreparative TLC (*n*-hexanes/EtOAc 3/1). [c] In parenthesis conversion after 7 days. [nr = no reaction; nd = not determined].

8. Control experiments using different additives



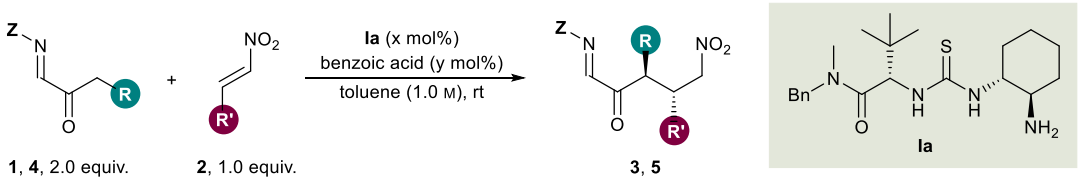
Toluene (1.0 M, 100 µL) was added to mixture of ketone **1D** (48 mg, 0.2 mmol), nitroalkene **2a** (15 mg, 0.1 mmol), organocatalyst **Ia** (8 mg, 0.04 mmol) and the corresponding additive (0.04 mmol) at room temperature. The resulting mixture was stirred at this temperature for 16 h. Conversions were determined by ^{1}H-NMR and enantiomeric ratios were determined by HPLC analysis.

Table S2

Entry	Additive	Conv. (%)[a]	ee (%)[b]
1	**Benzoic acid**	>95	>99
2[c]	**A1**	nr	nd
3	**A2**	33	98
4	**A3**	26	97
5	**A4**	<5	nd
6	**A5**	55	96
7	**A6**	<5	nd

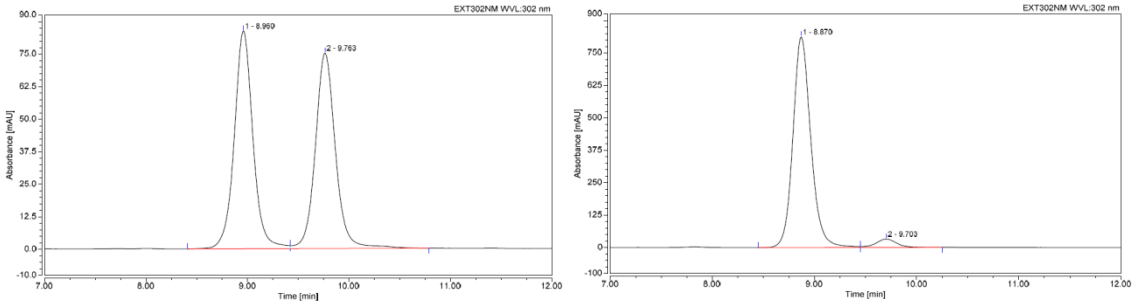
[a] Determined by ^{1}H NMR in the crude mixture. [b] Determined by HPLC analysis after isolation of the product by semipreparative TLC (*n*-hexanes/EtOAc 5/1). [c] Anthracene-9-carboxylic acid was not soluble in the reaction mixture. [nr = no reaction; nd = not determined].

9. General procedure for the catalytic stereoselective reactions of ketones 1A-D, 1F, 4 with nitroalkenes 2



Toluene (1.0 M) was added to mixture of the corresponding ketone **1A-D**, **1F**, **4** (2.0 equiv.), nitroalkene **2** (1.0 equiv.), catalyst **Ia** (x mol%) and benzoic acid (y mol%) at room temperature. The resulting mixture was stirred at this temperature until the consumption of the starting material. After this time, the resulting crude mixture was directly purified by flash chromatography (*n*-hexanes/EtOAc or toluene/EtOAc) to afford pure product **3**, **5**.

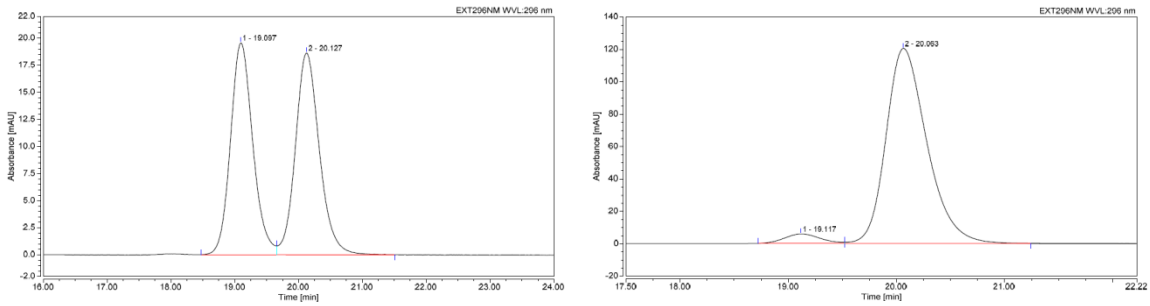
(*S*,*E*)-5-Nitro-4-phenyl-1-(pyrrolidin-1-ylimino)pentan-2-one, (*S*)-**3Aa**. Following the general procedure **9**, starting from **1A** (56 mg, 0.4 mmol), nitroalkene **2a** (30 mg, 0.2 mmol), 20 mol% of **Ia** (16 mg, 0.04 mmol) and 20 mol% of benzoic acid (4.9 mg, 0.04 mmol), compound (*S*)-**3Aa** was obtained as a pale yellow solid (35 mg, 60%; reaction ran for 7 days); mp. = 99-101 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.28 – 7.11 (m, 5H), 6.42 (s, 1H), 4.69 (dd, *J* = 12.5, 6.5 Hz, 1H), 4.56 (dd, *J* = 12.5, 8.5 Hz, 1H), 4.02 (dq, *J* = 8.5, 6.5 Hz, 1H), 3.44 – 3.23 (m, 4H), 3.17 (dd, *J* = 16.0, 6.5 Hz, 1H), 2.97 (dd, *J* = 16.0, 8.3 Hz, 1H), 2.06 – 1.81 (m, 4H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 195.5, 139.7, 128.7, 127.9, 127.5, 127.5, 79.9, 40.0, 39.2, 23.8. **HRMS** (ESI): m/z calcd for $C_{15}H_{20}O_3N_3$ [M^++H] 290.1499, found 290.1506. The enantiomeric excess was determined by HPLC using a Chiralpak IA column [*n*-hexanes/^{i}PrOH (80:20)]; flow rate 1 mL/min; τ_{major} = 8.9 min, τ_{minor} = 9.7 min (91% ee); $[\alpha]_D^{20}$ = −82.6 (c 1.0, $CHCl_3$).



No.	Retention Time min	Area mAU*min	Relative Area %
1	8.960	17.847	50.87
2	9.763	17.239	49.13

No.	Retention Time min	Area mAU*min	Relative Area %
1	8.870	165.029	95.56
2	9.703	7.662	4.44

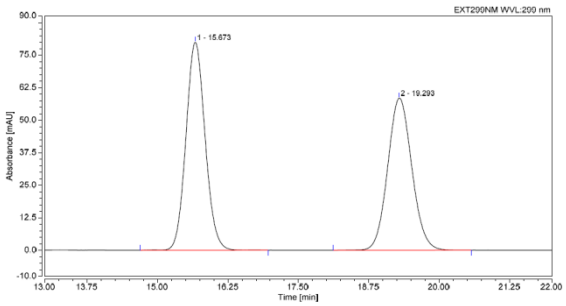
(*S*,*E*)-1-(2,2-Dibenzylhydrazineylidene)-5-nitro-4-phenylpentan-2-one, (*S*)-**3Ba**. Following the general procedure **9**, starting from **1B** (106 mg, 0.4 mmol), nitroalkene **2a** (30 mg, 0.2 mmol), 20 mol% of **Ia** (16 mg, 0.04 mmol) and 10 mol% of benzoic acid (2.4 mg, 0.02 mmol), compound (*S*)-**3Ba** was obtained as a brown oil (57 mg, 69%; reaction ran for 3 days). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.40 – 7.20 (m, 11H), 7.16 – 7.07 (m, 4H), 6.62 (s, 1H), 4.74 (dd, *J* = 12.4, 7.0 Hz, 1H), 4.68 – 4.55 (m, 5H), 4.16 – 4.02 (m, 1H), 3.34 (dd, *J* = 15.8, 7.0 Hz, 1H), 3.06 (dd, *J* = 15.8, 7.0 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 196.0, 139.4, 134.9, 128.9, 128.8, 128.5, 128.0, 127.6, 127.5, 127.3, 79.9, 40.2, 39.4. **HRMS** (ESI): m/z calcd for $C_{25}H_{25}O_3N_3Na$ [M^++Na] 438.1788, found 438.1782. The enantiomeric excess was determined by HPLC using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 20.1 min, τ_{minor} = 19.1 min (92% ee); $[\alpha]_D^{20}$ = −33.3 (c 0.5, $CHCl_3$).

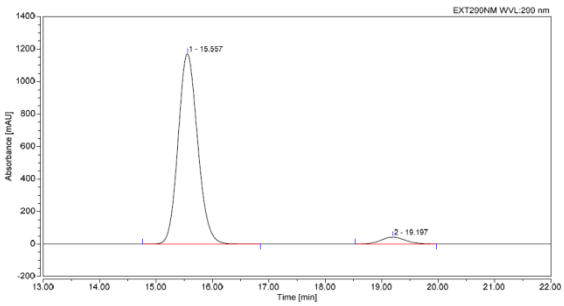


No.	Retention Time min	Area mAU*min	Relative Area %
1	19.097	7.918	49.31
2	20.127	8.138	50.69

No.	Retention Time min	Area mAU*min	Relative Area %
1	19.117	2.227	4.04
2	20.063	52.858	95.96

(*S*,*E*)-1-(2,2-Dibenzylhydrazineylidene)-5-nitro-4-(*p*-tolyl)pentan-2-one, (*S*)-**3Bb**. Following the general procedure **9**, starting from **1B** (106 mg, 0.4 mmol), nitroalkene **2b** (33 mg, 0.2 mmol), 20 mol% of **Ia** (16 mg, 0.04 mmol) and 10 mol% of benzoic acid (2.4 mg, 0.02 mmol), compound (*S*)-**3Bb** was obtained as a colorless oil (74 mg, 86%; reaction ran for 3 days). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.36 – 7.14 (m, 7H), 7.11 – 6.99 (m, 7H), 6.54 (s, 1H), 4.63 (dd, *J* = 12.3, 6.5 Hz, 1H), 4.58 – 4.42 (m, 5H), 4.04 – 3.89 (m, 1H), 3.24 (dd, *J* = 15.8, 7.0 Hz, 1H), 2.96 (dd, *J* = 15.8, 7.0 Hz, 1H), 2.24 (s, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 196.1, 137.2, 136.3, 134.9, 129.5, 128.9, 128.6, 128.0, 127.4, 127.3, 80.0, 39.8, 39.5, 21.1. **HRMS** (ESI): m/z calcd for $C_{26}H_{27}O_3N_3Na$ [M^++Na] 452.1945, found 452.1948. The enantiomeric excess was determined by HPLC using a Chiralpak IC column [*n*-hexanes/^{i}PrOH (70:30)]; flow rate 1 mL/min; τ_{major} = 15.6 min, τ_{minor} = 19.2 min (91% ee); $[\alpha]_D^{20}$ = −28.0 (c 1.0, $CHCl_3$).

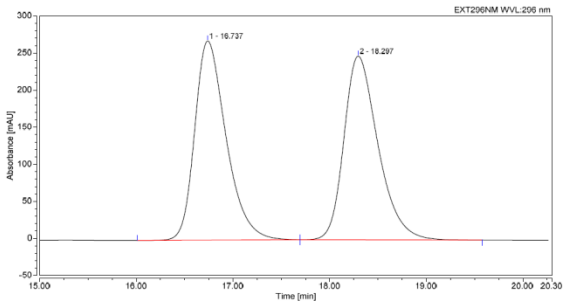


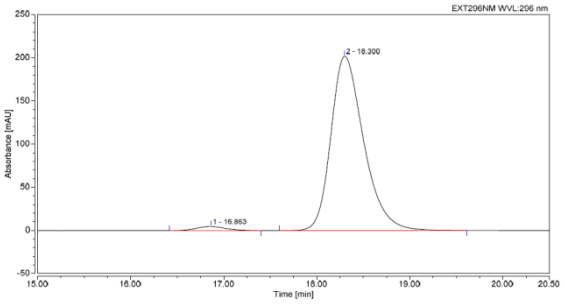


No.	Retention Time min	Area mAU*min	Relative Area %
1	15.673	31.529	52.06
2	19.293	29.032	47.94

No.	Retention Time min	Area mAU*min	Relative Area %
1	15.557	467.625	95.73
2	19.197	20.865	4.27

(*S*,*E*)-1-(2,2-Dibenzylhydrazineylidene)-4-(2,3-dimethoxyphenyl)-5-nitropentan-2-one, (*S*)-**3Bc**. Following the general procedure **9**, starting from **1B** (106 mg, 0.4 mmol), nitroalkene **2c** (43 mg, 0.2 mmol), 20 mol% of **Ia** (16 mg, 0.04 mmol) and 10 mol% of benzoic acid (2.4 mg, 0.02 mmol), compound (*S*)-**3Bc** was obtained as a colorless oil (85 mg, 89%; reaction ran for 3 days). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.30 – 7.13 (m, 6H), 7.11 – 6.96 (m, 4H), 6.88 (t, *J* = 8.0 Hz, 1H), 6.70 (ddd, *J* = 15.5, 8.0, 1.4 Hz, 2H), 6.53 (s, 1H), 4.66 (dd, *J* = 9.8, 4.5 Hz, 1H), 4.60 (dd, *J* = 9.8, 4.5 Hz, 1H), 4.51 (s, 4H), 4.39 – 4.24 (m, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.22 (dd, *J* = 16.1, 7.9 Hz, 1H), 3.03 (dd, *J* = 16.1, 7.9 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 196.4, 152.8, 147.1, 134.9, 132.7, 128.9, 128.5, 127.9, 127.4, 124.0, 120.0, 111.7, 78.9, 60.7, 55.6, 38.7, 35.0. **HRMS** (ESI): m/z calcd for $C_{27}H_{29}O_5N_3Na$ [M^++Na] 498.1999, found 498.1994. The enantiomeric excess was determined by HPLC using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 18.3 min, τ_{minor} = 16.7 min (96% ee); $[\alpha]_D^{20}$ = −27.1 (c 1.0, $CHCl_3$).

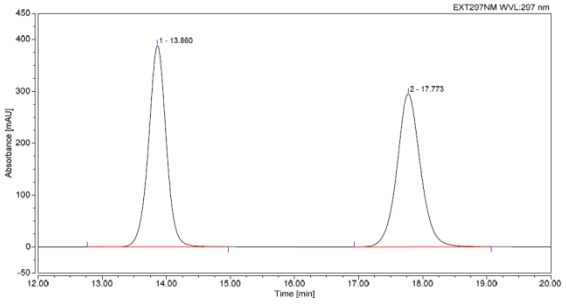


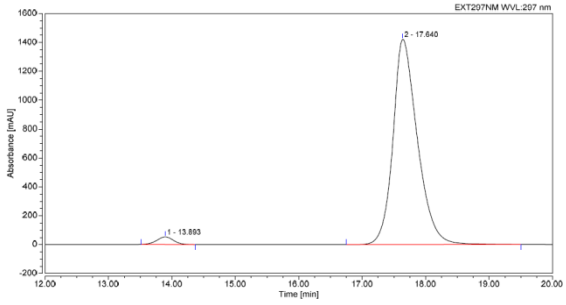


No.	Retention Time min	Area mAU*min	Relative Area %
1	16.737	101.137	49.93
2	18.297	101.413	50.07

No.	Retention Time min	Area mAU*min	Relative Area %
1	16.863	1.728	2.05
2	18.300	82.412	97.95

(*S*,*E*)-4-(2-Bromophenyl)-1-(2,2-dibenzylhydrazineylidene)-5-nitropentan-2-one, (*S*)-**3Bd**. Following the general procedure **9**, starting from **1B** (106 mg, 0.4 mmol), nitroalkene **2d** (46 mg, 0.2 mmol), 20 mol% of **Ia** (16 mg, 0.04 mmol) and 10 mol% of benzoic acid (2.4 mg, 0.02 mmol), compound (*S*)-**3Bd** was obtained as a colorless oil (95 mg, 96%; reaction ran for 3 days). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.53 – 7.43 (m, 1H), 7.30 – 7.12 (m, 8H), 7.10 – 6.95 (m, 5H), 6.52 (s, 1H), 4.72 – 4.61 (m, 2H), 4.59 – 4.43 (m, 5H), 3.25 – 3.15 (m, 1H), 3.13 (dd, *J* = 12.9, 4.5 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 195.8, 138.3, 134.9, 133.6, 129.0, 129.0, 128.4, 128.3, 128.0, 127.8, 127.4, 124.7, 78.1, 39.1, 38.2. **HRMS** (ESI): m/z calcd for $C_{25}H_{24}O_3N_3BrNa$ [M^++Na] 516.0893, found 516.0888. The enantiomeric excess was determined by HPLC using a Chiralpak IA column [*n*-hexanes/^{i}PrOH PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 17.6 min, τ_{minor} = 13.9 min (95% ee); $[\alpha]_D^{20}$ = −24.5 (c 1.0, $CHCl_3$).



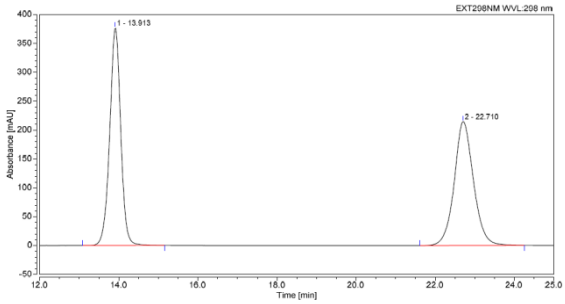


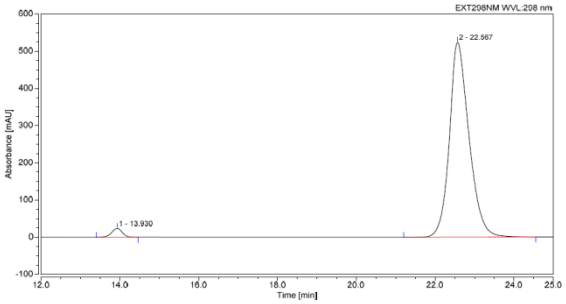
No.	Retention Time min	Area mAU*min	Relative Area %
1	13.860	123.933	49.61
2	17.773	125.900	50.39

No.	Retention Time min	Area mAU*min	Relative Area %
1	13.893	15.982	2.46
2	17.640	634.487	97.54

(*S*,*E*)-1-(2,2-Dibenzylhydrazineylidene)-4-(2,4-dichlorophenyl)-5-nitropentan-2-one, (*S*)-**3Bf**. Following the general procedure **9**, starting from **1B** (106 mg, 0.4 mmol), nitroalkene **2f** (44 mg, 0.2 mmol), 20 mol% of **Ia** (16 mg, 0.04 mmol) and 10 mol% of benzoic acid (2.4 mg, 0.02 mmol), compound (*S*)-**3Bf** was obtained as a colorless oil (70 mg, 72%; reaction ran for 3 days). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.28 – 7.13 (m, 6H), 7.12 – 7.06 (m, 2H), 7.06 – 6.94 (m, 4H), 6.51 (s, 1H), 4.72 – 4.60 (m, 2H), 4.59 – 4.47 (m, 4H), 4.47 – 4.36 (m, 1H), 3.18 (dd, *J* = 13.8, 5.3 Hz, 1H), 3.11 (dd, *J* = 13.8, 5.3 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 195.5, 135.1, 134.6, 133.8, 129.9, 129.4, 128.9, 128.3, 128.0, 127.4, 127.3, 77.7, 37.6, 36.4. **HRMS**

(ESI): m/z calcd for $C_{25}H_{23}O_3N_3ClNa$ [M^++Na] 506.1009, found 506.1004. The enantiomeric excess was determined by HPLC using a Chiralpak IA column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 22.6 min, τ_{minor} = 13.9 min (95% ee); $[\alpha]_D^{20}$ = −24.2 (c 1.0, $CHCl_3$).

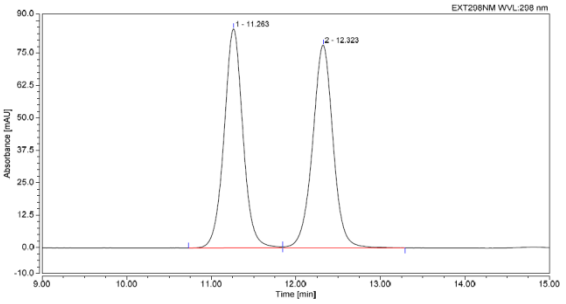


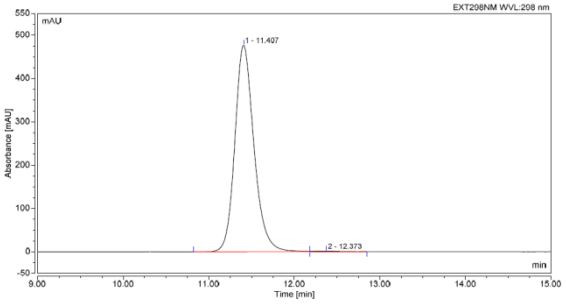


No.	Retention Time min	Area mAU*min	Relative Area %
1	13.913	121.459	50.13
2	22.710	120.820	49.87

No.	Retention Time min	Area mAU*min	Relative Area %
1	13.930	7.466	2.41
2	22.567	301.758	97.59

(*S*,*E*)-5-Nitro-4-phenyl-1-(piperidin-1-ylimino)pentan-2-one, (*S*)-**3Ca**. Following the general procedure **9**, starting from **1C** (62 mg, 0.4 mmol), nitroalkene **2a** (30 mg, 0.2 mmol), 10 mol% of **Ia** (8 mg, 0.02 mmol) and 5 mol% of benzoic acid (1.2 mg, 0.01 mmol), compound (*S*)-**3Ca** was obtained as a brown solid (52 mg, 85%, 92% ee; reaction performed at 1 mmol scale and subsequent recrystallization of the final product by slow evaporation of a solution of (*S*)-**3Ca** in *n*-pentane/Et_2O: 149 mg, 49%, >99% ee; reactions ran for 2 days); mp. = 61-63 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.34 – 7.21 (m, 5H), 6.78 (s, 1H), 4.75 (dd, *J* = 12.4, 6.4 Hz, 1H), 4.62 (dd, *J* = 12.4, 8.7 Hz, 1H), 4.16 – 4.02 (m, 1H), 3.36 – 3.22 (m, 5H), 3.07 (dd, *J* = 16.1, 8.7 Hz, 1H), 1.77 – 1.52 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 196.3, 139.6, 128.8, 128.6, 127.5, 79.9, 51.1, 40.0, 39.4, 24.8, 23.5. **HRMS** (ESI): m/z calcd for $C_{16}H_{21}O_3N_3Na$ [M^++Na] 326.1475, found 326.1473. The enantiomeric excess was determined by HPLC using a Chiralpak IA column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 11.4 min, τ_{minor} = 12.4 min (>99% ee); $[\alpha]_D^{20}$ = −107.6 (c 1.0, $CHCl_3$).

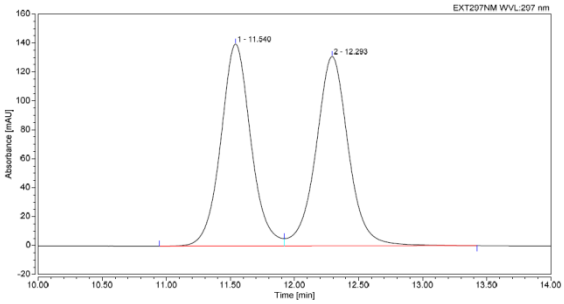


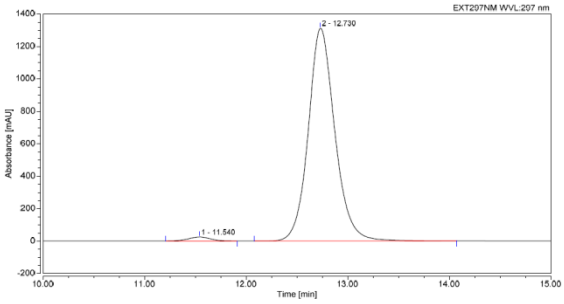


No.	Retention Time min	Area mAU*min	Relative Area %
1	11.263	21.847	49.87
2	12.323	21.958	50.13

No.	Retention Time min	Area mAU*min	Relative Area %
1	11.407	123.357	99.74
2	12.373	0.324	0.26

(*S*,*E*)-4-(2,3-Dimethoxyphenyl)-5-nitro-1-(piperidin-1-ylimino)pentan-2-one, (*S*)-**3Cc**. Following the general procedure **9**, starting from **1C** (62 mg, 0.4 mmol) and nitroalkene **2c** (43 mg, 0.2 mmol), 10 mol% of **Ia** (8 mg, 0.02 mmol) and 5 mol% of benzoic acid (1.2 mg, 0.01 mmol), compound (*S*)-**3Cc** was obtained as a yellow oil (66 mg, 90%; reaction ran for 2 days). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.02 – 6.94 (m, 1H), 6.85 – 6.75 (m, 3H), 4.77 (dd, *J* = 10.2, 4.9 Hz, 1H), 4.71 (dd, *J* = 10.2, 4.9 Hz, 1H), 4.45 – 4.33 (m, 1H), 3.92 (s, 3H), 3.85 (s, 3H), 3.37 – 3.22 (m, 5H), 3.11 (dd, *J* = 16.3, 8.1 Hz, 1H), 1.77 – 1.55 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 196.0, 138.3, 133.5, 128.9, 128.3, 128.1, 127.7, 124.6, 78.0, 51.0, 38.8, 38.2, 24.8, 23.5. **HRMS** (ESI): m/z calcd for $C_{18}H_{26}O_5N_3$ [M^++H] 364.1867, found 364.1866. The enantiomeric excess was determined by HPLC using a Chiralpak IA column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 12.7 min, τ_{minor} = 11.5 min (97% ee); $[\alpha]_D^{20}$ = −62.1 (c 0.5, $CHCl_3$).

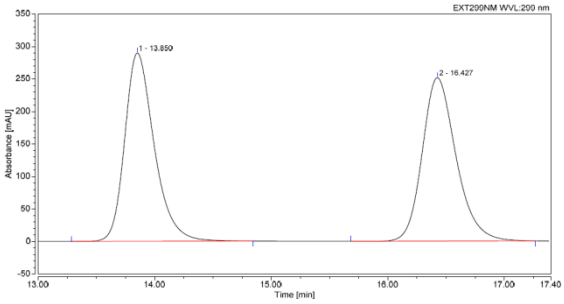


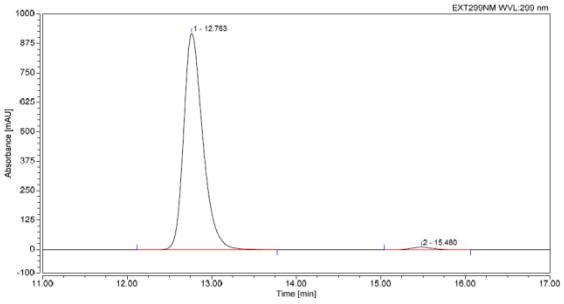


No.	Retention Time min	Area mAU*min	Relative Area %
1	11.540	37.875	49.68
2	12.293	38.370	50.32

No.	Retention Time min	Area mAU*min	Relative Area %
1	11.540	6.263	1.55
2	12.730	397.803	98.45

(*S*,*E*)-1-(2-Bromophenyl)-5-nitro-1-(piperidin-1-ylimino)pentan-2-one, (*S*)-**3Cd**. Following the general procedure **9**, starting from **1C** (62 mg, 0.4 mmol) and nitroalkene **2d** (46 mg, 0.2 mmol), 10 mol% of **Ia** (8 mg, 0.02 mmol) and 5 mol% of benzoic acid (1.2 mg, 0.01 mmol), compound (*S*)-**3Cd** was obtained as an orange oil (59 mg, 78%; reaction ran for 2 days). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.15 – 7.05 (m, 1H), 6.78 (s, 1H), 4.77 (d, *J* = 7.1 Hz, 2H), 4.65 – 4.53 (m, 1H), 3.38 – 3.30 (m, 4H), 3.30 – 3.14 (m, 2H), 1.77 – 1.55 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 196.0, 138.3, 133.5, 128.9, 128.3, 128.1, 127.7, 124.6, 78.0, 51.0, 38.8, 38.2, 24.8, 23.5. **HRMS** (ESI): m/z calcd for $C_{16}H_{20}O_3N_3BrNa$ [M^++Na] 404.0580, found 404.0577. The enantiomeric excess was determined by HPLC using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 12.8 min, τ_{minor} = 15.5 min (97% ee); $[\alpha]_D^{20}$ = −53.5 (c 0.5, $CHCl_3$).

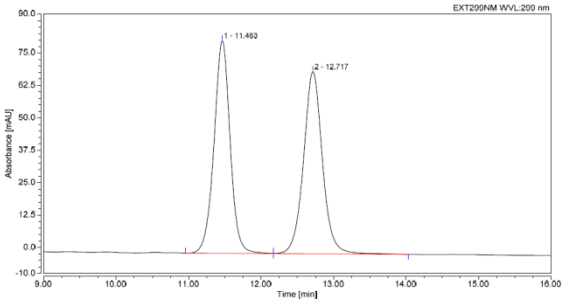


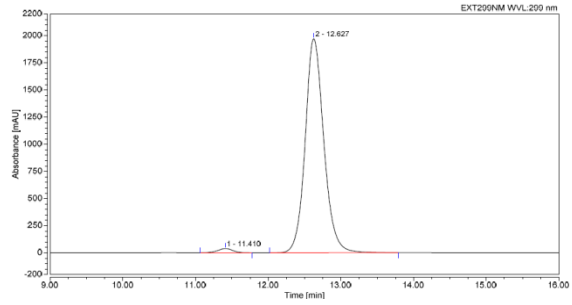


No.	Retention Time min	Area mAU*min	Relative Area %
1	13.850	84.979	50.07
2	16.427	84.735	49.93

No.	Retention Time min	Area mAU*min	Relative Area %
1	12.763	241.587	98.64
2	15.480	3.327	1.36

(*S*,*E*)-4-(2,4-Dichlorophenyl)-5-nitro-1-(piperidin-1-ylimino)pentan-2-one, (*S*)-**3Cf**. Following the general procedure **9**, starting from **1C** (62 mg, 0.4 mmol) and nitroalkene **2f** (44 mg, 0.2 mmol), 10 mol% of **Ia** (8 mg, 0.02 mmol) and 5 mol% of benzoic acid (1.2 mg, 0.01 mmol), compound (*S*)-**3Cf** was obtained as an orange oil (54 mg, 72%; reaction ran for 2 days). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.40 (t, *J* = 1.1 Hz, 1H), 7.21 (d, *J* = 1.1 Hz, 2H), 6.77 (s, 1H), 4.77 (d, *J* = 6.9 Hz, 2H), 4.59 – 4.46 (m, 1H), 3.37 – 3.29 (m, 4H), 3.26 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.18 (dd, *J* = 15.0, 5.5 Hz, 1H), 1.77 – 1.56 (m, 6H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 195.8, 135.4, 134.7, 133.8, 130.0, 129.3, 128.2, 127.4, 77.7, 51.1, 37.8, 36.2, 24.8, 23.5. **HRMS** (ESI): m/z calcd for $C_{16}H_{19}O_3N_3Cl_2Na$ [M^++Na] 394.0696, found 394.0693. The enantiomeric excess was determined by HPLC using a Chiralpak IA column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1mL/min; τ_{major} = 12.6 min, τ_{minor} = 11.4 min (97% ee); $[\alpha]_D^{20}$ = −52.4 (c 0.5, $CHCl_3$).



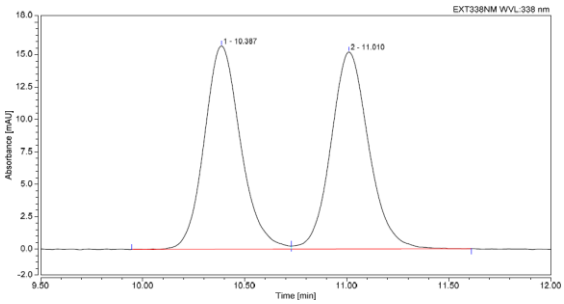


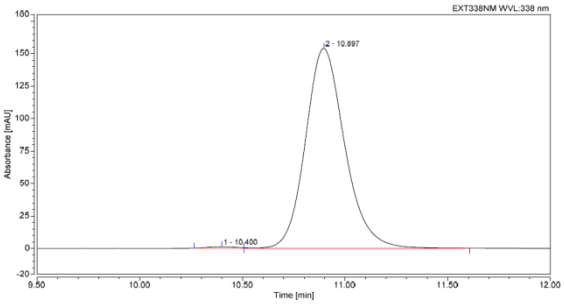
No.	Retention Time min	Area mAU*min	Relative Area %
1	11.463	21.122	49.84
2	12.717	21.257	50.16

No.	Retention Time min	Area mAU*min	Relative Area %
1	11.410	9.532	1.60
2	12.627	587.199	98.40

(*S*,*E*)-1-(2,2-Diphenylhydrazineylidene)-5-nitro-4-phenylpentan-2-one, (*S*)-**3Da**. Following the general procedure **9**, starting from **1D** (95 mg, 0.4 mmol), nitroalkene **2a** (30 mg, 0.2 mmol), 10 mol% of **Ia** (8 mg, 0.02 mmol) and 5 mol% of benzoic acid (1.2 mg, 0.01 mmol), compound (*S*)-**3Da** was obtained as a yellow solid (63 mg, 81%, >99% ee; reaction performed at 1 mmol scale: 362 mg, 93%, >99% ee; reaction ran for 1 day); mp. = 130-132 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.53 – 7.38 (m, 4H), 7.38 – 7.22 (m, 7H), 7.18 – 7.08 (m, 4H), 6.56 (s, 1H), 4.79 (dd, *J* = 12.5, 8.3 Hz, 1H), 4.69 (dd, *J* = 12.5, 8.3 Hz, 1H), 4.25 – 4.09 (m, 1H), 3.53 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.27 (dd, *J* = 16.4, 7.6 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 196.4, 139.2, 133.0, 130.0, 128.9, 127.7, 127.5, 79.8, 40.0, 39.8. **HRMS** (ESI): m/z calcd for $C_{23}H_{21}O_3N_3Na$ [M^++Na] 410.1475, found 410.1472. The enantiomeric excess was determined by HPLC

using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 10.9 min, τ_{minor} = 10.4 min (>99% ee); $[\alpha]_D^{20}$ = −126.5 (c 0.5, $CHCl_3$).

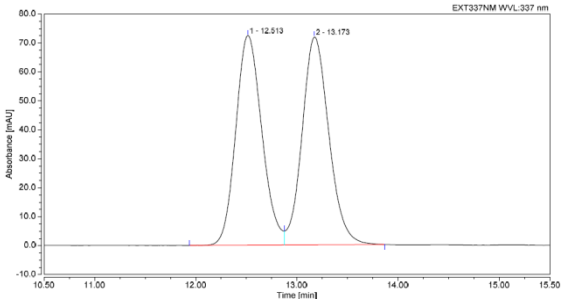


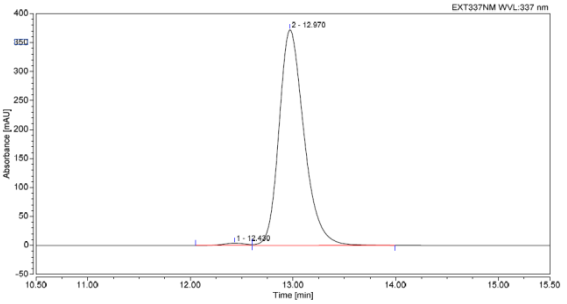


No.	Retention Time min	Area mAU*min	Relative Area %
1	10.387	3.242	49.77
2	11.010	3.273	50.23

No.	Retention Time min	Area mAU*min	Relative Area %
1	10.400	0.153	0.45
2	10.897	34.051	99.55

(*S*,*E*)-1-(2,2-Diphenylhydrazineylidene)-5-nitro-4-(*p*-tolyl)pentan-2-one, (*S*)-**3Db**. Following the general procedure **9**, starting from **1D** (95 mg, 0.4 mmol), nitroalkene **2b** (33 mg, 0.2 mmol), 10 mol% of **Ia** (8 mg, 0.02 mmol) and 5 mol% of benzoic acid (1.2 mg, 0.01 mmol), compound (*S*)-**3Db** was obtained as a yellow solid (70 mg, 87%; reaction ran for 1 day); mp. = 102-104 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.54 – 7.37 (m, 4H), 7.36 – 7.23 (m, 2H), 7.23 – 7.07 (m, 8H), 6.56 (s, 1H), 4.77 (dd, *J* = 12.4, 8.3 Hz, 1H), 4.66 (dd, *J* = 12.4, 8.3 Hz, 1H), 4.21 – 4.06 (m, 1H), 3.50 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.25 (dd, *J* = 16.4, 7.6 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 196.5, 137.4, 136.2, 133.1, 130.1, 129.7, 127.5, 80.0, 40.2, 39.5, 21.1. **HRMS** (ESI): m/z calcd for $C_{24}H_{23}O_3N_3Na$ [M^++Na] 424.1632, found 424.1629. The enantiomeric excess was determined by HPLC using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (95:5)]; flow rate 1 mL/min; τ_{major} = 13.0 min, τ_{minor} = 12.4 min (98% ee); $[\alpha]_D^{20}$ = −129.3 (c 0.5, $CHCl_3$).

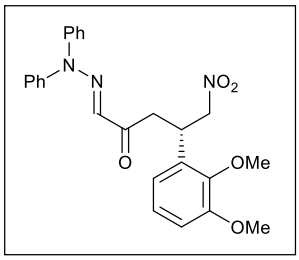




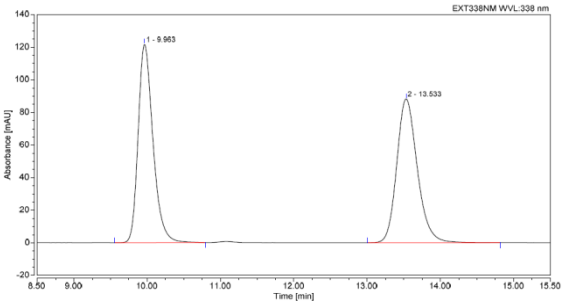
No.	Retention Time min	Area mAU*min	Relative Area %
1	12.513	21.614	49.54
2	13.173	22.015	50.46

No.	Retention Time min	Area mAU*min	Relative Area %
1	12.430	1.013	0.96
2	12.970	104.775	99.04

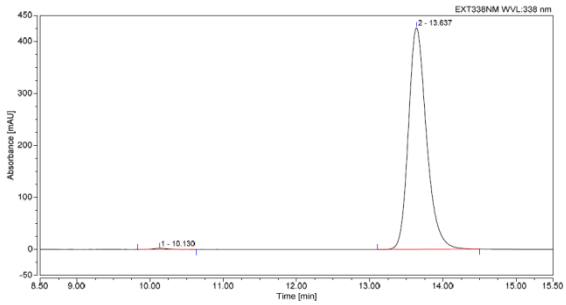
(*S*,*E*)-4-(2,3-Dimethoxyphenyl)-1-(2,2-diphenylhydrazineylidene)-5-nitropentan-2-one, (*S*)-**3Dc**.



Following the general procedure **9**, starting from **1D** (95 mg, 0.4 mmol) and nitroalkene **2c** (42 mg, 0.2 mmol), 10 mol% of **Ia** (8 mg, 0.02 mmol) and 5 mol% of benzoic acid (1.2 mg, 0.01 mmol), compound (*S*)-**3Dc** was obtained as an off-white solid (82 mg, 92%, >99% ee; reaction performed at 1 mmol scale: 383 mg, 86%; reaction ran for 1 day); mp. = 132-134 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.52 – 7.36 (m, 4H), 7.34 – 7.22 (m, 2H), 7.19 – 7.10 (m, 4H), 7.01 (dd, *J* = 8.4, 7.5 Hz, 1H), 6.89 – 6.79 (m, 2H), 6.57 (s, 1H), 4.78 (d, *J* = 7.7 Hz, 2H), 4.54 – 4.39 (m, 1H), 3.95 (s, 3H), 3.85 (s, 3H), 3.49 (dd, *J* = 16.6, 7.7 Hz, 1H), 3.36 (dd, *J* = 16.6, 7.7 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 196.9, 152.9, 147.2, 133.2, 132.5, 130.1, 124.1, 120.1, 111.9, 78.8, 60.8, 55.7, 39.2, 35.0. **HRMS** (ESI): m/z calcd for $C_{25}H_{25}O_5N_3Na$ [M^++Na] 470.1686, found 470.1683. The enantiomeric excess was determined by HPLC using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 13.6 min, τ_{minor} = 10.1 min (>99% ee); $[\alpha]_D^{20}$ = −124.2 (c 0.5, $CHCl_3$).

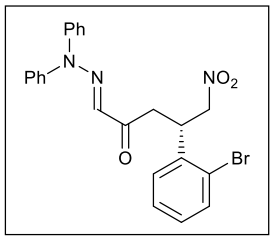


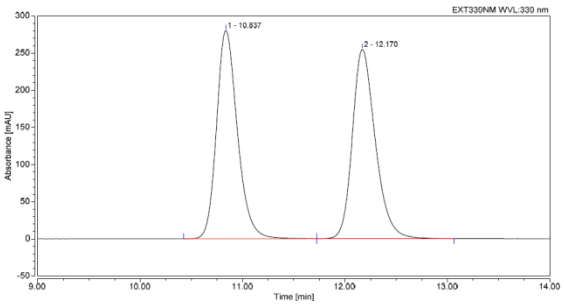
No.	Retention Time min	Area mAU*min	Relative Area %
1	9.963	28.575	49.92
2	13.533	28.672	50.08

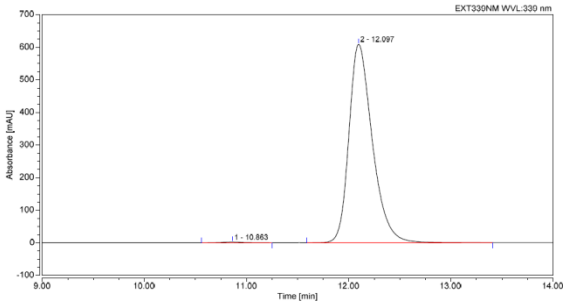


No.	Retention Time min	Area mAU*min	Relative Area %
1	10.130	0.566	0.46
2	13.637	121.767	99.54

(*S*,*E*)-4-(2-Bromophenyl)-1-(2,2-diphenylhydrazineylidene)-5-nitropentan-2-one, (*S*)-**3Dd**. Following the general procedure **9**, starting from **1D** (95 mg, 0.4 mmol), nitroalkene **2d** (48 mg, 0.2 mmol), 5 mol% of **Ia** (4 mg, 0.01 mmol) and 2.5 mol% of benzoic acid (0.6 mg, 0.005 mmol), compound (*S*)-**3Dd** was obtained as an orange oil (88 mg, 95%; reaction ran for 1 day). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.63 – 7.56 (m, 1H), 7.53 – 7.37 (m, 4H), 7.37 – 7.22 (m, 4H), 7.20 – 7.08 (m, 5H), 6.57 (s, 1H), 4.85 – 4.78 (m, 2H), 4.74 – 4.61 (m, 1H), 3.52 (dd, *J* = 16.6, 6.6 Hz, 1H), 3.43 (dd, *J* = 16.6, 6.6 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 196.1, 137.9, 133.6, 132.9, 130.0, 129.0, 128.2, 127.8, 124.5, 77.9, 38.6, 38.6. **HRMS** (ESI): m/z calcd for $C_{23}H_{20}O_3N_3BrNa$ [M^++Na] 488.0580, found 488.0577. The enantiomeric excess was determined by HPLC using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 12.1 min, τ_{minor} = 10.9 min (>99% ee); $[\alpha]_D^{20}$ = −82.8 (c 0.5, $CHCl_3$).



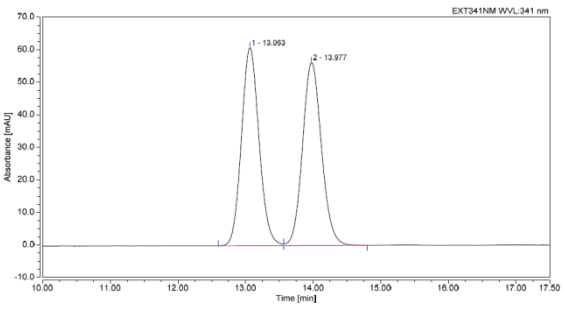


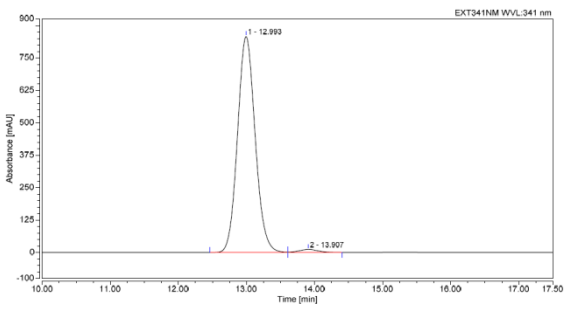


No.	Retention Time min	Area mAU*min	Relative Area %
1	10.837	66.345	50.03
2	12.170	66.257	49.97

No.	Retention Time min	Area mAU*min	Relative Area %
1	10.863	0.592	0.36
2	12.097	161.965	99.64

(*S*,*E*)-4-(4-Chlorophenyl)-1-(2,2-diphenylhydrazineylidene)-5-nitropentan-2-one, (*S*)-**3De**. Following the general procedure **9**, starting from **1D** (95 mg, 0.4 mmol), nitroalkene **2e** (38 mg, 0.2 mmol), 10 mol% of **Ia** (8 mg, 0.02 mmol) and 5 mol% of benzoic acid (1.2 mg, 0.01 mmol), compound (*S*)-**3De** was obtained as an off-white solid (71 mg, 84%; reaction ran for 1 day); mp. = 112-114 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.53 – 7.36 (m, 4H), 7.35 – 7.20 (m, 6H), 7.17 – 7.08 (m, 4H), 6.55 (s, 1H), 4.77 (dd, *J* = 12.6, 8.5 Hz, 1H), 4.66 (dd, *J* = 12.6, 8.5 Hz, 1H), 4.15 (dq, *J* = 12.6, 7.3 Hz, 1H), 3.49 (dd, *J* = 16.5, 7.3 Hz, 1H), 3.24 (dd, *J* = 16.5, 7.3 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 195.9, 137.7, 133.5, 132.9, 130.1, 129.1, 129.0, 79.5, 39.8, 39.2. **HRMS** (ESI): m/z calcd for $C_{23}H_{20}O_3N_3ClNa$ [M^++Na] 444.1085, found 444.1081. The enantiomeric excess was determined by HPLC using a Chiralpak IC column [*n*-hexanes/^{i}PrOH (80:20)]; flow rate 1 mL/min; τ_{major} = 13.0 min,τ_{minor} = 13.9 min (97% ee); $[\alpha]_D^{20}$ = −148.5 (c 0.5, $CHCl_3$).



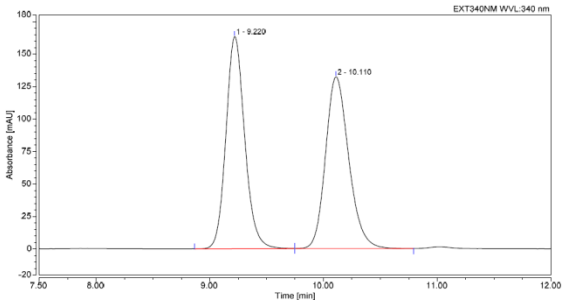


No.	Retention Time min	Area mAU*min	Relative Area %
1	13.063	18.248	49.97
2	13.977	18.272	50.03

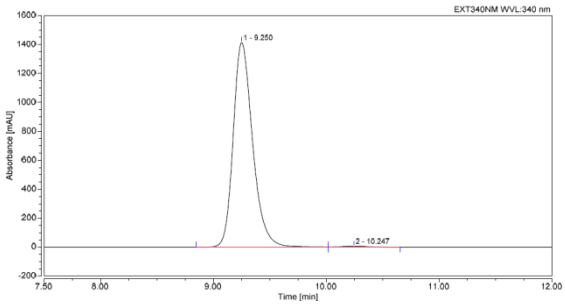
No.	Retention Time min	Area mAU*min	Relative Area %
1	12.993	249.933	98.50
2	13.907	3.804	1.50

(*S*,*E*)-4-(2,4-Dichlorophenyl)-1-(2,2-diphenylhydrazineylidene)-5-nitropentan-2-one, (*S*)-**3Df**. Following the general procedure **9**, starting from **1D** (95 mg, 0.4 mmol), nitroalkene **2f** (45 mg, 0.2 mmol), 5 mol% of **Ia** (4 mg, 0.01 mmol) and 2.5 mol% of benzoic acid (0.6 mg, 0.005 mmol), compound (*S*)-**3Df** was obtained as an off-white solid (90 mg, 99%; reaction ran for 1 day); mp. = 77-79 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.55 – 7.38 (m, 5H), 7.35 – 7.20 (m, 4H), 7.19 – 7.08 (m, 4H), 6.56 (s, 1H), 4.82 (d, *J* = 7.1 Hz, 2H), 4.66 – 4.54 (m, 1H), 3.50 (dd, *J* = 14.1, 4.1 Hz, 1H), 3.43 (dd, *J* = 14.0, 4.1 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 195.9, 135.0, 134.6, 134.0, 132.8, 130.1, 129.4, 127.5, 77.6, 38.2, 36.0. **HRMS** (ESI): m/z calcd for $C_{23}H_{19}O_3N_3Cl_2Na$

[M^++Na] 478.0696, found 478.0692. The enantiomeric excess was determined by HPLC using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 9.2 min, τ_{minor} = 10.2 min (99% ee); $[\alpha]_D^{20}$ = −114.3 (c 0.5, $CHCl_3$).

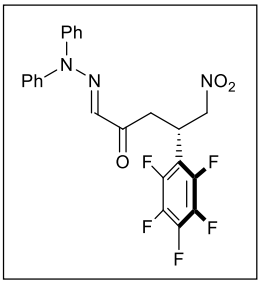


No.	Retention Time min	Area mAU*min	Relative Area %
1	9.220	31.341	50.02
2	10.110	31.317	49.98

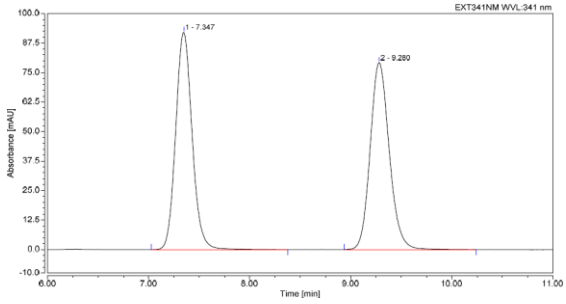


No.	Retention Time min	Area mAU*min	Relative Area %
1	9.250	281.382	99.50
2	10.247	1.427	0.50

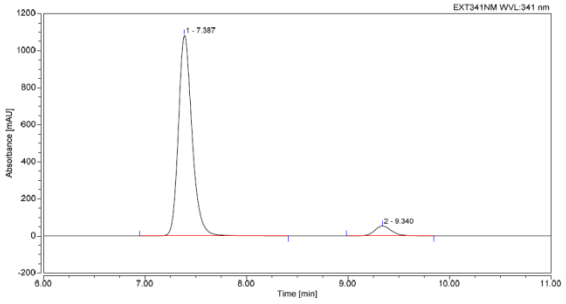
(*S*,*E*)-1-(2,2-Diphenylhydrazineylidene)-5-nitro-4-(perfluorophenyl)pentan-2-one, (*S*)-**3Dg**.



Following the general procedure **9**, starting from **1D** (95 mg, 0.4 mmol), nitroalkene **2g** (48 mg, 0.2 mmol), 5 mol% of **Ia** (4 mg, 0.01 mmol) and 2.5 mol% of benzoic acid (0.6 mg, 0.005 mmol), compound (*S*)-**3Dg** was obtained as an off-white solid (90 mg, 95%; reaction ran for 1 day); mp. = 137-139 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.56 – 7.38 (m, 4H), 7.31 (br s, 2H), 7.19 – 7.10 (m, 4H), 6.60 (s, 1H), 4.92 – 4.73 (m, 2H), 4.67 – 4.53 (m, 1H), 3.51 (dd, *J* = 17.0, 7.5 Hz, 1H), 3.42 (dd, *J* = 17.0, 7.5 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 194.9, 147.4 – 146.7 (m), 144.2 – 143.4 (m), 142.7 – 141.8 (m), 139.7 – 138.8 (m), 136.6 – 135.5 (m), 132.4, 130.1, 113.2 – 112.5 (m), 37.7, 30.0. **^{19}F NMR** (471 MHz, $CDCl_3$): δ –[141.03 – 141.22 (m, 2F)], –154.08 (t, *J* = 21.0 Hz, 1F), –[160.90 – 161.08 (m, 3F)]. **HRMS** (ESI): m/z calcd for $C_{23}H_{16}O_3N_3F_5Na$ [M^++Na] 500.1004, found 500.0997. The enantiomeric excess was determined by HPLC using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 7.4 min, τ_{minor} = 9.3 min (88% ee); $[\alpha]_D^{20}$ = −112.4 (c 0.5, $CHCl_3$).

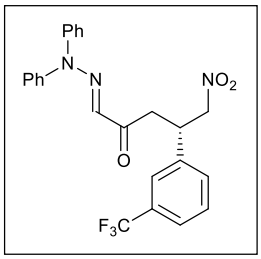


No.	Retention Time min	Area mAU*min	Relative Area %
1	7.347	17.337	50.07
2	9.280	17.287	49.93

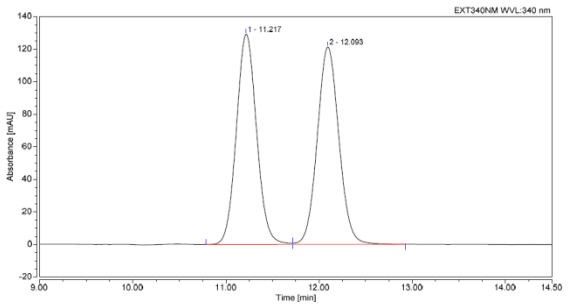


No.	Retention Time min	Area mAU*min	Relative Area %
1	7.387	168.477	94.14
2	9.340	10.481	5.86

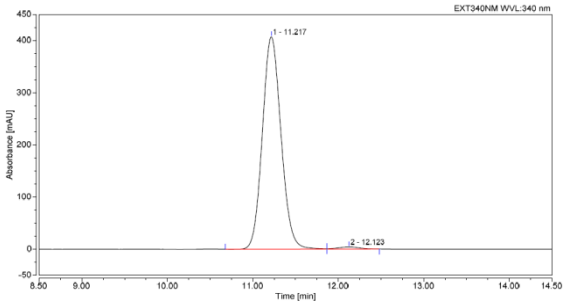
(*S*,*E*)-1-(2,2-Diphenylhydrazineylidene)-5-nitro-4-[3-(trifluoromethyl)phenyl]pentan-2-one, (*S*)-**3Dh**.



Following the general procedure **9**, starting from **1D** (95 mg, 0.4 mmol), nitroalkene **2h** (43 mg, 0.2 mmol), 10 mol% of **Ia** (8 mg, 0.02 mmol) and 5 mol% of benzoic acid (1.2 mg, 0.01 mmol), compound (*S*)-**3Dh** was obtained as a brown solid (75 mg, 82%, 98% ee; reaction performed at 1 mmol scale: 348 mg, 77%; reaction ran for 1 day); mp. = 50-52 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.64 – 7.38 (m, 8H), 7.38 – 7.23 (m, 2H), 7.19 – 7.08 (m, 4H), 6.58 (s, 1H), 4.83 (dd, *J* = 12.8, 6.6 Hz, 1H), 4.72 (dd, *J* = 12.8, 8.5 Hz, 1H), 4.35 – 4.19 (m, 1H), 3.57 (dd, *J* = 16.5, 7.2 Hz, 1H), 3.28 (dd, *J* = 16.5, 7.2 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 195.7, 140.3, 132.8, 131.2 (q, $J_{C,F}$ = 32.3 Hz), 131.1, 130.1, 129.4, 124.6 (q, $J_{C,F}$ = 3.5 Hz), 124.4 (q, $J_{C,F}$ = 3.5 Hz), 123.9 (q, $J_{C,F}$ = 272.6 Hz), 79.2, 39.7, 39.5. **^{19}F NMR** (471 MHz, $CDCl_3$): δ −62.64 (s, 3F). **HRMS** (ESI): m/z calcd for $C_{24}H_{20}O_3N_3F_3Na$ [M^++Na] 478.1349, found 478.1343. The enantiomeric excess was determined by HPLC using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 11.2 min, τ_{minor} = 12.1 min (98% ee); $[\alpha]_D^{20}$ = −128.1 (c 0.5, $CHCl_3$).

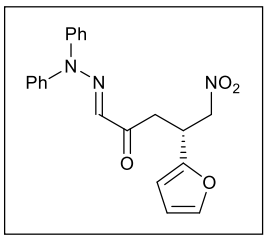


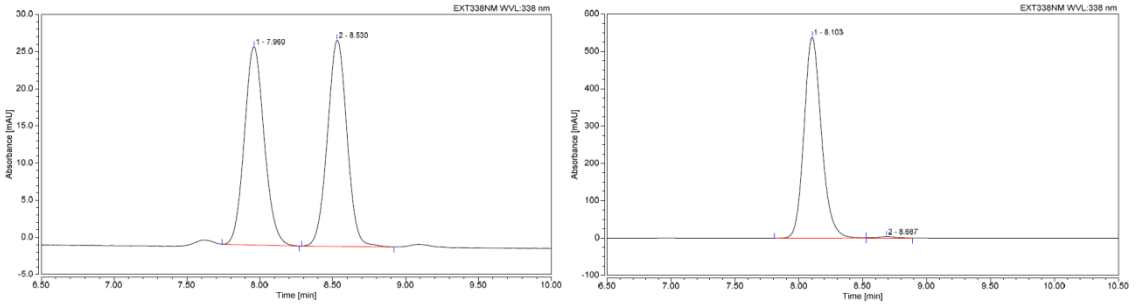
No.	Retention Time min	Area mAU*min	Relative Area %
1	11.217	32.516	49.91
2	12.093	32.633	50.09



No.	Retention Time min	Area mAU*min	Relative Area %
1	11.217	102.965	98.86
2	12.123	1.183	1.14

(*R*,*E*)-1-(2,2-Diphenylhydrazineylidene)-4-(furan-2-yl)-5-nitropentan-2-one, (*R*)-**3Di**. Following the general procedure **9**, starting from **1D** (95 mg, 0.4 mmol) and nitroalkene **2i** (28 mg, 0.2 mmol), 10 mol% of **Ia** (8 mg, 0.02 mmol) and 5 mol% of benzoic acid (1.2 mg, 0.01 mmol), compound (*R*)-**3Di** was obtained as a yellow solid (68 mg, 90%; reaction ran for 1 day). mp. = 137-139 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.61 – 7.39 (m, 4H), 7.39 – 7.23 (m, 3H), 7.22 – 7.11 (m, 4H), 6.61 (s, 1H), 6.30 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.19 (d, *J* = 3.3 Hz, 1H), 4.76 (d, *J* = 6.9 Hz, 2H), 4.34 – 4.19 (m, 1H), 3.52 (dd, *J* = 16.8, 6.9 Hz, 1H), 3.32 (dd, *J* = 16.8, 6.9 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 196.0, 152.2, 142.3, 132.8, 130.1, 110.4, 107.1, 77.5, 37.6, 33.6. **HRMS** (ESI): m/z calcd for $C_{21}H_{19}O_4N_3Na$ [M^++Na] 400.1268, found 400.1265. The enantiomeric excess was determined by HPLC using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 8.1 min, τ_{minor} = 8.7 min (98% ee); $[\alpha]_D^{20}$ = −83.7 (c 0.5, $CHCl_3$).

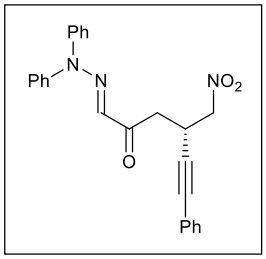




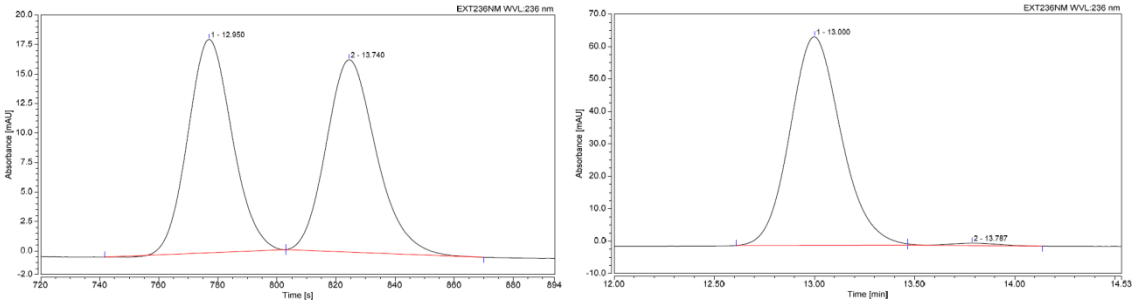
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.960	4.228	49.45
2	8.530	4.322	50.55

No.	Retention Time min	Area mAU*min	Relative Area %
1	8.103	85.346	99.22
2	8.687	0.669	0.78

(*S*,*E*)-1-(2,2-Diphenylhydrazineylidene)-4-(nitromethyl)-6-phenylhex-5-yn-2-one, (*S*)-**3Dj**. Following



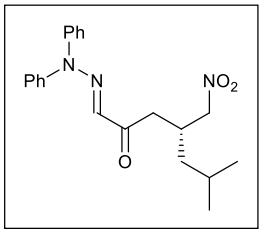
the general procedure **9**, starting from **1D** (95 mg, 0.4 mmol) and nitroalkene **2j** (35 mg, 0.2 mmol), 20 mol% of **Ia** (16 mg, 0.04 mmol) and 10 mol% of benzoic acid (2.4 mg, 0.02 mmol), compound (*S*)-**3Dj** was obtained as a pale brown solid (33 mg, 40%; reaction ran for 1 day); mp. = 109-111 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.52 – 7.35 (m, 6H), 7.34 – 7.23 (m, 5H), 7.20 – 7.12 (m, 4H), 6.67 (s, 1H), 4.72 (dd, *J* = 12.4, 6.2 Hz, 1H), 4.64 (dd, *J* = 12.4, 6.2 Hz, 1H), 4.11 – 3.98 (m, 1H), 3.49 – 3.33 (m, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 195.5, 132.7, 131.8, 130.1, 128.4, 128.2, 122.4, 86.3, 84.2, 77.8, 38.8, 27.1. **HRMS** (ESI): m/z calcd for $C_{25}H_{21}O_3N_3Na$ [M^++Na] 434.1475, found 434.1473. The enantiomeric excess was determined by HPLC using a Chiralpak ID column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 13.0 min, τ_{minor} = 13.8 min (98% ee); $[\alpha]_D^{20}$ = −166.3 (c 0.5, $CHCl_3$).



No.	Retention Time min	Area mAU*min	Relative Area %
1	12.950	5.228	49.51
2	13.740	5.332	50.49

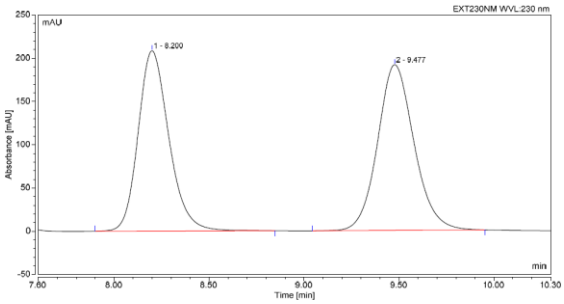
No.	Retention Time min	Area mAU*min	Relative Area %
1	13.000	19.028	98.85
2	13.787	0.222	1.15

(*R*,*E*)-1-(2,2-Diphenylhydrazineylidene)-6-methyl-4-(nitromethyl)heptan-2-one, (*R*)-**3Dk**. Following

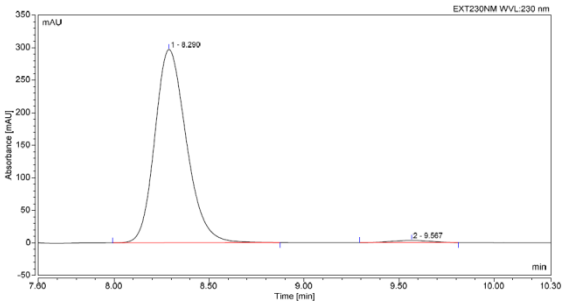


the general procedure **9**, starting from **1D** (95 mg, 0.4 mmol) and nitroalkene **2k** (26 mg, 0.2 mmol), 20 mol% of **Ia** (16 mg, 0.04 mmol) and 5 mol% of benzoic acid (1.2 mg, 0.01 mmol), compound (*R*)-**3Dk** was obtained as an off-white solid (38 mg, 52%; reaction ran for 1 day); mp. = 90-92 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.56 – 7.37 (m, 4H), 7.36 – 7.22 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 4H), 6.62 (s, 1H), 4.52 (dd, *J* = 12.0, 6.1 Hz, 1H), 4.45 (dd, *J* = 12.0, 6.1 Hz, 1H), 3.11 (dd, *J* = 16.9, 7.8 Hz, 1H), 3.04 (dd, *J* = 16.9, 5.3 Hz, 1H), 2.91 – 2.81 (m, 1H), 1.78 – 1.67 (m, 1H), 1.34 (td, *J* = 7.8, 2.0 Hz, 2H), 0.95 (d, *J* = 6.1 Hz, 3H), 0.93 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 197.8, 133.3, 130.1, 79.2, 41.0, 38.4, 31.6, 25.2, 22.6, 22.4. **HRMS** (ESI): m/z calcd for $C_{21}H_{25}O_3N_3Na$ [M^++Na] 390.1777, found 390.1781. The enantiomeric

excess was determined by HPLC using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (98:2)]; flow rate 1 mL/min; τ_{major} = 8.3 min, τ_{minor} = 9.6 min (97% ee); $[\alpha]_D^{20}$ = −1.5 (c 0.5, $CHCl_3$).

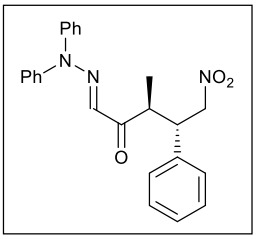


No.	Retention Time min	Area mAU*min	Relative Area %
1	8.200	39.063	47.82
2	9.477	42.626	52.18

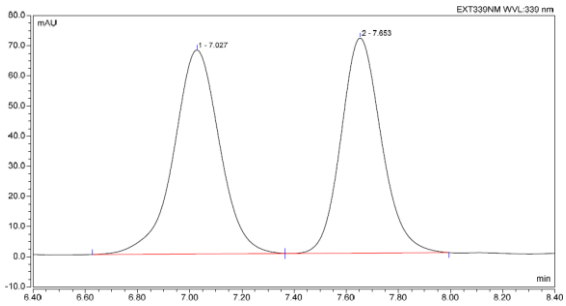


No.	Retention Time min	Area mAU*min	Relative Area %
1	8.290	57.079	98.58
2	9.567	0.824	1.42

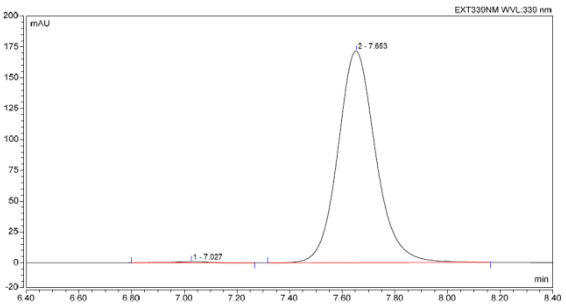
(3*S*,4*S*,*E*)-1-(2,2-Diphenylhydrazineylidene)-3-methyl-5-nitro-4-phenylpentan-2-one, (*S*,*S*)-**3Fa.**



Following the general procedure **9**, starting from **1F** (101 mg, 0.4 mmol), nitroalkene **2a** (30 mg, 0.2 mmol), 20 mol% of **Ia** (16 mg, 0.04 mmol) and 10 mol% of benzoic acid (2.4 mg, 0.02 mmol), compound (*S*,*S*)-**3Fa** was obtained as a pale yellow solid (40 mg, 50%, 99% ee, dr. = 13/1; reaction performed at 1 mmol scale followed by two chromatography columns: 177 mg, 44%, >99% ee, dr. >20/1; reactions ran for 5 days); mp. = 112-114 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.43 – 7.30 (m, 4H), 7.28 – 7.10 (m, 7H), 7.03 (d, *J* = 7.8 Hz, 4H), 6.32 (s, 1H), 4.80 (dd, *J* = 12.8, 5.1 Hz, 1H), 4.74 (dd, *J* = 12.8, 10.1 Hz, 1H), 4.21 – 4.13 (m, 1H), 3.85 (ddd, *J* = 10.1, 8.8, 5.1 Hz, 1H), 1.20 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 200.6, 138.5, 132.3, 130.1, 128.6, 128.1, 127.6, 77.7, 46.2, 42.4, 14.5. **HRMS** (ESI): m/z calcd for $C_{24}H_{23}O_3N_3Na$ [M^++Na] 424.1632, found 424.1626. The enantiomeric excess was determined by HPLC using a Chiralpak IA column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 7.6 min, τ_{minor} = 7.0 min (99% ee, dr. >20/1); $[\alpha]_D^{20}$ = −166.6 (c 1.0, $CHCl_3$).

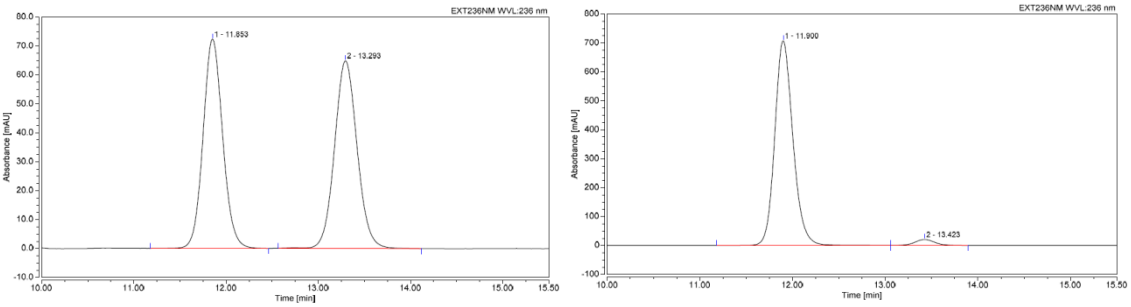


No.	Retention Time min	Area mAU*min	Relative Area %
1	7.027	13.776	51.94
2	7.653	12.745	48.06



No.	Retention Time min	Area mAU*min	Relative Area %
1	7.027	0.137	0.48
2	7.653	28.461	99.52

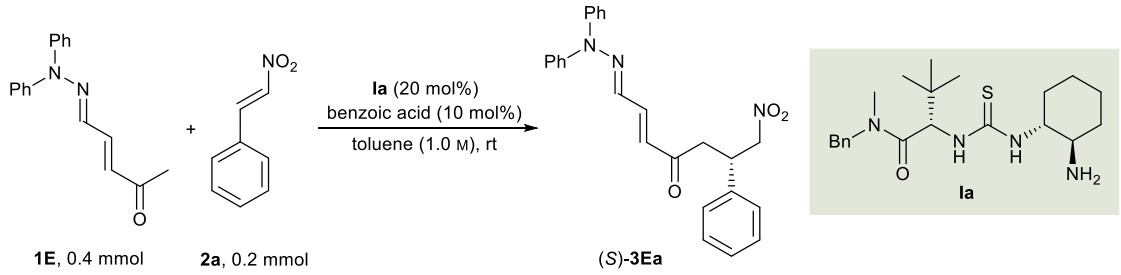
(*S*,*E*)-5-Nitro-2-oxo-4-phenylpentanal *O*-benzyl oxime, (*S*)-**5a**. Following the general procedure **9**, starting from **4** (71 mg, 0.4 mmol), nitroalkene **2a** (30 mg, 0.2 mmol), 10 mol% of **Ia** (8 mg, 0.02 mmol) and 5 mol% of benzoic acid (1.2 mg, 0.01 mmol), compound (*S*)-**5a** was obtained as a pale yellow oil (58 mg, 89%; reaction ran for 2 days). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.44 – 7.27 (m, 7H), 7.26 – 7.15 (m, 3H), 5.26 (s, 2H), 4.68 (dd, *J* = 12.5, 7.5 Hz, 1H), 4.59 (dd, *J* = 12.5, 7.5 Hz, 1H), 4.16 – 4.00 (m, 1H), 3.33 (dd, *J* = 17.1, 7.5 Hz, 1H), 3.12 (dd, *J* = 17.1, 7.5 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 195.0, 147.7, 138.4, 135.9, 129.0, 128.6, 128.6, 128.5, 127.9, 127.4, 79.5, 78.1, 40.7, 39.1. **HRMS** (ESI): m/z calcd for $C_{18}H_{18}O_4N_2Na$ [M^++Na] 349.1159, found 349.1160. The enantiomeric excess was determined by HPLC using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 11.9 min, τ_{minor} = 13.4 min (94% ee); $[\alpha]_D^{20}$ = −60.5 (c 0.5, $CHCl_3$).



No.	Retention Time min	Area mAU*min	Relative Area %
1	11.853	17.839	49.16
2	13.293	18.447	50.84

No.	Retention Time min	Area mAU*min	Relative Area %
1	11.900	161.100	96.90
2	13.423	5.149	3.10

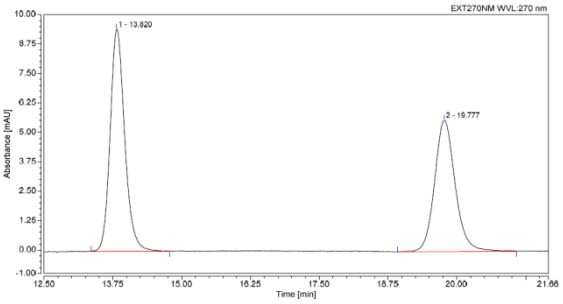
10. Synthesis of (*S*,1*E*,2*E*)-1-(2,2-diphenylhydrazineylidene)-7-nitro-6-phenylhept-2-en-4-one, (*S*)-**3Ea**



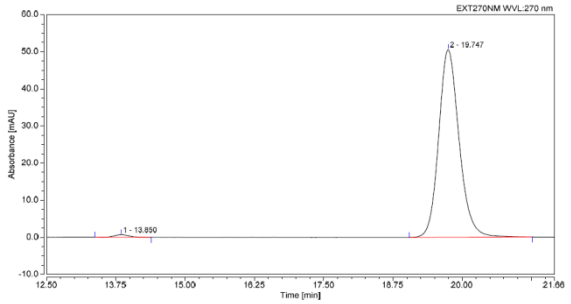
1E, 0.4 mmol **2a**, 0.2 mmol (*S*)-**3Ea**

Toluene (0.5 M, 400 µL) was added to mixture of **1E** (106 mg, 0.4 mmol), nitroalkene **2a** (30 mg, 0.2 mmol), 20 mol% of **Ia** (16 mg, 0.04 mmol) and 10 mol% of benzoic acid (2.4 mg, 0.02 mmol) at room temperature. The resulting mixture was stirred at this temperature for 48 h. After this time, the mixture was diluted with Et_2O and washed with aq. $NaHCO_3$ (3 x 5 mL, 5% w/w) and brine (1 x 15 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (*n*-hexanes/EtOAc 6/1 to 3/1) to afford pure product (*S*)-**3Ea** as a brown solid (58 mg, 70%, 98% ee; reaction performed at 1 mmol scale: 254 mg, 61%); mp. = 62-64 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.48 – 7.28 (m, 7H), 7.26 – 7.12 (m, 4H), 7.11 – 7.02 (m, 4H), 6.38 (d, *J* = 4.1 Hz, 1H), 5.29 (dd, *J* = 9.7, 4.2 Hz, 1H), 3.89 (td, *J* = 9.7, 5.9 Hz, 1H), 3.60 – 3.50 (m, 1H), 3.06 (ddd, *J* = 15.6, 5.9, 1.6 Hz, 1H), 2.90 (ddd, *J* = 15.6, 5.9, 1.6 Hz, 1H), 2.74 (dd, *J* = 15.6, 5.9 Hz, 1H), 2.62 (dd, *J* = 15.6, 9.7 Hz, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ 204.8, 143.1, 138.6, 131.9, 129.9, 129.1, 128.0, 127.2, 124.7, 122.1, 89.3, 44.9, 42.0, 41.6, 40.3. **HRMS** (ESI): m/z calcd for

$C_{25}H_{23}O_3N_3Na$ [M^++Na] 436.1632, found 436.1629. The enantiomeric excess was determined by HPLC using a Chiralpak IB column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 19.7 min, τ_{minor} = 13.8 min (98% ee); $[\alpha]_D^{20}$ = −226.6 (c 0.5, $CHCl_3$).

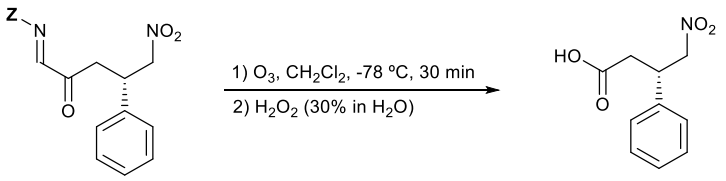


No.	Retention Time min	Area mAU*min	Relative Area %
1	13.820	2.893	54.39
2	19.777	2.426	45.61



No.	Retention Time min	Area mAU*min	Relative Area %
1	13.850	0.201	0.92
2	19.747	21.604	99.08

11. Synthesis of (*S*)-4-nitro-3-phenylbutanoic acid, (*S*)-**6a**



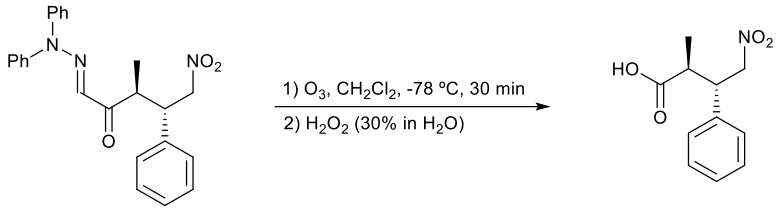
(*S*)-**3Ca** or (*S*)-**3Da**
0.5 mmol

(*S*)-**6a**

To a solution of Michael adduct [(*S*)-**3Ca** (152 mg, 0.5 mmol, >99% ee) or (*S*)-**3Da** (194 mg, 0.5 mmol, >99% ee)] in CH_2Cl_2 (5 mL) was applied a flow of ozone for 30 minutes at –78 ºC. After this time, aq. H_2O_2 (255 µL, 2.5 mmol, 30% w/w) was added and the resulting mixture was allowed to warm to room temperature. The mixture was then extracted with a saturated solution of $NaHCO_3$ (5 x 5 mL). The aqueous phase was washed with CH_2Cl_2 (3 x 10 mL), acidified with aq. HCl (2.0 M) until pH 0-1 and extracted with CH_2Cl_2 (5 x 10 mL). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was filtered through a small pad of silica gel (toluene/EtOAc 1/1) to afford (*S*)-**6a** as a colorless oil [from (*S*)-**3Ca**: 70 mg, 67%; from (*S*)-**3Da**: 53 mg, 51%]. The experimental data is in accordance with those reported in the literature.[12] **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.39 – 7.28 (m, 3H), 7.25 – 7.20 (m, 2H), 4.72 (dd, *J* = 12.6, 7.6 Hz, 1H), 4.63 (dd, *J* = 12.6, 7.6 Hz, 1H), 4.03 – 3.91 (m, 1H), 2.83 (d, *J* = 7.6 Hz, 1H), 2.83 (d, *J* = 7.6 Hz, 1H). $[\alpha]^{20}_D$ [from (*S*)-**3Ca**] = −15.2 (c 1.0, $CHCl_3$); $[\alpha]^{20}_D$ [from (*S*)-**3Da**] = −15.2 (c 1.0, $CHCl_3$). *Literature*: $[\alpha]^{20}_D$= −15.2 [c 1.0, $CHCl_3$, 99% ee (*S*)].

[12] (a) F. Felluga, V. Gombac, G. Pitacco and E. Valentin, *Tetrahedron: Asymmetry*, 2005, **16**, 1341; (b) O. V. Maltsev, A. S. Kucherenko, I. P. Beletskaya, V. A. Tartakovsky and S. G. Zlotin, *Eur. J. Org. Chem.*, 2010, 2927.

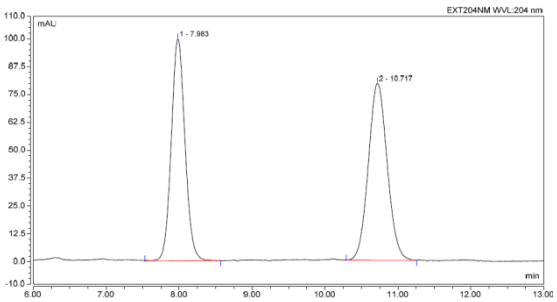
12. Synthesis of (2*S*,3*S*)-2-methyl-4-nitro-3-phenylbutanoic acid, (*S*,*S*)-6b



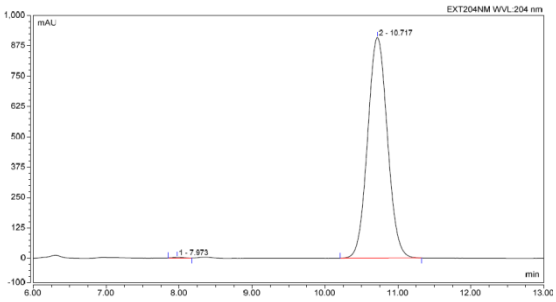
(*S*,*S*)-**3Fa**
0.25 mmol

(*S*,*S*)-**6b**

To a solution of Michael adduct (*S*,*S*)-**3Fa** (100 mg, 0.25 mmol, 99% ee, dr. >20/1) in CH_2Cl_2 (2.5 mL) was applied a flow of ozone for 30 minutes at –78 ºC. After this time, aq. H_2O_2 (128 µL, 1.25 mmol, 30% w/w) was added and the resulting mixture was allowed to warm to room temperature. The mixture was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was filtered through a small pad of silica gel (toluene/EtOAc 1/1) to afford (*S*,*S*)-**6b** as a pale brown solid (42 mg, 76%); mp. = 66-68 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.34 – 7.27 (m, 3H), 7.23 – 7.17 (m, 2H), 4.87 (dd, *J* = 13.1, 5.8 Hz, 1H), 4.78 (dd, *J* = 13.1, 9.3 Hz, 1H), 3.81 (dt, *J* = 9.3, 6.4 Hz, 1H), 2.98 – 2.89 (m, 1H), 1.25 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 178.1, 136.9, 128.9, 128.1, 128.0, 77.4, 46.1, 42.6, 14.5. **HRMS** (ESI): m/z calcd for $C_{11}H_{13}O_4NNa$ [M^++Na] 246.0737, found 246.0735. $[\alpha]_D^{20}$ = −16.4 (c 1.0, $CHCl_3$). The enantio- and diastereomeric excess were determined by HPLC after esterification with superdry MeOH (0.07 M, 2.0 equiv. of thionyl chloride, 70 ºC, 2 h) using a Chiralpak OD column [*n*-hexanes/^{i}PrOH (80:20)]; flow rate 1 mL/min; τ_{major} = 10.7 min, τ_{minor} = 8.0 min (>99% ee, dr. >20/1). The experimental data is in accordance with those reported in the literature.[13] **^{1}H NMR** of methyl ester, **6b'** (300 MHz, $CDCl_3$): δ 7.39 – 7.26 (m, 3H), 7.17 (d, *J* = 6.8 Hz, 2H), 4.87 (dd, *J* = 13.0, 5.9 Hz, 1H), 4.81 – 4.70 (m, 1H), 3.86 – 3.72 (m, 1H), 3.56 (s, 3H), 2.98 – 2.81 (m, 1H), 1.23 (d, *J* = 7.0 Hz, 3H).



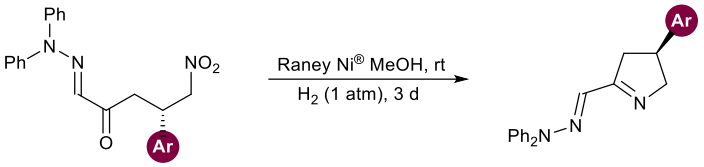
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.983	21.677	47.69
2	10.717	23.772	52.31



No.	Retention Time min	Area mAU*min	Relative Area %
1	7.973	0.322	0.11
2	10.717	285.110	99.89

[13] D. Yang, L. Wang, D. Li, F. Han, D. Zhao and R. Wang, *Chem. Eur. J.*, 2015, **21**, 1458.

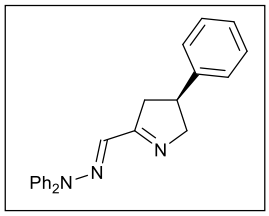
13. General procedure for the synthesis of imino-hydrazones (*S*)-7a-c



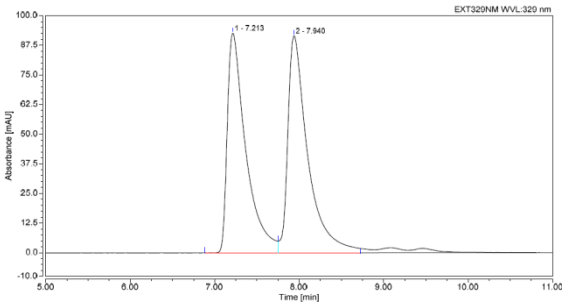
(*S*)-**3D**, 0.5 mmol (*S*)-**7a-c**

Michael adduct (*S*)-**3D** (0.5 mmol) was added to a suspension of Raney Ni® (0.25 mL, 50% in water) in MeOH (10 mL) at room temperature. The suspension was stirred for 72 hours under H_2 atmosphere (1 atm). After this time, the mixture was filtered through a celite pad and the solvent was eliminated under reduced pressure. The resulting residue was purified by flash chromatography (*n*-hexanes/EtOAc 3/1) to afford pure product (*S*)-**7a-c**.

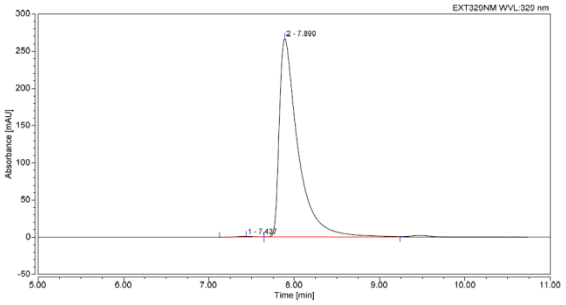
(*S*,*E*)-5-[(2,2-Diphenylhydrazineylidene)methyl]-3-phenyl-3,4-dihydro-2*H*-pyrrole, (*S*)-**7a**.



Following the general procedure **13**, starting from (*S*)-**3Da** (194 mg, 0.5 mmol, >99% ee), compound (*S*)-**7a** was obtained as a yellow solid (120 mg, 71%); mp. = 116-118 °C. **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 7.49 – 7.36 (m, 4H), 7.36 – 7.26 (m, 2H), 7.26 – 7.12 (m, 9H), 7.11 (s, 1H), 4.36 (ddt, *J* = 16.6, 8.1, 1.6 Hz, 1H), 3.91 (ddt, *J* = 16.6, 5.8, 1.6 Hz, 1H), 3.64 – 3.37 (m, 2H), 3.14 – 2.98 (m, 1H). **^{13}C NMR** (75.5 MHz, CD_2Cl_2): δ 173.1, 145.9, 143.4, 133.0, 130.4, 129.1, 127.4, 126.8, 125.8, 122.9, 70.1, 43.2, 43.0. **HRMS** (ESI): m/z calcd for $C_{23}H_{22}N_3$ [M^++H] 340.1808, found 340.1803. The enantiomeric excess was determined by HPLC using a Chiralpak ID column [*n*-hexanes/^{i}PrOH (90:10)]; flow rate 1 mL/min; τ_{major} = 7.9 min, τ_{minor} = 7.4 min (>99% ee); $[\alpha]_D^{20}$ = +269.8 (c 0.5, $CHCl_3$).

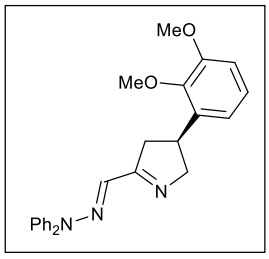


No.	Retention Time min	Area mAU*min	Relative Area %
1	7.213	23.443	48.44
2	7.940	24.949	51.56



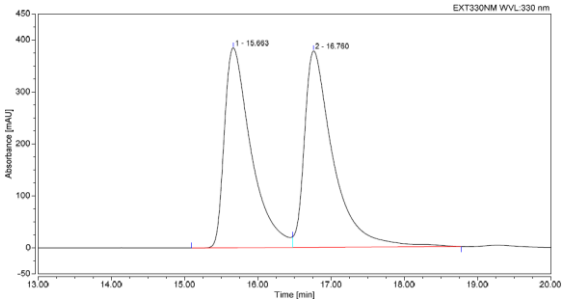
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.437	0.225	0.33
2	7.890	67.434	99.67

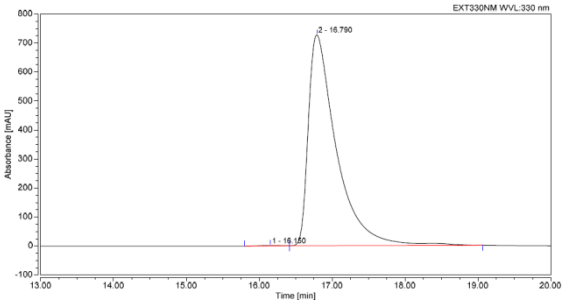
(*S*,*E*)-3-(2,3-Dimethoxyphenyl)-5-[(2,2-diphenylhydrazineylidene)methyl]-3,4-dihydro-2*H*-pyrrole,



(*S*)-**7b**. Following the general procedure **13**, starting from (*S*)-**3Dc** (224 mg, 0.5 mmol, >99% ee), compound (*S*)-**7b** was obtained as a yellow oil (134 mg, 67%, >99% ee). **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 7.47 – 7.36 (m, 4H), 7.25 – 7.12 (m, 6H), 7.11 (s, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.80 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.74 (dd, *J* = 8.0, 1.5 Hz, 1H), 4.40 – 4.25 (m, 1H), 3.85 (s, 3H), 3.98 – 3.82 (m, 2H), 3.81 (s, 3H), 3.48 – 3.32 (m, 1H), 3.10 – 2.97 (m, 1H). **^{13}C NMR** (75.5 MHz, CD_2Cl_2): δ 173.0, 153.4, 147.4, 143.4, 139.5, 133.1, 130.4, 125.8, 124.7, 122.9, 119.3, 111.0, 69.7, 61.2, 56.2, 42.7, 35.9. **HRMS** (ESI):

m/z calcd for $C_{25}H_{26}O_2N_3$ [M^++H] 400.2020, found 400.2016. The enantiomeric excess was determined by HPLC using a Chiralpak ID column [*n*-hexanes/^{i}PrOH (80:20)]; flow rate 0.5 mL/min; τ_{major} = 16.8 min, τ_{minor} = 15.7 (>99% ee); $[\alpha]_D^{20}$ = +202.7 (c 0.5, $CHCl_3$).

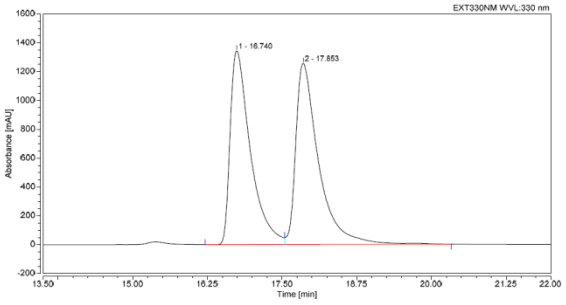


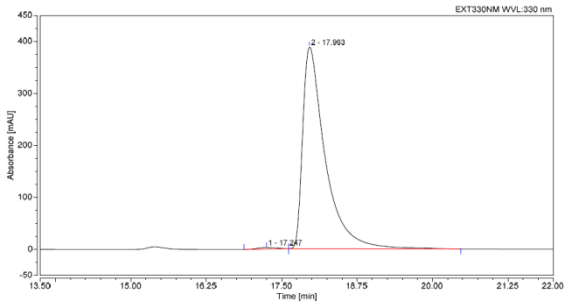


No.	Retention Time min	Area mAU*min	Relative Area %
1	15.663	162.165	48.58
2	16.760	171.662	51.42

No.	Retention Time min	Area mAU*min	Relative Area %
1	16.150	0.377	0.12
2	16.790	323.732	99.88

(*S*,*E*)-5-[(2,2-Diphenylhydrazineylidene)methyl]-3-[3-(trifluoromethyl)phenyl]-3,4-dihydro-2*H*-pyrrole, (*S*)-**7c**. Following the general procedure **13**, starting from (*S*)-**3Dh** (228 mg, 0.5 mmol, 97% ee), compound (*S*)-**7c** was obtained as a yellow oil (147 mg, 72%). **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 7.52 – 7.37 (m, 8H), 7.26 – 7.19 (m, 2H), 7.19 – 7.12 (m, 4H), 7.10 (s, 1H), 4.39 (ddt, *J* = 16.9, 8.3, 1.6 Hz, 1H), 3.93 (ddt, *J* = 16.9, 6.1, 1.6 Hz, 1H), 3.70 – 3.57 (m, 1H), 3.57 – 3.43 (m, 1H), 3.06 (ddt, *J* = 16.9, 6.1, 1.6 Hz, 1H). **^{13}C NMR** (75.5 MHz, CD_2Cl_2): δ 172.9, 147.0, 143.3, 132.7, 131.0, 130.5, 129.8, 125.9, 124.5 – 124.1 (m), 123.9 – 123.4 (m), 122.9, 69.9, 43.2, 42.8. **^{19}F NMR** (471 MHz, CD_2Cl_2): δ –62.83 (s, 3F). **HRMS** (ESI): m/z calcd for $C_{24}H_{21}N_3F_3$ [M^++H] 408.1682, found 408.1678. The enantiomeric excess was determined by HPLC using a Chiralpak ID column [*n*-hexanes/^{i}PrOH (95:5)]; flow rate 0.4 mL/min; τ_{major} = 18.0 min, τ_{minor} = 16.7 min (98% ee); $[\alpha]_D^{20}$ = +230.7 (c 0.5, $CHCl_3$).

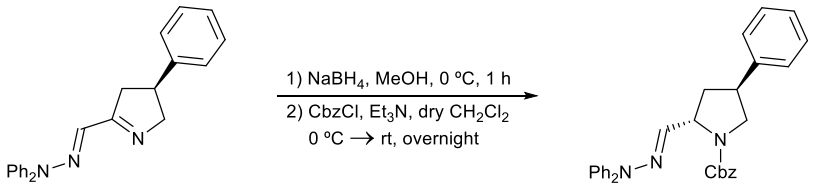




No.	Retention Time min	Area mAU*min	Relative Area %
1	16.740	526.146	48.57
2	17.853	557.047	51.43

No.	Retention Time min	Area mAU*min	Relative Area %
1	17.247	1.045	0.62
2	17.963	167.433	99.38

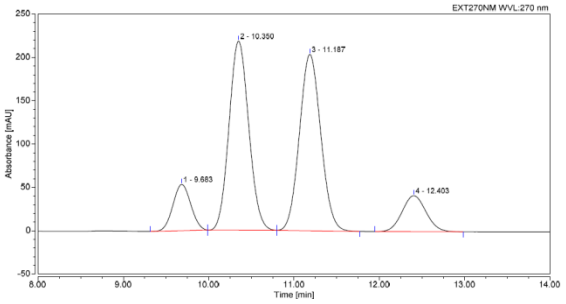
14. Synthesis of benzyl (2*S*,4*S*)-2-[(*E*)-(2,2-diphenylhydrazineylidene)methyl]-4-phenylpyrrolidine-1-carboxylate, (*S*,*S*)**-8**



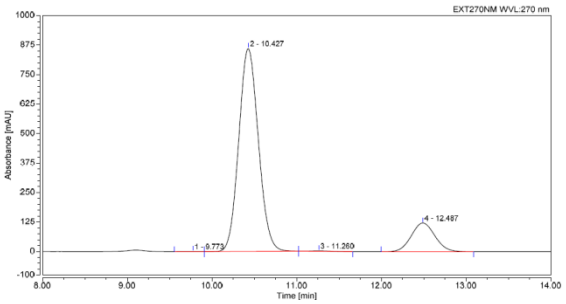
(*S*)-**7a**, 0.5 mmol (*S*,*S*)-**8**

Step 1: Sodium borohydride (60 mg, 1.5 mmol) was added to a solution of imino-hydrazone (*S*)-**7a** (170 mg, 0.5 mmol, >99% ee) in MeOH (10 mL) at 0 ºC. The resulting mixture was stirred at 0 ºC for 1 hour. After this time, the solvent was eliminated under reduced pressure. The mixture was then diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were washed with H_2O (1 x 50 mL) and brine (1 x 50 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to afford the (2*S*,4*S*)-2-[(*E*)-(2,2-diphenylhydrazineylidene)methyl]-4-phenylpyrrolidine as a yellow oil, which was used in the next step without further purification.

Step 2: Triethylamine (77 µL, 0.55 mmol) and benzyl chloroformate (77 µL, 0.525 mmol) were subsequently added to a solution of the crude pyrrolidine (~0.5 mmol) in dry CH_2Cl_2 (5 mL) at 0 ºC. The resulting mixture was allowed to warm to room temperature and stirred overnight. The mixture was then diluted with CH_2Cl_2 (15 mL) and washed with a saturated solution of NH_4Cl (1 x 15 mL), aq. $NaHCO_3$ (1 x 15 mL, 10% w/w) and brine (1 x 15 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (*n*-hexanes/EtOAc 5/1) to afford a diasteromeric mixture of (*S*,*S*)-**8** as an orange oil (199 mg, 84% in two steps). **^{1}H NMR** (300 MHz, $CDCl_3$). The compound exists as ~2.5:1 mixture of carbamate rotamers. *Signals corresponding to the major rotamer*: δ 7.43 – 7.29 (m, 9H), 7.27 – 7.07 (m, 8H), 7.06 – 6.90 (m, 3H), 6.39 (d, *J* = 5.0 Hz, 1H), 5.28 – 5.00 (m, 2H), 4.70 (ddd, *J* = 9.3, 7.0, 5.8 Hz, 1H), 4.24 – 3.91 (m, 1H), 3.60 – 3.29 (m, 2H), 2.72 – 2.49 (m, 1H), 2.40 – 2.00 (m, 1H). *Representative signals corresponding to the minor rotamer*: 6.65 (br s, 1H). **^{13}C NMR** (75.5 MHz, $CDCl_3$), *only resonance of the major rotamer shown*: δ 155.1, 143.6, 140.0, 138.1, 136.4, 129.7, 128.6, 128.4, 127.7, 127.6, 127.1, 126.9, 124.2, 122.2, 67.0, 59.7, 53.1, 42.4, 39.1. **HRMS** (ESI): m/z calcd for $C_{31}H_{30}O_2N_3$ [M^++H] 476.2333, found 476.2327. The enantio- and diastereomeric excess was determined by HPLC using a Chiralpak IC column [*n*-hexanes/^{i}PrOH (85:15)]; flow rate 1 mL/min; τ_{major} = 10.4 min, τ_{minor} = 11.3 min (>99% ee, dr. = 5.8/1); $[\alpha]_D^{20}$ = +13.6 (c 0.5, $CHCl_3$).

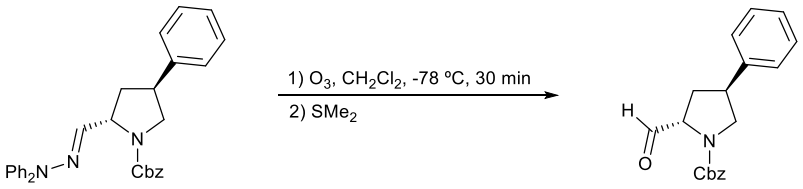


No.	Retention Time min	Area mAU*min	Relative Area %
1	9.683	12.964	9.01
2	10.350	58.415	40.61
3	11.187	58.999	41.01
4	12.403	13.473	9.37



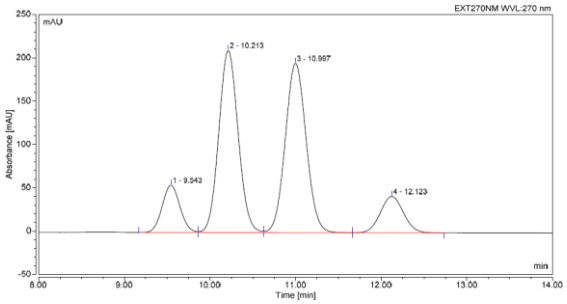
No.	Retention Time min	Area mAU*min	Relative Area %
1	9.773	0.099	0.04
2	10.427	230.366	85.23
3	11.260	0.454	0.17
4	12.487	39.372	14.57

15. Synthesis of benzyl (2*S*,4*S*)-2-formyl-4-phenylpyrrolidine-1-carboxylate, (*S*,*S*)-9

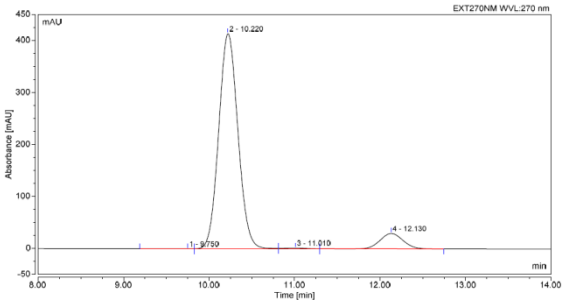


(*S*)-**8**, 0.25 mmol (*S*,*S*)-**9**

To a solution of (*S*)-**8** (119 mg, 0.25 mmol, >99% ee, dr. = 5.8/1) in CH_2Cl_2 (2.5 mL) was applied a flow of ozone for 30 minutes at –78 ºC. After this time, SMe_2 was added (92 µL, 1.25 mmol) and the resulting mixture was allowed to warm to room temperature. The solvent was eliminated under reduced pressure and the residue was purified by flash chromatography (*n*-hexanes/EtOAc 3/1) to afford a diasteromeric mixture of (*S*,*S*)-**9** as a yellow oil (60 mg, 78%). **^{1}H NMR** (300 MHz, CD_2Cl_2): the compound exists as ~1.1:1 mixture of carbamate rotamers. *Signals corresponding to the major rotamer*: δ 9.53 (d, *J* = 3.3 Hz, 1H), 7.45 – 7.19 (m, 10H), 5.19 (s, 2H), 4.39 – 4.23 (m, 1H), 4.21 – 3.97 (m, 1H), 3.60 – 3.34 (m, 2H), 2.63 – 2.40 (m, 1H), 2.16 – 1.92 (m, 1H). *Representative signals corresponding to the minor rotamer*: 9.47 (d, *J* = 3.3 Hz, 1H), 5.15 (s, 2H). **^{13}C NMR** (75.5 MHz, CD_2Cl_2): *signals corresponding to both rotamers*: δ 199.9, 199.8, 155.8, 154.8, 140.1, 137.2, 137.1, 129.3, 129.1, 128.7, 128.6, 128.5, 128.4, 127.8, 127.6, 127.5, 67.9, 66.1, 65.8, 53.9, 53.6, 44.1, 43.2, 35.8, 34.8. **HRMS** (ESI): m/z calcd for $C_{19}H_{19}O_3NNa$ [M^++Na] 332.1257, found 332.1257. The enantio- and diastereomeric excess was determined by HPLC after condensation with 1,1-diphenylhydrazine hydrochloride [1.2 equiv., THF/H_2O 10/1 (0.1 M), 0 ºC to rt, 1 h] using a Chiralpak IC column [*n*-hexanes/^{i}PrOH (85:15)]; flow rate 1 mL/min; τ_{major} = 10.2 min, τ_{minor} = 11.0 min (>99% ee, dr. = 12/1); $[\alpha]_D^{20}$ = +41.7 (c 0.5, $CHCl_3$). Relative configuration (*S*,*S*) was confirmed by ^{1}H and abcense of cross-peaks in the NOESY experiment.

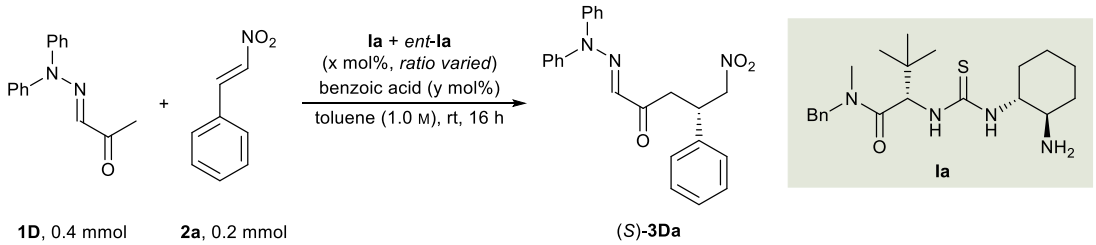


No.	Retention Time min	Area mAU*min	Relative Area %
1	9.543	13.180	9.64
2	10.213	55.096	40.28
3	10.997	55.316	40.44
4	12.123	13.199	9.65



No.	Retention Time min	Area mAU*min	Relative Area %
1	9.750	0.003	0.00
2	10.220	107.750	91.85
3	11.010	0.383	0.33
4	12.130	9.177	7.82

16. Non-linear effect experiments



Ia (10 mol%) and PhCOOH (5 mol%): Two solutions containing catalyst **Ia** or *ent*-**Ia** (78 mg, 0.2 mmol) and benzoic acid (12 mg, 0.1 mmol) were prepared in toluene (2.0 mL, 0.1 M). After complete solubilization, mixtures of stock solutions previously described were prepared according to **Table S3**, to afford stock solutions of **Ia** or *ent*-**Ia** (10 mol%) and benzoic acid (5 mol%) with different enantiomeric excesses. At this point, ketone **1D** (95 mg, 0.4 mmol) and nitroalkene **2a** (30 mg, 0.2 mmol) were subsequently added at room temperature. The resulting mixture was stirred at this temperature for 16 hours. Conversions were determined by ^{1}H NMR and enantiomeric ratios were determined by HPLC analysis.

Table S3

Entry	L-ent (µL)	D-ent (µL)	ee_{Ia} (%)[a]	Conv. (%)[b]	ee_{3Da} (%)[c]	ee_{THEOR} (%)
1	100	100	0	87	0	0
2	120	80	20	89	26	20
3	140	60	40	91	50	40
4	160	40	60	92	72	60
5	180	20	80	94	89	80
6	200	0	>99	>95	>99	>99

[a] The preparations of **Ia** and ***ent*-Ia** are assumed to be enantiomerically pure. [b] Determined by ^{1}H NMR in the crude mixture. [c] Determined by HPLC analysis after isolation of the product by semipreparative TLC (*n*-hexanes/EtOAc 5/1).

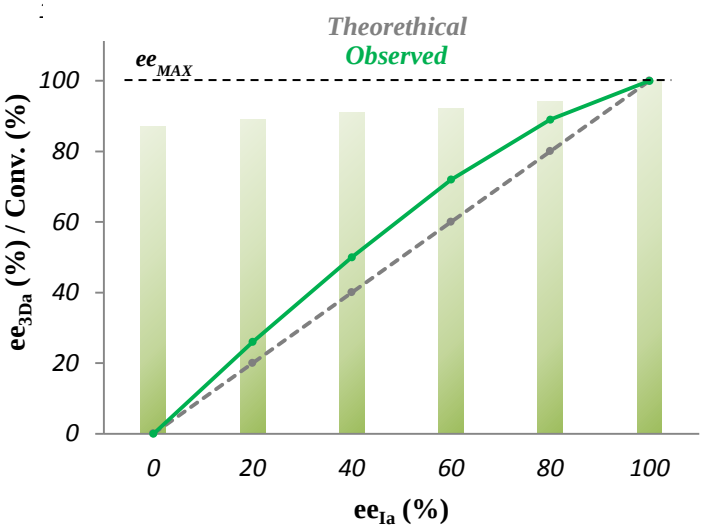


Figure S1 Relationship between catalyst and product enantiomeric excess [**Ia** (10 mol%) and PhCOOH (5 mol%)]. The solid green line represents the regression of the data obtained with catalyst **Ia** (**green** circles). The solid gray line represents the linear regression of the reaction (**gray** circles). Conversions are also represented (**green** columns)

Ia (20 mol%) and PhCOOH (20 mol%): Two solutions containing catalyst **Ia** or *ent*-**Ia** (156 mg, 0.4 mmol) and benzoic acid (49 mg, 0.4 mmol) were prepared in toluene (2.0 mL, 0.1 M). After complete solubilization, mixtures of stock solutions previously described were prepared according to **Table S4**, to afford stock solutions of **Ia** or *ent*-**Ia** (20 mol%) and benzoic acid (20 mol%) with different enantiomeric excesses. At this point, ketone **1D** (95 mg, 0.4 mmol) and nitroalkene **2a** (30 mg, 0.2 mmol) were subsequently added at room temperature. The resulting mixture was stirred at this temperature for 16 hours. Conversions were determined by ^{1}H-NMR and enantiomeric ratios were determined by HPLC analysis.

Table S4

Entry	L-ent (µL)	D-ent (µL)	ee_{Ia} (%)[a]	Conv. (%)[b]	ee_{3Da} (%)[c]	ee_{THEOR} (%)
1	100	100	0	19	0	0
2	120	80	20	36	61	20
3	140	60	40	43	83	40
4	160	40	60	80	97	60
5	180	20	80	90	98	80
6	200	0	>99	>95	>99	>99

[a] The preparations of **Ia** and ***ent*-Ia** are assumed to be enantiomerically pure. [b] Determined by ^{1}H NMR in the crude mixture. [c] Determined by HPLC analysis after isolation of the product by semipreparative TLC (*n*-hexanes/EtOAc 5/1).

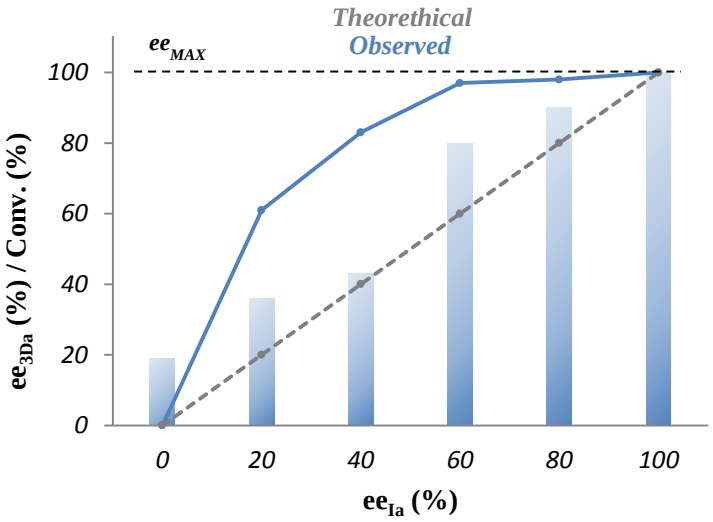


Figure S2 Relationship between catalyst and product enantiomeric excess [**Ia** (20 mol%) and PhCOOH (20 mol%)]. The solid blue line represents the regression of the data obtained with catalyst **Ia** (**blue** circles). The solid gray line represents the linear regression of the reaction (**gray** circles). Conversions are also represented (**blue** columns)

17. Diffusion coefficient equation and equation to calculate the increase of radius of the diffusing molecule

The molecular size can be estimated from the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\mu r}$$

(k = Boltzmann constant; μ = solvent viscosity; r = radius of the diffusing particle/molecule)

Equation 1

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To calculate the increase of the diffusing molecule radius in different solutions the **Equation 2** was used, which considers the diffusion coefficient of residual non deuterated toluene avoiding the error due to viscosity:

$$D_A = \frac{kT}{6\pi\mu_A r_A} \;\; ; \;\; D_B = \frac{kT}{6\pi\mu_B r_B}$$

$$\frac{D_A}{D_B} = \frac{\mu_B}{\mu_A}\frac{r_B}{r_A}$$

$$D(Tol)_A = \frac{kT}{6\pi\mu_A r(Tol)_A} \;\; ; \;\; D(Tol)_B = \frac{kT}{6\pi\mu_B r(Tol)_B}$$

$$\frac{D(Tol)_A}{D(Tol)_B} = \frac{\mu_B}{\mu_A}\frac{r(Tol)_B}{r(Tol)_A} \;\; ; \;\; r(Tol)_A = r(Tol)_B \;\; ; \;\; \frac{D(Tol)_A}{D(Tol)_B} = \frac{\mu_B}{\mu_A}$$

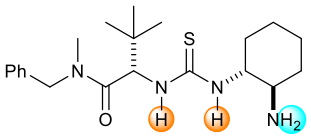
$$\frac{D_A}{D_B} = \frac{D(Tol)_A}{D(Tol)_B}\frac{r_B}{r_A}$$

$$\frac{r_B}{r_A} = \frac{D_A}{D_B}\frac{D(Tol)_B}{D(Tol)_A}$$

Equation 2

18. ^{1}H NMR spectra of Ia and *rac*-Ia at different concentrations

Four solutions containing catalyst **Ia** (1.9 – 78.1 mg, 0.005 – 0.2 mmol) in toluene-d_8 (0.5 mL, 0.01 – 0.40 M) or catalyst *rac*-**Ia** (39.1 mg, 0.1 mmol) in toluene-d_8 (0.5 mL, 0.2 M) were prepared and a ^{1}H NMR spectrum were recorded for each sample at 500 MHz. The change in chemical shifts could be observed for the N***H*** signals: In homochiral catalyst (**Ia**), the chemical shift of both primary amine (**blue** circles) and thioureido (**orange** circles) protons were shifted downfield from 1.44 → 3.14 ppm and 6.94 → 7.92 ppm, respectively (**Figure S3**, top). This concentration dependency is consistent with the self-aggregation of catalyst **Ia**. In heterochiral catalyst (*rac*-**Ia**), the chemical shift of both primary amine (**blue** circle) and a thioureido (**orange** circle) protons were shifted downfield from 2.82 → 4.27 ppm and 7.80 → 8.20 ppm, respectively (Figure **3**, bottom). These last results suggest a higher self-aggregation state of heterochiral catalyst (*rac*-**Ia**) in comparison with homochiral catalyst (**Ia**), as illustrated in the ^{1}H NMR DOSY experiment (**Table S5**, *vide infra*).



(*rac*)-**Ia**

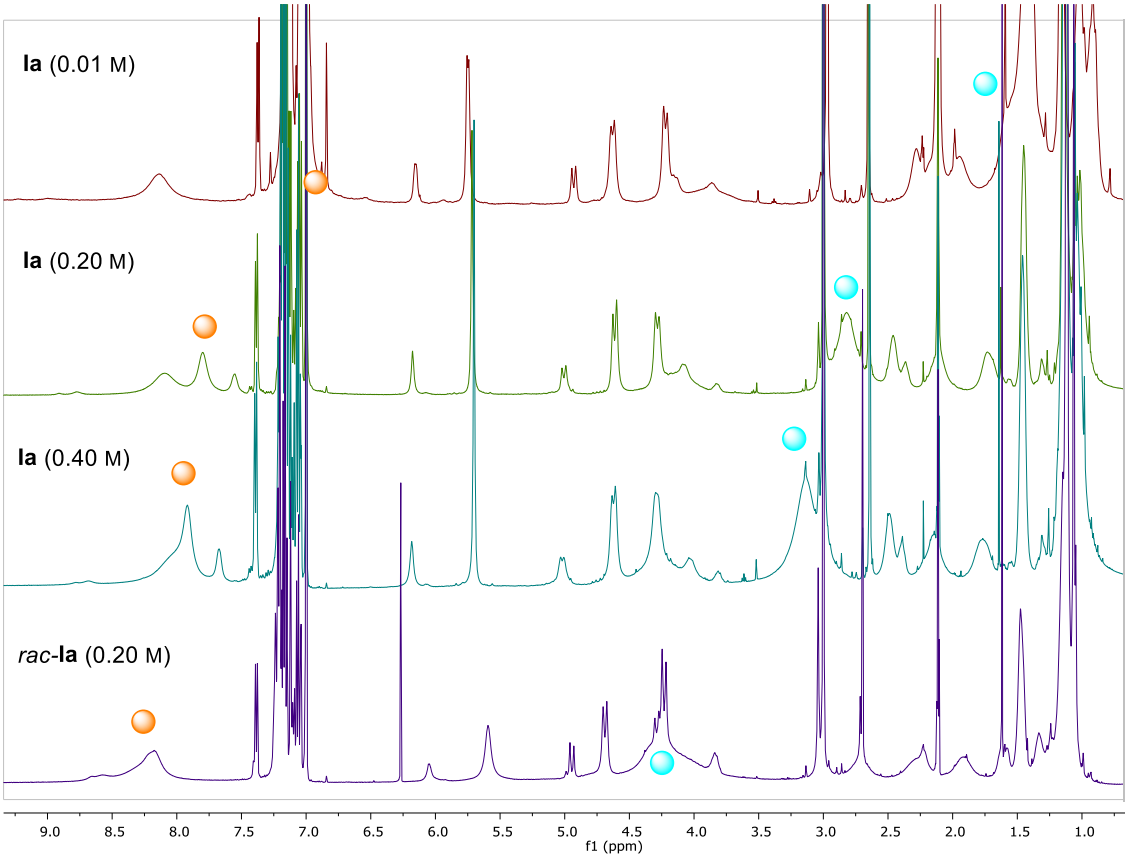


Figure S3 *Red spectrum*: ^{1}H NMR of catalyst **Ia** (0.01 M in toluene-d_8, 25ºC); *green spectrum*: ^{1}H NMR of catalyst **Ia** (0.20 M in toluene-d_8, 25ºC); *blue spectrum*: ^{1}H NMR of catalyst **Ia** (0.40 M in toluene-d_8, 25ºC); *purple spectrum*: ^{1}H NMR of catalyst *rac*-**Ia** (0.20 M in toluene- d_8, 25ºC)

19. ^{1}H NMR DOSY spectra of Ia and *rac*-Ia

Two solutions containing catalyst **Ia** (39.1 mg, 0.1 mmol) or catalyst *rac*-**Ia** (39.1 mg, 0.1 mmol) in toluene-d_8 (0.5 mL, 0.20 M) were prepared and a ^{1}H NMR DOSY spectrum were recorded for each sample at 500 MHz (**Figure S4**). The lower diffusion coefficient (D) in heterochiral catalyst (*rac*-**Ia**) suggests a higher self-aggregation (**Table S5**) in comparison with homochiral catalyst (**Ia**).

Ia *rac*-**Ia**

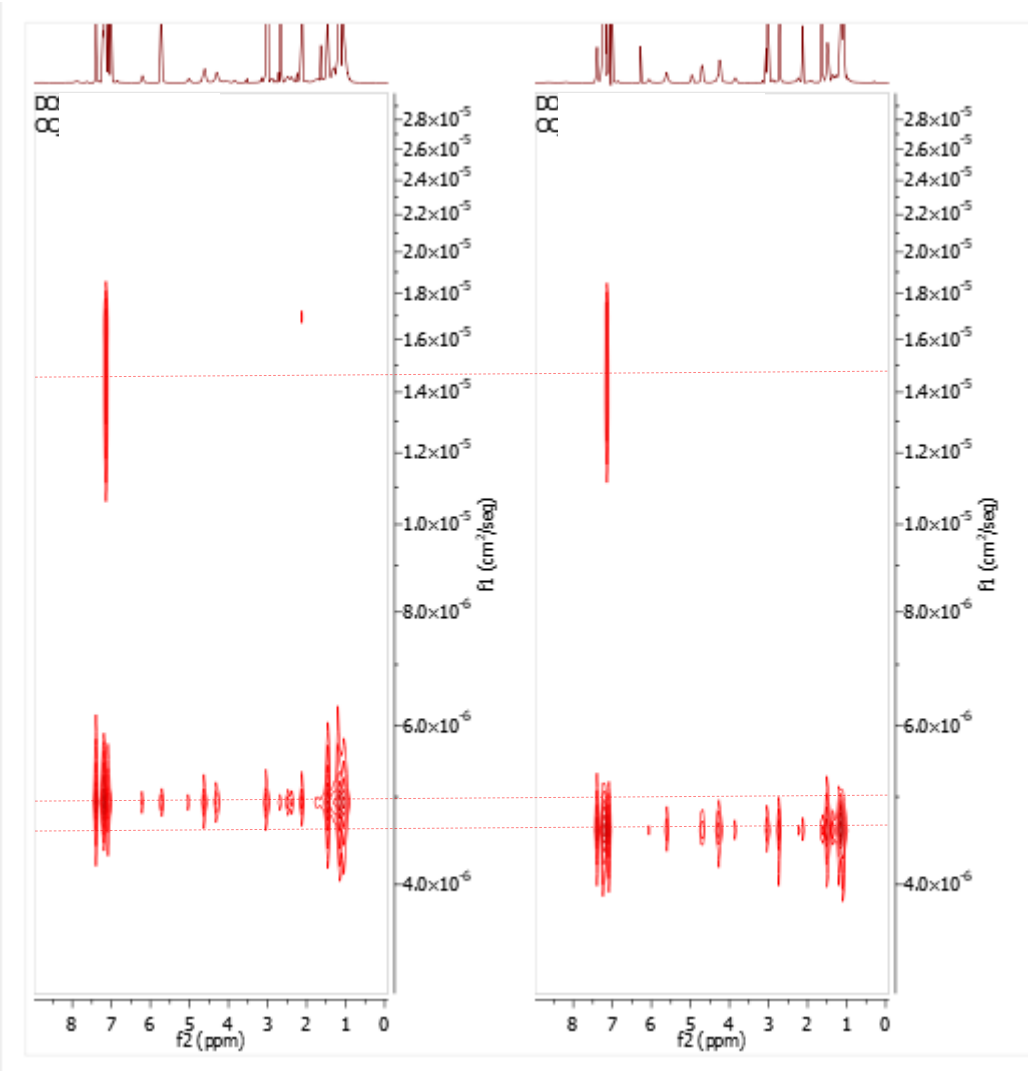


Figure S4 *Left*: ^{1}H NMR DOSY of catalyst **Ia** (0.20 M in toluene-d_8, 25ºC); *right*: ^{1}H NMR DOSY of catalyst *rac*-**Ia** (0.20 M in toluene-d_8, 25ºC)

Table S5

Entry	Solution	D_{Cat} (10^{-10} m^2s^{-1})[a]	D_{Tol} (10^{-9} m^2s^{-1})[b]
1	**Ia**	5.07	1.80
2	*rac*-**Ia**	4.70	1.80

[a]Diffusion coefficient D obtained by ^{1}H NMR DOSY. [b] D_{Tol} refers to residual non deuterated toluene.

20. NMR studies of Ia + PhCOOH

Three solutions containing catalyst **Ia** (39.1 mg, 0.1 mmol), benzoic acid (12.2 mg, 0.1 mmol) or a mixture of catalyst **Ia** (39.1 mg, 0.1 mmol) and benzoic acid (12.2 mg, 0.1 mmol) in toluene-d_8 (0.5 mL, 0.20 M) were prepared and a ^{1}H NMR spectrum were recorded for each sample at 500 MHz. The changes in both chemical shifts and multiplicities could be observed for the N***H*** signals: the chemical shift of both primary amine (**blue** circles) and thioureido (**yellow** and **orange** circles) protons were shifted downfield from 2.81 → 8.17 ppm, 7.82 (singlet) → 8.44 (doublet) ppm and 8.12 (singlet) → 9.44 (doublet) ppm, respectively (**Figure S5**). These results suggest the presence of the H-bonding complexation between **Ia** with benzoic acid, as illustrated in the ^{1}H NMR DOSY experiment (**Table S6**, *vide infra*).

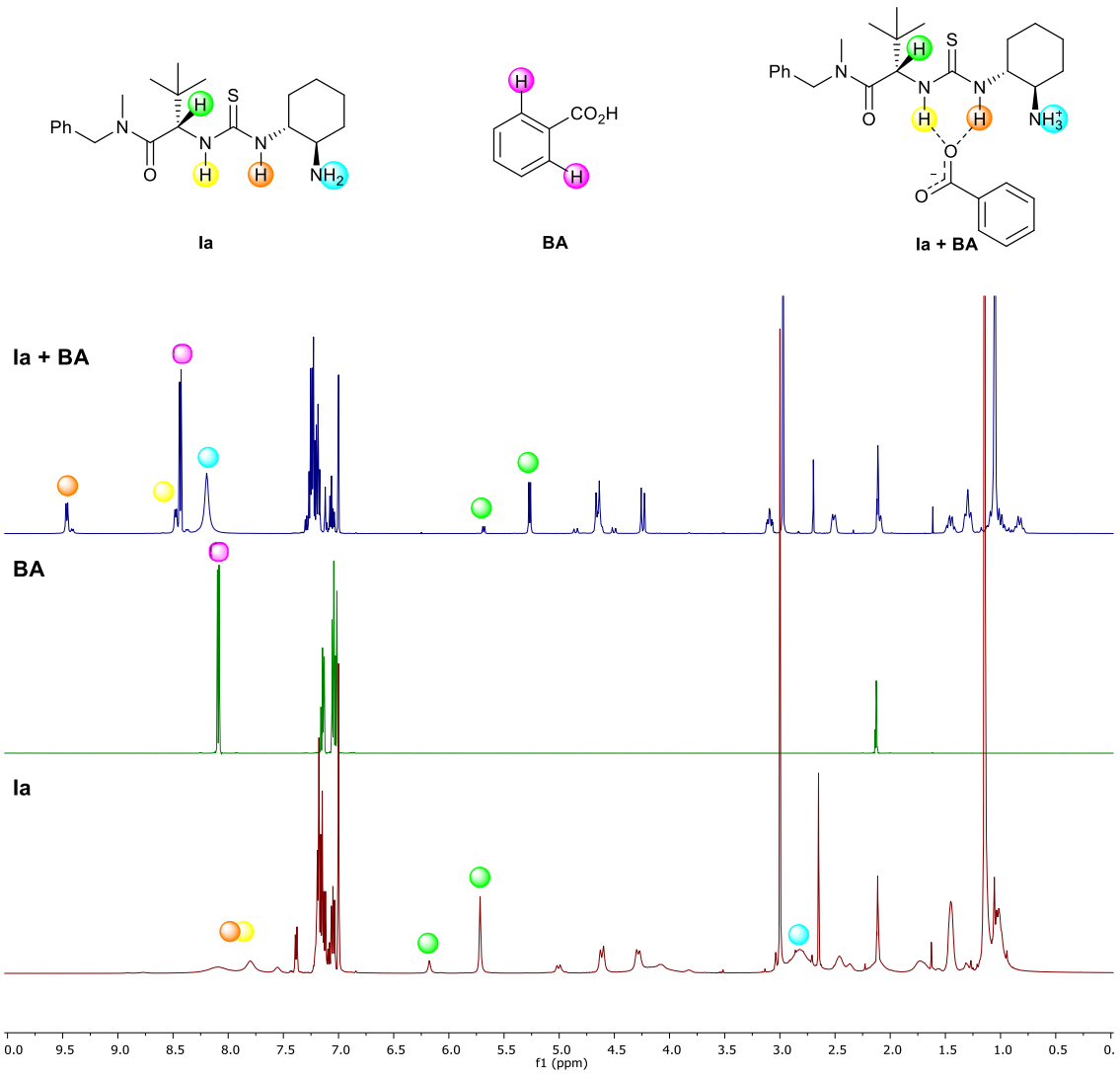
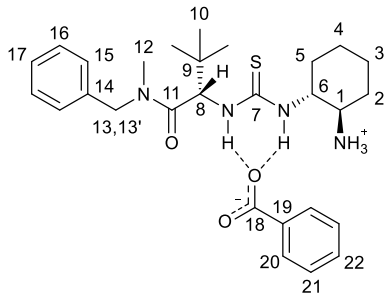


Figure S5 *Blue spectrum*: ^{1}H NMR of the mixture of catalyst **Ia** and benzoic acid (0.2 M in toluene-d_8, 25ºC); *green spectrum*: ^{1}H NMR of benzoic acid (0.2 M in toluene-d_8, 25ºC); *red spectrum*: ^{1}H NMR of catalyst **Ia** (0.2 M in toluene-d_8, 25ºC)

Characterization data of homochiral catalyst **Ia** + PhCOOH complex. **^{1}H NMR** (500 MHz, toluene-d_8):



the complex exists as a ~6.5:1 mixture of rotamers. *Signals corresponding to the major rotamer*: δ 9.42 (d, *J* = 8.0 Hz, 1H, N*H*-C_6), 8.46 (d, *J* = 7.5 Hz, 1H, N*H*-C_8), 8.44 – 8.36 (m, 2H, H_{19}), 8.16 (s, 3H, NH_3^+), 7.30 – 7.12 (m, 9H, H_{ar}), 5.25 (d, *J* = 7.6 Hz, 1H, H_8), 4.69 – 4.56 (m, 2H, H_{13} and H_6), 4.22 (d, *J* = 14.8 Hz, 1H, $H_{13'}$), 3.07 (td, *J* = 11.4, 4.1 Hz, 1H, H_1), 2.95 (s, 3H, H_{12}), 2.55 – 2.39 (m, 1H, H_5), 2.12 – 2.00 (m, 1H, H_2), 1.43 (m, 1H, $H_{2'}$), 1.36 – 1.19 (m, 2H, $H_{4,4'}$), 1.19 – 1.08 (m, 1H, H_3), 1.03 (s, 9H, H_{10}), 1.04 – 0.92 (m, 1H, $H_{5'}$), 0.92 – 0.73 (m, 1H, $H_{3'}$). *Representative signals corresponding to the minor rotamer*: δ 9.39 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 5.66 (d, *J* = 8.4 Hz, 1H), 4.83 (d, *J* = 15.2 Hz, 1H), 4.48 (d, *J* = 15.3 Hz, 1H). **^{13}C NMR** (126 MHz, toluene-d_8): *only signals corresponding to the major rotamer shown*: δ 184.7 (C_7), 173.8 (C_{11}), 173.60 (C_{18}), 137.3 (C_{19}), 130.9 (C_{ar}), 130.4 (C_{20}), 129.1 (C_{ar}), 128.8 (C_{ar}), 128.4(C_{ar}), 128.2 (C_{ar}), 127.6 (C_{ar}), 61.5 (C_8), 56.9 (C_6), 54.5 (C_1), 52.2 (C_{13}), 36.3 (C_{12}), 35.5 (C_9), 32.4 (C_5), 31.3 (C_2), 27.0 (C_{10}), 24.5 (C_3), 24.4 (C_4).

21. ^{1}H NMR DOSY spectra of Ia + PhCOOH

Three solutions containing catalyst **Ia** (39.1 mg, 0.1 mmol), benzoic acid (12.2 mg, 0.1 mmol) or a mixture of catalyst **Ia** (39.1 mg, 0.1 mmol) and benzoic acid (12.2 mg, 0.1 mmol) in toluene-d_8 (0.5 mL, 0.20 M) were prepared and a ^{1}H NMR DOSY spectrum were recorded for each sample at 500 MHz (**Figure S6**). The lower and convergent diffusion coefficient (D) of benzoic acid and homochiral catalyst (**Ia**) in the mixture suggests a high self-aggregation state (**Table S6**) between both species.

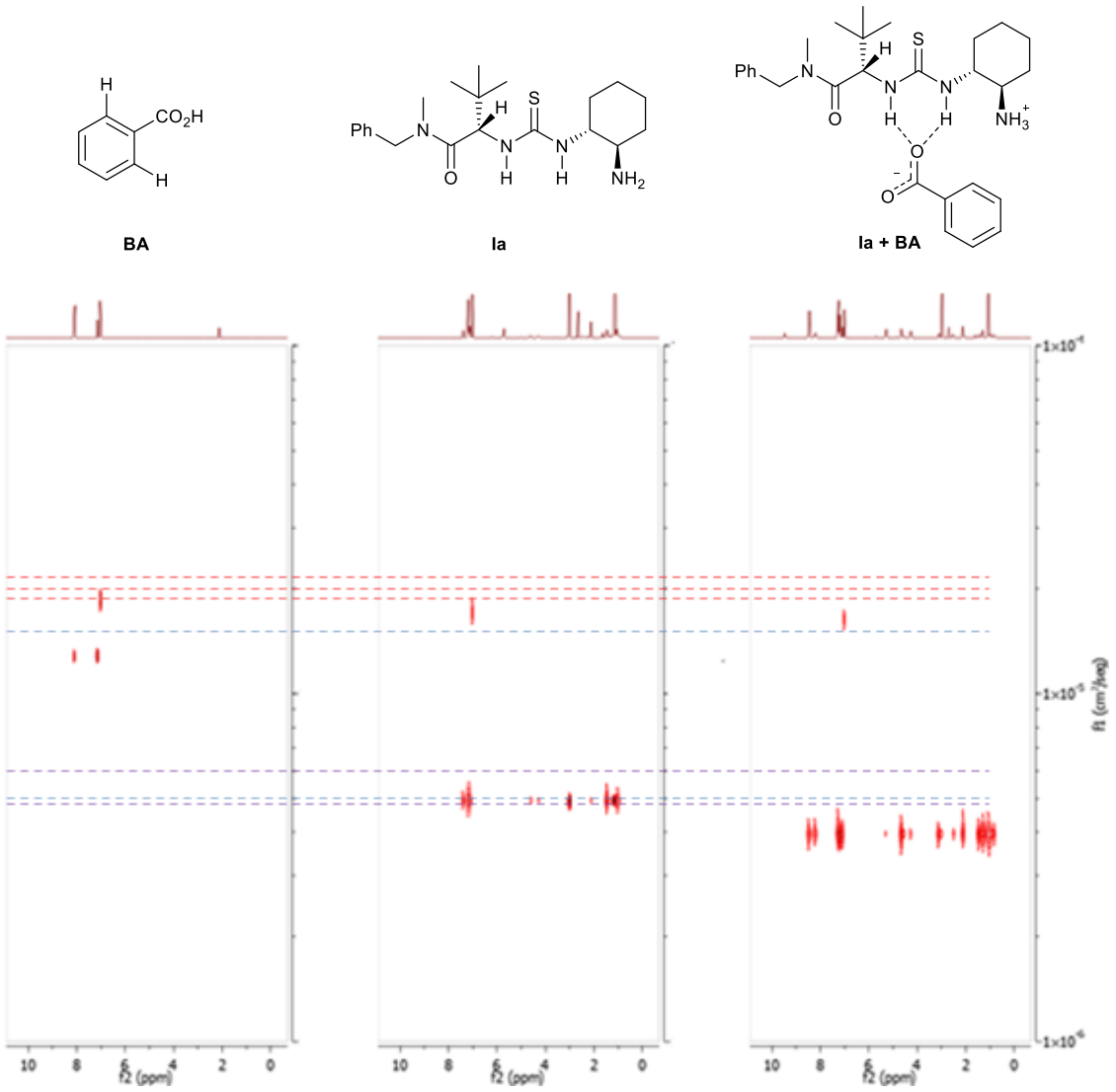


Figure S6 *Left*: ^{1}H NMR DOSY of benzoic acid (0.2 M in toluene-d_8, 25ºC); *centre*: ^{1}H NMR DOSY of catalyst **Ia** (0.2 M in toluene-d_8, 25ºC); *right*: ^{1}H NMR DOSY of catalyst **Ia**/benzoic acid (0.2 M in toluene-d_8, 25ºC)

Table S6

Entry	Solution	D_{PhCOOH} (10^{-10} m^2s^{-1})[a]	D_{Cat} (10^{-10} m^2s^{-1})[a]	D_{Tol} (10^{-9} m^2s^{-1})[b]
1	PhCOOH	12.90	-	2.02
2	**Ia**	-	5.07	1.80
3	**Ia** + PhCOOH	4.10	4.00	1.70

[a]Diffusion coefficient D obtained by ^{1}H NMR DOSY. [b] D_{Tol} refers to residual non deuterated toluene.

22. X-Ray diffraction analysis of *rac*-Ia + PhCOOH

Benzoic acid (12.2 mg, 0.1 mmol) was added to a solution of catalyst *rac*-**Ia** (39.1 mg, 0.1 mmol) in toluene-d_8 (0.5 mL, 0.20 M) and, an off-white precipitated was immediately formed (**Figure S7**, left). Suitable single crystal for X-ray diffraction analysis was obtained by simple recrystallization (90 ºC → room temperature) to afford heterodimer (*rac*-**Ia**/PhCOOH)$_2$ as a white solid; mp. = 203-205 ºC (**Figure S7**, right).

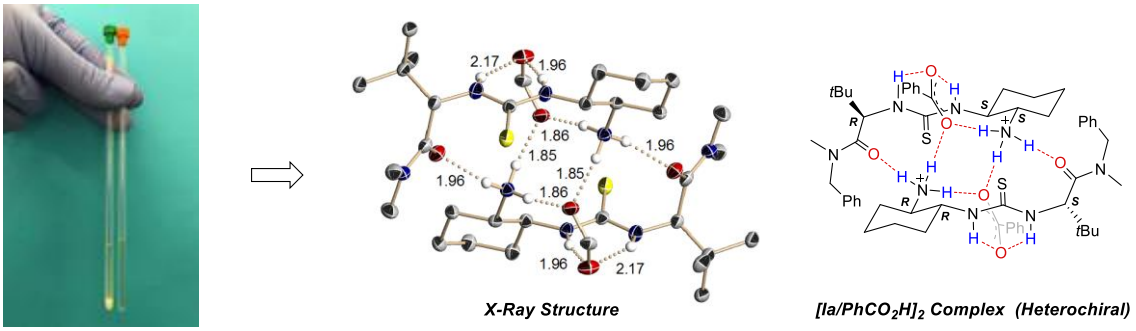


Figure S7 ORTEP plot of (*rac*-**Ia**/PhCOOH)$_2$ with thermal ellipsoids set at the 50% probability level. Most hydrogen atoms and phenyl rings are omitted for clarity

23. NMR studies of II + PhCOOH

Three solutions containing catalyst **II** (42.5 mg, 0.1 mmol), benzoic acid (12.2 mg, 0.1 mmol) or a mixture of catalyst **II** (42.5 mg, 0.1 mmol) and benzoic acid (12.2 mg, 0.1 mmol) in toluene-d_8 (0.5 mL, 0.20 M) were prepared and a ^{1}H NMR spectrum were recorded for each sample at 500 MHz (**Figure S8**). In this case, relevant changes in both chemical shifts and multiplicity for the N***H*** signals were not observed (**blue**, **yellow** and **orange** circles): the association of catalyst **II** and benzoic acid did not provide insights results, as illustrated in the ^{1}H NMR DOSY experiment (**Table S7**, *vide infra*).

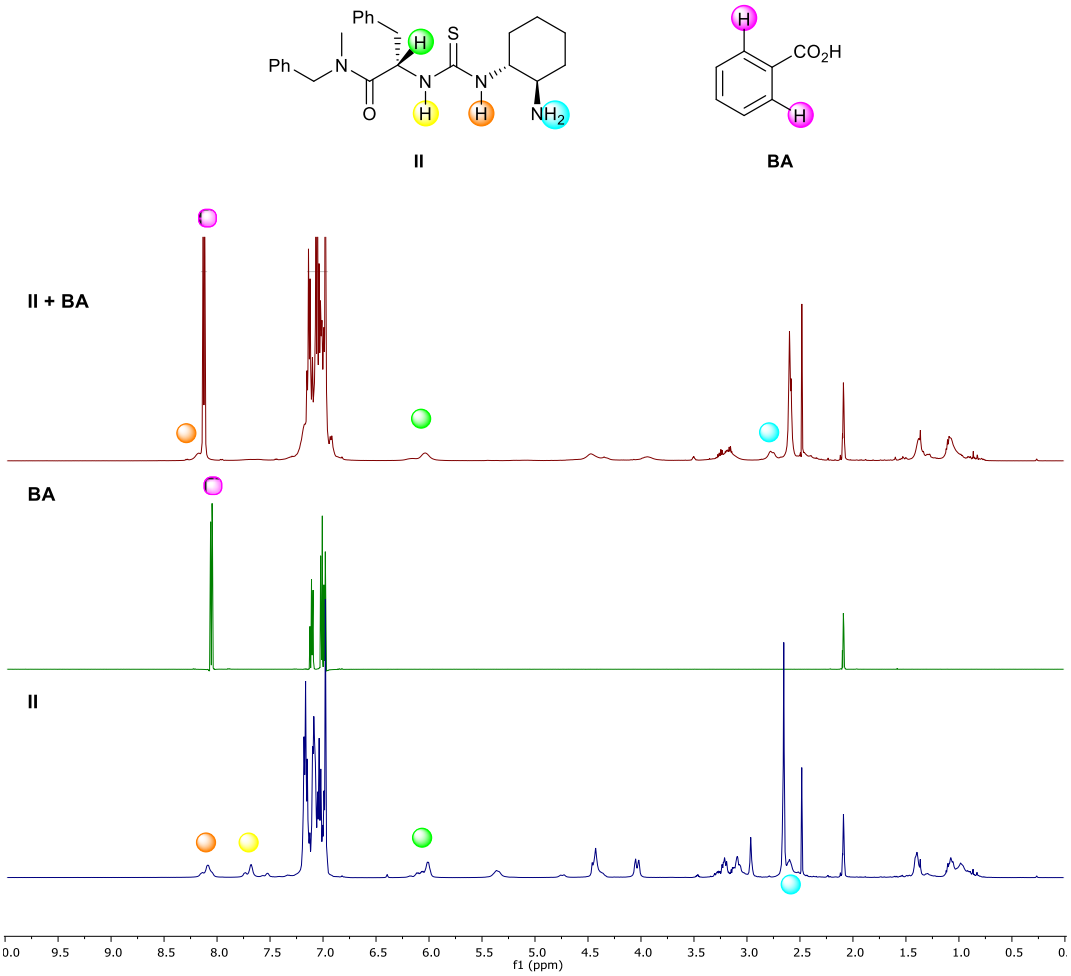


Figure S8 *Red spectrum*: ^{1}H NMR of the mixture of catalyst **II** and benzoic acid (0.2 M in toluene-d_8, 25ºC); *green spectrum*: ^{1}H NMR of benzoic acid (0.2 M in toluene-d_8, 25ºC); *blue spectrum*: ^{1}H NMR of catalyst **II** (0.2 M in toluene-d_8, 25ºC)

24. ^{1}H NMR DOSY spectra of II + PhCOOH

Three solutions containing catalyst **II** (42.5 mg, 0.1 mmol), benzoic acid (12.2 mg, 0.1 mmol) or a mixture of catalyst **II** (42.5 mg, 0.1 mmol) and benzoic acid (12.2 mg, 0.1 mmol) in toluene-d_8 (0.5 mL, 0.20 M) were prepared and a ^{1}H NMR DOSY spectrum were recorded for each sample at 500 MHz (**Figure S9**). The different diffusion coefficients (D) of benzoic acid and homochiral catalyst (**II**) in the mixture suggests poor or non self-aggregation state (**Table S7**) between both species.

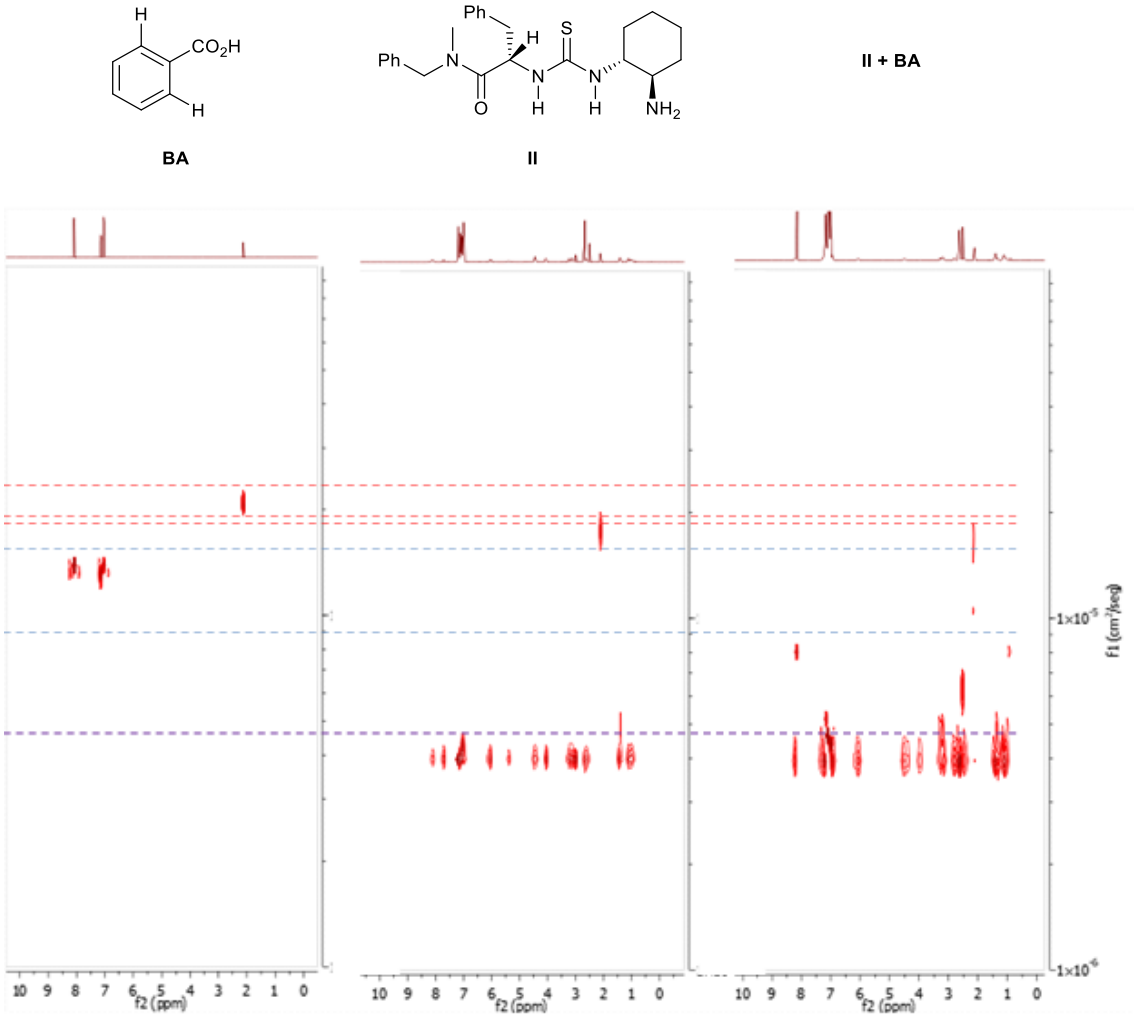


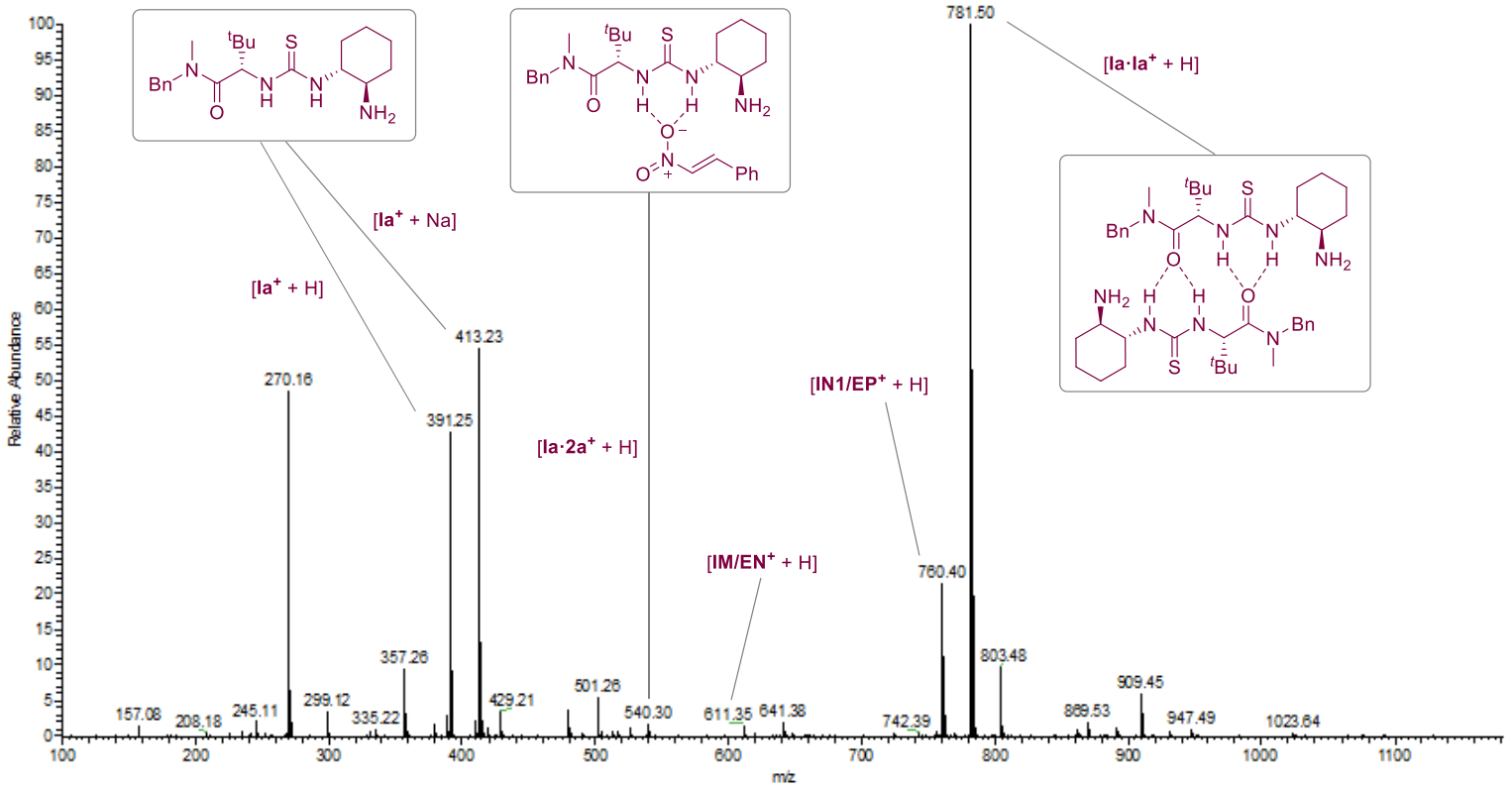
Figure S9 *Left*: ^{1}H NMR DOSY of benzoic acid (0.2 M in toluene-d_8, 25ºC); *centre*: ^{1}H NMR DOSY of catalyst **II** (0.2 M in toluene-d_8, 25ºC); right: ^{1}H NMR DOSY of catalyst **II**/benzoic acid (0.2 M in toluene-d_8, 25ºC)

Table S7

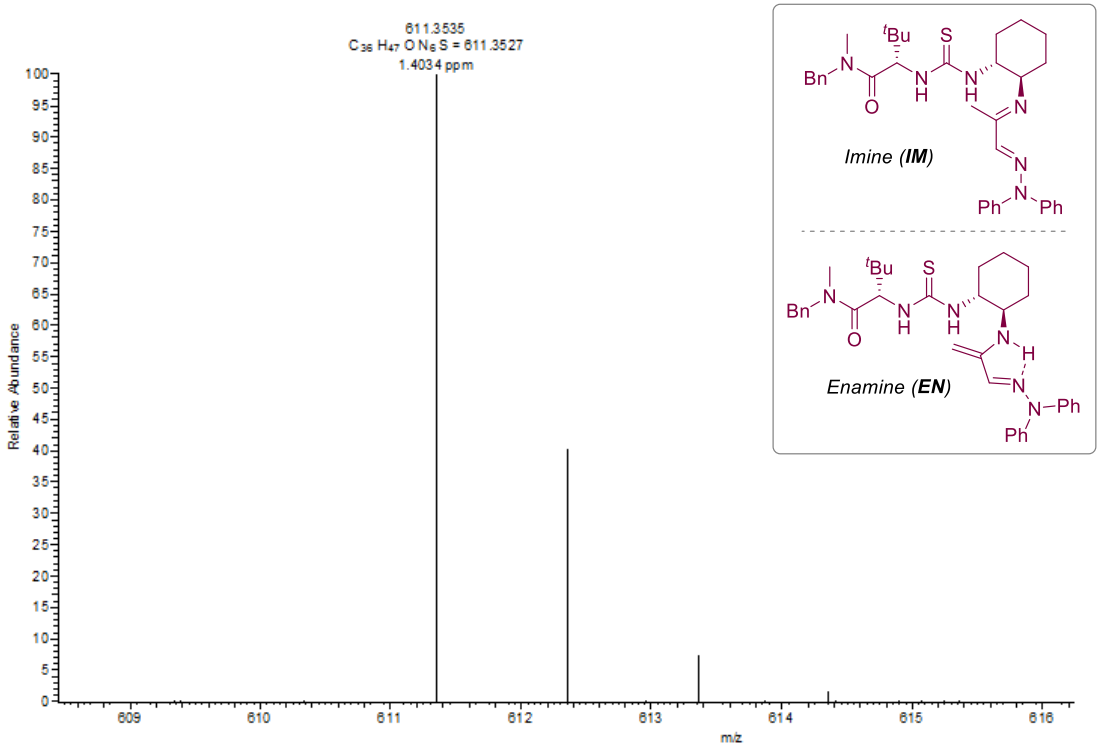
Entry	Solution	D_{PhCOOH} ($10^{-10}m^2s^{-1}$)[a]	D_{Cat} ($10^{-10}m^2s^{-1}$)[a]	D_{Tol} ($10^{-9}m^2s^{-1}$)[b]
1	PhCOOH	12.90	-	2.02
2	**II**	-	4.02	1.69
3	**II** + PhCOOH	7.63	3.87	1.67

[a]Diffusion coefficient D obtained by ^{1}H NMR DOSY. [b] D_{Tol} refers to residual non deuterated toluene.

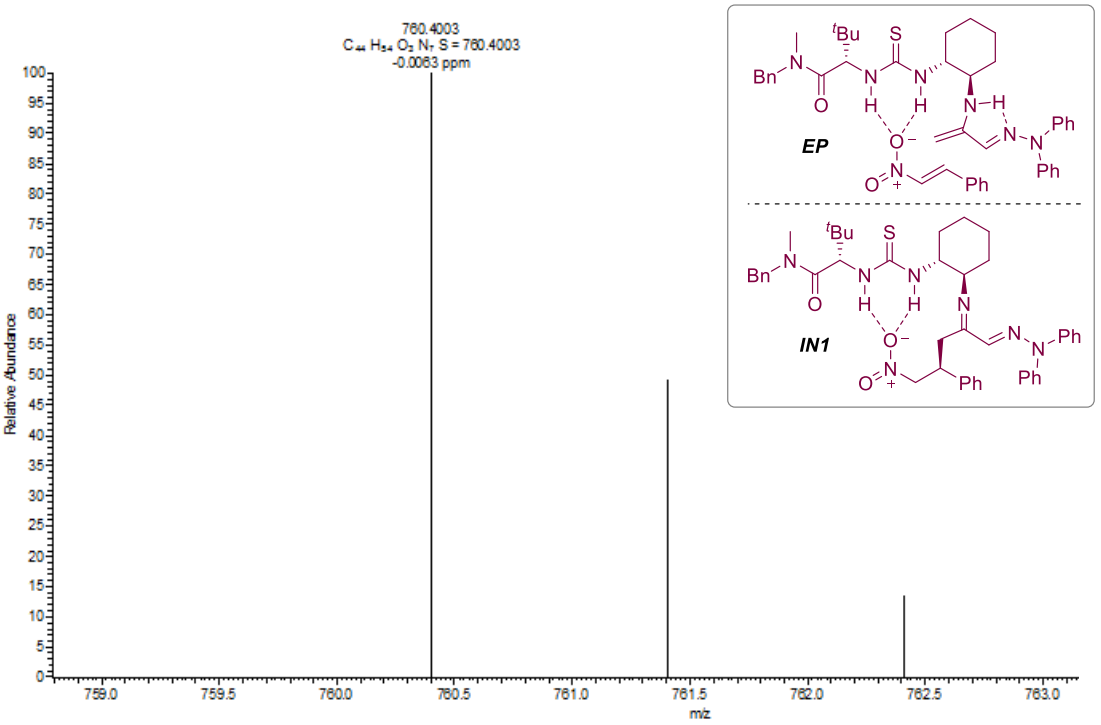
25. Mass spectra analysis



(+)-ESI-MS scan of the reaction between **1D** (0.2 mmol) and **2a** (0.1 mmol) in the presence of **Ia** (0.02 mmol) and PhCOOH (0.01 mmol) in toluene (1.0 M)



(+)-ESI-HRMS of **IM**/**EN** [M^+ + H]



(+)-ESI-HRMS of **IN1**/**EP** [M^+ + H]

26. Computational methods

All of the calculations were performed using the Gaussian09 program.[14] Computations were done using wb97xd functional[15] in conjunction with def2SVP and def2TZVP basis sets.[16] Geometry full optimizations were made at wb97xd/def2SVP level and then single point calculations at wb97xd/def2TZVP level were carried out in order to obtain more accurate values of the energies. Solvent effects (toluene) were considered using the PCM model.[17] The nature of stationary points was defined on the basis of calculations of normal vibrational frequencies (force constant Hessian matrix). The optimizations were carried out using the Berny analytical gradient optimization method.[18] Analytical second derivatives of the energy were calculated to classify the nature of transition structures, to determine the harmonic vibrational frequencies, and to provide zero-point vibrational energy corrections. The thermal and entropic contributions to the free energies were also obtained from the vibrational frequency calculations, using the unscaled frequencies. NCI (non-covalent interactions) were computed using the methodology previously described.[19] Quantitative data were obtained with the NCIPLOT4 program.[20] A density cutoff of ρ = 0.5 a.u. was applied and isosurfaces of s(r) =0.4 were colored by $sign(\lambda_2)\rho$ in the [-0.03,0.03] a.u. range using VMD software.[21] s(**r**) against $sign(\lambda_2)\rho(\mathbf{r})$ plots were generated with gnuplot software. Structural representations were generated using CYLView.[22]

Molecular dynamics simulations: All MD simulations were carried out using the AMBER18 package.[23] After assigned proper protonation states to benzoate and thiourea enantiomers, the corresponding structures were solvated in a pre-equilibrated truncated at 12 Å octahedral box filled with CHCL3BOX chloroform molecules using xleap of AMBERTools18. The force field parameters were taken from general AMBER force field (GAFF).[24] All obtained parameters were assigned with the antechamber module.[25] The solvated structure was then energy-minimized to avoid possible steric clashes. Two cycles of minimizations were performed with 5000 steps of each minimization. Periodic boundary conditions were applied with a cutoff distance of 8Å for nonbonded interaction. The minimized structure was heated

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over 100 ps from 0 to 300 K with a temperature coupling of 0.2 ps. The constant volume was maintained during the processes. Then the unrestrained equilibration of 200 ps with constant pressure and temperature conditions was carried out. The temperature and pressure were allowed to fluctuate around 300 K and 1 bar, respectively, with the corresponding coupling of 0.2 ps. The Langevin thermostat with a collision frequency of 5 ps^{-1} was used to keep the temperature constant, and the pressure was maintained at 1 bar with Berendsen's weak-coupling algorithm.[26] The SHAKE algorithm was applied to allow a time step of 2 fs.[27] Finally, production runs of 1 μs were carried out. The root mean square deviation (RMSD) curves were obtained to check whether equilibration is achieved. When assigning hydrogen bonds for the trajectory snapshots, we adopted geometric criteria with the angle X-H-X larger than 110º and the nonbonded distance H-X shorter than 3.0 Å.[28] During the production runs 500,000 structures for the corresponding simulation were saved for post-processing by uniformly sampling the trajectory.

Studies on association of thiourea-based catalysts

The stability of associated catalyst molecules was tested through MD simulations. Hetero- and homoquiral complexes **hetero-C** -formed by one molecule of protonated (*S*,*R*,*R*)-catalyst, one molecule of protonated (*R*,*S*,*S*)-catalyst and two molecules of benzoate-, and **homo-C** -formed by two molecules of protonated (*R*,*S*,*S*) and two molecules of benzoate- (**Figure S10**) were submitted to MD simulations of 1 microsecond.

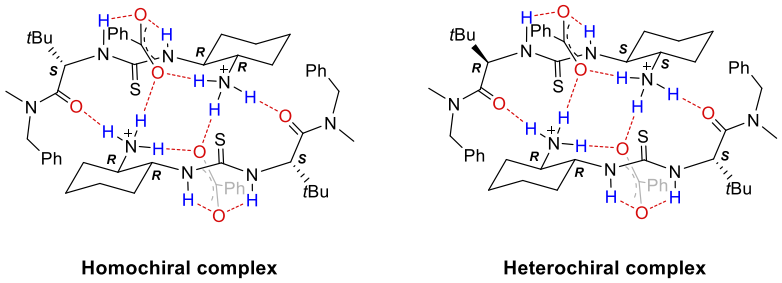

Figure S10 Hetero- and homoquiral complexes formed by two molecules of protonated catalyst and benzoic acid

During MD simulations, the stability of both complexes was confirmed as the corresponding dimers do not change during 1 microsecond (**Figure S11**). Moreover, simulations were also carried out putting together 4 molecules of protonated catalysts (2 couples of enantiomers) and four molecules of benzoate grouped in three ways: i) two enantiomeric homochiral complexes (*R*,*S*,*S*)/(*R*,*S*,*S*) and (*S*,*R*,*R*)/(*S*,*R*,*R*), ii) two heterochiral complexes (*R*,*S*,*S*)/(*S*,*R*,*R*) and (*R*,*S*,*S*)/(*S*,*R*,*R*), and iii) four separated complexes [2 x (*R*,*S*,*S)* and 2 x (*S*,*R*,*R*)] each one formed by a molecule of protonated catalyst and a benzoate. In all cases, a high stability was showed for hetero- and homochiral complexes, no interconversion between them being observed (**Figure S11**). Notably, MD simulations for the four separated complexes showed the grouping of the four complexes, a situation that was also partially observed in the simulations but, in any case the dimers were not dissociated.

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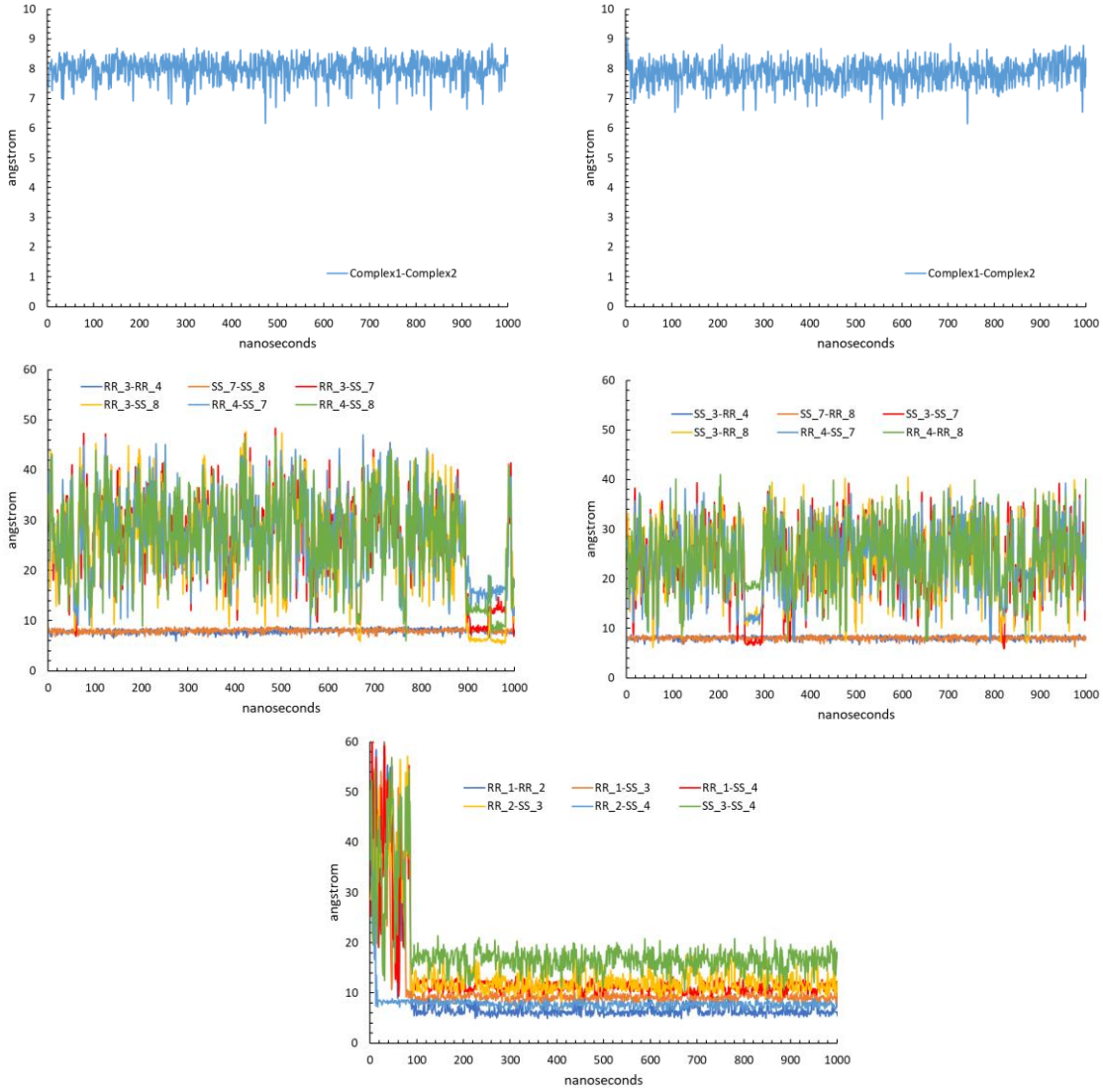
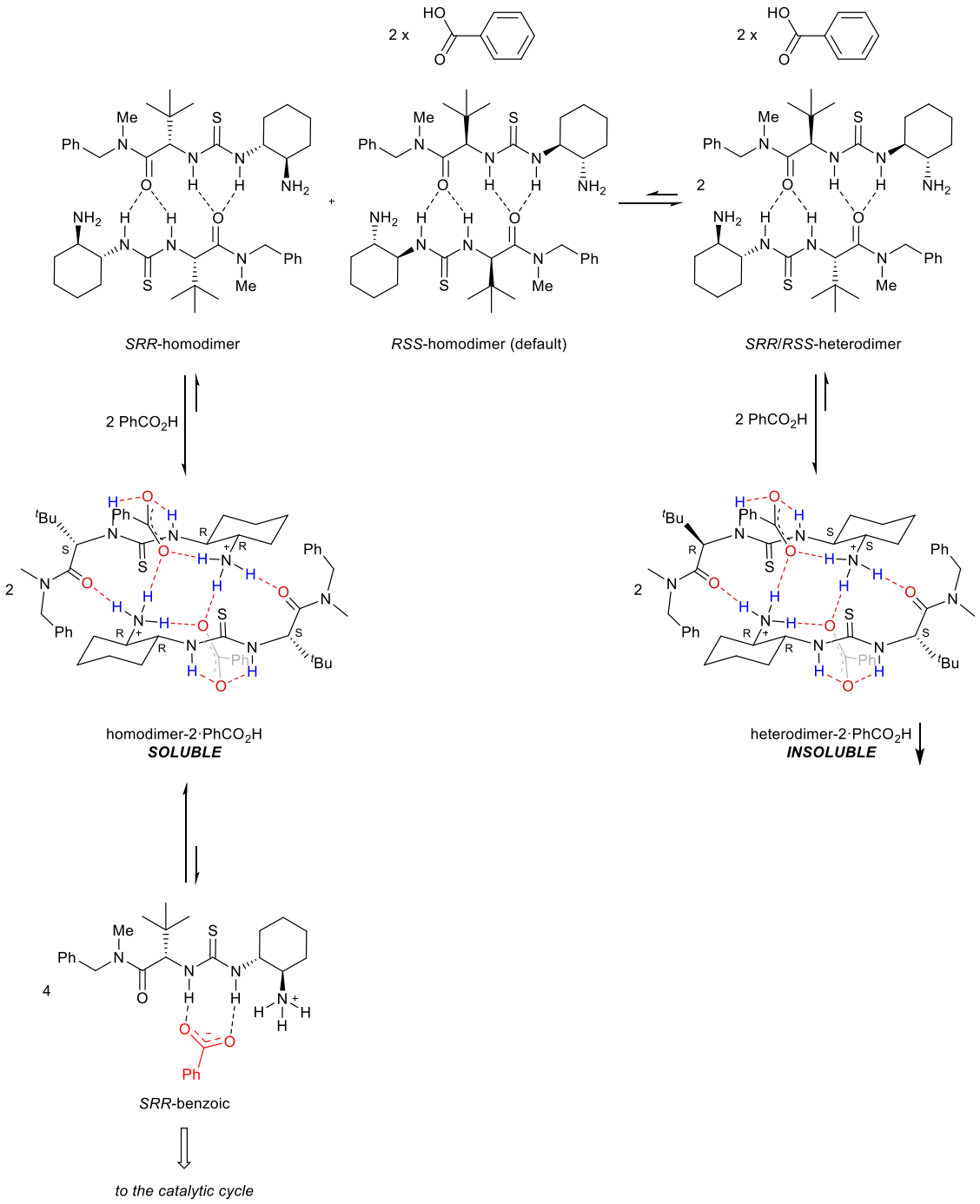


Figure S11 Distances between centers of mass of individual complexes catalyst-benzoate. *Top:* Hetero- (*left*) and homochiral dimers (*right*). *Center:* enantiomeric homochiral complexes (*R,S,S*)/(*R,S,S*) and (*S,R,R*)/(*S,R,R*) (*left*) heterochiral complexes (*R,S,S*)/(*S,R,R*) and (*R,S,S*)/(*S,R,R*) (*right*). *Bottom:* four separated complexes [2 x (*R,S,S)* and 2 x (*S,R,R*)] (*right*). RR_x and SS_y correspond to the different catalyst-benzoate complexes

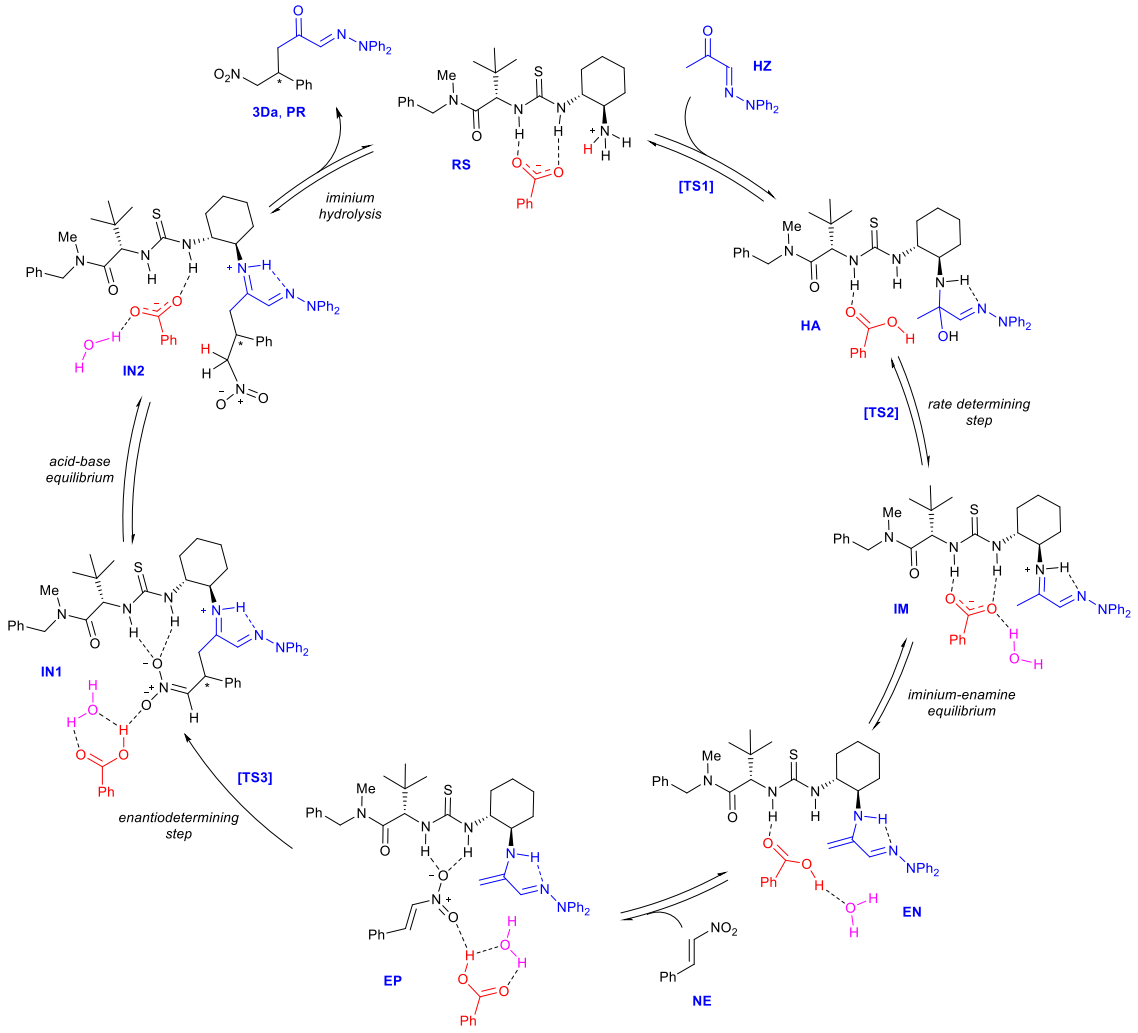
These studies cannot be considered conclusive since they only indicate the high stability of dimers. An equilibrium with the dissociate form can be present even with k(eq)<1; a small amount of dissociated form should be enough for entering into the catalytic cycle displacing the equilibrium (**Scheme S1**). The different solubility between the heterochiral complex (insoluble) from which an X-ray structure has been obtained and the homochiral complex (soluble) could explain the observed non-linear effects, i.e., precipitation of the insoluble heterochiral complex removes the minor amounts of (*R,S,S*)-enantiomers leaving pure (*S,R,R*)-enantiomer to form a soluble homochiral complex that provides dissociated form active in the catalytic cycle (**Scheme S1**).



Scheme S1 Equilibrium between complexes catalyst-benzoic acid

The catalytic cycle

A proposed catalytic cycle consistent with experimental observations is presented in **Scheme S2**. As noted, the resting state of the catalyst **RS**, consisted of a dissociated complex thiourea-benzoic **RS**, reacts with hydrazone **HZ** to form intermediate hemiaminal **HA** through a first transition structure **TS1**. The hemiaminal **HA** led to the iminium ion **IM** which equilibrates into the enamine **EN**. The formation of the iminium ion **IM** is a reversible process that proceeds via **TS2** and it is proposed to be rate-determining step on the basis of the observed dependence of the overall rate on the features of hydrazone *N*-substituents. The observed independence of the enantioselectivity on the characteristics of hydrazone *N*-substituents points to an encounter pair **EP** as the intermediate involved in the enantiodetermination through **TS3**. The formation of **IN1** takes place through an irreversible step. The formed **IN1** evolves to **IN2**, which after iminium hydrolysis regenerates **RS**.



Scheme S2 The proposed catalytic cycle

During the formation of the iminium **IM** two diastereomeric hemiaminals can be formed. These hemiaminals react with different barriers, the (*R*)-isomer being the most stable. This selectivity is irrelevant for the whole process since during the formation of the iminium salt any stereodifferentiation is lost and the step is reversible. The complete energy profile for the catalytic cycle is given in **Figure S12**.

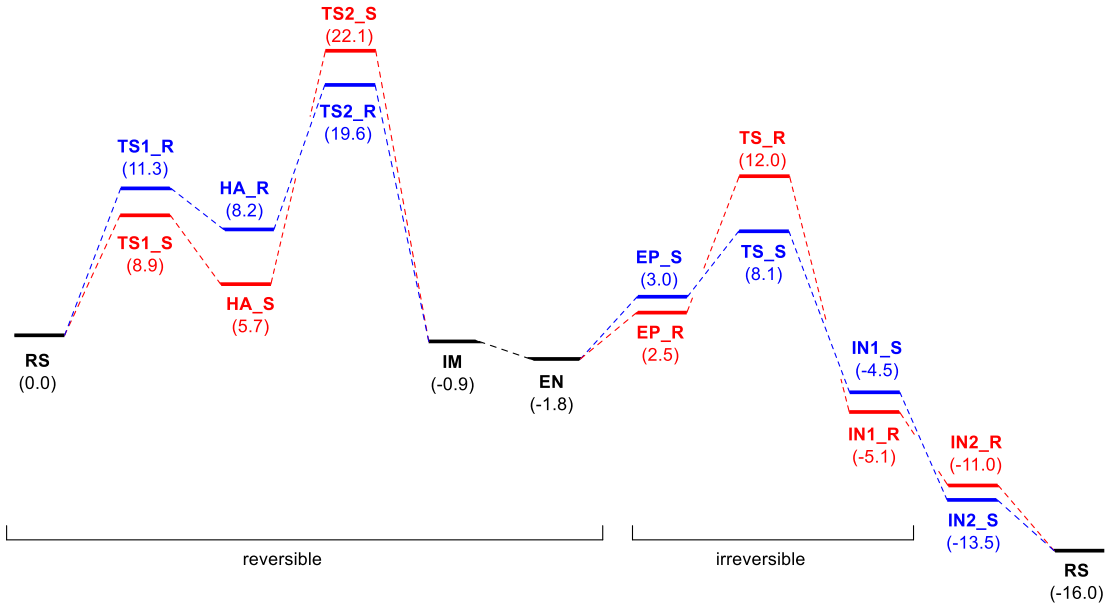


Figure S12 Energy profile (wb97xd/def2tzvp/pcm=toluene//wb97xd/def2svp/pcm=toluene) for the catalytic cycle illustrated in **Scheme S2**. Relative free energies are given in kcal/mol

The observed energy values for the enantiodetermining irreversible step agree with the experimentally observed obtention of the (*S*)-enantiomer.

Energies

Table S8 Absolute energies, in hartree, for the catalytic cycle illustrated in **Scheme S2**. (wb97xd/def2tzvp/pcm=toluene wb97xd/def2svp/pcm=toluene)

	E_0	G	im. freq
RS	-1933.497406	-1933.566777	
HZa	-764.473412	-764.518372	
NE	-514.036223	-514.071849	
TS1a-R	-2697.966472	-2698.057271	-201.5
TS1a-S	-2697.970014	-2698.060996	-254.3
HAa-R	-2697.968307	-2698.058828	
HAa-S	-2697.965772	-2698.055520	
TS2a-R	-2697.953488	-2698.044136	-272.9
TS2a-S	-2697.952765	-2698.040843	-243.9
IMa	-2697.989249	-2698.077203	
ENa	-2697.990413	-2698.078539	
EPa-R	-3212.027045	-3212.133557	
EPa-S	-3212.032385	-3212.133107	
TS3a-R	-3212.016358	-3212.118195	-299.9
TS3a-S	-3212.020427	-3212.123950	-308.3
IN1a-R	-3212.046213	-3212.146154	
IN1a-S	-3212.046835	-3212.145681	
IN2a-R	-3212.044018	-3212.143055	
IN2a-S	-3212.058401	-3212.159128	
PRa	-1278.534480	-1278.594441	

Transition structures

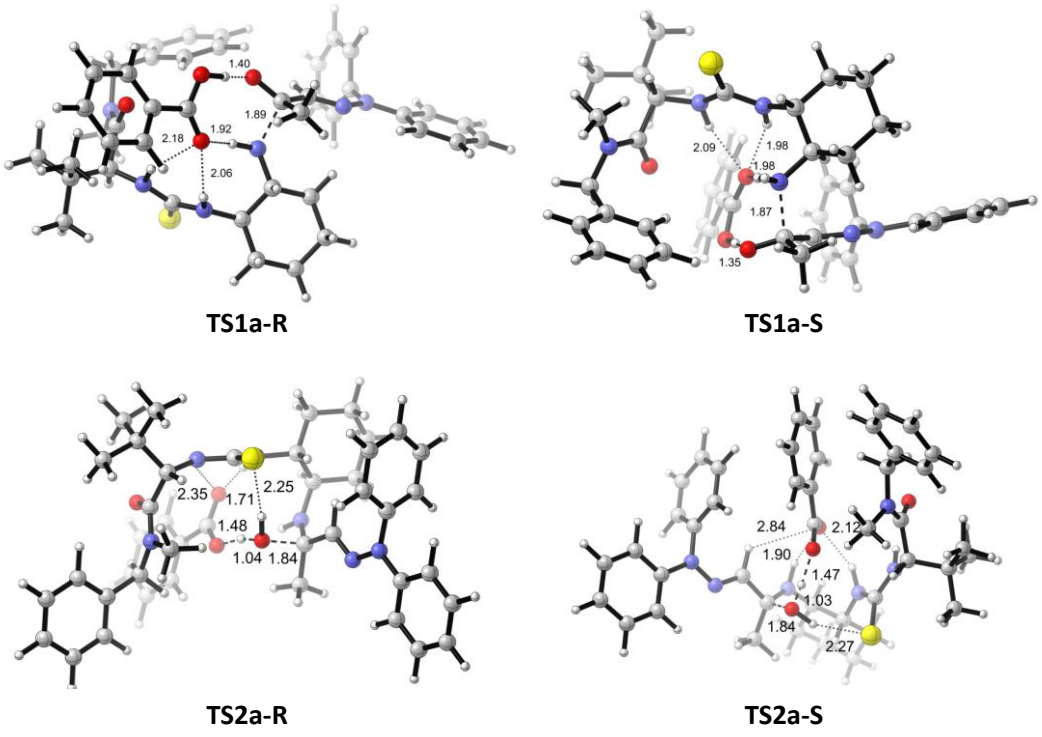


Figure S13 Optimized (wb97xd/def2svp/pcm=toluene) geometries of transition structures corresponding to the iminium formation for the catalytic cycle illustrated in **Scheme S2**. **TS2aR** and **TS2aS** correspond to the rate determining step

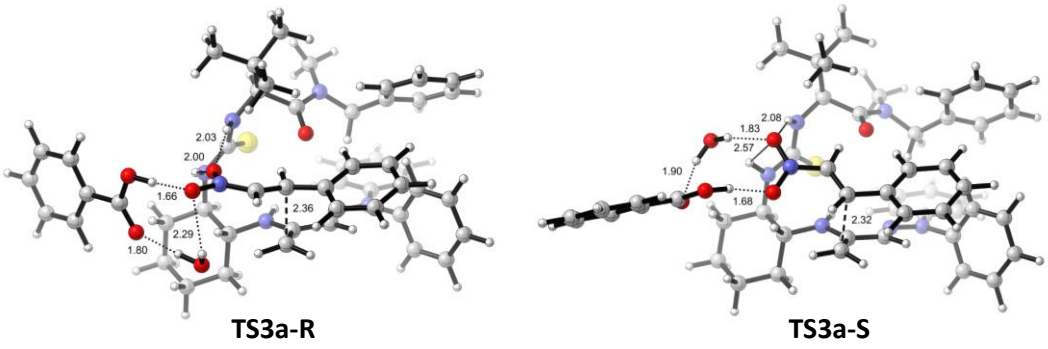
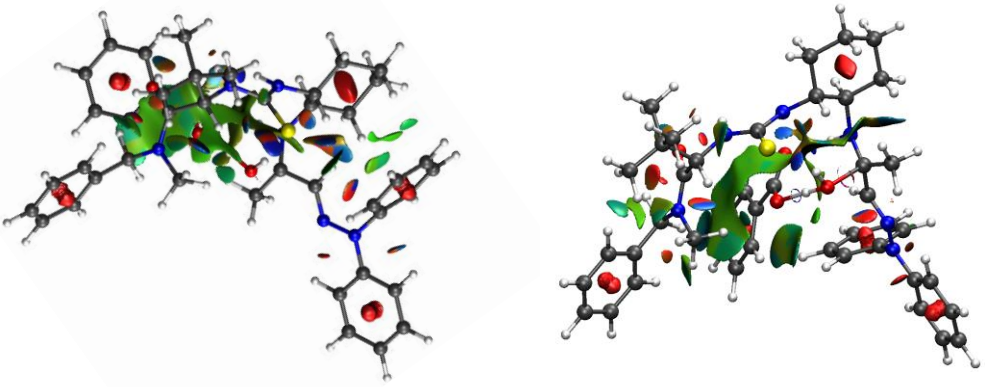


Figure S14 Optimized (wb97xd/def2svp/pcm=toluene) geometries of transition structures corresponding to the enantiodetermining step for the catalytic cycle illustrated in **Scheme S2**

NCI Calculations

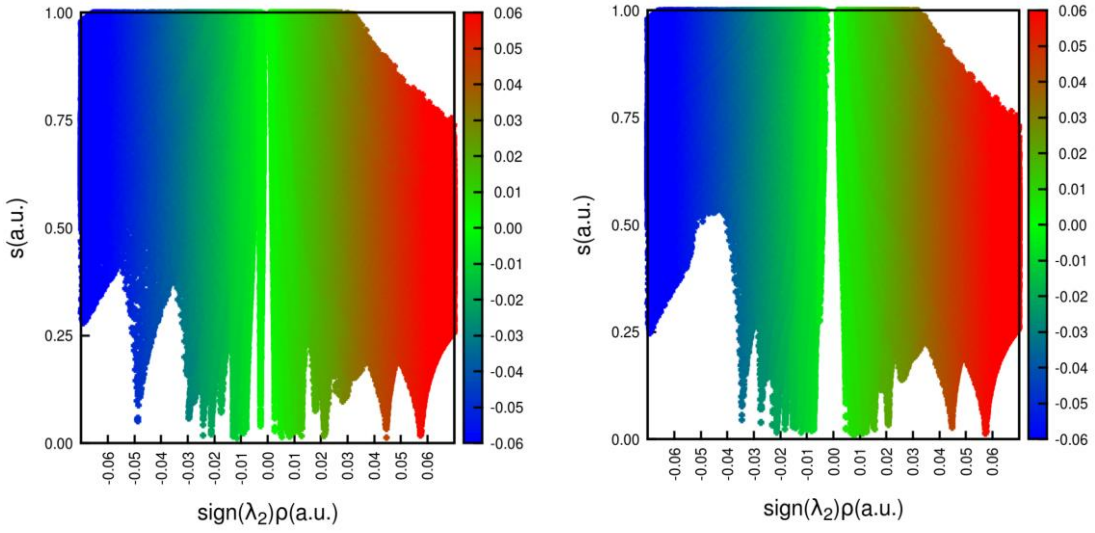
Quantitative[29] NCI calculations were carried out for the transition structures **TS2a-R** and **TS2a-S** corresponding to the rate-determining step (**Figure S15** and **Figure S16**; **Table S9**).



TS2a-R $\text{sign}(\lambda_2)\sigma(2.5) = -21.17$

TS2a-S $\text{sign}(\lambda_2)\sigma(2.5) = -21.18$

Figure S15 NCI analysis of **TS2a-R** and **TS2a-S**. Thin, delocalized green surface indicates van der Waals interactions. Small, lenticular, bluish surfaces indicate strong interactions such as hydrogen bonding. Steric clashes are shown as red isosurfaces



TS2a-R **TS2a-S**

[29] Integration of $\text{sign}(\lambda_2)\rho(n)$ provides information about interaction's energy, nature and the dominant contribution. Negative values for the total integration of $\text{sign}(\lambda_2)\rho(n)$ indicate that attractive interactions dominate the non-covalent interactions. The more negative value, the more attractive interactions there are. The interval [-0.1, -0.02] gives information about strong NCI (H-bond, halogen, etc.). The interval [-0.02, 0.02] gives information about van der Waals interactions. The interval [0.02, 1.00] gives information about repulsive interactions. According to the developers (see ref. 20) a value of n = 2.5 was selected.

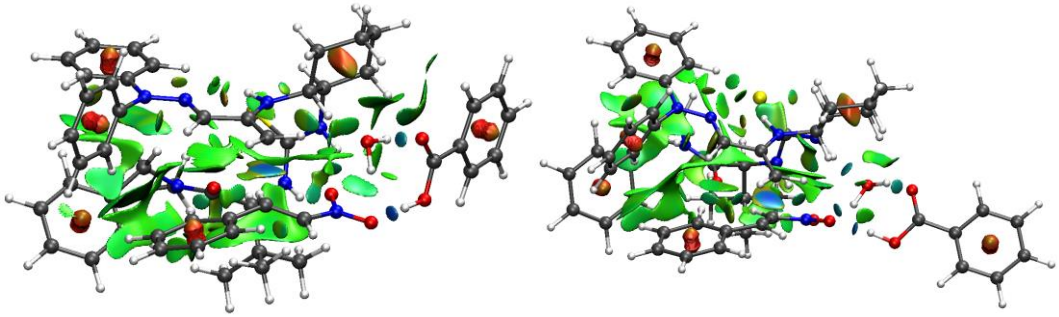
Figure S16 s(**r**) against *sign*(λ_2)ρ(**r**) plots for **TS2a-R** and **TS2a-S**. Quantitative analysis is given in **Table S9**. Blue area corresponds to strong NCI (H-bond, halogen, etc.); green area corresponds to van der Waals interactions and red area corresponds to repulsive interactions (steric clashes, etc.)

Table S9 Integration over the volumes of *sign*(λ_2)ρ(**n**) according to ref. 20 for **TS2a-R** and **TS2a-S**. A value of n = 2.5 has been selected.[a]

Interval	TS2a-R	TS2a-S
all	-21.17448074	-21.18277197
-0.1 to -0.02	-0.37719579	-0.38051784
-0.02 to 0.02	0.00675016	0.00658153
0.02 to 0.1	0.61184573	0.61475040

[a] Total integration of sign(λ2)ρ(n) was made for the whole interval [-0.5. 0.5]

Quantitative NCI calculations were also carried out for the transition structures **TS3a-R** and **TS3a-S** corresponding to the enantiodetermining step (**Figure S17** and **Figure S18**; **Table S10**).



TS3a-R

sign(λ_2)σ(2.5) = -25.40

TS3a-S

sign(λ_2)σ(2.5) = -25.44

Figure S17 NCI analysis of **TS3a-R** and **TS3a-S**. Thin, delocalized green surface indicates van der Waals interactions. Small, lenticular, bluish surfaces indicate strong interactions such as hydrogen bonding. Steric clashes are shown as red isosurfaces

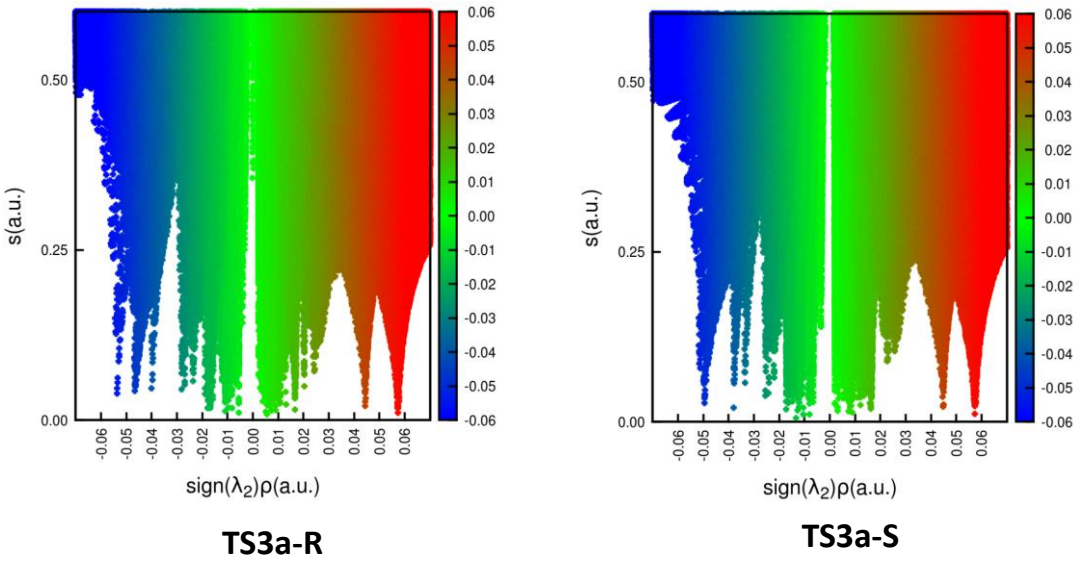


Figure S18 s(**r**) against *sign*(λ_2)ρ(**r**) plots for **TS3a-R** and **TS3a-S**. Quantitative analysis is given in **Table S10**. Blue area corresponds to strong NCI (H-bond, halogen, etc.); green area corresponds to van der Waals interactions and red area corresponds to repulsive interactions (steric clashes, etc.)

Table S10 Integration over the volumes of *sign*(λ_2)ρ(**n**) according to ref. 20 for **TS3a-R** and **TS3a-S**. A value of n = 2.5 has been selected.[a]

Interval	TS3a-R	TS3a-S
all	-5.63325533	-5.62630680
-0.1 to -0.02	-0.465045045	-0.46147514
-0.02 to 0.02	0.00776333	0.00786940
0.02 to 0.1	0.71220245	0.70916934

[a] Total integration of sign(λ2)ρ(n) was made for the whole interval [-0.5. 0.5]

In all the cases the same features have been observed. Negative values of total sign(λ2)ρ(**n**) indicate that attractive interactions dominate the non-covalent interactions. High negative values for the first interval [-0.1 to -0.02] indicate that strong non-covalent interactions stabilize the structures whereas the low values observed for the second interval [-0.02 to 0.02] indicate a scarce contribution of Van der Waals forces. On the other hand, the values observed for the third interval [0.02 to 0.1] points out a relevant role of repulsive interactions as expected for transition structures in which reagents are highly distorted.

Cartesian Coordinates

ENa

0 1

C	0	-0.2833030749	-2.5677111999	-0.2796668119
H	0	-0.3878030972	-2.3917792402	0.7979744810
C	0	-2.2153392064	-0.7517814100	2.3980819557
O	0	-2.3217217926	-1.9745810860	2.1156177759
O	0	-2.6322791471	0.1914665929	1.6844660121
H	0	0.1119153335	0.2983420052	-1.0762687635
H	0	-0.1850179164	0.6853983207	-2.5129661915
H	0	-2.5297740971	-2.3139823775	0.6192399262
N	0	-2.6090108302	-2.4396136313	-0.4467429515
O	0	0.4717940973	0.2159203097	-1.9679622856
N	0	0.8506493420	-2.7052293650	-0.8868616892
N	0	1.9874381699	-2.5730263872	-0.2564611960
C	0	-1.5329755763	-0.4048311812	3.7003045113
C	0	-1.0482091211	0.8875619156	3.9192005422
C	0	-1.3783882362	-1.3766587037	4.6929424342
C	0	-0.4228835885	1.2062837254	5.1231060762
H	0	-1.1411932504	1.6279454944	3.1239195943
C	0	-0.7720493619	-1.0534530513	5.9050446035
H	0	-1.7429640240	-2.3862100920	4.4958320380
C	0	-0.2938822618	0.2399528984	6.1221504941
H	0	-0.0364458394	2.2153699580	5.2847642466
H	0	-0.6667978462	-1.8134837023	6.6828833109
H	0	0.1853895899	0.4940524776	7.0708283906
C	0	3.1834749375	-2.7120372686	-1.0091872593
C	0	3.1310592445	-2.9277667310	-2.3919347697
C	0	4.4220302730	-2.6279365865	-0.3649447811
C	0	4.3128645062	-3.0599816385	-3.1138709856
H	0	2.1638955438	-2.9734791294	-2.8887419805
C	0	5.5963242487	-2.7652244062	-1.1016075490
H	0	4.4723819159	-2.4438232515	0.7080551002
C	0	5.5525953590	-2.9819774594	-2.4767167792
H	0	4.2613524260	-3.2209200829	-4.1928526775
H	0	6.5566513370	-2.6924350557	-0.5870454321
H	0	6.4756706779	-3.0855823352	-3.0501387003
C	0	2.0293060476	-2.1237852641	1.1087860472
C	0	2.0889071787	-3.0472961335	2.1509983058
C	0	1.9605854521	-0.7540613316	1.3610814610
C	0	2.0939960498	-2.5857960124	3.4662362216
H	0	2.1311621666	-4.1148615124	1.9263867696
C	0	1.9552681245	-0.3036920245	2.6776427882
H	0	1.9012462323	-0.0430392880	0.5360882002
C	0	2.0286875529	-1.2173302988	3.7280381336
H	0	2.1382071718	-3.2999112501	4.2908421323
H	0	1.8687619989	0.7660877512	2.8707738658
H	0	2.0081771061	-0.8596829893	4.7588263443
C	0	-3.9512489321	-2.1586227932	-0.9532577434
C	0	-4.0049564608	-0.8371302503	-1.7460208235
C	0	-4.6254408642	-3.3115391829	-1.7012558393
H	0	-4.5360774212	-1.9943520412	-0.0318836669
C	0	-5.4587778589	-0.4900113714	-2.0756909272
H	0	-3.4624384193	-0.9437256122	-2.6980596431
C	0	-6.0699712636	-2.9413552884	-2.0424232863
H	0	-4.0814163254	-3.5403535250	-2.6307402729
H	0	-4.5883810947	-4.2167882762	-1.0769581501
C	0	-6.1423188256	-1.6309105661	-2.8276871781
H	0	-5.4623576599	0.4359111583	-2.6694550952
H	0	-5.9959581447	-0.2769896431	-1.1350953039
H	0	-6.5356163261	-3.7599218396	-2.6115228084
H	0	-6.6483567815	-2.8396519777	-1.1078058866
H	0	-7.1904960614	-1.3695612241	-3.0370555138

H	0	-5.6516892230	-1.7644128023	-3.8078013318
H	0	-3.3088253124	0.0716049010	0.0567109427
C	0	-2.5187124623	1.1303419648	-1.4576811164
H	0	-1.8819251164	1.3947812910	0.4519499236
S	0	-2.3534951814	1.4562192112	-3.1235256684
N	0	-3.3380678459	0.1836868464	-0.9733617272
N	0	-1.8045088859	1.7653472864	-0.5031958686
C	0	0.3459771880	2.7623547183	-0.1042729844
O	0	0.4668849683	2.0809966200	0.9086304495
C	0	1.4165663518	4.0019453892	-1.9973054400
H	0	0.5856233707	3.6529504790	-2.6189762151
H	0	1.3697678984	5.0997542626	-1.9154644778
H	0	2.3465311446	3.7317714440	-2.5182421000
C	0	2.6760216269	3.3887885673	0.0226335657
H	0	3.0365100060	4.4313376396	0.0511927961
H	0	2.4665438381	3.0840530689	1.0568203513
C	0	-1.0606041474	2.9875999275	-0.6725200692
H	0	-1.0361703156	3.1920730130	-1.7482614384
C	0	-1.7854211025	4.1940262175	0.0205014646
C	0	-1.0131916457	5.4917866934	-0.2451272771
H	0	-0.9269699626	5.6929900706	-1.3242229049
H	0	-1.5440706401	6.3417795953	0.2098105379
H	0	-0.0006866191	5.4659198448	0.1856192941
C	0	-3.1867305244	4.3144743747	-0.5959219359
H	0	-3.8072177493	3.4381588293	-0.3582833600
H	0	-3.6976625200	5.2038062478	-0.1959754904
H	0	-3.1385553909	4.4066635195	-1.6915879488
C	0	-1.9177289063	3.9741907115	1.5335228058
H	0	-2.4321160675	3.0281105307	1.7622543238
H	0	-0.9373458705	3.9534652417	2.0308801558
H	0	-2.5090296262	4.7903209859	1.9765868601
N	0	1.4125362319	3.3646907224	-0.6940529710
C	0	3.7620086514	2.4998983265	-0.5493964410
C	0	3.4632467352	1.3787138730	-1.3289828229
C	0	5.1001571221	2.7870048837	-0.2574921794
C	0	4.4884159472	0.5581829818	-1.8008786624
H	0	2.4258632880	1.1371920414	-1.5792511230
C	0	6.1229061076	1.9625014174	-0.7224987078
H	0	5.3456120212	3.6674387928	0.3438232785
C	0	5.8182631954	0.8430641437	-1.4971883008
H	0	4.2413442146	-0.3176146154	-2.4047406534
H	0	7.1623533064	2.1989304635	-0.4828791841
H	0	6.6143628775	0.1919691257	-1.8652188111
H	0	-1.0534275427	-1.5578803726	-2.8709239326
C	0	-1.4850626294	-2.5644254975	-1.0902049806
C	0	-1.3566318327	-2.5751542203	-2.5735346492
H	0	-2.2806860235	-2.8488608957	-3.0876509947
H	0	-0.5420223244	-3.2466113999	-2.8675608015

EPa-R

0 1

C	0	2.5230883147	3.3709234260	-0.1956761617
C	0	3.1475323841	2.0966395912	0.4043340595
C	0	4.4404859770	2.4129329118	1.1631935747
C	0	5.4363475780	3.1539490698	0.2737054242
N	0	1.3500054991	2.9883629364	-0.9533721174
C	0	0.0651291719	3.2860629580	-0.6554536638
N	0	-0.8135862362	2.3842445910	-1.1473522800
C	0	-2.2364180361	2.5430465248	-1.2911541726
S	0	-0.3827314968	4.6601917450	0.2218681611
H	0	2.1816864449	4.0273207315	0.6213391233
H	0	5.7322069601	2.4956800269	-0.5629809557
H	0	6.3546821826	3.3821644534	0.8368516034
H	0	4.8737483964	1.4745538203	1.5434035199

H	0	4.1880679740	3.0267810036	2.0450557222
H	0	3.4173277741	1.4416205957	-0.4493152300
H	0	1.4860307811	2.1831970091	-1.5632427510
H	0	-0.4408075683	1.4889915240	-1.4523286831
H	0	-2.4981701832	3.4579674376	-0.7444998252
C	0	-2.6244321654	2.7271138024	-2.8016216827
C	0	-2.3385984656	1.4490318161	-3.6036255036
H	0	-2.9769421077	0.6101533244	-3.2890599418
H	0	-2.5234735910	1.6322076908	-4.6733716260
H	0	-1.2901970485	1.1303645439	-3.4992917706
C	0	-4.1056840023	3.0959847722	-2.9423726365
H	0	-4.7715894055	2.3183835057	-2.5419767407
H	0	-4.3363010416	4.0419963733	-2.4294049800
H	0	-4.3572500375	3.2258019612	-4.0058974159
C	0	-2.8863878357	1.3049515509	-0.6533656586
N	0	-4.0877324251	1.3990857996	-0.0338145261
O	0	-2.3051576095	0.2240068005	-0.7327139868
C	0	-4.8595716121	2.6092533844	0.1791392170
H	0	-5.8231784274	2.5530254840	-0.3515146740
H	0	-5.0489902601	2.7399537549	1.2539420349
H	0	-4.3243505270	3.4942452126	-0.1721548161
C	0	-4.6040276498	0.1971468406	0.5976545075
H	0	-3.7772847506	-0.3093068121	1.1103933061
H	0	-5.3026360607	0.5143335751	1.3849229815
C	0	-5.2929859748	-0.8024413755	-0.3066144313
C	0	-5.8073616340	-1.9699999853	0.2715156649
C	0	-5.4373025497	-0.6172008883	-1.6813900232
C	0	-6.4665468959	-2.9192410241	-0.5047212466
H	0	-5.6895022629	-2.1339137132	1.3465209199
C	0	-6.0869419761	-1.5722018894	-2.4655206473
H	0	-5.0340071263	0.2822705781	-2.1484152801
C	0	-6.6098527236	-2.7232079472	-1.8799733041
H	0	-6.8666889527	-3.8207634031	-0.0351915195
H	0	-6.1866135487	-1.4104377235	-3.5410940783
H	0	-7.1235003332	-3.4677816628	-2.4919050095
C	0	2.0150278353	0.0416374634	1.1955397856
C	0	2.9437134418	-0.8485952720	0.7726737352
H	0	2.7307389336	-1.9174970471	0.7883538071
H	0	3.9256306185	-0.5216300679	0.4374794780
N	0	2.1645123891	1.4020950593	1.1975422579
H	0	1.3520205330	1.9177352479	1.5179227565
C	0	4.8195348448	4.4329339107	-0.2929248471
H	0	5.5345268167	4.9494172040	-0.9518006655
H	0	4.5979307580	5.1274282973	0.5362199605
C	0	-1.7800927633	3.8782989391	-3.3683460123
H	0	-1.8790511467	4.7871691373	-2.7555717736
H	0	-0.7134837470	3.6151204160	-3.4063274436
H	0	-2.1054094458	4.1133783271	-4.3933722713
C	0	3.5307918464	4.1330991593	-1.0570813063
H	0	3.0556583783	5.0588421412	-1.4150292529
H	0	3.7623644866	3.5244459891	-1.9495265911
C	0	-0.1855747402	-1.8648324139	-1.8424829473
C	0	-0.9422802388	-3.0948429008	-1.6316189947
C	0	1.1417628550	-1.7979877088	-2.0475966207
H	0	-0.7690571649	-0.9382208157	-1.8483027466
C	0	-0.3249246753	-4.3449184366	-1.4389354863
C	0	-2.3447016131	-3.0157509977	-1.6713704565
N	0	1.7439409901	-0.5370053256	-2.3403587796
H	0	1.8606189910	-2.6223583638	-2.0422218962
C	0	-1.1051494885	-5.4881614350	-1.3071189625
H	0	0.7657068598	-4.4217227099	-1.3978661458
C	0	-3.1183082306	-4.1674998879	-1.5562453400
H	0	-2.8247073921	-2.0400366852	-1.7822548642
O	0	1.0644323103	0.4784723160	-2.3789153392
O	0	2.9399480226	-0.5185698579	-2.5840479718
C	0	-2.4988328415	-5.4043015995	-1.3766318463

H	0	-0.6230045723	-6.4558807163	-1.1544248547
H	0	-4.2058248002	-4.0894927536	-1.5963873487
H	0	-3.1041285225	-6.3087435480	-1.2819040833
C	0	0.7296043482	-0.4567548989	1.7142075487
H	0	0.6101841142	-1.5455504986	1.7856966495
N	0	-0.1662512481	0.3813809933	2.0740677287
N	0	-1.3352761141	-0.0120820937	2.6033968115
C	0	-2.2428611472	0.9883919745	2.9889279814
C	0	-3.3804517643	0.6681829542	3.7462782730
C	0	-2.0344883991	2.3230635546	2.6076580982
C	0	-4.2718640887	1.6691356954	4.1290353397
H	0	-3.5729230724	-0.3644801217	4.0388293059
C	0	-2.9304023309	3.3096423760	3.0014590199
H	0	-1.1770854967	2.5911250010	1.9926689463
C	0	-4.0538393633	2.9979831227	3.7700070231
H	0	-5.1474617610	1.3980988668	4.7239116132
H	0	-2.7414795925	4.3365044061	2.6791826836
H	0	-4.7524535433	3.7785234349	4.0778650088
C	0	-1.6084316924	-1.3993054211	2.8119195462
C	0	-1.3660914356	-1.9803708190	4.0582485366
C	0	-2.0640108449	-2.1760695615	1.7447953704
C	0	-1.6082618621	-3.3402658537	4.2438261792
H	0	-0.9946816405	-1.3582496437	4.8751014919
C	0	-2.2951715517	-3.5373242875	1.9334893368
H	0	-2.2130347061	-1.7031811738	0.7710438743
C	0	-2.0729545131	-4.1177951044	3.1823333106
H	0	-1.4271023508	-3.7955781421	5.2196922539
H	0	-2.6428608464	-4.1434208782	1.0952649450
H	0	-2.2553953823	-5.1847245326	3.3275370365
H	0	4.5619234160	-0.8751346378	-1.9053717638
O	0	5.4188954075	-0.7004097527	-1.4658644992
O	0	3.0378584477	-4.2772084108	-1.7351987701
C	0	5.8397510027	-1.7761839652	-0.8231601255
H	0	3.2886248307	-4.5192220617	-2.6324623572
H	0	3.8090750907	-3.7802681264	-1.4065695893
C	0	7.0280171593	-1.5258312215	0.0387058267
O	0	5.3006238547	-2.8612741114	-0.9121987613
C	0	7.5618570593	-0.2406363538	0.1914329888
C	0	7.5942817214	-2.6050659602	0.7255506537
C	0	8.6566095536	-0.0401520433	1.0280034029
H	0	7.1119900579	0.5981068088	-0.3405947929
C	0	8.6909558764	-2.4013596765	1.5574138446
H	0	7.1589851050	-3.5976761691	0.5983783963
C	0	9.2214562967	-1.1191096781	1.7091910814
H	0	9.0700474242	0.9628872085	1.1504341162
H	0	9.1328224625	-3.2438957350	2.0929868831
H	0	10.0800110744	-0.9592682298	2.3652331394

EPa-S

0 1

C	0	-1.9742790182	-3.1199698461	1.8585800466
C	0	-2.3641929671	-1.6318630539	1.9452039670
C	0	-2.9917395950	-1.3529436189	3.3194467055
C	0	-4.2149759737	-2.2315905270	3.5658758529
N	0	-1.3408965543	-3.4398578833	0.5976237159
C	0	-0.0140547550	-3.5017910780	0.3639041408
N	0	0.3137739672	-3.5660756312	-0.9508234666
C	0	1.6697576033	-3.4690053834	-1.4412041008
S	0	1.1516698526	-3.5367592765	1.5888981315
H	0	-1.2290489411	-3.3282316024	2.6421781928
H	0	-5.0017479183	-1.9554337406	2.8428478765
H	0	-4.6323670147	-2.0285225913	4.5641218231
H	0	-3.2619079840	-0.2896303552	3.3881522395
H	0	-2.2242591240	-1.5416998408	4.0908455143

H	0	-3.1379058508	-1.4437231505	1.1745098922
H	0	-1.9444857748	-3.4050685980	-0.2208128764
H	0	-0.4150629780	-3.2686728661	-1.5962523193
H	0	2.2794324113	-4.1449638047	-0.8299993565
C	0	1.7507818514	-3.9435789877	-2.9247711994
C	0	0.9207244582	-3.0558009932	-3.8661792665
H	0	1.3025859520	-2.0261423619	-3.8990241641
H	0	0.9589620125	-3.4692994662	-4.8855689904
H	0	-0.1409150567	-3.0045660543	-3.5788428346
C	0	3.2143338279	-3.9177010166	-3.3863383865
H	0	3.6579364721	-2.9135451935	-3.3034499250
H	0	3.8330561347	-4.6172437758	-2.8030969282
H	0	3.2795857850	-4.2231235872	-4.4413708746
C	0	2.1324396773	-2.0124344235	-1.2554658734
N	0	3.3689165645	-1.7198993505	-0.7970325324
O	0	1.3445090798	-1.1136715277	-1.5411623848
C	0	4.3579346464	-2.6851407243	-0.3547427495
H	0	4.2991585828	-2.8307864266	0.7353013319
H	0	4.2265871997	-3.6501660532	-0.8502672669
H	0	5.3592551662	-2.3148444277	-0.6161619833
C	0	3.6288016725	-0.3334108805	-0.4387676788
H	0	2.6881927003	0.0961524871	-0.0595900651
H	0	4.3383113142	-0.3344429165	0.3992988840
C	0	4.1547651044	0.5614103275	-1.5388476313
C	0	4.9083195771	1.6862280483	-1.1816251540
C	0	3.8577991033	0.3548102356	-2.8890604941
C	0	5.3366986279	2.5963529537	-2.1465305956
H	0	5.1572228904	1.8501681280	-0.1289976750
C	0	4.2944669079	1.2579818894	-3.8582278407
H	0	3.2662383417	-0.5122812381	-3.1856068635
C	0	5.0290116318	2.3852605726	-3.4910137927
H	0	5.9208965008	3.4695722586	-1.8473282789
H	0	4.0503407774	1.0826261945	-4.9082812246
H	0	5.3656178111	3.0939226435	-4.2507707043
C	0	-1.3104659523	0.5692665827	1.5471939336
C	0	-2.4466399974	1.2713434796	1.3127536660
H	0	-2.3961310188	2.3572829250	1.2262157208
H	0	-3.4235561476	0.7959697470	1.2239057027
N	0	-1.2234099156	-0.7924768308	1.6534453131
H	0	-0.3069060203	-1.1446405313	1.9210257848
C	0	-3.8719172799	-3.7137185244	3.4232311465
H	0	-4.7753151539	-4.3332797253	3.5323166625
H	0	-3.1876814332	-4.0067845207	4.2385507978
C	0	1.2344492963	-5.3880261643	-2.9949439148
H	0	1.7944765741	-6.0424827707	-2.3090444200
H	0	0.1704920786	-5.4526214568	-2.7274447198
H	0	1.3531399444	-5.7828894079	-4.0155914608
C	0	-3.2021579118	-4.0056524336	2.0812335652
H	0	-2.8953765805	-5.0604697405	2.0171473483
H	0	-3.9265532058	-3.8281339220	1.2660841840
C	0	-1.8498683386	1.0085333499	-1.5969794275
C	0	-0.9121103217	2.1182268694	-1.7483405593
C	0	-1.5451589171	-0.2944644873	-1.7605162206
H	0	-2.8943319099	1.2666512577	-1.4053102125
C	0	-1.4172861676	3.4255286672	-1.6626497450
C	0	0.4558609572	1.9280998628	-2.0182432687
N	0	-2.5677081303	-1.2671513006	-1.6403057451
H	0	-0.5590299420	-0.7250579802	-1.9384551640
C	0	-0.5846981118	4.5211489767	-1.8704639621
H	0	-2.4763336734	3.5757680208	-1.4380188725
C	0	1.2801631975	3.0260083550	-2.2405739406
H	0	0.8826624251	0.9227537421	-2.0429719429
O	0	-3.6821505995	-0.9527945315	-1.2470699704
O	0	-2.2938897809	-2.4309610822	-1.9347388311
C	0	0.7618696220	4.3214208677	-2.1741909640
H	0	-0.9899852866	5.5329765959	-1.8054532963

H	0	2.3378551657	2.8658542817	-2.4652854731
H	0	1.4126463391	5.1795128196	-2.3570981180
C	0	-0.0506167701	1.3159104273	1.7059290496
H	0	-0.0915605561	2.3979758686	1.5221219900
N	0	1.0063962988	0.7052095146	2.0849098642
N	0	2.1629273728	1.3582114878	2.2976177866
C	0	3.2764650614	0.6038441717	2.6999923928
C	0	4.5359796222	1.2126895404	2.8178460886
C	0	3.1579021923	-0.7728040676	2.9430206525
C	0	5.6544177409	0.4479921740	3.1459440037
H	0	4.6476859928	2.2827959379	2.6396869280
C	0	4.2845307489	-1.5193875350	3.2702865100
H	0	2.1889079123	-1.2568116846	2.8368229589
C	0	5.5431544787	-0.9230336930	3.3690113314
H	0	6.6270642667	0.9393184228	3.2246693748
H	0	4.1694640635	-2.5918493498	3.4460550745
H	0	6.4227600796	-1.5177114401	3.6224563467
C	0	2.2475416772	2.7784601340	2.1704626787
C	0	2.5327661280	3.3496929793	0.9310832146
C	0	2.0309133476	3.5876834071	3.2877945067
C	0	2.6166106652	4.7350808127	0.8109745083
H	0	2.6883475062	2.7033521415	0.0667269064
C	0	2.1131195863	4.9729374309	3.1632272130
H	0	1.8057301428	3.1209280294	4.2487635072
C	0	2.4085439132	5.5468466775	1.9256104894
H	0	2.8461818009	5.1792333278	-0.1593811130
H	0	1.9482114280	5.6074439250	4.0364224862
H	0	2.4760812438	6.6326899037	1.8306739539
H	0	-6.4671579679	-1.0969719844	-0.8386647008
O	0	-6.5027992426	-0.1349232595	-1.0826096247
O	0	-5.7317765106	-2.5252549087	-0.1617187352
C	0	-5.9457972679	0.5521662534	-0.1046964904
H	0	-4.9040157116	-2.3017536087	-0.6214129074
H	0	-5.6571679700	-2.0058662839	0.6550213625
C	0	-5.6473476267	1.9721003798	-0.4564119266
O	0	-5.6795590439	0.0722207270	0.9828748226
C	0	-5.6689655912	2.4083593806	-1.7861415728
C	0	-5.3043868641	2.8636715058	0.5648903700
C	0	-5.3433490640	3.7285666132	-2.0894957142
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C	0	-4.9861881893	4.1839852466	0.2600597240
H	0	-5.2845512222	2.5036570822	1.5947806252
C	0	-5.0054971022	4.6167800297	-1.0671689374
H	0	-5.3532498638	4.0664686137	-3.1276589951
H	0	-4.7210335255	4.8787424869	1.0594808645
H	0	-4.7533718742	5.6523502384	-1.3066214017

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C	0	-2.6898420000	-0.2727730000	-0.6024770000
C	0	-1.6244010000	-2.2456350000	-1.8038130000
H	0	-2.5499510000	0.6992180000	-0.1051820000
H	0	-0.6525650000	-2.6709780000	-2.0920810000
H	0	-2.1857460000	-2.9942340000	-1.2306270000
H	0	-2.1923320000	-2.0167980000	-2.7136300000
C	0	2.2391910000	-1.6868150000	-1.9113030000
O	0	1.8210740000	-2.0835000000	-0.7293290000
O	0	1.5618140000	-1.0303370000	-2.6817160000
H	0	0.0554920000	-0.3543370000	-2.1830290000
H	0	-0.3937260000	-0.3064540000	0.6310000000
H	0	0.9124130000	-1.6664600000	-0.4609230000
N	0	-0.5285250000	-1.2013500000	0.1510780000
C	0	-1.4055320000	-0.9542910000	-1.0237810000
O	0	-0.7715640000	0.0134370000	-1.8020760000

N	0	-3.8289880000	-0.7846250000	-0.8374940000
N	0	-4.9652210000	-0.1564240000	-0.4731260000
C	0	3.6211150000	-2.1334080000	-2.2479710000
C	0	4.2314280000	-3.1941530000	-1.5727270000
C	0	4.3119440000	-1.4590000000	-3.2583890000
C	0	5.5298820000	-3.5756050000	-1.9038040000
H	0	3.6841130000	-3.7221750000	-0.7899760000
C	0	5.6152070000	-1.8292920000	-3.5748320000
H	0	3.8166250000	-0.6333920000	-3.7711020000
C	0	6.2247050000	-2.8879870000	-2.8984800000
H	0	6.0039000000	-4.4080770000	-1.3797100000
H	0	6.1605640000	-1.2914170000	-4.3530100000
H	0	7.2467200000	-3.1797960000	-3.1504050000
C	0	-0.8304000000	-2.2642760000	1.1250040000
C	0	0.0479140000	-2.0552390000	2.3794720000
C	0	-2.2877180000	-2.4089650000	1.5888250000
H	0	-0.5349750000	-3.2212980000	0.6532280000
C	0	-0.0746930000	-3.2333390000	3.3458830000
H	0	-0.3158820000	-1.1500920000	2.8898790000
C	0	-2.4427530000	-3.5774050000	2.5630050000
H	0	-2.6051640000	-1.4661290000	2.0686610000
H	0	-2.9563350000	-2.5580690000	0.7327550000
C	0	-1.5252560000	-3.4401090000	3.7749340000
H	0	0.5686090000	-3.0392890000	4.2171260000
H	0	0.3081660000	-4.1486180000	2.8587940000
H	0	-3.4933080000	-3.6557890000	2.8814810000
H	0	-2.2084170000	-4.5172840000	2.0322230000
H	0	-1.6066780000	-4.3242870000	4.4254550000
H	0	-1.8460170000	-2.5737710000	4.3787520000
H	0	1.9319700000	-2.5167530000	1.5647640000
C	0	2.0212880000	-0.5669530000	2.0976980000
H	0	3.4178720000	-1.2255550000	0.8083640000
N	0	3.2565140000	-0.5339110000	1.5369640000
N	0	1.4305240000	-1.7833780000	2.0552040000
S	0	1.2883150000	0.7854810000	2.7951660000
C	0	4.0279410000	0.6822420000	1.3945400000
H	0	3.8498500000	1.2717900000	2.2988120000
C	0	3.5310420000	1.4312730000	0.1477060000
O	0	3.3372040000	0.7917040000	-0.8807090000
C	0	5.5568980000	0.3754180000	1.3428560000
C	0	5.9133170000	-0.6110160000	0.2231800000
H	0	5.4768410000	-1.6054350000	0.4009330000
H	0	5.5660420000	-0.2641190000	-0.7598450000
H	0	7.0047800000	-0.7481400000	0.1813230000
C	0	6.3263370000	1.6848380000	1.1260430000
H	0	6.0998080000	2.4181890000	1.9153140000
H	0	7.4092410000	1.4911750000	1.1548340000
H	0	6.0958220000	2.1425250000	0.1520630000
C	0	5.9605770000	-0.2240780000	2.6970350000
H	0	5.7693280000	0.4833110000	3.5192080000
H	0	5.3976160000	-1.1453100000	2.9060170000
H	0	7.0339120000	-0.4691490000	2.7021350000
C	0	3.3969220000	3.5706910000	1.4238470000
H	0	3.0038610000	3.0079090000	2.2791050000
H	0	4.4106110000	3.9413690000	1.6455350000
H	0	2.7347590000	4.4370170000	1.2908700000
C	0	2.9950030000	3.4865690000	-1.0123980000
H	0	3.6318600000	4.3817620000	-1.0958510000
H	0	3.2228320000	2.8212840000	-1.8536910000
N	0	3.3586180000	2.7755490000	0.2096030000
C	0	1.5347130000	3.8809560000	-1.0395400000
C	0	0.5483600000	2.8901210000	-1.1206050000
C	0	1.1441510000	5.2203040000	-0.9602650000
C	0	-0.7998560000	3.2359140000	-1.1268330000
H	0	0.8337380000	1.8385350000	-1.1905380000
C	0	-0.2082160000	5.5690340000	-0.9572040000

H	0	1.9066650000	6.0026900000	-0.9003450000
C	0	-1.1821040000	4.5760900000	-1.0391010000
H	0	-1.5466400000	2.4453610000	-1.2193550000
H	0	-0.4985780000	6.6202320000	-0.8914600000
H	0	-2.2413200000	4.8425830000	-1.0379530000
C	0	-4.9175530000	1.1568510000	0.0863220000
C	0	-4.8130140000	1.3242420000	1.4680600000
C	0	-4.9184020000	2.2676590000	-0.7602480000
C	0	-4.7084480000	2.6069280000	2.0038020000
H	0	-4.8108730000	0.4427990000	2.1126320000
C	0	-4.8203180000	3.5481540000	-0.2201240000
H	0	-4.9948200000	2.1160190000	-1.8387300000
C	0	-4.7108410000	3.7180420000	1.1605690000
H	0	-4.6223720000	2.7391520000	3.0841050000
H	0	-4.8293870000	4.4173900000	-0.8811470000
H	0	-4.6258850000	4.7219160000	1.5815870000
C	0	-6.1838830000	-0.7891760000	-0.7643490000
C	0	-7.3981750000	-0.1769960000	-0.4155230000
C	0	-6.2109530000	-2.0412310000	-1.4004480000
C	0	-8.6073720000	-0.8085110000	-0.6983750000
H	0	-7.3991300000	0.7951400000	0.0786850000
C	0	-7.4281290000	-2.6568580000	-1.6746510000
H	0	-5.2706420000	-2.5157090000	-1.6757830000
C	0	-8.6366140000	-2.0510240000	-1.3283810000
H	0	-9.5404820000	-0.3139660000	-0.4183320000
H	0	-7.4280930000	-3.6300250000	-2.1716810000
H	0	-9.5871820000	-2.5407530000	-1.5478440000

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C	0	-2.2959350000	-0.3192850000	1.7797420000
C	0	-1.7589650000	-2.5269520000	2.9282150000
H	0	-2.0536230000	0.7168850000	2.0495790000
H	0	-1.0215350000	-3.3420980000	2.9604920000
H	0	-1.8998820000	-2.1516800000	3.9497720000
H	0	-2.7178220000	-2.9058200000	2.5642580000
C	0	0.1841160000	1.5750780000	0.5046690000
O	0	-0.0585370000	0.5768410000	-0.2422320000
O	0	0.3001090000	1.5144290000	1.7438870000
H	0	0.0424990000	0.1058110000	2.4007950000
H	0	0.1550250000	-2.4458390000	0.9962000000
H	0	-0.2202930000	-0.9208070000	0.3759220000
N	0	-0.6320930000	-1.8371820000	0.7467760000
C	0	-1.2398330000	-1.3602000000	2.1020550000
O	0	-0.1808510000	-0.8092260000	2.7668510000
N	0	-3.3595110000	-0.6735170000	1.1742110000
N	0	-4.2815950000	0.2194820000	0.7889900000
C	0	0.2914510000	2.9199980000	-0.1621920000
C	0	0.0137130000	3.0640800000	-1.5235550000
C	0	0.6236110000	4.0451690000	0.5959930000
C	0	0.0603460000	4.3210000000	-2.1231550000
H	0	-0.2496790000	2.1798710000	-2.1070140000
C	0	0.6747230000	5.3020920000	-0.0010890000
H	0	0.8334680000	3.9118550000	1.6580810000
C	0	0.3901720000	5.4425440000	-1.3610170000
H	0	-0.1597230000	4.4271790000	-3.1877210000
H	0	0.9366410000	6.1789720000	0.5952410000
H	0	0.4278020000	6.4291730000	-1.8286710000
C	0	-1.4098120000	-2.4228350000	-0.3900020000
C	0	-0.4264480000	-2.7493590000	-1.5331550000
C	0	-2.2374680000	-3.6521430000	-0.0316930000
H	0	-2.0925270000	-1.6242850000	-0.7185370000
C	0	-1.1709450000	-3.2926210000	-2.7546600000
H	0	0.2695870000	-3.5326120000	-1.1866710000

C	0	-2.9665900000	-4.2014380000	-1.2587970000
H	0	-1.5796570000	-4.4269950000	0.3987320000
H	0	-2.9759920000	-3.3843400000	0.7307210000
C	0	-2.0061020000	-4.5182510000	-2.4007100000
H	0	-0.4208700000	-3.5282960000	-3.5236350000
H	0	-1.8171420000	-2.4954100000	-3.1619380000
H	0	-3.5380650000	-5.0957890000	-0.9683850000
H	0	-3.7052400000	-3.4534050000	-1.5959750000
H	0	-2.5602710000	-4.8687600000	-3.2841860000
H	0	-1.3352110000	-5.3419790000	-2.1013580000
H	0	-0.0670370000	-0.6819100000	-1.7395450000
C	0	1.7293040000	-1.5719800000	-1.9349180000
H	0	1.6249120000	0.3992590000	-1.5335240000
N	0	2.2393530000	-0.3189390000	-1.9243610000
N	0	0.3759560000	-1.5923390000	-1.8535250000
S	0	2.6533570000	-2.9804700000	-2.0516810000
C	0	3.6494330000	-0.0031610000	-1.8711290000
H	0	4.1829760000	-0.9421100000	-2.0478120000
C	0	3.9299850000	0.5381810000	-0.4645710000
O	0	3.2223230000	1.4358210000	-0.0214590000
C	0	4.0792590000	0.9878410000	-2.9949190000
C	0	3.2060030000	2.2483190000	-3.0136050000
H	0	2.1575750000	1.9992800000	-3.2355190000
H	0	3.2278190000	2.7768650000	-2.0509650000
H	0	3.5553400000	2.9336620000	-3.8016670000
C	0	5.5467780000	1.3784420000	-2.7791560000
H	0	6.1972890000	0.4901730000	-2.7415610000
H	0	5.8963520000	2.0098960000	-3.6101270000
H	0	5.6859910000	1.9487250000	-1.8478010000
C	0	3.9383740000	0.2519300000	-4.3339190000
H	0	4.5920150000	-0.6331960000	-4.3763260000
H	0	2.9031610000	-0.0873810000	-4.4884130000
H	0	4.2074070000	0.9177680000	-5.1686690000
C	0	5.7097210000	-1.1740300000	-0.1593910000
H	0	5.0543110000	-1.9600880000	-0.5591970000
H	0	6.4842450000	-0.9310590000	-0.9042140000
H	0	6.2062530000	-1.5882180000	0.7274030000
C	0	5.2358380000	0.5482040000	1.5697650000
H	0	6.3245290000	0.6803090000	1.6696020000
H	0	4.7626660000	1.5363670000	1.6179380000
N	0	4.9532680000	0.0008040000	0.2462620000
C	0	4.7112590000	-0.3367690000	2.6790870000
C	0	3.3294140000	-0.5082300000	2.8422970000
C	0	5.5832750000	-1.0210710000	3.5294480000
C	0	2.8356950000	-1.3541060000	3.8324870000
H	0	2.6379040000	0.0390660000	2.1948020000
C	0	5.0907860000	-1.8662160000	4.5260930000
H	0	6.6633470000	-0.8911540000	3.4129760000
C	0	3.7164040000	-2.0358110000	4.6760920000
H	0	1.7549570000	-1.4692820000	3.9366120000
H	0	5.7853550000	-2.3939960000	5.1838210000
H	0	3.3279800000	-2.6973270000	5.4541100000
C	0	-4.0733740000	1.6217740000	0.9861070000
C	0	-4.6998340000	2.2705770000	2.0506250000
C	0	-3.2184220000	2.3238860000	0.1331130000
C	0	-4.4793480000	3.6318640000	2.2536710000
H	0	-5.3594930000	1.7023240000	2.7092920000
C	0	-2.9946020000	3.6824220000	0.3451810000
H	0	-2.7123410000	1.7962000000	-0.6780770000
C	0	-3.6273290000	4.3360060000	1.4028050000
H	0	-4.9704550000	4.1427940000	3.0842880000
H	0	-2.3155250000	4.2277350000	-0.3136650000
H	0	-3.4485120000	5.4003860000	1.5679210000
C	0	-5.3869990000	-0.2637270000	0.0637670000
C	0	-5.6161190000	-1.6430570000	-0.0602880000
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C	0	-6.7045580000	-2.1073770000	-0.7925800000
H	0	-4.9359220000	-2.3408370000	0.4238330000
C	0	-7.3638780000	0.1501750000	-1.2738760000
H	0	-6.1149770000	1.7069430000	-0.4641900000
C	0	-7.5879240000	-1.2188770000	-1.4060110000
H	0	-6.8639190000	-3.1849270000	-0.8782120000
H	0	-8.0431920000	0.8642390000	-1.7449410000
H	0	-8.4411680000	-1.5892580000	-1.9770870000

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C	0	-2.9512072028	-2.0578636649	0.0003709014
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H	0	-1.7196540013	-3.5897570686	0.8834420913
H	0	-3.1709670711	-4.1839430010	0.0003918443
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H	0	-1.4423789007	4.9328894206	0.0001820710
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H	0	5.2872100065	-1.4201064191	-0.0004885055

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H	0	-0.5256477444	-2.0190848912	-4.4821113997
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C	0	4.9150940724	-1.5832009034	-0.5556027567
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H	0	5.5627403395	-1.2750919973	-4.3658550180
H	0	7.0059171790	-1.1639681347	-0.3099855621
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C	0	-3.2354689149	-1.6221979102	-2.5201052431
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H	0	-5.1360201446	1.2367874260	-2.9300985539
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H	0	1.6378002417	4.7675838018	-0.3003973004
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H	0	2.3839693696	3.9875522928	2.2096712909
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C	0	2.9707825774	2.0827120470	-0.5559863392
C	0	4.5179584248	3.2162878978	0.9025974171
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H	0	1.9572245858	1.7614060925	-0.8108103233
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C	0	5.3237919080	2.1660505853	-1.1180220479
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N	0	2.7454490188	1.2517057048	0.7142337652
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H	0	-2.6144943222	-0.5778029815	-2.9769211362
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H	0	-4.3730824553	-2.1175241072	-3.8028538473
H	0	-6.7739077942	-1.6498388850	-3.3195261080
C	0	0.0555695629	-0.8745395812	2.2939192823
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H	0	5.4112707286	1.9863177182	4.3827138731
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H	0	-5.6265907533	-2.6748734329	-0.0081156049
H	0	-6.6644724586	-3.3461493287	2.1542615869
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H	0	4.3404335660	-2.8112976954	1.7071984877
H	0	4.7816974007	-1.3950270398	1.6462825568
C	0	5.6370860184	0.7197947816	-1.8630580816
O	0	5.4039768094	-0.3122474587	0.2625608422
C	0	5.9430514473	0.5465809241	-3.2170018137
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H	0	-4.3223585874	-2.5969411187	0.0837796273
C	0	-5.5083220942	-1.5301969458	-2.0441648224
H	0	-3.5122662699	-1.7685911954	-2.7484146454
C	0	-5.6598146235	-4.0423726051	-1.7217168167
H	0	-3.6048079514	-4.3031976083	-2.3455743863
H	0	-3.9264502270	-4.9220985135	-0.7264781181
C	0	-6.0118528877	-2.8547776373	-2.6209840026
H	0	-5.7005068336	-0.6996958979	-2.7393570629
H	0	-6.0331021300	-1.2953347212	-1.1017998082
H	0	-5.9759331552	-4.9860794639	-2.1911223712
H	0	-6.2178735244	-3.9612669231	-0.7727332491
H	0	-7.0997198322	-2.8071492461	-2.7795621829
H	0	-5.5579807859	-3.0063778656	-3.6160195616
H	0	-3.4234686636	-0.2957351239	-0.2002034352
C	0	-2.6247800264	0.4567147029	-1.8833045863
H	0	-2.0083968062	1.0880805011	-0.0596619172
S	0	-2.4542992661	0.4601435908	-3.5804506502
N	0	-3.4468274703	-0.3856979027	-1.2321076734
N	0	-1.9284237941	1.2757819761	-1.0671297889
C	0	-0.0394311339	2.7136413113	-0.7196605338
O	0	0.0907552700	2.2912409303	0.4227296259
C	0	1.0100177244	3.6562720729	-2.7695759007
H	0	0.6599852232	2.7807499134	-3.3316114211
H	0	0.4284968820	4.5435293277	-3.0627519450
H	0	2.0561707103	3.8235724073	-3.0557833258
C	0	2.0633341031	3.8371573896	-0.5077456721
H	0	2.4667463476	4.7601770058	-0.9554592789
H	0	1.6633891287	4.1061111404	0.4795309731
C	0	-1.3863749819	2.5629702656	-1.4288239097
H	0	-1.2763469987	2.5796695732	-2.5198515457
C	0	-2.3700678374	3.7251800457	-1.0277684385
C	0	-1.8235954816	5.0721297251	-1.5160906518
H	0	-1.7236614613	5.0892669983	-2.6126255065
H	0	-2.5176799896	5.8788292510	-1.2355445452
H	0	-0.8450037545	5.3082591434	-1.0715101713
C	0	-3.7211298116	3.4680056255	-1.7122346220
H	0	-4.2178266989	2.5736400749	-1.3087310321
H	0	-4.3925515260	4.3232886818	-1.5402812149
H	0	-3.6062855166	3.3300830377	-2.7976283714
C	0	-2.5841279365	3.7792303695	0.4915286583
H	0	-2.9103188671	2.8074377901	0.8927198303
H	0	-1.6684843963	4.0718572162	1.0249756399
H	0	-3.3659384244	4.5178084894	0.7268146797
N	0	0.9574381735	3.3985393367	-1.3389713598
C	0	3.1920279847	2.8440411570	-0.3226849088
C	0	3.4469416865	1.8232114319	-1.2428908171
C	0	4.0363909557	2.9837532880	0.7842219528
C	0	4.5500232151	0.9859020124	-1.0746572828
H	0	2.7657489366	1.6510639992	-2.0801945131
C	0	5.1239889676	2.1322736381	0.9645794229
H	0	3.8339048648	3.7673718242	1.5199837729
C	0	5.3897766511	1.1352860581	0.0268485812
H	0	4.7481396213	0.2020040304	-1.8065593940

H	0	5.7650038611	2.2474441421	1.8415691323
H	0	6.2420682981	0.4651889911	0.1574067015
C	0	-0.2301247540	-4.2280902672	-2.7231863051
H	0	0.6974507469	-4.2289723668	-2.1380764101
C	0	0.1841792369	-4.1382182187	-4.1857911372
H	0	-0.6542808296	-4.0668130504	-4.8870541205
H	0	0.8470815158	-3.2749762843	-4.3375811361
C	0	-1.0254476703	-5.4700567522	-2.3682587178
C	0	-0.9641131862	-5.9553202540	-1.0564263194
C	0	-1.8747053512	-6.1091702122	-3.2778938258
C	0	-1.7449416772	-7.0365511235	-0.6555166958
H	0	-0.2922221102	-5.4772771671	-0.3383101898
C	0	-2.6531114690	-7.1964582555	-2.8812652270
H	0	-1.9405879402	-5.7680214223	-4.3133128053
C	0	-2.5966939043	-7.6588919121	-1.5680486146
H	0	-1.6839385919	-7.3975685353	0.3732694123
H	0	-3.3075545692	-7.6843966888	-3.6065824665
H	0	-3.2079968658	-8.5089415799	-1.2580726519
N	0	0.9845114506	-5.3330396228	-4.5990855238
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O	0	1.9005438934	-5.6610182425	-3.8797143359

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H	0	-2.2126512639	-3.7990882432	0.6997050387
H	0	-3.5284155573	-3.8534919916	-0.4774638841
C	0	-2.1077551630	-0.8260557336	0.3792517357
H	0	-2.5310044913	0.1775039212	0.5175817814
N	0	-0.8522687120	-1.0830862689	0.2995325686
N	0	0.0711309555	-0.1367874855	0.3333012734
C	0	-0.2882836676	1.2502006280	0.3110721650
C	0	-0.7185537108	1.8213312096	-0.8887136175
C	0	-0.2233672113	2.0065512459	1.4797492552
C	0	-1.0819684136	3.1652220433	-0.9144104587
H	0	-0.7696703602	1.2033388761	-1.7885797613
C	0	-0.5828223558	3.3534047105	1.4450730686
H	0	0.1140469760	1.5363998278	2.4053495605
C	0	-1.0119712972	3.9312756483	0.2505507054
H	0	-1.4197372875	3.6171954757	-1.8490275315
H	0	-0.5299626166	3.9524431066	2.3562592762
H	0	-1.2955980302	4.9854689914	0.2269438603
C	0	1.4176067632	-0.5391173902	0.1624680231
C	0	2.4031059863	0.4073057316	-0.1445016507
C	0	1.7745289789	-1.8884697325	0.2911133197
C	0	3.7226154702	-0.0002458491	-0.3329362855
H	0	2.1423024586	1.4611403263	-0.2446779164
C	0	3.0937536980	-2.2808592642	0.0896443079
H	0	1.0114425101	-2.6209712719	0.5490193098
C	0	4.0778524169	-1.3428145266	-0.2240589378
H	0	4.4791710747	0.7490899354	-0.5758978587
H	0	3.3525873869	-3.3376921101	0.1826882980
H	0	5.1116245557	-1.6563978427	-0.3798140257
C	0	-1.5470297994	-3.4241893493	-1.3240040269
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C	0	-1.6177648687	-4.8342784739	-1.9115362327
H	0	-1.5246800373	-5.5943671913	-1.1225526525
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C	0	-2.8812136031	-2.0328971830	-2.9895054664
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H	0	-3.7977396387	-2.5299662950	-2.6604454761
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H	0	0.4649392268	-1.9598853794	-2.3929771869
C	0	-1.8002080730	-0.3897584314	-4.3949231550
H	0	-3.9231408200	-0.7888768685	-4.4080314419
H	0	0.3419715418	-0.2205748317	-4.1567897887
H	0	-1.8592597731	0.3826220420	-5.1648738663
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O	0	0.6442209549	-4.9063159125	-2.4033041236
O	0	-0.7284261793	-5.4405531203	-3.9681258932

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C	0	1.6243037012	-1.9968235086	2.1763093965
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H	0	0.6335812872	-2.4689012772	2.2202497888
H	0	2.3227577166	-2.6362262899	1.6235523497
H	0	2.0027598757	-1.8824151744	3.2024412897
C	0	-2.2054444846	-1.2982654809	2.1667263694
O	0	-1.7330445694	-1.8027494969	1.1404662902
O	0	-1.5612022823	-0.4862312906	2.9303729292
H	0	-0.5900028388	-0.2402053333	2.5618277638
H	0	0.8660334349	-0.1591038336	-0.6649934256
H	0	-0.2260692429	-1.0217246614	0.2332800627
N	0	0.7467815391	-1.0056990788	-0.1039219790
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N	0	3.8721258871	-0.5721398363	1.0988666439
N	0	5.0017188777	0.0194469234	0.6830625480
C	0	-3.5911046376	-1.6336874823	2.6094925964
C	0	-4.1912961641	-2.8081987162	2.1493331927
C	0	-4.2972402124	-0.7740910671	3.4559184412
C	0	-5.4908740726	-3.1268198101	2.5353326532
H	0	-3.6292241057	-3.4679310958	1.4854071270
C	0	-5.6036233983	-1.0830852145	3.8234763205
H	0	-3.8190099379	0.1440553014	3.7983831076
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H	0	-5.9557955831	-4.0485735101	2.1795072330
H	0	-6.1619786117	-0.4030900961	4.4702694475
H	0	-7.2237951092	-2.5021809055	3.6607428309
C	0	0.9990701704	-2.2188191150	-0.8896536822
C	0	0.0509529189	-2.3069378723	-2.1027915227
C	0	2.4486110350	-2.3382620798	-1.3557857936
H	0	0.7751124232	-3.0647016455	-0.2160580495
C	0	0.2474202743	-3.6253491334	-2.8503134441
H	0	0.3013625087	-1.4852071947	-2.7930870405
C	0	2.6684247015	-3.6395300372	-2.1276240109
H	0	2.6857859354	-1.4722587629	-2.0005599120
H	0	3.1291911419	-2.2823655241	-0.4958189647
C	0	1.6994568730	-3.7799921233	-3.3015256376
H	0	-0.4367545785	-3.6417278355	-3.7116308230
H	0	-0.0390665977	-4.4643212583	-2.1913000920
H	0	3.7103365388	-3.6895518083	-2.4780908823
H	0	2.5310453562	-4.4902400612	-1.4370746519
H	0	1.8405301683	-4.7503735838	-3.8012577983
H	0	1.9243805691	-3.0040907966	-4.0537385100
H	0	-1.5946875064	-2.4802592089	-0.7965199900
C	0	-2.0969657018	-1.0663260510	-2.1439871556
H	0	-3.1325376116	-1.1961304217	-0.4171315782
N	0	-3.1800477494	-0.8228929903	-1.3659482221
N	0	-1.3187762984	-2.0804204844	-1.6919911367
S	0	-1.7457304162	-0.2112004959	-3.5585122461
C	0	-4.0337960950	0.3354248052	-1.5167316140

H	0	-3.8429586158	0.7245897870	-2.5206383517
C	0	-3.6227297721	1.3539868541	-0.4463225923
O	0	-3.5140771987	0.9837449181	0.7187561651
C	0	-5.5484763448	-0.0250752085	-1.4529165933
C	0	-5.8945592354	-0.8369761446	-0.2001711876
H	0	-5.3881945798	-1.8131254205	-0.2092202659
H	0	-5.6036388499	-0.3161101926	0.7228522472
H	0	-6.9777016574	-1.0325449170	-0.1665774082
C	0	-6.3708374317	1.2696968573	-1.4730961732
H	0	-6.1203658744	1.8917782410	-2.3469859512
H	0	-7.4442423423	1.0333221693	-1.5306388031
H	0	-6.2118921984	1.8703494290	-0.5643033609
C	0	-5.8734956867	-0.8550737364	-2.7019308991
H	0	-5.6969866940	-0.2787921271	-3.6235368567
H	0	-5.2477638524	-1.7589614519	-2.7450904874
H	0	-6.9287096834	-1.1694582713	-2.6909008628
C	0	-3.3282933674	3.1141269498	-2.1900093176
H	0	-2.8878477784	2.3567324826	-2.8508285324
H	0	-4.3123970613	3.4216141315	-2.5803984943
H	0	-2.6590723584	3.9847157702	-2.2176564554
C	0	-3.1477436747	3.6282169692	0.2265727981
H	0	-3.7057562625	4.5443326689	-0.0224022200
H	0	-3.5494191168	3.2240884275	1.1635004340
N	0	-3.4086581212	2.6410373520	-0.8181413505
C	0	-1.6751640214	3.9377720636	0.3847465056
C	0	-0.8260122711	3.0004323832	0.9873069498
C	0	-1.1310644717	5.1373763499	-0.0842990859
C	0	0.5345312260	3.2637230082	1.1217100557
H	0	-1.2350829979	2.0584622177	1.3599892649
C	0	0.2357888631	5.3972639990	0.0377868967
H	0	-1.7844843094	5.8823317558	-0.5482829189
C	0	1.0717719212	4.4598374549	0.6417684659
H	0	1.1556754835	2.5147413245	1.6152648217
H	0	0.6450579081	6.3381507654	-0.3376784999
H	0	2.1418842740	4.6573821630	0.7419222553
C	0	4.9853457845	1.3782706216	0.2387346474
C	0	4.6834858891	1.6650403409	-1.0943188023
C	0	5.2084184214	2.4108167066	1.1503951069
C	0	4.6062189328	2.9906656077	-1.5156775203
H	0	4.5087162746	0.8422020567	-1.7909214987
C	0	5.1332095414	3.7358999213	0.7238203996
H	0	5.4362409364	2.1658720715	2.1895363356
C	0	4.8308587527	4.0255668776	-0.6069684104
H	0	4.3683236103	3.2171361766	-2.5567944908
H	0	5.3090942060	4.5454308202	1.4350741961
H	0	4.7683047711	5.0641192278	-0.9384161888
C	0	6.1677771625	-0.7651925749	0.6186379761
C	0	7.3651648467	-0.2087646863	0.1447578115
C	0	6.1521576533	-2.1090202018	1.0246978591
C	0	8.5184943512	-0.9874962042	0.0763989093
H	0	7.3978349735	0.8341376800	-0.1721325604
C	0	7.3133272558	-2.8717383517	0.9486307797
H	0	5.2257712707	-2.5404551972	1.4002740235
C	0	8.5052952157	-2.3225579959	0.4746879575
H	0	9.4407665326	-0.5357360753	-0.2960711229
H	0	7.2824281307	-3.9158086496	1.2691349264
H	0	9.4119812173	-2.9277072565	0.4185642722

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C	0	2.3229819439	-0.7082699203	-1.5816649630
C	0	1.9488567406	-3.2355243653	-1.8806139107
H	0	1.9100095331	0.2716433477	-1.8462688102
H	0	1.1745838232	-3.9991386938	-1.7242679428

H	0	2.2730553353	-3.2907154293	-2.9299754412
H	0	2.8139406911	-3.4363311723	-1.2401938186
C	0	-0.5016465001	1.3224173018	-1.3142004613
O	0	-0.2525141383	0.7743286411	-0.2339136289
O	0	-0.4841075198	0.7071432376	-2.4442720891
H	0	-0.1603685690	-0.3381189805	-2.3626866181
H	0	0.2922038642	-2.7955004092	0.2219379370
H	0	0.0945516541	-1.1622074898	0.0133549888
N	0	0.7937938951	-1.9112895807	0.1115130382
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O	0	0.2739660423	-1.6120999687	-2.3054377043
N	0	3.5217230225	-0.8689222530	-1.1741833251
N	0	4.3352988280	0.1881957475	-1.0086231306
C	0	-0.7952183653	2.7859552774	-1.3753810370
C	0	-0.7870917729	3.5352737246	-0.1963865471
C	0	-1.0249925961	3.4214281646	-2.5986826299
C	0	-1.0110449352	4.9078660594	-0.2341996506
H	0	-0.5931621089	3.0296271969	0.7507865235
C	0	-1.2439456164	4.7965477138	-2.6386634501
H	0	-1.0262442898	2.8274496260	-3.5132717289
C	0	-1.2371475729	5.5404155834	-1.4578631819
H	0	-1.0094750611	5.4874013739	0.6913751898
H	0	-1.4235438304	5.2912007728	-3.5955043252
H	0	-1.4117649964	6.6182727678	-1.4908958555
C	0	1.6445667355	-1.6161968592	1.2744554709
C	0	0.8064777538	-1.3990664821	2.5502012471
C	0	2.7161254485	-2.6763765699	1.5047803780
H	0	2.1492973279	-0.6637144377	1.0395655670
C	0	1.7072931722	-1.0268547418	3.7298432049
H	0	0.2792161934	-2.3355347686	2.7960506035
C	0	3.6093733331	-2.3085070938	2.6882985832
H	0	2.2274932488	-3.6506521650	1.6856259855
H	0	3.3262735629	-2.7724733951	0.5983978979
C	0	2.7940083984	-2.0745837395	3.9585358770
H	0	1.0733656354	-0.9091953685	4.6212493020
H	0	2.1682189554	-0.0432516549	3.5273908572
H	0	4.3579334964	-3.0993834282	2.8467658326
H	0	4.1751514922	-1.3945577628	2.4346138849
H	0	3.4500303869	-1.7649794479	4.7861193563
H	0	2.3218078836	-3.0226746515	4.2695197699
H	0	0.0514454079	0.3573924526	1.6747963559
C	0	-1.5412248260	-0.5618673558	2.4951021680
H	0	-1.8149954120	0.9103295444	1.1421315810
N	0	-2.2849958581	0.3965956677	1.8900182549
N	0	-0.2101805975	-0.4009692626	2.3023239064
S	0	-2.1858835957	-1.8210581338	3.4166476138
C	0	-3.7253645520	0.3614164917	1.7660980003
H	0	-4.0691210884	-0.4642814121	2.3963076977
C	0	-4.0334422170	0.0990996725	0.2872591467
O	0	-3.4937546202	0.7961771573	-0.5666899652
C	0	-4.4073405824	1.6567327720	2.3015531042
C	0	-3.7994296181	2.9204384485	1.6819297135
H	0	-2.7436944674	3.0290570481	1.9717083086
H	0	-3.8486085250	2.9010787333	0.5847316128
H	0	-4.3343634488	3.8117389495	2.0454548473
C	0	-5.9075980340	1.5962995949	1.9878771296
H	0	-6.3666715680	0.6827365206	2.3979410720
H	0	-6.4237077626	2.4573589295	2.4391694056
H	0	-6.1010571046	1.6240880667	0.9044124846
C	0	-4.2036919913	1.6879575280	3.8217704241
H	0	-4.6793167843	0.8224403203	4.3082743174
H	0	-3.1329743480	1.6666968701	4.0743310207
H	0	-4.6382826961	2.6050628417	4.2492312553
C	0	-5.4189541220	-1.8715977998	0.9191194405
H	0	-4.6545523431	-2.1854129328	1.6423787338
H	0	-6.2993752484	-1.4902127052	1.4610003233

H	0	-5.7202752196	-2.7684130314	0.3621430004
C	0	-5.2454264527	-1.0961048511	-1.4319478309
H	0	-6.3336595972	-1.2500810396	-1.5014446633
H	0	-4.9949613431	-0.1684833241	-1.9607701159
N	0	-4.8956336912	-0.8993541941	-0.0281422206
C	0	-4.5101556742	-2.2648347970	-2.0501207613
C	0	-3.1195293109	-2.2066692683	-2.2129860567
C	0	-5.1874317399	-3.4239022643	-2.4373715970
C	0	-2.4222815616	-3.2862197585	-2.7489068094
H	0	-2.5806907047	-1.2997001051	-1.9269546272
C	0	-4.4921304155	-4.5085237359	-2.9766114621
H	0	-6.2735353632	-3.4802739283	-2.3182825367
C	0	-3.1090046177	-4.4413461732	-3.1308839483
H	0	-1.3398517367	-3.1964212315	-2.8650879192
H	0	-5.0356172099	-5.4080535758	-3.2751515741
H	0	-2.5639288561	-5.2886762715	-3.5537809682
C	0	3.8059195606	1.5127840452	-1.1307840294
C	0	3.7824231016	2.1462774351	-2.3726487130
C	0	3.2232854278	2.1229222480	-0.0164851408
C	0	3.1565708893	3.3862148472	-2.5034885842
H	0	4.2358836135	1.6509332509	-3.2332812757
C	0	2.6103917453	3.3651662743	-0.1502009394
H	0	3.2523911680	1.6138130099	0.9497186246
C	0	2.5654803946	3.9920941777	-1.3960157810
H	0	3.1219345015	3.8756002314	-3.4786719576
H	0	2.1482226018	3.8407628001	0.7166197761
H	0	2.0528472828	4.9504053153	-1.5036705810
C	0	5.6034624692	-0.0493547759	-0.4458276325
C	0	6.0348703100	-1.3559360756	-0.1688792729
C	0	6.4567029107	1.0264145493	-0.1589221375
C	0	7.2881977064	-1.5698691704	0.3966192068
H	0	5.3817659054	-2.1939929303	-0.4051537290
C	0	7.7088290122	0.7938691419	0.4059496827
H	0	6.1421853007	2.0475919748	-0.3770142413
C	0	8.1353036445	-0.5014837026	0.6920566102
H	0	7.6058827526	-2.5937616839	0.6071779359
H	0	8.3578981941	1.6451999289	0.6233106105
H	0	9.1168384854	-0.6774102109	1.1359365640

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C	0	3.2465564425	2.1205255942	0.9305725720
C	0	2.9691286604	-0.0978964194	-0.3148552817
H	0	2.9044098924	3.1431197483	1.1012058392
H	0	2.2200137070	-0.6131924757	-0.9311556287
H	0	3.9389355542	-0.1065461884	-0.8316721205
H	0	3.0686147801	-0.6122924909	0.6455125572
C	0	-0.7995844892	0.4422528051	-2.1315031569
O	0	-0.8412884075	1.6413822198	-2.4867516370
O	0	-0.2701587817	0.0042634624	-1.0704294845
H	0	0.3803308431	0.6528143881	0.0871929677
H	0	0.6692878237	1.7298113712	1.3038067976
H	0	1.7374375621	1.4083048044	-1.9276499108
N	0	2.1852649602	1.9898528615	-1.2274888523
C	0	2.5494189906	1.3319730720	-0.1082302238
O	0	1.0270626556	0.9374308845	0.8436693970
N	0	4.1767475241	1.5831284302	1.6233057386
N	0	4.8064359608	2.2884074238	2.5619157269
C	0	-1.4163664617	-0.5854559764	-3.0503880730
C	0	-1.2282612666	-1.9516197526	-2.8230592941
C	0	-2.1829567386	-0.1703302937	-4.1422504749
C	0	-1.8057986033	-2.8930559939	-3.6724816551
H	0	-0.6257053397	-2.2617394675	-1.9680072797
C	0	-2.7662972721	-1.1095685389	-4.9896640549

H	0	-2.3169242537	0.9002298522	-4.3050380915
C	0	-2.5787856214	-2.4726902311	-4.7557876021
H	0	-1.6561282148	-3.9595597152	-3.4886509348
H	0	-3.3730575776	-0.7788398758	-5.8357801046
H	0	-3.0371457725	-3.2098774664	-5.4193012030
C	0	5.8490389250	1.6613080002	3.2778258398
C	0	6.2339056355	0.3467935681	2.9781219388
C	0	6.5059237199	2.3542376443	4.3035228946
C	0	7.2617344421	-0.2547082873	3.6976653074
H	0	5.7210610923	-0.1917081205	2.1829136919
C	0	7.5343058570	1.7370532579	5.0128438100
H	0	6.2135184755	3.3750712390	4.5518540166
C	0	7.9213101681	0.4316447047	4.7178648179
H	0	7.5507593704	-1.2793340442	3.4527298783
H	0	8.0354437907	2.2911157102	5.8096656510
H	0	8.7270939354	-0.0472161316	5.2771660733
C	0	4.4967639967	3.6754006051	2.7417189904
C	0	3.4088514218	4.0497218112	3.5308358977
C	0	5.2302142371	4.6356091112	2.0411166567
C	0	3.0477458545	5.3935952297	3.6112950750
H	0	2.8367311621	3.2826646988	4.0558794451
C	0	4.8715381413	5.9786413768	2.1340370364
H	0	6.0739384634	4.3196141210	1.4241307153
C	0	3.7775839177	6.3563700576	2.9142716564
H	0	2.1862320282	5.6867908391	4.2135732673
H	0	5.4430463389	6.7323830518	1.5887502061
H	0	3.4899662697	7.4078054992	2.9765015831
C	0	2.0815247620	3.4278513227	-1.4897802770
C	0	1.0846431358	4.1798078304	-0.5874767667
C	0	3.4471027100	4.1266448037	-1.5379402634
H	0	1.6641064192	3.4727588016	-2.5094853746
C	0	0.9770674184	5.6478875045	-1.0137640374
H	0	1.4310758944	4.1693112498	0.4565222417
C	0	3.3126188121	5.5932050664	-1.9436108805
H	0	3.9326349777	4.0752582759	-0.5509741232
H	0	4.0957994031	3.5800508347	-2.2390854885
C	0	2.3422100426	6.3303515116	-1.0222995702
H	0	0.2850648476	6.1543831844	-0.3241928588
H	0	0.5228421027	5.6950631415	-2.0190902793
H	0	4.3035582377	6.0722998652	-1.9285580888
H	0	2.9484619326	5.6562145072	-2.9840809673
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H	0	2.7500083080	6.3414404198	0.0040664422
H	0	-0.4289503016	2.9587145757	-1.4707370841
C	0	-0.9576977150	3.2410374899	0.4467785243
H	0	-2.3001343662	2.4504150032	-0.8375509410
S	0	-0.4482864927	3.5336448180	2.0537551548
N	0	-0.1968794045	3.5156405020	-0.6223781198
N	0	-2.1392017971	2.6615761982	0.1482363065
C	0	-3.0517317017	0.4945459197	0.4500065202
O	0	-3.5159313915	0.3718692361	-0.6762881653
C	0	-1.9017464700	-0.4301065451	2.4509480274
H	0	-1.7942548472	-1.4346635210	2.8796930525
H	0	-0.8989437492	0.0141776227	2.3484075927
H	0	-2.4887976453	0.1612599414	3.1651698851
C	0	-2.4805811093	-1.8477364238	0.5127166734
H	0	-2.8473480560	-1.7134379955	-0.5140217703
H	0	-1.4193649155	-2.1350590356	0.4356564427
C	0	-2.9652073120	1.8985390871	1.0644993329
H	0	-2.4318250009	1.8894427098	2.0201258007
C	0	-4.3642100380	2.5326119737	1.3215279892
C	0	-5.2217814303	1.5184972023	2.0904579226
H	0	-5.4658829725	0.6444375272	1.4670067511
H	0	-4.7115459012	1.1650028636	3.0013538793
H	0	-6.1717230747	1.9796397537	2.4005218194
C	0	-4.1640654523	3.7890516067	2.1784812550

H	0	-3.4868627028	4.5013855531	1.6839930778
H	0	-5.1287650454	4.2925890355	2.3478550355
H	0	-3.7262674846	3.5432714162	3.1581748129
C	0	-5.0663132881	2.9204332996	0.0145369999
H	0	-4.4867827759	3.6815508120	-0.5299333109
H	0	-5.1970028563	2.0520530251	-0.6439903118
H	0	-6.0551413509	3.3512950296	0.2367793331
N	0	-2.5705994721	-0.5539204222	1.1654686509
C	0	-3.2707416933	-2.9329935427	1.2087247199
C	0	-2.8231622467	-4.2574638509	1.1752292129
C	0	-4.4729569147	-2.6470696715	1.8639125036
C	0	-3.5644752973	-5.2767651284	1.7718068793
H	0	-1.8799512514	-4.4936793370	0.6744195503
C	0	-5.2138855975	-3.6625572814	2.4659622882
H	0	-4.8251690702	-1.6136981965	1.9060148952
C	0	-4.7634238174	-4.9820444054	2.4202142895
H	0	-3.1998831295	-6.3059522967	1.7355195049
H	0	-6.1504931249	-3.4214479893	2.9739860264
H	0	-5.3433333632	-5.7780295899	2.8925449597

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C	0	3.2108242338	0.3428039883	-0.0511731526
C	0	3.7894213824	2.5418294823	1.1027121114
H	0	2.7863118786	-0.1105919630	-0.9568758978
H	0	3.3196730968	3.4657213679	1.4595110634
H	0	4.0361045584	1.9109612955	1.9620863894
H	0	4.7149978634	2.7894247523	0.5647532852
C	0	-0.1392139265	-0.1652140038	-0.9701148847
O	0	0.1988027681	0.6851406684	-1.8236347414
O	0	-0.0931761370	-0.0207414533	0.2825146664
H	0	0.8366371311	0.8971287312	0.9488000849
H	0	1.0171042681	2.2858099706	1.6999859167
H	0	1.7802875992	1.6763736862	-1.4600604331
N	0	2.3778631007	2.3288521943	-0.9341522289
C	0	2.8756677608	1.7743036437	0.1896398910
O	0	1.5352419980	1.4984836905	1.4170471044
N	0	3.9736727808	-0.2799231105	0.7604500768
N	0	4.3328790122	-1.5446462756	0.5464717507
C	0	-0.6174007772	-1.5186052030	-1.4525315742
C	0	-0.7046636454	-2.5882710484	-0.5554568930
C	0	-0.9375174313	-1.7213511681	-2.7962200104
C	0	-1.0941163498	-3.8508341613	-0.9975352390
H	0	-0.4582162457	-2.4093439886	0.4922064131
C	0	-1.3464121825	-2.9789639312	-3.2384574651
H	0	-0.8603066093	-0.8764613554	-3.4821882733
C	0	-1.4190493103	-4.0469590777	-2.3420879705
H	0	-1.1511498792	-4.6831637102	-0.2922808979
H	0	-1.6064652427	-3.1296994651	-4.2885087959
H	0	-1.7320824440	-5.0336924802	-2.6915603975
C	0	5.1743838206	-2.1604548926	1.4971257360
C	0	5.6144127610	-1.4569261868	2.6278866232
C	0	5.5706699505	-3.4937917955	1.3219407186
C	0	6.4395131371	-2.0826144598	3.5571156949
H	0	5.2997045566	-0.4243187080	2.7679176114
C	0	6.3978211209	-4.1047665571	2.2622414493
H	0	5.2312342939	-4.0576170232	0.4525529280
C	0	6.8401247837	-3.4080718434	3.3846608801
H	0	6.7728564101	-1.5203485315	4.4324837195
H	0	6.6958937189	-5.1444816441	2.1093056239
H	0	7.4872066975	-3.8920111466	4.1185666346
C	0	3.9807088808	-2.2060892538	-0.6740651460
C	0	4.8654240851	-2.1603289218	-1.7538402518
C	0	2.7419685069	-2.8333389251	-0.7991328796

C	0	4.5084935716	-2.7540857231	-2.9620871446
H	0	5.8286059376	-1.6597534908	-1.6354965712
C	0	2.3841229671	-3.4152563768	-2.0143069467
H	0	2.0567272578	-2.8446416554	0.0501459502
C	0	3.2668501391	-3.3779063048	-3.0926559007
H	0	5.1993120828	-2.7234668049	-3.8071113395
H	0	1.4056114932	-3.8877680453	-2.1184243729
H	0	2.9823813137	-3.8332922980	-4.0434283010
C	0	2.0558969446	3.7218641290	-1.2212424035
C	0	0.8796163999	4.2459450312	-0.3863826711
C	0	3.2474169726	4.6838297881	-1.1968556023
H	0	1.7084514086	3.6972658199	-2.2695712072
C	0	0.4970905762	5.6704623026	-0.8052270223
H	0	1.1716778008	4.2652872695	0.6762453821
C	0	2.8287101280	6.0796983698	-1.6569669992
H	0	3.6566792699	4.7660683493	-0.1805048006
H	0	4.0459115591	4.2750857862	-1.8345034971
C	0	1.6935505757	6.6177308881	-0.7866929236
H	0	-0.3018760225	6.0262761751	-0.1369740098
H	0	0.0707118511	5.6268274868	-1.8227032865
H	0	3.6965076783	6.7556266286	-1.6248575112
H	0	2.4980720243	6.0406139697	-2.7096148254
H	0	1.3857038488	7.6181680826	-1.1265115347
H	0	2.0534460907	6.7359180852	0.2504510124
H	0	-0.2381268538	2.7033721156	-1.3336201467
C	0	-1.1648251722	3.0620552882	0.4126226881
H	0	-2.3292768600	2.3713665943	-1.0914759060
S	0	-0.9215777110	3.4108494490	2.0560392353
N	0	-0.2407945305	3.3407390344	-0.5341826237
N	0	-2.2690847382	2.4768923821	-0.0800896813
C	0	-3.5322272128	0.4849303148	-0.2950230087
O	0	-3.6977780892	0.6847390142	-1.4939264416
C	0	-3.0605798032	-1.0699345232	1.5589574796
H	0	-2.9971324408	-2.1614616223	1.6437174246
H	0	-2.0412548589	-0.6655859704	1.6363383201
H	0	-3.6781961446	-0.7090789427	2.3962612486
C	0	-4.1146526528	-1.8270602814	-0.5936482657
H	0	-4.6724853517	-1.3575126952	-1.4151845731
H	0	-3.2667551702	-2.3518359008	-1.0575263418
C	0	-3.2685908811	1.6952736646	0.6152464946
H	0	-2.8534295304	1.4053681728	1.5881079647
C	0	-4.6100043202	2.4779192112	0.8657427269
C	0	-5.7109200365	1.4922375124	1.2813801785
H	0	-6.0035364787	0.8333565013	0.4501406353
H	0	-5.3967396118	0.8652981649	2.1311497580
H	0	-6.6086003639	2.0468784064	1.5935458545
C	0	-4.4001244169	3.4873473610	2.0005050471
H	0	-3.6098246795	4.2103807673	1.7572469677
H	0	-5.3348160697	4.0413682361	2.1820991480
H	0	-4.1079672095	2.9871829928	2.9364389647
C	0	-5.0551657436	3.2315665696	-0.3941006914
H	0	-4.3125957938	3.9913957142	-0.6802676957
H	0	-5.1968204524	2.5518769485	-1.2450558268
H	0	-6.0058426580	3.7510834770	-0.1975657170
N	0	-3.6387946891	-0.7447577681	0.2612574113
C	0	-4.9904865779	-2.8182934285	0.1349986075
C	0	-4.7929417395	-4.1906692695	-0.0416398213
C	0	-6.0261059653	-2.3912203311	0.9747626264
C	0	-5.6158014822	-5.1186540687	0.5982276652
H	0	-3.9814179567	-4.5339342915	-0.6886138456
C	0	-6.8448788881	-3.3144024233	1.6202830417
H	0	-6.1834358493	-1.3214299596	1.1280634091
C	0	-6.6433940636	-4.6830249059	1.4325577439
H	0	-5.4478914537	-6.1875542896	0.4479143414
H	0	-7.6471693494	-2.9640387572	2.2736647394
H	0	-7.2854409935	-5.4072911126	1.9387141503

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C	0	2.7534235114	-1.2392589905	-1.6771546660
C	0	2.1241508208	0.0664908232	-2.1948303339
C	0	2.3756963311	0.2652949926	-3.6944049119
C	0	3.8620855467	0.1848052910	-4.0284532654
N	0	2.6326506358	-1.2758264824	-0.2333488828
C	0	1.6231491765	-1.8487824099	0.4567631207
N	0	1.4367502983	-1.3088473025	1.6843702292
C	0	0.3557553938	-1.6768699115	2.5660937989
S	0	0.7035100592	-3.1421854612	-0.1282863066
H	0	2.1905253372	-2.0980658928	-2.0757359638
H	0	4.3914457245	1.0058307007	-3.5159912337
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TS3a-S

0 1

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O	0	-3.2875053247	1.1984876018	-1.1294452295
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C	0	2.8957549526	3.5384264395	-3.2652541905
H	0	1.8681315486	5.4323439486	-3.4392615890
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H	0	1.8120517871	2.9723515952	0.5385425546
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C	0	3.3381509063	-0.6919091436	3.1780193362
C	0	6.1218764295	-0.7965364601	3.1568516602
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C	0	4.0085594163	-1.7378385268	3.8026121106
H	0	2.2504057805	-0.6636859076	3.1671194187
C	0	5.4029569824	-1.8062354919	3.7929934925
H	0	7.2139641924	-0.8228088889	3.1471205887
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H	0	5.9219223563	-2.6325788105	4.2822772092
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C	0	5.0267048912	4.6185388116	1.2358944998
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O	0	-4.4596011010	-2.2950449271	-0.1411682124
C	0	-6.6082645407	0.4942916399	-0.4137145110
H	0	-4.1056677991	-1.7643397371	-0.8734434661
H	0	-5.1316079640	-1.7067621378	0.2387429042
C	0	-8.0815465215	0.7026412508	-0.5377091515
O	0	-6.1094756912	-0.1032117916	0.5242898084
C	0	-8.6345152694	1.4126304297	-1.6094776588
C	0	-8.9155837483	0.1692138978	0.4507152653
C	0	-10.0141862346	1.5853276299	-1.6890676762
H	0	-7.9775007588	1.8256583677	-2.3757713289
C	0	-10.2939071362	0.3433678950	0.3684351562
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H	0	-10.4456021189	2.1388570395	-2.5255980548
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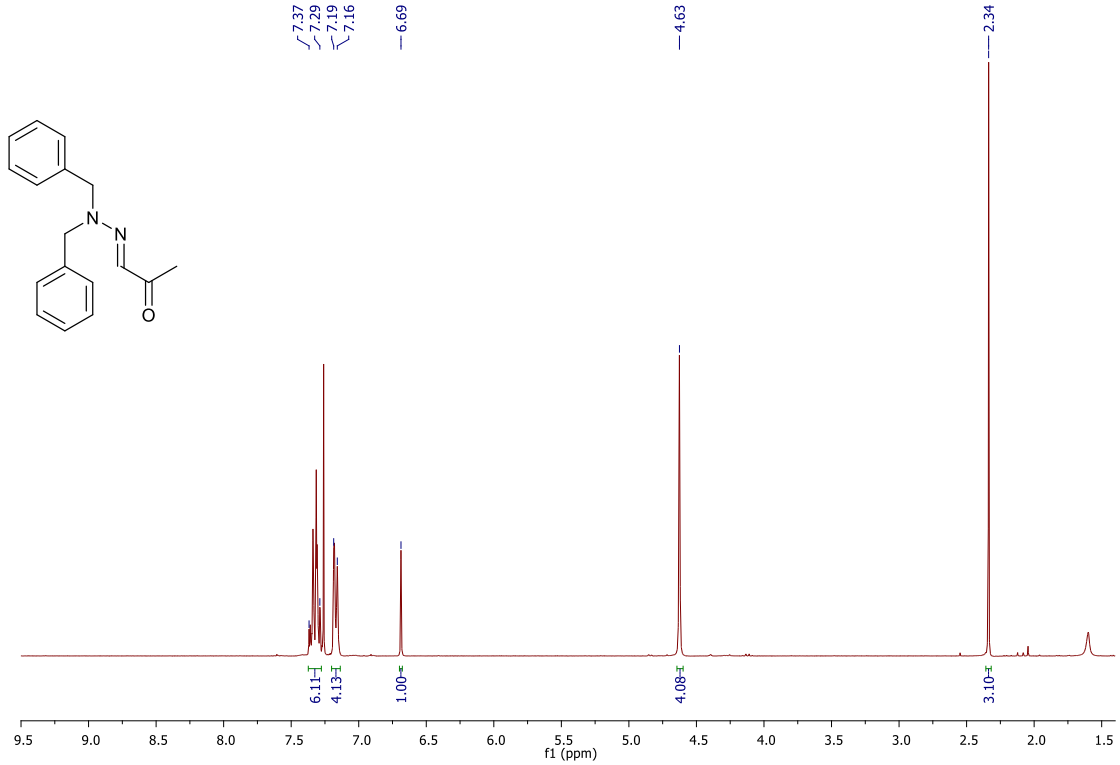
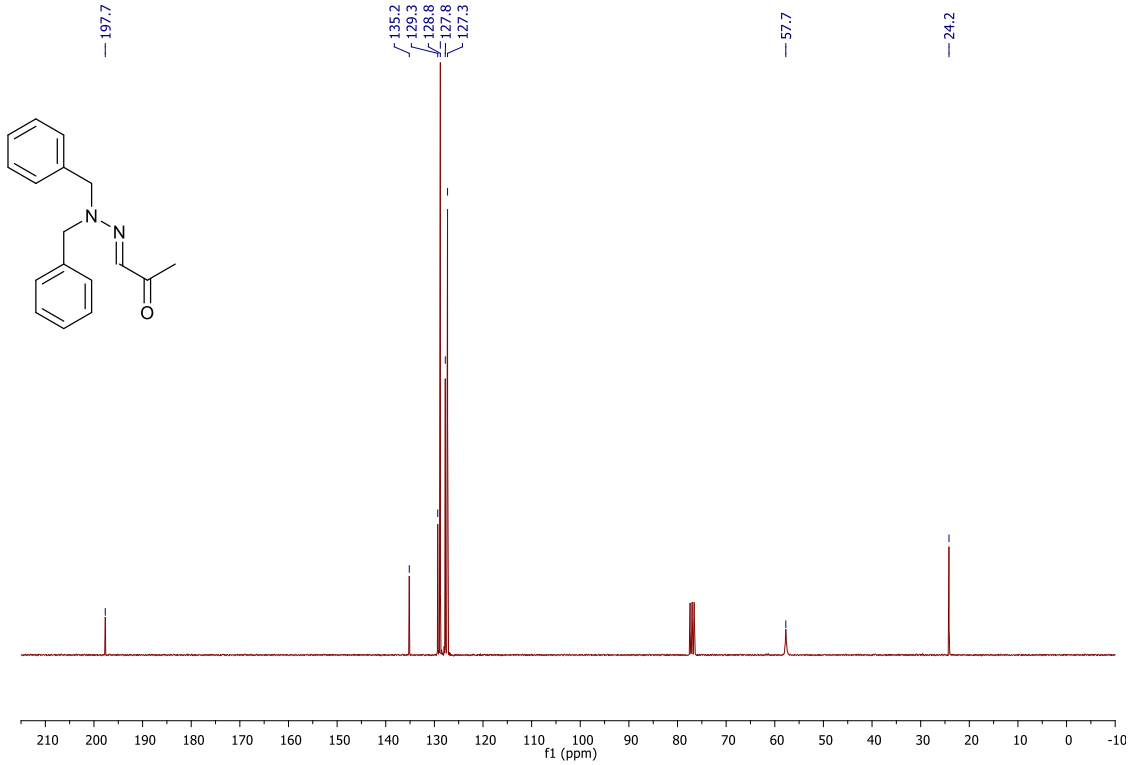
27. NMR spectra of new compounds

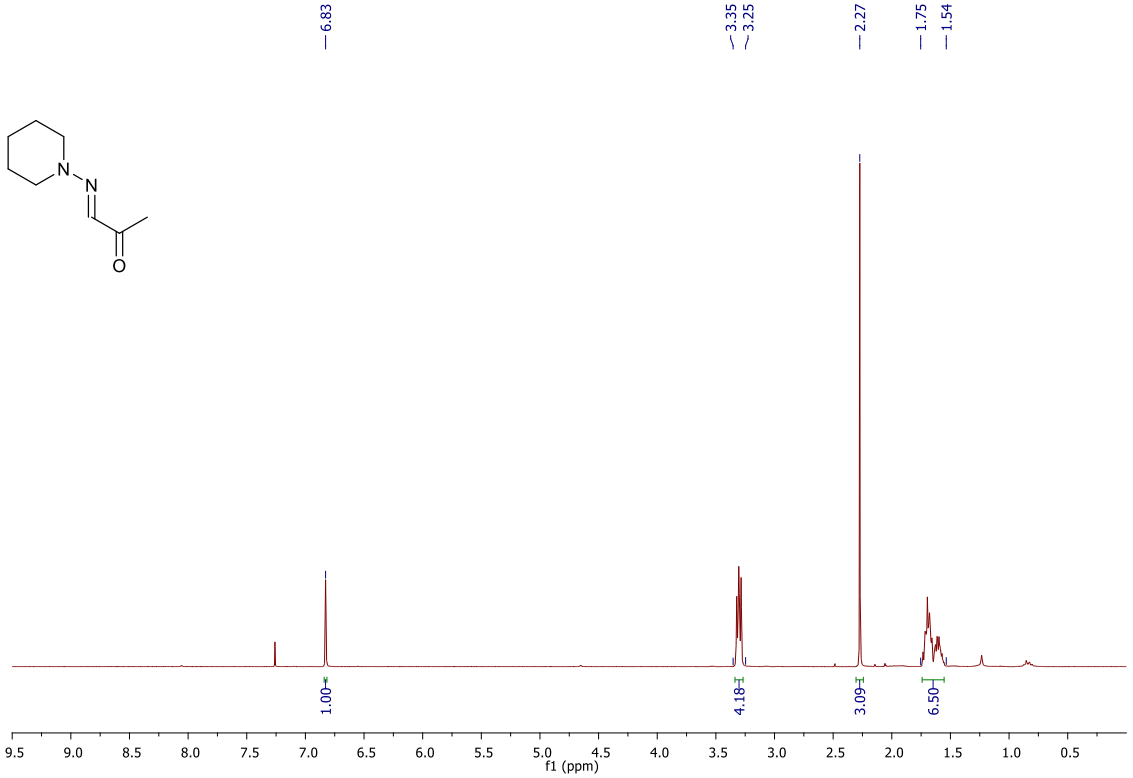
^{1}H NMR (300 MHz, $CDCl_3$) of **1B**



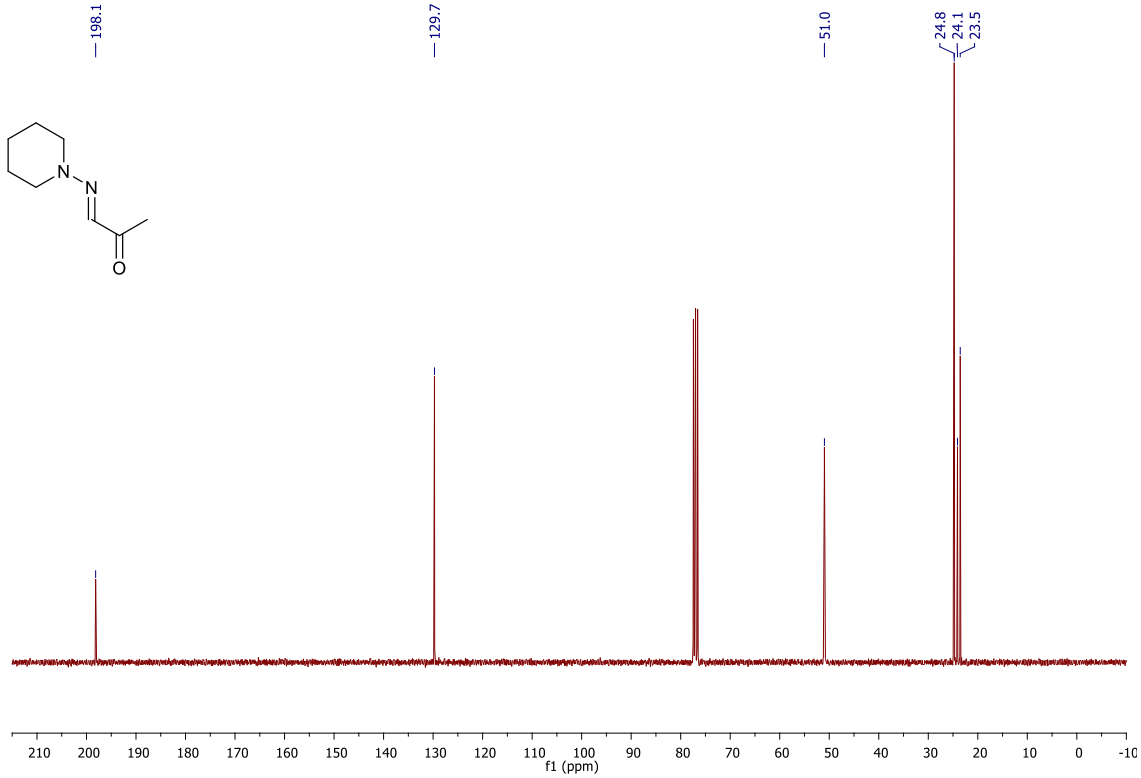
^{13}C NMR (75.5 MHz, $CDCl_3$) of **1B**



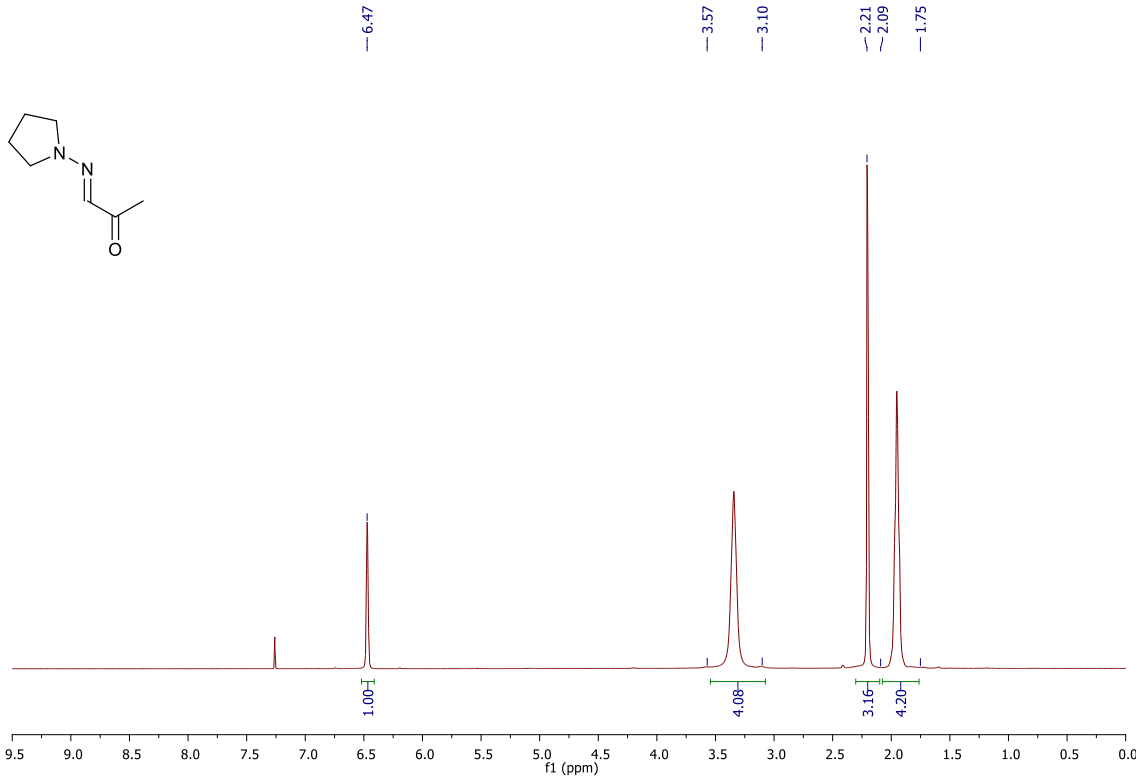
^{1}H NMR (300 MHz, $CDCl_3$) of **1C**



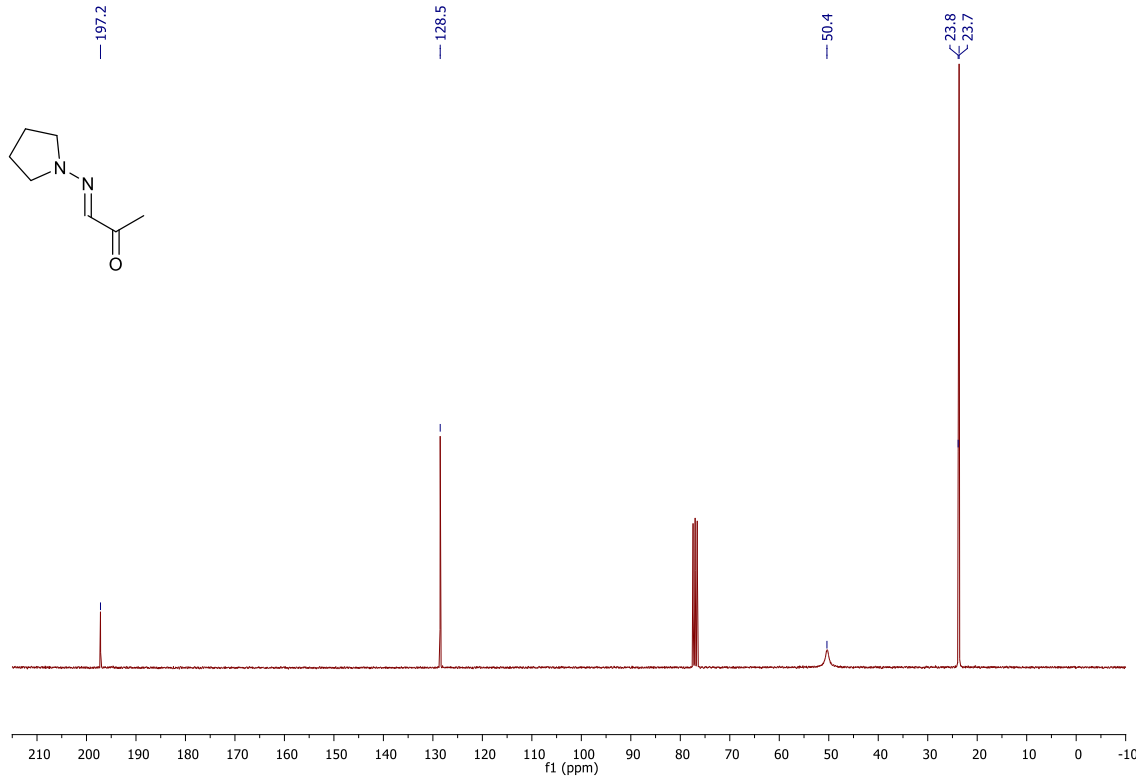
^{13}C NMR (75.5 MHz, $CDCl_3$) of **1C**



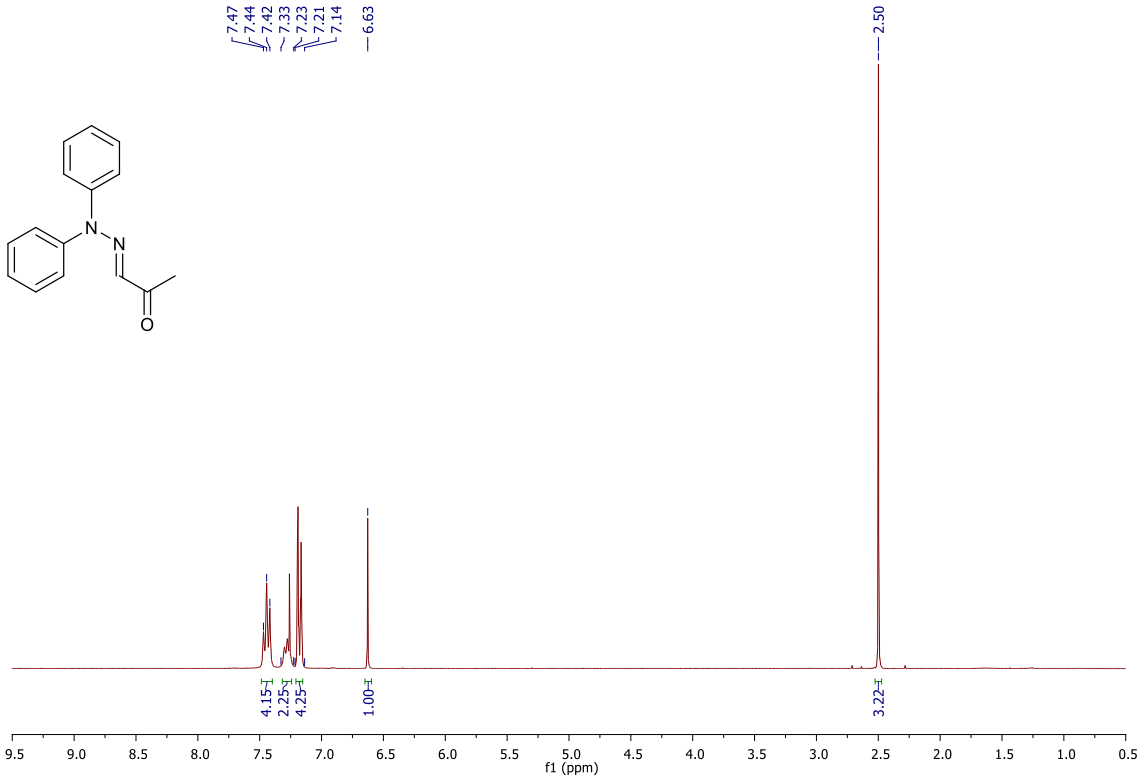
^{1}H NMR (300 MHz, $CDCl_3$) of **1A**



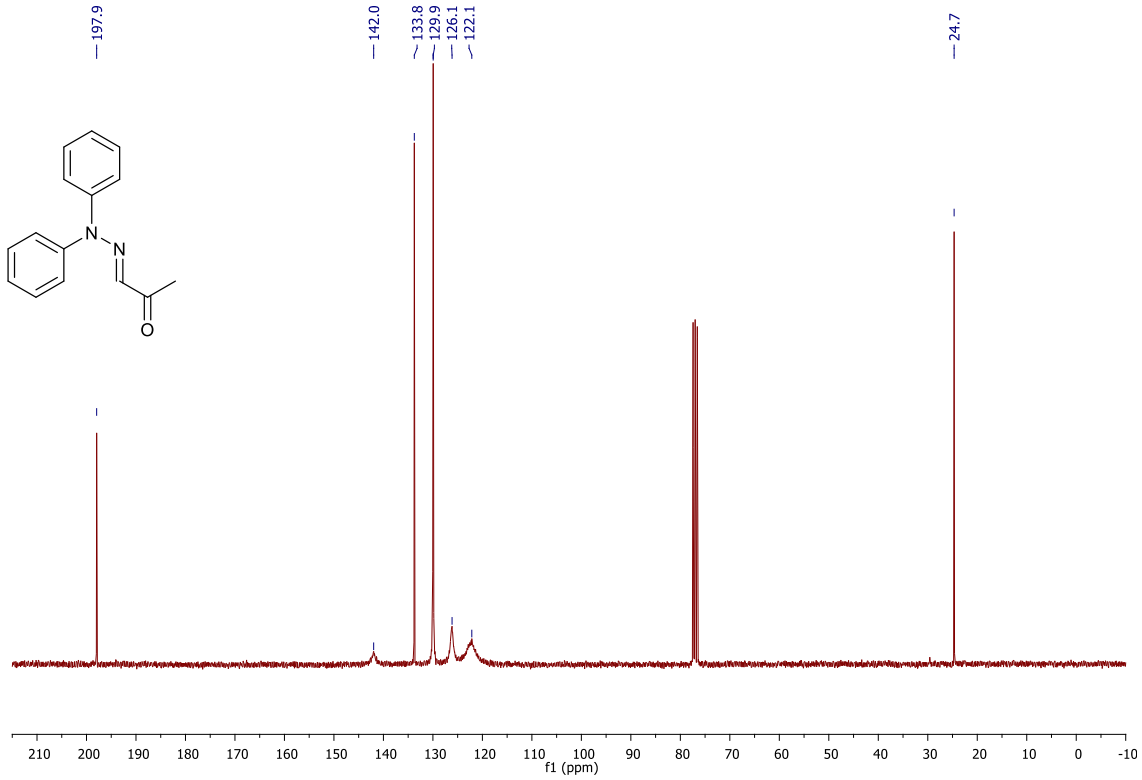
^{13}C NMR (75.5 MHz, $CDCl_3$) of **1A**



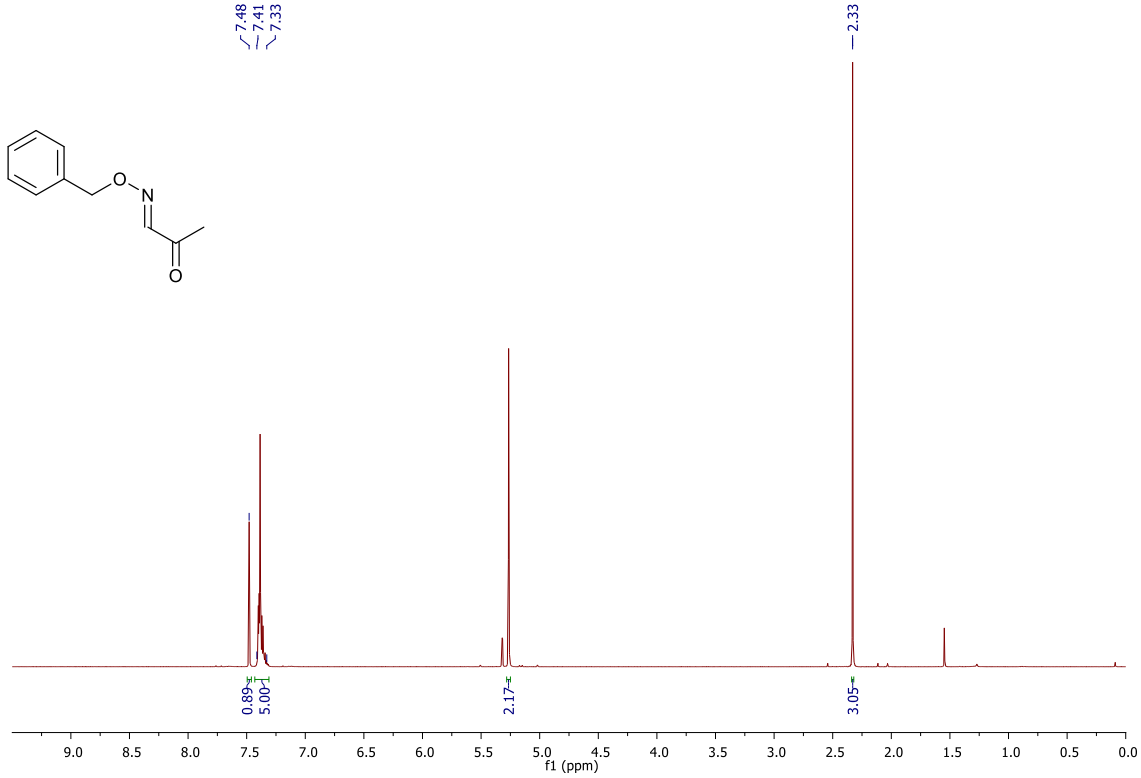
^{1}H NMR (300 MHz, $CDCl_3$) of **1D**



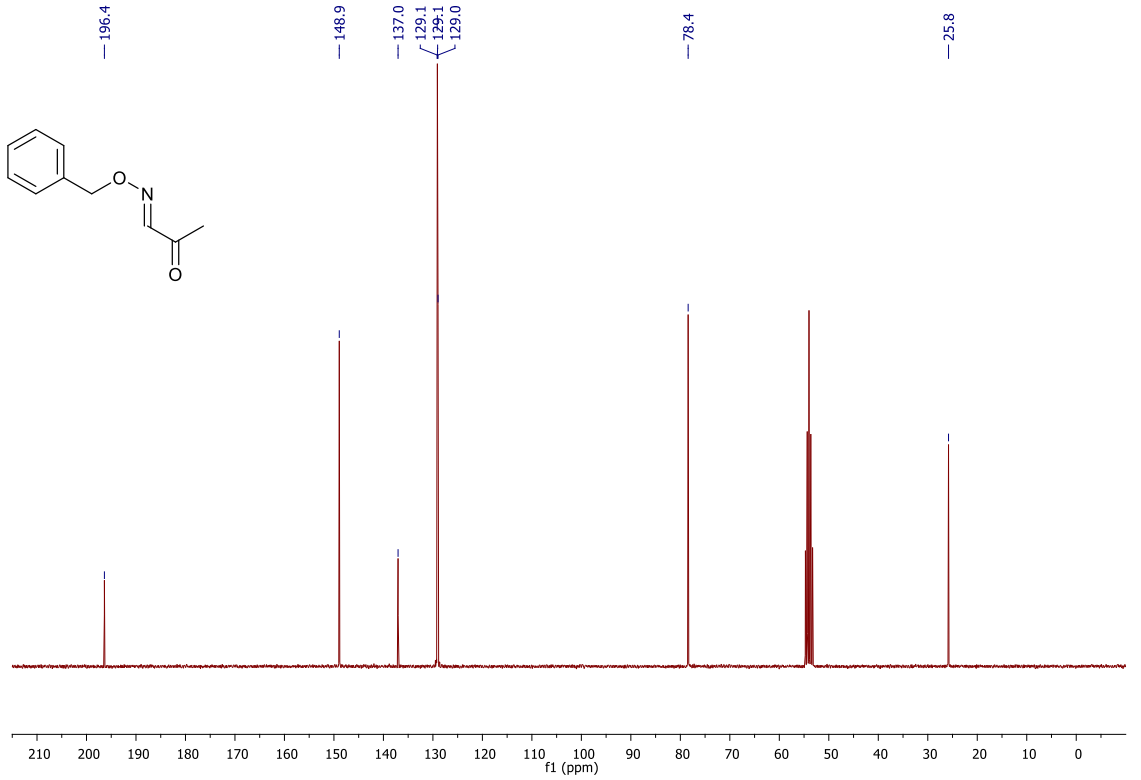
^{13}C NMR (75.5 MHz, $CDCl_3$) of **1D**



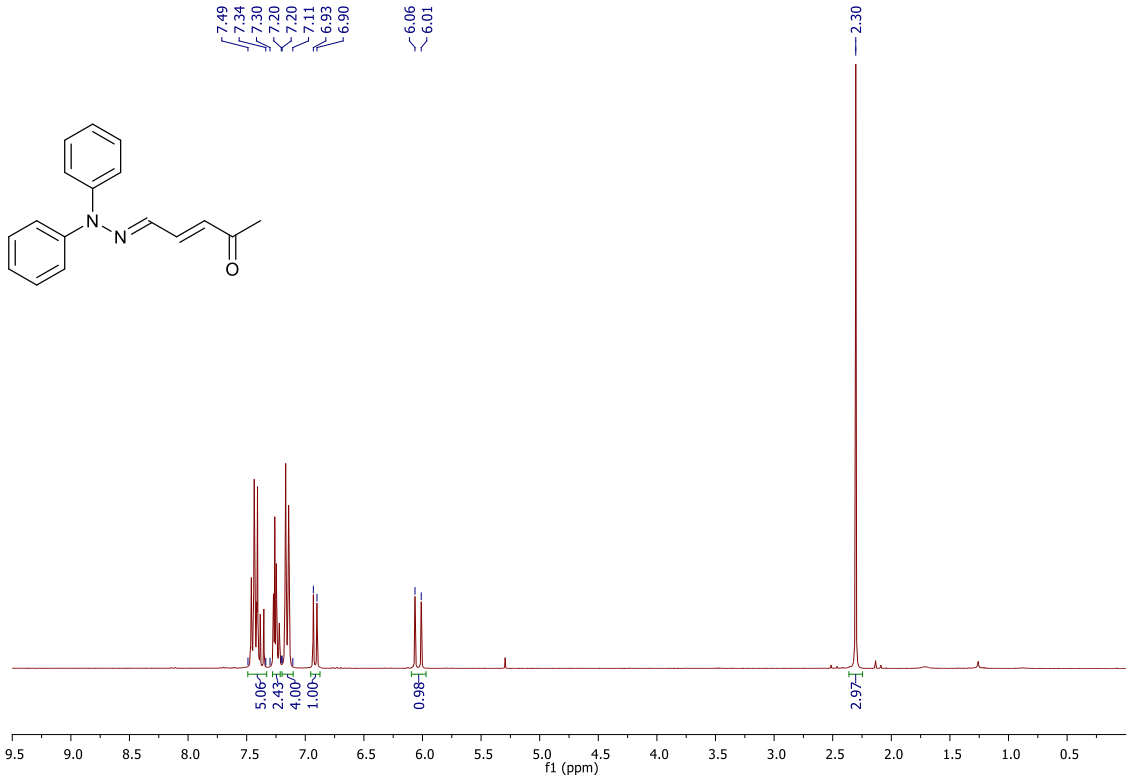
^{1}H NMR (300 MHz, CD_2Cl_2) of **4**



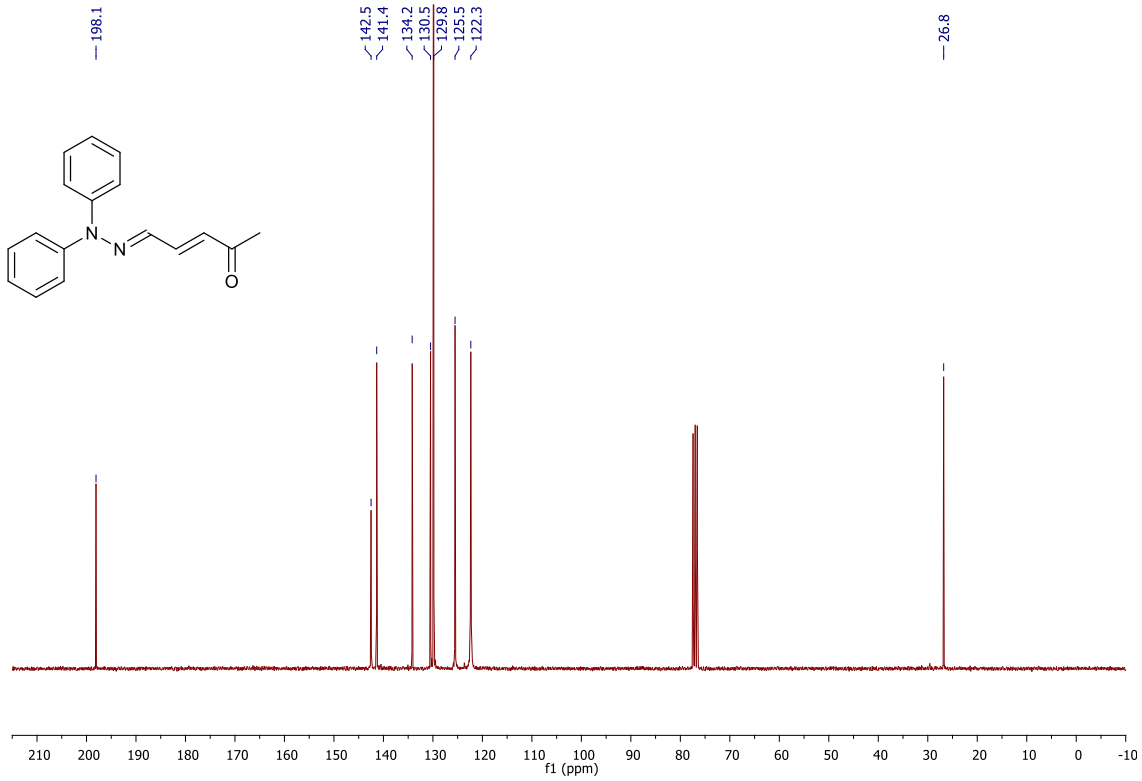
^{13}C NMR (75.5 MHz, CD_2Cl_2) of **4**



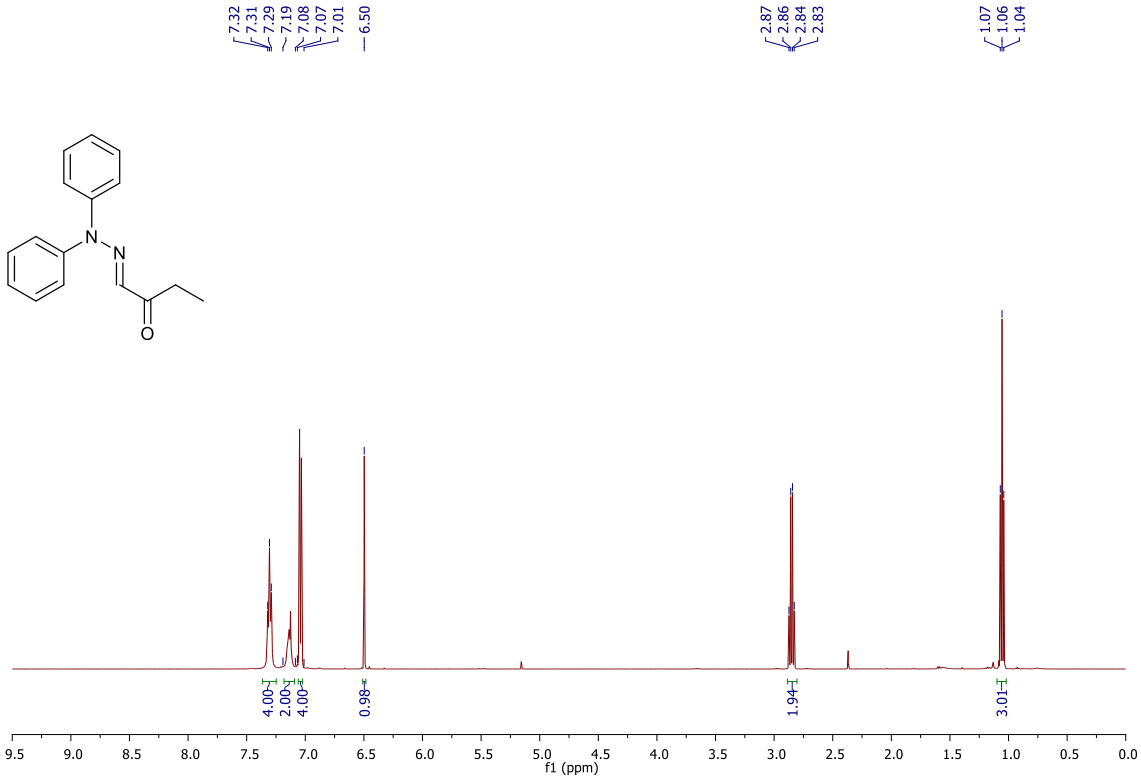
^{1}H NMR (300 MHz, $CDCl_3$) of **1E**



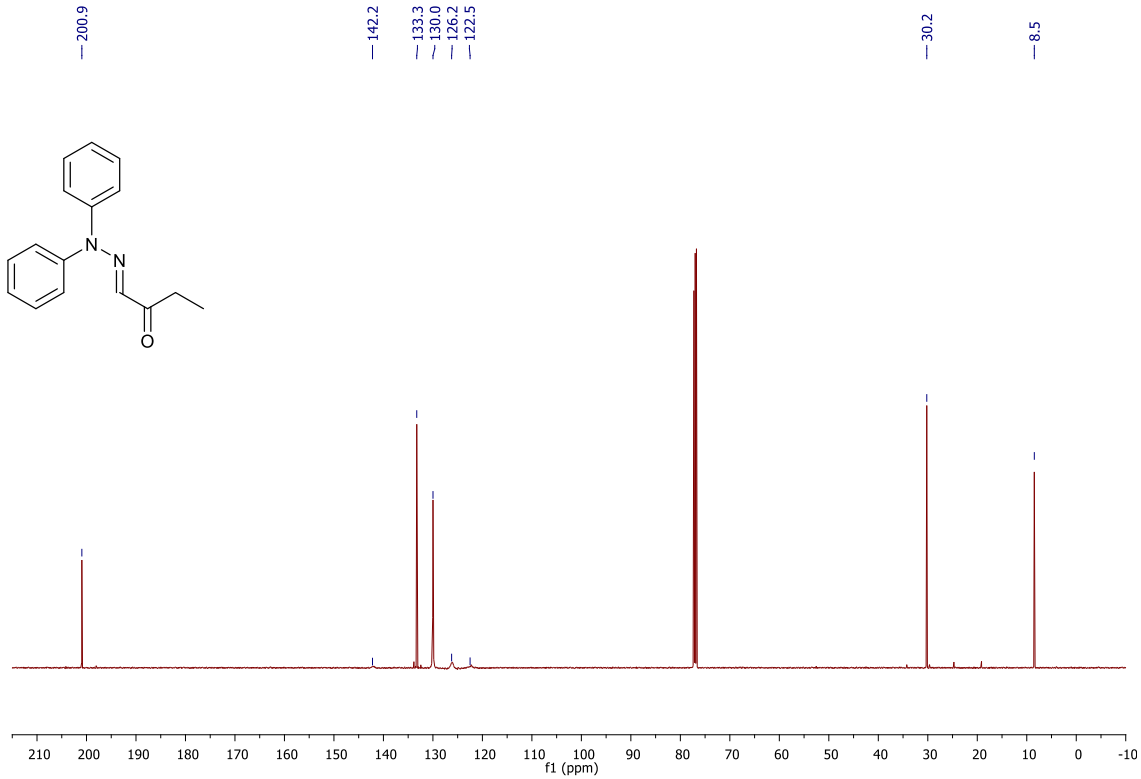
^{13}C NMR (75.5 MHz, $CDCl_3$) of **1E**



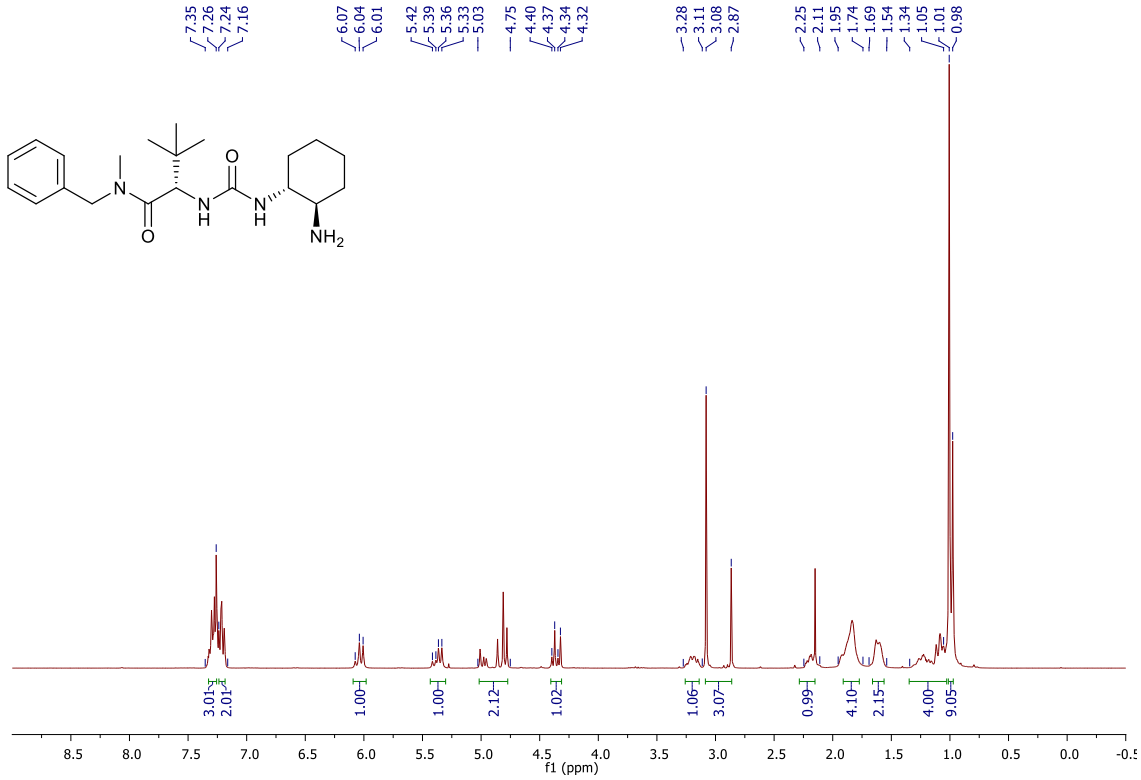
^{1}H NMR (500 MHz, $CDCl_3$) of **1F**



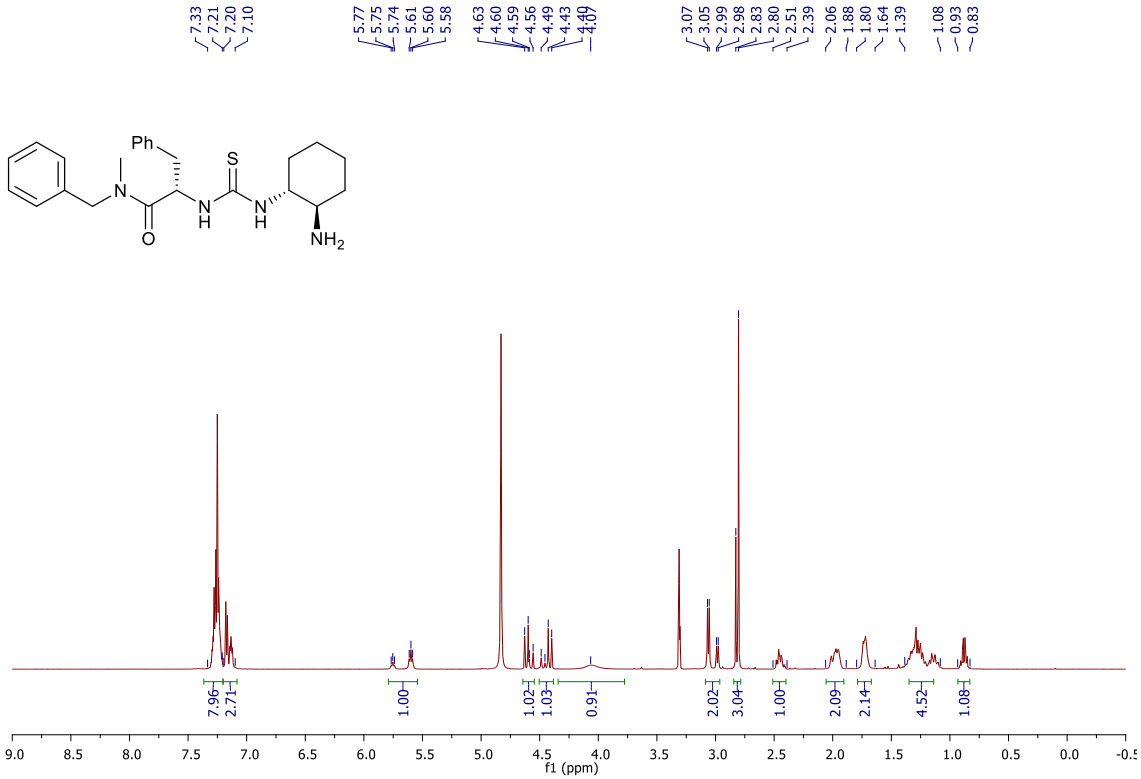
^{13}C NMR (126 MHz, $CDCl_3$) of **1F**



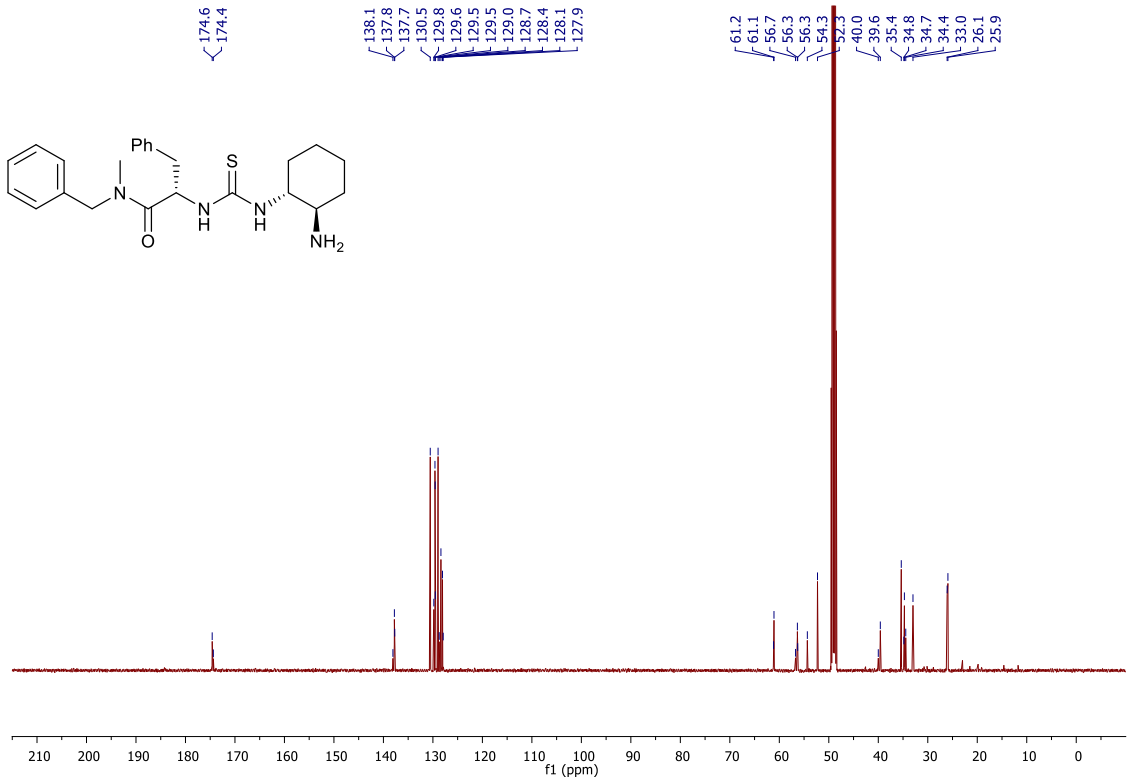
^{1}H NMR (300 MHz, $CDCl_3$) of **Ib**



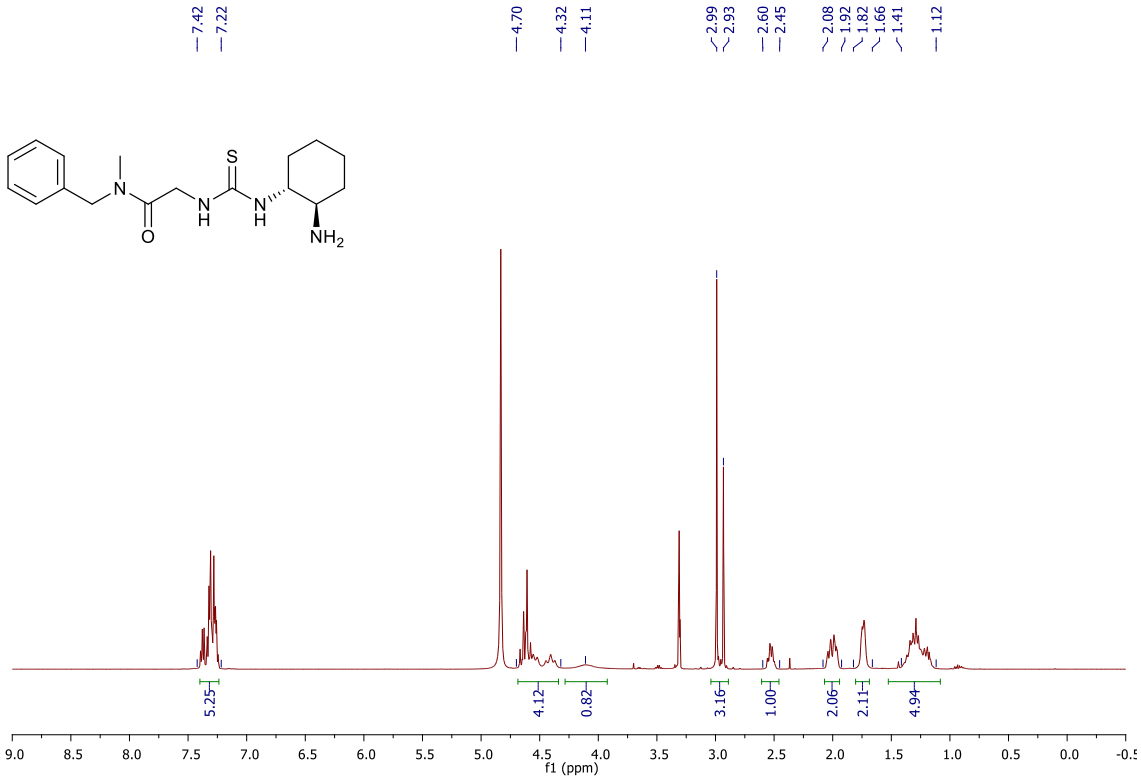
^{1}H NMR (500 MHz, CD_3OD) of **II**



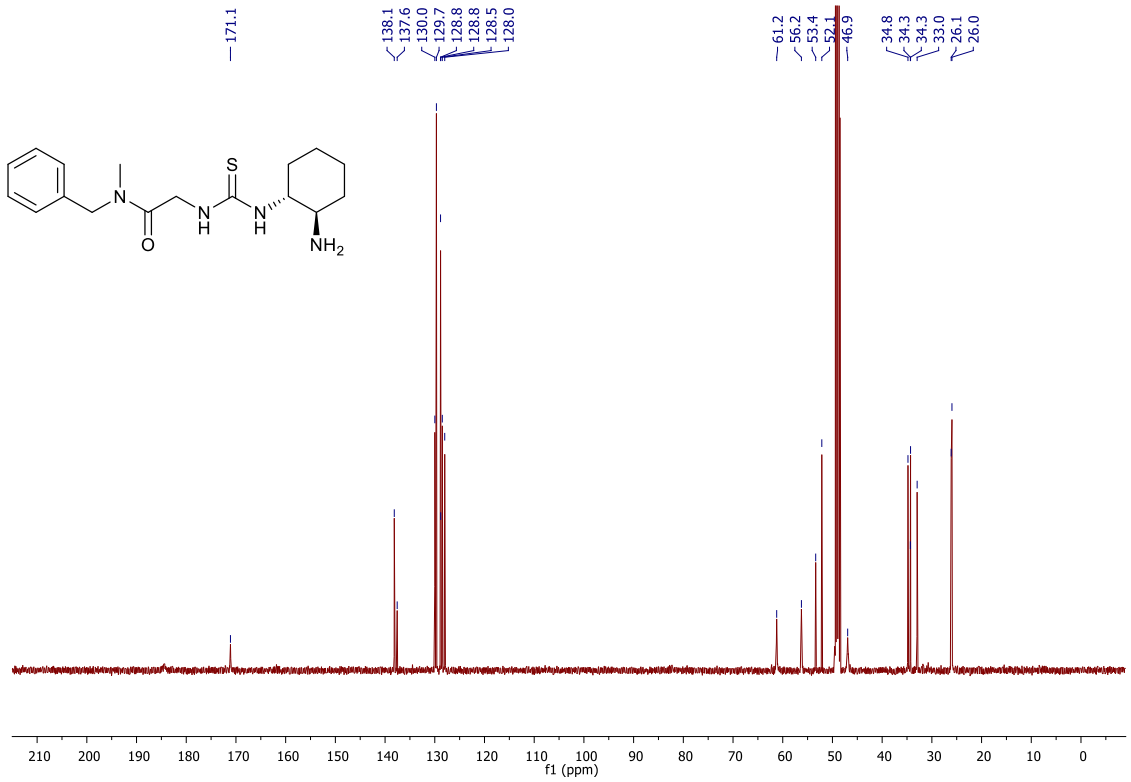
^{13}C NMR (126 MHz, CD_3OD) of **II**



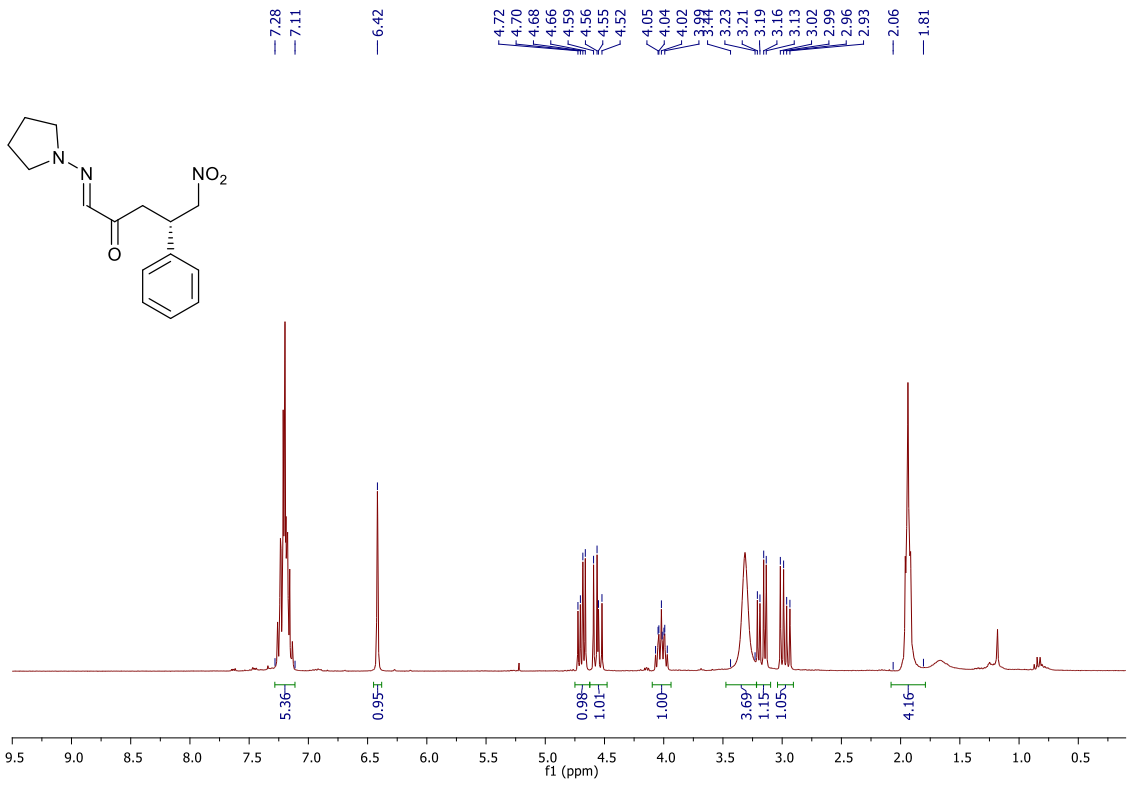
^{1}H NMR (500 MHz, CD_3OD) of **III**



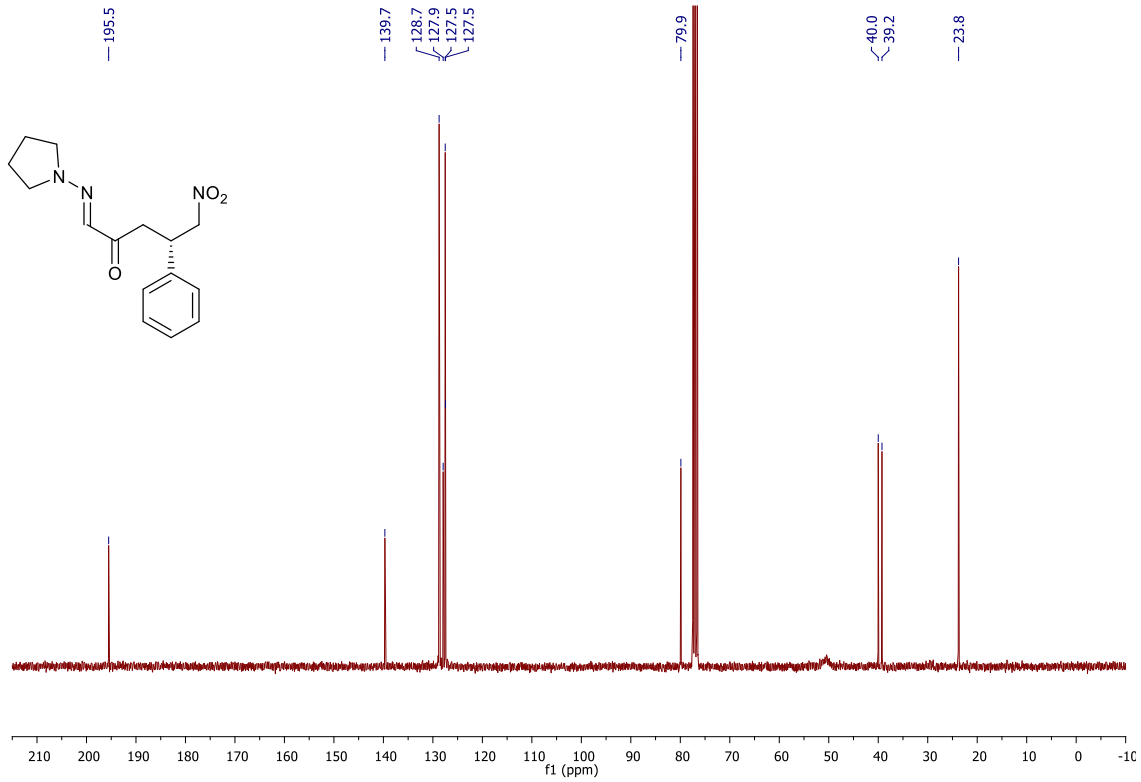
^{13}C NMR (126 MHz, CD_3OD) of **III**



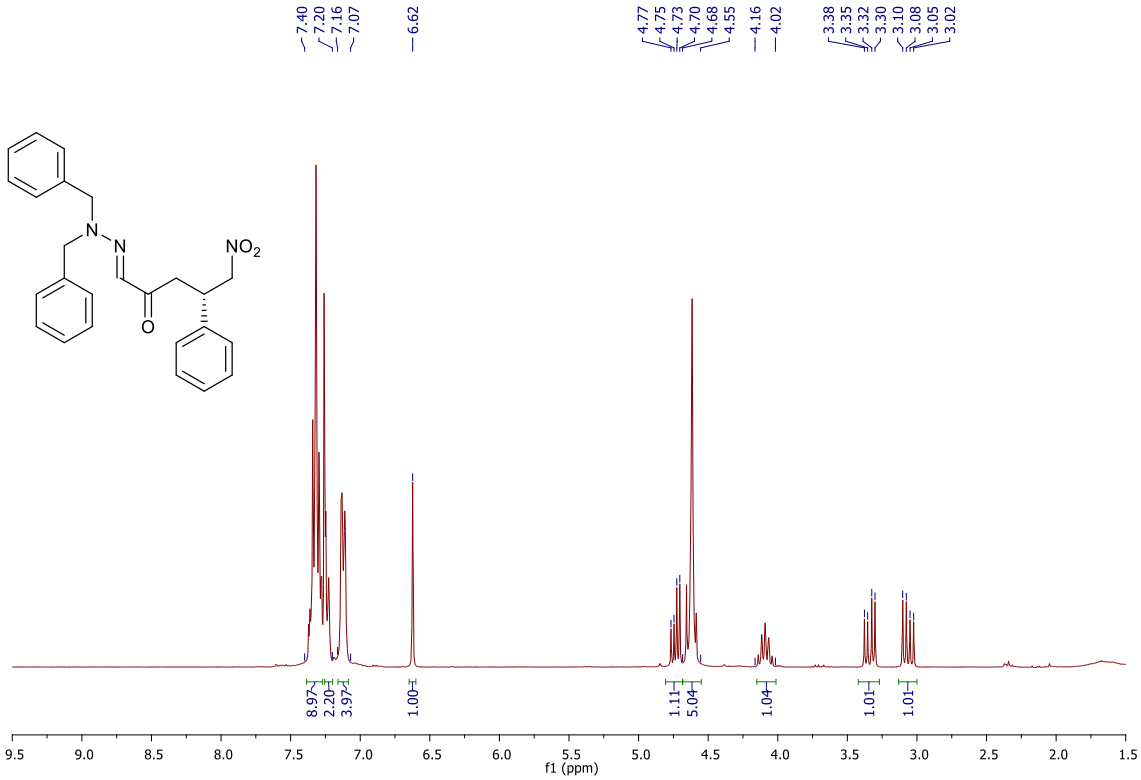
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Aa**



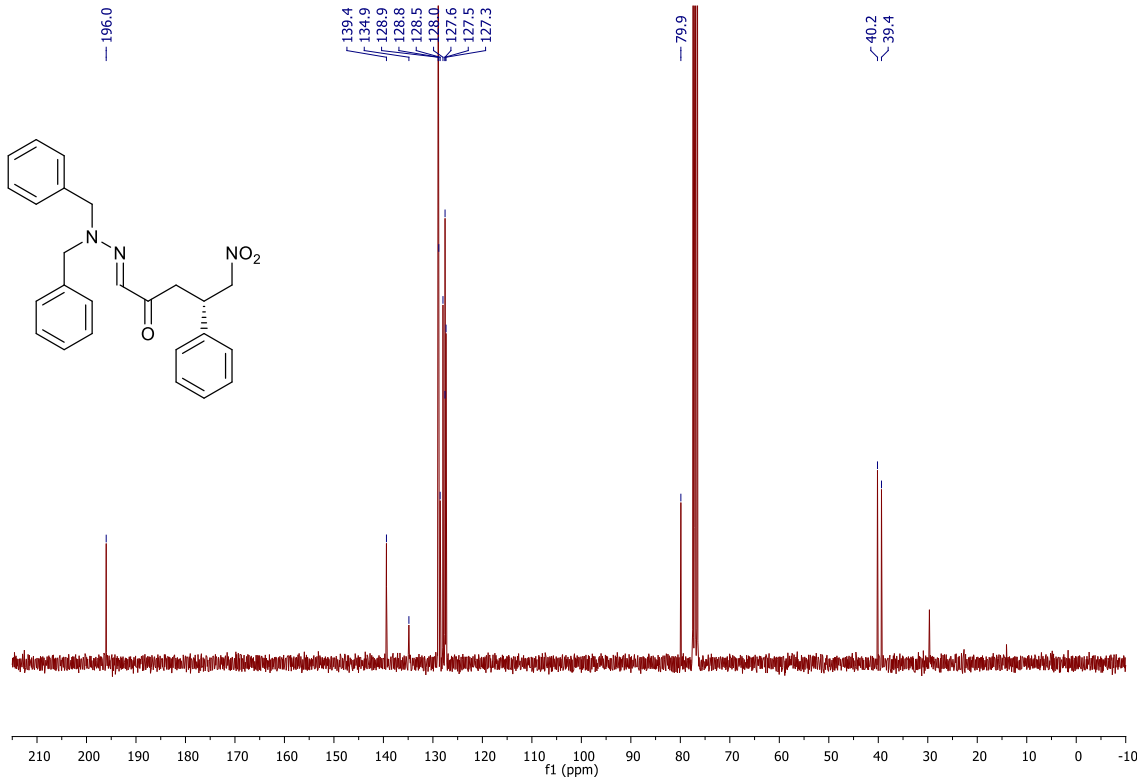
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Aa**



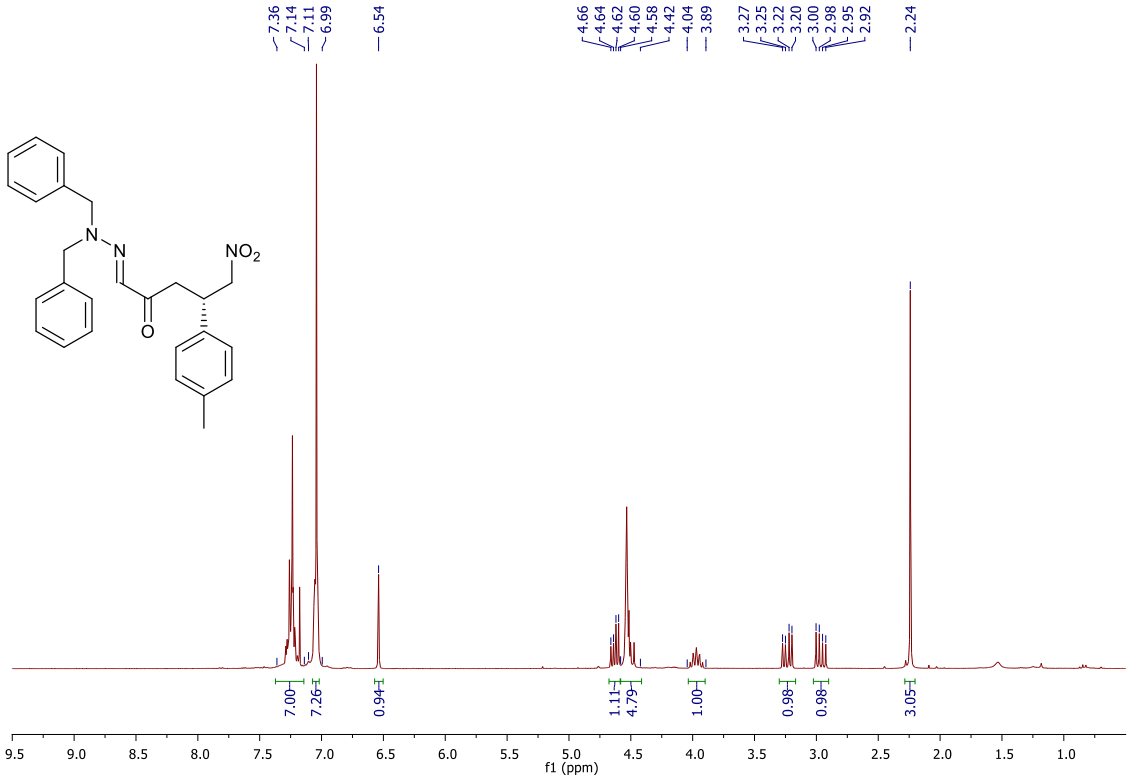
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Ba**



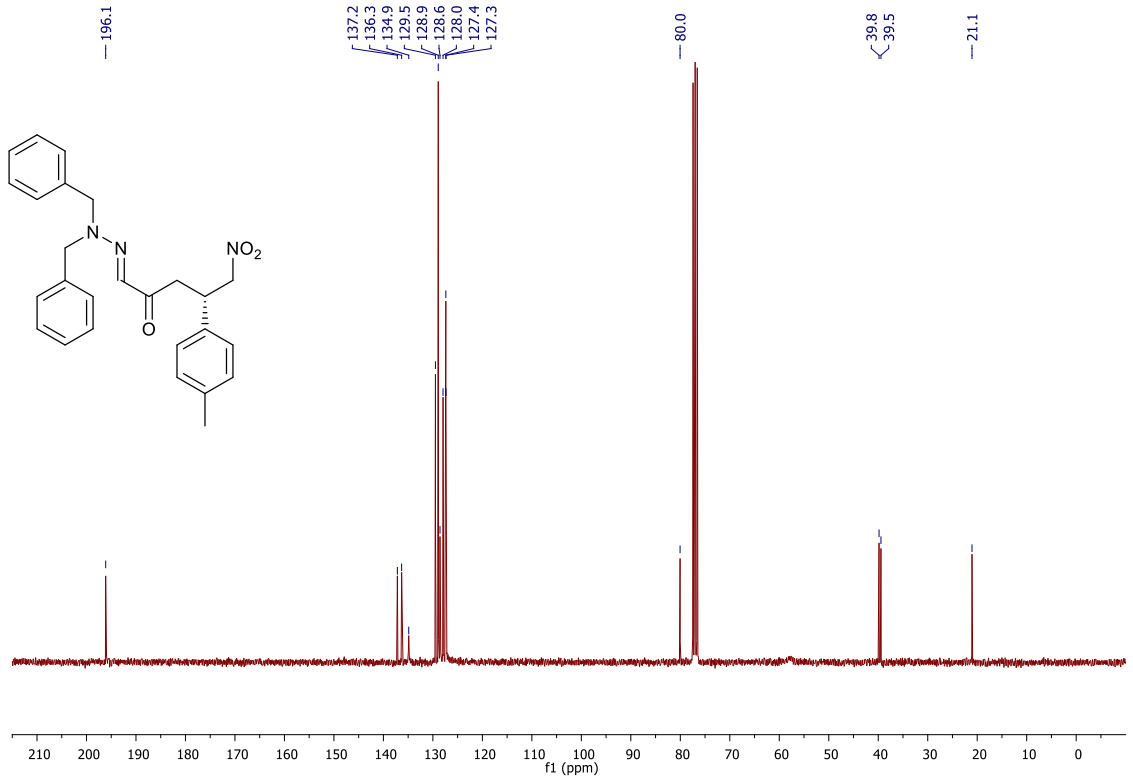
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Ba**



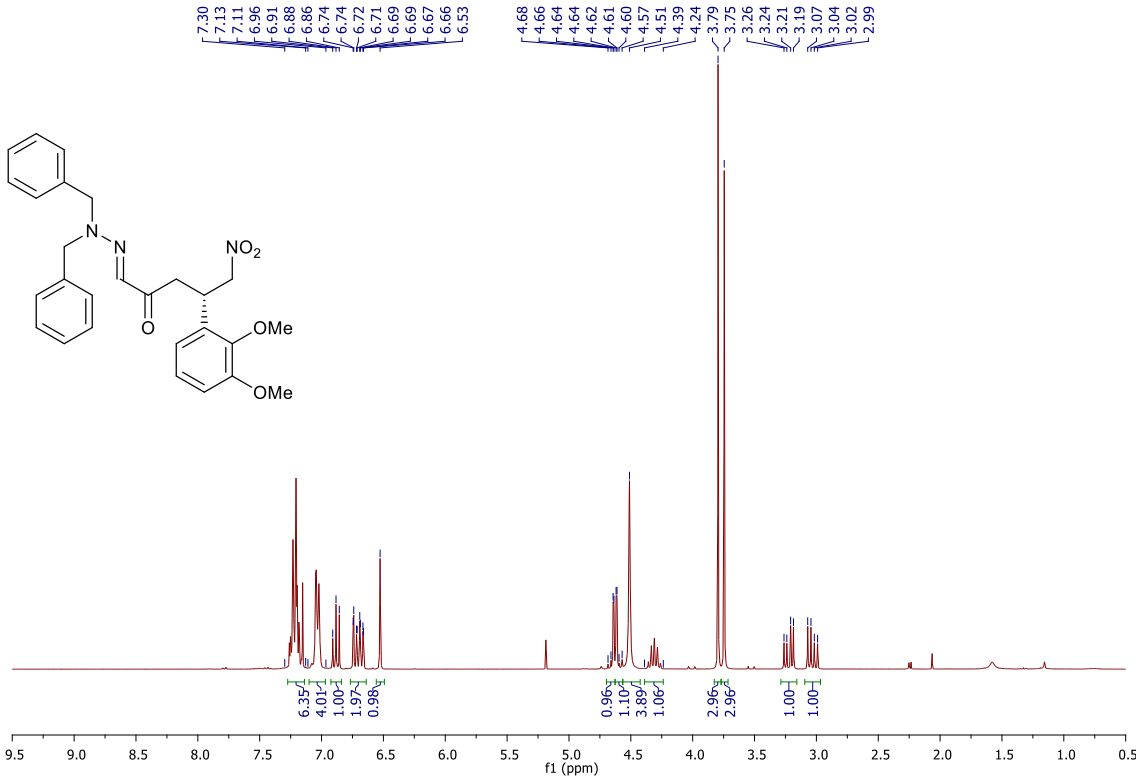
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Bb**



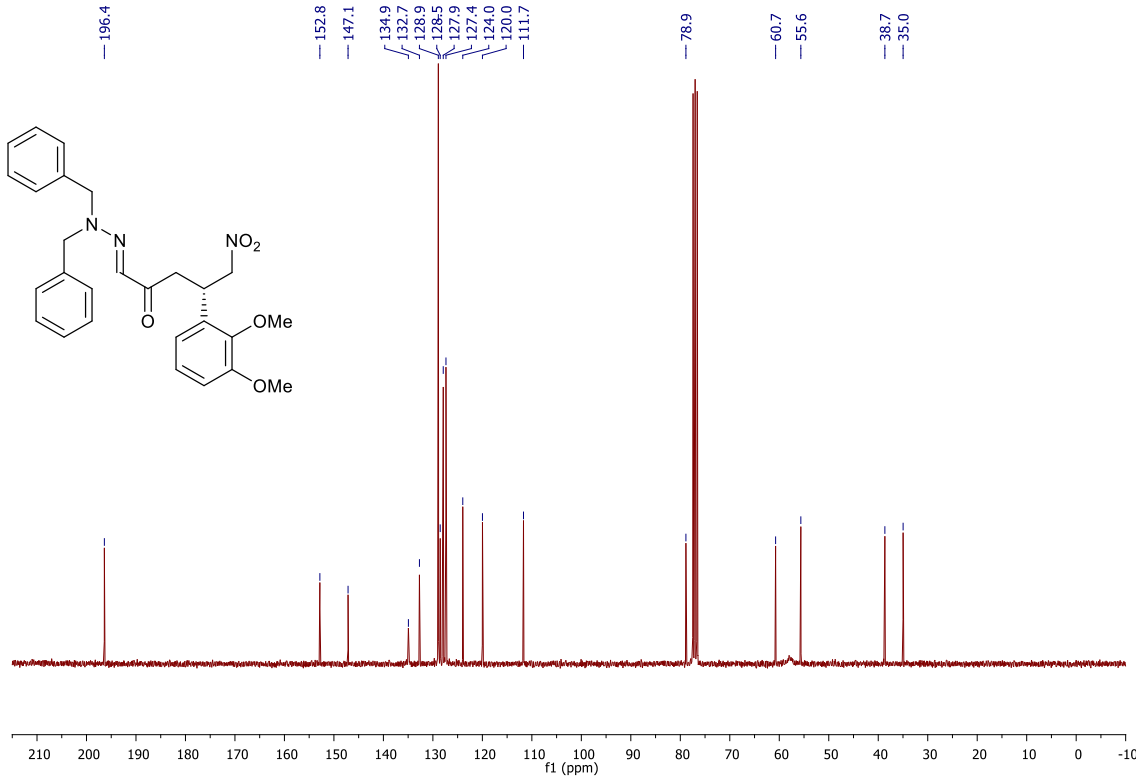
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Bb**



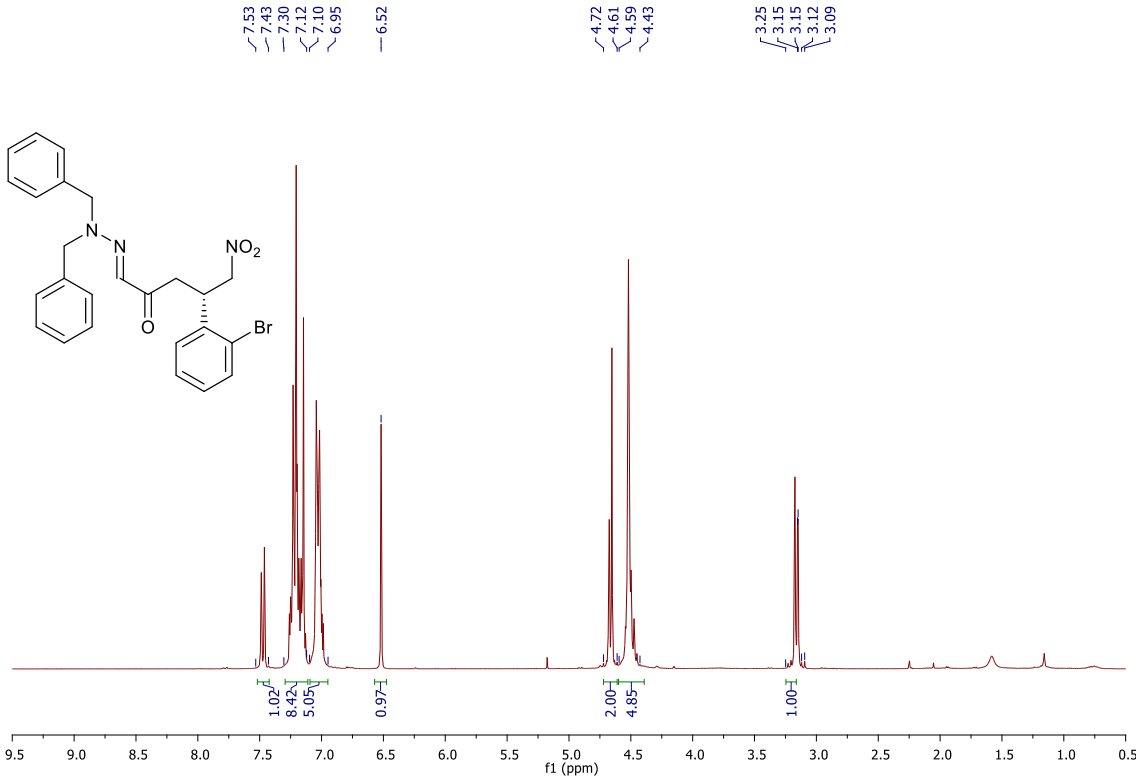
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Bc**



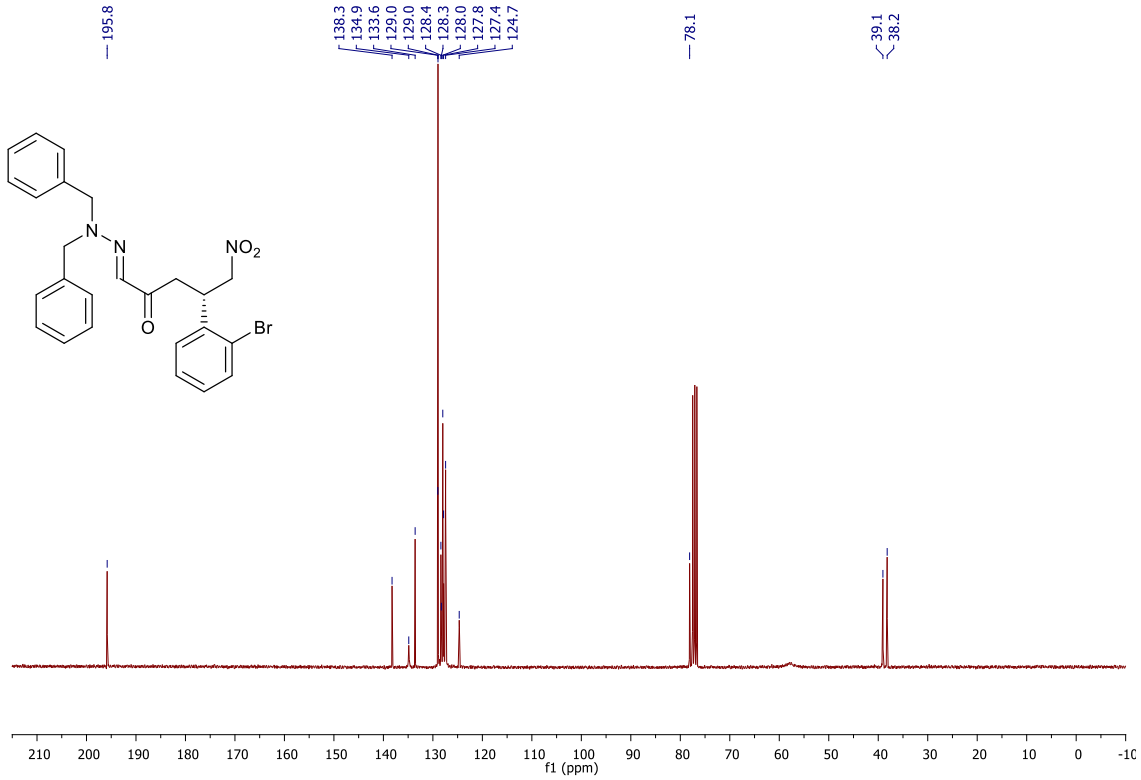
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Bc**



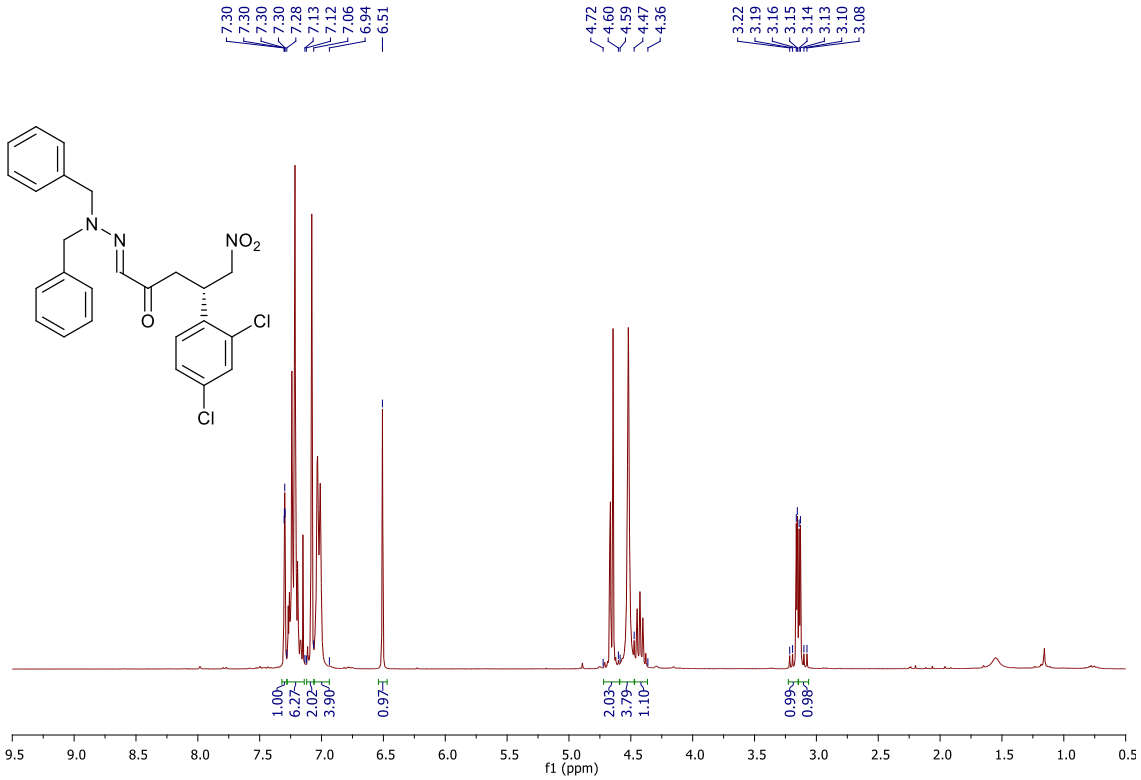
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Bd**



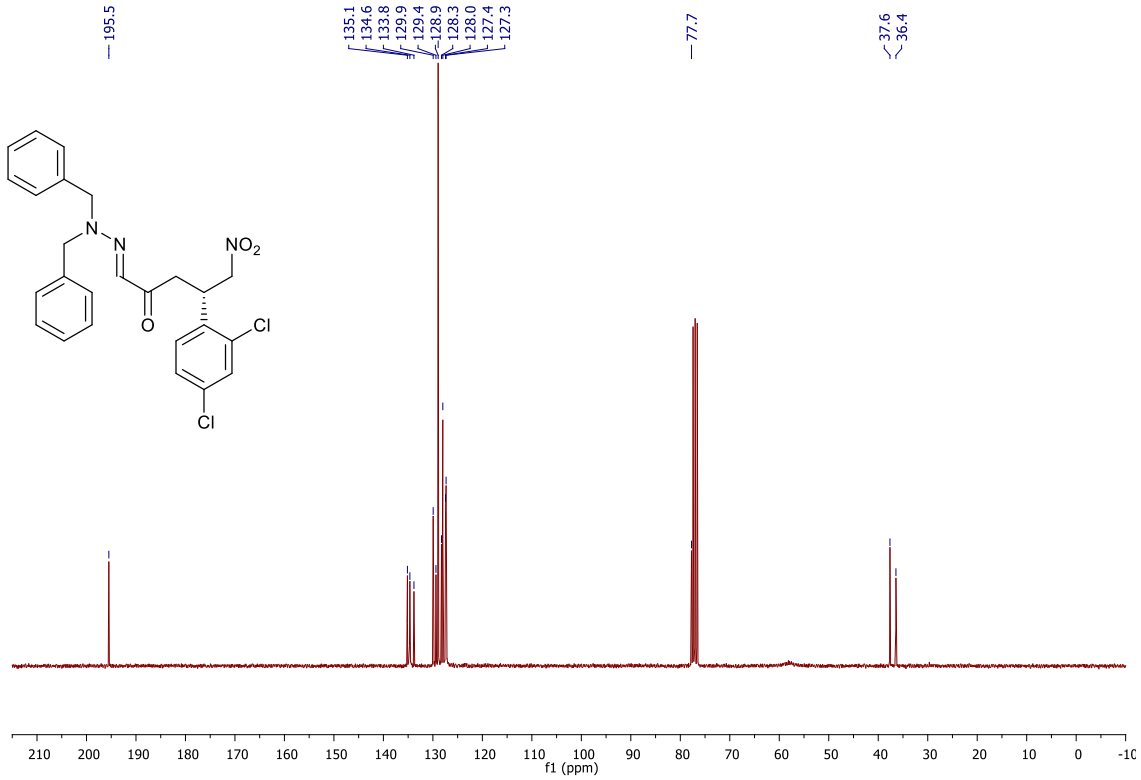
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Bd**



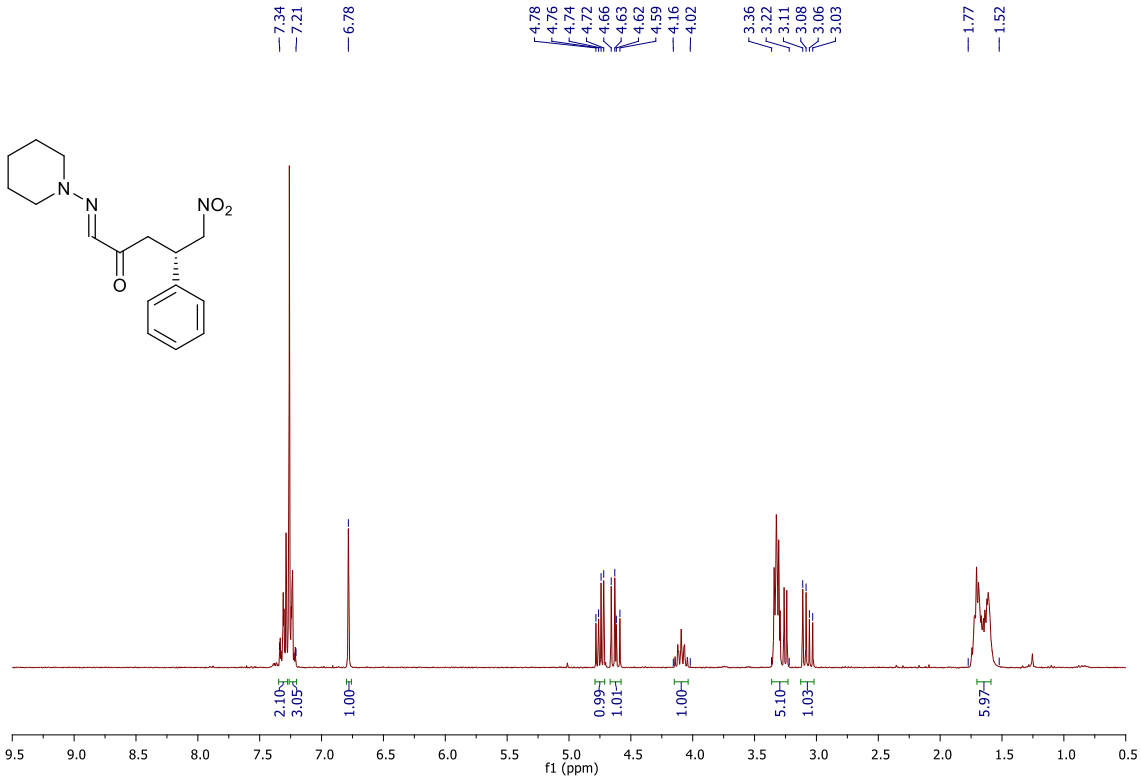
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Bf**



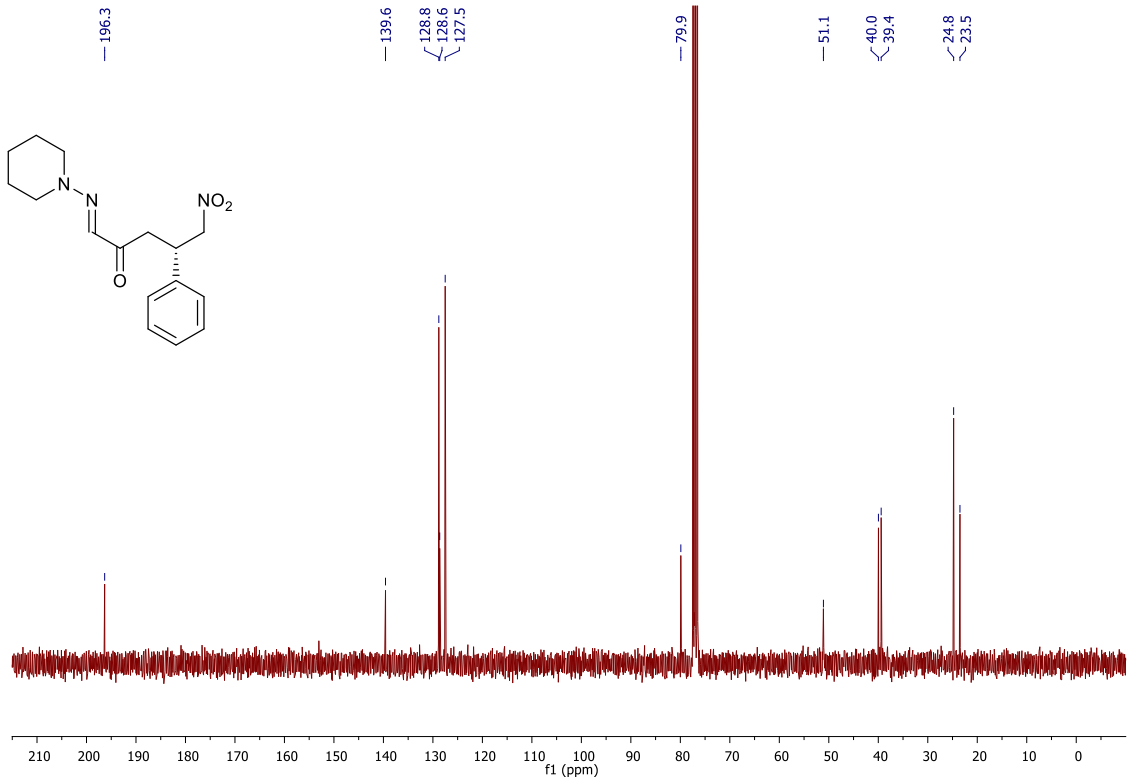
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Bf**



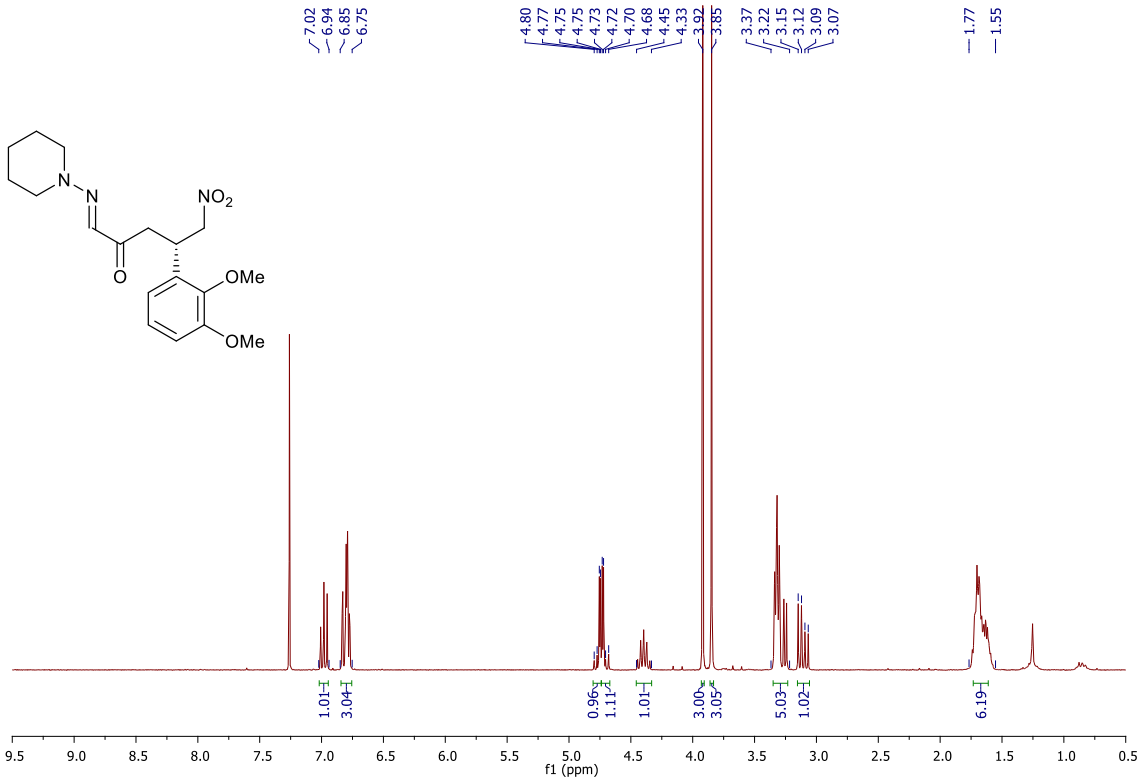
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Ca**



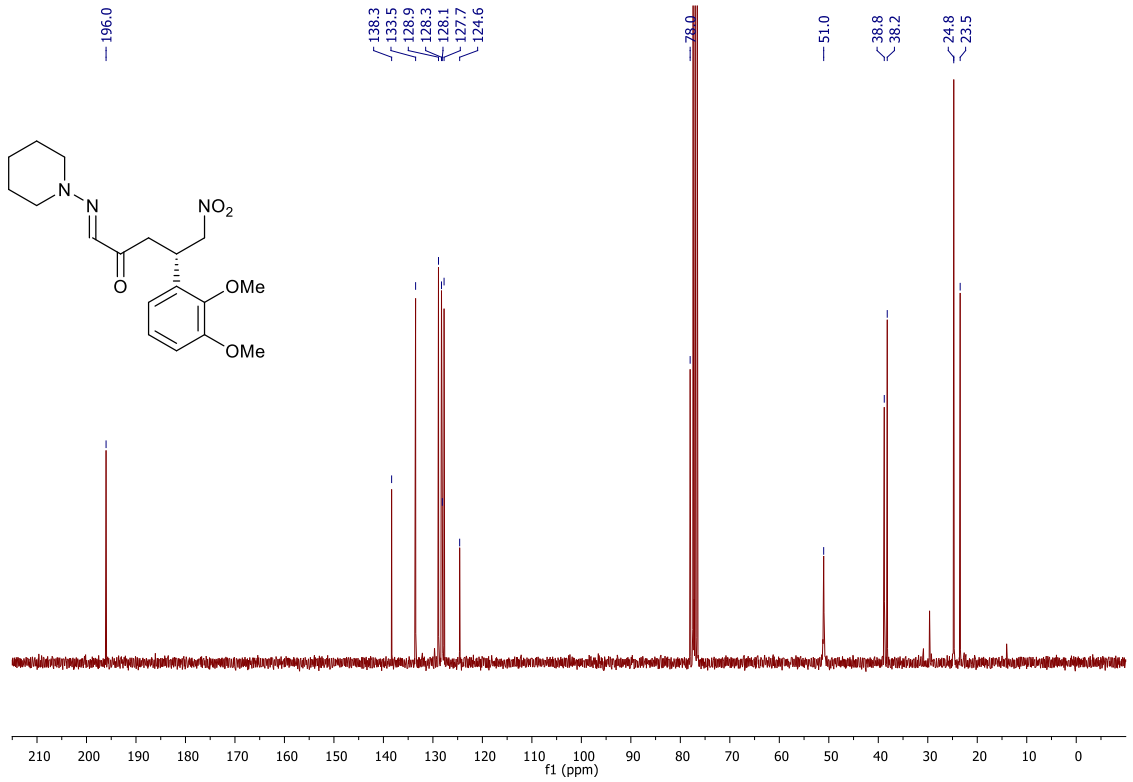
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Ca**



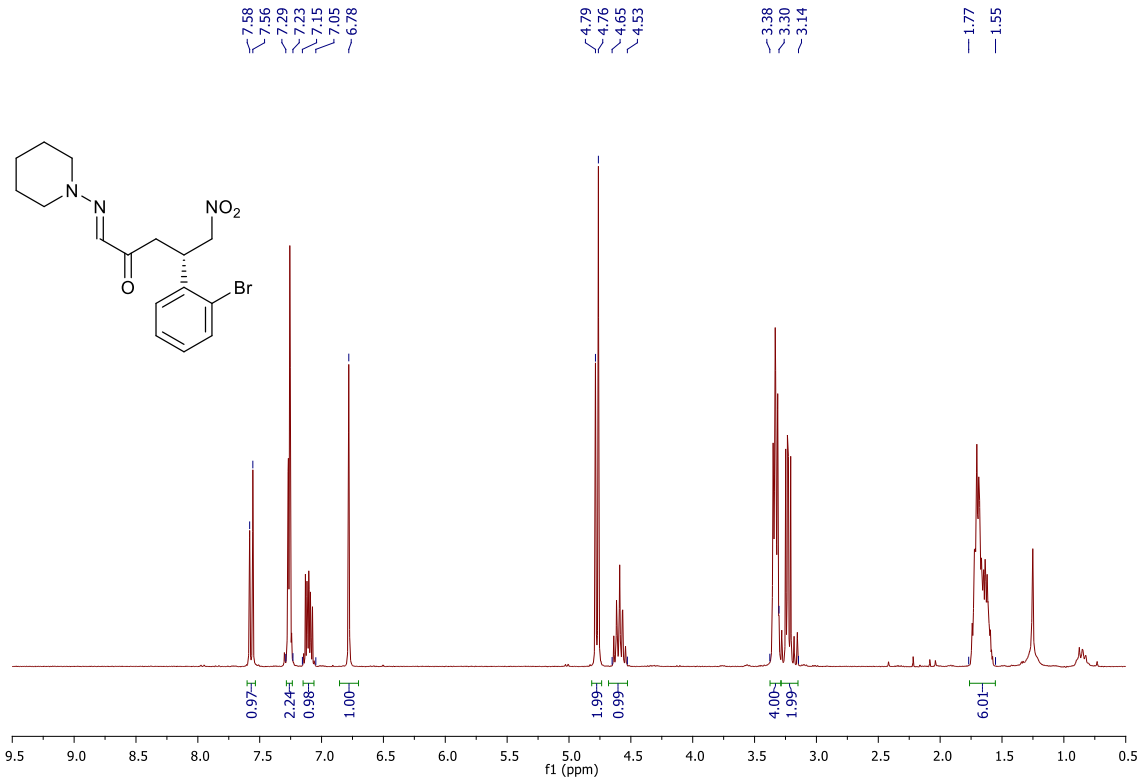
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Cc**



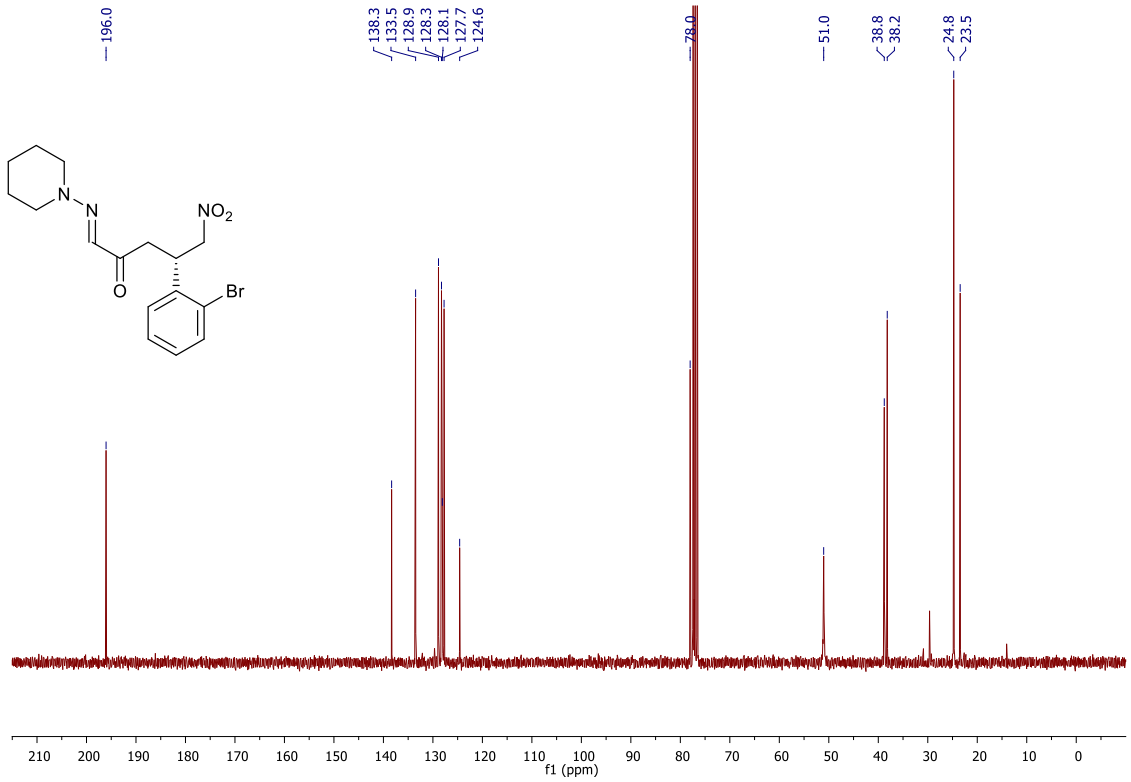
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Cc**



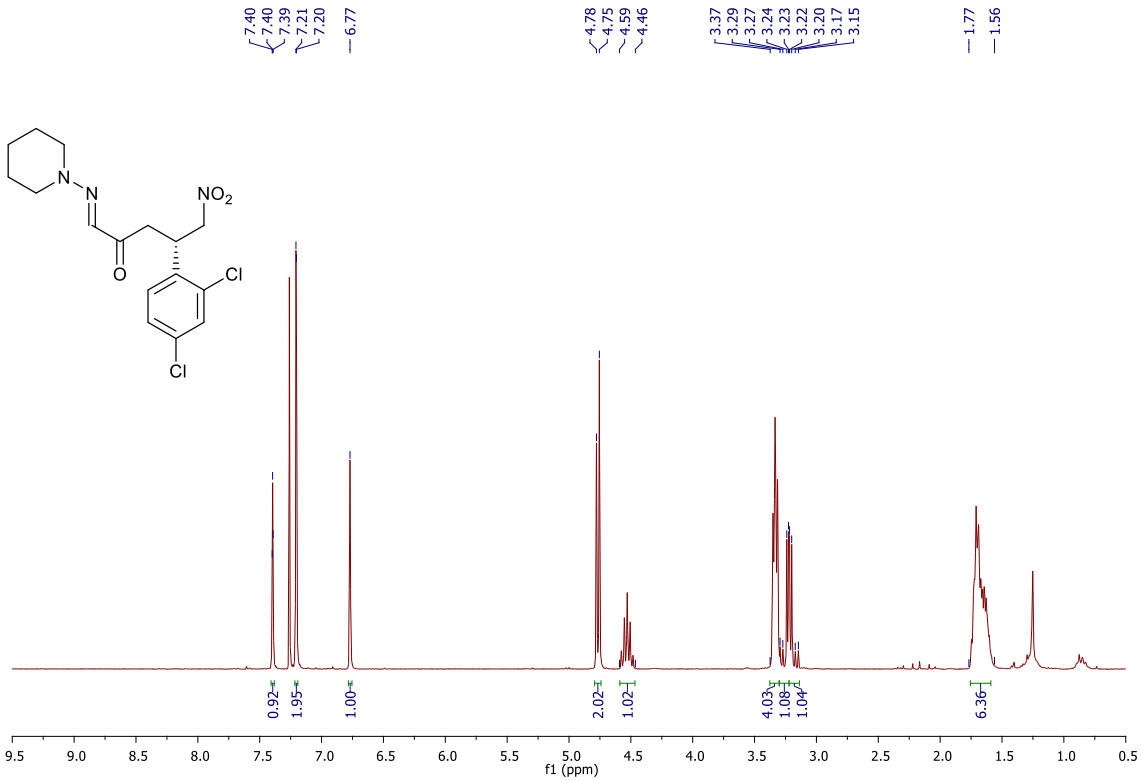
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Cd**



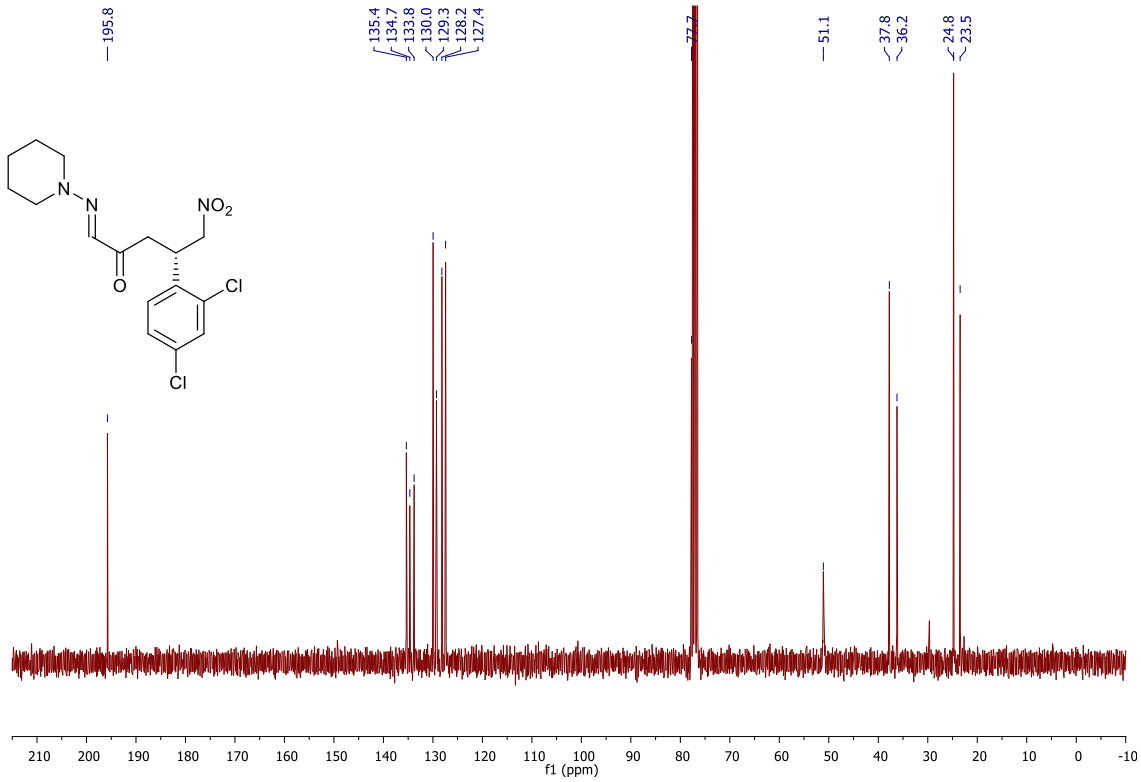
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Cd**



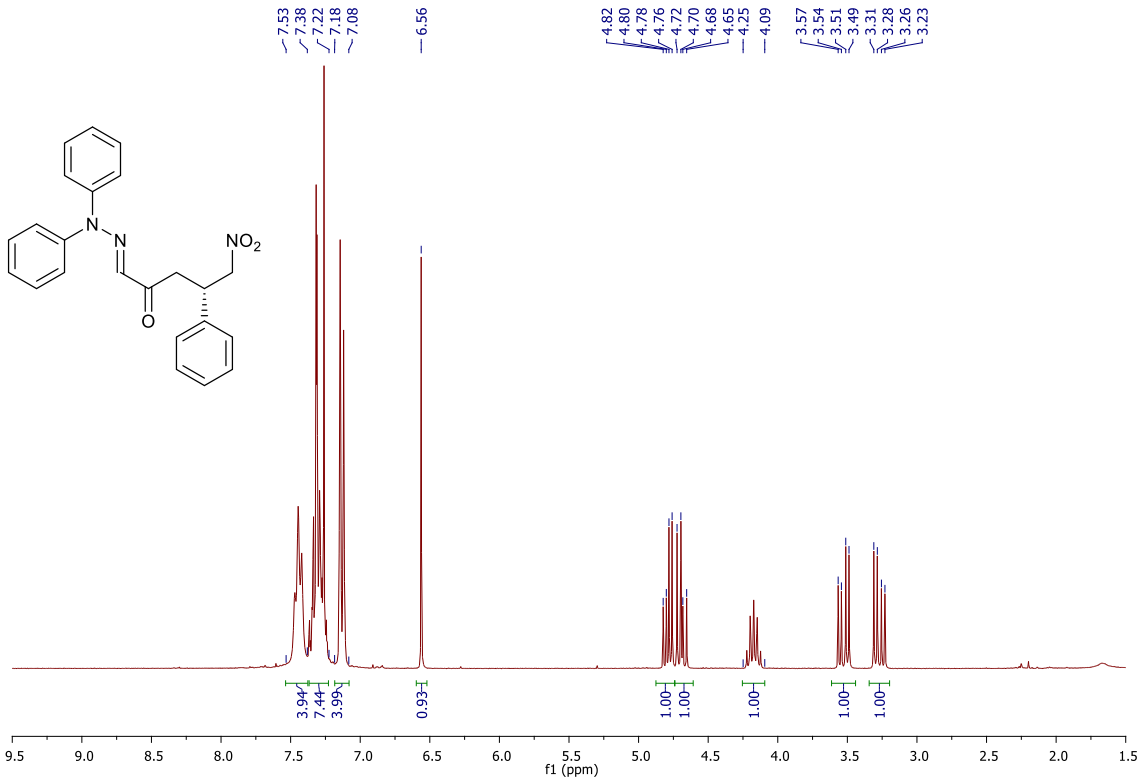
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Cf**



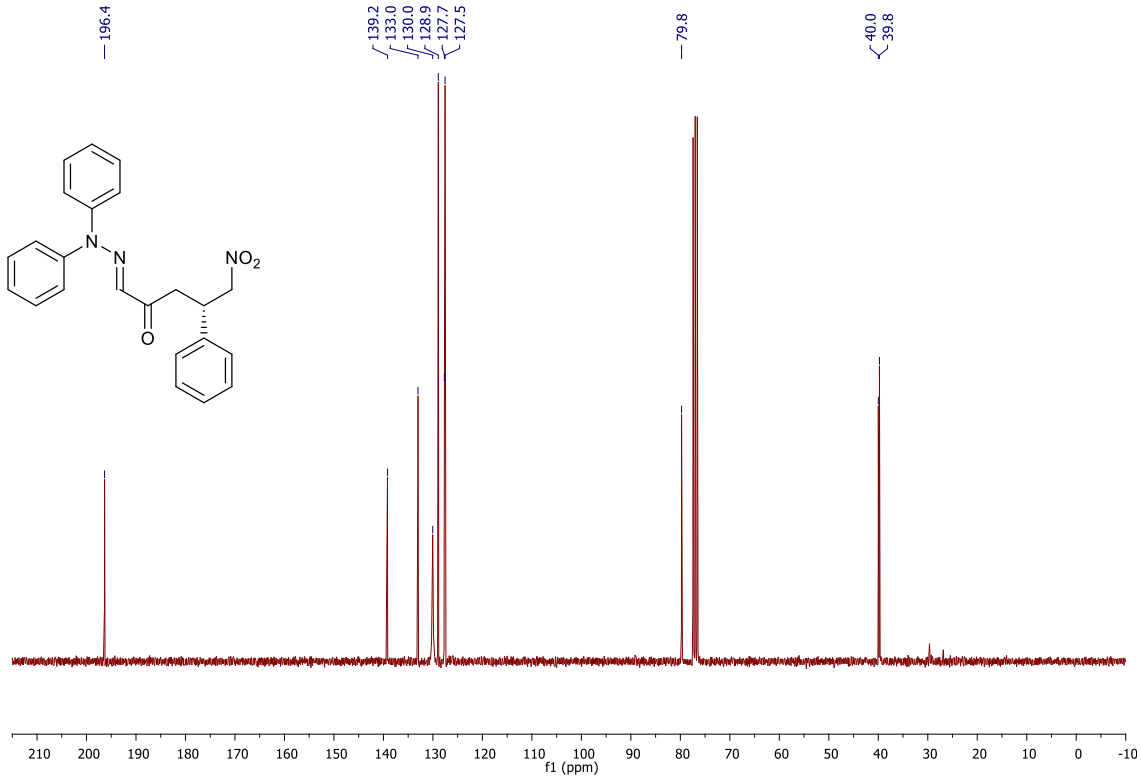
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Cf**



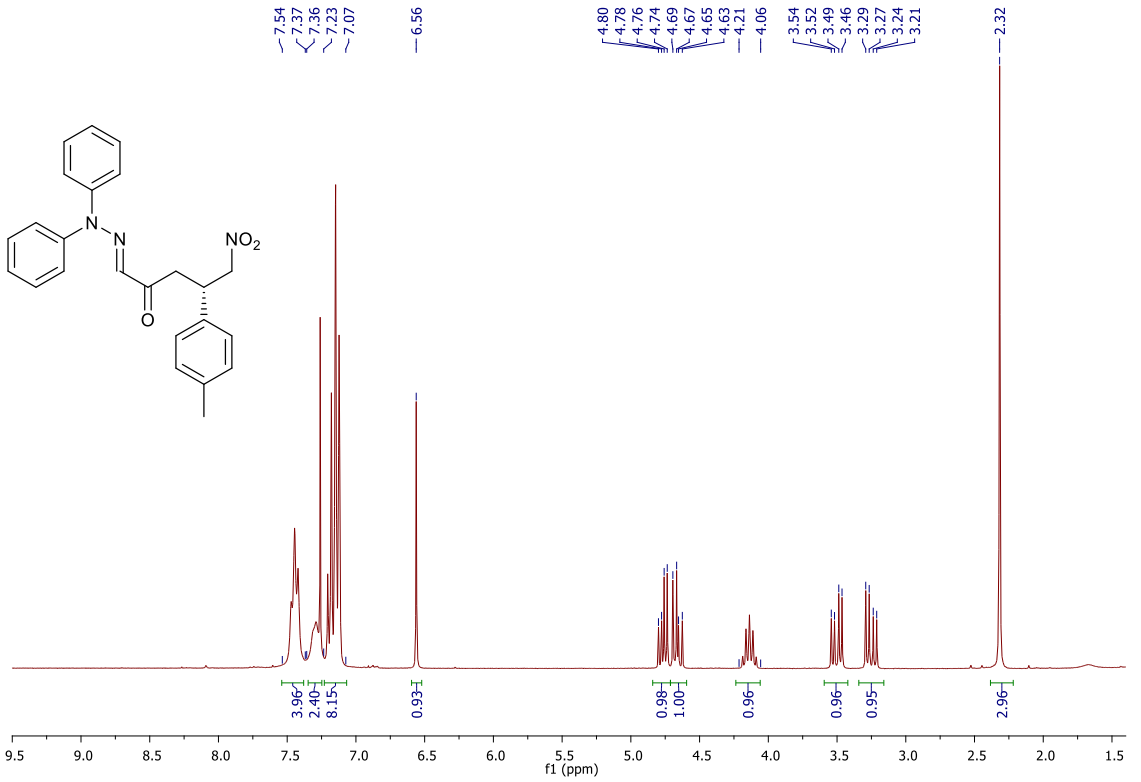
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Da**



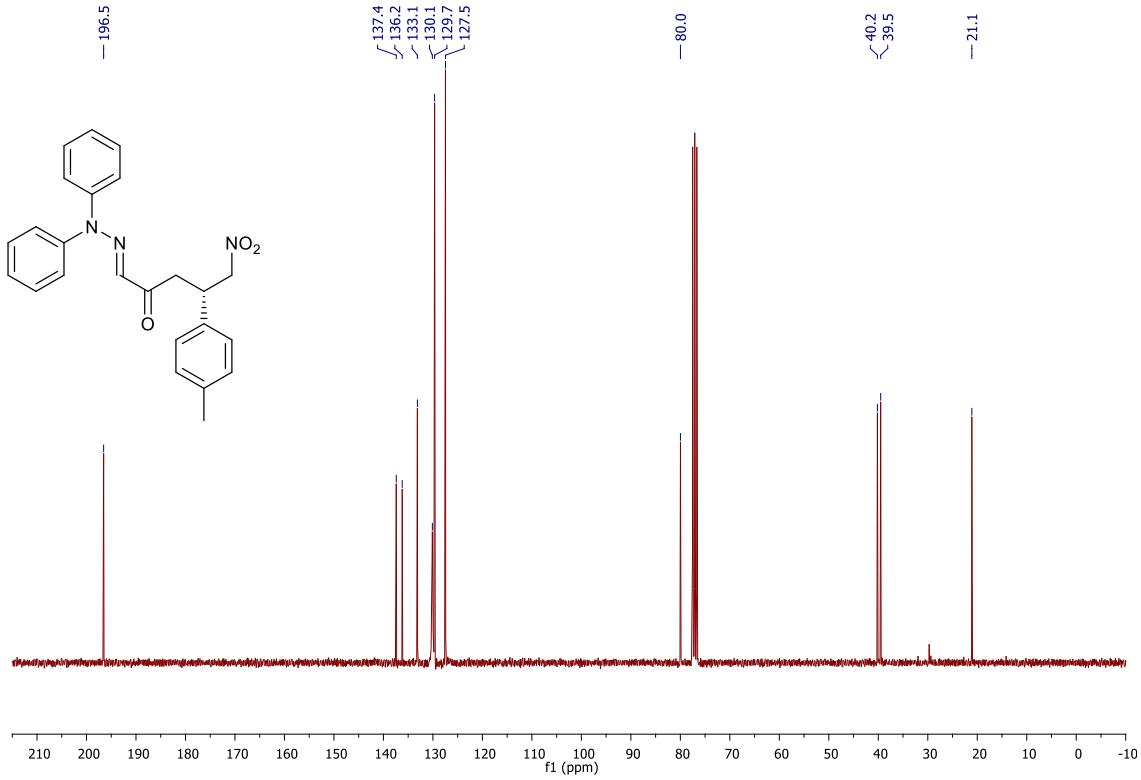
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Da**



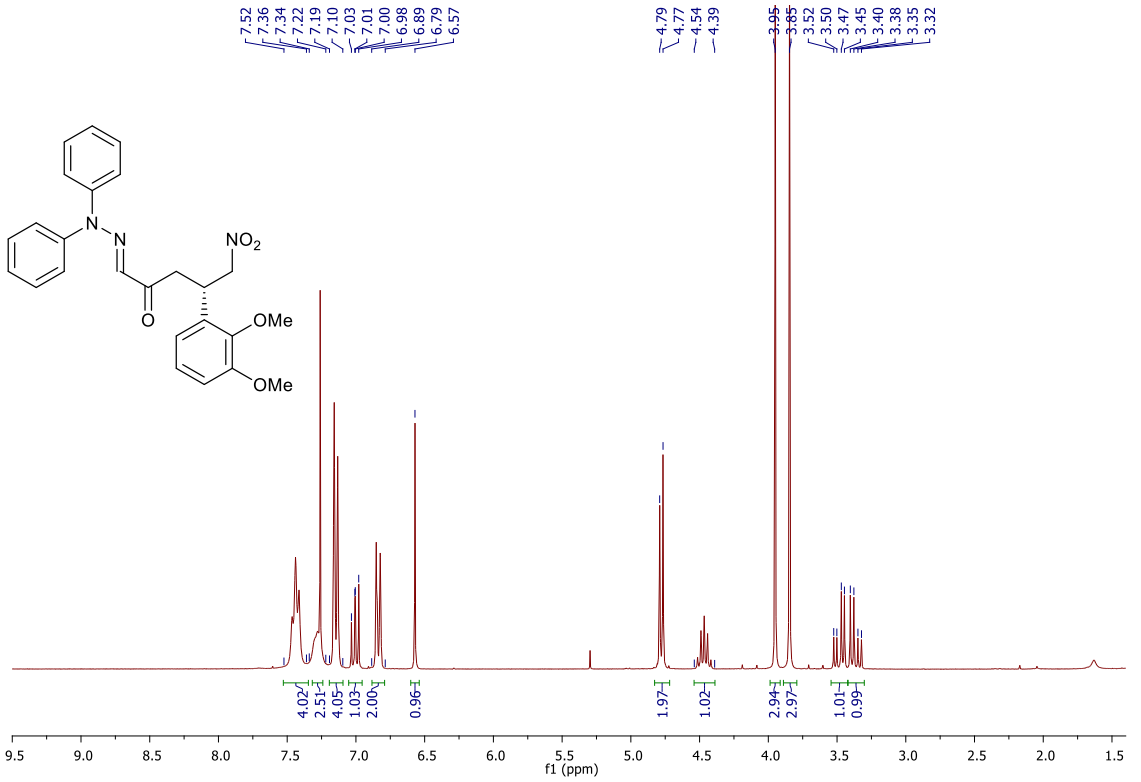
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Db**



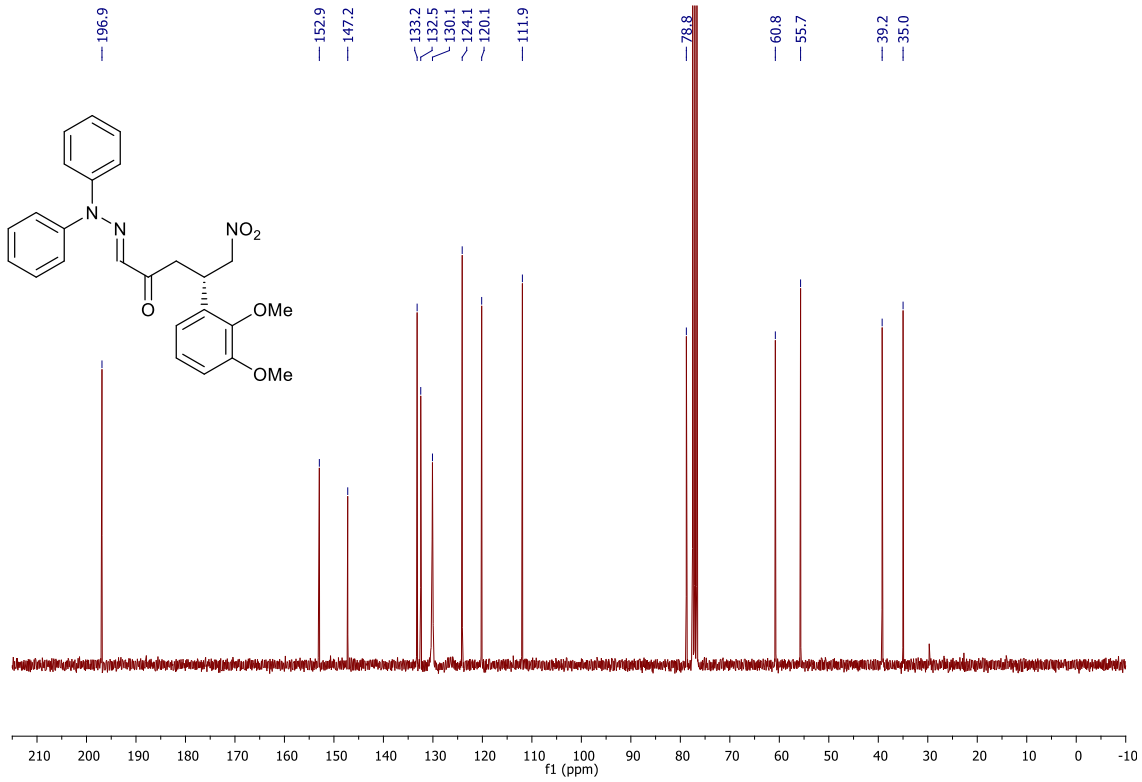
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Db**



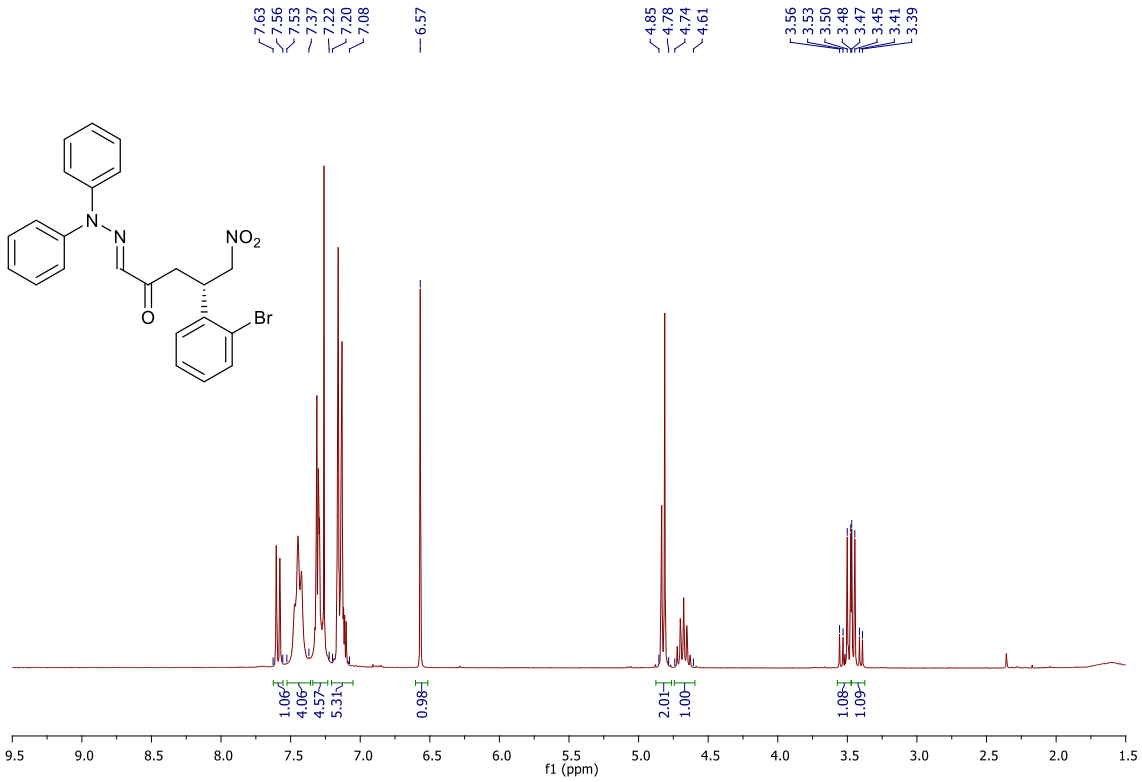
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Dc**



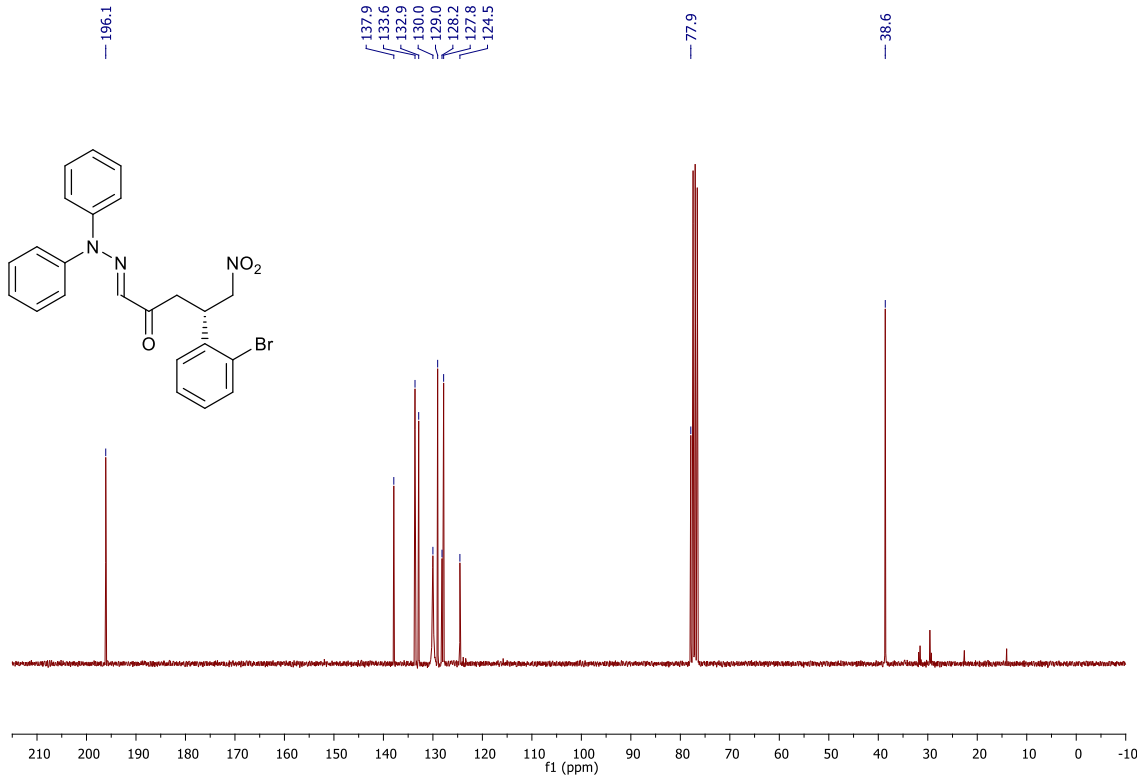
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Dc**



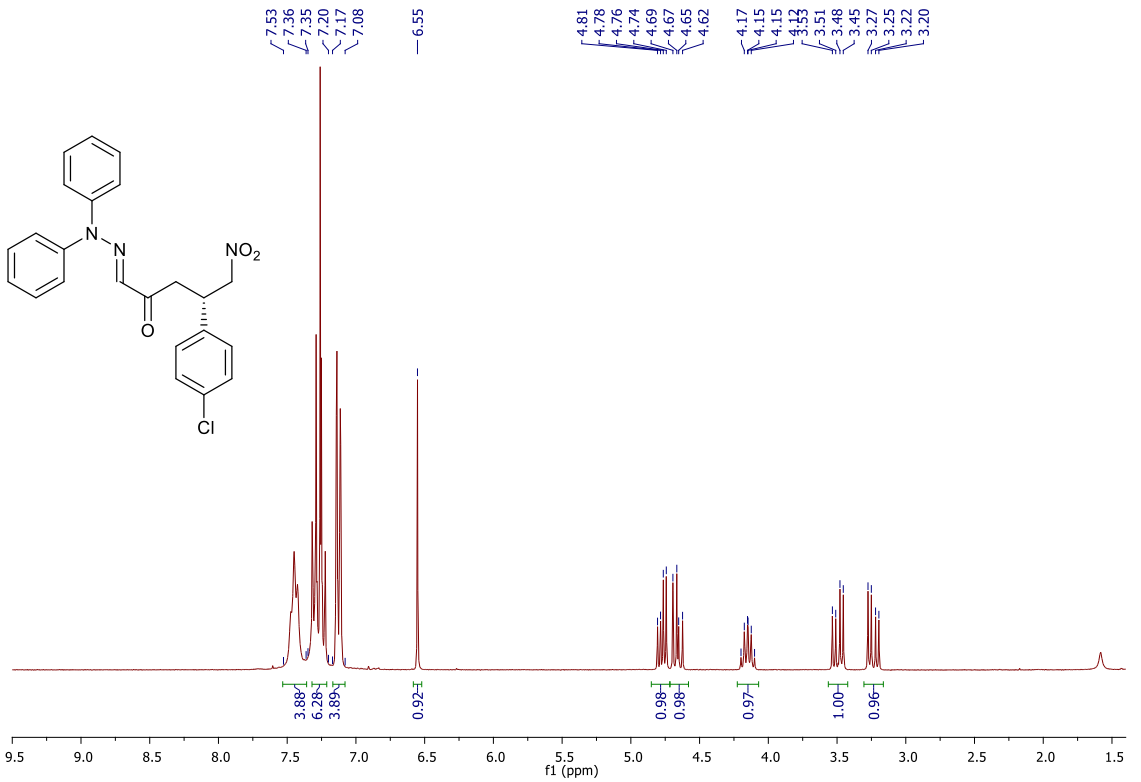
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Dd**



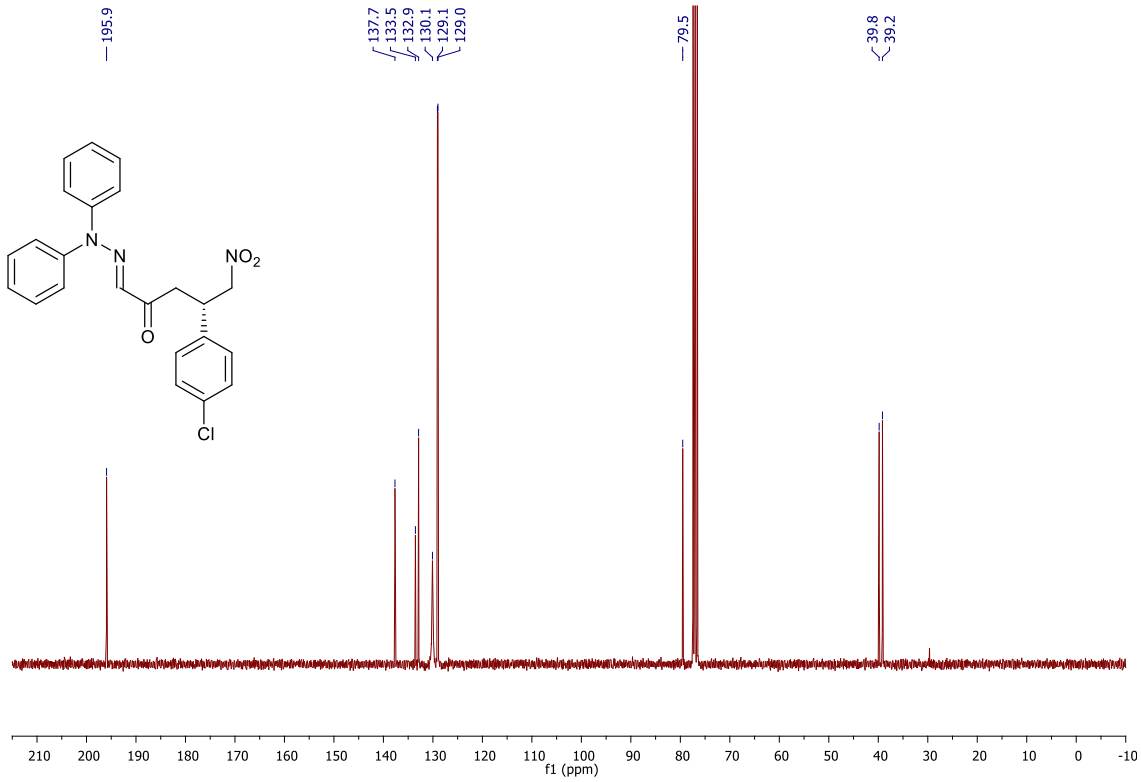
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Dd**



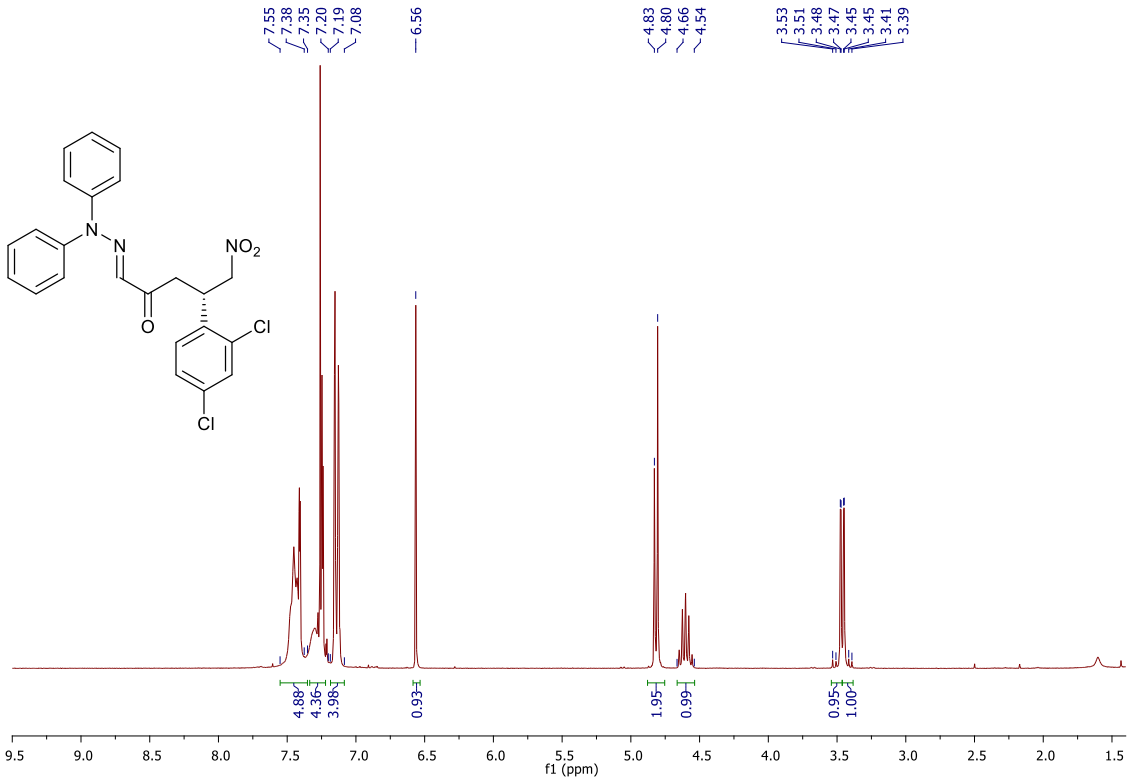
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3De**



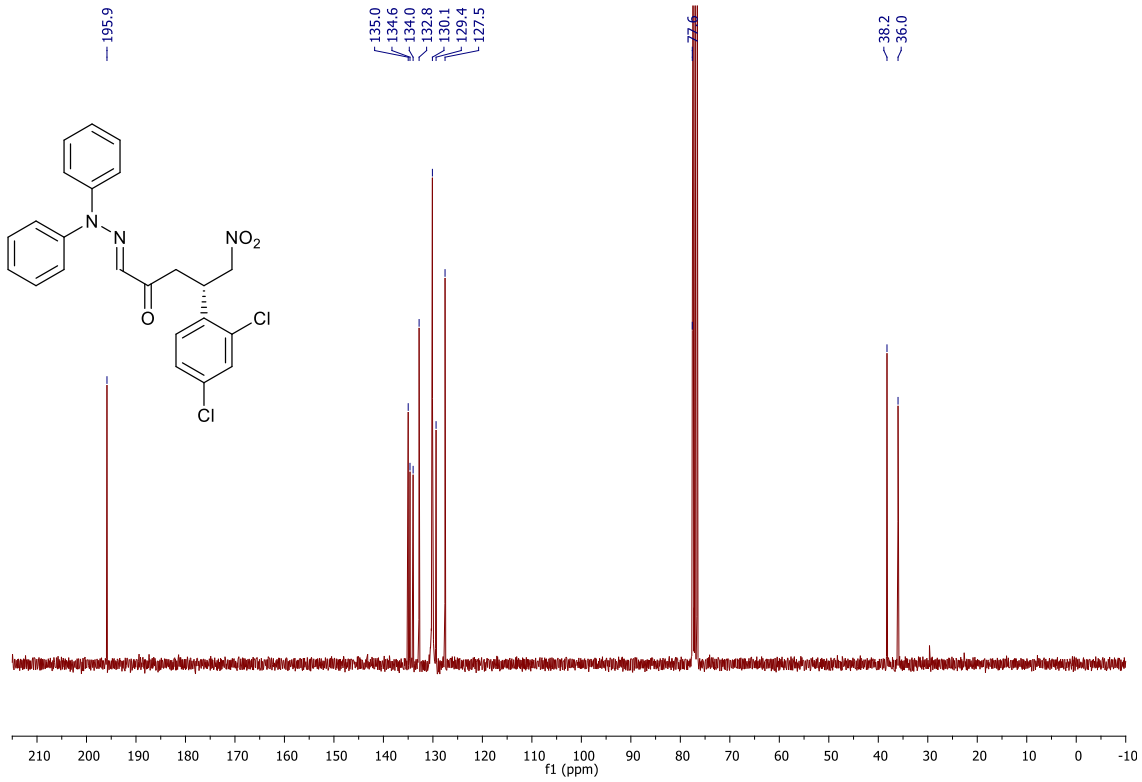
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3De**



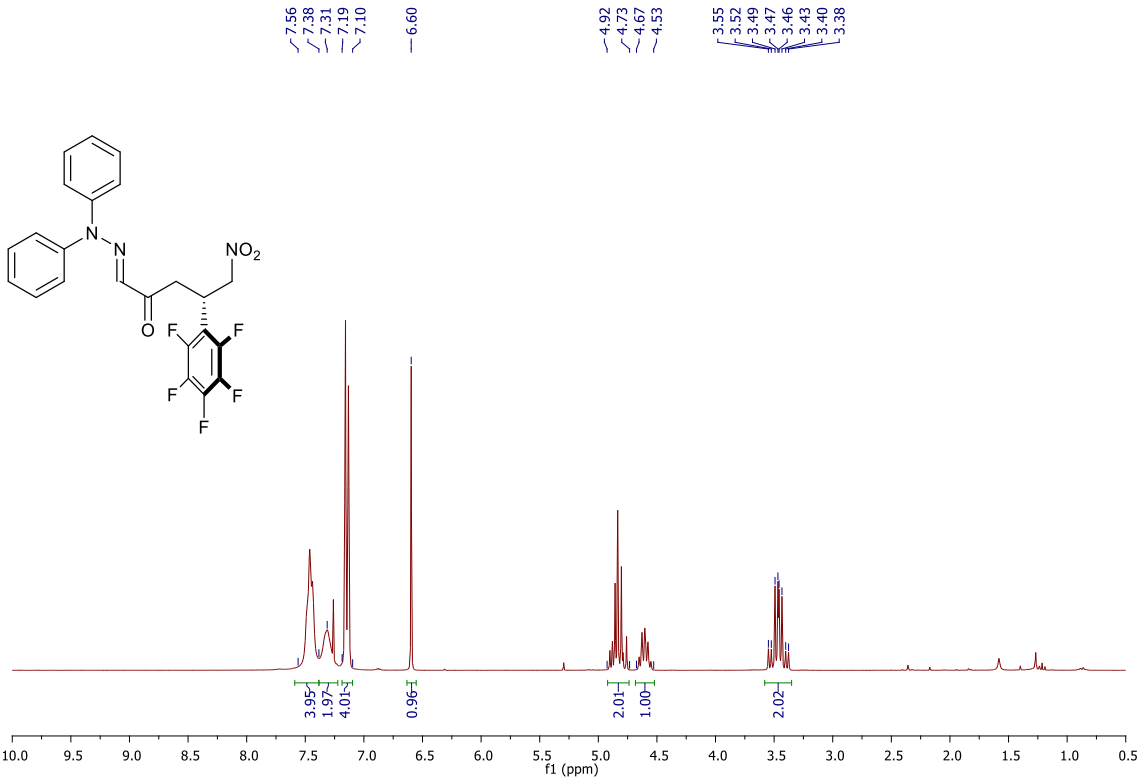
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Df**



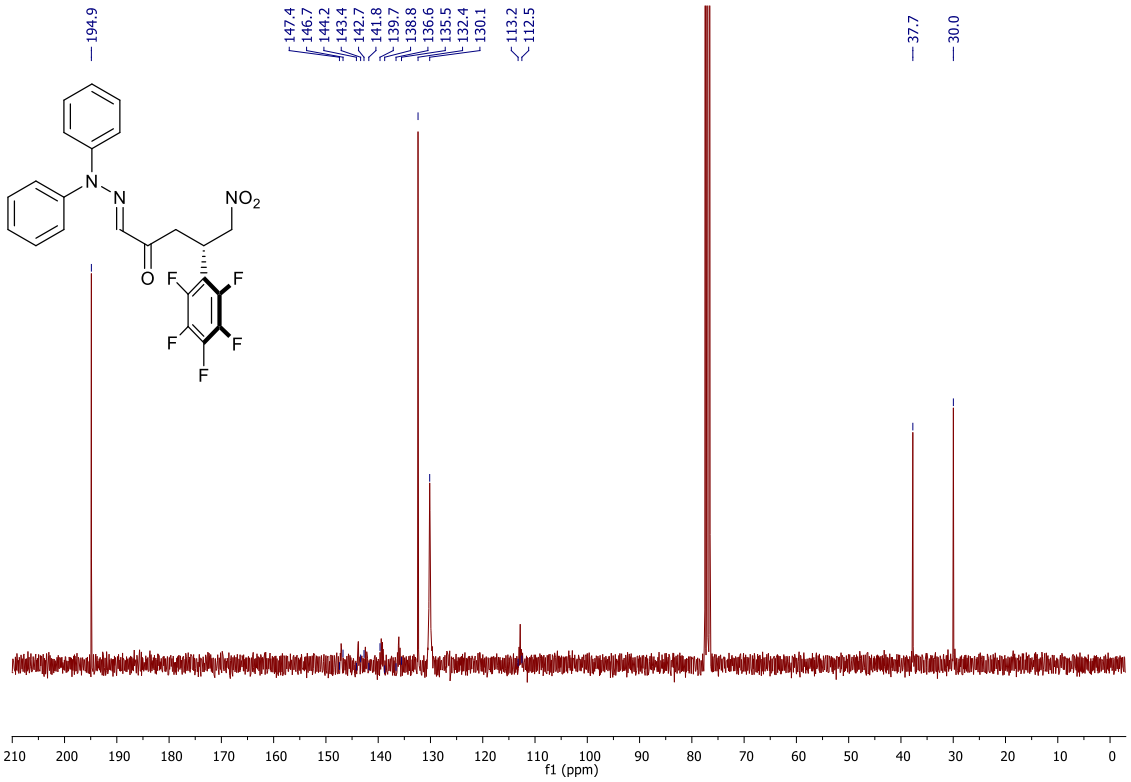
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Df**



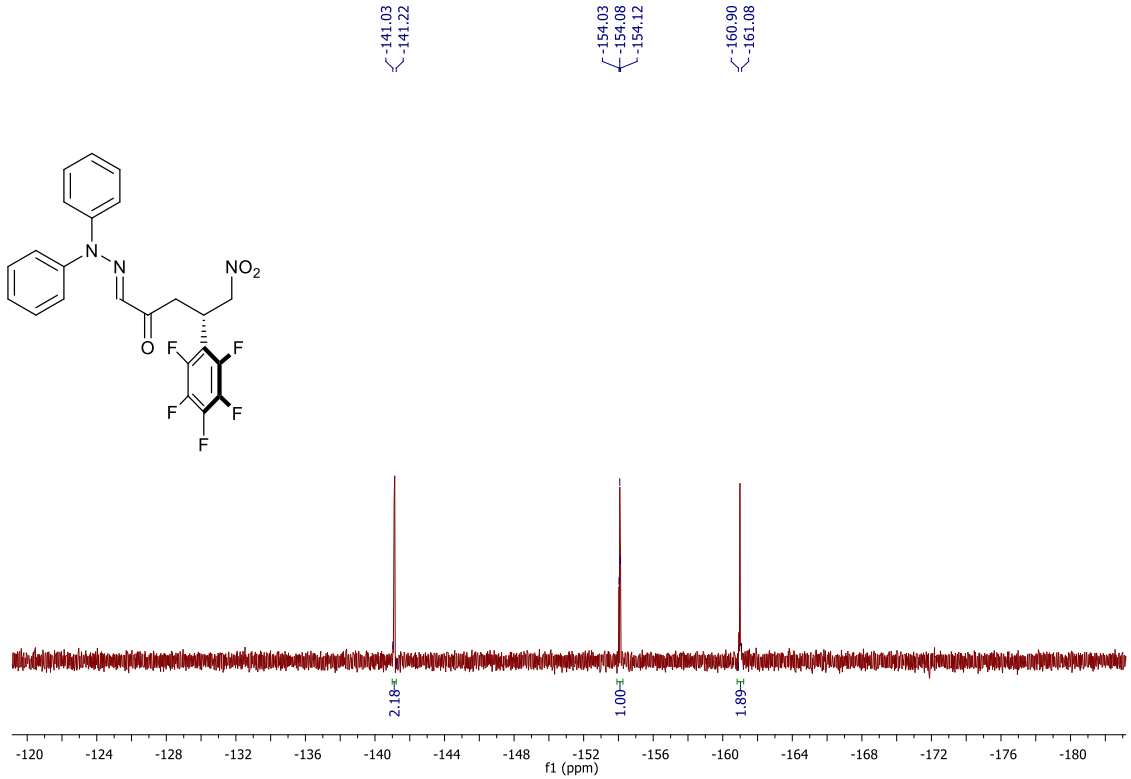
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Dg**



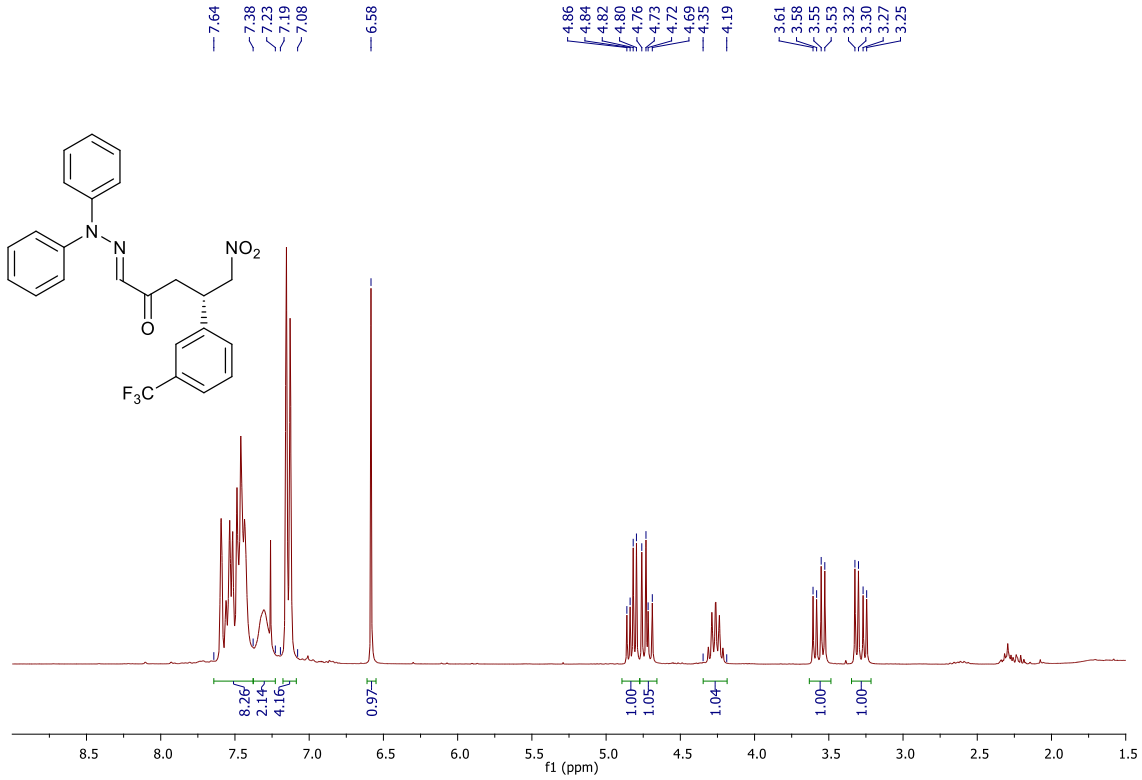
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Dg**



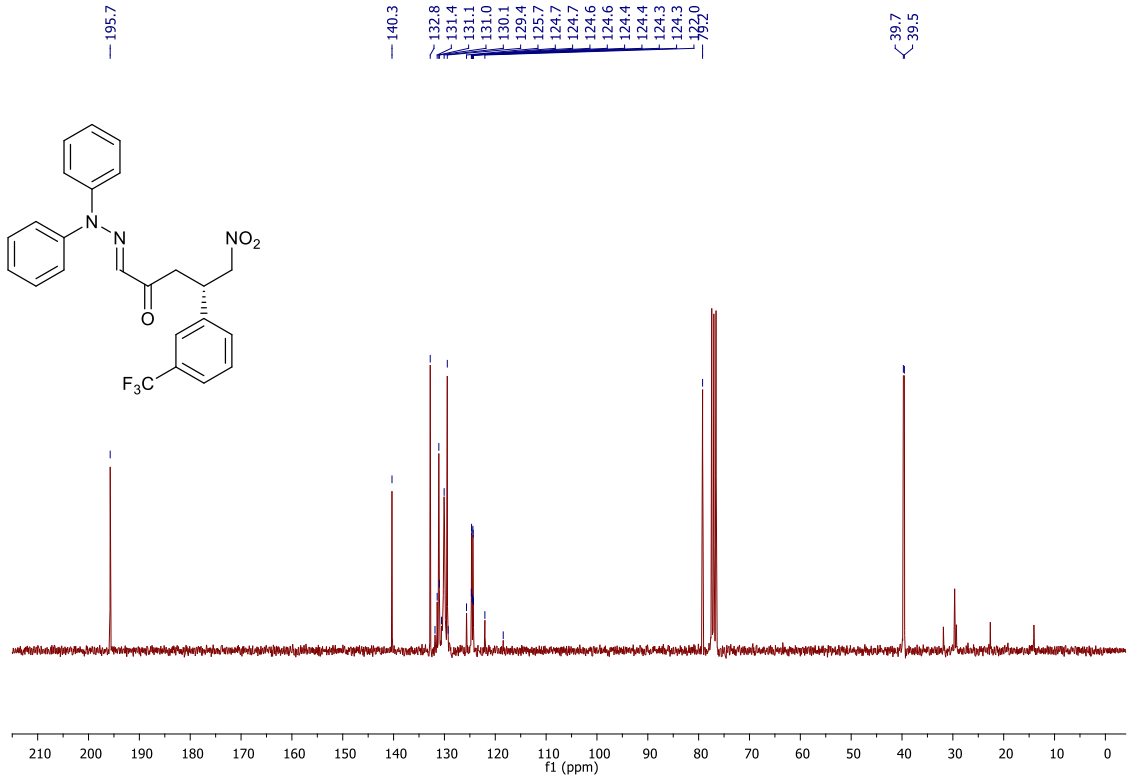
^{19}F NMR (471 MHz, $CDCl_3$) of (*S*)-**3Dg**



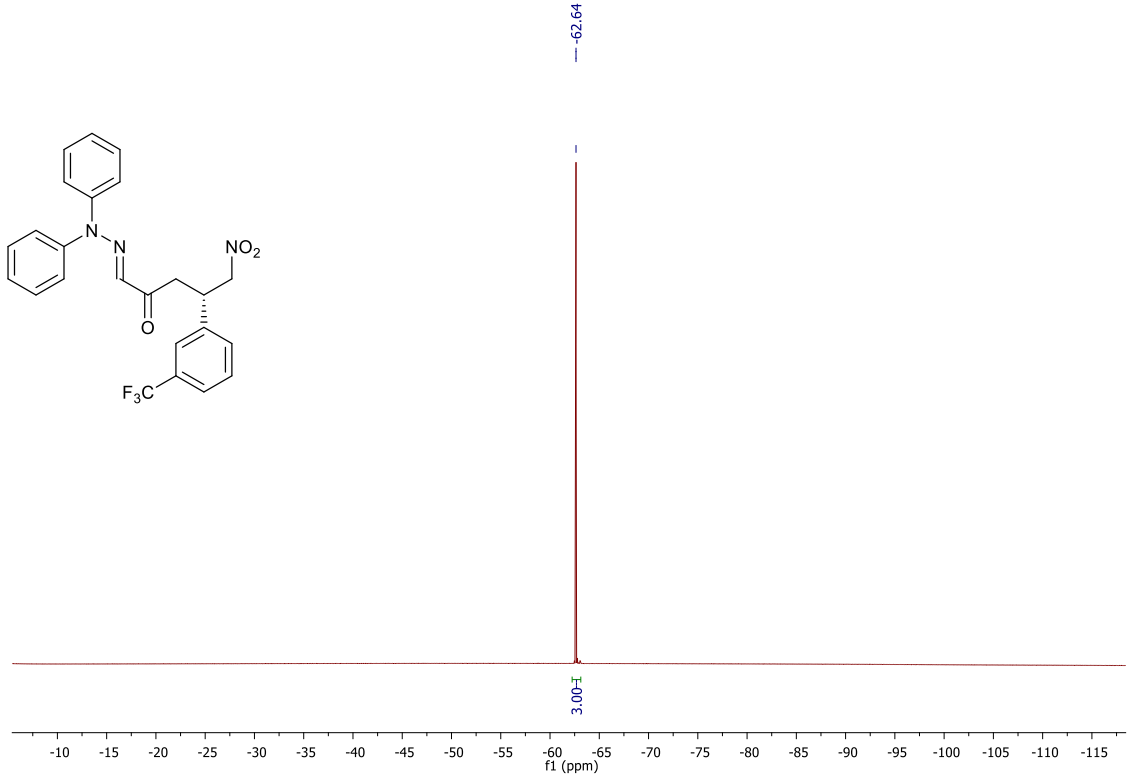
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Dh**



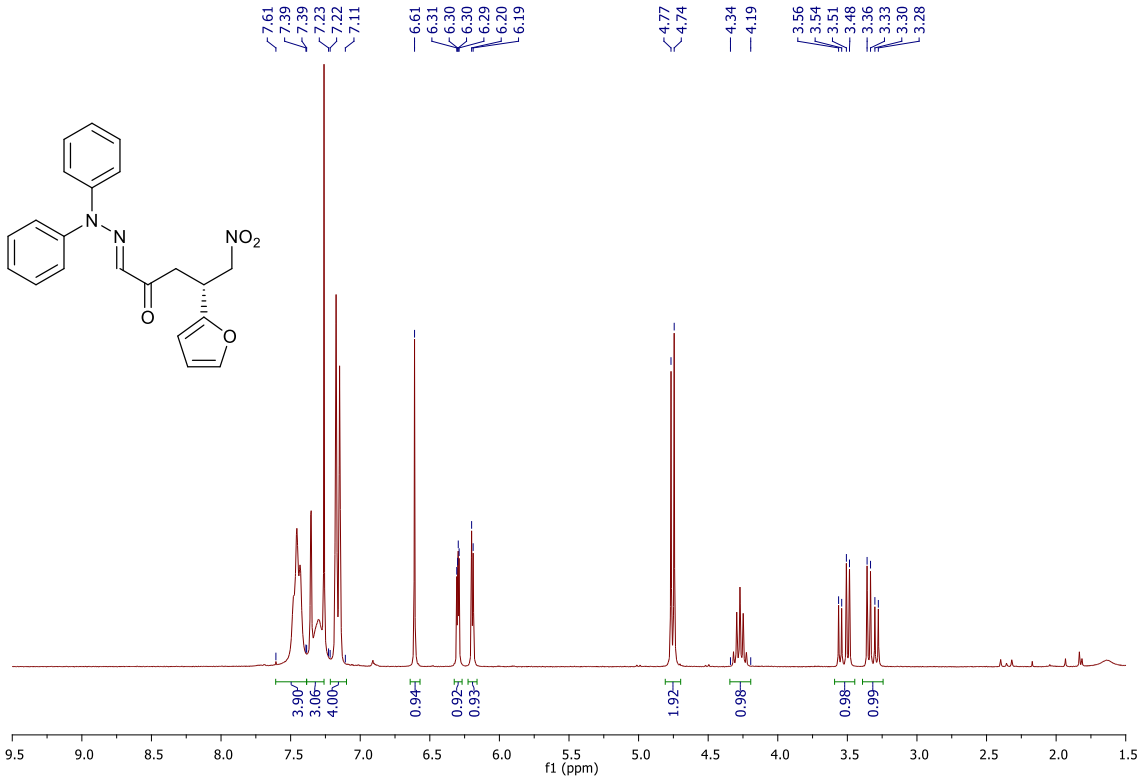
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Dh**



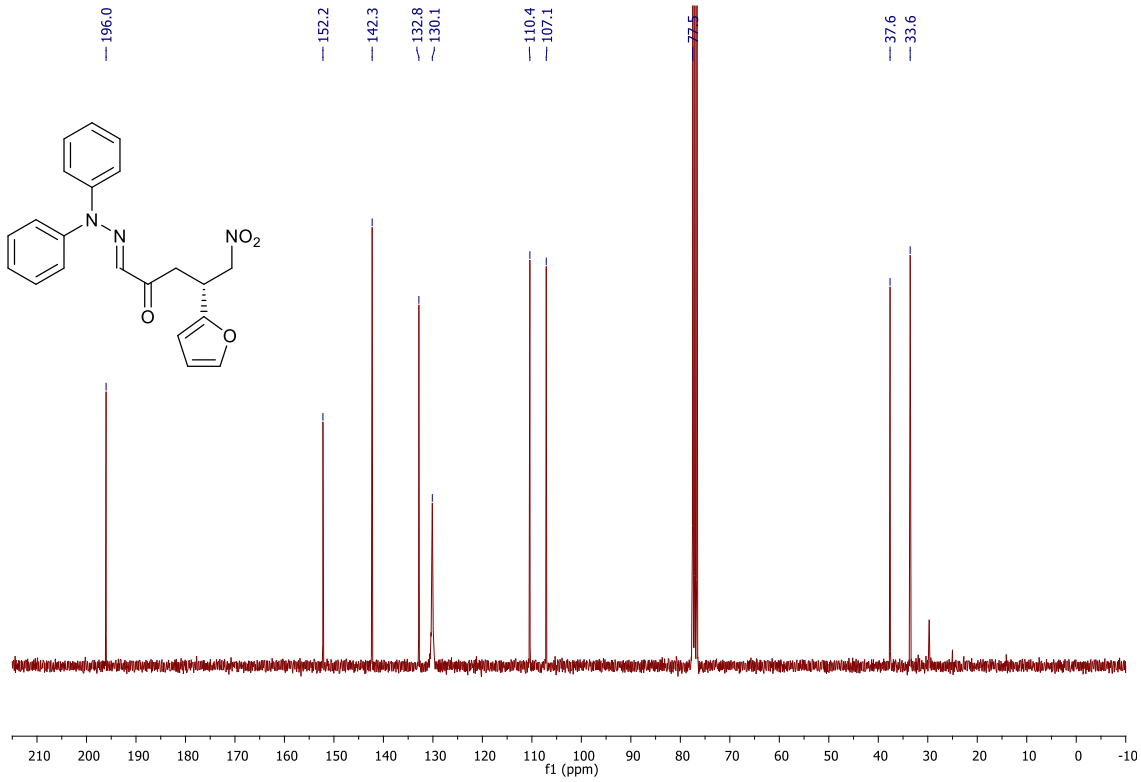
^{19}F NMR (471 MHz, $CDCl_3$) of (*S*)-**3Dh**



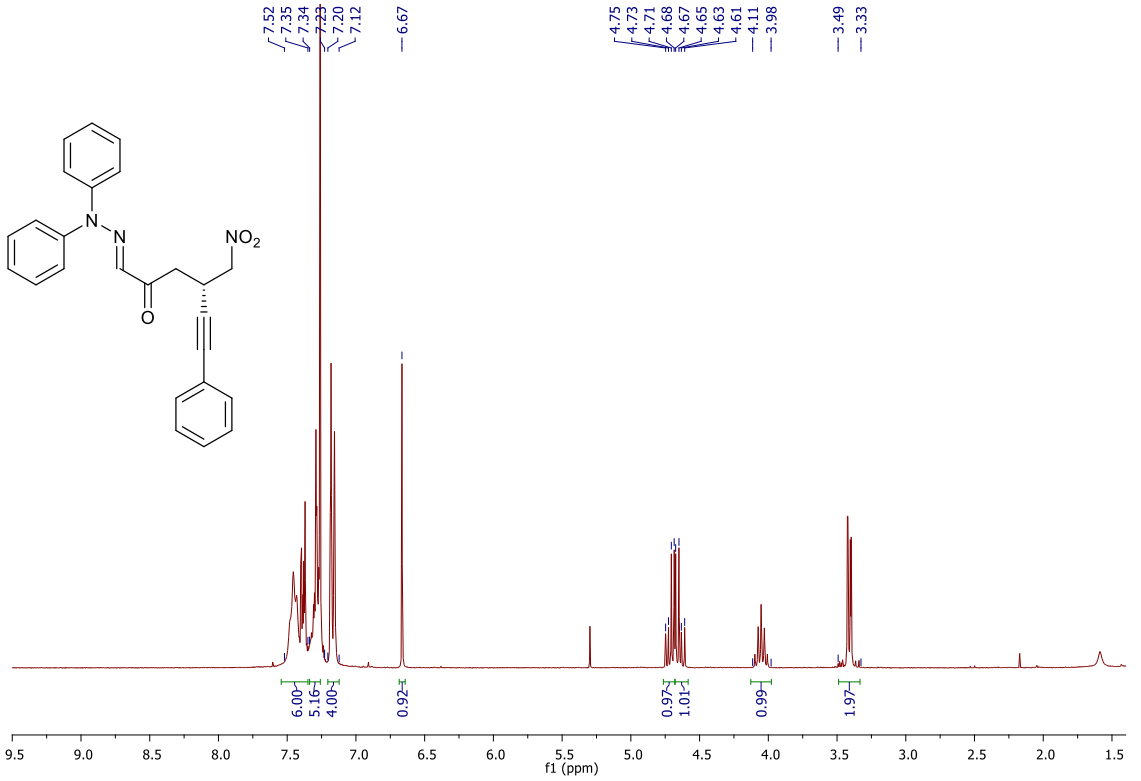
^{1}H NMR (300 MHz, $CDCl_3$) of (*R*)-**3Di**



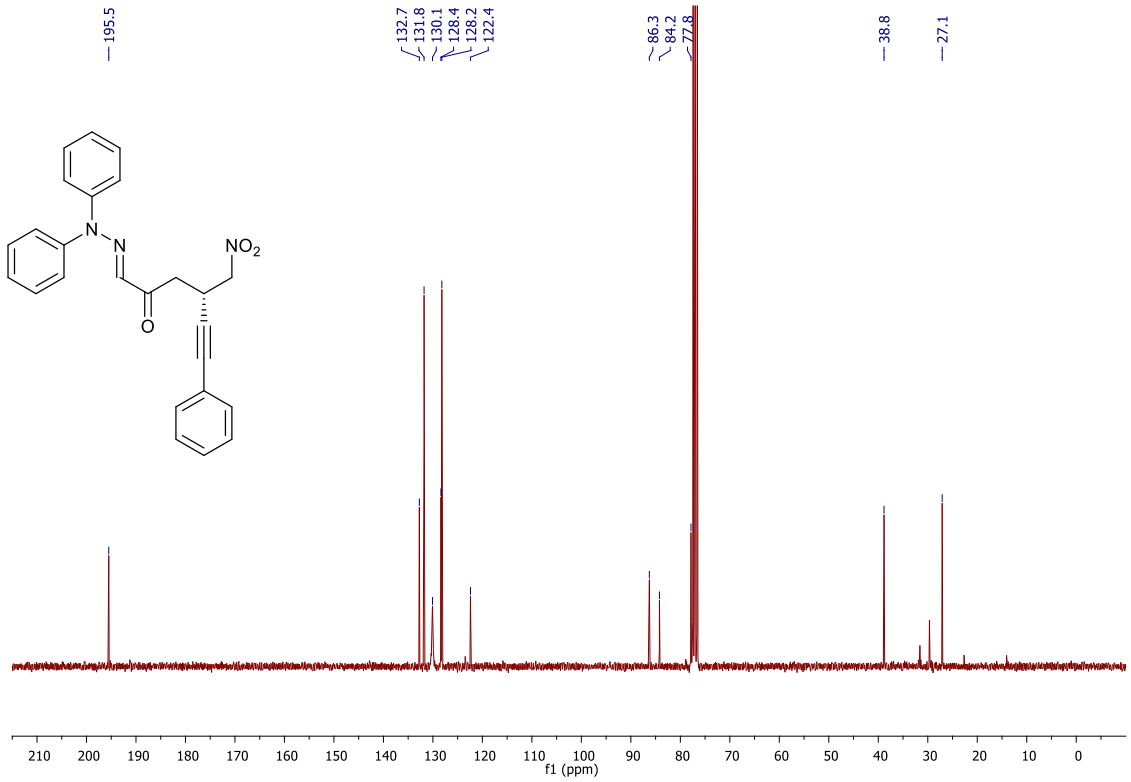
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*R*)-**3Di**



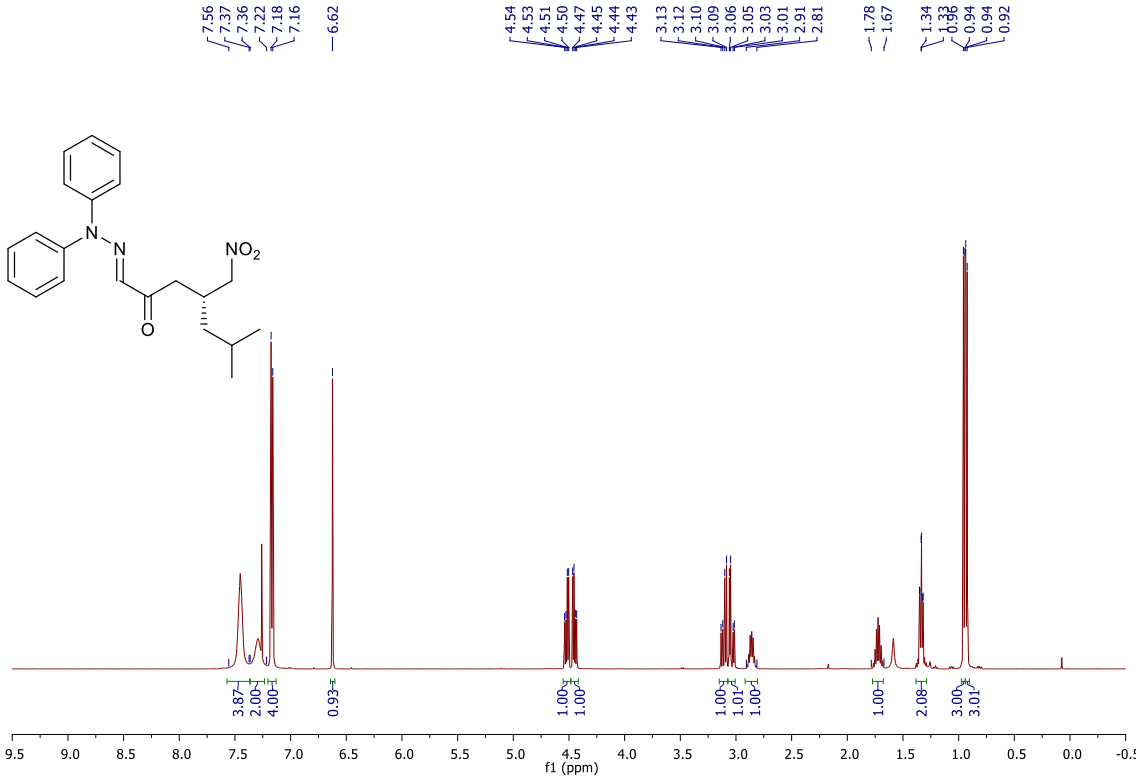
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Dj**



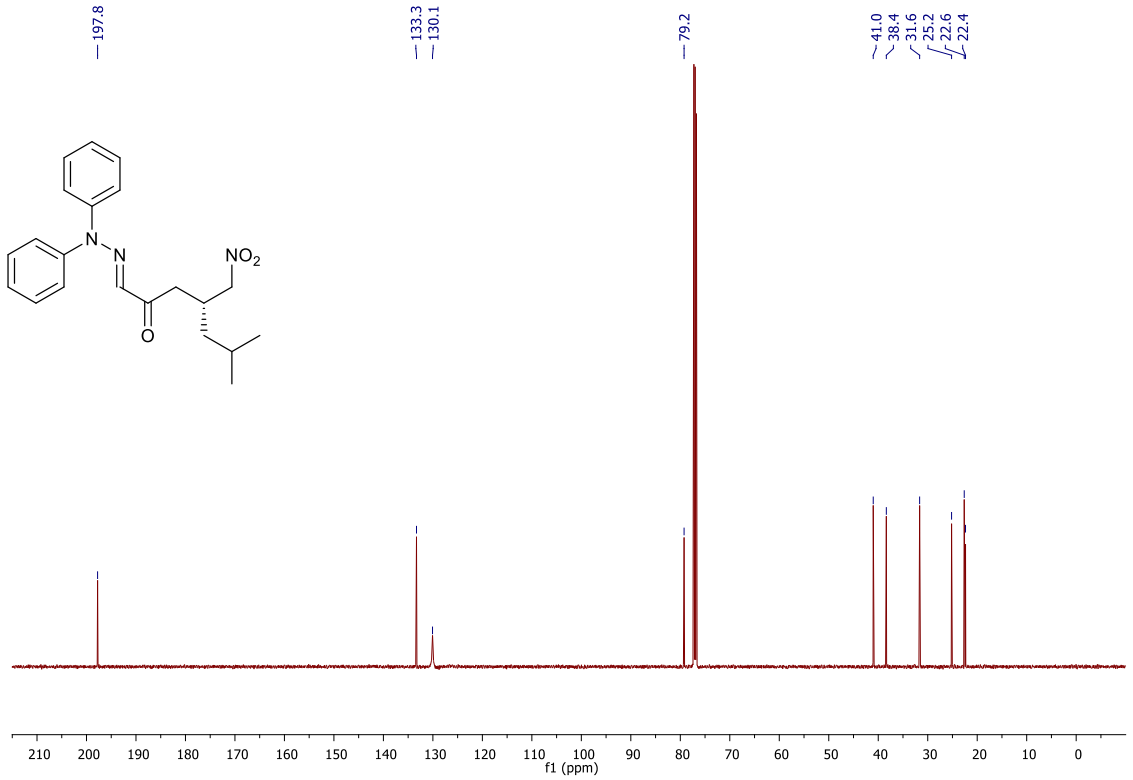
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Dj**



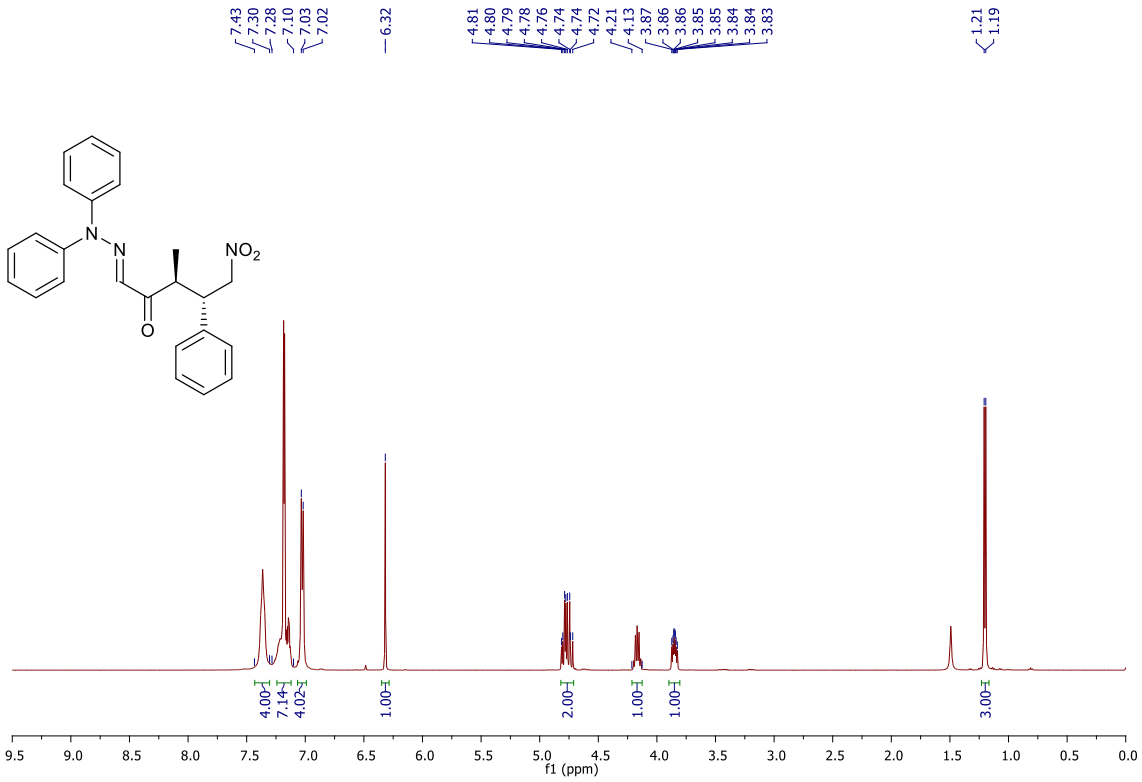
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**3Dk**



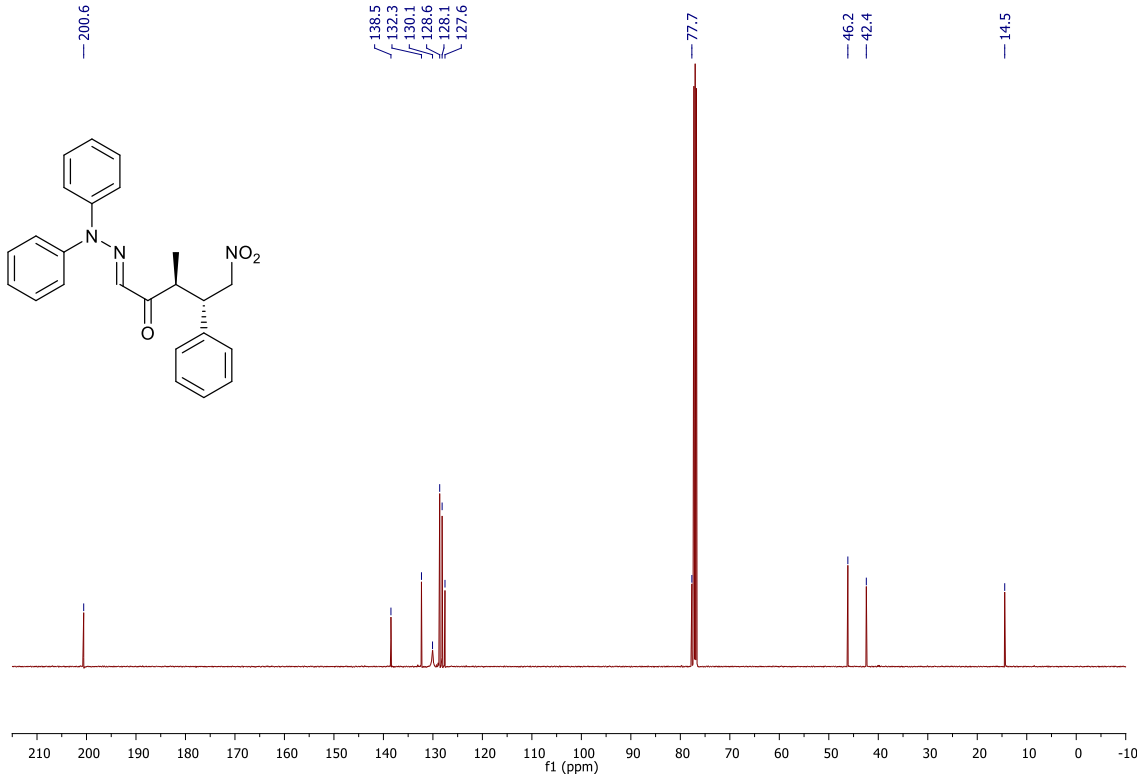
^{13}C NMR (126 MHz, $CDCl_3$) of (*R*)-**3Dk**



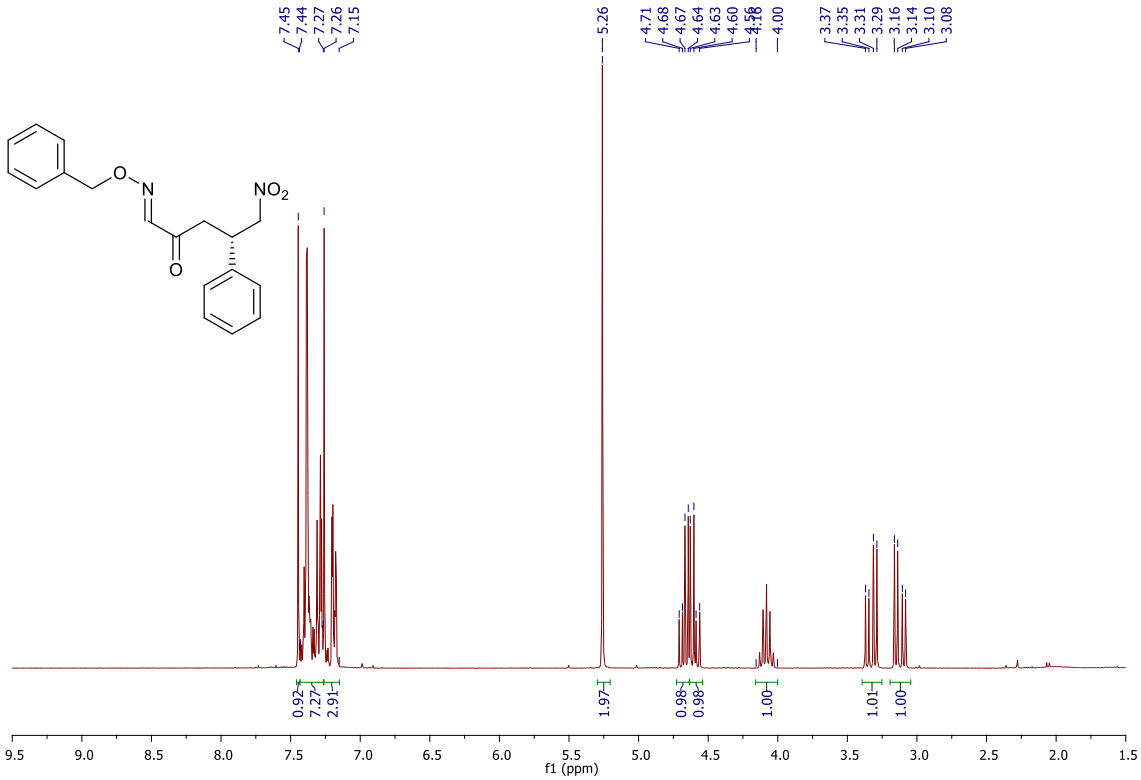
^{1}H NMR (500 MHz, $CDCl_3$) of (*S*,*S*)-**3Fa**



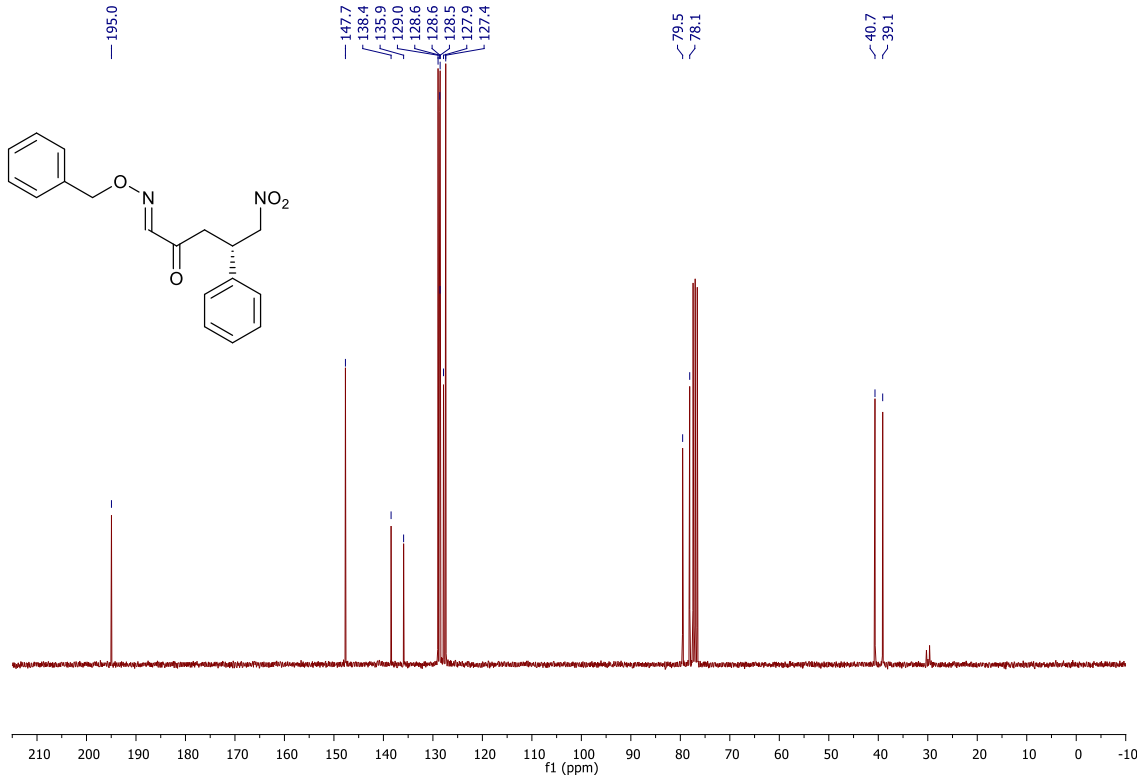
^{13}C NMR (126 MHz, $CDCl_3$) of (*S*,*S*)-**3Fa**



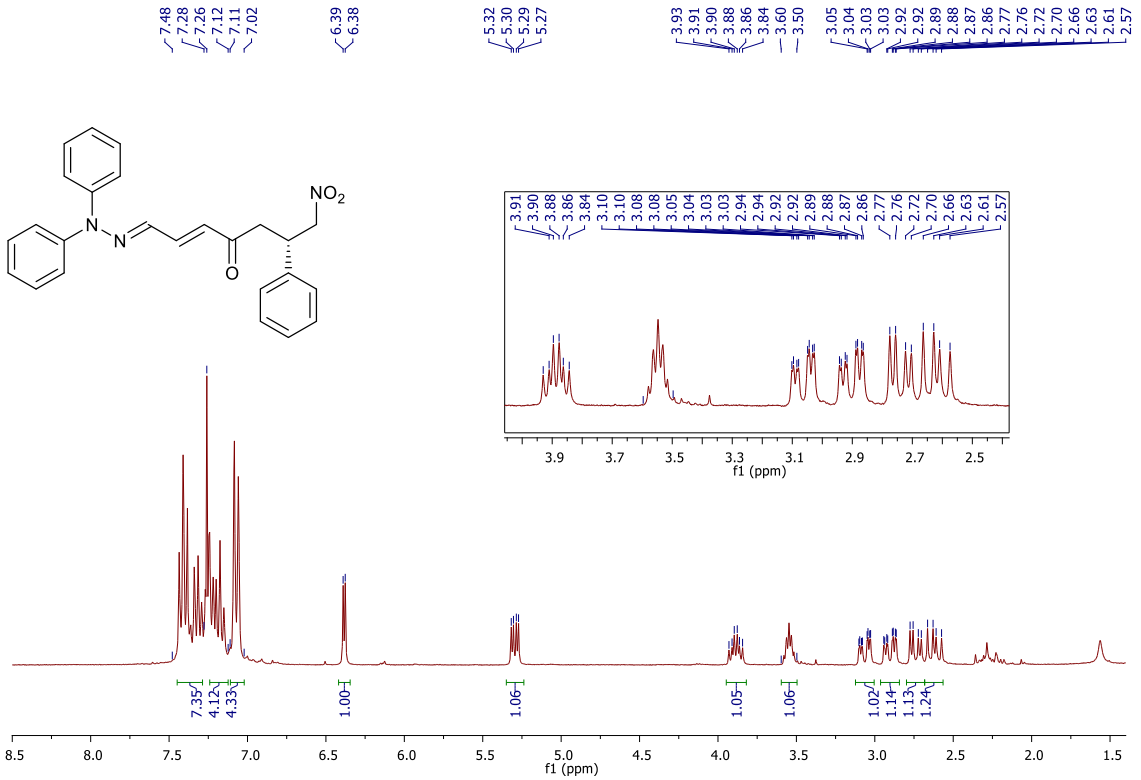
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**5a**



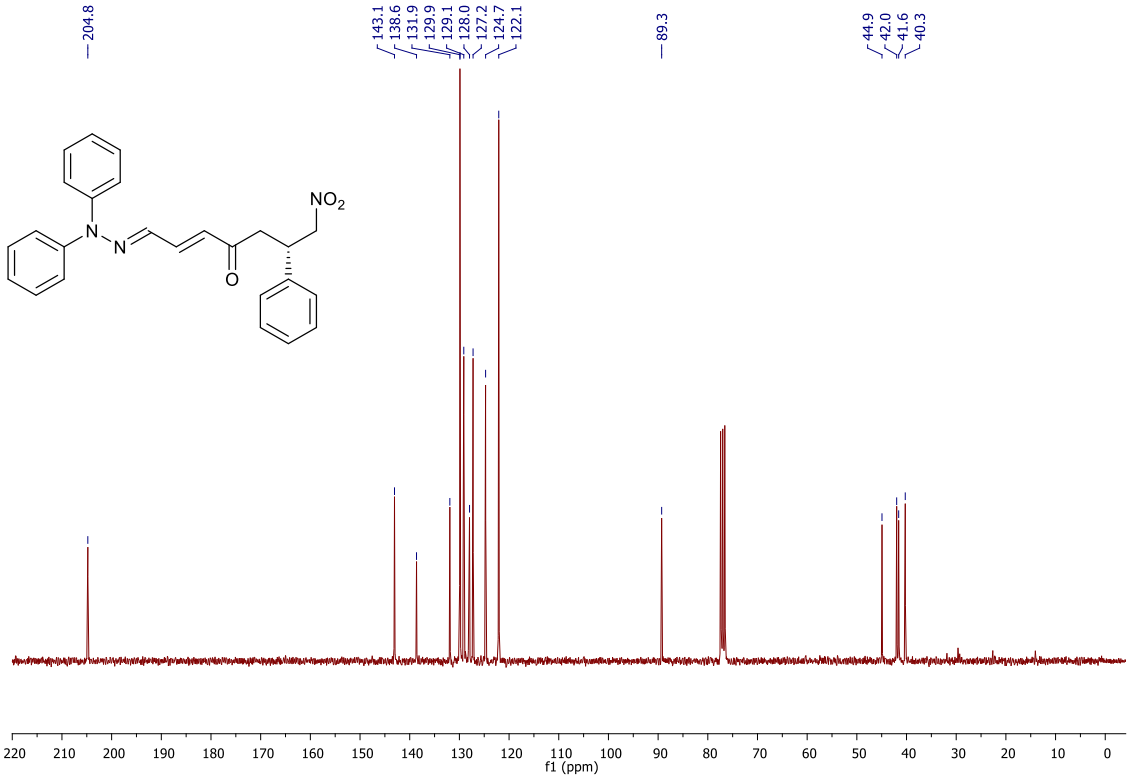
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**5a**



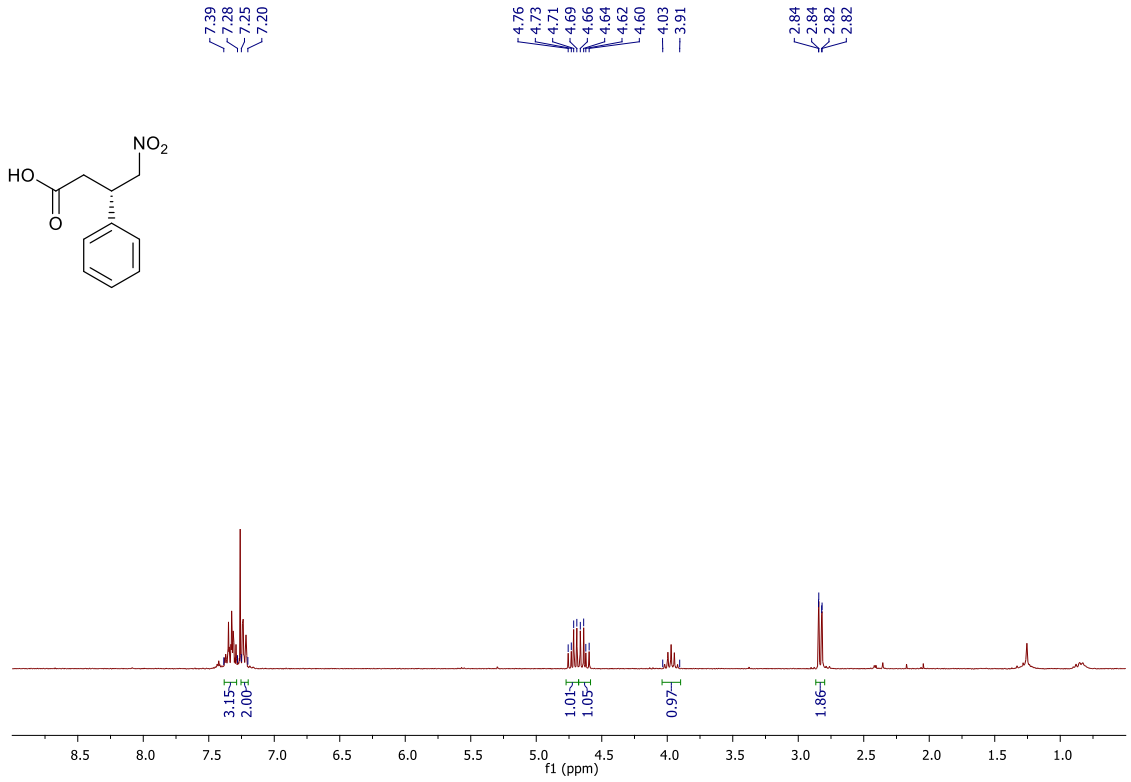
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**3Ea**



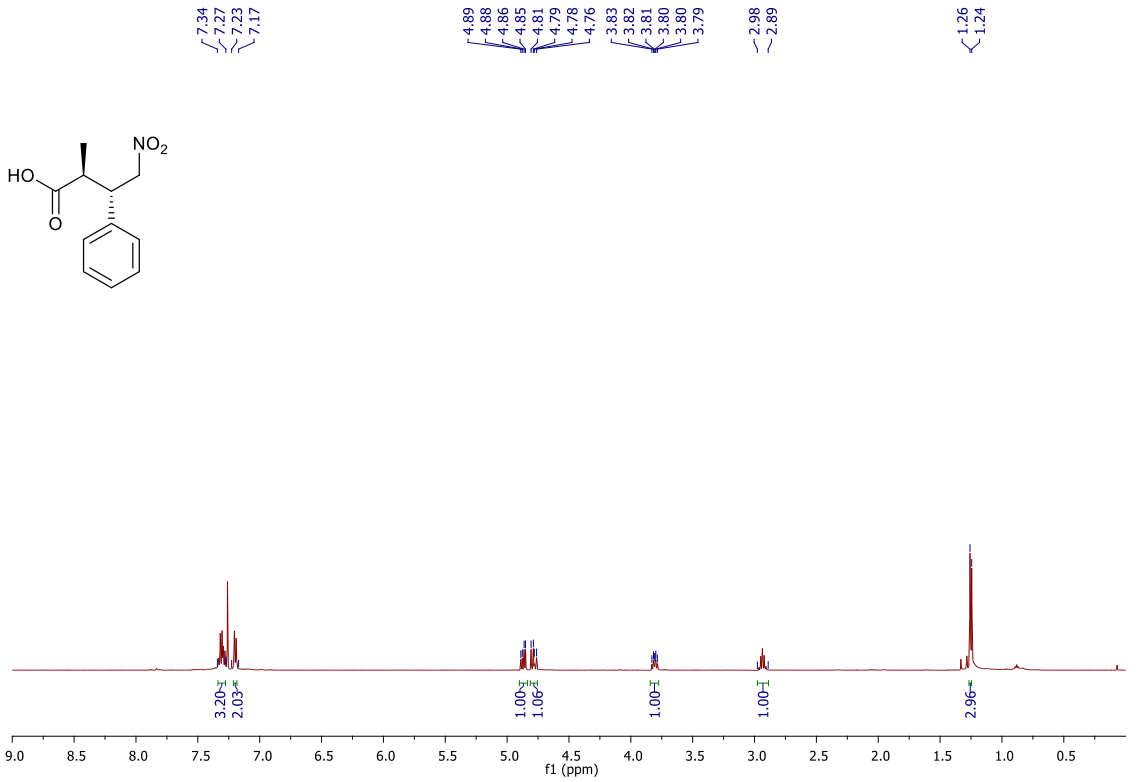
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*)-**3Ea**



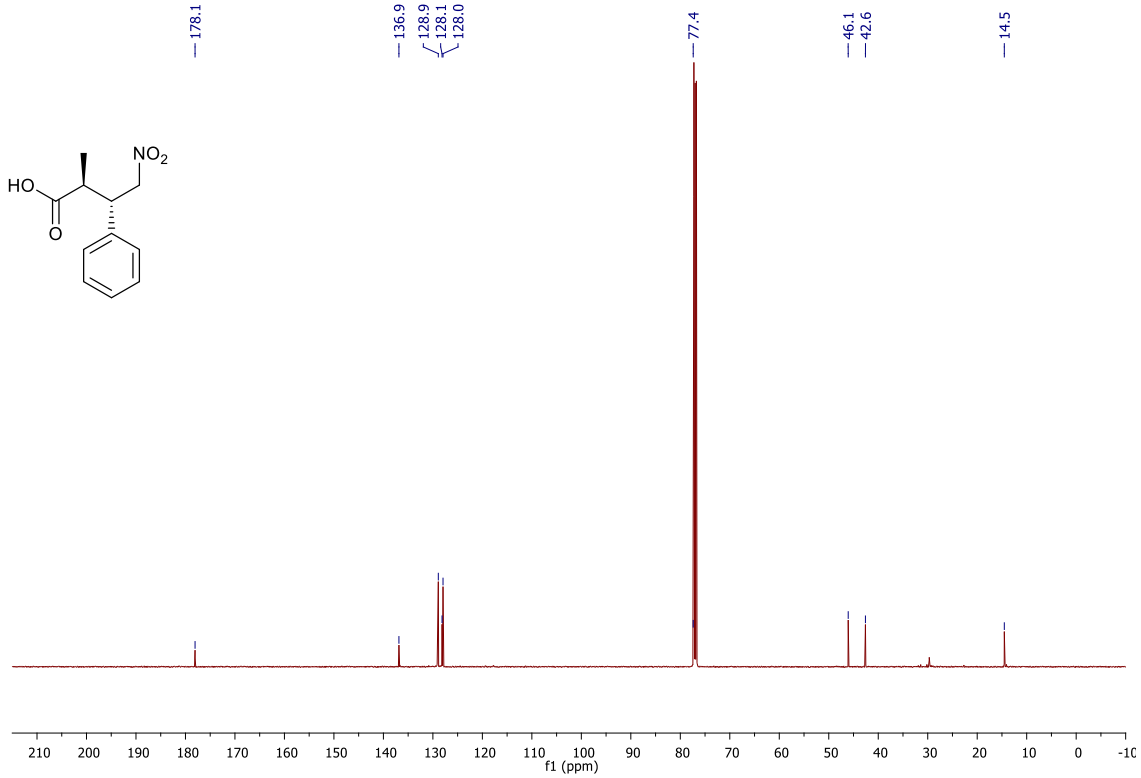
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*)-**6a**



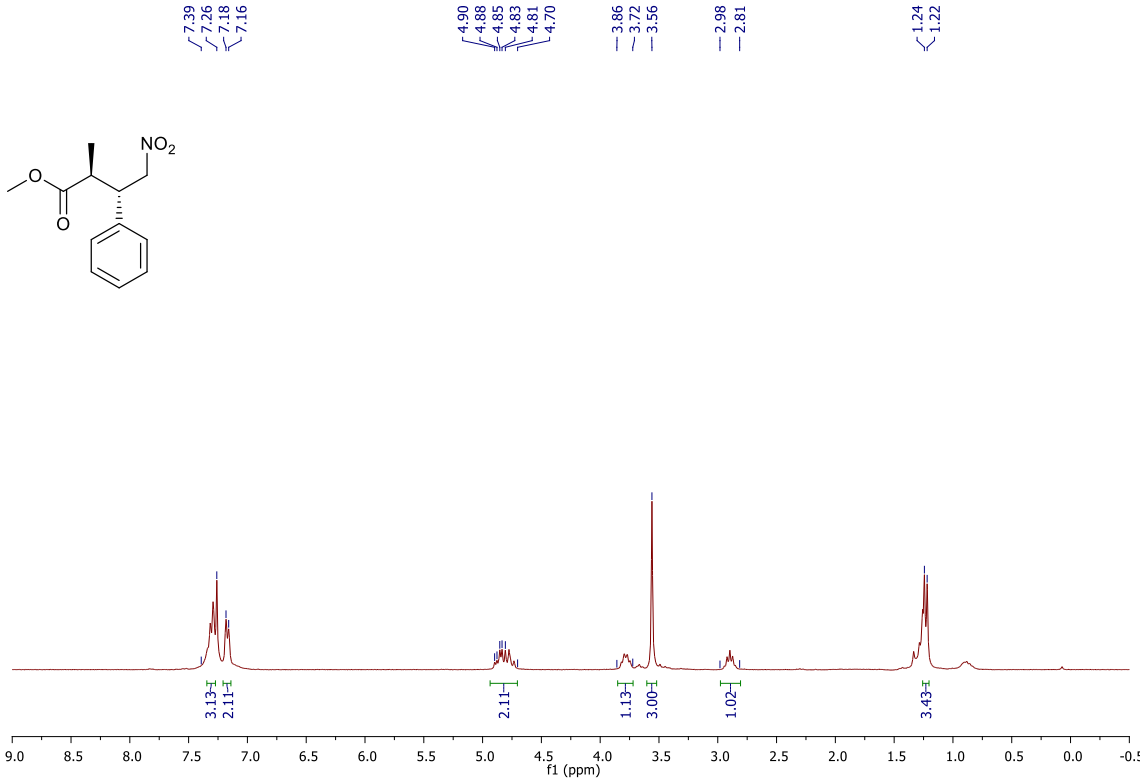
^{1}H NMR (500 MHz, $CDCl_3$) of (*S*,*S*)-**6b**



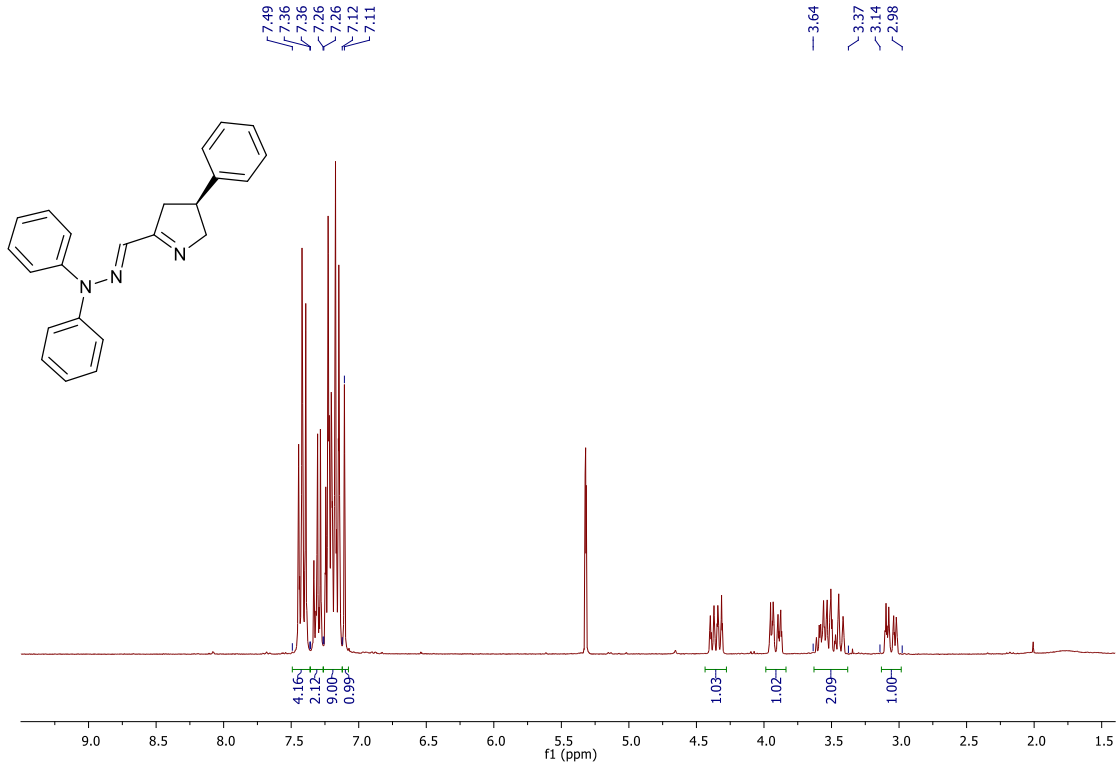
^{13}C NMR (126 MHz, $CDCl_3$) of (*S*,*S*)-**6b**



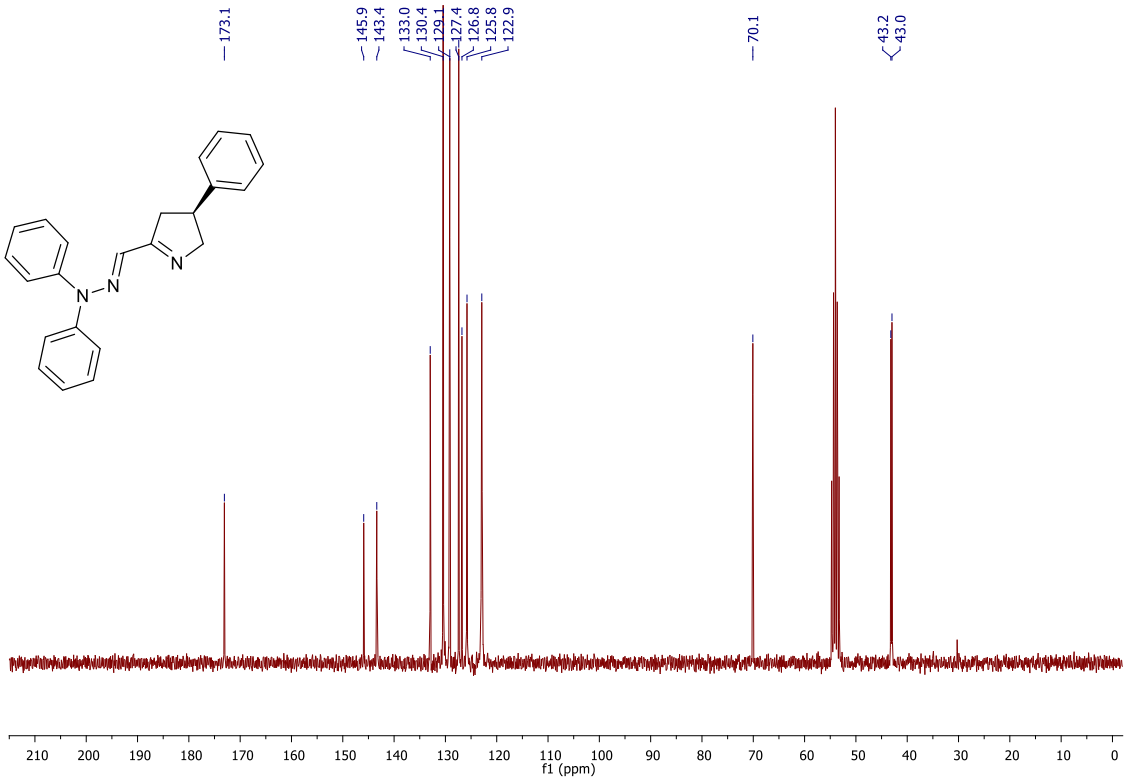
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*,*S*)-**6b'**



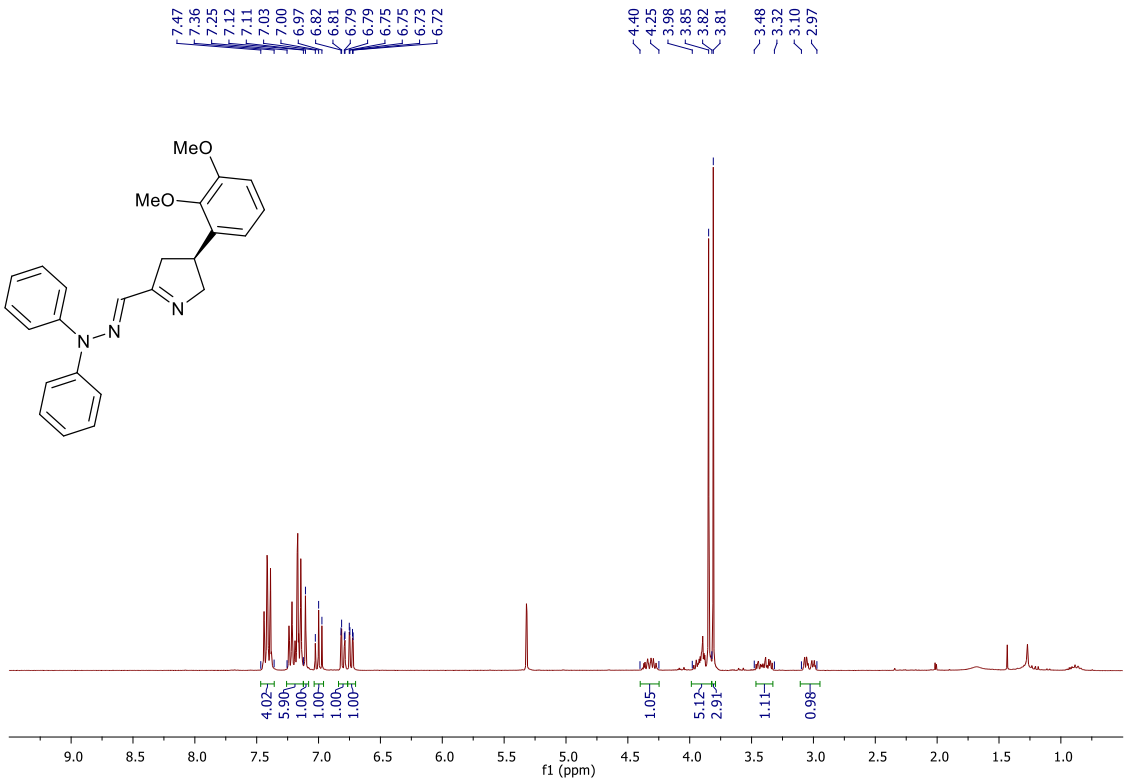
^{1}H NMR (300 MHz, CD_2Cl_2) of (*S*)-**7a**



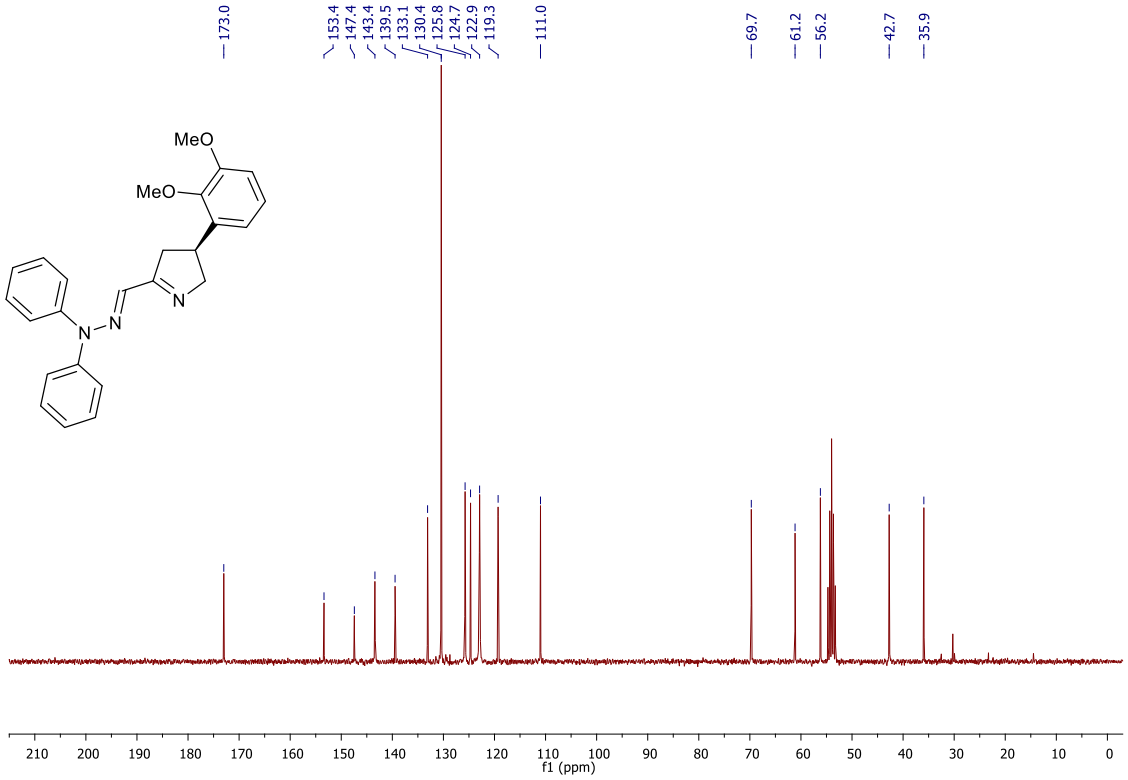
^{13}C NMR (75.5 MHz, CD_2Cl_2) of (*S*)-**7a**



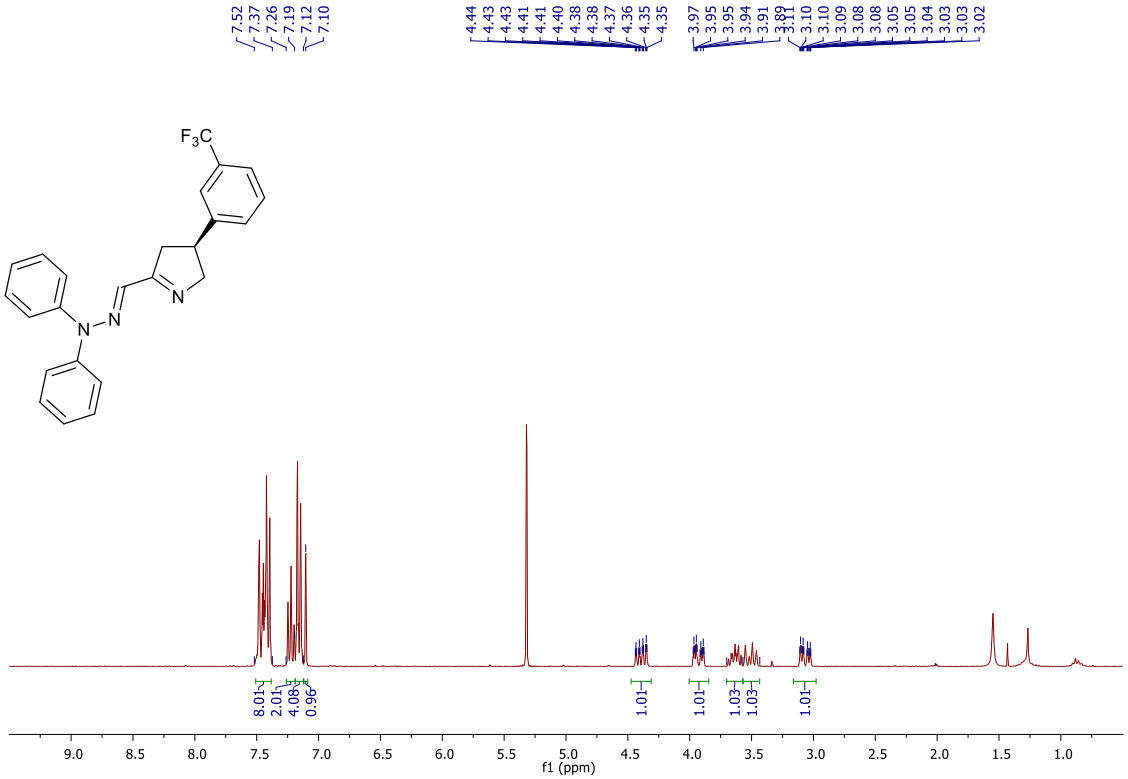
^{1}H NMR (300 MHz, CD_2Cl_2) of (*S*)-**7b**



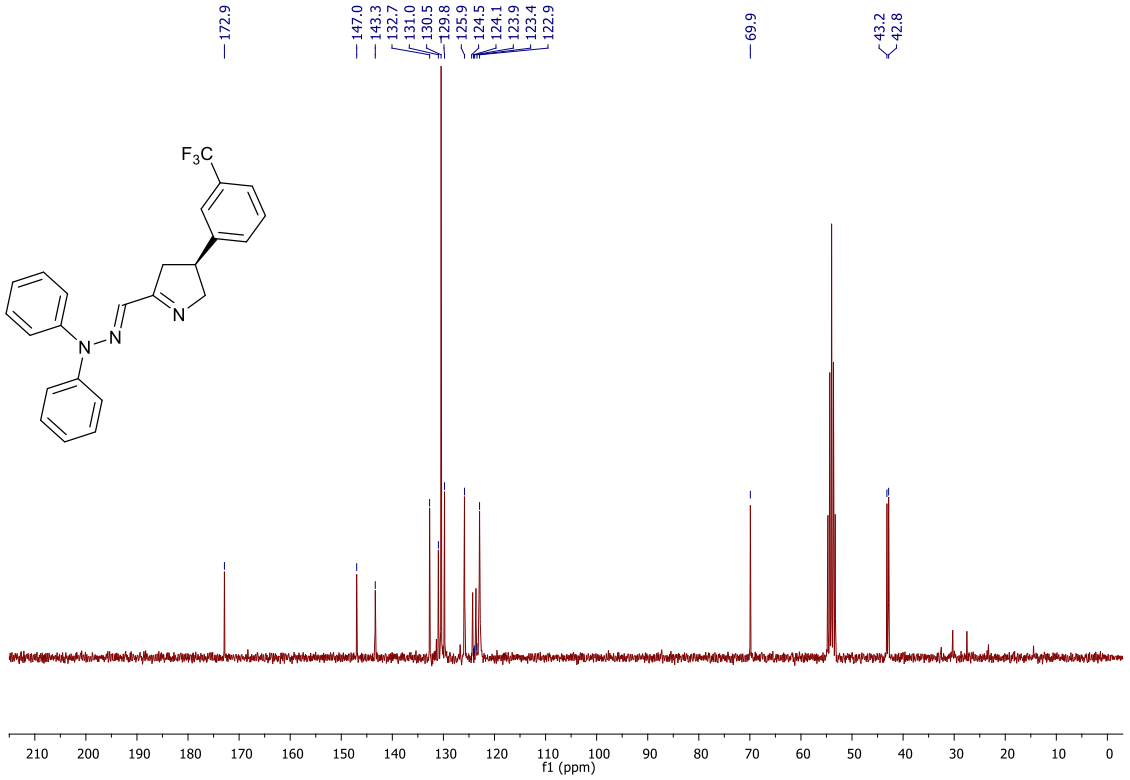
^{13}C NMR (75.5 MHz, CD_2Cl_2) of (*S*)-**7b**



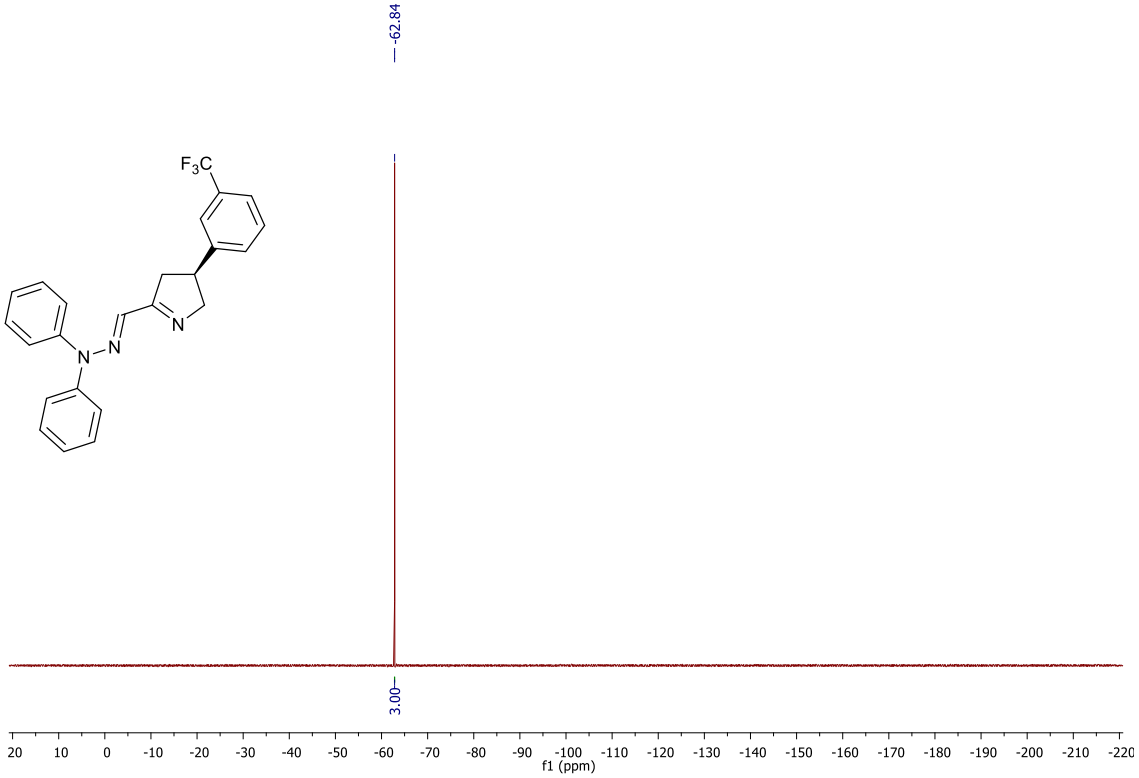
^{1}H NMR (300 MHz, CD_2Cl_2) of (*S*)-**7c**



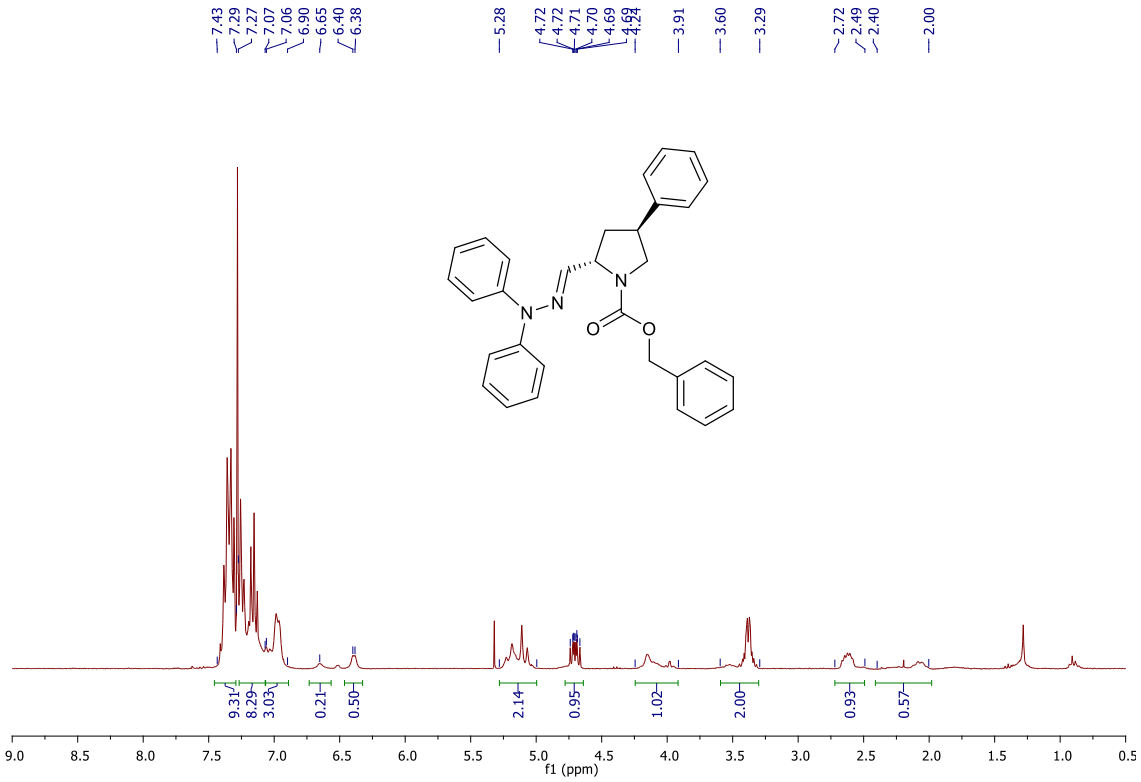
^{13}C NMR (75.5 MHz, CD_2Cl_2) of (*S*)-**7c**



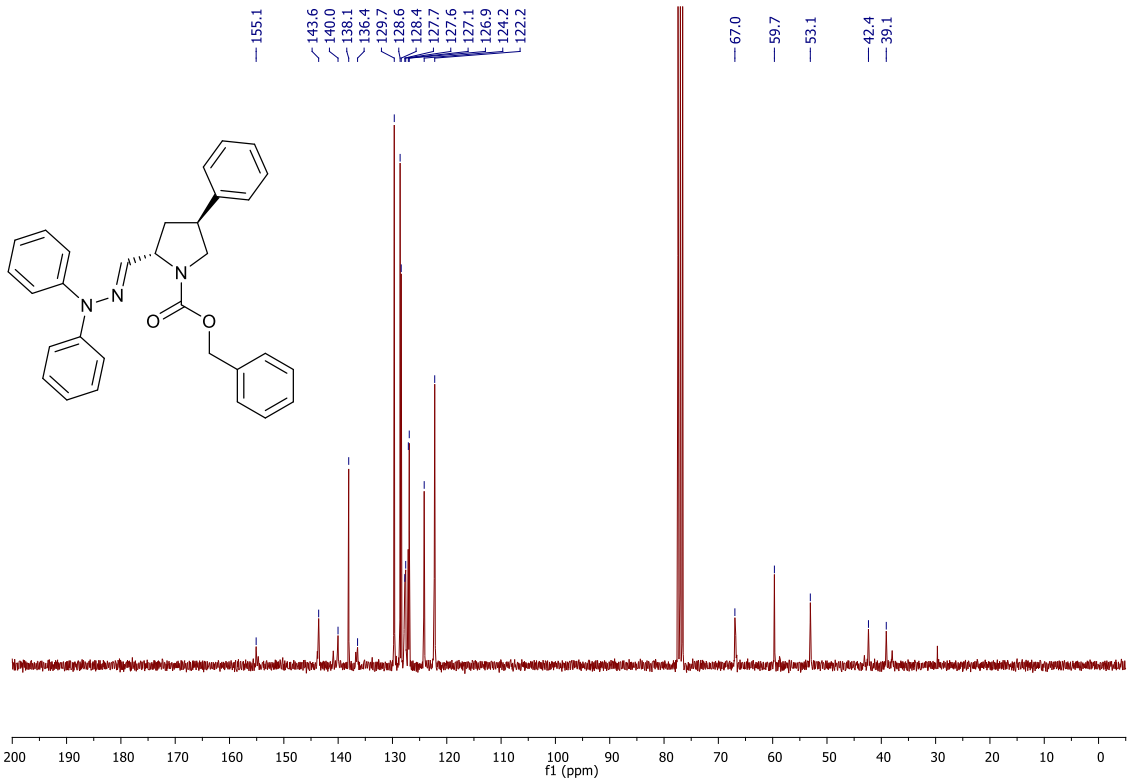
^{19}F NMR (471 MHz, CD_2Cl_2) of (*S*)-**7c**



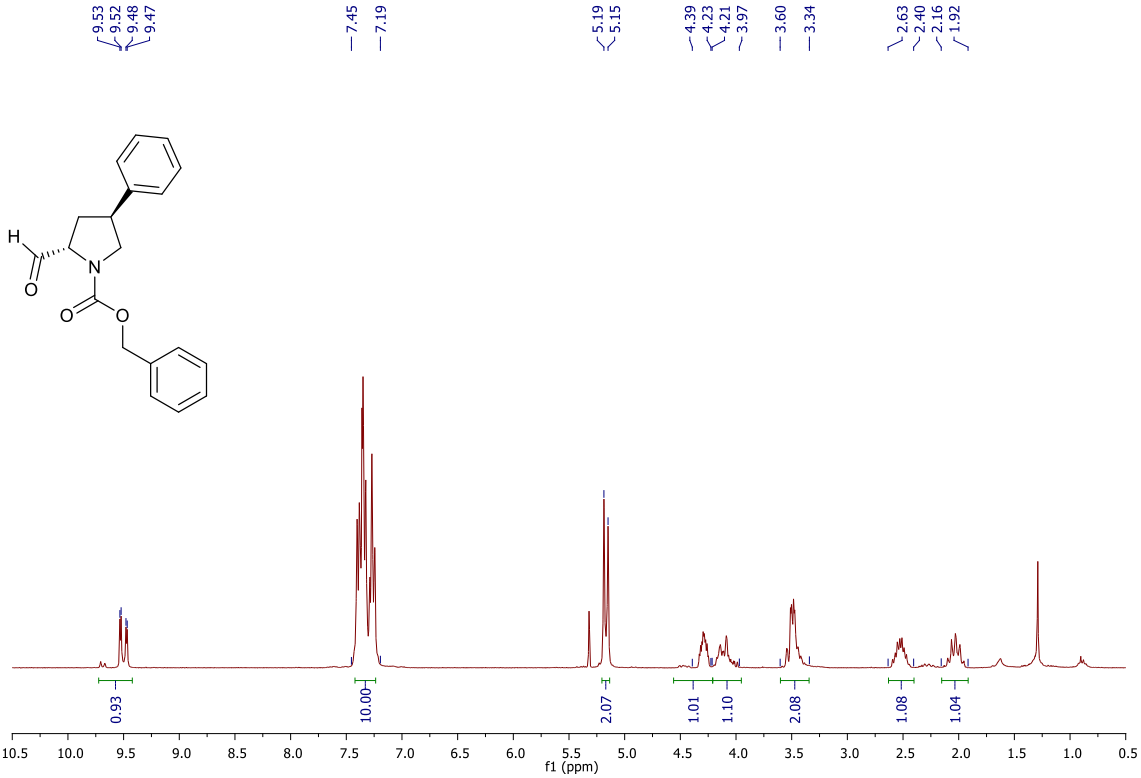
^{1}H NMR (300 MHz, $CDCl_3$) of (*S*,*S*)-**8**



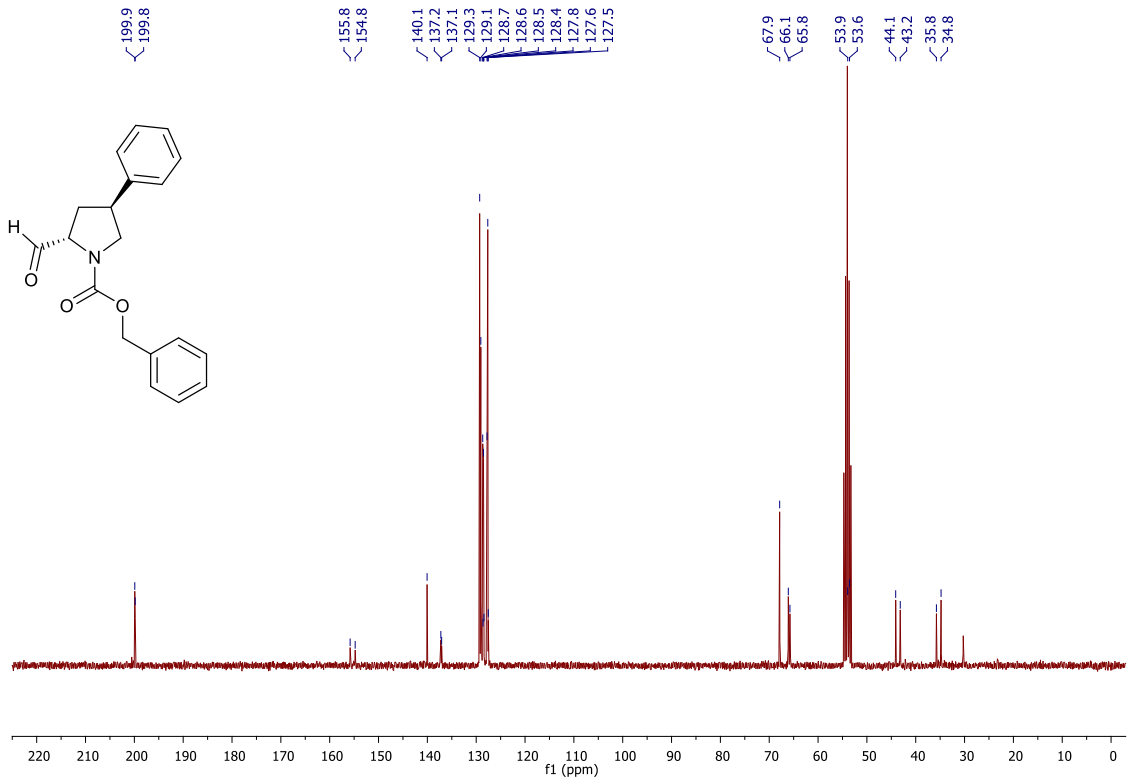
^{13}C NMR (75.5 MHz, $CDCl_3$) of (*S*,*S*)-**8**



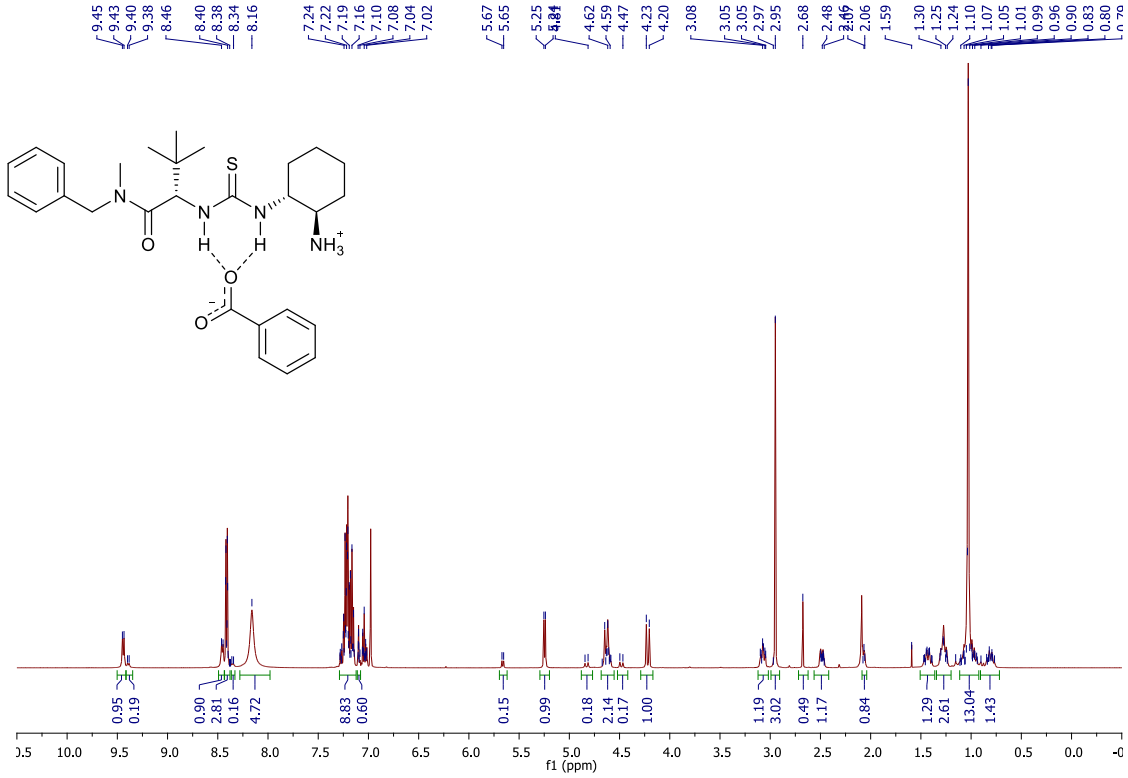
^{1}H NMR (300 MHz, CD_2Cl_2) of (*S*,*S*)-**9**



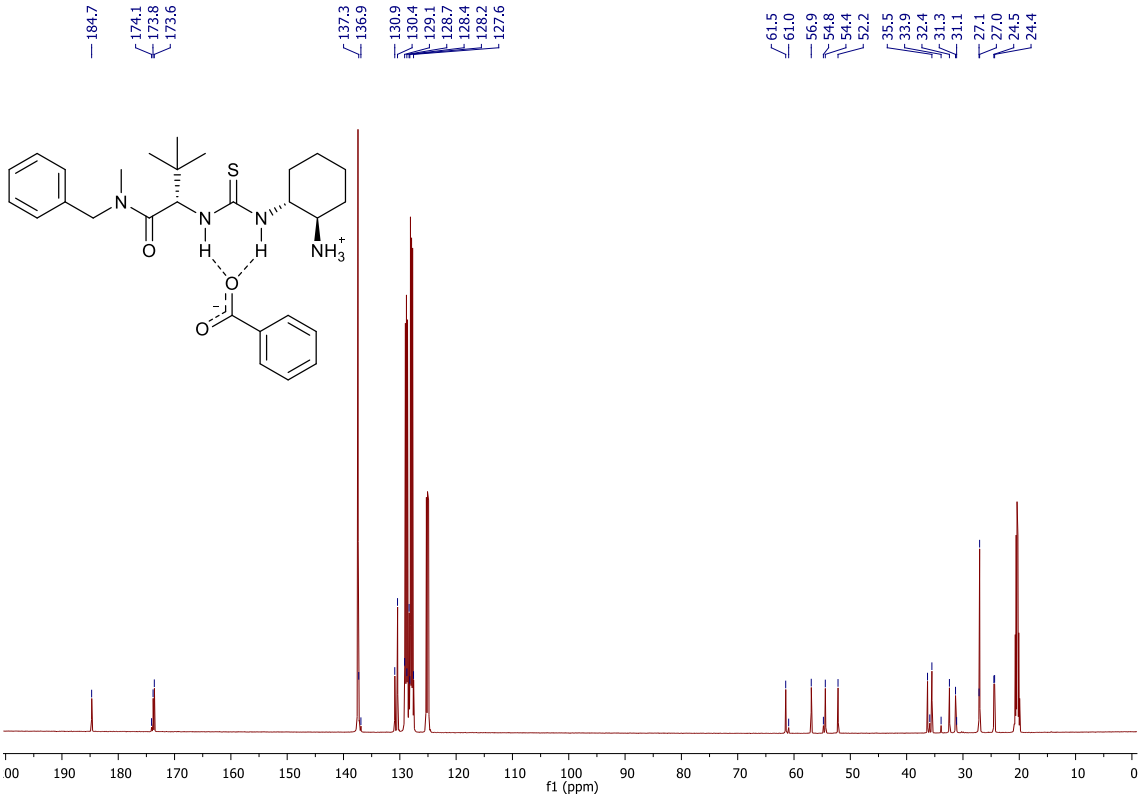
^{13}C NMR (75.5 MHz, CD_2Cl_2) of (*S*,*S*)-**9**



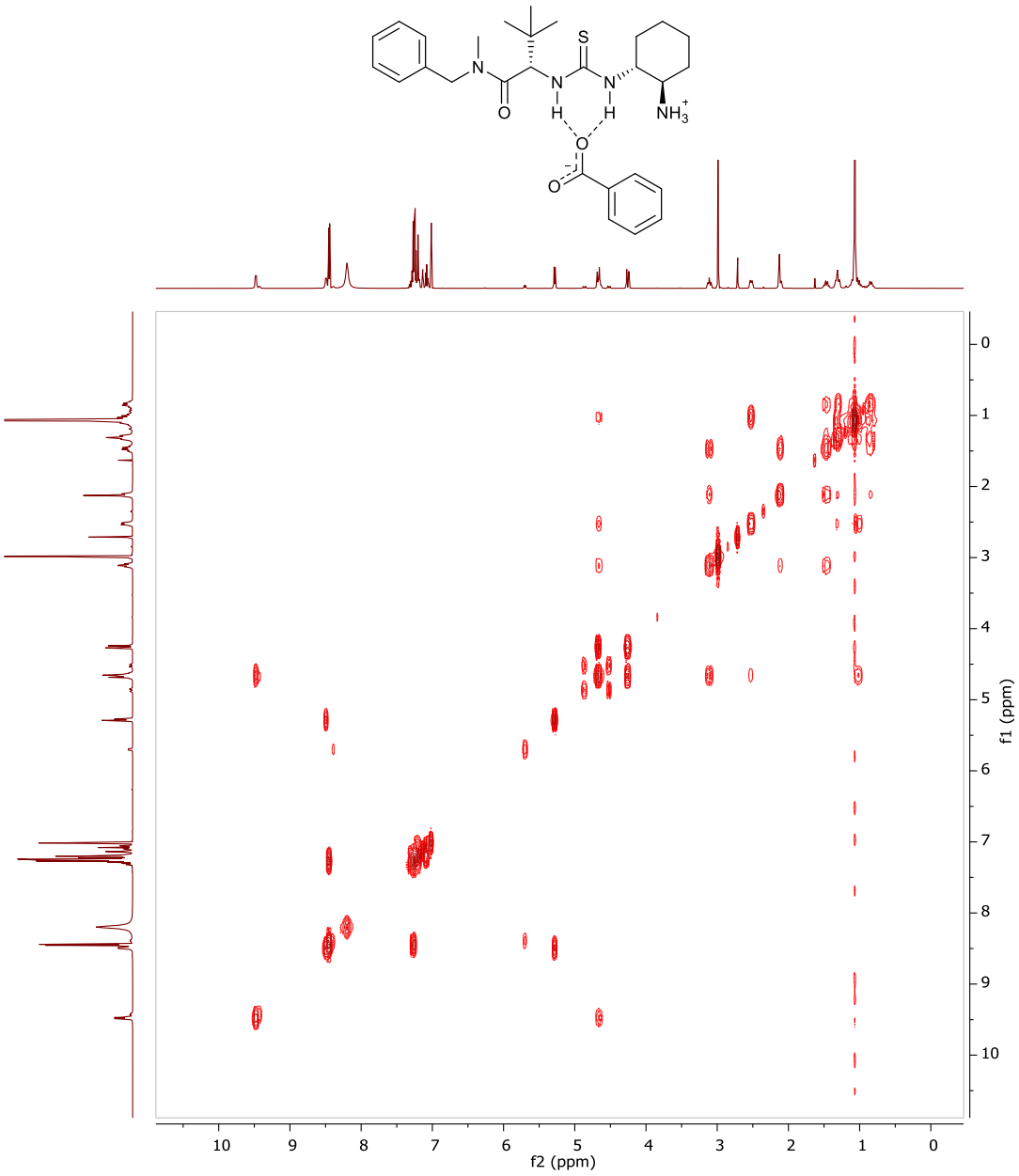
^{1}H NMR (500 MHz, toluene-d_8) of **Ia** + PhCOOH complex



^{13}C NMR (126 MHz, toluene-d_8) of **Ia** + PhCOOH complex



COSY (toluene-d_8) of **Ia** + PhCOOH complex



HSQC (toluene-d_8) of **Ia** + PhCOOH complex