Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Palladium-Catalyzed Denitrogenative Functionalization of Benzotriazoles with Alkenes and 1,3-Dienes

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1. General Information

NMR spectra were recorded on Bruker AV400 instrument. TMS was used as internal standard for ^{1}H NMR (0 ppm), and solvent signal was used as reference for ^{13}C NMR ($CDCl_3$, 77.16 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, td = triple doublet, qd = quarter doublet, m = multiplet. High-resolution mass spectra (HRMS) were recorded on a Waters Xevo G2 QTOF MS.

Reactions were monitored by Thin Layer Chromatography on plates (GF_{254}) supplied by Yantai Chemicals (China) using UV light as visualizing agent. If not specially mentioned, flash column chromatography uses silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China).

Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials.

The procedures for preparation of starting materials (benzotriazoles **1a-k**[1] , alkenes **2**[2], 1,3-dienes **4**[3]) referred to the known literatures listed in the references.

2. General Procedures for Pd-Catalyzed Denitrogenative Alkenylation of Benzotriazole

1) Procedure A (for Alkenylation products 3a-v)

A bottom of flask was sequentially charged with N-Tf-benzotriazole (0.30 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (16 mg, 0.015 mmol, 0.05 equiv), PPh_3 (24 mg, 0.09 mmol, 0.3 eq) and $AgBF_4$ (145 mg, 0.75 mmol, 2.5 eq) at N_2 atmosphere. The reaction was added freshly distilled MeCN (3.0 mL) followed by vinyl moiety (0.90 mmol, 3.0 eq) and then placed in an oil bath preheated to 90 ℃. The resulting solution was heated at this temperature for 8-12 hours before being cooled to room

1 Y. H. Wang, Y. F. Wu, Y. H. Li and Y. F. Tang, *Chem. Sci.* 2017, **8**, 3852.

2 (a) M. Takanori and Y. Itaru, *Chem. Commun.* 2015, **51**, 7393; (b) M. Soham, N. Togati, S. Upendra and M. Debabrata, *Org. Lett.* 2013, **15**, 3384.

3 (a) P. Fourgeaud, C. Midrier, J-P. Vors, J-N. Volle, J-L. Pirat and D. Virieux, *Tetrahedron*, 2010, **66**, 758; (b) B. J. Stokes, L. Y. Liao, A. M. D. Andrade, Q. F. Wang and M. S. Sigman, *Org. Lett.* 2014, **16**, 4666.

temperature and concentrated in vacuo. The residue was directly purified by flash chromatography (SiO_2, hexanes/EtOAc) to give the corresponding product (**3a-v**)**.**

2) Procedure B (for alkenylation product 3w)

A bottom of flask was sequentially charged with N-Tf-benzotriazole **1a** (75 mg, 0.30 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (16 mg, 0.015 mmol, 0.05 equiv), PPh_3 (24 mg, 0.09 mmol, 0.3 eq) and $AgBF_4$ (145 mg, 0.75 mmol, 2.5 eq) at N_2 atmosphere. The reaction was added freshly distilled MeCN (3.0 mL) followed by ethyl acrylate (1.80 mmol, 6.0 eq) and then placed in an oil bath preheated to 90 ℃. The resulting solution was heated at this temperature for 24 hours before being cooled to room temperature and concentrated in vacuo. The residue was directly purified by flash chromatography (SiO_2, hexanes/EtOAc) to give the corresponding product **3w.**

3) Procedure C (for alkenylation product 3x)

A bottom of flask was sequentially charged with N-Tf-benzotriazole **1a** (75 mg, 0.30 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (16 mg, 0.015 mmol, 0.05 equiv), PPh_3 (24 mg, 0.09 mmol, 0.3 eq) and $AgBF_4$ (145 mg, 0.75 mmol, 2.5 eq) at ethylene atmosphere. The reaction was added freshly distilled MeCN (3.0 mL) and then placed in an oil bath preheated to 90 ℃. The resulting solution was heated at this temperature for 12 hours before being cooled to room temperature and concentrated in vacuo. The residue was directly purified by flash chromatography (SiO_2, hexanes/EtOAc) to give the corresponding product **3x.**

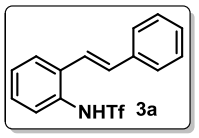
3. General Procedures for Pd-Catalyzed Denitrogenative Formal [3+2] Cyclization of Benzotriazole

Procedure for [3+2] cyclization products 5a-t

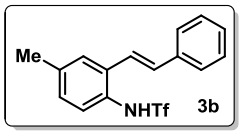
A bottom of flask was sequentially charged with 1,3-diene (0.45 mmol, 1.5 equiv), N-Tf-benzotriazole (0.30 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (16 mg, 0.015 mmol, 0.05 equiv), PPh_3 (24 mg, 0.09 mmol, 0.3 equiv) and $AgBF_4$ (145 mg, 0.75 mmol, 2.5 equiv) at N_2 atmosphere. The reaction was added freshly distilled MeCN (3.0 mL) and then placed in an oil bath preheated to 90 ℃. The resulting solution was heated at this temperature for 8-12 hours before being cooled to room temperature and concentrated in vacuo. The residue was directly purified by flash

chromatography (SiO_2, hexanes/EtOAc) to give the corresponding [3+2] cyclization product (**5a-t**).

4. Analysis Data of the Denitrogenative Alkenylation Products

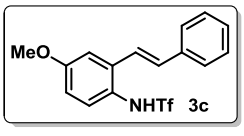


(*E*)-1,1,1-trifluoro-*N*-(2-styrylphenyl)methanesulfonamide (3a): The product was obtained as a white solid. Yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (s, 1H), 7.12 (d, *J* = 16.0 Hz, 1H), 7.29 (d, *J* = 6.8 Hz, 1H), 7.34-7.44 (m, 5H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 119.9 (q, *J* = 320.3 Hz), 121.9, 127.0, 127.0, 127.2, 128.7, 128.8, 128.9, 129.0, 130.8, 133.8, 134.3, 136.6; IR ν_{max} (film): 3674.26, 2987.09, 2900.17, 1651.02, 1405.56, 1393.47, 1381.39, 1249.70, 1228.65, 1065.76, 1056.63, 1008.16, 891.69 cm^{-1}; HRMS m/z calcd for $C_{15}H_{12}F_3NO_2S$ $[M-H]^+$: 326.0463; found: 326.0469.

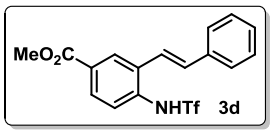


(*E*)-1,1,1-trifluoro-*N*-(4-methyl-2-styrylphenyl)methanesulfonamide (3b): The product was obtained as a colorless oil. Yield: 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 7.10 (d, *J* = 16.0 Hz, 1H), 7.15 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.30-7.36 (m, 3H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.53-7.56 (m, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 21.3, 120.0 (q, *J* = 320.4 Hz), 122.2, 126.9, 127.3, 127.6, 128.3, 128.6, 129.0, 129.6, 133.1, 134.4, 136.7, 139.1; IR ν_{max} (film): 2987.27, 1497.25, 1410.75, 1362.34, 1228.41, 1202.23, 1140.99, 1100.92, 1074.43, 961.96, 933.27 cm^{-1}; HRMS m/z calcd for $C_{16}H_{13}F_3NO_2S$ $[M-H]^+$: 340.0614; found: 340.0625.

(*E*)-1,1,1-trifluoro-*N*-(4-methoxy-2-styrylphenyl)methanesulfonamide (3c): The product

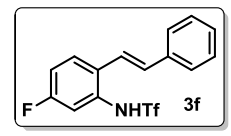


was obtained as a white solid. Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 6.58 (s, 1H), 6.87 (dd, *J* = 8.8 Hz, *J* = 2.8 Hz, 1H), 7.10 (d, *J* = 16.0 Hz, 1H), 7.21 (d, *J* = 2.8 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.34-7.36 (m, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 55.8, 111.4, 114.3, 119.9 (q, *J* = 320.4 Hz), 122.2, 124.7, 127.0, 128.7, 129.0, 130.0, 133.3, 136.6, 136.8, 160.0; IR ν_{max} (film): 3674.29, 3340.82, 2987.08, 2900.18, 1653.06, 1405.44, 1393.48, 1381.40, 1249.70, 1229.23, 1065.76, 1056.64, 1010.20, 891.72 cm^{-1}; HRMS m/z calcd for $C_{16}H_{14}F_3NO_3S$ $[M-H]^+$: 356.0568; found: 356.0578.

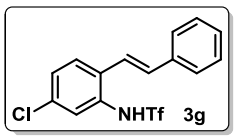


(*E*)-methyl 3-styryl-4-(trifluoromethylsulfonamido)benzoate (3d): The product was obtained as a white solid. Yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 3H), 7.23 (d, *J* = 16.8 Hz, 1H), 7.36 (d, *J* = 16.8 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.12 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 52.7, 119.9 (q, *J* = 320.4 Hz), 121.1, 126.8, 127.2, 128.9, 129.1, 129.3, 129.9, 130.4, 130.8, 135.6, 136.1, 139.0, 165.9; IR ν_{max} (film): 3674.25, 3328.57, 2987.10, 2900.17, 1655.10, 1405.52, 1393.47, 1381.29, 1249.71, 1229.14, 1065.76, 1056.63, 1010.20, 891.70 cm^{-1}; HRMS m/z calcd for $C_{17}H_{14}F_3NO_4S$ $[M-H]^+$: 384.0517; found: 384.0524.

(*E*)-1,1,1-trifluoro-*N*-(3-styryl-[1,1'-biphenyl]-4-yl)methanesulfonamide (3e): The product was obtained as a white solid. Yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 16.4 Hz, 1H), 7.33 (dd, *J* = 10.8 Hz, *J* = 3.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 3H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.52-7.55 (m, 4H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.86 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 119.9 (q, *J* = 320.5 Hz), 121.9, 125.6, 127.0, 127.3, 127.5, 127.6, 128.1, 128.8, 129.1, 129.1, 129.9, 133.9, 134.6, 136.5, 139.9, 142.0; IR ν_{max} (film): 3674.20, 3332.65, 2987.10, 2900.17, 1657.14, 1405.44, 1393.48, 1381.39, 1249.69, 1229.20, 1065.76, 1056.63, 1010.20, 891.71 cm^{-1}; HRMS m/z calcd for $C_{21}H_{16}F_3NO_2S$ $[M-H]^+$: 402.0776; found: 402.0780.

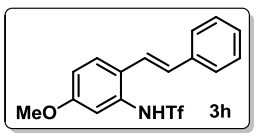


(*E*)-1,1,1-trifluoro-*N*-(5-fluoro-2-styrylphenyl)methanesulfonamide (3f): The product was obtained as a white solid. Yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 16.0 Hz, 1H), 7.12 (dt, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 7.20 (d, *J* = 16.0 Hz, 1H), 7.26 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.65 (dd, *J* = 8.8 Hz, *J* = 6.4 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 113.5 (d, *J* = 25.0 Hz), 115.9 (d, *J* = 21.3 Hz), 119.8 (q, *J* = 320.4 Hz), 120.8, 126.9, 128.5 (d, *J* = 8.8 Hz), 128.8, 129.1, 129.7 (d, *J* = 3.7 Hz), 132.0 (d, *J* = 10.2 Hz), 134.0 (d, *J* = 1.7 Hz), 136.3, 162.1 (d, *J* = 248.1 Hz); IR ν_{max} (film): 3674.17, 3332.65, 2987.11, 2900.17, 1651.02, 1405.51, 1393.47, 1381.36, 1249.69, 1229.28, 1065.76, 1056.64, 1008.16, 891.71 cm^{-1}; HRMS m/z calcd for $C_{15}H_{11}F_4NO_2S$ $[M-H]^+$: 344.0368; found: 344.0370.

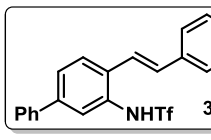


(*E*)-*N*-(5-chloro-2-styrylphenyl)-1,1,1-trifluoromethanesulfonamide (3g): The product was obtained as a white solid. Yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 1H), 7.05 (d, *J* = 16.0 Hz, 1H), 7.18 (d, *J* = 16.0 Hz, 1H), 7.31-7.34 (m, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.46 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 119.8 (q, *J* = 320.3 Hz), 120.7, 126.9, 127.0, 127.9, 129.0, 129.1, 129.1, 131.6, 132.5, 134.0, 134.3, 136.2; IR ν_{max} (film): 3674.14, 3338.78, 2987.14, 2900.15, 1653.06, 1405.32, 1393.50, 1249.69, 1228.96, 1065.76, 1056.66, 1012.24, 891.70 cm^{-1}; HRMS m/z calcd for $C_{15}H_{11}ClF_3NO_2S$ $[M-H]^+$: 360.0073; found: 360.0081.

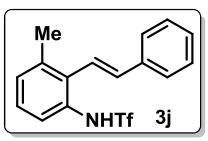
(*E*)-1,1,1-trifluoro-*N*-(5-methoxy-2-styrylphenyl)methanesulfonamide (3h): The product was obtained as a colorless oil. Yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.91 (dd, *J* = 8.8 Hz, *J* = 2.8 Hz, 1H), 6.95-6.99 (m, 2H), 7.20 (d, *J* = 16.0 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 55.7, 111.8, 115.1, 119.9 (q, *J* = 320.6 Hz), 121.6, 126.3, 126.7, 127.8, 128.3, 129.0, 131.7, 131.8, 136.9, 159.8; IR ν_{max} (film): 2969.21, 1610.24, 1505.77, 1416.84, 1368.07, 1291.69, 1271.04, 1229.16, 1197.15, 1162.88, 1140.08, 1102.45, 1036.97, 963.29, 904.33 cm^{-1}; HRMS m/z calcd for $C_{16}H_{13}F_3NO_3S$ $[M-H]^+$: 356.0580; found: 356.0576.



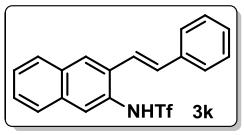
(*E*)-1,1,1-trifluoro-*N*-(4-styryl-[1,1'-biphenyl]-3-yl)methanesulfonamide (3i): The product was obtained as a colorless oil. Yield: 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 16.0 Hz, 1H), 7.31-7.42 (m, 5H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.59-7.62 (m, 3H), 7.67 (d, *J* = 0.8 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 120.0 (q, *J* = 319.9 Hz), 121.6, 125.9, 127.0, 127.1, 127.2, 127.4, 128.2, 128.7, 129.1, 129.2, 131.3, 133.0, 133.4, 136.7, 139.3, 141.8; IR ν_{max} (film): 2987.33, 2900.12, 1484.07, 1404.49, 1362.43, 1227.32, 1196.40, 1139.87, 1105.33, 1075.08, 957.74, 762.23 cm^{-1}; HRMS m/z calcd for $C_{21}H_{16}F_3NO_2S$ $[M-H]^+$: 402.0783; found: 402.0788.



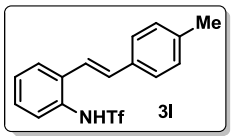
(*E*)-1,1,1-trifluoro-*N*-(3-methyl-2-styrylphenyl)methanesulfonamide (3j): The product was obtained as a white solid. Yield: 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 6.71 (d, *J* = 16.8 Hz, 1H), 6.90 (d, *J* = 16.8 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.39-7.43 (m, 3H), 7.51 (d, *J* = 7.6 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 20.9, 119.9 (q, *J* = 320.6 Hz), 120.1, 122.4, 126.8,



128.2, 128.7, 128.9, 129.1, 131.0, 132.0, 136.0, 137.6, 138.3; IR ν_{max} (film): 3674.14, 3330.61, 2987.07, 2900.17, 1657.14, 1405.42, 1393.51, 1381.59, 1249.70, 1228.89, 1065.74, 1056.59, 1010.20, 891.69 cm^{-1}; HRMS m/z calcd for $C_{16}H_{14}F_3NO_2S$ $[M-H]^+$: 340.0619; found: 340.0623.

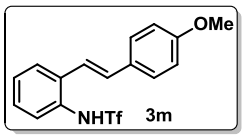


(*E*)-1,1,1-trifluoro-*N*-(3-styrylnaphthalen-2-yl)methanesulfonamide (3k): The product was obtained as a white solid. Yield: 62%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 16.0 Hz, 1H), 7.32-7.43 (m, 4H), 7.49-7.57 (m, 4H), 7.83-7.87 (m, 2H), 7.94 (s, 1H), 8.10 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 120.0 (q, *J* = 320.5 Hz), 122.2, 125.5, 126.4, 127.0, 127.1, 127.5, 127.9, 128.1, 128.7, 129.1, 129.1, 132.1, 132.9, 132.9, 134.2, 136.6; IR ν_{max} (film): 3674.21, 3326.53, 2987.09, 2900.17, 1655.10, 1405.43, 1393.47, 1381.42, 1249.71, 1229.18, 1065.75, 1056.64, 1010.20, 891.70 cm^{-1}; HRMS m/z calcd for $C_{19}H_{14}F_3NO_2S$ $[M-H]^+$: 376.0619; found: 376.0631.

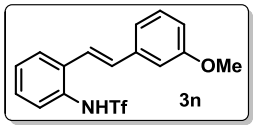


(*E*)-1,1,1-trifluoro-*N*-(2-(4-methylstyryl)phenyl)methanesulfonamide (3l): The product was obtained as a colorless oil. Yield: 76%; ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 7.05 (d, *J* = 16.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 16.0 Hz, 1H), 7.30 (dt, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.35 (dt, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.40-7.45 (m, 3H), 7.66 (dd, *J* = 7.6 Hz, *J* = 2.0 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 21.4, 120.0 (q, J = 320.5 Hz), 120.9, 126.9, 126.9, 127.2, 128.5, 128.8, 129.7, 130.8, 133.5, 133.9, 134.4, 138.8; IR ν_{max} (film): 3261.01, 2923.07, 1514.08, 1488.71, 1455.23, 1412.46, 1356.27, 1222.16, 1208.63, 1189.07, 1164.92, 1135.73, 1094.08, 967.29 cm^{-1}; HRMS m/z calcd for $C_{16}H_{13}F_3NO_2S$ $[M-H]^+$: 340.0614; found: 340.0625

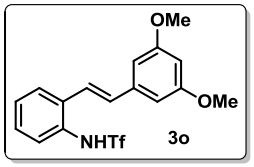
(*E*)-1,1,1-trifluoro-*N*-(2-(4-methoxystyryl)phenyl)methanesulfonamide (3m): The product was obtained as a colorless oil. Yield: 65%; ^1H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.89 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 16.0 Hz, 1H), 7.13 (d, *J* = 16.0 Hz, 1H), 7.24-7.29 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.41-7.44 (m, 3H), 7.64 (d, *J* = 7.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 55.5, 114.5, 119.6, 119.9 (q, *J* = 320.4 Hz), 126.6, 127.3, 128.2, 128.3, 128.8, 129.5, 130.6, 133.0, 134.6, 160.0; IR ν_{max} (film): 3674.17, 3332.65, 2987.10, 2900.17, 1653.06, 1405.42, 1393.48, 1381.38, 1249.73, 1229.05, 1065.76, 1056.63, 1008.16, 891.69 cm^{-1}; HRMS m/z calcd for $C_{16}H_{14}F_3NO_3S$ $[M-H]^+$: 356.0568; found: 356.0573.



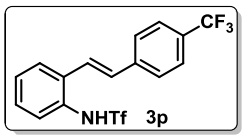
(*E*)-1,1,1-trifluoro-*N*-(2-(3-methoxystyryl)phenyl)methanesulfonamide (3n): The product was obtained as a colorless oil. Yield: 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.86 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 6.90 (s, 1H), 7.02-7.06 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.25-7.39 (m, 4H), 7.44 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.67 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 55.4, 112.1, 114.4, 119.6, 119.9 (q, *J* = 320.4 Hz), 122.3, 126.9, 127.4, 128.8, 128.9, 130.0, 130.9, 133.4, 134.2, 138.0, 160.1; IR ν_{max} (film): 3280.22, 1597.82, 1579.56, 1491.18, 1454.68, 1418.96, 1368.59, 1271.06, 1221.15, 1196.10, 1140.44, 1092.56, 1044.57, 959.41, 777.65 cm^{-1}; HRMS m/z calcd for $C_{16}H_{13}F_3NO_3S$ $[M-H]^+$: 356.0575; found: 356.0574.



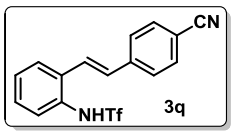
(*E*)-*N*-(2-(3,5-dimethoxystyryl)phenyl)-1,1,1-trifluoromethanesulfonamide (3o): The product was obtained as a colorless oil. Yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 6H), 6.41 (t, *J* = 2.0 Hz, 1H), 6.64 (d, *J* = 2.0 Hz, 2H), 6.98 (d, *J* = 16.0 Hz, 1H), 7.24 (d, *J* = 16.0 Hz, 1H), 7.30-7.39 (m, 2H), 7.45 (dd, *J* = 7.6 Hz, *J* = 2.0 Hz, 1H), 7.66 (dd, *J* = 7.6 Hz, *J* = 2.0 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 55.5, 100.9, 120.0 (q, *J* = 320.4 Hz), 122.5, 126.9, 127.6, 128.9, 128.9, 131.0, 133.3, 134.1, 138.6, 161.1; IR ν_{max} (film): 3334.74, 2945.28, 2834.75, 1591.64, 1456.46, 1418.48, 1374.98, 1222.53, 1196.88, 1145.24, 1017.57, 961.91 cm^{-1}; HRMS m/z calcd for $C_{17}H_{15}F_3NO_4S$ $[M-H]^+$: 386.0668; found: 386.0683.



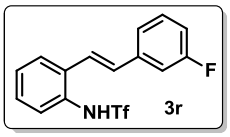
(*E*)-1,1,1-trifluoro-*N*-(2-(4-(trifluoromethyl)styryl)phenyl)methanesulfonamide (3p): The product was obtained as a white solid. Yield: 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 16.0 Hz, 1H), 7.34-7.45 (m, 4H), 7.59-7.63 (m, 4H), 7.71 (d, *J* = 7.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 119.9 (q, *J* = 320.3 Hz), 124.2 (q, *J* = 270.2 Hz), 124.6, 125.9 (q, *J* = 3.8 Hz), 127.0, 127.0, 127.8, 129.2, 129.4, 130.4 (q, *J* = 32.4 Hz), 130.9, 131.7, 134.1, 140.0; IR ν_{max} (film): 3674.16, 3336.73, 2987.11, 2900.17, 1653.06, 1405.43, 1393.48, 1381.32, 1249.70, 1229.06, 1065.78, 1056.65, 1008.16, 891.69 cm^{-1}; HRMS m/z calcd for $C_{16}H_{11}F_6NO_2S$ $[M-H]^+$: 394.0336; found: 394.0345.



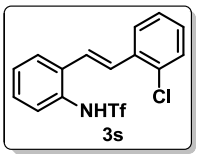
(*E*)-*N*-(2-(4-cyanostyryl)phenyl)-1,1,1-trifluoromethanesulfonamide (3q): The product was obtained as a white solid. Yield: 87%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.42 (d, *J* = 16.0 Hz, 1H), 7.46-7.53 (m, 3H), 7.77-7.85 (m, 5H), 7.95-7.98 (m, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 111.9, 119.4, 121.0 (q, *J* =



320.3 Hz), 127.2, 127.3, 128.2, 129.5, 129.7, 130.2, 130.7, 132.9, 133.5, 135.0, 142.6; IR ν_{max} (film): 2987.52, 2358.67, 2226.69, 1689.16, 1601.98, 1505.51, 1487.88, 1428.61, 1372.50, 1224.42, 1189.39, 1140.14, 1092.07, 954.22 cm^{-1}; HRMS m/z calcd for $C_{16}H_{10}F_3N_2O_2S$ $[M-H]^+$: 351.0416; found: 351.0421.

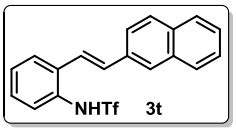


(*E*)-1,1,1-trifluoro-*N*-(2-(3-fluorostyryl)phenyl)methanesulfonamide (3r): The product was obtained as a colorless oil. Yield: 75%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.01-7.09 (m, 2H), 7.24 (dt, *J* = 10.0 Hz, *J* = 1.6 Hz, 1H), 7.31-7.43 (m, 5H), 7.47 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.71 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 113.4 (d, *J* = 21.8 Hz), 115.4 (d, *J* = 21.4 Hz), 120.0 (q, *J* = 320.4 Hz), 122.8 (d, *J* = 2.7 Hz), 123.5, 126.9, 127.6, 129.0, 129.1, 130.5 (d, *J* = 8.3 Hz), 131.0, 132.0 (d, *J* = 2.6 Hz), 134.1, 139.0 (d, *J* = 7.7 Hz), 163.3 (d, *J* = 244.5 Hz); IR ν_{max} (film): 3289.42, 1609.50, 1583.23, 1490.70, 1447.26, 1415.59, 1365.11, 1267.28, 1219.43, 1195.51, 1138.70, 1092.80, 959.46, 942.80, 780.25 cm^{-1}; HRMS m/z calcd for $C_{15}H_{10}F_4NO_2S$ $[M-H]^+$: 344.0371; found: 344.0372.

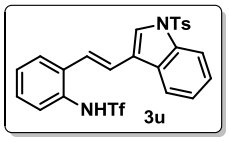


(*E*)-*N*-(2-(2-chlorostyryl)phenyl)-1,1,1-trifluoromethanesulfonamide (3s): The product was obtained as a colorless oil. Yield: 72%; ^1H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 1H), 7.25-7.46 (m, 7H), 7.49 (d, *J* = 16.0 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 119.9 (q, *J* = 320.4 Hz), 124.7, 126.9, 127.4, 127.4, 127.4, 129.1, 129.2, 129.6, 129.7, 130.1, 130.9, 133.9, 134.3, 134.8; IR ν_{max} (film): 3674.19, 3332.65, 2987.11, 2900.17, 1655.10, 1405.39, 1393.49, 1381.32, 1249.69, 1229.05, 1065.76, 1056.64, 1010.20, 891.71 cm^{-1}; HRMS m/z calcd for $C_{15}H_{11}ClF_3NO_2S$ $[M-H]^+$: 360.0073; found: 360.0078.

(*E*)-1,1,1-trifluoro-*N*-(2-(2-(naphthalen-2-yl)vinyl)phenyl)methanesulfonamide (3t): The product was obtained as a white solid. Yield: 85%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 16.0 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.37-7.48 (m, 5H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.81-7.84 (m, 4H); ^{13}C (100 MHz, $CDCl_3$) δ 119.9 (q, *J* = 320.4 Hz), 122.1, 123.3, 126.6, 126.7, 126.9, 127.4, 127.7, 127.9, 128.3, 128.8, 128.8, 128.9, 130.8, 133.5, 133.6, 133.7, 134.1, 134.4; IR ν_{max} (film): 3674.22, 3330.61, 2987.10, 2900.16, 1651.02, 1405.41, 1393.48, 1381.40, 1249.71, 1229.12, 1065.75, 1056.63, 1008.16, 891.69 cm^{-1}; HRMS m/z calcd for $C_{19}H_{14}F_3NO_2S$ $[M-H]^+$: 376.0619; found: 376.0632.

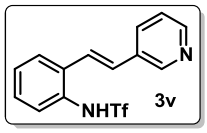


(*E*)-1,1,1-trifluoro-*N*-(2-(2-(1-tosyl-1*H*-indol-3-yl)vinyl)phenyl)methanesulfonamide (3u):

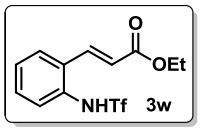


The product was obtained as a white solid. Yield: 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 6.73 (s, 1H), 7.14 (d, *J* = 16.4 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.30-7.41 (m, 5H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.72 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 21.8, 114.0, 119.9 (q, *J* = 320.2 Hz), 120.3, 120.5, 122.9, 124.1, 124.5, 125.4, 125.5, 126.7, 127.0, 127.5, 128.6, 128.8, 129.1, 130.2, 130.6, 134.8, 135.0, 135.7, 145.4; IR ν_{max} (film): 3674.14, 3330.61, 2987.12, 2900.16, 1655.10, 1405.33, 1393.49, 1381.26, 1249.70, 1229.16, 1065.75, 1056.64, 1010.20, 891.70 cm^{-1}; HRMS m/z calcd for $C_{24}H_{19}F_3N_2O_4S_2$ $[M-H]^+$: 519.0660; found: 519.0658.

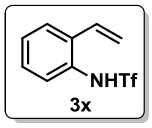
(*E*)-1,1,1-trifluoro-*N*-(2-(2-(pyridin-3-yl)vinyl)phenyl)methanesulfonamide (3v): The product



was obtained as a white solid. Yield: 66%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.00 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 16.4 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.45 (dd, *J* = 8.0 Hz, *J* = 5.2 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 16.8 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 4.4 Hz, 1H), 8.61 (s, 1H); ^{13}C (100 MHz, DMSO-d_6) δ 122.8 (q, *J* = 327.5 Hz), 123.3, 124.1, 125.5, 126.3, 127.2, 129.3, 129.6, 132.2, 134.8, 135.3, 145.3, 149.6, 149.7; IR ν_{max} (film): 2987.29, 2359.48, 2249.76, 2125.56, 1652.96, 1540.08, 1051.70, 1023.24, 1003.67, 820.68, 757.99 cm^{-1}; HRMS m/z calcd for $C_{14}H_{10}F_3N_2O_2S$ $[M-H]^+$: 327.0422; found: 327.0416.



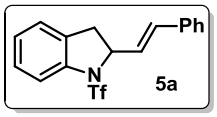
(*E*)-ethyl 3-(2-(trifluoromethylsulfonamido)phenyl)acrylate (3w): The product was obtained as a colorless oil. Yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.2 Hz, 3H), 4.28 (q, *J* = 7.2 Hz, 2H), 6.49 (d, *J* = 16.0 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 8.12 (d, *J* = 16.0 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 14.3, 61.4, 119.9 (q, *J* = 320.5 Hz), 121.8, 127.5, 128.0, 128.8, 131.1, 131.4, 132.8, 139.0, 167.3; IR ν_{max} (film): 3674.15, 3320.41, 2987.13, 2900.16, 1655.10, 1405.32, 1393.49, 1381.16, 1065.76, 1056.65, 1010.20, 891.70 cm^{-1}; HRMS m/z calcd for $C_{12}H_{12}F_3NO_4S$ $[M-H]^+$: 322.0361; found: 322.0368.



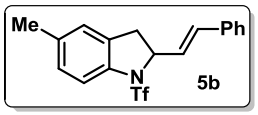
1,1,1-trifluoro-*N*-(2-vinylphenyl)methanesulfonamide (3x): The product was obtained as a colorless oil. Yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (d, *J* =

10.8 Hz, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 6.92 (dd, *J* = 17.6 Hz, *J* = 10.8 Hz, 1H), 7.32-7.35 (m, 2H), 7.42-7.44 (m, 1H), 7.53-7.56 (m, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 119.5, 119.9 (q, *J* = 320.3 Hz), 126.4, 127.2, 128.6, 129.1, 130.7, 131.1, 134.3; IR ν_{max} (film): 3674.16, 3326.53, 2987.14, 2900.15, 1655.10, 1405.30, 1393.49, 1249.69, 1229.22, 1065.76, 1056.66, 1012.24, 891.72 cm^{-1}; HRMS m/z calcd for $C_9H_8F_3NO_2S$ $[M-H]^+$: 250.0150; found: 250.0151.

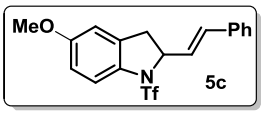
5. Analysis Data of the Denitrogenative [3+2] Cyclization Products



(*E*)-2-styryl-1-((trifluoromethyl)sulfonyl)indoline (5a): The product was obtained as a colorless oil. Yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (d, *J* = 16.0 Hz, 1H), 3.63 (dd, *J* = 16.0 Hz, *J* = 9.6 Hz, 1H), 5.23 (t, *J* = 8.4 Hz, 1H), 6.20 (dd, *J* = 15.6 Hz, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 15.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.23-7.34 (m, 7H), 7.47 (d, *J* = 7.2 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 35.7, 66.1, 115.7, 120.2 (q, *J* = 323.3 Hz), 125.7, 125.8, 126.9, 126.9, 128.4, 128.4, 128.7, 130.5, 132.9, 135.8, 139.0; IR ν_{max} (film): 3343.00, 1636.81, 1396.74, 1224.99, 1192.95, 1141.77, 1025.39, 963.82 cm^{-1}; HRMS m/z calcd for $C_{17}H_{13}F_3NO_2S$ $[M-H]^+$: 352.0619; found: 352.0626.

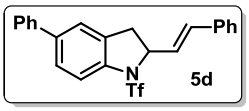


(*E*)-5-methyl-2-styryl-1-((trifluoromethyl)sulfonyl)indoline (5b): The product was obtained as a colorless oil. Yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.91 (d, *J* = 16.0 Hz, 1H), 3.59 (dd, *J* = 16.0 Hz, *J* = 9.2 Hz, 1H), 5.21 (t, *J* = 8.4 Hz, 1H), 6.18 (dd, *J* = 15.6 Hz, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 15.6 Hz, 1H), 7.03-7.05 (m, 2H), 7.21-7.36 (m, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 21.1, 35.7, 66.2, 115.4, 120.3 (q, *J* = 324.5 Hz), 126.4, 126.8, 126.9, 128.3, 128.7, 128.9, 130.6, 132.7, 135.7, 135.9, 136.6; IR ν_{max} (film): 3337.57, 2947.88, 2835.29, 1651.17, 1449.12, 1396.76, 1225.00, 1199.30, 1147.59, 1106.72, 1015.18 cm^{-1}; HRMS m/z calcd for $C_{18}H_{15}F_3NO_2S$ $[M-H]^+$: 366.0766; found: 366.0783.



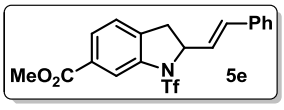
(*E*)-5-methoxy-2-styryl-1-((trifluoromethyl)sulfonyl)indoline (5c): The product was obtained as a colorless oil. Yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (d, *J* = 16.0 Hz, 1H), 3.61 (dd, *J* = 16.0 Hz, *J* = 9.2 Hz, 1H), 3.77 (s, 3H), 5.21 (t, *J* = 8.0 Hz, 1H), 6.19 (dd, *J* = 16.0 Hz, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.75-6.80 (m, 2H), 7.21-7.39 (m, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 35.9, 55.8, 66.3, 111.6, 113.3, 116.6, 120.3 (q, *J* = 323.6 Hz), 126.8, 126.8, 128.4, 128.7, 132.2, 132.3, 132.6, 135.9, 158.1; IR ν_{max} (film): 3373.14, 1487.91, 1394.84, 1225.29, 1196.71, 1143.82, 1037.17, 963.99 cm^{-1}; HRMS

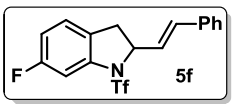
m/z calcd for $C_{18}H_{15}F_3NO_3S$ $[M-H]^+$: 382.0725; found: 382.0726.



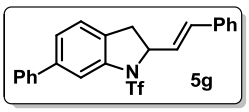
(*E*)-5-phenyl-2-styryl-1-((trifluoromethyl)sulfonyl)indoline (5d): The product was obtained as a white solid. Yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.03 (d, *J* = 16.0 Hz, *J* = 1.6 Hz, 1H), 3.69 (dd, *J* = 16.0 Hz, *J* = 9.6 Hz, 1H), 5.28 (t, *J* = 8.4 Hz, 1H), 6.24 (dd, *J* = 15.6 Hz, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 15.6 Hz, 1H), 7.23-7.58 (m, 13H); ^{13}C (100 MHz, $CDCl_3$) δ 35.8, 66.5, 115.8, 120.2 (q, *J* = 319.5 Hz), 124.5, 126.9, 127.1, 127.3, 127.4, 127.6, 128.4, 128.8, 129.0, 131.2, 133.0, 135.8, 138.3, 139.1, 140.3; IR ν_{max} (film): 3342.49, 2947.12, 2834.21, 1652.87, 1476.76, 1449.00, 1396.67, 1226.67, 1146.39, 1109.72, 1016.91 cm^{-1}; HRMS m/z calcd for $C_{23}H_{17}F_3NO_2S$ $[M-H]^+$: 428.0932; found: 428.0928.

(*E*)-methyl 2-styryl-1-((trifluoromethyl)sulfonyl)indoline-6-carboxylate (5e): The product was obtained as a colorless oil. Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90 (dd, *J* = 15.6 Hz, *J* = 1.6 Hz, 1H), 3.55 (dd, *J* = 15.6 Hz, *J* = 9.2 Hz, 1H), 3.79 (s, 3H), 5.23 (t, *J* = 8.4 Hz, 1H), 6.20 (dd, *J* = 15.6 Hz, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 15.2 Hz, 1H), 6.69 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 7.06 (s, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.22-7.35 (m, 5H); ^{13}C (100 MHz, $CDCl_3$) δ 35.0, 55.8, 67.0, 102.0, 111.7, 120.2 (q, *J* = 323.5 Hz), 122.2, 126.1, 126.9, 126.9, 128.4, 128.7, 132.8, 135.9, 140.1, 160.2; IR ν_{max} (film): 3329.35, 2948.49, 2836.21, 1646.78, 1397.69, 1225.55, 1204.26, 1107.47, 1015.00 cm^{-1}; HRMS m/z calcd for $C_{19}H_{15}F_3NO_4S$ $[M-H]^+$: 410.0674; found: 410.0670.



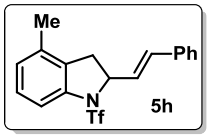


(*E*)-6-fluoro-2-styryl-1-((trifluoromethyl)sulfonyl)indoline (5f): The product was obtained as a colorless oil. Yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 (d, *J* = 16.0 Hz, 1H), 3.59 (dd, *J* = 16.0 Hz, *J* = 9.6 Hz, 1H), 5.26 (t, *J* = 8.4 Hz, 1H), 6.20 (dd, *J* = 16.0 Hz, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.84 (dt, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H), 7.17-7.37 (m, 7H); ^{13}C (100 MHz, $CDCl_3$) δ 35.1, 67.2, 104.1 (d, *J* = 28.4 Hz), 112.5 (d, *J* = 23.0 Hz), 120.1 (q, *J* = 325.7 Hz), 125.8 (d, *J* = 2.6 Hz), 126.4, 126.5, 126.9, 128.5, 128.8, 133.3, 135.7, 140.3 (d, *J* = 11.4 Hz), 162.8 (d, *J* = 244.0 Hz); IR ν_{max} (film): 3328.70, 2943.78, 2832.24, 1448.47, 1112.76, 1019.46 cm^{-1}; HRMS m/z calcd for $C_{17}H_{12}F_4NO_2S$ $[M-H]^+$: 370.0525; found: 370.0527.



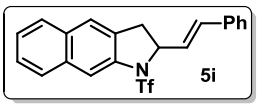
(*E*)-6-phenyl-2-styryl-1-((trifluoromethyl)sulfonyl)indoline (5g): The product was obtained as a white solid. Yield: 95%; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 3.02 (d, *J* = 16.0 Hz, 1H), 3.67 (dd, *J* = 16.0 Hz, *J* = 9.2 Hz, 1H), 5.29 (t, *J* = 8.4 Hz, 1H), 6.24 (dd, *J* = 16.0 Hz, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 7.23-7.37 (m, 8H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.70 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 35.5, 66.6, 114.4, 120.3 (q, *J* = 324.1 Hz), 124.8, 126.0, 126.8, 126.9, 127.4, 127.9, 128.4, 128.8, 129.0, 129.5, 133.0, 135.9, 139.8, 140.5, 142.1; IR ν_{max} (film): 3335.91, 2945.84, 2833.38, 1652.90, 1449.19, 1395.90, 1225.39, 1143.91, 1108.32, 1017.91 cm^{-1}; HRMS m/z calcd for $C_{23}H_{17}F_3NO_2S$ $[M-H]^+$: 428.0932; found: 428.0941.

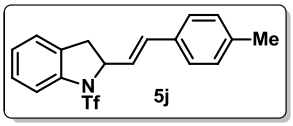


(*E*)-4-methyl-2-styryl-1-((trifluoromethyl)sulfonyl)indoline (5h): The product was obtained as a colorless oil. Yield: 90%; ^1H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 2.90 (d, *J* = 16.0 Hz, 1H), 3.50 (dd, *J* = 16.0 Hz, *J* = 9.6 Hz, 1H), 5.24 (t, *J* = 8.4 Hz, 1H), 6.20 (dd, *J* = 16.0 Hz, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.21-7.36 (m, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 18.8, 34.7, 65.9, 113.0, 120.2 (q, *J* = 322.1 Hz), 126.7, 126.9, 127.2, 128.4, 128.4, 128.7, 129.2, 132.7, 135.5, 135.9, 138.7; IR ν_{max} (film): 3329.72, 2945.21, 2833.17, 1652.89, 1449.08, 1399.28, 1113.07, 1017.05 cm^{-1}; HRMS m/z calcd for $C_{18}H_{15}F_3NO_2S$ $[M-H]^+$: 366.0776; found: 366.0777.

(*E*)-2-styryl-1-((trifluoromethyl)sulfonyl)-2,3-dihydro-1*H*-benzo[f]indole (5i): The product



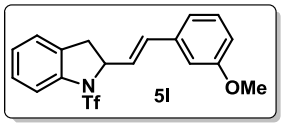
was obtained as a colorless oil. Yield: 75%; ^1H NMR (400 MHz, $CDCl_3$) δ 3.12 (d, *J* = 16.0 Hz, 1H), 3.73 (dd, *J* = 16.4 Hz, *J* = 9.2 Hz, 1H), 5.30 (t, *J* = 8.4 Hz, 1H), 6.20 (dd, *J* = 15.6 Hz, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 15.6 Hz, 1H), 7.20-7.33 (m, 5H), 7.43 (m, 2H), 7.68 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.87 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 35.5, 66.4, 112.6, 120.3 (q, *J* = 323.6 Hz), 124.8, 125.9, 126.6, 126.6, 126.9, 127.5, 128.1, 128.4, 128.7, 130.5, 131.7, 133.0, 133.5, 135.8, 137.2; IR ν_{max} (film): 3329.80, 2944.26, 2832.70, 1448.74, 1112.80, 1018.79 cm^{-1}; HRMS m/z calcd for $C_{21}H_{15}F_3NO_2S$ $[M-H]^+$: 402.0776; found: 402.0781.



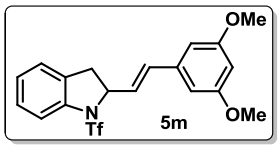
(*E*)-2-(4-methylstyryl)-1-((trifluoromethyl)sulfonyl)indoline (5j): The product was obtained as a colorless oil. Yield: 94%; ^1H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.96 (dd, *J* = 16.0 Hz, *J* = 1.2 Hz, 1H), 5.21 (t, *J* = 8.4 Hz, 1H), 6.14 (dd, *J* = 16.0 Hz, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H), 7.08-7.14 (m, 3H), 7.22-7.24 (m, 4H), 7.46 (d, *J* = 7.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 21.3, 35.8, 66.3, 115.7, 120.2 (q, *J* = 323.2 Hz), 125.7, 125.8, 126.8, 128.3, 129.4, 130.6, 132.8, 133.1,

138.3, 139.0; IR ν_{max} (film): 3362.97, 2987.34, 2900.27, 1394.98, 1225.68, 1193.32, 1142.08, 1100.70, 1065.72, 1049.87, 1026.80 cm^{-1}; HRMS m/z calcd for $C_{18}H_{15}F_3NO_2S$ $[M-H]^+$: 366.0776; found: 366.0772.

(*E*)-2-(4-methoxystyryl)-1-((trifluoromethyl)sulfonyl)indoline (5k): The product was obtained as a colorless oil. Yield: 83%; ^1H NMR (400 MHz, $CDCl_3$) δ 2.97 (dd, *J* = 16.0 Hz, *J* = 1.2 Hz, 1H), 3.62 (dd, *J* = 16.0 Hz, *J* = 9.2 Hz, 1H), 3.78 (s, 3H), 5.21 (t, *J* = 8.4 Hz, 1H), 6.06 (dd, *J* = 15.6 Hz, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 15.6 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.23-7.29 (m, 4H), 7.46 (d, *J* = 7.2 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 35.8, 55.4, 66.4, 114.2, 115.7, 120.2 (q, *J* = 323.8 Hz), 124.6, 125.6, 125.8, 128.1, 128.3, 128.6, 130.6, 132.5, 139.0, 159.9; IR ν_{max} (film): 3335.79, 2949.62, 1511.80, 1395.31, 1226.09, 1141.84, 1101.20, 1018.64 cm^{-1}; HRMS m/z calcd for $C_{18}H_{15}F_3NO_3S$ $[M-H]^+$: 382.0725; found: 382.0718.



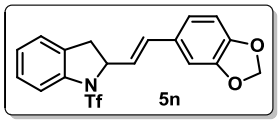
(*E*)-2-(3-methoxystyryl)-1-((trifluoromethyl)sulfonyl)indoline (5l): The product was obtained as a colorless oil. Yield: 81%; ^1H NMR (400 MHz, $CDCl_3$) δ 2.97 (dd, *J* = 16.0 Hz, *J* = 1.6 Hz, 1H), 3.63 (dd, *J* = 16.0 Hz, *J* = 9.2 Hz, 1H), 3.77 (s, 3H), 5.22 (t, *J* = 8.4 Hz, 1H), 6.19 (dd, *J* = 15.6 Hz, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.80 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 6.87 (s, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 7.12-7.25 (m, 5H), 7.47 (d, *J* = 7.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 35.7, 55.3, 66.1, 112.0, 114.2, 115.7, 119.5, 120.2 (q, *J* = 323.3 Hz), 125.7, 125.8, 127.1, 128.3, 129.1, 129.7, 130.5, 132.8, 137.3, 159.9; IR ν_{max} (film): 2987.34, 2900.30, 1394.34, 1226.11, 1193.29, 1141.63, 1100.68, 1065.74, 1049.71, 1026.90 cm^{-1}; HRMS m/z calcd for $C_{18}H_{15}F_3NO_3S$ $[M-H]^+$: 382.0725; found: 382.0723.



(*E*)-2-(3,5-dimethoxystyryl)-1-((trifluoromethyl)sulfonyl)indoline (5m): The product was obtained as a colorless oil. Yield: 81%; ^1H NMR (400 MHz, $CDCl_3$) δ 2.98 (dd, *J* = 16.0 Hz, *J* = 1.6 Hz, 1H), 3.64 (dd, *J* = 9.2 Hz, *J* = 1.6 Hz, 1H), 3.77 (s, 6H), 5.22 (t, *J* = 8.0 Hz, 1H), 6.18 (dd, *J* = 15.6 Hz, *J* = 8.0 Hz, 1H), 6.38 (t, *J* = 2.0 Hz, 1H), 6.50 (d, *J* = 2.0 Hz, 2H), 6.60 (d, *J* = 15.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.24-7.27 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 35.7, 55.5, 66.0, 100.8, 104.9, 115.7, 120.2 (q, *J* = 324.2 Hz), 125.7, 125.9, 127.3, 128.4, 130.5, 132.9, 137.9, 139.0, 161.1; IR ν_{max} (film): 2920.23, 2850.49, 1591.07, 1457.69, 1425.47, 1394.45, 1326.37,

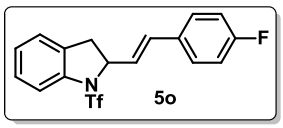
1295.68, 1224.45, 1191.94, 1140.94, 1100.15, 1065.25, 1023.46, 963.21, 829.36, 754.50 cm^{-1}; HRMS m/z calcd for $C_{19}H_{19}F_3NO_4S$ $[M+H]^+$: 414.0981; found: 414.0980.

(*E*)-2-(2-(benzo[d][1,3]dioxol-5-yl)vinyl)-1-((trifluoromethyl)sulfonyl)indoline (5n): The



5n

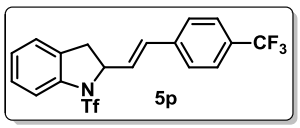
product was obtained as a colorless oil. Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96 (dd, *J* = 16.0 Hz, *J* = 1.6 Hz, 1H), 3.61 (dd, *J* = 16.0 Hz, *J* = 9.2 Hz, 1H), 5.19 (t, *J* = 8.4 Hz, 1H), 5.90 (s, 2H), 6.01 (dd, *J* = 15.6 Hz, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.22-7.25 (m, 2H), 7.45 (d, *J* = 7.2 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 35.8, 66.2, 101.3, 105.9, 108.4, 115.6, 120.2 (q, *J* = 329.3 Hz), 121.9, 125.0, 125.7, 125.8, 128.3, 130.2, 130.5, 132.6, 139.0, 147.9, 148.2; IR ν_{max} (film): 2899.94, 1504.14, 1488.84, 1480.08, 1461.85, 1446.43, 1249.80, 1223.08, 1189.30, 1140.39, 1099.87, 1023.43, 960.95, 929.49, 905.75, 864.69 cm^{-1}; HRMS m/z calcd for $C_{18}H_{13}F_3NO_4S$ $[M-H]^+$: 397.0606; found: 397.0605.



5o

(*E*)-2-(4-fluorostyryl)-1-((trifluoromethyl)sulfonyl)indoline (5o): The product was obtained as a colorless oil. Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (d, *J* = 16.0 Hz, *J* = 1.6 Hz, 1H), 3.64 (dd, *J* = 16.0 Hz, *J* = 9.2 Hz, 1H), 5.22 (t, *J* = 8.4 Hz, 1H), 6.12 (dd, *J* = 15.6 Hz, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.98 (t, *J* = 8.4 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.24-7.27 (m, 2H), 7.30-7.33 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 35.7, 66.1, 115.7 (d, *J* = 21.5 Hz), 115.7, 120.2 (q, *J* = 323.1 Hz), 125.8, 125.9, 126.6, 128.4, 128.4, 128.5, 130.4, 131.8, 132.0 (d, *J* = 2.9 Hz), 139.0, 162.8 (d, *J* = 246.4 Hz); IR ν_{max} (film): 3365.81, 2987.25, 1508.27, 1480.24, 1396.15, 1227.38, 1194.20, 1141.97, 1101.15, 1023.52, 965.11 cm^{-1}; HRMS m/z calcd for $C_{17}H_{12}F_4NO_2S$ $[M-H]^+$: 370.0525; found: 370.0524.

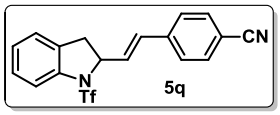
(*E*)-2-(4-(trifluoromethyl)styryl)-1-((trifluoromethyl)sulfonyl)indoline (5p): The product was



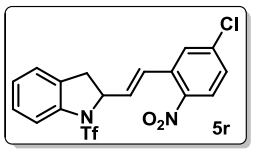
5p

obtained as a white solid. Yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00 (d, *J* = 16.0 Hz, 1H), 3.68 (dd, *J* = 16.0 Hz, *J* = 9.6 Hz, 1H), 5.26 (t, *J* = 8.4 Hz, 1H), 6.30 (dd, *J* = 16.0 Hz, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 16.0 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.26-7.29 (m, 2H), 7.44-7.49 (m, 3H), 7.55 (d, *J* = 8.4 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 35.7, 65.7, 115.8, 120.2 (q, *J* = 325.2 Hz), 124.2 (q, *J* = 270.3 Hz), 125.7 (q, *J* = 3.8 Hz), 125.9, 125.9, 127.1, 128.5, 129.5, 130.2, 130.2 (q, *J* = 32.4 Hz), 131.5, 139.0, 139.4; IR ν_{max} (film): 3330.72, 2944.85, 2833.25, 1448.43, 1404.49, 1017.86 cm^{-1}; HRMS m/z calcd for $C_{18}H_{12}F_6NO_2S$ $[M-H]^+$: 420.0493; found: 420.0497.

(*E*)-4-(2-(1-((trifluoromethyl)sulfonyl)indolin-2-yl)vinyl)benzonitrile (5q): The product was

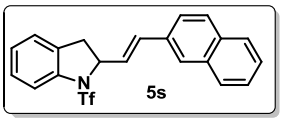


obtained as a colorless oil. Yield: 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.02 (dd, *J* = 16.0 Hz, *J* = 2.0 Hz, 1H), 3.71 (dd, *J* = 16.0 Hz, *J* = 9.6 Hz, 1H), 5.28 (t, *J* = 8.0 Hz, 1H), 6.35 (dd, *J* = 16.0 Hz, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.28-7.32 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 35.6, 65.5, 111.7, 115.7, 118.8, 120.2 (q, *J* = 323.1 Hz), 125.9, 126.0, 127.4, 128.6, 130.1, 130.7, 131.1, 132.6, 138.9, 140.3; IR ν_{max} (film): 3335.36, 2987.17, 1652.58, 1394.98, 1226.11, 1100.81, 1018.95 cm^{-1}; HRMS m/z calcd for $C_{18}H_{12}F_3N_2O_2S$ $[M-H]^+$: 377.0575; found: 377.0576.



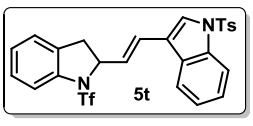
(*E*)-2-(5-chloro-2-nitrostyryl)-1-((trifluoromethyl)sulfonyl)indoline (5r): The product was obtained as a colorless oil. Yield: 45%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (dd, *J* = 16.0 Hz, *J* = 2.0 Hz, 1H), 3.71 (dd, *J* = 16.0 Hz, *J* = 9.2 Hz, 1H), 5.28 (t, *J* = 8.0 Hz, 1H), 6.20 (dd, *J* = 15.6 Hz, *J* = 8.0 Hz, 1H), 7.15-7.20 (m, 2H), 7.26-7.30 (m, 2H), 7.37-7.39 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 7.48-7.51 (m, 2H), 7.95 (d, *J* = 8.4 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 35.6, 65.3, 115.7, 120.2 (q, *J* = 323.3 Hz), 125.9, 126.0, 126.5, 127.7, 128.6, 128.9, 129.0, 130.0, 133.3, 133.9, 138.9, 139.9, 146.0; IR ν_{max} (film): 2987.28, 2900.15, 2361.83, 1558.49, 1540.10, 1521.11, 1507.01, 1394.59, 1227.22, 1065.78 cm^{-1}; HRMS m/z calcd for $C_{17}H_{11}ClF_3N_2O_4S$ $[M-H]^+$: 431.0092; found: 431.0092.

(*E*)-2-(2-(naphthalen-2-yl)vinyl)-1-((trifluoromethyl)sulfonyl)indoline (5s): The product was



obtained as a colorless oil. Yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (dd, *J* = 16.0 Hz, *J* = 1.6 Hz, 1H), 3.62 (dd, *J* = 16.0 Hz, *J* = 9.2 Hz, 1H), 5.26 (t, *J* = 8.4 Hz, 1H), 6.29 (dd, *J* = 16.0 Hz, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.22-7.26 (m, 2H), 7.39-7.44 (m, 2H), 7.49 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.70-7.75 (m, 4H); ^{13}C (100 MHz, $CDCl_3$) δ 35.7, 66.2, 115.7, 120.2 (q, *J* = 324.6 Hz), 123.5, 125.7, 125.9, 126.3, 126.5, 127.1, 127.3, 127.8, 128.2, 128.4, 128.4, 130.5, 133.0, 133.3, 133.4, 133.6, 139.0; IR ν_{max} (film): 3362.42, 2987.28, 1394.77, 1225.71, 1193.62, 1141.27, 1100.74, 1065.71, 1025.81 cm^{-1}; HRMS m/z calcd for $C_{21}H_{15}F_3NO_2S$ $[M-H]^+$: 402.0776; found: 402.0777.

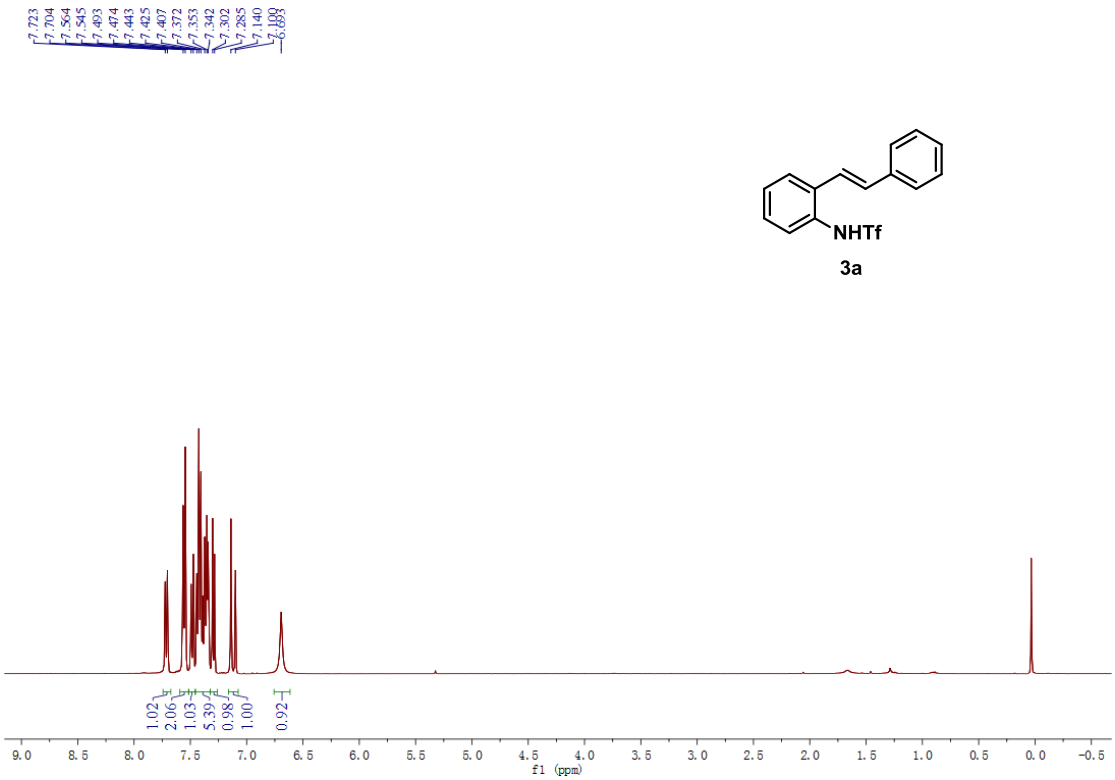
(*E*)-1-tosyl-3-(2-(1-((trifluoromethyl)sulfonyl)indolin-2-yl)vinyl)-1*H*-indole (5t): The product



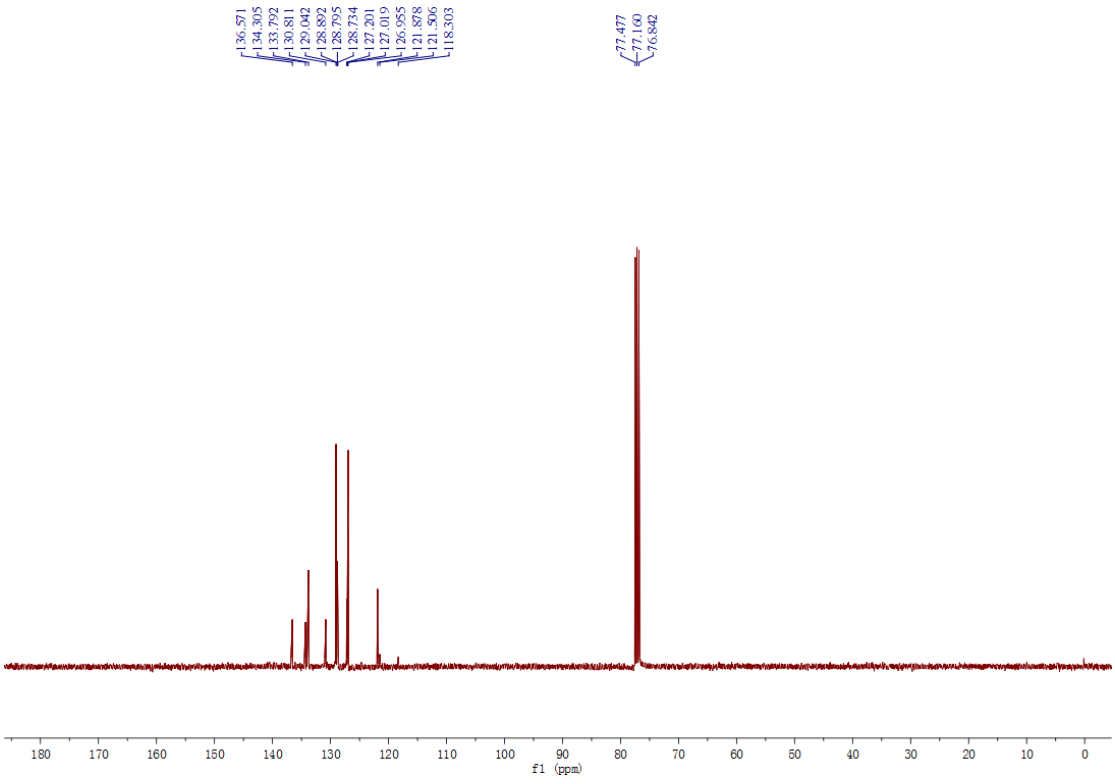
was obtained as a colorless oil. Yield: 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 3.00 (dd, *J* = 16.0 Hz, *J* = 1.6 Hz, 1H), 3.66 (dd, *J* = 16.0

Hz, *J* = 9.6 Hz, 1H), 5.24 (t, *J* = 8.4 Hz, 1H), 6.27 (dd, *J* = 16.0 Hz, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 15.6 Hz, 1H), 7.13-7.33 (m, 8H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.59 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 21.6, 35.8, 66.4, 113.8, 115.7, 119.1, 120.2 (q, *J* = 322.5 Hz), 120.4, 123.7, 125.0, 125.2, 125.8, 125.9, 127.0, 127.9, 128.3, 128.4, 128.7, 129.1, 130.1, 130.4, 135.1, 135.5, 145.3; IR ν_{max} (film): 3361.95, 2987.48, 1652.82, 1394.56, 1224.90, 1175.50, 1141.80, 1018.18 cm^{-1}; HRMS m/z calcd for $C_{26}H_{22}F_3N_2O_4S_2$ $[M+H]^+$: 547.0973; found: 547.0969.

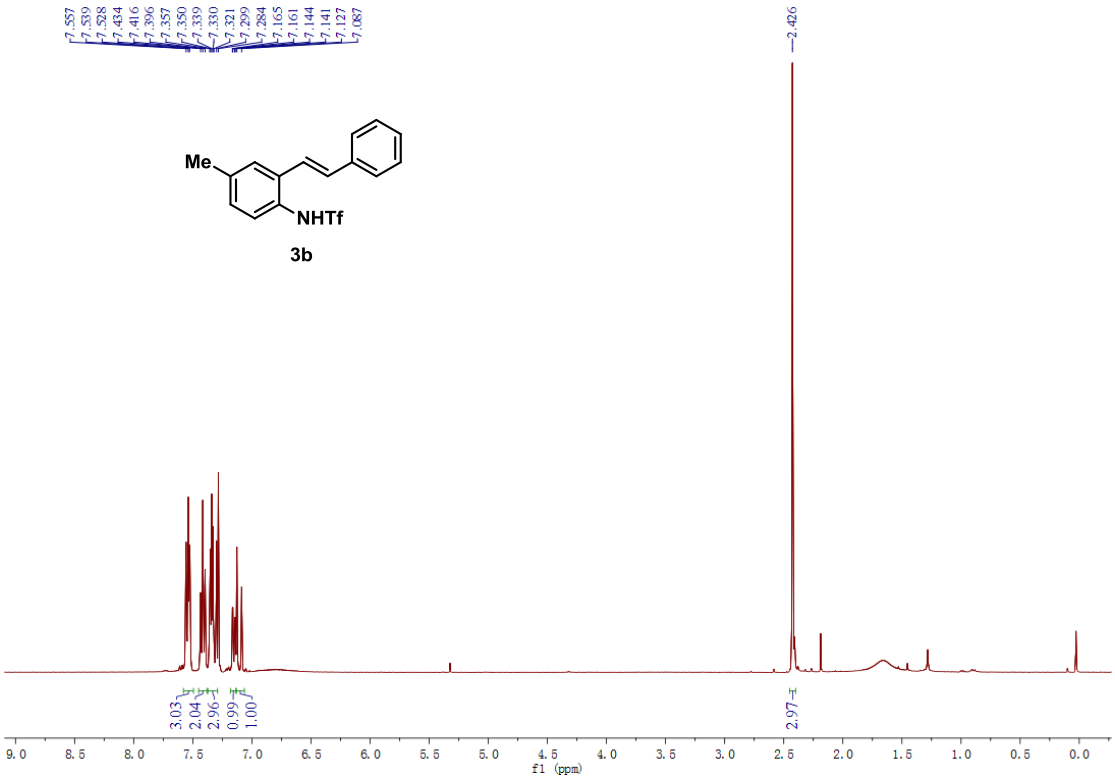
6. NMR Spectra of the Pd-Catalyzed Denitrogenative Alkenylation Products



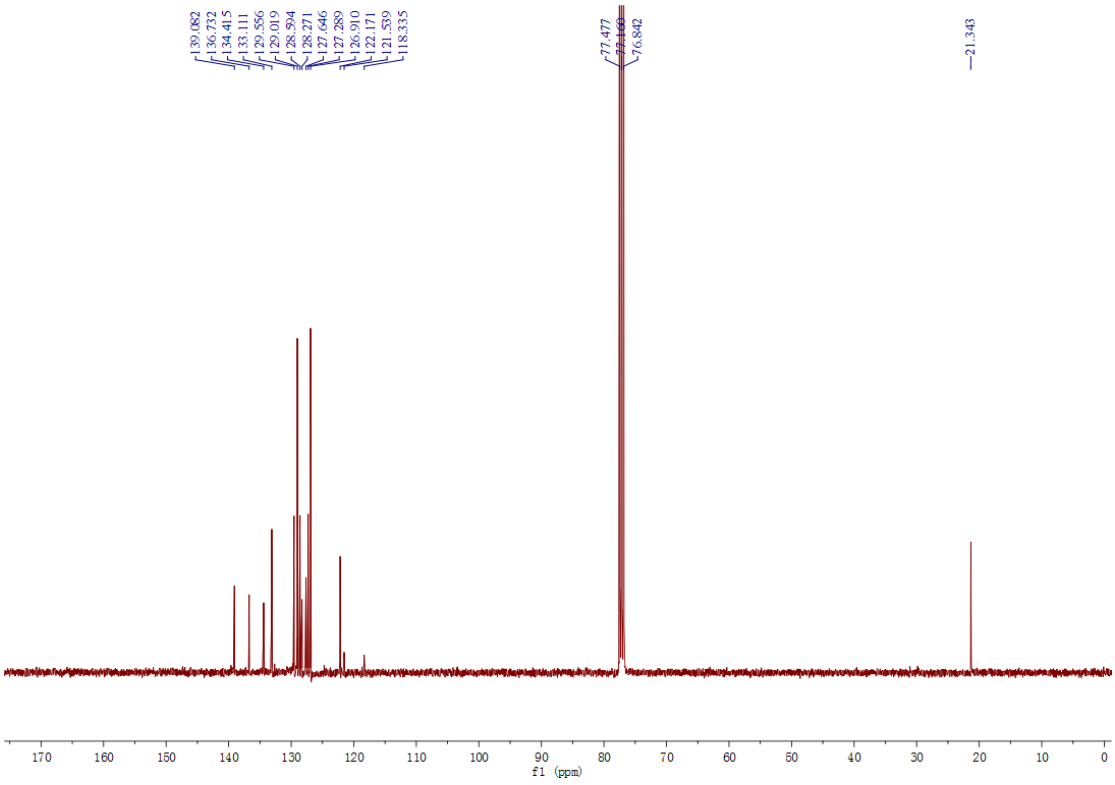
^{1}H NMR Spectrum for **3a** ($CDCl_3$, 400 MHz)



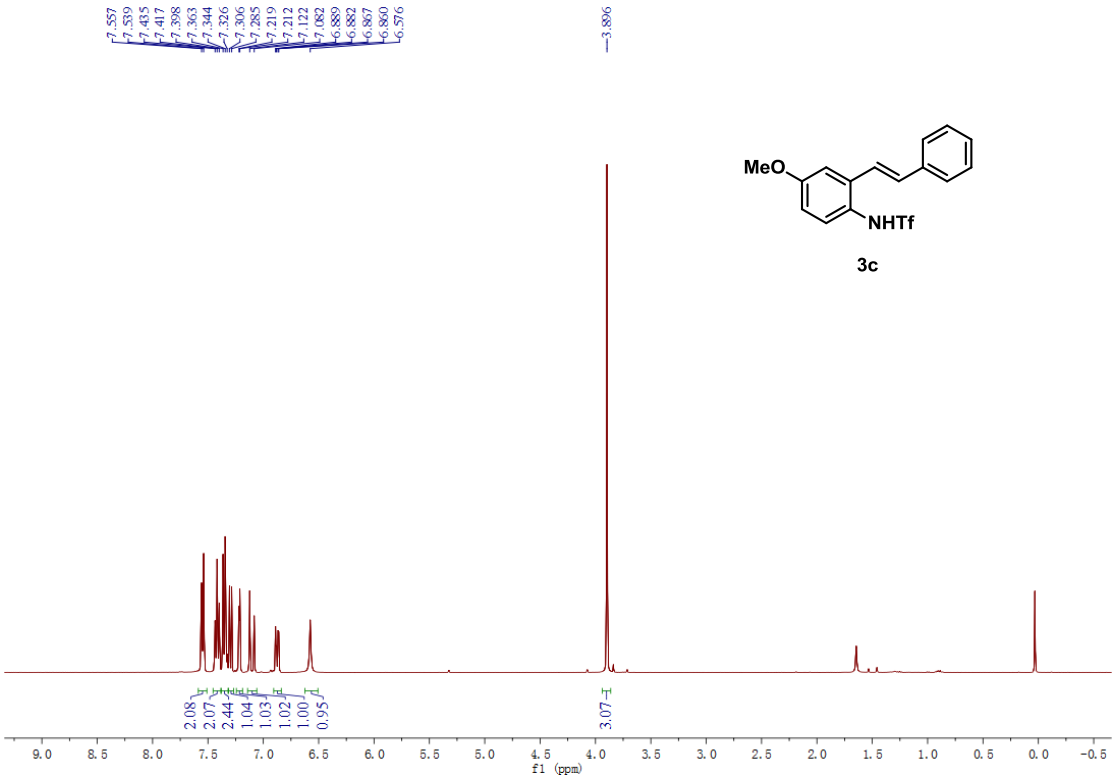
^{13}C NMR Spectrum for **3a** ($CDCl_3$, 100 MHz)



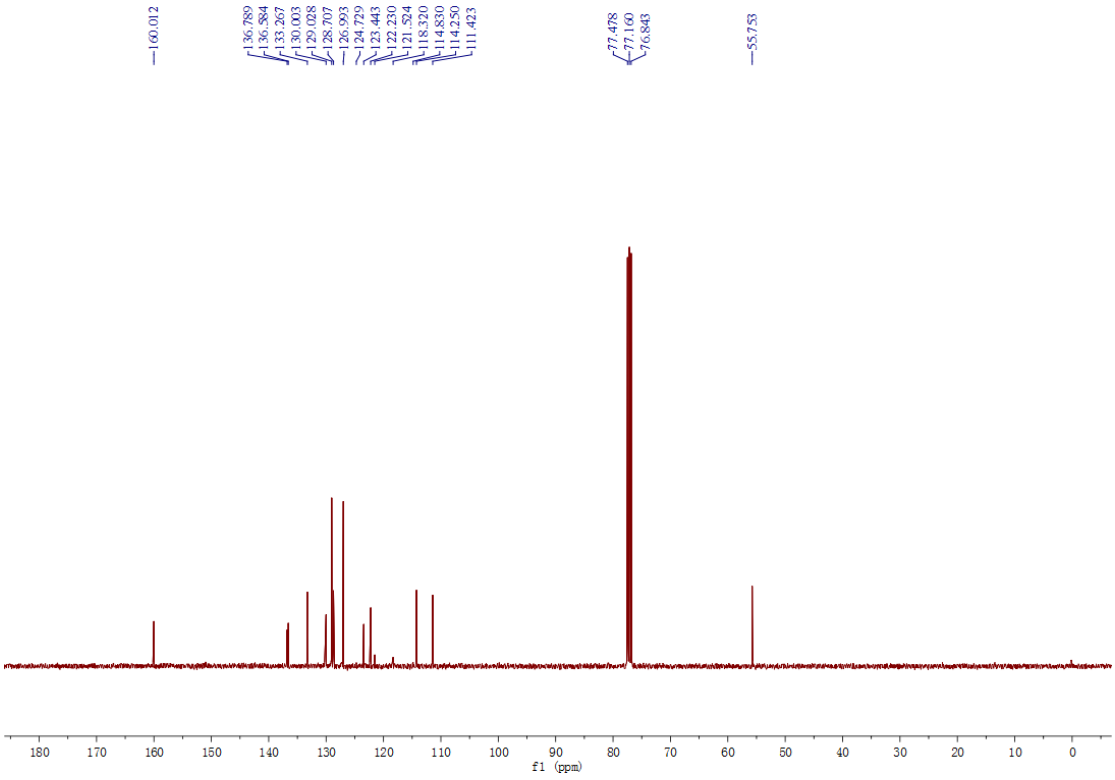
^{1}H NMR Spectrum for **3b** ($CDCl_3$, 400 MHz)



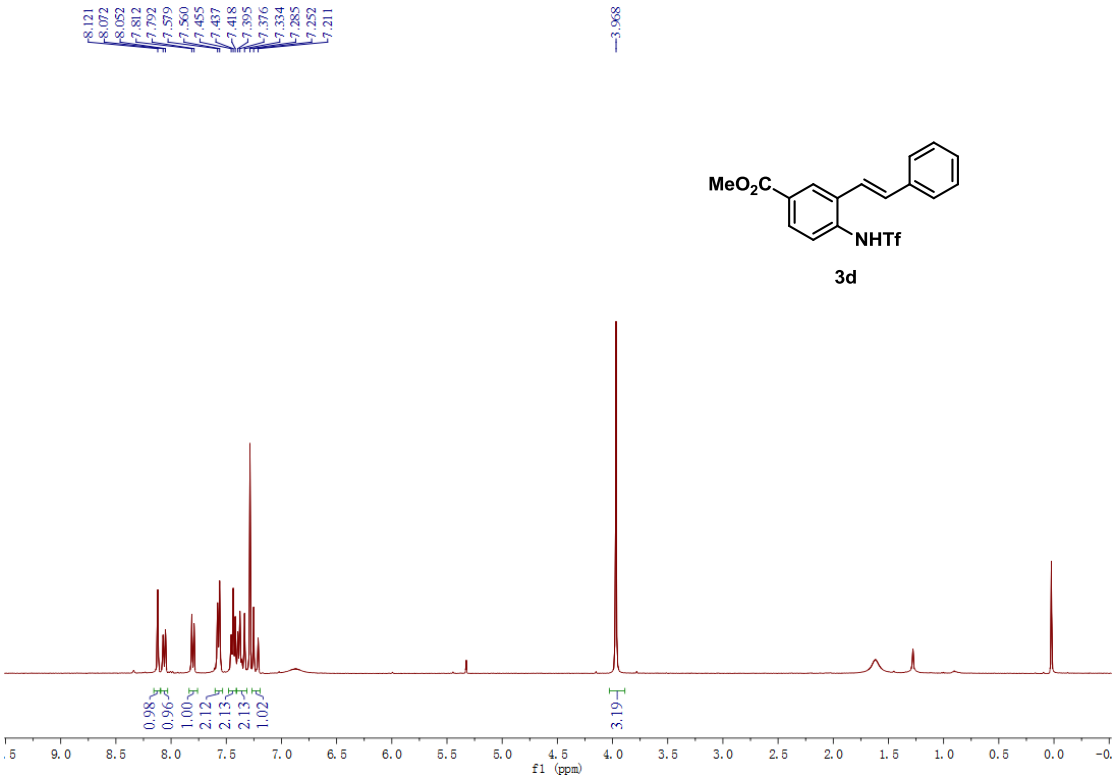
^{13}C NMR Spectrum for **3b** ($CDCl_3$, 100 MHz)



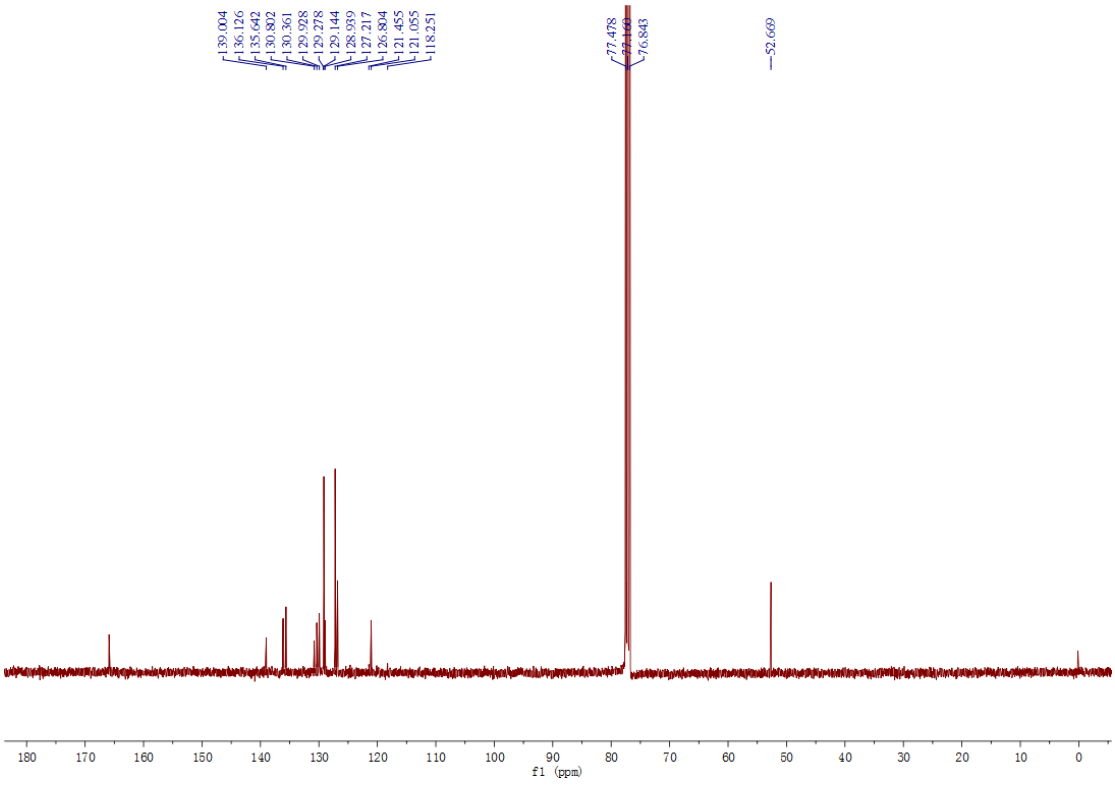
^{1}H NMR Spectrum for **3c** ($CDCl_3$, 400 MHz)



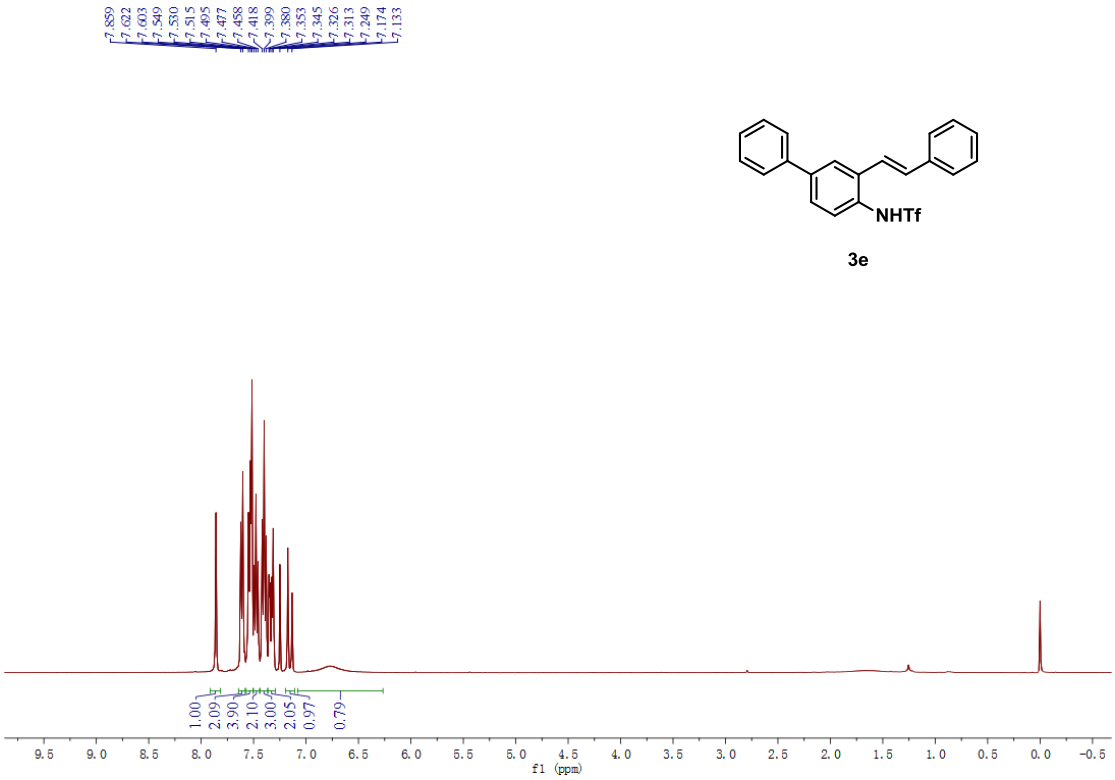
^{13}C NMR Spectrum for **3c** ($CDCl_3$, 100 MHz)



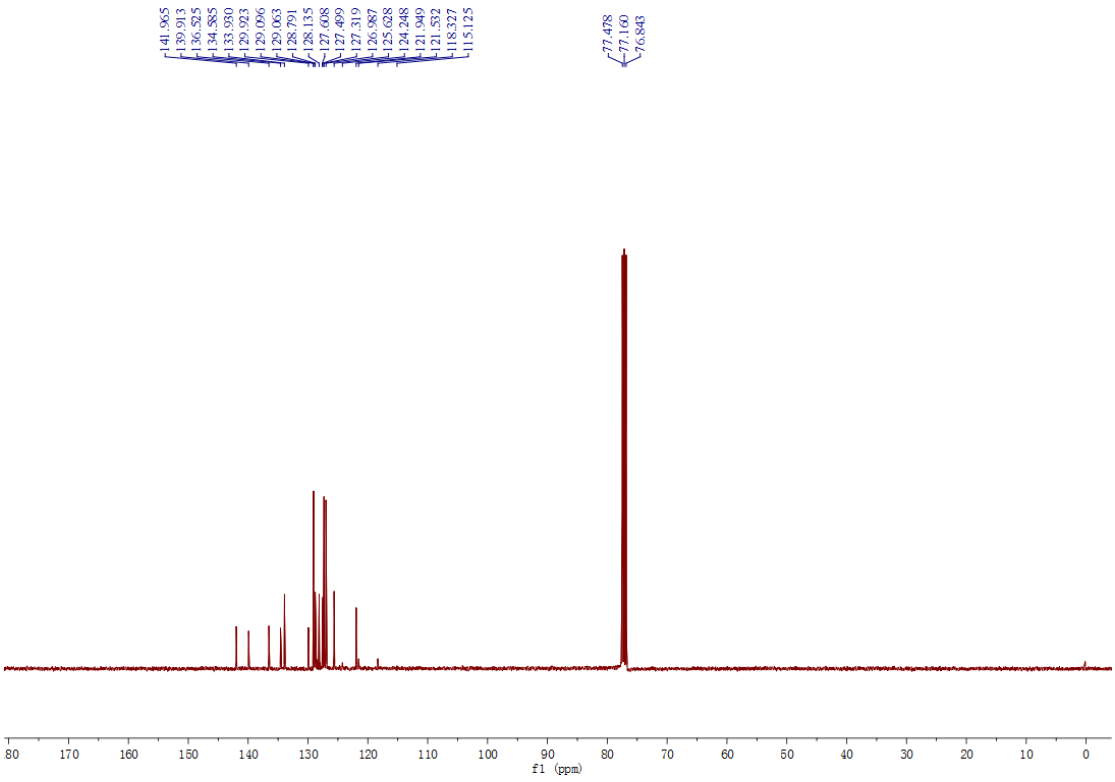
^{1}H NMR Spectrum for **3d** ($CDCl_3$, 400 MHz)



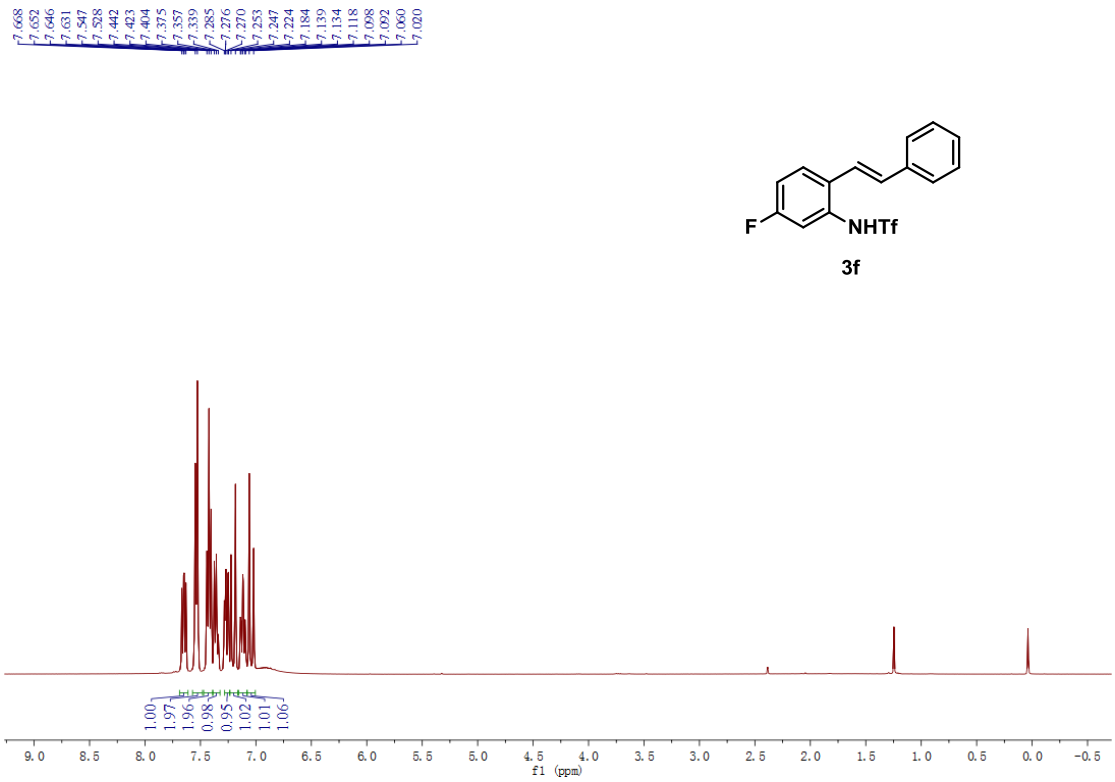
^{13}C NMR Spectrum for **3d** ($CDCl_3$, 100 MHz)



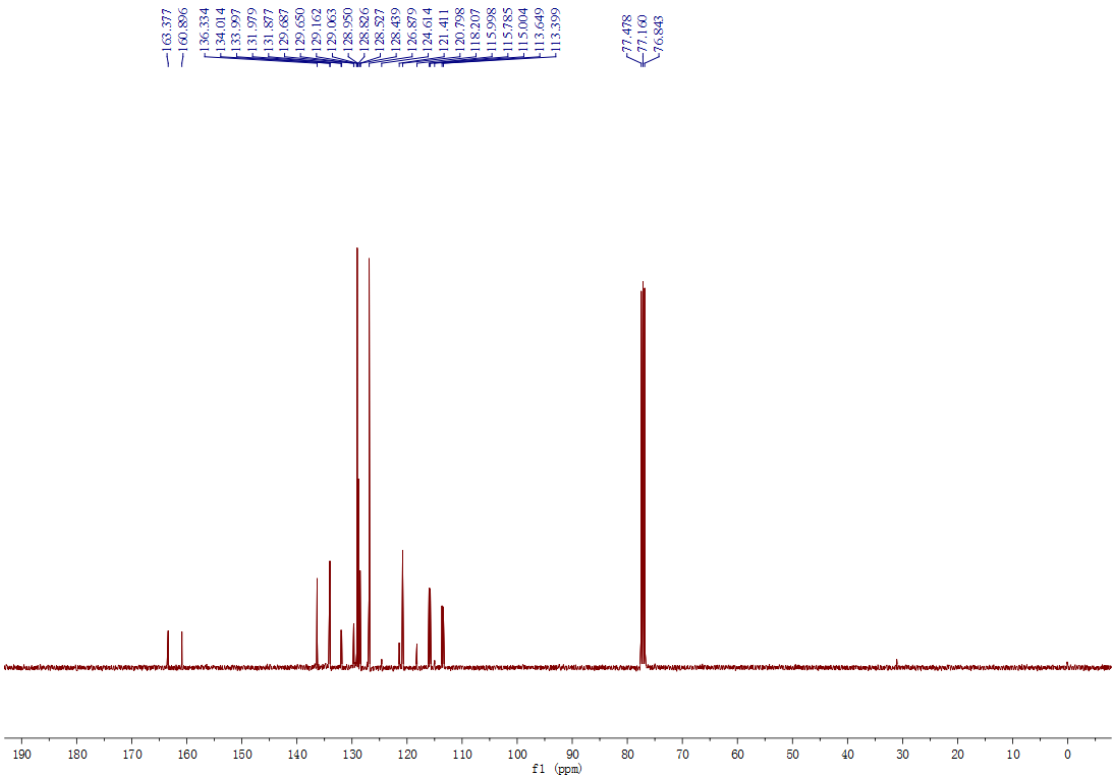
^{1}H NMR Spectrum for **3e** ($CDCl_3$, 400 MHz)



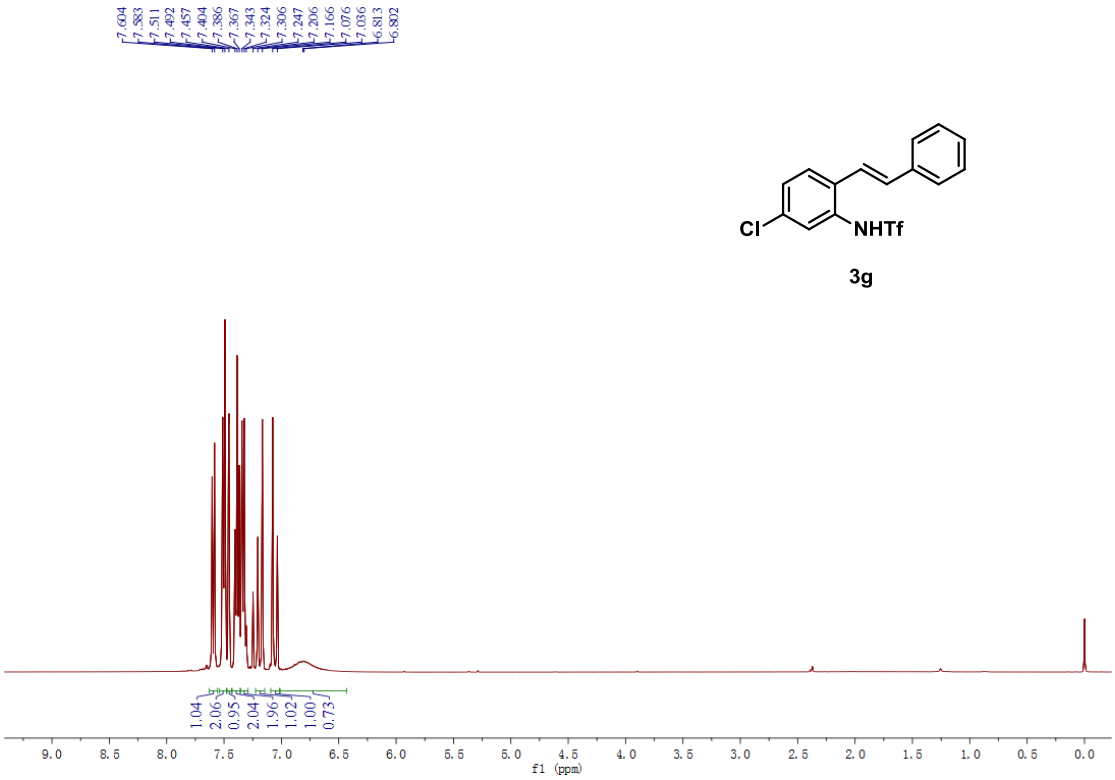
^{13}C NMR Spectrum for **3e** ($CDCl_3$, 100 MHz)



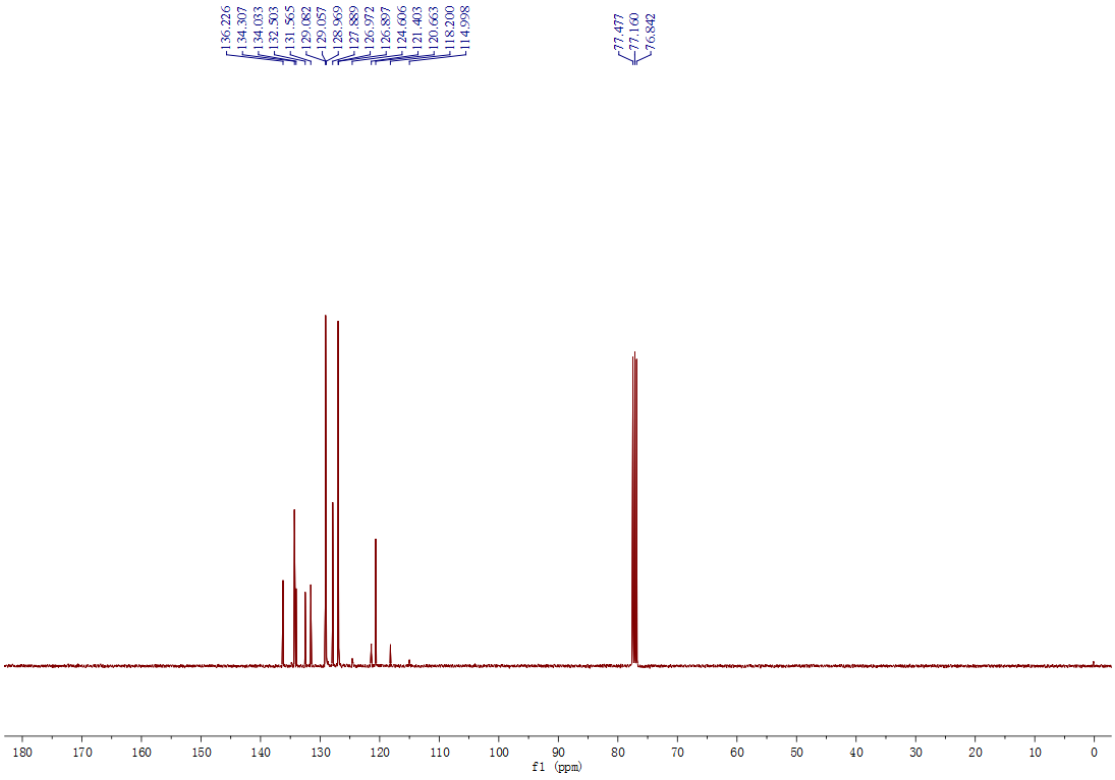
^{1}H NMR Spectrum for **3f** ($CDCl_3$, 400 MHz)



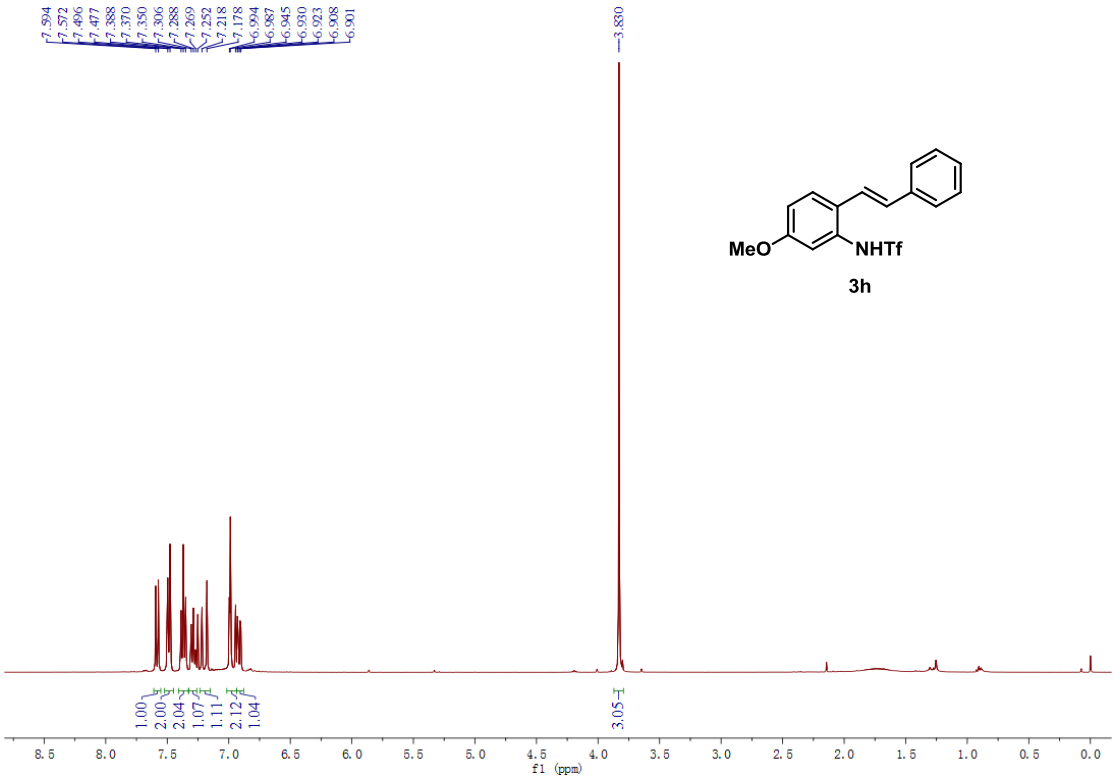
^{13}C NMR Spectrum for **3f** ($CDCl_3$, 100 MHz)



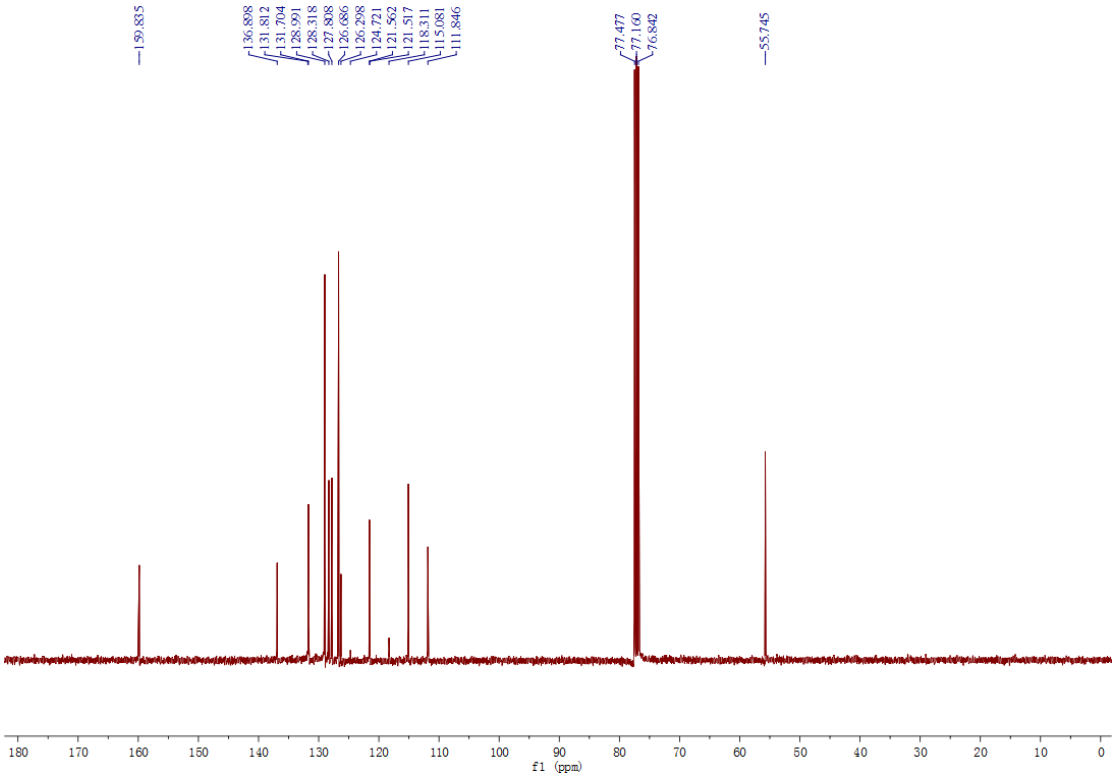
^{1}H NMR Spectrum for **3g** ($CDCl_3$, 400 MHz)



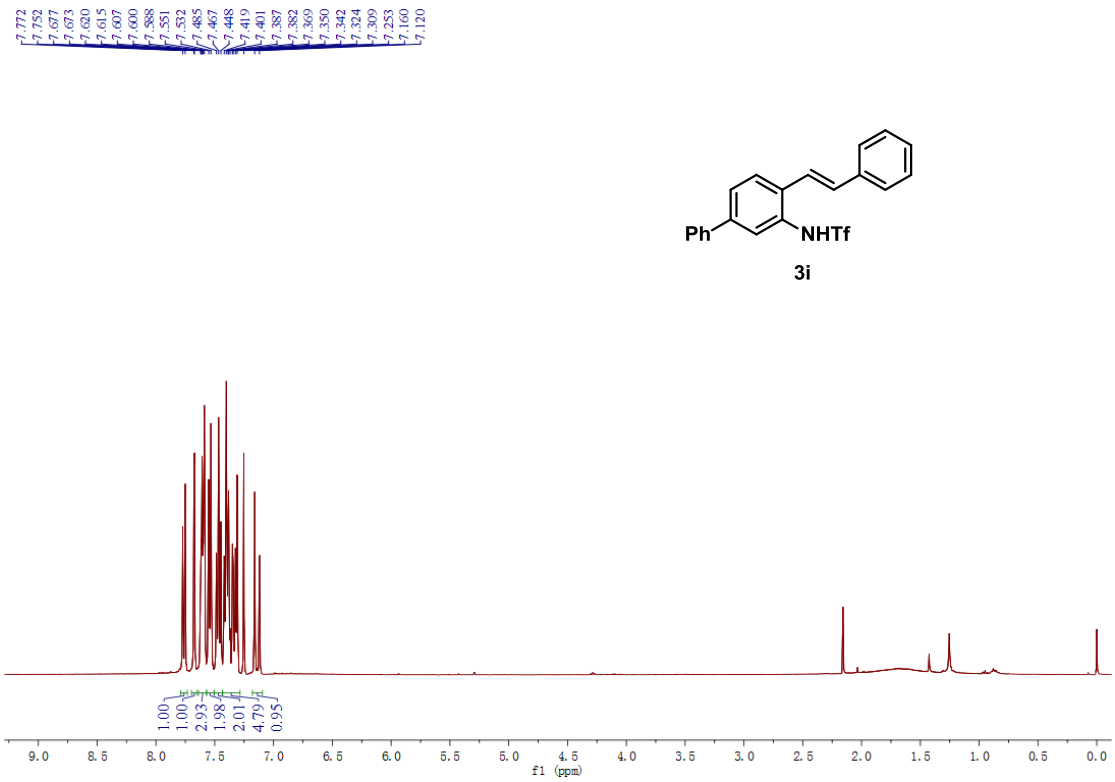
^{13}C NMR Spectrum for **3g** ($CDCl_3$, 100 MHz)



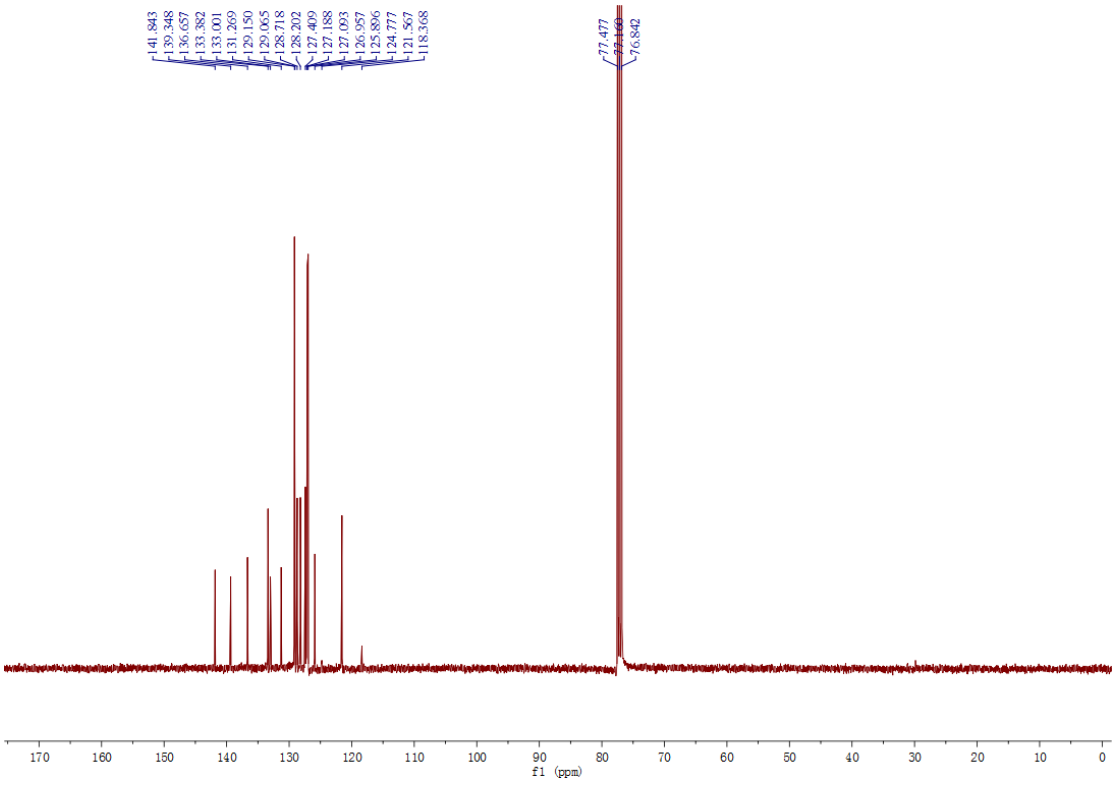
^{1}H NMR Spectrum for **3h** ($CDCl_3$, 400 MHz)



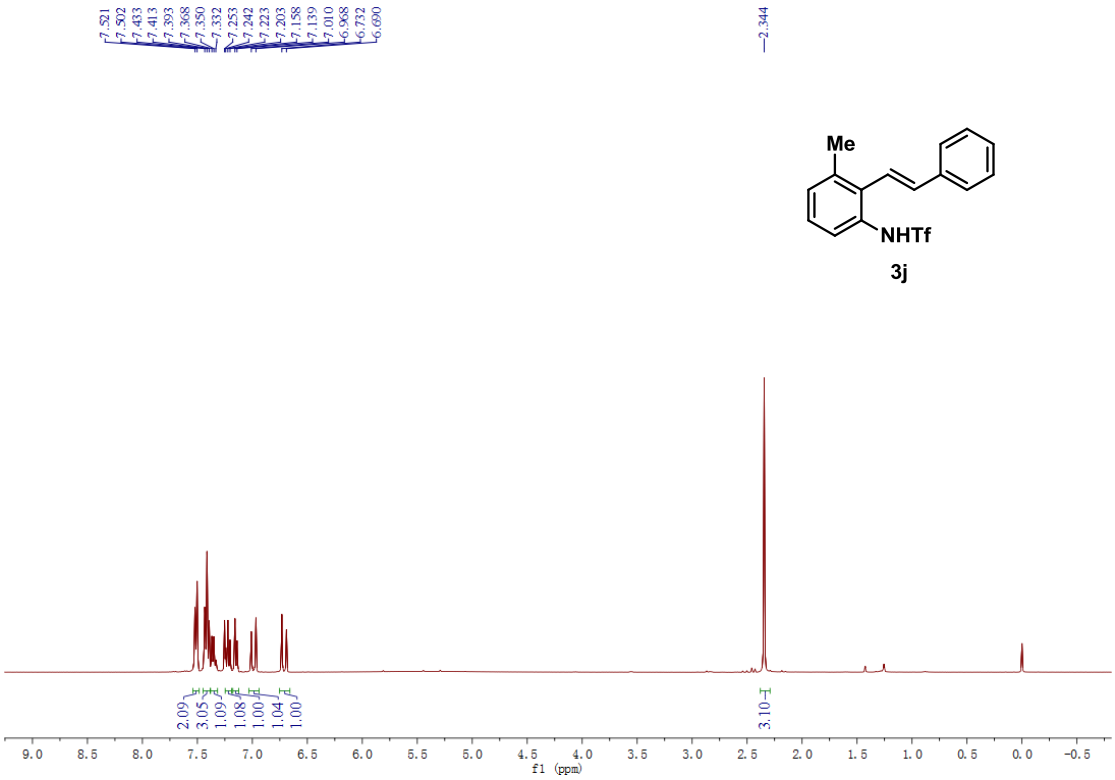
^{13}C NMR Spectrum for **3h** ($CDCl_3$, 100 MHz)



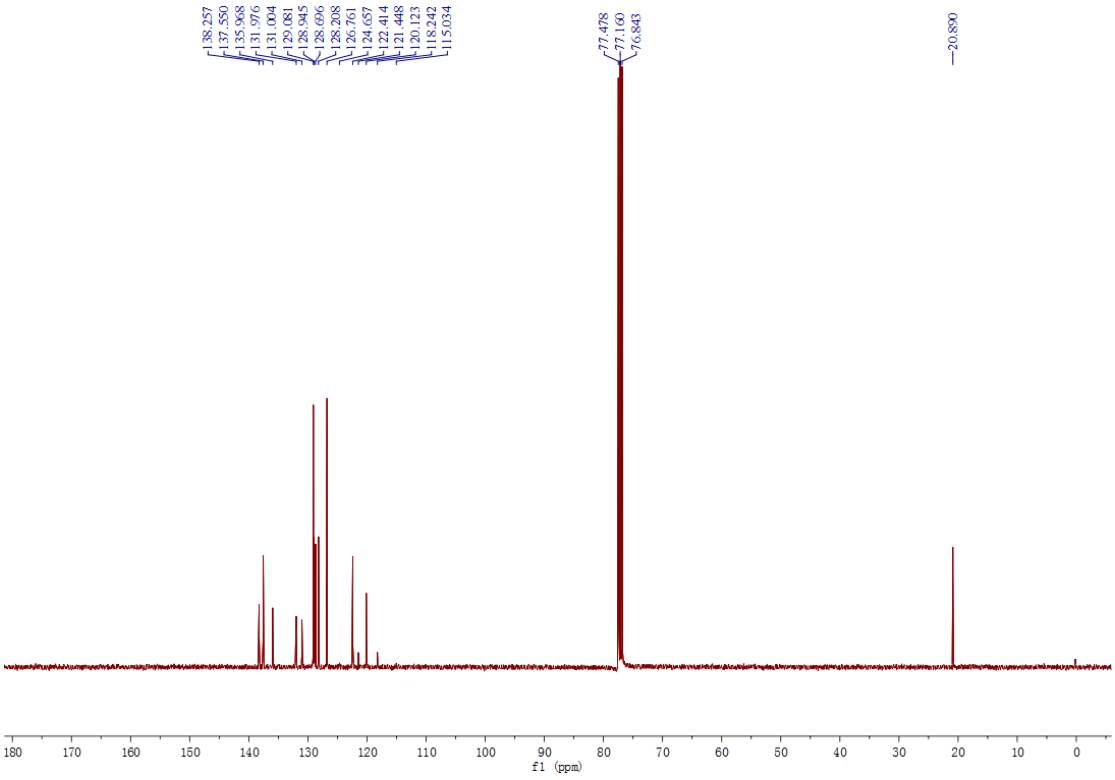
^{1}H NMR Spectrum for **3i** ($CDCl_3$, 400 MHz)



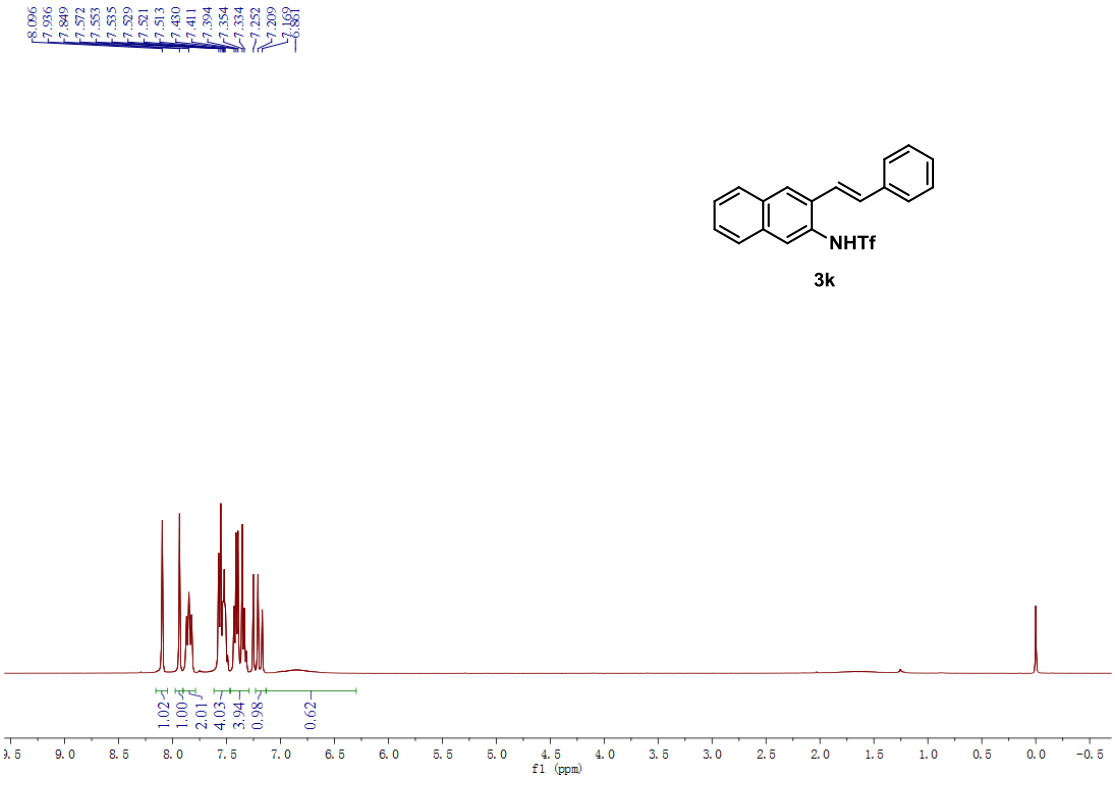
^{13}C NMR Spectrum for **3i** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum for **3j** ($CDCl_3$, 400 MHz)

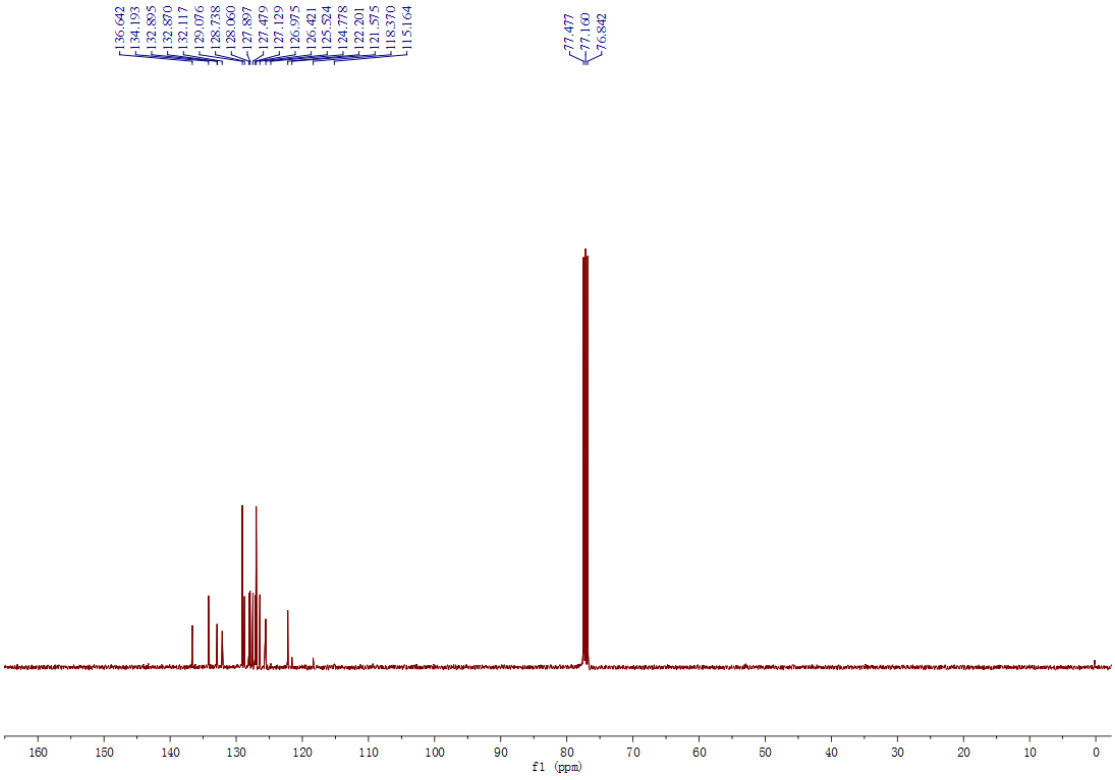


^{13}C NMR Spectrum for **3j** ($CDCl_3$, 100 MHz)

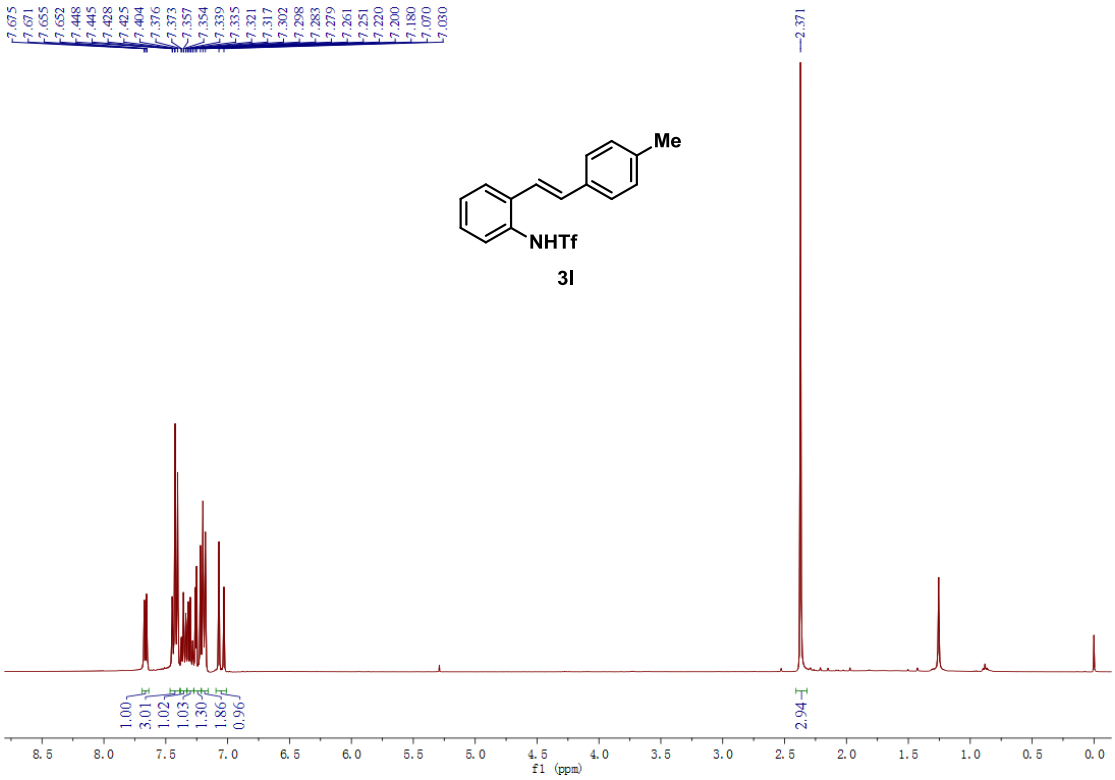


3k

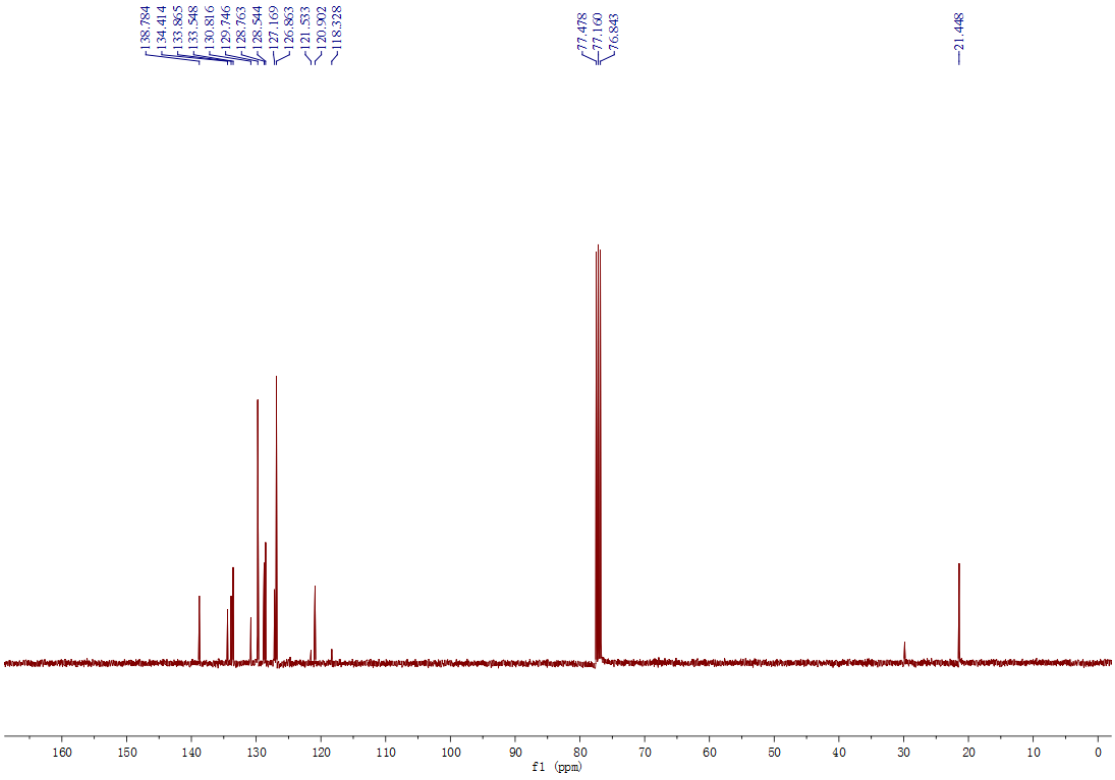
^{1}H NMR Spectrum for **3k** ($CDCl_3$, 400 MHz)



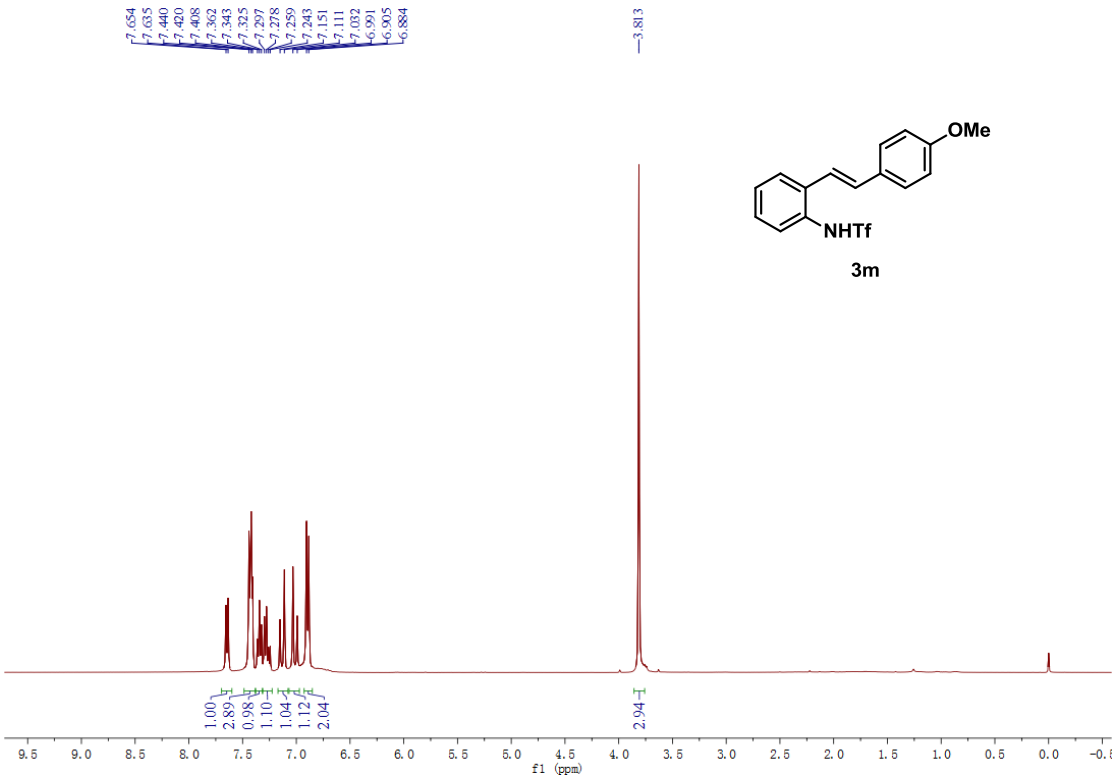
^{13}C NMR Spectrum for **3k** ($CDCl_3$, 100 MHz)



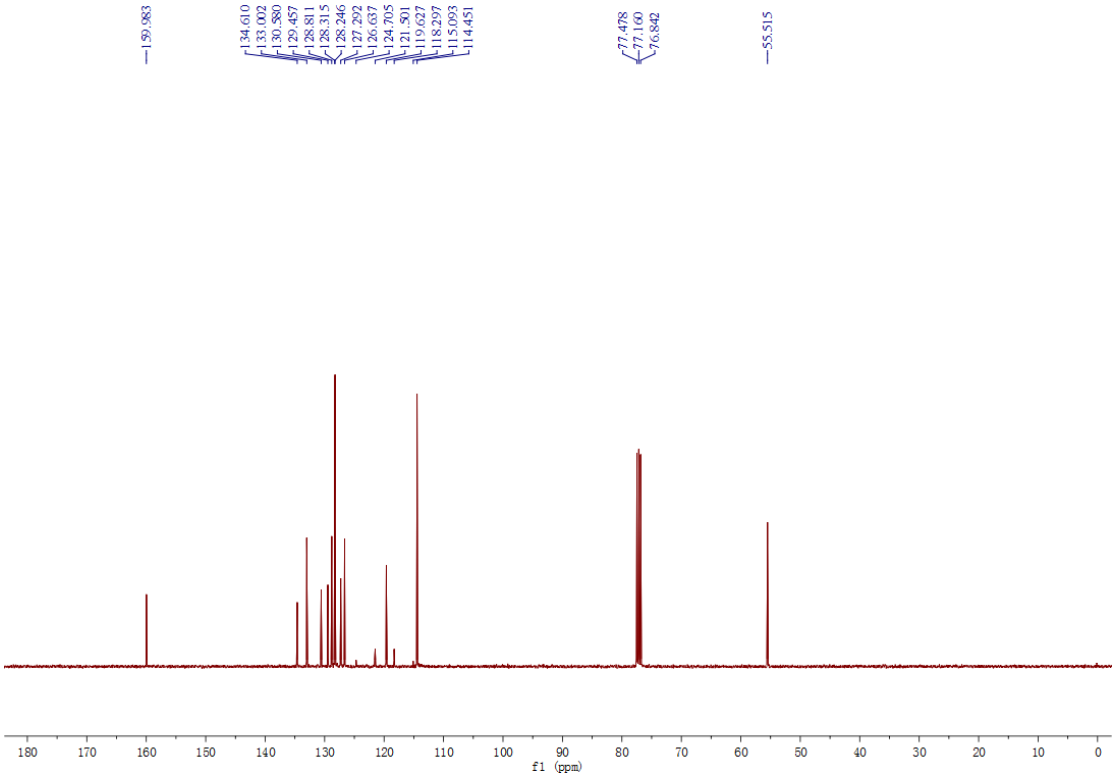
^{1}H NMR Spectrum for **3l** ($CDCl_3$, 400 MHz)



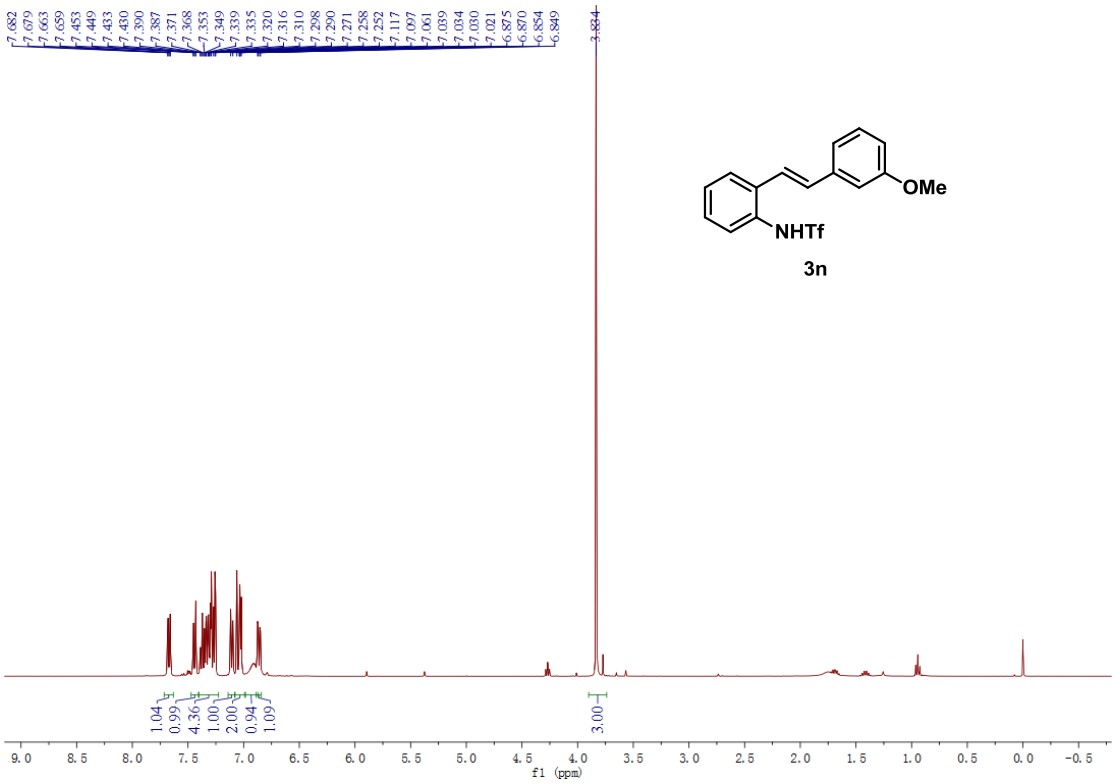
^{13}C NMR Spectrum for **3l** ($CDCl_3$, 100 MHz)



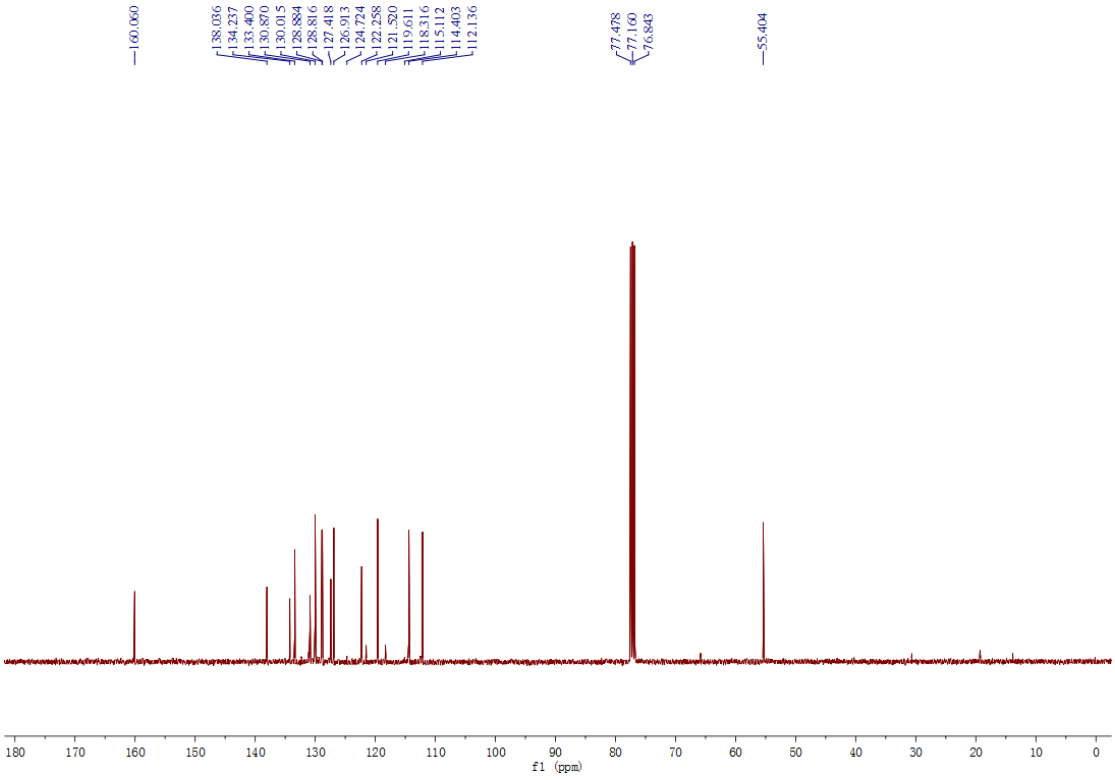
^{1}H NMR Spectrum for **3m** ($CDCl_3$, 400 MHz)



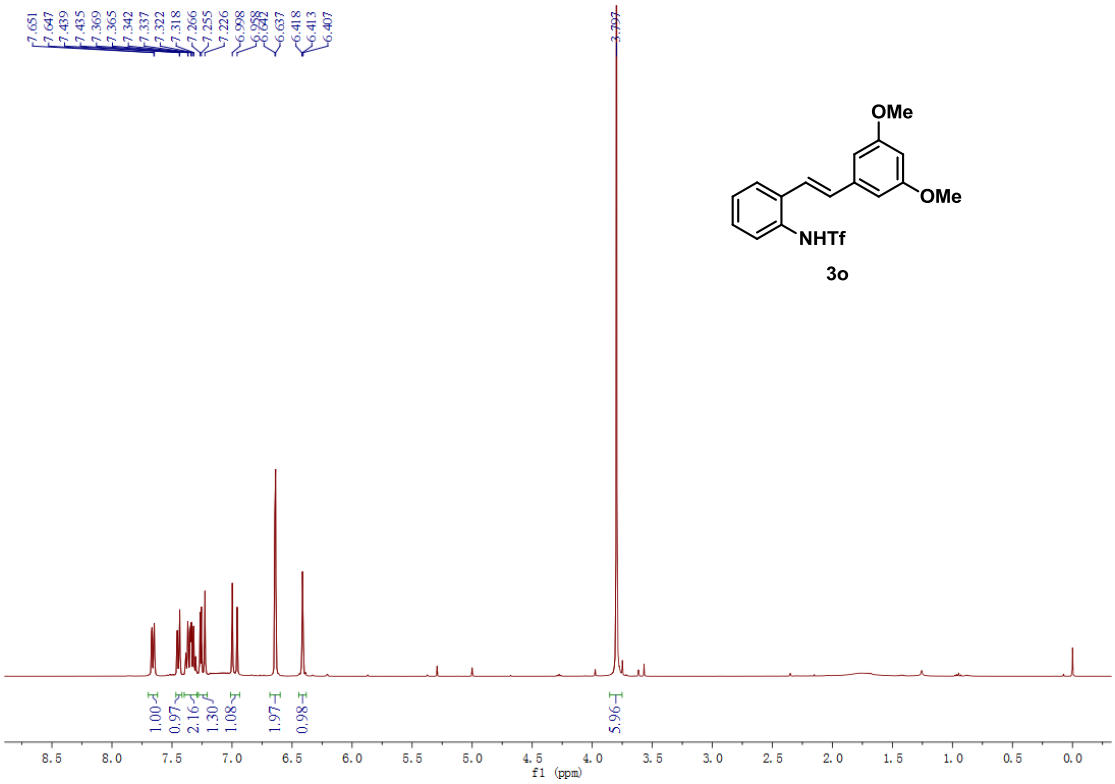
^{13}C NMR Spectrum for **3m** ($CDCl_3$, 100 MHz)



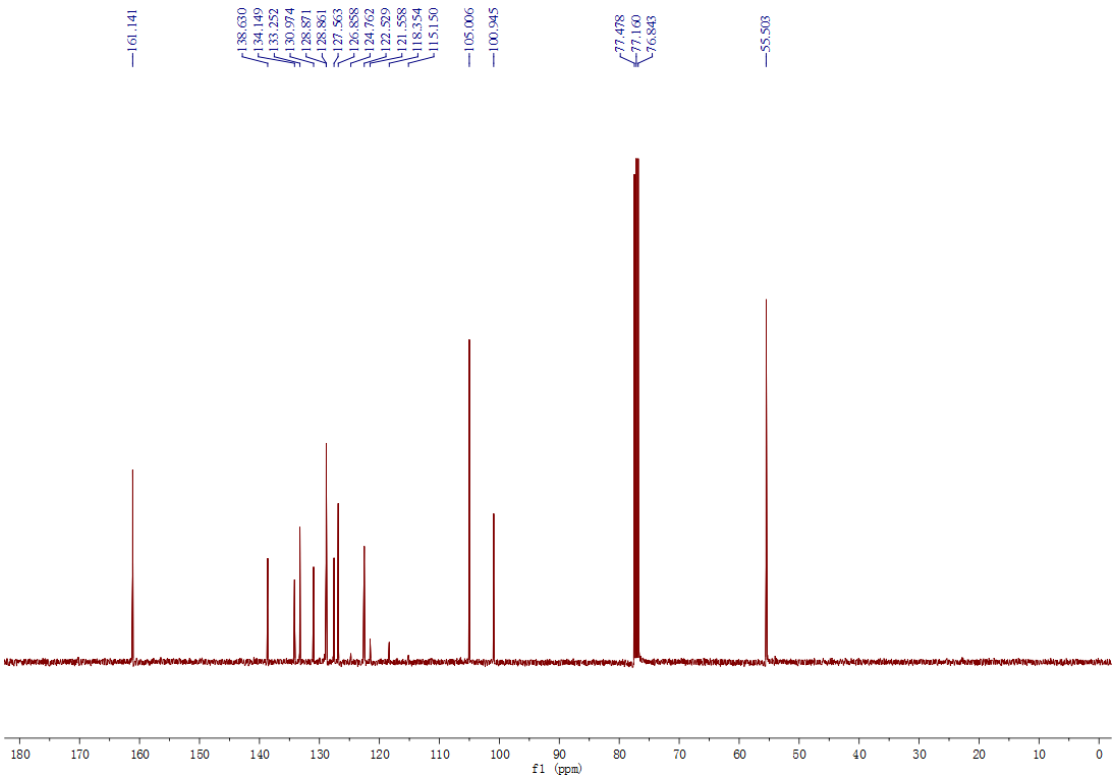
^{1}H NMR Spectrum for **3n** ($CDCl_3$, 400 MHz)



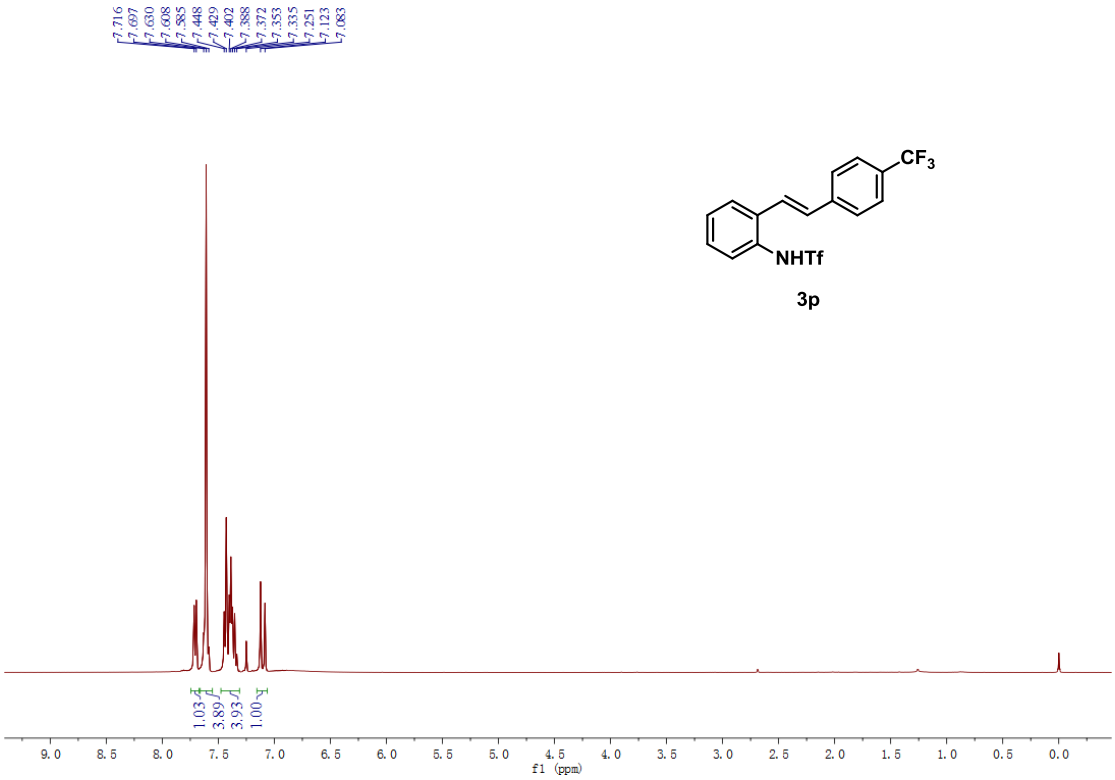
^{13}C NMR Spectrum for **3n** ($CDCl_3$, 100 MHz)



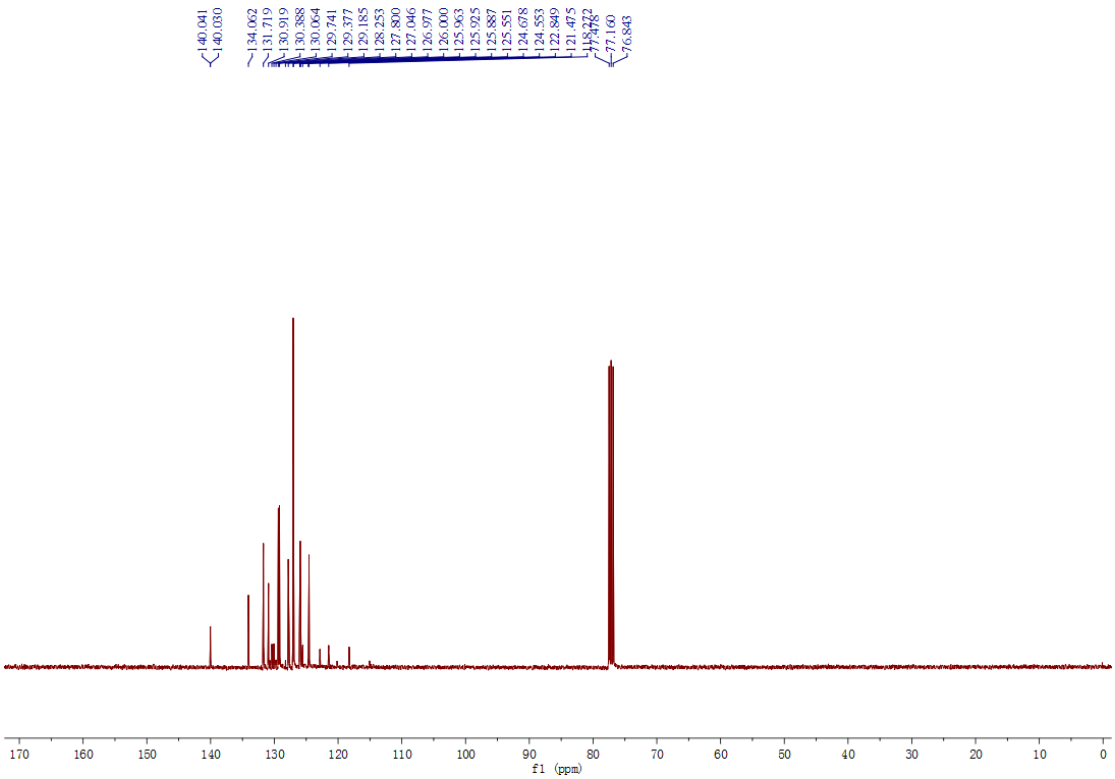
^{1}H NMR Spectrum for **3o** ($CDCl_3$, 400 MHz)



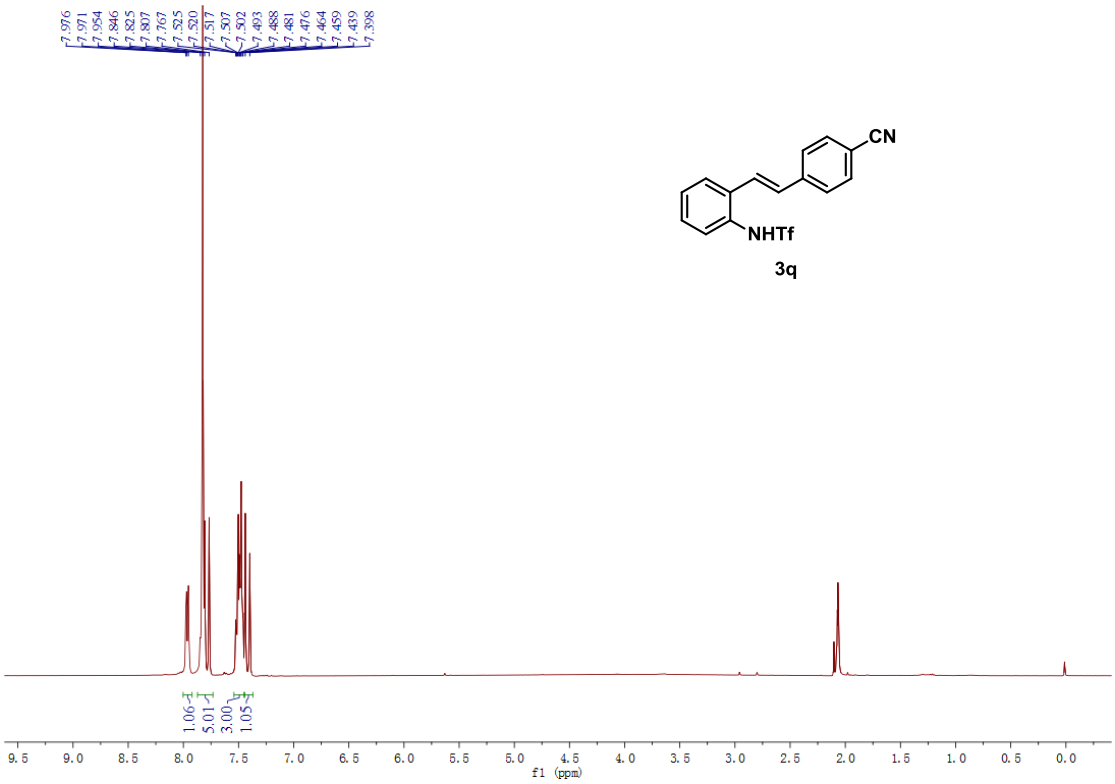
^{13}C NMR Spectrum for **3o** ($CDCl_3$, 100 MHz)



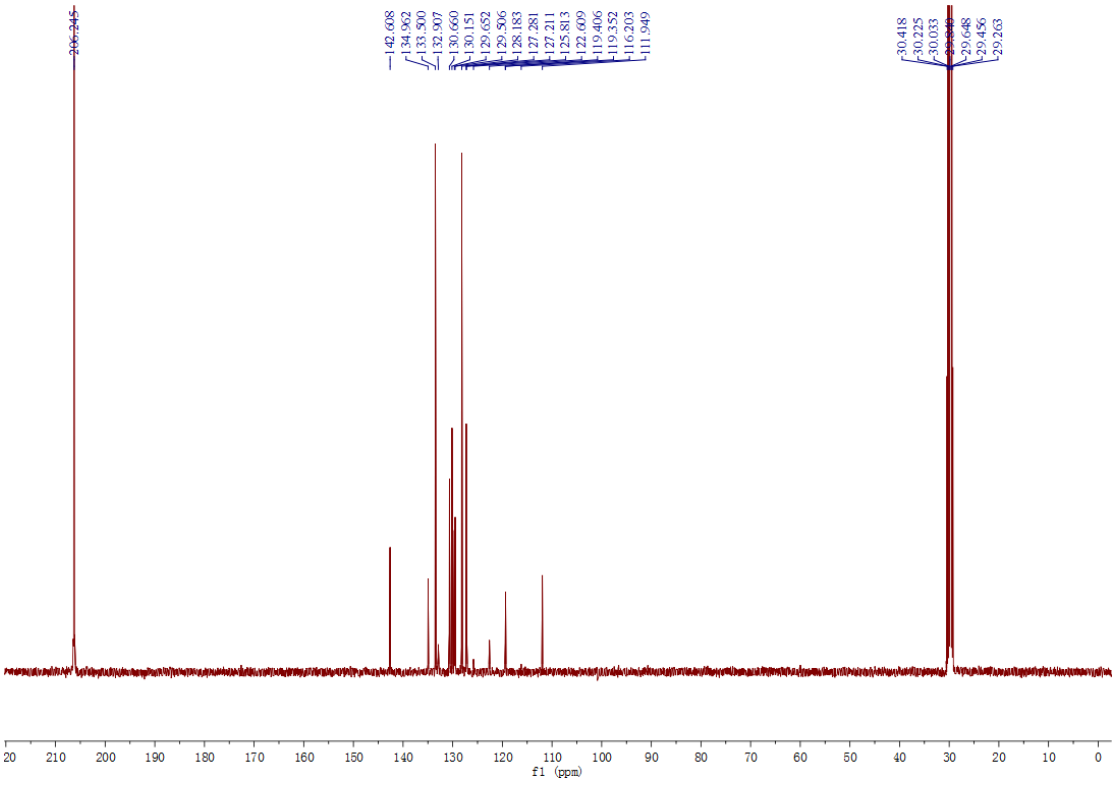
^{1}H NMR Spectrum for **3p** ($CDCl_3$, 400 MHz)



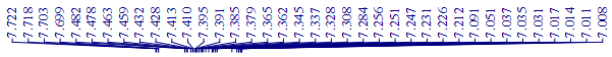
^{13}C NMR Spectrum for **3p** ($CDCl_3$, 100 MHz)

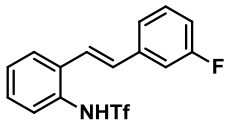


^{1}H NMR Spectrum for **3q** (Acetone-d_6, 400 MHz)

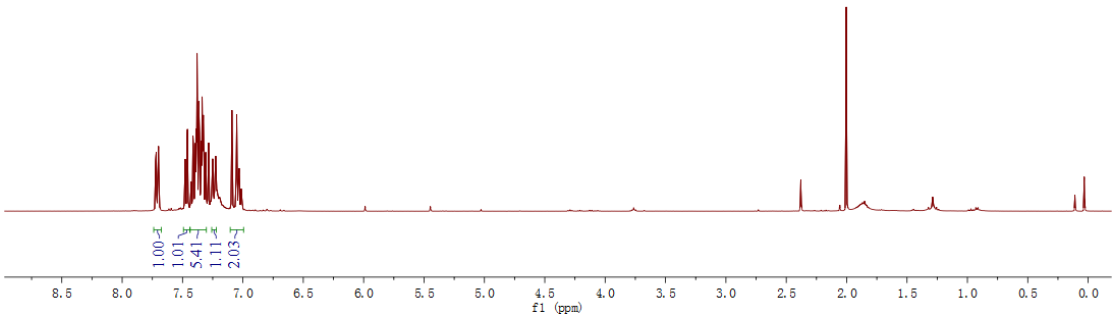


^{13}C NMR Spectrum for **3q** (Acetone-d_6, 100 MHz)

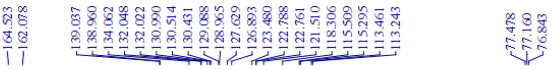


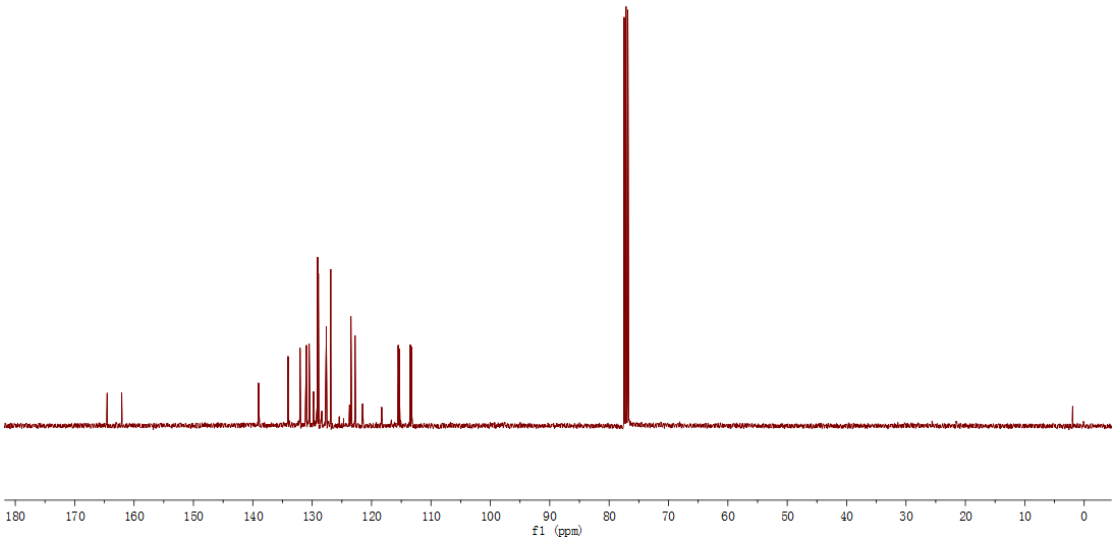


3r

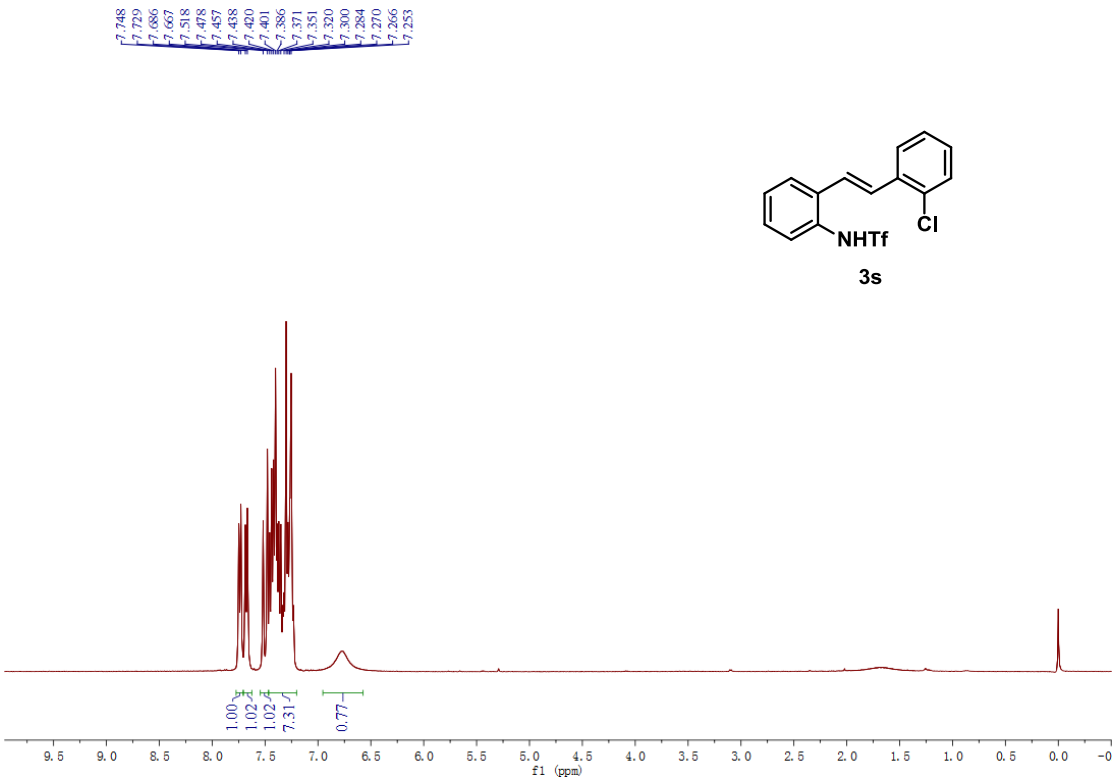


^{1}H NMR Spectrum for **3r** ($CDCl_3$, 400 MHz)

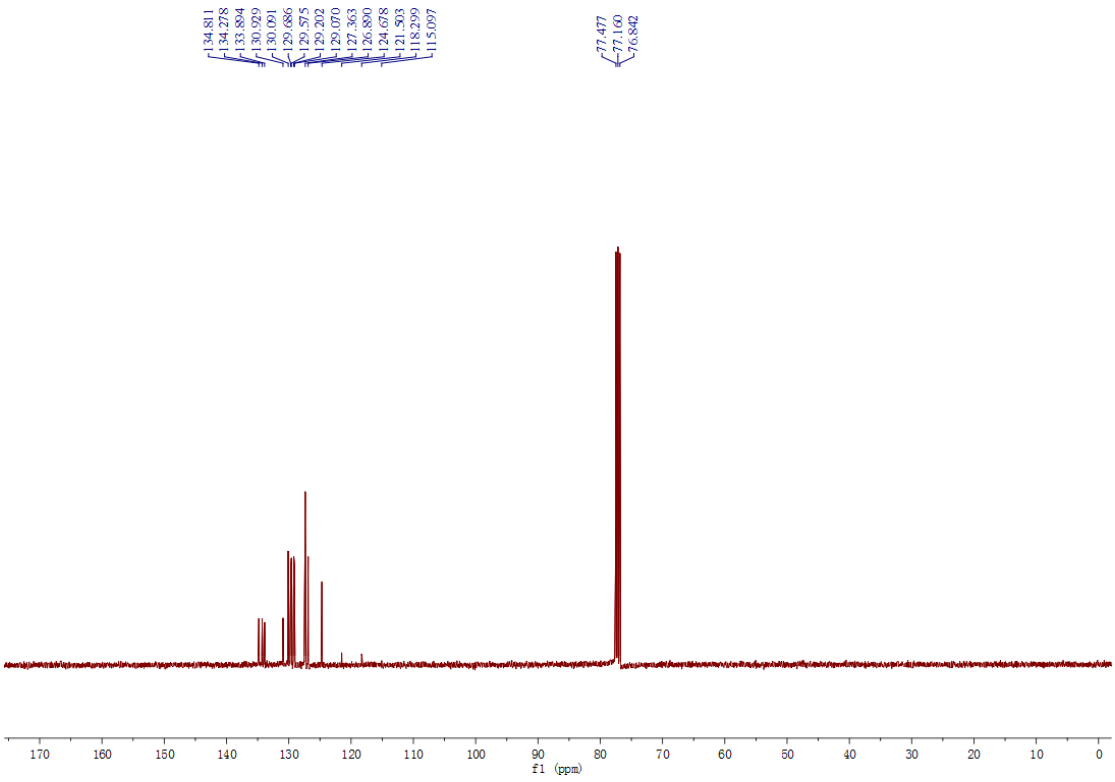




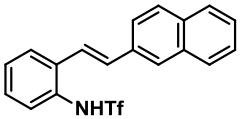
^{13}C NMR Spectrum for **3r** ($CDCl_3$, 100 MHz)



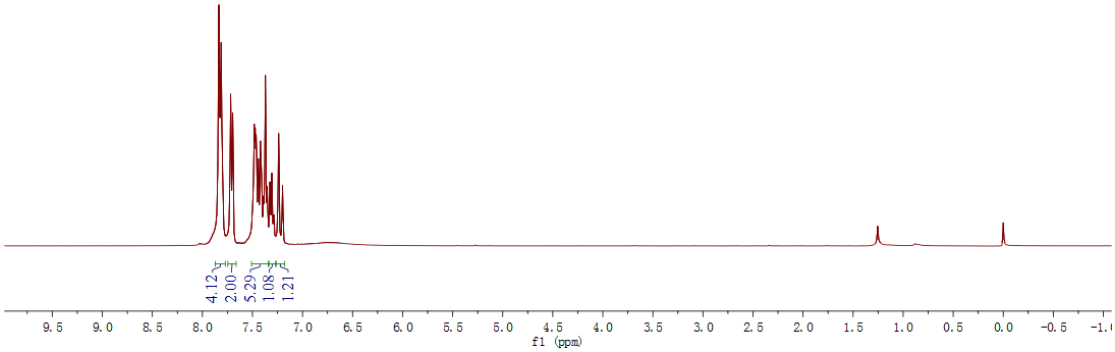
^{1}H NMR Spectrum for **3s** ($CDCl_3$, 400 MHz)



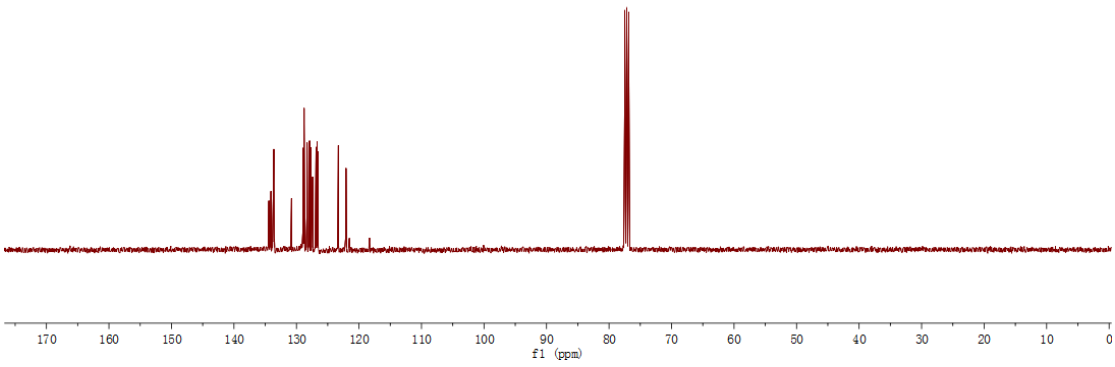
^{13}C NMR Spectrum for **3s** ($CDCl_3$, 100 MHz)



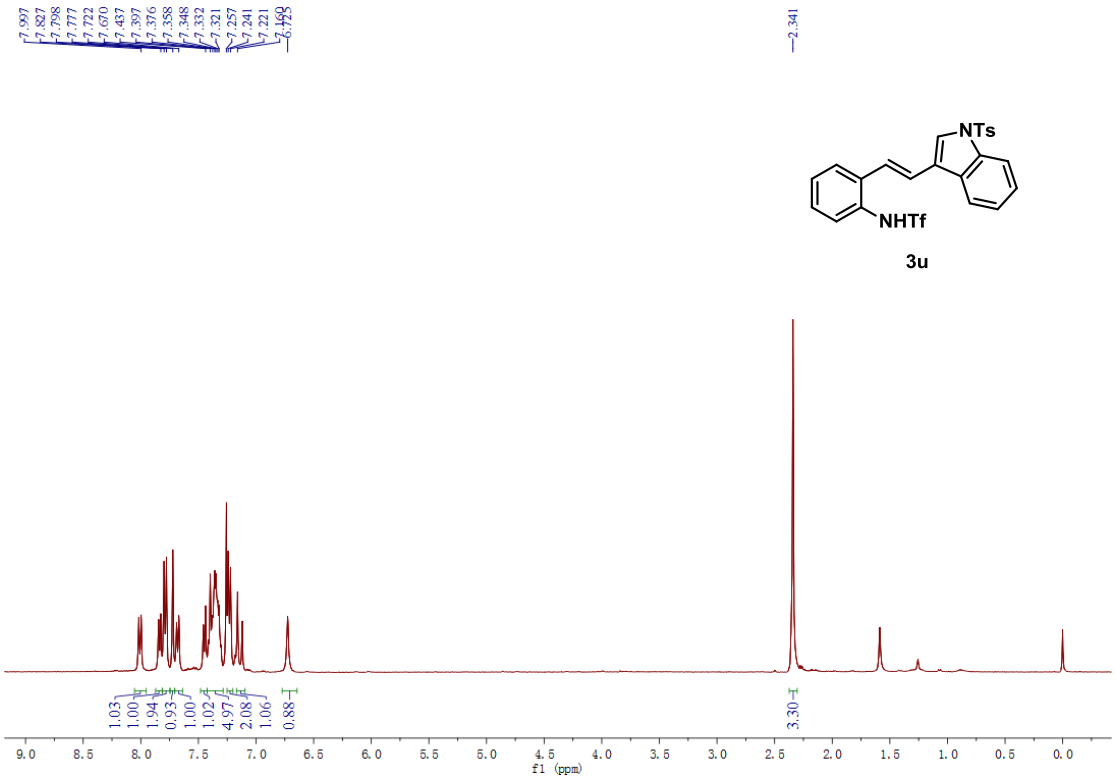
3t



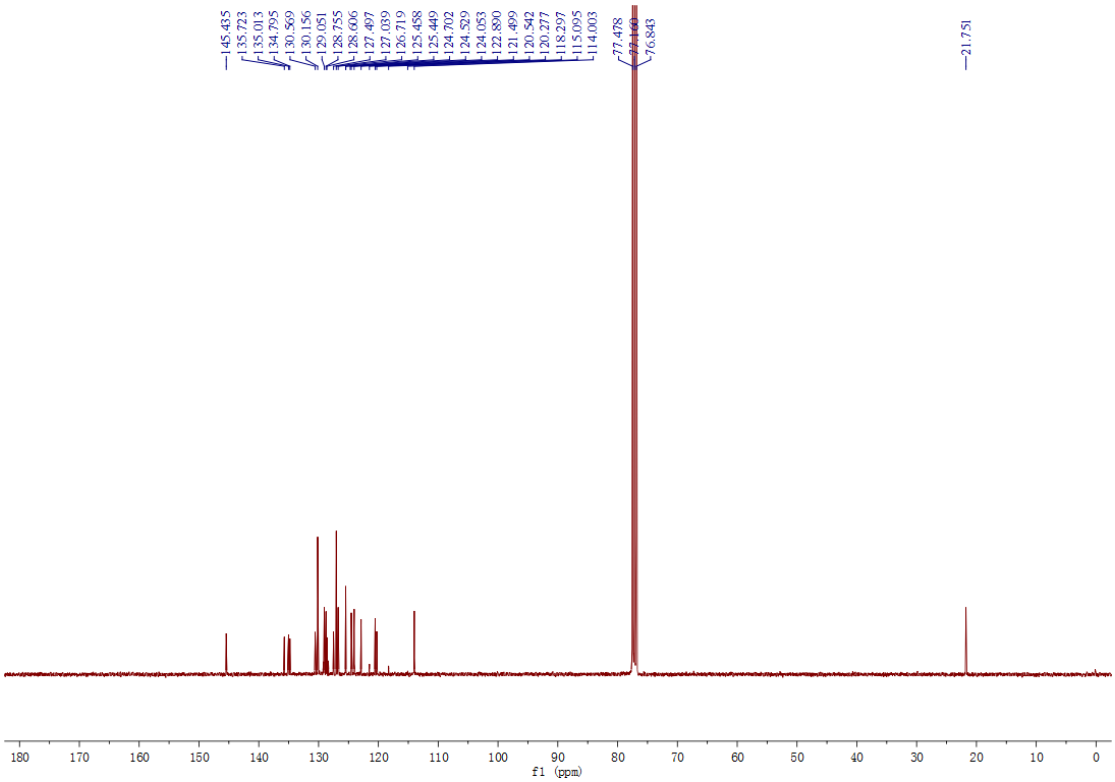
^{1}H NMR Spectrum for **3t** ($CDCl_3$, 400 MHz)



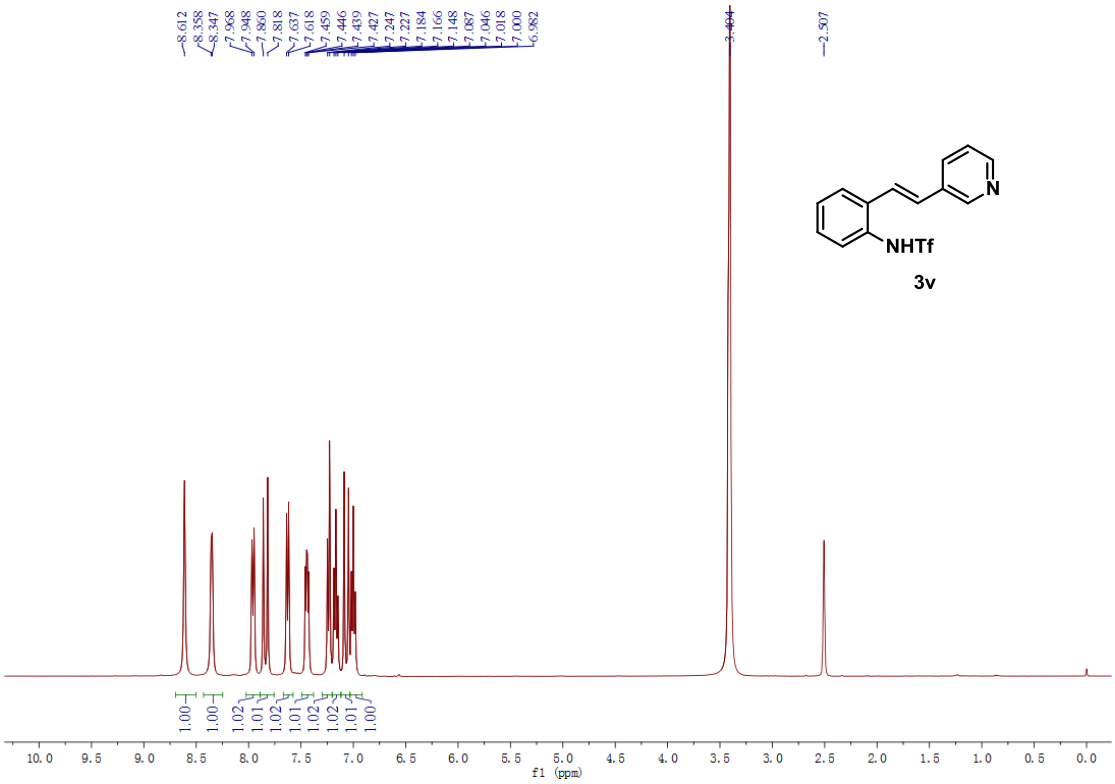
^{13}C NMR Spectrum for **3t** ($CDCl_3$, 100 MHz)



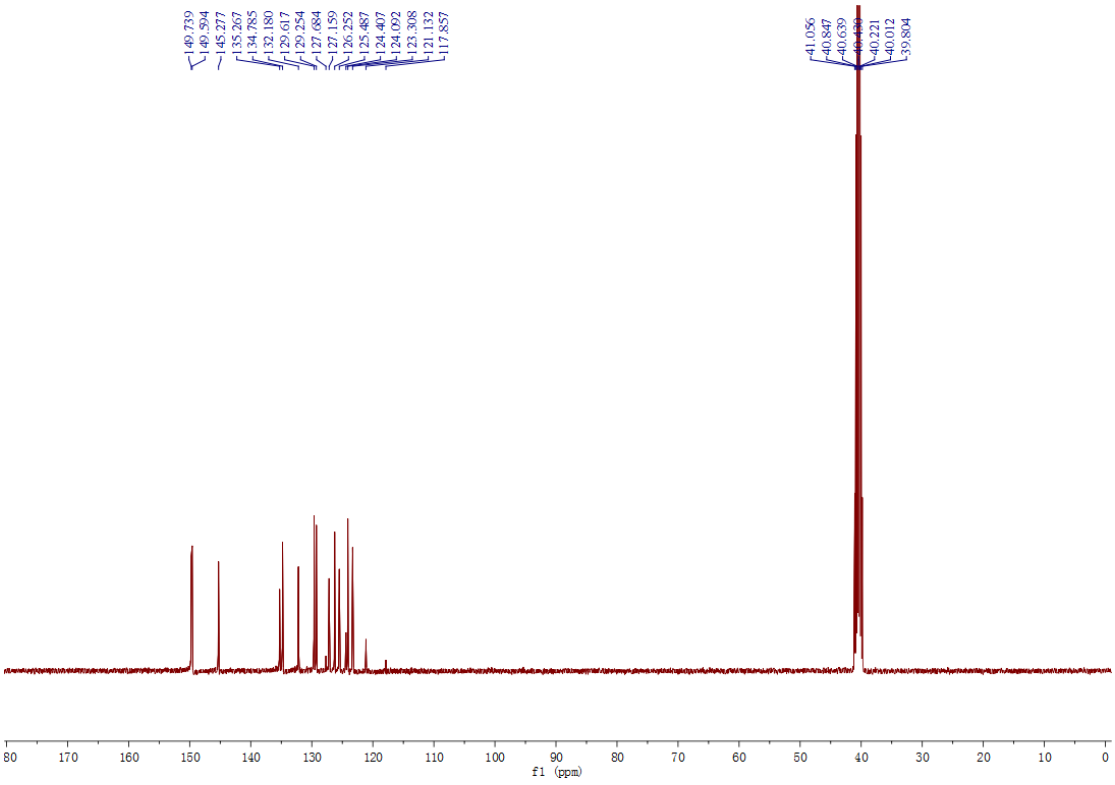
^{1}H NMR Spectrum for **3u** ($CDCl_3$, 400 MHz)



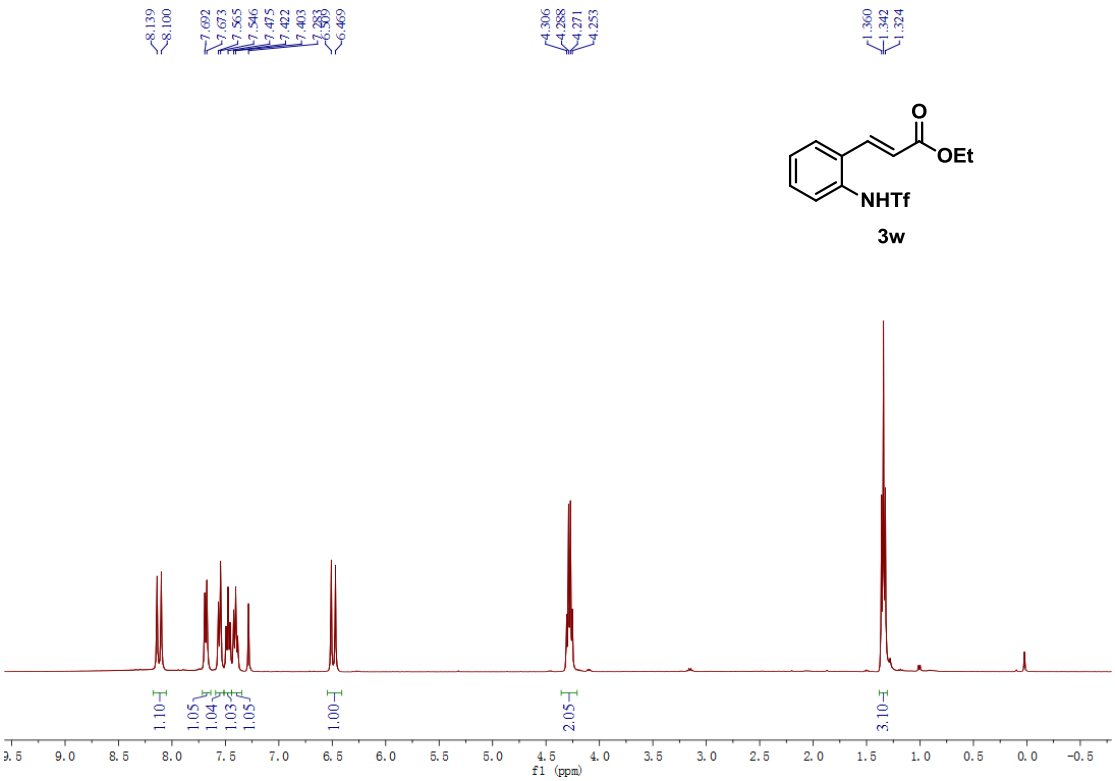
^{13}C NMR Spectrum for **3u** ($CDCl_3$, 100 MHz)



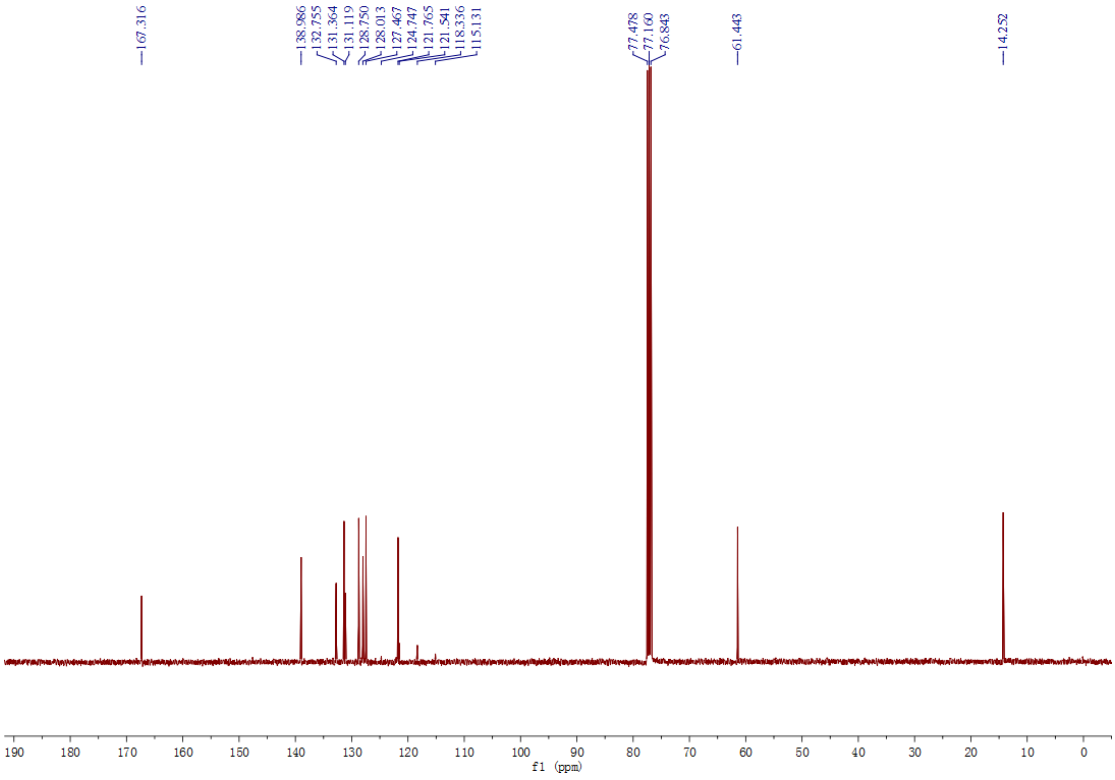
^{1}H NMR Spectrum for **3v** (DMSO-d_6, 400 MHz)



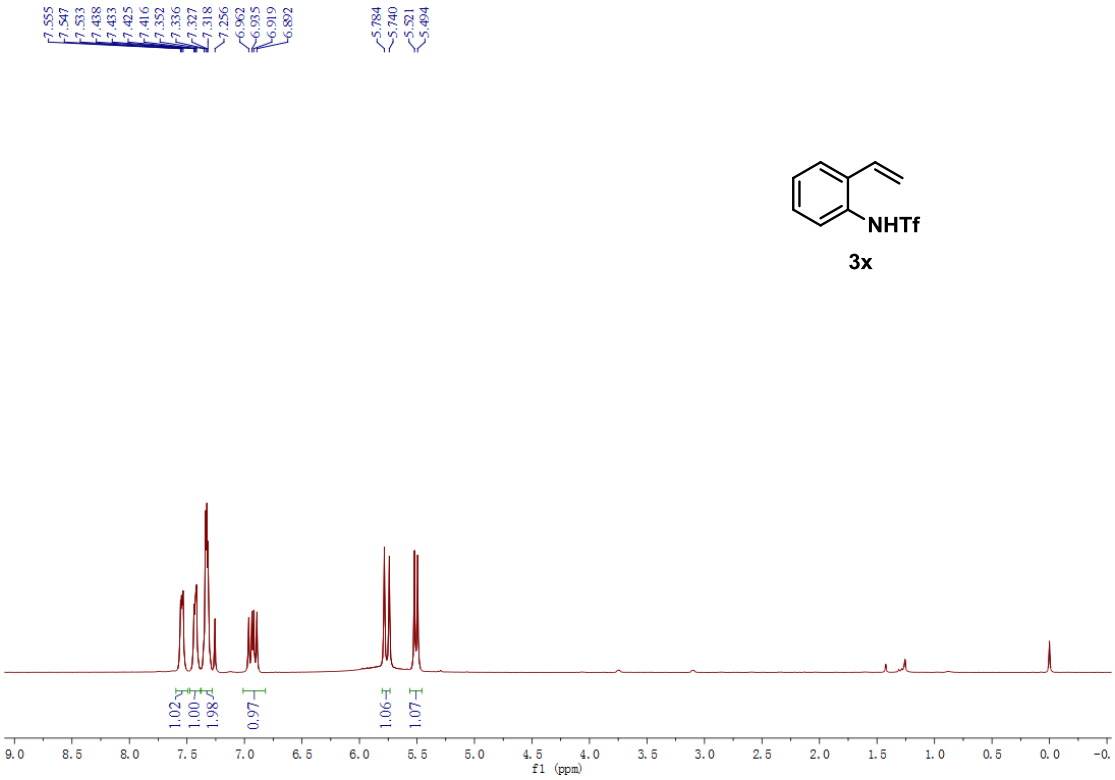
^{13}C NMR Spectrum for **3v** (DMSO-d_6, 100 MHz)



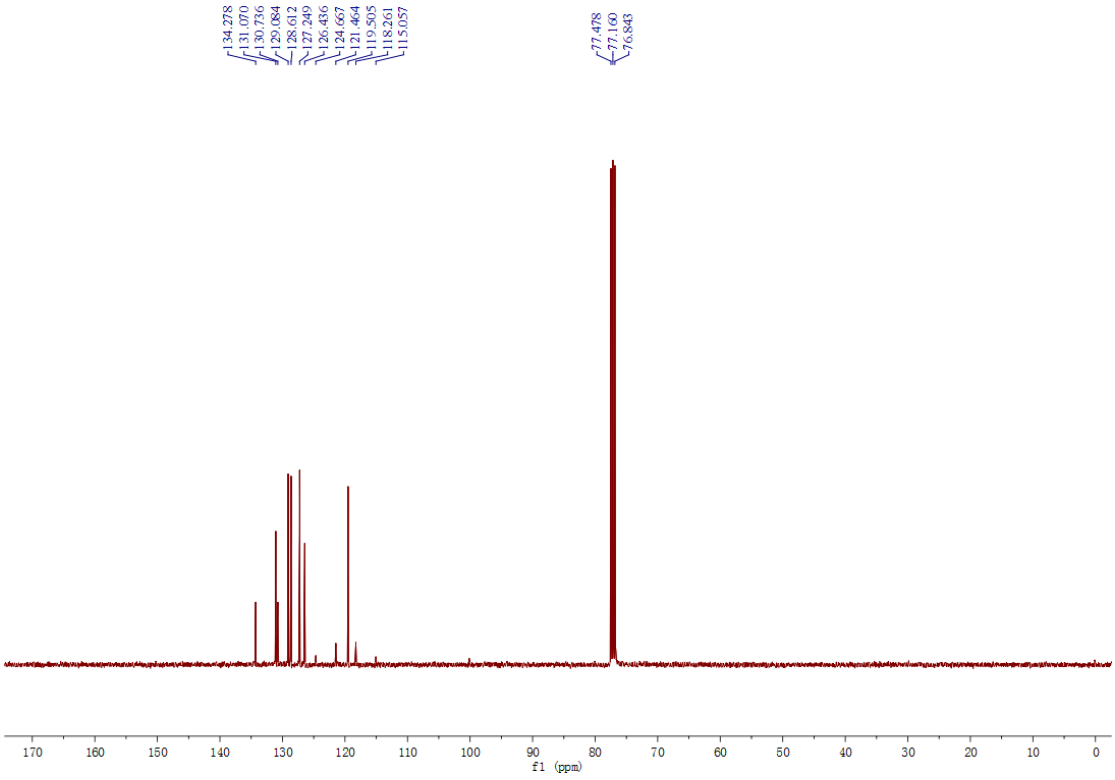
^{1}H NMR Spectrum for **3w** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum for **3w** ($CDCl_3$, 100 MHz)

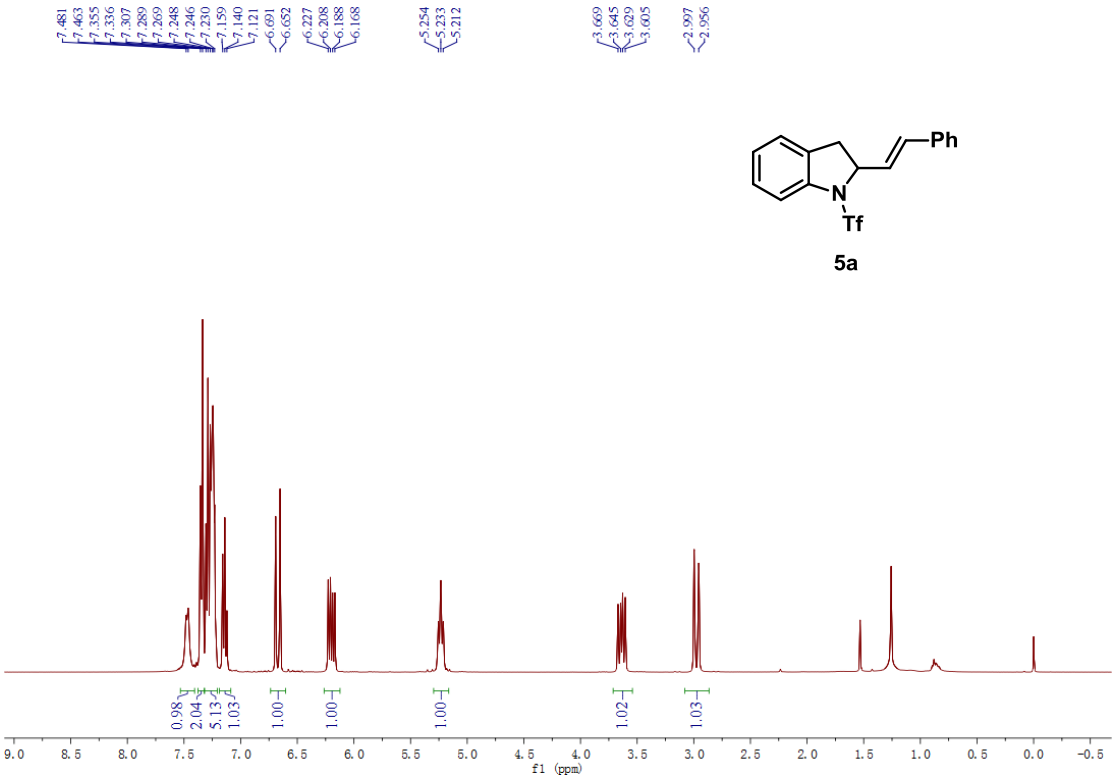


^{1}H NMR Spectrum for **3x** ($CDCl_3$, 400 MHz)

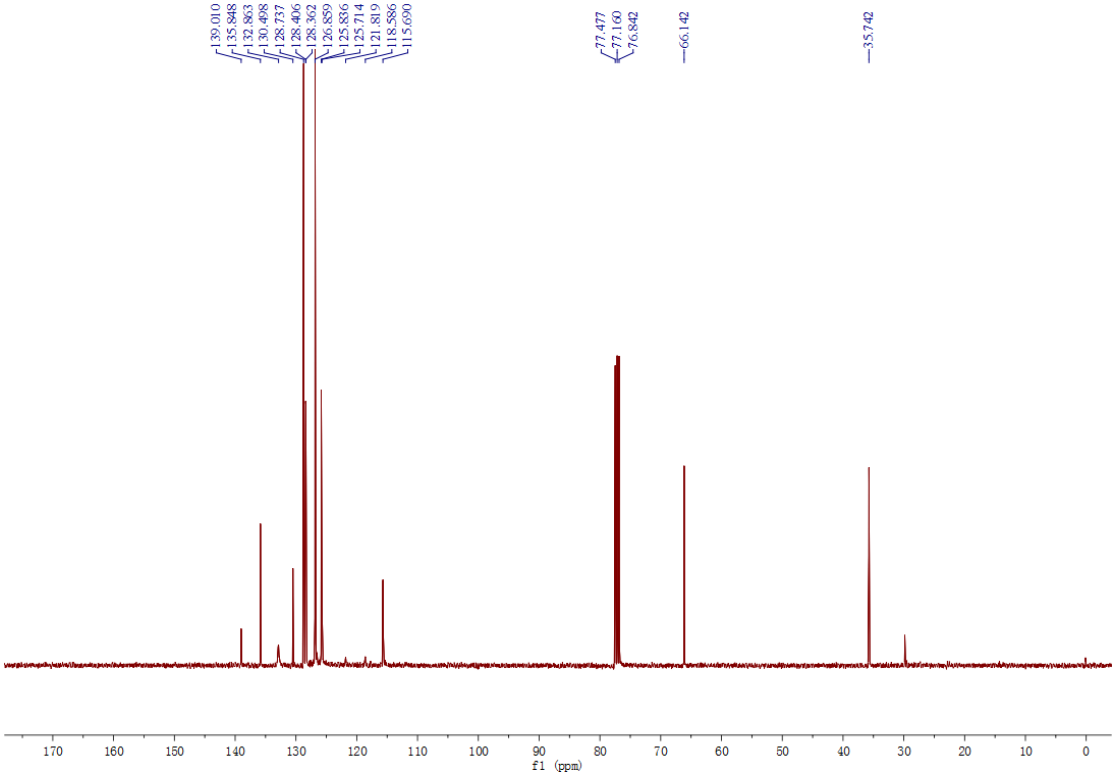


^{13}C NMR Spectrum for **3x** ($CDCl_3$, 100 MHz)

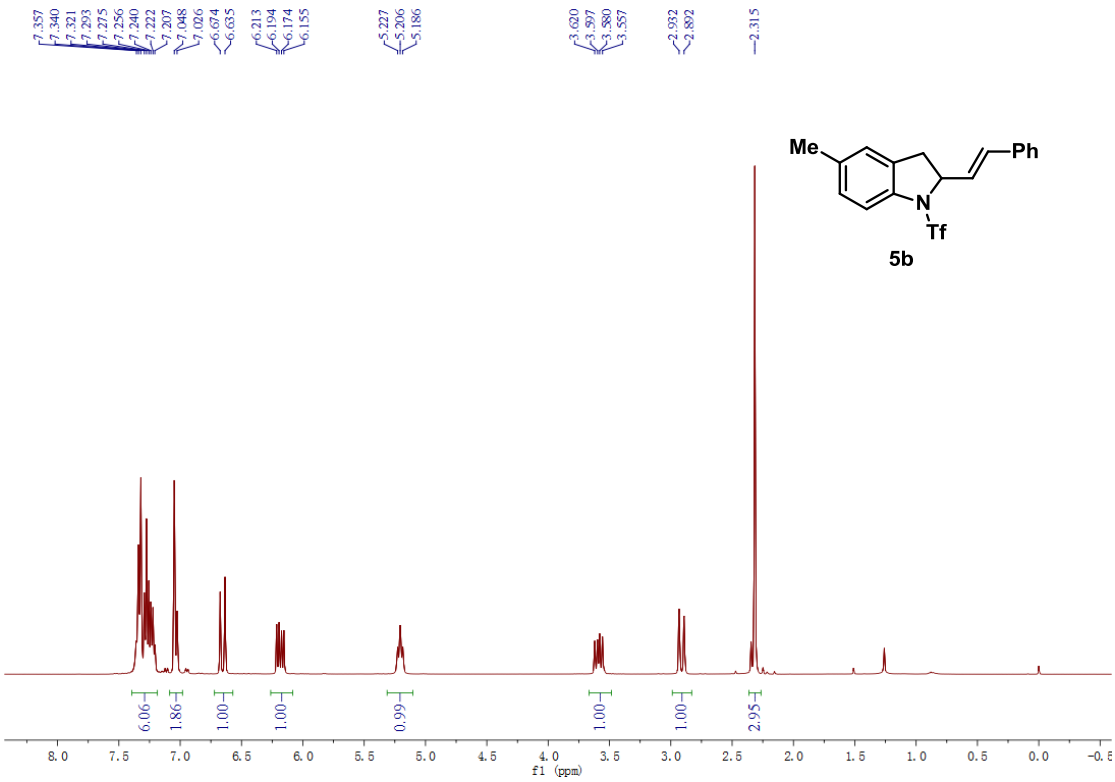
7. NMR Spectra of the Pd-Catalyzed Denitrogenative Formal [3+2] Cyclization Products



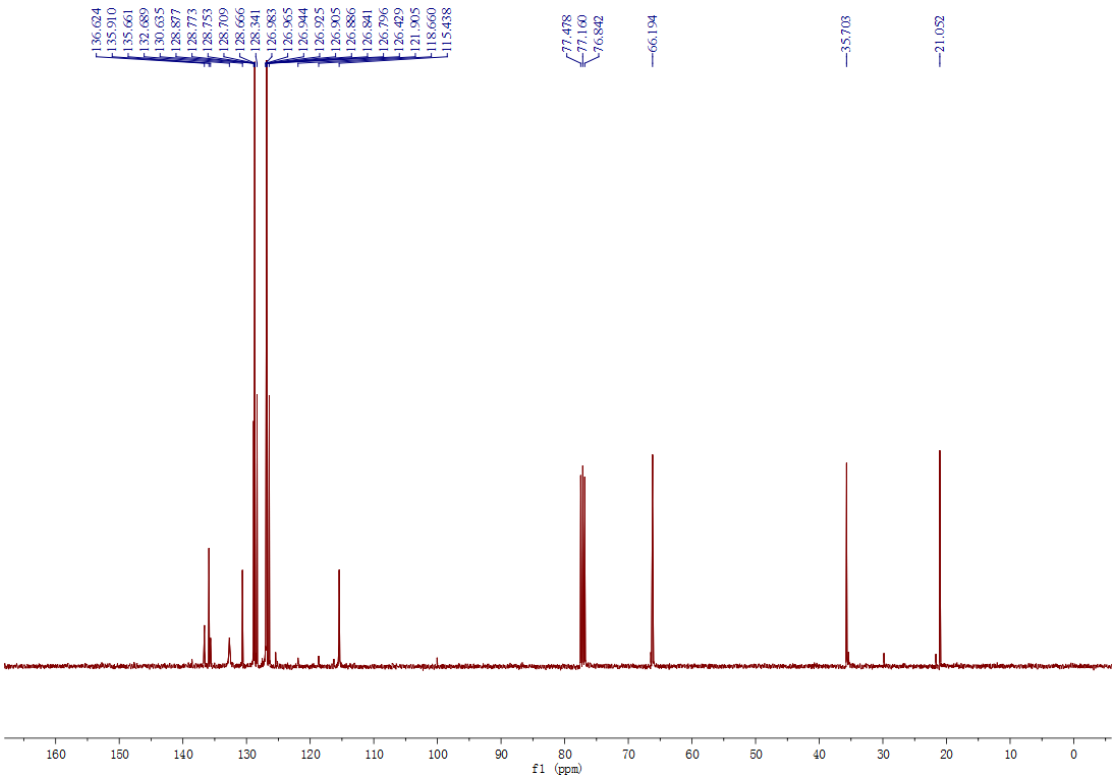
^{1}H NMR Spectrum for **5a** ($CDCl_3$, 400 MHz)



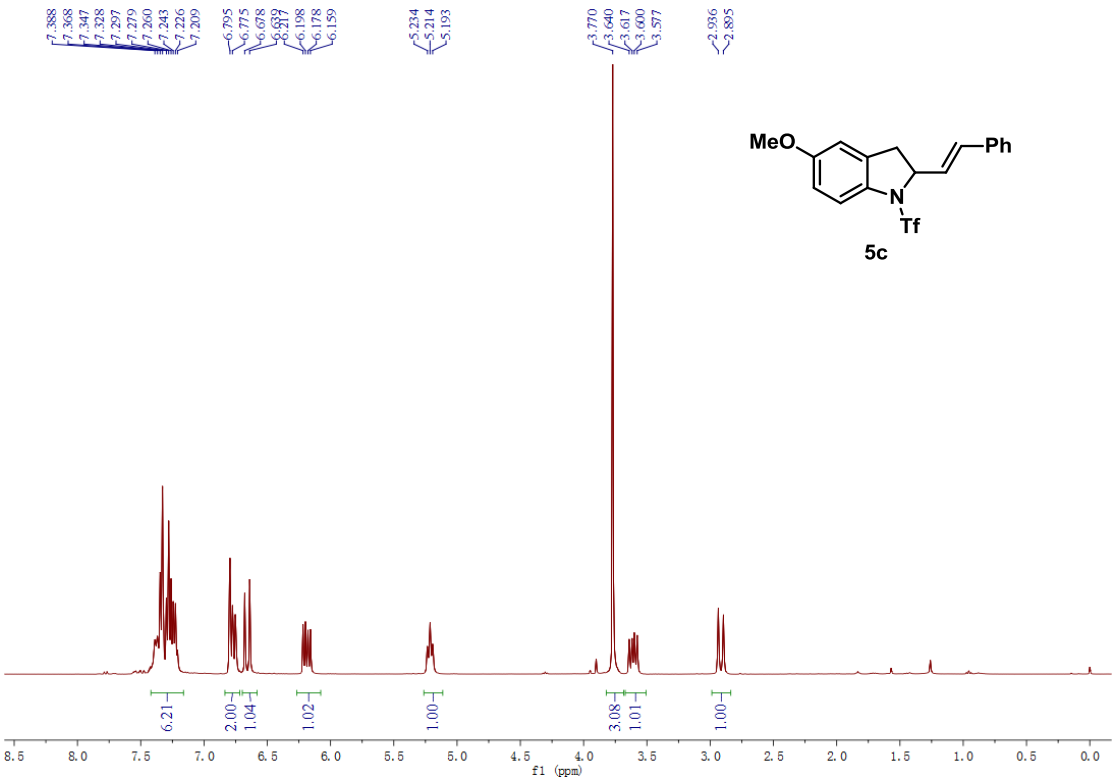
^{13}C NMR Spectrum for **5a** ($CDCl_3$, 100 MHz)



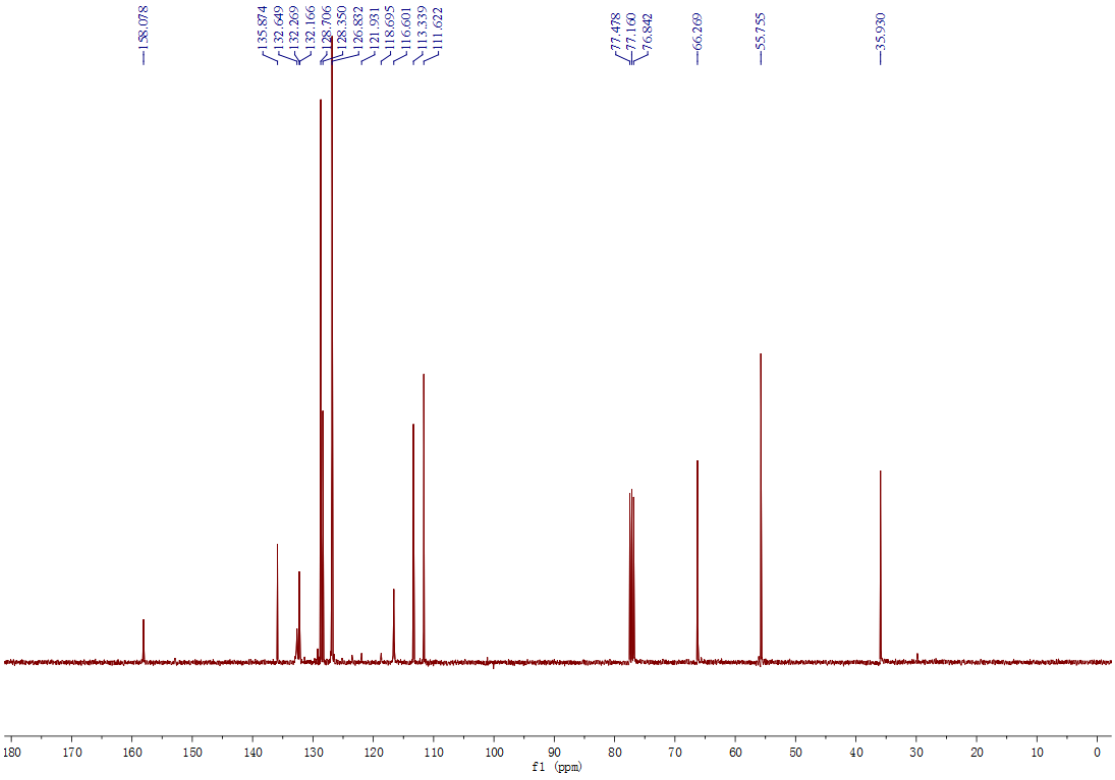
^{1}H NMR Spectrum for **5b** ($CDCl_3$, 400 MHz)



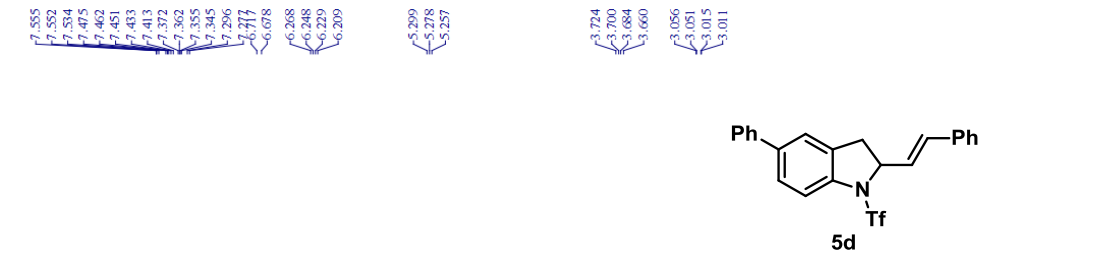
^{13}C NMR Spectrum for **5b** ($CDCl_3$, 100 MHz)



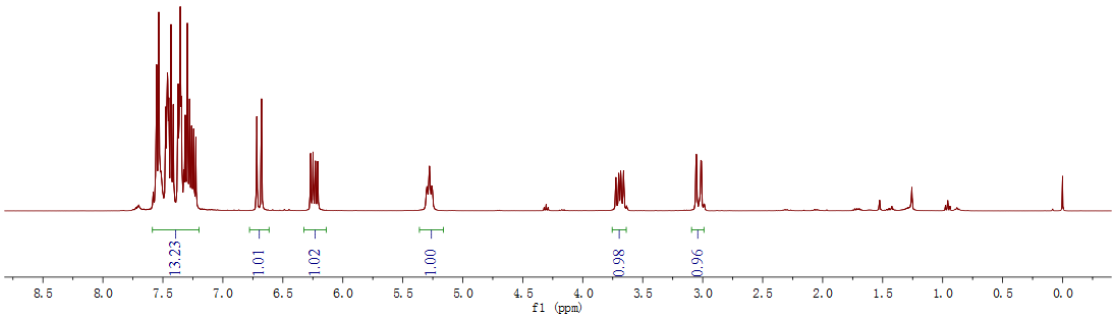
^{1}H NMR Spectrum for **5c** ($CDCl_3$, 400 MHz)



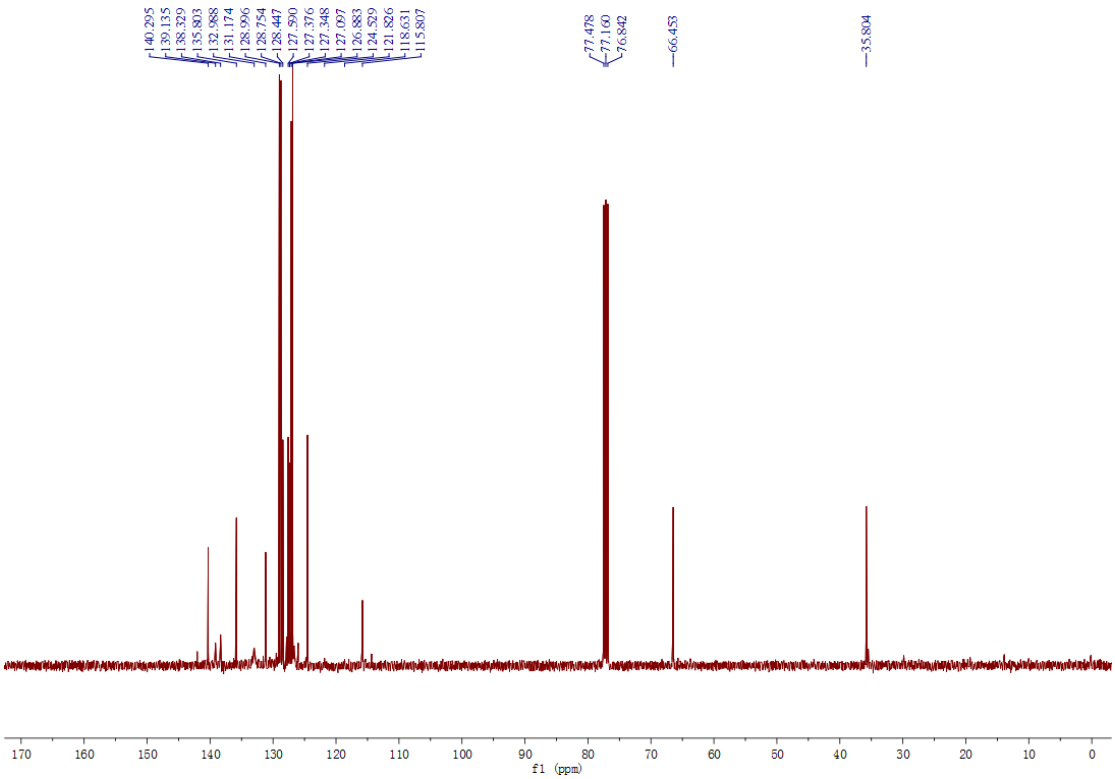
^{13}C NMR Spectrum for **5c** ($CDCl_3$, 100 MHz)



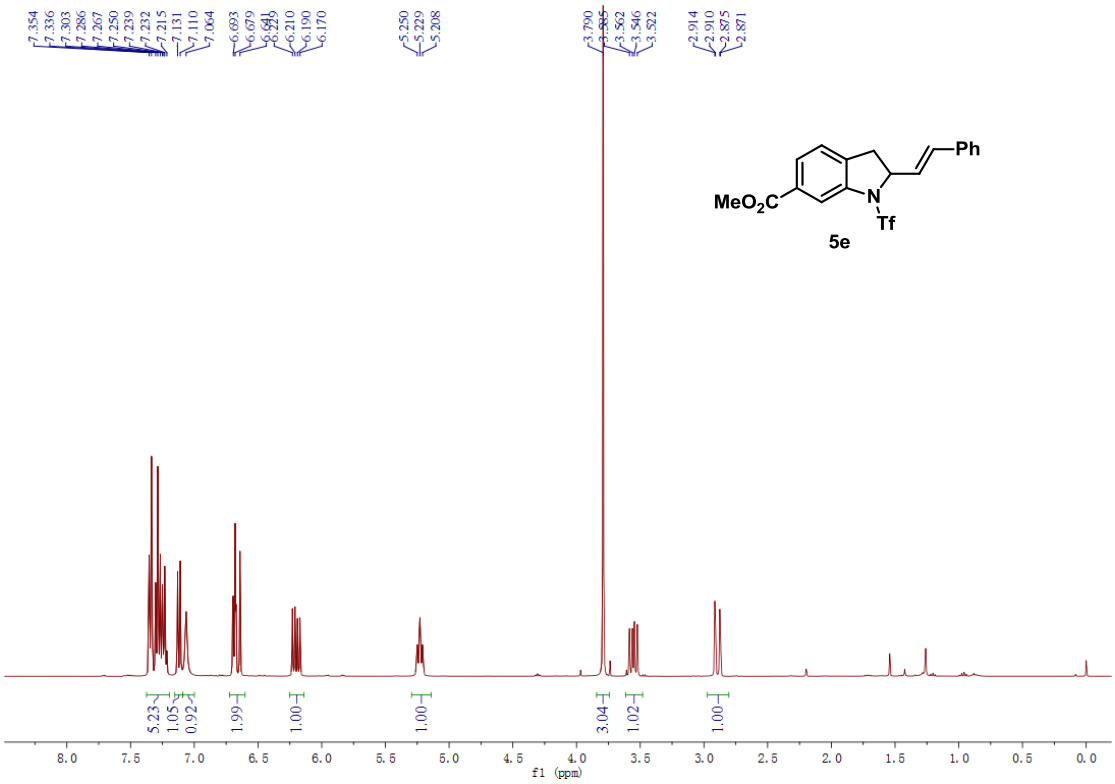
5d



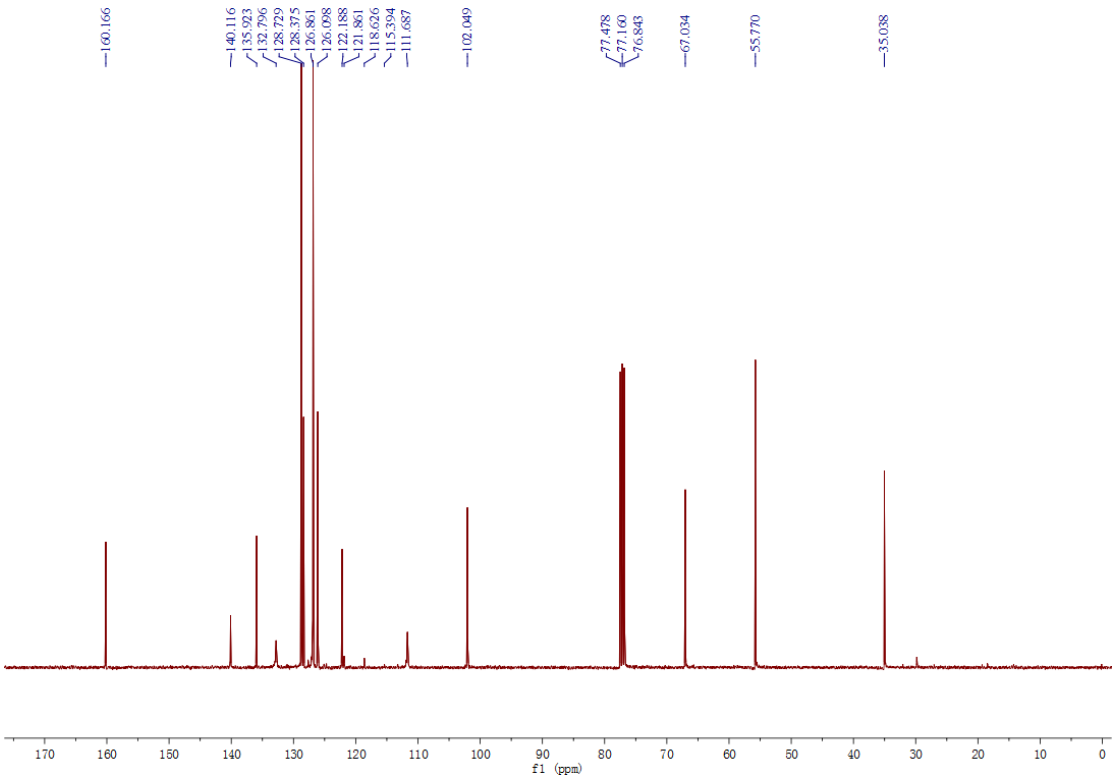
^{1}H NMR Spectrum for **5d** ($CDCl_3$, 400 MHz)



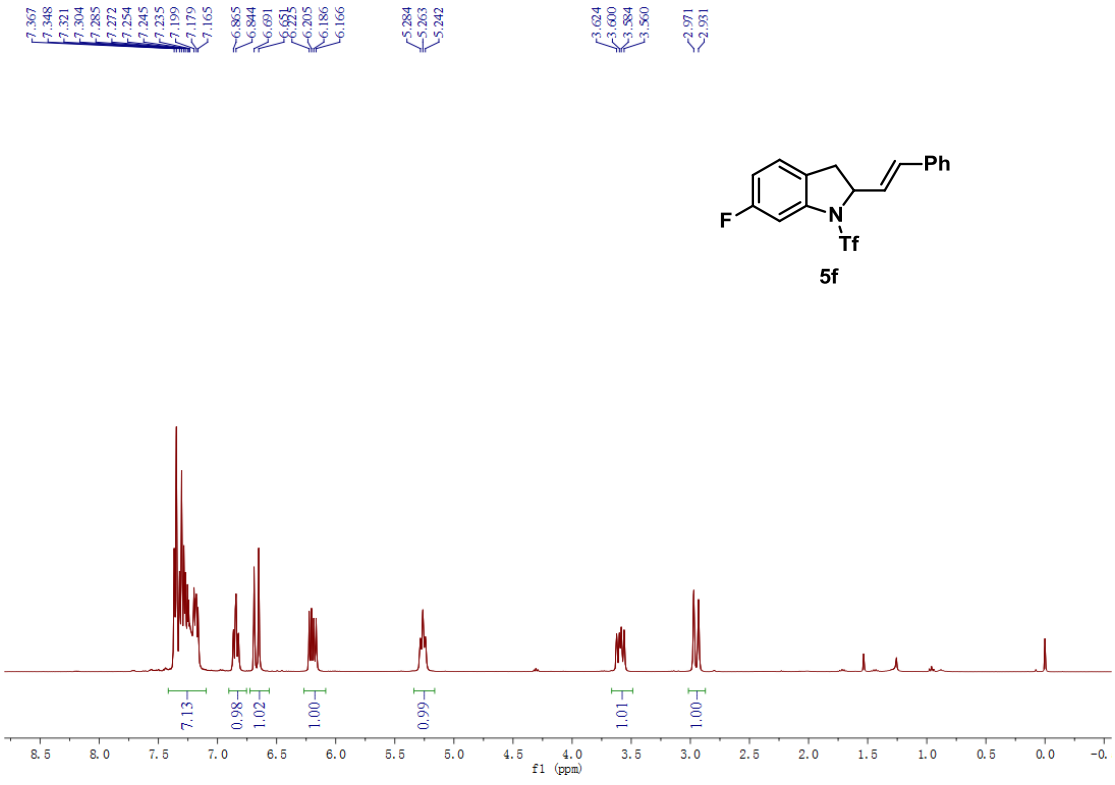
^{13}C NMR Spectrum for **5d** ($CDCl_3$, 100 MHz)



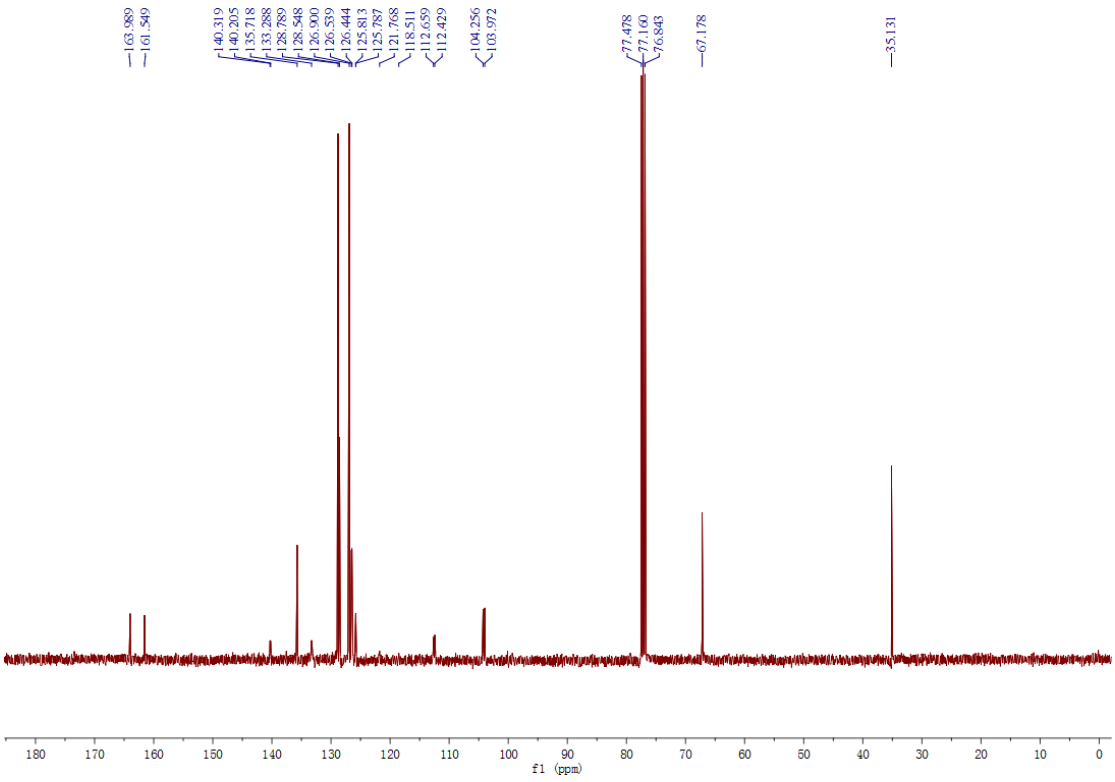
^{1}H NMR Spectrum for **5e** ($CDCl_3$, 400 MHz)



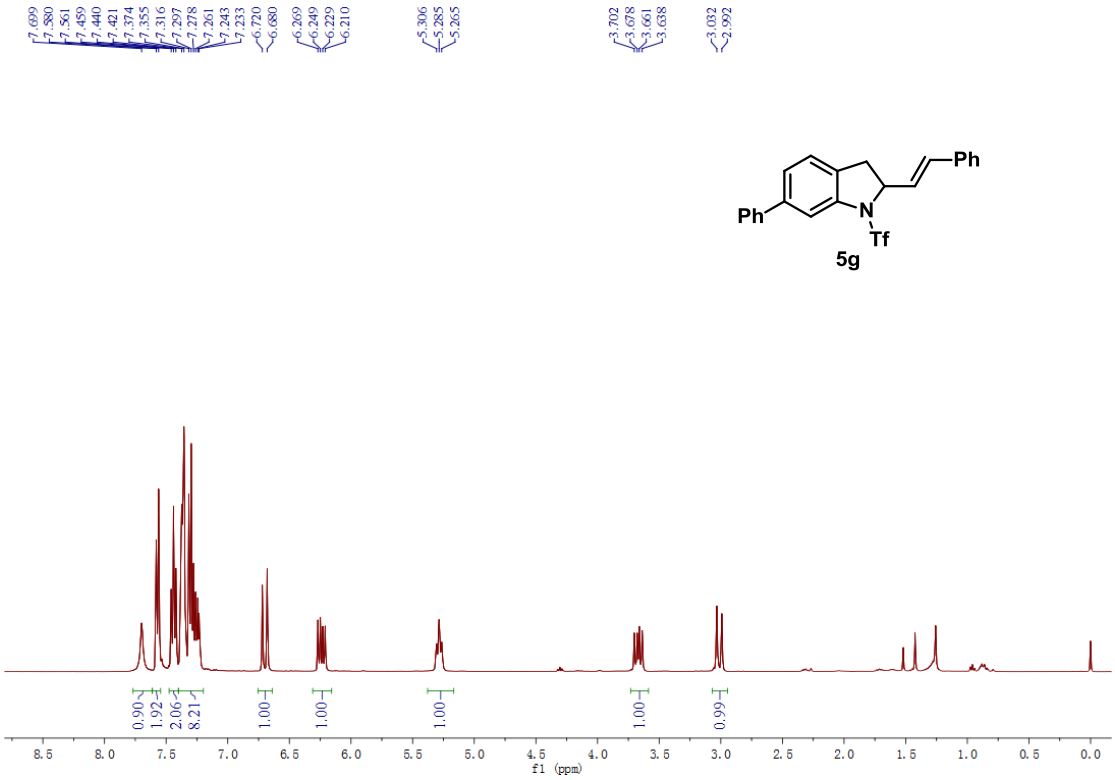
^{13}C NMR Spectrum for **5e** ($CDCl_3$, 100 MHz)



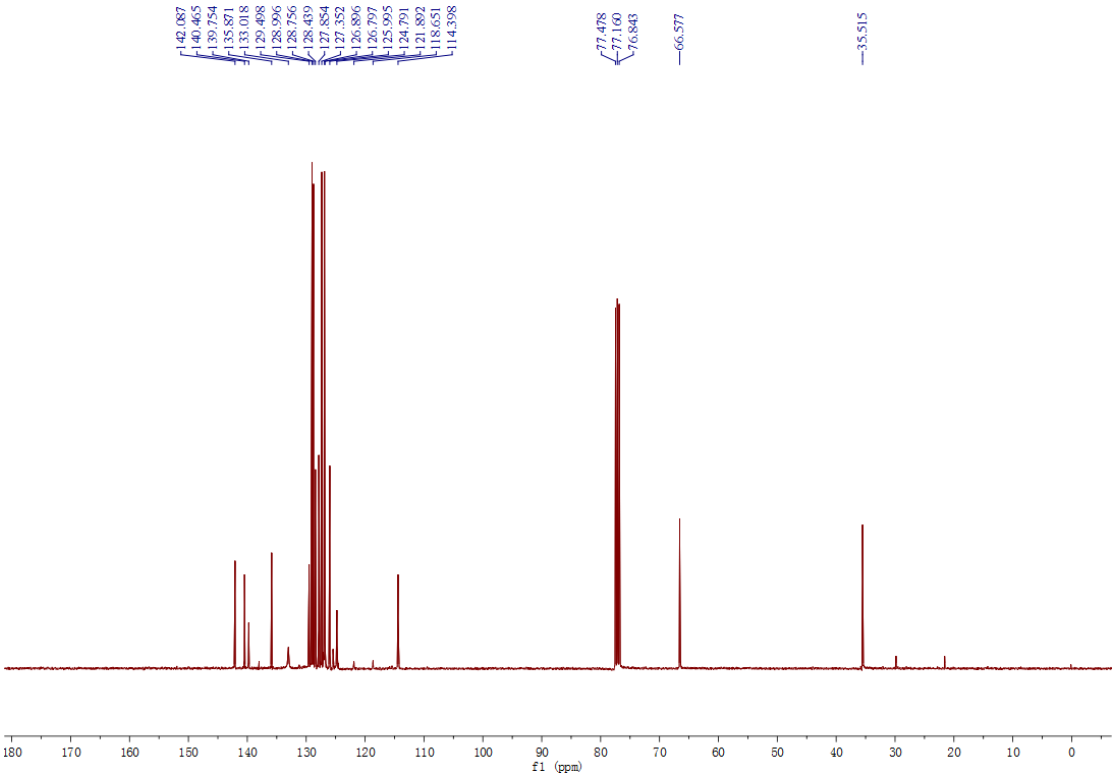
^{1}H NMR Spectrum for **5f** ($CDCl_3$, 400 MHz)



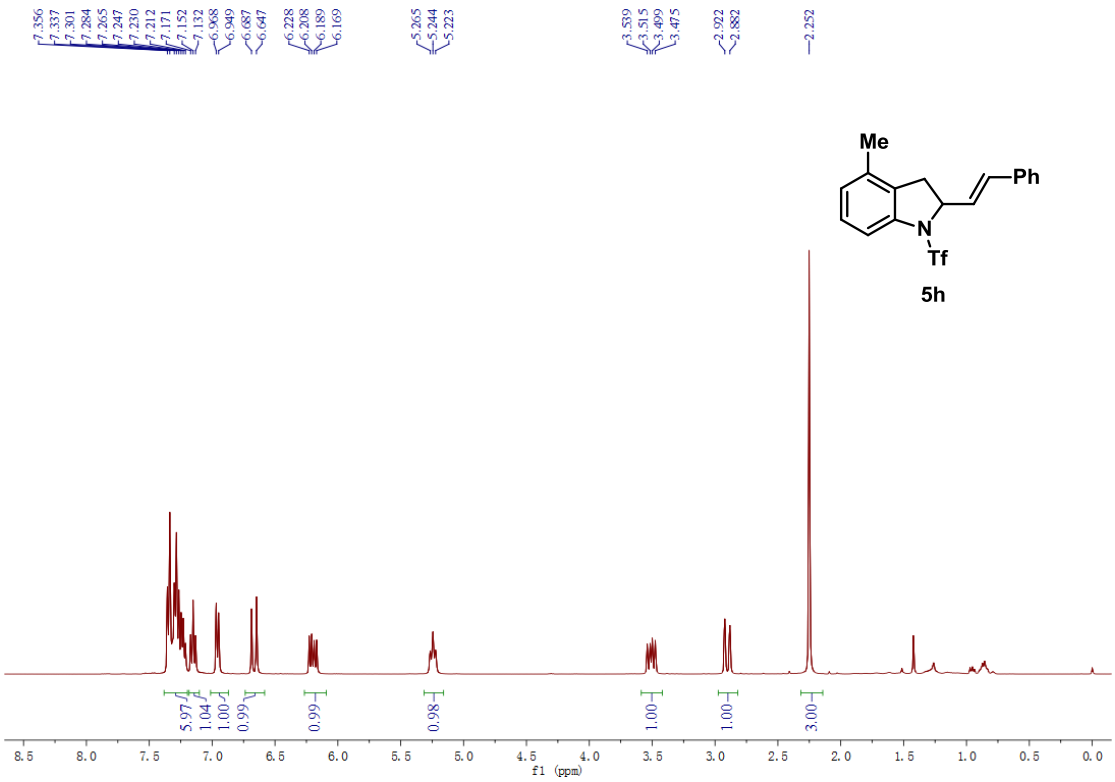
^{13}C NMR Spectrum for **5f** ($CDCl_3$, 100 MHz)



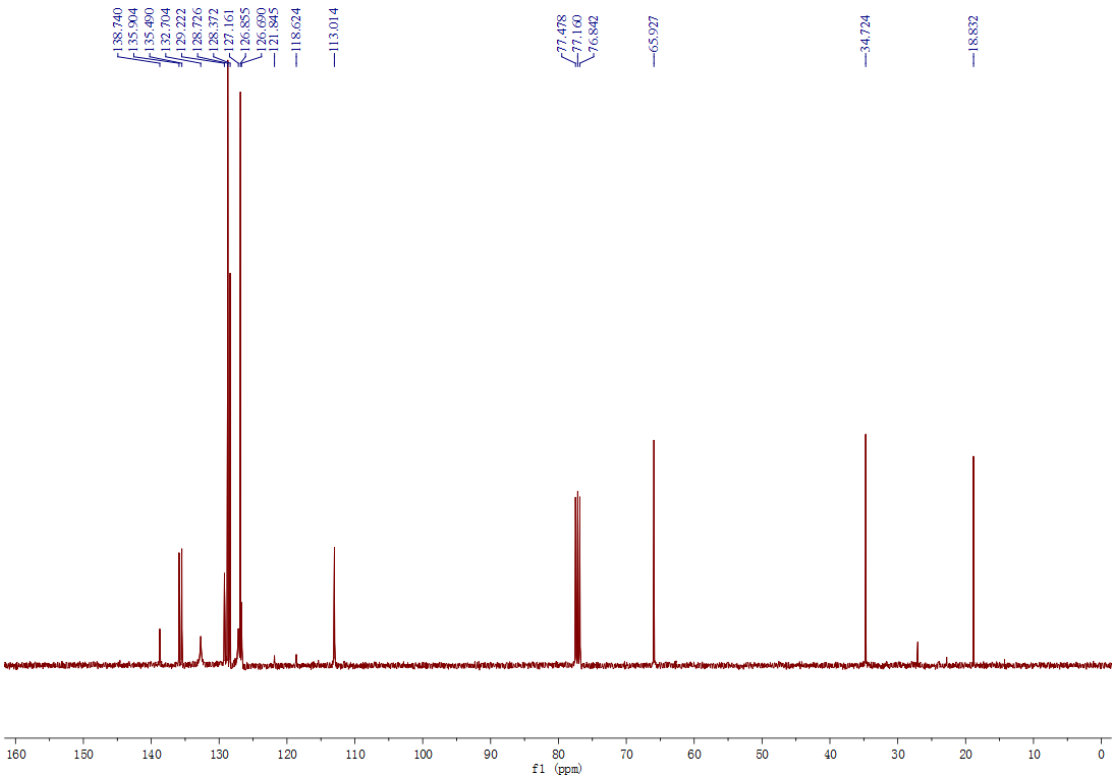
^{1}H NMR Spectrum for **5g** ($CDCl_3$, 400 MHz)



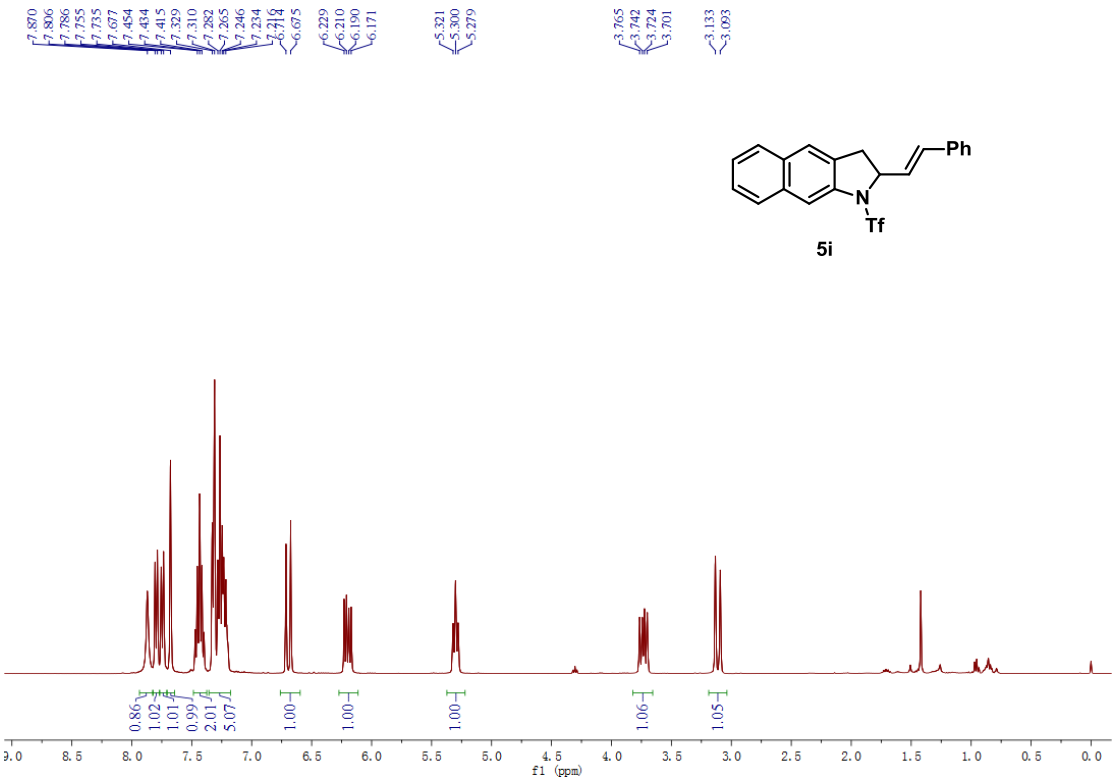
^{13}C NMR Spectrum for **5g** ($CDCl_3$, 100 MHz)



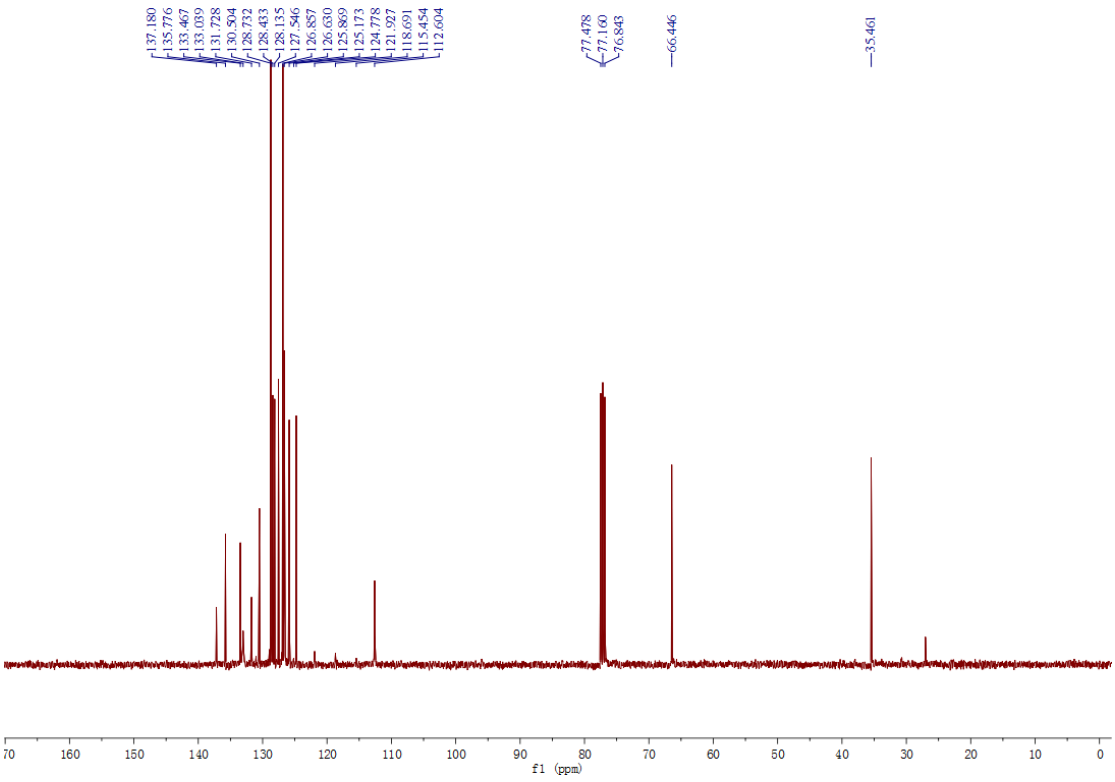
^{1}H NMR Spectrum for **5h** ($CDCl_3$, 400 MHz)



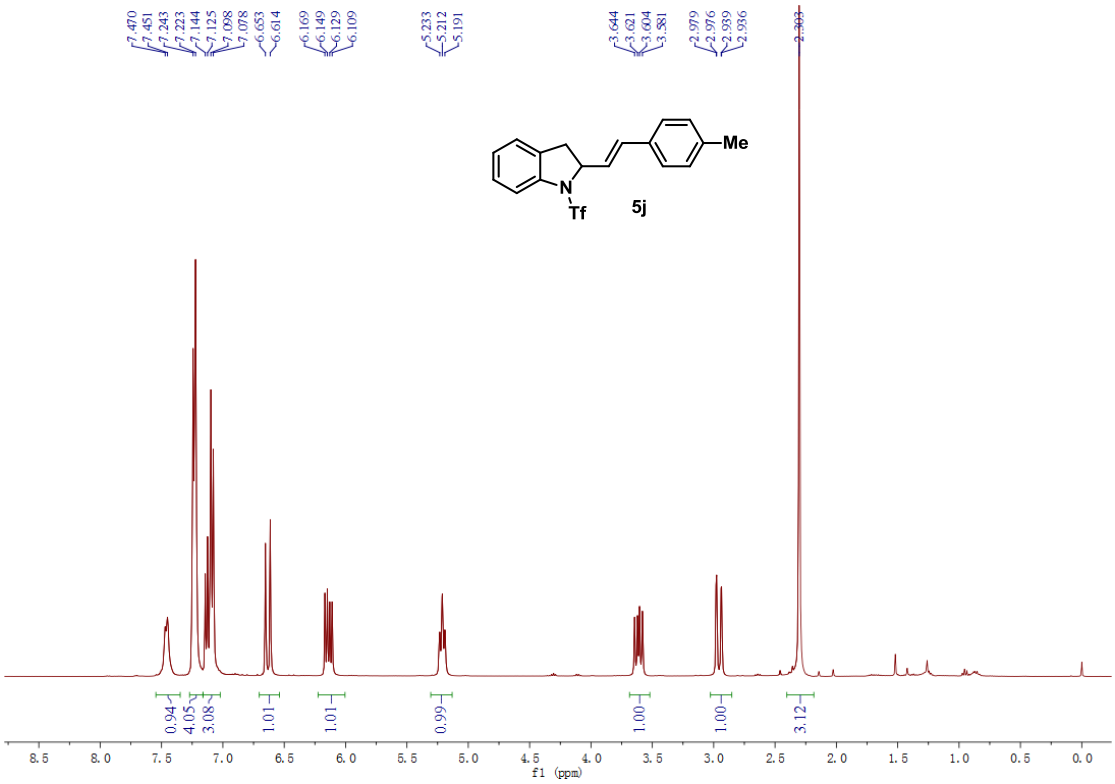
^{13}C NMR Spectrum for **5h** ($CDCl_3$, 100 MHz)



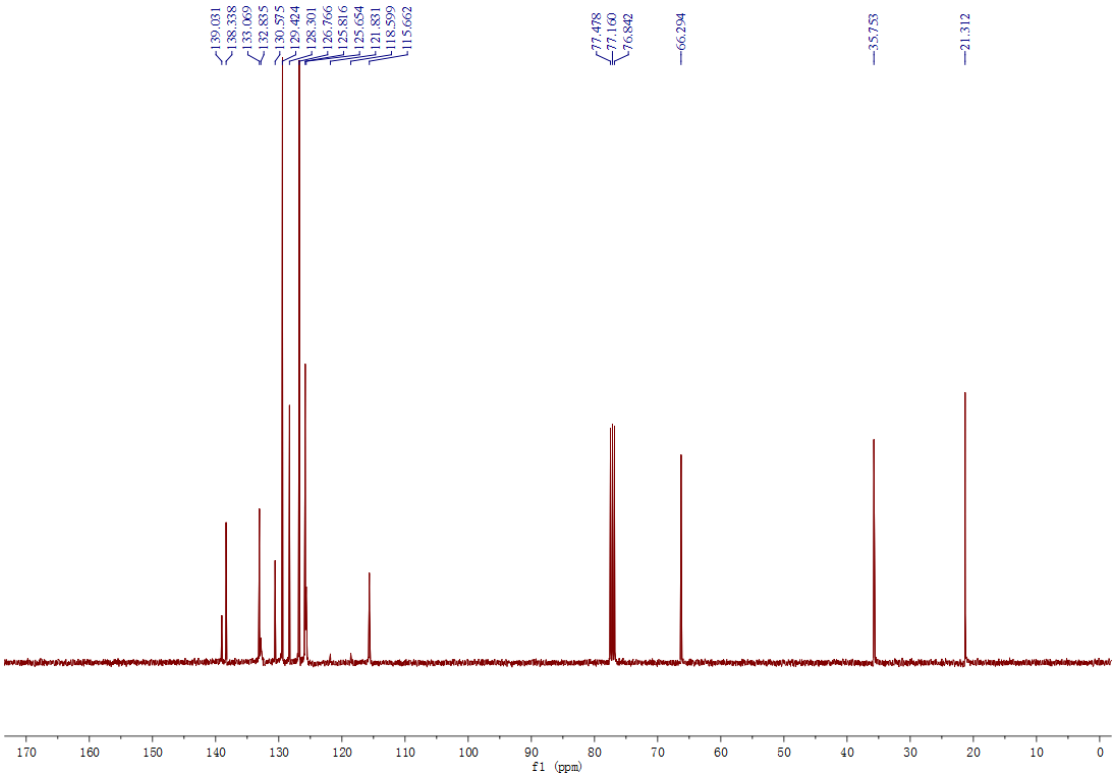
^{1}H NMR Spectrum for **5i** ($CDCl_3$, 400 MHz)



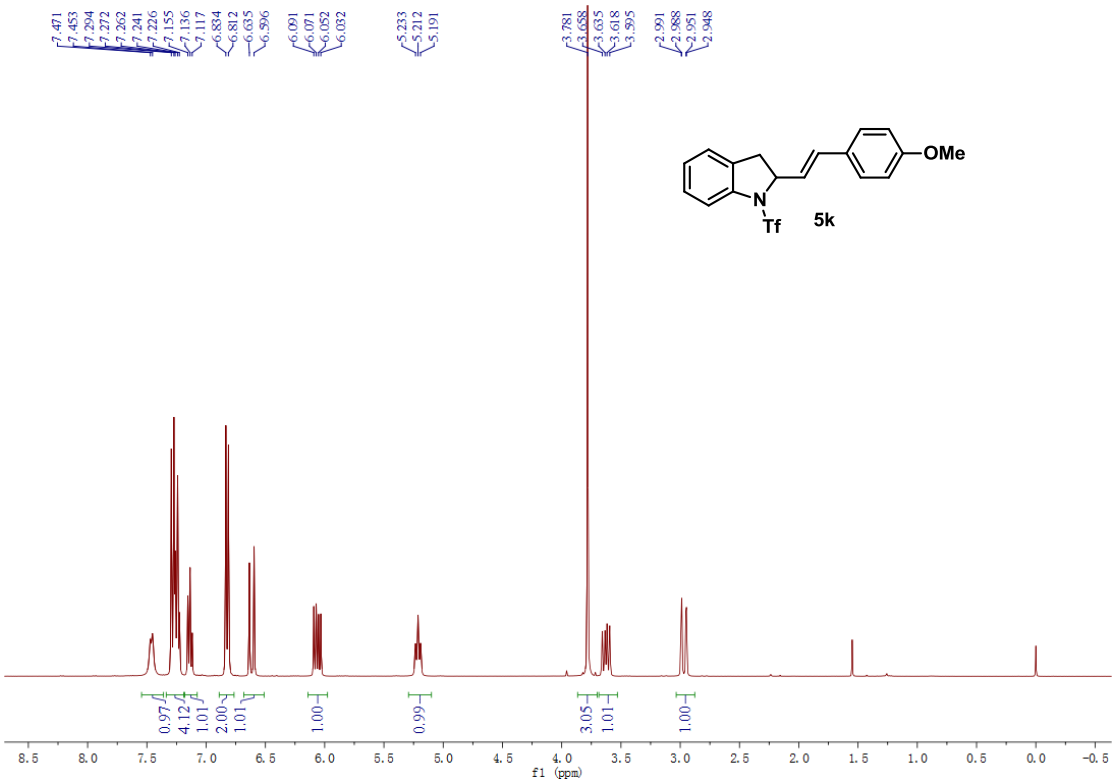
^{13}C NMR Spectrum for **5i** ($CDCl_3$, 100 MHz)



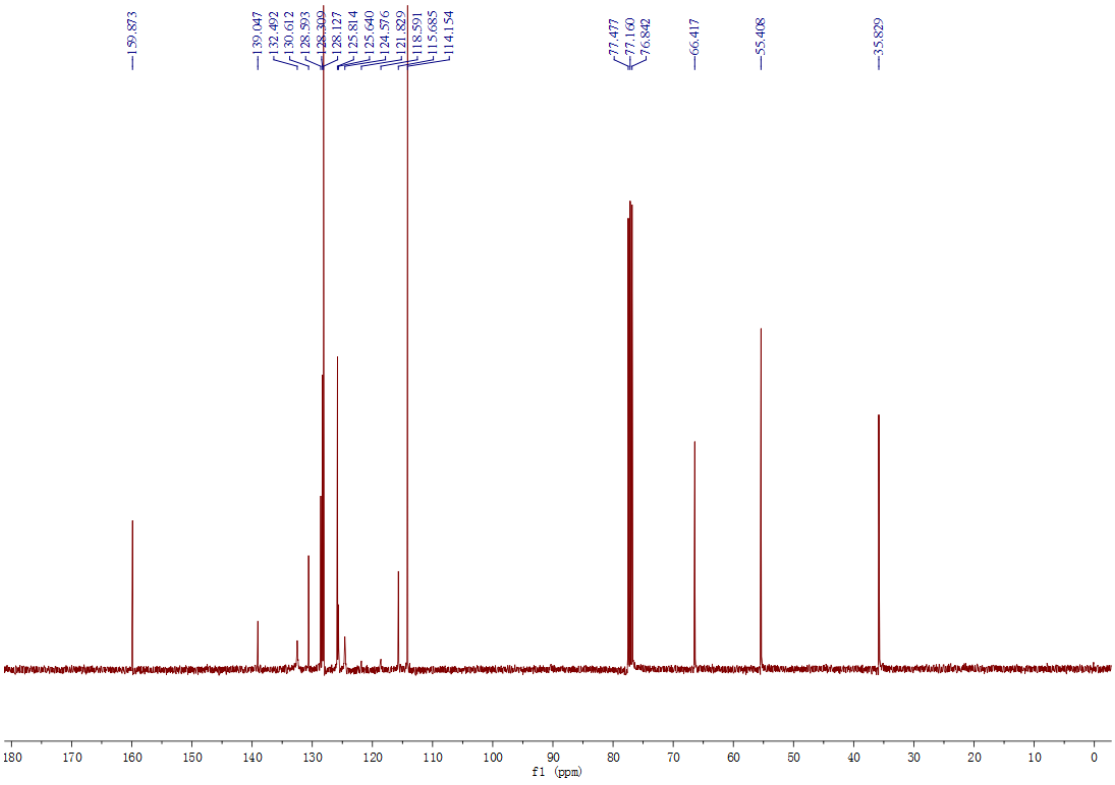
^{1}H NMR Spectrum for **5j** ($CDCl_3$, 400 MHz)



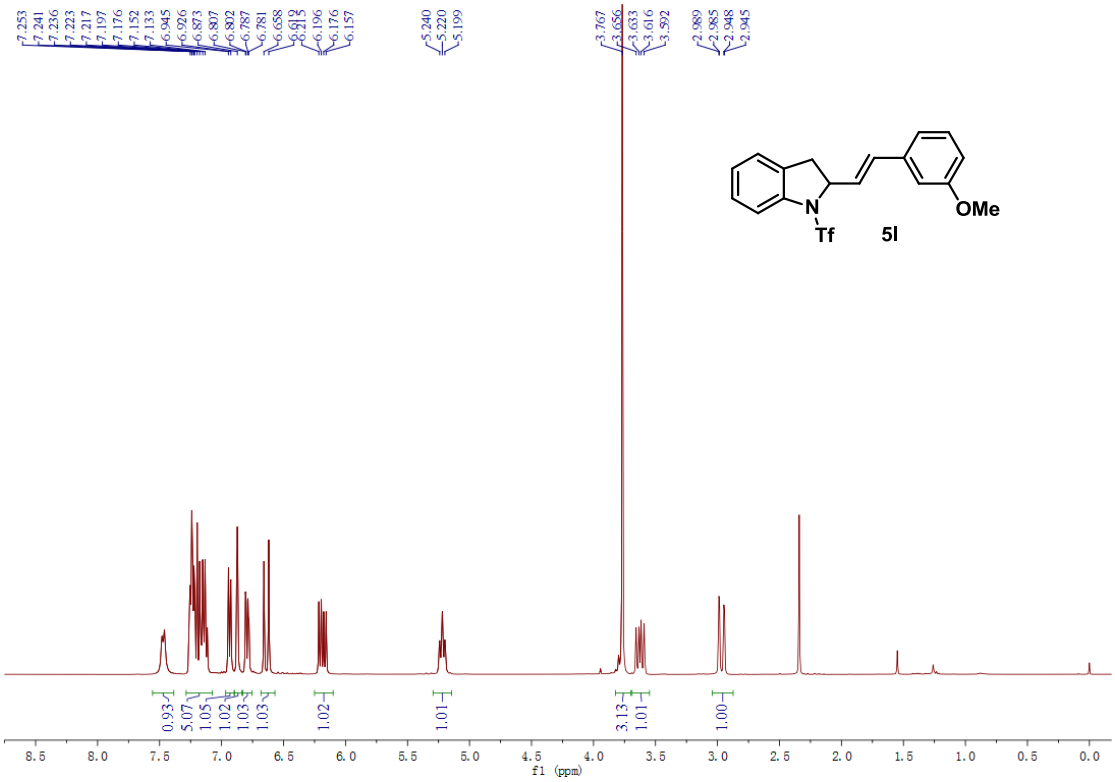
^{13}C NMR Spectrum for **5j** ($CDCl_3$, 100 MHz)



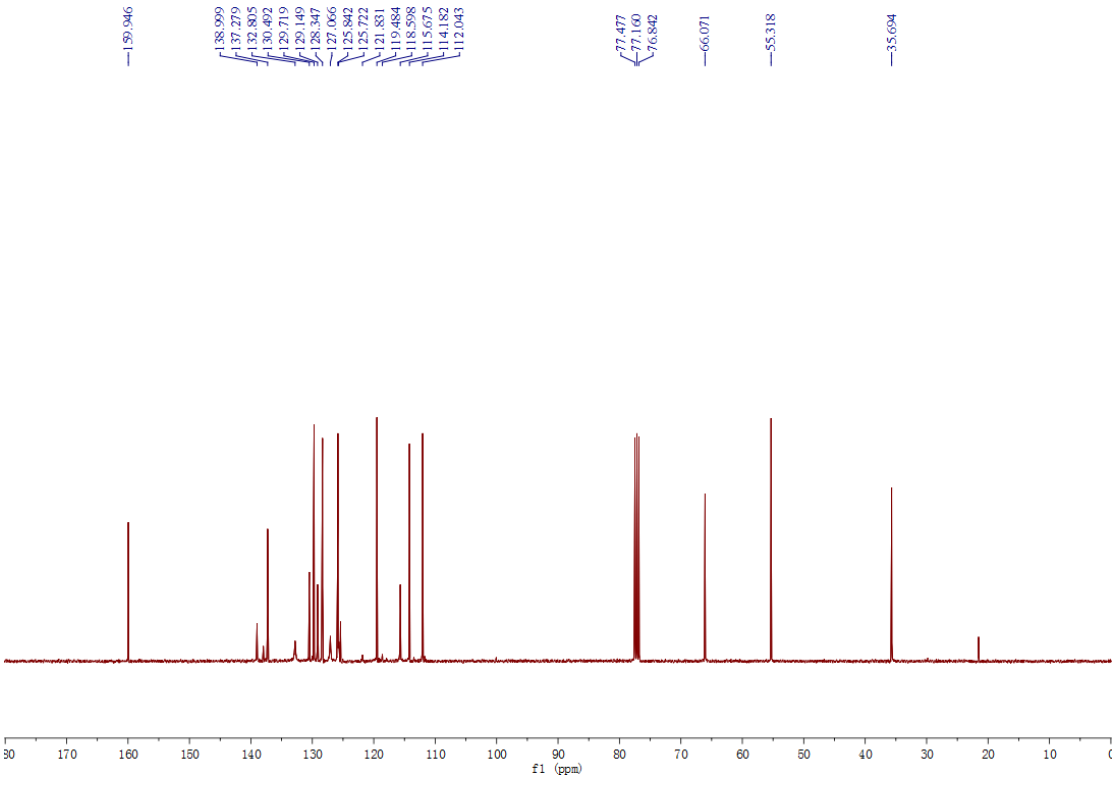
^{1}H NMR Spectrum for **5k** ($CDCl_3$, 400 MHz)



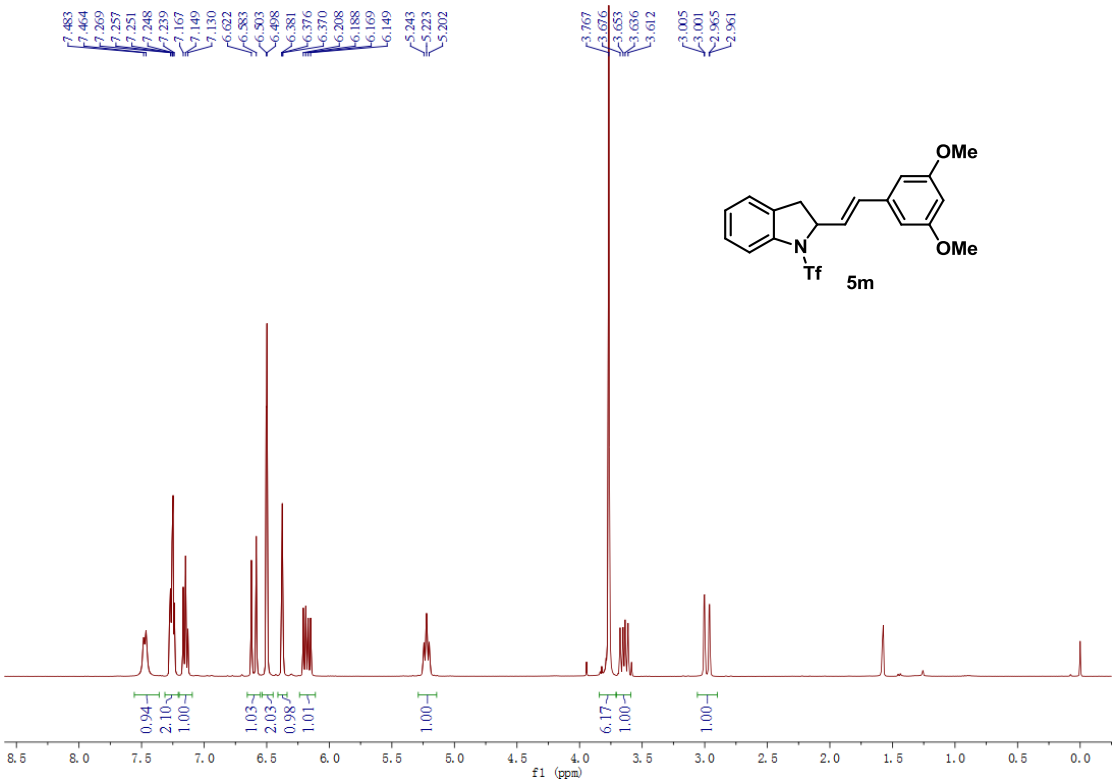
^{13}C NMR Spectrum for **5k** ($CDCl_3$, 100 MHz)



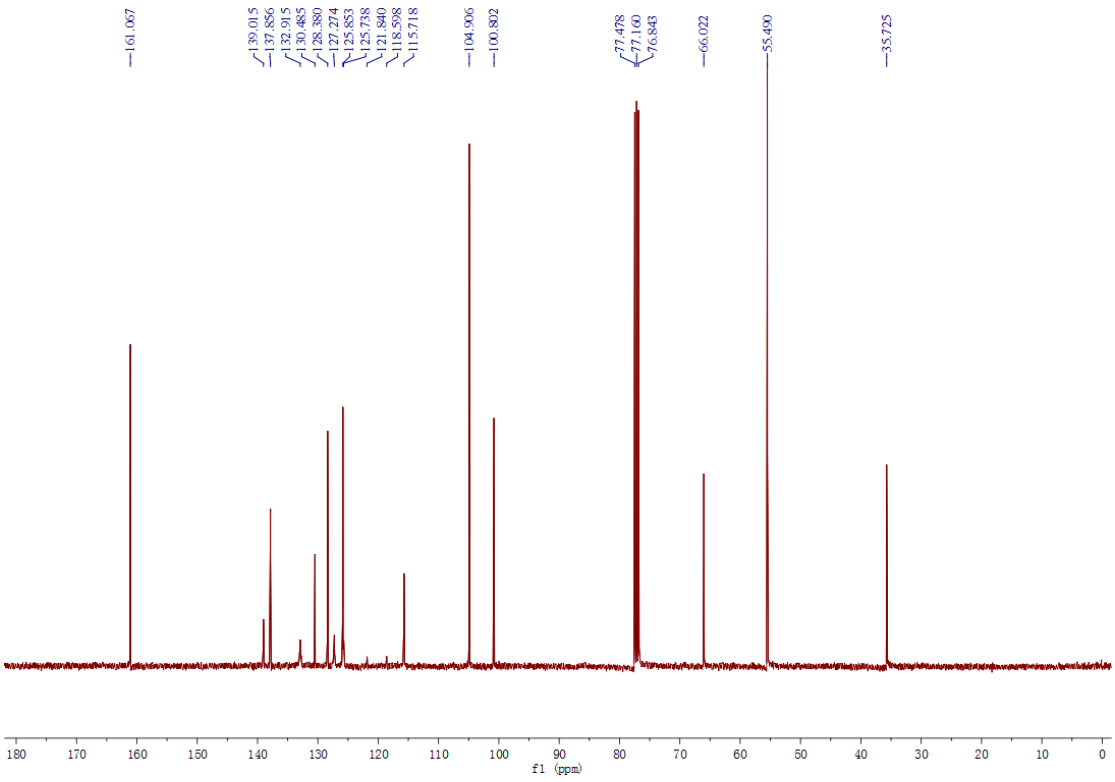
^{1}H NMR Spectrum for **5l** ($CDCl_3$, 400 MHz)



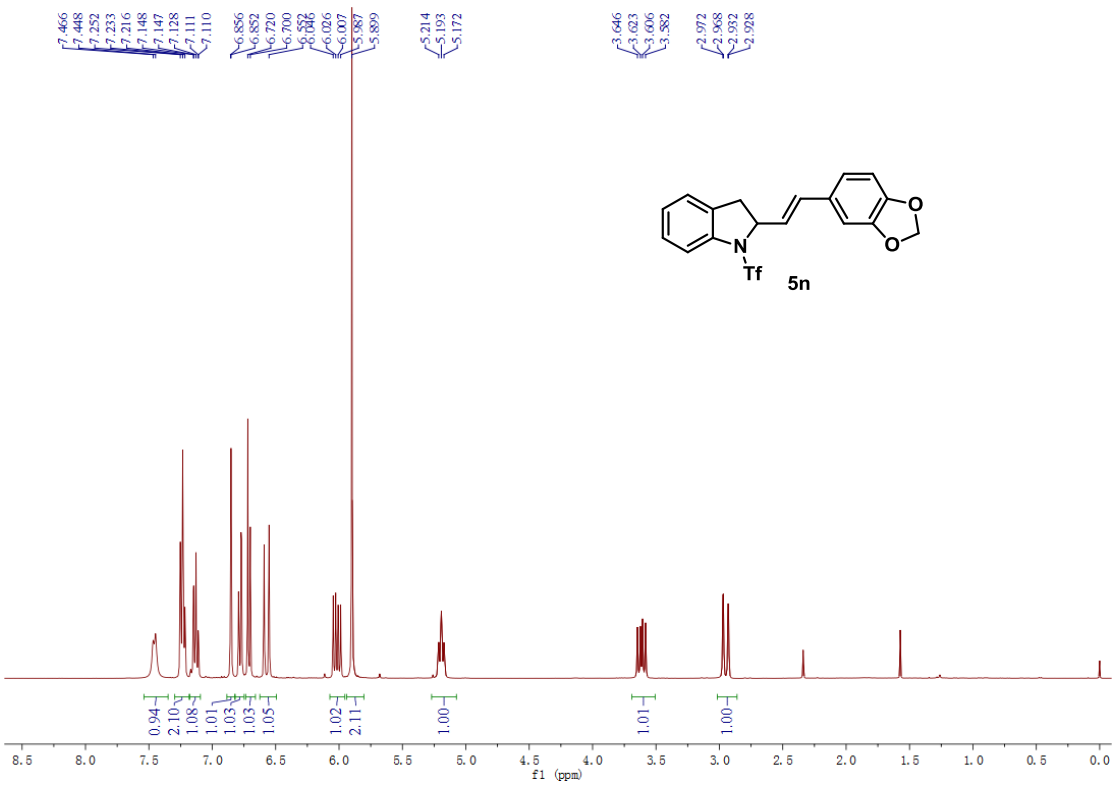
^{13}C NMR Spectrum for **5l** ($CDCl_3$, 100 MHz)



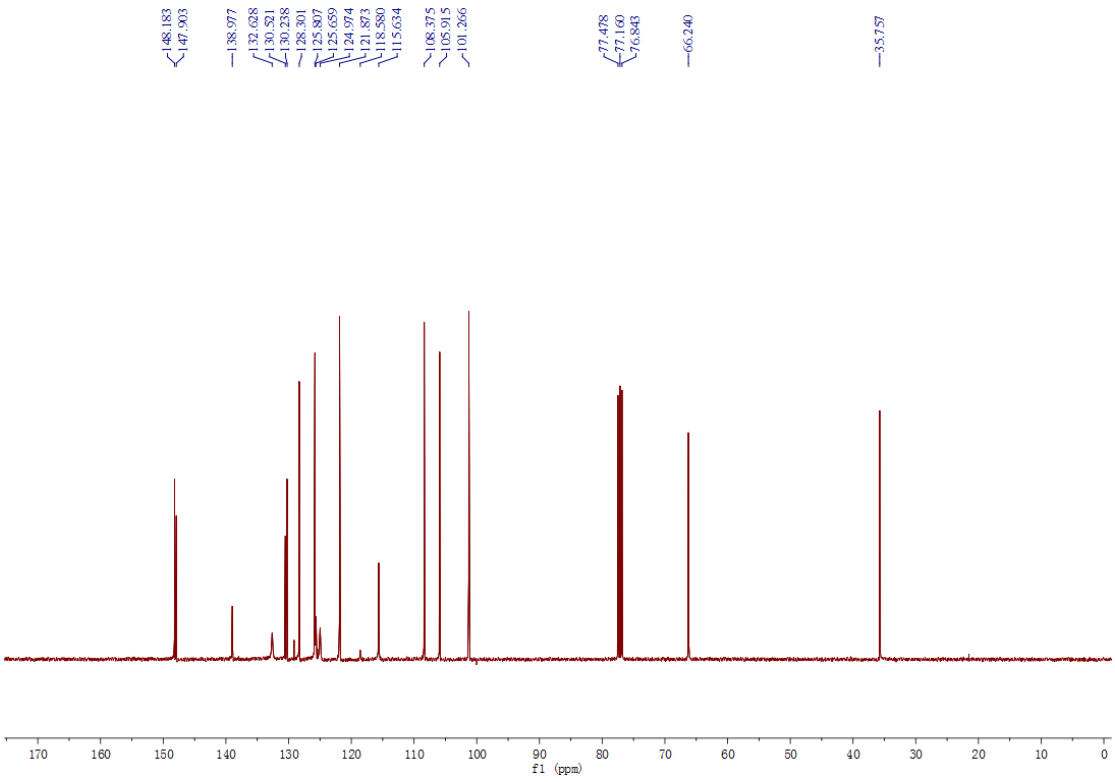
^{1}H NMR Spectrum for **5m** ($CDCl_3$, 400 MHz)



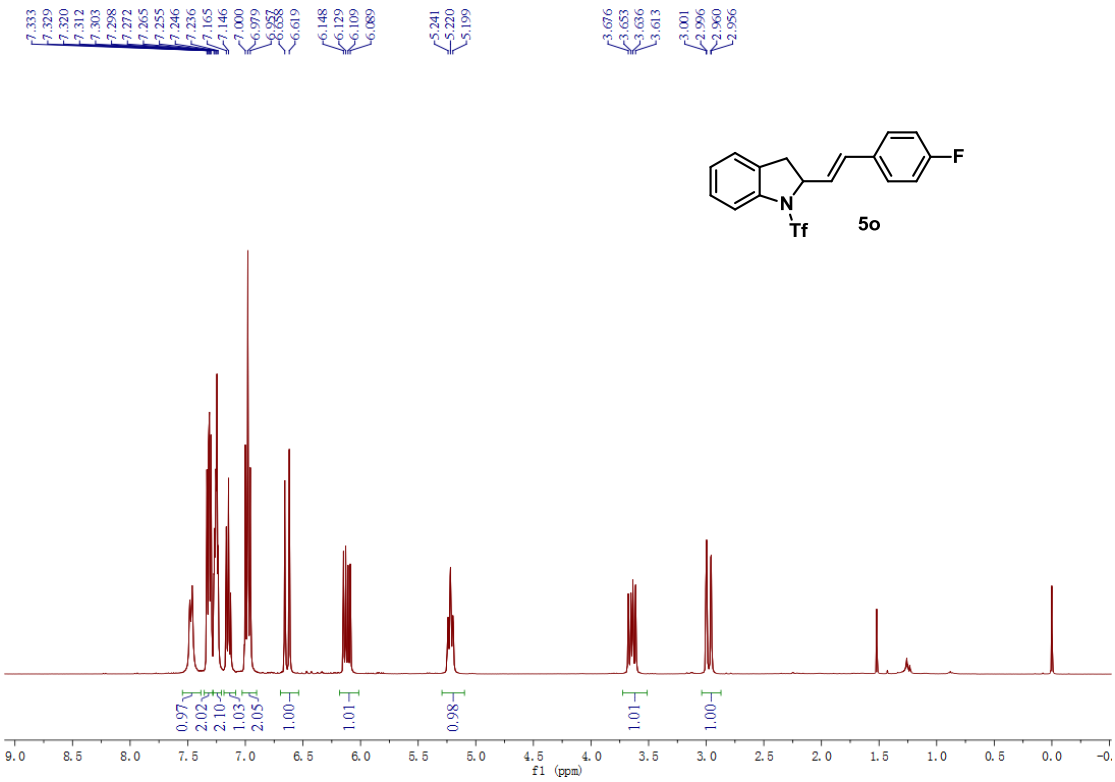
^{13}C NMR Spectrum for **5m** ($CDCl_3$, 100 MHz)



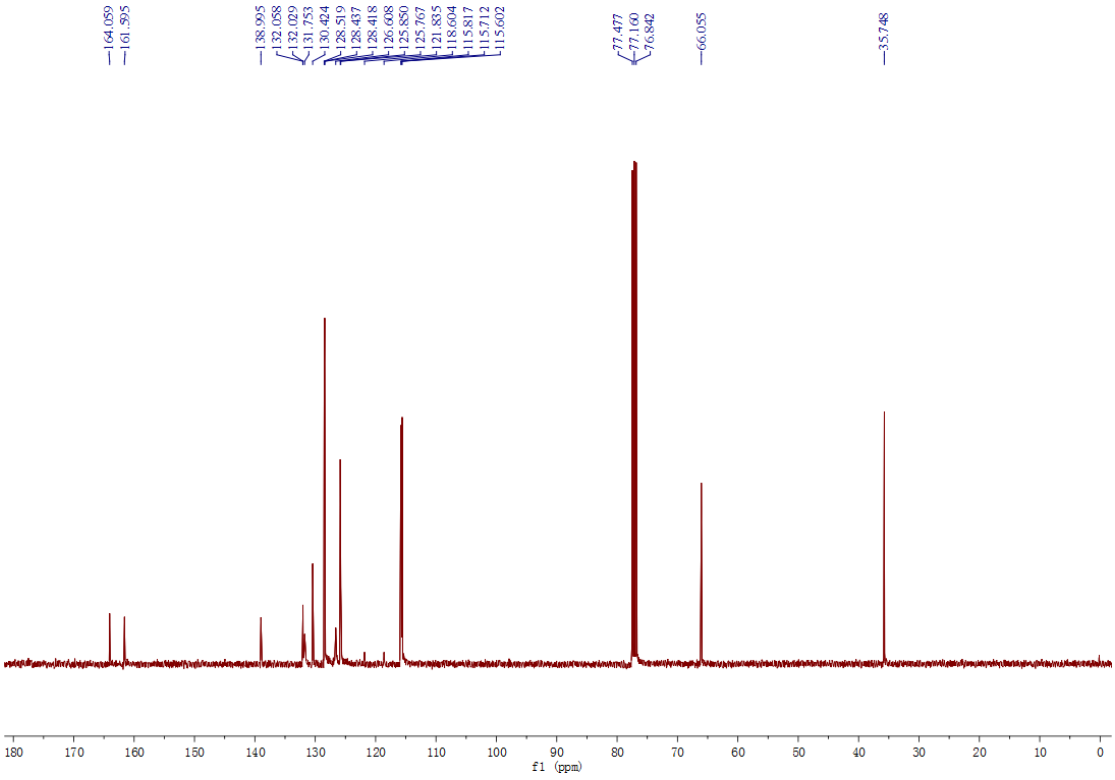
^{1}H NMR Spectrum for **5n** ($CDCl_3$, 400 MHz)



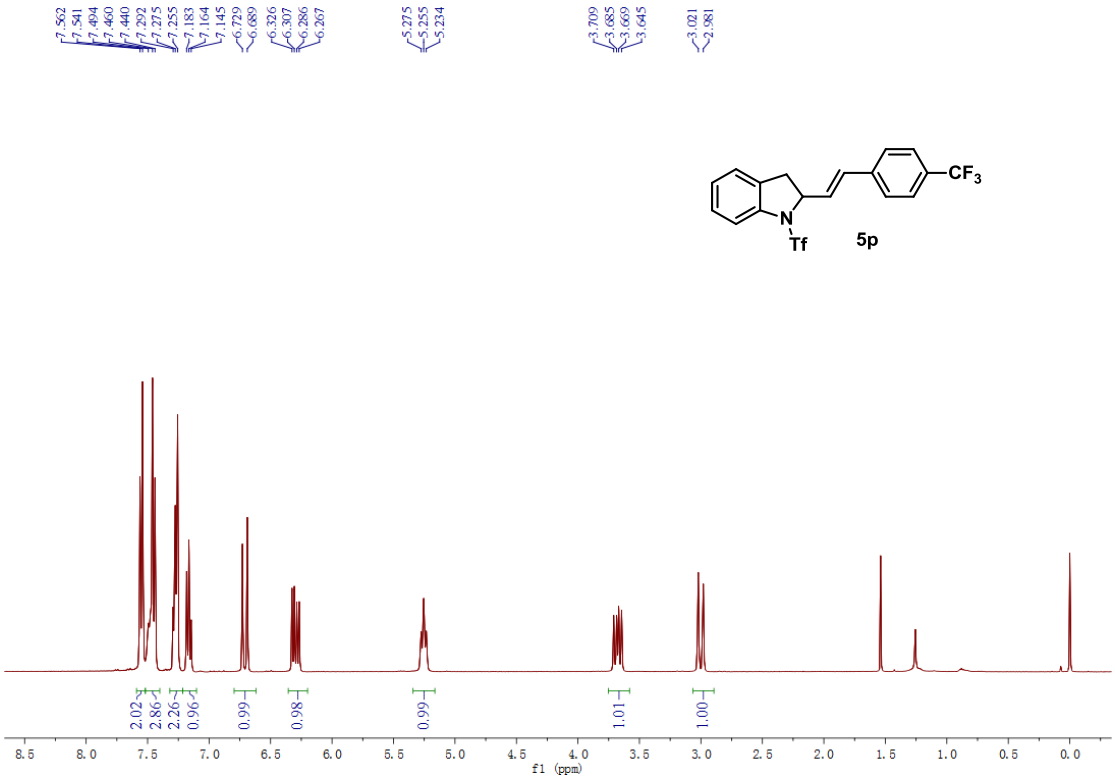
^{13}C NMR Spectrum for **5n** ($CDCl_3$, 100 MHz)



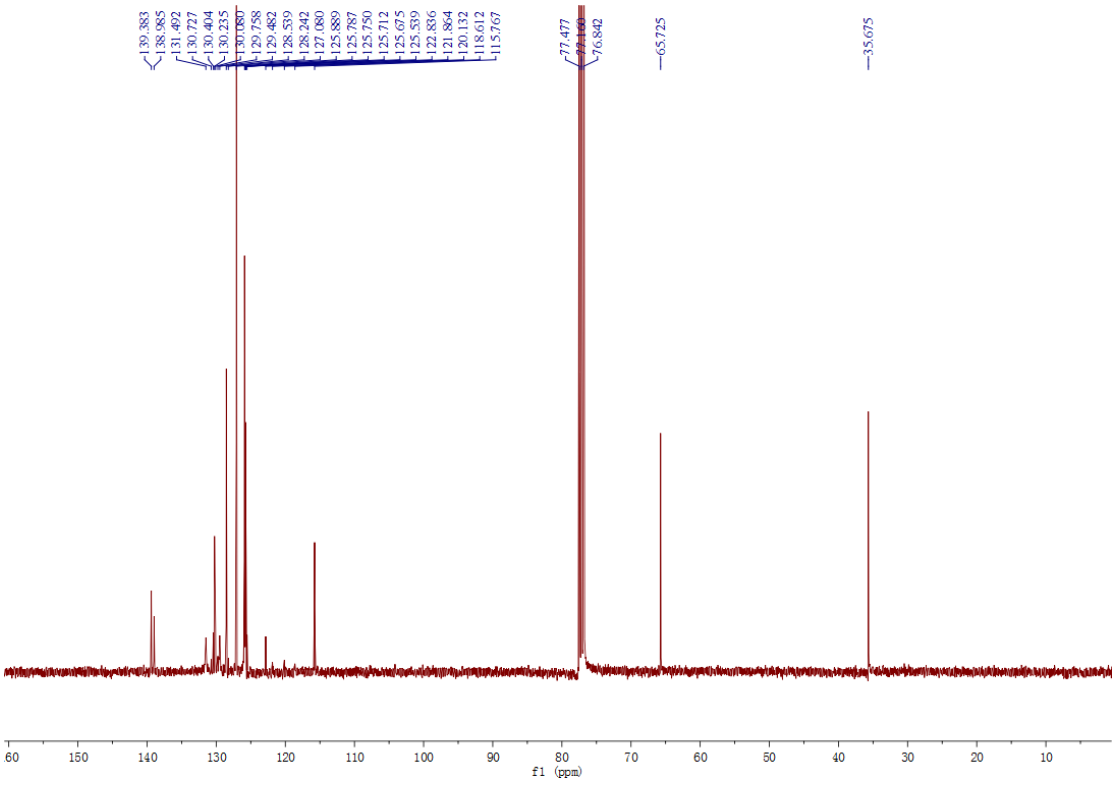
^{1}H NMR Spectrum for **5o** ($CDCl_3$, 400 MHz)



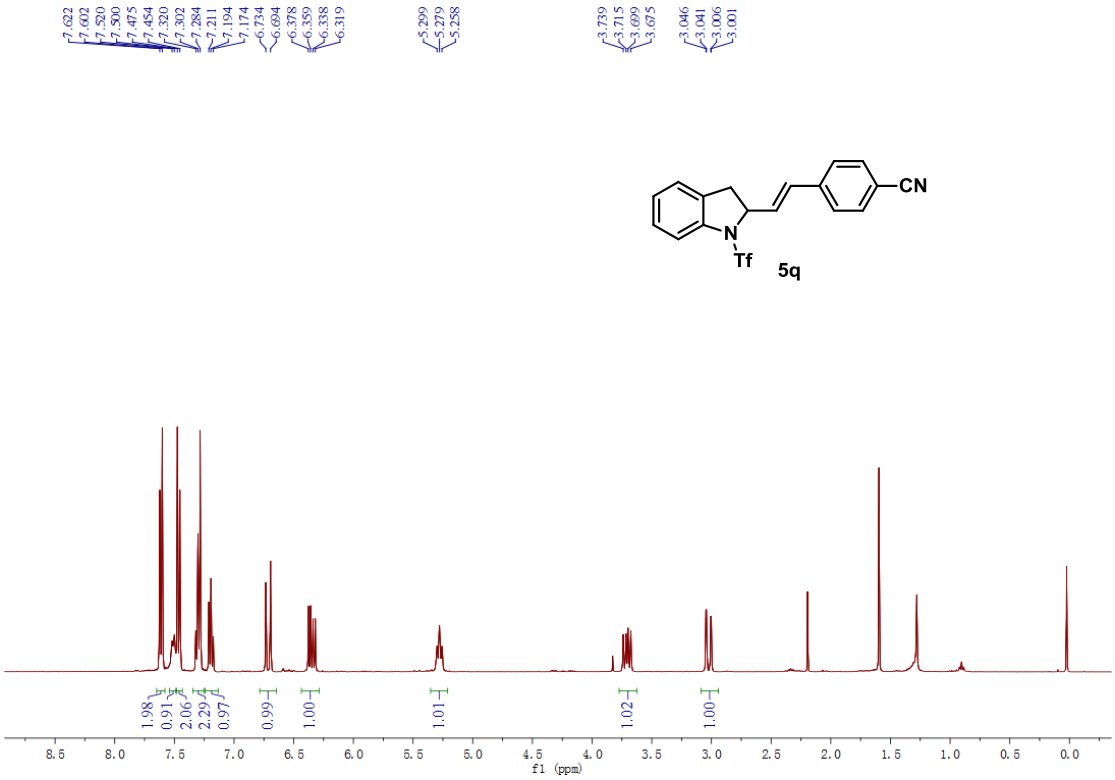
^{13}C NMR Spectrum for **5o** ($CDCl_3$, 100 MHz)



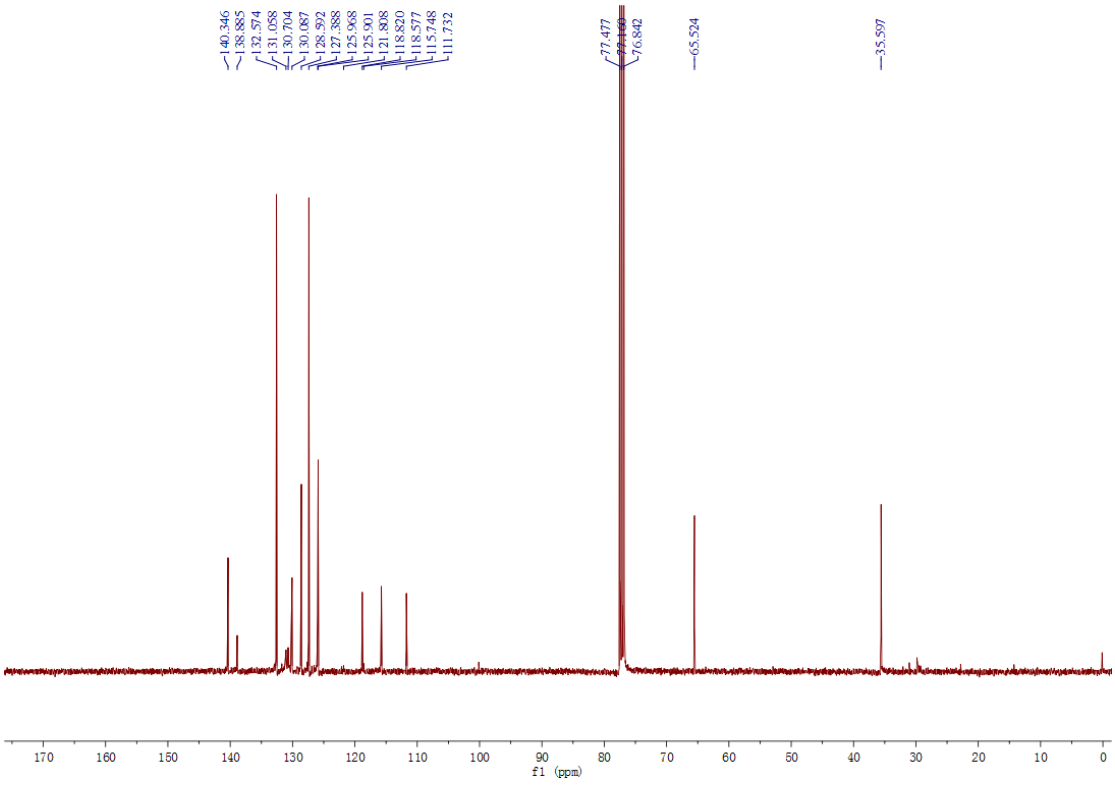
^{1}H NMR Spectrum for **5p** ($CDCl_3$, 400 MHz)



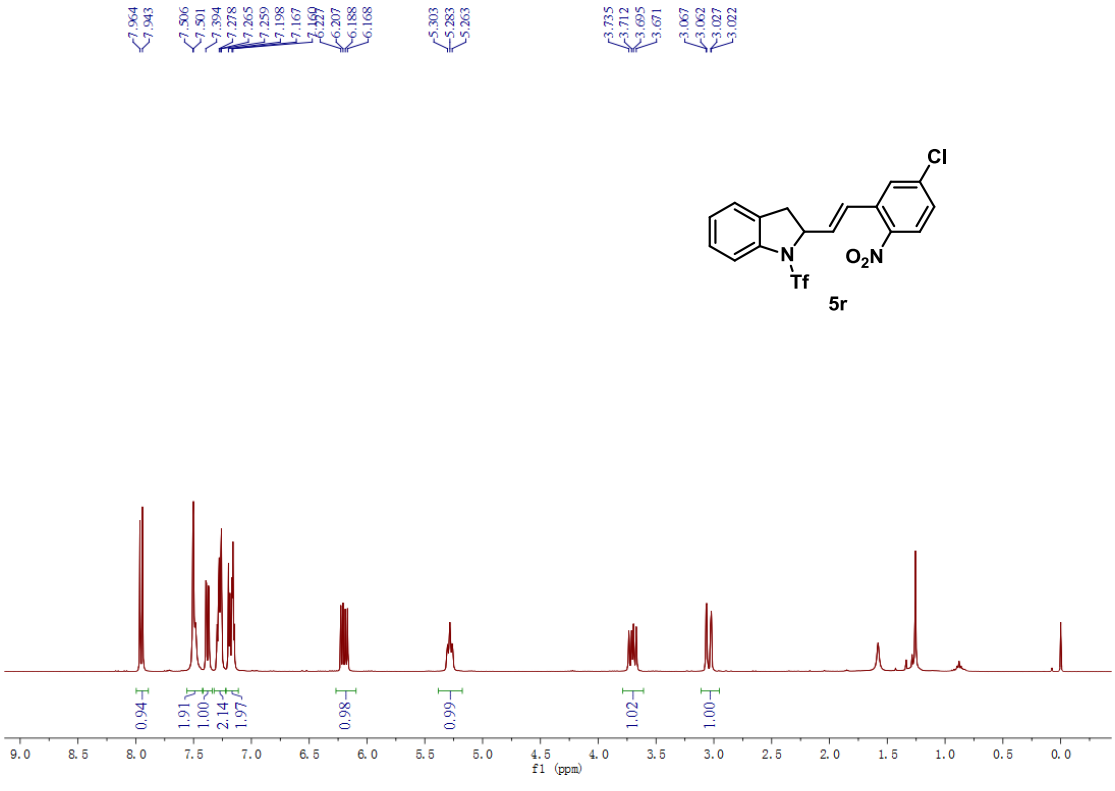
^{13}C NMR Spectrum for **5p** ($CDCl_3$, 100 MHz)



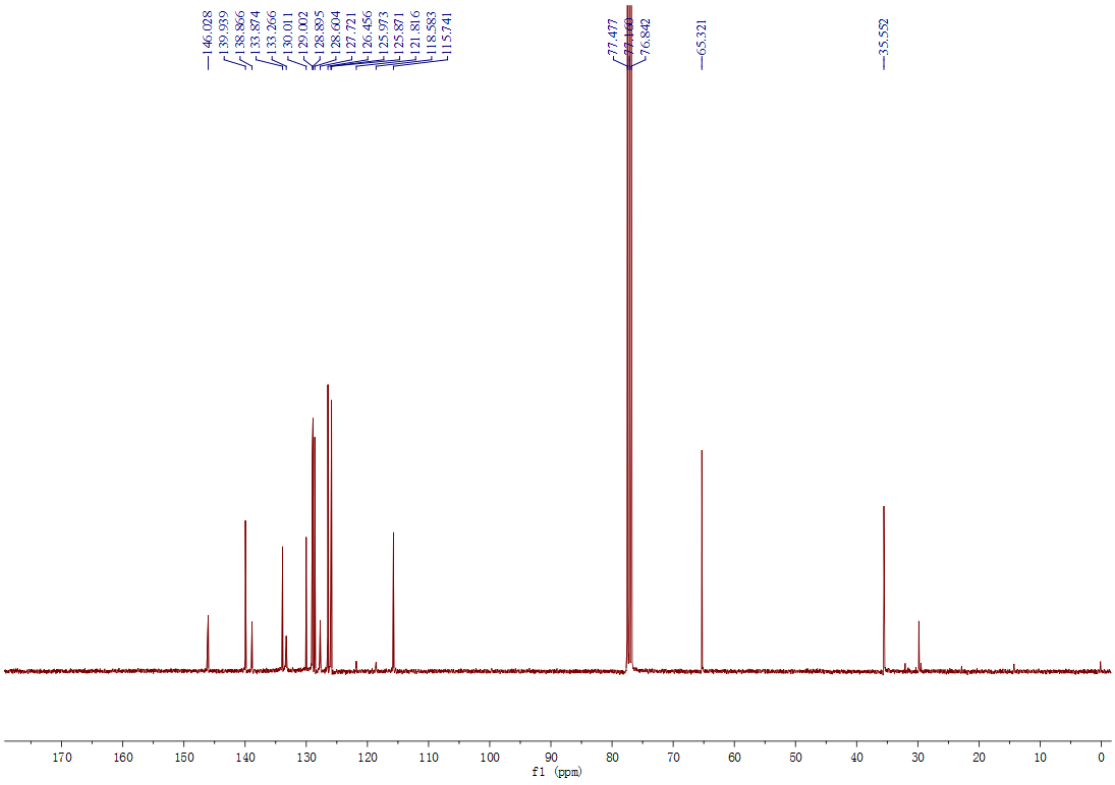
^{1}H NMR Spectrum for **5q** ($CDCl_3$, 400 MHz)



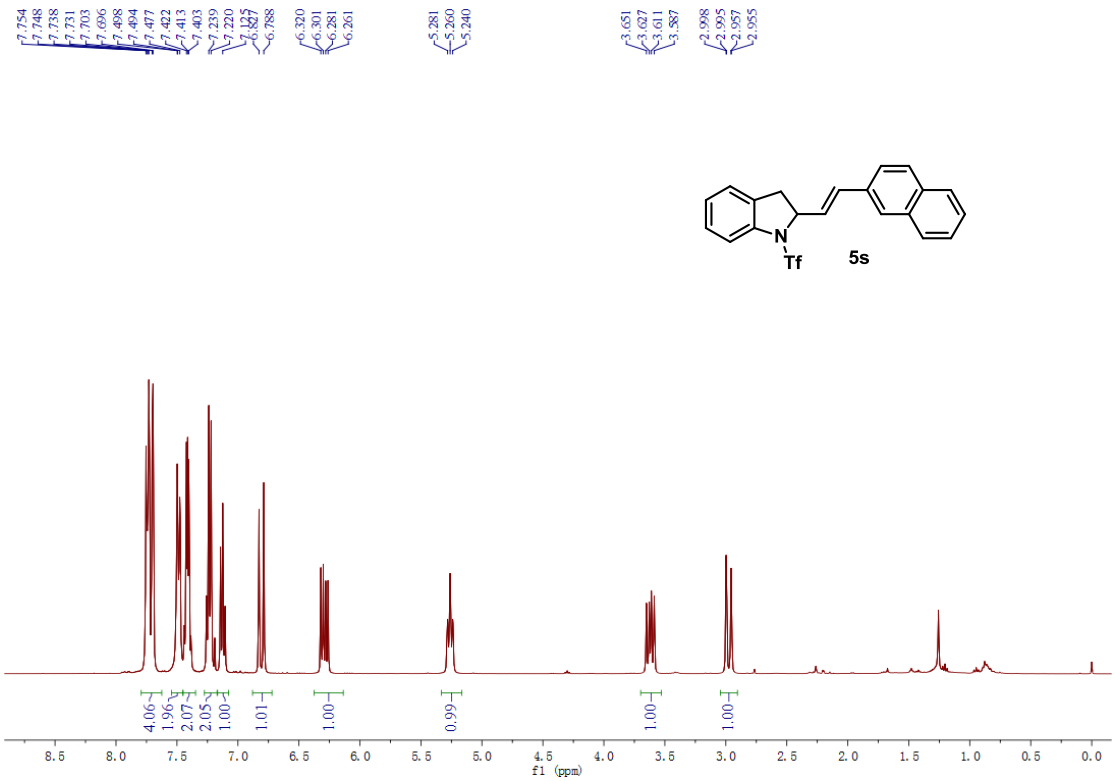
^{13}C NMR Spectrum for **5q** ($CDCl_3$, 100 MHz)



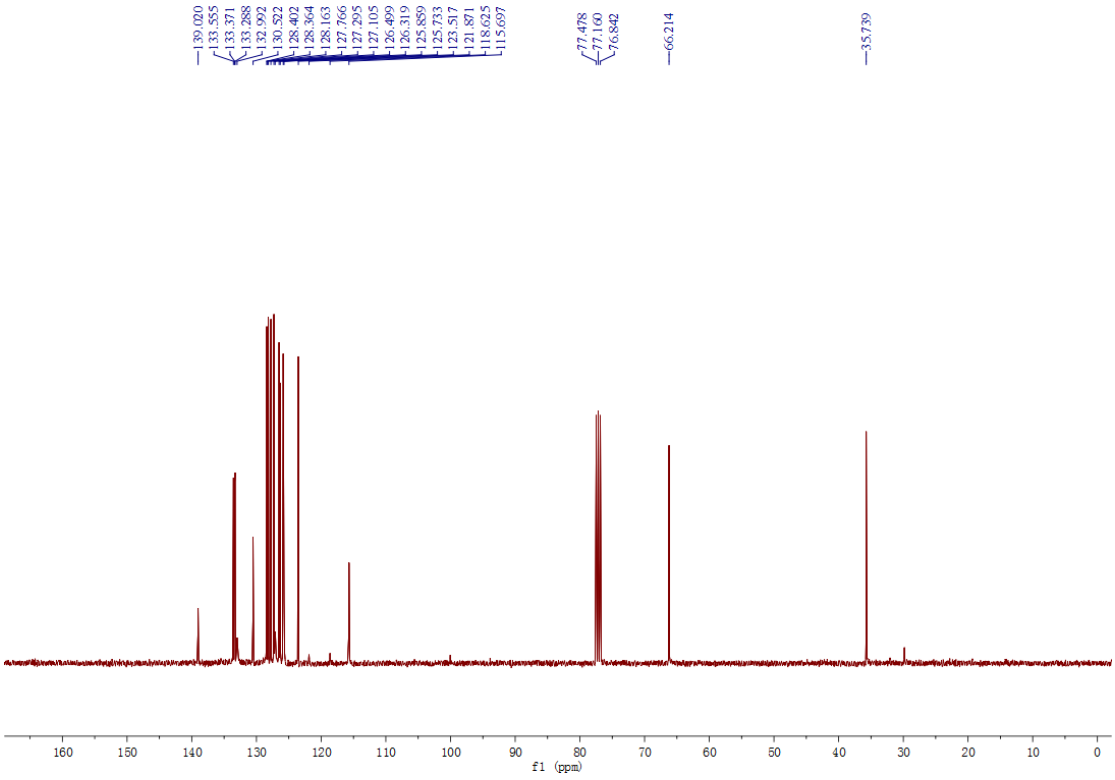
^{1}H NMR Spectrum for **5r** ($CDCl_3$, 400 MHz)



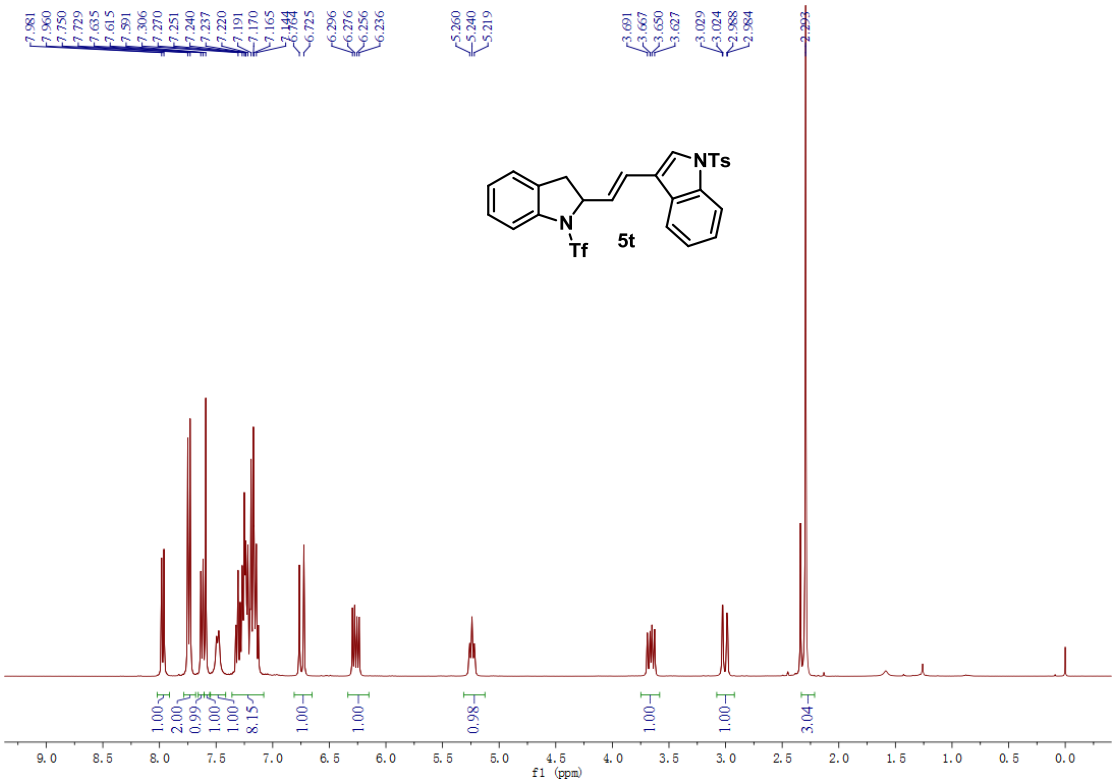
^{13}C NMR Spectrum for **5r** ($CDCl_3$, 100 MHz)



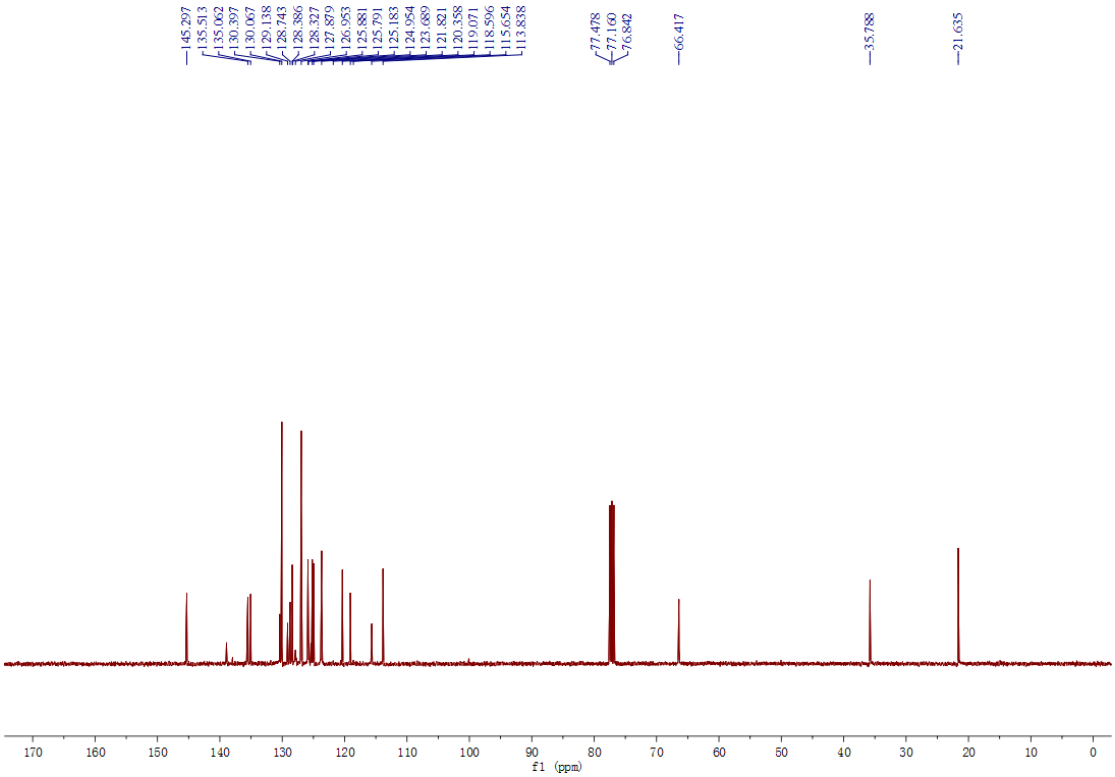
^{1}H NMR Spectrum for **5s** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum for **5s** ($CDCl_3$, 100 MHz)

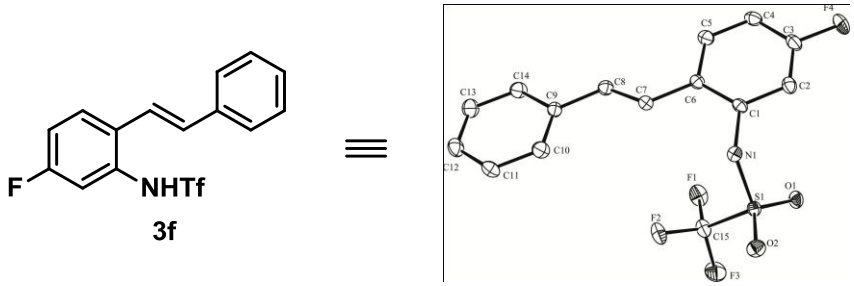


^{1}H NMR Spectrum for **5t** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum for **5t** ($CDCl_3$, 100 MHz)

8. X-ray Crystallographic Structure and Data



X-ray crystallographic structure and data of **3f**

Compound	**3f**
formula	$C_{15}\ H_{11}\ F_4NO_2S$
FW	345.31
crystal system	monoclinic
space group	*P b c a*
a/Å	9.3189 (6)
b/Å	17.4284 (11)
c/Å	17.8836 (16)
α/deg	90
β/deg	90
γ/deg	90
V/Å^3	2904.5 (4)
Z	8
D_c/g cm^{-3}	1.579
μ/mm^{-1}	0.276
R_1[a] ($I > 2\sigma$)	0.0522 (2021)
wR_2[b] (all data)	0.1427 (2844)
GOF	1.032

9. Computational study

A) Computation methods

The calculations were performed with the Gaussian 09 program package[4] and ORCA 4.0.1 program. The geometry optimizations of the intermediates and transition states were performed using the M06 functional with LANL2TZ(f) for Pd and Ag atoms, and def2-SV(P) for others. DFT-D3 dispersion correction with Becke-Johnson damping was used during optimization.[5] Higher level of single point electronic energies for those structures were calculated at DSD-PBEP86-D3/def2-TZVP level with RI approximation using the corresponding auxiliary basis set.[6] Solvation effects were also accounted using SMD solvation model at M05-2X/6-31G(d) level in MeCN.[7] The vibrational harmonic frequencies and thermal corrections were calculated using the same level as the optimization, the latter was calculated at 80^{o}C; the former confirmed the optimized geometrical structures are the minima of PES, and transition states, the first order saddle points. All energies mentioned are solvated Gibbs free energies in MeCN (ΔGsol, $\Delta Gsol^{\neq}$). The Laplacian bond order was calculated using Multiwfn 3.4.1 program (dev. version), using the wavefunction at optimization level.

B) Thermodynamic property of the products

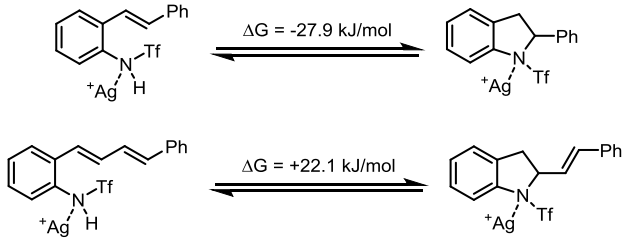


Figure 9B. Gibbs free energy difference of product – Ag^{+} complex

C) Mechanism, and activation Gibbs free energy of nucleophilic attack and β-hydride elimination pathways

It is understandable that the release of N_2, forming intermediate **IM1**, is a spontaneous process with the help of $AgBF_4$ tilts isomerization of benzotriazole towards the ring-opened form. Starting

4 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, E. R. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas; J. B. Foresman, J. B. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision D.01*. Wallingford CT, 2009.

5 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.* 2011**, 32**, 1456.

6 (a) F. Neese, F. Wennmohs, A. Hansen and U. Becker, *Chem. Phys.* 2009**, 356**, 98; (b) F. Weigend, *PCCP* 2006**, 8**, 1057.

7 (a) Y. Zhao, N. E. Schultz and D. G. Truhlar, *J. Chem. Theory Comput.* 2006**, 2**, 364; (b) A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B* 2009**, 113**, 6378.

from there, alkene insertion, forming intermediate **IM2a** and **IM2b**, further lowers the energy to about 100 kJ/mol relative to **IM1**, shown in Figure 9C.

For the monoene substrates, styrene as an example, the computation estimates a $\Delta\Delta G^{\neq}$ of 82.3 kJ/mol favoring the β-elimination pathway via **TS2**. While for the diene substrates, approximately 20.4 kJ/mol advantage tilts towards the nucleophilic attack pathway via **TS1'**. The reason of such difference has been discussed in the main text.

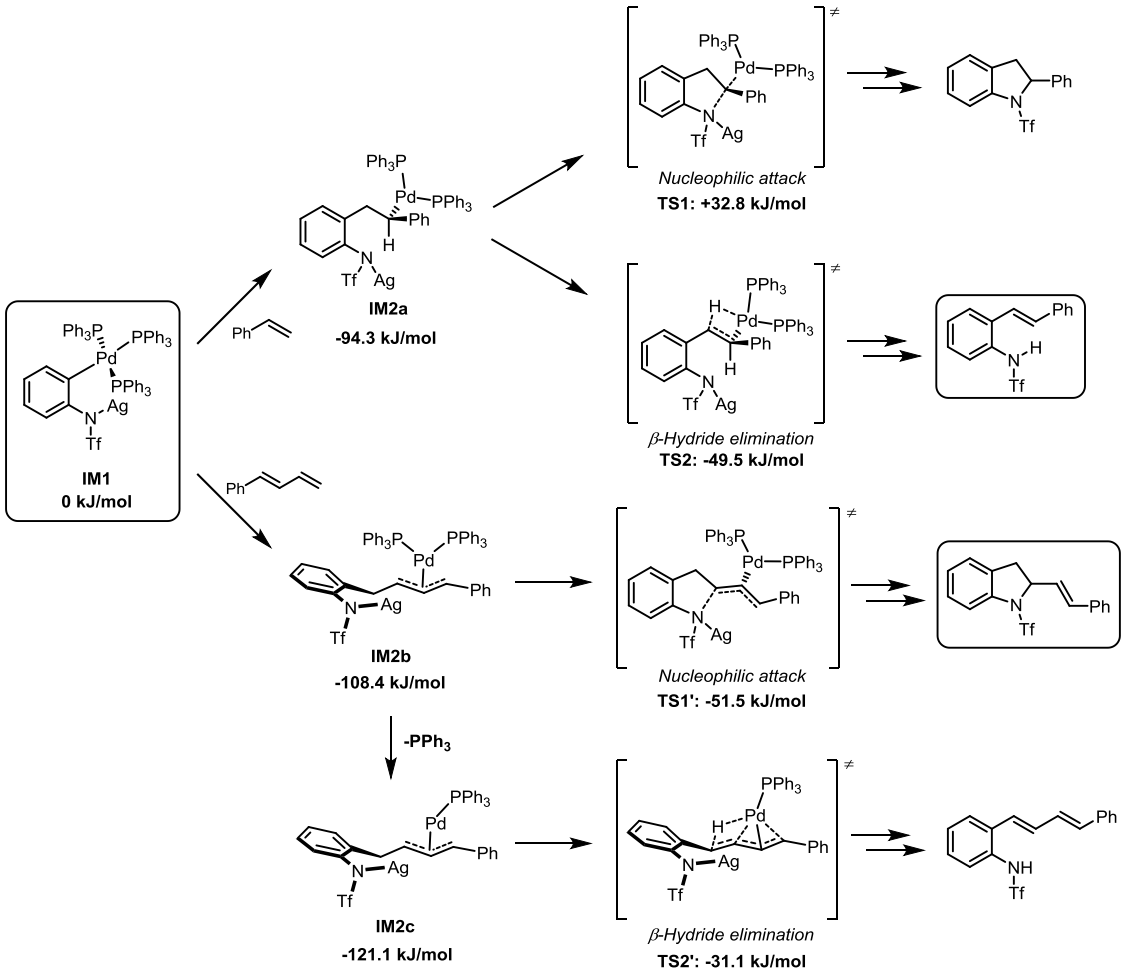
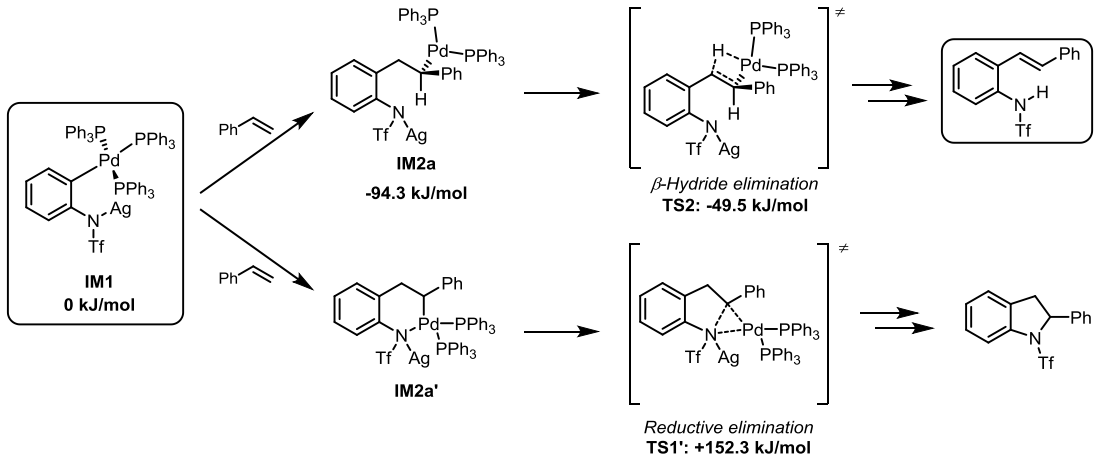


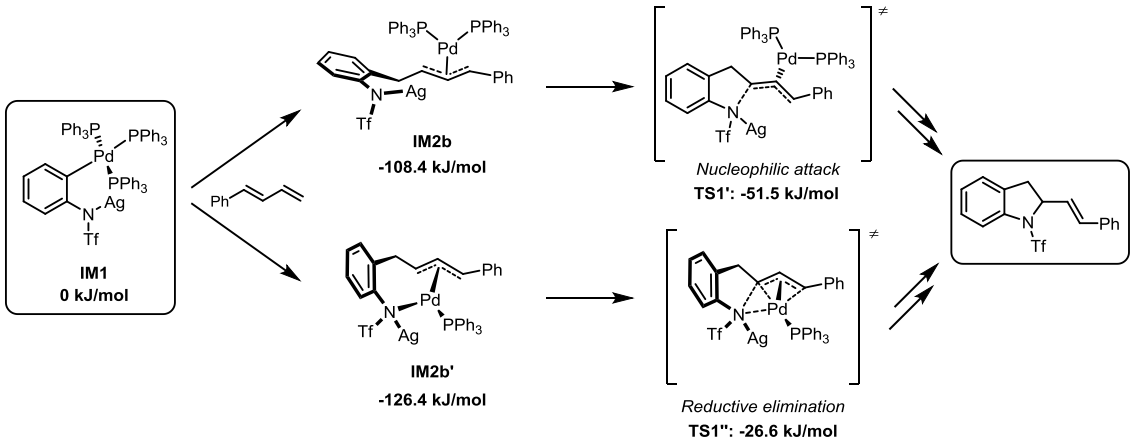
Figure 9C. Activation Gibbs free energy of nucleophilic attack and β-hydride elimination pathways for monoene substrats

D) The possibility of reductive elimination mechanism

There is a possibility of a reductive elimination mechanism, which give the same product as nucleophilic attack pathway. However, it is unlikely to happen according to the computation results. The reductive elimination transition state for the monoene substrates **TS1'** has been located with a Gibbs free energy of +152.3 kJ/mol relative to **IM1**. The steric hindrance of the 3-member-ring-like TS is likely to be the cause of such high energy.



For the diene substrates, the reductive elimination mechanism will lead to the same formal [3+2] product, via **IM2b'** and **TS1"**. But the activation Gibbs free energy of a reductive elimination pathway is much higher than that of a nucleophilic attack. This result coincides with the fact that Tsuji-Trost allylation with similar nucleophile typically undergoes a double inversion process, giving the product with net retention of configuration.



E) Energies and geometries

Species	PPh_3	IM1	Styrene	IM2a
Optimization Level	M06-D3/[def2-SV(P)+LANL2TZ(f)]			
Electronic Energy Level	DSD-PBEP86/def2-TZVP			
Electronic Energy (kJ/mol)	-2718325.44	-11950602.73	-811993.22	-10044288.64
Imaginaries	0	0	0	0
H Correction (kJ/mol)	773.13	2702.63	374.54	2298.05
S (J/mol Ƙ)	606.08	1628.73	361.74	1513.04
G Correction (kJ/mol)	559.09	2127.44	246.79	1763.72
Solvation Gibbs Free Energy (kJ/mol)	-59.16	-345.66	-30.28	-341.49
Solvated Gibbs Free Energy (kJ/mol)	-2717825.51	-11948820.95	-811776.71	-10042866.41

Species	TS1’	TS2	TS1	(E)-butadien-1-ylbenzene
Optimization Level		M06-D3/[def2-SV(P)+LANL2TZ(f)]		
Electronic Energy Level		DSD-PBEP86/def2-TZVP		
Electronic Energy (kJ/mol)	-10044093.15	-10044243.74	-10044206.15	-1014973.66
Imaginaries	1	1	1	0
H Correction (kJ/mol)	2294.29	2285.66	2295.21	470.11
S (J/mol Ƙ)	1459.49	1499.81	1474.14	415.40
G Correction (kJ/mol)	1778.87	1756.00	1774.62	323.41
Solvation Gibbs Free Energy (kJ/mol)	-305.51	-333.90	-307.86	-38.08
Solvated Gibbs Free Energy (kJ/mol)	-10042619.80	-10042821.64	-10042739.39	-1014688.32

Species	IM2b’	IM2b	IM2c	TS1''
Optimization Level		M06-D3/[def2-SV(P)+LANL2TZ(f)]		
Electronic Energy Level		DSD-PBEP86/def2-TZVP		
Electronic Energy (kJ/mol)	-7528896.87	-10247290.02	-7528792.21	-7528804.26
Imaginaries	0	0	0	1
H Correction (kJ/mol)	1611.53	2397.85	1611.80	1605.78
S (J/mol Ƙ)	1144.29	1520.33	1206.51	1174.86
G Correction (kJ/mol)	1207.42	1860.95	1185.72	1190.88
Solvation Gibbs Free Energy (kJ/mol)	-295.16	-363.07	-372.91	-271.47
Solvated Gibbs Free Energy (kJ/mol)	-7527984.62	-10245792.14	-7527979.40	-7527884.85

Species	TS1'	TS2'
Optimization Level	M06-D3/[def2-SV(P)+LANL2TZ(f)]	
Electronic Energy Level	DSD-PBEP86/def2-TZVP	
Electronic Energy (kJ/mol)	-10247254.31	-7528694.66
Imaginaries	1	1
H Correction (kJ/mol)	2386.84	1594.42
S (J/mol Ƙ)	1557.70	1210.52
G Correction (kJ/mol)	1836.74	1166.92
Solvation Gibbs Free Energy (kJ/mol)	-317.67	-361.60
Solvated Gibbs Free Energy (kJ/mol)	-10245735.24	-7527889.35

Triphenylphosphane

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C	-0.853112	1.400828	-0.433058	C	1.949507	0.805265	0.704812
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C	-2.217302	2.415999	1.296488	H	-2.818430	2.314234	2.207980
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C	-1.277475	3.793124	-0.449333	H	-1.140175	4.774913	-0.917902
C	-0.693961	2.663550	-1.020523	H	-0.099344	2.762904	-1.939568
C	-0.800620	-1.451965	-0.444315	H	0.823068	-2.040984	0.871651
C	-0.196606	-2.257437	0.527633	H	-0.399107	-3.967542	1.832603
C	-0.885487	-3.342916	1.073411	H	-2.727979	-4.477363	1.098969
C	-2.186832	-3.628872	0.663851	H	-3.821025	-3.048422	-0.635441
C	-2.797648	-2.831084	-0.306481	H	-2.587829	-1.141135	-1.633881
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C	2.667094	-0.756879	-0.988756	H	5.227914	-0.037038	1.144782
C	3.940045	-0.793011	-0.422649	H	3.446481	1.392856	2.146309
C	4.223996	-0.019954	0.704172	H	1.176189	1.436496	1.161209

IM1

C	1.617017	-1.013373	4.029482	C	-2.847923	-3.780037	-1.273221
C	2.979125	-1.146532	3.775195	C	-3.495208	-4.084564	-2.470403
C	3.458399	-1.047356	2.472608	C	-3.232685	-3.342793	-3.622637
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C	1.215546	-0.642376	1.643823	C	-1.683593	-1.974673	-2.380430
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N	3.028216	-0.803963	0.044505	C	-1.916683	-4.415599	1.933268
Pd	-0.339369	-0.043067	0.388915	C	-2.635490	-4.894267	3.025801
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F	5.717877	0.675405	0.791811	C	-2.425522	1.766295	2.362939
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C	0.481977	-3.516845	0.040306	C	-4.302789	3.801739	2.140182
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C	2.794703	-5.074735	-0.320195	C	-1.724131	1.673243	-2.749764
C	1.965465	-4.804678	-1.404792	C	-1.803944	2.267968	-4.007816
C	0.802833	-4.039892	-1.231455	C	-2.983938	2.896602	-4.399677
C	-1.935205	-2.721487	-1.222395	C	-4.085740	2.904610	-3.540791

C	-4.005938	2.299349	-2.289347
C	-4.117629	-0.213094	-0.207104
C	-4.638513	-0.767331	-1.384164
C	-5.750284	-1.605991	-1.339936
C	-6.346150	-1.920119	-0.118583
C	-5.838684	-1.368643	1.056873
C	-4.741083	-0.510383	1.011976
H	1.218301	-1.097993	5.047529
H	3.686511	-1.330086	4.593181
H	4.530499	-1.165830	2.290364
H	-0.309560	-0.616754	3.178033
H	1.078610	-3.436647	2.129729
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H	3.704358	-5.669472	-0.458211
H	2.201633	-5.201686	-2.398701
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P	0.750483	2.174216	0.299136
C	1.725105	2.356583	-1.243980
C	1.704527	1.341218	-2.202146
C	2.409016	1.459795	-3.398534
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C	-0.256805	3.727293	0.246804
C	-0.604582	4.442001	1.399768
C	-1.376833	5.599011	1.309651
C	-1.826564	6.054216	0.070832
C	-1.482867	5.352491	-1.083674
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C	1.918709	2.469606	1.682445
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Styrene

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H	4.006365	-0.010543	0.000074
H	2.812515	1.427001	0.000262

IM2a

C	1.355097	3.268418	2.565399
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C	3.562526	2.290980	2.473608
C	3.234019	1.600336	1.297509
C	1.937414	1.747994	0.757297
C	1.018942	2.578652	1.401181
N	4.138487	0.712729	0.676879
C	1.546665	0.953168	-0.454990
C	1.232106	-0.482996	-0.135259
Pd	-0.759216	0.137373	-0.346699
C	1.692809	-1.541535	-1.047531
C	1.737857	-1.369245	-2.443427
C	2.221932	-2.378350	-3.269022
C	2.686817	-3.582816	-2.731097
C	2.649698	-3.779757	-1.352346
C	2.152922	-2.772877	-0.512481
S	5.545735	1.186587	0.145519
O	6.346834	-0.016294	-0.149682
O	6.182151	2.317200	0.820328
C	5.206434	1.859924	-1.552171
F	4.439473	2.937515	-1.465191
F	6.334762	2.188911	-2.157553
F	4.577735	0.954398	-2.294683
P	-1.543837	-1.717299	0.800550
C	-1.493380	-3.242313	-0.194705
C	-1.852832	-4.481107	0.354990
C	-1.829651	-5.624493	-0.439354
C	-1.470620	-5.535697	-1.786474
C	-1.137456	-4.302186	-2.342882
C	-1.146305	-3.156988	-1.546462
C	-3.266129	-1.697433	1.424125
C	-3.580681	-1.439051	2.762883
C	-4.911724	-1.442170	3.180941
C	-5.935086	-1.698753	2.270543
C	-5.626818	-1.957440	0.934014
C	-4.300215	-1.958014	0.512705
C	-0.470833	-1.935944	2.265205
C	0.291365	-3.086119	2.489421
C	1.235526	-3.111153	3.518395
C	1.415314	-1.997553	4.335662
C	0.643492	-0.851361	4.128695
C	-0.285979	-0.817161	3.094265
P	-2.727088	1.485137	-0.692743
C	-2.210262	3.166185	-1.222568
C	-1.355461	3.243226	-2.332216
C	-0.891564	4.476112	-2.780071
C	-1.267184	5.645786	-2.115129
C	-2.117353	5.575502	-1.013488
C	-2.592147	4.340522	-0.566989
C	-3.876872	0.980323	-2.021178
C	-3.758339	-0.301515	-2.568572
C	-4.617186	-0.715396	-3.586766
C	-5.592162	0.155977	-4.069185
C	-5.703764	1.444037	-3.540565
C	-4.848105	1.858305	-2.523124
C	-3.733749	1.775325	0.806384
C	-5.130048	1.704129	0.831595
C	-5.821215	1.934075	2.022727
C	-5.127400	2.248750	3.189690
C	-3.733199	2.321946	3.171453
C	-3.040648	2.075566	1.989402
H	0.616543	3.915513	3.052793
H	2.915123	3.651080	4.017392
H	4.564094	2.159957	2.896613
H	0.014858	2.685577	0.965415
H	0.644947	1.482065	-0.941445
H	2.298435	1.032229	-1.264190
H	1.398094	-0.739710	0.923523
H	1.380609	-0.429032	-2.884299
H	2.243878	-2.222993	-4.353851
H	3.074471	-4.367494	-3.390178
H	2.993374	-4.724554	-0.915360
H	2.043499	-2.963583	0.566396
H	-2.158379	-4.551757	1.407618
H	-2.103948	-6.593185	-0.006149
H	-1.460229	-6.438183	-2.408422
H	-0.868099	-4.227256	-3.402918
H	-0.882491	-2.179617	-1.973781
H	-2.789991	-1.243829	3.496902
H	-5.146077	-1.242626	4.233201

H	-6.979424	-1.699911	2.603767
H	-6.424518	-2.164868	0.211341
H	-4.069721	-2.179439	-0.536995
H	0.178101	-3.965263	1.844514
H	1.838568	-4.013127	3.674313
H	2.159865	-2.020480	5.139643
H	0.770823	0.022461	4.777349
H	-0.857984	0.103601	2.911703
H	-1.047355	2.323363	-2.851149
H	-0.224772	4.524518	-3.648659
H	-0.895032	6.617181	-2.460743
H	-2.418128	6.491578	-0.491737
H	-3.265774	4.301605	0.298287
H	-2.979427	-0.979584	-2.194837
H	-4.516669	-1.722738	-4.007358
H	-6.266347	-0.166433	-4.871194
H	-6.462964	2.132955	-3.928387
H	-4.937993	2.874292	-2.115501
H	-5.690102	1.460333	-0.079873
H	-6.915403	1.867150	2.033604
H	-5.674684	2.431945	4.121674
H	-3.180011	2.563526	4.086501
H	-1.942331	2.123937	1.985054
Ag	4.140261	-1.525458	0.105489

TS1’

C	4.128382	-4.401896	2.002643
C	4.624851	-3.158511	1.611217
C	3.931073	-2.373497	0.689197
C	2.728789	-2.839874	0.146786
C	2.259116	-4.110127	0.509840
C	2.941713	-4.880838	1.444782
N	1.891080	-2.111327	-0.735059
C	1.041149	-4.522244	-0.251117
C	0.063925	-3.416792	-0.390304
Pd	-0.608847	-0.625557	0.566548
C	-0.656298	-2.862276	0.728695
C	-0.059697	-2.365273	1.937540
C	-0.859901	-2.276475	3.110617
C	-2.186393	-2.649246	3.096209
C	-2.785579	-3.129730	1.901621
C	-2.058008	-3.206294	0.740548
S	2.622521	-1.702004	-2.096630
O	3.513807	-2.706683	-2.673697
O	3.152084	-0.309731	-2.083928
C	1.218134	-1.566461	-3.291818
F	0.340184	-0.668954	-2.882153
F	1.713487	-1.185176	-4.452037
F	0.617729	-2.733157	-3.441031
P	-2.510878	0.085129	-0.885766
C	-3.388981	-1.330216	-1.677501
C	-4.675876	-1.730164	-1.295882
C	-5.246740	-2.885555	-1.832551
C	-4.546532	-3.652636	-2.762185
C	-3.263615	-3.262754	-3.150588
C	-2.687752	-2.119818	-2.602121
C	-2.416659	1.375127	-2.198675
C	-2.297770	2.714655	-1.797196
C	-2.124820	3.729504	-2.734113
C	-2.044680	3.420833	-4.093038
C	-2.149733	2.092422	-4.502126
C	-2.337468	1.076322	-3.563701
C	-3.804070	0.751796	0.242476
C	-4.865391	1.553291	-0.200349
C	-5.841318	1.989557	0.694231
C	-5.784426	1.612000	2.037075
C	-4.741846	0.801489	2.483712
C	-3.752404	0.385567	1.593116
P	0.147001	1.452799	1.499360
C	1.754613	1.526560	2.415631
C	2.662113	0.463964	2.242351
C	3.969776	0.560671	2.740948
C	4.366589	1.700504	3.435798
C	3.454506	2.736328	3.648357
C	2.159810	2.654914	3.139289
C	0.595106	2.604369	0.118782
C	0.776622	2.010035	-1.143139
C	1.264644	2.751491	-2.225352
C	1.541349	4.106410	-2.059549
C	1.335734	4.712418	-0.816302
C	0.878412	3.969518	0.270658
C	-1.004651	2.350076	2.597243
C	-1.851915	3.366205	2.139585
C	-2.827235	3.901024	2.981007
C	-2.963424	3.429233	4.285836
C	-2.121764	2.415840	4.749626
C	-1.154109	1.872331	3.908437
H	4.672350	-5.005077	2.738159

H	5.563657	-2.782967	2.035310
H	4.327499	-1.390822	0.400757
H	2.547822	-5.864575	1.727298
H	1.326444	-4.881617	-1.259591
H	0.502368	-5.349119	0.258983
H	-0.472567	-3.359536	-1.350152
H	1.030055	-2.310322	2.037268
H	-0.391107	-1.930276	4.040610
H	-2.783394	-2.586069	4.013882
H	-3.839286	-3.434361	1.899162
H	-2.511163	-3.587811	-0.183513
H	-5.243764	-1.146684	-0.561131
H	-6.253041	-3.185909	-1.517296
H	-4.998843	-4.558157	-3.183086
H	-2.698695	-3.857965	-3.878074
H	-1.667391	-1.845203	-2.892860
H	-2.352382	2.969297	-0.731105
H	-2.040619	4.769625	-2.395443
H	-1.902149	4.216584	-4.833493
H	-2.093761	1.838745	-5.567378
H	-2.428228	0.041433	-3.914826
H	-4.937535	1.840218	-1.257522
H	-6.660296	2.624487	0.336050
H	-6.555007	1.954918	2.737582
H	-4.688348	0.496945	3.536080
H	-2.919543	-0.235944	1.952885
H	2.325029	-0.475946	1.778296
H	4.663397	-0.277791	2.604102
H	5.386647	1.776851	3.828348
H	3.759443	3.626767	4.209848
H	1.461437	3.486575	3.298551
H	0.483383	0.959243	-1.278982
H	1.395694	2.266038	-3.201378
H	1.912274	4.699673	-2.903016
H	1.549750	5.779794	-0.687602
H	0.755209	4.458765	1.245034
H	-1.750594	3.752288	1.117634
H	-3.486175	4.695226	2.610338
H	-3.731032	3.850084	4.945838
H	-2.225137	2.039152	5.773885
H	-0.508082	1.061753	4.275241
Ag	3.013455	1.072808	-0.178195

TS2

C	-1.412243	3.957240	-1.727234
C	-2.123281	3.567323	-2.863109
C	-2.748436	2.327550	-2.885151
C	-2.672340	1.440895	-1.796837
C	-1.882980	1.797994	-0.675800
C	-1.300894	3.077506	-0.658640
N	-3.374860	0.213391	-1.858457
C	-1.704091	0.900701	0.500961
C	-1.532768	-0.485671	0.402475
Pd	0.553732	0.360981	0.550562
C	-1.825532	-1.450489	1.471364
C	-1.875060	-1.106130	2.832027
C	-2.190312	-2.064662	3.790578
C	-2.460545	-3.382941	3.412908
C	-2.419084	-3.735730	2.063821
C	-2.105206	-2.776563	1.104399
S	-4.961841	0.198905	-1.838333
O	-5.426469	-1.068093	-2.420798
O	-5.629633	1.449417	-2.198684
C	-5.384876	0.006914	-0.047280
F	-4.873778	1.017005	0.643128
F	-6.696650	-0.000736	0.120589
F	-4.889344	-1.125393	0.424895
P	1.602520	-1.687274	-0.286288
C	1.646261	-2.977263	1.005798
C	2.154404	-4.260833	0.758698
C	2.214918	-5.195577	1.788548
C	1.790733	-4.851068	3.074553
C	1.304584	-3.570683	3.330798
C	1.226525	-2.638566	2.295620
C	3.346571	-1.699384	-0.875148
C	3.706784	-1.686438	-2.226149
C	5.052868	-1.658809	-2.594197
C	6.050196	-1.635215	-1.620940
C	5.698087	-1.651229	-0.270395
C	4.356331	-1.690226	0.099142
C	0.622478	-2.353294	-1.689640
C	-0.020745	-3.599624	-1.656479
C	-0.860582	-3.989827	-2.696656
C	-1.052961	-3.150464	-3.806867
C	-0.400389	-1.900522	-3.849263
C	0.411237	-1.501093	-2.779712
P	2.420347	1.786339	0.533003
C	2.055718	3.556730	0.854959

C	1.503169	3.893008	2.099262
C	1.152949	5.209743	2.378670
C	1.346162	6.204691	1.415956
C	1.906156	5.877566	0.183855
C	2.264706	4.557027	-0.098286
C	3.732172	1.400881	1.738346
C	3.522066	0.348124	2.634067
C	4.499646	0.014033	3.570361
C	5.690846	0.736867	3.615206
C	5.891676	1.812306	2.746721
C	4.911538	2.155204	1.818833
C	3.095922	1.788518	-1.166894
C	4.456154	1.780121	-1.489254
C	4.856498	1.837341	-2.825084
C	3.907630	1.903021	-3.843970
C	2.547492	1.908580	-3.528391
C	2.144884	1.847028	-2.197526
H	-0.926308	4.938868	-1.679202
H	-2.199633	4.233164	-3.730388
H	-3.329596	2.015828	-3.760423
H	-0.718055	3.381467	0.221715
H	-0.125590	1.641772	1.216031
H	-2.081469	1.303589	1.454219
H	-1.500299	-0.915055	-0.607295
H	-1.649328	-0.080156	3.150897
H	-2.222388	-1.781478	4.849311
H	-2.706126	-4.133376	4.173262
H	-2.634681	-4.765407	1.754873
H	-2.091991	-3.045408	0.038481
H	2.510938	-4.529412	-0.244611
H	2.604575	-6.200455	1.588476
H	1.847017	-5.587896	3.884068
H	0.978853	-3.293212	4.340059
H	0.835515	-1.629628	2.489097
H	2.940436	-1.699750	-3.010715
H	5.319802	-1.652713	-3.657636
H	7.105699	-1.608999	-1.915640
H	6.471388	-1.639850	0.507587
H	4.096940	-1.724688	1.164273
H	0.115475	-4.272526	-0.802246
H	-1.359728	-4.964409	-2.658837
H	-1.640672	-3.494907	-4.667012
H	-0.498527	-1.255017	-4.730371
H	0.874648	-0.505684	-2.803963
H	1.333011	3.111913	2.854043
H	0.719145	5.462617	3.352986
H	1.058812	7.240158	1.632192
H	2.065403	6.653713	-0.573525
H	2.701745	4.316793	-1.075117
H	2.580718	-0.216896	2.592382
H	4.327750	-0.818206	4.263137
H	6.465095	0.472040	4.344679
H	6.818885	2.394587	2.797863
H	5.062692	3.020703	1.160669
H	5.216737	1.727557	-0.701968
H	5.925710	1.824395	-3.067651
H	4.228636	1.946920	-4.891046
H	1.793801	1.956234	-4.323390
H	1.072139	1.849034	-1.952710
Ag	-2.662325	-1.584649	-2.892915

TS1

C	0.658860	4.769244	1.690810
C	1.357868	4.270980	2.792449
C	2.046336	3.060999	2.703702
C	2.040033	2.371870	1.491428
C	1.319256	2.851338	0.392086
C	0.628274	4.055369	0.491646
N	2.641694	1.080436	1.292168
C	1.329432	1.919044	-0.778391
C	1.503511	0.538709	-0.215575
Pd	-0.059805	-1.661995	-1.015042
C	2.035969	-0.576855	-0.976399
C	2.681694	-0.395934	-2.241125
C	3.303416	-1.447183	-2.869568
C	3.354052	-2.727479	-2.259478
C	2.776736	-2.928452	-1.026547
C	2.080903	-1.876991	-0.371375
S	4.225115	1.058119	0.784331
O	4.481518	2.030129	-0.270690
O	4.629809	-0.332358	0.641527
C	5.262700	1.672841	2.216940
F	4.978667	1.012074	3.323257
F	6.517927	1.443947	1.886655
F	5.094323	2.962761	2.412750
P	-0.830568	-3.581588	0.233816
C	-0.182945	-5.239377	-0.199936
C	-0.297701	-6.344435	0.654720

C	0.170240	-7.591272	0.248246	H	0.376182	1.970523	-1.339989
C	0.742738	-7.746483	-1.017077	H	2.137279	2.173852	-1.490194
C	0.845497	-6.654945	-1.877477	H	0.740714	0.272315	0.530691
C	0.383568	-5.402965	-1.468890	H	2.663381	0.587274	-2.725679
C	-2.613675	-3.941530	0.503756	H	3.773997	-1.293236	-3.847489
C	-3.224378	-4.078311	1.755186	H	3.874122	-3.550067	-2.764553
C	-4.596455	-4.322315	1.841905	H	2.854220	-3.904268	-0.530225
C	-5.366318	-4.441935	0.685185	H	1.903940	-1.966982	0.711300
C	-4.758139	-4.334895	-0.567081	H	-0.759541	-6.228393	1.644791
C	-3.391060	-4.085549	-0.653861	H	0.082591	-8.452714	0.920708
C	-0.164227	-3.177251	1.896615	H	1.107515	-8.730295	-1.334817
C	1.039319	-3.721996	2.368100	H	1.287670	-6.776009	-2.873109
C	1.671642	-3.185761	3.489252	H	0.460871	-4.536647	-2.141851
C	1.100025	-2.098238	4.177190	H	-2.636642	-3.992855	2.677696
C	-0.125987	-1.565607	3.719226	H	-5.066342	-4.421079	2.827584
C	-0.736814	-2.094372	2.582679	H	-6.444391	-4.626744	0.759314
P	-1.927119	-0.317071	-1.647070	H	-5.350663	-4.440294	-1.484420
C	-1.650745	1.232173	-2.602489	H	-2.916172	-4.001139	-1.640715
C	-0.737938	1.149588	-3.662940	H	1.507261	-4.565827	1.845623
C	-0.445284	2.271401	-4.434912	H	2.609452	-3.624210	3.849139
C	-1.057576	3.492161	-4.146582	H	1.538368	-1.747327	5.121392
C	-1.979629	3.578499	-3.103237	H	-0.608183	-0.748393	4.268998
C	-2.282619	2.452679	-2.336803	H	-1.670640	-1.642365	2.220576
C	-3.302450	-1.058089	-2.611391	H	-0.239193	0.191987	-3.874975
C	-2.999745	-2.144031	-3.440401	H	0.274026	2.195220	-5.258588
C	-3.983373	-2.710395	-4.251873	H	-0.816906	4.380985	-4.741556
C	-5.279414	-2.196738	-4.233884	H	-2.469188	4.534092	-2.880690
C	-5.586845	-1.107967	-3.414693	H	-3.010381	2.535933	-1.519623
C	-4.602002	-0.534042	-2.613702	H	-1.979066	-2.554635	-3.441315
C	-2.643399	0.215110	-0.043625	H	-3.735819	-3.562215	-4.896149
C	-3.665393	-0.511118	0.581684	H	-6.056457	-2.645013	-4.864210
C	-4.037658	-0.218429	1.895150	H	-6.603429	-0.697779	-3.404760
C	-3.388185	0.790585	2.605908	H	-4.854440	0.330549	-1.985286
C	-2.365054	1.517287	1.992481	H	-4.169837	-1.329298	0.049096
C	-1.998548	1.231561	0.680060	H	-4.842233	-0.793887	2.368282
H	0.112865	5.715849	1.774162	H	-3.681301	1.013009	3.638510
H	1.356522	4.822447	3.739374	H	-1.848389	2.319392	2.535266
H	2.572535	2.646812	3.572758	H	-1.196810	1.815793	0.211635
H	0.049598	4.423882	-0.364813	Ag	2.091905	-0.425490	2.860436

(E)-butadien-1-ylbenzene

C	-3.252996	0.388202	0.000138	C	-0.932392	1.076477	-0.000171
C	-2.852327	-0.947599	0.000147	C	-2.285562	1.397245	-0.000030
C	-1.497049	-1.268625	-0.000000	H	-4.318624	0.646016	0.000243
C	-0.510985	-0.266502	-0.000144	H	-3.602176	-1.747589	0.000270

H	-1.183552	-2.320667	-0.000001
H	-0.188231	1.882505	-0.000334
H	-2.591803	2.450245	-0.000059
C	0.894542	-0.663106	-0.000253
H	1.073435	-1.750316	-0.000603
C	1.975398	0.146414	0.000040
H	1.855627	1.241530	0.000422
C	3.334399	-0.355699	-0.000126
H	3.447353	-1.451720	-0.000515
C	4.427533	0.424807	0.000167
H	4.341974	1.521771	0.000555
H	5.439496	-0.000797	0.000030

IM2b’

C	-3.435866	-4.332316	-1.025840
C	-3.297184	-3.396049	-2.046340
C	-2.940670	-2.087052	-1.730597
C	-2.723797	-1.687816	-0.406567
C	-2.877575	-2.630941	0.629964
C	-3.229127	-3.942084	0.296535
N	-2.265151	-0.345367	-0.162788
C	1.043568	-1.567562	2.361156
C	-0.136383	-2.323640	2.120227
C	-1.353999	-1.715062	2.447542
C	-2.710623	-2.231376	2.069502
Pd	-0.286968	-0.482156	0.974300
S	-3.390669	0.780969	0.135896
O	-4.713201	0.241320	0.441643
O	-3.279325	1.870518	-0.853762
C	-2.882657	1.676754	1.696473
F	-1.632672	2.104915	1.629844
F	-3.683004	2.717859	1.818552
F	-3.018618	0.908106	2.760881
C	2.398460	-1.947330	1.947576
C	2.654910	-2.965617	1.013672
C	3.960334	-3.271937	0.641930
C	5.034635	-2.564349	1.186400
C	4.794588	-1.550679	2.114527
C	3.489297	-1.250080	2.493499
P	1.332128	0.809305	-0.230309
C	0.705164	2.046537	-1.453241
C	0.646502	1.785512	-2.841975
C	0.075554	2.731072	-3.710691
C	-0.416604	3.934703	-3.212274
C	-0.334636	4.204448	-1.844502
C	0.212238	3.269827	-0.970224
C	2.431206	1.843106	0.795331
C	2.177071	1.910320	2.169268
C	2.962180	2.718170	2.992003
C	4.003319	3.463770	2.442281
C	4.243289	3.424563	1.067062
C	3.453498	2.628357	0.242075
C	2.323337	-0.341225	-1.252999
C	1.604435	-1.366799	-1.888536
C	2.251354	-2.272390	-2.725602
C	3.631980	-2.183357	-2.910014
C	4.357047	-1.189030	-2.255207
C	3.707799	-0.266095	-1.434305
H	-3.705668	-5.369403	-1.255639
H	-3.458106	-3.679322	-3.092598
H	-2.831829	-1.346768	-2.539206
H	-3.342819	-4.674611	1.105735
H	1.002847	-0.862291	3.207255
H	-0.118360	-3.233324	1.501147
H	-1.332401	-0.973388	3.262750
H	-3.459805	-1.456672	2.318502
H	-2.953697	-3.097543	2.717771
H	1.825548	-3.524513	0.562436
H	4.140303	-4.067997	-0.090530
H	6.061097	-2.803089	0.883506
H	5.630500	-0.990194	2.549399
H	3.300157	-0.456556	3.227854
H	1.114251	0.884213	-3.261251
H	0.048577	2.521718	-4.785998
H	-0.854749	4.671773	-3.894089
H	-0.706367	5.157385	-1.451286
H	0.266513	3.498903	0.101506
H	1.346160	1.329873	2.593696
H	2.755794	2.765971	4.067282
H	4.625952	4.093877	3.087966
H	5.046943	4.028987	0.631041
H	3.624576	2.632757	-0.842131
H	0.519555	-1.458442	-1.719427
H	1.675507	-3.060070	-3.224810
H	4.147306	-2.900933	-3.558906
H	5.444018	-1.125618	-2.382584
H	4.298175	0.508449	-0.932087
Ag	-1.387448	0.636960	-2.190430

IM2b

C	3.962931	-2.937084	-2.364205
C	5.022437	-2.821877	-1.465750
C	5.150254	-1.667260	-0.699660
C	4.237033	-0.610508	-0.825399
C	3.150986	-0.723035	-1.720771
C	3.044159	-1.894897	-2.480182
N	4.328376	0.524060	0.019180
C	-0.246906	2.543941	0.073267
C	0.523918	2.029432	-0.976362
C	1.355654	0.904026	-0.773786
C	2.179611	0.407910	-1.939605
Pd	-0.755323	0.336644	-0.302922
S	5.593312	1.478060	0.040511
O	6.827346	0.945057	-0.538522
O	5.643365	2.174903	1.330962
C	5.140818	2.831589	-1.140354
F	4.001425	3.404126	-0.779652
F	6.087761	3.755853	-1.168449
F	4.997957	2.334600	-2.362156
C	-1.186233	3.662100	0.010942
C	-1.467954	4.366831	-1.171671
C	-2.385778	5.412357	-1.167761
C	-3.044946	5.771032	0.010823
C	-2.763889	5.089448	1.195834
C	-1.835209	4.053965	1.194804
P	-3.141934	0.467274	-0.153504
C	-4.042618	-1.048487	-0.689283
C	-3.711808	-1.586791	-1.942871
C	-4.331388	-2.744202	-2.406168
C	-5.295749	-3.382663	-1.624691
C	-5.622518	-2.861089	-0.375074
C	-4.996108	-1.705971	0.095336
C	-3.835312	0.940696	1.467488
C	-2.927278	1.149892	2.513495
C	-3.374873	1.508680	3.783877
C	-4.739515	1.664846	4.019652
C	-5.654152	1.456866	2.986131
C	-5.208029	1.093489	1.717360
C	-3.708861	1.699224	-1.400693
C	-3.032660	1.702743	-2.630652
C	-3.438307	2.545805	-3.662677
C	-4.509375	3.418354	-3.469575
C	-5.158906	3.451580	-2.236635
C	-4.764031	2.596982	-1.206900
H	3.853917	-3.835721	-2.982618
H	5.751786	-3.633098	-1.355464
H	5.965796	-1.567897	0.025582
H	2.216250	-1.985326	-3.195019
H	0.062155	2.265546	1.096532
H	0.364195	2.387987	-2.006206
H	1.768401	0.771318	0.239157
H	2.757433	1.285821	-2.304246
H	1.504588	0.146179	-2.778496
H	-0.953970	4.104195	-2.103977
H	-2.590000	5.956886	-2.097300
H	-3.772357	6.591107	0.005419
H	-3.266420	5.371769	2.128711
H	-1.597851	3.529162	2.128574
H	-2.952082	-1.104227	-2.570615
H	-4.052926	-3.150782	-3.386039
H	-5.786498	-4.292627	-1.988931
H	-6.368581	-3.361639	0.253718
H	-5.260286	-1.329644	1.089887
H	-1.850002	1.037481	2.325392
H	-2.650794	1.668884	4.590864
H	-5.095431	1.948423	5.016892
H	-6.728347	1.574180	3.169166
H	-5.942611	0.917456	0.922326
H	-2.167712	1.040491	-2.778421
H	-2.903217	2.528816	-4.619248
H	-4.828667	4.085735	-4.278385
H	-5.985981	4.151371	-2.068572
H	-5.288813	2.650658	-0.247074
P	-0.403855	-1.972735	0.161299
C	-1.707342	-2.838734	1.137198
C	-0.123040	-3.008968	-1.311415
C	1.025969	-2.089950	1.326635
C	-2.101756	-2.262215	2.353786
C	-2.328145	-4.020084	0.717230
C	-0.348821	-2.390861	-2.548614
C	0.221523	-4.368764	-1.278682
C	1.075061	-1.121307	2.343073
C	2.021168	-3.073860	1.287536
C	-3.079065	-2.862406	3.142537
H	-1.649636	-1.323684	2.696865
C	-3.302261	-4.624889	1.513729

H	-2.062914	-4.483725	-0.239656	H	-3.776653	-5.551914	1.170071
C	-0.237486	-3.114443	-3.734496	C	0.120215	-4.460992	-3.693024
H	-0.616295	-1.323940	-2.573795	H	-0.423159	-2.620356	-4.695123
C	0.352556	-5.085441	-2.465887	H	0.626063	-6.146071	-2.431289
H	0.365583	-4.885084	-0.321871	C	3.065589	-2.161007	3.276014
C	2.074917	-1.160737	3.331706	H	2.032680	-0.464870	4.180544
H	0.324078	-0.319417	2.381593	H	3.811382	-3.874173	2.186042
C	3.037145	-3.101118	2.244993	H	-4.445699	-4.530313	3.346958
H	2.032089	-3.827565	0.493305	H	0.215061	-5.032012	-4.623844
C	-3.677964	-4.053029	2.727112	H	3.840413	-2.207802	4.049607
H	-3.377284	-2.389918	4.086452	Ag	3.448046	0.228895	1.998082

IM2c

C	4.490132	-4.210424	1.468823	C	-4.175458	-1.218545	1.300467
C	5.552574	-3.365478	1.787255	C	-3.489482	-2.184226	2.048316
C	5.496294	-2.017591	1.445292	C	-4.102937	-2.793021	3.141539
C	4.389962	-1.492507	0.760555	C	-5.401290	-2.430657	3.500407
C	3.314646	-2.346787	0.428574	C	-6.085909	-1.462178	2.765226
C	3.382560	-3.693430	0.799936	C	-5.477929	-0.857122	1.666263
N	4.295520	-0.116730	0.460719	C	-4.074205	1.091161	-0.467433
C	-0.108388	1.060489	0.871255	C	-4.540670	1.456123	-1.735788
C	0.913471	0.366898	0.142800	C	-5.059329	2.733202	-1.948190
C	1.247628	-0.930861	0.522981	C	-5.119505	3.649204	-0.898518
C	2.105113	-1.827814	-0.309323	C	-4.652118	3.290078	0.367197
Pd	-0.957744	-0.743398	0.040751	C	-4.118839	2.022019	0.580755
S	5.370097	0.630581	-0.428426	H	4.521917	-5.271701	1.740931
O	6.707185	0.040360	-0.490409	H	6.429859	-3.754621	2.317719
O	5.231532	2.078436	-0.214702	H	6.316288	-1.343521	1.713274
C	4.753079	0.413830	-2.163928	H	2.544273	-4.353718	0.541400
F	3.528722	0.909333	-2.291455	H	-0.192854	0.825713	1.946686
F	5.548552	1.033937	-3.019483	H	1.277552	0.752651	-0.822781
F	4.720049	-0.875853	-2.471086	H	1.039257	-1.253467	1.559160
C	-0.616420	2.375054	0.479995	H	2.394369	-1.297239	-1.236848
C	-0.679355	2.787346	-0.863429	H	1.488074	-2.696219	-0.618078
C	-1.116014	4.066739	-1.185315	H	-0.401234	2.089257	-1.663501
C	-1.488099	4.957981	-0.174399	H	-1.171086	4.374402	-2.235803
C	-1.436163	4.558326	1.160697	H	-1.827835	5.967762	-0.432718
C	-1.016301	3.271289	1.484941	H	-1.732877	5.252061	1.955708
P	-3.312412	-0.535637	-0.159085	H	-0.977036	2.949403	2.533393
C	-3.839468	-1.592843	-1.555320	H	-1.881095	-1.481211	-2.477547
C	-2.902395	-1.884244	-2.554750	H	-2.521427	-2.903018	-4.421296
C	-3.260287	-2.679419	-3.643344	H	-4.835433	-3.819773	-4.586861
C	-4.554317	-3.189754	-3.734835	H	-6.509416	-3.305052	-2.812194
C	-5.492060	-2.903353	-2.740350	H	-5.883025	-1.886668	-0.877302
C	-5.138674	-2.107070	-1.653806	H	-2.460514	-2.457234	1.768539

H	-3.561230	-3.549357	3.721097
H	-5.883662	-2.903853	4.363679
H	-7.105410	-1.175161	3.047777
H	-6.023965	-0.098617	1.090516
H	-4.505140	0.740910	-2.567335
H	-5.424081	3.011722	-2.943674
H	-5.533705	4.650247	-1.066545
H	-4.695194	4.007803	1.195078
H	-3.741904	1.748772	1.576483
Ag	2.997464	1.438773	1.425780

TS1''

C	3.663419	-3.068516	3.453759
C	3.586305	-1.686894	3.638185
C	3.335377	-0.838316	2.559737
C	3.184069	-1.391975	1.286667
C	3.270988	-2.779490	1.091201
C	3.502374	-3.616002	2.178948
N	2.859363	-0.701285	0.099300
C	-0.129714	-1.805463	-1.712306
C	0.804090	-2.444533	-0.885153
C	2.204149	-2.301119	-1.078440
C	3.137571	-3.214134	-0.346182
Pd	0.390299	-0.345406	-0.034312
S	3.554657	0.637748	-0.387637
O	3.519432	1.731869	0.620174
O	3.131105	0.951147	-1.745981
C	5.376201	0.288715	-0.521791
F	5.546260	-0.777461	-1.279917
F	5.971536	1.322916	-1.078323
F	5.897724	0.068366	0.667833
C	-1.556593	-2.104262	-1.785620
C	-2.205964	-2.973837	-0.888705
C	-3.567685	-3.222078	-1.011999
C	-4.312898	-2.595600	-2.015691
C	-3.682391	-1.731850	-2.911828
C	-2.314559	-1.500941	-2.804640
P	-1.455107	0.982954	0.424760
C	-1.352925	2.418744	1.602682
C	-1.654205	2.306702	2.966429
C	-1.428133	3.381245	3.827328
C	-0.899271	4.578146	3.346326
C	-0.605051	4.707514	1.988431
C	-0.832948	3.640791	1.115707
C	-2.237936	1.767692	-1.026564
C	-1.612705	1.646029	-2.270936
C	-2.174510	2.237981	-3.402666
C	-3.364802	2.954029	-3.292631
C	-3.980764	3.102162	-2.047510
C	-3.415643	2.522061	-0.915447
C	-2.677413	-0.139111	1.208805
C	-2.182048	-1.013179	2.190112
C	-3.033854	-1.900378	2.843039
C	-4.388652	-1.939393	2.508278
C	-4.881985	-1.092571	1.517864
C	-4.033090	-0.194066	0.869673
H	3.848630	-3.726583	4.310468
H	3.711097	-1.259260	4.639733
H	3.261395	0.246416	2.702772
H	3.562600	-4.700558	2.026226
H	0.272187	-1.223152	-2.557880
H	0.475315	-3.155442	-0.111670
H	2.543944	-1.820358	-2.006257
H	4.129721	-3.205691	-0.835951
H	2.746319	-4.248142	-0.405057
H	-1.640452	-3.464192	-0.087229
H	-4.058900	-3.908666	-0.312386
H	-5.389302	-2.785790	-2.099420
H	-4.258306	-1.242582	-3.706233
H	-1.810093	-0.840611	-3.520187
H	-2.069092	1.373970	3.367201
H	-1.670269	3.276762	4.891213
H	-0.723207	5.416393	4.029685
H	-0.210009	5.650819	1.594317
H	-0.638863	3.772218	0.040904
H	-0.672311	1.081318	-2.346469
H	-1.678373	2.135747	-4.374832
H	-3.811216	3.415605	-4.181040
H	-4.906150	3.682518	-1.956566
H	-3.891014	2.667655	0.063726
H	-1.110738	-0.999440	2.441162
H	-2.634494	-2.571839	3.611785
H	-5.060103	-2.641337	3.016205
H	-5.941318	-1.130383	1.237835
H	-4.440999	0.451463	0.083257
Ag	1.225378	2.070450	1.169116

TS1'

C	4.443948	-3.431265	-2.491181
C	5.313099	-2.338621	-2.465707
C	5.152670	-1.331387	-1.513665
C	4.123383	-1.443526	-0.579337
C	3.234694	-2.525879	-0.613720
C	3.399923	-3.524337	-1.569094
N	3.797380	-0.435669	0.381374
C	0.915424	1.201258	0.113946
C	1.212506	-0.162627	-0.226810
C	1.892405	-0.990695	0.707398
C	2.139057	-2.443712	0.406666
S	4.540985	-0.498178	1.846749
O	4.726077	-1.855138	2.346739
O	3.937287	0.525384	2.692231
C	6.280763	0.123463	1.565174
F	6.267344	1.262433	0.889069
F	6.821275	0.331880	2.747624
F	6.996121	-0.765305	0.907947
C	1.115791	2.278351	-0.874939
C	0.785885	2.129588	-2.237363
C	1.059148	3.140970	-3.149733
C	1.685570	4.323942	-2.739266
C	2.030522	4.488630	-1.401685
C	1.744802	3.478946	-0.472003
H	4.571103	-4.212252	-3.249730
H	6.118342	-2.260241	-3.205046
H	5.815425	-0.456478	-1.497113
H	2.700087	-4.369073	-1.599509
H	1.179611	1.500755	1.145005
H	1.337293	-0.435150	-1.289490
H	1.812087	-0.687296	1.762415
H	1.207839	-2.905081	0.022621
H	2.420741	-2.982472	1.331534
H	0.300381	1.204016	-2.574025
H	0.784239	3.006609	-4.202450
H	1.899118	5.114489	-3.467243
H	2.513032	5.412824	-1.062285
H	1.968297	3.635464	0.593802
Ag	3.698015	1.754776	-0.440609
Pd	-0.876927	0.077119	0.191554
P	-2.617480	1.664407	0.347992
P	-1.978008	-2.049606	-0.036233
C	-3.731362	1.502456	-1.099723
C	-3.112197	1.405649	-2.356596
H	-2.017742	1.479211	-2.430684
C	-3.869896	1.222765	-3.509704
H	-3.371425	1.153956	-4.483622
C	-5.259218	1.115932	-3.420300
H	-5.858409	0.960953	-4.325078
C	-5.880842	1.197799	-2.175558
H	-6.970763	1.105909	-2.097101
C	-5.123213	1.392084	-1.018237
H	-5.629938	1.437221	-0.046590
C	-2.081264	3.423129	0.334133
C	-1.331706	3.863759	1.435601
H	-1.122698	3.174318	2.266699
C	-0.848624	5.167970	1.485796
H	-0.271084	5.501002	2.356331
C	-1.088647	6.043634	0.424064
H	-0.701508	7.068726	0.458344
C	-1.819017	5.608158	-0.679477
H	-2.011022	6.289915	-1.516415
C	-2.319735	4.304297	-0.724723
H	-2.903242	3.982833	-1.596673
C	-3.682669	1.598348	1.835172
C	-4.666616	2.565806	2.086625
H	-4.822128	3.390892	1.378490
C	-5.450603	2.483377	3.234389
H	-6.221982	3.239387	3.421605
C	-5.251421	1.443244	4.145586
H	-5.868537	1.384232	5.049754
C	-4.262165	0.489584	3.911918
H	-4.094093	-0.320216	4.631381
C	-3.478624	0.569189	2.759944
H	-2.689174	-0.173524	2.575705
C	-1.165751	-2.916677	-1.441675
C	-0.817306	-2.132550	-2.551498
H	-1.047532	-1.056932	-2.548412
C	-0.174431	-2.700573	-3.649139
H	0.089900	-2.075730	-4.510231
C	0.141740	-4.060075	-3.643504
H	0.657556	-4.508837	-4.500598
C	-0.194348	-4.845900	-2.541454
H	0.055664	-5.913299	-2.530056
C	-0.847277	-4.279671	-1.445472
H	-1.098291	-4.911968	-0.585083
C	-1.756962	-3.145740	1.414869
C	-0.874138	-2.731657	2.420113

H	-0.362590	-1.762694	2.319638
C	-0.651925	-3.531307	3.540810
H	0.040945	-3.195832	4.321168
C	-1.318178	-4.749370	3.667819
H	-1.146472	-5.378977	4.548610
C	-2.210151	-5.164257	2.676674
H	-2.739602	-6.118750	2.778661
C	-2.432585	-4.366240	1.556722
H	-3.141182	-4.697475	0.785998
C	-3.771411	-2.202642	-0.409122
C	-4.250530	-2.410916	-1.707898
H	-3.551652	-2.571448	-2.538454
C	-5.623577	-2.423000	-1.959518
H	-5.983980	-2.587046	-2.982158
C	-6.531429	-2.230649	-0.919696
H	-7.609267	-2.241622	-1.119613
C	-6.061256	-2.022938	0.378627
H	-6.767680	-1.872116	1.203547
C	-4.692409	-2.005452	0.631681
H	-4.337219	-1.845135	1.658408

TS2'

C	-2.625505	-3.359887	-2.683931
C	-4.000641	-3.358082	-2.449508
C	-4.572443	-2.382655	-1.638365
C	-3.776903	-1.407213	-1.019668
C	-2.379893	-1.430096	-1.229901
C	-1.826390	-2.394271	-2.077375
N	-4.330446	-0.341478	-0.284036
C	0.447168	2.644993	-1.351776
C	-0.418479	1.845290	-0.655264
C	-1.053883	0.716561	-1.291136
C	-1.557012	-0.387242	-0.564675
Pd	0.768299	-0.252886	-0.703097
S	-5.283465	-0.572561	0.963734
O	-5.960380	-1.867175	1.020649
O	-6.034974	0.655683	1.232722
C	-4.114478	-0.655907	2.402595
F	-3.423612	0.473202	2.504880
F	-4.781053	-0.847087	3.527609
F	-3.260091	-1.656053	2.233512
C	1.338170	3.644393	-0.788231
C	1.609053	3.724161	0.591900
C	2.480366	4.687314	1.083952
C	3.099507	5.589137	0.212464
C	2.849822	5.514330	-1.158120
C	1.984234	4.543992	-1.654392
P	2.797735	-1.006493	0.146569
C	2.729130	-1.527645	1.893461
C	1.888842	-0.802454	2.749378
C	1.831099	-1.116743	4.104405
C	2.600275	-2.167183	4.608926
C	3.429015	-2.897711	3.758408
C	3.499480	-2.577921	2.401926
C	3.616691	-2.359389	-0.759640
C	2.819472	-3.403547	-1.247152
C	3.404782	-4.474014	-1.919425
C	4.786026	-4.501919	-2.117037
C	5.582564	-3.462278	-1.636775
C	5.002403	-2.392503	-0.956497
C	3.966129	0.400005	0.118326
C	4.746814	0.767346	1.219535
C	5.583222	1.881436	1.140116
C	5.645621	2.630235	-0.034498
C	4.869966	2.265997	-1.137584
C	4.027202	1.160503	-1.059478
H	-2.173407	-4.115247	-3.336424
H	-4.641467	-4.114172	-2.918162
H	-5.655273	-2.354059	-1.482076
H	-0.739874	-2.391715	-2.241660
H	0.485162	2.523274	-2.446204
H	-0.556095	1.966552	0.430356
H	-1.111864	0.699980	-2.392653
H	-1.750023	-0.214850	0.506532
H	-0.199301	-1.408774	-0.154877
H	1.148430	3.008383	1.284439
H	2.689779	4.731918	2.158920
H	3.788234	6.346357	0.604877
H	3.339062	6.213359	-1.845974
H	1.789915	4.474833	-2.731952
H	1.275371	0.017245	2.346103
H	1.176467	-0.542689	4.770123
H	2.549822	-2.419703	5.674427
H	4.031204	-3.724448	4.152466
H	4.160884	-3.154095	1.742432
H	1.730995	-3.376149	-1.099090
H	2.776401	-5.288282	-2.298073
H	5.246110	-5.340620	-2.652378

H	6.667402	-3.483629	-1.791253	H	6.299715	3.508356	-0.091529
H	5.637735	-1.582184	-0.576091	H	4.911775	2.855406	-2.061163
H	4.709282	0.181980	2.146961	H	3.406901	0.879816	-1.924196
H	6.191596	2.166298	2.006301	Ag	-4.003888	1.816070	-0.646114