Supporting Information

Auto-Tandem Palladium/Phosphine Cooperative Catalysis: Synthesis of Bicyclo[3.1.0]hexenes by Selective Activation of Morita–Baylis–Hillman Carbonates

Yue Wang,[a] Manman Song,[a] Er-Qing Li,*[a] and Zheng Duan*[a]

a College of Chemistry, Green Catalysis Center, International Phosphorus Laboratory, International Joint Research Laboratory for Functional Organophosphorus Materials of Henan Province, Zhengzhou University, Zhengzhou 450001, P. R. China. E-mail: lierqing@zzu.edu.cn. duanzheng@zzu.edu.cn.

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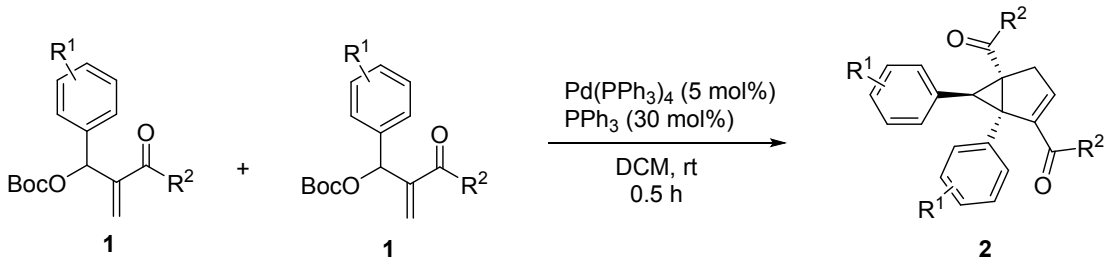
1. General experimental details.

NMR spectra were obtained using Bruker AV300 spectrometer (100 ppm of ^{13}C NMR was produced by machine). Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS. HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-Tof HR-MS spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Melting Point: heating rate: 4°C/min, the thermometer was not corrected. Silica gel (200-300 mesh) was used for the chromatographic separations. All commercially available reagents were used without further purification. Morita-Baylis-Hillman (MBH) carbonates were prepared according to the literature procedures. [1]

1 (a) S. Kayal, S. Mukherjee, *Org. Lett.* **2017**, *19*, 4944; (b) S. H. Kim, S. H. Ki, C. H. Lim, J. N. Kim, *Bull. Korean Chem. Soc.* **2002**, *33*, 2023; (c) K. Oh, J.-Y. Li, *Synthesis* , **2011**, *12*,1960; (d) X. Wang, P. Guo, Z. Han, X. Wang, Z. Wang, K. L. Ding, *J. Am. Chem. Soc*. **2014**, *136*, 405.

2. General procedure for compounds 2.

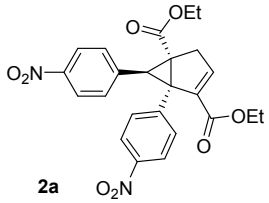


1 **1** **2**

To a dry flask filled with nitrogen were added **1** (0.2 mmol) in 2 mL CH_2Cl_2， then PPh_3 (0.03 mmol) and $Pd(PPh_3)_4$ (0.005 mmol) were added. This solution was stirred at room temperature for 0.5 h, and monitored by TLC (ethyl acetate /petroleum ether). After complete conversion, the product **2** was obtained by flash chromatography on silica gel (ethyl acetate /petroleum ether).

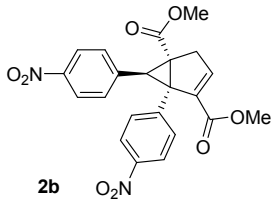
3. Analytical date for compounds 2.

Diethyl 5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-dicarboxylate (2a)



Prepared according to the general procedure as described above in 61% yield (28.4 mg). It was purified by column chromatography (EtOAc/PE = 1:4) to afford a yellow solid. Mp = 85.4-86.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (dd, J = 12.8, 8.5 Hz, 4H), 7.54 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 6.41 (d, J = 2.6 Hz, 1H), 4.12 (s, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.94 (q, J = 7.1 Hz, 2H), 3.67 (dd, J = 21.0, 2.6 Hz, 1H), 2.46 (dd, J = 21.0, 2.6 Hz, 1H), 1.11 (t, J = 7.1 Hz, 3H), 0.92 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 163.1, 147.3, 147.2, 144.4, 143.6, 140.7, 136.3, 130.9, 130.0, 123.8, 123.5, 61.5, 60.9, 53.9, 43.6, 36.1, 33.5, 14.0, 13.9 ppm; IR (film) ν_{max} 2980, 1707, 1601, 1518, 1464, 1371, 1343, 1296, 1240, 1174, 1150, 1094, 1040, 1013, 980, 852, 772, 747, 722, 701 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}N_2O_8^+$ $[M+H]^+$: 467.1449, found 467.1448.

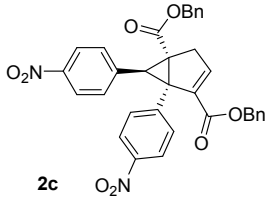
Dimethyl 5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-dicarboxylate (2b)



Prepared according to the general procedure as described above in 57% yield (25.1 mg). It was purified by column chromatography (EtOAc/PE = 1:4) to afford a yellow solid. Mp = 68.9-69.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (dd, J = 11.8, 8.8 Hz, 4H), 7.52 (d, J = 8.7 Hz, 2H), 7.48 – 7.38 (m, 2H), 6.40 (t, J = 2.5 Hz, 1H), 4.11 (s, 1H), 3.67 (dd, J = 20.6, 2.2 Hz, 1H), 3.62 (s, 3H), 3.50 (s, 3H), 2.48 (dd, J = 21.0, 2.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 163.6, 147.3, 143.9, 143.6, 140.5, 136.0, 130.9, 129.9, 123.8, 123.6, 54.0, 52.5, 52.0, 43.6, 36.3, 33.6 ppm; IR (film) ν_{max} 2920, 2851, 1715, 1599, 1515, 1436, 1344, 1257, 1192, 1149, 1108, 1041, 1015,

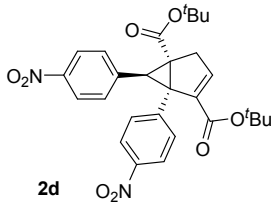
993, 922, 884, 772, 747, 722, 701 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{18}N_2NaO_8^+$ $[M+Na]^+$: 461.0955, found 461.0958.

Dibenzyl 5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-dicarboxylate (2c)



Prepared according to the general procedure as described above in 55% yield (32.6 mg). It was purified by column chromatography (EtOAc/PE = 1:3) to afford a yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 9.0 Hz, 2H), 7.44 – 7.12 (m, 10H), 7.08 (dd, J = 7.9, 1.7 Hz, 2H), 7.01 – 6.86 (m, 2H), 6.46 (t, J = 2.4 Hz, 1H), 5.09 (d, J = 12.1 Hz, 1H), 4.95 (dd, J = 11.8 ,8.1 Hz, 2H), 4.84 (d, J = 11.8 Hz, 1H), 4.09 (s, 1H), 3.69 (dd, J = 20.9, 2.5 Hz, 1H), 2.47 (dd, J = 21.0, 2.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 162.7, 147.3, 147.1, 144.4, 143.7, 140.5, 136.1, 135.2, 134.7, 130.9, 129.7, 128.7, 128.6, 128.5, 128.4, 128.3, 123.8, 123.5, 67.4, 66.6, 53.9, 43.5, 36.1, 33.7 ppm; IR (film) ν_{max} 2922, 1710, 1599, 1514, 1455, 1344, 1247, 1143, 1090, 1028, 986, 906, 853, 770, 747, 695 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{26}N_2NaO_8^+$ $[M+Na]^+$: 613.1581, found 613.1585.

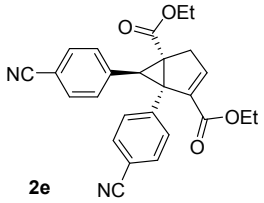
Di-tert-butyl 5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-dicarboxylate (2d)



Prepared according to the general procedure as described above in 45% yield (23.5 mg). It was purified by column chromatography (EtOAc/PE = 1:10) to afford a yellow solid. Mp = 186.5-187.6 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, J = 8.6 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 6.34 (t, J = 2.5 Hz, 1H), 4.06 (s, 1H), 3.58 (dd, J = 20.9, 2.5 Hz, 1H), 2.38 (dd, J = 20.8, 2.5 Hz, 1H), 1.27 (s, 9H), 1.13 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 162.3, 147.2, 147.0, 145.1, 143.3, 141.2, 137.7, 131.0, 130.0, 123.6, 123.4, 82.1, 81.6,

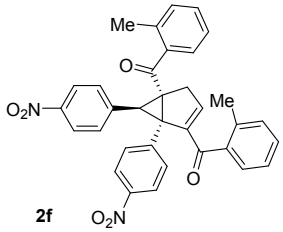
53.4, 44.5, 35.5, 33.4, 27.9, 27.7 ppm; IR (film) ν_{max} 2920, 1702, 1621, 1600, 1520, 1455, 1392, 1364, 1345, 1278, 1253, 1138, 1095, 1024, 1012, 983, 949, 870, 852, 845, 776, 728, 716, 701,671, 526 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{30}N_2NaO_8^+$ $[M+Na]^+$: 545.1894, found 545.1896.

Diethyl 5,6-bis(4-cyanophenyl)bicyclo[3.1.0]hex-3-ene-1,4-dicarboxylate (2e)



Prepared according to the general procedure as described above in 60% yield (25.6 mg). It was purified by column chromatography (EtOAc/PE = 1:4) to afford a white oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (dd, J = 10.7, 8.4 Hz, 4H), 7.46 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 7.9 Hz, 2H), 6.40 (t, J = 2.4 Hz, 1H), 4.09 – 4.01 (m, 2H), 3.91 (q, J = 7.1 Hz, 2H), 3.63 (dd, J = 20.9, 2.6 Hz, 1H), 2.42 (dd, J = 20.9, 2.5 Hz, 1H), 1.09 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 163.1, 143.6, 142.5, 138.8, 136.3, 132.3, 132.0, 130.8, 129.9, 118.7, 118.5, 111.4, 111.3, 61.4, 60.8, 54.1, 43.4, 36.1, 33.5, 14.0, 13.8 ppm; IR (film) ν_{max} 3326, 2973, 2882, 1648, 1380, 1327, 1272, 1088, 1047, 880, 644 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{23}N_2O_4^+$ $[M+H]^+$: 427.1652, found 427.1653.

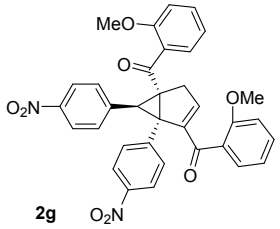
(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis(*o*-tolylmethanone) (2f)



Prepared according to the general procedure as described above in 38% yield (21.2 mg). It was purified by column chromatography (EtOAc/PE = 1:3) to afford a yellow solid. Mp = 159.5-161.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (t, J = 8.5 Hz, 4H), 7.59 (t, J = 8.9 Hz, 4H), 7.37 – 7.30 (m, 3H), 7.24 – 7.17 (m, 4H), 7.03 – 6.95 (m, 1H), 6.02 (t, J = 2.6 Hz, 1H), 4.50 (s, 1H), 3.58 (dd, J = 21.1, 2.6 Hz, 1H), 2.66 (dd, J = 21.1, 2.5 Hz, 1H), 2.30 (s, 3H), 2.17 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.4,

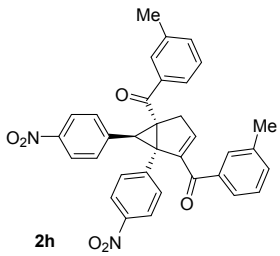
193.74, 147.5, 147.5, 147.2, 145.3, 143.3, 141.0, 137.8, 137.5, 137.3, 136.0, 131.5, 131.5, 131.1, 130.9, 130.5, 129.5, 128.6, 125.9, 125.6, 125.1, 123.7, 58.3, 51.7, 37.2, 36.1, 20.0, 19.5 ppm; IR (film) ν_{max} 1659, 1599, 1514, 1455, 1342, 1242, 1108, 1057, 1014, 981, 945, 889, 874, 853, 831, 813, 792, 760, 742, 729, 712, 664 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{27}N_2O_6^+$ $[M+H]^+$: 559.1864, found 559.1861.

(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis((2-methoxyphenyl)methanone) (2g)



Prepared according to the general procedure as described above in 49% yield (29 mg). It was purified by column chromatography (EtOAc/PE = 1:3) to afford a yellow solid. Mp = 104.2-105.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.9, 2.4 Hz, 4H), 7.66 – 7.50 (m, 4H), 7.45 – 7.31 (m, 2H), 7.10 (dd, J = 7.4, 1.8 Hz, 1H), 6.96 – 6.80 (m, 4H), 6.65 (dd, J = 7.5, 1.8 Hz, 1H), 6.00 (t, J = 2.5 Hz, 1H), 4.32 (s, 1H), 3.90 (s, 3H), 3.80 (s, 3H), 3.55 (dd, J = 21.1, 2.6 Hz, 1H), 2.58 (dd, J = 21.1, 2.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 192.3, 156.9, 156.2, 147.3, 147.0, 145.2, 143.9, 141.5, 132.3, 132.1, 131.0, 130.1, 128.7, 128.2, 123.5, 123.3, 121.2, 120.4, 111.5, 110.8, 57.8, 55.7, 55.4, 52.4, 38.0, 35.2 ppm; IR (film) ν_{max} 1652, 1598, 1515, 1487, 1463, 1435, 1343, 1289, 1245, 1180, 1107, 1067, 1044, 1018, 890, 852, 752, 664 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{27}N_2O_8^+$ $[M+H]^+$: 591.1762, found 591.1760.

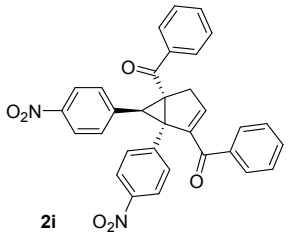
(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis(*m*-tolylmethanone) (2h)



Prepared according to the general procedure as described above in 62% yield (34.5 mg). It was purified by column chromatography (EtOAc/PE = 1:3) to afford a yellow

oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 8.7 Hz, 2H), 8.08 (d, J = 8.7 Hz, 2H), 7.74 – 7.58 (m, 4H), 7.50 (d, J = 8.8 Hz, 2H), 7.41 – 7.28 (m, 6H), 6.21 (t, J = 2.4 Hz, 1H), 4.48 (s, 1H), 3.80 (dd, J = 20.9, 2.5 Hz, 1H), 2.71 (dd, J = 21.0, 2.5 Hz, 1H), 2.41 (s, 3H), 2.37 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 191.5, 147.3, 147.1, 144.8, 143.3, 143.1, 141.0, 138.8, 138.7, 137.6, 136.8, 134.2, 133.4, 131.0, 129.5, 129.0, 128.7, 128.5, 128.4, 126.5, 124.9, 123.8, 123.7, 57.2, 51.1, 37.5, 35.5, 21.4 ppm; HRMS (ESI) calcd for $C_{34}H_{27}N_2O_6^+$ $[M+H]^+$: 559.1864, found 559.1862.

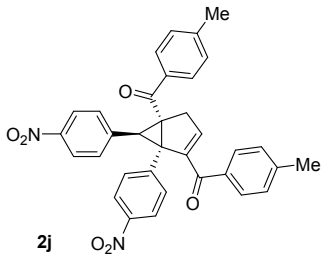
(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis(phenylmethanone) (2i)



2i

Prepared according to the general procedure as described above in 62% yield (33 mg). It was purified by column chromatography (EtOAc/PE = 1:3) to afford a yellow solid. Mp = 125.7-126.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.90 – 7.80 (m, 2H), 7.67 – 7.37 (m, 12H), 6.24 (t, *J* = 2.5 Hz, 1H), 4.51 (s, 1H), 3.81 (dd, *J* = 21.0, 2.5 Hz, 1H), 2.74 (dd, *J* = 21.0, 2.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 191.4, 147.3, 147.1, 145.1, 143.3, 143.1, 141.0, 137.5, 136.8, 133.4, 132.7, 131.0, 129.2, 129.0, 128.7, 128.7, 128.0, 123.8, 57.3, 51.0, 37.5, 35.5 ppm; IR (film) ν_{max} 1647, 1598,1519, 1447, 1425, 1347, 1273, 1244, 983, 945, 904, 886, 871, 855, 828, 816, 793, 765, 753, 730,713, 694, 665 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{23}N_2O_6^+$ $[M+H]^+$: 531.1551, found 531.1548.

(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis(*p*-tolylmethanone) (2j)

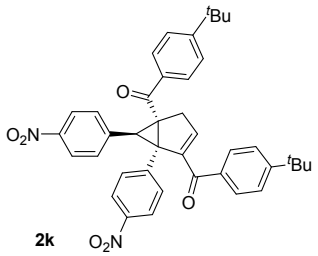


2j

Prepared according to the general procedure as described above in 61% yield (34.1 mg). It was purified by column chromatography (EtOAc/PE = 1:3) to afford a yellow

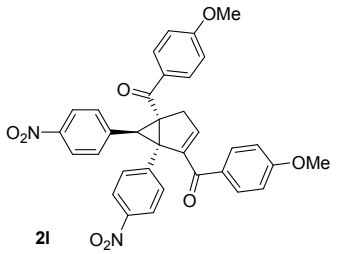
solid. Mp = 136.7-137.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 8.7 Hz, 2H), 8.06 (d, J = 8.9 Hz, 2H), 7.78 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.47 (t, J = 8.5 Hz, 4H), 7.35 – 7.18 (m, 4H), 6.19 (t, J = 2.4 Hz, 1H), 4.47 (s, 1H), 3.77 (dd, J = 20.8, 2.5 Hz, 1H), 2.70 (dd, J = 20.9, 2.4 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 190.9, 147.3, 147.0, 144.4, 144.1, 143.7, 143.4, 143.2, 141.1, 134.9, 134.0, 131.1, 129.4, 129.4, 129.3, 128.8, 128.3, 56.9, 51.0, 37.7, 35.0, 21.7, 21.7 ppm; IR (film) ν_{max} 1655, 1638, 1600, 1516, 1407, 1343, 1276, 1254, 1171, 1107, 1061, 1013, 977, 947, 901, 888, 872, 848, 829, 805, 780, 746, 728, 668, 649 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{27}N_2O_6^+$ [M+H]$^+$: 559.1864, found 559.1862.

(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis((4-(tert-butyl)phenyl)methanone) (2k)



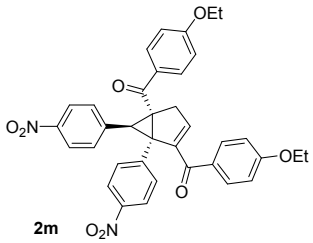
Prepared according to the general procedure as described above in 41% yield (26.5 mg). It was purified by column chromatography (EtOAc/PE = 1:4) to afford a yellow solid. Mp = 142.1-142.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J = 8.8 Hz, 2H), 8.06 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.57 – 7.44 (m, 8H), 6.23 (t, J = 2.4 Hz, 1H), 4.50 (s, 1H), 3.80 (dd, J = 20.9, 2.5 Hz, 1H), 2.69 (dd, J = 20.9, 2.4 Hz, 1H), 1.34 (s, 9H), 1.33 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 190.9, 157.4, 156.6, 147.3, 147.1, 144.3, 143.4, 143.2, 141.1, 134.9, 134.0, 131.1, 129.2, 128.8, 128.1, 125.7, 125.7, 123.7, 123.7, 57.1, 51.2, 37.7, 35.2, 35.2, 35.0, 31.1 ppm; IR (film) ν_{max} 1645,1600, 1517, 1407, 1344, 1268, 1178, 1107, 1061, 1015, 976, 889, 850, 802, 775, 731, 705, 671 cm^{-1}; HRMS (ESI) calcd for $C_{40}H_{39}N_2O_6^+$ [M+H]$^+$: 643.2803, found 643.2802.

(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis((4-methoxyphenyl)methanone) (2l)



Prepared according to the general procedure as described above in 70% yield (41.3 mg). It was purified by column chromatography (EtOAc/PE = 1:3) to afford a yellow solid. Mp = 126-127.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (dd, J = 8.8, 2.3 Hz, 2H), 8.04 (dd, J = 8.8, 2.7 Hz, 2H), 7.92 (d, J = 8.9 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.9 Hz, 2H), 7.46 (d, J = 8.9 Hz, 2H), 7.08 – 6.86 (m, 4H), 6.18 (t, J = 2.3 Hz, 1H), 4.44 (s, 1H), 3.88 (d, J = 2.2 Hz, 3H), 3.85 (d, J = 2.2 Hz, 3H), 3.75 (dd, J = 20.8, 2.5 Hz, 1H), 2.70 (dd, J = 20.9, 2.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.1, 189.7, 164.0, 163.3, 147.2, 147.0, 143.4, 143.3, 143.1, 141.2, 131.6, 131.1, 130.7, 130.3, 129.0, 128.6, 123.7, 123.7, 114.0, 113.9, 56.4, 55.6, 55.5, 51.0, 38.1, 34.6 ppm; IR (film) ν_{max} 1637, 1596, 1513, 1346, 1250, 1165, 1109, 1032, 888, 846, 771, 749, 613 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{27}N_2O_8^+$ $[M+H]^+$: 591.1762, found 591.1760.

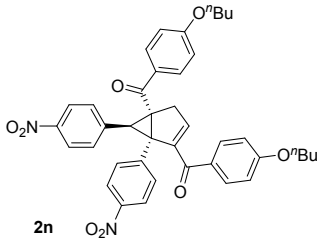
(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis((4-ethoxyphenyl)methanone) (2m)



Prepared according to the general procedure as described above in 65% yield (40.2 mg). It was purified by column chromatography (EtOAc/PE = 1:3) to afford a yellow solid. Mp = 112.7-113.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J = 8.7 Hz, 2H), 8.03 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 6.93 (dd, J = 16.2, 8.9 Hz, 4H), 6.19 (t, J = 2.3 Hz, 1H), 4.44 (s, 1H), 4.18 – 4.00 (m, 4H), 3.76 (dd, J = 20.8, 2.4 Hz, 1H), 2.71 (dd, J = 20.9, 2.4 Hz, 1H), 1.44 (td, J = 7.0, 4.4 Hz, 6H) ppm; ^{13}C NMR (75 MHz,

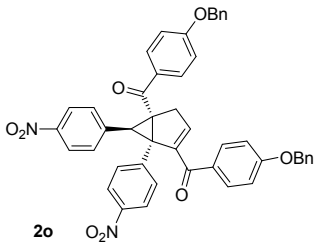
$CDCl_3$) δ 195.0, 189.7, 163.4, 162.8, 147.2, 146.9, 143.4, 143.4, 143.1, 141.3, 131.6, 131.1, 130.7, 130.1, 128.8, 128.7, 123.7, 123.7, 114.4, 114.3, 63.9, 63.9, 56.4, 51.0, 38.1, 34.6, 14.6 ppm; IR (film) ν_{max} 2982, 1641, 1596, 1515, 1421, 1343, 1244, 1163, 1111, 1040, 976, 888, 847, 771, 748, 729,642 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{31}N_2O_8^+$ $[M+H]^+$: 619.2075, found 619.2078.

(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis((4-butoxyphenyl)methanone) (2n)



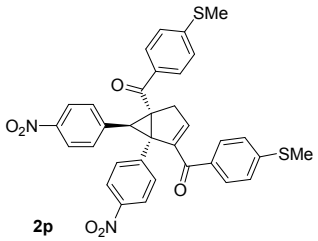
Prepared according to the general procedure as described above in 64% yield (43.1 mg). It was purified by column chromatography (EtOAc/PE = 1:3) to afford a yellow solid. Mp = 112.7-113.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 8.5 Hz, 2H), 7.91 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 6.93 (dd, J = 16.3, 8.5 Hz, 4H), 6.17 (t, J = 2.5 Hz, 1H), 4.43 (s, 1H), 4.02 (dt, J = 9.3, 6.5 Hz, 4H), 3.75 (dd, J = 20.7, 2.5 Hz, 1H), 2.70 (dd, J = 20.9, 2.5 Hz, 1H), 1.96 – 1.69 (m, 4H), 1.49 (ddt, J = 10.1, 7.3, 2.9 Hz, 4H), 0.98 (t, J = 7.4 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 189.7, 163.6, 163.0, 147.2, 147.0, 143.4, 143.4, 143.0, 141.3, 131.6, 131.2, 130.7, 130.0, 128.8, 128.6, 123.7, 123.7, 114.4, 114.4, 68.1, 68.1, 56.4, 51.0, 38.1, 34.6, 31.1, 19.2, 13.8 ppm; IR (film) ν_{max} 2958, 1641, 1596, 1571, 1515, 1466, 1421, 1343, 1247, 1163, 1111, 1062, 1015, 969, 889, 847, 771, 749, 708, 644, 625 cm^{-1}; HRMS (ESI) calcd for $C_{40}H_{39}N_2O_8^+$ $[M+H]^+$: 675.2701, found 675.2701.

(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis((4-(benzyloxy)phenyl)methanone) (2o)



Prepared according to the general procedure as described above in 61% yield (45 mg). It was purified by column chromatography (EtOAc/PE = 1:2) to afford a yellow solid. Mp = 107.4-108.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 8.7 Hz, 2H), 8.03 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.50 – 7.32 (m, 12H), 7.01 (dd, J = 15.5, 8.8 Hz, 4H), 6.16 (t, J = 2.3 Hz, 1H), 5.14 (s, 2H), 5.11 (s, 2H), 4.43 (s, 1H), 3.73 (dd, J = 20.8, 2.4 Hz, 1H), 2.69 (dd, J = 20.9, 2.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 189.7, 163.1, 162.5, 147.2, 147.0, 143.4, 143.2, 143.2, 141.2, 136.0, 135.9, 131.6, 131.1, 130.7, 130.5, 129.3, 128.8, 128.7, 128.7, 128.7, 128.4, 128.4, 127.5, 127.4, 123.7, 123.7, 114.9, 114.9, 70.2, 70.2, 56.5, 51.0, 38.0, 34.7 ppm; IR (film) ν_{max} 1645, 1595, 1514, 1454, 1419, 1343, 1245, 1163, 1110, 1013, 888, 845, 771, 734, 696, 654 cm^{-1}; HRMS (ESI) calcd for $C_{46}H_{35}N_2O_8^+$ $[M+H]^+$: 743.2388, found 743.2388.

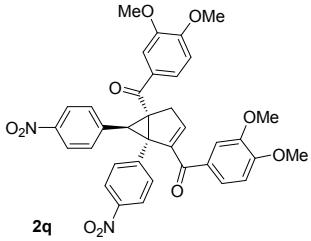
(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis((4-(methylthio)phenyl)methanone) (2p)



Prepared according to the general procedure as described above in 65% yield (40.6 mg). It was purified by column chromatography (EtOAc/PE = 1:2) to afford a yellow solid. Mp = 120.2-121.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 8.7 Hz, 2H), 8.05 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.53 – 7.43 (m, 4H), 7.31 – 7.22 (m, 4H), 6.20 (t, J = 2.4 Hz, 1H), 4.46 (s, 1H), 3.75 (dd, J = 20.9, 2.5 Hz, 1H), 2.72 (dd, J = 20.9, 2.4 Hz, 1H), 2.52 (s, 3H), 2.51 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6, 190.1, 147.3, 147.0, 146.9, 146.1, 143.7, 143.3, 143.1, 141.0, 133.5, 132.5, 131.1, 129.6, 128.7, 128.0, 125.1, 125.0, 123.8, 123.7,

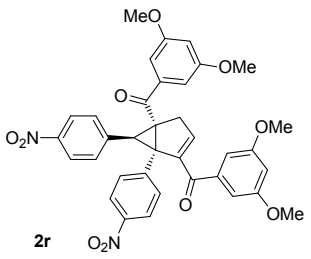
56.8, 51.0, 37.8, 34.9, 14.8, 14.7 ppm; IR (film) ν_{max} 1641, 1586, 1552, 1513, 1401, 1342, 1252, 1180, 1090, 1013, 971, 887, 842, 799, 763, 727, 702, 625 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{27}N_2O_6S_2^+$ $[M+H]^+$: 623.1305, found 623.1304.

(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis((3,4-dimethoxyphenyl)methanone) (2q)



Prepared according to the general procedure as described above in 75% yield (49 mg). It was purified by column chromatography (EtOAc/PE = 1:1) to afford a yellow solid. Mp = 154.9-155.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 8.3 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H), 7.71 – 7.60 (m, 3H), 7.47 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 1.9 Hz, 1H), 7.24 (d, J = 2.0 Hz, 1H), 7.14 (d, J = 2.0 Hz, 1H), 6.90 (dd, J = 8.4, 4.9 Hz, 2H), 6.20 (t, J = 2.3 Hz, 1H), 4.42 (s, 1H), 3.96 – 3.83 (m, 12H), 3.78 (dd, J = 21.3, 2.4 Hz, 1H), 2.73 (dd, J = 20.9, 2.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.1, 189.6, 153.9, 153.2, 149.5, 149.2, 147.2, 147.0, 143.4, 143.0, 142.8, 141.2, 131.1, 130.4, 129.1, 128.6, 124.3, 123.7, 123.7, 122.6, 111.2, 111.0, 109.9, 109.8, 56.4, 56.2, 56.1, 56.0, 56.0, 50.9, 38.3, 34.7 ppm; IR (film) ν_{max} 1659, 1634, 1592, 1579, 1511, 1463, 1419, 1342, 1293, 1264, 1220,1181, 1166, 1146, 1133, 1112, 1065, 1023, 990, 955, 913, 882, 844, 817, 771, 685, 638 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{31}N_2O_{10}^+$ $[M+H]^+$: 651.1973, found 651.1975.

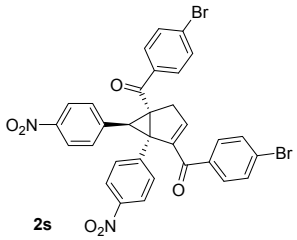
(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis((3,5-dimethoxyphenyl)methanone) (2r)



Prepared according to the general procedure as described above in 67% yield (43.6

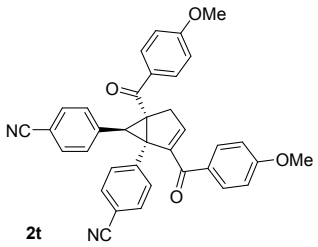
mg). It was purified by column chromatography (EtOAc/PE = 1:1) to afford a yellow solid. Mp = 114.3-115.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (t, J = 8.6 Hz, 4H), 7.65 – 7.46 (m, 4H), 7.25 – 7.19 (m, 1H), 6.70 (d, J = 8.4 Hz, 1H), 6.49 – 6.41 (m, 3H), 6.36 (dd, J = 8.5, 2.2 Hz, 1H), 5.99 (t, J = 2.5 Hz, 1H), 4.28 (s, 1H), 3.88 (s, 3H), 3.80 (s, 9H), 3.59 (dd, J = 21.1, 2.6 Hz, 1H), 2.56 (dd, J = 20.9, 2.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.7, 191.0, 163.4, 163.4, 159.2, 158.1, 147.2, 146.8, 145.7, 145.2, 144.3, 141.9, 131.3, 131.1, 130.5, 130.0, 123.5, 123.3, 121.5, 121.6, 105.2, 104.4, 99.0, 98.2, 57.6, 55.7, 55.6, 55.5, 55.4, 52.3, 37.5, 35.6 ppm; IR (film) ν_{max} 1645, 1597, 1515, 1462, 1416, 1343, 1309, 1264, 1208, 1160, 1108, 1066, 1026, 975, 923, 882, 852, 831, 773, 704, 645 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{31}N_2O_{10}^+$ $[M+H]^+$: 651.1973, found 651.1974.

(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis((4-bromophenyl)methanone) (2s)



Prepared according to the general procedure as described above in 38% yield (26.1 mg). It was purified by column chromatography (EtOAc/PE = 1:4) to afford a yellow solid. Mp = 135.8-136.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, J = 8.7 Hz, 2H), 8.11 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.6 Hz, 2H), 7.66 – 7.55 (m, 6H), 7.47 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 6.20 (t, J = 2.5 Hz, 1H), 4.46 (s, 1H), 3.74 (dd, J = 21.0, 2.6 Hz, 1H), 2.75 (dd, J = 20.9, 2.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.0, 190.0, 147.4, 147.3, 144.6, 143.1, 142.5, 140.4, 136.0, 135.4, 132.1, 130.9, 130.5, 129.5, 128.9, 128.7, 127.9, 123.9, 123.9, 57.4, 50.6, 37.4, 35.6 ppm; IR (film) ν_{max} 1747, 1667, 1583, 1515, 1396, 1341, 1250, 1172, 1108, 1070, 1010, 972, 887, 845, 788, 746, 701, 626 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{21}Br_2N_2O_6^+$ $[M+H]^+$: 686.9761, found 686.9759.

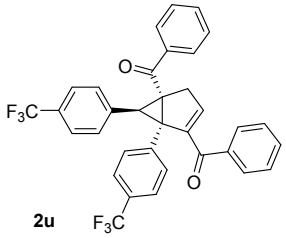
4,4'-(2,5-bis(4-methoxybenzoyl)bicyclo[3.1.0]hex-2-ene-1,6-diyl)dibenzonitrile (2t)



2t

Prepared according to the general procedure as described above in 68% yield (37.5 mg). It was purified by column chromatography (EtOAc/PE = 1:3) to afford a white solid. Mp = 126-127.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, J = 8.9 Hz, 2H), 7.59 – 7.55 (m, 6H), 7.53 – 7.36 (m, 4H), 6.95 (dd, J = 18.1, 8.8 Hz, 4H), 6.16 (t, J = 2.4 Hz, 1H), 4.37 (s, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.72 (dd, J = 20.6, 2.5 Hz, 1H), 2.66 (dd, J = 20.8, 2.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3, 189.8, 163.9, 163.2, 143.4, 143.2, 141.2, 139.2, 132.2, 132.2, 131.6, 131.0, 130.7, 130.4, 129.1, 128.5, 118.7, 118.6, 114.0, 113.9, 111.2, 111.1, 56.6, 55.6, 55.5, 50.7, 37.9, 34.6 ppm; IR (film) ν_{max} 2926, 1646, 1595, 1569, 1507, 1463, 1419, 1311, 1254, 1162, 1115, 1062, 976, 902, 886, 834, 805, 774, 676, 644, 614 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{27}N_2O_4^+$ $[M+H]^+$: 551.1965, found 551.1963.

(5,6-bis(4-(trifluoromethyl)phenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis(phenylmethanone) (2u)

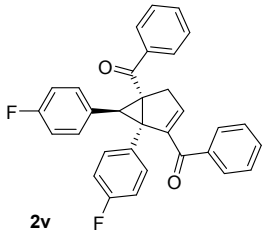


2u

Prepared according to the general procedure as described above in 47% yield (27.2 mg). It was purified by column chromatography (EtOAc/PE = 1:5) to afford a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.78 (m, 2H), 7.57 (s, 5H), 7.52 – 7.34 (m, 11H), 6.18 (t, J = 2.5 Hz, 1H), 4.47 (s, 1H), 3.78 (dd, J = 20.8, 2.5 Hz, 1H), 2.68 (dd, J = 20.8, 2.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1, 191.4, 144.9, 143.5, 139.9, 139.9, 137.9, 137.7, 137.7, 137.4, 133.1, 132.2, 130.4, 129.8 (d, J = 2.8 Hz), 129.4 (d, J = 2.9 Hz), 129.2, 128.6, 128.5, 128.5, 127.9, 125.5, 125.5, 125.4, 125.4, 57.7, 50.3, 37.1, 35.4 ppm; IR (film) ν_{max} 1646, 1410, 1322, 1247, 1162, 1108, 1066, 1018, 884, 744, 703, 670, 592, 578 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{23}F_6O_2^+$ $[M+H]^+$:

577.1597, found 577.1599.

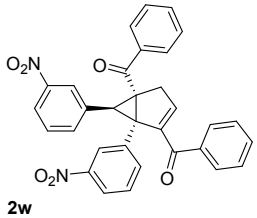
(5,6-bis(4-fluorophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis(phenylmethanone) (2v)



2v

Prepared according to the general procedure as described above in 32% yield (15 mg). It was purified by column chromatography (EtOAc/PE = 1:20) to afford a white solid. Mp = 71.2-72.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 2H), 7.60 – 7.51 (m, 1H), 7.49 – 7.36 (m, 9H), 7.35 – 7.27 (m, 2H), 6.98 (t, J = 8.7 Hz, 2H), 6.88 (t, J = 8.7 Hz, 2H), 6.10 (t, J = 2.5 Hz, 1H), 4.31 (s, 1H), 3.74 (dd, J = 20.6, 2.6 Hz, 1H), 2.63 (dd, J = 20.7, 2.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.0, 191.6, 163.7, 163.6, 144.4, 143.7, 138.2, 137.9, 132.8, 131.8, 131.7, 131.6, 130.0, 129.9, 129.3, 129.3, 129.1, 128.5, 128.3, 127.8, 115.5, 115.2, 58.0, 49.8, 36.7, 35.5 ppm; IR (film) ν_{max} 1645, 1597, 1509, 1447, 1349, 1219, 1156, 1061, 987, 882, 833, 792, 741, 697, 531 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{23}F_2O_2^+$ $[M+H]^+$: 477.1661, found 477.1659.

(5,6-bis(3-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis(phenylmethanone) (2w)

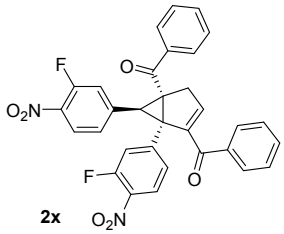


2w

Prepared according to the general procedure as described above in 42% yield (22.3 mg). It was purified by column chromatography (EtOAc/PE = 1:3) to afford a white solid. Mp = 167.5-168.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 – 8.18 (m, 2H), 8.13 (dd, J = 8.2, 2.1 Hz, 1H), 8.04 (dd, J = 8.1, 2.1 Hz, 1H), 7.83 (dd, J = 7.6, 5.5 Hz, 3H), 7.73 (d, J = 7.9 Hz, 1H), 7.62 – 7.38 (m, 10H), 6.21 (t, J = 2.6 Hz, 1H), 4.49 (s, 1H), 3.81 (dd, J = 21.0, 2.5 Hz, 1H), 2.69 (dd, J = 21.1, 2.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 191.5, 148.4, 148.2, 145.2, 143.5, 137.9, 137.7, 137.1, 136.4,

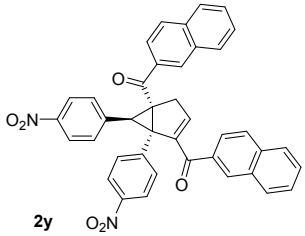
135.3, 134.4, 133.2, 132.5, 129.6, 129.5, 129.0, 128.7, 127.9, 125.0, 123.3, 122.7, 122.7, 57.3, 50.3, 37.3, 35.2 ppm; IR (film) ν_{max} 2926, 1668, 1628, 1597, 1525, 1446, 1347, 1248, 1161, 1095, 1057, 1027, 993, 938, 883, 855, 809, 771, 734, 719, 690, 669, 638, 606,583 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{23}N_2O_6^+$ $[M+H]^+$: 531.1551, found 531.1551.

(5,6-bis(3-fluoro-4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis(phenylmethanone) (2x)



Prepared according to the general procedure as described above in 52% yield (29.6 mg). It was purified by column chromatography (EtOAc/PE = 1:3) to afford a white solid. Mp = 114.9-115.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (dt, J = 22.4, 8.1 Hz, 2H), 7.86 (d, J = 7.4 Hz, 3H), 7.62 – 7.45 (m, 9H), 7.38 (t, J = 10.0 Hz, 2H), 7.23 (d, J = 4.3 Hz, 1H), 6.28 (t, J = 2.5 Hz, 1H), 4.41 (s, 1H), 3.81 (dd, J = 21.1, 2.5 Hz, 1H), 2.75 (dd, J = 21.0, 2.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.3, 191.2, 157.3, 153.7, 145.1, 144.6 (d, J = 7.7 Hz), 143.0, 142.2 (d, J = 8.3 Hz), 137.2, 136.6 (d, J = 7.6 Hz), 136.4, 136.3 (d, J = 7.1 Hz), 133.7, 133.0, 129.1, 128.9, 128.0, 126.4, 126.1 (d, J = 3.8 Hz), 124.0 (d, J = 3.9 Hz), 120.0, 119.7, 118.2, 117.9, 56.6, 51.1, 37.6, 35.0 ppm; IR (film) ν_{max} 1645, 1598, 1520, 1447, 1343, 1246, 1064, 975, 899, 838, 740, 697 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{21}F_2N_2O_6^+$ $[M+H]^+$: 567.1362, found 567.1366.

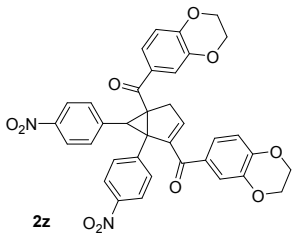
(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis(naphthalen-2-ylmethanone) (2y)



Prepared according to the general procedure as described above in 43% yield (27 mg).

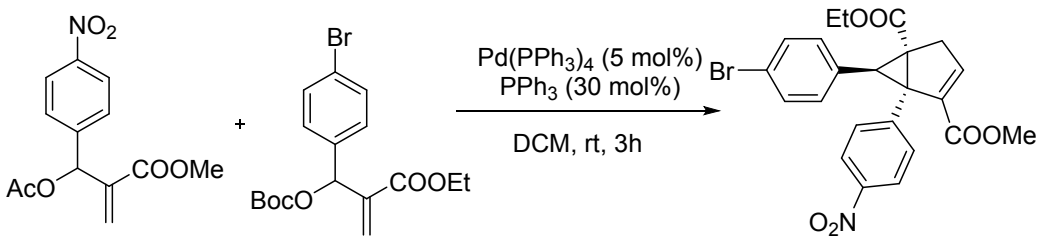
It was purified by column chromatography (EtOAc/PE = 1:2) to afford a yellow solid. Mp = 123.2-124.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, J = 8.7 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H), 8.10 (dd, J = 8.2, 1.7 Hz, 1H), 7.99 – 7.91 (m, 3H), 7.87 – 7.82 (m, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.66 – 7.61 (m, 3H), 7.60 – 7.40 (m, 6H), 7.23 (dd, J = 7.1, 1.3 Hz, 1H), 6.06 (t, J = 2.5 Hz, 1H), 4.57 (s, 1H), 3.69 (dd, J = 21.1, 2.5 Hz, 1H), 2.70 (dd, J = 21.2, 2.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.3, 193.0, 147.6, 147.5, 147.3, 145.5, 143.3, 140.9, 135.8, 135.3, 133.8, 133.6, 132.4, 131.3, 130.8, 130.4, 130.3, 129.6, 128.7, 128.5, 128.0, 127.8, 127.4, 126.8, 126.8, 124.7, 124.7, 124.4, 124.3, 123.9, 123.8, 123.8, 58.5, 51.9, 37.6, 36.1 ppm; IR (film) ν_{max} 1645, 1598, 1515, 1342, 1276, 1239, 1107, 1014, 943, 893, 853, 778, 734, 702, 583 cm^{-1}; HRMS (ESI) calcd for $C_{40}H_{27}N_2O_6^+$ $[M+H]^+$: 631.1864, found 631.1862.

(5,6-bis(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-diyl)bis((2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)methanone) (2z)



Prepared according to the general procedure as described above in 43% yield (28 mg). It was purified by column chromatography (EtOAc/ petroleum ether = 1:2) to afford a yellow solid. Mp = 163.5-164.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, J = 8.8 Hz, 2H), 8.04 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H), 7.52 – 7.42 (m, 4H), 7.14 – 7.11 (m, 2H), 7.04 – 6.81 (m, 2H), 6.20 (t, J = 2.3 Hz, 1H), 4.43 (s, 1H), 4.39 – 4.17 (m, 8H), 3.76 (dd, J = 20.8, 2.5 Hz, 1H), 2.68 (dd, J = 20.8, 2.4 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.8, 189.6, 148.5, 147.9, 147.2, 147.0, 143.6, 143.4, 143.2, 143.1, 141.2, 131.1, 131.0, 129.8, 128.7, 123.7, 123.7, 123.4, 122.3, 118.7, 117.9, 117.5, 117.4, 64.7, 64.6, 64.1, 64.1, 56.6, 51.16, 38.06, 34.5 ppm; IR (film) ν_{max} 1660, 1600, 1581, 1508, 1425, 1343, 1288, 1259, 1109, 1066, 890, 853, 829, 795, 775, 747, 714, 688 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{27}N_2O_{10}^+$ $[M+H]^+$: 647.1660, found 647.1660.

4. Synthesis of compound 6.

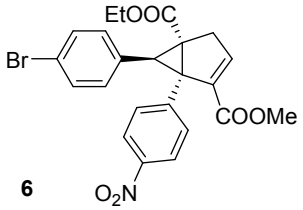


3 **4** **6**

To a dried Schlenk tube equipped with a stir bar were added compound **4** (77 mg, 0.2 mmol) and PPh_3 (8 mg, 0.03 mmol) in 2 mL CH_2Cl_2. Then compound **3** (28 mg, 0.1 mmol) and $Pd(PPh_3)_4$ (5 mg, 0.005 mmol) were added. This solution was stirred at room temperature for 3 h, and monitored by TLC (ethyl acetate /petroleum ether). After complete conversion, the product **6** was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1:6): 5 mg as a white solid（10% yield）.

1-ethyl 4-methyl 6-(4-bromophenyl)-5-(4-nitrophenyl)bicyclo[3.1.0]hex-3-ene-1,4-

dicarboxylate (6)



6

Mp = 112.3-113.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 6.42 (t, J = 2.5 Hz, 1H), 4.00 (s, 1H), 3.91 (q, J = 7.2 Hz, 2H), 3.61 (dd, J = 21.0, 2.3 Hz, 1H), 3.60 (s, 3H), 2.46 (dd, J = 21.0, 2.4 Hz, 1H), 0.89 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 163.7, 147.1, 144.9, 144.1, 135.8, 131.9, 131.7, 131.6, 130.0, 123.5,

121.4, 61.3, 53.9, 51.8, 43.4, 36.2, 33.5, 13.9 ppm; IR (film) ν_{max} 2925, 1710, 1596, 1519, 1489, 1460, 1368, 1346, 1297, 1262, 1241, 1173, 1145, 1090, 1072, 1041, 982, 933, 863, 852, 808, 792, 767, 757, 699, 536 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{20}BrNNaO_6^+$ $[M+Na]^+$: 508.0366, found 508.0364.

5. Mechanistic Investigations

5.1 HRMS study

Dectection of intermediate D： To a dry flask filled with nitrogen were added **1** (0.2 mmol) in 2 mL CH_2Cl_2， then PPh_3 (0.03 mmol) and $Pd(PPh_3)_4$ (0.005 mmol) were added. This solution was stirred at room temperature for 10 mins. Then a small aliquot was injected in the machine for mass spectrometry. As shown in Figure S1, the proposed intermediate **D** can be found with MW = 729.2371 ($[M+H]_+$).

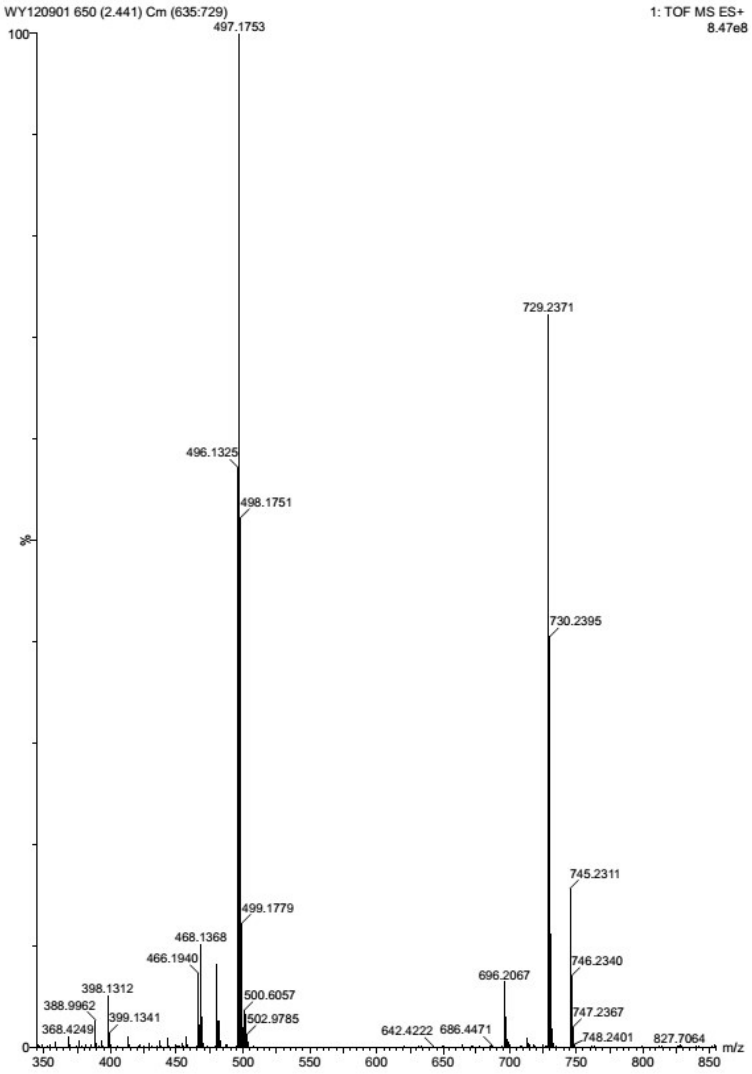
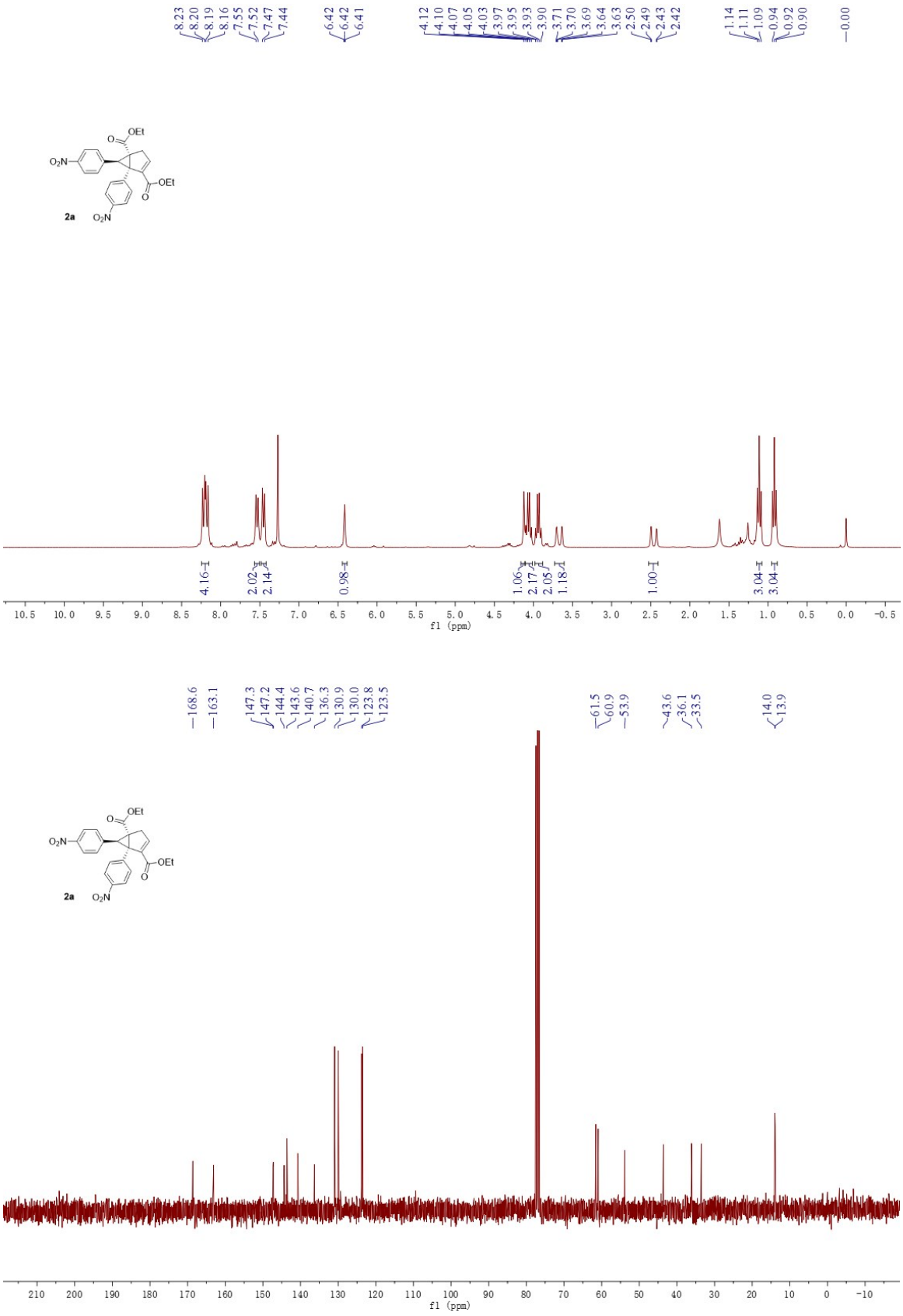
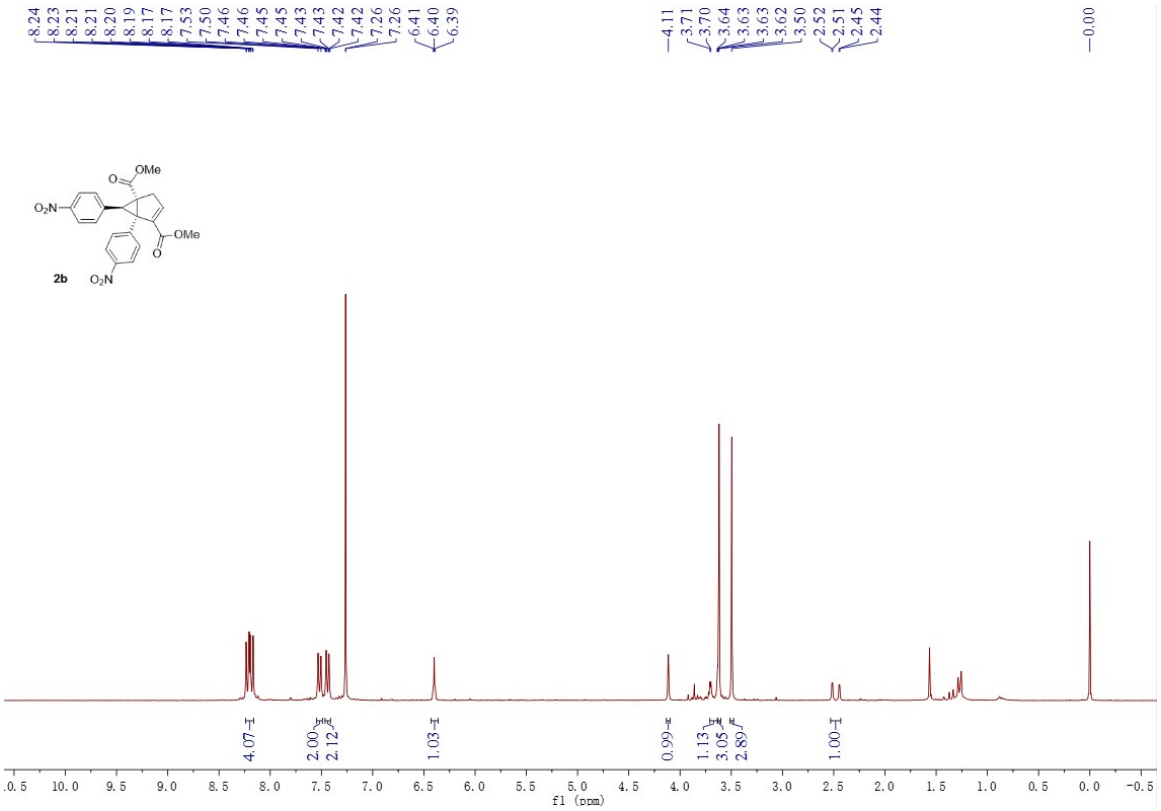


Figure S1. HRMS analysis of the intermediate **D.**

6. ^{1}H, ^{13}C NMR spectra for compounds

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7.43
7.43
7.42
7.42
7.26
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3.63
3.62
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2.52
2.51
2.45
2.44
0.00
OMe
O
O2N
OMe
O
2b
O2N
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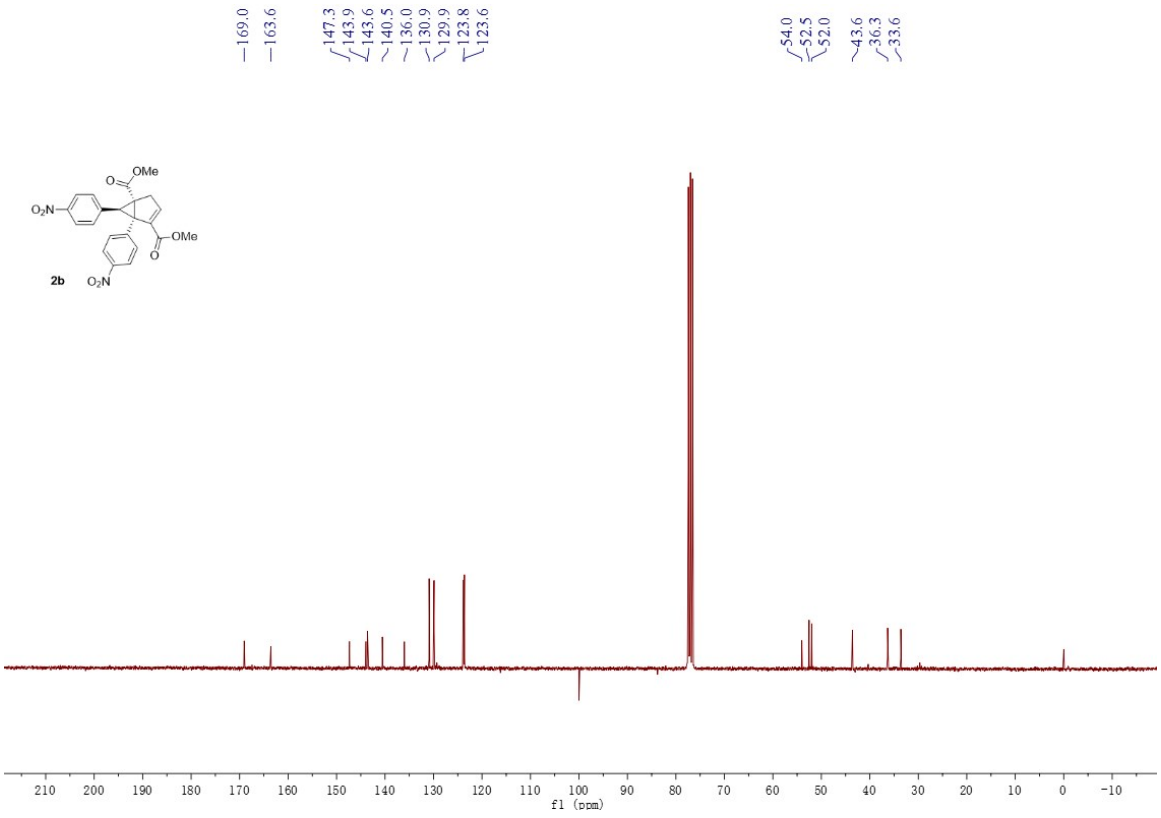
2.12
1.03
0.99
1.13
3.05
2.89
1.00
f1 (ppm)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136.0
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123.8
123.6
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33.6
OMe
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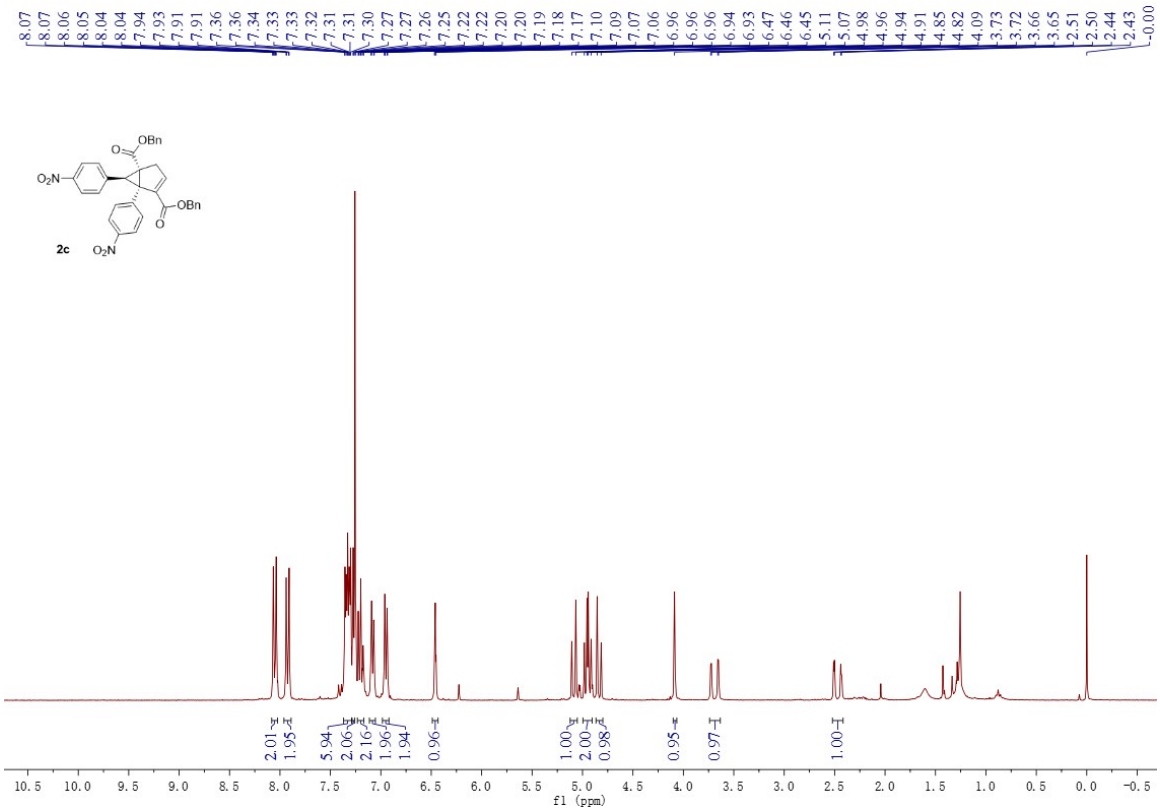
O2N
OMe
O
2b
O2N
f1 (ppm)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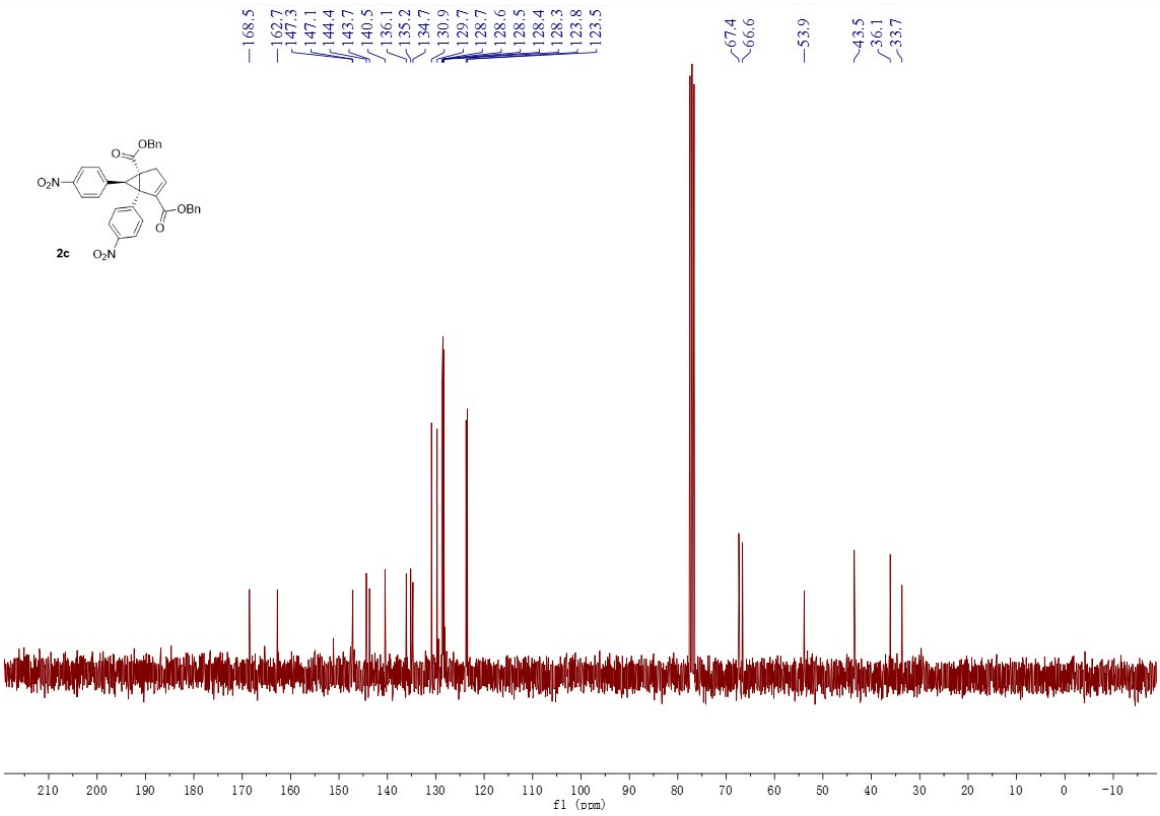
OBn
O2N
OBn
O
O
2c
O2N
2.01 1.95 5.94 2.06 2.16 1.96 1.94 0.96 1.00 2.00 0.98 0.95 0.97 1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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67.4 66.6 53.9 43.5 36.1 33.7
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OBn
O
O
2c
O2N
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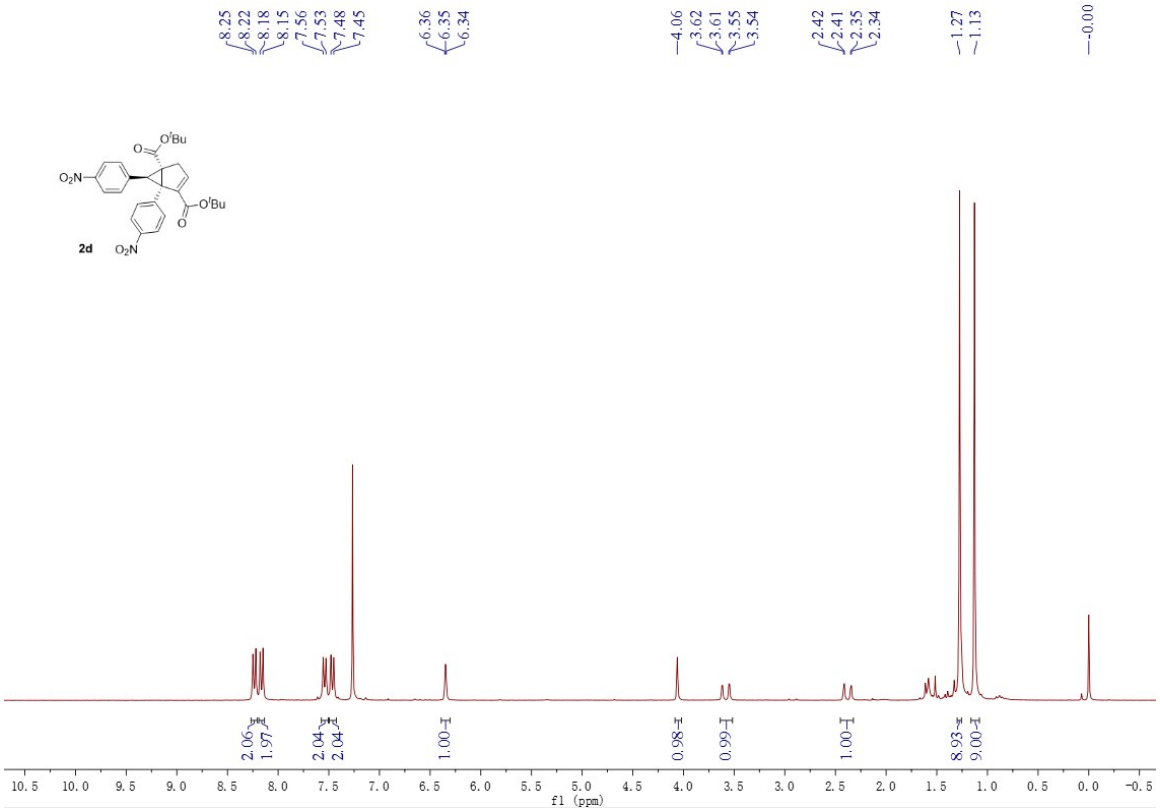
f1 (ppm)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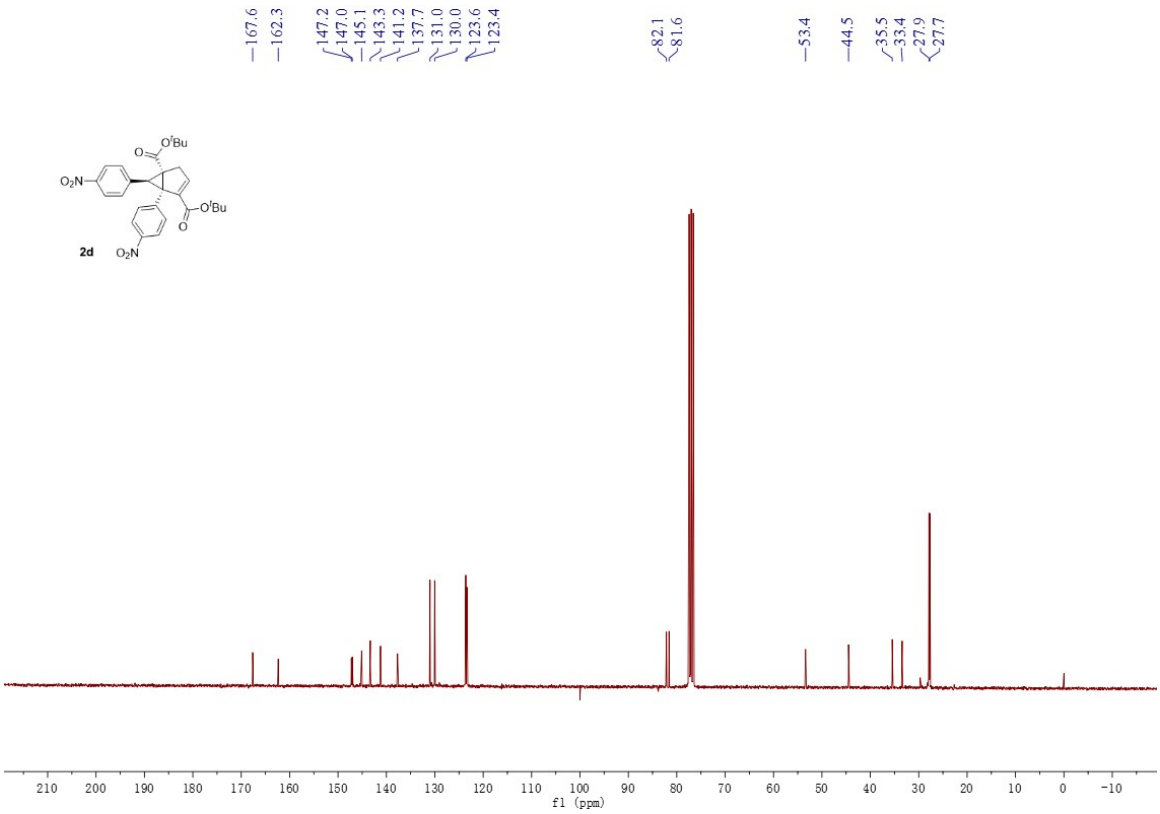
f1 (ppm)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33.4
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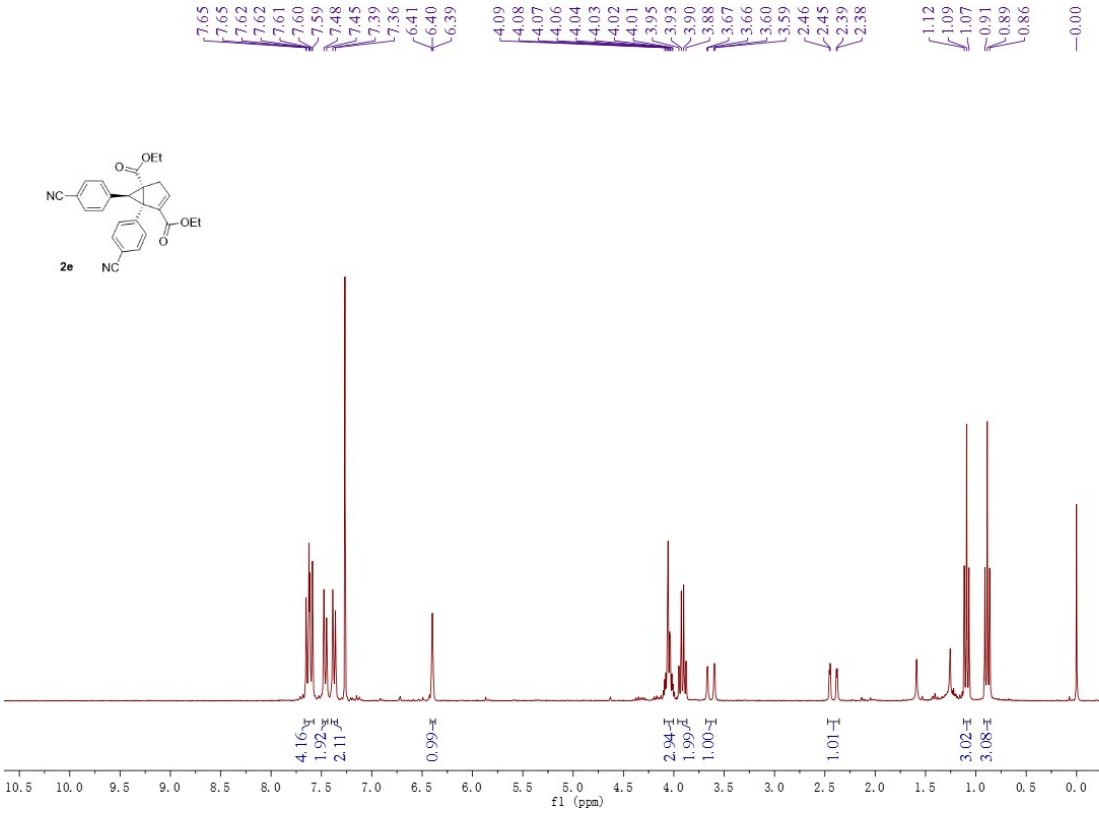
27.7
2d
f1 (ppm)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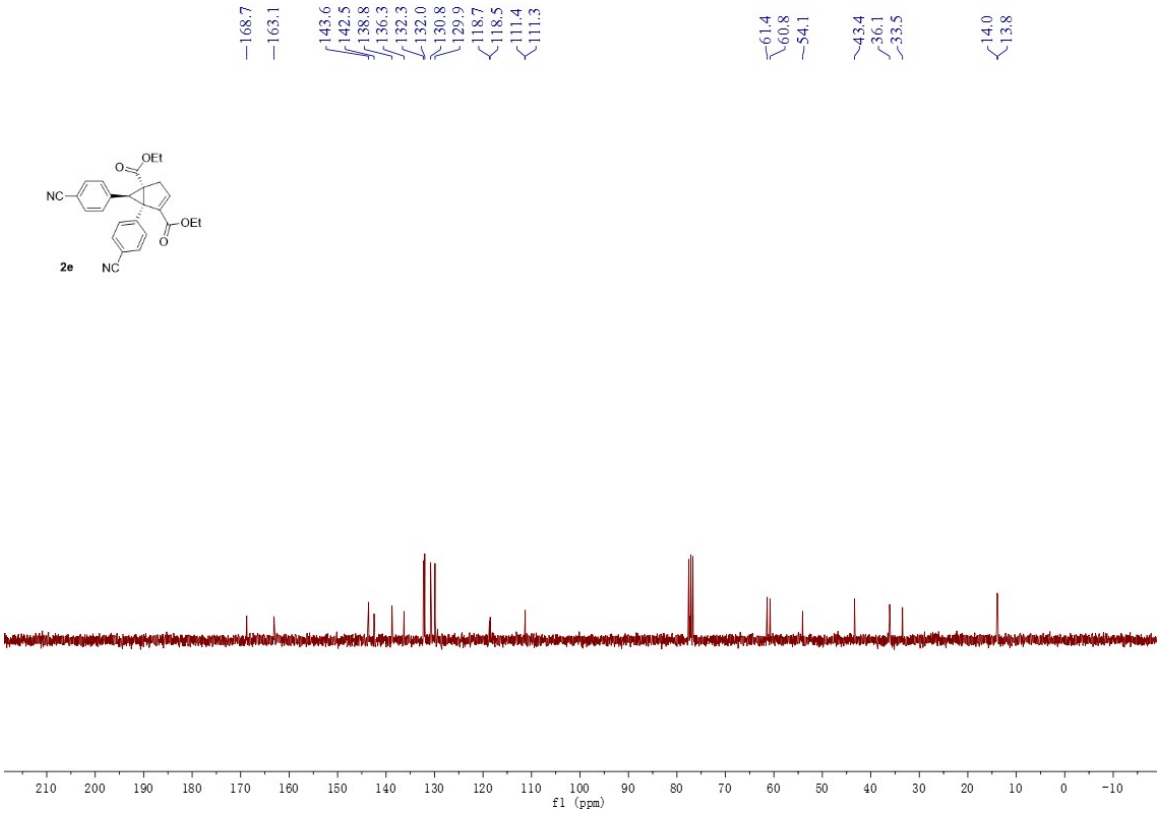
3.08
f1 (ppm)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NC
OEt
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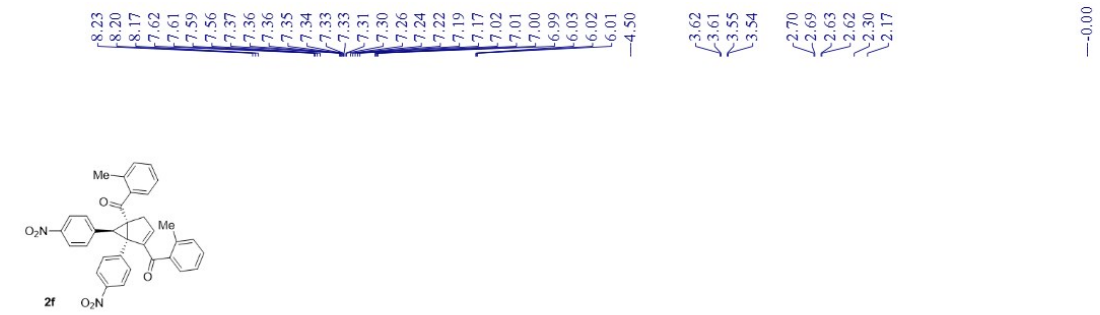
NC
f1 (ppm)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O2N
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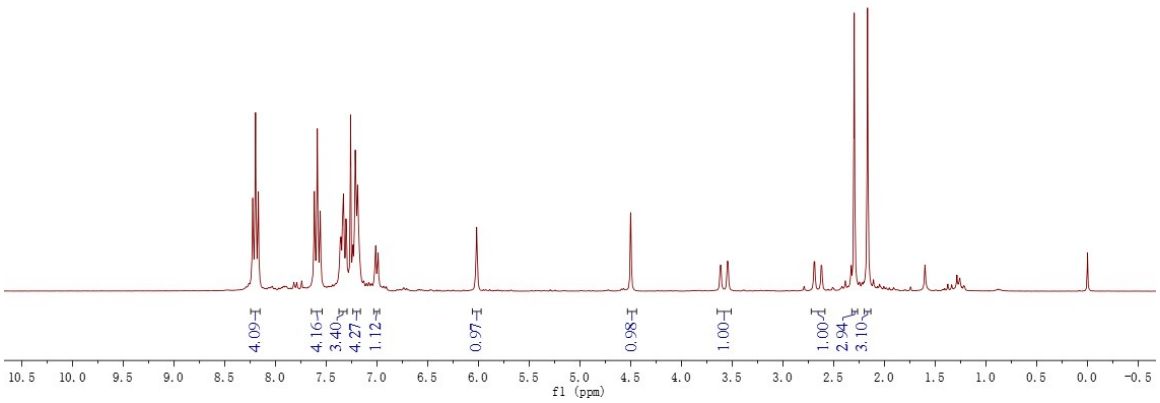
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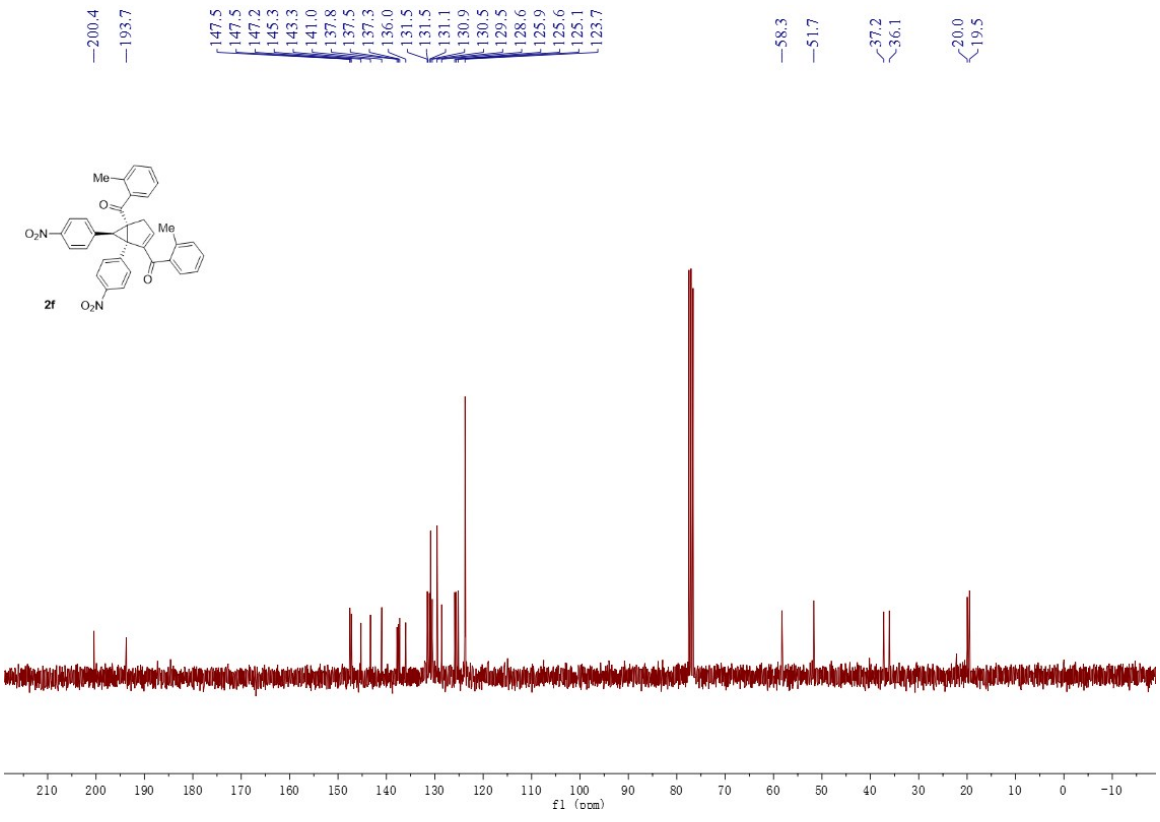
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128.6
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125.1
123.7
58.3
51.7
37.2
36.1
20.0
19.5
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f1 (ppm)

Me
O
Me
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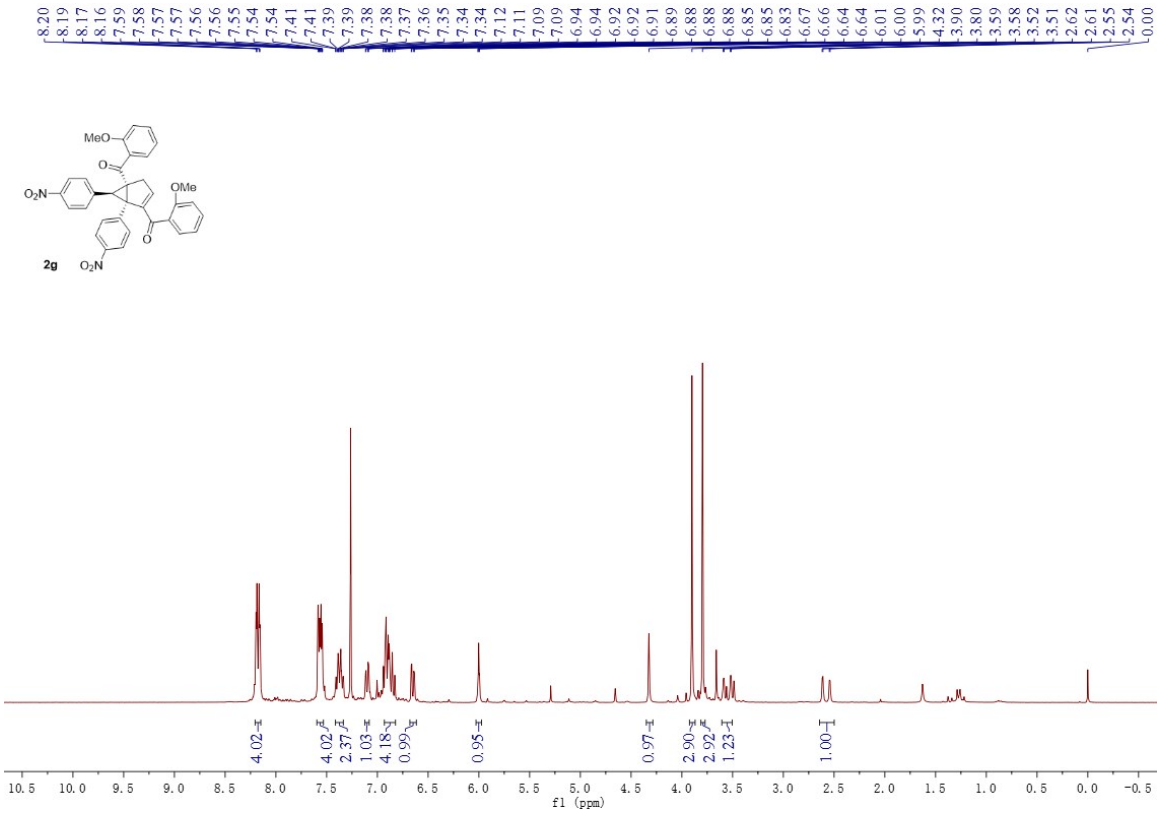
O2N
O2N
2f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MeO
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O2N
OMe
O
2g
O2N
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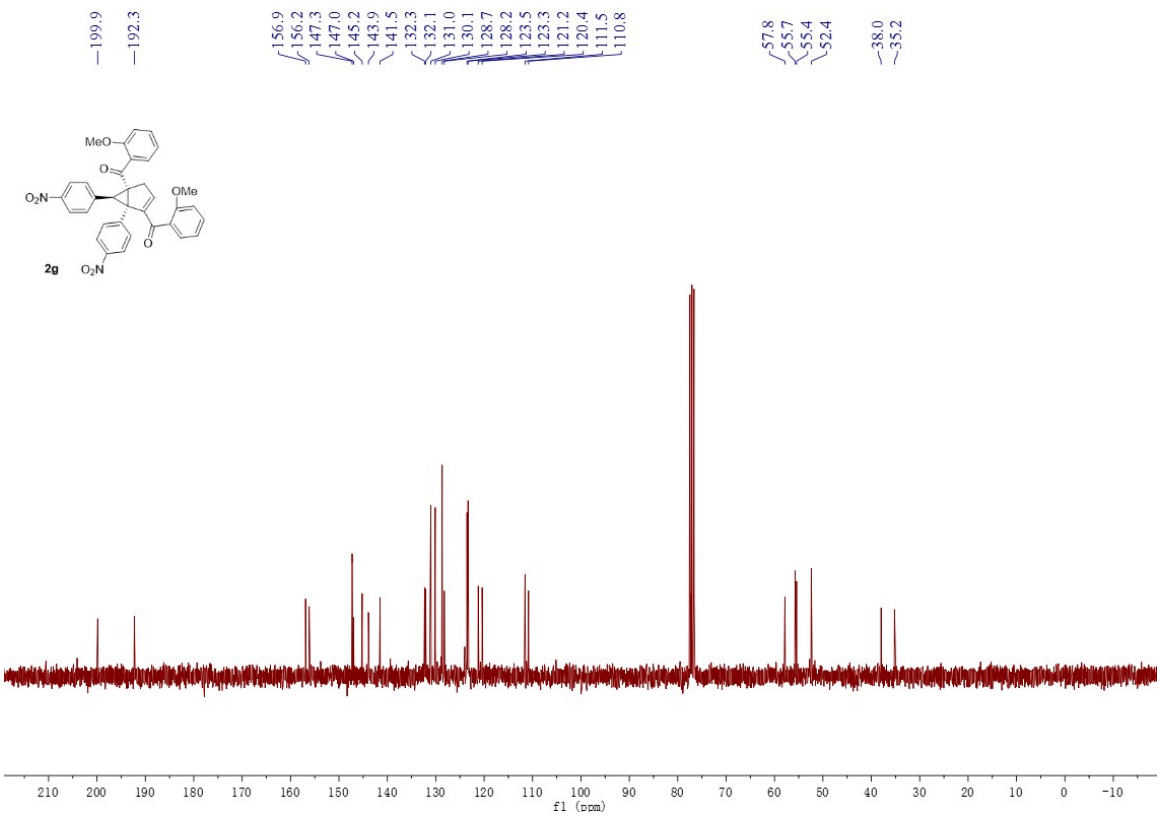
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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O
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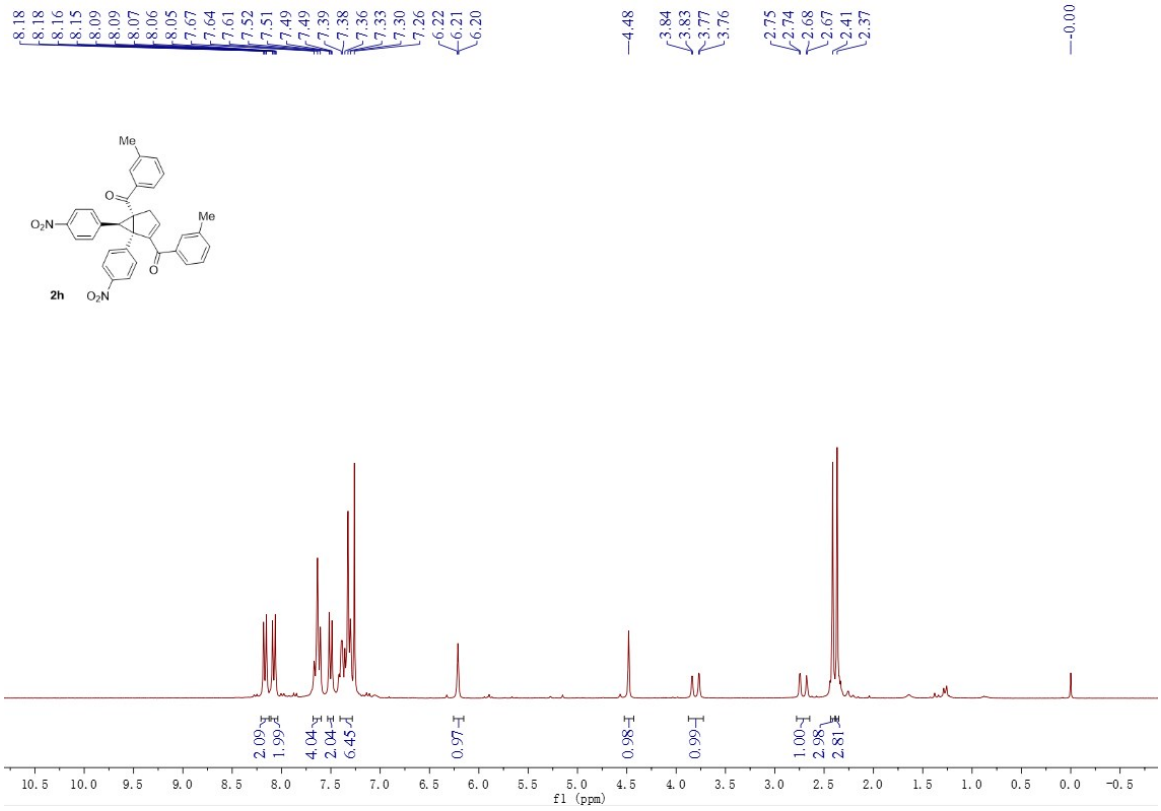
OMe
O
2g
O2N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.33
7.30
7.26
6.22
6.21
6.20
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3.83
3.77
3.76
2.75
2.74
2.68
2.67
2.41
2.37
0.00
Me
O
O2N
Me
O
2h
O2N
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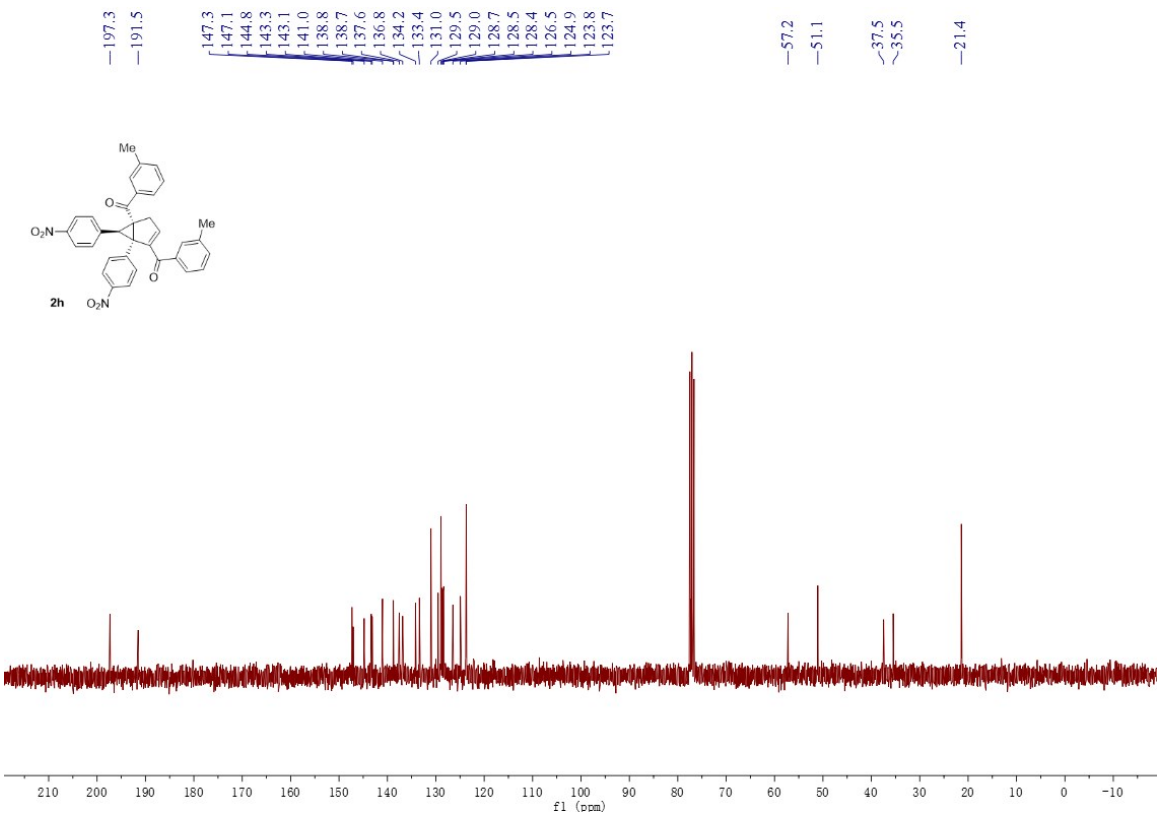
1.99
4.04
2.04
6.45
0.97
0.98
0.99
1.00
2.98
2.81
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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131.0
129.5
129.0
128.7
128.5
128.4
126.5
124.9
123.8
123.7
57.2
51.1
37.5
35.5
21.4
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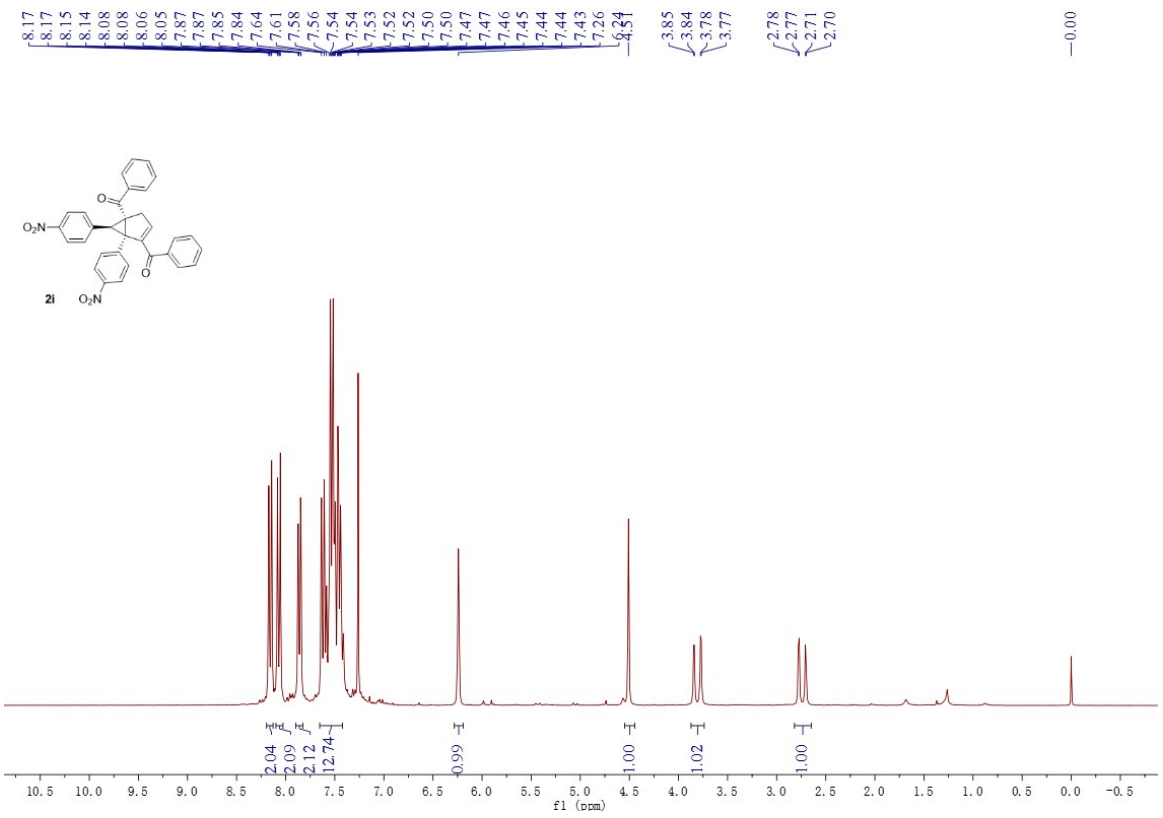
Me
O
2h
O2N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.64
7.61
7.58
7.56
7.54
7.54
7.53
7.52
7.52
7.50
7.50
7.47
7.47
7.46
7.45
7.44
7.44
7.43
7.26
6.24
4.51
3.85
3.84
3.78
3.77
2.78
2.77
2.71
2.70
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2.09
2.12
12.74
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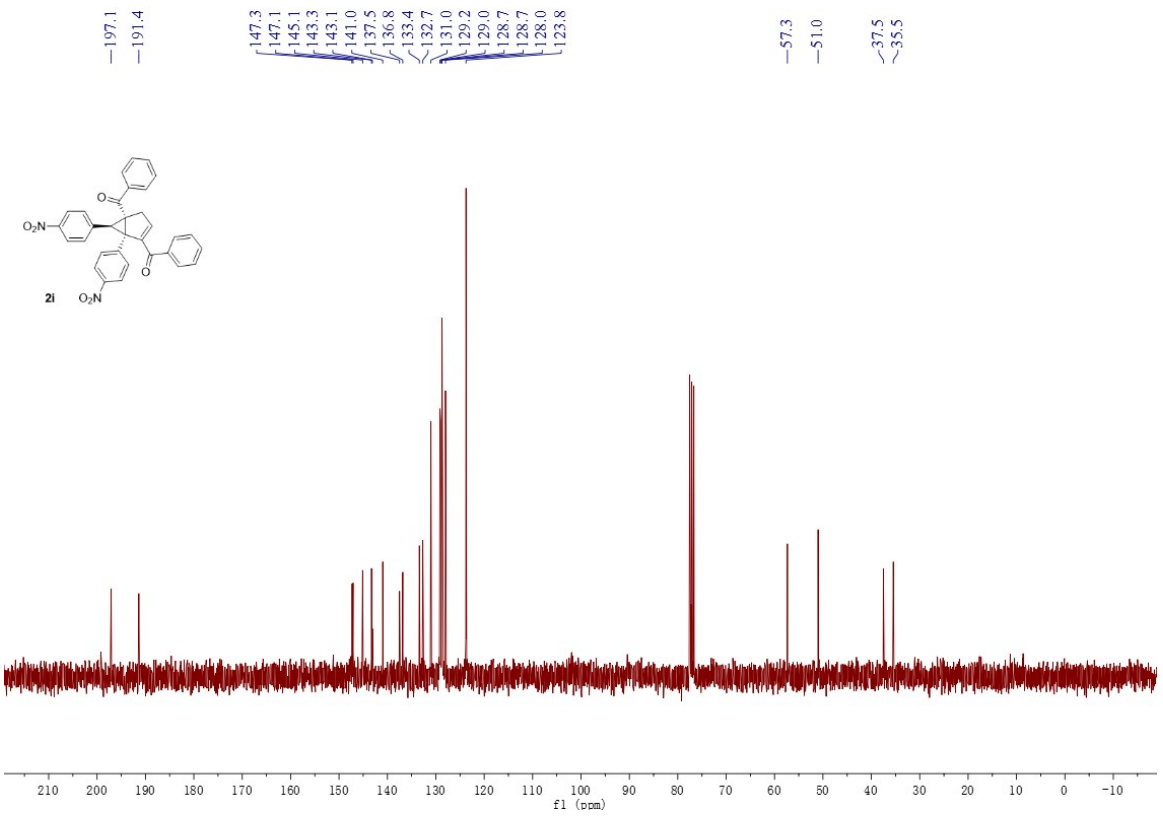
1.00
f1 (ppm)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143.1
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131.0
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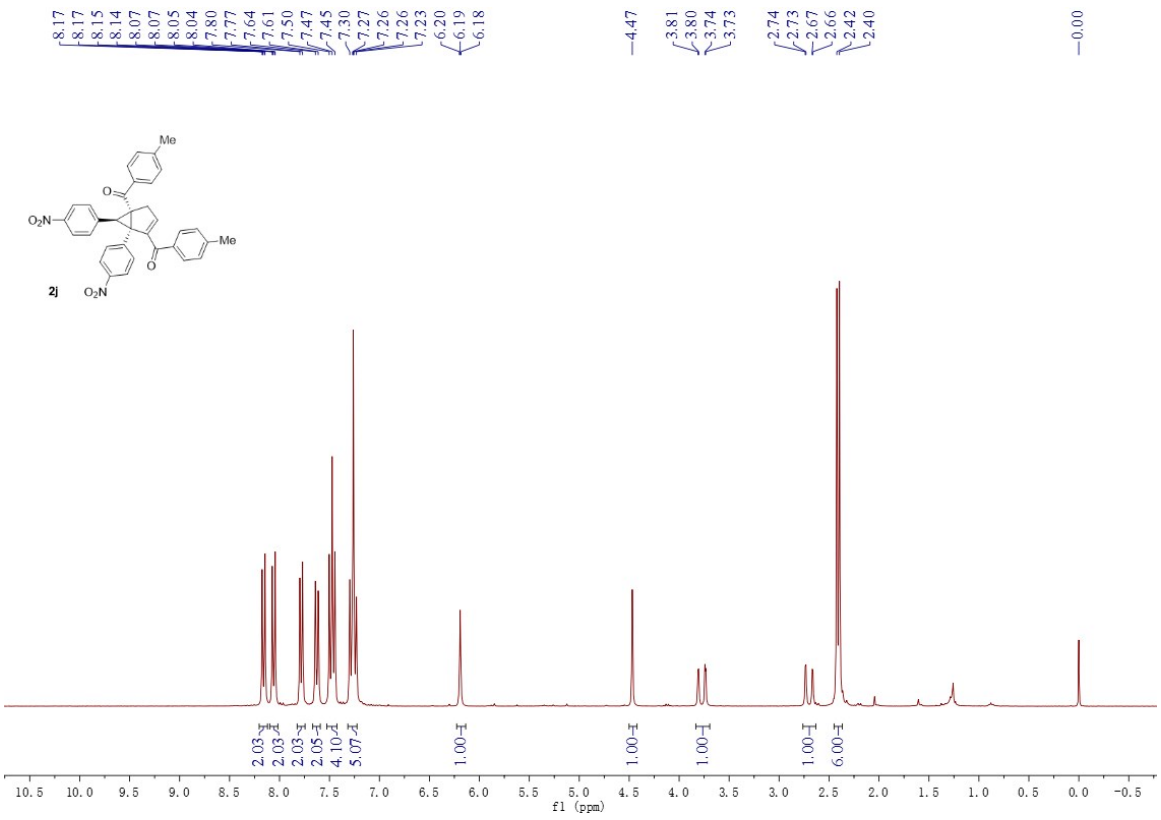
128.7
128.0
123.8
57.3
51.0
37.5
35.5
2i
f1 (ppm)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7.50
7.47
7.45
7.30
7.27
7.26
7.26
7.23
6.20
6.19
6.18
4.47
3.81
3.80
3.74
3.73
2.74
2.73
2.67
2.66
2.42
2.40
0.00
Me
O
O2N
Me
O
2j
O2N
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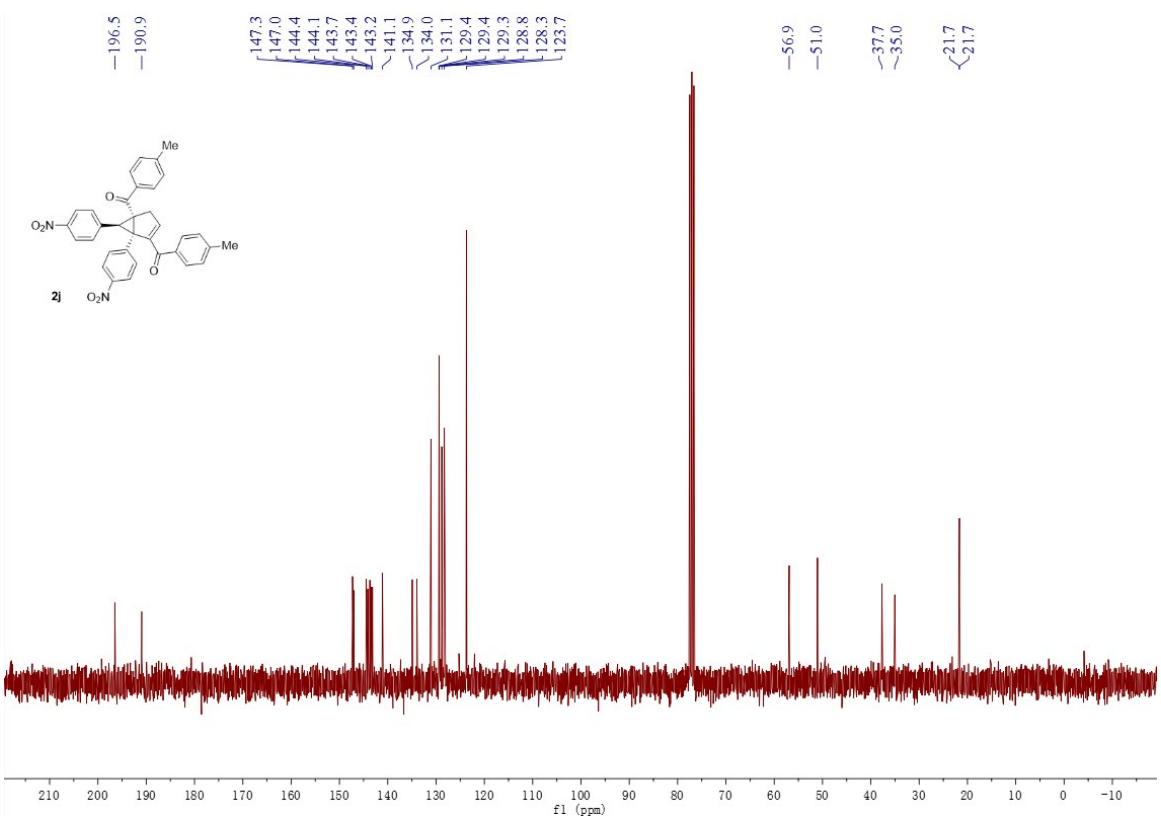
2.05
4.10
5.07
1.00
1.00
1.00
1.00
6.00
f1 (ppm)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134.0
131.1
129.4
129.4
129.3
128.8
128.3
123.7
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51.0
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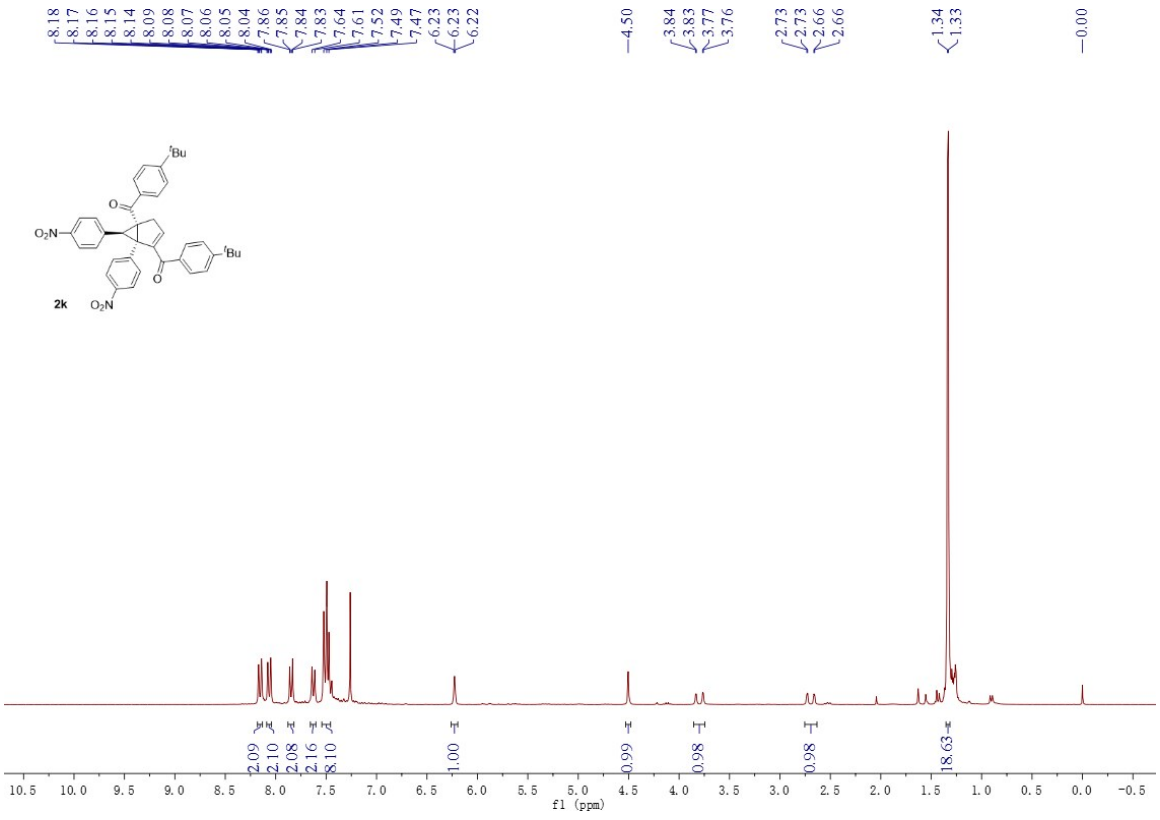
35.0
21.7
21.7
Me
O
O2N
Me
O
2j
O2N
f1 (ppm)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8.07
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8.05
8.04
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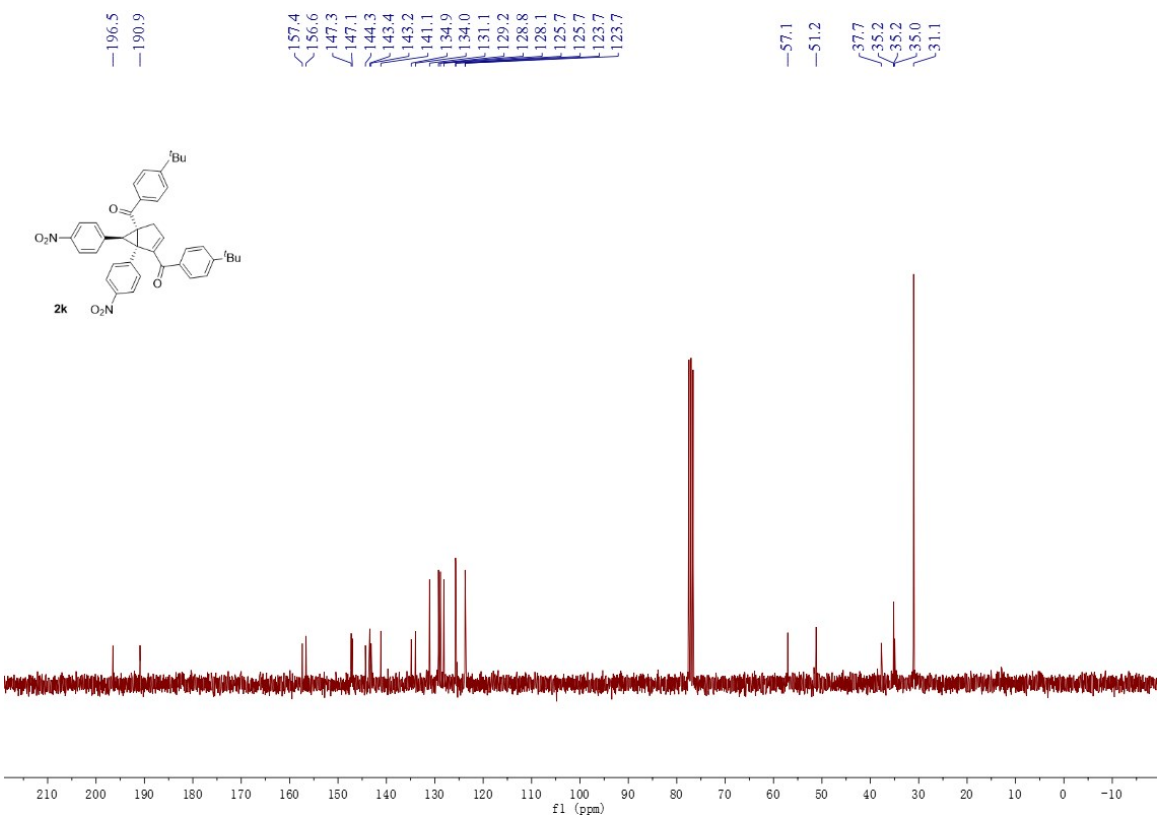
7.85
7.84
7.83
7.64
7.61
7.52
7.49
7.47
6.23
6.23
6.22
4.50
3.84
3.83
3.77
3.76
2.73
2.73
2.66
2.66
1.34
1.33
0.00
2k
2.09
2.10
2.08
2.16
8.10
1.00
0.99
0.98
0.98
18.63
f1 (ppm)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157.4
156.6
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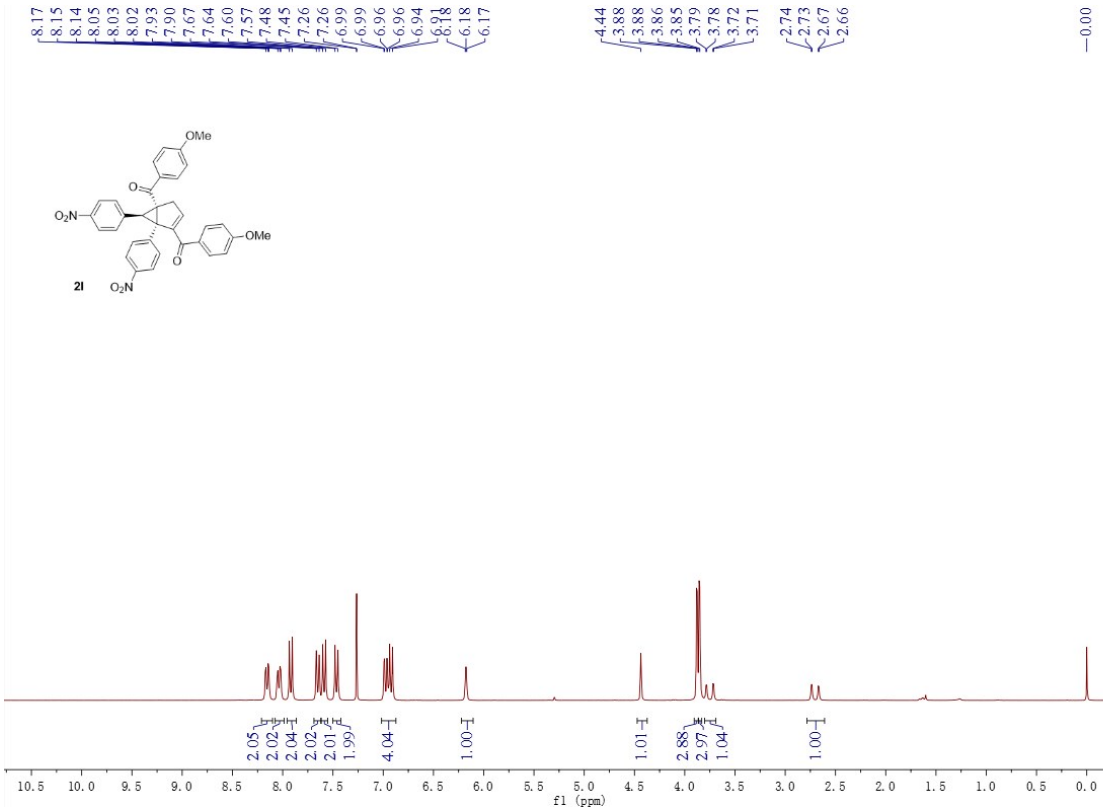
147.1
144.3
143.4
143.2
141.1
134.9
134.0
131.1
129.2
128.8
128.1
125.7
125.7
123.7
123.7
57.1
51.2
37.7
35.2
35.2
35.0
31.1
2k
f1 (ppm)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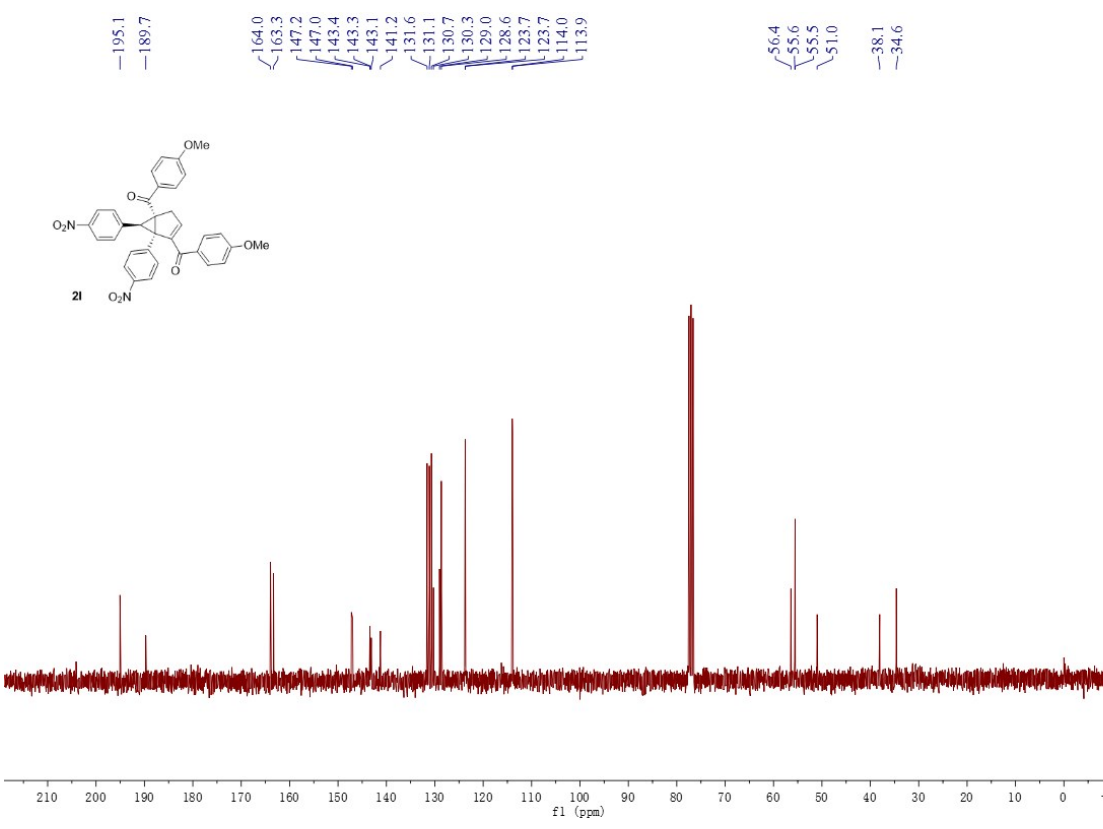
7.45
7.26
7.26
6.99
6.99
6.96
6.96
6.94
6.91
6.18
6.18
6.17
4.44
3.88
3.88
3.86
3.85
3.79
3.78
3.72
3.71
2.74
2.73
2.67
2.66
0.00
OMe
O
O2N
OMe
O
2l
O2N
2.05
2.02
2.04
2.02
2.01
1.99
4.04
1.00
1.01
2.88
2.97
1.04
1.00
f1 (ppm)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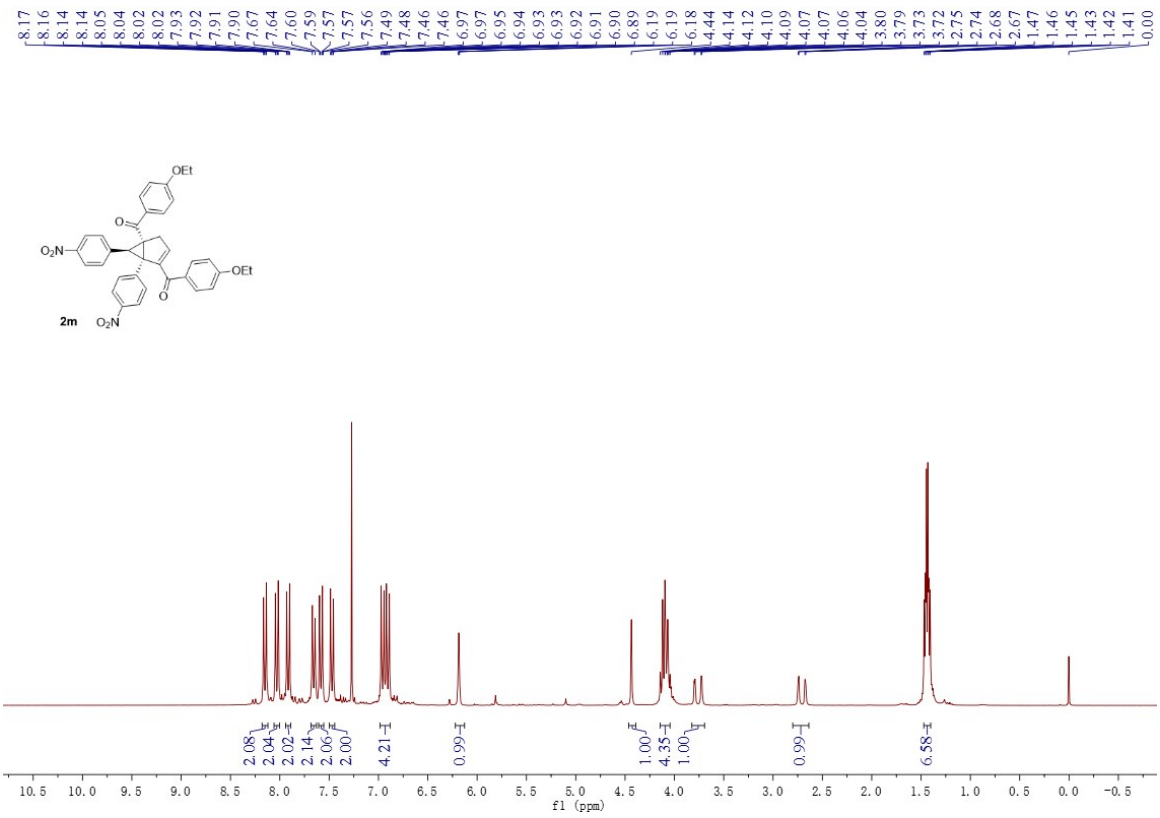
141.2
131.6
131.1
130.7
130.3
129.0
128.6
123.7
123.7
114.0
113.9
56.4
55.6
55.5
51.0
38.1
34.6
OMe
O
O2N
OMe
O
2l
O2N
f1 (ppm)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7.64
7.60
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7.57
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7.56
7.49
7.48
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7.46
6.97
6.97
6.95
6.94
6.93
6.93
6.92
6.91
6.90
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6.19
6.18
4.44
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4.09
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4.07
4.06
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2.68
2.67
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1.45
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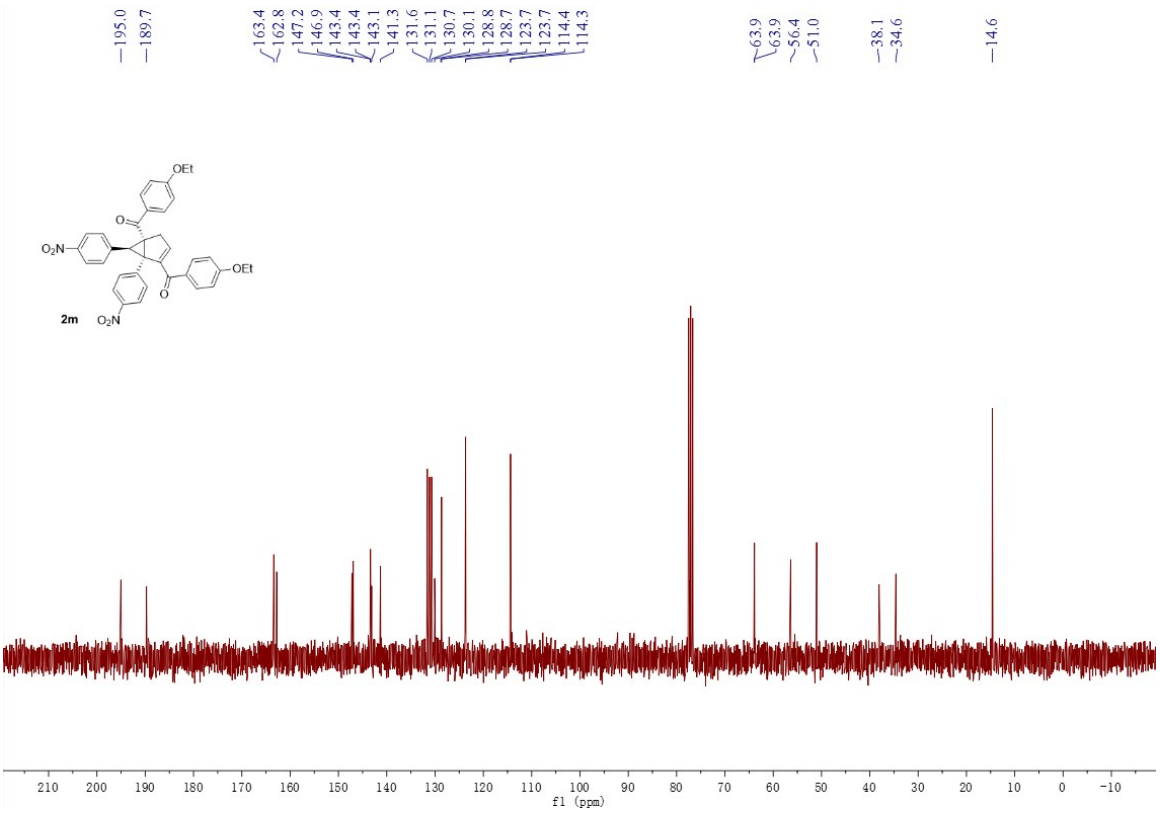
1.42
1.41
0.00
OEt
O
O2N
OEt
O
2m
O2N
2.08
2.04
2.02
2.14
2.06
2.00
4.21
0.99
1.00
4.35
1.00
0.99
6.58
f1 (ppm)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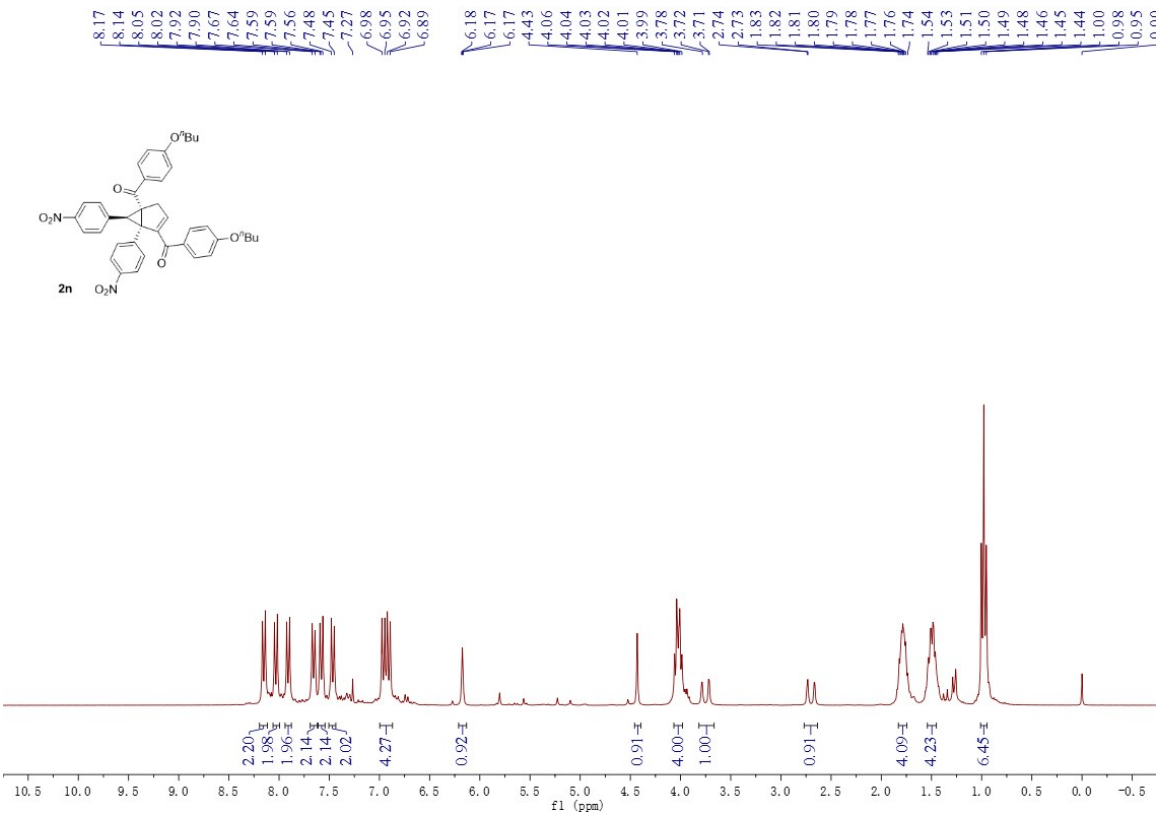
131.1
130.7
130.1
128.8
128.7
123.7
123.7
114.4
114.3
63.9
63.9
56.4
51.0
38.1
34.6
14.6
OEt
O
O2N
OEt
O
2m
O2N
f1 (ppm)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7.59
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7.45
7.27
6.98
6.95
6.92
6.89
6.18
6.17
6.17
4.43
4.06
4.04
4.03
4.02
4.01
3.99
3.78
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3.71
2.74
2.73
1.83
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.74
1.54
1.53
1.51
1.50
1.49
1.48
1.46
1.45
1.44
1.00
0.98
0.95
O^{n}Bu
O
O$_2$N
O^{n}Bu
O
2n
O$_2$N
2.20
1.98
1.96
2.14
2.14
2.02
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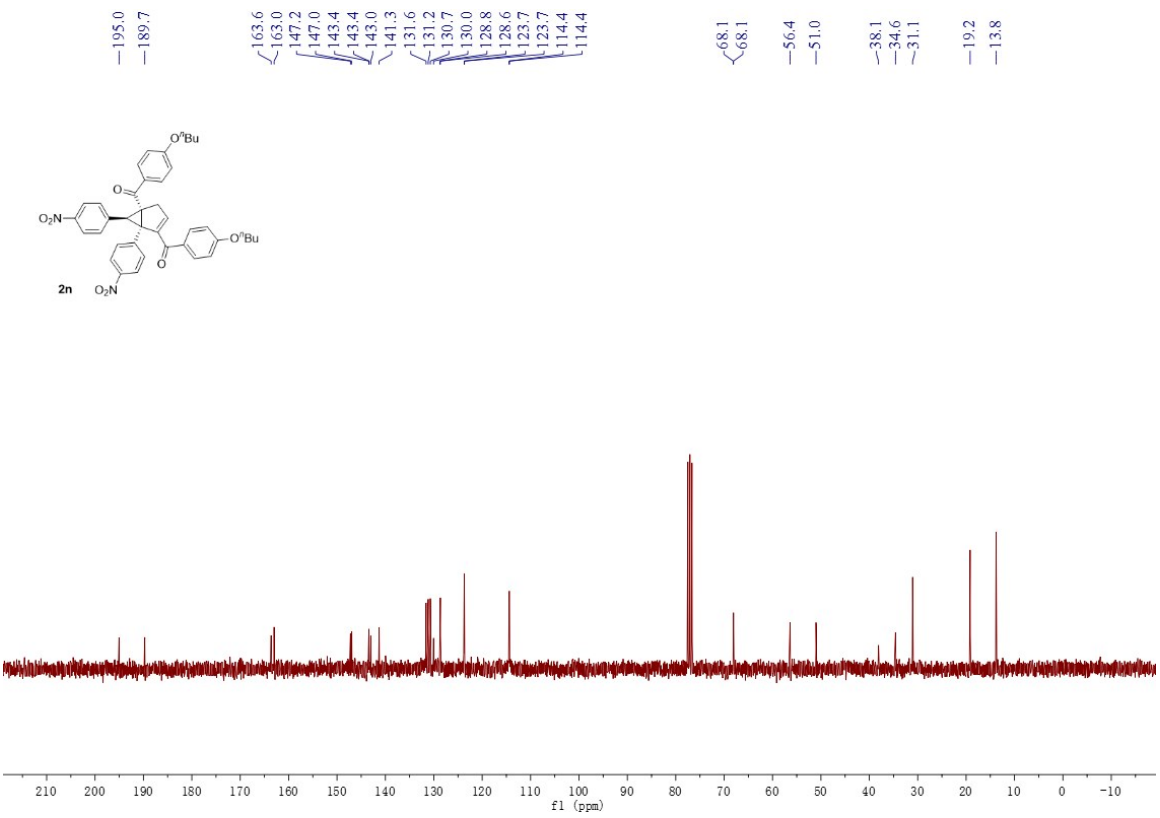
0.92
0.91
4.00
1.00
0.91
4.09
4.23
6.45
f1 (ppm)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163.0
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143.4
143.0
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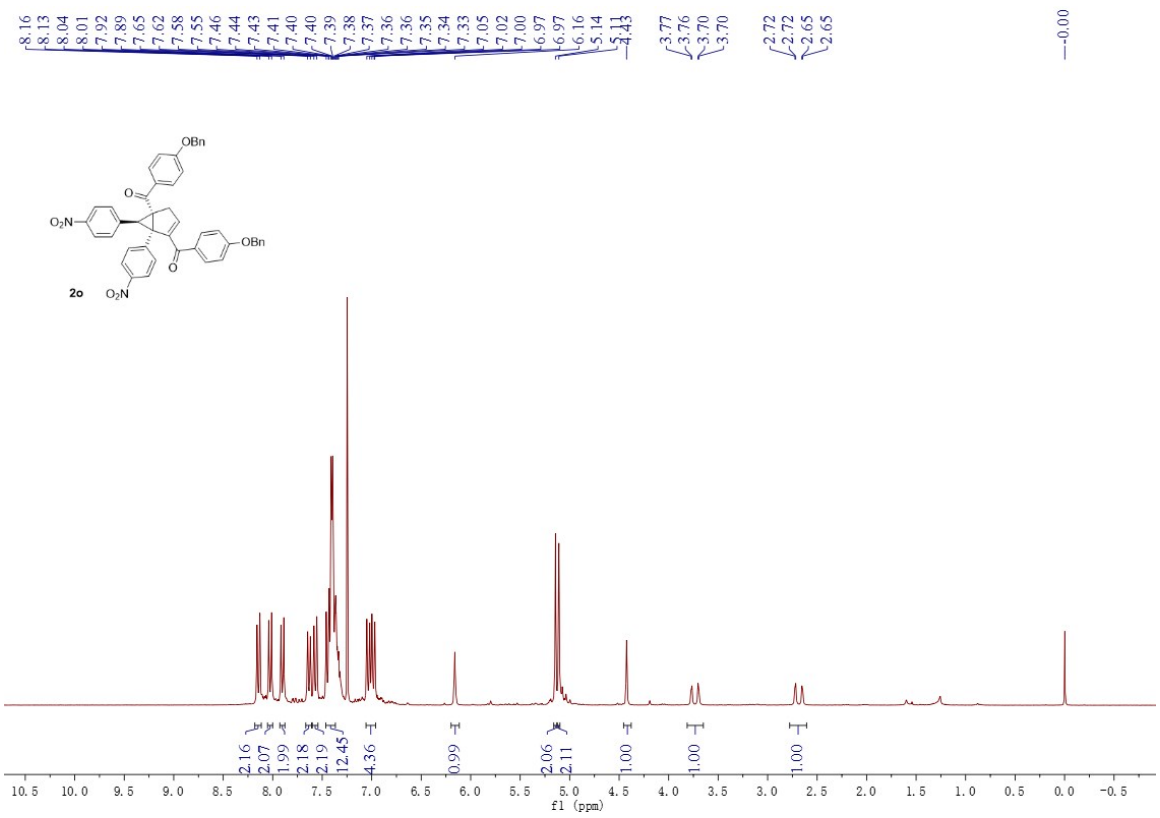
131.6
131.2
130.7
130.0
128.8
128.6
123.7
123.7
114.4
114.4
68.1
68.1
56.4
51.0
38.1
34.6
31.1
19.2
13.8
O^{n}Bu
O
O$_2$N
O^{n}Bu
O
2n
O$_2$N
f1 (ppm)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7.43
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7.40
7.40
7.39
7.38
7.37
7.36
7.36
7.35
7.34
7.33
7.05
7.02
7.00
6.97
6.97
6.16
5.14
5.11
4.43
3.77
3.76
3.70
3.70
2.72
2.72
2.65
2.65
0.00
OBn
O
O2N
OBn
O
2o
O2N
2.16
2.07
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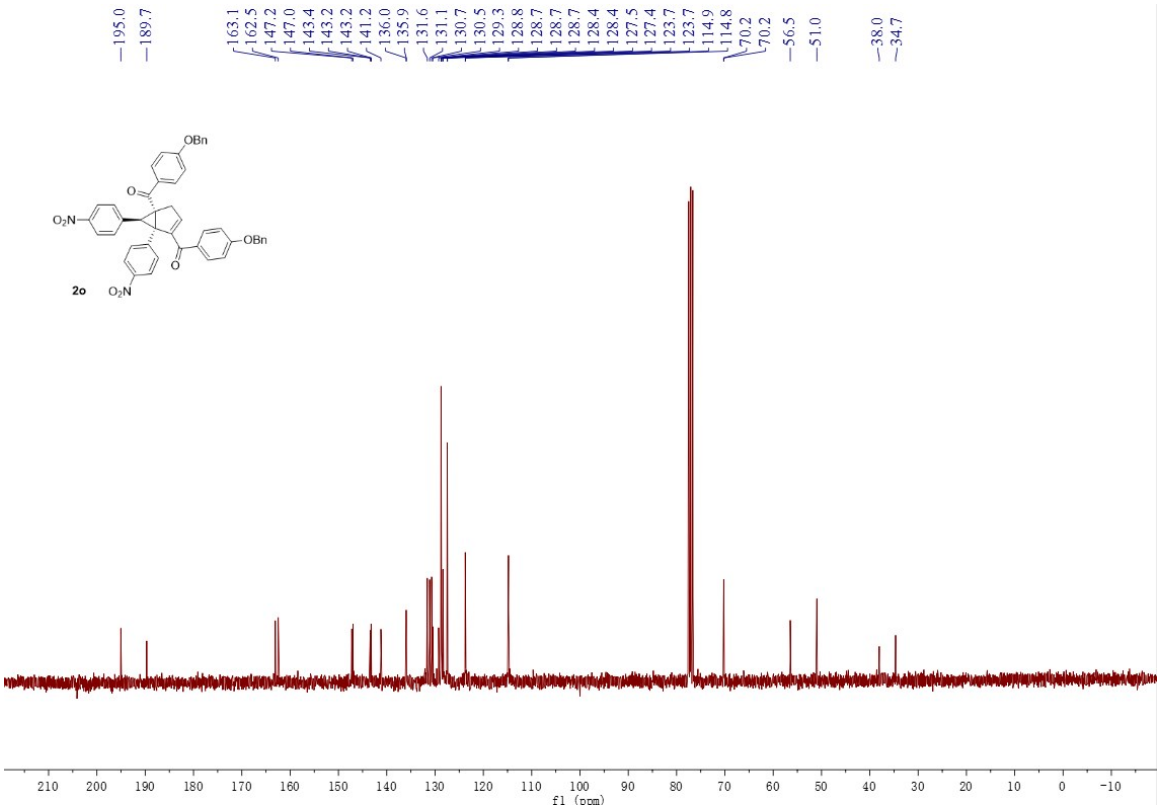
2.19
12.45
4.36
0.99
2.06
2.11
1.00
1.00
1.00
f1 (ppm)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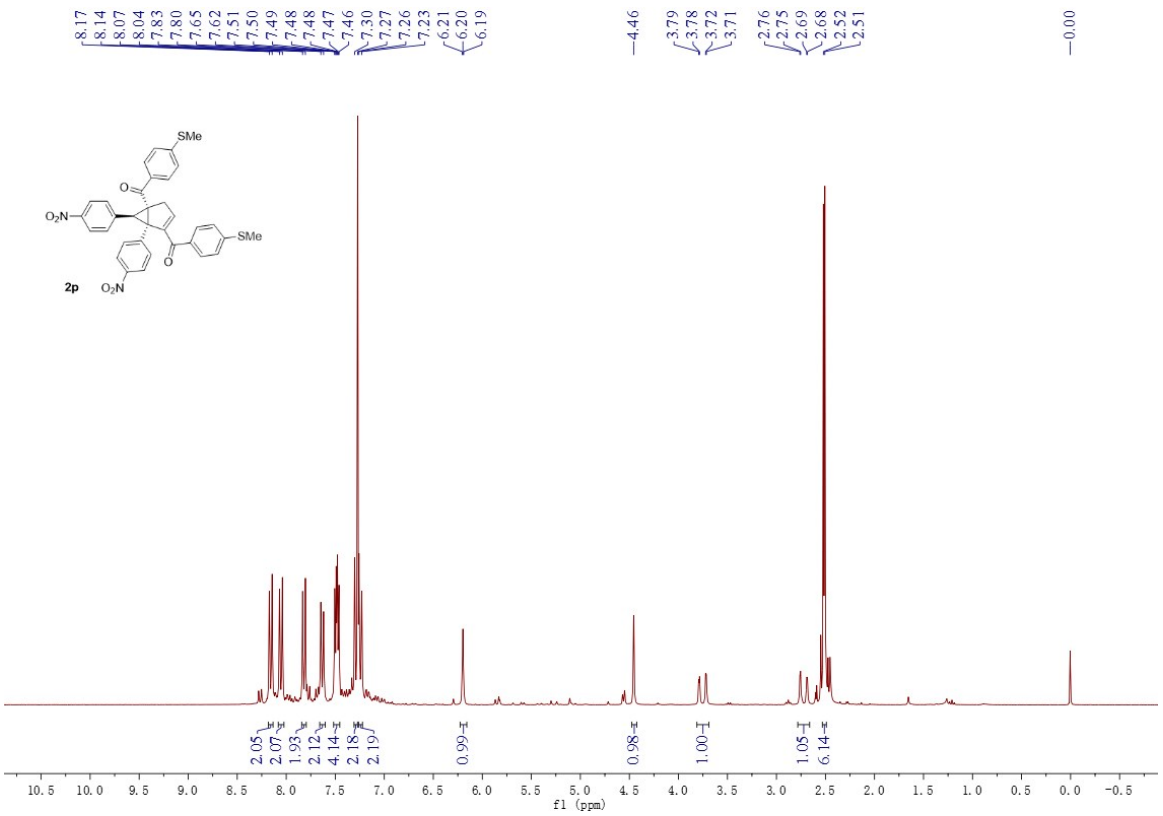
162.5
147.2
147.0
143.4
143.2
143.2
141.2
136.0
135.9
131.6
131.1
130.7
130.5
129.3
128.8
128.7
128.7
128.4
128.4
127.5
127.4
123.7
123.7
114.9
114.8
70.2
70.2
56.5
51.0
38.0
34.7
OBn
O
O2N
OBn
O
2o
O2N
f1 (ppm)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7.48
7.48
7.47
7.46
7.30
7.27
7.26
7.23
6.21
6.20
6.19
4.46
3.79
3.78
3.72
3.71
2.76
2.75
2.69
2.68
2.52
2.51
0.00
SMe
O
O2N
SMe
O
2p
O2N
2.05
2.07
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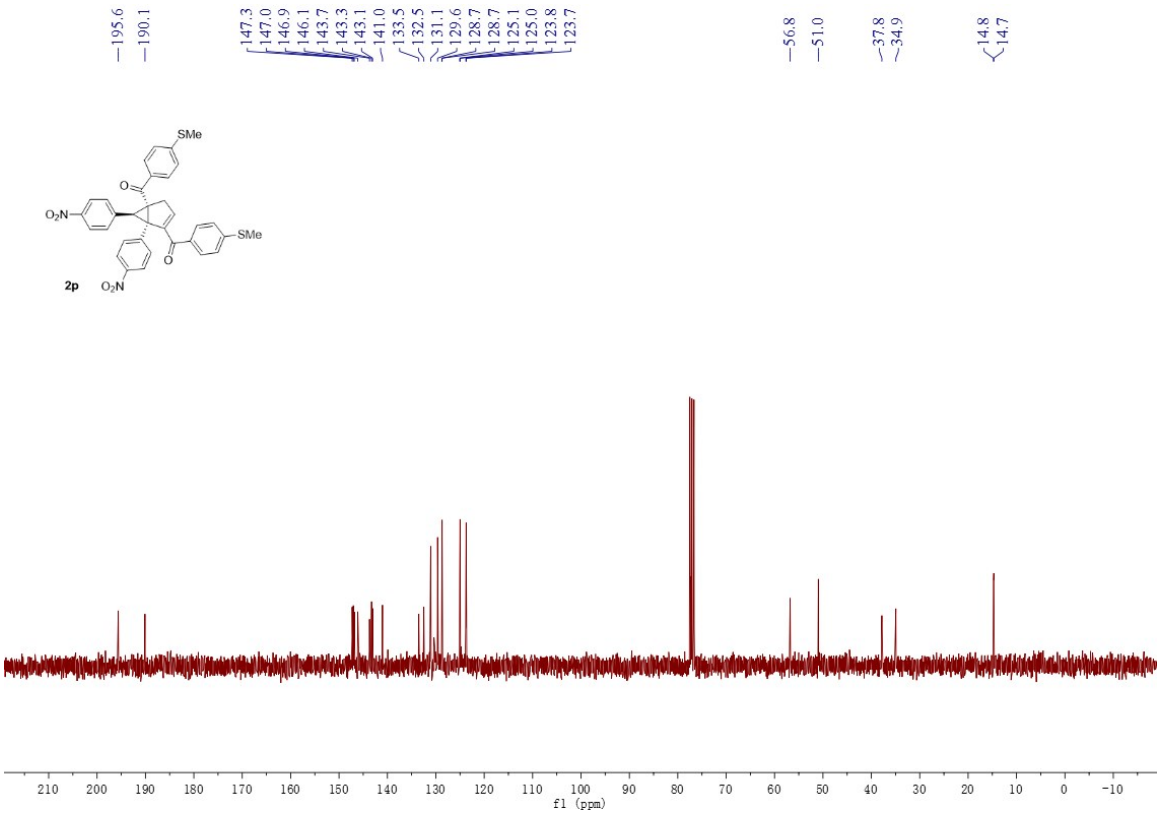
4.14
2.18
2.19
0.99
0.98
1.00
1.05
6.14
f1 (ppm)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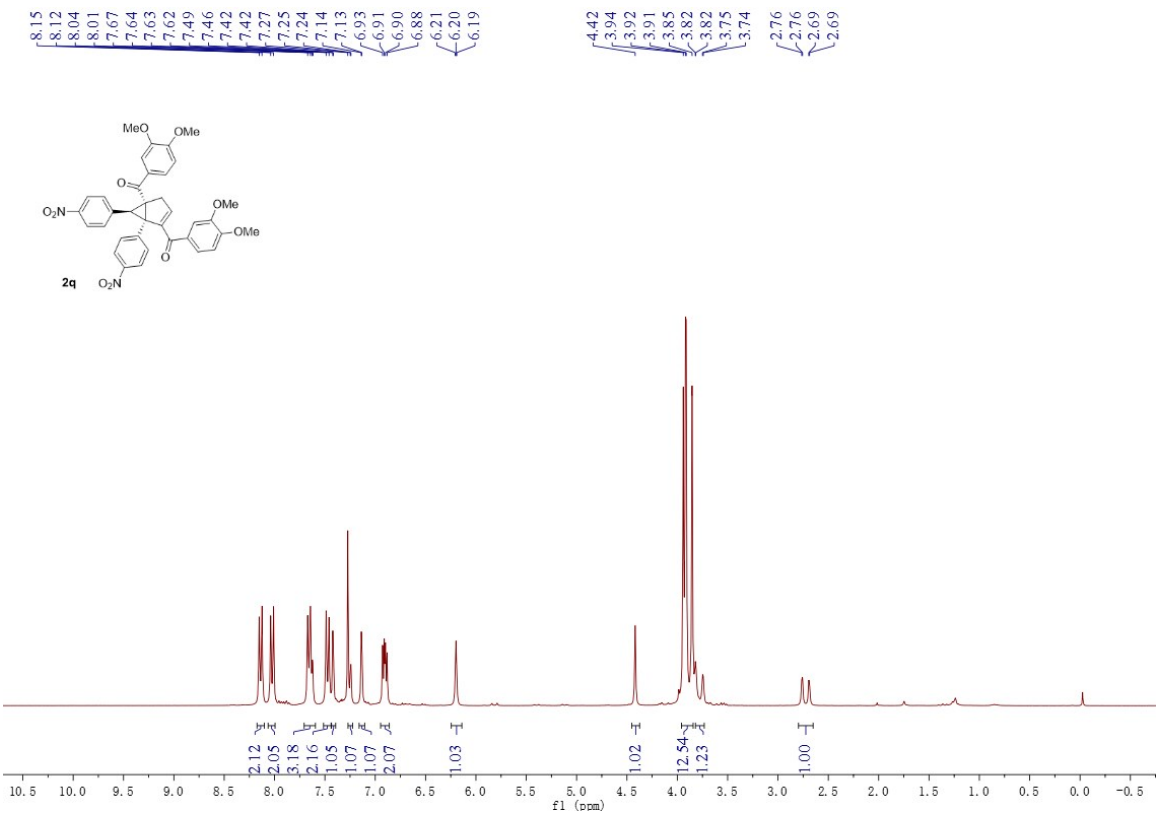
132.5
131.1
129.6
128.7
128.7
125.1
125.0
123.8
123.7
56.8
51.0
37.8
34.9
14.8
14.7
SMe
O
O2N
SMe
O
2p
O2N
f1 (ppm)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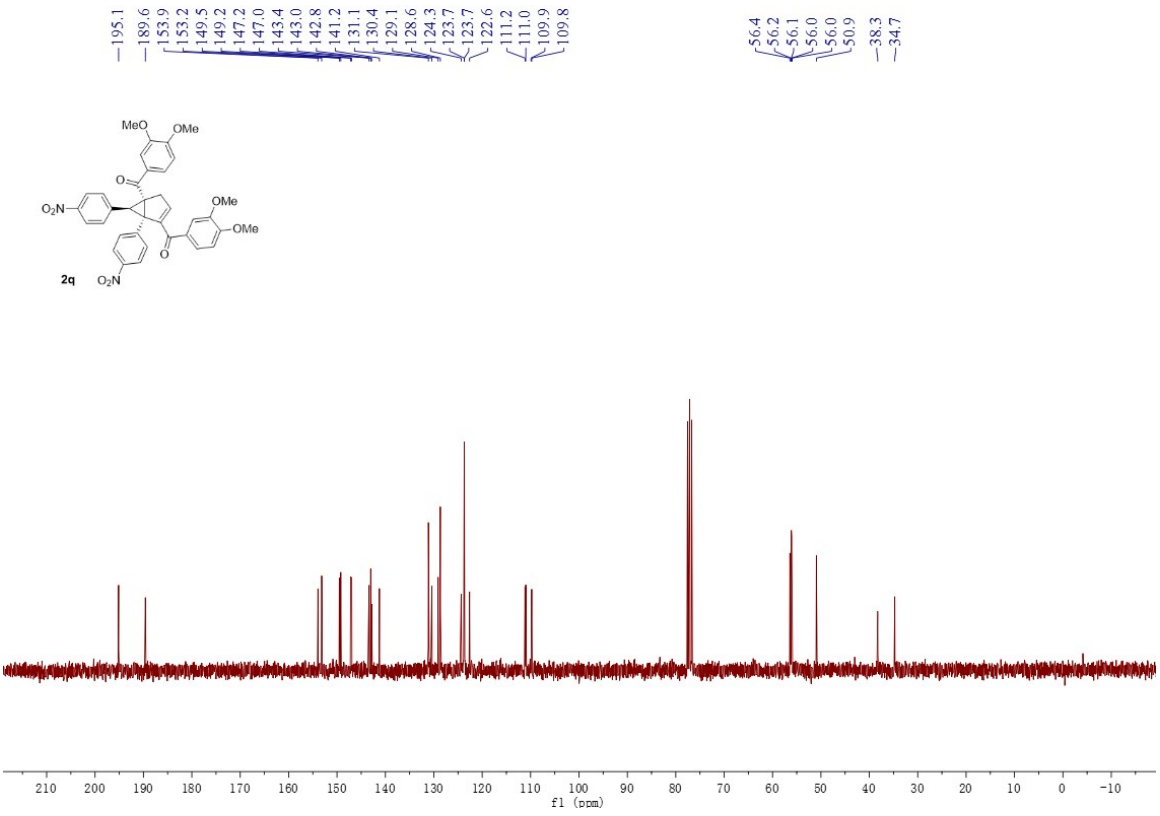
7.27
7.25
7.24
7.14
7.13
6.93
6.91
6.90
6.88
6.21
6.20
6.19
4.42
3.94
3.92
3.91
3.85
3.82
3.82
3.75
3.74
2.76
2.76
2.69
2.69
MeO
OMe
O
O2N
OMe
OMe
O
2q
O2N
2.12
2.05
3.18
2.16
1.05
1.07
1.07
2.07
1.03
1.02
12.54
1.23
1.00
f1 (ppm)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153.2
149.5
149.2
147.2
147.0
143.4
143.0
142.8
141.2
131.1
130.4
129.1
128.6
124.3
123.7
123.7
122.6
111.2
111.0
109.9
109.8
56.4
56.2
56.1
56.0
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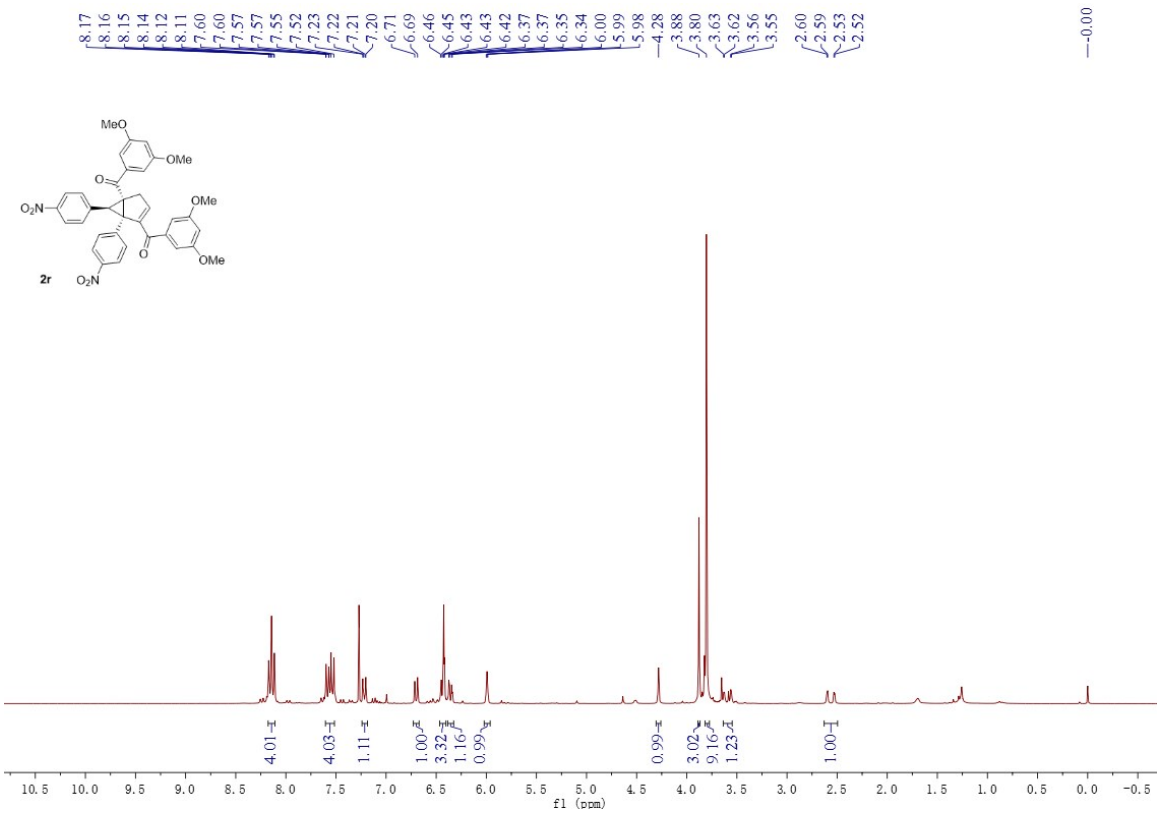
50.9
38.3
34.7
MeO
OMe
O
O2N
OMe
OMe
O
2q
O2N
f1 (ppm)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7.22
7.21
7.20
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6.69
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6.45
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6.43
6.42
6.37
6.37
6.35
6.34
6.00
5.99
5.98
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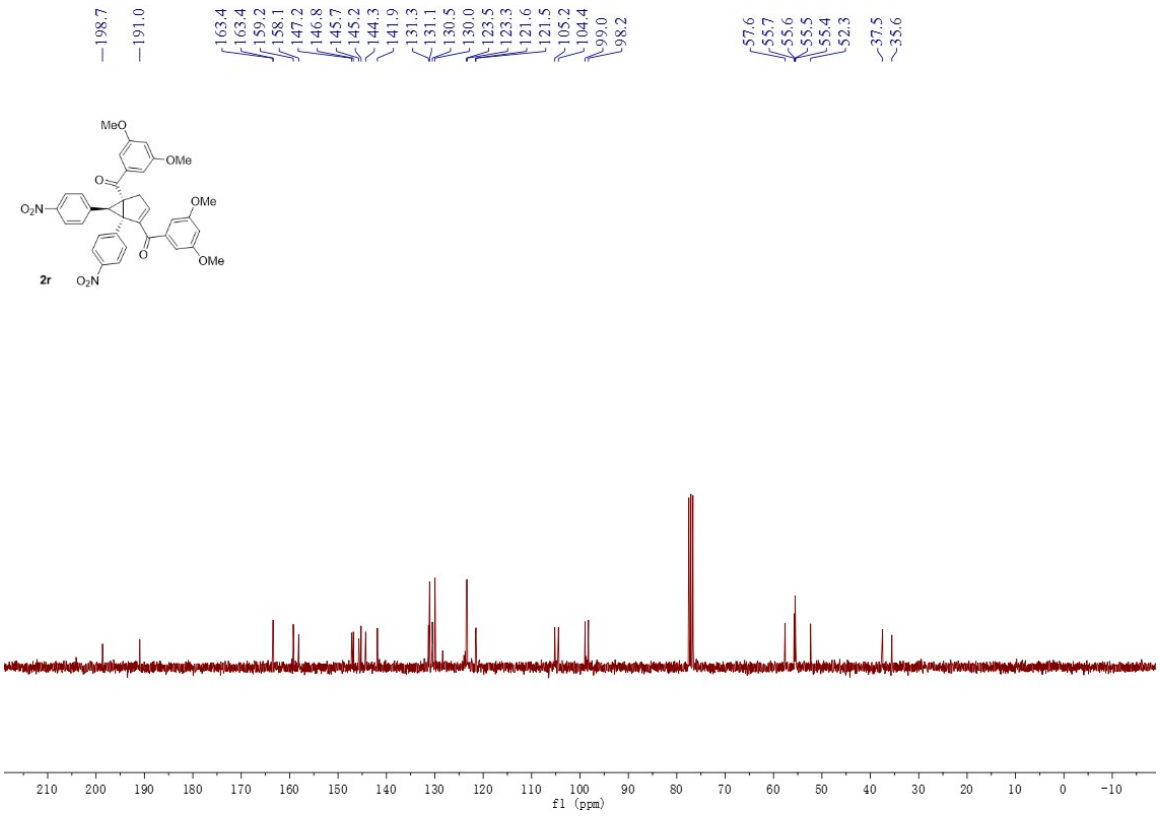
3.88
3.80
3.63
3.62
3.56
3.55
2.60
2.59
2.53
2.52
0.00
MeO
OMe
O
O2N
OMe
O
OMe
2r
O2N
4.01
4.03
1.11
1.00
3.32
1.16
0.99
0.99
3.02
9.16
1.23
1.00
f1 (ppm)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130.0
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105.2
104.4
99.0
98.2
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55.7
55.6
55.5
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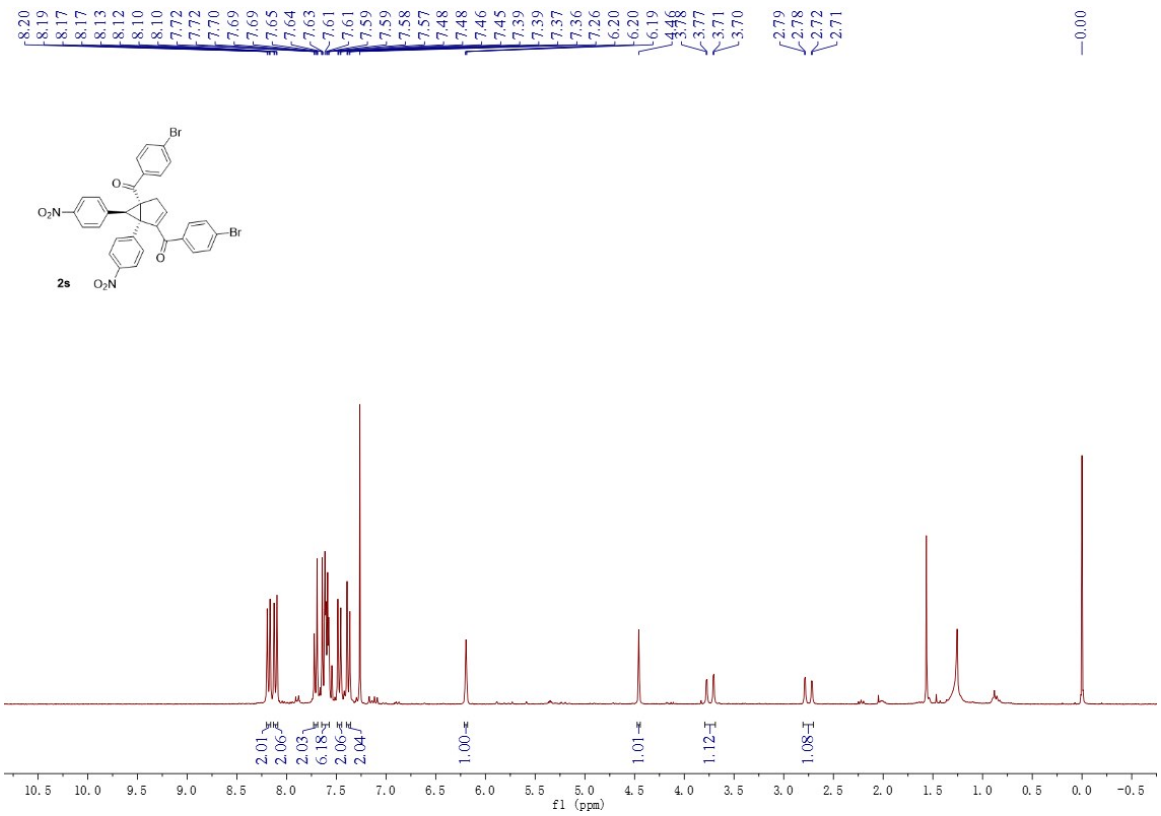
OMe
O
O2N
OMe
O
OMe
2r
O2N
f1 (ppm)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7.69
7.65
7.64
7.63
7.61
7.61
7.59
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7.58
7.57
7.48
7.48
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7.45
7.39
7.39
7.37
7.36
7.26
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6.19
4.46
3.78
3.77
3.71
3.70
2.79
2.78
2.72
2.71
0.00
Br
O
O2N
Br
O
2s
O2N
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2.03
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2.06
2.04
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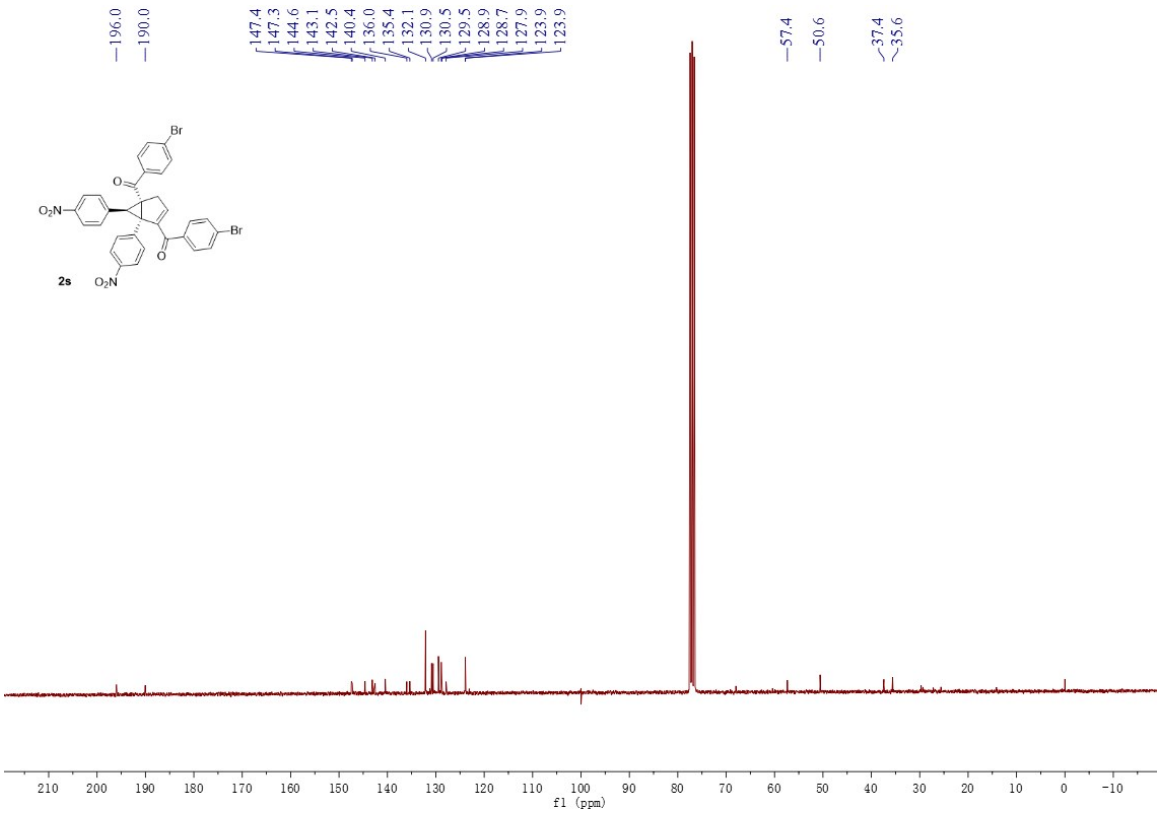
1.08
f1 (ppm)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128.7
127.9
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123.9
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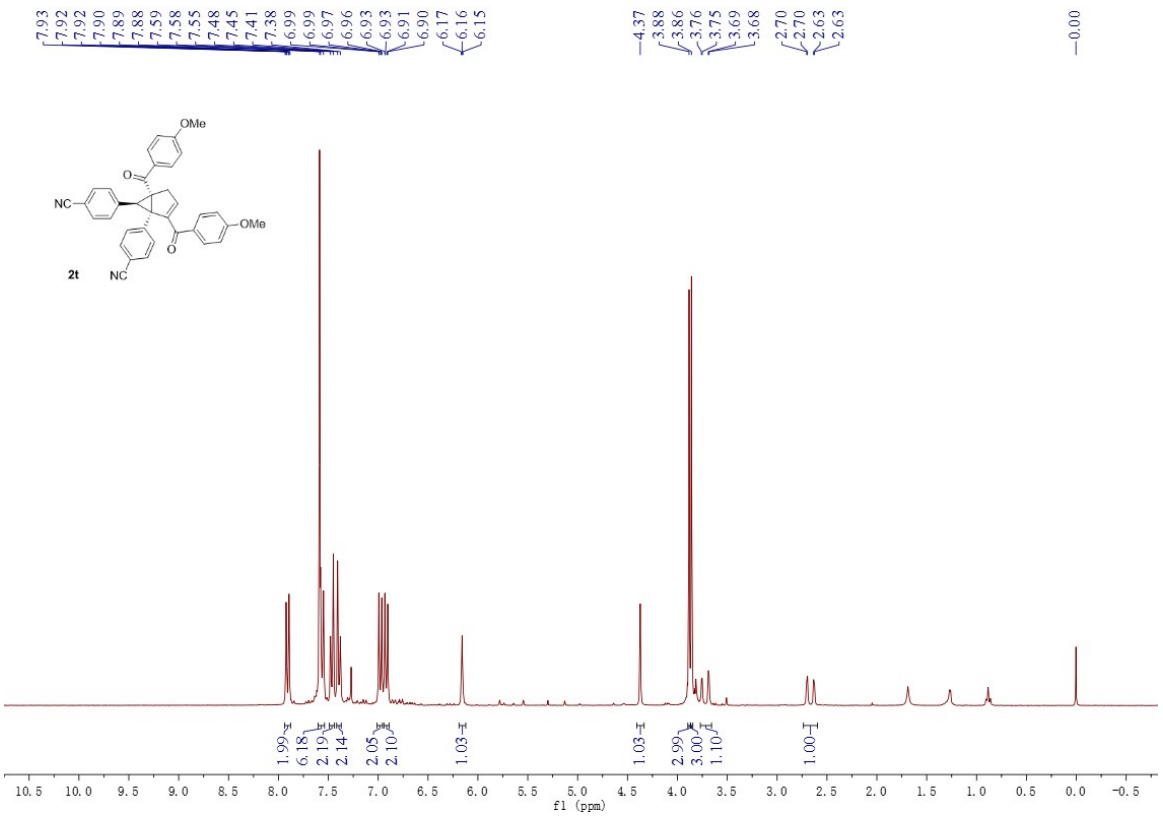
50.6
37.4
35.6
Br
O
O2N
Br
O
2s
O2N
f1 (ppm)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7.38
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6.99
6.97
6.96
6.93
6.93
6.91
6.90
6.17
6.16
6.15
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3.88
3.86
3.76
3.75
3.69
3.68
2.70
2.70
2.63
2.63
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OMe
O
NC
OMe
O
2t
NC
1.99
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1.03
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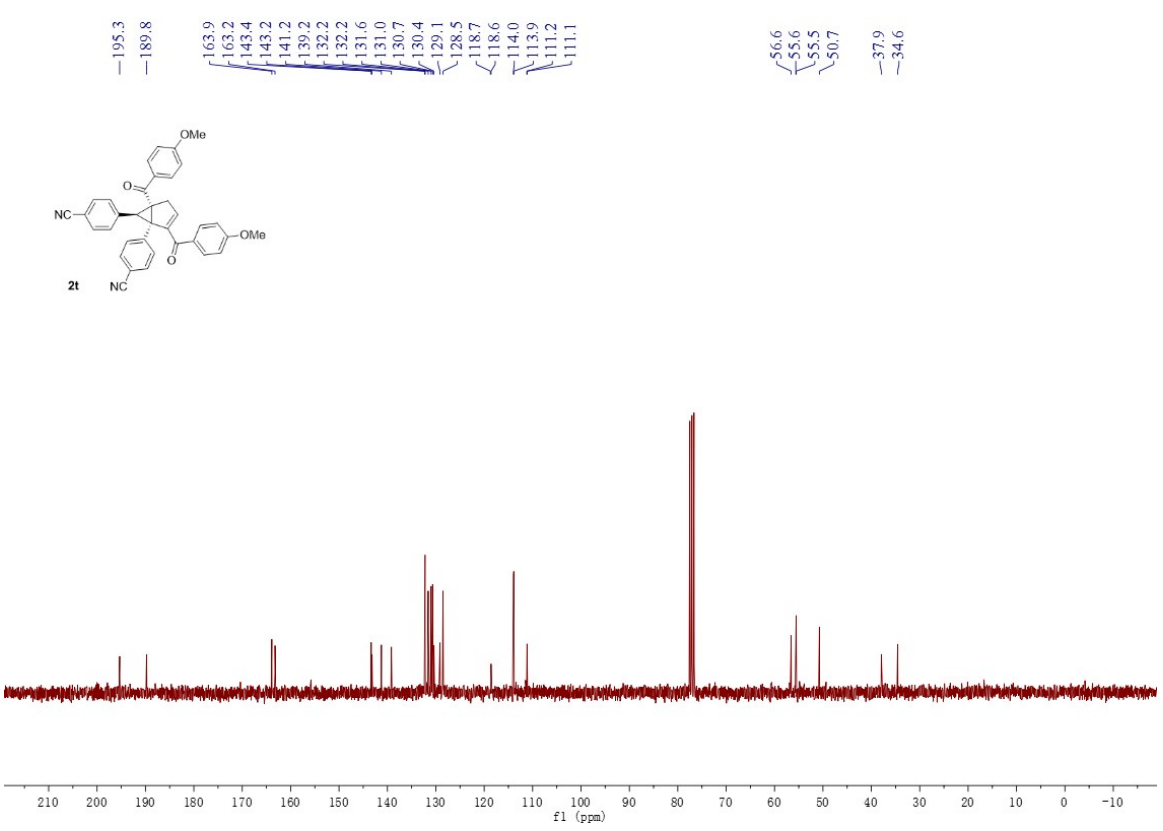
1.00
f1 (ppm)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118.6
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113.9
111.2
111.1
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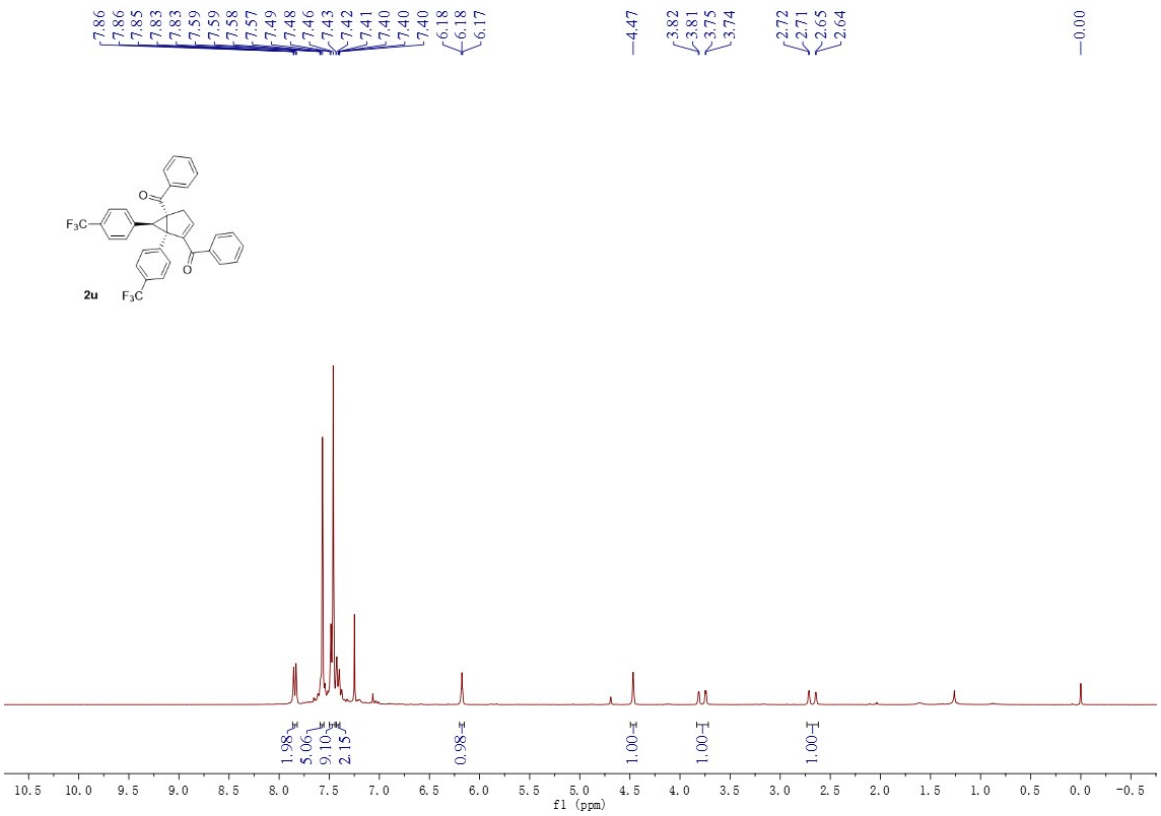
34.6
OMe
O
NC
OMe
O
2t
NC
f1 (ppm)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6.18
6.17
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3.81
3.75
3.74
2.72
2.71
2.65
2.64
0.00
F3C
O
O
2u
F3C
1.98
5.06
9.10
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0.98
1.00
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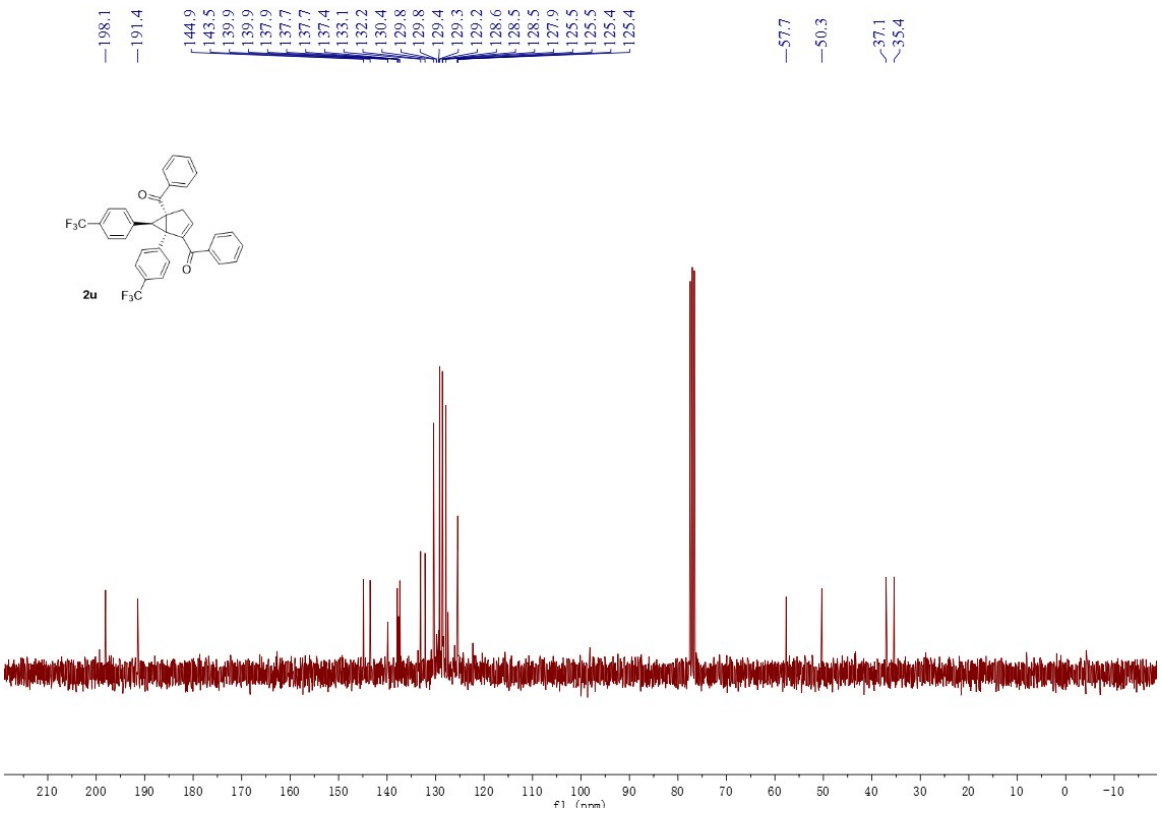
1.00
f1 (ppm)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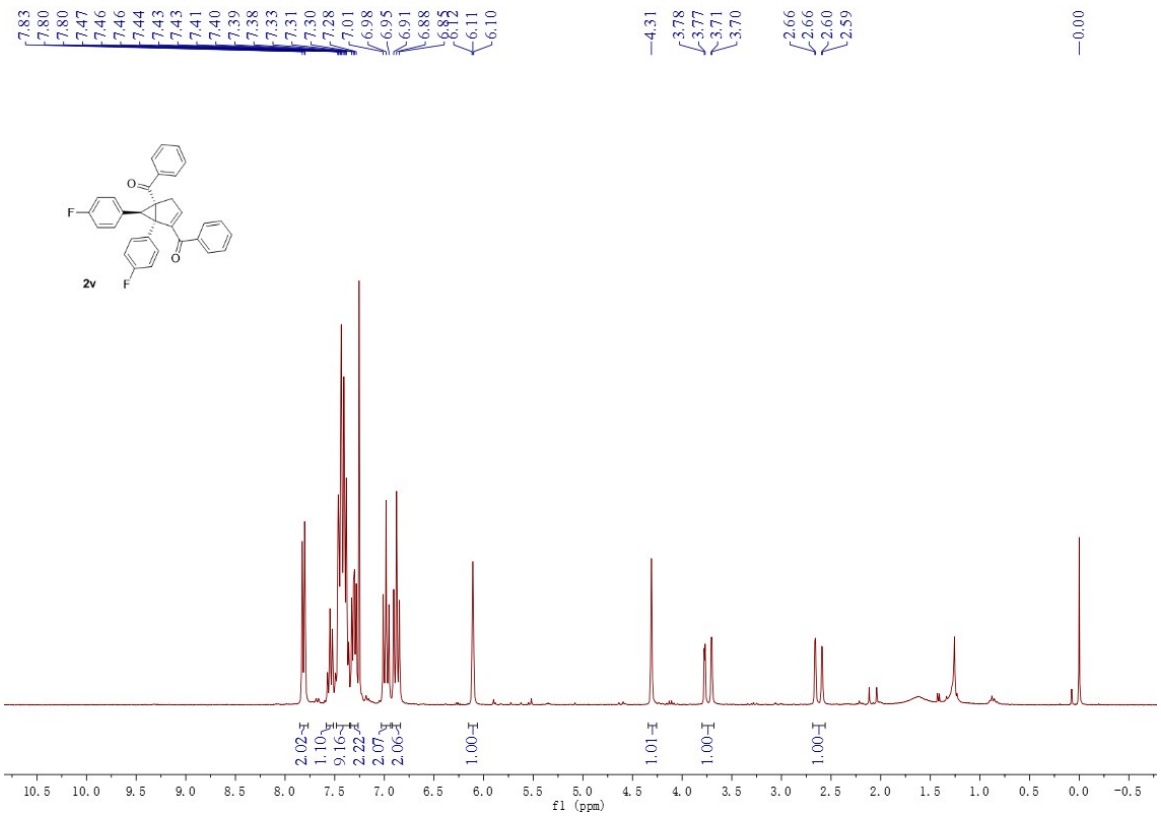
F3C
O
O
2u
F3C
f1 (ppm)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7.31
7.30
7.28
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6.95
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6.12
6.11
6.10
4.31
3.78
3.77
3.71
3.70
2.66
2.66
2.60
2.59
0.00
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2.02
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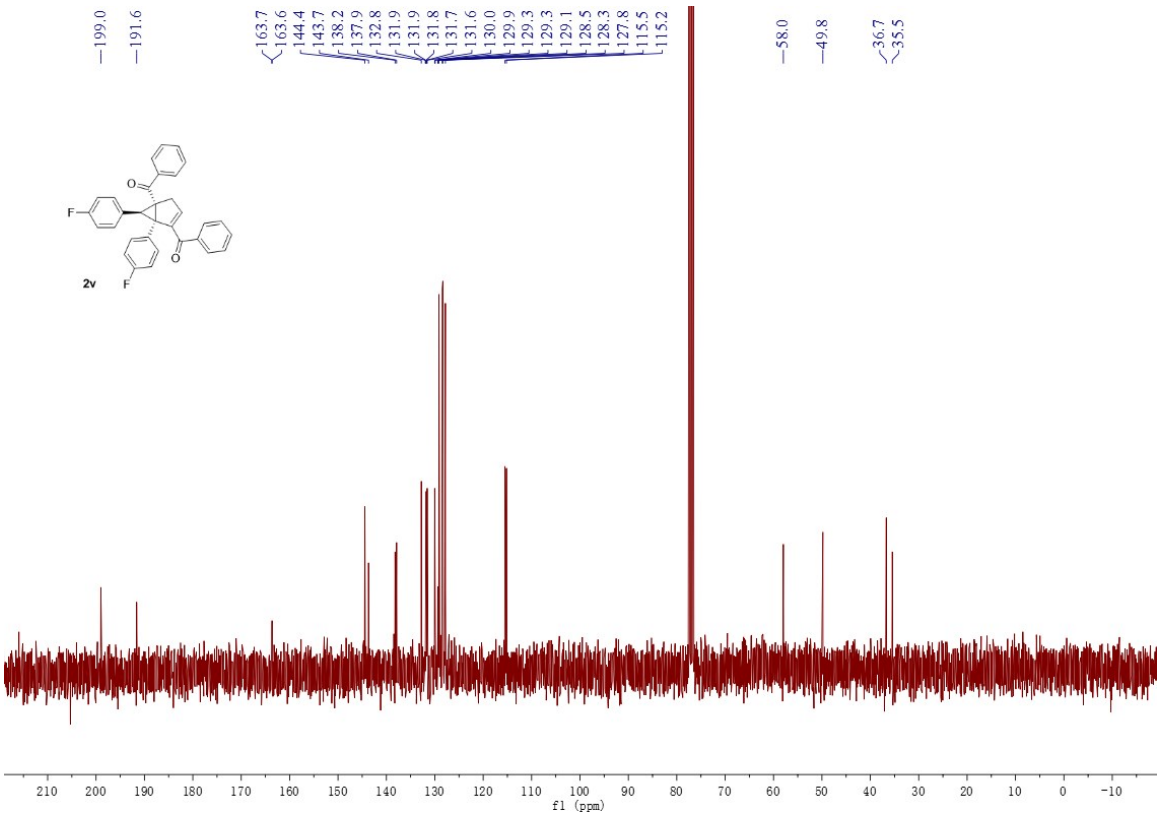
2.22
2.07
2.06
1.00
1.01
1.00
1.00
f1 (ppm)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131.7
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129.9
129.3
129.3
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128.3
127.8
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115.2
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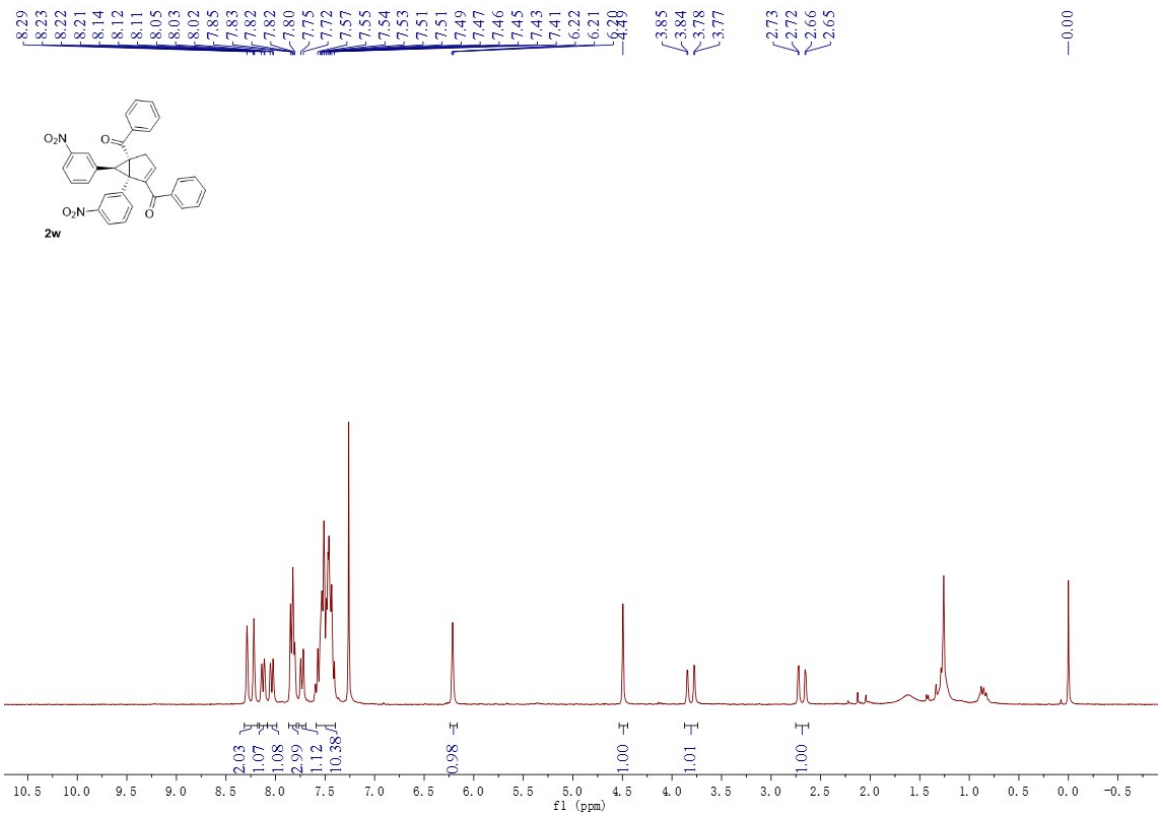
49.8
36.7
35.5
2v
f1 (ppm)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8.02
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7.54
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7.51
7.51
7.49
7.47
7.46
7.45
7.43
7.41
6.22
6.21
6.20
4.49
3.85
3.84
3.78
3.77
2.73
2.72
2.66
2.65
0.00
O2N
O
O2N
O
2w
2.03
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1.12
10.38
0.98
1.00
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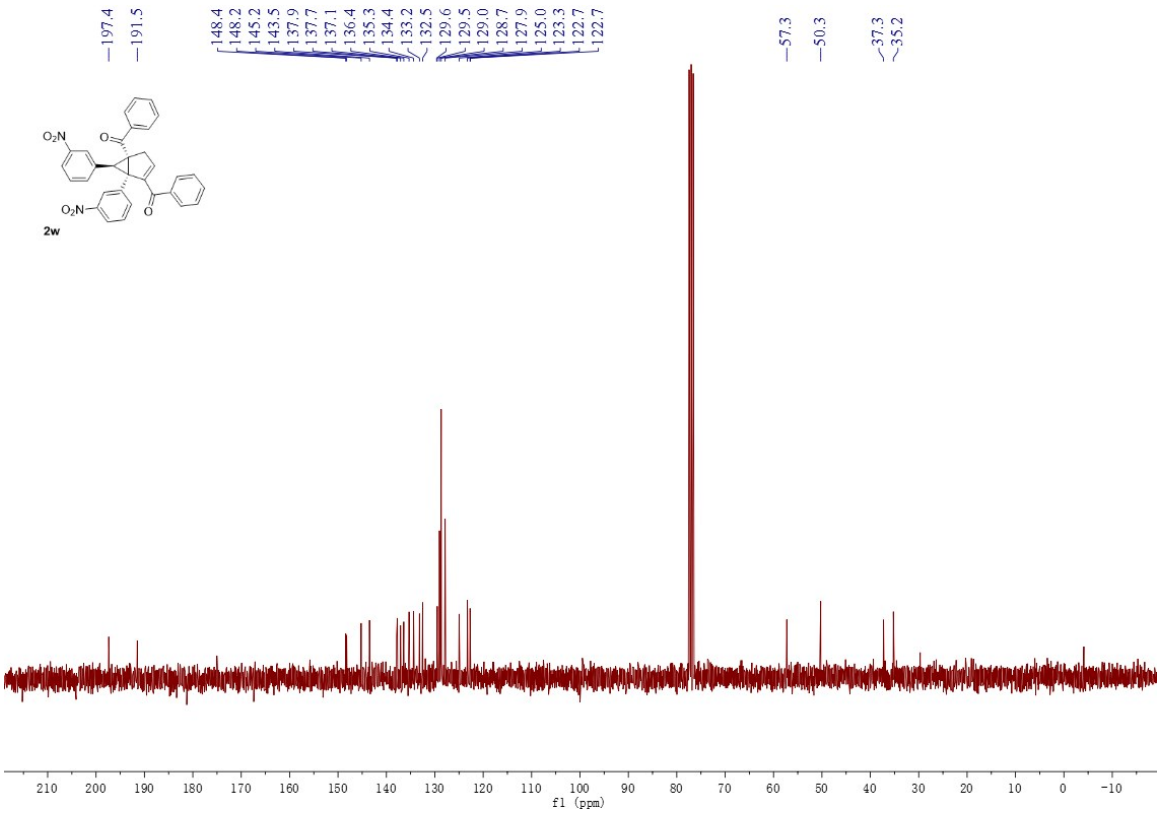
1.00
f1 (ppm)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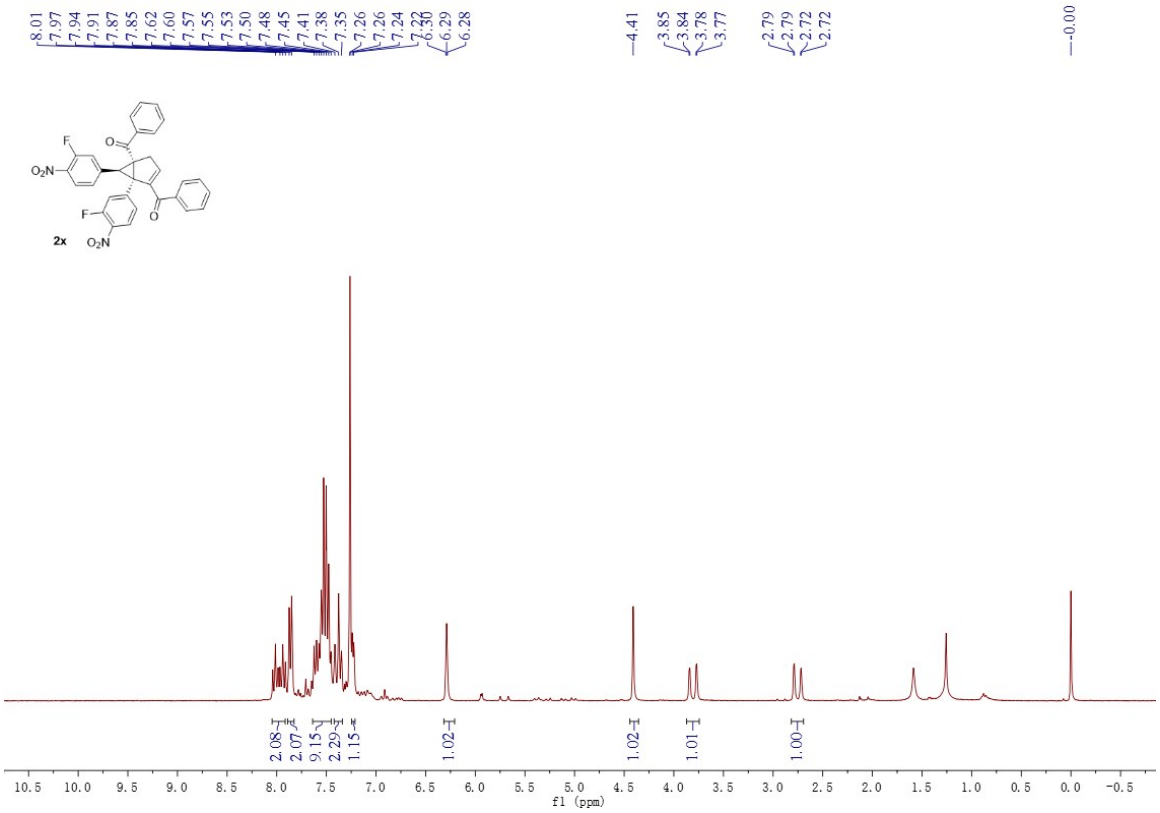
134.4
133.2
132.5
129.6
129.5
129.0
128.7
127.9
125.0
123.3
122.7
122.7
57.3
50.3
37.3
35.2
O2N
O
O2N
O
2w
f1 (ppm)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6.30
6.29
6.28
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3.85
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3.78
3.77
2.79
2.79
2.72
2.72
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1.02
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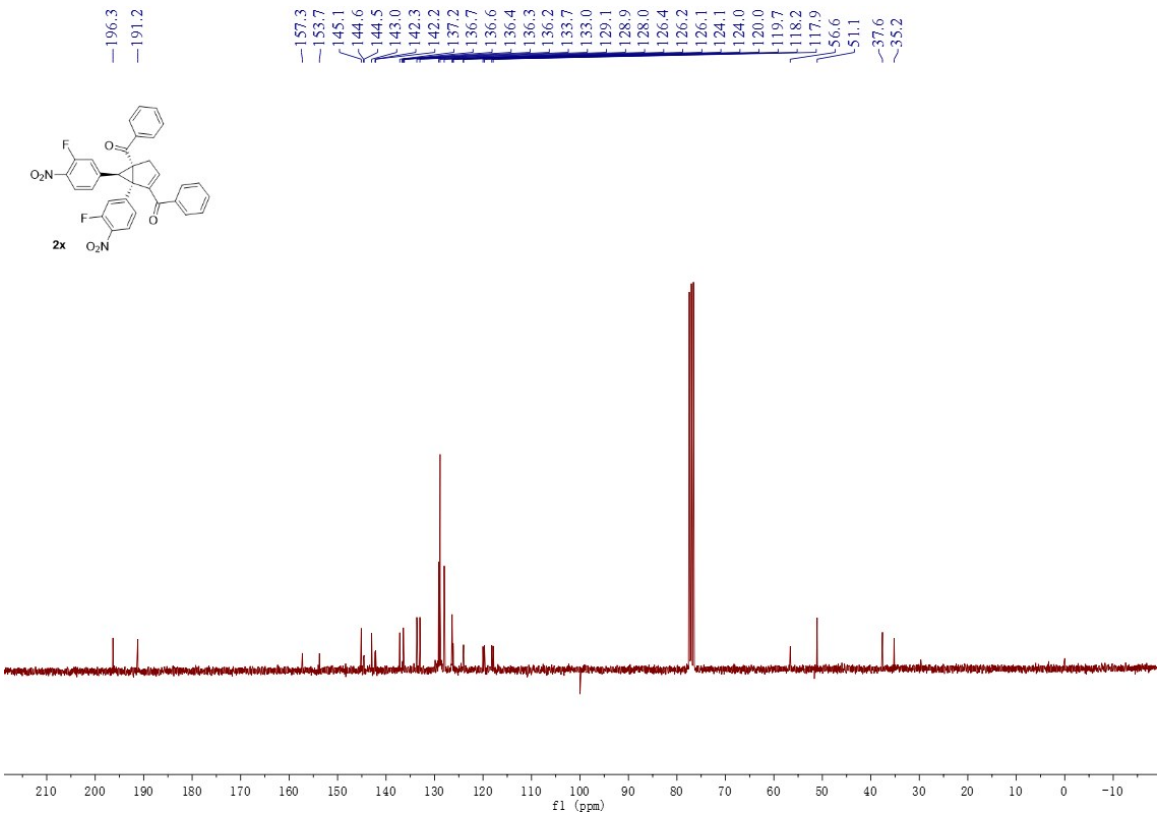
1.00
f1 (ppm)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144.6
144.5
143.0
142.3
142.2
137.2
136.7
136.6
136.4
136.3
136.2
133.7
133.0
129.1
128.9
128.0
126.4
126.2
126.1
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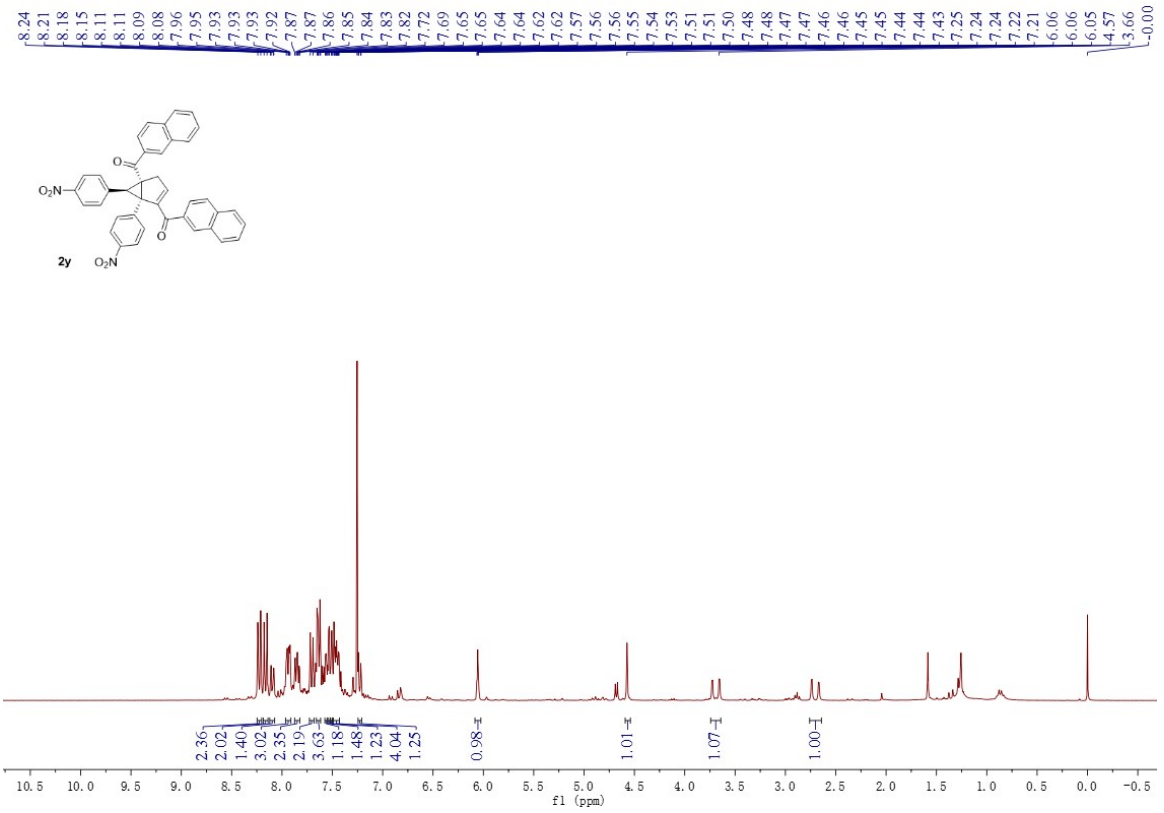
118.2
117.9
56.6
51.1
37.6
35.2
2x
f1 (ppm)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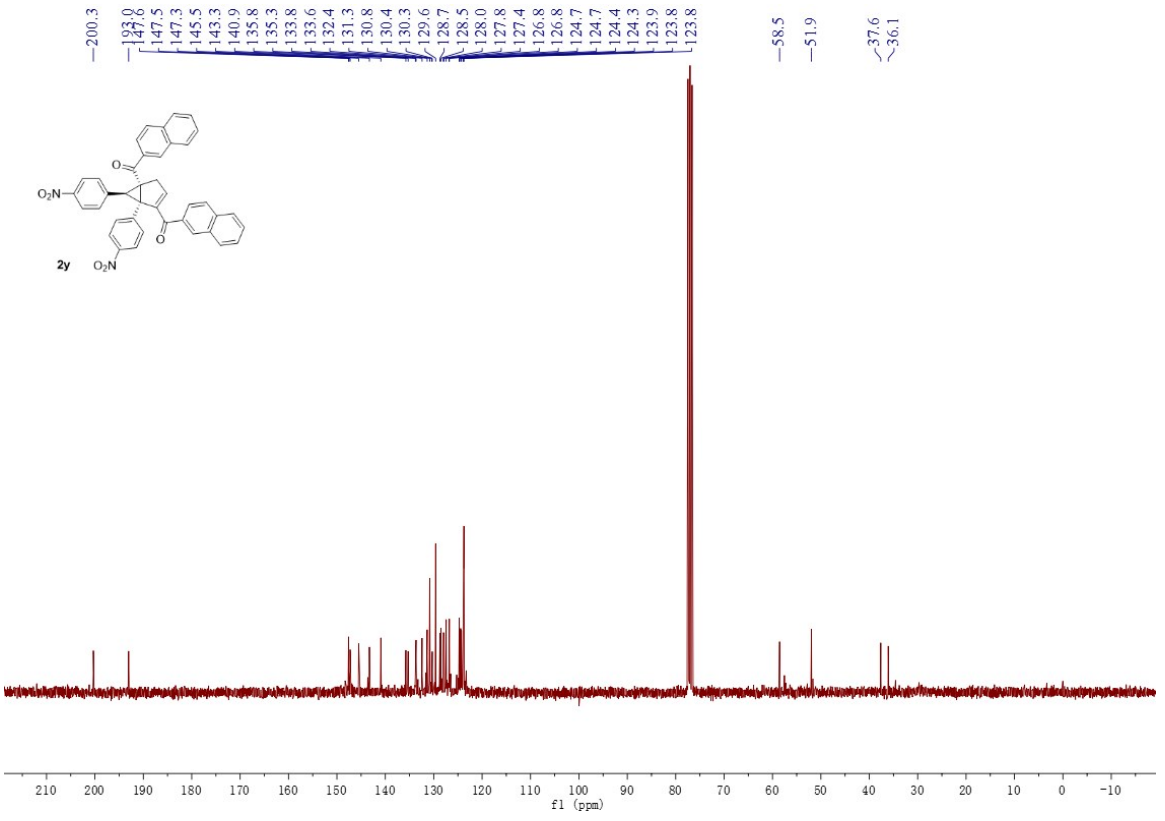
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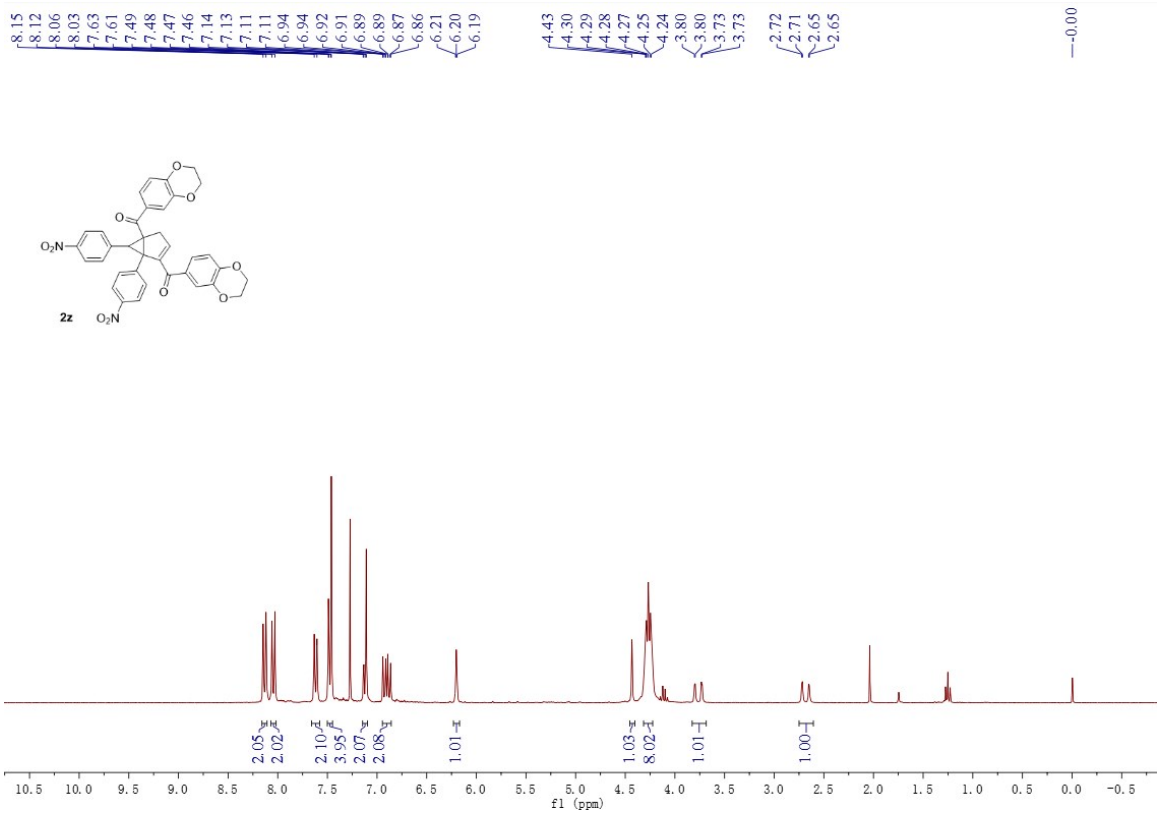
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7.11
7.11
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6.92
6.91
6.89
6.89
6.87
6.86
6.21
6.20
6.19
4.43
4.30
4.29
4.28
4.27
4.25
4.24
3.80
3.80
3.73
3.73
2.72
2.71
2.65
2.65
0.00
2z
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2.08
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8.02
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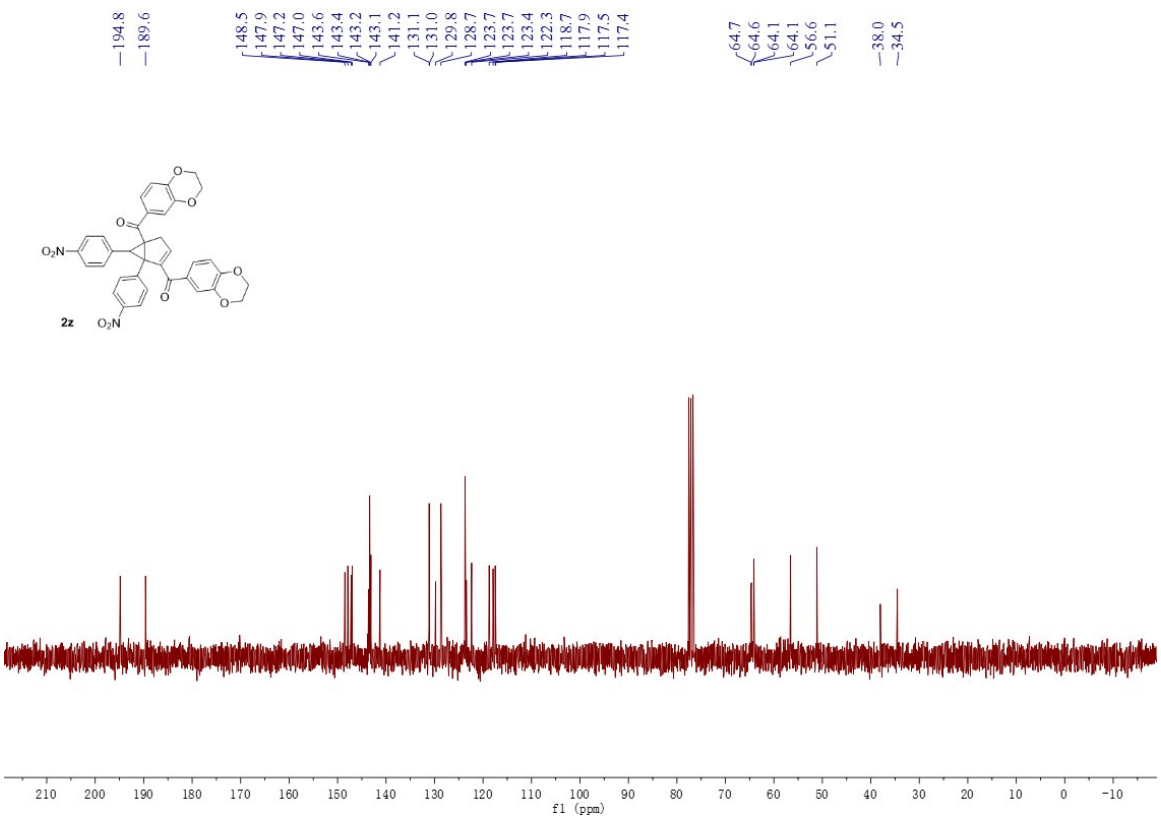
1.00
f1 (ppm)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128.7
123.7
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123.4
122.3
118.7
117.9
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64.1
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51.1
38.0
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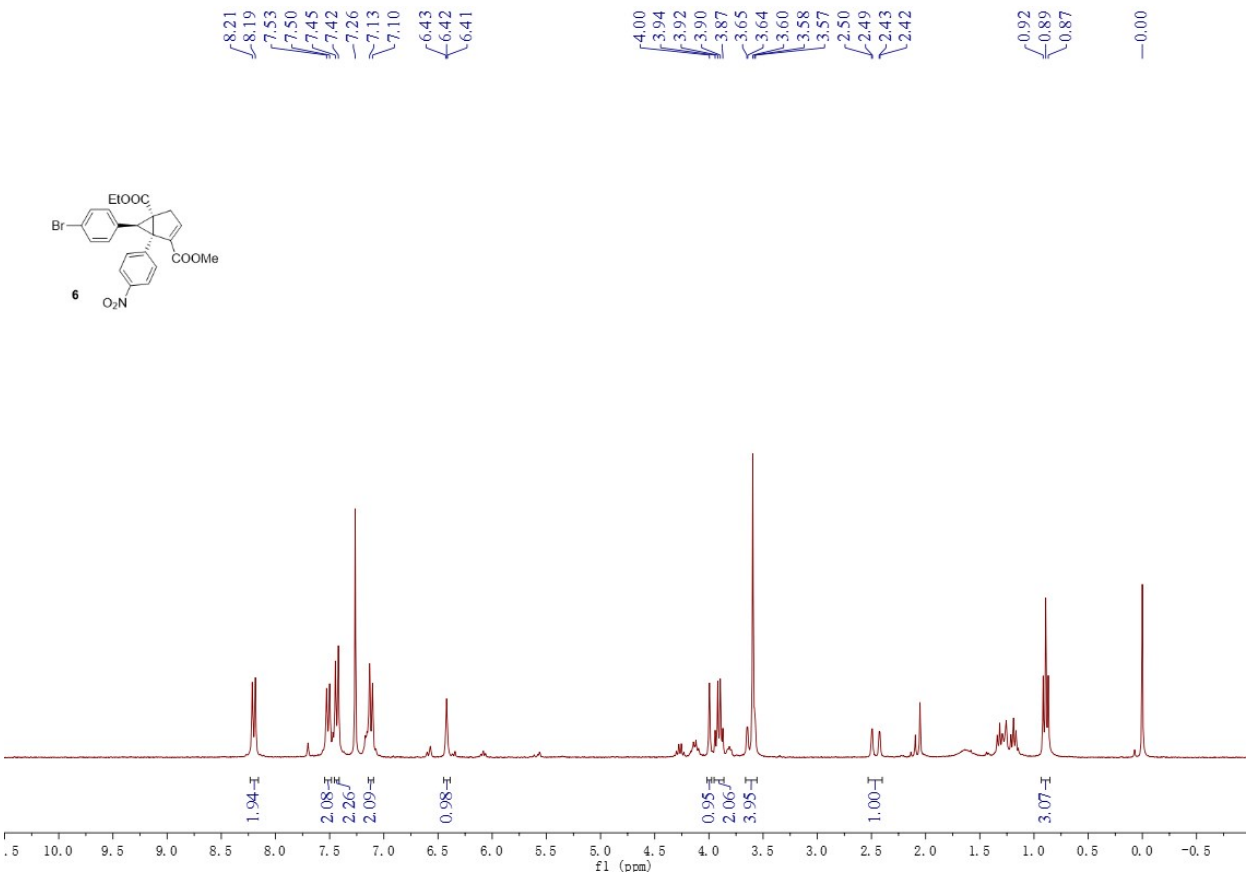
2z
f1 (ppm)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3.90
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3.65
3.64
3.60
3.58
3.57
2.50
2.49
2.43
2.42
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0.87
0.00
EtOOC
Br
COOMe
6
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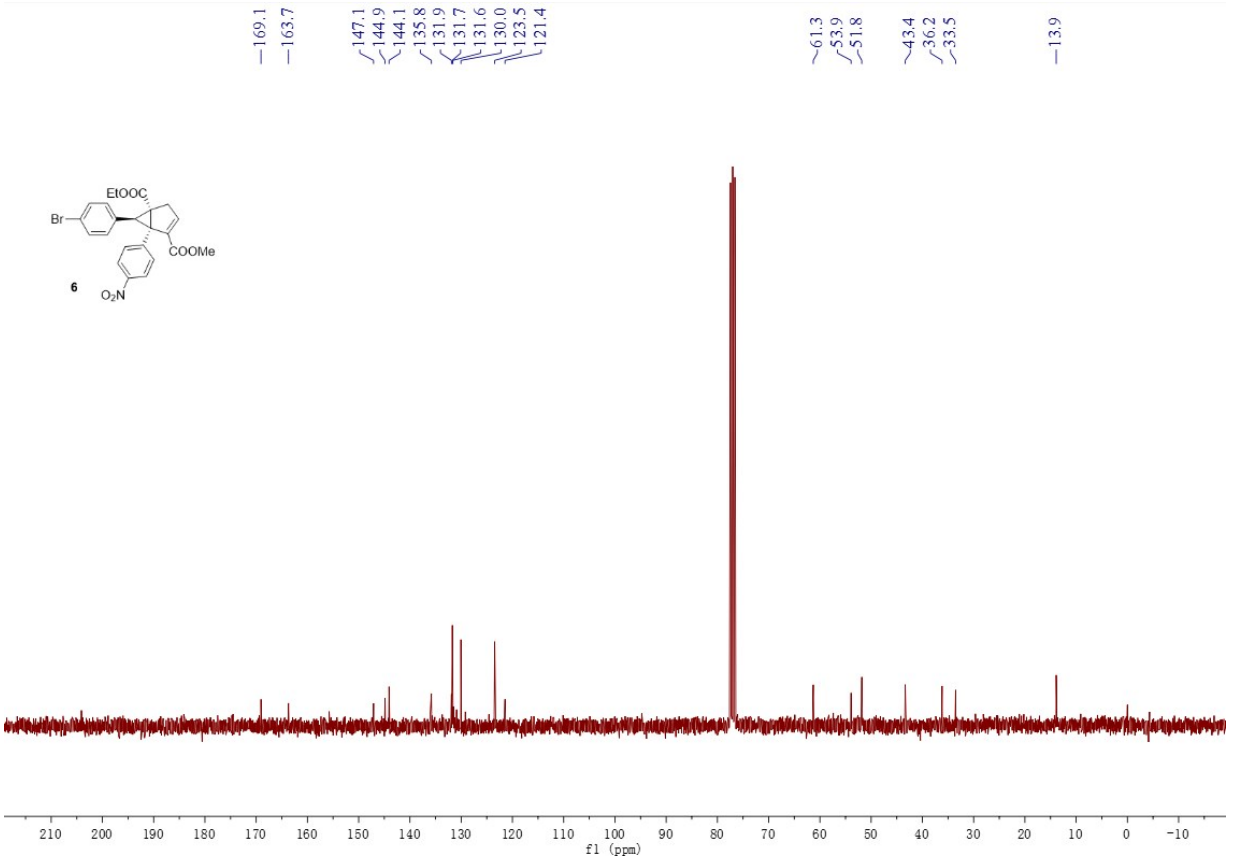
2.26
2.09
0.98
0.95
2.06
3.95
1.00
3.07
f1 (ppm)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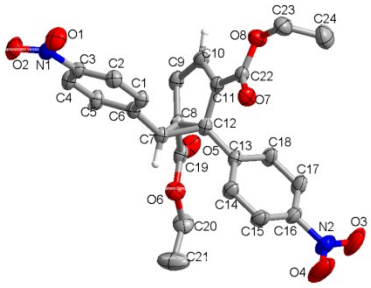
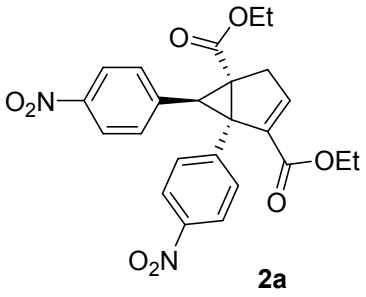
130.0
123.5
121.4
61.3
53.9
51.8
43.4
36.2
33.5
13.9
EtOOC
Br
COOMe
6
O2N
f1 (ppm)

7. X-ray crystal structure of 2a and 6.

Yellow crystals suitable for X-ray diffraction were grown by n-hexane/dichloromethane solution of **2a** inside a penicillin bottle.





2a

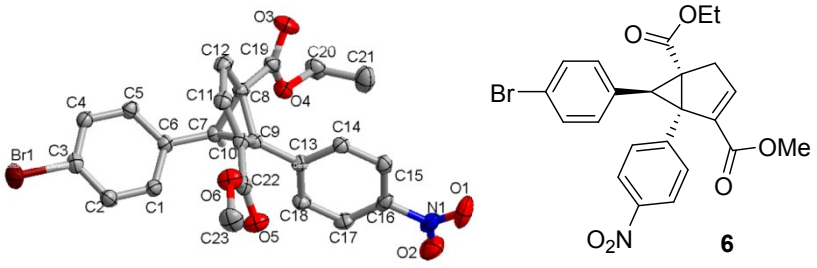
Crystal data and structure refinement for 2a (CCDC 1911493).

Identification code	**2a**
Empirical formula	$C_{24}H_{22}N_2O_8$
Formula weight	466.43
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.6988(3)
b/Å	13.6615(2)
c/Å	14.5332(3)
α/°	90
β/°	105.162(2)
γ/°	90
Volume/Å^3	2625.17(9)
Z	4
ρ_{calc}g/cm^3	1.180
μ/mm^{-1}	0.754
F(000)	976.0
Crystal size/mm^3	0.15 × 0.1 × 0.08

Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.898 to 134.166
Index ranges	$-14 \leq h \leq 16$, $-16 \leq k \leq 10$, $-17 \leq l \leq 16$
Reflections collected	10184
Independent reflections	4697 [R_{int} = 0.0287, R_{sigma} = 0.0330]
Data/restraints/parameters	4697/2/317
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0510, wR_2 = 0.1473
Final R indexes [all data]	R_1 = 0.0629, wR_2 = 0.1596
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.20

X-ray crystal structure of 6

White crystals suitable for X-ray diffraction were grown by n-hexane/dichloromethane solution of **6** inside a penicillin bottle.



Crystal data and structure refinement for 6 (CCDC 1937397).

Identification code	**6**
Empirical formula	$C_{23}H_{20}BrNO_6$
Formula weight	486.31
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.8322(4)
b/Å	9.5496(3)

c/Å	21.3416(8)
α/°	90
β/°	99.283(4)
γ/°	90
Volume/Å^3	2178.73(14)
Z	4
ρ_{calc}g/cm^3	1.483
μ/mm^{-1}	2.915
F(000)	992.0
Crystal size/mm^3	0.19 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.39 to 134.118
Index ranges	-12 ≤ h ≤ 11, -11 ≤ k ≤ 8, -23 ≤ l ≤ 25
Reflections collected	9143
Independent reflections	3875 [R_{int} = 0.0639, R_{sigma} = 0.0555]
Data/restraints/parameters	3875/0/282
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0541, wR_2 = 0.1398
Final R indexes [all data]	R_1 = 0.0617, wR_2 = 0.1518
Largest diff. peak/hole / e Å^{-3}	0.46/-0.72