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Supporting Information

α-Diazo Sulfonium Triflates: Synthesis, Structure, and Application to the Synthesis of 1-(Dialkylamino)-1,2,3-triazoles

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Supporting Information

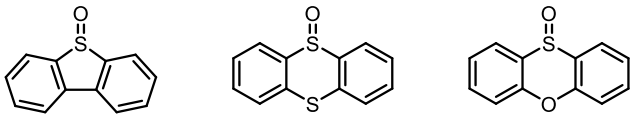
Contents

1. General methods

All dry solvents were obtained from a solvent purification system MBSPS7 from M.Braun. All reactions were carried out under nitrogen atmosphere unless stated otherwise. Ethyl diazoacetate (contains ≥13 wt. % dichloromethane) was purchased from Aldrich (E22201-20G) and used without further purification. Hydrogen peroxide solution (contains inhibitor, 30 wt. % in H_2O, ACS reagent) was purchased from Sigma-Aldrich (216763-500ML) and used without further purification. The photocatalysts $[Ru(bpy)_3][PF_6]_2$[1], $Ir(ppy)_3$,[2] $[Ir(ppy)_2(dtbbpy)][PF_6]$[3] and 4CzIPN[4] were prepared following the literature procedures. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_3CN on Bruker AVANCE III HD, Bruker AVANCE NEO 400 or Bruker AVANCE NEO 600 NMR spectrometer. ^1H NMR spectra were recorded with tetramethylsilane (δ = 0.00 ppm) or CD_3CN (δ = 1.94 ppm) as internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.16 ppm) or CD_3CN (δ = 1.32 ppm) as internal reference. High resolution mass spectra (ESI) were measured on a Bruker maXis II mass spectrometer or a Bruker micrOTOF benchtop ESI-TOF mass spectrometer. IR spectra were recorded on JASCO FT/IR-4600 Fourier Transform Infrared Spectrometer at room temperature, and the stretching frequencies are reported in wavenumbers (cm^{-1}). UV/Vis spectra were recorded on JASCO V-650 spectrophotometer. Differential scanning calorimetry (DSC) data were recorded on Mettler Toledo TGA/DSC 3^+ STAR^e System. Column chromatography was performed either on Merck 60 (40-63 μm) silica gel or by using Biotage One automated column chromatography system with CHROMABOND® Flash BT 15g (or 25g) SiOH 40-63 μm from Macherey-Nagel. Thin-layer chromatography (TLC) analysis was performed using POLYGRAM® SIL G/UV254 TLC plates from Macherey-Nagel and visualized by UV irradiation and/or phosphomolybdic acid staining. All commercially available compounds (Acros, ABCR, Alfa Aesar, Aldrich, Fluorochem, TCI) were used as received unless stated otherwise.

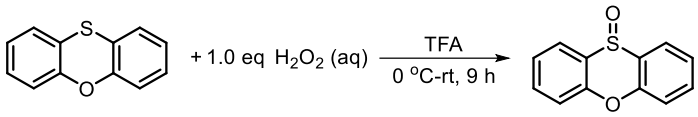
2. Synthetic procedures

2.1 Synthesis of sulfoxides



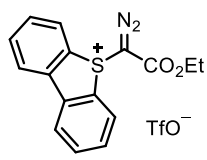
2

Dibenzo[*b*,*d*]thiophene 5-oxide (**2**)[5] and thianthrene 5-oxide[6] were prepared according to the previously reported literature procedures. Phenoxathiine 10-oxide was prepared according to the following procedure:

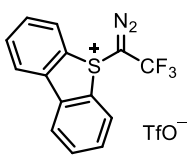


To a suspension of phenoxathiine (2.00 g, 10 mmol, 1.0 equiv.) in trifluoroacetic acid (10 mL) was added dropwise H_2O_2 (30 wt. %, 1.02 mL, 10 mmol, 1.0 equiv.) at 0 °C. After this, the ice bath was removed and the reaction was allowed to warm up to room temperature. The reaction was stirred for an additional 9 hours, then diluted with H_2O, and finally extracted with dichloromethane and dried over Na_2SO_4. Evaporation of the organic solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: dichloromethane/methanol = 50:1) to afford phenoxathiine 10-oxide (1.99 g, 92% yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94-7.91 (m, 2H), 7.65-7.59 (m, 2H), 7.45-7.35 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6, 133.9, 131.2, 125.0, 123.8, 118.9. The spectroscopic data are in agreement with those previously reported.[7]

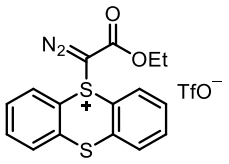
2.2 Synthesis of sulfonium salt 1



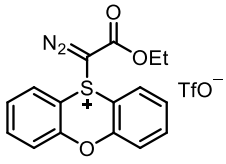
1a



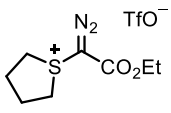
1b



1c

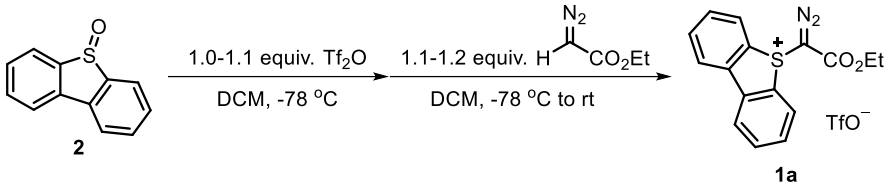


1d



1e

2.2.1 Procedure for the synthesis of 5-(1-diazo-2-ethoxy-2-oxoethyl)-5*H*-dibenzo-[*b*,*d*]-thiophen-5-ium trifluoromethanesulfonate (1a)

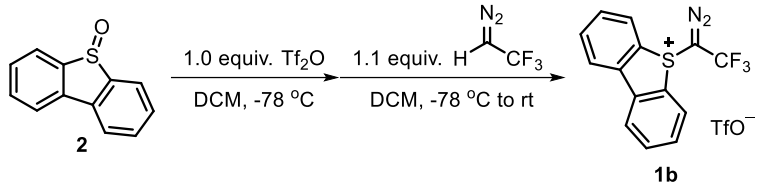


Tf_2O (1.68 mL, 10 mmol, 1.0 equiv.) was added dropwise over 30 minutes with a syringe pump to a solution of dibenzo[*b*,*d*]thiophene 5-oxide (**2**) (2.00 g, 10 mmol, 1.0 equiv.) in dry dichloromethane (100 mL) at −78 °C under N_2. After stirring the resulting mixture for one hour, a solution of ethyl diazoacetate (contains ≥13 wt. % dichloromethane, 1.33 mL, 11 mmol, 1.1 equiv.) in dichloromethane (10 mL) was added dropwise over 30 minutes by a syringe pump and the mixture was further stirred at −78 °C for one additional hour. Then, the cooling system was removed, and the resulting mixture was further stirred at room temperature for 30 minutes. The reaction was then quenched with water, extracted with dichloromethane and dried over Na_2SO_4. Evaporation of the organic solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: dichloromethane/methanol = 25:1) to afford **1a** (2.74 g, 61% yield) as a pale yellow solid.

A procedure for the synthesis of sulfonium salt **1a** without using column chromatography was also developed: Tf_2O (1.85 mL, 11 mmol, 1.1 equiv.) was added dropwise over 30 minutes by a syringe pump to a solution of dibenzo[*b*,*d*]thiophene 5-oxide (**2**) (2.00 g, 10 mmol, 1.0 equiv.) in dry dichloromethane (100 mL) at -78 °C under N_2. After stirring the resulting mixture for one additional hour, a solution of ethyl diazoacetate (contains ≥13 wt. % dichloromethane, 12 mmol, 1.2 equiv, 1.45 mL) in dichloromethane (10 mL) was added dropwise over 30 minutes using a syringe pump and the mixture was further stirred at -78 °C for two additional hours. Then, the cooling system was removed, and the resulting mixture was further stirred at room temperature for 30 minutes. Then, diethyl ether (200 mL) was added slowly to the above reaction mixture with continuous stirring. Filtration of the suspension afforded a light yellow solid, which was further washed with diethyl ether (3 × 50 mL). A suspension of the collected solid in dichloromethane (20 mL) was further subjected to sonication for 5 minutes applying an ultrasonic cleaner. Filtration of the suspension afforded **1a** as a pale yellow solid, which was further washed with dichloromethane (3 × 5 mL), and finally dried under vacuum furnishing 2.52 g (56% yield) of **1a**. ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 8.32-8.28 (m, 2H), 8.25-8.22 (m, 2H), 7.94-7.88 (m, 2H), 7.78-7.73 (m, 2H), 3.89 (q, J = 7.2 Hz, 2H), 0.86 (t, J = 7.2 Hz,

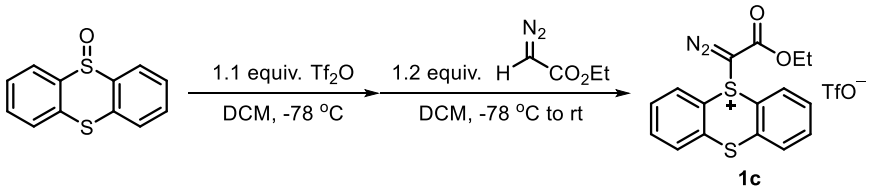
3H). ^{13}C NMR (75 MHz, acetonitrile-d_3) δ 159.1, 140.2, 135.6, 132.3, 129.6, 129.0, 124.9, 124.3, 122.1 (q, J = 318.6 Hz), 64.4, 13.9; ^{19}F NMR (282 MHz, acetonitrile-d_3) δ -79.2; IR (neat): 2155, 1712, 1448, 1254, 1225, 1167, 1149, 1078, 1029, 1008, 777, 764, 755, 732, 705, 635, 614, 572, 544, 517, 473, 420 cm^{-1}; HRMS calculated m/z for $C_{16}H_{13}N_2O_2S^+$ [M-OTf]: 297.0692, found (ESI) 297.0683.

2.2.2 Procedure for the synthesis of 5-(1-diazo-2,2,2-trifluoroethyl)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium trifluoromethanesulfonate (1b)



Tf_2O (841 μL, 5 mmol, 1.0 equiv.) was added dropwise over 30 minutes with a syringe pump to a solution of dibenzo[*b*,*d*]thiophene 5-oxide (**2**) (1.00 g, 5 mmol, 1.0 equiv.) in dry dichloromethane (40 mL) at -78 °C under N_2. After stirring the resulting mixture for additional 30 minutes, 2-diazo-1,1,1-trifluoroethane[8, 9] (17.6 mL of 0.312 M in DCM, 5.5 mmol, 1.1 equiv.) was added dropwise over 30 minutes by a syringe pump and the mixture was further stirred at –78 °C for two additional hours. Then, the cooling was removed, and the resulting mixture was further stirred at room temperature for 30 minutes. Diethyl ether (120 mL) was subsequently added to the above reaction mixture with continuous stirring. Filtration of the suspension afforded a light yellow solid, which was further washed with diethyl ether (3 × 30 mL). A suspension of the collected solid in dichloromethane (10 mL) was further subjected to sonication for 5 minutes using an ultrasonic cleaner. Filtration of the suspension afforded **1b** as an off-white solid, which was finally dried under vacuum furnishing 1.34 g (61% yield) of **1b**. ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 8.43-8.40 (m, 2H), 8.27-8.24 (m, 2H), 7.98-7.93 (m, 2H), 7.84-7.78 (m, 2H); ^{13}C NMR (75 MHz, acetonitrile-d_3) δ 139.4, 136.4, 132.8, 129.6, 128.8, 125.6, 123.1(q, J = 272.1 Hz), 122.1 (q, J = 318.8 Hz); ^{19}F NMR (282 MHz, acetonitrile-d_3) δ -55.3, -79.3; IR (neat): 3086, 3070, 2200, 2143, 1447, 1298, 1258, 1221, 1130, 1007, 758, 627, 509, 418 cm^{-1}; HRMS calculated m/z for $C_{14}H_8F_3N_2S^+$ [M-OTf]: 293.0355, found (ESI) 293.0356.

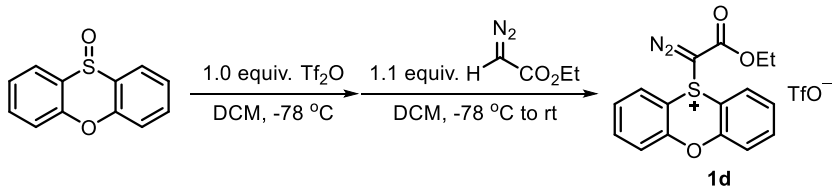
2.2.3 Procedure for the synthesis of 5-(1-diazo-2-ethoxy-2-oxoethyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (1c)



1c

Tf_2O (925 μL, 5.5 mmol, 1.1 equiv.) was added dropwise over 30 minutes with a syringe pump to a solution of thianthrene 5-oxide (1.16 g, 5 mmol, 1.0 equiv.) in dry dichloromethane (40 mL) at –78 °C under N_2. After stirring the resulting mixture for one additional hour, a solution of ethyl diazoacetate (contains ≥13 wt. % dichloromethane, 725 μL, 6 mmol, 1.2 equiv.) in dichloromethane (4 mL) was added dropwise over 30 minutes using a syringe pump and the mixture was further stirred at –78 °C for two additional hours. Then, the cooling was removed, and the resulting mixture was further stirred at room temperature for 30 minutes. The reaction was quenched with water, extracted with dichloromethane and dried over Na_2SO_4. Evaporation of the organic solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: dichloromethane/methanol = 20:1) to afford **1c** (772 mg, 32% yield) as a yellow solid. ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 8.21-8.17 (m, 2H), 8.00-7.96 (m, 2H), 7.88-7.82 (m, 2H), 7.78-7.72 (m, 2H), 4.28 (q, J = 7.1 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, acetonitrile-d_3) δ 160.6, 137.1, 136.0, 134.4, 131.6, 130.9, 122.1 (q, J = 320.8 Hz), 118.4. ^{19}F NMR (282 MHz, acetonitrile-d_3) δ -79.3; IR (neat): 3078, 2998, 2107, 1739, 1692, 1450, 1297, 1268, 1258, 1236, 1225, 1144, 1028, 754, 733, 633, 515, 474 cm^{-1}; HRMS calculated *m/z* for $C_{16}H_{13}N_2O_2S_2^+$ [M-OTf]: 329.0413, found (ESI) 329.0414.

2.2.4 Procedure for the synthesis of 10-(1-diazo-2-ethoxy-2-oxoethyl)-10*H*-phenoxathiin-10-ium trifluoromethanesulfonate (1d)

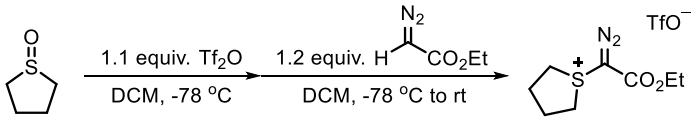


1d

Tf_2O (841 μL, 5.0 mmol, 1.0 equiv.) was added dropwise within 30 minutes with a syringe pump to a solution of phenoxathiine 10-oxide (1.08 g, 5.0 mmol, 1.0 equiv.) in dry dichloromethane (40 mL) at –78 °C under N_2. After stirring the resulting mixture for one

additional hour, a solution of ethyl diazoacetate (contains ≥13 wt. % dichloromethane, 665 μL, 5.5 mmol, 1.1 equiv.) in dichloromethane (5 mL) was added dropwise within 30 minutes using a syringe pump and the mixture was further stirred at –78 °C for three additional hours. Then, the cooling was removed, and the resulting mixture was further stirred at room temperature for 30 minutes. The reaction was quenched with water, extracted with dichloromethane and dried over Na_2SO_4. Evaporation of the organic solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: dichloromethane/methanol = 20:1) to afford **1d** (1.52 g, 66% yield) as an off-white solid. ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 8.18-8.15 (m, 2H), 7.89-7.83 (m, 2H), 7.59-7.51 (m, 4H), 4.05 (q, J = 7.1 Hz, 2H), 1.08 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, acetonitrile-d_3) δ 159.8, 153.3, 137.9, 132.1, 127.8, 122.1 (q, J = 318.9 Hz), 120.4, 102.8, 64.7, 14.1; ^{19}F NMR (282 MHz, acetonitrile-d_3) δ -79.2; IR (neat): 3084, 2153, 1712, 1471, 1255, 1234, 1221, 1153, 1029, 786, 760, 734, 632, 515 cm^{-1}; HRMS calculated m/z for $C_{16}H_{13}N_2O_3S^+$ [M-OTf]: 313.0641, found (ESI) 313.0644.

2.2.5 Procedure for the synthesis of 1-(1-diazo-2-ethoxy-2-oxoethyl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (1e)

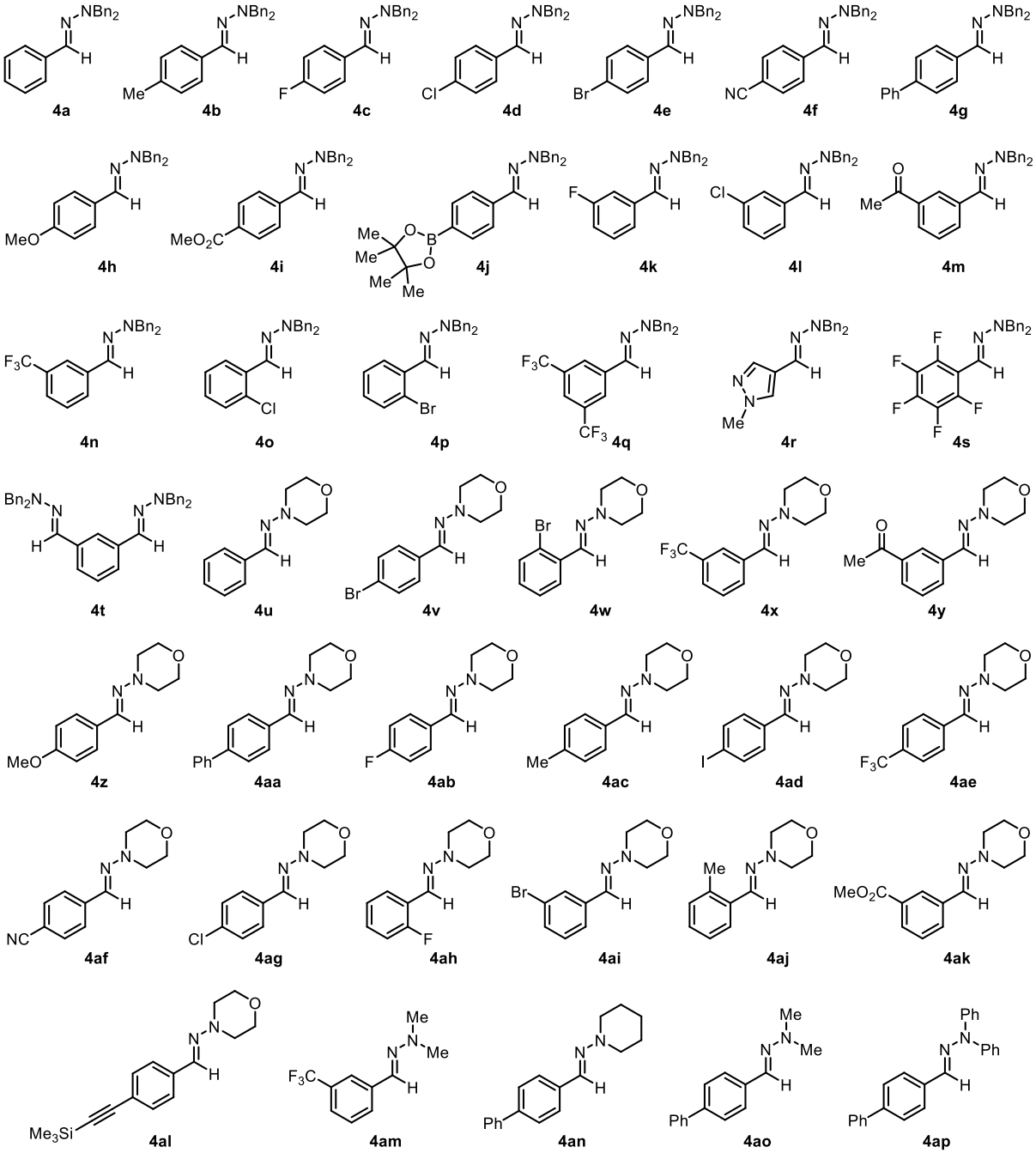


1e

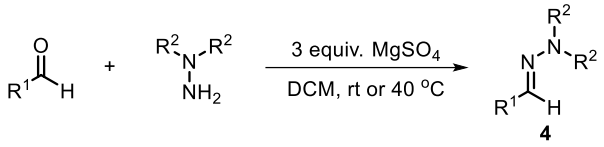
Tf_2O (925 μL, 5.5 mmol, 1.1 equiv.) was added dropwise over 30 minutes with a syringe pump to a solution of tetrahydrothiophene 1-oxide (450 μL, 5.0 mmol, 1.0 equiv.) in dry dichloromethane (40 mL) at -78 °C under N_2. After stirring the resulting mixture for one additional hour, a solution of ethyl diazoacetate (contains ≥13 wt. % dichloromethane, 725 μL, 6.0 mmol, 1.2 equiv.) in dichloromethane (5 mL) was added dropwise over 30 minutes using a syringe pump and the mixture was further stirred at –78 °C for four additional hours. Then, the cooling was removed, and the resulting mixture was further stirred at room temperature for 30 minutes. Then, diethyl ether (40 mL) was added slowly to the above reaction mixture with continuous stirring. Filtration of the suspension afforded a white solid, which was further washed with diethyl ether (3 × 10 mL), and finally dried under vacuum furnishing 908 mg (52% yield) of **1e**. ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 4.32 (q, J = 7.1 Hz, 2H), 3.89-3.80 (m, 2H), 3.72-3.63 (m, 2H), 2.57-2.45 (m, 2H), 2.23-2.09 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, acetonitrile-d_3) δ 161.0, 122.1 (q, J = 320.8 Hz), 64.7, 47.4, 29.6, 14.4; ^{19}F NMR (282 MHz, acetonitrile-d_3) δ -79.3; IR (neat): 3006, 2994, 2955, 2116, 1703, 1466,

1452, 1426, 1396, 1370, 1290, 1268, 1250, 1223, 1207, 1167, 1145, 1096, 1081, 1027, 954, 883, 860, 801, 757, 736, 634, 574, 536, 513, 405 cm^{-1}; HRMS calculated *m*/*z* for $C_8H_{13}N_2O_2S^+$ [M-OTf]: 201.0692, found (ESI) 201.0691.

2.3 Preparation of aldehyde-derived hydrazones 4



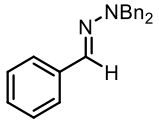
Hydrazones **4ab,**[10] **4ac**[10] and **4ao**[11] were prepared according to the previously reported literature procedures. The other hydrazones were synthesized by modified procedures of the reported method, which are described below.[12]



4

To a solution of aldehyde (1.0 equiv.) in dry DCM was added hydrazine (1.0-1.1 equiv.) and anhydrous $MgSO_4$ (3 equiv.). The resulting reaction mixture was stirred at room temperature or 40 °C with TLC monitoring until the reaction was completed. Then, the reaction mixture was filtered through a pad of celite. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel to afford hydrazones **4**.

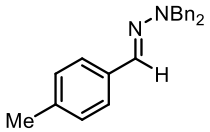
2.3.1 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-benzylidenehydrazine (4a)



4a

A mixture of benzaldehyde (203 μL, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 °C for 23 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4a** in 98% yield (588 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.32-7.17 (m, 14H), 4.52 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 137.1, 132.0, 128.7, 128.5, 127.8, 127.3, 125.7, 58.0. The spectroscopic data are in agreement with those previously reported.[13]

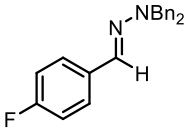
2.3.2 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-(4-methylbenzylidene)-hydrazine (4b)



4b

A mixture of 4-methylbenzaldehyde (236 μL, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 °C for 16 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4b** in 74% yield (463 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.33-7.20 (m, 10H), 7.16 (s, 1H), 7.10-7.08 (m, 2H), 4.48 (s, 4H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 137.2, 134.3, 132.5, 129.3, 128.6, 127.8, 127.3, 125.7, 58.0, 21.4. The spectroscopic data are in agreement with those previously reported.[14]

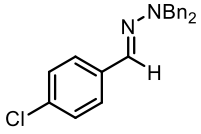
2.3.3 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-(4-fluorobenzylidene)-hydrazine (4c)



4c

A mixture of 4-fluorobenzaldehyde (215 μL, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 °C for 20 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4c** in 99% yield (630 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47-7.42 (m, 2H), 7.34-7.21 (m, 10H), 7.13 (s, 1H), 6.99-6.93 (m, 2H), 4.50 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3 (d, $^1J_{C\text{-}F}$ = 246.2 Hz), 137.7, 133.3 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 130.9, 128.7, 127.8, 127.4, 127.1 (d, $^3J_{C\text{-}F}$ = 7.9 Hz), 115.5 (d, $^2J_{C\text{-}F}$ = 21.7 Hz), 58.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ 114.9; IR (neat): 3030, 2974, 2829, 1739, 1603, 1574, 1506, 1495, 1452, 1433, 1365, 1346, 1319, 1260, 1227, 1215, 1116, 1092, 1072, 1028, 969, 953, 912, 890, 861, 841, 827, 800, 793, 748, 732, 700, 632, 621, 606, 570, 538, 528, 464 cm^{-1}; HRMS calculated *m*/*z* for $C_{21}H_{20}FN_2^+$ $[M+H]^+$: 319.1605, found (ESI) 319.1605.

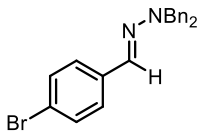
2.3.4 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-(4-chlorobenzylidene)-hydrazine (4d)



4d

A mixture of 4-chlorobenzaldehyde (281 mg, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 °C for 20 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4d** in 44% yield (295 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.38 (m, 2H), 7.34-7.21 (m, 12H), 7.09 (s, 1H), 4.51 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 135.7, 132.7, 130.3, 128.73, 128.66, 127.7, 127.4, 126.8, 58.0; IR (neat): 3030, 2859, 1581, 1557, 1491, 1452, 1342, 1321, 1255, 1115, 1098, 1088, 1072, 970, 946, 884, 833, 820, 799, 751, 732, 694, 620, 607, 550, 520, 506, 454 cm^{-1}; HRMS calculated *m*/*z* for $C_{21}H_{20}ClN_2^+$ $[M+H]^+$: 335.1310, found (ESI) 335.1310.

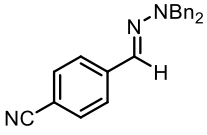
2.3.5 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-(4-bromobenzylidene)-hydrazine (4e)



4e

A mixture of 4-bromobenzaldehyde (637 mg, 3 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (555 mg, 3 mmol, 1.0 equiv.), $MgSO_4$ (1.08 g, 9 mmol, 3 equiv.) and DCM (30 mL) was stirred at room temperature for 24 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4e** in 80% yield (909 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.23 (m, 14H), 7.07 (s, 1H), 4.51 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 136.1, 131.6, 130.2, 128.7, 127.7, 127.4, 127.1, 120.8, 58.0; IR (neat): 3030, 2963, 2853, 1739, 1587, 1487, 1451, 1344, 1114, 1097, 1069, 970, 946, 883, 832, 818, 800, 751, 732, 694, 677, 607, 547, 516, 449 cm^{-1}; HRMS calculated *m*/*z* for $C_{21}H_{20}BrN_2^+$ $[M+H]^+$: 379.0804, found (ESI) 379.0801.

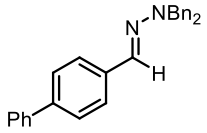
2.3.6 Synthesis and characterization of (*E*)-4-((2,2-dibenzylhydrazineylidene)methyl)-benzonitrile (4f)



4f

A mixture of 4-formylbenzonitrile (262 mg, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 °C for 16 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) afforded **4f** in 99% yield (643 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.50 (m, 4H), 7.33-7.23 (m, 10H), 7.06 (s, 1H), 4.59 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7, 136.9, 132.3, 128.8, 128.2, 127.61, 127.57, 125.6, 119.5, 109.5, 58.0; IR (neat): 3027, 2933, 2218, 1739, 1573, 1538, 1493, 1452, 1379, 1345, 1325, 1229, 1217, 1126, 1105, 1076, 878, 833, 807, 760, 742, 732, 698, 656, 643, 578, 556, 544, 529, 466, 425 cm^{-1}; HRMS calculated *m*/*z* for $C_{22}H_{20}N_3^+$ $[M+H]^+$: 326.1652, found (ESI) 326.1652.

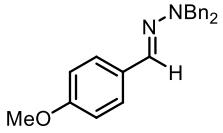
2.3.7 Synthesis and characterization of (*E*)-2-([1,1'-biphenyl]-4-ylmethylene)-1,1-dibenzylhydrazine (4g)



4g

A mixture of [1,1'-biphenyl]-4-carbaldehyde (364 mg, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 ºC for 23 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4g** in 98% yield (738 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.51 (m, 6H), 7.44-7.38 (m, 2H), 7.34-7.20 (m, 12H), 4.54 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0, 140.0, 137.7, 136.2, 131.4, 128.9, 128.7, 127.8, 127.35, 127.26, 127.0, 126.1, 58.0; IR (neat): 3057, 3030, 2853, 1739, 1577, 1488, 1449, 1434, 1345, 1317, 1262, 1103, 1070, 1028, 971, 951, 891, 857, 838, 796, 765, 755, 737, 728, 721, 699, 690, 642, 606, 554, 545, 492, 452 cm^{-1}; HRMS calculated m/z for $C_{27}H_{25}N_2^+$ $[M+H]^+$: 377.2012, found (ESI) 377.2013.

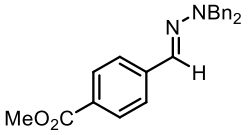
2.3.8 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-(4-methoxybenzylidene)-hydrazine (4h)



4h

A mixture of 4-methoxybenzaldehyde (243 μL, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 ºC for 22 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) afforded **4h** in 98% yield (648 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 7.34-7.21 (m, 10H), 7.17 (s, 1H), 6.86-6.81 (m, 2H), 4.47 (s, 4H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 138.0, 132.6, 130.0, 128.6, 127.9, 127.2, 127.0, 114.0, 58.2, 55.4; IR (neat): 3030, 2838, 1606, 1511, 1493, 1453, 1348, 1308, 1253, 1110, 1097, 1069, 1028, 966, 956, 893, 822, 811, 801, 746, 731, 694, 632, 607, 528, 461 cm^{-1}; HRMS calculated m/z for $C_{22}H_{23}N_2O^+$ $[M+H]^+$: 331.1805, found (ESI) 331.1803.

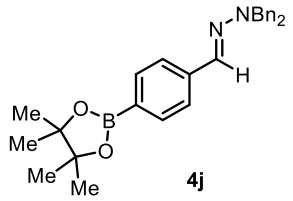
2.3.9 Synthesis and characterization of methyl (*E*)-4-[(2,2-dibenzylhydrazineylidene)-methyl]benzoate (4i)



4i

A mixture of methyl 4-formylbenzoate (328 mg, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 ºC for 16 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) afforded **4i** in 97% yield (694 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.34-7.22 (m, 10H), 7.13 (s, 1H), 4.57 (s, 4H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 141.6, 137.2, 129.9, 129.6, 128.8, 128.2, 127.6, 127.5, 125.2, 58.0, 52.1; IR (neat): 3030, 2832, 1721, 1453, 1346, 1273, 1256, 1107, 1098, 1070, 970, 899, 884, 819, 801, 752, 733, 694, 620, 608, 551, 519, 454 cm^{-1}; HRMS calculated *m*/*z* for $C_{23}H_{23}N_2O_2^+$ $[M+H]^+$: 359.1754, found (ESI) 359.1754.

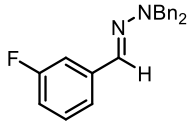
2.3.10 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)hydrazine (4j)



4j

A mixture of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (464 mg, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 ºC for 18 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) afforded **4j** in 81% yield (691 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.32-7.24 (m, 10H), 7.15 (s, 1H), 4.53 (s, 4H), 1.33 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.8, 137.6, 135.1, 131.5, 128.7, 127.8, 127.4, 124.9, 83.8, 58.0, 25.0; IR (neat): 2971, 2840, 1583, 1397, 1346, 1317, 1271, 1153, 1140, 1118, 1096, 1085, 1072, 972, 958, 894, 856, 832, 795, 741, 702, 662, 654, 607, 549, 456 cm^{-1}; HRMS calculated *m*/*z* for $C_{27}H_{32}BN_2O_2^+$ $[M+H]^+$: 427.2551, found (ESI) 427.2557.

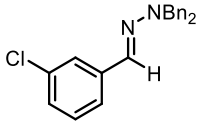
2.3.11 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-(3-fluorobenzylidene)-hydrazine (4k)



4k

A mixture of 3-fluorobenzaldehyde (212 μL, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 °C for 16 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4k** in 98% yield (627 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.15 (m, 13H), 7.09 (s, 1H), 6.88-6.81 (m, 1H), 4.53 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3 (d, $^1J_{C\text{-}F}$ = 244.4 Hz), 139.6 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 137.4, 130.0 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 129.9 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 128.8, 127.7, 127.4, 121.6 (d, $^4J_{C\text{-}F}$ = 2.6 Hz), 113.9 (d, $^2J_{C\text{-}F}$ = 21.7 Hz), 111.6 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 58.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.7; IR (neat): 2835, 1591, 1565, 1493, 1445, 1429, 1346, 1321, 1260, 1154, 1138, 1108, 1069, 975, 969, 951, 905, 882, 865, 778, 747, 735, 699, 685, 650, 609, 476, 458, 422 cm^{-1}; HRMS calculated *m*/*z* for $C_{21}H_{20}FN_2^+$ $[M+H]^+$: 319.1605, found (ESI) 319.1607.

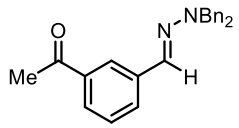
2.3.12 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-(3-chlorobenzylidene)-hydrazine (4l)



4l

A mixture of 3-chlorobenzaldehyde (227 μL, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 °C for 18 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4l** in 99% yield (663 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.51 (m, 1H), 7.34-7.10 (m, 13H), 7.05 (s, 1H), 4.53 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 137.4, 134.6, 129.71, 129.67, 128.8, 127.7, 127.4, 127.0, 125.3, 123.8, 58.0; IR (neat): 3033, 2843, 1583, 1494, 1454, 1345, 1252, 1105, 1071, 968, 957, 902, 878, 782, 755, 736, 713, 693, 683, 652, 608, 547, 472, 450, 437 cm^{-1}; HRMS calculated *m*/*z* for $C_{21}H_{20}ClN_2^+$ $[M+H]^+$: 335.1310, found (ESI) 335.1308.

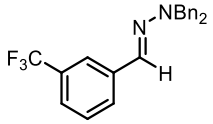
2.3.13 Synthesis and characterization of (*E*)-1-{3-[(2,2-dibenzylhydrazineylidene)-methyl]phenyl}ethan-1-one (4m)



4m

A mixture of 3-acetylbenzaldehyde (296 mg, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 °C for 15 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) afforded **4m** in 96% yield (659 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01-8.00 (m, 1H), 7.78-7.72 (m, 2H), 7.40-7.24 (m, 11H), 7.18 (s, 1H), 4.56 (s, 4H), 2.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.5, 137.7, 137.5, 137.4, 130.2, 129.8, 128.8, 127.7, 127.5, 126.9, 125.6, 58.1, 26.9; IR (neat): 3057, 3027, 2998, 2968, 2939, 1739, 1674, 1560, 1359, 1274, 1230, 1217, 1200, 937, 753, 695, 603, 587, 551 cm^{-1}; HRMS calculated *m*/*z* for $C_{23}H_{23}N_2O^+$ $[M+H]^+$: 343.1805, found (ESI) 343.1807.

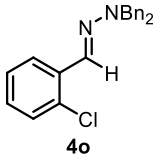
2.3.14 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-[3-(trifluoromethyl)benzylidene]hydrazine (4h)



4n

A mixture of 3-(trifluoromethyl)benzaldehyde (268 μL, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 °C for 16 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4n** in 73% yield (540 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.63 (d, J = 7.3 Hz, 1H), 7.41-7.21 (m, 12H), 7.13 (s, 1H), 4.56 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 137.3, 130.9 (q, $^2J_{C\text{-}F}$ = 32.1 Hz), 129.4, 128.9, 128.8, 128.6, 127.7, 127.5, 124.4 (q, $^1J_{C\text{-}F}$ = 270.7 Hz), 123.5 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 122.2 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 58.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.7; IR (neat): 3033, 2974, 2933, 1737, 1557, 1343, 1326, 1215, 1149, 1140, 1109, 1094, 1068, 1028, 977, 902, 799, 746, 729, 695, 670, 651, 627, 553, 456 cm^{-1}; HRMS calculated *m*/*z* for $C_{22}H_{20}F_3N_2^+$ $[M+H]^+$: 369.1573, found (ESI) 369.1574.

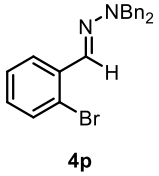
2.3.15 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-(2-chlorobenzylidene)-hydrazine (4o)



4o

A mixture of 2-chlorobenzaldehyde (225 μL, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 °C for 16 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4o** in 99% yield (665 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98-7.94 (m, 1H), 7.54 (s, 1H), 7.35-7.17 (m, 12H), 7.11-7.06 (m, 1H), 4.56 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 134.3, 132.3, 129.6, 128.7, 128.1, 127.93, 127.88, 127.4, 126.8, 125.8, 58.2; IR (neat): 3025, 2968, 1739, 1574, 1548, 1452, 1439, 1365, 1353, 1228, 1217, 1205, 1029, 972, 749, 731, 694, 456 cm^{-1}; HRMS calculated *m*/*z* for $C_{21}H_{20}ClN_2^+$ $[M+H]^+$: 335.1310, found (ESI) 335.1312.

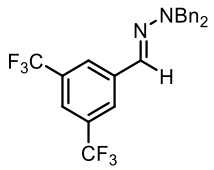
2.3.16 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-(2-bromobenzylidene)-hydrazine (4p)



4p

A mixture of 2-bromobenzaldehyde (233 μL, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 °C for 16 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4p** in 96% yield (727 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.48 (s, 1H), 7.42 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.36-7.21 (m, 11H), 7.04-6.98 (m, 1H), 4.56 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 135.8, 132.9, 130.8, 128.7, 128.3, 127.9, 127.5, 127.4, 126.2, 122.7, 58.4; IR (neat): 3057, 3030, 2936, 1741, 1568, 1547, 1128, 1018, 874, 753, 731, 701, 695, 649, 611, 555, 451, 420 cm^{-1}; HRMS calculated *m*/*z* for $C_{21}H_{20}BrN_2^+$ $[M+H]^+$: 379.0804, found (ESI) 379.0801.

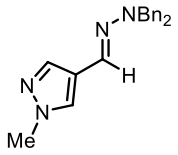
2.3.17 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-[3,5-bis(trifluoromethyl)-benzylidene]hydrazine (4q)



4q

A mixture of 3,5-bis(trifluoromethyl)benzaldehyde (378 mg, 1.56 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (365 mg, 1.72 mmol, 1.1 equiv.), $MgSO_4$ (563 mg, 4.68 mmol, 3 equiv.) and DCM (20 mL) was stirred at room temperature for 20 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4q** in 84% yield (571 mg) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.62 (s, 1H), 7.36-7.23 (m, 10H), 7.10 (s, 1H), 4.61 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.5, 136.8, 131.8 (q, J = 33.2 Hz), 128.9, 127.7, 127.6, 126.9, 125.0 (q, J = 3.9 Hz), 123.7 (q, J = 272.7 Hz), 119.9 (p, J = 3.8 Hz), 58.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.9; IR (neat): 3064, 3033, 1561, 1453, 1340, 1274, 1168, 1122, 1074, 889, 843, 730, 696, 681, 639 cm^{-1}; HRMS calculated *m*/*z* for $C_{23}H_{19}F_6N_2^+$ $[M+H]^+$: 437.1447, found (ESI) 437.1447.

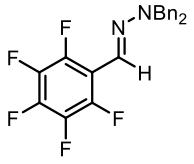
2.3.18 Synthesis and characterization of (*E*)-4-[(2,2-dibenzylhydrazineylidene)methyl]-1-methyl-1*H*-pyrazole (4r)



4r

A mixture of 1-methyl-1*H*-pyrazole-4-carbaldehyde (253 mg, 2.3 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (537 mg, 2.53 mmol, 1.1 equiv.), $MgSO_4$ (831 mg, 6.9 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 ºC for 16 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 2:1) afforded **4r** in 99% yield (695 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.44 (s, 1H), 7.34-7.21 (m, 10H), 7.11 (s, 1H), 4.40 (s, 4H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 137.4, 128.6, 127.8, 127.5, 127.2, 126.4, 120.9, 58.2, 39.1; IR (neat): 3030, 2960, 2921, 2840, 1739, 1450, 1171, 1063, 965, 816, 807, 756, 697, 660, 607, 542 cm^{-1}; HRMS calculated *m*/*z* for $C_{19}H_{21}N_4^+$ $[M+H]^+$: 305.1761, found (ESI) 305.1762.

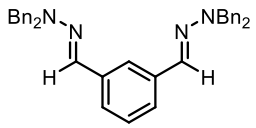
2.3.19 Synthesis and characterization of (*E*)-1,1-dibenzyl-2-[(perfluorophenyl)methylene]hydrazine (4s)



4s

A mixture of 2,3,4,5,6-pentafluorobenzaldehyde (247 μL, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (467 mg, 2.2 mmol, 1.1 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at 40 ºC for 16 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4s** in 91% yield (710 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.24 (m, 10H), 6.98 (s, 1H), 4.59 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6-142.8 [m, Ar*C*(2,6)F], 139.3 [dtt, *J* = 252.6, 13.7, 4.7 Hz, Ar*C*(4)F], 139.3-136.4 [m, Ar*C*(3,5)F], 136.6, 128.9, 127.7, 117.4 [q, *J* = 3.1 Hz], 112.5 [td, *J* = 12.1, 4.1 Hz, Ar*C*(1)], 57.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ -144.9 [m, Ar(2,6)*F*], -158.5 [t, *J* = 20.8 Hz, Ar(4)*F*], -163.7 [m, Ar(3,5)*F*]; IR (neat): 3025, 2968, 1739, 1559, 1519, 1488, 1451, 1417, 1385, 1367, 1351, 1339, 1217, 1170, 1156, 1029, 1011, 957, 879, 854, 776, 732, 705, 694, 630, 576, 538, 460, 432 cm^{-1}; HRMS calculated *m*/*z* for $C_{21}H_{16}F_5N_2^+$ $[M+H]^+$: 391.1228, found (ESI) 391.1229.

2.3.20 Synthesis and characterization of 1,3-bis[(*E*)-(2,2-dibenzylhydrazineylidene)-methyl]benzene (4t)

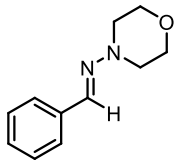


4t

A mixture of isophthalaldehyde (268 mg, 2 mmol, 1.0 equiv.), 1,1-dibenzylhydrazine (892 mg, 4.2 mmol, 2.1 equiv.), $MgSO_4$ (1.44 g, 12 mmol, 6 equiv.) and DCM (20 mL) was stirred at 40 ºC for 20 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4t** in 99% yield (1.03 g) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.54 (m, 1H), 7.40-7.37 (m, 2H), 7.33-7.19 (m, 21H), 7.15 (s, 2H), 4.50 (s, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.7, 137.2, 132.0, 128.7, 127.7, 127.3, 124.5, 123.2, 58.0; IR (neat): 3057, 3025, 2936, 2845, 1591, 1563, 1494, 1453, 1442, 1352, 1342, 1326, 1312, 1287, 1273, 1260, 1118, 1107, 1070, 1029, 978, 971, 951, 914, 903, 896, 873, 810, 793, 757, 730, 694, 669, 653, 622, 607, 546, 466, 455, 433 cm^{-1}; HRMS calculated *m*/*z* for $C_{36}H_{35}N_4^+$ $[M+H]^+$: 523.2856,

found (ESI) 523.2857.

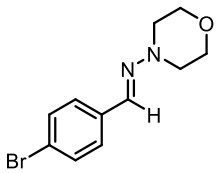
2.3.21 Synthesis and characterization of (*E*)-*N*-morpholino-1-phenylmethanimine (4u)



4u

A mixture of benzaldehyde (508 μL, 5 mmol, 1.0 equiv.), morpholin-4-amine (482 μL, 5 mmol, 1.0 equiv.), $MgSO_4$ (1.81 g, 15 mmol, 3 equiv.) and DCM (25 mL) was stirred at room temperature for 48 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded **4u** in 68% yield (643 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.58 (m, 3H), 7.37-7.25 (m, 3H), 3.90-3.86 (m, 4H), 3.19-3.15 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.4, 136.1, 128.7, 128.5, 126.3, 66.6, 52.0. The spectroscopic data are in agreement with those previously reported.[10]

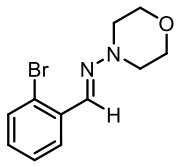
2.3.22 Synthesis and characterization of (*E*)-1-(4-bromophenyl)-*N*-morpholinomethanimine (4v)



4v

A mixture of 4-bromobenzaldehyde (555 mg, 3 mmol, 1.0 equiv.), morpholin-4-amine (322 mg, 3.15 mmol, 1.05 equiv.), $MgSO_4$ (1.08 g, 9 mmol, 3 equiv.) and DCM (15 mL) was stirred at room temperature for 24 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded **4v** in 97% yield (785 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.46 (m, 4H), 3.90-3.86 (m, 4H), 3.19-3.15 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.1, 134.6, 131.8, 127.7, 122.2, 66.5, 51.8. The spectroscopic data are in agreement with those previously reported.[10]

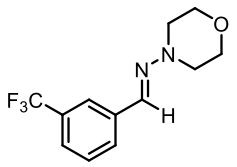
2.3.23 Synthesis and characterization of (*E*)-1-(2-bromophenyl)-*N*-morpholinomethanimine (4w)



4w

A mixture of 2-bromobenzaldehyde (370 mg, 2 mmol, 1.0 equiv.), morpholin-4-amine (214 mg, 2.1 mmol, 1.05 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (20 mL) was stirred at room temperature for 24 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded **4w** in 89% yield (477 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.86 (s, 1H), 7.51 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.30-7.24 (m, 1H), 7.11 (td, *J* = 7.7, 1.8 Hz, 1H), 3.90-3.86 (m, 4H), 3.23-3.20 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.8, 134.7, 132.9, 129.4, 127.5, 126.8, 123.4, 66.5, 51.8. The spectroscopic data are in agreement with those previously reported.[10]

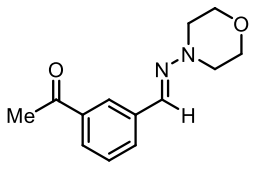
2.3.24 Synthesis and characterization of (*E*)-*N*-morpholino-1-(3-(trifluoromethyl)-phenyl)methanimine (4x)



4x

A mixture of 3-(trifluoromethyl)benzaldehyde (756 mg, 4.34 mmol, 1.0 equiv.), morpholin-4-amine (443 mg, 4.34 mmol, 1.0 equiv.), $MgSO_4$ (1.57 g, 13.0 mmol, 3 equiv.) and DCM (20 mL) was stirred at room temperature for 24 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded **4x** in 75% yield (841 mg) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87-7.86 (m, 1H), 7.76-7.73 (m, 1H), 7.56 (s, 1H), 7.53-7.42 (m, 2H), 3.90-3.87 (m, 4H), 3.22-3.19 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 133.8, 131.1 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 129.3 (q, $^4J_{C\text{-}F}$ = 1.5 Hz), 129.1, 124.7 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 122.8 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 66.5, 51.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.8. The spectroscopic data are in agreement with those previously reported.[15]

2.3.25 Synthesis and characterization of (*E*)-1-{3-[(morpholinoimino)methyl]-phenyl}ethan-1-one (4y)

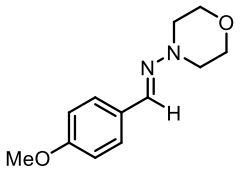


4y

A mixture of 3-acetylbenzaldehyde (296 mg, 2 mmol, 1.0 equiv.), morpholin-4-amine (204 mg, 2 mmol, 1.0 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (15 mL) was stirred at room temperature for 24 h. Column chromatography on silica gel (eluent: hexane to

hexane/ethyl acetate = 3:1) afforded **4y** in 93% yield (432 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16-8.14 (m, 1H), 7.87-7.79 (m, 2H), 7.60 (s, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 3.90-3.87 (m, 4H), 3.22-3.18 (m, 4H), 2.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1, 137.5, 136.6, 134.5, 130.4, 128.9, 127.9, 126.1, 66.4, 51.7, 26.8; IR (neat): 2971, 2867, 1738, 1676, 1569, 1451, 1427, 1359, 1271, 1227, 1216, 1199, 1114, 1096, 1069, 1004, 917, 865, 806, 800, 690, 668, 588, 520 cm^{-1}; HRMS calculated *m/z* for $C_{13}H_{17}N_2O_2^+$ $[M+H]^+$: 233.1285, found (ESI) 233.1286.

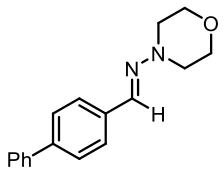
2.3.26 Synthesis and characterization of (*E*)-1-(4-methoxyphenyl)-*N*-morpholino-methanimine (4z)



4z

A mixture of 4-methoxybenzaldehyde (953 mg, 7 mmol, 1.0 equiv.), morpholin-4-amine (715 mg, 7 mmol, 1.0 equiv.), $MgSO_4$ (2.53 g, 21 mmol, 3 equiv.) and DCM (30 mL) was stirred at room temperature for 17 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **4z** in 58% yield (893 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.57-7.52 (m, 2H), 6.91-6.86 (m, 2H), 3.90-3.87 (m, 4H), 3.82 (s, 3H), 3.16-3.13 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 136.9, 128.9, 127.7, 114.2, 66.7, 55.5, 52.3. The spectroscopic data are in agreement with those previously reported.[10]

2.3.27 Synthesis and characterization of (*E*)-1-([1,1'-biphenyl]-4-yl)-*N*-morpholinomethanimine (4aa)

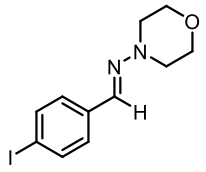


4aa

A mixture of [1,1'-biphenyl]-4-carbaldehyde (911 mg, 5 mmol, 1.0 equiv.), morpholin-4-amine (562 mg, 5.5 mmol, 1.1 equiv.), $MgSO_4$ (1.81 g, 15 mmol, 3 equiv.) and DCM (20 mL) was stirred at room temperature for 20 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded **4aa** in 98% yield (1.30 g) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.57 (m, 7H), 7.46-7.41 (m, 2H), 7.36-7.31 (m, 1H), 3.90-3.87 (m, 4H), 3.21-3.17 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1, 140.8, 135.9, 135.1, 128.9, 127.5,

127.4, 127.1, 126.7, 66.6, 52.0; IR (neat): 2952, 2853, 1587, 1447, 1355, 1263, 1114, 1092, 1067, 996, 900, 862, 833, 763, 733, 721, 694, 659, 601, 514, 500, 490 cm^{-1}; HRMS calculated *m/z* for $C_{17}H_{19}N_2O^+$ $[M+H]^+$: 267.1492, found (ESI) 267.1493.

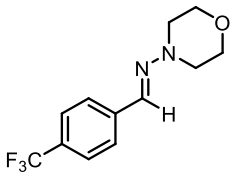
2.3.28 Synthesis and characterization of (*E*)-1-(4-iodophenyl)-*N*-morpholinomethanimine (4ad)



4ad

A mixture of 4-iodobenzaldehyde (464 mg, 2 mmol, 1.0 equiv.), morpholin-4-amine (214 mg, 2.1 mmol, 1.05 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (15 mL) was stirred at room temperature for 18 h. Column chromatography on silica gel (eluent: hexane/ethyl acetate/DCM = 5:1:1) afforded **4ad** in 39% yield (246 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.65 (m, 2H), 7.48 (s, 1H), 7.34-7.32 (m, 2H), 3.90-3.86 (m, 4H), 3.19-3.16 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 135.7, 134.7, 127.9, 93.9, 66.5, 51.8. The spectroscopic data are in agreement with those previously reported.[14]

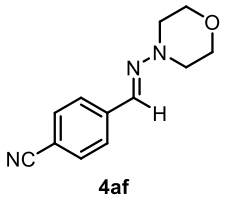
2.3.29 Synthesis and characterization of (*E*)-*N*-morpholino-1-(4-(trifluoromethyl)-phenyl)methanimine (4ae)



4ae

A mixture of 4-(trifluoromethyl)benzaldehyde (540 mg, 3.1 mmol, 1.0 equiv.), morpholin-4-amine (333 mg, 3.26 mmol, 1.05 equiv.), $MgSO_4$ (1.12 g, 9.3 mmol, 3 equiv.) and DCM (15 mL) was stirred at room temperature for 18 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded **4ae** in 99% yield (796 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.54 (s, 1H), 3.90-3.87 (m, 4H), 3.23-3.20 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6 (q, $^5J_{C\text{-}F}$ = 1.6 Hz), 133.6, 129.8 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 126.2, 125.6 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.3 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 66.5, 51.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.4. The spectroscopic data are in agreement with those previously reported.[10]

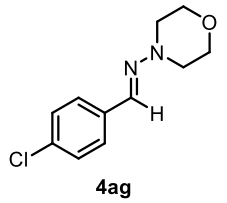
2.3.30 Synthesis and characterization of (*E*)-4-((morpholinoimino)methyl)benzonitrile (4af)



4af

A mixture of 4-formylbenzonitrile (393 mg, 3 mmol, 1.0 equiv.), morpholin-4-amine (322 mg, 3.15 mmol, 1.05 equiv.), $MgSO_4$ (1.08 g, 9 mmol, 3 equiv.) and DCM (15 mL) was stirred at room temperature for 20 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **4af** in 98% yield (634 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.65 (m, 2H), 7.62-7.59 (m, 2H), 7.50 (s, 1H), 3.91-3.88 (m, 4H), 3.26-3.22 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 132.55, 132.50, 126.4, 119.2, 111.0, 66.4, 51.5. The spectroscopic data are in agreement with those previously reported.[10]

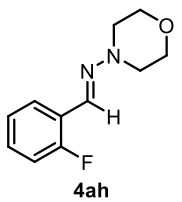
2.3.31 Synthesis and characterization of (*E*)-1-(4-chlorophenyl)-*N*-morpholinomethanimine (4ag)



4ag

A mixture of 4-chlorobenzaldehyde (281 mg, 2 mmol, 1.0 equiv.), morpholin-4-amine (214 mg, 2.1 mmol, 1.05 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (10 mL) was stirred at room temperature for 15 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded **4ag** in 97% yield (438 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.48 (m, 3H), 7.31-7.28 (m, 2H), 3.87-3.84 (m, 4H), 3.16-3.13 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.6, 134.4, 133.8, 128.8, 127.3, 66.4, 51.7. The spectroscopic data are in agreement with those previously reported.[10]

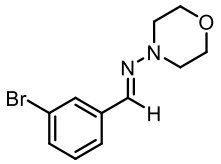
2.3.32 Synthesis and characterization of (*E*)-1-(2-fluorophenyl)-*N*-morpholinomethanimine (4ah)



4ah

A mixture of 2-fluorobenzaldehyde (248 mg, 2 mmol, 1.0 equiv.), morpholin-4-amine (214 mg, 2.1 mmol, 1.05 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (10 mL) was stirred at room temperature for 16 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **4ah** in 99% yield (412 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (t, *J* = 7.7 Hz, 1H), 7.78 (s, 1H), 7.26-6.99 (m, 3H), 3.89-3.86 (m, 4H), 3.21-3.18 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7 (d, *J* = 249.0 Hz), 129.6 (d, *J* = 8.4 Hz), 128.7 (d, *J* = 5.2 Hz), 125.9 (d, *J* = 3.3 Hz), 124.3 (d, *J* = 3.4 Hz), 123.8 (d, *J* = 9.9 Hz), 115.6 (d, *J* = 21.2 Hz), 66.5, 51.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -122.8. The spectroscopic data are in agreement with those previously reported.[14]

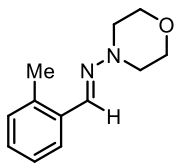
2.3.33 Synthesis and characterization of (*E*)-1-(3-bromophenyl)-*N*-morpholinomethanimine (4ai)



4ai

A mixture of 3-bromobenzaldehyde (370 mg, 2 mmol, 1.0 equiv.), morpholin-4-amine (214 mg, 2.1 mmol, 1.05 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (10 mL) was stirred at room temperature for 16 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded **4ai** in 95% yield (512 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.77 (m, 1H), 7.48-7.46 (m, 2H), 7.40-7.37 (m, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 3.89-3.86 (m, 4H), 3.19-3.16 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 133.9, 131.1, 130.2, 128.9, 125.0, 123.0, 66.5, 51.8. The spectroscopic data are in agreement with those previously reported.[14]

2.3.34 Synthesis and characterization of (*E*)-*N*-morpholino-1-(*o*-tolyl)methanimine (4aj)

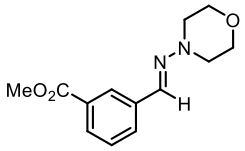


4aj

A mixture of 2-methylbenzaldehyde (240 mg, 2 mmol, 1.0 equiv.), morpholin-4-amine (214 mg, 2.1 mmol, 1.05 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (10 mL) was stirred at room temperature for 24 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded **4aj** in 99% yield (404 mg) as a white solid. ^{1}H NMR (300

MHz, $CDCl_3$) δ 7.79-7.76 (m, 2H), 7.19-7.10 (m, 3H), 3.88-3.84 (m, 4H), 3.17-3.13 (m, 4H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.4, 134.8, 133.9, 130.6, 128.1, 126.2, 125.6, 66.4, 52.0, 19.6. The spectroscopic data are in agreement with those previously reported.[10]

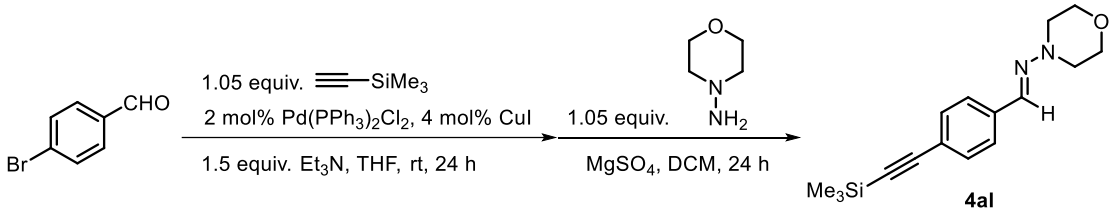
2.3.35 Synthesis and characterization of methyl (*E*)-3-[(morpholinoimino)methyl]benzoate (4ak)



4ak

A mixture of methyl 3-formylbenzoate (328 mg, 2 mmol, 1.0 equiv.), morpholin-4-amine (214 mg, 2.1 mmol, 1.05 equiv.), $MgSO_4$ (6 mmol, 722 mg, 3 equiv.) and DCM (10 mL) was stirred at room temperature for 22 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **4ak** in 99% yield (490 mg) as a white solid. ^1H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.94 (d, J = 7.7 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.59 (s, 1H), 7.41 (t, J = 7.8 Hz, 1H), 3.97 (s, 3H), 3.92-3.86 (m, 4H), 3.21-3.18 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 136.5, 134.6, 130.6, 130.1, 129.2, 128.7, 127.6, 66.5, 52.2, 51.7. The spectroscopic data are in agreement with those previously reported.[16]

2.3.36 Synthesis and characterization of (*E*)-*N*-morpholino-1-{4-[(trimethylsilyl)ethynyl]-phenyl}methanimine (4al)



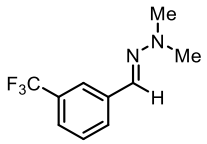
4al

To a 100 mL oven-dried Schlenk tube equipped with a stirring bar was added $Pd(PPh_3)_2Cl_2$ (56.2 mg, 0.08 mmol, 2 mol%), CuI (30.5 mg, 0.16 mmol, 4 mol%) and 4-bromobenzaldehyde (740 mg, 4.0 mmol, 1.0 equiv.). The Schlenk tube was then evacuated and backfilled with N_2 three times. After this, 30 mL of dry THF was added under N_2, followed by the addition of ethynyltrimethylsilane (582 μL, 4.2 mmol, 1.05 equiv.) and triethylamine (834 μL, 6 mmol, 1.5 equiv.). The resulting reaction mixture was stirred at room temperature for 24 h, then filtered through a pad of celite. The obtained organic phase was extracted with ethyl acetate, washed with brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 40:1)

to afford 4-((trimethylsilyl)ethynyl)benzaldehyde, which was used for the next step.

Morpholin-4-amine (429 mg, 4.2 mmol, 1.05 equiv.) and $MgSO_4$ (1.44 g, 12 mmol, 3 equiv.) were added sequentially to a stirred solution of the above obtained aldehyde in DCM (30 mL). The resulting solution was stirred at room temperature for 24 h, then filtered through a pad of celite. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) to afford **4al** in 46% yield (530 mg) as a light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.51 (m, 3H), 7.46-7.42 (m, 2H), 3.89-3.86 (m, 4H), 3.20-3.16 (m, 4H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2, 135.0, 132.3, 126.0, 122.8, 105.3, 95.3, 66.5, 51.8, 0.1. The spectroscopic data are in agreement with those previously reported.[16]

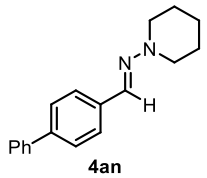
2.3.37 Synthesis and characterization of (*E*)-1,1-dimethyl-2-[3-(trifluoromethyl)benzylidene]hydrazine (4am)



4am

A mixture of 3-(trifluoromethyl)benzaldehyde (348 mg, 2 mmol, 1.0 equiv.), 1,1-dimethylhydrazine (126 mg, 2.1 mmol, 1.05 equiv.), $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and DCM (10 mL) was stirred at room temperature for 24 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **4am** in 74% yield (320 mg) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82-7.81 (m, 1H), 7.72-7.66 (m, 1H), 7.45-7.37 (m, 2H), 7.18 (s, 1H), 3.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 131.0 (q, J = 32.1 Hz), 130.0, 129.0, 128.6 (q, J = 1.4 Hz), 124.4 (q, J = 272.3 Hz), 123.5 (q, J = 3.9 Hz), 122.2 (q, J = 3.9 Hz), 42.8; IR (neat): 2864, 1566, 1445, 1324, 1280, 1207, 1160, 1116, 1093, 1066, 1039, 908, 796, 696, 666, 632, 536 cm^{-1}; HRMS calculated m/z for $C_{10}H_{12}F_3N_2^+$ $[M+H]^+$: 217.0947, found (ESI) 217.0948.

2.3.38 Synthesis and characterization of (*E*)-1-([1,1'-biphenyl]-4-yl)-*N*-(piperidin-1-yl)-methanimine (4an)

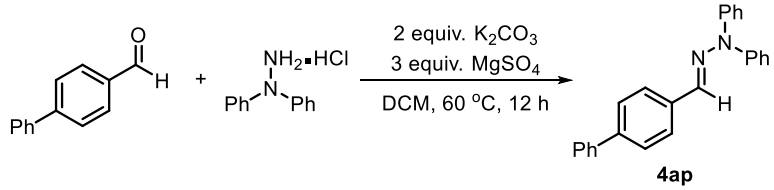


4an

A mixture of [1,1'-biphenyl]-4-carbaldehyde (729 mg, 4 mmol, 1.0 equiv.), piperidin-1-

amine (401 mg, 4 mmol, 1.0 equiv.), $MgSO_4$ (1.44 g, 12 mmol, 3 equiv.) and DCM (20 mL) was stirred at room temperature for 24 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 8:1) afforded **4an** in 97% yield (1.03 g) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.55 (m, 7H), 7.45-7.40 (m, 2H), 7.35-7.29 (m, 1H), 3.20-3.16 (m, 4H), 1.79-1.72 (m, 4H), 1.60-1.50 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0, 140.5, 135.9, 134.2, 128.9, 127.34, 127.29, 127.1, 126.5, 52.2, 25.3, 24.3; IR (neat): 3030, 2936, 2818, 1739, 1486, 1445, 1377, 1363, 1354, 1229, 1079, 987, 898, 884, 857, 833, 758, 721, 690, 556, 514, 491 cm^{-1}; HRMS calculated *m/z* for $C_{18}H_{21}N_2^+$ $[M+H]^+$: 265.1699, found (ESI) 265.1702.

2.3.39 Synthesis and characterization of (*E*)-2-([1,1'-biphenyl]-4-ylmethylene)-1,1-diphenylhydrazine (4ap)



4ap

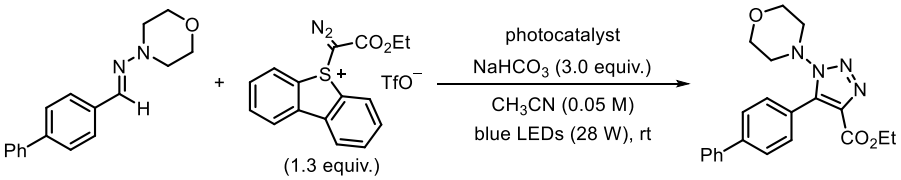
To a solution of [1,1'-biphenyl]-4-carbaldehyde (364 mg, 2 mmol, 1.0 equiv.) in dry DCM (30 mL) was added *N*,*N*-diphenylhydrazinium chloride (441 mg, 2 mmol, 1.0 equiv.), anhydrous $MgSO_4$ (722 mg, 6 mmol, 3 equiv.) and K_2CO_3 (553 mg, 4 mmol, 2 equiv.). The resulting mixture was refluxed at 60 °C for 12 h. Then, the reaction mixture was filtered through a pad of celite. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) to afford **4ap** in 95% yield (663 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.65 (m, 2H), 7.62-7.55 (m, 4H),7.46-7.40 (m, 6H), 7.36-7.30 (m, 1H), 7.23-7.17 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 140.9, 140.8, 135.4, 135.2, 130.0, 128.9, 127.5, 127.3, 127.1, 126.8, 124.7, 122.7; IR (neat): 3060, 3027, 1585, 1574, 1494, 1483, 1382, 1297, 1234, 1202, 1169, 1092, 1068, 907, 831, 765, 744, 725, 697, 687, 644, 623, 574, 554, 508, 489 cm^{-1}; HRMS calculated *m/z* for $C_{25}H_{21}N_2^+$ $[M+H]^+$: 349.1699, found (ESI) 349.1689.

2.4 Optimizations details for the synthesis of triazoles 5

2.4.1 Evaluation of photocatalysts

To a 10 mL oven-dried Schlenk tube equipped with a stirring bar was added photocatalyst, $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4aa** (53.3 mg, 0.2 mmol, 1.0 equiv.). The Schlenk tube was then evacuated and backfilled with N_2 three times after which dry acetonitrile (4 mL) was added under N_2. The tube was sealed and degassed by three freeze-pump-thaw cycles under N_2. After that, the reaction tube was placed in a photoreactor equipped with blue LED strips (wavelength range: 430-435 nm, 28 W). A mini-fan was kept on top to maintain room temperature. The resulting mixture was stirred at room temperature for the appropriate time as indicated in Table S1. Then, the reaction was quenched with water, extracted with DCM, washed with brine and the organic phase was dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated under the reduced pressure and the residue was subjected to column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1). The fractions containing **5ac** were all combined. The solvent was then removed under the reduced pressure to afford a residue. The NMR yields were obtained by ^1H NMR analysis of the residue using CH_2Br_2 (0.2 mmol, 14.0 μL, 1.0 equiv.) as the internal standard in $CDCl_3$. The results were summarized in Table S1.

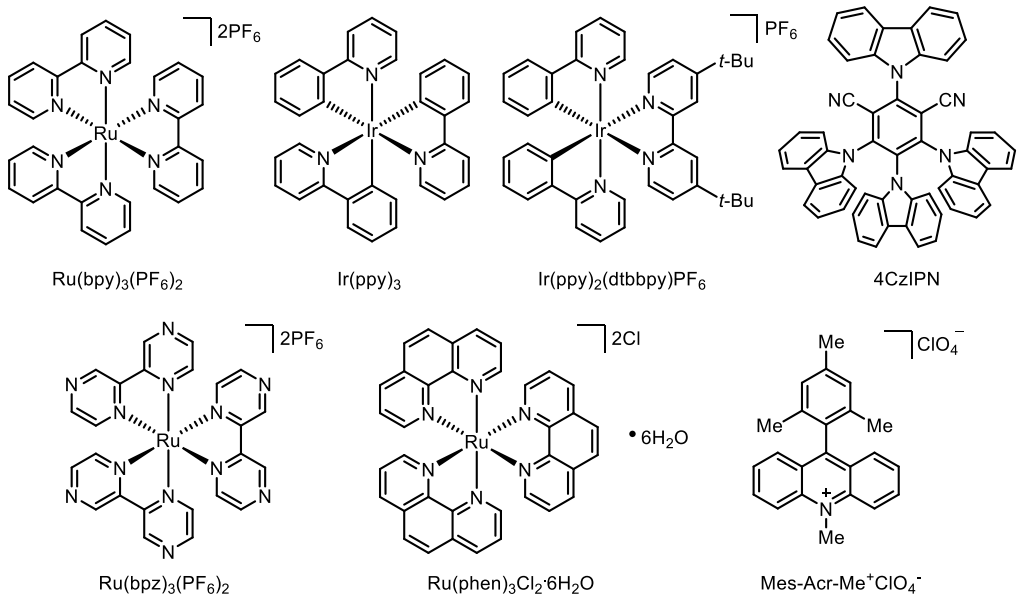
Table S1: Evaluation of photocatalysts



4aa **1a** **5ac**

entry	photocatalyst (mol%)	time (h)	yield (%)[a]
1	no photocatalyst	16	11
2	$Ru(bpy)_3(PF_6)_2$ (1)	22	57
3	$Ir(ppy)_3$ (1)	21	13
4	$Ir(ppy)_2(dtbbpy)PF_6$ (1)	21	17
5	4CzIPN (1)	11	20
6	$Ru(bpz)_3(PF_6)_2$ (1)	15	54
7	$Ru(phen)_3Cl_2{\cdot}6H_2O$ (1)	15	52
8	$Ru(bpy)_3(PF_6)_2$ (3)	14	58
9	$Ru(bpy)_3(PF_6)_2$ (5)	14	59
10	Mes-Acr-$Me^+ClO_4^-$ (5)	15	59

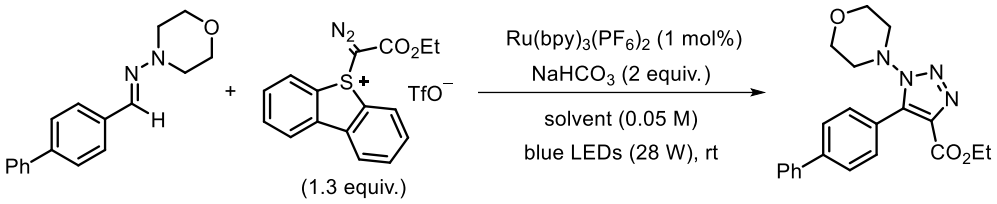
[a] ^1H NMR yield with CH_2Br_2 as the internal standard.



2.4.2 Evaluation of solvents

To a 10 mL oven-dried Schlenk tube equipped with a stirring bar was added $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (33.6 mg, 0.4 mmol, 2.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4aa** (53.3 mg, 0.2 mmol, 1.0 equiv.). The Schlenk tube was then evacuated and backfilled with N_2 three times after which dry solvents (4 mL) was added under N_2. The tube was sealed and degassed by three freeze-pump-thaw cycles under N_2. After that, the reaction tube was placed in a photoreactor equipped with blue LED strips (wavelength range: 430-435 nm, 28 W). A mini-fan was kept on top to maintain room temperature. The resulting mixture was stirred at room temperature for the appropriate time as indicated in Table S2. Then, the reaction was quenched with water, extracted with DCM, washed with brine and the organic phase was dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated under the reduced pressure and the residue was subjected to column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1). The fractions containing **5ac** were all combined. The solvent was then removed under the reduced pressure to afford a residue. The NMR yields were obtained by ^1H NMR analysis of the residue using CH_2Br_2 (0.2 mmol, 14.0 μL, 1.0 equiv.) as the internal standard in $CDCl_3$. The results were summarized in Table S2.

Table S2: Evaluation of solvents



4aa **1a** **5ac**

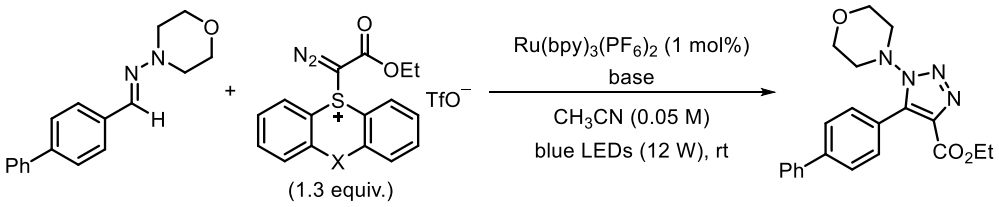
entry	solvent	time (h)	yield (%)[a]
1	CH_3CN	22	57
2	THF	12	15
3	MeOH	12	37
4	Acetone	15	50
5	DMF	13	30
6	DMSO	13	0
7	$CHCl_3$	13	19
8	CH_3CN/DCE (1:1)	19	54

[a] ^{1}H NMR yield with CH_2Br_2 as the internal standard.

2.4.3 Evaluation of bases and reagents

To a 10 mL oven-dried Schlenk tube equipped with a stirring bar was added $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), bases, **1** (0.26 mmol, 1.3 equiv.) and **4aa** (53.3 mg, 0.2 mmol, 1.0 equiv.). The Schlenk tube was then evacuated and backfilled with N_2 three times after which dry CH_3CN (4 mL) was added under N_2. The tube was sealed and degassed by three freeze-pump-thaw cycles under N_2. After that, the reaction tube was placed in a photoreactor equipped with blue LED strips (wavelength range: 430-435 nm, 12 W). A mini-fan was kept on top to maintain room temperature. The resulting mixture was stirred at room temperature for the appropriate time as indicated in Table S3. Then, the reaction mixture was quenched with water, extracted with DCM, washed with brine and the organic phase was dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated under the reduced pressure and the residue was subjected to column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1). The fractions containing **5ac** were all combined. The solvent was then removed under the reduced pressure to afford a residue. The NMR yields were obtained by ^{1}H NMR analysis of the residue using CH_2Br_2 (0.2 mmol, 14.0 μL, 1.0 equiv.) as the internal standard in $CDCl_3$. The results were summarized in Table S3.

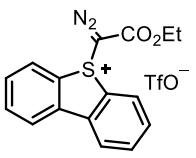
Table S3: Evaluation of bases and reagents 1



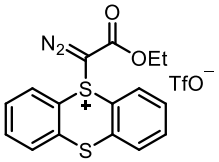
4aa **1** **5ac**

entry	reagent **1**	base (equiv.)	time (h)	yield (%)[a]
1	**1a**	$NaHCO_3$ (2)	15	57
2	**1a**	Cs_2CO_3 (2)	8	9
3	**1a**	Na_3PO_4 (2)	8	47
4	**1a**	K_2CO_3 (2)	18	36
5	**1a**	K_3PO_4 (2)	18	31
6	**1a**	KH_2PO_4 (2)	18	30
7	**1a**	Na_2HPO_4 (2)	18	47
8	**1a**	$PhCO_2Na$ (2)	19	24
9	**1a**	$KHCO_3$ (2)	19	43
10	**1a**	NaOAc (2)	19	30
11	**1a**	$NaHCO_3$ (3)	17	57
12	**1a**	no base	20	8
13[b]	**1a**	$NaHCO_3$ (3)	17	55
14	**1c**	$NaHCO_3$ (3)	17	56
15	**1d**	$NaHCO_3$ (3)	11	41
16[c]	**1a**	$NaHCO_3$ (3)	10	20

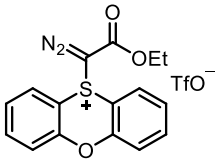
[a] ^1H NMR yield with CH_2Br_2 as the internal standard. [b] 5 mol% $Zn(NTf_2)_2$ was added. [c] A solution of **1a** in CH_3CN (2 mL) was added by a syring pump over 3 h.



1a



1c



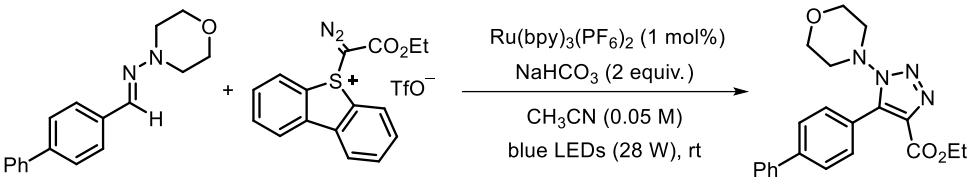
1d

2.4.4 Evaluation of appropriate stoichiometry

To a 10 mL oven-dried Schlenk tube equipped with a stirring bar was added $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (33.6 mg, 0.4 mmol, 2.0 equiv.), **1a** and **4aa**. The Schlenk tube was then evacuated and backfilled with N_2 three times after which dry CH_3CN (4 mL) was added under N_2. The tube was sealed and degassed by three freeze-pump-thaw cycles under N_2. After that, the reaction tube was placed in a photoreactor equipped with blue LED strips (wavelength range: 430-435 nm, 28 W). A mini-fan was kept on top to maintain room temperature. The resulting mixture was stirred at room temperature for the appropriate time as

indicated in Table S4. Then, the reaction mixture was quenched with water, extracted with DCM, washed with brine and the organic phase was dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated under the reduced pressure and the residue was subjected to column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1). The fractions containing **5ac** were all combined. The solvent was then removed under the reduced pressure to afford a residue. The NMR yields were obtained by ^1H NMR analysis of the residue using CH_2Br_2 (0.2 mmol, 14.0 μL, 1.0 equiv.) as the internal standard in $CDCl_3$. The results were summarized in Table S4.

Table S4: Evaluation of stoichiometry



4aa **1a** **5ac**

entry	equiv. **4aa**	equiv. **1a**	time (h)	yield (%)[a]
1	1.3	1.0	22	22
2	1.0	1.2	19	54
3	1.0	1.3	22	57
4	1.0	1.5	13	51

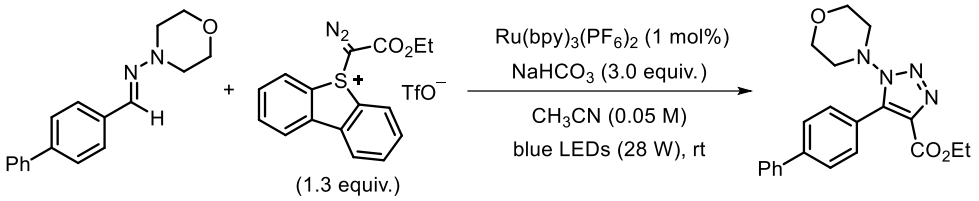
[a] ^1H NMR yield with CH_2Br_2 as the internal standard.

2.4.5 Evaluation of additives and concentration

To a 10 mL oven-dried Schlenk tube equipped with a stirring bar was added $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.), **4aa** (53.3 mg, 0.2 mmol, 1.0 equiv.) and additives. The Schlenk tube was then evacuated and backfilled with N_2 three times after which dry CH_3CN was added under N_2. The tube was sealed and degassed by three freeze-pump-thaw cycles under N_2. After that, the reaction tube was placed in a photoreactor equipped with blue LED strips (wavelength range: 430-435 nm, 28 W). A mini-fan was kept on top to maintain room temperature. The resulting mixture was stirred at room temperature for the appropriate time as indicated in Table S5. Then, the reaction was quenched with water, extracted with DCM, washed with brine and the organic phase was dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated under the reduced pressure and the residue was subjected to column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1). The fractions containing **5ac** were all combined. The solvent was then removed under the reduced pressure to afford a residue. The NMR yields were

obtained by ^{1}H NMR analysis of the residue using CH_2Br_2 (0.2 mmol, 14.0 μL, 1.0 equiv.) as the internal standard in $CDCl_3$. The results were summarized in Table S5.

Table S5: Evaluation of additives and concentration



4aa **1a** **5ac**

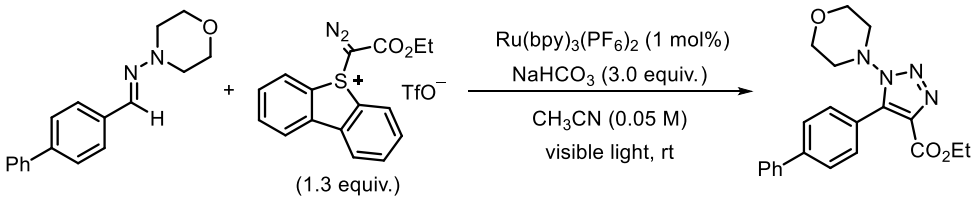
entry	concentration **4aa**/(mol/L)	additive (equiv.)	time (h)	yield (%)[a]
1	0.05	-	22	57
2[b]	0.05	4Å MS	17	56
3	0.05	MgO (3.0)	17	54
4	0.025	-	17	57
5	0.1	-	21	53

[a] ^{1}H NMR yield with CH_2Br_2 as the internal standard. [b] 50 mg 4Å MS was used.

2.4.6 Evaluation of light sources

To a 10 mL oven-dried Schlenk tube equipped with a stirring bar was added $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4aa** (53.3 mg, 0.2 mmol, 1.0 equiv.). The Schlenk tube was then evacuated and backfilled with N_2 three times after which dry CH_3CN (4 mL) was added under N_2. The tube was sealed and degassed by three freeze-pump-thaw cycles under N_2. After that, the reaction tube was placed in a photoreactor equipped with blue or white LED strips. A mini-fan was kept on top to maintain room temperature. The resulting mixture was stirred at room temperature for the appropriate time as indicated in Table S6. Then, the reaction was quenched with water, extracted with DCM, washed with brine and the organic phase was dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated under the reduced pressure and the residue was subjected to column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1). The fractions containing **5ac** were all combined. The solvent was then removed under the reduced pressure to afford a residue. The NMR yields were obtained by ^{1}H NMR analysis of the residue using CH_2Br_2 (0.2 mmol, 14.0 μL, 1.0 equiv.) as the internal standard in $CDCl_3$. The results were summarized in Table S6.

Table S6: Evaluation of light sources



4aa **1a** **5ac**

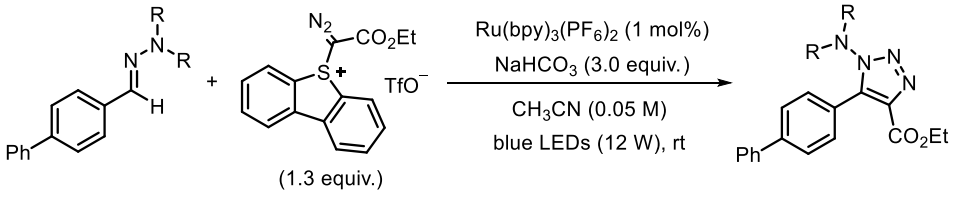
entry	visible light	time (h)	yield (%)[a]
1	no light	16	0
2	blue LEDs (5 W)	15	55
3	blue LEDs (12 W)	17	57
4	blue LEDs (28 W)	22	57
5	white LEDs	16	57

[a] ^{1}H NMR yield with CH_2Br_2 as the internal standard.

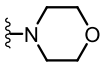
2.4.7 Evaluation of hydrazones

To a 10 mL oven-dried Schlenk tube equipped with a stirring bar was added $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4** (0.2 mmol, 1.0 equiv.). The Schlenk tube was then evacuated and backfilled with N_2 three times after which dry CH_3CN (4 mL) was added under N_2. The tube was sealed and degassed by three freeze-pump-thaw cycles under N_2. After that, the reaction tube was placed in a photoreactor equipped with blue LED strips (wavelength range: 430-435 nm, 12 W). A mini-fan was kept on top to maintain room temperature. The resulting mixture was stirred at room temperature for the appropriate time as indicated in Table S7. Then, the reaction was quenched with water, extracted with DCM, washed with brine and the organic phase was dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated under the reduced pressure and the residue was subjected to column chromatography on silica gel. The fractions containing **5** were all combined. The solvent was then removed under the reduced pressure to afford a residue. The NMR yields were obtained by ^{1}H NMR analysis of the residue using CH_2Br_2 (0.2 mmol, 14.0 μL, 1.0 equiv.) as the internal standard in $CDCl_3$. The results were summarized in Table S7.

Table S7: Evaluation of hydrazones

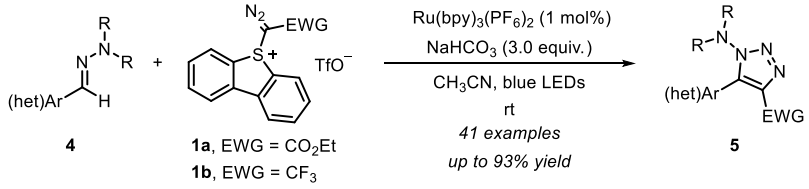


4 **1a** **5**

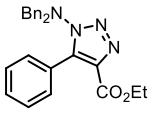
entry	hydrazone		time (h)	yield (%)[a]
1	**4aa**		17	57
2	**4an**		23	40
3	**4ao**		23	46
4	**4ap**		19	messy
5	**4g**		12	81[b]

[a] ^{1}H NMR yield with CH_2Br_2 as the internal standard. [b] Isolated yield.

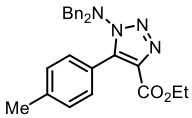
2.5 Synthesis and characterization of triazoles 5



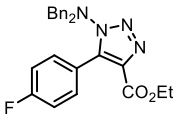
4 **1a**, EWG = CO_2Et **1b**, EWG = CF_3 **5**



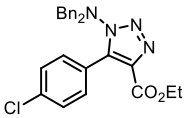
5a; 87%



5b; 83%



5c; 92%



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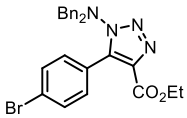

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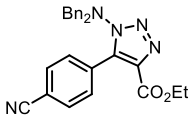

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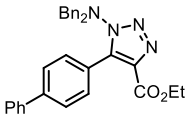
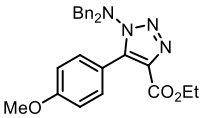
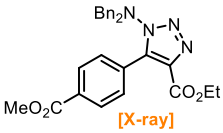


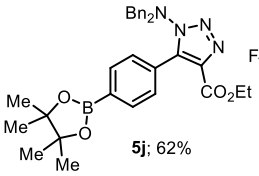
5g; 81%



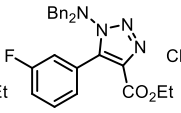
5h; 86%



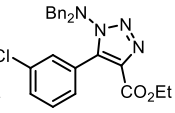
[X-ray] **5i**; 92%



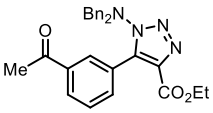
5j; 62%



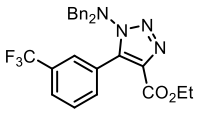
5k; 84%



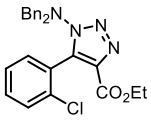
5l; 86%



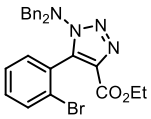
5m; 93%



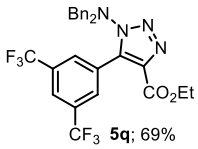
5n; 92%



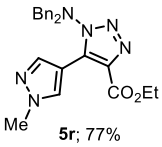
5o; 86%



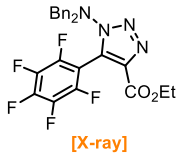
5p; 85%



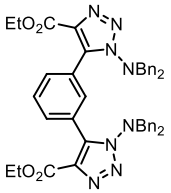
5q; 69%



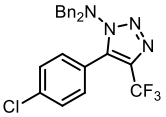
5r; 77%



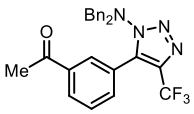
[X-ray] **5s**; 52%



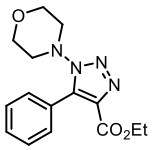
5t; 66%



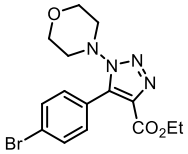
5u; 90%



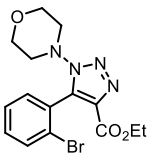
5v; 72%



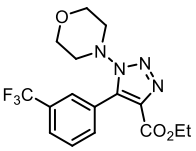
5w; 56%



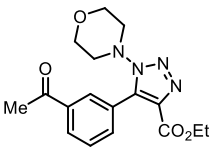
5x; 62%



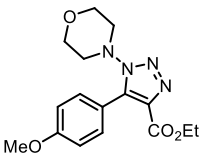
[X-ray] **5y**; 61%



5z; 71%



5aa; 65%



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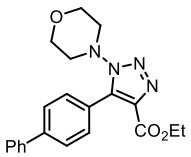

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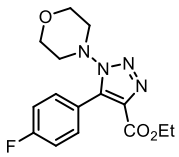
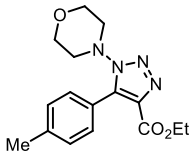
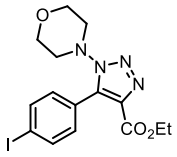


5ad; 59%



5ae; 51%



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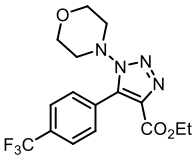

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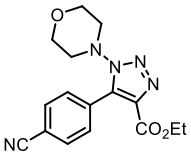

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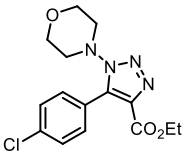

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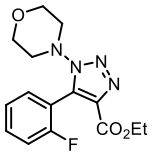
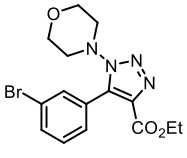


5aj; 69%



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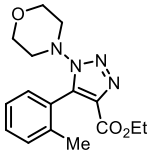

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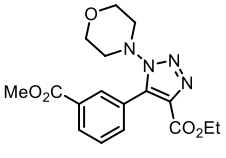


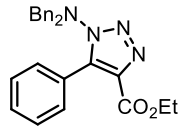
5am; 64%

5an; 44%

5ao; 71%

Typical procedure for the photoredox-catalyzed C(sp^2)-H diazomethylation of hydrazones to triazoles **5**: To a 10 mL oven-dried Schlenk tube equipped with a stirring bar was added $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1** (0.26 mmol, 1.3 equiv.) and **4** (0.2 mmol, 1.0 equiv.). The Schlenk tube was then evacuated and backfilled with N_2 three times after which dry CH_3CN (4 mL) was added under N_2. Then, the reaction tube was placed in a photoreactor equipped with blue LED strips (wavelength range: 430-435 nm, 12 W). A mini-fan was kept on top to maintain room temperature. The resulting mixture was stirred at room temperature for 8-19 hours. Then, the reaction was quenched with water, extracted with DCM, washed with brine and the organic phase was dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under the reduced pressure to afford a residue, which was purified by column chromatography on silica gel to afford the desired products.

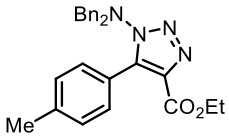
2.5.1 Synthesis and characterization of ethyl 1-(dibenzylamino)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (5a)



5a

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4a** (60.1 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 12 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5a** in 87% yield (71.5 mg) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.33 (m, 1H), 7.27-7.15 (m, 8H), 7.00-6.96 (m, 4H), 6.46-6.42 (m, 2H), 4.45 (bs, 4H), 4.21 (q, J = 7.1 Hz, 2H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 141.7, 134.9, 134.7, 130.1, 129.7, 129.3, 128.6, 128.2, 127.3, 125.2, 62.3, 61.0, 14.0. IR (neat): 3033, 2971, 1724, 1491, 1454, 1428, 1376, 1365, 1335, 1228, 1216, 1193, 1054, 1028, 749, 694 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{25}H_{25}N_4O_2^+$ $[M+H]^+$: 413.1972, found 413.1973.

2.5.2 Synthesis and characterization of 5b

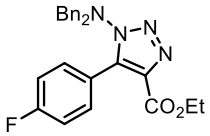


5b

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol,

3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4b** (62.9 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 9 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5b** in 83% yield (70.4 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.22-7.15 (m, 6H), 7.03-6.97 (m, 6H), 6.43-6.41 (m, 2H), 4.43 (bs, 4H), 4.21 (q, J = 7.1 Hz, 2H), 2.37 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 141.8, 139.4, 134.9, 134.6, 130.0, 129.7, 128.6, 128.2, 128.0, 122.1, 62.3, 61.0, 21.5, 14.1. IR (neat): 3035, 2971, 1725, 1715, 1455, 1438, 1366, 1334, 1214, 1201, 1183, 1060, 750, 700, 501 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{26}H_{27}N_4O_2^+$ $[M+H]^+$: 427.2129, found 427.2128.

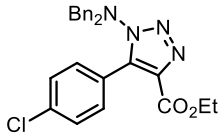
2.5.3 Synthesis and characterization of ethyl 1-(dibenzylamino)-5-(4-fluorophenyl)-1*H*-1,2,3-triazole-4-carboxylate (5c)



5c

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4c** (63.7 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 10 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5c** in 92% yield (78.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.26-7.15 (m, 6H), 6.98-6.93 (m, 4H), 6.89-6.84 (m, 2H), 6.41-6.36 (m, 2H), 4.44 (bs, 4H), 4.21 (q, J = 7.1 Hz, 2H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3 (d, $^1J_{C\text{-}F}$ = 249.8 Hz), 160.8, 140.9, 134.8, 134.6, 132.1(d, $^3J_{C\text{-}F}$ = 8.5 Hz), 129.7, 128.6, 128.3, 121.0 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 114.4 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 62.5, 61.1, 14.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.2. IR (neat): 3033, 2977, 1721, 1498, 1455, 1438, 1378, 1365, 1335, 1295, 1228, 1219, 1192, 1159, 1055, 1028, 848, 835, 814, 793, 752, 730, 697, 615, 514 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{25}H_{24}FN_4O_2^+$ $[M+H]^+$: 431.1878, found 431.1876.

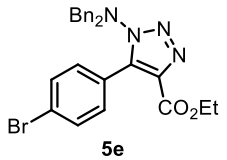
2.5.4 Synthesis and characterization of ethyl 5-(4-chlorophenyl)-1-(dibenzylamino)-1*H*-1,2,3-triazole-4-carboxylate (5d)



5d

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4d** (67.0 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 9 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5d** in 88% yield (79.0 mg) as a white solid. ^1H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.26-7.13 (m, 8H), 6.98-6.95 (m, 4H), 6.32-6.29 (m, 2H), 4.45 (bs, 4H), 4.21 (q, J = 7.1 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 140.8, 135.6, 134.71, 134.65, 131.4, 129.7, 128.6, 128.3, 127.5, 123.5, 62.6, 61.1, 14.1. IR (neat): 3030, 2968, 1738, 1719, 1486, 1480, 1456, 1436, 1377, 1365, 1329, 1229, 1217, 1196, 1089, 1058, 1017, 998, 821, 792, 742, 704, 694, 523, 496 cm^{-1}; HRMS (ESI) calcd *m/z* for $C_{25}H_{24}ClN_4O_2^+$ $[M+H]^+$: 447.1582, found 447.1577.

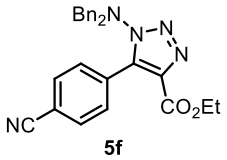
2.5.5 Synthesis and characterization of ethyl 5-(4-bromophenyl)-1-(dibenzylamino)-1*H*-1,2,3-triazole-4-carboxylate (5e)



5e

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4e** (75.9 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 13 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5e** in 90% yield (88.4 mg) as a white solid. ^1H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.32-7.28 (m, 2H), 7.26-7.15 (m, 6H), 6.97-6.94 (m, 4H), 6.25-6.21 (m, 2H), 4.45 (bs, 4H), 4.21 (q, J = 7.1 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 50 °C) δ 160.8, 140.7, 134.9, 134.8, 131.8, 130.6, 129.8, 128.7, 128.4, 124.3, 124.0, 62.7, 61.0, 14.1. IR (neat): 3033, 2992, 1717, 1478, 1456, 1436, 1328, 1195, 1069, 1057, 1029, 1015, 996, 972, 846, 821, 791, 742, 726, 703, 693, 521, 493 cm^{-1}; HRMS (ESI) calcd *m/z* for $C_{25}H_{24}BrN_4O_2^+$ $[M+H]^+$: 491.1077, found 491.1077.

2.5.6 Synthesis and characterization of ethyl 5-(4-cyanophenyl)-1-(dibenzylamino)-1*H*-1,2,3-triazole-4-carboxylate (5f)

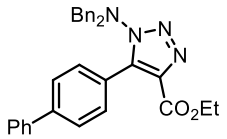


5f

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol,

3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4f** (65.1 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 9 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5f** in 91% yield (79.4 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.42-7.40 (m, 2H), 7.29-7.24 (m, 2H), 7.21-7.17 (m, 4H), 6.94-6.92 (m, 4H), 6.38-6.36 (m, 2H), 4.48 (bs, 4H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 140.1, 134.8, 134.5, 130.78, 130.76, 129.80, 129.76, 128.7, 128.5, 118.3, 113.0, 62.8, 61.3, 14.0. IR (neat): 3030, 2968, 2225, 1738, 1717, 1496, 1444, 1378, 1365, 1337, 1330, 1230, 1216, 1197, 1058, 1032, 1015, 994, 849, 834, 760, 740, 700, 565, 546, 522 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{26}H_{24}N_5O_2^+$ $[M+H]^+$: 438.1925, found 438.1926.

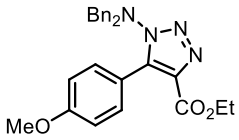
2.5.7 Synthesis and characterization of ethyl 5-([1,1'-biphenyl]-4-yl)-1-(dibenzylamino)-1*H*-1,2,3-triazole-4-carboxylate (5g)



5g

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4g** (75.3 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 12 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5g** in 81% yield (79.0 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.63-7.60 (m, 2H), 7.48-7.42 (m, 4H), 7.38-7.34 (m, 1H), 7.25-7.15 (m, 6H), 7.01-6.98 (m, 4H), 6.61-6.58 (m, 2H), 4.46 (bs, 4H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 142.1, 141.5, 140.4, 134.9, 134.6, 130.6, 129.7, 128.9, 128.6, 128.2, 127.8, 127.2, 125.9, 124.0, 62.4, 61.1, 14.1. IR (neat): 3064, 3030, 2968, 2856, 1737, 1716, 1216, 1194, 1065, 1056, 856, 763, 749, 699, 600, 513 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{31}H_{29}N_4O_2^+$ $[M+H]^+$: 489.2285, found 489.2283.

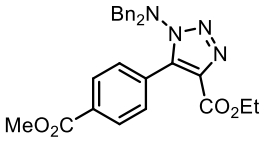
2.5.8 Synthesis and characterization of ethyl 1-(dibenzylamino)-5-(4-methoxyphenyl)-1*H*-1,2,3-triazole-4-carboxylate (5h)



5h

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4h** (66.1 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 10 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5h** in 86% yield (76.0 mg) as a white solid. ^1H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.24-7.15 (m, 6H), 7.01-6.98 (m, 4H), 6.76-6.72 (m, 2H), 6.51-6.47 (m, 2H), 4.43 (bs, 4H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 160.4, 141.5, 134.9, 134.4, 131.6, 129.6, 128.6, 128.2, 117.1, 112.8, 62.2, 60.9, 55.3, 14.1. IR (neat): 3064, 3033, 2966, 1714, 1611, 1501, 1437, 1300, 1253, 1190, 1065, 1030, 1019, 853, 791, 760, 750, 695, 622, 596, 502 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{26}H_{27}N_4O_3^+$ $[M+H]^+$: 443.2078, found 443.2077.

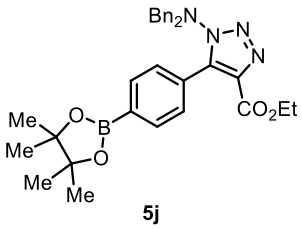
2.5.9 Synthesis and characterization of ethyl 1-(dibenzylamino)-5-[4-(methoxycarbonyl)-phenyl]-1*H*-1,2,3-triazole-4-carboxylate (5i)



5i

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4i** (71.7 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 8 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5i** in 92% yield (86.8 mg) as a white solid. ^1H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.85-7.82 (m, 2H), 7.27-7.23 (m, 2H), 7.20-7.16 (m, 4H), 6.97-6.94 (m, 4H), 6.45-6.42 (m, 2H), 4.45 (bs, 4H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 160.6, 140.8, 134.8, 134.6, 130.7, 130.1, 129.73, 129.69, 128.7, 128.34, 128.30, 62.6, 61.1, 52.3, 14.0. IR (neat): 2966, 1737, 1717, 1705, 1565, 1438, 1365, 1280, 1228, 1217, 1199, 1113, 1062, 1051, 855, 767, 753, 709, 696 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{27}H_{27}N_4O_4^+$ $[M+H]^+$: 471.2027, found 471.2021.

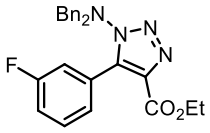
2.5.10 Synthesis and characterization of ethyl 1-(dibenzylamino)-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1*H*-1,2,3-triazole-4-carboxylate (5j)



5j

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4j** (85.3 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 8 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5j** in 62% yield (67.3 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.65-7.62 (m, 2H), 7.25-7.15 (m, 6H), 6.99-6.96 (m, 4H), 6.46-6.43 (m, 2H), 4.43 (bs, 4H), 4.20 (q, J = 7.1 Hz, 2H), 1.37 (s, 12H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 141.7, 134.8, 133.6, 129.8, 129.3, 128.7, 128.3, 127.8, 84.1, 62.5, 61.0, 25.0, 14.1. IR (neat): 2979, 2931, 1736, 1718, 1578, 1397, 1358, 1327, 1228, 1200, 1144, 1088, 1058, 1028, 856, 849, 751, 743, 696, 669, 654, 522 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{31}H_{36}BN_4O_4^+$ $[M+H]^+$: 539.2824, found 539.2822.

2.5.11 Synthesis and characterization of ethyl 1-(dibenzylamino)-5-(3-fluorophenyl)-1*H*-1,2,3-triazole-4-carboxylate (5k)

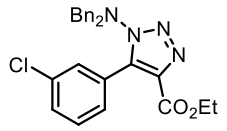


5k

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4k** (63.7 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 9 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5k** in 84% yield (72.3 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.27-7.11 (m, 7H), 7.05-7.00 (m, 1H), 6.98-6.95 (m, 4H), 6.22-6.19 (m, 1H), 6.04-6.01 (m, 1H), 4.45 (bs, 4H), 4.21 (q, J = 7.1 Hz, 2H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6 (d, $^1J_{C\text{-}F}$ = 244.3 Hz), 160.7, 140.5 (d, $^4J_{C\text{-}F}$ = 2.5 Hz), 134.73, 134.70, 129.8, 128.8, 128.7, 128.4, 127.0 (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 125.8 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 117.3 (d, $^2J_{C\text{-}F}$ = 23.5 Hz), 116.3 (d, $^2J_{C\text{-}F}$ = 20.9 Hz), 62.6,

61.1, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.0. IR (neat): 3030, 2974, 2864, 1738, 1714, 1457, 1338, 1226, 1212, 1186, 1057, 1031, 866, 838, 780, 748, 696, 682, 524, 518 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{25}H_{24}N_4O_2F^+$ $[M+H]^+$: 431.1878, found 431.1875.

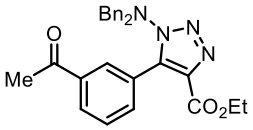
2.5.12 Synthesis and characterization of ethyl 5-(3-chlorophenyl)-1-(dibenzylamino)-1*H*-1,2,3-triazole-4-carboxylate (5l)



5l

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4l** (67.0 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 10 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5l** in 86% yield (76.6 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 50 ^{o}C) δ 7.31-7.17 (m, 7H), 7.11-7.07 (m, 1H), 6.97-6.95 (m, 4H), 6.29-6.26 (m, 2H), 4.45 (bs, 4H), 4.22-4.17 (m, 2H), 1.20-1.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 140.5, 134.7, 134.6, 133.1, 130.1, 129.8, 129.4, 128.7, 128.42, 128.38, 128.2, 126.7, 62.6, 61.1, 14.0. IR (neat): 3030, 2968, 1728, 1455, 1442, 1379, 1364, 1339, 1229, 1215, 1199, 1061, 889, 794, 769, 752, 720, 696, 682, 518 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{25}H_{24}ClN_4O_2^+$ $[M+H]^+$: 447.1582, found 447.1574.

2.5.13 Synthesis and characterization of ethyl 5-(3-acetylphenyl)-1-(dibenzylamino)-1*H*-1,2,3-triazole-4-carboxylate (5m)

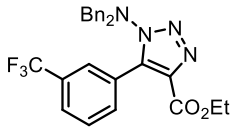


5m

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4m** (68.5 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 10 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5m** in 93% yield (84.2 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 50 ^{o}C) δ 7.95-7.92 (m, 1H), 7.30-7.13 (m, 8H), 6.98-6.95 (m, 4H), 6.63-6.60 (m, 1H), 4.46 (bs, 4H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 160.7, 140.7, 136.3, 134.70, 134.66, 134.6, 130.3, 129.7, 129.0, 128.6, 128.3, 127.6, 125.6, 62.5, 61.1, 26.7, 14.0.

IR (neat): 3033, 2979, 2244, 1721, 1684, 1454, 1264, 1239, 1229, 1190, 1057, 752, 731, 697, 667, 588 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{27}H_{27}N_4O_3^+$ $[M+H]^+$: 455.2078, found 455.2071.

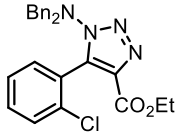
2.5.14 Synthesis and characterization of ethyl 1-(dibenzylamino)-5-(3-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole-4-carboxylate (5n)



5n

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4n** (73.7 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 10 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded **5n** in 92% yield (88.2 mg) as a white solid. ^1H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.29-7.14 (m, 7H), 6.95-6.93 (m, 4H), 6.75 (s, 1H), 6.56 (d, *J* = 7.9 Hz, 1H), 4.47 (bs, 4H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 140.3, 134.8, 134.5, 133.6 (q, *J* = 1.4 Hz), 129.77, 129.76 (q, *J* = 32.5 Hz), 128.7, 128.5, 127.7, 127.1 (q, *J* = 3.8 Hz), 126.0 (q, *J* = 3.7 Hz), 125.9, 123.8 (q, *J* = 272.6 Hz), 62.7, 61.2, 13.9. IR (neat): 3030, 2971, 1729, 1455, 1442, 1380, 1329, 1276, 1228, 1216, 1199, 1166, 1124, 1095, 1074, 1060, 1022, 903, 848, 752, 695, 651, 559, 525 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{26}H_{24}F_3N_4O_2^+$ $[M+H]^+$: 481.1846, found 481.1843.

2.5.15 Synthesis and characterization of ethyl 5-(2-chlorophenyl)-1-(dibenzylamino)-1*H*-1,2,3-triazole-4-carboxylate (5o)

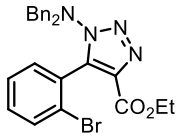


5o

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4o** (67.0 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 9 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5o** in 86% yield (76.6 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.43-7.41 (m, 1H), 7.36 (td, *J* = 7.7, 1.6 Hz, 1H), 7.27-7.18 (m, 6H), 7.06 (td, *J* = 7.5, 1.4 Hz, 1H), 6.99-6.97 (m, 4H), 5.94 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.51-4.48 (m, 2H), 4.33-4.30 (m, 2H), 4.23-4.16 (m, 2H), 1.14

(t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 138.6, 135.8, 135.4, 133.8, 132.0, 130.9, 129.5, 128.8, 128.7, 128.2, 126.1, 125.5, 61.5 (br), 61.0, 13.9. IR (neat): 3067, 3033, 2974, 2862, 1725, 1454, 1442, 1378, 1337, 1193, 1057, 1029, 750, 730, 697, 655 cm^{-1}; HRMS (ESI) calcd m/z for $C_{25}H_{24}ClN_4O_2^+$ $[M+H]^+$: 447.1582, found 447.1580.

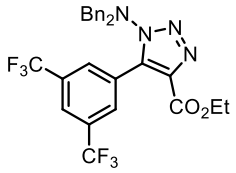
2.5.16 Synthesis and characterization of ethyl 5-(2-bromophenyl)-1-(dibenzylamino)-1*H*-1,2,3-triazole-4-carboxylate (5p)



5p

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4p** (75.9 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 10 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **5p** in 85% yield (83.4 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.63-7.60 (m, 1H), 7.30-7.19 (m, 7H), 7.11-7.07 (m, 1H), 6.99-6.97 (m, 4H), 5.83-5.81 (m, 1H), 4.52-4.48 (m, 2H), 4.35-4.32 (m, 2H), 4.22-4.17 (m, 2H), 1.15-1.11 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 140.1, 135.7, 135.4, 132.0, 131.0, 129.6, 128.7, 128.2, 127.8, 126.7, 123.5, 61.5 (br), 61.0, 13.9. IR (neat): 3033, 2979, 2859, 1724, 1470, 1454, 1436, 1336, 1193, 1058, 1029, 750, 729, 697, 646 cm^{-1}; HRMS (ESI) calcd m/z for $C_{25}H_{24}BrN_4O_2^+$ $[M+H]^+$: 491.1077, found 491.1073.

2.5.17 Synthesis and characterization of ethyl 5-(3,5-bis(trifluoromethyl)phenyl)-1-(dibenzylamino)-1*H*-1,2,3-triazole-4-carboxylate (5q)

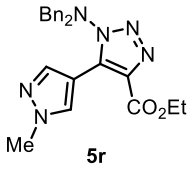


5q

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4q** (87.3 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 9 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded **5q** in 69% yield (75.2 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 60 °C) δ 7.79 (s, 1H), 7.25-7.21 (m, 2H), 7.17-7.13 (m, 4H), 6.93-6.89 (m, 6H), 4.51 (bs, 4H), 4.21 (q, J = 7.1 Hz, 2H), 1.17 (t,

J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 138.9, 135.0, 134.1, 130.7 (q, $^2J_{C\text{-}F}$ = 33.6 Hz), 130.6 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 129.9, 128.9, 128.8, 127.0, 123.04 (m), 123.01 (q, $^1J_{C\text{-}F}$ = 271.2 Hz), 63.2, 61.5, 13.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.5. IR (neat): 3004, 2968, 2945, 1739, 1727, 1455, 1435, 1367, 1277, 1228, 1217, 1203, 1178, 1130, 1109, 1063, 1046, 1029, 902, 755, 699, 680 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{27}H_{23}F_6N_4O_2^+$ $[M+H]^+$: 549.1720, found 549.1715.

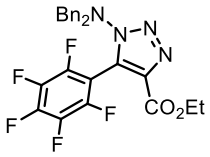
2.5.18 Synthesis and characterization of ethyl 1-(dibenzylamino)-5-(1-methyl-1*H*-pyrazol-4-yl)-1*H*-1,2,3-triazole-4-carboxylate (5r)



5r

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4r** (60.9 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 9 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 1:1) afforded **5r** in 77% yield (63.8 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.74 (s, 1H), 7.65 (s, 1H), 7.20-7.14 (m, 6H), 7.10-7.06 (m, 4H), 4.50 (bs, 4H), 4.34 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6, 139.7, 134.6, 134.4, 132.55, 132.53, 129.8, 128.5, 128.2, 105.4, 62.4, 61.2, 39.0, 14.3. IR (neat): 2974, 2856, 1738, 1710, 1452, 1445, 1365, 1227, 1200, 1176, 1162, 1046, 981, 757, 712, 698, 520 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{23}H_{25}N_6O_2^+$ $[M+H]^+$: 417.2034, found 417.2032.

2.5.19 Synthesis and characterization of ethyl 1-(dibenzylamino)-5-(perfluorophenyl)-1*H*-1,2,3-triazole-4-carboxylate (5s)

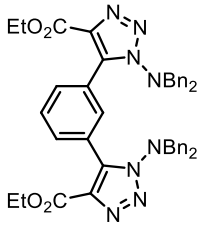


5s

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4s** (78.1 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 9 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) afforded **5s** in 52% yield (52.7 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.20 (m, 6H), 7.05-7.02

(m, 4H), 4.41 (bs, 4H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 145.8-143.1 [m, Ar*C*(2,6)F], 142.5 [dtt, *J* = 257.7, 13.0, 4.9 Hz, Ar*C*(4)F], 138.8-136.0 [m, Ar*C*(3,5)F], 136.8, 134.8, 129.2, 128.8, 128.5, 127.3 (m), 102.1 [td, *J* = 17.3, 4.1 Hz, Ar*C*(1)], 61.70, 61.68, 14.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -134.9 [m, Ar(2,6)*F*], -150.1 [tt, *J* = 20.9, 3.4 Hz, Ar(4)*F*], -162.0 [m, Ar(3,5)*F*]. IR (neat): 3001, 2971, 1737, 1720, 1517, 1508, 1496, 1455, 1377, 1365, 1338, 1310, 1235, 1217, 1186, 1111, 1055, 1029, 985, 854, 821, 755, 709, 700, 684, 521 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{25}H_{20}N_4O_2F_5^+$ $[M+H]^+$: 503.1501, found 503.1504.

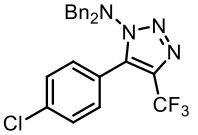
2.5.20 Synthesis and characterization of diethyl 5,5'-(1,3-phenylene)bis[1-(dibenzylamino)-1*H*-1,2,3-triazole-4-carboxylate] (5t)



5t

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 2 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 6.0 equiv.), **1a** (102.7 mg, 0.23 mmol, 2.3 equiv.) and **4t** (52.3 mg, 0.1 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 19 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5t** in 66% yield (49.2 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 50 ºC) δ 7.14-7.09 (m, 4H), 7.06-6.99 (m, 9H), 6.87-6.84 (m, 8H), 6.39 (dd, *J* = 7.8, 1.7 Hz, 2H), 5.88-5.87 (m, 1H), 4.34-4.27 (m, 12H), 1.28 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 140.8, 134.9, 134.8, 131.4, 130.7, 129.7, 128.5, 128.2, 126.7, 124.8, 62.2, 61.1, 14.2. IR (neat): 3035, 2968, 1727, 1455, 1439, 1378, 1364, 1335, 1229, 1216, 1187, 1062, 756, 732, 697, 516 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{44}H_{43}N_8O_4^+$ $[M+H]^+$: 747.3402, found 747.3387.

2.5.21 Synthesis and characterization of *N*,*N*-dibenzyl-5-(4-chlorophenyl)-4-(trifluoromethyl)-1*H*-1,2,3-triazol-1-amine (5u)

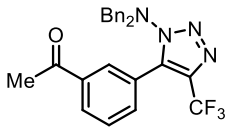


5u

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol,

3.0 equiv.), **1b** (115.0 mg, 0.26 mmol, 1.3 equiv.) and **4d** (67.0 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 11 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) afforded **5u** in 90% yield (79.4 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.13 (m, 8H), 6.98-6.94 (m, 4H), 6.19-6.15 (m, 2H), 4.46 (bs, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2 (q, J = 2.4 Hz), 136.2, 134.7, 134.2 (q, J = 38.4 Hz), 131.1, 129.8, 128.8, 128.5, 128.1, 122.3, 120.6 (q, J = 268.5 Hz), 62.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -59.8. IR (neat): 3030, 2968, 2864, 1739, 1613, 1581, 1492, 1445, 1352, 1184, 1159, 1128, 1092, 1045, 985, 908, 831, 749, 737, 697, 511, 496 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{23}H_{19}ClF_3N_4^+$ $[M+H]^+$: 443.1245, found 443.1242.

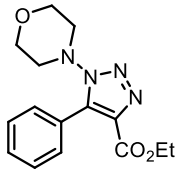
2.5.22 Synthesis and characterization of 1-{3-[1-(dibenzylamino)-4-(trifluoromethyl)-1*H*-1,2,3-triazol-5-yl]phenyl}ethan-1-one (5v)



5v

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1b** (115.0 mg, 0.26 mmol, 1.3 equiv.) and **4m** (68.5 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 15 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded **5v** in 72% yield (64.9 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.96-7.93 (m, 1H), 7.31-7.11 (m, 8H), 6.96-6.94 (m, 4H), 6.54-6.51 (m, 1H), 4.47 (bs, 4H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9, 137.2 (q, J = 2.2 Hz), 136.8, 134.5, 134.2, 134.1 (q, J = 38.3 Hz), 129.73, 129.67, 129.5, 128.7, 128.5, 128.2, 124.4, 120.7 (q, J = 268.4 Hz), 62.7, 26.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -59.6. IR (neat): 3033, 2971, 1739, 1684, 1446, 1432, 1381, 1360, 1230, 1216, 1189, 1158, 1122, 1049, 1003, 798, 748, 739, 697, 687, 589, 524 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{25}H_{22}F_3N_4O^+$ $[M+H]^+$: 451.1740, found 451.1742.

2.5.23 Synthesis and characterization of ethyl 1-morpholino-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (5w)

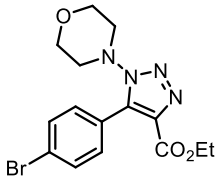


5w

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol,

3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4u** (38.1 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 13 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5w** in 56% yield (34.1 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.46 (m, 5H), 4.35 (q, J = 7.1 Hz, 2H), 3.79-3.76 (m, 4H), 3.38-3.35 (m, 4H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 138.9, 135.1, 130.3, 130.1, 128.1, 125.1, 66.6, 61.2, 55.8, 14.2. IR (neat): 3060, 3004, 2969, 2925, 2855, 1737, 1726, 1715, 1577, 1571, 1491, 1453, 1389, 1372, 1348, 1340, 1287, 1274, 1260, 1215, 1205, 1107, 1063, 1033, 1022, 1005, 912, 850, 791, 764, 755, 699, 689, 559, 510, 478 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{15}H_{19}N_4O_3^+$ $[M+H]^+$: 303.1452, found 303.1454.

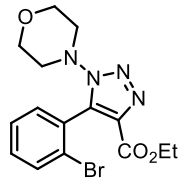
2.5.24 Synthesis and characterization of ethyl 5-(4-bromophenyl)-1-morpholino-1*H*-1,2,3-triazole-4-carboxylate (5x)



5x

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4v** (53.8 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 14 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5x** in 62% yield (47.6 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66-7.62 (m, 2H), 7.40-7.36 (m, 2H), 4.36 (q, J = 7.1 Hz, 2H), 3.80-3.77 (m, 4H), 3.37-3.34 (m, 4H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 137.9, 135.1, 131.9, 131.5, 124.8, 123.9, 66.5, 61.4, 55.9, 14.3. IR (neat): 2966, 2856, 1725, 1712, 1610, 1484, 1454, 1341, 1202, 1105, 1064, 1035, 1023, 998, 914, 851, 822, 788, 560, 487 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{15}H_{18}BrN_4O_3^+$ $[M+H]^+$: 381.0557, found 381.0555.

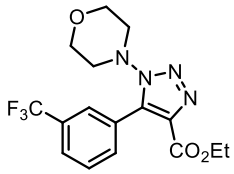
2.5.25 Synthesis and characterization of ethyl 5-(2-bromophenyl)-1-morpholino-1*H*-1,2,3-triazole-4-carboxylate (5y)



5y

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4w** (53.8 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 14 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5y** in 61% yield (46.5 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.71 (m, 1H), 7.47-7.36 (m, 2H), 7.23-7.20 (m, 1H), 4.36-4.20 (m, 2H), 3.76-3.66 (m, 4H), 3.48-3.41 (m, 2H), 3.36-3.29 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 138.5, 136.0, 132.9, 131.41, 131.36, 128.1, 127.3, 123.8, 66.6, 61.2, 55.8, 14.1. IR (neat): 2968, 2928, 1730, 1658, 1563, 1454, 1375, 1200, 1104, 1071, 1031, 1018, 849, 766, 558 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{15}H_{18}BrN_4O_3^+$ $[M+H]^+$: 381.0557, found 381.0556.

2.5.26 Synthesis and characterization of ethyl 1-morpholino-5-[3-(trifluoromethyl)-phenyl]-1*H*-1,2,3-triazole-4-carboxylate (5z)

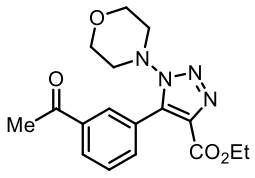


5z

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4x** (51.6 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 16 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5z** in 71% yield (52.7 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.73 (m, 3H), 7.68-7.62 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.80-3.77 (m, 4H), 3.40-3.37 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 137.3, 135.3, 133.9 (q, *J* = 1.5 Hz), 130.7 (q, *J* = 32.8 Hz), 128.7, 127.4 (q, *J* = 4.0 Hz), 126.8 (q, *J* = 3.7 Hz), 125.9, 123.8 (q, *J* = 272.5 Hz), 66.5, 61.5, 55.9, 14.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.8. IR (neat): 2971, 2901, 2867, 1732, 1458, 1328, 1271, 1199, 1179, 1162, 1108, 1071, 1037, 1025, 912, 850, 806, 791, 699, 556 cm^{-}

[1]; HRMS (ESI) calcd *m/z* for $C_{16}H_{18}F_3N_4O_3^+$ $[M+H]^+$: 371.1326, found 371.1328.

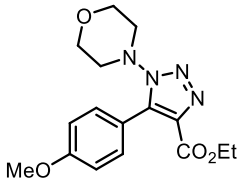
2.5.27 Synthesis and characterization of ethyl 5-(3-acetylphenyl)-1-morpholino-1*H*-1,2,3-triazole-4-carboxylate (5aa)



5aa

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4y** (46.5 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 13 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 2:1) afforded **5aa** in 65% yield (44.6 mg) as a white solid. ^1H NMR (300 MHz, $CDCl_3$) δ 8.15-8.08 (m, 2H), 7.75-7.71 (m, 1H), 7.65-7.59 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.80-3.77 (m, 4H), 3.41-3.38 (m, 4H), 2.66 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 161.0, 137.9, 137.0, 135.2, 134.8, 130.4, 129.9, 128.5, 125.6, 66.6, 61.4, 55.9, 26.7, 14.3. IR (neat): 2979, 2862, 1722, 1685, 1560, 1467, 1278, 1258, 1239, 1198, 1106, 1065, 1037, 1014, 794, 692, 588, 561 cm^{-1}; HRMS (ESI) calcd *m/z* for $C_{17}H_{21}N_4O_4^+$ $[M+H]^+$: 345.1557, found 345.1558.

2.5.28 Synthesis and characterization of ethyl 5-(4-methoxyphenyl)-1-morpholino-1*H*-1,2,3-triazole-4-carboxylate (5ab)

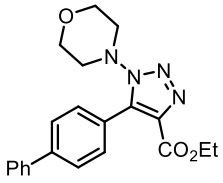


5ab

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4z** (44.1 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 12 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5ab** in 41% yield (27.4 mg) as a white solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.02-6.99 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 3.81-3.78 (m, 4H), 3.38-3.34 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 161.0, 138.8, 134.7, 131.9, 116.8, 113.6, 66.6, 61.2, 55.7, 55.4, 14.3. IR (neat): 2974, 2923, 2860, 2840, 1718, 1612, 1580, 1567, 1505,

1464, 1455, 1446, 1388, 1370, 1342, 1297, 1274, 1253, 1196, 1175, 1122, 1107, 1091, 1065, 1033, 1018, 992, 911, 851, 832, 814, 794, 779, 627, 616, 562, 530, 507 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{16}H_{21}N_4O_4^+$ $[M+H]^+$: 333.1557, found 333.1557.

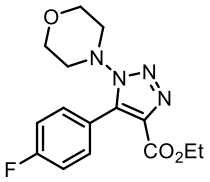
2.5.29 Synthesis and characterization of ethyl 5-([1,1'-biphenyl]-4-yl)-1-morpholino-1*H*-1,2,3-triazole-4-carboxylate (5ac)



5ac

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4aa** (53.3 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 12 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5ac** in 56% yield (42.5 mg) as a white solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.74-7.70 (m, 2H), 7.68-6.64 (m, 2H), 7.60-7.56 (m, 2H), 7.51-7.45 (m, 2H), 7.43-7.37 (m, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.82-3.79 (m, 4H), 3.41-3.38 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 142.9, 140.2, 138.7, 135.1, 130.8, 129.0, 128.0, 127.3, 126.8, 123.7, 66.6, 61.3, 55.9, 14.3. IR (film): 2970, 2927, 2901, 2860, 2361, 1725, 1486, 1456, 1444, 1374, 1344, 1295, 1267, 1227, 1202, 1111, 1065, 1036, 1018, 912, 853, 793, 768, 732, 698, 563 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{21}H_{23}N_4O_3^+$ $[M+H]^+$: 379.1765, found 379.1770.

2.5.30 Synthesis and characterization of ethyl 5-(4-fluorophenyl)-1-morpholino-1*H*-1,2,3-triazole-4-carboxylate (5ad)

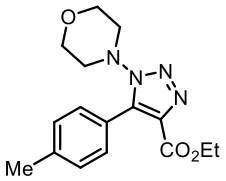


5ad

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4ab** (41.6 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 13 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5ad** in 59% yield (37.6 mg) as a white solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.53-7.48 (m, 2H), 7.22-7.17 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.80-3.77 (m, 4H), 3.38-3.35 (m, 4H), 1.33 (t, *J* = 7.1 Hz,

3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7 (d, $^1J_{C\text{-}F}$ = 251.1 Hz), 161.1, 138.0, 135.0, 132.5 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 121.0 (d, $^4J_{C\text{-}F}$ = 3.6 Hz), 115.5 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 66.6, 61.3, 55.8, 14.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -109.9. IR (neat): 2963, 2934, 2917, 2898, 2860, 1721, 1712, 1615, 1597, 1572, 1501, 1464, 1443, 1394, 1386, 1373, 1340, 1289, 1262, 1254, 1234, 1223, 1199, 1160, 1130, 1111, 1065, 1032, 1022, 1003, 925, 910, 868, 852, 835, 813, 789, 730, 720, 691, 626, 615, 560, 517, 494, 457, 411 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{15}H_{18}FN_4O_3^+$ $[M+H]^+$: 321.1357, found 321.1359.

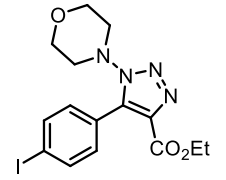
2.5.31 Synthesis and characterization of ethyl 1-morpholino-5-(*p*-tolyl)-1*H*-1,2,3-triazole-4-carboxylate (5ae)



5ae

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4ac** (40.9 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 13 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5ae** in 51% yield (32.2 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.31-7.27 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.80-3.77 (m, 4H), 3.38-3.34 (m, 4H), 2.44 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 140.3, 139.0, 134.9, 130.2, 128.9, 121.9, 66.6, 61.2, 55.8, 21.6, 14.3. IR (neat): 2982, 2901, 2855, 1708, 1618, 1578, 1506, 1465, 1443, 1393, 1370, 1345, 1295, 1266, 1250, 1200, 1187, 1165, 1120, 1107, 1063, 1035, 1013, 990, 915, 849, 819, 794, 773, 730, 720, 703, 694, 561, 515, 496, 486, 427 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{16}H_{21}N_4O_3^+$ $[M+H]^+$: 317.1608, found 317.1612.

2.5.32 Synthesis and characterization of ethyl 5-(4-iodophenyl)-1-morpholino-1*H*-1,2,3-triazole-4-carboxylate (5af)

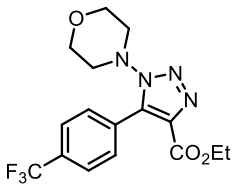


5af

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4ad** (63.2 mg, 0.2 mmol, 1.0 equiv.) in

CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 13 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5af** in 65% yield (55.5 mg) as a white solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.86-7.82 (m, 2H), 7.26-7.22 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.80-3.77 (m, 4H), 3.37-3.34 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 138.0, 137.4, 135.1, 131.9, 124.5, 96.8, 66.5, 61.4, 55.9, 14.3. IR (neat): 2981, 2897, 2856, 1716, 1600, 1485, 1274, 1266, 1200, 1106, 1064, 1035, 1013, 991, 850, 822, 795, 557 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{15}H_{18}IN_4O_3^+$ $[M+H]^+$: 429.0418, found 429.0420.

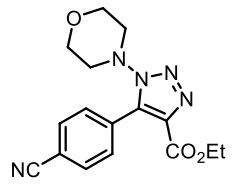
2.5.33 Synthesis and characterization of ethyl 1-morpholino-5-[4-(trifluoromethyl)-phenyl]-1*H*-1,2,3-triazole-4-carboxylate (5ag)



5ag

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4ae** (51.6 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 13 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5ag** in 60% yield (44.4 mg) as a white solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.81-3.78 (m, 4H), 3.40-3.36 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 137.6, 135.4, 132.1 (q, *J* = 32.7 Hz), 130.9, 128.8 (q, *J* = 1.2 Hz), 125.2 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.5 Hz), 66.5, 61.5, 56.0, 14.2. IR (neat): 2979, 2912, 2851, 1728, 1714, 1587, 1453, 1326, 1207, 1162, 1104, 1064, 1034, 1022, 1002, 852, 841, 560 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{16}H_{18}F_3N_4O_3^+$ $[M+H]^+$: 371.1326, found 371.1326.

2.5.34 Synthesis and characterization of ethyl 5-(4-cyanophenyl)-1-morpholino-1*H*-1,2,3-triazole-4-carboxylate (5ah)

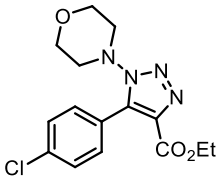


5ah

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol,

3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4af** (43.1 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 13 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 2:1) afforded **5ah** in 40% yield (26.3 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.79 (m, 2H), 7.66-7.62 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.80-3.77 (m, 4H), 3.39-3.36 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 137.1, 135.5, 131.9, 131.2, 129.7, 118.2, 114.0, 66.5, 61.7, 56.0, 14.3. IR (neat): 2971, 2859, 2223, 1731, 1458, 1446, 1394, 1374, 1347, 1266, 1189, 1110, 1096, 1068, 1035, 1022, 911, 853, 835, 793, 728, 558 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{16}H_{18}N_5O_3^+$ $[M+H]^+$: 328.1404, found 328.1406.

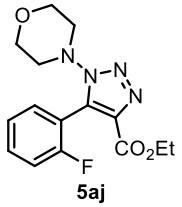
2.5.35 Synthesis and characterization of ethyl 5-(4-chlorophenyl)-1-morpholino-1*H*-1,2,3-triazole-4-carboxylate (5ai)



5ai

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4ag** (44.9 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 16 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5ai** in 64% yield (43.2 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.43 (m, 4H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.80-3.77 (m, 4H), 3.38-3.34 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 137.8, 136.4, 135.1, 131.7, 128.5, 123.4, 66.6, 61.4, 55.9, 14.3. IR (neat): 2968, 2915, 2862, 2372, 2322, 1725, 1713, 1488, 1455, 1202, 1106, 1064, 1036, 1022, 999, 851, 824, 788, 561 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{15}H_{18}ClN_4O_3^+$ $[M+H]^+$: 337.1062, found 337.1064.

2.5.36 Synthesis and characterization of ethyl 5-(2-fluorophenyl)-1-morpholino-1*H*-1,2,3-triazole-4-carboxylate (5aj)

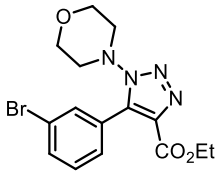


5aj

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4ah** (41.6 mg, 0.2 mmol, 1.0 equiv.) in

CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 11 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5aj** in 69% yield (44.3 mg) as a white solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.57-7.49 (m, 1H), 7.40-7.34 (m, 1H), 7.31-7.18 (m, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.77-3.74 (m, 4H), 3.38-3.35 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6, 160.0 (d, *J* = 250.3 Hz), 136.0, 134.2, 132.3 (d, *J* = 8.4 Hz), 132.1 (d, *J* = 1.9 Hz), 124.0 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 21.5 Hz), 113.9 (d, *J* = 15.0 Hz), 66.7, 61.3, 55.8, 14.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.9. IR (neat): 2974, 2898, 2859, 1728, 1584, 1459, 1377, 1348, 1224, 1194, 1107, 1070, 1038, 918, 849, 820, 772, 563 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{15}H_{18}FN_4O_3^+$ $[M+H]^+$: 321.1357, found 321.1360.

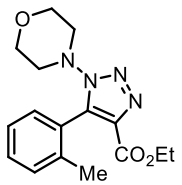
2.5.37 Synthesis and characterization of ethyl 5-(3-bromophenyl)-1-morpholino-1*H*-1,2,3-triazole-4-carboxylate (5ak)



5ak

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4ai** (53.8 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 15 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5ak** in 66% yield (50.3 mg) as a white solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.66-7.62 (m, 2H), 7.46-7.35 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.81-3.78 (m, 4H), 3.38-3.35 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 137.2, 135.2, 133.2, 133.1, 129.6, 129.0, 126.9, 121.9, 66.5, 61.4, 55.9, 14.2. IR (neat): 3057, 2979, 2901, 2862, 1735, 1563, 1265, 1195, 1105, 1070, 1038, 1019, 899, 849, 790, 752, 723, 693, 561 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{15}H_{18}BrN_4O_3^+$ $[M+H]^+$: 381.0557, found 381.0556.

2.5.38 Synthesis and characterization of ethyl 1-morpholino-5-(*o*-tolyl)-1*H*-1,2,3-triazole-4-carboxylate (5al)

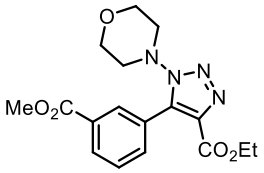


5al

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol,

3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4aj** (40.9 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 15 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5al** in 44% yield (27.6 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.38 (m, 1H), 7.34-7.25 (m, 2H), 7.11-7.08 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.71 (t, *J* = 4.7 Hz, 4H), 3.41-3.25 (m, 4H), 2.11 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 139.0, 137.3, 135.9, 130.2, 130.1, 129.9, 125.7, 125.6, 66.5, 61.1, 55.8, 19.9, 14.1. IR (neat): 2992, 2968, 2923, 2864, 2370, 2325, 1729, 1437, 1375, 1199, 1107, 1031, 769 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{16}H_{21}N_4O_3^+$ $[M+H]^+$: 317.1608, found 317.1609.

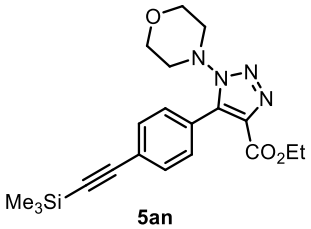
2.5.39 Synthesis and characterization of ethyl 5-[3-(methoxycarbonyl)phenyl]-1-morpholino-1*H*-1,2,3-triazole-4-carboxylate (5am)



5am

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4ak** (49.7 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 15 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 2:1) afforded **5am** in 64% yield (46.4 mg) as a colorless sticky oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20-8.17 (m, 2H), 7.74-7.71 (m, 1H), 7.62-7.57 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 3.80-3.77 (m, 4H), 3.40-3.37 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 160.9, 137.9, 135.2, 134.7, 131.6, 131.1, 130.2, 128.3, 125.4, 66.5, 61.4, 55.9, 52.5, 14.2. IR (neat): 2968, 2862, 1718, 1563, 1437, 1276, 1263, 1236, 1196, 1107, 1064, 1033, 757, 720, 691, 560 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{17}H_{21}N_4O_5^+$ $[M+H]^+$: 361.1506, found 361.1507.

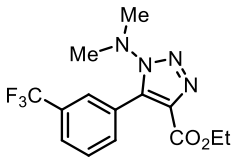
2.5.40 Synthesis and characterization of ethyl 1-morpholino-5-{4-[(trimethylsilyl)-ethynyl]phenyl}-1H-1,2,3-triazole-4-carboxylate (5an)



5an

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4al** (57.3 mg, 0.2 mmol, 1.0 equiv.) in CH_3CN (4 mL) was stirred at room temperature under blue light irradiation for 13 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5an** in 44% yield (35.4 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.56 (m, 2H), 7.45-7.42 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.78-3.75 (m, 4H), 3.36-3.33 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 138.2, 135.2, 131.6, 130.2, 125.05, 124.96, 104.3, 96.7, 66.6, 61.3, 55.8, 14.3, -0.0. IR (neat): 2960, 2894, 2856, 2150, 1720, 1498, 1248, 1211, 1108, 1068, 1035, 1019, 853, 838, 759, 672, 559 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{20}H_{27}N_4O_3Si^+$ $[M+H]^+$: 399.1847, found 399.1846.

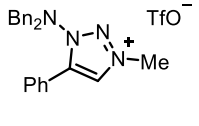
2.5.41 Synthesis and characterization of ethyl 1-(dimethylamino)-5-[3-(trifluoro-methyl)phenyl]-1*H*-1,2,3-triazole-4-carboxylate (5ao)



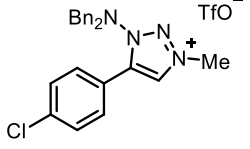
5ao

A mixture of $Ru(bpy)_3(PF_6)_2$ (2.2 mg, 0.0026 mmol, 1 mol%), $NaHCO_3$ (65.5 mg, 0.78 mmol, 3.0 equiv.), **1a** (150.9 mg, 0.338 mmol, 1.3 equiv.) and **4am** (56.2 mg, 0.26 mmol, 1.0 equiv.) in CH_3CN (5.2 mL) was stirred at room temperature under blue light irradiation for 14 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) afforded **5ao** in 71% yield (60.2 mg) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.72-7.61 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.02 (s, 6H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 137.4, 135.3, 133.7 (q, *J* = 1.5 Hz), 130.7 (q, *J* = 32.8 Hz), 128.7, 127.3 (q, *J* = 4.0 Hz), 126.7 (q, *J* = 3.7 Hz), 126.3, 123.9 (q, *J* = 272.5 Hz), 61.4, 47.7, 14.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.7. IR (neat): 2974, 1714, 1576, 1442, 1344, 1329, 1319, 1273, 1182, 1167, 1122, 1096, 1078, 1047, 1027, 905, 807, 698 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{14}H_{16}F_3N_4O_2^+$ $[M+H]^+$: 329.1220, found 329.1219.

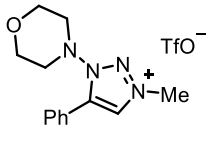
2.6 Synthesis and characterization of 1,2,3-triazolium salts 7



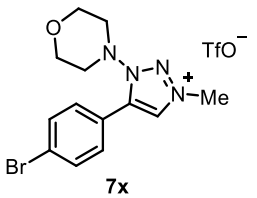
7a



7d



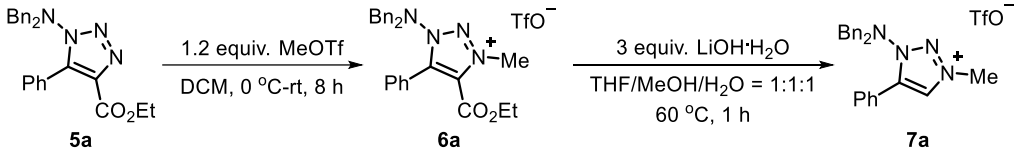
7w



7x

The carbene salts **7** were synthesized by modified previously reported procedures,[17] which are described below.

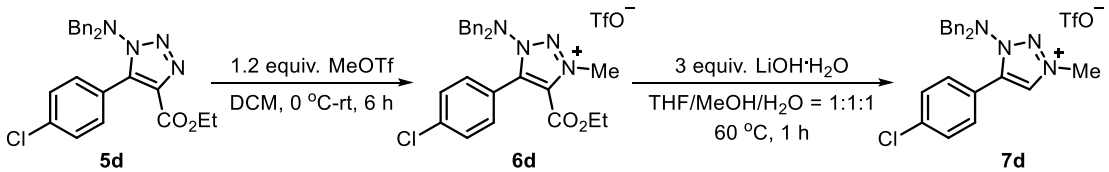
2.6.1 Procedure for the preparation of 1-(dibenzylamino)-3-methyl-5-phenyl-1*H*-1,2,3-triazol-3-ium trifluoromethanesulfonate (7a)



A solution of **5a** (743 mg, 1.8 mmol, 1.0 equiv.) in dry CH_2Cl_2 (30 mL) was cooled to 0 °C under N_2. Then, MeOTf (245 μL, 2.16 mmol, 1.2 equiv.) dissolved in CH_2Cl_2 (5 mL) was added over one hour using a syringe pump. After that, the mixture was stirred at room temperature for additional 7 hours. Evaporation of the organic solvent under the reduced pressure afforded crude **6a**, which was used directly in the next step without further purification.

To a stirred solution of the above crude **6a** in a THF/MeOH/H_2O mixture (15 mL, 1/1/1 volume ratio) was added LiOH·H_2O (227 mg, 5.4 mmol, 3 equiv.). The resulting suspension was stirred at 60 °C for one hour. Then, the reaction was diluted with water, extracted with CH_2Cl_2 and the organic phase was dried over anhydrous Na_2SO_4. Evaporation of the solvents under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: CH_2Cl_2 to CH_2Cl_2/MeOH = 10:1) to afford **7a** in 89% yield (804 mg) over two steps as a colorless sticky oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.49-7.43 (m, 1H), 7.37-7.31 (m, 2H), 7.28-7.17 (m, 8H), 7.06-7.01 (m, 4H), 4.45 (s, 3H), 4.44 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 133.0, 131.5, 129.4, 129.3, 129.1, 129.00, 128.97, 128.8, 121.5, 120.8 (q, J = 320.3 Hz), 62.3, 41.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ -78.3. IR (neat): 3102, 3064, 3035, 1610, 1584, 1493, 1453, 1256, 1223, 1148, 1028, 756, 742, 698, 635, 597, 572, 562, 517, 493 cm^{-1}; HRMS (ESI) calcd m/z for $C_{23}H_{23}N_4^+$ [M-OTf$^-$]$^+$: 355.1917, found 355.1920.

2.6.2 Procedure for the preparation of 5-(4-chlorophenyl)-1-(dibenzylamino)-3-methyl-1*H*-1,2,3-triazol-3-ium trifluoromethanesulfonate (7d)

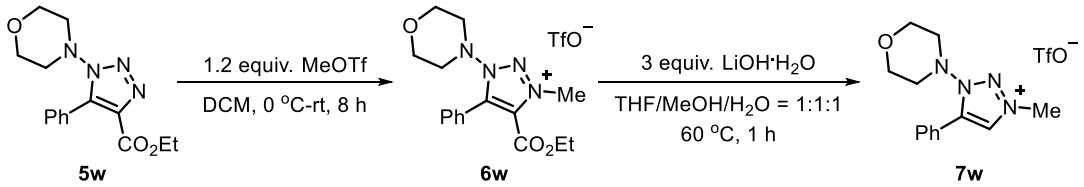


A solution of **5d** (626 mg, 1.4 mmol, 1.0 equiv.) in dry CH_2Cl_2 (20 mL) was cooled to 0 °C

under N_2. Then, MeOTf (190 μL, 1.68 mmol, 1.2 equiv.) dissolved in CH_2Cl_2 (5 mL) was added over one hour using a syringe pump. After that, the mixture was stirred at room temperature for additional 5 hours. Evaporation of the organic solvent under the reduced pressure afforded crude **6d**, which was used directly in the next step without further purification.

To a stirred solution of the above crude **6d** in a THF/MeOH/H_2O mixture (15 mL, 1/1/1 volume ratio) was added LiOH·H_2O (176 mg, 4.2 mmol, 3 equiv.). The resulting suspension was stirred at 60 °C for one hour. Then, the reaction was diluted with water, extracted with CH_2Cl_2 and the organic phase was dried over anhydrous Na_2SO_4. Evaporation of the solvents under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: CH_2Cl_2 to CH_2Cl_2/MeOH = 10:1) to afford **7d** in 89% yield (670 mg) over two steps as a colorless sticky oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.31-7.19 (m, 8H), 7.16-7.12 (m, 2H), 7.05-7.00 (m, 4H), 4.46 (s, 3H), 4.45 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2, 138.0, 133.0, 130.5, 129.6, 129.4, 129.1, 120.7 (q, J = 320.3 Hz), 120.0, 62.5, 41.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -78.4. IR (neat): 3078, 3030, 2971, 1739, 1613, 1488, 1450, 1373, 1365, 1273, 1254, 1220, 1157, 1092, 1027, 827, 821, 756, 702, 637, 572, 517, 503 cm^{-1}; HRMS (ESI) calcd *m/z* for $C_{23}H_{22}ClN_4^+$ $[M\text{-}OTf^-]^+$: 389.1528, found 389.1528.

2.6.3 Procedure for the preparation of 3-methyl-1-morpholino-5-phenyl-1*H*-1,2,3-triazol-3-ium trifluoromethanesulfonate (7w)

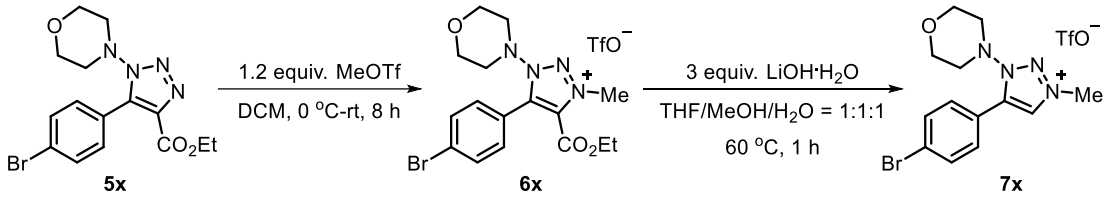


A solution of **5w** (327 mg, 1.08 mmol, 1.0 equiv.) in dry CH_2Cl_2 (10 mL) was cooled to 0 °C under N_2. Then, MeOTf (147 μL, 1.296 mmol, 1.2 equiv.) dissolved in CH_2Cl_2 (4 mL) was added over one hour using a syringe pump. After that, the mixture was stirred at room temperature for additional 7 hours. Evaporation of the organic solvent under the reduced pressure afforded crude **6w**, which was used directly in the next step without further purification.

To a stirred solution of the above crude **6w** in a THF/MeOH/H_2O mixture (6 mL, 1/1/1 volume ratio) was added LiOH·H_2O (136 mg, 3.24 mmol, 3 equiv.). The resulting suspension was stirred at 60 °C for one hour. Then, the reaction was diluted with CH_2Cl_2, dried directly over anhydrous Na_2SO_4, followed by filtration. Evaporation of the solvents under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent:

CH_2Cl_2 to CH_2Cl_2/MeOH = 10:1) to afford **7w** in 71% yield (304 mg) over two steps as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.86-7.82 (m, 2H), 7.56-7.48 (m, 3H), 4.35 (s, 3H), 3.87-3.84 (m, 4H), 3.42-3.39 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2, 131.9, 129.4, 129.3, 128.8, 121.6, 120.6 (q, J = 320.3 Hz), 66.2, 55.9, 41.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -78.5. IR (neat): 3088, 3033, 2864, 1739, 1488, 1367, 1264, 1223, 1204, 1146, 1104, 1033, 1017, 906, 782, 694, 634, 573, 556, 516 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{13}H_{17}N_4O^+$ $[M\text{-}OTf^-]^+$: 245.1397, found 245.1397.

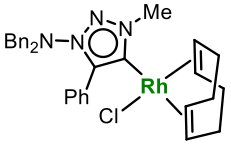
2.6.4 Procedure for the preparation of 5-(4-bromophenyl)-3-methyl-1-morpholino-1*H*-1,2,3-triazol-3-ium trifluoromethanesulfonate (7x)



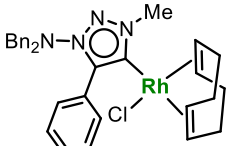
A solution of **5x** (252 mg, 0.66 mmol, 1.0 equiv.) in dry CH_2Cl_2 (15 mL) was cooled to 0 °C under N_2. Then, MeOTf (89.7 μL, 0.792 mmol, 1.2 equiv.) dissolved in CH_2Cl_2 (4 mL) was added over one hour by a syringe pump. After that, the mixture was stirred at room temperature for additional 7 hours. Evaporation of the organic solvent under the reduced pressure afforded crude **6x**, which was used directly in the next step without further purification.

To a stirred solution of the above crude **6x** in a THF/MeOH/H_2O mixture (6 mL, 1/1/1 volume ratio) was added LiOH·H_2O (83.1 mg, 1.98 mmol, 3 equiv.). The resulting suspension was stirred at 60 ºC for one hour. Then, the reaction was diluted with CH_2Cl_2, dried directly over anhydrous Na_2SO_4, followed by filtration. Evaporation of the solvents under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: CH_2Cl_2 to CH_2Cl_2/MeOH = 10:1) to afford **7x** in 61% yield (190 mg) over two steps as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.76-7.73 (m, 2H), 7.67-7.64 (m, 2H), 4.37 (s, 3H), 3.89-3.86 (m, 4H), 3.43-3.40 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.5, 132.8, 130.4, 129.9, 126.9, 120.7, 120.6 (q, J = 320.3 Hz), 66.3, 56.1, 41.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -78.5. IR (neat): 3108, 2971, 2870, 1739, 1603, 1491, 1370, 1277, 1255, 1225, 1158, 1148, 1107, 1075, 1029, 1007, 903, 847, 828, 635, 594, 573, 562, 517, 487 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{13}H_{16}BrN_4O^+$ $[M\text{-}OTf^-]^+$: 323.0502, found 323.0502.

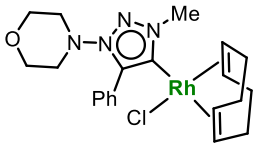
2.7 Synthesis and characterization of rhodium complexes 8



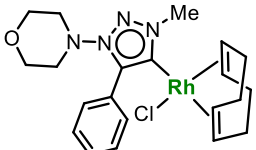
8a



8d



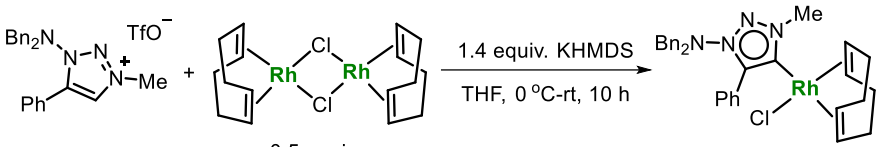
8w



8x

The rhodium complexes **8** were synthesized using modified reported procedures,[18, 19] which are described below.

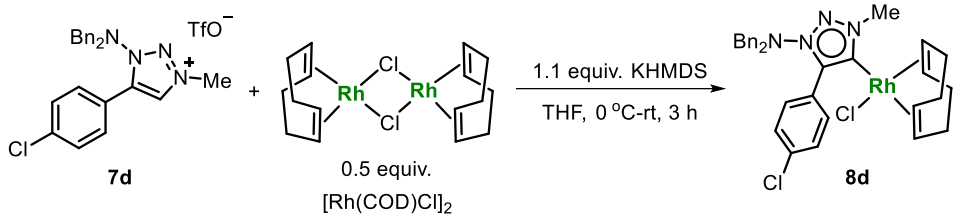
2.7.1 Procedure for the preparation of (1*Z*,5*Z*)-cycloocta-1,5-diene [1-(dibenzylamino)-3-methyl-5-phenyl-2,3-dihydro-1*H*-1,2,3-triazol-4-yl]rhodium(I) chloride (8a)



7a 0.5 equiv. $[Rh(COD)Cl]_2$ **8a**

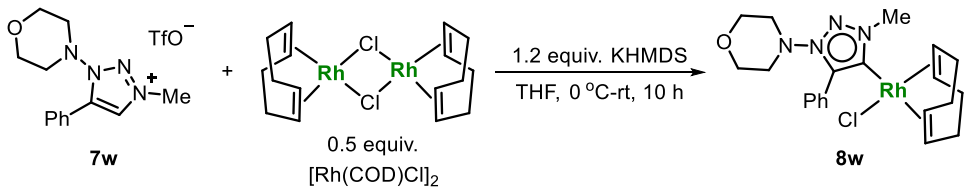
THF (4 mL) was added to a solid mixture of $[Rh(COD)Cl]_2$ (49.3 mg, 0.1 mmol, 0.5 equiv.) and KHMDS (55.9 mg, 0.28 mmol, 1.4 equiv.) under a N_2 atmosphere. The resulting solution was stirred for 5 minutes at 0 °C. Then, **7a** (101 mg, 0.2 mmol, 1.0 equiv.) was added in one portion. The resulting mixture was stirred at 0 °C for one hour, then stirred at room temperature for an additional 9 hours and filtered through a pad of celite. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2/MeOH = 100:1) to afford **8a** in 60% yield (71.6 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 55 ºC) δ 7.88-7.85 (m, 2H), 7.36-7.32 (m, 3H), 7.23-7.18 (m, 6H), 7.00 (bs, 4H), 4.93 (bs, 2H), 4.54 (s, 3H), 4.23 (bs, 4H), 2.76-2.72 (m, 2H), 2.25-1.65 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 55 ºC) δ 171.8 (d, J = 46.9 Hz), 143.2 (d, J = 2.6 Hz), 134.2, 130.4, 129.4, 128.9, 128.8, 128.5, 127.5, 127.4, 96.6 (d, J = 7.1 Hz), 68.2 (br), 61.6, 42.8, 32.7 (br), 29.1. IR (film): 3030, 2932, 2912, 2872, 2827, 2213, 1496, 1454, 1430, 1296, 1279, 1260, 1065, 1028, 907, 863, 753, 725, 694, 643, 630, 615, 607, 568, 524, 499, 448 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{31}H_{34}ClN_4NaRh^+$ $[M+Na]^+$: 623.1419, found 623.1424.

2.7.2 Procedure for the preparation of (1*Z*,5*Z*)-cycloocta-1,5-diene [5-(4-chlorophenyl)-1-(dibenzylamino)-3-methyl-2,3-dihydro-1*H*-1,2,3-triazol-4-yl]rhodi-um(I) chloride (8d)



THF (2 mL) was added to a solid mixture of $[Rh(COD)Cl]_2$ (24.7 mg, 0.05 mmol, 0.5 equiv.) and KHMDS (21.9 mg, 0.11 mmol, 1.1 equiv.) under a N_2 atmosphere. The resulting solution was stirred for 10 minutes at 0 °C. Then a solution of **7d** (53.9 mg, 0.1 mmol, 1.0 equiv.) dissolved in THF (1 mL) was added dropwise over 30 minutes using a syringe pump. The mixture was further stirred at 0 °C for 30 minutes, and then at room temperature for an additional 2 hours. After that, the reaction mixture was filtered through a pad of celite. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2/MeOH = 100:1) to afford **8d** in 60% yield (38.4 mg) as a yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$, 55 °C) δ 7.83-7.80 (m, 2H), 7.30-7.28 (m, 2H), 7.24-7.20 (m, 6H), 6.97 (bs, 4H), 4.94 (bs, 2H), 4.55 (s, 3H), 4.24 (bs, 4H), 3.01 (bs, 1H), 2.50-2.18 (m, 4H), 1.82-1.50 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$, 55 °C) δ 172.3 (d, J = 46.8 Hz), 142.4, 135.1, 134.1, 131.6, 129.5, 128.9, 128.7, 127.7, 126.0, 97.1 (d, J = 7.1 Hz), 68.5 (br), 62.0 (br), 42.9, 33.4 (br), 32.4 (br), 29.1. IR (film): 3062, 3031, 2988, 2931, 2913, 2873, 2827, 1711, 1602, 1519, 1496, 1455, 1430, 1362, 1331, 1305, 1290, 1268, 1220, 1090, 1065, 1029, 1015, 994, 831, 816, 747, 735, 728, 699, 679, 639, 602, 528, 503, 485 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{31}H_{33}ClN_4Rh^+$ $[M\text{-}Cl]^+$: 599.1443, found 599.1443.

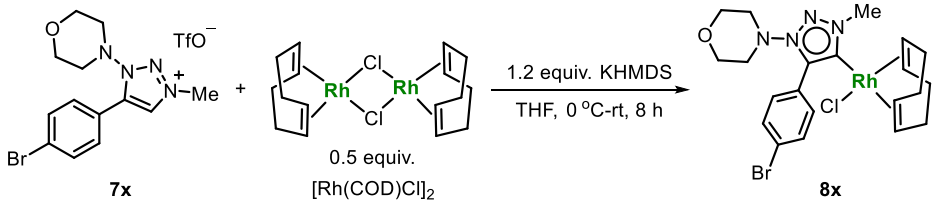
2.7.3 Procedure for the preparation of (1*Z*,5*Z*)-cycloocta-1,5-diene (3-methyl-1-morpholino-5-phenyl-2,3-dihydro-1*H*-1,2,3-triazol-4-yl)rhodium(I) chloride (8w)



THF (4 mL) was added to a solid mixture of $[Rh(COD)Cl]_2$ (49.3 mg, 0.1 mmol, 0.5 equiv.) and KHMDS (47.9 mg, 0.24 mmol, 1.2 equiv.) under a N_2 atmosphere. The resulting solution was stirred at 0 °C for 5 minutes. Then **7w** (78.9 mg, 0.2 mmol, 1.0 equiv.) was added in one portion. The resulting mixture was stirred at 0 °C for one hour, and then at room temperature

for an additional 9 hours. Then, the reaction mixture was filtered through a pad of celite. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2/MeOH = 50:1) to afford **8w** in 70% yield (68.3 mg) as a yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$, 55 °C) δ 8.48-8.46 (m, 2H), 7.53-7.50 (m, 2H), 7.47-7.45 (m, 1H), 5.04-4.97 (m, 2H), 4.53 (s, 3H), 3.82 (t, *J* = 4.7 Hz, 4H), 3.31-3.09 (m, 5H), 2.62 (bs, 1H), 2.32-2.28 (m, 3H), 1.86-1.74 (m, 4H), 1.64-1.58 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, 55 °C) δ 172.4 (d, *J* = 46.7 Hz), 140.5 (d, *J* = 2.5 Hz), 130.0, 129.3, 128.0, 127.5, 96.9, 69.1 (br), 67.8 (br), 66.5, 55.8, 42.8, 33.5 (br), 32.0 (br), 29.1 (br). IR (film): 2962, 2929, 2913, 2865, 2827, 1710, 1456, 1430, 1403, 1331, 1306, 1264, 1215, 1108, 1071, 1060, 1016, 994, 911, 863, 849, 768, 732, 693, 564, 487, 449 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{21}H_{28}ClN_4NaORh^+$ $[M+Na]^+$: 513.0899, found 513.0888.

2.7.4 Procedure for the preparation of (1*Z*,5*Z*)-cycloocta-1,5-diene [5-(4-bromo- phenyl)-3-methyl-1-morpholino-2,3-dihydro-1*H*-1,2,3-triazol-4-yl]rhodium(I) chloride (8x)

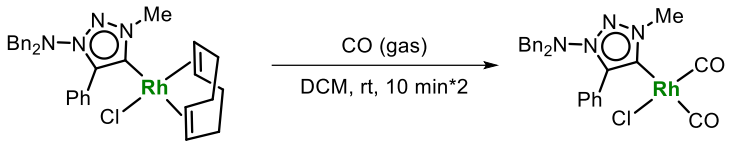


THF (4 mL) was added to a solid mixture of $[Rh(COD)Cl]_2$ (49.3 mg, 0.1 mmol, 0.5 equiv.) and KHMDS (47.9 mg, 0.24 mmol, 1.2 equiv.) under a N_2 atmosphere. The resulting solution was stirred at 0 °C for 5 minutes. Then **7x** (94.7 mg, 0.2 mmol, 1.0 equiv.) was added in one portion. The resulting mixture was stirred at 0 °C for one hour, and then stirred at room temperature for additional 7 hours. Then, the reaction mixture was filtered through a pad of celite. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2/MeOH = 50:1) to afford **8x** in 81% yield (92.6 mg) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47-8.43 (m, 2H), 7.69-7.65 (m, 2H), 5.07 (bs, 1H), 4.95 (bs, 1H), 4.53 (s, 3H), 3.85 (t, *J* = 4.7 Hz, 4H), 3.27-3.19 (m, 5H), 2.60 (bs, 1H), 2.36-2.28 (m, 3H), 1.89-1.87 (m, 4H), 1.67-1.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6 (d, *J* = 46.8 Hz), 139.4 (d, *J* = 2.5 Hz), 131.39, 131.35, 126.2, 123.9, 97.5 (d, *J* = 7.2 Hz), 97.2 (d, *J* = 7.3 Hz), 69.3 (d, *J* = 14.6 Hz), 68.0 (d, *J* = 14.5 Hz), 66.5, 55.8, 43.0, 33.5, 32.1, 29.5, 28.9. IR (film): 2959, 2929, 2916, 2862, 2829, 2218, 1702, 1594, 1455, 1429, 1415, 1391, 1304, 1286, 1263, 1108, 1070, 1008, 909, 864, 849, 826, 724, 685, 671, 644, 633, 622, 613, 563, 516, 489 cm^{-1}; HRMS (ESI) calcd *m*/*z* for $C_{21}H_{27}BrClN_4NaORh^+$ $[M+Na]^+$: 591.0004,

found 590.9997.

2.8 Synthesis and characterization of rhodium dicarbonyl complexes 9

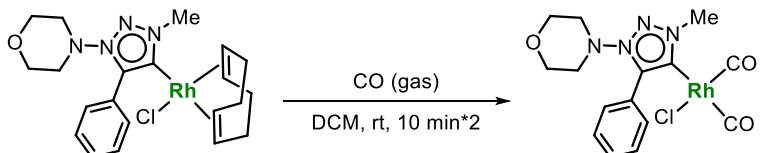
2.8.1 Procedure for the preparation of [1-(dibenzylamino)-3-methyl-5-phenyl-2,3-dihydro-1*H*-1,2,3-triazol-4-yl]rhodium(I) chloride dicarbonyl (9a)



8a **9a**

CO was bubbled through a solution of **8a** (39.2 mg, 0.0652 mmol, 1.0 equiv.) in DCM (10 mL) for 10 min. The solvent was then removed under reduced pressure and the residue was dried in high vacuum. In order to ensure reaction completion, the residue was again dissolved in DCM (10 mL) and CO was bubbled through the solution for a second time for an additional 10 min. After this, the solvent was removed until residual volume of approximately 1 mL, and hexane (40 mL) was slowly added to form a suspension. Filtration of the reaction mixture through a pad of celite afforded a light yellow solution. The solvent was then removed under reduced pressure, and the residue was dried in high vacuum to afford **9a** in 75% yield (26.8 mg) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.21 (m, 11H), 7.03-6.99 (m, 4H), 4.43 (s, 3H), 4.30 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.9 (d, J = 54.2 Hz), 183.0 (d, J = 75.3 Hz), 162.1 (d, J = 39.5 Hz), 146.1 (d, J = 3.1 Hz), 133.9, 130.6, 129.6, 129.3, 129.0, 128.7, 127.8, 126.3, 61.8, 43.5. IR (film): 2953, 2067, 1990, 1771, 1644, 1431, 1361, 1263, 1156, 1027, 861, 800, 735, 696, 568, 523, 494 cm^{-1}; HRMS (ESI) calcd m/z for $C_{25}H_{22}N_4O_2Rh^+$ [M-Cl]$^+$: 513.0792, found 513.0798.

2.8.2 Procedure for the preparation of [5-(4-bromophenyl)-3-methyl-1-morpholino-2,3-dihydro-1*H*-1,2,3-triazol-4-yl]rhodium(I) chloride dicarbonyl (9x)



8x **9x**

CO was bubbled through a solution of **8x** (82.6 mg, 0.145 mmol, 1.0 equiv.) in DCM (20 mL) for 10 min. The solvent was then removed under reduced pressure, and the residue was dried in high vacuum. Once again the residue was dissolved in DCM (20 mL), and CO was bubbled through the solution for an additional 10 minutes ensuring the reaction completion.

The solvent was then removed until the residual volume of approximately 2 mL, and hexane (80 mL) was added to to form a suspension. Filtration of the reaction mixture afforded a light yellow solution. The solvent was then removed under reduced pressure and the residue was dried in high vacuum to afford **9x** in 72% yield (53.7 mg) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99-7.96 (m, 2H), 7.66-7.63 (m, 2H), 4.40 (s, 3H), 3.87-3.84 (m, 4H), 3.32-3.29 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.5 (d, J = 54.3 Hz), 182.9 (d, J = 75.1 Hz), 162.9 (d, J = 39.7 Hz), 142.2 (d, J = 3.1 Hz), 131.8, 131.7, 125.1, 124.8, 66.4, 55.9, 43.6. IR (film): 2957, 2071, 1992, 1456, 1392, 1261, 1158, 1109, 1073, 1009, 912, 826, 564 cm^{-1}; HRMS (ESI) calcd *m/z* for $C_{15}H_{15}BrN_4O_3Rh^+$ $[M\text{-}Cl]^+$: 480.9377, found 480.9372.

3. Stern-Volmer fluorescence quenching studies

Fluorescence quenching experiments were performed on JASCO FP-8500 Fluorescence Spectrometer. The measurements were carried out mixing a 0.05 mM solution of $Ru(bpy)_3(PF_6)_2$ in MeCN (3 mL) with the appropriate amount of quencher in a quartz cuvette equipped with a septum under nitrogen atmosphere. The solvent used was previously degassed with nitrogen for 10 minutes. All solutions were irradiated at λ = 452 nm (absorption maximum of $Ru(bpy)_3(PF_6)_2$) and the emission intensity at 593 nm was observed (emission maximum). Plots were constructed according to the Stern-Volmer equation and K_{sv} was calculated[20].

Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + K_{sv}[Q]$$

Increasing amounts of reagent **1a** were added to a solution of $Ru(bpy)_3(PF_6)_2$ in MeCN (0.05 mM). After each addition, an emission spectrum of the solution was recorded. The results in Figure S1 indicate that **1a** quenches emission of $[Ru(bpy)_3]^{2+}$*.

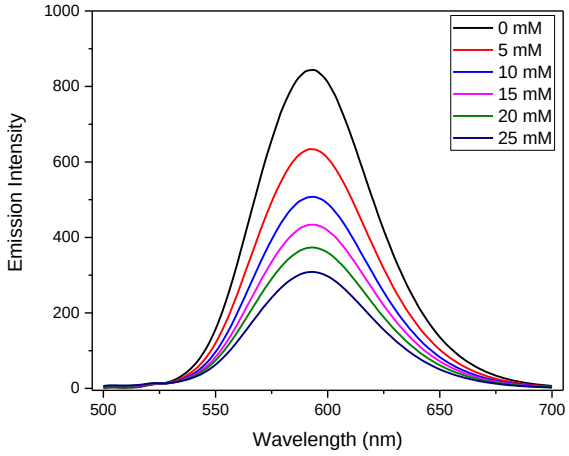


Figure S1. Emission spectrum of $[Ru(bpy)_3]_2^{+}$* varying concentration of **1a**.

The Stern-Volmer plot reported in Figure S2 shows a linear correlation between the amounts of **1a** and the ratio I_0/I with a constant K_{sv} of 67.08 M^{-1}.

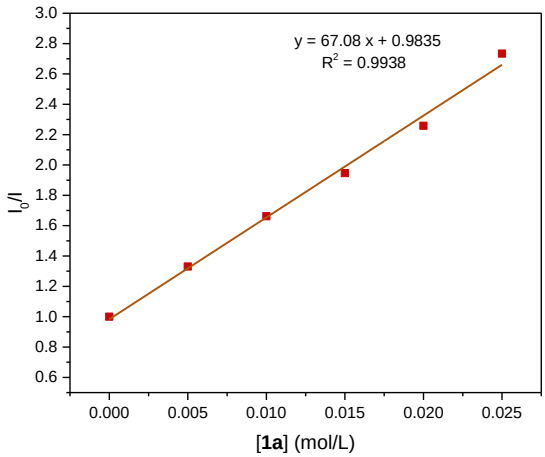


Figure S2. Stern-Volmer plot of $Ru(bpy)_3(PF_6)_2$ quenching with varying [**1a**].

4. Cyclic voltammetry measurements

Cyclic voltammetry data[21] was measured using VersaSTAT 4 Potentiostat Galvanostat electrochemical analyser. All cyclic voltammetry experiments were performed under argon atmosphere. The cell setup consisted of a glassy carbon working electrode, platinum coil counter electrode, and Ag/AgCl reference electrode. All measurements were performed in dry MeCN or DMSO, which had been degassed by bubbling N_2 for 30 minutes prior to measurements. 0.1 M tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte. Unless otherwise stated, each measurement consisted of an oxidative scan, followed by the reverse reductive scan. Ferrocene was added at the end of the measurements as an internal standard to determine the precise potential scale. Potential values are given versus the saturated calomel electrode (SCE). Irreversible reduction waves were obtained; therefore, the reduction potentials were obtained from the maximum, $E_{p,max}$.

*Sulfonium salt **1a**:*

The cyclic voltammogram for a solution of **1a** in DMSO [0.1 M $(n\text{-}Bu)_4NPF_6$] is shown in Figure S3. The sweep rate is 500 mV/s. The reduction potential ($E_{1/2}^{red}$) was normalized to the ferrocene/ferrocenium (Fc/Fc+) redox couple and then converted to saturated calomel electrode (SCE) by adding 0.435 V.[22] The reduction potential of **1a** was determined to be −0.939 V *vs* Fc/Fc^+ or −0.504 V *vs* SCE.

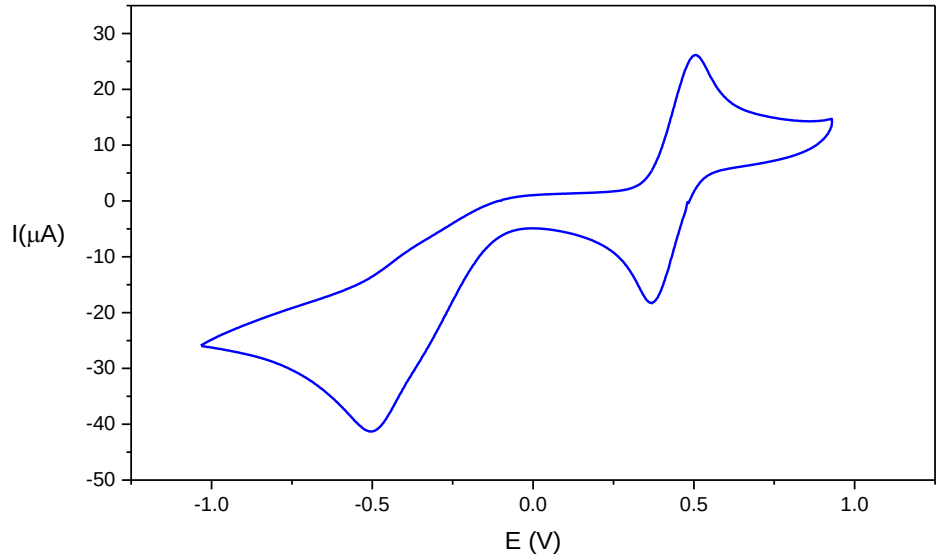


Figure S3. Cyclic voltammogram of **1a** with ferrocene as an internal standard

*Sulfonium salt **1e**:*

The cyclic voltammogram for a solution of **1e** in CH_3CN [0.1 M $(n\text{-}Bu)_4NPF_6$] is shown in Figure S4. The sweep rate is 200 mV/s. The reduction potential ($E_{1/2}^{red}$) was normalized to the ferrocene/ferrocenium (Fc/Fc+) redox couple and then converted to saturated calomel electrode (SCE) by adding 0.382 V.[23] The reduction potential of **1e** was determined to be −1.088 V *vs* Fc/Fc^+ or −0.706 V *vs* SCE.

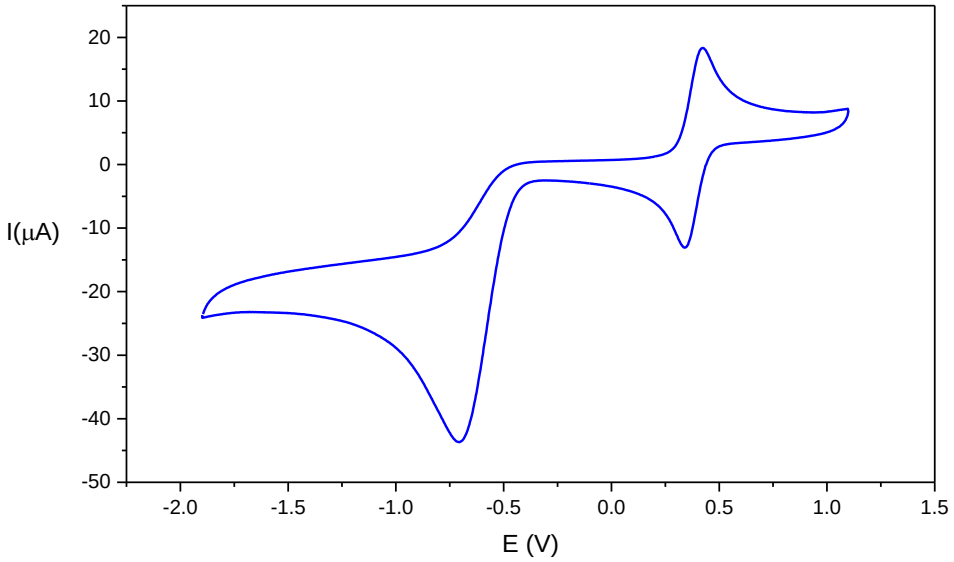


Figure S4. Cyclic voltammogram of **1e** with ferrocene as an internal standard

5. Quantum yield measurement

5.1 Determination of the photon flux

The photon flux of the LED setup was determined using standard ferrioxalate actinometry[23]

following a modified literature procedure.[24]

Solutions prepared:

0.05 M H_2SO_4 aqueous solution:

In a 1L volumetric flask, 2.81 mL of conc. H_2SO_4 (95% w/w, 17.8 M) was added to 400 mL of deionized water. Then, deionized water was added until the 1L graduation mark was reached.

0.006 Mferrioxalate solution:

In a darkened room, potassium ferrioxalate ($K_3FeC_2O_4 \cdot 3H_2O$, 737 mg, 1.5 mmol) was added to a 250 mL volumetric flask. Then, the above 0.05 M H_2SO_4 aqueous solution was added until the 250 mL graduation mark was reached. The mixture was shaken violently to ensure homogeneity. Then, the solution was covered by aluminum foil and stored in the dark.

Buffer solution:

To a 100 mL volumetric flask was added NaOAc (7.30 g, 89.0 mmol) and 50 mL deionized water. Then, 1.0 mL of conc. H_2SO_4 (95% w/w, 17.8 M) was added dropwise. After this, deionized water was added until the 100 mL graduation mark was reached. The mixture was completely dissolved by using ultrasonic cleaner for 5 minutes.

Measurements:

While being careful to minimize exposure to background light, 4.0 mL of the 0.006 M ferrioxalate solution was added to a 10 mL Schlenk tube. The tube was positioned 5 cm from a single PR160L-440 nm Kessil LED lamp (λ_{max} = 440 nm, 25% of the maximum intensity) and irradiated for 10 seconds. Immediately after irradiation, 0.50 mL of the solution was transferred to a foil-covered 10 mL volumetric flask containing 10 mg of 1,10-phenanthroline and 0.50 mL of the buffer solution. Deionized water was then added to the flask to make a total volume of 10 mL. The flask was shaken to ensure efficient mixing and the solution was stored in the dark for approximately one hour. 1.0 mL of the solution was transferred to a quartz cuvette (1.0 cm path length) and the absorbance at λ = 510 nm was measured by UV/Vis spectroscopy (Figure S5). A non-irradiated sample and other samples with different irradiation time (20 s, 30 s) were also prepared and the absorbance at 510 nm was measured.

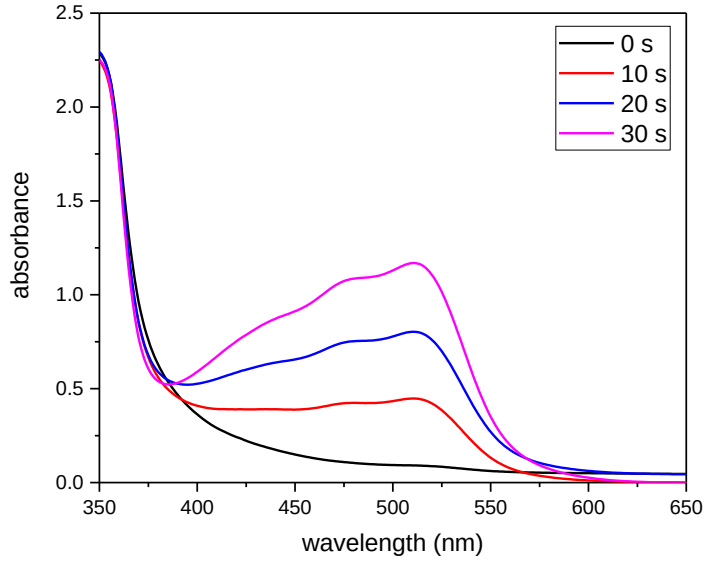


Figure S5. Actinometry: UV/Vis spectra of ferrioxalate/1,10-phenanthroline solutions

The moles of ferrous ions formed in the irradiated volume are given by

$$\text{moles } Fe^{2+} = \frac{V_1 \times V_3 \times \Delta A(510\ nm)}{V_2 \times l \times \varepsilon(510\ nm)}$$

where V_1 is the irradiated volume (4 mL), V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (0.5 mL), V_3 is the final volume after complexation with phenanthroline (10 mL), l is the optical pathlength of the irradiation cell (1.0 cm), ΔA(510 nm) is the difference in absorbance at λ = 510 nm between the irradiated and non-irradiated ferrioxalate/1,10-phenanthroline solutions, and ε(510 nm) is the molar absorptivity of the $Fe(phen)_3^{2+}$ complex at λ = 510 nm (11,100 $L \cdot mol^{-1} \cdot cm^{-1}$).

The moles of Fe^{2+} were plotted as a function of time (Figure S6):

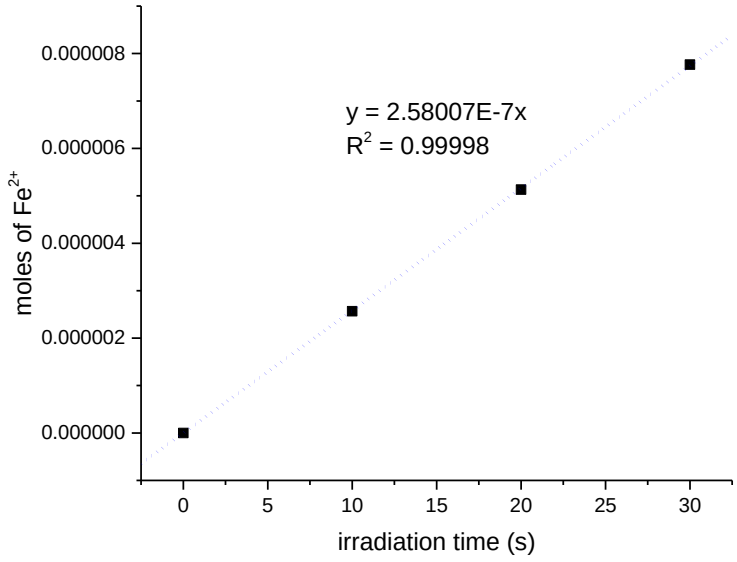


Figure S6. Actinometry: Moles of Fe^{2+} formed vs. irradiation time

The photon flux was then calculated using:

$$\text{photon flux} = \frac{moles\ Fe^{2+}}{\Phi t f}$$

where Φ is the quantum yield of the ferrioxalate actinometer (approximated as 1.11, which was reported for a 0.006 M solution at λ = 436 nm),[23] t is the irradiation time, and f is the fraction of light absorbed at 440 nm (0.3821).

The fraction of light absorbed was determined by the following equation:

$$f = 1 - 10^{-A}$$

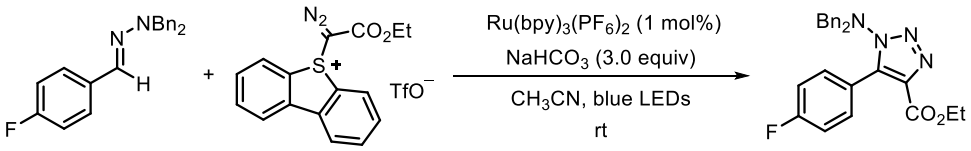
where A is the measured absorbance (0.2091) of the 0.006 M solution of potassium ferrioxalate at 440 nm.

Table S8. Calculation of radiant flux.

irradiation time (s)	Absorbance (A)	ΔA	moles Fe^{2+} (mol)	radiant flux (Einstein/s)
non-irradiation	0.091	–	–	–
10	0.448	0.356	2.56685E-06	6.052E-07
20	0.803	0.712	5.12959E-06	6.048E-07
30	1.169	1.077	7.76497E-06	6.103E-07

The average radiant flux is 6.07×10^{-7} Einstein/s.

5.2 Determination of the quantum yield



To a 10 mL oven-dried Schlenk tube equipped with a stirring bar was added $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv) and **4c** (63.7 mg, 0.2 mmol, 1.0 equiv). The Schlenk tube was then evacuated and backfilled with N_2 three times after which CH_2Br_2 (0.2 mmol, 14.0 μL, 1.0 equiv) and acetonitrile (4 mL) were added under N_2. The tube was positioned 5 cm from a single PR160L-440 nm Kessil LED lamp (λ_{max} = 440 nm, 25% of the maximum intensity). The reaction was stirred at 500 rpm and approximate 0.1 mL reaction mixture was taken by a syringe every 5 minutes, which was diluted with $CDCl_3$, and comparison of the integration of the internal standard CH_2Br_2 (4.97 ppm, s, 2H) with that of the formed product (4.20 ppm, q, J = 7.1 Hz, 2H) revealed yields of **5c**.

The quantum yield (Φ) was then calculated using:

$$\Phi = \frac{moles\ of\ product}{photon\ flux \cdot t \cdot f}$$

where flux is the photon flux determined by ferrioxalate actinometry (6.07×10^{-7} Einstein/s), t is the time, and f is the fraction of light absorbed by $Ru(bpy)_3(PF_6)_2$ at 440 nm.

A 1.0×10^{-4} M solution of $Ru(bpy)_3(PF_6)_2$ in acetonitrile was prepared, and the absorbance of the solution at 440 nm was 2.168. The fraction of light absorbed at 440 nm was calculated:

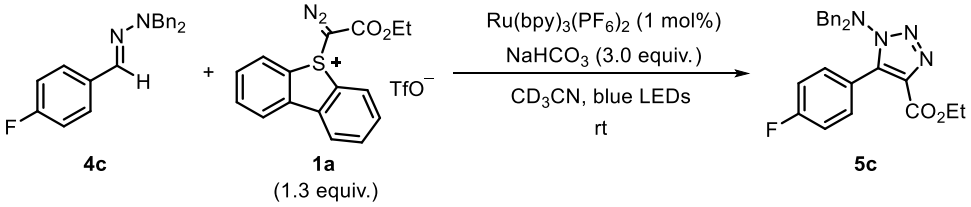
$$f = 1 - 10^{-A} = 0.9932$$

Table S9. Calculation of quantum yield.

reaction time (s)	yield (%)	moles of product (mol)	quantum yield Φ
300	17	3.40E-05	0.188
600	32	6.40E-05	0.177
900	47	9.40E-05	0.173
1200	68	1.36E-04	0.188
1500	88	1.76E-04	0.195

The average quantum yield is 0.18.

6. Light on/off experiment



To a 10 mL oven-dried Schlenk tube equipped with a stirring bar was added $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (116.1 mg, 0.26 mmol, 1.3 equiv.) and **4c** (63.7 mg, 0.2 mmol, 1.0 equiv.). The Schlenk tube was then evacuated and backfilled with N_2 three times after which CH_2Br_2 (0.2 mmol, 14.0 μL, 1.0 equiv.) and CD_3CN (4 mL) were added under N_2. Then, the reaction tube was placed in a photoreactor equipped with blue LED strips (wavelength range: 430-435 nm, 12 W). A mini-fan was kept on top to maintain room temperature. The reaction mixture was stirred at room temperature, and the light was turned on and off every 15 minutes. During each on/off shift, approximate 0.4 mL reaction mixture was taken by a syringe, which was directly transferred into an NMR tube over a syringe filter (additional CD_3CN was added if it is necessary). Comparison of the integration of the internal standard CH_2Br_2 (5.09 ppm, s, 2H) with that of the formed product (4.12 ppm,

q, J = 7.1 Hz, 2H) revealed yields of **5c** (Figure S7).

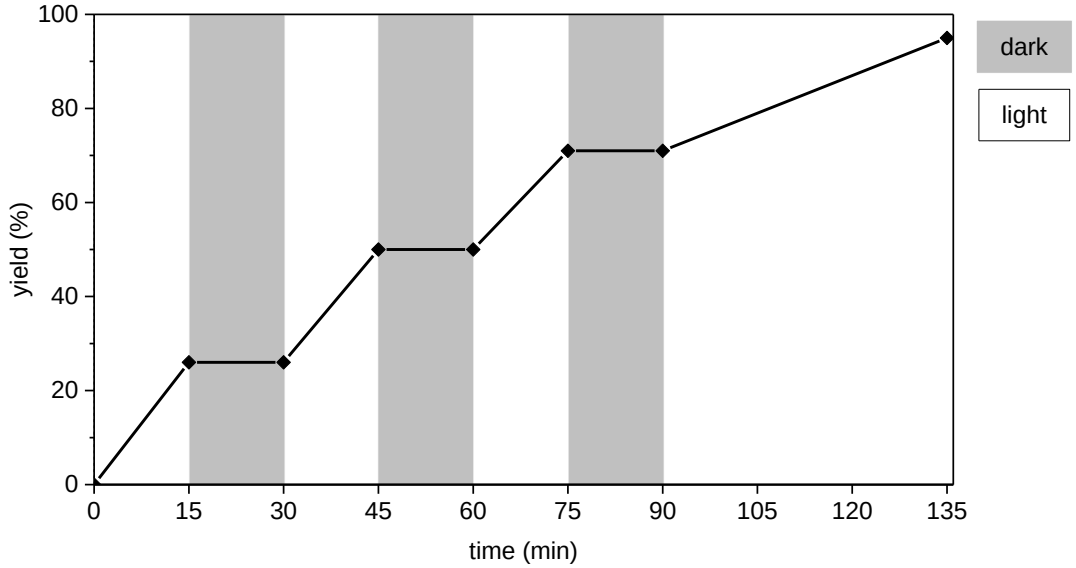
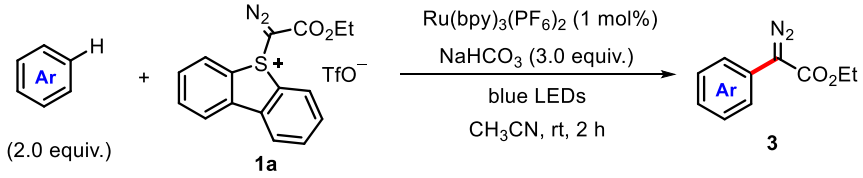


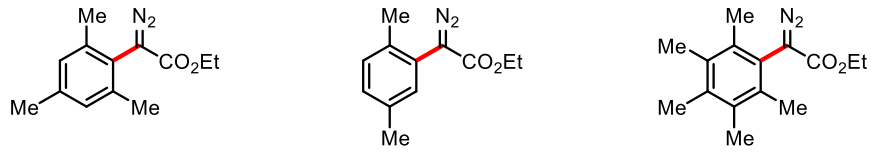
Figure S7. Time profile of the reaction with and without light

The light on/off experiment verified the necessity of continuous irradiation of visible light, which suggested that chain propagation might not be involved in the mechanistic pathway.

7. Other control experiments

7.1 Photoredox-catalyzed C-H diazomethylation of arenes

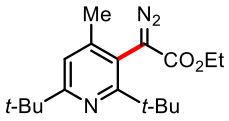




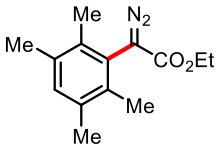
3a, 73%

3b, 58%[a]

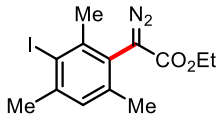
3c, 75%



3d, 44%[b]



3e, 59%



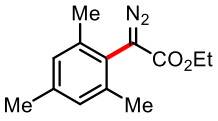
3f, 52%

[a] 10 equiv. *p*-xylene was used. [b] 3 equiv. 2,6-di-*tert*-butyl-4-methylpyridine was used.

Typical procedure for the photoredox catalyzed C-H diazomethylation of arenes: To a 10 mL oven-dried Schlenk tube equipped with a stirring bar was added $Ru(bpy)_3(PF_6)_2$ (1.7 mg,

0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.) and **1a** (89.3 mg, 0.2 mmol, 1.0 equiv.). The Schlenk tube was then evacuated and backfilled with N_2 three times after which CH_3CN (2 mL) and arenes (0.4 mmol, 2.0 equiv.) were added under N_2. After that, the reaction mixture was placed in a photoreactor equipped with blue LED strips (wavelength range: 430-435 nm, 9 W). A mini-fan was kept on top to maintain room temperature. Two hours later, the reaction mixture was passed through a short pad of celite and eluted with dichloromethane. The combined solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford **3**.

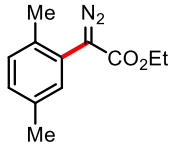
7.1.1 Synthesis and characterization of ethyl 2-diazo-2-mesitylacetate (3a)



3a

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (89.3 mg, 0.2 mmol, 1.0 equiv.) and mesitylene (55.6 μL, 0.4 mmol, 2.0 equiv.) in CH_3CN (2 mL) was stirred at room temperature with blue light for 2 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **3a** in 73% yield (33.8 mg) as a yellowish oil. ^1H NMR (300 MHz, $CDCl_3$) δ 6.87 (s, 2H), 4.19 (q, J = 7.2 Hz, 2H), 2.22 (s, 3H), 2.21 (s, 6H), 1.21 (t, J = 7.2 Hz, 3H). The spectroscopic data are in agreement with those previously reported.[25]

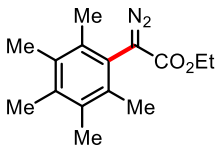
7.1.2 Synthesis and characterization of ethyl 2-diazo-2-(2,5-dimethylphenyl)acetate (3b)



3b

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (89.3 mg, 0.2 mmol, 1.0 equiv.) and *p*-xylene (247 μL, 2.0 mmol, 10.0 equiv.) in CH_3CN (2 mL) was stirred at room temperature with blue light for 2 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **3b** in 58% yield (25.4 mg) as a yellowish oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 7.15-7.13 (m, 1H), 7.08-7.06 (m, 1H), 4.29 (q, J = 7.2 Hz, 2H), 2.32 (s, 3H), 2.26 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). The spectroscopic data are in agreement with those previously reported.[25]

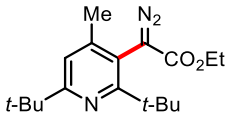
7.1.3 Synthesis and characterization of ethyl 2-diazo-2-(2,3,4,5,6-pentamethylphenyl) acetate (3c)



3c

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (89.3 mg, 0.2 mmol, 1.0 equiv.) and 1,2,3,4,5-pentamethylbenzene (59.3 mg, 0.4 mmol, 2.0 equiv.) in CH_3CN (2 mL) was stirred at room temperature with blue light for 2 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **3c** in 75% yield (39.3 mg) as a yellowish oil. ^1H NMR (300 MHz, $CDCl_3$) δ 4.27 (q, J = 7.1 Hz, 2H), 2.27 (s, 6H), 2.25 (s, 3H), 2.23 (s, 6H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0 (br), 137.3, 135.2, 133.3, 121.9, 61.0, 18.1, 17.1, 17.0, 14.8. IR (neat): 2971, 2927, 2079, 1820, 1738, 1698, 1682, 1445, 1366, 1335, 1277, 1257, 1205, 1171, 1108, 1067, 1018, 927, 827, 739, 708, 614, 538, 514, 470, 419 cm^{-1}; HRMS (ESI) calcd *m/z* for $C_{15}H_{20}N_2O_2Na^+$ $[M+Na]^+$: 283.1417, found 283.1422.

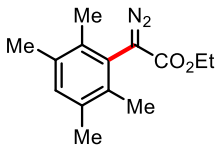
7.1.4 Synthesis and characterization of ethyl 2-(2,6-di-*tert*-butyl-4-methylpyridin-3-yl)-2-diazoacetate (3d)



3d

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (89.3 mg, 0.2 mmol, 1.0 equiv.) and 2,6-di-*tert*-butyl-4-methylpyridine (123.2 mg, 0.6 mmol, 3.0 equiv.) in CH_3CN (2 mL) was stirred at room temperature with blue light for 2 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **3d** in 44% yield (28.1 mg) as a light yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.07 (s, 1H), 4.31-4.24 (m, 2H), 2.28 (s, 3H), 1.41 (s, 9H), 1.33 (s, 9H), 1.31-1.25 (m, 3H). The spectroscopic data are in agreement with those previously reported.[25]

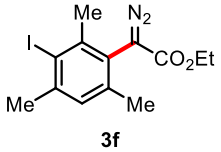
7.1.5 Synthesis and characterization of ethyl 2-diazo-2-(2,3,5,6-tetramethylphenyl)acetate (3e)



3e

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (89.3 mg, 0.2 mmol, 1.0 equiv.) and 1,2,4,5-tetramethylbenzene (53.7 mg, 0.4 mmol, 2.0 equiv.) in CH_3CN (2 mL) was stirred at room temperature with blue light for 2 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **3e** in 59% yield (29.1 mg) as a yellowish oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.03 (s, 1H), 4.27 (q, J = 7.1 Hz, 2H), 2.25 (s, 6H), 2.21 (s, 6H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7 (br), 135.7, 134.4, 133.2, 124.2, 61.1, 20.4, 16.9, 14.7. IR (neat): 2971, 2921, 2868, 2078, 1698, 1682, 1603, 1465, 1445, 1409, 1384, 1365, 1333, 1263, 1200, 1170, 1106, 1020, 977, 873, 803, 757, 741, 722, 581, 531, 519, 462, 431, 420 cm^{-1}; HRMS (ESI) calcd *m/z* for $C_{14}H_{19}N_2O_2^+$ $[M+H]^+$: 247.1441, found 247.1438.

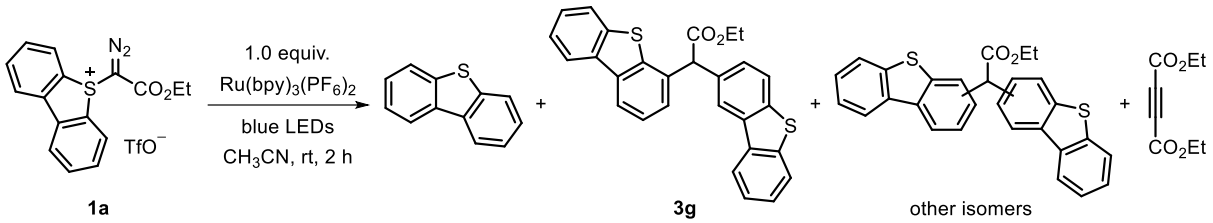
7.1.6 Synthesis and characterization of ethyl 2-diazo-2-(3-iodo-2,4,6-trimethylphenyl) acetate (3f)



3f

A mixture of $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv.), **1a** (89.3 mg, 0.2 mmol, 1.0 equiv.) and 2-iodo-1,3,5-trimethylbenzene (98.4 mg, 0.4 mmol, 2.0 equiv.) in CH_3CN (2 mL) was stirred at room temperature with blue light for 2 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) afforded **3f** in 52% yield (37.2 mg) as a yellowish oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.05 (s, 1H), 4.27 (q, J = 7.1 Hz, 2H), 2.54 (s, 3H), 2.46 (s, 3H), 2.26 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1 (br), 144.1, 143.2, 139.6, 129.3, 121.8, 106.2, 61.3, 30.2, 28.0, 20.0, 14.7. IR (neat): 2977, 2920, 2081, 1823, 1685, 1444, 1366, 1323, 1262, 1214, 1169, 1139, 1093, 1036, 1024, 954, 862, 822, 764, 744, 641, 604, 586, 546, 526, 470, 418 cm^{-1}; HRMS (ESI) calcd *m/z* for $C_{13}H_{16}N_2O_2I^+$ $[M+H]^+$: 359.0251, found 359.0249.

7.2 Stoichiometric reaction



To a 3 mL oven-dried Schlenk tube equipped with a stirring bar was added $Ru(bpy)_3(PF_6)_2$ (43.0 mg, 0.05 mmol, 1.0 equiv.) and **1a** (22.3 mg, 0.05 mmol, 1.0 equiv.). The Schlenk tube was then evacuated and backfilled with N_2 three times after which CH_3CN (0.5 mL) was added under N_2. After that, the reaction mixture was placed in a photoreactor equipped with blue LED strips (wavelength range: 430-435 nm, 9 W). A mini-fan was kept on top to maintain room temperature. After two hours, the reaction mixture was passed through a short pad of celite and eluted with dichloromethane. The solvent was then removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) to afford dibenzo[*b*,*d*]thiophene (4.8 mg, 52% yield) as a white solid and a colorless mixture (3.0 mg). The mixture was further subjected to preparative HPLC, affording **3g** (1.2 mg, 11% yield) as a colorless oil and other isomers. Diethyl but-2-ynedioate was observed in trace amount. Characterization of **3g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35-8.33 (m, 1H), 8.08-8.04 (m, 2H), 7.91-7.82 (m, 4H), 7.47-7.39 (m, 6H), 7.30-7.27 (m, 1H), 6.29 (s, 1H), 4.39-4.21 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 140.7, 140.1, 140.0, 138.9, 136.3, 135.4, 135.3, 135.2, 134.2, 133.6, 127.9, 127.1, 126.4, 126.3, 126.2, 125.0, 124.6, 124.5, 123.4, 123.2, 123.0, 122.4, 122.2, 121.9, 61.8, 55.0, 14.4. IR (film): 3060, 2979, 1734, 1562, 1469, 1440, 1366, 1294, 1231, 1179, 1158, 1081, 1025, 907, 764, 732, 620, 507, 496, 483, 469, 443, 431, 419 cm^{-1}; HRMS calculated *m*/*z* for $C_{28}H_{21}O_2S_2^+$ [M+H]: 453.0977, found (ESI) 453.0961.

8. Differential scanning calorimetry (DSC) of sulfonium salts 1

Experimental method of the DSC analysis of sulfonium salts: from 25 °C to 500 °C, 15 °C/min, air as the working gas.

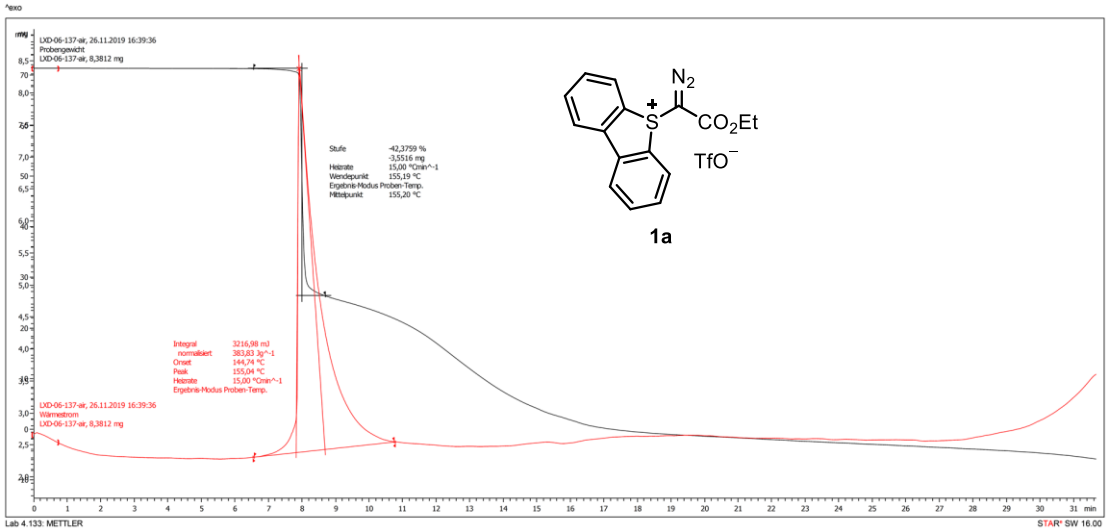


Figure S8. DSC measurement curve for **1a**.

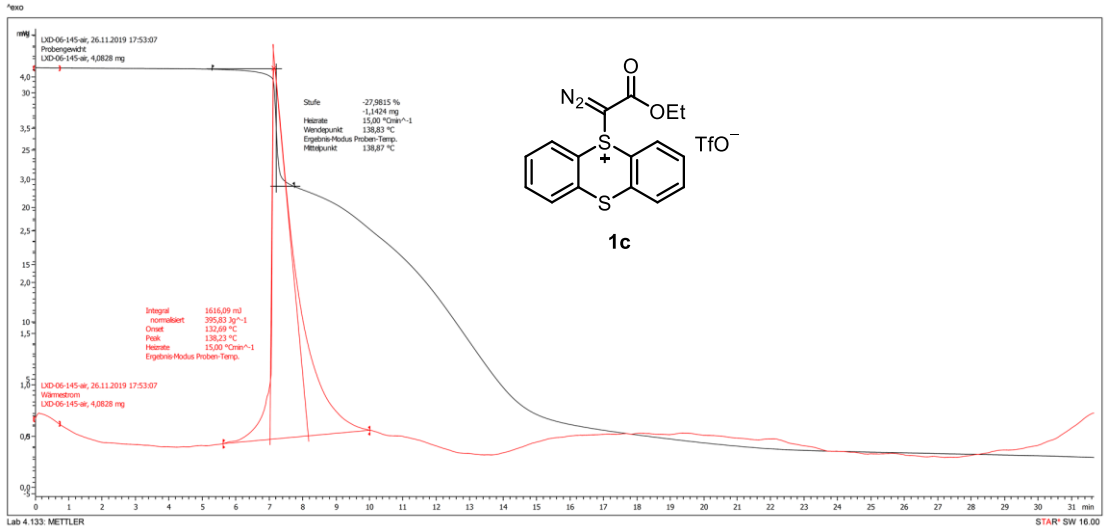


Figure S9. DSC measurement curve for **1c**.

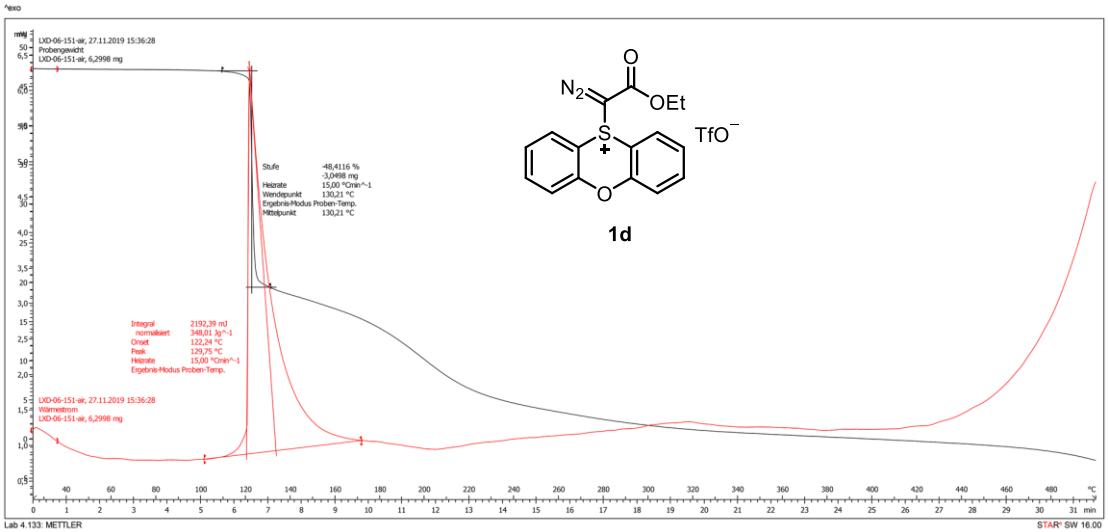


Figure S10. DSC measurement curve for **1d**.

9. Single crystal X-ray diffraction analysis

9.1 General remarks

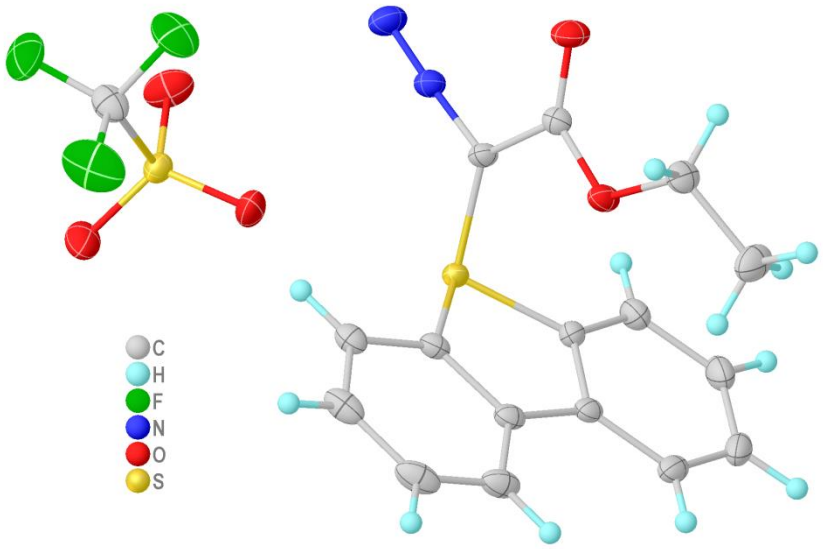
Data collection was done on two dual source equipped Bruker D8 Venture four-circle-diffractometer from Bruker AXS GmbH; used X-ray sources: microfocus IμS 2.0 Cu/Mo and microfocus IμS 3.0 Ag/Mo from Incoatec GmbH with mirror optics HELIOS and single-hole collimator from Bruker AXS GmbH; used detector: Photon III CE14 (Cu/Mo) and Photon III HE (Ag/Mo) from Bruker AXS GmbH.

Used programs: APEX3 Suite (v2018.7-2) for data collection and therein integrated programs SAINT V8.38A (Integration) und SADABS 2016/2 (Absorption correction) from Bruker AXS GmbH; structure solution was done with SHELXT, refinement with SHELXL-2018/3;[26] OLEX2 was used for data finalization.[27]

Special Utilities: SMZ1270 stereomicroscope from Nikon Metrology GmbH was used for sample preparation; crystals were mounted on MicroMounts or MicroLoops from MiTeGen in NVH oil; for sensitive samples the X-TEMP 2 System was used for picking of crystals;[28] crystals were cooled to given temperature with Cryostream 800 from Oxford Cryosystems.

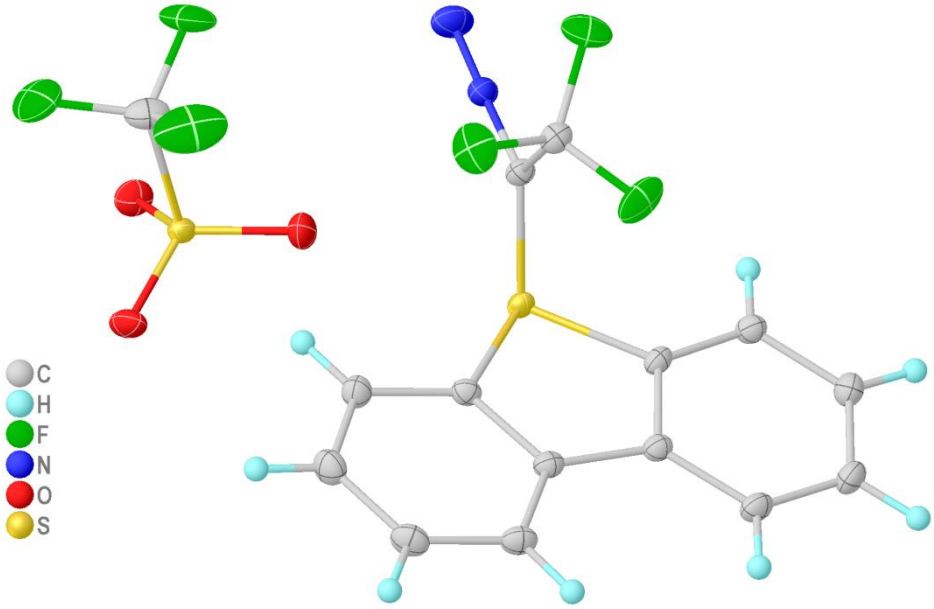
Compound Identifier	CCDC number
1a	2009414
1b	2041657
1c	2009416
1d	2009417
5i	2041658
5s	2041659
5y	2041660
5ab	2009418
7w	2041661
7x	2041662
8w	2041663
8x	2041664

9.2 Crystal data and structure refinement for 1a



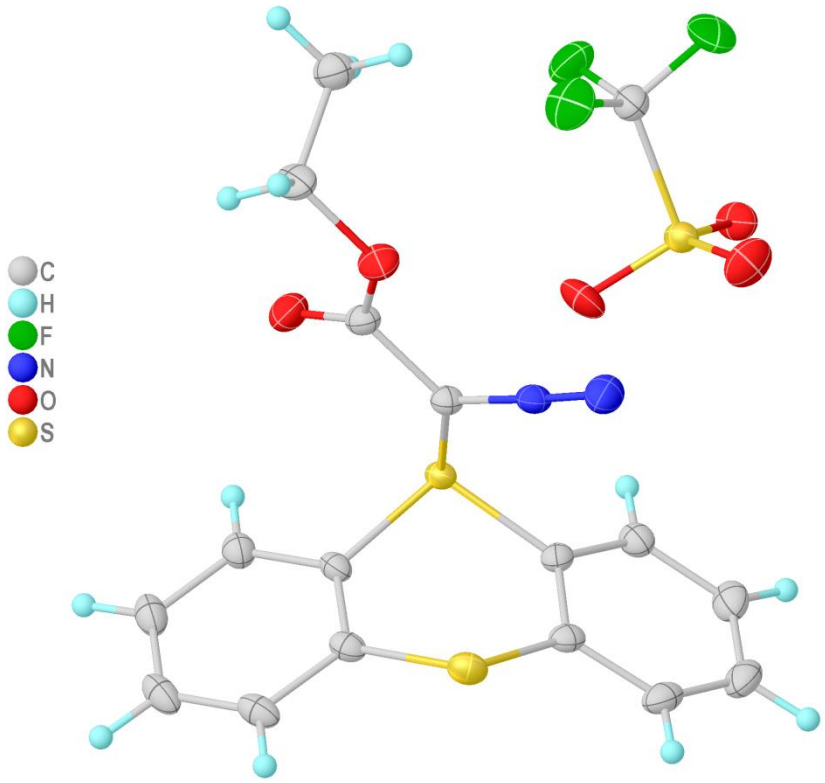
Empirical formula	$C_{17}H_{13}F_3N_2O_5S_2$
Formula weight	446.41
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	8.8866(8)
b/Å	10.5241(8)
c/Å	11.8134(10)
α/°	110.309(3)
β/°	108.409(3)
γ/°	101.173(3)
Volume/Å^3	924.22(14)
Z	2
ρ_{calc}g/cm^3	1.604
μ/mm^{-1}	0.351
F(000)	456.0
Crystal size/mm^3	0.308 × 0.181 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.39 to 61.086
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 15, -16 ≤ l ≤ 15
Reflections collected	38735
Independent reflections	5371 [R_{int} = 0.0279, R_{sigma} = 0.0189]
Data/restraints/parameters	5371/0/264
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0799
Final R indexes [all data]	R_1 = 0.0386, wR_2 = 0.0843
Largest diff. peak/hole / e Å^{-3}	0.56/-0.39

9.3 Crystal data and structure refinement for 1b



Empirical formula	$C_{15}H_8F_6N_2O_3S_2$
Formula weight	442.35
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	7.6962(8)
b/Å	10.7945(12)
c/Å	11.2457(11)
α/°	64.258(4)
β/°	85.031(5)
γ/°	81.268(5)
Volume/Å^3	831.56(15)
Z	2
ρ_{calc}g/cm^3	1.767
μ/mm^{-1}	0.406
F(000)	444.0
Crystal size/mm^3	0.328 × 0.313 × 0.19
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.224 to 57.418
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected	21188
Independent reflections	4285 [R_{int} = 0.0202, R_{sigma} = 0.0178]
Data/restraints/parameters	4285/0/253
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0249, wR_2 = 0.0656
Final R indexes [all data]	R_1 = 0.0254, wR_2 = 0.0660
Largest diff. peak/hole / e Å^{-3}	0.44/-0.37

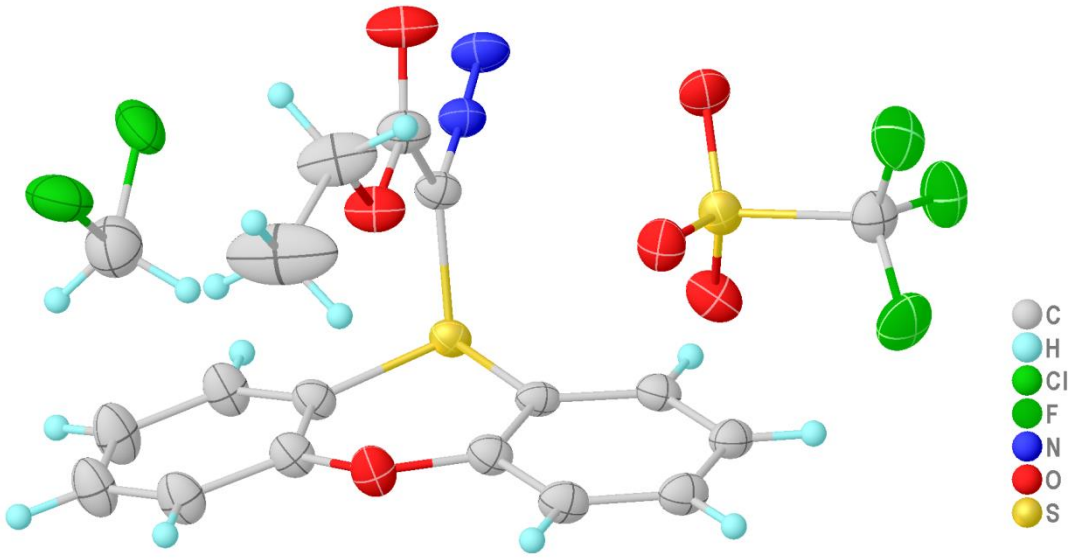
9.4 Crystal data and structure refinement for 1c



Empirical formula	$C_{17}H_{13}F_3N_2O_5S_3$
Formula weight	478.47
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	9.3754(9)
b/Å	10.0246(10)
c/Å	11.2424(11)
α/°	102.665(3)
β/°	107.668(3)
γ/°	91.868(3)
Volume/Å^3	976.68(17)
Z	2
ρ_{calc}g/cm^3	1.627
μ/mm^{-1}	0.441
F(000)	488.0
Crystal size/mm^3	0.204 × 0.187 × 0.122
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.918 to 61.084
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $-16 \leq l \leq 15$
Reflections collected	56639
Independent reflections	5924 [R_{int} = 0.0255, R_{sigma} = 0.0144]
Data/restraints/parameters	5924/0/272

Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0290, wR_2 = 0.0787
Final R indexes [all data]	R_1 = 0.0327, wR_2 = 0.0817
Largest diff. peak/hole / e $Å^{-3}$	0.47/-0.41

9.5 Crystal data and structure refinement for 1d

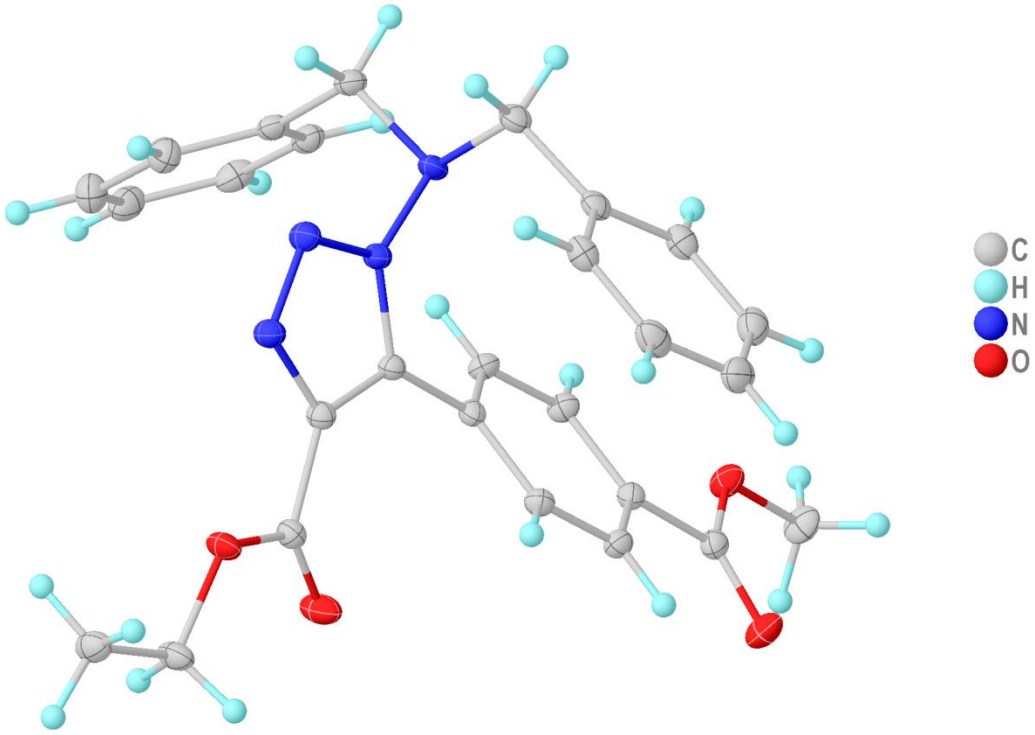


Empirical formula	$C_{17.04}H_{13.07}Cl_{0.07}F_3N_2O_6S_2$*
Formula weight	465.51
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.3106(18)
b/Å	15.392(2)
c/Å	13.213(2)
α/°	90
β/°	106.098(5)
γ/°	90
Volume/$Å^3$	2014.6(6)
Z	4
ρ_{calc}g/cm^3	1.535
μ/mm^{-1}	0.339
F(000)	950.0
Crystal size/mm^3	0.598 × 0.043 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.158 to 57.446
Index ranges	$-13 \leq h \leq 13$, $-20 \leq k \leq 20$, $-17 \leq l \leq 17$
Reflections collected	46638
Independent reflections	5200 [R_{int} = 0.0424, R_{sigma} = 0.0243]
Data/restraints/parameters	5200/28/301
Goodness-of-fit on F^2	1.106

Final R indexes [I>=2σ (I)]	R_1 = 0.0481, wR_2 = 0.1259
Final R indexes [all data]	R_1 = 0.0618, wR_2 = 0.1366
Largest diff. peak/hole / e Å^{-3}	0.37/-0.55

*: DCM molecule on special position with occupation far below 1 leads to the non-integer sum formula. It is assumed, that the DCM can relatively freely evaporate from the lattice without major damage to the crystal.

9.6 Crystal data and structure refinement for 5i

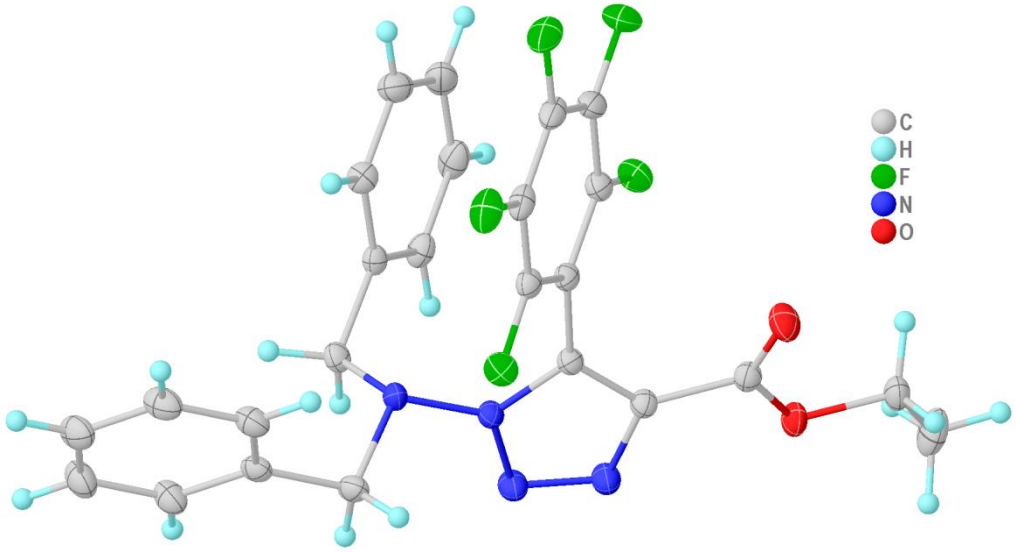


Empirical formula	$C_{27}H_{26}N_4O_4$
Formula weight	470.52
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.9095(11)
b/Å	11.8073(18)
c/Å	24.960(4)
α/°	90
β/°	91.947(6)
γ/°	90
Volume/Å^3	2329.7(6)
Z	4
ρ_{calc}g/cm^3	1.341
μ/mm^{-1}	0.092
F(000)	992.0
Crystal size/mm^3	0.378 × 0.275 × 0.254

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.75 to 61.052
Index ranges	-11 ≤ h ≤ 11, 0 ≤ k ≤ 16, 0 ≤ l ≤ 35
Reflections collected	7673
Independent reflections	7673 [R_{int} = ?*, R_{sigma} = 0.0206]
Data/restraints/parameters	7673/0/319
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0359, wR_2 = 0.0884
Final R indexes [all data]	R_1 = 0.0412, wR_2 = 0.0928
Largest diff. peak/hole / e $Å^{-3}$	0.44/-0.25

*: Integrated and refined as non-merohedral twin.

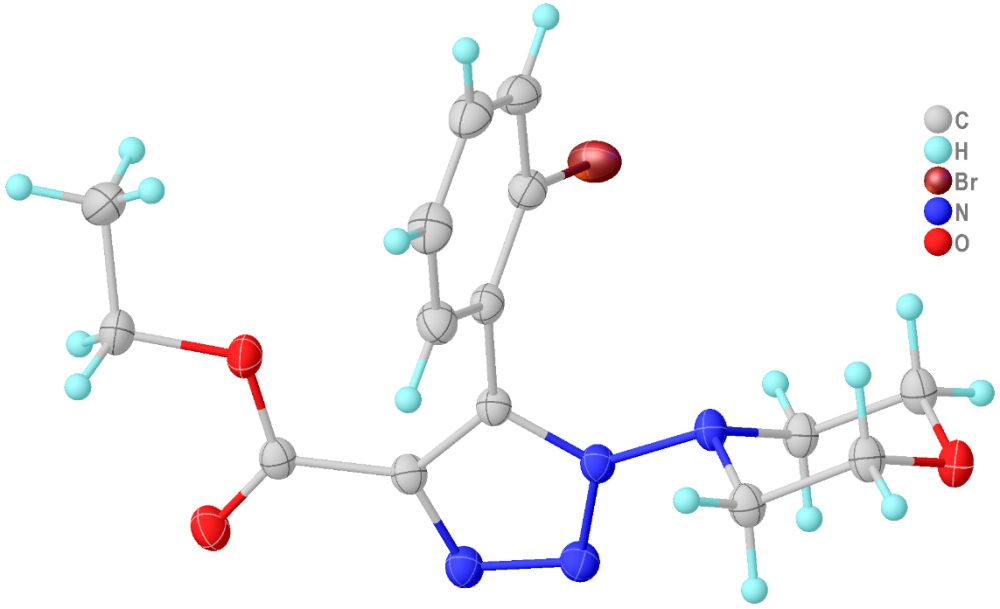
9.7 Crystal data and structure refinement for 5s



Empirical formula	$C_{25}H_{19}F_5N_4O_2$
Formula weight	502.44
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	7.6176(7)
b/Å	12.0476(10)
c/Å	13.1839(15)
α/°	85.199(3)
β/°	87.319(3)
γ/°	74.947(4)
Volume/$Å^3$	1163.9(2)
Z	2
ρ_{calc}g/cm^3	1.434
μ/mm^{-1}	0.120
F(000)	516.0
Crystal size/mm^3	0.289 × 0.241 × 0.072
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	4.508 to 61.082
Index ranges	$-10 \leq h \leq 10$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$
Reflections collected	85023
Independent reflections	7118 [R_{int} = 0.0190, R_{sigma} = 0.0104]
Data/restraints/parameters	7118/0/326
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0335, wR_2 = 0.0923
Final R indexes [all data]	R_1 = 0.0362, wR_2 = 0.0953
Largest diff. peak/hole / e $Å^{-3}$	0.44/-0.22

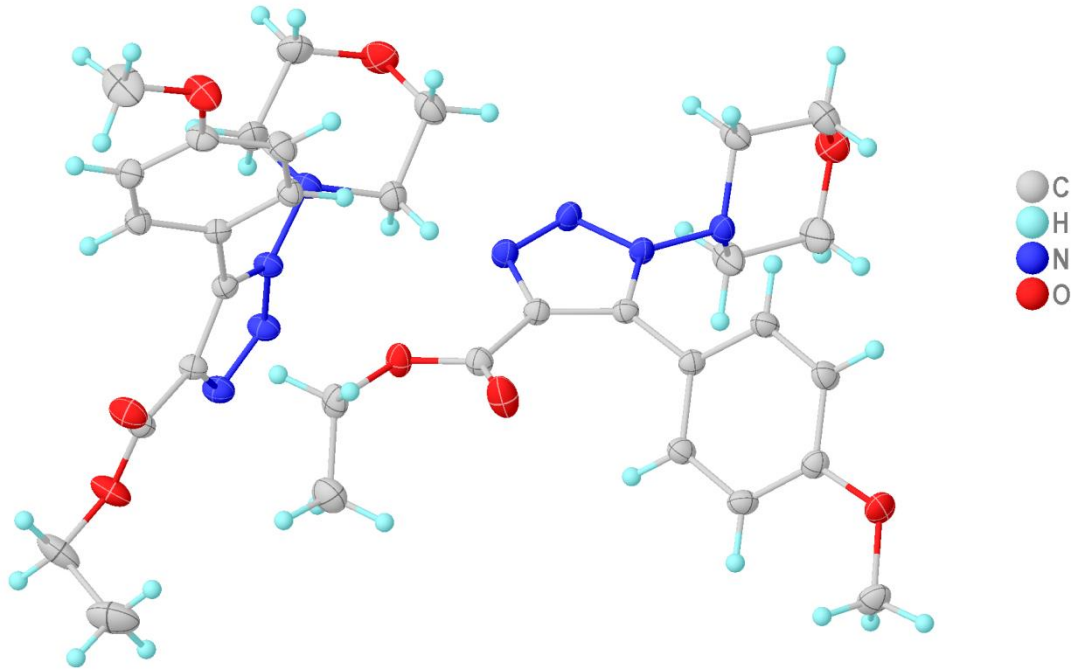
9.8 Crystal data and structure refinement for 5y



Empirical formula	$C_{15}H_{17}BrN_4O_3$
Formula weight	381.24
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.5088(5)
b/Å	8.6800(6)
c/Å	19.6924(11)
α/°	90
β/°	100.540(2)
γ/°	90
Volume/$Å^3$	1597.92(17)
Z	4
$\rho_{calc}g/cm^3$	1.585
μ/mm^{-1}	2.593
F(000)	776.0
Crystal size/mm^3	0.34 × 0.272 × 0.203
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.144 to 61.084

Index ranges	$-13 \leq h \leq 13, -12 \leq k \leq 12, -28 \leq l \leq 28$
Reflections collected	59669
Independent reflections	4880 [R_{int} = 0.0259, R_{sigma} = 0.0134]
Data/restraints/parameters	4880/0/209
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0242, wR_2 = 0.0667
Final R indexes [all data]	R_1 = 0.0258, wR_2 = 0.0679
Largest diff. peak/hole / e $Å^{-3}$	1.04/-0.50

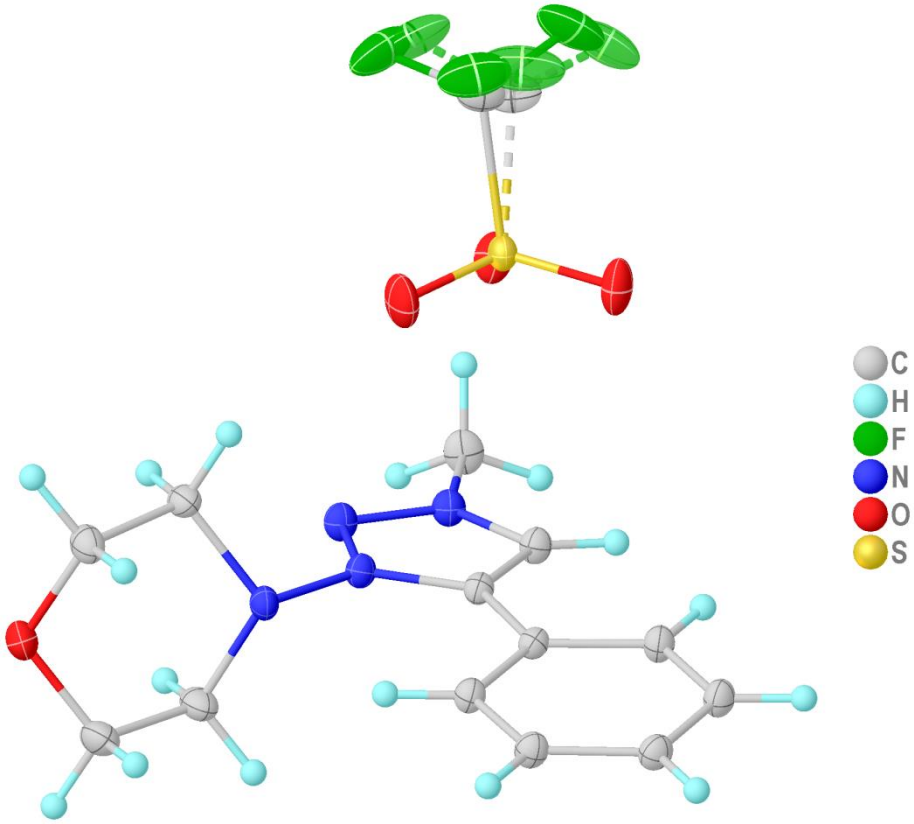
9.9 Crystal data and structure refinement for 5ab



Empirical formula	$C_{16}H_{20}N_4O_4$
Formula weight	332.36
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.1940(8)
b/Å	11.0232(7)
c/Å	27.2006(19)
α/°	90
β/°	99.377(2)
γ/°	90
Volume/$Å^3$	3311.5(4)
Z	8
ρ_{calc}g/cm^3	1.333
μ/mm^{-1}	0.098
F(000)	1408.0
Crystal size/mm^3	0.382 × 0.343 × 0.282

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.994 to 59.2
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -37 ≤ l ≤ 37
Reflections collected	159503
Independent reflections	9310 [R_{int} = 0.0221, R_{sigma} = 0.0133]
Data/restraints/parameters	9310/0/438
Goodness-of-fit on F^2	1.109
Final R indexes [I>=2σ (I)]	R_1 = 0.0397, wR_2 = 0.1048
Final R indexes [all data]	R_1 = 0.0423, wR_2 = 0.1067
Largest diff. peak/hole / e $Å^{-3}$	0.35/-0.21

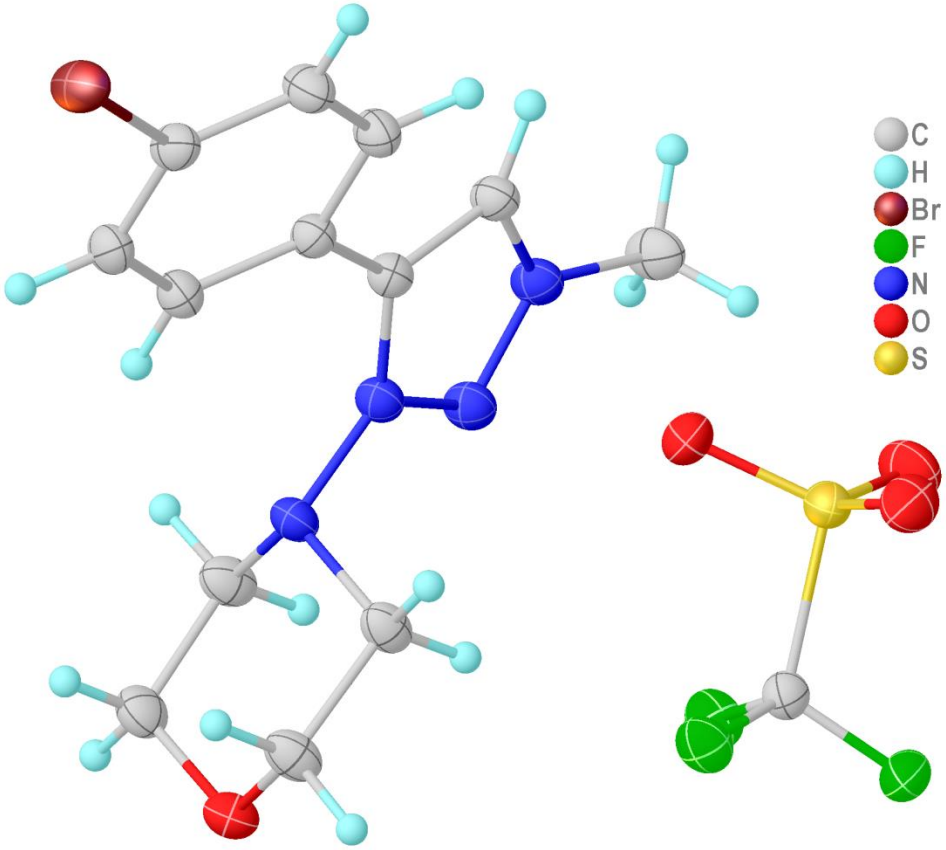
9.10 Crystal data and structure refinement for 7w



Empirical formula	$C_{14}H_{17}F_3N_4O_4S$
Formula weight	394.37
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	9.1707(7)
b/Å	9.3189(8)
c/Å	10.6588(7)
α/°	78.592(2)
β/°	88.611(2)
γ/°	72.022(3)

Volume/Å^3	848.66(11)
Z	2
ρ_{calc}g/cm^3	1.543
μ/mm^{-1}	0.251
F(000)	408.0
Crystal size/mm^3	0.308 × 0.304 × 0.26
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.674 to 66.59
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	140969
Independent reflections	6497 [R_{int} = 0.0273, R_{sigma} = 0.0121]
Data/restraints/parameters	6497/10/276
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0281, wR_2 = 0.0811
Final R indexes [all data]	R_1 = 0.0289, wR_2 = 0.0818
Largest diff. peak/hole / e Å^{-3}	0.51/-0.37

9.11 Crystal data and structure refinement for 7x

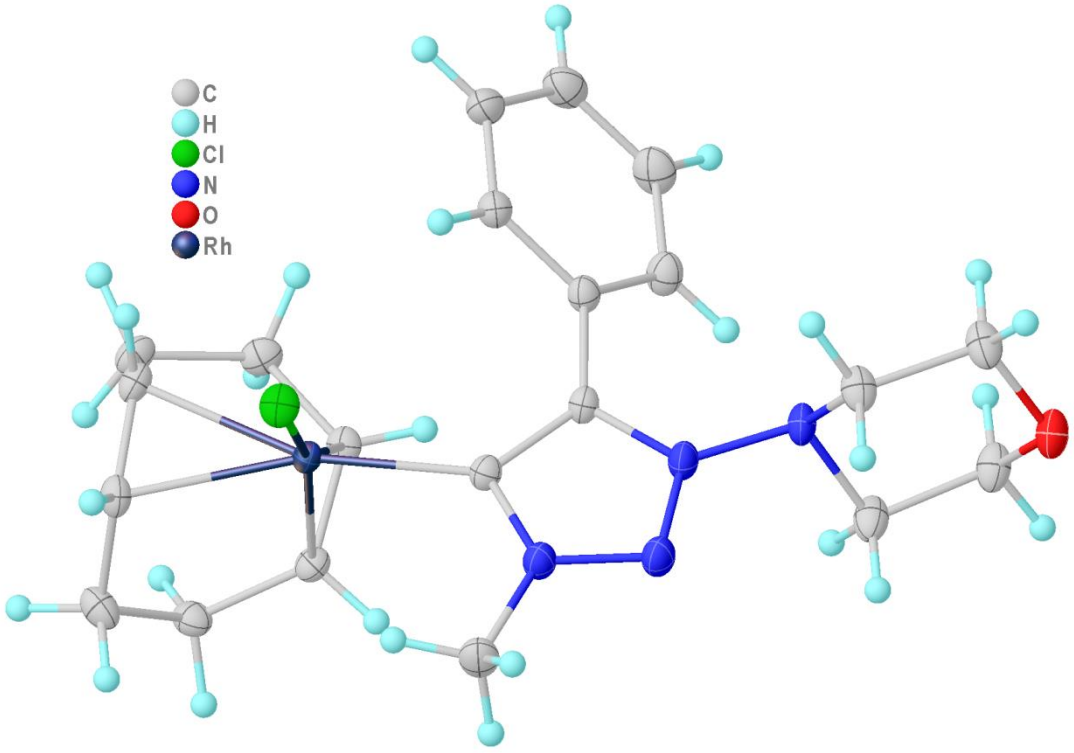


Empirical formula	$C_{14}H_{16}BrF_3N_4O_4S$
Formula weight	473.28
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$

a/Å	11.1233(15)
b/Å	12.0528(19)
c/Å	13.966(2)
α/°	90
β/°	98.295(5)
γ/°	90
Volume/Å^3	1852.8(5)
Z	4
ρ_{calc}g/cm^3	1.697
μ/mm^{-1}	2.389
F(000)	952.0
Crystal size/mm^3	0.551 × 0.401 × 0.322
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.386 to 61.144
Index ranges	-15 ≤ h ≤ 15, 0 ≤ k ≤ 17, 0 ≤ l ≤ 19
Reflections collected	7040
Independent reflections	7040 [R_{int} = ?*, R_{sigma} = 0.0219]
Data/restraints/parameters	7040/0/246
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0259, wR_2 = 0.0764
Final R indexes [all data]	R_1 = 0.0310, wR_2 = 0.0787
Largest diff. peak/hole / e Å^{-3}	0.40/-0.45

*: Integrated and refined as non-merohedral twin.

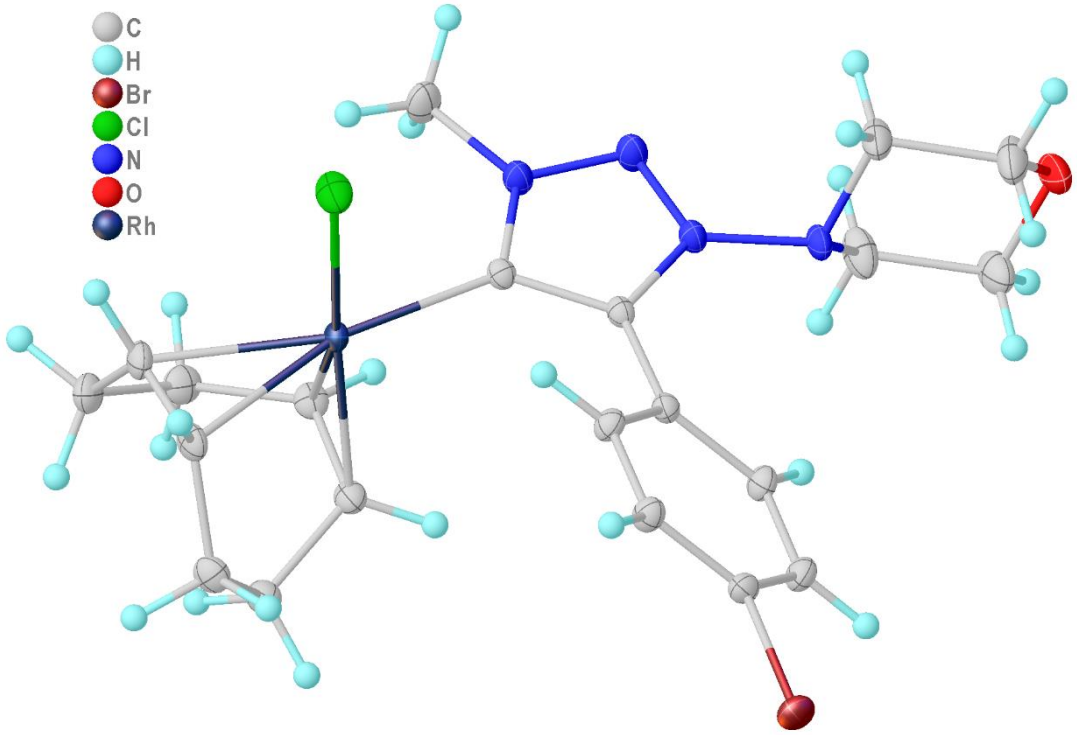
9.12 Crystal data and structure refinement for 8w



Empirical formula	$C_{21}H_{28}ClN_4ORh$

Formula weight	490.83
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.1685(9)
b/Å	9.7210(4)
c/Å	13.0030(7)
α/°	90
β/°	93.961(2)
γ/°	90
Volume/Å^3	2164.95(19)
Z	4
ρ_{calc}g/cm^3	1.506
μ/mm^{-1}	0.931
F(000)	1008.0
Crystal size/mm^3	0.35 × 0.258 × 0.048
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.756 to 65.29
Index ranges	$-25 \leq h \leq 25$, $-12 \leq k \leq 14$, $-19 \leq l \leq 19$
Reflections collected	63799
Independent reflections	7753 [R_{int} = 0.0236, R_{sigma} = 0.0154]
Data/restraints/parameters	7753/0/268
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0187, wR_2 = 0.0460
Final R indexes [all data]	R_1 = 0.0209, wR_2 = 0.0474
Largest diff. peak/hole / e Å^{-3}	0.44/-0.70

9.13 Crystal data and structure refinement for 8x



Empirical formula	$C_{21}H_{27}BrClN_4ORh$
Formula weight	569.73
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.4156(9)
b/Å	9.6081(4)
c/Å	14.3393(7)
α/°	90
β/°	113.468(2)
γ/°	90
Volume/Å^3	2200.93(18)
Z	4
ρ_{calc}g/cm^3	1.719
μ/mm^{-1}	2.733
F(000)	1144.0
Crystal size/mm^3	0.547 × 0.381 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.948 to 61.072
Index ranges	$-24 \leq h \leq 24$, $-13 \leq k \leq 13$, $-20 \leq l \leq 20$
Reflections collected	67001
Independent reflections	6746 [R_{int} = 0.0252, R_{sigma} = 0.0140]
Data/restraints/parameters	6746/0/263
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0198, wR_2 = 0.0498

Final R indexes [all data]	R_1 = 0.0214, wR_2 = 0.0507
Largest diff. peak/hole / e Å^{-3}	0.77/-0.84

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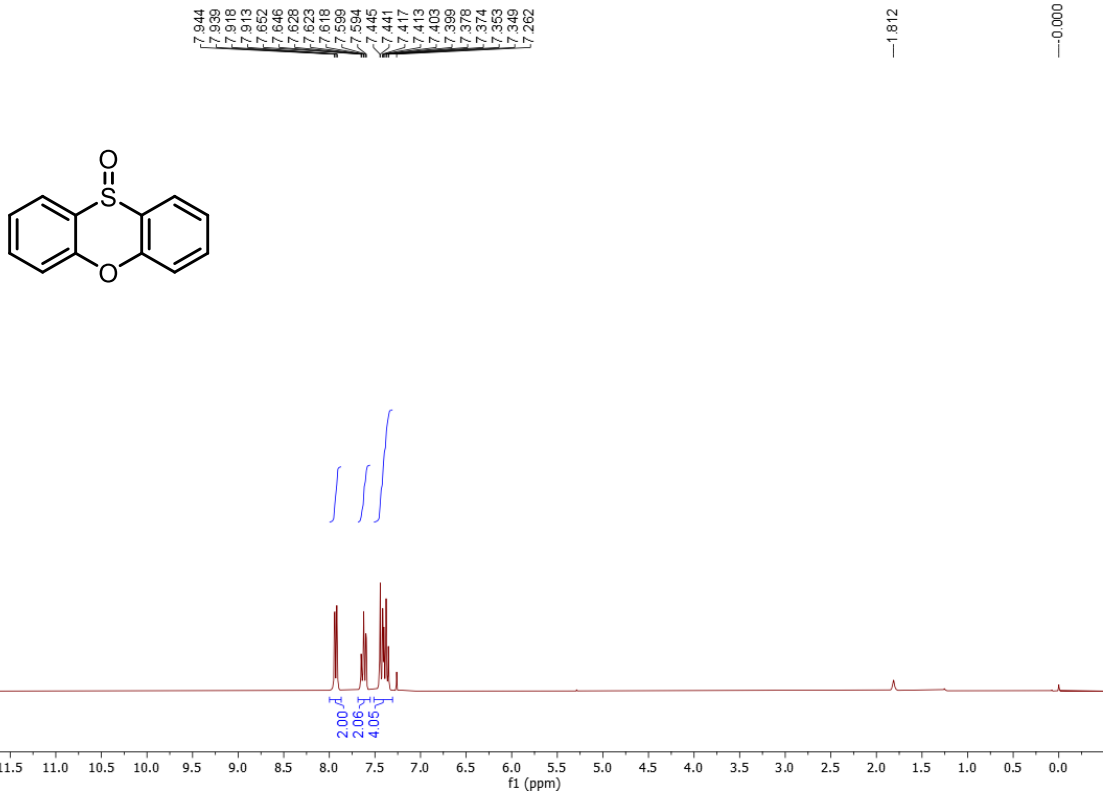
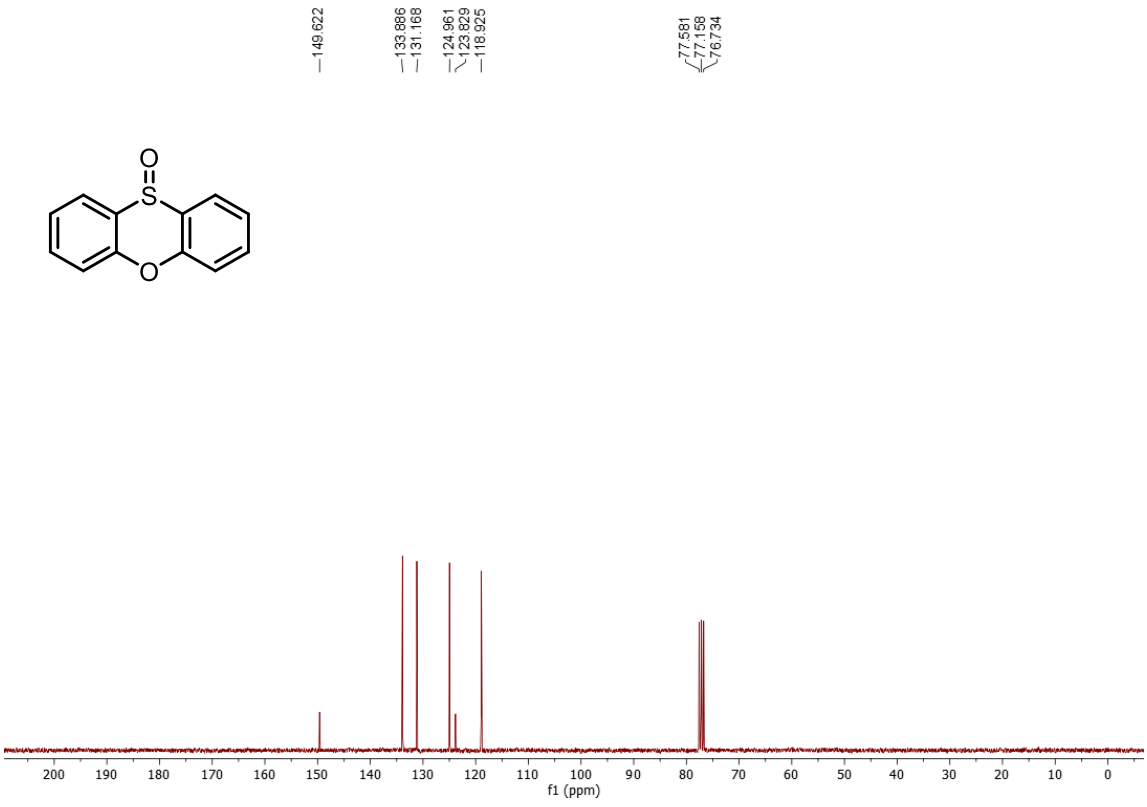
11. NMR spectra

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



^{13}C NMR (75 MHz, $CDCl_3$)



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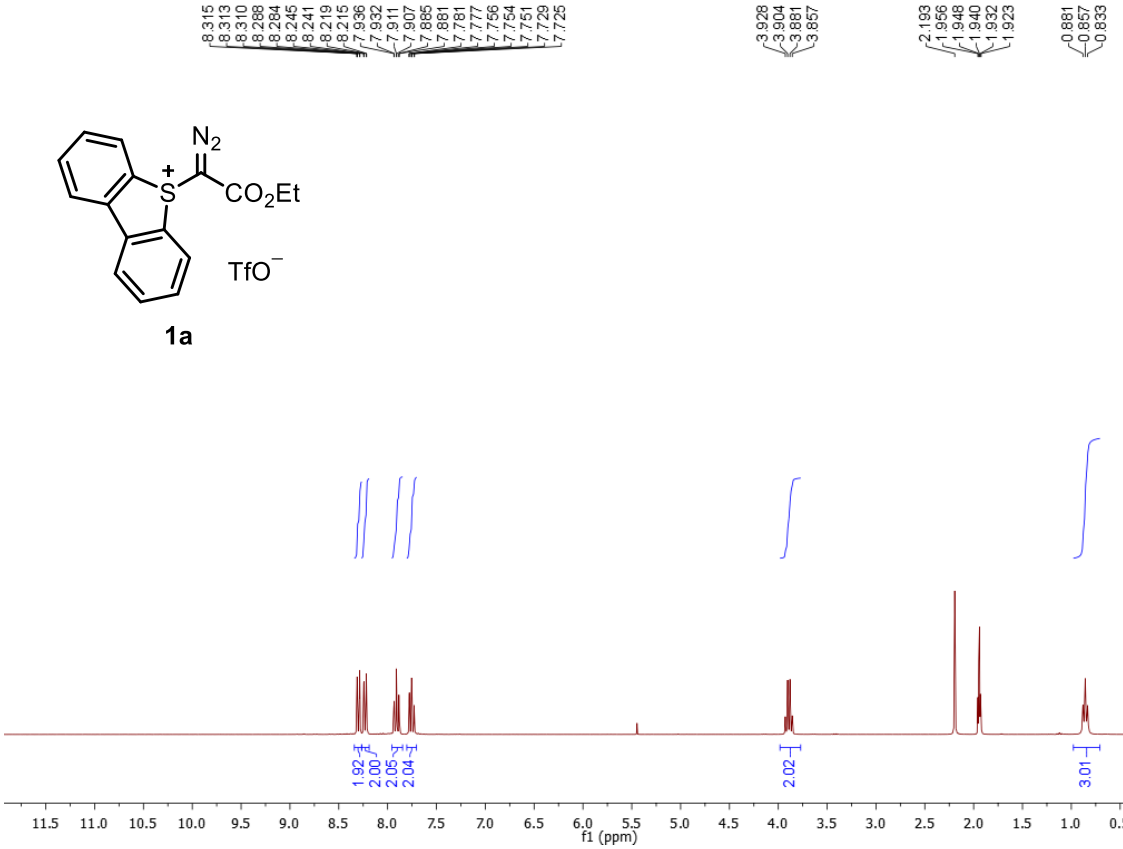
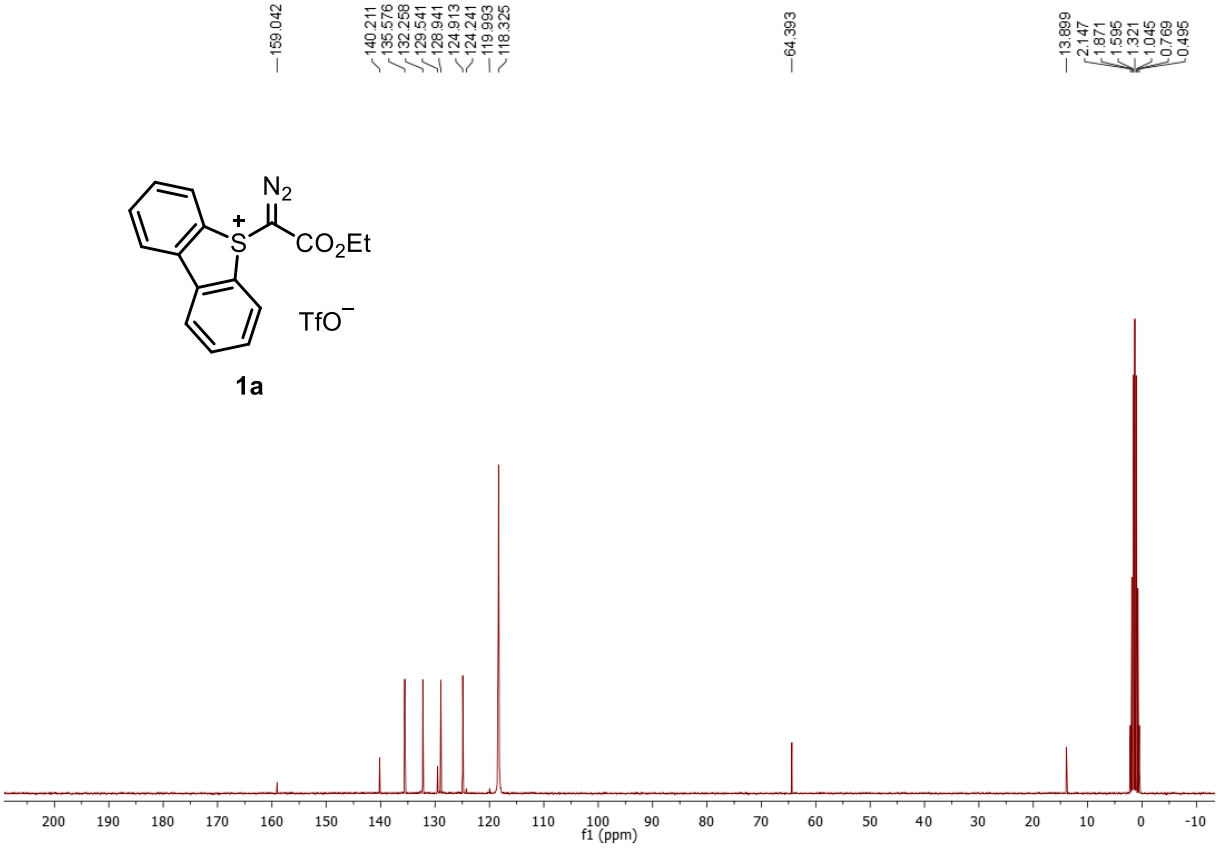


1a

^{13}C NMR (75 MHz, CD_3CN)



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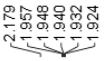

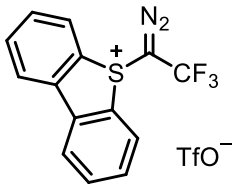

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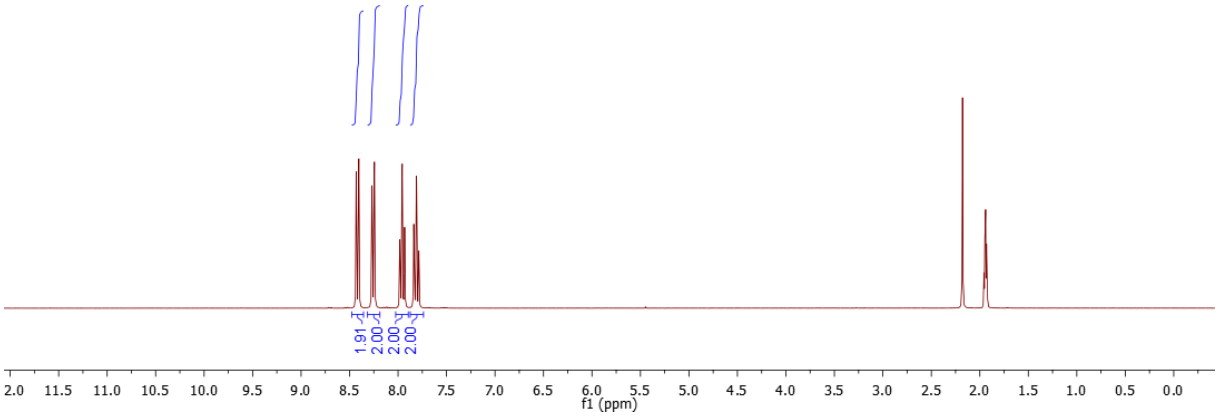
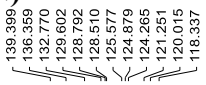
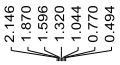
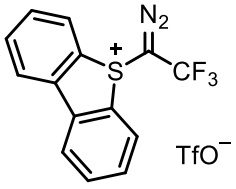


^{13}C NMR (75 MHz, CD_3CN)







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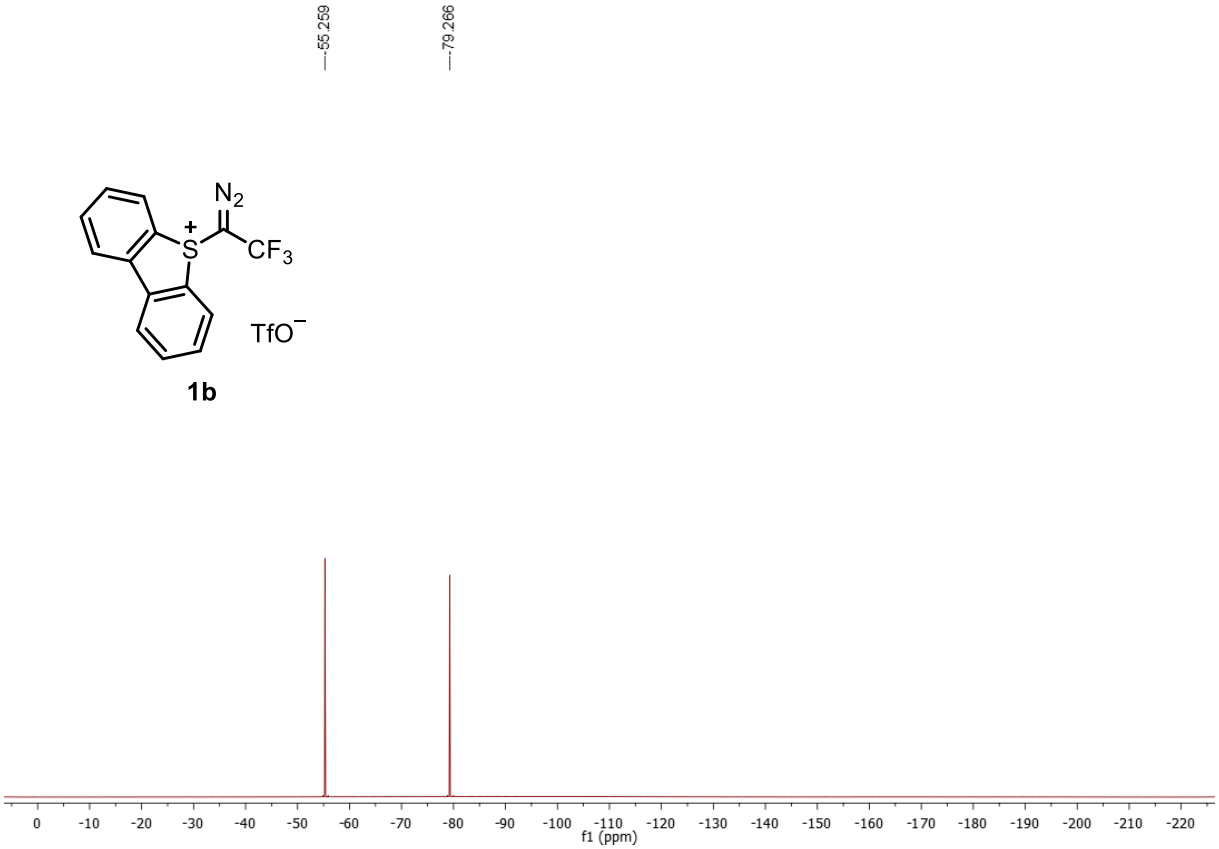
^{19}F NMR (282 MHz, CD_3CN)



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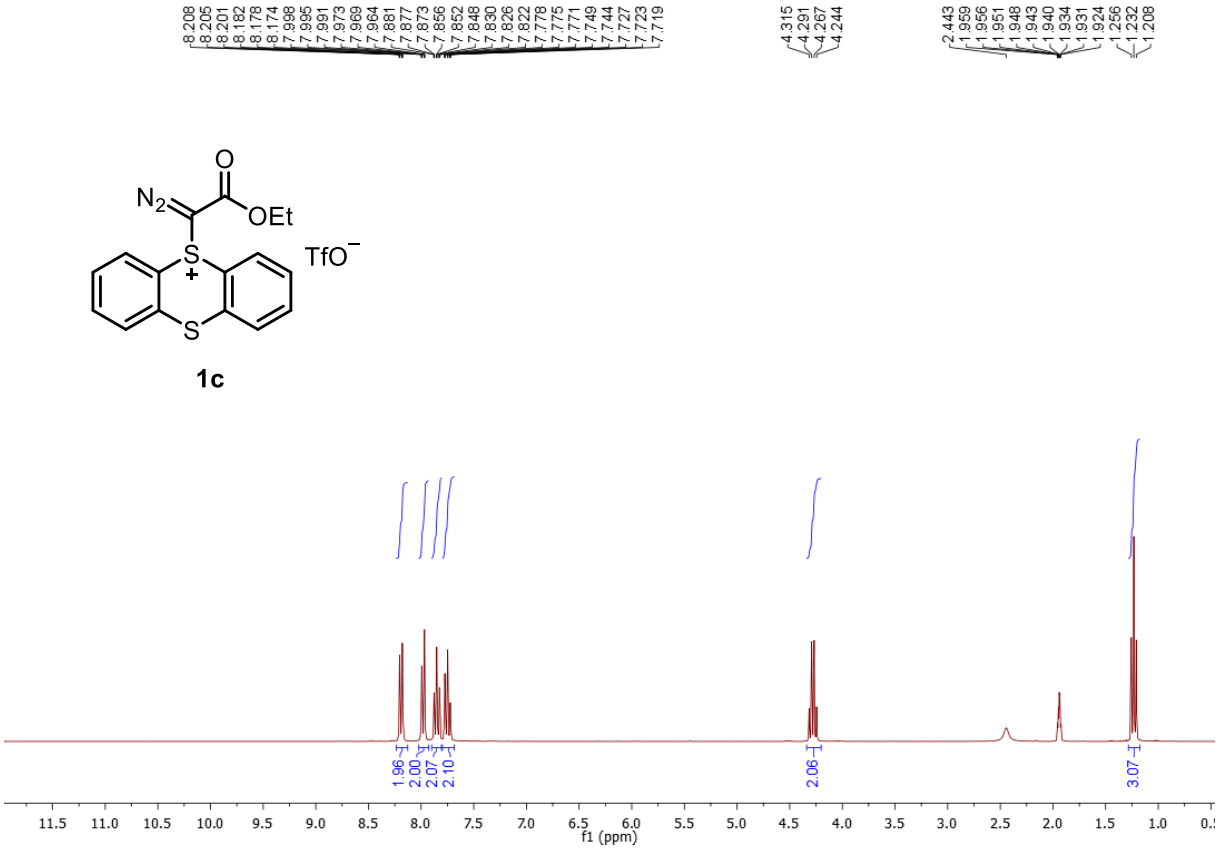
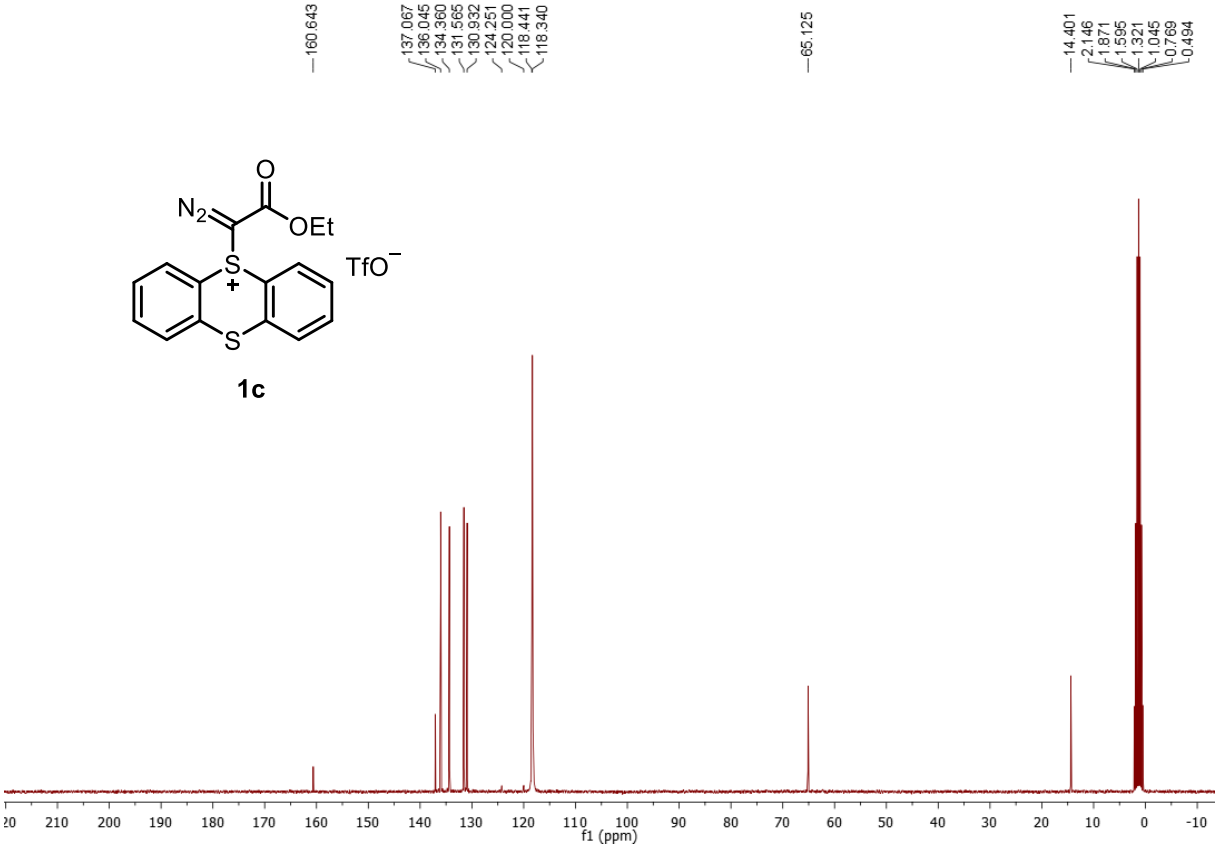


^{13}C NMR (75 MHz, CD_3CN)



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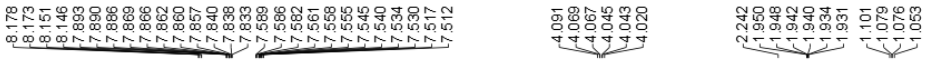

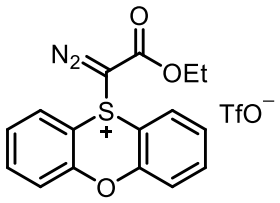

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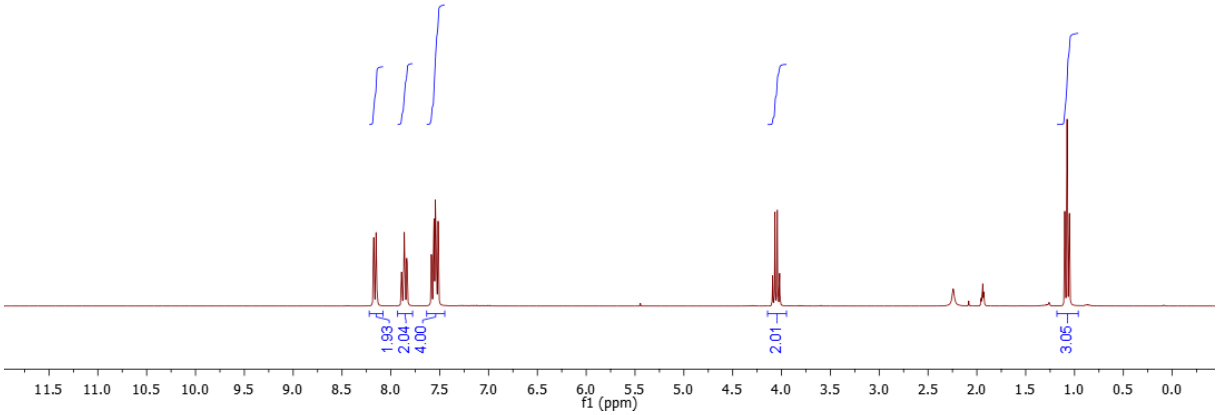

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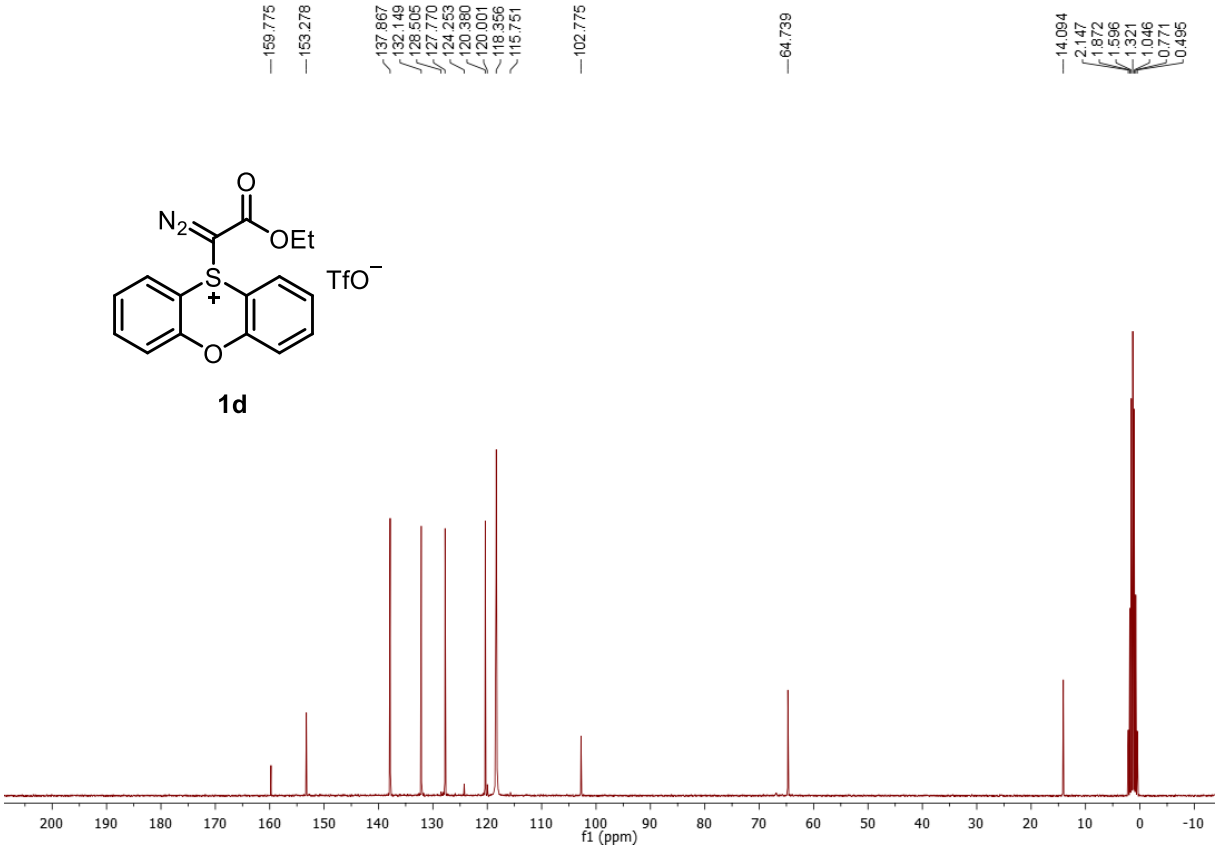

1d

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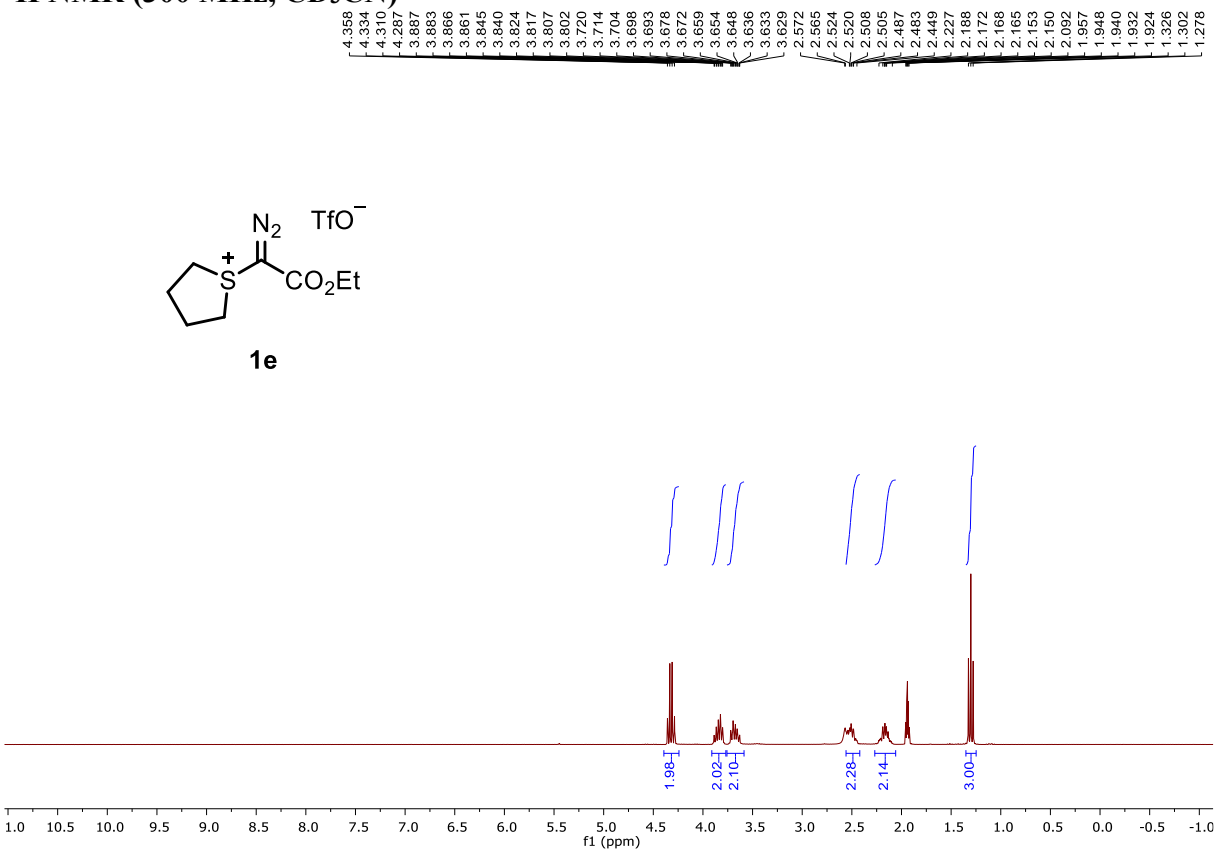
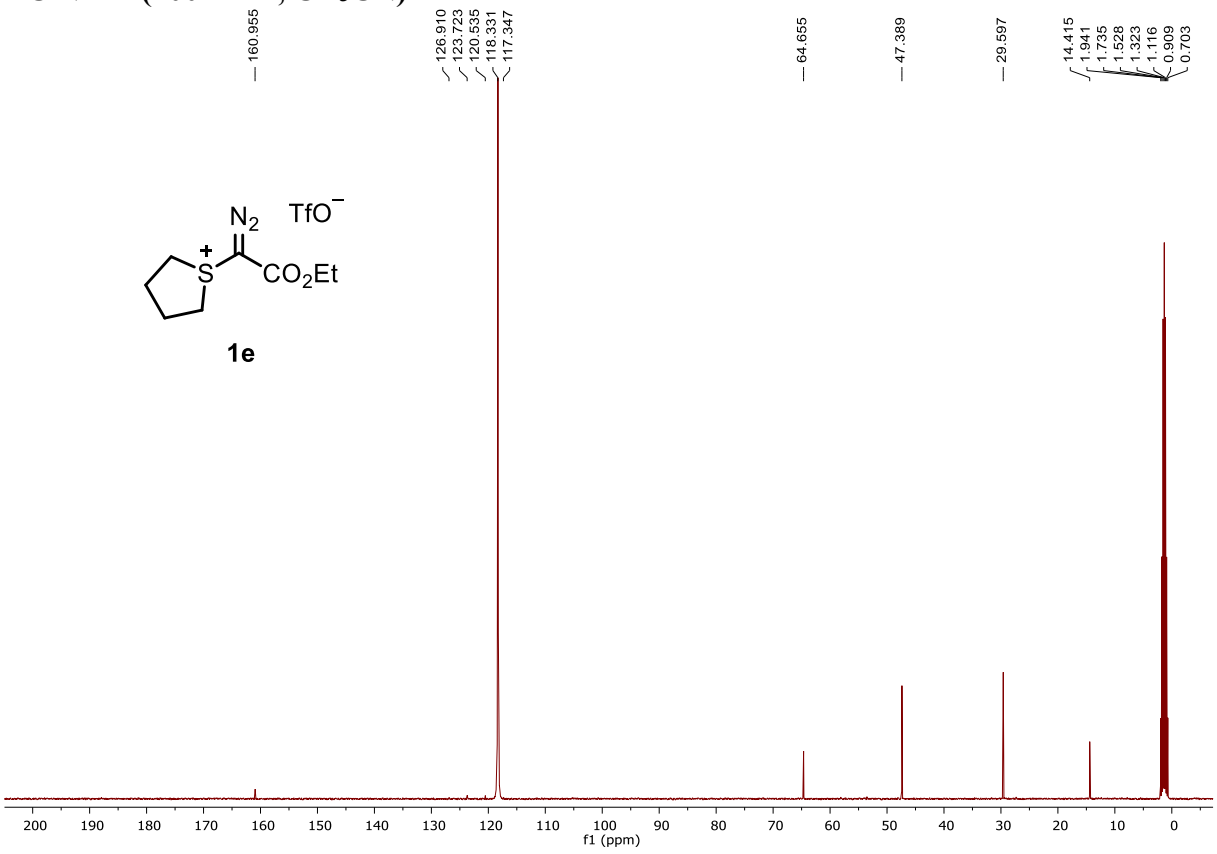


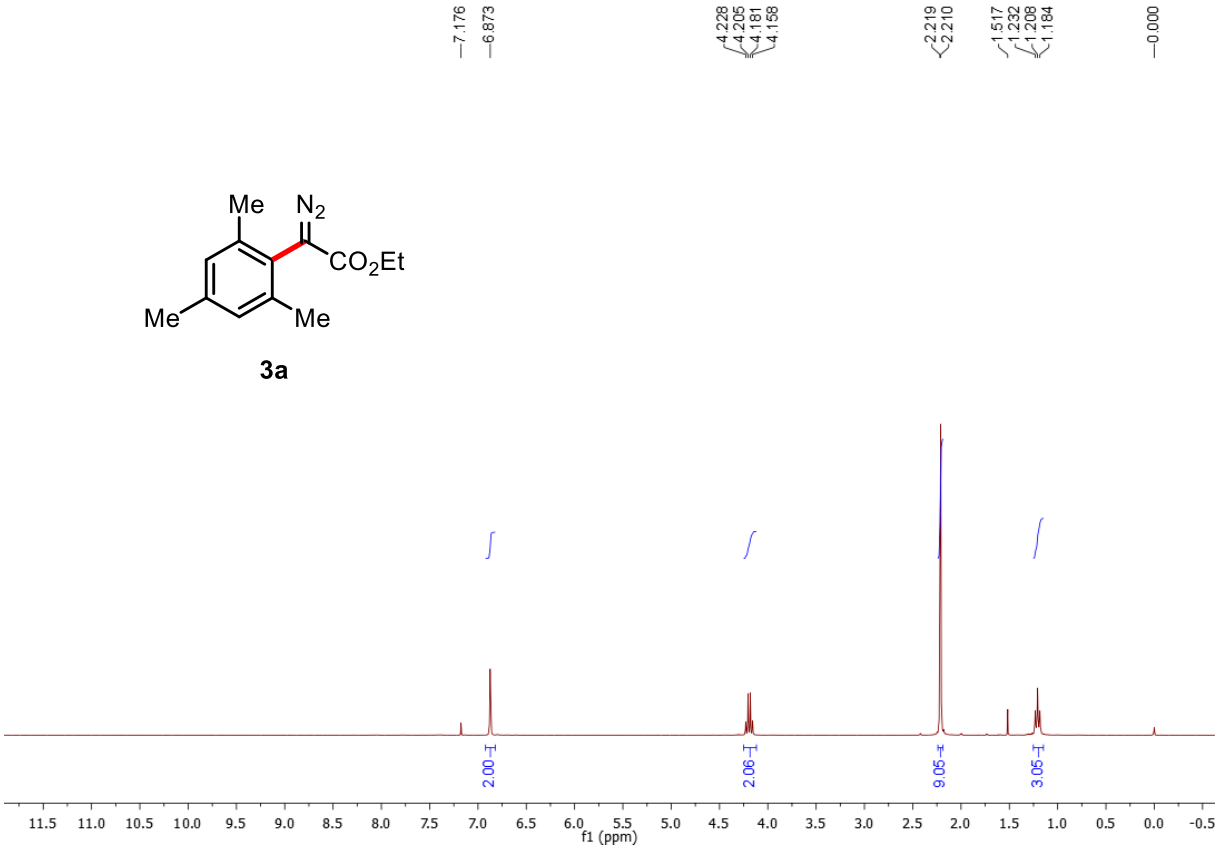
1e

^{13}C NMR (100 MHz, CD_3CN)



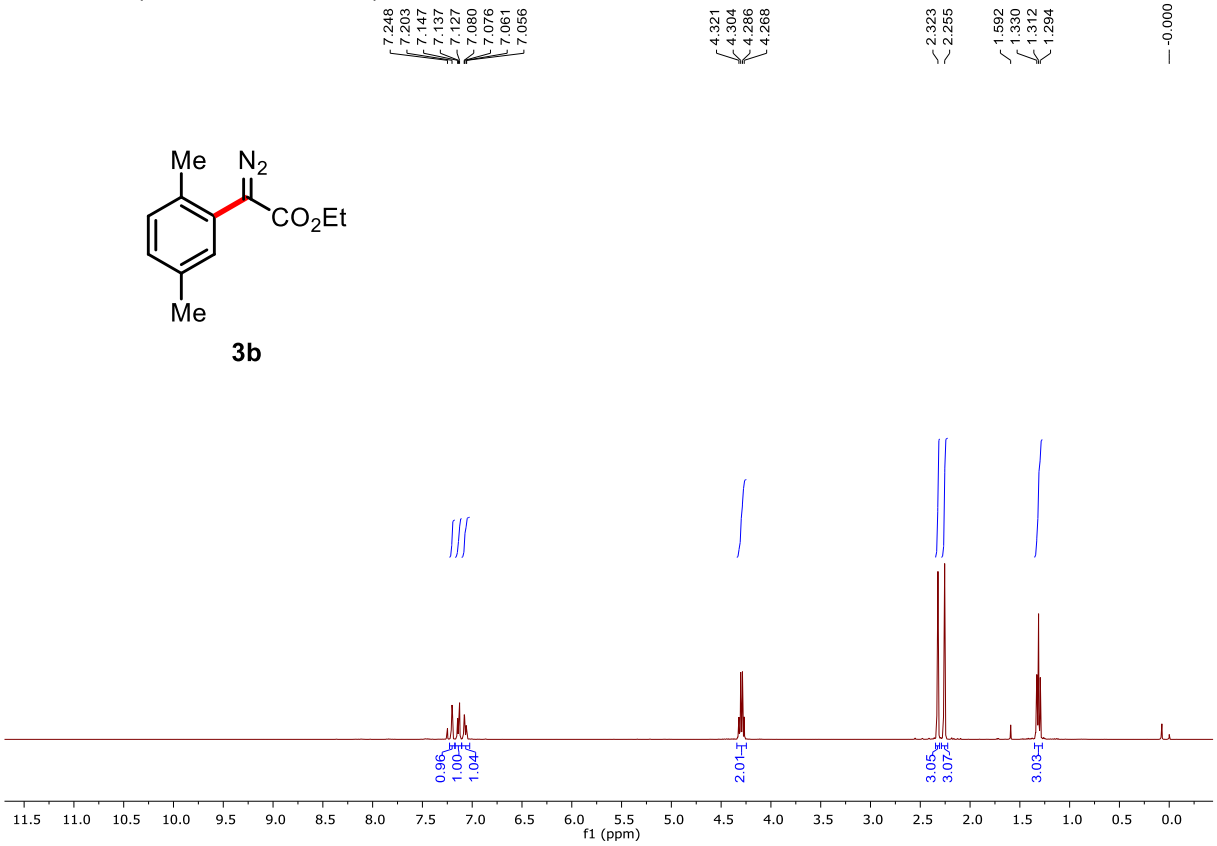
1e

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



3a

^{1}H NMR (400 MHz, $CDCl_3$)



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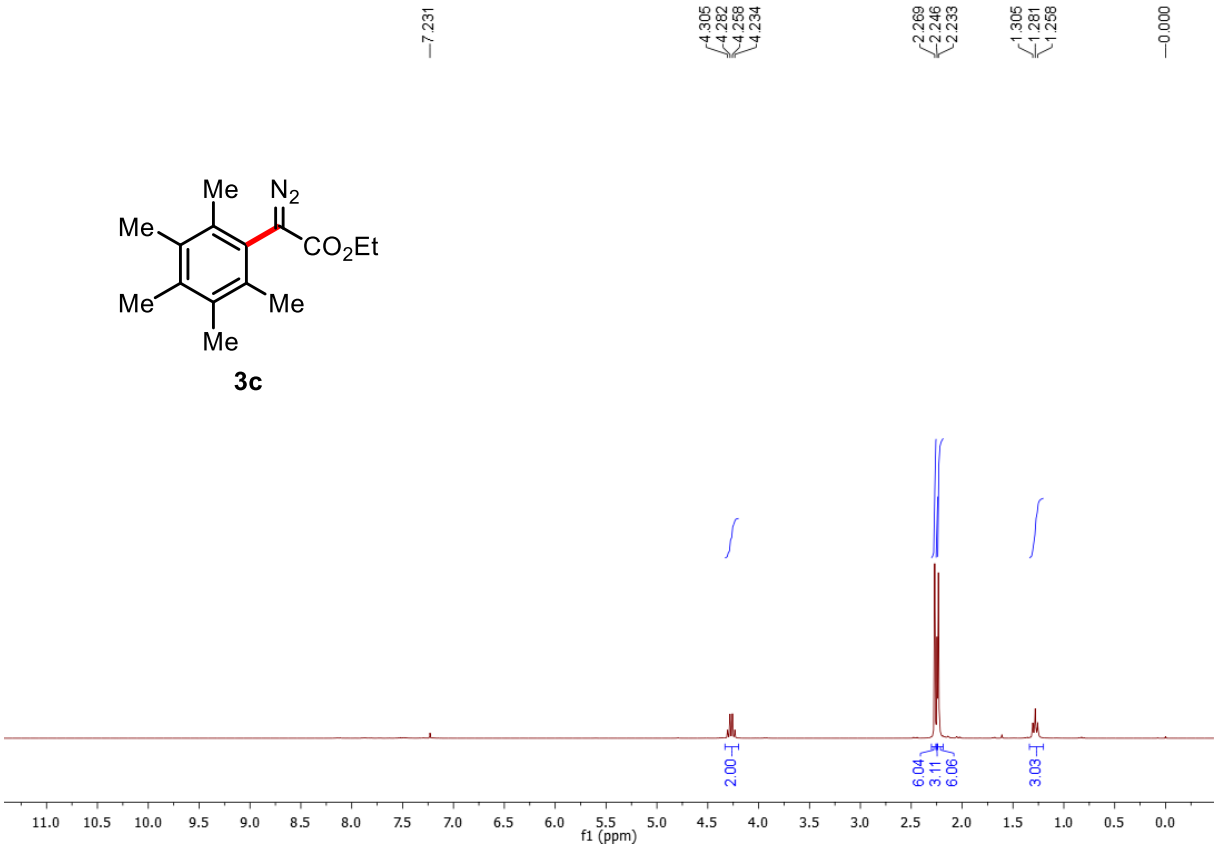

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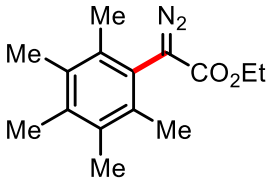

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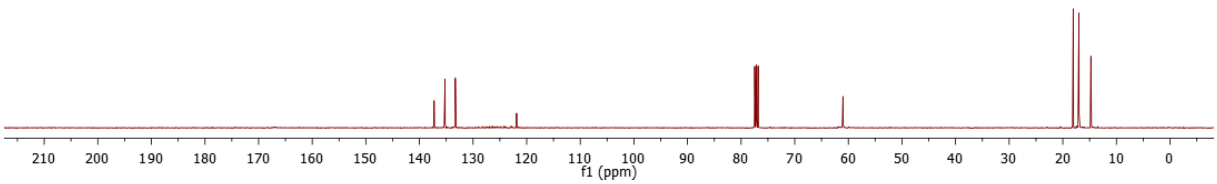

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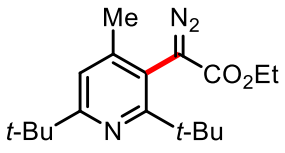

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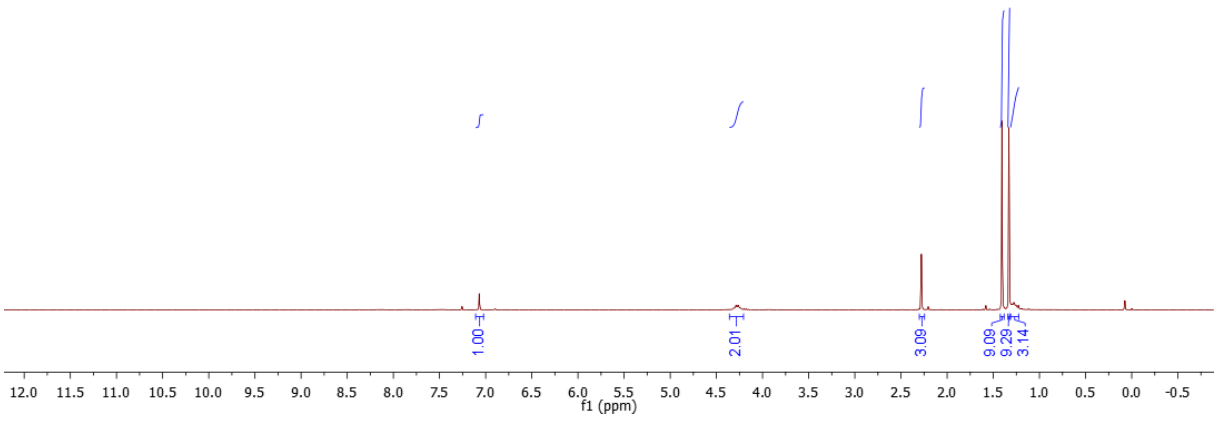

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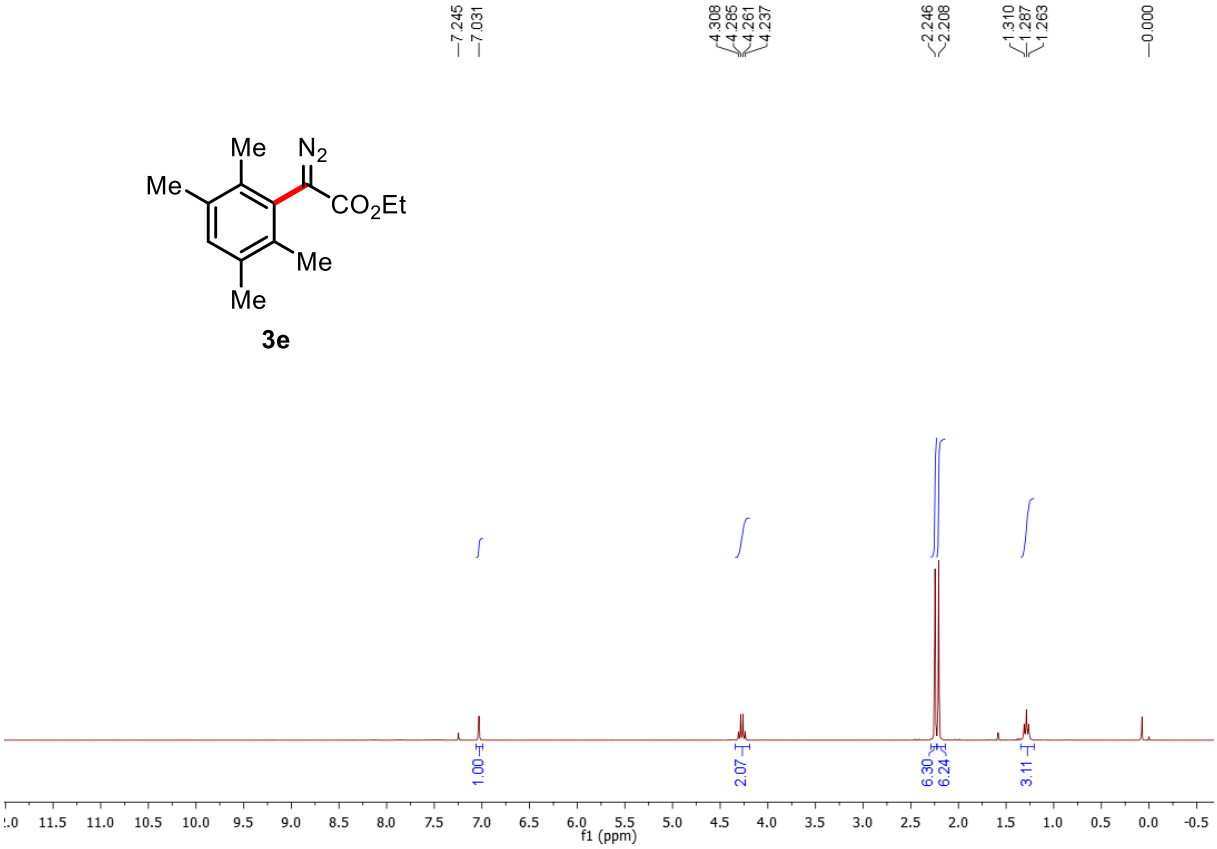

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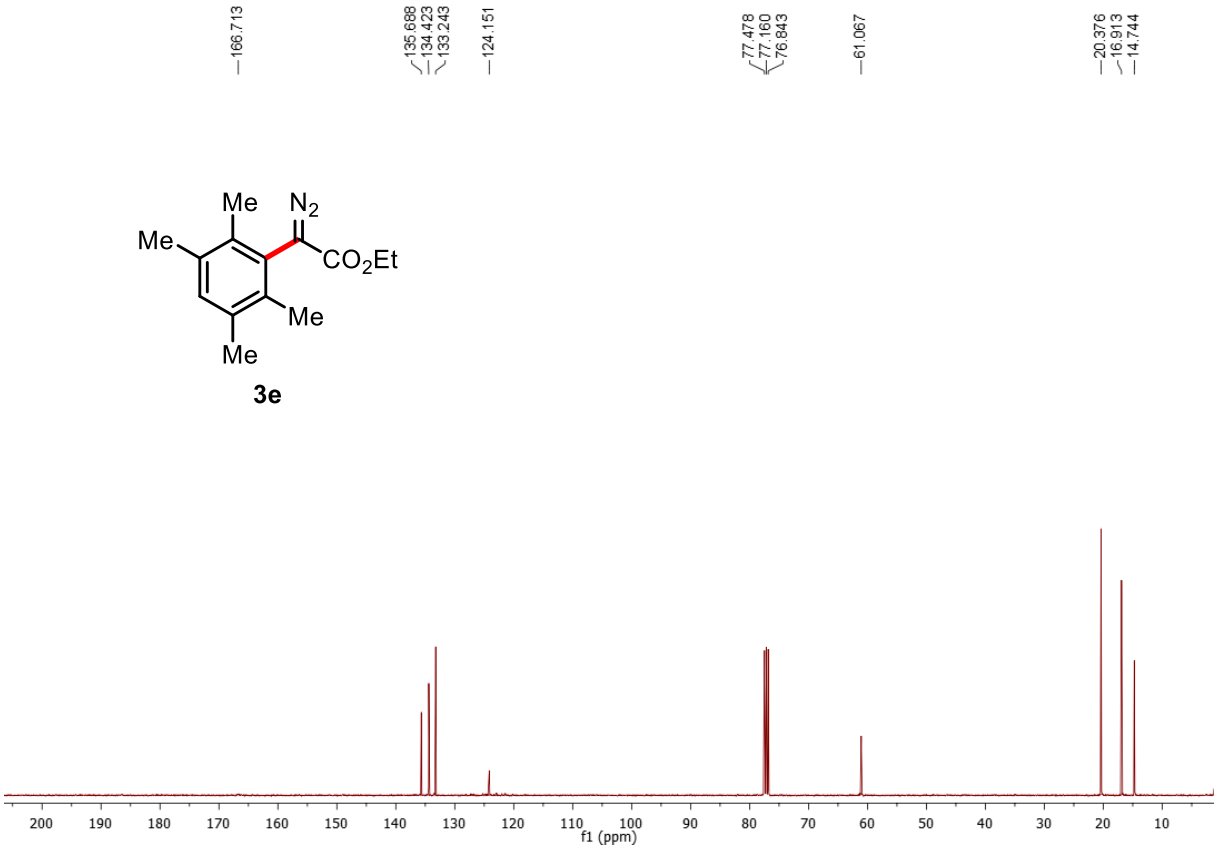
^{13}C NMR (100 MHz, $CDCl_3$)



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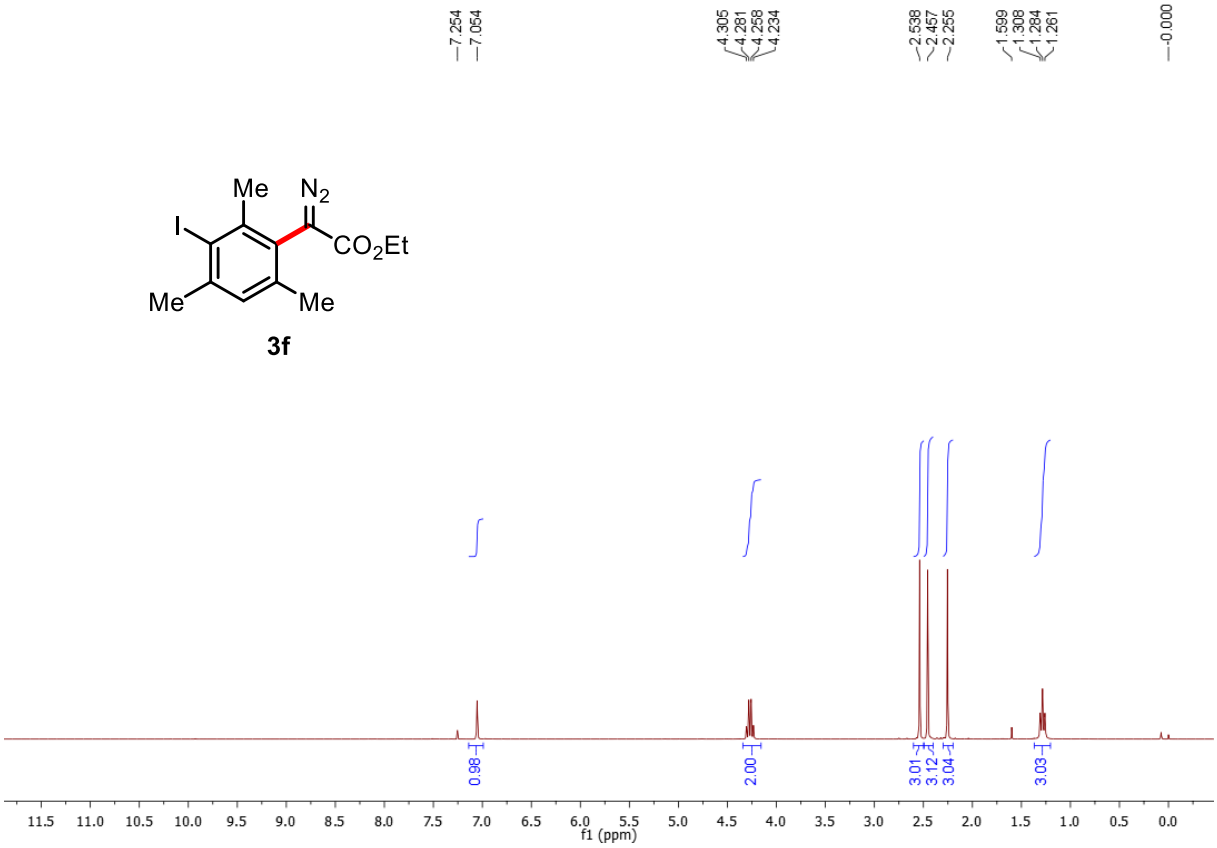

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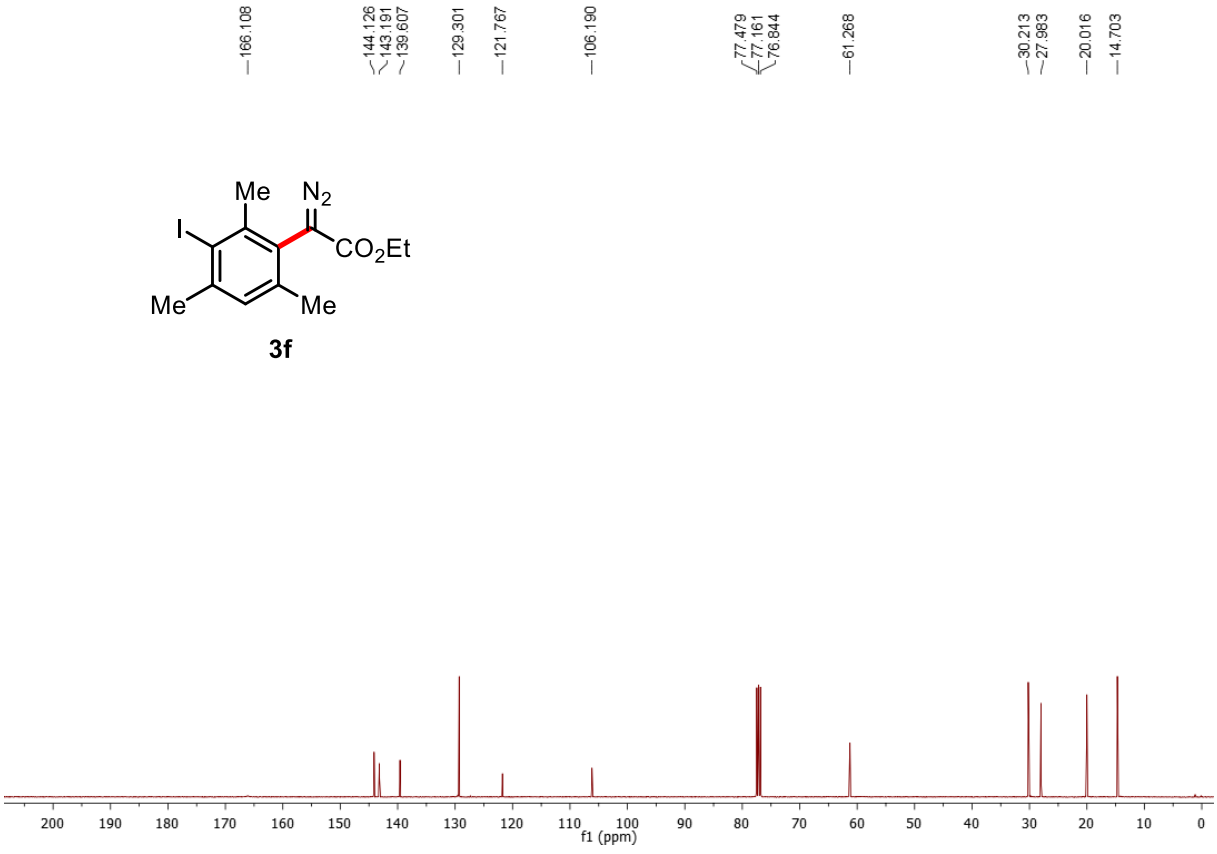

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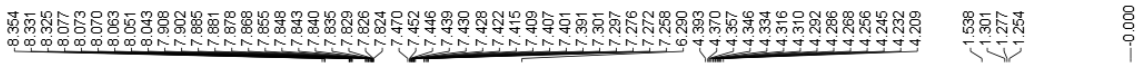

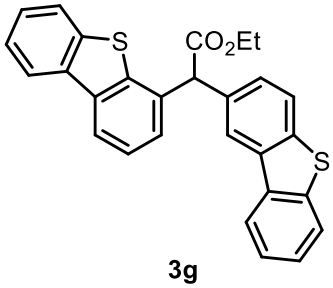

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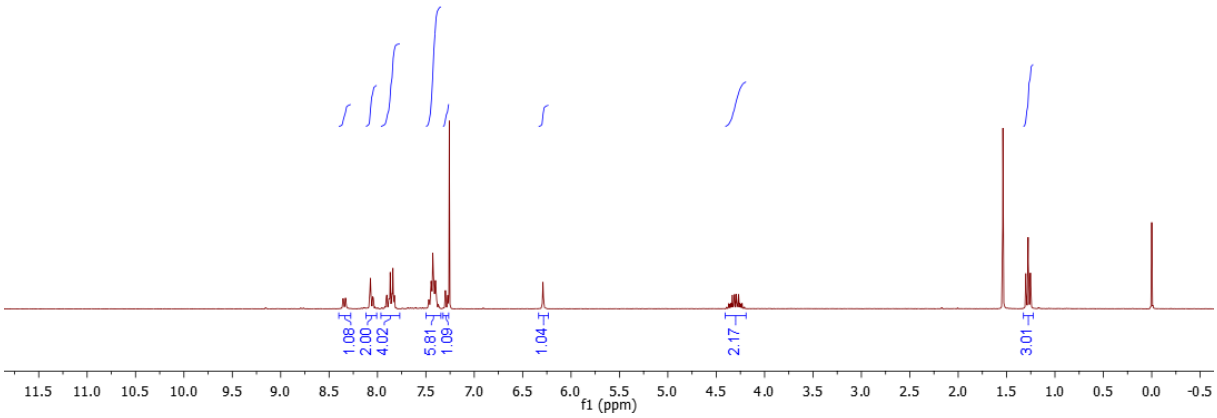

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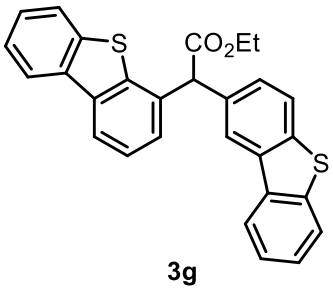

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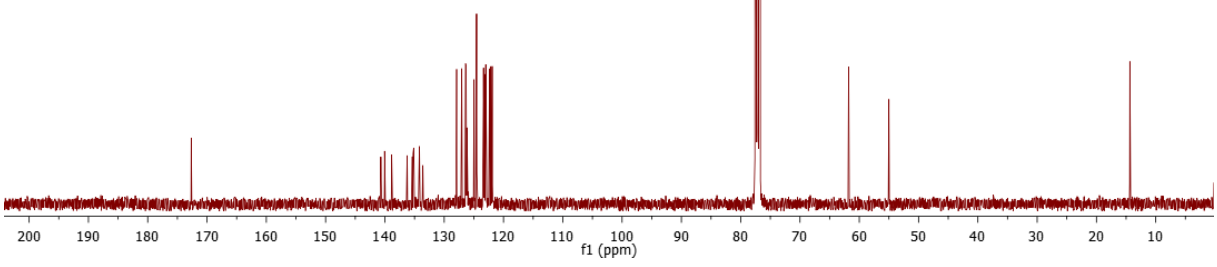

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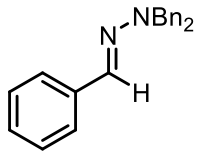

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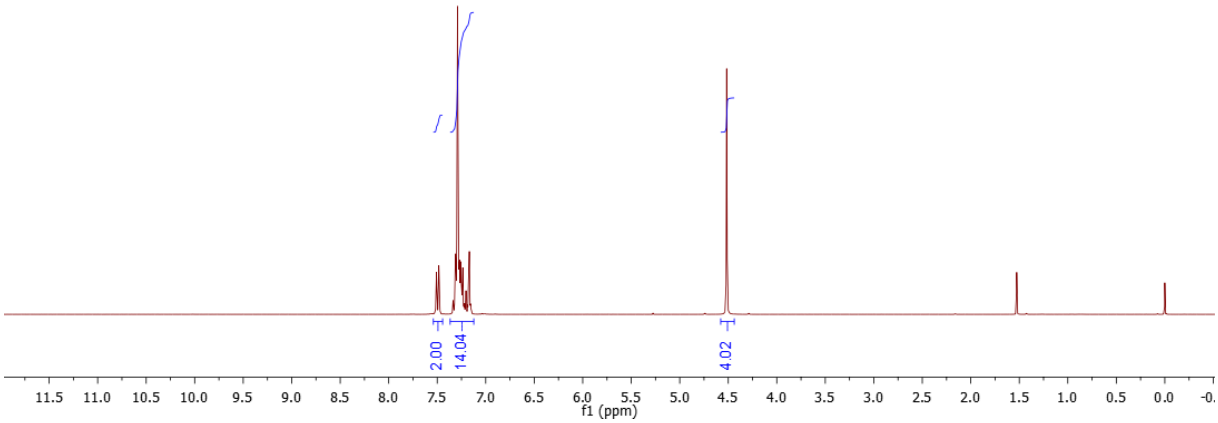

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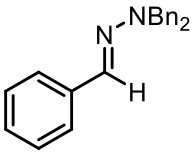

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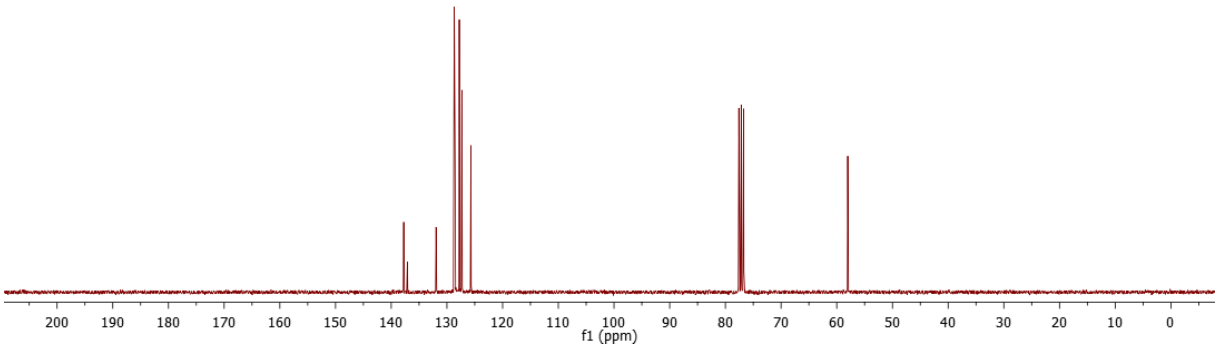

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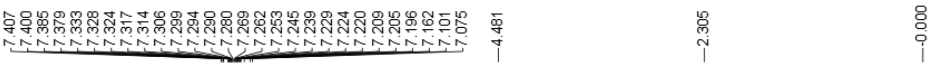

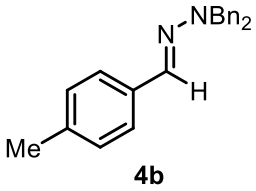

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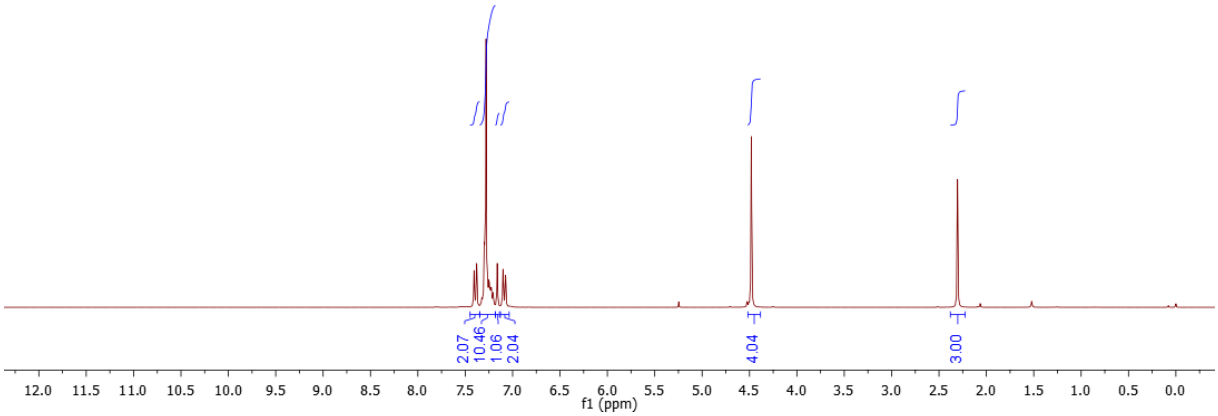

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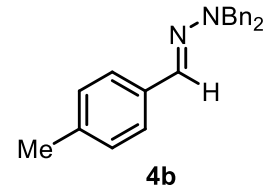

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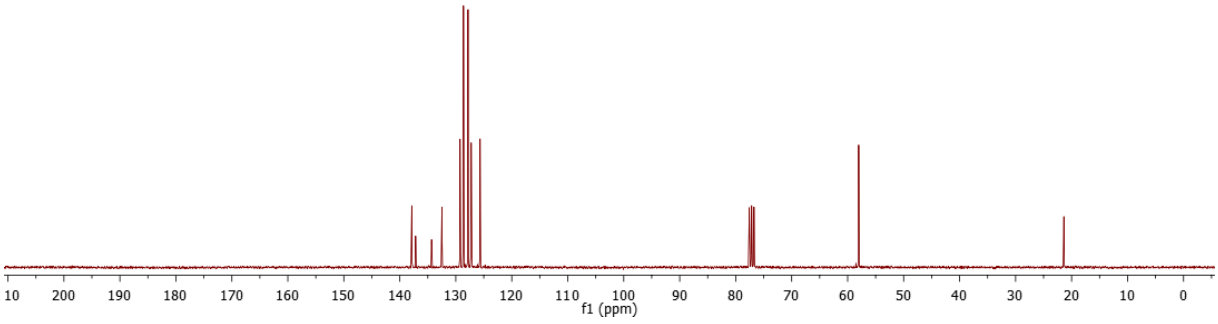

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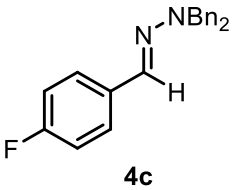

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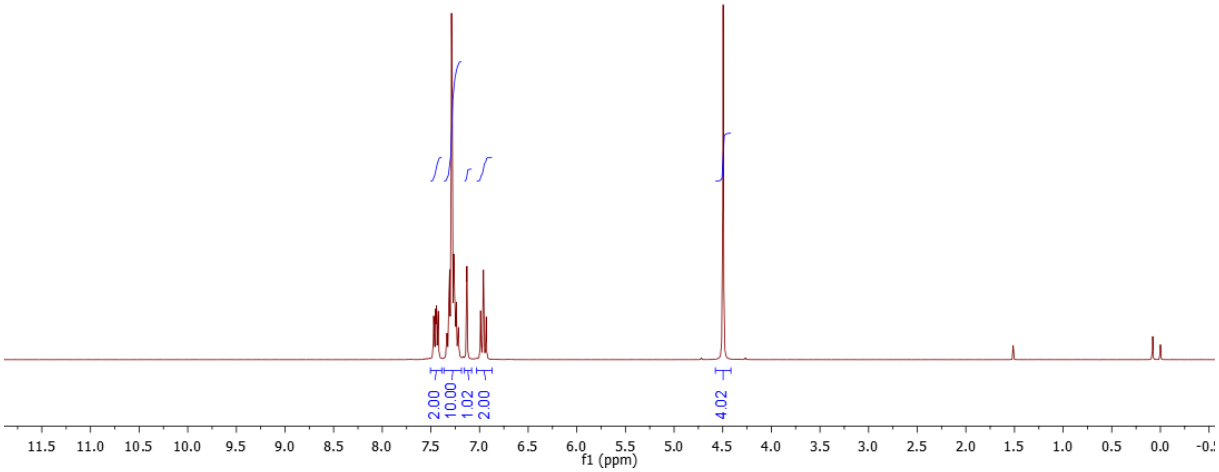

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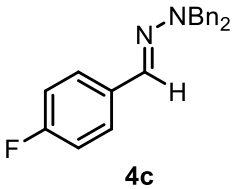

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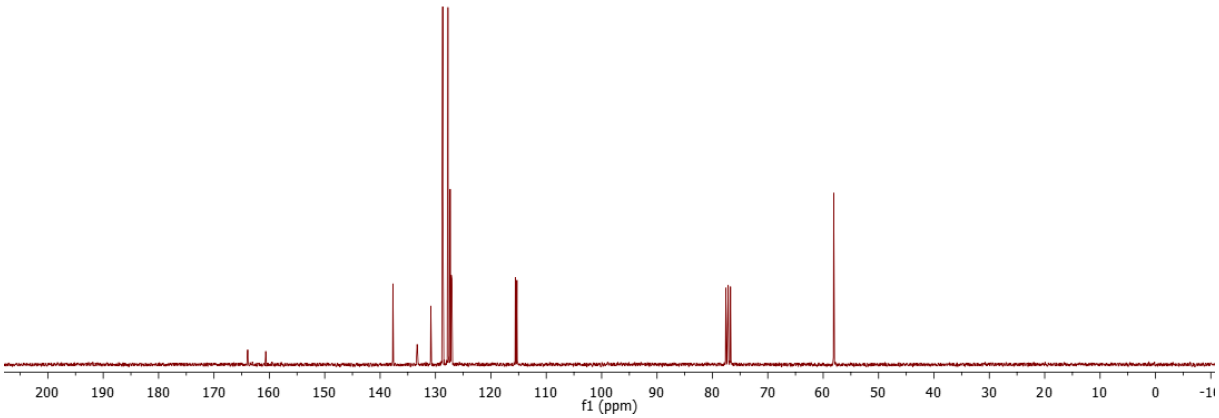

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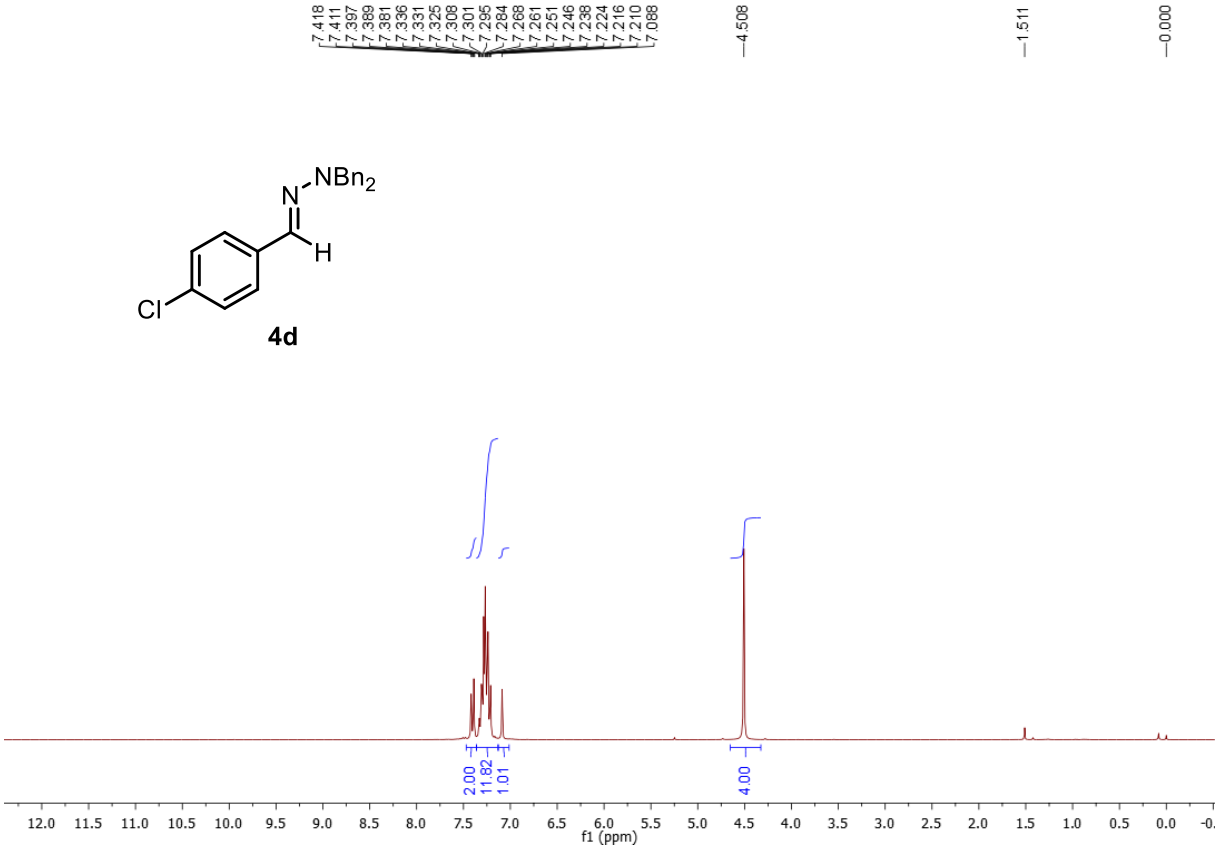

4d

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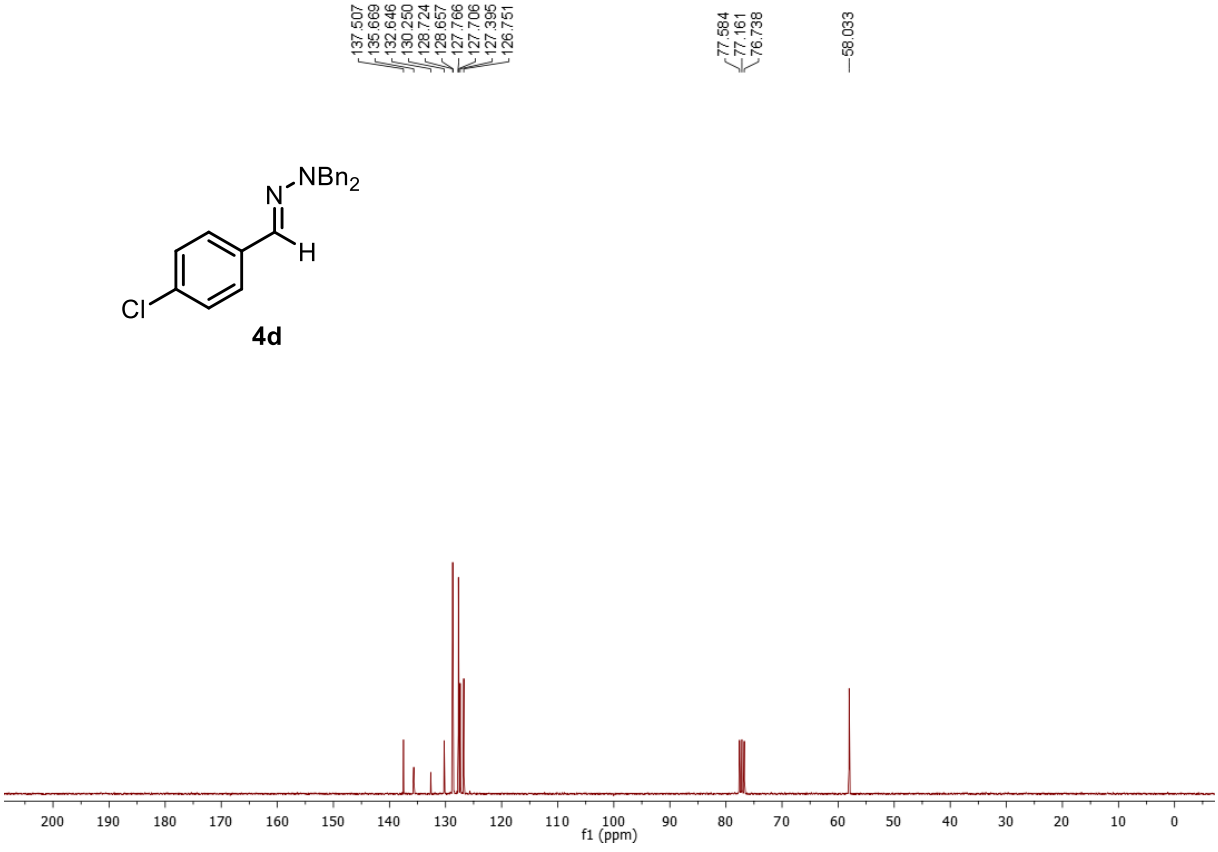
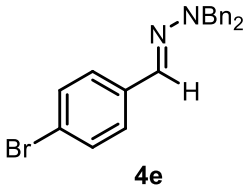


4d

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



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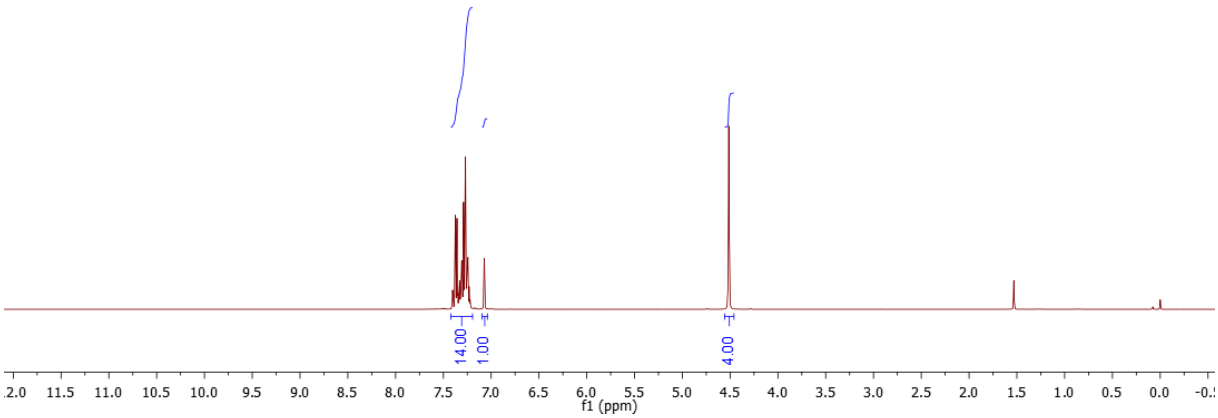
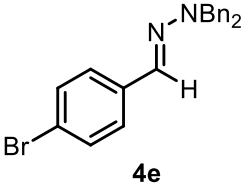


^{13}C NMR (75 MHz, $CDCl_3$)



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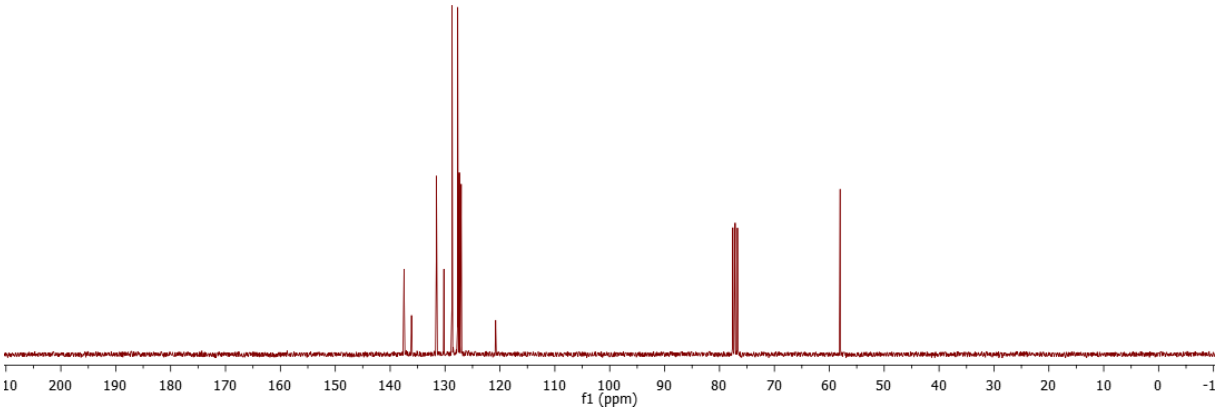
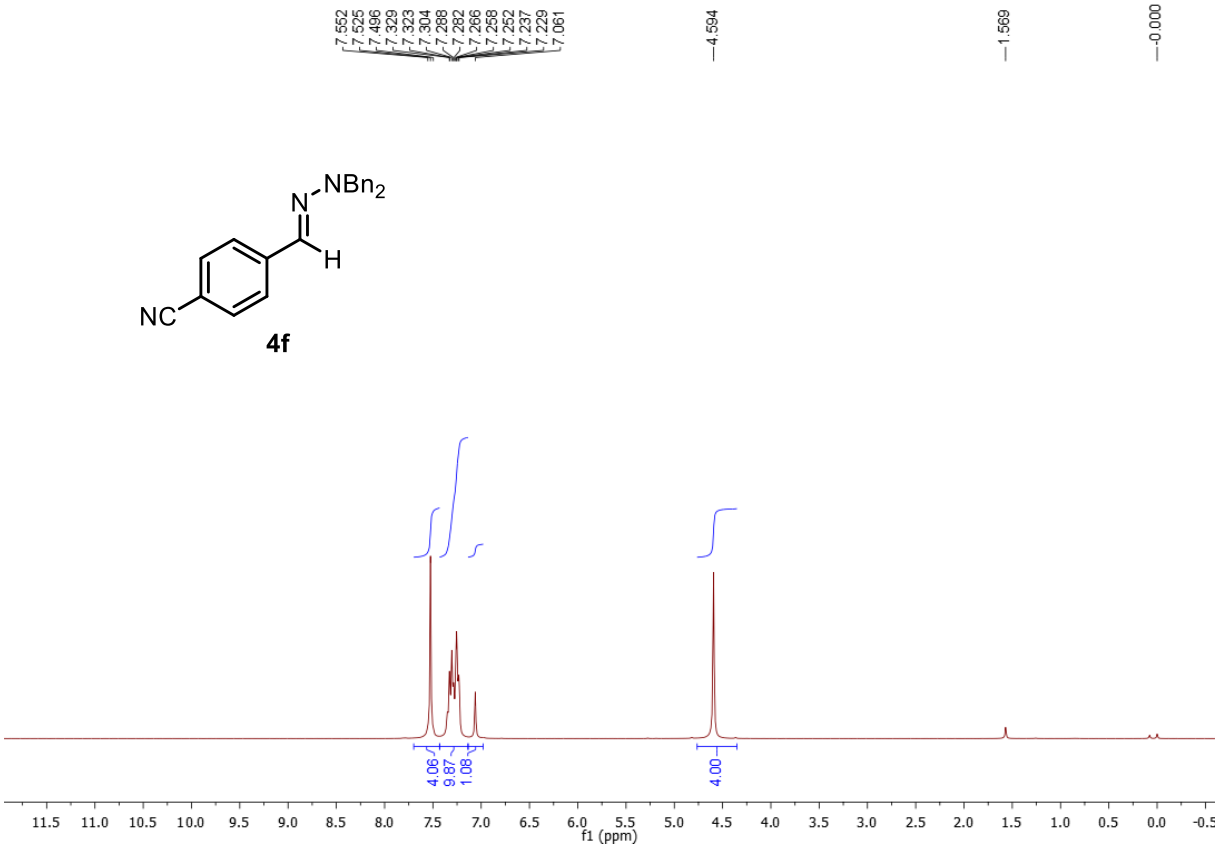
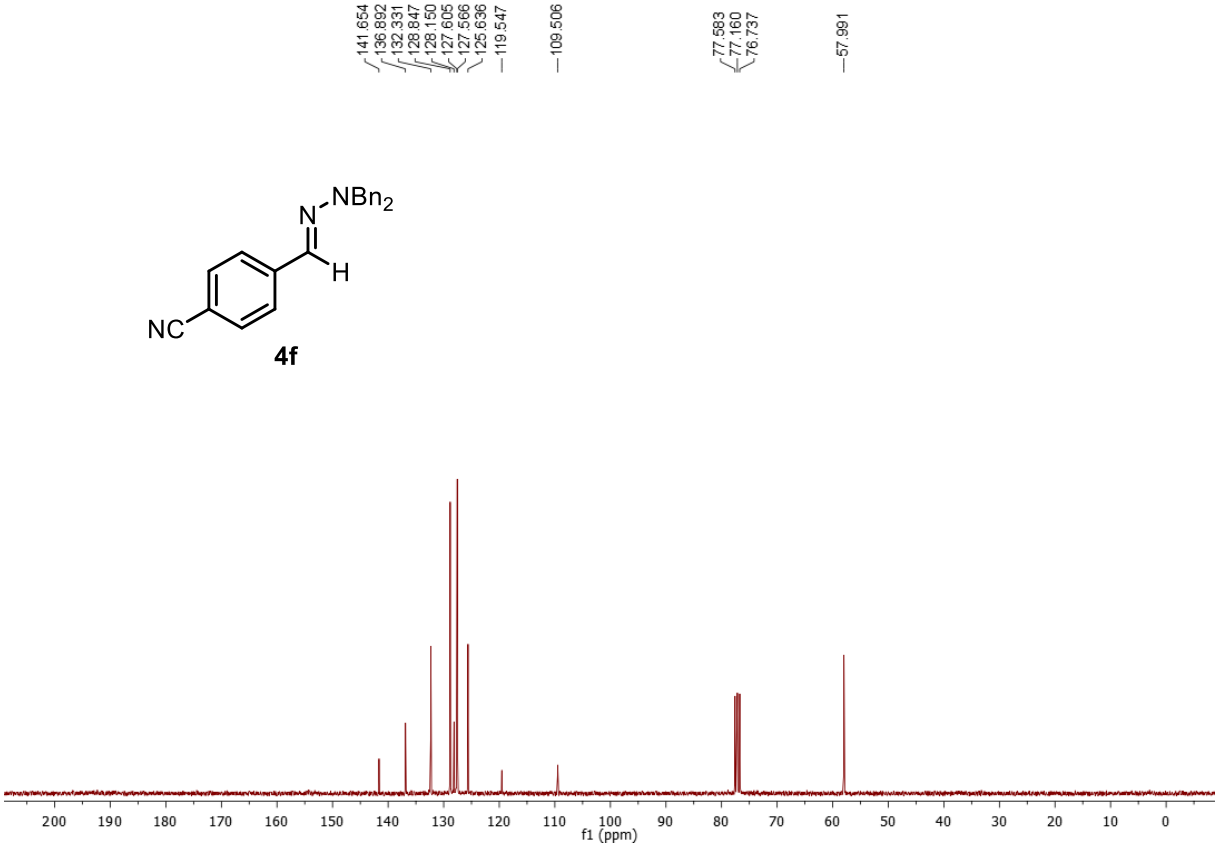


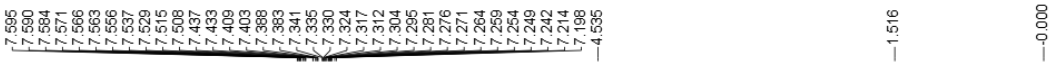
^{1}H NMR (300 MHz, $CDCl_3$)

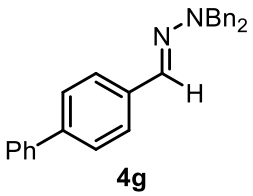


^{13}C NMR (75 MHz, $CDCl_3$)



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





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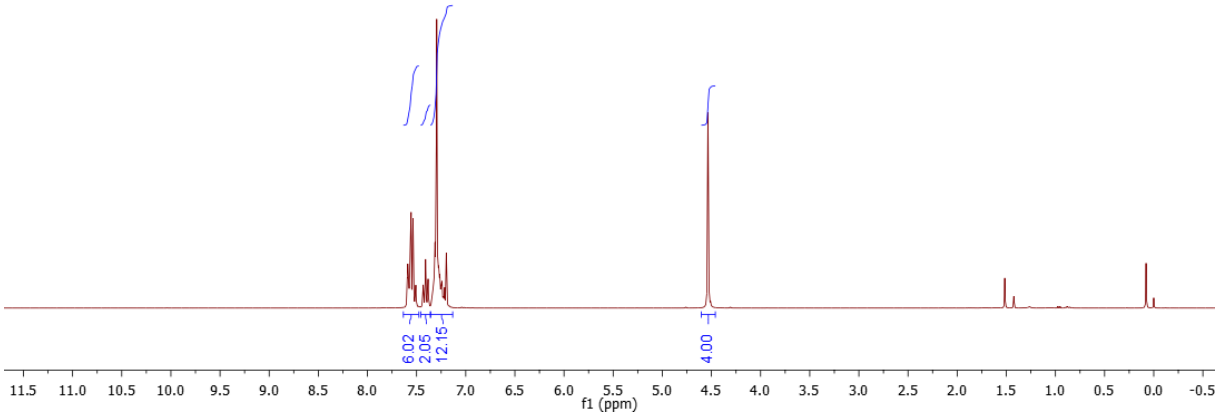
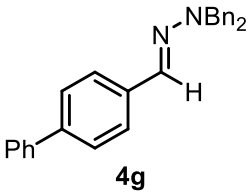


^{13}C NMR (75 MHz, $CDCl_3$)



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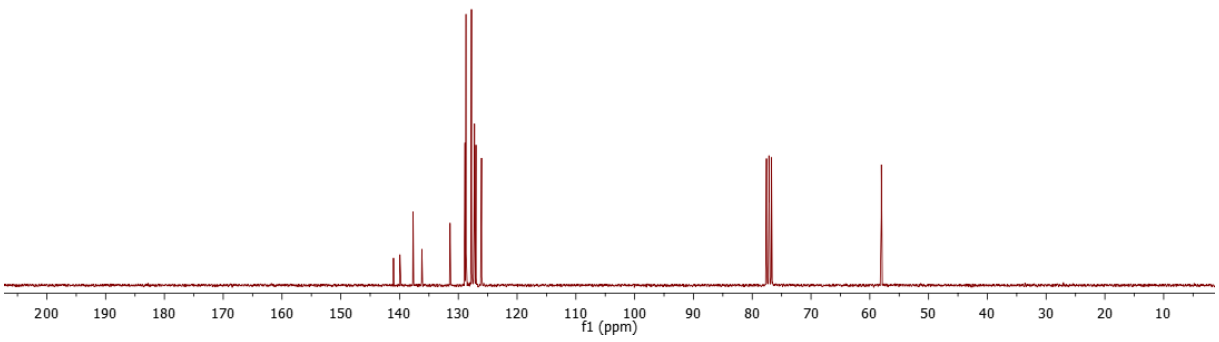
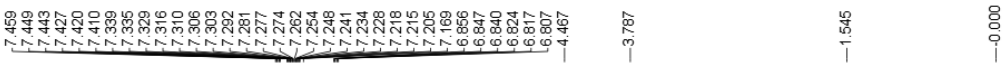
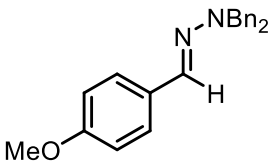


^{1}H NMR (300 MHz, $CDCl_3$)





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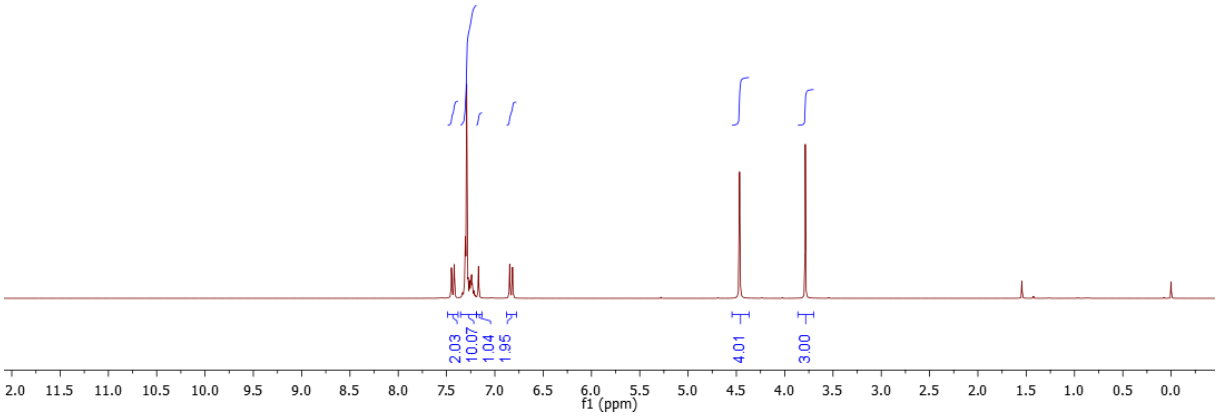
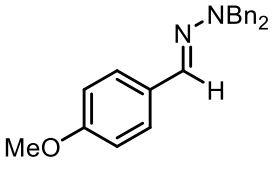


^{13}C NMR (75 MHz, $CDCl_3$)



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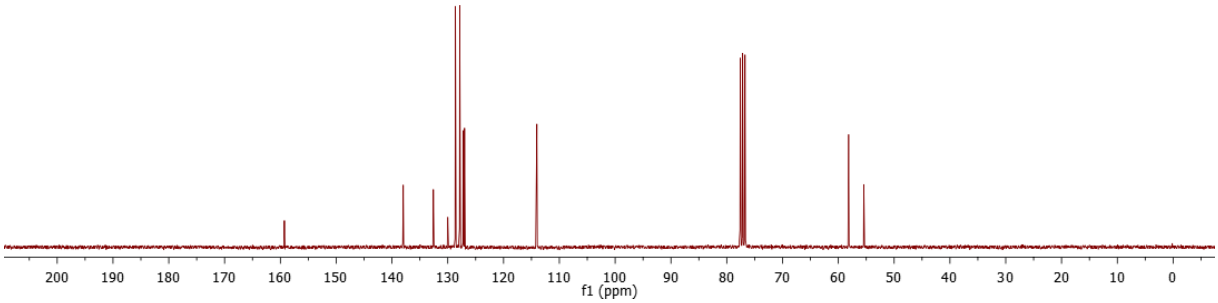
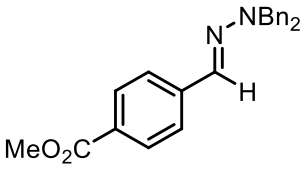


^{1}H NMR (300 MHz, $CDCl_3$)



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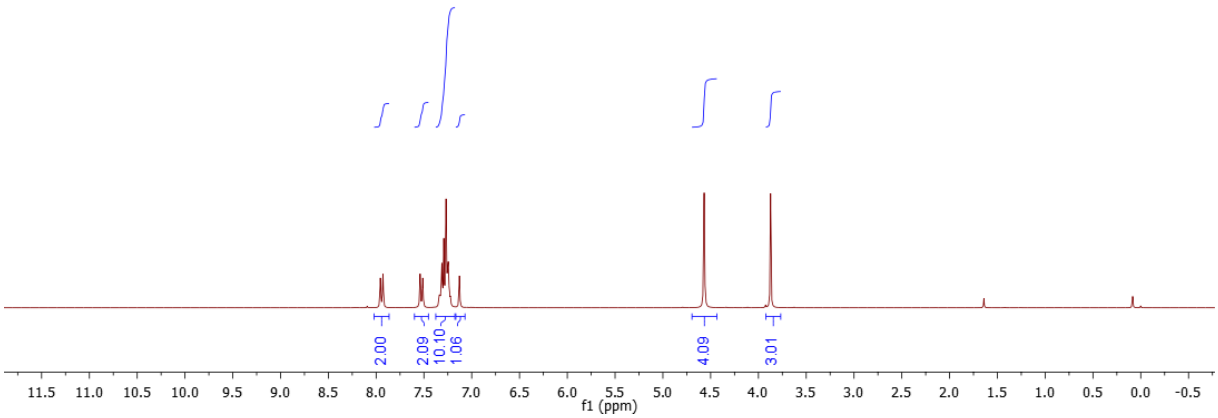
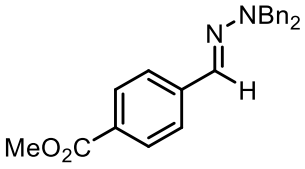


^{13}C NMR (75 MHz, $CDCl_3$)



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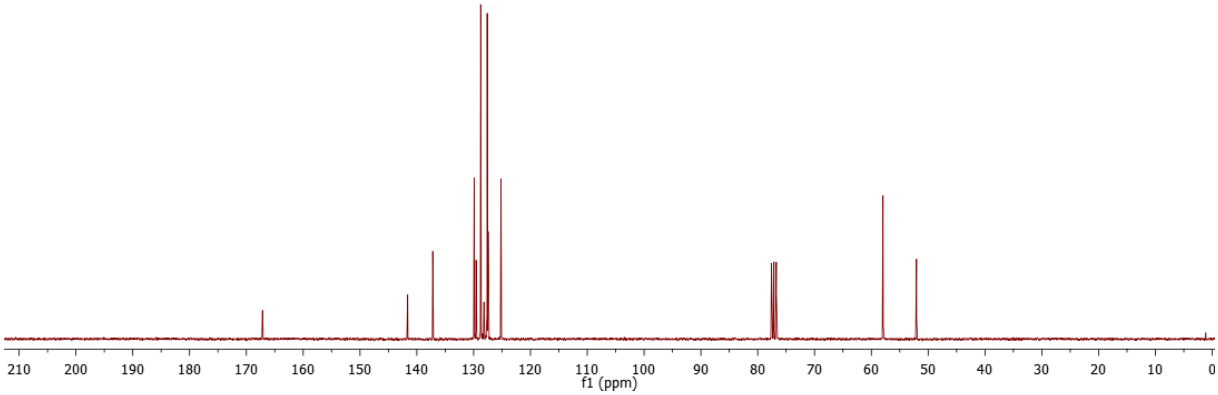
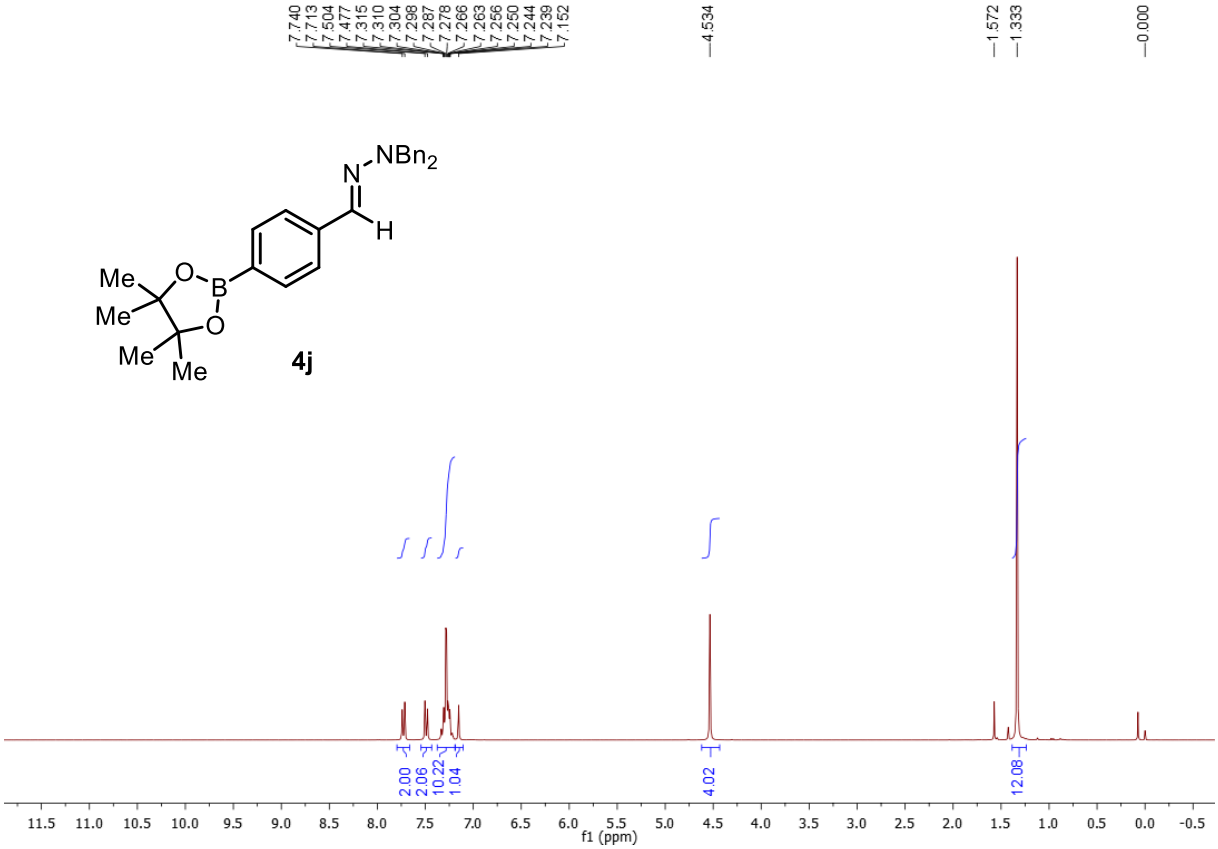
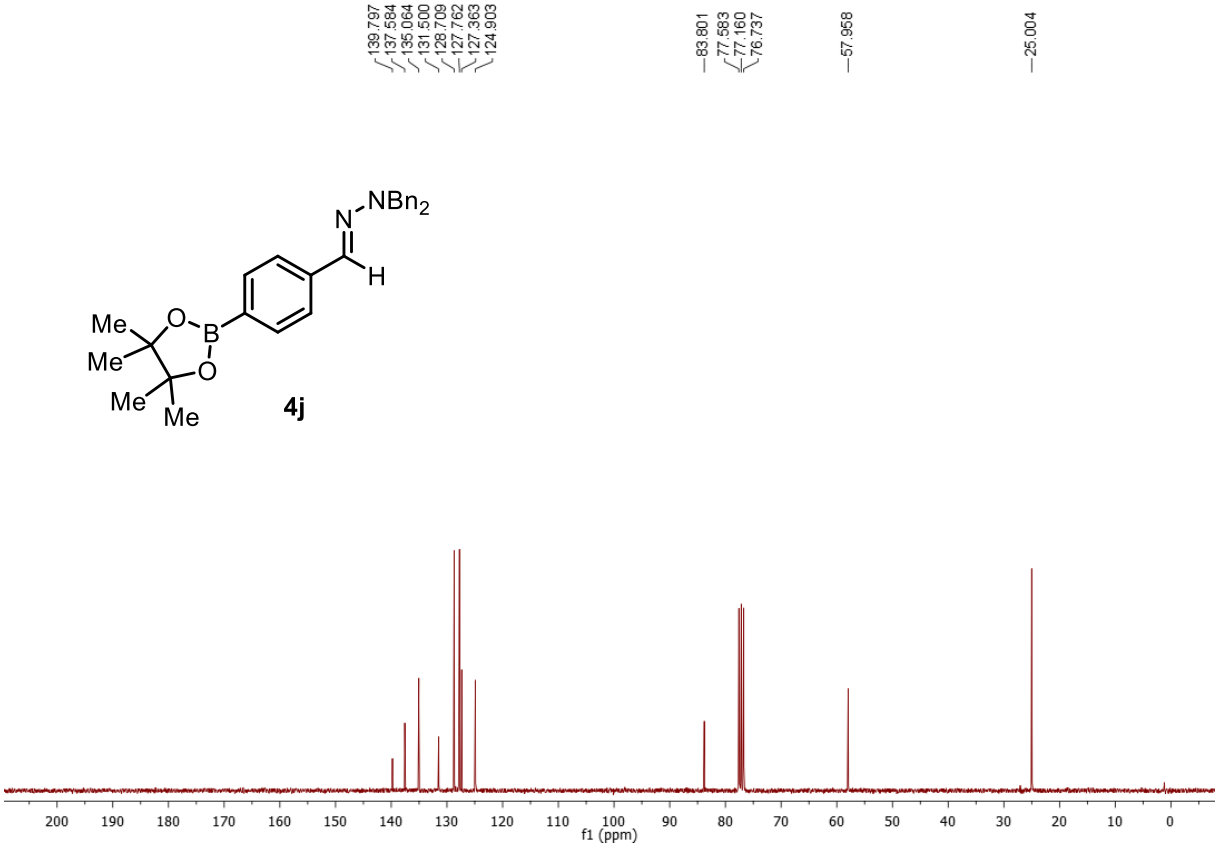


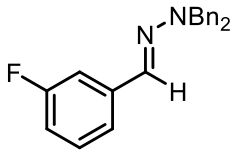
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



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



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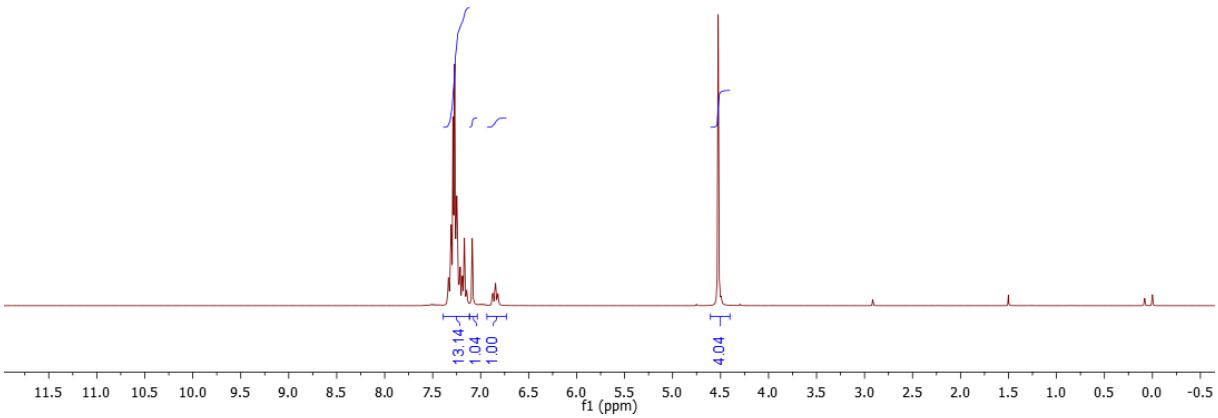
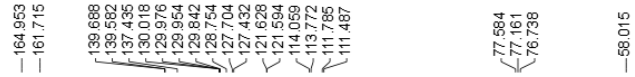
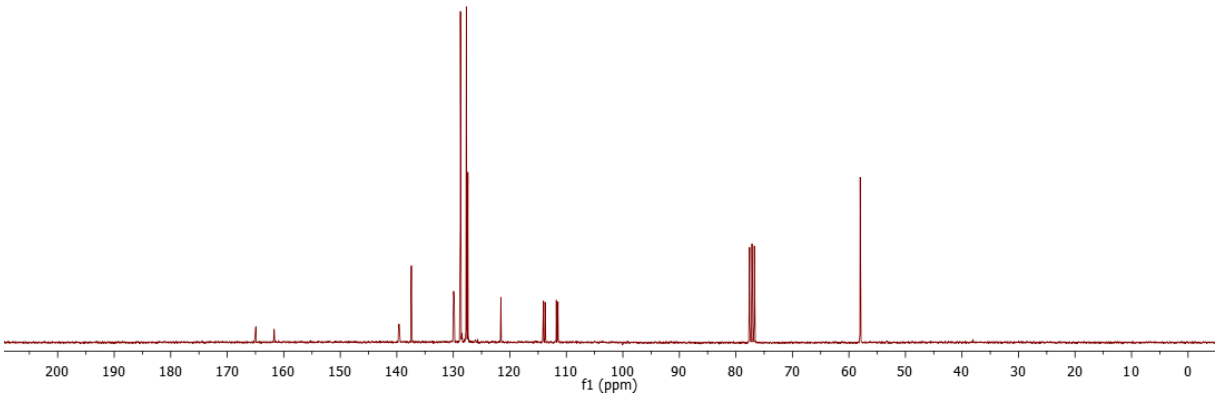
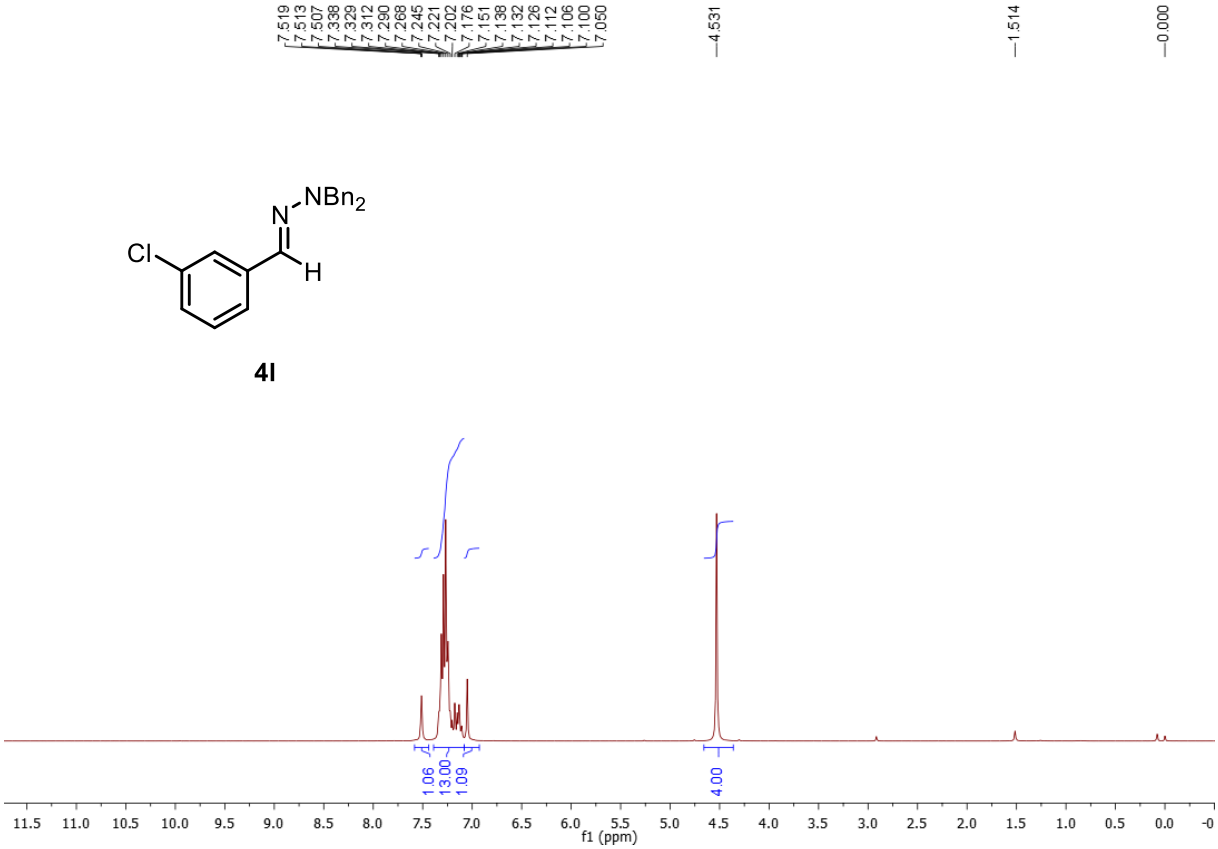


^{13}C NMR (75 MHz, $CDCl_3$)

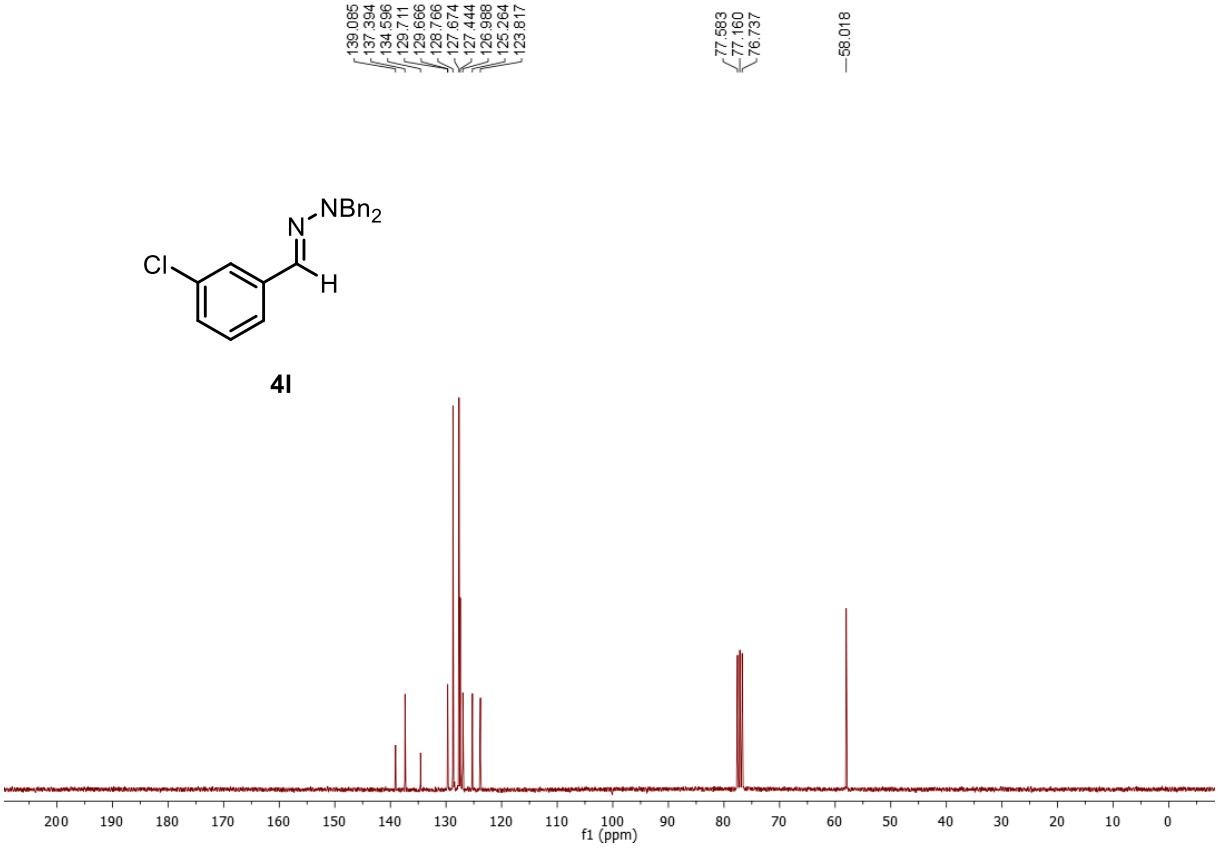




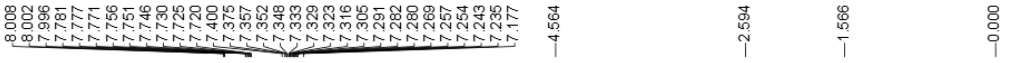
^{1}H NMR (300 MHz, $CDCl_3$)

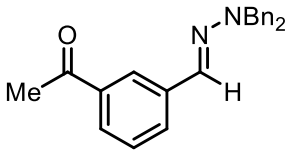


^{13}C NMR (75 MHz, $CDCl_3$)



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





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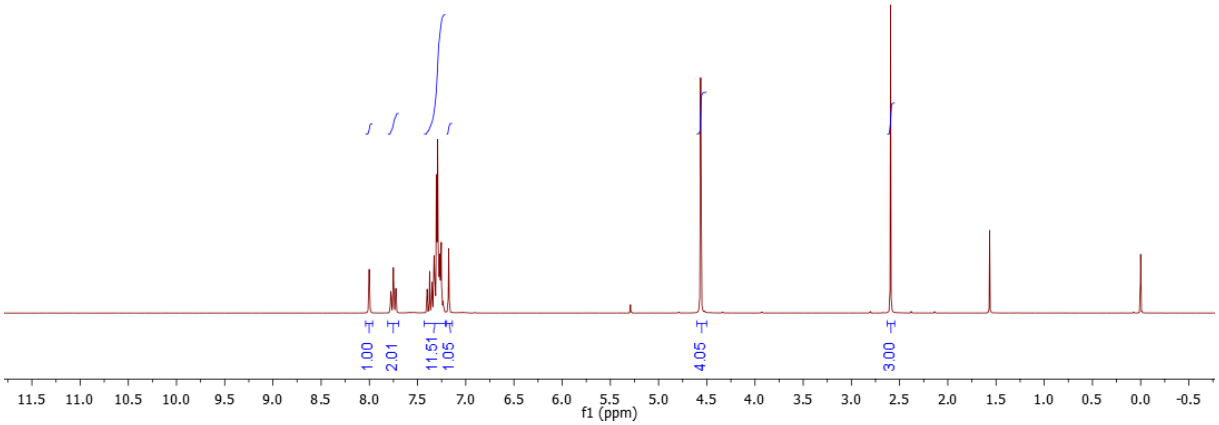
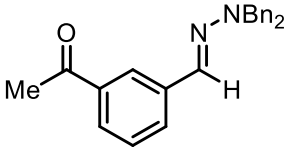


^{13}C NMR (75 MHz, $CDCl_3$)



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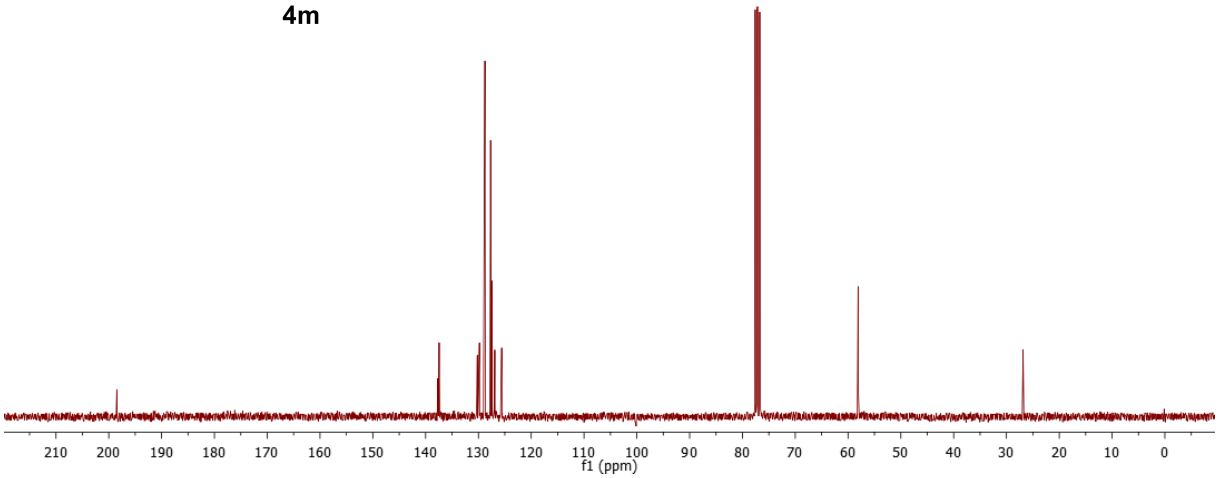
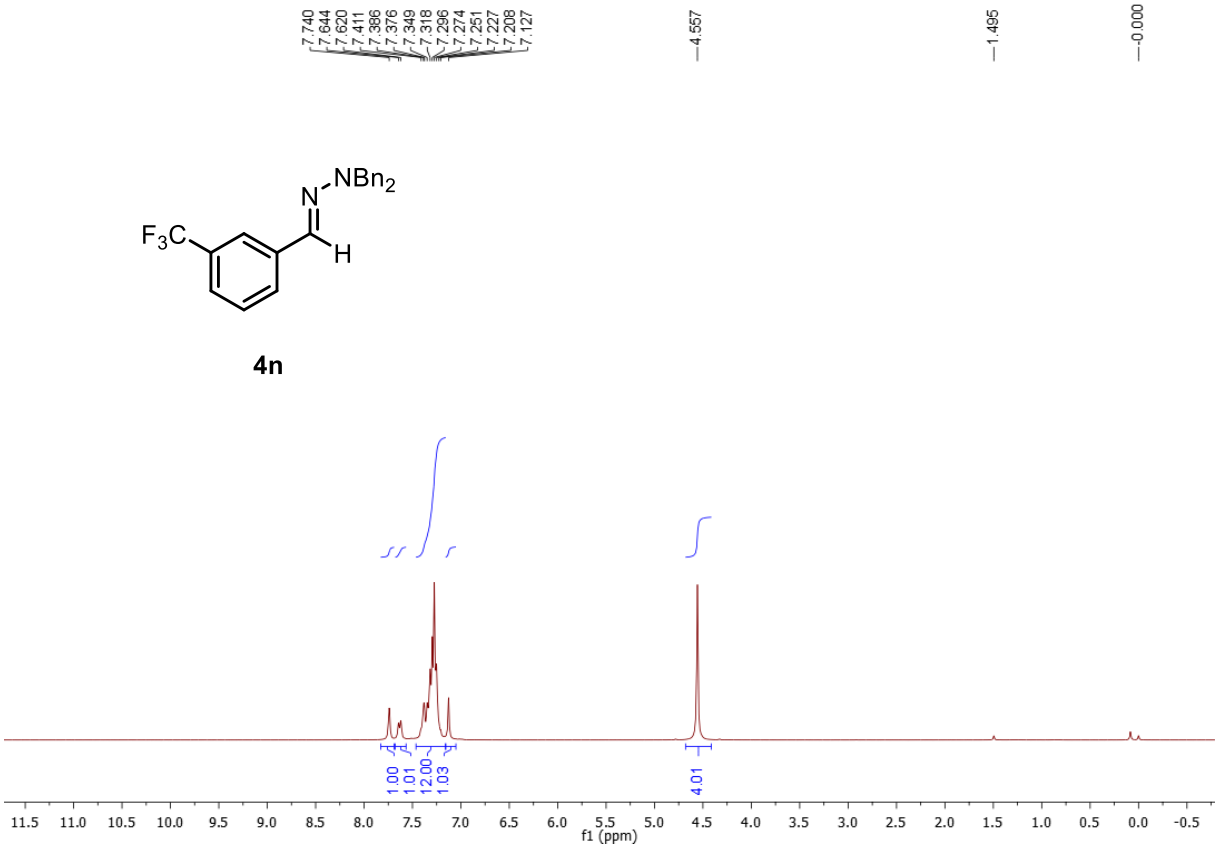
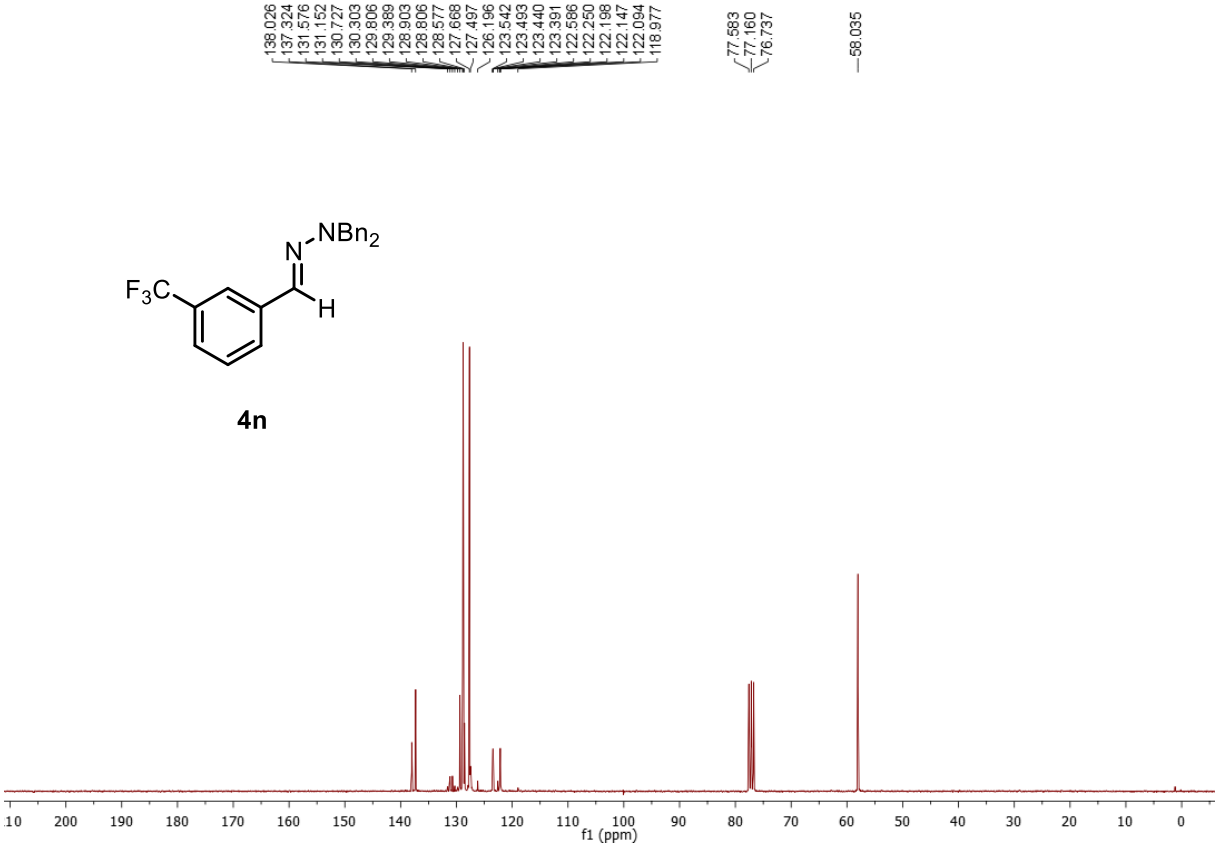


^{1}H NMR (300 MHz, $CDCl_3$)



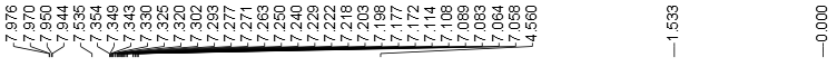
4n

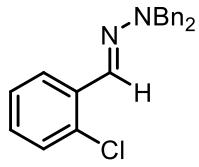
^{13}C NMR (75 MHz, $CDCl_3$)



4n

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





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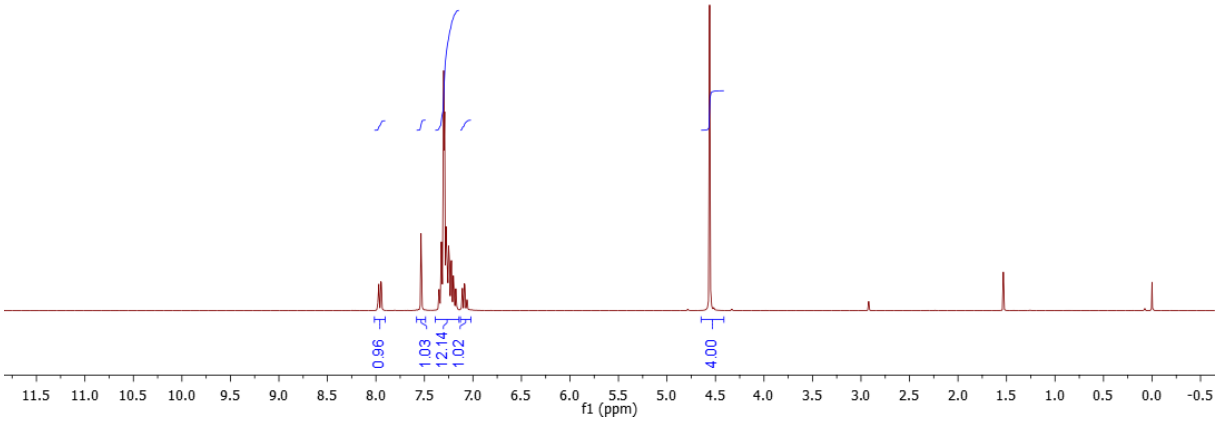
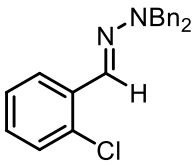


^{13}C NMR (75 MHz, $CDCl_3$)



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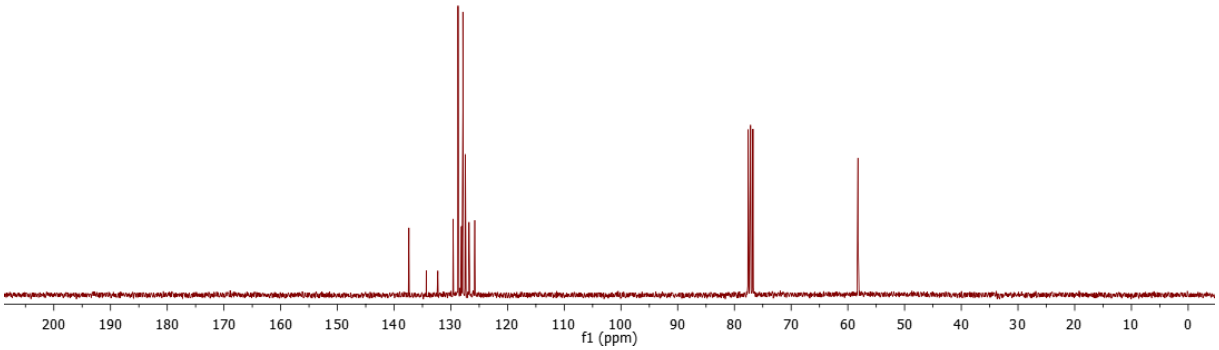
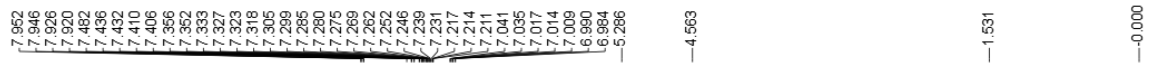
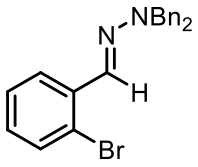


^{1}H NMR (300 MHz, $CDCl_3$)





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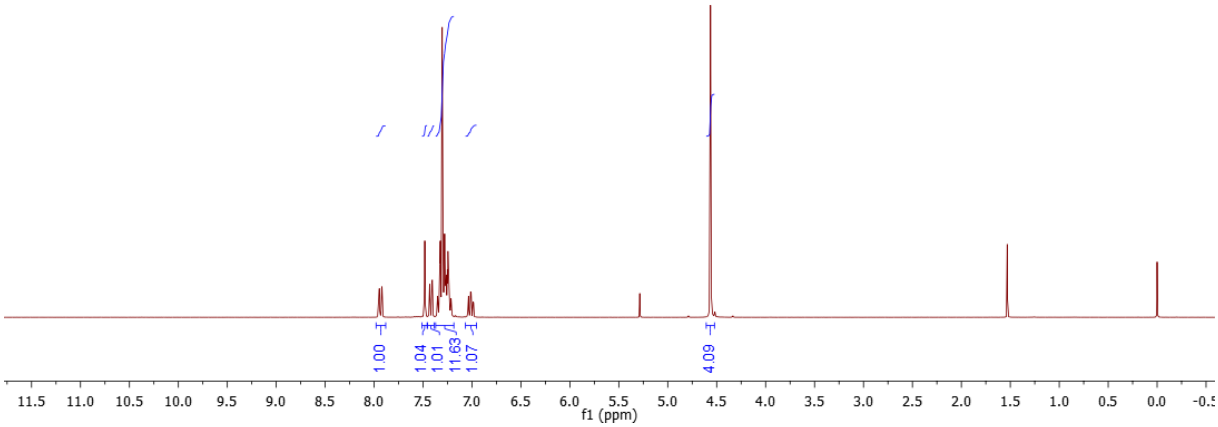
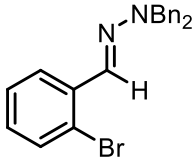


^{13}C NMR (75 MHz, $CDCl_3$)



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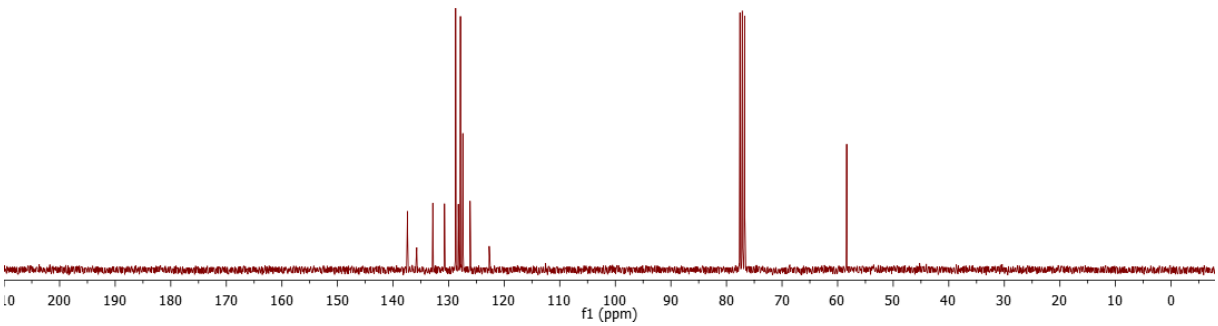
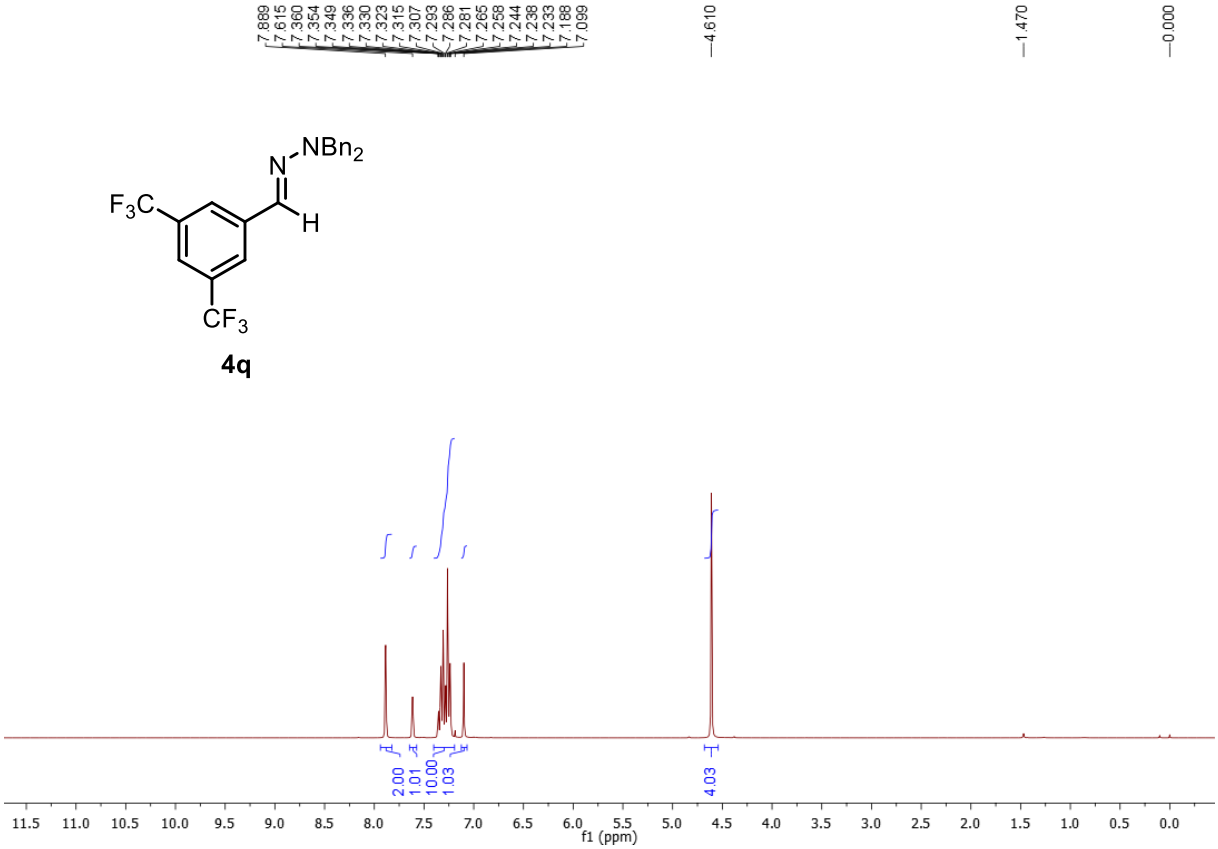
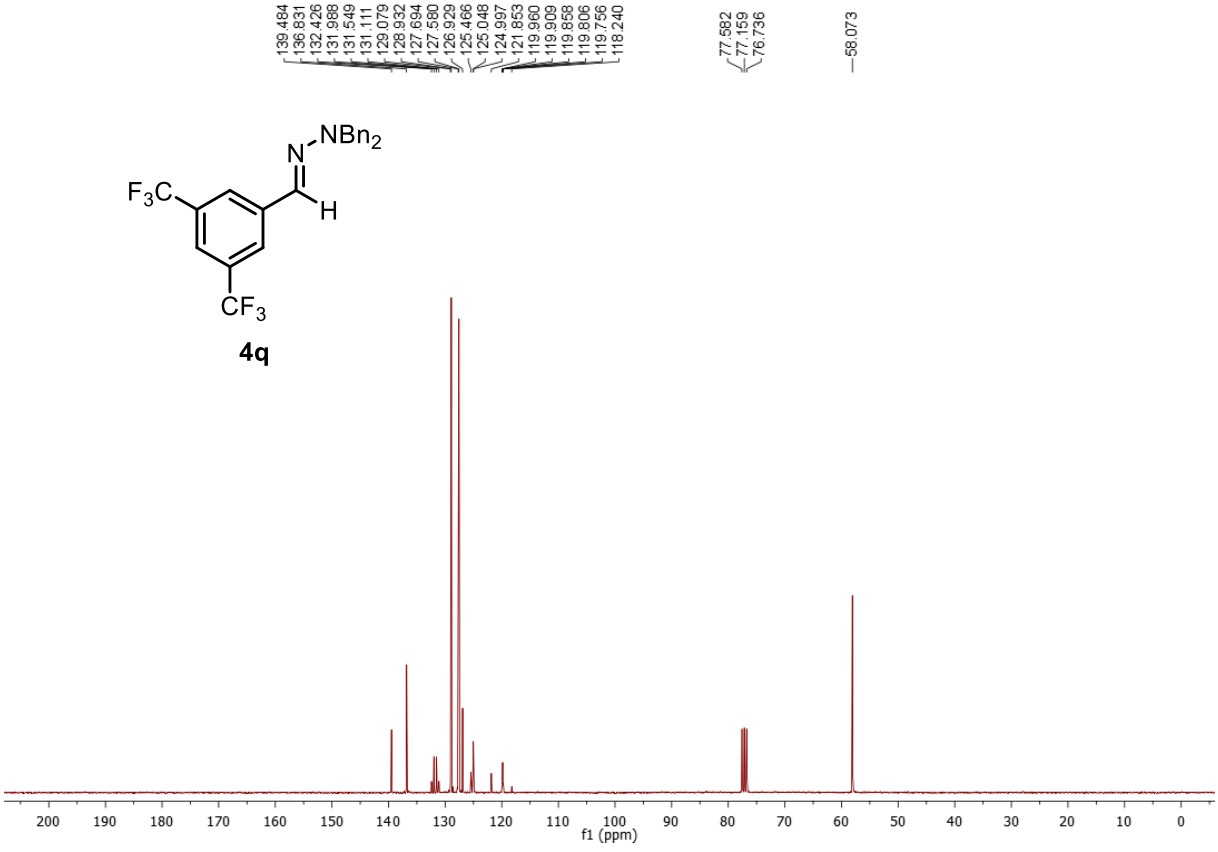


^{1}H NMR (300 MHz, $CDCl_3$)



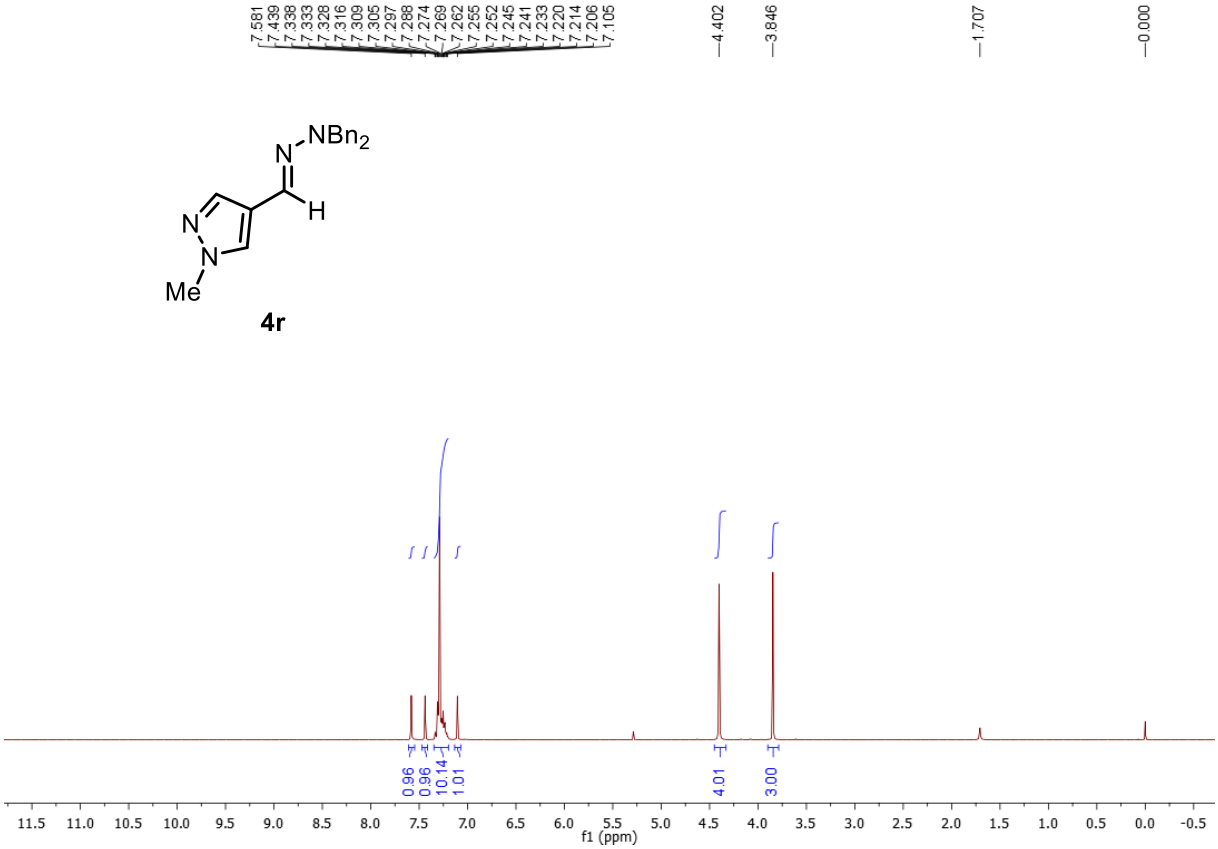
4q

^{13}C NMR (75 MHz, $CDCl_3$)



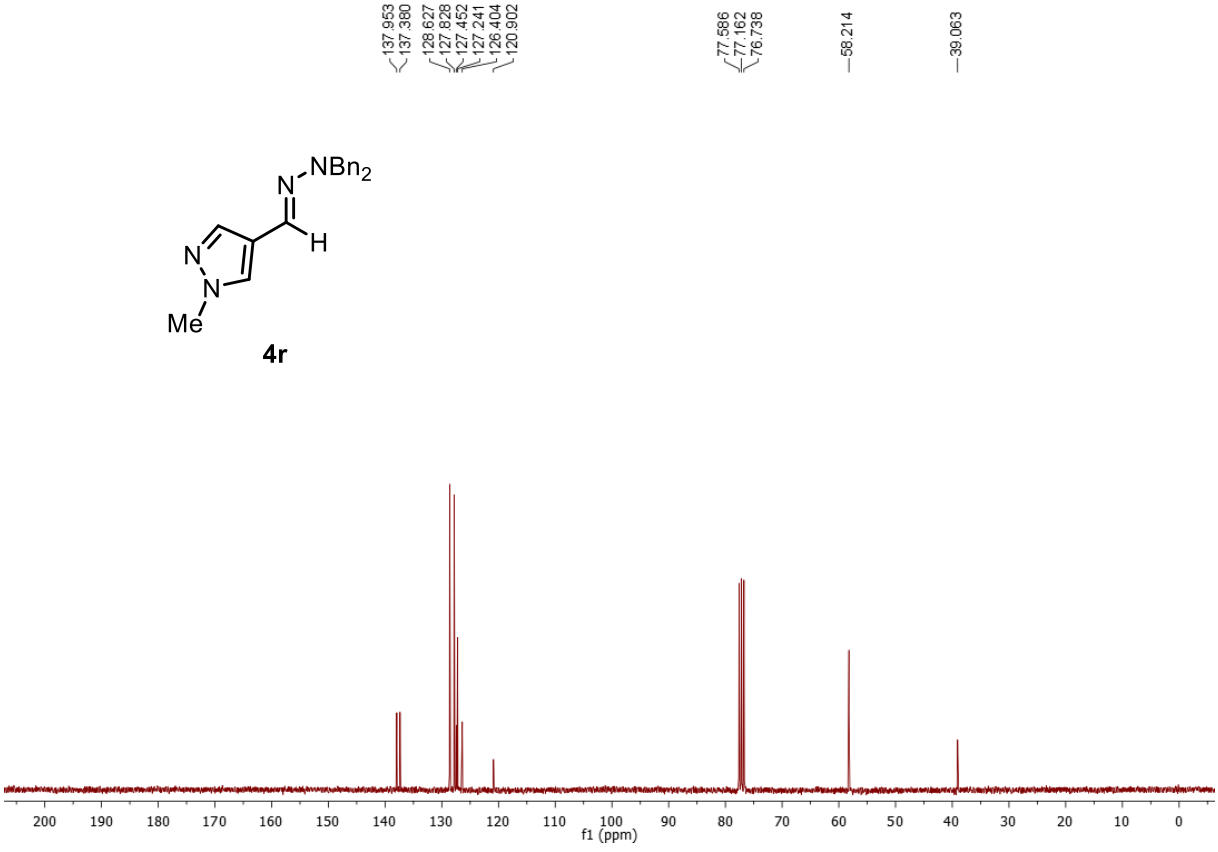
4q

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



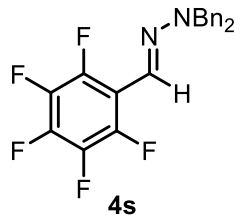
4r

^{13}C NMR (75 MHz, $CDCl_3$)

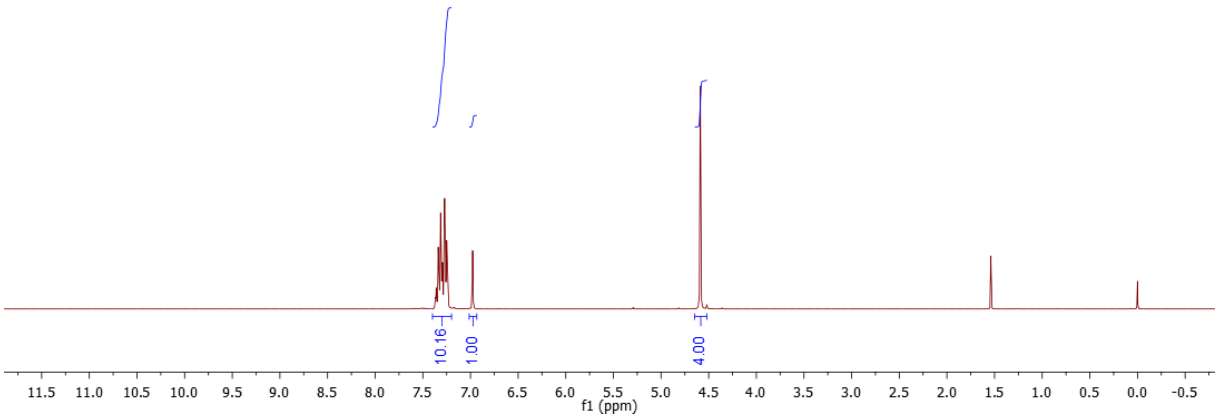


4r

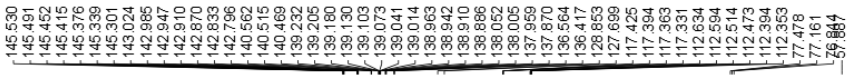
^{1}H NMR (300 MHz, $CDCl_3$)

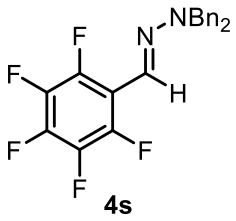


4s



^{13}C NMR (100 MHz, $CDCl_3$)





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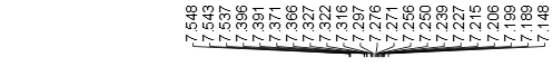
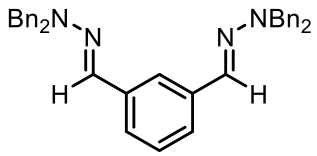
^{1}H NMR (300 MHz, $CDCl_3$)





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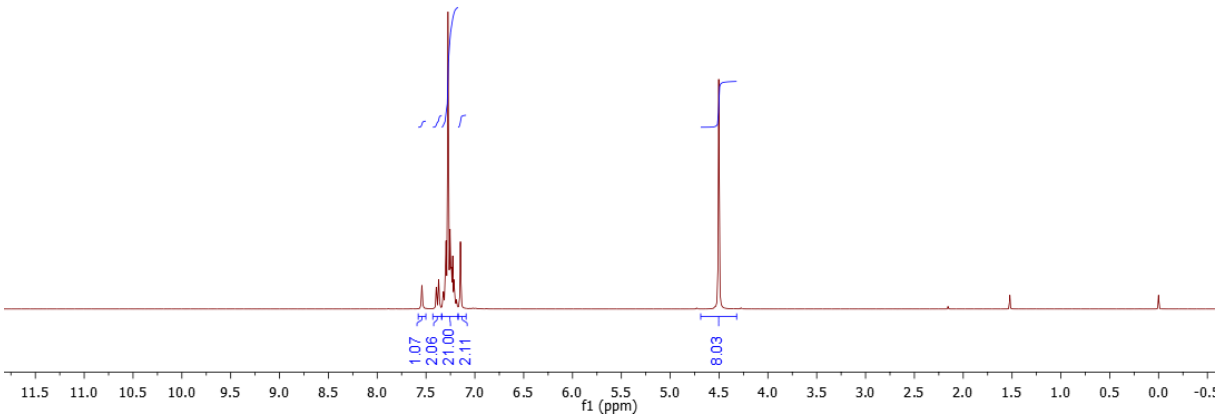
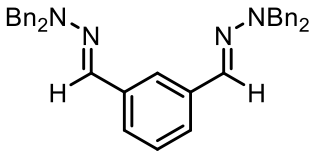


^{13}C NMR (75 MHz, $CDCl_3$)



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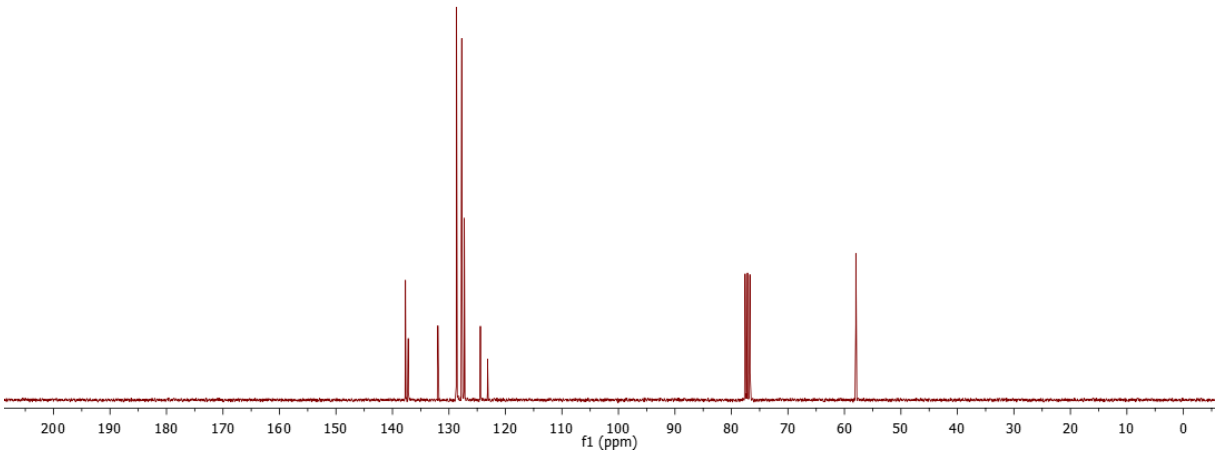
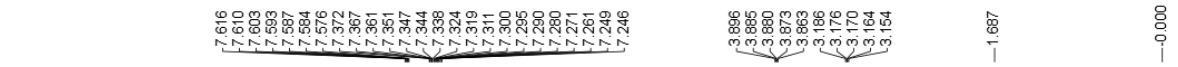
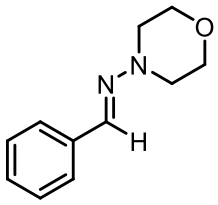


^{1}H NMR (300 MHz, $CDCl_3$)





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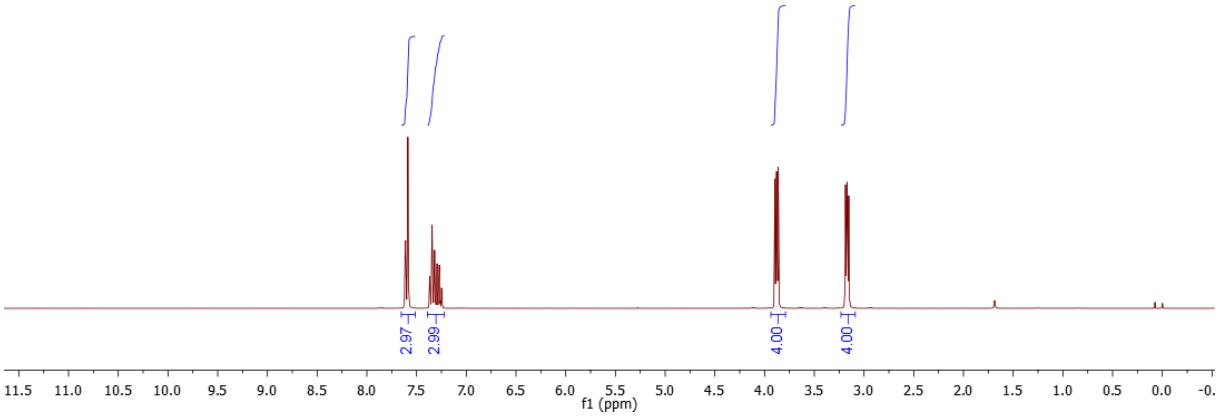
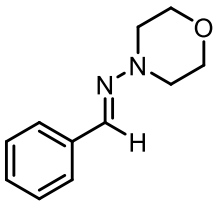


^{13}C NMR (75 MHz, $CDCl_3$)



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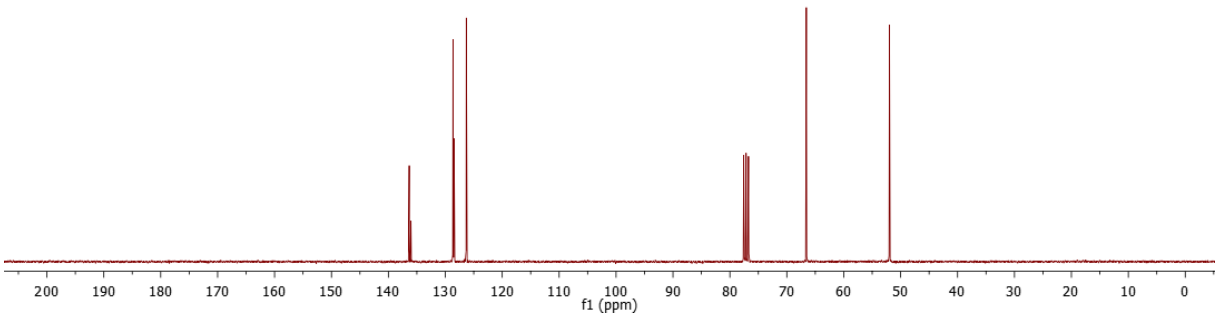
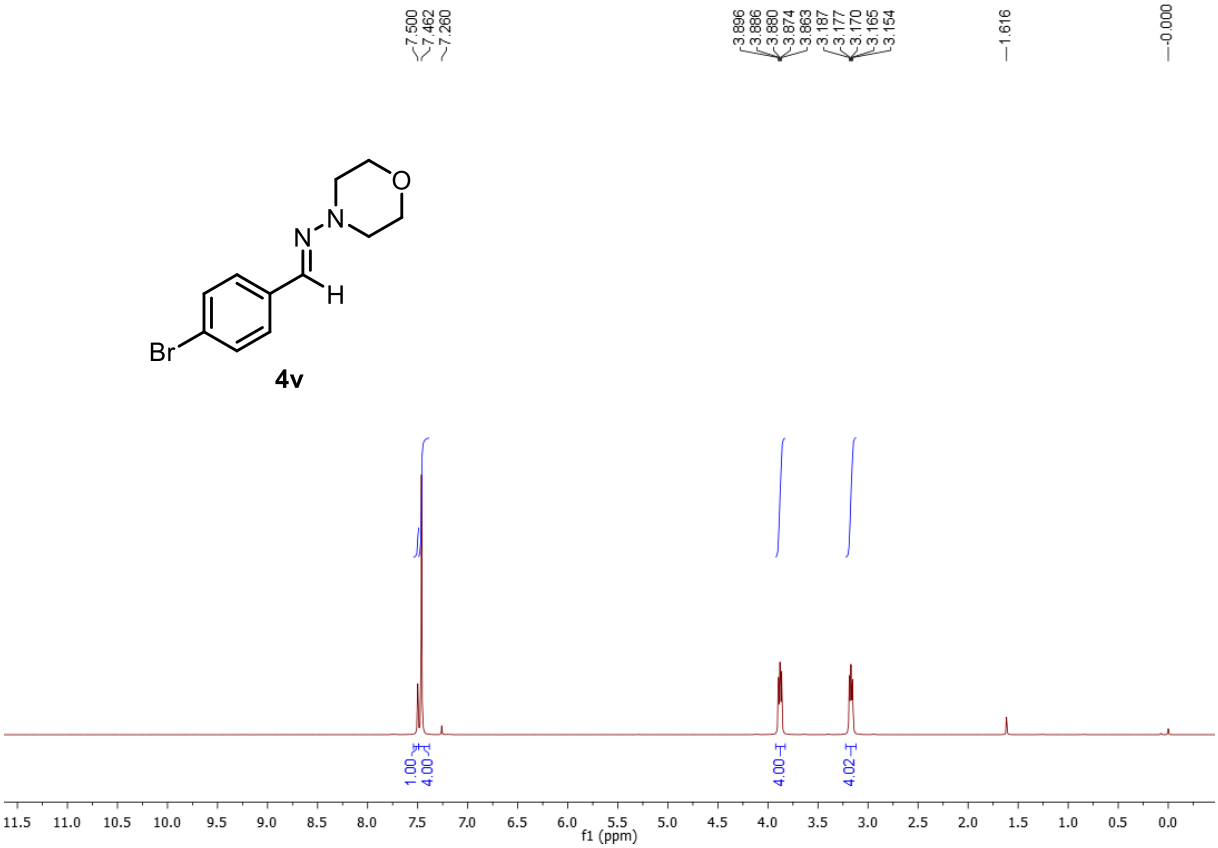
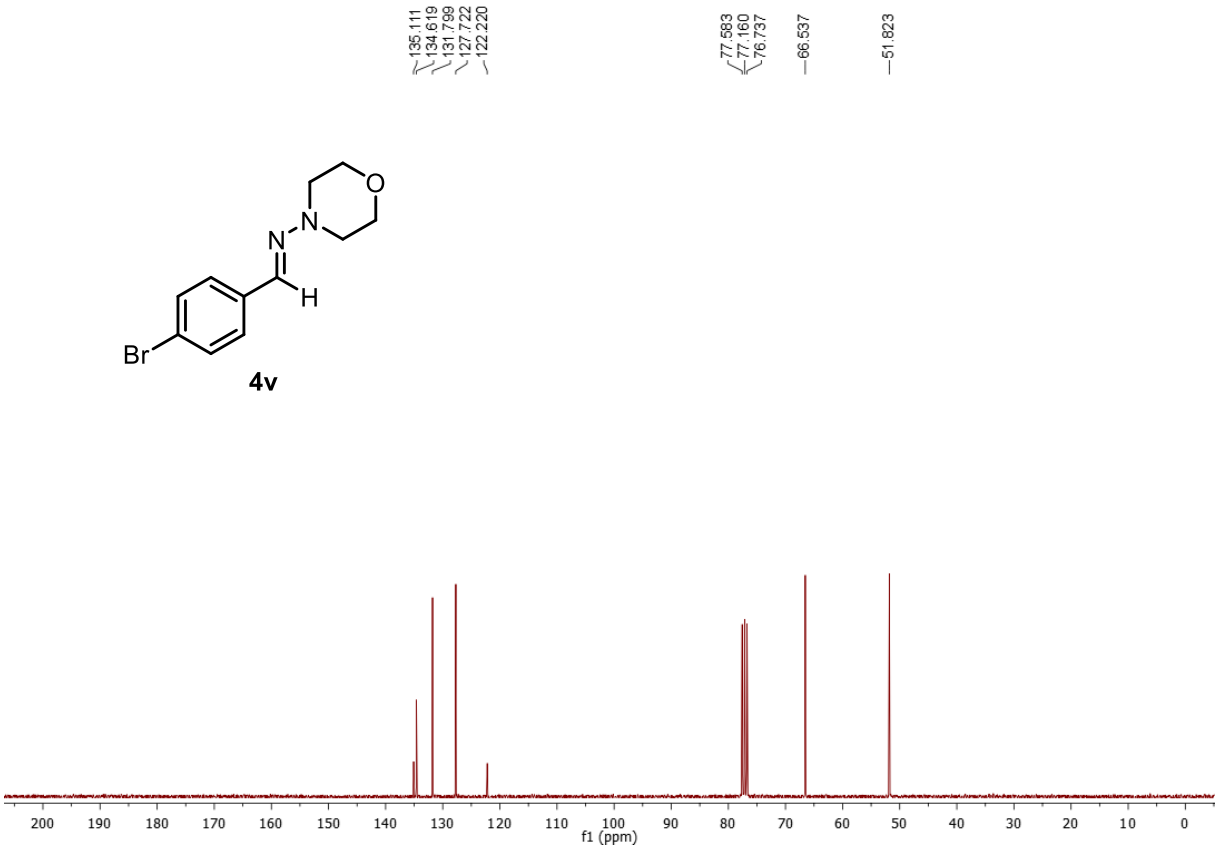


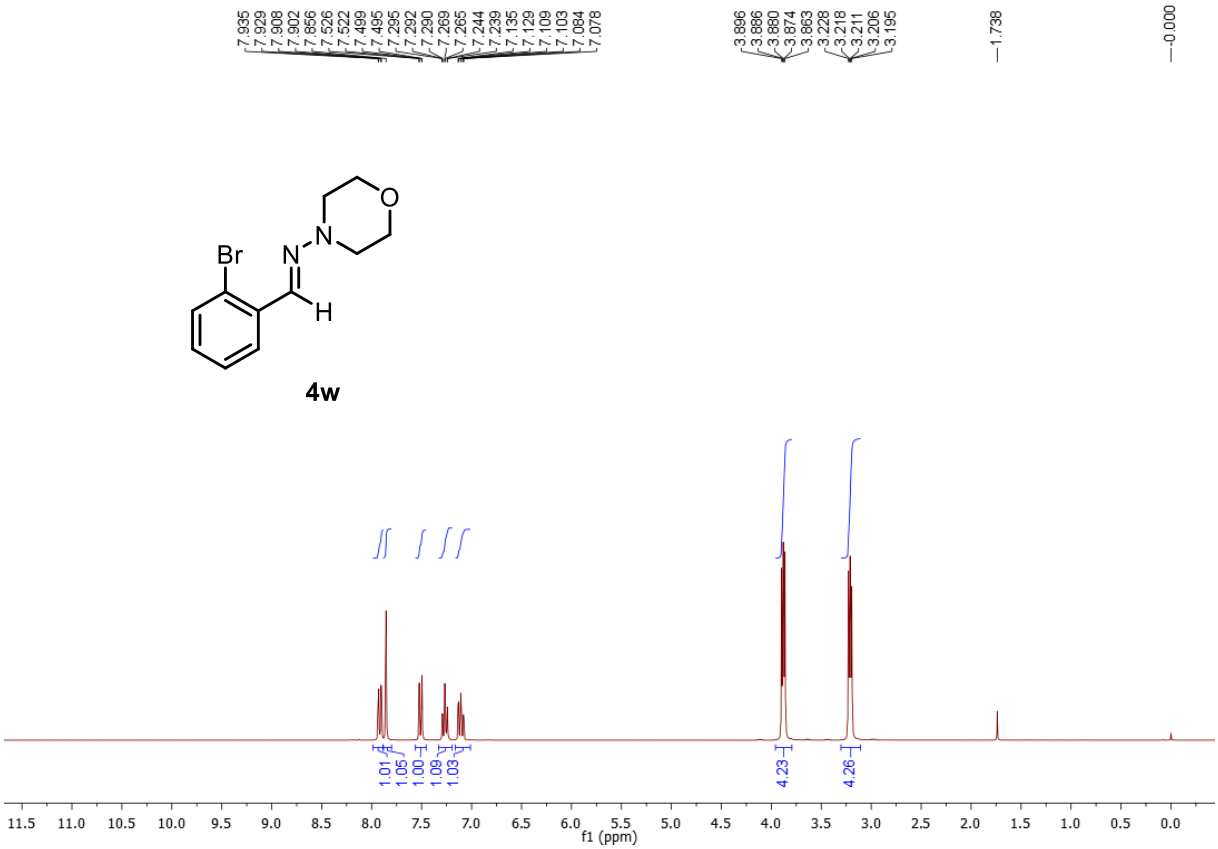
^{1}H NMR (300 MHz, $CDCl_3$)



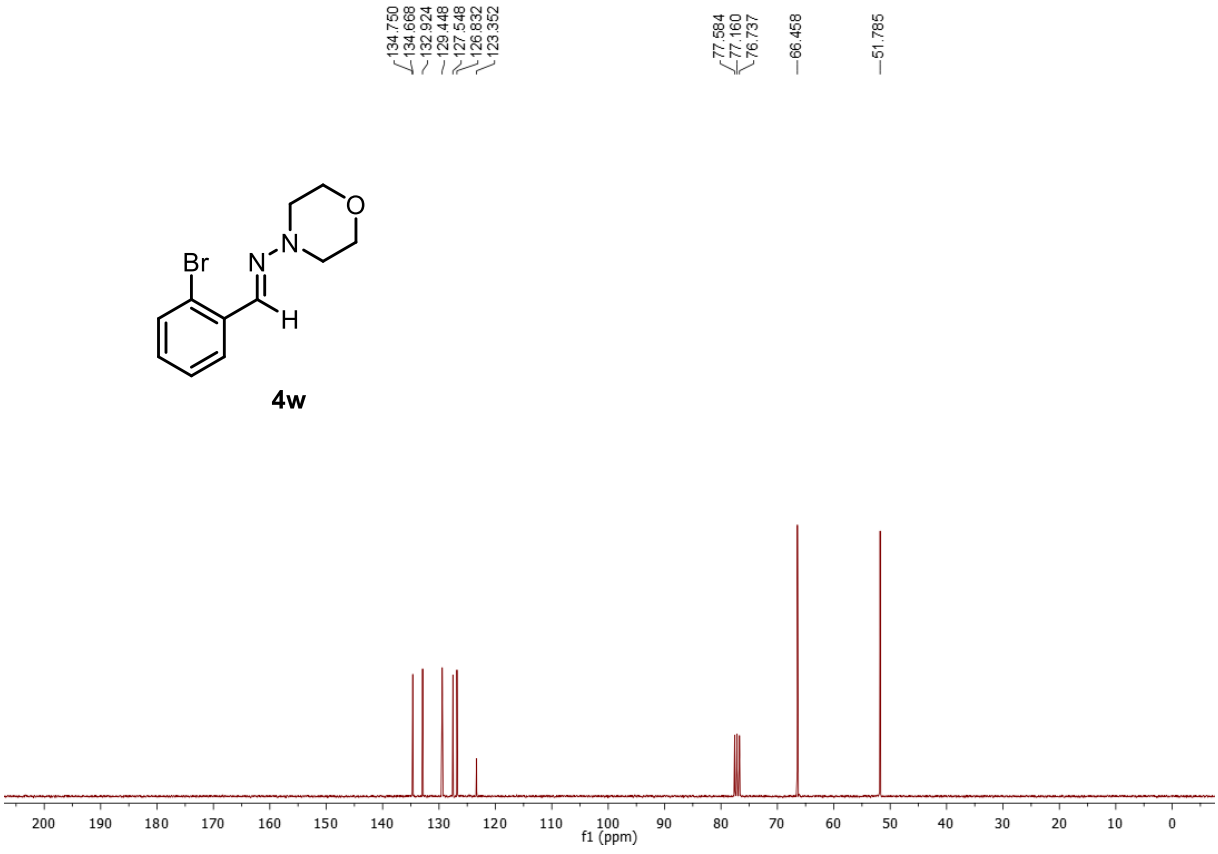
^{13}C NMR (75 MHz, $CDCl_3$)



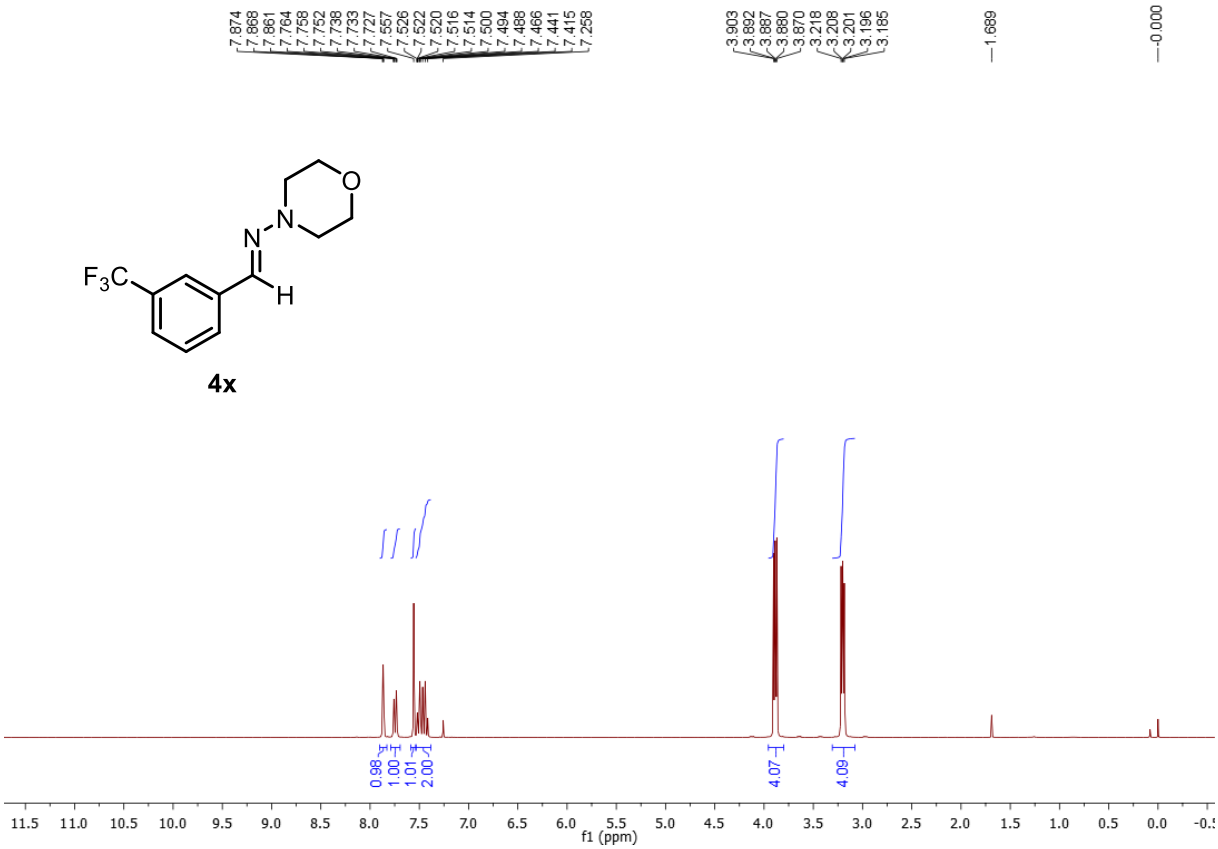
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

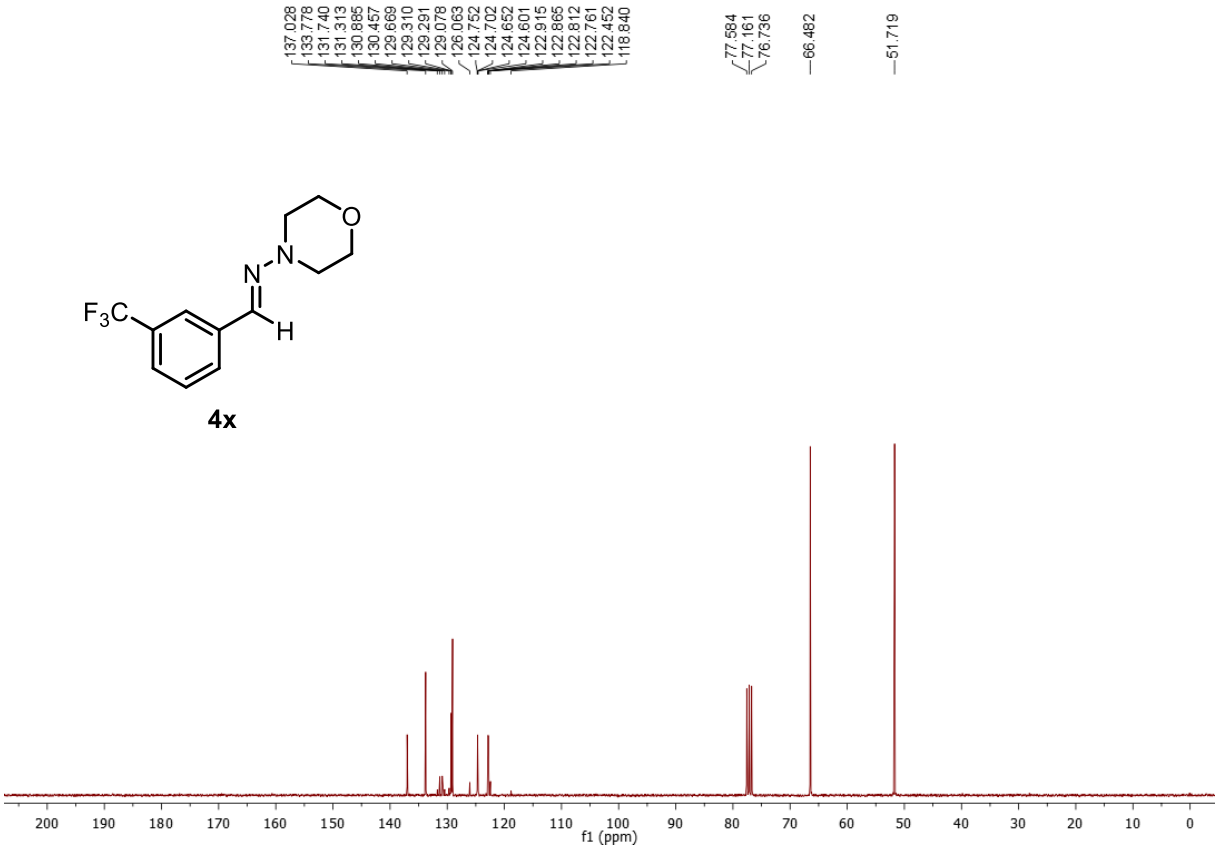


^{1}H NMR (300 MHz, $CDCl_3$)



4x

^{13}C NMR (75 MHz, $CDCl_3$)



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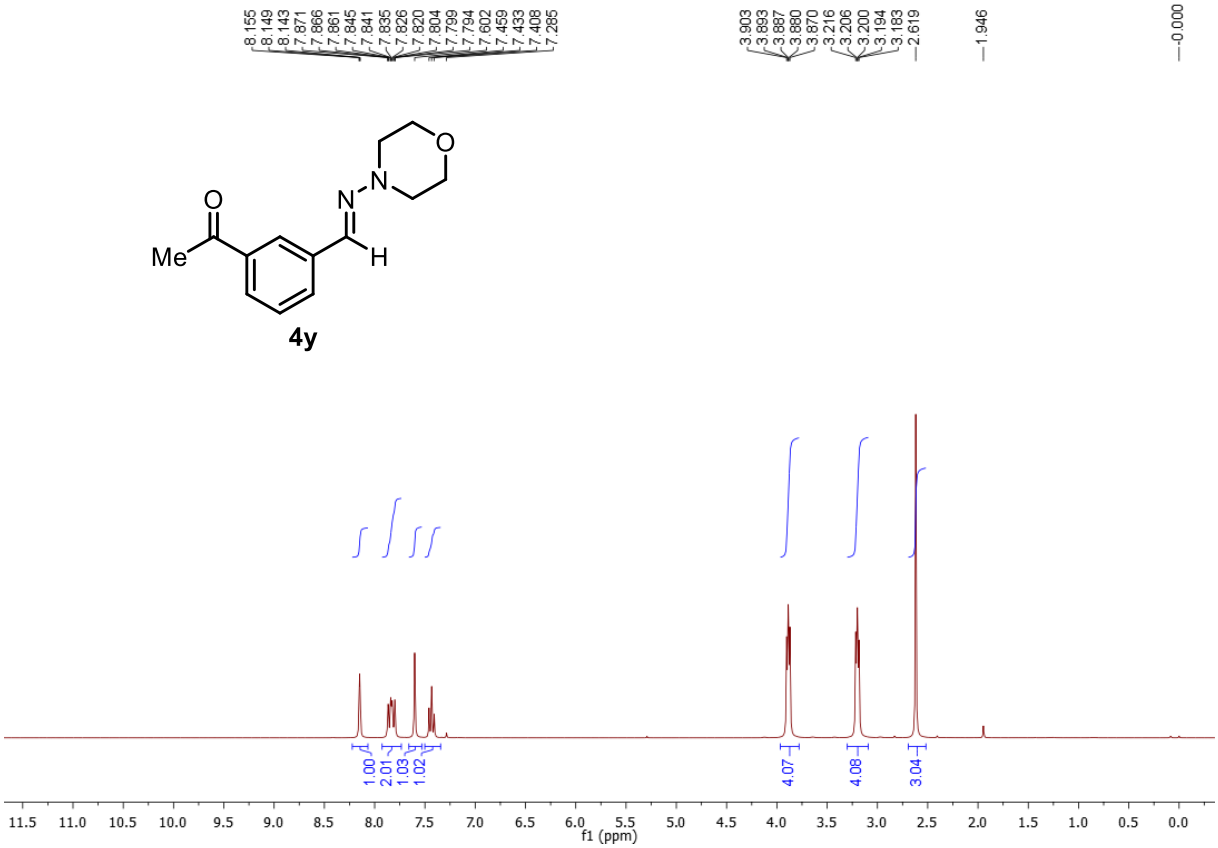
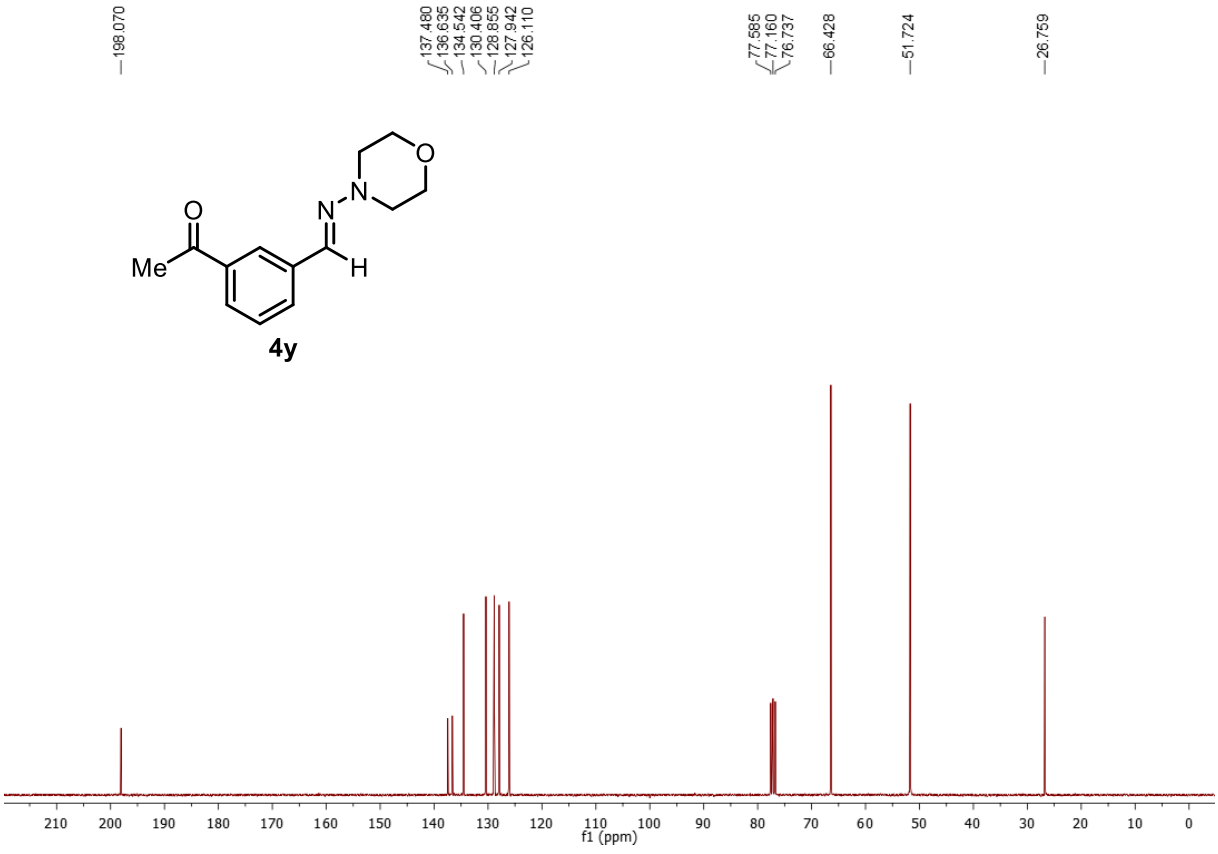
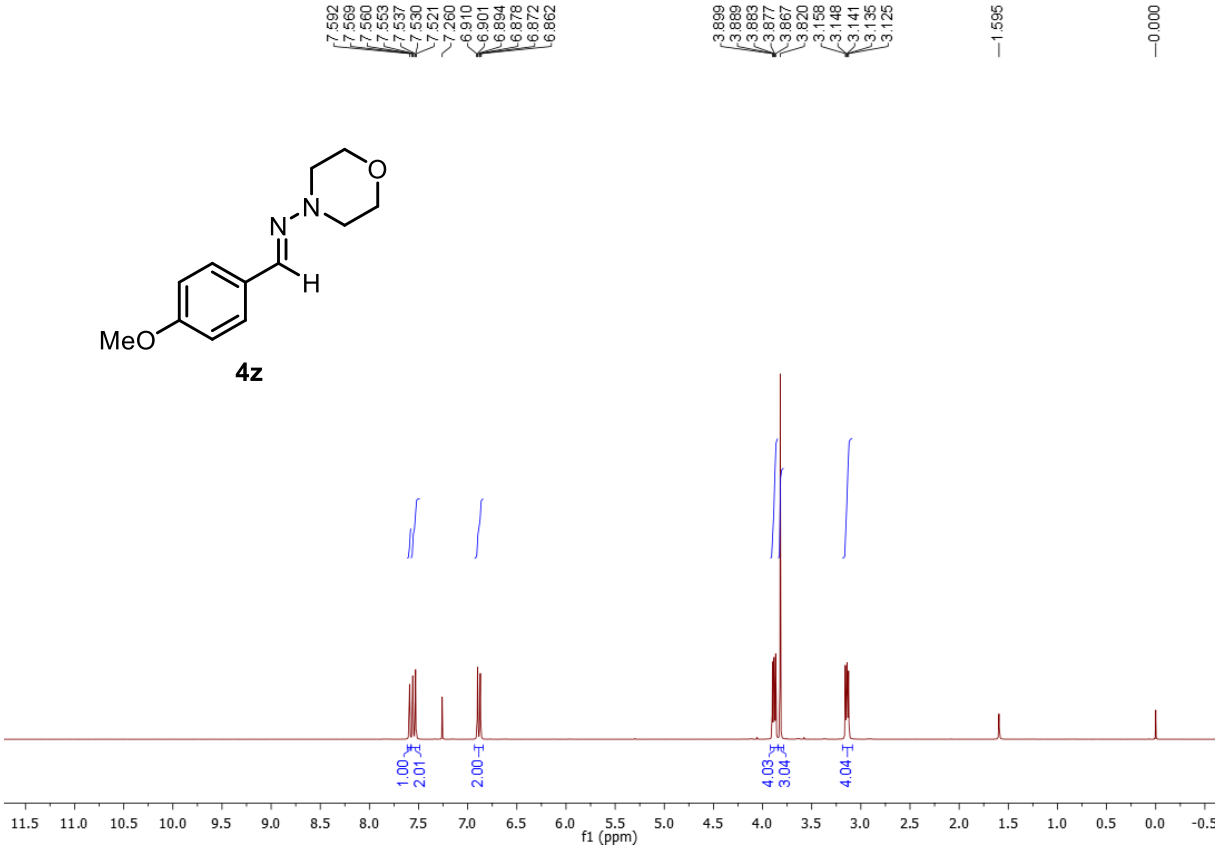
^{1}H NMR (300 MHz, $CDCl_3$)



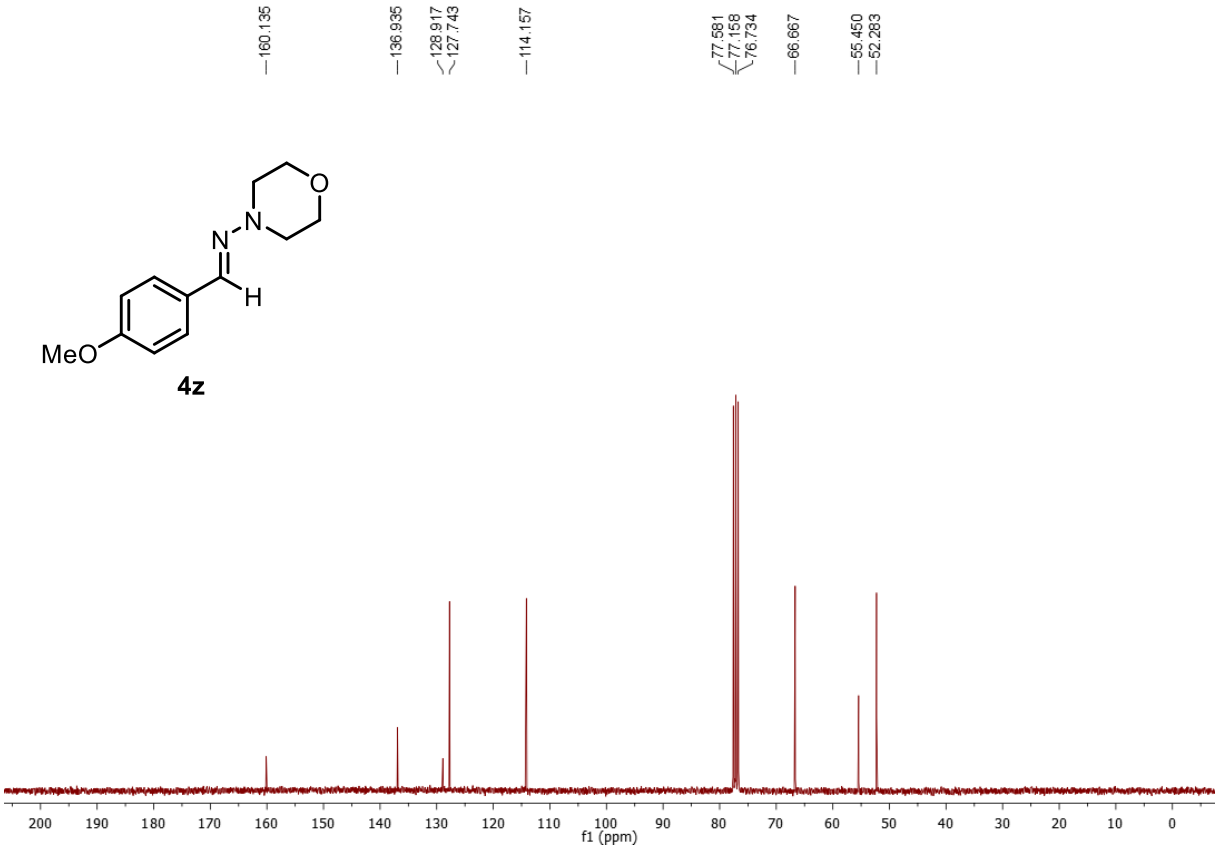
^{13}C NMR (75 MHz, $CDCl_3$)



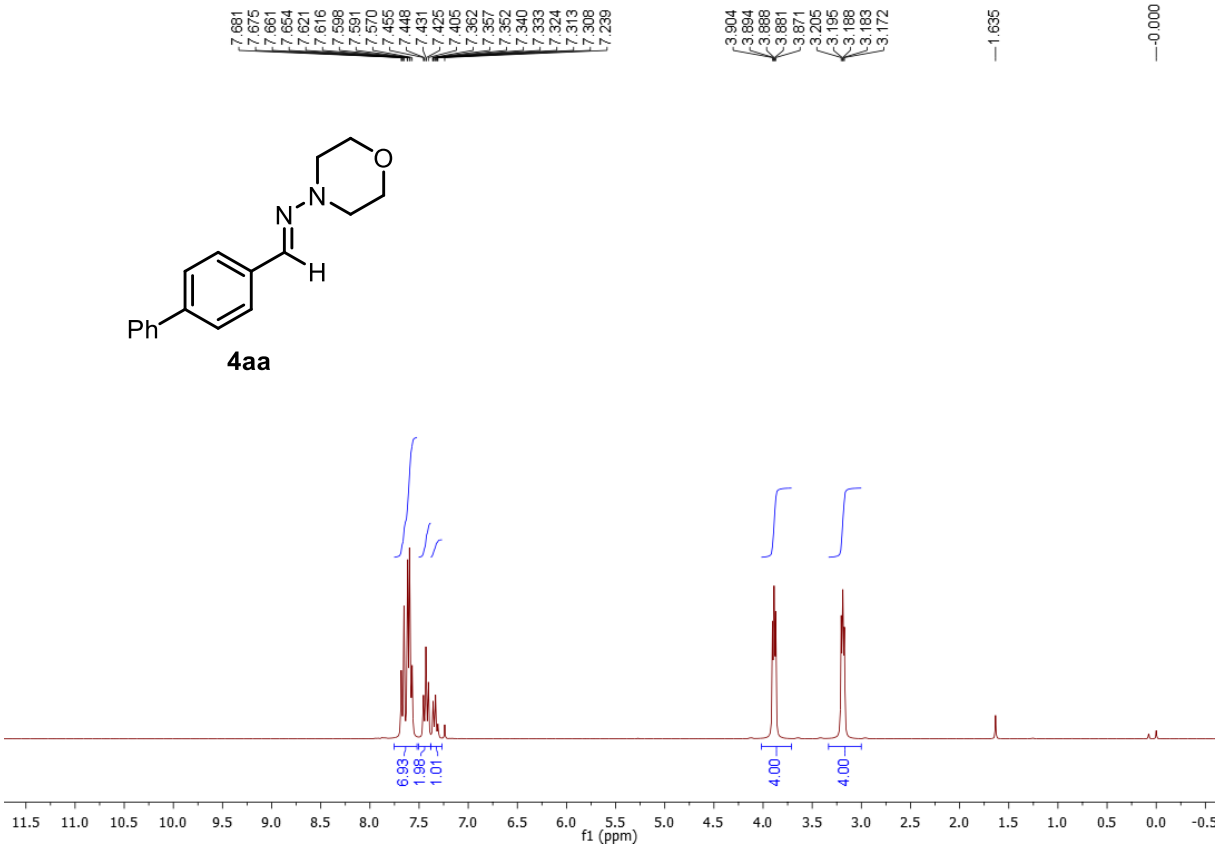
^{1}H NMR (300 MHz, $CDCl_3$)



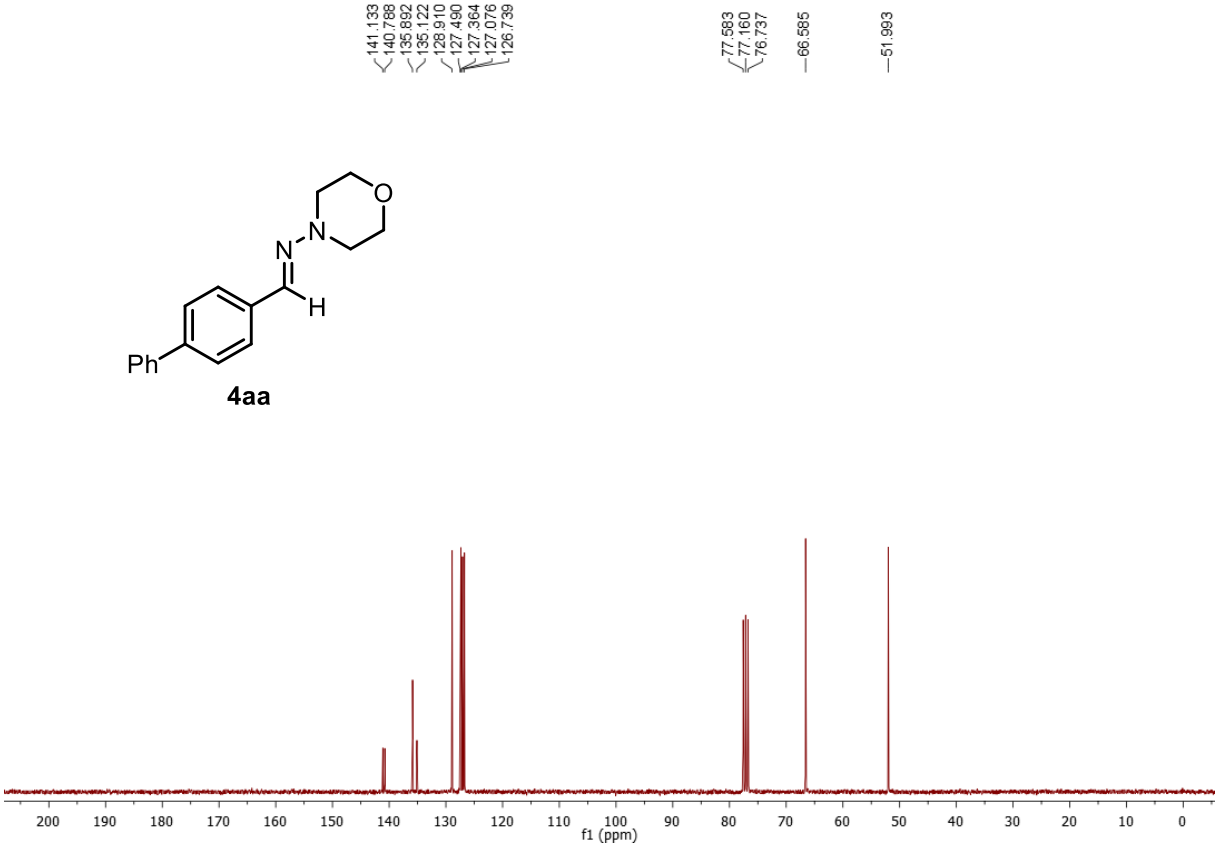
^{13}C NMR (75 MHz, $CDCl_3$)



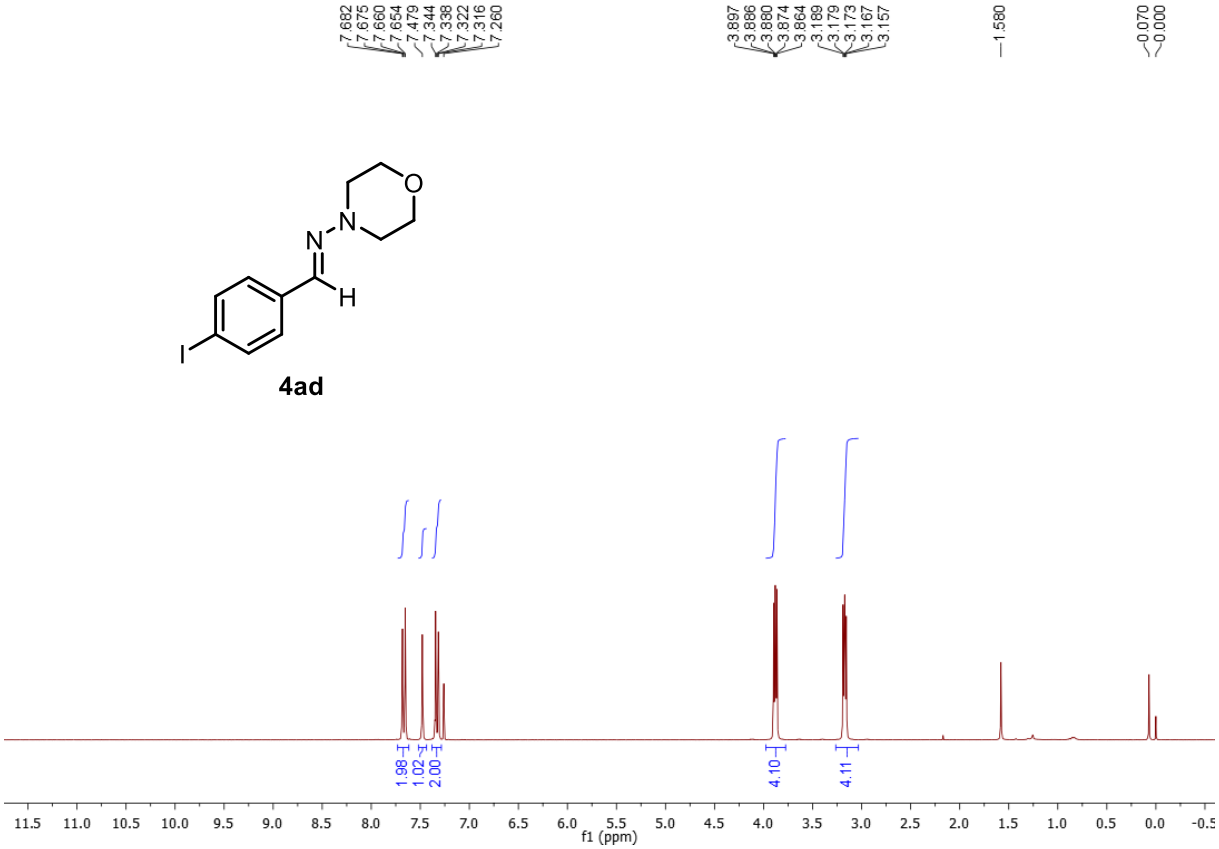
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

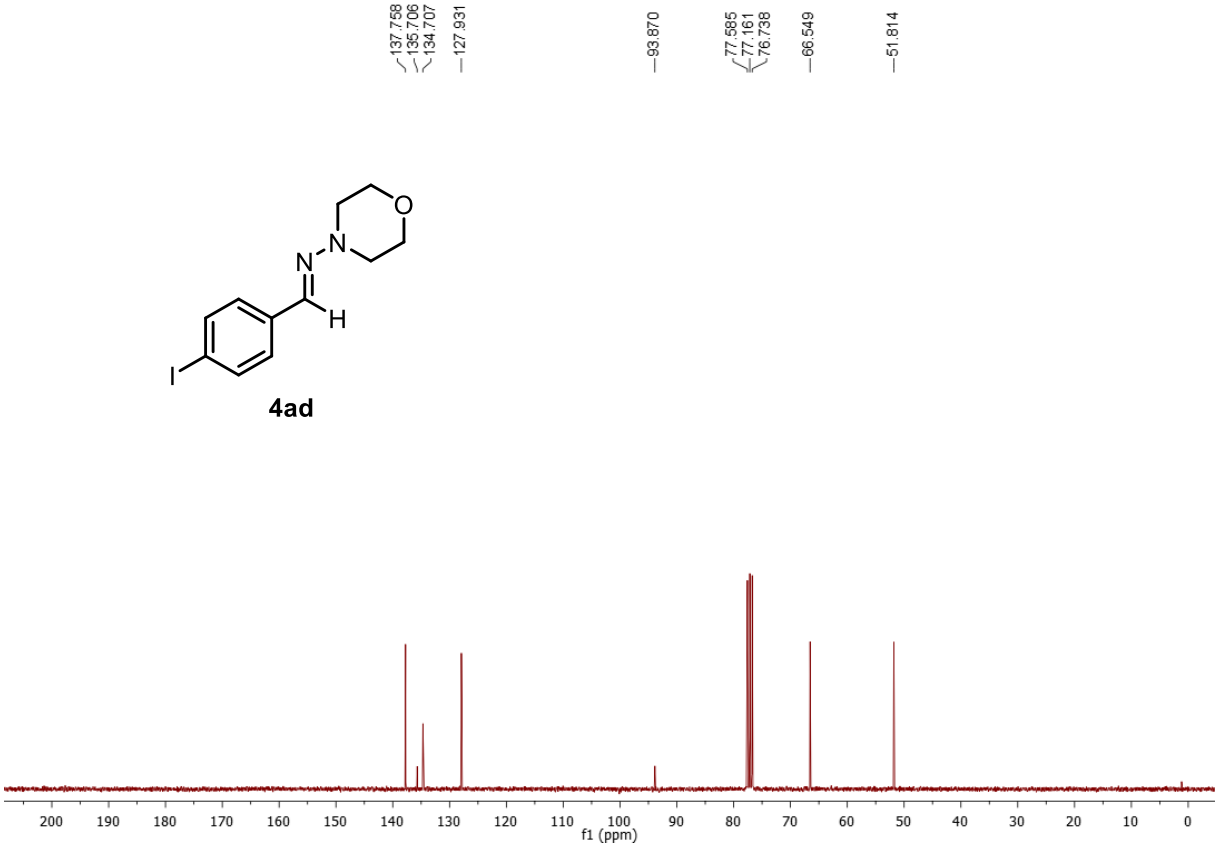


^{1}H NMR (300 MHz, $CDCl_3$)



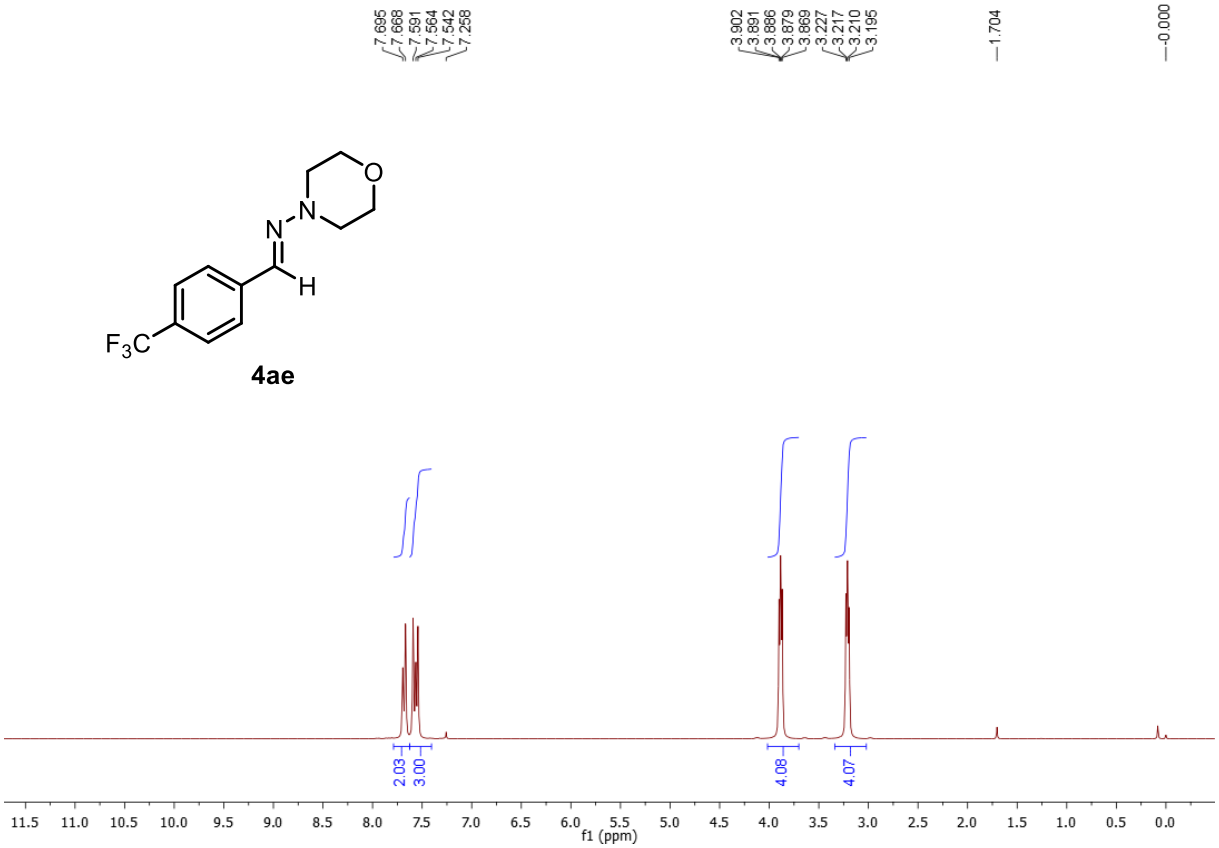
4ad

^{13}C NMR (75 MHz, $CDCl_3$)

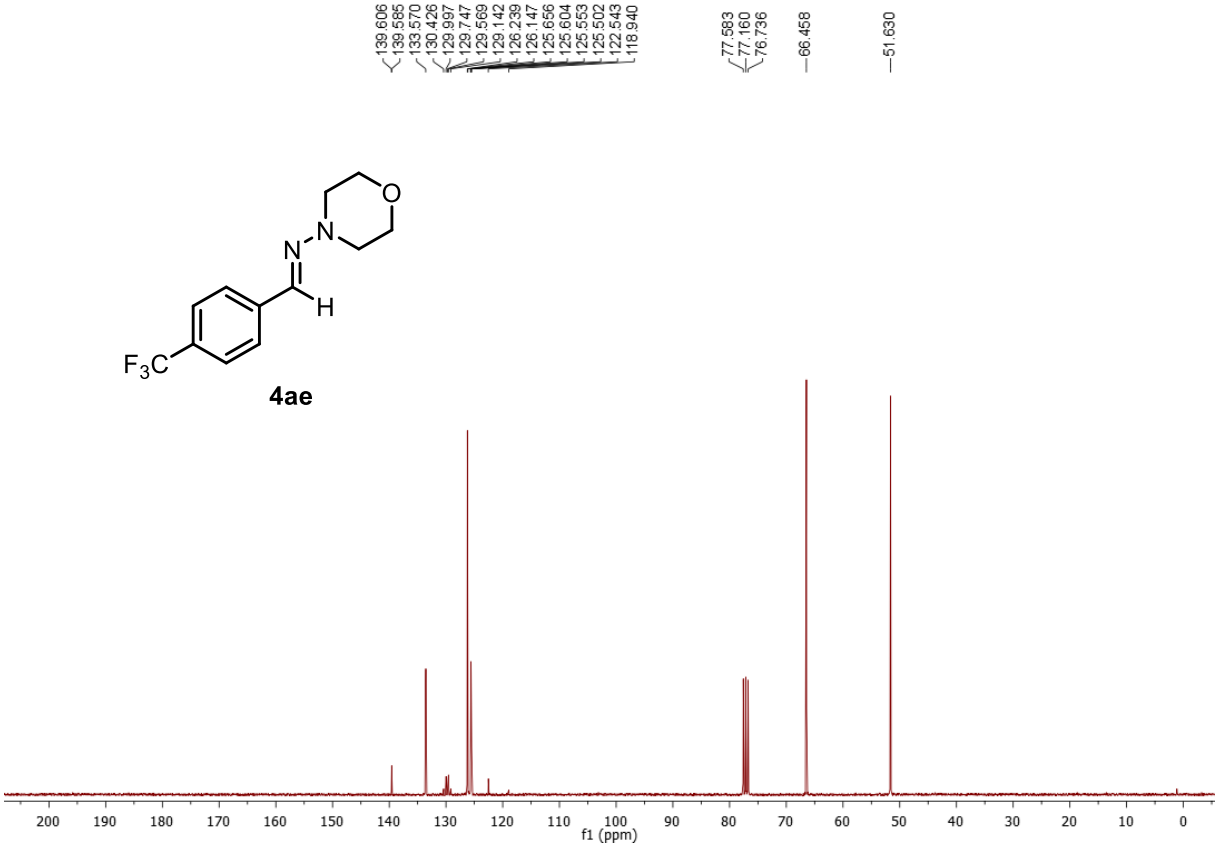


4ad

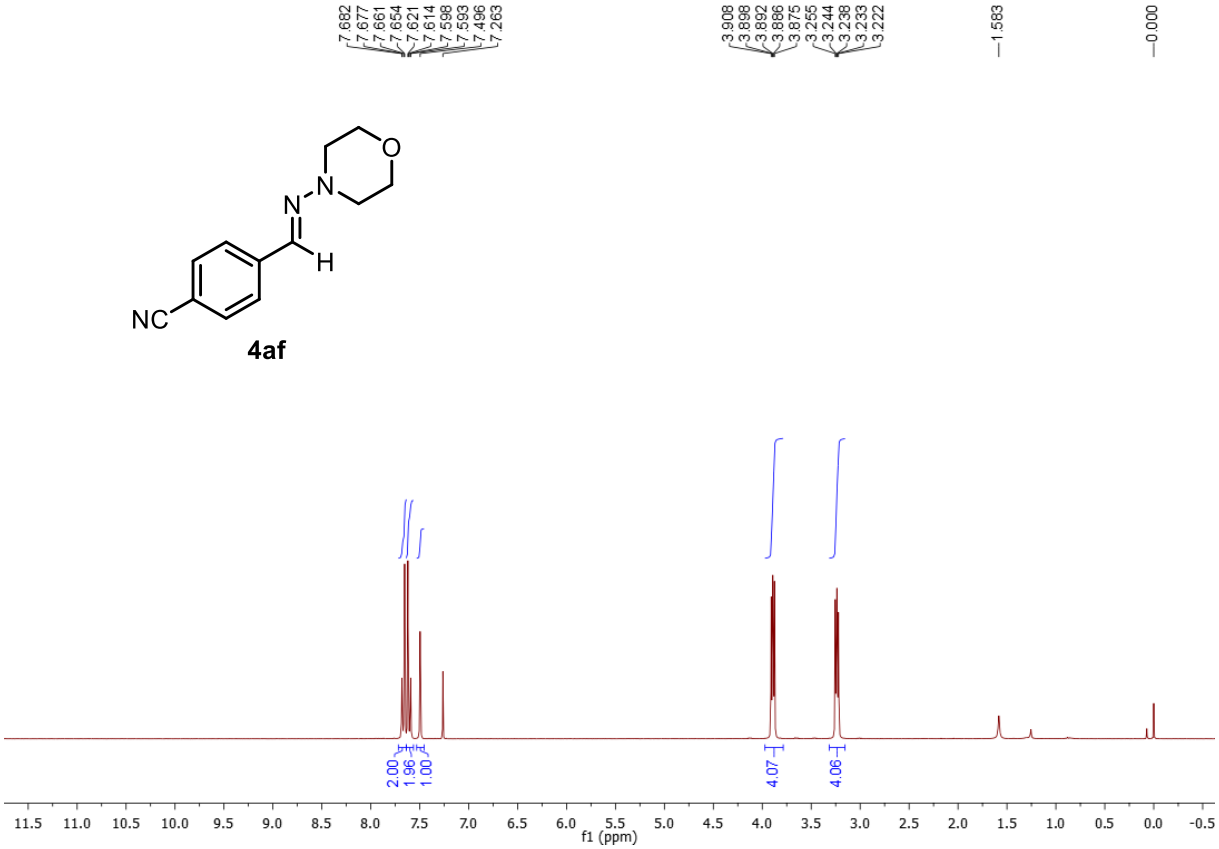
^{1}H NMR (300 MHz, $CDCl_3$)



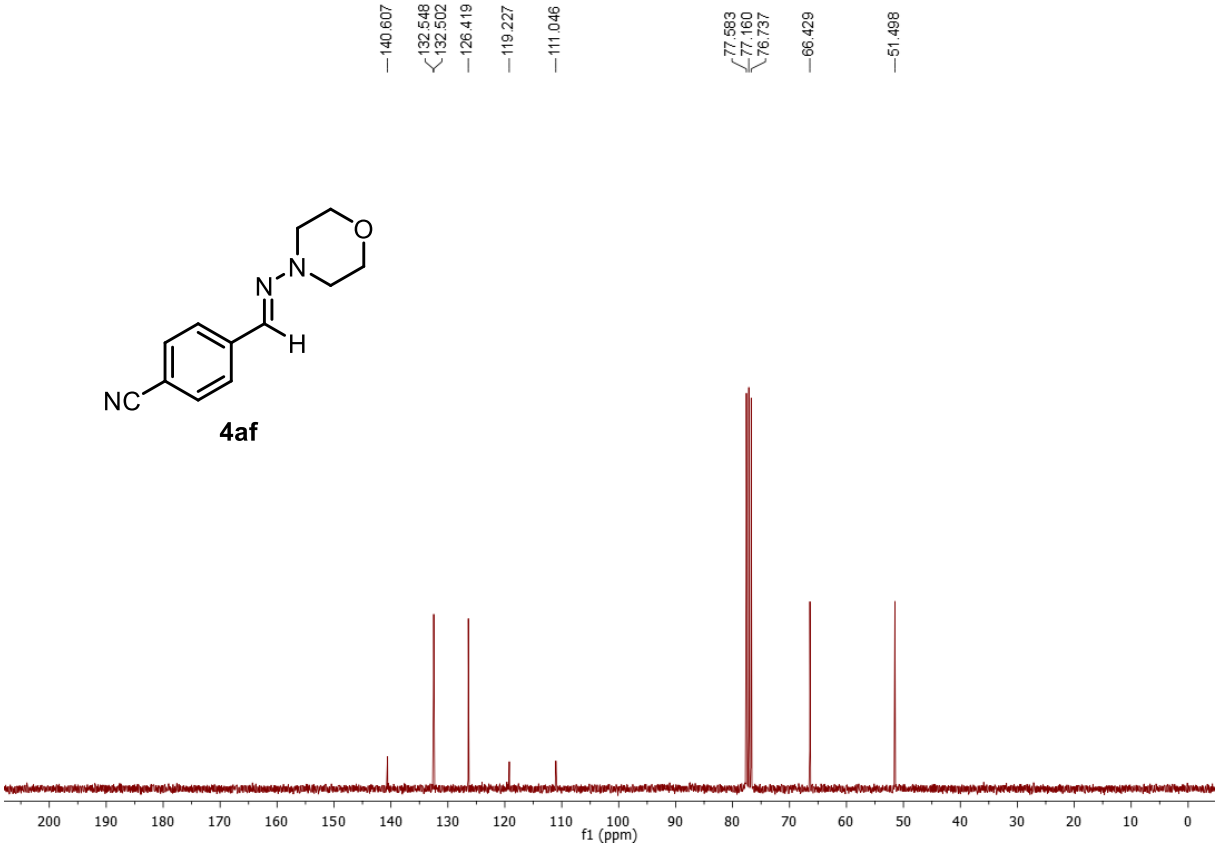
^{13}C NMR (75 MHz, $CDCl_3$)



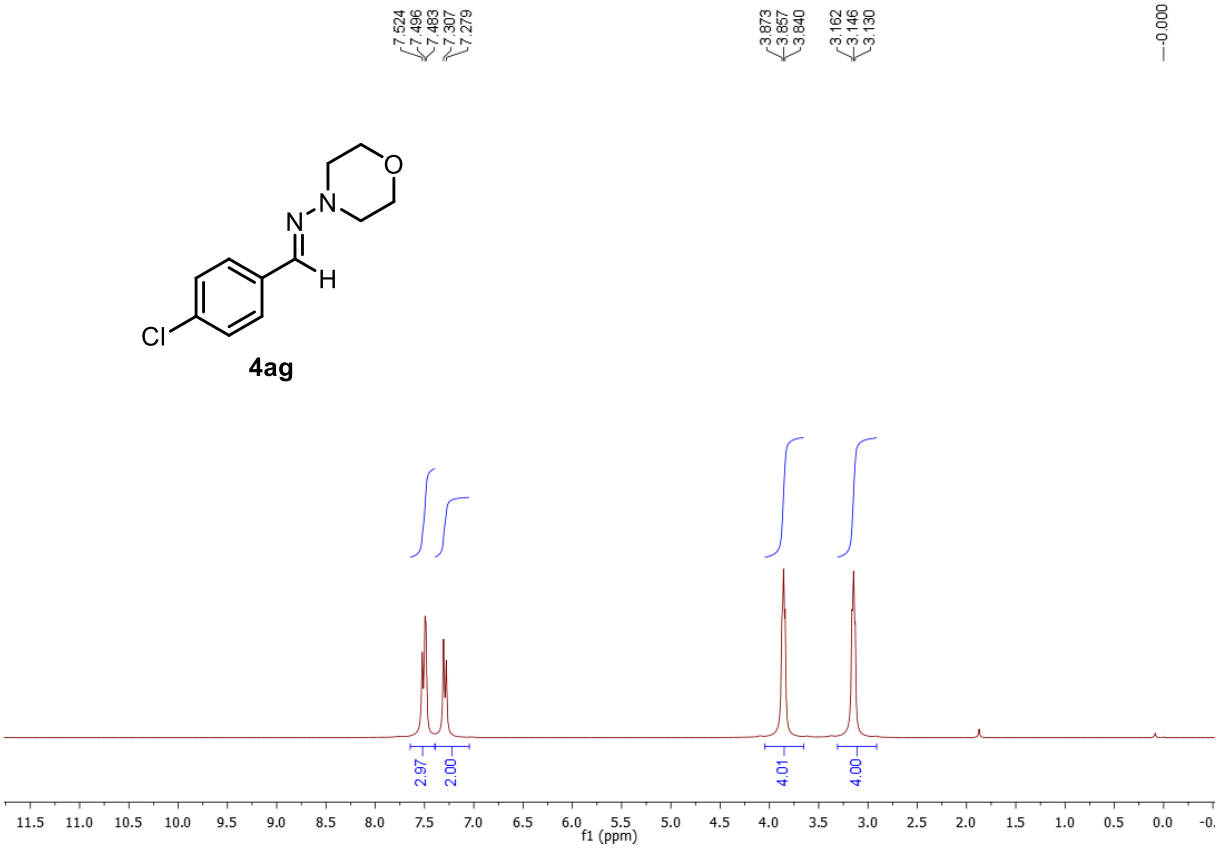
^{1}H NMR (300 MHz, $CDCl_3$)



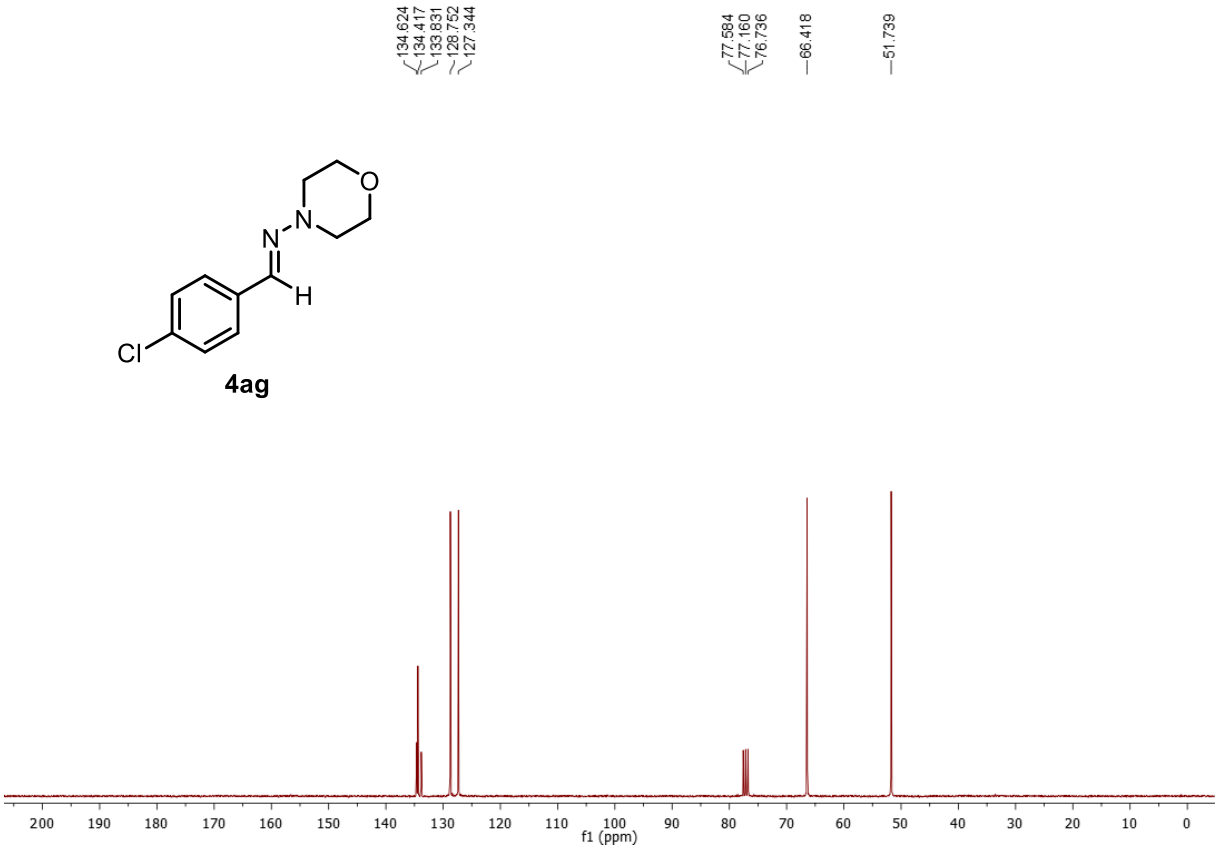
^{13}C NMR (75 MHz, $CDCl_3$)



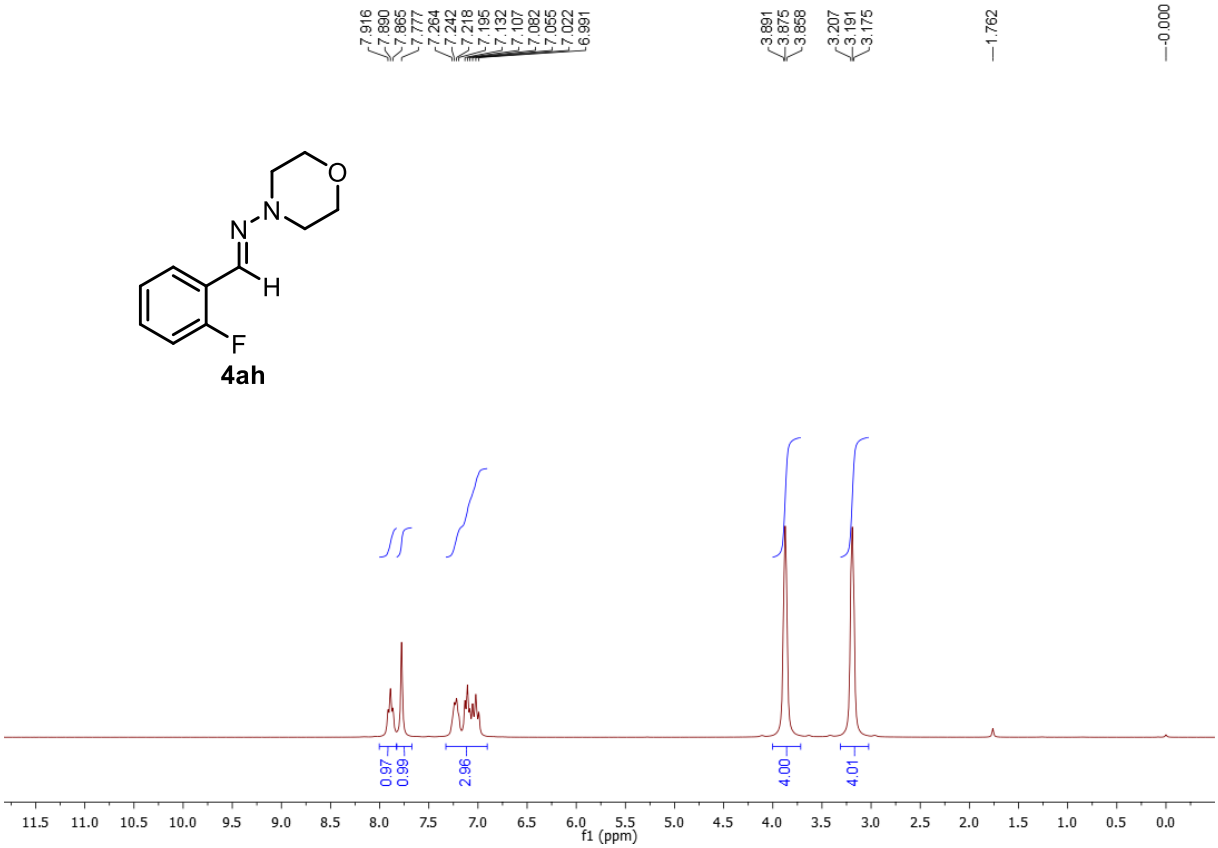
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

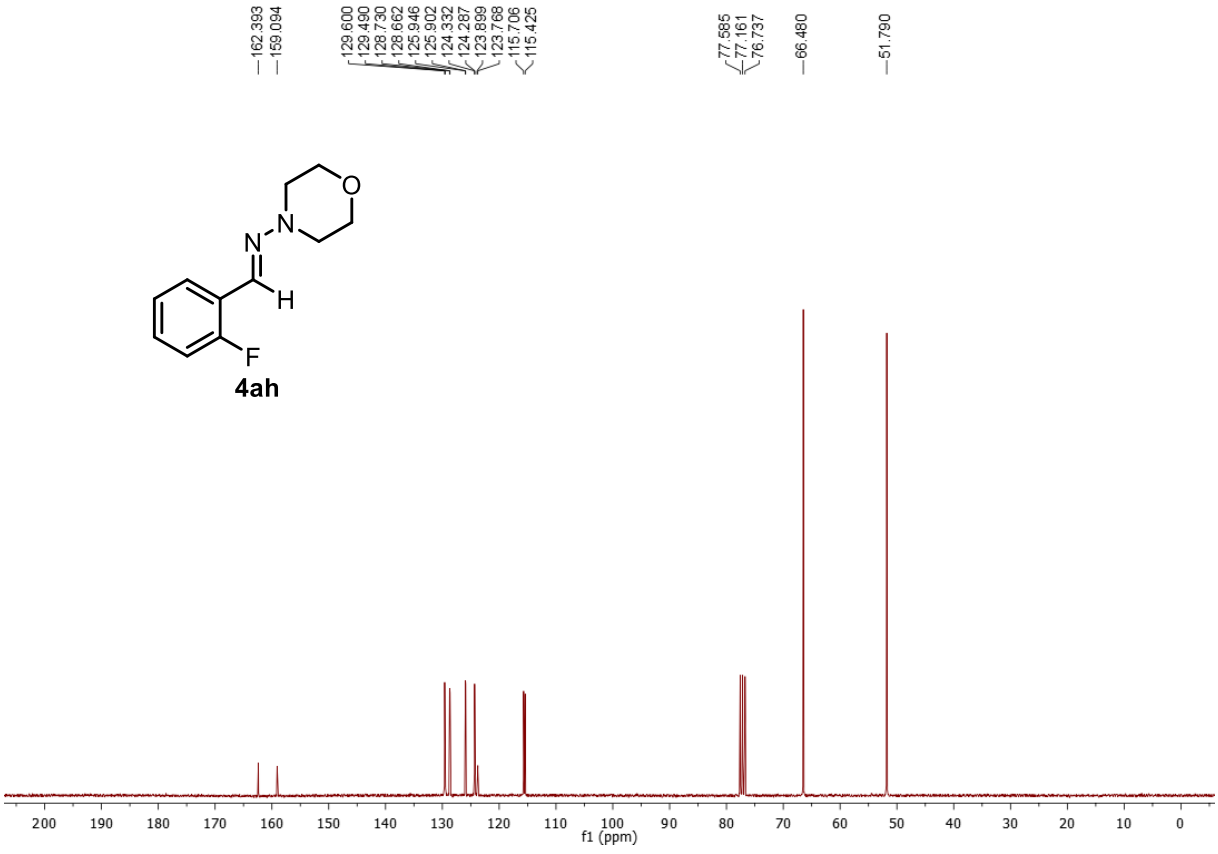


^{1}H NMR (300 MHz, $CDCl_3$)



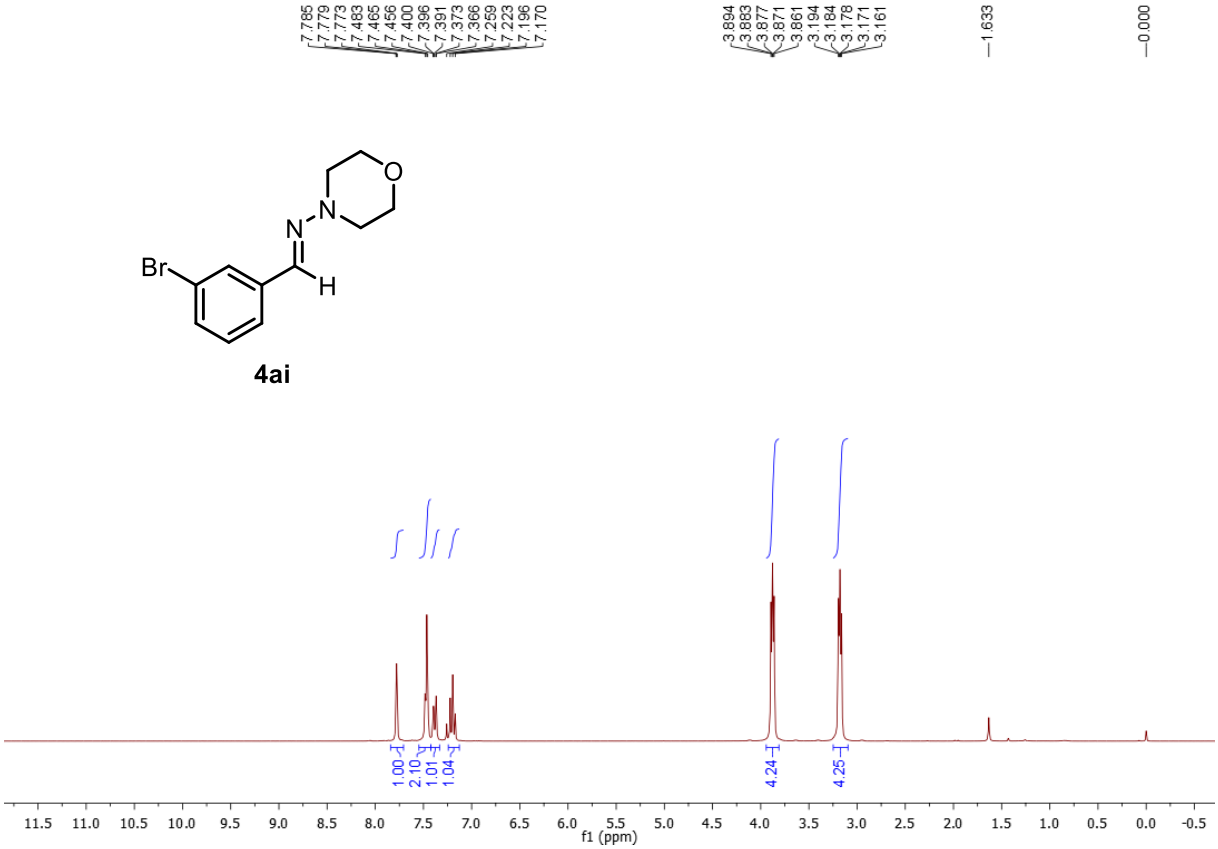
4ah

^{13}C NMR (75 MHz, $CDCl_3$)

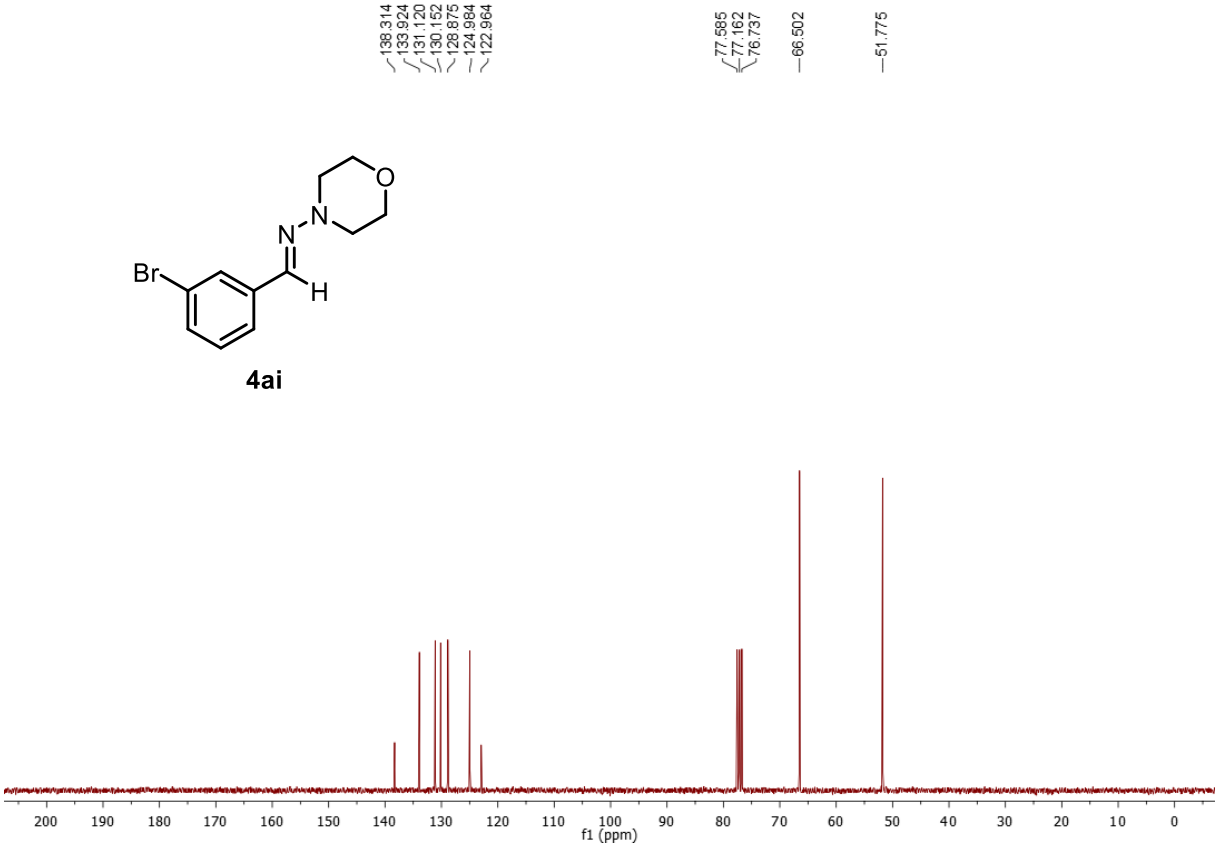


4ah

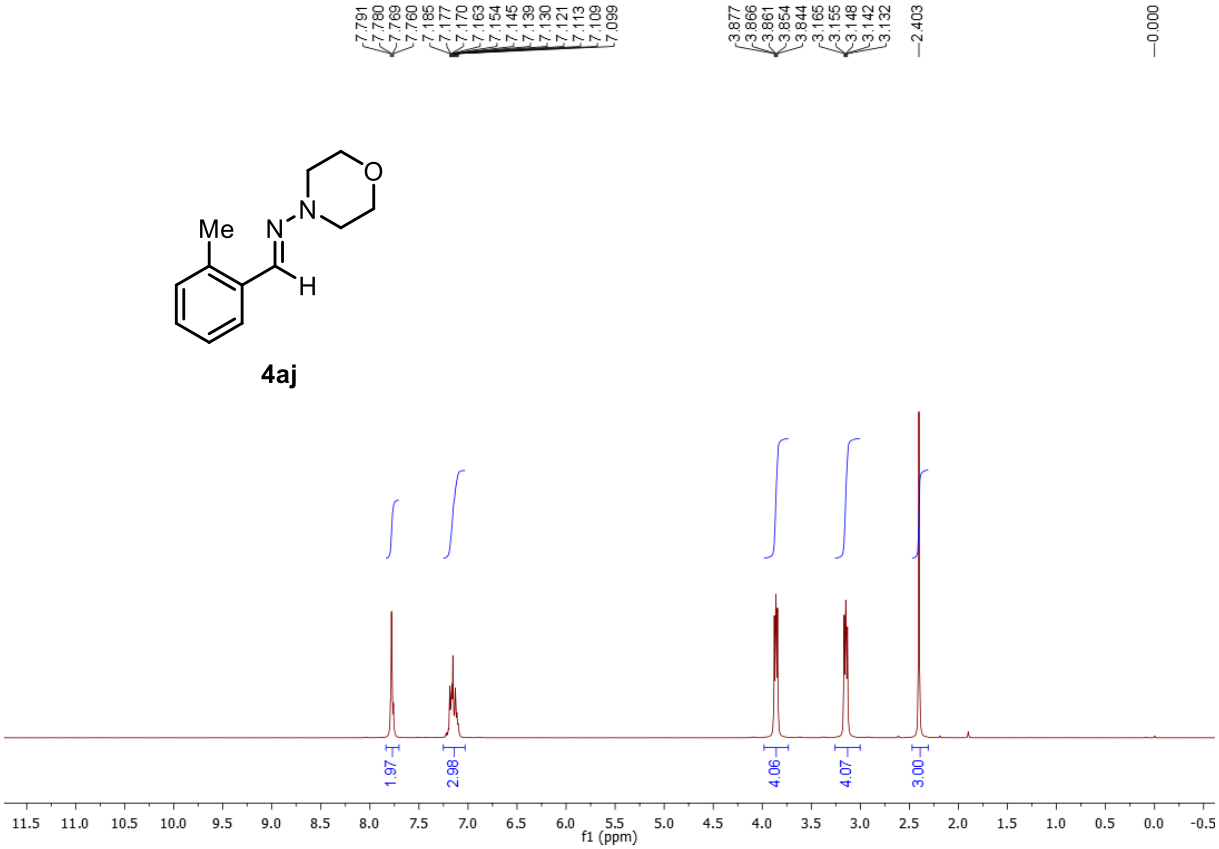
^{1}H NMR (300 MHz, $CDCl_3$)



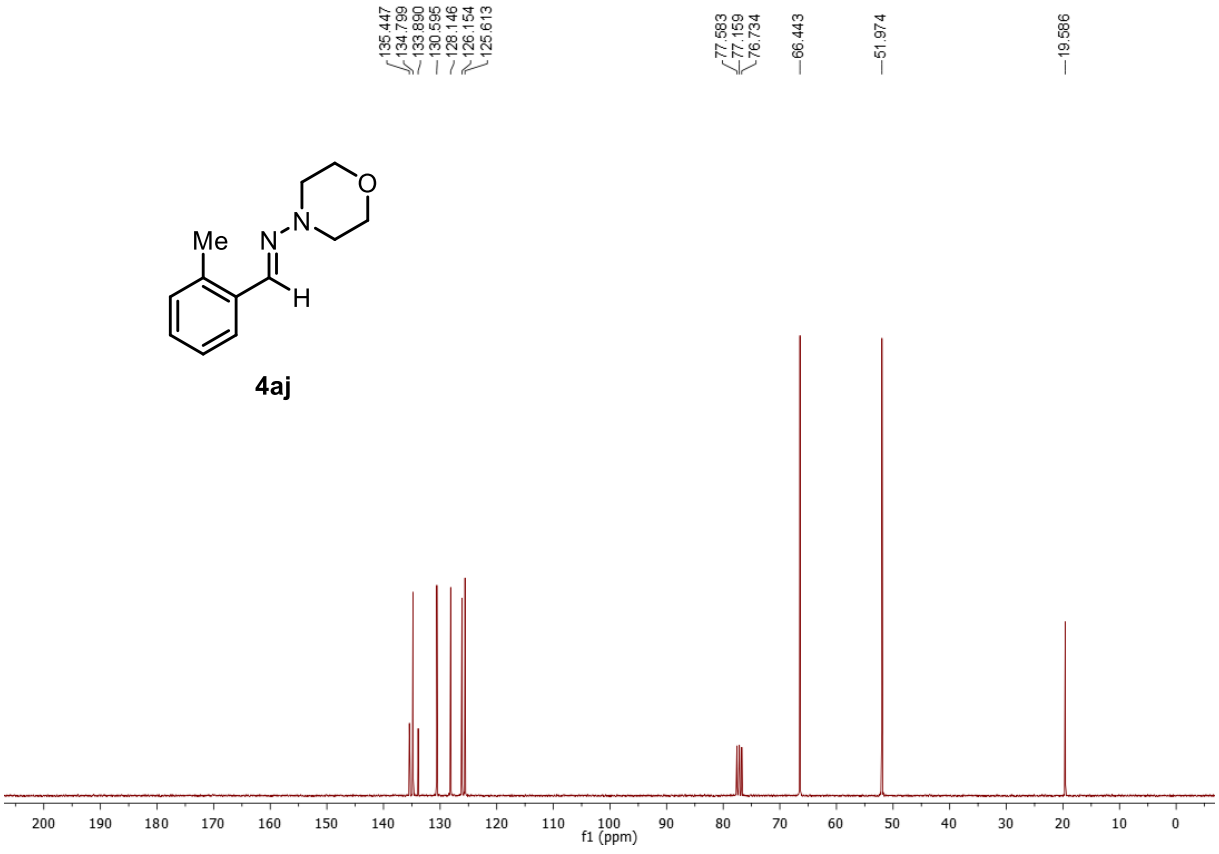
^{13}C NMR (75 MHz, $CDCl_3$)



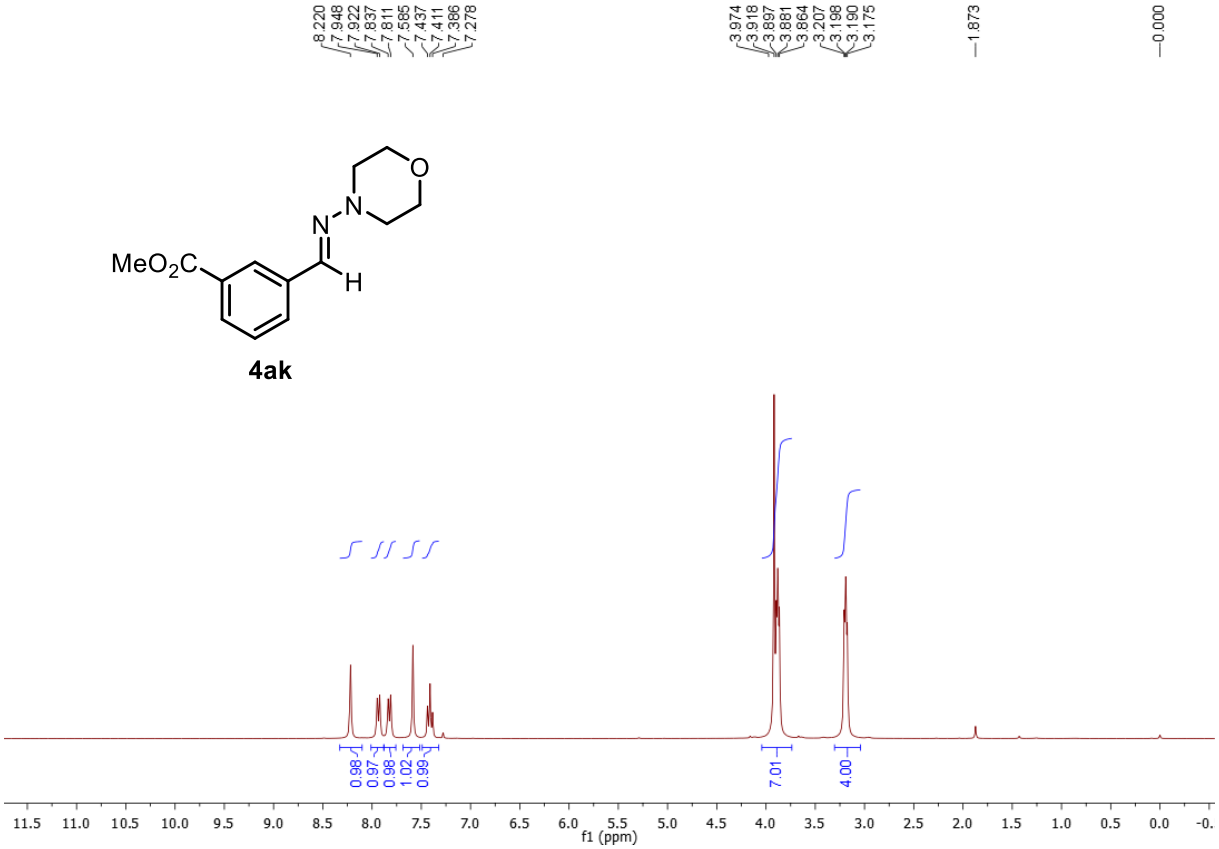
^{1}H NMR (300 MHz, $CDCl_3$)



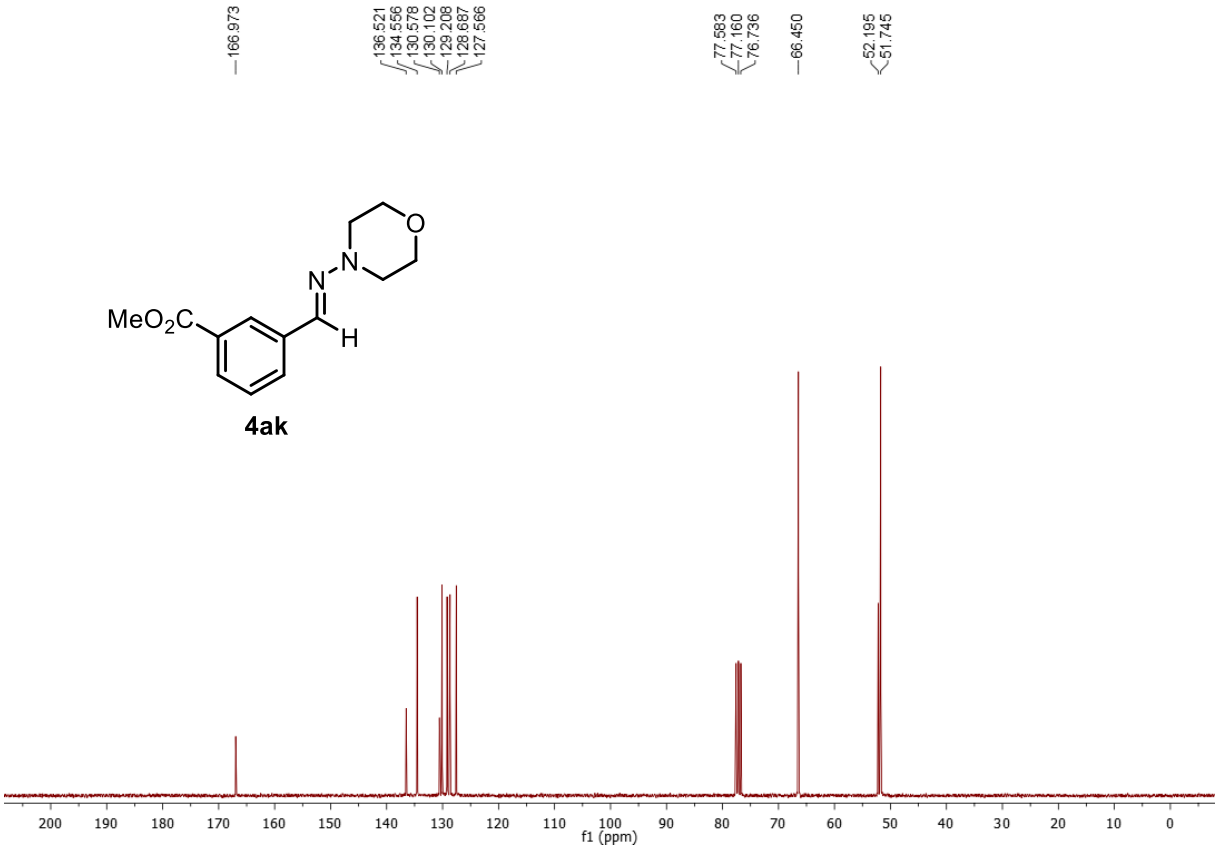
^{13}C NMR (75 MHz, $CDCl_3$)



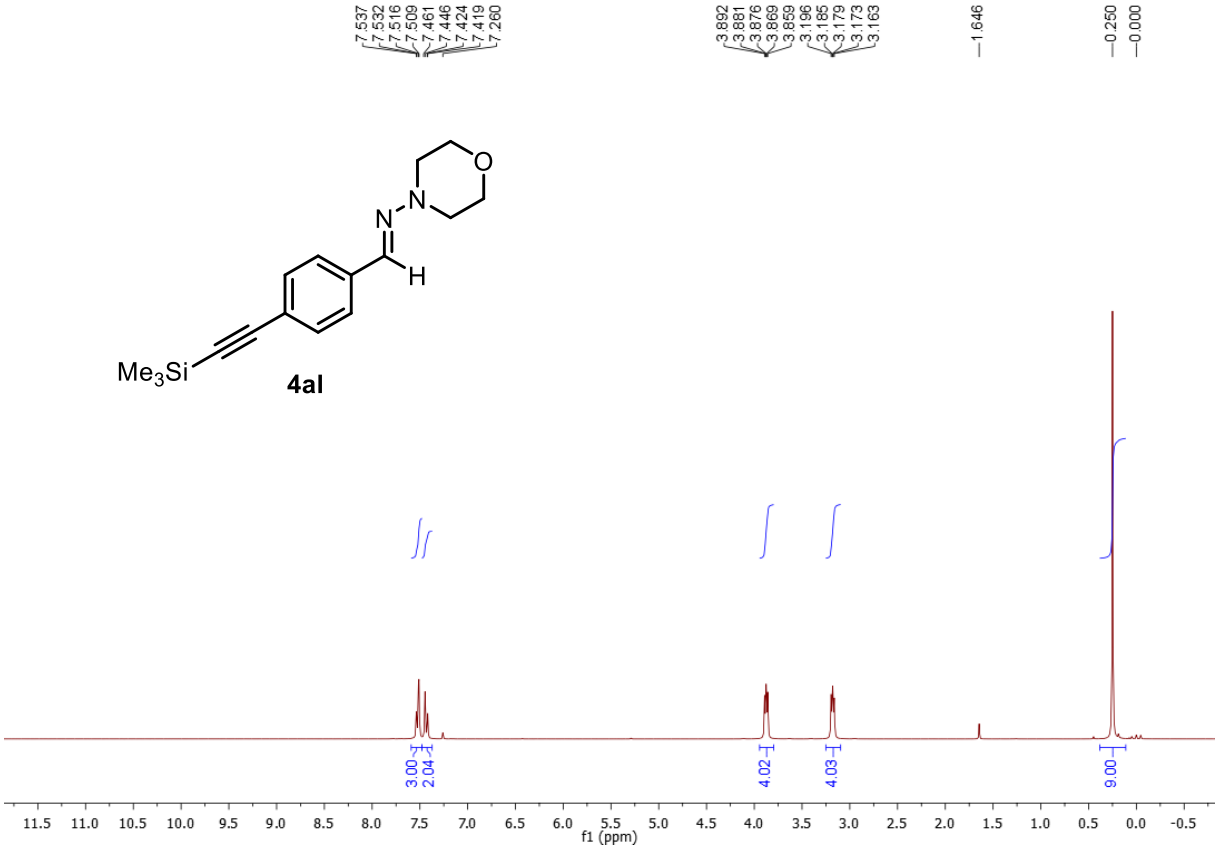
^{1}H NMR (300 MHz, $CDCl_3$)



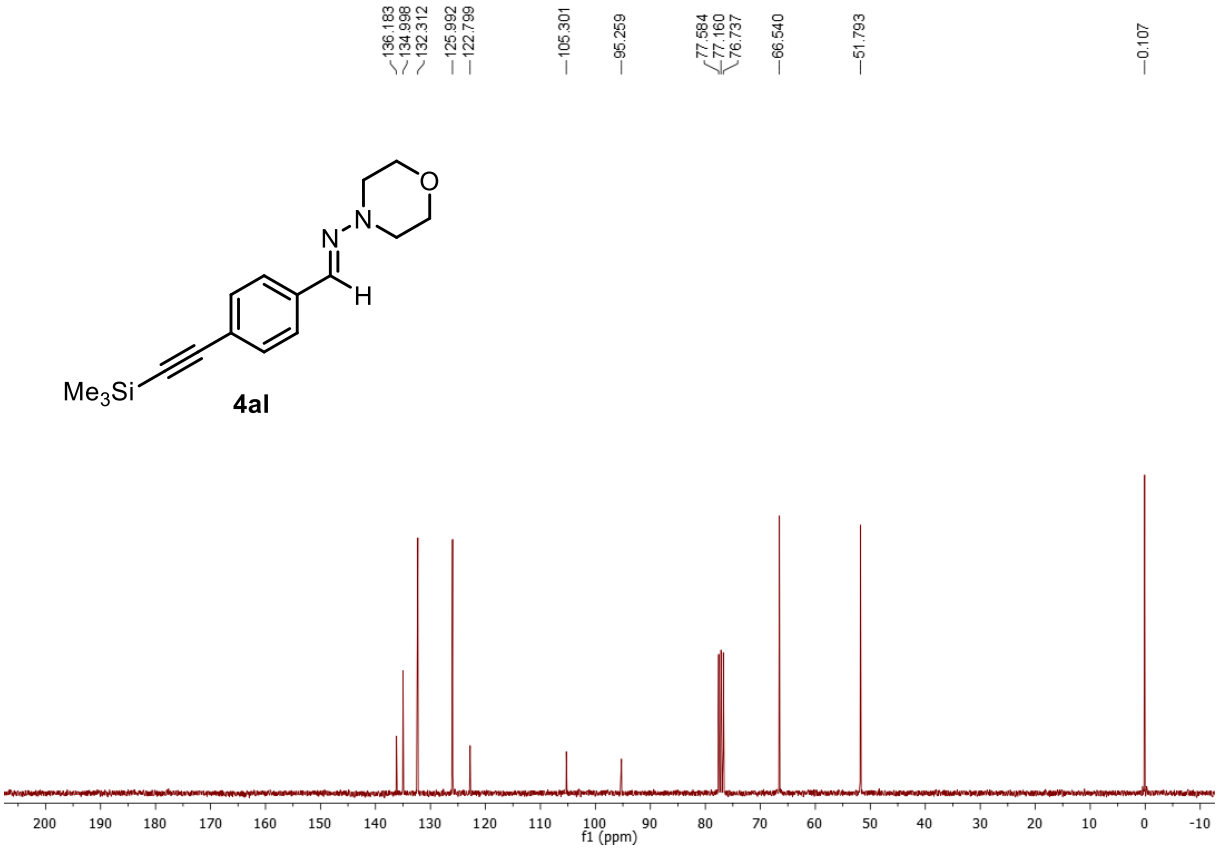
^{13}C NMR (75 MHz, $CDCl_3$)



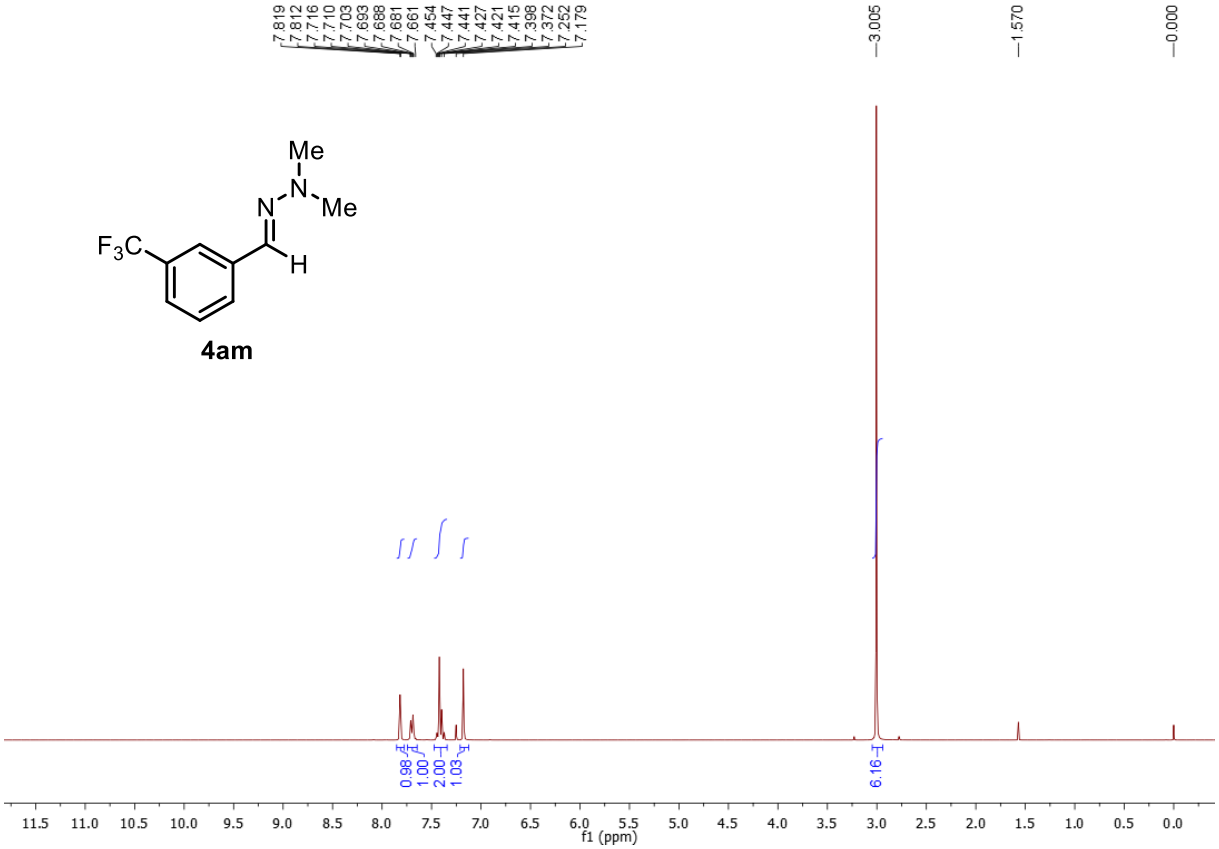
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

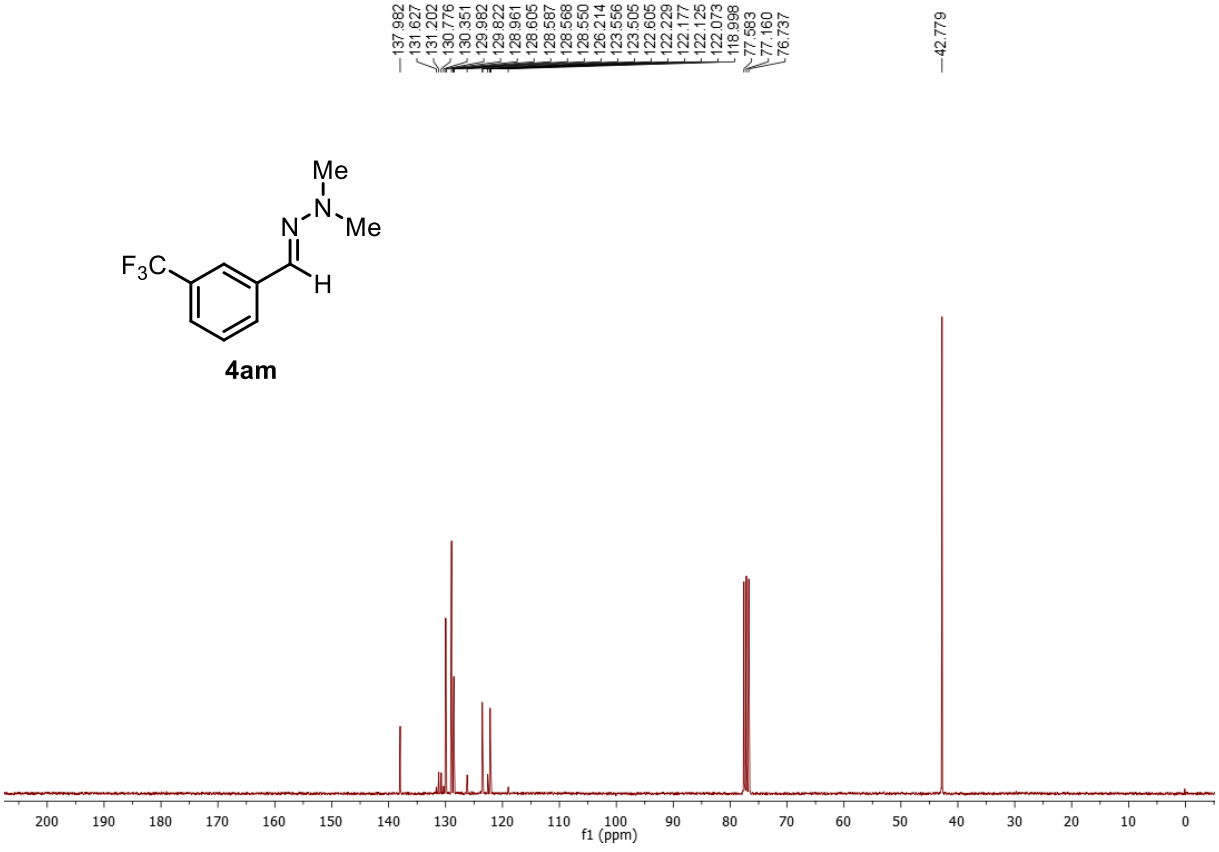


^{1}H NMR (300 MHz, $CDCl_3$)



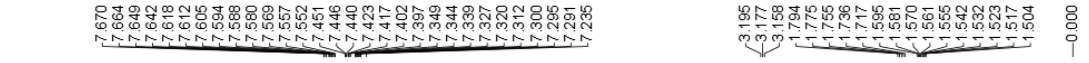
4am

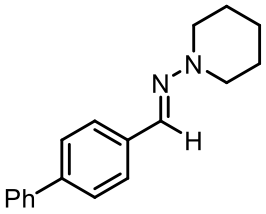
^{13}C NMR (75 MHz, $CDCl_3$)



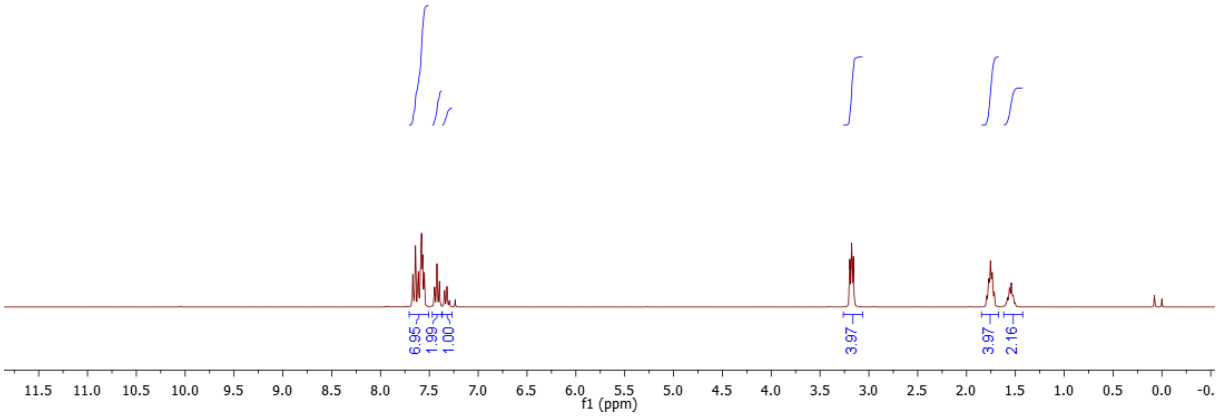
4am

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

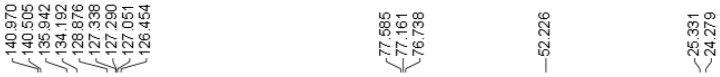


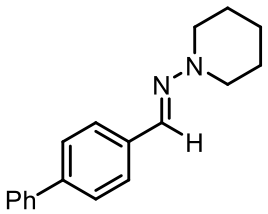


4an



^{13}C NMR (75 MHz, $CDCl_3$)





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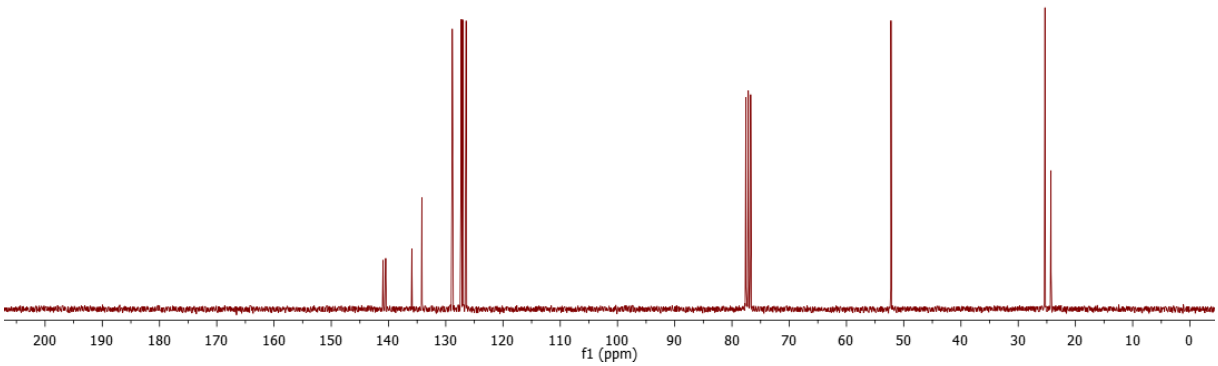
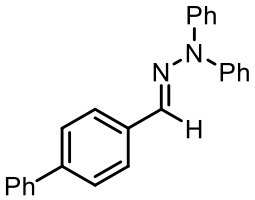
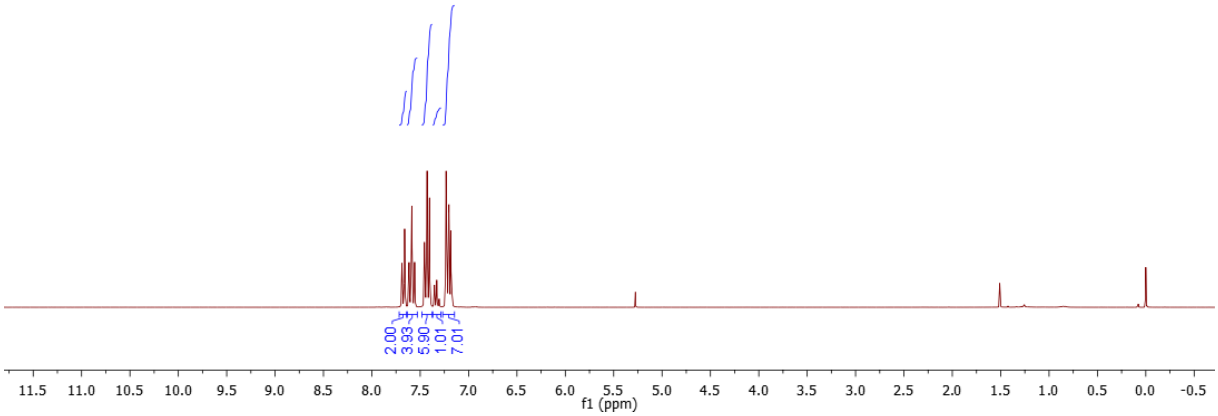


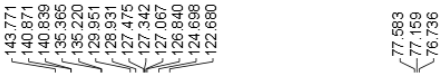
^{1}H NMR (300 MHz, $CDCl_3$)

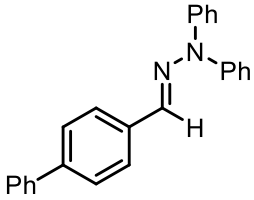


4ap



^{13}C NMR (75 MHz, $CDCl_3$)





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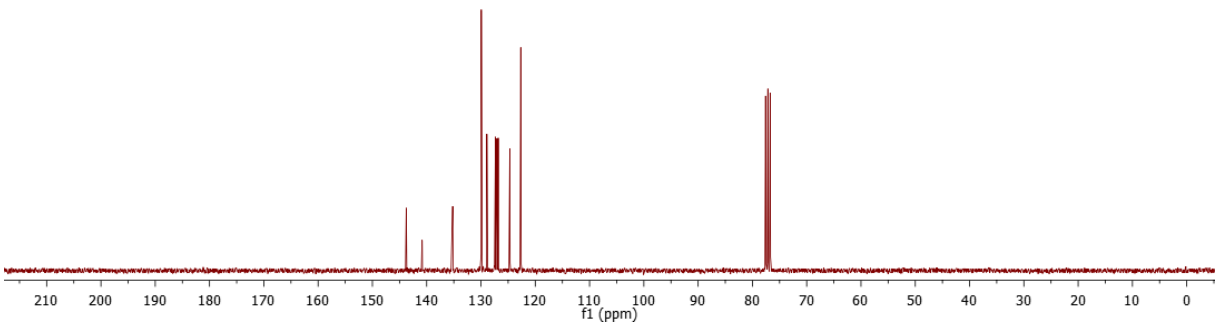
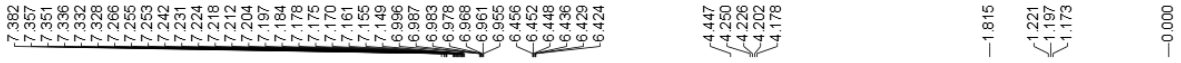
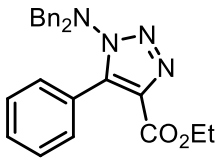
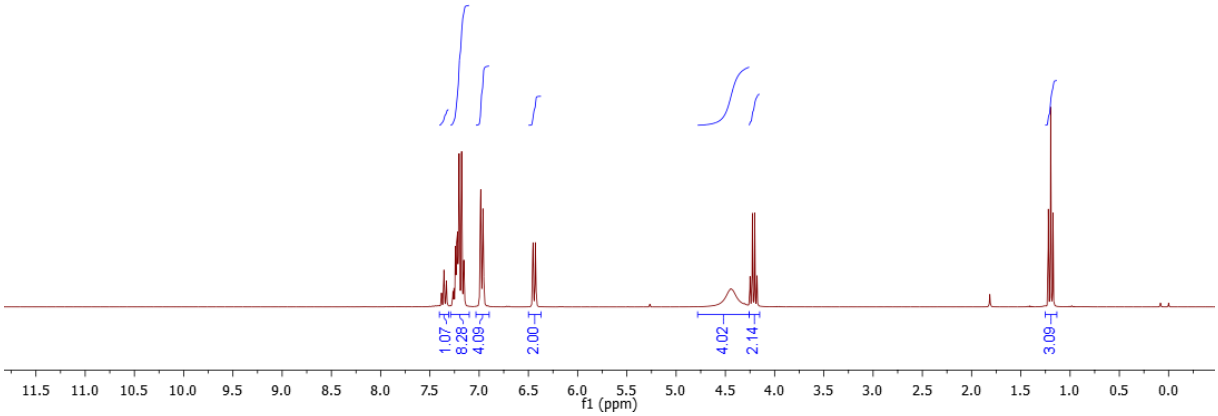


^{1}H NMR (300 MHz, $CDCl_3$)

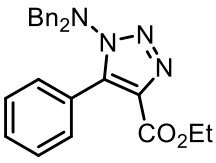




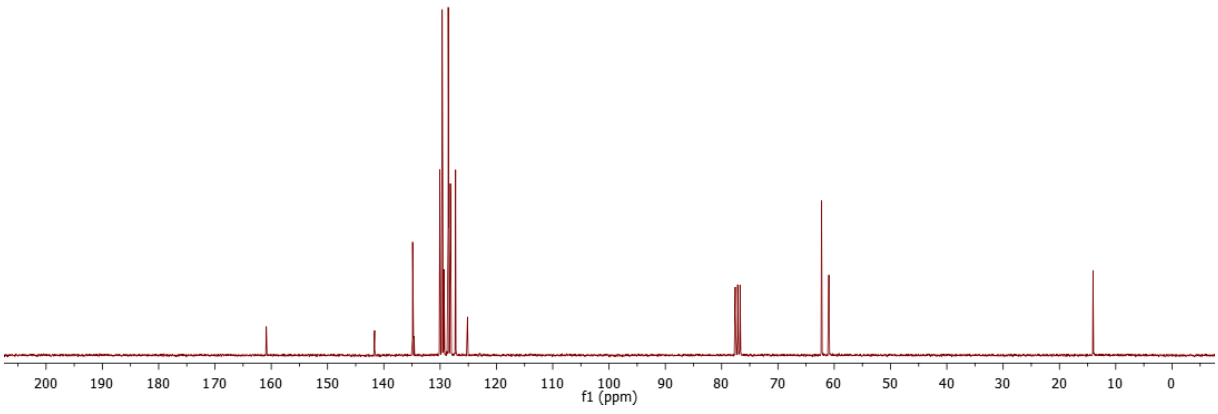
5a



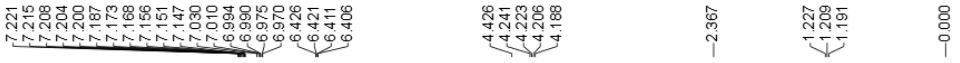
^{13}C NMR (75 MHz, $CDCl_3$)

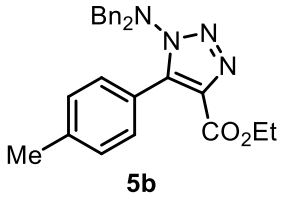


5a



^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)





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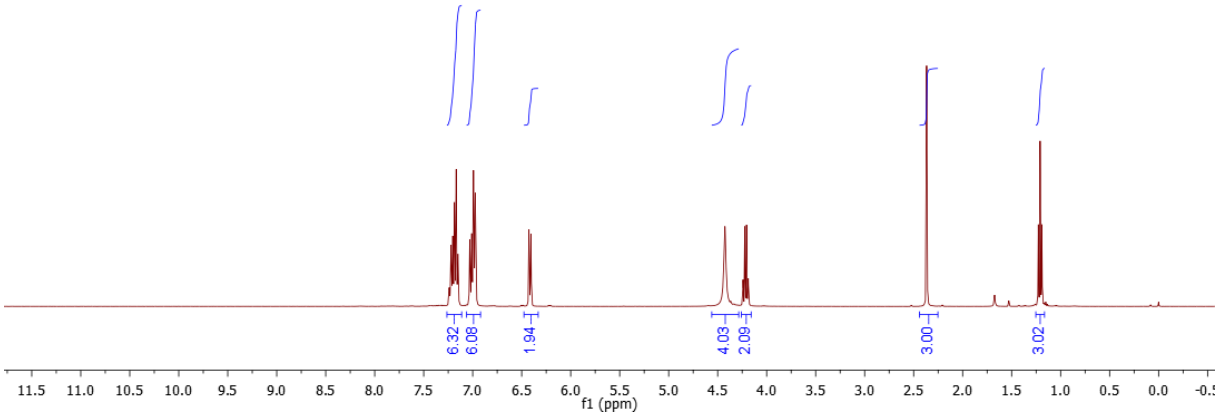
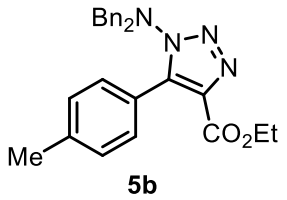


^{13}C NMR (75 MHz, $CDCl_3$)



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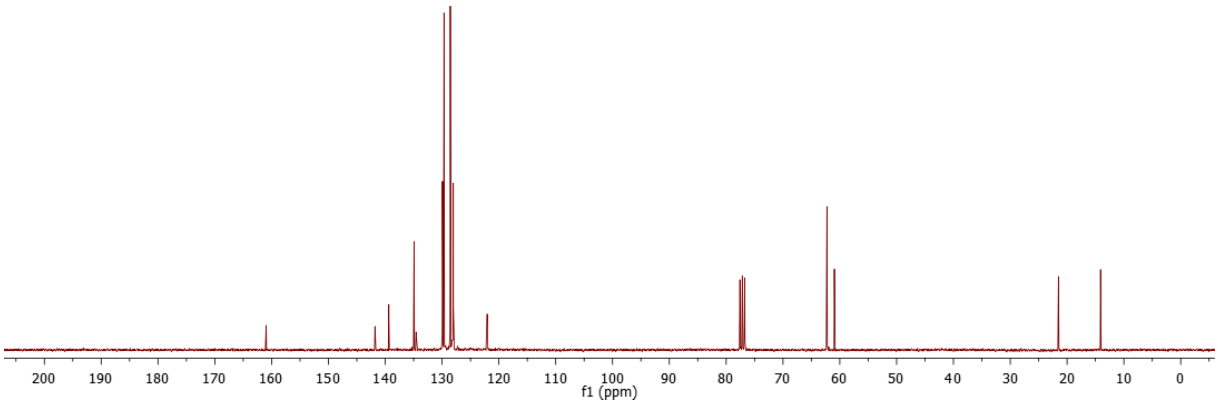
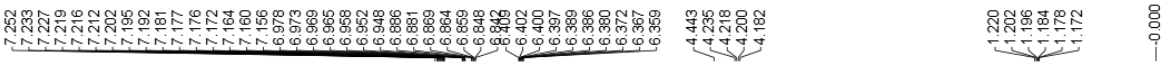
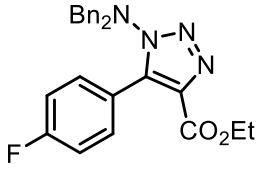


^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)





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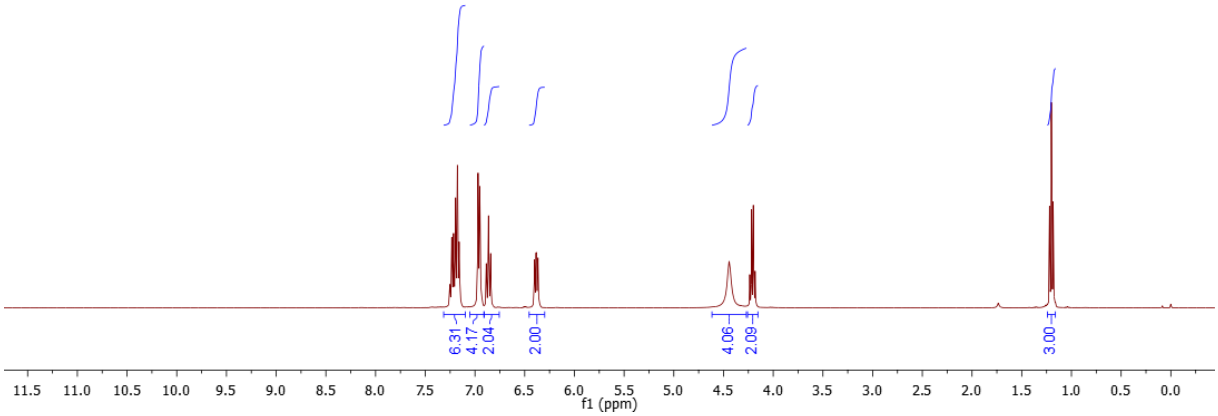
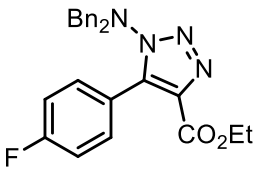


^{13}C NMR (100 MHz, $CDCl_3$)



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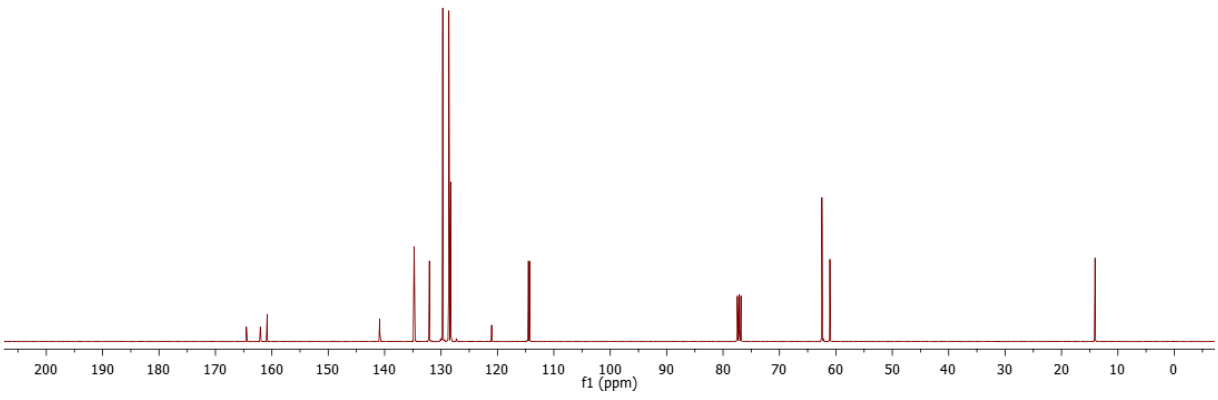
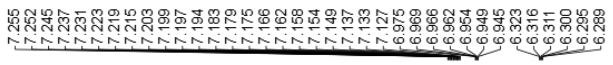
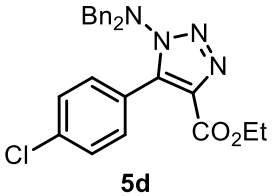


^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)





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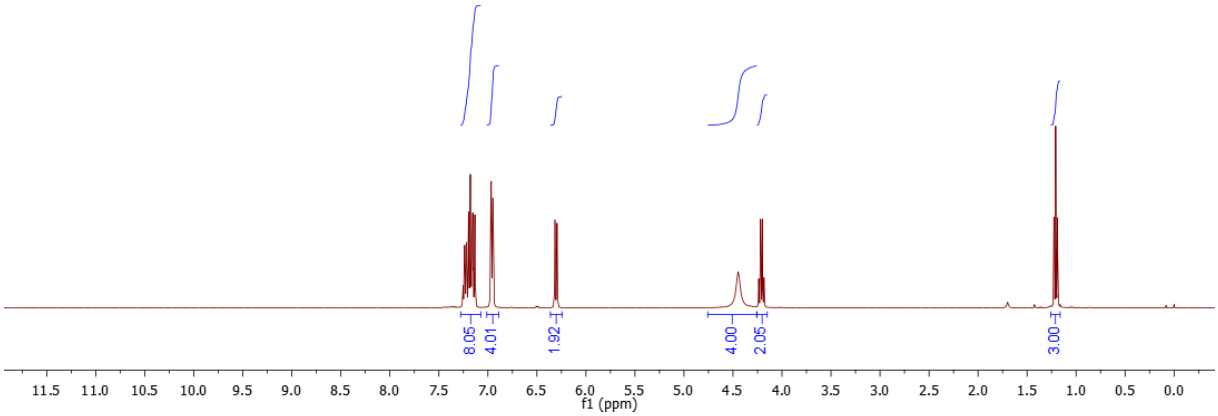
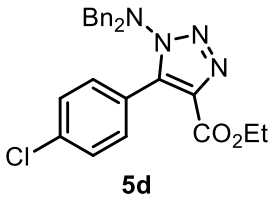


^{13}C NMR (75 MHz, $CDCl_3$)



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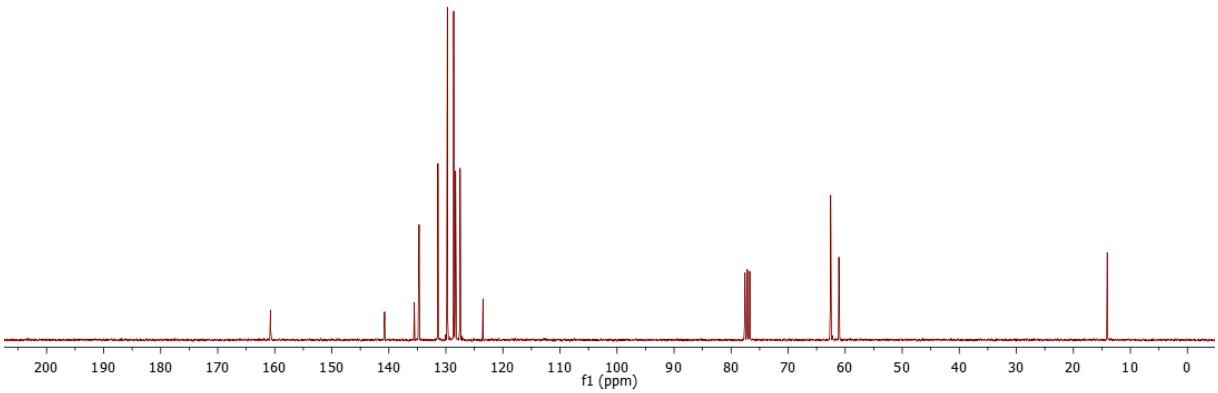
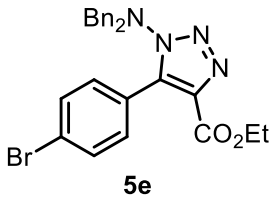


^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)



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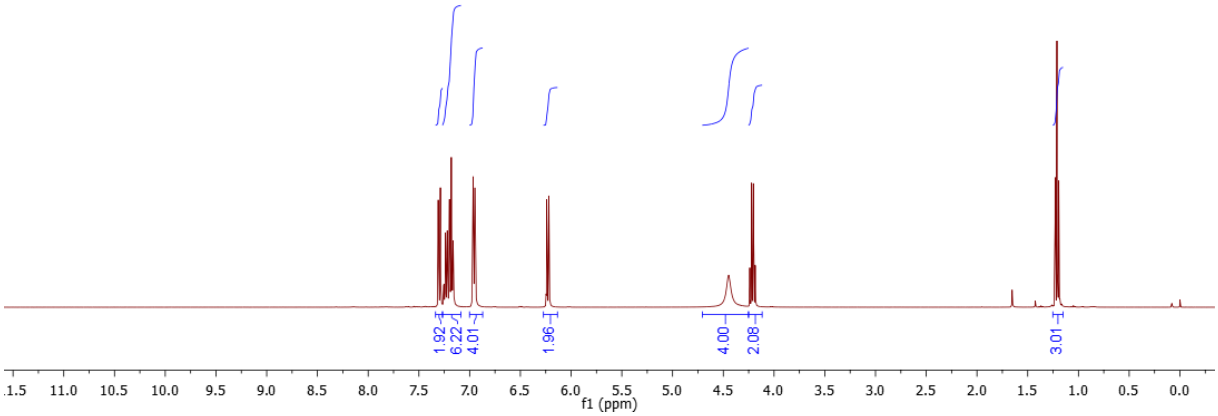
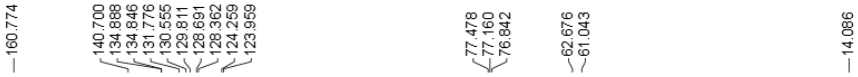
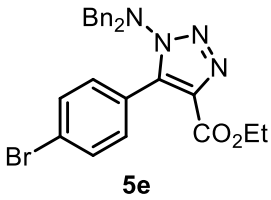


^{13}C NMR (100 MHz, $CDCl_3$, 50 °C)





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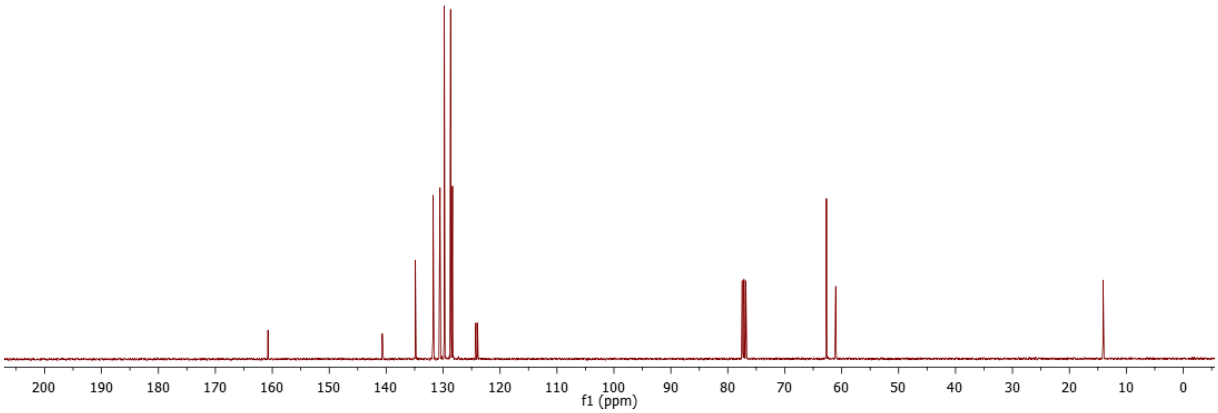
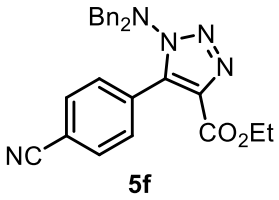


^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)



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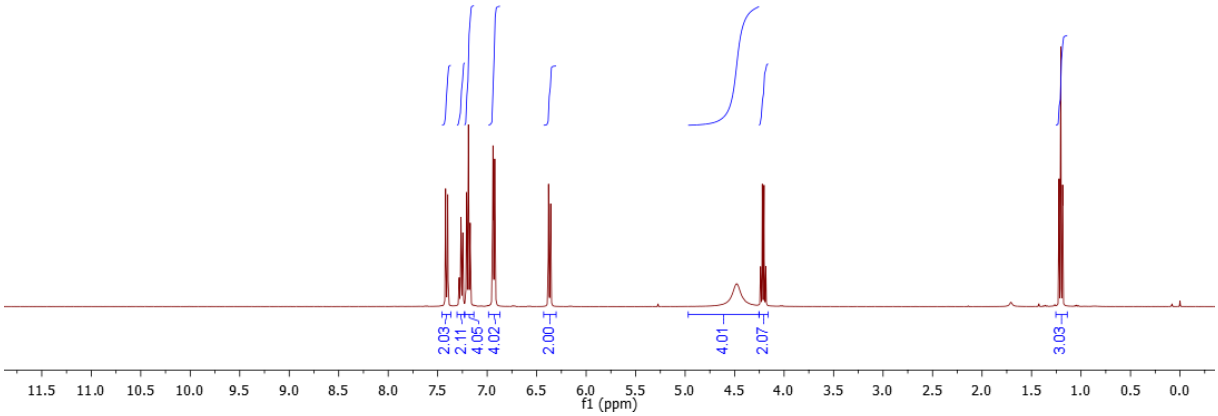
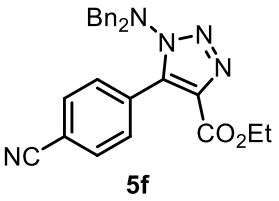


^{13}C NMR (75 MHz, $CDCl_3$)



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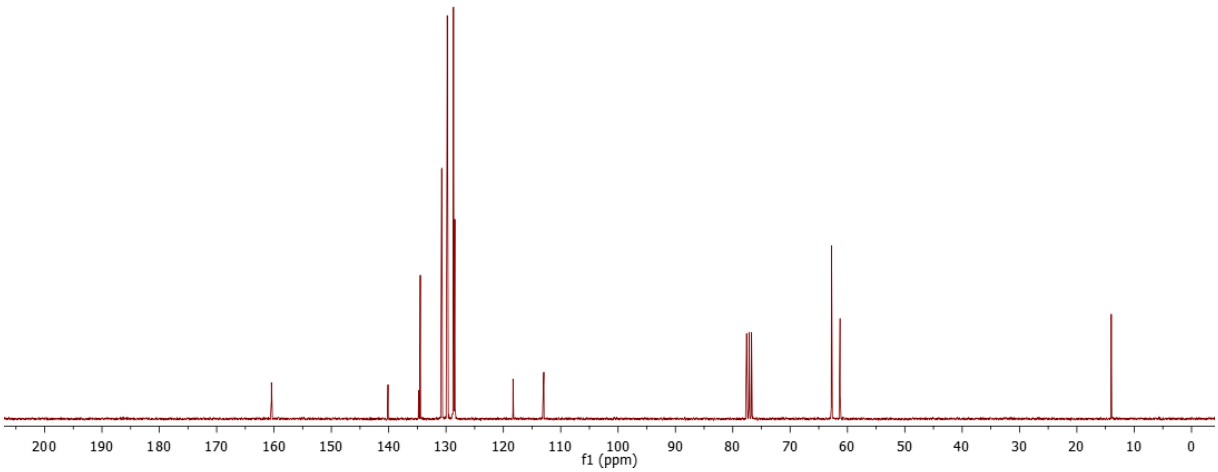
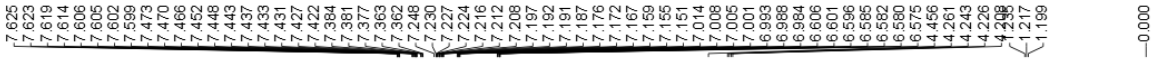
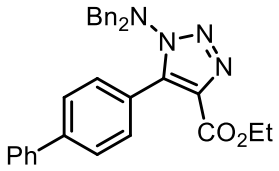


^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)





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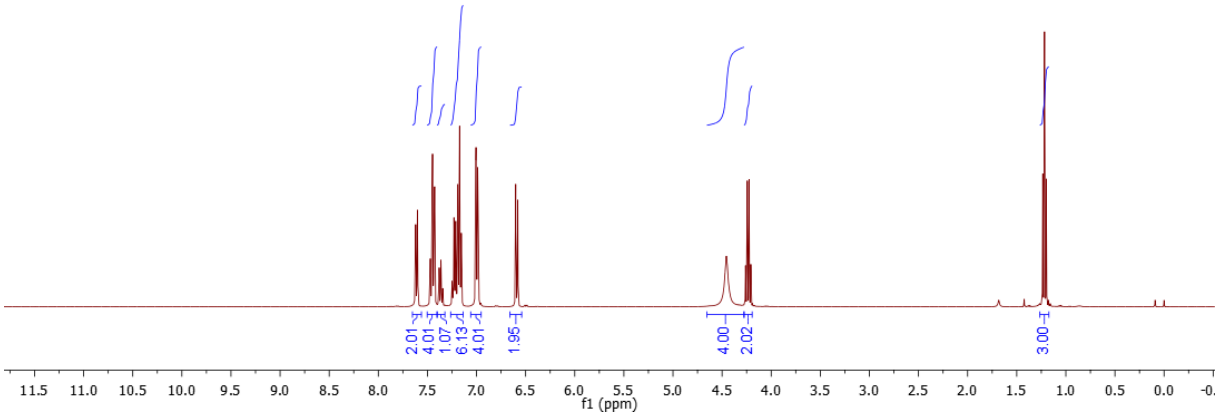
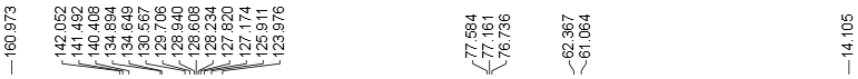
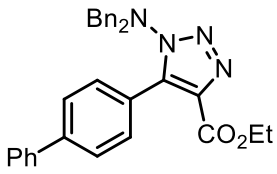


^{13}C NMR (75 MHz, $CDCl_3$)





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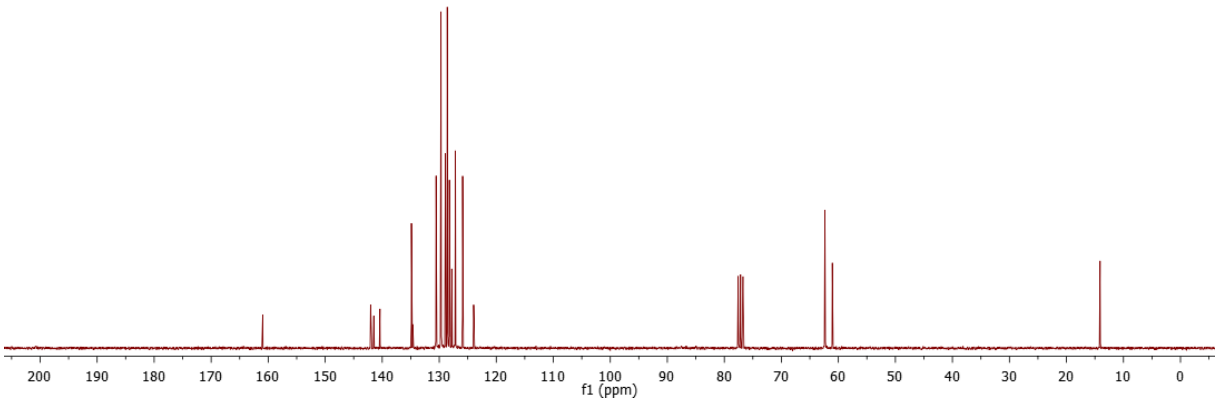
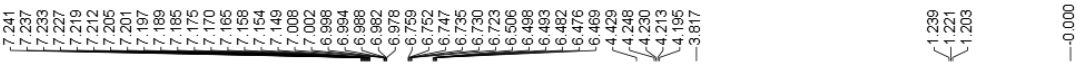
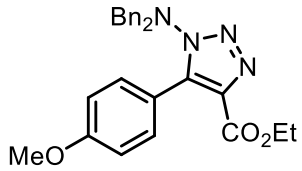


^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)





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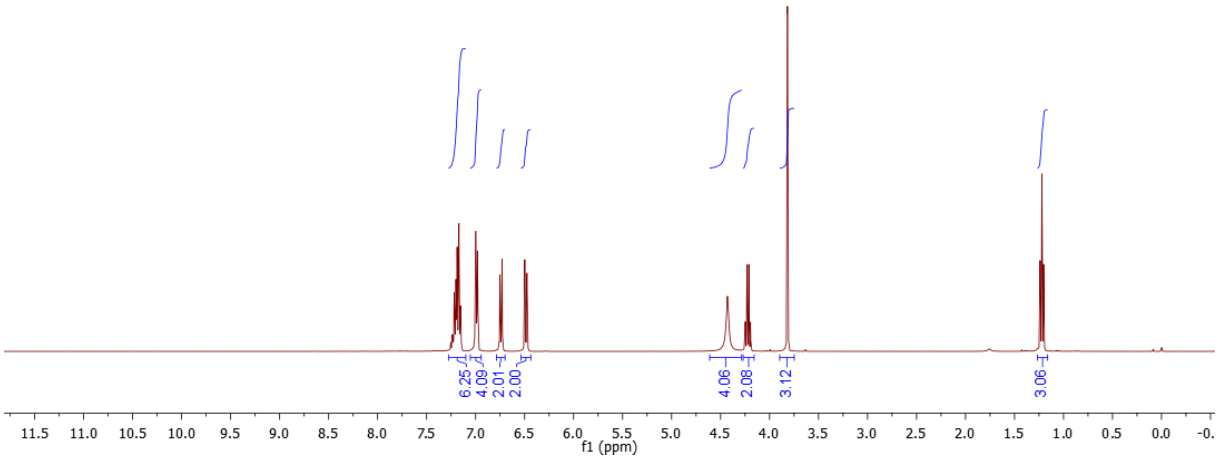
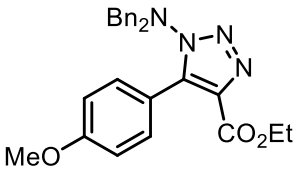


^{13}C NMR (75 MHz, $CDCl_3$)



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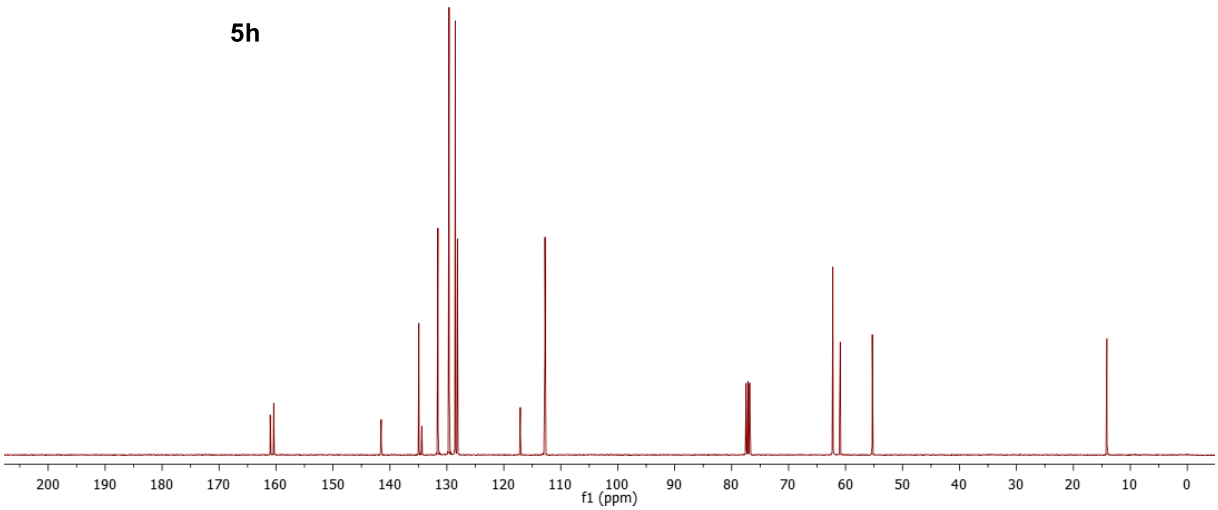
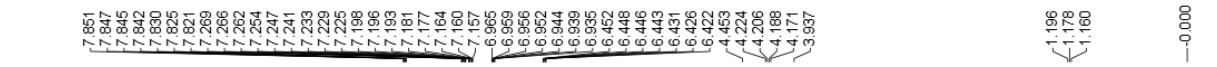
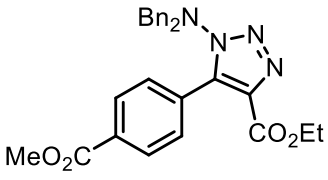


^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)





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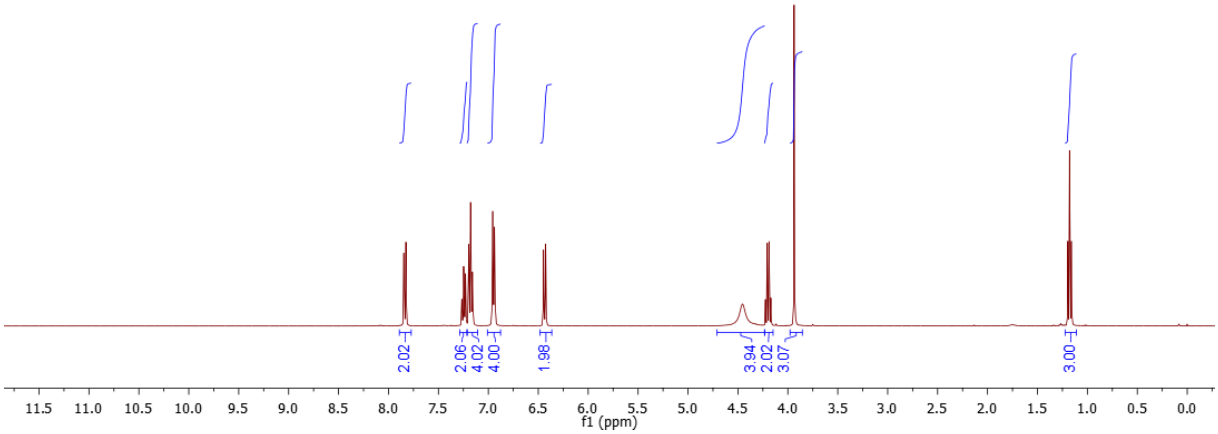
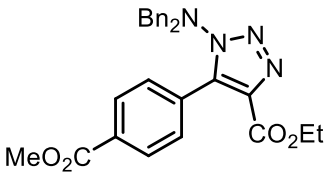


^{13}C NMR (75 MHz, $CDCl_3$)



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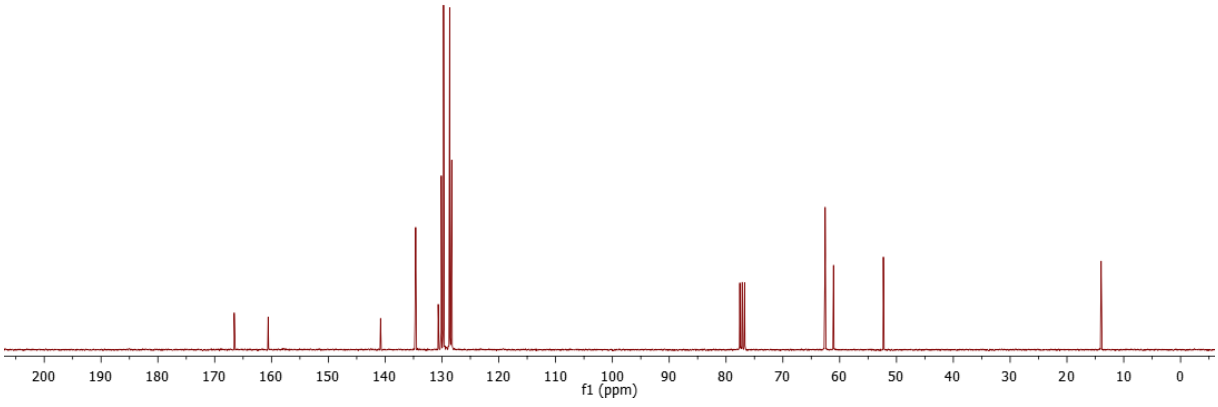
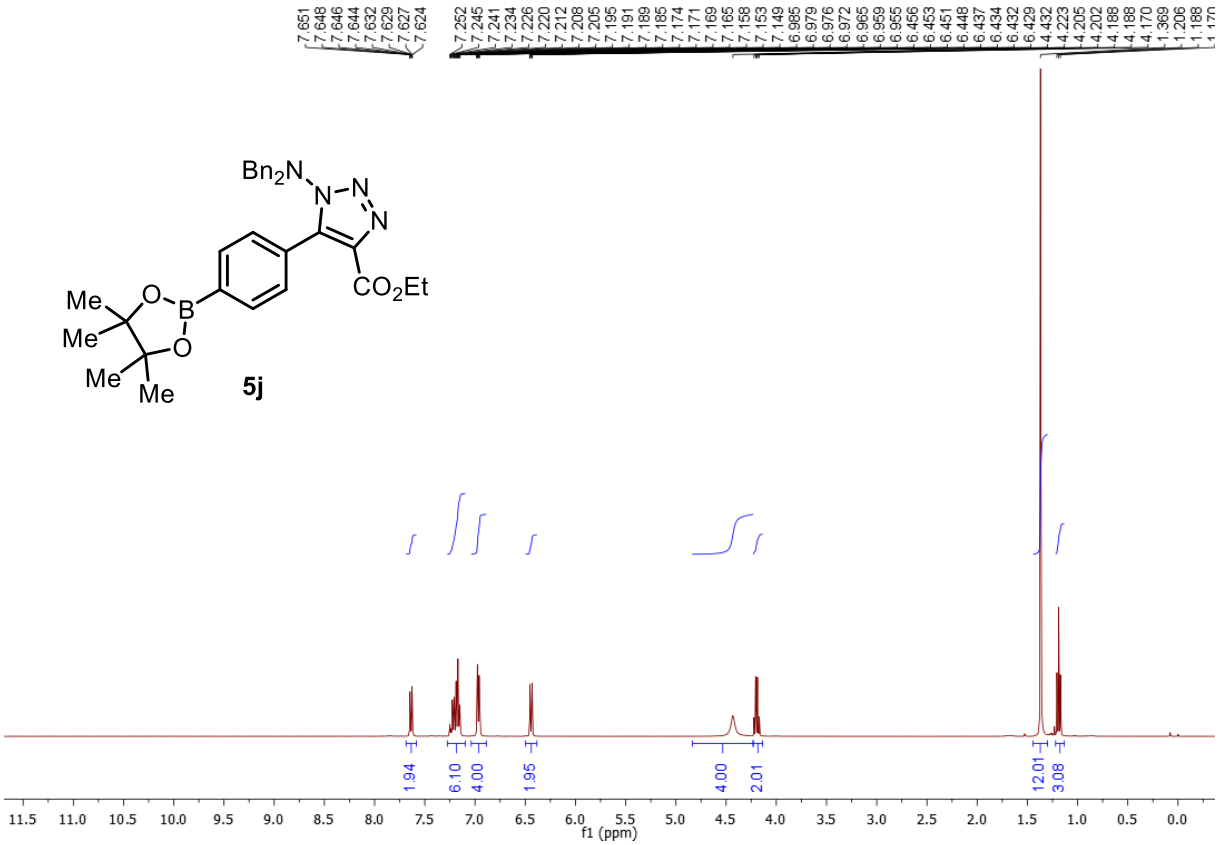
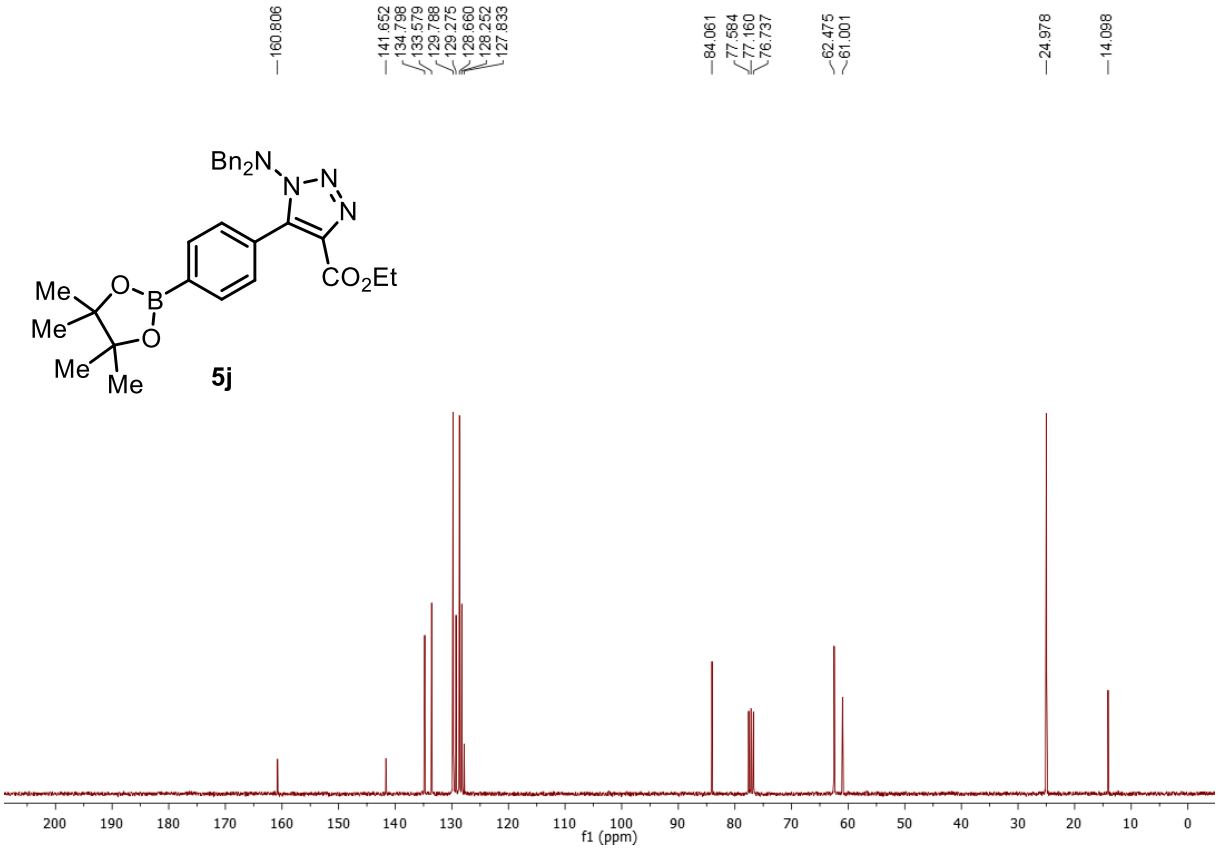


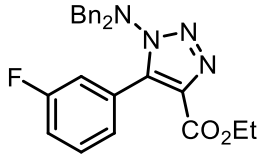
^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)



^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)



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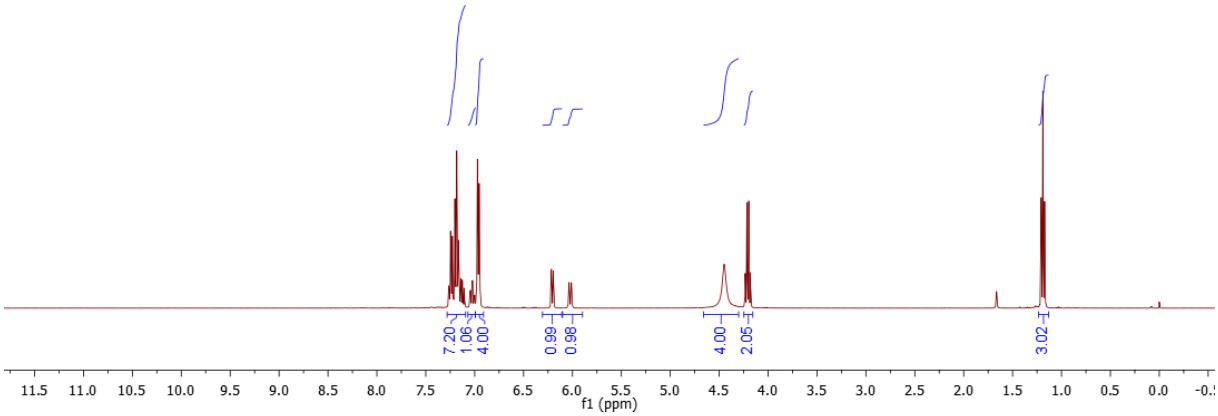
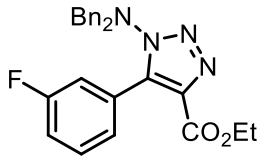


^{13}C NMR (75 MHz, $CDCl_3$)



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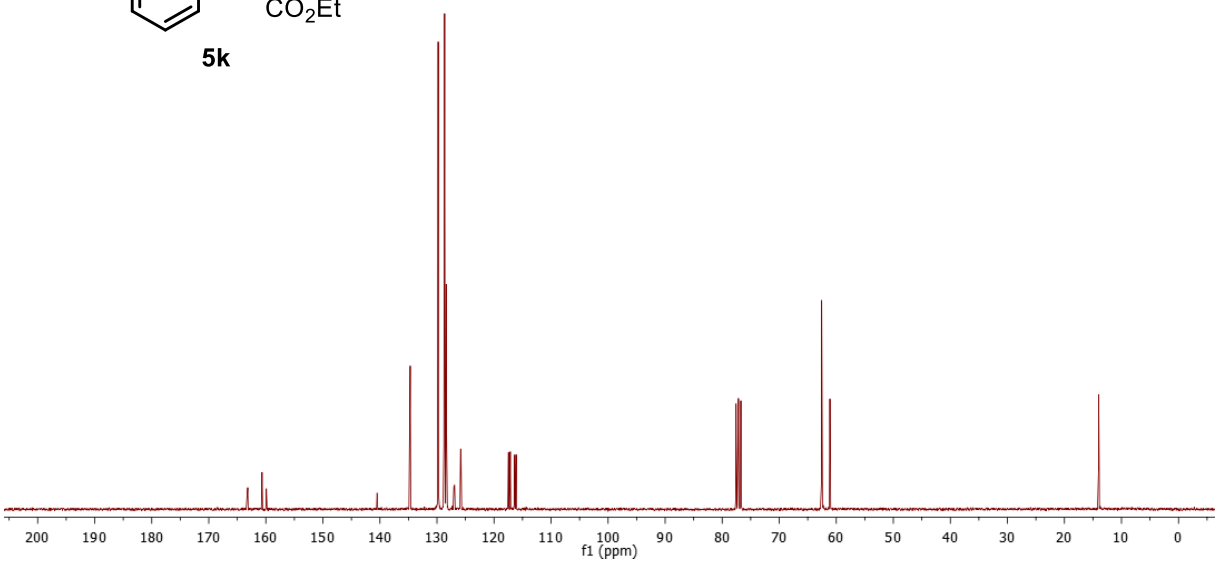
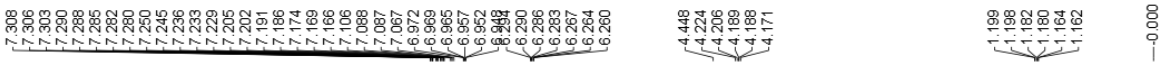
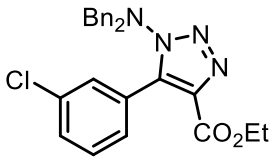


^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)





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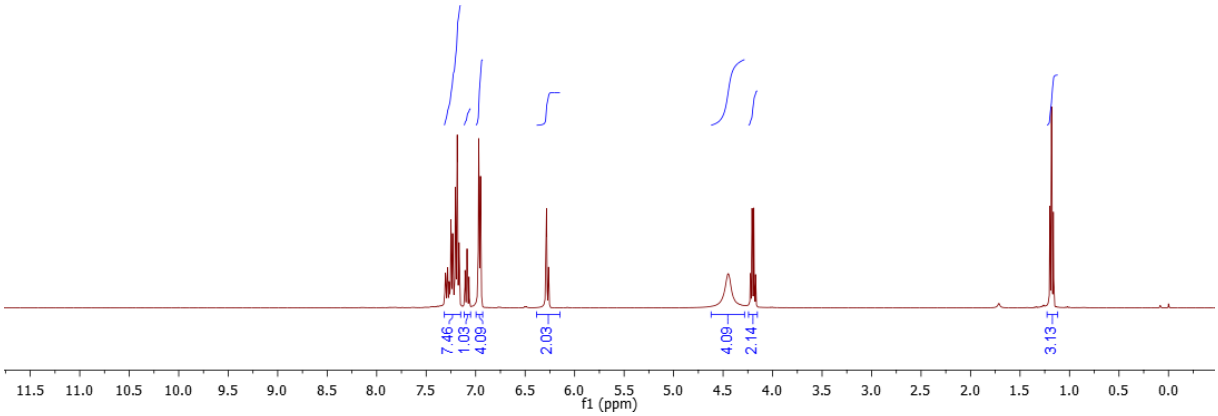
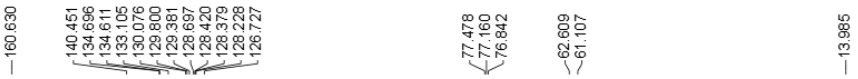
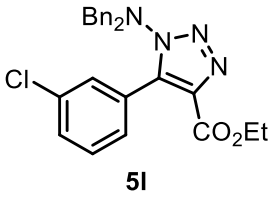


^{13}C NMR (75 MHz, $CDCl_3$)





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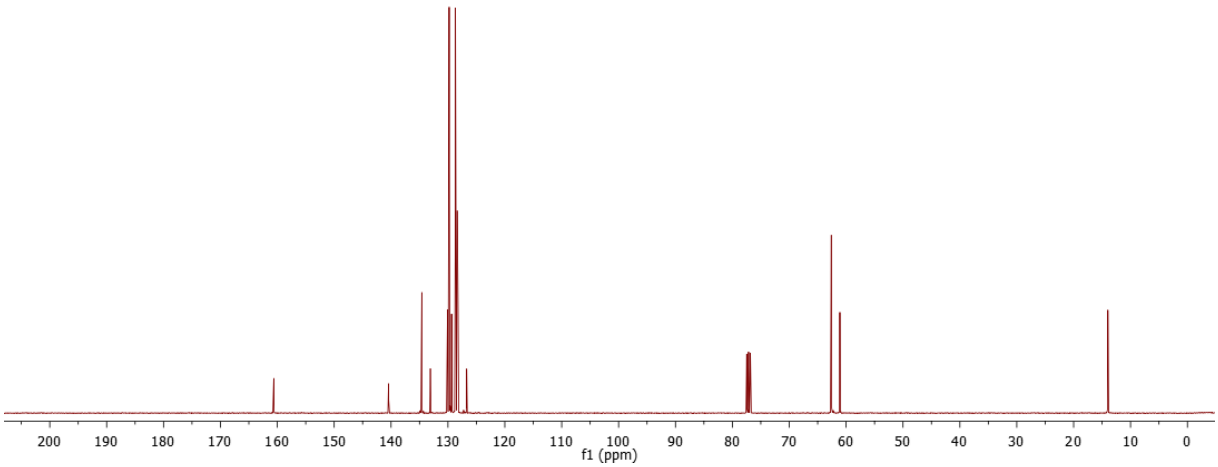
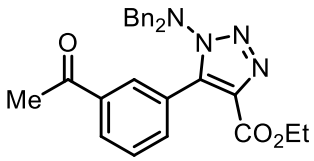


^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)



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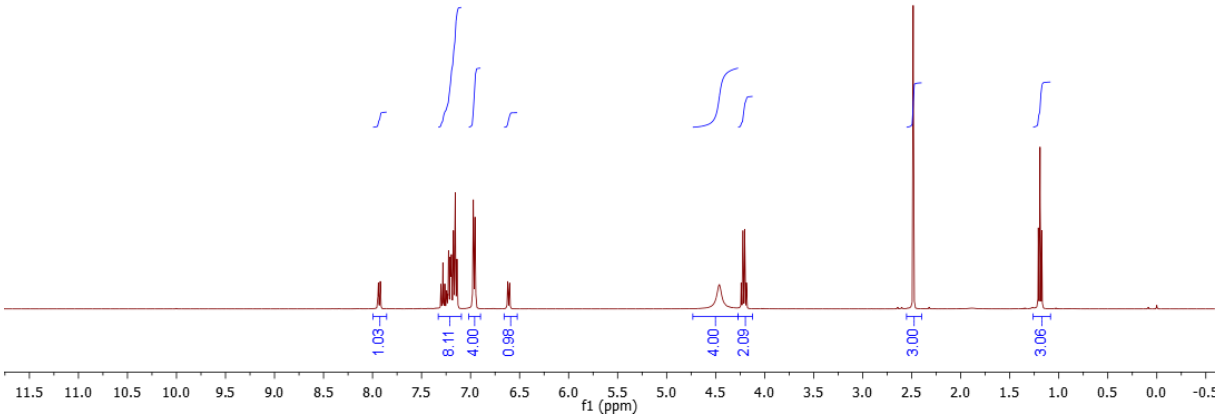
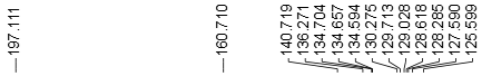
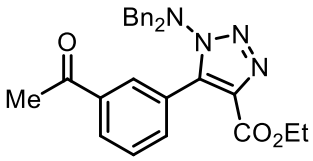


^{13}C NMR (75 MHz, $CDCl_3$)





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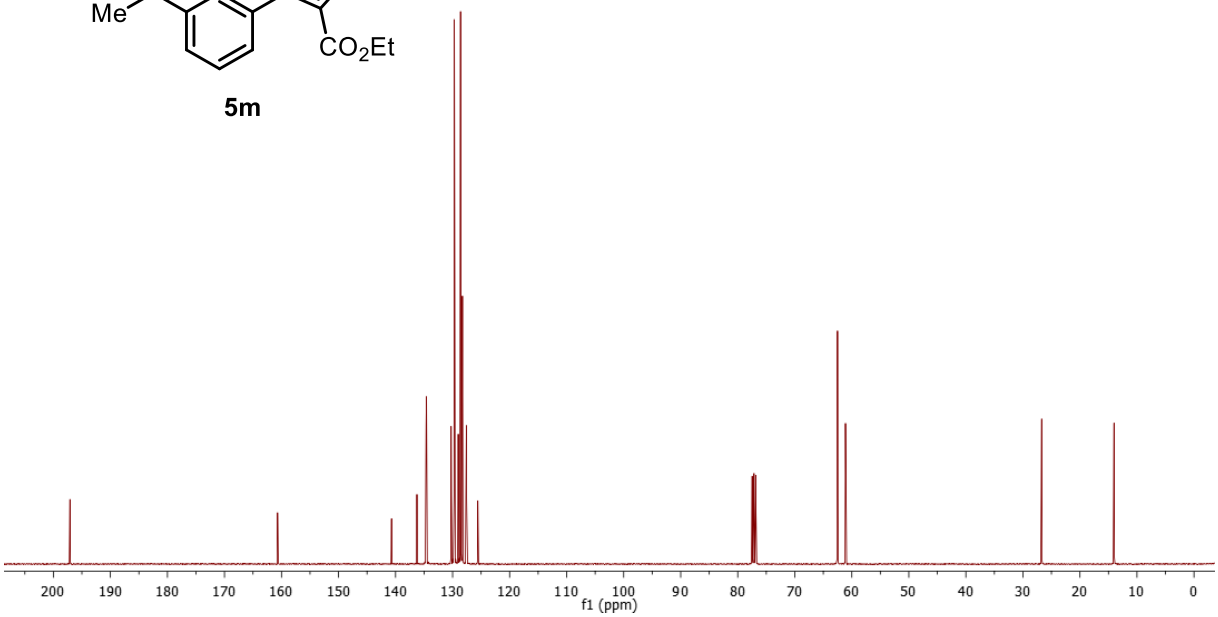
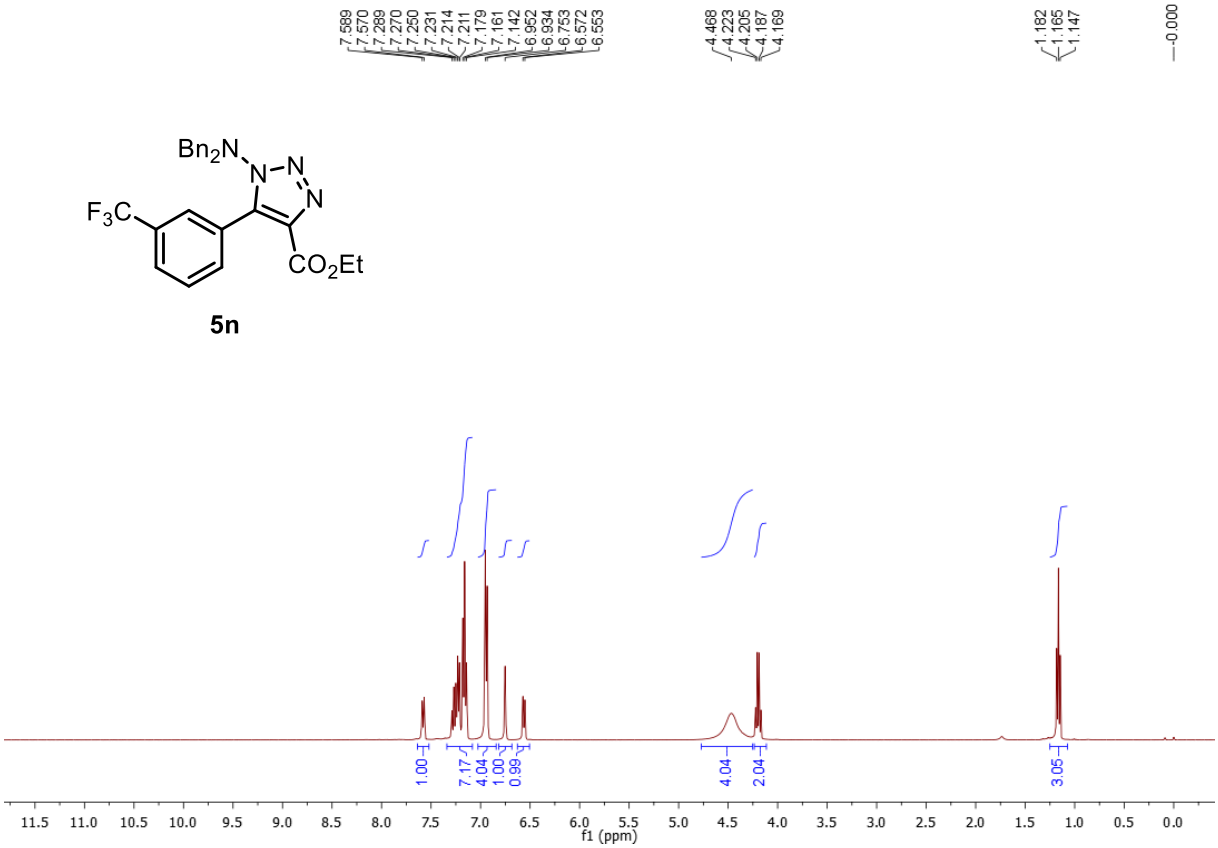
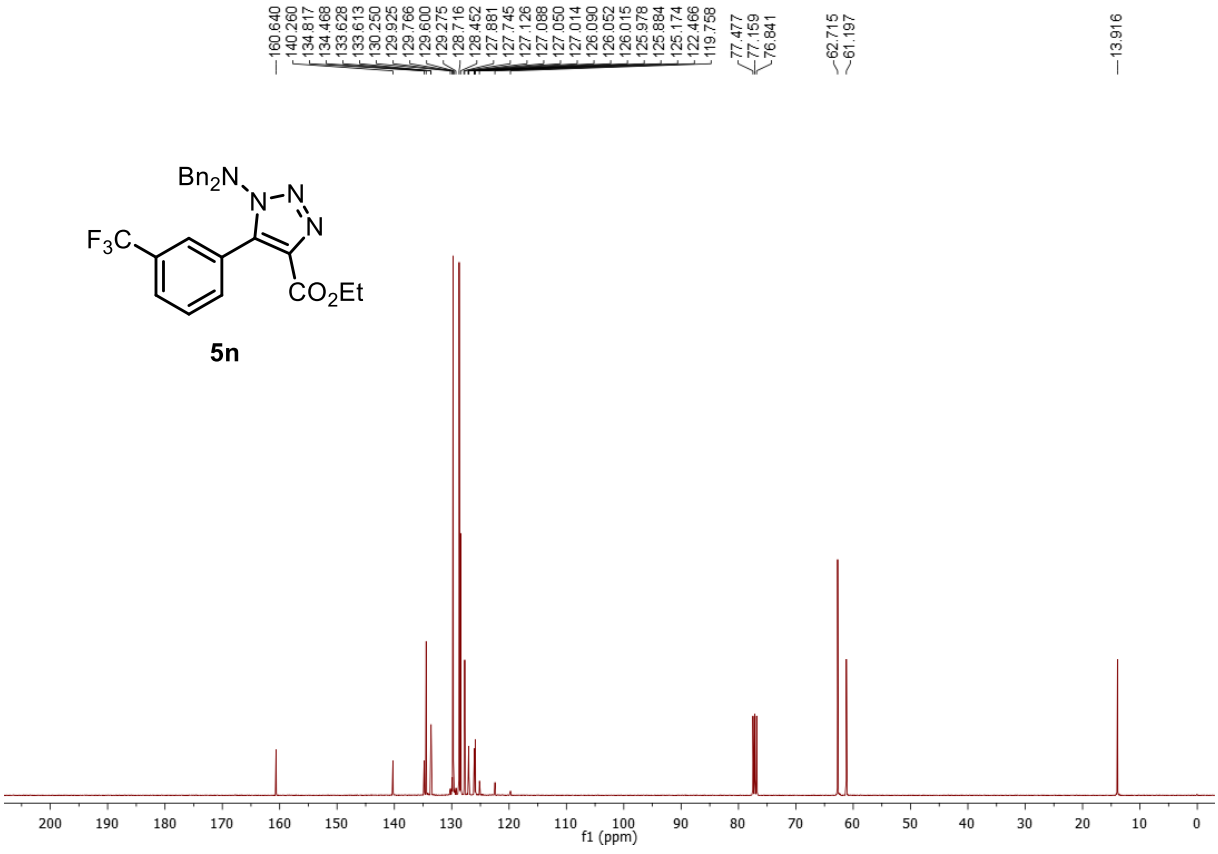


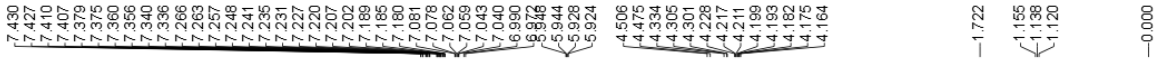
^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)

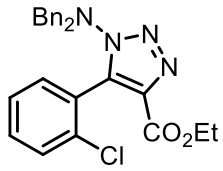


^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)





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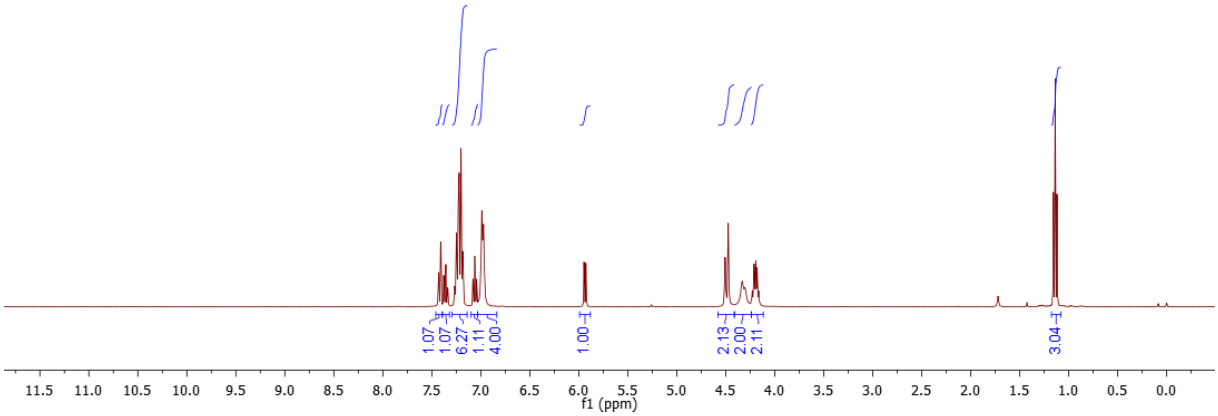
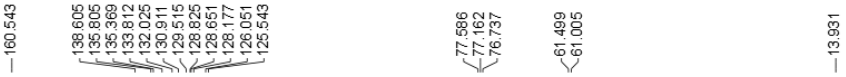
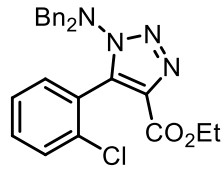


^{13}C NMR (75 MHz, $CDCl_3$)





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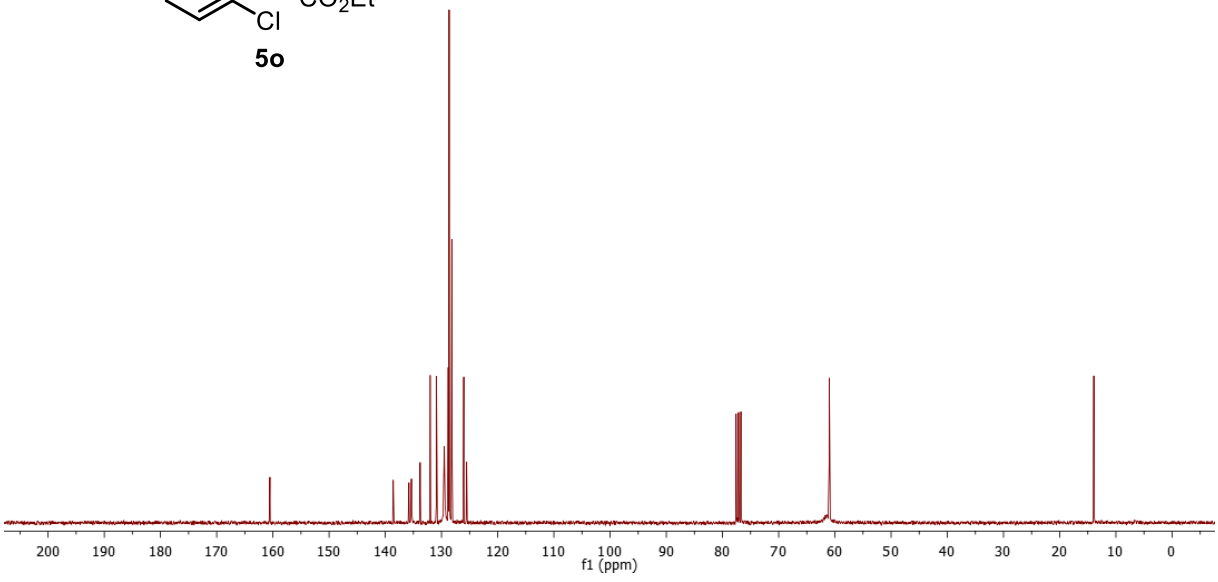
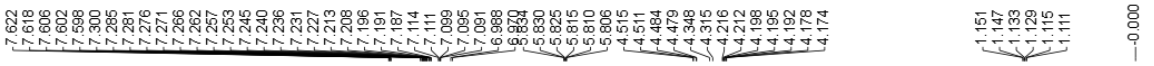
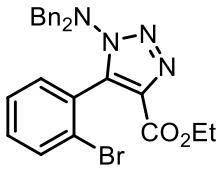


^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)





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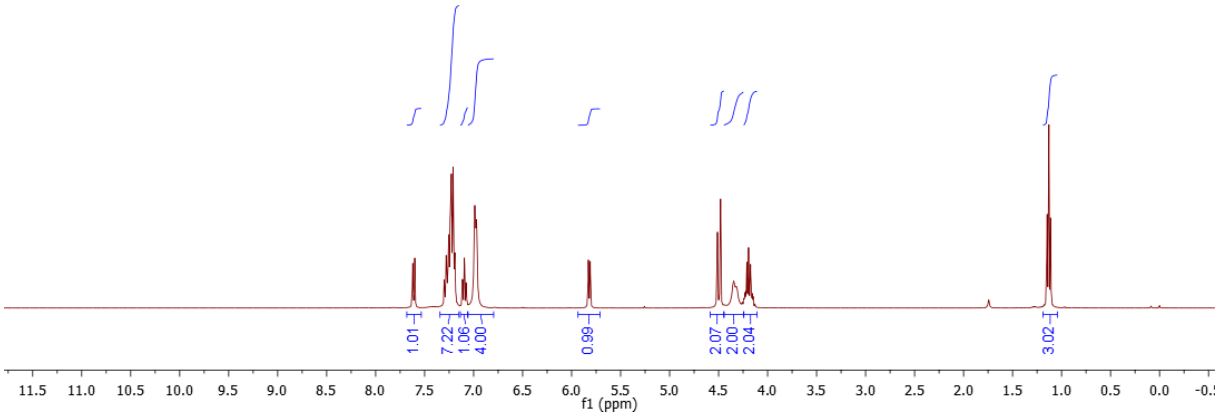
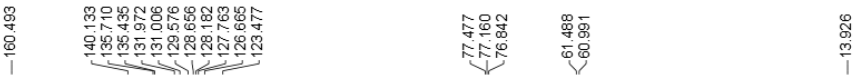
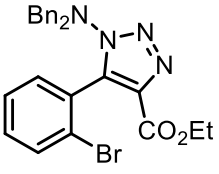


^{13}C NMR (75 MHz, $CDCl_3$)





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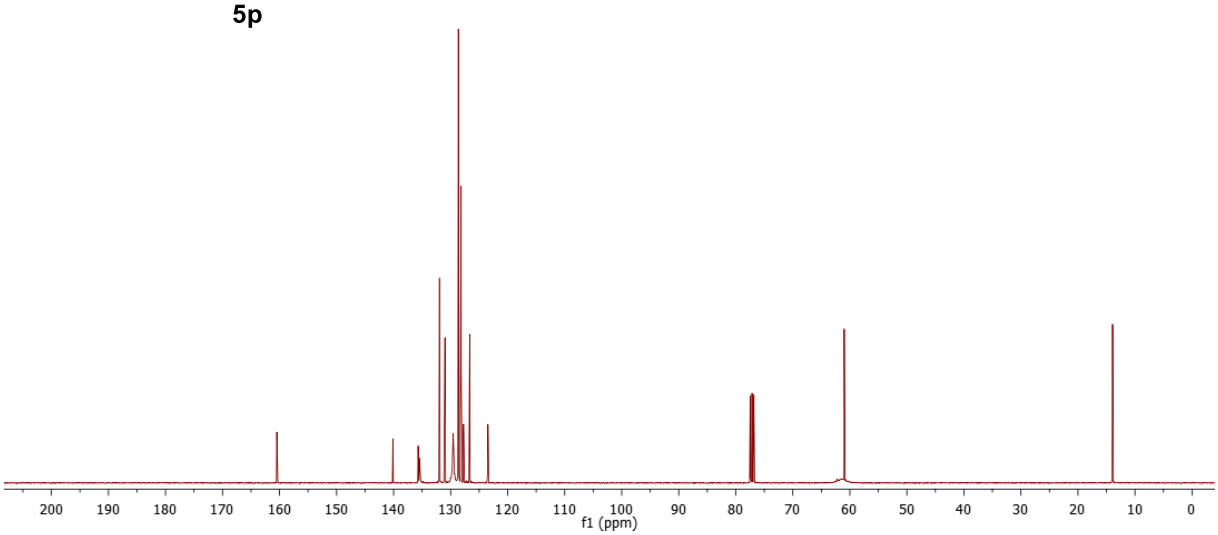
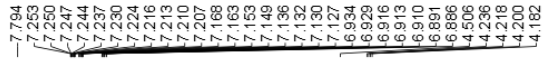
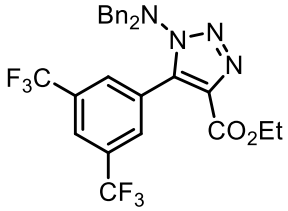


^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)





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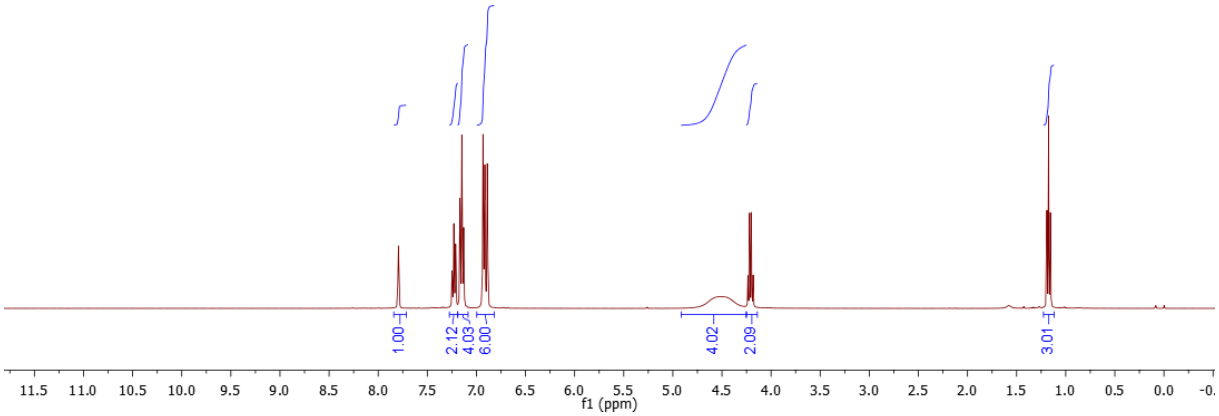
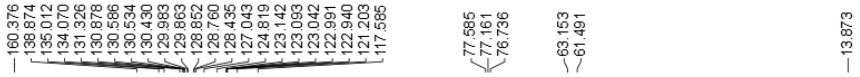
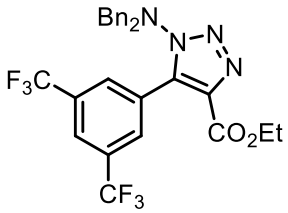


^{13}C NMR (75 MHz, $CDCl_3$)





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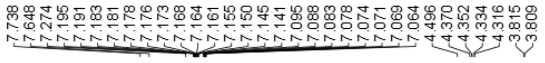
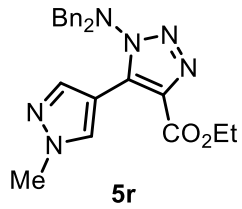
^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)





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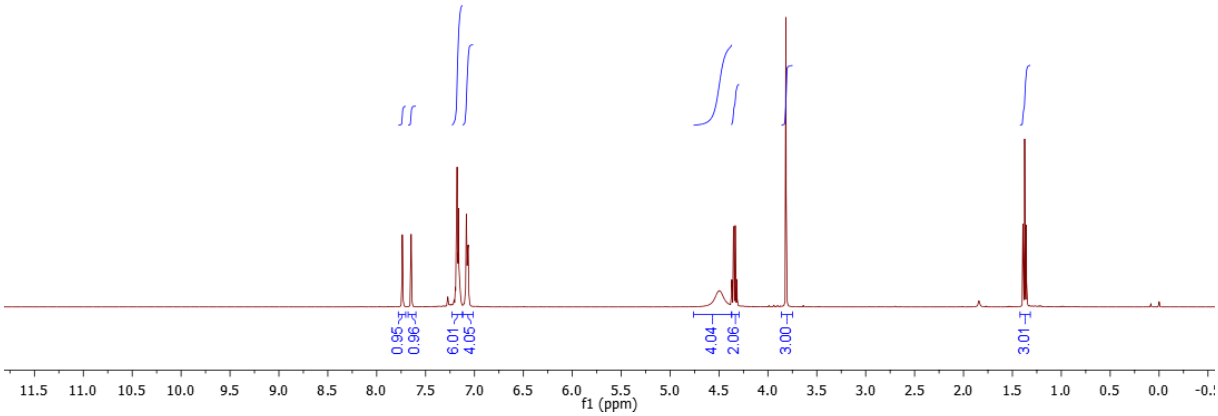
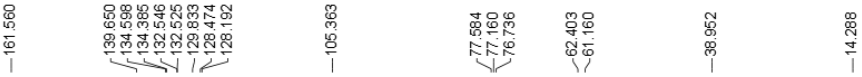
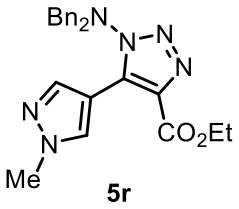


^{13}C NMR (75 MHz, $CDCl_3$)





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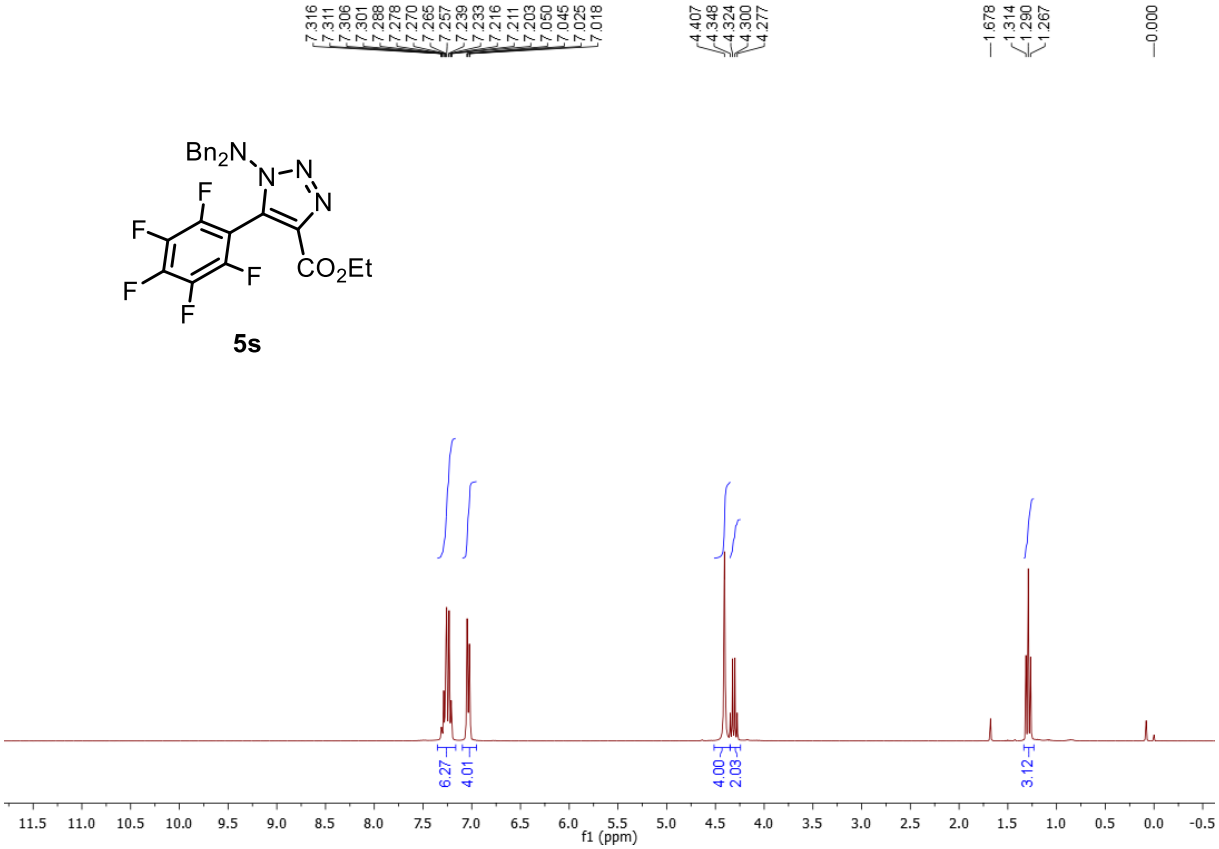
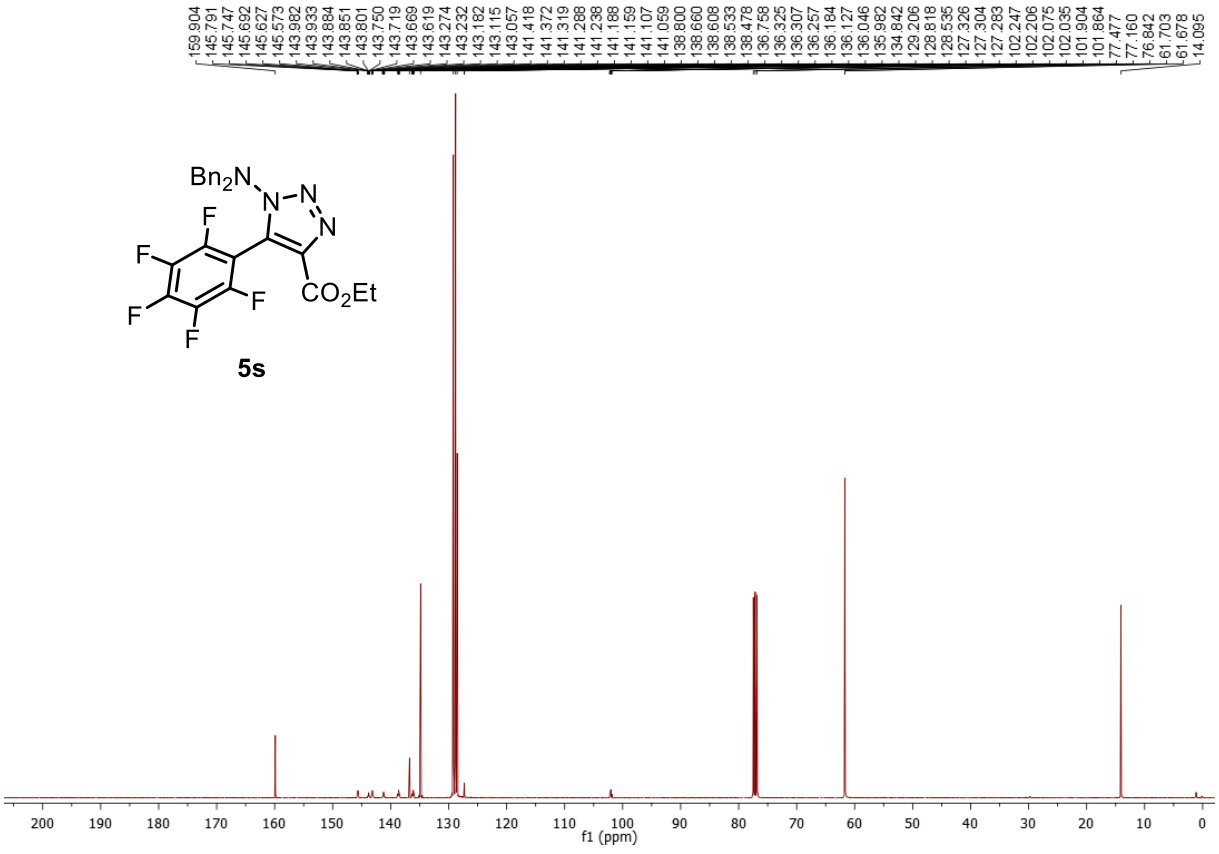
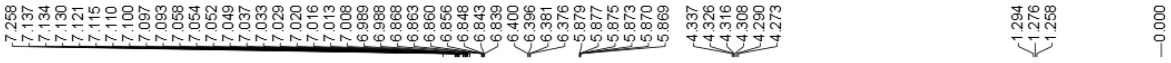
^{1}H NMR (300 MHz, $CDCl_3$)

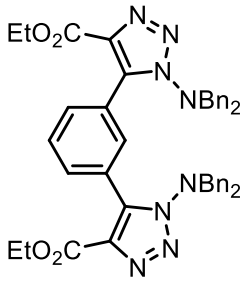


^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)





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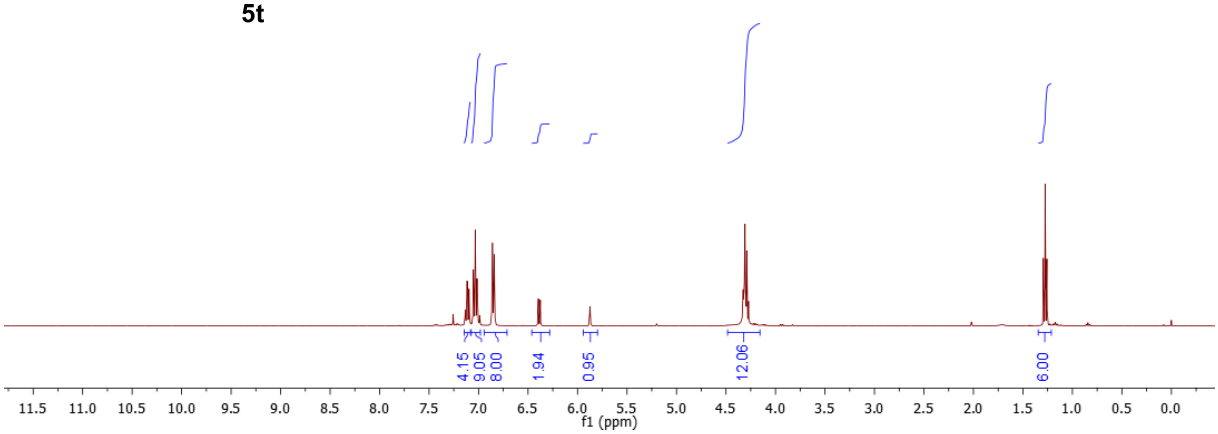
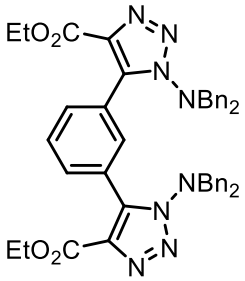


^{13}C NMR (75 MHz, $CDCl_3$)



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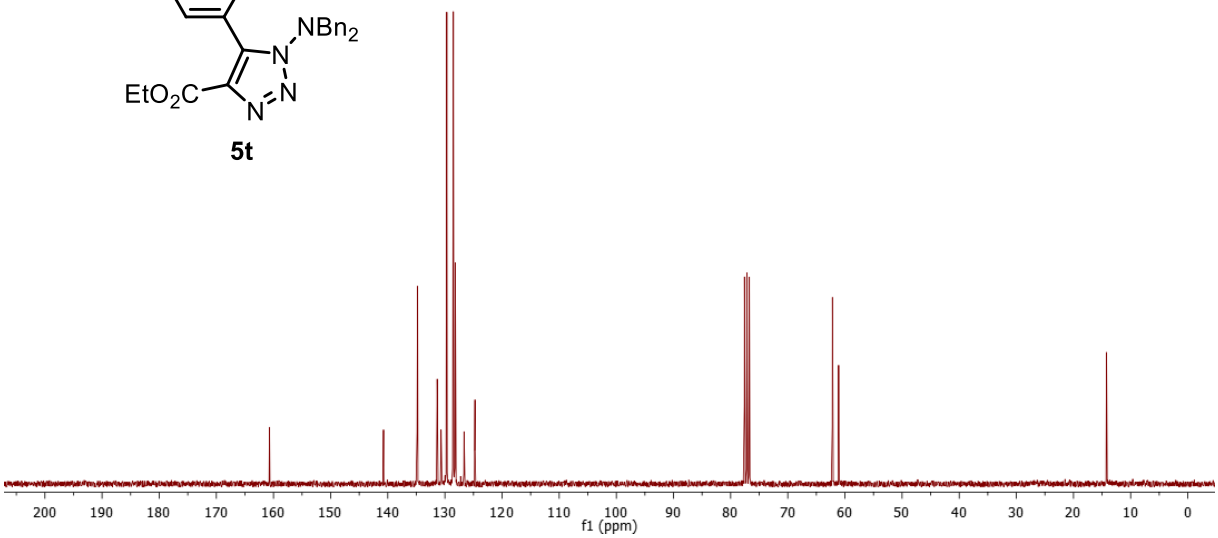
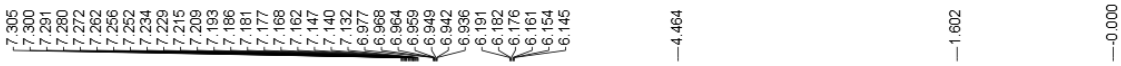
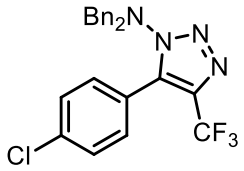


^{1}H NMR (300 MHz, $CDCl_3$)





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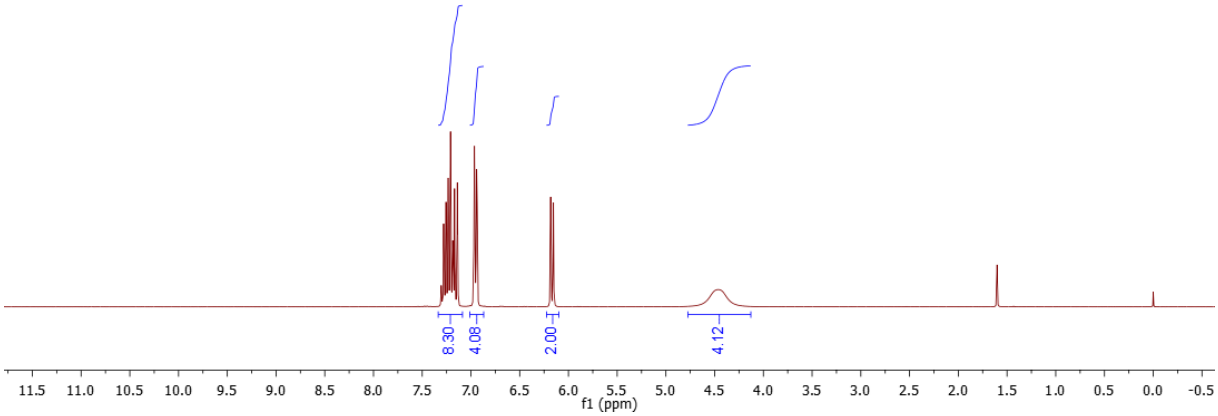
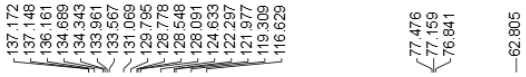
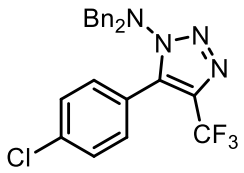


^{13}C NMR (75 MHz, $CDCl_3$)





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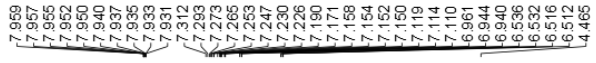
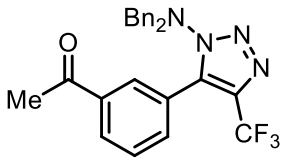
^{1}H NMR (400 MHz, $CDCl_3$, 50 °C)





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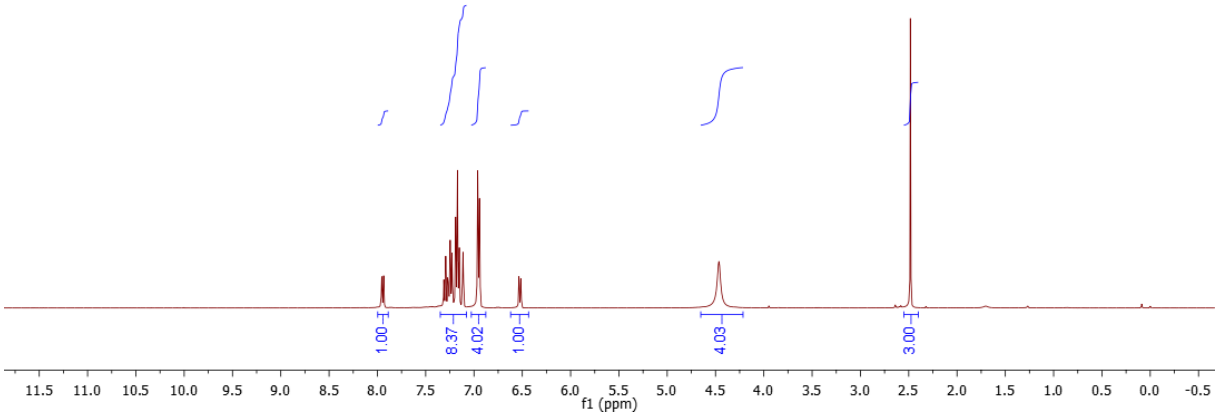
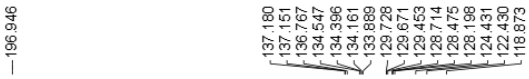
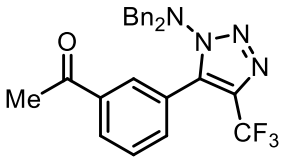


^{13}C NMR (75 MHz, $CDCl_3$)





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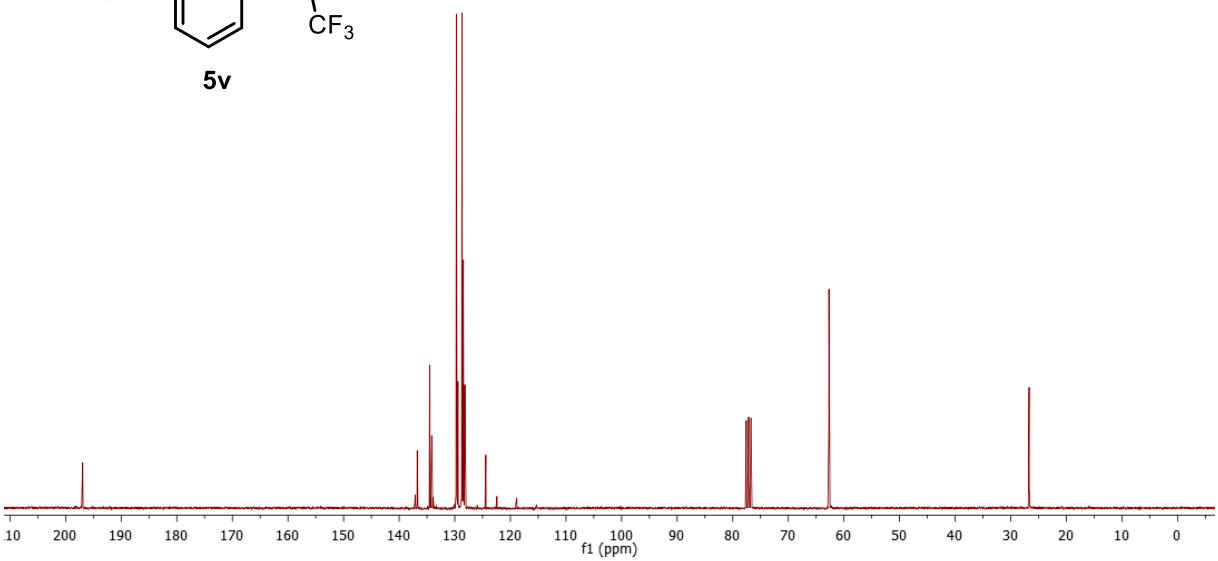
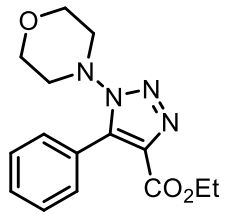


^{1}H NMR (300 MHz, $CDCl_3$)



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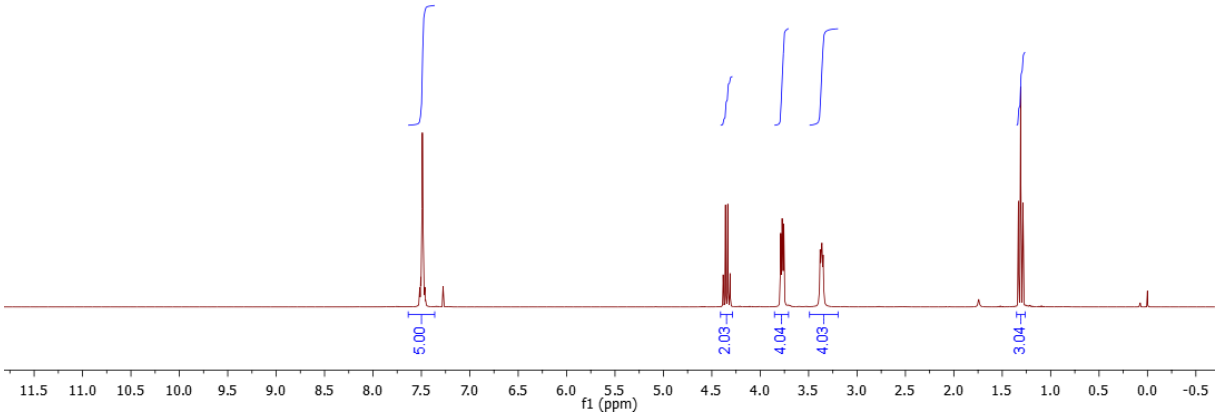
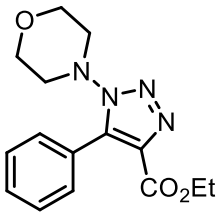


^{13}C NMR (75 MHz, $CDCl_3$)



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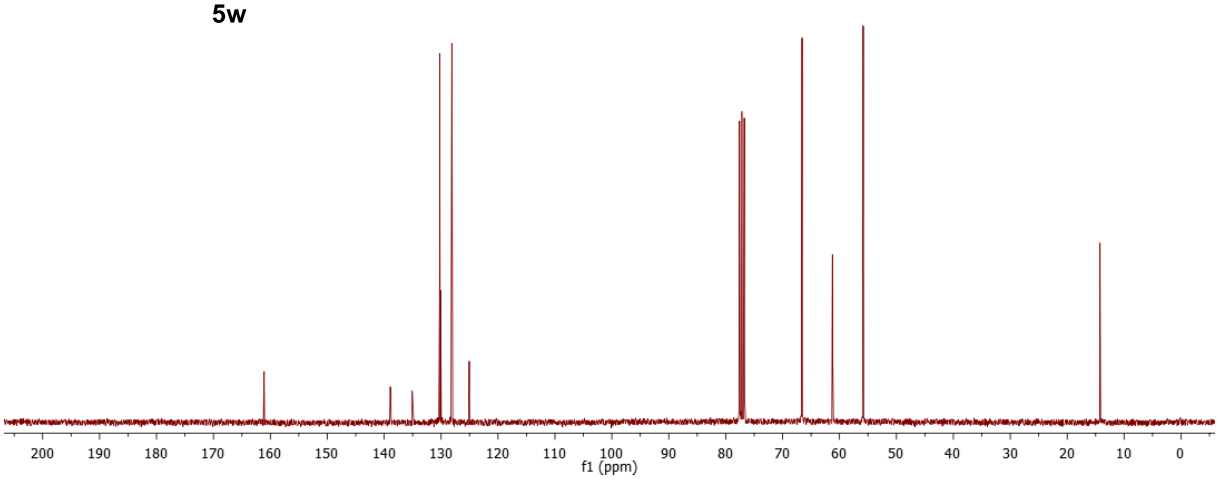
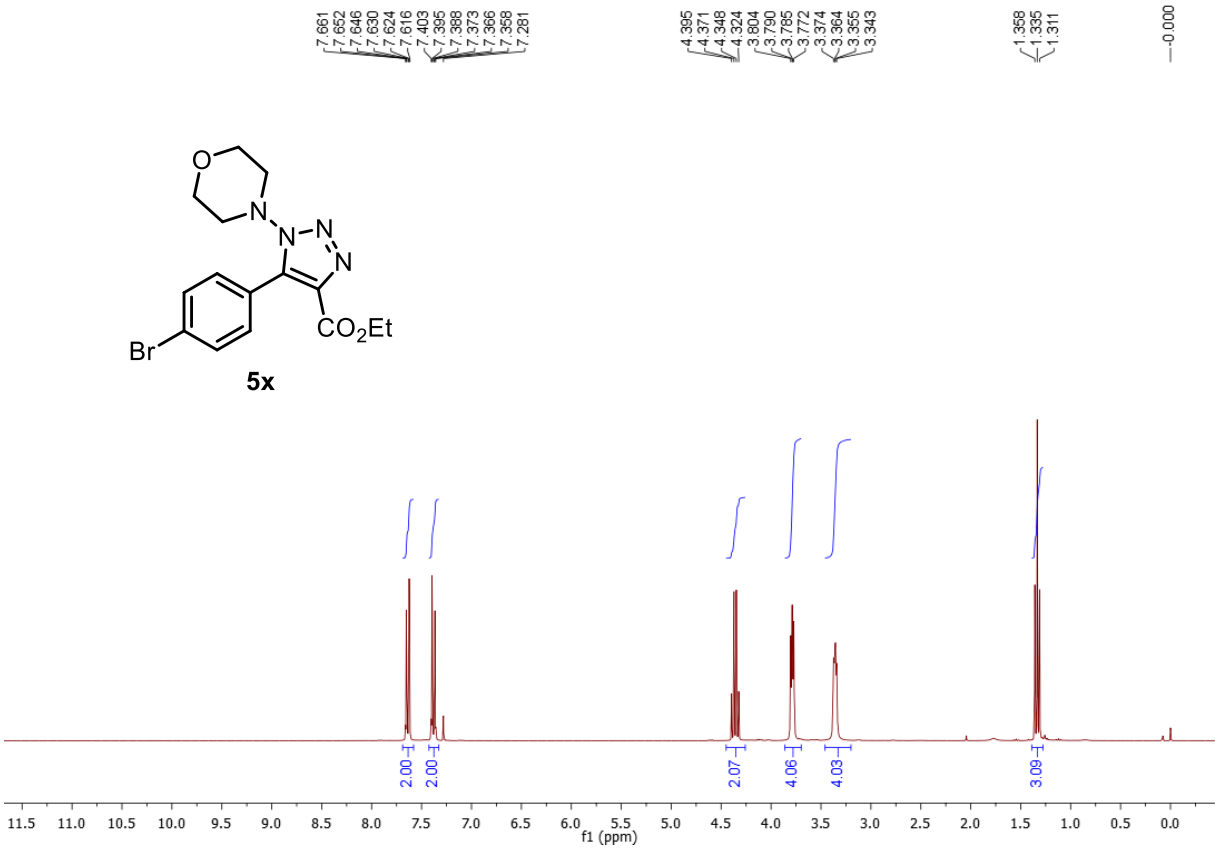
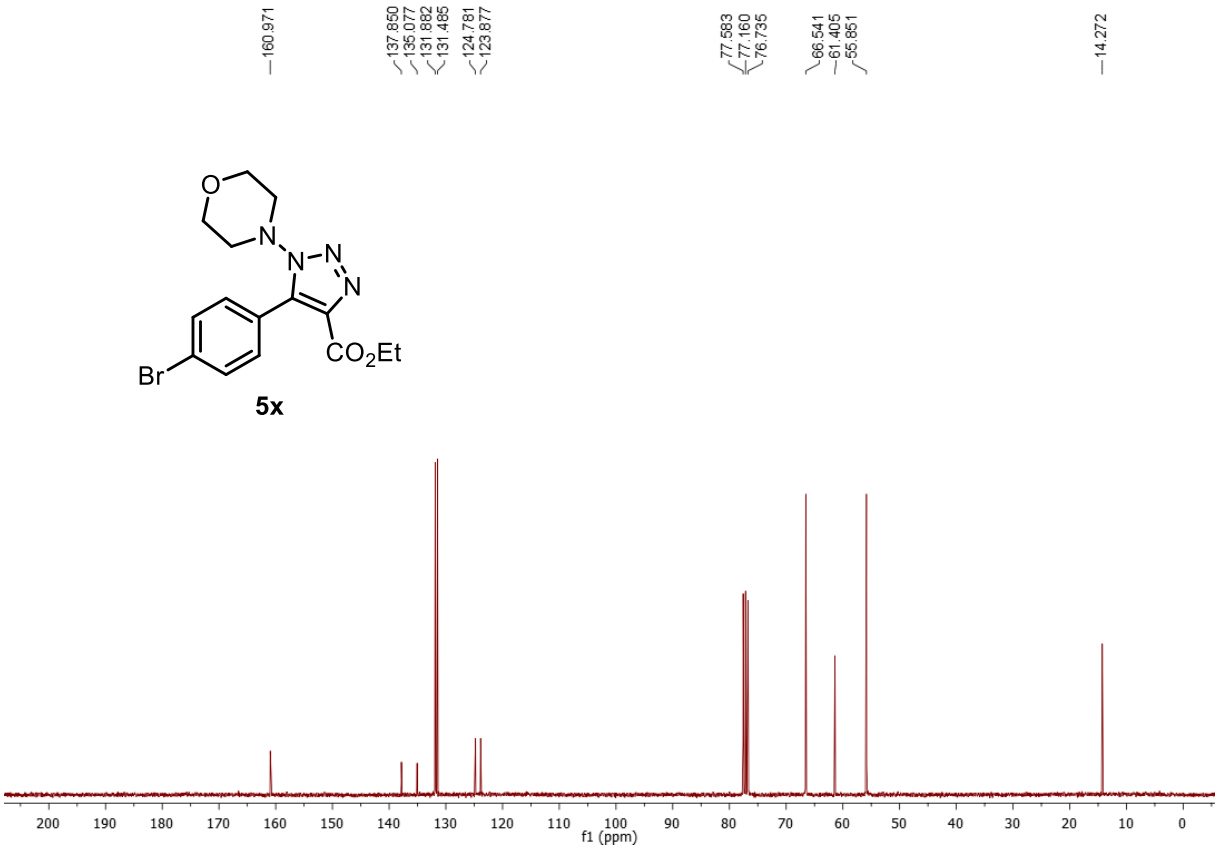


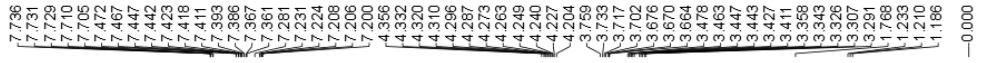
^{1}H NMR (300 MHz, $CDCl_3$)

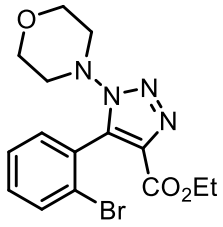


^{13}C NMR (75 MHz, $CDCl_3$)



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





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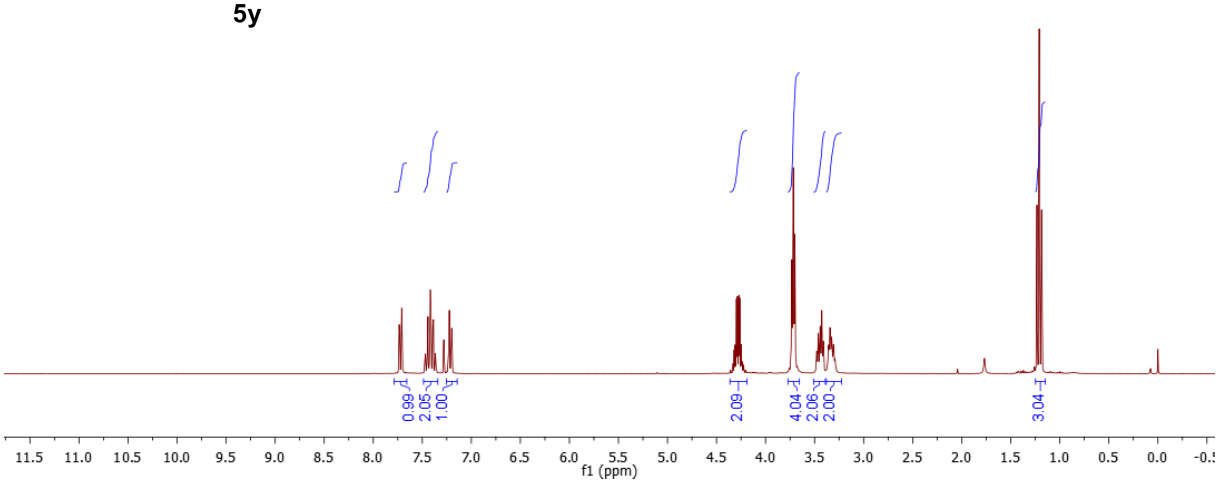
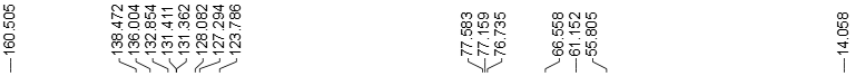
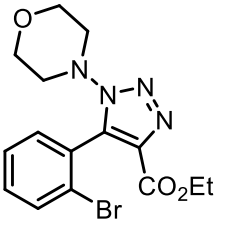


^{13}C NMR (75 MHz, $CDCl_3$)





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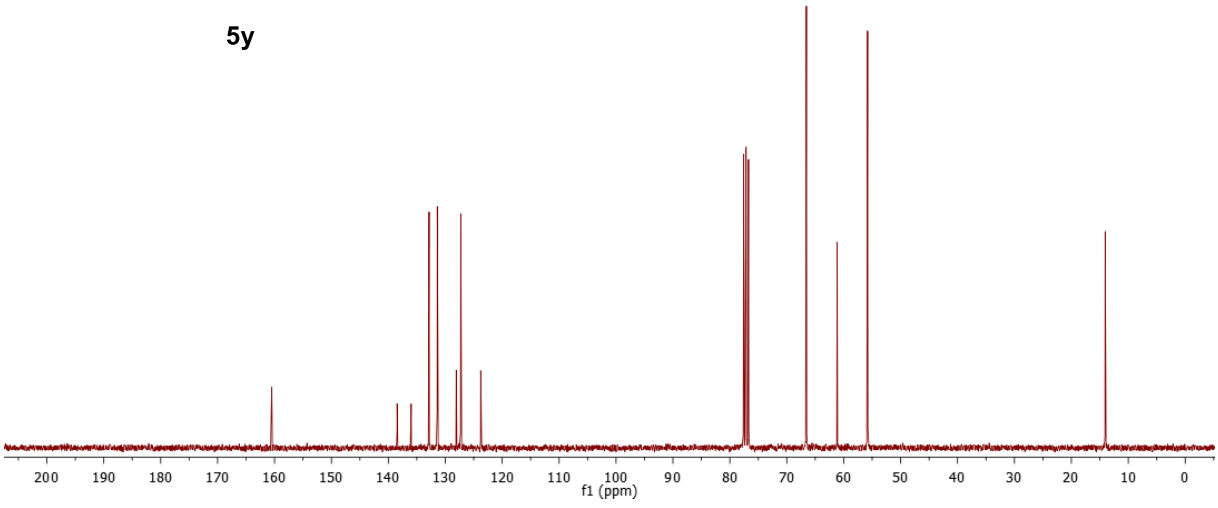
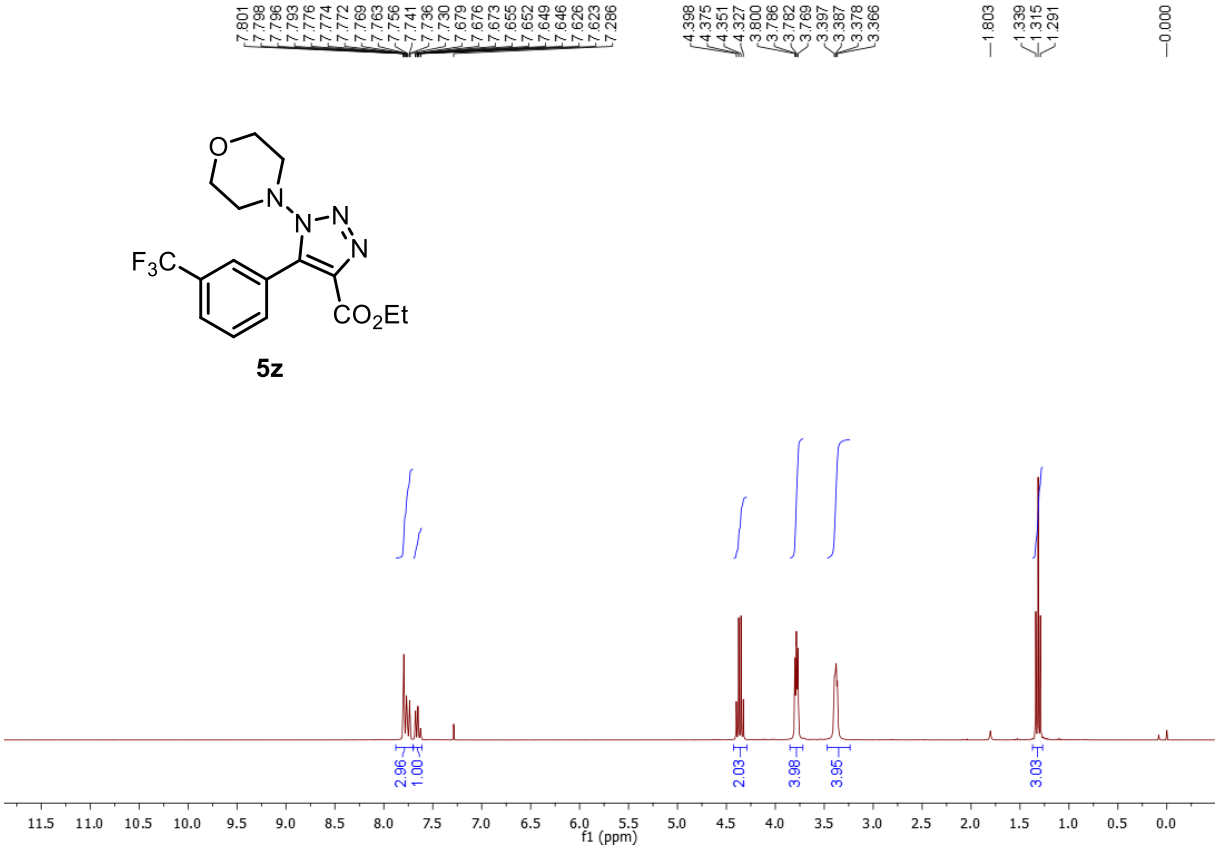


^{1}H NMR (300 MHz, $CDCl_3$)



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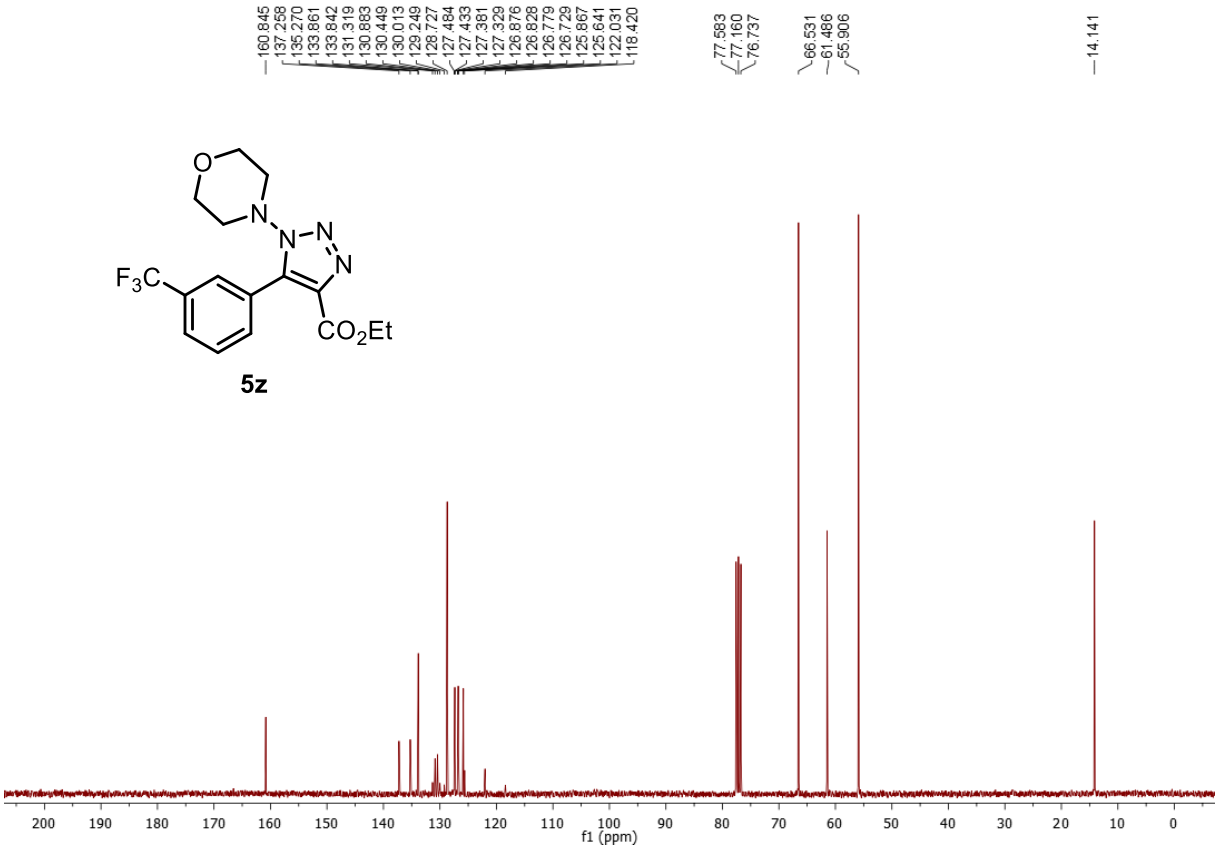
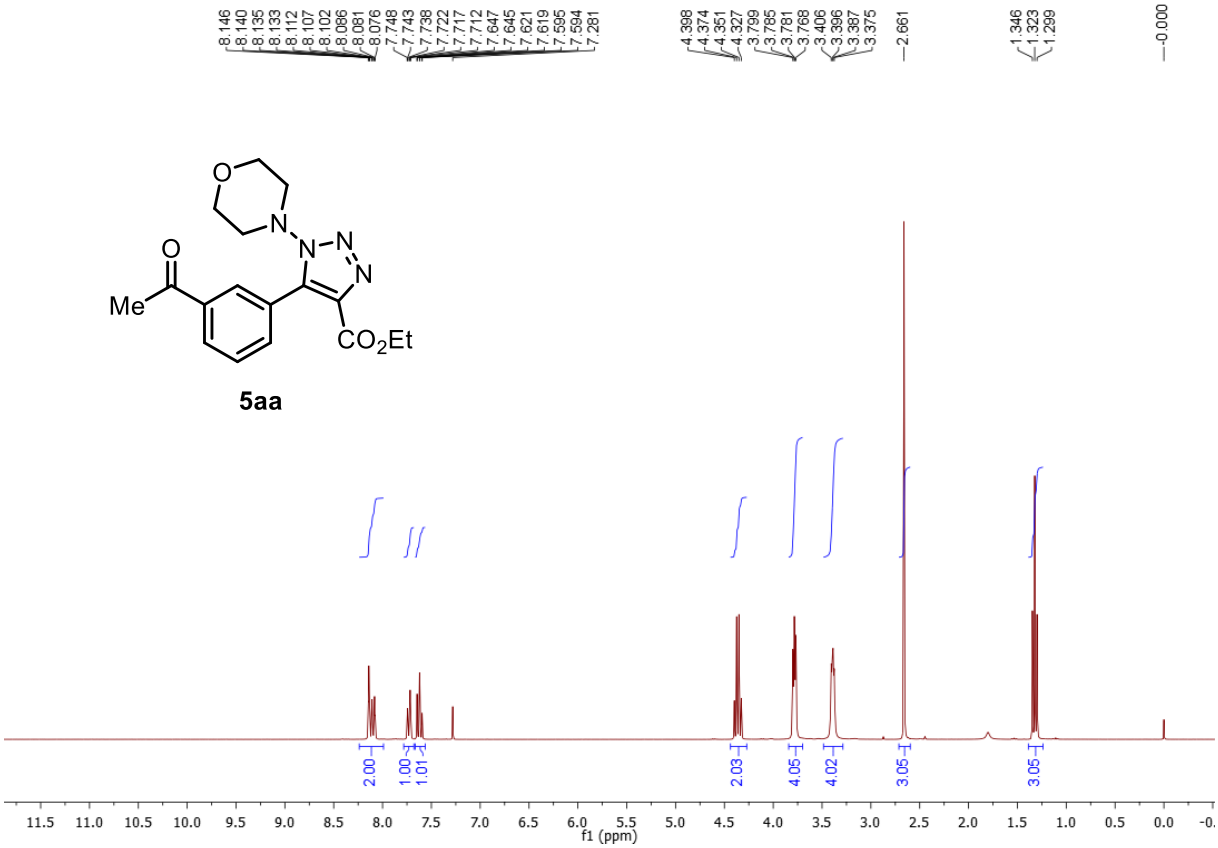
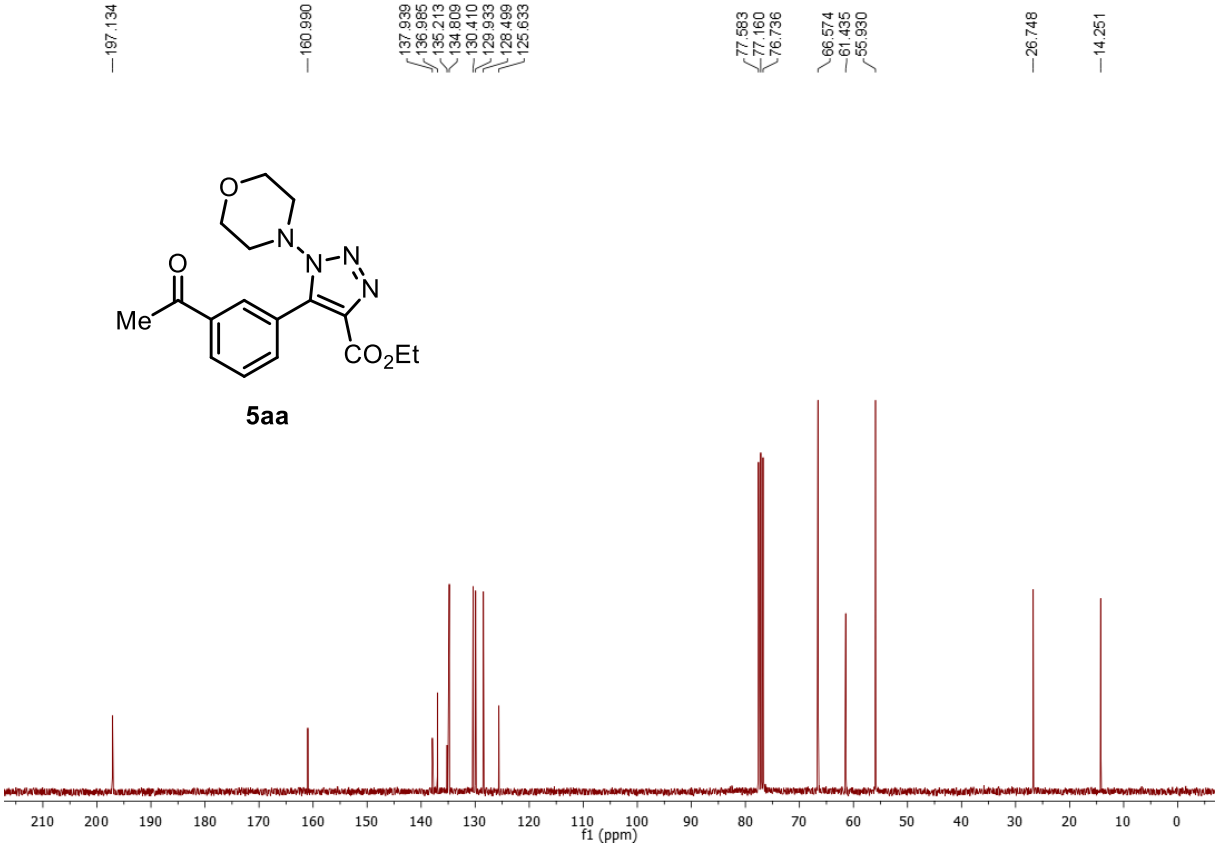


^{1}H NMR (300 MHz, $CDCl_3$)



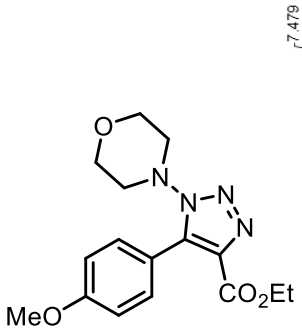
5aa

^{13}C NMR (75 MHz, $CDCl_3$)



5aa

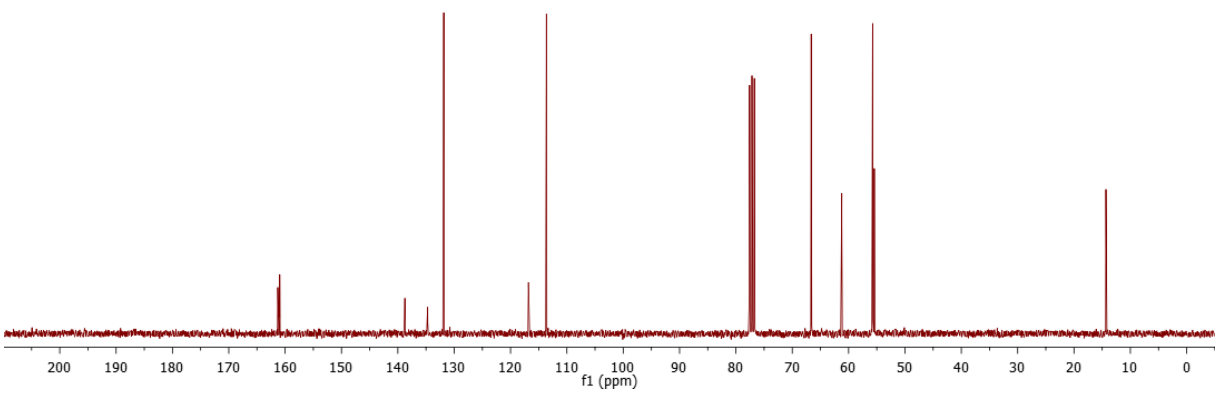
^{1}H NMR (300 MHz, $CDCl_3$)



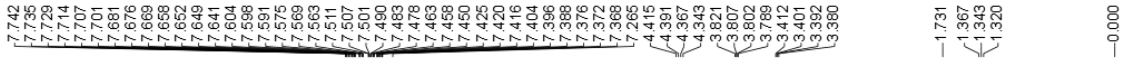
5ab

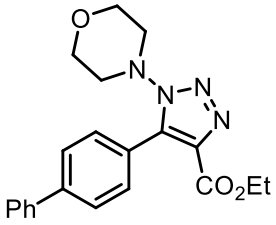
^{13}C NMR (75 MHz, $CDCl_3$)

5ab



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





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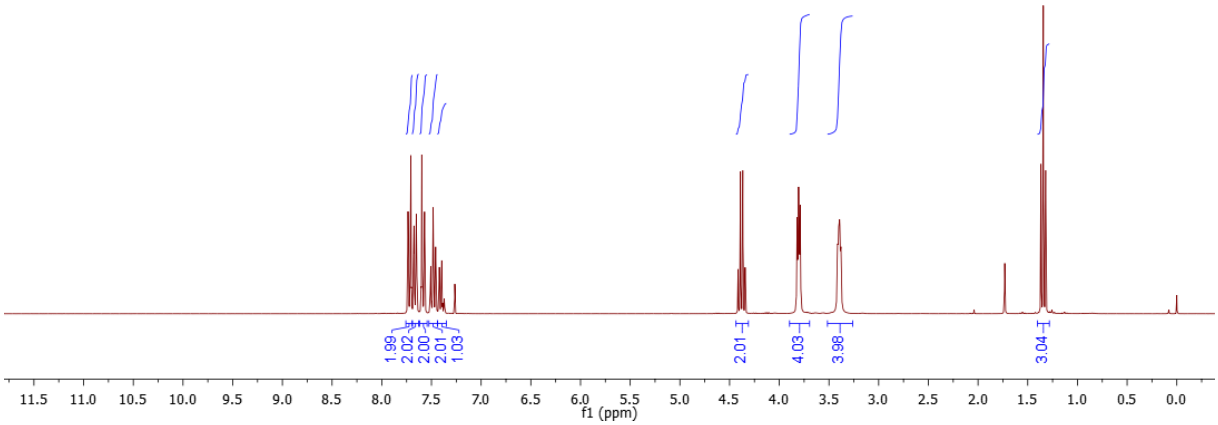
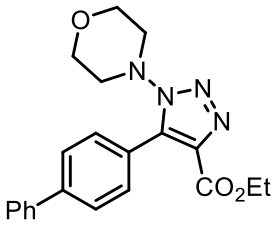


^{13}C NMR (75 MHz, $CDCl_3$)



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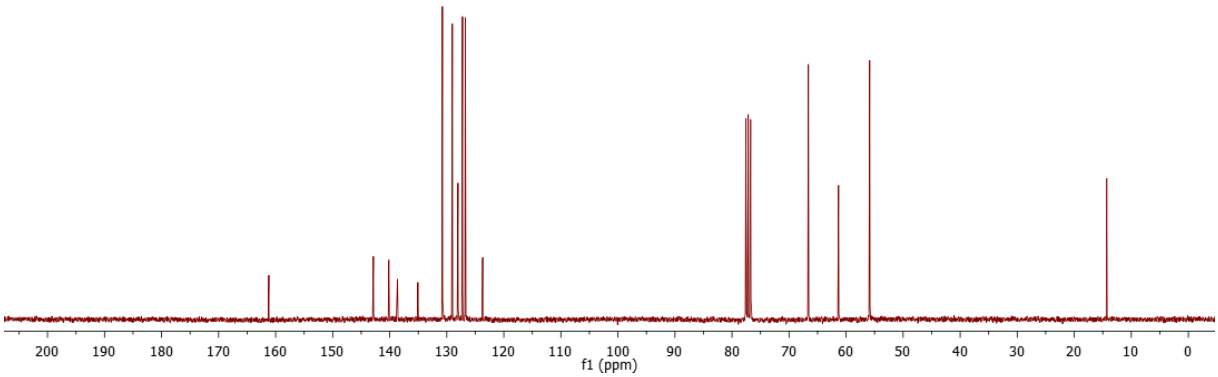
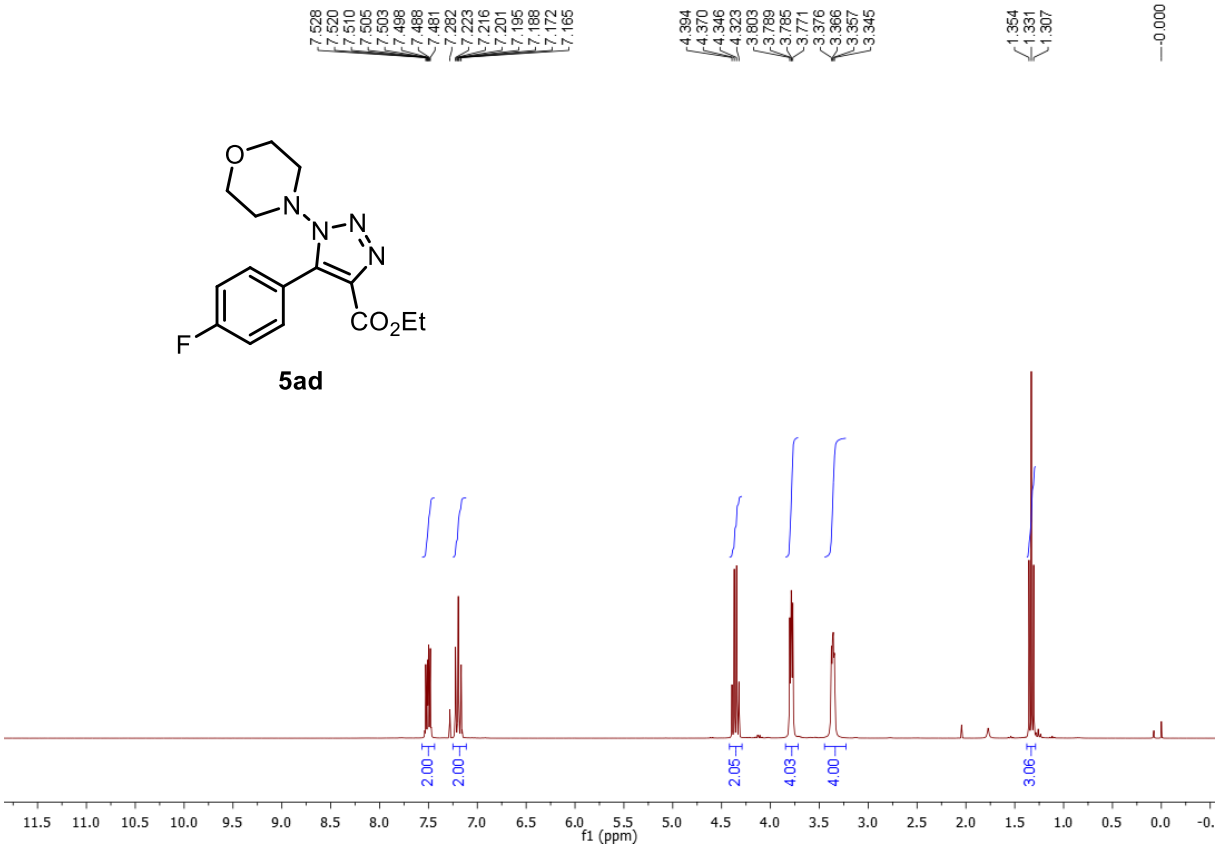
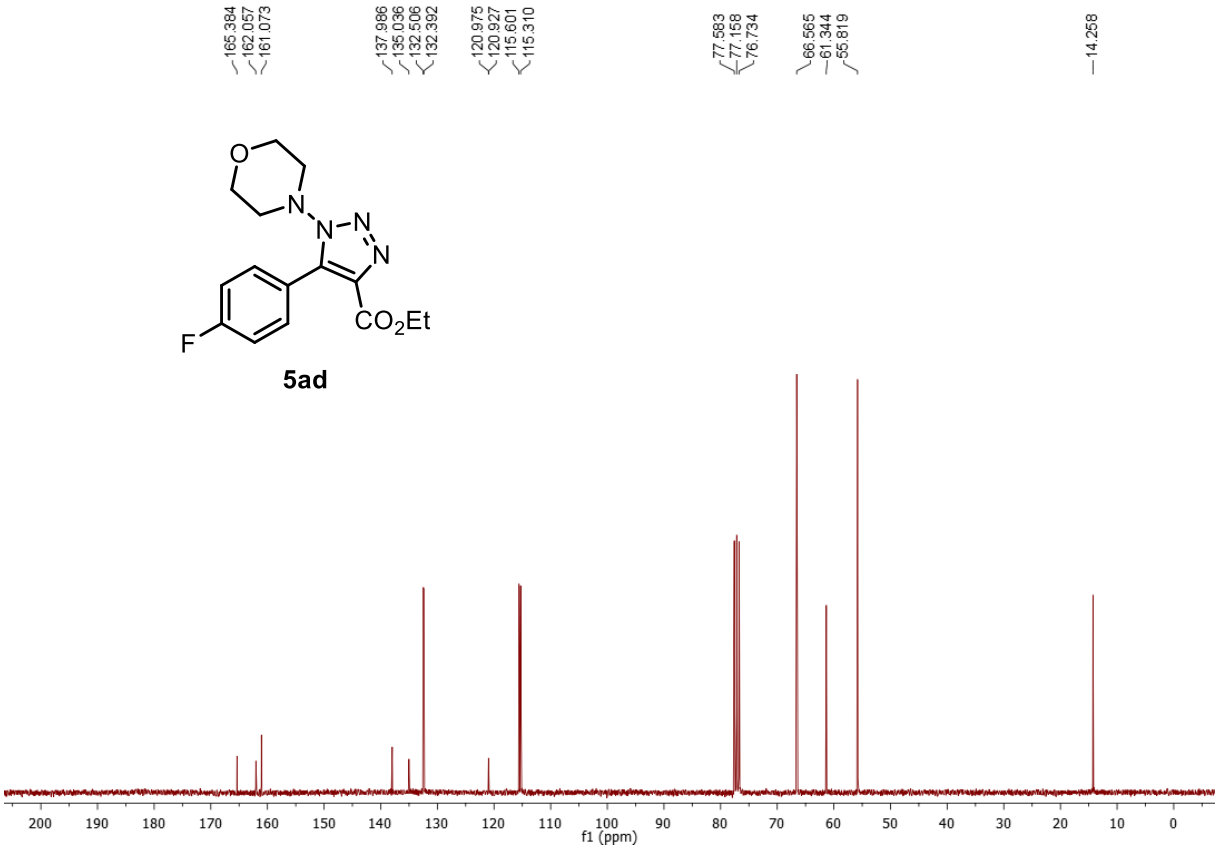


^{1}H NMR (300 MHz, $CDCl_3$)



5ad

^{13}C NMR (75 MHz, $CDCl_3$)



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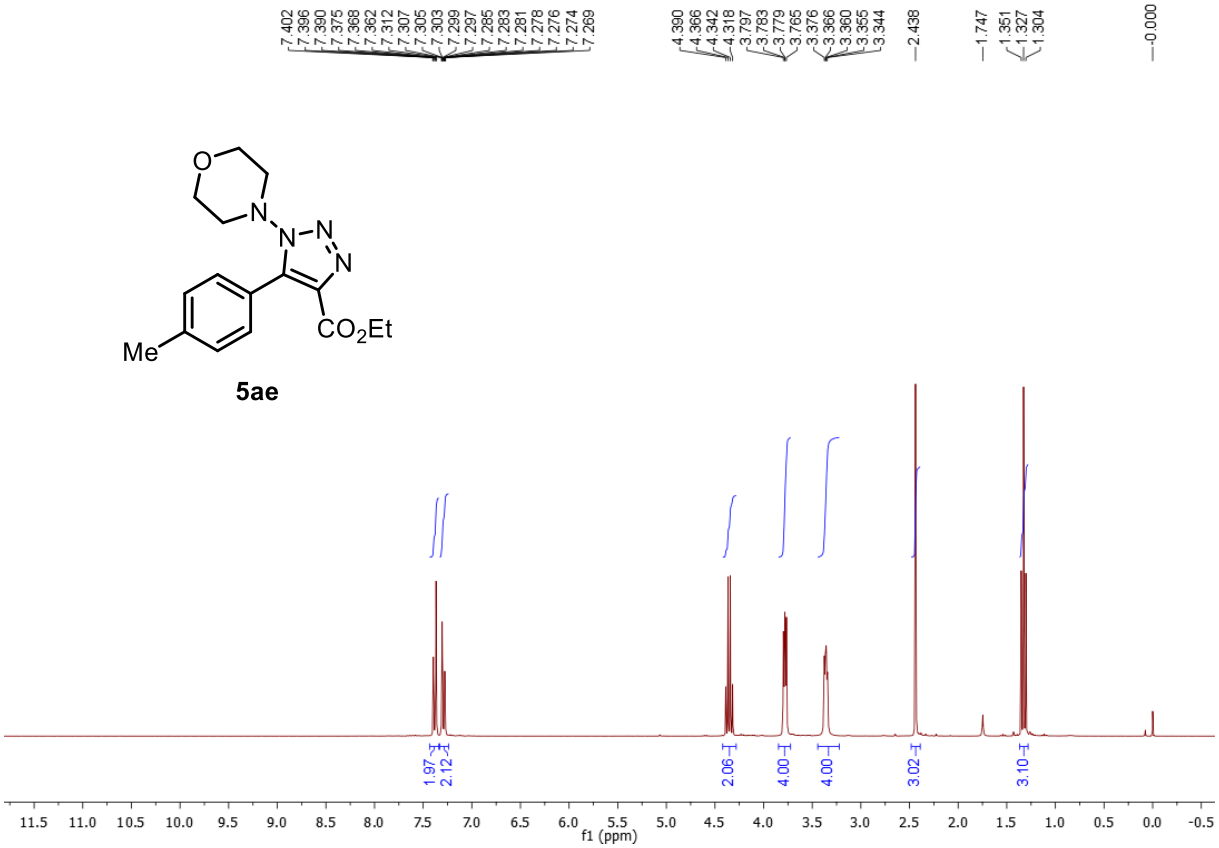

5ae

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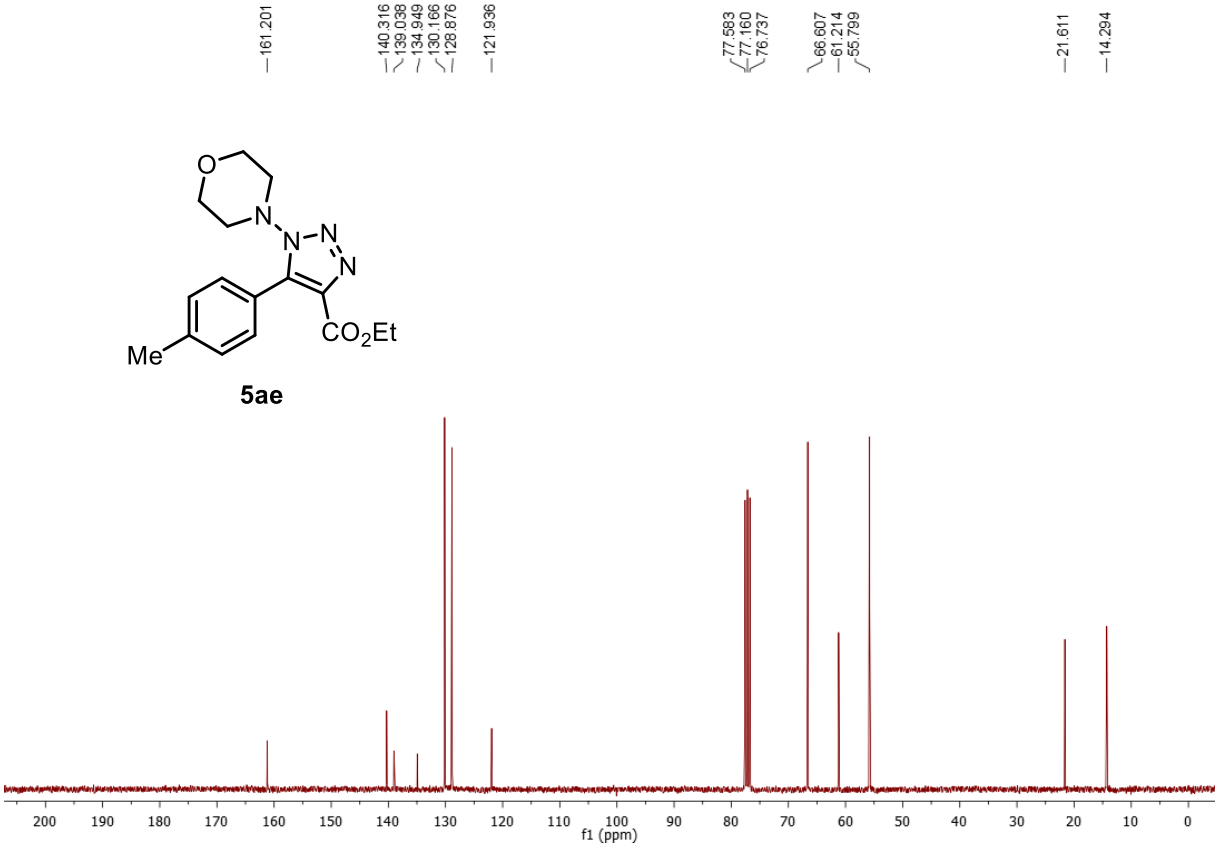

5ae

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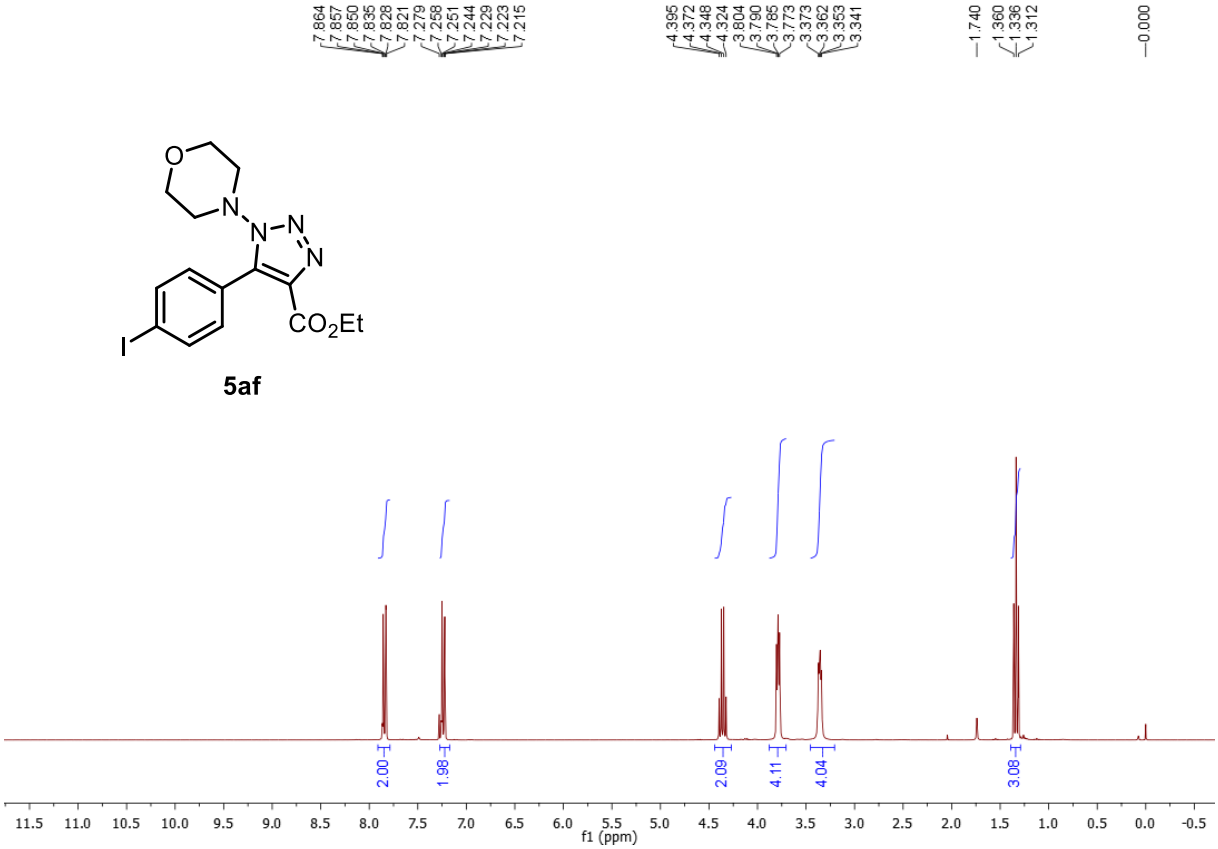
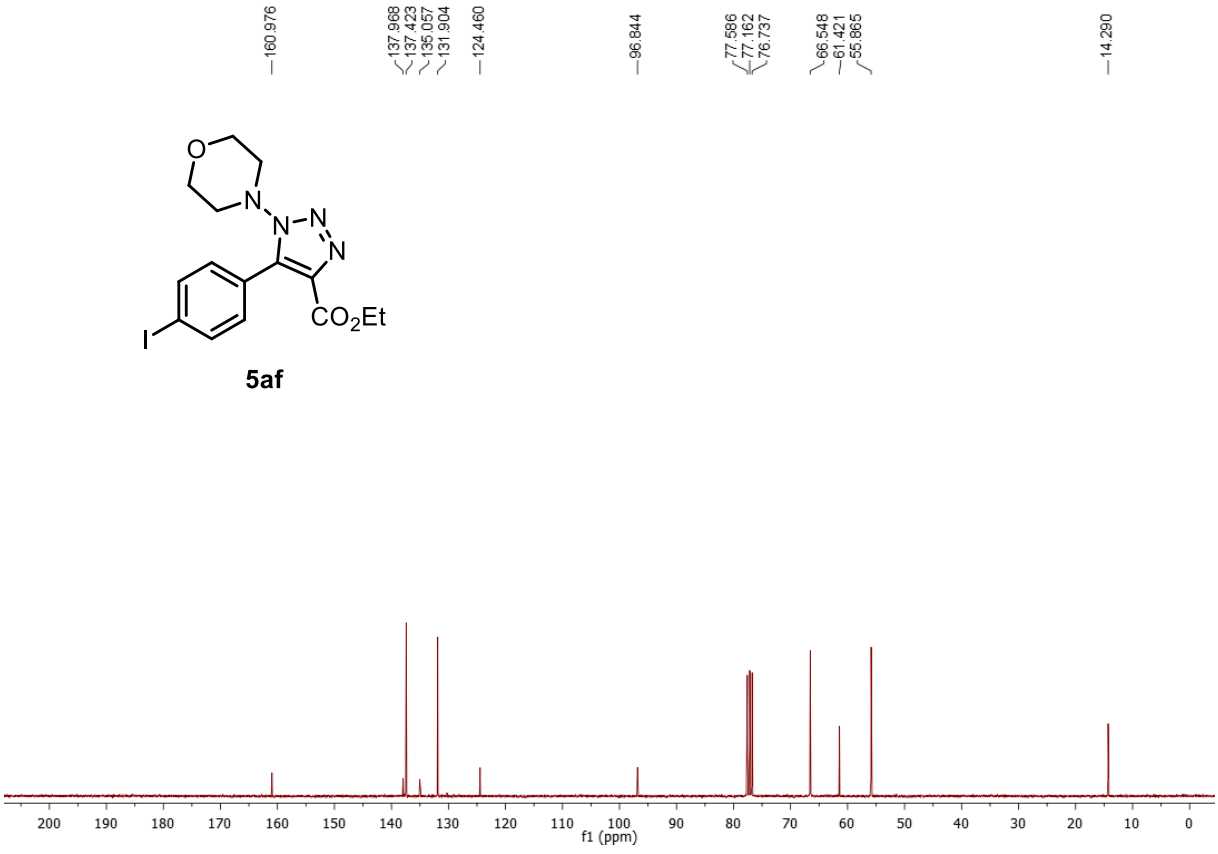


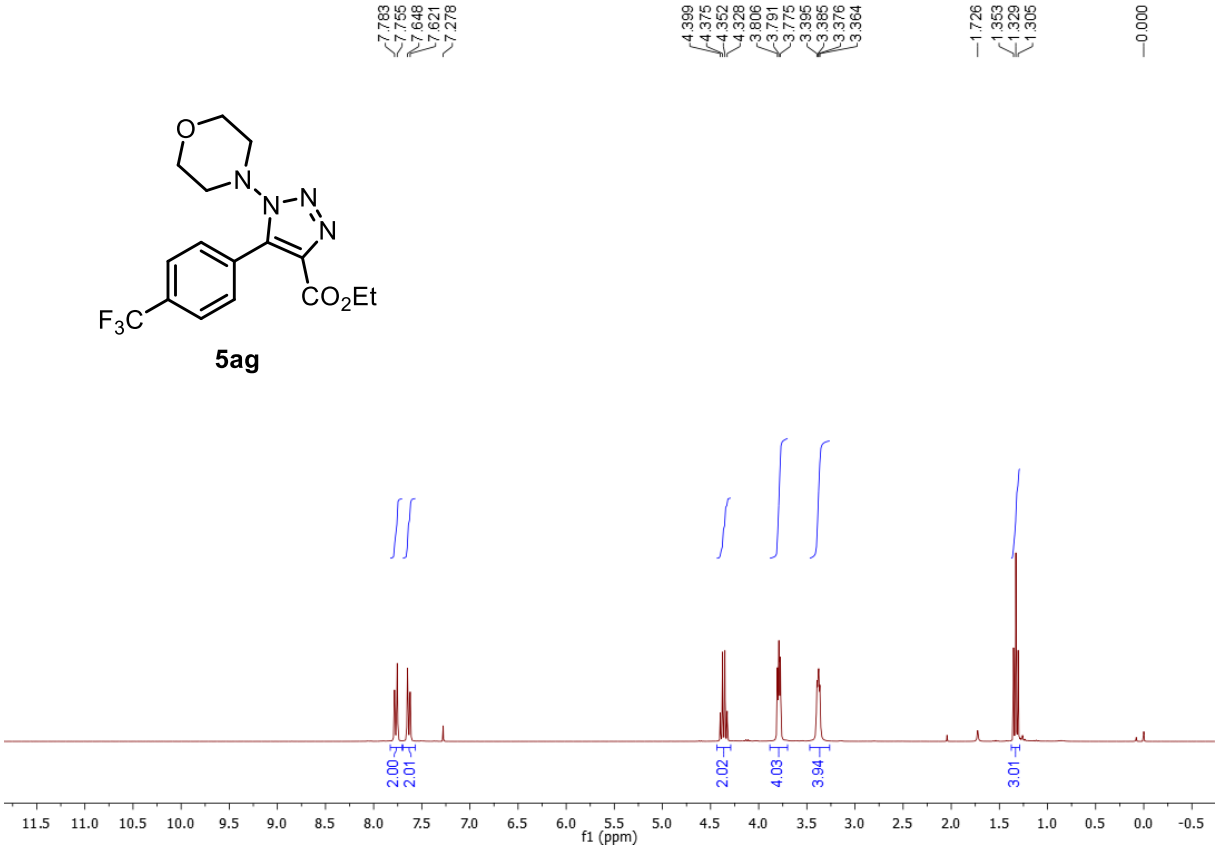
5af

^{13}C NMR (75 MHz, $CDCl_3$)



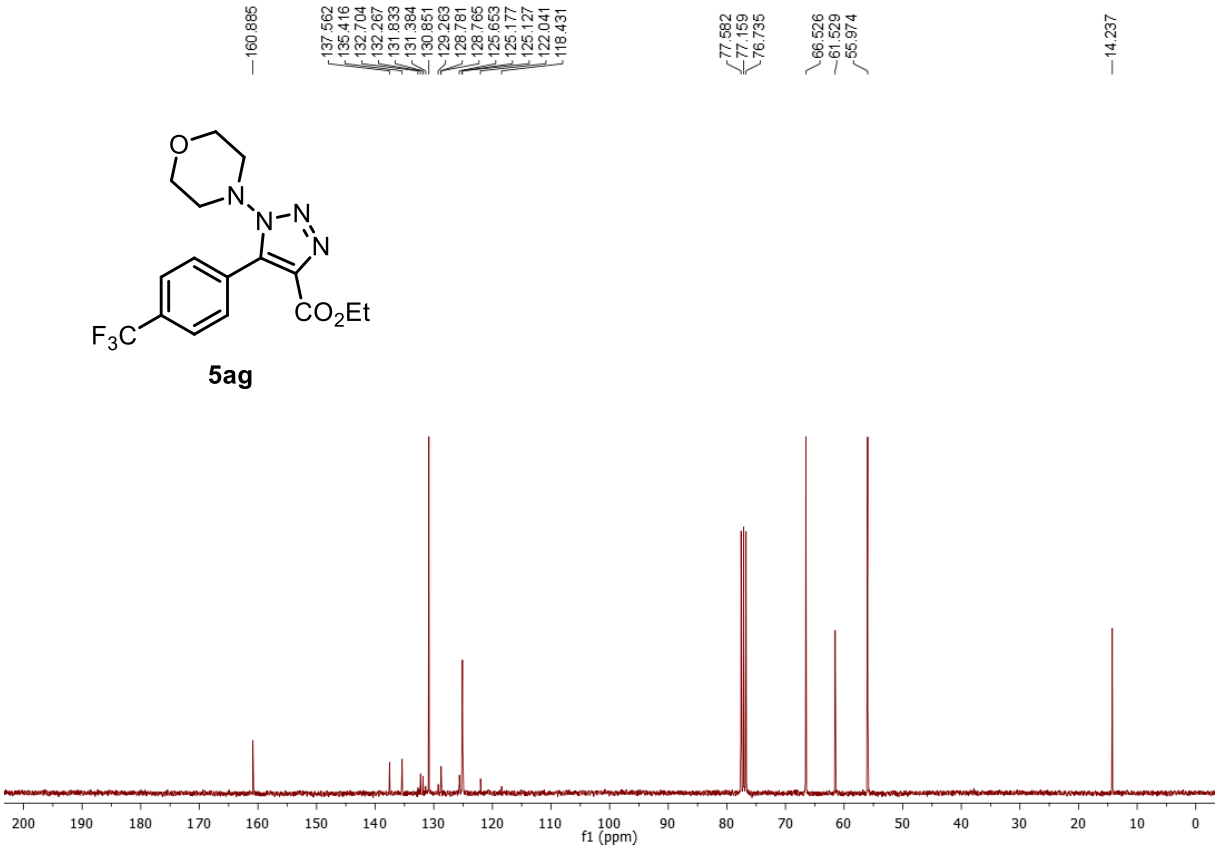
5af

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



5ag

^{13}C NMR (75 MHz, $CDCl_3$)



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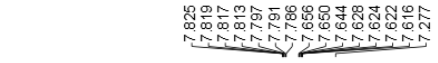
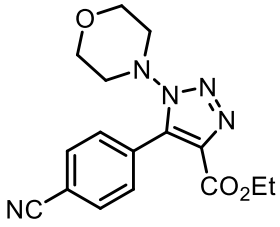
^{1}H NMR (300 MHz, $CDCl_3$)





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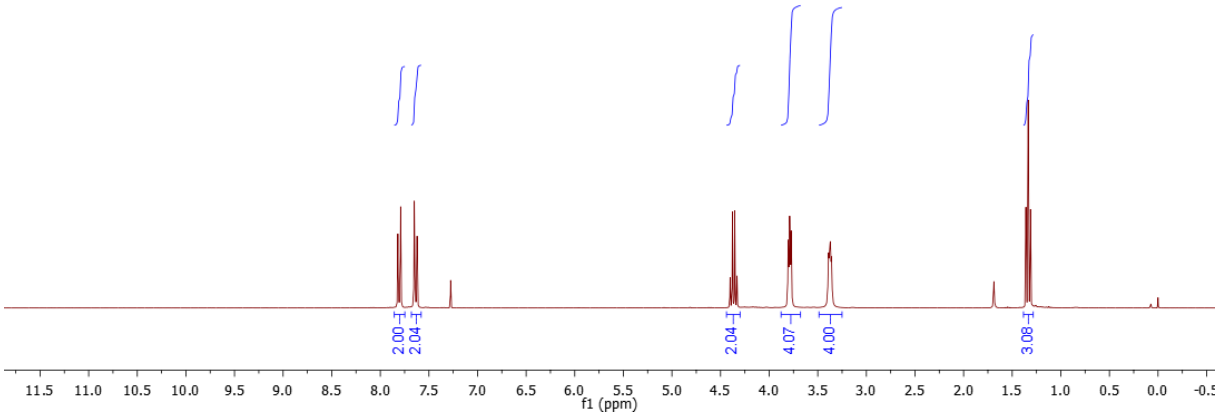
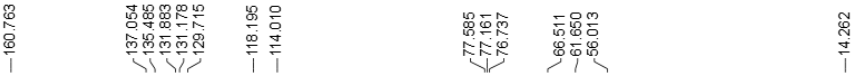
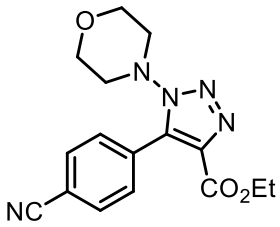


^{13}C NMR (75 MHz, $CDCl_3$)





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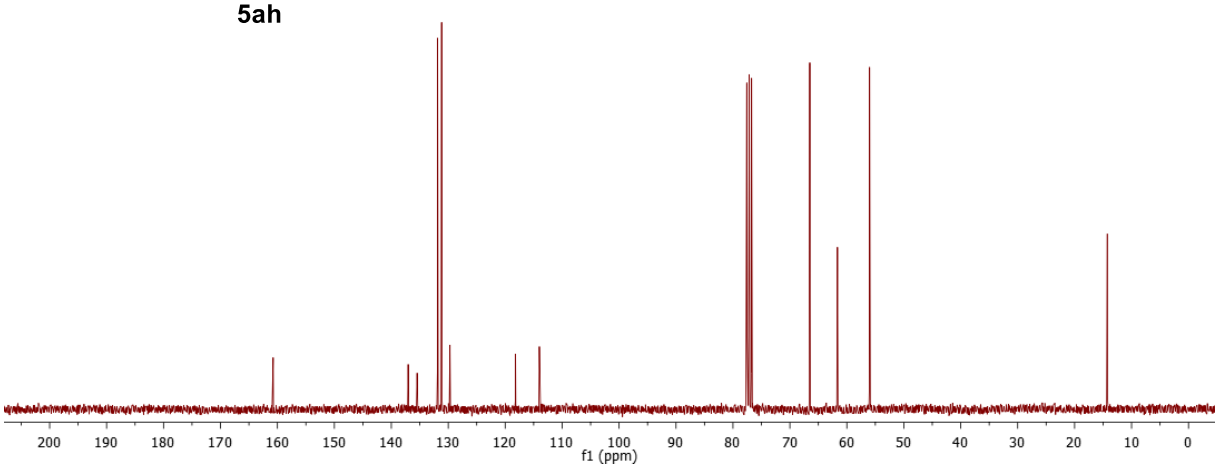
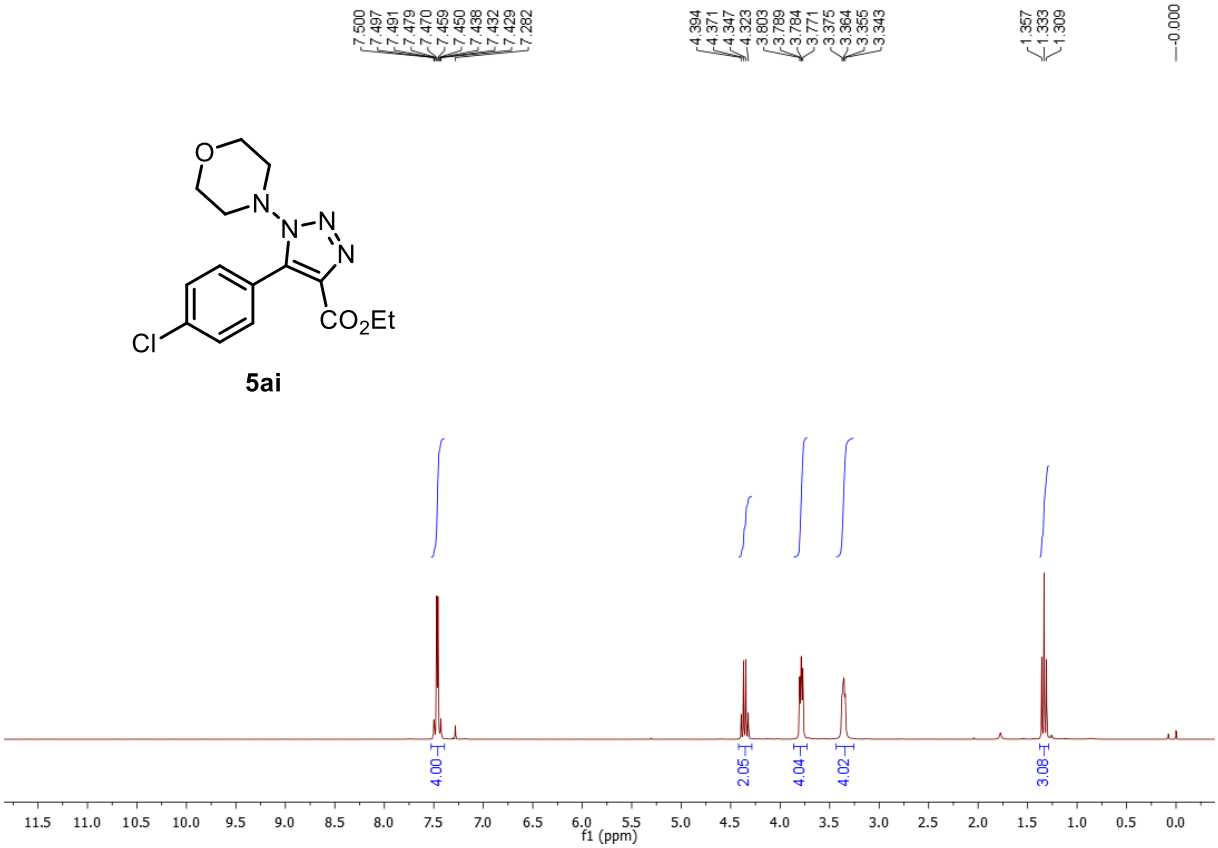
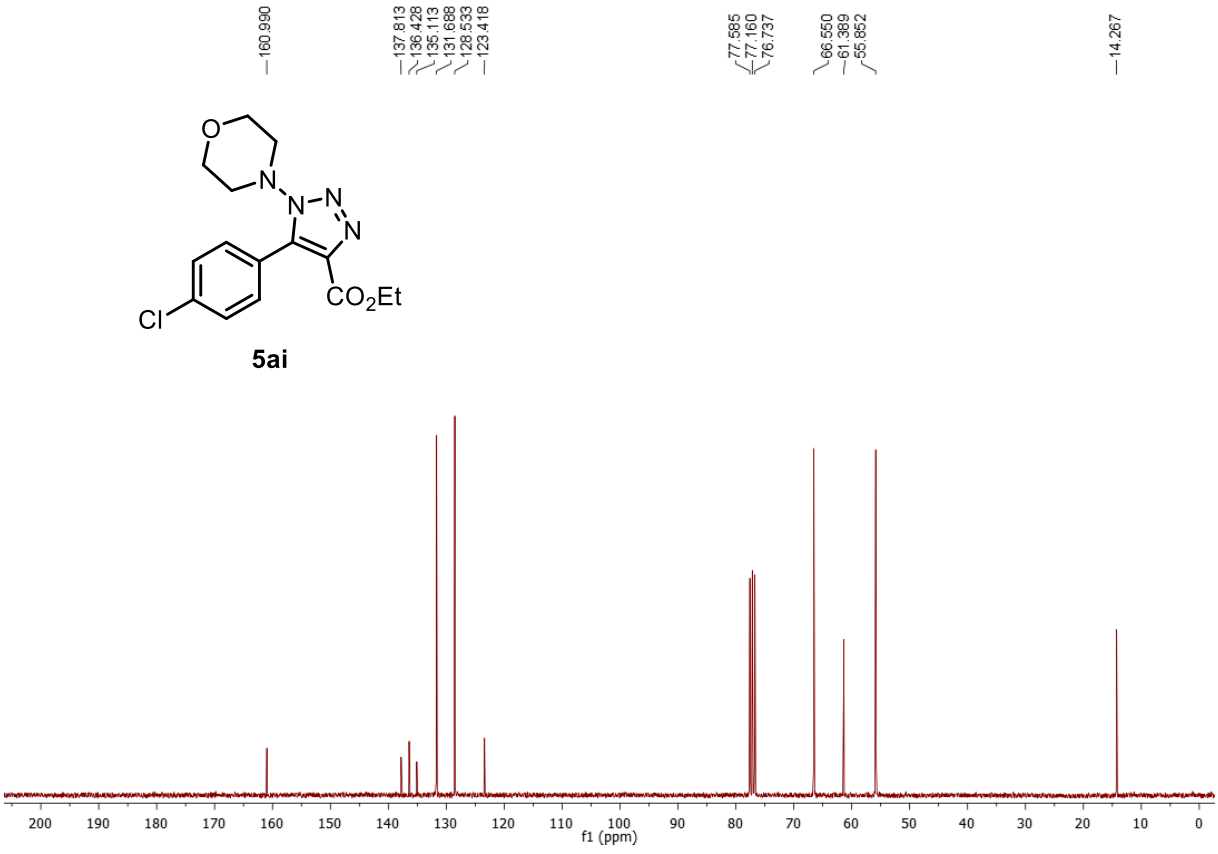


^{1}H NMR (300 MHz, $CDCl_3$)



5ai

^{13}C NMR (75 MHz, $CDCl_3$)



5ai

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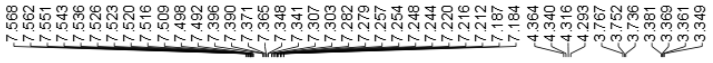

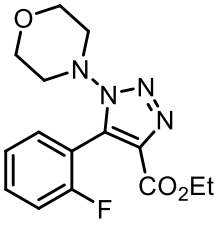

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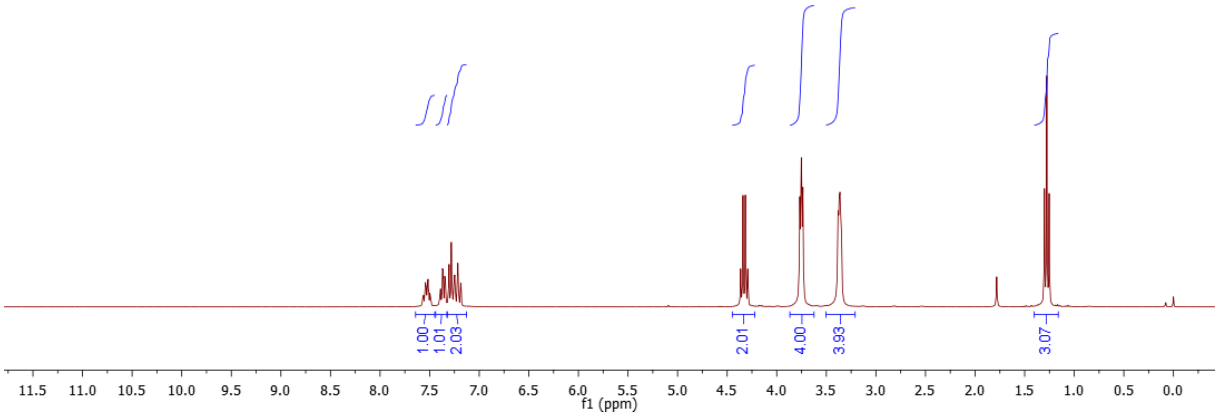
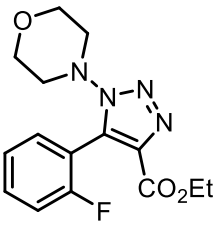


^{13}C NMR (75 MHz, $CDCl_3$)



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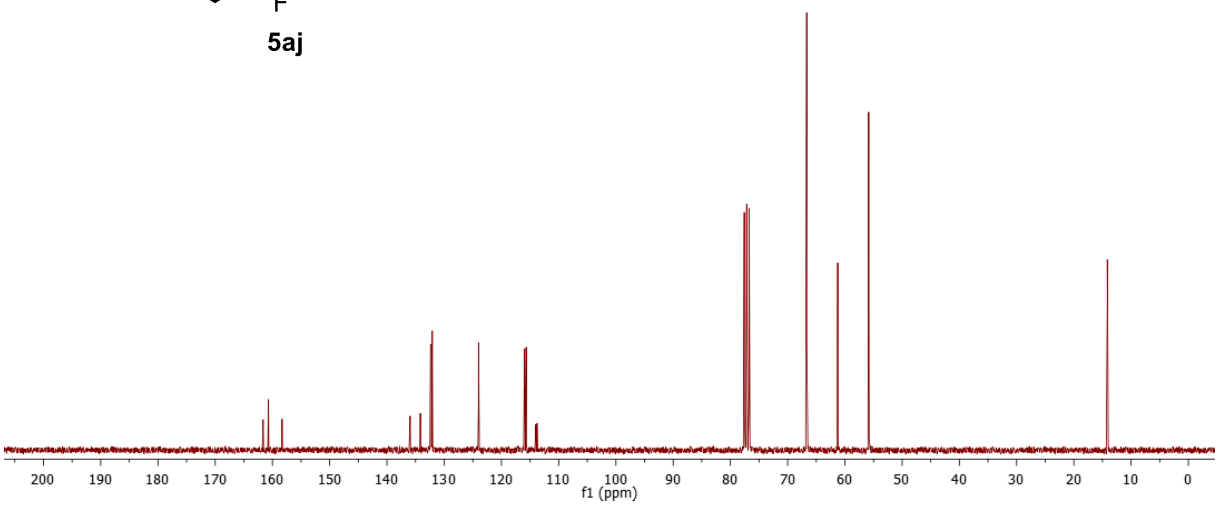
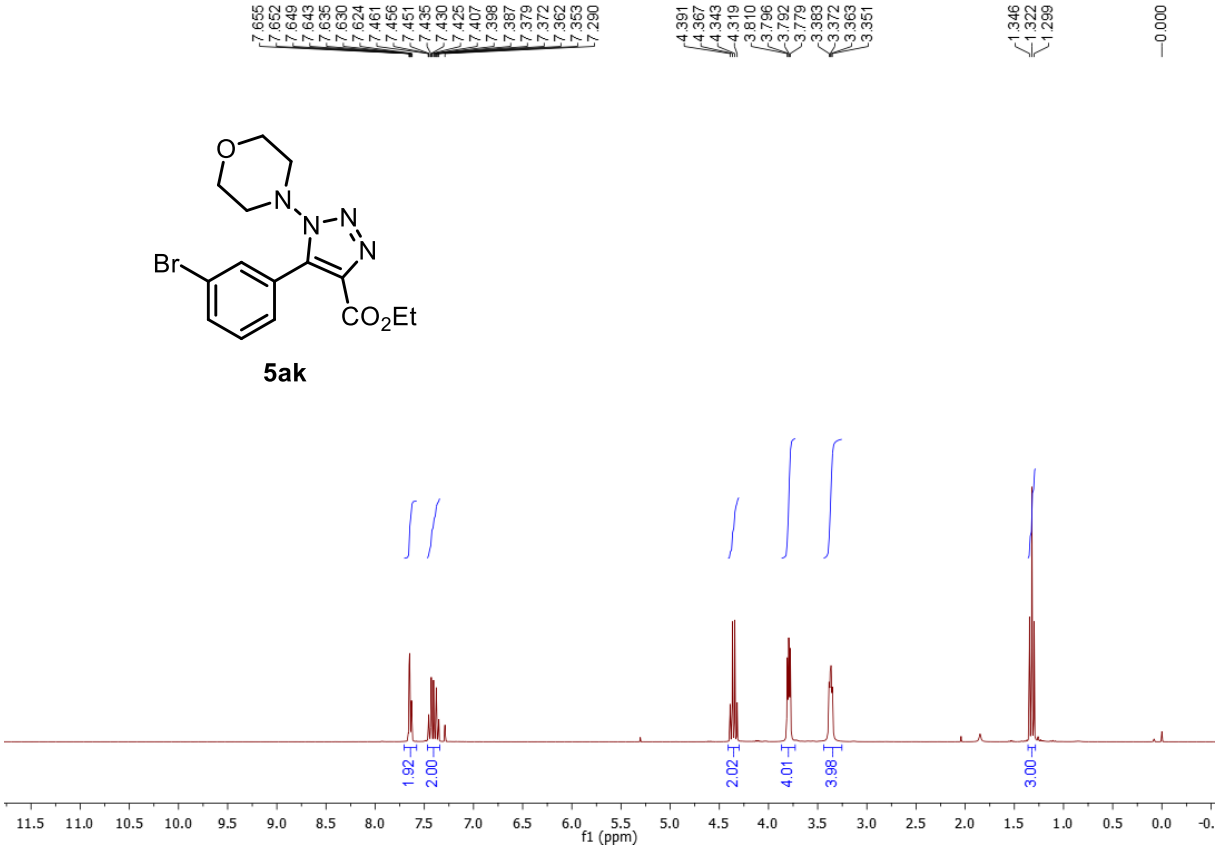
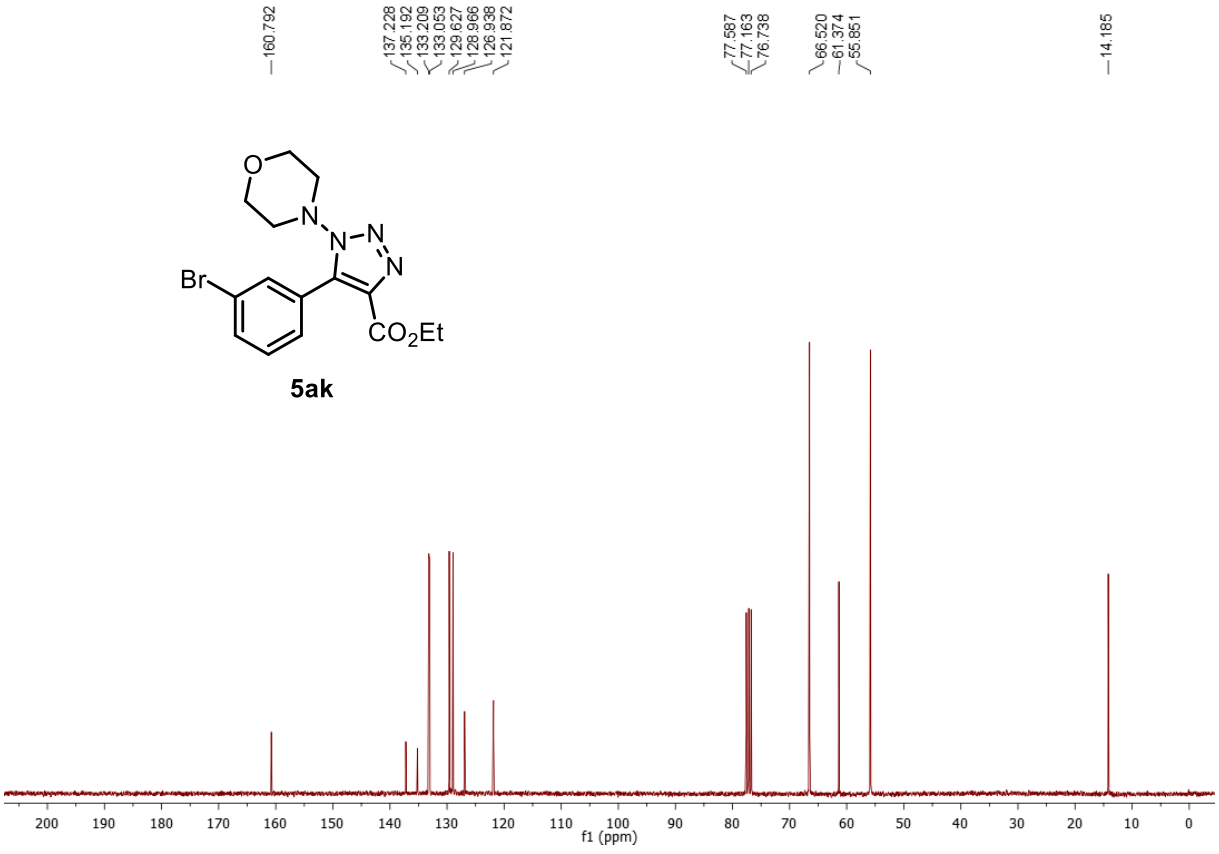


^{1}H NMR (300 MHz, $CDCl_3$)



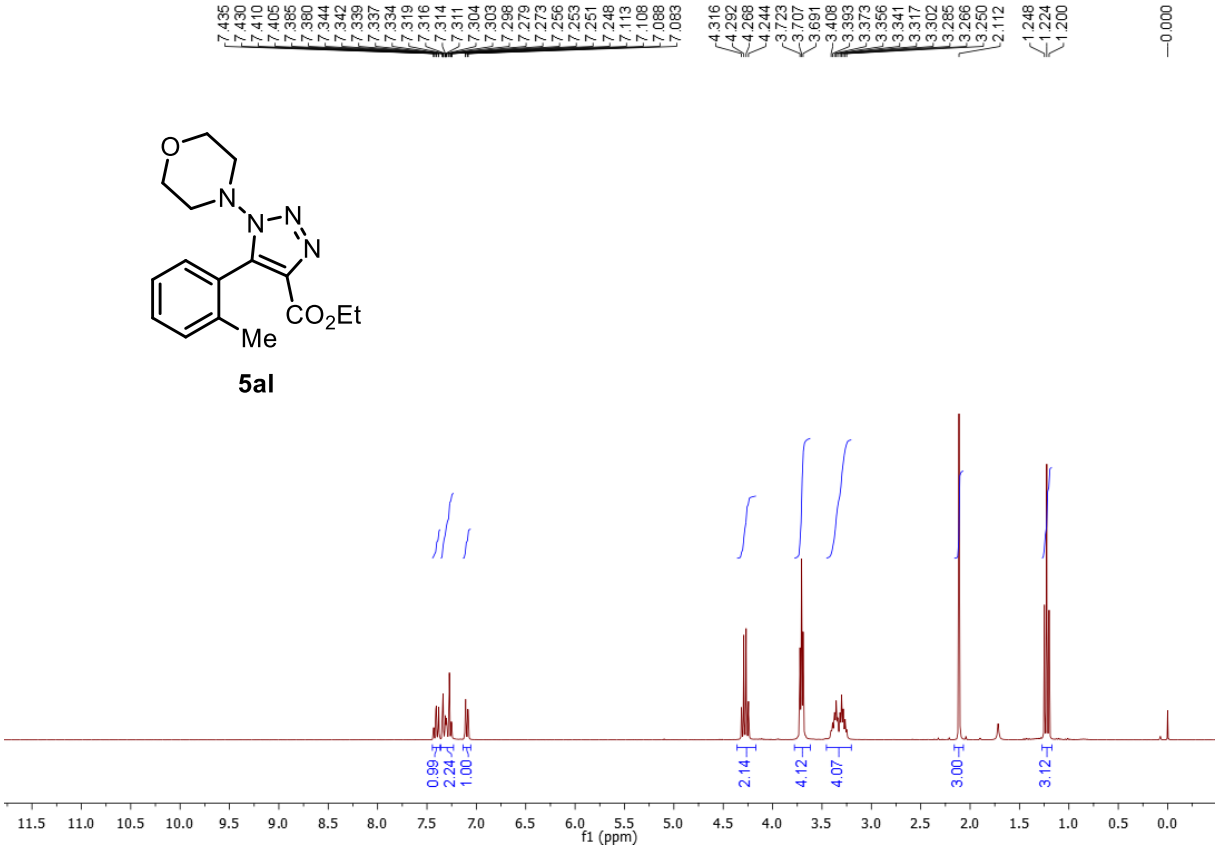
5ak

^{13}C NMR (75 MHz, $CDCl_3$)



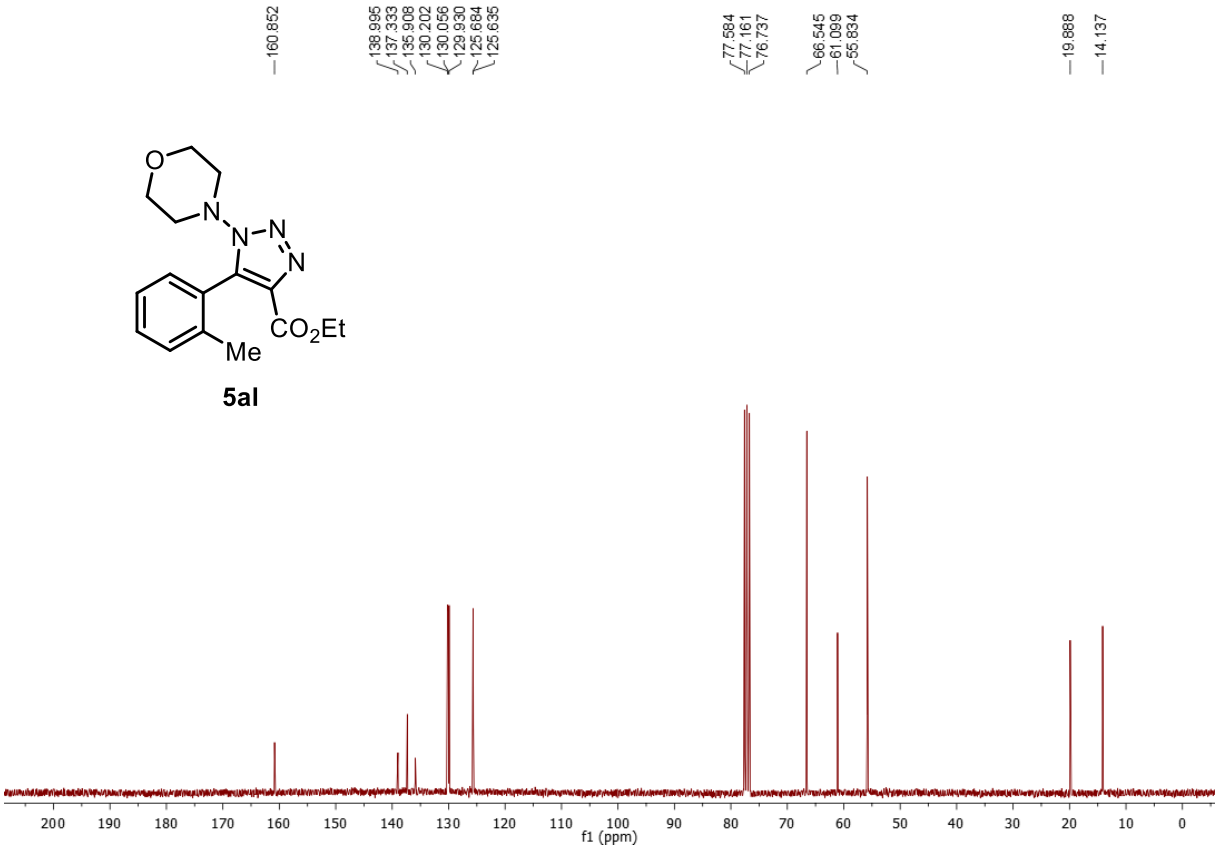
5ak

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



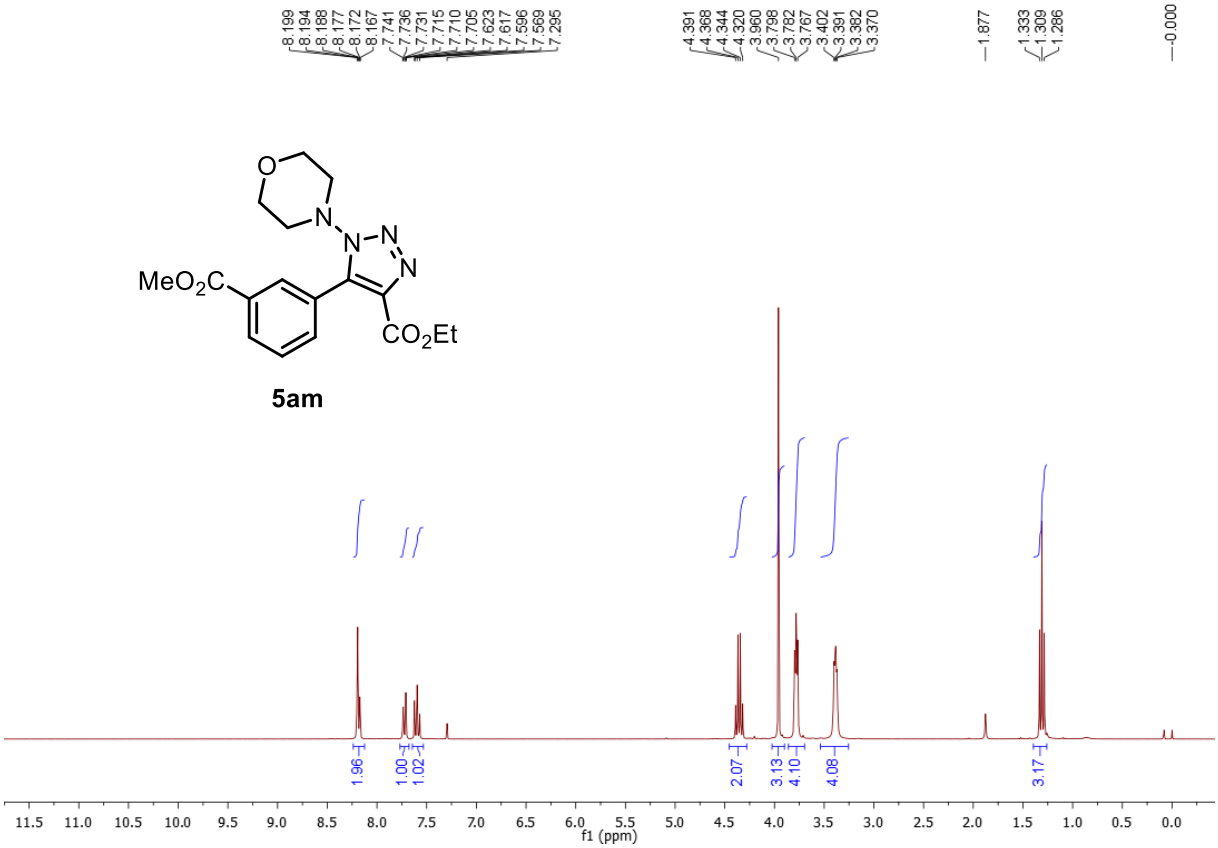
5aI

^{13}C NMR (75 MHz, $CDCl_3$)

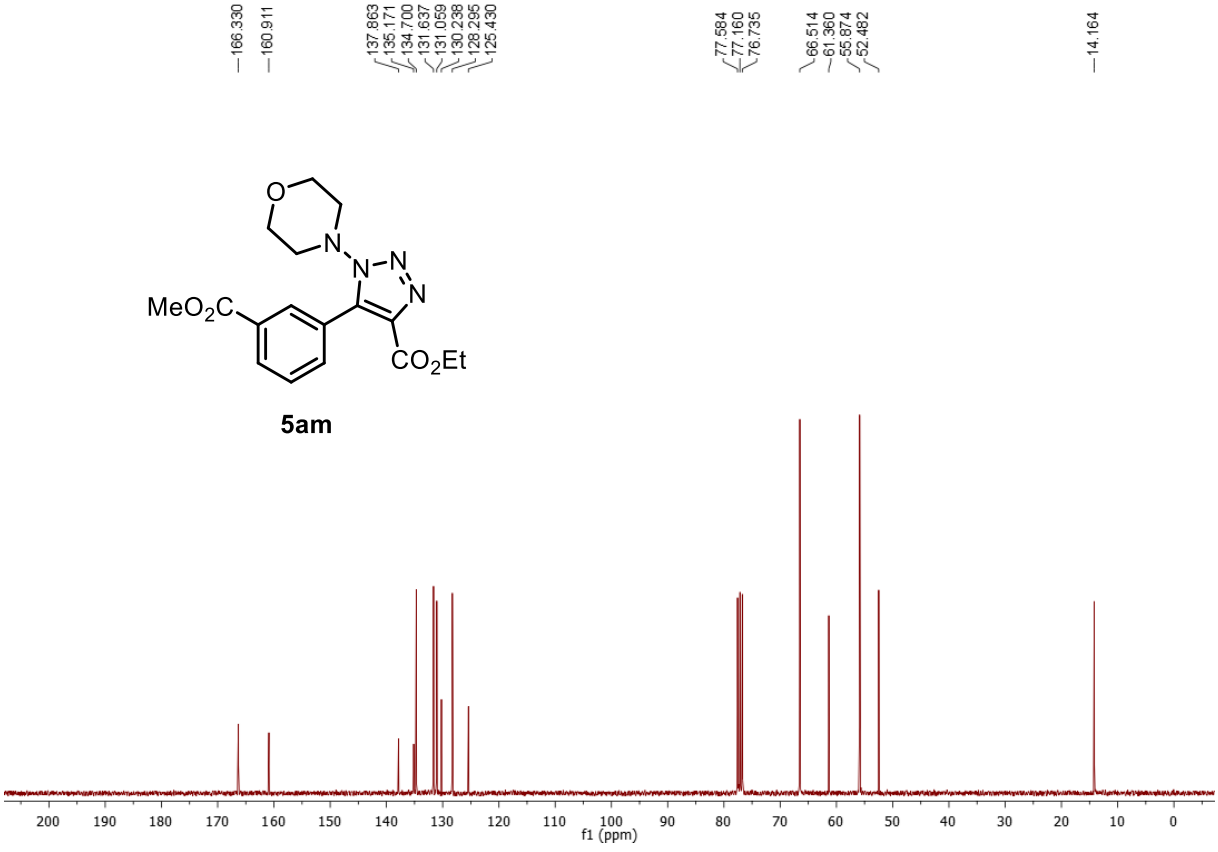


5aI

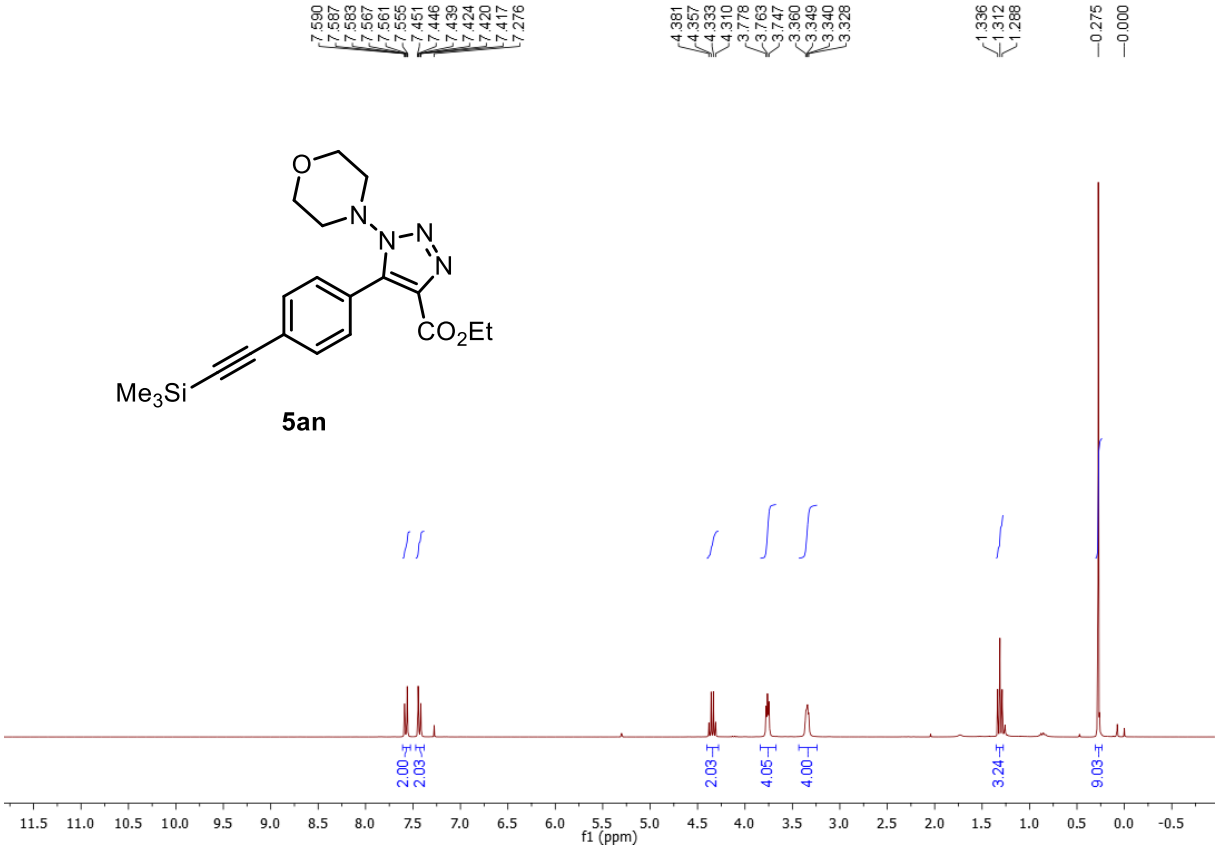
^{1}H NMR (300 MHz, $CDCl_3$)



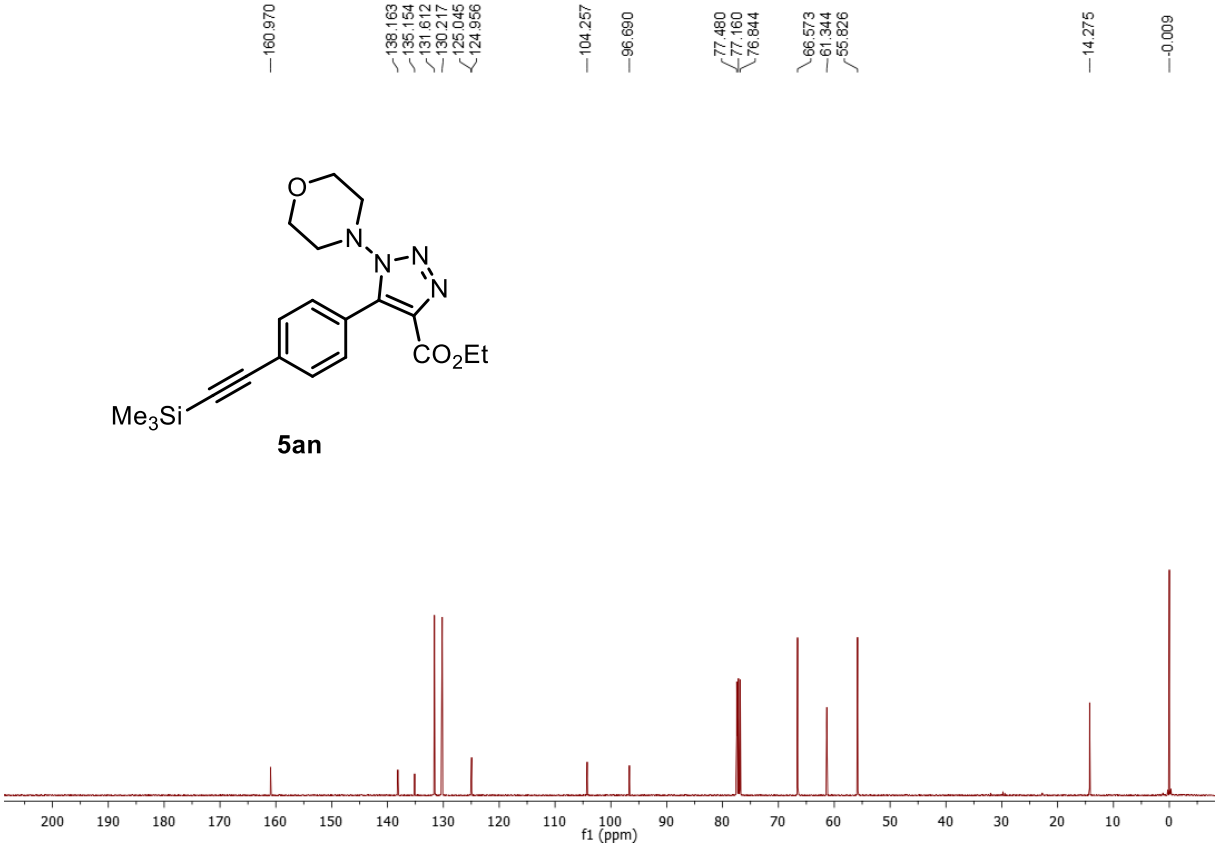
^{13}C NMR (75 MHz, $CDCl_3$)



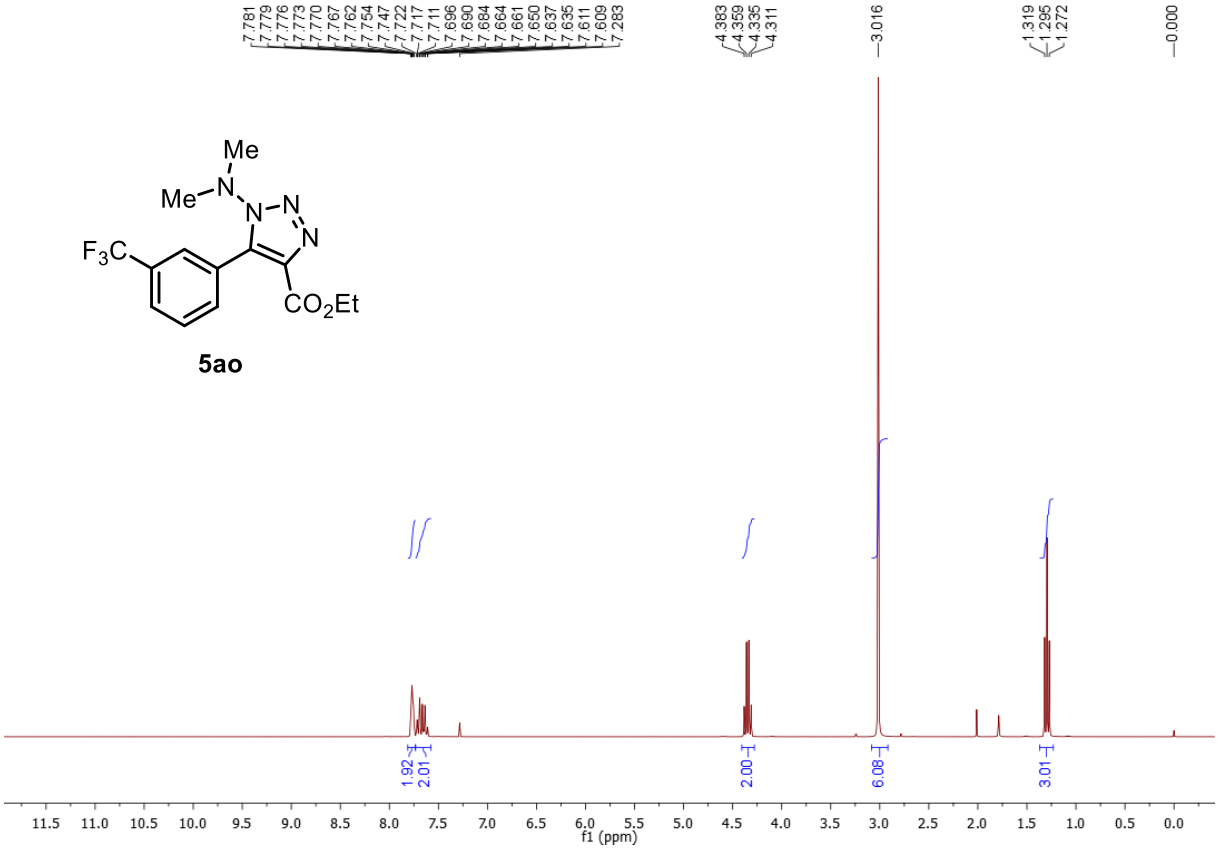
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

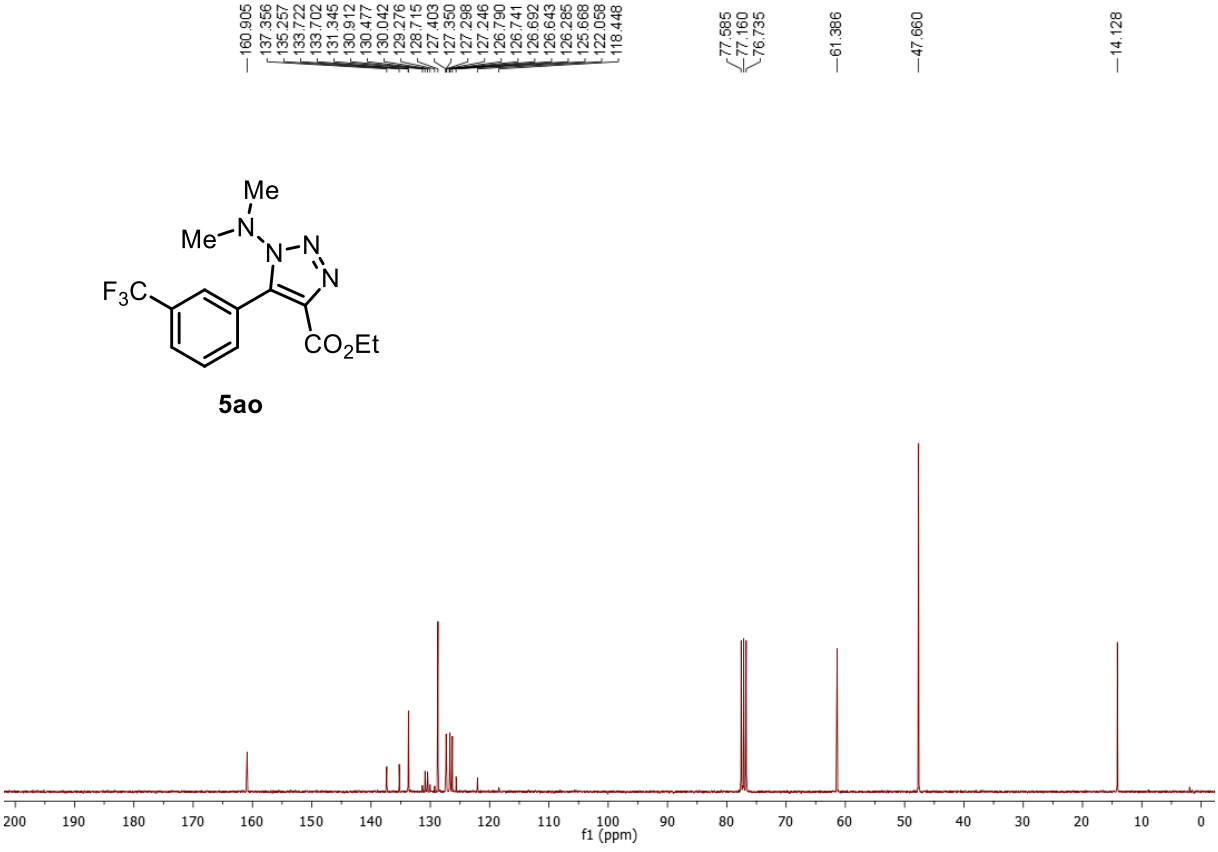


^{1}H NMR (300 MHz, $CDCl_3$)



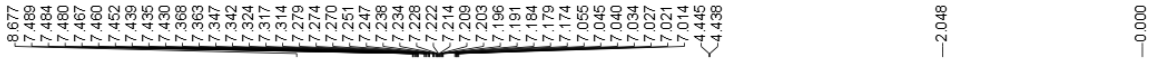
5ao

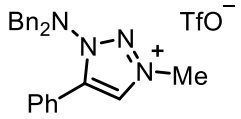
^{13}C NMR (75 MHz, $CDCl_3$)



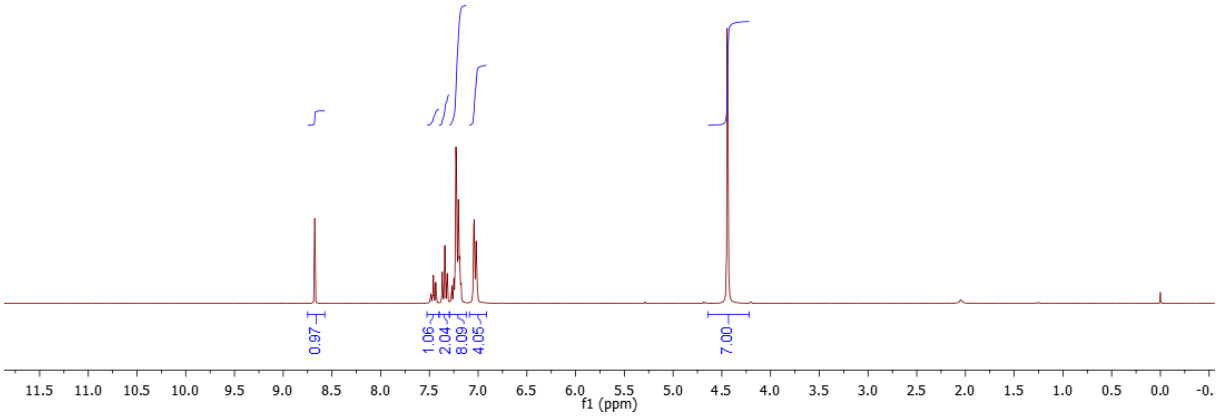
5ao

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

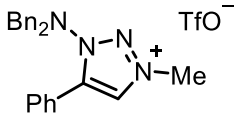




7a

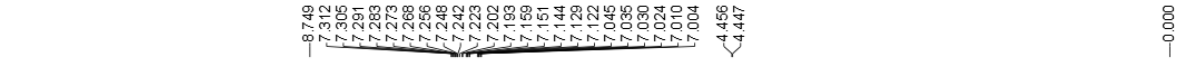


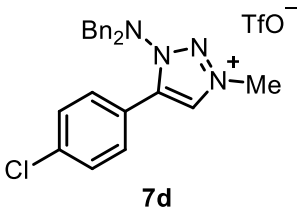
^{13}C NMR (75 MHz, $CDCl_3$)



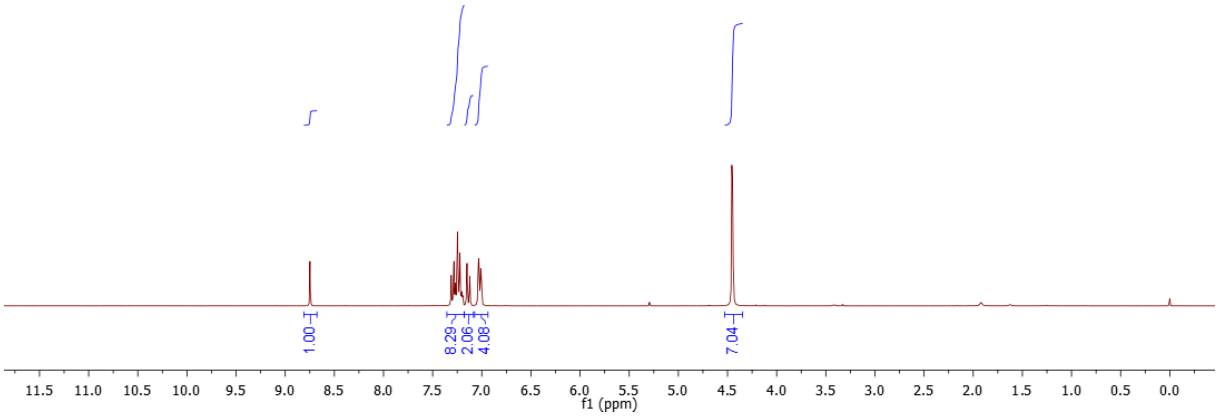
7a

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

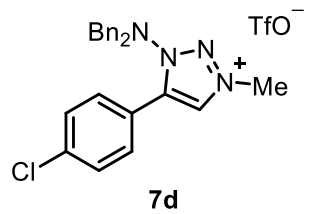




7d

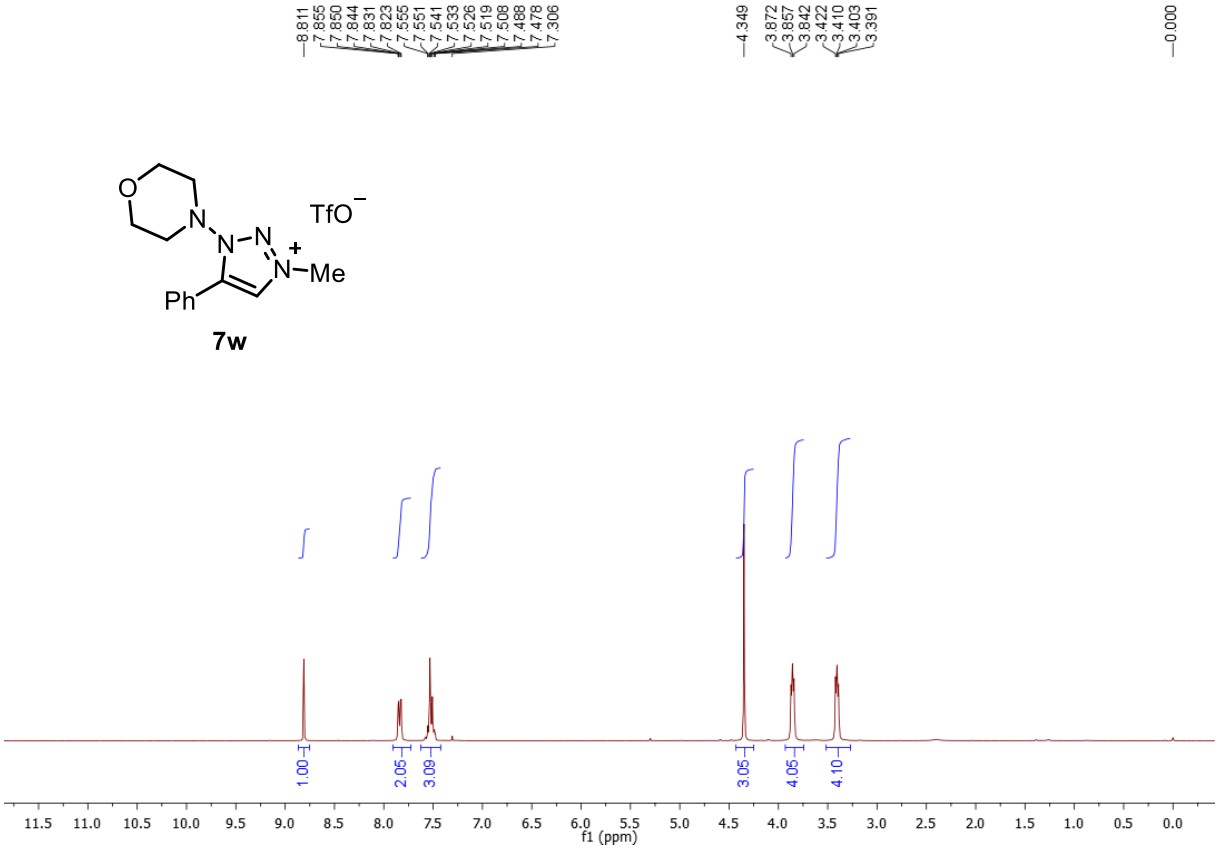


^{13}C NMR (75 MHz, $CDCl_3$)



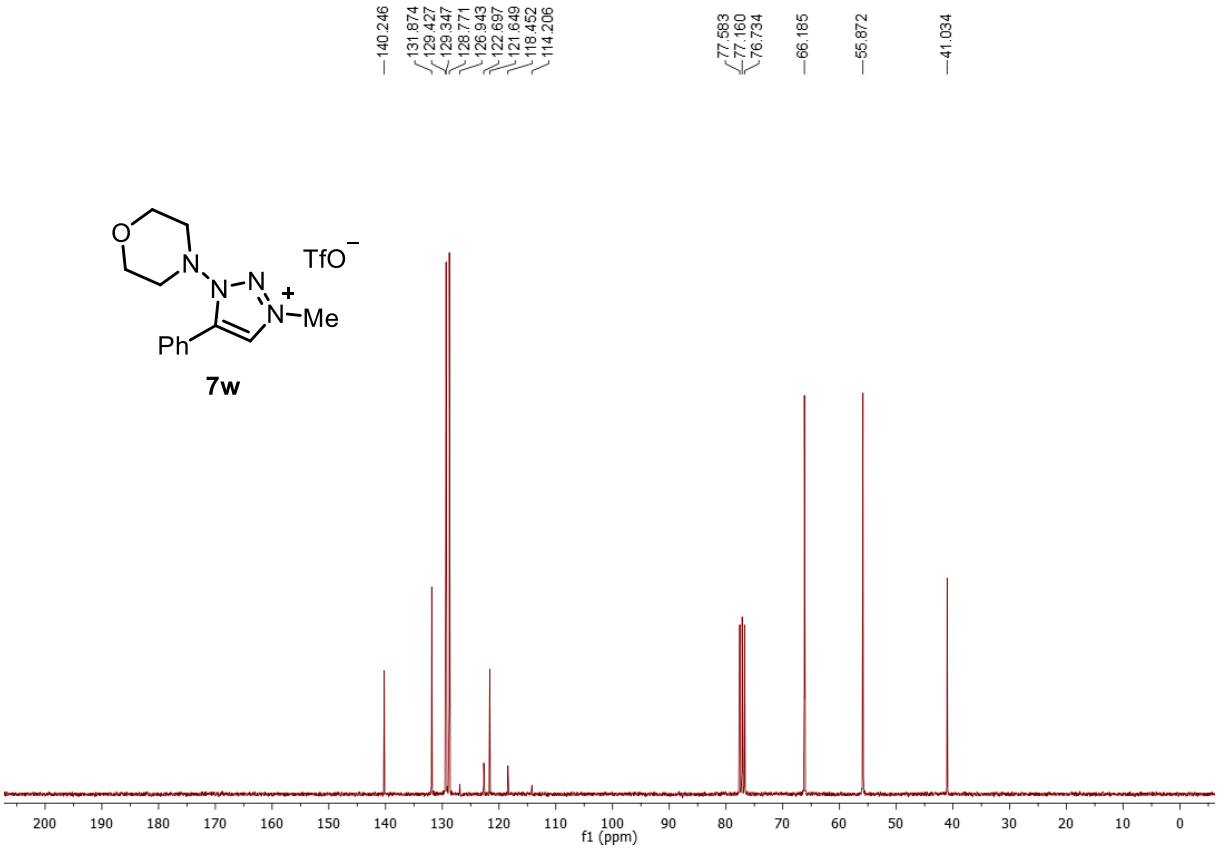
7d

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



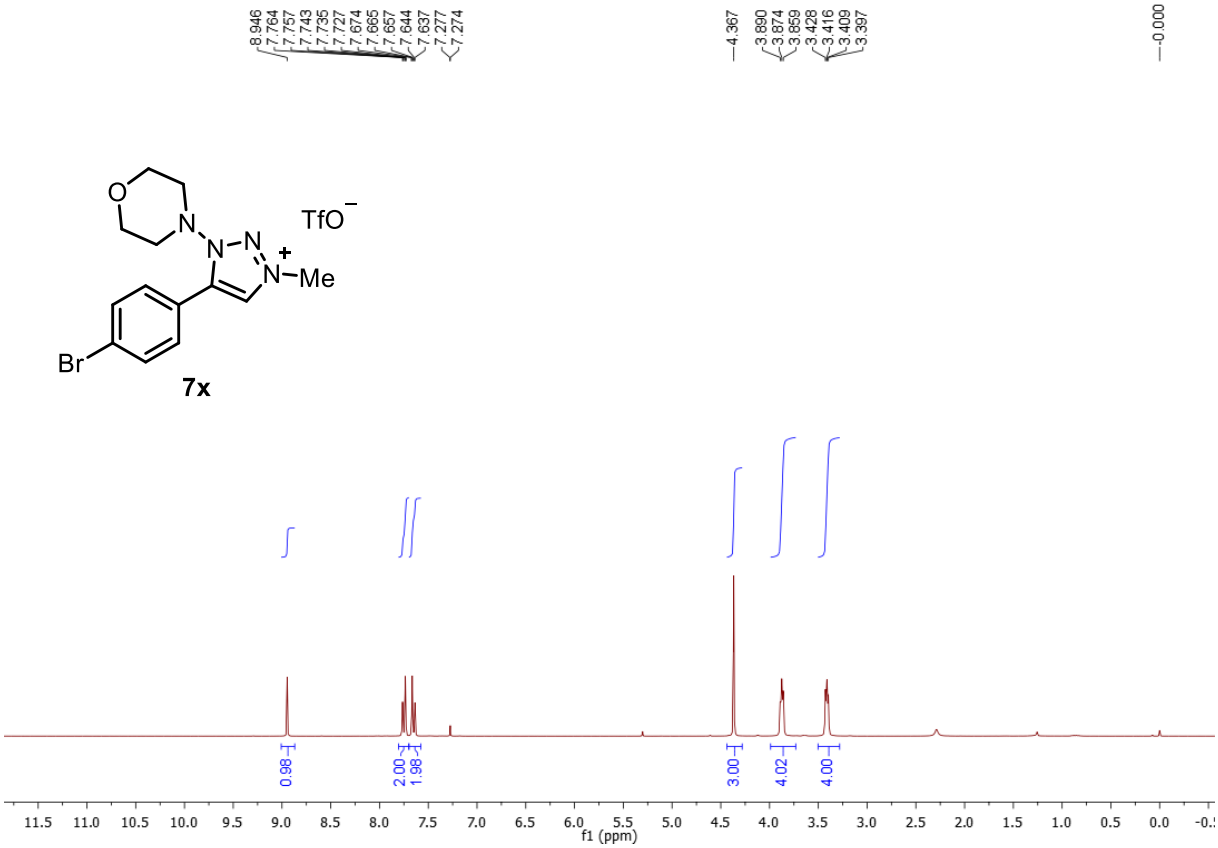
7w

^{13}C NMR (75 MHz, $CDCl_3$)

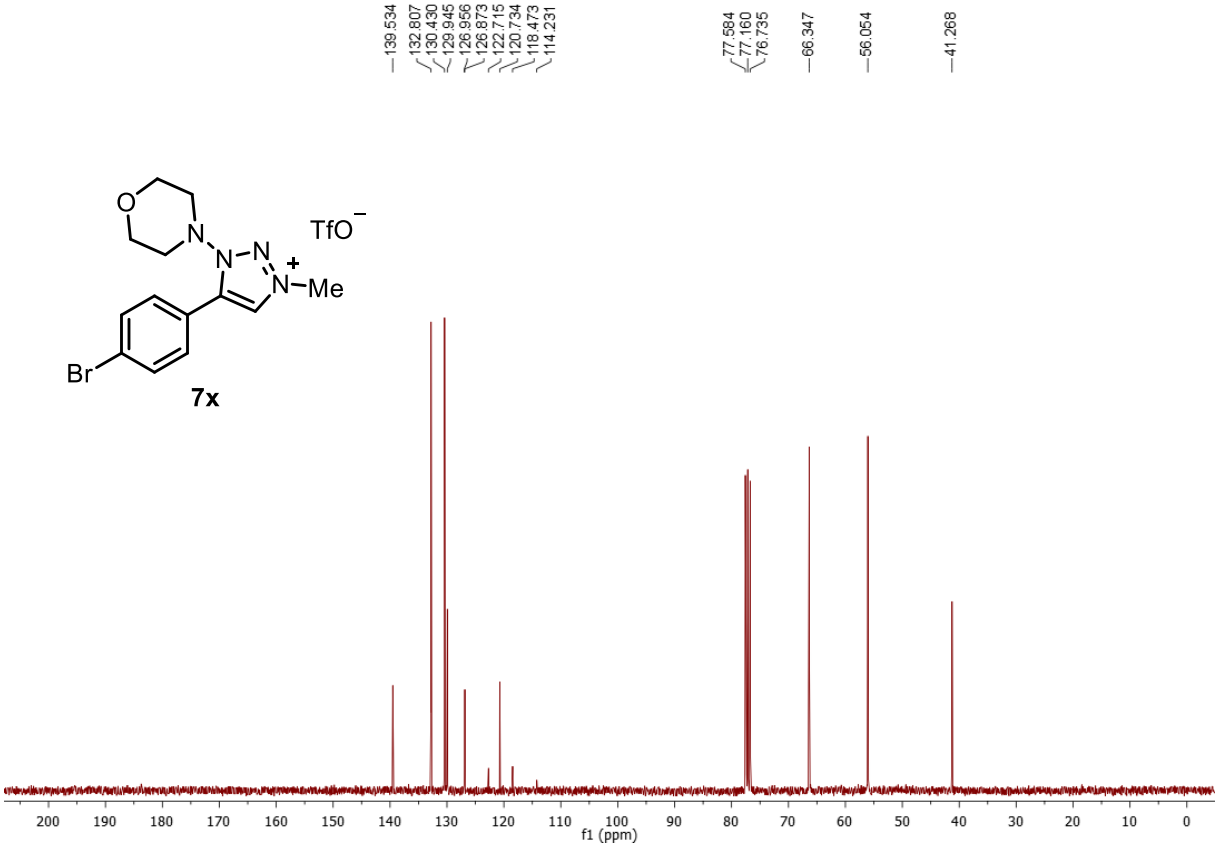


7w

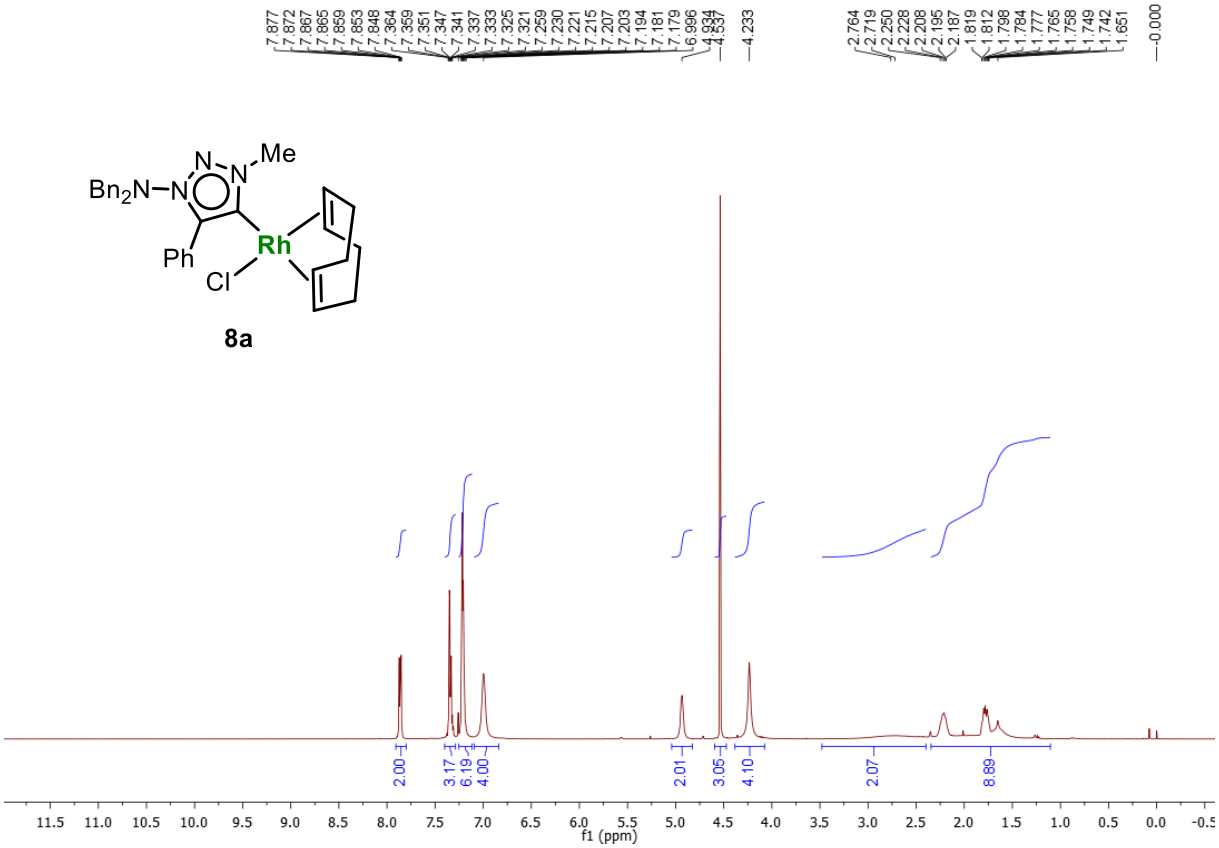
^{1}H NMR (300 MHz, $CDCl_3$)



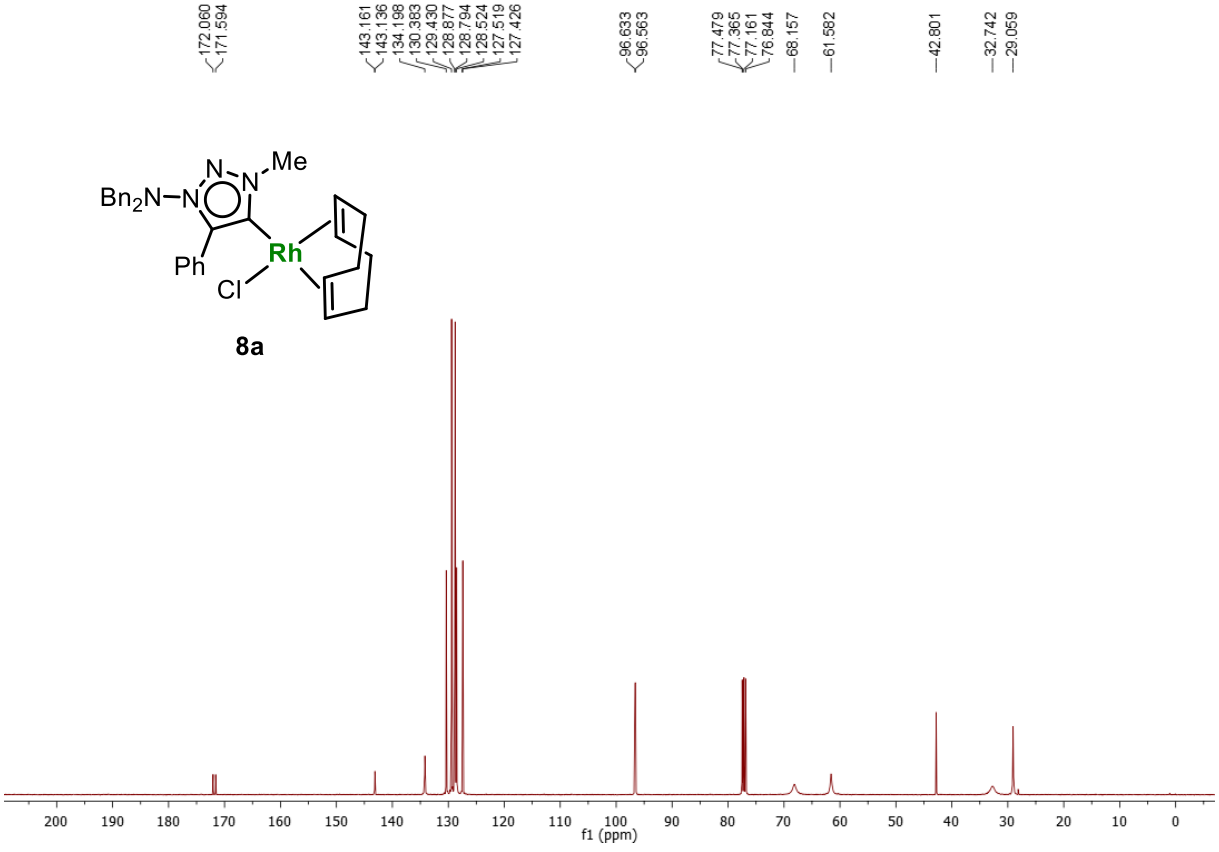
^{13}C NMR (75 MHz, $CDCl_3$)



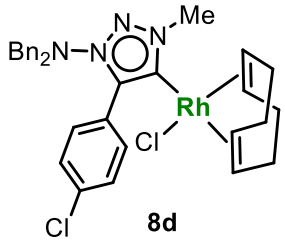
^{1}H NMR (400 MHz, $CDCl_3$, 55 °C)



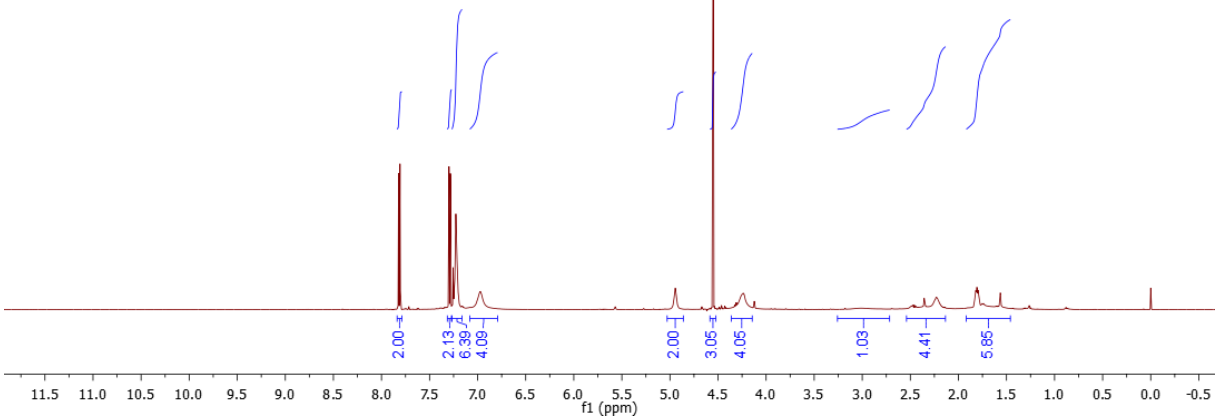
^{13}C NMR (100 MHz, $CDCl_3$, 55 °C)



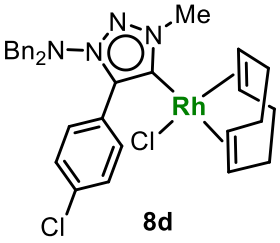
^{1}H NMR (600 MHz, $CDCl_3$, 55 °C)



8d



^{13}C NMR (150 MHz, $CDCl_3$, 55 °C)



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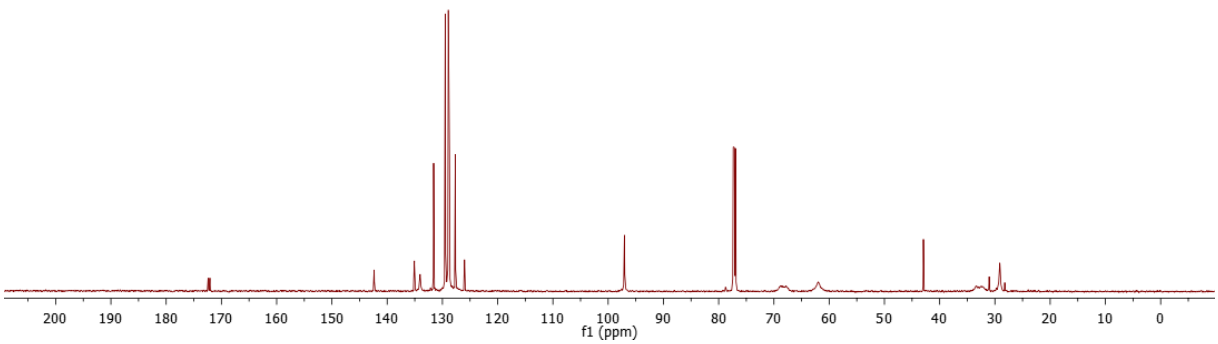
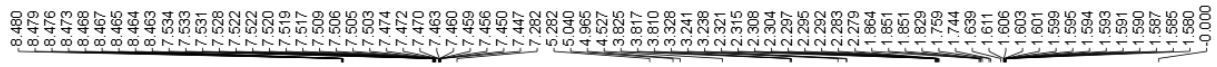
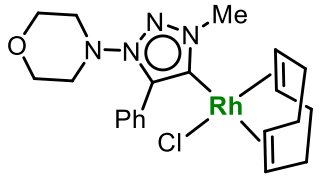


^{1}H NMR (600 MHz, $CDCl_3$, 55 °C)





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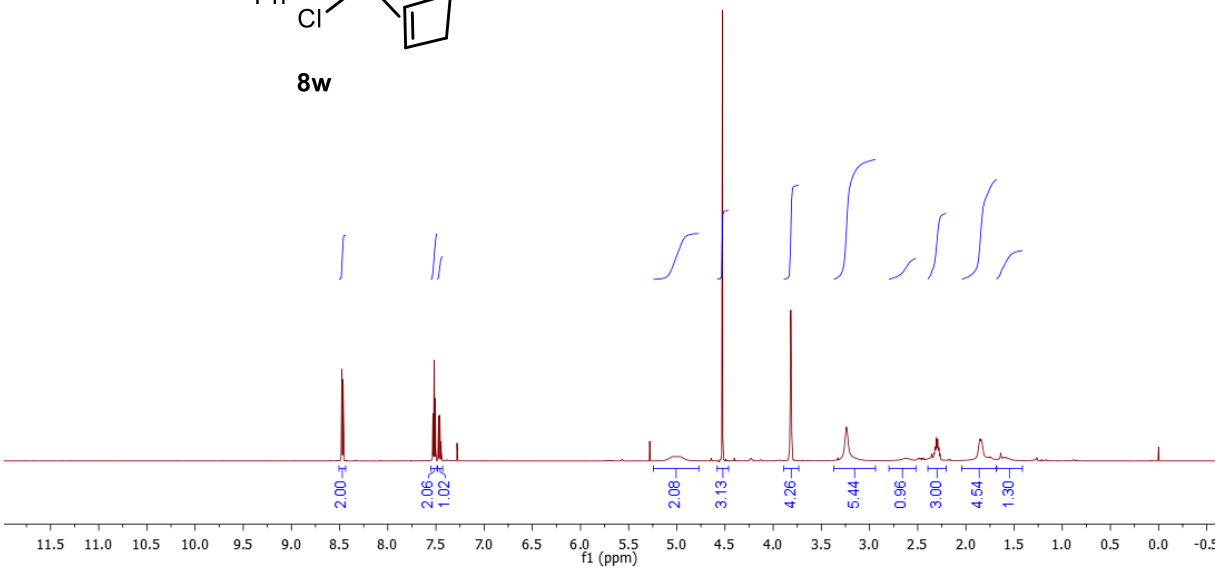
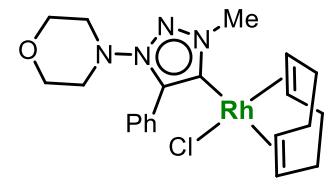


^{13}C NMR (150 MHz, $CDCl_3$, 55 °C)



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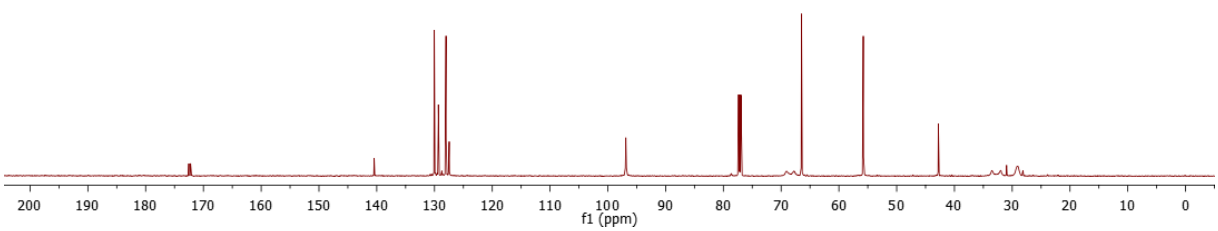
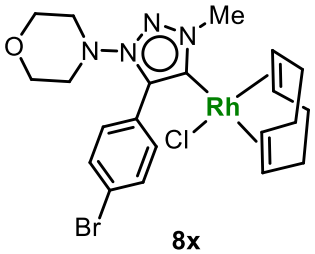
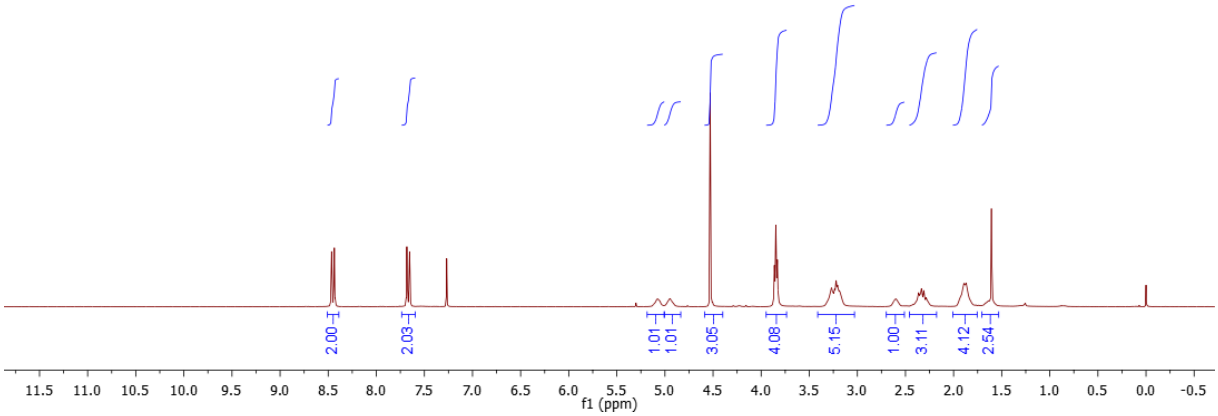


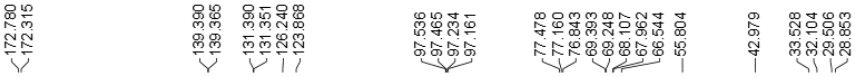
^{1}H NMR (300 MHz, $CDCl_3$)

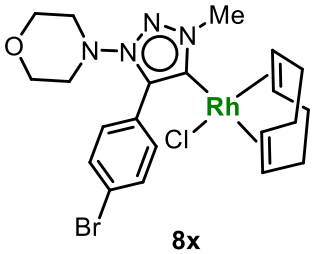


8x



^{13}C NMR (75 MHz, $CDCl_3$)





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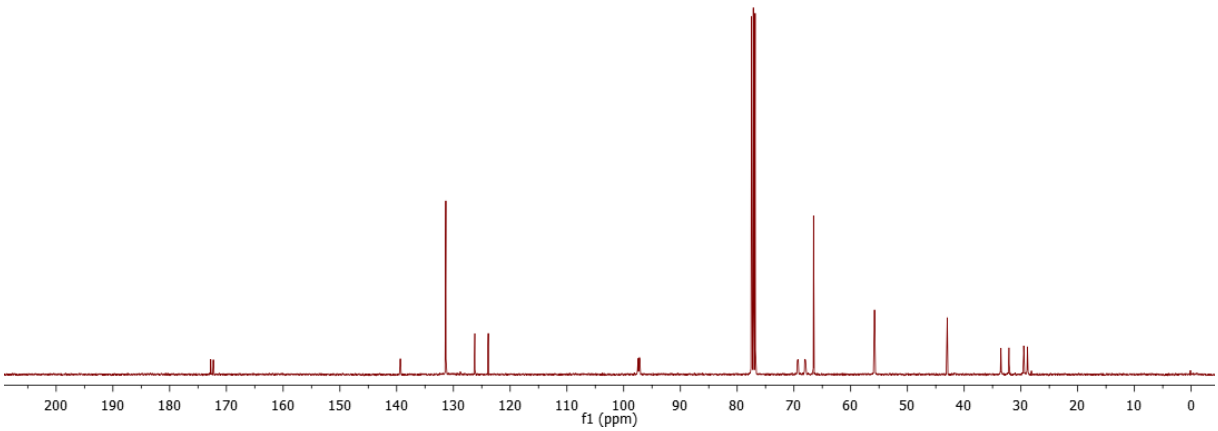
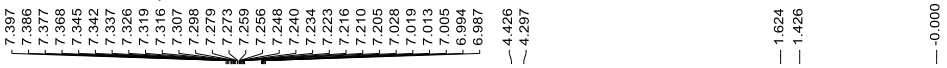
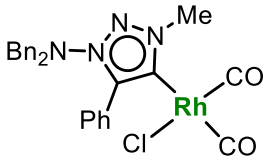
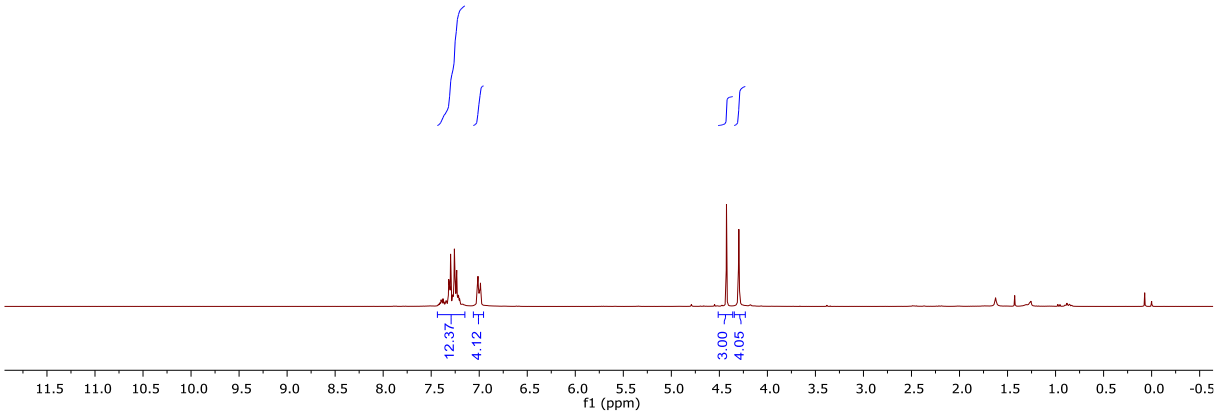


^{1}H NMR (300 MHz, $CDCl_3$)

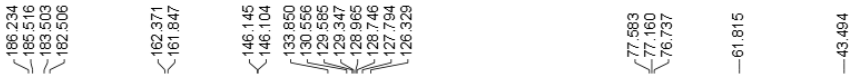


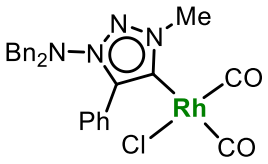


9a



^{13}C NMR (75 MHz, $CDCl_3$)





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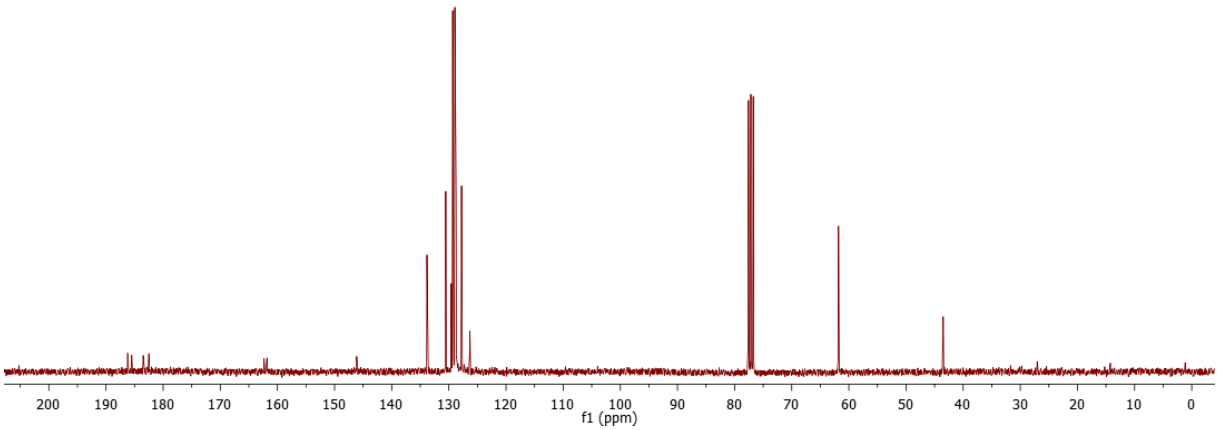
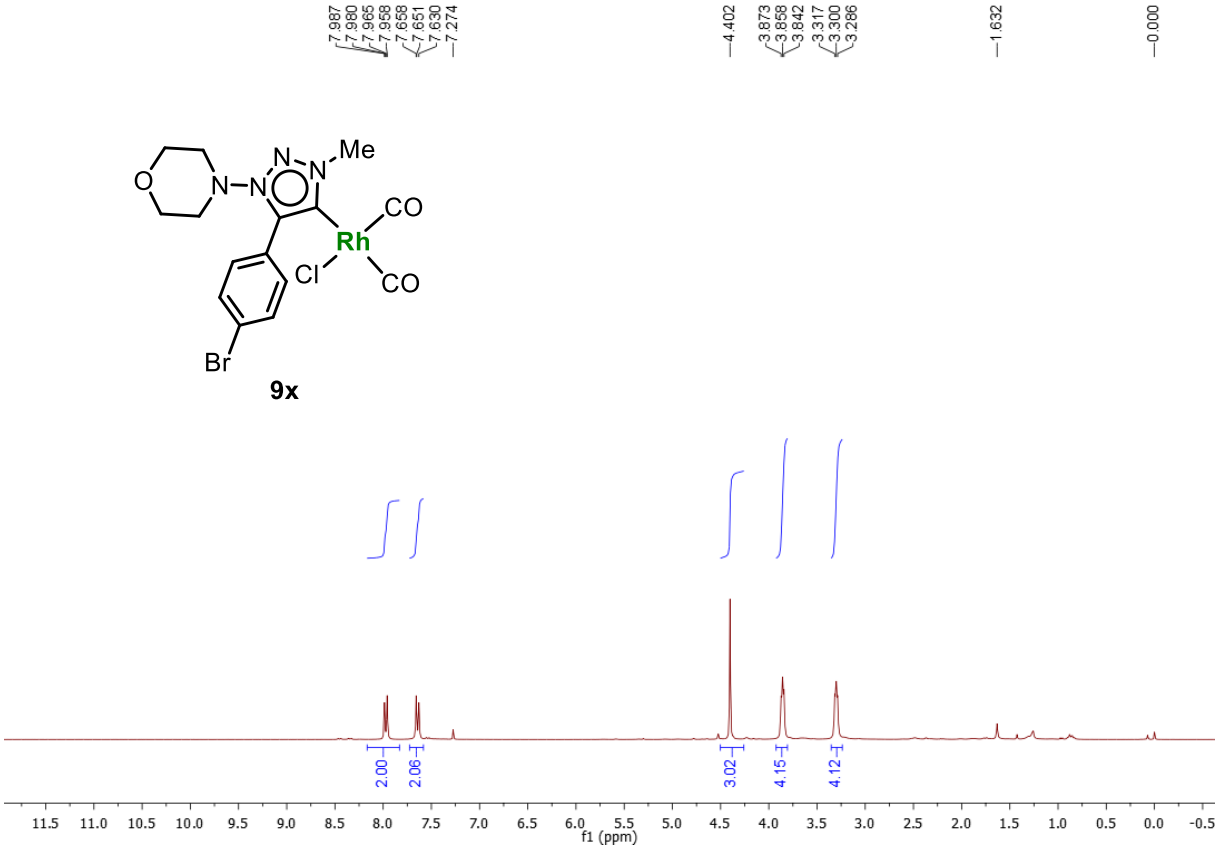
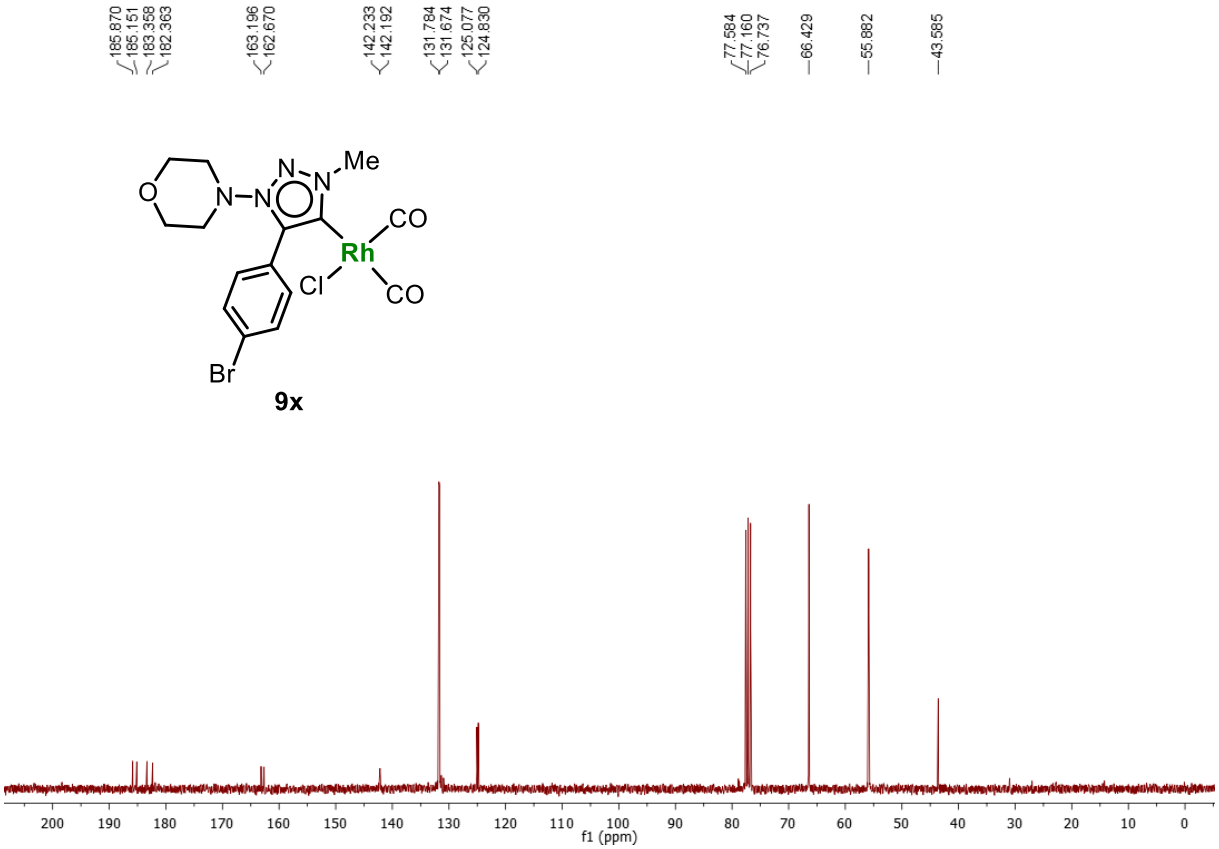


^{1}H NMR (300 MHz, $CDCl_3$)



9x

^{13}C NMR (75 MHz, $CDCl_3$)



9x