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Supplementary Information

Brønsted Acid Catalysis of Photosensitized Cycloadditions

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Table of Contents

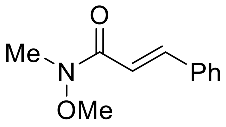
1. General Information

Reagent Preparation: MeCN, THF, CH_2Cl_2, and toluene were purified by elution through alumina as described by Grubbs.[1] Acetic acid, chloroacetic acid, trifluoroacetic acid, *p*-toluenesulfonic acid monohydrate, and $Ru(bpy)_3Cl_2$•$6H_2O$ were purchased from Sigma Aldrich and used without further purification. All styrenes, 2,3-dimethylbutadiene, phenyl vinyl sulfide, methylenecyclopentane, and indene were purchased from Sigma Aldrich and distilled prior to use. Unless indicated below, all other compounds or solvents were purchased and used as received. Manual flash-column chromatography (FCC) was performed with Silicycle 40-63 Å (230-40 mesh) silica. Automated flash-column chromatography was performed with a Teledyne ISCO CombiFlashR_f+ Lumen system. Photochemical reactions were carried out with a 15 W EagleLight PAR38 blue LED flood light (500 lumens) unless otherwise indicated.

Product Characterization: Diastereomer ratios for reactions were determined by ^{1}H NMR analysis of crude reaction mixtures vs. a phenanthrene internal standard. ^{1}H and ^{13}C NMR data were obtained using a Bruker Avance-500 spectrometer with DCH cryoprobe and are referenced to tetramethylsilane (0.0 ppm) and $CDCl_3$ (77.0 ppm), respectively. This instrument and supporting facilities are funded by Paul J. Bender, Margaret M. Bender, and the University of Wisconsin. ^{19}F NMR data were obtained using Bruker Avance-400 spectrometer. This instrument and supporting facilities are funded by the NSF (CHE-1048642) and the University of Wisconsin. NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sext = sextet, sept = septet, m = multiplet), coupling constant(s) in Hz, integration. NMR spectra were obtained at 298 K unless otherwise noted. FT-IR spectra were obtained using a Bruker Tensor 27 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Melting points (mp) were obtained using a Stanford Research Systems DigiMelt MPA160 melting point apparatus and are uncorrected. Mass spectrometry was performed with a Thermo Q Exactive™ Plus using ESI-TOF (electrospray ionization-time of flight). This instrument and supporting facilities are funded by the NIH (1S10 OD020022-1) and the University of Wisconsin.

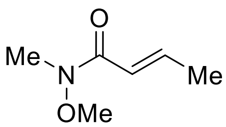
2. Substrate Synthesis

N-Methoxy-N-methylcinnamide: A flame-dried 50 mL round bottom flask (RBF) was charged with



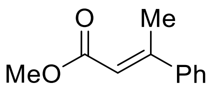
cinnamoyl chloride (8.64 g, 52.0 mmol, 1.0 equiv.) and *N,O*-dimethylhydroxylamine hydrochloride (5.34 g, 54.7 mmol, 1.05 mmol) in dry CH_2Cl_2 (150 mL). The mixture was cooled to 0 °C and pyridine (9.20 mL, 114.4 mmol, 2.2 equiv.) added slowly. The reaction was then warmed to room temperature and stirred overnight. Then 1 M HCl was added, the organic layer separated, and the aqueous layer extracted with additional EtOAc (3x25 mL). The combined organics were washed with sat. aq. $NaHCO_3$ (25 mL) and sat. aq. NaCl (25 mL). After drying over Na_2SO_4, the crude material was concentrated. Purification by FCC (1:1 Et_2O/pentanes) gave 8.14 g (42.6 mmol, 82% yield) of a viscous oil which solidified after extended drying on high-vacuum. The compound was consistent with reported spectroscopic data.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 15.9 Hz, 1H), 7.59–7.56 (m, 2H), 7.41–7.36 (m, 3H), 7.04 (d, *J* = 15.9 Hz, 1H), 3.77(s, 3H), 3.32 (s, 3H).

N-Methoxy-N-methylcrotonamide: A flame-dried 250 mL RBF was charged with crotonoyl chloride



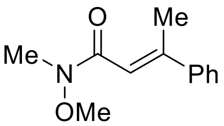
(4.79 mL, 50.0 mmol, 1.0 equiv.) and *N,O*-dimethylhydroxylamine hydrochloride (5.15 g, 52.5 mmol, 1.05 mmol) in dry CH_2Cl_2 (100 mL). The mixture was cooled to 0 °C and pyridine (8.90 mL, 33.0 mmol, 2.2 equiv.) added slowly. The resulting slurry was warmed to room temperature and stirred overnight. Subsequently, 1 M HCl was added and the resulting biphase separated and the aqueous layer extracted with EtOAc (50 mL). The combined organics were washed with sat. aq. $NaHCO_3$ (50 mL) and sat. aq. NaCl (50 mL). After drying over Na_2SO_4, the crude material was concentrated. Purification by FCC (1:1 EtOAc/hexanes) gave 2.48 g (19.0 mmol, 38% yield) of a viscous oil. The compound was consistent with reported spectroscopic data.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (dq, *J* = 15.3, 6.9 Hz, 1H), 6.42 (dq, *J* = 15.3, 1.6 Hz, 1H), 3.70 (s, 3H), 3.24 (s, 3H), 1.91 (dd, *J* = 6.9, 1.6 Hz, 3H).

(*E*)-Methyl 3-phenylbut-2-enoate: A flame-dried 100 mL RBF was charged with phenylboronic acid



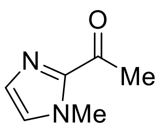
(1.22 g, 10.0 mmol, 1.0 equiv.), Pd(OAc)2 (45.0 mg, 0.2 mmol, 0.02 equiv.), and 1,3-bis(diphenylphosphino)propane (dPPP)(123.7 mg, 0.3 mmol, 0.03 equiv.). The flask was purged with N_2 and dry acetone (30 mL) added, followed by methyl crotonate (2.1 mL, 20.0 mmol, 2.0 equiv.) and trifluoroacetic acid (0.23 mL, 3.0 mmol, 0.3 equiv.). The light orange solution was heated to reflux (70 °C). After 30 minutes, the solution had become an intense blood-red color. The reflux was continued for 20 h. Upon cooling the reaction mixture to room temperature, the solvent was removed *via* rotary evaporation. The residue was taken up in CH_2Cl_2 (30 mL), washed once with H_2O (10 mL), dried over Na_2SO_4, and concentrated. The crude orange oil was purified by FCC (gradient 1:49 to 1:24 Et_2O/pentanes) to give 850 mg (4.8 mmol, 48% yield) of a colorless oil. The compound was consistent with reported spectroscopic data.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2H), 7.40–7.35 (m, 3H), 6.14 (q, *J* = 1.3 Hz, 1H), 3.76 (s, 3H), 2.58 (d, *J* = 1.3 Hz, 3H).

(E)-N-Methyl-N-methoxy-3-phenylbut-2-enamide: A flame dried 25-mL RBF was charged with (E)-



Methyl 3-phenylbut-2-enoate (529 mg, 3.0 mmol, 1.0 equiv.), *N,O*-dimethylhydroxylamine hydrochloride (585 mg, 6.0 mmol, 2.0 equiv.), and dry THF (5 mL). This suspension was cooled to 0 °C and iPrMgCl (2.0 M in THF) (6 mL, 12.0 mmol, 4.0 equiv.) added over ~20 min. At this point, the reaction was stirred at 0 °C for 1 hour, then slowly quenched by sat. aq. NH_4Cl. The reaction mixture was transferred to a separatory funnel with EtOAc (80 mL) and H_2O added (10 mL). The organic layer was separated and the aqueous washed with EtOAc (2x10 mL). The combined organics were washed with sat. aq. NaCl (20 mL), dried over Na_2SO_4, and concentrated. The residue was purified by FCC (1:1 Et_2O/pentanes) to give 553 mg (2.7 mmol, 90% yield) of a viscous oil. The compound was consistent with reported spectroscopic data.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.46 (m, 2H), 7.40–7.33 (m, 3H), 6.57 (s, 1H), 3.71 (s, 3H), 3.27 (s, 3H), 2.53 (d, *J* = 1.2 Hz, 3H).

2-Acetyl-1-methylimidazole: A solution of 1-methylimidazole (0.84 mL, 10.5 mmol, 1.05 equiv.) in

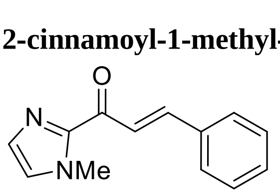


dry THF (25 mL) was prepared in a flame-dried 100 mL RBF. After cooling to –78 °C, recently titrated nBuLi (5.5 mL, 1.91 M in hexanes, 10.5 mmol, 1.05 equiv.) was added portionwise. The reaction was warmed to 0 °C for 30 minutes before returning to –78 °C. A solution of 4-acetylmorpholine (1.15 mL, 10.0 mmol, 1.0 equiv.) in THF (25 mL) was prepared in a flame-dried 50 mL conical bottom flask and added to the solution of deprotonated 1-methylimidazole *via* cannula. The reaction was warmed to room temperature and stirred overnight. The solution was then stirred vigorously and glacial acetic acid (2 mL) added dropwise. This was transferred to separatory funnel with EtOAc (100 mL), the washed with sat. aq. $NaHCO_3$ (30 mL) and sat. aq. NaCl (30 mL). Each wash was back-extracted with additional EtOAc (1x30 mL). The combined organics were dried over Na_2SO_4 and concentrated. Purification by FCC (2:3 EtOAc/pentanes) gave 700 mg (5.6 mmol, 56% yield) of a colorless oil. The compound was consistent with reported spectroscopic data.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 1H), 7.03 (s, 1H), 4.00 (s, 3H), 2.66 (s, 3H).

General Method A for the Preparation of Cinnamoyl Methylimidazole Derivatives: A flame-dried RBF was charged with *N*-methylimidazole (1.05 equiv.) and dry THF, then cooled to –78 °C. Recently titrated nBuLi (in hexanes, 1.05 equiv.) was added portionwise. The reaction was warmed to 0 °C for 30 minutes, then returned to –78 °C. A solution of the Weinreb amide (1.0 equiv.) in THF was prepared in a flame-dried conical bottom flask and added to the solution of deprotonated 1-methylimidazole *via* cannula. The reaction was warmed to room temperature and stirred overnight. The resulting solution was stirred vigorously and glacial acetic acid added dropwise. This solution was transferred to separatory funnel with EtOAc and shaken with water. The organic layer was separated and the aqueous extracted with additional EtOAc (2-3x). The combined organics were washed with sat. aq. $NaHCO_3$ and sat. aq. NaCl, dried over Na_2SO_4, and concentrated. Products were purified as indicated below.

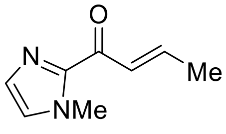
General Method B for the Preparation of Cinnamoyl Methylimidazole Derivatives: A RBF was charged with 2-acetyl-1-methylimidazole (1.0 equiv.), EtOH, and H_2O. This solution was sparged briefly with N_2 (~5 minutes). Freshly distilled aromatic aldehyde (1.0-1.1 equiv.) was then added to the solution, followed by a catalytic quantity of KOH. This was then stirred under N_2 for 12-16 h (overnight). The crude reaction mixture was then diluted with CH_2Cl_2 and transferred to separatory funnel and shaken with H_2O. The organic layer was separated and the aqueous extracted with additional CH_2Cl_2 (2-3x). The combined organics were dried over Na_2SO_4 and concentrated. The resulting solids were usually quite pure by ^{1}H NMR. Purification by FCC was performed with 1:1 Et_2O/pentanes.

2-cinnamoyl-1-methyl-1*H*-imidazole (1): Prepared using general method A using 1-methylimidazole



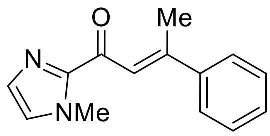
(0.71 mL, 8.93 mmol, 1.05 equiv.) and nBuLi (3.6 mL, 2.50 M in hexanes, 8.93 mmol, 1.05 equiv.) in THF (30 mL), and *N*-methoxy-*N*-methylcinnamide (1.62 g, 8.50 mmol, 1.0 equiv.) in THF (10 mL). Purified by flash column chromatography with 1:1 Et_2O/pentanes. Yield: 1.32 g (6.2 mmol, 73% yield) of an off-white solid. The compound was consistent with reported spectroscopic data.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 16.0 Hz, 1H), 7.83 (d, *J* = 16.0 Hz, 1H), 7.72–7.68 (m, 2H), 7.43–7.38 (m, 3H), 7.23 (s, 1H), 7.09 (s, 1H), 4.10 (s, 3H).

2-crotonoyl-1-methyl-1*H*-imidazole: Prepared using general method A using 1-methylimidazole

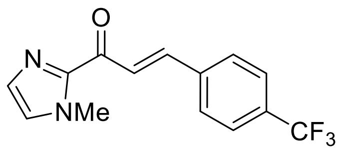


(1.51 mL, 18.9 mmol, 1.05 equiv.) and nBuLi (10.6 mL, 1.78 M in hexanes, 18.9 mmol, 1.05 equiv.) in THF (50 mL), and *N*-methoxy-*N*-methylcrotonamide (2.32 g, 18.0 mmol, 1.0 equiv.) in THF (50 mL). Purified by flash column chromatography with 1:9 EtOAc/pentanes. Yield: 1.28 g (8.5 mmol, 47% yield) of a colorless oil. The compound was consistent with reported spectroscopic data.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dq, *J* = 15.6, 1.6 Hz, 1H), 6.18 (s, 1H), 7.13 (dq, *J* = 15.6, 6.9 Hz, 1H), 7.05 (s, 1H), 4.05 (s, 3H), 1.99 (dd, *J* = 6.9, 1.6 Hz, 3H).

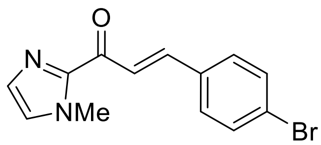
2-(3-methylcinnamoyl)-1-methyl-1*H*-imidazole: Prepared using general method A using 1-methylimidazole (0.18 mL, 2.2 mmol, 1.05 equiv.) and nBuLi (1.4 mL, 1.6 M in hexanes, 2.2 mmol, 1.05 equiv.) in THF (10 mL), and (*E*)-*N*-Methyl-*N*-methoxy-3-phenylbut-2-enamide (431 mg, 2.1 mmol, 1.0 equiv.) in THF (2 mL). Purified by flash column chromatography with 1:1 Et2O/pentanes. Yield: 280 mg (1.2 mmol, 59% yield) of an off-white solid (mp = 71 – 73 °C). ν_{max} (film) / cm^{-1} 2954, 1648, 1596, 1447, 1403, 1291, 1224, 1155, 1039, 947, 917, 850. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (q, *J* = 1.2 Hz, 1H), 7.64–7.61 (m, 2H), 7.42–7.36 (m, 3H), 7.16 (s, 1H), 7.02(s, 1H), 4.09 (s, 3H), 2.68 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.11, 156.00, 144.98, 142.67, 129.18, 128.72, 128.44, 126.81, 126.71, 121.81, 36.50, 18.52. HRMS (ESI) calculated for $[C_{14}H_{15}N_2O]^+$ ($M+H^+$) - requires *m/z* 227.1179, found 227.1175.



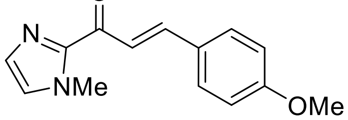
(*E*)-3-(4-trifluoromethylphenyl)-1-(1-methyl-1*H*-imidazol-2-yl)prop-2-en-1-one: Prepared using general method B using 2-acetyl-1-methylimidazole (328.0 mg, 3.0 mmol, 1.0 equiv.), 4-trifluoromethylbenzaldehyde (0.45 mL, 3.3 mmol, 1.1 equiv.), KOH (½ pellet, ~25 mg), EtOH (12 mL), and H_2O (6 mL). Purified by flash column chromatography with 1:1 Et_2O/pentanes. Yield: 442 mg (1.59 mmol, 53% yield) of an off-white solid (mp = 85 – 88 °C). ν_{max} (film) / cm^{-1} 1663, 1610, 1403, 1320, 1280, 1163, 1108, 1067, 1015, 984, 956, 919, 831. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 16.0 Hz, 1H), 7.81 (d, *J* = 16.0 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.24 (s, 1H), 7.11 (s, 1H), 4.11 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.98, 143.85, 141.21, 138.28 (q, *J* = 1.3 Hz), 131.74 (q, *J* = 32.7 Hz), 129.58, 128.74, 127.59, 125.78 (q, *J* = 3.8 Hz), 125.08, 123.87 (q, *J* = 272.4 Hz), 36.40. ^{19}F NMR (337 MHz, $CDCl_3$) δ –62.82. HRMS (ESI) calculated for $[C_{14}H_{12}F_3N_2O]^+$ ($M+H^+$) requires *m/z* 281.0896, found 281.0890.



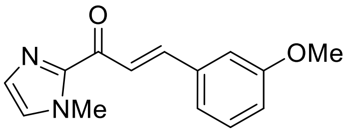
(*E*)-3-(4-bromophenyl)-1-(1-methyl-1*H*-imidazol-2-yl)prop-2-en-1-one: Prepared using general method B using 2-acetyl-1-methylimidazole (377.9 mg, 3.0 mmol, 1.0 equiv.), 4-bromobenzaldehyde (558.0 mg, 3.0 mmol, 1.0 equiv.), KOH (1 pellet, ~50 mg), and EtOH (6 mL). Purified by flash column chromatography with 1:1 Et_2O/pentanes. Yield: 561 mg (1.92 mmol, 64% yield) of an off-white solid. The compound was consistent with reported spectroscopic data.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 16.0 Hz, 1H), 7.74 (d, *J* = 16.0 Hz, 1H), 7.57–7.52 (m, 4H), 7.22 (s, 1H), 7.09 (s, 1H), 4.10 (s, 3H).



(*E*)-3-(4-methoxyphenyl)-1-(1-methyl-1*H*-imidazol-2-yl)prop-2-en-1-one: Prepared using general method B using 2-acetyl-1-methylimidazole (372.7 mg, 3.0 mmol, 1.0 equiv.), 4-methoxybenzaldehyde (0.26 mL, 3.0 mmol, 1.0 equiv.), KOH (½ pellet, ~25 mg), and EtOH (6 mL). Purified by flash column chromatography with 1:1 Et_2O/pentanes. Yield: 382 mg (1.59 mmol, 53% yield) of an off-white solid. The compound was consistent with reported spectroscopic data.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 15.9 Hz, 1H), 7.80 (d, *J* = 15.9 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.21 (s, 1H), 7.07 (s, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 4.10 (s, 3H), 3.85 (s, 3H).

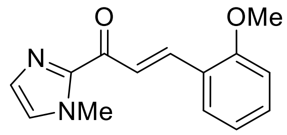


(*E*)-3-(3-methoxyphenyl)-1-(1-methyl-1*H*-imidazol-2-yl)prop-2-en-1-one: Prepared using general



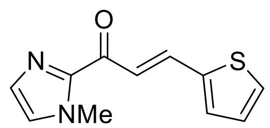
method B using 2-acetyl-1-methylimidazole (327.4 mg, 3.0 mmol, 1.0 equiv.), 3-methoxybenzaldehyde (0.41 mL, 3.3 mmol, 1.1 equiv.), KOH (½ pellet, ~25 mg), EtOH (12 mL), and H_2O (6 mL). Purified by flash column chromatography with 1:1 Et_2O/pentanes. Yield: 531 mg (2.19 mmol, 73% yield) of an off-white solid (mp = 91 – 94 °C). ν_{max} (film) / cm^{-1} 2957, 1658, 1601, 1464, 1400, 1287, 1249, 1156, 1081, 1020, 992, 918, 838.0. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 16.1 Hz, 1H), 7.80 (d, *J* = 16.1 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.28 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.23 (s, 1H), 7.21 (t, *J* = 1.8 Hz, 1H), 7.09 (s, 1H), 6.95 (ddd, *J* = 7.8 2.4, 1.2 Hz, 1H), 4.10 (s, 1H), 3.86 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.46, 159.89 144.03, 143.42, 136.27, 129.80, 129.32, 127.30, 122.90, 121.76, 116.80, 112.95, 55.40, 36.40. HRMS (ESI) calculated for $[C_{14}H_{15}N_2O_2]^+$ (M+H^+) requires *m/z* 243.1128, found 243.1125.

(*E*)-3-(2-methoxyphenyl)-1-(1-methyl-1*H*-imidazol-2-yl)prop-2-en-1-one: Prepared using general



method B using 2-acetyl-1-methylimidazole (499.6 mg, 4.0 mmol, 1.0 equiv.), 2-methoxybenzaldehyde (0.41 mL, 4.4 mmol, 1.1 equiv.), KOH (½ pellet, ~25 mg), and EtOH (8 mL). Purified by flash column chromatography with 1:1 Et_2O/pentanes. Yield: 877 mg (3.6 mmol, 90% yield) of an off-white solid (mp = 136 – 139°C). The compound **not consistent** with reported spectroscopic data[7], and therefore is independently characterized here.[8] ν_{max} (film) / cm^{-1} 2944, 1654, 1593, 1464, 1401, 1314, 1289, 1245, 1157, 1051, 1019, 920, 810. ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 16.2 Hz, 1H), 8.09 (d, *J* = 16.2 Hz, 1H), 7.76 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.37 (ddd, *J* = 8.9, 7.6, 1.6 Hz, 1H), 7.21 (s, 1H), 7.07 (s, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 8.9 Hz, 1H), 4.10 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.91, 158.73, 144.23, 138.48, 131.77, 129.18, 128.62, 127.04, 123.95, 122.83, 120.63, 111.11, 55.56, 36.37. HRMS (ESI) calculated for $[C_{14}H_{15}N_2O_2]^+$ (M+H^+) requires *m/z* 243.1128, found 243.1124.

(*E*)-1-(1-methyl-1*H*-imidazol-2-yl)-3-(thiophen-2-yl)prop-2-en-1-one: Prepared using general

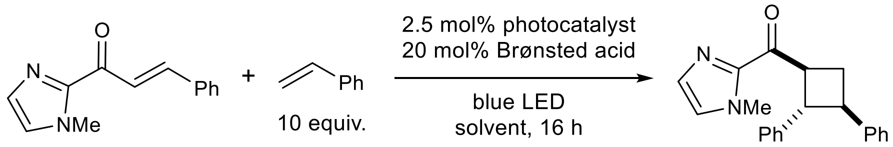


method B using 2-acetyl-1-methylimidazole (280.0 mg, 2.25 mmol, 1.0 equiv.), 2-thiophenecarboxaldehyde (0.23 mL, 3.0 mmol, 1.0 equiv.), KOH (1 pellet, ~50 mg), and EtOH (5 mL). Purified by flash column chromatography with 1:1 Et_2O/pentanes. Yield: 250 mg (1.15 mmol, 51% yield) of an off-white solid. The compound was consistent with reported spectroscopic data.[7] ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 15.7 Hz, 1H), 7.84 (d, *J* = 15.7 Hz, 1H), 7.42 (d, *J* = 5.0 Hz, 1H), 7.38 (d, *J* = 3.5 Hz, 1H), 7.22 (s, 1H), 7.08 (s, 1H), 7.08 (dd, *J* = 5.0, 3.5 Hz, 1H), 4.09 (s, 3H).

3. Optimization and Additional Experiments

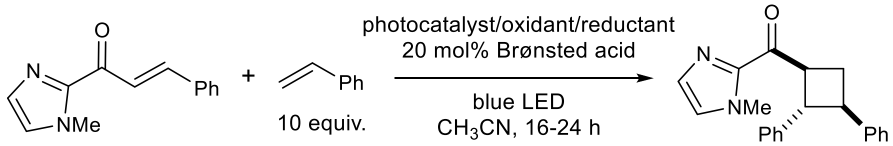
Experiments for Optimization/Control Studies: Reactions carried out for optimization purposes were carried on a small scale (0.1 mmol). A representative procedure follows. An oven-dried 2 dram vial with a stir bar was charged with cinnamoyl imidazole (0.10 mmol, 1.0 equiv.), *p*-toluenesulfonic acid monohydrate (0.02 mmol, 0.2 equiv.), and $Ru(bpy)_3Cl_2•6H_2O$ (0.0025 mmol, 0.025 equiv.). These were dissolved in MeCN (2 mL, 0.05 M in cinnamoyl imidazole) before addition of styrene (1.0 mmol, 10.0 equiv.). The solution was sealed with a septum and degassed by bubbling dry N_2 through the solution for 10 minutes. The septum was additionally covered with parafilm and the reaction mixture subjected to irradiation by a blue LED lamp for 16-24 h. The resulting mixture was then diluted with 4 mL of reagent grade Et_2O and passed through a short plug of silica to remove the photocatalyst. Phenanthrene (approx. 0.1 mmol) was added to the mixture for preliminary analysis by ^1H NMR and the solvent removed under reduced pressure. NOTE: All results obtained for both Table S1 and S2 were prepared using this general approach, though the specific reagents/quantities do differ. All oxidants and reductants used in Table S2 were used as received, excluding SmI_2, which was prepared according to Proctor.[9]

Table S1. Optimization Experiments



Entry	Photocatalyst	Acid	Solvent	Yield	d.r.
1	$Ru(bpy)_3Cl_2$	none	CH_3CN	11%	2:1
2	$Ru(bpy)_3Cl_2$	CH_3CO_2H	CH_3CN	17%	2:1
3	$Ru(bpy)_3Cl_2$	$ClCH_2CO_2H$	CH_3CN	28%	2:1
4	$Ru(bpy)_3Cl_2$	CF_3CO_2H	CH_3CN	68%	2:1
5	$Ru(bpy)_3Cl_2$	*p*-TsOH	CH_3CN	75%	2:1
6	none	none	CH_3CN	0%	-
7	none	*p*-TsOH	CH_3CN	trace	-
8	$Ru(bpy)_3(PF_6)_2$	*p*-TsOH	CH_2Cl_2	70%	2:1

Table S2. Control Experiments



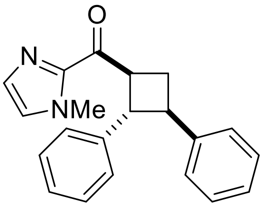
Entry	Photocatalyst/Oxidant/Reductant	Acid	Time	Yield	d.r.
1	$Ru(deeb)_3(PF_6)_2$ (2.5 mol%)	*p*-TsOH	24 h	51%	2:1
2	Benzil (100 mol%)	*p*-TsOH	16 h	57%	2:1
3	Benzil (100 mol%)	none	16 h	69%	2:1
4	TDAE or $Co(Cp)_2$ or SmI_2 (100 mol%)	*p*-TsOH	24 h	0%	-
5	CAN, $Mn(OAc)_3$, $Fe(acac)_3$ (100 mol%)	*p*-TsOH	24 h	0%	-

TDAE = tetrakis(dimethylamino)ethylene, CAN = cerium ammonium nitrate

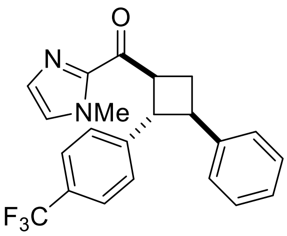
4. [2+2] Photocycloaddition Reactions

Isolation Scale Experiments: An oven-dried Schlenk tube with a stir bar was charged with cinnamoyl imidazole (0.40 mmol, 1 equiv.), *p*-toluenesulfonic acid monohydrate (0.08 mmol, 0.2 equiv.), and Ru(bpy)$_3$Cl$_2$•6H$_2$O (0.01 mmol, 0.025 equiv.). These were dissolved in dry MeCN (8 mL, 0.05 M in cinnamoyl imidazole) before addition of alkene (4.0 mmol, 10 equiv.). The Schlenk tube was then sealed with a glass stopper and degassed *via* freeze-pump-thaw technique (3 x 5 minutes). Following the final thaw, the reaction mixture was subjected to irradiation by a blue LED lamp for 24 h. The resulting mixture was then diluted with 10-12 mL of Et$_2$O and passed through a short plug of silica to remove the photocatalyst. Phenanthrene (0.1 mmol) was added to the mixture for preliminary analysis by ^{1}H NMR and the solvent removed under reduced pressure. After recombining the NMR sample, the residue was purified by FCC with 1:1 Et2O/pentanes to give a mixture of diastereomers. For most reactions, these diastereomers could be further separated through additional purification – for specifics see each reaction.

(2,3-diphenylcyclobutyl)(1-methyl-1H-imidazol-2-yl)methanone (2): Prepared according to general procedure for isolation scale experiments using 84.6 mg (0.4 mmol) 2-cinnamoyl-1-methyl-1*H*-imidazole, 15.1 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 7.4 mg (0.01 mmol) Ru(bpy)$_3$Cl$_2$•6H$_2$O, and 0.45 mL (4.0 mmol) styrene in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et$_2$O/pentanes to give 86 mg (0.27 mmol, 68% yield) of two diastereomers (1.8:1 d.r.). Separation of diastereomers for characterization purposes was achieved by automated FCC (ISCO) using a continuous gradient of 15% → 100% EtOAc in hexanes. Major Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 3027, 2932, 2360, 1666, 1602, 1495, 1456, 1409, 1290, 1235, 1155, 1077, 1022, 947, 913, 855, 754, 698, 662. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31–7.25 (m, 8 H), 7.23–7.16 (m, 2H), 7.15 (d, *J* = 0.8 Hz, 1H), 7.04 (s, 1H), 4.57 (td, *J* = 9.8, 8.7 Hz, 1H), 4.08 (t, *J* = 9.8 Hz, 1H), 4.03 (s, 3H), 3.63 (td, *J* = 10.1, 8.1 Hz), 2.83 (dt, *J* = 10.3, 8.5 Hz, 1H), 2.31 (q, *J* = 10.2 Hz, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 192.44, 143.58, 142.63, 142.52, 129.40, 128.38, 128.36, 127.25, 126.96, 126.94, 126.42 (2C), 48.56, 44.97, 43.48, z36.18, 31.92. HRMS (ESI) calculated for $[C_{21}H_{21}N_2O]^+$ (M+H$^+$) requires *m/z* 317.1648, found 317.1646. Minor Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 3027, 1666, 1495, 1455, 1406, 1289, 1229, 1154, 1030, 913, 838, 734, 696, 634. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.18 (d, *J* = 0.8 Hz, 1H), 7.14–7.02 (m, 8H), 6.99–6.98 (m, 3H), 5.05 (q, *J* = 9.0 Hz, 1H), 4.47 (t, *J* = 9.3 Hz, 1H), 4.04 (s, 3H), 4.03–3.96 (m, 1H), 2.78–2.74 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 193.05, 142.57, 140.74, 139.62, 129.40, 128.23, 127.93, 127.84, 127.64, 127.34, 125.80, 125.78, 45.75, 43.74, 41.96, 36.24, 28.61. HRMS (ESI) calculated for $[C_{21}H_{21}N_2O]^+$ (M+H$^+$) requires *m/z* 317.1648, found 317.1646.

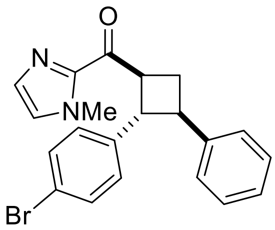


(1-methyl-1H-imidazol-2-yl)(3-phenyl-2-(4-(trifluoromethyl)phenyl)cyclobutyl)methanone (3): Prepared according to general procedure for isolation scale experiments using 113.2 mg (0.4 mmol) (E)-3-(4-trifluoromethylphenyl)-1-(1-methyl-1*H*-imidazol-2-yl)prop-2-en-1-one, 13.0 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 7.8 mg (0.01 mmol) Ru(bpy)$_3$Cl$_2$•6H$_2$O, and 0.48 mL (4.0 mmol) styrene in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et$_2$O/pentanes to give 91 mg (0.24 mmol, 60% yield) of two diastereomers (1.8:1 d.r.). Separation of diastereomers for characterization purposes was achieved by automated FCC (ISCO) using a continuous gradient of 15% → 100% EtOAc in hexanes. Major Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2950, 1667, 1619, 1409, 1325, 1236, 1163, 1117, 1068, 1018, 912, 858, 775, 699, 666. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.34–2.29 (m, 4H), 7.23 (tt, *J* = 6.8, 1.9 Hz, 1H), 7.16 (d, *J* = 0.8 Hz, 1H), 7.07 (s, 1H), 4.57 (td, *J* = 9.8, 8.7 Hz, 1H), 4.11 (t, *J* = 9.9 Hz, 1H), 3.62 (td, 9.9, 8.5 Hz), 2.85 (dt, *J* = 10.2, 8.5 Hz, 1H), 2.37 (q, *J* = 10.3 Hz). ^{13}C NMR (125

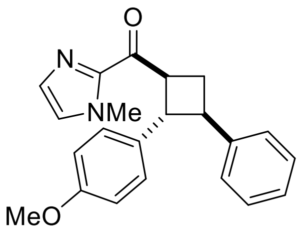


MHz, $CDCl_3$) δ 191.94, 146.46 (q, *J* = 1.2 Hz), 142.98, 142.45, 129.54, 128.53, 127.46, 127.24, 126.91, 126.70, 125.33 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 271.7 Hz), 48.38, 44.72, 43.50, 36.18, 31.84. ^{19}F NMR (377 MHz, $CDCl_3$) δ –62.39. HRMS (ESI) calculated for $[C_{22}H_{20}F_3N_2O]^+$ $(M+H^+)$ requires *m/z* 385.1522, found 385.1517. Minor Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2947, 1668, 1619, 1456, 1409, 1326, 1291, 1162, 1115, 1068, 1017, 913, 847, 774, 699, 668. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 0.7 Hz, 1H), 7.16–7.13 (m, 2H), 7.10–7.05 (m, 6H), 5.05 (q, *J* = 9.0 Hz, 1H), 4.49 (t, *J* = 9.3 Hz, 1Hf), 4.05 (s, 3H), 4.03–3.99 (m, 1H), 2.81–2.74 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.50, 143.84 (q, *J* = 1.2 Hz), 142.41, 140.15, 129.55, 128.17, 128.11, 128.09, 127.52, 126.18, 124.54 (q, *J* = 3.8 Hz), 124.25 (q, 272.0 Hz), 45.51 43.78, 41.95, 36.24, 28.53. ^{19}F NMR (377 MHz, $CDCl_3$) δ –62.37. HRMS (ESI) calculated for $[C_{22}H_{20}F_3N_2O]^+$ $(M+H^+)$ requires *m/z* 385.1522, found 385.1519.

(2-(4-bromophenyl)-3-phenylcyclobutyl)(1-methyl-1H-imidazol-2-yl)methanone (4): Prepared according to general procedure for isolation scale experiments using 116.4 mg (0.4 mmol) (E)-3-(4-bromophenyl)-1-(1-methyl-1*H*-imidazol-2-yl)prop-2-en-1-one, 13.9 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 7.3 mg (0.01 mmol) $Ru(bpy)_3Cl_2•6H_2O$, and 0.48 mL (4.0 mmol) styrene in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et_2O/pentanes to give 93 mg (0.24 mmol, 59% yield) of two diastereomers (1.8:1 d.r.). Separation of major diastereomer for characterization purposes was achieved by automated FCC (ISCO) using a continuous gradient of 10% → 50% EtOAc in hexanes. Major Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2945, 1664, 1488, 1406, 1289, 1235, 1155, 1073, 1010, 911, 856, 824, 771, 699, 670, 622. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.33–2.27 (m, 4H), 7.22 (tt, *J* = 7.0, 1.8 Hz, 1H), 7.16–7.14 (m, 3H), 7.05 (s, 1H), 4.52 (q, *J* = 9.5 Hz, 1H), 4.03 (s, 3H), 4.00 (t, *J* = 9.8 Hz, 1H), 3.56 (td, *J* = 10.1, 8.2 Hz, 1H), 2.81 (dt, *J* = 10.3, 8.3 Hz, 1H), 2.33 (q, *J* = 10.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.09, 143.15, 142.51, 141.46, 131.42, 129.48, 128.71, 128.47, 127.38, 126.88, 126.59, 120.24, 48.25, 44.85, 43.56, 36.17, 31.65. HRMS (ESI) calculated for $[C_{21}H_{20}BrN_2O]^+$ $(M+H^+)$ requires *m/z* 395.0754, found 395.0753. Minor Diastereomer: Unable to separate from major diastereomer cleanly.

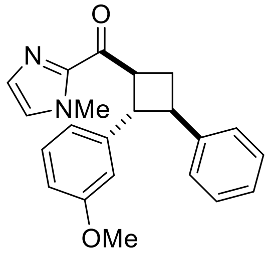


(2-(4-methoxyphenyl)-3-phenylcyclobutyl)(1-methyl-1H-imidazol-2-yl)methanone(5): Prepared according to general procedure for isolation scale experiments using 97.6 mg (0.4 mmol) (E)-3-(4-methoxyphenyl)-1-(1-methyl-1*H*-imidazol-2-yl)prop-2-en-1-one, 15.4 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 7.7 mg (0.01 mmol) $Ru(bpy)_3Cl_2•6H_2O$, and 0.46 mL (4.0 mmol) styrene in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et_2O/pentanes to give 83 mg (0.24 mmol, 60% yield) of two diastereomers (1.8:1 d.r.). Separation of diastereomers for characterization purposes was achieved by manual FCC using a gradient of 1:2 → 1:1 Et_2O/pentanes. Major Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2928, 1665, 1611, 1513, 1457, 1408, 1291, 1248, 1178, 1155, 1033, 912, 858, 831, 776, 700. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.29 (m, 4H), 7.22–7.18(m, 3H), 7.15 (s, 1H), 7.04(s, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.52 (q, *J* = 9.5 Hz, 1H), 4.03 (s, 3H), 3.99 (t, *J* = 9.7 Hz, 1H), 3.58 (q, *J* = 9.3 Hz, 1H), 2.81 (q, *J* = 8.8 Hz, 1H), 2.30 (q, *J* = 10.2 Hz, 1H) . ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.52, 158.20, 143.62, 142.69, 134.71, 129.37, 128.35, 128.00, 127.22, 126.92, 126.36, 113.75, 55.23, 48.28, 45.28, 43.79, 36.17, 31.59. HRMS (ESI) calculated for $[C_{22}H_{23}N_2O_2]^+$ $(M+H^+)$ requires *m/z* 347.1754, found 347.1753. Minor Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2935, 1164, 1611, 1512, 1455, 1405, 1290, 1247, 1178, 1154, 1032, 912, 835, 775, 699. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (s, 1H), 7.16–7.13 (m, 2H), 7.09–7.05 (m, 3H), 7.04 (s, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 2H), 4.98 (q, *J* = 8.8 Hz, 1H), 4.39 (t, *J* = 9.2 Hz, 1H), 4.03(s, 3H), 3.95 (td, *J* = 8.9, 4.8 Hz, 1H), 3.67 (s, 3H), 2.78–2.69 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.13, 157.66, 142.63, 140.77, 131.85, 129.39, 128.25, 127.88,

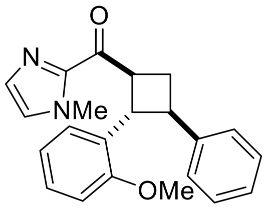


127.30, 125.77, 113.07, 55.05, 45.31, 44.28, 41.99, 36.23, 28.31. HRMS (ESI) calculated for $[C_{22}H_{23}N_2O_2]^+$ $(M+H^+)$ requires *m/z* 347.1754, found 347.1753.

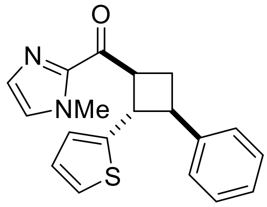
(2-(3-methoxyphenyl)-3-phenylcyclobutyl)(1-methyl-1H-imidazol-2-yl)methanone (6): Prepared according to general procedure for isolation scale experiments using 97.9 mg (0.4 mmol) (E)-3-(3-methoxyphenyl)-1-(1-methyl-1*H*-imidazol-2-yl)prop-2-en-1-one, 15.4 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 7.8 mg (0.01 mmol) $Ru(bpy)_3Cl_2$•$6H_2O$, and 0.46 mL (4.0 mmol) styrene in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et_2O/pentanes to give 98 mg (0.28 mmol, 71% yield) of two diastereomers (1.7:1 d.r.). Separation of major diastereomer for characterization purposes was achieved by automated FCC (ISCO) using a continuous gradient of 10% → 100% EtOAc in hexanes. Major Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2927, 1666, 1601, 1491, 1456, 1409, 1289, 1158, 1045, 879, 773, 699. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.29 (m, 4H), 7.23–7.15 (m, 3H), 7.05 (s, 1H), 6.88–6.85 (m, 2H), 6.72 (dd, *J* = 8.2, 2.0 Hz, 1H), 4.56 (td, 9.6, 8.7 Hz, 1H), 4.05 (t, *J* = 9.7 Hz, 1H), 4.03 (s, 3H), 3.61 (td, *J* = 10.1, 8.2 Hz, 1H), 2.82 (dt, *J* = 10.1, 8.5 Hz, 1H), 2.32 (q, *J* = 10.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.39, 159.59, 144.23, 143.56, 142.64, 129.39, 129.36, 128.39, 127.27, 126.97, 126.43, 119.30, 112.61, 111.86, 55.15, 48.67, 44.88, 43.44, 36.18, 31.76. HRMS (ESI) calculated for $[C_{22}H_{23}N_2O_2]^+$ $(M+H^+)$ requires *m/z* 347.1754, found 347.1752. Minor Diastereomer: Unable to separate from major diastereomer cleanly.



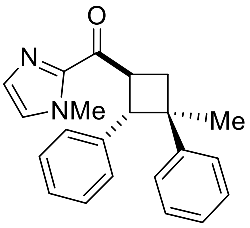
(2-(2-methoxyphenyl)-3-phenylcyclobutyl)(1-methyl-1H-imidazol-2-yl)methanone (7): Prepared according to general procedure for isolation scale experiments using 98.0 mg (0.4 mmol) (E)-3-(2-methoxyphenyl)-1-(1-methyl-1*H*-imidazol-2-yl)prop-2-en-1-one, 15.2 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2$•$6H_2O$, and 0.46 mL (4.0 mmol) styrene in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et_2O/pentanes to give 88 mg (0.25 mmol, 63% yield) of two diastereomers (1.7:1 d.r.). Separation of diastereomers for characterization purposes was achieved by manual FCC using a gradient of 1:2 → 1:1 Et_2O/pentanes. Major Diastereomer: White solid (mp = 109–112 °C). ν_{max} (film) / cm^{-1} 2928, 1665, 1601, 1492, 1457, 1409, 1289, 1246, 1154, 1125, 1051, 1028, 911, 859, 752, 699, 663. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.32–7.29 (m, 3H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.14 (td, *J* = 7.5, 1.8 Hz, 1H), 7.11 (s, 1H), 7.04 (s, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 4.57 (q, *J* = 9.0 Hz, 1H), 4.22 (t, *J* = 9.5 Hz, 1H), 4.09 (s, 3H), 3.74 (q, *J* = 9.4 Hz, 1H), 3.33 (s, 3H), 2.70 (dt, *J* = 10.2, 8.3 Hz, 1H), 2.38 (q, *J* = 9.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.07, 157.24, 144.24, 143.32, 130.66, 129.11, 128.23, 127.38, 127.19, 127.10, 126.91, 126.18, 120.31, 109.86, 54.43, 45.29, 43.74, 41.16, 36.26, 31.46. HRMS (ESI) calculated for $[C_{22}H_{23}N_2O_2]^+$ $(M+H^+)$ requires *m/z* 347.1454, found 347.1454. Minor Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2933, 1664, 1602, 1493, 1455, 1406, 1290, 1245, 1155, 1122, 1030, 913, 839, 752, 699, 668. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (s, 1H), 7.17 (d, *J* = Hz, 1H), 7.12 (d, *J* = Hz, 2H), 7.08–7.05 (m, 2H), 7.05 (s, 1H), 7.00–6.95 (m, 2H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 5.20 (q, *J* = 9.4 Hz, 1H), 4.62 (t, *J* = 9.4 Hz, 1H), 4.01 (s, 3H), 3.99 (td, *J* = 9.4, 3.8 Hz, 1H), 3.65 (s, 3H), 2.81 (dt, 11.7, 9.0 Hz, 1H), 2.62 (ddd, *J* = 11.6, 9.5, 3.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.35, 156.76, 142.83, 141.71, 129.35, 128.07, 127.95, 127.65, 127.45, 127.31, 126.98, 125.59, 119.75, 109.16, 54.79, 41.90, 41.89, 41.79, 36.26, 28.93. HRMS (ESI) calculated for $[C_{22}H_{23}N_2O_2]^+$ $(M+H^+)$ requires *m/z* 347.1754, found 347.1754.



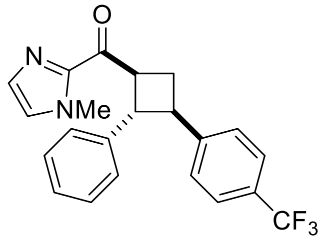
(1-methyl-1H-imidazol-2-yl)(3-phenyl-2-(thiophen-2-yl)cyclobutyl)methanone (8): Prepared according to general procedure for isolation scale experiments using 88.5 mg (0.4 mmol) (E)-1-(1-methyl-1*H*-imidazol-2-yl)-3-(thiophen-2-yl)prop-2-en-1-one, 16.2 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 8.4 mg (0.01 mmol) $Ru(bpy)_3Cl_2$•$6H_2O$, and 0.46 mL (4.0 mmol) styrene in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et_2O/pentanes to give 47 mg (0.15 mmol, 36% yield) of two diastereomers (1.7:1 d.r.). Separation of diastereomers for characterization purposes was achieved by automated FCC (ISCO) using a continuous gradient of 15% → 100% EtOAc in hexanes. Major Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2946, 1665, 1456, 1408, 1289, 1235, 1155, 1079, 1020, 903, 855, 775, 698, 662. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.30 (m, 4H), 7.23–7.20 (m, 1H), 7.16 (d, *J* = 0.8 Hz, 1H), 7.12 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.05 (s, 1H), 6.93 (dt, *J* = 3.4, 1.0 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.5 Hz, 1H), 4.53 (td, *J* = 9.6, 8.7 Hz, 1H), 4.19 (t, *J* = 9.6 Hz, 1H), 4.03(s, 3H), 3.64 (td, *J* = 10.0, 8.1 Hz, 1H), 2.83 4.53 (dt, *J* = 10.4, 8.5 Hz, 1H), 2.32 (q, *J* = 10.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.73, 146.55, 142.84, 142.54, 129.48, 128.39, 127.29, 126.82, 126.81, 126.57, 123.75, 123.60, 47.05, 45.35, 44.17, 36.15, 31.24. HRMS (ESI) calculated for $[C_{19}H_{19}N_2OS]^+$ ($M+H^+$) requires *m/z* 323.1213, found 323.1210. Minor Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2944, 1667, 1495, 1455, 1408, 1290, 1235, 1155, 1078, 1032, 907, 849, 775, 698. ^{1}H NMR (50fz0 MHz, $CDCl_3$) δ 7.22–7.17 (m, 5H), 7.14–7.11 (m, 1H), 7.06 (s, 1H), 6.93 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.71 (dd, *J* = 4.9, 3.6 Hz, 1H), 6.64 (dt, *J* = 3.5, 1.1 Hz, 1H), 4.88(q, *J* = 8.6 Hz, 1H), 4.62 (t, *J* = 8.8 Hz, 1H), 4.05 (s, 3H), 3.97 (td, *J* = 9.1, 5.1Hz, 1H), 2.86 (ddd, *J* = 11.8, 10.2, 5.0 Hz, 1H), 2.68 (dt, *J* = 12.0, 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.30, 143.45, 142.43, 140.16, 129.51, 128.17, 127.94, 127.34, 126.22, 126.19, 124.90, 123.77, 46.71, 42.47, 41.28, 36.23, 28.37. HRMS (ESI) calculated for $[C_{19}H_{19}N_2OS]^+$ ($M+H^+$) requires *m/z* 323.1213, found 323.1210.



(1-methyl-1H-imidazol-2-yl)((3-methyl-2,3-diphenylcyclobutyl)methanone (12): Prepared according to general procedure for isolation scale experiments using 86.0 mg (0.4 mmol) 2-cinnamoyl-1-methyl-1*H*-imidazole, 15.6 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 8.1 mg (0.01 mmol) $Ru(bpy)_3Cl_2$•$6H_2O$, and 0.52 mL (4.0 mmol) α-methylstyrene in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et_2O/pentanes to give 70.5 mg (0.21 mmol, 53 % yield) of two diastereomers (2.1:1 d.r.). Separation of diastereomers for characterization purposes was achieved by manual FCC using a gradient of 1:3 → 1:1 Et_2O/pentanes. Major Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2959, 1665, 1496, 1444, 1408, 1291, 1234, 1155, 1080, 1030, 914, 839, 767, 699, 664. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.38 (m, 2H), 7.36–7.28 (m, 6H). 7.23–7.19 (m, 1H), 7.19 (s, 1H), 7.04 (s, 1H), 4.98 (q, *J* = 9.5 Hz, 1H), 4.27(d, *J* = 10.1 Hz, 1H), 2.62 (t, *J* = 10.2 Hz), 2.45 (dd, *J* = 10.3, 9.3 Hz), 1.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.85, 150.44, 142.80, 139.42, 129.34, 128.30, 128.22, 128.10, 127.35, 126.44, 125.79, 125.41, 50.66, 43.32, 40.40, 37.24, 36.20, 23.97. HRMS (ESI) calculated for $[C_{22}H_{23}N_2O]^+$ ($M+H^+$) requires *m/z* 331.1805, found 331.1800. Minor Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2956, 1667, 1602, 1496, 1452, 1408, 1291, 1155, 1031, 984, 915, 765, 698, 662. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 0.8 Hz, 1H), 7.13–7.10 (m, 2H), 7.07–7.03 (m, 6H), 7.02 (s, 1H), 6.91 (dd, *J* = 8.0, 1.7 Hz, 2H), 4.78 (q, *J* = 9.5 Hz, 1H), 4.01 (d, *J* = 10.0 Hz, 1H), 4.00 (s, 3H), 3.11 (dd, *J* = 11.6, 9.1 Hz, 1H), 2.34 (dd, *J* = 11.6, 9.7 Hz, 1H), 1.68 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.94, 143.32, 142.80, 139.47, 129.37, 128.20, 127.62, 127.59, 127.28, 127.23, 126.17, 125.59, 54.02 45.88, 40.98, 36.20, 35.54, 31.41. HRMS (ESI) calculated for $[C_{22}H_{23}N_2O]^+$ ($M+H^+$) requires *m/z* 331.1805, found 331.1802.

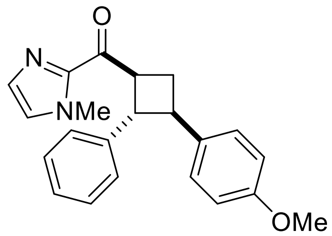


(1-methyl-1H-imidazol-2-yl)(2-phenyl-3-(4-(trifluoromethyl)phenyl)cyclobutyl)methanone (13):



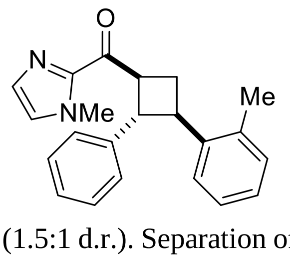
Prepared according to general procedure for isolation scale experiments using 85.4 mg (0.4 mmol) 2-cinnamoyl-1-methyl-1*H*-imidazole, 16.2 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 8.0 mg (0.01 mmol) $Ru(bpy)_3Cl_2$•$6H_2O$, and 0.59 mL (4.0 mmol) 4-trifluoromethylstyrene in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et_2O/pentanes to give 105 mg (0.27 mmol, 68% yield) of two diastereomers (1.7:1 d.r.). Separation of diastereomers for characterization purposes was achieved by automated FCC (ISCO) using a continuous gradient of 15% → 100% EtOAc in hexanes. <u>Major Diastereomer</u>: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2945, 1667, 1619, 1410, 1325, 1236, 1163, 1121, 1068, 1017, 912, 834, 770, 699. ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.28–7.27 (m, 4H), 7.21–7.18 (m, 1H), 7.15 (s, 1H), 7.05 (s, 1H), 4.61 (q, *J* = 9.3 Hz, 1H), 4.07 (t, *J* = 9.9 Hz, 1H), 4.03 (s, 3H), 3.68, (q, *J* = 9.3 Hz, 1H), 2.86 (dt, *J* = 10.2, 8.4 Hz, 1H), 2.36 (q, *J* = 10.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.07, 147.59 (q, *J* = 1.2 Hz), 142.52, 141.94, 129.50, 128.51, 127.40, 127.25, 126.89, 126.71, 125.34 (q, *J* = 3.7 Hz), 124.29 (q, *J* = 272.2 Hz), 48.63, 44.88, 43.23, 36.18, 31.50. ^{19}F NMR (377 MHz, $CDCl_3$) δ –62.34. HRMS (ESI) calculated for $[C_{22}H_{20}F_3N_2O]^+$ $(M+H^+)$ requires *m/z* 385.1522, found 385.1518. <u>Minor Diastereomer</u>: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2937, 1669, 1618, 1409, 1325, 1162, 1115, 1069, 1017, 914, 837, 773, 699, 642. ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.19–7.16 (m, 3H), 7.09–7.05 (m, 3H), 7.02–6.97 (m, 3H), 5.05 (q, *J* = 8.8 Hz, 1H), 4.51 (t, *J* = 9.4 Hz, 1H), 4.07–4.02 (m, 1H), 4.04 (s, 3H), 2.82–2.73 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.62, 145.08 (q, *J* = 1.3 Hz), 142.47, 139.02, 129.51, 128.46, 127.89, 127.78, 127.47, 126.14, 124.73 (q, *J* = 3.8 Hz), 124.25 (q, *J* = 272.3 Hz), 45.70, 43.50, 41.84, 36.24, 28.47. ^{19}F NMR (377 MHz, $CDCl_3$) δ –62.34. HRMS (ESI) calculated for $[C_{22}H_{20}F_3N_2O]^+$ $(M+H^+)$ requires *m/z* 385.1522, found 385.1519.

(3-(4-methoxyphenyl)-2-phenylcyclobutyl)(1-methyl-1H-imidazol-2-yl)methanone (14): Prepared



according to general procedure for isolation scale experiments using 84.5 mg (0.4 mmol) 2-cinnamoyl-1-methyl-1*H*-imidazole, 15.0 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 7.6 mg (0.01 mmol) $Ru(bpy)_3Cl_2$•$6H_2O$, and 0.53 mL (4.0 mmol) 4-methoxystyrene in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et_2O/pentanes to give 97 mg (0.28 mmol, 70% yield) of two diastereomers (1.5:1 d.r.). Separation of major diastereomer for characterization purposes was achieved by manual FCC using a gradient of 1:2 → 1:1 Et_2O/pentanes. <u>Major Diastereomer</u>: White solid (mp = 83–85 °C). ν_{max} (film) / cm^{-1} 2934, 1666, 1611, 1513, 1409, 1291, 1248, 1177, 1033, 829, 699. ^1H NMR (500 MHz, $CDCl_3$) δ 7.27–7.23 (m, 6H), 7.18–7.15 (m, 1H), 7.15 (s, 1H), 7.04 (s, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.56 (td, *J* = 9.7, 8.6 Hz, 1H), 4.04–4.00 (m, 1H), 4.03 (s, 3H), 3.79 (s, 3H), 3.54 (td, *J* = 10.1, 8.2 Hz, 1H), 2.80 (dt, *J* = 10.2, 8.4 Hz, 1H), 2.27 (q, *J* = 10.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.55, 158.22, 142.67, 142.56, 135.76, 129.39, 128.33, 128.01, 127.25, 126.90, 126.37, 113.78, 55.27, 48.97, 44.72, 43.05, 36.18, 32.23. HRMS (ESI) calculated for $[C_{22}H_{23}N_2O_2]^+$ $(M+H^+)$ requires *m/z* 347.1754, found 547.1754. <u>Minor Diastereomer</u>: Unable to separate from major diastereomer cleanly.

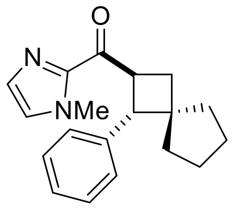
(1-methyl-1H-imidazol-2-yl)(2-phenyl-3-(o-tolyl)cyclobutyl)methanone (15): Prepared according to



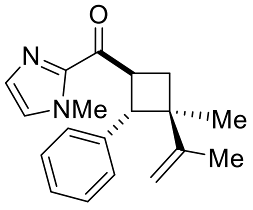
general procedure for isolation scale experiments using 85.0 mg (0.4 mmol) 2-cinnamoyl-1-methyl-1*H*-imidazole, 15.8 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 7.2 mg (0.01 mmol) $Ru(bpy)_3Cl_2$•$6H_2O$, and 0.52 mL (4.0 mmol) 2-methylstyrene in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et_2O/pentanes to give 79 mg (0.24 mmol, 60% yield) of two diastereomers (1.5:1 d.r.). Separation of major diastereomer for characterization purposes was achieved by automated

FCC (ISCO) using a continuous gradient of 15% → 100% EtOAc in hexanes. Major Diastereomer: White solid (mp = 94–97 °C). ν_{max} (film) / cm^{-1} 2949, 1666, 1458, 1409, 1289, 1235, 1155, 1024, 913, 856, 754, 699, 662. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.27–7.24 (m, 2H), 7.22–7.19 (m, 1H), 7.18–7.15 (m, 2H), 7.15–7.11 (m, 2H), 7.04 (s, 1H), 4.53 (q, *J* = 9.1 Hz, 1H), 4.29 (t, *J* = 9.9 Hz, 1H), 4.03 (s, 3H), 3.81 (td, *J* = 10.1, 8.1 Hz, 1H), 2.95 (dt, *J* = 10.1, 8.4 Hz, 1H), 2.22 (s, 3H), 2.11 (q, *J* = 10.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ. HRMS (ESI) calculated for $[C_{22}H_{23}N_2O]^+$ (M+H$^+$) requires *m/z* 331.1805, found 331.1801. Minor Diastereomer: Unable to separate from major diastereomer cleanly.

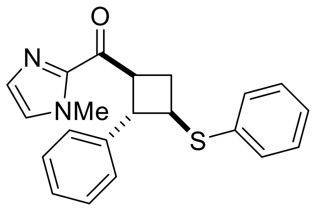
(1-methyl-1H-imidazol-2-yl)(1-phenylspiro[3.4]octan-2-yl)methanone (16): Prepared according to general procedure for isolation scale experiments using 85.4 mg (0.4 mmol) 2-cinnamoyl-1-methyl-1*H*-imidazole, 16.4 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 7.5 mg (0.01 mmol) $Ru(bpy)_3Cl_2•6H_2O$, and 0.42 mL (4.0 mmol) methylenecyclohexane in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et_2O/pentanes to give 35 mg (0.12 mmol, 30% yield) of a single diastereomer (>10:1 d.r.). White solid (mp = 100–105 °C). ν_{max} (film) / cm^{-1} 2931, 1665, 1497, 1407, 1289, 1154, 1031, 915, 765, 699. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.26 (m, 4H), 7.19–7.15 (m, 1H), 7.16 (s, 1H), 7.02 (s, 1H), 4.79 (q, *J* = 9.5 Hz, 1H), 3.98 (s, 3H), 3.91 (d, *J* = 10.0 Hz, 1H), 2.21 (t, *J* = 9.6 Hz, 1H), 2.06 (t, *J* = 9.8 Hz, 1H), 1.83–1.72 (m, 2H), 1.55–1.45 (m, 4H), 1.32–1.27(m, 2H) . ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.10, 142.85, 139.90, 129.24, 128.04, 127.76, 127.18, 126.15, 49.02, 48.57, 40.44, 39.70, 38.19, 36.19, 33.34. HRMS (ESI) calculated for $[C_{19}H_{23}N_2O]^+$ (M+H$^+$) requires *m/z* 295.1805, found 295.1805.



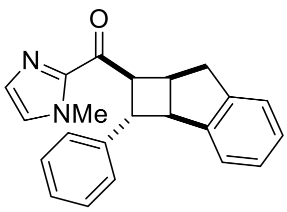
(1-methyl-1H-imidazol-2-yl)(3-methyl-2-phenyl-3-(prop-1-en-2-yl)cyclobutyl)methanone (17): Prepared according to general procedure for isolation scale experiments using 84.9 mg (0.4 mmol) 2-cinnamoyl-1-methyl-1*H*-imidazole, 15.1 mg (0.08 mmol) *p*-toluekknesulfonic acid monohydrate, 7.4 mg (0.01 mmol) $Ru(bpy)_3Cl_2•6H_2O$, and 0.45 mL (4.0 mmol) 2,3-dimethylbutadiene in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et_2O/pentanes to give 78 mg (0.26 mmol, 66% yield) of two diastereomers (7:1 d.r.). Separation of major diastereomer for characterization purposes was achieved by manual FCC using a gradient of 1:2 → 1:1 Et_2O/pentanes. Major Diastereomer: White solid (mp = 100–103 °C). ν_{max} (film) / cm^{-1} 2962, 1665, 1513, 1407, 1290, 1239, 1154, 1031, 915, 838, 767, 699. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.25 (m, 4H), 7.19–7.16 (m, 1H), 7.18 (s, 1H), 7.04 (s, 1H), 4.91 (s, 1H), 4.84 (m, 1H), 4.79 (q, *J* = 9.5 Hz, 1H), 4.13 (d, *J* = 9.9 Hz, 1H), 3.99 (s, 3H), 2.28 (t, *J* = 9.8 Hz, 1H), 2.19 (t, *J* = 9.7 Hz, 1H), 1.78 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.07, 152.58, 142.78, 139.94, 129.30, 128.17, 127.97, 127.27, 126.14, 108.79, 47.67, 44.93, 39.92, 36.20, 36.11, 21.29, 18.99. HRMS (ESI) calculated for $[C_{19}H_{23}N_2O]^+$ (M+H$^+$) requires *m/z* 295.1805, found 295.1806. Minor Diastereomer: Unable to separate from major diastereomer cleanly.



(1-methyl-1H-imidazol-2-yl)(2-phenyl-3-(phenylthio)cyclobutyl)methanone (18): Prepared according to general procedure for isolation scale experiments using 85.1 mg (0.4 mmol) 2-cinnamoyl-1-methyl-1*H*-imidazole, 16.0 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 7.6 mg (0.01 mmol) $Ru(bpy)_3Cl_2•6H_2O$, and 0.52 mL (4.0 mmol) phenyl vinyl sulfide in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et_2O/pentanes to give 110 mg (0.31 mmol, 79% yield) of two diastereomers (1.4:1 d.r.). Separation of diastereomers for characterization purposes was achieved by manual FCC using a gradient of 10% → 30% EtOAc in pentanes. Major Diastereomer: White solid (mp = 81–84 °C). ν_{max} (film) / cm^{-1} 2944, 1665, 1583, 1496, 1479, 1438, 1407, 1289, 1233, 1155, 1090, 1024, 845, 740, 699. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.30–7.27 (m, 4H), 7.25–

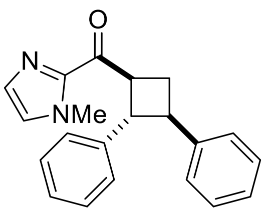


7.16 (m, 4H), 7.12 (s, 1H), 7.02 (s, 1H), 4.49 (q, *J* = 9.4 Hz, 1H), 3.99 (s, 3H), 3.93 (t, *J* = 9.5 Hz, 1H), 3.85 (td, *J* = 9.6, 7.5 Hz, 1H), 2.94 (dt, *J* = 10.7, 8.2 Hz, 1H), 2.20 (q, *J* = 10.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.73, 142.28, 141.01, 135.18, 130.84, 129.44, 128.82, 128.44, 127.31, 126.96, 126.82, 126.56, 48.39, 45.20, 44.76, 36.11, 33.99. HRMS (ESI) calculated for $[C_{21}H_{21}N_2OS]^+$ (M+H$^+$) requires *m/z* 349.1369, found 349.1369. Minor Diastereomer: White solid (mp = 105–107 °C). ν_{max} (film) / cm^{-1} 2939, 1664, 1585, 1480, 1438, 1407, 1289, 1224, 1155, 1026, 915, 837, 739, 697. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), z7.22 (t, *J* = 7.3 Hz, 1H), 7.18–7.15 (m, 3H), 7.11–7.07 (m, 3H), 7.04 (s, 1H), 5.14 (q, *J* = 9.0 Hz, 1H), 4.47 (t, *J* = 8.5 Hz, 1H), 4.36 (td, *J* = 8.0, 3.3 Hz, 1H), 4.01 (s, 3H), 2.76 (dt, *J* = 11.9, 7.9 Hz, 1H), 2.47 (ddd, *J* = 12.1, 9.7, 3.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.29, 142.38, 138.28, 136.12, 129.53, 129.16, 128.61, 128.27, 127.93, 127.41, 126.89, 125.59, 44.41, 43.62, 43.59, 36.17, 31.85. HRMS (ESI) calculated for $[C_{21}H_{21}N_2OS]^+$ (M+H$^+$) requires *m/z* 349.1369, found 349.1369.



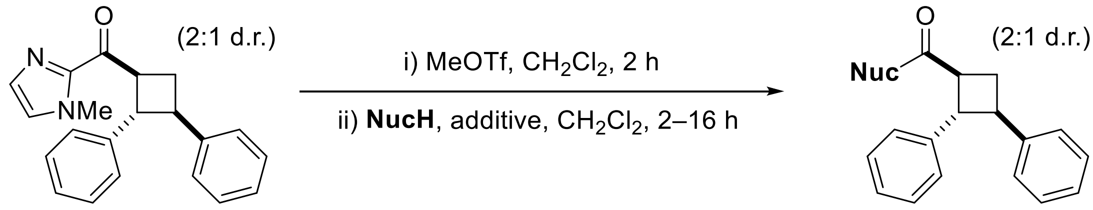
(1-methyl-1H-imidazol-2-yl)(2-phenyl-2,2a,7,7a-tetrahydro-1H-cyclobuta[*a*]inden-1-yl)methanone (19): Prepared according to general procedure for isolation scale experiments using 84.5 mg (0.4 mmol) 2-cinnamoyl-1-methyl-1*H*-imidazole, 15.8 mg (0.08 mmol) *p*-toluenesulfonic acid monohydrate, 7.6 mg (0.01 mmol) $Ru(bpy)_3Cl_2$•$6H_2O$, and 0.47 mL (4.0 mmol) indene in MeCN with a total volume of 8 mL (0.05 M). Isolation of products was performed by FCC with 1:1 Et_2O/pentanes to give 82 mg (0.25 mmol, 62% yield) of two diastereomers (1.1:1 d.r.). Separation of diastereomers for characterization purposes was achieved by manual FCC using a gradient of 10% → 30% EtOAc in pentanes. Major Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1} 2923, 1663, 1407, 1291, 1154, 872, 772, 699, 662. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.6 Hz, 1H), 7.16–7.09 (m, 5H), 7.02 (s, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.41 (d, *J* = 7.6 Hz, 1H), 4.55 (dd, *J* = 9.7, 7.5 Hz, 1H), 4.44 (t, *J* = 9.5 Hz, 1H), 4.10 (t, *J* = 7.7 Hz, 1H), 4.00 (s, 3H), 3.43 (d, *J* = 16.3 Hz, 1H), 3.24 (q, *J* = 7.1 Hz, 1H), 3.15 (dd, *J* = 16.5, 7.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.50, 144.35, 142.99, 141.57, 139.28, 129.32, 128.18, 127.68, 127.33 (2C), 126.86, 126.15, 125.67, 125.61, 49.85, 48.56, 43.35, 39.89, 38.32, 36.15. HRMS (ESI) calculated for $[C_{22}H_{21}N_2O]^+$ (M+H$^+$) requires *m/z* 329.1648, found 329.1648. Minor Diastereomer: Viscous oil/semisolid. ν_{max} (film) / cm^{-1}, 2955, 1665, 1496, 1458, 1407, 1289, 1154, 1007, 917, 866, 756, 699. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.31 (m, 4H), 7.23–7.14 (m, 6H), 7.04 (s, 1H), 4.69 (t, *J* = 9.3 Hz, 1H), 4.01 (s, 3H), 3.98 (dd, *J* = 9.0, 7.0 Hz, 1H), 3.93 (t, *J* = 7.1 Hz, 1H), 3.86–3.80 (m, 1H), 3.09 (dd, *J* = 17.5, 10.0 Hz, 1H), 2.93 (dd, *J* = 17.5, 5.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.63, 146.03, 145.11, 143.58, 142.62, 129.37, 128.49, 126.82, 126.76, 126.67, 126.66, 126.25, 124.98, 123.57, 50.71, 49.72, 46.24, 39.47, 36.10, 34.19. HRMS (ESI) calculated for $[C_{22}H_{21}N_2O]^+$ (M+H$^+$) requires *m/z* 329.1648, found 329.1648.

5. Derivatization of Cyclobutane Products



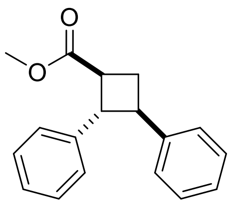
Large Scale Synthesis of 2: A 50 mL RBF with a stir bar was charged with 427.3 mg (2.0 mmol) 2-cinnamoyl-1-methyl-1*H*-imidazole, 79.3 mg (0.40 mmol) *p*-toluenesulfonic acid monohydrate, 37.5 mg (0.05 mmol) $Ru(bpy)_3Cl_2$•$6H_2O$, and dry MeCN (40 mL), then fitted with a septum. A volume 2.3 mL (20.0 mmol) styrene was added and the reaction sparged with N_2 for 20 minutes. The reaction was then stirred in front of a of a blue LED lamp for 48 h (under N_2). The resulting mixture was diluted with 50 mL Et_2O, pushed through a short plug of silica, and the plug washed with 50 mL Et_2O. The resulting colorless solution was concentrated and purified by FCC with 1:1 Et_2O/pentanes to give 410 mg (1.3 mmol, 64% yield) of a viscous oil composed of two diastereomers (~2:1 d.r.).

Scheme S1. General two-step procedure for imidazole cleavage

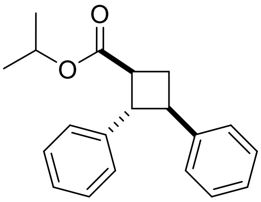


General Procedure for [2+2] Cycloadduct Derivatizations: An oven-dried 1.5 dram vial with a small stir bar was charged with cyclobutane **2** (0.20–0.30 mmol, 1.0 equiv.) as a 2:1 mixture of diastereomers. This vial was fitted with a cap with a Teflon septum, then CH_2Cl_2 added (0.1–0.2 M in cyclobutane). This solution was stirred under a flow of N_2 for 5 minutes before freshly distilled MeOTf (1.2-1.4 equiv.) was added. The reaction mixture was sealed and stirred for 2 hours. At this point the starting material appeared entirely consumed or trace by TLC. The solvent and any remaining MeOTf were removed under vacuum and the resulting colorless solid dried under high vacuum for 30 minutes. After redissolving the salt in CH_2Cl_2 (0.1–0.2 M in cyclobutane), nucleophile (20.0–45.0 equiv.) was added. For ROH nucleophiles, 1,4-diazabicyclo[2.2.2]octane (DABCO, 0.2 equiv.) was also added. The reactions were then stirred for 2–16 h. Upon completion, the mixtures were directly concentrated and then purified by FCC.

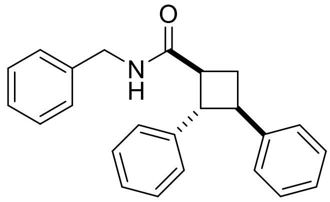
Methyl-2,3-diphenylcyclobutane-1-carboxylate (20): Prepared according to general procedure for derivatizations using 95.0 mg (0.30 mmol) cyclobutane **2** (2:1 mixture of diastereomers), 40 µL (0.36 mmol) MeOTf, and 1.5 mL (0.2 M) CH_2Cl_2 for the methylation step. For the nucleophile displacement step, 0.57 mL (14.0 mmol) MeOH, 8.2 mg DABCO (0.07 mmol), and 1.5 (0.2 M) CH_2Cl_2 were used. Reaction time: 2 hours. The resulting mixture was purified by FCC with 5% Et_2O in pentanes to give 66.7 mg (0.25 mmol, 83% yield) clear oil composed of two diastereomers (2:1 d.r.). Spectroscopic data for the major diastereomer was consistent with that previously reported.[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.19 (m, 10H), 3.85 (t, J = 9.7 Hz, 1H), 3.72 (s, 3H), 3.53 (td, J = 10.1, 8.3 Hz, 1H) 3.20 (td, J = 9.7, 8.4 Hz, 1H), 2.62 (dt, J = 10.6, 8.3 Hz, 1H) 2.41 (q, J = 10.4 Hz, 1H).



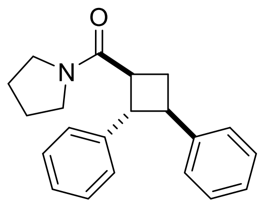
Isopropyl-2,3-diphenylcyclobutane-1-carboxylate (21): Prepared according to general procedure for derivatization experiments using 96.5 mg (0.30 mmol) cyclobutane **2** (2:1 mixture of diastereomers), 40 µL (0.36 mmol) MeOTf, and 1.5 mL (0.2 M) CH_2Cl_2 for the methylation step. For the nucleophile displacement step, 0.91 mL (12.0 mmol) *i*PrOH, 6.2 mg DABCO (0.06 mmol), and 1.5 (0.2 M) CH_2Cl_2 were used. Reaction time: 2 hours. The resulting mixture was purified by FCC with 5% Et_2O in pentanes to give 76.7 mg (0.26 mmol, 85% yield) clear oil composed of two diastereomers (2:1 d.r.). Spectroscopic data for the major diastereomer was consistent with that previously reported. [10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.19 (m, 10H), 5.06 (sept, J = 6.4 Hz, 1H), 3.84 (t, J = 9.9 Hz, 1H), 3.55 (td, J = 10.1, 8.3 Hz, 1H), 3.12 (td, J = 9.8, 8.4 Hz, 1H), 2.62 (dt, J = 10.5, 8.4 Hz, 1H), 2.38 (q, J = 10.4 Hz, 1H), 1.25 (d, J = 6.3 Hz, 3H), 1.24 (d, J = 6.3 Hz, 3H).



***N*-benzyl-2,3-diphenylcyclobutane-1-carboxamide (22):** Prepared according to general procedure for derivatizations using 61.1 mg (0.19 mmol) cyclobutane **2** (2:1 mixture of diastereomers), 30 µL (0.27 mmol) MeOTf, and 2.0 mL (0.1 M) CH_2Cl_2 for the methylation step. For the nucleophile displacement step, 0.44 mL (4.0 mmol) benzylamine and 2.0 mL (0.1 M) CH_2Cl_2 were used. Reaction time: 16 hours. The resulting mixture was purified by FCC with 1:1 Et_2O/pentanes to give 53.4 mg (0.16 mmol, 81% yield) of two diastereomers (2:1 d.r.). Separation of these diastereomers for characterization purposes was achieved by automated FCC (ISCO) using a continuous gradient of 15% → 100% EtOAc in hexanes. Major Diastereomer: White solid (mp = 144–146 °C). ν_{max} (film) / cm^{-1} 3277, 3028, 2927, 1640, 1603, 1543, 1495, 1454, 1358, 1249, 1080, 1029. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.19 (m, 15H), 5.57 (br s, 1H), 4.50–4.42 (m, 2H), 3.81(t, *J* = 9.7 Hz, 1H), 3.57 (td, *J* = 10.1, 8.3 Hz, 1H), 2.94 (td, *J* = 9.6, 8.0 Hz, 1H), 2.59–2.48 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.97, 143.17, 142.09, 138.26, 128.71, 128.66, 128.40, 127.76, 127.52, 126.85 (2C), 126.83, 126.51, 51.38, 44.41, 43.61, 42.86, 28.77. HRMS (ESI) calculated for $[C_{24}H_{24}NO]^+$ ($M+H^+$) requires *m/z* 342.1852, found 342.1850. Minor Diastereomer: Colorless oil. ν_{max} (film) / cm^{-1} 3277, 3060, 3028, 1638, 1603, 1541, 1495, 1454, 1388, 1357, 1245, 1074, 1029, 1013, 910. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.27 (m, 3H), 7.21 (d, *J* = 7.0 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 2H), 7.09 –7.02 (m, 4H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 7.0 Hz, 2H), 5.60 (br s, 1H), 4.50–4.39 (m, 2H), 4.24 (t, *J* = 9.2 Hz, 1H), 3.99 (td, *J* = 9.3, 4.0 Hz, 1H), 3.48 (q, *J* = 8.9 Hz, 1H), 2.86 (dt, *J* = 12.0, 8.8 Hz, 1H), 2.59 (ddd, *J* = 12.2, 8.7, 4.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.73, 140.20, 139.26, 138.25, 128.70, 128.07, 127.94, 127.91, 127.84, 127.65, 127.48, 126.32, 125.93, 48.11, 43.57, 42.85, 42.16, 26.12. HRMS (ESI) calculated for $[C_{24}H_{24}NO]^+$ ($M+H^+$) requires *m/z* 342.1852, found 342.1849.



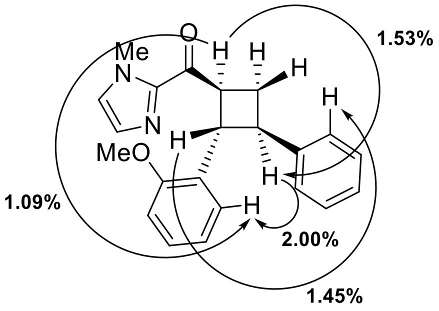
(2,3-diphenylcyclobutyl)(pyrrolidin-1-yl)methanone (23): Prepared according to general procedure for derivatization experiments using 85.2 mg (0.27 mmol) cyclobutane **2** (2:1 mixture of diastereomers), 40 µL (0.36 mmol) MeOTf, and 2.0 mL (0.1 M) CH_2Cl_2 for the methylation step. The reaction time for this step was 2 hours. For the nucleophile displacement step, 0.44 mL (5.4 mmol) pyrrolidine and 2.0 mL (0.1 M) CH_2Cl_2 were used. The reaction time for this step was 16 hours. The resulting mixture was purified by FCC with 1:1 EtOAc/pentanes with 2% Et_3N to give 58.9 mg (0.19 mmol, 72% yield) of two diastereomers (2:1 d.r.). Separation of these diastereomers for characterization purposes was achieved by manual FCC using 1:1 EtOAc/pentanes with 2% Et_3N. Major Diastereomer: White solid (mp = 99–101 °C). ν_{max} (film) / cm^{-1} 2973, 2872, 1628, 1495, 1434, 1341, 1226, 1190, 1030, 914, 843. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.27 (m, 8H), 7.22–7.17 (m, 2H), 4.01 (t, *J* = 9.8 Hz, 1H), 3.59 (td, *J* = 10.1, 8.4 Hz, 1H), 3.50–3.47 (m, 2H), 3.35–3.30 (m, 1H), 3.24–3.17 (m, 2H), 2.60 (dt, *J* = 10.3, 8.3 Hz, 1H), 2.40 (q, *J* = 10.2 Hz, 1H), 1.91–1.79 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.68, 143.50, 142.91, 128.44, 128.34, 126.95, 126.88, 126.50, 126.38, 49.98, 46.09, 45.81, 42.85, 42.72, 29.43, 26.06, 24.24. HRMS (ESI) calculated for $[C_{21}H_{24}NO]^+$ ($M+H^+$) requires *m/z* 306.1852, found 306.1848. Minor Diastereomer: White solid (mp = 97–99 °C). ν_{max} (film) / cm^{-1} 2928, 2872, 1629, 1496, 1432, 1342, 1227, 1192, 1031, 1009, 914. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.3 Hz, 2H), 7.08–7.00 (m, 4H), 6.96 (d, *J* = 7.4 Hz, 2H), 6.88 (d, *J* = 7.1 Hz, 2H), 4.32 (dd, *J* = 9.6, 8.0 Hz, 1H), 4.04 (td, *J* = 9.4, 5.3 Hz, 1H), 3.62 (q, *J* = 8.3 Hz, 1H), 3.55–3.46 (m, 2H), 3.40–3.36 (m, 1H), 3.29–3.24 (m, 1H), 2.82 (ddd, *J* = 11.8, 8.8, 7.8 Hz, 1H), 2.62 (ddd, *J* = 11.8, 9.2, 5.2 Hz, 1H), 1.93–1.79 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.32, 140.79, 140.09, 128.03, 127.99, 127.82, 127.72, 125.98, 125.74, 47.33, 46.29, 42.92, 41.82, 40.98, 26.39, 26.07, 24.27. HRMS (ESI) calculated for $[C_{21}H_{24}NO]^+$ ($M+H^+$) requires *m/z* 306.1852, found 306.1849.



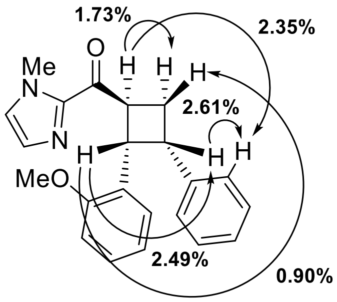
6. Assignment of Diastereomers by 1D-NOE

Figure S1. Observed NOE enhancements

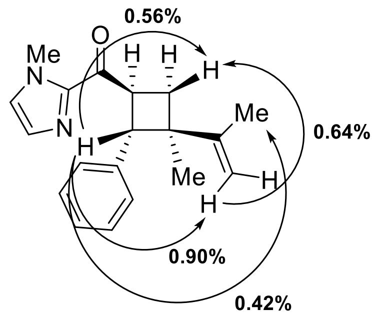
Major Diastereomer(1.7:1)
(in C_6D_6)



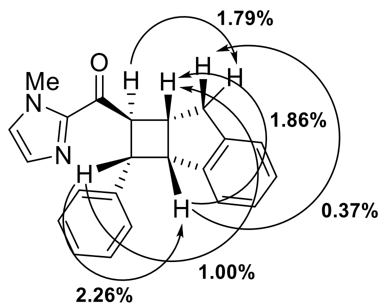
Minor Diastereomer(1.7:1)
(in C_6D_6)



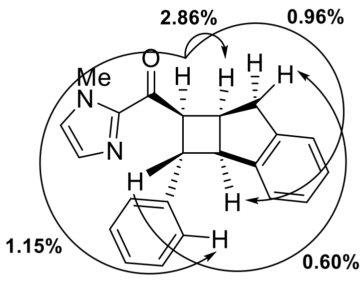
Major Diastereomer(7:1)
(in $CDCl_3$)



Major Diastereomer (1.1:1)
(in C_6D_6)

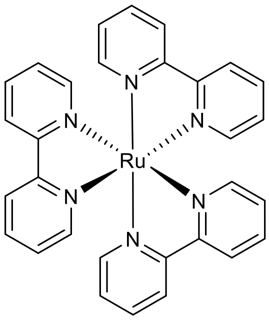


Minor Diastereomer (1.1:1)
(in C_6D_6)

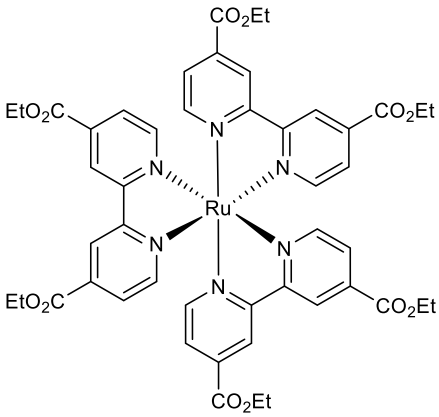


7. Photocatalyst Data

Figure S2. Summary of physical data for ruthenium photocatalysts

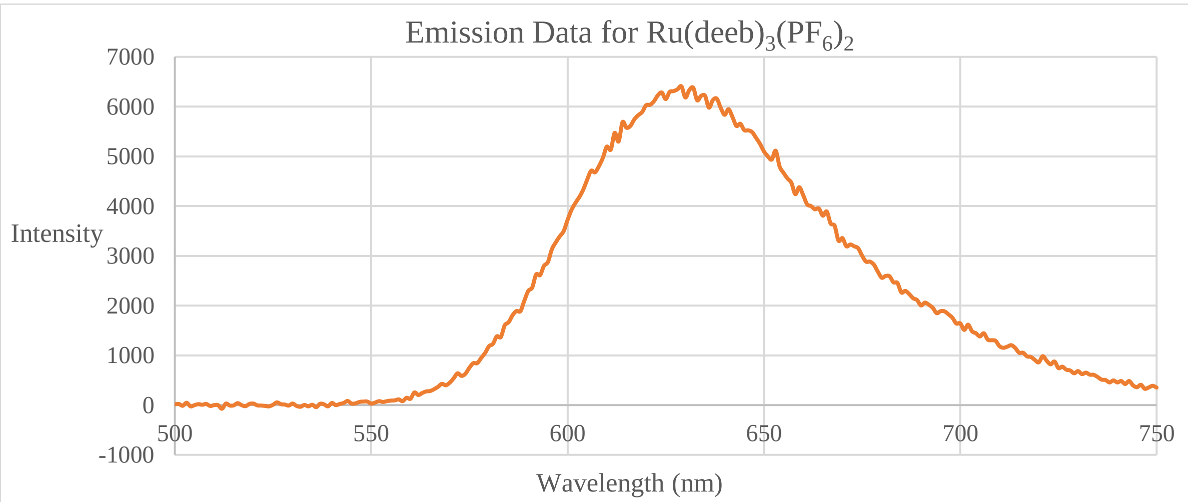


$Ru(bpy)_3Cl_2$**)**
E_0 (2+*/3+) = –0.81
λ_{max} = 613 nm
E_T = 46.6 kcal/mol



$Ru(4\text{-}deeb)_3(PF_6)_2$
E_0 (2+*/3+) = –0.28
λ_{max} = 630 nm
E_T = 45.4 kcal/mol

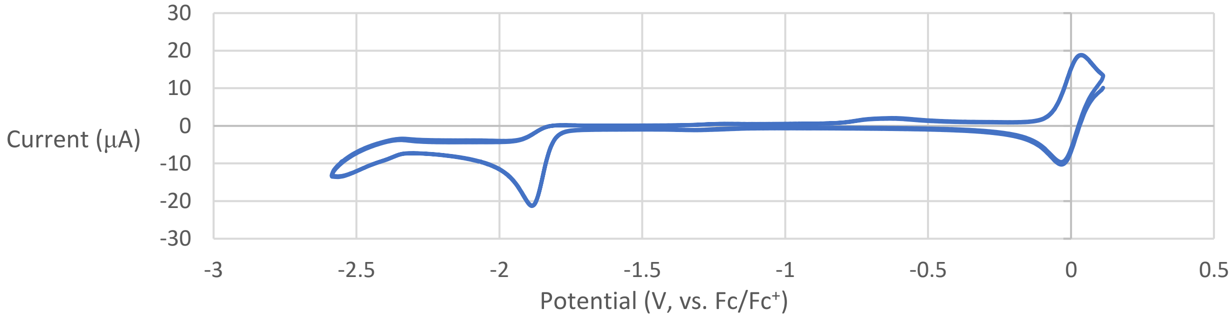
Figure S3. Fluorescence spectrum of $Ru(deeb)_3(PF_6)_2$



8. Electrochemical Data

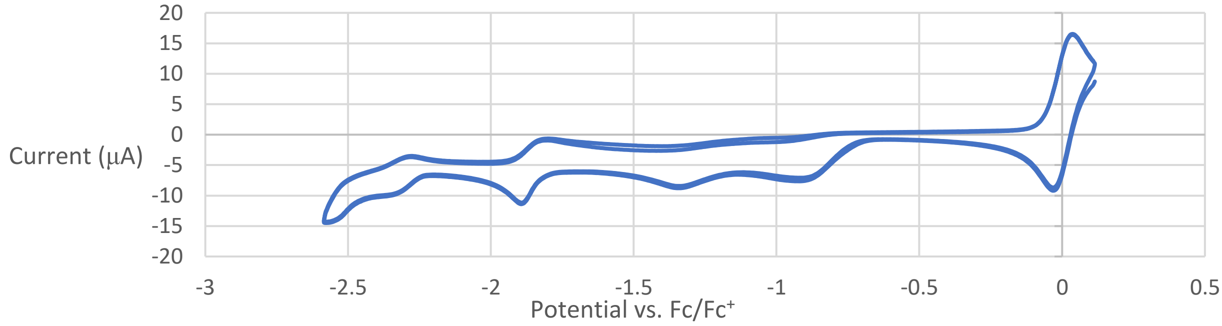
Instrument Details: All electrochemical data was acquired on a Pine Research Instrumentation Wavenow Potentiostat in MeCN with 0.1 M Bu_4NPF_6 and 1 mM substrate using a platinum auxiliary electrode, a glassy carbon working electrode, and a Ag/AgNO3 reference electrode. All data was referenced versus the ferrocene/ferrocenium (Fc/Fc^+) redox couple through added ferrocene. Data acquired in two passes at a scan rate of 0.05 V/s.

Figure S4. CV for cinnamoyl-1-methylimidazole (**1**)



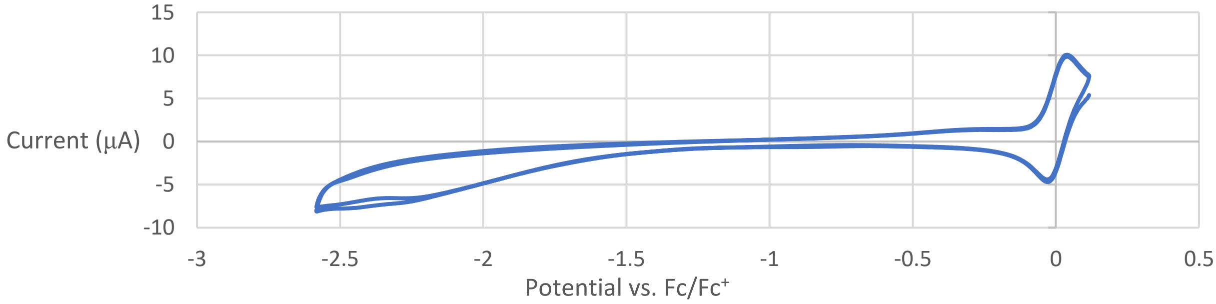
Reduction of **1**: $E_{1/2}$ (vs. Fc/Fc^+) = –1.84 V → $E_{1/2}$ (vs. SCE) = –1.54 V

Figure S5. CV for cinnamoyl-1-methylimidazole (**1**) + *p*-toluenesulfonic acid monohydrate (*p*-TsOH)



Reduction of **1** + *p*-TsOH: $E_{1/2}$ (vs. Fc/Fc^+) = –0.81 V → $E_{1/2}$ (vs. SCE) = –0.51 V

Figure S6. Electrochemical data for *p*-toluenesulfonic acid monohydrate



9. Fluorescence Quenching Data

Experimental Details: All fluorescence data was acquired on an ISS PC1 photon counting spectrofluorimeter with a 300 W high-pressure xenon arc lamp. Stock solutions of $Ru(bpy)_3Cl_2•6H_2O$, cinnamoyl-1-methylimidazole **(1)**, *p*-toluenesulfonic acid monohydrate (*p*-TsOH), and a 1:1 mixture of **1** and *p*-TsOH were prepared in HPLC-grade CH_3CN. Stock solutions were combined by volume to give 2.0 mL samples which each contained $5x10^{-5}$ M $Ru(bpy)_3Cl_2•6H_2O$, as well as the concentration of reagents indicated in the "concentration" column of each table. After preparing these solutions in separate vials, the volume was transferred to a 1 cm path cuvette, which was fitted with an appropriate septum, and sparged for 10 minutes prior to data acquisition. Samples were excited @ 450 nm, then collected from 460-700 nm. Intensities were recorded at 610 nm (λ_{max} of $Ru(bpy)_3Cl_2$), repeated three-fold, and then averaged.

Table S3. Blank, contents: $5x10^{-5}$ M $Ru(bpy)_3Cl_2•6H_2O$

Entry	Concentration, M	Intensity	Average	F/F_0
0-1	N/A	10135	10195	1.000
0-2	N/A	10168		
0-3	N/A	10282		

Table S4. Sample 1, Contents: $5x10^{-5}$ M $Ru(bpy)_3Cl_2•6H_2O$, indicated concentration **1**

Entry	Concentration, M	Intensity	Average	F/F_0
1A-1	0.005	9416	9470	1.077
1A-2	0.005	9475		
1A-3	0.005	9519		
1B-1	0.010	9108	9033	1.129
1B-2	0.010	8972		
1B-3	0.010	9018		
1C-1	0.015	8943	8932	1.141
1C-2	0.015	8893		
1C-3	0.015	8960		
1D-1	0.020	8550	8393	1.215
1D-2	0.020	8273		
1D-3	0.020	8356		
1E-1	0.025	7967	8062	1.265
1E-2	0.025	8139		
1E-3	0.025	8081		

Table S5. Sample 2, Contents: $5x10^{-5}$ M $Ru(bpy)_3Cl_2•6H_2O$, indicated concentration *p*-TsOH

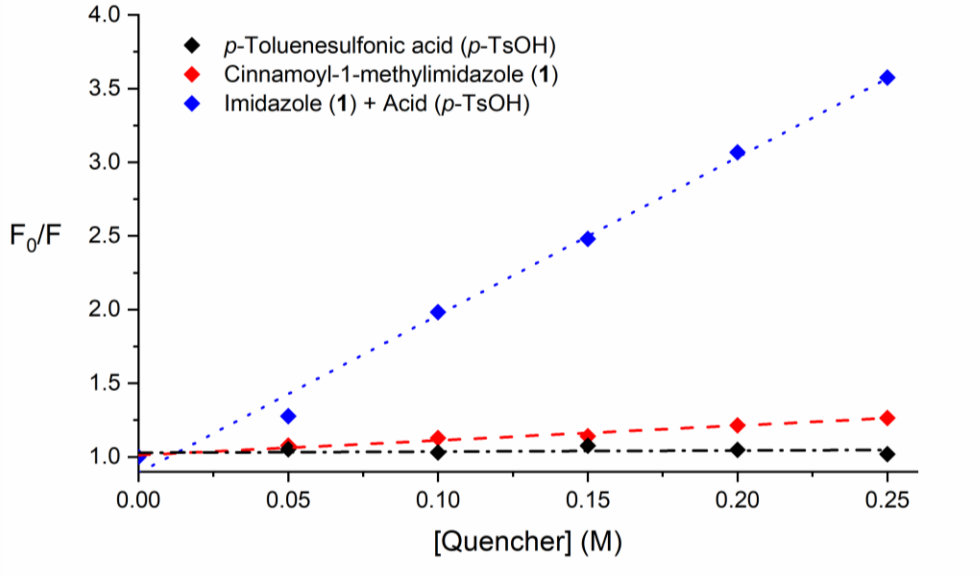
Entry	Concentration, M	Intensity	Average	F/F_0
2A-1	0.005	9861	9697	1.051
2A-2	0.005	9591		
2A-3	0.005	9638		
2B-1	0.010	9968	9884	1.031
2B-2	0.010	9952		
2B-3	0.010	9732		

2C-1	0.015	9644	9467	1.077
2C-2	0.015	9343		
2C-3	0.015	9413		
2D-1	0.020	9673	9719	1.049
2D-2	0.020	9709		
2D-3	0.020	9770		
2E-1	0.025	10016	10006	1.019
2E-2	0.025	9779		
2E-3	0.025	10223		

Table S6. Sample 3, Contents: 5x10^{-5} M Ru(bpy)$_3$Cl$_2$•6H$_2$O, indicated concentration 1 and *p*-TsOH

Entry	Concentration, M	Intensity	Average	F/F$_0$
3A-1	0.005	7928	7979	1.278
3A-2	0.005	8133		
3A-3	0.005	7876		
3B-1	0.010	5228	5143	1.982
3B-2	0.010	5128		
3B-3	0.010	5072		
3C-1	0.015	4366	3941	2.480
3C-2	0.015	4024		
3C-3	0.015	3941		
3D-1	0.020	3317	3394	3.068
3D-2	0.020	3257		
3D-3	0.020	3394		
3E-1	0.025	2875	2902	3.575
3E-2	0.025	2779		
3E-3	0.025	2902		

Figure S7. Stern-Volmer quenching of Ru(bpy)$_3$Cl$_2$•6H$_2$O by *p*-TsOH, **1**, and **1** + *p*-TsOH



10. Computational Data

General details: The calculations for the present Brønsted acid co-catalyzed photocyclization were carried out using density functional theory[11] (DFT) implemented in the Jaguar 9.1 suite program.[12] Geometry optimization were performed with B3LYP-D3[13–15] levels of theory and 6-31G** basis set.[16] For the Ru metal center, Los Alamos LACVP**[17–19] basis set which is including effective core potentials was applied. Once in the optimized geometries, the single point energies were re-evaluated using triple-ζ quality of basis set, cc-pVTZ(-f)[20], where Ru metal was evaluated with LACV3P** basis set. Vibrational frequencies were evaluated using the optimized structures at the same level as the geometry optimizations. Zero-point energies and entropy correction terms were derived from frequency calculations. Solvation correction energies were calculated from the self-consistent reaction field (SCRF) approximations,[21–23] which is the solution for the linearized Poisson-Boltzmann equations with the proper dielectric constants (ε=37.5 for acetonitrile). Transition states were found by using the quadratic synchronous transit search method (QST).[24] Finally, the solution phase Gibbs free energies were computed as follows:

$$G(Sol) = G(gas) + G^{solv} \quad (1)$$
$$G(gas) = H(gas) - TS(gas) \quad (2)$$
$$H(Gas) = E(SCF) + ZPE \quad (3)$$
$$\Delta G(Sol) = \Sigma G(Sol) \text{ for products} - \Sigma G(Sol) \text{ for reactants} \quad (4)$$

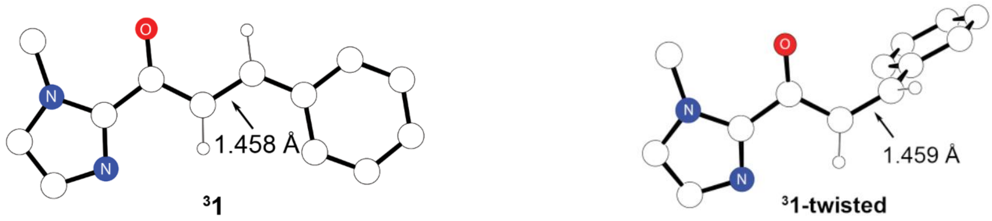
G(Sol) is the solvation corrected Gibbs free energy; G(gas) is the gas phase free energy; H(gas) is the enthalpy in the gas phase; T is the temperature (298.15 K); S(gas) is the entropy in the gas phase; E(SCF) is the electronic energy converged from the self-consistent field method; ZPE is the vibrational zero-point energy; and S for the vibrational entropy correction. Note that here entropy refers specifically to the vibrational/rotational/translational entropy of the solute(s). The solvent entropies are implicitly included in the continuum model.

Evaluation of triplet energies: To evaluate the triplet energies of substrates (**1** and **1H$^+$**) and photocatalyst, we optimized both singlet ground state and the first triplet state geometries. Gibbs free energy of each state was assessed as mentioned previously, and triplet energies were computed through eqn. 5:

$$E_T = G(T_1) - G(S_0) \quad (5)$$

Note that for the triplet state geometries of alkenes, two major conformers were found for **1**, but not with **1H$^+$**. Two structures – planar and twisted geometries of **^{3}1** are shown in Figure S8.

Figure S8. Planar and twisted structures of ^{3}**1**.

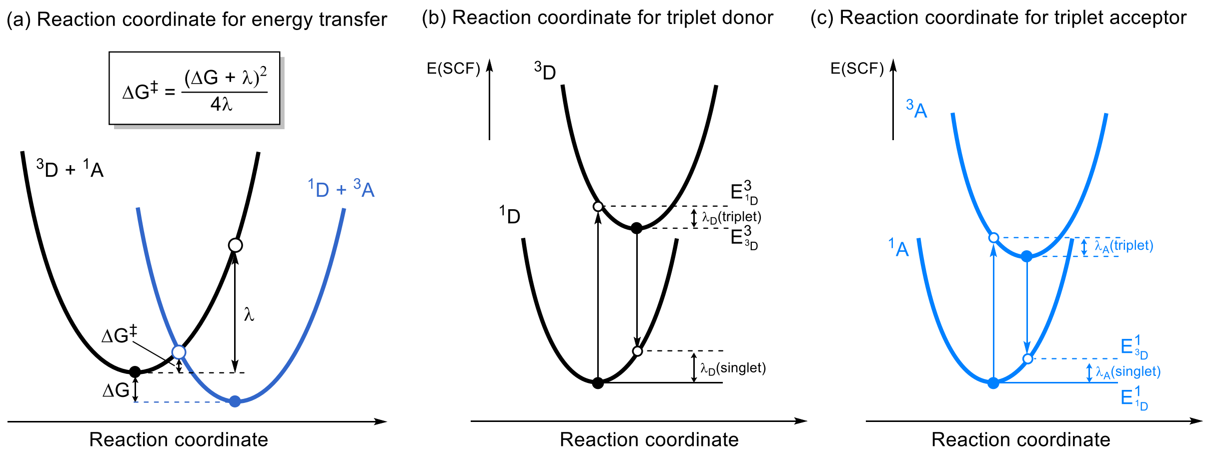


E_T = 47.57 kcal/mol E_T = 46.51 kcal/mol

Evaluation of vertical reorganization energies and Marcus energy transfer barrier: The potential energy surface model to express the vertical Dexter energy transfer process is shown in Figure S9a. The black parabolic surface represents the state before energy transfer, where the donor molecule is its triplet state (^{3}D) and the acceptor molecule is in its singlet state (^{1}A). After the energy transfer, the spin states are swapped to a donor singlet (^{1}D) and acceptor triplet (^{3}A) respectively, as drawn in blue. Energy transfer occurs at the point where the two curves cross, and the energy barrier for this process can be estimated by equation shown in Figure S9a.

Vertical reorganization energy was evaluated by following Nelson's four point model.[25] As described in Figure S9, the vertical reorganization energy for triplet donor can be assessed as λ_D(triplet), which is the structural reorganization cost required for ^{3}D to ^{1}D geometry change. Similarly, for triplet acceptor molecule, λ_A(singlet) should be assessed, as they changes their geometry from ^{1}A to ^{3}A.

Figure S9. Reaction coordinate for triplet donor and acceptor for evaluating vertical reorganization energy.



Hence, the reorganization energy of each was calculated using the four-point model with B3LYP-D3/cc-pVTZ(-f) level. Total reorganization energy for the Dexter energy transfer can be computed as below:

$$\lambda = \lambda_D(\text{triplet}) + \lambda_A(\text{singlet}) \quad (6)$$

$$\lambda_D(\text{triplet}) = E^3_{1_D} - E^3_{3_D} \quad (7)$$

$$\lambda_A(\text{singlet}) = E^1_{3_A} - E^1_{1_A} \quad (8)$$

Where E^y_x is the SCF converged energy of the state y (y = 1 for singlet, 3 for triplet) in gas-phase optimized geometry of x. (x = ^{1}D/^{3}D for singlet/triplet donor, ^{1}A/^{3}A for singlet/triplet acceptor) The computed vertical reorganization energies of **^{1}1(≡^{1}I)**, **^{1}1H^{+}(≡^{1}IV)** and ^{3}Ru(bpy)$_3^{2+}$ are enumerated in Table S7.

Table S7. Computed vertical reorganization energies

	$E^3_{1_D}$ (eV)	$E^3_{3_D}$ (ev)	λ$_D$ (kcal/mol)
^{3}Ru(bpy)$_3$$^{2+}$	-42998. 422	-42999.379	22.07
	$E^1_{3_A}$ (eV)	$E^1_{1_A}$ (ev)	λ$_A$ (kcal/mol)
^{1}1	-18709.127	-18709.588	10.63
^{1}1H+	-18719.670	-18719.945	6.34

Energies, Coordinates, and Vibrational Frequencies of Optimized Structures

Table S8. Computed energies of the optimized geometries

	E(SCF)/(eV)	**ZPE/(kcal/mol)**	**S(gas)/(cal/mol·K)**	**G(solv)/(kcal/mol)**
	cc-pVTZ(-f)/LACV3P**	6-31G**/LACVP**	6-31G**/LACVP**	6-31G**/LACVP**
^{1}Ru(bpy)$_3$$^{2+}$	-43001.434	304.61	186.44	-126.09
^{3}Ru(bpy)$_3$$^{2+}$	-42999.379	303.16	197.92	-124.76
***p*-TsOH**	-24370.111	89.12	101.30	-14.86
***p*-TsO$^-$**	-24356.299	82.02	101.33	-68.14
(^{1}1)	-18709.588	140.91	120.05	-11.29
^{3}1	-18707.348	138.57	124.88	-11.59
^{3}1-twisted	-18707.369	138.34	124.81	-11.96
^{3}1-TS	-27136.678	223.92	158.71	-12.96
^{3}24	-27137.473	225.61	158.14	-12.01
^{1}25	-27137.520	225.50	155.67	-11.84
^{1}25-TS	-27137.293	225.30	151.35	-12.52
^{1}2	-27139.053	228.73	153.88	-11.75
(^{1}1H$^+$)	-18719.945	149.19	120.26	-55.46
^{3}1H$^+$	-18717.982	147.14	125.46	-52.69
^{3}1H$^+$-TS	-27147.439	232.45	159.34	-52.05
^{3}24H$^+$	-27147.760	233.67	158.91	-56.12
^{1}25H$^+$	-27147.790	233.57	149.28	-56.39
^{1}25H$^+$-TS	-27147.605	233.68	150.26	-55.99
^{1}2H$^+$	-27149.598	236.83	152.79	-51.15

Table S9. Cartesian coordinates of the optimized geometries.

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^{1}Ru(bpy)$_{3}^{2+}$

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C	-1.657469869	4.599597454	-0.029567523
C	-0.707512379	4.232200623	-0.982709825
C	-0.221517518	2.930230379	-0.972596109
C	-1.560348511	2.357465744	0.857971132
C	-2.085834026	3.652616024	0.896282613
C	-1.948890448	1.282713532	1.796257257
C	-1.630765676	-0.951297641	2.412594795
C	-2.553867102	-0.847897649	3.446117163
C	-3.193097115	0.374445766	3.653684139
C	-2.885608196	1.446836114	2.821198463
C	-2.696708202	-0.660598397	-1.260902405
C	-3.589166880	-0.919300616	-2.293882370
C	-3.112140656	-0.928623378	-3.604739904
C	-1.761641979	-0.679989994	-3.833192825
C	-0.910181224	-0.427489042	-2.752832174
C	0.537198544	-0.154718295	-2.891168356
C	1.211892128	-0.133930489	-4.115607738
C	2.577458858	0.133084789	-4.148361206
C	3.248594522	0.373282224	-2.949468613
C	2.526077271	0.340640992	-1.762533188
C	0.189963460	-3.040341139	-0.245138884
C	1.972304702	1.521496773	1.865329385
C	3.009477854	1.656298876	2.779964685
C	3.674900055	0.509367347	3.214356899
C	3.278662682	-0.730301976	2.719995260
C	2.227575302	-0.802324712	1.800024509
C	1.734086394	-2.066658497	1.215160728
C	2.262300730	-3.325209856	1.521079779
C	1.727521896	-4.461018085	0.919066429
C	0.672083974	-4.316782951	0.018073989
H	-2.060475349	5.607342243	-0.006708314
H	-0.346834213	4.938145161	-1.723294258
H	0.514951646	2.595405579	-1.693727374
H	-2.824355602	3.924315214	1.641095281
H	-1.108811140	-1.878944993	2.209144115
H	-2.763265848	-1.708897829	4.071919918
H	-3.919588089	0.492877543	4.451559067
H	-3.373628855	2.402438402	2.971907377
H	-3.018784523	-0.639377892	-0.226466238
H	-4.634347439	-1.106322169	-2.071248055
H	-3.780687571	-1.124486923	-4.437300205
H	-1.377966046	-0.683115780	-4.846469879
H	0.680012345	-0.325120926	-5.039583683
H	3.107765675	0.151554659	-5.095314503
H	4.312479496	0.584081531	-2.928864241
H	3.000190496	0.522974312	-0.805132151
H	-0.628276050	-2.875339270	-0.936866283
H	1.425085545	2.381263733	1.496548891
H	3.285376787	2.640813351	3.142291784
H	4.489410400	0.578122556	3.928600550
H	3.785466194	-1.629846811	3.047951221
H	3.082859278	-3.422366381	2.221604824
H	2.129296780	-5.442708015	1.149688840
H	0.227009103	-5.174651623	-0.474681169
N	-0.631032586	2.010957003	-0.076884821
N	-1.333060026	0.082738906	1.601669431
N	-1.388154626	-0.421127886	-1.476819992
N	1.203511238	0.087599665	-1.726505280
N	1.586971045	0.325105071	1.380213141
N	0.699776292	-1.938606977	0.336593151
Ru	0.027806319	0.021382269	0.007655812

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^{3}Ru(bpy)$_{3}^{2+}$

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C	-1.936032534	4.536324024	-0.083726056
C	-1.022511244	4.133548737	-1.057990432
C	-0.486106068	2.854931116	-0.974950790
C	-1.680144668	2.382421494	0.981348574
C	-2.269612789	3.650905609	0.936772108
C	-1.988420248	1.398227453	2.051561832
C	-1.883083344	-0.822984099	2.725327015
C	-2.503953934	-0.544560313	3.939927816
C	-2.860834599	0.777016819	4.210267067
C	-2.596689224	1.761082888	3.259984255
C	-2.631384611	-0.485204607	-1.418367982
C	-3.545995951	-0.681468070	-2.445496559
C	-3.071179390	-0.745855570	-3.755595684
C	-1.704448223	-0.619855404	-3.986398697
C	-0.827830672	-0.444841743	-2.909581661
C	0.641766191	-0.313551694	-3.089470625
C	1.296464205	-0.673272669	-4.274263859
C	2.676984787	-0.510834873	-4.365389824
C	3.377115488	-0.002816677	-3.270505428
C	2.659378290	0.311935335	-2.119996786
C	0.562859774	-2.965176582	-0.618780255
C	1.612350941	1.395965338	2.274149179
C	2.533009529	1.497633219	3.308787584
C	3.274583340	0.367897630	3.657849550
C	3.070755005	-0.819100261	2.960519075
C	2.132570267	-0.862125635	1.925013900
C	1.840808272	-2.067367792	1.127825618
C	2.476513386	-3.298589945	1.312675357
C	2.133954048	-4.379717350	0.506018460
C	1.158924341	-4.211499214	-0.478297919
H	-2.390333652	5.521256447	-0.122052059
H	-0.734252930	4.789684296	-1.871832371
H	0.217179358	2.484410048	-1.712732315
H	-3.001040697	3.937813759	1.682331800
H	-1.569971800	-1.832082272	2.469912529
H	-2.696158648	-1.339835763	4.652056694
H	-3.332638025	1.041067481	5.151456356
H	-2.846350193	2.794270515	3.470432043
H	-2.944952726	-0.412948012	-0.382616043
H	-4.602656364	-0.772677660	-2.219505548
H	-3.754809618	-0.882425487	-4.587451935
H	-1.325336576	-0.637559772	-5.000833988
H	0.748359382	-1.089833260	-5.110314846
H	3.198665857	-0.783996761	-5.277188301
H	4.451693058	0.141798571	-3.303149939
H	3.155576229	0.696098804	-1.232495785
H	-0.195533767	-2.780819893	-1.370486856
H	1.008441925	2.241726398	1.967111588
H	2.662277222	2.441296101	3.827193737
H	4.001589298	0.409554541	4.462561607

H	3.639207363	-1.702673435	3.224002123
H	3.233846188	-3.416855097	2.078010082
H	2.622216940	-5.339121819	0.643684864
H	0.863925159	-5.028541088	-1.127465248
N	-0.798652947	1.998918891	0.018818231
N	-1.634715676	0.118075721	1.804263234
N	-1.305777311	-0.375605077	-1.637889147
N	1.330335140	0.165961593	-2.030925751
N	1.413313389	0.249156073	1.593813896
N	0.888842046	-1.915868402	0.162344456
Ru	0.033224087	0.004679526	0.019114867

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***p*-TsOH**

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C	-3.909461021	0.087634914	-1.301102161
C	-4.901912212	-0.642064273	-0.627754748
C	-2.919746161	0.731659710	-0.546642840
H	-5.665424824	-1.159643173	-1.202280402
H	-2.137423277	1.288829446	-1.054581523
C	-4.920924664	-0.718608797	0.761212170
C	-2.920313597	0.668601871	0.845548987
H	-5.677700520	-1.292166233	1.284584880
H	-2.153278112	1.159733891	1.434172273
C	-3.930353880	-0.049564689	1.482805014
C	-3.928541899	0.190889686	-2.806713820
H	-2.947540283	0.463469744	-3.205130577
H	-4.235987186	-0.752607465	-3.268326283
H	-4.641890049	0.958572924	-3.131108522
S	-3.943365812	-0.143426701	3.257040501
O	-4.679003716	-1.328527451	3.703764915
O	-2.610447407	0.132988691	3.787150383
O	-4.898898125	1.180127025	3.513310671
H	-5.241266727	1.085560203	4.586587429

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***p*-TsO⁻**

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C	-3.935457230	-0.015764803	-1.332505584
C	-5.077348709	-0.411128342	-0.621300519
C	-2.816570997	0.403838187	-0.601749480
H	-5.960253239	-0.736025333	-1.171120048
H	-1.921185970	0.721104860	-1.135157347
C	-5.100435257	-0.388242513	0.773101926
C	-2.835266352	0.428690493	0.793777645
H	-5.988220692	-0.675339282	1.328014612
H	-1.978525519	0.773868024	1.363841772
C	-3.975940466	0.027650680	1.490480065
C	-3.931199789	-0.004220272	-2.845211983
H	-2.910915613	-0.007105505	-3.244049072
H	-4.454311848	-0.875275731	-3.257440805
H	-4.433000088	0.888126373	-3.244465351
S	-3.976434469	-0.003313641	3.315807819
O	-3.486042976	-1.367406487	3.651330948
O	-3.042726994	1.094311833	3.688036680
O	-5.400592327	0.240665719	3.673270226

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^{1}1

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N	0.115229376	-0.118081972	-3.039816856
C	-0.023184463	1.028723717	-2.374508142
C	0.231319815	-1.083942652	-2.090475321
C	0.162775934	-0.524187982	-0.827671170
N	0.001965524	0.821029663	-1.012326360
H	0.217448115	-0.957290649	0.160076588
H	0.356701761	-2.127005100	-2.346743107
C	-0.119392820	1.816444755	0.050719399
H	-1.074213147	2.337256670	-0.027932940
H	-0.048572648	1.302303076	1.011327147
H	0.673216701	2.560254574	-0.036988609
C	-0.190237895	2.355970860	-2.990581751
O	-0.318542510	3.368569136	-2.293561459
C	-0.189184904	2.375805616	-4.465725422
H	-0.066802882	1.421971798	-4.965116024
C	-0.324595809	3.541696072	-5.127821922
H	-0.431062132	4.435194016	-4.513179779
C	-0.333467841	3.745752573	-6.574998856
C	-0.207099199	2.692103624	-7.502269268
C	-0.470412463	5.055099010	-7.072043419
C	-0.220259115	2.943450689	-8.869272232
C	-0.480493963	5.307366371	-8.442064285
C	-0.355957627	4.251730442	-9.346067429
H	-0.108552679	1.671137691	-7.148686409
H	-0.565566421	5.878720760	-6.369138718
H	-0.126597106	2.117754936	-9.568895340
H	-0.589084744	6.325577259	-8.804203987
H	-0.368382871	4.443560600	-10.415128708

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N	0.115783721	-0.122301444	-3.070152760
C	-0.021965532	1.017331481	-2.392442703
C	0.228648886	-1.100982308	-2.129063368
C	0.159313485	-0.557447731	-0.862831593
N	-0.000152193	0.795110583	-1.034797788
H	0.210064217	-1.000289798	0.120486721
H	0.352791071	-2.141143799	-2.397757292
C	-0.121897861	1.779056311	0.037571844
H	-1.075008869	2.304068804	-0.035508748
H	-0.055927634	1.253856182	0.992666125
H	0.673189282	2.521570921	-0.037071031
C	-0.180459350	2.351775885	-2.998603344
O	-0.307620734	3.388387442	-2.294828415
C	-0.181026638	2.398250580	-4.426435471
H	-0.065579697	1.460458398	-4.956147671
C	-0.327135414	3.664039612	-5.135107040
H	-0.431255817	4.542419434	-4.505757809
C	-0.334969342	3.804393053	-6.516732693
C	-0.202408791	2.692720890	-7.432068825
C	-0.480864614	5.115364552	-7.106479168
C	-0.216887668	2.891204596	-8.796857834
C	-0.491354614	5.289877415	-8.469974518
C	-0.359793901	4.182434082	-9.337229729
H	-0.093635969	1.688718796	-7.038929462
H	-0.581860662	5.968582630	-6.441636086
H	-0.116755195	2.039309740	-9.463614464
H	-0.602577388	6.286951542	-8.886676788
H	-0.370182335	4.327147007	-10.412937164

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N	0.582259417	-0.070431262	-3.074938774
C	0.072959624	1.032967091	-2.529695988
C	0.542016566	-1.016982794	-2.097745419
C	-0.000232956	-0.488276362	-0.942099631
N	-0.298800468	0.818843126	-1.221707463
H	-0.194345638	-0.917775333	0.029454475
H	0.898991466	-2.024484396	-2.261451721
C	-0.896523595	1.773368478	-0.290447533
H	-1.845582366	2.140473843	-0.682344496
H	-1.054389238	1.267664671	0.664162695
H	-0.237805232	2.631783724	-0.154862866
C	-0.100060716	2.325484276	-3.222489834
O	-0.603977144	3.307269096	-2.648343086
C	0.351860076	2.367248297	-4.598653316
H	0.816857338	1.464574456	-4.992835999
C	0.209743261	3.563113451	-5.422719479
H	1.012181640	4.300229073	-5.387488365
C	-0.915828526	3.840764284	-6.236068249
C	-2.027116776	2.951798439	-6.308786392
C	-0.967913508	5.028669357	-7.020025730
C	-3.115237236	3.239154577	-7.117838860
C	-2.062115908	5.304180622	-7.824771404
C	-3.144152403	4.414090633	-7.881836414
H	-2.011924982	2.040245056	-5.718274117
H	-0.132432312	5.722676754	-6.978756428
H	-3.951752186	2.546954632	-7.158593178
H	-2.080171347	6.216747761	-8.414194107
H	-3.999000788	4.633162975	-8.514685631

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N	1.185414791	0.122632220	-2.624961376
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C	1.660435319	-0.793473244	-1.731309772
C	0.993330359	-0.678587794	-0.529499412
N	0.080803528	0.333740890	-0.693680704
H	1.074236989	-1.221078992	0.400444895
H	2.447444916	-1.488572955	-1.990167975
C	-0.802496076	0.852197826	0.347273856
H	-1.822822332	0.922568500	-0.027251752
H	-0.760158956	0.171200141	1.200419664
H	-0.479945689	1.850519776	0.646991074
C	-0.494663060	1.966412306	-2.507730961
O	-1.228036880	2.658721924	-1.765677214
C	-0.248391643	2.310784578	-3.883170366
H	0.251445115	1.575900435	-4.502816200
C	-0.948781490	3.445044994	-4.471593380
H	-1.606455922	3.982853889	-3.795443773
C	-0.826441288	3.884927273	-5.799517632
C	0.035369396	3.260544062	-6.759778500
C	-1.581008315	5.018038750	-6.247432232
C	0.126480296	3.740188122	-8.055565834
C	-1.480955124	5.482960224	-7.544507027
C	-0.625875056	4.851721287	-8.465818405
H	0.623792291	2.396904469	-6.468286514
H	-2.244067907	5.509831905	-5.540318489
H	0.787677586	3.246953964	-8.763020515
H	-2.068283319	6.342892170	-7.854886055
H	-0.550113738	5.219393253	-9.484356880
C	1.919074297	3.337296009	-3.531961679
C	1.675404310	4.273303986	-2.564915657
H	1.915101886	3.632741213	-4.574775219
H	2.315229416	2.353185177	-3.307034016
H	1.334390044	5.255675316	-2.885859013
C	1.724451184	4.059790611	-1.129948616
C	1.247477174	5.073024273	-0.270035684
C	2.223880768	2.874654055	-0.543602645
C	1.253312707	4.908625126	1.110284328
C	2.230350971	2.714236736	0.837137759
C	1.743601203	3.725976229	1.672919273
H	0.855547667	5.989418983	-0.703473985
H	2.599791765	2.074055433	-1.170073986
H	0.872905552	5.699673176	1.750116110
H	2.614419460	1.792124271	1.263749003
H	1.750346780	3.595482111	2.751169443

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N	1.729790449	0.308447003	-2.577512264
C	0.756077051	0.971654713	-1.953379273
C	2.096881151	-0.690013528	-1.729698896
C	1.343564391	-0.632833064	-0.570506454
N	0.489244282	0.422903627	-0.718506038
H	1.344010234	-1.239177465	0.322944641
H	2.872388840	-1.399858236	-1.982350111
C	-0.442118436	0.914278388	0.294143289
H	-1.454732895	0.944180250	-0.106289774
H	-0.394397020	0.244837090	1.154979825
H	-0.156934872	1.924290419	0.594099343
C	0.087400623	2.174661875	-2.467573166
O	-0.863194823	2.675349951	-1.876174331
C	0.699379325	2.797606468	-3.719506264
H	0.998339772	1.983576894	-4.390089035
C	-0.254703194	3.741353989	-4.377628803
H	-1.051169276	4.136999130	-3.755599022
C	-0.161908135	4.171892166	-5.720084667
C	0.839239717	3.706268549	-6.623189926
C	-1.101941228	5.118646145	-6.225131035
C	0.889947891	4.163403034	-7.931948185
C	-1.041529298	5.566822529	-7.534214020
C	-0.044690203	5.095556259	-8.400967598
H	1.571191311	2.979554176	-6.285181522
H	-1.877280116	5.486783981	-5.558037281
H	1.663246274	3.791712761	-8.598937035
H	-1.772010684	6.288122177	-7.890536308
H	0.001858802	5.449266911	-9.426482201
C	2.050710440	3.520467997	-3.301768303
C	1.846359849	4.570213795	-2.259165525
H	2.447469234	3.975313902	-4.215649605
H	2.755753040	2.747182846	-2.986899376
H	1.431139708	5.516632557	-2.597118378
C	1.994753480	4.389139175	-0.862433791
C	1.599624991	5.428590298	0.031102516
C	2.507333517	3.193264008	-0.275863707

C	1.687375784	5.274354458	1.404816270
C	2.588772774	3.049965858	1.102367401
C	2.177892208	4.081872463	1.956579328
H	1.207050920	6.351956844	-0.386817694
H	2.837378025	2.379291058	-0.910826743
H	1.369216561	6.082215786	2.058158159
H	2.980026245	2.125152826	1.518530726
H	2.243493319	3.962046385	3.033870935

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N	1.676574230	0.416210771	-2.537428141
C	0.701372862	1.093351364	-1.930487037
C	2.077330589	-0.529079437	-1.645731807
C	1.344791889	-0.422807336	-0.476314098
N	0.465947866	0.605061352	-0.664975226
H	1.375182509	-0.978394508	0.449028611
H	2.860541344	-1.238143563	-1.875442743
C	-0.433937758	1.153006792	0.347420007
H	-1.456650615	1.170001268	-0.026516251
H	-0.365040421	0.528338611	1.239595056
H	-0.133273616	2.174401760	0.589357138
C	0.010214211	2.262593746	-2.489130974
O	-0.952634633	2.766874075	-1.921206594
C	0.628160357	2.862894297	-3.746148825
H	1.001653314	2.047294140	-4.374138832
C	-0.333698779	3.727793455	-4.472810268
H	-1.177000523	4.105746746	-3.902848005
C	-0.187957019	4.135391712	-5.819512367
C	0.895087183	3.719276667	-6.647865772
C	-1.151335716	5.011044502	-6.400673389
C	0.999821603	4.156424999	-7.960650921
C	-1.037600517	5.438881397	-7.713183403
C	0.039577320	5.017702103	-8.506226540
H	1.647269011	3.045211792	-6.250603676
H	-1.987508059	5.341995239	-5.789935112
H	1.835444331	3.823526382	-8.570454597
H	-1.788210273	6.105504036	-8.129167557
H	0.127758414	5.355086327	-9.534543037
C	1.959102631	3.651131153	-3.287065744
C	1.731520653	4.578115940	-2.151816368
H	2.294900656	4.196506977	-4.175143242
H	2.707252264	2.889676571	-3.057314396
H	1.194898009	5.497832775	-2.374049664
C	1.984425426	4.298314095	-0.784029782
C	1.545069575	5.217587471	0.213590518
C	2.641054630	3.116691589	-0.329314381
C	1.731571913	4.965634346	1.563561201
C	2.819550991	2.873727322	1.025382876
C	2.367175341	3.788958311	1.985183716
H	1.040394425	6.126608849	-0.103228994
H	2.997621298	2.385904312	-1.046234488
H	1.377699614	5.683632851	2.298526287
H	3.316868782	1.959916472	1.339684486
H	2.510380745	3.591616392	3.043441296

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N	1.796099901	-0.197537228	-2.653477430
C	0.895712972	0.482380360	-1.945598602
C	2.146234989	-1.260049582	-1.878902316
C	1.459399343	-1.225142479	-0.679137886
N	0.662012994	-0.115257077	-0.724867225
H	1.474413276	-1.875733852	0.182527900
H	2.868005276	-1.994722247	-2.207955837
C	-0.216319904	0.352816731	0.345603853
H	-1.258886576	0.309293389	0.028917693
H	-0.060040887	-0.282672614	1.219550133
H	0.017617121	1.390450120	0.590007007
C	0.225576684	1.719329238	-2.374472857
O	-0.728196740	2.165427208	-1.744393945
C	0.804689050	2.407873392	-3.608375549
H	0.822602630	1.652622581	-4.405954838
C	-0.013656041	3.629486084	-3.955610752
H	-0.731949151	3.953123808	-3.211041689
C	-0.000759275	4.284912586	-5.214732170
C	0.797261059	3.857023478	-6.311547756
C	-0.809049964	5.440430641	-5.409979343
C	0.786554992	4.546997070	-7.516714573
C	-0.811091781	6.123414040	-6.615871429
C	-0.012018047	5.684813976	-7.680812836
H	1.416766882	2.971747875	-6.211118221
H	-1.430121303	5.785028458	-4.587132454
H	1.403949142	4.196705818	-8.339615822
H	-1.438033342	7.002957344	-6.735390186
H	-0.014625521	6.220968246	-8.625109673
C	2.254929066	2.927416086	-3.349854708
C	2.113930225	4.305926323	-2.748157263
H	2.770520449	3.005437136	-4.310681343
H	2.839053869	2.232025385	-2.740423679
H	2.199851990	5.156056881	-3.416398048
C	1.952882648	4.572427750	-1.361397982
C	1.712256551	5.903797150	-0.918670952
C	2.016611814	3.559293509	-0.363466471
C	1.523973465	6.195679188	0.422903240
C	1.832100153	3.863064766	0.978910863
C	1.577791572	5.178112984	1.385555267
H	1.663957238	6.697837353	-1.659672618
H	2.228471279	2.535125017	-0.650609612
H	1.333338380	7.220824718	0.728963137
H	1.894842386	3.070571423	1.720536828
H	1.430478692	5.409273148	2.436281681

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N	-0.369583756	0.091638878	-3.712664127
C	-0.111663640	1.013916850	-2.784065008
C	0.351086110	-1.003740788	-3.357180595
C	1.058986783	-0.753121436	-2.195469379
N	0.762059212	0.530233741	-1.833198667
H	1.729438901	-1.365582466	-1.611205220
H	0.331777900	-1.915092826	-3.938469172
C	1.304185510	1.235770345	-0.674270689
H	0.493964702	1.600270748	-0.042706914
H	1.934217095	0.541990578	-0.114393629
H	1.890188813	2.097457647	-0.997291803
C	-0.650468647	2.379629612	-2.777533531

O	-0.337795258	3.188007116	-1.903095841
C	-1.569316506	2.771062374	-3.905749798
H	-1.882744908	1.905789614	-4.490016460
C	-1.024263859	3.916953564	-4.814867496
H	-0.365684807	4.544239521	-4.200205803
C	-0.367015511	3.613070965	-6.132510185
C	0.125260741	2.340215206	-6.444048882
C	-0.228980616	4.641819954	-7.077349663
C	0.744640231	2.102634668	-7.673590183
C	0.387172103	4.402775288	-8.304087639
C	0.878037572	3.129973412	-8.607064247
H	0.019699354	1.527426958	-5.731693268
H	-0.613257229	5.631919384	-6.846544266
H	1.119535923	1.108201027	-7.901239395
H	0.483810842	5.209780216	-9.025591850
H	1.359941721	2.942893982	-9.562732697
C	-2.754115582	3.706125498	-3.540650129
C	-2.452099323	4.556076050	-4.805459499
H	-3.744803667	3.250790596	-3.469266415
H	-2.535938025	4.252777100	-2.620040178
H	-3.014060497	4.161733627	-5.659030914
C	-2.567109346	6.053541183	-4.770949841
C	-1.977890730	6.797751904	-3.737692595
C	-3.228125334	6.743897438	-5.795717716
C	-2.048555613	8.189463615	-3.731292725
C	-3.299911499	8.138091087	-5.793327332
C	-2.709128141	8.865649223	-4.760097980
H	-1.451959252	6.283051014	-2.937795639
H	-3.684355021	6.180412769	-6.606267452
H	-1.582962751	8.749039650	-2.924599886
H	-3.815686703	8.654090881	-6.598655224
H	-2.763345003	9.950592995	-4.754743099

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N	0.065397322	-0.213681832	-2.924163103
C	-0.033623263	1.011449695	-2.363708019
C	0.188838899	-1.177279234	-1.953268290
C	0.164855301	-0.513870776	-0.758227706
N	0.026651511	0.831116915	-1.028244019
H	0.235313281	-0.885510683	0.251935452
H	0.280296654	-2.227542400	-2.181257010
C	-0.042527683	1.876053214	0.014172458
H	-1.002206445	2.388513803	-0.049277715
H	0.071546622	1.385331631	0.981502473
H	0.753928006	2.602370262	-0.145828217
C	-0.194479302	2.335618496	-3.058727741
O	-0.341803253	3.317879677	-2.333297729
C	-0.163825095	2.341194153	-4.509630680
H	0.002419107	1.414693713	-5.053743362
C	-0.331593484	3.518486738	-5.176106930
H	-0.483286887	4.396724224	-4.547710896
C	-0.332678586	3.749715567	-6.603113651
C	-0.156447679	2.722652435	-7.557857990
C	-0.519927263	5.073919773	-7.057189465
C	-0.167910337	3.014893532	-8.913661003
C	-0.529780388	5.364602089	-8.416899681
C	-0.354012728	4.335696220	-9.346416473
H	-0.012389988	1.694577575	-7.238006115
H	-0.656366229	5.870738506	-6.330221176
H	-0.032474391	2.219874144	-9.640811920
H	-0.674106479	6.386634827	-8.752475739
H	-0.361930311	4.558391094	-10.408986092
H	0.038667522	-0.390057743	-3.920508146

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^{3}1H^{+}

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N	-0.318701804	-0.196710140	-2.849495173
C	-0.099451452	1.014316320	-2.270716667
C	-0.030307444	-1.214175701	-1.961655498
C	0.378163218	-0.611969769	-0.813138247
N	0.333794087	0.757288456	-1.011564493
H	0.697790980	-1.037601709	0.124393851
H	-0.131299421	-2.255741119	-2.219990969
C	0.701021552	1.750063896	0.012346744
H	-0.140576810	2.415626764	0.199996233
H	0.962355137	1.205687284	0.919565618
H	1.544557214	2.344378233	-0.334746271
C	-0.283568323	2.343427658	-2.850985289
O	0.114103913	3.360116243	-2.196408510
C	-0.919822931	2.490793705	-4.119139194
H	-1.314923406	1.616628885	-4.630048275
C	-1.068954825	3.771909237	-4.715794086
H	-0.655241251	4.603561878	-4.154542923
C	-1.721808791	4.034277916	-5.932885647
C	-2.347498894	3.021971941	-6.745142460
C	-1.776094198	5.392961502	-6.407001972
C	-2.964670658	3.351981640	-7.931175232
C	-2.395650625	5.706335068	-7.594590187
C	-2.995646477	4.691160679	-8.370883942
H	-2.342337370	1.987252116	-6.421007633
H	-1.311347961	6.169045448	-5.806658268
H	-3.433332443	2.579471111	-8.532305717
H	-2.425103903	6.735002995	-7.938545704
H	-3.483268023	4.941729069	-9.307363510
H	-0.621180415	-0.332069039	-3.802249908

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^{3}1H^{+}-TS

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N	1.123260498	-0.005723800	-2.632698774
C	0.368194431	0.931641877	-1.992878795
C	1.479524732	-1.015118718	-1.759648204
C	0.927237272	-0.692513049	-0.559485018
N	0.240092516	0.497856200	-0.711245596
H	0.956560552	-1.212343454	0.384490103
H	2.073335648	-1.862370014	-2.061636209
C	-0.461657286	1.191842198	0.378395140
H	-1.502205849	1.352253199	0.102509297
H	-0.392071158	0.562433064	1.266140342
H	0.006732326	2.158443928	0.558138490
C	-0.206315175	2.161064386	-2.529773474
O	-0.857750535	2.910696745	-1.765352488
C	0.093417451	2.544799089	-3.898055077
H	0.579778790	1.827890277	-4.556465626
C	-0.700766683	3.573484421	-4.502633095
H	-1.392877698	4.075794220	-3.833504438
C	-0.625922918	4.007843971	-5.849501610

C	0.300836295	3.485345125	-6.798303604
C	-1.514758945	5.031492710	-6.290242195
C	0.328514218	3.959298134	-8.099800110
C	-1.482839823	5.494170666	-7.594751835
C	-0.561429977	4.963638306	-8.509408951
H	0.999227762	2.707808495	-6.504835129
H	-2.228917360	5.443161488	-5.582625866
H	1.043058634	3.550406694	-8.807615280
H	-2.172764301	6.270858288	-7.909404278
H	-0.535447359	5.329008102	-9.530900955
C	1.984929919	3.644889593	-3.515850306
C	1.726388812	4.447240829	-2.411720514
H	1.955386043	4.083544731	-4.506363869
H	2.608470917	2.761702538	-3.418099642
H	1.221907020	5.393504620	-2.587451458
C	1.953420639	4.087674618	-1.040096402
C	1.428736210	4.915831089	-0.016494334
C	2.684348822	2.933616877	-0.658349454
C	1.620804429	4.604350090	1.322054863
C	2.878543854	2.629900694	0.681703806
C	2.349910975	3.462568521	1.677538753
H	0.859243035	5.798046112	-0.293187231
H	3.123349190	2.291916847	-1.414908051
H	1.209668875	5.248468876	2.092693806
H	3.454786062	1.752492785	0.959120274
H	2.511271954	3.225812674	2.724760294
H	1.348264217	0.017336167	-3.615360022

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[3]24H+

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N	1.586710811	0.155257225	-2.614762306
C	0.756486654	1.001365542	-1.961938977
C	1.932089925	-0.897058487	-1.801060915
C	1.285237789	-0.687482476	-0.616184235
N	0.559746563	0.477500588	-0.732312083
H	1.280768752	-1.272108197	0.289997548
H	2.584186792	-1.693834901	-2.120974064
C	-0.216030970	1.089375734	0.360963255
H	-1.247514844	1.229950309	0.044940226
H	-0.160731375	0.419339955	1.218076587
H	0.225516483	2.056194067	0.605687797
C	0.155399278	2.258388042	-2.480464697
O	-0.677725017	2.822905779	-1.789146662
C	0.699773610	2.836484909	-3.763339758
H	0.951111436	2.032671452	-4.471497536
C	-0.263703376	3.794280529	-4.381237984
H	-1.043260336	4.181281090	-3.735187054
C	-0.180002049	4.263298035	-5.710292816
C	0.810795367	3.830899000	-6.640004635
C	-1.132679224	5.222711086	-6.164931297
C	0.843367755	4.334722996	-7.931432724
C	-1.092794418	5.714993954	-7.458013535
C	-0.104156643	5.277879238	-8.351203918
H	1.554818273	3.097204208	-6.343179226
H	-1.899968743	5.563457012	-5.475137234
H	1.608846545	3.994629383	-8.622490883
H	-1.830437899	6.443531513	-7.780344009
H	-0.072600827	5.667944908	-9.363432884
C	2.100255013	3.553481102	-3.400102377
C	1.960457683	4.568797112	-2.326298952
H	2.422348738	4.020824432	-4.334567070
H	2.833997250	2.779422522	-3.150444508
H	1.530949116	5.524883270	-2.610726595
C	2.191741943	4.330141068	-0.949953556
C	1.806371808	5.312528133	0.009330950
C	2.771691084	3.125858307	-0.451883554
C	1.967415810	5.094536781	1.367344856
C	2.934512377	2.920415163	0.912505031
C	2.529561043	3.895879507	1.832470536
H	1.364331484	6.240262508	-0.342699140
H	3.136253119	2.372507811	-1.142892122
H	1.658422470	5.857148647	2.075631618
H	3.399117231	2.004044294	1.266645551
H	2.663897514	3.732644320	2.897076368
H	1.896420717	0.288785577	-3.568006516

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[1]25H+

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N	1.491951227	0.308413267	-2.575487137
C	0.685898304	1.191026211	-1.946312308
C	1.869234204	-0.690675080	-1.712410688
C	1.269201040	-0.404218763	-0.517677605
N	0.535305977	0.747744739	-0.681618869
H	1.304843903	-0.926886439	0.424837083
H	2.508458138	-1.507546425	-2.006901026
C	-0.183770761	1.440881610	0.403580189
H	-1.234652877	1.539154172	0.140029430
H	-0.062631682	0.847486734	1.308616996
H	0.253930986	2.430736780	0.540101230
C	0.079913683	2.432658911	-2.510348320
O	-0.774750113	2.992797613	-1.847436905
C	0.663544476	3.002469301	-3.777277708
H	1.026944757	2.203110456	-4.437835693
C	-0.322872430	3.851420641	-4.489876747
H	-1.151202917	4.235124111	-3.904236078
C	-0.206643209	4.236416340	-5.845791340
C	0.873250723	3.840278387	-6.686943054
C	-1.213498116	5.067805290	-6.417915821
C	0.933909357	4.252481461	-8.010052681
C	-1.144090176	5.470311642	-7.740951061
C	-0.070606396	5.067409515	-8.547699928
H	1.665727854	3.207780123	-6.296954155
H	-2.046595335	5.383040428	-5.795596600
H	1.766824841	3.940674305	-8.633157730
H	-1.925274134	6.101288795	-8.153809547
H	-0.017693125	5.385159492	-9.584052086
C	2.023782969	3.814867020	-3.336627007
C	1.851287961	4.635339737	-2.122048378
H	2.257000208	4.425041199	-4.212514400
H	2.820329189	3.073398352	-3.225216389
H	1.291518211	5.560469151	-2.227179050
C	2.184201002	4.216098309	-0.804718792
C	1.723403692	4.974246979	0.311030656
C	2.941998243	3.042649746	-0.520293951
C	1.986744046	4.577025890	1.613202929
C	3.204712629	2.655533075	0.788466215
C	2.726658344	3.411991358	1.865901589
H	1.146375775	5.875830173	0.126079038

H	3.357450247	2.455065489	-1.333014846
H	1.619982719	5.175599575	2.441546917
H	3.803471804	1.768116593	0.974843681
H	2.941556454	3.110347033	2.886002064
H	1.761303425	0.380321294	-3.547885180

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^{125}H^{+}-TS

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N	0.981047332	-0.115204491	-2.406836271
C	0.652573228	1.066904306	-1.837122679
C	1.153340816	-1.079565763	-1.441883326
C	0.924288034	-0.462881684	-0.245288253
N	0.613909543	0.855264783	-0.503903449
H	0.955836654	-0.853144944	0.759528399
H	1.414652228	-2.099272966	-1.675087929
C	0.355718106	1.874668717	0.529633522
H	-0.662944615	2.246200085	0.432432175
H	0.506091475	1.404627323	1.501083374
H	1.052228689	2.702485561	0.390270889
C	0.362215877	2.359533310	-2.518309116
O	-0.127719507	3.254514217	-1.847766399
C	0.689212859	2.470735312	-3.992470264
H	0.105233908	1.683936477	-4.501453400
C	0.340259850	3.850540638	-4.495512009
H	0.096466780	4.591082573	-3.743883371
C	0.171078160	4.185135841	-5.863446236
C	0.282121837	3.245023727	-6.924920559
C	-0.121685274	5.534950733	-6.207602501
C	0.121121071	3.639119387	-8.245612144
C	-0.279818177	5.918714046	-7.529359818
C	-0.156944647	4.975323677	-8.558324814
H	0.479067713	2.199087858	-6.708252430
H	-0.219110623	6.268393993	-5.411811829
H	0.206555650	2.904628992	-9.040842056
H	-0.503109336	6.954265594	-7.767192841
H	-0.281538099	5.277518272	-9.593242645
C	2.219110489	2.292795181	-4.299157143
C	2.843367100	3.630492926	-4.006410599
H	2.317637444	2.068225145	-5.363019943
H	2.685825586	1.462327957	-3.753931284
H	3.019309759	4.299828053	-4.840325832
C	3.238547087	4.038142204	-2.704507828
C	3.565509319	5.400387287	-2.453658104
C	3.316780090	3.134353876	-1.606760859
C	3.902448416	5.834142208	-1.182642460
C	3.666625500	3.578587055	-0.335843414
C	3.948617697	4.929464340	-0.111220255
H	3.526182890	6.107297421	-3.277710676
H	3.169075012	2.071816444	-1.771488190
H	4.135504723	6.881155491	-1.014960647
H	3.750019550	2.866501331	0.481160223
H	4.222363949	5.273131847	0.881170273
H	1.074732780	-0.256457508	-3.403736830

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^{1}2H^{+}

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N	-0.910197854	0.936228395	-4.094486237
C	-0.376114279	1.095040679	-2.866492748
C	-2.069754601	0.212534115	-4.013898849
C	-2.246312857	-0.087466046	-2.689943552
N	-1.196008563	0.468820244	-1.995384455
H	-3.025506020	-0.644920290	-2.194367409
H	-2.668846369	-0.022949046	-4.878977299
C	-1.018716335	0.383534521	-0.533246517
H	-1.053238153	1.383712888	-0.103884786
H	-1.823339105	-0.234643698	-0.136899456
H	-0.050727740	-0.062614828	-0.308238566
C	0.880257845	1.841676474	-2.521034718
O	1.131996870	2.031269073	-1.344530702
C	1.686305285	2.347386122	-3.674377441
H	1.879272580	1.532806516	-4.382271767
C	1.063213348	3.590486526	-4.427257061
H	0.543350160	4.215211391	-3.692872047
C	0.189157382	3.383833408	-5.629448414
C	0.543980300	2.475245476	-6.644402027
C	-1.023708582	4.080260754	-5.750133514
C	-0.296739608	2.266116619	-7.741121292
C	-1.858026028	3.879462719	-6.850100994
C	-1.500411034	2.967069626	-7.845266342
H	1.492106915	1.945368052	-6.591814518
H	-1.308925033	4.789754391	-4.977899551
H	-0.004606071	1.566691041	-8.518611908
H	-2.787880898	4.434492588	-6.929646015
H	-2.150577545	2.808647156	-8.700070381
C	2.946410418	3.194092751	-3.399208784
C	2.529091358	4.132106781	-4.569409847
H	3.910759449	2.690047741	-3.477330923
H	2.878152847	3.681566000	-2.424700737
H	2.947636127	3.749971628	-5.506997108
C	2.712429762	5.621363640	-4.496364117
C	2.388129950	6.335328579	-3.333960772
C	3.153822184	6.329885960	-5.620368958
C	2.505622387	7.723529339	-3.296659708
C	3.271375179	7.719671249	-5.586577415
C	2.947001219	8.419833183	-4.424336910
H	2.041964531	5.807664871	-2.448123693
H	3.404736519	5.789545536	-6.529930592
H	2.254421473	8.262856483	-2.388168573
H	3.615923882	8.253878593	-6.466935635
H	3.038208485	9.501325607	-4.395525455
H	-0.538288891	1.373692155	-4.944337368

Table S10. Vibrational frequencies of all optimized geometries

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$^{1}Ru(bpy)_3^{2+}$

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34.70 35.50 37.91 39.23 40.18 51.65
84.52 84.93 89.47 116.09 117.77 122.70
154.10 174.23 179.43 180.38 193.43 195.17
229.20 230.82 254.29 270.60 270.95 281.16
322.15 332.84 333.22 360.84 367.67 372.81
434.38 436.03 438.58 443.88 444.66 459.38
466.39 477.95 479.32 492.39 493.13 494.43
565.18 565.55 567.55 647.82 652.81 655.17
658.91 660.75 662.48 668.48 670.86 677.41
746.43 749.56 749.95 763.30 763.73 765.86
768.33 775.35 780.02 787.17 788.23 788.72
824.07 824.40 825.93 907.50 907.85 909.60
914.96 915.37 917.91 984.73 985.49 986.74
987.36 987.83 989.28 1026.66 1027.13 1027.55
1027.73 1031.35 1031.57 1031.90 1032.00 1033.94
1038.71 1040.73 1051.98 1056.93 1060.19 1061.88
1090.83 1093.49 1094.33 1100.05 1101.66 1102.30
1139.32 1139.58 1141.28 1157.10 1157.70 1158.38
1202.97 1203.51 1203.74 1214.67 1215.23 1215.86
1302.53 1303.37 1305.64 1306.01 1306.77 1308.20
1324.62 1325.15 1325.51 1338.97 1339.59 1340.14
1347.34 1347.63 1349.19 1465.76 1466.71 1466.91
1486.15 1486.43 1486.75 1505.67 1510.56 1511.47
1528.23 1528.52 1529.23 1611.10 1611.67 1612.18
1620.86 1621.30 1622.09 1647.81 1648.72 1649.03
1654.25 1656.01 1656.47 3211.47 3211.76 3211.80
3212.84 3212.94 3213.13 3221.76 3222.20 3222.76
3223.60 3223.91 3224.20 3229.11 3229.96 3230.25
3234.35 3235.98 3236.31 3236.76 3237.25 3237.80
3239.93 3241.44 3241.81

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$^{3}Ru(bpy)_3^{2+}$

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28.62 29.95 30.98 33.70 36.62 47.84
61.82 80.17 84.00 91.11 92.47 104.18
123.66 126.99 142.69 150.88 155.34 177.37
182.56 210.59 213.07 223.77 256.65 257.13
261.03 281.30 311.41 351.32 359.36 377.59
414.50 415.85 422.78 430.51 435.93 437.11
446.55 460.86 464.45 481.74 482.75 484.23
562.92 564.13 566.18 635.75 642.67 643.99
659.00 661.44 661.82 663.03 669.84 689.18
743.52 749.39 751.98 758.75 759.63 761.55
771.80 778.27 780.70 783.95 786.06 787.01
824.07 826.88 827.97 907.15 913.36 913.85
915.34 920.11 921.32 985.00 986.64 988.30
988.91 994.93 995.32 1017.79 1025.58 1028.22
1028.41 1030.08 1030.31 1031.40 1032.61 1033.06
1033.19 1034.17 1056.41 1057.62 1058.09 1059.98
1088.03 1088.72 1092.76 1100.54 1103.30 1103.71
1135.41 1137.74 1139.68 1151.94 1152.64 1158.02
1201.08 1201.23 1203.96 1212.96 1213.36 1214.79
1304.18 1305.29 1307.31 1309.32 1310.16 1312.38
1321.11 1321.97 1327.39 1338.80 1339.34 1342.42
1346.54 1347.09 1349.64 1463.77 1464.06 1466.39
1480.93 1481.34 1485.75 1507.63 1510.61 1511.42
1522.22 1522.88 1527.81 1609.56 1612.22 1612.78
1619.85 1625.88 1626.42 1640.27 1640.88 1649.71
1652.32 1653.48 1656.41 3187.63 3188.17 3212.44
3212.93 3213.81 3213.85 3214.61 3215.82 3219.83
3220.06 3225.50 3226.26 3226.71 3227.47 3231.06
3231.69 3231.92 3233.92 3234.91 3238.63 3239.54
3240.51 3242.29 3242.71

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***p*-TsOH**

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40.63 51.91 99.58 164.89 216.48 283.90
305.87 360.57 379.09 416.24 465.86 477.86
534.08 549.96 646.53 656.03 713.40 775.23
822.22 834.18 856.93 976.69 984.93 1020.31
1035.37 1064.95 1082.86 1102.95 1153.23 1160.30
1223.31 1235.86 1330.77 1341.10 1359.36 1427.84
1444.76 1448.23 1500.69 1505.58 1539.48 1631.60
1657.01 2045.45 3040.66 3102.49 3131.60 3185.83
3188.19 3223.65 3225.02

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***p*-TsO^{-}**

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29.77 53.60 89.25 164.61 206.55 272.72
317.94 352.37 390.28 417.02 480.47 529.40
555.10 568.30 651.24 660.73 717.30 811.33
831.01 854.63 964.01 974.74 992.82 1009.73
1042.05 1060.67 1121.00 1135.39 1206.60 1219.64
1220.74 1231.32 1325.74 1347.80 1420.72 1436.32
1500.54 1508.45 1535.75 1624.45 1655.85 3015.13
3069.91 3100.46 3142.28 3145.09 3206.02 3207.83

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^{1}1

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25.75 41.03 60.03 97.73 115.54 149.20
185.25 204.39 215.86 238.30 285.71 310.18
407.57 412.60 454.07 500.28 546.57 587.66
629.80 632.41 667.46 701.63 711.10 751.59
766.34 791.37 798.50 853.64 865.84 907.33
911.83 935.81 937.53 975.91 1000.75 1013.91
1042.60 1047.86 1060.88 1084.99 1105.73 1116.18
1152.53 1197.34 1198.81 1217.86 1242.82 1256.89
1322.58 1335.37 1348.41 1371.53 1374.47 1407.06
1451.98 1463.15 1486.57 1492.15 1504.03 1527.58
1540.08 1551.56 1630.46 1655.83 1668.48 1732.41
3075.74 3159.10 3164.06 3164.93 3176.28 3182.98
3193.16 3203.76 3210.91 3227.82 3251.76 3278.94

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^{3}1

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18.20 42.09 59.63 69.79 123.91 132.52
183.06 189.36 214.46 229.74 291.41 301.49
400.11 403.44 450.69 466.31 533.35 544.86
571.14 610.96 636.38 653.40 708.10 708.88
747.14 749.21 777.53 793.74 804.88 836.34
858.95 870.50 877.92 933.83 969.01 976.13
985.65 1022.16 1055.29 1079.85 1105.62 1113.48
1152.47 1153.60 1180.19 1195.95 1221.14 1252.47
1265.76 1330.56 1354.11 1367.42 1379.80 1397.60
1430.77 1457.61 1463.51 1479.87 1487.20 1498.18
1517.68 1542.41 1559.18 1560.42 1586.88 1630.10
3074.66 3161.52 3163.33 3179.65 3185.77 3196.95
3203.96 3209.60 3219.23 3238.91 3250.20 3280.39

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^{3}1-twisted

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21.37 29.08 50.82 67.36 141.62 142.47
164.13 201.06 229.10 255.24 273.57 317.71
396.69 409.51 473.41 485.33 536.61 558.14
594.83 621.49 626.29 645.30 688.67 706.63
710.09 761.03 765.30 783.76 835.18 838.37
846.91 864.67 900.69 932.18 968.24 989.25
992.35 1023.40 1045.69 1077.49 1105.95 1113.22
1135.44 1152.50 1189.60 1193.88 1195.65 1231.59
1251.55 1327.50 1336.49 1362.82 1371.84 1403.67
1422.59 1456.67 1463.27 1487.72 1492.02 1501.86
1514.04 1524.54 1549.86 1595.37 1616.75 1623.60
3076.21 3136.59 3160.31 3164.15 3164.95 3173.31
3178.28 3188.90 3195.31 3206.76 3252.48 3279.74

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^{3}1-TS

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-231.06 14.40 36.00 42.20 52.58 57.12
67.38 81.03 100.14 106.44 136.36 159.54
188.61 189.55 208.83 219.30 250.84 267.28
299.05 311.25 335.86 403.50 413.60 417.93
454.48 458.57 482.75 486.06 546.35 569.79
577.17 620.80 622.30 629.57 653.62 676.24

687.89 709.09 725.92 739.46 743.77 749.12
782.30 787.88 799.23 803.03 809.72 828.35
853.92 855.01 886.25 892.65 931.10 937.21
966.86 969.99 980.19 982.01 984.90 989.59
1001.04 1009.04 1036.67 1048.40 1060.89 1068.72
1087.21 1106.21 1110.68 1125.51 1155.04 1160.92
1187.14 1192.84 1194.70 1208.99 1217.87 1241.08
1247.79 1260.40 1309.75 1326.39 1347.53 1351.90
1365.13 1370.38 1373.51 1394.07 1451.35 1453.85
1462.27 1477.92 1488.76 1494.18 1498.25 1502.50
1520.44 1532.06 1550.13 1551.79 1575.93 1587.91
1599.91 1616.64 1628.01 1646.78 3072.54 3156.82
3164.34 3173.11 3173.18 3175.36 3176.34 3179.39
3183.66 3190.76 3193.99 3199.32 3202.44 3205.73
3209.91 3221.46 3227.99 3248.61 3269.42 3278.83

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^{3}24

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12.74 28.97 41.18 49.49 58.60 72.43
76.32 107.05 126.37 148.60 155.46 185.13
192.49 199.22 234.27 248.21 287.31 309.04
334.03 402.69 408.90 415.90 427.20 454.17
484.56 489.38 512.97 559.03 563.02 577.04
625.11 626.01 633.66 668.09 682.36 691.68
701.97 707.92 719.37 750.41 768.52 770.39
771.03 783.33 813.43 834.54 841.44 865.31
876.30 897.88 899.66 903.15 929.56 967.27
969.11 971.67 987.46 988.19 992.41 993.70
1017.19 1044.49 1048.02 1072.39 1081.66 1098.65
1105.13 1122.00 1148.06 1154.61 1189.00 1190.45
1194.55 1197.14 1201.02 1208.62 1234.20 1249.75
1261.10 1267.42 1322.02 1338.77 1343.48 1344.47
1360.69 1365.09 1366.16 1407.78 1442.09 1448.40
1460.63 1464.62 1489.26 1492.70 1497.98 1507.12
1509.40 1522.75 1527.44 1529.74 1550.65 1593.79
1594.32 1618.05 1619.10 1751.03 3057.14 3064.37
3076.15 3120.29 3159.34 3170.93 3171.54 3174.22
3176.07 3177.62 3177.81 3189.01 3189.85 3198.74
3202.43 3203.61 3207.45 3219.21 3253.12 3280.10

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^{1}25

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15.26 29.03 42.35 54.20 57.87 69.59
77.84 105.91 125.05 136.96 154.76 186.75
193.05 201.68 235.59 250.56 273.47 308.75
327.92 404.12 408.60 415.27 428.31 455.77
485.89 491.09 504.74 557.09 561.91 577.28
626.43 626.75 631.94 659.23 681.26 693.02
696.35 709.49 723.08 743.58 769.94 771.98
772.59 780.37 814.26 835.52 842.59 851.70
866.51 896.98 899.60 904.47 930.38 965.51
968.07 972.76 987.81 988.54 993.83 994.48
1006.47 1033.85 1048.82 1052.50 1082.23 1100.45
1104.84 1119.10 1154.15 1155.26 1182.93 1189.33
1190.96 1197.17 1202.13 1208.66 1234.67 1250.54
1261.45 1271.20 1316.52 1335.11 1343.00 1343.40
1359.13 1365.45 1366.56 1408.96 1441.29 1449.24
1460.91 1465.76 1488.76 1491.71 1499.39 1506.76
1510.59 1523.61 1528.33 1532.71 1551.14 1595.20
1596.30 1619.85 1621.51 1752.90 3061.94 3074.77
3076.89 3128.56 3158.40 3168.08 3171.54 3172.52
3177.94 3178.47 3179.34 3188.97 3189.63 3196.86
3199.28 3203.03 3207.46 3217.52 3253.47 3280.23

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^{1}25-TS

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-244.77 25.40 36.59 43.52 51.85 57.93
63.37 91.19 112.81 130.82 177.96 181.75
195.30 198.32 226.43 234.99 244.80 303.04
331.20 392.62 408.98 416.43 419.73 440.68
490.75 498.23 526.69 553.85 575.27 585.17
599.68 627.56 628.91 637.61 673.05 693.95
696.00 699.82 734.37 746.20 763.39 766.38
770.99 790.67 802.36 837.92 841.63 865.96
873.02 900.09 902.17 920.97 941.93 968.54
970.10 982.75 988.27 988.59 996.43 998.52
1016.53 1048.25 1051.52 1068.56 1082.60 1091.29
1105.22 1127.79 1133.39 1155.36 1190.25 1191.63
1194.21 1199.67 1204.71 1209.79 1216.23 1246.34
1257.09 1260.41 1314.26 1335.87 1342.36 1345.11
1355.23 1366.40 1366.97 1406.57 1437.97 1441.22
1455.89 1463.55 1490.50 1494.77 1496.00 1509.02
1512.66 1525.43 1526.74 1528.56 1550.91 1600.02
1600.89 1624.98 1626.57 1742.71 3034.00 3072.88
3074.20 3117.16 3159.51 3164.04 3169.32 3171.58
3173.91 3177.81 3187.94 3189.16 3199.60 3201.17
3202.56 3207.44 3209.90 3216.37 3254.00 3280.40

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^{1}2

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10.98 25.32 38.23 44.60 47.77 58.93
86.31 133.53 144.16 149.91 157.14 195.73
213.53 234.99 237.02 254.23 298.26 343.34
371.70 414.67 416.78 418.30 444.46 459.77
513.56 534.57 555.59 626.17 631.79 632.96
636.59 654.89 681.29 710.61 716.70 717.97
747.19 767.96 772.13 781.73 792.39 823.61
863.43 869.15 869.64 871.52 926.50 928.17
938.30 943.99 975.67 980.19 985.05 993.92
1000.37 1003.35 1014.63 1015.32 1026.79 1050.89
1060.08 1062.71 1078.03 1092.69 1105.74 1109.70
1124.69 1141.78 1152.20 1195.82 1195.98 1198.04
1216.97 1223.43 1227.20 1240.23 1243.73 1252.41
1257.93 1272.29 1276.33 1330.86 1338.68 1343.79
1361.61 1368.53 1377.45 1383.00 1408.23 1418.53
1454.55 1463.52 1487.53 1489.77 1496.12 1504.69
1508.01 1528.19 1542.62 1546.08 1551.61 1638.60
1640.83 1664.18 1665.58 1735.91 3041.69 3065.84
3076.65 3080.05 3133.74 3147.15 3161.53 3168.29
3169.32 3169.77 3174.04 3178.34 3183.55 3188.85
3191.99 3197.44 3202.95 3203.61 3255.01 3280.82

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^{1}1H$^+$

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25.76 37.04 63.61 90.44 113.16 185.27
194.98 203.64 214.75 259.50 289.54 318.08
407.26 408.56 442.68 486.52 535.57 588.28
623.71 628.45 637.53 670.73 688.69 690.40
749.41 772.16 790.49 792.46 841.13 853.47
880.83 907.35 946.89 947.45 987.64 1012.42
1021.20 1038.84 1045.52 1054.89 1103.01 1122.44
1123.87 1147.46 1154.27 1204.91 1221.26 1236.77
1256.18 1295.47 1317.79 1344.68 1362.22 1377.01
1389.70 1424.26 1465.90 1485.29 1490.67 1495.28
1505.73 1536.46 1538.65 1614.66 1623.52 1638.18
1658.38 1730.25 3090.18 3158.96 3172.92 3184.89
3186.88 3188.62 3190.11 3200.03 3209.32 3219.54
3297.73 3314.24 3638.68

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^{3}1H$^+$

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13.01 39.77 61.15 75.80 131.64 157.13
180.56 207.12 216.24 234.59 280.56 316.89
389.46 403.36 449.66 460.73 510.06 539.92
567.04 575.25 598.52 619.12 647.53 687.93
692.12 747.77 774.89 787.34 799.78 823.99
861.84 874.07 876.65 921.46 940.34 986.09
986.83 1008.30 1023.66 1044.91 1105.58 1115.62
1129.84 1139.90 1150.82 1178.83 1205.04 1222.71
1245.03 1269.32 1298.28 1303.81 1348.64 1377.36
1384.87 1401.32 1419.38 1458.18 1462.48 1486.44
1497.53 1506.25 1526.82 1535.30 1556.98 1583.59
1621.13 1642.79 3096.20 3182.79 3190.31 3195.35
3199.73 3202.95 3212.65 3213.60 3219.43 3226.70
3301.26 3319.24 3675.21

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^{3}1H$^+$-TS

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-262.01 14.93 33.43 37.46 51.93 56.61
64.16 74.39 89.21 123.41 143.86 178.71

183.12 193.04 205.56 232.66 253.79 263.93
310.38 319.51 356.93 406.85 408.65 410.32
456.78 462.08 484.03 489.08 535.81 542.49
565.59 580.46 605.71 615.63 622.77 624.32
681.15 682.32 690.30 710.40 743.75 745.41
763.50 785.51 799.16 812.46 817.57 839.80
846.23 855.18 858.27 899.54 922.73 932.26
937.91 953.99 980.42 984.33 995.93 1005.04
1006.89 1011.57 1013.52 1042.68 1045.62 1048.65
1071.11 1100.28 1113.69 1124.75 1127.67 1136.09
1152.26 1187.57 1200.18 1200.89 1208.49 1217.59
1238.91 1242.32 1260.88 1288.64 1289.35 1301.65
1351.56 1355.09 1370.40 1374.13 1379.65 1398.56
1452.36 1456.98 1479.22 1484.71 1491.32 1500.77
1510.23 1513.32 1524.39 1526.74 1544.75 1565.41
1591.48 1594.00 1609.44 1621.84 1624.74 1636.21
3093.65 3154.67 3163.05 3186.50 3188.52 3189.25
3189.43 3190.94 3196.87 3197.17 3201.38 3202.80
3203.94 3208.63 3211.32 3219.56 3220.44 3259.09
3299.73 3318.11 3678.17

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^{3}24H$^+$

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13.20 27.96 35.79 50.89 57.13 70.65
84.09 103.66 122.81 155.87 164.30 184.96
192.38 196.55 231.65 259.42 280.18 313.18
330.81 397.49 409.04 411.61 422.26 451.24
479.50 485.46 501.10 549.78 562.87 577.85
615.52 624.17 625.19 633.13 656.56 674.78
688.26 689.60 695.43 708.54 739.13 765.35
767.61 773.70 784.82 801.81 831.52 836.27
842.61 876.53 894.91 911.74 912.41 932.60
962.77 973.24 975.81 993.66 995.15 1002.36
1004.26 1012.21 1035.54 1048.04 1052.95 1081.74
1100.87 1117.77 1122.61 1136.79 1152.58 1154.78
1165.97 1195.04 1196.86 1205.07 1209.38 1232.48
1233.09 1258.91 1267.63 1295.95 1305.56 1327.76
1344.85 1346.48 1366.07 1367.16 1369.39 1416.70
1449.39 1457.96 1463.67 1486.50 1489.39 1490.64
1499.60 1506.09 1507.55 1522.89 1527.42 1536.63
1595.03 1595.74 1613.05 1618.93 1619.16 1742.89
3000.61 3056.30 3093.96 3116.97 3177.89 3178.19
3184.55 3185.99 3189.13 3195.62 3197.06 3197.79
3204.08 3204.45 3204.95 3216.41 3217.41 3218.54
3299.81 3317.00 3644.95

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^{1}25H$^+$

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9.07 24.88 38.50 53.09 64.51 66.74
86.99 96.53 120.12 153.92 175.99 182.38
195.61 199.68 237.32 256.69 266.92 311.73
325.55 400.06 409.76 410.26 421.50 452.42
478.89 489.26 493.16 535.96 556.78 573.34
600.17 621.82 621.98 624.82 651.47 670.03
685.30 689.89 691.65 706.42 734.18 767.14
769.51 775.36 783.01 797.45 823.63 831.93
840.77 879.32 893.11 911.84 913.33 936.72
956.11 975.23 975.65 987.90 994.88 997.96
1002.77 1003.74 1027.52 1048.71 1050.08 1084.40
1103.57 1117.40 1121.00 1137.91 1153.36 1159.79
1165.08 1194.60 1197.21 1205.32 1211.03 1229.14
1237.73 1260.04 1266.64 1295.63 1305.26 1319.85
1342.67 1344.10 1365.27 1368.04 1369.20 1423.70
1444.02 1460.50 1466.21 1485.17 1487.97 1489.62
1500.26 1506.68 1508.31 1522.62 1528.40 1541.65
1595.40 1597.31 1620.08 1620.53 1620.68 1764.50
3014.29 3070.06 3095.19 3127.30 3177.05 3179.01
3184.24 3187.74 3187.86 3191.65 3196.60 3196.85
3203.71 3204.02 3206.69 3211.23 3216.51 3217.46
3300.27 3316.89 3641.17

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^{1}25H$^+$-TS

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-217.42 27.87 38.54 49.25 54.44 58.20
73.79 91.86 122.60 130.39 181.82 192.85

197.53 208.29 232.51 246.98 259.57 307.63
335.56 393.63 408.23 414.02 421.44 434.47
484.41 494.49 509.81 548.68 567.00 580.13
592.42 618.12 626.27 627.21 645.72 666.93
681.78 691.98 697.66 717.41 741.62 755.36
770.36 771.71 795.02 798.83 836.50 838.49
870.81 876.81 909.81 914.42 919.32 941.58
971.92 974.51 977.26 998.10 999.94 1004.57
1005.00 1014.46 1048.26 1051.42 1065.66 1085.29
1097.80 1119.08 1127.73 1134.20 1143.90 1155.41
1182.32 1196.52 1198.52 1205.29 1211.53 1219.74
1229.34 1254.55 1258.17 1298.14 1301.81 1330.06
1343.49 1348.37 1359.43 1369.00 1370.21 1418.04
1439.37 1450.38 1462.45 1488.27 1492.60 1493.36
1497.91 1508.37 1510.42 1524.78 1526.59 1537.26
1599.68 1602.67 1618.34 1626.02 1627.40 1740.29
2966.77 3033.93 3090.30 3126.55 3174.62 3179.42
3183.32 3184.28 3187.70 3195.77 3197.14 3198.40
3203.34 3204.50 3216.42 3217.35 3220.81 3230.01
3300.11 3317.23 3647.01

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^{1}2H$^+$

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19.64 30.89 34.61 46.00 48.84 63.03
75.26 135.65 144.22 148.56 173.05 194.95
209.75 229.60 233.69 252.50 315.15 364.53
370.72 379.50 414.89 415.81 417.89 478.29
516.39 517.20 546.80 623.19 630.27 631.57
632.02 637.95 654.48 695.09 713.71 716.63
730.98 752.99 770.19 773.89 787.06 798.70
815.48 858.73 863.55 871.32 885.90 919.99
929.31 939.14 952.04 955.76 973.68 978.56
990.76 1009.28 1013.21 1014.52 1015.94 1020.32
1048.13 1059.68 1060.02 1074.36 1097.30 1114.12
1117.55 1128.96 1138.32 1151.27 1162.38 1198.44
1200.51 1202.58 1219.52 1222.11 1235.62 1238.23
1239.62 1243.94 1263.02 1272.69 1306.76 1320.58
1335.47 1346.82 1367.07 1367.54 1380.62 1396.90
1422.98 1431.58 1466.06 1486.57 1493.97 1495.25
1498.83 1505.37 1513.32 1537.35 1543.48 1544.43
1630.62 1634.24 1642.86 1655.27 1663.64 1781.89
3060.46 3065.97 3077.47 3098.14 3102.67 3161.10
3168.35 3174.76 3175.01 3184.49 3191.39 3193.73
3197.05 3198.63 3200.94 3205.53 3213.20 3216.79
3298.67 3315.81 3374.

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[8] The NMR shifts in ref. 6 DO NOT match our ^{1}H and ^{13}C data above. Instead, the previously reported data for the *ortho*-OMe substrate is consistent with our reported data for the *meta*-OMe substrate. To rule out error, we established that the simple coupling patterns for our *ortho*-OMe and *meta*-OMe substrates are, in fact, completely consistent with their structure. We believe this singular substrate has been misidentified in ref. 6.

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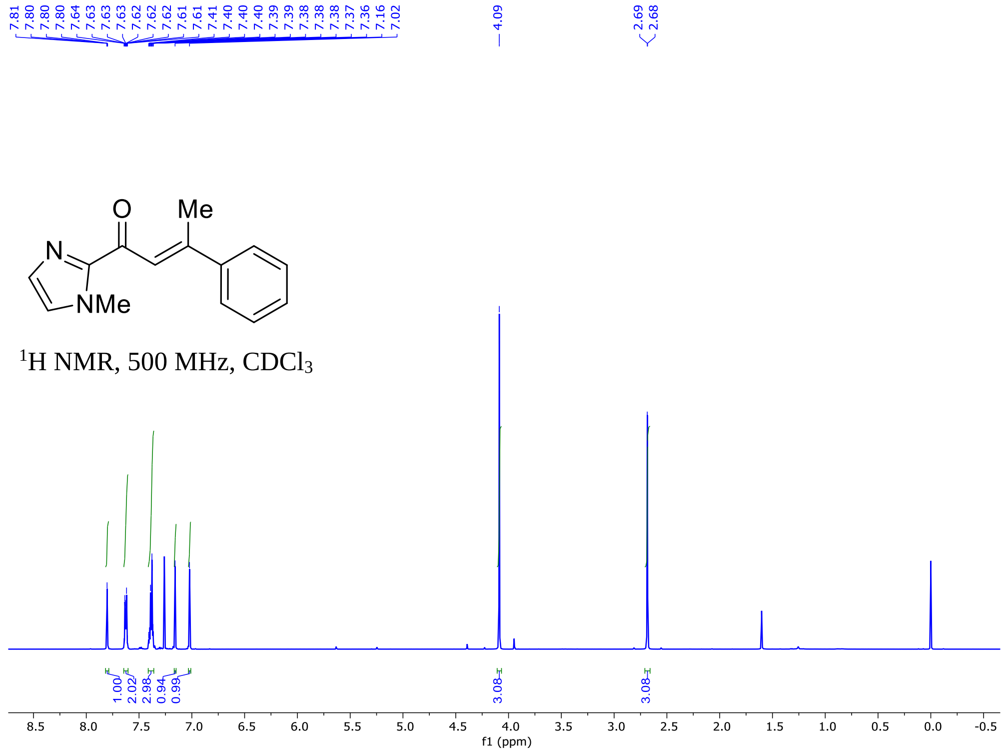
12. NMR Data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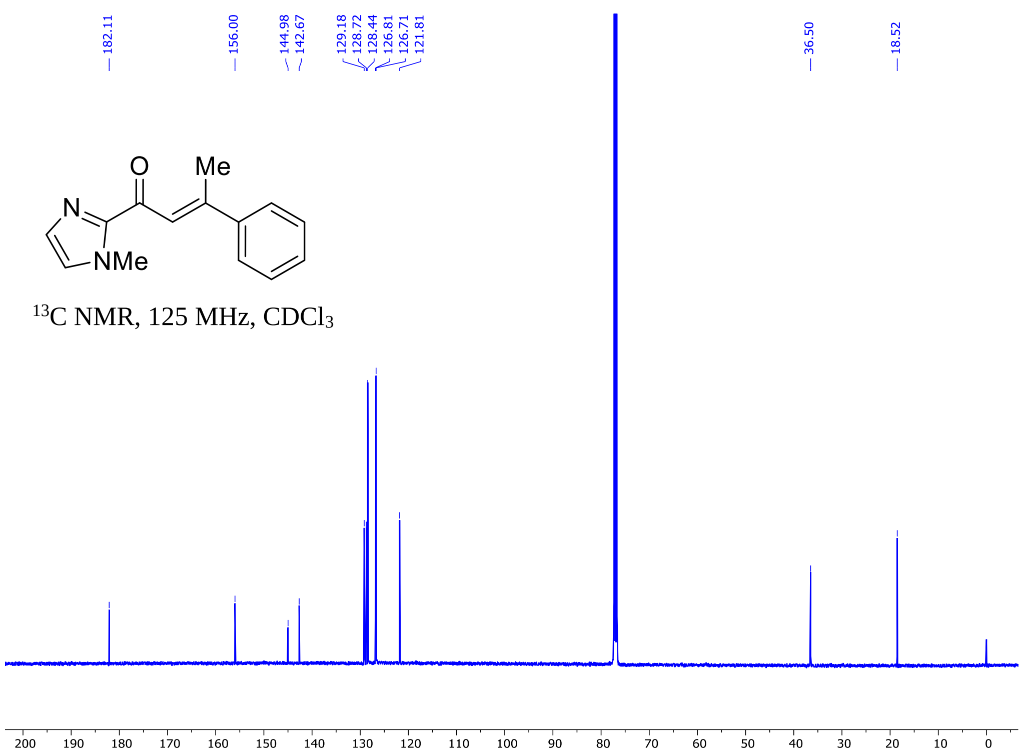
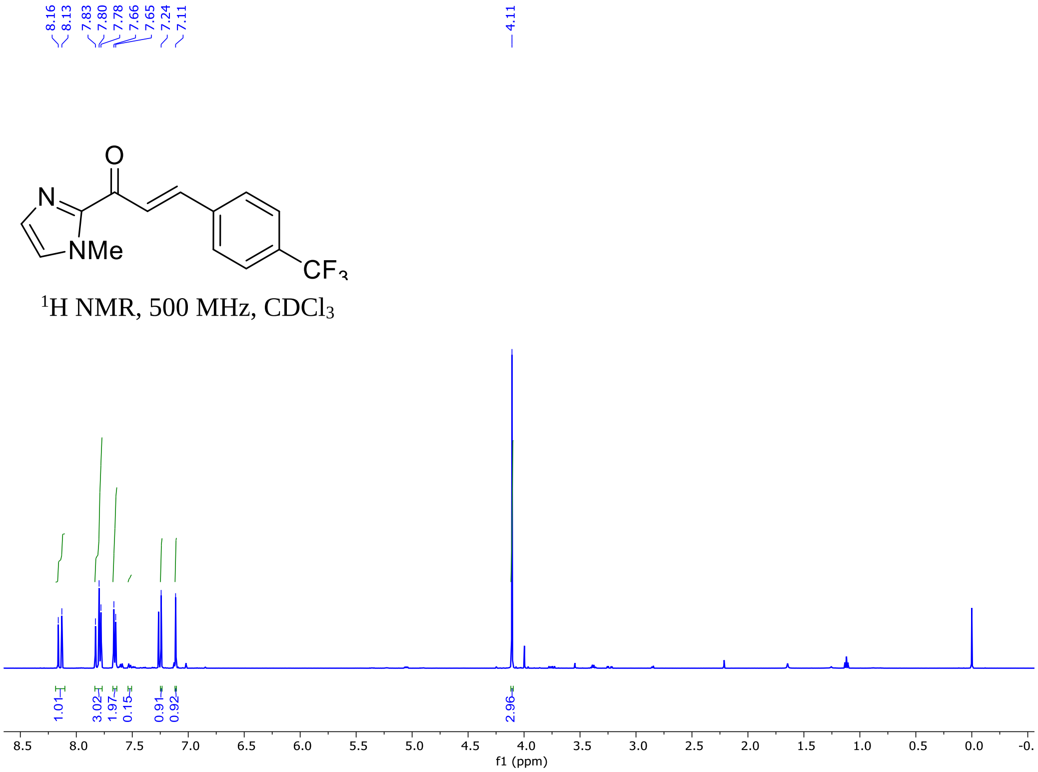
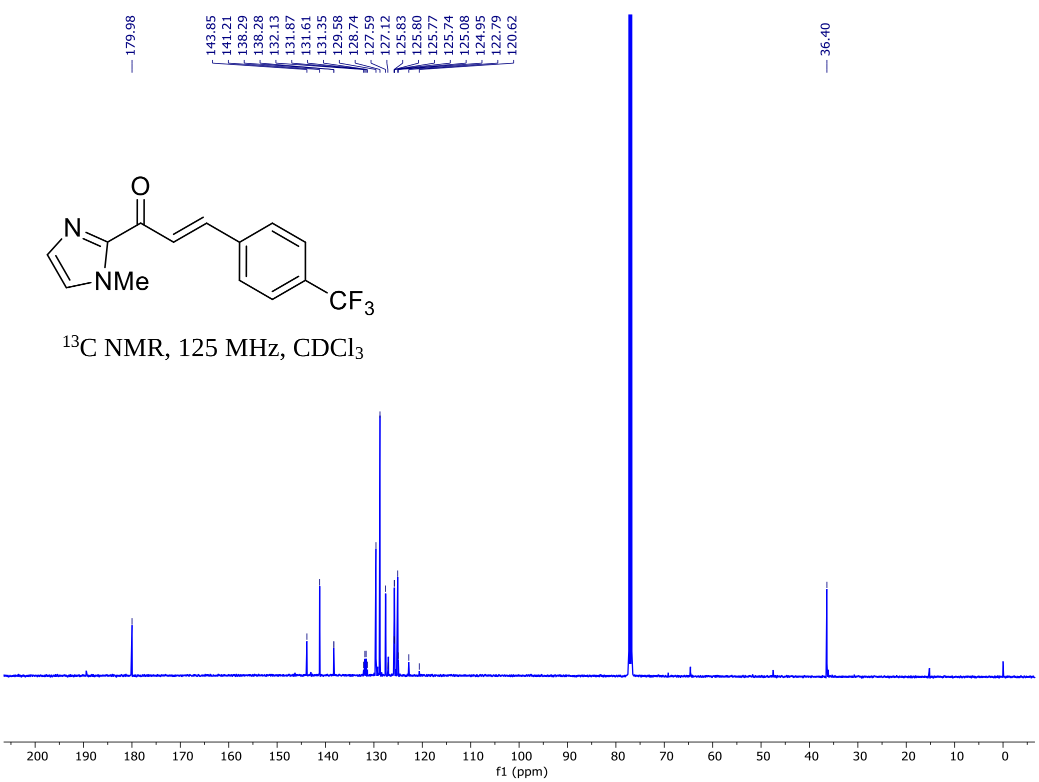
4.09
2.69 2.68
O
Me
N
NMe
^{1}H NMR, 500 MHz, CDCl$_3$
1.00 2.02 2.98 0.94 0.99
3.08
3.08
f1 (ppm)


182.11
156.00
144.98 142.67
129.18 128.72 128.44 126.81 126.71 121.81
36.50
18.52
O
Me
N
NMe
^{13}C NMR, 125 MHz, CDCl$_3$
f1 (ppm)


8.16
8.13
7.83
7.80
7.78
7.66
7.65
7.24
7.11
4.11
O
N
NMe
CF3
^{1}H NMR, 500 MHz, $CDCl_3$
1.01
3.02
1.97
0.15
0.91
0.92
2.96
f1 (ppm)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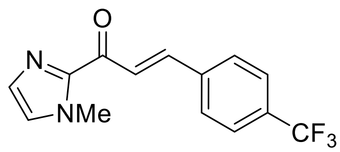
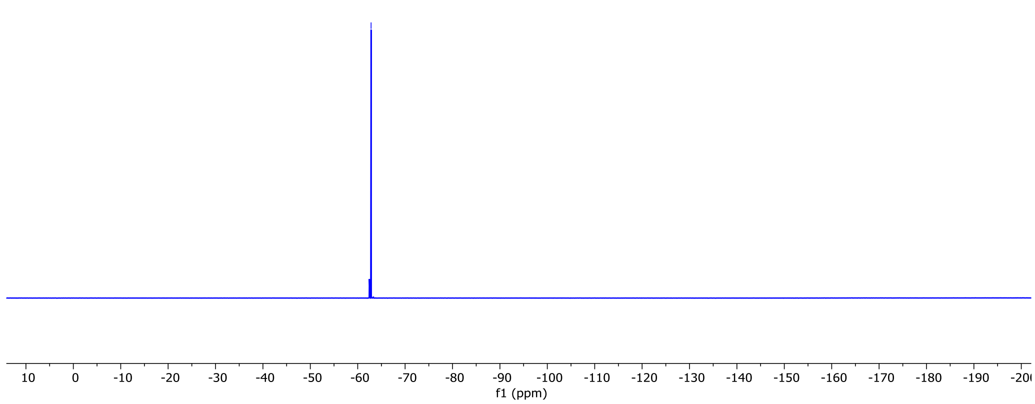
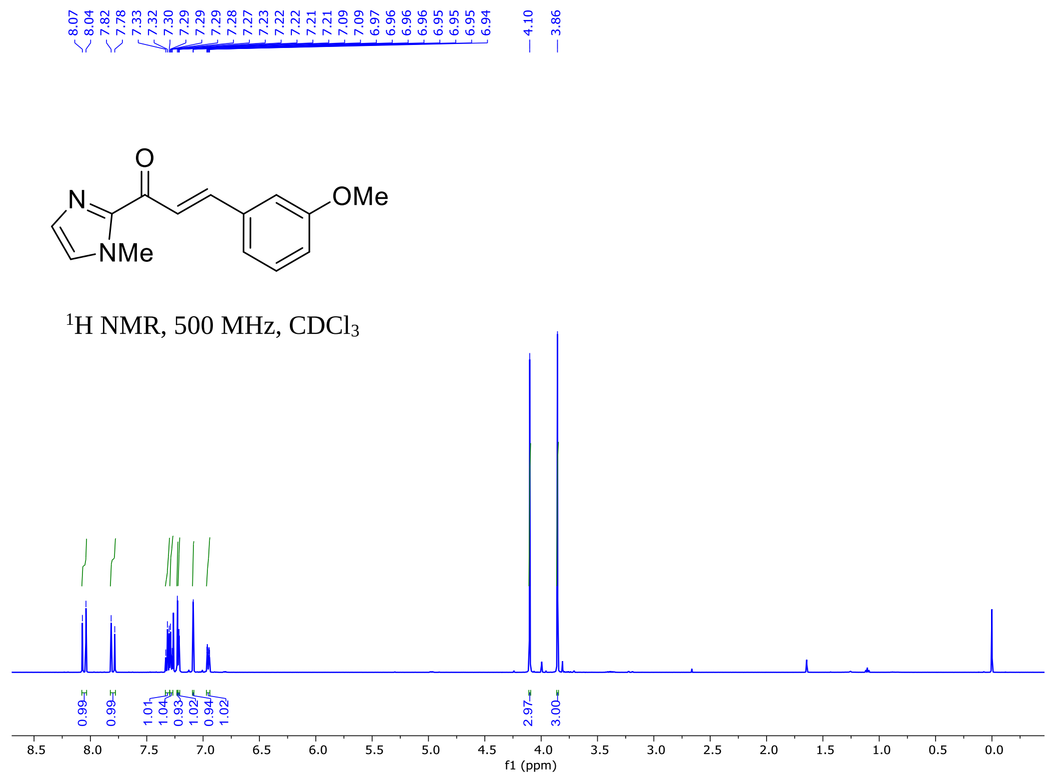
143.85
141.21
138.29
138.28
132.13
131.87
131.61
131.35
129.58
128.74
127.59
127.12
125.83
125.80
125.77
125.74
125.08
124.95
122.79
120.62
36.40
O
N
NMe
CF3
^{13}C NMR, 125 MHz, $CDCl_3$
f1 (ppm)

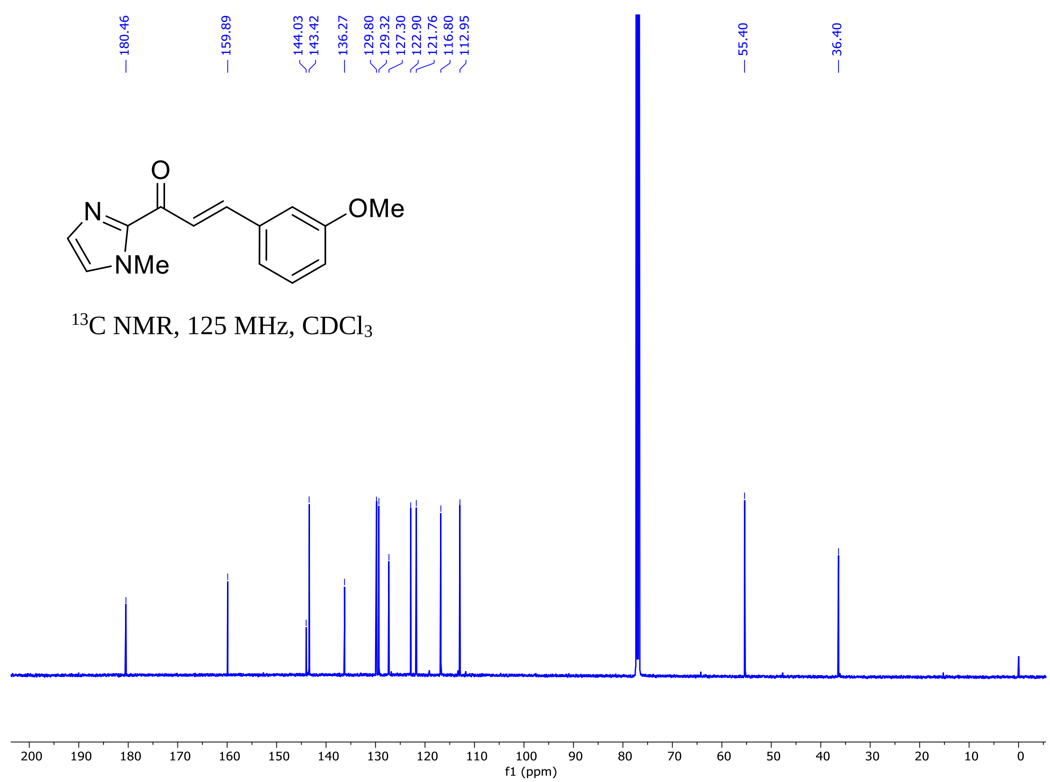


^{19}F NMR, 377 MHz, $CDCl_3$

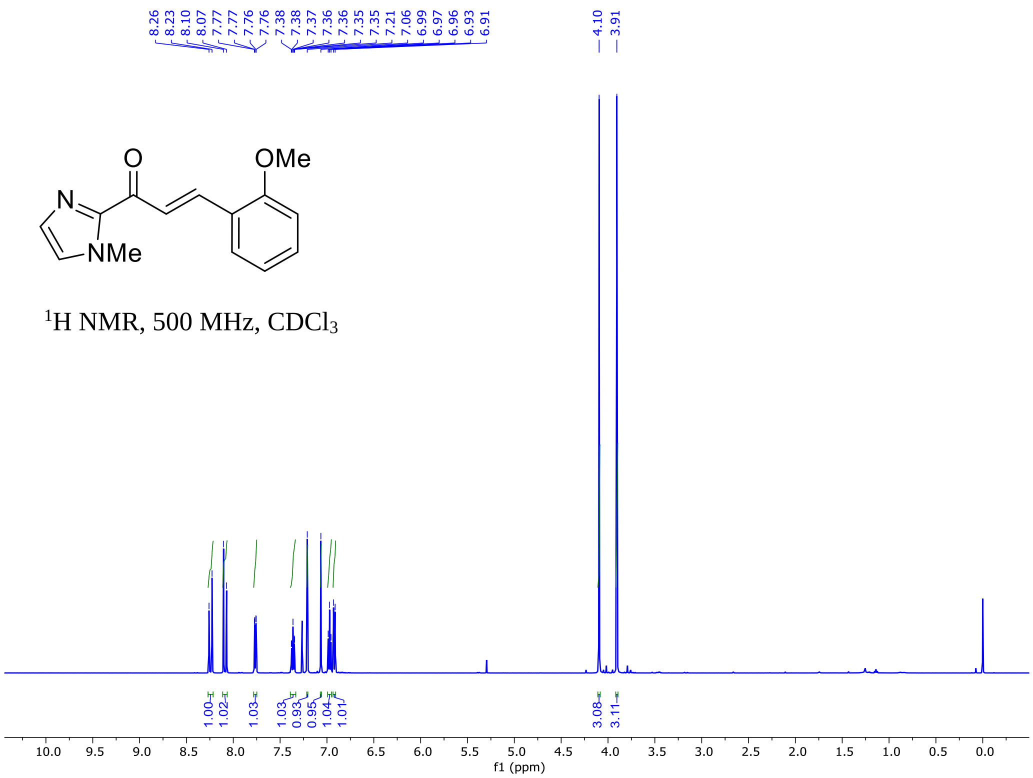


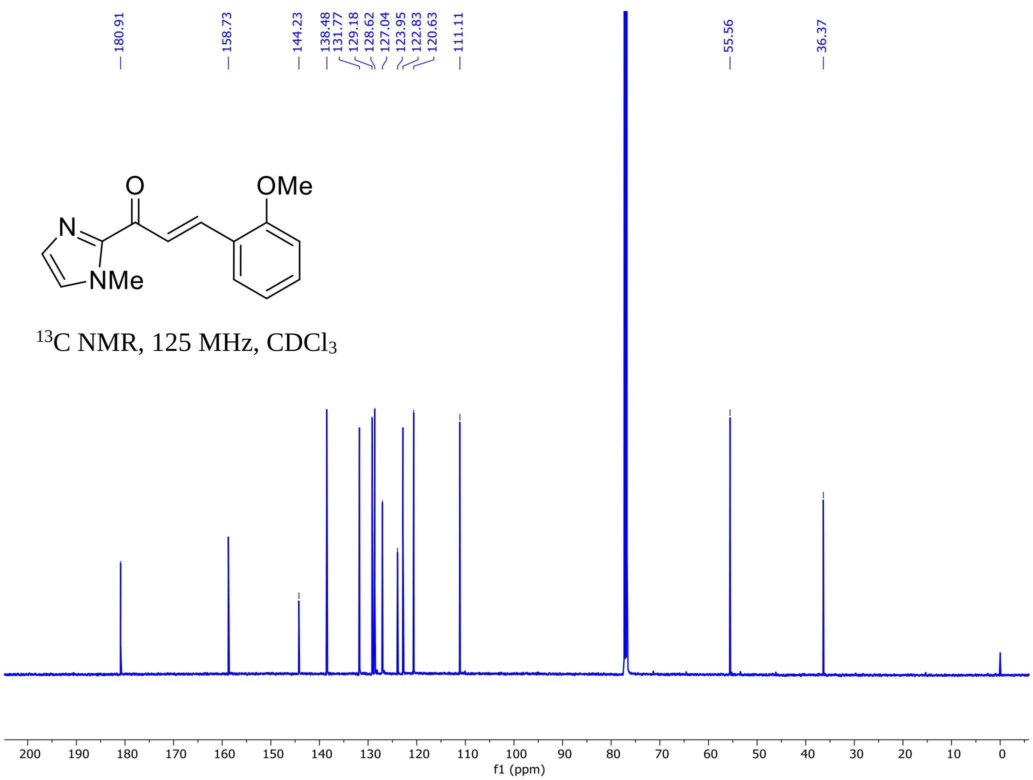


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$


8.26
8.23
8.10
8.07
7.77
7.77
7.76
7.76
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.21
7.06
6.99
6.97
6.96
6.93
6.91
4.10
3.91
O
OMe
N
NMe
^{1}H NMR, 500 MHz, $CDCl_3$
1.00
1.02
1.03
1.03
0.93
0.95
1.04
1.01
3.08
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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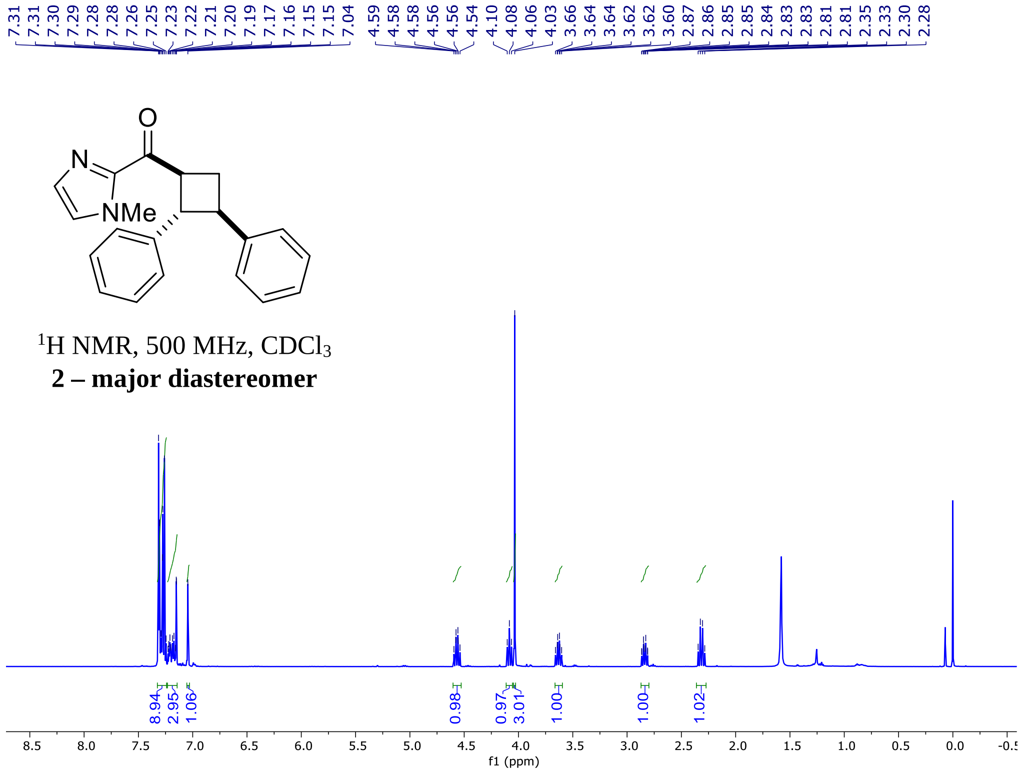
144.23
138.48
131.77
129.18
128.62
127.04
123.95
122.83
120.63
111.11
55.56
36.37
O
OMe
N
NMe
^{13}C NMR, 125 MHz, $CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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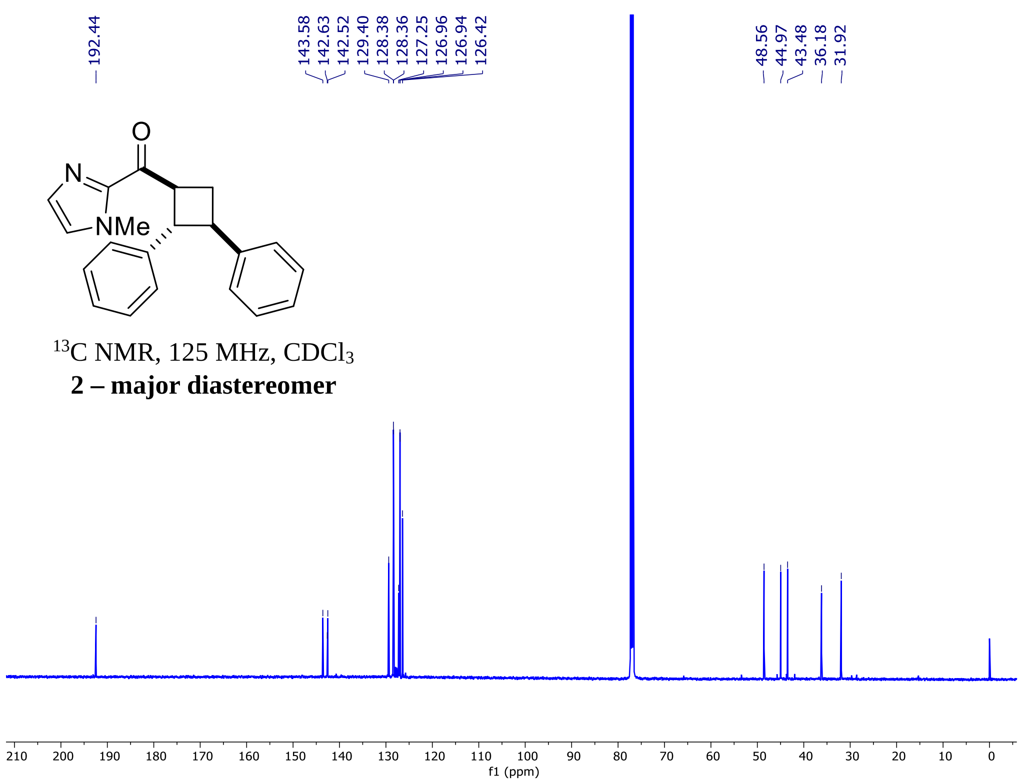
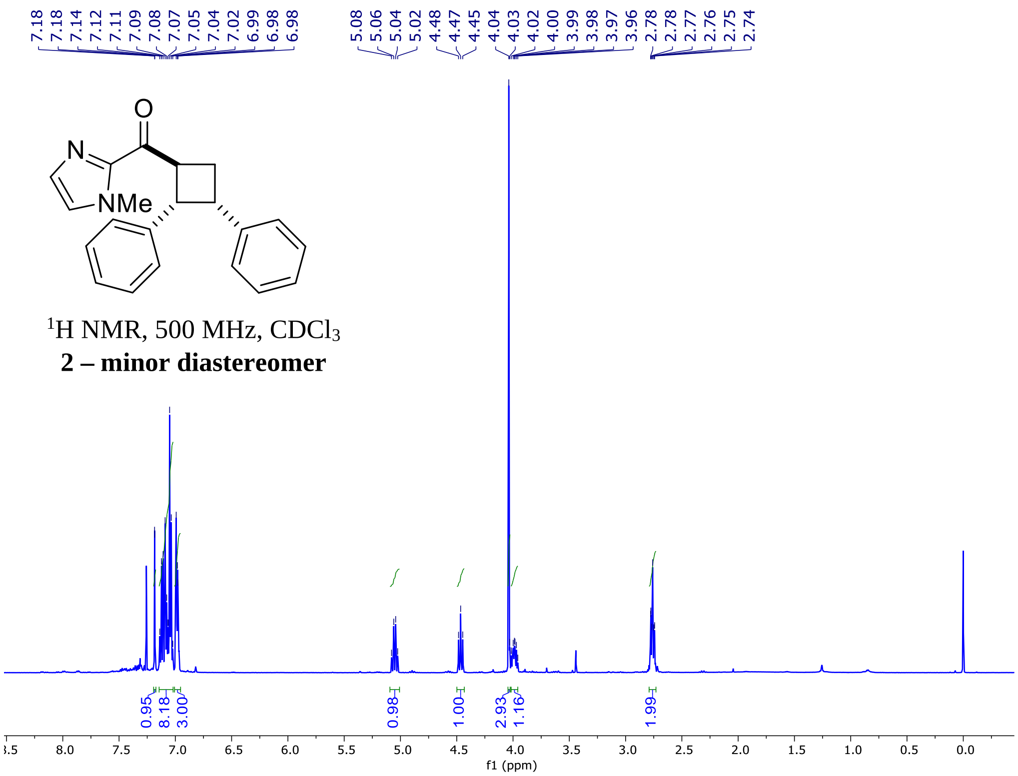
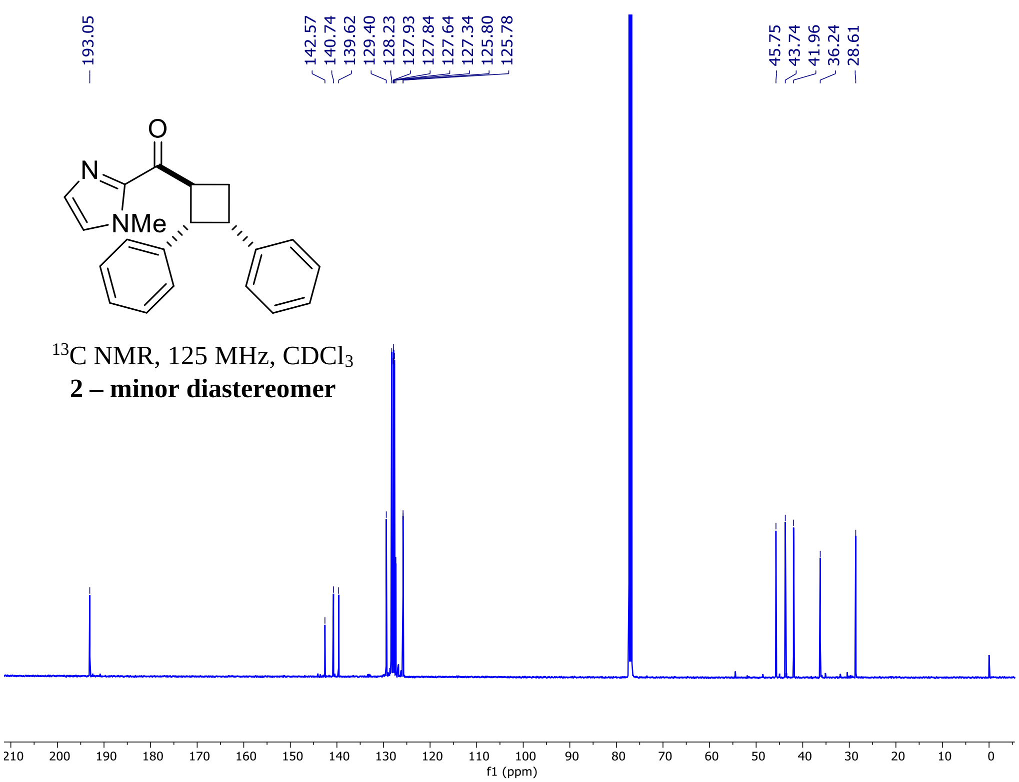
O
N
NMe
^{1}H NMR, 500 MHz, $CDCl_3$
2 – major diastereomer
8.94 2.95 1.06 0.98 0.97 3.01 1.00 1.00 1.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

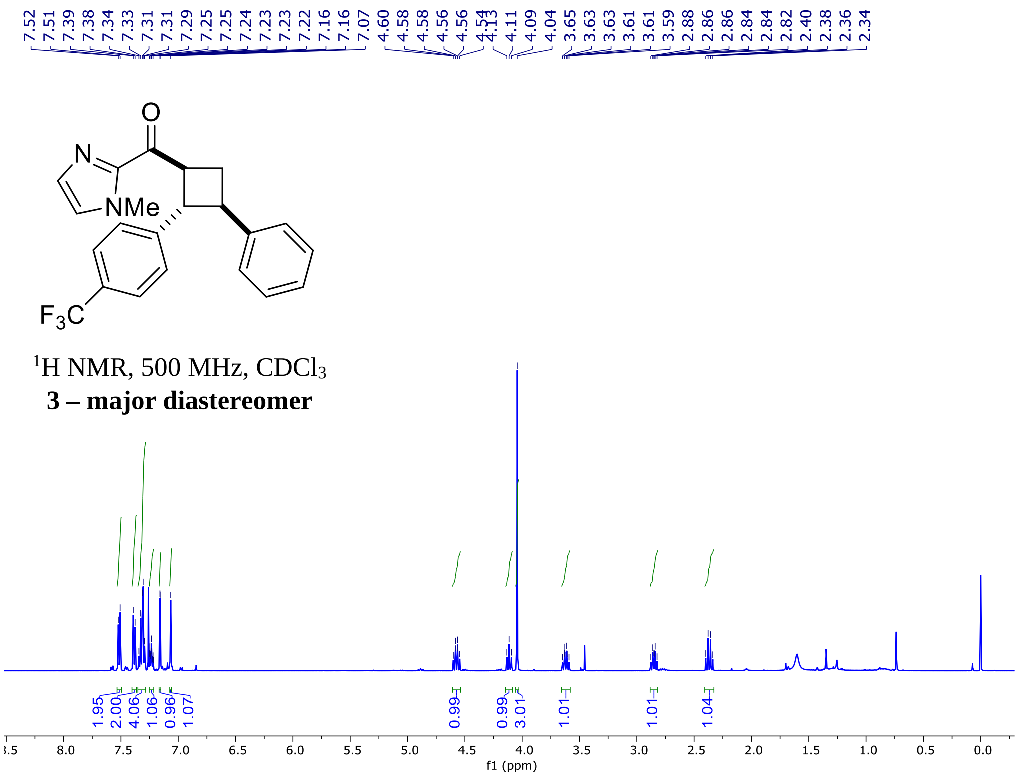

192.44
143.58 142.63 142.52 129.40 128.38 128.36 127.25 126.96 126.94 126.42
48.56 44.97 43.48 36.18 31.92
O
N
NMe
^{13}C NMR, 125 MHz, $CDCl_3$
2 – major diastereomer
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



^{1}H NMR, 500 MHz, $CDCl_3$
2 – minor diastereomer
NMe
f1 (ppm)

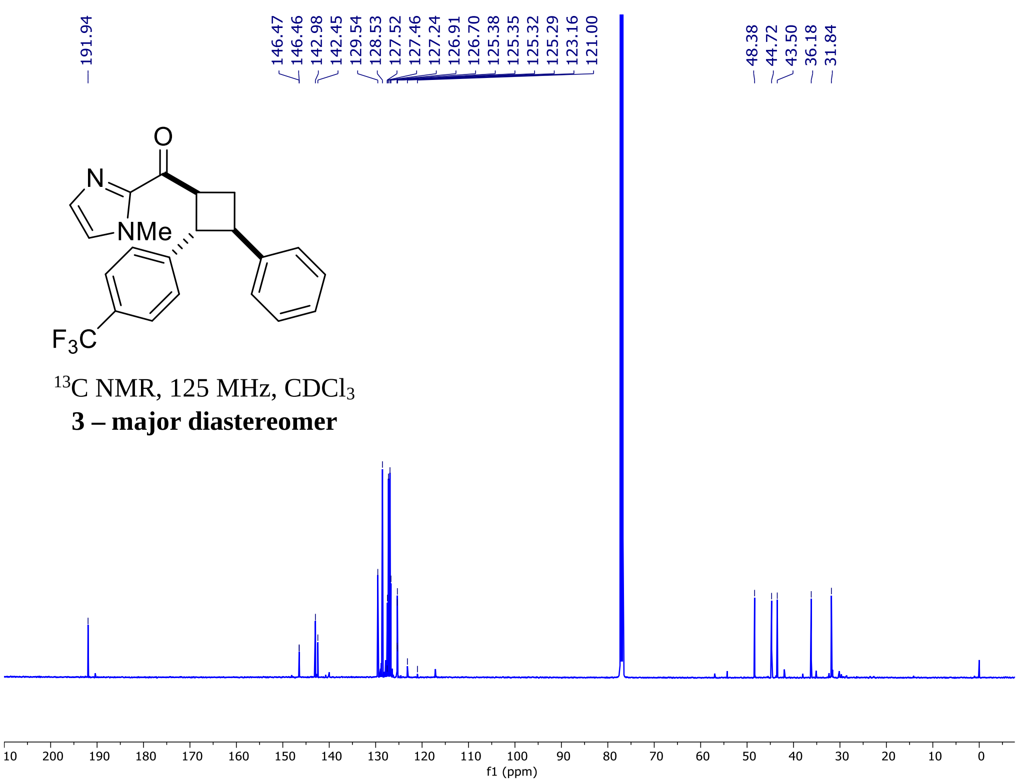


^{13}C NMR, 125 MHz, $CDCl_3$
2 – minor diastereomer
NMe
f1 (ppm)



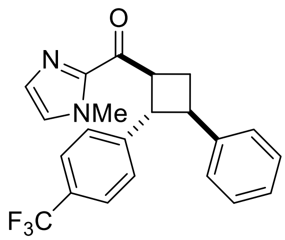
^{1}H NMR, 500 MHz, $CDCl_3$

3 – major diastereomer



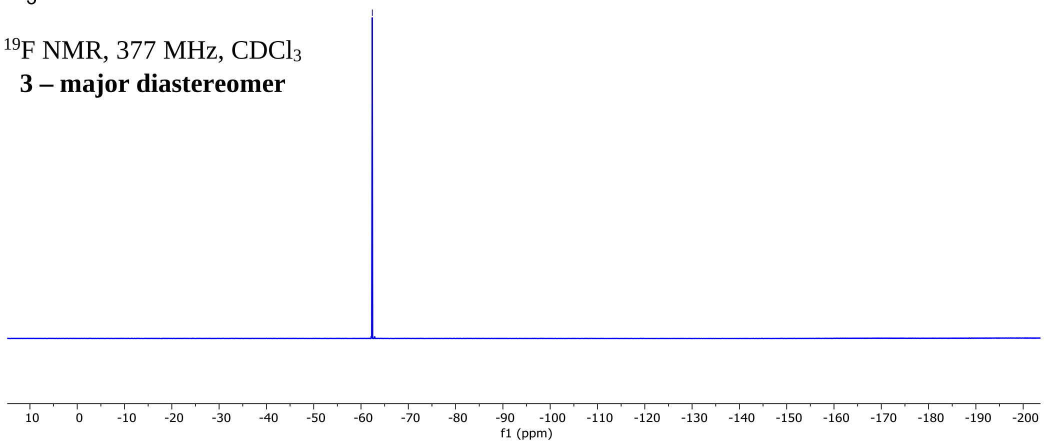
^{13}C NMR, 125 MHz, $CDCl_3$

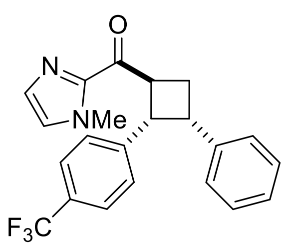
3 – major diastereomer



^{19}F NMR, 377 MHz, $CDCl_3$

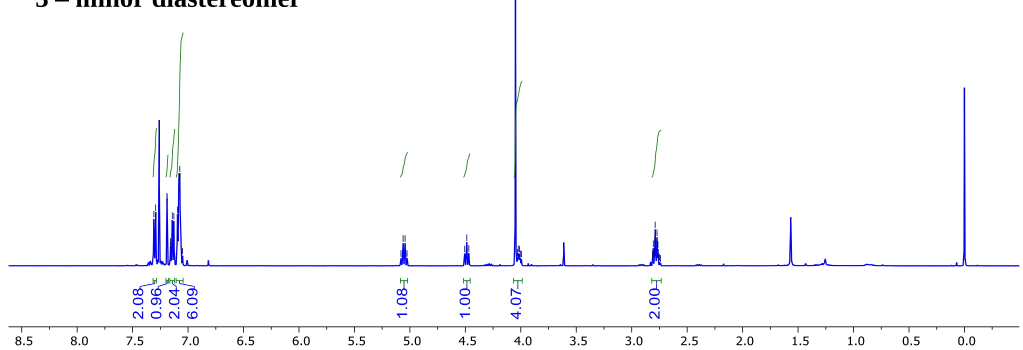
3 – major diastereomer

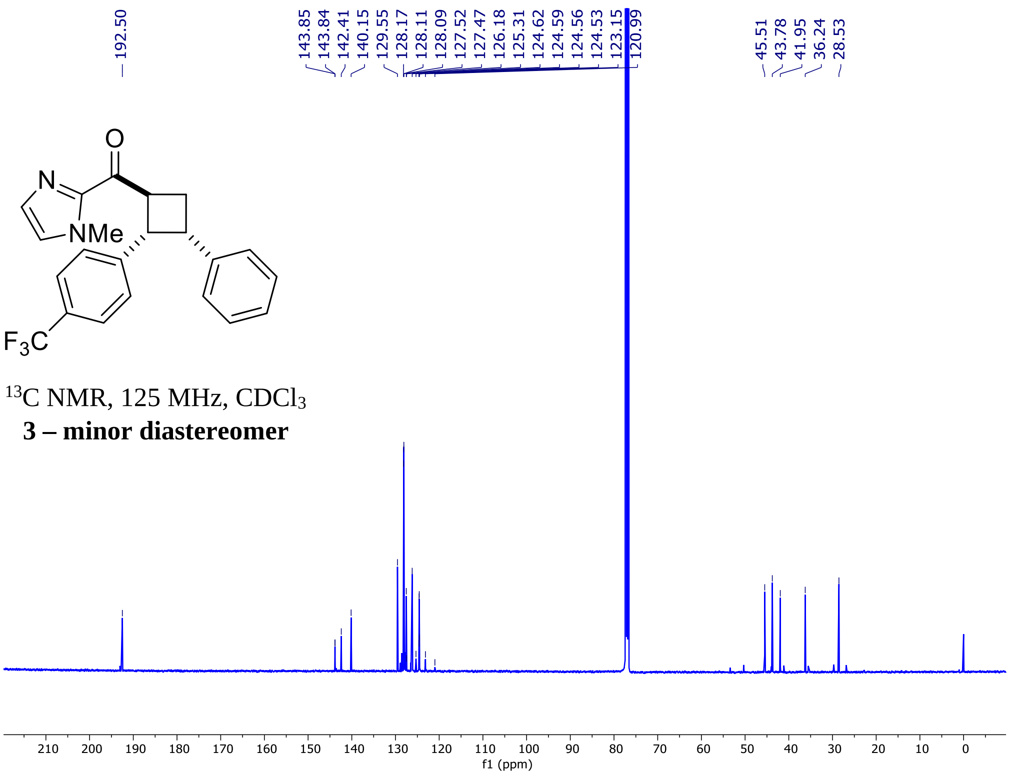


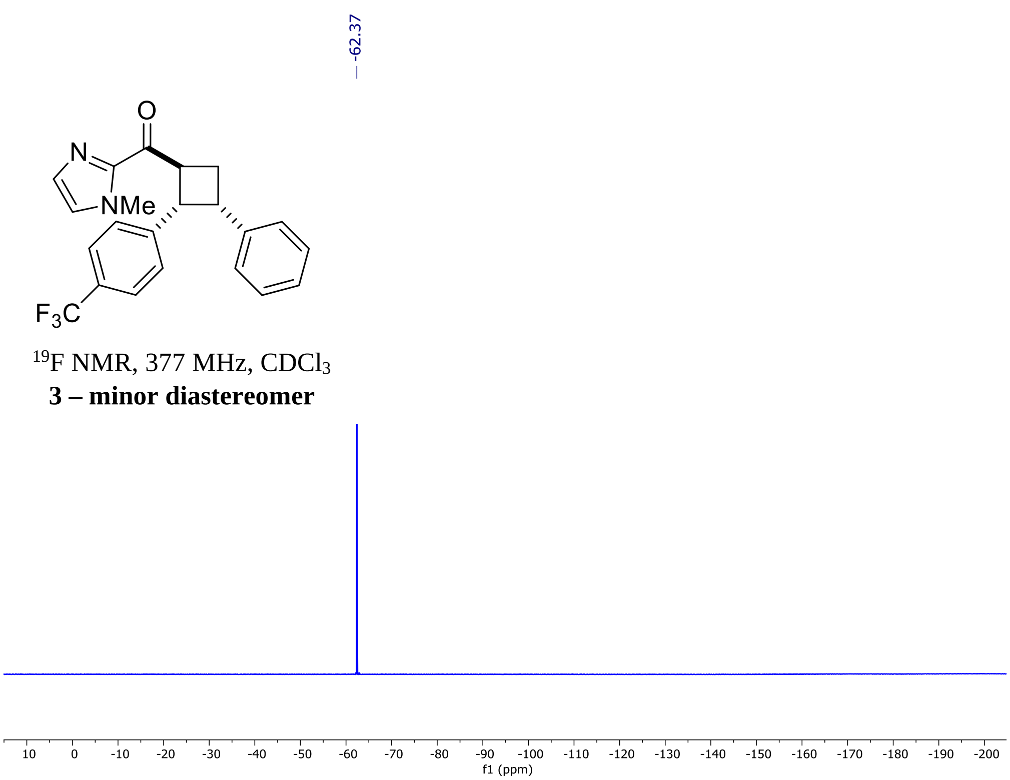


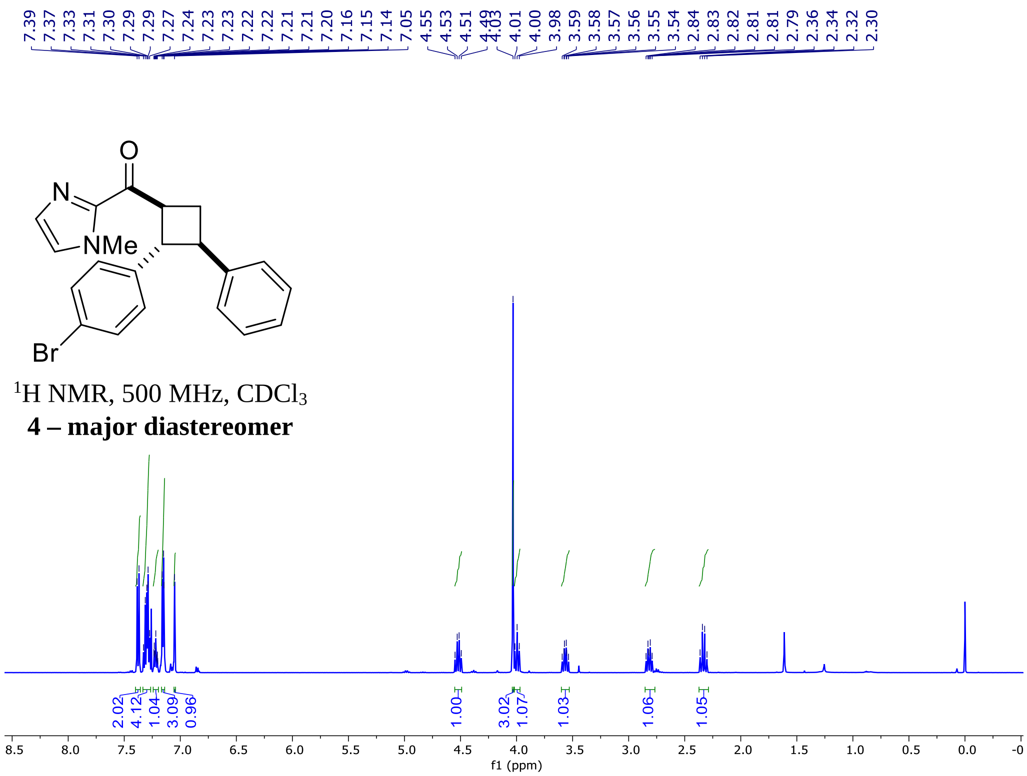
^{1}H NMR, 500 MHz, $CDCl_3$

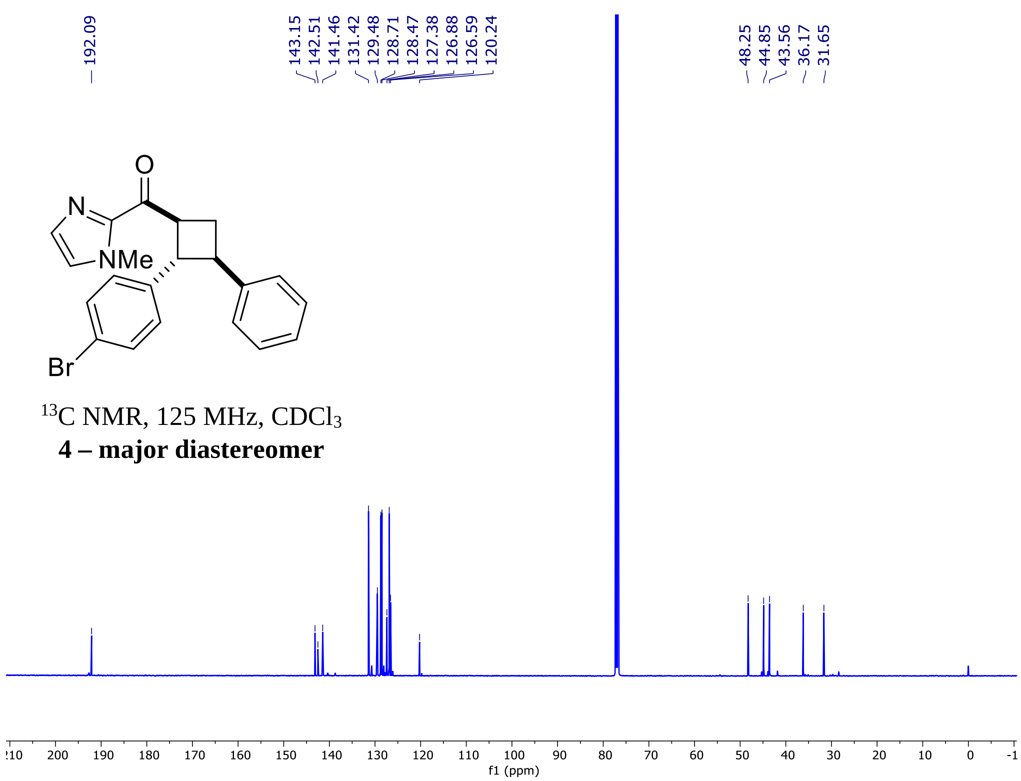
3 – minor diastereomer

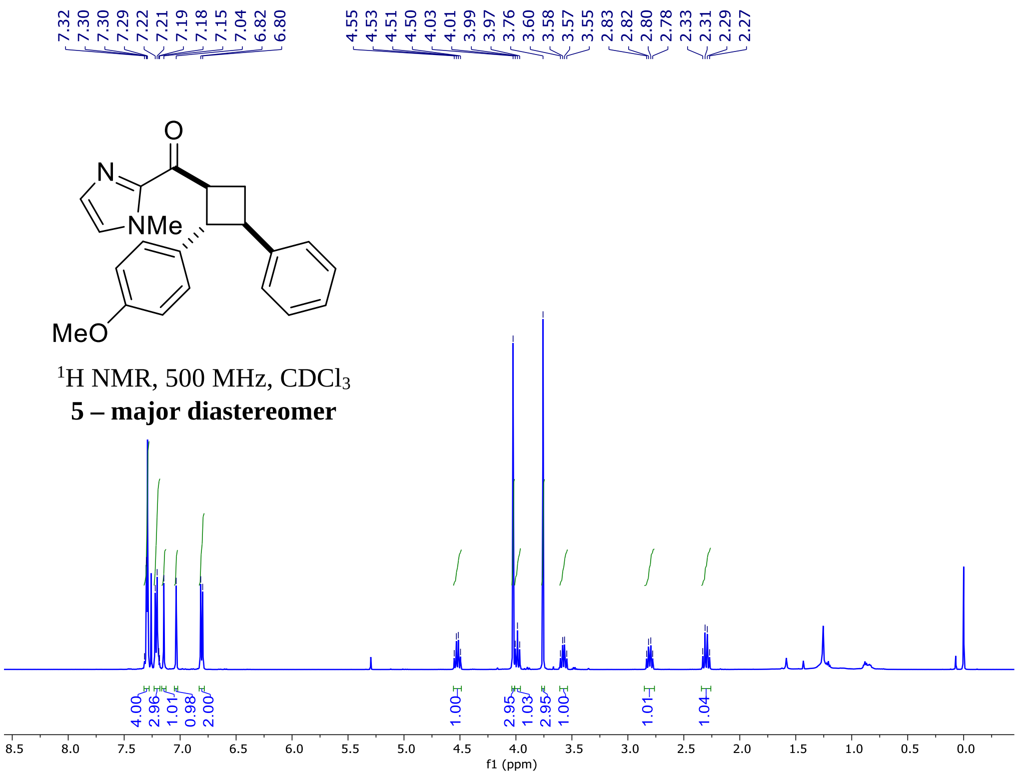



192.50
143.85
143.84
142.41
140.15
129.55
128.17
128.11
128.09
127.52
127.47
126.18
125.31
124.62
124.59
124.56
124.53
123.15
120.99
45.51
43.78
41.95
36.24
28.53
O
N
NMe
F3C
13C NMR, 125 MHz, CDCl3
3 – minor diastereomer
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.37
O
N
NMe
F3C
19F NMR, 377 MHz, CDCl3
3 – minor diastereomer
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

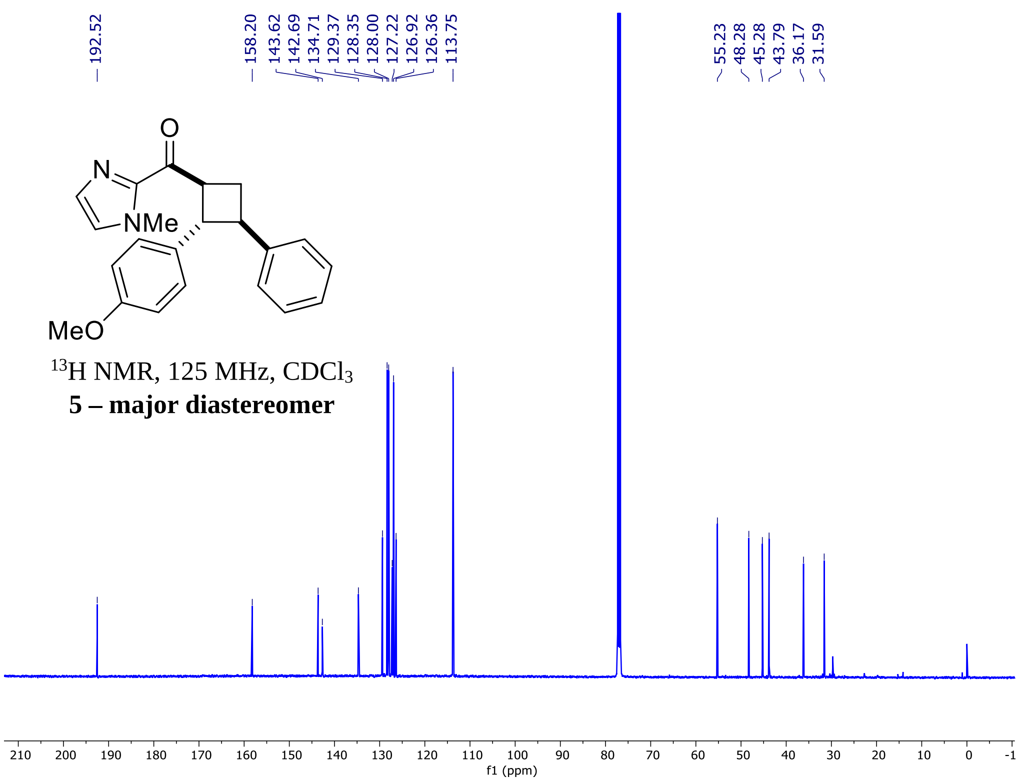

7.39 7.37 7.33 7.31 7.30 7.29 7.29 7.27 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.16 7.15 7.14 7.05 4.55 4.53 4.51 4.49 4.03 4.01 4.00 3.98 3.59 3.58 3.57 3.56 3.55 3.54 2.84 2.83 2.82 2.81 2.81 2.79 2.36 2.34 2.32 2.30
O
N
NMe
Br
^{1}H NMR, 500 MHz, $CDCl_3$
4 – major diastereomer
2.02 4.12 1.04 3.09 0.96 1.00 3.02 1.07 1.03 1.06 1.05
f1 (ppm)


192.09
143.15 142.51 141.46 131.42 129.48 128.71 128.47 127.38 126.88 126.59 120.24
48.25 44.85 43.56 36.17 31.65
O
N
NMe
Br
^{13}C NMR, 125 MHz, $CDCl_3$
4 – major diastereomer
f1 (ppm)



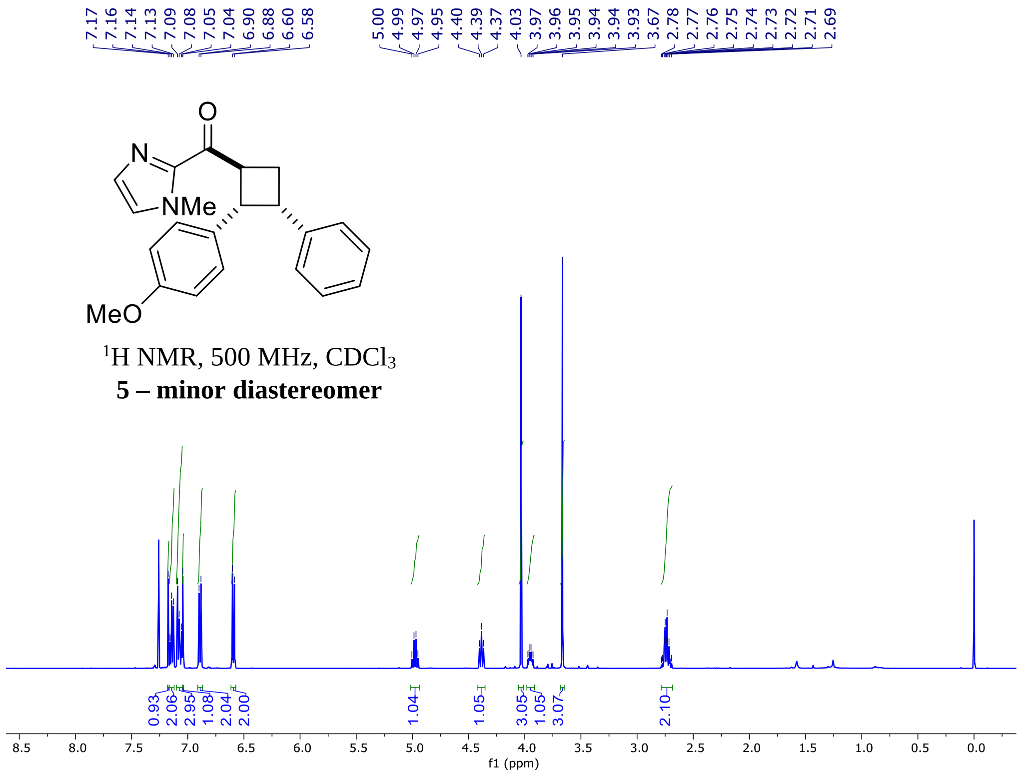
^{1}H NMR, 500 MHz, $CDCl_3$

5 – major diastereomer



^{13}H NMR, 125 MHz, $CDCl_3$

5 – major diastereomer



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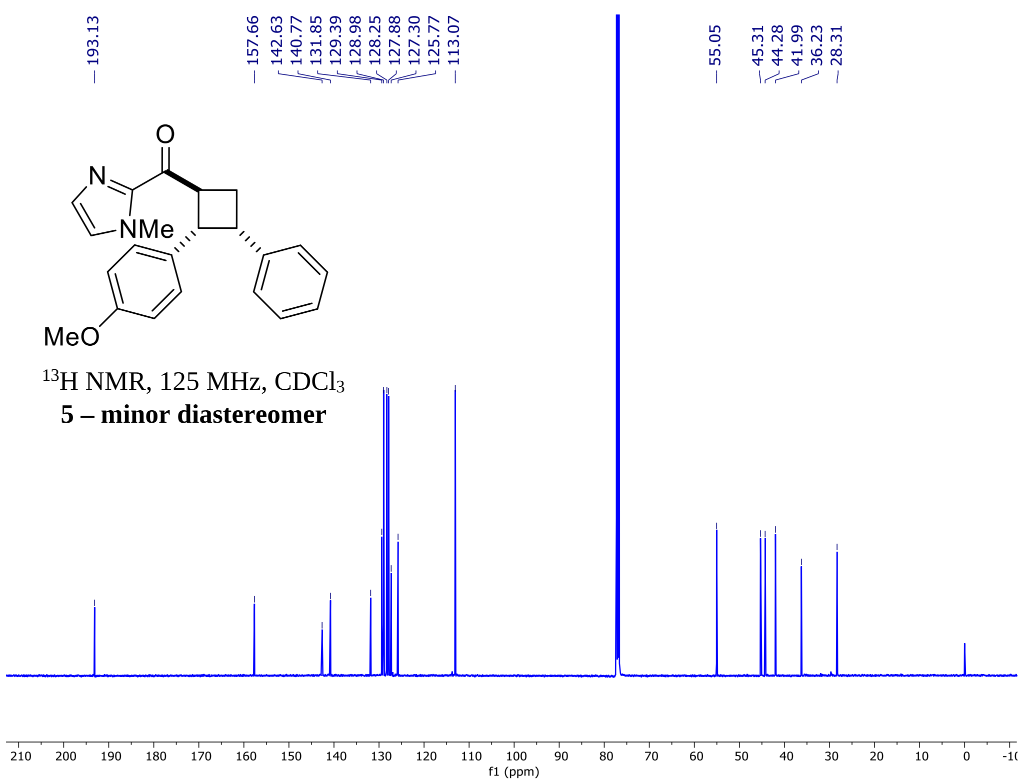
5 – minor diastereomer



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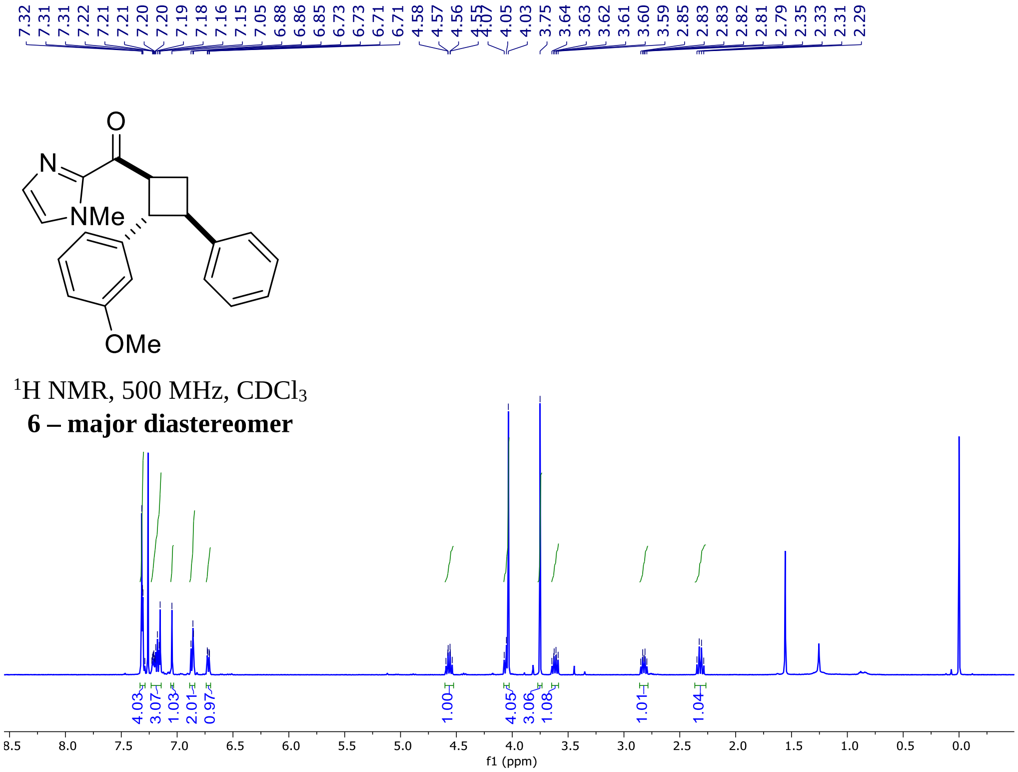
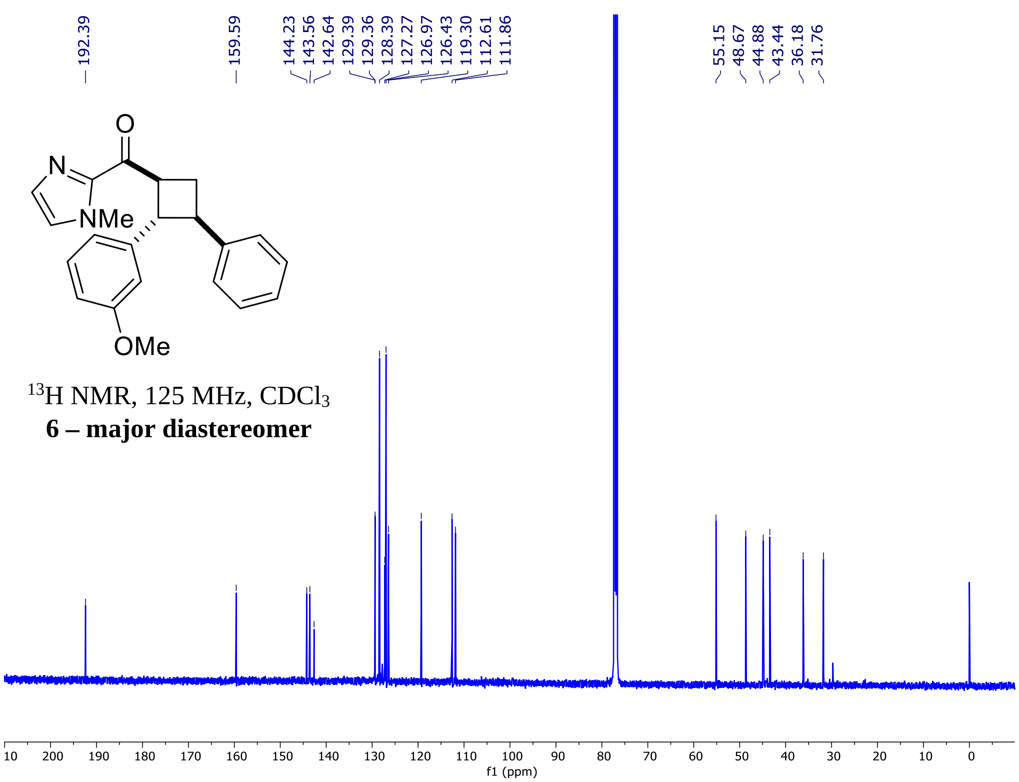
5 – minor diastereomer



^{1}H NMR, 500 MHz, $CDCl_3$
6 – major diastereomer



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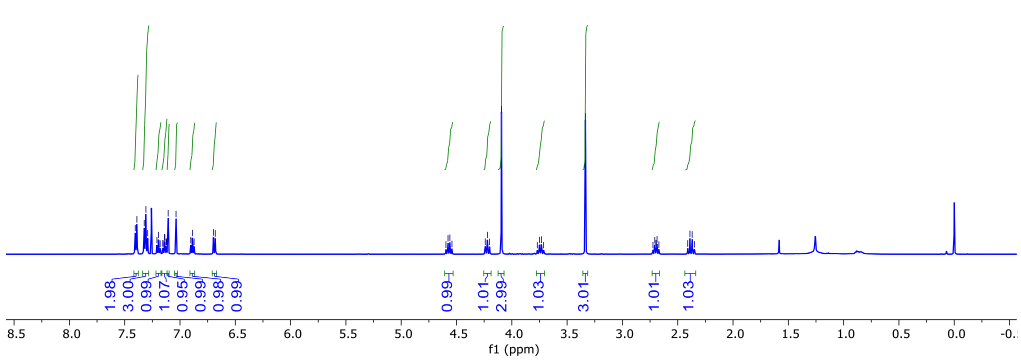
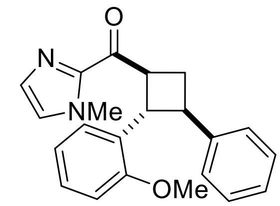
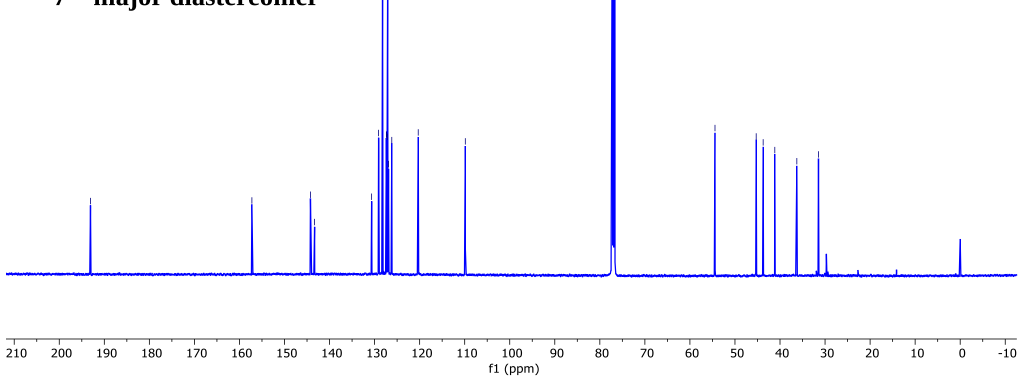
6 – major diastereomer

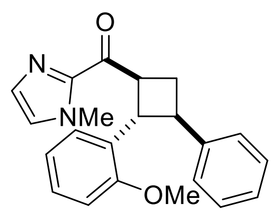




^{1}H NMR, 500 MHz, $CDCl_3$

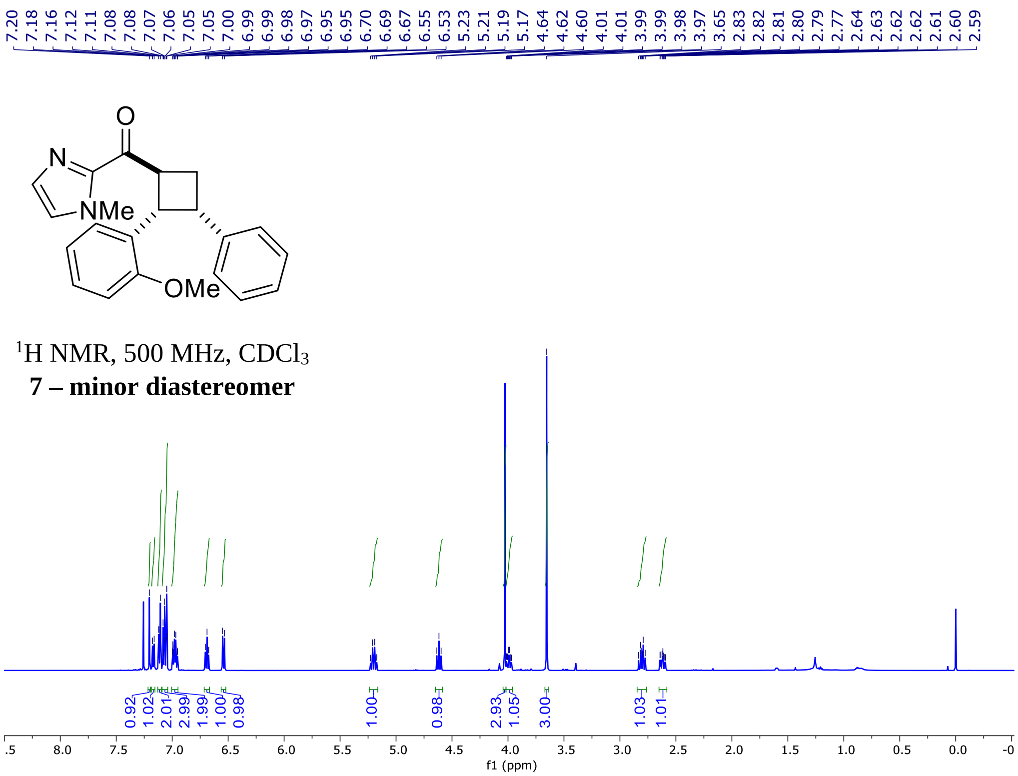
7 – major diastereomer





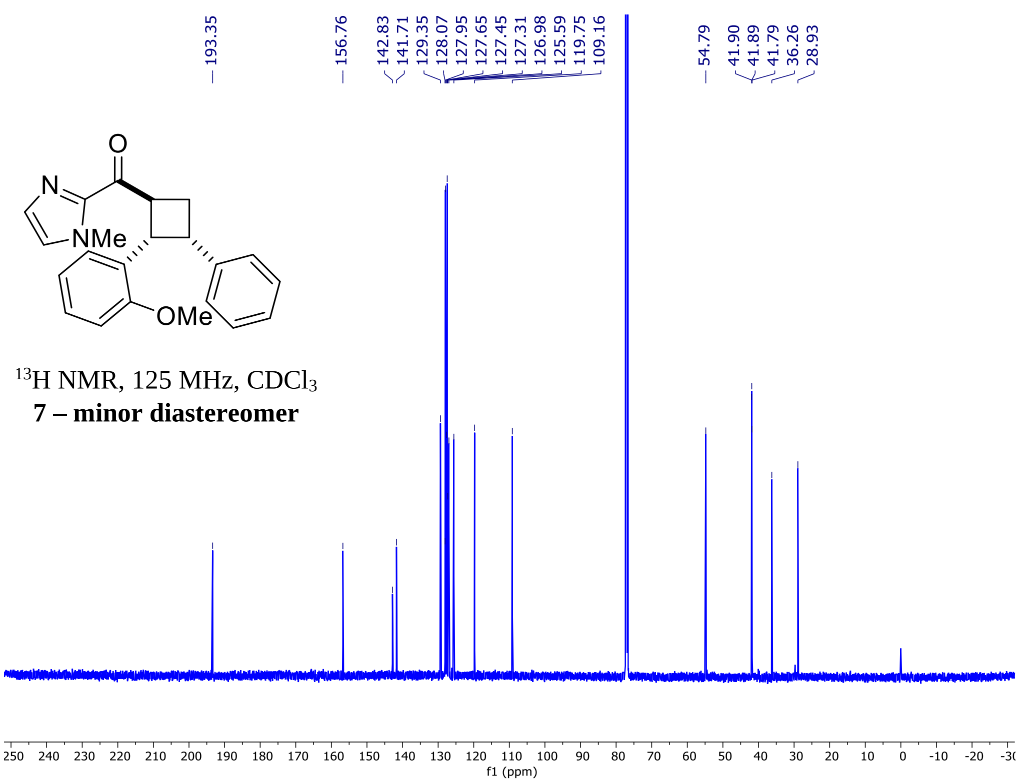
^{13}H NMR, 125 MHz, $CDCl_3$

7 – major diastereomer



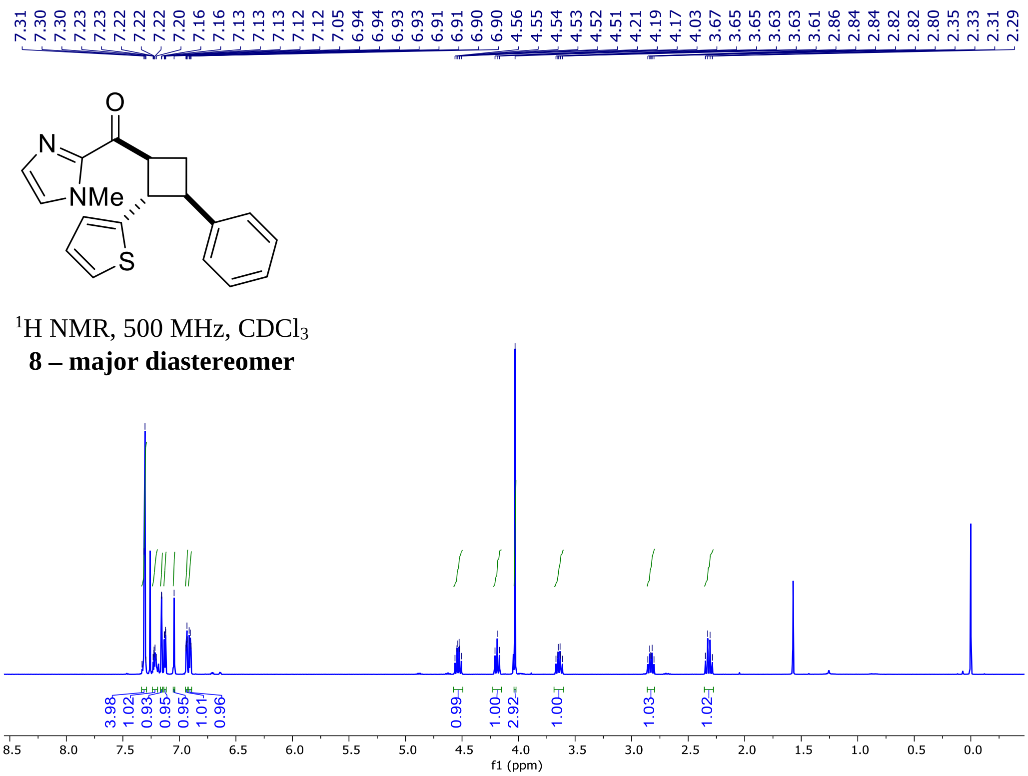
^{1}H NMR, 500 MHz, $CDCl_3$

7 – minor diastereomer



^{13}H NMR, 125 MHz, $CDCl_3$

7 – minor diastereomer



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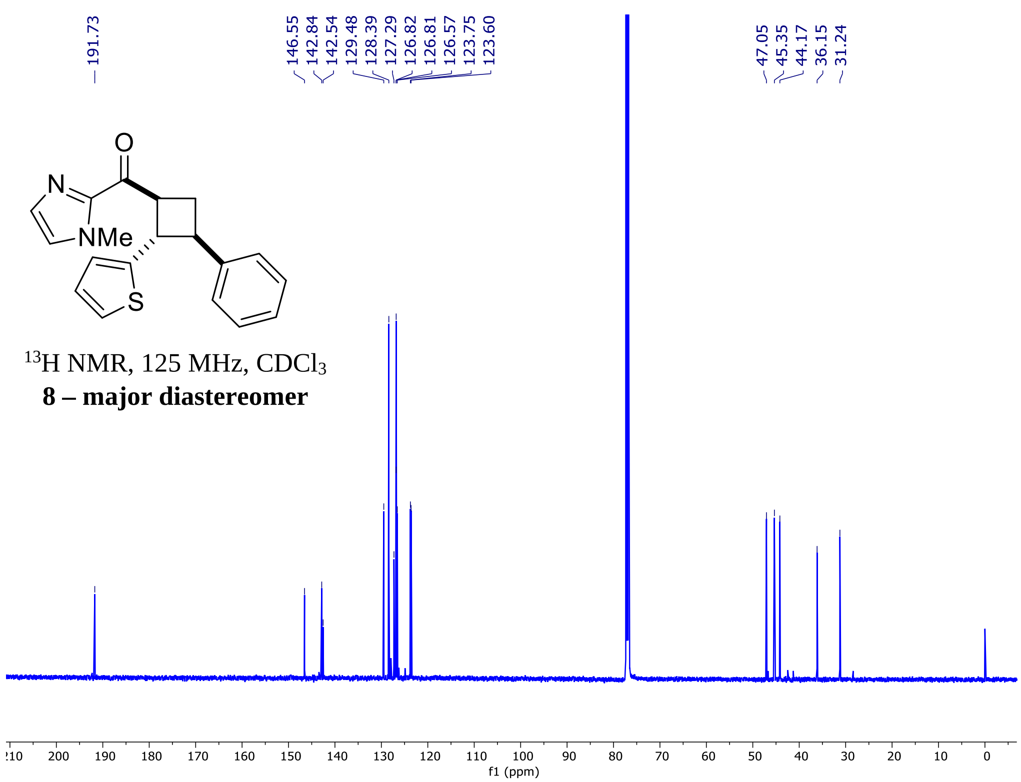
8 – major diastereomer



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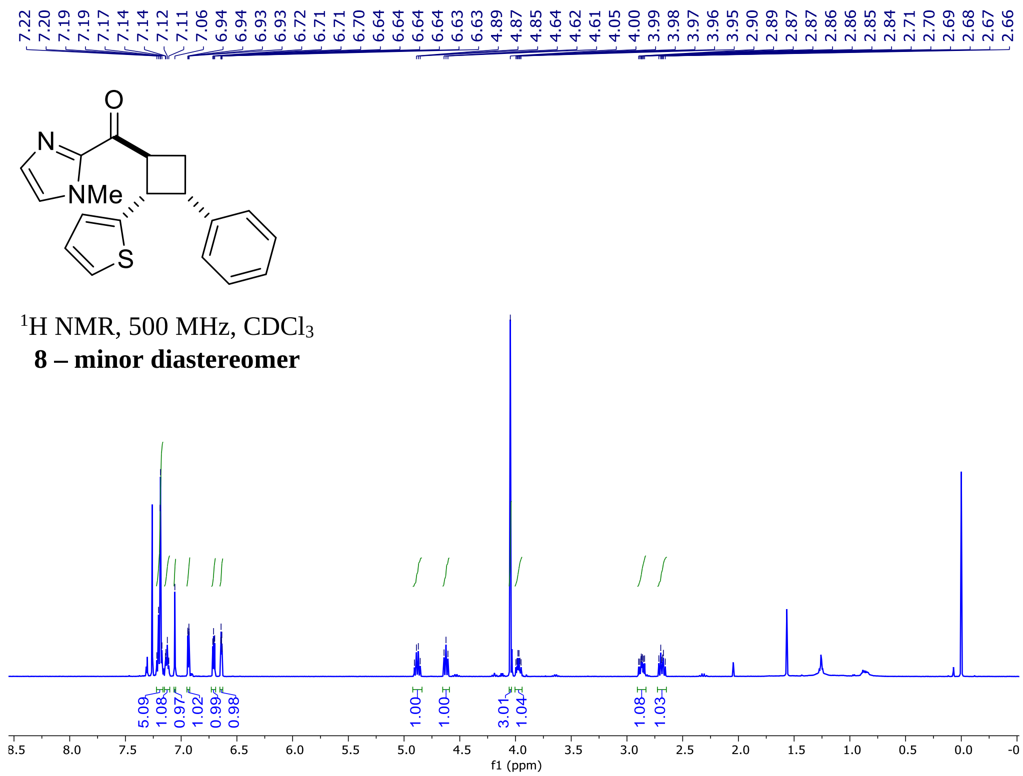
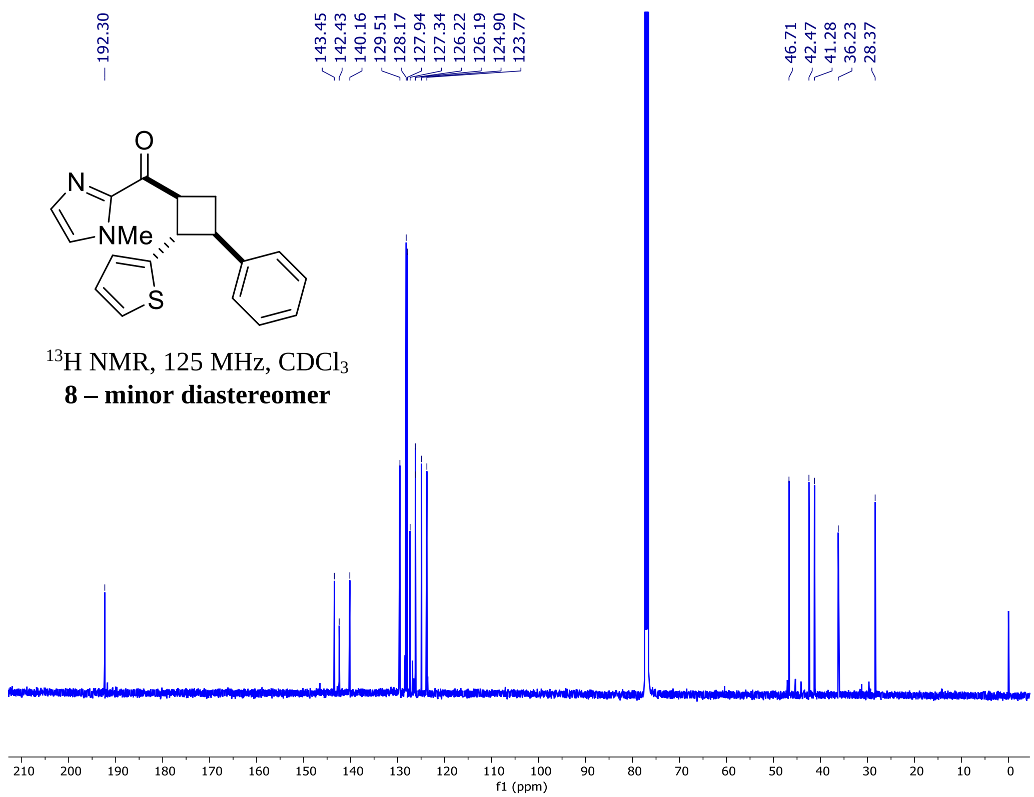
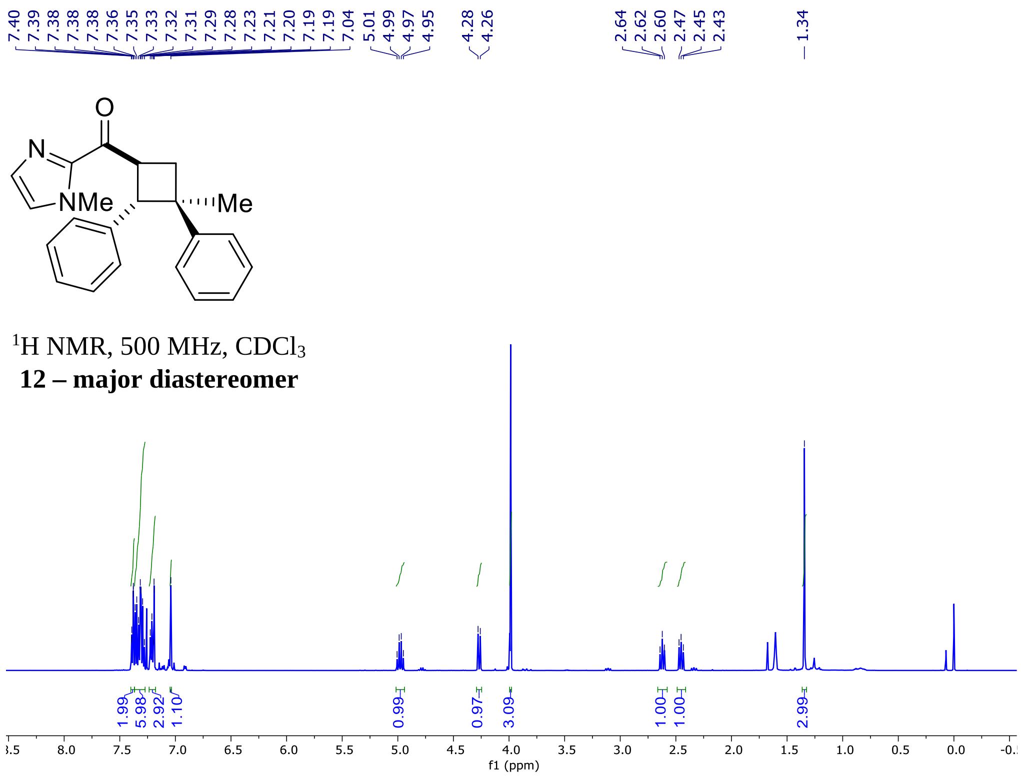
8 – major diastereomer

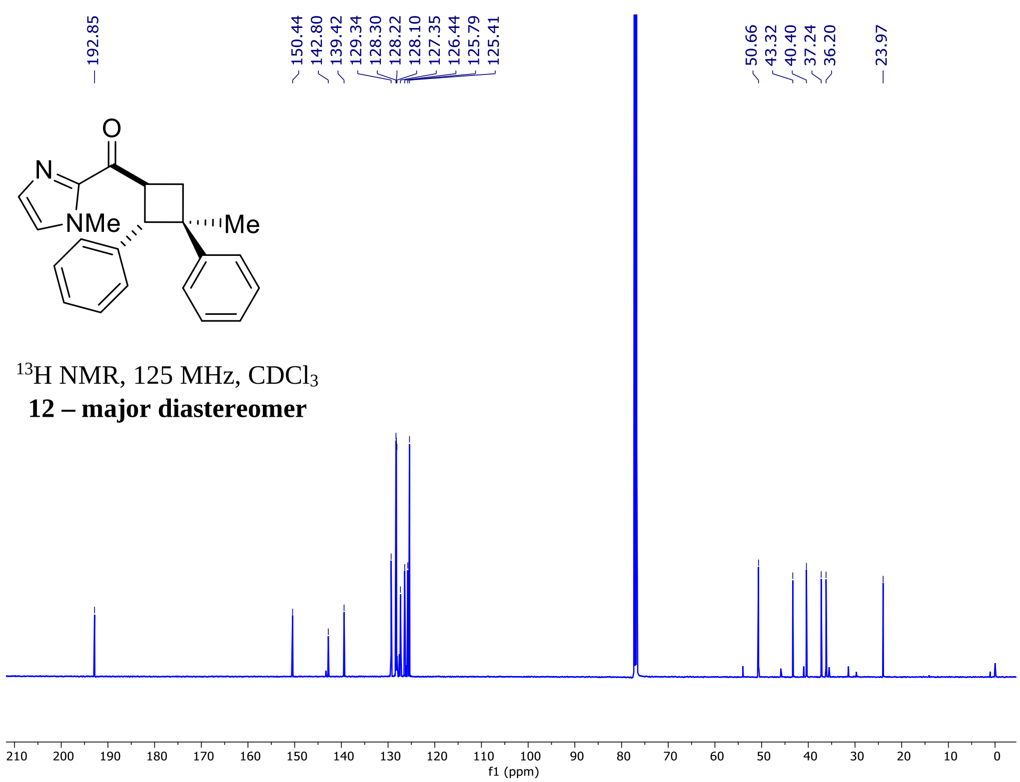

7.22 7.20 7.19 7.19 7.17 7.14 7.14 7.12 7.11 7.06 6.94 6.94 6.93 6.93 6.72 6.71 6.71 6.70 6.64 6.64 6.64 6.63 6.63 4.89 4.87 4.85 4.64 4.62 4.61 4.05 4.00 3.99 3.98 3.97 3.96 3.95 2.90 2.89 2.87 2.87 2.86 2.85 2.84 2.71 2.70 2.69 2.68 2.67 2.66
O
N
NMe
S
^{1}H NMR, 500 MHz, CDCl$_3$
8 – minor diastereomer
5.09 1.08 0.97 1.02 0.99 0.98 1.00 1.00 3.01 1.04 1.08 1.03
f1 (ppm)


192.30
143.45 142.43 140.16 129.51 128.17 127.94 127.34 126.22 126.19 124.90 123.77
46.71 42.47 41.28 36.23 28.37
O
N
NMe
S
^{13}H NMR, 125 MHz, CDCl$_3$
8 – minor diastereomer
f1 (ppm)



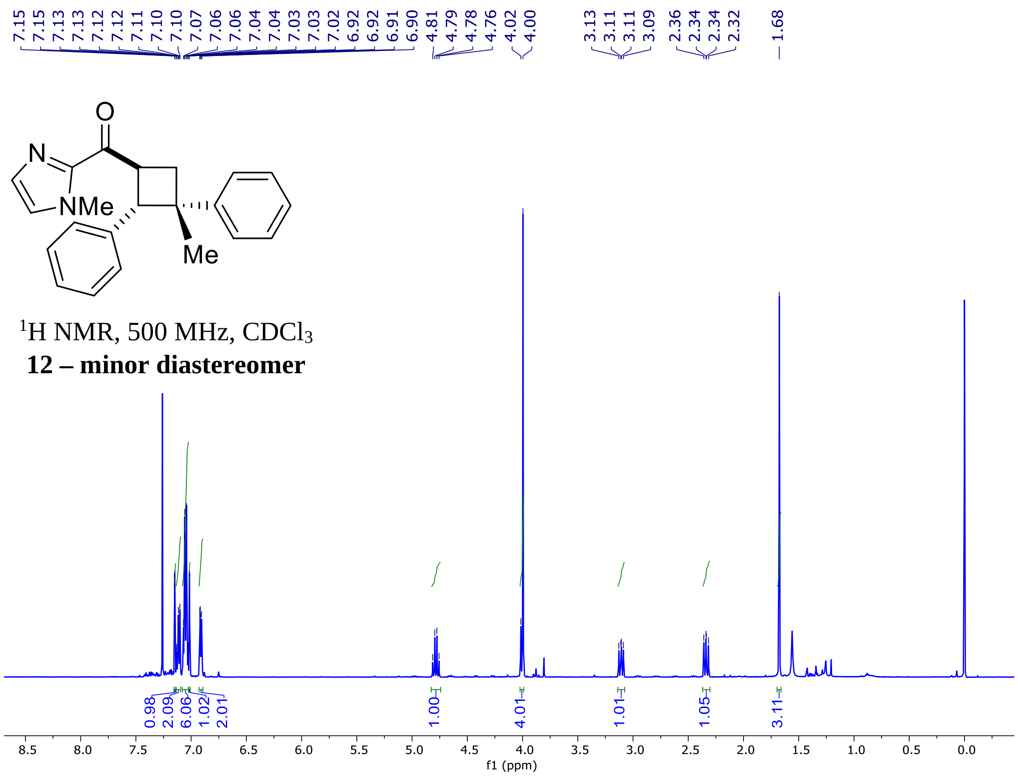
^{1}H NMR, 500 MHz, $CDCl_3$

12 – major diastereomer



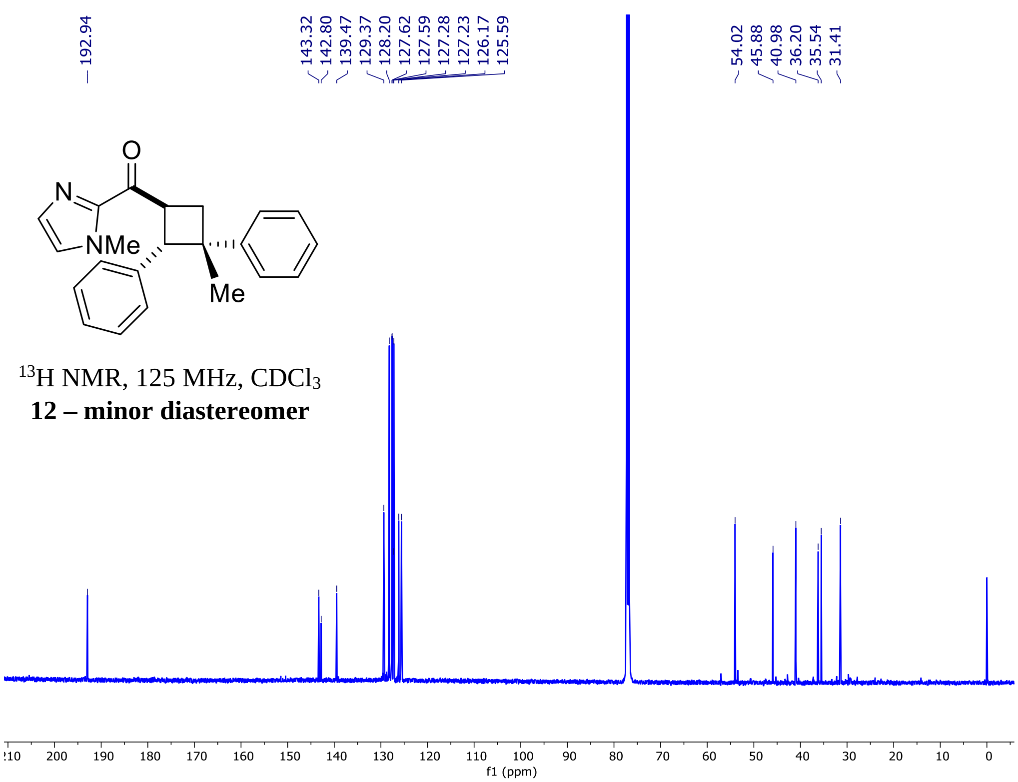
^{13}H NMR, 125 MHz, $CDCl_3$

12 – major diastereomer



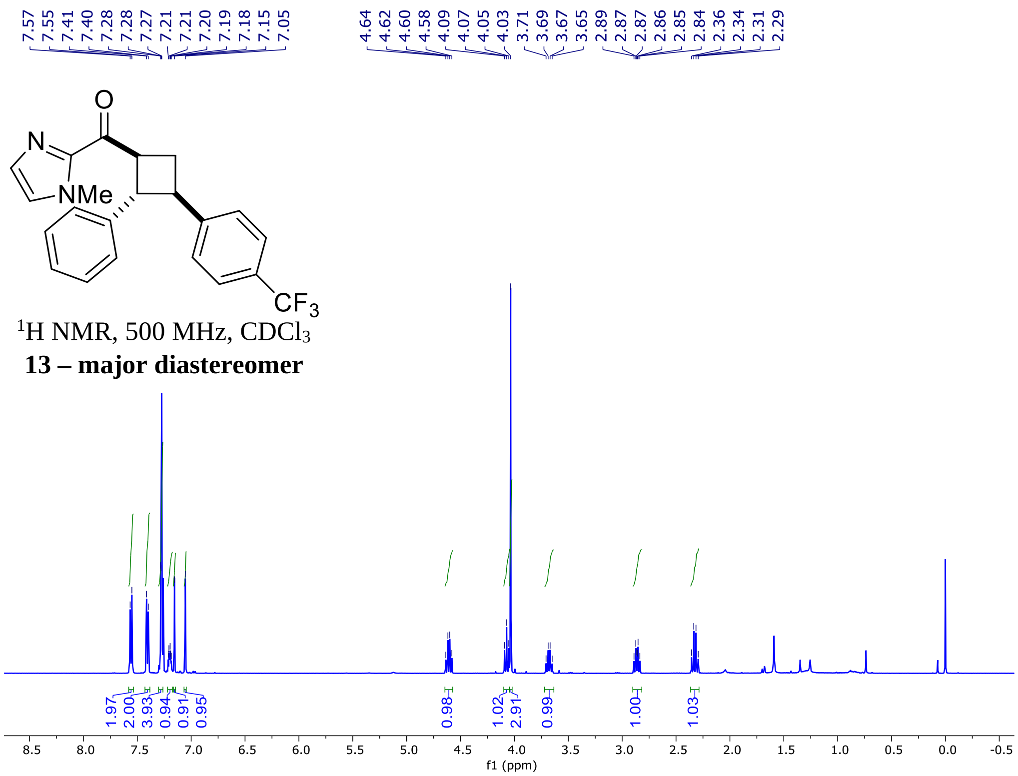
^{1}H NMR, 500 MHz, $CDCl_3$

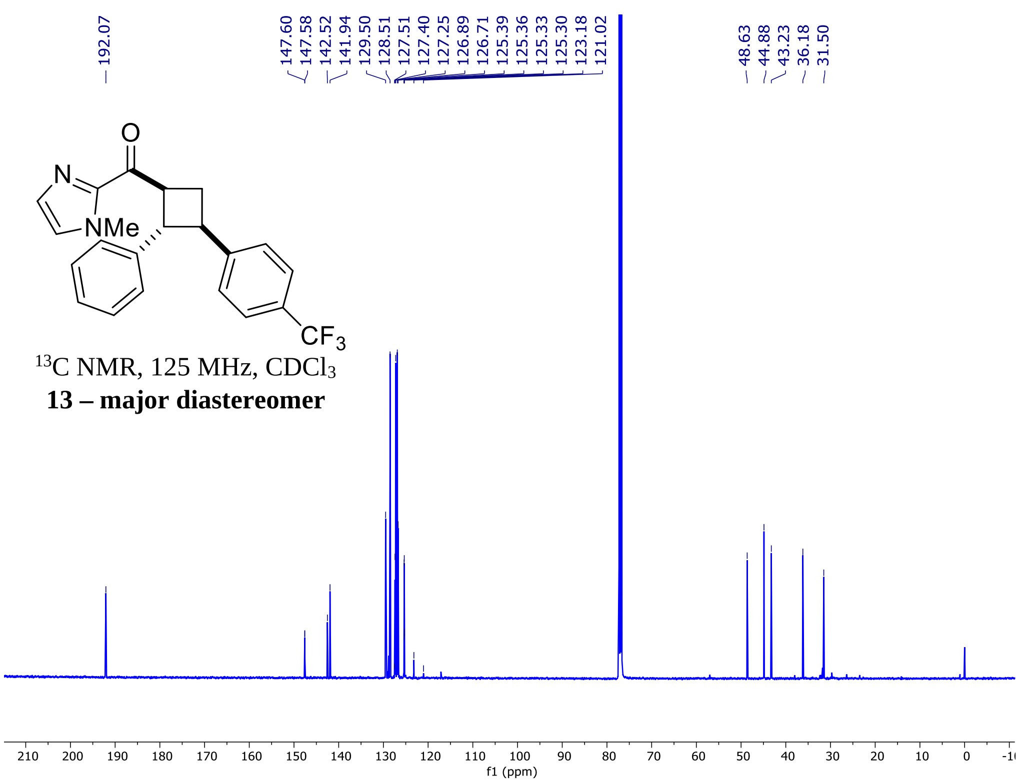
12 – minor diastereomer

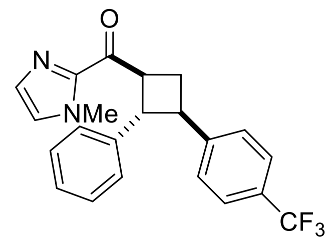


^{13}H NMR, 125 MHz, $CDCl_3$

12 – minor diastereomer

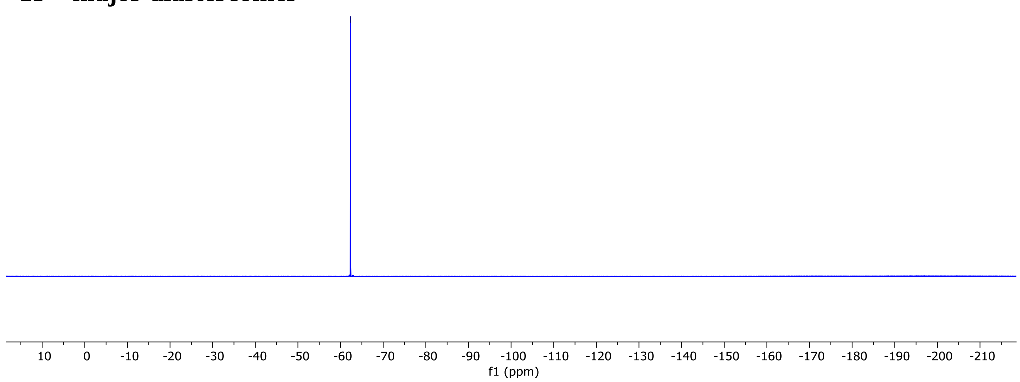

7.57 7.55 7.41 7.40 7.28 7.28 7.27 7.21 7.21 7.20 7.19 7.18 7.15 7.05
4.64 4.62 4.60 4.58 4.09 4.07 4.05 4.03 3.71 3.69 3.67 3.65 2.89 2.87 2.87 2.86 2.85 2.84 2.36 2.34 2.31 2.29
O
N
NMe
CF_3
^{1}H NMR, 500 MHz, $CDCl_3$
13 – major diastereomer
1.97 2.00 3.93 0.94 0.91 0.95
0.98 1.02 2.91 0.99 1.00 1.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

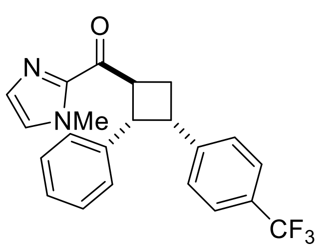

192.07
147.60 147.58 142.52 141.94 129.50 128.51 127.51 127.40 127.25 126.89 126.71 125.39 125.36 125.33 125.30 123.18 121.02
48.63 44.88 43.23 36.18 31.50
O
N
NMe
CF_3
^{13}C NMR, 125 MHz, $CDCl_3$
13 – major diastereomer
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



^{19}F NMR, 377 MHz, $CDCl_3$

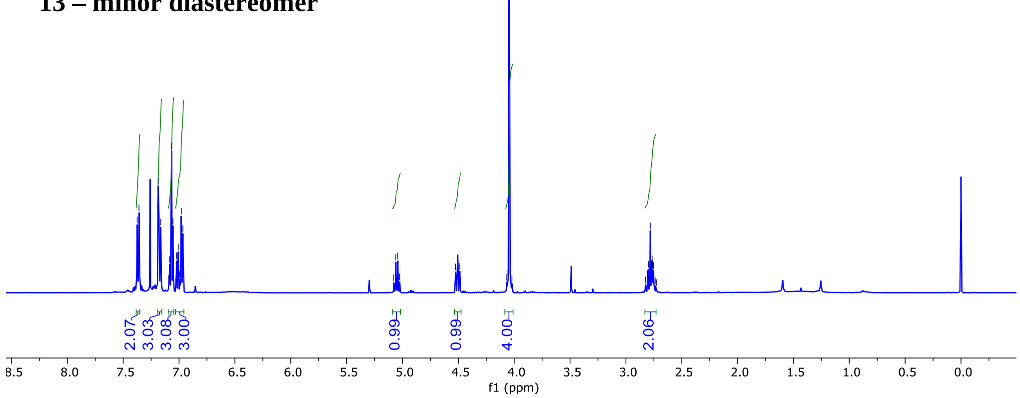
13 – major diastereomer

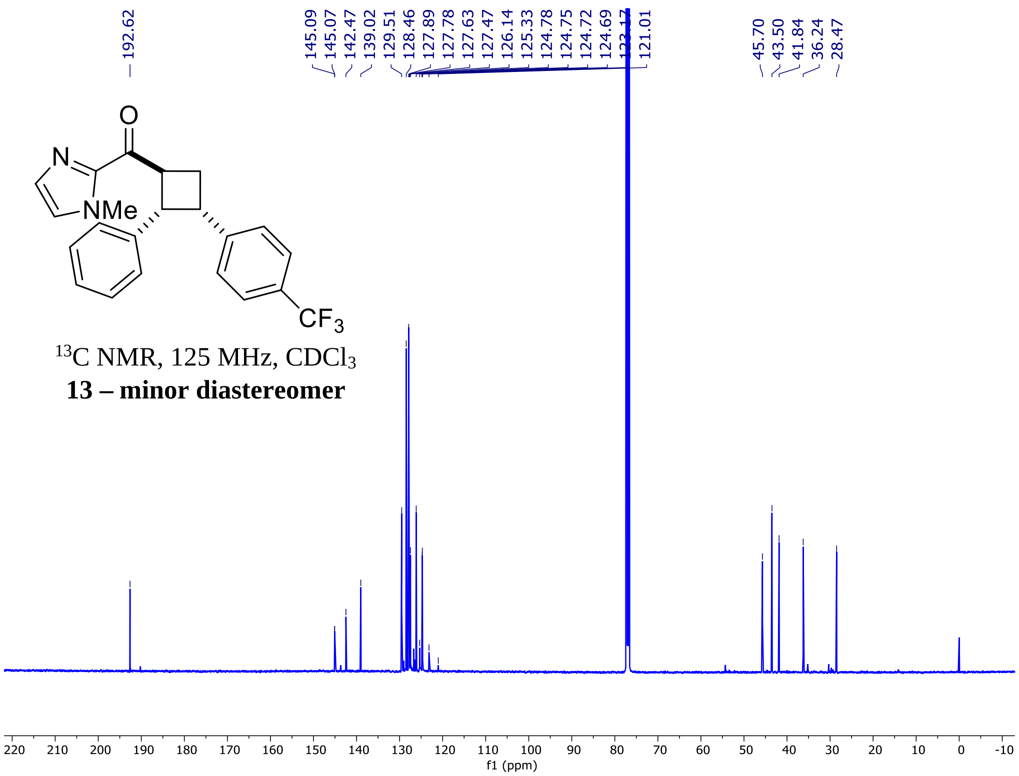




^{1}H NMR, 500 MHz, $CDCl_3$

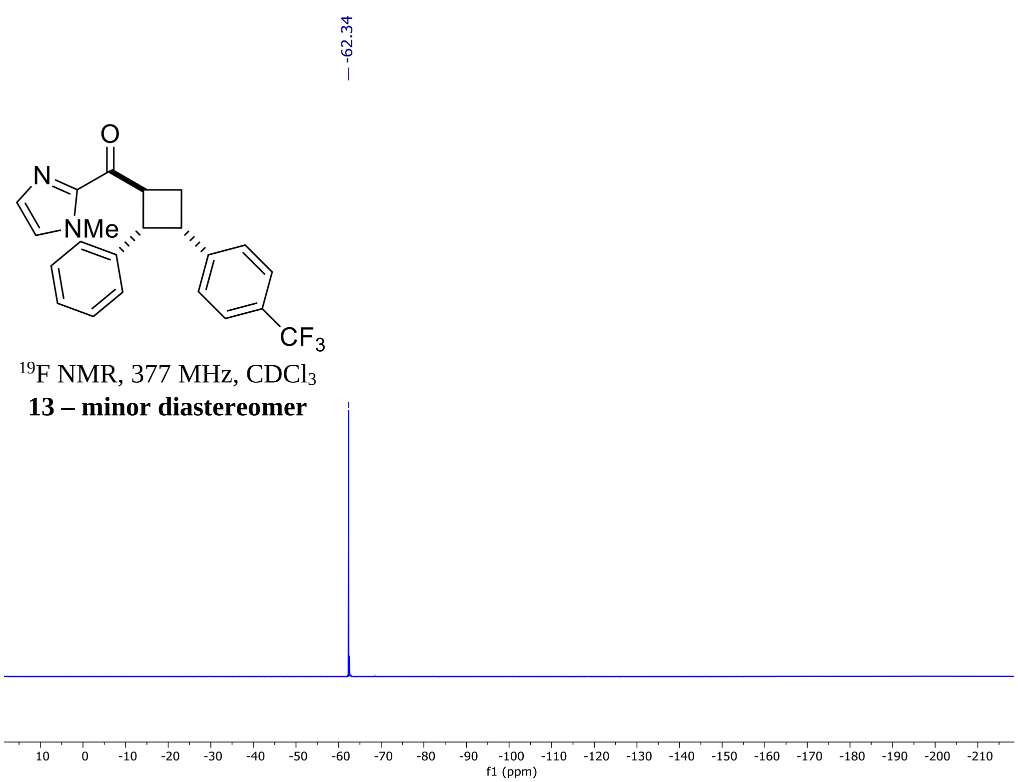
13 – minor diastereomer





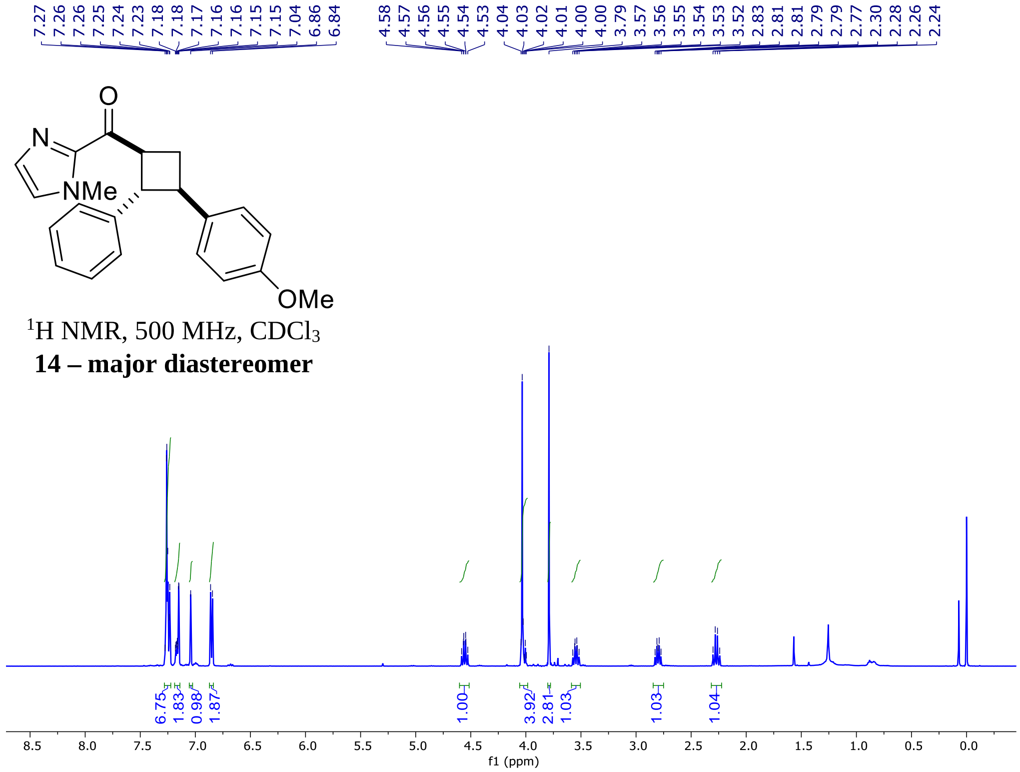
^{13}C NMR, 125 MHz, $CDCl_3$

13 – minor diastereomer



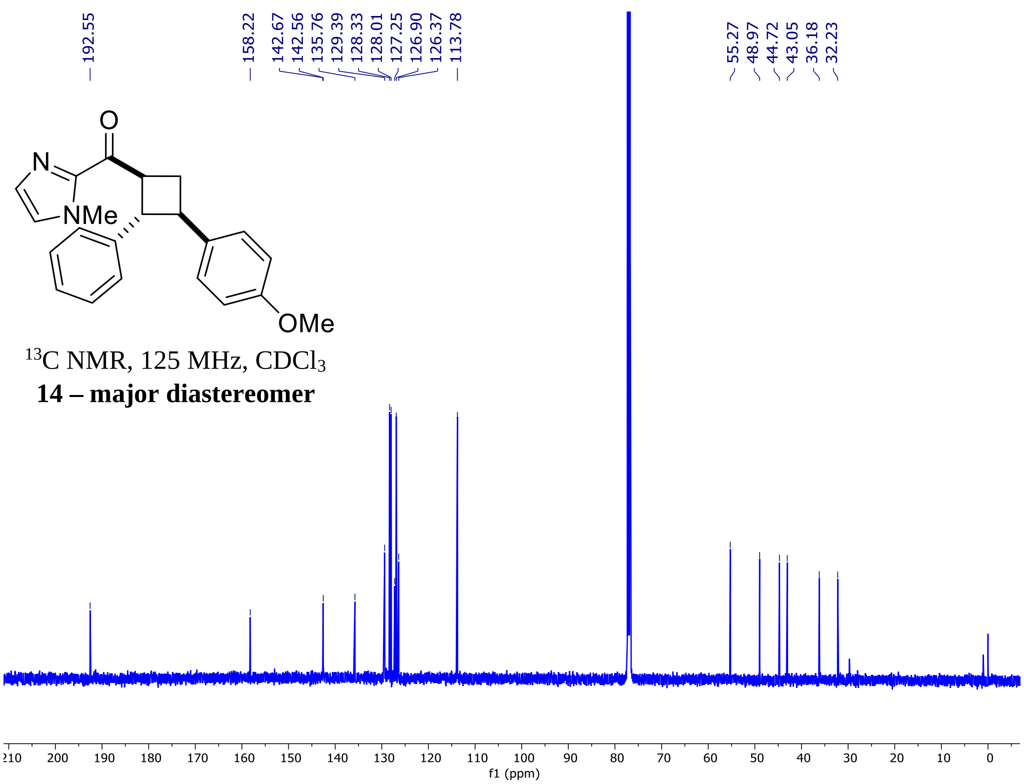
^{19}F NMR, 377 MHz, $CDCl_3$

13 – minor diastereomer



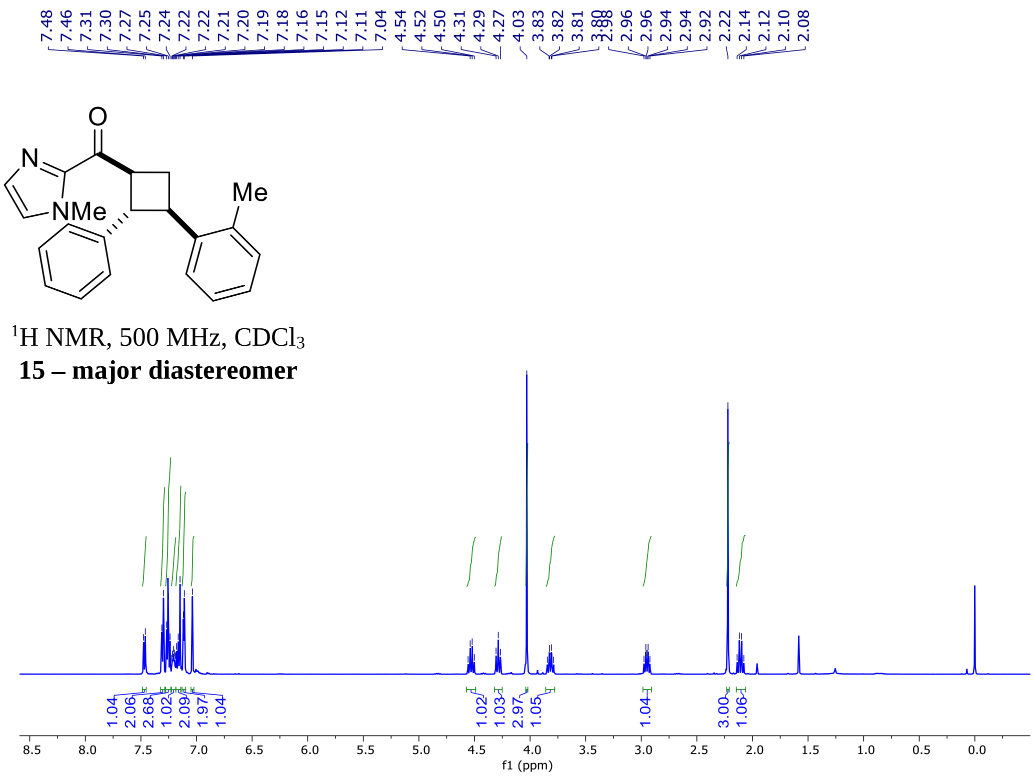
^{1}H NMR, 500 MHz, $CDCl_3$

14 – major diastereomer



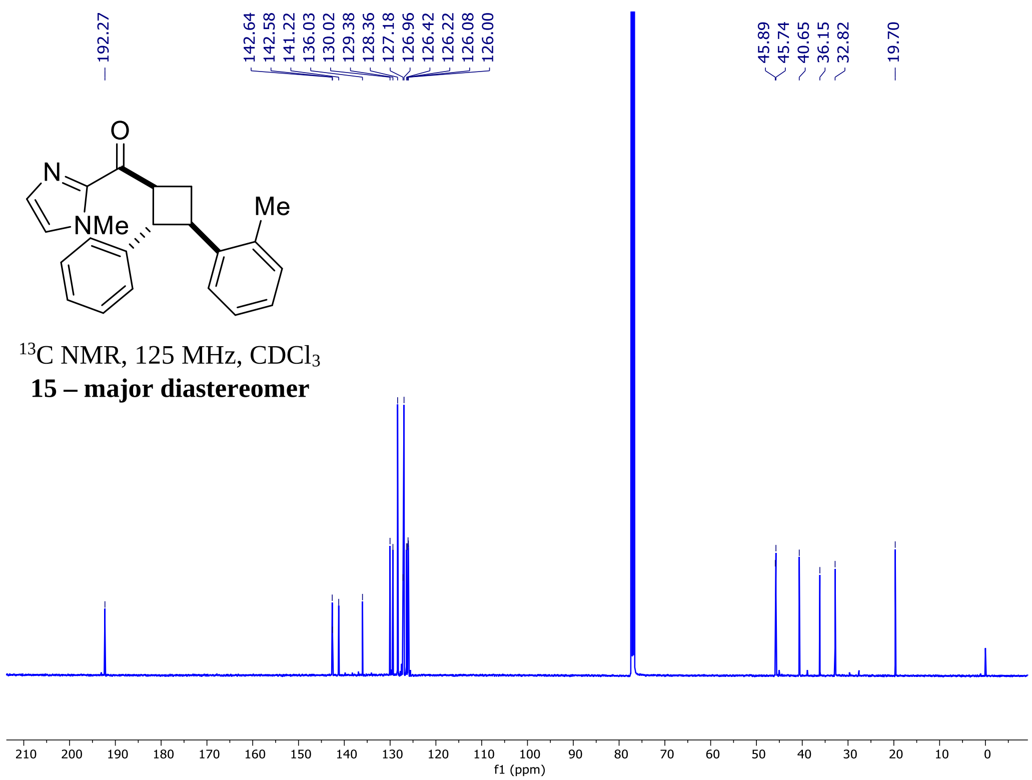
^{13}C NMR, 125 MHz, $CDCl_3$

14 – major diastereomer



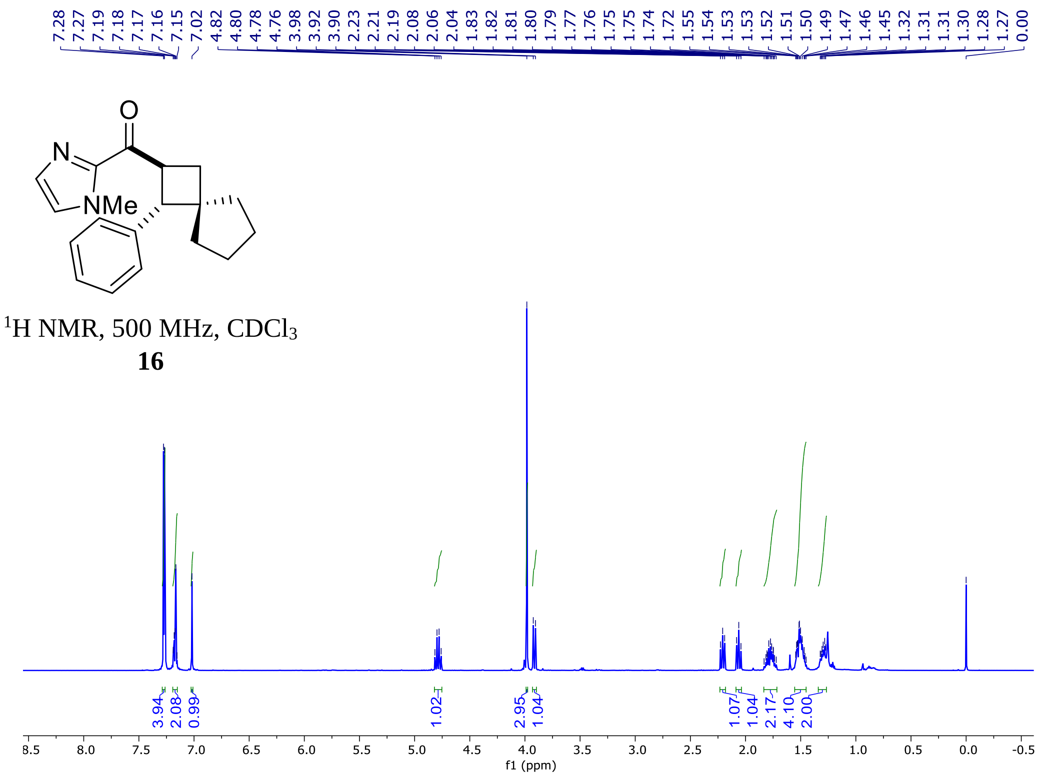
^{1}H NMR, 500 MHz, $CDCl_3$

15 – major diastereomer



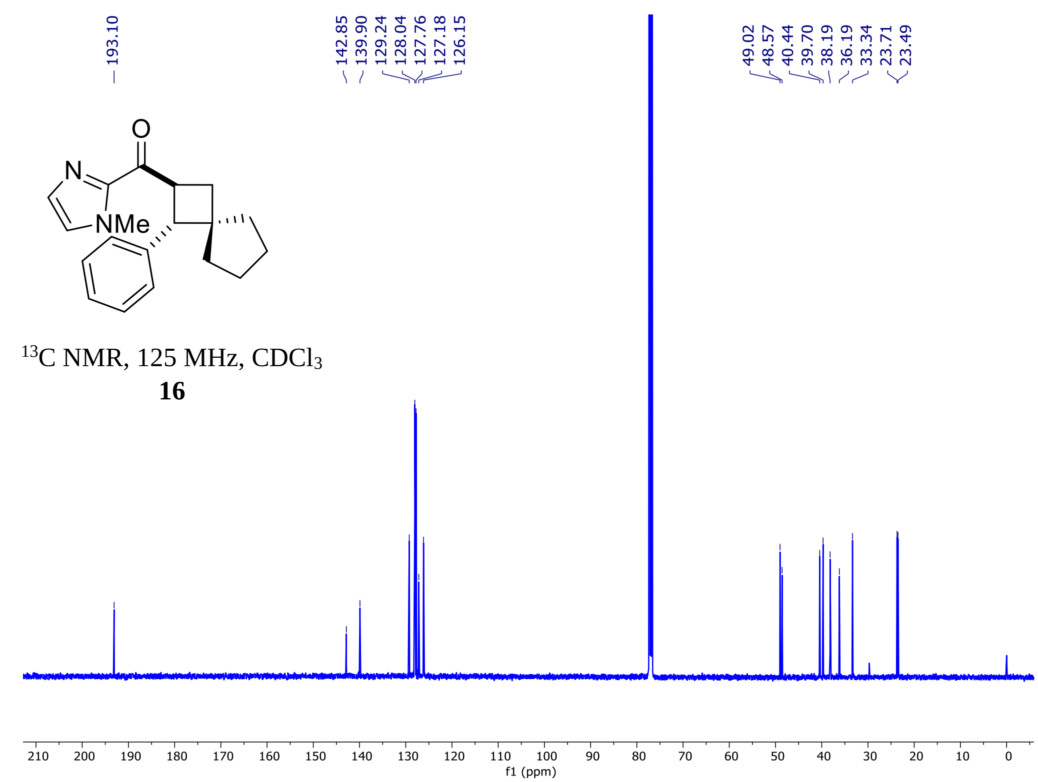
^{13}C NMR, 125 MHz, $CDCl_3$

15 – major diastereomer



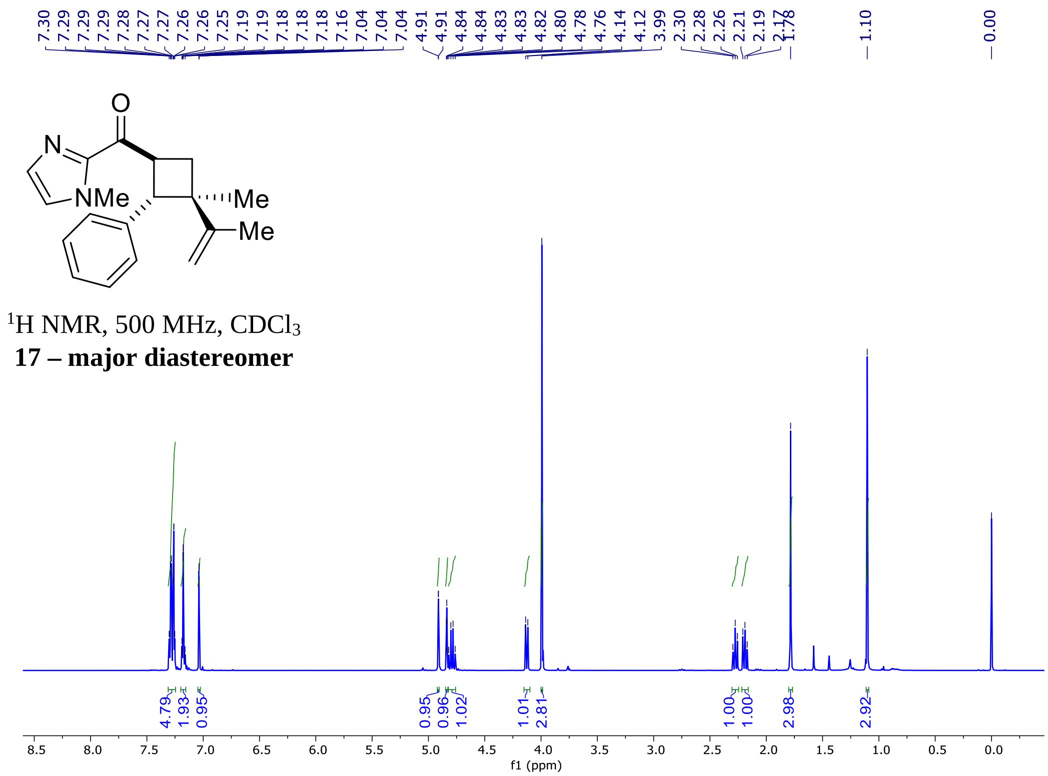
^{1}H NMR, 500 MHz, CDCl$_3$

16



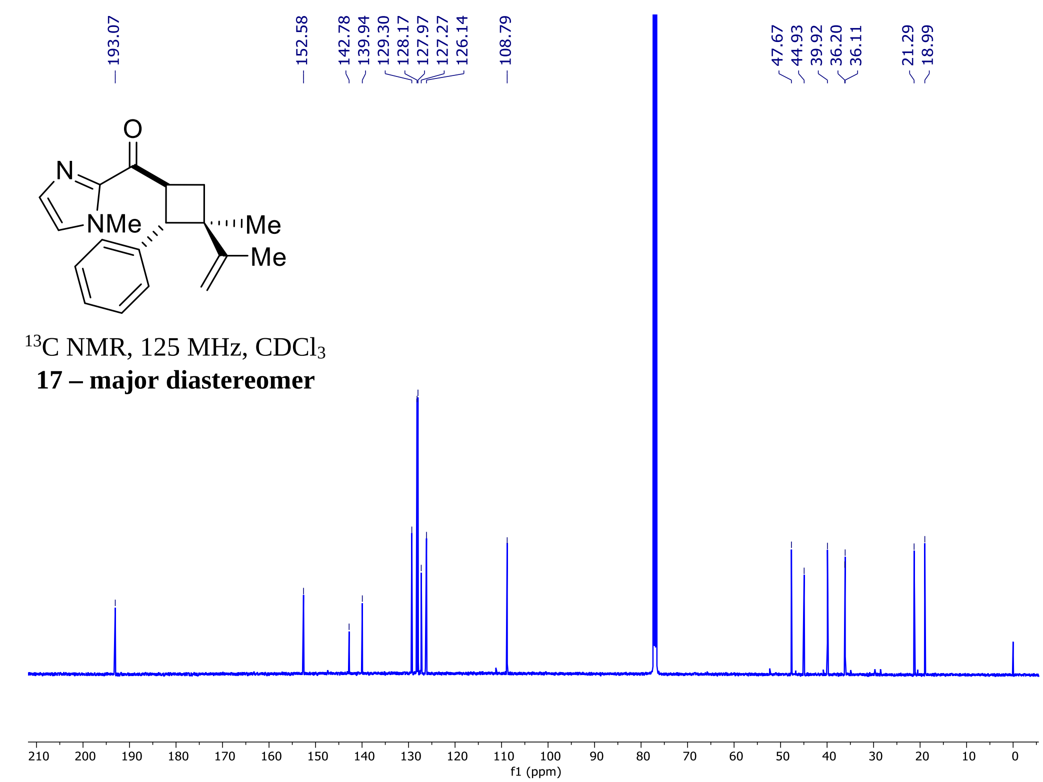
^{13}C NMR, 125 MHz, CDCl$_3$

16



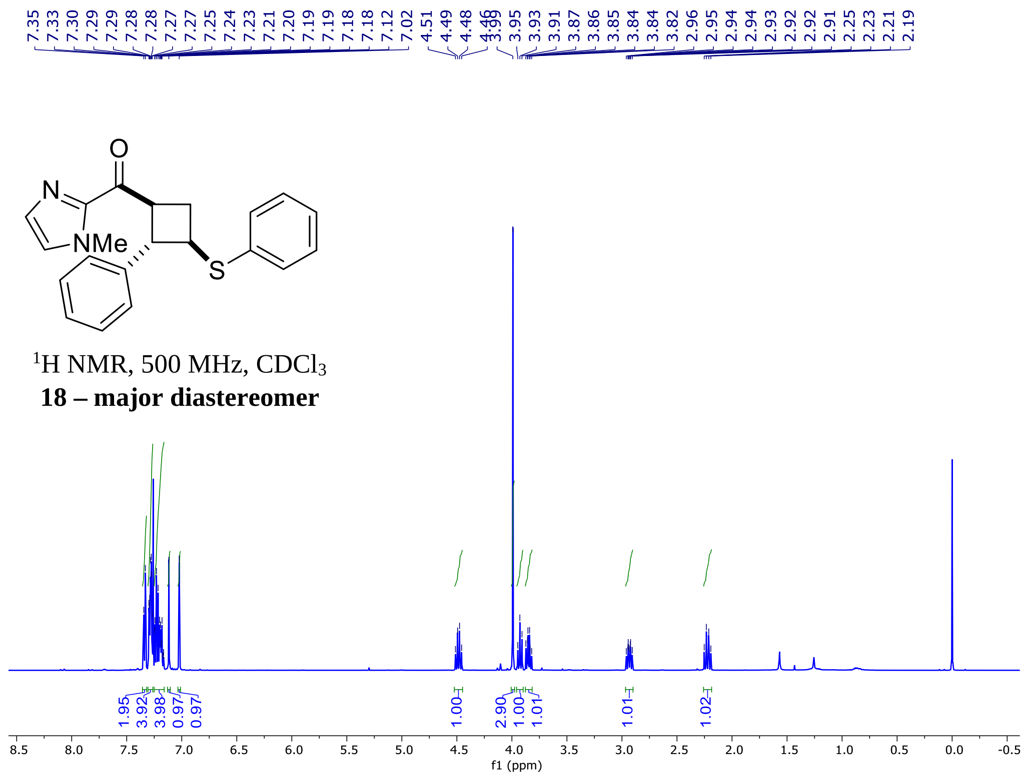
^{1}H NMR, 500 MHz, $CDCl_3$

17 – major diastereomer

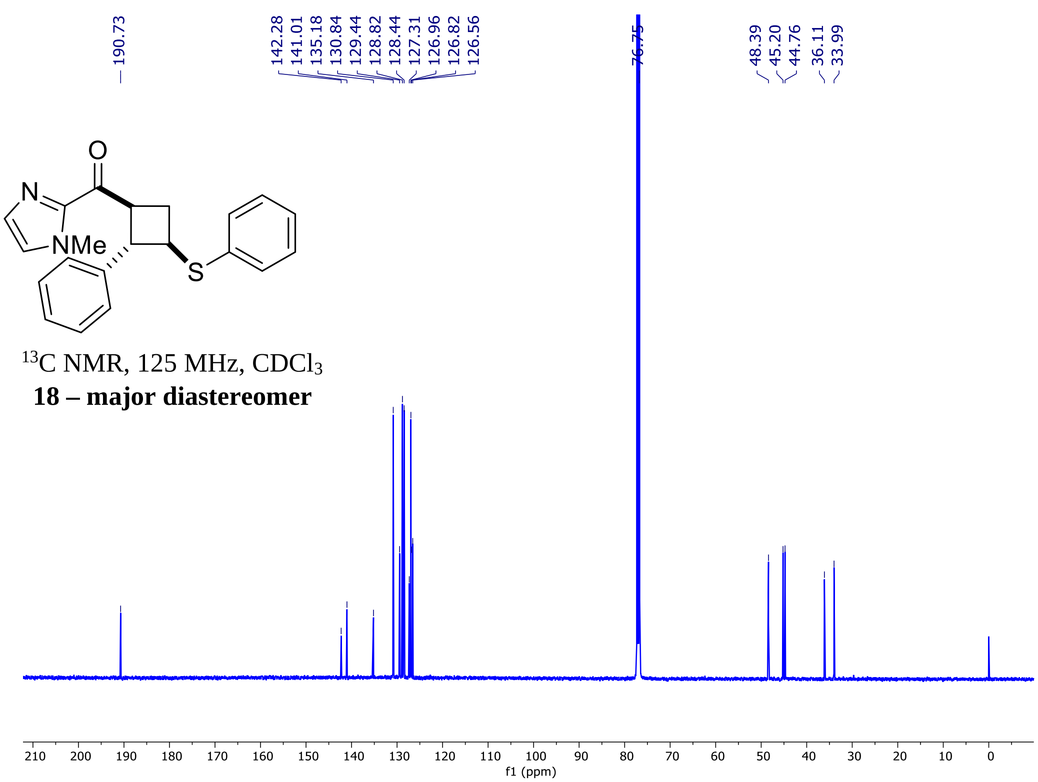


^{13}C NMR, 125 MHz, $CDCl_3$

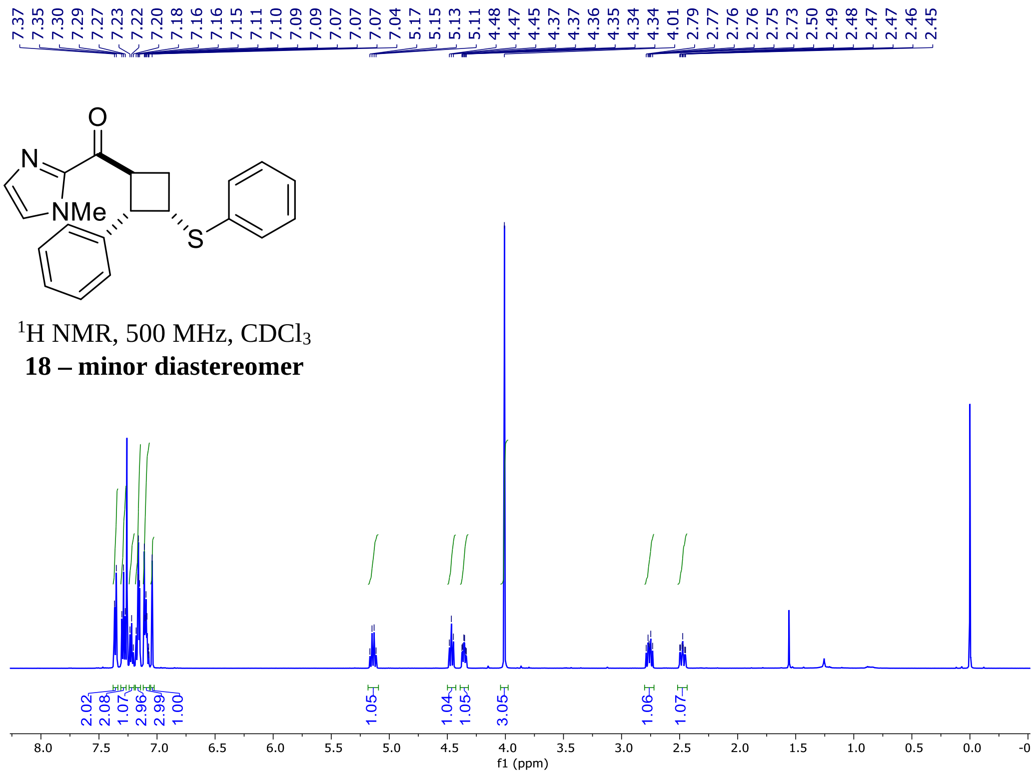
17 – major diastereomer

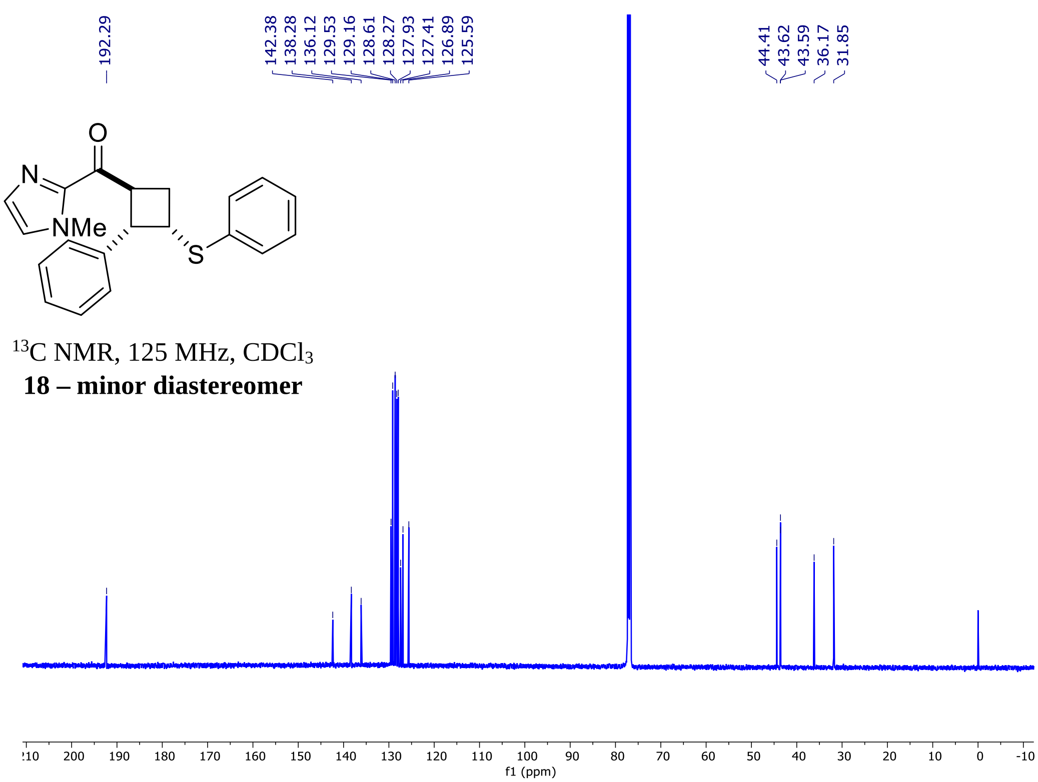


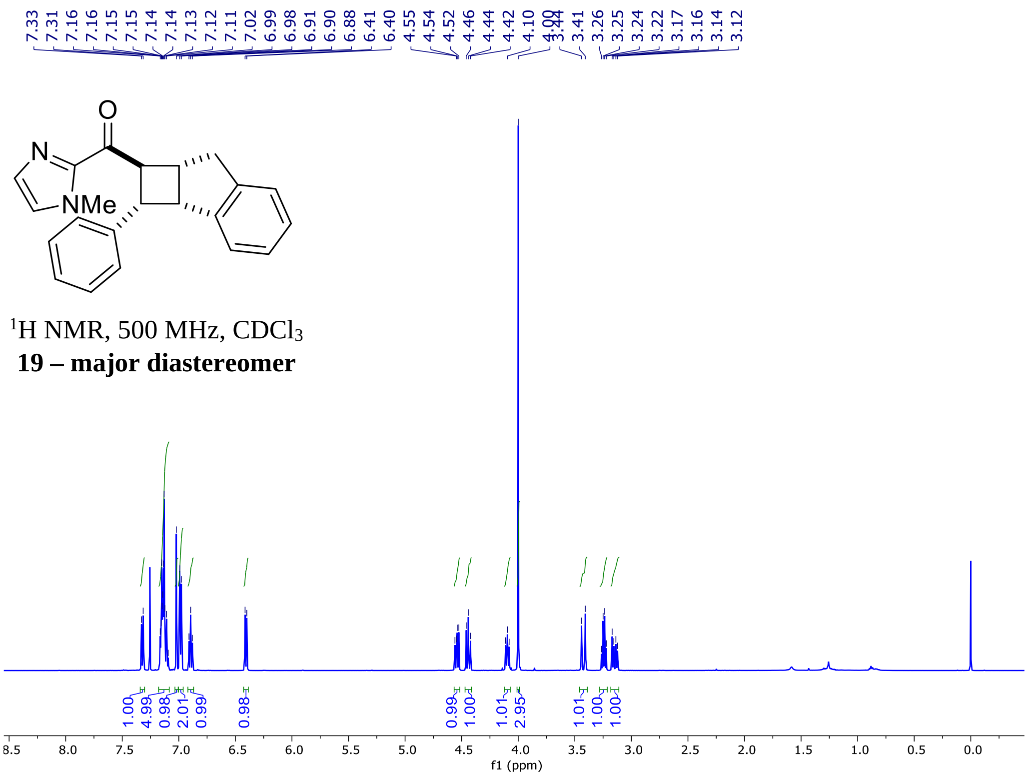
^{1}H NMR, 500 MHz, $CDCl_3$
18 – major diastereomer



^{13}C NMR, 125 MHz, $CDCl_3$
18 – major diastereomer

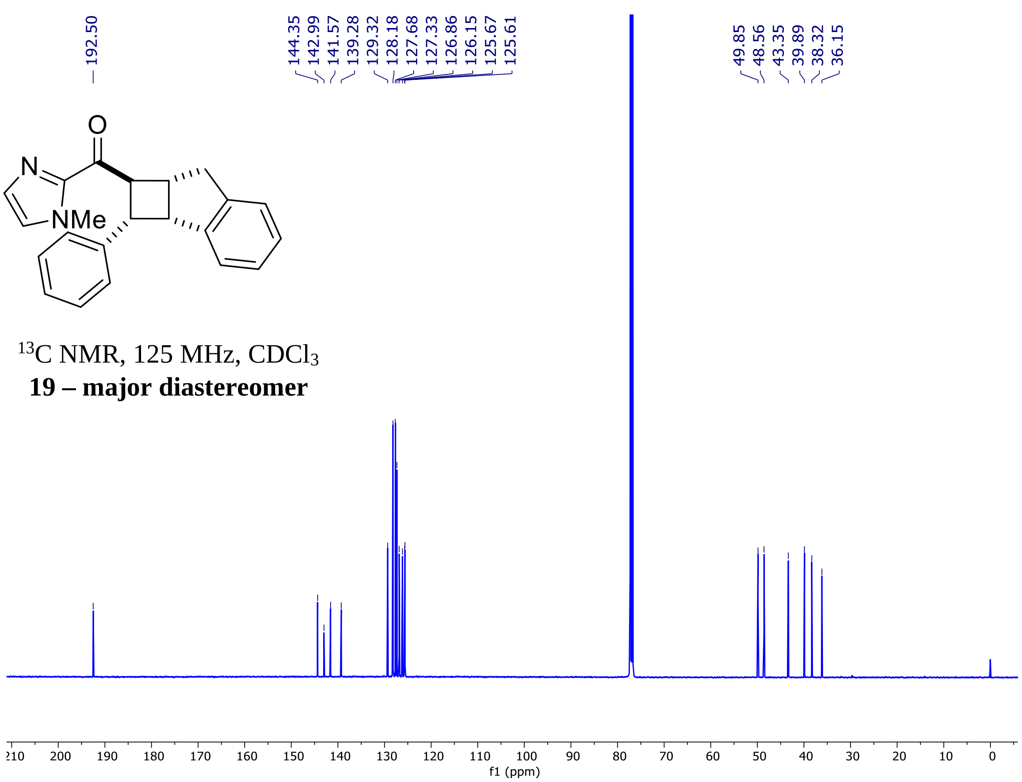

7.37
7.35
7.30
7.29
7.27
7.23
7.22
7.20
7.18
7.16
7.16
7.15
7.11
7.10
7.09
7.09
7.07
7.07
7.04
5.17
5.15
5.13
5.11
4.48
4.47
4.45
4.37
4.37
4.36
4.35
4.34
4.34
4.01
2.79
2.77
2.76
2.75
2.73
2.50
2.49
2.48
2.47
2.47
2.46
2.45
O
N
NMe
S
^{1}H NMR, 500 MHz, $CDCl_3$
18 – minor diastereomer
2.02
2.08
1.07
2.96
2.99
1.00
1.05
1.04
1.05
3.05
1.06
1.07
f1 (ppm)


192.29
142.38
138.28
136.12
129.53
129.16
128.61
128.27
127.93
127.41
126.89
125.59
44.41
43.62
43.59
36.17
31.85
O
N
NMe
S
^{13}C NMR, 125 MHz, $CDCl_3$
18 – minor diastereomer
f1 (ppm)



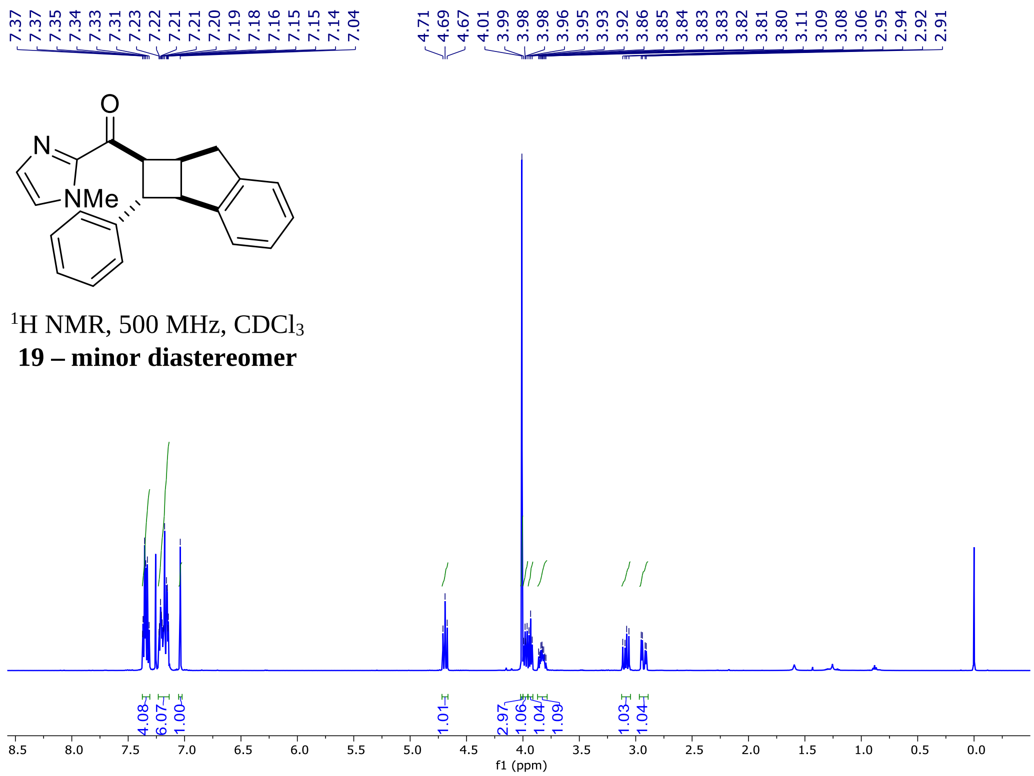
[1]H NMR, 500 MHz, $CDCl_3$

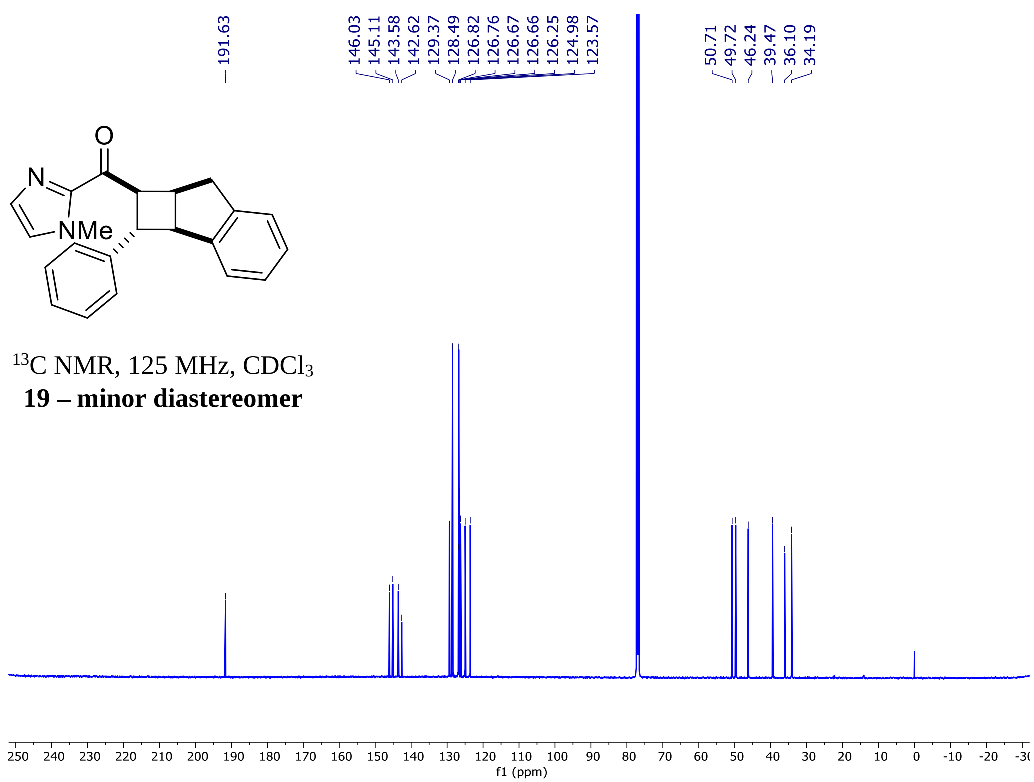
19 – major diastereomer

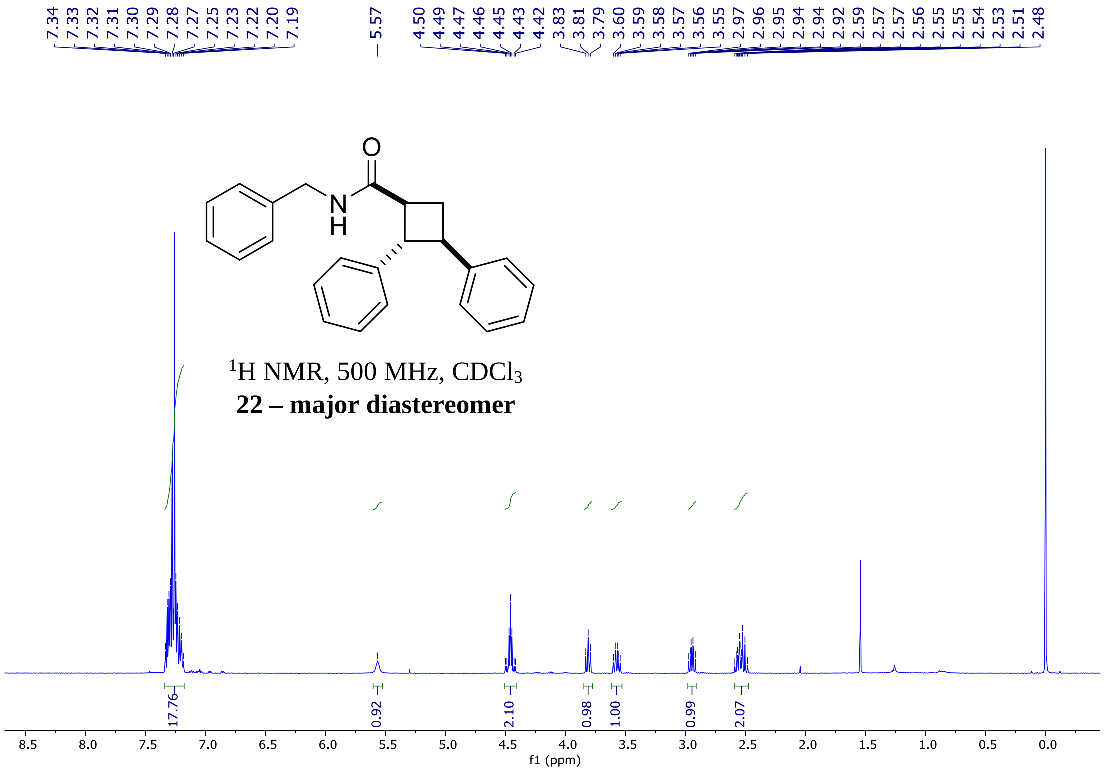


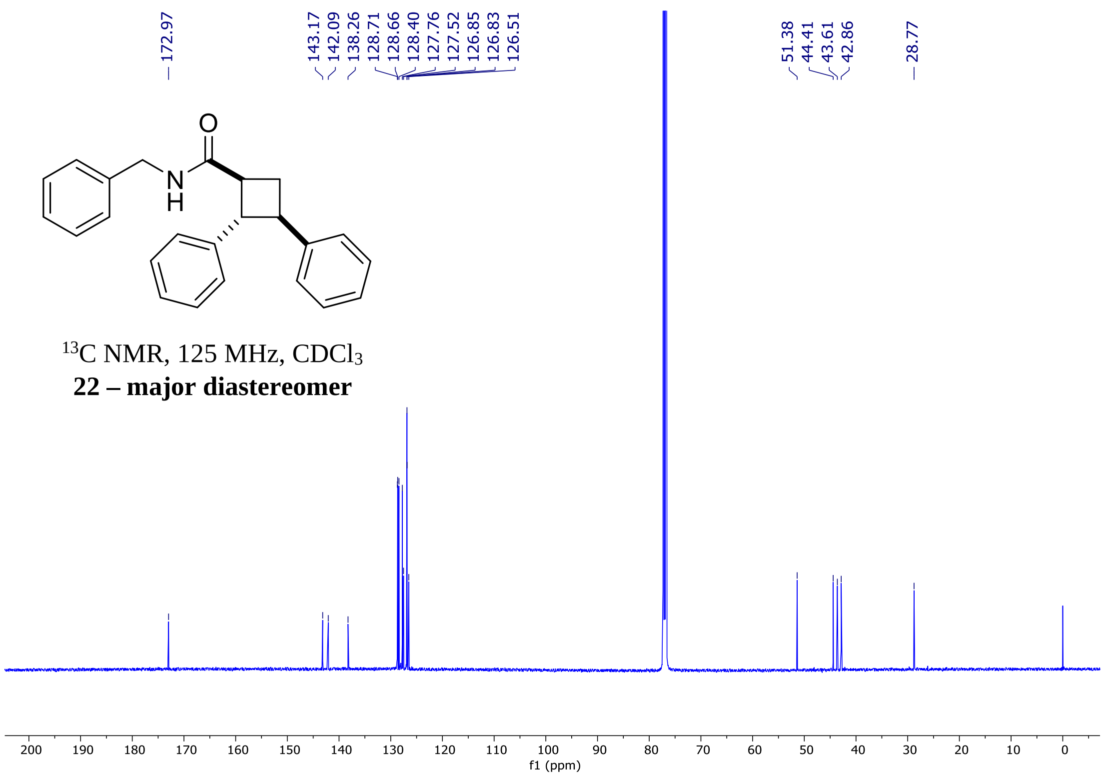
[13]C NMR, 125 MHz, $CDCl_3$

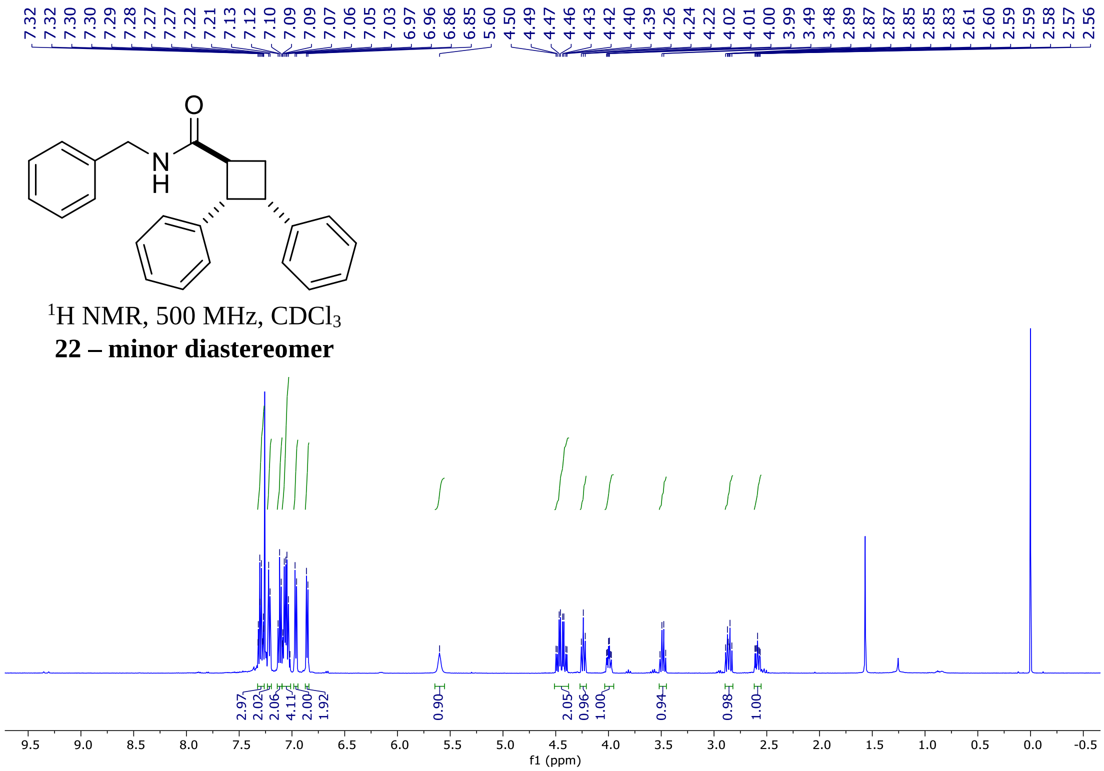
19 – major diastereomer

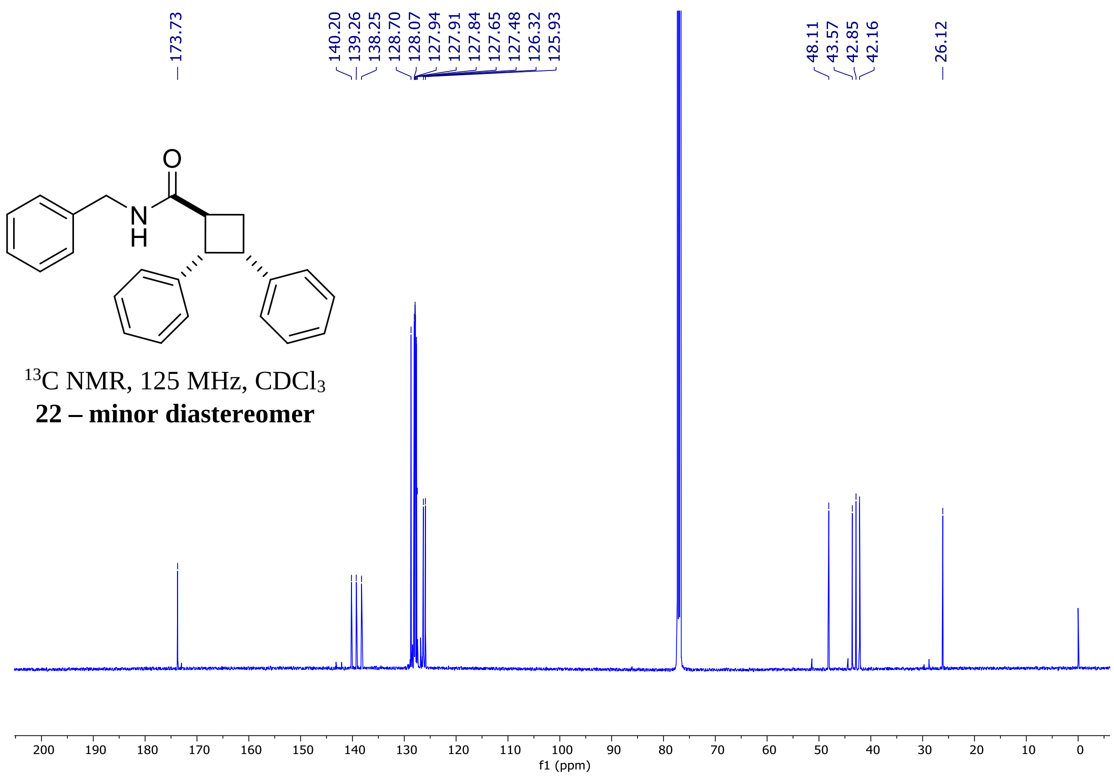

7.37 7.37 7.35 7.34 7.33 7.31 7.23 7.22 7.21 7.21 7.20 7.19 7.18 7.16 7.15 7.15 7.14 7.04
4.71 4.69 4.67 4.01 3.99 3.98 3.98 3.96 3.95 3.93 3.92 3.86 3.85 3.84 3.83 3.83 3.82 3.81 3.80 3.11 3.09 3.08 3.06 2.95 2.94 2.92 2.91
O
N
NMe
¹H NMR, 500 MHz, CDCl₃
19 – minor diastereomer
4.08 6.07 1.00 1.01 2.97 1.06 1.04 1.09 1.03 1.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

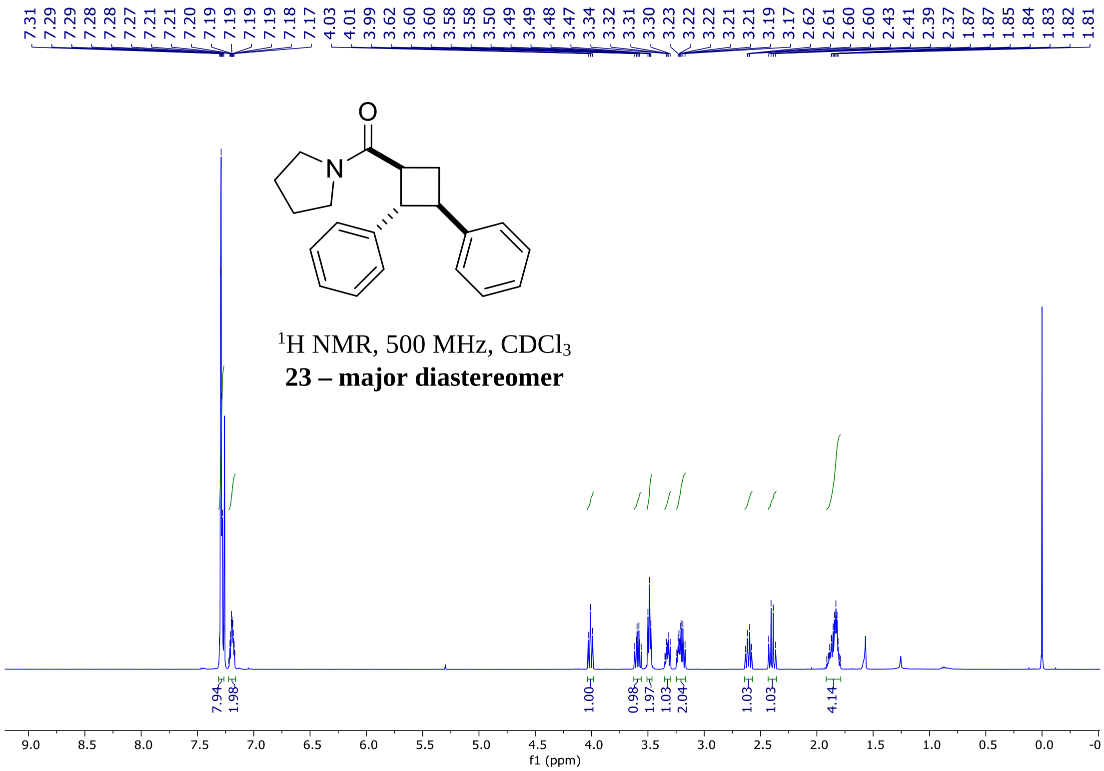

191.63
146.03 145.11 143.58 142.62 129.37 128.49 126.82 126.76 126.67 126.66 126.25 124.98 123.57
50.71 49.72 46.24 39.47 36.10 34.19
O
N
NMe
¹³C NMR, 125 MHz, CDCl₃
19 – minor diastereomer
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

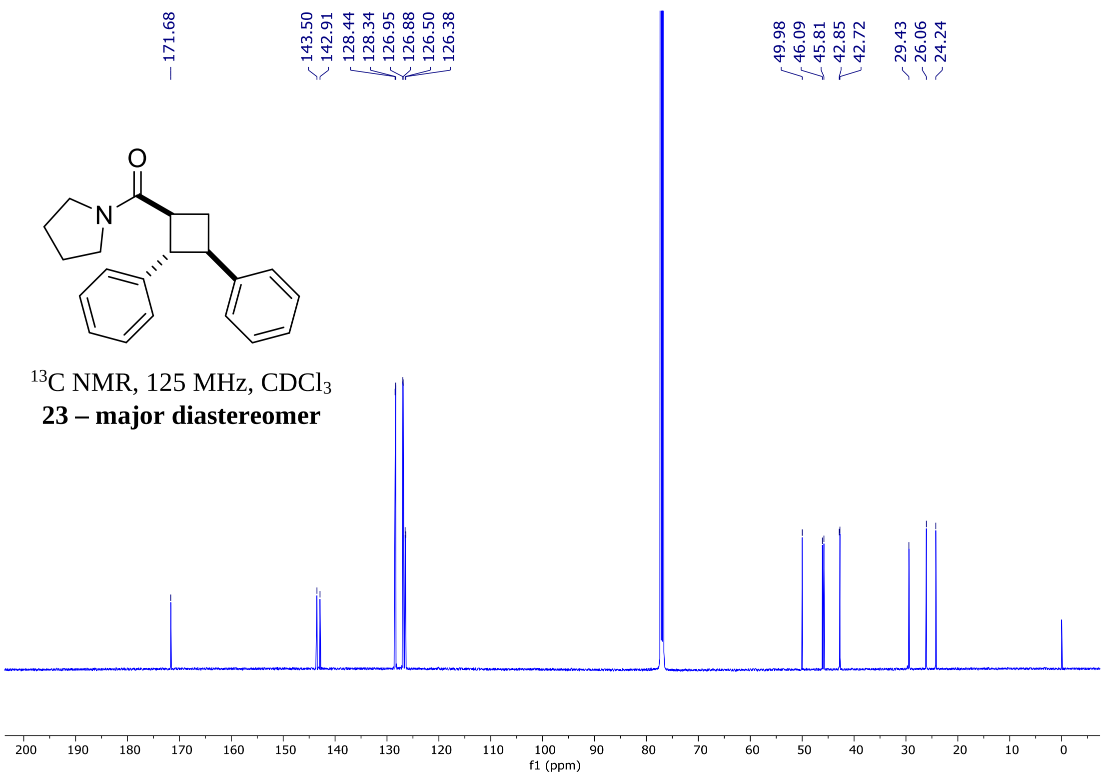

7.34 7.33 7.32 7.31 7.30 7.29 7.28 7.27 7.25 7.23 7.22 7.20 7.19
5.57
4.50 4.49 4.47 4.46 4.45 4.43 4.42 3.83 3.81 3.79 3.60 3.59 3.58 3.57 3.56 3.55 2.97 2.96 2.95 2.94 2.94 2.92 2.59 2.57 2.57 2.56 2.55 2.55 2.54 2.53 2.51 2.48
O
N
H
^{1}H NMR, 500 MHz, $CDCl_3$
22 – major diastereomer
17.76
0.92
2.10
0.98
1.00
0.99
2.07
f1 (ppm)

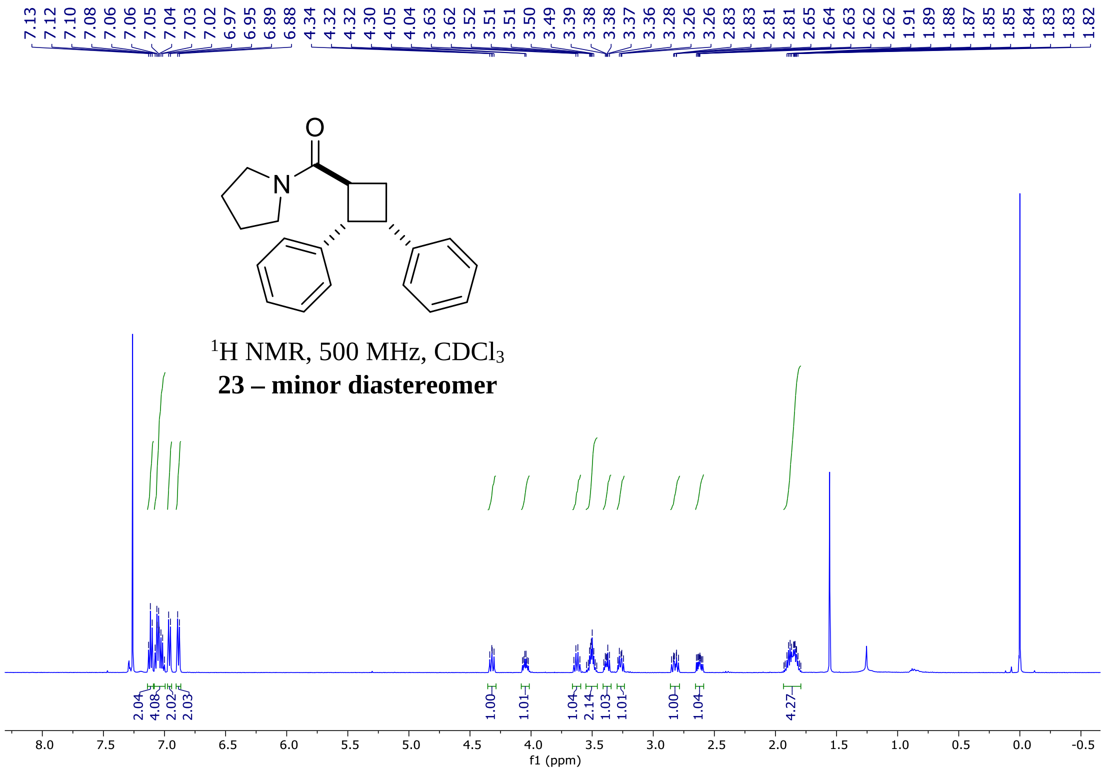

172.97
143.17 142.09 138.26 128.71 128.66 128.40 127.76 127.52 126.85 126.83 126.51
51.38 44.41 43.61 42.86
28.77
O
N
H
^{13}C NMR, 125 MHz, $CDCl_3$
22 – major diastereomer
f1 (ppm)

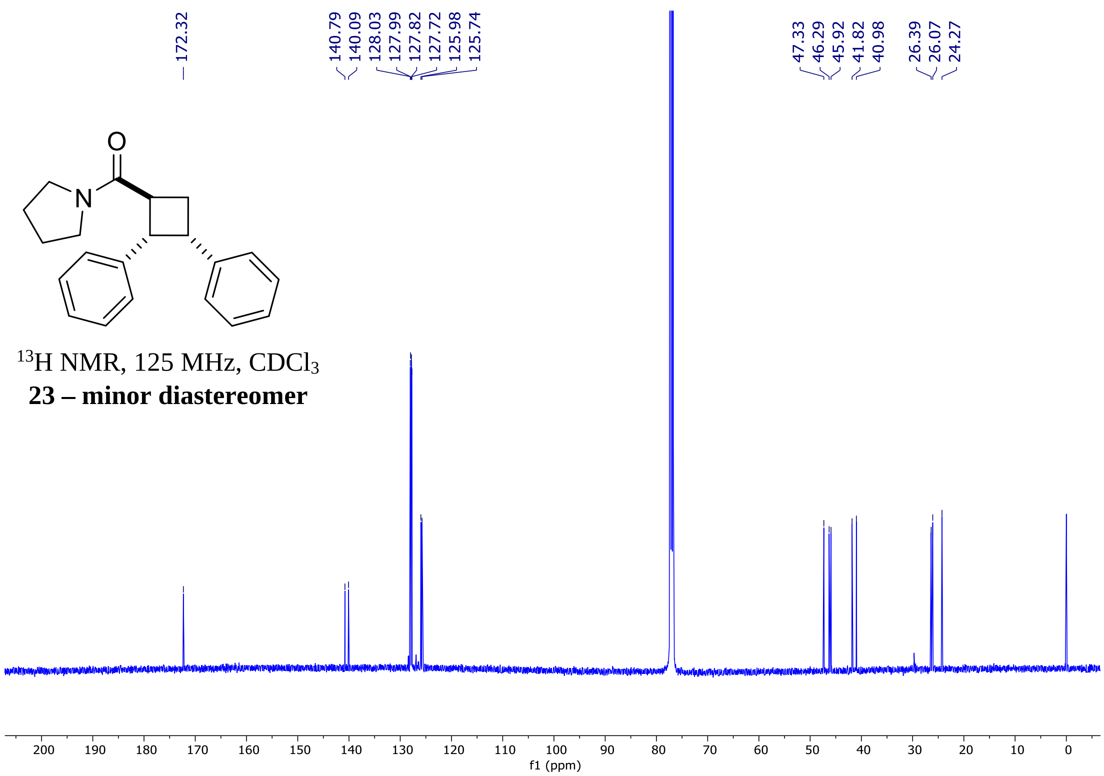

7.32 7.32 7.30 7.30 7.29 7.28 7.27 7.27 7.22 7.21 7.13 7.12 7.10 7.09 7.09 7.07 7.06 7.05 7.03 6.97 6.96 6.86 6.85 5.60 4.50 4.49 4.47 4.46 4.43 4.42 4.40 4.39 4.26 4.24 4.22 4.02 4.01 4.00 3.99 3.49 3.48 2.89 2.87 2.87 2.85 2.85 2.83 2.61 2.60 2.59 2.59 2.58 2.57 2.56
O
N
H
^{1}H NMR, 500 MHz, CDCl$_3$
22 – minor diastereomer
2.97 2.02 2.06 4.11 2.00 1.92 0.90 2.05 0.96 1.00 0.94 0.98 1.00
f1 (ppm)


173.73 140.20 139.26 138.25 128.70 128.07 127.94 127.91 127.84 127.65 127.48 126.32 125.93 48.11 43.57 42.85 42.16 26.12
O
N
H
^{13}C NMR, 125 MHz, CDCl$_3$
22 – minor diastereomer
f1 (ppm)


7.31 7.29 7.29 7.28 7.28 7.27 7.21 7.20 7.19 7.19 7.19 7.18 7.17 4.03 4.01 3.99 3.62 3.60 3.60 3.58 3.58 3.50 3.49 3.49 3.48 3.47 3.34 3.32 3.31 3.30 3.23 3.22 3.22 3.21 3.21 3.19 3.17 2.62 2.61 2.60 2.60 2.43 2.41 2.39 2.37 1.87 1.87 1.85 1.84 1.83 1.82 1.81
O
N
^{1}H NMR, 500 MHz, $CDCl_3$
23 – major diastereomer
7.94 1.98 1.00 0.98 1.97 1.03 2.04 1.03 1.03 4.14
f1 (ppm)


171.68
143.50 142.91 128.44 128.34 126.95 126.88 126.50 126.38
49.98 46.09 45.81 42.85 42.72
29.43 26.06 24.24
O
N
^{13}C NMR, 125 MHz, $CDCl_3$
23 – major diastereomer
f1 (ppm)


7.13 7.12 7.10 7.08 7.06 7.06 7.05 7.04 7.03 7.02 6.97 6.95 6.89 6.88 4.34 4.32 4.32 4.30 4.05 4.04 3.63 3.62 3.52 3.51 3.51 3.50 3.49 3.39 3.38 3.38 3.37 3.36 3.28 3.26 3.26 2.83 2.83 2.81 2.81 2.65 2.64 2.63 2.62 2.62 1.91 1.89 1.88 1.87 1.85 1.85 1.84 1.83 1.83 1.82
O
N
^{1}H NMR, 500 MHz, CDCl$_3$
23 – minor diastereomer
2.04 4.08 2.02 2.03 1.00 1.01 1.04 2.14 1.03 1.01 1.00 1.04 4.27
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


172.32
140.79 140.09 128.03 127.99 127.82 127.72 125.98 125.74
47.33 46.29 45.92 41.82 40.98 26.39 26.07 24.27
O
N
^{13}H NMR, 125 MHz, CDCl$_3$
23 – minor diastereomer
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)