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Supporting Information

Palladium Catalysed [3+2]-Annulation Reaction of Vinylcyclopropanes with Pentafulvenes: Synthesis of Polysubstituted Spiro[4,4]nona-6,8-dienes

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1. General Information 2

2. Procedure for the palladium catalysed [2+3]-annulation reaction 3

3. Procedure for the Diels-Alder reactions of annulation products 3

4. Procedure for the RCM reaction of annulation product **3ao** 4

5. Procedure for the synthesis of thiobarbital **8** 4

6. Characterization data of compounds 5

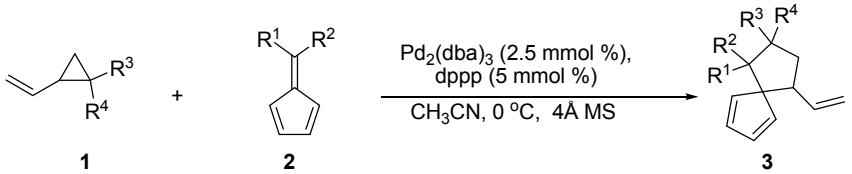
7. Crystallographic information of compounds *anti-endo*-**5** and *syn-endo*-**6** 17

8. Copies of ^{1}H NMR and ^{13}C NMR spectrogram 19

1. General Information

Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on silica gel plates with F-254 indicator and compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^{1}H NMR, ^{13}C NMR spectra were recorded on 400 MHz or 100 MHz spectrometers. The spectra were recorded in $CDCl_3$ as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to either the residual solvent peak or TMS as an internal standard. Data for ^{1}H NMR were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = double, t = triplet, m = multiplet, dd = double doublet, br = broad), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR were reported as chemical shift. HRMS were performed on Bruker Apex II mass instrument (ESI).

2. Procedure for the palladium catalysed [2+3]-annulation reaction

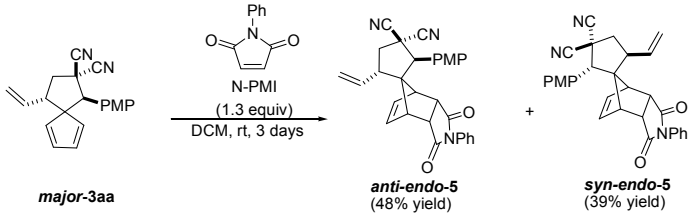


1a, R^3 = CN; R^4 = CN; **1b**, R^3 = CO_2Me; R^4 = CN;
1c, R^3 = $CO_2{}^iPr$, R^4 = CN; **1d**, R^3 = $CO_2{}^tBu$, R^4 = CN;

Under an atmosphere of dry nitrogen, tris(dibenzylideneacetone)dipalladium (Pd_2dba_3) (4.6 mg, 0.005 mmol), 1,3-bis (diphenylphosphino) propane (4.1 mg, 0.01 mmol), 4 Å MS (100 mg), and 0.5 mL of anhydrous CH_3CN were added into an oven-dried reaction tube equipped with a stir bar, and the solution was stirred at 30 °C for half an hour. When the solution changed to green, the reaction tube was cooled to 0 °C. Next, a solution of vinylcyclopropane **1** (0.4 mmol) and pentafulvene **2** (0.2 mmol) in anhydrous CH_3CN (1.5 mL) was transferred into the reaction tube via syringe, and mixture was stirred at 0°C until the material exhausted completely. Filtration of the reaction mixture through silica gel and removal of the solvent in vacuo offered the crude mixture of products. Isolation of this mixture by silica gel chromatography offered the title products. The dr value was determined by ^{1}H NMR spectrum of the diastereomeric mixture of products

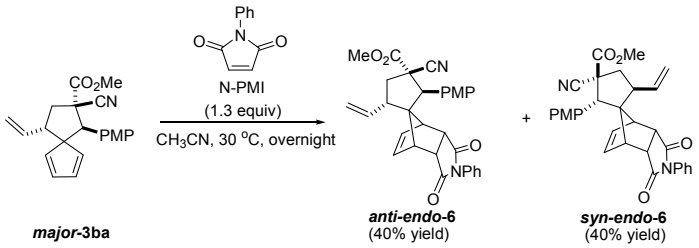
For the reaction of vinylcyclopropane **1e** with pentafulvene **2a**, the solvent was changed into dimethyl sulfoxide and the temperature was increased to 30 °C.

3. Procedure for the Diels-Alder reactions of annulation products



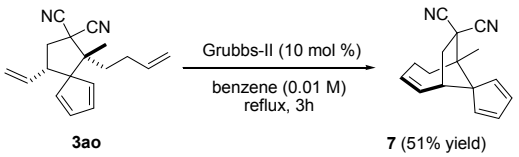
In a 5 mL reaction tube equipped with a stir bar was charged with the compound ***major*-3aa** (60.4

mg, 0.20 mmol) and the N-phenyl maleimide (45.0 mg, 0.26 mmol) in DCM (0.2 M). Then the solution was stirred at ambient temperature for 3 days. After completion of the reaction as detected by TLC, the mixture was concentrated under reduced pressure, the product ***anti-endo*-5** was isolated in 48% yield (45.9 mg, 0.10 mmol) and the product ***syn-endo-5*** was isolated in 39% yield (36.8 mg, 0.08 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:5 / V:V).



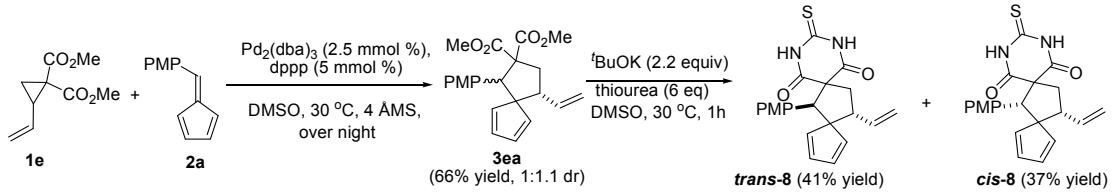
In a 5 mL reaction tube equipped with a stir bar was charged with the compound ***major*-3ba** (67.2 mg, 0.20 mmol) and the N-phenyl maleimide (45.0 mg, 0.26 mmol) in DCM (0.2 M). Then the solution was stirred at 30 °C for overnight. After completion of the reaction as detected by TLC, the mixture was concentrated under reduced pressure, the product ***anti-endo-6*** was isolated in 40% yield (40.8 mg, 0.08 mmol) and the product ***syn-endo-6*** was isolated in 40% yield (39.5 mg, 0.08 mmol) by silica gel chromatography(EtOAc:petroleum ether:DCM = 1:10:4/V:V:V).

4. Procedure for the RCM reaction of annulation product 3ao



In a 5 mL reaction tube equipped with a stir bar, Grubbs-II catalyst (8.5 mg, 0.01 mmol) was added to a stirred solution of **3ao** (26.5 mg, 0.1 mmol) in anhydrous benzene (1 mL) under argon. The mixture was refluxed for 3h with stirring. After completion of the reaction as detected by TLC, distilled water was added, and the mixture was extracted with EtOAc (10×3 mL). The combined organic phase was washed with brine, dried over Na_2SO_4. After filtration, the solvent was removed by rotary evaporator, and the product **7** was isolated as a colorless oil in 51% yield (13.5 mg, 0.05 mmol) by silica gel chromatography (EtOAc:petroleum ether =1:15/ V:V).

5. Procedure for the synthesis of thiobarbital 8

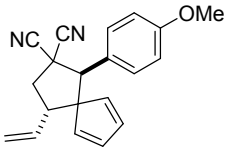


The compound **3ea** was prepared according to general procedure with vinylcyclopropane **1e** (94.4 mg, 0.8 mmol) and pentafulvene **2a** (72.2 mg, 0.4 mmol) in DMSO (0.1 M) at 30°C for 10h. After completion of the reaction as detected by TLC, the product mixture was isolated in 66% yield (99.2 mg, 0.26 mmol) with 1:1.1 dr as a colorless oil by silica gel chromatography (EtOAc: petroleum ether =1:35 /V:V).

Thiourea (91.3 mg, 1.2 mmol) and *t*-BuOK (49.4 mg, 0.44 mmol) were added into the solution of **3ea** (73.7 mg, 0.2 mmol) in 0.4 mL DMSO, and the reaction mixture was stirred at 30 °C for 1 hour. Then the reaction mixture was diluted with 10 mL of hydrochloric acid (0.1 N) and extracted with EtOAc (10×3 mL). The combined organic phase was washed with water and brine successively, and dried over Na_2SO_4. After removal of the solvent in vacuo, the products ***trans*-8** and ***cis*-8** was isolated respectively in 41% and 37% yields by silica gel chromatography (EtOAc:petroleum ether = 1:5/V:V).

6. Characterization data of compounds

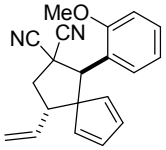
1-(4-Methoxyphenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3aa)



The products *trans*-**3aa** and *cis*-**3aa** were obtained in 98% total yield (59.2 mg, 0.19 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product *trans*-**3aa** is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 4.8 Hz, 1H), 6.30 (d, *J* = 5.2 Hz, 1H), 6.25–6.20 (m, 2H), 5.82–5.74 (m, 1H), 5.13–5.06 (m, 2H), 4.06 (s, 1H), 3.76 (s, 3H), 3.24 (dd, *J* = 14.8, 7.2 Hz, 1H), 3.03 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.73 (dd, *J* = 14.0, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 139.2, 138.2, 136.4, 132.5, 132.4, 130.0, 124.6, 116.5,

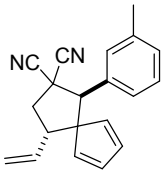
116.3, 116.0, 113.7, 67.9, 59.2, 55.2, 46.6, 43.0, 40.2. HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}N_2O$ $[M+H]^+$ 303.1492, found: 303.1484.

1-(2-Methoxyphenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ab)



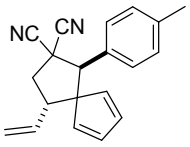
The products *trans*-**3ab** and *cis*-**3ab** were obtained in 90% total yield (54.4 mg, 0.18 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product *trans*-**3ab** is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.30–7.26 (m, 1H), 6.89–6.86 (m, 2H), 6.64 (td, *J* = 3.2, 1.6 Hz, 1H), 6.33–6.31 (m, 1H), 6.27–6.23 (m, 2H), 5.82 (ddd, *J* = 17.2, 10.4, 7.6 Hz, 1H), 5.12–5.07 (m, 2H), 4.89 (s, 1H), 3.84 (s, 3H), 3.25 (dd, *J* = 14.8, 7.2 Hz, 1H), 3.07 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.78 (dd, *J* = 14.0, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 139.3, 138.4, 136.5, 132.3, 131.9, 130.0, 129.0, 121.9, 120.2, 116.7, 116.6, 116.3, 110.8, 68.3, 55.6, 50.2, 47.4, 44.2, 39.4. HRMS (ESI) m/z calcd. for $C_{20}H_{19}N_2O$ $[M+H]^+$ 303.1492, found 303.1499.

1-(3-Methoxyphenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ac)



The products *trans*-**3ac** and *cis*-**3ac** were obtained in 85% total yield (51.4 mg, 0.17 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product *trans*-**3ac** is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (t, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.91–6.88 (m, 1H), 6.87–6.85 (m, 1H), 6.62–6.60 (m, 1H), 6.33–6.31 (m, 1H), 6.30–6.28 (m, 1H), 6.26–6.24 (m, 1H), 5.82–5.73 (m, 1H), 5.14–5.07 (m, 2H), 4.06 (s, 1H), 3.77 (s, 3H), 3.27 (dd, *J* = 14.8, 7.6 Hz, 1H), 3.05 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.76 (dd, *J* = 14.0, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 139.3, 138.2, 136.2, 134.3, 132.6, 132.4, 129.4, 121.0, 116.6, 116.3, 116.0, 114.4, 114.3, 67.9, 59.5, 55.3, 46.8, 43.4, 39.8. HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}N_2O$ $[M+H]^+$ 303.1492, found 303.1499.

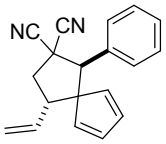
1-(P-tolyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ad)



The products *trans*-**3ad** and *cis*-**3ad** were obtained in 97% total yield (57.2 mg, 0.194 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product *trans*-**3ad** is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 6.8 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.62–6.02 (m, 1H), 6.31–6.29 (m,

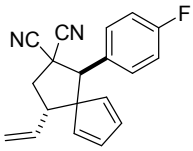
1H), 6.27–6.21 (m, 2H), 5.81–5.73 (m, 1H), 5.13–5.07 (m, 2H), 4.05 (s, 1H), 3.27 (dd, J = 14.8, 7.2 Hz, 1H), 3.04 (dd, J = 14.0, 7.6 Hz, 1H), 2.74 (dd, J = 14.0, 7.6 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3, 138.9, 138.2, 136.3, 132.5, 132.4, 129.8, 129.1, 128.6, 116.6, 116.3, 116.0, 67.9, 59.5, 46.8, 43.3, 40.1, 21.2. HRMS (ESI) m/z calcd. for $C_{20}H_{19}N_2$ $[M+H]^+$ 287.1543, found 287.1540.

1-Phenyl-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ae)



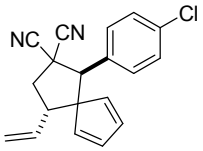
The products *trans*-**3ae** and *cis*-**3ae** were obtained in 90% total yield (48.0 mg, 0.18 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product *trans*-**3ae** is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.29 (m, 5H), 6.61 (d, J = 5.2 Hz, 1H), 6.30 (d, J = 5.2 Hz, 1H), 6.23–6.26 (m, 2H), 5.77 (ddd, J = 17.6, 10.4, 7.6 Hz, 1H), 5.12 (d, J = 8.0 Hz, 1H), 5.09 (d, J = 14.4 Hz, 1H), 4.08 (s, 1H), 3.28 (dd, J = 14.8, 7.6 Hz, 1H), 3.06 (dd, J = 14.0, 7.6 Hz, 1H), 2.76 (dd, J = 14.0, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2, 138.1, 136.2, 132.8, 132.6, 132.5, 131.0, 129.1, 128.7, 128.4, 116.6, 116.2, 116.0, 67.8, 59.7, 46.8, 43.4, 39.9, 19.3. HRMS (ESI) m/z calcd. for $C_{19}H_{16}N_2Na$ $[M+Na]^+$ 295.1206, found 295.1208.

1-(4-Fluorophenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3af)



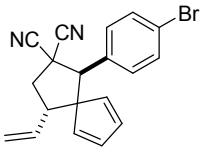
The products *trans*-**3af** and *cis*-**3af** were obtained in 96% total yield (55.7 mg, 0.192 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product *trans*-**3af** is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.35 (m, 2H), 6.98 (t, J = 8.4 Hz, 2H), 6.64 (d, J =5.2 Hz, 1H), 6.32 (d, J = 5.2 Hz, 1H), 6.26 (d, J = 5.2 Hz, 1H), 6.20 (d, J = 5.2 Hz, 1H), 5.79 (ddd, J = 17.6, 10.4, 7.2 Hz, 1H), 5.16–5.09 (m, 2H), 4.08 (s, 1H), 3.24 (dd, J =14.4, 7.2 Hz, 1H), 3.05 (dd, J = 14.0, 7.2 Hz, 1H), 2.76 (dd, J = 14.0, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3 (d, J = 247.0 Hz, 1C), 161.8, 138.9, 138.0, 136.3, 132.8, 130.5 (d, J = 8.2 Hz, 1C), 128.4 (d, J = 3.0 Hz, 1C), 116.7, 116.0, 115.8, 115.4 (d, J = 21.0 Hz, 1C), 67.8, 58.9, 46.6, 43.0, 39.9. HRMS (ESI) m/z calcd. for $C_{19}H_{16}FN_2$ $[M+H]^+$ 291.1292, found 291.1292.

1-(4-Chlorophenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ag)



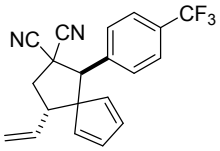
The products *trans*-**3ag** and *cis*-**3ag** were obtained in 95% total yield (58.2 mg, 0.19 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product *trans*-**3ag** is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 5.2 Hz, 1H), 6.32 (d, *J* = 5.2 Hz, 1H), 6.26 (d, *J* = 5.2 Hz, 1H), 6.20 (d, *J* = 5.2 Hz, 1H), 5.78 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.15–5.08 (m, 2H), 4.06 (s, 1H), 3.24 (dd, *J* =14.2, 7.2 Hz, 1H), 3.05 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.75 (dd, *J* = 14.0, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 138.0, 136.2, 135.0, 132.8, 132.7, 131.0, 130.0, 128.6, 116.7, 116.0, 115.8, 67.7, 58.9, 46.6, 43.0, 39.7. HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{16}ClN_2$ $[M+H]^+$ 307.0997, found 307.0997.

1-(4-Bromophenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ah)



The products *trans*-**3ah** and *cis*-**3ah** were obtained in 91% total yield (63.7 mg, 0.18 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product *trans*-**3ah** is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 5.2 Hz, 1H), 6.32 (d, *J* =5.2 Hz, 1H), 6.26 (d, *J* = 5.2 Hz, 1H), 6.20 (d, *J* = 5.2 Hz, 1H), 5.78 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.15–5.08 (m, 2H), 4.05 (s, 1H), 3.24 (dd, *J* =14.4, 7.2 Hz, 1H), 3.05 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.76 (dd, *J* = 14.0, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 138.0, 136.2, 132.8, 131.6, 131.5, 130.3, 123.3, 116.8, 115.9, 115.8, 67.6, 59.0, 46.6, 43.1, 39.6. HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{16}BrN_2$ $[M+H]^+$ 351.0491, found 351.0493.

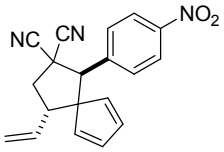
1-(4-(Trifluoromethyl)phenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ai)



The products *trans*-**3ai** and *cis*-**3ai** were obtained in 76% total yield (51.7 mg, 0.15 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product *trans*-**3ai** is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 5.2 Hz, 1H), 6.33 (d, *J* = 5.2 Hz, 1H), 6.28 (d, *J* = 5.2 Hz, 1H), 6.22 (d, *J* = 5.2 Hz, 1H), 5.80 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.17–5.10 (m, 2H), 4.14 (s, 1H), 3.28 (dd, *J* = 14.8, 7.2 Hz, 1H), 3.08 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.78 (dd, *J* = 14.0, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 137.9, 136.6,

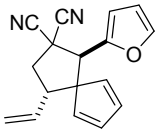
136.1, 133.0, 129.1, 125.5, 125.4, 122.5, 116.9, 115.8, 115.7, 67.7, 59.1, 46.7, 43.3, 39.6. HRMS (ESI) calcd for $C_{20}H_{16}F_3N_2Na$ $[M+Na]^+$ 363.1080, found 363.1080.

1-(4-Nitrophenyl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3aj)



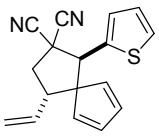
The products *trans*-**3aj** and *cis*-**3aj** were obtained in 68% total yield (43.1 mg, 0.14 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:20/ V:V). The major product *trans*-**3aj** is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 5.6 Hz, 1H), 6.35 (d, *J* = 5.6 Hz, 1H), 6.29 (d, *J* = 5.6 Hz, 1H), 6.23 (d, *J* = 5.2 Hz, 1H), 5.80 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.19–5.11 (m, 2H), 4.19 (s, 1H), 3.29 (dd, *J* = 14.4, 7.2 Hz, 1H), 3.09 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.80 (dd, *J* = 14.0, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 139.7, 138.6, 137.8, 136.0, 133.3, 133.2, 129.6, 123.6, 117.1, 115.5, 67.7, 58.8, 46.7, 43.3, 39.3. HRMS (ESI) calcd for $C_{19}H_{15}N_3O_2Na$ $[M+Na]^+$ 340.1056, found 340.1057.

1-(Furan-2-yl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ak)



The products *trans*-**3ak** and *cis*-**3ak** were obtained in 84% total yield (44.1 mg, 0.168 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product *trans*-**3ak** is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 0.8 Hz, 1H), 6.40–6.33 (m, 4H), 6.28 (d, *J* = 3.2 Hz, 1H), 6.21 (d, *J* = 5.2 Hz, 1H), 5.57 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.09–5.04 (m, 2H), 4.13 (s, 1H), 3.60 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.09 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.71 (dd, *J* = 14.0, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 143.1, 138.3, 137.3, 134.5, 132.7, 117.2, 116.7, 115.0, 110.6, 109.8, 68.4, 53.3, 47.4, 43.8, 38.7. HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{15}N_2O$ $[M+H]^+$ 263.1179, found 263.1177.

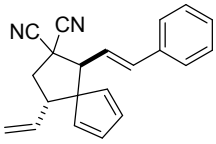
1-(Thiophen-2-yl)-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3al)



The products *trans*-**3al** and *cis*-**3al** were obtained in 92 % total yield (51.2 mg, 0.184 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). The major product *trans*-**3al** is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 5.2 Hz, 1H), 7.14 (d, *J* = 3.2 Hz, 1H), 6.97–6.94 (m, 1H), 6.63 (d, *J* = 5.6 Hz, 1H), 6.39 (d, *J* = 5.6 Hz, 1H), 6.32 (d, *J* = 5.2 Hz, 1H), 6.23 (d, *J* = 5.2 Hz, 1H), 5.78 (ddd, *J* = 17.6,

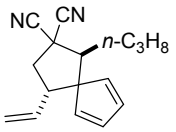
10.4, 7.2 Hz, 1H), 5.14–5.08 (m, 2H), 4.45 (s, 1H), 3.28 (dd, J = 14.4, 7.2 Hz, 1H), 3.04 (dd, J = 14.0, 7.6 Hz, 1H), 2.74 (dd, J = 14.0, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 137.7, 136.3, 133.9, 133.6, 133.1, 128.1, 126.7, 125.9, 116.8, 116.0, 115.6, 68.1, 55.3, 46.5, 42.7, 41.2. HRMS (ESI) *m/z* calcd. for $C_{17}H_{14}N_2SNa$ $[M+Na]^+$ 301.0770, found 301.0773.

(*E*)-1-Styryl-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3am)



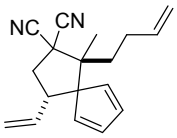
The product *cis*-**3am** were obtained in 93% yield (55.5 mg, 0.186 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.25 (m, 5H), 6.54–6.50 (m, 2H), 6.36 (d, J = 5.6 Hz, 1H), 6.32 (d, J = 5.2 Hz, 1H), 6.21 (d, J = 5.6 Hz, 1H), 6.03 (dd, J = 15.6, 9.6 Hz, 1H), 5.70 (ddd, J = 17.2, 10.0, 7.2 Hz, 1H), 5.08–5.02 (m, 2H), 3.59 (d, J = 9.2 Hz, 1H), 3.24 (dd, J =15.2, 7.6 Hz, 1H), 2.94 (dd, J = 13.6, 6.8 Hz, 1H), 2.61 (dd, J = 13.6, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 137.6, 136.2, 135.7, 135.6, 132.9, 132.6, 128.7, 128.4, 126.9, 119.8, 116.4, 116.0, 115.1, 67.7, 57.9, 46.4, 43.1, 39.9. HRMS (ESI) m/z calcd. for $C_{21}H_{19}N_2$ $[M+H]^+$ 299.1543, found 299.1548.

1-Propyl-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3an)



The products *trans*-**3an** and *cis*-**3an** were obtained in 92% total yield (43.8 mg, 0.184 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:50/ V:V). The major product *trans*-**3an** is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.40–6.35 (m, 2H), 6.30 (dt, J = 5.2, 1.6 Hz, 1H), 6.17 (dt, J = 5.6, 1.6 Hz, 1H), 5.63 (ddd, J = 17.6, 10.4, 7.6 Hz, 1H), 5.03–4.96 (m, 2H), 3.10 (dd, J = 15.2, 7.6 Hz, 1H), 2.94 (dd, J = 8.8, 5.6 Hz, 1H), 2.84 (dd, J =13.2, 6.4 Hz, 1H), 2.52 (dd, J = 13.6, 8.8 Hz, 1H), 1.65–1.52 (m, 1H), 1.48–1.38 (m, 1H), 1.31–1.21(m, 2H), 0.88 (t, J = 7.2, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 138.8, 135.3, 132.3, 131.6, 116.7, 116.1, 115.0, 67.1, 53.3, 47.0, 43.3, 38.6, 30.7, 20.9, 13.9. HRMS (ESI) calcd for $C_{16}H_{18}N_2Na$ $[M+Na]^+$ 261.1362, found 261.1361.

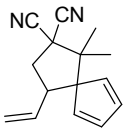
1-(But-3-en-1-yl)-1-methyl-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ao)



The diastereomeric mixture of the product **3ao** was obtained in 72% total yield (38.0 mg, 0.144 mmol) by silica gel chromatography (EtOAc:petroleum ether =

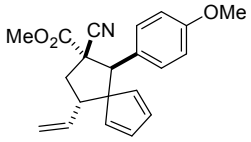
1:50/ V:V). The major product is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.55 (ddd, *J* = 5.2, 2.4, 1.6 Hz, 1H), 6.32–6.27 (m, 2H), 6.26–6.24 (m, 1H), 5.77–5.70 (m, 1H), 5.52 (ddd, *J* = 17.2, 11.2, 8.0 Hz, 1H), 5.04–4.95 (m, 2H), 4.91–4.84 (m, 2H), 3.35–3.30 (m, 1H), 2.84 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.60 (dd, *J* = 13.6, 10.8 Hz, 1H), 2.14–2.05 (m, 1H), 2.00–1.92 (m, 1H), 1.83 (td, *J* = 18.4, 13.6, 4.8 Hz, 1H), 1.7 (td, *J* = 16.4, 12.0, 4.0 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 137.9, 137.4, 135.7, 131.6, 130.7, 116.1, 115.6, 115.4, 70.2, 55.3, 45.4, 45.1, 41.7, 36.8, 28.5, 22.8. HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{21}N_2[M+H]^+$ 265.1699, found 265.1703.

1,1-Dimethyl-4-vinylspiro[4.4]nona-6,8-diene-2,2-dicarbonitrile (3ap)



The product **3ap** was obtained in 97% yield (45.8 mg, 0.19 mmol) as a colorless oil by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.54 (d, *J* = 4.8 Hz, 1H), 6.44 (d, *J* = 5.2 Hz, 1H), 6.34 (d, *J* = 5.6 Hz, 1H), 6.14–6.13 (m, 1H), 5.34 (ddd, *J* = 17.2, 9.6, 7.2 Hz, 1H), 4.91–4.88 (m, 2H), 3.36 (dd, *J* = 17.6, 9.6 Hz, 1H), 3.02 (dd, *J* = 14.8, 9.6 Hz, 1H), 2.69 (dd, *J* = 14.8, 10.0 Hz, 1H), 1.51 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7, 133.9, 133.8, 132.7, 117.3, 116.7, 115.6, 72.7, 52.9, 46.1, 44.1, 43.0, 26.7, 21.5. HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{17}N_2$ $[M+H]^+$ 225.1386, found 225.1387.

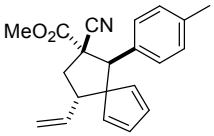
Methyl 2-cyano-1-(4-methoxyphenyl)-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3ba)



The diastereomeric mixture of **3ba** was obtained in 90% total yield (57.4 mg, 0.18 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:50/ V:V). The major product is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 2.0 Hz, 2H), 6.76–6.73 (m, 3H), 6.23–6.19 (m, 2H), 6.16 (dt, *J* = 7.2, 1.6 Hz, 1H), 5.81 (ddd, *J* = 16.8, 10.4, 8.0 Hz, 1H), 5.00–4.96 (m, 2H), 4.13 (s, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.32 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.80 (dd, *J* = 17.6, 7.2 Hz, 1H), 2.55 (dd, *J* = 13.6, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 159.3, 140.5, 139.6, 137.4, 131.4, 131.3, 130.0, 126.6, 120.0, 115.2, 113.3, 68.2, 58.0, 55.1, 54.1, 53.9, 46.7, 43.0. HRMS (ESI) *m*/*z* calcd.

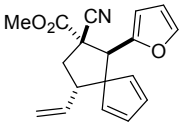
for $C_{21}H_{22}NO_3$ $[M+H]^+$ 336.1594, found 336.1603.

Methyl 2-cyano-1-(p-tolyl)-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3bd)



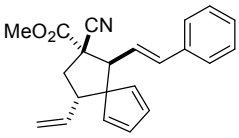
The diastereomeric mixture of **3bd** was obtained in 90% total yield (57.4 mg, 0.18 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:50/ V:V). The major product is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 5.6 Hz, 1H), 6.23 (d, *J* = 5.2 Hz, 1H), 6.19 (d, *J* = 5.2 Hz, 1H), 6.16 (d, *J* = 5.2 Hz, 1H), 5.81 (ddd, *J* = 17.2, 10.4, 8.4 Hz, 1H), 5.00–4.96 (m, 2H), 4.14 (s, 1H), 3.74 (s, 3H), 3.34 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.80 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.56 (dd, *J* = 13.6, 8.8 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 140.6, 139.6, 137.8, 137.3, 131.6, 131.4, 131.3, 128.7, 128.6, 120.0, 115.3, 68.2, 58.2, 54.0, 53.8, 46.9, 43.2, 21.2. HRMS (ESI) *m/z* calcd. for $C_{21}H_{22}NO_2$ $[M+H]^+$ 320.1645, found 320.1652.

Methyl 2-cyano-1-(furan-2-yl)-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3bk)



The diastereomeric mixture of **3bk** was obtained in 67% total yield (39.5 mg, 0.13 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:50/ V:V). The major product is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 5.2 Hz, 1H), 7.03 (d, *J* = 3.2 Hz, 1H), 6.87 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.77 (d, *J* = 5.2 Hz, 1H), 6.30 (d, *J* = 5.6 Hz, 1H), 6.25–6.21 (m, 2H), 5.83 (ddd, *J* = 17.6, 9.2, 7.6 Hz, 1H), 5.00–4.96 (m, 2H), 4.56 (s, 1H), 3.80 (s, 3H), 3.30 (dd, *J* =16.0, 8.0 Hz, 1H), 2.82 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.54 (dd, *J* = 13.6, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 140.4, 139.1, 137.4, 136.0, 132.2, 132.1, 126.9, 126.4, 124.7, 119.5, 115.5, 68.3, 55.0, 54.1, 53.7, 46.6, 42.7. HRMS (ESI) calcd for $C_{18}H_{17}NO_3K$ $[M+K]^+$ 334.0840 found 334.0870.

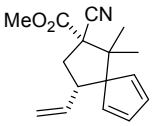
(*E*)-Methyl 2-cyano-1-styryl-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3bm)



The diastereomeric mixture of **3bm** was obtained in 95% total yield (62.9 mg, 0.19 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:50/ V:V).The major product is a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.19 (m, 5H), 6.64–6.61 (m, 1H), 6.30–6.22 (m, 4H), 6.10 (dd, *J* = 15.2, 9.2 Hz, 1H), 5.73 (ddd, *J* = 17.6, 9.6, 8.0 Hz, 1H), 4.97–4.93 (m, 2H), 3.83 (s, 3H), 3.64 (d, *J* = 9.6 Hz,

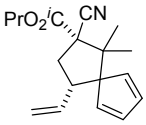
1H), 3.27 (dd, J = 16.4, 8.0 Hz, 1H), 2.71 (dd, J = 13.6, 7.2 Hz, 1H), 2.49 (dd, J = 13.6, 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ169.1, 139.1, 138.7, 136.7, 136.3, 133.8, 131.8, 131.6, 128.6, 127.9, 126.7, 122.0, 118.9, 115.2, 68.1, 56.4, 54.0, 46.8, 42.7. HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{22}NO_2[M+H]^+$ 332.1645, found 332.1653.

Methyl 2-cyano-1,1-dimethyl-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3bp)



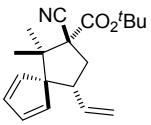
The product **3bp** was obtained in 58% total yield (29.8 mg, 0.116 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V) as a coless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46 (ddd, J = 5.6, 2.4, 1.6 Hz, 1H), 6.35 (dt, J = 5.6, 1.6 Hz, 1H), 6.22 (dt, J = 5.6, 1.6 Hz, 1H), 6.16 (ddd, J = 5.2, 2.0, 1.2 Hz, 1H), 5.39 (ddd, J = 17.2, 10.0, 7.2 Hz, 1H), 4.97–4.87 (m, 2H), 3.84 (s, 3H), 3.32–3.25 (m, 1H), 2.90 (dd, J = 13.6, 12.4 Hz, 1H), 2.60 (dd, J = 14.0, 7.2 Hz, 1H), 1.55 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 138.3, 137.9, 134.9, 132.6, 131.2, 120.4, 116.1, 72.9, 56.4, 53.6, 52.3, 46.6, 41.8, 29.8, 22.5. HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{20}NO_2$ $[M+H]^+$ 258.1489, found 258.1497.

Isopropyl 2-cyano-1,1-dimethyl-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3cp)



The product **3cp** was obtained in 31% yield (17.7 mg, 0.062 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46 (d, J = 5.2 Hz, 1H), 6.34 (d, J = 5.6 Hz, 1H), 6.21 (d, J = 5.2 Hz, 1H), 6.18 (d, J = 5.2 Hz, 1H), 5.44–5.34 (m, 1H), 5.14–5.08 (m, 1H), 4.95–4.86 (m, 2H), 3.29–3.23 (m, 1H), 2.89 (t, J = 14.0 Hz, 1H), 2.58 (dd, J = 14.0, 7.2 Hz, 1H), 1.52 (s, 3H), 1.35 (d, J = 6.4 Hz, 3H), 1.30 (d, J = 6.0 Hz, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 138.5, 138.2, 135.2, 132.3, 131.0, 120.5, 115.6, 73.0, 71.3, 56.6, 52.0, 46.3, 41.7, 29.6, 22.8, 21.7, 21.6. HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{23}NO_2Na$ $[M+Na]^+$ 308.1621, found 308.1626.

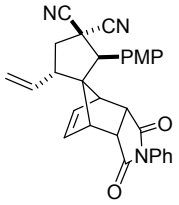
***tert*-Butyl 2-cyano-1,1-dimethyl-4-vinylspiro[4.4]nona-6,8-diene-2-carboxylate (3dp)**



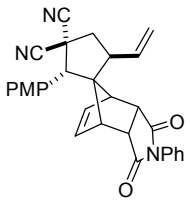
The product **3dp** was obtained in 30% yield (17.9mg, 0.06 mmol) by silica gel chromatography (EtOAc:petroleum ether = 1:35/ V:V) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46 (ddd, J = 5.2, 2.0, 1.2 Hz, 1H), 6.34–6.31 (m, 1H),

6.21–6.18 (m, 2H), 5.40 (ddd, J = 17.6, 10.4, 7.2 Hz, 1H), 4.94–4.85 (m, 2H), 3.28–3.21 (m, 1H), 2.84 (dd, J = 14.0, 12.4 Hz, 1H), 2.55 (dd, J = 14.0, 7.2 Hz, 1H), 1.53 (s, 9H), 1.50 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 138.6, 138.5, 135.4, 132.1, 131.0, 120.9, 115.7, 84.3, 73.0, 57.2, 51.9, 46.2, 41.5, 29.5, 27.9, 23.0. HRMS (ESI) m/z calcd. for $C_{19}H_{25}NO_2Na$ $[M+Na]^+$ 322.1778, found 322.1785.

Diels-Alder cycloadducts of 3aa (5)

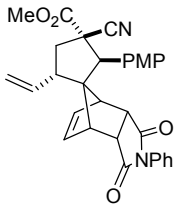


***anti-endo*-5** as a white solid. m.p.: 148−152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.29 (m, 4H), 7.21 (dd, J = 8.4, 2.4 Hz, 1H), 7.06–7.00 (m, 3H), 6.95 (dd, J = 8.4, 2.4 Hz, 1H), 6.25 (dd, J = 5.6, 2.8 Hz, 1H), 6.02 (dd, J = 5.6, 2.8 Hz, 1H), 5.95 (dt, J = 16.8, 10.0 Hz, 1H), 5.04 (dd, J = 10.4, 0.4 Hz, 1H), 4.92 (d, J = 16.8 Hz, 1H), 3.85 (s, 3H), 3.69 (s, 1H), 3.58 (s, 1H), 3.54 (dd, J = 7.6, 4.4 Hz, 1H), 3.40 (s, 1H), 3.21 (td, J = 9.2, 6.0 Hz, 1H), 2.90–2.79 (m, 2H), 2.39 (dd, J = 14.0, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 160.5, 140.6, 137.0, 132.7, 131.7, 129.2, 128.8, 127.9, 126.5, 126.4, 116.9, 116.2, 115.3, 114.8, 114.3, 79.6, 59.5, 55.4, 52.0, 51.1, 48.0, 44.8, 44.6, 42.6, 40.4. HRMS (ESI) m/z calcd. for $C_{30}H_{25}N_3O_3Na$ $[M+Na]^+$ 498.1788, found 498.1798.



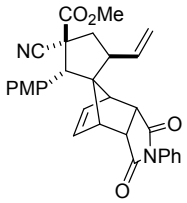
***syn-endo*-5** as a white solid. m.p.: 156−160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.33 (m, 3H), 7.21 (d, J = 8.0 Hz, 1H), 7.04 (d, J = 7.6 Hz, 2H), 6.97–6.92 (m, 2H), 6.85 (d, J = 8.0 Hz, 1H), 6.27–6.17 (m, 2H), 5.80 (dd, J = 6.0, 2.8 Hz, 1H), 5.33–5.25 (m, 2H), 3.92 (dd, J = 7.2, 4.4 Hz, 1H), 3.81 (s, 4H), 3.78 (s, 1H), 3.40–3.35 (m, 2H), 3.10–3.00 (m, 2H), 2.48 (dd, J = 12.4, 2.8 Hz, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 159.8, 138.4, 135.3, 134.3, 132.8, 131.7, 129.3, 128.8, 127.8, 126.5, 118.0, 117.0, 114.9, 114.5, 114.3, 79.4, 61.1, 55.3, 53.2, 51.1, 47.5, 46.1, 44.7, 44.0, 38.9. HRMS (ESI) m/z calcd. for $C_{30}H_{25}N_3O_3Na$ $[M+Na]^+$ 498.1788, found 498.1810.

Diels-Alder cycloadducts of 3ba (6)



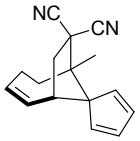
***anti-endo*-6** as a white solid. m.p.: 217−220 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, J = 8.4, 2.0 Hz, 1H), 7.41–7.31 (m, 3H), 7.09–7.03 (m, 4H), 6.87 (dd, J = 8.4, 2.4 Hz, 1H), 6.19 (dd, J = 5.6, 2.4 Hz, 1H), 6.07 (dd, J = 5.6, 3.2 Hz,

1H), 5.66–5.57 (m, 1H), 4.92–4.86 (m, 2H), 3.85 (s, 3H), 3.79 (s, 3H), 3.62 (s, 1H), 3.44–3.39 (m, 3H), 3.18 (dd, *J* = 18.0, 8.4 Hz, 1H), 2.82 (dd, *J* = 7.2, 4.8 Hz, 1H), 2.49 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.29 (dd, *J* = 13.2, 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 169.2, 159.7, 140.8, 135.3, 133.1, 132.0, 131.0, 129.1, 128.8, 128.5, 126.5, 118.8, 114.7, 113.7, 107.9, 79.7, 67.7, 57.2, 55.3, 54.1, 51.0, 50.6, 49.2, 45.0, 44.4, 41.8. HRMS (ESI) m/z calcd. for $C_{31}H_{28}N_2O_5Na$ $[M+Na]^+$ 531.1890, found 531.1889.



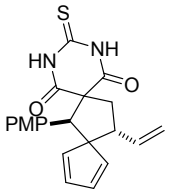
***syn-endo*-6** as a colorless solid. m.p.: 209−212 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 6.8, 1.6 Hz, 1H), 7.37–7.31 (m, 3H), 7.04–7.02 (m, 2H), 6.91 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.75 (ddd, *J* = 14.4, 8.4, 1.6 Hz, 2H), 6.06–5.97 (m, 1H), 5.86 (dd, *J* = 6.0, 3.2 Hz, 1H), 5.66 (dd, *J* = 5.6, 2.4 Hz, 1H), 5.30 (d, *J* = 16.8 Hz, 1H), 5.20 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.86–3.83 (m, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 3.65 (s, 1H), 3.60 (s, 1H), 3.51 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.40 (s, 1H), 3.03 (dd, *J* = 18.0, 8.8 Hz, 1H), 2.64 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.36 (dd, *J* = 13.6, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 169.1, 158.9, 138.5, 135.0, 132.2, 131.7, 131.3, 129.1, 128.7, 128.2, 126.5, 119.4, 117.2, 114.4, 113.8, 79.3, 58.9, 55.2, 54.0, 52.6, 52.1, 50.4, 48.1, 45.7, 44.4, 43.1. HRMS (ESI) m/z calcd. for $C_{31}H_{28}N_2O_5Na$ $[M+Na]^+$ 531.1890, found 531.1889.

RCM-derivative of 3ao (7)



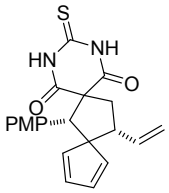
as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.08 (dd, *J* = 9.6, 5.6 Hz, 1H), 6.00 (dd, *J* = 9.6, 5.6 Hz, 1H), 5.80 (dd, *J* = 9.6, 5.6 Hz, 1H), 5.70–5.64 (m, 2H), 5.39–5.36 (m, 1H), 2.95–2.88 (m, 2H), 2.44–2.36 (m, 1H), 2.23–2.18 (m, 2H), 1.87–1.82 (m, 1H), 1.76–1.68 (m, 1H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.1, 127.4, 125.8, 125.4, 124.7, 122.8, 116.5, 115.6, 52.5, 48.9, 44.4, 44.3, 43.3, 30.3, 22.8, 17.7. HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{17}N_2$ $[M+H]^+$ 237.1386, found 237.1392.

Thiobarbital derivatives from 3ea (8)



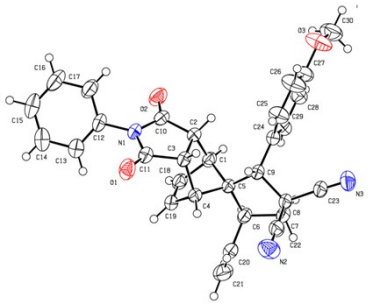
***trans*-8** as a white waxy substance. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.17 (s, 1H), 8.74 (s, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.76 (ddd, *J* = 3.2, 2.0, 1.2 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.32–6.30 (m, 1H), 6.18–6.16 (m, 2H), 6.04 (ddd, *J* = 18.4, 10.0,

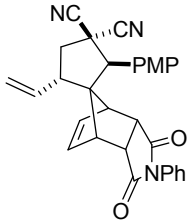
8.8 Hz, 1H), 5.05–4.98 (m, 2H), 4.14 (s, 1H), 3.73 (s, 3H), 3.42 (dd, J = 15.6, 7.6 Hz, 1H), 2.90 (dd, J = 13.6, 7.6 Hz, 1H), 2.63 (dd, J = 13.6, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.4, 170.6, 169.0, 159.7, 140.2, 139.9, 138.2, 131.2, 131.1, 130.1, 127.0, 115.6, 113.7, 70.7, 64.5, 55.3, 49.7, 38.1, 29.8. HRMS (ESI) m/z calcd. for $C_{21}H_{20}N_2O_3SNa$ $[M+Na]^+$ 403.1087, found 403.1098.



***cis*-8** as a white waxy substance. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.20 (s, 1H), 8.71 (s, 1H), 7.06–7.03 (m, 3H), 6.66 (d, J = 8.8 Hz, 2H), 6.36 (d, J = 5.2 Hz, 1H), 6.24 (d, J = 5.2 Hz, 1H), 6.03 (d, J = 5.2 Hz, 1H), 5.97 (t, J = 4.0 Hz, 1H), 5.50–5.41 (m, 1H), 5.03–4.92 (m, 2H), 4.18 (s, 1H), 3.72 (s, 3H), 3.48–3.41 (m, 1H), 2.85 (t, J = 12.8 Hz, 1H), 2.67 (dd, J = 13.6, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.4, 171.8, 169.0, 159.9, 138.8, 136.2, 134.6, 133.1, 132.8, 129.6, 125.6, 116.4, 113.7, 71.6, 67.4, 62.1, 55.3, 50.2, 38.2. HRMS (ESI) m/z calcd. for $C_{21}H_{20}N_2O_3SNa$ $[M+Na]^+$ 403.1087, found 403.1097.

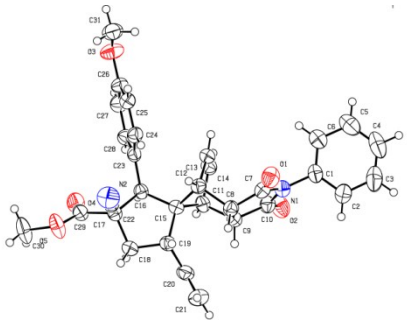
7. Crystallographic information of compounds *anti-endo*-5 and *syn-endo*-6

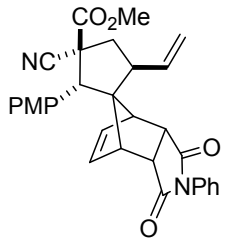




***anti-endo*-5**
CCDC 1906465

Bond precision:	C-C = 0.0031 A	Wavelength = 1.54184	
Cell:	a = 8.9859 (13)	b = 10.004 (2)	c = 15.8029 (18)
	alpha=97.570 (13)	beta = 90.211 (11)	gamma = 115.564 (17)
Temperature:	293 K		
	Calculated	Reported	
Volume	1296.5 (4)	1296.5 (4)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C30H25N3O3 [+ solvent]	C30H25N3O3	
Sum formula	C30H25N3O3 [+ solvent]	C30H25N3O3	
Mr	475.53	475.53	
Dx,g cm-3	1.246	1.246	
Z	2	2	
Mu (mm-1)	0.654	0.654	
F000	500.0	500.0	
F000'	501.48		
h, k, lmax	10,11,18	10,11,18	
Nref	4471	4466	
Tmin, Tmax	0.889, 0.913	0.889, 1.000	
Tmin'	0.872		
Correction method = # Reported T Limits: Tmin = 0.889 Tmax = 1.000 AbsCorr = MULTI-SCAN			
Data completeness = 0.999	Theta (max) = 66.600		
R (reflections) = 0.0458 (3530)	wR2 (reflections) = 0.1273 (4466)		
S = 1.029	Npar = 334		





***syn-endo*-6**
CCDC 1893180

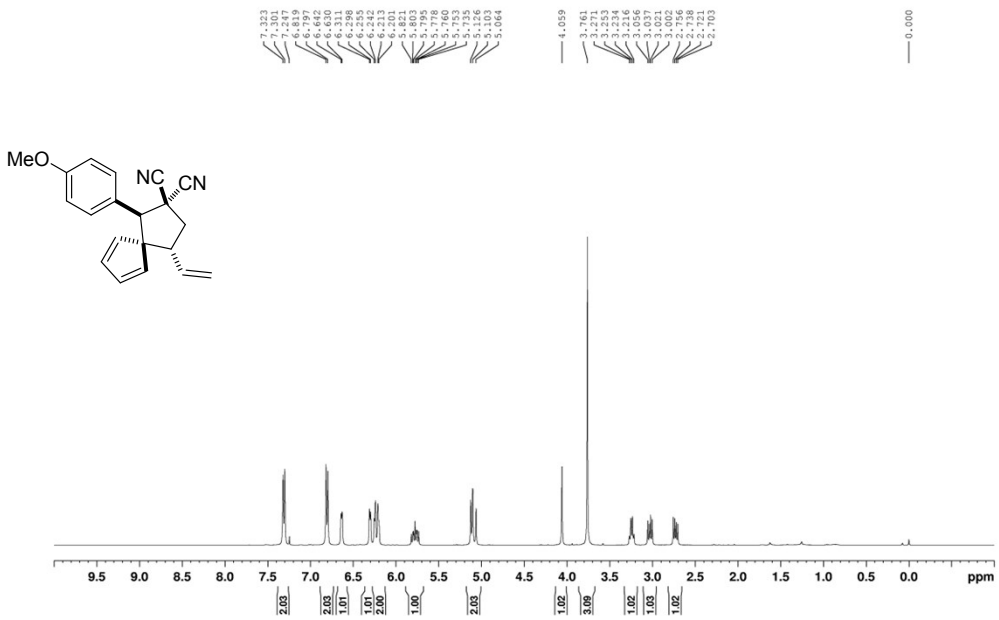
Bond precision:	C-C = 0.0063 A	Wavelength = 0.71073	
Cell:	a = 21.4324 (12)	b = 13.5256 (8)	c = 8.8733 (5)
	alpha = 90	beta = 90	gamma = 90
	Calculated	Reported	
Volume	2572.3 (3)	2572.2 (3)	
Space group	P n a 21	P n a 21	
Hall group	P 2c -2n	P 2c -2n	
Moiety formula	$C_{31}H_{28}N_2O_5$	$C_{31}H_{28}N_2O_5$	
Sum formula	$C_{31}H_{28}N_2O_5$	$C_{31}H_{28}N_2O_5$	
Mr	508.55	508.55	
Dx,g cm^{-3}	1.313	1.313	
Z	4	4	
Mu (mm^{-1})	0.090	0.090	
F000	1072.0	1072.0	
F000'	1072.51		
h, k, lmax	26,16,10	26,16,10	
Nref	5056 [2702]	3845	
Tmin, Tmax	0.984, 0.989	0.666, 1.000	
Tmin'	0.984		
	Calculated	Reported	
Volume	2572.3 (3)	2572.2 (3)	

Correction method = # Reported T Limits: Tmin = 0.666 Tmax = 1.000 AbsCorr = MULTI-SCAN

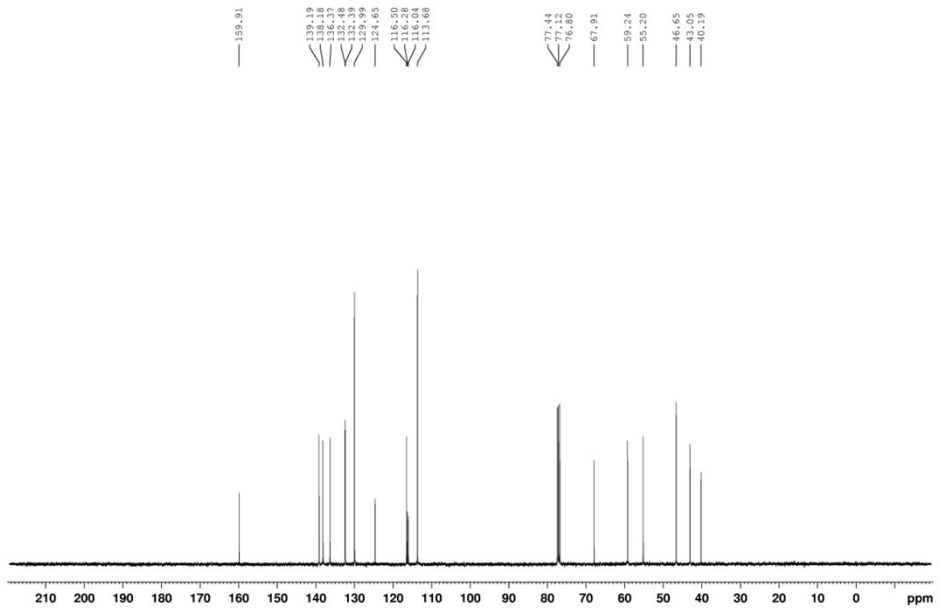
Data completeness = 1.42/0.76	Theta (max) = 26.022
R (reflections)= 0.0502 (2699)	wR2 (reflections) = 0.1086 (3845)
S = 1.055	Npar = 345

8. Copies of ^{1}H NMR and ^{13}C NMR spectrogram

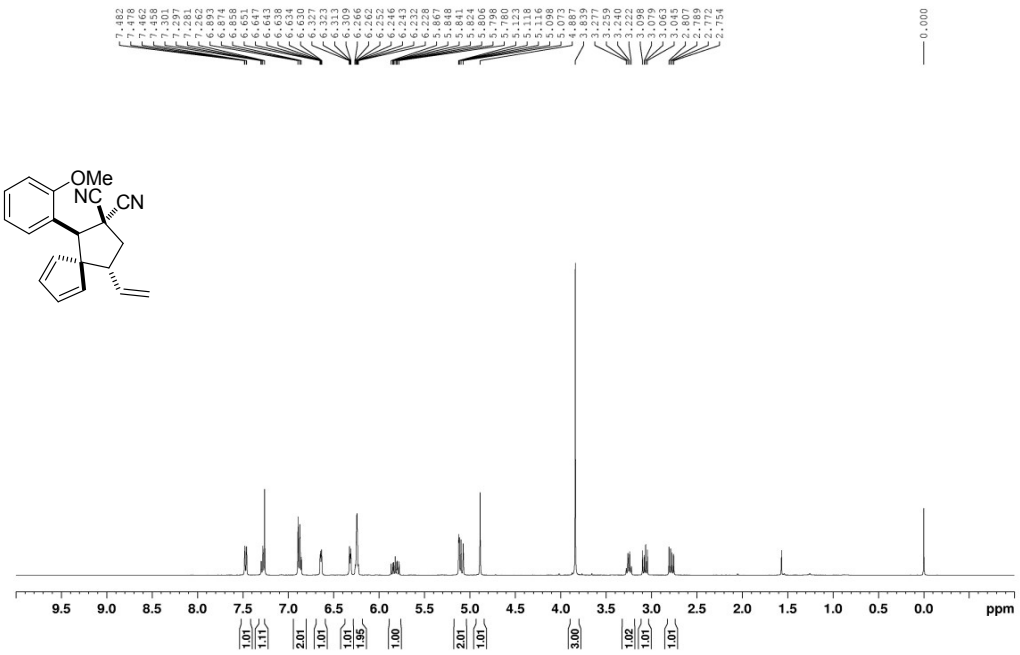
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans*-3aa



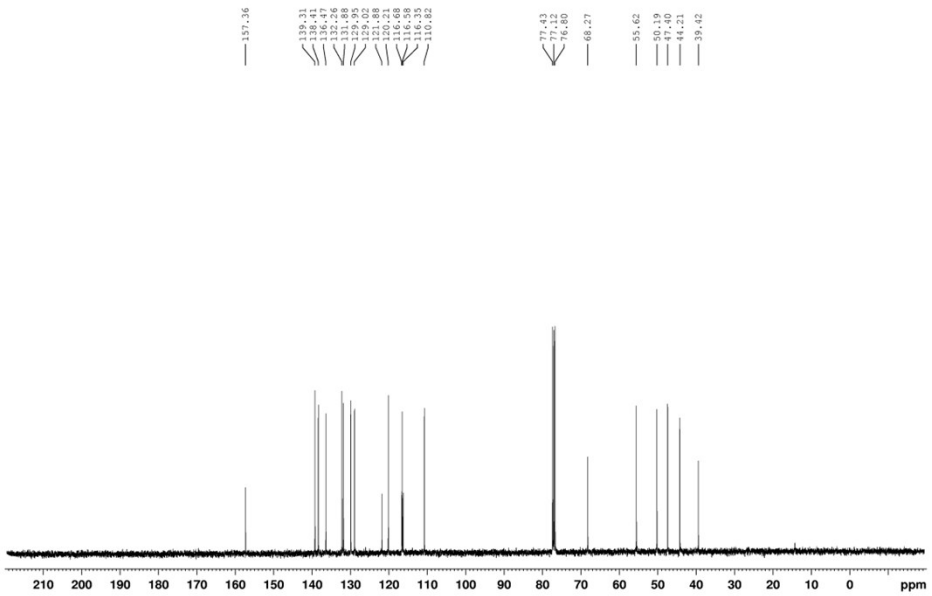
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans* -3aa



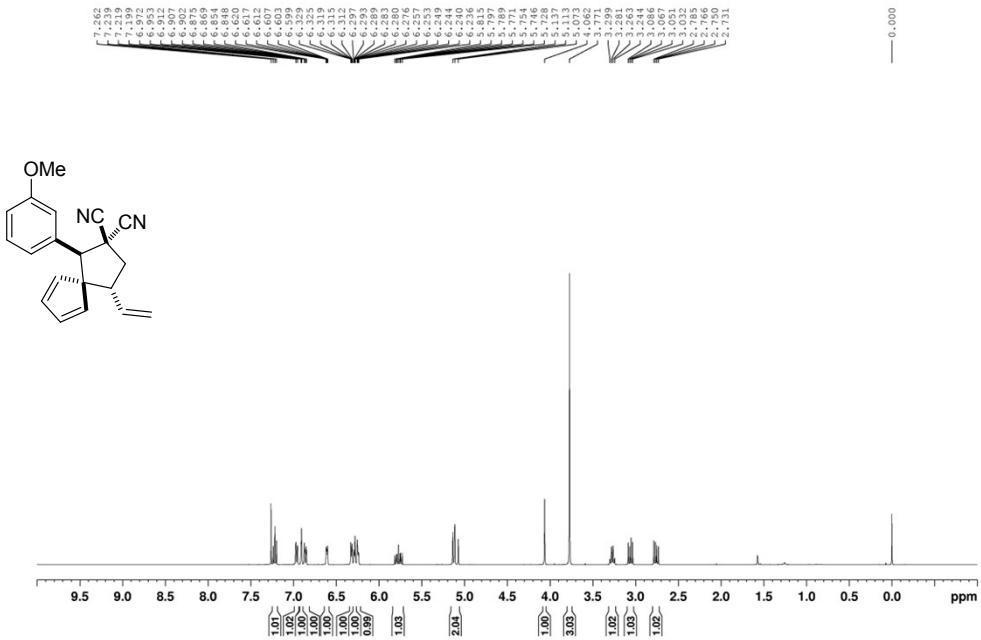
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans* -3ab



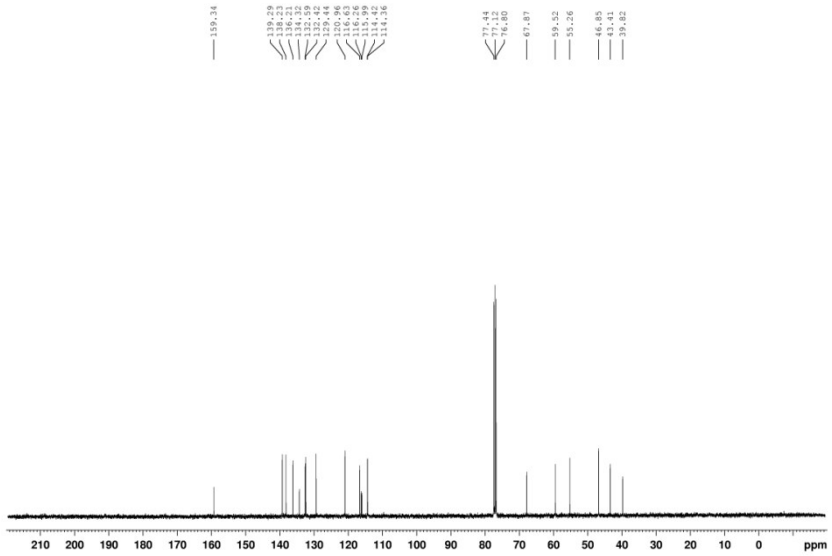
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans* -3ab



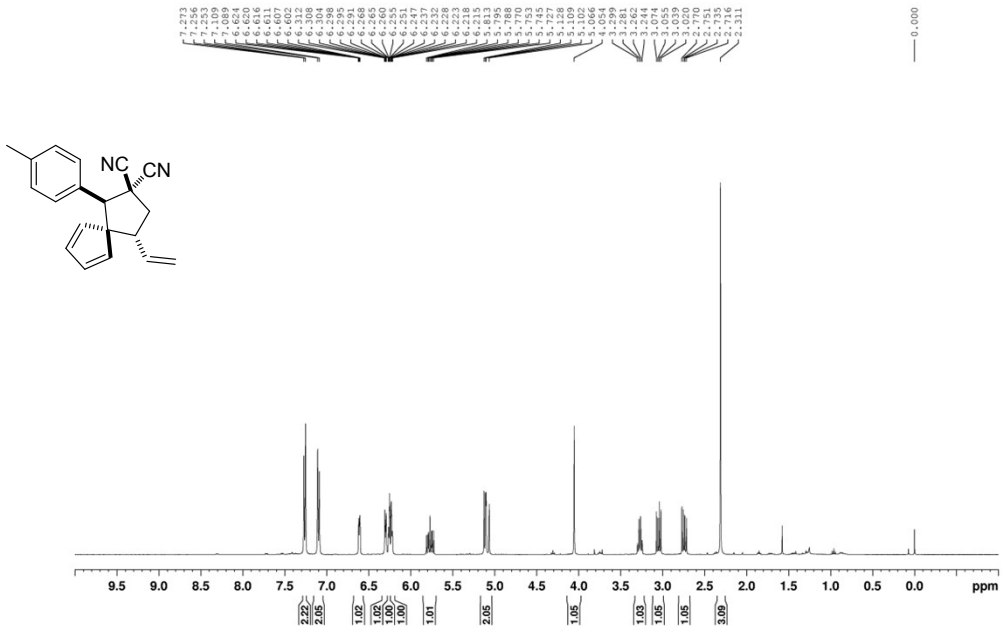
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans* -3ac



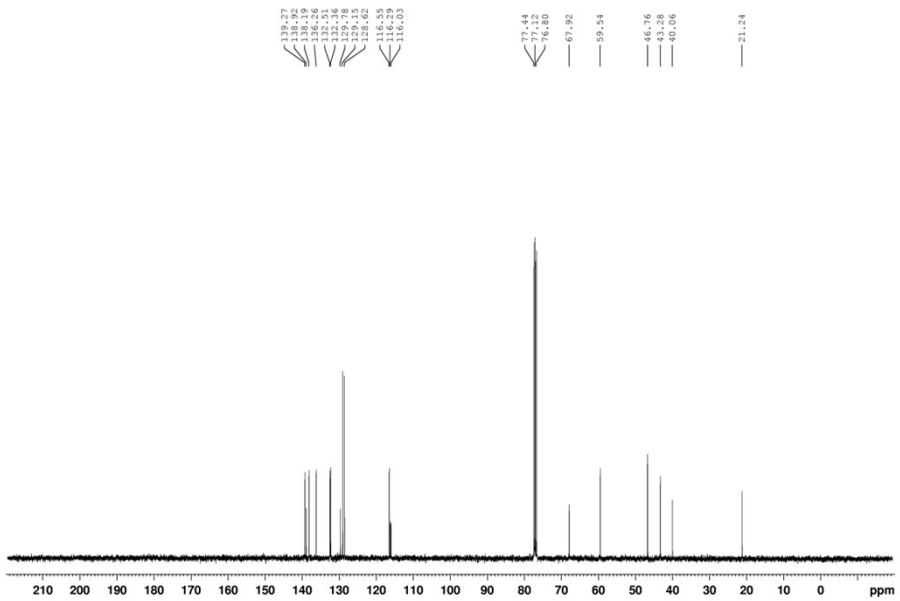
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans* -3ac



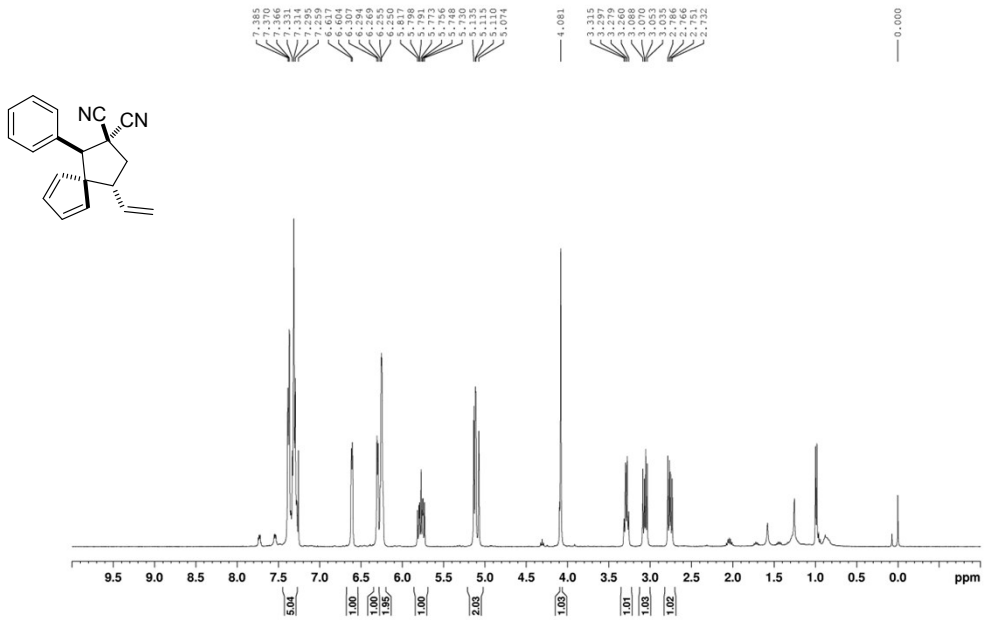
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans* -3ad



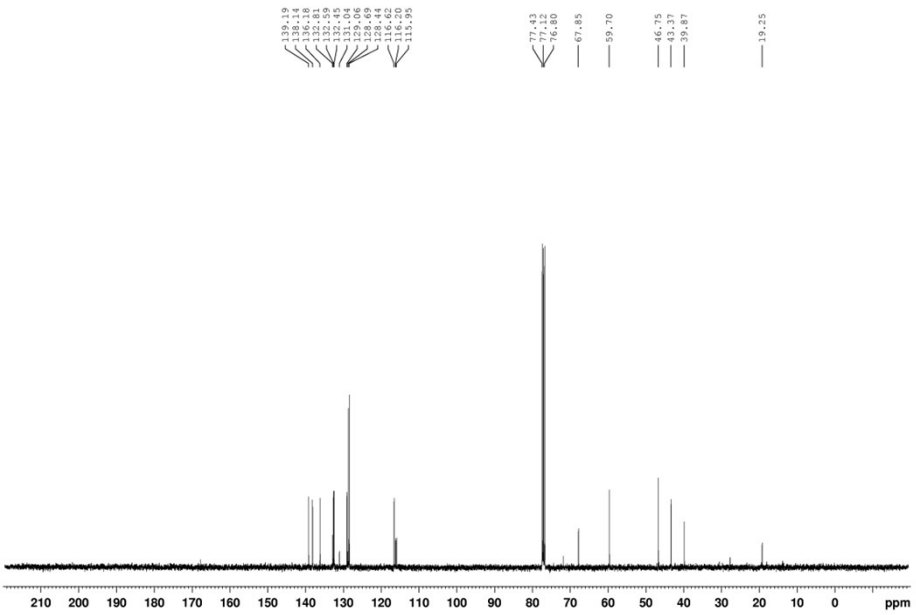
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans* -3ad



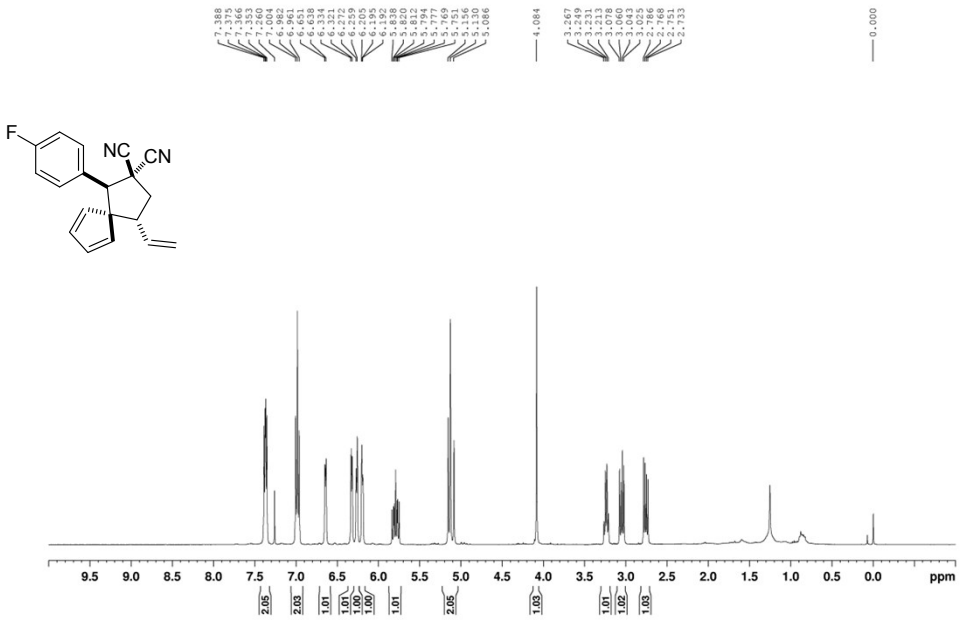
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans* -3ae



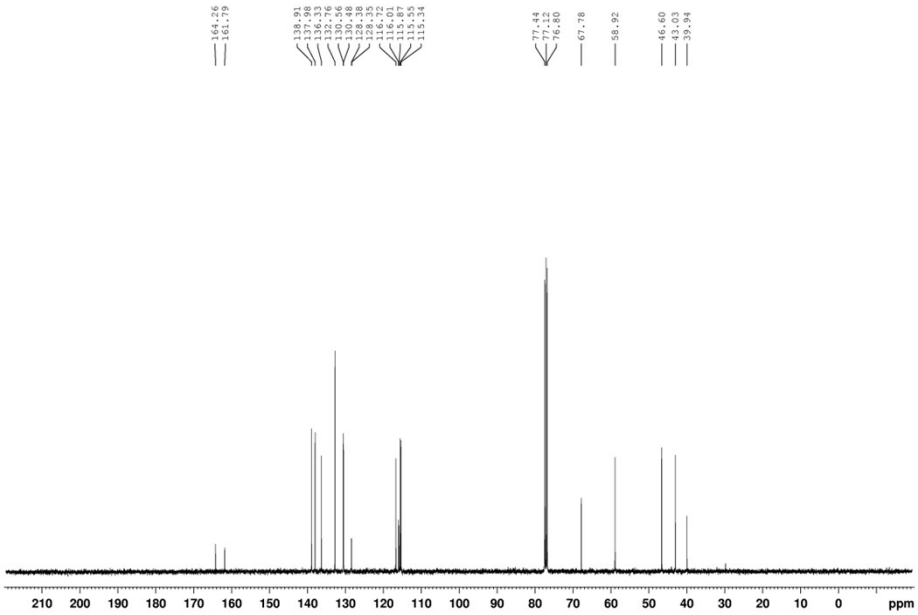
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans* -3ae



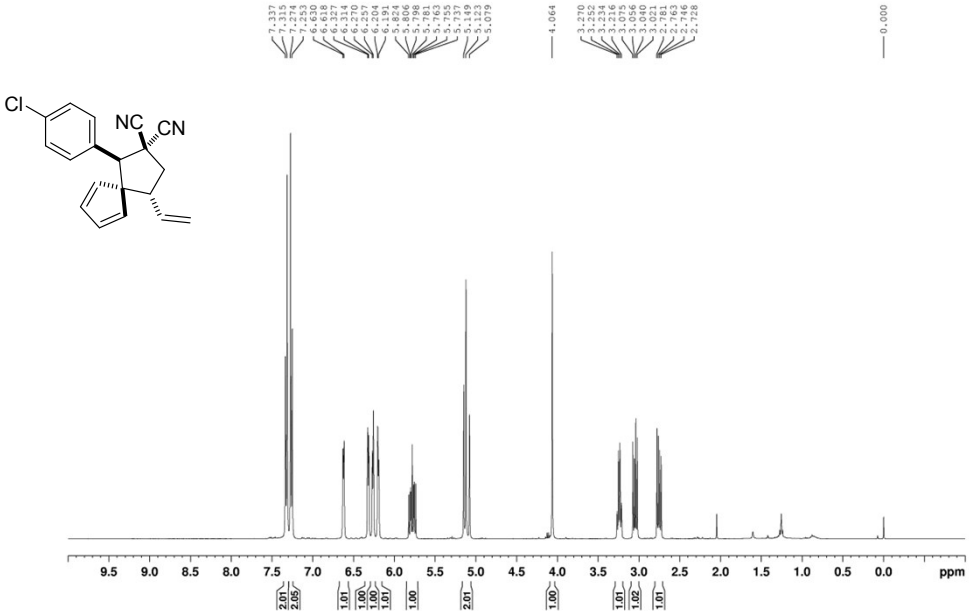
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans* -3af



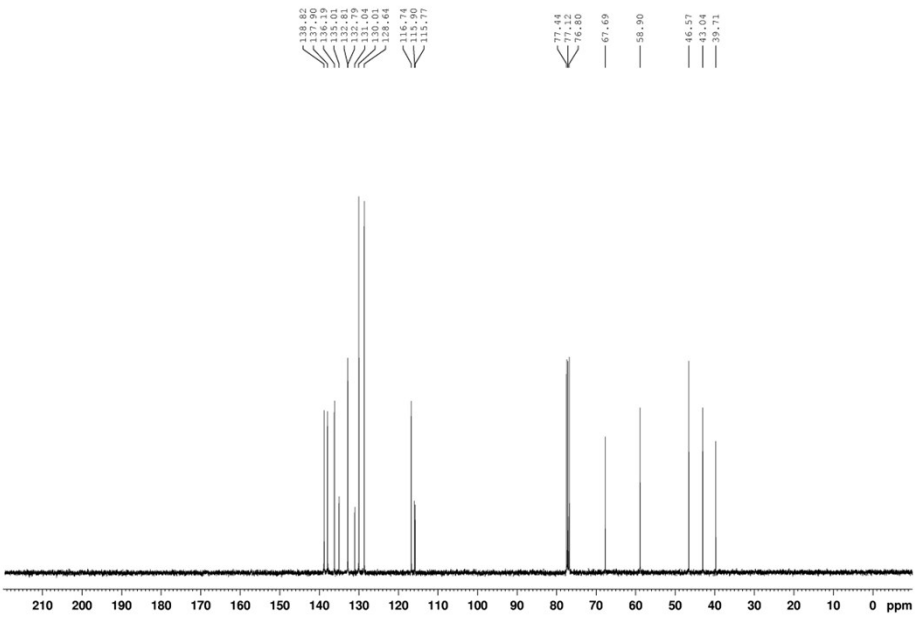
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans* -3af



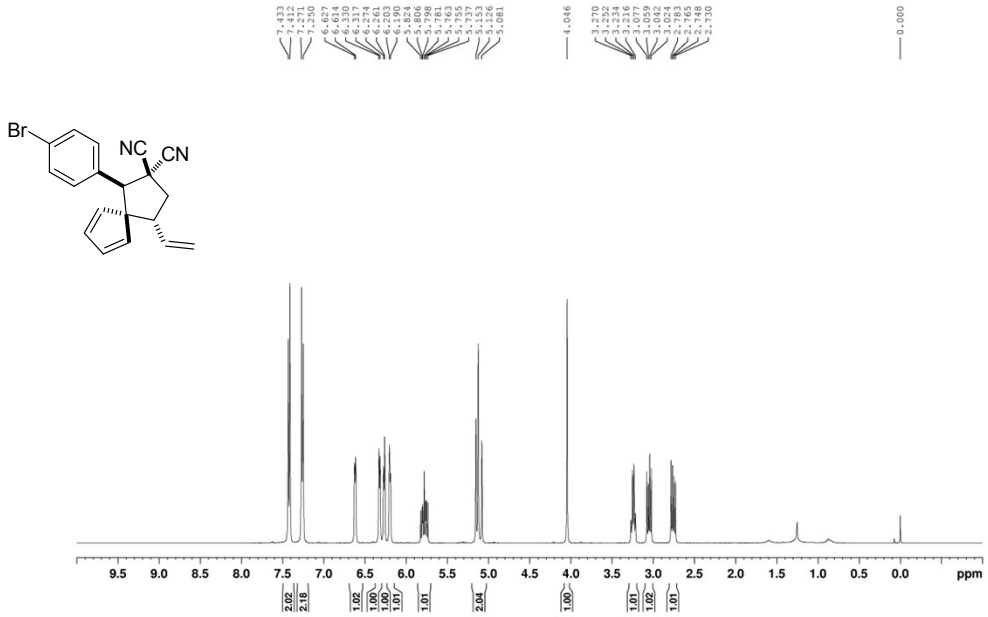
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans* -3ag



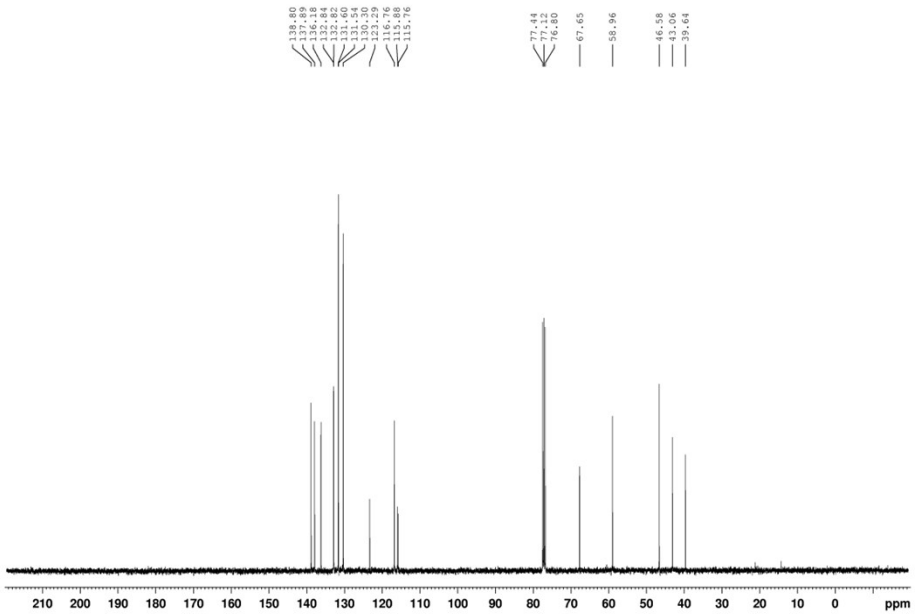
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans* -3ag



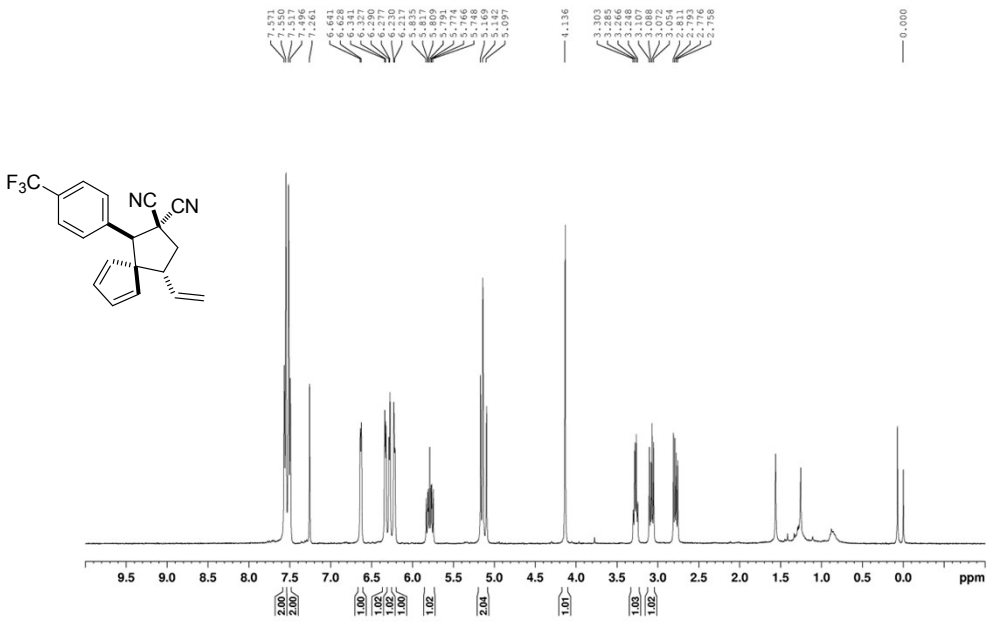
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans* -3ah



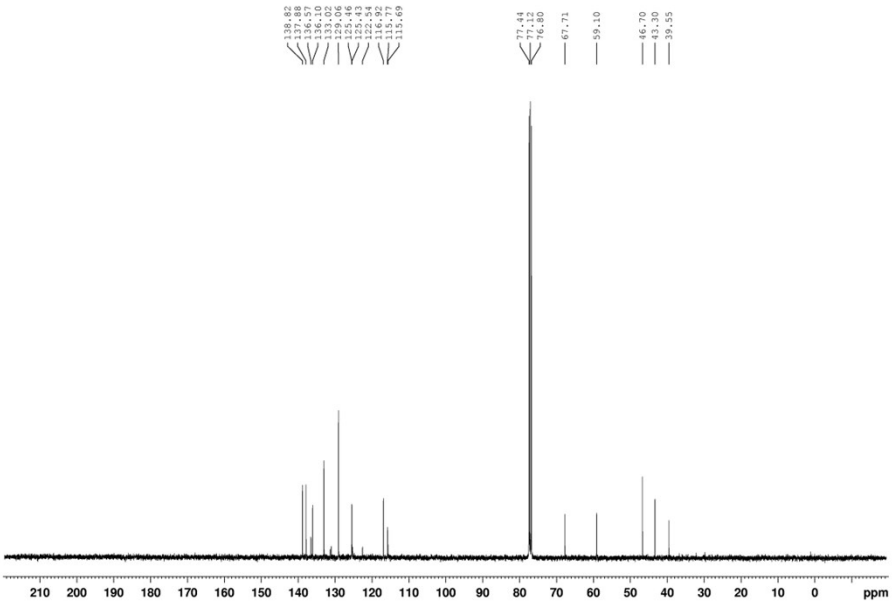
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans*-3ah



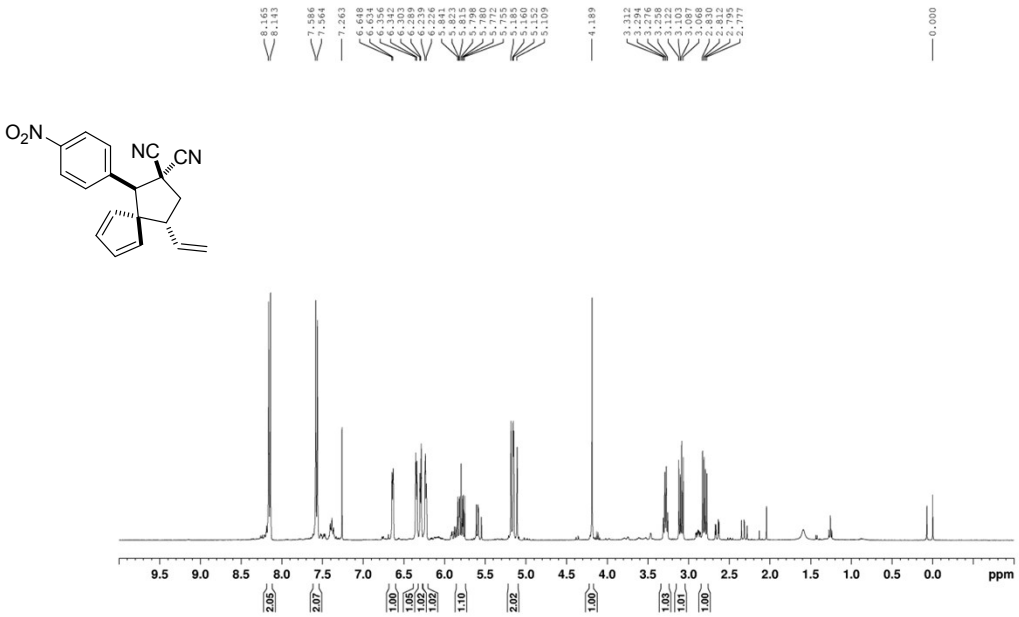
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans* -3ai



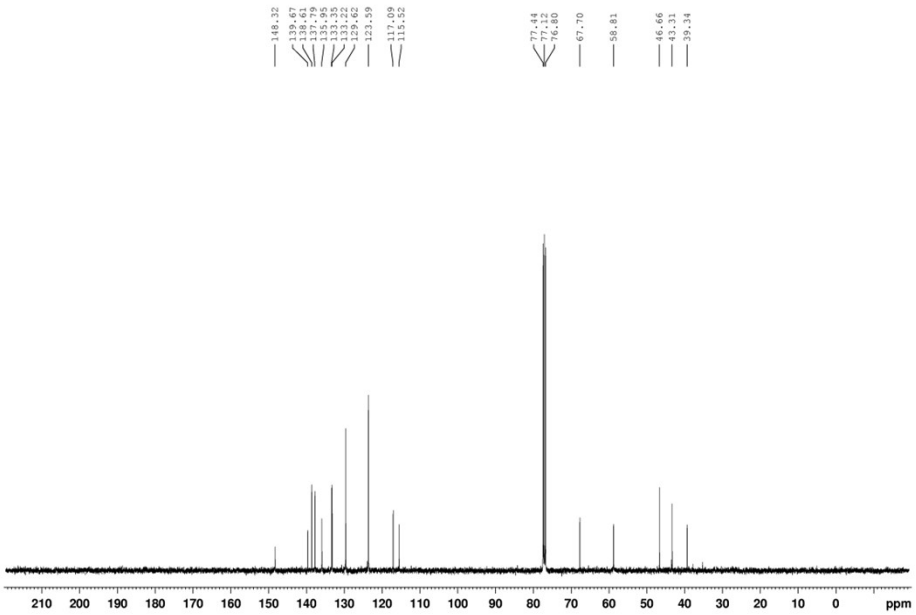
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans* -3ai



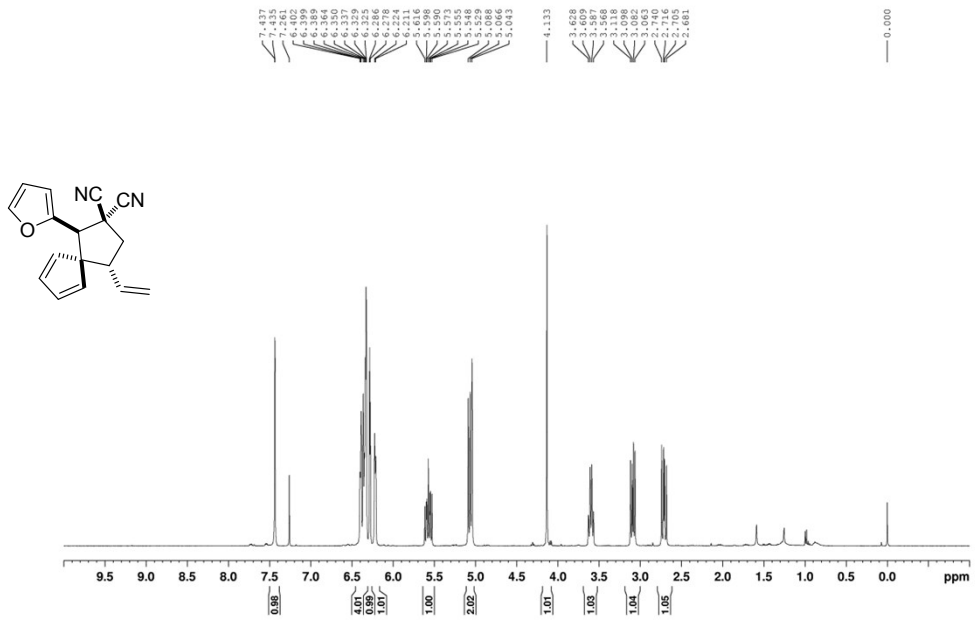
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans* -3aj



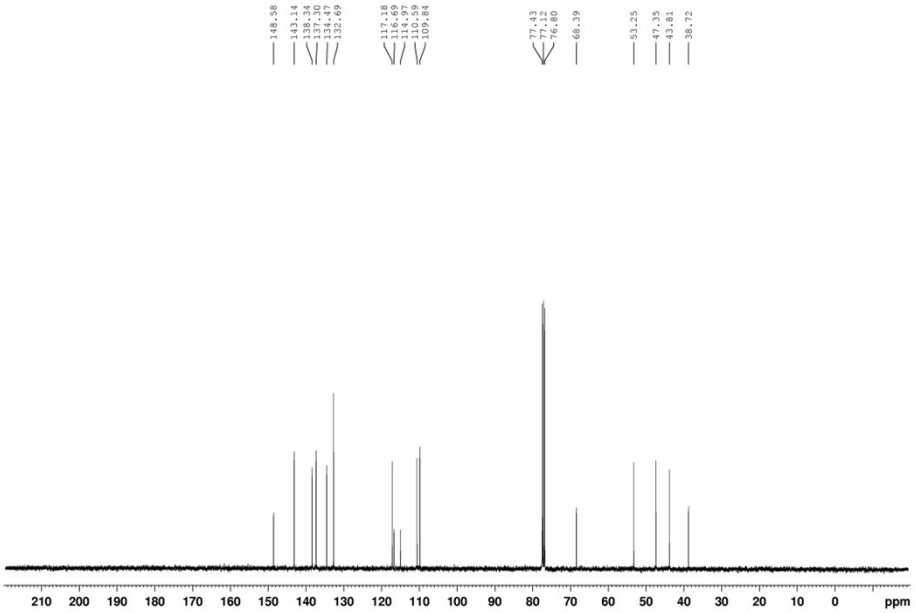
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans* -3aj



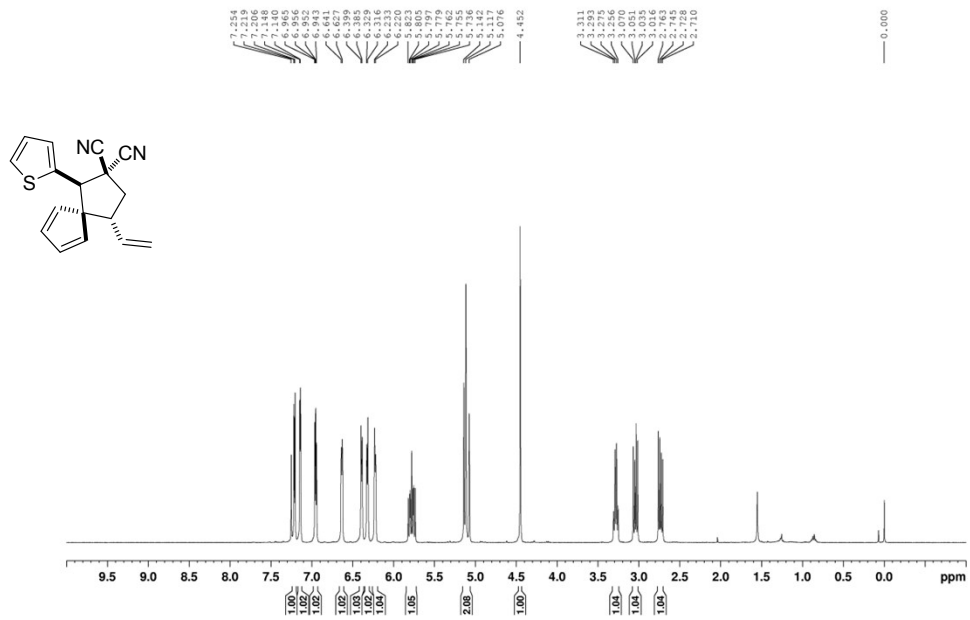
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans* -3ak



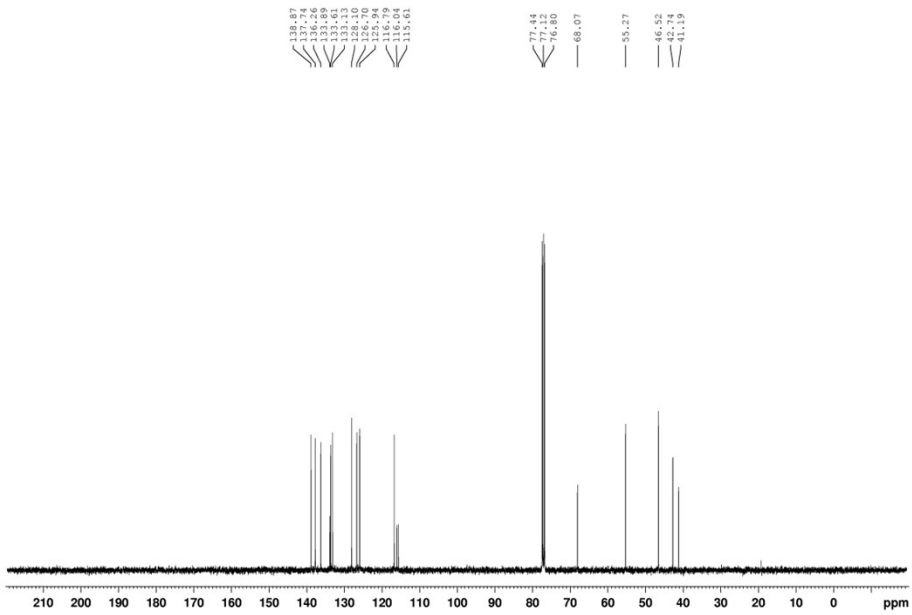
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans* -3ak



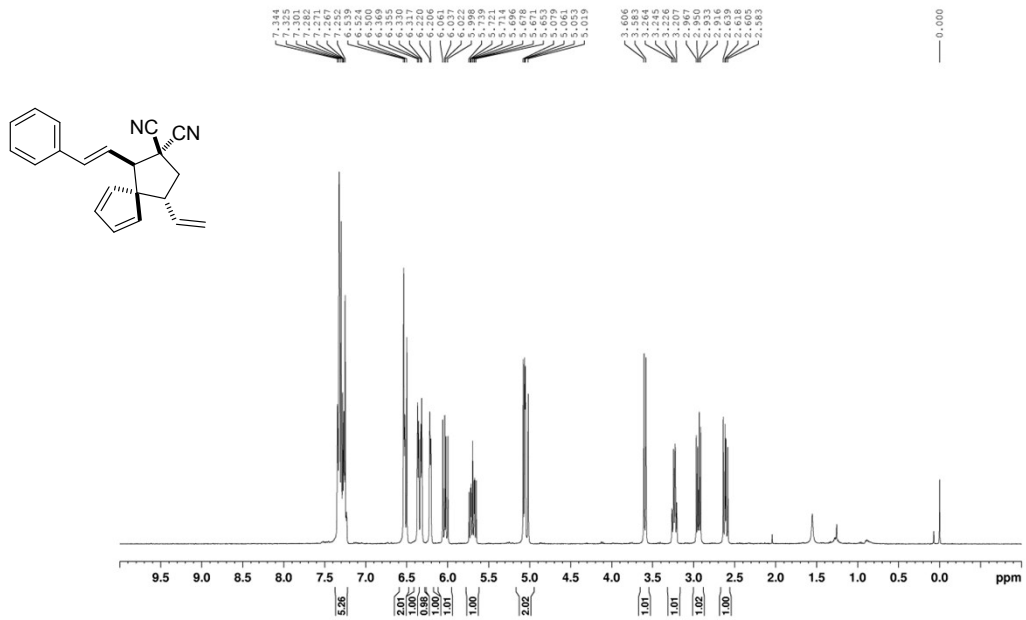
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans* -3al



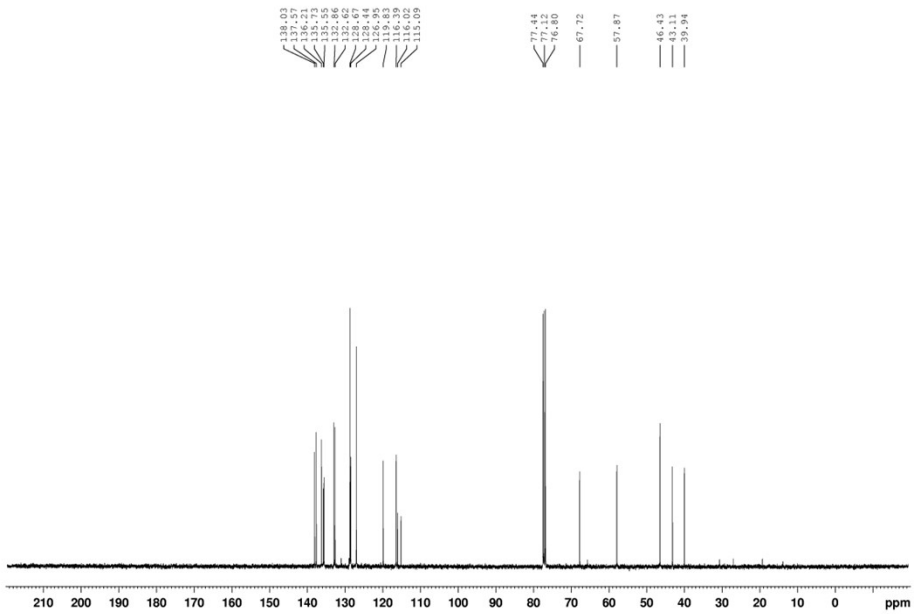
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans* -3al



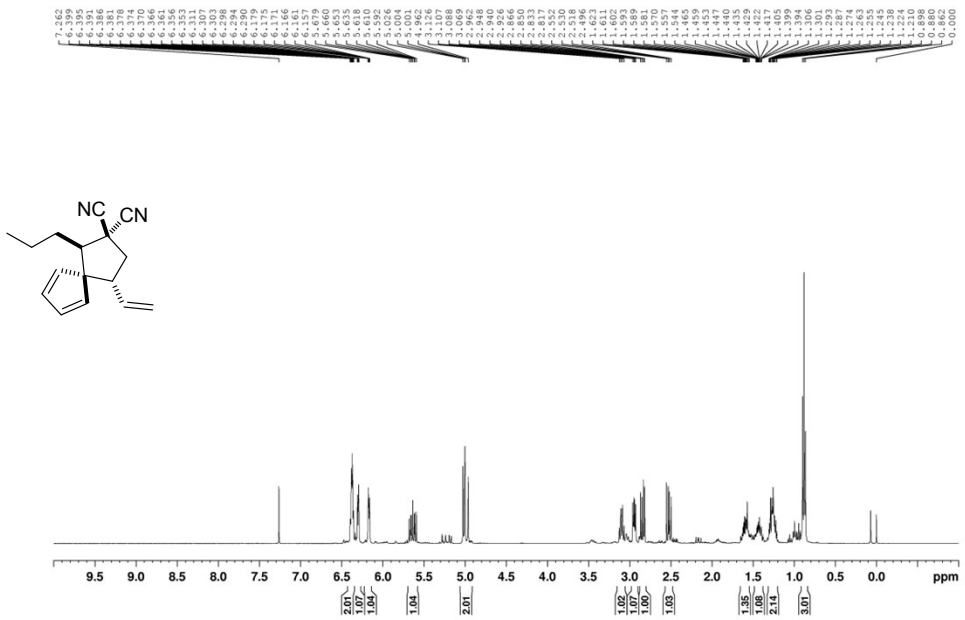
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans* -3am



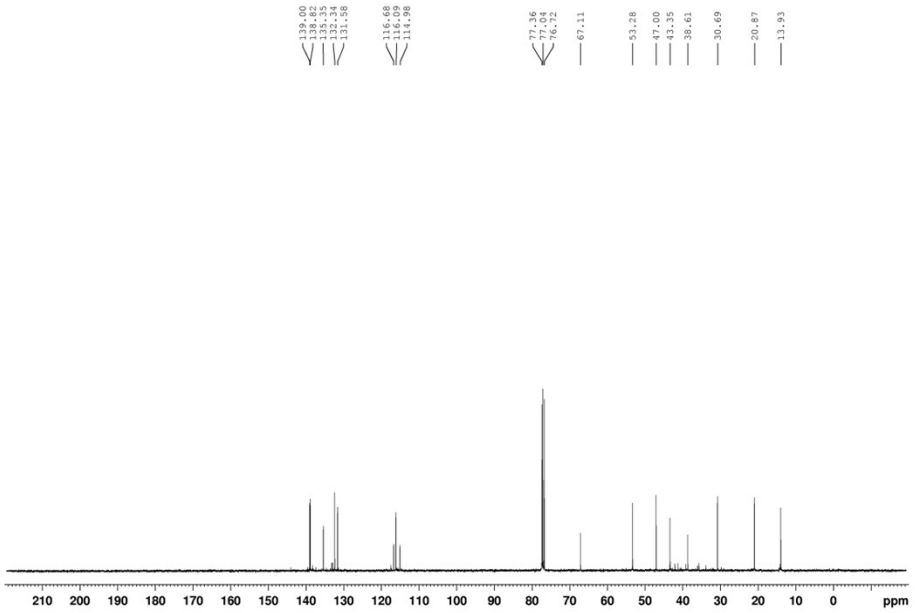
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans* -3am



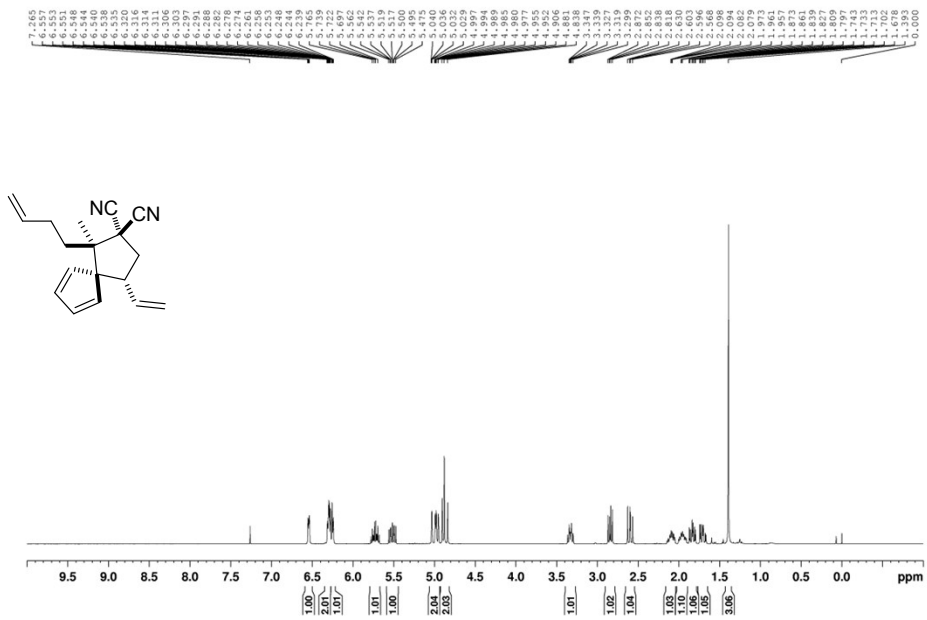
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans* -3an



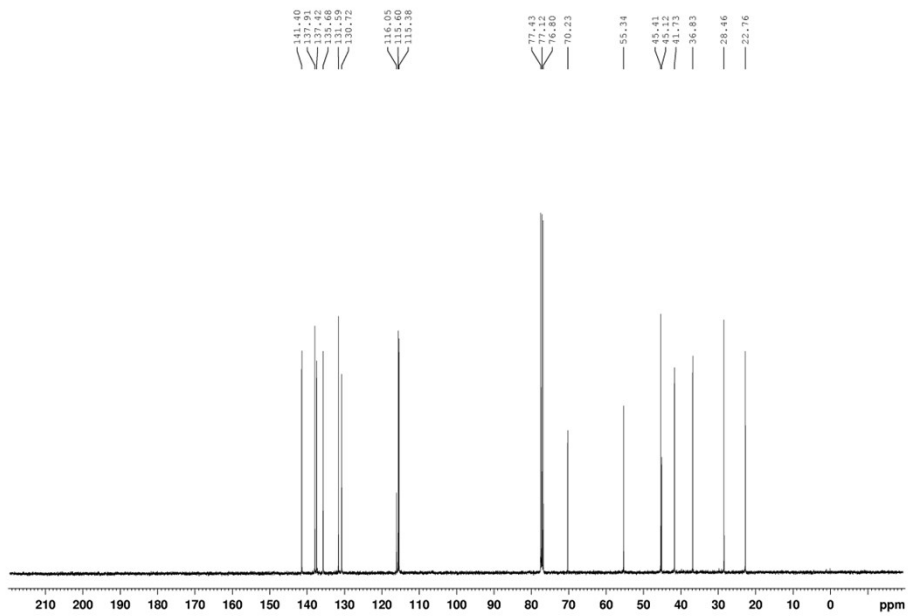
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans* -3an



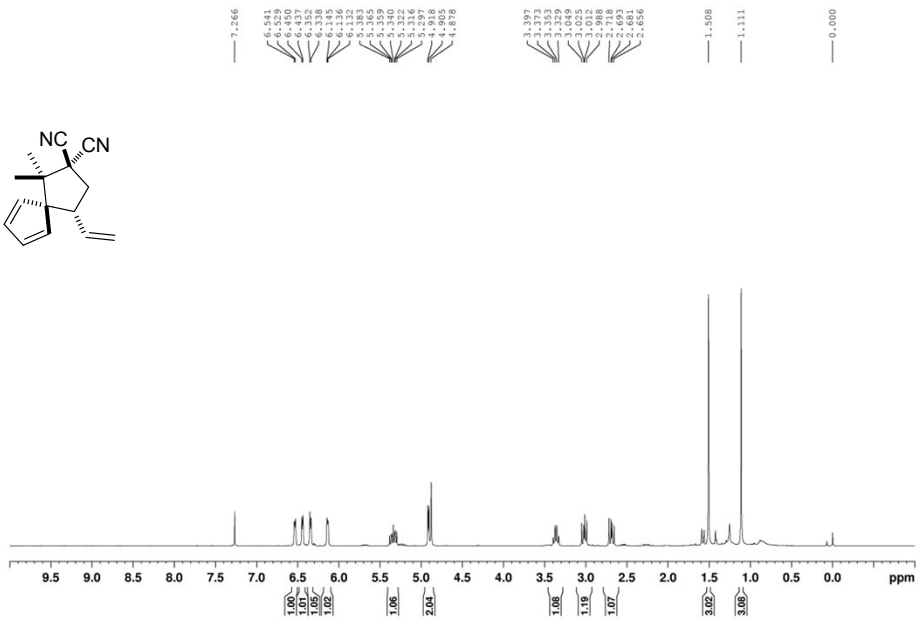
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *major*-3ao



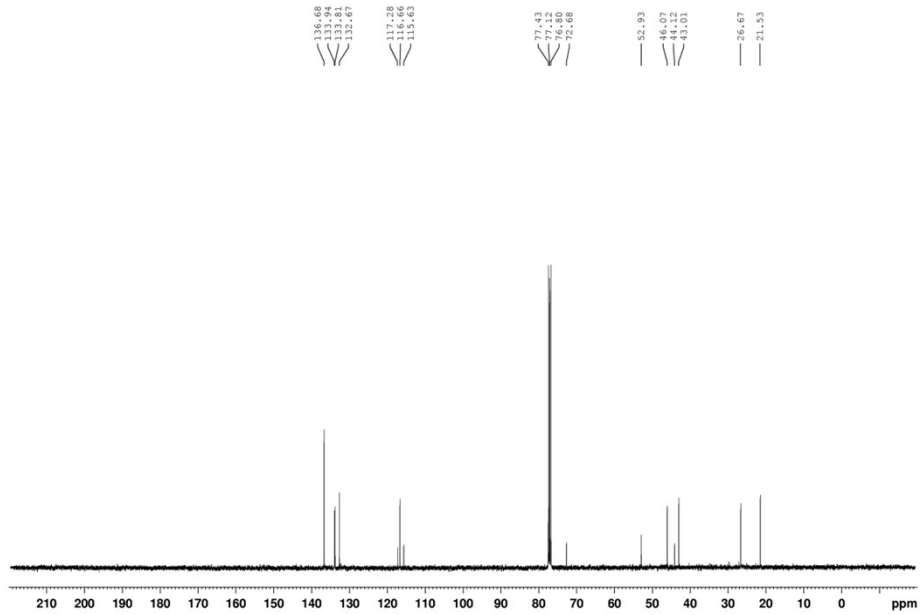
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *major*-3ao



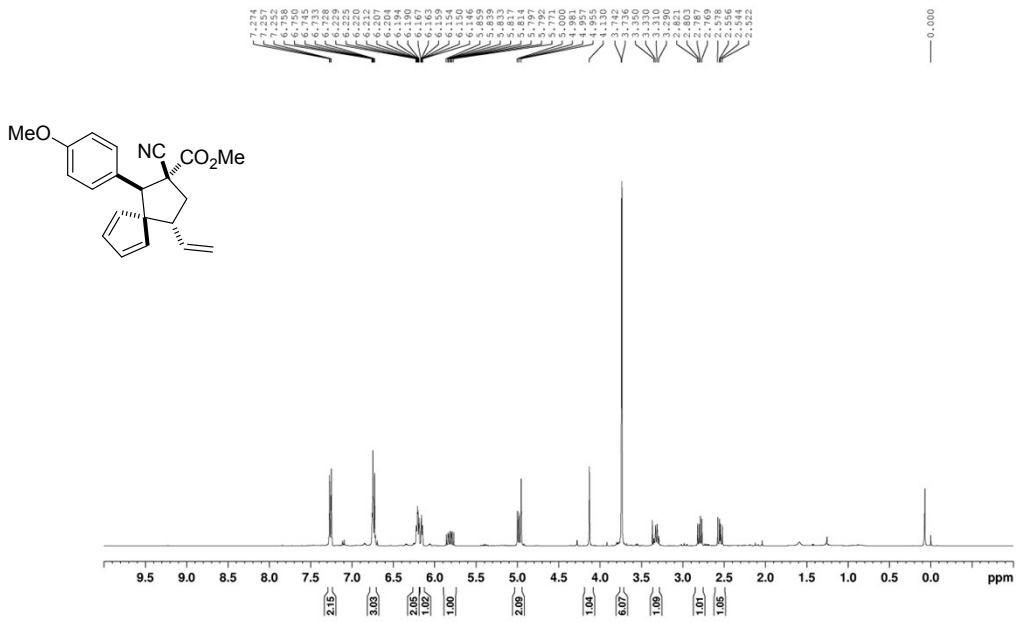
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 3ap



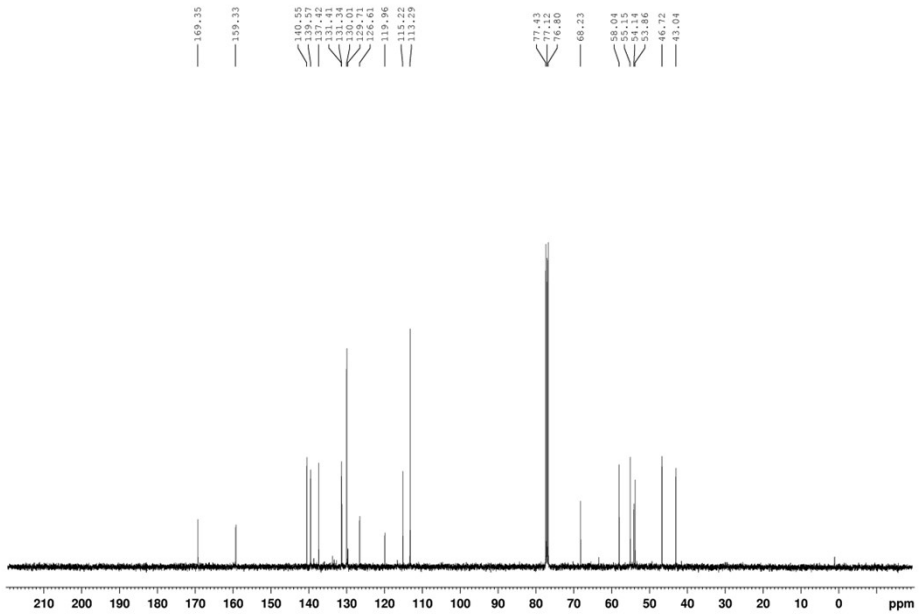
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 3ap



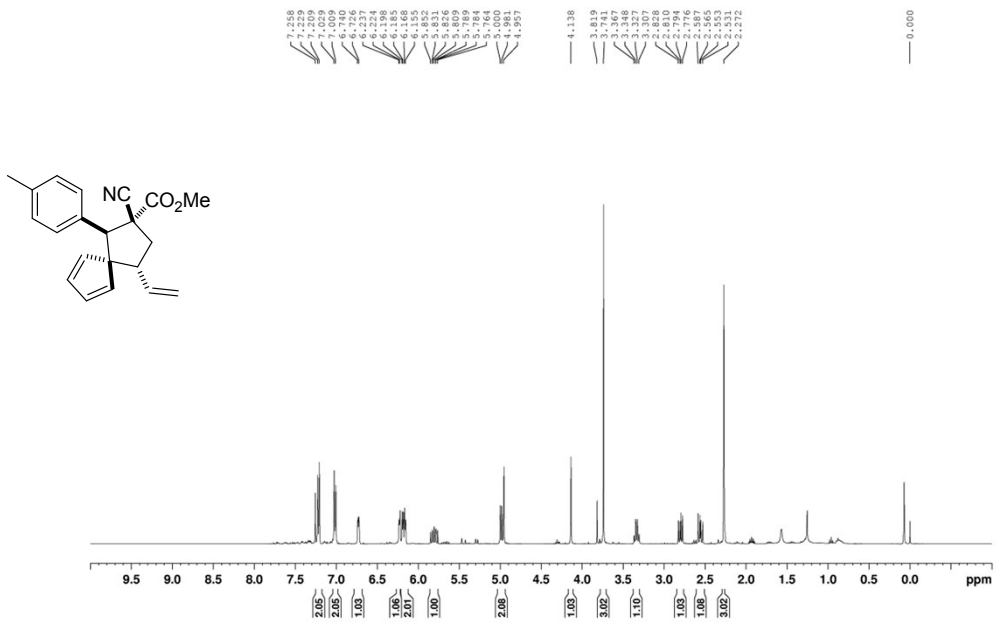
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *major*-3ba



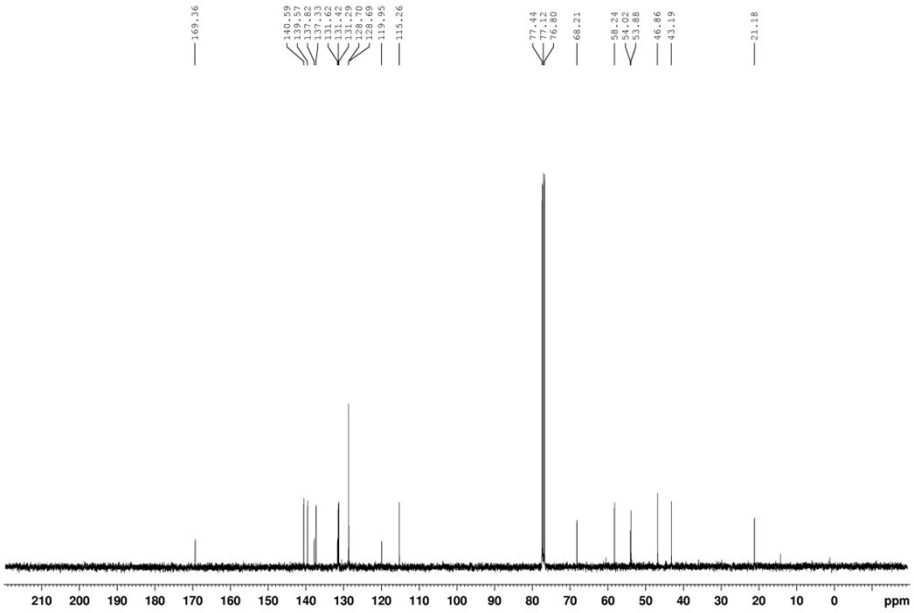
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *major*-3ba



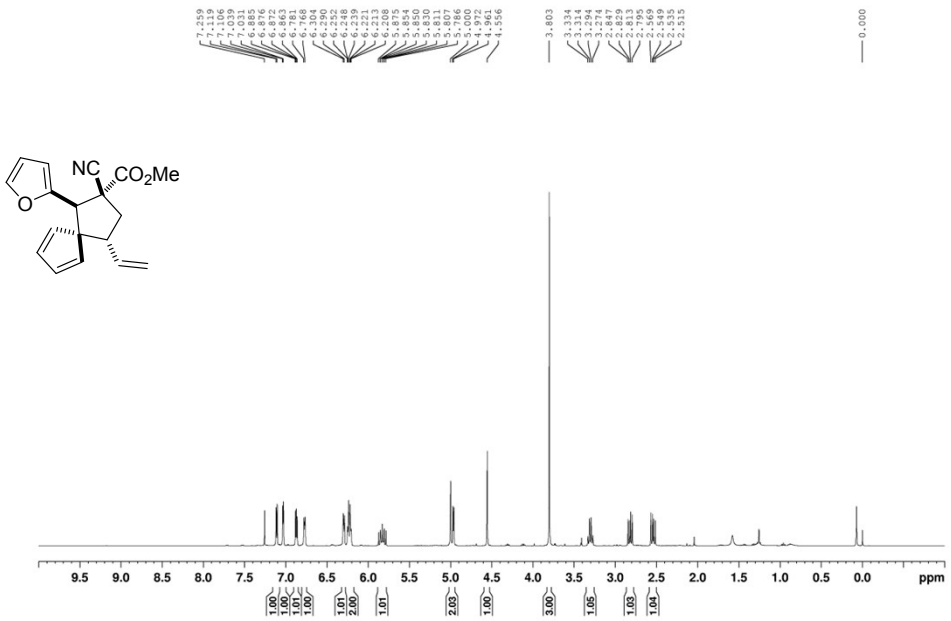
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *major*-3bd



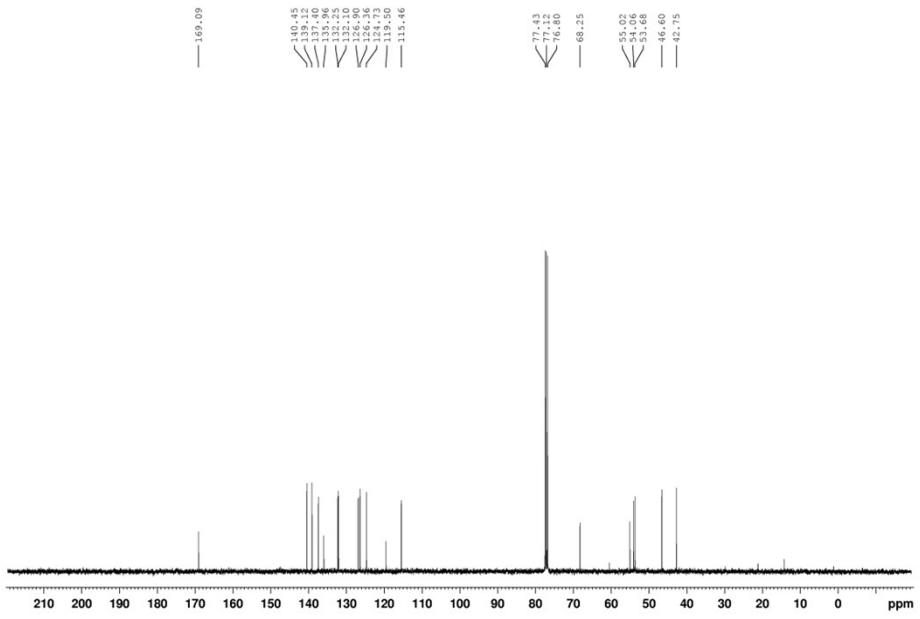
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *major*-3bd



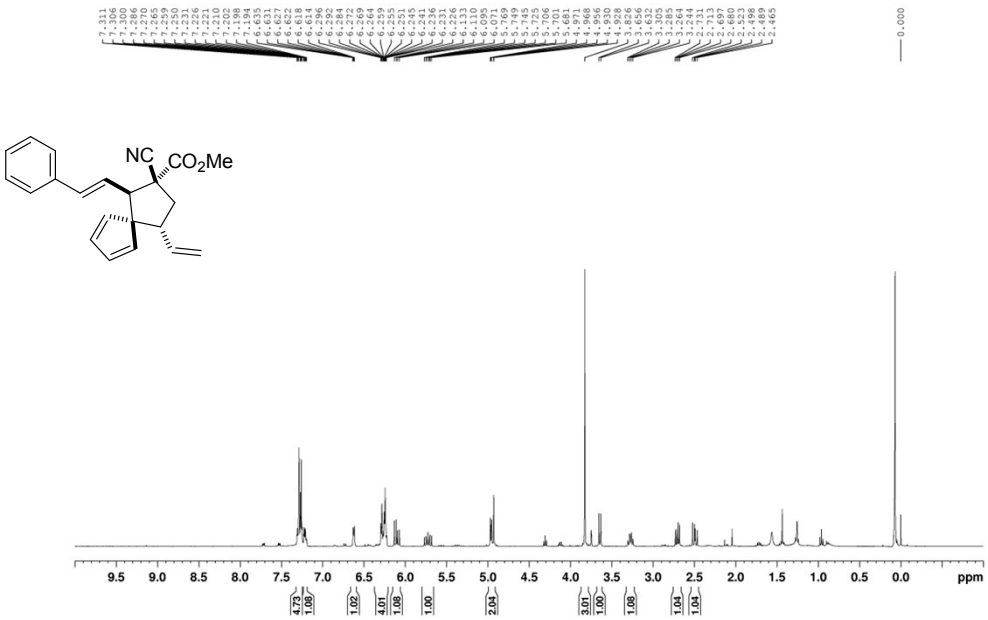
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *major*-3bk



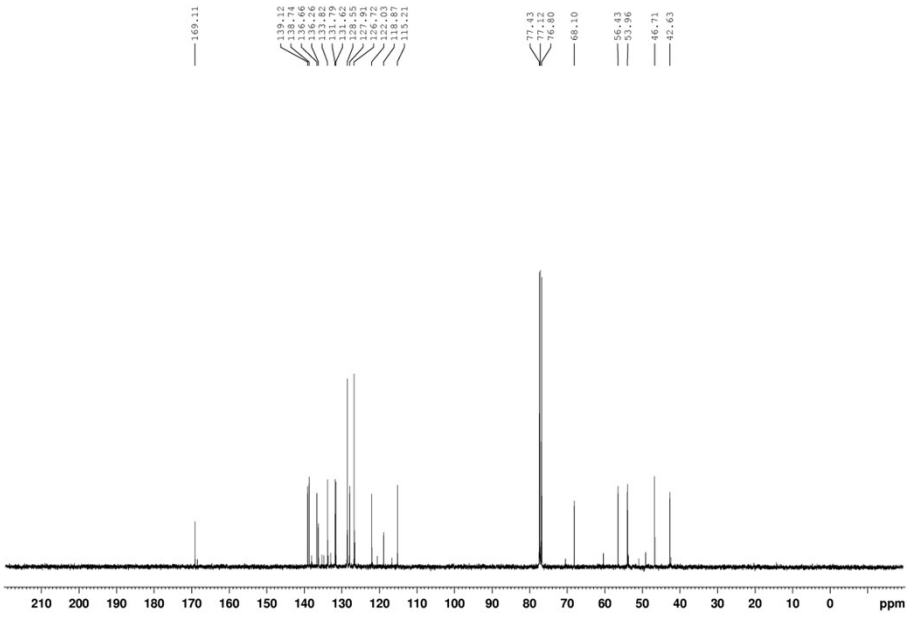
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *major*-3bk



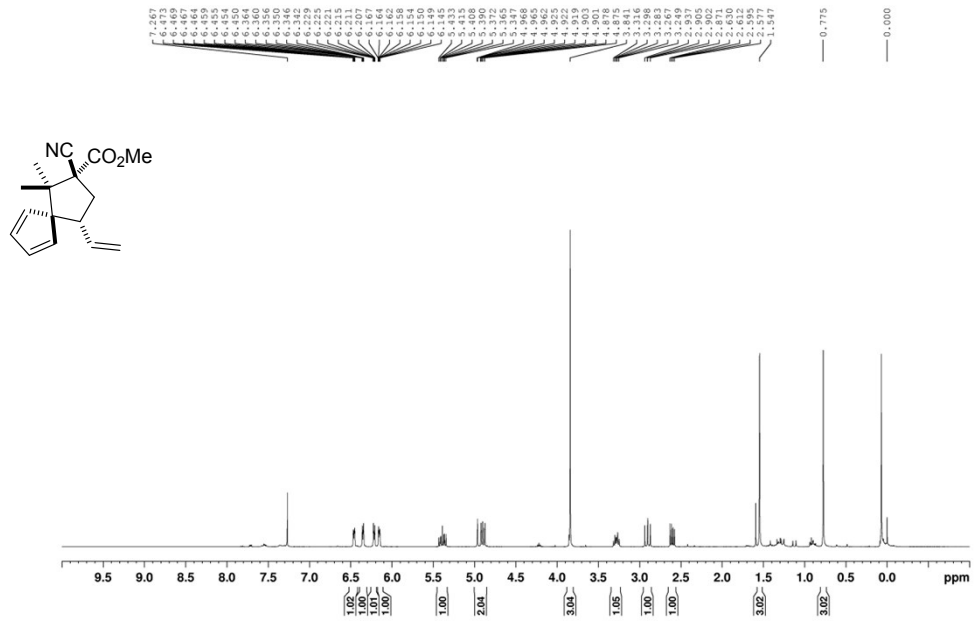
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *major*-3bm



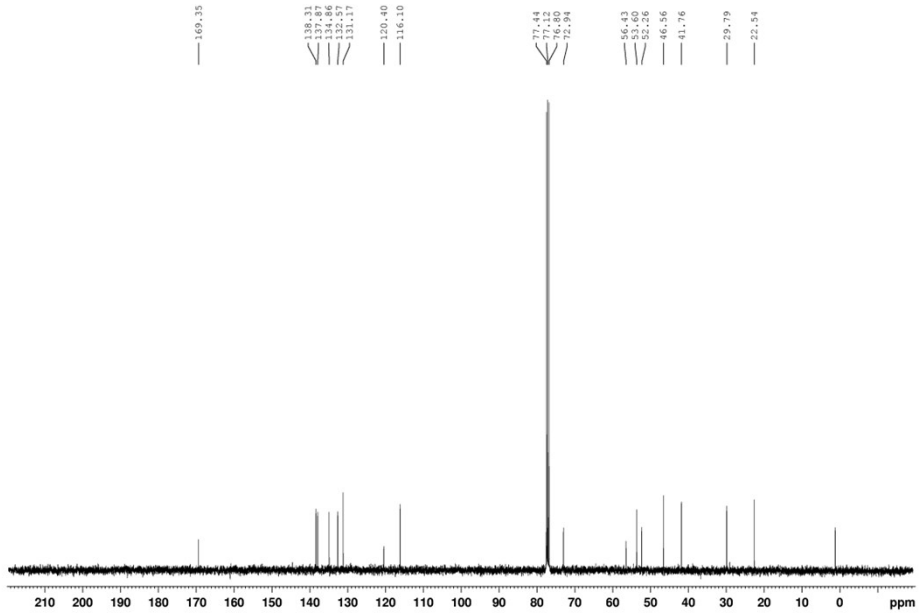
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *major*-3bm



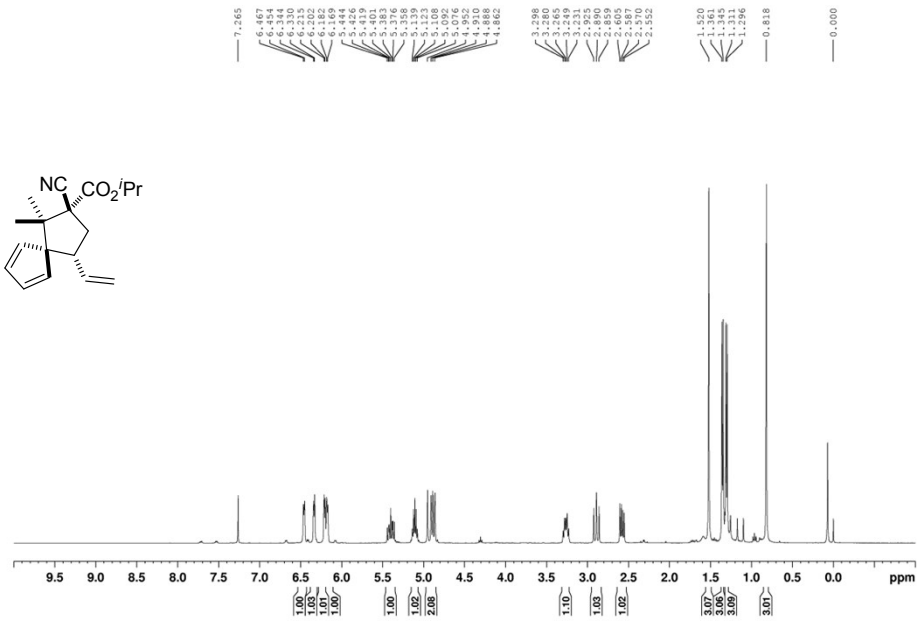
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 3bp



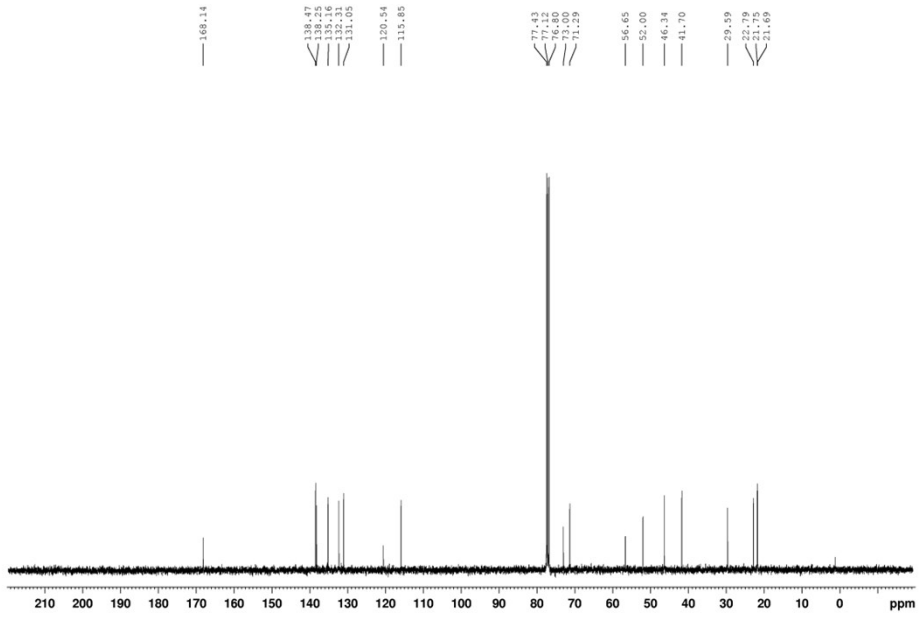
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 3bp



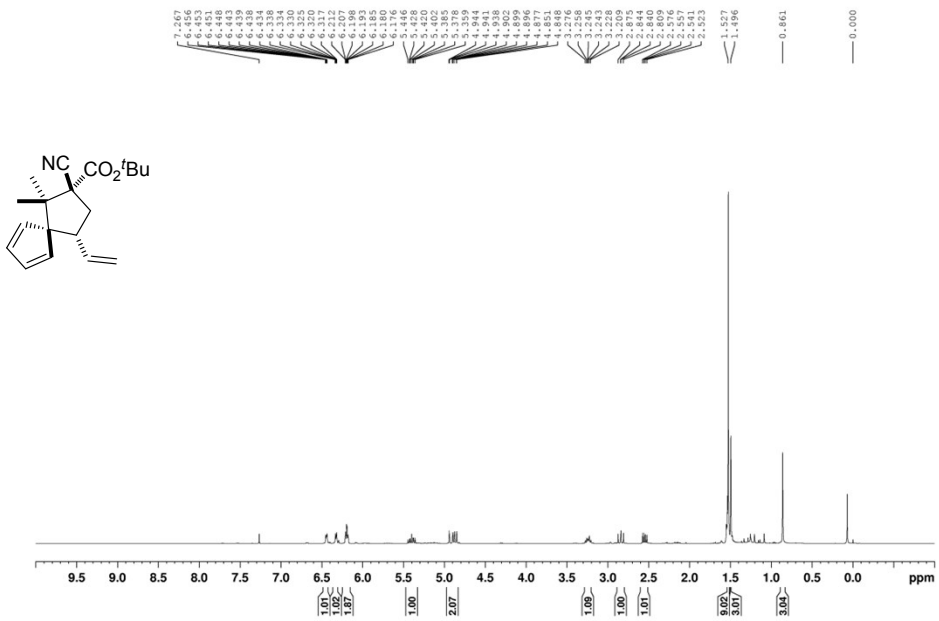
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 3cp



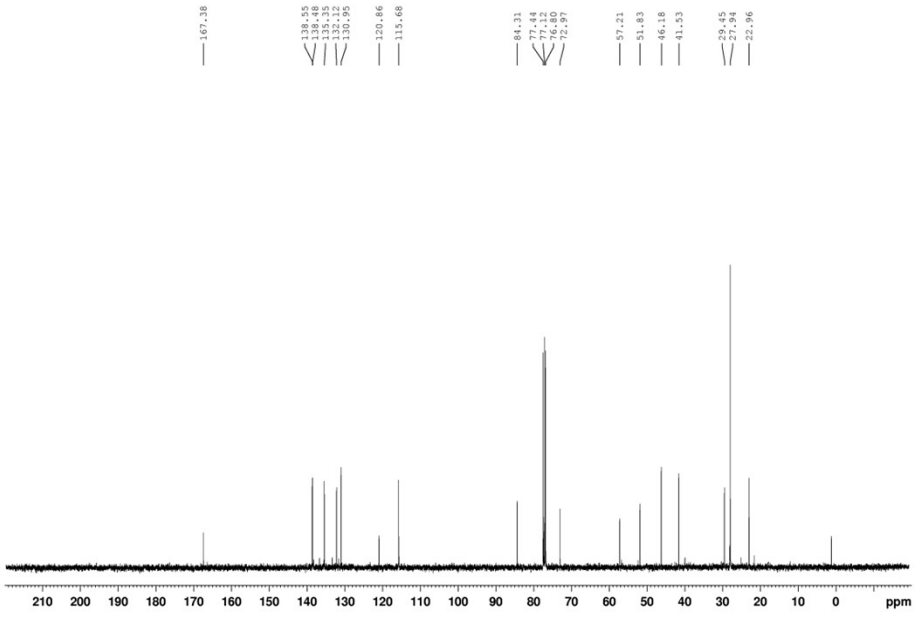
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 3cp



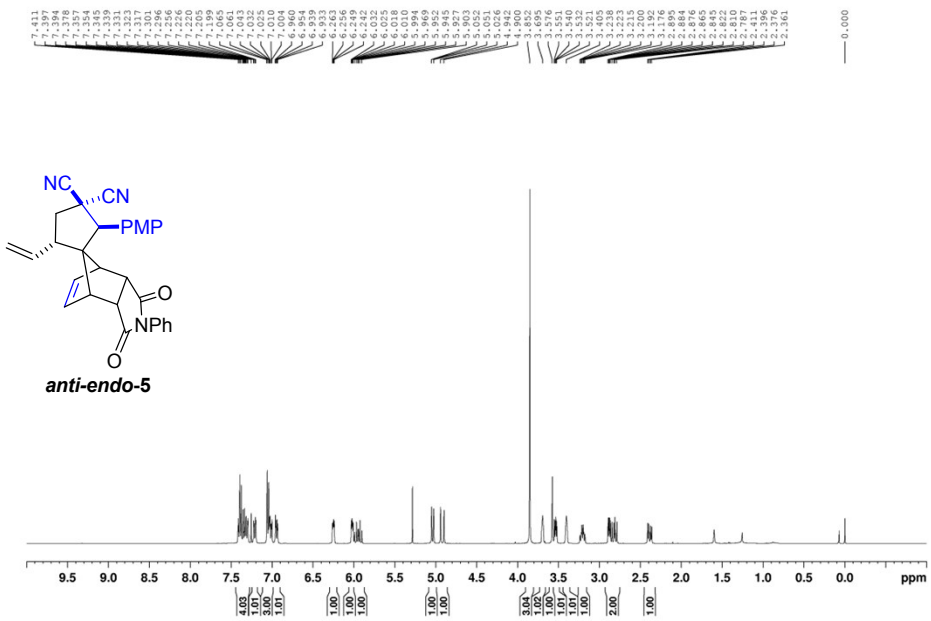
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 3dp



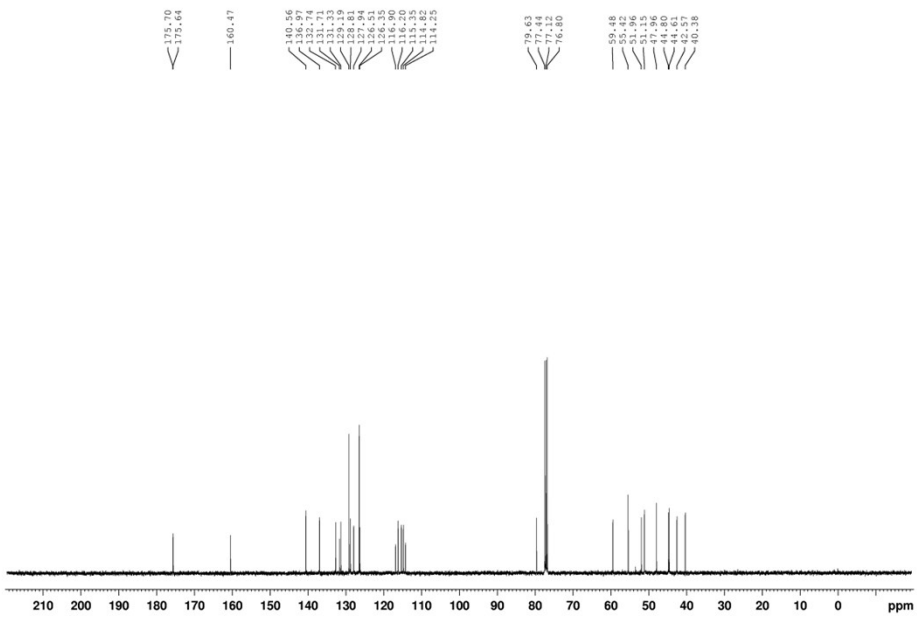
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 3dp



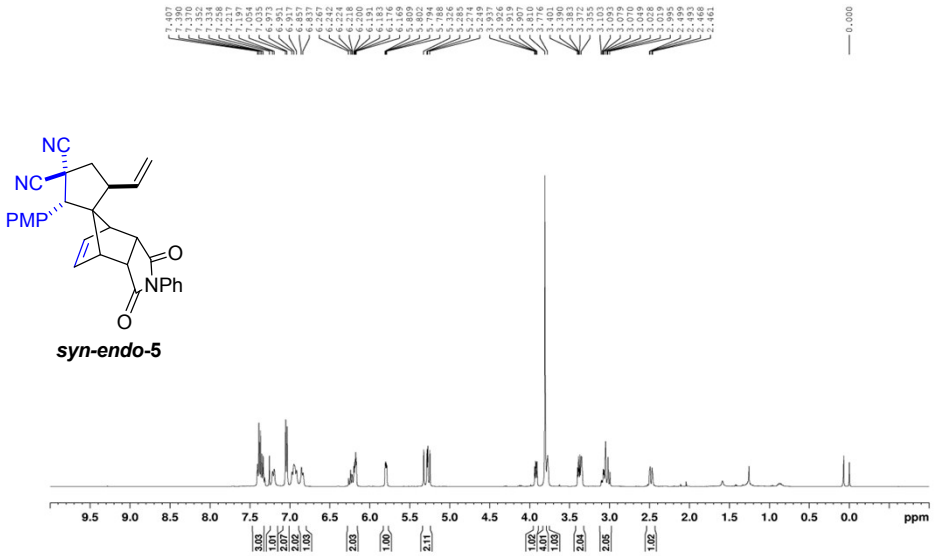
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *anti-endo*-5



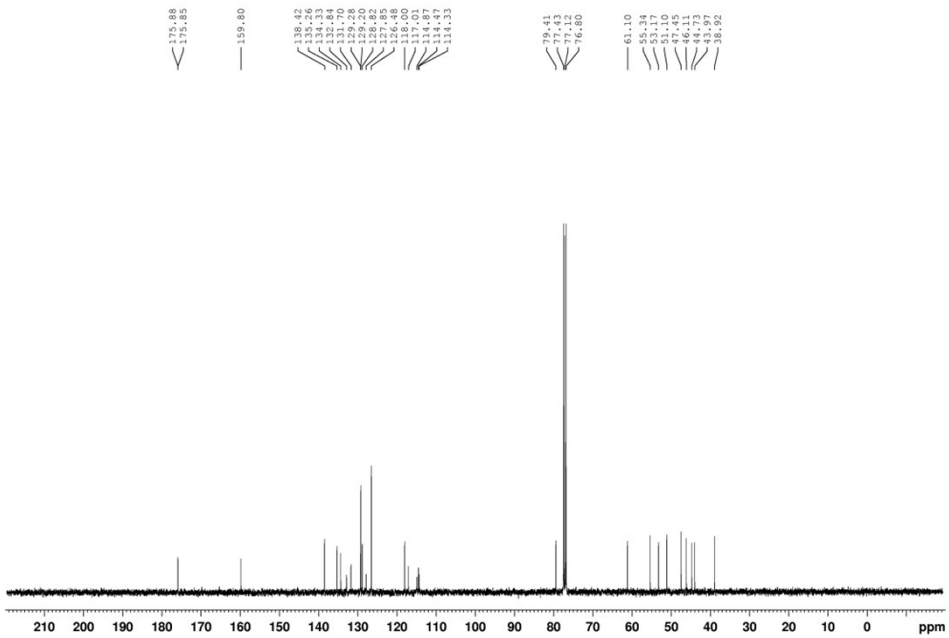
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *anti-endo-5*



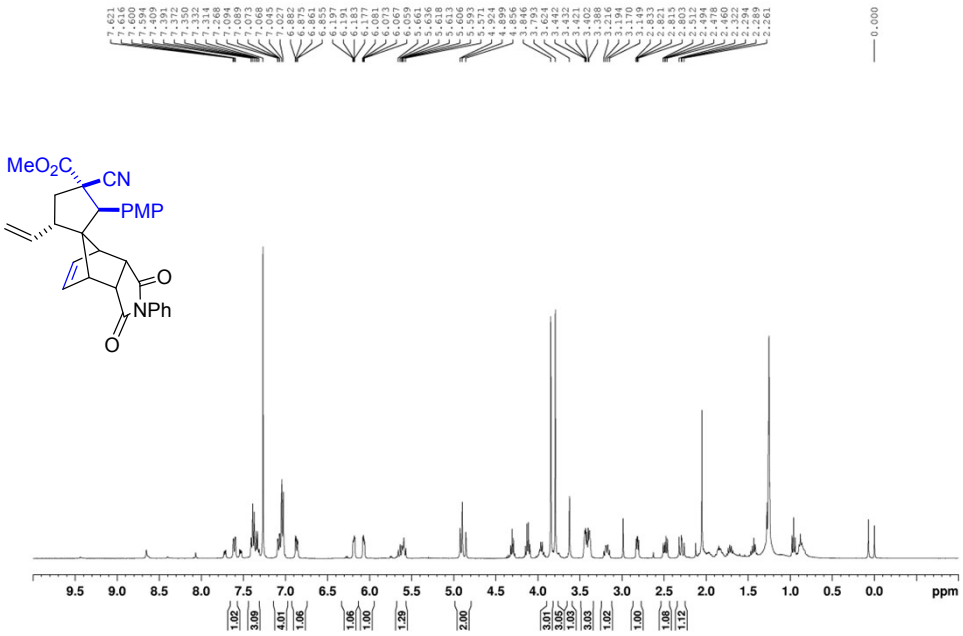
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *syn-endo-5*



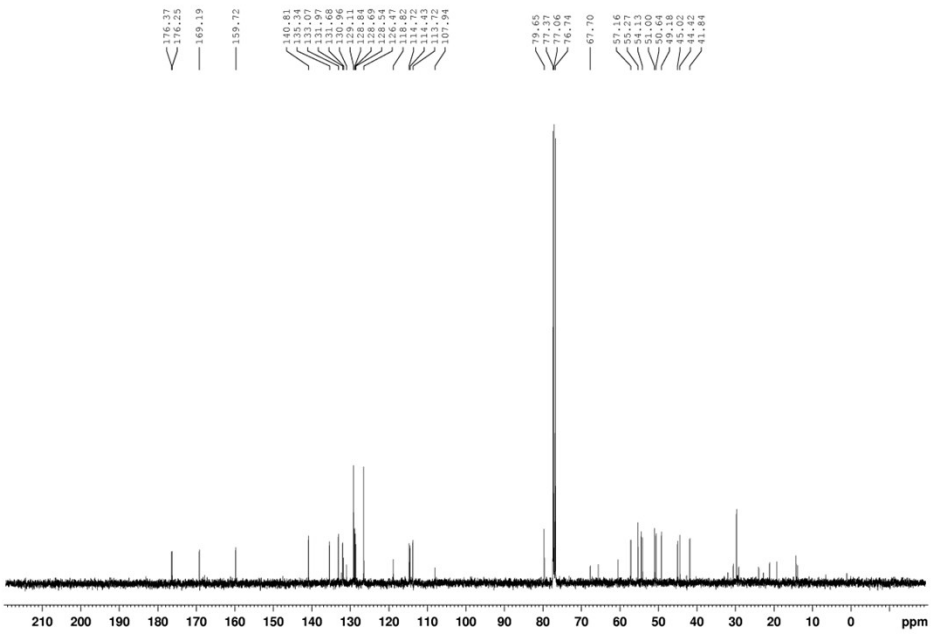
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *syn-endo-5*



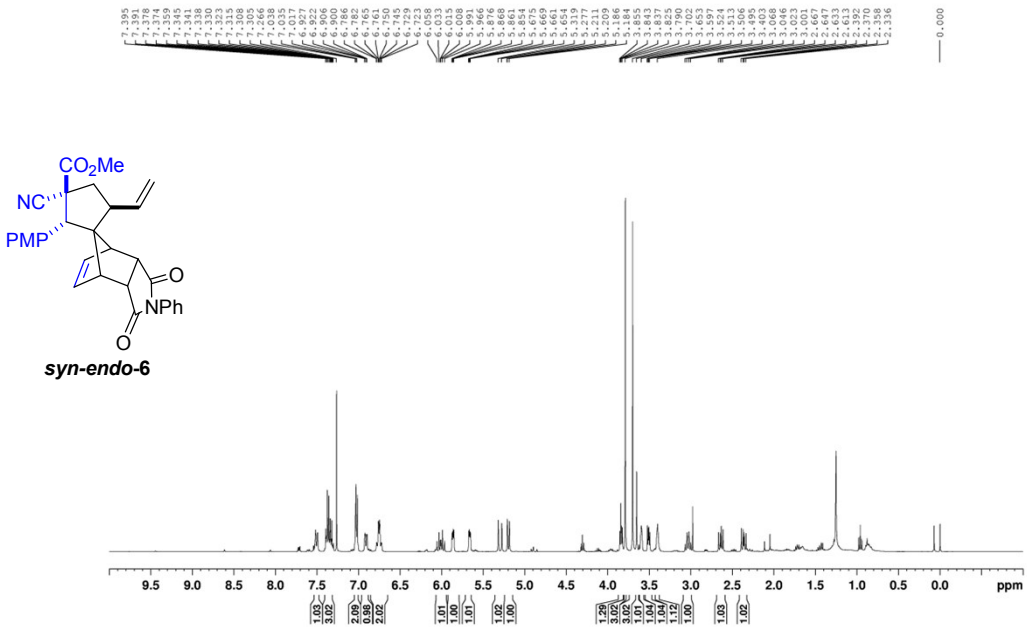
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *anti-endo-6*



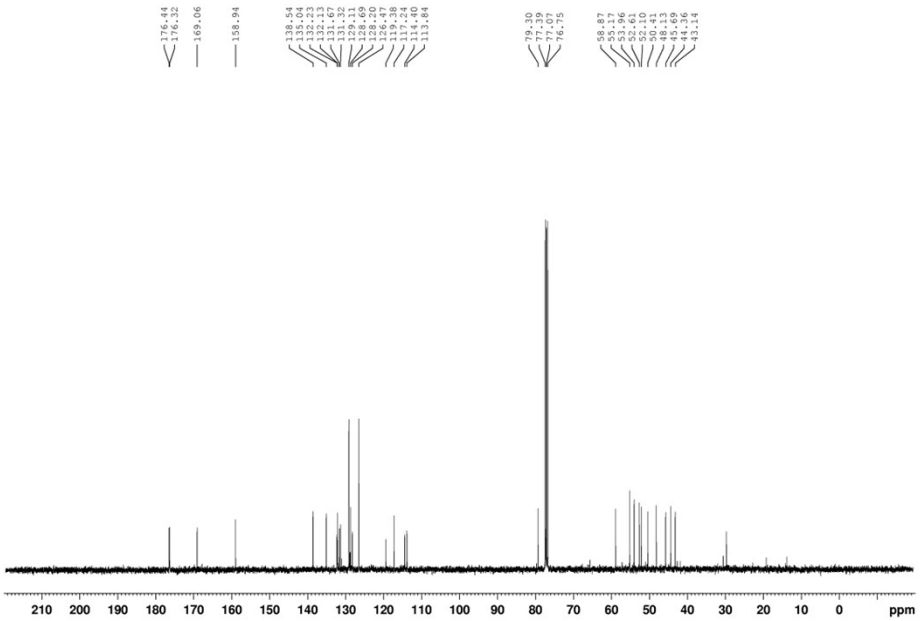
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *anti-endo-6*



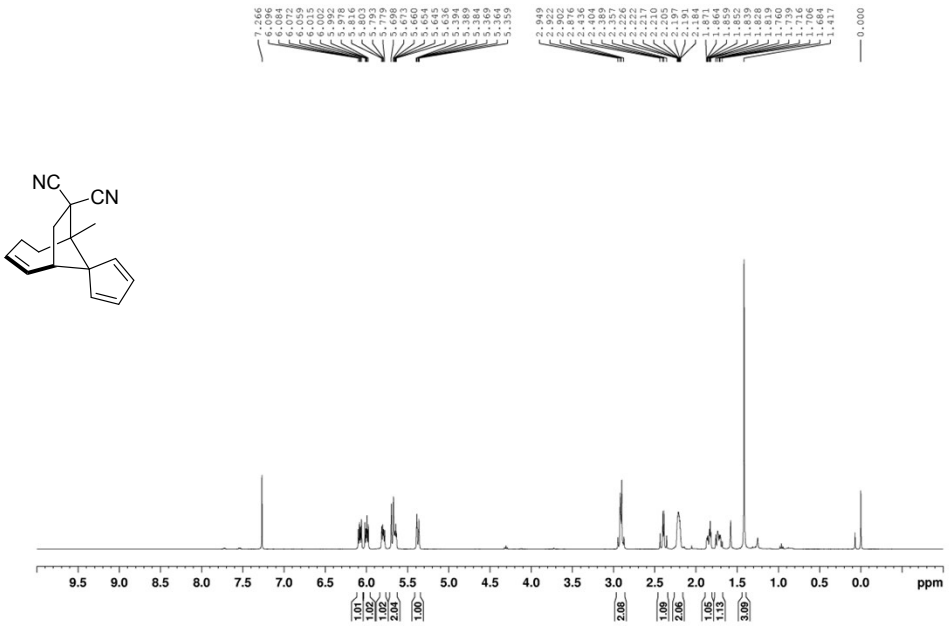
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *syn-endo-6*



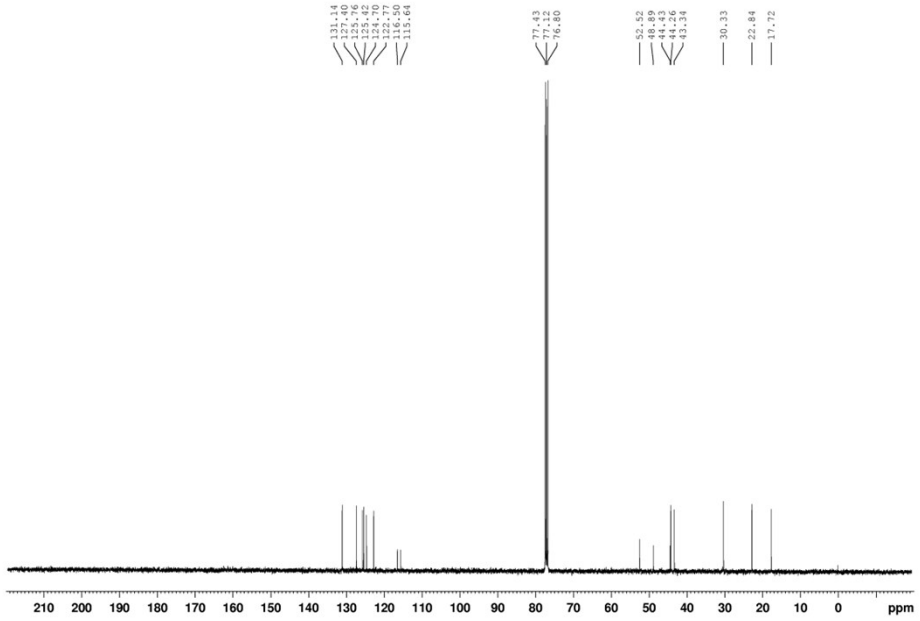
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *syn-endo-6*



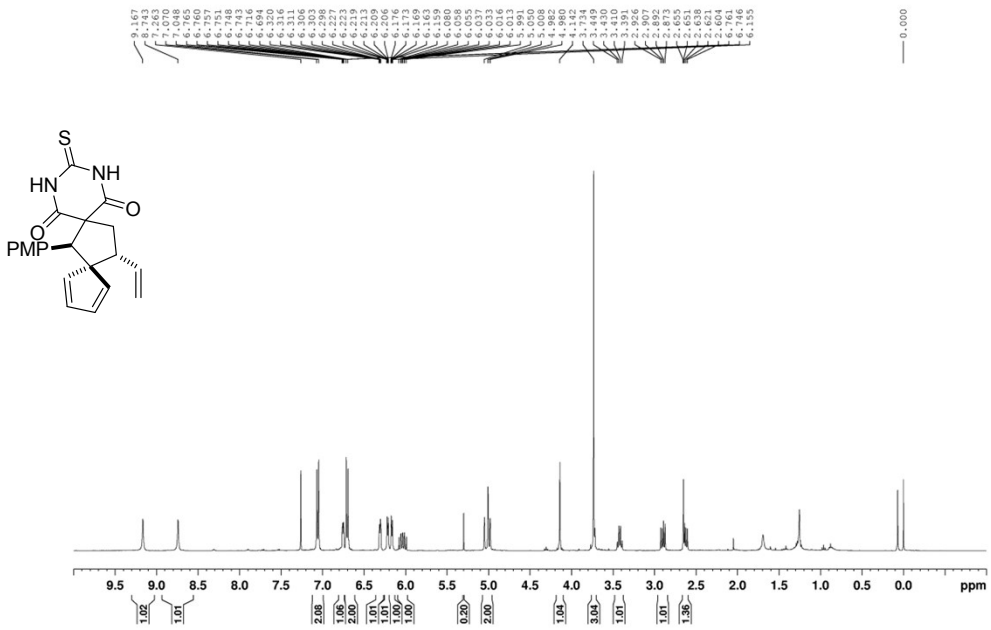
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound 7



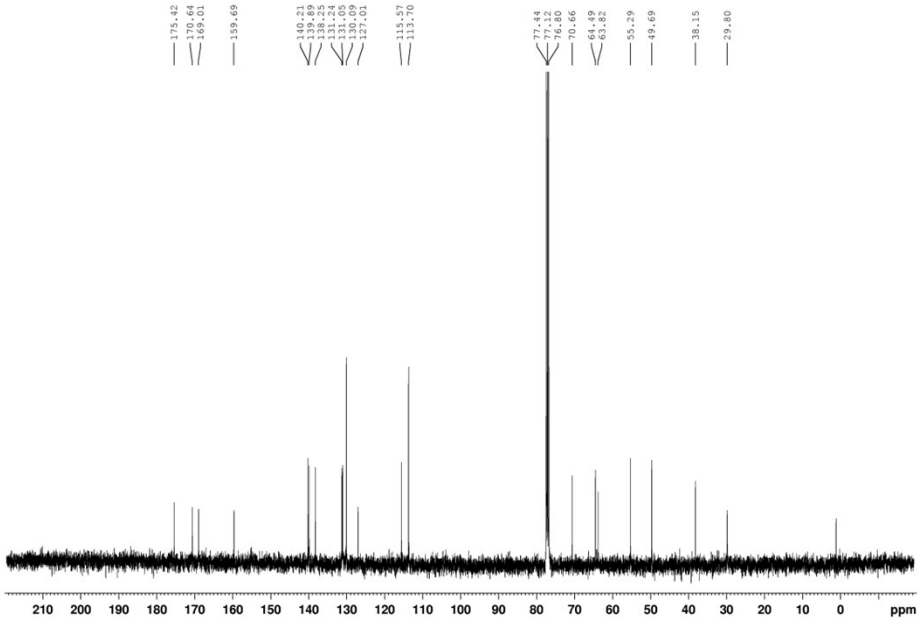
^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound 7



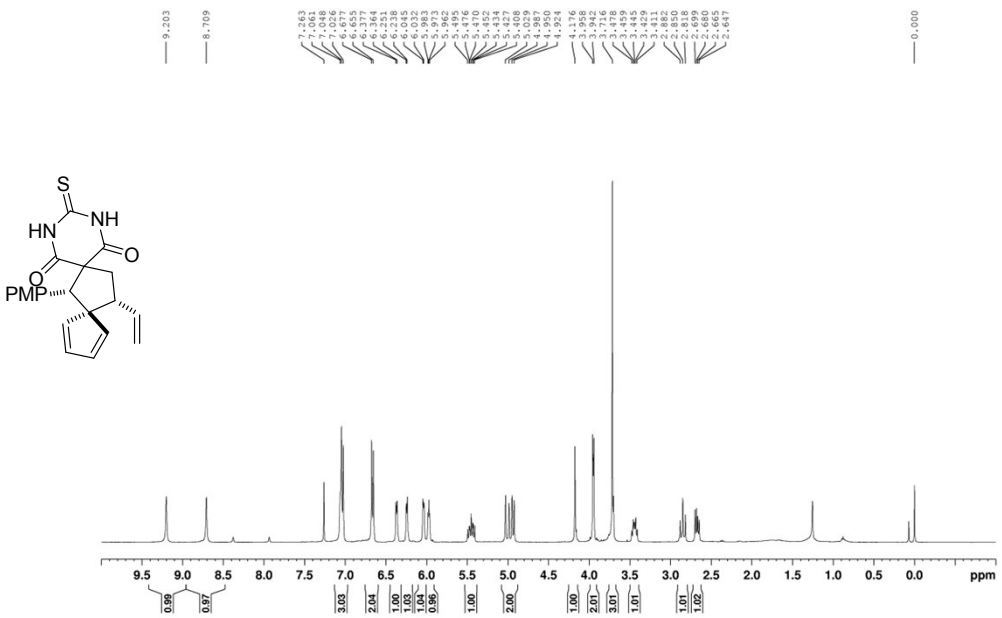
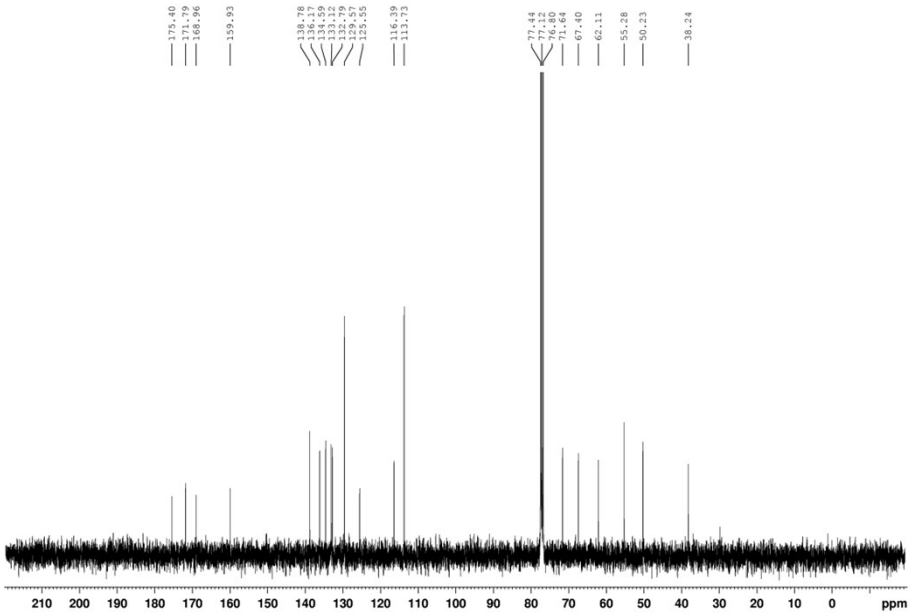
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *trans*-8



^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *trans*-8



^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound *cis*-8



^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound *cis*-8