Supplementary Information

Cationic rhodium(I)/bisphosphine complex-catalyzed cyclization of 1,6-diynes with carboxylic acids

Ken Tanaka,* Shunsuke Saitoh, Hiromi Hara, and Yu Shibata

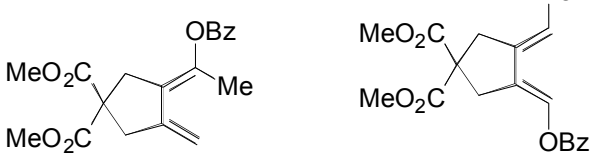
Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

I. General

Anhydrous CH_2Cl_2 (No. 27,099-7) and $(CH_2Cl)_2$ (No. 28,450-5) were obtained from Aldrich and used as received. 1,6-Diynes **1a**,[1] **1b**,[1] **1c**,[1] **1d**,[2] **1e**,[1] **1f**,[3] 1,7-diynes **1g**,[4] and triyne **6**[5] were prepared according to the literatures. All other reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring.

II. Compound Characterization Data

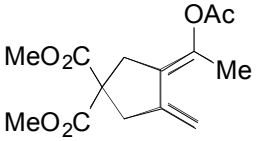
3-(1-Benzoyloxyethylidene)-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3aa, 3aa/4aa = 95:5)



major **3aa** minor **4aa**

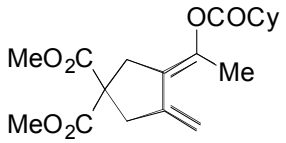
Reaction time: 16 h; Yellow oil; IR (neat) 2955, 1731, 1602, 1270 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) major **3aa**: δ 8.11 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 5.23 (s, 1H), 5.19 (s, 1H), 3.72 (s, 6H), 3.12–3.05 (m, 2H), 3.08–2.98 (m, 2H), 2.25–2.20 (m, 3H); minor **4aa**: δ 8.11 (d, J = 7.2 Hz, 2H), 7.79–7.75 (m, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 5.96–5.89 (m, 1H), 3.77 (s, 6H), 3.29–3.26 (m, 2H), 3.08–2.98 (m, 2H), 1.78–1.72 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.4, 164.1, 142.9, 142.8, 133.4, 130.0, 129.5, 128.5, 124.7, 110.2, 56.9, 52.9, 52.8, 43.0, 37.5, 18.9, 14.9; HRMS (ESI) calcd for $C_{19}H_{20}O_6Na$ $[M+Na]^+$ 367.1152, found 367.1119.

3-(1-Acetoxyethylidene)-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ab)



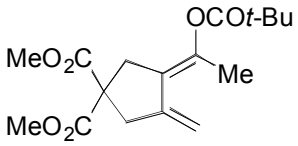
Reaction time: 16 h; Colorless solid; Mp 50.9–52.9 °C; IR (KBr) 2956, 1735, 1674, 1185 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.18 (s, 1H), 5.12 (s, 1H), 3.73 (s, 6H), 3.07–3.03 (m, 2H), 3.03–2.95 (m, 2H), 2.17 (s, 3H), 2.11–2.08 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.4, 168.5, 142.8, 142.5, 124.4, 110.2, 56.9, 52.8, 42.9, 37.4, 20.8, 18.7; HRMS (ESI) calcd for $C_{14}H_{18}O_6Na$ $[M+Na]^+$ 305.0996, found 305.0999.

3-(1-Cyclohexanecarbonyloxyethylidene)-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ac)



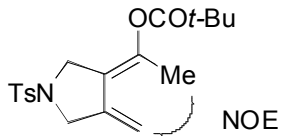
Reaction time: 16 h; Pale yellow oil; IR (neat) 2934, 2856, 1737, 1680, 1123 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.17 (s, 1H), 5.10 (s, 1H), 3.73 (s, 6H), 3.06–3.01 (m, 2H), 2.99–2.93 (m, 2H), 2.47–2.35 (tt, J = 11.1, 3.6 Hz, 1H), 2.07 (s, 3H), 2.04–1.93 (m, 2H), 1.84–1.72 (m, 2H), 1.73–1.62 (m, 1H), 1.58–1.41 (m, 2H), 1.39–1.20 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.6, 171.5, 142.9, 142.7, 124.1, 109.9, 56.9, 52.8, 43.0, 42.9, 37.3, 28.9, 25.6, 25.3, 18.8; HRMS (ESI) calcd for $C_{19}H_{26}O_6Na$ $[M+Na]^+$ 373.1622, found 373.1651.

3-[1-(2,2-Dimethylpropionyloxy)ethylidene]-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ad)



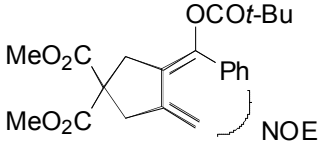
Reaction time: 16 h; Pale yellow oil; IR (neat) 2957, 2360, 1739, 1124 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.17 (s, 1H), 5.10 (s, 1H), 3.73 (s, 6H), 3.08–3.02 (m, 2H), 3.00–2.94 (m, 2H), 2.09–2.04 (m, 3H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.0, 171.5, 142.9, 142.7, 124.0, 109.9, 56.9, 52.8, 43.0, 38.9, 37.2, 27.0, 18.7; HRMS (ESI) calcd for $C_{17}H_{24}O_6Na$ $[M+Na]^+$ 347.1465, found 347.1484.

2,2-Dimethylpropionic acid 1-[4-methylene-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]ethyl ester (3bd)

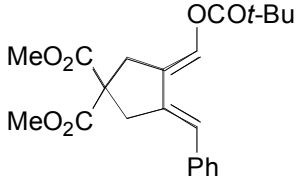


Reaction time: 16 h; Colorless solid; Mp 98.3–99.0 °C; IR (KBr) 3462, 2974, 2847, 1739, 1684 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.68 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5,12 (s, 2H), 4.00–3.94 (m, 2H), 3.93–3.87 (m, 2H), 2.43 (s, 3H), 2.01 (s, 3H), 1.27 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 175.9, 143.8, 143.2, 139.2, 132.5, 129.7, 127.7, 121.5, 109.5, 54.5, 50.6, 39.0, 26.9, 21.5, 18.6; HRMS (ESI) calcd for $C_{19}H_{25}NO_4SNa$ $[M+Na]^+$ 386.1397, found 386.1397.

3-[(2,2-Dimethylpropionyloxy)phenylmethylene]-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3cd, 3cd/4cd = 85:15)



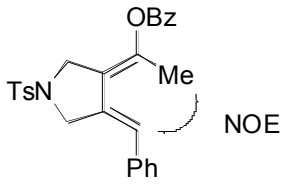
major **3cd**



minor **4cd**

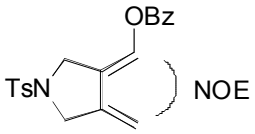
Reaction time: 16 h; Pale yellow oil; IR (neat) 2956, 1739, 1435, 1111 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) major **3cd**: δ 7.47–7.41 (m, 2H), 7.37–7.28 (m, 3H), 4.88–4.83 (m, 1H), 4.68 (t, J = 2.0 Hz, 1H), 3.76 (s, 6H), 3.10 (s, 2H), 3.05 (t, J = 2.0 Hz, 2H), 1.23 (s, 9H); minor **4cd**: δ 7.75 (t, J = 2.4 Hz, 1H), 7.47–7.41 (m, 2H), 7.37–7.28 (m, 3H), 6.79 (t, J = 2.7 Hz, 1H), 3.73 (s, 6H), 3.37 (d, J = 2.4 Hz, 2H), 3.16 (d, J = 2.7 Hz, 2H), 1.29 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 175.6, 171.4, 142.8, 141.3, 135.1, 129.8, 129.3, 129.1, 129.0, 128.73, 128.68, 128.4, 128.3, 128.0, 125.9, 110.3, 56.8, 53.4, 53.3, 53.1, 53.0, 52.9, 52.8, 42.9, 38.8, 37.9, 27.0, 26.94, 26.90, 26.86; HRMS (ESI) calcd for $C_{22}H_{26}O_6Na$ $[M+Na]^+$ 409.1622, found 409.1629.

Benzoic acid 1-[4-benzylidene-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]ethyl ester (3da)



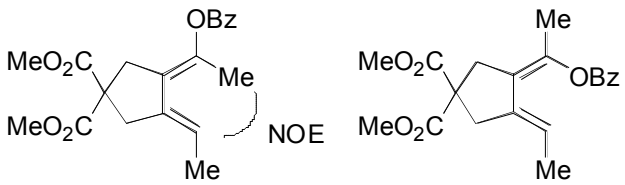
Reaction time: 16 h; Pale yellow solid; Mp 147.8–149.5 °C; IR (KBr) 3064, 2836, 1725, 1492 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.10 (d, J = 7.8 Hz, 2H), 7.70–7.61 (m, 3H), 7.51 (t, J = 7.8 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.29 (t, J = 7.8 Hz, 3H), 7.17 (d, J = 7.8 Hz, 2H), 6.61 (s, 1H), 4.31–4.28 (m, 2H), 4.07–3.98 (m, 2H), 2.41 (s, 3H), 2.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.0, 143.7, 141.9, 136.4, 133.8, 132.9, 132.4, 130.1, 130.0, 129.7, 128.9, 128.60, 128.57, 128.5, 128.4, 127.65, 127.57, 126.6, 124.3, 52.4, 49.4, 21.4, 19.1; HRMS (ESI) calcd for $C_{27}H_{25}NO_4SNa$ $[M+Na]^+$ 482.1397, found 482.1364.

Benzoic acid 4-methylene-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidenemethyl ester (3ea)



Reaction time: 16 h; Colorless solid; Mp 151.2–151.8 °C; IR (neat) 2836, 1736, 1344 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.07 (d, J = 7.5 Hz, 2H), 7.82 (t, J = 2.5 Hz, 1H), 7.75 (d, J = 8.1 Hz, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 5.42–5.35 (m, 1H), 4.98–4.92 (m, 1H), 4.24 (d, J = 2.5 Hz, 2H), 4.03–3.99 (m, 2H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.7, 144.0, 138.8, 134.1, 132.5, 130.0, 129.8, 129.2, 128.7, 128.2, 127.8, 120.1, 104.3, 53.4, 49.7, 21.5; HRMS (ESI) calcd for $C_{20}H_{19}NO_4SNa$ $[M+Na]^+$ 392.0927, found 392.0928.

3-(1-Benzoyloxyethylidene)-4-ethylidenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3fa: *E*/*Z* = 95:5)

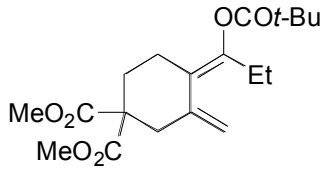


major minor

Reaction time: 16 h; Colorless oil; IR (neat) 2953, 1735, 1435, 1272 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) *E*-isomer: δ 8.11 (dd, J = 7.5, 0.9 Hz, 2H), 7.60 (tt, J = 7.5, 0.9 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H),

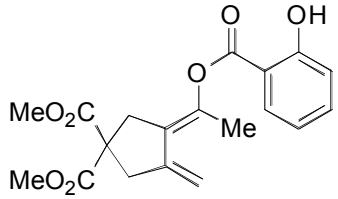
5.81–5.67 (m, 1H), 3.72 (s, 6H), 3.07–3.03 (m, 2H), 3.04–2.99 (m, 2H), 2.18 (s, 3H), 1.79 (d, J = 6.9 Hz, 3H); *Z*-isomer: δ 8.11 (dd, J = 7.5, 0.9 Hz, 2H), 7.60 (tt, J = 7.5, 0.9 Hz, 1H). 7.48 (t, J = 7.5 Hz, 2H), 5.48 (q, J = 7.8 Hz, 1H), 3.71 (s, 6H), 3.04–2.97 (m, 2H), 2.96 (t, J = 1.5 Hz, 2H), 2.02–1.98 (m, 3H), 1.72 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.7 164.3, 140.2, 135.4, 133.3, 129.9, 129.7, 128.4, 125.5, 121.5, 56.9, 52.8, 38.2, 37.4, 18.9, 15.4; HRMS (ESI) calcd for $C_{20}H_{22}O_6Na$ $[M+Na]^+$ 381.1309, found 381.1296.

4-[1-(2,2-Dimethylpropionyloxy)propylidene]-3-methylenecyclohexane-1,1-dicarboxylic acid dimethyl ester (3gd)



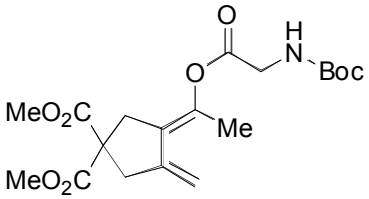
Reaction time: 64 h; Colorless solid; Mp 51.2–52.5 °C; IR (neat) 2973, 1739, 1251, 1125 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.09–5.05 (m, 1H), 4.93–4.88 (m, 1H), 3.72 (s, 6H), 2.80 (s, 2H), 2.41 (q, J = 7.5 Hz, 2H), 2.24–2.16 (m, 2H), 2.14–2.07 (m, 2H), 1.28 (s, 9H), 0.98 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.3, 171.1, 144.4, 140.6, 125.3, 114.6, 56.4, 52.6, 40.8, 39.0, 30.8, 27.2, 24.6, 23.4, 12.1; HRMS (ESI) calcd for $C_{19}H_{28}O_6Na$ $[M+Na]^+$ 375.1778, found 375.1762.

3-[1-(2-Hydroxybenzoyloxy)ethylidene]-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ag)



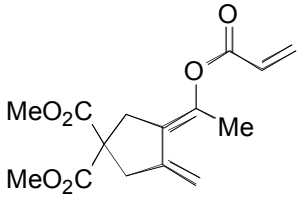
Reaction time: 64 h; Pale yellow oil; IR (neat) 3224, 2954, 1737, 1683 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.56 (s, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.51 (t, J = 8.1 Hz, 1H), 7.01 (d, J = 8.1 Hz, 1H), 6.93 (t, J = 8.1Hz, 1H), 5.28–5.23 (m, 1H), 5.23–5.18 (m, 1H), 3.72 (s, 6H), 3.12–3.05 (m, 2H), 3.07–3.00 (m, 2H), 2.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.3, 168.0, 162.0, 142.6, 142.0, 136.3, 130.2, 125.4, 119.3, 117.7, 111.8, 110.8, 56.9, 52.9, 42.9, 37.5, 18.8; HRMS (ESI) calcd for $C_{19}H_{20}O_7Na$ $[M+Na]^+$ 383.1101, found 383.1106.

3-[1-(2-*tert*-Butoxycarbonylaminoacetoxy)ethylidene]-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ah)



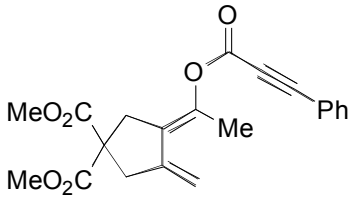
Reaction time: 20 h; Pale yellow oil; IR (neat) 3396, 2979, 1737, 1153 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.20 (s, 1H), 5.13 (s, 1H), 5.09–4.96 (m, 1H), 4.07–3.97 (m, 2H), 3.72 (s, 6H), 3.08–3.01 (m, 2H), 3.00–2.93 (m, 2H), 2.13–2.07 (m, 3H), 1.46 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.3, 168.0, 155.5, 142.6, 142.1, 124.8, 110.5, 80.0, 56.8, 52.8, 42.8, 42.3, 37.3, 28.2, 18.5; HRMS (ESI) calcd for $C_{19}H_{27}NO_8Na$ $[M+Na]^+$ 420.1629, found 420.1625.

3-(1-Acryloyloxyethylidene)-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ai)



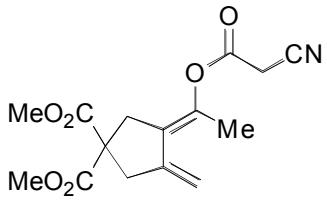
Reaction time: 16 h; Pale yellow oil; IR (neat) 2955, 2362, 1736, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.51 (dd, J = 17.1, 1.5 Hz, 1H), 6.20 (dd, J = 17.1, 10.4 Hz, 1H), 5.94 (dd, J = 10.4, 1.5 Hz, 1H), 5.23–5.15 (m, 1H), 5.20–5.09 (m, 1H), 3.72 (s, 6H), 3.10–3.03 (m, 2H), 3.01–2.96 (m, 2H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.4, 163.5, 142.8, 142.4, 132.1, 127.8, 124.6, 110.2, 56.9, 52.8, 42.9, 37.4, 18.7; HRMS (ESI) calcd for $C_{15}H_{18}O_6Na$ $[M+Na]^+$ 317.0996, found 317.1004.

3-Methylene-4-[1-(3-phenylpropynoyloxy)ethylidene]cyclopentane-1,1-dicarboxylic acid dimethyl ester (3aj)



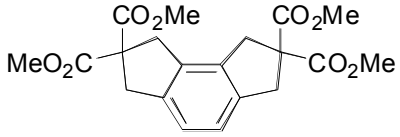
Reaction time: 16 h; Pale yellow oil; IR (neat) 3417, 2954, 2218, 1738 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.63 (d, J = 6.9 Hz, 2H), 7.49 (t, J = 6.9 Hz, 1H), 7.40 (t, J = 6.9 Hz, 2H), 5.26–5.21 (m, 1H), 5.19–5.14 (m, 1H), 3.73 (s, 6H), 3.12–3.05 (m, 4H), 2.17 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.3, 151.3, 142.6, 141.9, 133.1, 130.9, 128.6, 125.4, 119.2, 110.8, 87.7, 80.2, 56.9, 52.8, 42.8, 37.6, 18.6: HRMS (ESI) calcd for $C_{21}H_{20}O_6Na$ $[M+Na]^+$ 391.1152, found 391.1146.

3-[1-(2-Cyanoacetoxy)ethylidene]-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ak)



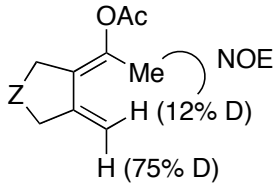
Reaction time: 16 h; Pale yellow oil; IR (neat) 2957, 1732, 1683 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.24 (s, 1H), 5.16 (s, 1H), 3.74 (s, 6H), 3.59 (s, 2H), 3.09–3.04 (m, 2H), 3.01–2.96 (m, 2H), 2.16–2.12 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 160.6, 142.2, 142.0, 125.5, 112.6, 111.3, 56.8, 52.9, 52.5, 42.6, 37.3, 24.5, 18.3; HRMS (ESI) calcd for $C_{15}H_{17}NO_6Na$ $[M+Na]^+$ 330.0948, found 330.0937.

1,3,6,8-Tetrahydroasindacene-2,2,7,7-tetracarboxylic acid tetramethyl ester (8)[5]



Reaction time: 3 h; Colorless solid; Mp 137.0–138.3 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.01 (s, 2H), 3.75 (s, 12H), 3.57 (s, 4H), 3.51 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.1, 138.8, 135.5, 122.8, 60.3, 53.0, 40.4, 39.0.

3-(1-Acetoxyethylidene)-4-(monodeuteriummethylene)cyclopentane-1,1-dicarboxylic acid dimethyl ester (*d*-3ab)

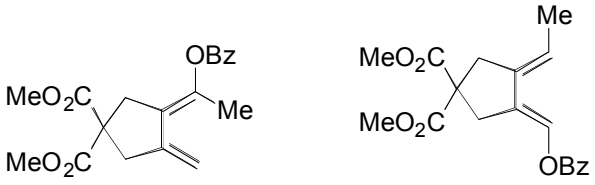


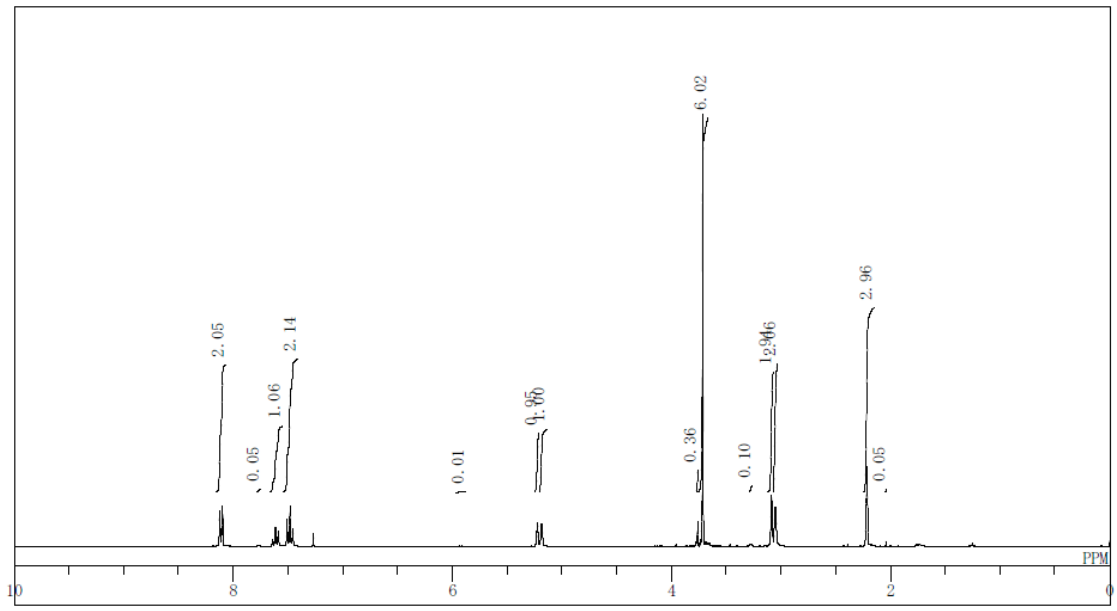
Reaction time: 16 h; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.18 (s, 0.25H), 5.10 (s, 0.88H), 3.73 (s, 6H), 3.07–3.03 (m, 2H), 3.01–2.95 (m, 2H), 2.17 (s, 3H), 2.11–2.08 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.3, 168.4, 142.74, 142.65, 142.5, 124.3, 110.1, 109.8, 109.5, 56.8, 52.8, 42.84, 42.78, 37.4, 20.7, 18.7.

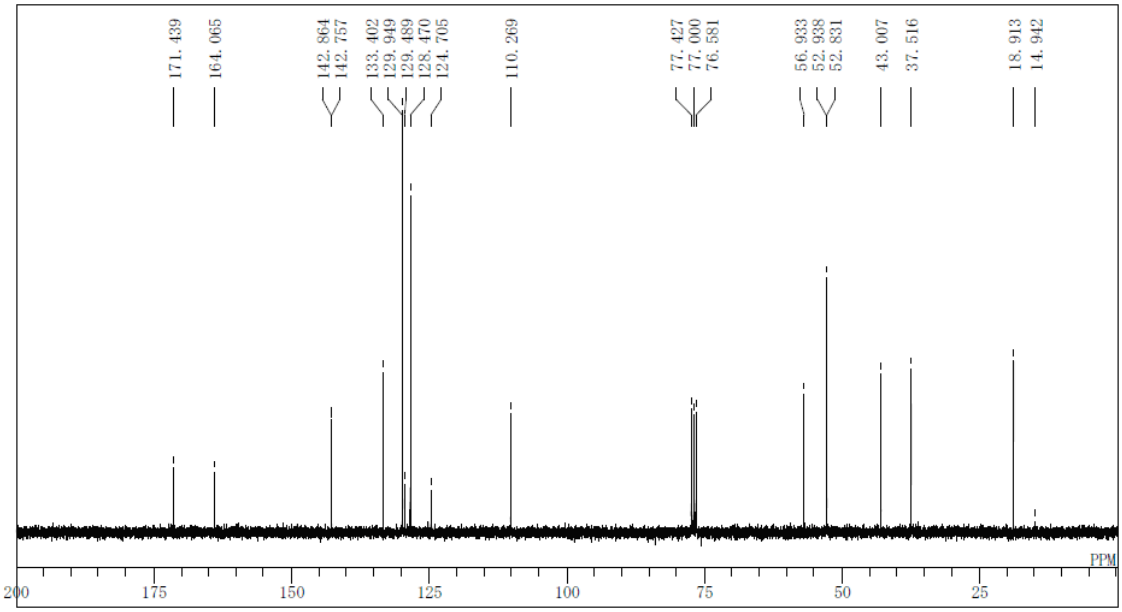
III. References

(1) K. Itoh, Y. Yamamoto, R. Ogawa, *Chem. Commun.*, **2000**, 549.
(2) T. Shibata, A. Kawachi, M. Ogawa, Y. Kuwata, K. Tsuchikama, K. Endo, *Tetrahedron*, 2007, **63**, 12853.
(3) K. Tanaka, Y. Otake, M. Hirano, *Org. Lett.*, 2007, **9**, 3953.
(4) C**.** González-Rodríguez, J. A. Varela, L. Castedo, C. Saá, *J. Am. Chem. Soc.*, 2007, **129**, 12916.
(5) Y. Yamamoto, T. Arakawa, R. Ogawa, K. Itoh, *J. Am. Chem. Soc.*, 2003, **125**, 12143.

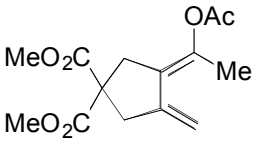
3-(1-Benzoyloxyethylidene)-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3aa, 3aa/4aa = 95:5)

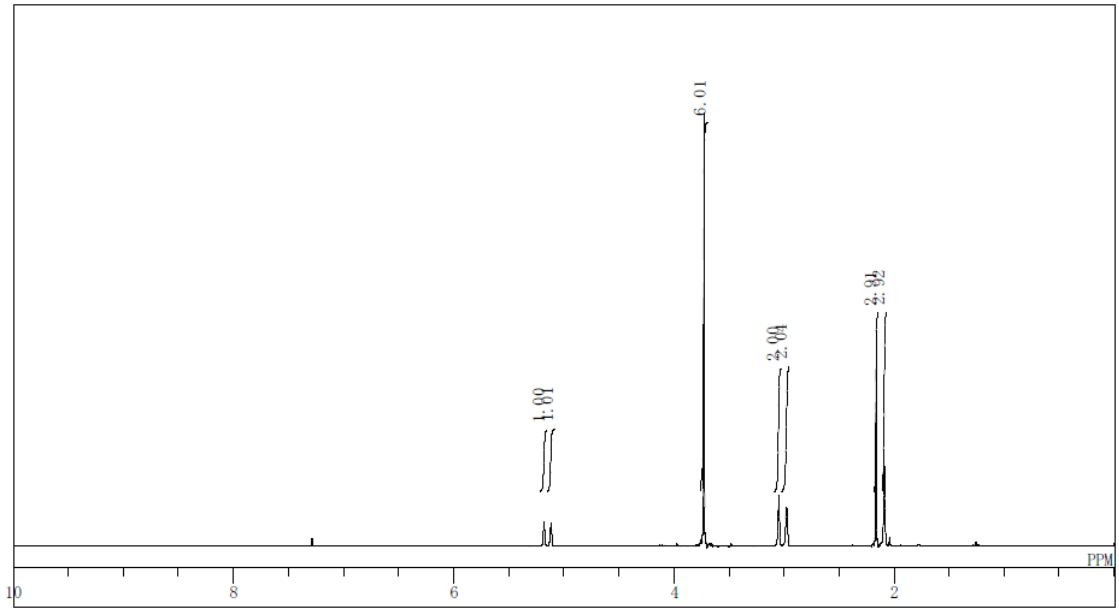


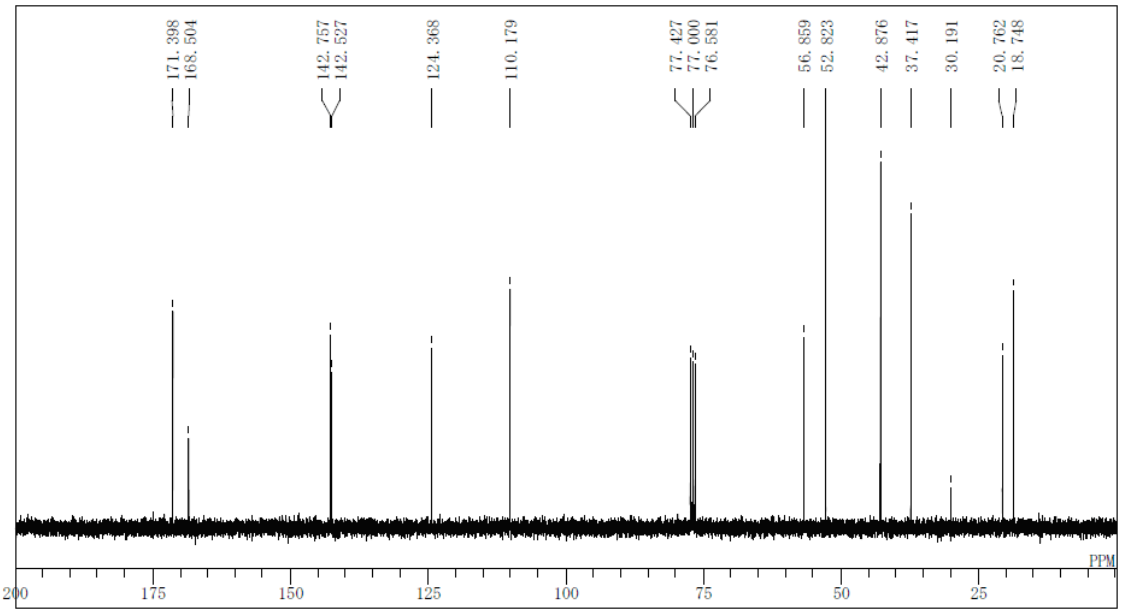




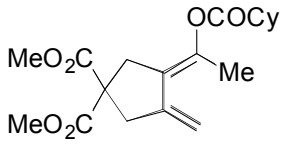
3-(1-Acetoxyethylidene)-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ab)

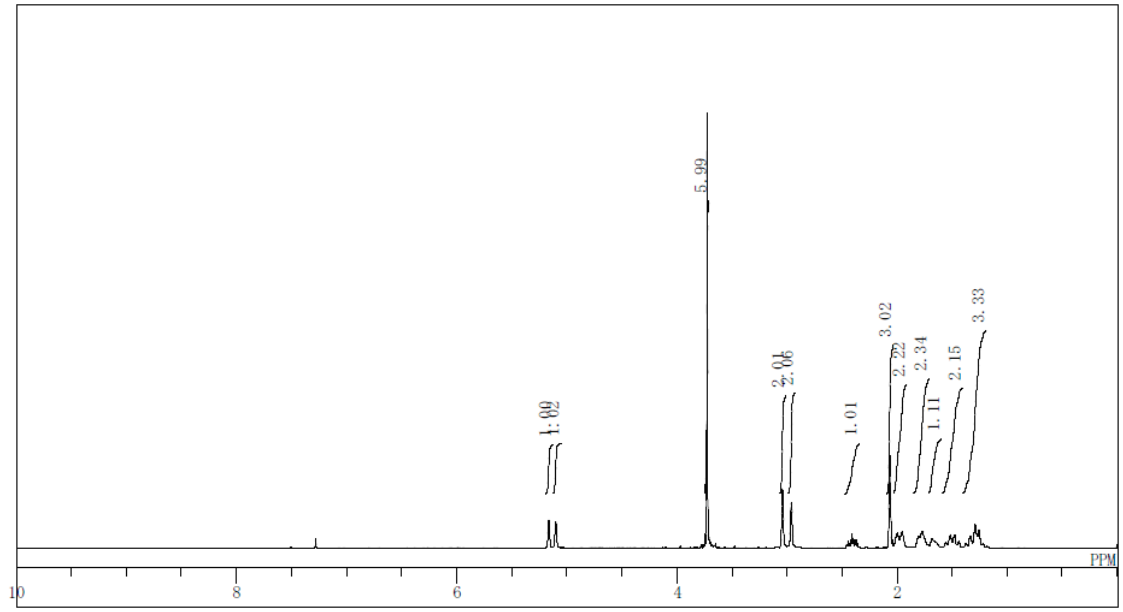


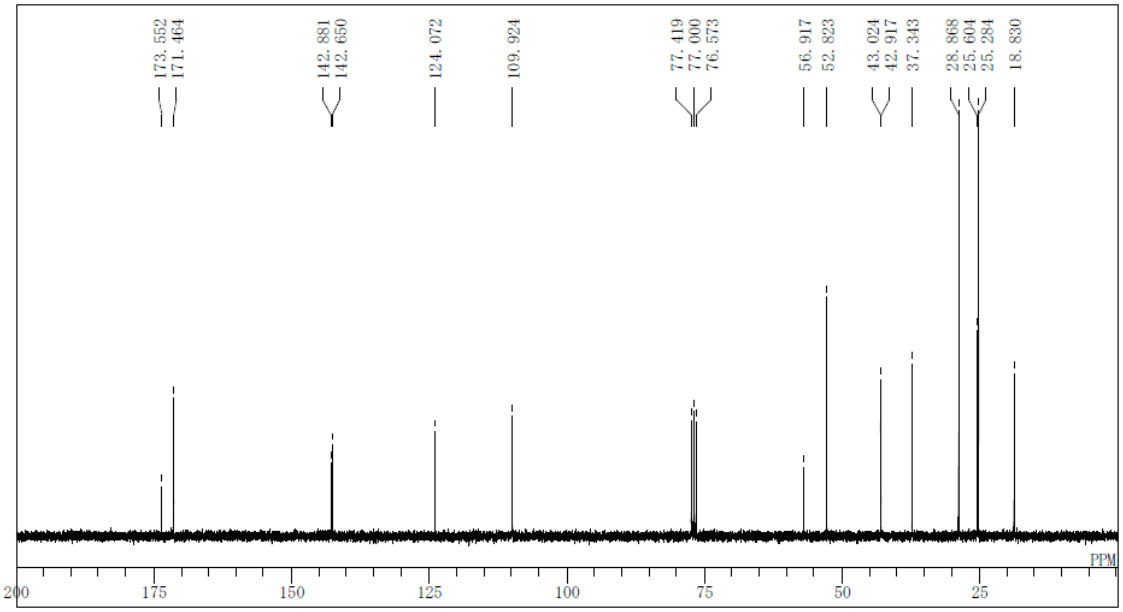




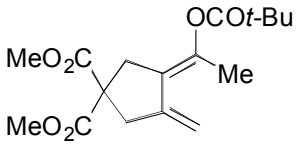
3-(1-Cyclohexanecarbonyloxyethylidene)-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ac)

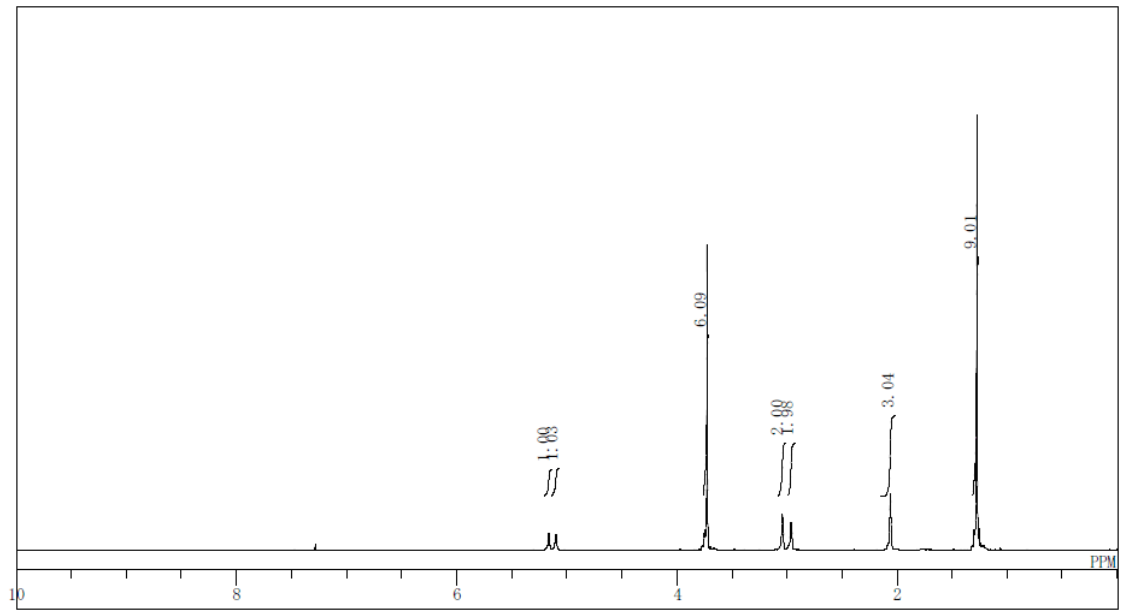


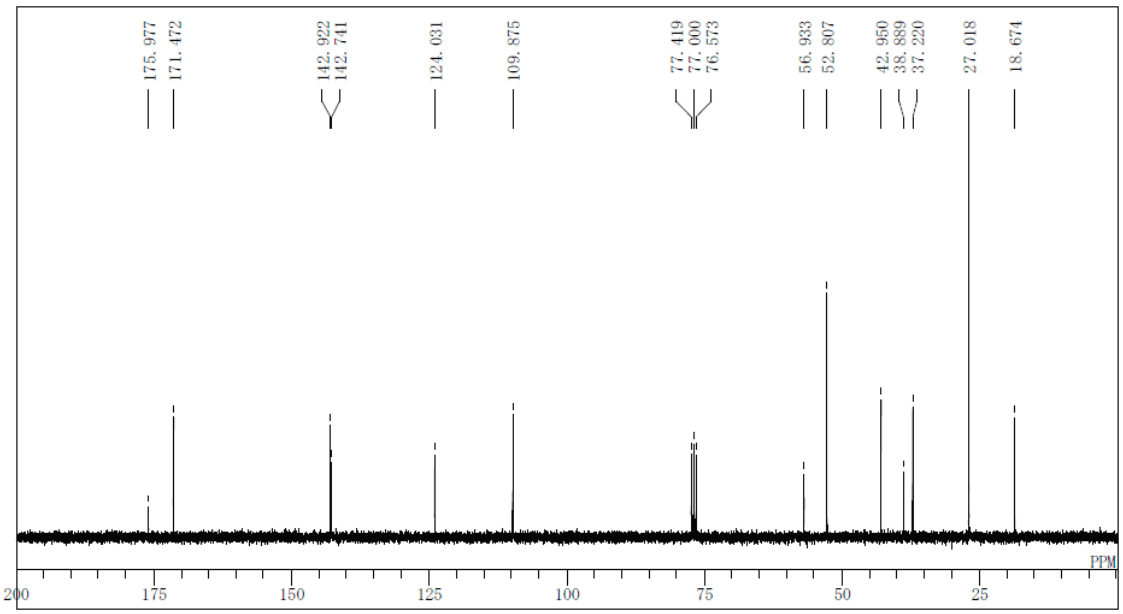




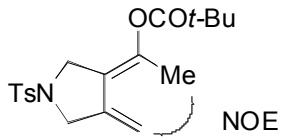
3-[1-(2,2-Dimethylpropionyloxy)ethylidene]-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ad)

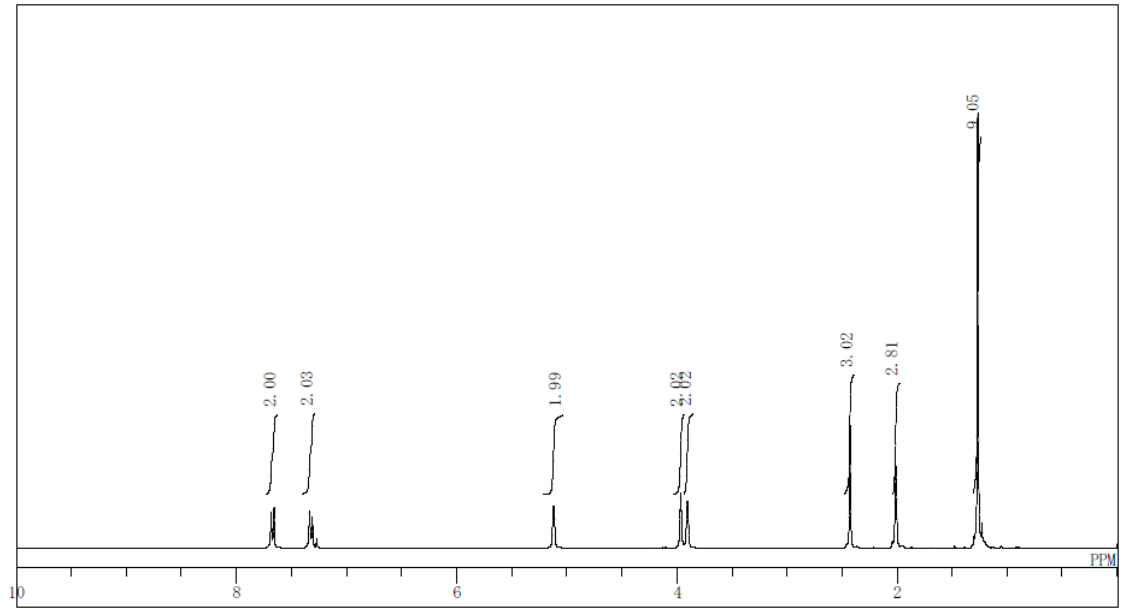


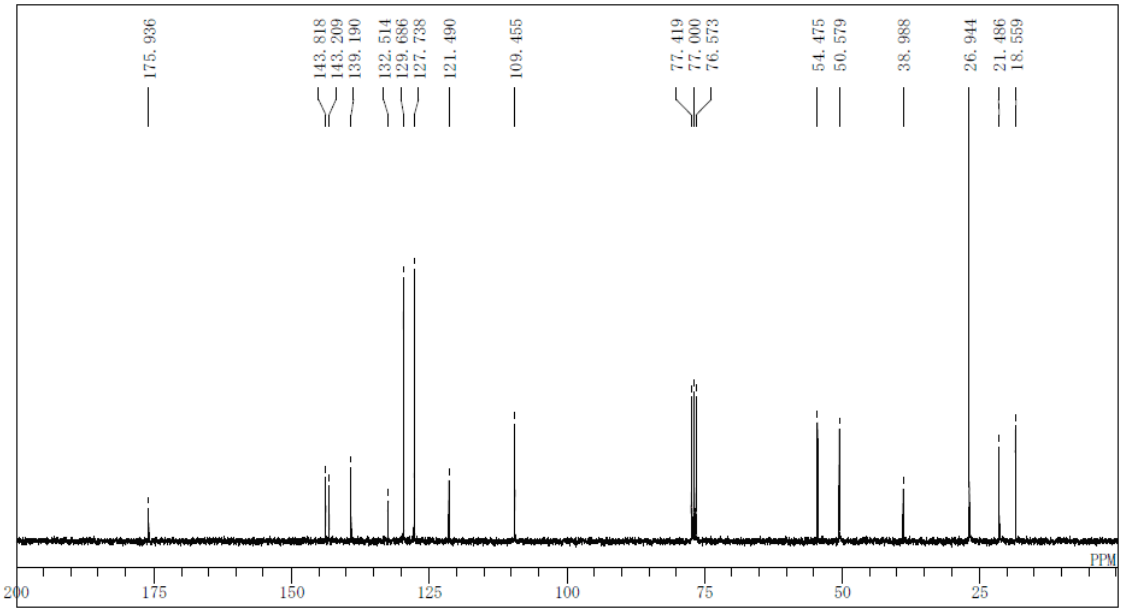




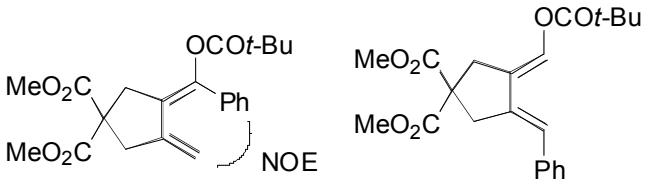
2,2-Dimethylpropionic acid 1-[4-methylene-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]ethyl ester (3bd)

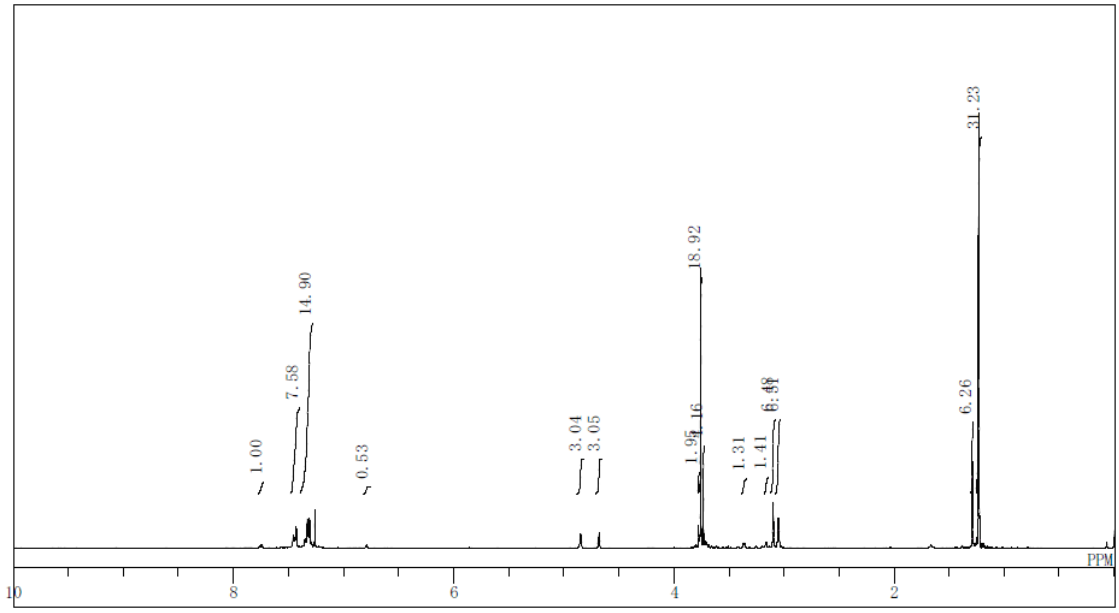


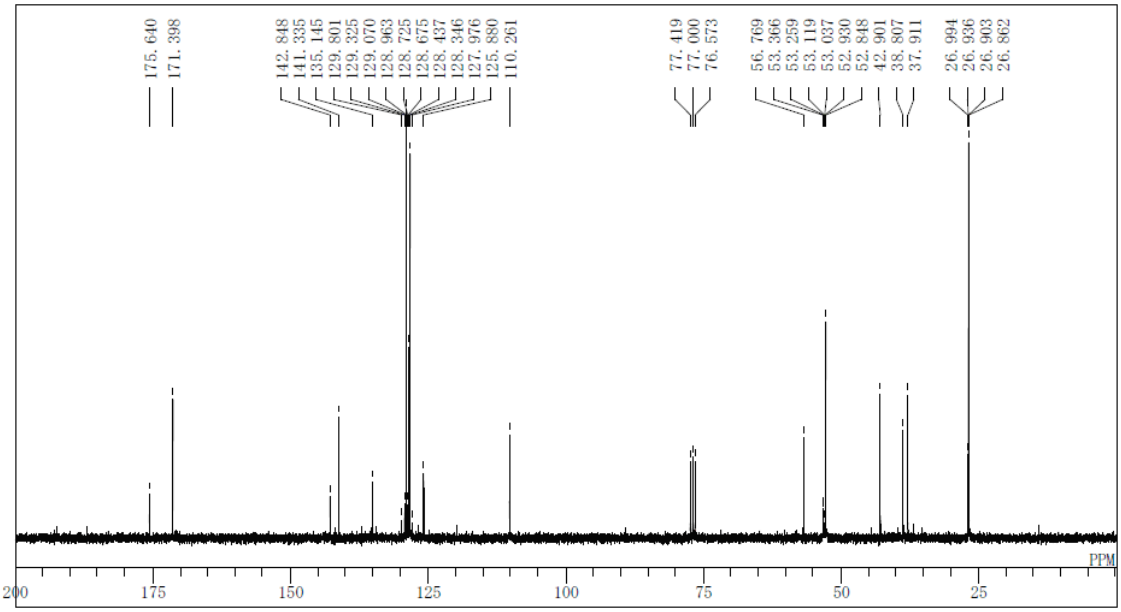




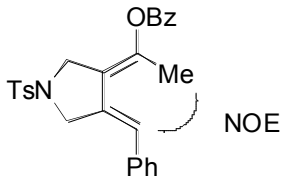
3-[(2,2-Dimethylpropionyloxy)phenylmethylene]-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3cd, 3cd/4cd = 85:15)

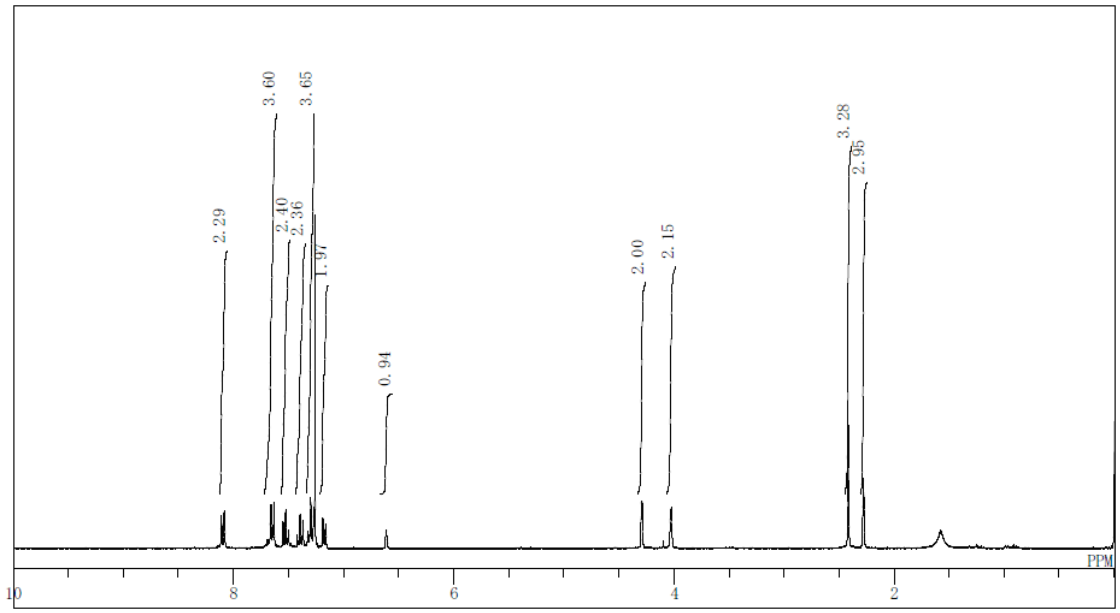


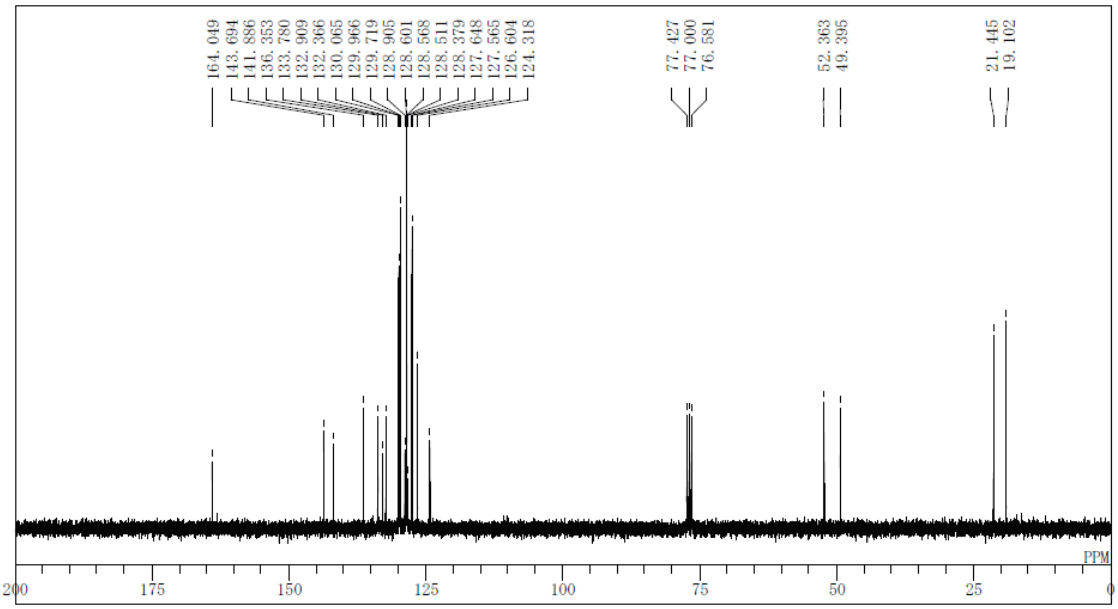




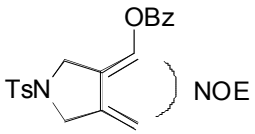
Benzoic acid 1-[4-benzylidene-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidene]ethyl ester (3da)

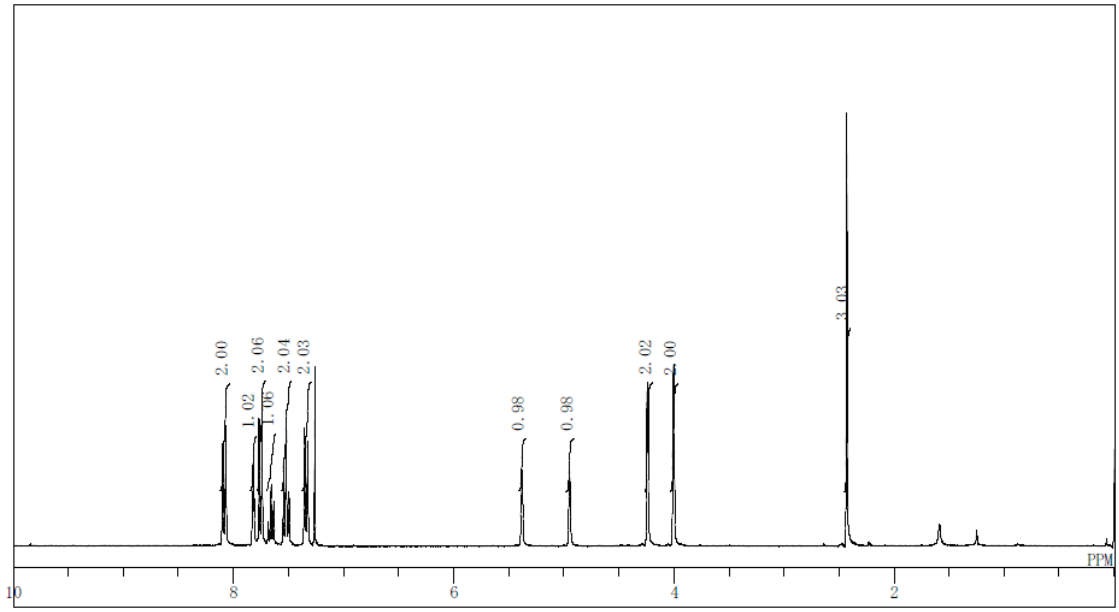


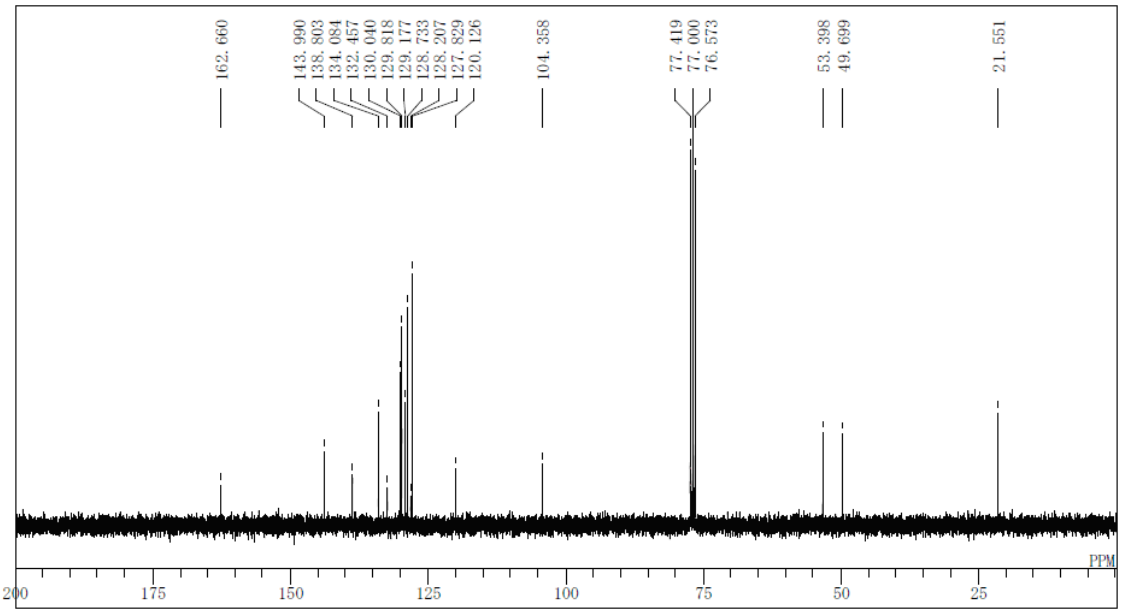




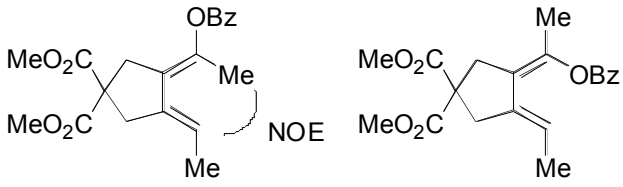
Benzoic acid 4-methylene-1-(toluene-4-sulfonyl)pyrrolidin-3-ylidenemethyl ester (3ea)

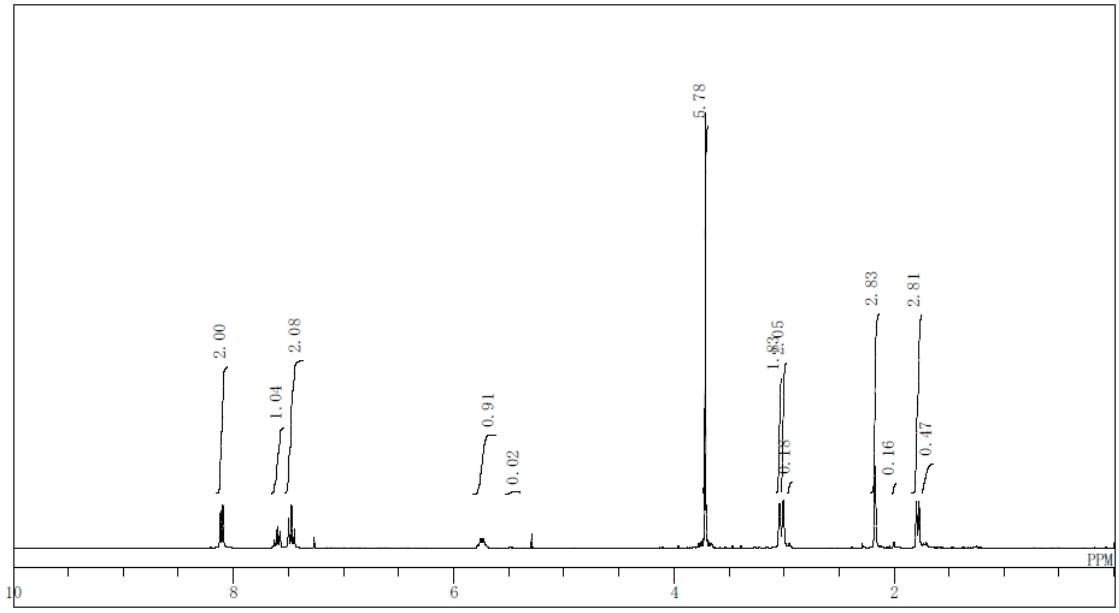


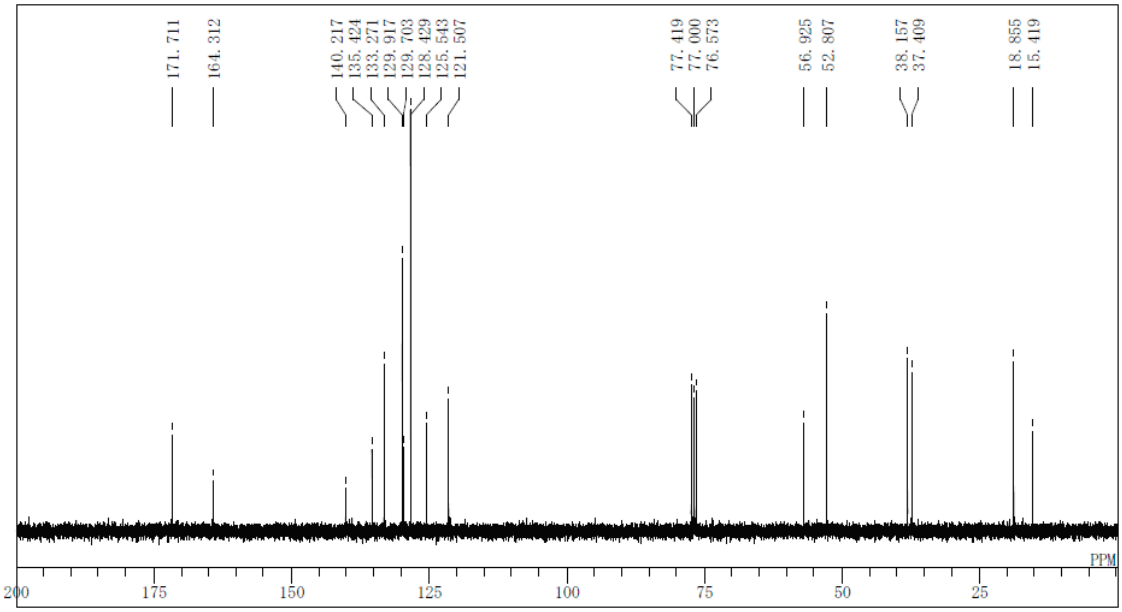




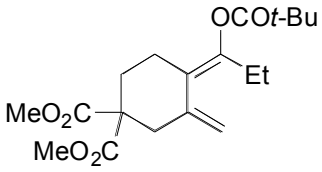
3-(1-Benzoyloxyethylidene)-4-ethylidenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3fa: *E*/*Z* = 95:5)

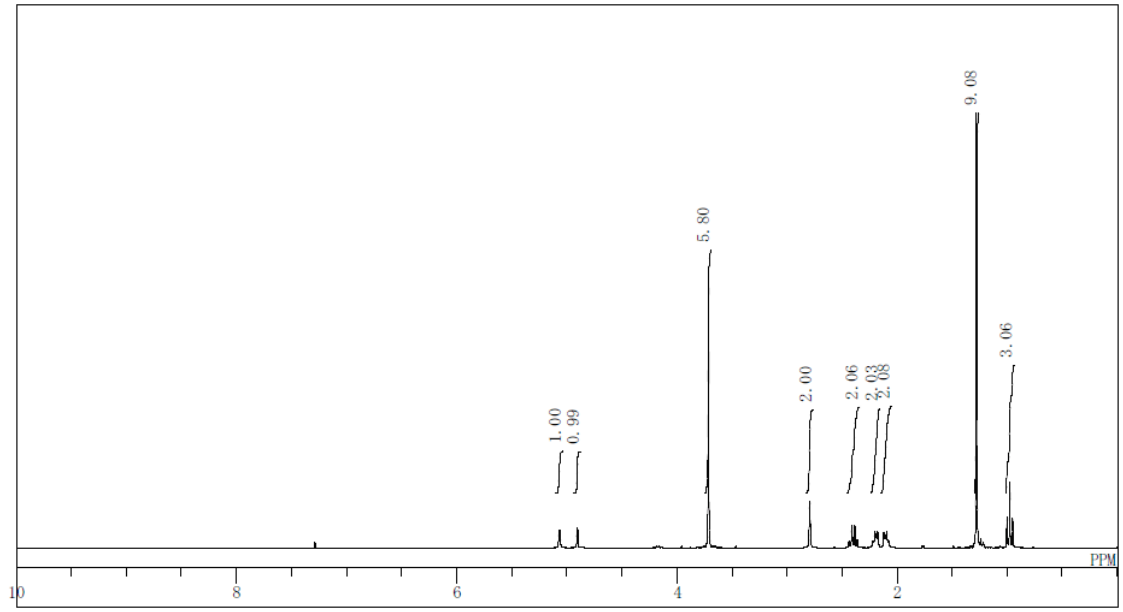


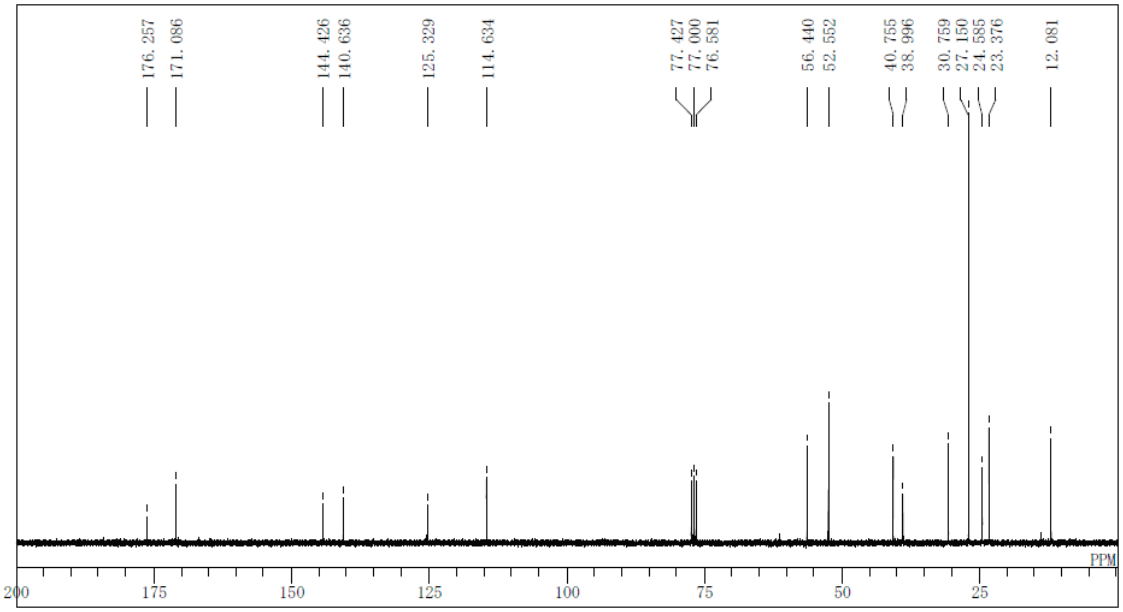




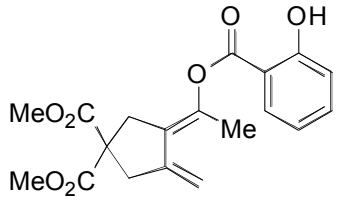
4-[1-(2,2-Dimethylpropionyloxy)propylidene]-3-methylenecyclohexane-1,1-dicarboxylic acid dimethyl ester (3gd)

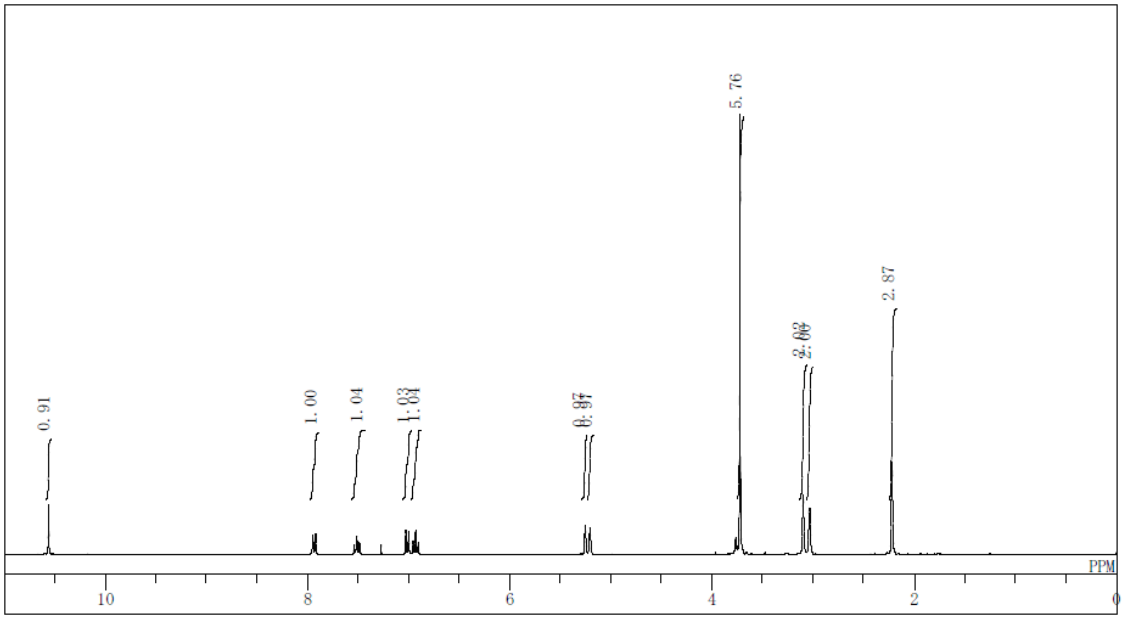


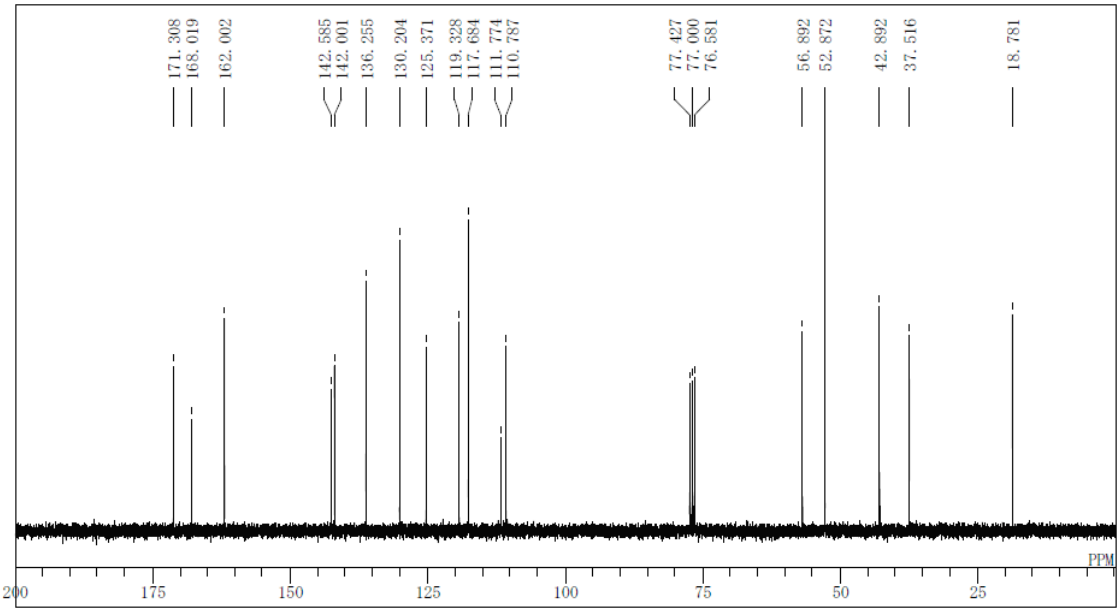




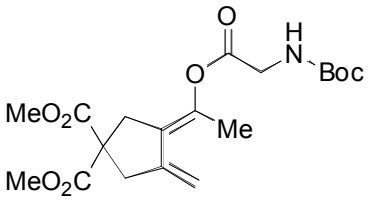
3-[1-(2-Hydroxybenzoyloxy)ethylidene]-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ag)

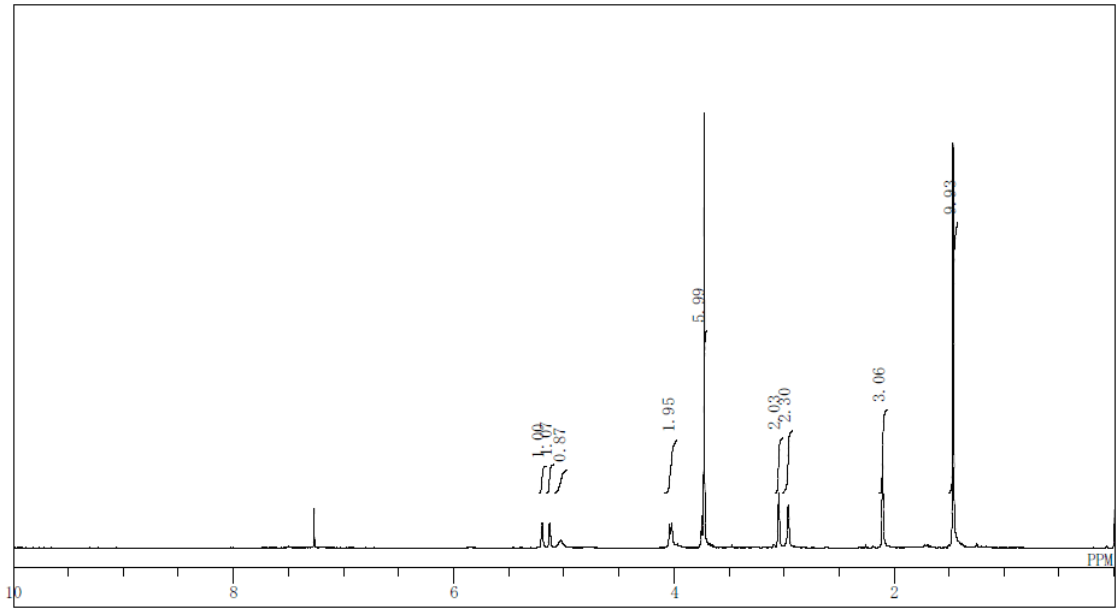


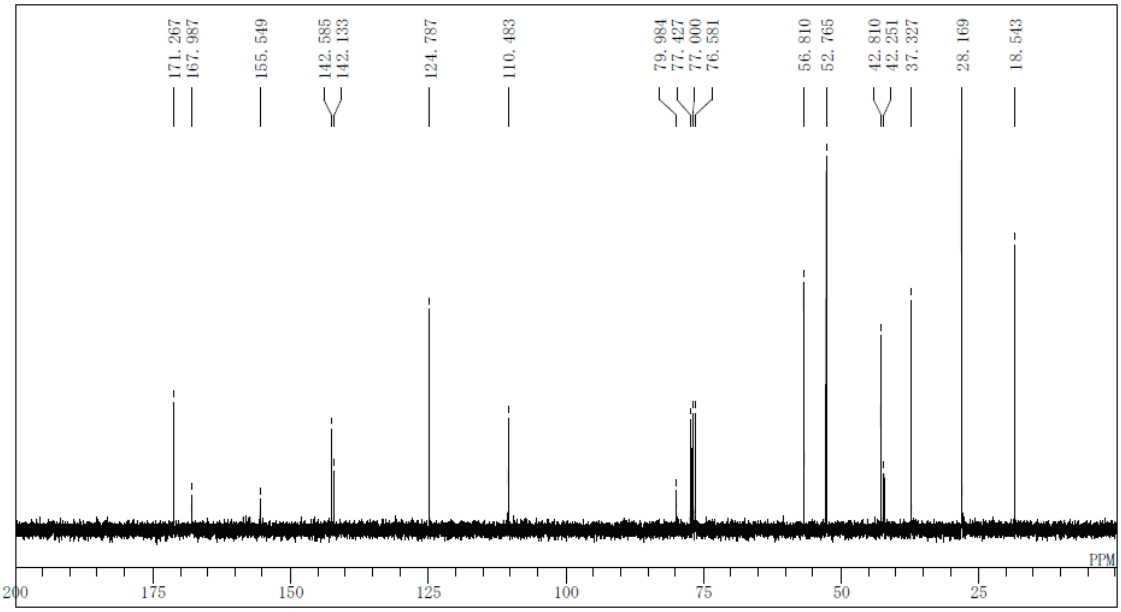




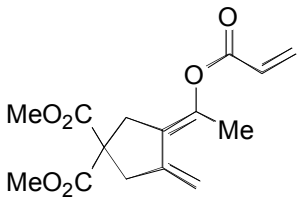
3-[1-(2-*tert*-Butoxycarbonylaminoacetoxy)ethylidene]-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ah)

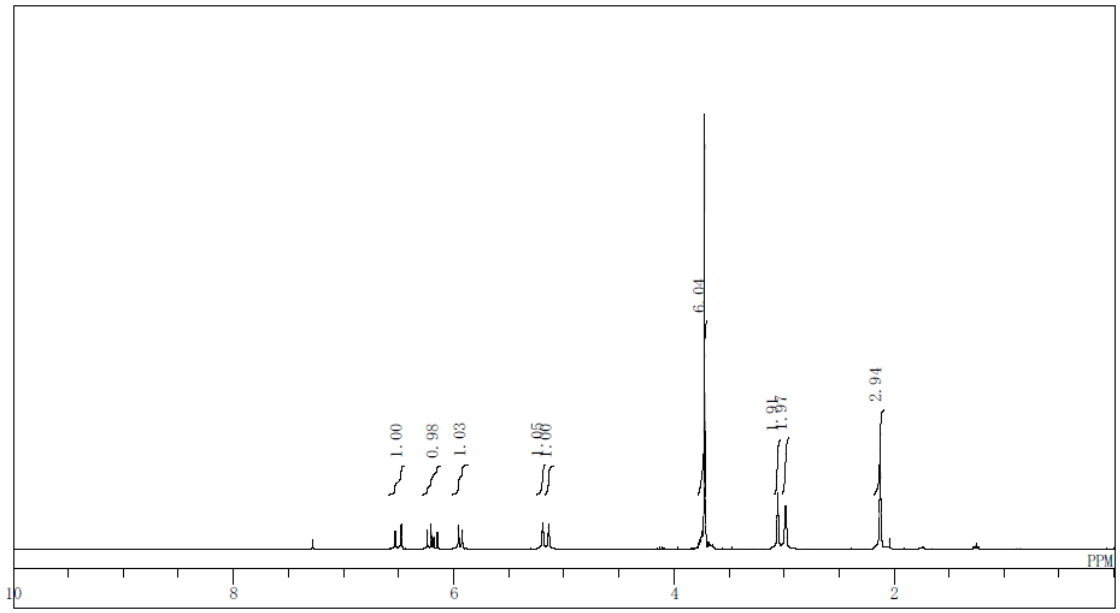


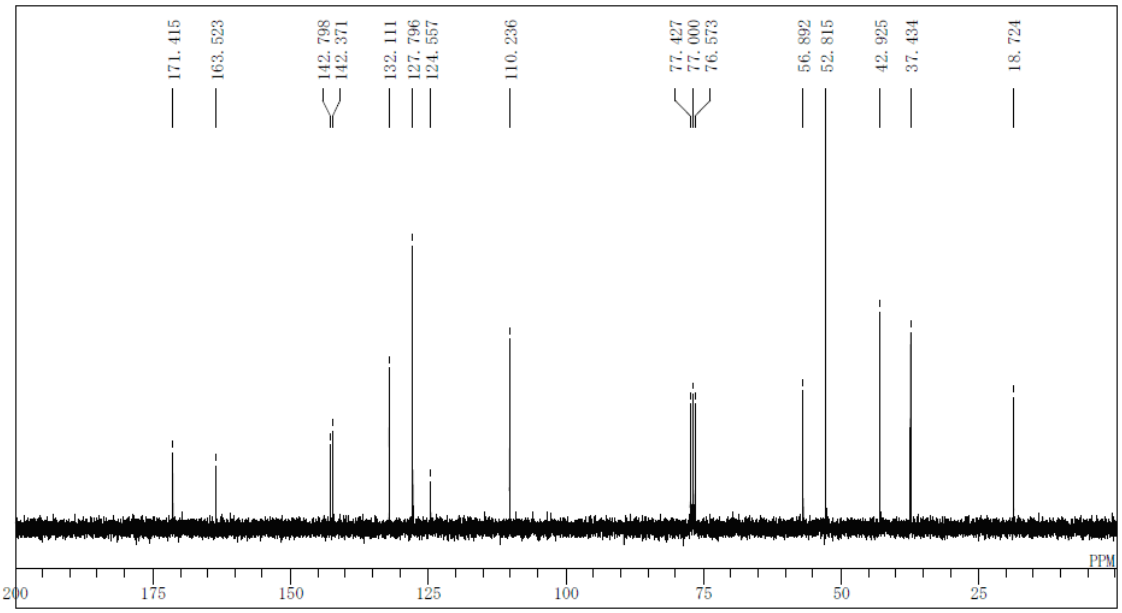




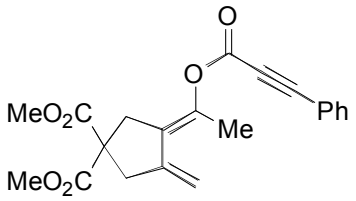
3-(1-Acryloyloxyethylidene)-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ai)

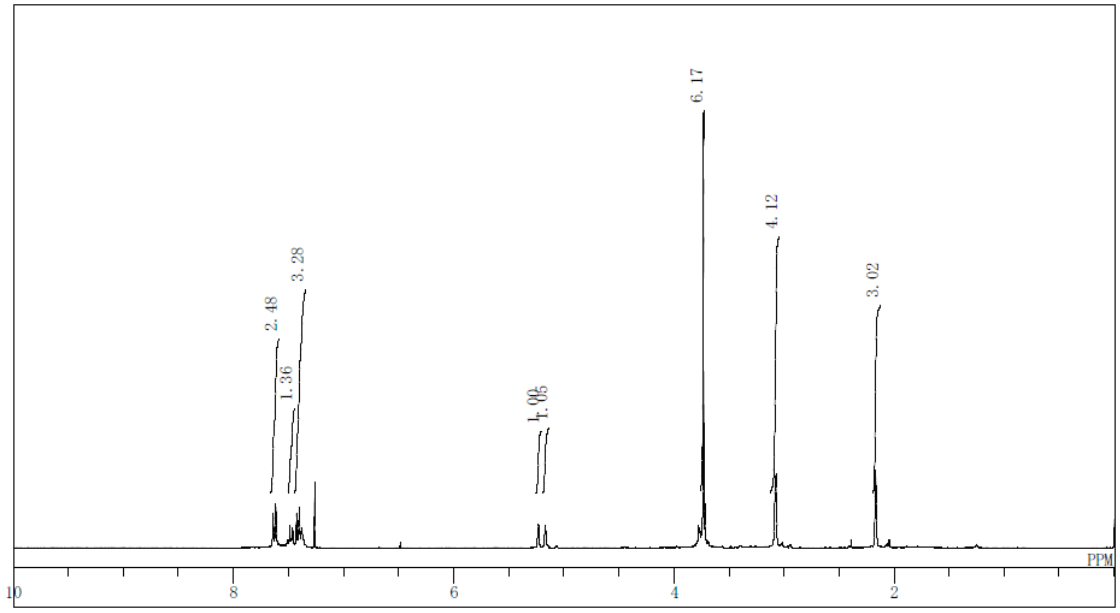


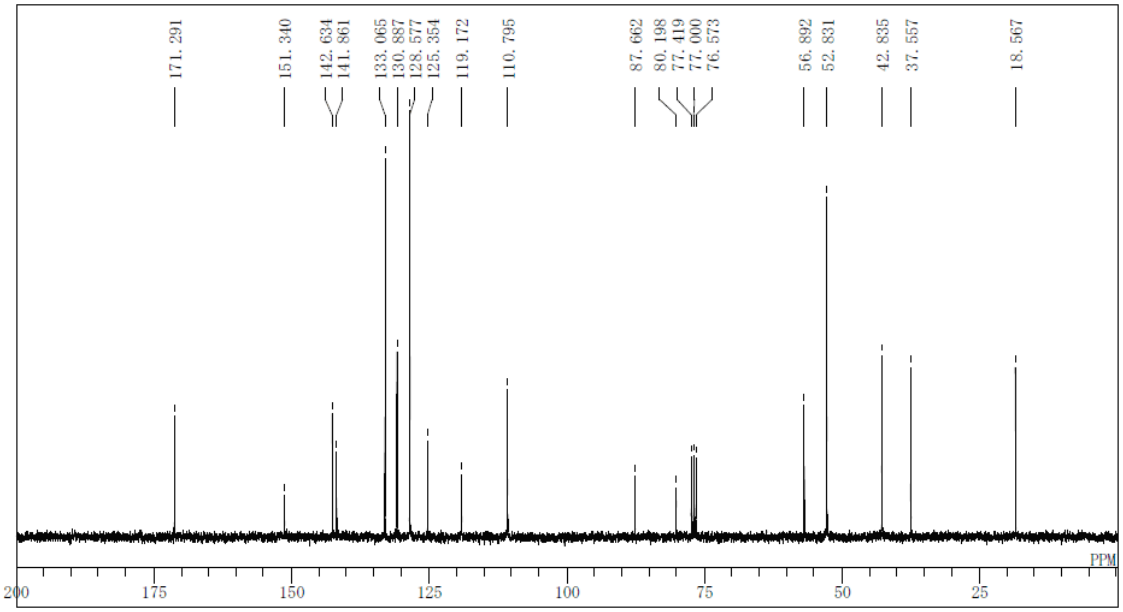




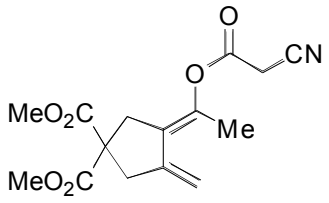
3-Methylene-4-[1-(3-phenylpropynoyloxy)ethylidene]cyclopentane-1,1-dicarboxylic acid dimethyl ester (3aj)

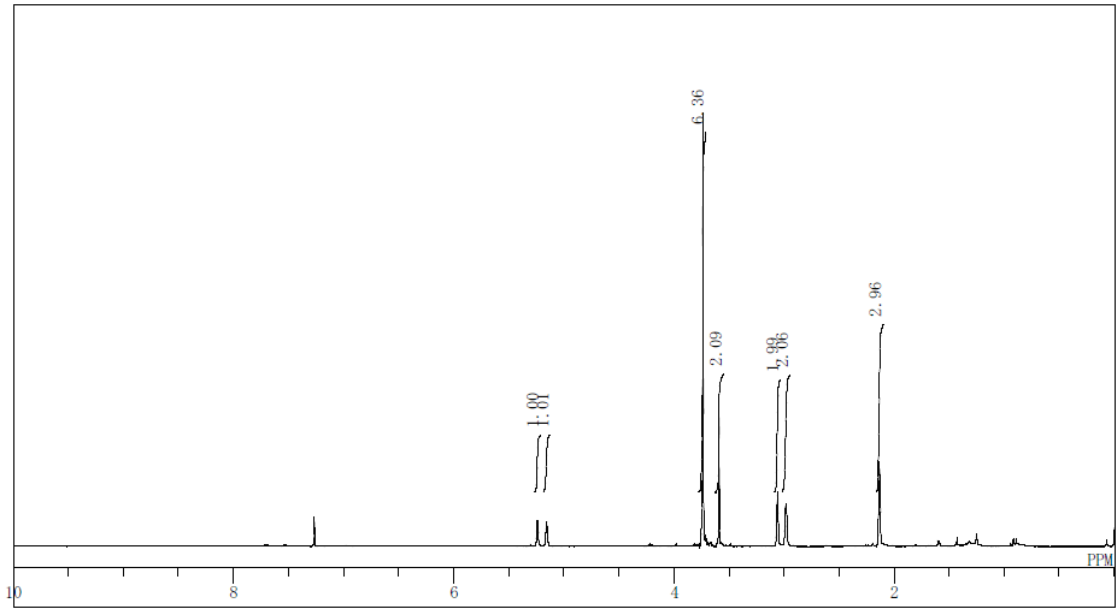


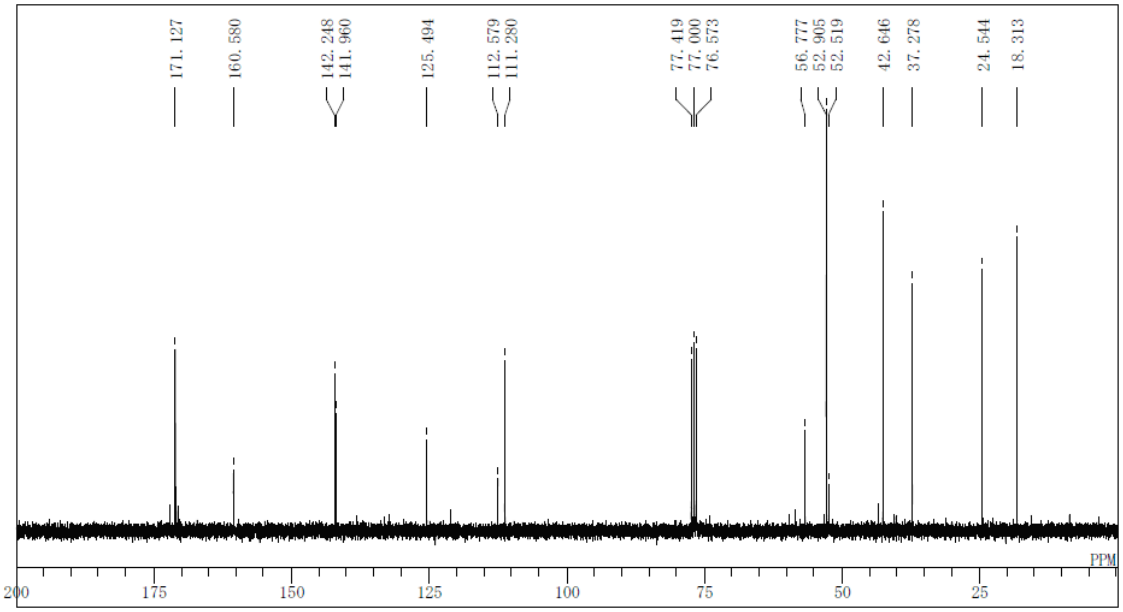




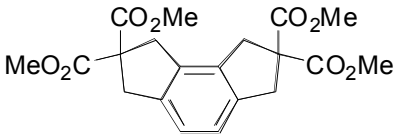
3-[1-(2-Cyanoacetoxy)ethylidene]-4-methylenecyclopentane-1,1-dicarboxylic acid dimethyl ester (3ak)

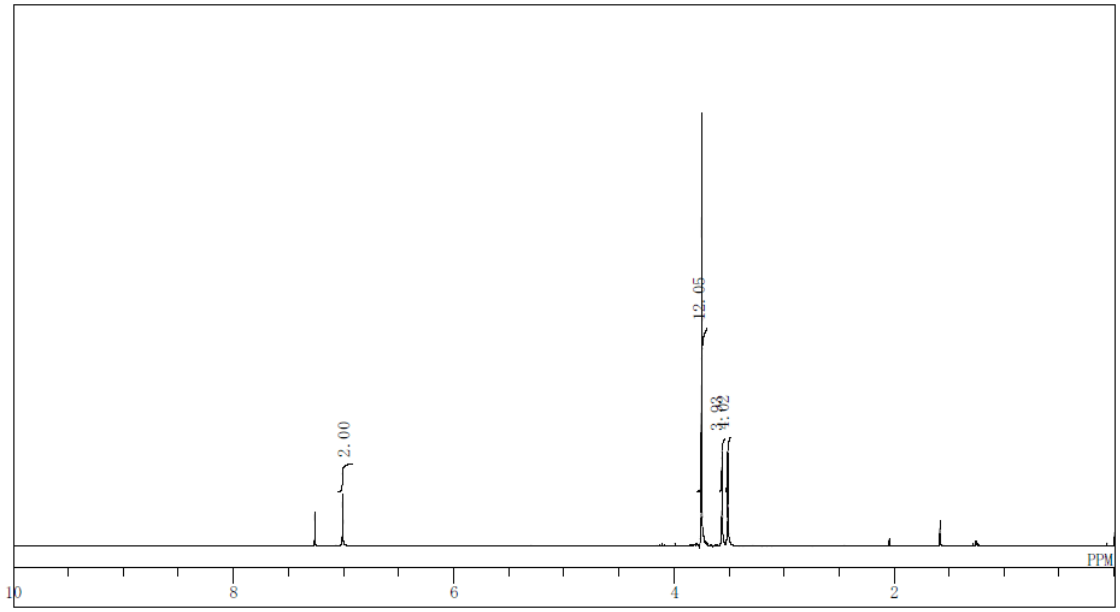


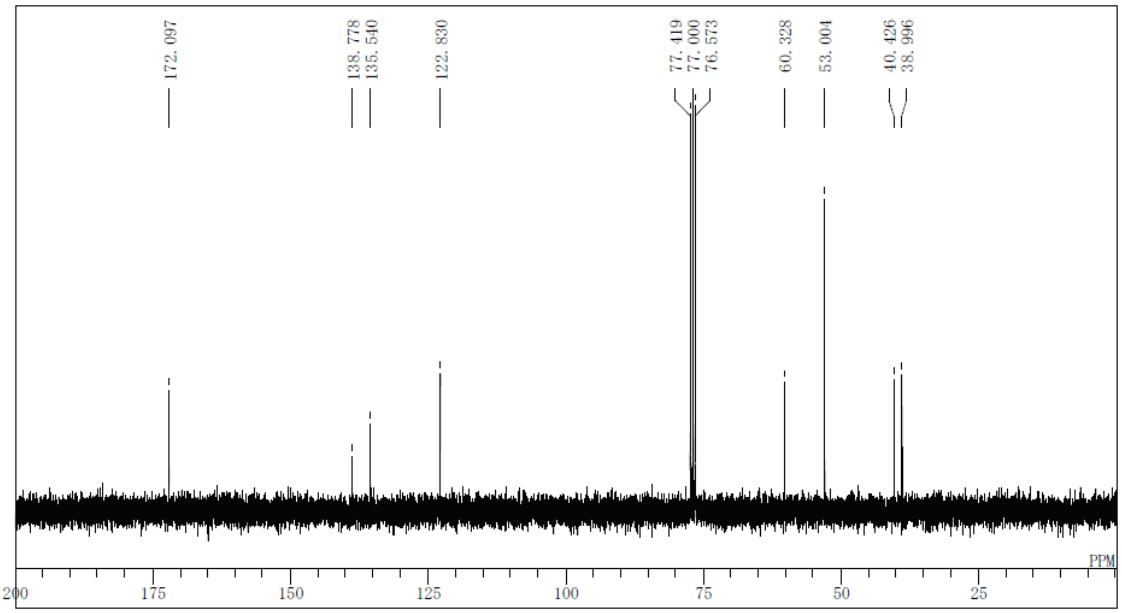




1,3,6,8-Tetrahydroasindacene-2,2,7,7-tetracarboxylic acid tetramethyl ester (8)







3-(1-Acetoxyethylidene)-4-(monodeuteriummethylene)cyclopentane-1,1-dicarboxylic acid dimethyl ester (*d*-3ab)