Intramolecular Alder-Ene Reaction of Cyclopropene with Alkenes

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Supporting Information

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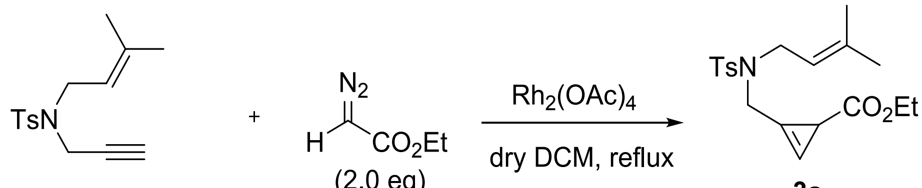
I. General Information and Materials

NMR spectra were recorded using Bruker AV-300 / AV-400 / AV-500 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets), coupling constants (Hz) and integration. High resolution mass spectra were acquired on an agilent 6230 spectrometer and were obtained by peak matching. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gelplates with UV254 fluorescent indicator and/or by exposure to phosphormolybdic acid/ninhydrine followed by brief heating with a heat gun. Liquid chromatography (flash chromatography) was performed on 60Å (40–60 μm) mesh silica gel (SiO_2). All reactions were carried out under nitrogen with anhydrous solvents in oven-dried glassware, unless otherwise noted. All reagents were commercially obtained and, where appropriate, purified prior to use.

II. Preparation and Characterization of Substrates

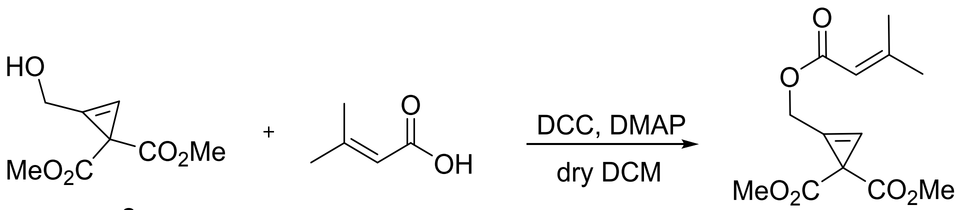
A. **Typical procedure for Cyclopropenation**



s1 **3a**

Typical synthetic procedure a (with **3a** as an example): [1] A mixture of enyne **s1** (500 mg, 1.8 mmol) and $Rh_2(OAc)_4$ (40 mg, 0.05 mmol) in DCM (8 mL) was stirred and refluxed under nitrogen for 5 min. A solution of diazocompound in DCM (1 mL) was added slowly over 5 h. Until substrate **s1** was consumed as indicated by TLC, the resulting reaction mixture was concentrated. Purification of the crude product by flash column chromatography (silica gel; PE: EtOAc = 20: 1) afforded **3a** (254 mg, 37% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.16 (d, J = 1.4 Hz, 1H), 5.11–4.99 (m, 1H), 4.39–4.26 (m, 2H), 4.10–4.00 (m, 2H), 3.82 (d, J = 7.2 Hz, 2H), 2.40 (s, 3H), 1.99 (d, J = 1.2 Hz, 1H), 1.66 (s, 3H), 1.57 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.2, 143.4, 138.6, 137.1, 129.6, 127.5, 118.2, 110.9, 98.5, 60.5, 44.8, 41.7, 25.9, 21.6, 20.4, 17.8, 14.4. **HRMS** (ESI) *m/z* Calculated for $C_{19}H_{25}NNaO_4S^+$ $[M + Na]^+$ 386.1397, found 386.1393.

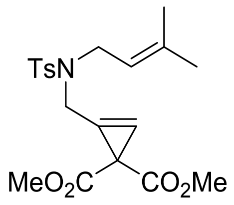
1. A. López-Rodríguez, G. Dominguez and J. Pérez-Castells, *J. Org. Chem.*, **2019**, *84*, 924.



s2 **3r**

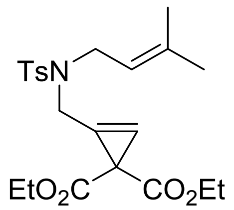
Typical synthetic procedure b (with **3r** as an example): A mixture of **s2** (167 mg, 0.90 mmol), 3-Methyl-2-butenoic acid (100 mg, 1.00 mmol), DCC (206 mg, 1 mmol) and DMAP (11 mg, 0.09 mmol) in DCM (3 mL) was stirred under nitrogen overnight. Until substrate **s2** was consumed as indicated by TLC. The resulting reaction mixture was washed with ammonium chloride aqueous solution and extracted with DCM (3 × 10 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography (silica gel; PE: EtOAc = 10: 1 afforded **3r** (168 mg, 63% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.69 (s, 1H), 5.71 (s, 1H), 5.09 (d, J = 1.4 Hz, 2H), 3.71 (s, 6H), 2.17 (s, 3H), 1.92 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 165.5, 158.9, 114.8, 110.4, 97.2, 55.6, 52.4, 33.0, 27.6, 20.4. **HRMS** (ESI) *m/z* Calculated for $C_{13}H_{16}NaO_6^+$ $[M + Na]^+$ 291.0839, found 291.0842. **IR** (KBr, thin film): 2956, 2920, 2850, 1728, 1652, 1259, 1138, 738 cm^{-1}.

B. Cyclopropene Substrates



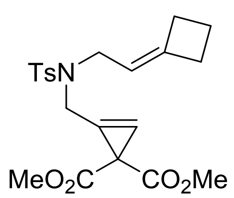
3b

3b: According to the procedure described for the preparation of **3a**, enyne (300 mg, 1.08 mmol) was converted into **3b** (124 mg, 28% yield). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H), 6.08 (s, 1H), 5.05 (t, J = 7.2 Hz, 1H), 4.37 (s, 2H), 3.83 (d, J = 7.3 Hz, 2H), 3.67 (s, 6H), 2.41 (s, 3H), 1.67 (s, 3H), 1.57 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 143.6, 138.9, 136.9, 129.6, 127.6, 118.0, 109.9, 97.4, 52.4, 44.8, 40.9, 32.8, 25.9, 21.6, 17.7. **HRMS** (ESI) *m/z* Calculated for $C_{20}H_{25}NNaO_6S^+$ $[M + Na]^+$ 430.1295, found 430.1296. **IR** (KBr, thin film): 2922, 2849, 1644, 1437, 1342, 1246, 1157, 543 cm^{-1}.



3c

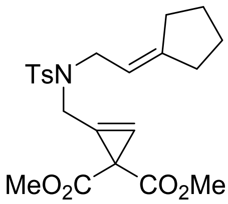
3c: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.80 mmol) was converted into **3c** (136 mg, 17% yield). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 6.07 (s, 1H), 5.07 (t, J = 7.0 Hz, 1H), 4.39 (s, 2H), 4.13 (q, J = 7.1 Hz, 4H), 3.84 (d, J = 7.2 Hz, 2H), 2.41 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H), 1.24 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 143.6, 138.9, 137.1, 129.7, 127.7, 118.1, 110.2, 97.6, 61.3, 44.8, 41.1, 33.2, 25.9, 21.6, 17.8, 14.2. **HRMS** (ESI) *m/z* Calculated for $C_{22}H_{29}NNaO_6S^+$ $[M + Na]^+$ 458.1608, found 458.1608.



3d

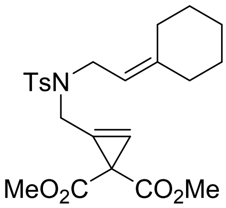
3d: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.73 mmol) was converted into **3d** (115 mg, 16% yield). White soild. Mp: 38.4~40.5 ^{o}C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 6.10 (s, 1H), 5.08–4.90 (m, 1H), 4.40 (s, 2H), 3.73 (d, J = 7.3 Hz, 2H), 3.70 (s, 6H), 2.67–2.54 (m, 4H), 2.42 (s, 3H), 1.98–1.85 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 147.9, 143.6, 137.0, 129.7, 127.6, 113.6, 110.0, 97.3, 52.4, 45.0, 41.0, 32.9, 31.2, 29.2, 21.6, 17.1. **HRMS** (ESI) *m/z* Calculated for $C_{21}H_{25}NNaO_6S^+$ $[M + Na]^+$

442.1295, found 442.1296.



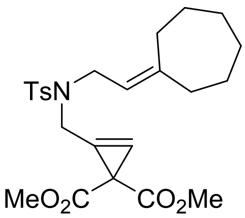
3e

3e: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.65 mmol) was converted into **3e** (140 mg, 20% yield). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 6.08 (s, 1H), 5.21–5.06 (m, 1H), 4.38 (s, 2H), 3.83 (d, *J* = 7.0 Hz, 2H), 3.67 (s, 6H), 2.41 (s, 3H), 2.20 (t, *J* = 6.8 Hz, 2H), 2.13 (t, *J* = 6.7 Hz, 2H), 1.67–1.51 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170., 150.5, 143.6, 137.0, 129.6, 127.6, 113.5, 110.0, 97.3, 52.4, 46.5, 41.1, 33.9, 32.9, 28.6, 26.3, 26.1, 21.6. **HRMS** (ESI) *m/z* Calculated for $C_{22}H_{27}NNaO_6S^+$ $[M + Na]^+$ 456.1451, found 456.1455.



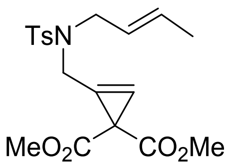
3f

3f: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.58 mmol) was converted into **3f** (180 mg, 25% yield). White soild. Mp: 63.8~65.8 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 9.5 Hz, 2H), 6.08 (s, 1H), 4.98 (t, *J* = 7.1 Hz, 1H), 4.35 (s, 2H), 3.82 (d, *J* = 7.3 Hz, 2H), 3.65 (s, 6H), 2.38 (s, 3H), 2.02 (d, *J* = 4.6 Hz, 4H), 1.47 (s, 4H), 1.41 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 146.8, 143.5, 136.9, 129.6, 127.5, 114.6, 109.9, 97.4, 52.3, 43.8, 40.6, 37.1, 32.8, 28.5, 28.3, 27.8, 26.5, 21.5. **HRMS** (ESI) *m/z* Calculated for $C_{23}H_{29}NNaO_6S^+$ $[M + Na]^+$ 470.1608, found 470.1604.



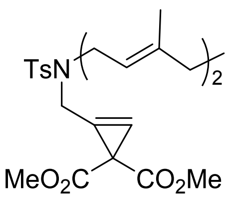
3g

3g: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.51 mmol) was converted into **3g** (147 mg, 21% yield). Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* =7.6 Hz, 2H), 6.07 (s, 1H), 5.04 (t, *J* = 6.6 Hz, 1H), 4.37 (s, 2H), 3.82 (d, *J* = 7.0 Hz, 2H), 3.65 (s, 6H), 2.39 (s, 3H), 2.15 (s, 3H), 1.57–1.35 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 148.4, 143.6, 137.0, 129.7, 127.7, 118.2, 110.0, 97.5, 52.4, 44.5, 41.1, 37.8, 32.9, 29.8, 29.7, 29.1, 29.0, 27.1, 21.6. **HRMS** (ESI) *m/z* Calculated for $C_{24}H_{31}NNaO_6S^+$ $[M + Na]^+$ 484.1764, found 484.1765.



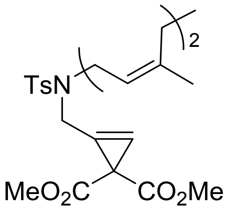
3h

3h: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.90 mmol) was converted into **3h** (164 mg, 22% yield). White soild. Mp: 61.8~64.2 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.03 (s, 1H), 5.66–5.49 (m, 1H), 5.35–5.22 (m, 1H), 4.38 (s, 2H), 3.76 (d, *J* = 6.8 Hz, 2H), 3.66 (s, 6H), 2.40 (s, 3H), 1.62 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 143., 136.8, 132.1, 129.7, 127.5, 124.4, 109.6, 97.4, 52.4, 49.1, 40.7, 32.7, 21.6, 17.7. **HRMS** (ESI) *m/z* Calculated for $C_{19}H_{23}NNaO_6S^+$ $[M + Na]^+$ 416.1138, found 416.1134. **IR** (KBr, thin film): 2900, 2849, 1718, 1654, 1437, 1260, 1159, 543 cm^{-1}.



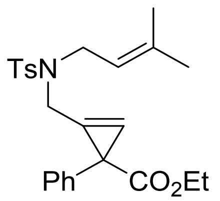
3i

3i: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.51 mmol) was converted into **3i** (160 mg, 23% yield). Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.06 (s, 1H), 5.08–4.92 (m, 2H), 4.36 (d, *J* = 1.2 Hz, 2H), 3.85 (d, *J* = 7.3 Hz, 2H), 3.65 (s, 6H), 2.39 (s, 3H), 2.07–1.91 (m, 4H), 1.63 (s, 3H), 1.55 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 143.6, 142.4, 137.0, 131.9, 129.6, 127.6, 123.7, 117.7, 109.8, 97.4, 52.3, 44.6, 40.7, 39.6, 32.8, 26.2, 25.7, 21.6, 17.7, 16.0. **HRMS** (ESI) *m/z* Calculated for $C_{25}H_{33}NNaO_6S^+$ $[M + Na]^+$ 498.1921, found 498.1923.



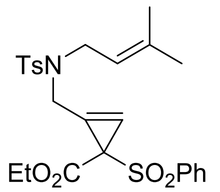
3j

3j: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.51 mmol) was converted into **3j** (124 mg, 18% yield). Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.09 (s, 1H), 5.12–4.95 (m, 2H), 4.36 (d, *J* = 1.1 Hz, 2H), 3.82 (d, *J* = 6.9 Hz, 2H), 3.66 (s, 6H), 2.41 (s, 3H), 2.04–1.93 (m, 4H), 1.68 (s, 3H), 1.65 (s, 3H), 1.56 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 143.6, 142.3, 136.9, 132.2, 129.7, 127., 123.6, 118.8, 100.0, 97.5, 52.4, 44.6, 41.0, 32.7, 31.8, 26.5, 25.8, 23.6, 21.6, 17.7. **HRMS** (ESI) *m/z* Calculated for $C_{25}H_{33}NNaO_6S^+$ $[M + Na]^+$ 498.1921, found 498.1919.



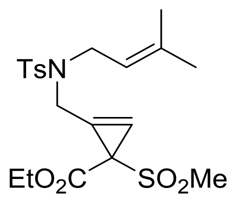
3k

3k: According to the procedure described for the preparation of **3a** ($Rh_2(piv)_4$ was used to substitute $Rh_2(OAc)_4$), enyne (500 mg, 1.90 mmol) was converted into **3k** (137 mg, 16% yield). Yellow oil. **¹H NMR** (300 MHz, $CDCl_3$) δ 7.70–7.64 (m, 2H), 7.31–7.17 (m, 5H), 7.16–7.09 (m, 2H), 6.38 (t, *J* = 1.6 Hz, 1H), 5.06–4.96 (m, 1H), 4.57 –4.22 (m, 2H), 4.17-4.08 (m, 2H), 3.81 (d, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.62 (d, *J* = 0.7 Hz, 3H), 1.44 (d, *J* = 0.7 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (75 MHz, $CDCl_3$) δ 174.3, 143.5, 140.4, 138.7, 137.2, 129.6, 128.3, 128.1, 127.7, 126.7, 118.2, 116.5, 101.0, 61.0, 44.8, 41.5, 33.9, 25.8, 21.6, 17.7, 14.4. **HRMS** (ESI) *m/z* Calculated for $C_{25}H_{29}NNaO_4S^+$ $[M + Na]^+$ 462.1710, found 462.1711.



3l

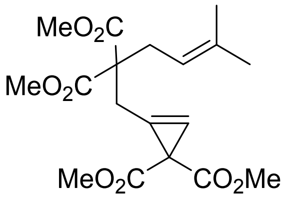
3l: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.80 mmol) was converted into **3l** (305 mg, 34% yield). Colorless oil. **¹H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.1 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.64–7.58 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.13 (s, 1H), 5.13–5.04 (m, 1H), 4.46 (s, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.90 (d, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.68 (s, 3H), 1.63 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (100 MHz, $CDCl_3$) δ 167.0, 143.7, 139.8, 139.4, 136.6, 133.6, 129.7, 129.0, 128.9, 127.7, 117.7, 97.6, 62.1, 52.3, 45.1, 41.2, 25.9, 21.6, 17.9, 14.0. **HRMS** (ESI) *m/z* Calculated for $C_{25}H_{29}NNaO_6S_2^+$ $[M + Na]^+$ 526.1329, found 526.1329. **IR** (KBr, thin film): 2922, 2949, 1646, 1445, 1303, 1245, 1146, 543 cm^{-1}.



3m

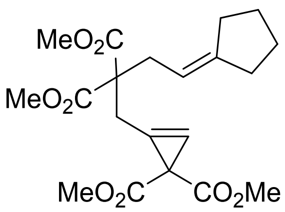
3m: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.80 mmol) was converted into **3m** (245 mg, 31% yield). Colorless oil. **¹H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.46 (s, 1H), 4.94 (t, *J* = 7.0 Hz, 1H), 4.43 (d, J = 18.3 Hz, 1H), 4.31–4.22 (m, 3H), 3.86 (qd, J = 15.0, 7.3 Hz, 2H), 3.24 (s, 3H), 2.43 (s, 3H), 1.66 (s, 3H), 1.62 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$)δ 167.7, 143.9, 139.5, 136.7, 129.8, 127.5, 117.4, 111.6, 97.3, 62.5, 50.9, 45.2, 41.9, 40.5, 25.9, 21.6, 17.9, 14.2. **HRMS** (ESI) *m/z* Calculated for $C_{20}H_{27}NNaO_6S_2^+$ $[M + Na]^+$ 464.1172, found 464.1177. **IR** (KBr, thin film): 3147, 2921, 2851, 1726, 1633, 1136, 724, 541 cm^{-1}.



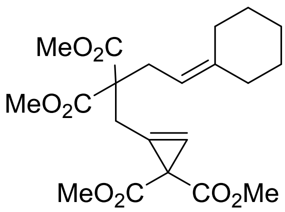
3n

3n: According to the procedure described for the preparation of **3a**, enyne (500 mg, 2.10 mmol) was converted into **3n** (160 mg, 30 % yield). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.46 (s, 1H), 4.89 (t, J = 7.6 Hz, 1H), 3.69 (s, 6H), 3.67 (s, 6H), 3.11 (d, J = 1.2 Hz, 2H), 2.71 (d, J = 7.6 Hz, 2H), 1.67 (s, 3H), 1.57 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.1, 170.5, 137.0, 116.9, 110.8, 96.8, 56.5, 52.9, 52.3, 32.1, 31.3, 27.6, 26.2, 17.9. **HRMS** (ESI) *m/z* Calculated for $C_{18}H_{24}NaO_8^+$ $[M + Na]^+$ 391.1363, found 391.1364.



3o

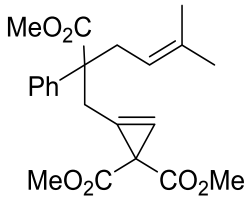
3o: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.89 mmol) was converted into **3o** (89 mg, 12% yield). Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.47 (s, 1H), 5.03 (s, 1H), 3.71 (s, 6H), 3.69 (s, 6H), 3.14 (s, 2H), 2.72 (d, J = 7.5 Hz, 2H), 2.21 (t, J = 6.8 Hz, 2H), 2.14 (t, J = 6.9 Hz, 2H), 1.70–1.50 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.2, 170.6,148.9, 112.4, 110.9, 96.8, 56.5, 52.9, 52.3, 33.9, 33.1, 32.1, 28.9, 27.7, 26.4, 26.3. **HRMS** (ESI) *m/z* Calculated for $C_{20}H_{26}NaO_8^+$ $[M + Na]^+$ 417.1520, found 417.1516.



3p

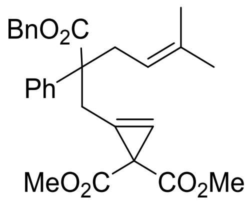
3p: According to the procedure described for the preparation of **3a**, enyne (300 mg, 1.08 mmol) was converted into **3p** (80 mg, 21% yield). White soild. Mp: 37.8~40.4 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.47 (s, 1H), 4.86 (t, J = 7.7 Hz, 1H), 3.70 (s, 6H), 3.68 (s, 6H), 3.14 (s, 2H), 2.72 (d, J = 7.7 Hz, 2H), 2.12–1.96 (m, 4H), 1.56–1.36 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 170.5, 145.1, 113.5, 110.8, 97.0, 56.6, 52.9, 52.3, 37.6, 32.1, 30.4, 28.9, 28.7, 28.0, 27.5, 26.8. **HRMS** (ESI) *m/z* Calculated for

$C_{21}H_{28}NaO_8^+$ [M + Na]$^+$ 431.1676, found 431.1679.



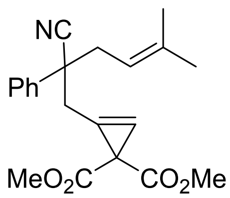
3q

3q: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.95 mmol) was converted into **3q** (200 mg, 27% yield). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.21 (m, 5H), 6.26 (s, 1H), 4.86 (t, *J* = 7.3 Hz, 1H), 3.64 (s, 3H), 3.62 (s, 3H), 3.60 (s, 3H), 3.28 (s, 2H), 2.91 (dd, *J* = 14.5, 7.7 Hz, 1H), 2.76 (dd, *J* = 14.4, 7.0 Hz, 1H), 1.64 (s, 3H), 1.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.8, 171.3, 171.3, 140.8, 136.0, 128.5, 127.3, 126.4, 118.2, 111.8, 96.3, 53.3, 52.4, 52.2, 52.2, 33.9, 32.1, 30.0, 26.2, 18.0. **HRMS** (ESI) *m/z* Calculated for $C_{22}H_{26}NaO_6^+$ [M + Na]$^+$ 409.1622, found 409.1623.



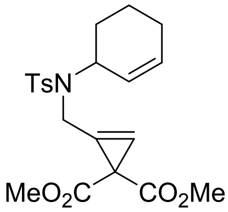
3r

3r: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.50 mmol) was converted into **3r** (181 mg, 26% yield). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.22 (m, 8H), 7.19–7.12 (m, 2H), 6.19 (s, 1H), 5.13 (d, *J* = 12.4 Hz, 1H), 5.06 (d, *J* = 12.4 Hz, 1H), 4.86 (t, *J* = 7.3 Hz, 1H), 3.64 (s, 3H), 3.58 (s, 3H), 3.33 (s, 2H), 2.96 (dd, *J* = 14.4 Hz, 7.3 Hz, 1H), 2.79 (dd, *J* = 14.5 Hz, 7.2 Hz, 1H), 1.62 (s, 3H), 1.49 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1, 171.3, 171.2, 140.6, 136.0, 135.7, 128.4, 128.4, 128.1, 128.1, 127.2, 126.4, 118.2, 111.7, 96.4, 66.9, 53.2, 52.2, 52.1, 33.7, 32.1, 29.9, 26.1, 18.0. **HRMS** (ESI) *m/z* Calculated for $C_{28}H_{30}NaO_6^+$ [M + Na]$^+$ 485.1935, found 485.1944.



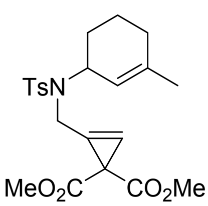
3s

3s: According to the procedure described for the preparation of **3a**, enyne (500 mg, 2.24 mmol) was converted into **3s** (150 mg, 19% yield). Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45–7.30 (m, 5H), 6.47 (s, 1H), 5.07 (t, *J* = 7.1 Hz, 1H), 3.68 (s, 3H), 3.59 (s, 3H), 3.30 (d, *J* = 17.1 Hz, 1H), 3.23 (d, *J* = 17.1 Hz, 1H), 2.78 (dd, *J* = 14.4, 8.1 Hz, 1H), 2.64 (dd, *J* = 14.3, 6.9 Hz, 1H), 1.69 (s, 3H), 1.53 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.0, 170.9, 138.1, 137.3, 128.9, 128.3, 126.2, 121.4, 116.8, 110.3, 98.5, 52.4, 52.3, 46.5, 39.7, 33.7, 32.4, 26.0, 18.2. **HRMS** (ESI) *m/z* Calculated for $C_{21}H_{23}NNaO_4^+$ [M + Na]$^+$ 376.1519, found 376.1516.



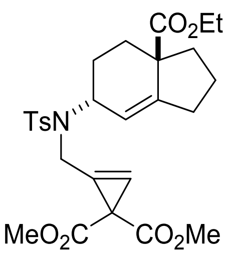
3u

3u: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.73 mmol) was converted into **3u** (159 mg, 22% yield). White soild. Mp: 38.7~40.4 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.32 (s, 1H), 5.88–5.75 (m, 1H), 5.10 (d, *J* = 10.2 Hz, 1H), 4.59–4.48 (m 1H), 4.36 (dd, *J* = 18.8, 1.3 Hz, 1H), 4.14 (dd, *J* = 18.8, 1.3 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 2.40 (s, 3H), 1.97–1.78 (m, 3H), 1.78–1.66 (m, 1H), 1.62–1.47 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 170.8, 143.6, 137.9, 133.7, 129.8, 127.3, 126.8, 112.6, 96.7, 55.4, 52.4, 38.5, 34.1, 28.4, 24.5, 21.6, 21.5. **HRMS** (ESI) *m/z* Calculated for $C_{21}H_{25}NNaO_6S^+$ [M + Na]$^+$ 442.1295, found 442.1290.



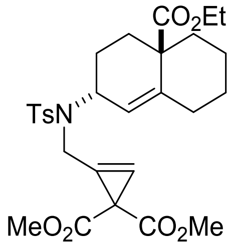
3v

3v: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.65 mmol) was converted into **3v** (194 mg, 27% yield). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.30 (s, 1H), 4.85 (s, 1H), 4.54–4.45 (m, 1H), 4.35 (d, *J* = 18.8 Hz, 1H), 4.15 (d, *J* = 18.8 Hz, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 2.41 (s, 3H), 1.95–1.66 (m, 5H), 1.56 (s, 3H), 1.49–1.33 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 170.8, 143.5, 141.7, 138.0, 129.7, 127.3, 120.9, 112.7, 96.6, 55.9, 52.4, 52.4, 38.4, 34.1, 29.5, 28.2, 23.7, 21.6, 21.6. **HRMS** (ESI) *m/z* Calculated for $C_{22}H_{27}NNaO_6S^+$ [M + Na]$^+$ 456.1451, found 456.1447.



3w

3w: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.25 mmol) was converted into **3w** (120 mg, 20% yield). Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 6.27 (s, 1H), 5.10 (s, 1H), 4.48 (s, 1H), 4.41 (d, *J* =19.1 Hz, 1H), 4.24 (d, *J* =19.1 Hz, 1H), 4.14–4.01 (m, 2H), 3.70 (s, 3H), 3.68 (s, 3H), 2.58–2.44 (m, 1H), 2.40 (s, 3H), 2.34–2.11 (m, 3H), 1.82–(m, 2H), 1.68–1.57 (m, 2H), 1.43–1.31 (m, 1H), 1.26–1.16 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.0, 170.8, 170.7, 150.3, 143.6, 137.8, 129.8, 127.4, 118.1, 112.3, 96.7, 61.0, 52.5, 52.4, 52.4, 51.1, 39.6, 38.3, 34.1, 30.9, 28.6, 26.8, 21.7, 21.6, 14.3. **HRMS** (ESI) *m/z* Calculated for $C_{27}H_{33}NNaO_8S^+$ [M + Na]$^+$ 554.1819, found 554.1819.

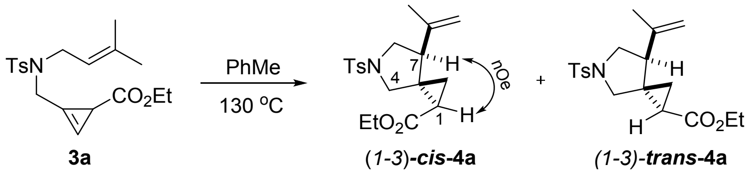


3x

3x: According to the procedure described for the preparation of **3a**, enyne (500 mg, 1.20 mmol) was converted into **3x** (238 mg, 35% yield). Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.31 (s, 1H), 5.08 (s, 1H), 4.49 (s, 1H), 4.41 (d, *J* =18.9 Hz, 1H), 4.23 (d, *J* =18.9 Hz, 1H), 4.13 (m, 2H), 3.71 (s, 3H), 3.69 (s, 3H), 2.41 (s, 3H), 2.25–2.16 (m, 1H), 2.13–2.00 (m, 2H), 1.88–1.51 (m, 6H), 1.41–1.27 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.18–1.07 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.3, 170.8, 170.7, 146.0, 143.6, 137.8, 129.8, 127.4, 120.9, 112.5, 96.9, 60.9, 53.8, 52.4, 52.4, 48.2, 39.2, 36.8, 34.4, 34.1, 32.5, 27.95, 25.9, 23.7, 21.6, 14.3. **HRMS** (ESI) *m/z* Calculated for $C_{28}H_{35}NNaO_8S^+$ [M + Na]$^+$ 568.1976, found 568.1979. **IR** (KBr, thin film): 3144, 2951, 2858, 1725, 1436, 1285, 1158, 547 cm^{-1}.

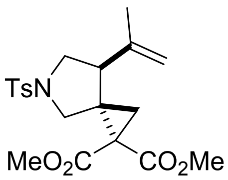
III. Intramolecular Alder-Ene Reaction

A. Typical procedure



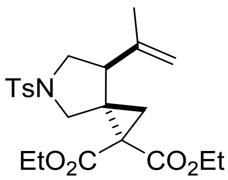
Typical intramolecular ene reaction procedure: A stirred solution of **3a** (60 mg, 0.165 mmol) in dry toluene (1.65 mL) under N_2 was heated to reflux for 4.5 h. After cooling to room temperature, volatiles were removed in vacuum and the residue was purified by column chromatography (silica gel; PE : EtOAc = 10 : 1) to give inseparable mixture of two isomers (*1-3*)-***cis*-4a** and (*1-3*)-***trans*-4a** (total 55 mg, 92%). The area of one methylene-H peak at δ 1.52 in cis isomer was compared with that peak at δ1.65 in trans isomer to derive a ^{1}H NMR ratio of cis/trans = 5.6 : 1. (*1-3*)-***cis*-4a**: **^{1} H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.75 (t, *J* = 1.4 Hz, 1H), 4.61 (s, 1H), 4.15–3.97 (m, 2H), 3.44–3.23 (m, 4H), 2.61 (dd, *J* = 7.6, 5.9 Hz, 1H), 2.42 (s, 3H), 1.60 (s, 3H), 1.52 (dd, *J* =8.7, 5.9 Hz, 1H), 1.22 (t, *J* = 7.1Hz, 3H), 1.14 (t, *J* = 5.3Hz, 1H), 0.99 (dd, *J* =8.7, 5.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 143.7, 141.9, 132.8, 129.7, 127.9, 114.9, 60.8, 51.5, 51.4, 51.3, 33.1, 25.4, 21.6, 19.9, 17.4, 14.3. (*1-3*)-***trans*-4a**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.36–7.32 (m, 2H), 4.74 (t, 1H), 4.59 (s, 1H), 4.14–3.97 (m, 2H), 3.50 (dd, *J* = 10.0, 7.6 Hz, 1H), 3.44–3.23 (m, 3H), 2.44–2.42 (m, 1H), 2.41–2.38 (m, 3H), 1.65 (dd, *J* = 8.7, 5.8 Hz, 1H), 1.58 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.18–1.15 (m, 1H), 0.88 (dd, *J* = 8.7, 4.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 143.0, 141.9, 133.0, 129.7, 127.9, 114.4, 60.9, 52.3, 52.2, 51.9, 32.6, 22.9, 21.5, 19.6, 16.1, 14.4. **HRMS** (ESI) *m/z* Calculated for $C_{19}H_{25}NNaO_4S^+$ [M + Na]$^+$ 386.1397, found 386.1388. **IR** (KBr, thin film): 3076, 2981, 2922, 1720, 1645, 1347, 1162, 664 cm^{-1}.

B. Spiro[2.4]heptane products



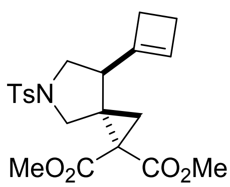
4b

4b: According to the typical procedure, **3b** (80 mg, 0.196 mmol) was converted into **4b** (66 mg, 83% yield) as a white soild. Mp: 80.5~83.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.74 (s, 1H), 4.53 (s, 1H), 3.69 (s, 3H), 3.69 (s, 3H), 3.47–3.34 (m, 2H), 3.28–3.14 (m, 2H), 2.76 (dd, *J* = 7.8, 2.9 Hz, 1H), 2.44 (s, 3H), 1.67 (s, 3H), 1.64 (d, *J* = 5.7 Hz, 1H), 1.54 (d, *J* = 5.6 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.8, 167.5, 143.9, 143.3, 132.3, 129.8, 128.1, 114.9, 53.0, 52.7, 52.4, 52.1, 47.6, 38.8, 38.3, 23.5, 21.7, 19.3. **HRMS** (ESI) *m/z* Calculated for $C_{20}H_{25}NNaO_6S^+$ [M + Na]$^+$ 430.1295, found 430.1294. **IR** (KBr, thin film): 3036, 2957, 2857, 1731, 1646, 1345, 1168, 664 cm^{-1}.



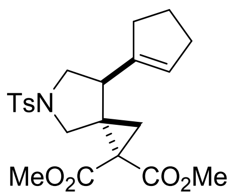
4c

4c: According to the typical procedure, **3c** (78 mg, 0.179 mmol) was converted into **4c** (66 mg, 85% yield) as a white soild. Mp: 97.4~99.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 1H), 4.54 (s, 1H), 4.23–4.03 (m, 4H), 3.46–3.31 (m, 2H), 3.30–3.19 (m, 2H), 2.79 (dd, *J* = 7.7, 2.6 Hz, 1H), 2.44 (s, 3H), 1.66 (s, 3H), 1.61 (d, *J* = 5.5 Hz, 1H), 1.51 (d, *J* = 5.6 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 167.2, 143.9, 143.5, 132.4, 129.8, 128.1, 114.8, 62.0, 61.7, 52.2, 52.1, 47.5, 38.6, 38.5, 23.1, 21.7, 19.4, 14.2. **HRMS** (ESI) *m/z* Calculated for $C_{22}H_{29}NNaO_6S^+$ [M + Na]$^+$ 458.1608, found 458.1606. **IR** (KBr, thin film): 3074, 2982, 2923, 1720, 1646, 1342, 1161, 551 cm^{-1}.



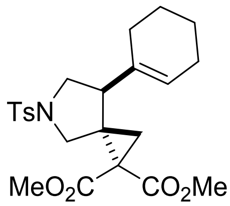
4d

4d: According to the typical procedure, **3d** (42 mg, 0.100 mmol) was converted into **4d** (35 mg, 83% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.62 (s, 1H), 3.69 (s, 6H), 3.47–3.27 (m, 4H), 2.67 (s, 1H), 243 (s, 3H), 2.35–2.13 (m, 4H), 1.65 (d, *J* = 5.7 Hz, 1H), 1.55 (d, *J* = 5.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 167.7, 146.1, 143.7, 133.5, 131.8, 129.7, 127.8, 53.0, 52.7, 51.3, 50.6, 42.1, 39.2, 37.3, 30.1, 26.7, 21.7, 21.6. **HRMS** (ESI) *m/z* Calculated for $C_{21}H_{25}NNaO_6S^+$ [M + Na]$^+$ 442.1295, found 442.1296. **IR** (KBr, thin film): 2954, 2922, 2851, 1725, 1655, 1160, 663, 547 cm^{-1}.



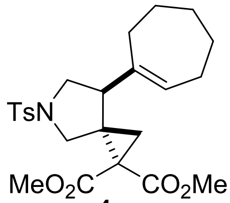
4e

4e: According to the typical procedure, **3e** (60 mg, 0.139 mmol) was converted into **4e** (56 mg, 93% yield) as a white soild. Mp: 81.3~83.8 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.28 (s, 1H), 3.67 (s, 6H), 3.42–3.20 (m, 4H), 2.84 (dd, *J* = 6.2, 3.6 Hz, 1H), 2.42 (s, 3H), 2.23–2.05 (m, 4H), 1.88–1.70 (m, 2H), 1.56 (d, *J* = 5.6 Hz, 1H) , 1.51 (d, *J* = 5.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 167.6, 143.7, 141.6, 132.9, 129.7, 128.6, 127.9, 52.9, 52.6, 52.1, 51.4, 42.3, 39.4, 38.0, 32.6, 32.1, 23.4, 22.6, 21.6. **HRMS** (ESI) *m/z* Calculated for $C_{22}H_{27}NNaO_6S^+$ [M + Na]$^+$ 456.1451, found 456.1455. **IR** (KBr, thin film): 3049, 2960, 2863, 1720, 1596, 1162, 661, 549 cm^{-1}.



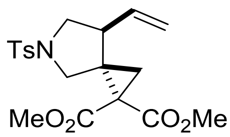
4f

4f: According to the typical procedure, **3f** (90 mg, 0.200 mmol) was converted into **4f** (82 mg, 91% yield) as a white soild. Mp: 111.3~113.5 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.21 (s, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 3.45–3.26 (m, 2H), 3.27–3.11 (m, 2H), 2.62 (dd, *J* = 7.8, 3.1 Hz, 1H), 2.43 (s, 3H), 1.97–1.73 (m, 4H), 1.62–1.54 (m, 2H), 1.53–1.43 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.9, 167.5, 143.8, 135.6, 132.3, 129.7, 128.0, 126.2, 52.9, 52.6, 52.5, 52.1, 48.1, 38.9, 38.2, 25.3, 25.2, 23.3, 22.7, 22.2, 21.7. **HRMS** (ESI) *m/z* Calculated for $C_{23}H_{29}NNaO_6S^+$ [M + Na]$^+$ 470.1608, found 470.1605. **IR** (KBr, thin film): 2926, 2855, 1729, 1598, 1436, 1348, 1163, 549 cm^{-1}.



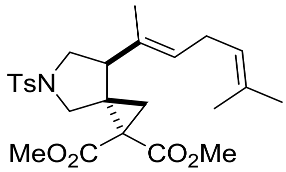
4g

4g: According to the typical procedure, **3g** (51 mg, 0.111 mmol) was converted into **4g** (36 mg, 71% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.38 (t, *J* = 6.4 Hz, 1H), 3.69 (s, 3H), 3.63 (s, 3H), 3.45–3.17 (m, 4H), 2.83 (dd, *J* = 8.2, 5.2 Hz, 1H), 2.44 (s, 3H), 2.05–1.94 (m, 4H), 1.83–1.69 (m, 1H), 1.67–1.40 (m, 5H), 1.36–1.21 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 167.1, 143.8, 140.9, 132.5, 132.2, 129.8, 128.0, 53.0, 52.8, 52.5, 52.0, 49.8, 38.5, 37.3, 32.6, 29.8, 28.4, 27.2, 26.8, 23.9, 21.7. **HRMS** (ESI) *m/z* Calculated for $C_{24}H_{31}NNaO_6S^+$ $[M + Na]^+$ 484.1764, found 484.1768. **IR** (KBr, thin film): 2923, 2854, 1739, 1634, 1456, 1377, 1164, 549 cm^{-1}.



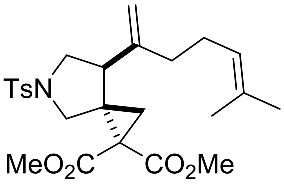
4h

4h: According to the typical procedure, **3h** (80 mg, 0.203 mmol) was converted into **4h** (63 mg, 79% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.46–5.30 (m, 1H), 5.03 (dd, *J* = 10.2, 1.3 Hz, 1H), 4.97–4.87 (m, 1H), 3.70 (s, 3H), 3.65 (s, 3H), 3.49 (dd, *J* = 9.7, 7.4 Hz, 1H), 3.44 (d, *J* = 11.3 Hz, 1H), 3.37 (d, *J* = 11.3 Hz, 1H), 3.15 (dd, *J* = 9.7, 6.5 Hz, 1H), 2.83 (dd, *J* = 15.7, 7.1 Hz, 1H), 2.45 (s, 3H), 1.57 (d, *J* = 5.7 Hz, 1H), 1.41 (d, *J* = 5.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.9, 167.1, 143.9, 134.6, 133.0, 129.8, 127.9, 119.0, 53.2, 53.0, 52.5, 52.1, 44.9, 38.8, 36.6, 21.9, 21.7. **HRMS** (ESI) *m/z* Calculated for $C_{19}H_{23}NNaO_6S^+$ $[M + Na]^+$ 416.1138, found 416.1139. **IR** (KBr, thin film): 2935, 2922, 1738, 1652, 1435, 1345, 1160, 549 cm^{-1}.



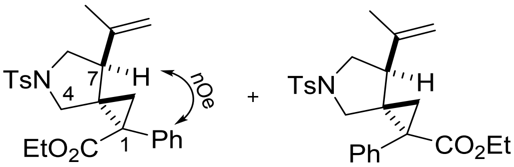
4i

4i: According to the typical procedure, **3i** (72 mg, 0.156 mmol) was converted into **4i** (55 mg, 76% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz,2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.00–4.93 (m, 1H), 4.90 (t, *J* = 7.0 Hz, 1H), 3.68 (s, 3H), 3.64 (s, 3H), 3.42 (d, *J* = 11.0 Hz, 1H), 3.32 (dd, *J* = 9.8, 3.8 Hz, 1H), 3.22 (d, *J* = 8.4 Hz, 1H), 3.17 (d, *J* = 10.9 Hz, 1H), 2.77 (dd, *J* = 8.3, 3.7 Hz, 1H), 2.58 (t, *J* = 7.1 Hz, 1H), 2.44 (s, 3H), 1.65 (s, 3H), 1.61 (d, *J* = 5.5 Hz, 1H), 1.57 (s, 1H), 1.56 (s, 1H), 1.44 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 167.3, 143.9, 132.3, 132.2, 132.1, 129.8, 128.9, 128.1, 122.2, 52.9, 52.9, 52.6, 52.1, 49.1, 38.5, 37.7, 27.0, 25.7, 23.9, 21.7, 17.8, 13.1. **HRMS** (ESI) *m/z* Calculated for $C_{25}H_{33}NNaO_6S^+$ [M + Na]$^+$ 498.1921, found 498.1918. **IR** (KBr, thin film): 2955, 2926, 1730, 1638, 1163, 1095, 667, 549 cm^{-1}.



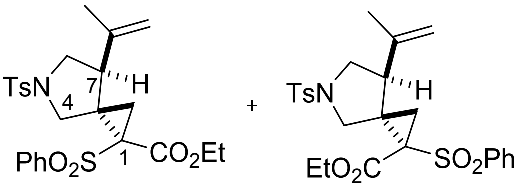
4j

4j: According to the typical procedure, **3j** (63 mg, 0.156 mmol) was converted into **4j** (55 mg, 87% yield) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.03 (t, *J* = 6.8 Hz, 1H), 4.80 (d, *J* = 1.5 Hz, 1H), 4.65 (s, 1H), 3.68 (s, 6H), 3.41 (d, *J* = 11.2 Hz, 1H), 3.37–3.28 (m, 2H), 3.26 (d, *J* = 11.1 Hz, 1H), 2.73 (dd, *J* = 7.3, 3.5 Hz, 1H), 2.44 (s, 3H), 2.16–1.97 (m, 2H), 1.97–1.81 (m, 2H), 1.68 (s, 3H), 1.61 (d, *J* = 5.7 Hz, 1H), 1.59 (s, 3H), 1.55 (d, *J* = 5.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 167.6, 147.3, 143.8, 132.7, 132.2, 129.8, 128.0, 123.7, 113.1, 53.0, 52.8, 52.7, 52.0, 47.3, 39.5, 38.5, 33.0, 26.3, 25.8, 23.2, 21.7, 17.9. **HRMS** (ESI) *m/z* Calculated for $C_{25}H_{33}NNaO_6S^+$ [M + Na]$^+$ 498.1921, found 498.1920. **IR** (KBr, thin film): 2954, 2924, 1727, 1640, 1435, 1162, 663, 548 cm^{-1}.



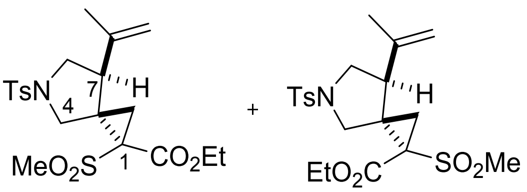
(*1-3*)-***cis*-4k** (*1-3*)-***trans*-4k**

4k: According to the typical procedure, **3k** (60 mg, 0.136 mmol) was converted into inseparable mixture of two isomers (*1-3*)**-*cis*-4k** and (*1-3*)**-*trans*-4k** (total 42 mg, 70 % yield). The area of one alkenyl-H peak at δ 4.43 in cis isomer was compared with that peak at δ 4.75 in trans isomer to derive a ^{1}H NMR ratio of cis/trans = 5.1 : 1. (*1-3*)**-*cis*-4k**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.29–7.21 (m, 3H), 7.10–7.02 (m, 2H), 4.43 (s, 1H), 4.16–3.94 (m, 2H), 3.72 (s, 1H), 3.41 (dd, *J* = 20.4, 11.2 Hz, 2H), 3.32–3.18 (m, 2H), 2.47 (s, 3H), 2.24 (dd, *J* = 7.8, 3.7 Hz, 1H), 1.63 (d, *J* = 5.3 Hz, 1H), 1.46 (s, 3H), 1.41 (d, *J* = 5.4 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.4, 143.8, 143.7, 135.2, 132.8, 131.2, 129.8, 128.2, 128.1, 127.6, 114.3, 61.6, 52.7, 51.9, 47.8, 39.6, 38.4, 21.7, 21.7, 19.2, 14.3. (*1-3*)**-*trans*-4k**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.30–7.21 (m, 3H), 7.15–7.11 (m, 2H), 4.75 (s, 1H), 4.64 (s, 1H), 4.18–3.94 (m, 2H), 3.52 (dd, *J* = 9.8, 7.5 Hz, 1H), 3.47–3.33 (m, 1H), 2.94 (d, *J* = 10.4 Hz, 1H), 2.77 (d, *J* = 10.4 Hz, 1H), 2.71 (dd, *J* = 7.4, 2.5 Hz, 1H), 2.47 (s, 3H), 1.89–1.86 (m, 1H), 1.64 (s, 3H), 1.35 (d, *J* = 5.8 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.0, 144.3, 143.6, 135.6, 133.2, 131.1, 129.7, 128.5, 127.9, 127.8, 113.5, 61.4, 52.4, 51.3, 47.3, 41.0, 38.3, 20.3, 20.3, 19.3, 13.9. **HRMS** (ESI) *m/z* Calculated for $C_{25}H_{29}NNaO_4S^+$ [M + Na]$^+$ 462.1710, found 462.1709. **IR** (KBr, thin film): 3061, 2924, 2853, 1716, 1645, 1164, 1094, 550 cm-1.



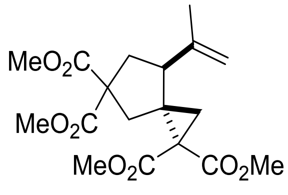
(*1-3*)-***cis*-4l** (*1-3*)-***trans*-4l**

4l: According to the typical procedure, **3l** (100 mg, 0.200 mmol) was converted into inseparable mixture of two isomers (*1-3*)-***cis*-4l** and (*1-3*)-***trans*-4l** (total 40 mg, 40 % yield). The area of one alkenyl-H peak at δ 4.72 in major isomer was compared with that peak at δ 4.86 in minor isomer to derive a ^{1}H NMR dr = 3.2 : 1. (*1-3*)-***cis*-4l**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.67–7.59 (m, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.72 (s, 1H), 4.45 (s, 1H), 4.03–3.87 (m, 2H), 3.82 (d, *J* = 11.0 Hz, 1H), 3.64 (d, *J* = 11.0 Hz, 1H), 3.32 (dd, *J* = 9.8, 3.0 Hz, 1H), 3.13 (dd, *J* = 9.9, 8.0 Hz, 1H), 2.56 (dd, *J* = 7.9, 2.9 Hz, 1H), 2.45 (s, 3H), 2.17 (d, *J* = 6.2 Hz, 1H), 1.82 (d, *J* = 6.2 Hz, 1H), 1.65 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.9, 144.1, 142.7, 134.0, 131.6, 129.9, 129.0, 128.7, 128.1, 115.4, 62.5, 55.0, 51.9, 51.7, 48.3, 39.1, 22.2, 21.6, 18.9, 13.7. (*1-3*)-***trans*-4l**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 5.8 Hz, 2H), 7.67–7.59 (m, 3H), 7.52–7.47 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.86 (s, 1H), 4.82 (s, 1H), 4.32–4.06 (m, 2H), 3.63–3.59 (m, 1H), 3.49 (dd, *J* = 9.7, 1.6 Hz, 1H), 3.44–3.37 (m, 2H), 2.88 (d, *J* = 11.1 Hz, 1H), 2.43 (s, 3H), 2.21 (d, *J* = 6.1 Hz, 1H), 2.07 (d, *J* = 6.1 Hz, 1H), 1.73 (s, 3H), 1.05–1.01 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 143.3, 142.6, 139.1, 133.9, 131.6, 129.7, 129.0, 128.3, 127.7, 114.8, 62.8, 55.6, 52.8, 52.4, 45.5, 41.9, 29.7, 21.6, 20.5, 13.8. **HRMS** (ESI) *m/z* Calculated for $C_{25}H_{29}NNaO_6S_2^+$ $[M + Na]^+$ 526.1329, found 526.1332. **IR** (KBr, thin film): 2923, 2951, 1727, 1320, 1155, 1094, 664, 548 cm-1.



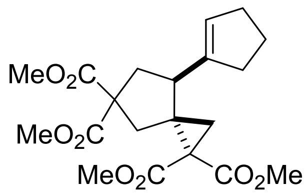
(*1-3*)-***cis*-4m** (*1-3*)-***trans*-4m**

4m: According to the typical procedure, **3m** (133 mg, 0.301 mmol) was converted into was converted into (*1-3*)-***cis*-4m** and (*1-3*)-***trans*-4m**. Isolation by flash chromatography (silica gel; PE : EtOAc = 4 : 1) gave dr 5.2/1. (*1-3*)-***cis*-4m**: 94 mg, 71% yield, yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.72 (s, 1H), 4.48 (s, 1H), 4.35–4.21 (m, 2H), 3.84 (d, *J* = 11.7 Hz, 1H), 3.62 (dd, *J* = 10.1, 8.3 Hz, 1H), 3.21 (s, 3H), 3.05–2.93 (m, 2H), 2.51 (dd, *J* = 8.3, 4.8 Hz, 1H), 2.43 (s, 3H), 2.02 (d, *J* = 6.7 Hz, 1H), 1.81 (d, *J* = 6.6 Hz, 1H), 1.44 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 144.4, 141.8, 131.6, 130.0, 128.0, 115.5, 63.1, 54.1, 51.4, 49.9, 48.2, 42.5, 39.4, 21.7, 19.4, 16.2, 14.1. (*1-3*)-***trans*-4m**: 18 mg, 14% yield, colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.79 (s, 1H), 4.70 (s, 1H), 4.38 – 4.21 (m, 2H), 3.47 (dd, J = 10.2, 7.7 Hz, 1H), 3.38 – 3.27 (m, 3H), 3.14 (s, 3H), 3.05 (d, J = 11.4 Hz, 1H), 2.45 (s, 3H), 2.02 (d, J = 6.5 Hz, 1H), 1.98 (d, J = 6.5 Hz, 1H), 1.59 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 144.2, 143.1, 132.9, 129.9, 127.8, 115.1, 63.4, 54.6, 52.5, 52.0, 45.1, 43.0, 41.7, 21.7, 20.3, 18.4, 14.2. **HRMS** (ESI) *m/z* Calculated for $C_{20}H_{27}NNaO_6S_2^+$ [M + Na]$^+$ 464.1172, found 464.1171. **IR** (KBr, thin film): 2955, 2924, 2853, 1728, 1645, 1462, 1377, 1094 cm^{-1}.



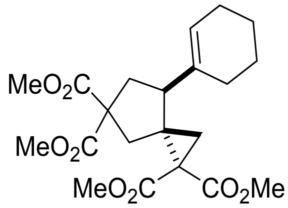
4n

4n: According to the typical procedure, **3n** (74 mg, 0.200 mmol) was converted into **4n** (63 mg, 85% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ4.73 (s, 1H), 4.55 (s, 1H), 3.73 (s, 3H), 3.73 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 2.79 (t, J = 8.7 Hz, 1H), 2.72–2.57 (m, 2H), 2.31 (d, J = 14.4 Hz, 1H), 2.23 (dd, J = 13.1, 9.1 Hz, 1H), 1.65 (s, 3H), 1.63 (d, J = 5.4 Hz, 1H), 1.46 (d, J = 5.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 171.4, 169.2, 167.6, 144.0, 114.7, 59.8, 52.9, 52.9, 52.7, 52.4, 48.3, 40.2, 39.7, 39.1, 38.8, 22.7, 18.6. **HRMS** (ESI) *m/z* Calculated for $C_{18}H_{24}NaO_8^+$ [M + Na]$^+$ 391.1363, found 391.1365. **IR** (KBr, thin film): 3078, 2955, 2849, 1735, 1646, 1436, 1241, 1108 cm^{-1}.



4o

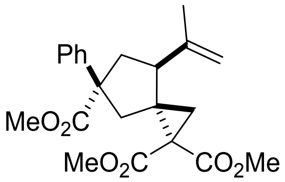
4o: According to the typical procedure, **3o** (60 mg, 0.152 mmol) was converted into **4o** (50 mg, 83% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.28 (s, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.69 (s, 6H), 2.92 (t, J = 8.2 Hz, 1H), 2.65 (d, J = 14.5 Hz, 1H), 2.59 (dd, J = 13.2, 8.3 Hz, 1H), 2.37 (d, J = 14.5 Hz, 1H), 2.29–2.18 (m, 4H), 2.17–2.06 (m, 1H), 1.93–1.75 (m, 2H), 1.59 (d, J = 5.3 Hz, 1H), 1.45 (d, J = 5.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.8, 171.7, 169.3, 167.8, 143.2, 128.3, 59.7, 52.9, 52.7, 52.4, 42.5, 40.7, 39.1, 38.4, 32.2, 31.9, 23.6, 22.6. **HRMS** (ESI) *m/z* Calculated for $C_{20}H_{26}NaO_8^+$ [M + Na]$^+$ 417.1520, found 417.1515. **IR** (KBr, thin film): 2999, 2954 , 2848 , 1736 , 1436 , 1262 , 1107 , 1075 cm^{-1}.



4p

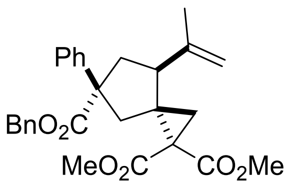
4p: According to the typical procedure, **3p** (65 mg, 0.159 mmol) was converted into **4p**

(49 mg, 75% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.23 (s, 1H), 3.73 (s, 6H), 3.69 (s, 6H), 2.74–2.62 (m, 2H), 2.62–2.52 (m, 1H), 2.31–2.18 (m, 2H), 1.93 (s, 3H), 1.85–1.63 (m, 2H), 1.58 (d, J = 5.2 Hz, 2H), 1.53–1.43 (m, 2H), 1.41 (d, J = 5.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 171.5, 169.3, 167.6, 136.1, 126.0, 59.8, 52.9, 52.8, 52.6, 52.4, 48.6, 40.3, 39.6, 39.1, 38.90 25.3, 24.8, 22.8, 22.6, 22.5. **HRMS** (ESI) *m/z* Calculated for $C_{21}H_{28}NaO_8^+$ [M + Na]$^+$ 431.1676, found 431.1678. **IR** (KBr, thin film): 2997, 2952, 2856, 1732, 1435, 1251, 1106, 1063 cm^{-1}.



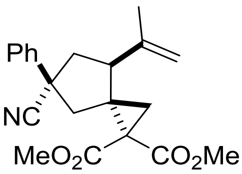
4q

4q: According to the typical procedure, **3q** (80 mg, 0.207 mmol) was converted into **4q** (72 mg, 90% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.22 (m, 5H), 4.73 (s, 1H), 4.55 (d, J = 1.7 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.64 (s, 3H), 3.20 (dd, J = 13.8, 2.7 Hz, 1H), 3.10–3.02 (m, 1H), 2.89 (dd, J = 10.1, 8.1 Hz, 1H), 2.08 (d, J = 13.8 Hz, 1H), 2.00 (dd, J = 12.3, 10.3 Hz, 1H), 1.68 (d, J = 5.4 Hz, 1H), 1.63 (s, 3H), 1.50 (d, J = 5.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.9, 169.6, 167.6, 144.4, 141.7, 128.6, 127.4, 126.9, 114.7, 57.7, 52.6, 52.6, 52.4, 48.6, 41.5, 40.3, 40.1, 39.9, 23.0, 18.3. **HRMS** (ESI) *m/z* Calculated for $C_{22}H_{26}NaO_6^+$ [M + Na]$^+$ 409.1622, found 409.1626. **IR** (KBr, thin film): 2951, 2922, 2851, 1728, 1642, 1433, 1238, 1106 cm^{-1}.



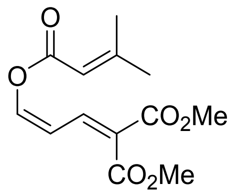
4r

4r: According to the typical procedure, **3r** (72 mg, 0.159 mmol) was converted into **4r** (59 mg, 82% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41–7.35 (m, 2H), 7.35–7.23 (m, 6H), 7.18–7.13 (m, 2H), 5.30 (d, J = 13.0 Hz, 1H), 4.98 (d, J = 13.0 Hz, 1H), 4.76 (s, 1H), 4.58 (d, J = 1.5 Hz, 1H), 3.72 (s, 3H), 3.60 (s, 3H), 3.30 (dd, J = 13.9, 2.6 Hz, 1H), 3.15–3.07 (m, 1H), 2.99 (dd, J = 10.0, 8.1 Hz, 1H), 2.13 (d, J = 13.9 Hz, 1H), 2.06 (dd, J = 12.3, 10.3 Hz, 1H), 1.68 (d, J = 5.3 Hz, 1H), 1.65 (s, 3H), 1.51 (d, J = 5.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1, 169.6, 167.6, 144.4, 141.7, 136.3, 128.6, 128.5, 127.8, 127.4, 127.2, 126.9, 114.7, 66.7, 57.8, 52.6, 52.3, 48.6, 41.2, 40.2, 40.1, 40.0, 23.1, 18.4. **HRMS** (ESI) *m/z* Calculated for $C_{28}H_{30}NaO_6^+$ [M + Na]$^+$ 485.1935, found 485.1945. **IR** (KBr, thin film): 3065, 2921, 2851, 1731, 1645, 1260, 1105, 697 cm^{-1}.



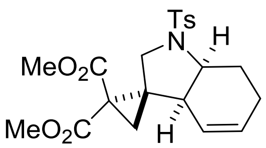
4s

4s: According to the typical procedure, **3s** (72 mg, 0.203 mmol) was converted into **4s** (36 mg, 50% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.48–7.29 (m, , 5H), 4.85 (s, 1H), 4.69 (s, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.34 (dd, *J* = 10.0, 8.0 Hz, 1H), 2.94 (dd, *J* = 14.3, 2.5 Hz, 1H), 2.75 (ddd, *J* = 13.2, 8.1, 2.5 Hz, 1H), 2.33 (d, *J* = 14.3 Hz, 1H), 2.24 (dd, *J* = 13.1, 10.1 Hz, 1H), 1.70 (s, 3H), 1.66 (d, *J* = 5.5 Hz, 1H), 1.58 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.6, 167.6, 143.1, 138.3, 129.1, 128.4, 126.1, 122.6, 115.6, 53.1, 52.7, 48.2, 46.7, 44.8, 43.4, 39.5, 39.3, 22.7, 18.9. **HRMS** (ESI) *m/z* Calculated for $C_{21}H_{23}NNaO_4^+$ [M + Na]$^+$ 376.1519, found 376.1517. **IR** (KBr, thin film): 2954, 2923, 2852, 1719, 1637, 1260, 1108, 696 cm^{-1}.



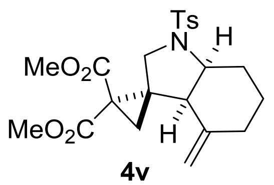
4t

4t: According to the typical procedure, **3t** (55 mg, 0.200 mmol) was converted into **4t** (28 mg, 51% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (s, 1H), 5.68 (s, 1H), 5.50 (d, *J* = 1.7 Hz, 1H), 5.38 (d, *J* = 1.7 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 2.19 (s, 3H), 1.96 (d, *J* = 0.7 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.0, 164.1, 163.1, 161.4, 148.2, 136.6, 125.4, 116.0, 114.5, 52.9, 52.7, 27.7, 20.6. **HRMS** (ESI) *m/z* Calculated for $C_{13}H_{16}NaO_6^+$ [M + Na]$^+$ 291.0839, found 291.0839. **IR** (KBr, thin film): 2956, 2925, 2854, 1735, 1637, 1259, 1116, 1068 cm^{-1}.



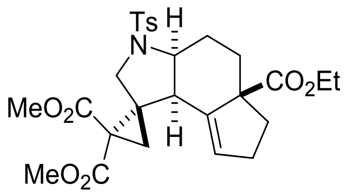
4u

4u: According to the typical procedure, **3u** (84 mg, 0.200 mmol) was converted into **4u** (58 mg, 69% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.92–5.80 (m, 1H), 5.01–4.89 (m, 1H), 3.98–3.88 (m, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 3.59 (d, *J* = 11.5 Hz, 1H), 3.54 (d, *J* = 11.5 Hz, 1H), 2.46 (ddd, *J* = 6.6, 4.1, 2.0 Hz, 1H), 2.42 (s, 3H), 2.23–2.07 (m, 1H), 2.06–1.78 (m, 3H), 1.61 (d, *J* = 5.5 Hz, 1H) , 1.50 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 167.7, 143.4, 135.5, 132.3, 129.8, 127.5, 122.6, 59.0, 53.0, 52.8, 51.2, 41.2, 39.1, 35.6, 29.8, 26.4, 22.8, 21.7. **HRMS** (ESI) *m/z* Calculated for $C_{21}H_{25}NNaO_6S^+$ [M + Na]$^+$ 442.1295, found 442.1293. **IR** (KBr, thin film): 2921, 2850, 1719, 1648, 1437, 1109, 662, 546 cm^{-1}.



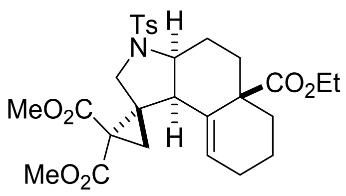
4v

4v: According to the typical procedure, **3v** (87 mg, 0.200 mmol) was converted into **4v** (50 mg, 57% yield) as a white soild. Mp: 60.1~63.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.78 (s, 1H), 4.44 (s, 1H), 3.95 (dt, *J* = 11.6, 6.0 Hz, 1H), 3.78–3.69(m, 4H), 3.57 (s, 3H), 3.51 (d, *J* = 12.5 Hz, 1H), 2.83 (d, *J* = 6.8 Hz, 1H), 2.44 (s, 3H), 2.16–2.04 (m, 1H), 1.99–1.81 (m, 2H), 1.79–1.66 (m, 1H), 1.57 (d, *J* = 5.4 Hz, 1H), 1.55–1.45 (m, 2H), 1.27–1.20 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 166.2, 143.5, 142.9, 136.1, 129.9, 127.3, 115.6, 62.6, 53.0, 52.0, 51.6, 47.7, 36.6, 36.0, 32.9, 28.7, 24.1, 23.9, 21.7. **HRMS** (ESI) *m/z* Calculated for $C_{22}H_{27}NNaO_6S^+$ [M + Na]$^+$ 456.1451, found 456.1451. **IR** (KBr, thin film): 3084, 2925, 2856, 1719, 1643, 1432, 1158, 548 cm^{-1}.



4w

4w: According to the typical procedure, **3w** (80 mg, 0.150 mmol) was converted into **4w** (60 mg, 75% yield) as white solid, Mp: 89.7~91.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 5.77 (s, 1H), 4.22–3.97 (m, 2H), 3.73–3.65 (m, 3H), 3.63 (s, 3H), 3.58 (s, 3H), 2.64–2.54 (m, 1H), 2.48–2.43 (m, 1H), 2.42 (s, 3H), 2.38–2.24 (m, 3H), 2.16 (d, *J* = 13.1 Hz, 1H), 1.90 (d, *J* = 5.6 Hz, 1H), 1.89–1.80 (m, 1H), 1.80–1.69 (m, 1H), 1.68 (d, *J* = 5.6 Hz, 1H), 1.65–1.54 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.0, 168.9, 167.5, 143.3, 139.8, 134.3, 129.5, 127.8, 127.4, 61.2, 60.7, 58.1, 52.8, 52.6, 49.5, 45.2, 38.8, 37.1, 36.6, 31.7, 30.3, 25.8, 21.7, 21.1, 14.3. **HRMS** (ESI) *m/z* Calculated for $C_{27}H_{33}NNaO_8S^+$ [M + Na]$^+$ 554.1819, found 554.1819. **IR** (KBr, thin film): 2926, 2854, 1720, 1654, 1437, 1341, 1160, 694 cm^{-1}.

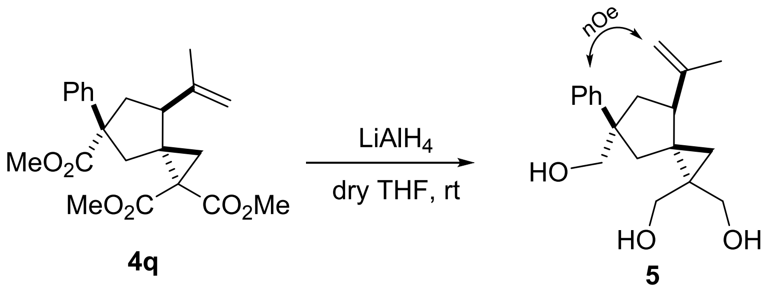


4x

4x: According to the typical procedure, **3x** (80 mg, 0.146 mmol) was converted into **4x** (47 mg, 59% yield) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.90 (s, 1H), 4.21–4.00 (m, 2H), 3.72–3.66 (m, 3H), 3.62 (s, 3H), 3.55 (s, 3H), 2.41 (s, 3H), 2.41–2.34 (m, 2H), 2.17–2.04 (m, 3H), 1.98–1.92 (m, 1H), 1.90 (d, *J* = 5.6 Hz, 1H), 1.74 (d, *J* = 5.6 Hz, 1H), 1.66–1.57(m, 2H), 1.55–1.46 (m, 1H), 1.45–1.26 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$)

δ 175.9, 169.0, 167.4, 143.2, 134.5, 133.3, 129.5, 127.8, 124.5, 61.9, 60.8, 52.7, 52.6, 49.5, 47.9, 47.1, 38.4, 36.5, 35.5, 31.7, 26.1, 25.1, 22.0, 21.7, 19.2, 14.3. **HRMS** (ESI) *m/z* Calculated for $C_{28}H_{35}NNaO_8S^+$ $[M + Na]^+$ 568.1976, found 568.1979. **IR** (KBr, thin film): 2928, 1722, 1435, 1343, 1239, 1161, 690, 550 cm^{-1}.

IV. Derivatization Experiment



$LiAlH_4$ (24 mg, 0.644 mmol) in THF (1 mL) was stirred at 0 °C under nitrogen. A solution of compound **4q** (42 mg, 0.011 mmol) in THF (1 mL) was added slowly. Until substrate **4q** was consumed as indicated by TLC, the resulting reaction mixture was quench carefully with ammonium chloride aqueous solution and extracted with EtOAc (3 × 2 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. Purification of the crude product by flash column chromatography (silica gel; PE: EtOAc = 2: 1 afforded **5** (22 mg, 68% yield) as a colorless oil. **^{1}H NMR** (400 MHz, DMSO) δ 7.29–7.20 (m, 4H), 7.19–7.12 (m, 1H), 5.04 (br, 2H), 4.67 (s, 2H), 4.44 (br, 1H), 3.89 (d, *J* = 11.6 Hz, 1H), 3.59 (d, *J* = 10.9 Hz, 1H), 3.49 (d, *J* = 10.8 Hz, 1H), 3.40 (d, *J* = 9.9 Hz, 2H), 3.31 (d, *J* = 11.6 Hz, 1H), 2.97 (t, *J* = 9.0 Hz, 1H), 2.30 (dd, *J* = 13.0, 2.0 Hz, 1H), 2.25–2.14 (m, 1H), 1.81 (d, *J* = 12.9 Hz, 1H), 1.75 (dd, *J* = 12.8, 9.4 Hz, 1H), 1.60 (s, 3H) , 0.41 (d, *J* = 4.7 Hz, 1H), 0.24 (d, *J* = 4.6 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO) δ 148.1, 147.9, 127.6, 127.0, 125.5, 112.6, 79.2, 67.1, 62.9, 60.79, 60.76, 51.6, 47.2, 32.7, 31.3, 19.0, 17.8. **HRMS** (ESI) *m/z* Calculated for $C_{19}H_{26}NaO_3^+$ $[M + Na]^+$ 325.1774, found 325.1771. **IR** (KBr, thin film): 2955, 2853, 1732, 1634, 1463, 1377, 1021, 700 cm^{-1}.

V. Computational Studies

Computational methods

The B3LYP[1] density functional method (DFT) was employed to carry out all the calculations. The 6-31G(d)[2] basis set was used for all atoms. Vibrational frequency analyses at the same level of the theory were performed on all the optimized geometries to characterize them as local minima (no imaginary frequency) or transition states (one imaginary frequency). In addition, intrinsic reaction coordinate (IRC) calculations were used to verify that the transition state connect with appropriate reactant and product.[3] The gas-phase Gibbs energies for all species were obtained at 298.15 K and 1 atm at their respective optimized structures. Solution phase single-point energies were calculated based on the optimized structures with the M06-2X[4] method, SMD solvation model,[5] and 6-311++G(d,p) basis set. The Gibbs energy was determined by adding the single-point energy and the gas-phase thermal correction to the Gibbs energy obtained from the vibrational frequency analyses. All calculations were carried out with the Gaussian 09 suite of programs.[6]

References

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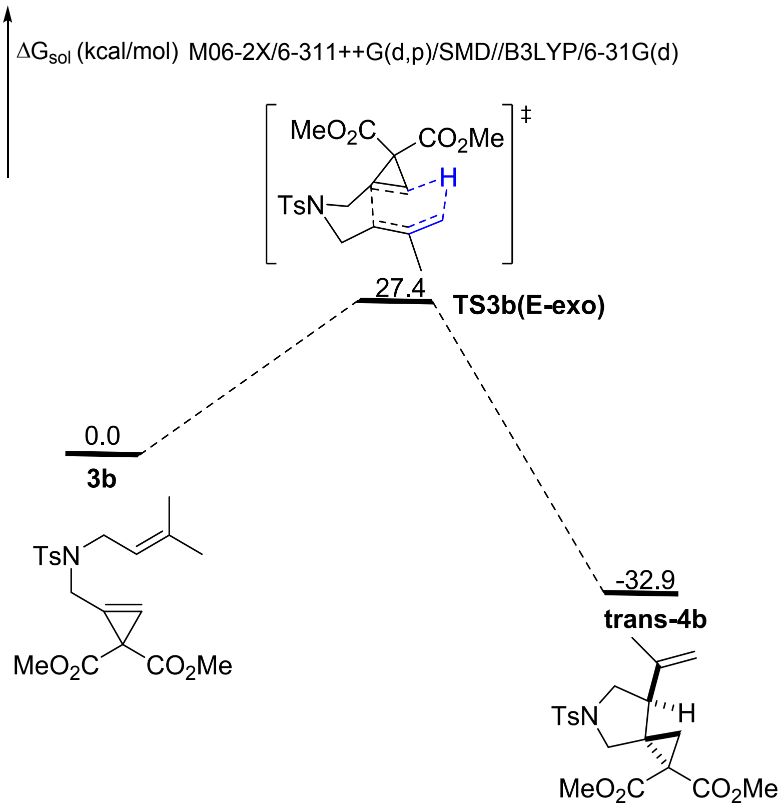

Figure S1. The energy profile of the ene reaction of **3b**.

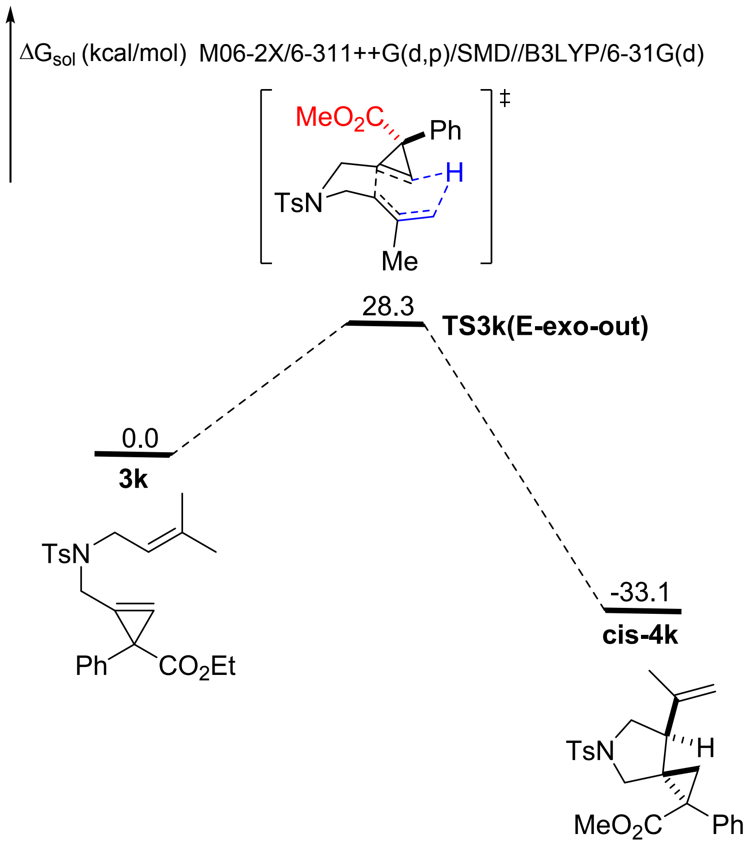

Figure S2. The energy profile of the ene reaction of **3k**.

Cartesian Coordinates and Energies

TS3b(E-exo)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.311937	1.010574	1.578871
2	6	0	-3.693431	-0.161209	1.148052
3	6	0	-3.175793	-0.222973	-0.148389
4	6	0	-3.277424	0.872305	-1.010321
5	6	0	-3.898540	2.036150	-0.561105
6	6	0	-4.424946	2.125138	0.735269
7	1	0	-4.720713	1.057950	2.585422
8	1	0	-3.631205	-1.029555	1.795345
9	1	0	-2.894399	0.801436	-2.022856
10	1	0	-3.981513	2.887678	-1.232028
11	6	0	-5.128652	3.377673	1.200402
12	1	0	-4.744595	4.266742	0.689943
13	1	0	-6.205637	3.322464	0.993471
14	1	0	-5.012706	3.526238	2.279016
15	16	0	-2.330035	-1.709327	-0.697936
16	8	0	-2.795594	-2.817602	0.141241
17	8	0	-2.412030	-1.750071	-2.159052
18	7	0	-0.701563	-1.513665	-0.328718
19	6	0	-0.280291	-1.579116	1.079779
20	1	0	-0.789548	-2.423144	1.549758
21	1	0	-0.549491	-0.661948	1.626740
22	6	0	1.223060	-1.739826	1.056936
23	6	0	1.863765	-2.923825	0.685953
24	6	0	3.294867	-2.845547	0.550161
25	1	0	3.384885	-2.039794	-0.359625
26	1	0	3.832057	-2.300861	1.329237
27	1	0	3.806861	-3.764288	0.257479
28	6	0	1.138280	-4.065731	0.024499
29	1	0	1.620305	-5.017907	0.272323
30	1	0	0.082960	-4.120632	0.300875
31	1	0	1.173175	-3.961859	-1.070103
32	6	0	0.080648	-0.539363	-1.107274
33	1	0	-0.012961	-0.784673	-2.165909
34	1	0	-0.281238	0.487635	-0.957709
35	6	0	1.526282	-0.609136	-0.655177
36	6	0	2.556451	0.510367	-0.477328
37	6	0	2.746470	-0.770620	-1.240970
38	1	0	3.092967	-0.937871	-2.252334
39	6	0	3.237482	0.718722	0.860679
40	8	0	4.278252	0.214363	1.221569
41	8	0	2.492188	1.528056	1.651483
42	6	0	3.075946	1.852754	2.923421
43	1	0	4.033126	2.362604	2.785043
44	1	0	3.238682	0.949318	3.517491
45	1	0	2.359102	2.510924	3.415569
46	6	0	2.342113	1.757982	-1.297136
47	8	0	1.595526	1.825947	-2.253755
48	8	0	3.121264	2.779291	-0.886106
49	6	0	3.008430	3.991075	-1.650448
50	1	0	3.703187	4.692852	-1.188476
51	1	0	3.278564	3.811664	-2.694294
52	1	0	1.986308	4.376494	-1.608297
53	1	0	1.769789	-1.078817	1.723638

Zero-point correction= 0.423349 (Hartree/Particle)
Thermal correction to Energy= 0.452461
Thermal correction to Enthalpy= 0.453405
Thermal correction to Gibbs Free Energy= 0.360476
Sum of electronic and zero-point Energies= -1680.847303

Sum of electronic and thermal Energies= -1680.818191
Sum of electronic and thermal Enthalpies= -1680.817246
Sum of electronic and thermal Free Energies= -1680.910176
M06-2X /6-311++G (d, p)/SMD// B3LYP /6-31G(d) energy= -1681.133876

TS3b(E-endo)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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3	6	0	-2.542400	-1.050375	0.188827
4	6	0	-3.794698	-1.081225	-0.426492
5	6	0	-4.665818	-0.007772	-0.251032
6	6	0	-4.305331	1.098540	0.530038
7	1	0	-2.732444	1.964080	1.725201
8	1	0	-1.164118	0.071517	1.414099
9	1	0	-4.068824	-1.930596	-1.042880
10	1	0	-5.639492	-0.027898	-0.734475
11	6	0	-5.268762	2.242709	0.739118
12	1	0	-5.939152	2.041391	1.585175
13	1	0	-4.742274	3.177674	0.956910
14	1	0	-5.898420	2.403111	-0.142281
15	16	0	-1.479016	-2.488731	0.030825
16	8	0	-1.390284	-3.191874	1.316388
17	8	0	-1.912760	-3.217332	-1.171078
18	7	0	0.025080	-1.777783	-0.188068
19	6	0	1.200299	-2.453281	0.429125
20	1	0	1.139122	-3.542566	0.312164
21	1	0	1.208745	-2.236431	1.498776
22	6	0	2.418629	-1.926703	-0.292385
23	1	0	2.555458	-2.382080	-1.273100
24	6	0	3.593540	-1.425144	0.269840
25	6	0	4.544506	-0.932995	-0.687636
26	1	0	4.758162	-1.584667	-1.538570
27	1	0	3.847846	-0.064466	-1.276974
28	1	0	5.442595	-0.453927	-0.297021
29	6	0	3.755897	-1.114518	1.735091
30	1	0	4.374560	-0.224212	1.878586
31	1	0	2.800292	-0.961948	2.243925
32	1	0	4.262468	-1.951319	2.236583
33	6	0	0.310006	-1.137369	-1.482062
34	1	0	0.436488	-1.867544	-2.294365
35	1	0	-0.513739	-0.471302	-1.749527
36	6	0	1.561125	-0.339113	-1.272978
37	6	0	1.696209	1.115786	-0.832610
38	6	0	2.486273	0.429691	-1.916866
39	1	0	2.683425	0.722597	-2.940096
40	6	0	2.340544	1.531274	0.475667
41	8	0	3.464315	1.963478	0.607130
42	8	0	1.473544	1.384948	1.507962
43	6	0	1.903069	1.949764	2.757736
44	1	0	2.120880	3.014287	2.636852
45	1	0	2.797005	1.443010	3.128984
46	1	0	1.070181	1.804278	3.446553
47	6	0	0.602857	2.042860	-1.310486
48	8	0	-0.062620	1.851386	-2.308719
49	8	0	0.473452	3.136579	-0.531417
50	6	0	-0.536220	4.071699	-0.947410
51	1	0	-0.482480	4.894556	-0.234080
52	1	0	-0.336467	4.426312	-1.961598
53	1	0	-1.522177	3.600116	-0.921120

Zero-point correction= 0.423344 (Hartree/Particle)
Thermal correction to Energy= 0.452177
Thermal correction to Enthalpy= 0.453121

Thermal correction to Gibbs Free Energy= 0.361910
Sum of electronic and zero-point Energies= -1680.839254
Sum of electronic and thermal Energies= -1680.810421
Sum of electronic and thermal Enthalpies= -1680.809477
Sum of electronic and thermal Free Energies= -1680.900688
M06-2X /6-311++G (d, p)/SMD// B3LYP /6-31G(d) energy= -1681.127348

TS3b(Z-exo)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.434989	0.816715	0.766474
2	6	0	-2.338215	-0.044034	0.763002
3	6	0	-2.450557	-1.282593	0.128488
4	6	0	-3.639575	-1.660087	-0.499082
5	6	0	-4.726338	-0.788921	-0.479238
6	6	0	-4.645320	0.458112	0.156481
7	1	0	-3.347490	1.786163	1.251496
8	1	0	-1.399197	0.254823	1.217840
9	1	0	-3.699574	-2.616836	-1.006697
10	1	0	-5.650903	-1.079964	-0.972036
11	6	0	-5.839146	1.382361	0.196079
12	1	0	-6.416121	1.332652	-0.733533
13	1	0	-6.519192	1.110669	1.014278
14	1	0	-5.537440	2.422686	0.354728
15	16	0	-1.098091	-2.465835	0.167804
16	8	0	-1.032079	-3.088297	1.496173
17	8	0	-1.240235	-3.306731	-1.030219
18	7	0	0.250436	-1.482944	0.037707
19	6	0	1.420291	-1.666128	0.952756
20	1	0	1.248532	-2.570778	1.541676
21	1	0	1.490548	-0.818831	1.638795
22	6	0	2.616228	-1.824098	0.052638
23	1	0	2.442396	-2.675185	-0.610306
24	6	0	3.958405	-1.444417	0.095114
25	6	0	4.932722	-2.229740	-0.766195
26	1	0	5.293332	-1.625861	-1.610519
27	1	0	5.814574	-2.518474	-0.181775
28	1	0	4.485854	-3.142827	-1.169430
29	6	0	4.388078	-0.168070	0.510882
30	1	0	5.453170	0.057159	0.472285
31	1	0	3.782546	0.521005	-0.559595
32	1	0	3.866957	0.354617	1.307837
33	6	0	0.595106	-0.965095	-1.315076
34	1	0	0.831352	-1.769791	-2.020024
35	1	0	-0.257348	-0.402690	-1.710052
36	6	0	1.742227	-0.057366	-1.062956
37	6	0	1.624638	1.396299	-0.572779
38	6	0	2.730369	0.817855	-1.423605
39	1	0	3.129081	1.179761	-2.366866
40	6	0	1.894973	1.907317	0.830122
41	8	0	2.848757	2.576199	1.161553
42	8	0	0.910547	1.549738	1.690253
43	6	0	1.022139	2.102841	3.014314
44	1	0	1.002191	3.194817	2.970551
45	1	0	1.952800	1.782309	3.489316
46	1	0	0.160654	1.722319	3.563292
47	6	0	0.578165	2.193753	-1.314420
48	8	0	0.256289	1.982415	-2.466159
49	8	0	0.051727	3.181623	-0.561664
50	6	0	-0.945609	3.988659	-1.211626
51	1	0	-1.213893	4.758337	-0.487557
52	1	0	-0.541488	4.438308	-2.121745
53	1	0	-1.816540	3.379812	-1.468519

Zero-point correction= 0.422105 (Hartree/Particle)

Thermal correction to Energy=	0.451353
Thermal correction to Enthalpy=	0.452297
Thermal correction to Gibbs Free Energy=	0.358915
Sum of electronic and zero-point Energies=	-1680.813269
Sum of electronic and thermal Energies=	-1680.784021
Sum of electronic and thermal Enthalpies=	-1680.783077
Sum of electronic and thermal Free Energies=	-1680.876459

M06-2X /6-311++G (d, p)/SMD// B3LYP /6-31G(d) energy= -1681.096936

TS3b(Z-endo)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.748779	0.727864	0.601933
2	6	0	-4.430233	0.496912	0.999508
3	6	0	-3.642723	-0.380597	0.258285
4	6	0	-4.158728	-1.037032	-0.863766
5	6	0	-5.473061	-0.794437	-1.245079
6	6	0	-6.289590	0.090539	-0.519955
7	1	0	-6.365730	1.413360	1.177452
8	1	0	-4.012482	0.986044	1.872778
9	1	0	-3.534966	-1.723358	-1.426911
10	1	0	-5.876948	-1.301336	-2.118349
11	6	0	-7.716886	0.336543	-0.947237
12	1	0	-7.764688	0.713826	-1.976006
13	1	0	-8.304153	-0.589486	-0.917224
14	1	0	-8.209789	1.066470	-0.298286
15	16	0	-1.971389	-0.738113	0.801943
16	8	0	-1.700053	0.130415	1.962168
17	8	0	-1.799199	-2.189449	0.919396
18	7	0	-1.077781	-0.261326	-0.569874
19	6	0	-0.906997	1.211039	-0.732472
20	1	0	-1.361893	1.725253	0.115653
21	1	0	-1.452924	1.512898	-1.634307
22	6	0	0.549681	1.640447	-0.894634
23	1	0	0.895949	1.609039	-1.927718
24	6	0	1.148879	2.606558	-0.086090
25	6	0	2.228906	3.503881	-0.639742
26	1	0	3.078325	3.585539	0.048630
27	1	0	2.598470	3.157483	-1.607752
28	1	0	1.830908	4.520426	-0.771201
29	6	0	1.002213	2.512417	1.338555
30	1	0	1.477860	3.292451	1.935212
31	1	0	0.027538	2.221070	1.736218
32	1	0	1.608925	1.445489	1.519357
33	6	0	0.187680	-0.974242	-0.789531
34	1	0	0.110157	-1.991149	-0.402351
35	1	0	0.362356	-1.026715	-1.870344
36	6	0	1.288574	-0.214045	-0.100864
37	6	0	2.766743	-0.438937	0.089969
38	6	0	1.757331	-0.113290	1.172409
39	1	0	1.531778	-0.603550	2.110285
40	6	0	3.794153	0.557363	-0.414382
41	8	0	3.906481	0.908181	-1.570120
42	8	0	4.603678	0.982202	0.578597
43	6	0	5.703434	1.808565	0.164863
44	1	0	5.344447	2.736460	-0.288197
45	1	0	6.325447	1.277647	-0.560819
46	1	0	6.268316	2.020193	1.073416
47	6	0	3.237984	-1.873480	0.021369
48	8	0	2.537147	-2.835225	0.259350
49	8	0	4.539854	-1.964243	-0.323428
50	6	0	5.066169	-3.299310	-0.405308
51	1	0	6.111751	-3.183442	-0.691563
52	1	0	4.983471	-3.802408	0.561518
53	1	0	4.522803	-3.878724	-1.156173

Zero-point correction= 0.423182 (Hartree/Particle)
Thermal correction to Energy= 0.452209
Thermal correction to Enthalpy= 0.453153
Thermal correction to Gibbs Free Energy= 0.359806
Sum of electronic and zero-point Energies= -1680.837312
Sum of electronic and thermal Energies= -1680.808286
Sum of electronic and thermal Enthalpies= -1680.807341
Sum of electronic and thermal Free Energies= -1680.900689
M06-2X /6-311++G (d, p)/SMD// B3LYP /6-31G(d) energy= -1681.121951

TS3k(E-exo-out)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.239080	-1.095311	-1.947400
2	6	0	-3.663883	0.103911	-1.531774
3	6	0	-3.336302	0.273438	-0.184000
4	6	0	-3.590130	-0.740319	0.743932
5	6	0	-4.166002	-1.932585	0.309617
6	6	0	-4.492312	-2.133283	-1.039284
7	1	0	-4.506072	-1.223299	-2.993588
8	1	0	-3.499069	0.914492	-2.233759
9	1	0	-3.368195	-0.578118	1.793383
10	1	0	-4.375521	-2.717191	1.032679
11	6	0	-5.090107	-3.439739	-1.503729
12	1	0	-5.705884	-3.898679	-0.723387
13	1	0	-5.713355	-3.302073	-2.393119
14	1	0	-4.303990	-4.160909	-1.764187
15	16	0	-2.548448	1.794914	0.355774
16	8	0	-2.905675	2.841464	-0.606093
17	8	0	-2.798146	1.935850	1.792082
18	7	0	-0.891758	1.571216	0.193731
19	6	0	-0.307427	1.508340	-1.154405
20	1	0	-0.734763	2.317286	-1.750823
21	1	0	-0.534425	0.553094	-1.653524
22	6	0	1.186364	1.645959	-0.960436
23	1	0	1.797984	0.931857	-1.505731
24	6	0	1.797859	2.853522	-0.612312
25	6	0	3.208861	2.772337	-0.320207
26	1	0	3.698704	3.707330	-0.039670
27	1	0	3.203048	2.027109	0.628968
28	1	0	3.808643	2.196255	-1.029523
29	6	0	1.028955	4.054032	-0.129174
30	1	0	1.541544	4.977236	-0.422594
31	1	0	0.003055	4.085353	-0.502422
32	1	0	0.966937	4.058290	0.969599
33	6	0	-0.205740	0.694761	1.155839
34	1	0	-0.369175	1.089446	2.159964
35	1	0	-0.605349	-0.330253	1.119701
36	6	0	1.272989	0.647238	0.810155
37	6	0	2.250200	-0.550404	0.826522
38	6	0	2.429740	0.774427	1.524528
39	1	0	2.643012	1.005129	2.560570
40	6	0	1.840821	-1.748518	1.659565
41	8	0	2.008384	-2.911574	1.359175
42	8	0	1.243917	-1.372481	2.821819
43	6	0	0.831996	-2.452429	3.673100
44	1	0	0.372175	-1.981136	4.542515
45	1	0	0.113917	-3.097167	3.158940
46	1	0	1.693554	-3.055129	3.972637
47	6	0	3.081751	-0.938281	-0.374415
48	6	0	4.423653	-0.552798	-0.464328
49	6	0	2.537810	-1.715715	-1.407793
50	6	0	5.203344	-0.919007	-1.563996
51	1	0	4.855820	0.036949	0.339588

52	6	0	3.311175	-2.080106	-2.509288
53	1	0	1.504642	-2.045548	-1.340227
54	6	0	4.647744	-1.681592	-2.591695
55	1	0	6.245062	-0.612307	-1.613724
56	1	0	2.872274	-2.680931	-3.301731
57	1	0	5.251376	-1.967571	-3.449040

Zero-point correction= 0.461690 (Hartree/Particle)
Thermal correction to Energy= 0.490756
Thermal correction to Enthalpy= 0.491700
Thermal correction to Gibbs Free Energy= 0.399385
Sum of electronic and zero-point Energies= -1683.986514
Sum of electronic and thermal Energies= -1683.957449
Sum of electronic and thermal Enthalpies= -1683.956504
Sum of electronic and thermal Free Energies= -1684.048820
M06-2X /6-311++G (d, p)/SMD// B3LYP /6-31G(d) energy= -1684.291041

TS3k(E-exo-in)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.260040	0.809150	1.780475
2	6	0	-3.722741	-0.322860	1.172004
3	6	0	-3.189966	-0.218583	-0.116114
4	6	0	-3.198779	1.002754	-0.794346
5	6	0	-3.740618	2.124840	-0.169220
6	6	0	-4.278160	2.048209	1.122966
7	1	0	-4.680177	0.728004	2.780167
8	1	0	-3.735536	-1.284407	1.674288
9	1	0	-2.807898	1.062070	-1.804513
10	1	0	-3.752865	3.074671	-0.698218
11	6	0	-4.894759	3.260432	1.779405
12	1	0	-5.981584	3.280554	1.624429
13	1	0	-4.722141	3.262510	2.860908
14	1	0	-4.489181	4.189893	1.367307
15	16	0	-2.446855	-1.659844	-0.890506
16	8	0	-3.050309	-2.847025	-0.278447
17	8	0	-2.459468	-1.435617	-2.337867
18	7	0	-0.830464	-1.682237	-0.439759
19	6	0	-0.475704	-2.028929	0.945424
20	1	0	-1.051550	-2.911274	1.233492
21	1	0	-0.720548	-1.214288	1.645316
22	6	0	1.016103	-2.273434	0.942039
23	1	0	1.582240	-1.806493	1.740426
24	6	0	1.599334	-3.397931	0.350357
25	6	0	3.042822	-3.407415	0.303506
26	1	0	3.259387	-2.429845	-0.363925
27	1	0	3.551086	-3.117109	1.223711
28	1	0	3.499159	-4.279755	-0.169737
29	6	0	0.841497	-4.332565	-0.555432
30	1	0	1.249572	-5.346921	-0.482022
31	1	0	-0.228633	-4.365698	-0.338675
32	1	0	0.941499	-4.022641	-1.606624
33	6	0	0.073654	-0.687265	-1.038977
34	1	0	0.069221	-0.831991	-2.121476
35	1	0	-0.259830	0.340608	-0.830166
36	6	0	1.468924	-0.862620	-0.462458
37	6	0	2.476606	0.265304	-0.113395
38	6	0	2.716439	-0.926553	-1.010332
39	1	0	3.085645	-0.971005	-2.027874
40	6	0	3.147497	0.268678	1.242663
41	8	0	3.484454	-0.713631	1.878145
42	8	0	3.361075	1.522067	1.702224
43	6	0	4.021283	1.607966	2.974310
44	1	0	5.002687	1.128404	2.931289
45	1	0	3.425519	1.122497	3.752204

46	1	0	4.122892	2.674539	3.177288
47	6	0	2.235396	1.625921	-0.736193
48	6	0	2.932563	2.017969	-1.885455
49	6	0	1.285033	2.508908	-0.200885
50	6	0	2.692705	3.256149	-2.483755
51	1	0	3.674075	1.349505	-2.315101
52	6	0	1.037076	3.743831	-0.799555
53	1	0	0.745949	2.229804	0.700766
54	6	0	1.741107	4.122424	-1.944601
55	1	0	3.249982	3.542458	-3.372003
56	1	0	0.294798	4.411783	-0.369861
57	1	0	1.549499	5.084661	-2.412006

Zero-point correction= 0.461940 (Hartree/Particle)
Thermal correction to Energy= 0.490946
Thermal correction to Enthalpy= 0.491891
Thermal correction to Gibbs Free Energy= 0.398981
Sum of electronic and zero-point Energies= -1683.984513
Sum of electronic and thermal Energies= -1683.955506
Sum of electronic and thermal Enthalpies= -1683.954562
Sum of electronic and thermal Free Energies= -1684.047472
M06-2X /6-311++G (d, p)/SMD// B3LYP /6-31G(d) energy= -1684.286818

3b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.246345	-0.997602	0.799006
2	6	0	-1.865056	-1.131036	0.894908
3	6	0	-1.234599	-2.170244	0.204892
4	6	0	-1.970720	-3.071681	-0.563687
5	6	0	-3.355313	-2.924717	-0.641735
6	6	0	-4.013171	-1.888625	0.031959
7	1	0	-3.739060	-0.184801	1.327162
8	1	0	-1.281410	-0.424739	1.475155
9	1	0	-1.459953	-3.869169	-1.092419
10	1	0	-3.931928	-3.625469	-1.240291
11	6	0	-5.507945	-1.711465	-0.085571
12	1	0	-5.997035	-2.634738	-0.411369
13	1	0	-5.952152	-1.409350	0.869197
14	1	0	-5.753249	-0.932326	-0.819254
15	16	0	0.531626	-2.438804	0.373875
16	8	0	0.852244	-2.786629	1.763062
17	8	0	0.943559	-3.339477	-0.714591
18	7	0	1.134721	-0.863738	0.140881
19	6	0	2.416907	-0.551158	0.838647
20	1	0	2.336118	-1.012303	1.826502
21	1	0	2.428375	0.530654	0.984980
22	6	0	3.647767	-1.045594	0.126439
23	1	0	3.687487	-2.126625	-0.010907
24	6	0	4.680259	-0.313434	-0.323572
25	6	0	5.864304	-0.984459	-0.979446
26	1	0	6.019687	-0.601338	-1.997640
27	1	0	6.790114	-0.775537	-0.425265
28	1	0	5.740451	-2.070014	-1.037181
29	6	0	4.796460	1.188687	-0.212626
30	1	0	5.629990	1.459834	0.450418
31	1	0	5.032921	1.623093	-1.193789
32	1	0	3.896637	1.679848	0.163839
33	6	0	1.023606	-0.371371	-1.240870
34	1	0	1.895412	-0.651844	-1.845047
35	1	0	0.133297	-0.810571	-1.703096
36	6	0	0.854758	1.103458	-1.247567
37	6	0	0.009376	2.189490	-0.601960
38	6	0	1.123394	2.306414	-1.622561

39	1	0	1.659707	3.031575	-2.213616
40	6	0	0.340352	2.546427	0.826722
41	8	0	1.453168	2.848698	1.210850
42	8	0	-0.719042	2.418749	1.651211
43	6	0	-0.460819	2.715210	3.035390
44	1	0	-0.107676	3.743535	3.145482
45	1	0	0.292062	2.033389	3.438800
46	1	0	-1.415150	2.580002	3.544813
47	6	0	-1.412078	2.327897	-1.098432
48	8	0	-1.932103	1.556790	-1.878041
49	8	0	-2.010544	3.445222	-0.639190
50	6	0	-3.355950	3.653931	-1.097031
51	1	0	-3.682734	4.583797	-0.630710
52	1	0	-3.382228	3.738903	-2.186724
53	1	0	-3.998118	2.823630	-0.791048

Zero-point correction= 0.426021 (Hartree/Particle)
Thermal correction to Energy= 0.456756
Thermal correction to Enthalpy= 0.457700
Thermal correction to Gibbs Free Energy= 0.360112
Sum of electronic and zero-point Energies= -1680.889167
Sum of electronic and thermal Energies= -1680.858431
Sum of electronic and thermal Enthalpies= -1680.857487
Sum of electronic and thermal Free Energies= -1680.955076
M06-2X /6-311++G (d, p)/SMD// B3LYP /6-31G(d) energy= -1681.177114

trans-4b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.191344	0.855423	1.727146
2	6	0	-3.578671	-0.294515	1.233427
3	6	0	-3.133706	-0.316557	-0.091261
4	6	0	-3.302243	0.797137	-0.918607
5	6	0	-3.917046	1.938385	-0.406864
6	6	0	-4.370828	1.987149	0.918726
7	1	0	-4.543439	0.871681	2.755867
8	1	0	-3.466357	-1.176956	1.854446
9	1	0	-2.975599	0.756741	-1.952352
10	1	0	-4.052954	2.803787	-1.050947
11	6	0	-5.068677	3.215343	1.452726
12	1	0	-4.731545	4.122705	0.941198
13	1	0	-6.154757	3.143827	1.307632
14	1	0	-4.892469	3.342680	2.525904
15	16	0	-2.296289	-1.774773	-0.723616
16	8	0	-2.708822	-2.912843	0.101590
17	8	0	-2.439834	-1.769187	-2.180302
18	7	0	-0.658617	-1.565917	-0.419140
19	6	0	-0.164586	-1.611865	0.961660
20	1	0	-0.471644	-2.541519	1.442037
21	1	0	-0.539885	-0.763334	1.557158
22	6	0	1.365633	-1.490307	0.776693
23	6	0	2.074866	-2.833043	0.685314
24	6	0	3.130111	-3.079460	1.469746
25	1	0	3.559072	-1.275093	-0.986032
26	1	0	3.510404	-2.342078	2.172061
27	1	0	3.661883	-4.026703	1.426566
28	6	0	1.566702	-3.847947	-0.309627
29	1	0	2.167353	-4.761852	-0.273447
30	1	0	0.520193	-4.115214	-0.122806
31	1	0	1.601738	-3.455174	-1.333407
32	6	0	0.088223	-0.527859	-1.150288
33	1	0	0.077438	-0.740418	-2.218865
34	1	0	-0.344647	0.469522	-0.994434
35	6	0	1.487030	-0.630230	-0.519717
36	6	0	2.445422	0.587237	-0.532551

37	6	0	2.730209	-0.668908	-1.339908
38	1	0	2.635737	-0.569514	-2.417260
39	6	0	3.275153	0.819451	0.707503
40	8	0	4.378291	0.362862	0.910575
41	8	0	2.597281	1.566529	1.605445
42	6	0	3.319852	1.890937	2.805498
43	1	0	4.221786	2.459744	2.564797
44	1	0	3.604882	0.982165	3.342011
45	1	0	2.635357	2.492372	3.404164
46	6	0	2.071540	1.791649	-1.342518
47	8	0	1.345999	1.767785	-2.317130
48	8	0	2.688195	2.906616	-0.903943
49	6	0	2.429271	4.096782	-1.669037
50	1	0	3.009085	4.883189	-1.185763
51	1	0	2.748805	3.962016	-2.705422
52	1	0	1.363267	4.337329	-1.652136
53	1	0	1.776863	-0.949040	1.632610

Zero-point correction= 0.430050 (Hartree/Particle)
Thermal correction to Energy= 0.459119
Thermal correction to Enthalpy= 0.460063
Thermal correction to Gibbs Free Energy= 0.366725
Sum of electronic and zero-point Energies= -1680.937455
Sum of electronic and thermal Energies= -1680.908387
Sum of electronic and thermal Enthalpies= -1680.907443
Sum of electronic and thermal Free Energies= -1681.000780
M06-2X /6-311++G (d, p)/SMD// B3LYP /6-31G(d) energy= -1681.236159

3k

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.846562	-0.595023	-0.538051
2	6	0	-4.536327	-0.352711	-0.954898
3	6	0	-3.676389	0.351627	-0.114621
4	6	0	-4.113200	0.826074	1.126100
5	6	0	-5.421312	0.575685	1.524663
6	6	0	-6.309128	-0.137150	0.700850
7	1	0	-6.518969	-1.146517	-1.190316
8	1	0	-4.179380	-0.698028	-1.919217
9	1	0	-3.436304	1.384578	1.764291
10	1	0	-5.764092	0.941195	2.489767
11	6	0	-7.733170	-0.379839	1.140530
12	1	0	-7.777206	-0.728195	2.178675
13	1	0	-8.324482	0.543258	1.085039
14	1	0	-8.226104	-1.126409	0.510627
15	16	0	-2.006185	0.719379	-0.662670
16	8	0	-1.873421	0.187428	-2.027476
17	8	0	-1.712525	2.128672	-0.382109
18	7	0	-1.073772	-0.164167	0.439622
19	6	0	-1.142944	-1.643527	0.366698
20	1	0	-2.190880	-1.890161	0.156385
21	1	0	-0.945558	-2.003667	1.381055
22	6	0	-0.248573	-2.306051	-0.647701
23	1	0	-0.431808	-1.991339	-1.673278
24	6	0	0.694003	-3.234469	-0.420486
25	6	0	1.466719	-3.833001	-1.571937
26	1	0	1.331757	-4.922989	-1.612337
27	1	0	1.154903	-3.416268	-2.534508
28	1	0	2.543834	-3.655364	-1.450800
29	6	0	1.093589	-3.770712	0.932897
30	1	0	2.163787	-3.594411	1.105314
31	1	0	0.543389	-3.325851	1.765647
32	1	0	0.943469	-4.858143	0.978511
33	6	0	0.189257	0.449796	0.865715
34	1	0	-0.028371	1.447791	1.260914

35	1	0	0.563622	-0.154326	1.701279
36	6	0	1.256269	0.593477	-0.158026
37	6	0	2.720423	1.021896	-0.272181
38	6	0	1.734397	0.620723	-1.353967
39	1	0	1.606077	0.512247	-2.419643
40	6	0	3.039383	2.493572	-0.117424
41	8	0	4.097461	2.954628	0.260428
42	8	0	1.981174	3.266577	-0.457913
43	6	0	2.194416	4.680707	-0.356793
44	1	0	1.250154	5.138421	-0.652985
45	1	0	2.454123	4.960435	0.668209
46	1	0	3.002310	4.997363	-1.022443
47	6	0	3.807070	0.066632	0.168198
48	6	0	4.121363	-1.049084	-0.617544
49	6	0	4.486254	0.234989	1.384466
50	6	0	5.082389	-1.974355	-0.206455
51	1	0	3.603786	-1.194609	-1.562449
52	6	0	5.443696	-0.689851	1.800628
53	1	0	4.276279	1.103235	1.999630
54	6	0	5.746411	-1.799168	1.008581
55	1	0	5.317482	-2.826187	-0.840117
56	1	0	5.957920	-0.540239	2.746689
57	1	0	6.495908	-2.516575	1.332532

Zero-point correction= 0.463505 (Hartree/Particle)
Thermal correction to Energy= 0.494554
Thermal correction to Enthalpy= 0.495499
Thermal correction to Gibbs Free Energy= 0.395138
Sum of electronic and zero-point Energies= -1684.026515
Sum of electronic and thermal Energies= -1683.995466
Sum of electronic and thermal Enthalpies= -1683.994522
Sum of electronic and thermal Free Energies= -1684.094883
M06-2X /6-311++G (d, p)/SMD// B3LYP /6-31G(d) energy= -1684.331911

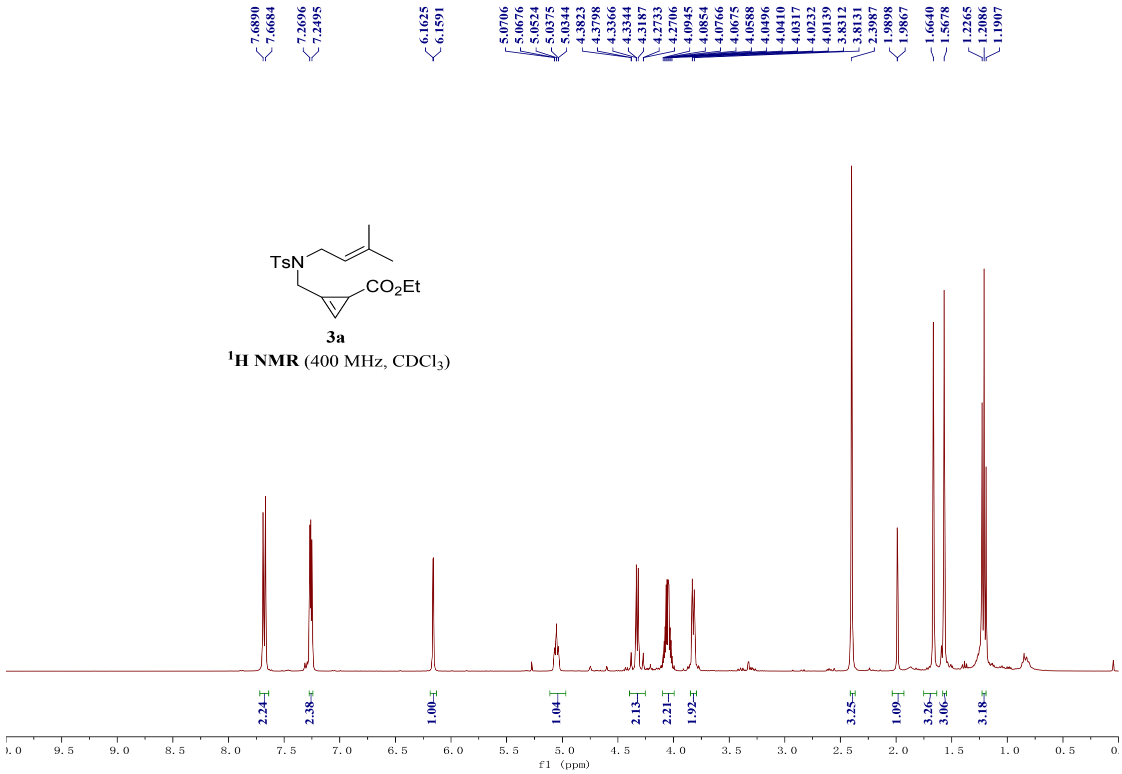
cis-4k

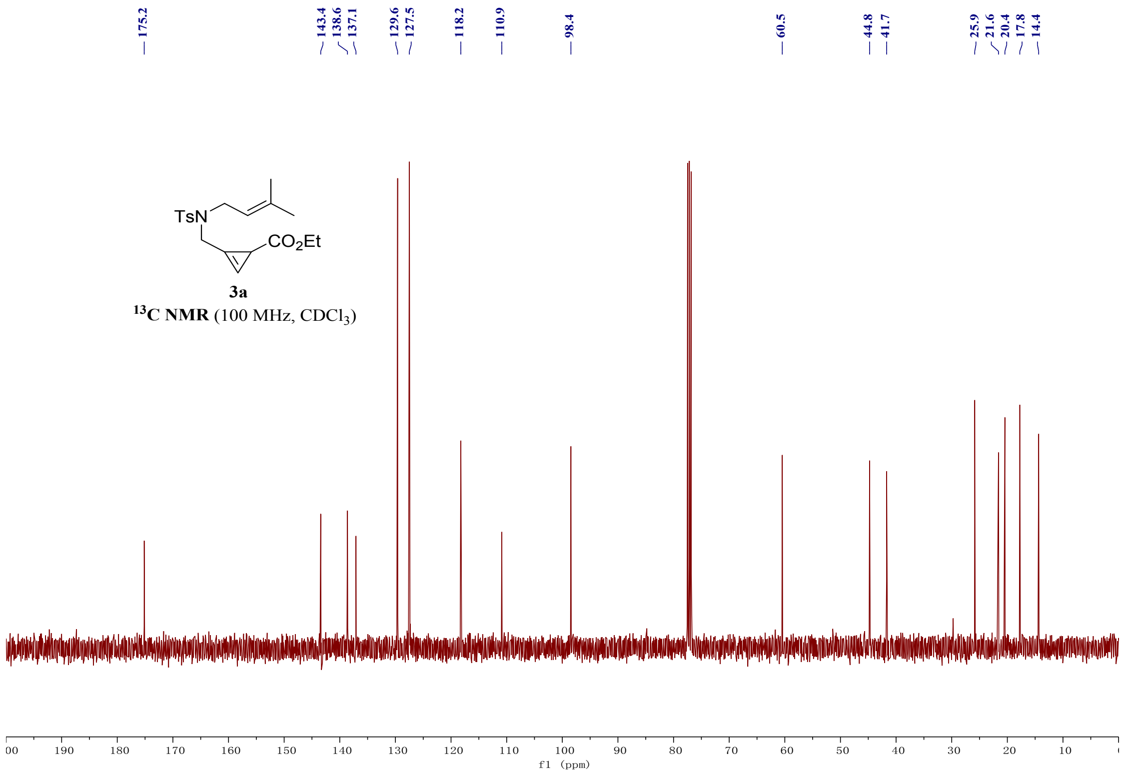
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.186866	-1.015801	-2.042169
2	6	0	-3.635019	0.170630	-1.562679
3	6	0	-3.329393	0.282200	-0.203578
4	6	0	-3.582917	-0.777213	0.672204
5	6	0	-4.135207	-1.955763	0.174515
6	6	0	-4.438223	-2.098276	-1.187159
7	1	0	-4.436267	-1.098659	-3.097239
8	1	0	-3.471371	1.015369	-2.223460
9	1	0	-3.379346	-0.661003	1.731457
10	1	0	-4.343933	-2.776008	0.857129
11	6	0	-5.008908	-3.390386	-1.720713
12	1	0	-5.632669	-3.891938	-0.973612
13	1	0	-5.617274	-3.221361	-2.614978
14	1	0	-4.207941	-4.088764	-1.997592
15	16	0	-2.569480	1.787481	0.415862
16	8	0	-2.927070	2.871242	-0.502021
17	8	0	-2.835472	1.856856	1.854474
18	7	0	-0.908964	1.590964	0.264974
19	6	0	-0.299790	1.524304	-1.070109
20	1	0	-0.564806	2.410282	-1.648724
21	1	0	-0.630151	0.629606	-1.623015
22	6	0	1.210639	1.424322	-0.754013
23	1	0	1.693697	0.801274	-1.510851
24	6	0	1.910925	2.775027	-0.745035
25	6	0	2.995889	2.966613	-1.504605
26	1	0	3.517122	3.920808	-1.521393
27	1	0	3.230599	1.443457	1.184440
28	1	0	3.402341	2.179802	-2.135211

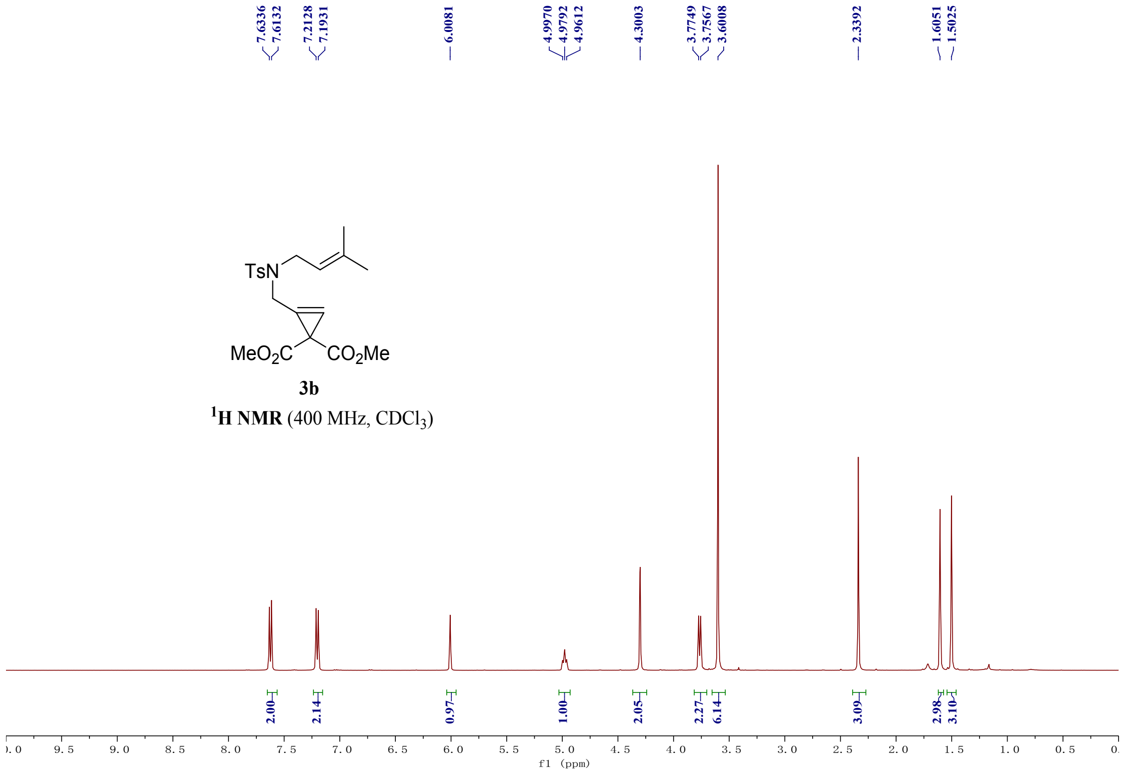
29	6	0	1.352517	3.866817	0.135236
30	1	0	1.948697	4.780496	0.049823
31	1	0	0.314873	4.107412	-0.124031
32	1	0	1.339864	3.562669	1.189262
33	6	0	-0.211298	0.644795	1.148993
34	1	0	-0.309635	0.965098	2.186179
35	1	0	-0.631370	-0.369991	1.056409
36	6	0	1.232480	0.697341	0.621559
37	6	0	2.197715	-0.502820	0.855065
38	6	0	2.404026	0.834647	1.539753
39	1	0	2.224827	0.880841	2.608438
40	6	0	1.639715	-1.645610	1.668311
41	8	0	1.538142	-2.789632	1.278124
42	8	0	1.226467	-1.257006	2.899624
43	6	0	0.639475	-2.292410	3.705475
44	1	0	0.347871	-1.806271	4.636812
45	1	0	-0.231879	-2.722892	3.205089
46	1	0	1.366698	-3.085821	3.895285
47	6	0	3.123190	-0.946718	-0.248315
48	6	0	4.479415	-0.600230	-0.236395
49	6	0	2.642882	-1.736633	-1.304760
50	6	0	5.335089	-1.020137	-1.257179
51	1	0	4.873827	-0.003485	0.581051
52	6	0	3.494936	-2.156153	-2.325109
53	1	0	1.599086	-2.033662	-1.315512
54	6	0	4.844803	-1.797360	-2.306188
55	1	0	6.385111	-0.741257	-1.227782
56	1	0	3.104640	-2.767091	-3.134819
57	1	0	5.508813	-2.124136	-3.102004

Zero-point correction= 0.468204 (Hartree/Particle)
Thermal correction to Energy= 0.497260
Thermal correction to Enthalpy= 0.498204
Thermal correction to Gibbs Free Energy= 0.405423
Sum of electronic and zero-point Energies= -1684.077621
Sum of electronic and thermal Energies= -1684.048565
Sum of electronic and thermal Enthalpies= -1684.047620
Sum of electronic and thermal Free Energies= -1684.140401
M06-2X /6-311++G (d, p)/SMD// B3LYP /6-31G(d) energy= -1684.395003

VI. NMR Spectra of Compounds

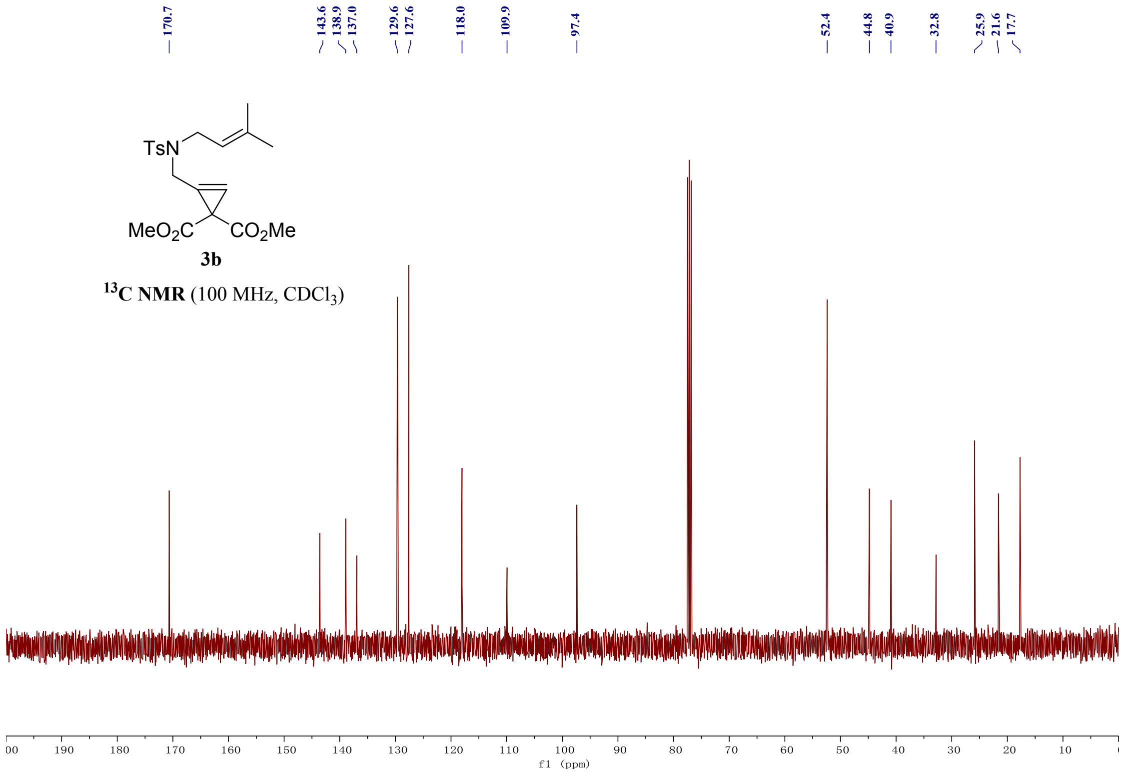






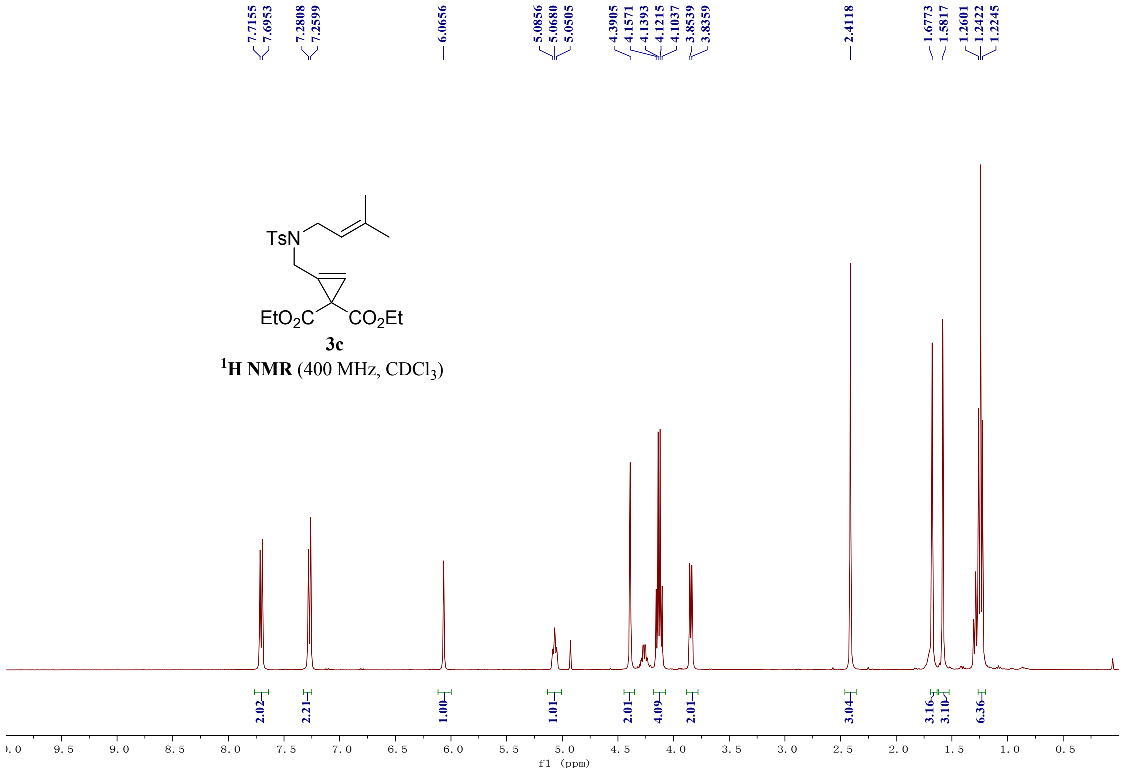
3b

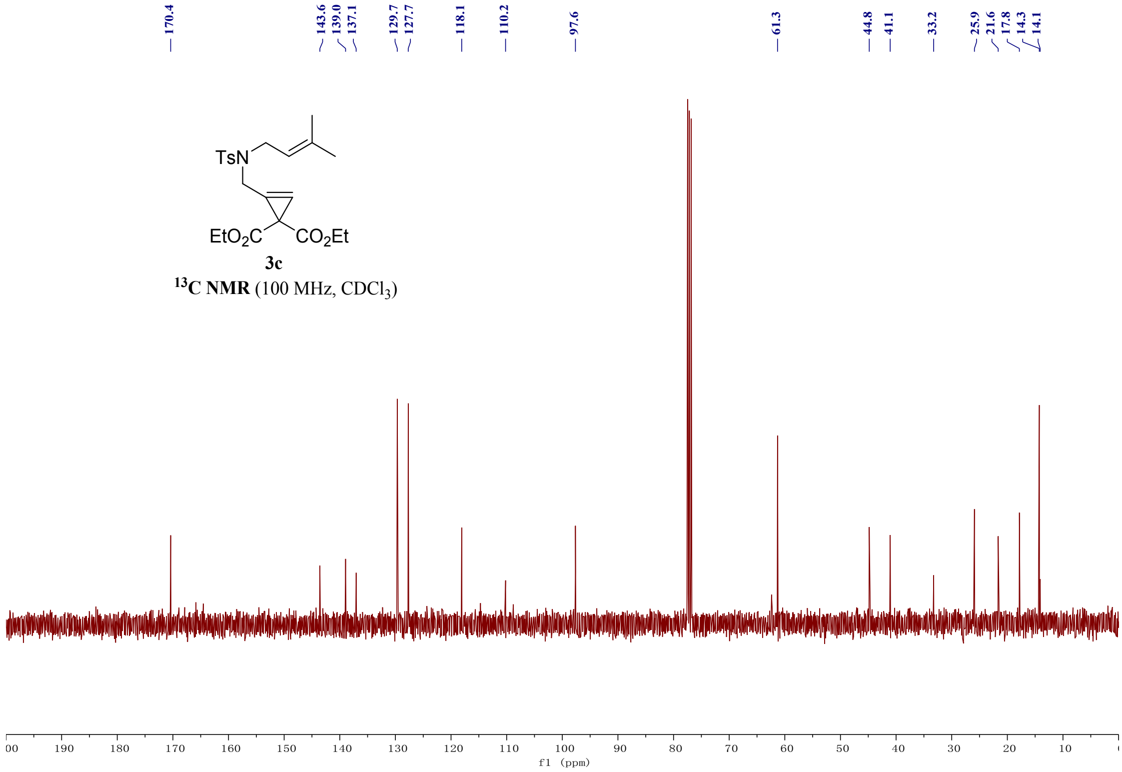
[1]H NMR (400 MHz, $CDCl_3$)

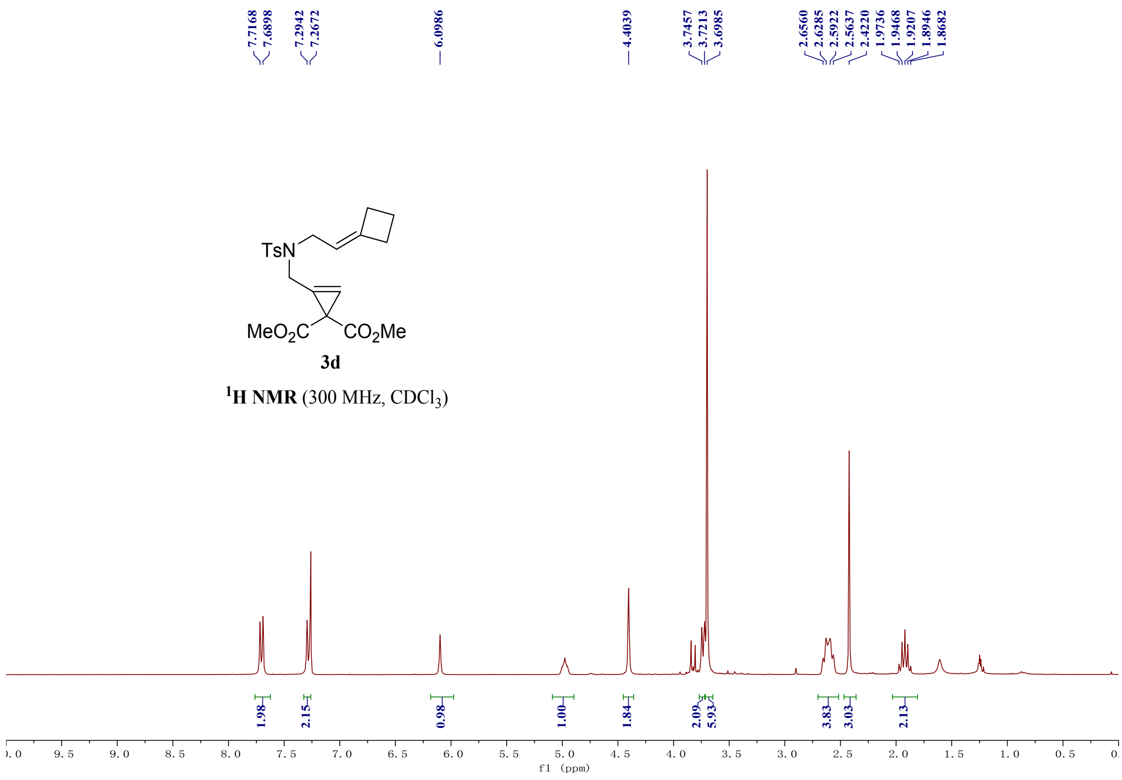


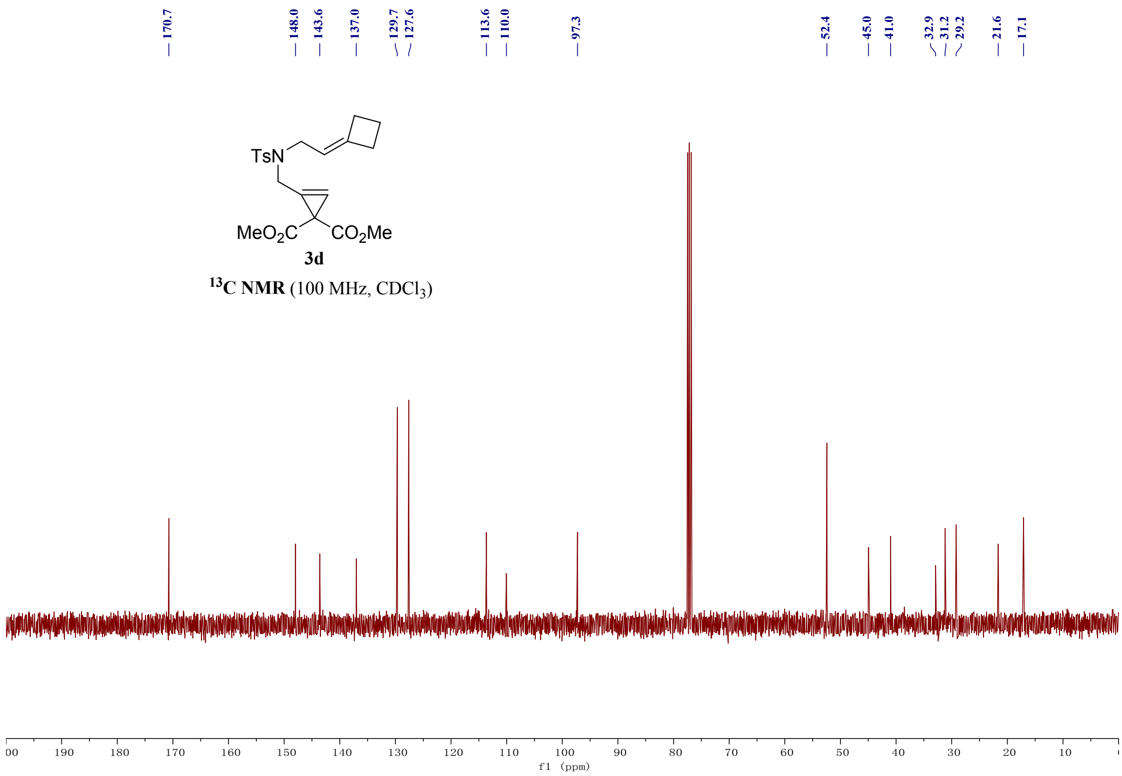
3b

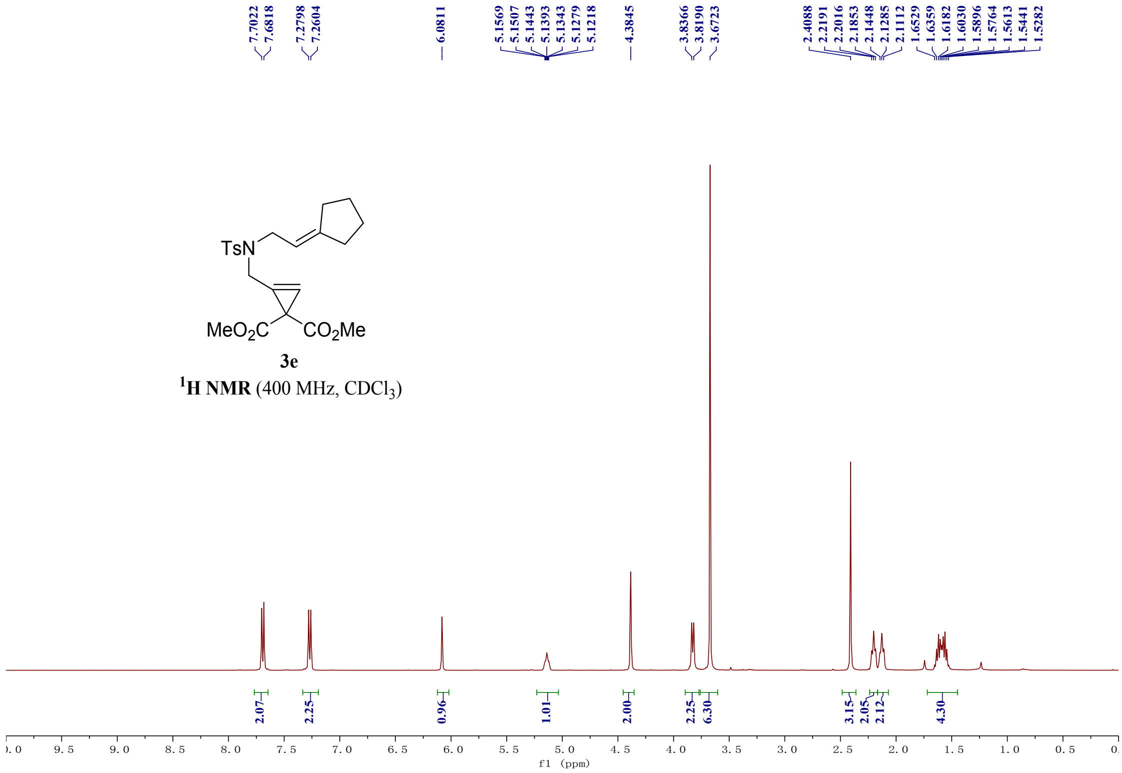
[13]C NMR (100 MHz, $CDCl_3$)


7.7155
7.6953
7.2808
7.2599
6.0656
5.0856
5.0680
5.0505
4.3905
4.1571
4.1393
4.1215
4.1037
3.8539
3.8359
2.4118
1.6773
1.5817
1.2601
1.2422
1.2245
TsN
EtO2C
CO2Et
3c
1H NMR (400 MHz, CDCl3)
2.02
2.21
1.00
1.01
2.01
4.09
2.01
3.04
3.16
3.10
6.36
f1 (ppm)


170.4
143.6
139.0
137.1
129.7
127.7
118.1
110.2
97.6
61.3
44.8
41.1
33.2
25.9
21.6
17.8
14.3
14.1
TsN
EtO2C
CO2Et
3c
13C NMR (100 MHz, CDCl3)
f1 (ppm)

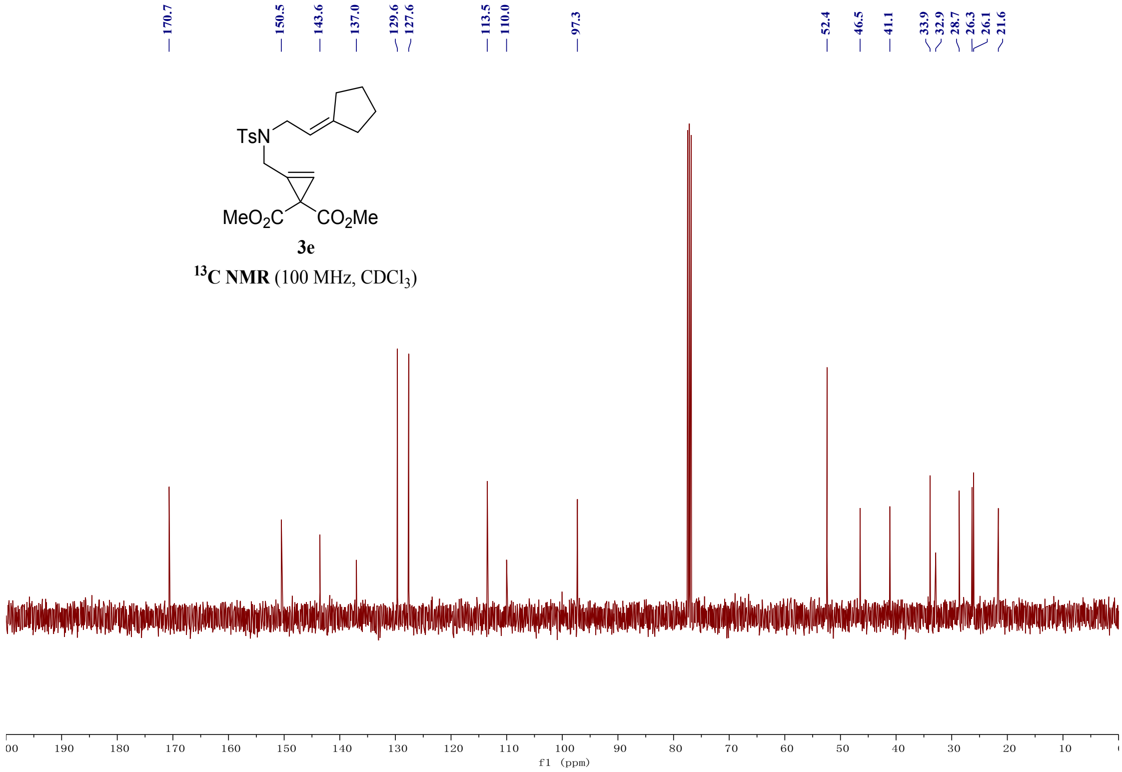

7.7168
7.6898
7.2942
7.2672
6.0986
4.4039
3.7457
3.7213
3.6985
2.6560
2.6285
2.5922
2.5637
2.4220
1.9736
1.9468
1.9207
1.8946
1.8682
TsN
MeO2C
CO2Me
3d
1H NMR (300 MHz, CDCl3)
1.98
2.15
0.98
1.00
1.84
2.09
5.93
3.83
3.03
2.13
f1 (ppm)


170.7
148.0
143.6
137.0
129.7
127.6
113.6
110.0
97.3
52.4
45.0
41.0
32.9
31.2
29.2
21.6
17.1
TsN
MeO2C
CO2Me
3d
13C NMR (100 MHz, CDCl3)
f1 (ppm)



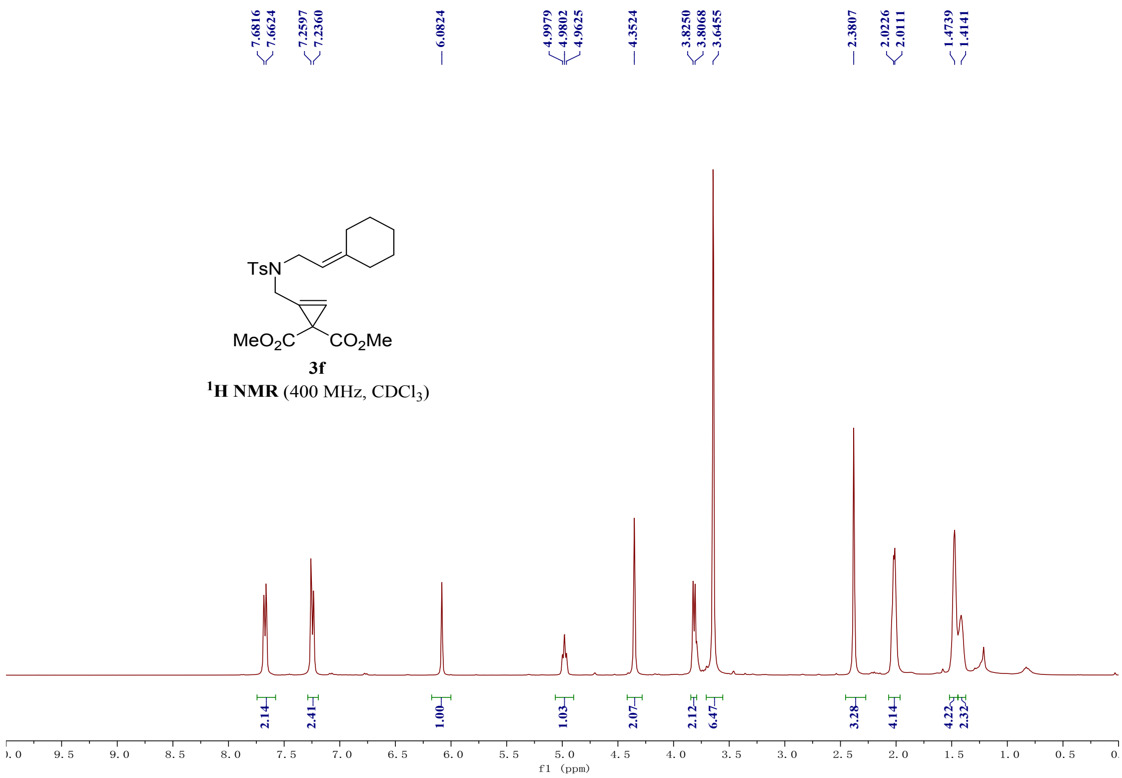
3e

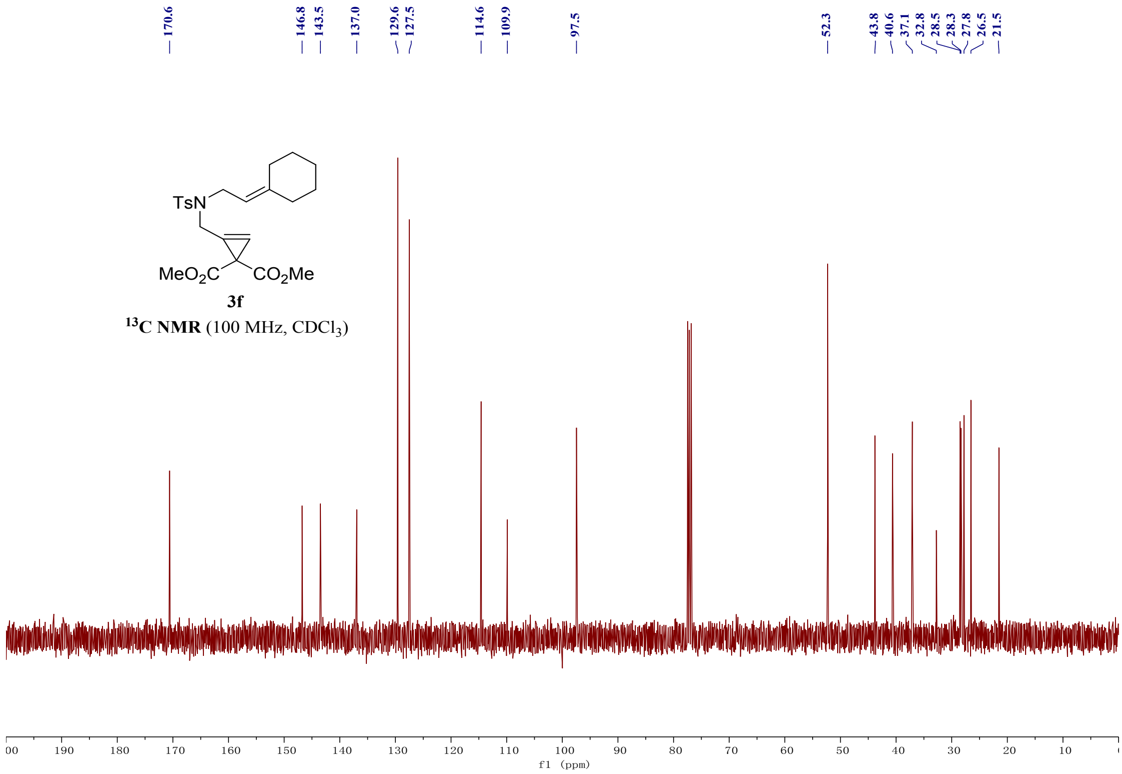
^{1}H NMR (400 MHz, $CDCl_3$)

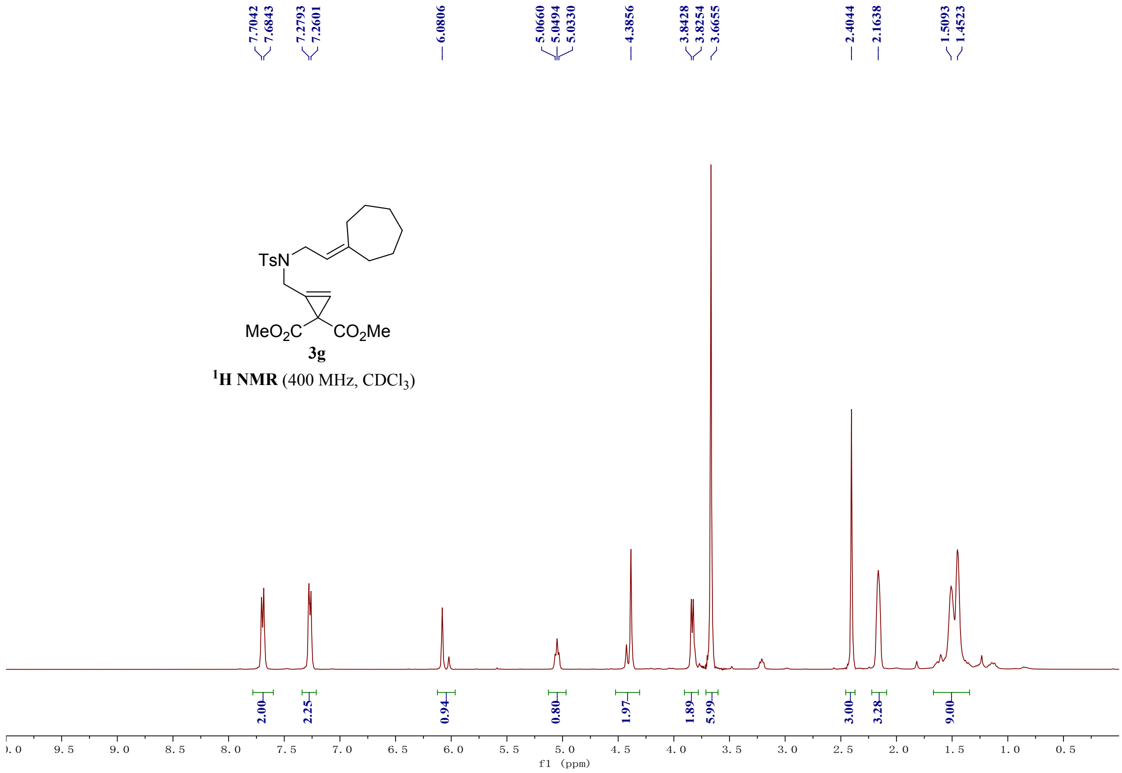


3e

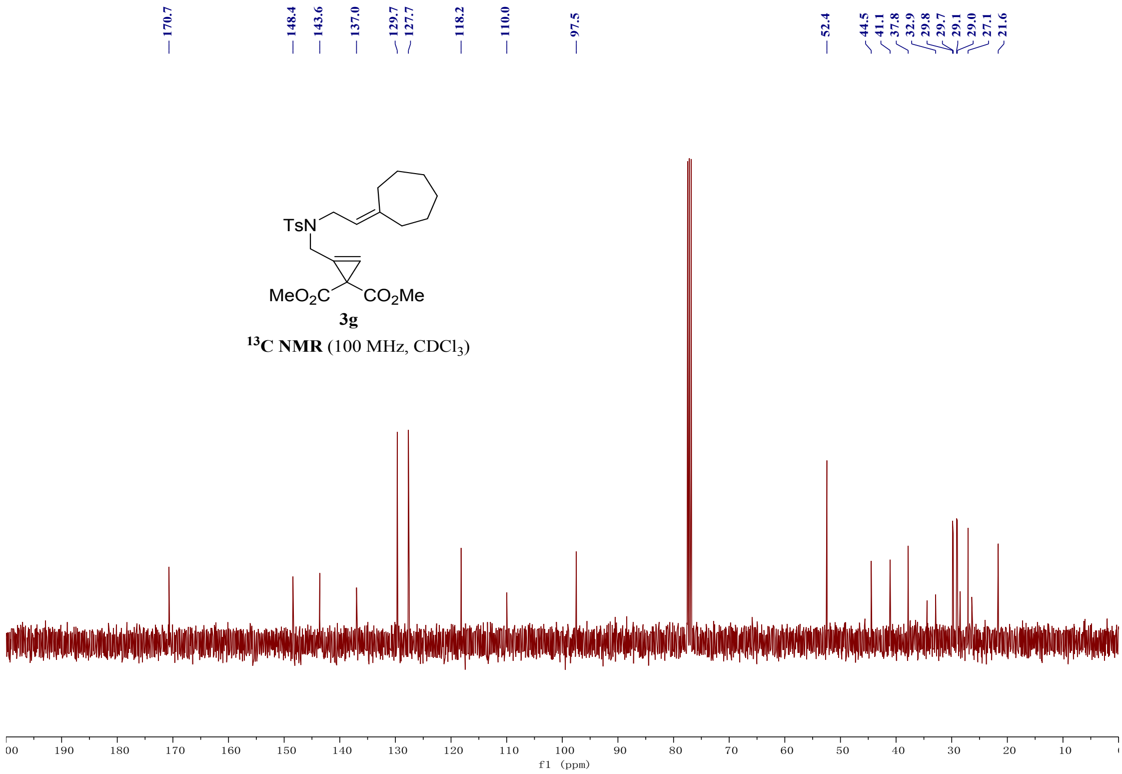
^{13}C NMR (100 MHz, $CDCl_3$)


7.6816
7.6624
7.2597
7.2360
6.0824
4.9979
4.9802
4.9625
4.3524
3.8250
3.8068
3.6455
2.3807
2.0226
2.0111
1.4739
1.4141
TsN
MeO2C
CO2Me
3f
1H NMR (400 MHz, CDCl3)
2.14
2.41
1.00
1.03
2.07
2.12
6.47
3.28
4.14
4.22
2.32
f1 (ppm)

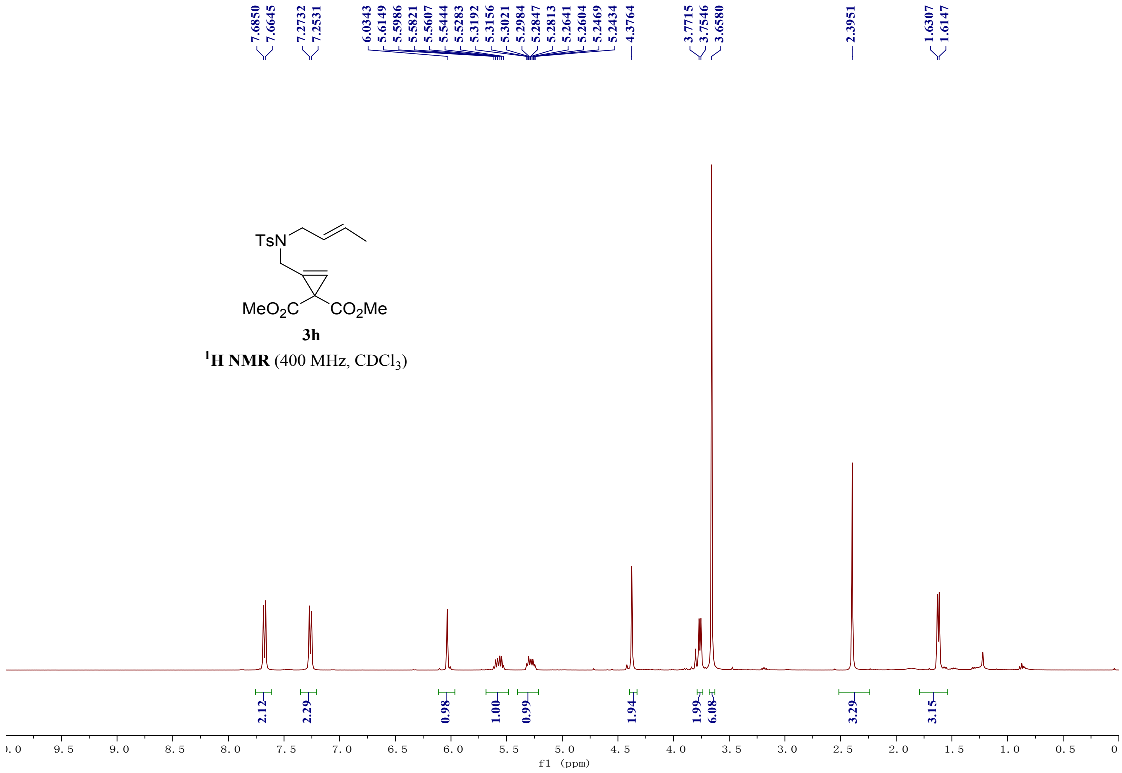

170.6
146.8
143.5
137.0
129.6
127.5
114.6
109.9
97.5
52.3
43.8
40.6
37.1
32.8
28.5
28.3
27.8
26.5
21.5
TsN
MeO2C
CO2Me
3f
13C NMR (100 MHz, CDCl3)
f1 (ppm)



7.7042
7.6843
7.2793
7.2601
6.0806
5.0660
5.0494
5.0330
4.3856
3.8428
3.8254
3.6655
2.4044
2.1638
1.5093
1.4523
TsN
MeO2C
CO2Me
3g
1H NMR (400 MHz, CDCl3)
2.00
2.25
0.94
0.80
1.97
1.89
5.99
3.00
3.28
9.00
f1 (ppm)



170.7
148.4
143.6
137.0
129.7
127.7
118.2
110.0
97.5
52.4
44.5
41.1
37.8
32.9
29.8
29.7
29.1
29.0
27.1
21.6
TsN
MeO2C
CO2Me
3g
13C NMR (100 MHz, CDCl3)
f1 (ppm)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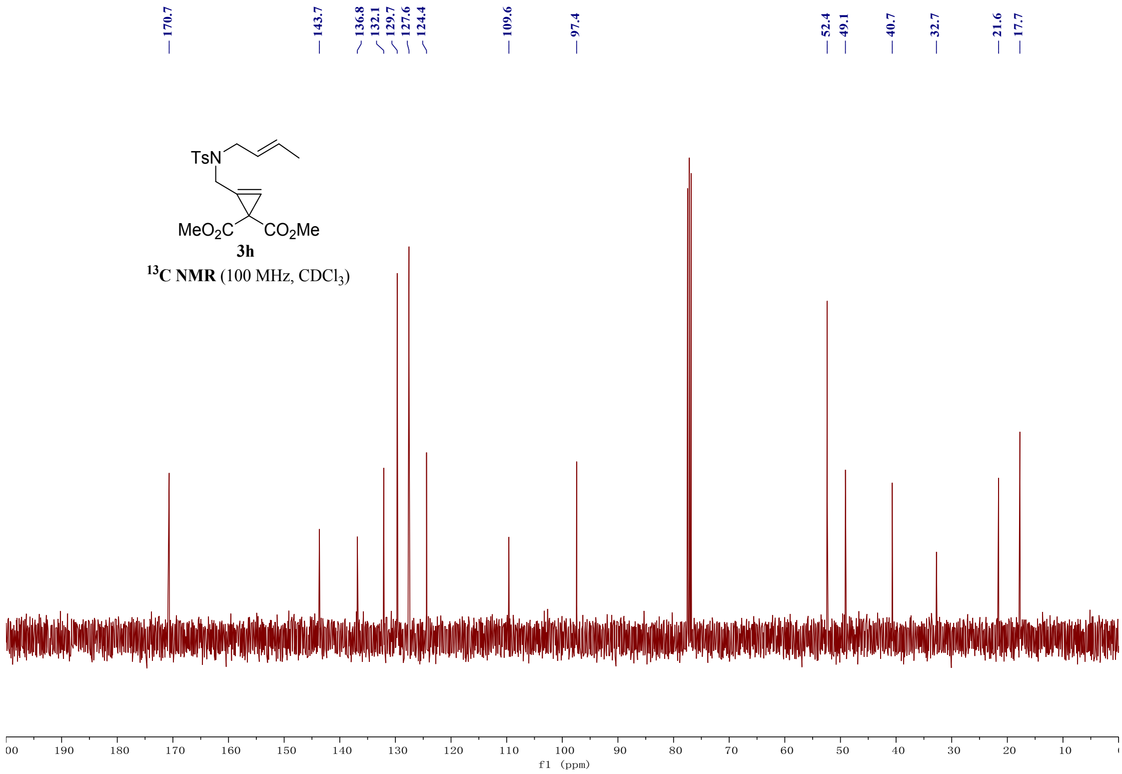
7.6645
7.2732
7.2531
6.0343
5.6149
5.5986
5.5821
5.5607
5.5444
5.5283
5.3192
5.3156
5.3021
5.2984
5.2847
5.2813
5.2641
5.2604
5.2469
5.2434
4.3764
3.7715
3.7546
3.6580
2.3951
1.6307
1.6147
TsN
MeO2C
CO2Me
3h
1H NMR (400 MHz, CDCl3)
2.12
2.29
0.98
1.00
0.99
1.94
1.99
6.08
3.29
3.15
f1 (ppm)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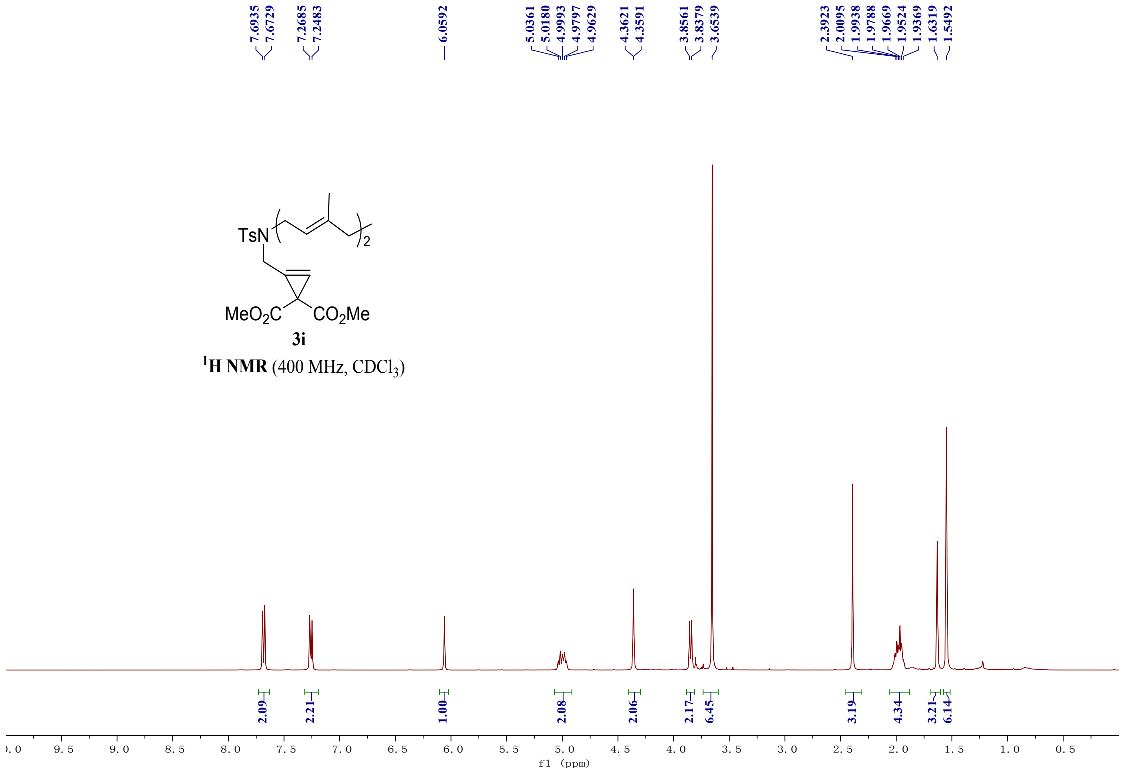
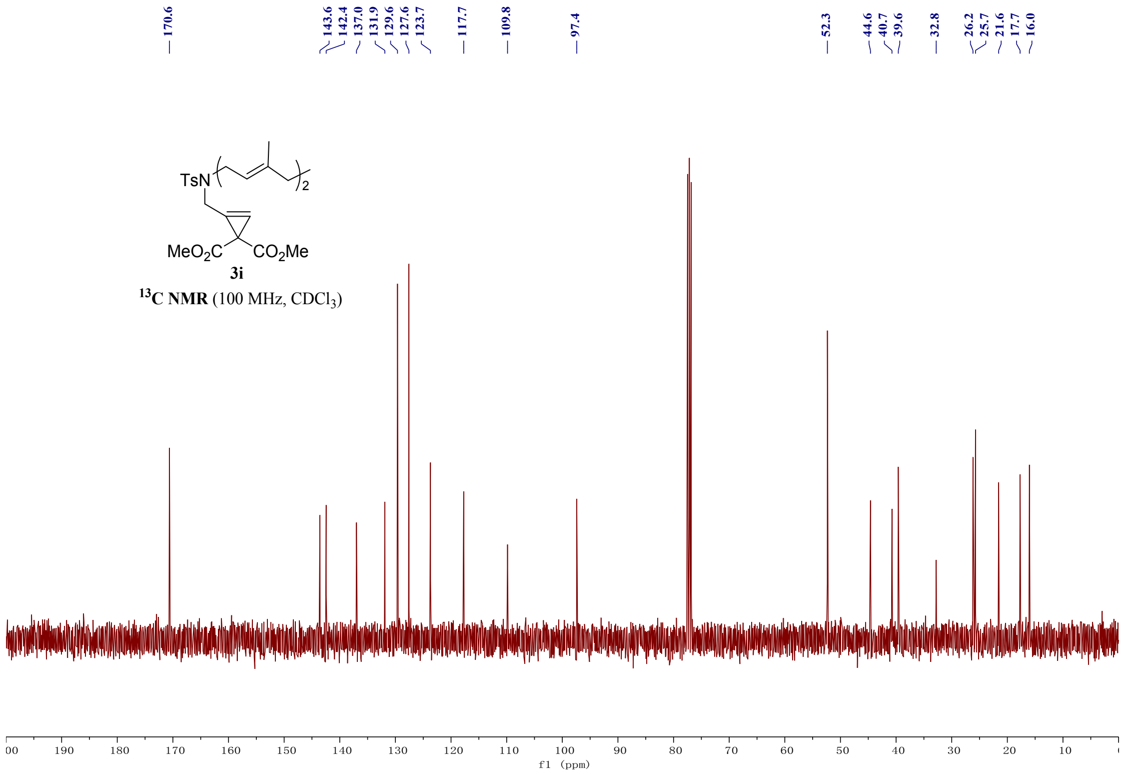
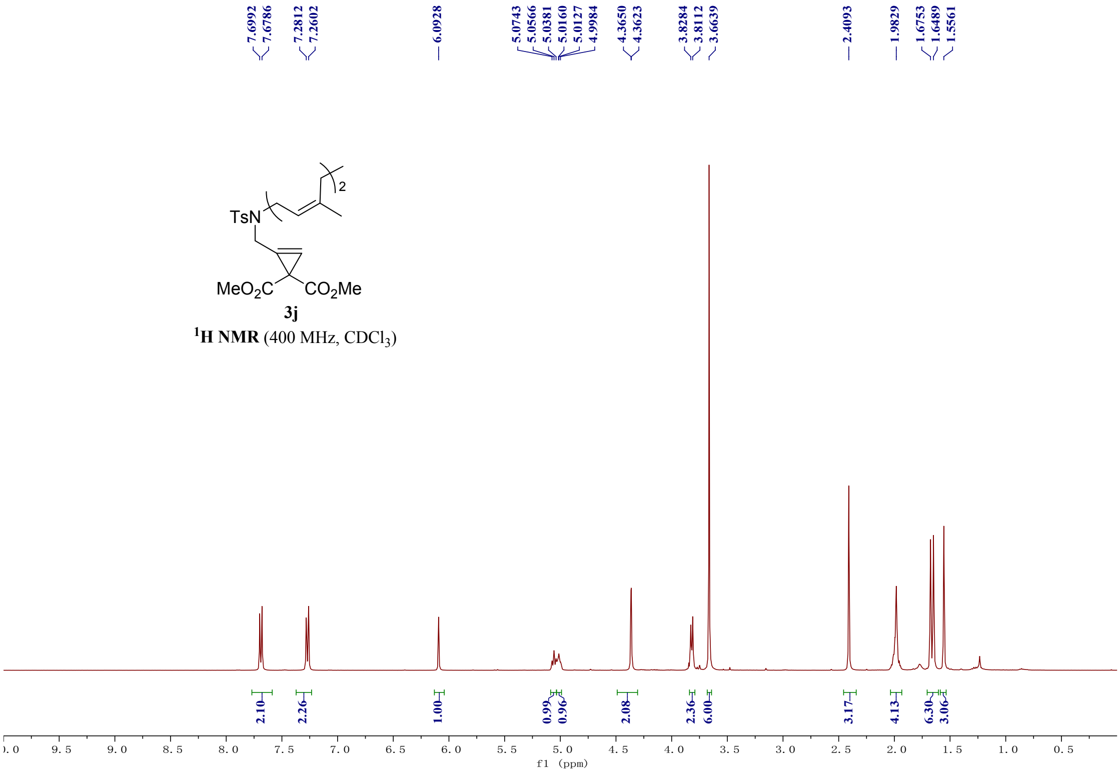
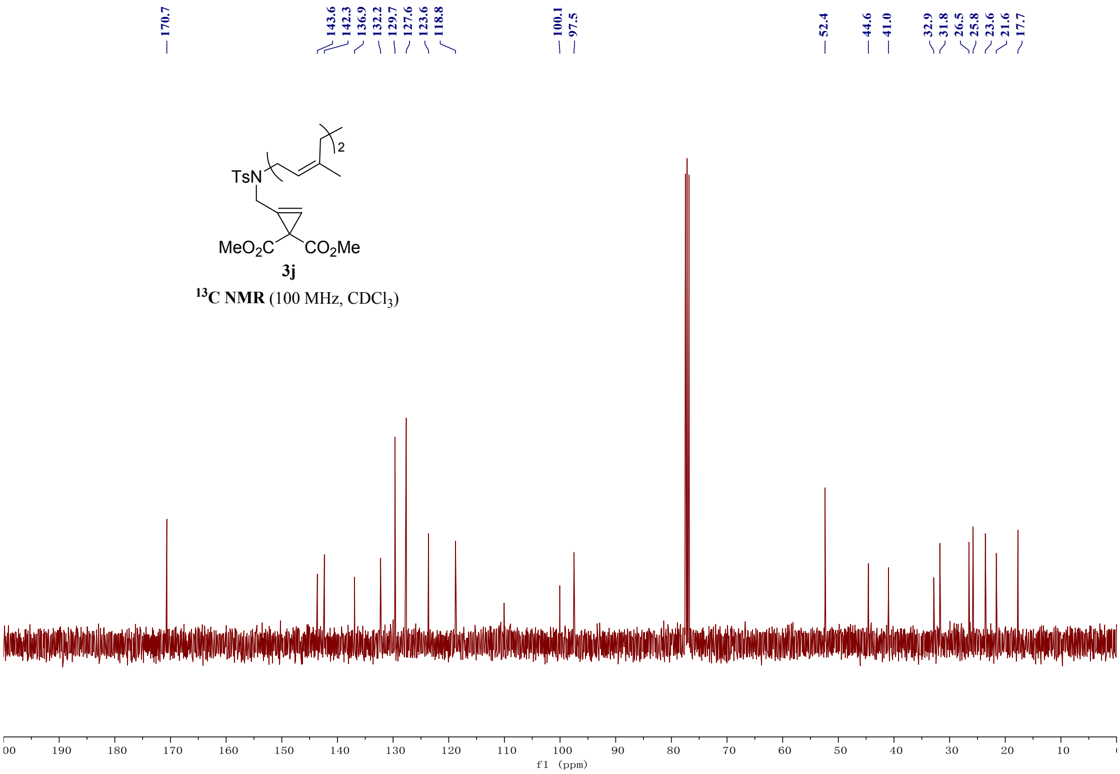
143.7
136.8
132.1
129.7
127.6
124.4
109.6
97.4
52.4
49.1
40.7
32.7
21.6
17.7
TsN
MeO2C
CO2Me
3h
13C NMR (100 MHz, CDCl3)
f1 (ppm)


TsN
MeO2C
CO2Me
3i
1H NMR (400 MHz, CDCl3)
f1 (ppm)

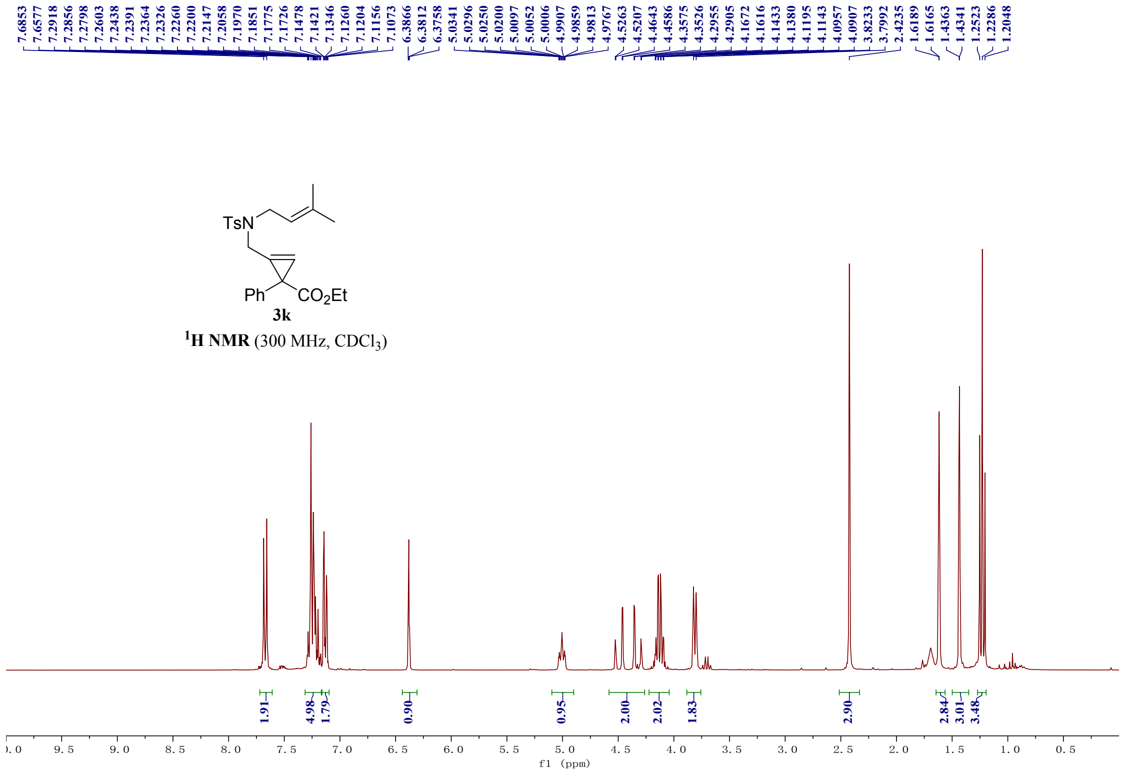

TsN
MeO2C
CO2Me
3i
13C NMR (100 MHz, CDCl3)
f1 (ppm)

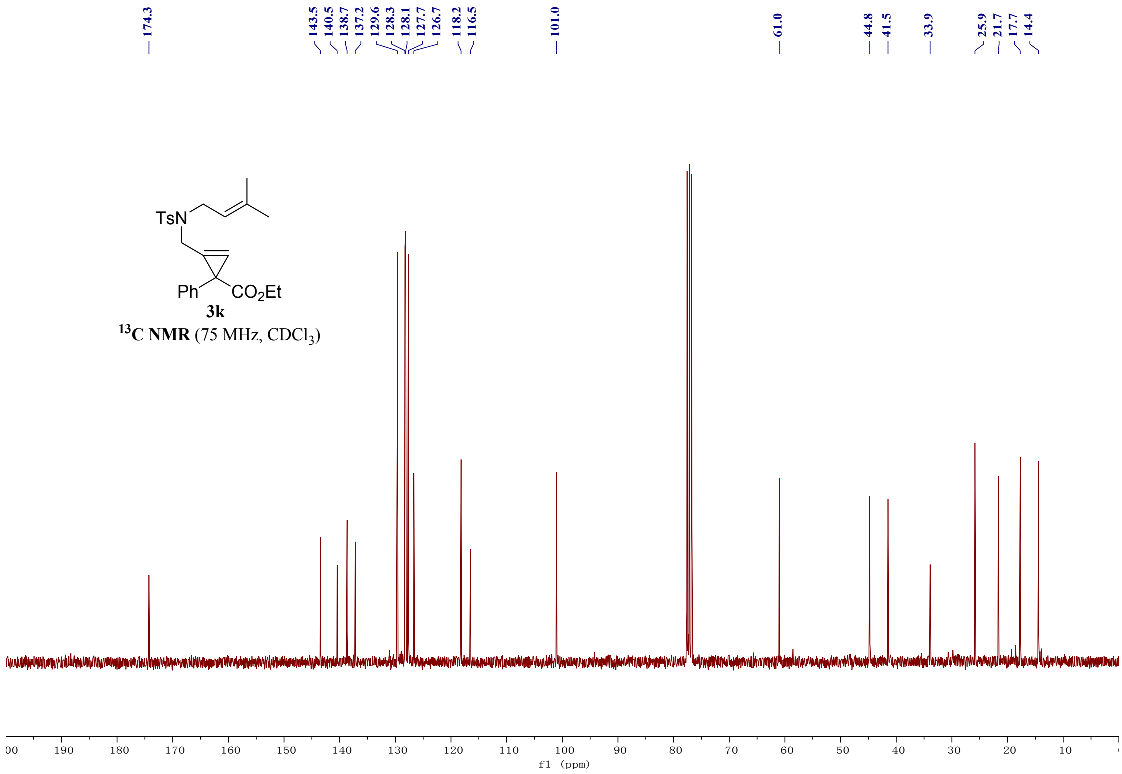


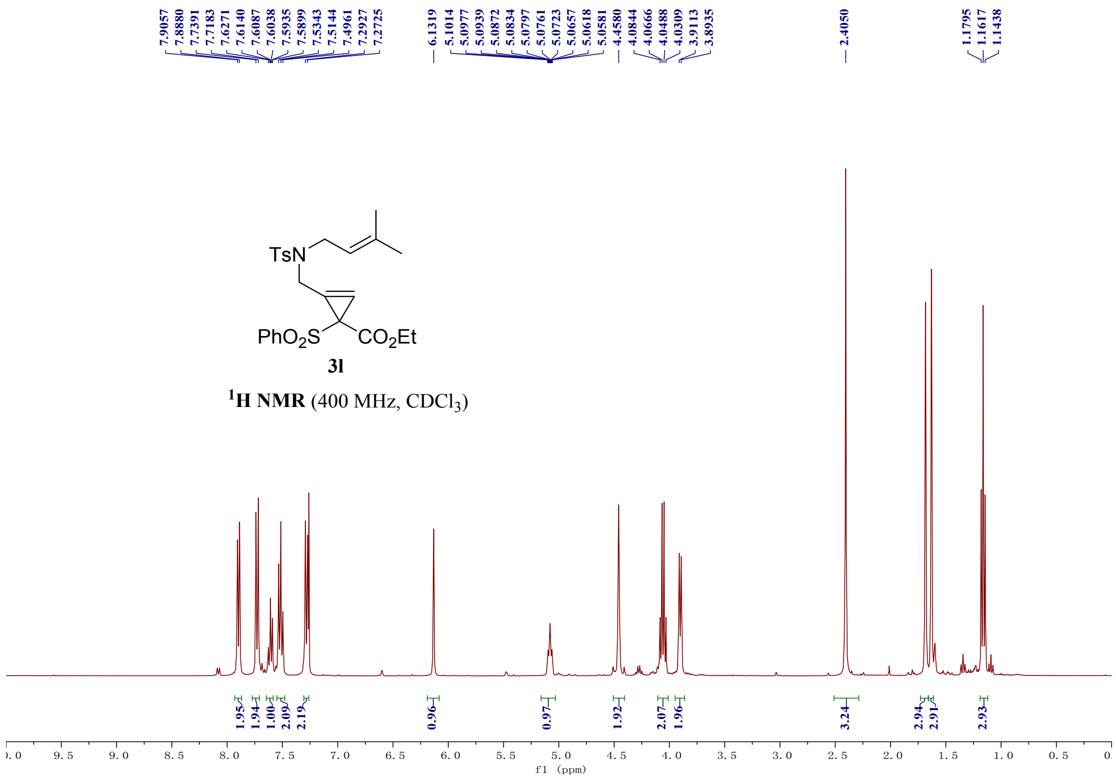
7.6992
7.6786
7.2812
7.2602
6.0928
5.0743
5.0566
5.0381
5.0160
5.0127
4.9984
4.3650
4.3623
3.8284
3.8112
3.6639
2.4093
1.9829
1.6753
1.6489
1.5561
TsN
2
MeO2C
CO2Me
3j
1H NMR (400 MHz, CDCl3)
2.10
2.26
1.00
0.99
0.96
2.08
2.36
6.00
3.17
4.13
6.30
3.06
f1 (ppm)

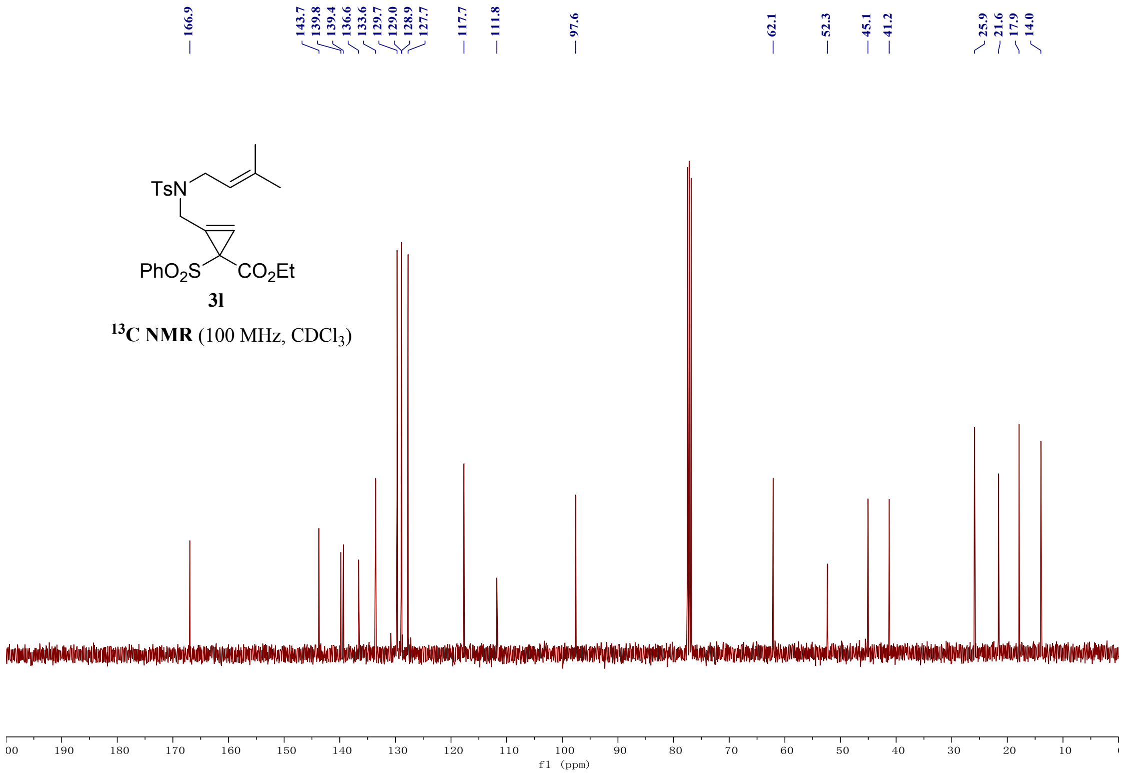


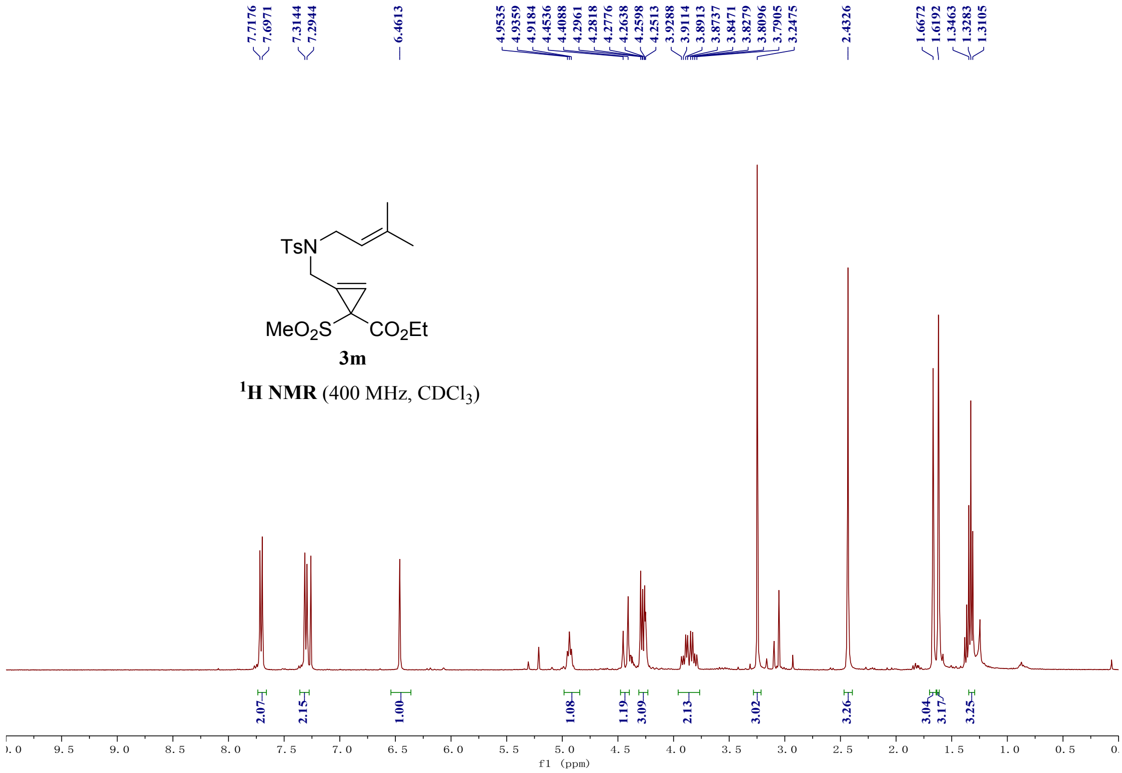
170.7
143.6
142.3
136.9
132.2
129.7
127.6
123.6
118.8
100.1
97.5
52.4
44.6
41.0
32.9
31.8
26.5
25.8
23.6
21.6
17.7
TsN
2
MeO2C
CO2Me
3j
13C NMR (100 MHz, CDCl3)
f1 (ppm)


TsN
Ph
CO2Et
3k
1H NMR (300 MHz, CDCl3)
f1 (ppm)


174.3
143.5
140.5
138.7
137.2
129.6
128.3
128.1
127.7
126.7
118.2
116.5
101.0
61.0
44.8
41.5
33.9
25.9
21.7
17.7
14.4
TsN
Ph
CO2Et
3k
13C NMR (75 MHz, CDCl3)
f1 (ppm)


7.9057
7.8880
7.7391
7.7183
7.6271
7.6140
7.6087
7.6038
7.5935
7.5899
7.5343
7.5144
7.4961
7.2927
7.2725
6.1319
5.1014
5.0977
5.0939
5.0872
5.0834
5.0797
5.0761
5.0723
5.0657
5.0618
5.0581
4.4580
4.0844
4.0666
4.0488
4.0309
3.9113
3.8935
2.4050
1.1795
1.1617
1.1438
TsN
PhO2S
CO2Et
3l
1H NMR (400 MHz, CDCl3)
1.95
1.94
1.00
2.09
2.19
0.96
0.97
1.92
2.07
1.96
3.24
2.94
2.91
2.93
f1 (ppm)


166.9
143.7
139.8
139.4
136.6
133.6
129.7
129.0
128.9
127.7
117.7
111.8
97.6
62.1
52.3
45.1
41.2
25.9
21.6
17.9
14.0
TsN
PhO2S
CO2Et
3l
13C NMR (100 MHz, CDCl3)
f1 (ppm)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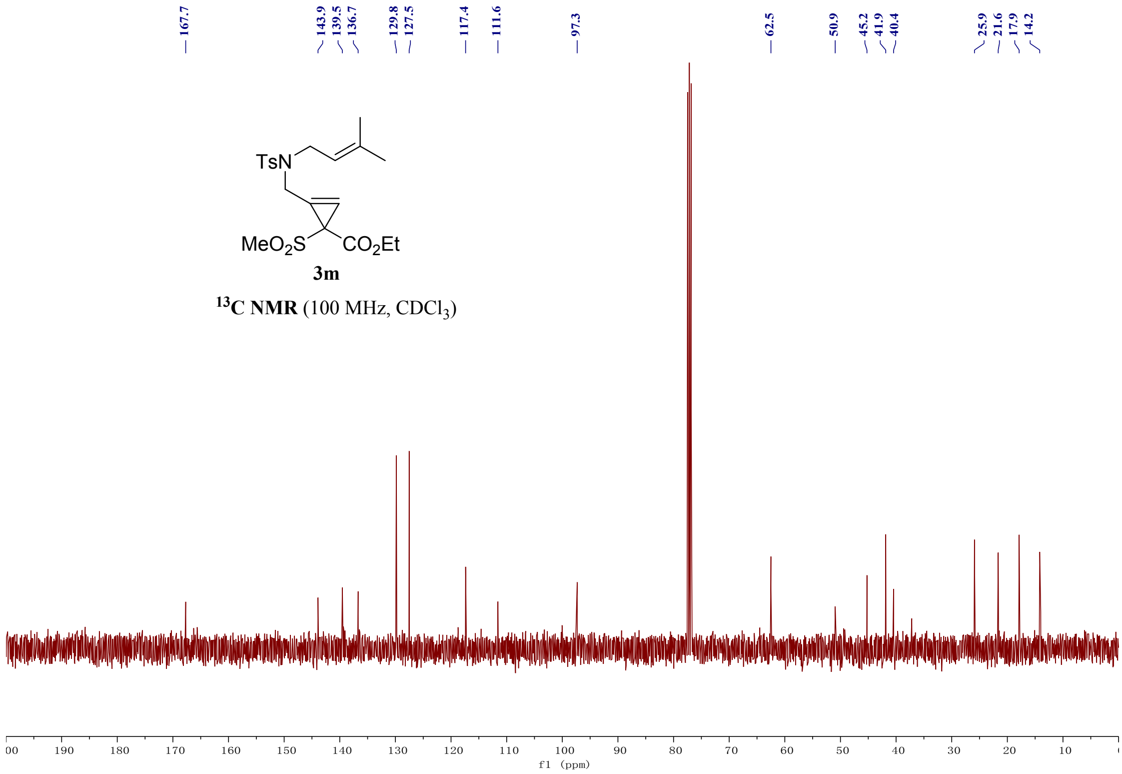
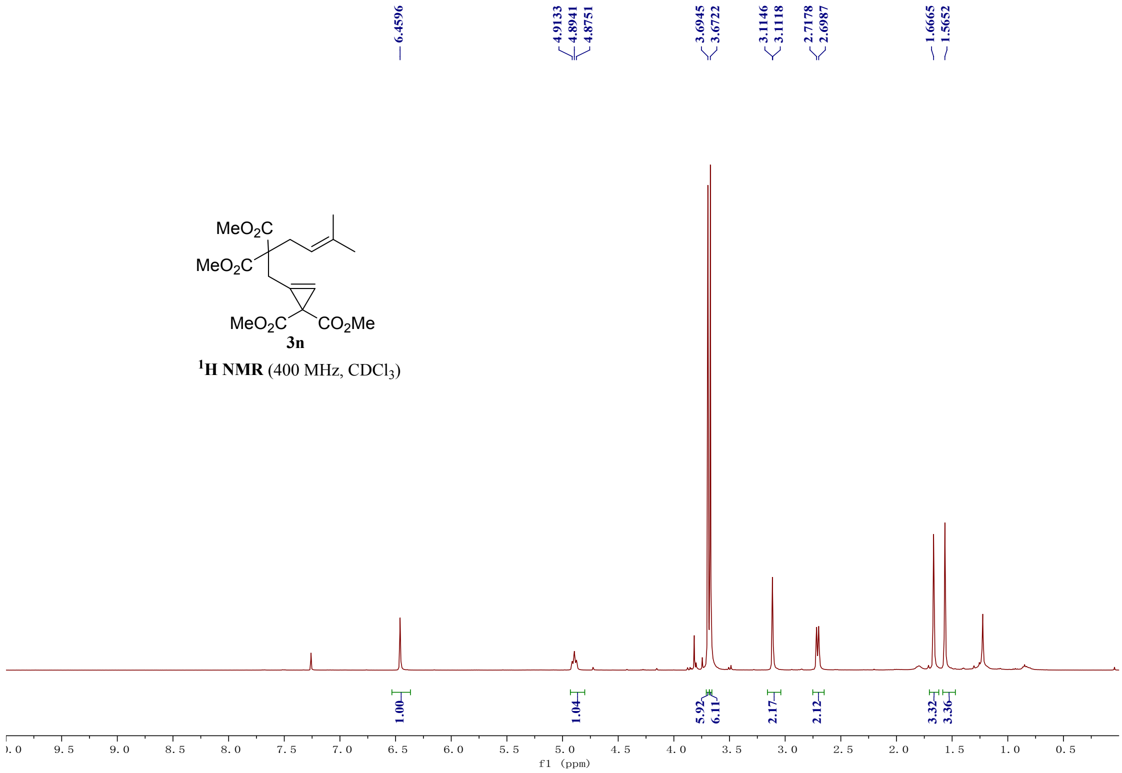
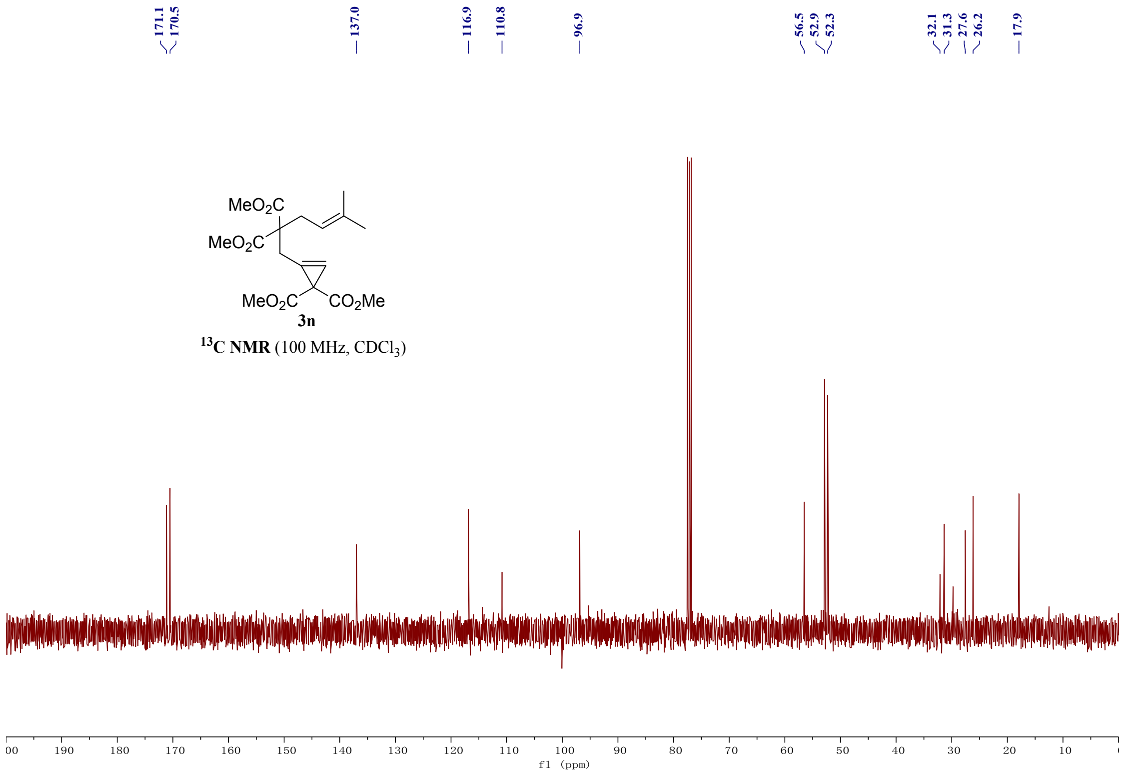
7.6971
7.3144
7.2944
6.4613
4.9535
4.9359
4.9184
4.4536
4.4088
4.2961
4.2818
4.2776
4.2638
4.2598
4.2513
3.9288
3.9114
3.8913
3.8737
3.8471
3.8279
3.8096
3.7905
3.2475
2.4326
1.6672
1.6192
1.3463
1.3283
1.3105
TsN
MeO2S
CO2Et
3m
1H NMR (400 MHz, CDCl3)
2.07
2.15
1.00
1.08
1.19
3.09
2.13
3.02
3.26
3.04
3.17
3.25
f1 (ppm)

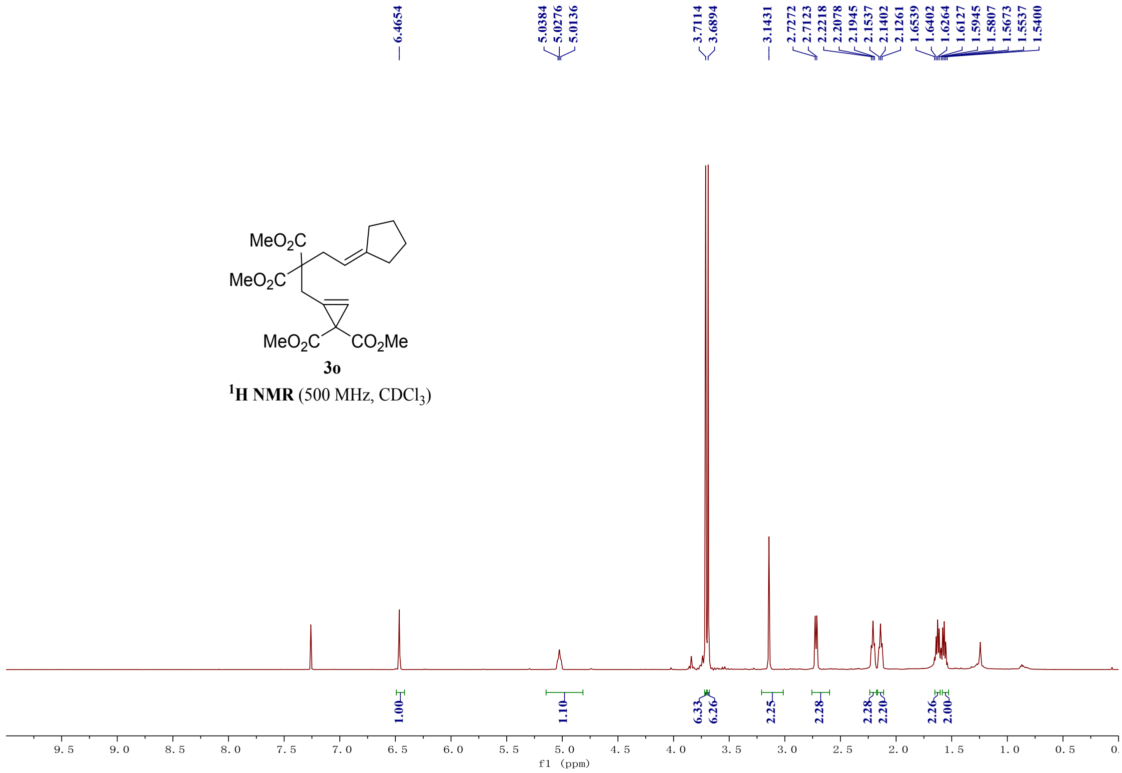

167.7
143.9
139.5
136.7
129.8
127.5
117.4
111.6
97.3
62.5
50.9
45.2
41.9
40.4
25.9
21.6
17.9
14.2
TsN
MeO2S
CO2Et
3m
13C NMR (100 MHz, CDCl3)
f1 (ppm)



6.4596
4.9133
4.8941
4.8751
3.6945
3.6722
3.1146
3.1118
2.7178
2.6987
1.6665
1.5652
MeO2C
MeO2C
MeO2C
CO2Me
3n
1H NMR (400 MHz, CDCl3)
1.00
1.04
5.92
6.11
2.17
2.12
3.32
3.36
f1 (ppm)



171.1
170.5
137.0
116.9
110.8
96.9
56.5
52.9
52.3
32.1
31.3
27.6
26.2
17.9
MeO2C
MeO2C
MeO2C
CO2Me
3n
13C NMR (100 MHz, CDCl3)
f1 (ppm)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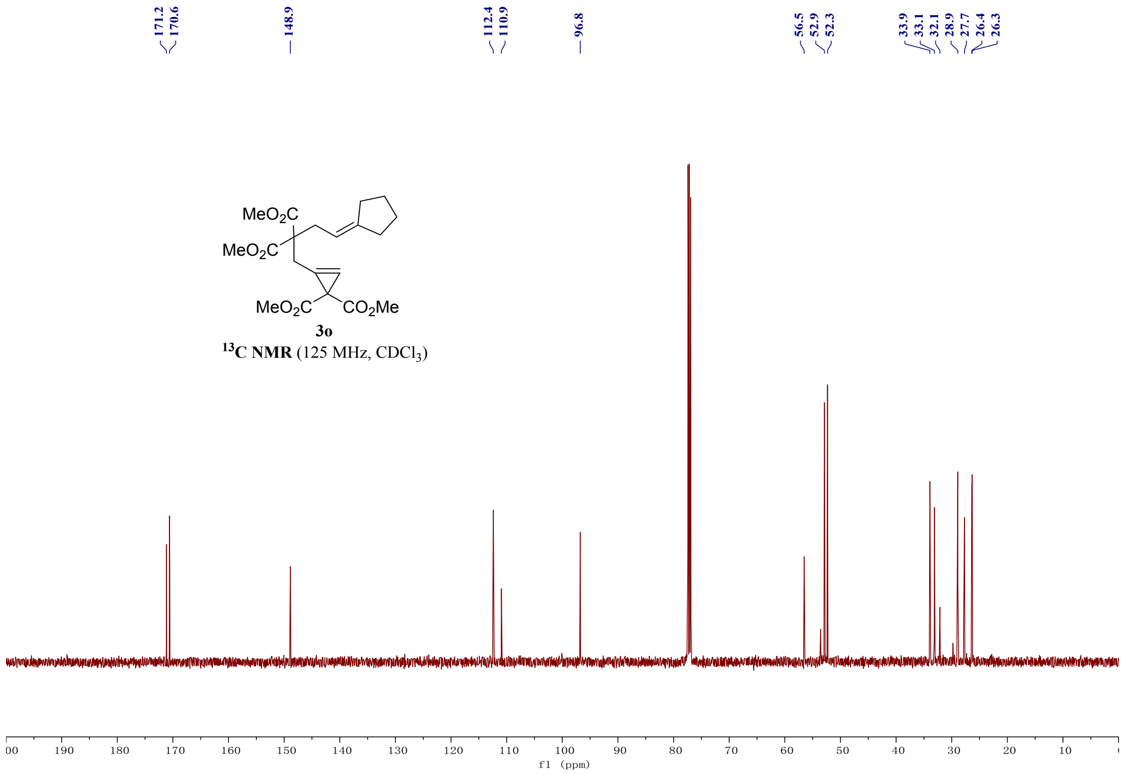
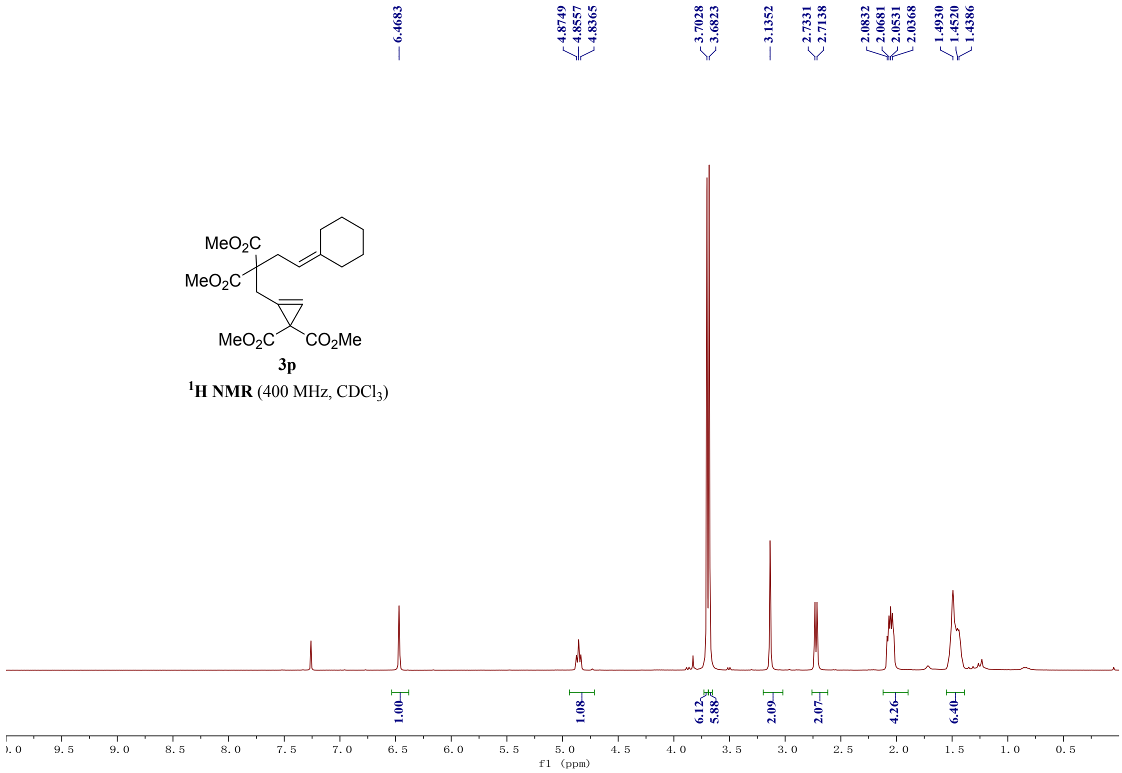
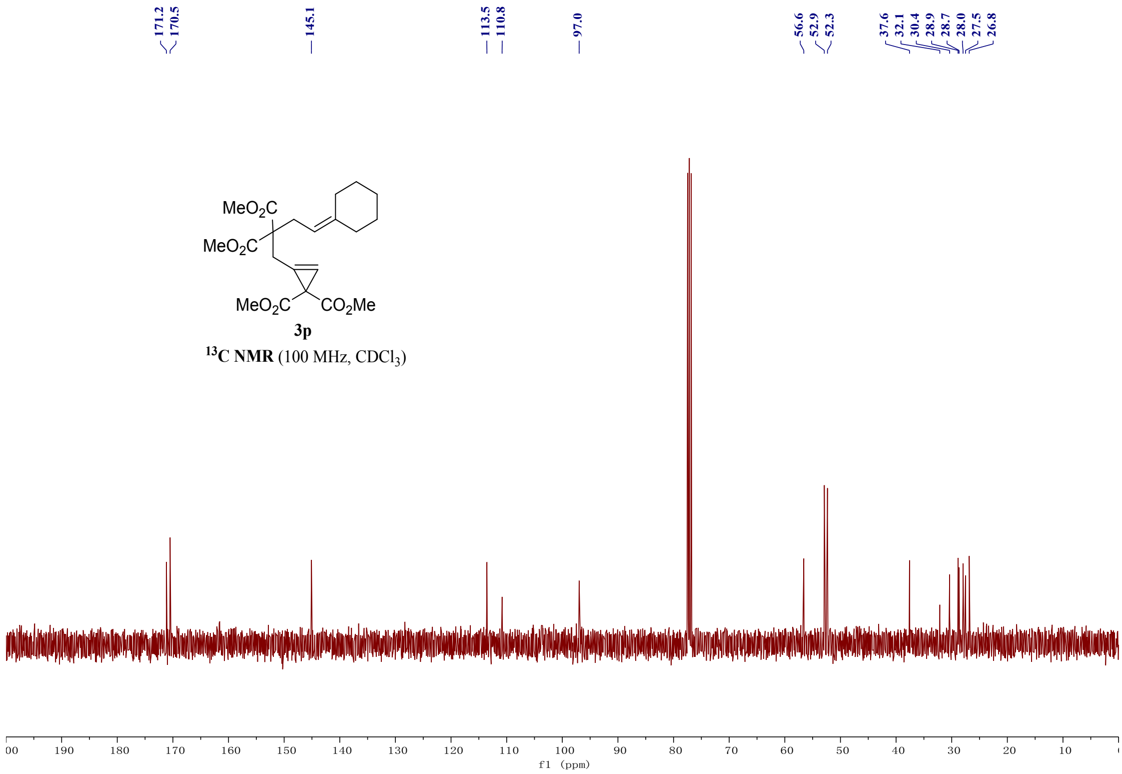
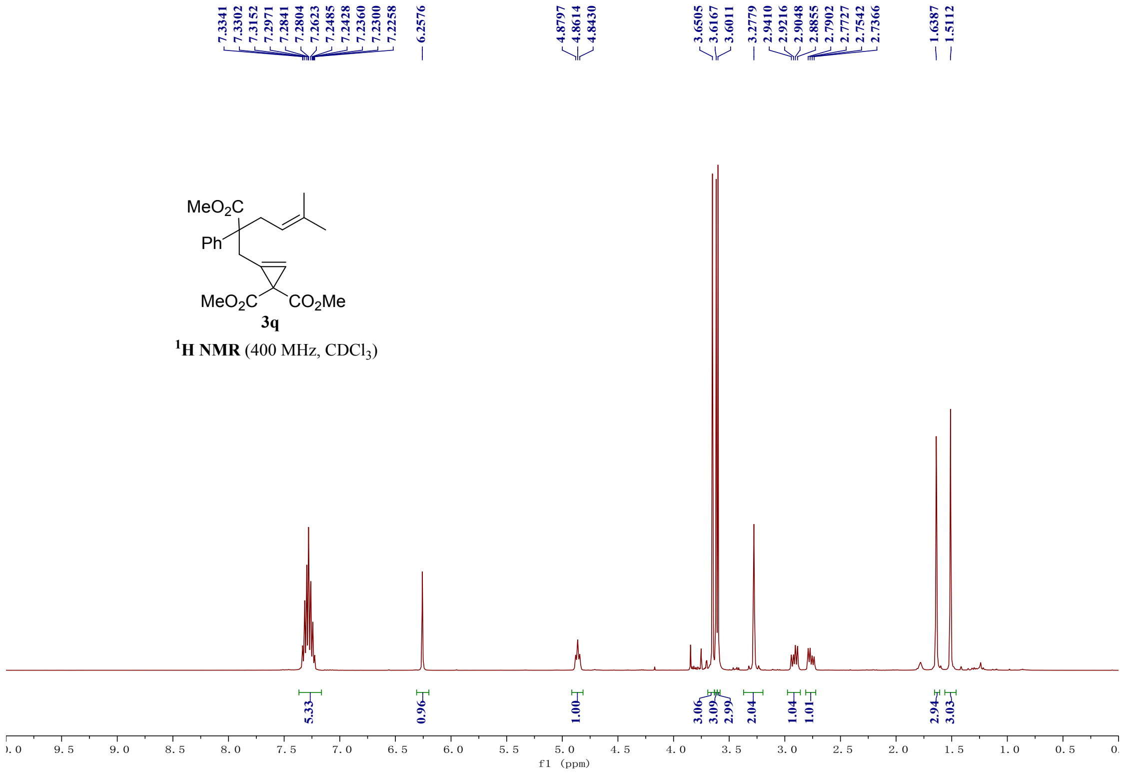
5.0384
5.0276
5.0136
3.7114
3.6894
3.1431
2.7272
2.7123
2.2218
2.2078
2.1945
2.1537
2.1402
2.1261
1.6539
1.6402
1.6264
1.6127
1.5945
1.5807
1.5673
1.5537
1.5400
MeO_2C
MeO_2C
MeO_2C
CO_2Me
3o
^{1}H NMR (500 MHz, $CDCl_3$)
1.00
1.10
6.33
6.26
2.25
2.28
2.28
2.20
2.26
2.00
f1 (ppm)


171.2
170.6
148.9
112.4
110.9
96.8
56.5
52.9
52.3
33.9
33.1
32.1
28.9
27.7
26.4
26.3
MeO_2C
MeO_2C
MeO_2C
CO_2Me
3o
^{13}C NMR (125 MHz, $CDCl_3$)
f1 (ppm)


6.4683
4.8749
4.8557
4.8365
3.7028
3.6823
3.1352
2.7331
2.7138
2.0832
2.0681
2.0531
2.0368
1.4930
1.4520
1.4386
MeO2C
MeO2C
MeO2C
CO2Me
3p
1H NMR (400 MHz, CDCl3)
1.00
1.08
6.12
5.88
2.09
2.07
4.26
6.40
f1 (ppm)


171.2
170.5
145.1
113.5
110.8
97.0
56.6
52.9
52.3
37.6
32.1
30.4
28.9
28.7
28.0
27.5
26.8
MeO2C
MeO2C
MeO2C
CO2Me
3p
13C NMR (100 MHz, CDCl3)
f1 (ppm)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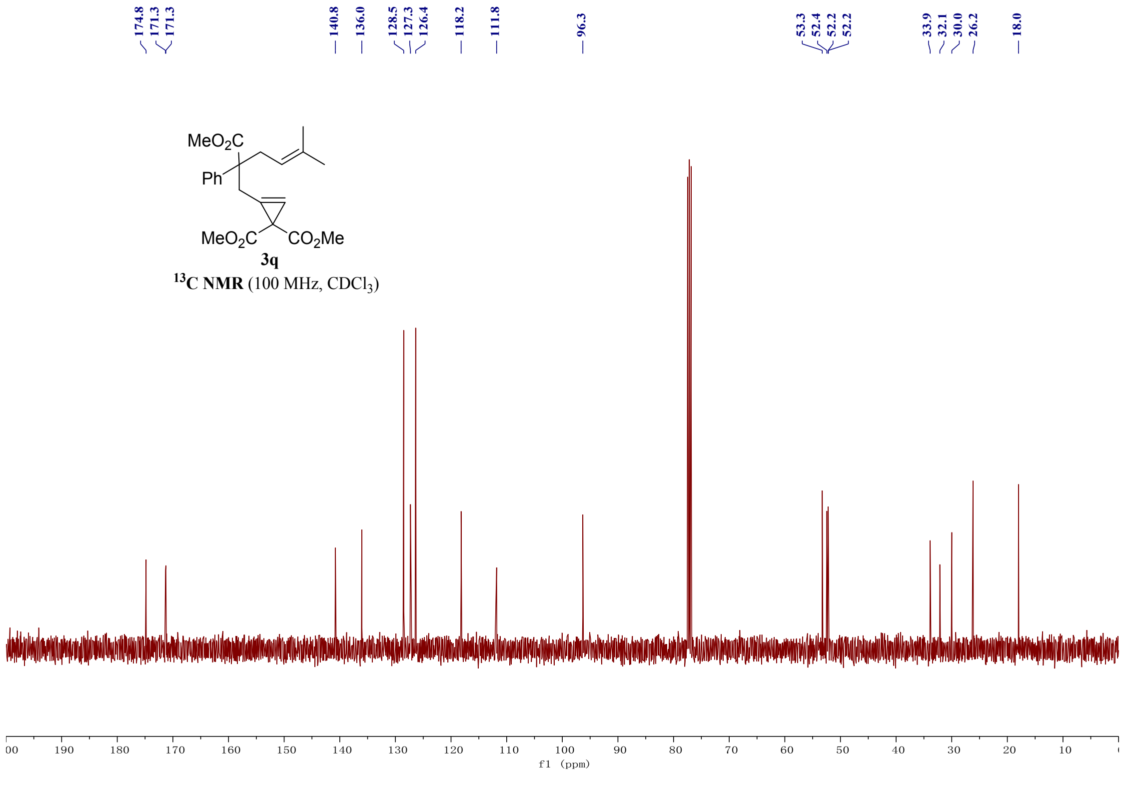
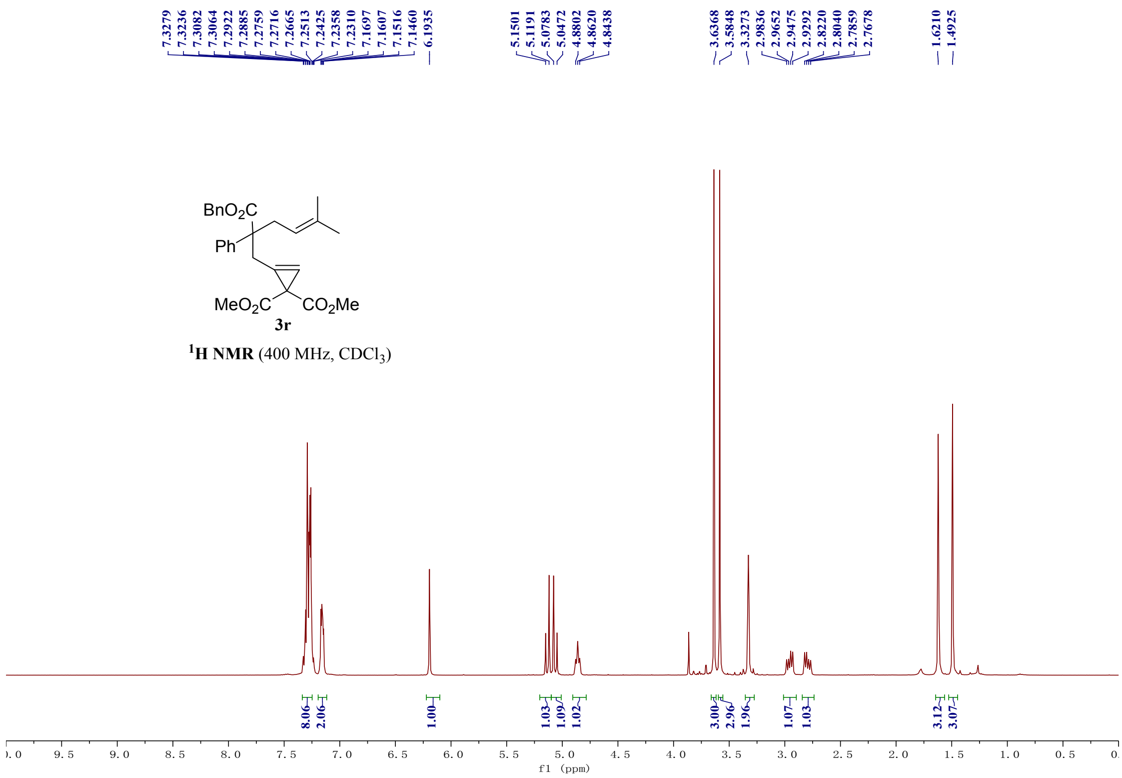
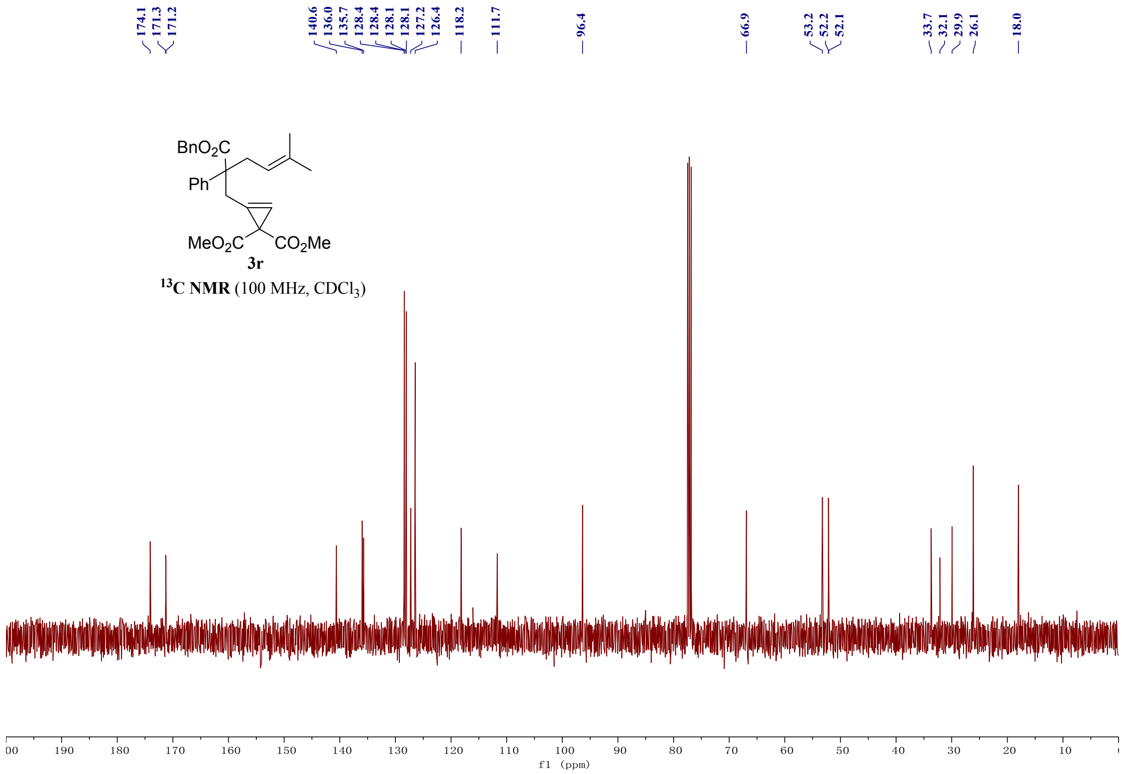
7.3302
7.3152
7.2971
7.2841
7.2804
7.2623
7.2485
7.2428
7.2360
7.2300
7.2258
6.2576
4.8797
4.8614
4.8430
3.6505
3.6167
3.6011
3.2779
2.9410
2.9216
2.9048
2.8855
2.7902
2.7727
2.7542
2.7366
1.6387
1.5112
MeO2C
Ph
MeO2C
CO2Me
3q
1H NMR (400 MHz, CDCl3)
5.33
0.96
1.00
3.06
3.09
2.99
2.04
1.04
1.01
2.94
3.03
f1 (ppm)

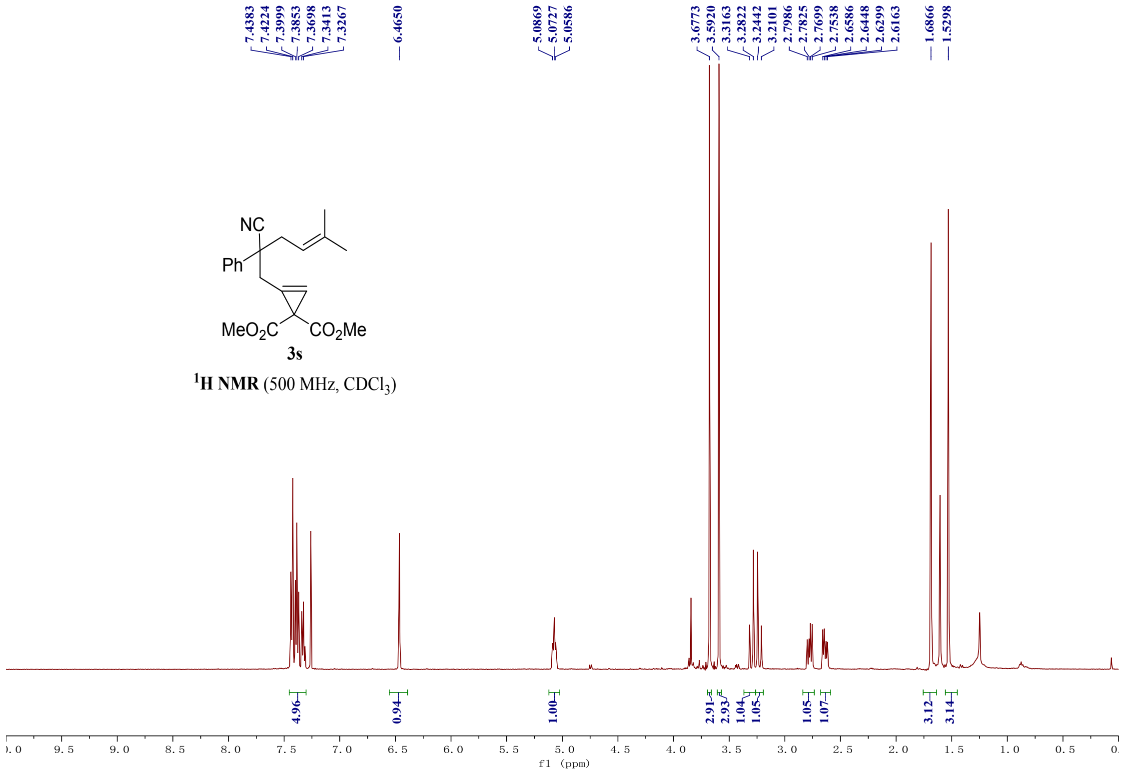

174.8
171.3
171.3
140.8
136.0
128.5
127.3
126.4
118.2
111.8
96.3
53.3
52.4
52.2
52.2
33.9
32.1
30.0
26.2
18.0
MeO2C
Ph
MeO2C
CO2Me
3q
13C NMR (100 MHz, CDCl3)
f1 (ppm)



BnO$_2$C
Ph
MeO$_2$C
CO$_2$Me
3r
^{1}H NMR (400 MHz, CDCl$_3$)



BnO$_2$C
Ph
MeO$_2$C
CO$_2$Me
3r
^{13}C NMR (100 MHz, CDCl$_3$)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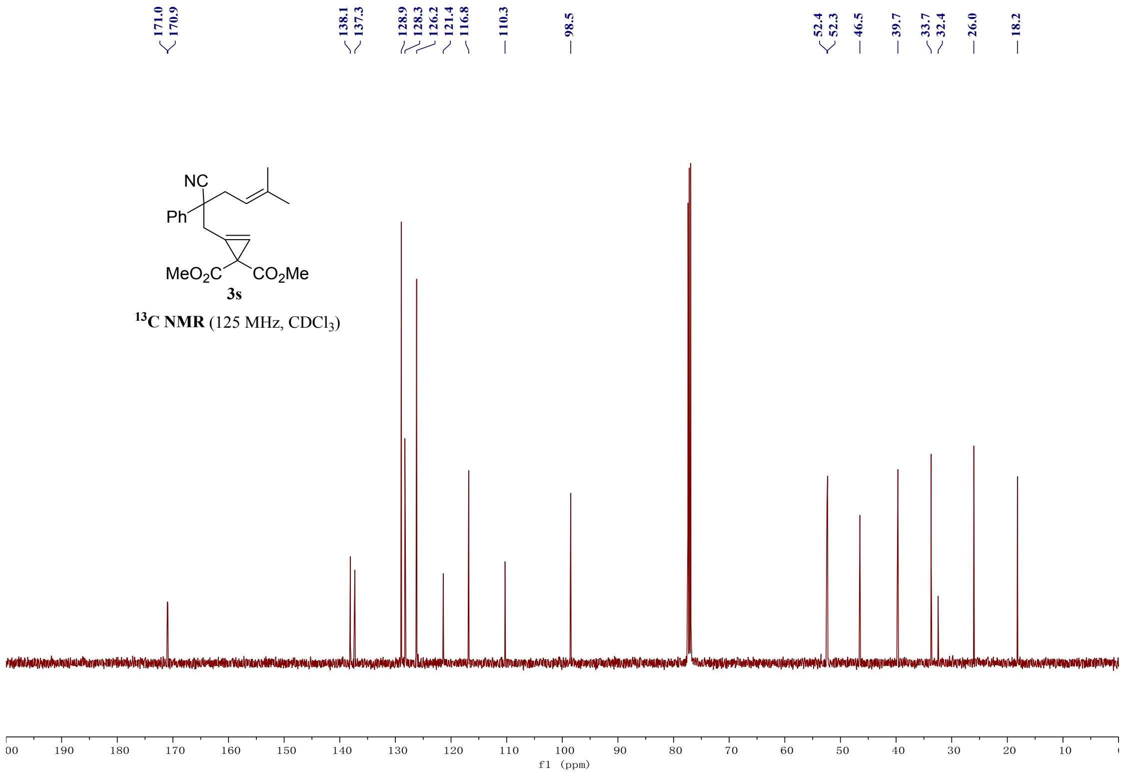
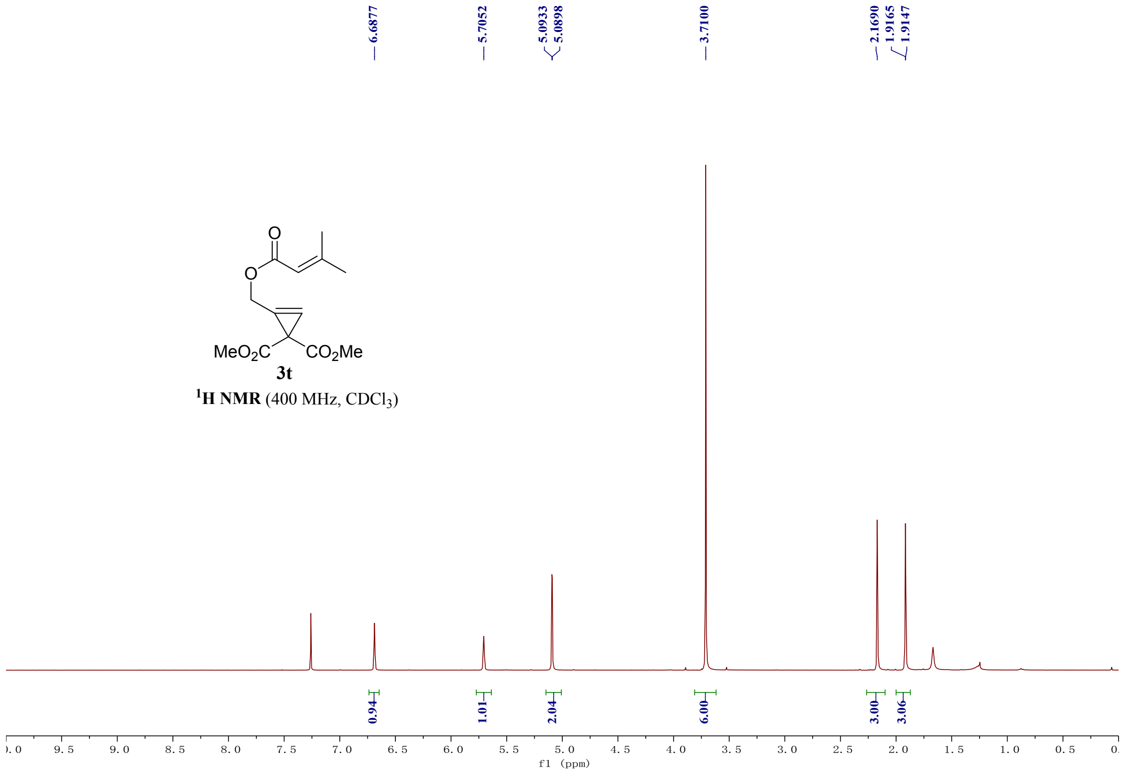
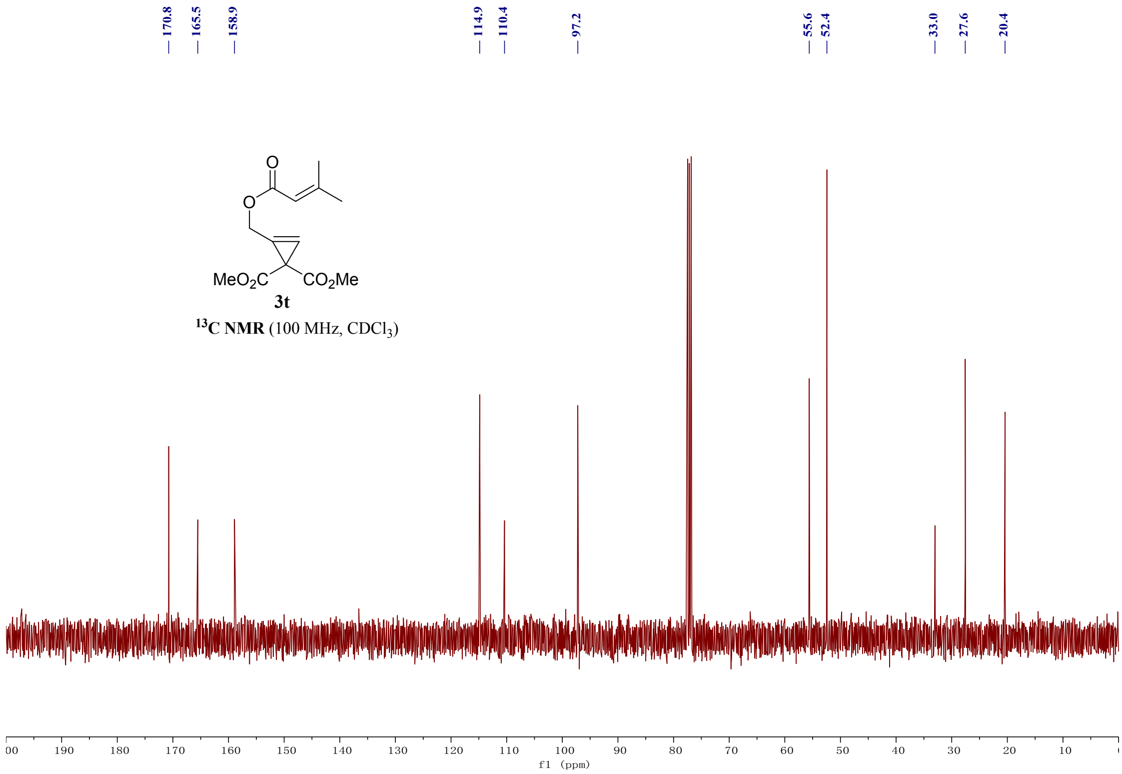
7.4224
7.3999
7.3853
7.3698
7.3413
7.3267
6.4650
5.0869
5.0727
5.0586
3.6773
3.5920
3.3163
3.2822
3.2442
3.2101
2.7986
2.7825
2.7699
2.7538
2.6586
2.6448
2.6299
2.6163
1.6866
1.5298
NC
Ph
MeO2C
CO2Me
3s
1H NMR (500 MHz, CDCl3)
4.96
0.94
1.00
2.91
2.93
1.04
1.05
1.05
1.07
3.12
3.14
f1 (ppm)


171.0
170.9
138.1
137.3
128.9
128.3
126.2
121.4
116.8
110.3
98.5
52.4
52.3
46.5
39.7
33.7
32.4
26.0
18.2
NC
Ph
MeO2C
CO2Me
3s
13C NMR (125 MHz, CDCl3)
f1 (ppm)



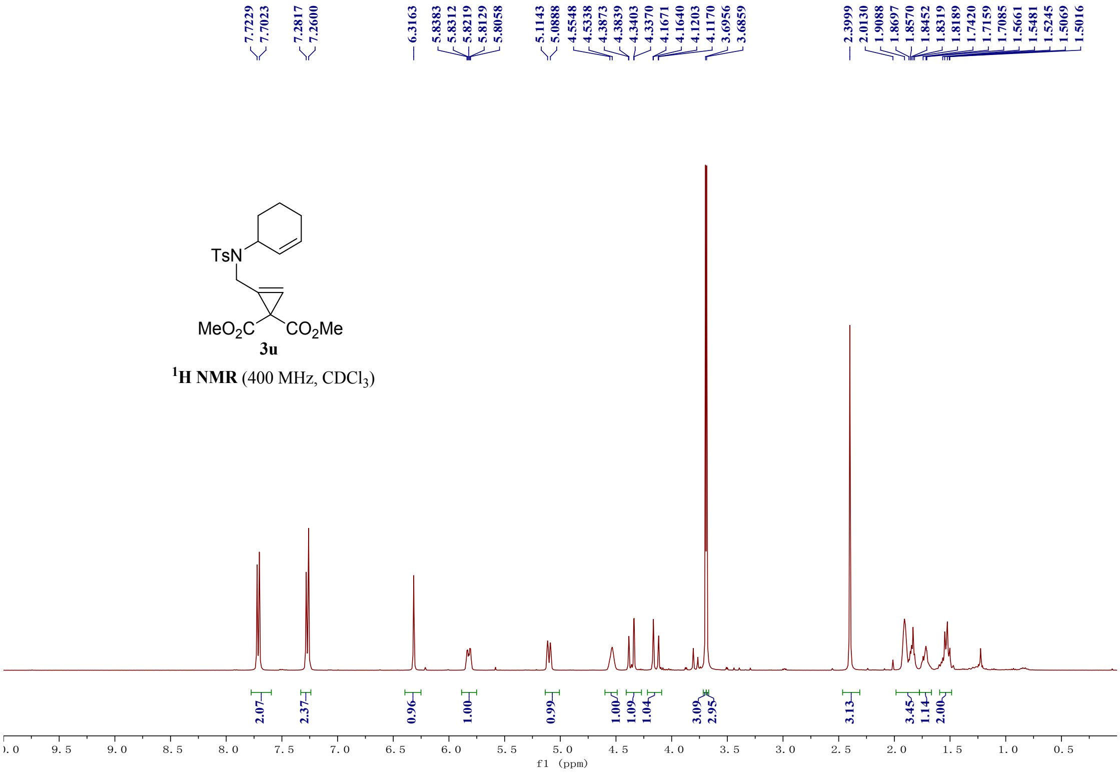
3t

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



3t

^{13}C NMR (100 MHz, $CDCl_3$)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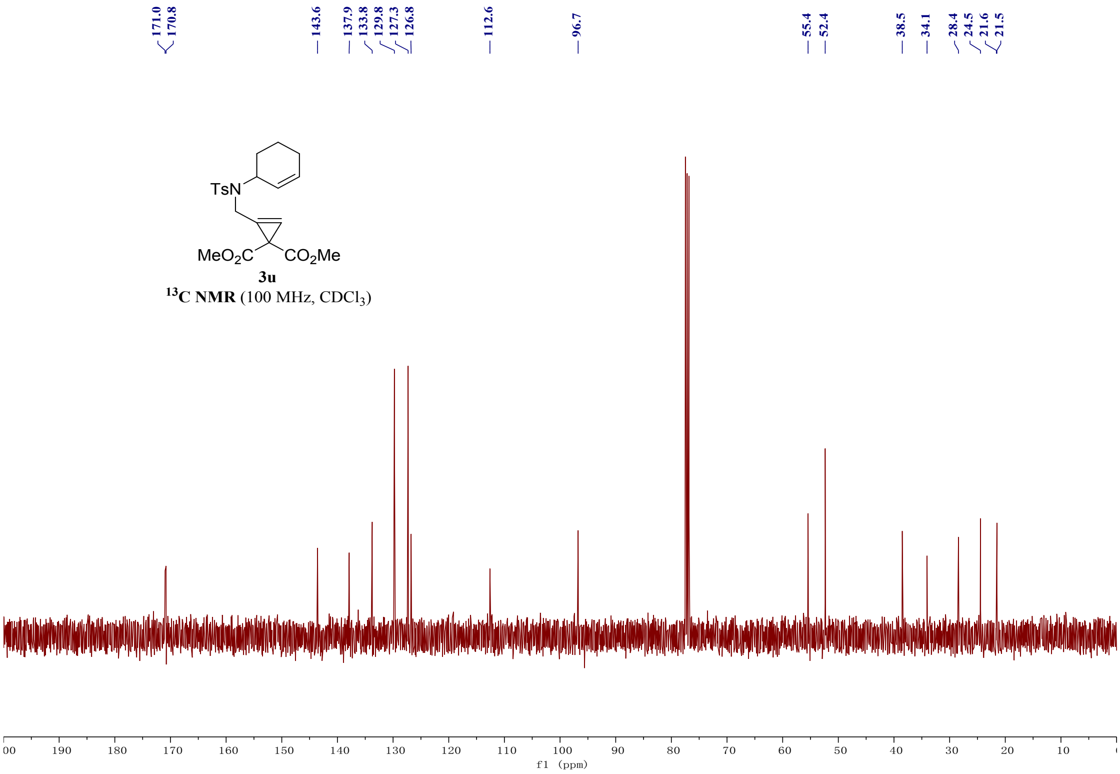
7.7023
7.2817
7.2600
6.3163
5.8383
5.8312
5.8219
5.8129
5.8058
5.1143
5.0888
4.5548
4.5338
4.3873
4.3839
4.3403
4.3370
4.1671
4.1640
4.1203
4.1170
3.6956
3.6859
2.3999
2.0130
1.9088
1.8697
1.8570
1.8452
1.8319
1.8189
1.7420
1.7159
1.7085
1.5661
1.5481
1.5245
1.5069
1.5016
TsN
MeO2C
CO2Me
3u
1H NMR (400 MHz, CDCl3)
2.07
2.37
0.96
1.00
0.99
1.00
1.09
1.04
3.09
2.95
3.13
3.45
1.14
2.00
f1 (ppm)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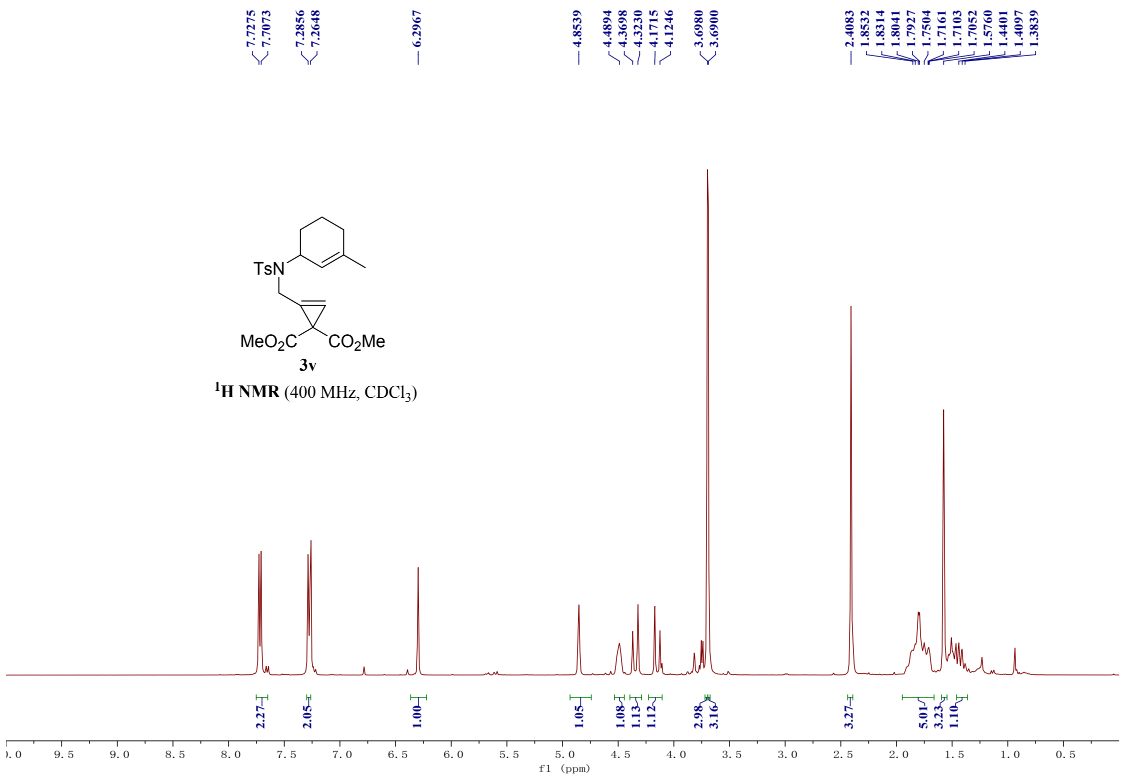
170.8
143.6
137.9
133.8
129.8
127.3
126.8
112.6
96.7
55.4
52.4
38.5
34.1
28.4
24.5
21.6
21.5
TsN
MeO2C
CO2Me
3u
13C NMR (100 MHz, CDCl3)
f1 (ppm)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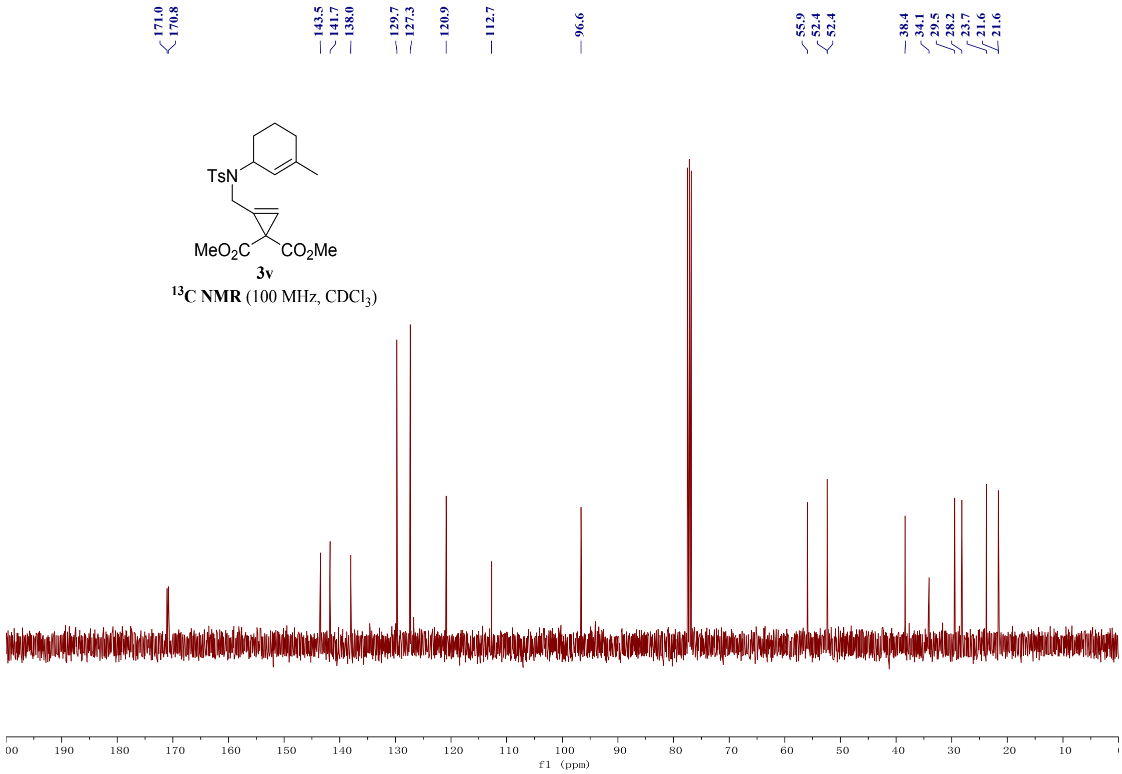
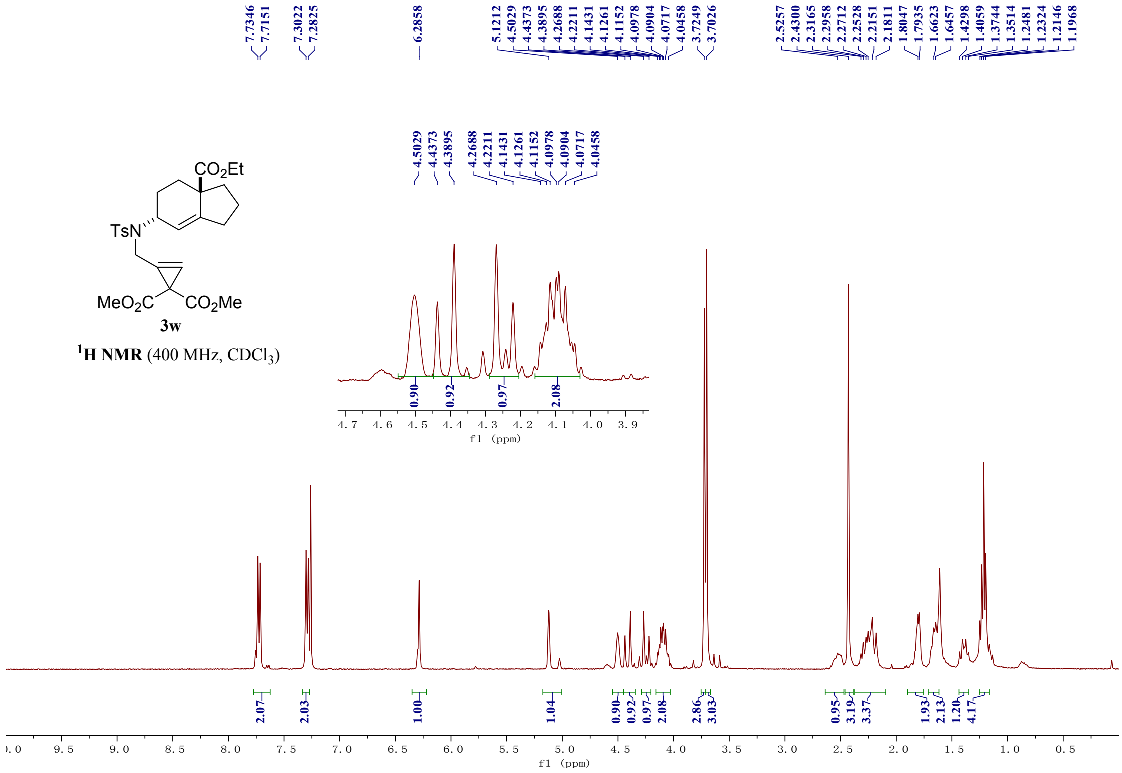
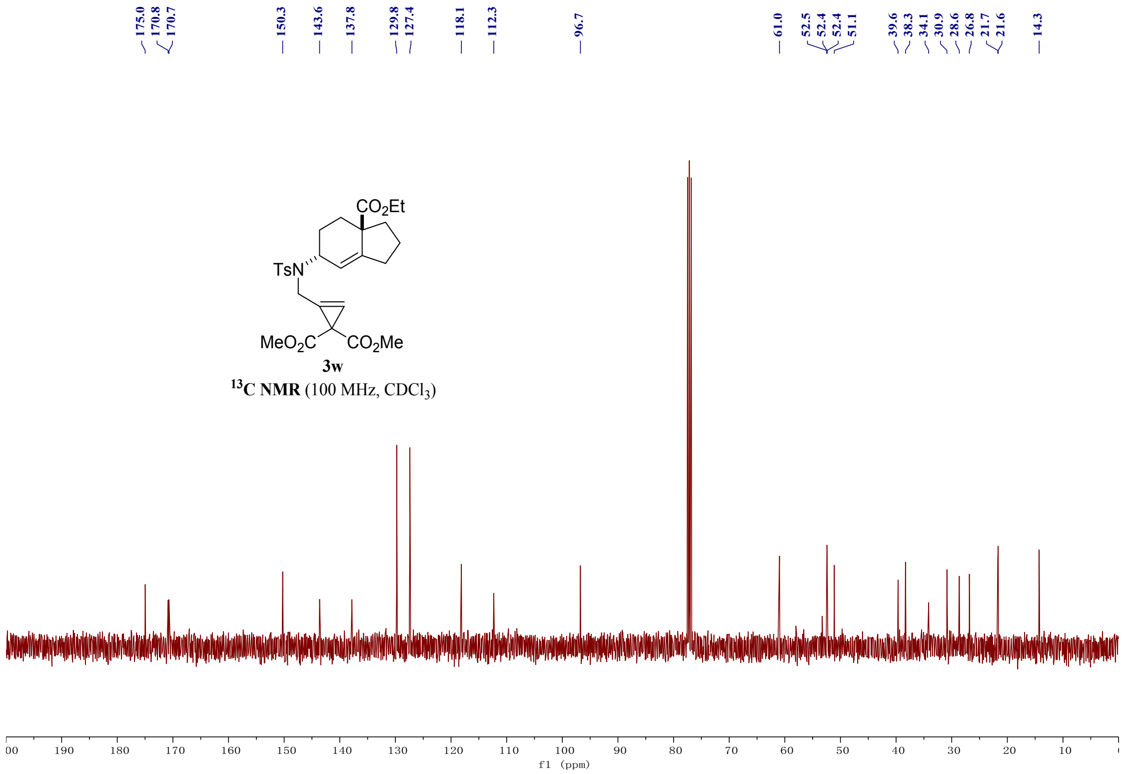
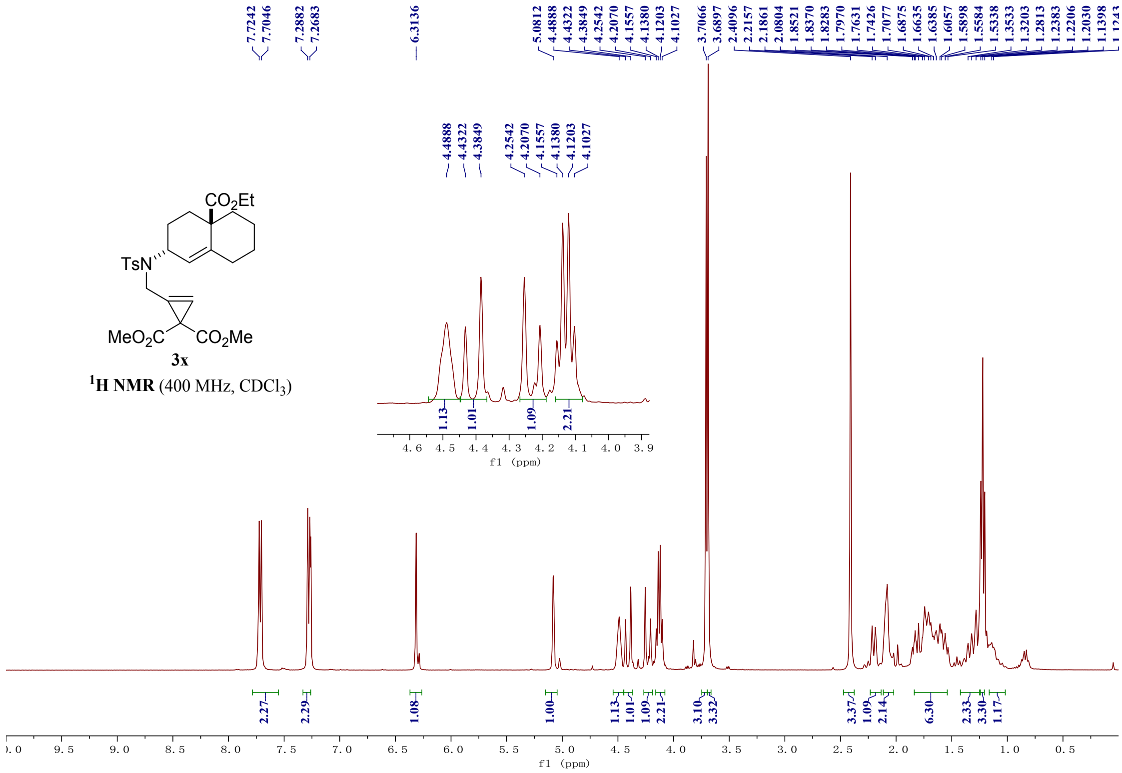
7.7073
7.2856
7.2648
6.2967
4.8539
4.4894
4.3698
4.3230
4.1715
4.1246
3.6980
3.6900
2.4083
1.8532
1.8314
1.8041
1.7927
1.7504
1.7161
1.7103
1.7052
1.5760
1.4401
1.4097
1.3839
TsN
MeO2C
CO2Me
3v
1H NMR (400 MHz, CDCl3)
2.27
2.05
1.00
1.05
1.08
1.13
1.12
2.98
3.16
3.27
5.01
3.23
1.10
f1 (ppm)


171.0
170.8
143.5
141.7
138.0
129.7
127.3
120.9
112.7
96.6
55.9
52.4
52.4
38.4
34.1
29.5
28.2
23.7
21.6
21.6
TsN
MeO2C
CO2Me
3v
13C NMR (100 MHz, CDCl3)
f1 (ppm)

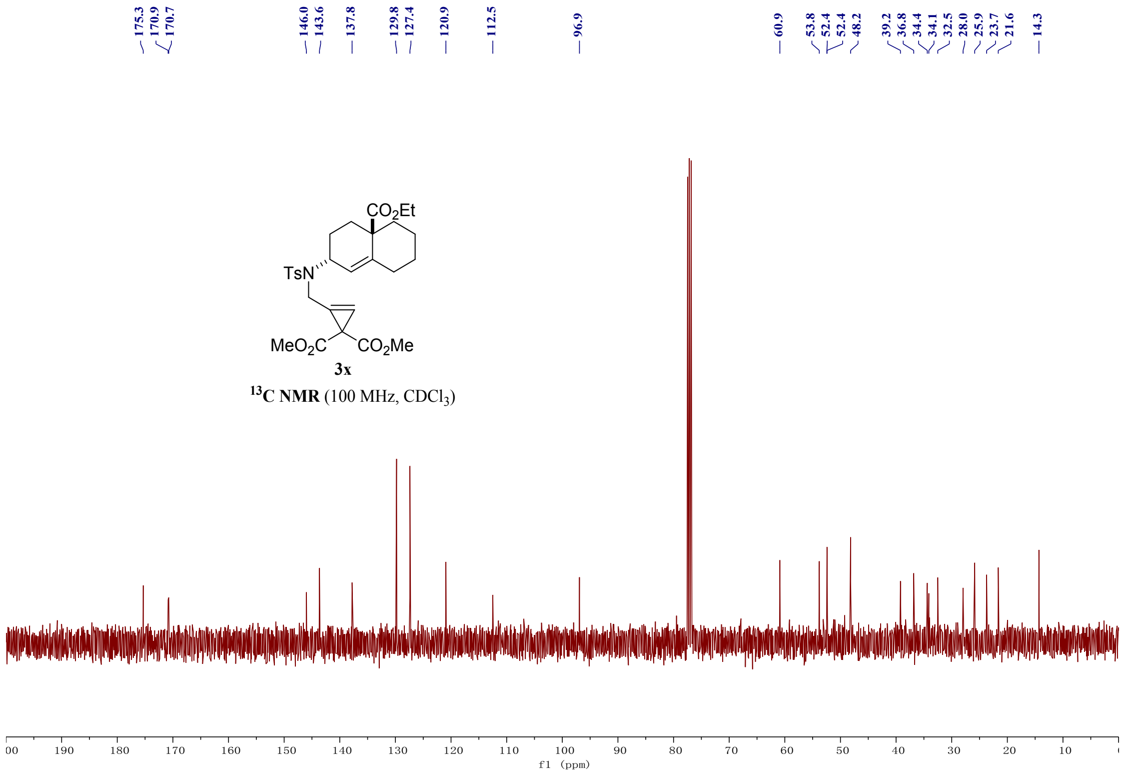

CO2Et
TsN
MeO2C
CO2Me
3w
1H NMR (400 MHz, CDCl3)
7.7346
7.7151
7.3022
7.2825
6.2858
5.1212
4.5029
4.4373
4.3895
4.2688
4.2211
4.1431
4.1261
4.1152
4.0978
4.0904
4.0717
4.0458
3.7249
3.7026
2.5257
2.4300
2.3165
2.2958
2.2712
2.2528
2.2151
2.1811
1.8047
1.7935
1.6623
1.6457
1.4298
1.4059
1.3744
1.3514
1.2481
1.2324
1.2146
1.1968
0.90
0.92
0.97
2.08
f1 (ppm)
2.07
2.03
1.00
1.04
2.86
3.03
0.95
3.19
3.37
1.93
2.13
1.20
4.17
f1 (ppm)


175.0
170.8
170.7
150.3
143.6
137.8
129.8
127.4
118.1
112.3
96.7
61.0
52.5
52.4
52.4
51.1
39.6
38.3
34.1
30.9
28.6
26.8
21.7
21.6
14.3
CO2Et
TsN
MeO2C
CO2Me
3w
13C NMR (100 MHz, CDCl3)
f1 (ppm)



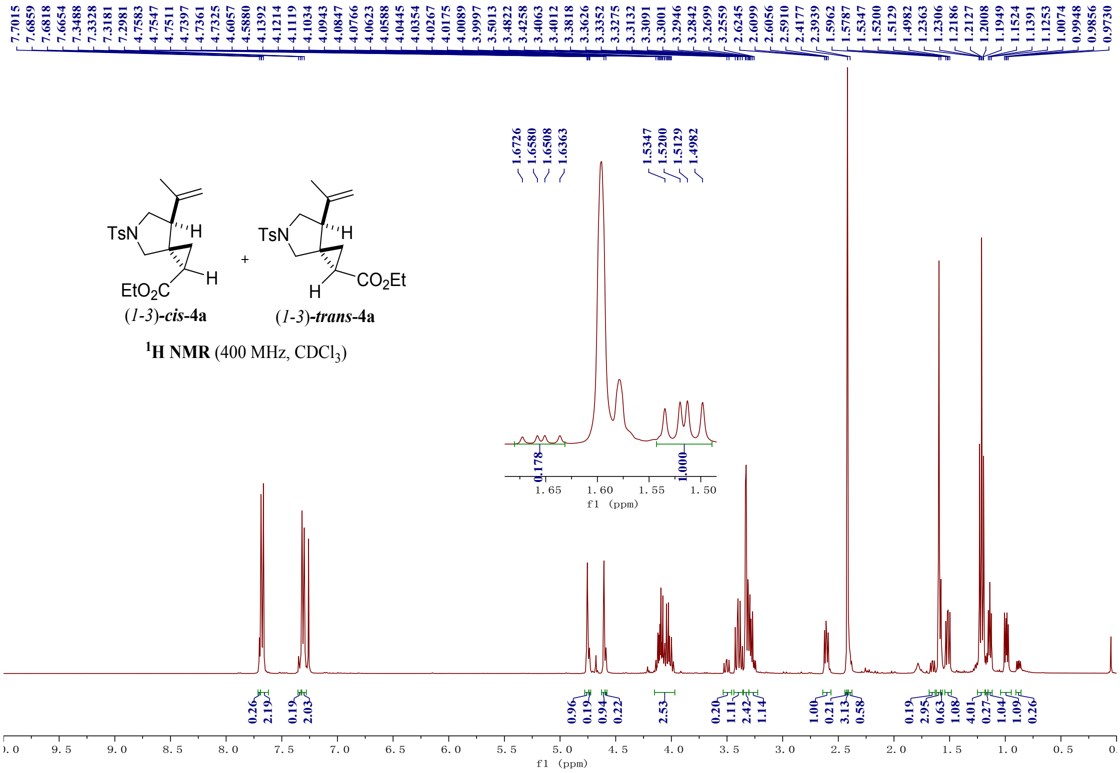
3x

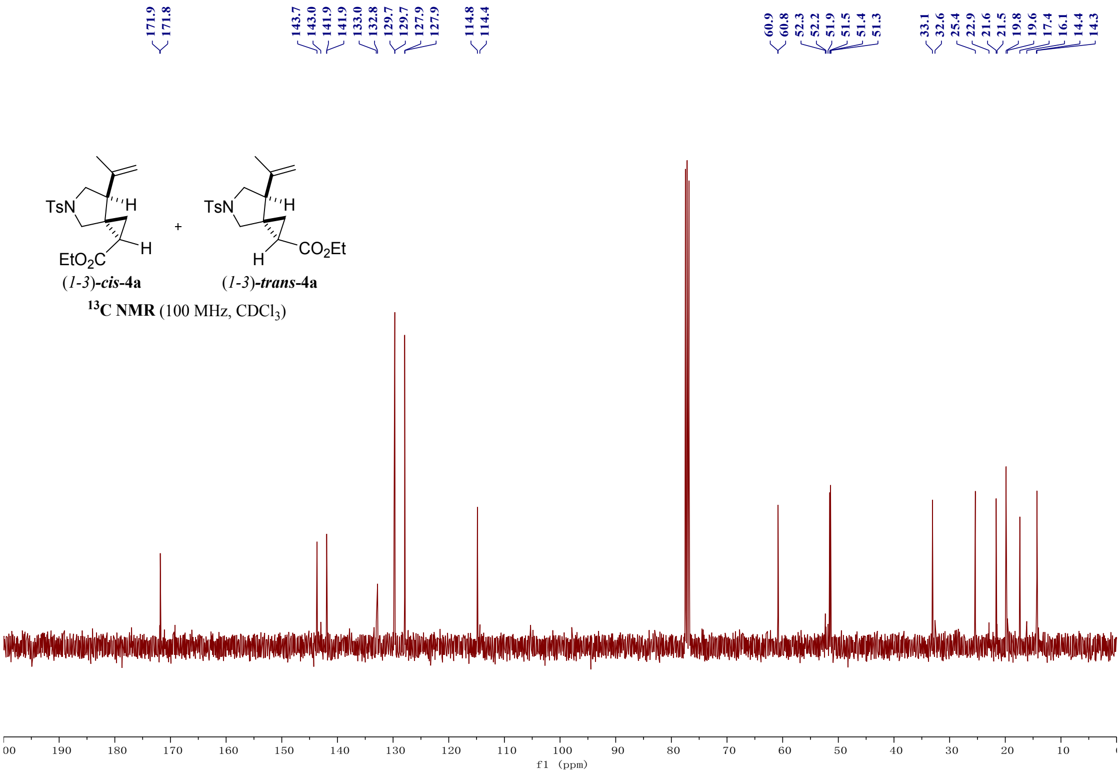
^{1}H NMR (400 MHz, $CDCl_3$)



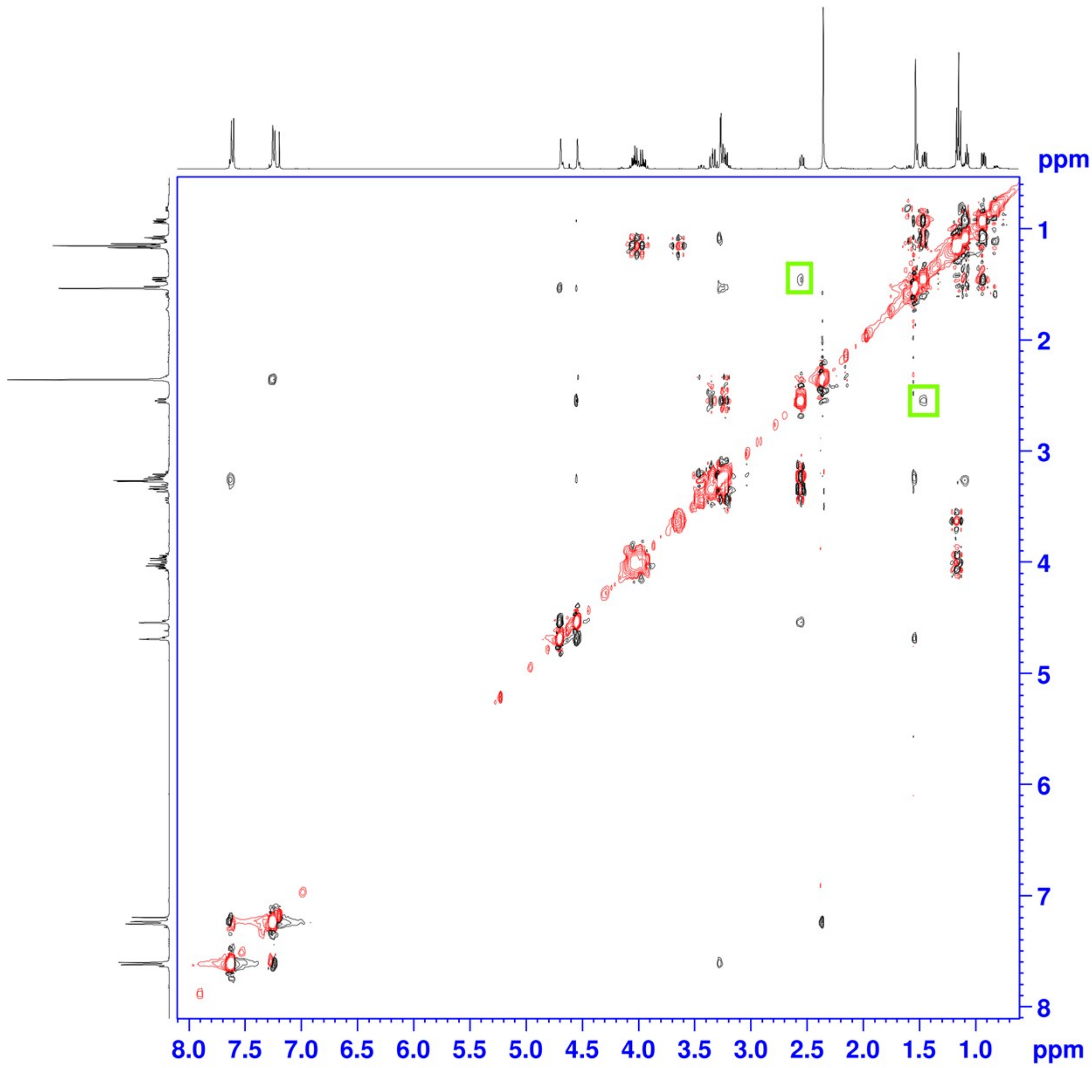
3x

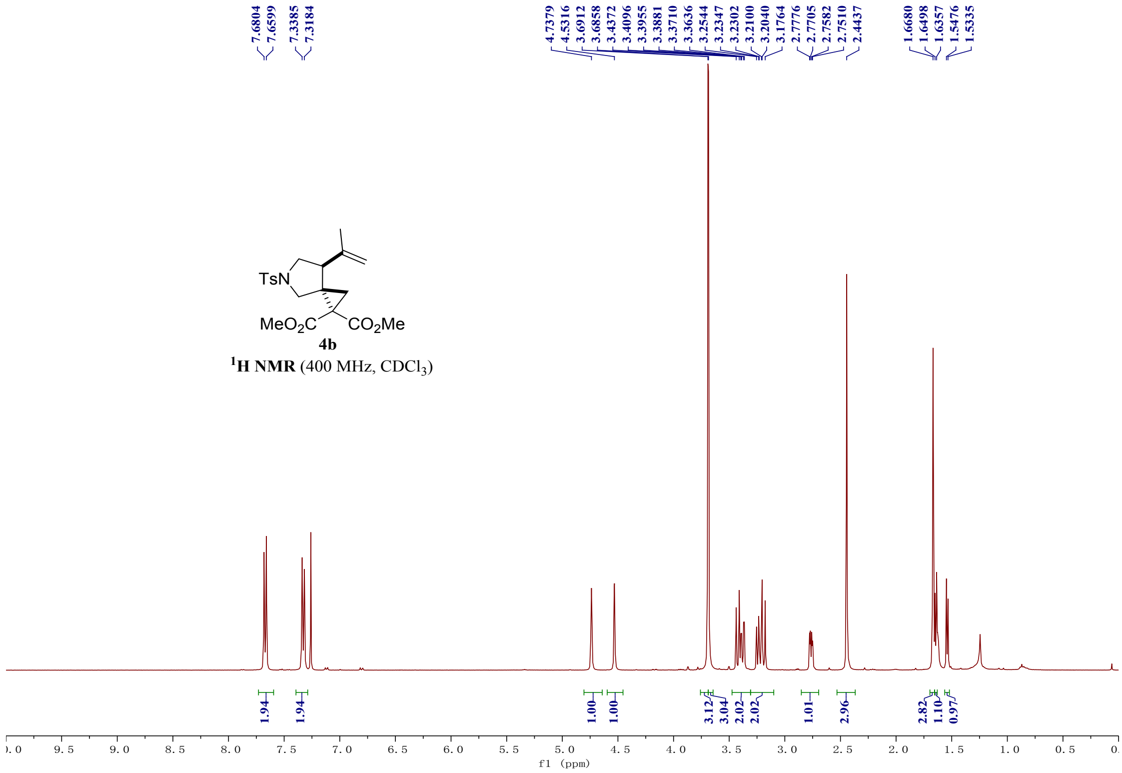
^{13}C NMR (100 MHz, $CDCl_3$)


7.7015 7.6859 7.6818 7.6654 7.3488 7.3328 7.3181 7.2981 4.7583 4.7547 4.7511 4.7397 4.7361 4.7325 4.6057 4.5880 4.1392 4.1214 4.1119 4.1034 4.0943 4.0847 4.0766 4.0623 4.0588 4.0445 4.0354 4.0267 4.0175 4.0089 3.9997 3.5013 3.4822 3.4258 3.4063 3.4012 3.3818 3.3626 3.3352 3.3275 3.3132 3.3091 3.3001 3.2946 3.2842 3.2699 3.2559 2.6245 2.6099 2.6056 2.5910 2.4177 2.3939 1.5962 1.5787 1.5347 1.5200 1.5129 1.4982 1.2363 1.2306 1.2186 1.2127 1.2008 1.1949 1.1524 1.1391 1.1253 1.0074 0.9948 0.9856 0.9730
TsN
H
EtO2C
H
(1-3)-cis-4a
+
TsN
H
H
CO2Et
(1-3)-trans-4a
1H NMR (400 MHz, CDCl3)
1.6726 1.6580 1.6508 1.6363
1.5347 1.5200 1.5129 1.4982
0.178
1.000
f1 (ppm)
0.26 2.19 0.19 2.03 0.96 0.19 0.94 0.22 2.53 0.20 1.11 2.42 1.14 1.00 0.21 3.13 0.58 0.19 2.95 0.63 1.08 4.01 0.27 1.04 1.09 0.26
f1 (ppm)


171.9 171.8 143.7 143.0 141.9 141.9 133.0 132.8 129.7 129.7 127.9 127.9 114.8 114.4 60.9 60.8 52.3 52.2 51.9 51.5 51.4 51.3 33.1 32.6 25.4 22.9 21.6 21.5 19.8 19.6 17.4 16.1 14.4 14.3
TsN
H
EtO2C
H
(1-3)-cis-4a
+
TsN
H
H
CO2Et
(1-3)-trans-4a
13C NMR (100 MHz, CDCl3)
f1 (ppm)

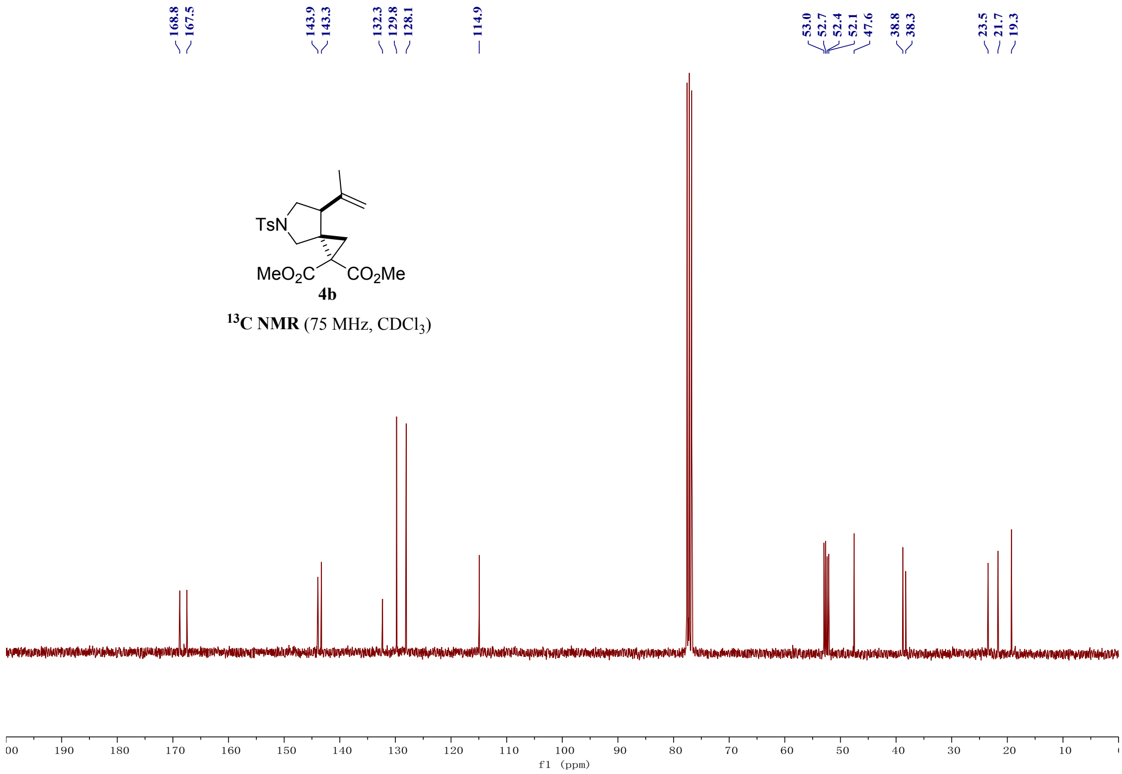
[1]H-[1]H NOESY of 4a





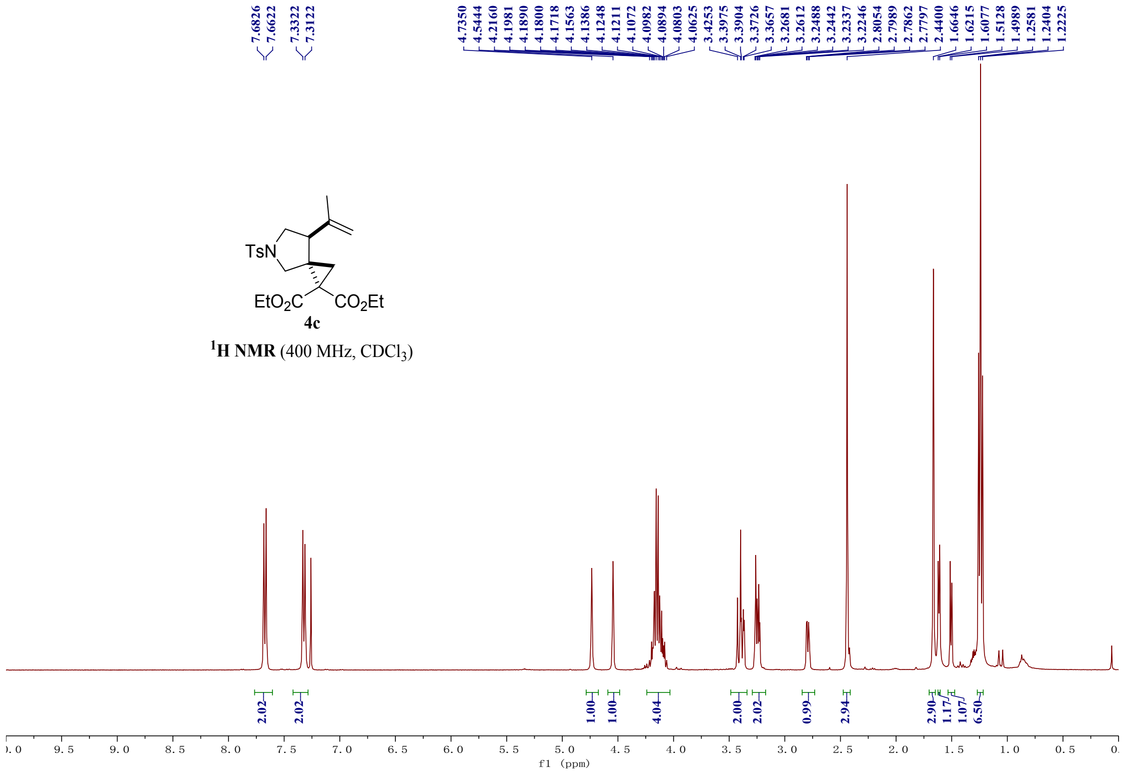
4b

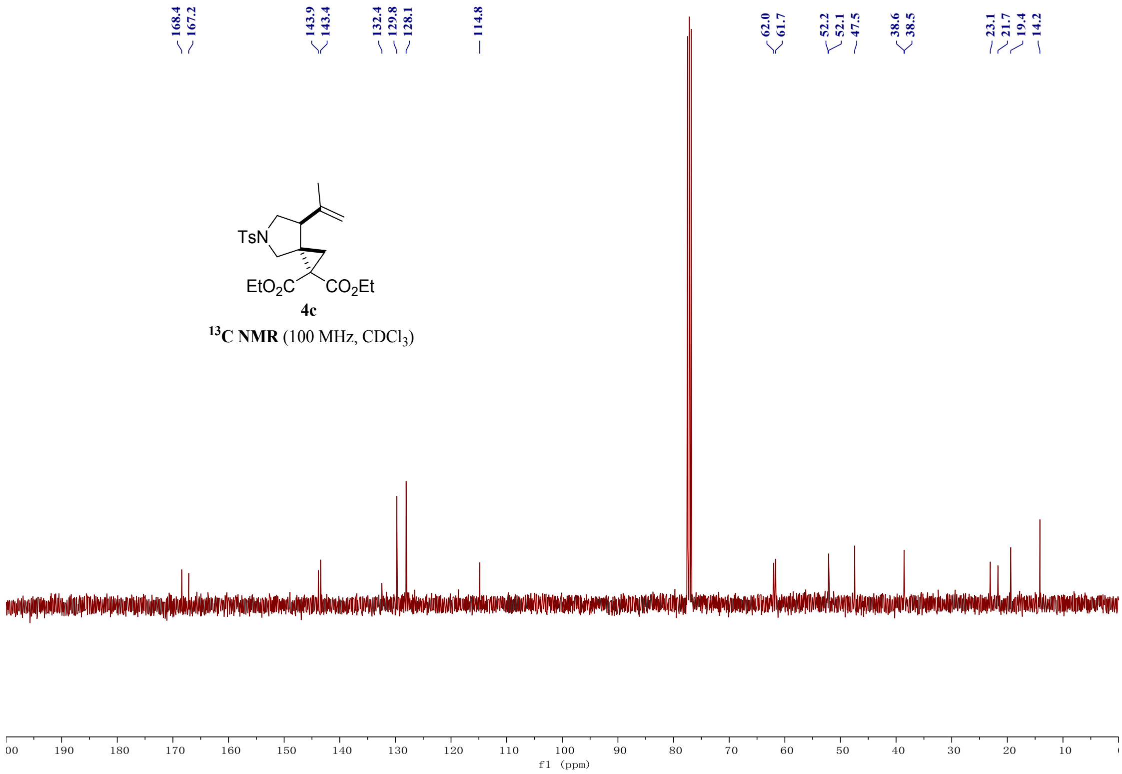
[1]H NMR (400 MHz, $CDCl_3$)

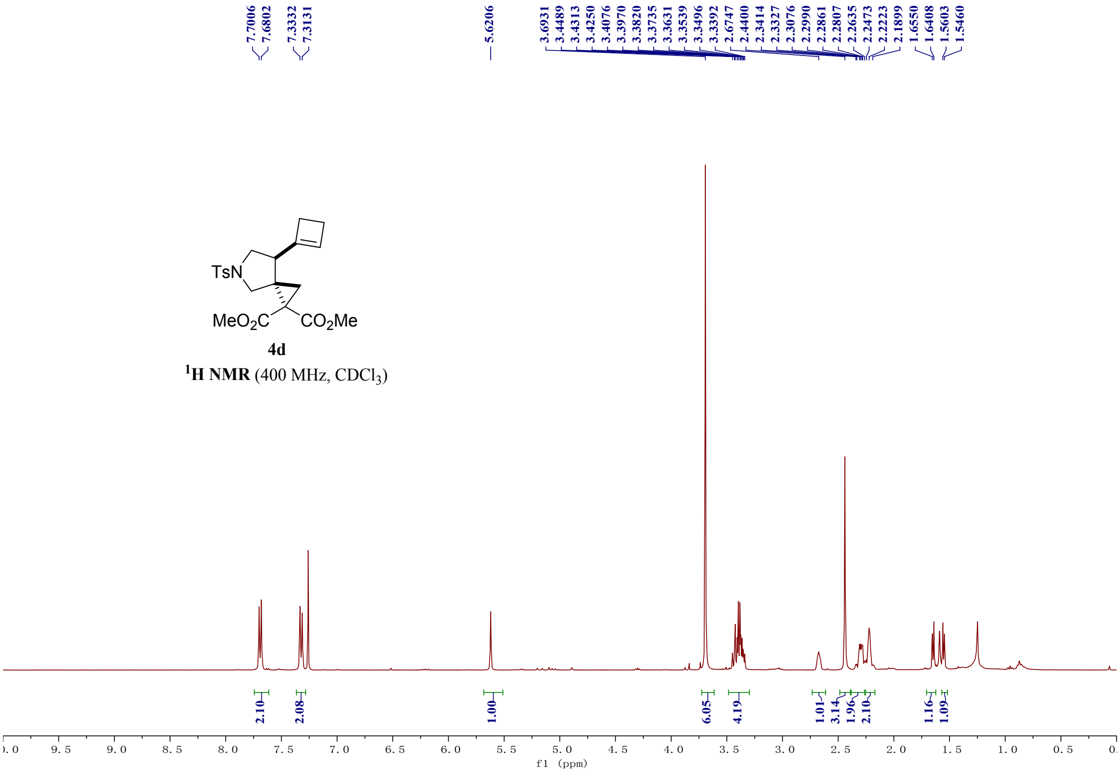


4b

[13]C NMR (75 MHz, $CDCl_3$)

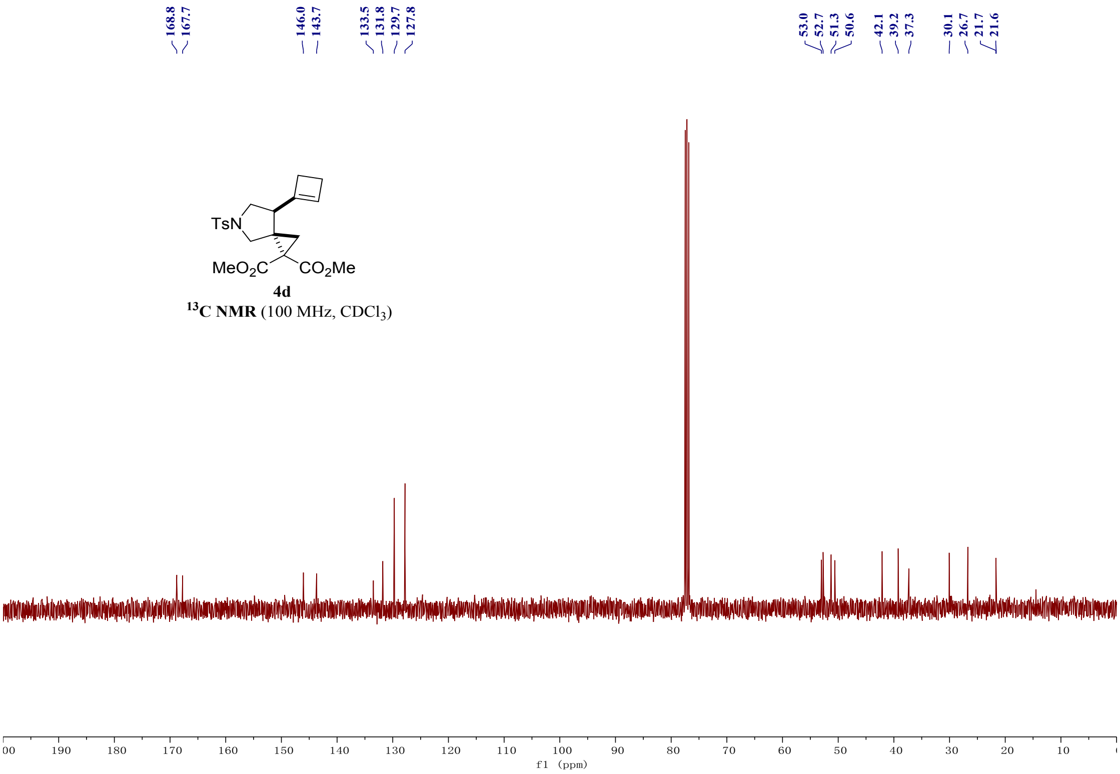

7.6826
7.6622
7.3322
7.3122
4.7350
4.5444
4.2160
4.1981
4.1890
4.1800
4.1718
4.1563
4.1386
4.1248
4.1211
4.1072
4.0982
4.0894
4.0803
4.0625
3.4253
3.3975
3.3904
3.3726
3.3657
3.2681
3.2612
3.2488
3.2442
3.2337
3.2246
2.8054
2.7989
2.7862
2.7797
2.4400
1.6646
1.6215
1.6077
1.5128
1.4989
1.2581
1.2404
1.2225
TsN
EtO2C
CO2Et
4c
1H NMR (400 MHz, CDCl3)
2.02
2.02
1.00
1.00
4.04
2.00
2.02
0.99
2.94
2.90
1.17
1.07
6.50
f1 (ppm)


168.4
167.2
143.9
143.4
132.4
129.8
128.1
114.8
62.0
61.7
52.2
52.1
47.5
38.6
38.5
23.1
21.7
19.4
14.2
TsN
EtO2C
CO2Et
4c
13C NMR (100 MHz, CDCl3)
f1 (ppm)



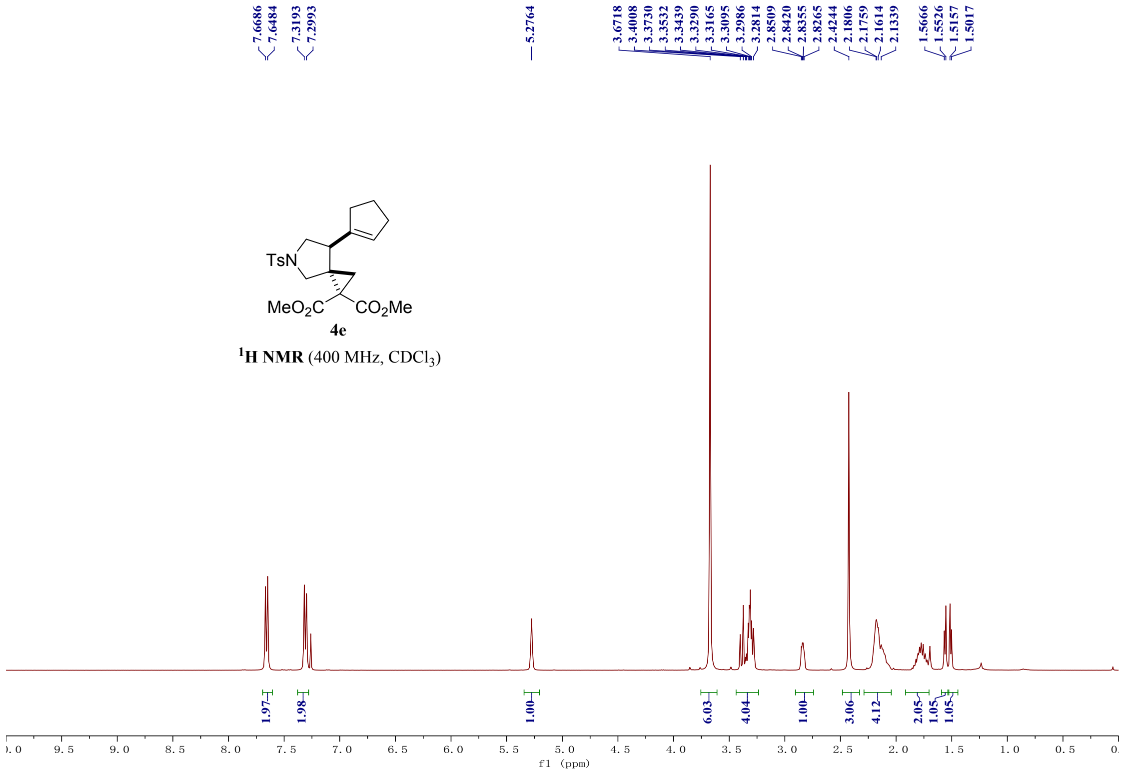
4d

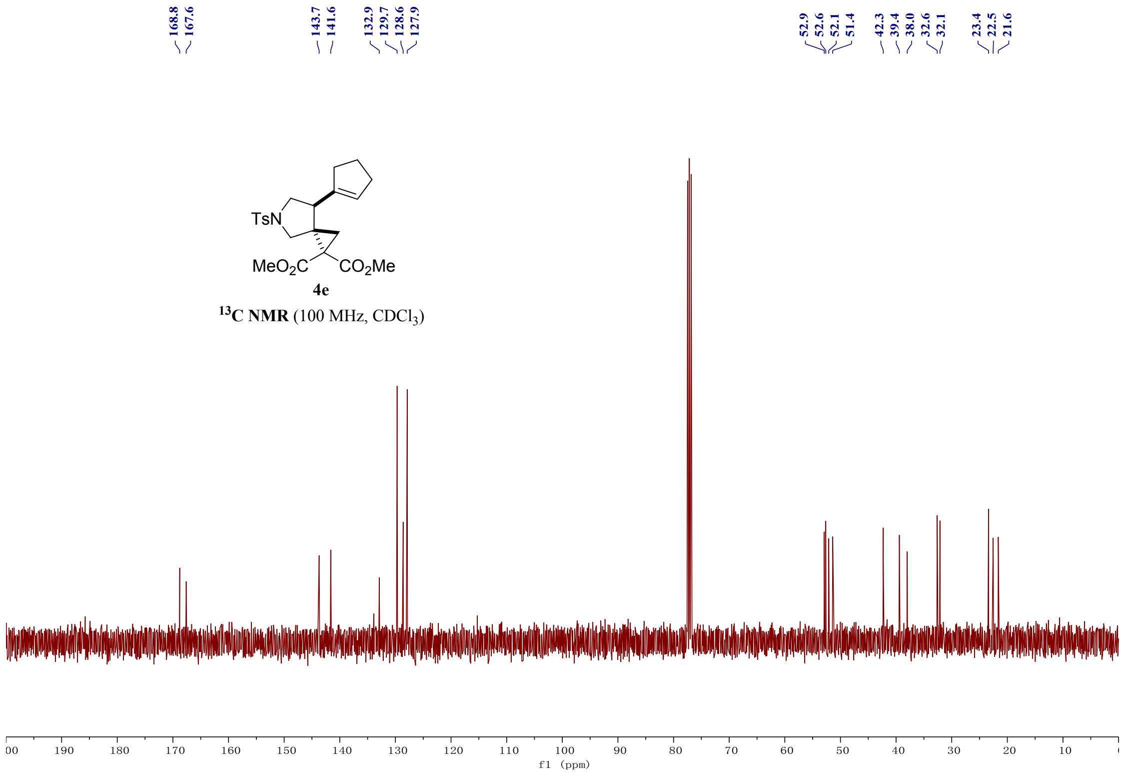
^{1}H NMR (400 MHz, $CDCl_3$)

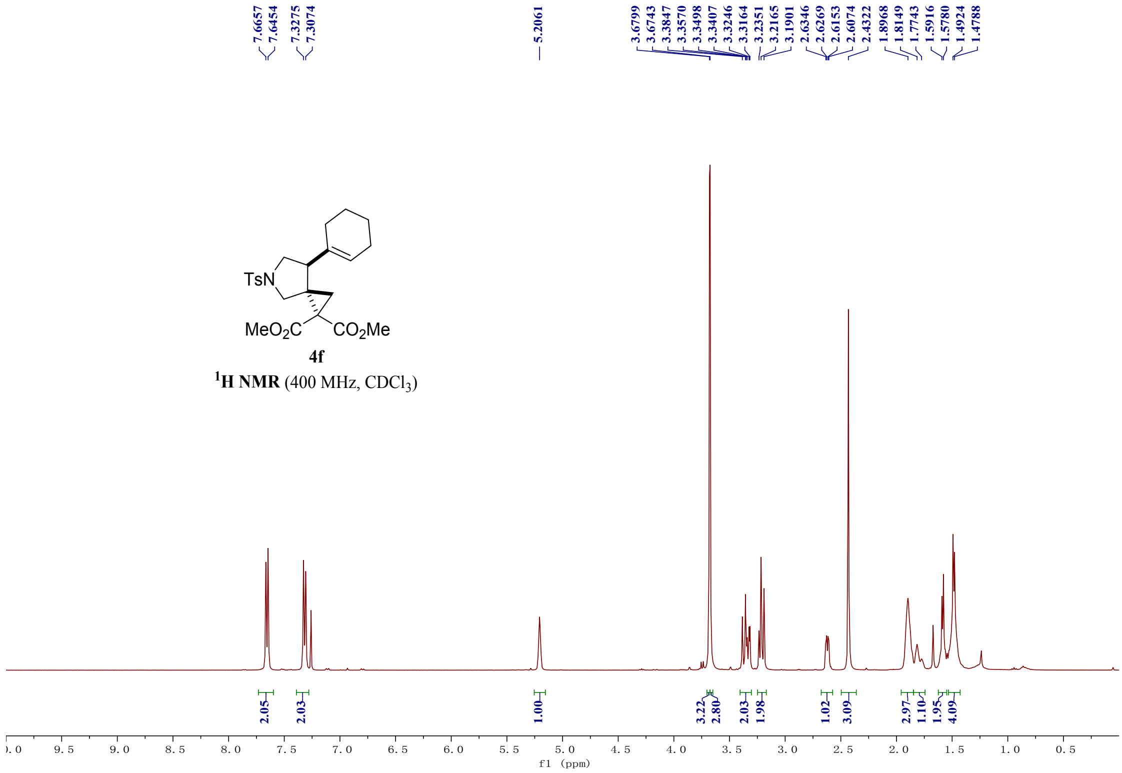


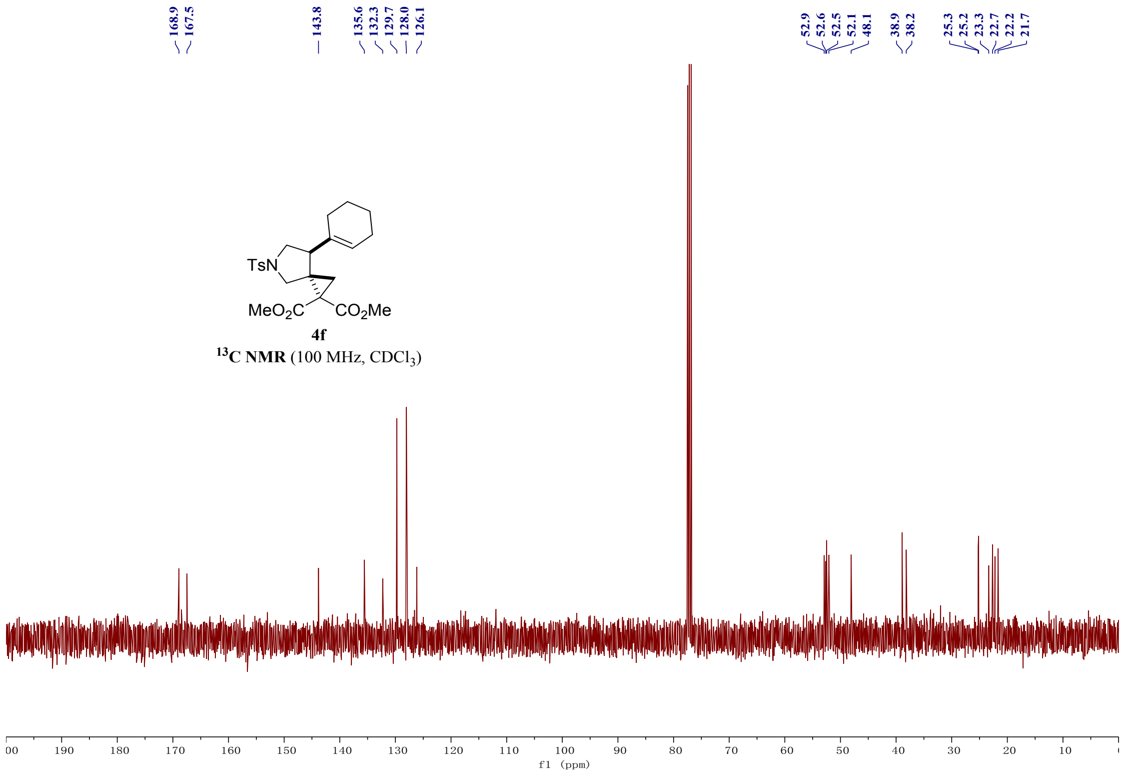
4d

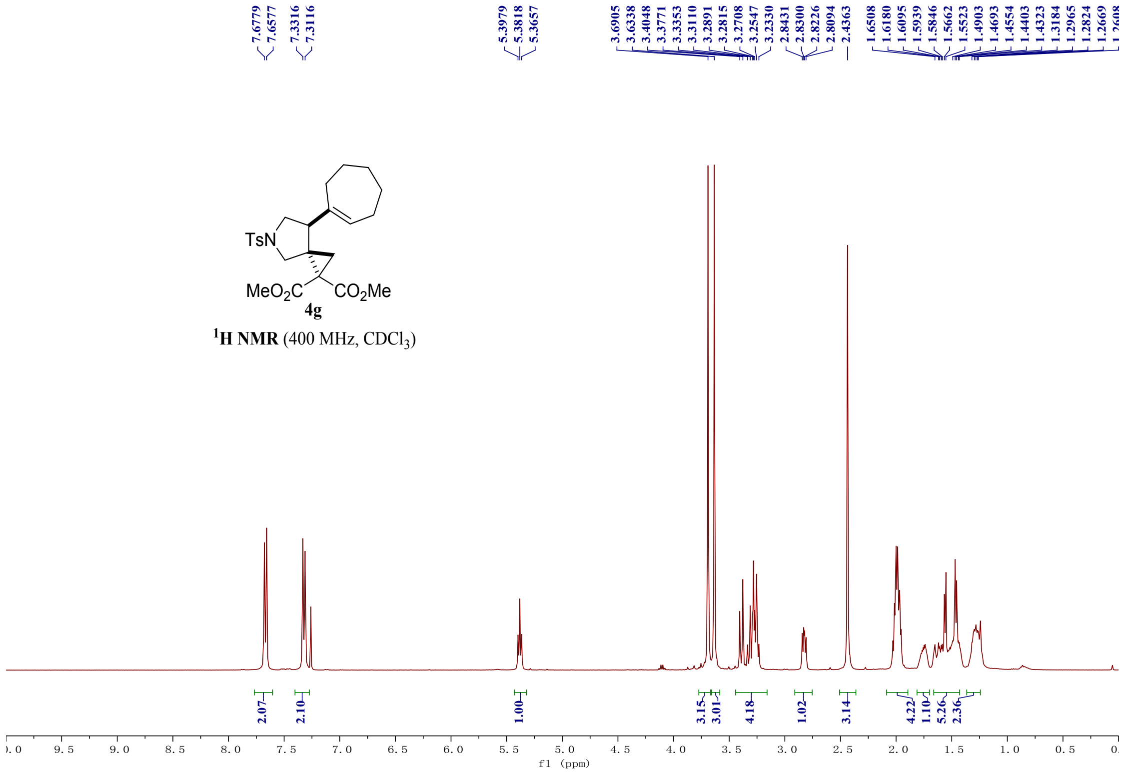
^{13}C NMR (100 MHz, $CDCl_3$)

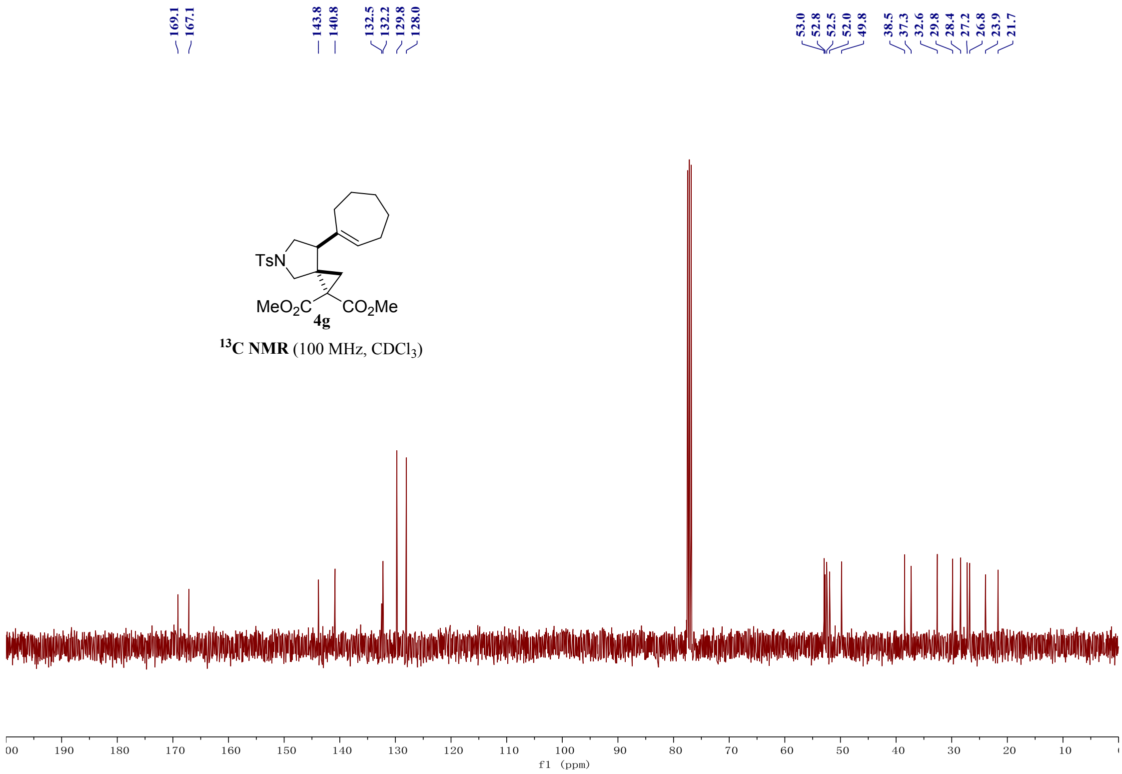

7.6686
7.6484
7.3193
7.2993
5.2764
3.6718
3.4008
3.3730
3.3532
3.3439
3.3290
3.3165
3.3095
3.2986
3.2814
2.8509
2.8420
2.8355
2.8265
2.4244
2.1806
2.1759
2.1614
2.1339
1.5666
1.5526
1.5157
1.5017
TsN
MeO2C
CO2Me
4e
1H NMR (400 MHz, CDCl3)
1.97
1.98
1.00
6.03
4.04
1.00
3.06
4.12
2.05
1.05
1.05
f1 (ppm)

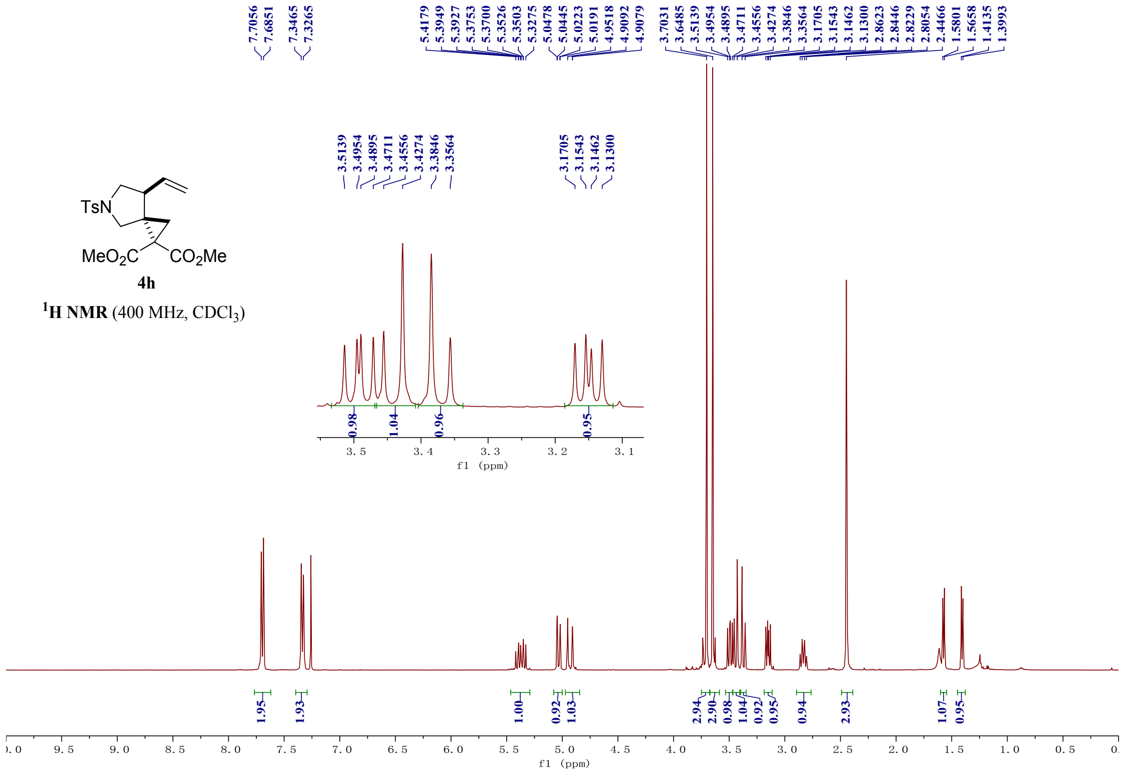

168.8
167.6
143.7
141.6
132.9
129.7
128.6
127.9
52.9
52.6
52.1
51.4
42.3
39.4
38.0
32.6
32.1
23.4
22.5
21.6
TsN
MeO2C
CO2Me
4e
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.6657
7.6454
7.3275
7.3074
5.2061
3.6799
3.6743
3.3847
3.3570
3.3498
3.3407
3.3246
3.3164
3.2351
3.2165
3.1901
2.6346
2.6269
2.6153
2.6074
2.4322
1.8968
1.8149
1.7743
1.5916
1.5780
1.4924
1.4788
TsN
MeO2C
CO2Me
4f
1H NMR (400 MHz, CDCl3)
2.05
2.03
1.00
3.22
2.80
2.03
1.98
1.02
3.09
2.97
1.10
1.95
4.09
f1 (ppm)

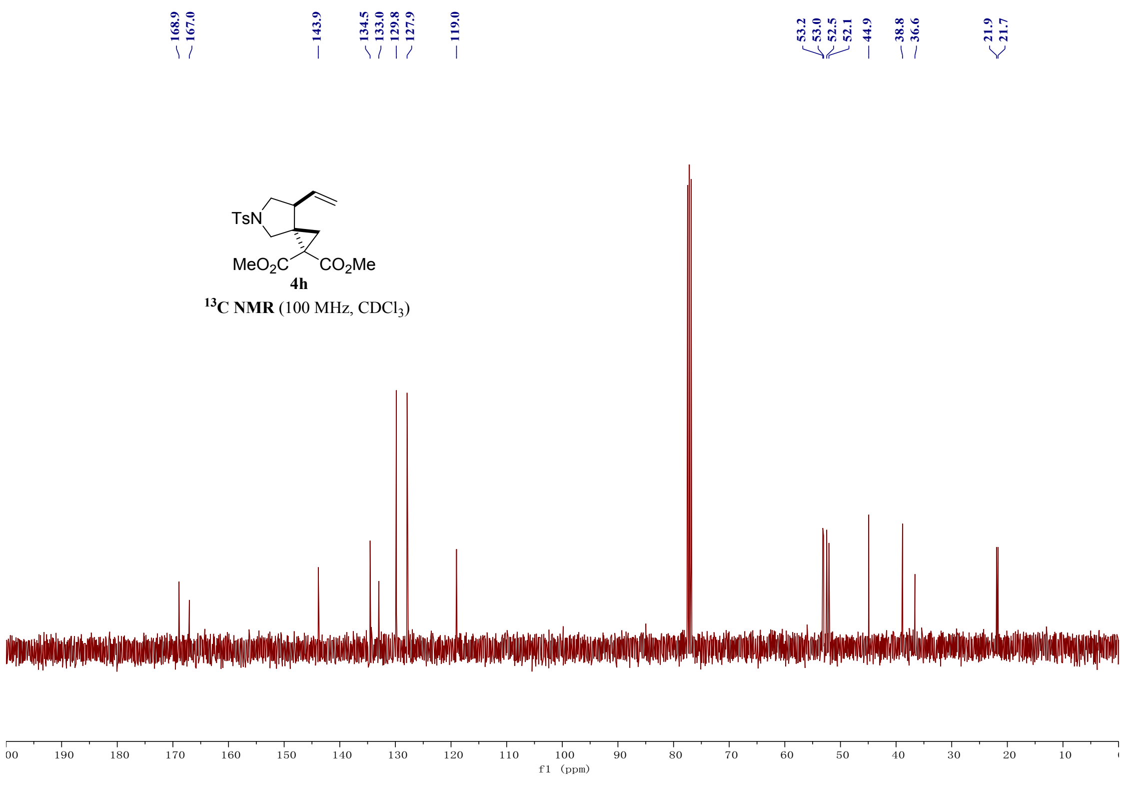

168.9
167.5
143.8
135.6
132.3
129.7
128.0
126.1
52.9
52.6
52.5
52.1
48.1
38.9
38.2
25.3
25.2
23.3
22.7
22.2
21.7
TsN
MeO2C
CO2Me
4f
13C NMR (100 MHz, CDCl3)
f1 (ppm)


TsN
MeO2C
CO2Me
4g
1H NMR (400 MHz, CDCl3)
f1 (ppm)

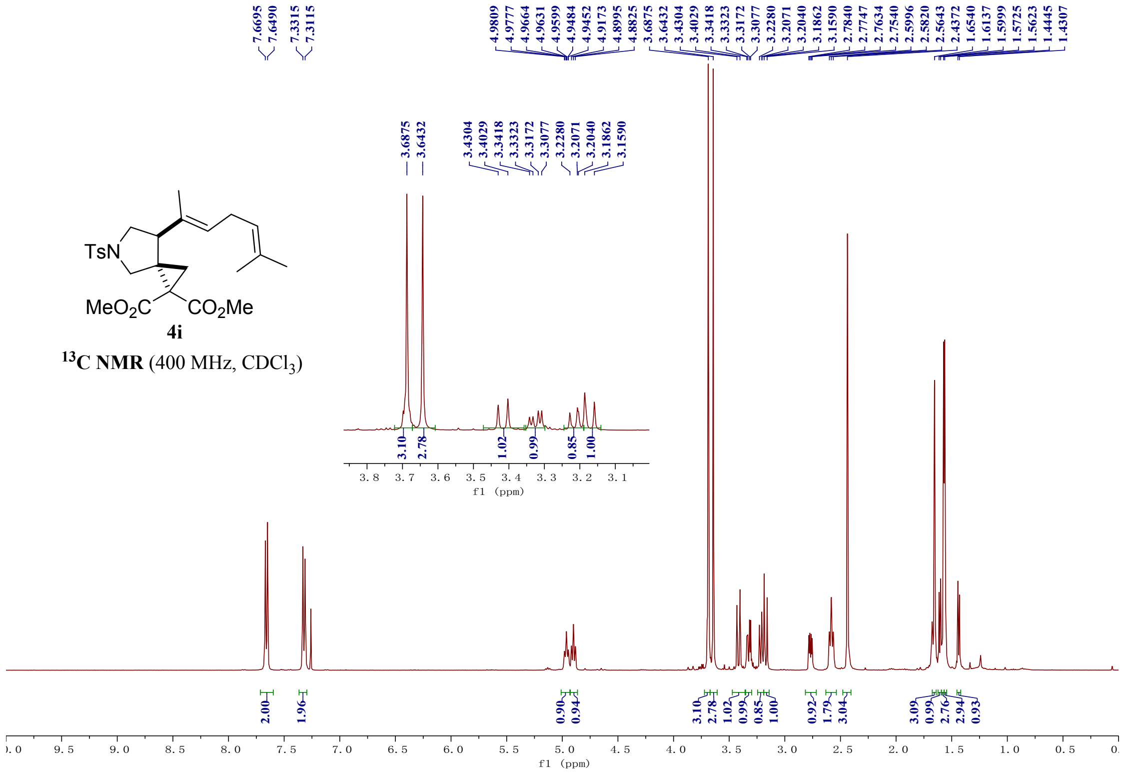

TsN
MeO2C
CO2Me
4g
13C NMR (100 MHz, CDCl3)
f1 (ppm)

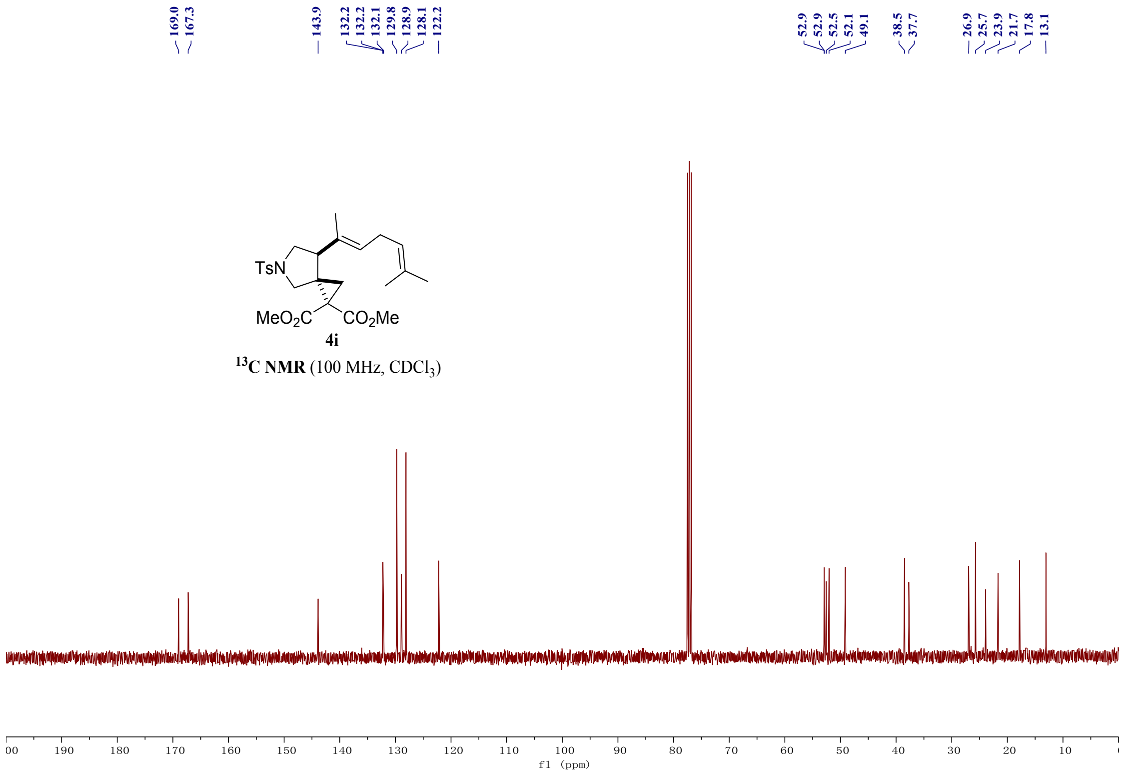


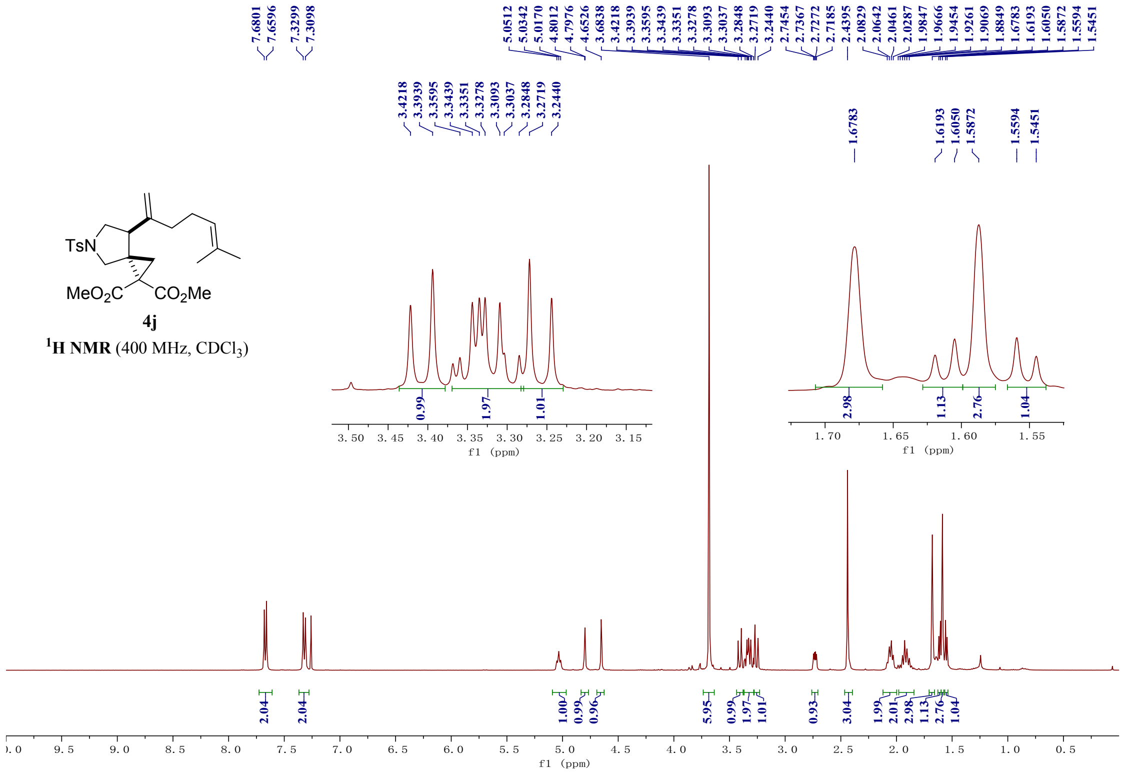
7.7056
7.6851
7.3465
7.3265
5.4179
5.3949
5.3927
5.3753
5.3700
5.3526
5.3503
5.3275
5.0478
5.0445
5.0223
5.0191
4.9518
4.9092
4.9079
3.7031
3.6485
3.5139
3.4954
3.4895
3.4711
3.4556
3.4274
3.3846
3.3564
3.1705
3.1543
3.1462
3.1300
2.8623
2.8446
2.8229
2.8054
2.4466
1.5801
1.5658
1.4135
1.3993
TsN
MeO2C
CO2Me
4h
1H NMR (400 MHz, CDCl3)
1.95
1.93
1.00
0.92
1.03
2.94
2.90
0.98
1.04
0.92
0.95
0.94
2.93
1.07
0.95
f1 (ppm)

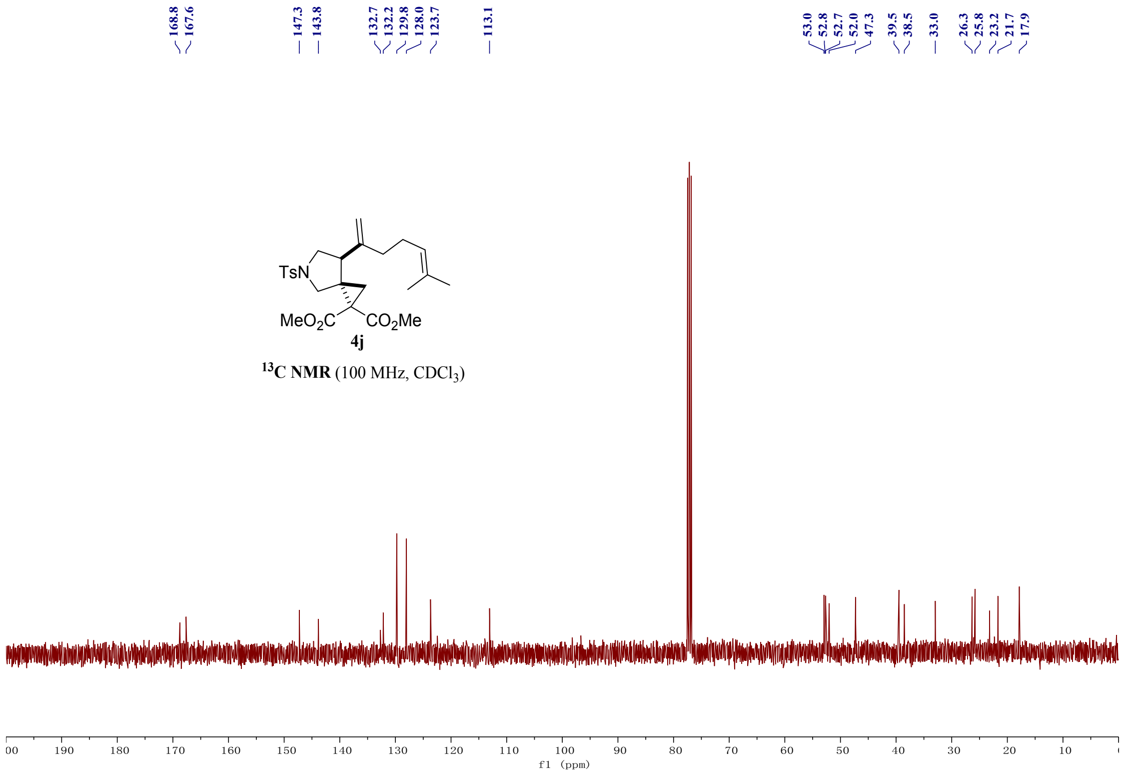


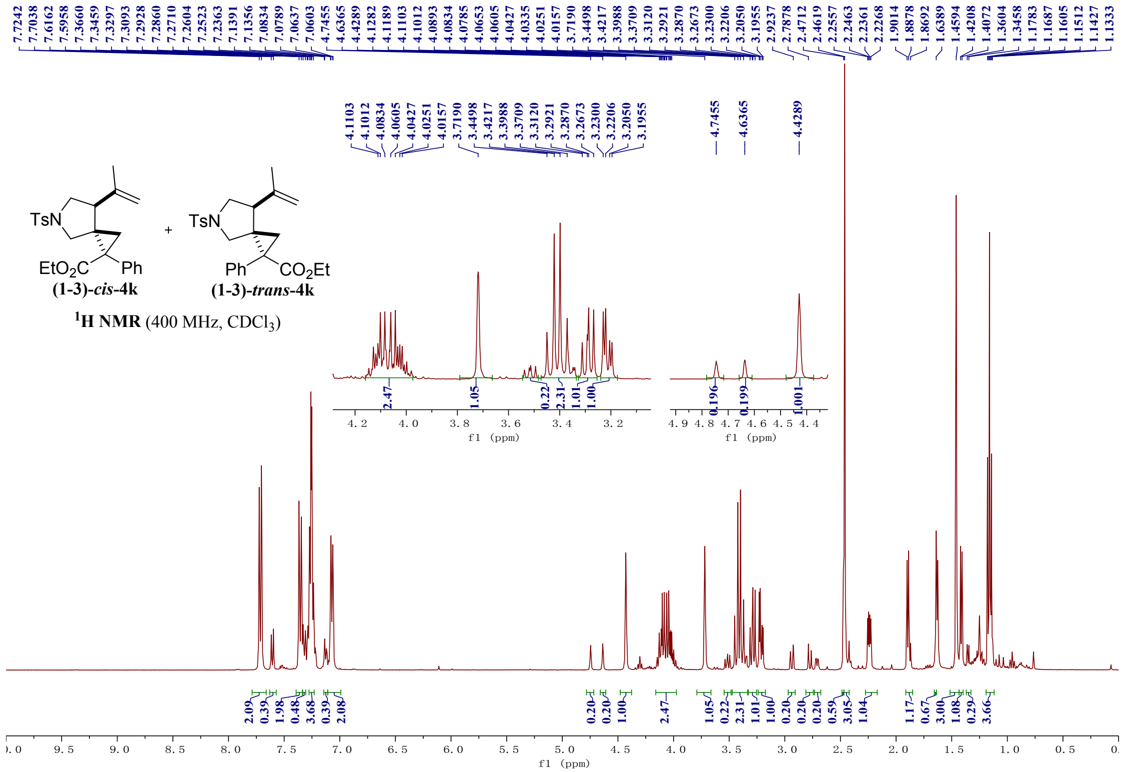
168.9
167.0
143.9
134.5
133.0
129.8
127.9
119.0
53.2
53.0
52.5
52.1
44.9
38.8
36.6
21.9
21.7
TsN
MeO2C
CO2Me
4h
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.6695
7.6490
7.3315
7.3115
4.9809
4.9777
4.9664
4.9631
4.9599
4.9484
4.9452
4.9173
4.8995
4.8825
3.6875
3.6432
3.4304
3.4029
3.3418
3.3323
3.3172
3.3077
3.2280
3.2071
3.2040
3.1862
3.1590
2.7840
2.7747
2.7634
2.7540
2.5996
2.5820
2.5643
2.4372
1.6540
1.6137
1.5999
1.5725
1.5623
1.4445
1.4307
TsN
MeO2C
CO2Me
4i
13C NMR (400 MHz, CDCl3)
f1 (ppm)

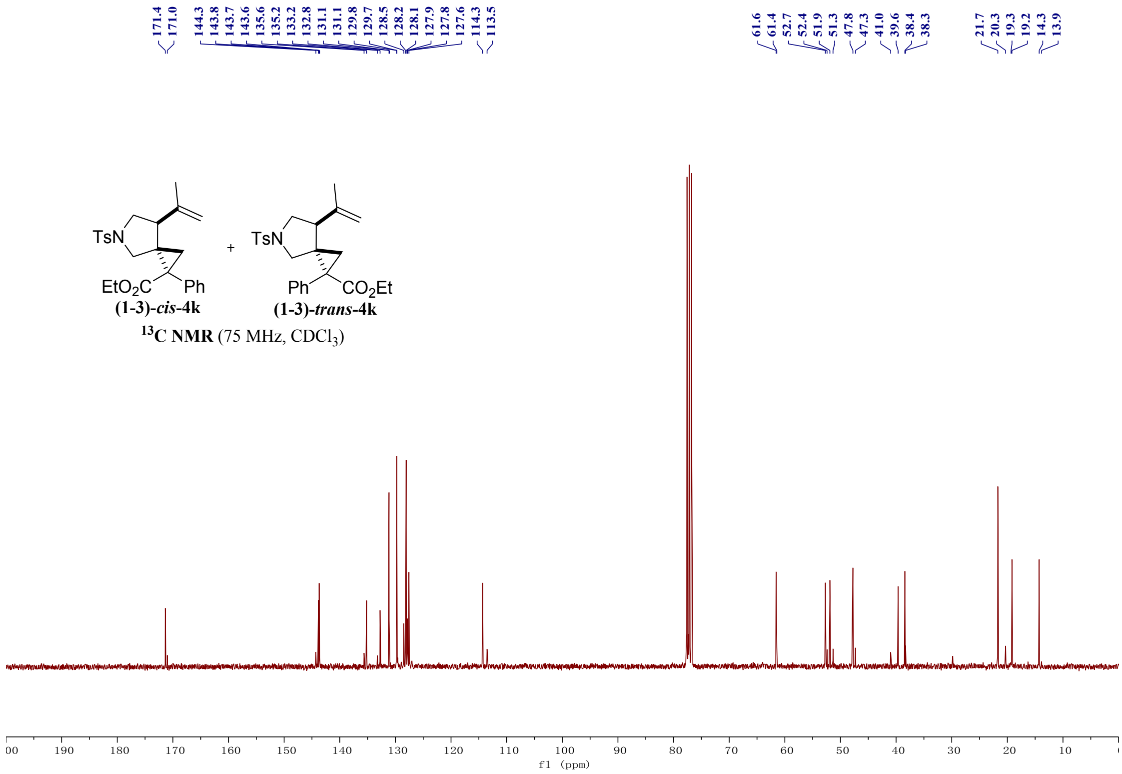

169.0
167.3
143.9
132.2
132.2
132.1
129.8
128.9
128.1
122.2
52.9
52.9
52.5
52.1
49.1
38.5
37.7
26.9
25.7
23.9
21.7
17.8
13.1
TsN
MeO2C
CO2Me
4i
13C NMR (100 MHz, CDCl3)
f1 (ppm)


TsN
MeO2C
CO2Me
4j
1H NMR (400 MHz, CDCl3)
f1 (ppm)


TsN
MeO2C
CO2Me
4j
13C NMR (100 MHz, CDCl3)
f1 (ppm)

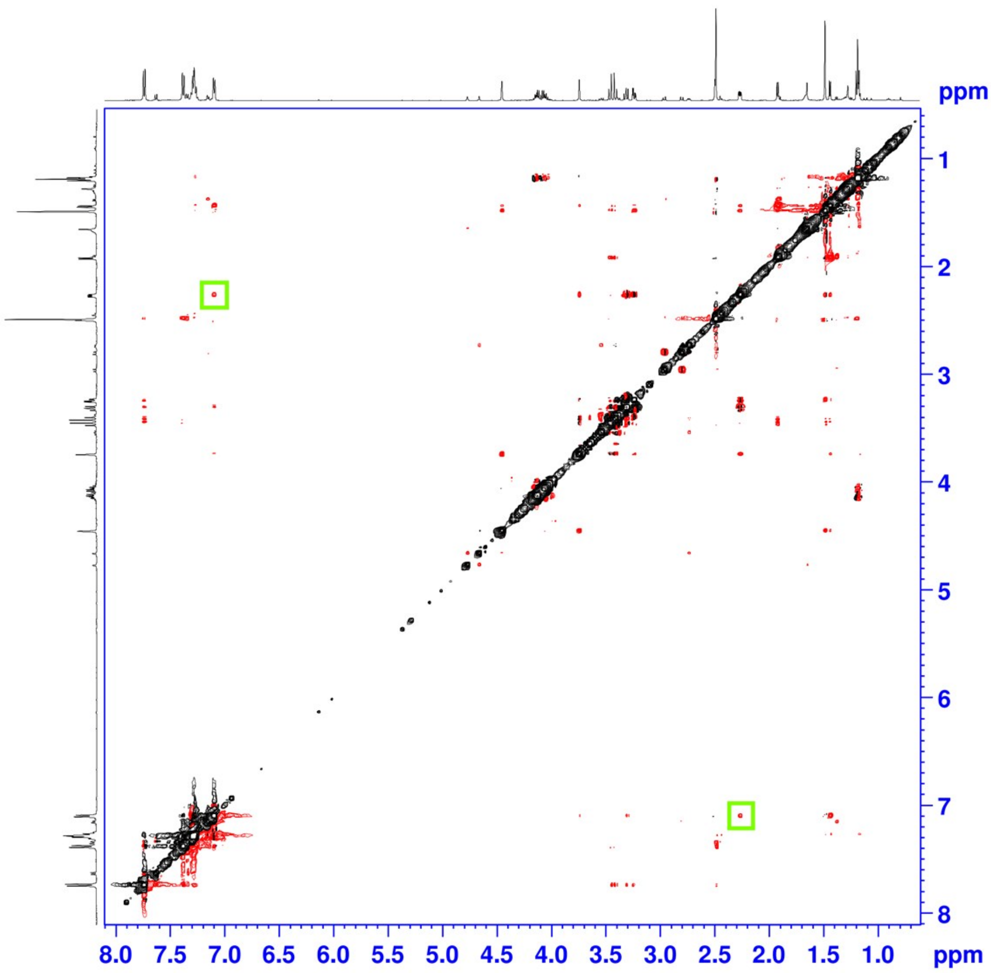


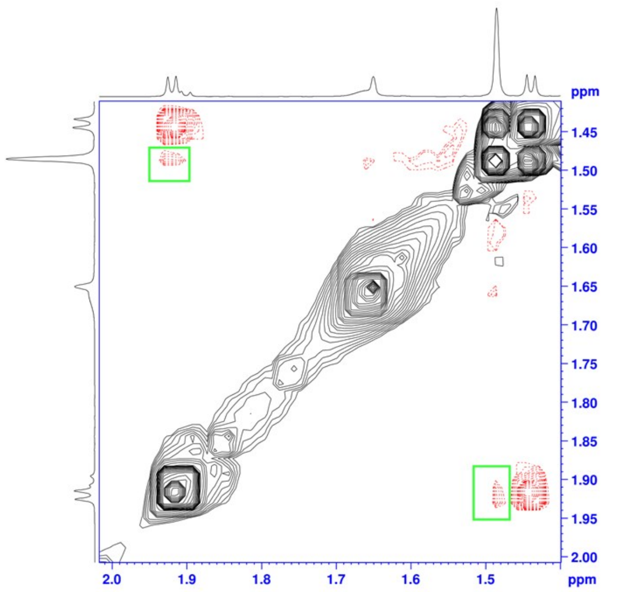
7.7242 7.7038 7.6162 7.5958 7.3660 7.3459 7.3297 7.3093 7.2928 7.2860 7.2710 7.2604 7.2523 7.2363 7.1391 7.1356 7.0834 7.0789 7.0637 7.0603 4.7455 4.6365 4.4289 4.1282 4.1189 4.1103 4.1012 4.0893 4.0834 4.0785 4.0653 4.0605 4.0427 4.0335 4.0251 4.0157 3.7190 3.4498 3.4217 3.3988 3.3709 3.3120 3.2921 3.2870 3.2673 3.2300 3.2206 3.2050 3.1955 2.9237 2.7878 2.4712 2.4619 2.2557 2.2463 2.2361 2.2268 1.9014 1.8878 1.8692 1.6389 1.4594 1.4208 1.4072 1.3604 1.3458 1.1783 1.1687 1.1605 1.1512 1.1427 1.1333
TsN
EtO2C
Ph
(1-3)-cis-4k
+
TsN
Ph
CO2Et
(1-3)-trans-4k
1H NMR (400 MHz, CDCl3)
f1 (ppm)

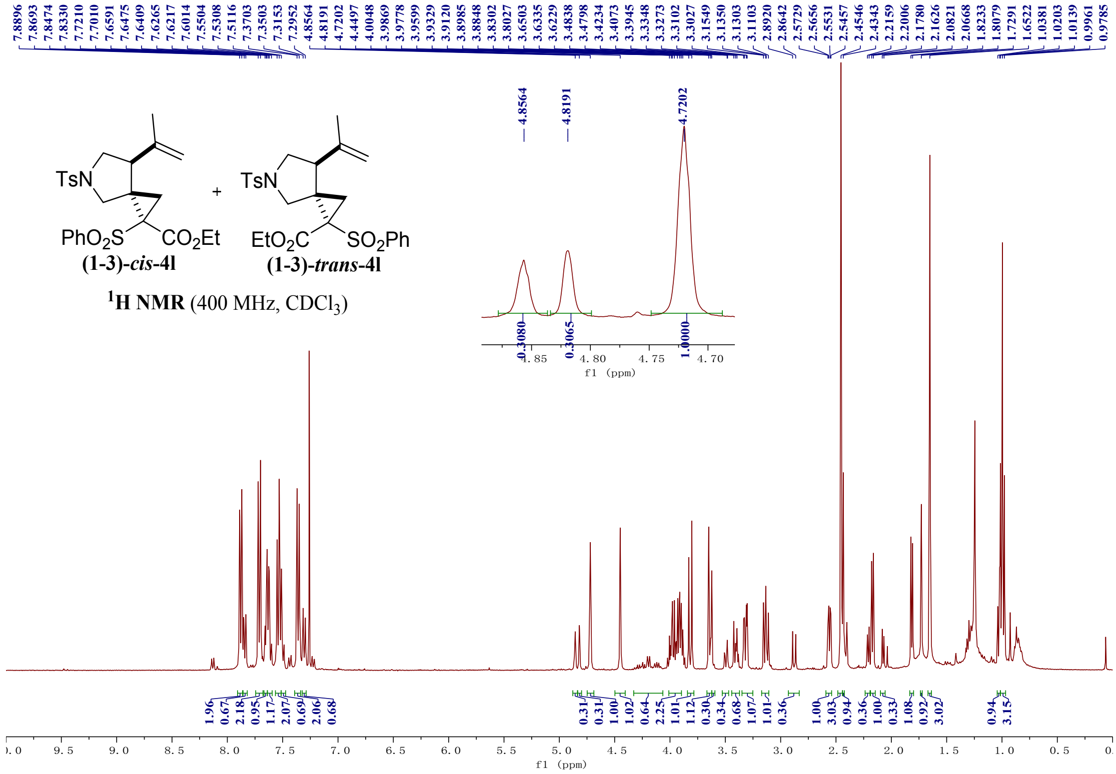


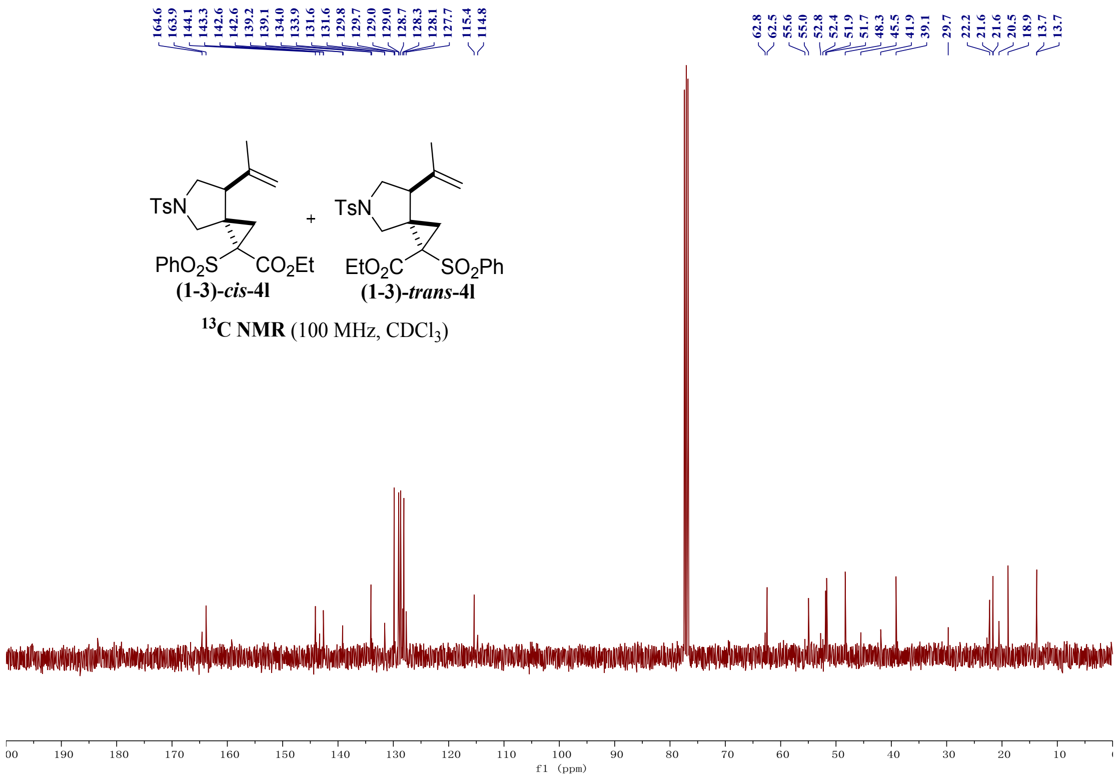
171.4 171.0 144.3 143.8 143.7 143.6 135.6 135.2 133.2 132.8 131.1 131.1 129.8 129.7 128.5 128.2 128.1 127.9 127.8 127.6 114.3 113.5 61.6 61.4 52.7 52.4 51.9 51.3 47.8 47.3 41.0 39.6 38.4 38.3 21.7 20.3 19.3 19.2 14.3 13.9
TsN
EtO2C
Ph
(1-3)-cis-4k
+
TsN
Ph
CO2Et
(1-3)-trans-4k
13C NMR (75 MHz, CDCl3)
f1 (ppm)

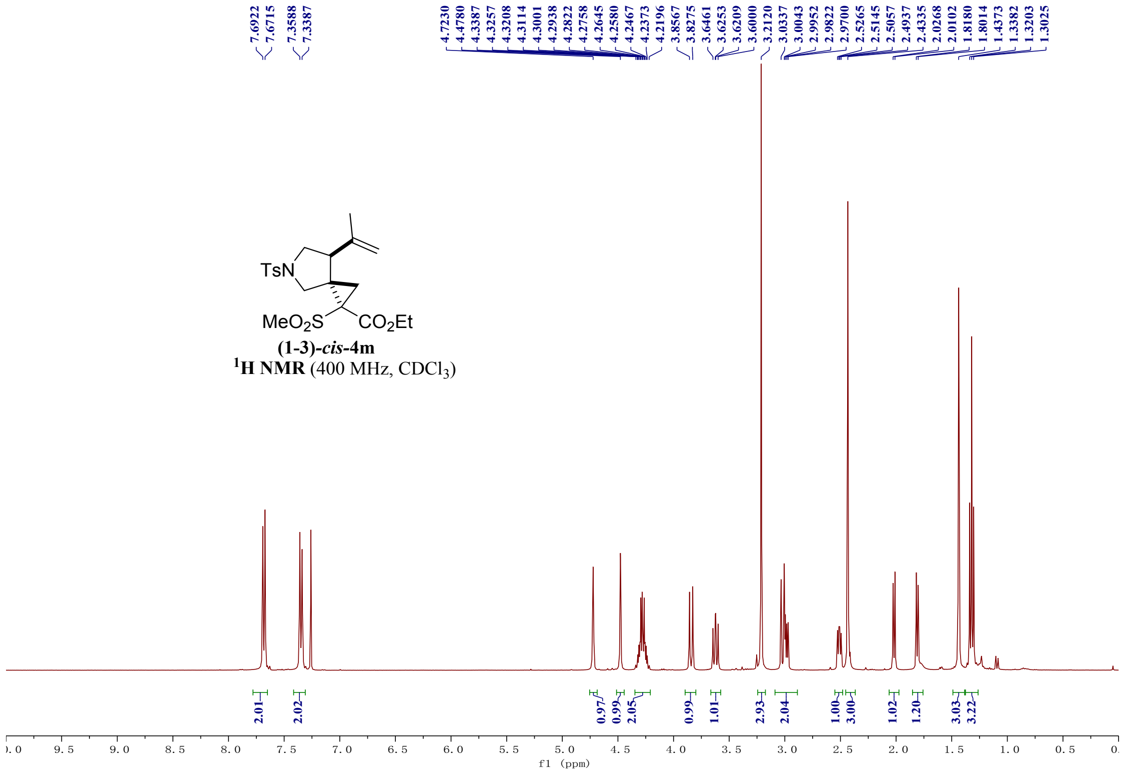
[1]H-[1]H NOESY of 4k

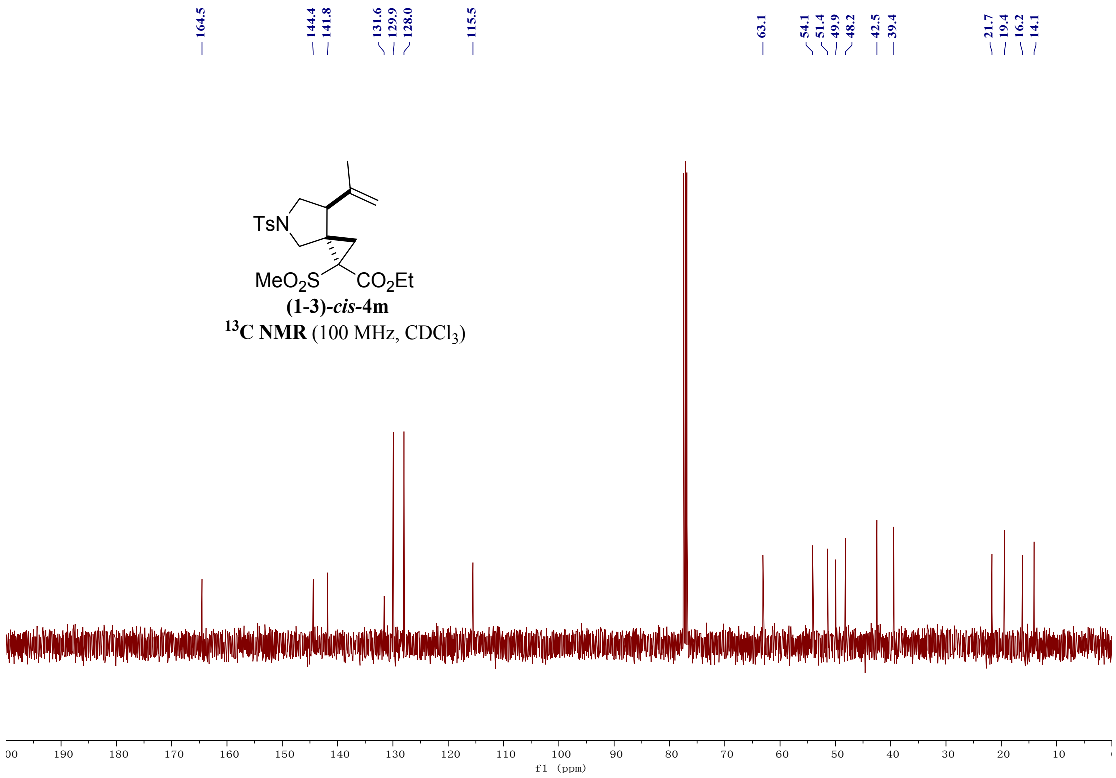




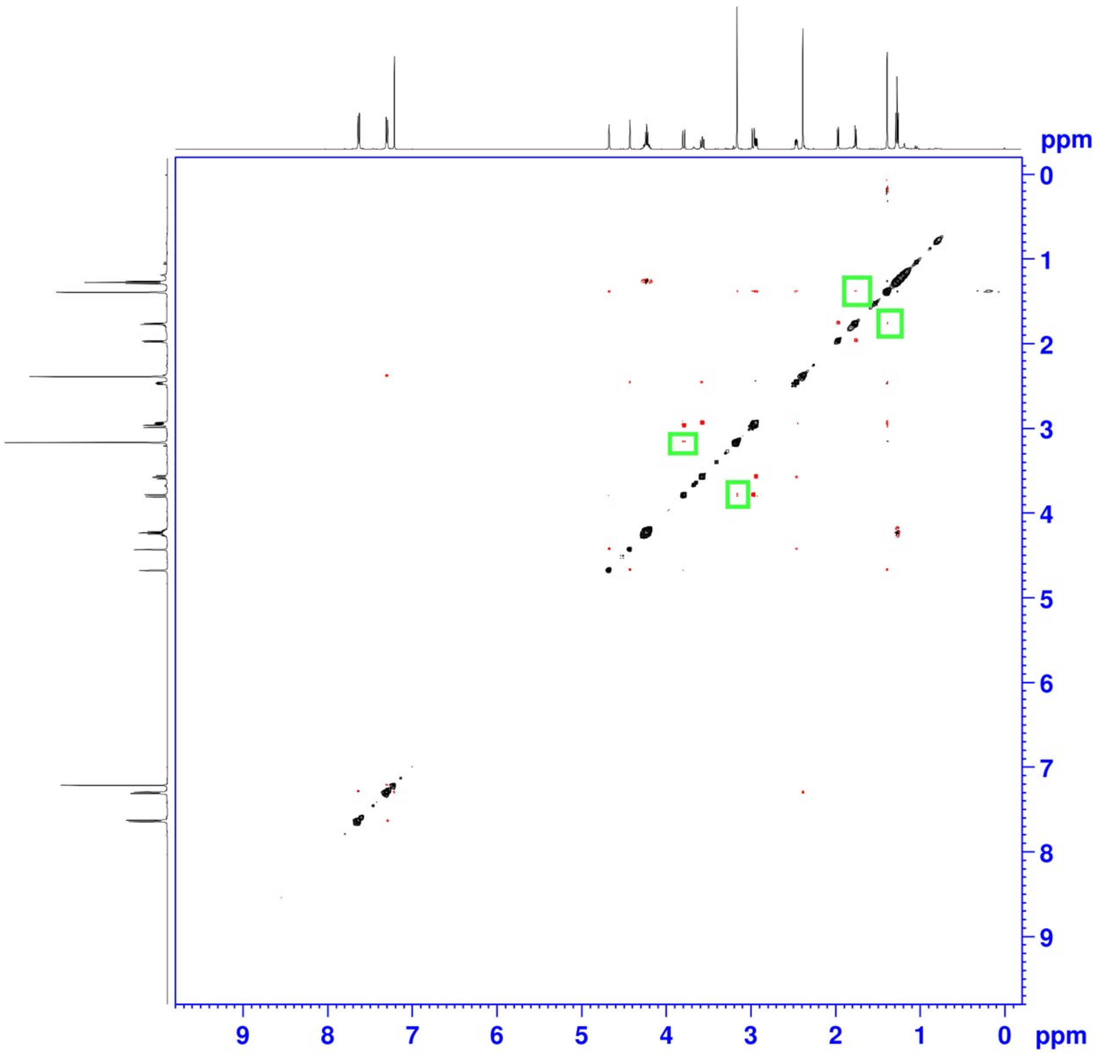


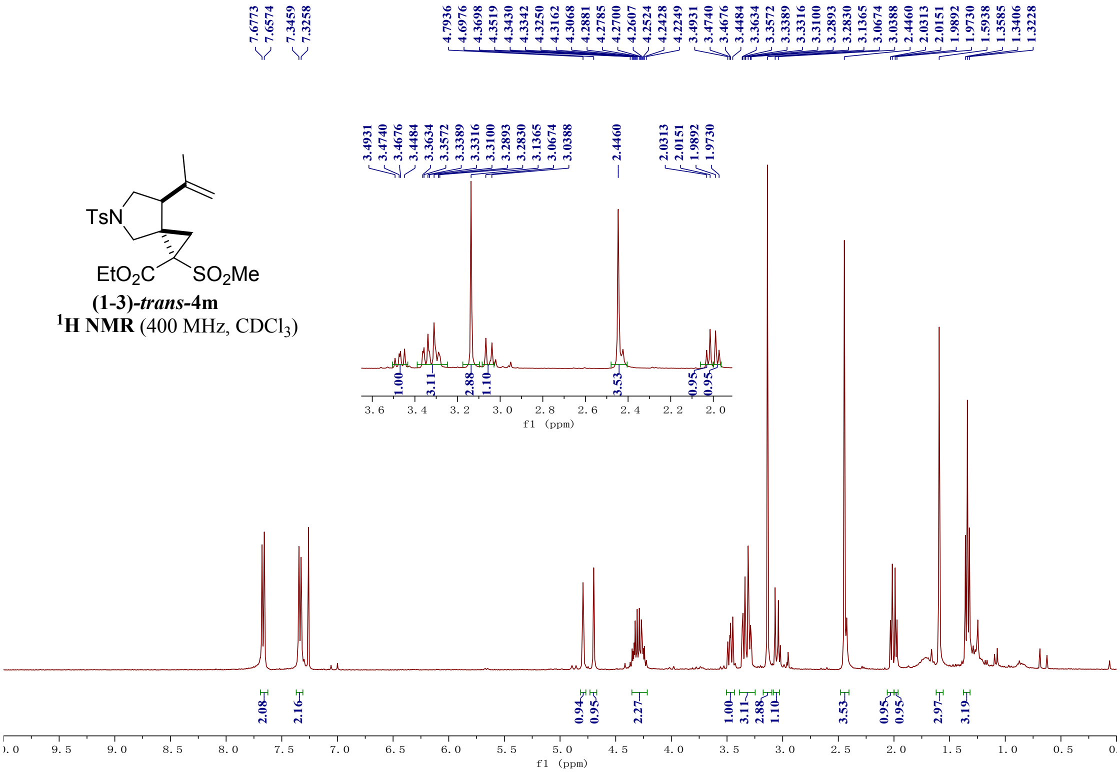



7.6922
7.6715
7.3588
7.3387
4.7230
4.4780
4.3387
4.3257
4.3208
4.3114
4.3001
4.2938
4.2822
4.2758
4.2645
4.2580
4.2467
4.2373
4.2196
3.8567
3.8275
3.6461
3.6253
3.6209
3.6000
3.2120
3.0337
3.0043
2.9952
2.9822
2.9700
2.5265
2.5145
2.5057
2.4937
2.4335
2.0268
2.0102
1.8180
1.8014
1.4373
1.3382
1.3203
1.3025
TsN
MeO2S
CO2Et
(1-3)-cis-4m
1H NMR (400 MHz, CDCl3)
2.01
2.02
0.97
0.99
2.05
0.99
1.01
2.93
2.04
1.00
3.00
1.02
1.20
3.03
3.22
f1 (ppm)


164.5
144.4
141.8
131.6
129.9
128.0
115.5
63.1
54.1
51.4
49.9
48.2
42.5
39.4
21.7
19.4
16.2
14.1
TsN
MeO2S
CO2Et
(1-3)-cis-4m
13C NMR (100 MHz, CDCl3)
f1 (ppm)

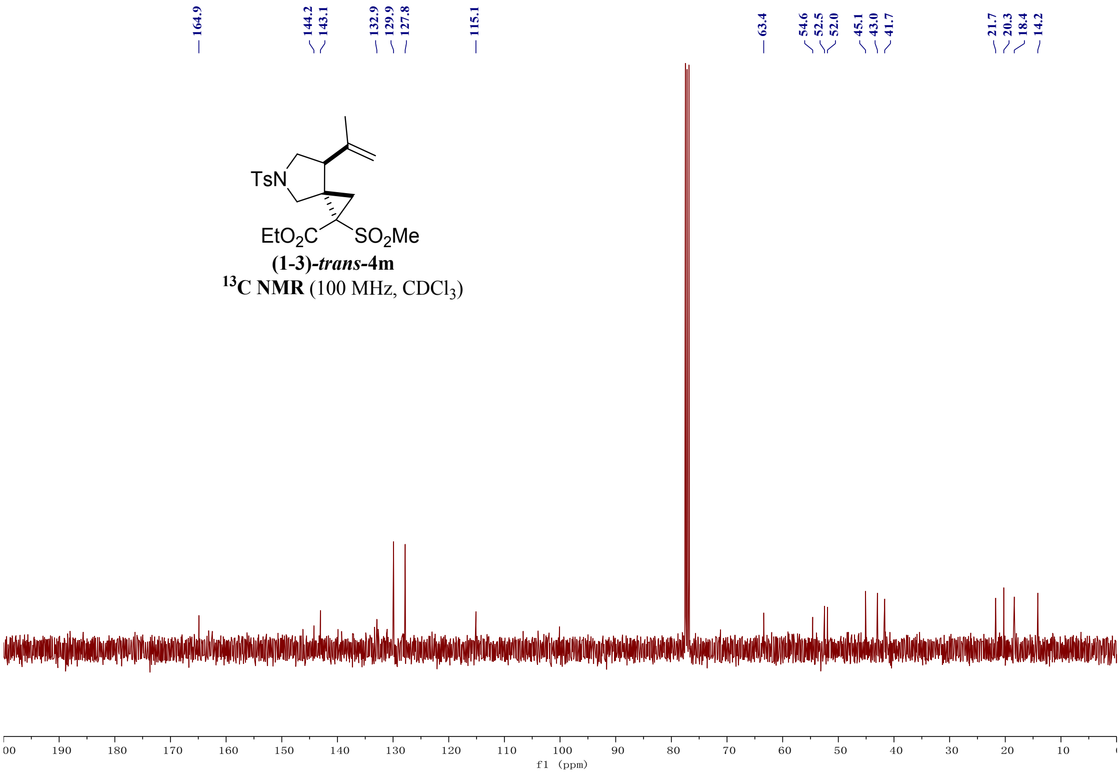
[1]H-[1]H NOESY of (1-3)-*cis*-4m





(1-3)-*trans*-4m

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

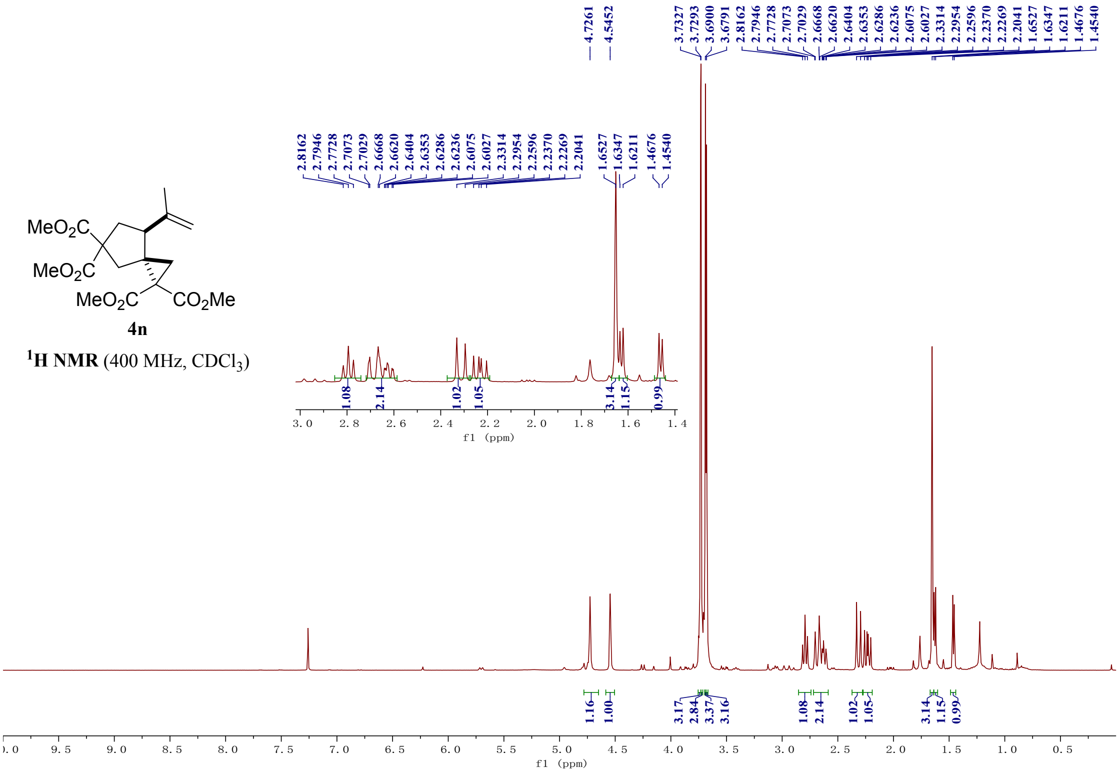


(1-3)-*trans*-4m

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

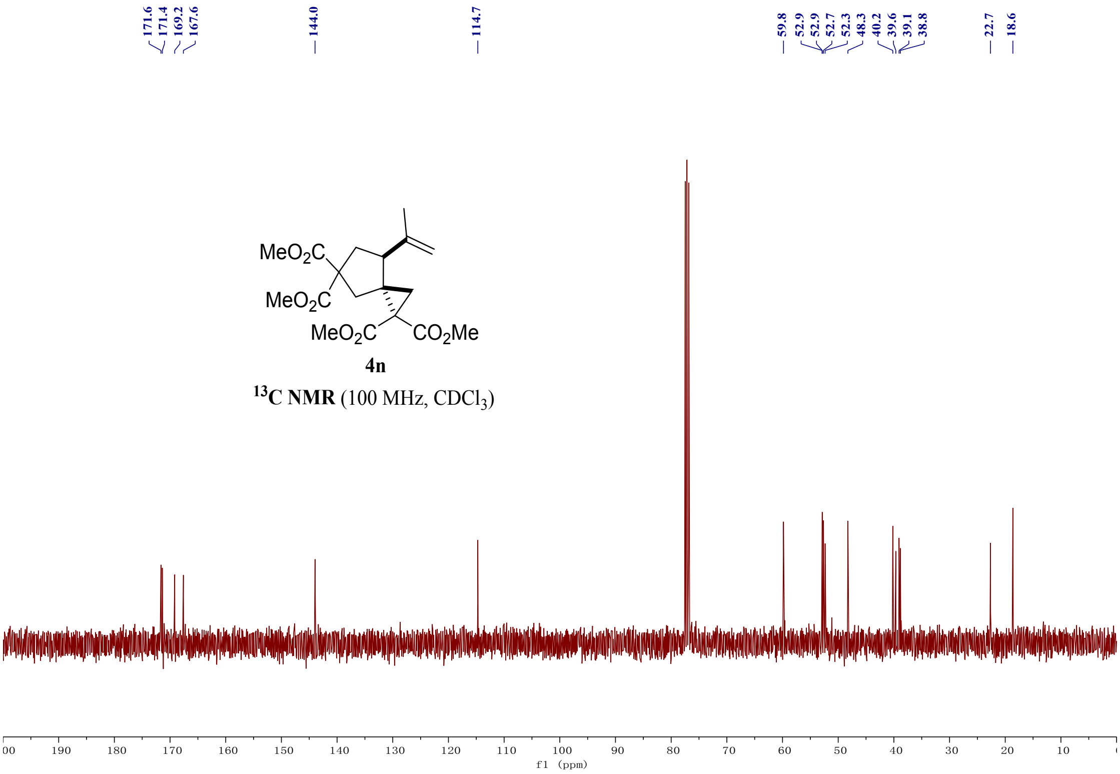
4n

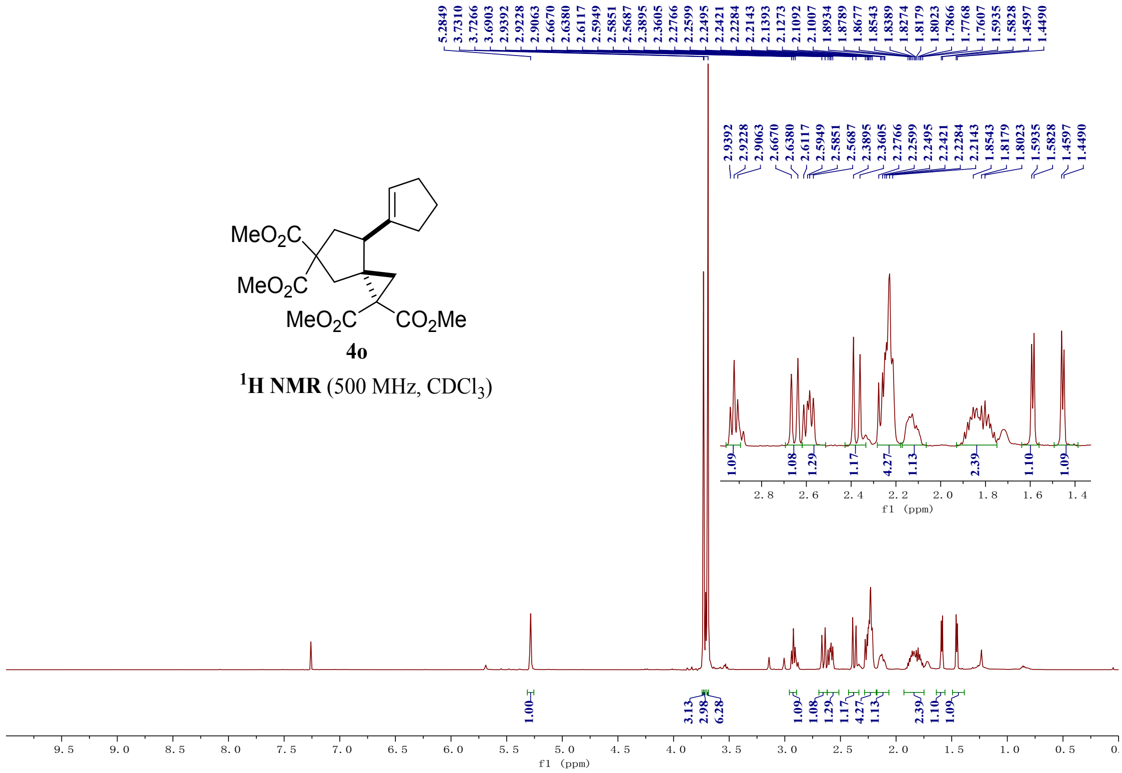
[1]**H NMR** (400 MHz, $CDCl_3$)

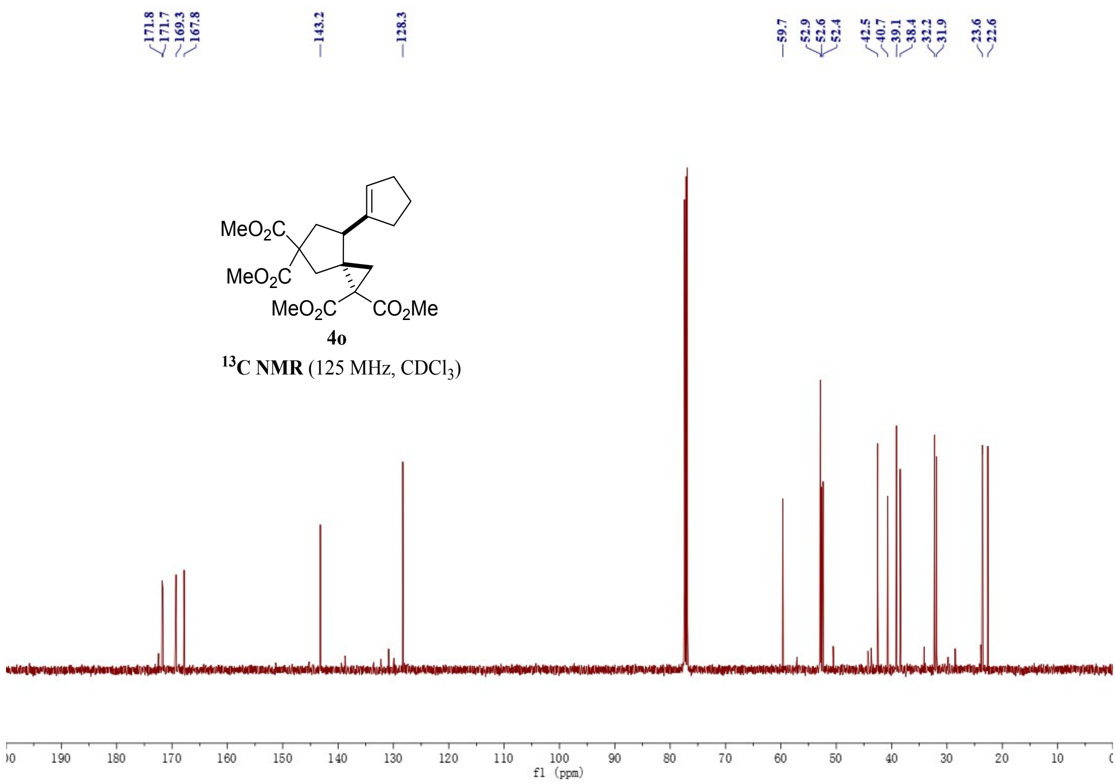


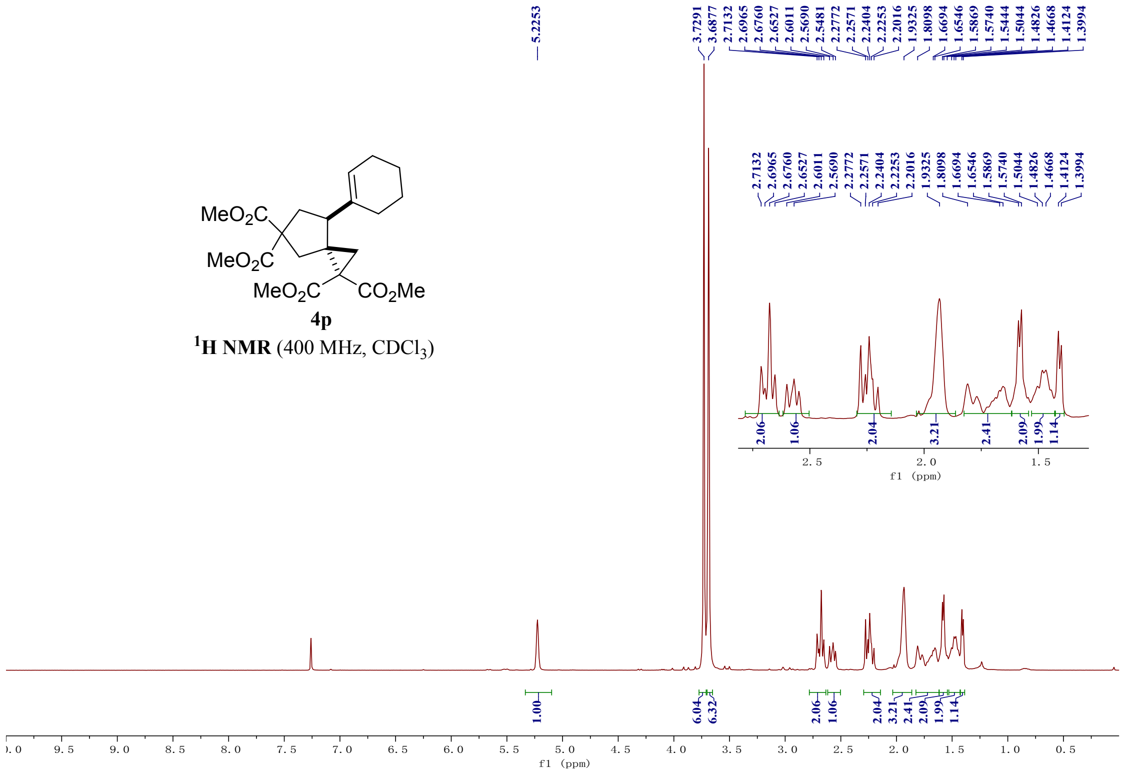
4n

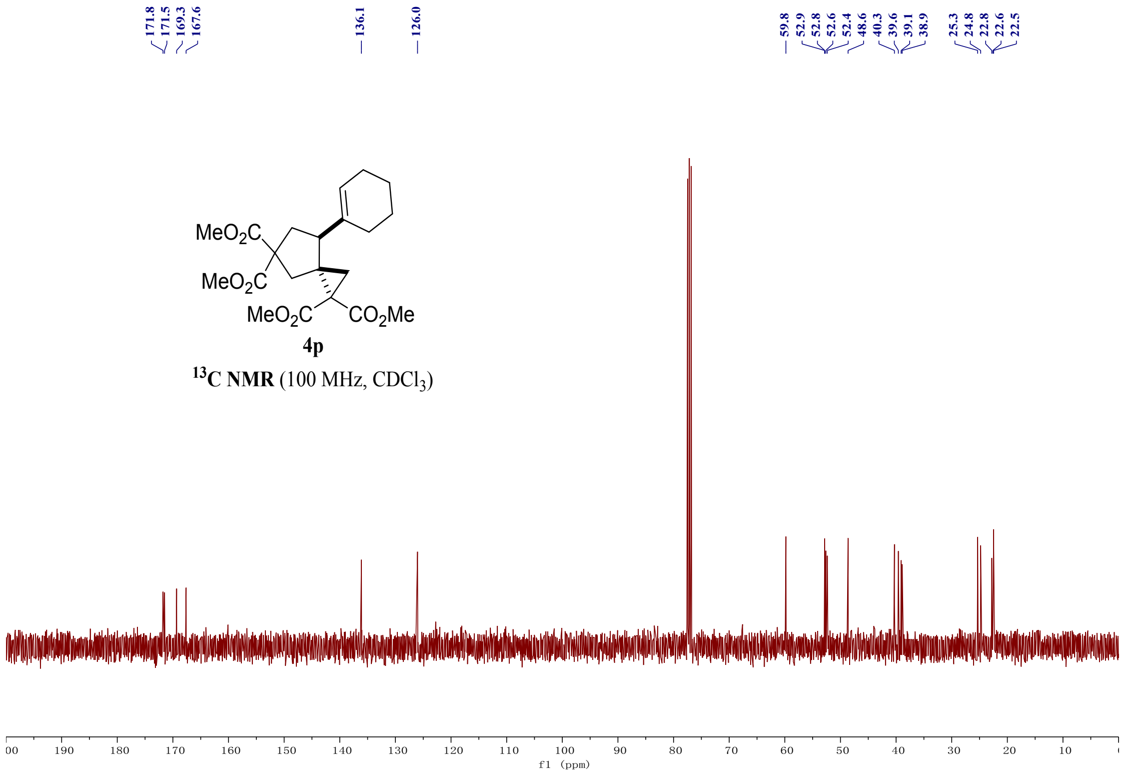
[13]**C NMR** (100 MHz, $CDCl_3$)

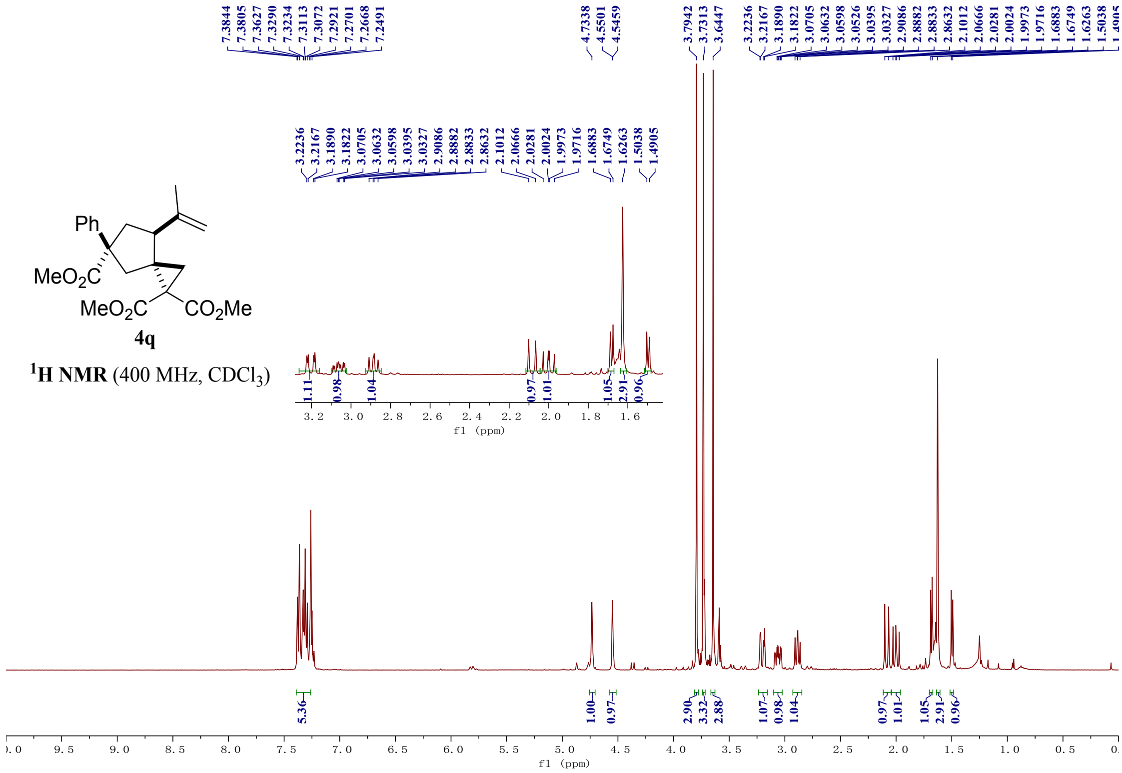



MeO2C
MeO2C
MeO2C
CO2Me
4o
1H NMR (500 MHz, CDCl3)
5.2849 3.7310 3.7266 3.6903 2.9392 2.9228 2.9063 2.6670 2.6380 2.6117 2.5949 2.5851 2.5687 2.3895 2.3605 2.2766 2.2599 2.2495 2.2421 2.2284 2.2143 2.1393 2.1273 2.1092 2.1007 1.8934 1.8789 1.8677 1.8543 1.8389 1.8274 1.8179 1.8023 1.7866 1.7768 1.7607 1.5935 1.5828 1.4597 1.4490
1.00 3.13 2.98 6.28 1.09 1.08 1.29 1.17 4.27 1.13 2.39 1.10 1.09
f1 (ppm)


171.8 171.7 169.3 167.8 143.2 128.3 59.7 52.9 52.6 52.4 42.5 40.7 39.1 38.4 32.2 31.9 23.6 22.6
MeO2C
MeO2C
MeO2C
CO2Me
4o
13C NMR (125 MHz, CDCl3)
f1 (ppm)

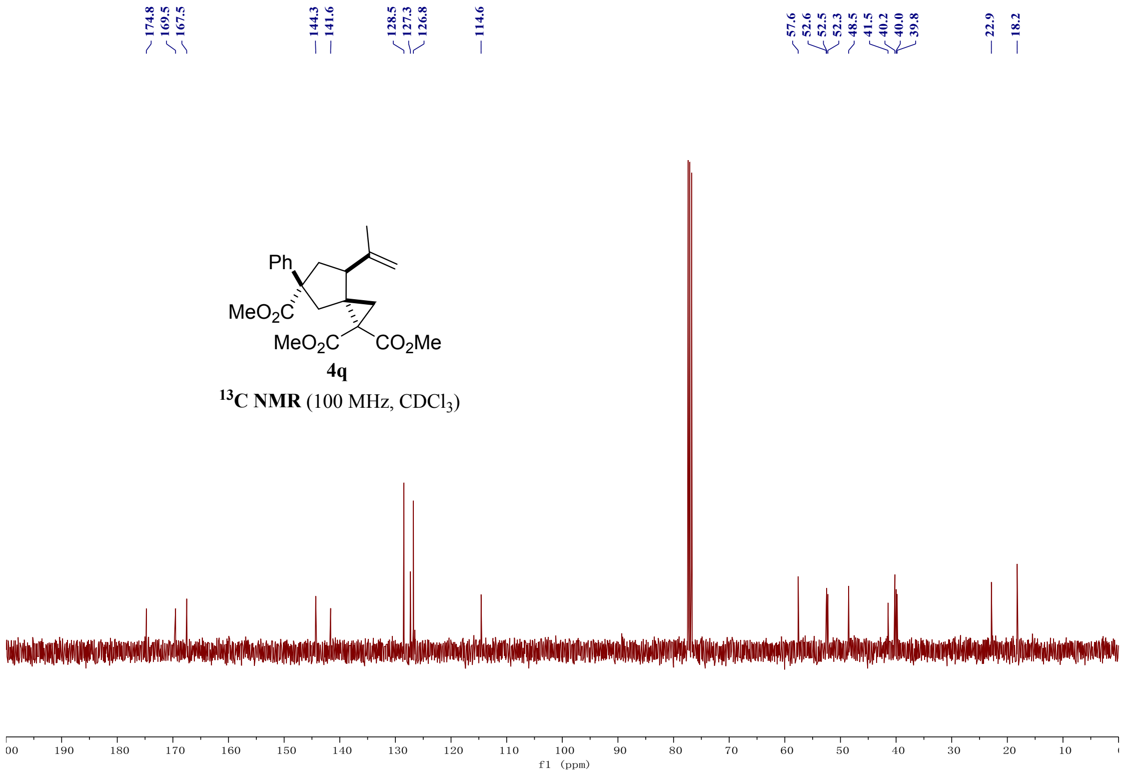

MeO2C
MeO2C
MeO2C
CO2Me
4p
1H NMR (400 MHz, CDCl3)
5.2253
3.7291
3.6877
2.7132
2.6965
2.6760
2.6527
2.6011
2.5690
2.5481
2.2772
2.2571
2.2404
2.2253
2.2016
1.9325
1.8098
1.6694
1.6546
1.5869
1.5740
1.5444
1.5044
1.4826
1.4668
1.4124
1.3994
1.00
6.04
6.32
2.06
1.06
2.04
3.21
2.41
2.09
1.99
1.14
f1 (ppm)


MeO2C
MeO2C
MeO2C
CO2Me
4p
13C NMR (100 MHz, CDCl3)
171.8
171.5
169.3
167.6
136.1
126.0
59.8
52.9
52.8
52.6
52.4
48.6
40.3
39.6
39.1
38.9
25.3
24.8
22.8
22.6
22.5
f1 (ppm)



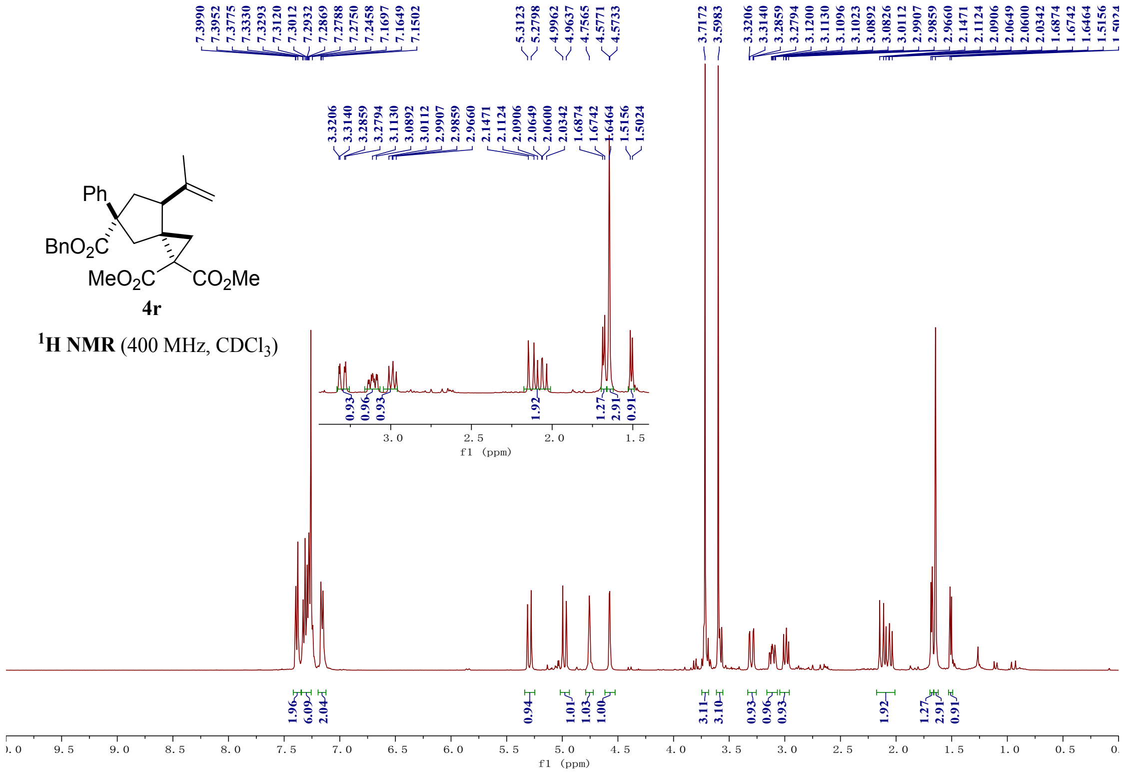
4q

[1]H NMR (400 MHz, $CDCl_3$)

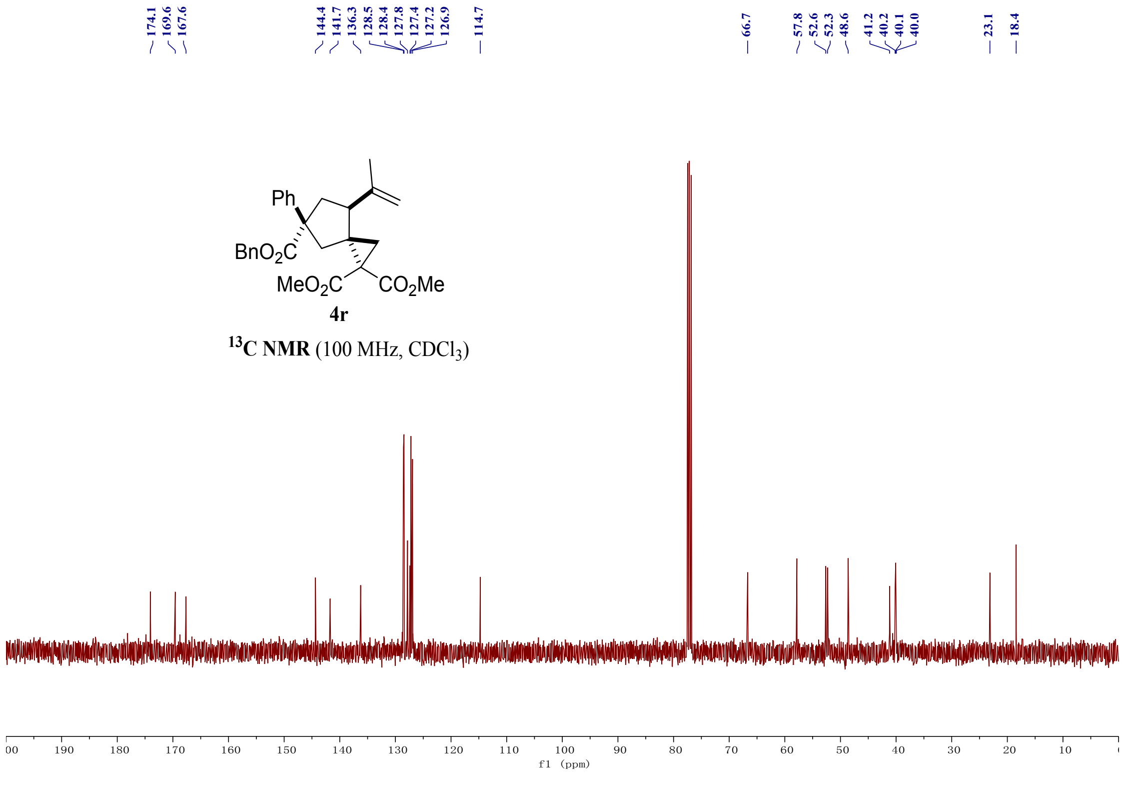


4q

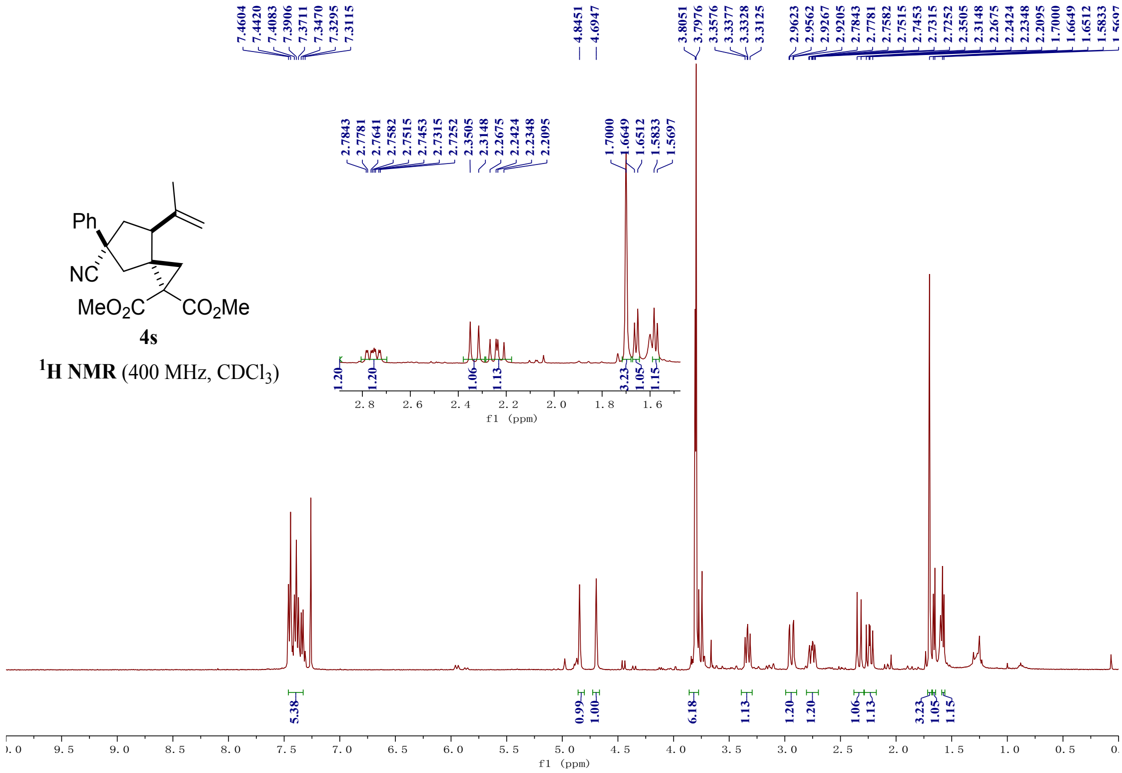
[13]C NMR (100 MHz, $CDCl_3$)



Ph
BnO2C
MeO2C
CO2Me
4r
1H NMR (400 MHz, CDCl3)
7.3990
7.3952
7.3775
7.3330
7.3293
7.3120
7.3012
7.2932
7.2869
7.2788
7.2750
7.2458
7.1697
7.1649
7.1502
5.3123
5.2798
4.9962
4.9637
4.7565
4.5771
4.5733
3.7172
3.5983
3.3206
3.3140
3.2859
3.2794
3.1200
3.1130
3.1096
3.1023
3.0892
3.0826
3.0112
2.9907
2.9859
2.9660
2.1471
2.1124
2.0906
2.0649
2.0600
2.0342
1.6874
1.6742
1.6464
1.5156
1.96
6.09
2.04
0.94
1.01
1.03
1.00
3.11
3.10
0.93
0.96
0.93
1.92
1.27
2.91
0.91
f1 (ppm)

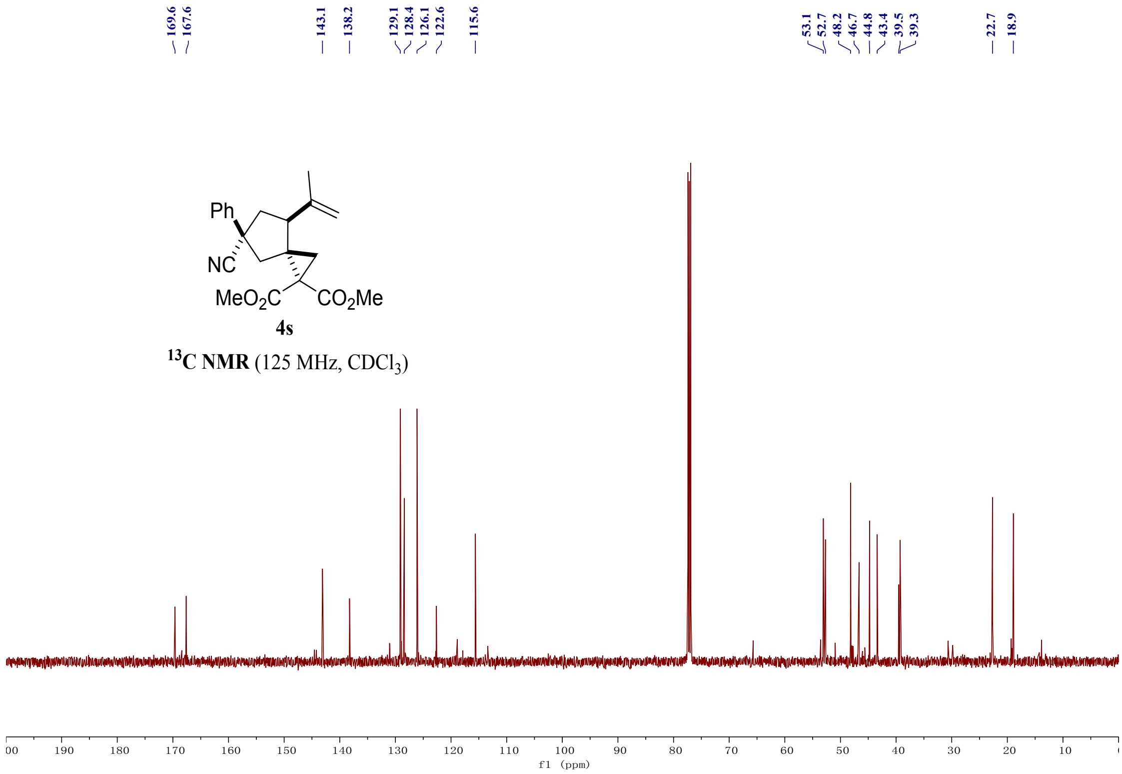


174.1
169.6
167.6
144.4
141.7
136.3
128.5
128.4
127.8
127.4
127.2
126.9
114.7
66.7
57.8
52.6
52.3
48.6
41.2
40.2
40.1
40.0
23.1
18.4
Ph
BnO2C
MeO2C
CO2Me
4r
13C NMR (100 MHz, CDCl3)
f1 (ppm)



4s

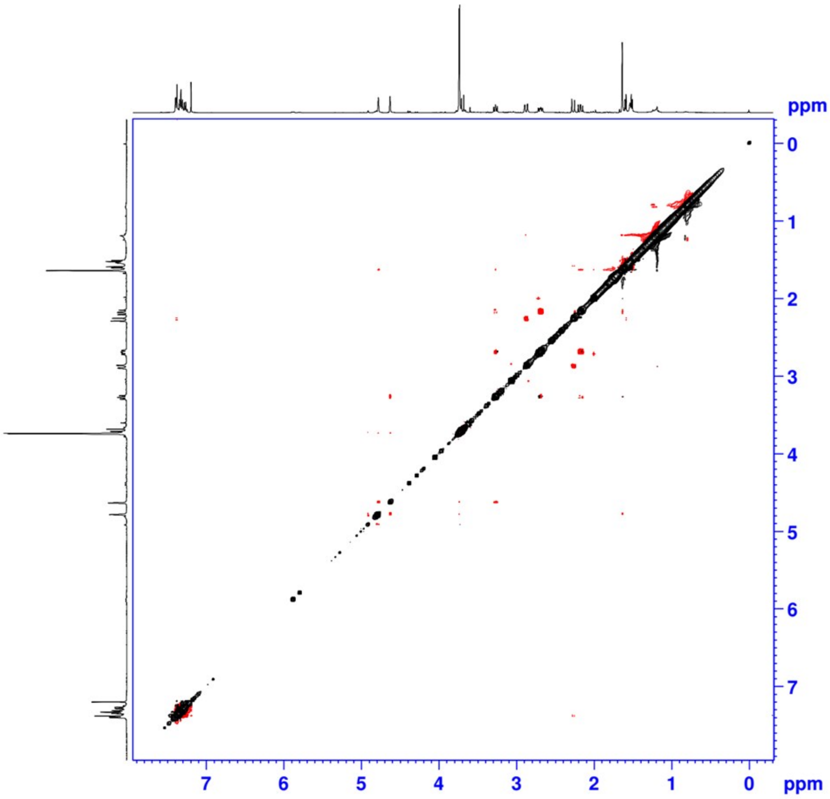
^{1}H NMR (400 MHz, $CDCl_3$)

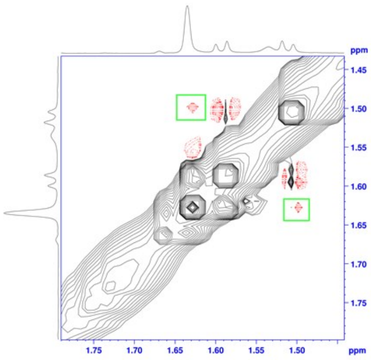


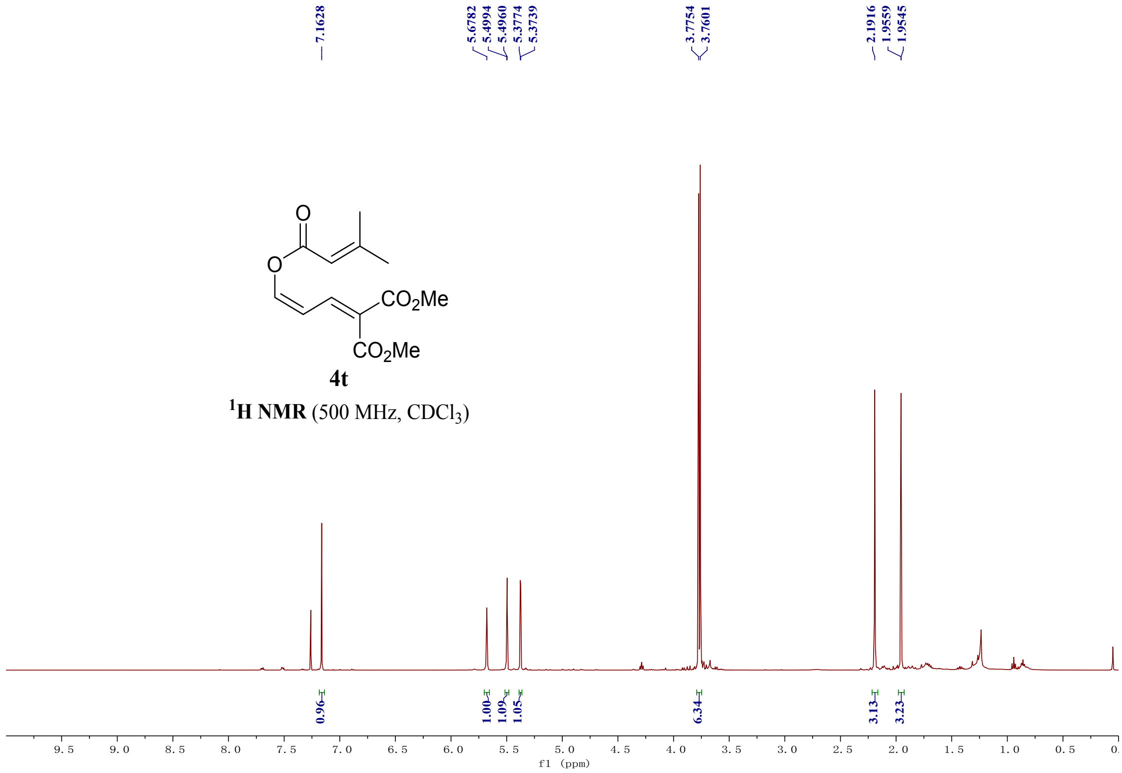
4s

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

^{1}H-^{1}H NOESY of 4s

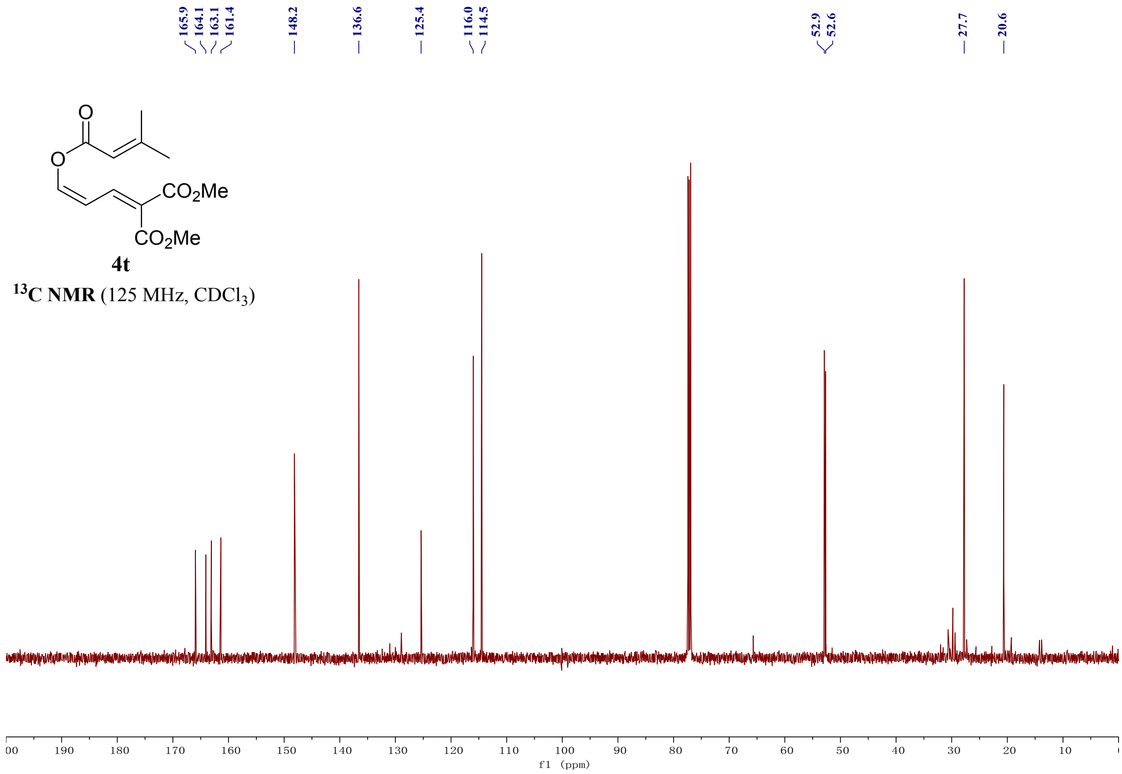






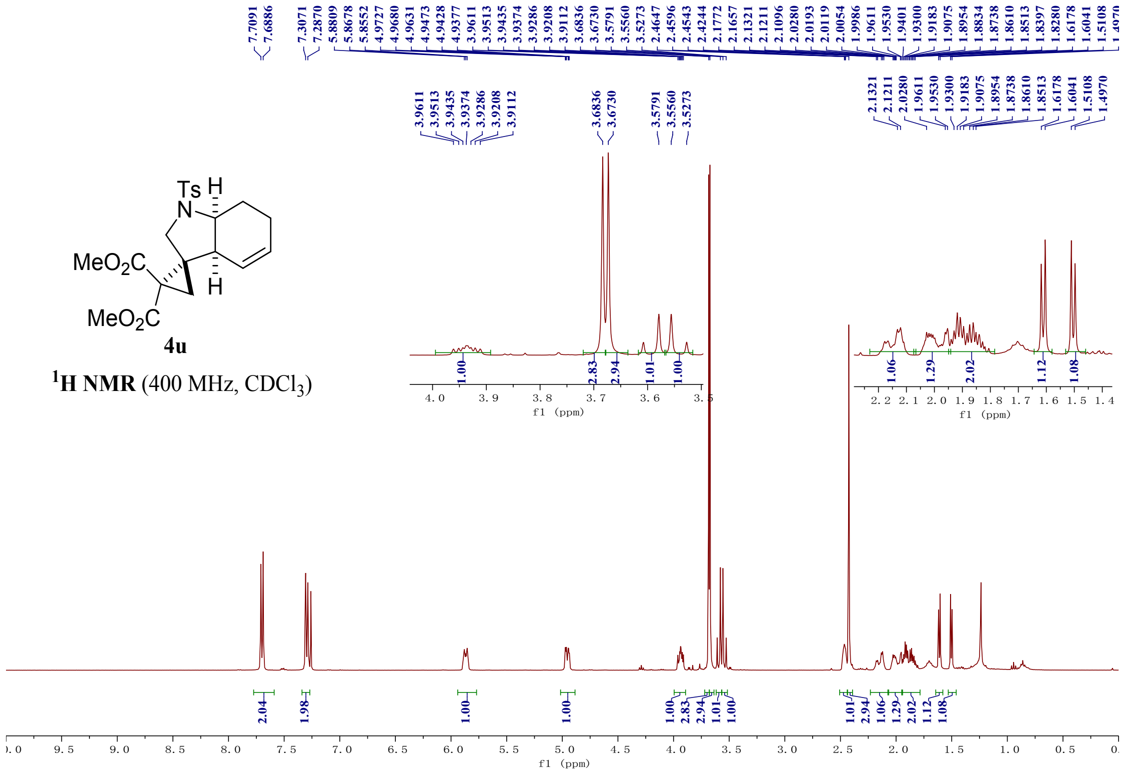
4t

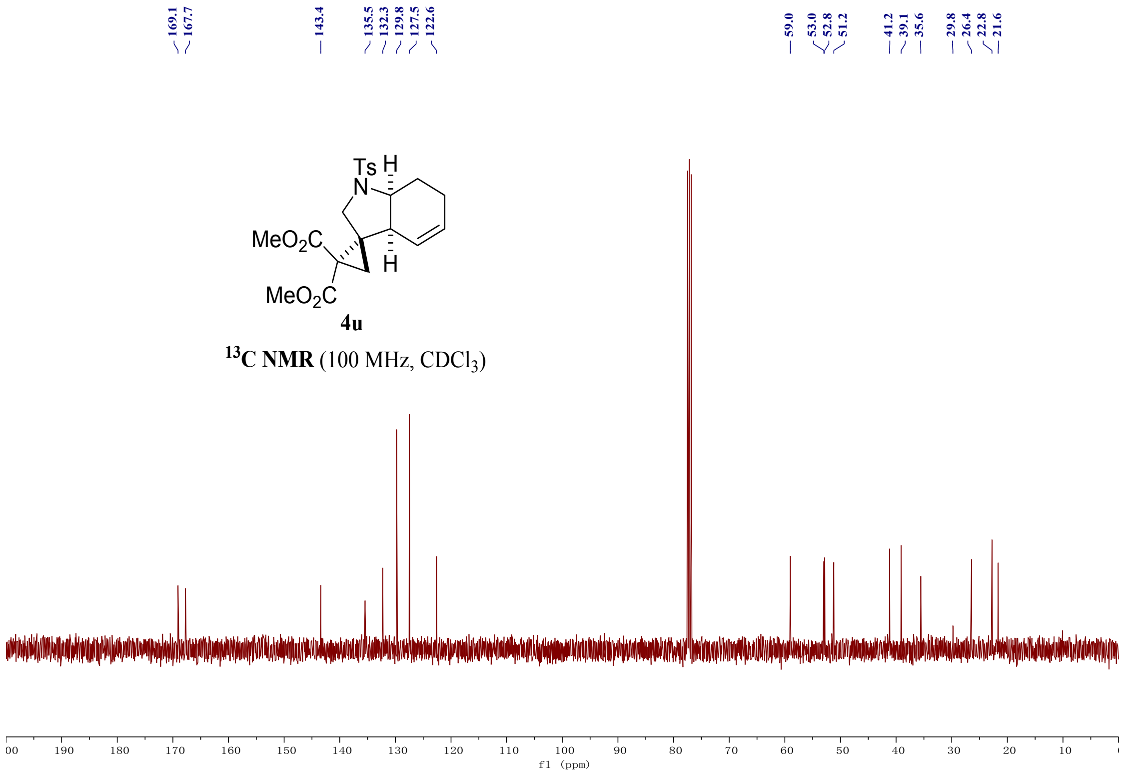
[1]**H NMR** (500 MHz, $CDCl_3$)



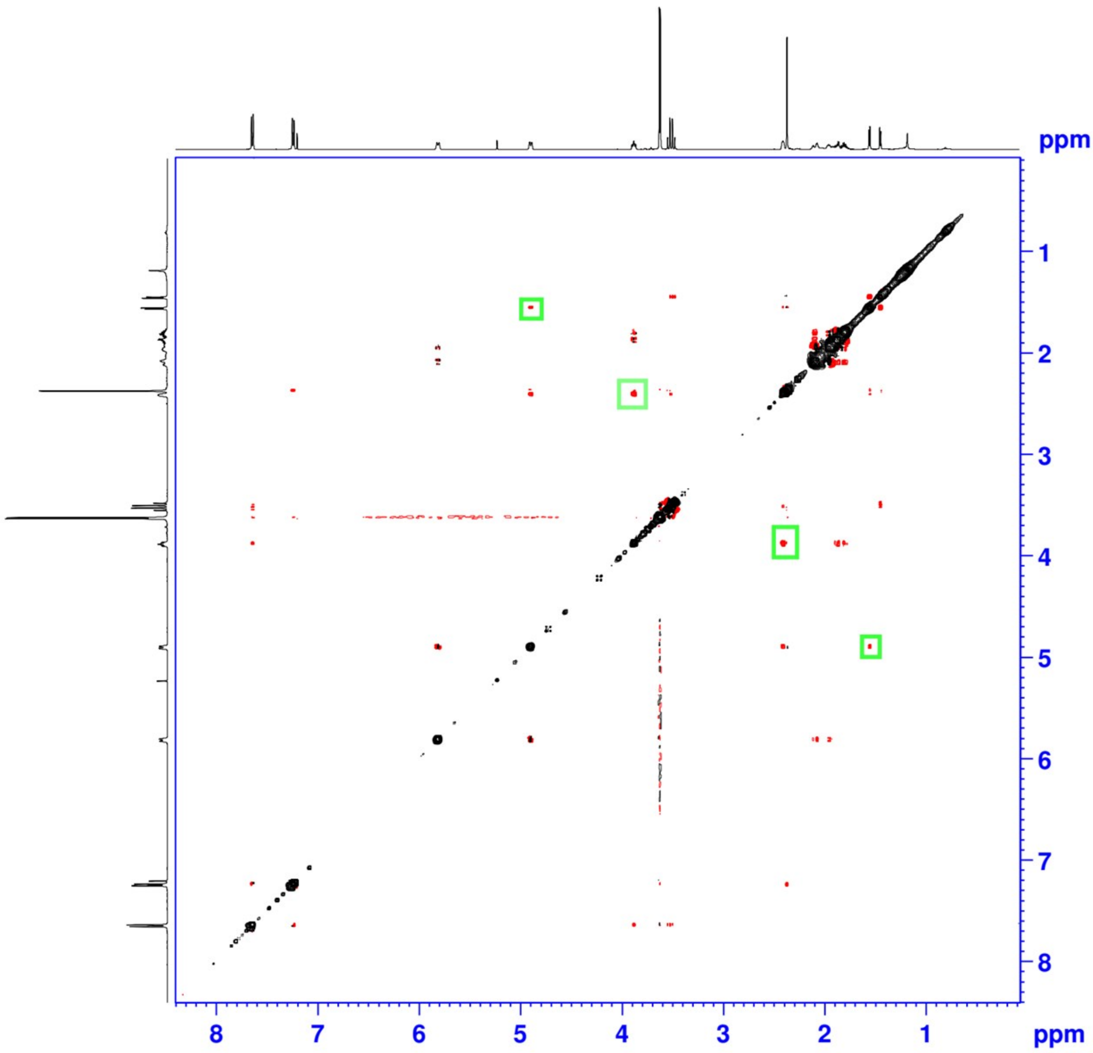
4t

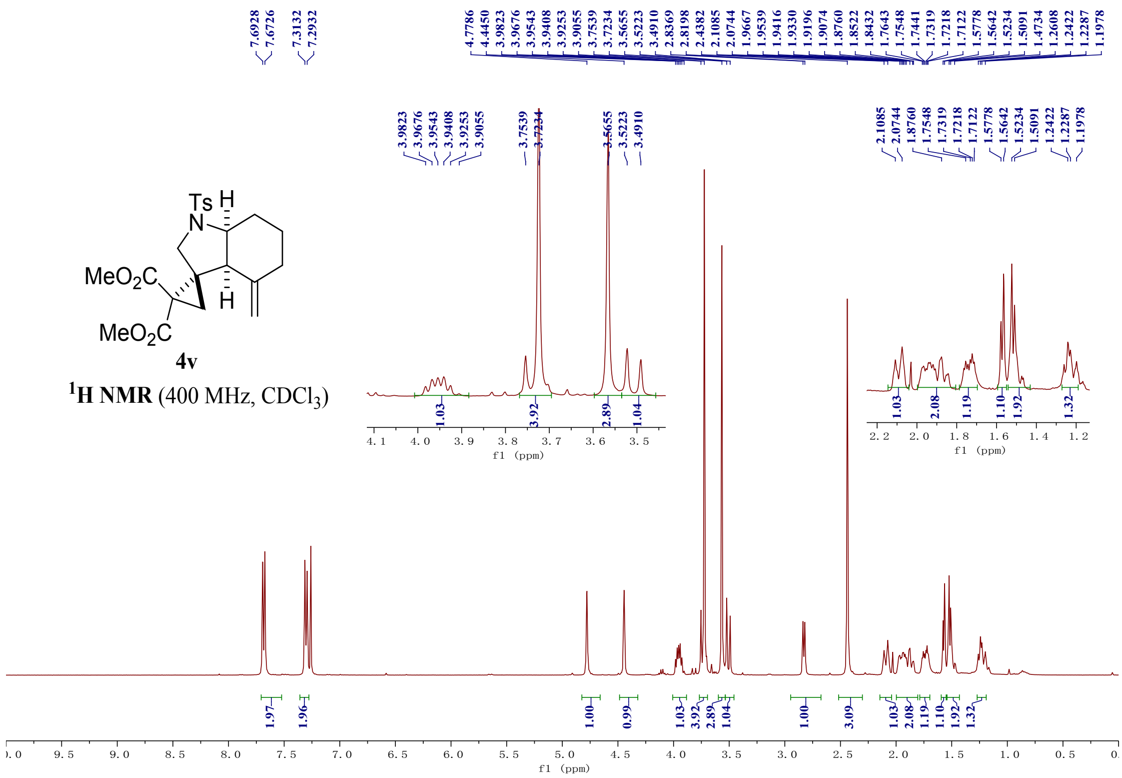
[13]**C NMR** (125 MHz, $CDCl_3$)


4u
1H NMR (400 MHz, CDCl3)
7.7091
7.6886
7.3071
7.2870
5.8809
5.8678
5.8552
4.9727
4.9680
4.9631
4.9473
4.9428
4.9377
3.9611
3.9513
3.9435
3.9374
3.9286
3.9208
3.9112
3.6836
3.6730
3.5791
3.5560
3.5273
2.4647
2.4596
2.4543
2.4244
2.1772
2.1657
2.1321
2.1211
2.1096
2.0280
2.0193
2.0119
2.0054
1.9986
1.9611
1.9530
1.9401
1.9300
1.9183
1.9075
1.8954
1.8834
1.8738
1.8610
1.8513
1.8397
1.8280
1.6178
1.6041
1.5108
1.4970
f1 (ppm)


4u
13C NMR (100 MHz, CDCl3)
169.1
167.7
143.4
135.5
132.3
129.8
127.5
122.6
59.0
53.0
52.8
51.2
41.2
39.1
35.6
29.8
26.4
22.8
21.6
f1 (ppm)

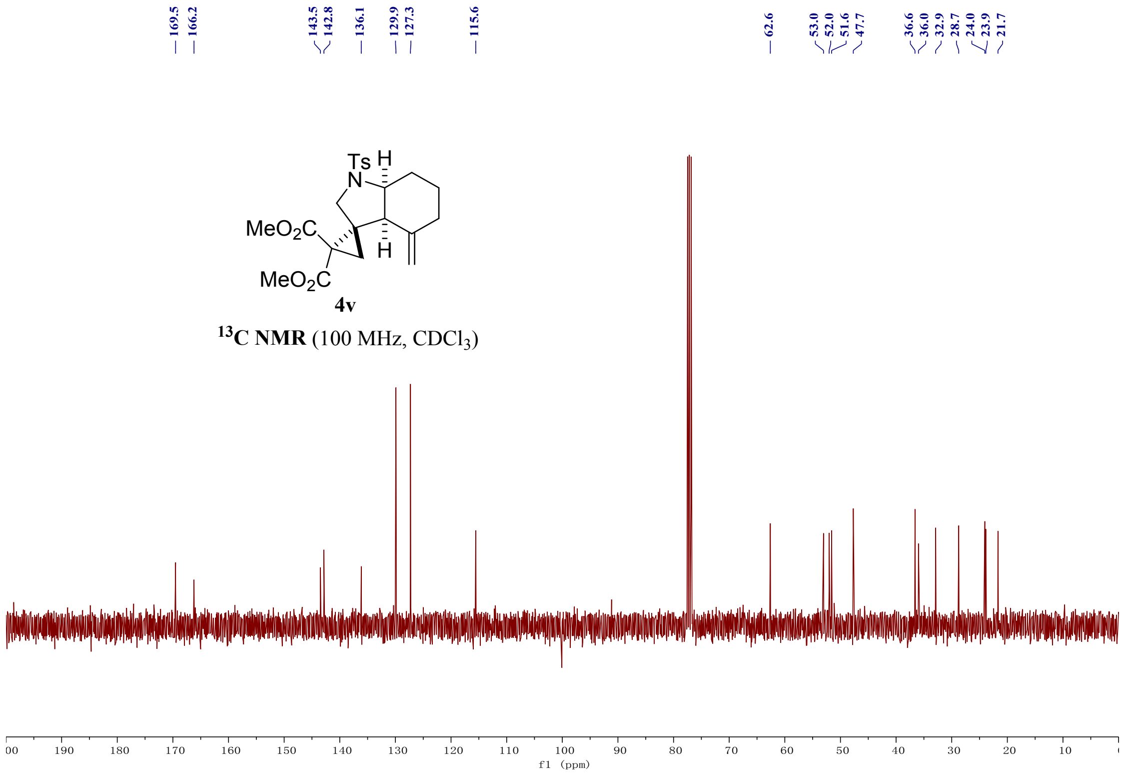
^{1}H-^{1}H NOESY of 4u





4v

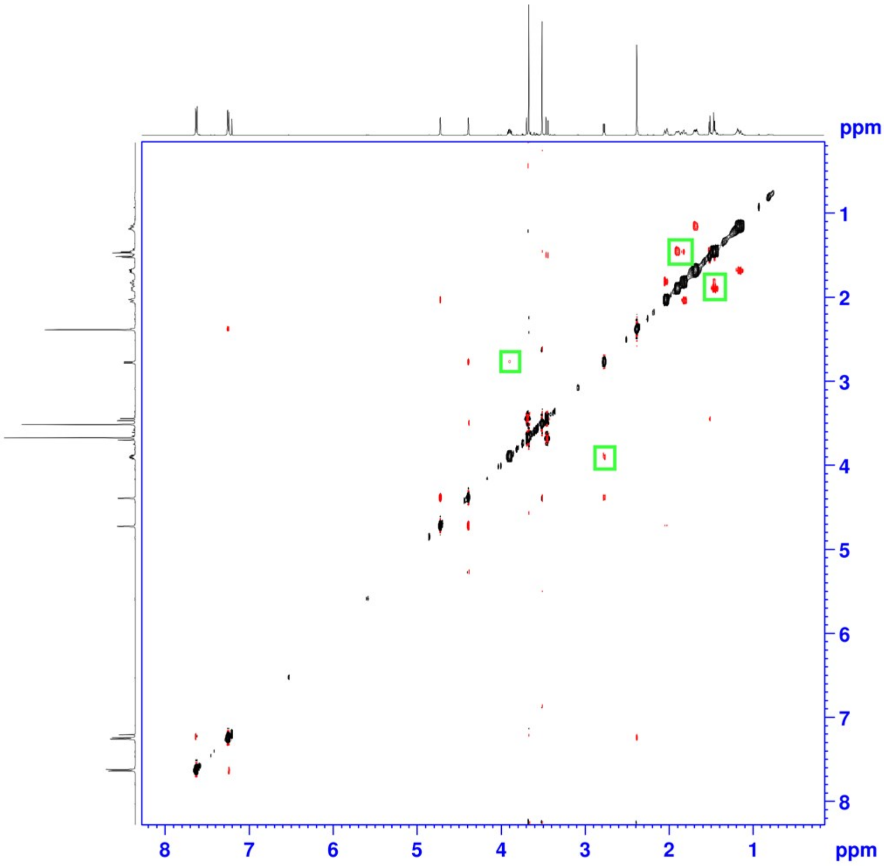
[1]**H NMR** (400 MHz, $CDCl_3$)

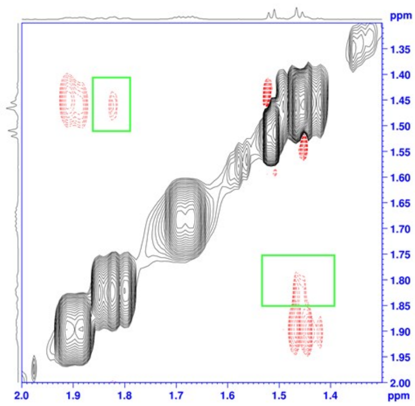


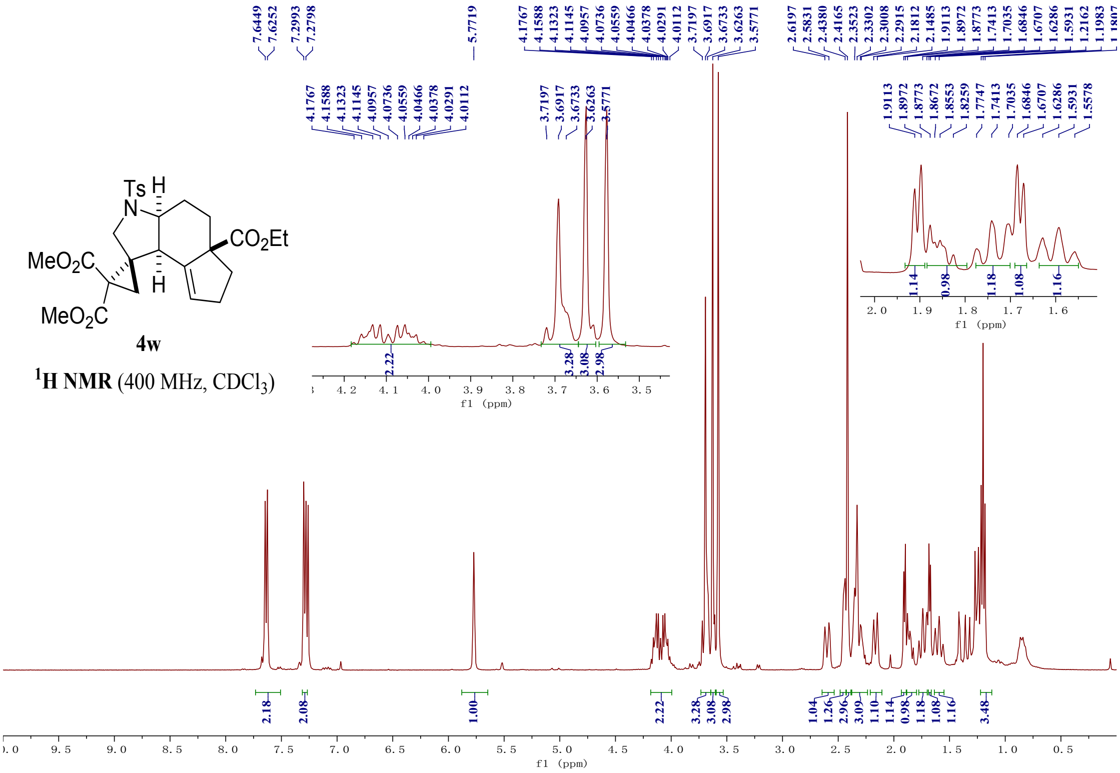
4v

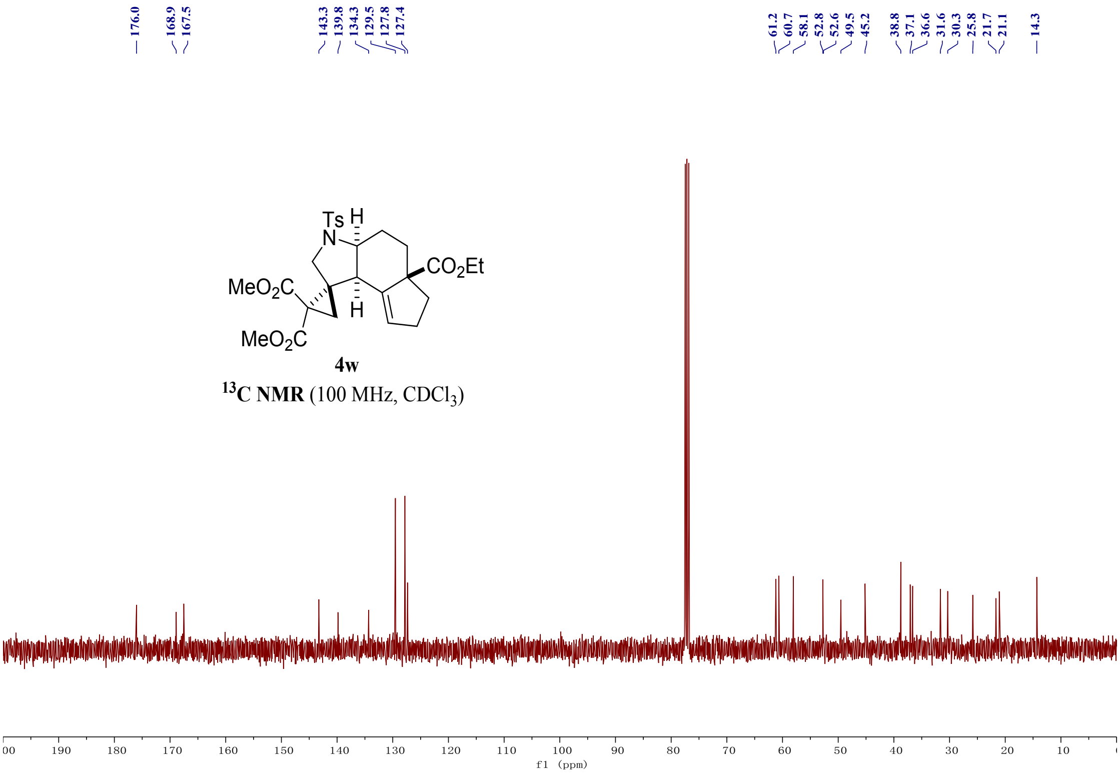
[13]**C NMR** (100 MHz, $CDCl_3$)

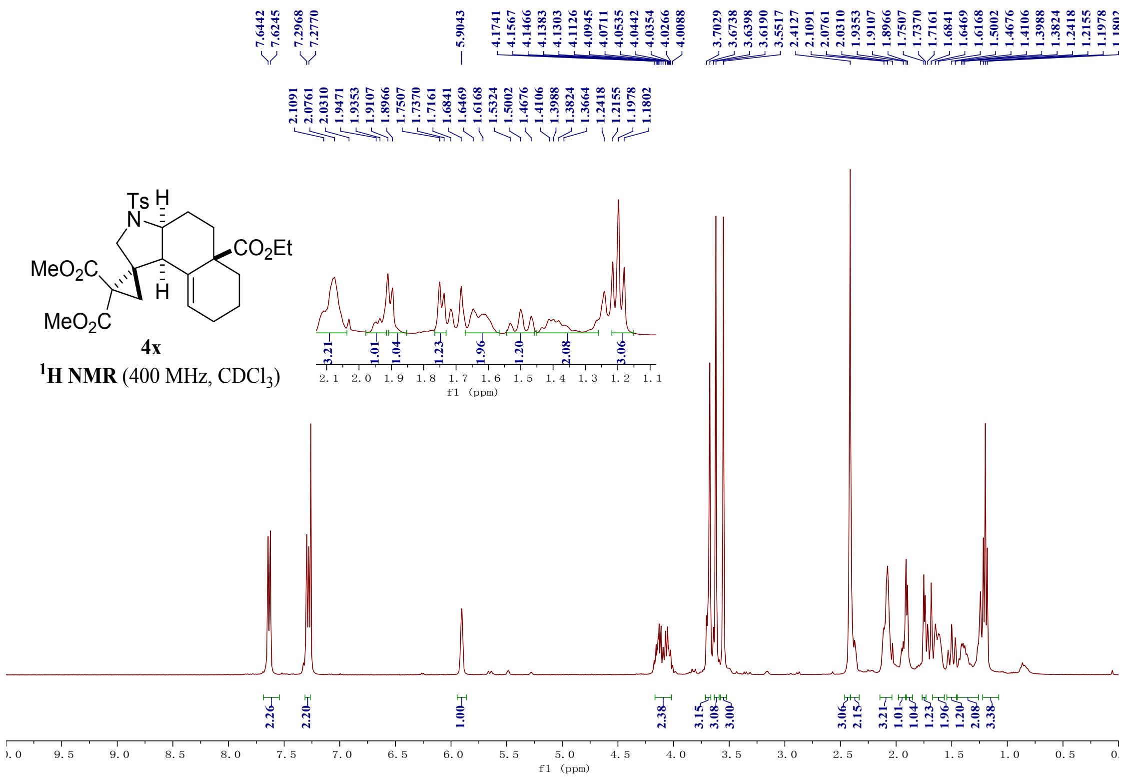
^{1}H-^{1}H NOESY of 4v

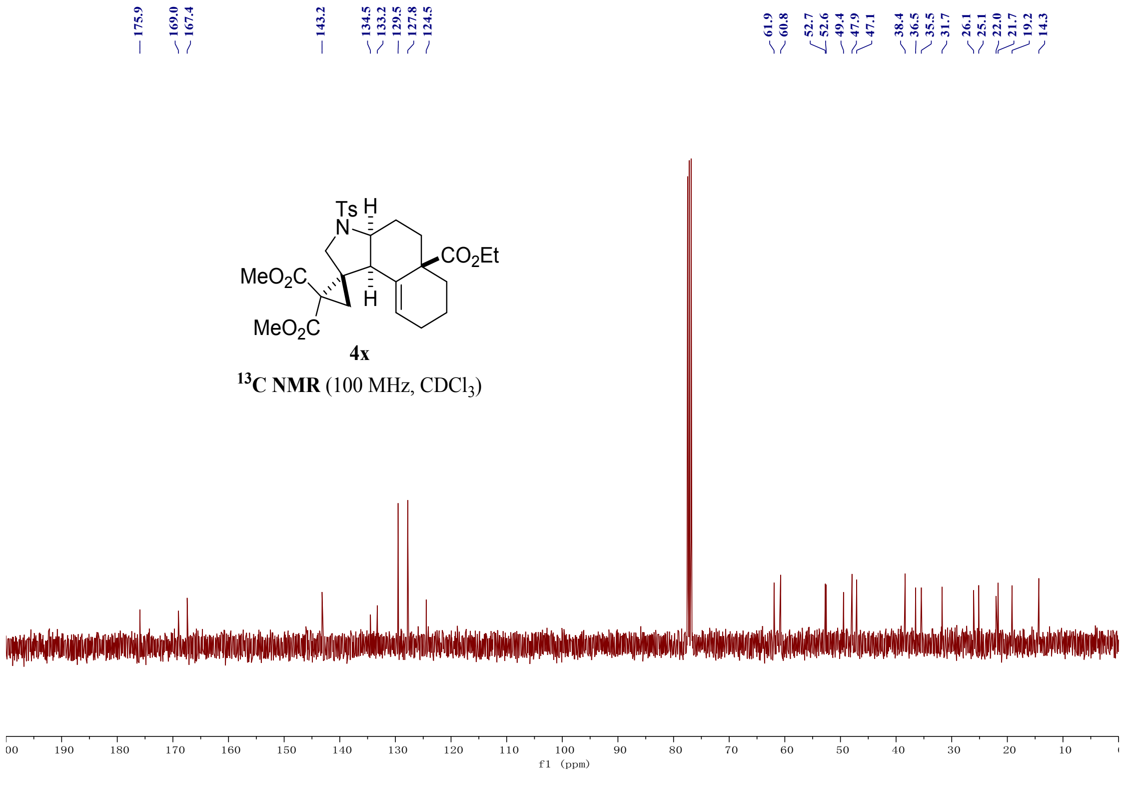


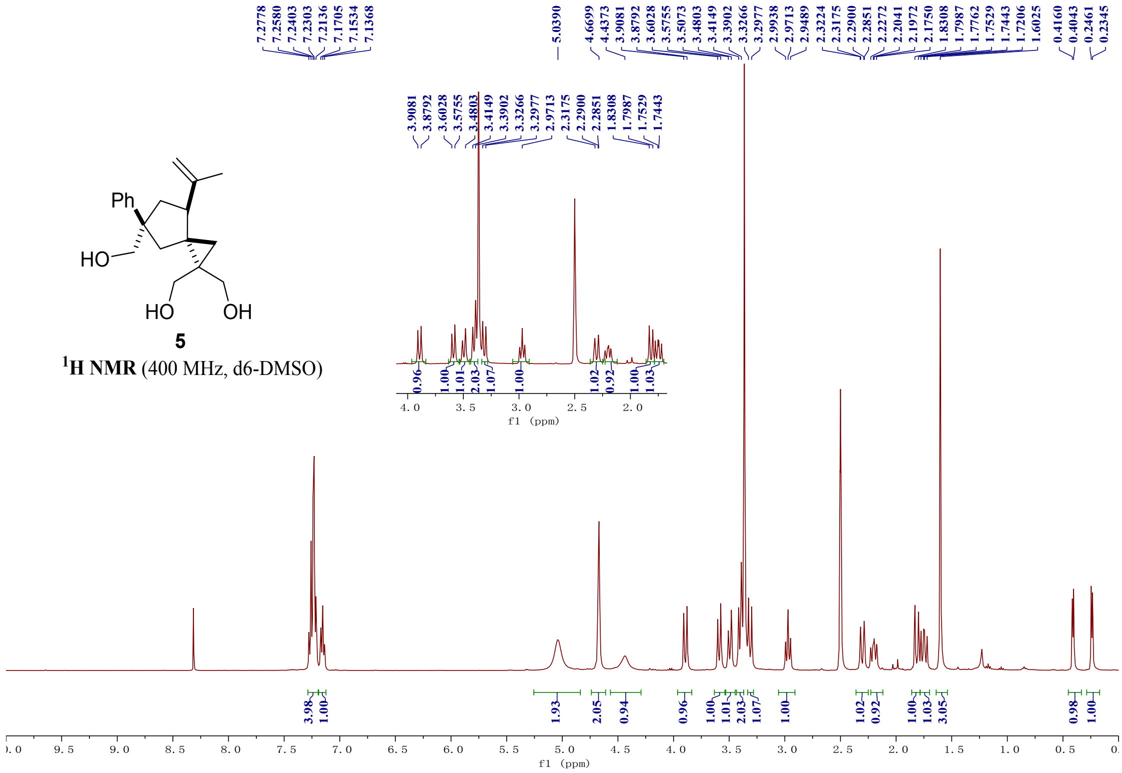



4w
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


176.0
168.9
167.5
143.3
139.8
134.3
129.5
127.8
127.4
61.2
60.7
58.1
52.8
52.6
49.5
45.2
38.8
37.1
36.6
31.6
30.3
25.8
21.7
21.1
14.3
4w
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

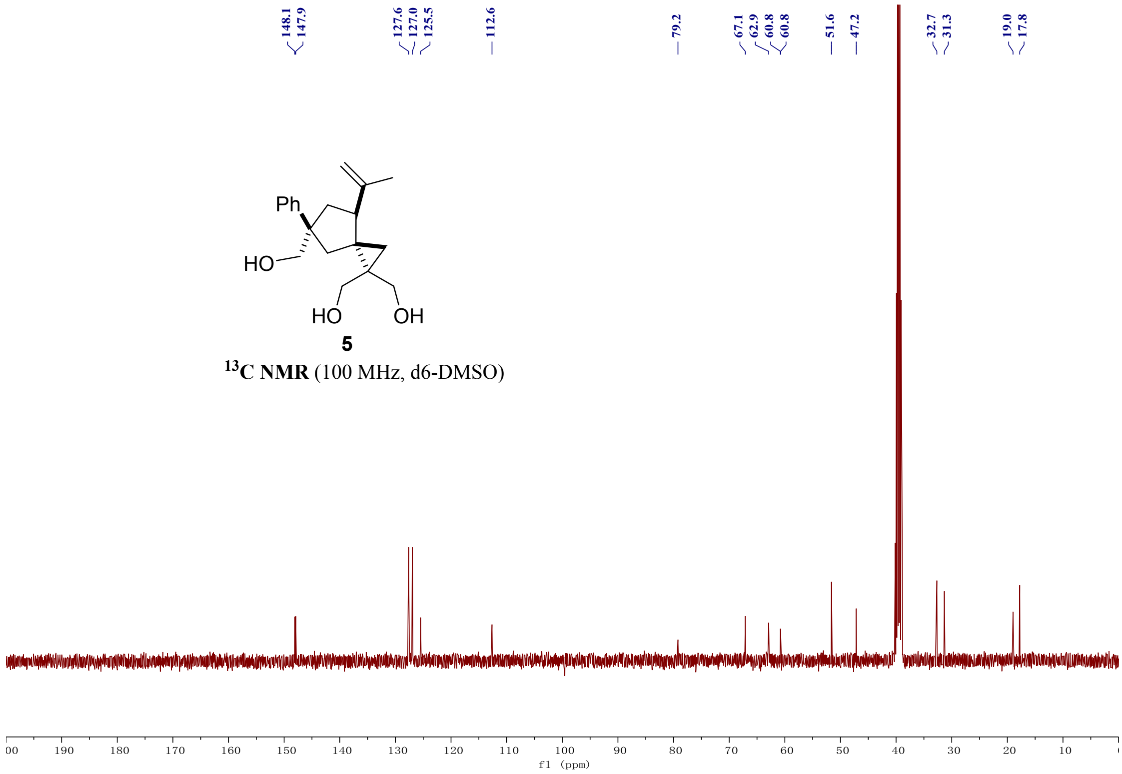

7.6442
7.6245
7.2968
7.2770
5.9043
4.1741
4.1567
4.1466
4.1383
4.1303
4.1126
4.0945
4.0711
4.0535
4.0442
4.0354
4.0266
4.0088
3.7029
3.6738
3.6398
3.6190
3.5517
2.4127
2.1091
2.0761
2.0310
1.9353
1.9107
1.8966
1.7507
1.7370
1.7161
1.6841
1.6469
1.6168
1.5002
1.4676
1.4106
1.3988
1.3824
1.2418
1.2155
1.1978
Ts
H
N
MeO2C
CO2Et
H
MeO2C
4x
1H NMR (400 MHz, CDCl3)
f1 (ppm)
f1 (ppm)


175.9
169.0
167.4
143.2
134.5
133.2
129.5
127.8
124.5
61.9
60.8
52.7
52.6
49.4
47.9
47.1
38.4
36.5
35.5
31.7
26.1
25.1
22.0
21.7
19.2
14.3
Ts
H
N
MeO2C
CO2Et
H
MeO2C
4x
13C NMR (100 MHz, CDCl3)
f1 (ppm)



5

[1]H NMR (400 MHz, d6-DMSO)



5

[13]C NMR (100 MHz, d6-DMSO)

[1]H-[1]H NOESY of 5