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Supporting Information

Palladium-Catalyzed Denitrogenative Cycloadditions and Alkenylations of Benzotriazoles with Alkynes

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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, dt = triple 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]) referred to the known literatures listed in the references.

2. General Procedures for the Denitrogenative Formal [2+2+1] Cyclization

A bottom of flask was sequentially charged with N-Tf-benzotriazole (0.30 mmol, 1.0 equiv), alkyne (0.60 mmol, 2.0 equiv), $Pd(TFA)_2$ (5 mg, 0.015 mmol, 0.05 equiv) and $AgBF_4$ (233 mg, 1.2 mmol, 4.0 eq) at N_2 atmosphere. The freshly distilled MeCN (3.0 mL) was added and then the flask was placed in an oil bath preheated to 100 °C. The resulting solution was heated at this temperature for 4-12 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 (**3a-q**).

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

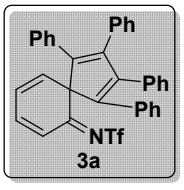
3. General Procedures for the Denitrogenative Formal [2+2+2] Cyclization

A bottom of flask was sequentially charged with N-Tf-benzotriazole (0.30 mmol, 1.0 equiv), alkyne (0.60 mmol, 2.0 equiv), $Pd(PhCN)_2Cl_2$ (6 mg, 0.015 mmol, 0.05 equiv) and $AgBF_4$ (233 mg, 1.2 mmol, 4.0 eq) at N_2 atmosphere. The freshly distilled MeCN (3.0 mL) was added and then the flask was placed in an oil bath preheated to 100 °C. The resulting solution was heated at this temperature for 12-72 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 (**4a-h**).

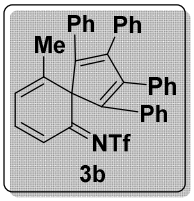
4. General Procedures for the Denitrogenative Alkenylation

A bottom of flask was sequentially charged with N-Tf-benzotriazole (0.30 mmol, 1.0 equiv), alkyne (2.4 mmol, 8.0 equiv), $Pd(dppf)_2Cl_2$ (12.3 mg, 0.015 mmol, 0.05 equiv) and $AgBF_4$ (233 mg, 1.2 mmol, 4.0 eq) at N_2 atmosphere. The freshly distilled MeCN (3.0 mL) was added and then the flask was placed in an oil bath preheated to 100 °C. The resulting solution was heated at this temperature for 2-6 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 (**6a-h**).

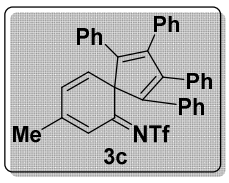
5. Analysis Data of the Denitrogenative Formal [2+2+1] Cyclization Products

(*E*)-1,1,1-trifluoro-*N*-(1,2,3,4-tetraphenylspiro[4.5]deca-1,3,7,9-tetraen-6-ylidene)methanesulfonamide (3a): 

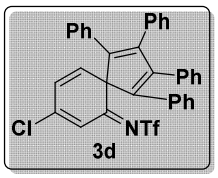
The product was obtained as a red solid. Yield: 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (dd, J = 8.8 Hz, J = 5.6 Hz, 1H), 6.65 (d, J = 8.8 Hz, 1H), 6.89-6.92 (m, 8H), 7.05-7.26 (m, 14H); ^{13}C (100 MHz, $CDCl_3$) δ 72.6, 119.0 (q, J = 317.6 Hz), 123.7, 123.8, 127.5, 127.8, 128.1, 128.2, 129.2, 129.8, 133.9, 134.7, 143.4, 143.8, 147.1, 149.7, 183.5; IR ν_{max} (film): 3674.48, 2987.12, 2900.26, 1631.30, 1552.08, 1517.50, 1441.92, 1405.79, 1393.49, 1381.44, 1349.27, 1264.36, 1217.98, 1159.35, 1123.17, 1056.65, 904.12, 798.34 cm^{-1}; HRMS m/z calcd for $C_{35}H_{23}F_3NO_2S$ $[M-H]^+$: 578.1402; found: 578.1396.

(*E*)-1,1,1-trifluoro-*N*-(10-methyl-1,2,3,4-tetraphenylspiro[4.5]deca-1,3,7,9-tetraen-6-ylidene)methanesulfonamide (3b): 

The product was obtained as an orange solid. Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (s, 3H), 6.41 (d, *J* = 6.0 Hz, 1H), 6.86-6.92 (m, 8H), 6.96 (d, *J* = 9.6 Hz, 1H), 7.02 (d, *J* = 6.4 Hz, 1H), 7.06-7.14 (m, 12H); ^{13}C (100 MHz, $CDCl_3$) δ 19.2, 75.8, 119.1 (q, *J* = 317.4 Hz), 121.6, 123.0, 127.5, 127.8, 128.2, 128.3, 129.0, 129.7, 133.5, 134.9, 146.0, 147.3, 150.0, 154.4, 185.1; IR ν_{max} (film): 3674.58, 2987.20, 2900.35, 1639.75, 1558.57, 1507.47, 1441.46, 1410.82, 1345.96, 1215.75, 1191.91, 1122.73, 1073.91, 961.94 cm^{-1}; HRMS m/z calcd for $C_{36}H_{25}F_3NO_2S$ $[M-H]^+$: 592.1558; found: 592.1562.

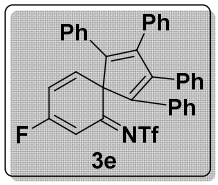
(*E*)-1,1,1-trifluoro-*N*-(8-methyl-1,2,3,4-tetraphenylspiro[4.5]deca-1,3,7,9-tetraen-6-ylidene)methanesulfonamide (3c): 

The product was obtained as an orange solid. Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3H), 6.50 (d, *J* = 9.2 Hz, 1H), 6.65 (d, *J* = 9.2 Hz, 1H), 6.93-6.96 (m, 9H), 7.12-7.17 (m, 12H); ^{13}C (100 MHz, $CDCl_3$) δ 24.3, 71.7, 119.1 (q, *J* = 315.5 Hz), 122.1, 127.4, 127.6, 127.7, 128.0, 128.1, 129.2, 129.8, 133.9, 134.8, 142.5, 143.9, 149.6, 162.0, 182.6; IR ν_{max} (film): 3674.50, 2987.22, 2900.27, 1636.48, 1509.36, 1441.70, 1410.62, 1341.90, 1215.55, 1192.08, 1122.71, 1056.71, 946.62, 831.28 cm^{-1}; HRMS m/z calcd for $C_{36}H_{25}F_3NO_2S$ $[M-H]^+$: 592.1558; found: 592.1560.

(*E*)-*N*-(8-chloro-1,2,3,4-tetraphenylspiro[4.5]deca-1,3,7,9-tetraen-6-ylidene)-1,1,1-trifluoromethanesulfonamide (3d): 

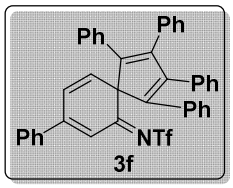
The product was obtained as an orange solid. Yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (d, *J* = 2.0 Hz, 1H), 6.91-6.97 (m, 9H), 7.05 (d, *J* = 10.0 Hz, 1H), 7.12-7.19 (m, 12H); ^{13}C (100 MHz, $CDCl_3$) δ 73.5, 118.9 (q, *J* = 317.4 Hz), 124.8, 127.7, 127.9, 128.0, 128.2, 128.4, 129.1, 129.7, 133.4, 134.4, 136.6, 143.8, 147.5, 149.6, 181.6; IR ν_{max} (film): 3674.53, 2987.16, 2900.26, 1624.51, 1556.32, 1527.13, 1488.43, 1441.68, 1406.00, 1354.29, 1264.39, 1196.44, 1125.36, 1074.46, 1027.35, 902.15, 821.80 cm^{-1}; HRMS m/z calcd for $C_{35}H_{22}F_3NO_2SCl$ $[M-H]^+$: 612.1012; found: 612.1005.

(*E*)-1,1,1-trifluoro-*N*-(8-fluoro-1,2,3,4-tetraphenylspiro[4.5]deca-1,3,7,9-tetraen-6-



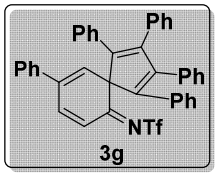
ylidene)methanesulfonamide (3e): The product was obtained as an orange solid. Yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53-6.58 (m, 1H), 6.85-6.97 (m, 10H), 7.10-7.20 (m, 12H); ^{13}C (100 MHz, $CDCl_3$) δ 72.4, 107.0 (d, J = 21.5 Hz), 118.9 (q, J = 321.0 Hz), 119.9 (d, J = 32.3 Hz), 127.7, 128.1, 128.1, 128.4, 129.1, 129.8, 133.5, 134.4, 143.2, 148.1 (d, J = 14.9 Hz), 150.4, 176.0 (d, J = 284.3 Hz), 183.7; IR ν_{max} (film): 3674.51, 2987.19, 2900.24, 1637.20, 1521.29, 1442.29, 1405.64, 1393.54, 1350.09, 1206.26, 1173.31, 1122.33, 1074.65, 1056.59, 1027.25, 845.43 cm^{-1}; HRMS m/z calcd for $C_{35}H_{22}F_4NO_2S$ $[M-H]^+$: 596.1386; found: 596.1381.

(*E*)-1,1,1-trifluoro-*N*-(1,2,3,4,8-pentaphenylspiro[4.5]deca-1,3,7,9-tetraen-6-

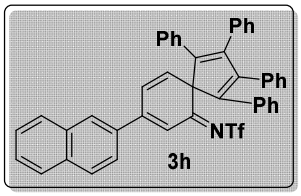


ylidene)methanesulfonamide (3f): The product was obtained as an orange solid. Yield: 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, J = 9.6 Hz, 1H), 6.97-7.03 (m, 9H), 7.12-7.20 (m, 12H), 7.33 (s, 1H), 7.45-7.55 (m, 5H); ^{13}C (100 MHz, $CDCl_3$) δ 72.0, 119.1 (q, J = 317.4 Hz), 119.8, 125.2, 127.5, 127.7, 127.7, 128.1, 128.1, 129.2, 129.3, 129.9, 131.9, 134.0, 134.8, 137.0, 143.5, 144.1, 149.6, 158.7, 182.5; IR ν_{max} (film): 3674.96, 3055.24, 1628.04, 1594.67, 1504.23, 1441.54, 1341.25, 1264.63, 1189.61, 1121.35, 1072.51, 1026.03, 947.64, 932.99 cm^{-1}; HRMS m/z calcd for $C_{41}H_{27}F_3NO_2S$ $[M-H]^+$: 654.1715; found: 654.1794.

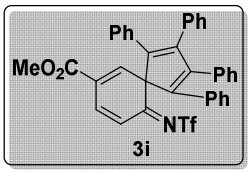
(*E*)-1,1,1-trifluoro-*N*-(1,2,3,4,9-pentaphenylspiro[4.5]deca-1,3,7,9-tetraen-6-



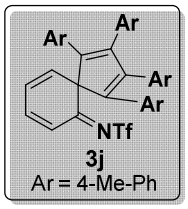
ylidene)methanesulfonamide (3g): The product was obtained as an orange solid. Yield: 41%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 1H), 6.96-6.97 (m, 8H), 7.10-7.21 (m, 13H), 7.35 (d, J = 7.6 Hz, 2H), 7.41-7.46 (m, 4H); ^{13}C (100 MHz, $CDCl_3$) δ 72.7, 119.0 (q, J = 317.4 Hz), 124.2, 125.8, 127.5, 127.8, 128.1, 128.2, 128.7, 129.2, 129.2, 129.8, 133.9, 134.7, 136.3, 137.6, 137.9, 144.1, 148.7, 149.5, 183.2; IR ν_{max} (film): 3674.60, 2987.24, 2900.30, 1636.66, 1554.82, 1522.11, 1494.01, 1442.00, 1409.41, 1393.46, 1351.59, 1217.95, 1196.36, 1126.80, 1074.63, 1056.64, 1027.24, 908.29, 828.40 cm^{-1}; HRMS m/z calcd for $C_{41}H_{27}F_3NO_2S$ $[M-H]^+$: 654.1715; found: 654.1718.

(*E*)-1,1,1-trifluoro-*N*-(8-(naphthalen-2-yl)-1,2,3,4-tetraphenylspiro[4.5]deca-1,3,7,9-tetraen-6-ylidene)methanesulfonamide (3h): 

The product was obtained as an orange solid. Yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, *J* = 9.2 Hz, 1H), 6.97-6.99 (m, 4H), 7.02-7.04 (m, 4H), 7.11-7.21 (m, 13H), 7.47 (s, 1H), 7.58-7.61 (m, 3H), 7.88-7.94 (m, 3H), 8.08 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 72.1, 119.2 (q, *J* = 317.3 Hz), 119.8, 123.9, 125.1, 127.3, 127.5, 127.7, 127.9, 128.1, 128.2, 128.5, 128.6, 129.2, 129.3, 129.3, 129.9, 133.0, 134.0, 134.9, 134.9, 143.5, 144.3, 149.6, 158.4, 182.3; IR ν_{max} (film): 3674.45, 2987.14, 2900.26, 1621.55, 1501.61, 1441.18, 1406.55, 1393.41, 1342.49, 1241.29, 1201.04, 1120.89, 1065.87, 1056.63, 1027.31, 931.99, 857.88 cm^{-1}; HRMS m/z calcd for $C_{45}H_{29}F_3NO_2S$ $[M-H]^+$: 704.1949; found: 704.1951.

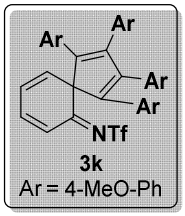
methyl (*E*)-1,2,3,4-tetraphenyl-10-(((trifluoromethyl)sulfonyl)imino)spiro[4.5]deca-1,3,6,8-tetraene-7-carboxylate (3i): 

The product was obtained as an orange solid. Yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3H), 6.75 (d, *J* = 9.2 Hz, 1H), 6.90-6.93 (m, 8H), 7.04 (d, *J* = 9.6 Hz, 1H), 7.10-7.20 (m, 12H), 7.66 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 53.5, 72.6, 119.0 (q, *J* = 317.5 Hz), 122.2, 124.7, 127.6, 127.9, 128.1, 128.3, 129.0, 129.8, 133.7, 134.5, 143.2, 144.2, 144.8, 149.9, 164.5, 183.8; IR ν_{max} (film): 3674.49, 2987.16, 2900.27, 1730.65, 1634.83, 1525.86, 1441.37, 1406.15, 1381.53, 1358.21, 1253.88, 1218.71, 1125.36, 1074.71, 1027.37, 830.11 cm^{-1}; HRMS m/z calcd for $C_{37}H_{25}F_3NO_4S$ $[M-H]^+$: 636.1456; found: 636.1468.

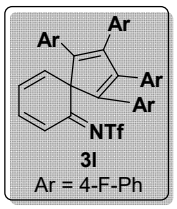
(*E*)-1,1,1-trifluoro-*N*-(1,2,3,4-tetra-p-tolylspiro[4.5]deca-1,3,7,9-tetraen-6-ylidene)methanesulfonamide (3j): 

The product was obtained as a dark red solid. Yield: 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 6H), 2.24 (s, 6H), 6.53-6.63 (m, 2H), 6.77-6.80 (m, 8H), 6.87-6.91 (m, 8H), 7.02-7.14 (m, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 21.3, 21.4, 72.7, 119.1 (q, *J* = 317.0 Hz), 123.4, 123.7, 128.8, 128.8, 129.0, 129.7, 131.3, 132.1, 136.9, 137.3, 143.0, 144.1, 147.0, 149.5, 184.0; IR ν_{max} (film): 3674.47, 2987.15, 2900.26, 1630.90, 1552.18, 1515.78, 1450.45, 1405.59, 1393.51, 1381.41, 1352.04, 1219.53, 1196.10, 1125.45, 1065.78, 1027.45, 903.27 cm^{-1}; HRMS m/z calcd for $C_{39}H_{33}F_3NO_2S$ $[M+H]^+$: 636.2196; found: 636.2194.

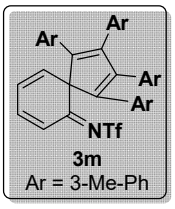
(*E*)-1,1,1-trifluoro-*N*-(1,2,3,4-tetrakis(4-methoxyphenyl)spiro[4.5]deca-1,3,7,9-tetraen-6-ylidene)methanesulfonamide (3k): The product was obtained as a brown solid. Yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (d, *J* = 9.6 Hz, 12H), 6.59 (dd, *J* = 8.8 Hz, *J* = 6.0 Hz, 1H), 6.64-6.69 (m, 9H), 6.83-6.86 (m, 8H), 7.07 (d, *J* = 10.0 Hz, 1H), 7.17 (dd, *J* = 9.6 Hz, *J* = 5.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 55.2, 55.2, 72.7, 113.5, 123.3, 123.6, 126.8, 127.5, 130.4, 131.2, 142.1, 144.5, 147.2, 148.7, 158.7, 158.8, 184.3; IR ν_{max} (film): 3674.53, 2987.16, 2900.25, 1405.74, 1393.48, 1381.83, 1249.47, 1229.33, 1065.79, 1056.62, 1027.48, 891.70 cm^{-1}; HRMS m/z calcd for $C_{39}H_{31}F_3NO_6S$ $[M-H]^+$: 698.1902; found: 698.1910.



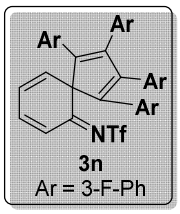
(*E*)-1,1,1-trifluoro-*N*-(1,2,3,4-tetrakis(4-fluorophenyl)spiro[4.5]deca-1,3,7,9-tetraen-6-ylidene)methanesulfonamide (3l): The product was obtained as an orange solid. Yield: 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61-6.67 (m, 2H), 6.83-6.92 (m, 16H), 7.09 (d, *J* = 9.6 Hz, 1H), 7.16-7.21 (m, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 72.5, 115.4 (d, *J* = 2.7 Hz), 115.7 (d, *J* = 2.7 Hz), 119.0 (q, *J* = 317.4 Hz), 123.8, 124.1, 129.5 (d, *J* = 3.5 Hz), 130.1 (d, *J* = 3.4 Hz), 130.8 (d, *J* = 8.1 Hz), 131.5 (d, *J* = 8.0 Hz), 142.4, 143.2, 147.2, 148.4, 162.3 (d, *J* = 247.4 Hz), 163.5, 182.9; IR ν_{max} (film): 3674.61, 2987.20, 2900.29, 1630.47, 1598.80, 1552.89, 1500.58, 1404.17, 1350.48, 1217.43, 1192.14, 1156.81, 1122.94, 1094.51, 904.82 cm^{-1}; HRMS m/z calcd for $C_{35}H_{19}F_7NO_2S$ $[M-H]^+$: 650.1103; found: 650.1025.



(*E*)-1,1,1-trifluoro-*N*-(1,2,3,4-tetra-m-tolylspiro[4.5]deca-1,3,7,9-tetraen-6-ylidene)methanesulfonamide (3m): The product was obtained as an orange solid. Yield: 56%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (s, 6H), 2.13 (s, 6H), 6.54 (ddd, *J* = 8.0 Hz, *J* = 5.6 Hz, *J* = 1.2 Hz, 1H), 6.61 (dt, *J* = 8.8 Hz, *J* = 1.2 Hz, 1H), 6.70-6.73 (m, 8H), 6.90-7.00 (m, 8H), 7.03-7.11 (m, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 21.4, 21.4, 72.7, 119.1 (q, *J* = 317.3 Hz), 123.4, 123.7, 126.3, 126.9, 127.8, 127.9, 128.0, 128.4, 129.8, 130.5, 134.0, 134.8, 137.3, 137.5, 143.3, 144.0, 146.9, 149.8, 183.9; IR ν_{max} (film): 3674.55, 2987.12, 2900.34, 1630.51, 1600.49, 1551.20, 1514.98, 1482.26, 1451.45, 1406.80, 1393.52, 1347.89, 1264.76, 1218.12, 1189.21, 1158.95, 1122.59, 1065.79, 1056.40, 982.41, 904.64, 883.55 cm^{-1}; HRMS m/z calcd for $C_{39}H_{33}F_3NO_2S$ $[M+H]^+$: 636.2184; found: 636.2191.

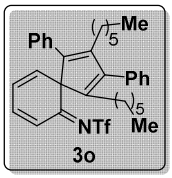


(*E*)-1,1,1-trifluoro-*N*-(1,2,3,4-tetrakis(3-fluorophenyl)spiro[4.5]deca-1,3,7,9-tetraen-6-ylidene)methanesulfonamide (3n): The product was obtained as an orange solid. Yield: 77%; ^{1}H

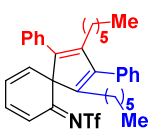


NMR (400 MHz, $CDCl_3$) δ 6.56-6.70 (m, 10H), 6.85-6.92 (m, 4H), 7.08-7.20 (m, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 72.2, 115.2 (d, J = 21.0 Hz), 115.4 (d, J = 21.0 Hz), 115.8 (d, J = 22.0 Hz), 116.4 (d, J = 22.0 Hz), 119.0 (q, J = 317.0 Hz), 123.9, 124.5, 124.8 (d, J = 3.0 Hz), 125.4 (d, J = 3.0 Hz), 130.1 (d, J = 8.5 Hz), 130.2 (d, J = 8.4 Hz), 135.1 (d, J = 8.0 Hz), 135.9 (d, J = 8.0 Hz), 141.5, 143.9 (d, J = 2.0 Hz), 147.1, 148.5 (d, J = 2.0 Hz), 161.4 (d, J = 245.4 Hz), 162.6 (d, J = 245.2 Hz), 182.1; IR ν_{max} (film): 3674.56, 2987.20, 2900.27, 1632.29, 1606.56, 1580.68, 1554.14, 1519.25, 1479.36, 1434.66, 1393.50, 1350.05, 1264.83, 1248.61, 1218.29, 1190.52, 1157.14, 1122.18, 1075.97, 1056.76, 914.20, 891.20 cm^{-1}; HRMS m/z calcd for $C_{35}H_{21}F_7NO_2S$ $[M+H]^+$: 652.1181; found: 652.1185.

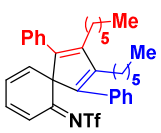
(*E*)-*N*-(1,3-dihexyl-2,4-diphenylspiro[4.5]deca-1,3,7,9-tetraen-6-ylidene)-1,1,1-



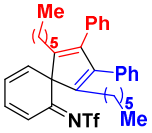
trifluoromethanesulfonamide (3o): The product was obtained as a red solid. Yield: 43%; ^1H NMR (400 MHz, $CDCl_3$) δ 0.75 (t, J = 7.2 Hz, 3H), 0.81 (t, J = 7.2 Hz, 3H), 0.94-1.09 (m, 12H), 1.14-1.20 (m, 4H), 1.93-2.06 (m, 2H), 2.15-2.25 (m, 2H), 6.39 (d, J = 9.2 Hz, 1H), 6.57 (dd, J = 9.2 Hz, J = 6.4 Hz, 1H), 7.08-7.10 (m, 3H), 7.20-7.30 (m, 6H), 7.36-7.40 (m, 1H), 7.43-7.46 (m, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 14.1, 14.1, 22.3, 22.5, 26.8, 27.4, 28.4, 28.8, 29.2, 29.5, 31.2, 31.3, 72.6, 119.0 (q, J = 317.4 Hz), 122.6, 123.4, 127.6, 127.6, 128.3, 128.5, 128.9, 129.0, 134.8, 135.9, 140.2, 144.9, 145.3, 147.3, 150.0, 150.1, 183.9; IR ν_{max} (film): 3674.57, 2956.22, 2923.93, 1630.43, 1551.26, 1516.61, 1491.92, 1441.96, 1393.55, 1350.70, 1218.66, 1191.81, 1158.55, 1124.44, 1073.49, 1056.72, 907.07 cm^{-1}; HRMS m/z calcd for $C_{35}H_{39}F_3NO_2S$ $[M-H]^+$: 594.2732; found: 594.2659.



3o



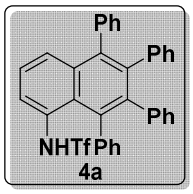
3o'



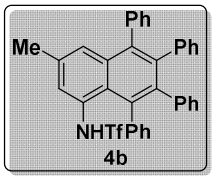
3o''

Note: Theoretically, the above reaction may lead to the formation of three possible regio-isomers **3o**, **3o'** and **3o''**. For **3o'** and **3o''**, their ^1H-NMR and ^{13}C-NMR spectra should be simpler than that of **3o**, since the two alkene moieties (in red and blue) are chemically equivalent. However, in practice, the alkene moieties of the obtained product show two groups of signals in the ^1H-NMR and ^{13}C-NMR spectra, which indicate that they bear different chemical environment. As a result, the product could be assigned to be **3o**.

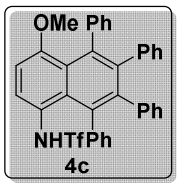
6. Analysis Data of the Denitrogenative Formal [2+2+2] Cyclization Products



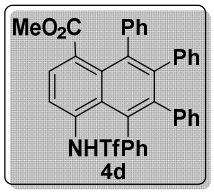
1,1,1-trifluoro-*N*-(5,6,7,8-tetraphenylnaphthalen-1-yl)methanesulfonamide (4a): The product was obtained as a yellow solid. Yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78-6.88 (m, 10H), 7.21-7.41 (m, 12H), 7.63 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 119.7 (q, J = 319.4 Hz), 121.3, 121.3, 124.8, 125.6, 125.7, 126.7, 126.8, 126.9, 127.2, 127.8, 128.3, 129.1, 130.6, 130.8, 131.0, 131.1, 131.2, 134.1, 134.1, 139.4, 139.6, 139.8, 139.9, 140.2, 142.0; IR ν_{max} (film): 3674.49, 3272.36, 2987.09, 2900.28, 1491.45, 1441.46, 1393.59, 1339.87, 1264.10, 1217.50, 1199.20, 1139.41, 1073.80, 1056.59, 1027.56, 963.45, 894.97 cm^{-1}; HRMS m/z calcd for $C_{35}H_{23}F_3NO_2S$ $[M-H]^+$: 578.1402; found: 578.1401.



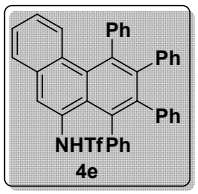
1,1,1-trifluoro-*N*-(3-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)methanesulfonamide (4b): The product was obtained as a yellow solid. Yield: 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 6.76-6.86 (m, 10H), 7.19-7.37 (m, 12H), 7.53 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 21.8, 119.7 (q, J = 321.3 Hz), 123.0, 123.2, 125.6, 126.1, 126.7, 126.7, 126.8, 127.8, 128.2, 129.1, 130.4, 130.8, 131.0, 131.2, 131.3, 133.9, 134.2, 135.6, 139.1, 139.6, 139.7, 139.8, 140.1, 140.3, 141.0; IR ν_{max} (film): 3674.49, 3271.19, 2987.09, 2900.30, 1493.16, 1441.34, 1405.70, 1393.69, 1382.25, 1346.08, 1249.70, 1225.09, 1196.08, 1139.36, 1065.83, 1056.38, 1027.47, 892.59 cm^{-1}; HRMS m/z calcd for $C_{36}H_{25}F_3NO_2S$ $[M-H]^+$: 592.1558; found: 592.1569.



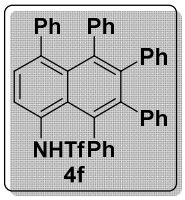
1,1,1-trifluoro-*N*-(4-methoxy-5,6,7,8-tetraphenylnaphthalen-1-yl)methanesulfonamide (4c): The product was obtained as a white solid. Yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (s, 3H), 6.13 (s, 1H), 6.70-6.85 (m, 11H), 7.04-7.12 (m, 5H), 7.17 (d, J = 7.2 Hz, 2H), 7.26-7.31 (m, 3H), 7.53 (d, J = 8.4 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 55.7, 105.8, 119.7 (q, J = 321.3 Hz), 122.4, 125.1, 125.4, 125.5, 125.6, 125.9, 126.3, 126.5, 126.6, 127.7, 128.9, 129.1, 129.6, 130.7, 131.0, 131.3, 134.2, 137.8, 139.7, 139.9, 140.6, 140.9, 142.3, 143.5, 157.2; IR ν_{max} (film): 3674.45, 3293.01, 2987.13, 2900.30, 1601.54, 1569.65, 1490.63, 1451.96, 1441.39, 1409.94, 1393.38, 1382.20, 1320.20, 1260.48, 1223.07, 1195.57, 1138.68, 1066.61, 1045.66, 1027.69, 904.16 cm^{-1}; HRMS m/z calcd for $C_{36}H_{25}F_3NO_3S$ $[M-H]^+$: 608.1507; found: 608.1523.



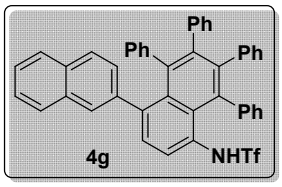
methyl 5,6,7,8-tetraphenyl-4-((trifluoromethyl)sulfonamido)-1-naphthoate (4d): The product was obtained as a white solid. Yield: 79%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 6.75-6.88 (m, 10H), 7.19-7.35 (m, 10H), 8.23 (s, 1H), 8.38 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 52.6, 119.7 (q, J = 320.9 Hz), 120.7, 125.9, 126.0, 126.8, 126.9, 127.0, 127.2, 127.3, 127.9, 128.5, 129.2, 129.7, 130.7, 130.9, 131.0, 131.2, 133.5, 134.2, 138.5, 139.2, 139.5, 139.6, 140.7, 141.4, 144.2, 166.2; IR ν_{max} (film): 3674.47, 3267.68, 2987.12, 2900.26, 1723.70, 1439.39, 1405.87, 1393.65, 1380.84, 1262.32, 1224.96, 1140.04, 1065.80, 1056.25, 1027.36, 891.88 cm^{-1}; HRMS m/z calcd for $C_{37}H_{25}F_3NO_4S$ $[M-H]^+$: 636.1456; found: 636.1458.



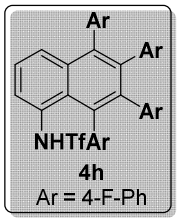
1,1,1-trifluoro-*N*-(5,6,7,8-tetraphenylphenanthren-9-yl)methanesulfonamide (4e): The product was obtained as a white solid. Yield: 52%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (s, 1H), 6.70-6.73 (m, 4H), 6.87-6.90 (m, 5H), 7.02-7.09 (m, 3H), 7.17-7.18 (m, 5H), 7.31-7.32 (m, 3H), 7.42 (t, J = 7.2 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.86 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 119.7 (q, J = 321.5 Hz), 124.3, 125.6, 125.6, 125.7, 126.6, 126.7, 126.8, 126.9, 128.0, 128.2, 128.3, 128.4, 129.2, 129.2, 130.0, 131.1, 131.2, 131.3, 131.6, 132.1, 134.7, 138.8, 139.4, 140.0, 140.3, 141.2, 142.8; IR ν_{max} (film): 3674.48, 3283.55, 2987.12, 2900.29, 1494.08, 1441.36, 1404.09, 1393.75, 1328.27, 1227.10, 1197.37, 1139.72, 1065.98, 1056.20, 1027.49, 928.14 cm^{-1}; HRMS m/z calcd for $C_{39}H_{25}F_3NO_2S$ $[M-H]^+$: 628.1558; found: 628.1571.



1,1,1-trifluoro-*N*-(4,5,6,7,8-pentaphenylnaphthalen-1-yl)methanesulfonamide (4f): The product was obtained as a white solid. Yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (d, J = 7.2 Hz, 2H), 6.61-6.67 (m, 6H), 6.73-6.75 (m, 2H), 6.78-6.80 (m, 3H), 6.86-6.87 (m, 3H), 6.95 (m, 5H), 7.26-7.34 (m, 5H), 7.63 (d, J = 7.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 119.7 (q, J = 321.3 Hz), 121.2, 125.4, 125.6, 125.7, 125.8, 126.5, 126.5, 126.7, 127.2, 127.3, 128.2, 129.1, 129.6, 129.9, 130.1, 131.0, 131.1, 131.1, 132.5, 133.1, 133.7, 139.6, 139.7, 139.8, 140.3, 140.8, 140.9, 141.3, 141.4, 143.7; IR ν_{max} (film): 3674.50, 3274.55, 2987.14, 2900.31, 1598.56, 1489.76, 1441.30, 1409.85, 1393.50, 1381.00, 1314.30, 1225.00, 1194.14, 1138.44, 1066.14, 1056.65, 1027.39, 975.23, 900.33 cm^{-1}; HRMS m/z calcd for $C_{41}H_{27}F_3NO_2S$ $[M-H]^+$: 654.1715; found: 654.1730.

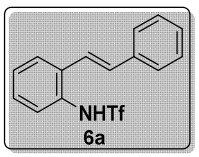


1,1,1-trifluoro-*N*-(5,6,7,8-tetraphenyl-[1,2'-binaphthalen]-4-yl)methanesulfonamide (4g): The product was obtained as a white solid. Yield: 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30-6.37 (m, 2H), 6.46-6.53 (m, 2H), 6.59-6.66 (m, 4H), 6.76 (m, 5H), 6.87 (m, 3H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.29-7.42 (m, 9H), 7.60-7.68 (m, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 119.8 (q, *J* = 321.2 Hz), 121.2, 125.3, 125.4, 125.5, 125.7, 125.8, 126.0, 126.3, 126.5, 126.8, 126.8, 127.3, 127.4, 127.6, 128.3, 128.9, 129.2, 129.7, 130.3, 131.0, 131.1, 131.7, 132.0, 132.6, 132.6, 133.3, 133.8, 139.6, 139.8, 139.8, 140.4, 140.7, 141.0, 141.0, 141.1, 141.5; IR ν_{max} (film): 3674.50, 3273.16, 2970.40, 2900.45, 1599.55, 1490.13, 1441.05, 1411.12, 1393.29, 1380.69, 1312.81, 1223.79, 1197.33, 1138.89, 1073.70, 1056.61, 1027.62, 987.13, 904.08 cm^{-1}; HRMS m/z calcd for $C_{45}H_{29}F_3NO_2S$ $[M-H]^+$: 704.1871; found: 704.1874.



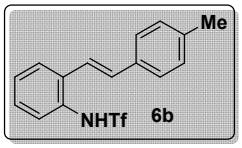
1,1,1-trifluoro-*N*-(5,6,7,8-tetrakis(4-fluorophenyl)naphthalen-1-yl)methanesulfonamide (4h): The product was obtained as a white solid. Yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61-6.66 (m, 4H), 6.69 (dd, *J* = 8.4 Hz, *J* = 5.6 Hz, 2H), 6.75 (dd, *J* = 7.6 Hz, *J* = 5.6 Hz, 2H), 6.99 (t, *J* = 8.4 Hz, 2H), 7.06 (t, *J* = 8.4 Hz, 2H), 7.15 (dd, *J* = 7.6 Hz, *J* = 5.6 Hz, 2H), 7.20 (dd, *J* = 7.6 Hz, *J* = 5.6 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 114.2 (d, *J* = 21.3 Hz), 114.3 (d, *J* = 21.3 Hz), 115.1 (d, *J* = 21.3 Hz), 116.4 (d, *J* = 21.4 Hz), 119.6 (q, *J* = 321.0 Hz), 122.8, 125.6, 126.1, 127.4, 130.4, 132.3 (d, *J* = 7.8 Hz), 132.3 (d, *J* = 8.1 Hz), 132.4 (d, *J* = 8.1 Hz), 132.6 (d, *J* = 7.9 Hz), 133.8, 134.3, 134.9 (d, *J* = 3.5 Hz), 135.3 (d, *J* = 3.6 Hz), 135.6 (d, *J* = 3.5 Hz), 135.9 (d, *J* = 3.7 Hz), 139.1, 139.3, 141.4, 161.0 (d, *J* = 244.7 Hz), 161.9 (d, *J* = 245.4 Hz), 162.3 (d, *J* = 248.7 Hz); IR ν_{max} (film): 3674.44, 3290.08, 2987.09, 2900.26, 1603.76, 1508.12, 1450.52, 1405.42, 1393.47, 1381.03, 1221.97, 1156.14, 1139.19, 1065.80, 1056.61, 892.28 cm^{-1}; HRMS m/z calcd for $C_{35}H_{19}F_7NO_2S$ $[M-H]^+$: 650.1103; found: 650.1025.

7. Analysis Data of the Denitrogenative Alkenylation Products



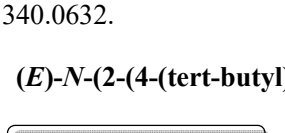
(*E*)-1,1,1-trifluoro-*N*-(2-styrylphenyl)methanesulfonamide (6a): The product was obtained as a white solid. Yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (s, 1H), 7.09 (d, *J* = 16.0 Hz, 1H), 7.26 (d, *J* = 6.4 Hz, 1H), 7.31-7.42 (m, 5H), 7.45 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.51-7.54 (m, 2H), 7.69 (dd, *J* = 9.6 Hz, *J* = 1.6 Hz, 1H);

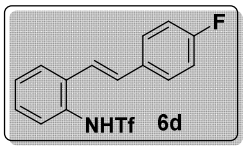
^{13}C (100 MHz, $CDCl_3$) δ 119.9 (q, *J* = 320.3 Hz), 121.9, 126.9, 127.0, 127.0, 127.2, 128.7, 128.8, 128.9, 129.1, 130.8, 133.8, 134.3, 136.6; IR ν_{max} (film): 3284.16, 2987.47, 1496.67, 1411.79, 1365.73, 1222.57, 1192.62, 1138.74, 960.86 cm^{-1}; HRMS m/z calcd for $C_{15}H_{11}F_3NO_2S$ $[M-H]^+$: 326.0485; found: 326.0483.



(*E*)-1,1,1-trifluoro-*N*-(2-(4-methylstyryl)phenyl)methanesulfonamide (6b): The product was obtained as a white solid. Yield: 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 6.63 (s, 1H), 7.06 (d, *J* = 16.4 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 16.4 Hz, 1H), 7.31 (dt, *J* = 7.6 Hz, *J* = 2.0 Hz, 1H), 7.36 (dt, *J* = 7.6 Hz, *J* = 2.0 Hz, 1H), 7.42 (dd, *J* = 6.0 Hz, *J* = 2.0 Hz, 2H), 7.46 (dd, *J* = 7.6 Hz, *J* = 2.0 Hz, 1H), 7.66 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 21.5, 119.9 (q, *J* = 320.4 Hz), 120.8, 126.9, 127.0, 127.1, 128.6, 128.8, 129.8, 130.7, 133.8, 133.8, 134.4, 138.8; IR ν_{max} (film): 3674.49, 3260.38, 2987.37, 2900.30, 1513.79, 1487.44, 1454.55, 1411.14, 1356.79, 1188.95, 1136.12, 1065.89, 965.26, 939.08 cm^{-1}; HRMS m/z calcd for $C_{16}H_{13}F_3NO_2S$ $[M-H]^+$: 340.0631; found: 340.0632.

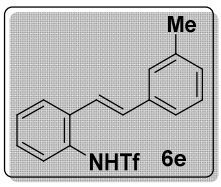
(*E*)-*N*-(2-(4-(tert-butyl)styryl)phenyl)-1,1,1-trifluoromethanesulfonamide (6c): The product was obtained as a white solid. Yield: 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 9H), 6.69 (s, 1H), 7.07 (d, *J* = 16.4 Hz, 1H), 7.24 (d, *J* = 16.0 Hz, 1H), 7.30 (dt, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.36 (dt, *J* = 7.6 Hz, *J* = 2.0 Hz, 1H), 7.40-7.46 (m, 5H), 7.66 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 31.4, 34.9, 119.9 (q, *J* = 320.5 Hz), 121.0, 126.0, 126.7, 126.9, 127.1, 128.6, 128.8, 130.7, 133.6, 133.8, 134.4, 152.1; IR ν_{max} (film): 3281.84, 2962.26, 1484.79, 1411.26, 1363.56, 1189.32, 1138.34, 1108.70, 1089.78, 961.48 cm^{-1}; HRMS m/z calcd for $C_{19}H_{19}F_3NO_2S$ $[M-H]^+$: 382.1100; found: 382.1103.



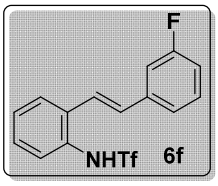


(*E*)-1,1,1-trifluoro-*N*-(2-(4-fluorostyryl)phenyl)methanesulfonamide (6d): The product was obtained as a white solid. Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (s, 1H), 7.03-7.11 (m, 3H), 7.21 (d, *J* = 16.0 Hz, 1H), 7.33 (dt, *J* = 7.6 Hz, *J* = 2.0 Hz, 1H), 7.38 (dt, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.44 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.46-7.52 (m, 2H), 7.66 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 116.1 (d, *J* = 21.6 Hz), 119.9 (q, *J* = 320.3 Hz), 121.8 (d, *J* = 2.5 Hz), 126.9, 127.4, 128.6 (d, *J* = 8.0 Hz), 128.9, 129.0, 130.8, 132.4, 132.8 (d, *J* = 3.5 Hz), 134.3, 163.0 (d, *J* = 247.2 Hz); IR ν_{max} (film):

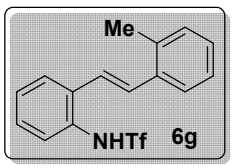
3674.41, 3285.69, 2987.28, 2900.25, 1598.45, 1508.02, 1409.09, 1366.42, 1189.18, 1157.76, 1135.27, 1065.85, 960.86, 937.75 cm^{-1}; HRMS m/z calcd for $C_{15}H_{10}F_4NO_2S$ $[M-H]^+$: 344.0384; found: 344.0383.



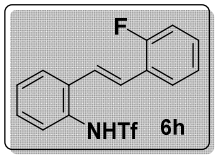
(*E*)-1,1,1-trifluoro-*N*-(2-(3-methylstyryl)phenyl)methanesulfonamide (6e): The product was obtained as a white solid. Yield: 68%; ^1H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 6.66 (s, 1H), 7.05 (d, J = 16.0 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 7.25-7.34 (m, 5H), 7.37 (dt, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.45 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.66 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 21.6, 119.9 (q, J = 320.3 Hz), 121.6, 124.1, 127.0, 127.0, 127.7, 128.7, 128.8, 128.9, 129.6, 130.8, 134.0, 134.3, 136.5, 138.7; IR ν_{max} (film): 3674.48, 3279.03, 2987.37, 1489.04, 1409.47, 1366.19, 1219.50, 1191.64, 1137.68, 1088.86, 1046.67, 959.14 cm^{-1}; HRMS m/z calcd for $C_{16}H_{13}F_3NO_2S$ $[M-H]^+$: 340.0635; found: 340.0633.



(*E*)-1,1,1-trifluoro-*N*-(2-(3-fluorostyryl)phenyl)methanesulfonamide (6f): The product was obtained as a white solid. Yield: 51%; ^1H NMR (400 MHz, $CDCl_3$) δ 6.63 (s, 1H), 7.00-7.07 (m, 2H), 7.21 (dt, J = 10.0 Hz, J = 2.4 Hz, 1H), 7.28-7.42 (m, 5H), 7.46 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.69 (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): 3289.03, 1609.66, 1583.43, 1490.77, 1415.11, 1366.08, 1220.96, 1197.36, 1140.06, 959.95 cm^{-1}; HRMS m/z calcd for $C_{15}H_{10}F_4NO_2S$ $[M-H]^+$: 344.0391; found: 344.0388.

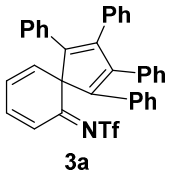


(*E*)-1,1,1-trifluoro-*N*-(2-(2-methylstyryl)phenyl)methanesulfonamide (6g): The product was obtained as a white solid. Yield: 54%; ^1H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 6.69 (s, 1H), 7.16 (d, J = 16.0 Hz, 1H), 7.19-7.25 (m, 3H), 7.30-7.35 (m, 2H), 7.38 (dt, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.59 (m, 1H), 7.67 (dd, J = 7.6 Hz, J = 2.0 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 20.0, 119.9 (q, J = 320.6 Hz), 123.3, 125.7, 126.6, 126.9, 127.3, 128.6, 128.8, 128.8, 130.7, 130.9, 131.8, 134.5, 135.7, 136.3; IR ν_{max} (film): 3674.54, 3277.73, 2987.23, 2900.30, 1491.62, 1409.49, 1364.92, 1190.62, 1136.84, 1090.17, 1045.77, 960.10 cm^{-1}; HRMS m/z calcd for $C_{16}H_{13}F_3NO_2S$ $[M-H]^+$: 340.0631; found: 340.0632.

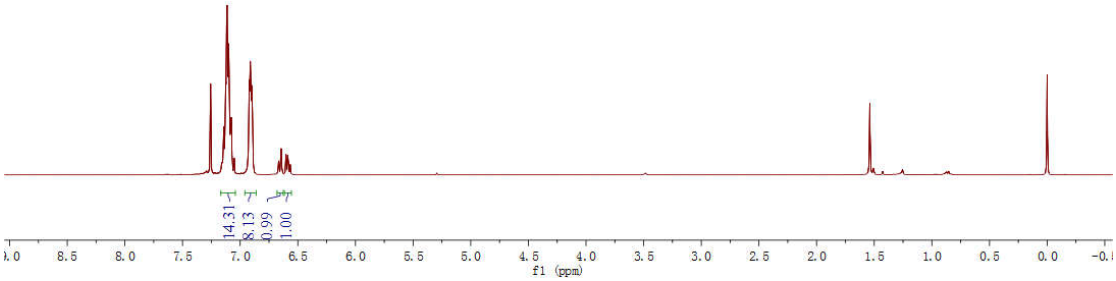


(*E*)-1,1,1-trifluoro-*N*-(2-(2-fluorostyryl)phenyl)methanesulfonamide (6h): The product was obtained as a white solid. Yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (s, 1H), 7.10 (ddd, *J* = 10.8 Hz, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 7.18 (dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.24 (d, *J* = 16.4 Hz, 1H), 7.27-7.33 (m, 1H), 7.35 (dd, *J* = 7.6 Hz, *J* = 2.0 Hz, 1H), 7.37-7.42 (m, 2H), 7.46 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.59 (dt, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.71 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 116.1 (d, *J* = 22.0 Hz), 119.9 (q, *J* = 320.3 Hz), 124.4 (d, *J* = 5.7 Hz), 124.6 (d, *J* = 3.6 Hz), 126.1 (d, *J* = 3.3 Hz), 127.0, 127.4, 127.7 (d, *J* = 3.3 Hz), 129.0, 129.1, 129.9, 130.0, 130.9, 134.4, 160.8 (d, *J* = 249.1 Hz); IR ν_{max} (film): 3674.52, 3284.49, 2987.28, 2900.27, 1491.89, 1455.45, 1409.89, 1365.46, 1190.00, 1136.00, 1091.42, 1049.20, 962.41, 939.71 cm^{-1}; HRMS m/z calcd for $C_{15}H_{10}F_4NO_2S$ $[M-H]^+$: 344.0361; found: 344.0364.

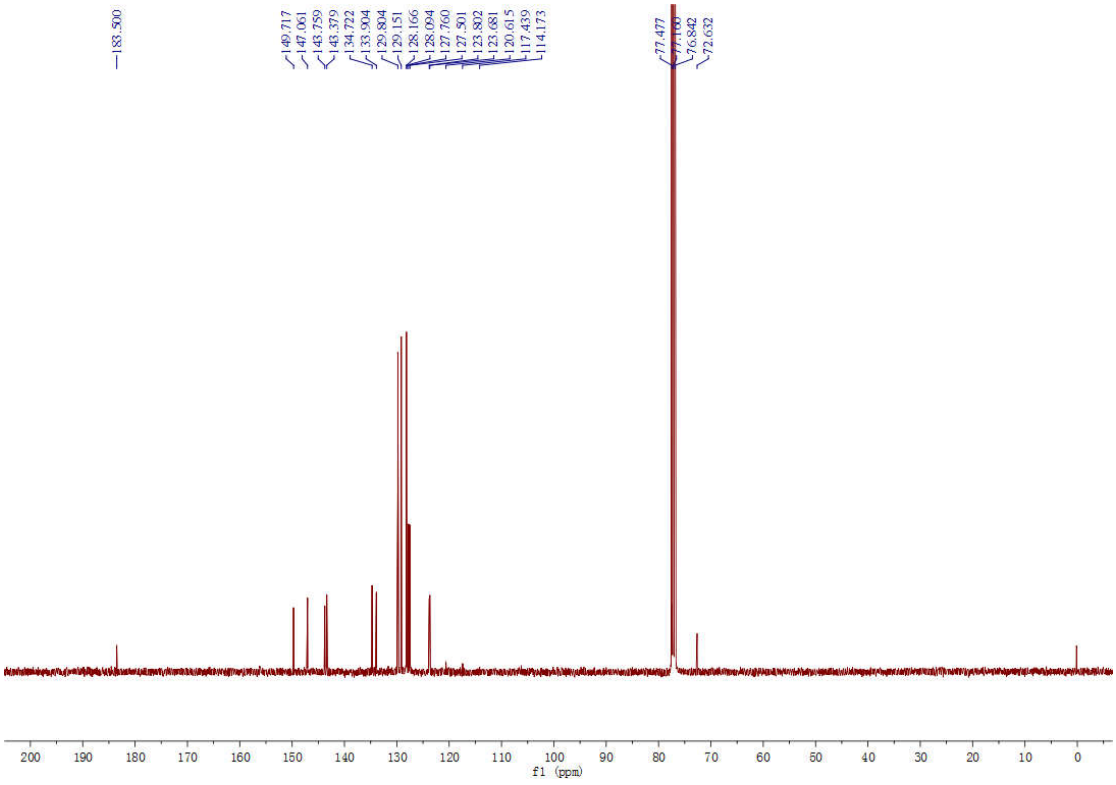
8. NMR Spectra of the Denitrogenative Formal [2+2+1] Cyclization Products



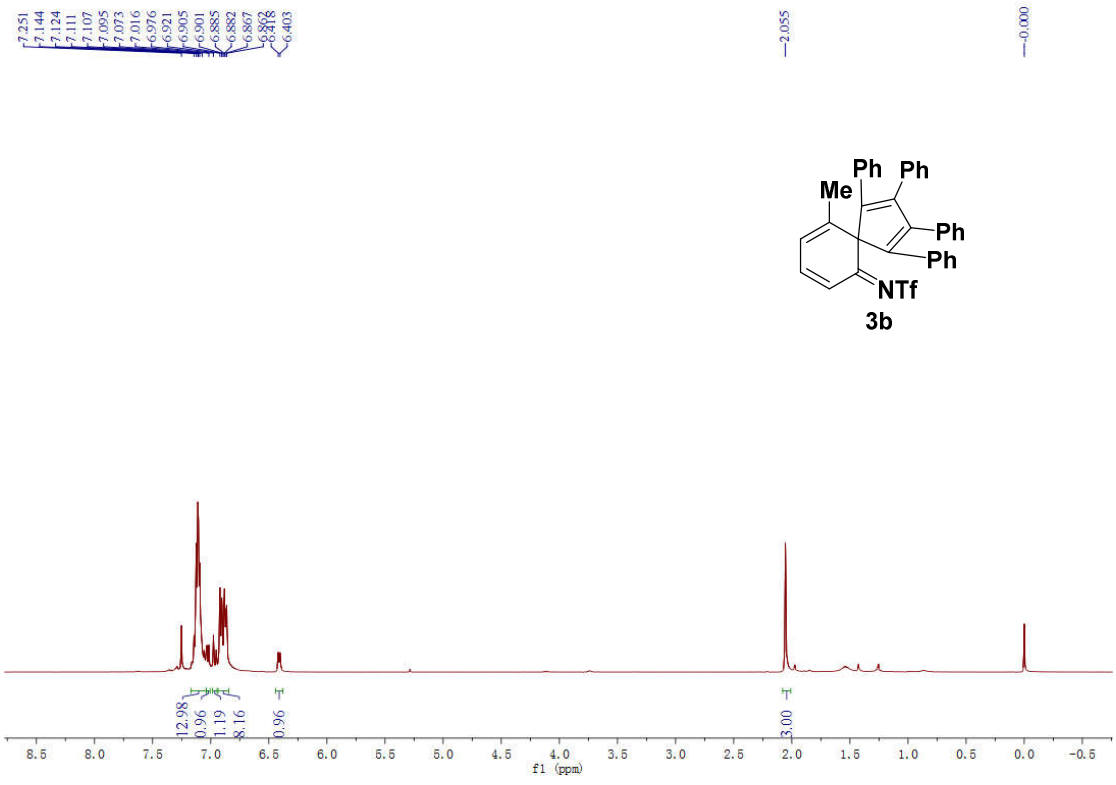
3a



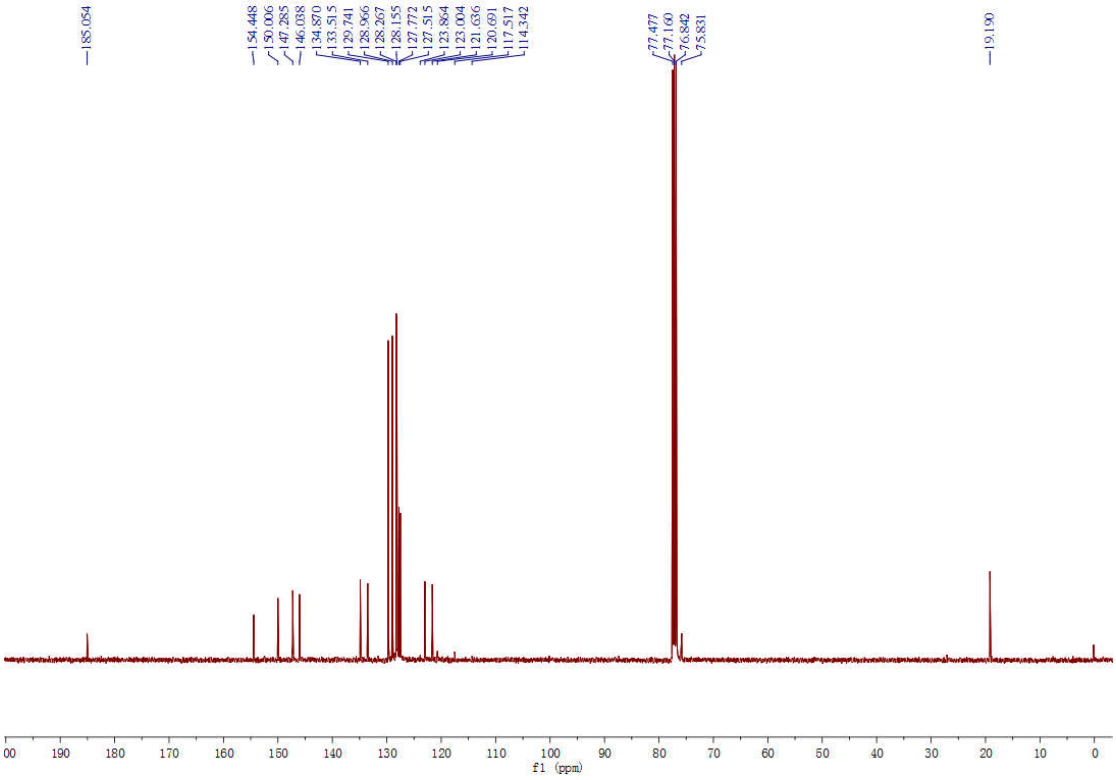
^{1}H NMR Spectrum for **3a** ($CDCl_3$, 400 MHz)



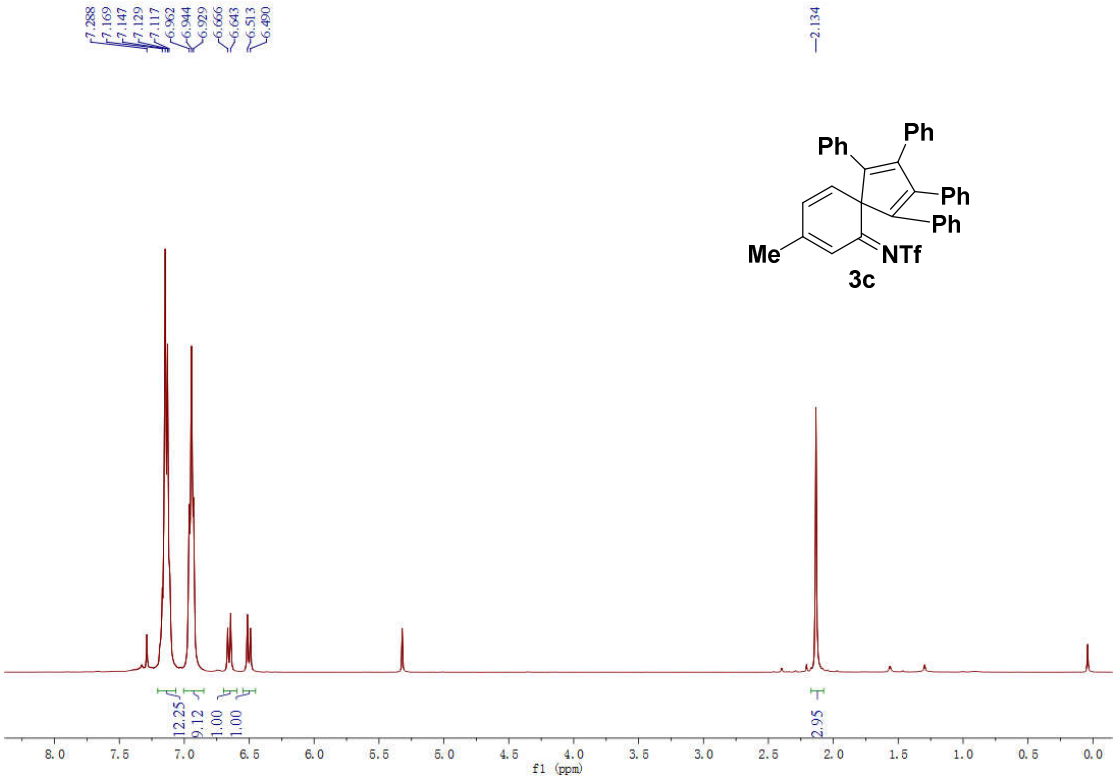
^{13}C NMR Spectrum for **3a** ($CDCl_3$, 100 MHz)



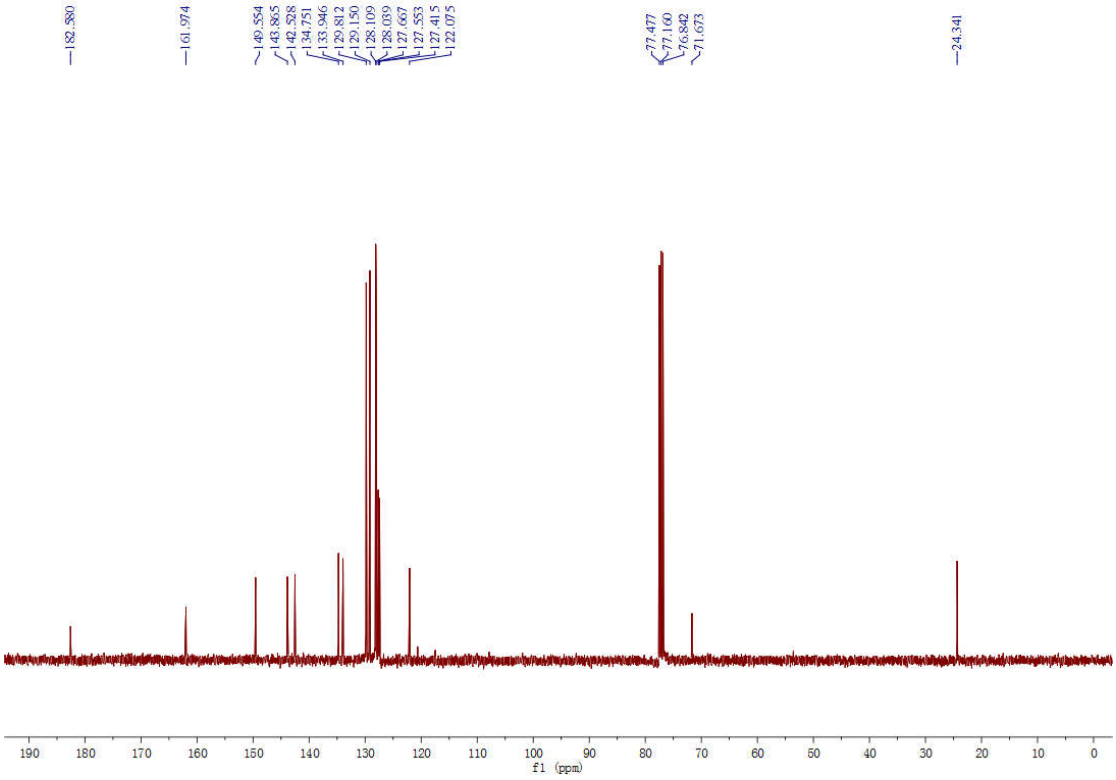
^{1}H NMR Spectrum for **3b** ($CDCl_3$, 400 MHz)



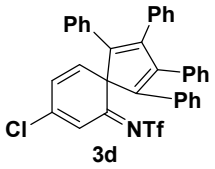
^{13}C NMR Spectrum for **3b** ($CDCl_3$, 100 MHz)



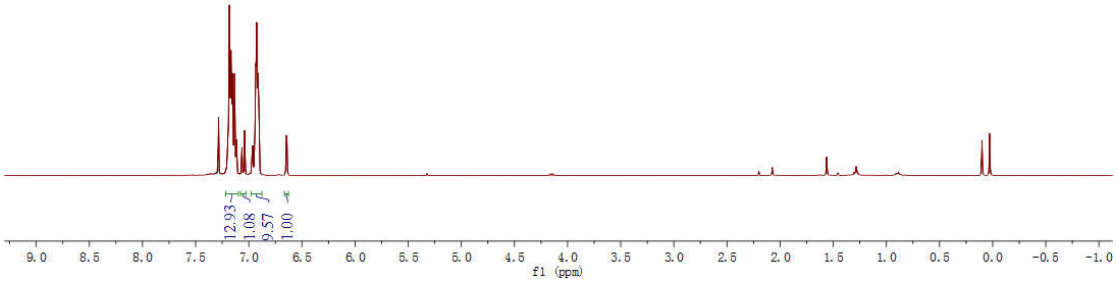
^{1}H NMR Spectrum for **3c** ($CDCl_3$, 400 MHz)



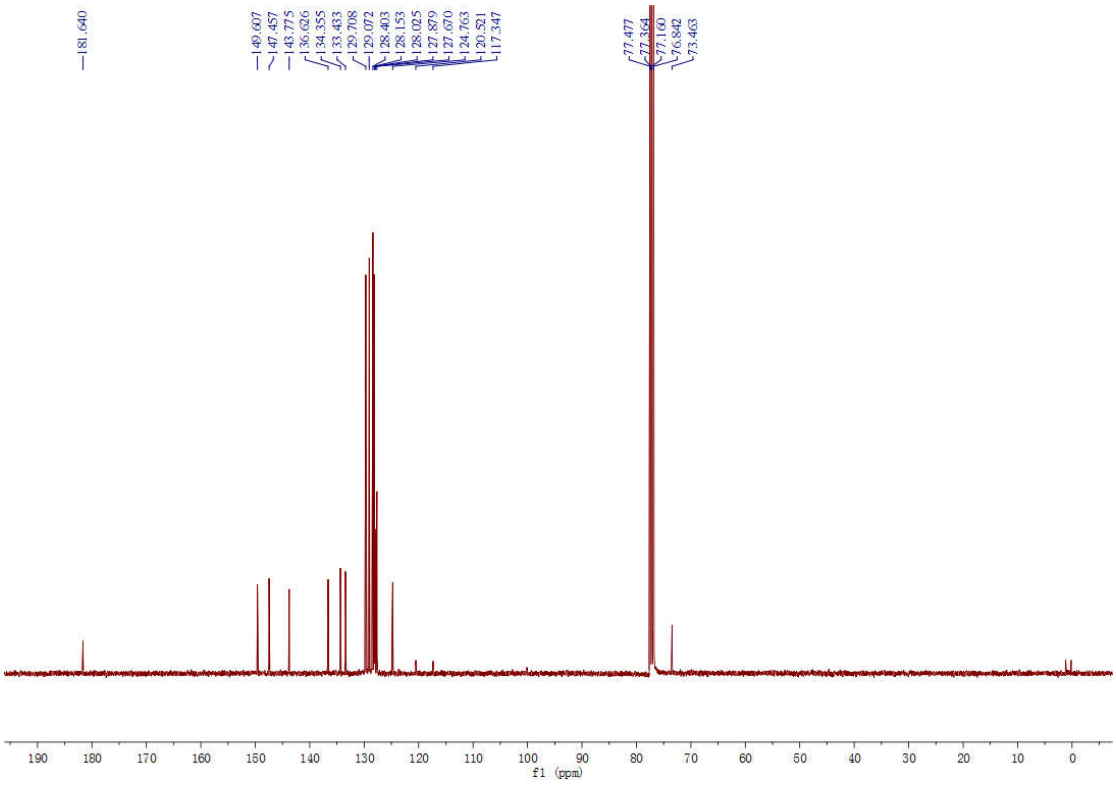
^{13}C NMR Spectrum for **3c** ($CDCl_3$, 100 MHz)



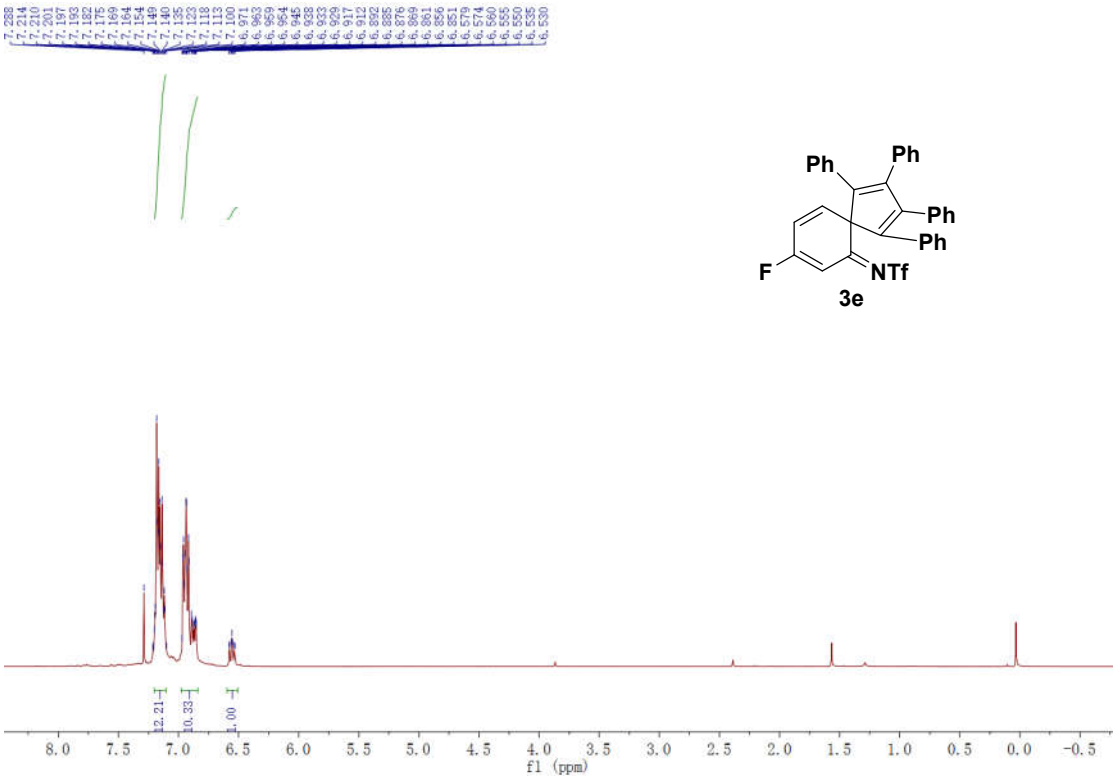
3d



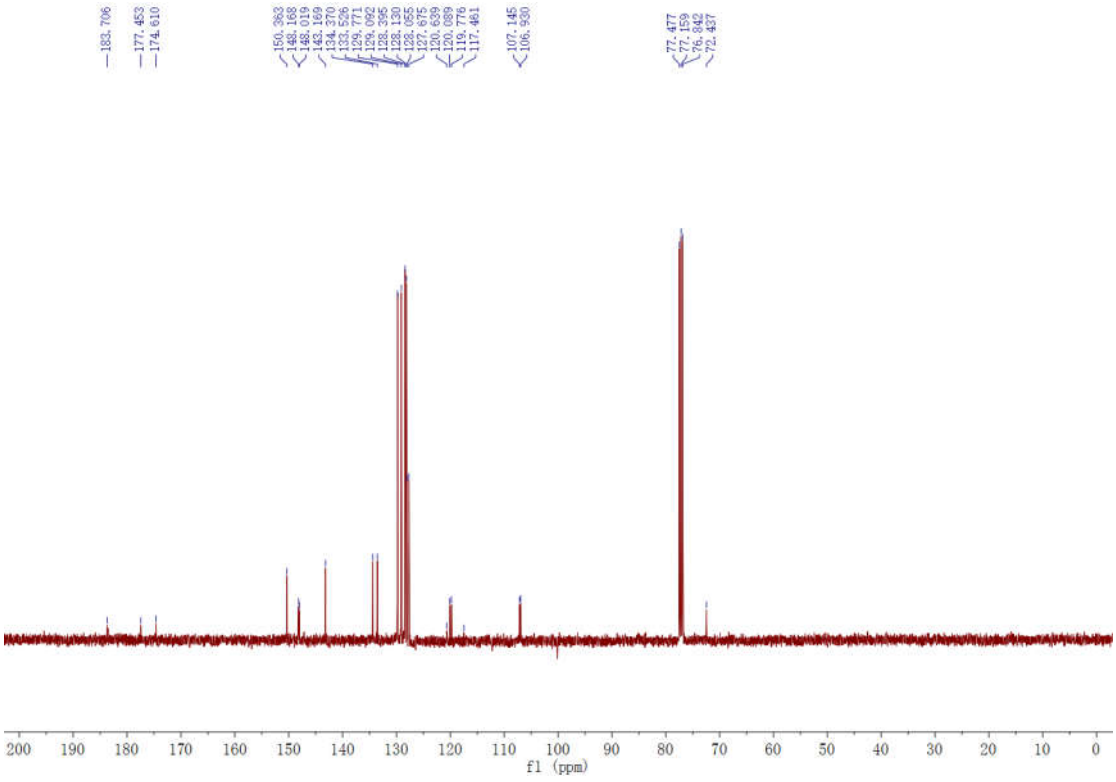
^{1}H NMR Spectrum for **3d** ($CDCl_3$, 400 MHz)



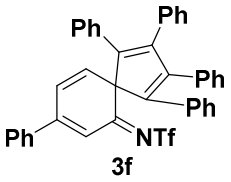
^{13}C NMR Spectrum for **3d** ($CDCl_3$, 100 MHz)



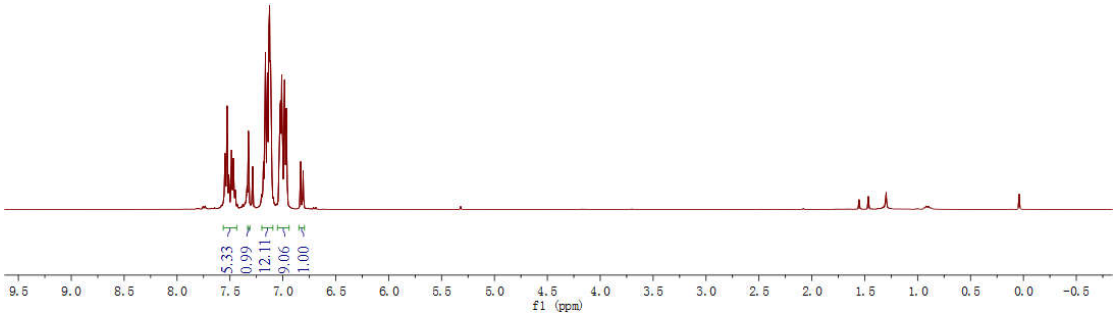
^{1}H NMR Spectrum for **3e** ($CDCl_3$, 400 MHz)



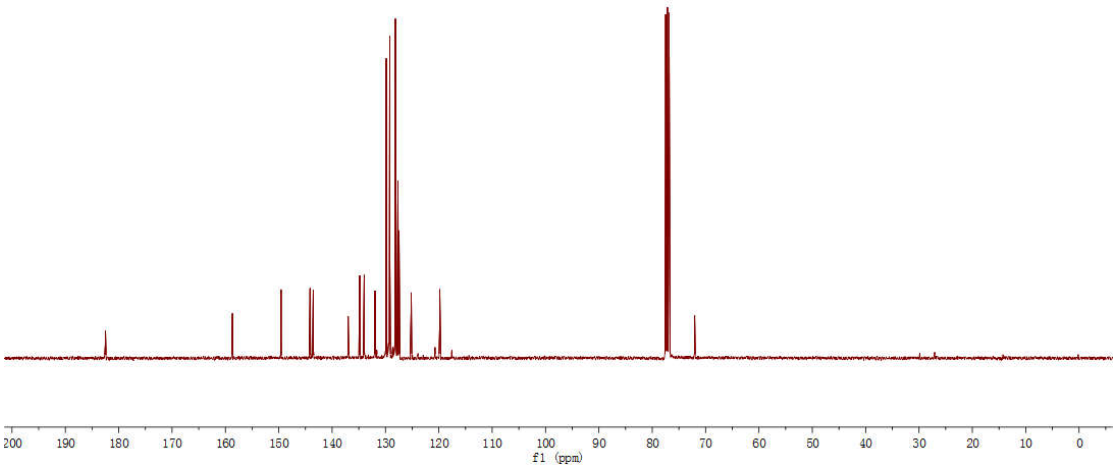
^{13}C NMR Spectrum for **3e** ($CDCl_3$, 100 MHz)



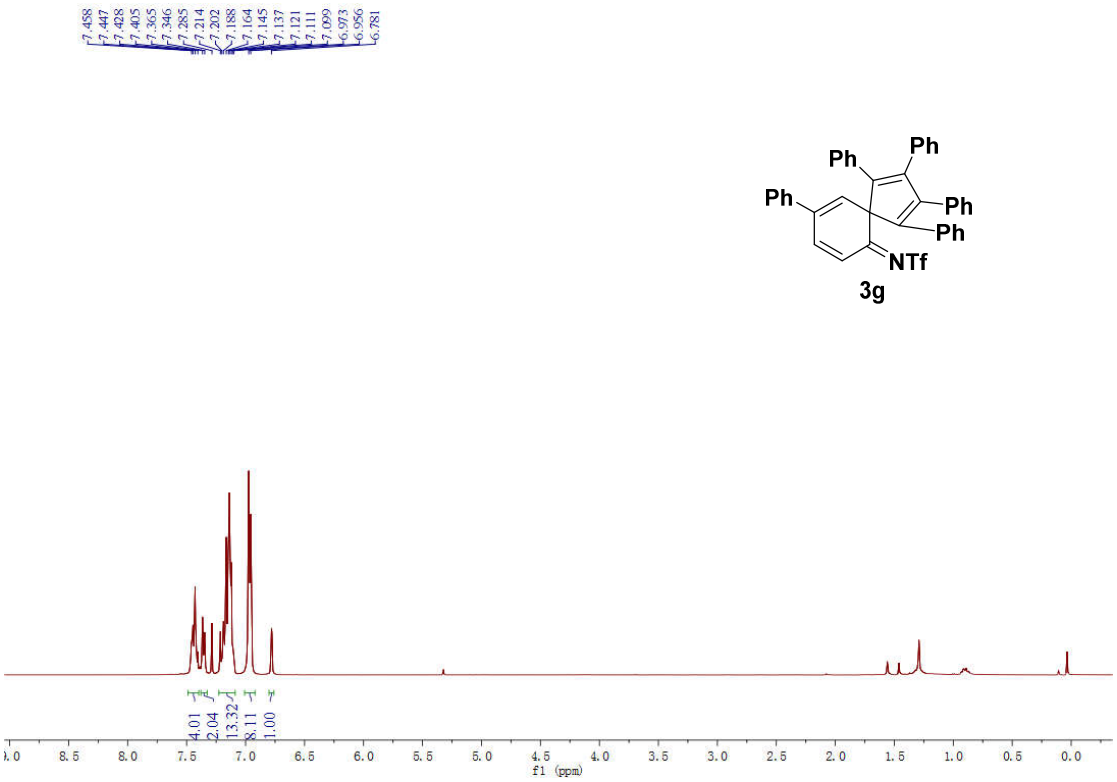
3f



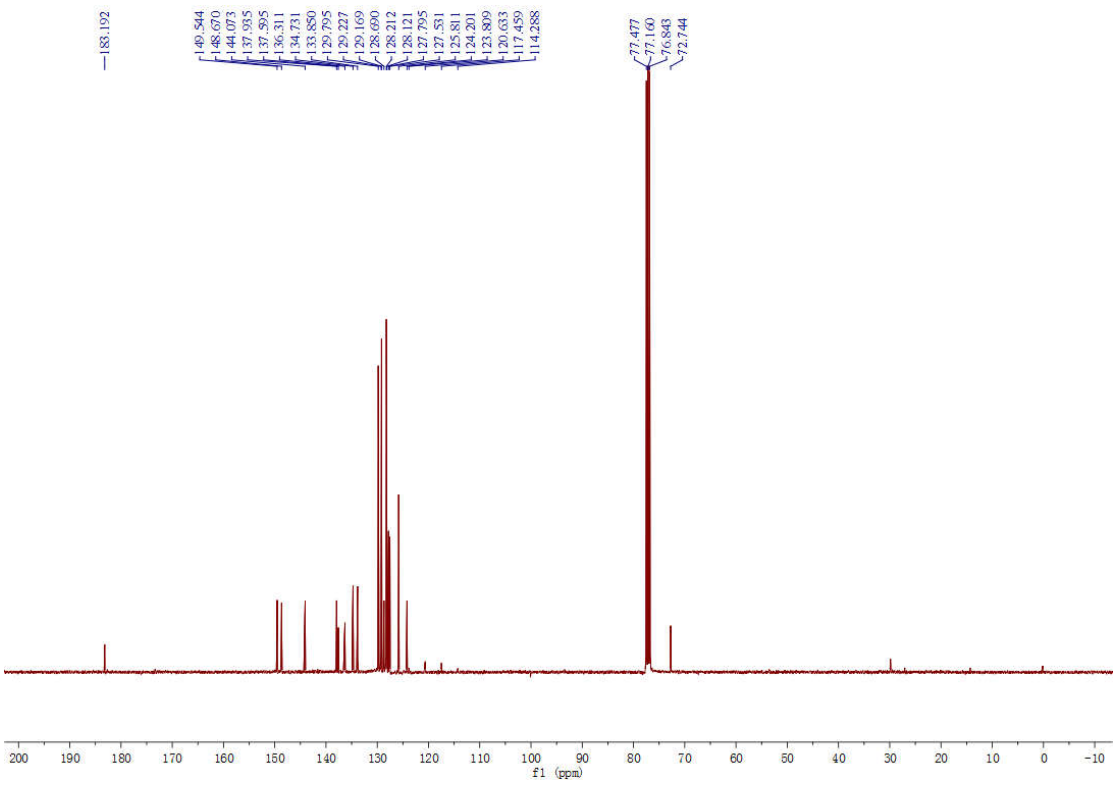
^{1}H NMR Spectrum for **3f** ($CDCl_3$, 400 MHz)



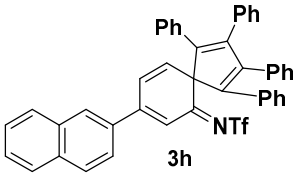
^{13}C NMR Spectrum for **3f** ($CDCl_3$, 100 MHz)



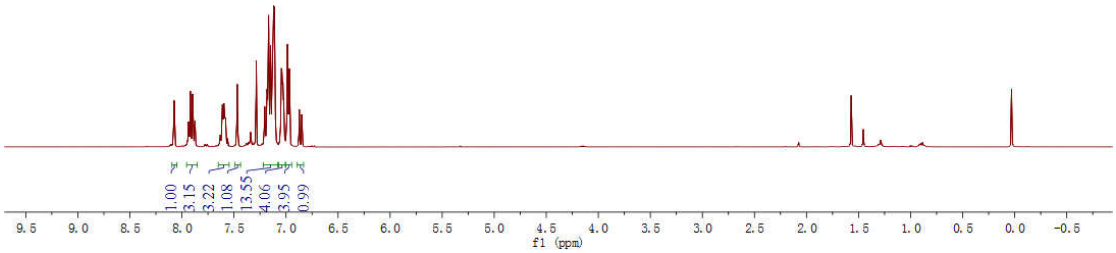
^{1}H NMR Spectrum for **3g** ($CDCl_3$, 400 MHz)



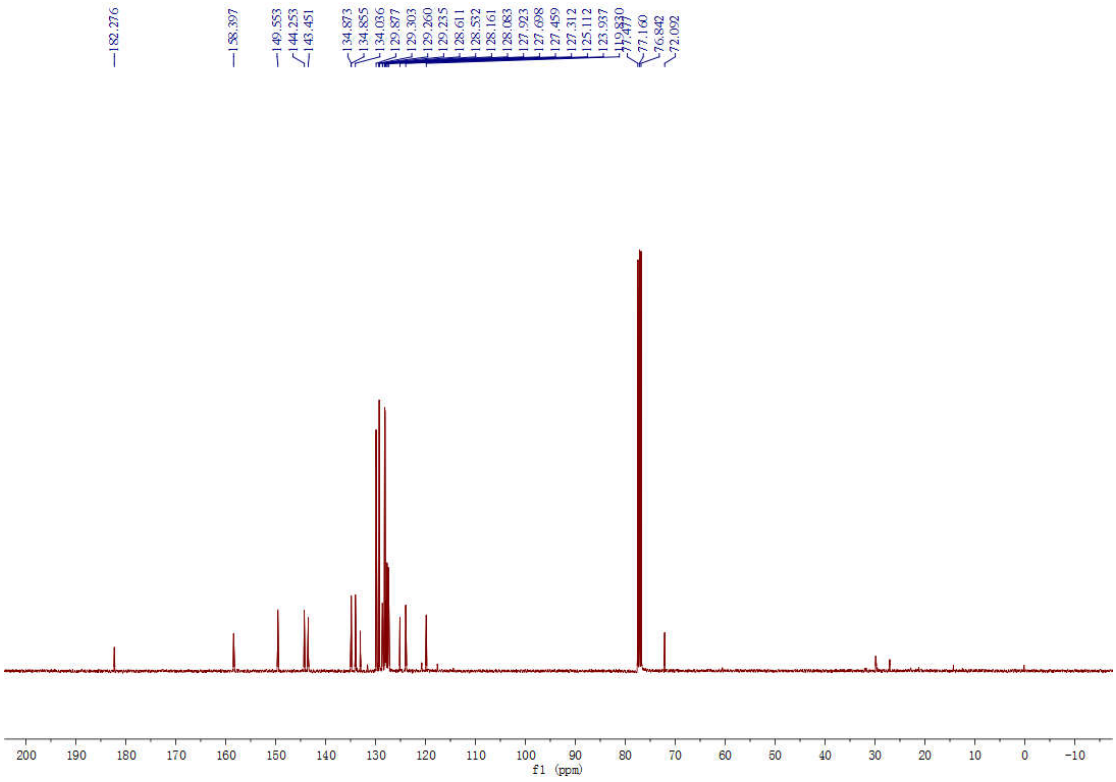
^{13}C NMR Spectrum for **3g** ($CDCl_3$, 100 MHz)



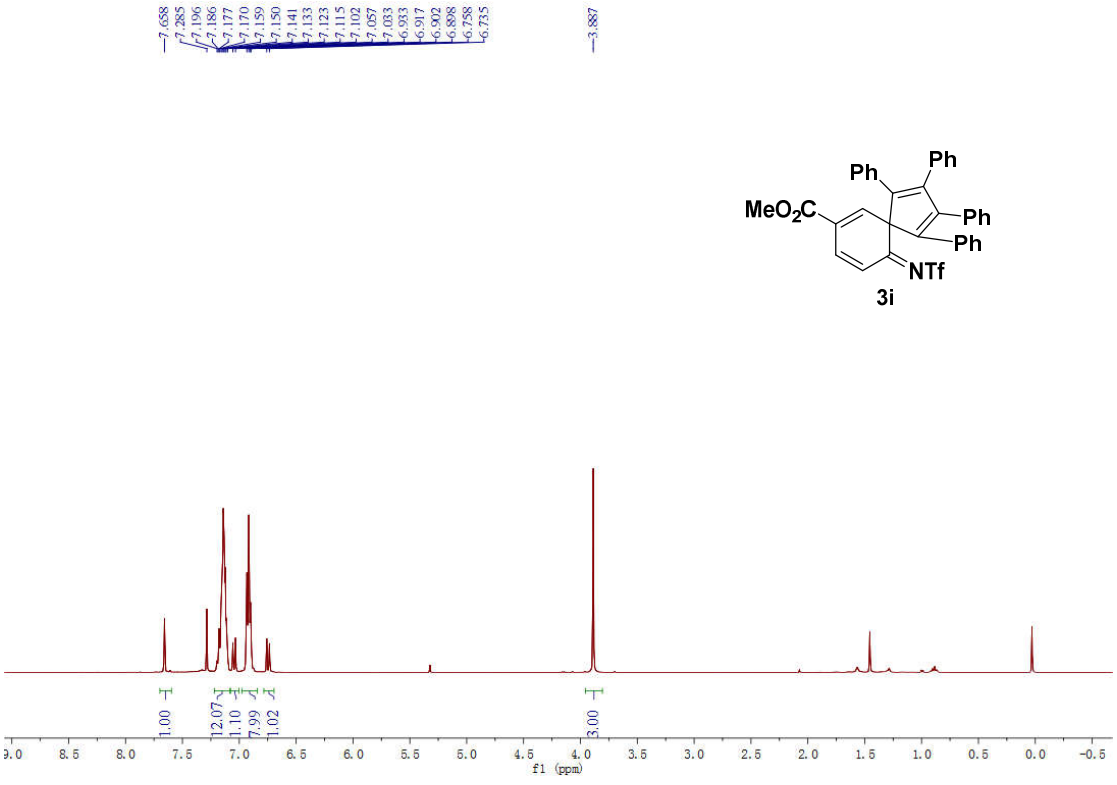
3h



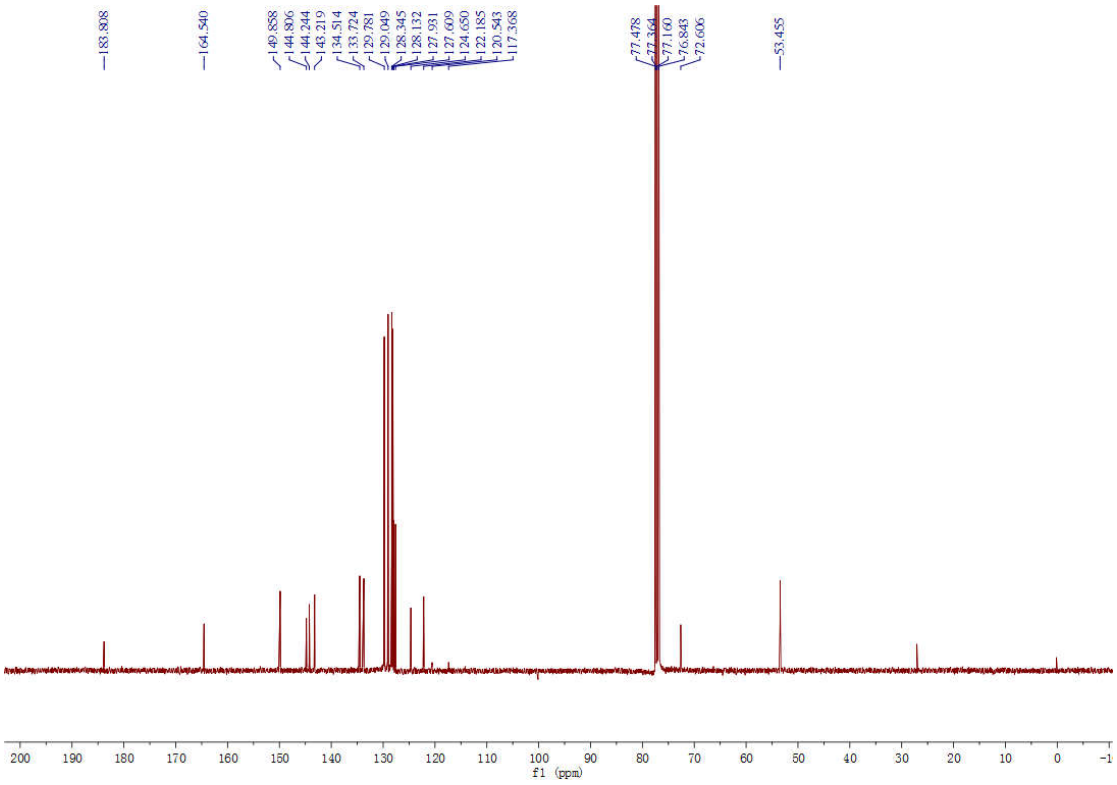
^{1}H NMR Spectrum for **3h** ($CDCl_3$, 400 MHz)



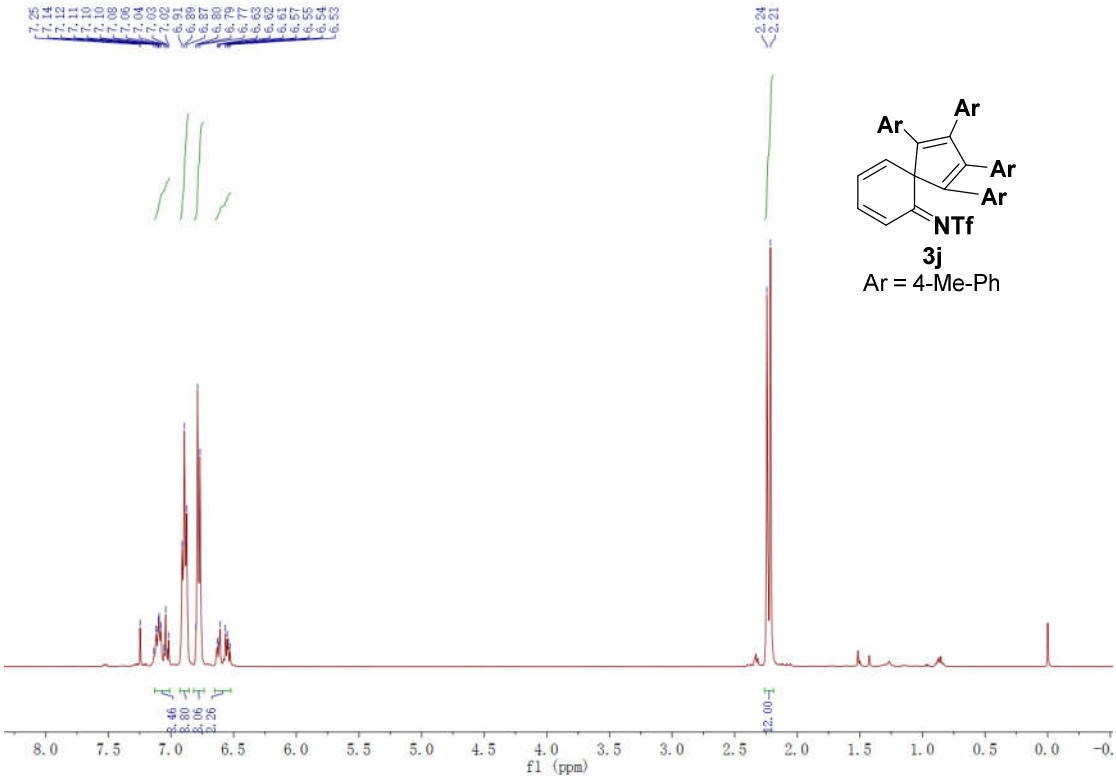
^{13}C NMR Spectrum for **3h** ($CDCl_3$, 100 MHz)



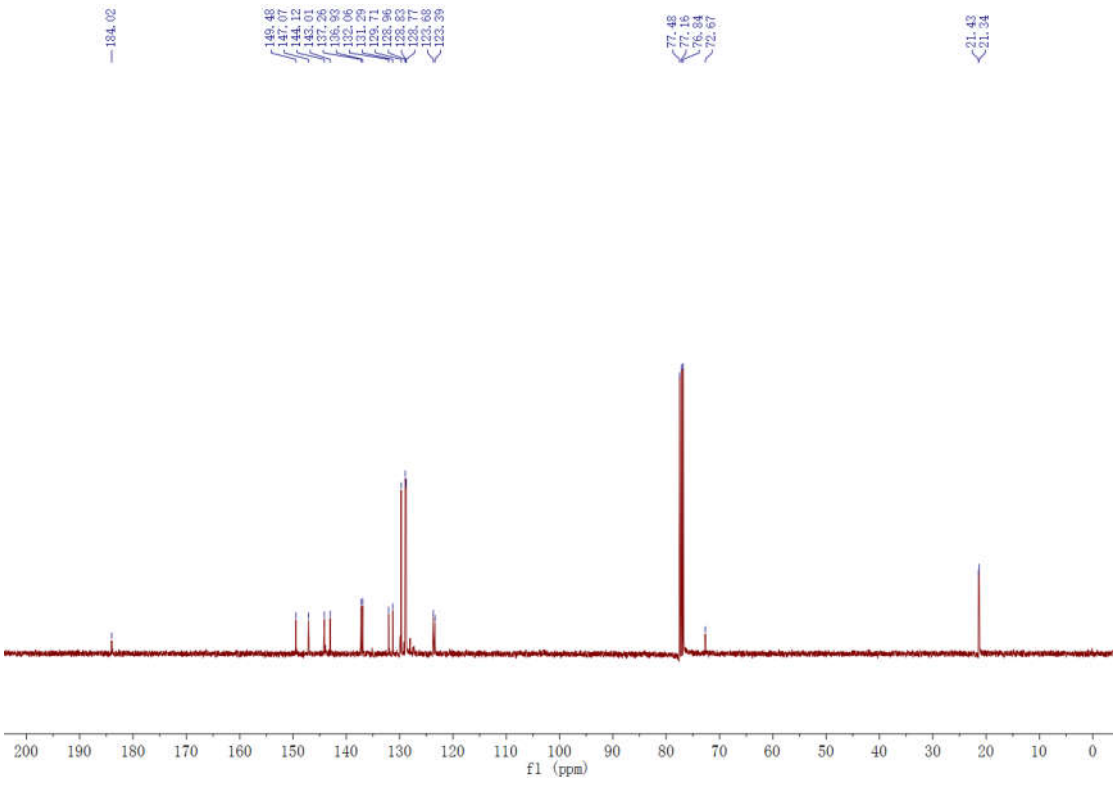
^{1}H NMR Spectrum for **3i** ($CDCl_3$, 400 MHz)



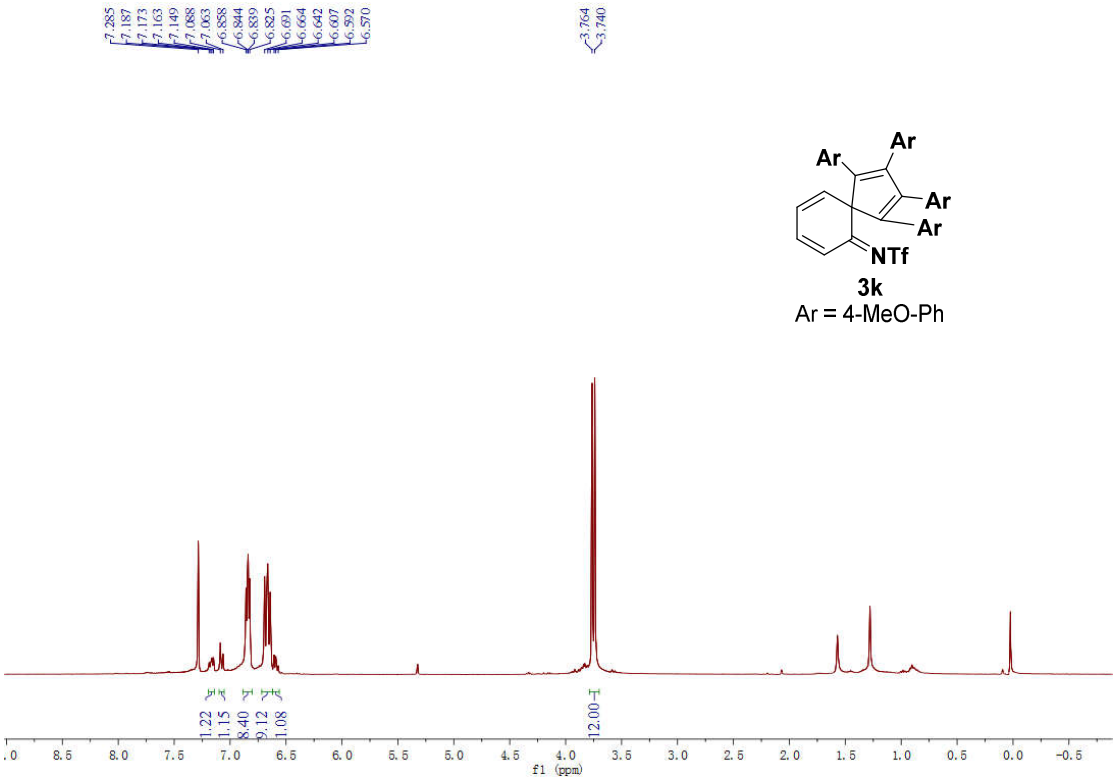
^{13}C NMR Spectrum for **3i** ($CDCl_3$, 100 MHz)



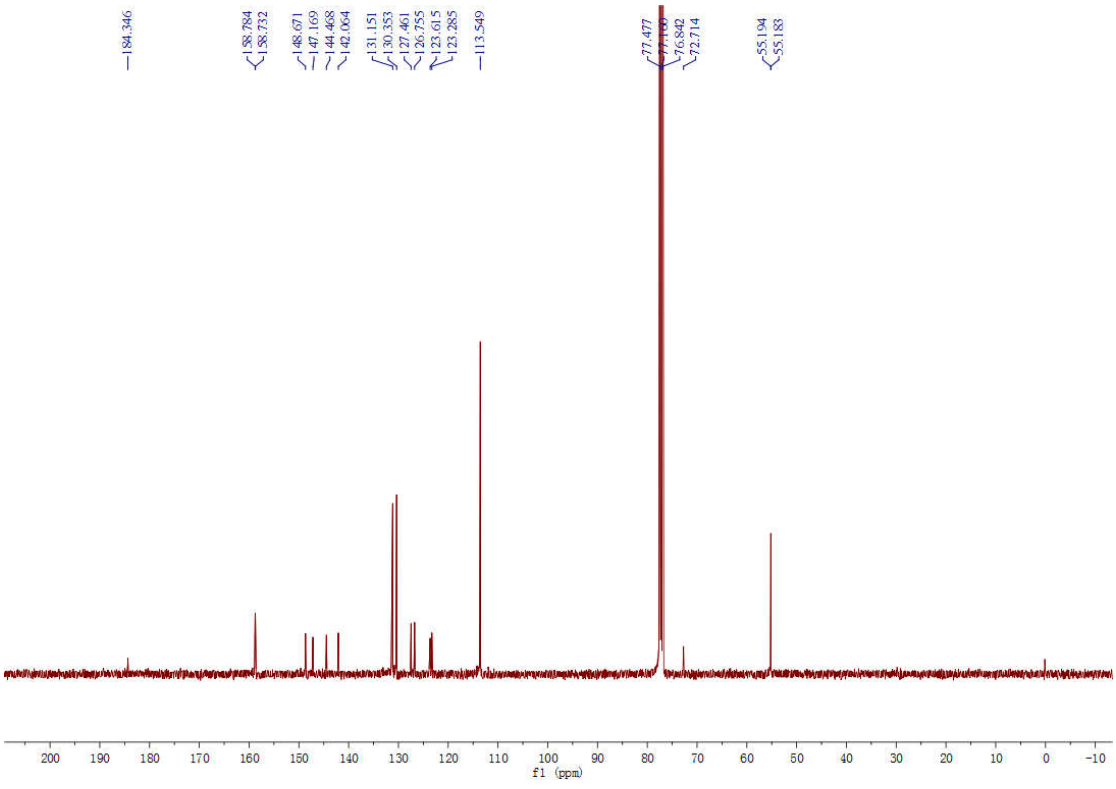
^{1}H NMR Spectrum for **3j** ($CDCl_3$, 400 MHz)



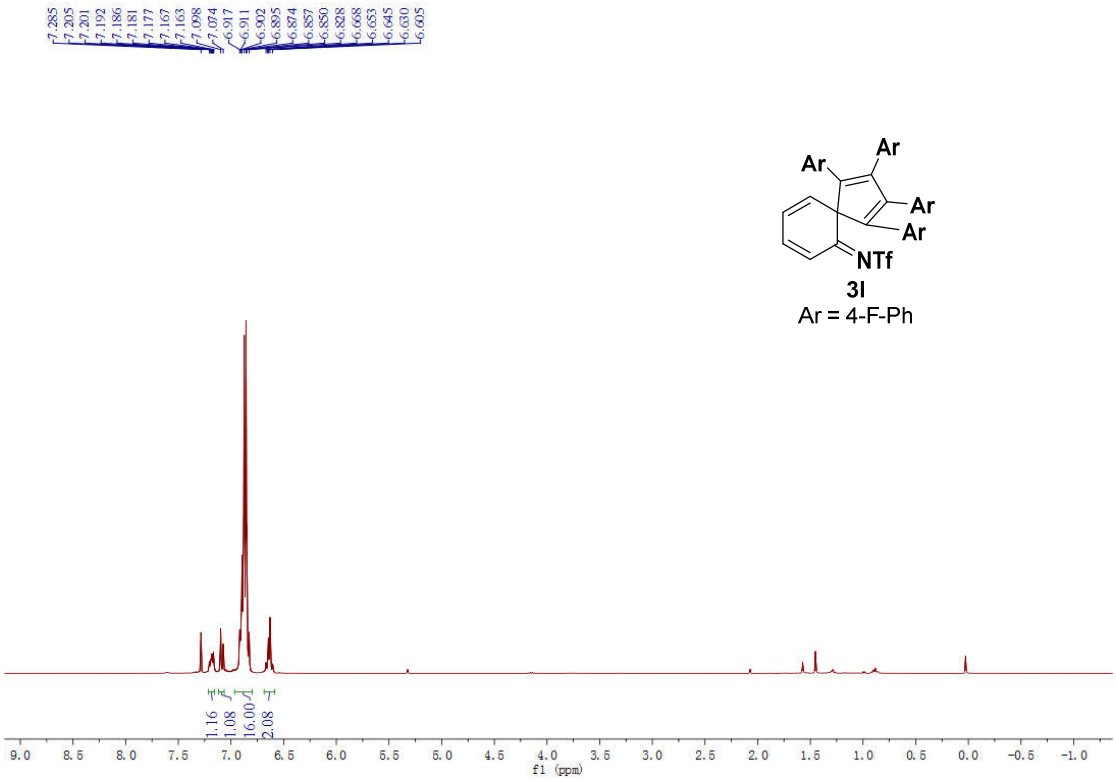
^{13}C NMR Spectrum for **3j** ($CDCl_3$, 100 MHz)



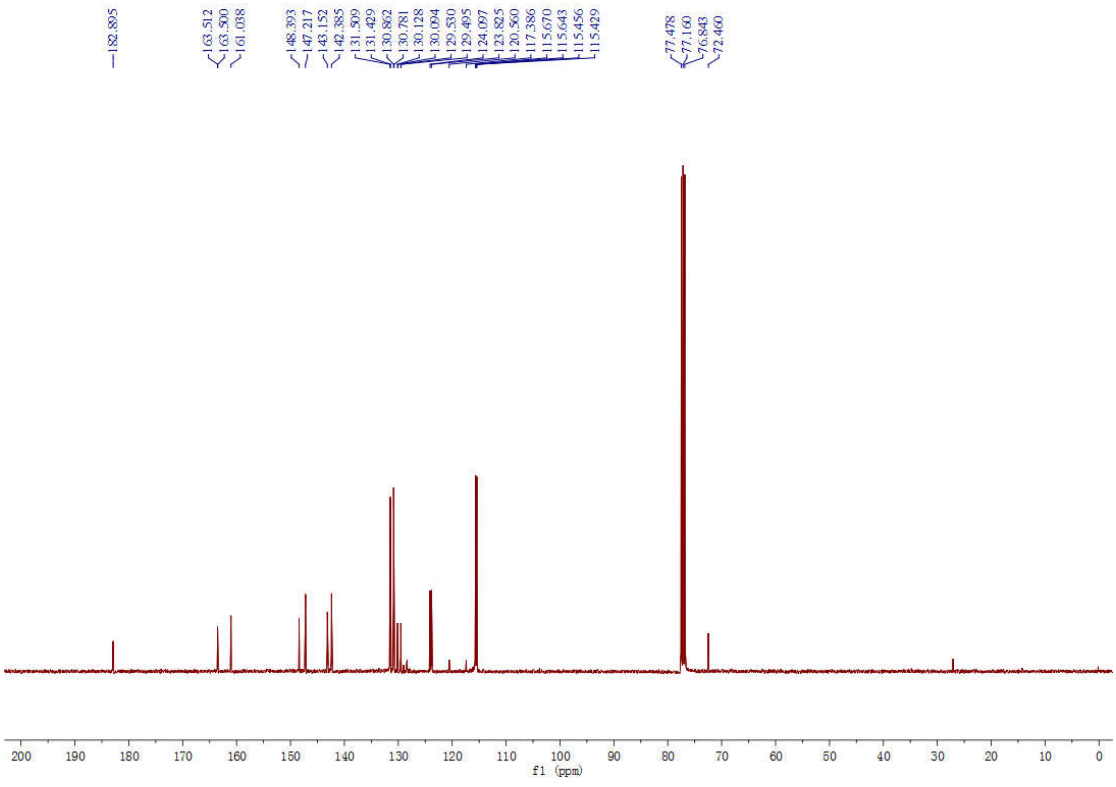
^{1}H NMR Spectrum for **3k** ($CDCl_3$, 400 MHz)



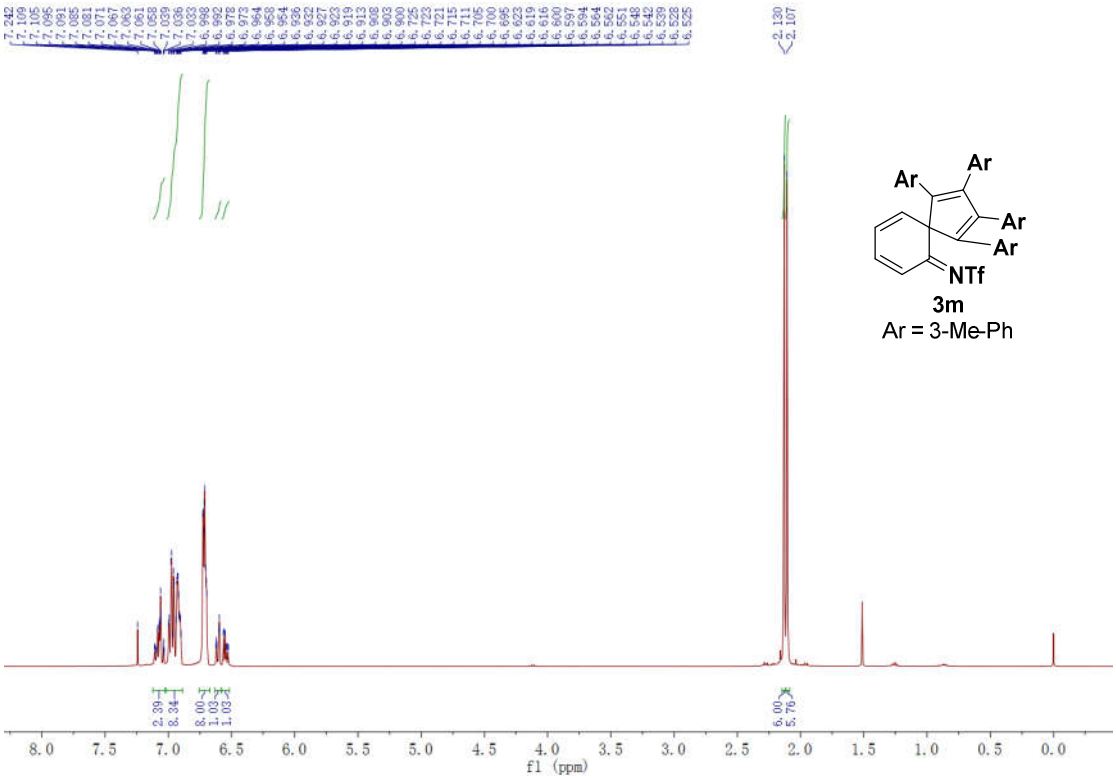
^{13}C NMR Spectrum for **3k** ($CDCl_3$, 100 MHz)



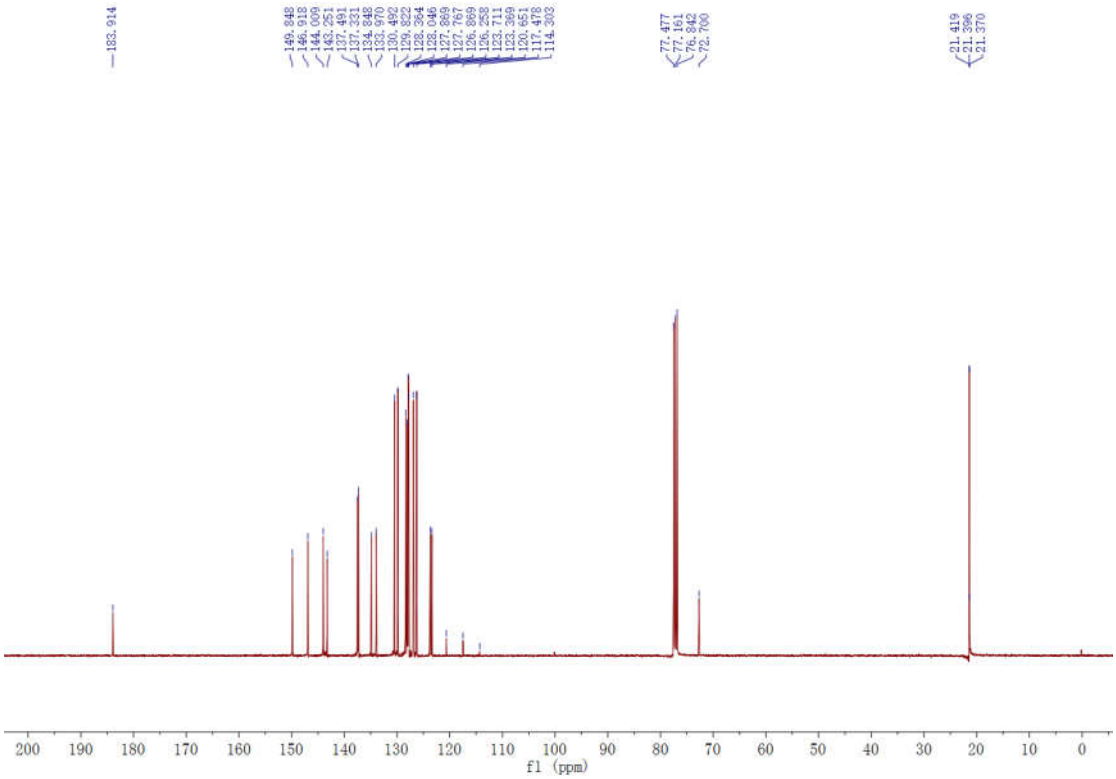
^{1}H NMR Spectrum for **3l** ($CDCl_3$, 400 MHz)



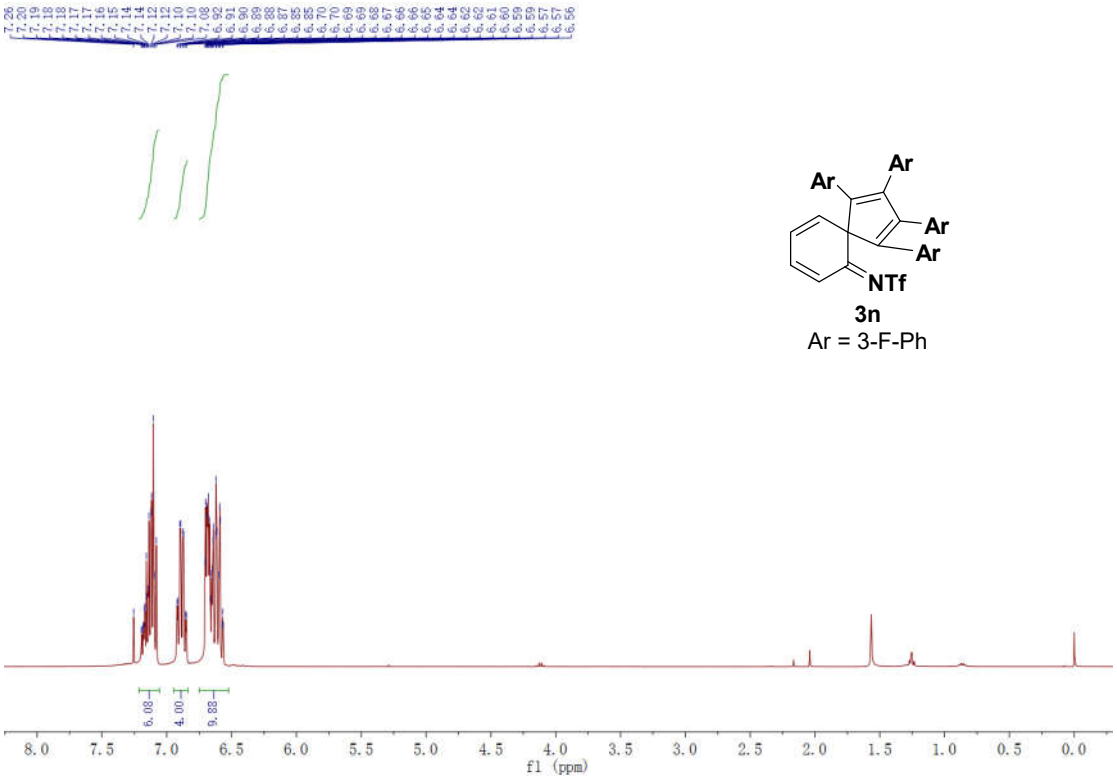
^{13}C NMR Spectrum for **3l** ($CDCl_3$, 100 MHz)



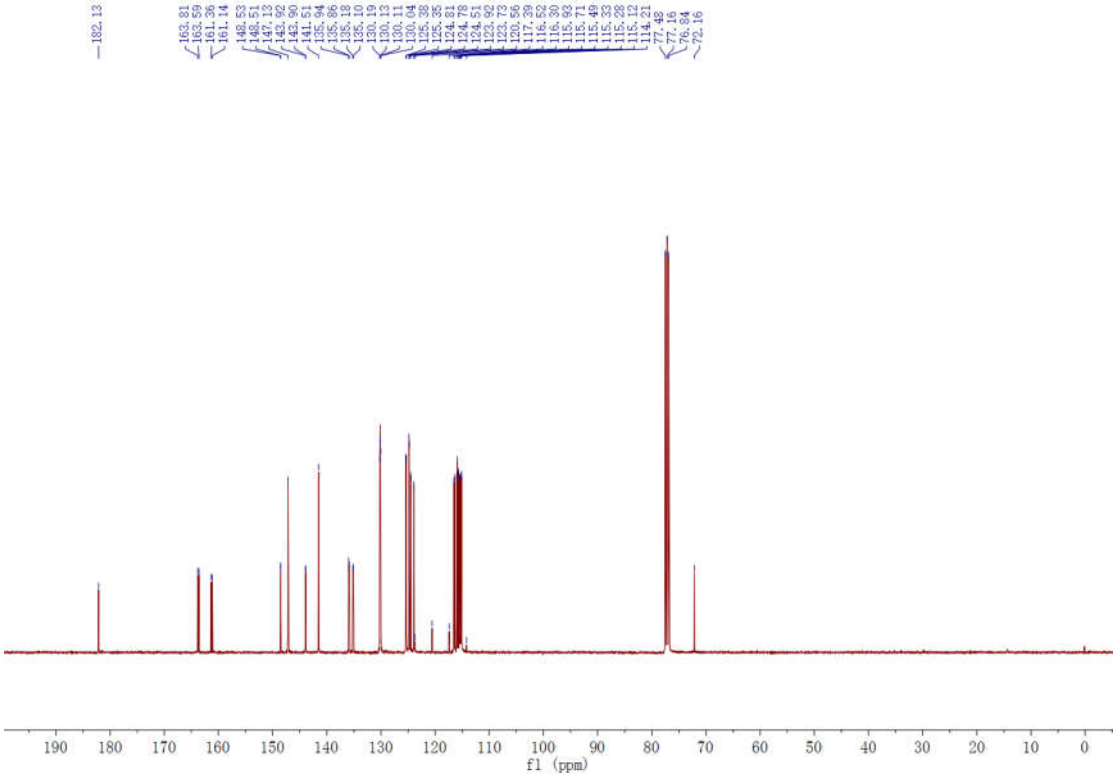
^{1}H NMR Spectrum for **3m** ($CDCl_3$, 400 MHz)



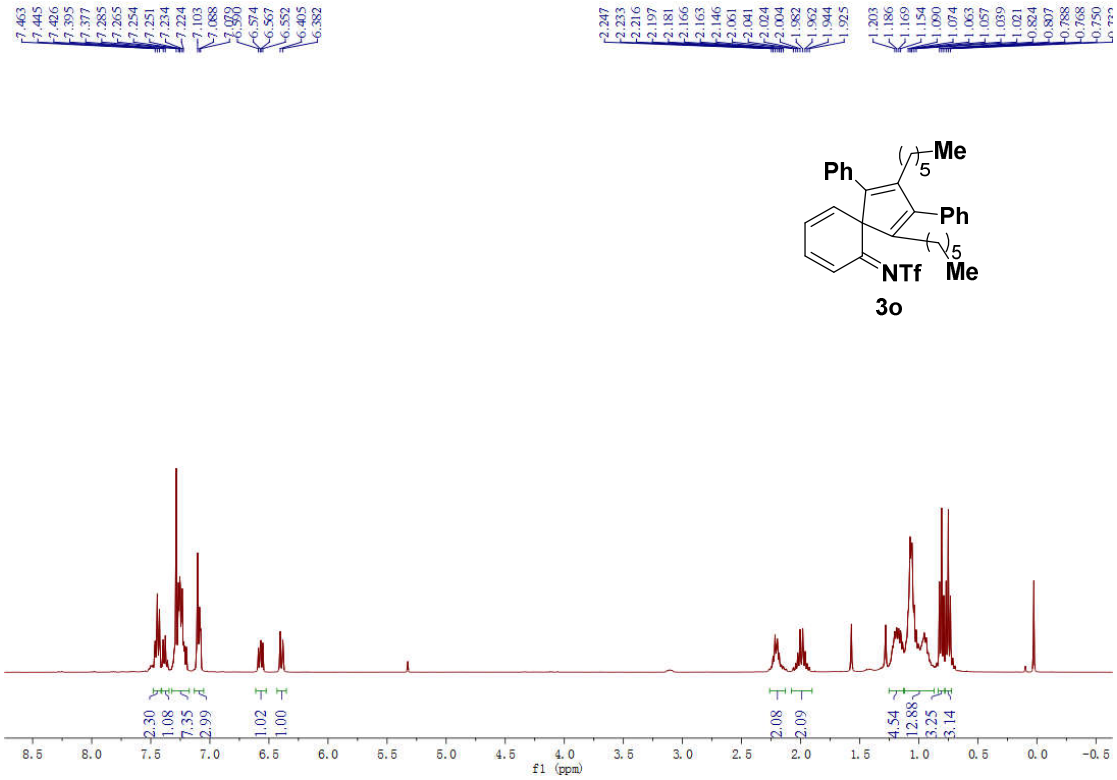
^{13}C NMR Spectrum for **3m** ($CDCl_3$, 100 MHz)



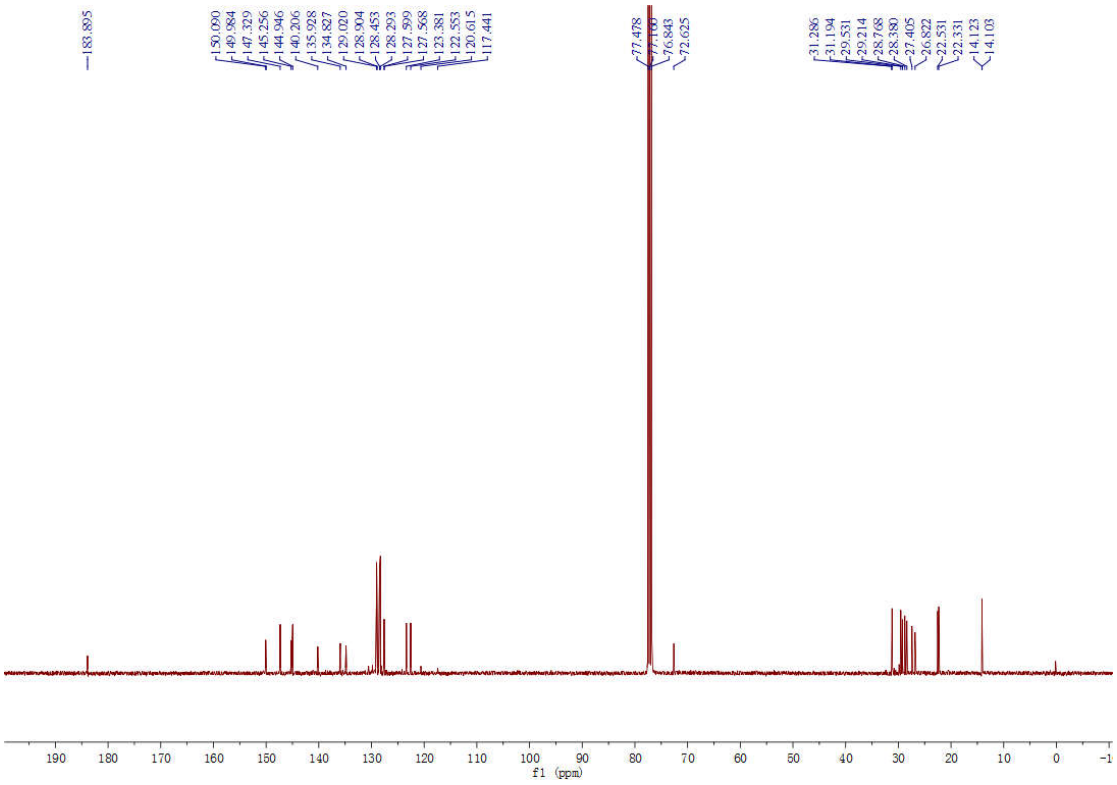
^{1}H NMR Spectrum for **3n** ($CDCl_3$, 400 MHz)



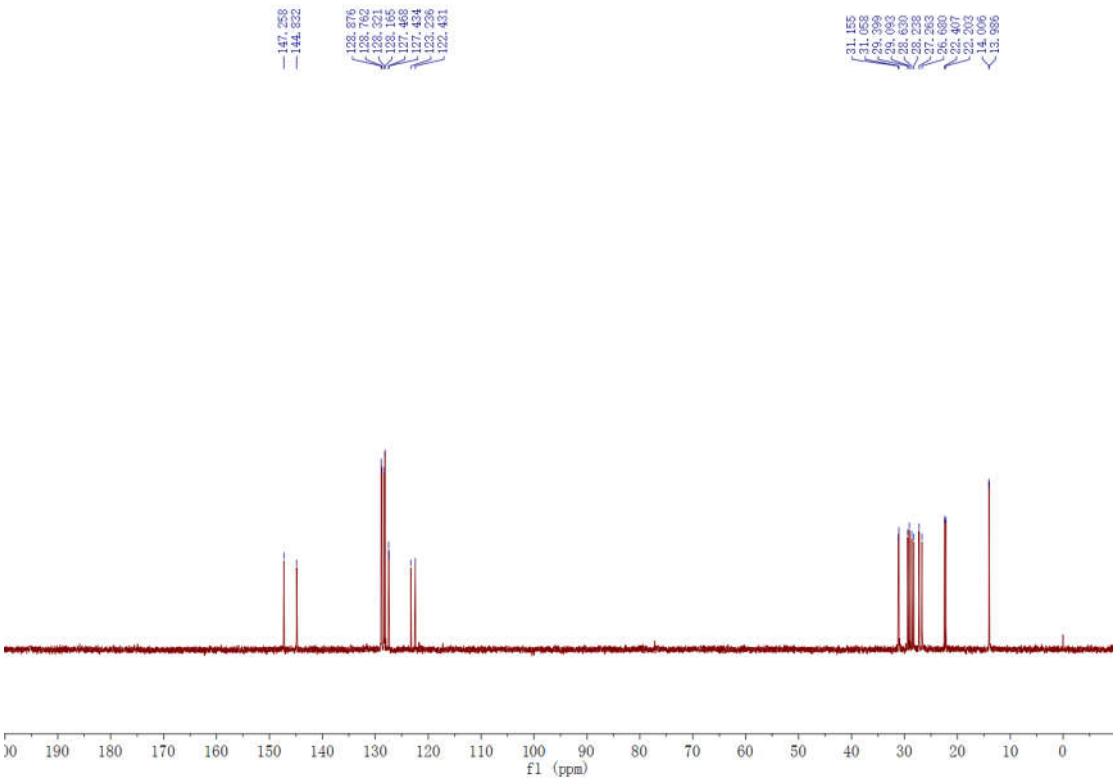
^{13}C NMR Spectrum for **3n** ($CDCl_3$, 100 MHz)



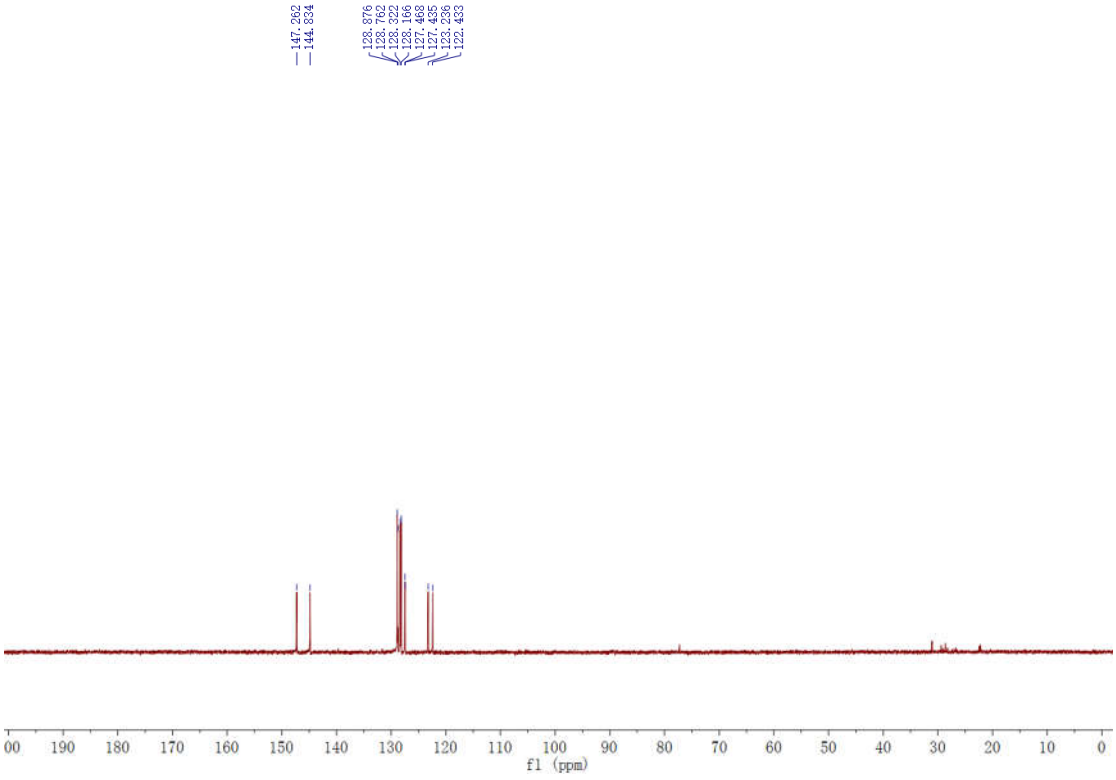
^{1}H NMR Spectrum for **3o** ($CDCl_3$, 400 MHz)



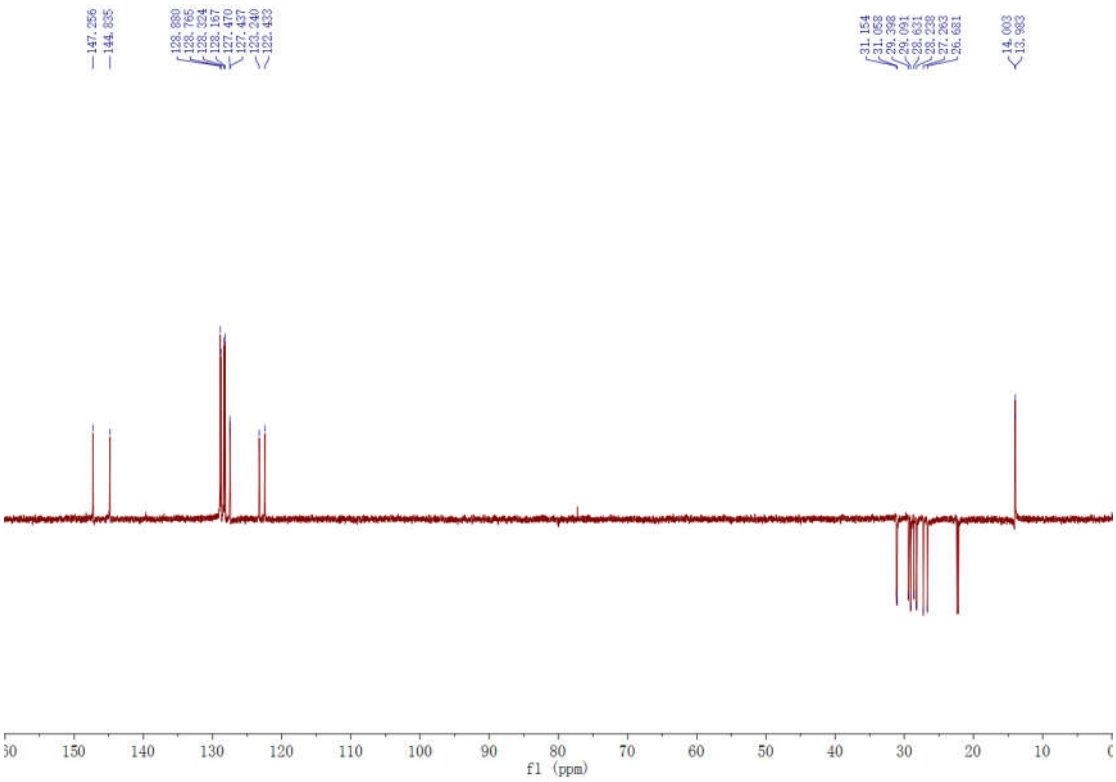
^{13}C NMR Spectrum for **3o** ($CDCl_3$, 100 MHz)



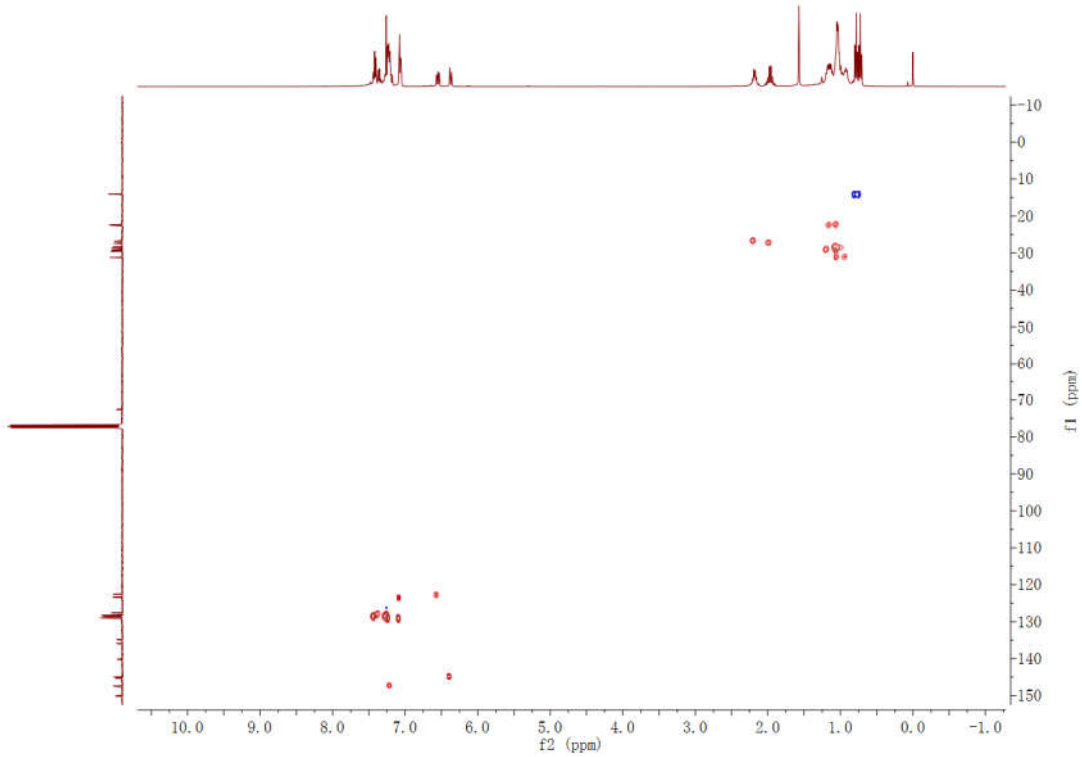
DEPT-45 NMR Spectrum for **3o** ($CDCl_3$, 100 MHz)



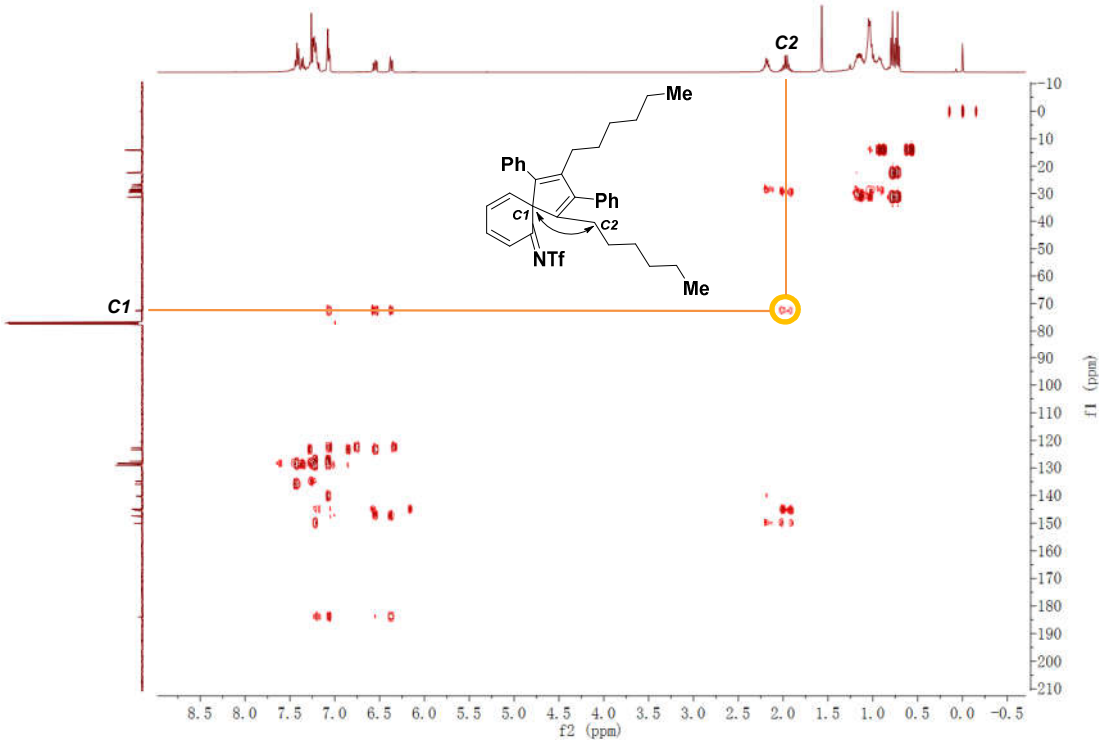
DEPT-90 NMR Spectrum for **3o** ($CDCl_3$, 100 MHz)



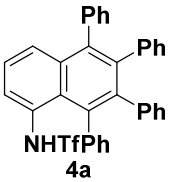
DEPT-135 NMR Spectrum for **3o** ($CDCl_3$, 100 MHz)

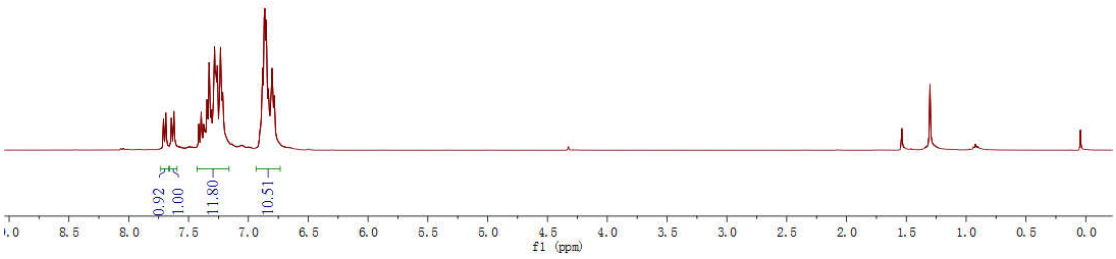


HSQC NMR Spectrum for **3o** ($CDCl_3$)

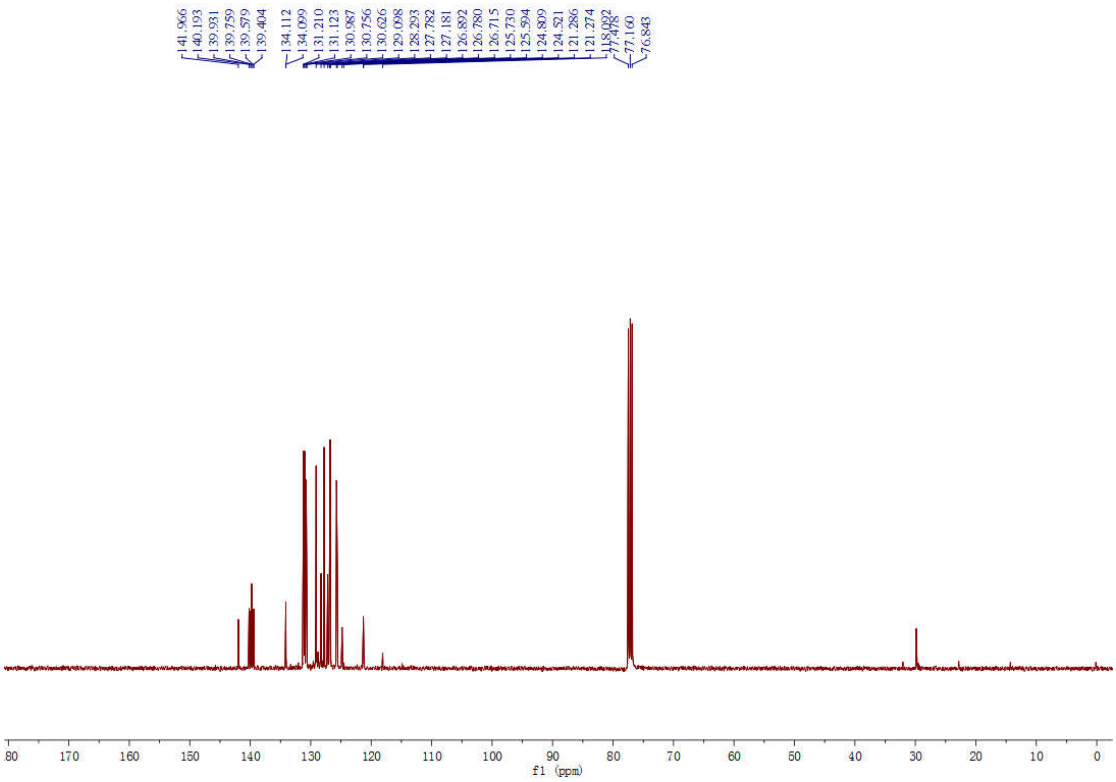


HMBC NMR Spectrum for **3o** ($CDCl_3$)

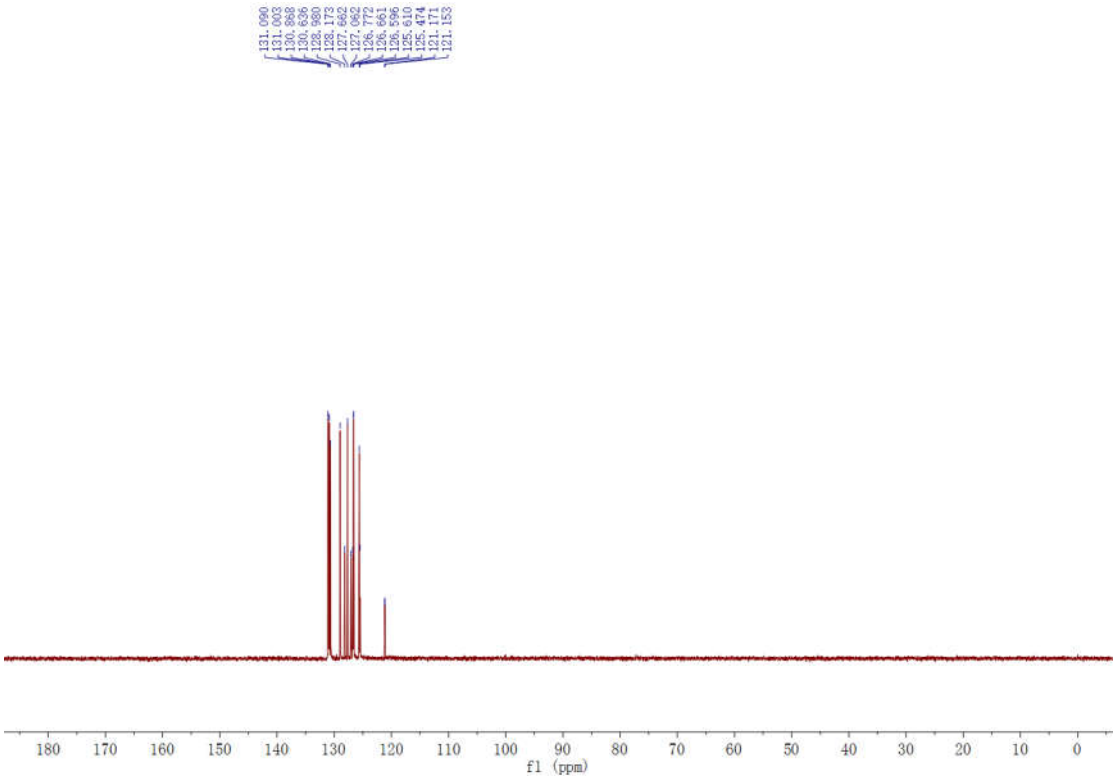




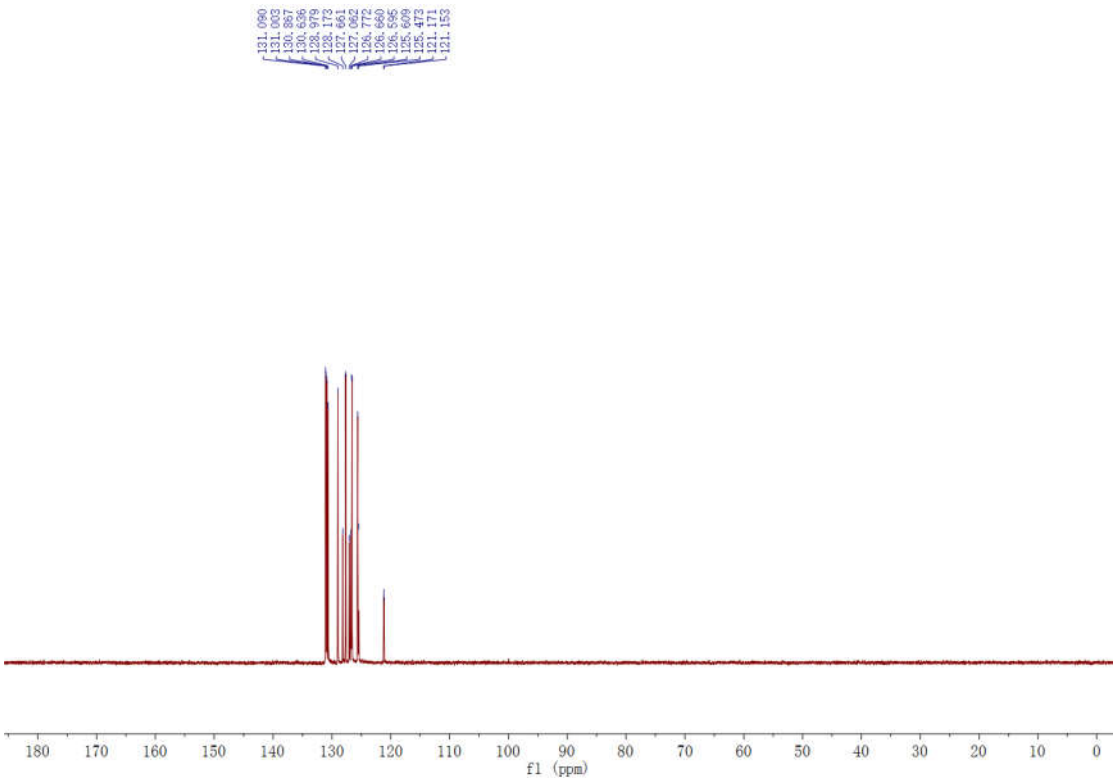
^{1}H NMR Spectrum for **4a** ($CDCl_3$, 400 MHz)



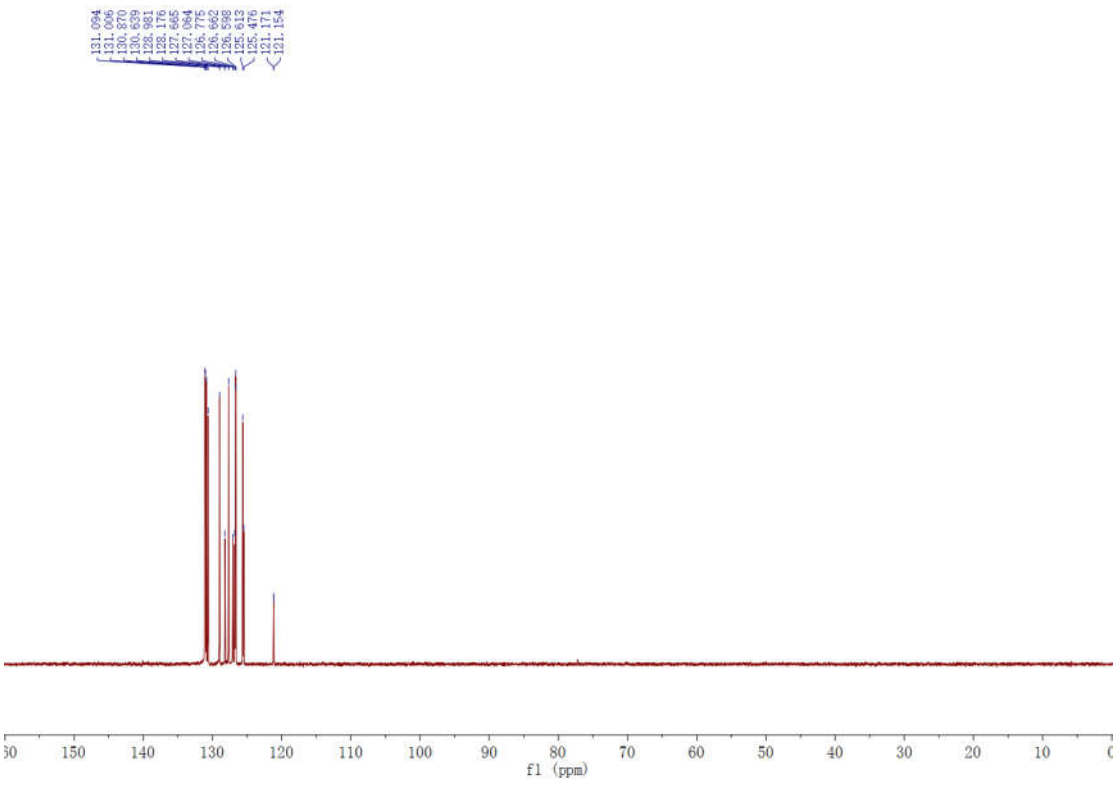
^{13}C NMR Spectrum for **4a** ($CDCl_3$, 100 MHz)



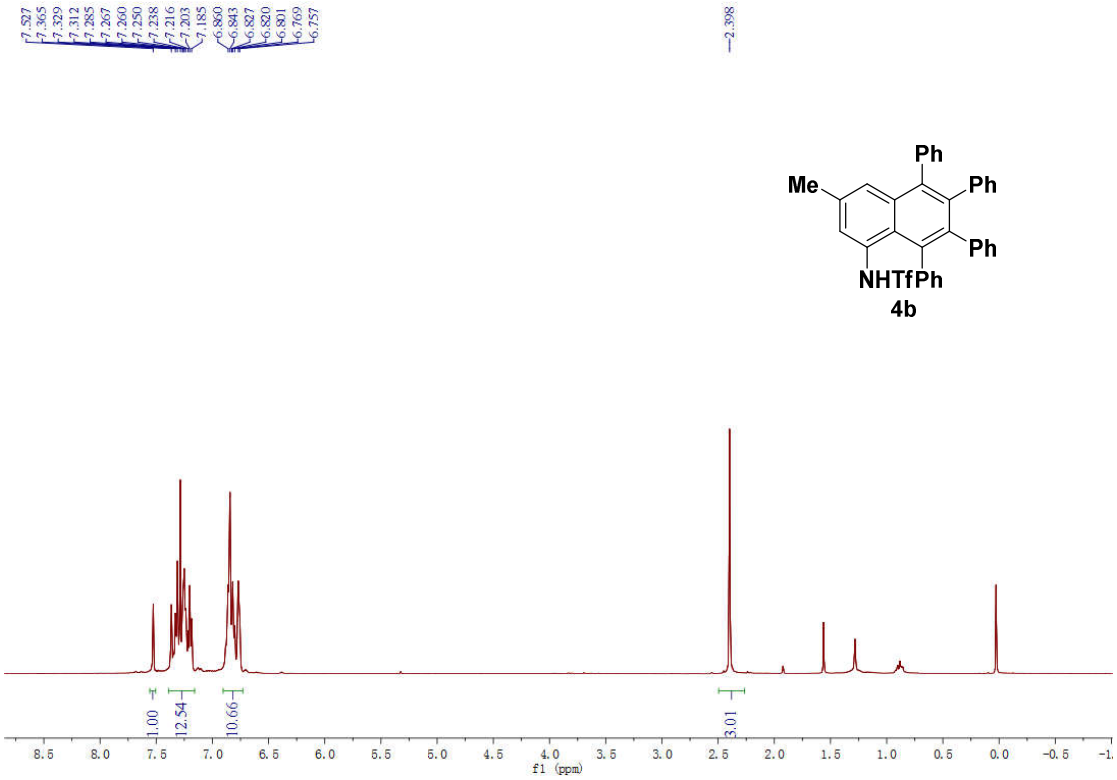
DEPT-45 NMR Spectrum for **4a** ($CDCl_3$, 100 MHz)



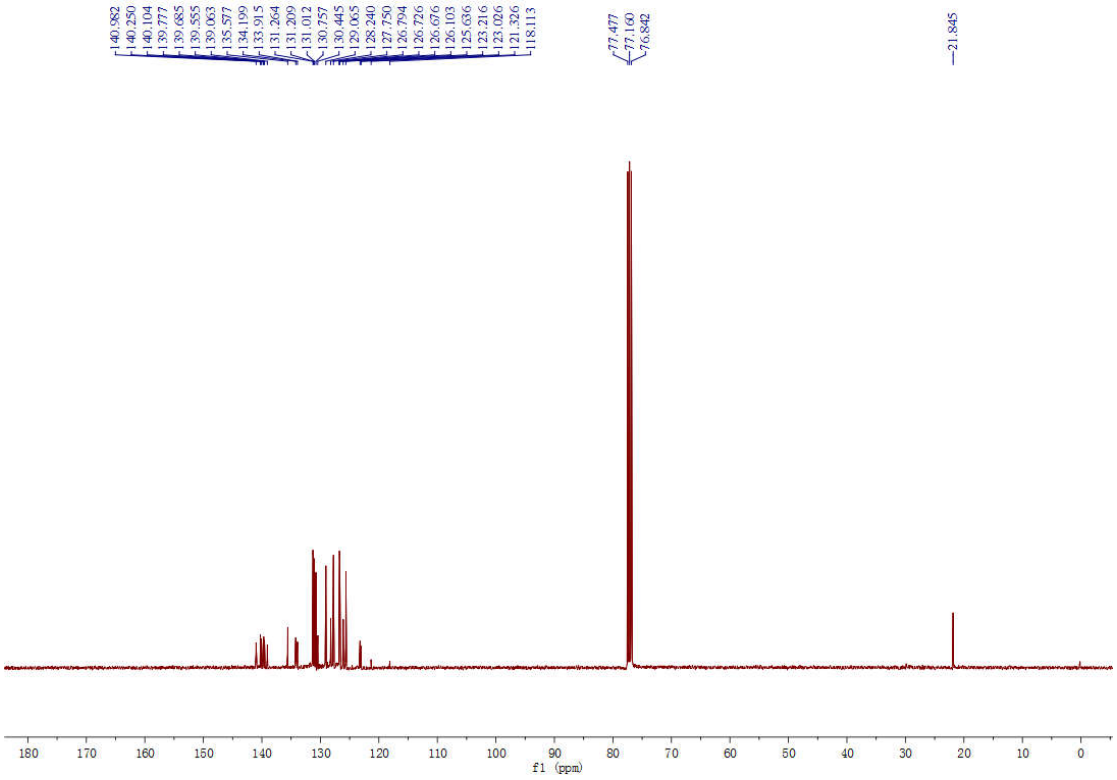
DEPT-90 NMR Spectrum for **4a** ($CDCl_3$, 100 MHz)



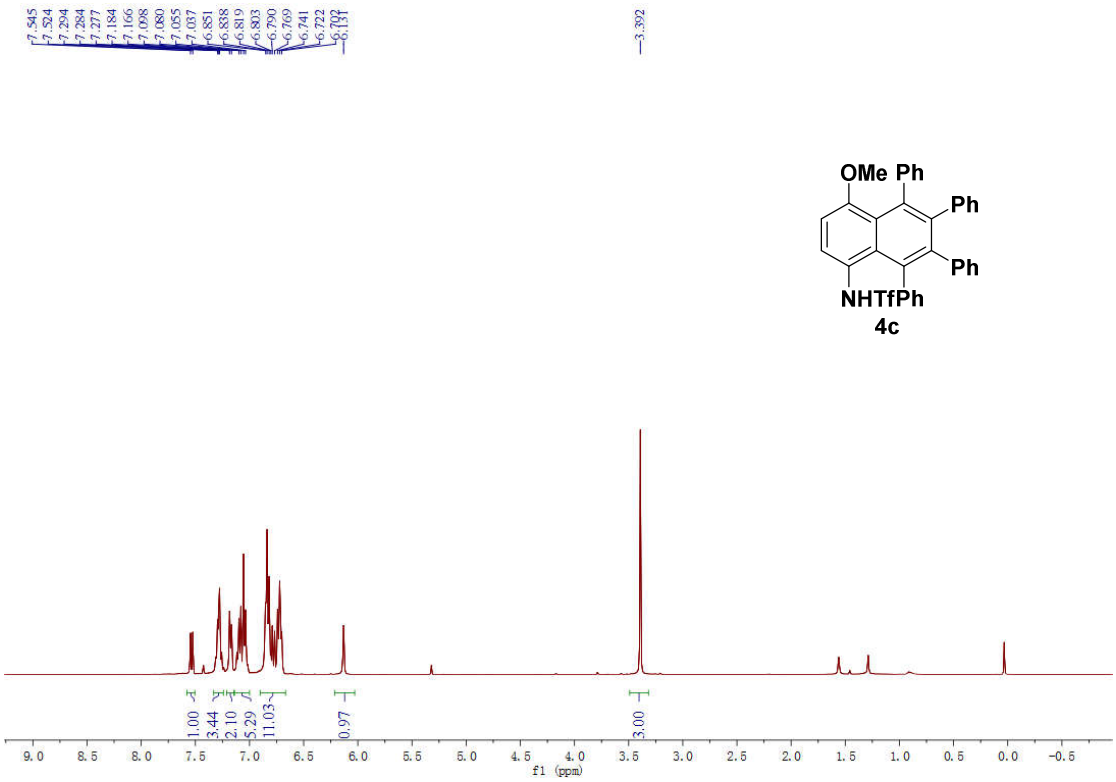
DEPT-135 NMR Spectrum for **4a** ($CDCl_3$, 100 MHz)



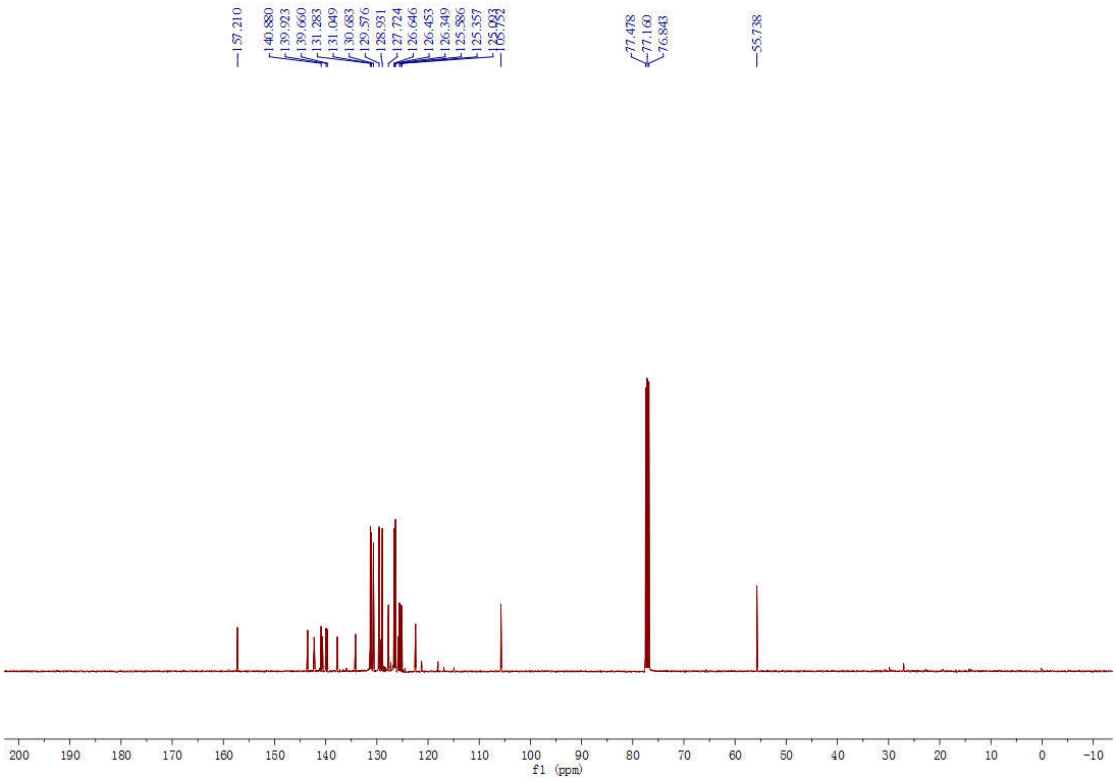
^{1}H NMR Spectrum for **4b** ($CDCl_3$, 400 MHz)



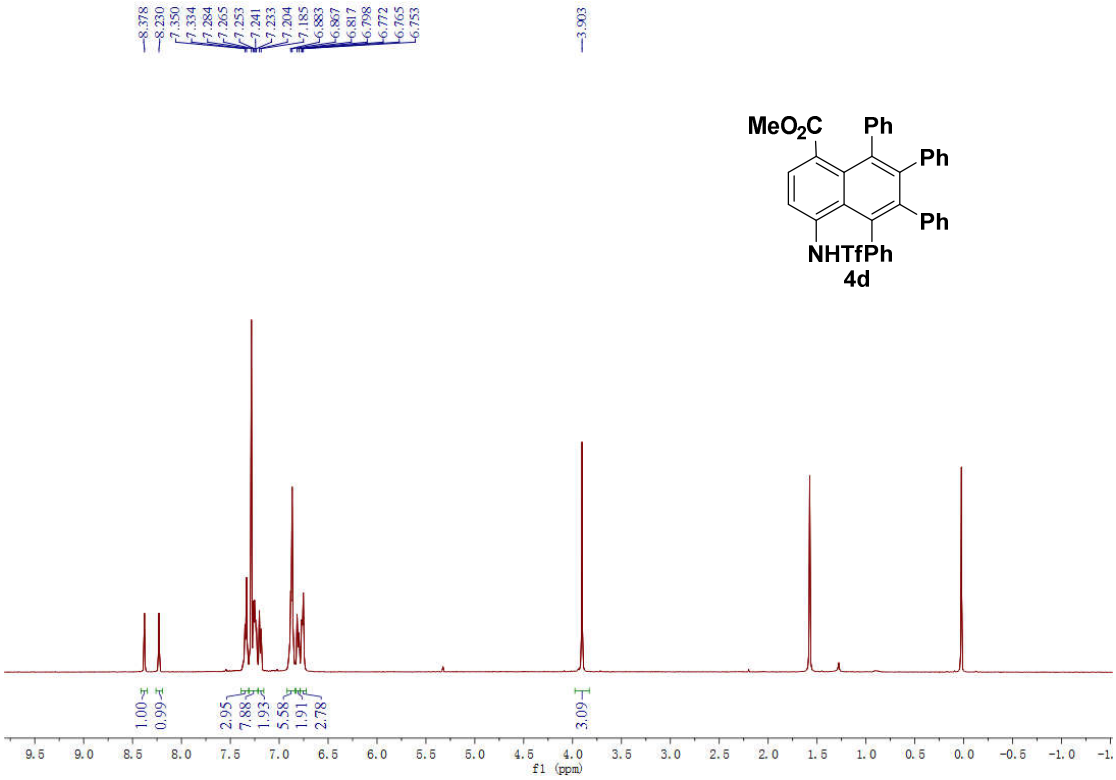
^{13}C NMR Spectrum for **4b** ($CDCl_3$, 100 MHz)



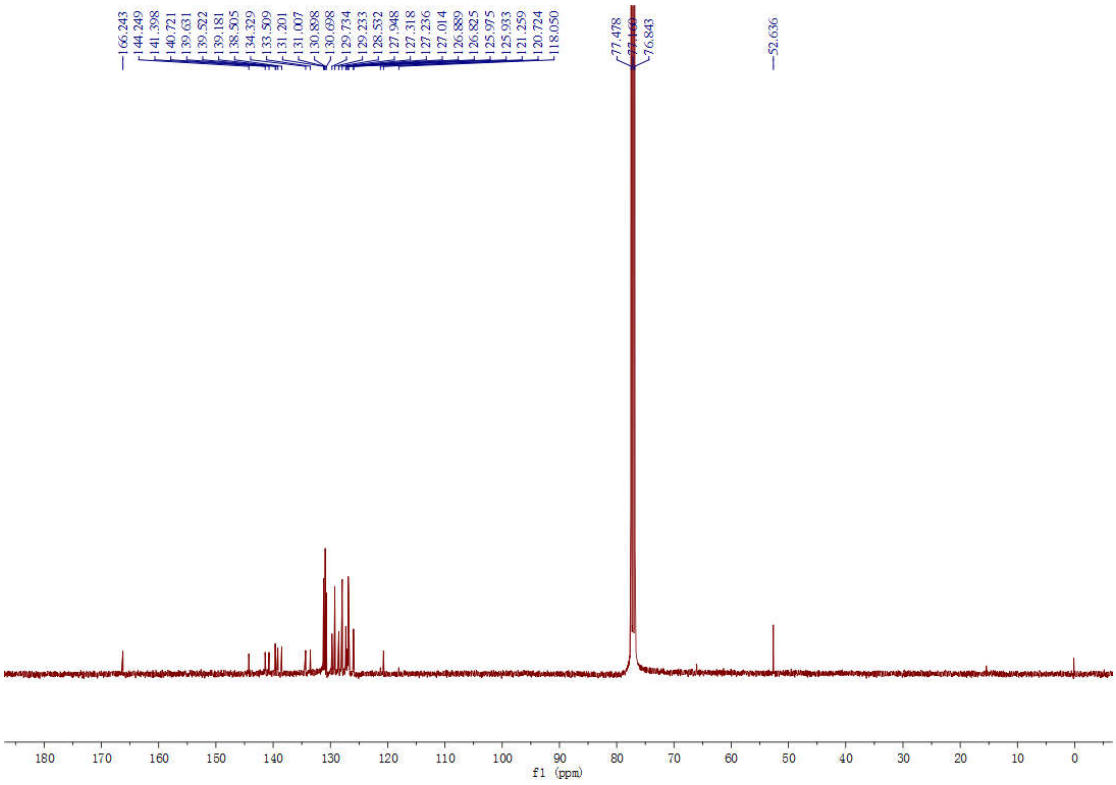
^{1}H NMR Spectrum for **4c** ($CDCl_3$, 400 MHz)



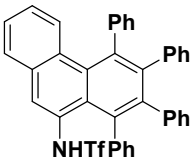
^{13}C NMR Spectrum for **4c** ($CDCl_3$, 100 MHz)



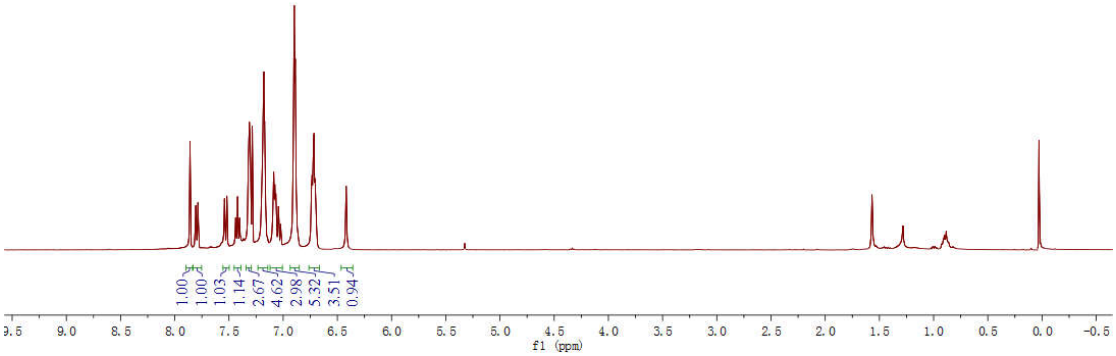
^{1}H NMR Spectrum for **4d** ($CDCl_3$, 400 MHz)



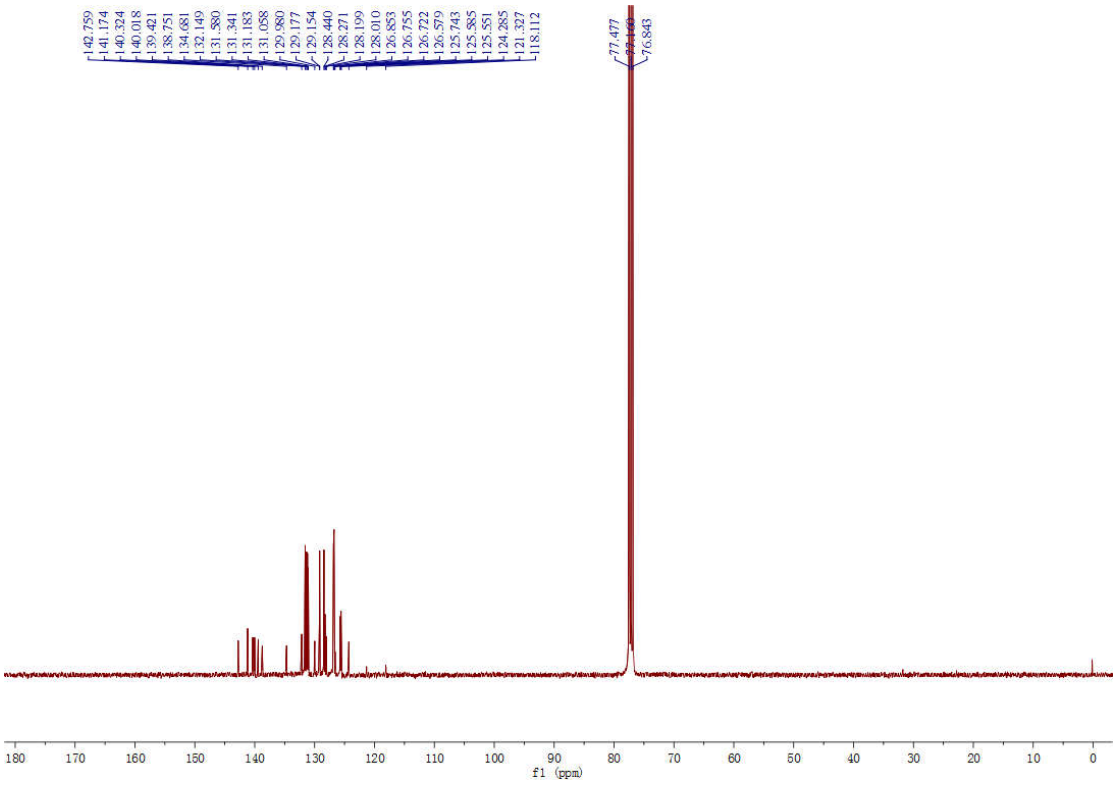
^{13}C NMR Spectrum for **4d** ($CDCl_3$, 100 MHz)



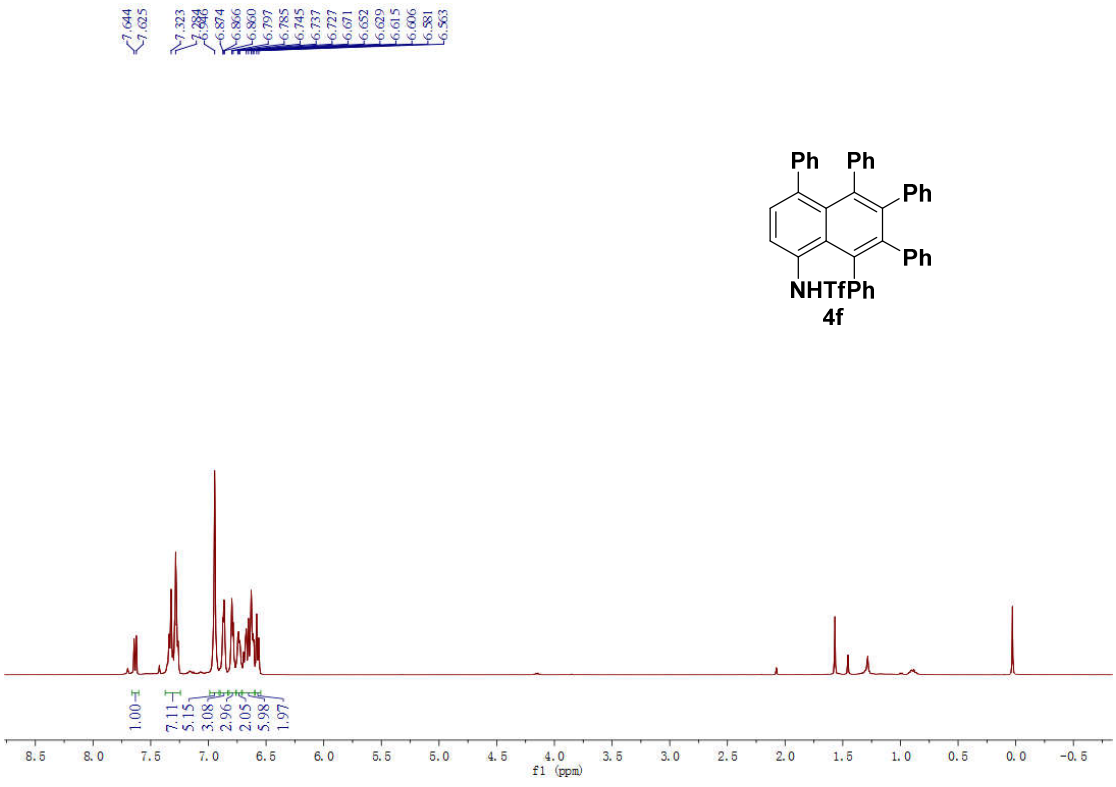
4e



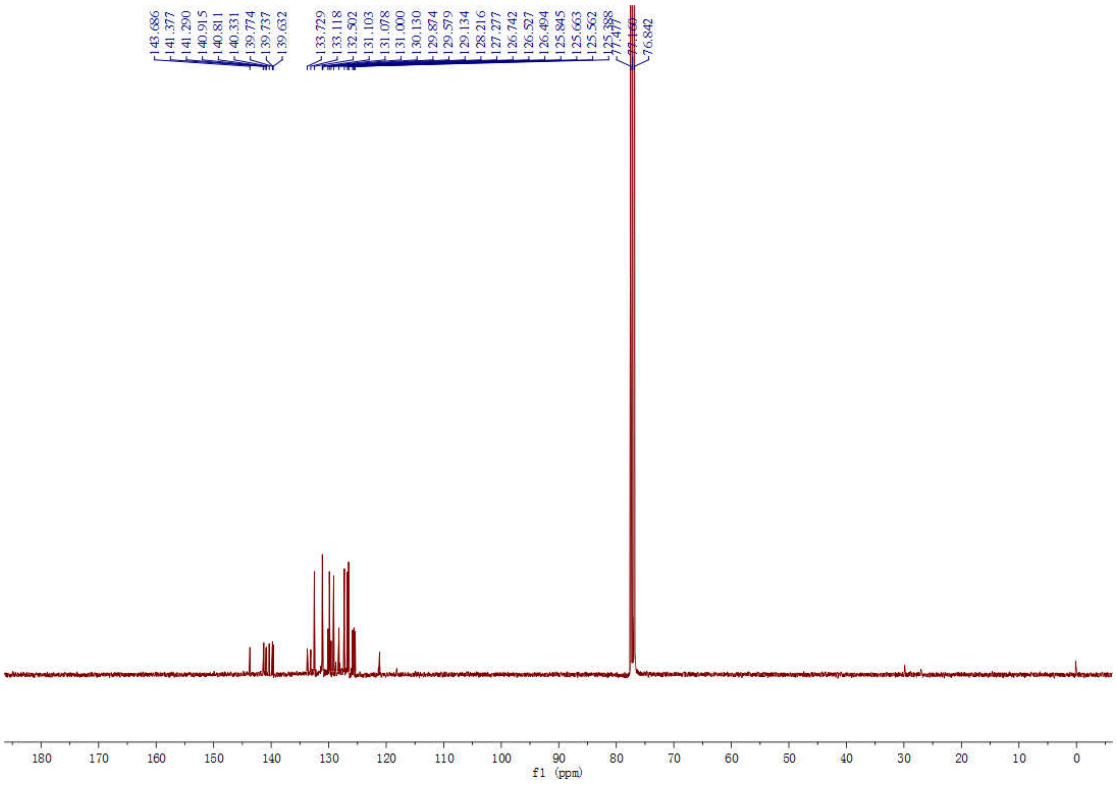
^{1}H NMR Spectrum for **4e** ($CDCl_3$, 400 MHz)



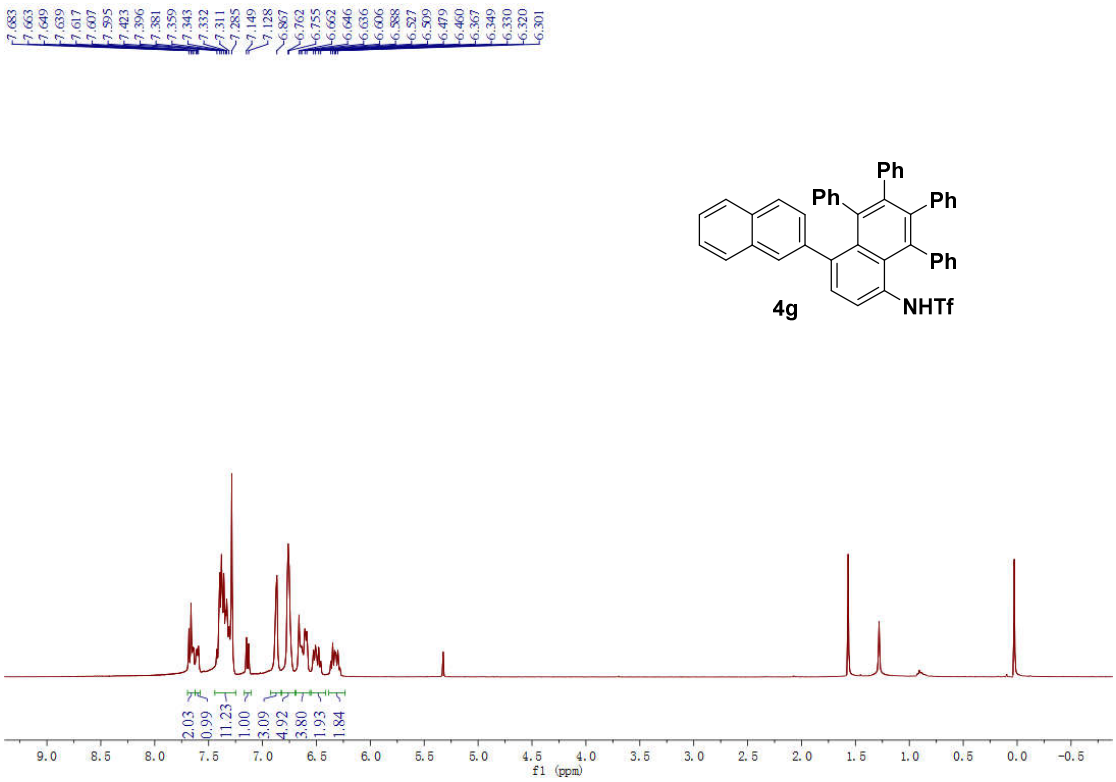
^{13}C NMR Spectrum for **4e** ($CDCl_3$, 100 MHz)



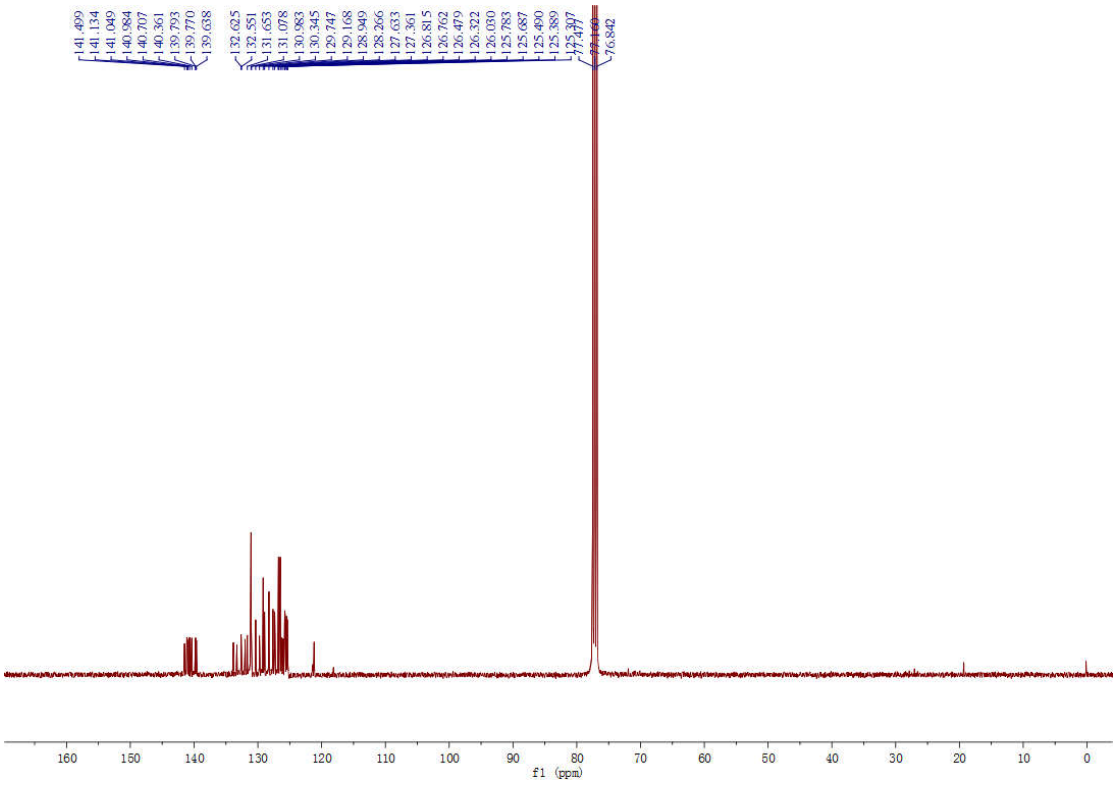
^{1}H NMR Spectrum for **4f** ($CDCl_3$, 400 MHz)



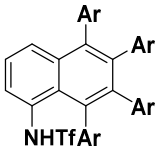
^{13}C NMR Spectrum for **4f** ($CDCl_3$, 100 MHz)



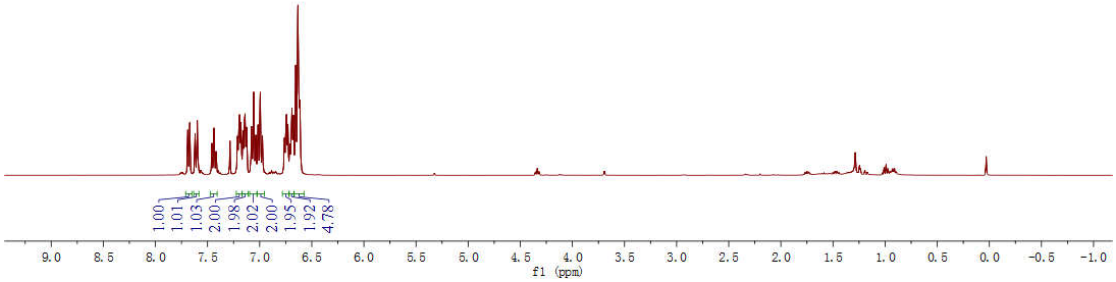
^{1}H NMR Spectrum for **4g** ($CDCl_3$, 400 MHz)



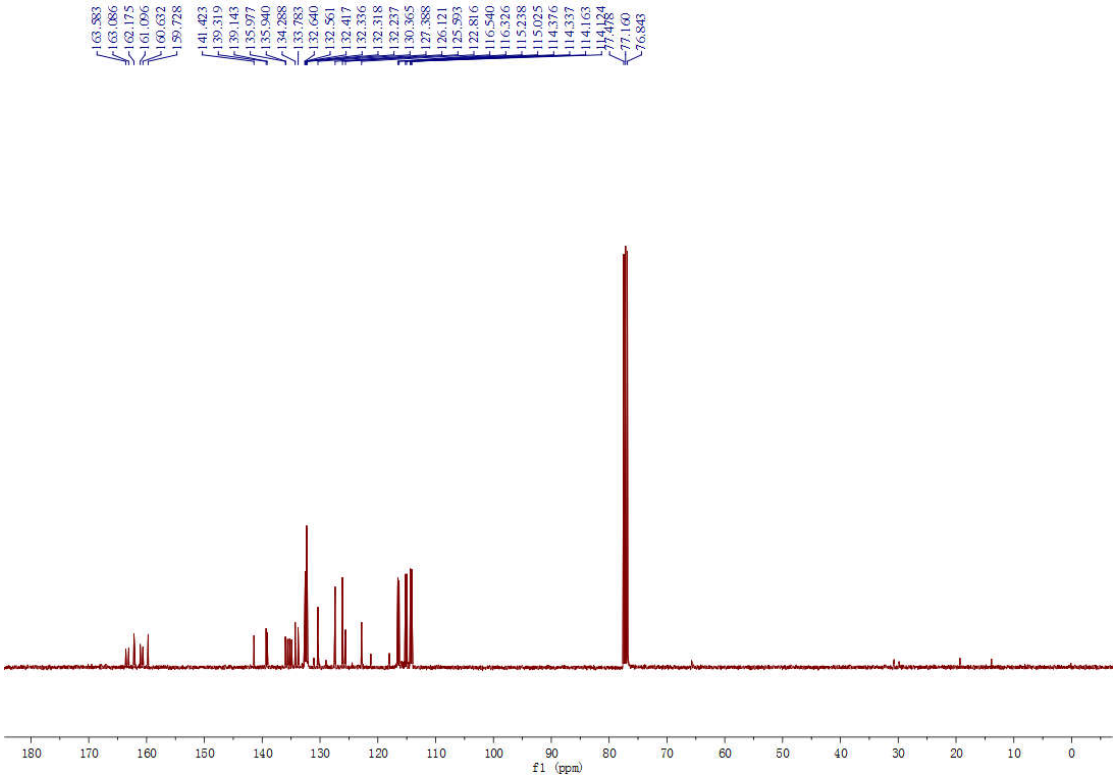
^{13}C NMR Spectrum for **4g** ($CDCl_3$, 100 MHz)



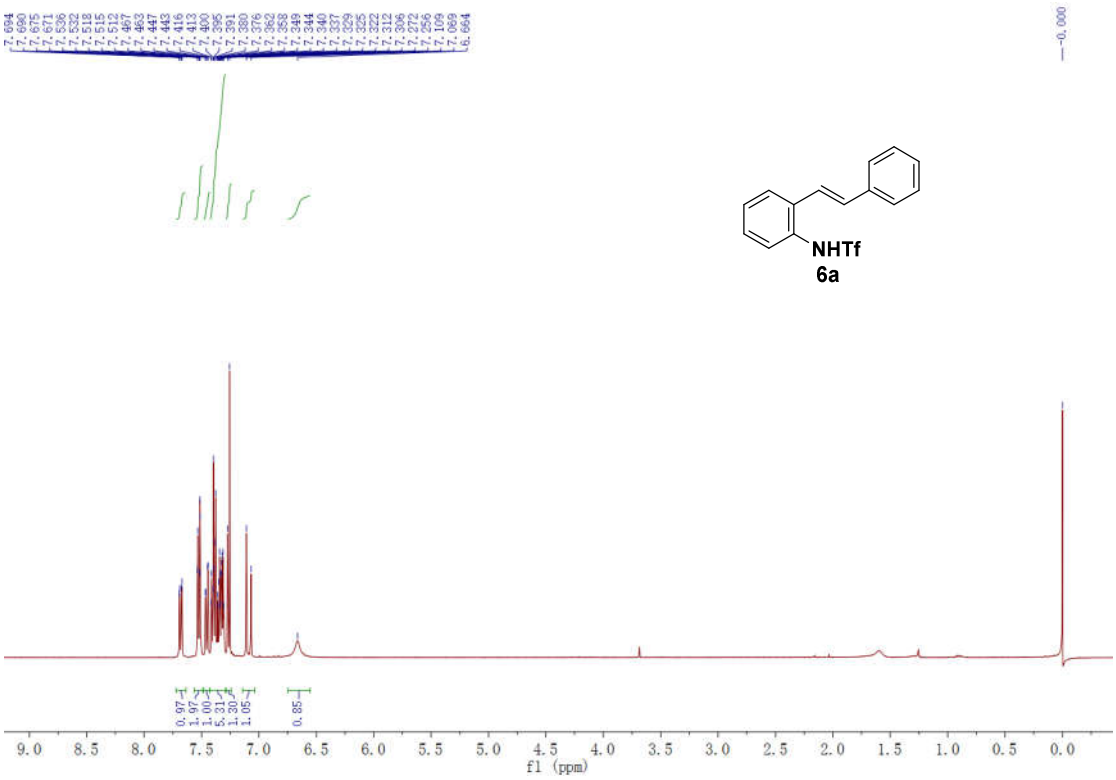
4h
Ar = 4-F-Ph



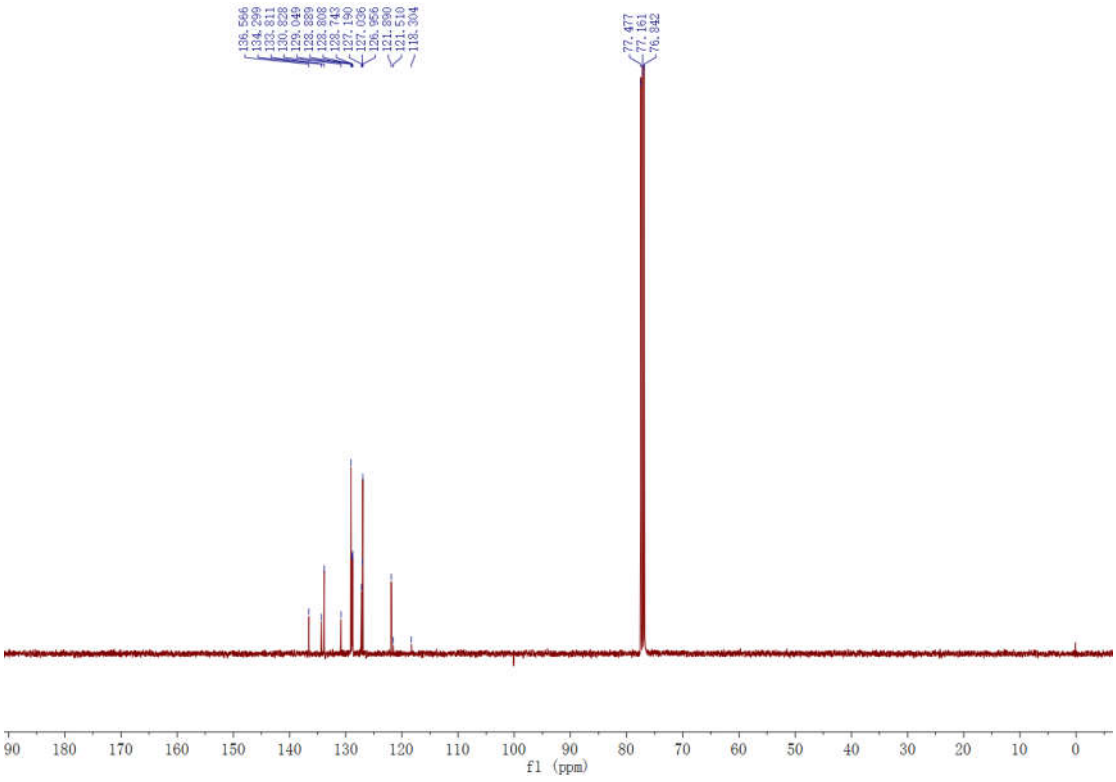
^{1}H NMR Spectrum for **4h** ($CDCl_3$, 400 MHz)



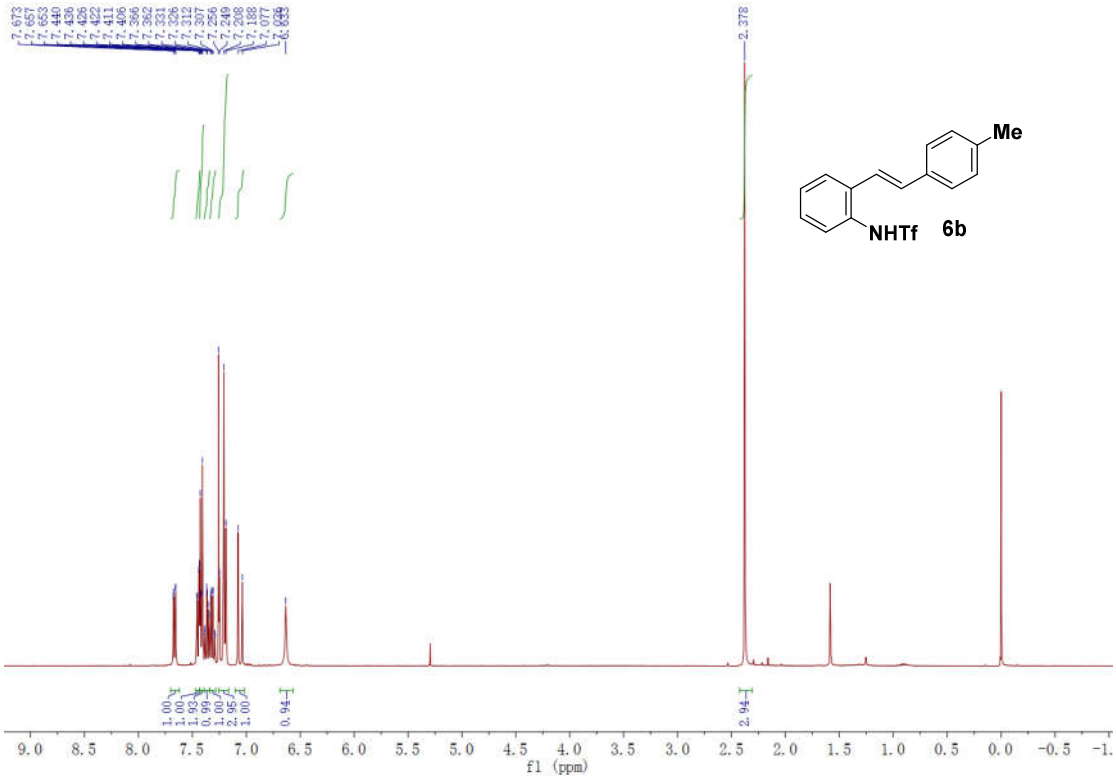
^{13}C NMR Spectrum for **4h** ($CDCl_3$, 100 MHz)



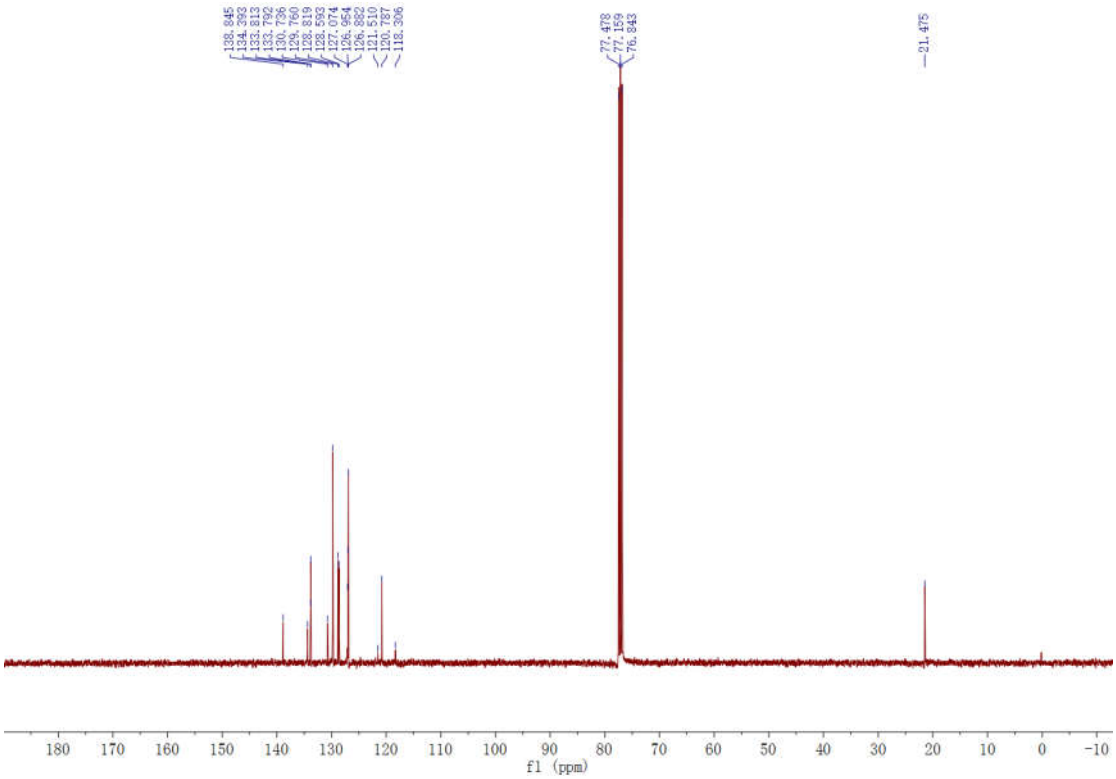
^{1}H NMR Spectrum for **6a** ($CDCl_3$, 400 MHz)



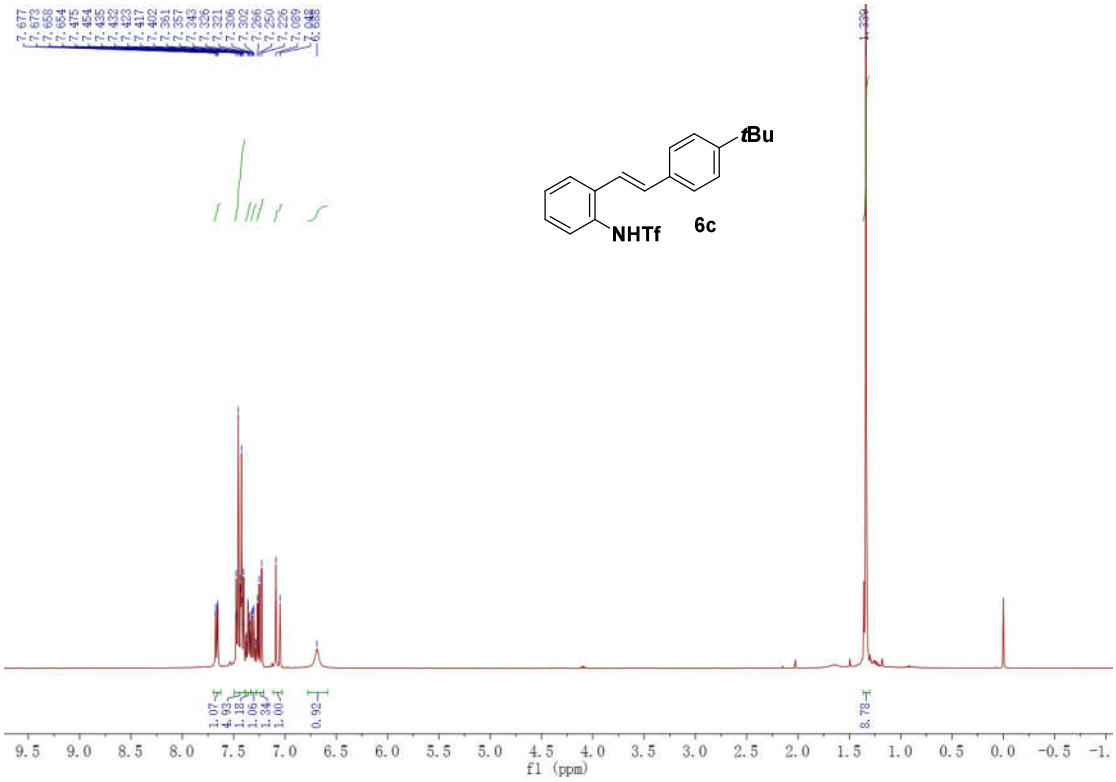
^{13}C NMR Spectrum for **6a** ($CDCl_3$, 100 MHz)



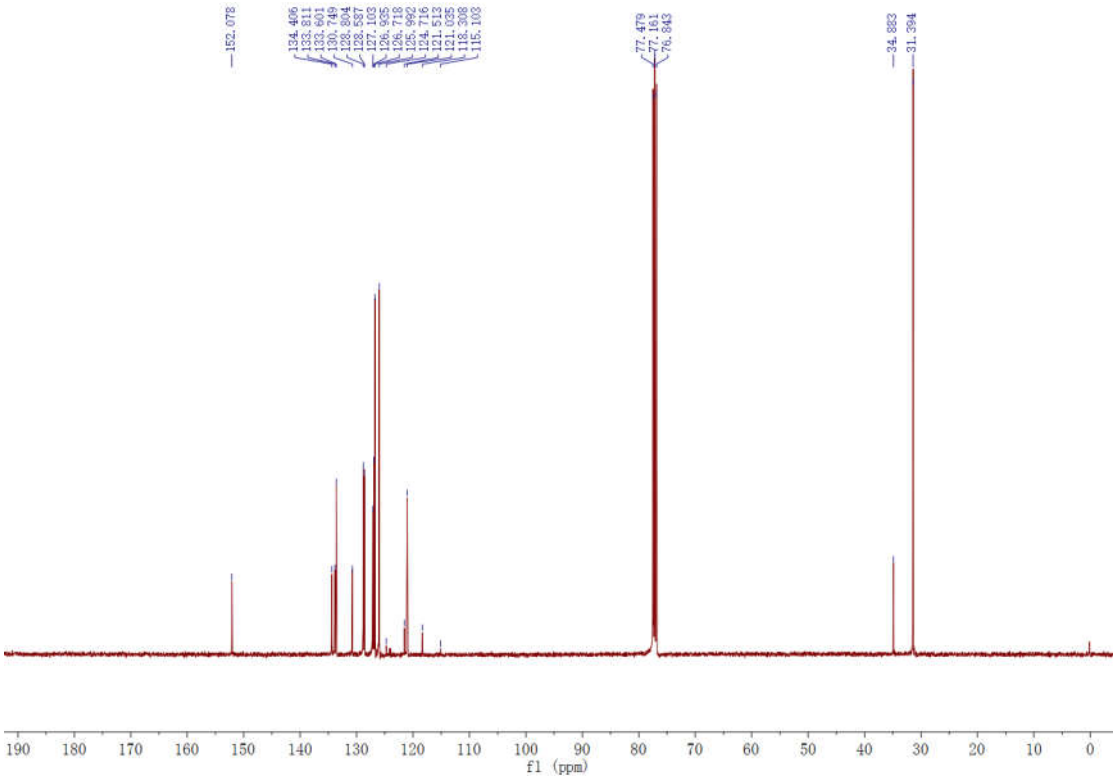
^{1}H NMR Spectrum for **6b** ($CDCl_3$, 400 MHz)



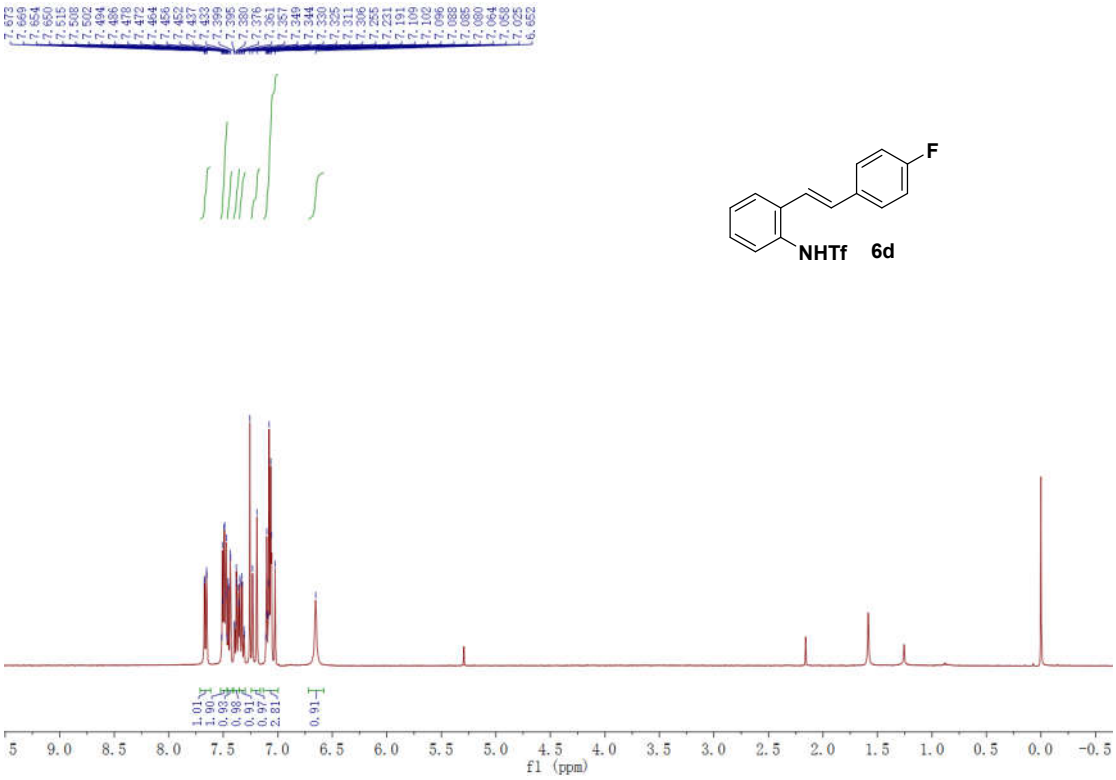
^{13}C NMR Spectrum for **6b** ($CDCl_3$, 100 MHz)



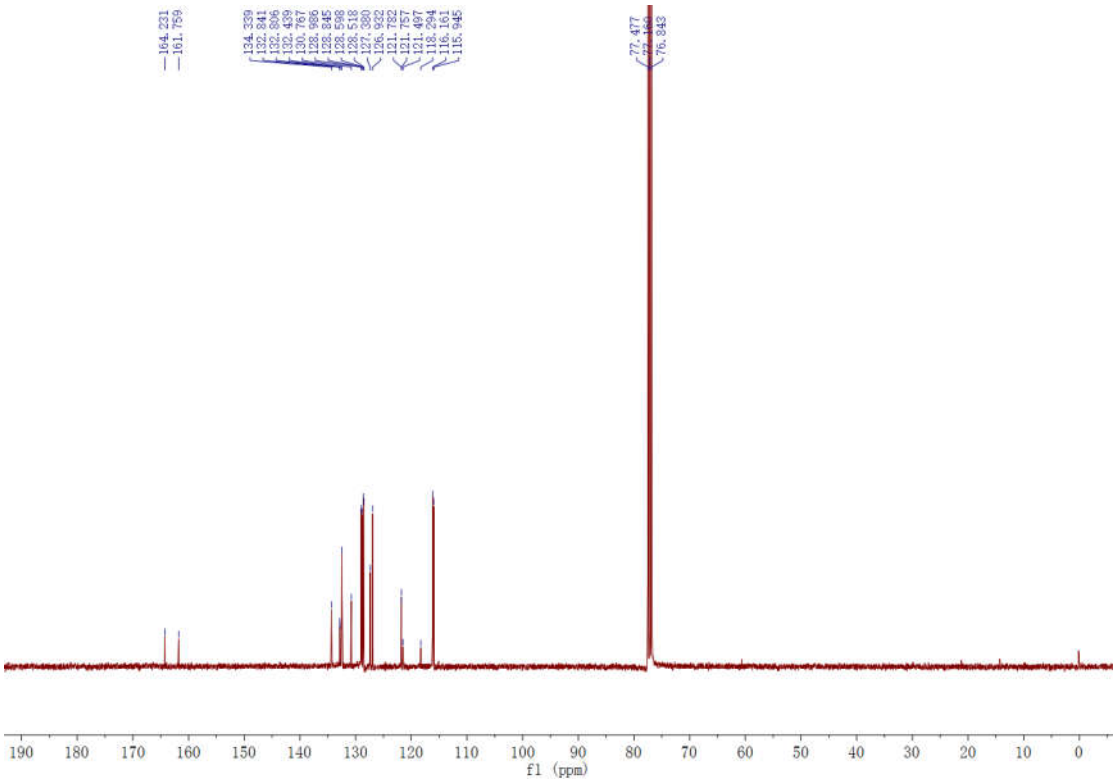
^{1}H NMR Spectrum for **6c** ($CDCl_3$, 400 MHz)



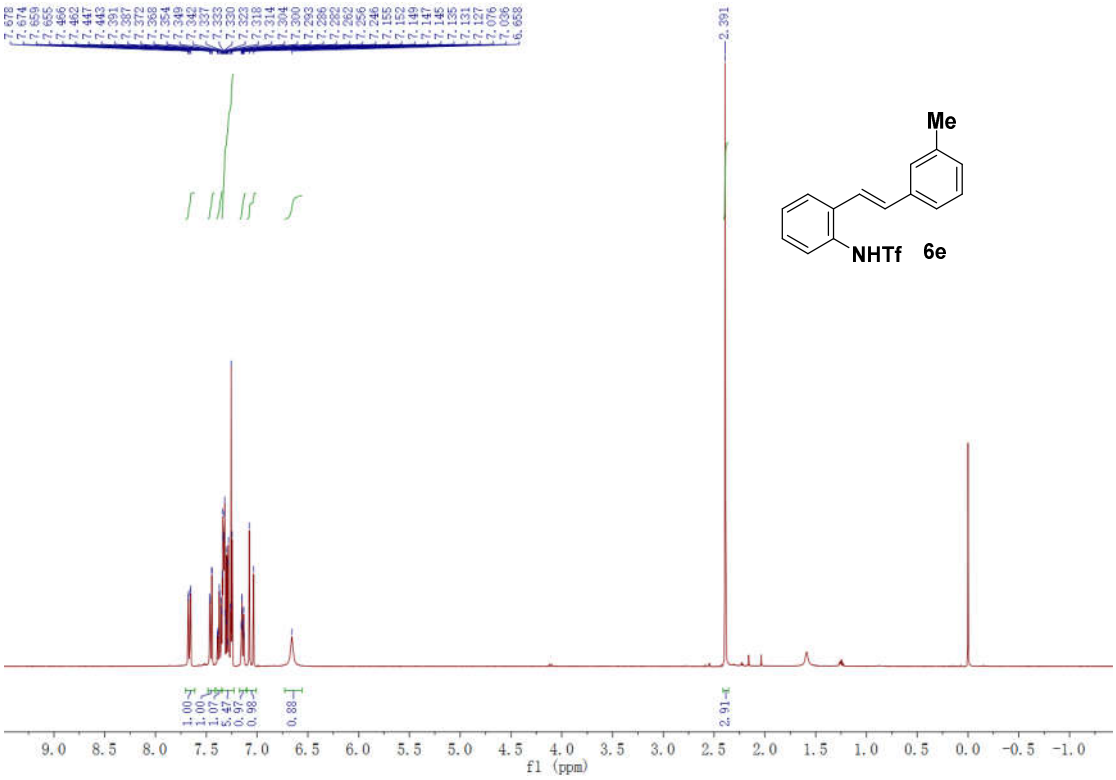
^{13}C NMR Spectrum for **6c** ($CDCl_3$, 100 MHz)



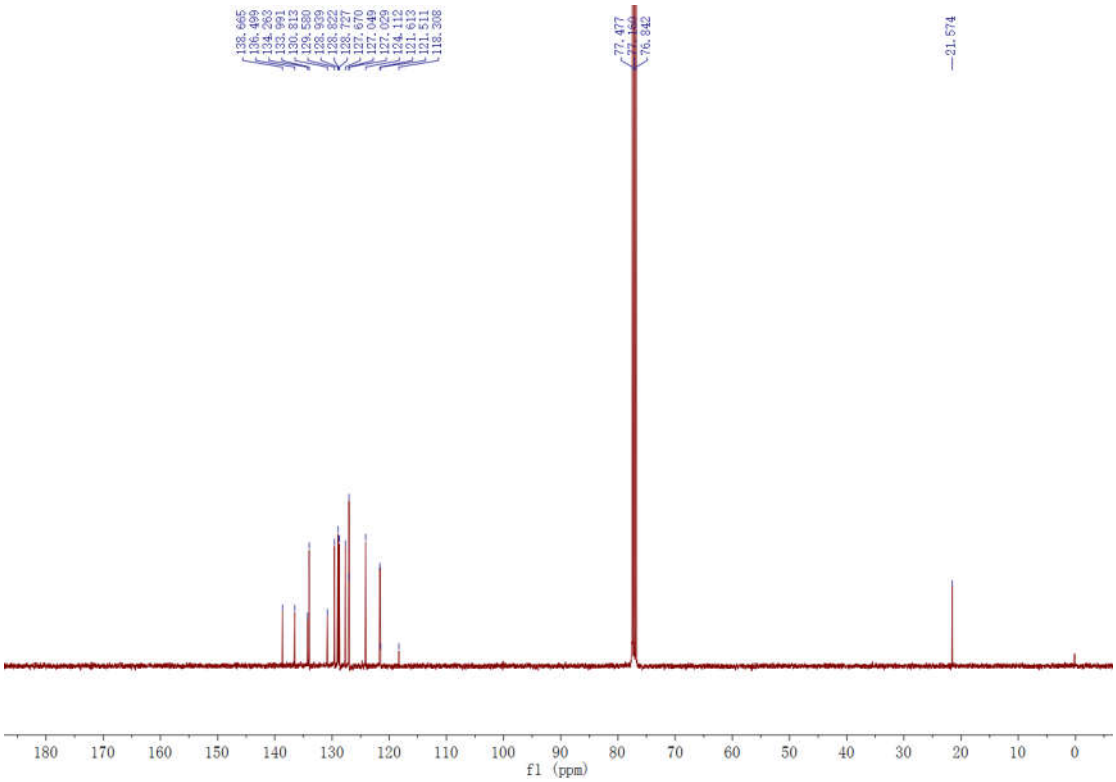
^{1}H NMR Spectrum for **6d** ($CDCl_3$, 400 MHz)



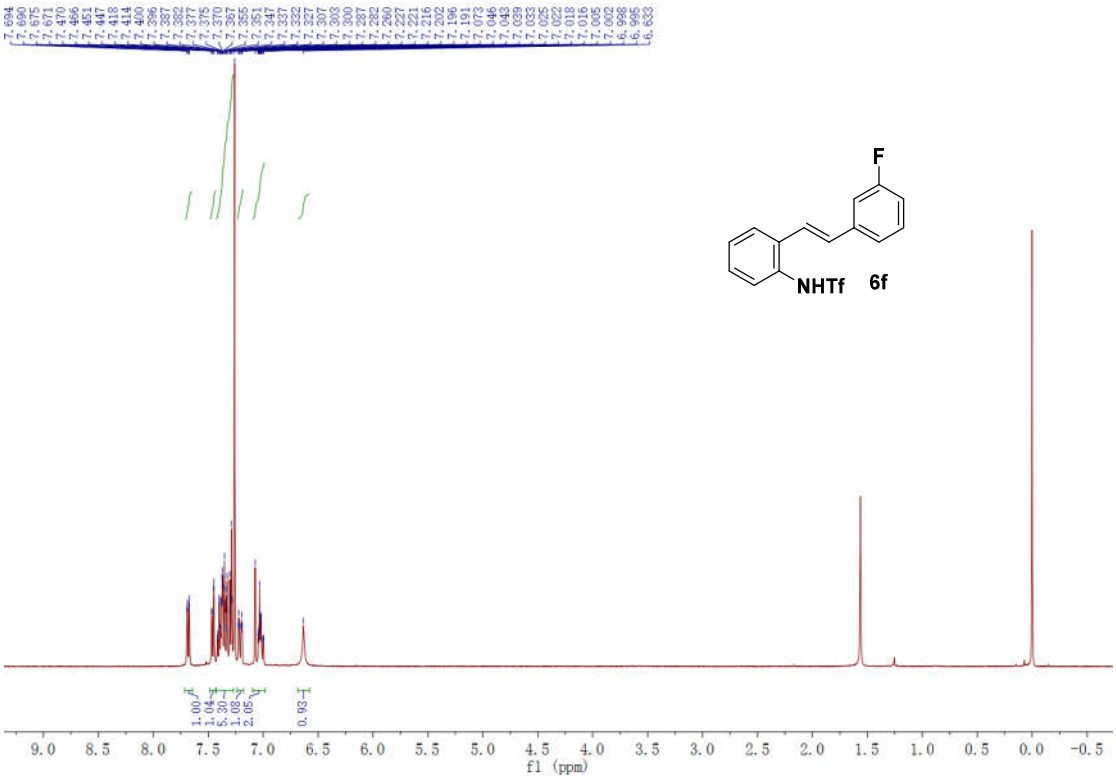
^{13}C NMR Spectrum for **6d** ($CDCl_3$, 100 MHz)



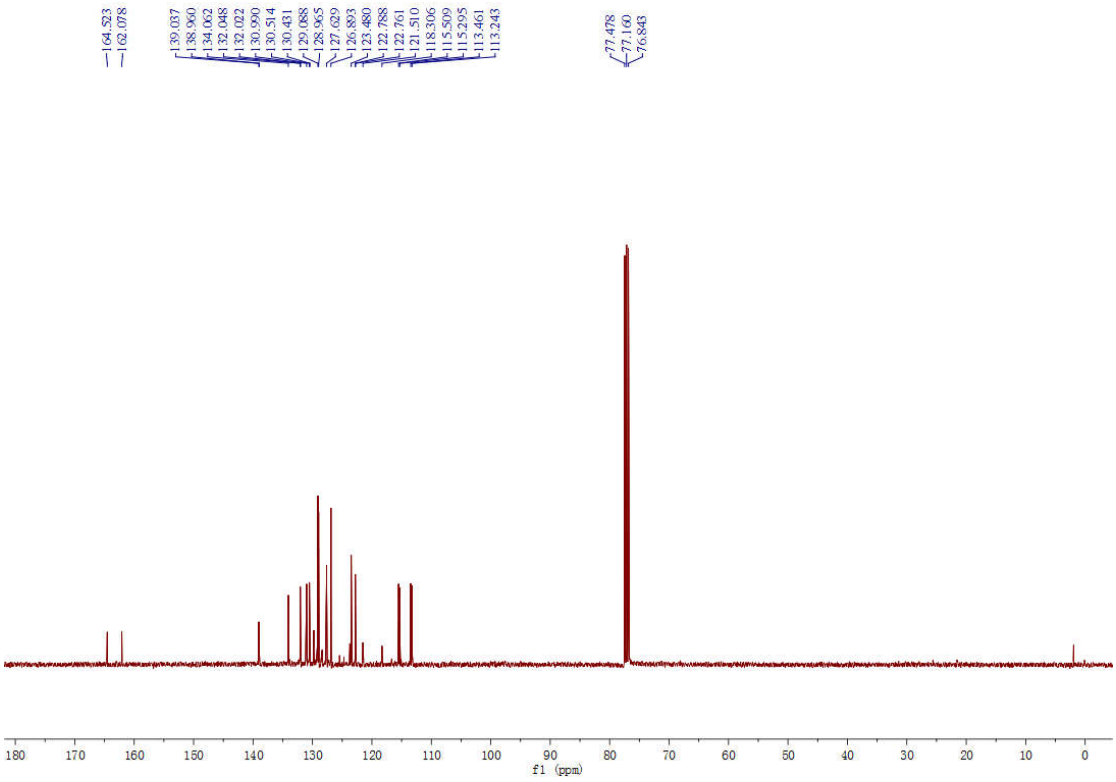
^{1}H NMR Spectrum for **6e** ($CDCl_3$, 400 MHz)



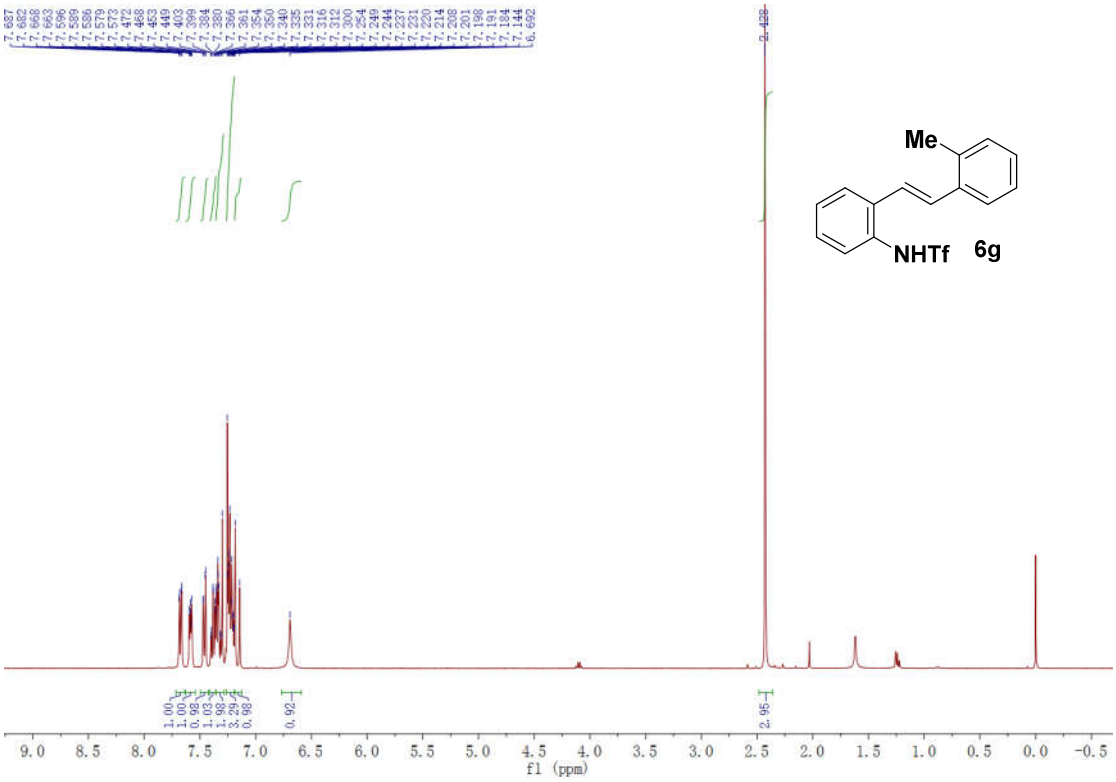
^{13}C NMR Spectrum for **6e** ($CDCl_3$, 100 MHz)



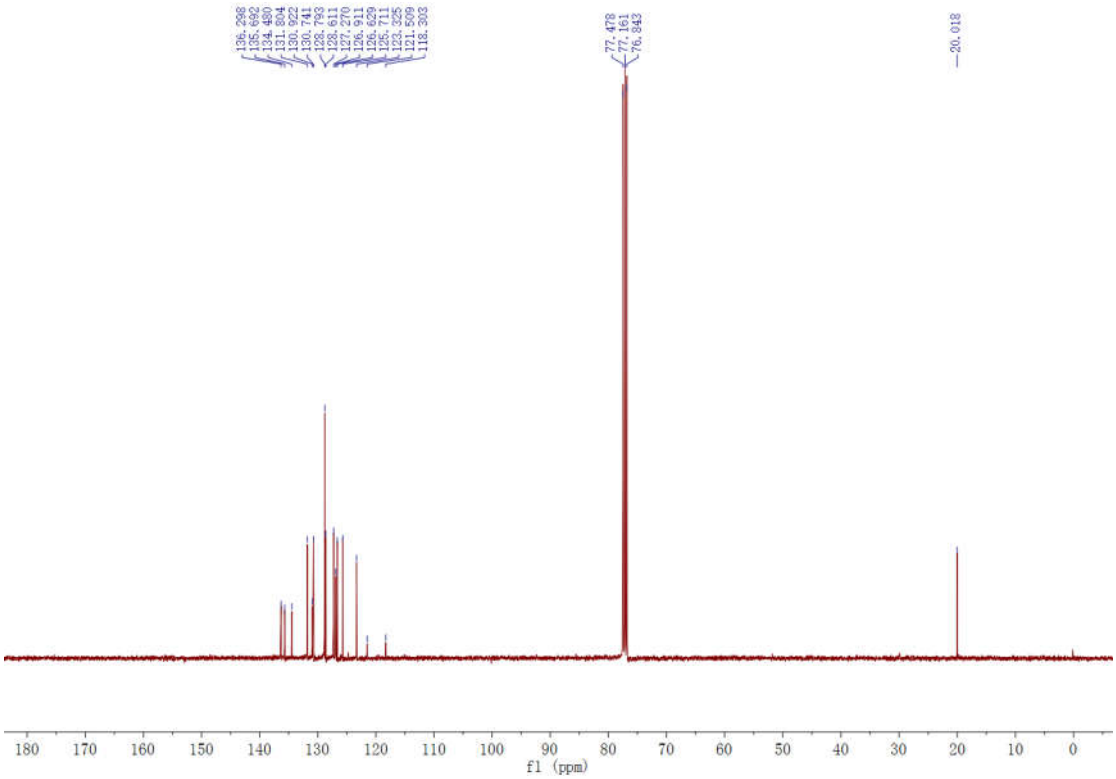
^{1}H NMR Spectrum for **6f** ($CDCl_3$, 400 MHz)



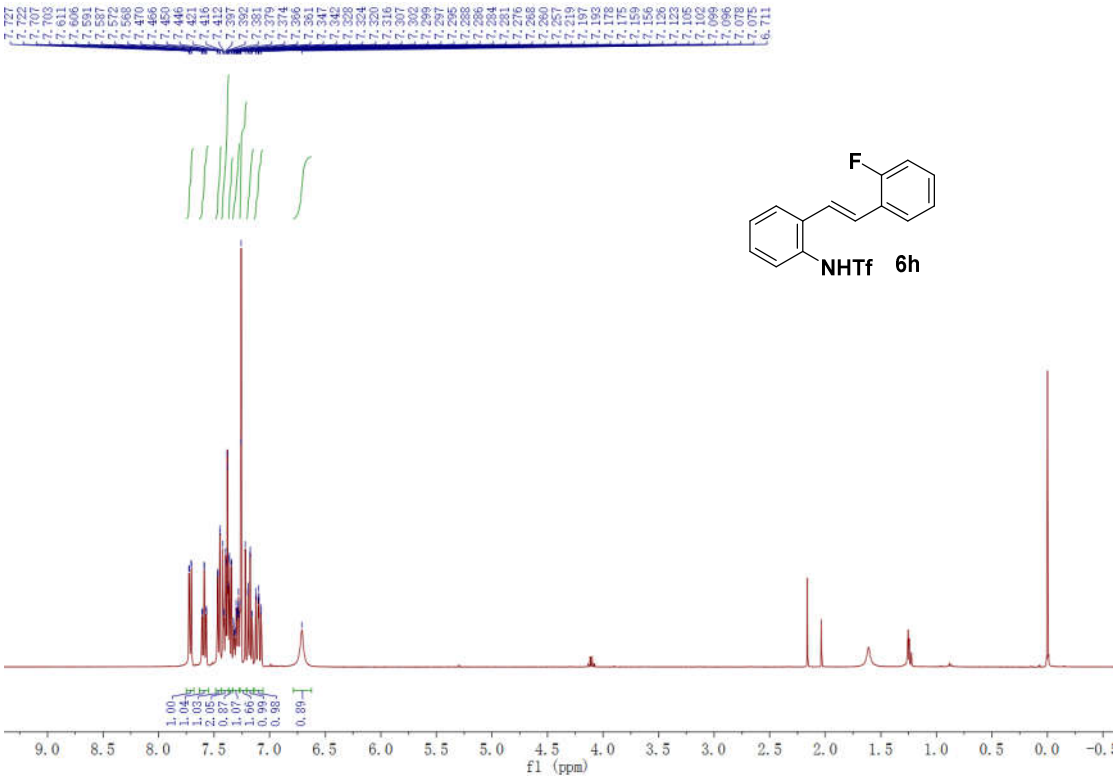
^{13}C NMR Spectrum for **6f** ($CDCl_3$, 100 MHz)



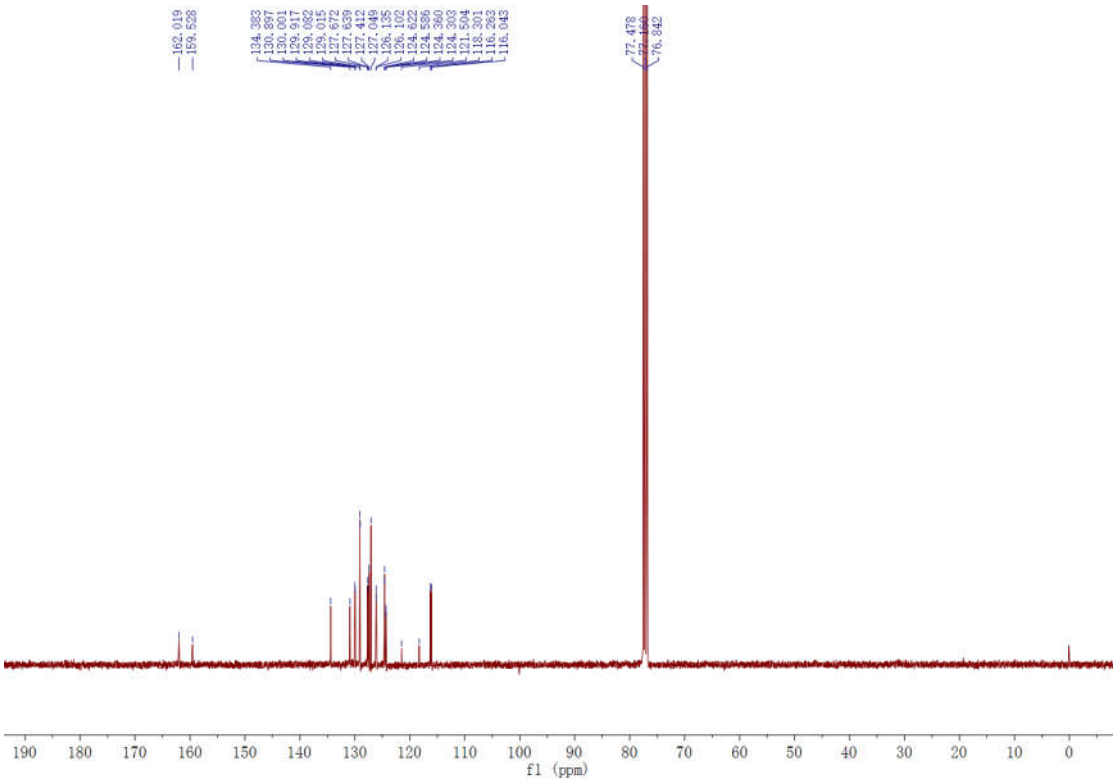
^{1}H NMR Spectrum for **6g** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum for **6g** ($CDCl_3$, 100 MHz)

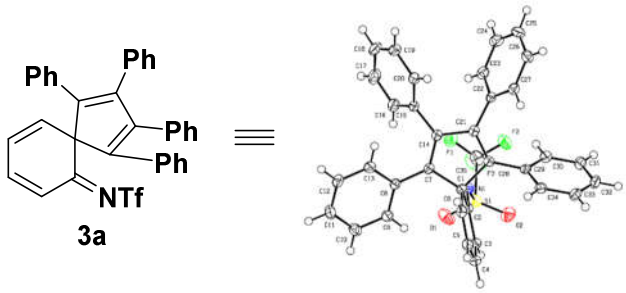


^{1}H NMR Spectrum for **6h** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum for **6h** ($CDCl_3$, 100 MHz)

9. X-ray Crystallographic Structure and Data



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

Compound	**3a**
formula	$C_{35}H_{24}F_3NO_2S$
FW	579.61
crystal system	monoclinic
space group	*P 1 21/n 1*
a/Å	9.1091 (2)
b/Å	14.3255 (3)
c/Å	22.0866 (5)
α/deg	90
β/deg	101.388 (2)
γ/deg	90
V/Å^3	2825.39 (11)
Z	4
D_c/g cm^{-3}	1.363
μ/mm^{-1}	1.473
R_1[a] ($I > 2\sigma$)	0.0349 (5034)
wR_2[b] (all data)	0.0910 (5423)
GOF	1.038