Electronic Supplementary Material (ESI) for ChemComm.

Phosphine catalyzed [3+2] cyclization/Michael addition of allenoate with CS_2 to form 2-thineyl vinyl sulfide

Weihong Fei [a†], Ping Xu [a†], Jie Hou [a] and Weijun Yao* [a]

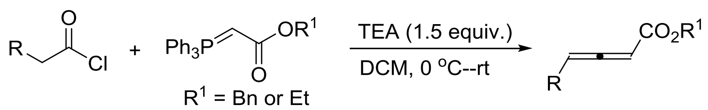
[a] Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, 310018, P.R. China.
[†] The authors contribute equally to this work.
Email: Orgywj@zstu.edu.cn;

Table of contents

A. General information

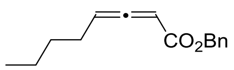
Unless otherwise specified, all reactions were carried out with dry solvents in anhydrous conditions. THF, toluene, dichloromethane and acetonitrile were dried by activated molecular sieve (4 Å). All chemicals were used without further purification as commercially available unless otherwise noted. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm). High resolution mass spectra (HRMS) were recorded on a Waters TOFMS GCT Premier using ESI ionization. Petroleum ether (PE) refers to the fraction with boiling point in the range 60 – 90 ^{o}C.

B. Preparation and analytical data of allenoate 1 and 3



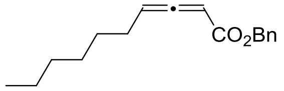
Allenoate **1** and **3** was prepared from corresponding substituted acetyl chloride with phosphonium ylide according to the reported procedure. [1, 2] The ^{1}H NMR spectra of known compounds were consistent with the literature reported. The analytical data of new compounds (**1e**, **1h**, **1i, 3b, 3c**, **3f**, **3g**, **3h** and **3i**) were as follow.

Benzyl octa-2,3-dienoate **1e**



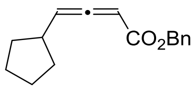
Colourless oil; it is a unseparated mixture with alkynoate, and the ratio is 2.3:1 from crude ^{1}H NMR. The NMR details as follow: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 5H), 5.66 – 5.59 (m, 1.25H, allenoate), 5.27 – 5.09 (m, 2H), 3.30 (t, *J* = 2.4 Hz, 0.54H, alkynoate), 2.24 – 2.10 (m, 2H), 1.53 – 1.31 (m, 4H), 0.95 – 0.84 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) for allenoate: δ 212.6, 166.1, 136.0, 128.5, 128.2, 95.5, 88.0, 66.4, 30.8, 27.1, 22.0, 13.8 ppm; for alkynoate: δ 168.8, 135.5, 128.5, 128.33 128.1, 128.1, 84.0, 71.2, 67.0, 30.7, 26.1, 21.9, 18.4, 13.6 ppm; IR (film) *v* = 2958, 2932, 2026, 1960, 1722, 1631 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{19}O_2$ $[M+H]^+$ = 231.1380, found = 231.1395.

Benzyl deca-2,3-dienoate **1h**



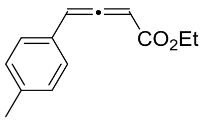
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 5.66 – 5.61 (m, 2H), 5.22 (d, *J* = 12.5 Hz, 1H), 5.18 (d, *J* = 12.5 Hz, 1H), 2.19 – 2.11 (m, 2H), 1.52 – 1.42 (m, 2H), 1.39 – 1.25 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.6, 166.0, 136.0, 128.4, 128.0, 127.9, 95.5, 87.9, 66.3, 31.4, 28.6, 28.5, 27.4, 22.5, 14.0 ppm; IR (film) *v* = 2959, 2929, 2026, 1960, 1720, 1631 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{23}O_2$ $[M+H]^+$ = 259.1693, found = 259.1704.

Benzyl 4-cyclopentylbuta-2,3-dienoate **1i**



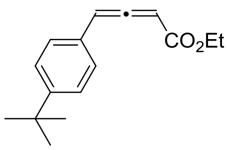
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 5H), 5.71 – 5.63 (m, 2H), 5.22 (d, *J* = 12.5 Hz, 1H), 5.14 (d, *J* = 12.5 Hz, 1H), 2.68 – 2.55 (m, 1H), 1.88- 1.80 (m, 2H), 1.70 – 1.53 (m, 4H), 1.49 – 1.37 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.9, 166.0, 136.1, 128.4, 128.0, 128.0, 100.3, 88.6, 66.3, 38.1, 32. 7, 32.4, 24.7 ppm; IR (film) *v* = 2955, 2869, 2026, 1958, 1720, 1631 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{19}O_2$ $[M+H]^+$ = 243.1380, found = 243.1396.

Ethyl 4-(p-tolyl)buta-2,3-dienoate **3b**



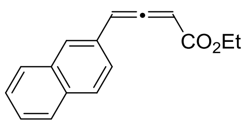
yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.61 (d, *J* = 6.4 Hz, 1H), 6.02 (d, *J* = 6.4 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.6, 165.17, 137.9, 129.5, 128.0, 127.3, 98.4, 91.7, 61.0, 21.2, 14.1 ppm; IR (film) *v* = 2980, 2924, 2026, 1729, 1631, 1590 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{15}O_2$ $[M+H]^+$ = 203.1067, found = 203.1081;

Ethyl 4-(4-(tert-butyl)phenyl)buta-2,3-dienoate **3c**



Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 6.4 Hz, 1H), 6.02 (d, *J* = 6.3 Hz, 1H), 4.23 (qd, *J* = 7.1, 2.2 Hz, 2H), 1.33 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.7, 165.1, 151.3, 128.1, 127.2, 125.8, 98.3, 91.7, 61.0, 34.6, 31.2, 14.2 ppm; IR (film) *v* = 2963, 2026, 1733, 1632, 1592, 1386 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{21}O_2$ $[M+H]^+$ = 245.1536, found = 245.1548.

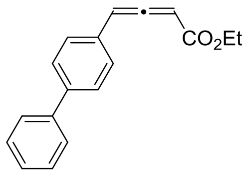
Ethyl 4-(naphthalen-2-yl)buta-2,3-dienoate **3f**



Pale yellow gel; it is a unseparated mixture with alkynoate, and the ratio is 9:1 from crude ^{1}H NMR..^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 3H), 7.72 (s, 1H), 7.47 (dd, *J* = 11.1, 7.0 Hz, 3H), 6.80 (d, *J* = 6.2 Hz, 1H), 6.11 (d, *J* = 6.2 Hz, 1H), 4.27 (q, *J* = 7.0 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm;.

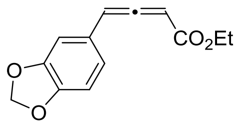
^{13}C NMR (101 MHz, $CDCl_3$) δ 215.1, 165.0, 133.5, 133.0, 131.6, 128.5, 127.8, 127.7, 126.8, 126.4, 126.2, 124.8, 99.0, 92.1, 61.1, 14.2 ppm; IR (KBr) v = 2980, 2026, 1718, 1632, 1596, 1351 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{15}O_2$ $[M+H]^+$ = 239.1067, found = 239.1080.

Ethyl 4-([1,1'-biphenyl]-4-yl)buta-2,3-dienoate **3g**



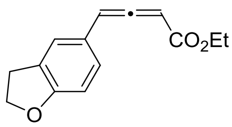
White solid, m.p. 59.8-62.1 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 4H), 7.45 (t, J = 7.5 Hz, 2H), 7.40-7.34 (m, 3H), 6.68 (d, J = 6.4 Hz, 1H), 6.06 (d, J = 6.3 Hz, 1H), 4.25 (qd, J = 7.1, 1.6 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.9, 165.0, 140.9, 140.4, 130.1, 128.8, 127.9, 127.5, 127.5, 126.9, 98.3, 92.0, 61.2, 14.2 ppm; IR (KBr) v = 3031, 2978, 2026, 1943, 1714, 1632 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{17}O_2$ $[M+H]^+$ = 265.1223 found = 265.1236.

Ethyl 4-(benzo[d][1,3]dioxol-5-yl)buta-2,3-dienoate **3h**



Pale yellow oil; it is a mixture containing 14% unseparated alkynoate from ^{1}HNMR. ^1H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 1H), 6.75 (s, 2H), 6.54 (d, J = 6.3 Hz, 1H), 5.98 (d, J = 6.3 Hz, 1H), 5.94 (s, 2H), 4.20 (qd, J = 7.1, 1.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.4, 165.0, 148.2, 147.7, 124.8, 121.6, 108.5, 107.2, 101.2, 98.6, 92.1, 61.1, 14.2 ppm; IR (film) v = 2980, 2903, 2026, 1718, 1632, 1603cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{13}O_4$ $[M+H]^+$ = 233.0808, found = 233.0822.

Ethyl 4-(2,3-dihydrobenzofuran-5-yl)buta-2,3-dienoate **3i**



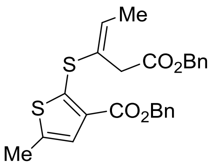
pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 7.04 (d, J = 8.2 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 6.58 (d, J = 6.3 Hz, 1H), 5.99 (d, J = 6.3 Hz, 1H), 4.58 (t, J = 8.7 Hz, 2H), 4.22 (qd, J = 7.1, 2.0 Hz, 2H), 3.20 (t, J = 8.7 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.6, 165.3, 160.3, 128.0, 127.7, 123.9, 122.9, 109.5, 109.2, 98.5, 91.8, 71.5, 61.0, 29.5, 14.2 ppm; IR (film) v = 2980, 2026, 1716, 1632, 1593, 1385 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{15}O_3$ $[M+H]^+$ = 231.1016, found = 231.1029.

C. General procedure for the DPPE catalyzed tandem reaction

To a dried sealed tube with a magnetic stirring bar were added allenoate**1** or **3** (0.4 mmol) and CS_2 (2 mL), followed by the addition of DPPE (0.04 mmol, 15.9 mg) at room temperature. The resulting mixture was sealed and stirred overnight at room temperature. After the completely consumption of allenoate monitored by TLC, the mixture was purified directly by column chromatography on silica gel with PE/Ea as eluent to afford product **2** or **4.**

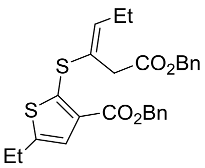
D. Analytical data of products 1 or 3

Benzyl (E)-2-((5-(benzyloxy)-5-oxopent-2-en-3-yl)thio)-5-methylthiophene-3-carboxylate **2a**



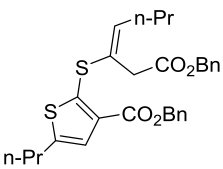
Crude ^{1}HNMR show the E/Z ratio is more than 19:1. pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 2H), 7.40 – 7.29 (m, 8H), 7.06 (s, 1H), 6.42 (q, *J* = 7.0 Hz, 1H), 5.29 (s, 2H), 5.12 (s, 2H), 3.49 (s, 2H), 2.35 (s, 3H), 1.81 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 162.5, 146.0, 140.6, 137.6, 136.1, 135.6, 128.5, 128.2, 128.1, 128.0, 127.4, 126.2, 66.7, 66.2, 37.6, 15.5, 15.2 ppm; IR (film) *v* = 3033, 2917, 1736, 1701, 1455, 1232 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{25}O_4S_2$[M+H]$^+$ = 453.1189, found = 453.1193.

Benzyl (E)-2-((1-(benzyloxy)-1-oxohex-3-en-3-yl)thio)-5-ethylthiophene-3-carboxylate **2b**



Crude ^{1}HNMR show the E/Z ratio is more than 19:1. pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.0 Hz, 2H), 7.39 – 7.31 (m, 8H), 7.09 (s, 1H), 6.34 (t, *J* = 7.5 Hz, 1H), 5.29 (s, 2H), 5.11 (s, 2H), 3.49 (s, 2H), 2.70 (q, *J* = 7.5 Hz, 2H), 2.19 (p, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.5 Hz, 3H), 1.04 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 162. 7, 147.7, 145.0, 136.2, 135.7, 128.5, 128.2, 128.2, 128.1, 128.0, 127.2, 125.6, 124. 7, 66.8, 66.2, 37.9, 23.3, 15.4, 13.1 ppm; IR (film) *v* = 3032, 2967, 1737, 1701, 1497, 1455 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{29}O_4S_2$[M+H]$^+$ = 481.1502, found = 481.1505.

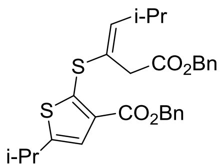
Benzyl (E)-2-((1-(benzyloxy)-1-oxohept-3-en-3-yl)thio)-5-propylthiophene-3-carboxylate **2c**



Crude ^{1}HNMR show the E/Z ratio is more than 19:1. pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ

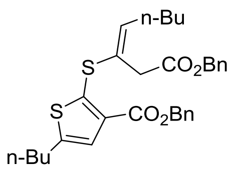
7.44 (d, *J* = 7.1 Hz, 2H), 7.40 – 7.29 (m, 8H), 7.08 (s, 1H), 6.35 (t, *J* = 7.5 Hz, 1H), 5.29 (s, 2H), 5.11 (s, 2H), 3.49 (s, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.15 (q, *J* = 7.4 Hz, 2H), 1.69 – 1.56 (m, 2H), 1.55 – 1.38 (m, 2H), 0.93 (tt, *J* = 11.9, 5.9 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 162.6, 146.3, 146.0, 143.3, 136.1, 135.6, 128.4, 128.2, 128.1, 128.1, 128.0, 126.3, 125.2, 66.7, 66.1, 38.0, 32.0, 31.9, 24.4, 21.9, 13.7, 13.5 ppm; IR (film) *v* = 2959, 2930, 1736, 1702, 1455, 1250 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{33}O_4S_2[M+H]^+$ = 509.1815, found = 509.1822 .

Benzyl (E)-2-((1-(benzyloxy)-5-methyl-1-oxohex-3-en-3-yl)thio)-5-isopropylthiophene-3-carboxylate **2d**



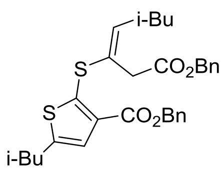
Crude ^{1}HNMR show the E/Z ratio is 10:1 and it is an unseparated mixture. pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.30 (m, 8H), 7.09 (s, 1H), 6.18 (d, *J* = 10.1 Hz, 1H), 5.30 (d, *J* = 4.7 Hz, 2H), 5.12 (s, 2H), 3.50 (s, 2H), 3.09 – 2.95 (m, 1H), 2.64 – 2.55 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 6H), 1.04 (d, *J* = 6.6 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 162.7, 153.3, 150.5, 146.1, 136.2, 135.6, 128.5, 128.2, 128.2, 128.1, 128.0, 124.1, 122.9, 66.8, 66.1, 38.1, 30.0, 29.6, 24.2, 22.0 ppm; IR (film) *v* = 3033, 2961, 1738, 1702, 1456, 1324 cm^{-1};HRMS (ESI) m/z calcd for $C_{29}H_{33}O_4S_2[M+H]^+$ = 509.1815, found = 509.1823 .

Benzyl (E)-2-((1-(benzyloxy)-1-oxooct-3-en-3-yl)thio)-4-butylcyclopenta-1,4-diene-1-carboxylate **2e**



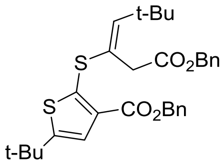
Crude ^{1}HNMR show the E/Z ratio is more than 19:1. pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.1 Hz, 2H), 7.39 – 7.30 (m, 8H), 7.07 (s, 1H), 6.35 (t, *J* = 7.5 Hz, 1H), 5.29 (s, 2H), 5.11 (s, 2H), 3.48 (s, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.17 (q, *J* = 7.3 Hz, 2H), 1.58 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.44 – 1.28 (m, 6H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 162.7, 146.6, 143.5, 136.2, 135.7, 128.5, 128.2, 128.2, 128.1, 128.0, 127.0, 126.2, 125.0, 66.8, 66.2, 38.0, 33.3, 30.7, 29.7, 29.7, 22.3, 22.0, 13.8, 13.7 ppm; IR (film) *v* = 2956, 2929, 2857, 1739, 1704, 1456 cm^{-1}; HRMS (ESI) m/z calcd for $C_{31}H_{37}O_4S_2[M+H]^+$ = 537.2128, found = 537.2138.

Benzyl (E)-2-((1-(benzyloxy)-6-methyl-1-oxohept-3-en-3-yl)thio)-5-isobutylthiophene-3-carboxylate **2f**



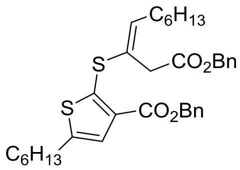
Crude ^{1}HNMR show the E/Z ratio is more than 19:1. pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.38 -7.31 (m, 8H), 7.08 (s, 1H), 6.38 (t, *J* = 9.3 Hz, 1H), 5.31 (s, 2H), 5.12 (s, 2H), 3.50 (s, 2H), 2.54 (d, *J* = 3.3 Hz, 2H), 2.08 (t, *J* = 7.0 Hz, 2H), 1.83 – 1.71 (m, 2H), 0.97 – 0.89 (m,12H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 162.7, 146.3, 145.6, 142.1, 136.1, 135.6, 128.4, 128.2, 128.1, 128.0, 127.1, 127.0, 125.6, 66.7, 66.26, 39.2, 38.9, 38.0, 30.3, 28.3, 22.4, 22.1 ppm; IR (film) *v* = 2956, 2925, 1739, 1704, 1495, 1454 cm^{-1}; HRMS (ESI) m/z calcd for $C_{31}H_{37}O_4S_2[M+H]^+$ = 537.2128, found = 537.2133.

Benzyl (E)-2-((1-(benzyloxy)-5,5-dimethyl-1-oxohex-3-en-3-yl)thio)-5-(tert-butyl)thiophene-3-carboxylate **2g**



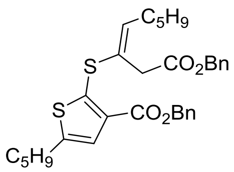
Crude ^{1}HNMR show the E/Z ratio is more than 19:1. white powder, m.p. = 45.5 – 47.4 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.1 Hz, 2H), 7.42 – 7.30 (m, 8H), 7.06 (s, 1H), 6.45 (s, 1H), 5.32 (s, 2H), 5.14 (s, 2H), 3.69 (s, 2H), 1.33 (s, 9H), 1.19 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 162.8, 156.1, 154.4, 146.8, 136.2, 135.6, 128.4, 128.2, 128.1, 128.0, 126.2, 124.2, 123.5, 66.7, 66.1, 38. 8, 34.8, 34.6, 32.0, 30.1, 29.6 ppm; IR (KBr) *v* = 3033, 2961, 1740, 1704, 1456, 1364 cm^{-1}; HRMS (ESI) m/z calcd for $C_{31}H_{37}O_4S_2[M+H]^+$ = 537.2128, found = 537.2136.

Benzyl (E)-2-((1-(benzyloxy)-1-oxodec-3-en-3-yl)thio)-5-hexylthiophene-3-carboxylate **2h**



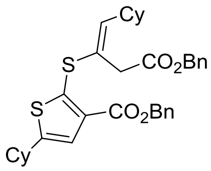
Crude ^{1}HNMR show the E/Z ratio is more than 19:1. pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.1 Hz, 2H), 7.39 – 7.30 (m, 8H), 7.07 (s, 1H), 6.36 (t, *J* = 7.5 Hz, 1H), 5.29 (s, 2H), 5.11 (s, 2H), 3.49 (s, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.17 (q, *J* = 7.3 Hz, 2H), 1.67 – 1.53 (m, 2H), 1.47 – 1.40 (m, 2H), 1.38 – 1.19 (m, 14H), 0.98 – 0.83 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 162.7, 146.8, 146.2, 143.5, 136.2, 135.6, 128.4, 128.27, 128.1, 128.1, 128.0, 127.0, 126.2, 125.0, 66.7, 66.1, 38.0, 31.6, 31.4, 31.2, 30.0, 29.9, 28.9, 28.6, 28.5, 22.6, 22.5, 14.0, 14.0 ppm; IR (film) *v* = 2954, 2927, 2855, 1740, 1705, 1456 cm^{-1}; HRMS (ESI) m/z calcd for $C_{35}H_{45}O_4S_2[M+H]^+$ = 593.2754, found = 593.2764.

Benzyl (E)-2-((4-(benzyloxy)-1-cyclopentyl-4-oxobut-1-en-2-yl)thio)-5-cyclopentylthiophene-3-carboxylate **2i**



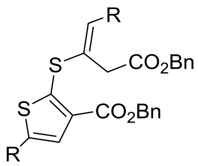
Crude ^{1}HNMR show the E/Z ratio is more than 19:1. pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.29 (m, 8H), 7.10 (s, 1H), 6.29 (d, *J* = 9.8 Hz, 1H), 5.30 (s, 2H), 5.12 (s, 2H), 3.52 (s, 2H), 3.17 – 3.02 (m, 1H), 2.69 (h, *J* = 8.1 Hz, 1H), 2.10 – 2.02 (m, 2H), 1.89 – 1.54 (m, 12H), 1.42 – 1.32 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 162.7, 151.6, 148.1, 146.2, 136.2, 135.7, 128.4, 128.1, 128.1, 128.0, 128.0, 126.7, 124.7, 123.4, 66.7, 66.1, 41.0, 40.7, 38.2, 34.9, 32.8, 25.3, 25.0 ppm; IR (film) v = 2954, 2868, 1736, 1702, 1451, 1223 cm^{-1}; HRMS (ESI) m/z calcd for $C_{33}H_{37}O_4S_2[M+H]^+$ = 561.2128, found = 561.2133.

Benzyl (E)-2-((4-(benzyloxy)-1-cyclohexyl-4-oxobut-1-en-2-yl)thio)-5-cyclohexylthiophene-3-carboxylate **2j**



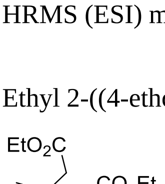
Crude [1]HNMR show the E/Z ratio is more than 19:1. pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.0 Hz, 2H), 7.41 – 7.29 (m, 8H), 7.08 (s, 1H), 6.19 (d, J = 9.9 Hz, 1H), 5.29 (s, 2H), 5.11 (s, 2H), 3.50 (s, 2H), 2.73 – 2.56 (m, 1H), 2.32 – 2.22 (m, 1H), 2.01 – 1.92 (m, 2H), 1.84 – 1.77 (m, 2H), 1.75 – 1.63 (m, 6H), 1.37 – 1.13 (m, 10H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 162.7, 151.8, 149.5, 145.9, 136.2, 135.6, 128.4, 128.2, 128.1, 128.0, 126.6, 124.0, 123.3, 66.7, 66.1, 39.4, 39.3, 38.2, 34.8, 31.9, 26.2, 25.7, 25.4 ppm; IR (film) v = 2925, 2850, 1738, 1702, 1448, 1245 cm^{-1}; HRMS (ESI) m/z calcd for $C_{35}H_{41}O_4S_2[M+H]^+$ = 589.2441, found = 589.2441.

Benzyl (E)-2-((1-(benzyloxy)-1-oxo-6-phenylhex-3-en-3-yl)thio)-5-phenethylthiophene-3-carboxylate **2k**



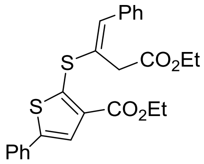
Crude [1]HNMR show the E/Z ratio is more than 19:1. pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.0 Hz, 2H), 7.41 – 7.27 (m, 12H), 7.24 – 7.15 (m, 6H), 7.09 (s, 1H), 6.35 (t, J = 7.4 Hz, 1H), 5.29 (s, 2H), 5.11 (s, 2H), 3.41 (s, 2H), 3.00 – 2.95 (m, 2H), 2.93 – 2.87 (m, 2H), 2.74 (t, J = 7.6 Hz, 2H), 2.49 (q, J = 7.5 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 162. 6, 145.9, 144.8, 142.3, 140.8, 140.5, 136.1, 135.6, 128.4, 128.4, 128.2, 128.1, 128.1, 127.3, 126.6, 126.38, 126.1, 125.9, 66.8, 66.2, 38.0, 37.4, 34.6, 31.8, 31.6 ppm; IR (film) v = 3027, 2921, 1735, 1701, 1496, 1453 cm^{-1}; HRMS (ESI) m/z calcd for $C_{39}H_{37}O_4S_2[M+H]^+$ = 633.2128, found = 633.2139

Ethyl 2-((4-ethoxy-4-oxobut-1-en-2-yl)thio)thiophene-3-carboxylate **2l**



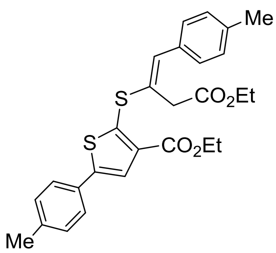
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 5.5 Hz, 1H), 7.17 (d, J = 5.5 Hz, 1H), 5.65 (s, 1H), 5.61 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 3.36 (s, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 162.6, 143.3, 136.3, 130.9, 129.8, 125.1, 124.5, 61.0, 60.7, 42.1, 14.2, 14.0 ppm; IR (film) v = 2981, 2935, 1736, 1702, 1509, 1445 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{16}NaO_4S_2[M+Na]^+$ = 323.0382, found = 323.0398.

Ethyl (E)-2-((4-ethoxy-4-oxo-1-phenylbut-1-en-2-yl)thio)-5-phenylthiophene-3-carboxylate **4a**



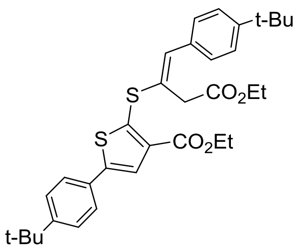
Crude ^{1}HNMR show the E/Z ratio is more than 19:1. white solid, m.p. = 64.7 - 66.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.45 – 7.32 (m, 8H), 7.29 (d, *J* = 7.2 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.67 (s, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 162.8, 146.1, 142.8, 142.0, 135.6, 133.1, 129.7, 128.9, 128.8, 128.6, 128.4, 128.3, 127.9, 125.4, 125.0, 61.2, 60.8, 38.7, 14.4, 14.1 ppm; IR (KBr) *v* = 3030, 2927, 1735, 1702, 1441, 1225 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{24}NaO_4S_2[M+Na]^+$ = 475.1008, found = 475.1012.

Ethyl (E)-2-((4-ethoxy-4-oxo-1-(p-tolyl)but-1-en-2-yl)thio)-5-(p-tolyl)thiophene-3-carboxylate **4b**



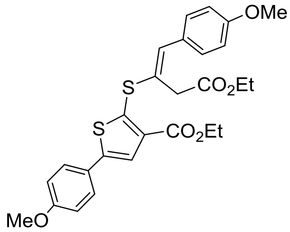
Crude ^{1}HNMR show the E/Z ratio is more than 19:1. white solid, m.p. = 65.3-67.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.36 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.67 (s, 2H), 2.38 (s, 3H), 2.35 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 162.8, 146.0, 143.1, 142.0, 138.3, 137.8, 132.7, 130.4, 129.6, 129.3, 128.9, 128.4, 127.8, 125.2, 124.4, 61.2, 60.7, 38.8, 21.2, 21.1, 14.4, 14.1 ppm; IR (KBr) *v* = 2980, 2922, 1735, 1702, 1441, 1224 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{28}NaO_4S_2[M+Na]^+$ = 503.1321, found = 503.1331

Ethyl (E)-5-(4-(tert-butyl)phenyl)-2-((1-(4-(tert-butyl)phenyl)-4-ethoxy-4-oxobut-1-en-2-yl)thio)thiophene-3-carboxylate **4c**



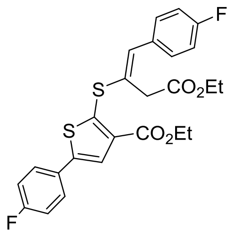
Crude ^{1}HNMR show the E/Z ratio is more than 19:1. pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.47 – 7.42 (m, 4H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.37 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.34 (s, 9H), 1.33 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 162.9, 151.5, 151.1, 146.3, 143.1, 142.0, 132.8, 130.4, 129.4, 128.3, 127.8, 125.8, 125.6, 125.2, 124.5, 61.2, 60.8, 38.9, 34.7, 34.6, 31.2, 14.4, 14.1 ppm; IR (film) *v* = 2962, 2902, 1735, 1702, 1507, 1438 cm^{-1}; HRMS (ESI) m/z calcd for $C_{33}H_{40}NaO_4S_2[M+Na]^+$ = 587.2260, found = 587.2266.

Ethyl (E)-2-((4-ethoxy-1-(4-methoxyphenyl)-4-oxobut-1-en-2-yl)thio)-5-(4-methoxyphenyl)thiophene-3-carboxylate **4d**



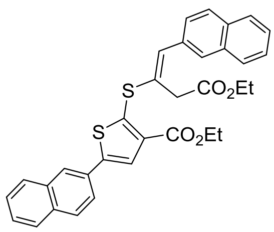
Crude ^{1}HNMR show the E/Z ratio is 12:1. pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.43 (d, *J* = 8.7 Hz, 21H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.32 (s, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.66 (s, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 162.8, 159.6, 159.4, 145.7, 142.7, 141.8, 130.9, 129.9, 129.3, 128.1, 126.7, 126.0, 123.8, 114.3, 114.0, 61.2, 61.0, 60.7, 55.3, 55.2, 38.8, 14.4, 14.1 ppm; IR (film) *v* = 2932, 2834, 1732, 1699, 1606, 1507 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{28}NaO_6S_2[M+Na]^+$ = 535.1220, found = 535.1226.

Ethyl (E)-2-((4-ethoxy-1-(4-fluorophenyl)-4-oxobut-1-en-2-yl)thio)-5-(4-fluorophenyl)thiophene-3-carboxylate **4e**



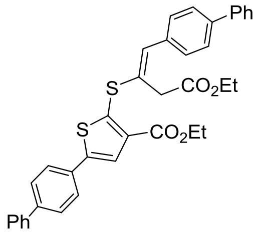
Crude ^{1}HNMR show the E/Z ratio is more than 19:1. pale yellow gel; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.51 – 7.45 (m, 2H), 7.39 -7.36 (m, 2H), 7.32 (s, 1H), 7.13 – 7.03 (m, 4H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.61 (s, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 162.7, 162.6 (d, J_{C-F} = 248.9 Hz), 162.5 (d, J_{C-F} = 248.2 Hz), 141.5, 141.5, 141.2, 131.6 (d, J_{C-F} = 2.7 Hz), 130.3 (d, J_{C-F} = 8.2 Hz), 129.4 (d, J_{C-F} = 3.5 Hz), 128.8, 128.8, 127.2 (d, J_{C-F} = 8.1 Hz), 125.0, 116.0 (d, J_{C-F} = 22.0 Hz), 115.7 (d, J_{C-F} = 21.6 Hz), 61.4, 60.9, 38.6, 14.4, 14.1 ppm; IR (film) *v* = 2988, 2917, 1736, 1700, 1655, 1507 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}F_2NaO_4S_2[M+Na]^+$ = 511.0820, found = 511.0829.

Ethyl (E)-2-((4-ethoxy-1-(naphthalen-2-yl)-4-oxobut-1-en-2-yl)thio)-5-(naphthalen-2-yl)thiophene-3-carboxylate **4f**



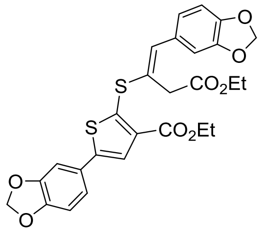
Crude ^{1}HNMR show the E/Z ratio is more than 19:1. pale yellow gel; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.90 – 7.79 (m, 6H), 7.78 (s, 1H), 7.67 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.57 (s, 1H), 7.55 – 7.50 (m, 3H), 7.49 – 7.44 (m, 2H), 4.42 (q, J = 7.1 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 3.78 (s, 2H), 1.45 (t, J = 7.1 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 162.8, 146.4, 142.9, 142.2, 133.44 133.2, 133.0, 132.9, 132.8, 130.5, 129.9, 129.0, 128.7, 128.3, 128.3, 128.0, 127.9, 127.7, 126.7, 126.6, 126.5, 126.2, 126.1, 125.4, 123.9, 123.5, 61.3, 60.9, 38.9, 14.4, 14.2 ppm; IR (film) v = 3063, 2980, 2923, 1733, 1701, 1596 cm^{-1}; HRMS (ESI) m/z calcd for $C_{33}H_{28}NaO_4S_2$ $[M+Na]^+$ = 575.1321, found = 575.1324

Ethyl (E)-5-([1,1'-biphenyl]-4-yl)-2-((1-([1,1'-biphenyl]-4-yl)-4-ethoxy-4-oxobut-1-en-2-yl)thio)thiophene-3-carboxylate **4g**



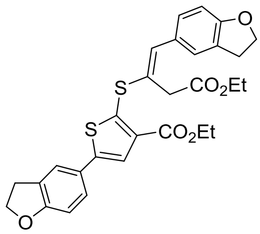
Crude ^{1}HNMR show the E/Z ratio is 14:1. pale yellow gel; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.67 (s, 1H), 7.65 – 7.58 (m, 10H), 7.50 (d, J = 7.9 Hz, 2H), 7.46 (d, J = 6.3 Hz, 2H), 7.44 (d, J = 6.8 Hz, 2H), 7.37 (dd, J = 14.1, 7.2 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.74 (s, 2H), 1.44 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 162.8, 146.2, 142.4, 141.7, 141.2, 140.7, 140.3, 140.2, 134.5, 132.1, 129.9, 129.8, 129.0, 128.8, 127.6, 127.5, 127.3, 127.0, 126.9, 125.8, 125.1, 125.0, 61.3, 60.9, 38.9, 14.4, 14.1 ppm; IR (film) v = 3030, 2980, 1734, 1701, 1487, 1438 cm^{-1}; HRMS (ESI) m/z calcd for $C_{37}H_{32}NaO_4S_2$ $[M+Na]^+$ = 627.1634, found = 627.1641.

Ethyl (E)-5-(benzo[d][1,3]dioxol-5-yl)-2-((1-(benzo[d][1,3]dioxol-5-yl)-4-ethoxy-4-oxobut-1-en-2-yl)-thio)thiophene-3-carboxylate **4h**



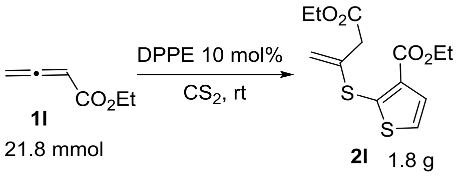
Crude ^{1}HNMR show the E/Z ratio is more than 19:1. pale yellow gel; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.27 (s, 1H), 6.99 (s, 1H), 6.99 – 6.96 (m, 1H), 6.90 (s, 1H), 6.88 (d, J = 8.5 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.78 (d, J = 8.6 Hz, 1H), 5.99 (s, 2H), 5.98 (s, 2H), 4.35 (q, J = 7.1 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.64 (s, 2H), 1.39 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 162.8, 148.2, 147.9, 147.7, 147.6, 145.7, 145.6, 142.7, 142.7, 141.9, 129.6, 127.5, 124.3, 122.9, 119.4, 108.6, 108.6, 108.5, 106.0, 101.3, 101.3, 61.3, 60.8, 38.8, 14.4, 14.1 ppm; IR (film) v = 2980, 2920, 1734, 1701, 1502, 1489 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{24}NaO_8S_2$ $[M+Na]^+$ = 563.0805, found = 563.0813.

Ethyl (E)-5-(2,3-dihydrobenzofuran-5-yl)-2-((1-(2,3-dihydrobenzofuran-5-yl)-4-ethoxy-4-oxobut-1-en-2-yl)thio)thiophene-3-carboxylate **4i**



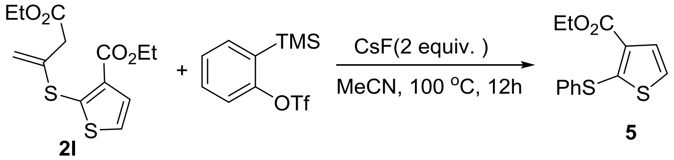
Crude [1]HNMR show the E/Z ratio is more than 19:1. pale yellow gel; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.35 (s, 1H), 7.31 (s, 1H), 7.27 – 7.25 (m, 2H), 7.17 (d, J = 8.3 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 4.60 (td, J = 8.7, 6.2 Hz, 4H), 4.35 (q, J = 7.1 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.67 (s, 2H), 3.23 (q, J = 8.3 Hz, 4H), 1.39 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 170.2, 162.9, 160.4, 160.1, 143.4, 142.3, 130.4, 129.0, 128.1, 127.9, 127.6, 126.1, 126.0, 125.7, 125.2, 123.6, 122.3, 109.5, 109.4, 71.5, 71.5, 61.2, 60.7, 38.9, 29.5, 29.5, 14.4, 14.1 ppm; IR (film) v = 2980, 2922, 1734, 1701, 1611, 1491 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{28}NaO_6S_2[M+Na]^+$ = 559.1220, found = 559.1222.

E. Gram scale synthesis of 2l



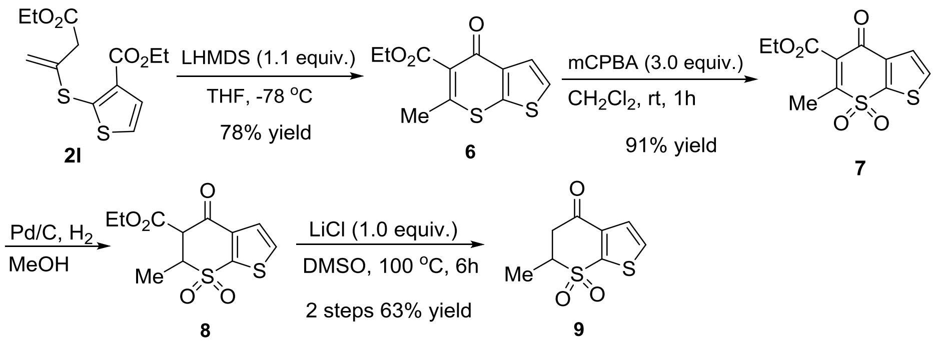
To a dried 100 mL round-bottomed flask with a magnetic stirring bar were added ethyl buta-2,3-dienoate **1l** (21.8 mmol, 2.44g) and CS_2 (50 mL), followed by the addition of DPPE (2.18 mmol, 0.87 g) at room temperature. The resulting mixture was stirred overnight. After the completely consumption of **1l** monitored by TLC, the mixture was evaporated to remove CS_2 and the residue was purified by column chromatography on silica gel with PE/Ea = 10:1 as eluent to afford product **2l** (1.8g, 55% yield) as a yellow oil.

F. Reaction of 2l with benzyne



To a dried sealed tube with a magnetic stirring bar were added CsF (0.4 mmol, 60.8 mg) and acetonitrile (1.5 mL), followed by the addition of **2l** (0.2 mmol, 60.1 mg) and benzyne precursor (0.3 mmol, 89.5 mg). The resulting mixture was sealed and stirred at 100 °C. After the completely consumption of **1l** monitored by TLC (about 12 h), the mixture was evaporated to remove solvent and the residue was purified by column chromatography on silica gel with PE/Ea = 10:1 as eluent to afford product **5** (22.7 mg, 55% yield) as a white powder, m.p. = 46.0-48.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.43 – 7.42 (m, 3H), 7.38 (d, *J* = 5.4 Hz, 1H), 6.95 (d, *J* = 5.4 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 151.0, 134.5, 133.2, 129.7, 129.2, 127.2, 122.7, 60.7, 14.4 ppm; IR (KBr) *v* = 2980, 2927, 1698, 1509, 1421, 1260 cm^{-1};HRMS (ESI) m/z calcd for $C_{13}H_{13}O_2S_2[M+H]^+$ = 265.0351, found = 265.0365.

G. Transformation of 2l



Step 1

To the solution of **2l** (5 mmol, 1.502 g) in 25 mL anhydrous THF was added dropwise LHMDS (5.5 mmol, 5.5 mL, 1 mol/L in THF) over 15 min at -78 °C under Nitrogen atmosphere. The mixture was stirred at the same temperature for one hour, and then was warmed to 0 °C and kept stirring. After the completely consumption of **2l** monitored by TLC (about one hour), 20 mL saturated NH_4Cl aqueous solution was added and separated. The aqueous phase was extracted by Ea (20 mL×2), and the organic phase was combined, dried by Na_2SO_4 and filtered. The filtrate was concentrated under vacuum to remove solvent and the residue was purified by column chromatography on silica gel with PE/Ea = 5:1 as eluent to afford product **6** (0.992 g, 78% yield) as a white powder, m.p. = 102.8-103.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 5.4 Hz, 1H), 7.42 (d, *J* = 5.4 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 165.9, 147.4, 142.6, 137.1, 132.2, 125.9, 125.3, 61.9, 21.0, 14.2 ppm; IR (film) *v* = 3109, 2920, 1934, 1683, 1647, 1507cm^{-1}; HRMS (ESI) m/z calcd for $C_{11}H_{11}O_3S_2[M+H]^+$ = 255.0144, found = 255.0149.

Step 2

To the solution of **6** (3.6 mmol, 0.916g g) in 25 mL anhydrous DCM was added mCPBA (10.8 mmol, 1.86g) and the resulting mixture was stirred at room temperature. After the completely consumption of **6** monitored by TLC (about one hour), the mixture was concentrated under vacuum to remove solvent and the residue was purified by column chromatography on silica gel with PE/Ea = 5:1 as eluent to afford product **7** (0.938 g, 91% yield) as a white powder, m.p. = 118.2-121.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 5.1 Hz, 1H), 7.56 (d, *J* = 5.1 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 162.3, 150.9, 144.0, 137.4, 133.8, 130.8, 126.2, 62.7, 14.0, 11.6 ppm; IR (film) *v* = 2927, 2814, 2026, 1724, 1661, 1631cm^{-1}; HRMS (ESI) m/z calcd for $C_{11}H_{11}O_5S_2$[M+H]$^+$ = 287.0042, found = 287.0044.

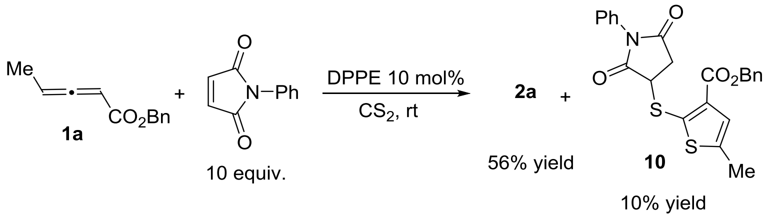
Step 3

To a 25 mL round-bottomed flask with a magnetic stirring bar were added compound **7** (2 mmol, 0.572 g) and 10% Pd/C (60 mg), followed by the addition of 10 mL Methanol. The RBF was connected with vacuum bump and Hydrogen balloon. After switched 4 times of vacuum and Hydrogen, the mixture was stirred at room temperature overnight. when compound **7** was completely consumed monitored by TLC, the mixture was filtered through a short pad of Celite and the filtrate was concentrated under vacuum to remove solvent to afford crude product **8**, which was used directly in the next step.

Step 4

To the solution of above product **8** in 10 mL DMSO was added LiCl (2 mmol, 84.8 mg), and the resulting solution was stirred at 100 ^{o}C. After the completely consumption of **8** monitored by TLC (about 6 hour), the mixture was cooled to room temperature, then added 20 mL water and 20 mL ether. After separation, the aqueous phase was extracted by ether (20 mL ×2). The organic phase was combined, washed by brine, dried by Na_2SO_4 and filtered. The filtrate was concentrated under vacuum to remove solvent and the residue was purified by column chromatography on silica gel with PE/Ea = 5:1 as eluent to afford product **9** (272.5 mg, 63% yield in two steps) as a white powder, m.p. = 99.9 – 102 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 5.1 Hz, 1H), 7.48 (d, *J* = 5.1 Hz, 1H), 3.86 (ddd, *J* = 9.3, 6.9, 4.6 Hz, 1H), 3.41 – 3.03 (m, 2H), 1.56 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.5, 146.8, 139.8, 130.6, 126.1, 58.0, 44. 7, 11.7; HRMS (ESI) m/z calcd for $C_8H_9O_3S_2$[M+H]$^+$ = 216.9988, found = 216.9989.

H. Control experiment with Maleimide



To a dried sealed tube with a magnetic stirring bar were added allenoate **1a** (0.4 mmol, 75.3 mg), N-phenyl Maleimide (4 mmol, 692.7 mg) and CS_2 (2 mL). After the mixture became clear, DPPE (0.04 mmol, 15.9 mg) was added and the mixture was stirred at room temperature overnight. When allenoate **1a** was completely consumed monitored by TLC, the mixture was purified directly by column chromatography on silica gel with PE/Ea as eluent to afford product **2a** (50.7 mg, 56% yield) and **10** (17.5 mg, 10% yield) as a yellow solid, m.p. = 137.2 – 139.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.35 (m, 8H), 7.27 – 7.24 (m, 2H), 7.20 (s, 1H), 5.30 (s, 2H), 4.43 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.22 (dd, *J* = 19.0, 9.2 Hz, 1H), 2.88 (dd, *J* = 19.0, 4.0 Hz, 1H), 2.43 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 173.3, 162.2, 142.6, 135.6, 135.0, 134.6, 131.5, 129.2, 128.8, 128.6, 128.4, 128.2, 126.3, 66.8, 44.7, 35.3, 15.4 ppm; IR (KBr) *v* = 2914, 2843, 1783, 1716, 1702, 1495 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{19}NNaO_4S_2[M+Na]^+$ = 460.0648, found = 460.0655.

I. X-Ray crystallographic analysis of 4a

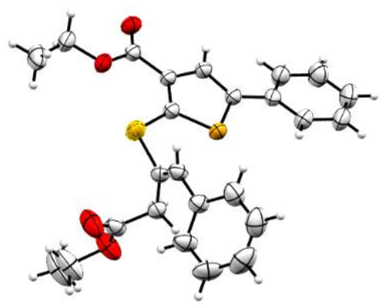


Figure 1. X-ray structure of **4a**

Table 1. Crystal data and structure refinement for **4a** (CCDC 2018743)

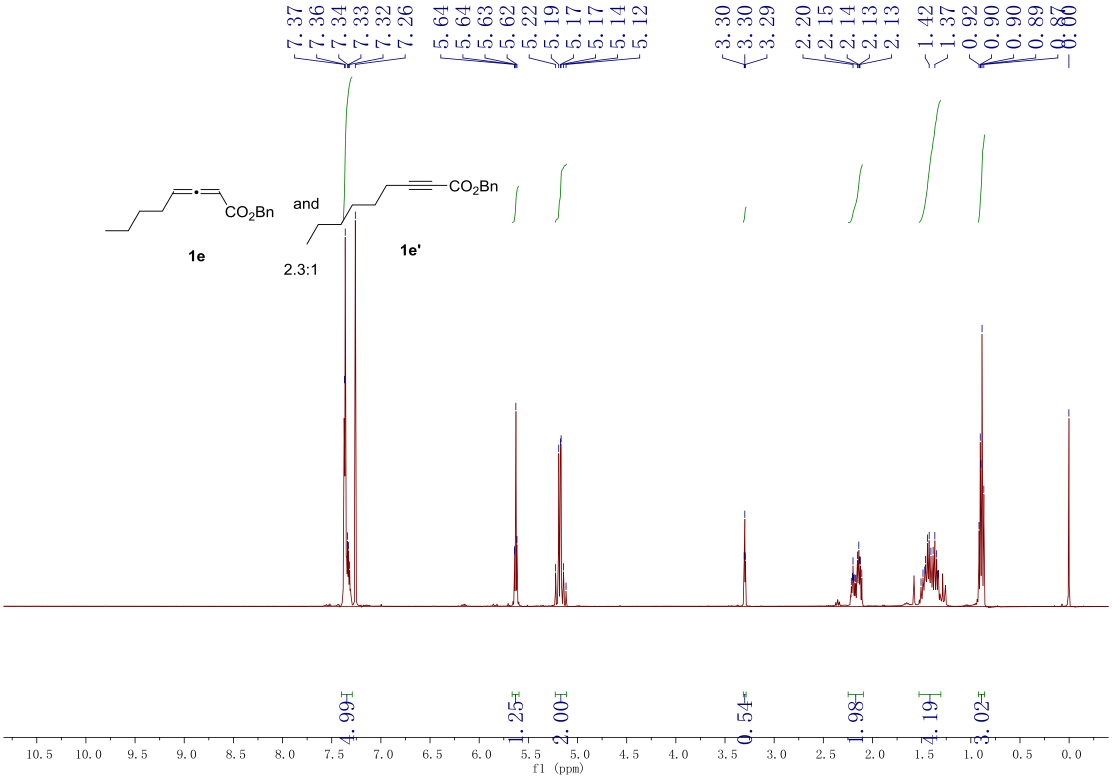
Empirical formula	$C_{25}H_{24}O_4S_2$
Formula weight	452.56
Temperature	296K
Wavelength	0.71073 Å

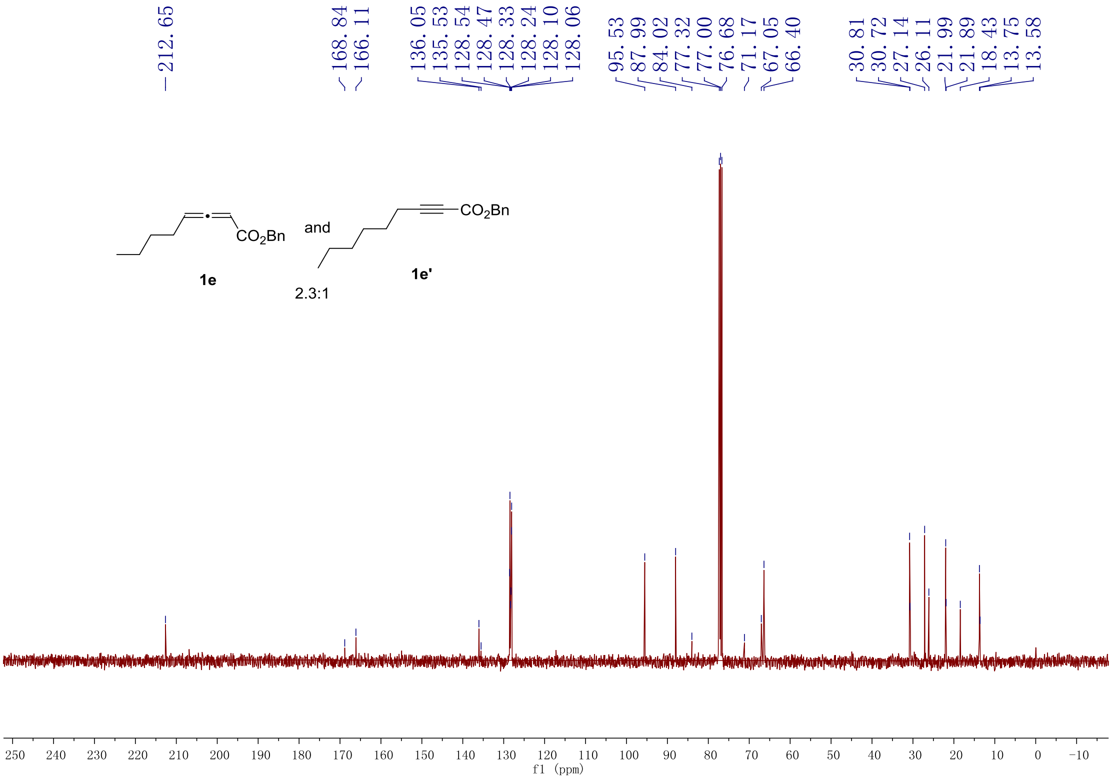
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 10.917 (3) Å α= 90 °.
	b = 7.526 (3) Å β= 100.154 °.
	c = 26.688 (11) Å γ = 90 °.
Volume	2320.1 (14) $Å^3$
Z	4
Density (calculated)	1.296 Mg/m^3
Absorption coefficient	0.258 mm^{-1}
F(000)	952
Crystal size	0.664 x 0.305 x 0.16 mm^3
Theta range for data collection	2.576 to 30.548 °.
Index ranges	-15<=h<=15, -10<=k<=10, -40<=l<=40
Reflections collected	38600
Independent reflections	7096 [R(int) = 0.0330]
Completeness to theta = 25.242 °	99.9 %
Absorption correction	multi-scan from equivalents
Max. and min. transmission	1.00000 and 0.9073
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7096 / 0 / 282
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1241
R indices (all data)	R1 = 0.0614, wR2 = 0.1377
Largest diff. peak and hole	0.454 and -0. 408 e.$Å^{-3}$

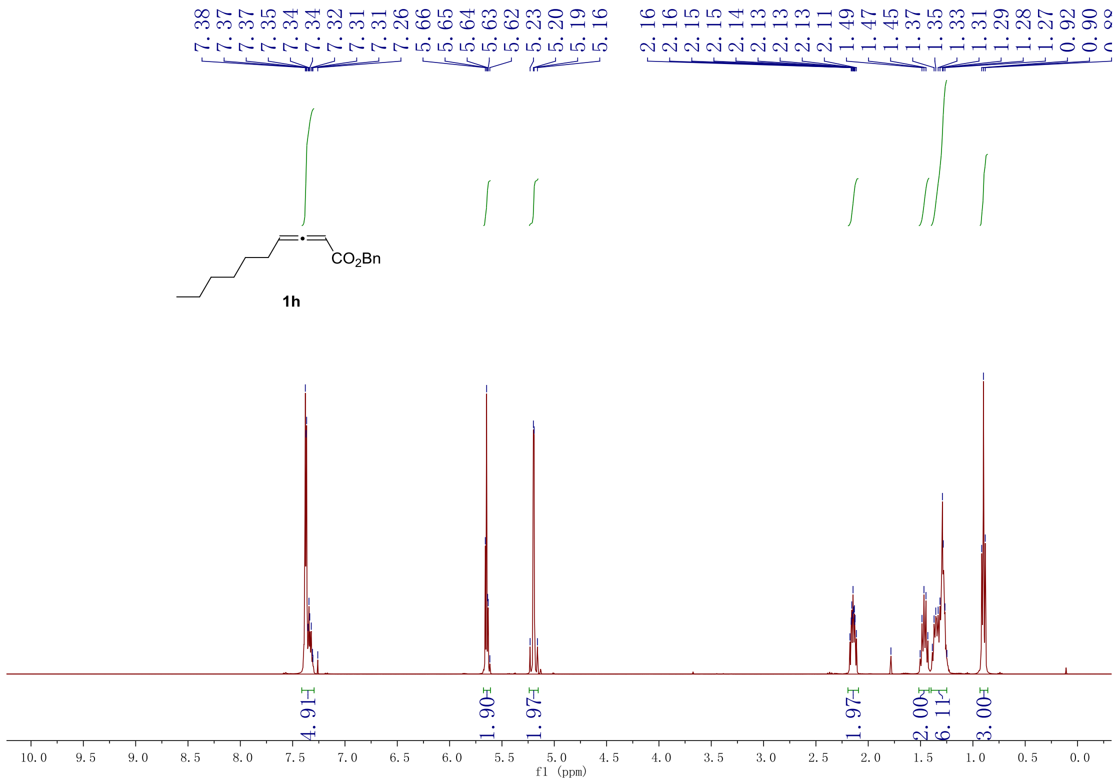
J. Reference

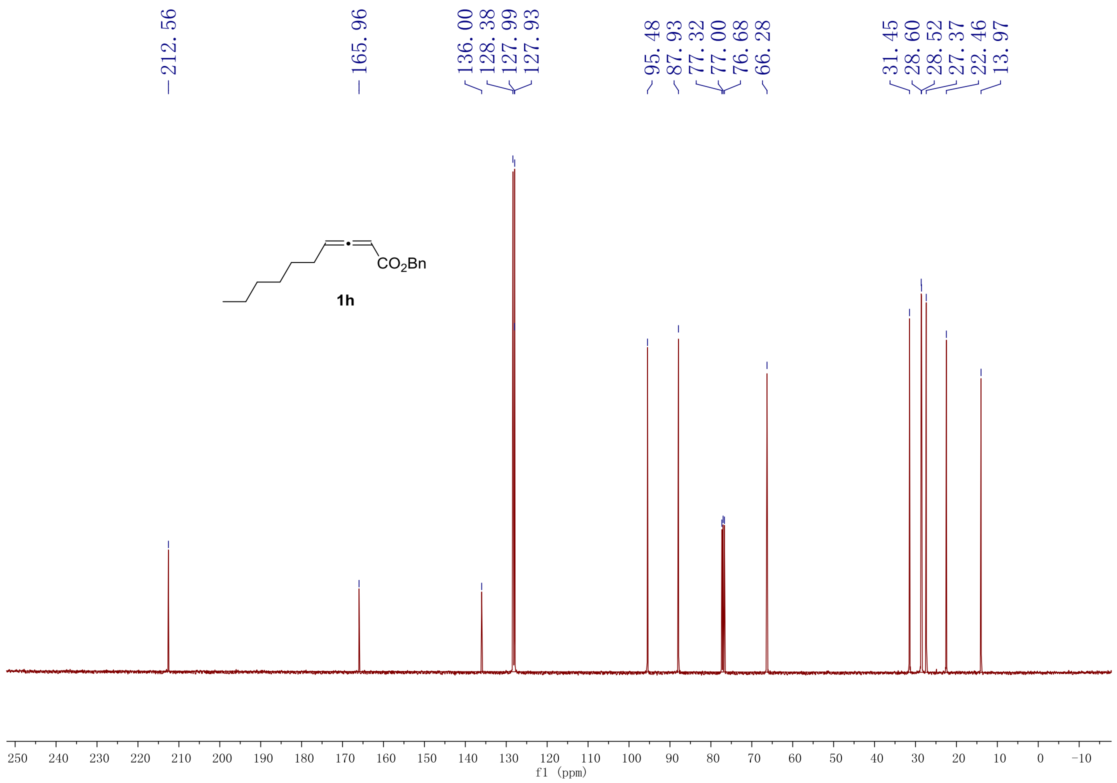
1. Rout, L.; Harned, A. M. *Chem. Eur. J.* **2009**, *15*, 12926 – 12928.
2. Kalek, M.; Fu. G. C. *J. Am. Chem. Soc.* **2015**, *137*, 9438 – 9442.

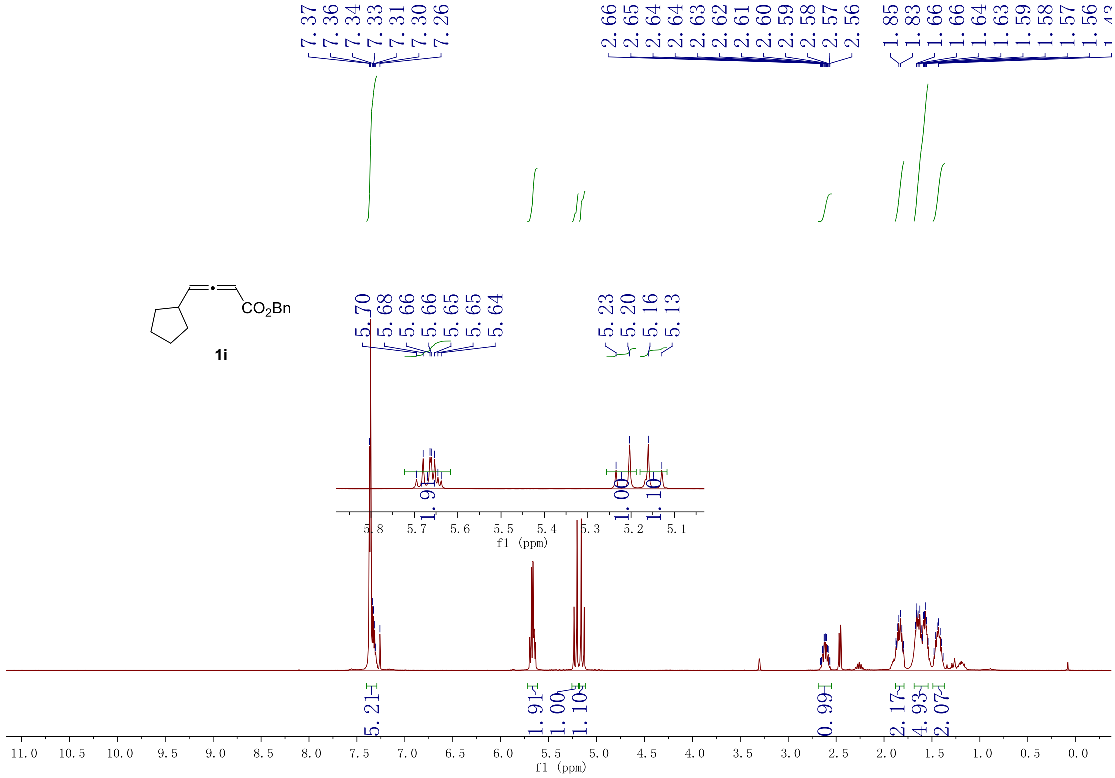
K. Spectra

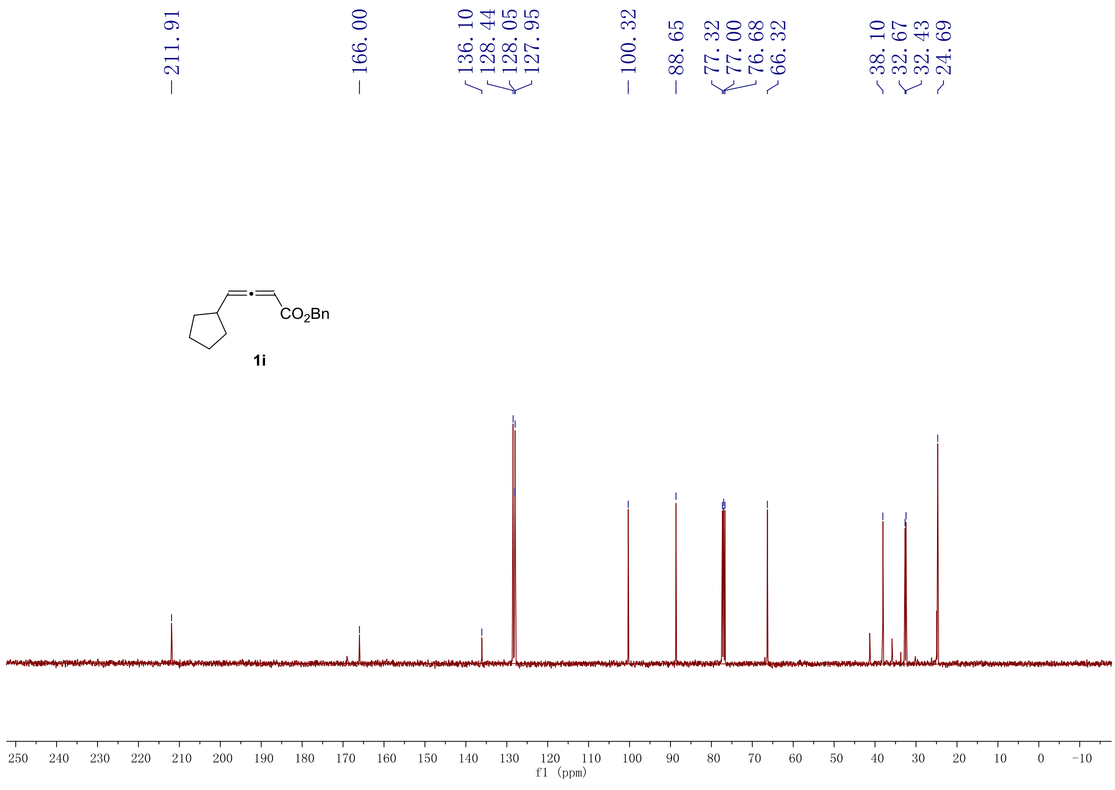


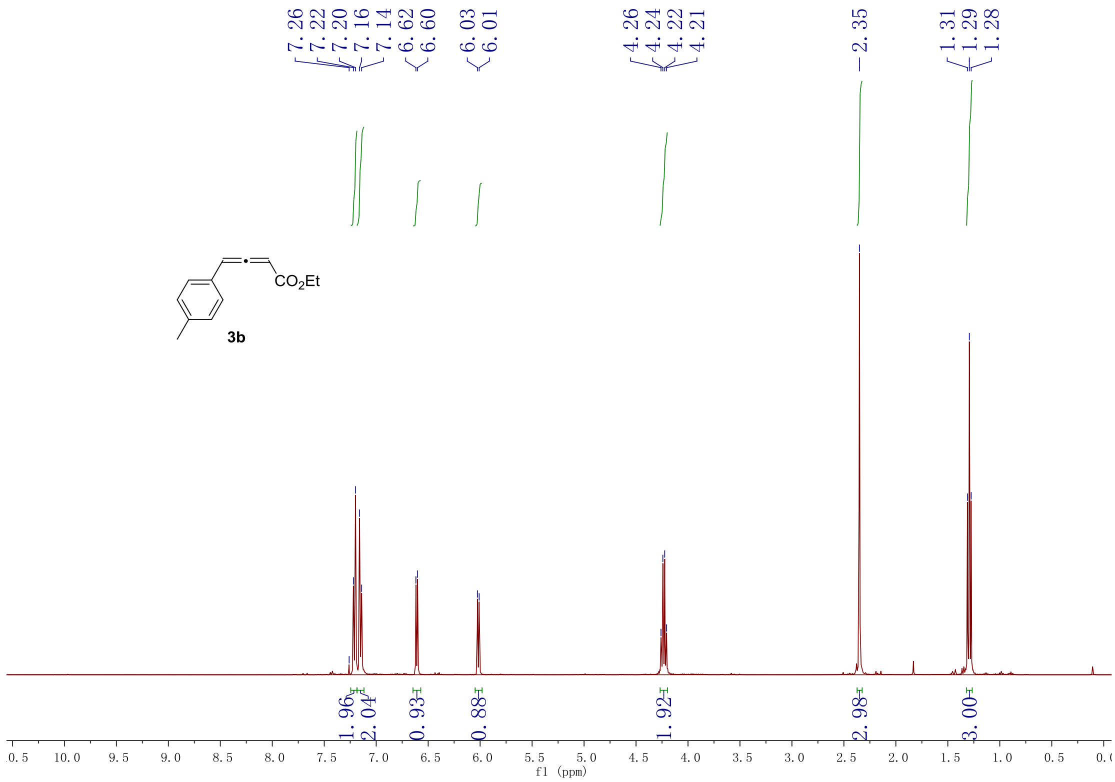


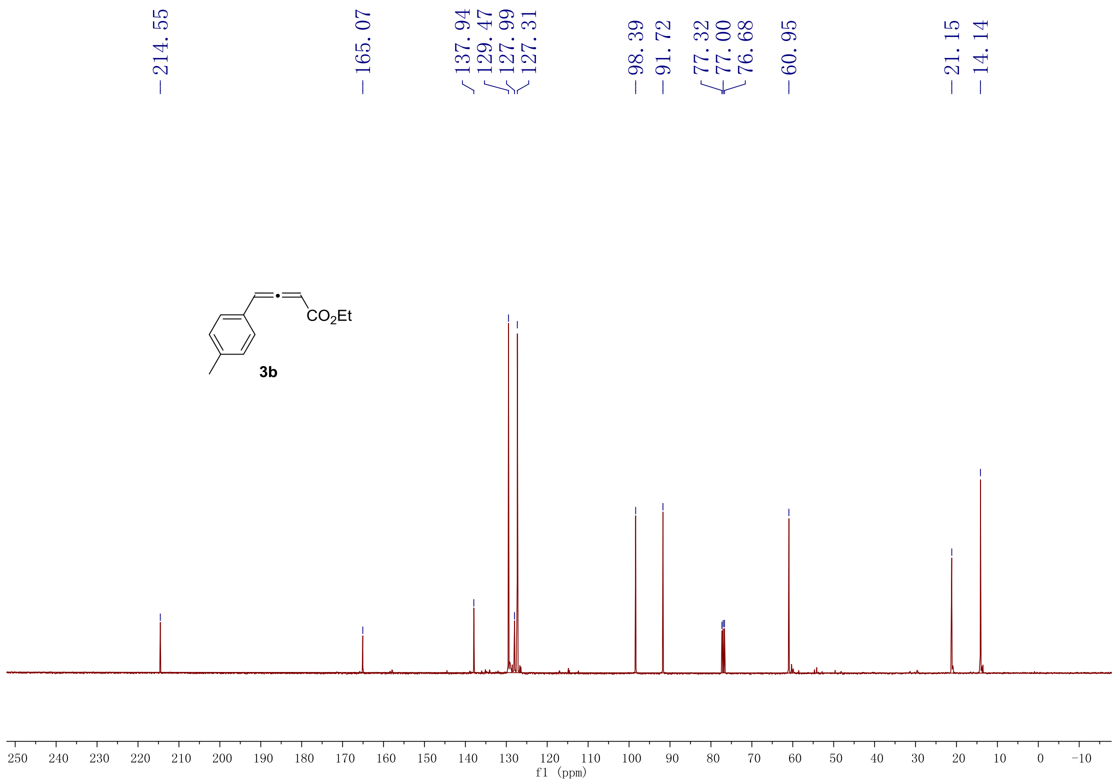


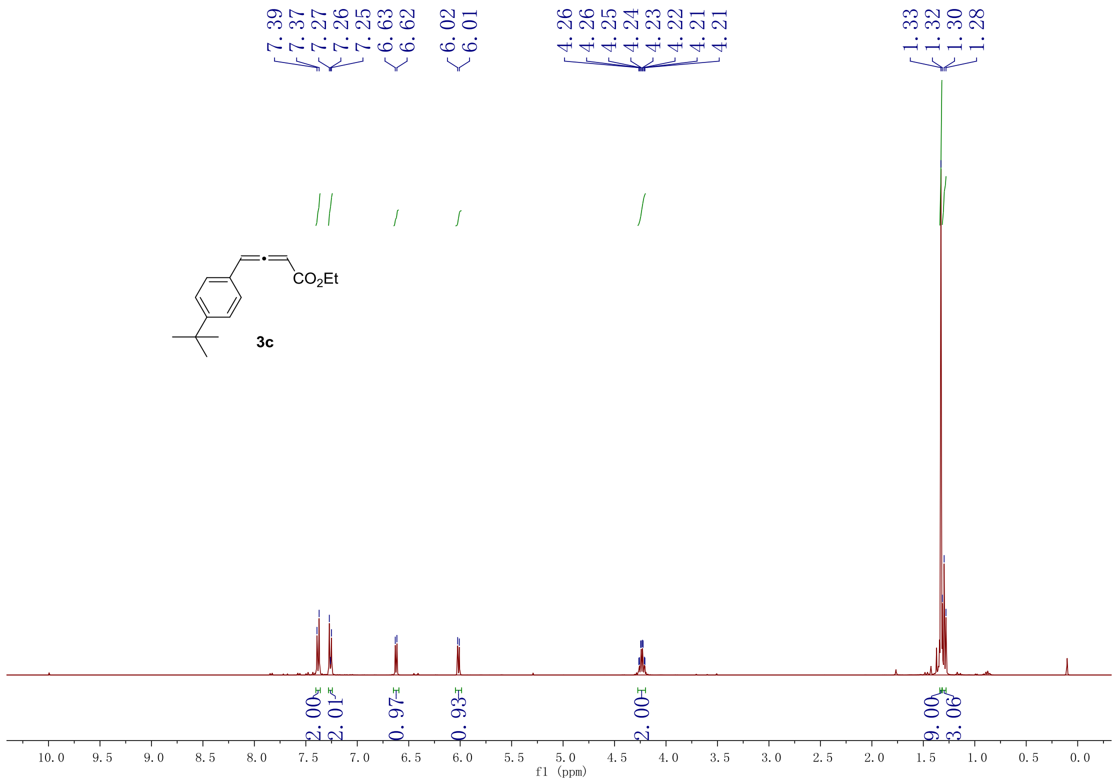


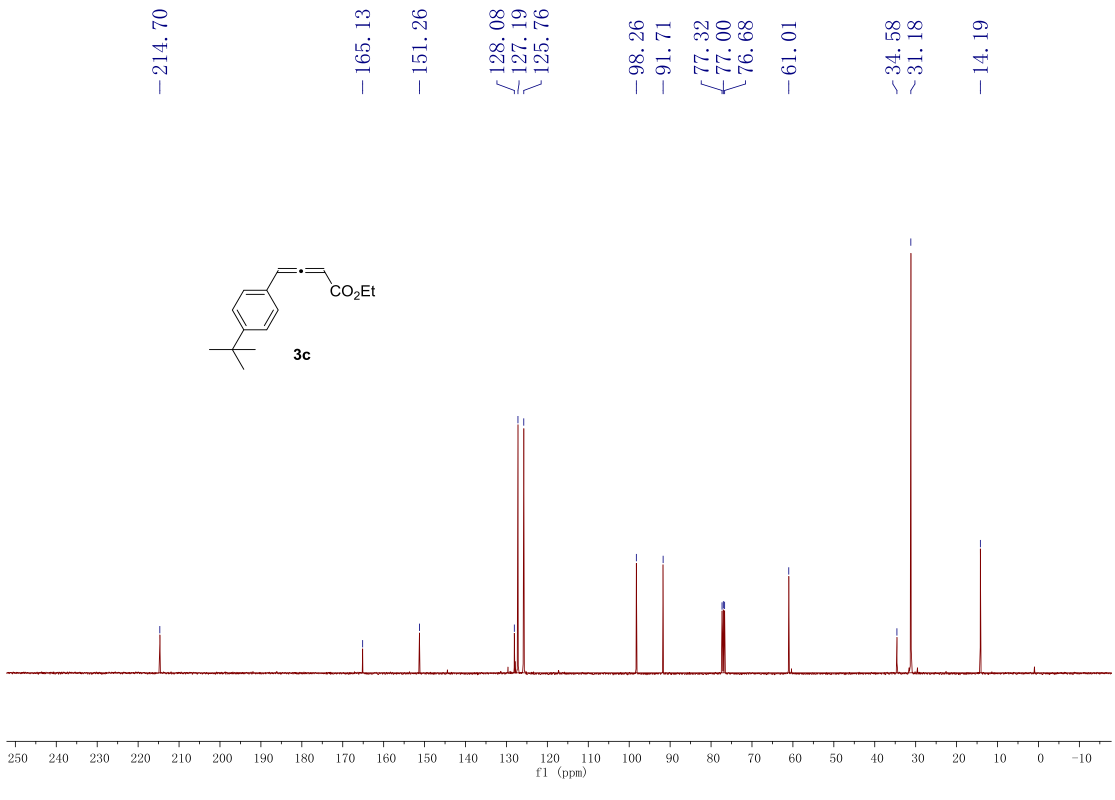

7.37
7.36
7.34
7.33
7.31
7.30
7.26
2.66
2.65
2.64
2.64
2.63
2.62
2.61
2.60
2.59
2.58
2.57
2.56
1.85
1.83
1.66
1.66
1.64
1.63
1.59
1.58
1.57
1.56
5.70
5.68
5.66
5.66
5.65
5.65
5.64
5.23
5.20
5.16
5.13
CO2Bn
1i
1.91
1.00
1.10
5.21
1.91
1.00
1.10
0.99
2.17
4.93
2.07
f1 (ppm)

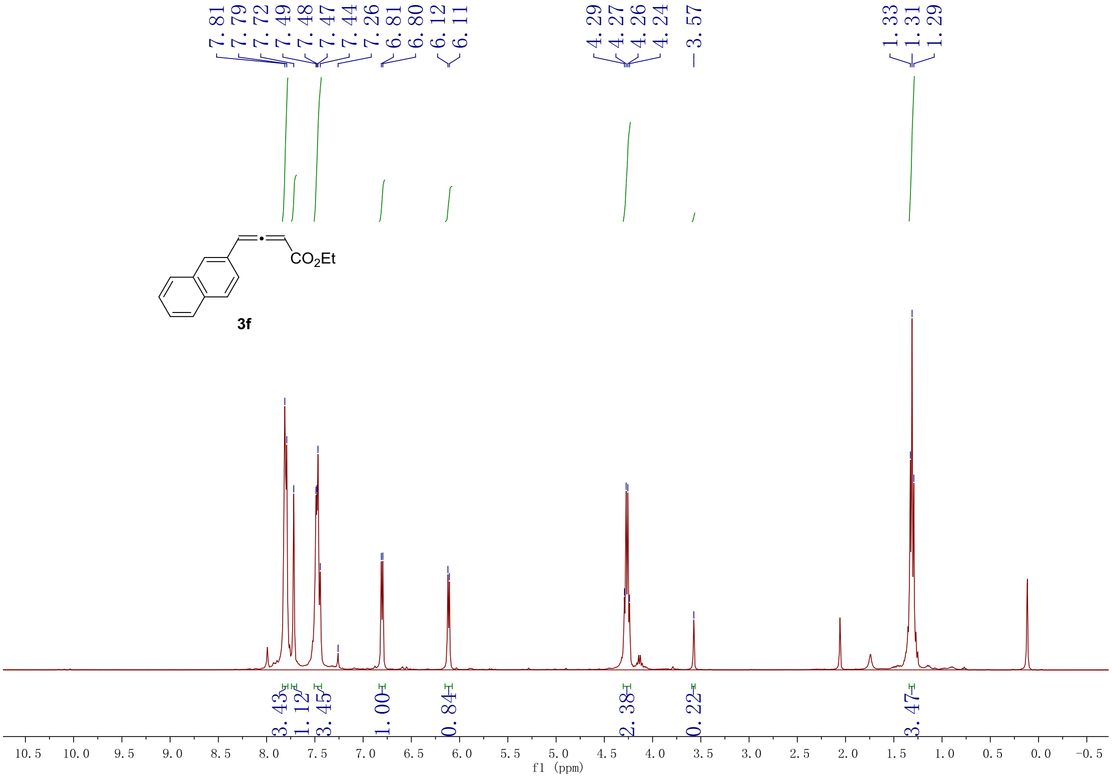

211.91
166.00
136.10
128.44
128.05
127.95
100.32
88.65
77.32
77.00
76.68
66.32
38.10
32.67
32.43
24.69
CO2Bn
1i
f1 (ppm)

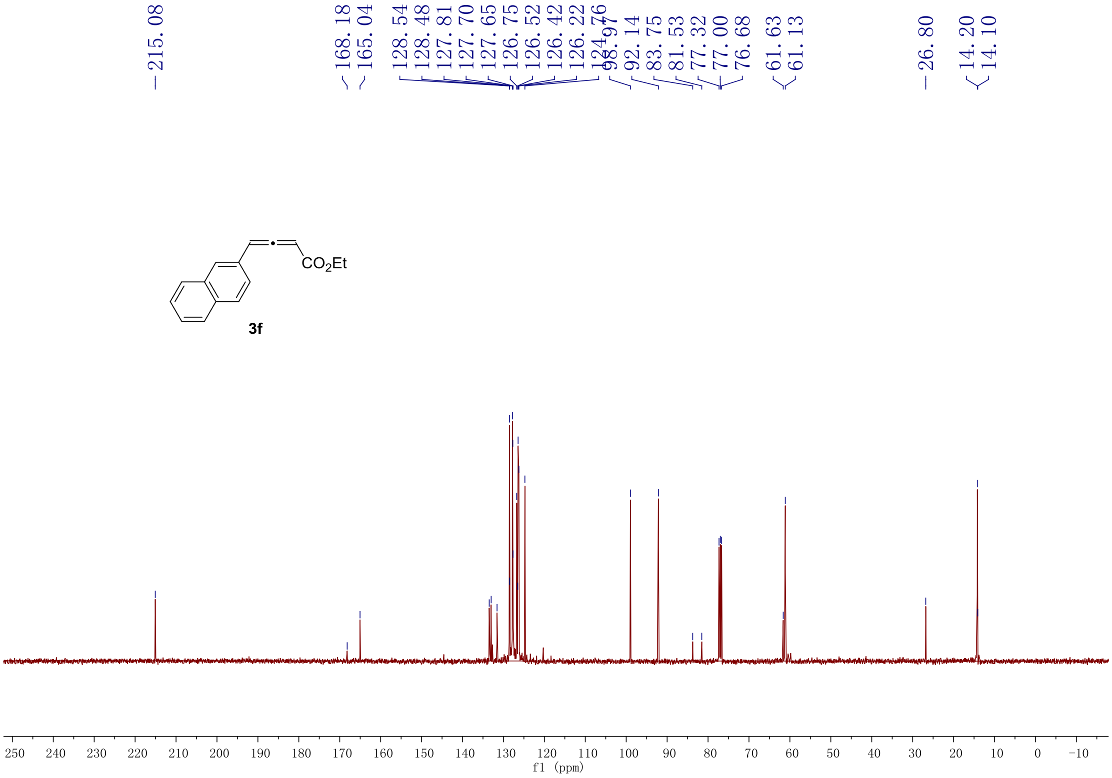

7.26
7.22
7.20
7.16
7.14
6.62
6.60
6.03
6.01
4.26
4.24
4.22
4.21
2.35
1.31
1.29
1.28
CO2Et
3b
1.96
2.04
0.93
0.88
1.92
2.98
3.00
f1 (ppm)

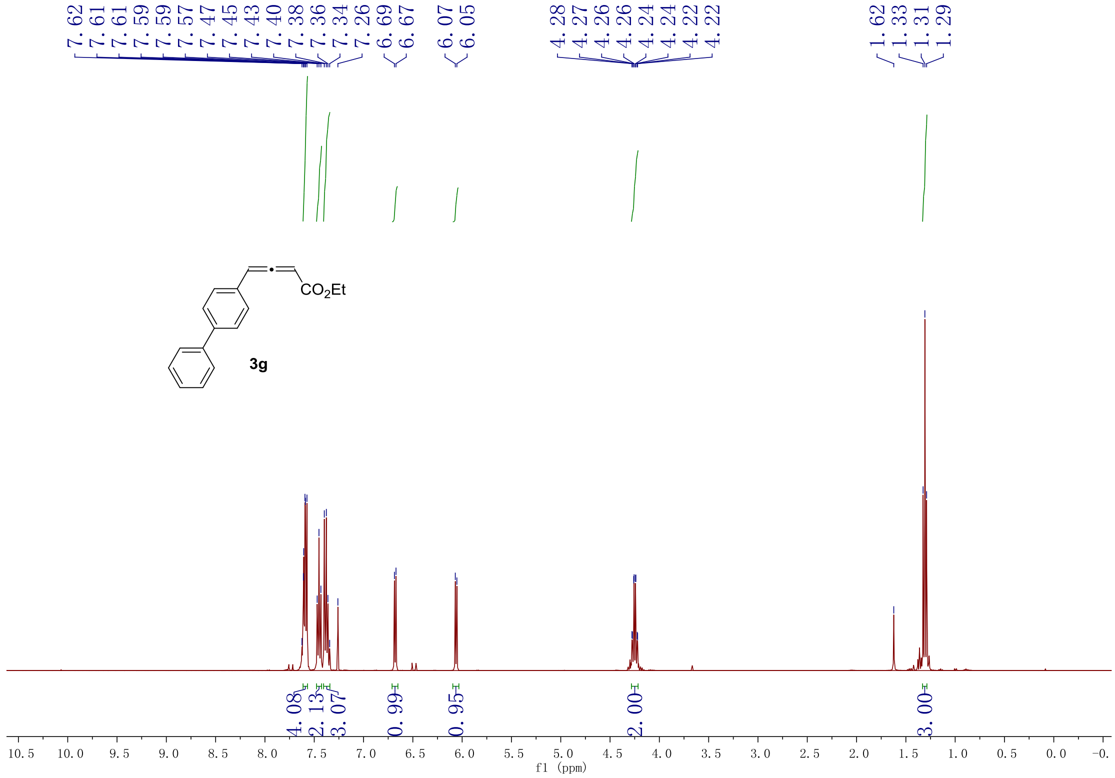

214.55
165.07
137.94
129.47
127.99
127.31
98.39
91.72
77.32
77.00
76.68
60.95
21.15
14.14
CO2Et
3b
f1 (ppm)

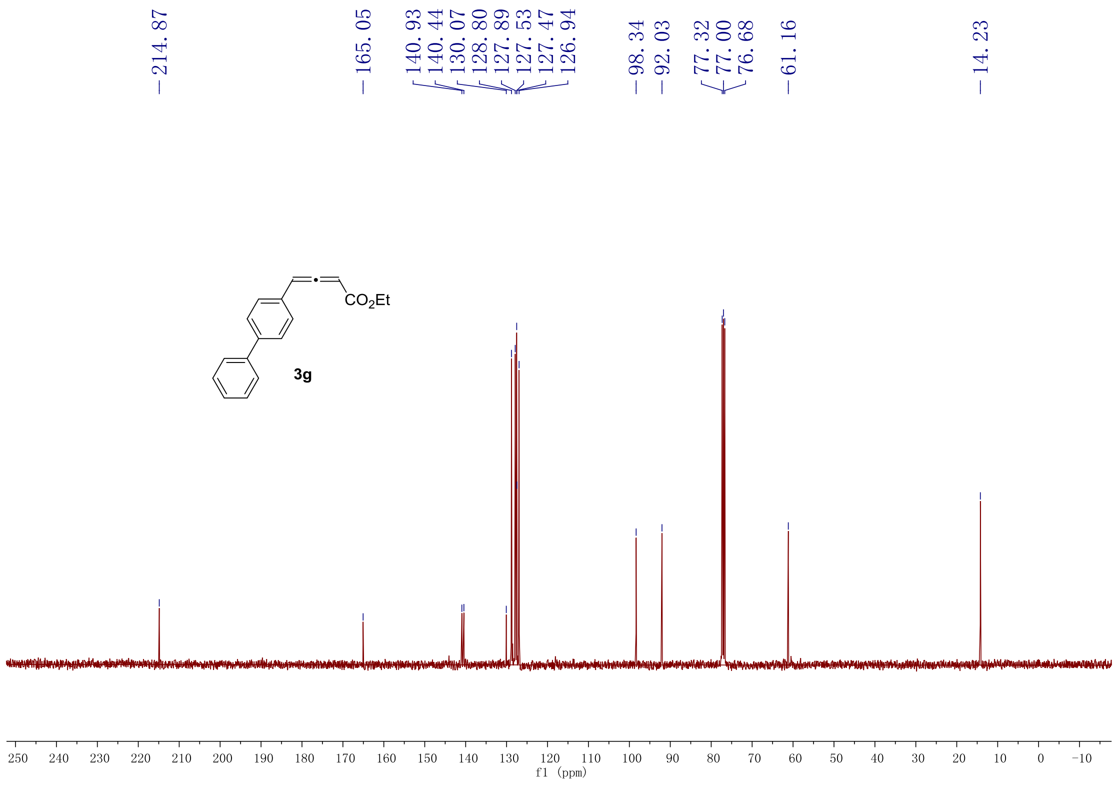

7.39
7.37
7.27
7.26
7.25
6.63
6.62
6.02
6.01
4.26
4.26
4.25
4.24
4.23
4.22
4.21
4.21
1.33
1.32
1.30
1.28
CO_2Et
3c
2.00
2.01
0.97
0.93
2.00
9.00
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

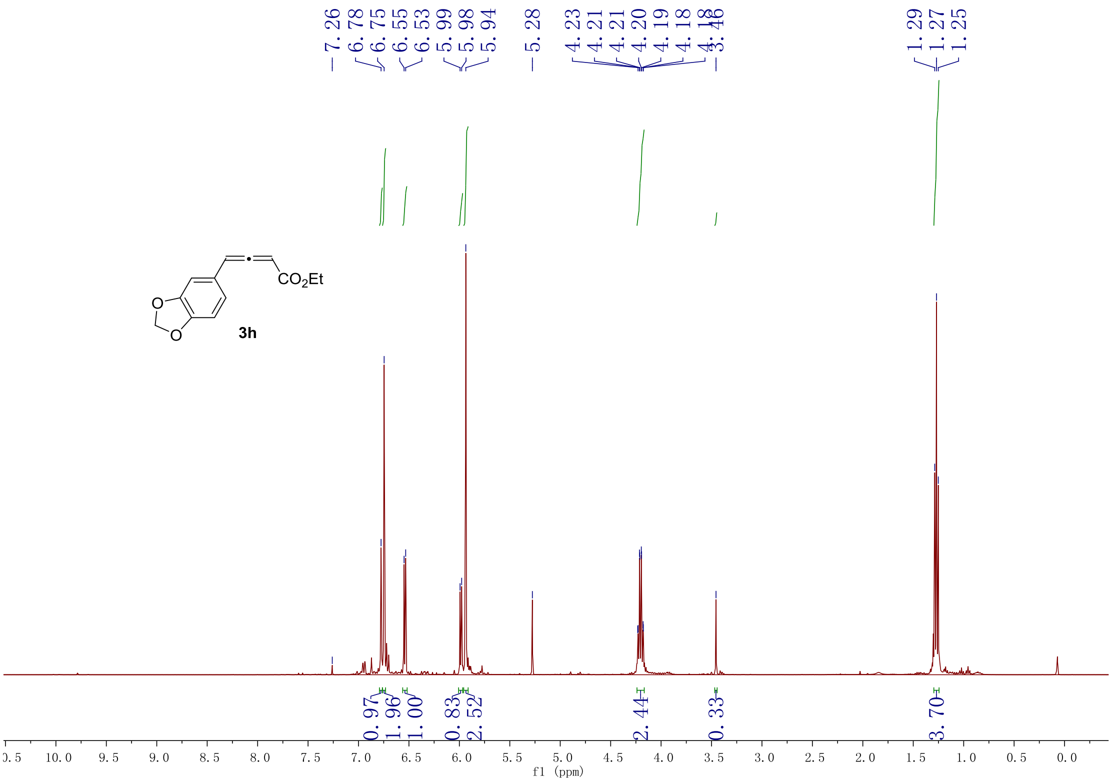

214.70
165.13
151.26
128.08
127.19
125.76
98.26
91.71
77.32
77.00
76.68
61.01
34.58
31.18
14.19
CO_2Et
3c
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

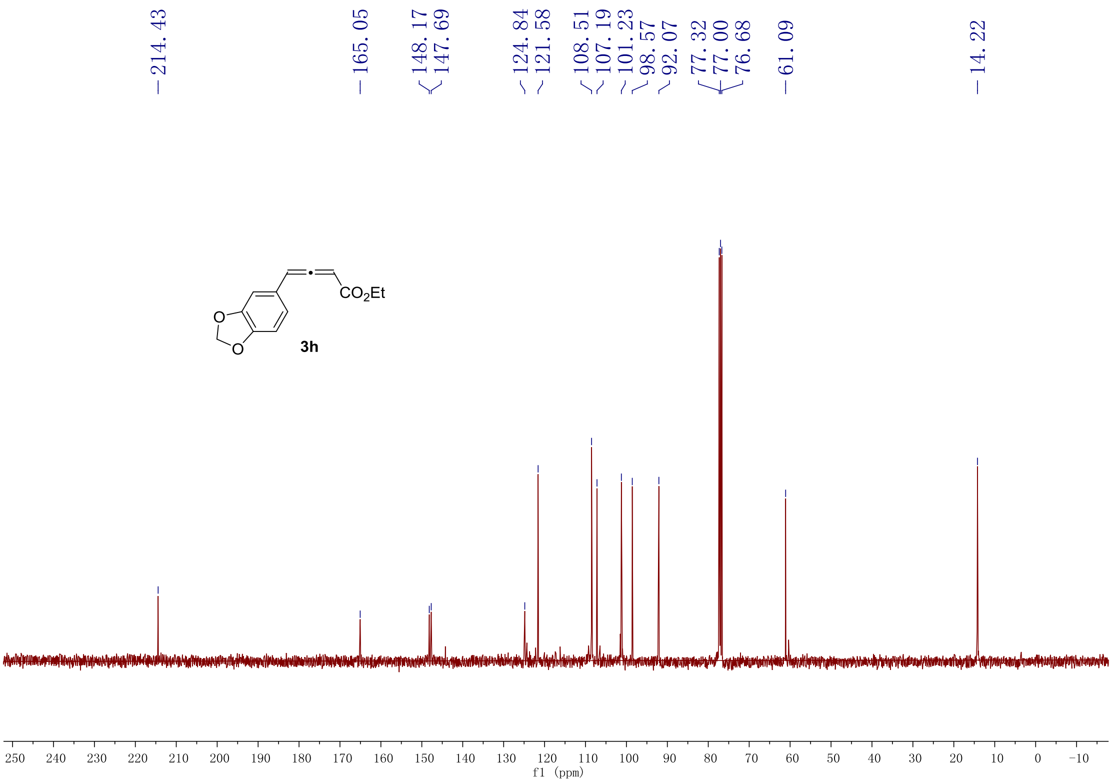

7.81 7.79 7.72 7.49 7.48 7.47 7.44 7.26 6.81 6.80 6.12 6.11
4.29 4.27 4.26 4.24 3.57
1.33 1.31 1.29
CO2Et
3f
3.43 1.12 3.45 1.00 0.84 2.38 0.22 3.47
f1 (ppm)

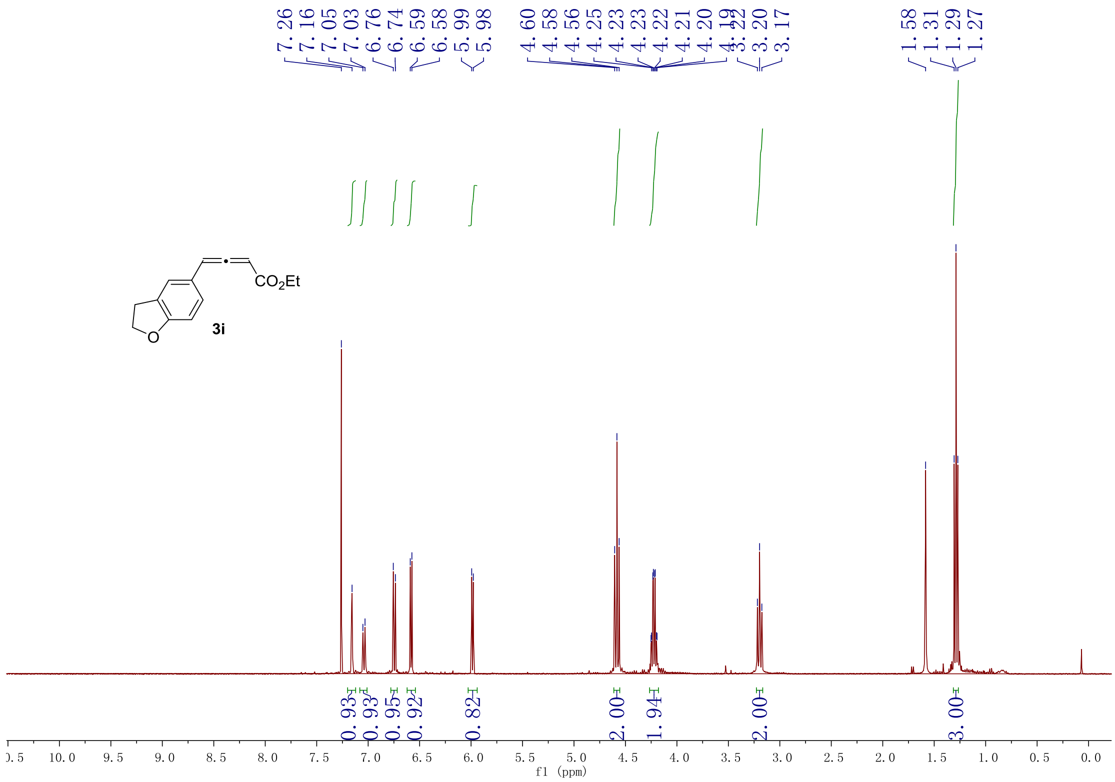

215.08
168.18 165.04 128.54 128.48 127.81 127.70 127.65 126.75 126.52 126.42 126.22 124.76 98.97 92.14 83.75 81.53 77.32 77.00 76.68 61.63 61.13
26.80 14.20 14.10
CO2Et
3f
f1 (ppm)

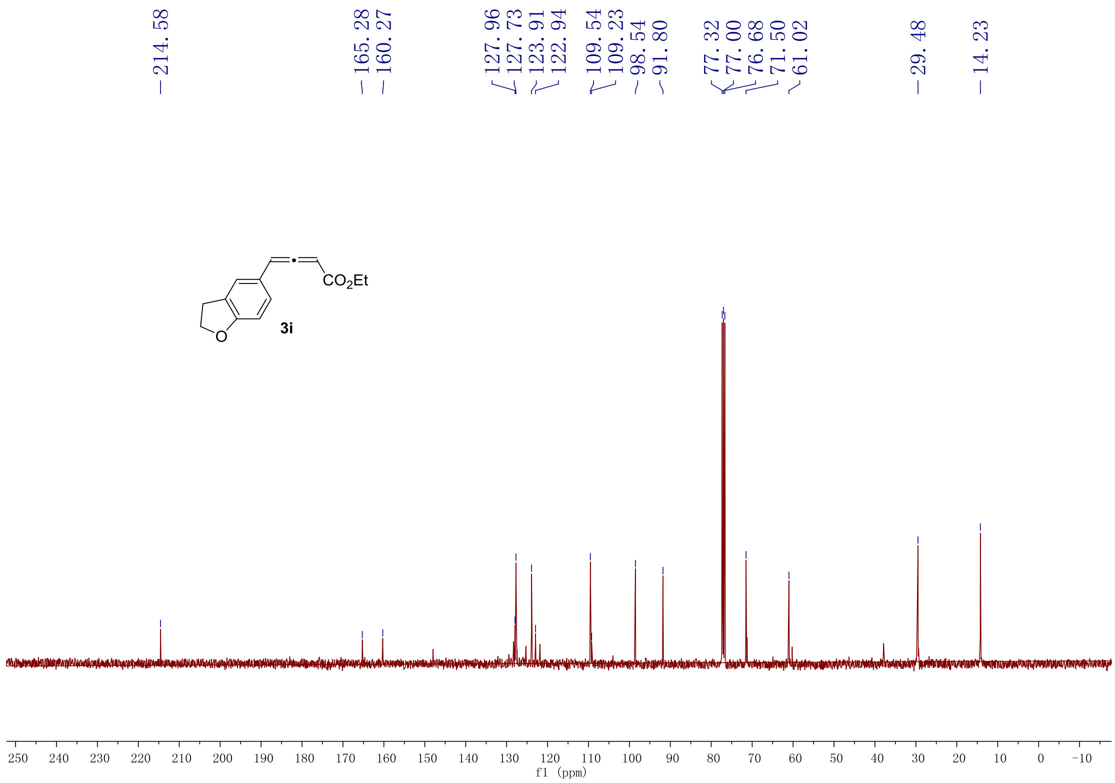

7.62 7.61 7.61 7.59 7.59 7.57 7.47 7.45 7.43 7.40 7.38 7.36 7.34 7.26 6.69 6.67 6.07 6.05 4.28 4.27 4.26 4.26 4.24 4.24 4.22 4.22 1.62 1.33 1.31 1.29
CO2Et
3g
4.08 2.13 3.07 0.99 0.95 2.00 3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

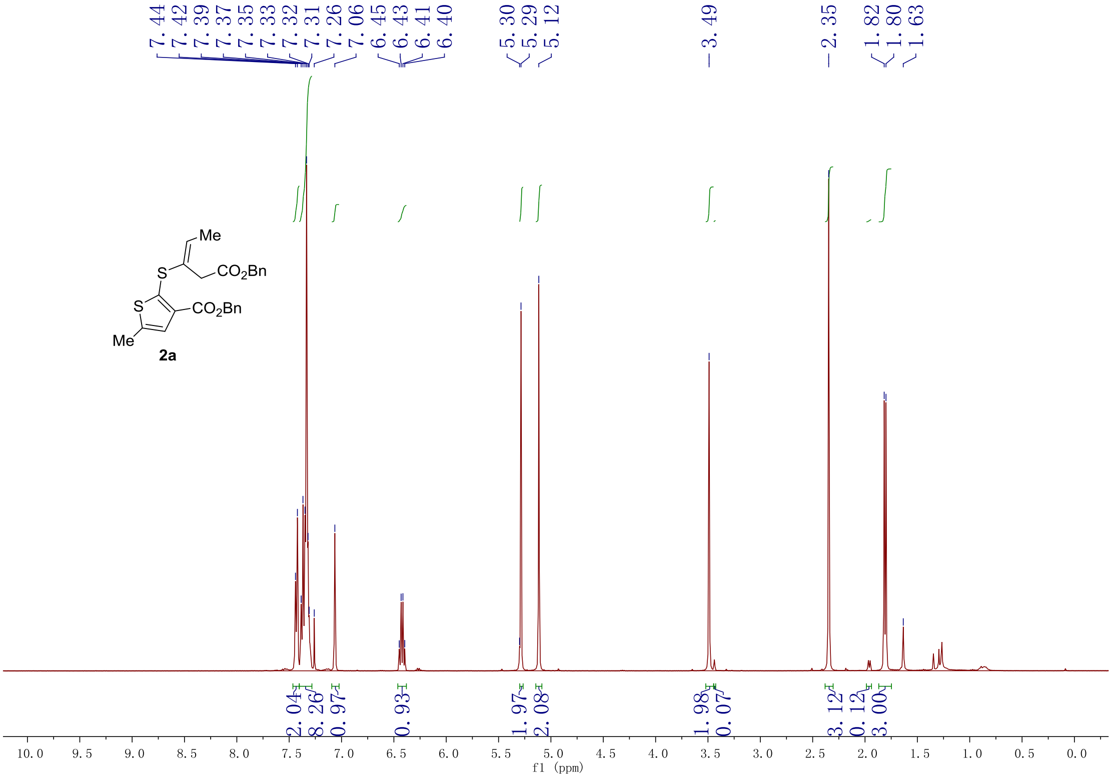

214.87 165.05 140.93 140.44 130.07 128.80 127.89 127.53 127.47 126.94 98.34 92.03 77.32 77.00 76.68 61.16 14.23
CO2Et
3g
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

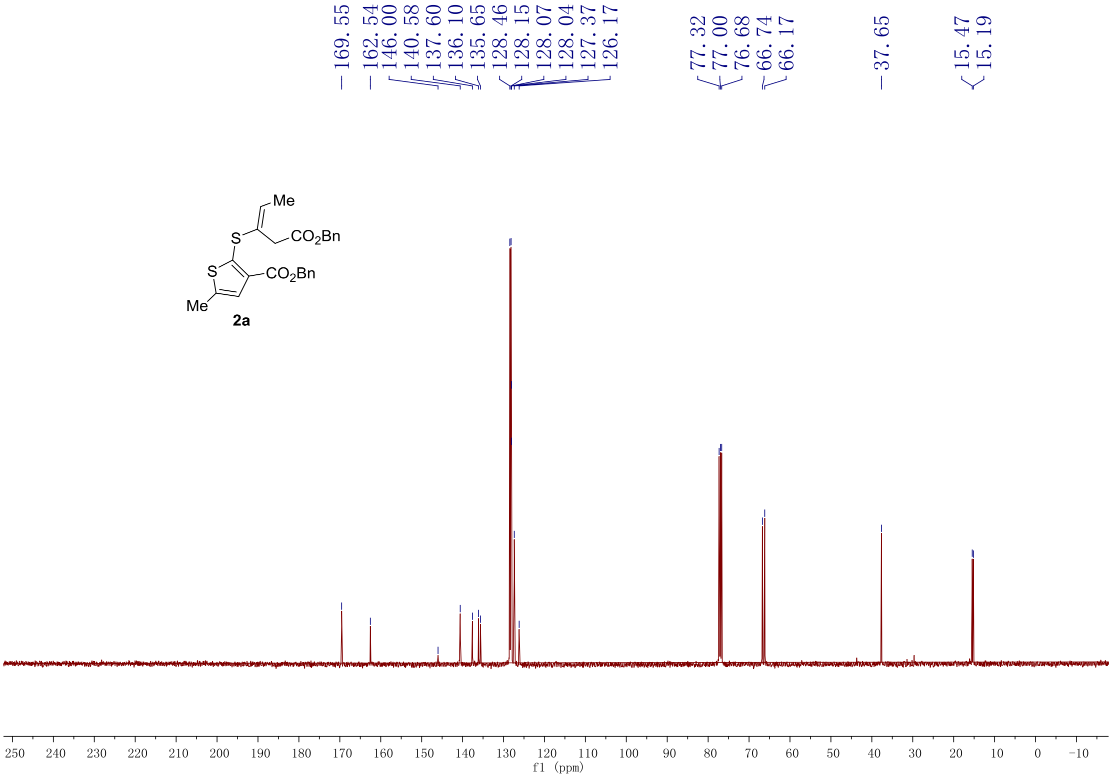

7.26
6.78
6.75
6.55
6.53
5.99
5.98
5.94
5.28
4.23
4.21
4.21
4.20
4.19
4.18
4.18
3.46
1.29
1.27
1.25
CO2Et
3h
0.97
1.96
1.00
0.83
2.52
2.44
0.33
3.70
f1 (ppm)

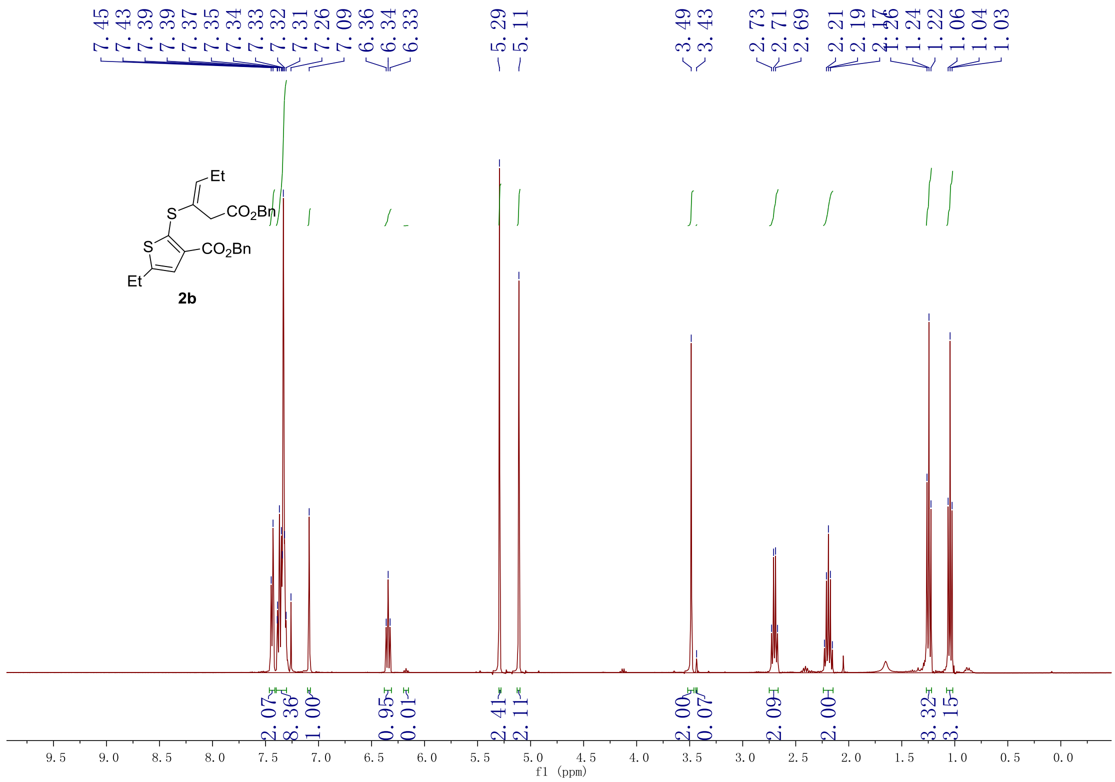

214.43
165.05
148.17
147.69
124.84
121.58
108.51
107.19
101.23
98.57
92.07
77.32
77.00
76.68
61.09
14.22
CO2Et
3h
f1 (ppm)

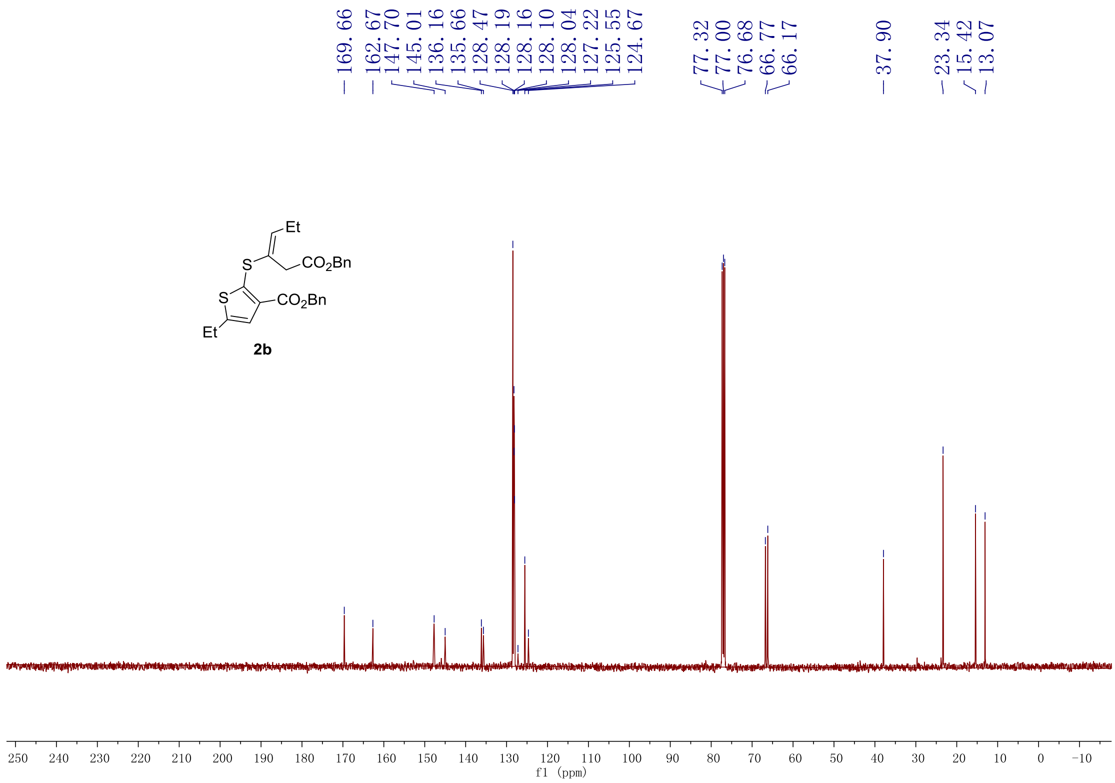

7.26 7.16 7.05 7.03 6.76 6.74 6.59 6.58 5.99 5.98 4.60 4.58 4.56 4.25 4.23 4.23 4.22 4.21 4.20 4.19 3.22 3.20 3.17 1.58 1.31 1.29 1.27
CO2Et
3i
0.93 0.93 0.95 0.92 0.82 2.00 1.94 2.00 3.00
f1 (ppm)

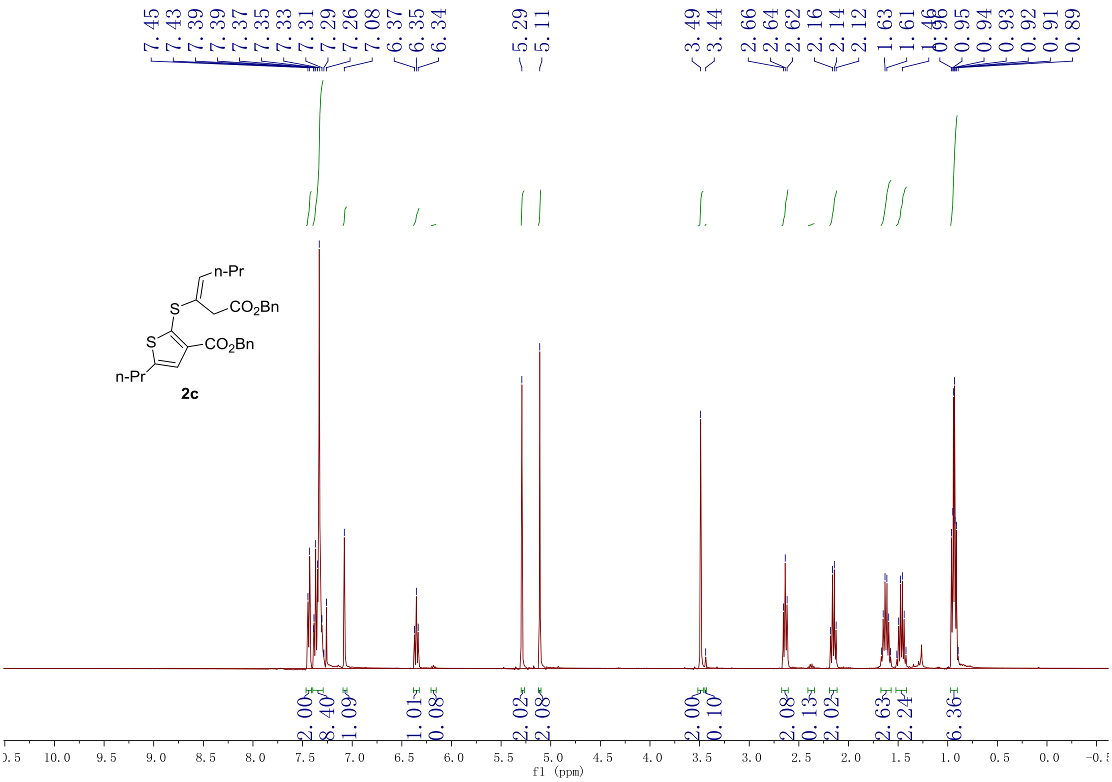

214.58 165.28 160.27 127.96 127.73 123.91 122.94 109.54 109.23 98.54 91.80 77.32 77.00 76.68 71.50 61.02 29.48 14.23
CO2Et
3i
f1 (ppm)

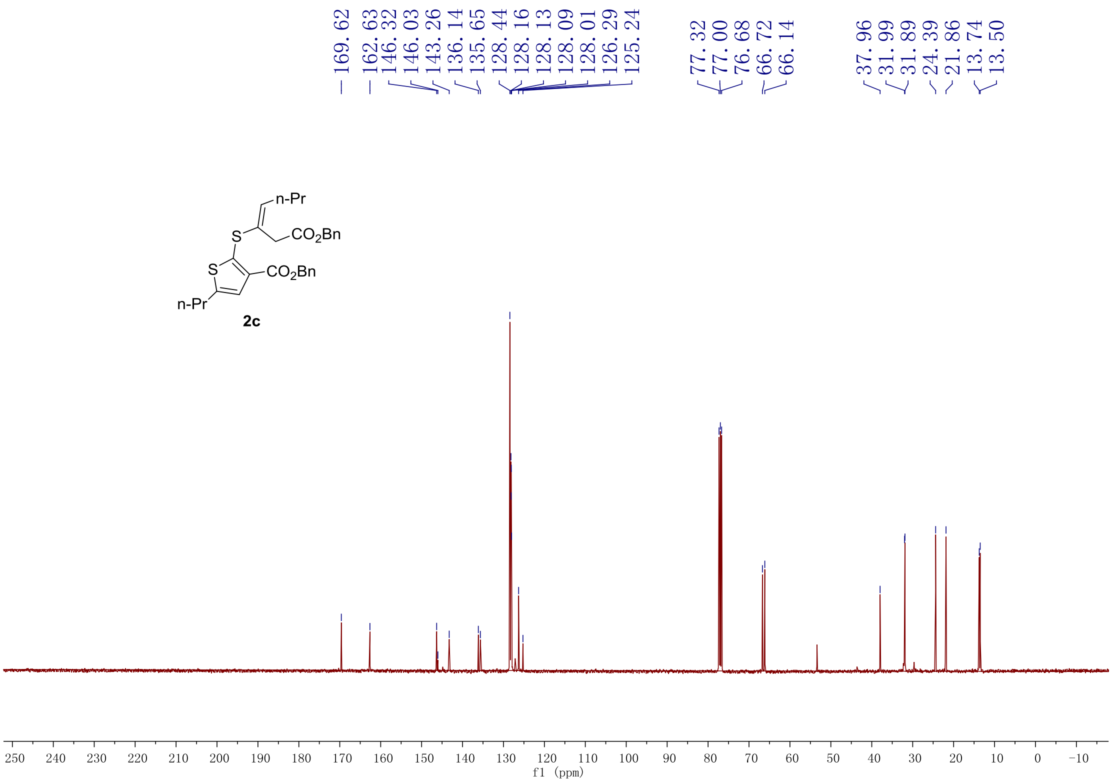

7.44 7.42 7.39 7.37 7.35 7.33 7.32 7.31 7.26 7.06 6.45 6.43 6.41 6.40 5.30 5.29 5.12 3.49 2.35 1.82 1.80 1.63
Me
S
CO_2Bn
S
CO_2Bn
Me
2a
2.04 8.26 0.97 0.93 1.97 2.08 1.98 0.07 3.12 0.12 3.00
f1 (ppm)

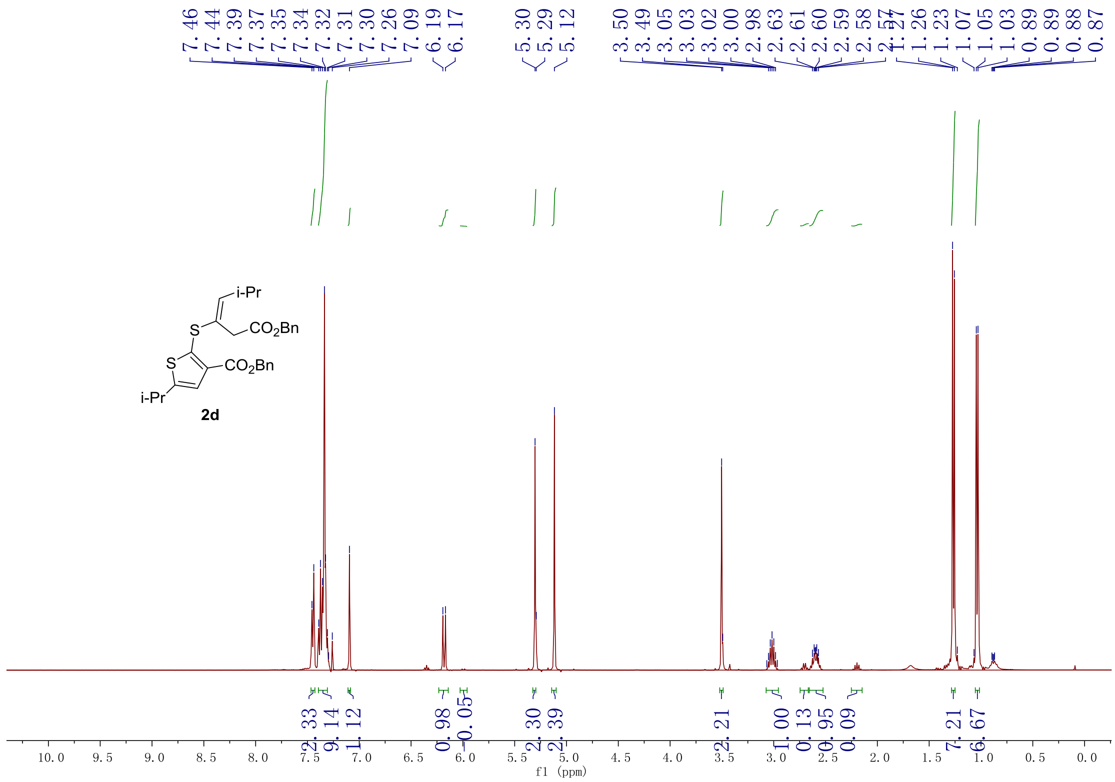

169.55 162.54 146.00 140.58 137.60 136.10 135.65 128.46 128.15 128.07 128.04 127.37 126.17 77.32 77.00 76.68 66.74 66.17 37.65 15.47 15.19
Me
S
CO_2Bn
S
CO_2Bn
Me
2a
f1 (ppm)

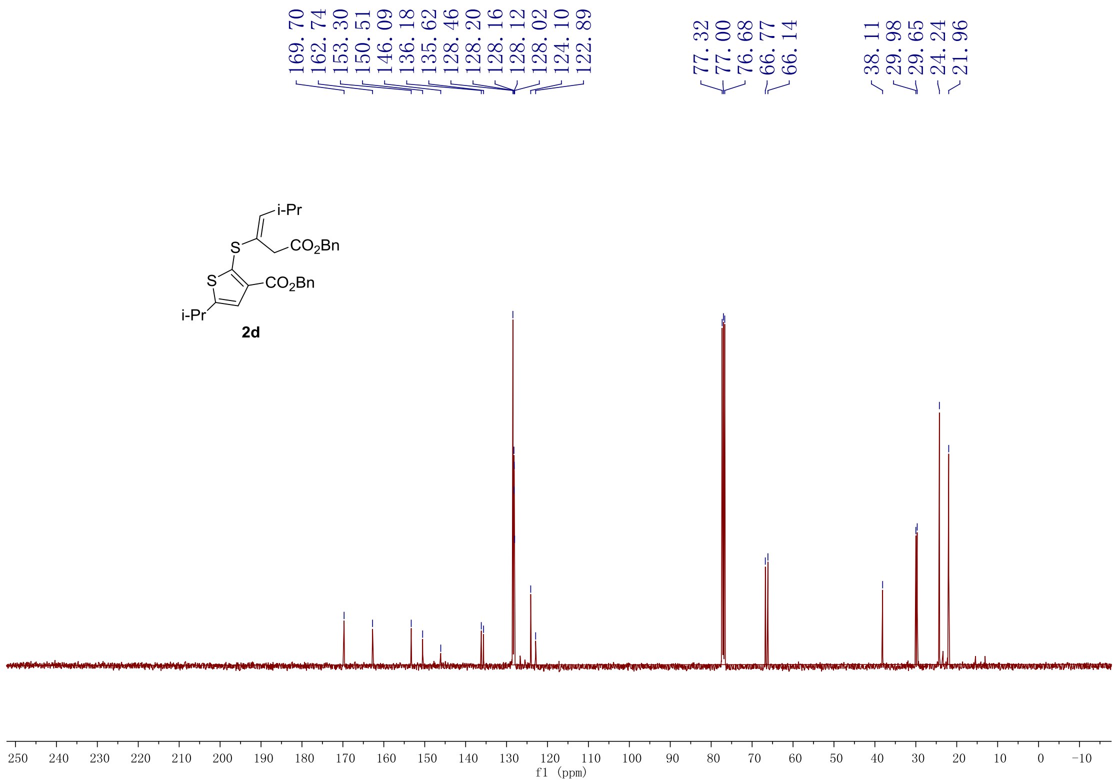

7.45 7.43 7.39 7.39 7.37 7.35 7.34 7.33 7.32 7.31 7.26 7.09 6.36 6.34 6.33 5.29 5.11 3.49 3.43 2.73 2.71 2.69 2.21 2.19 2.17 1.26 1.24 1.22 1.06 1.04 1.03
Et
S
CO2Bn
S
CO2Bn
Et
2b
2.07 8.36 1.00 0.95 0.01 2.41 2.11 2.00 0.07 2.09 2.00 3.32 3.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

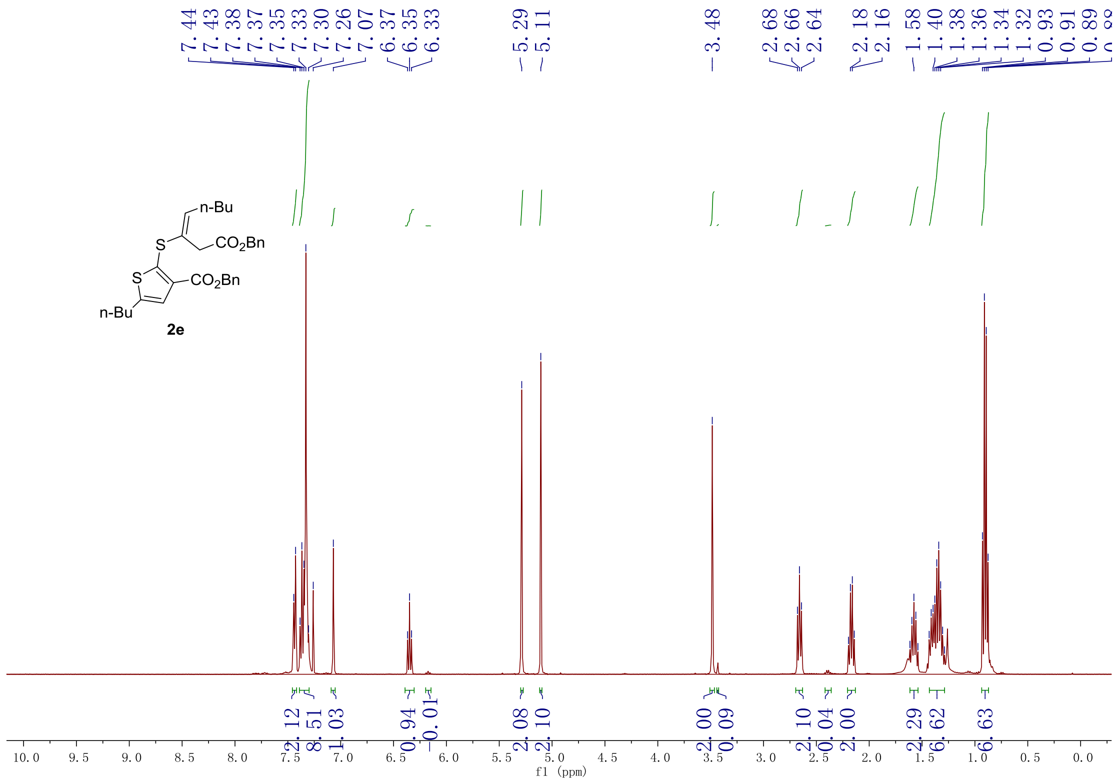

169.66 162.67 147.70 145.01 136.16 135.66 128.47 128.19 128.16 128.10 128.04 127.22 125.55 124.67 77.32 77.00 76.68 66.77 66.17 37.90 23.34 15.42 13.07
Et
S
CO2Bn
S
CO2Bn
Et
2b
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

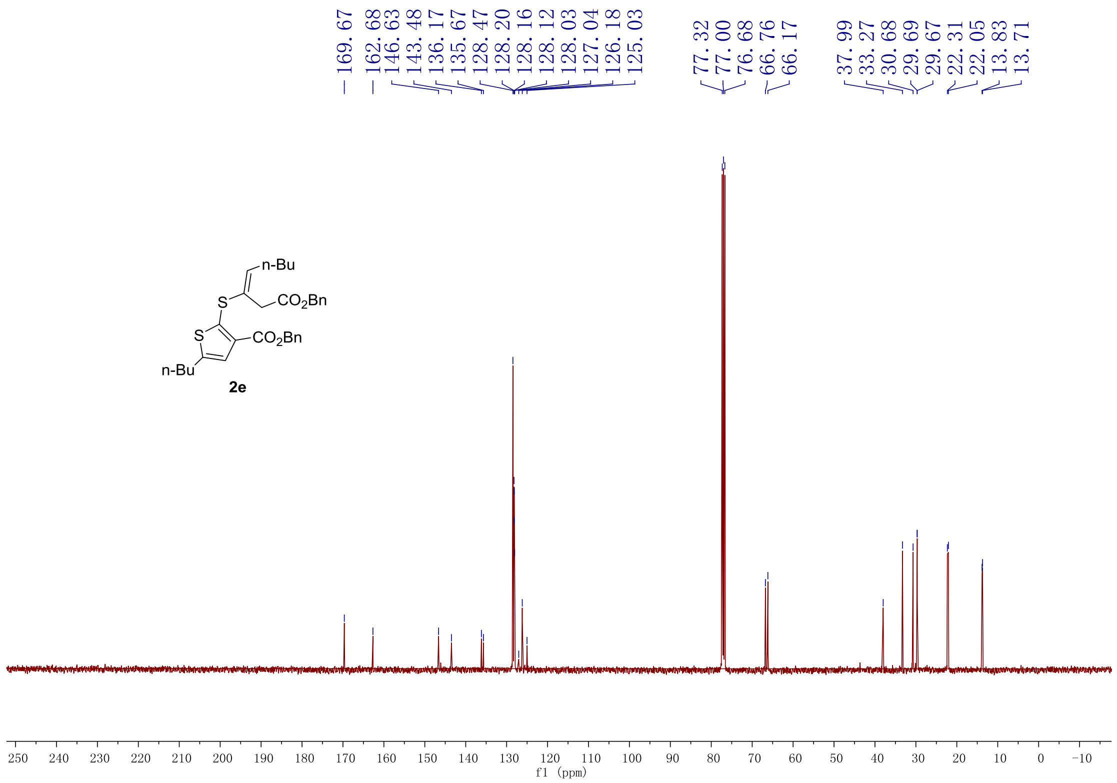


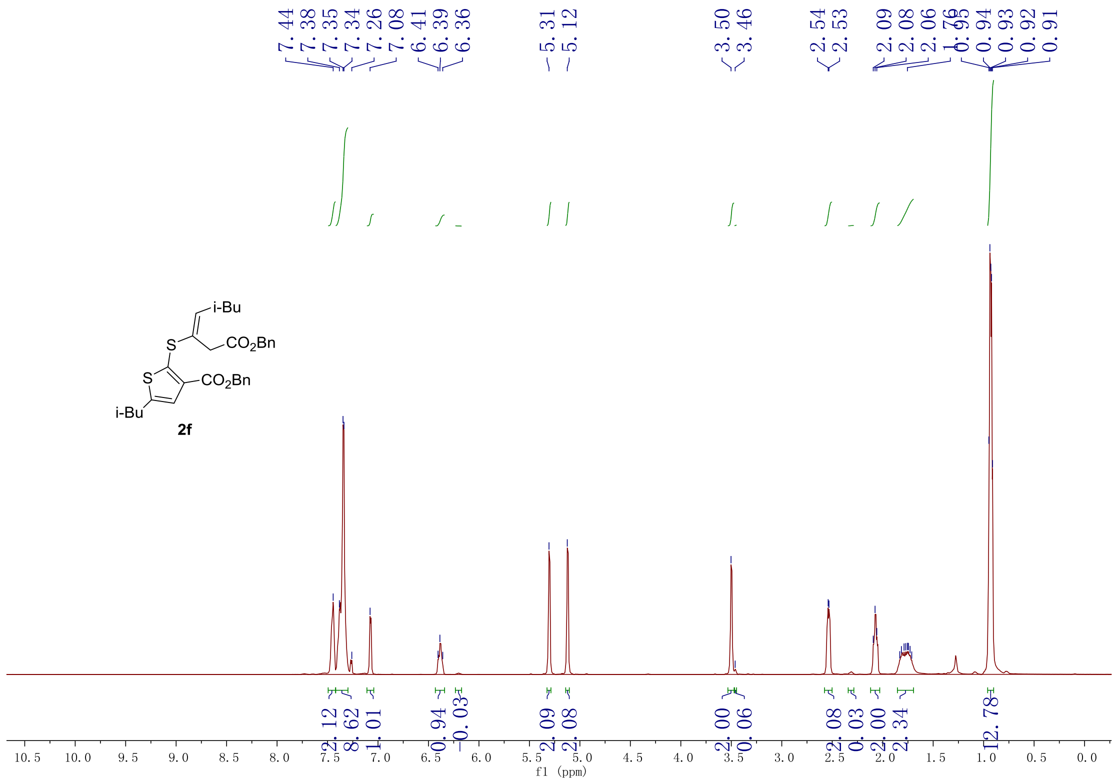


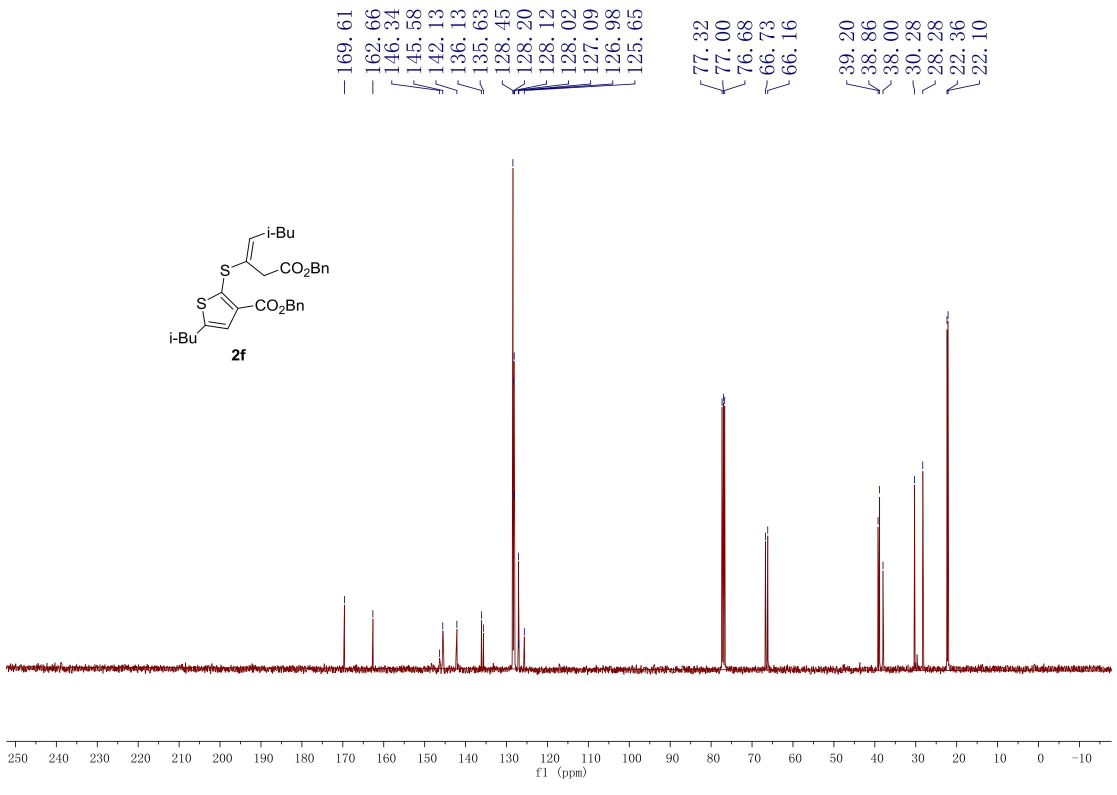

7.46 7.44 7.39 7.37 7.35 7.34 7.32 7.31 7.30 7.26 7.09 6.19 6.17 5.30 5.29 5.12 3.50 3.49 3.05 3.03 3.02 3.00 2.98 2.63 2.61 2.60 2.59 2.58 2.57 1.27 1.26 1.23 1.07 1.05 1.03 0.89 0.88 0.87
i-Pr
S
CO2Bn
S
CO2Bn
i-Pr
2d
2.33 9.14 1.12 0.98 0.05 2.30 2.39 2.21 1.00 0.13 0.95 0.09 7.21 6.67
f1 (ppm)

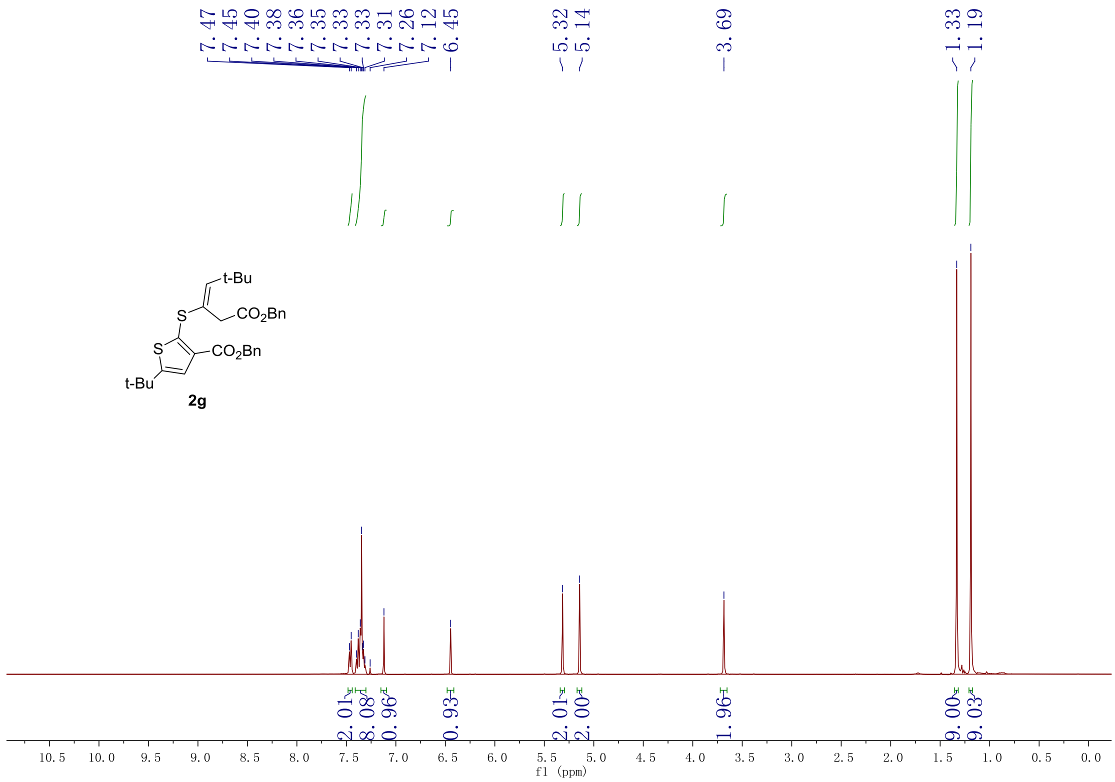

169.70 162.74 153.30 150.51 146.09 136.18 135.62 128.46 128.20 128.16 128.12 128.02 124.10 122.89 77.32 77.00 76.68 66.77 66.14 38.11 29.98 29.65 24.24 21.96
i-Pr
S
CO2Bn
S
CO2Bn
i-Pr
2d
f1 (ppm)

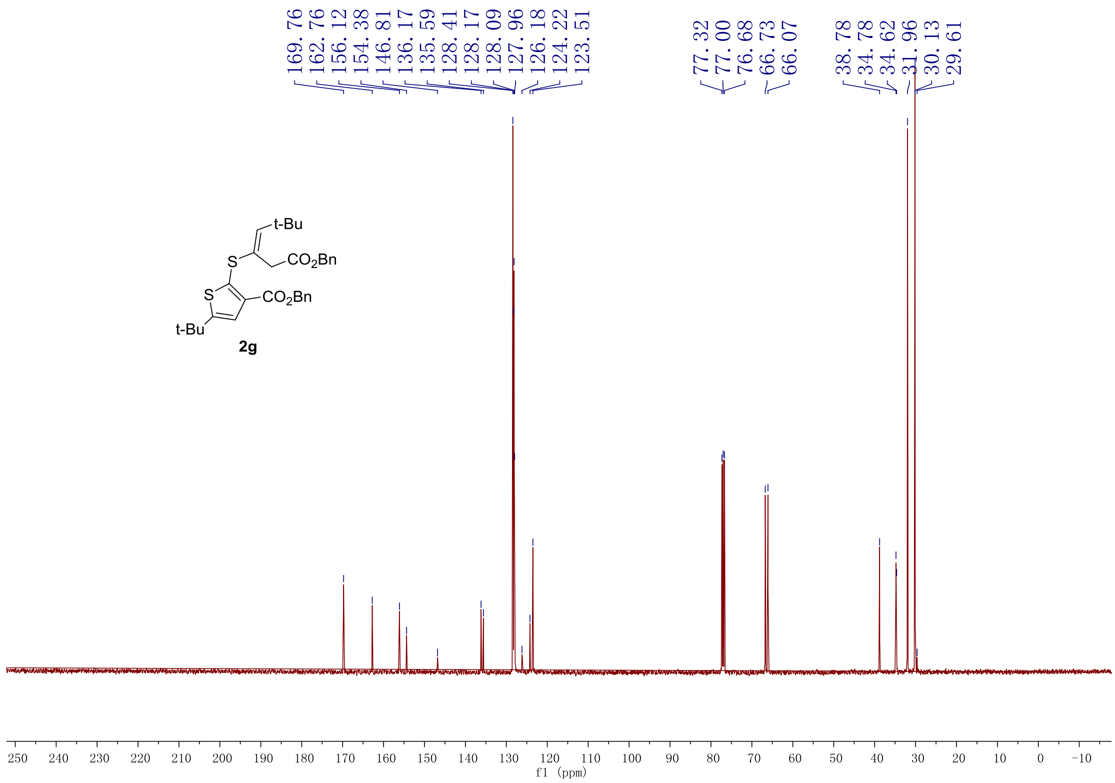


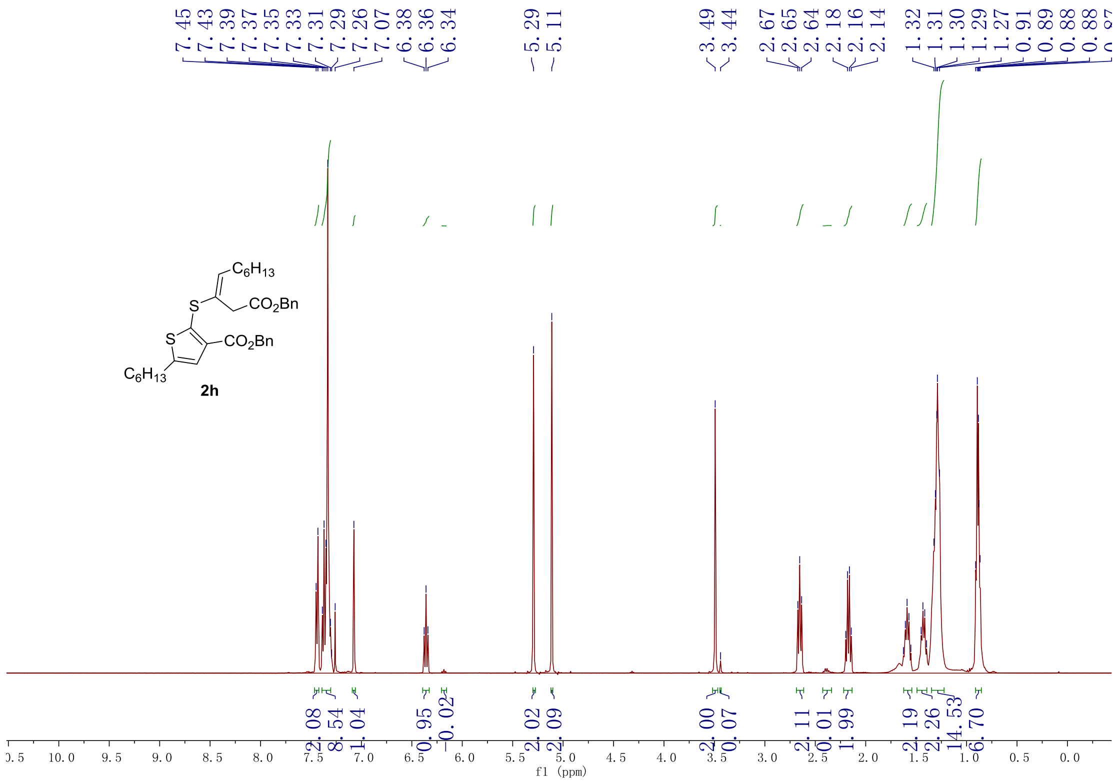


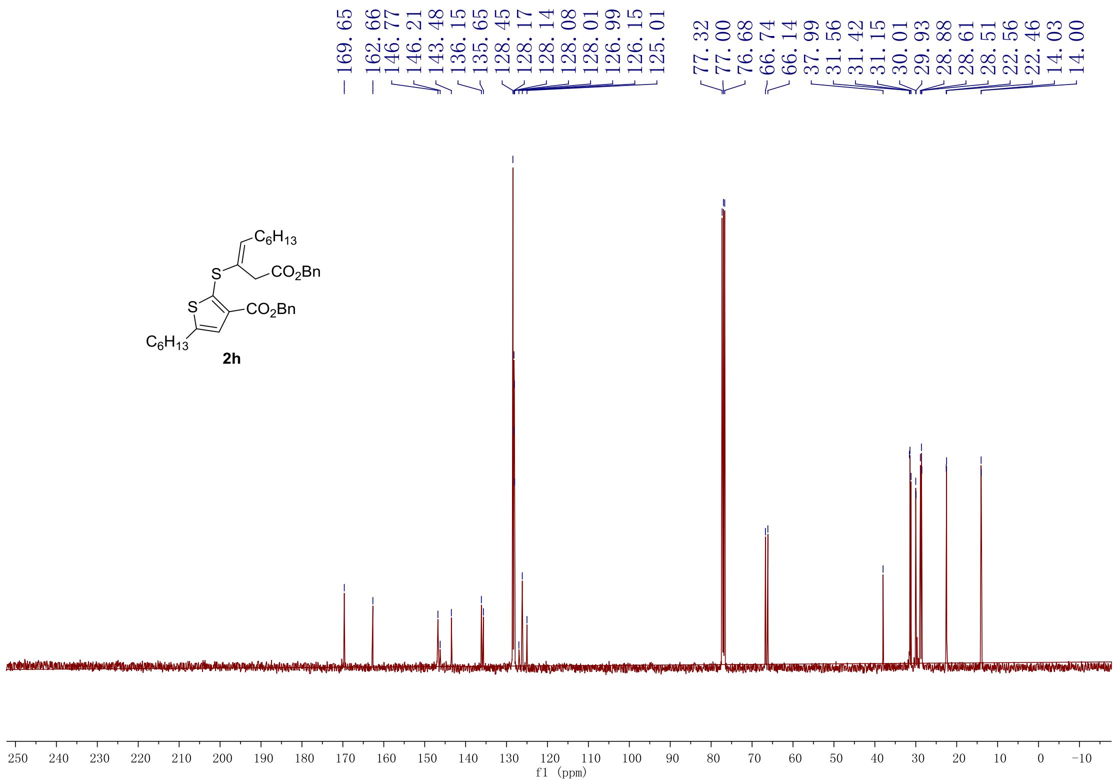

7.44 7.38 7.35 7.34 7.26 7.08 6.41 6.39 6.36
5.31 5.12
3.50 3.46
2.54 2.53
2.09 2.08 2.06 1.76 1.95 0.94 0.93 0.92 0.91
i-Bu
S
CO2Bn
S
CO2Bn
i-Bu
2f
2.12 8.62 1.01 0.94 0.03 2.09 2.08 2.00 0.06 2.08 0.03 2.00 2.34 12.78
f1 (ppm)

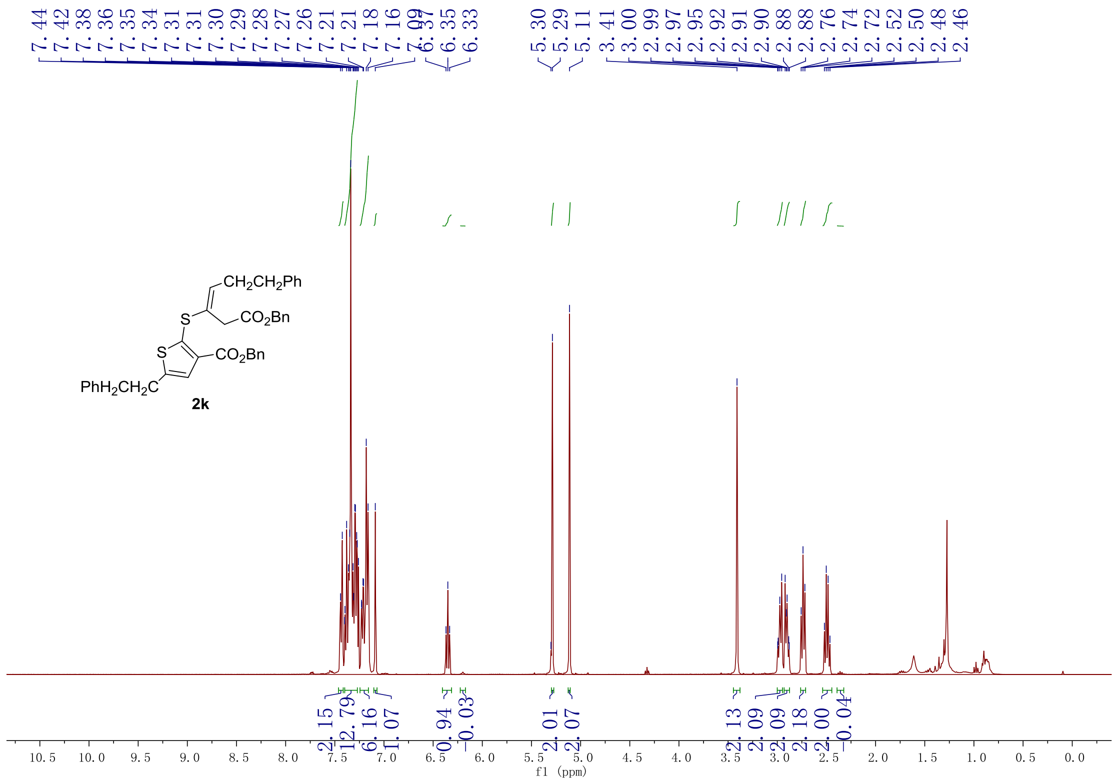

169.61 162.66 146.34 145.58 142.13 136.13 135.63 128.45 128.20 128.12 128.02 127.09 126.98 125.65
77.32 77.00 76.68 66.73 66.16
39.20 38.86 38.00 30.28 28.28 22.36 22.10
i-Bu
S
CO2Bn
S
CO2Bn
i-Bu
2f
f1 (ppm)

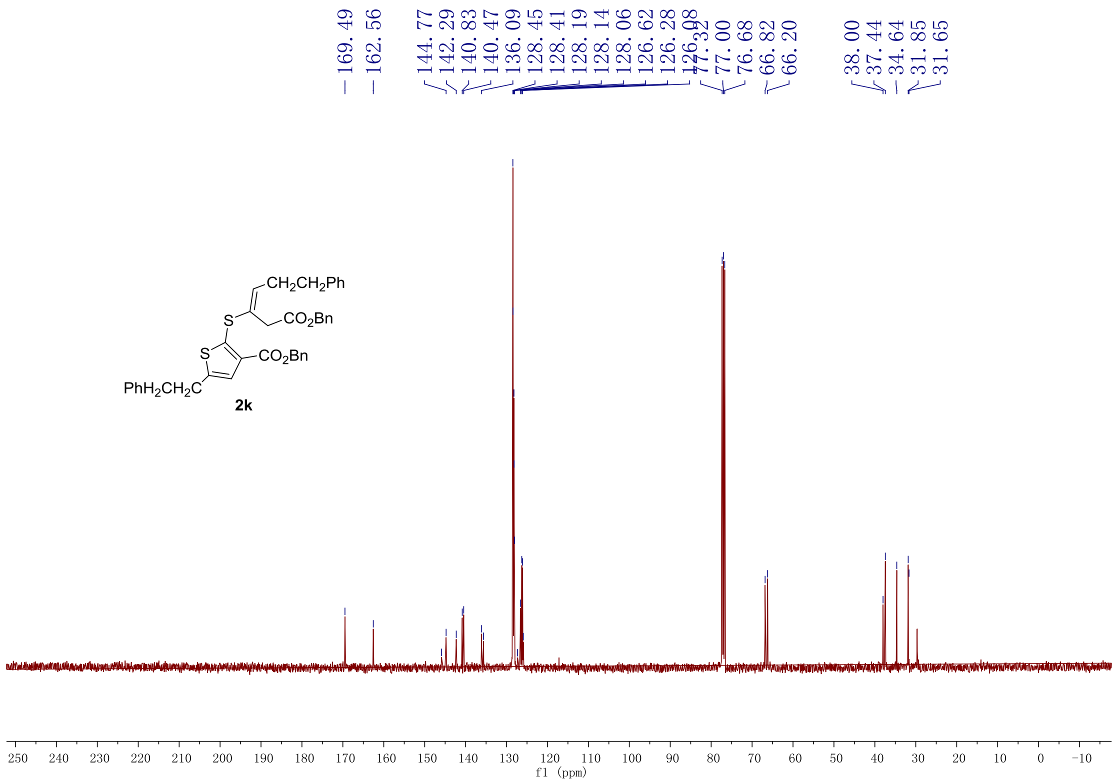

7.47
7.45
7.40
7.38
7.36
7.35
7.33
7.33
7.31
7.26
7.12
6.45
5.32
5.14
3.69
1.33
1.19
2.01
8.08
0.96
0.93
2.01
2.00
1.96
9.00
9.03
f1 (ppm)
t-Bu
CO2Bn
CO2Bn
t-Bu
2g

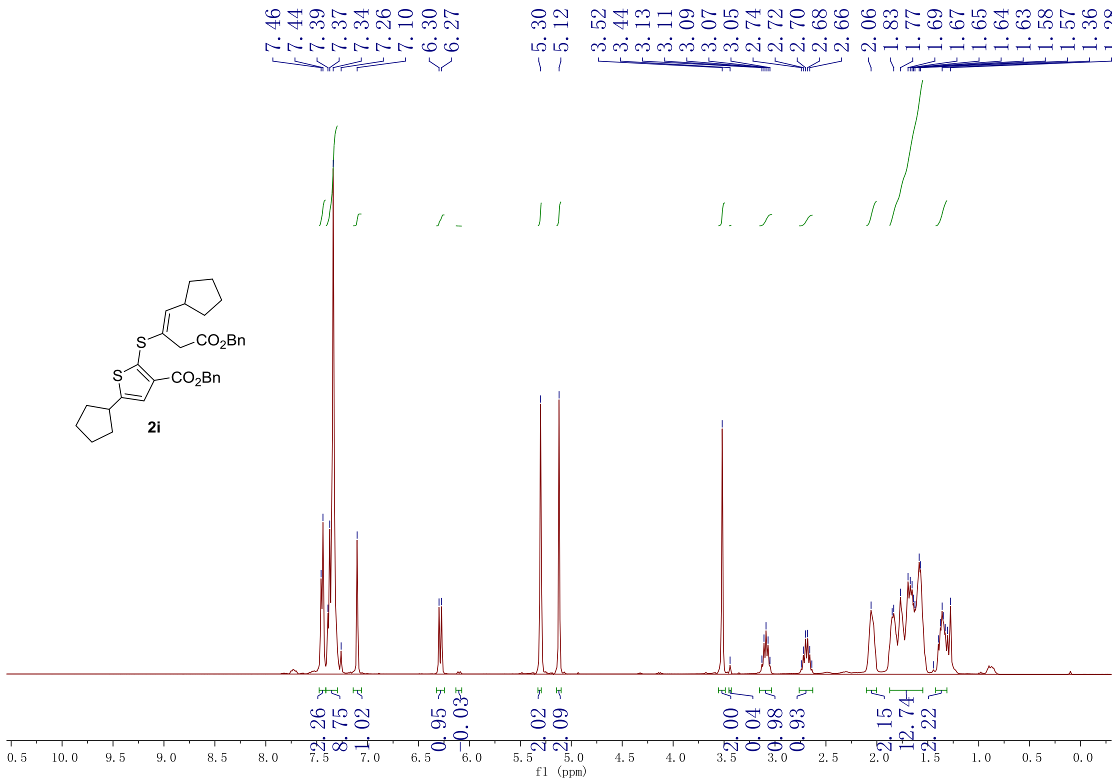

169.76
162.76
156.12
154.38
146.81
136.17
135.59
128.41
128.17
128.09
127.96
126.18
124.22
123.51
77.32
77.00
76.68
66.73
66.07
38.78
34.78
34.62
31.96
30.13
29.61
f1 (ppm)
t-Bu
CO2Bn
CO2Bn
t-Bu
2g

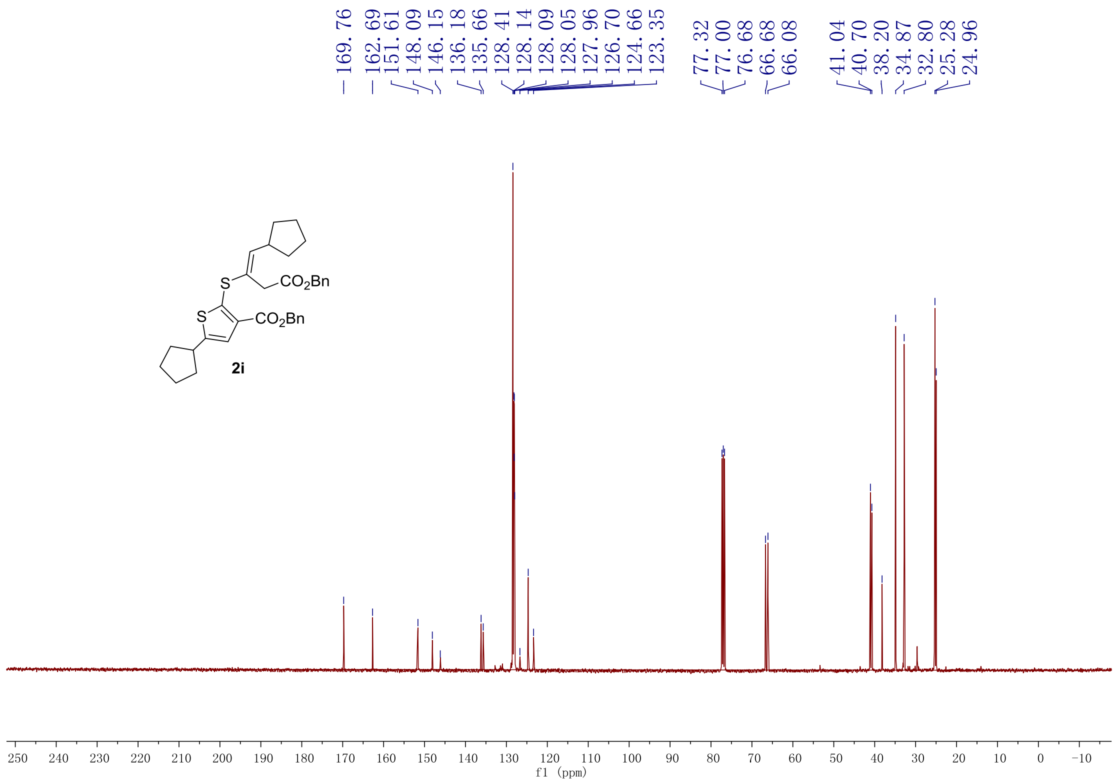


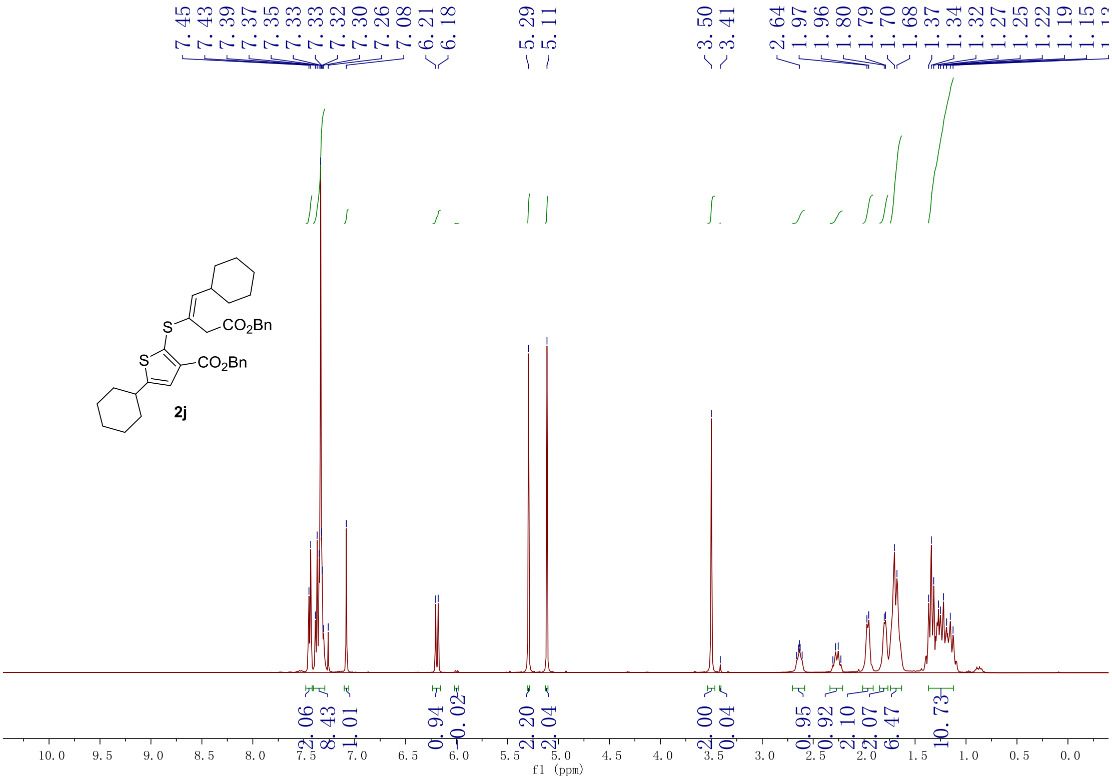


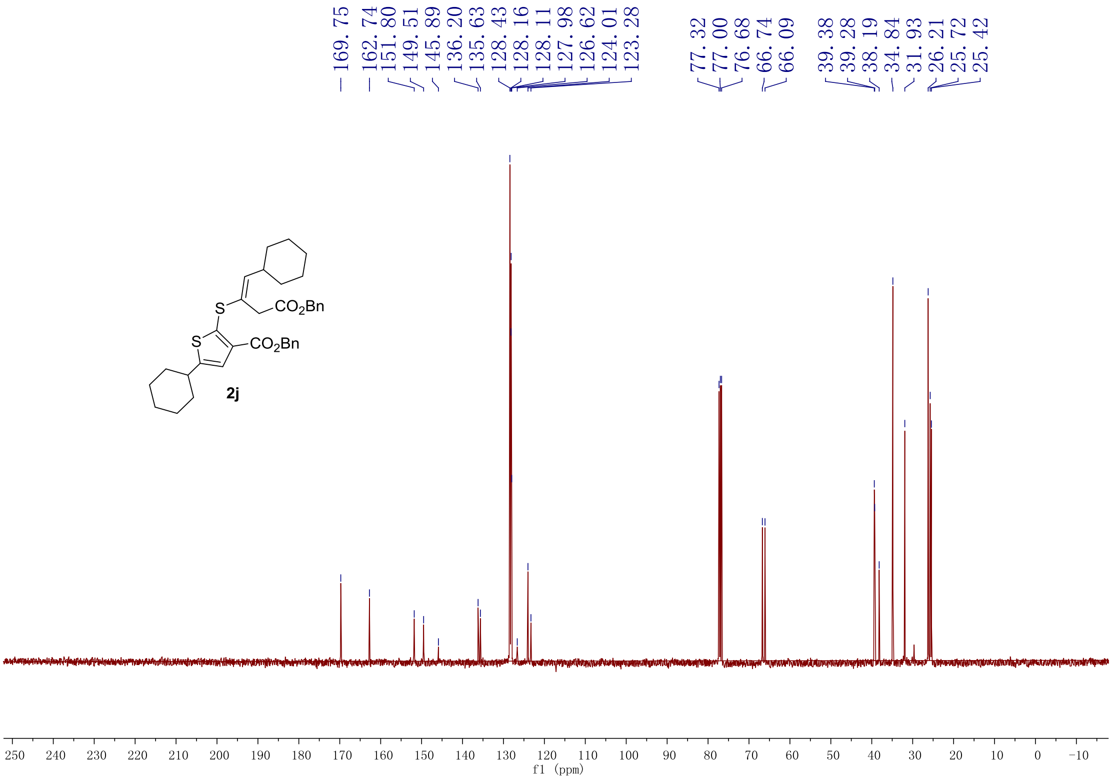

7.44 7.42 7.38 7.36 7.35 7.34 7.31 7.31 7.30 7.29 7.28 7.27 7.26 7.21 7.21 7.18 7.16 7.09 6.37 6.35 6.33
5.30 5.29 5.11 3.41 3.00 2.99 2.97 2.95 2.92 2.91 2.90 2.88 2.88 2.76 2.74 2.72 2.52 2.50 2.48 2.46
CH2CH2Ph
S
CO2Bn
S
CO2Bn
PhH2CH2C
2k
2.15 12.79 6.16 1.07 0.94 0.03 2.01 2.07 2.13 2.09 2.09 2.18 2.00 0.04
f1 (ppm)

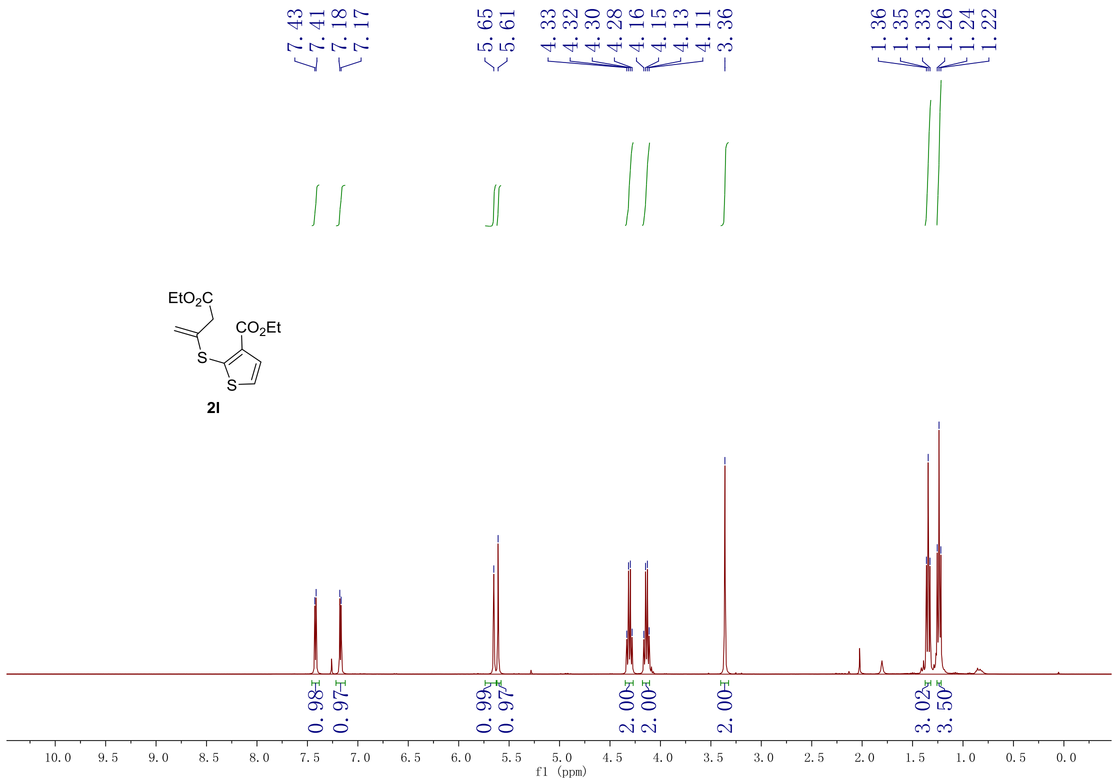

169.49 162.56 144.77 142.29 140.83 140.47 136.09 128.45 128.41 128.19 128.14 128.06 126.62 126.28 126.08 77.32 77.00 76.68 66.82 66.20 38.00 37.44 34.64 31.85 31.65
CH2CH2Ph
S
CO2Bn
S
CO2Bn
PhH2CH2C
2k
f1 (ppm)

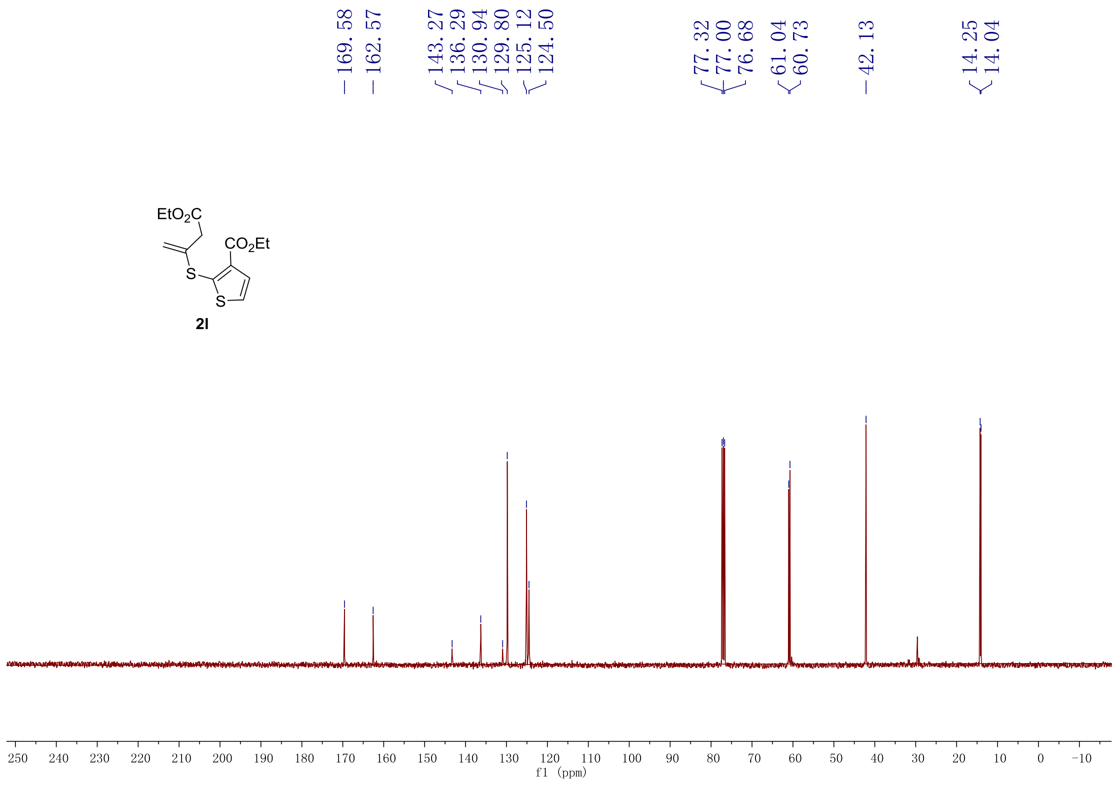


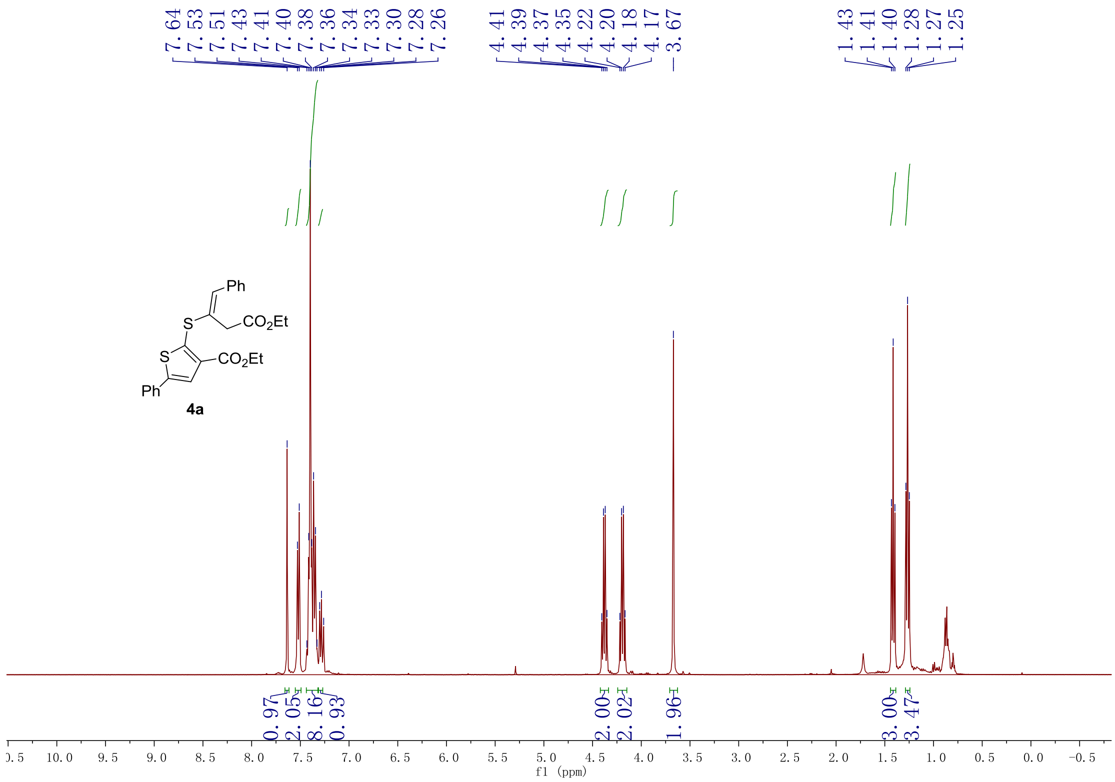


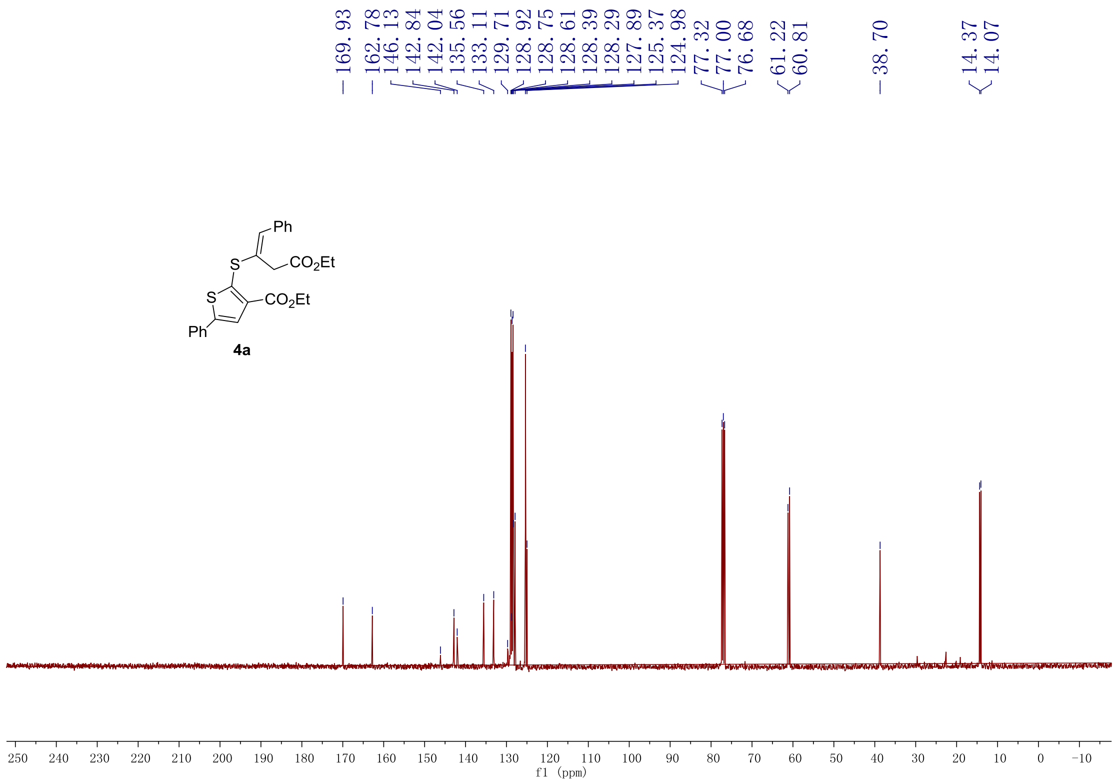

7.45
7.43
7.39
7.37
7.35
7.33
7.33
7.32
7.30
7.26
7.08
6.21
6.18
5.29
5.11
3.50
3.41
2.64
1.97
1.96
1.80
1.79
1.70
1.68
1.37
1.34
1.32
1.27
1.25
1.22
1.19
1.15
CO2Bn
S
S
CO2Bn
2j
2.06
8.43
1.01
0.94
0.02
2.20
2.04
2.00
0.04
0.95
0.92
2.10
2.07
6.47
10.73
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

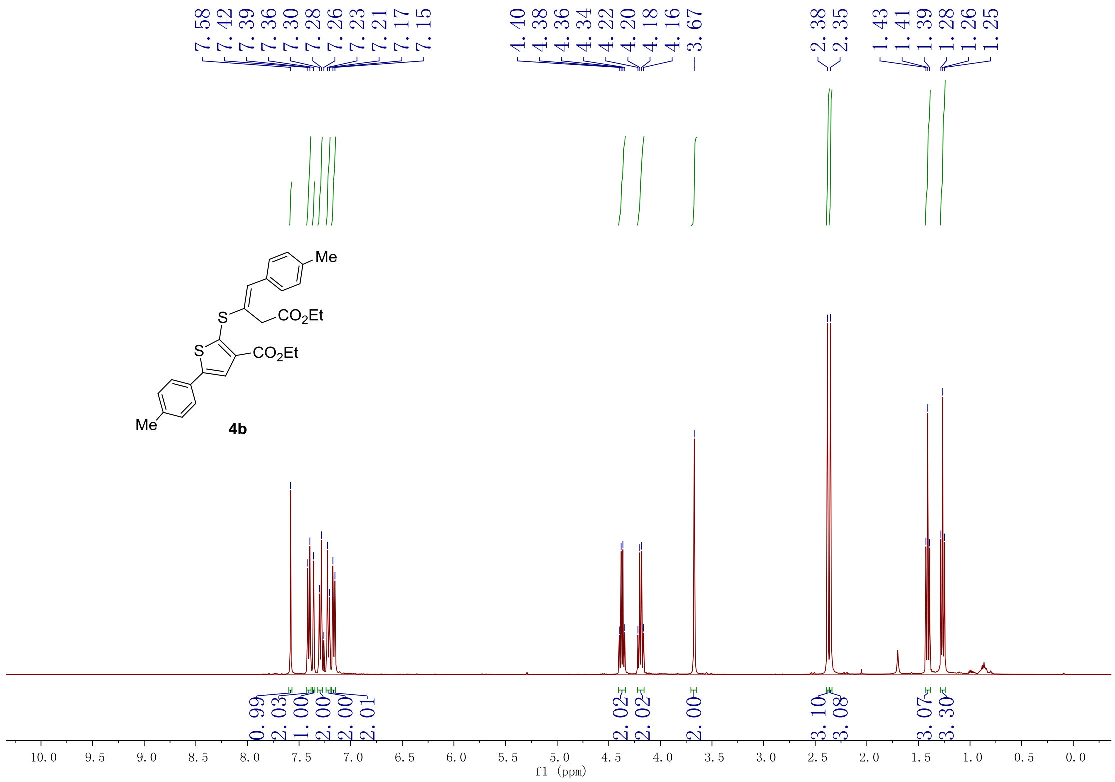

169.75
162.74
151.80
149.51
145.89
136.20
135.63
128.43
128.16
128.11
127.98
126.62
124.01
123.28
77.32
77.00
76.68
66.74
66.09
39.38
39.28
38.19
34.84
31.93
26.21
25.72
25.42
CO2Bn
S
S
CO2Bn
2j
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.43
7.41
7.18
7.17
5.65
5.61
4.33
4.32
4.30
4.28
4.16
4.15
4.13
4.11
3.36
1.36
1.35
1.33
1.26
1.24
1.22
EtO_2C
CO_2Et
S
S
2l
0.98
0.97
0.99
0.97
2.00
2.00
2.00
3.02
3.50
f1 (ppm)

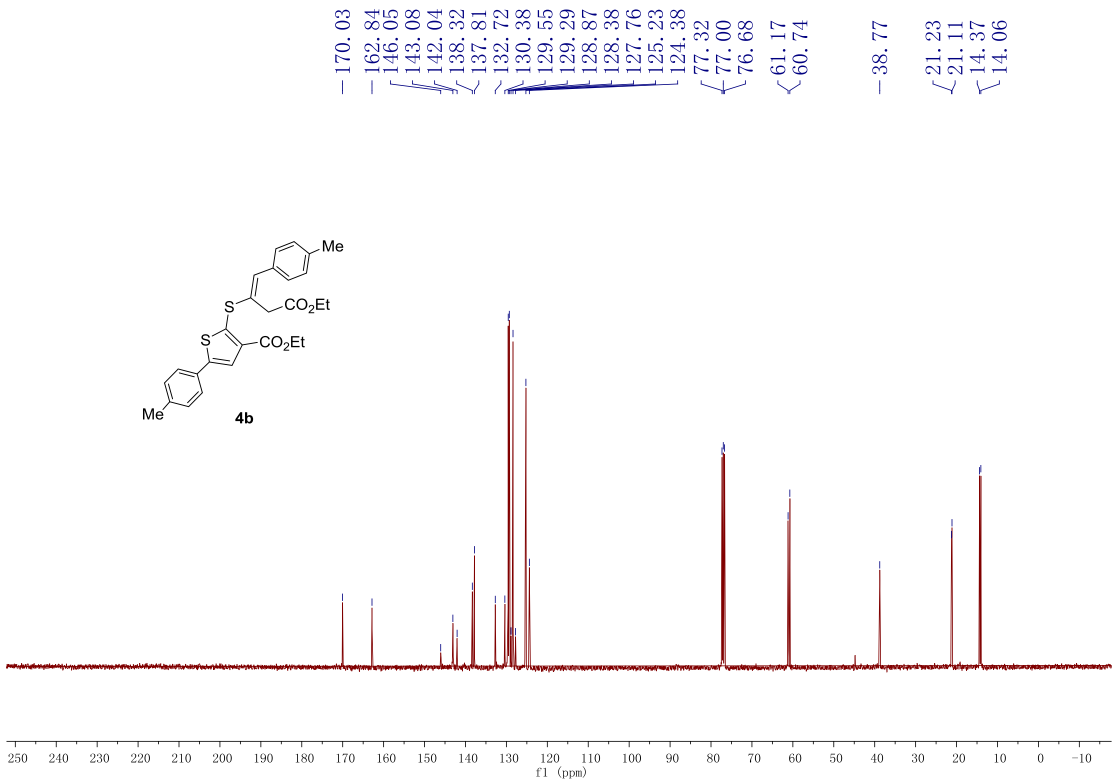

169.58
162.57
143.27
136.29
130.94
129.80
125.12
124.50
77.32
77.00
76.68
61.04
60.73
42.13
14.25
14.04
EtO_2C
CO_2Et
S
S
2l
f1 (ppm)


7.64
7.53
7.51
7.43
7.41
7.40
7.38
7.36
7.34
7.33
7.30
7.28
7.26
4.41
4.39
4.37
4.35
4.22
4.20
4.18
4.17
3.67
1.43
1.41
1.40
1.28
1.27
1.25
Ph
S
CO2Et
S
CO2Et
Ph
4a
0.97
2.05
8.16
0.93
2.00
2.02
1.96
3.00
3.47
f1 (ppm)

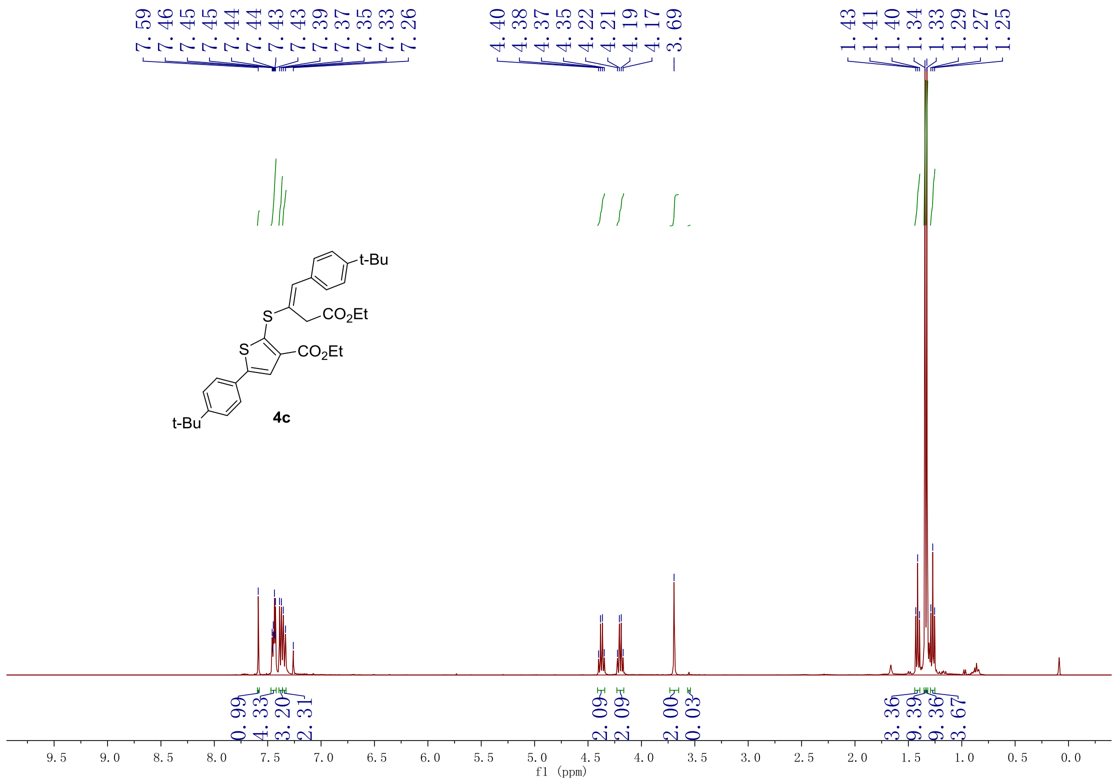

169.93
162.78
146.13
142.84
142.04
135.56
133.11
129.71
128.92
128.75
128.61
128.39
128.29
127.89
125.37
124.98
77.32
77.00
76.68
61.22
60.81
38.70
14.37
14.07
Ph
S
CO2Et
S
CO2Et
Ph
4a
f1 (ppm)


7.58
7.42
7.39
7.36
7.30
7.28
7.26
7.23
7.21
7.17
7.15
4.40
4.38
4.36
4.34
4.22
4.20
4.18
4.16
3.67
2.38
2.35
1.43
1.41
1.39
1.28
1.26
1.25
Me
S
CO2Et
S
CO2Et
Me
0.99
2.03
1.00
2.00
2.00
2.01
2.02
2.02
2.00
3.10
3.08
3.07
3.30
f1 (ppm)

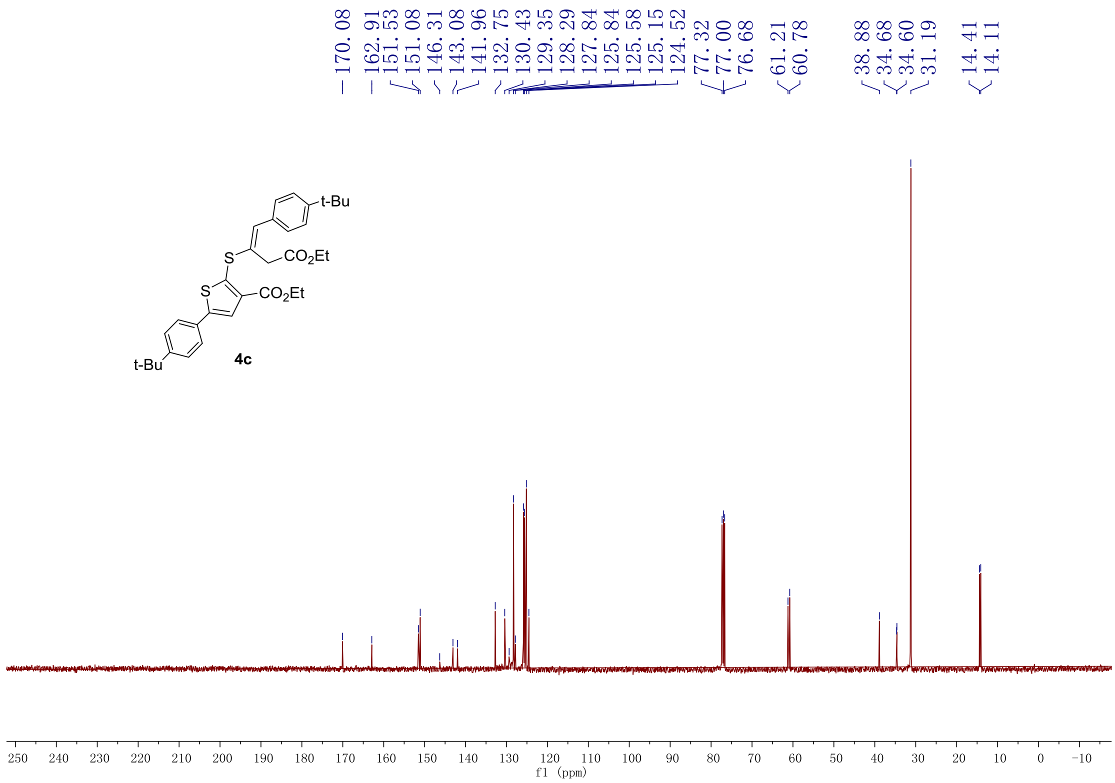
4b


170.03
162.84
146.05
143.08
142.04
138.32
137.81
132.72
130.38
129.55
129.29
128.87
128.38
127.76
125.23
124.38
77.32
77.00
76.68
61.17
60.74
38.77
21.23
21.11
14.37
14.06
Me
S
CO2Et
S
CO2Et
Me
f1 (ppm)

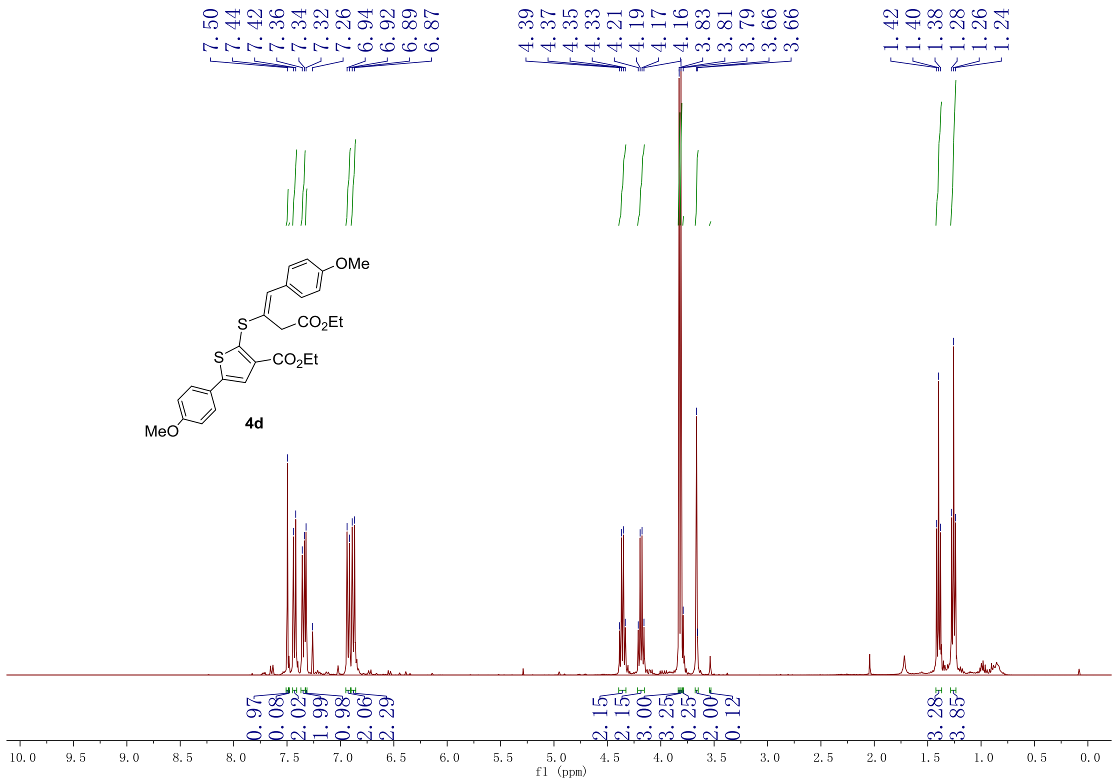
4b

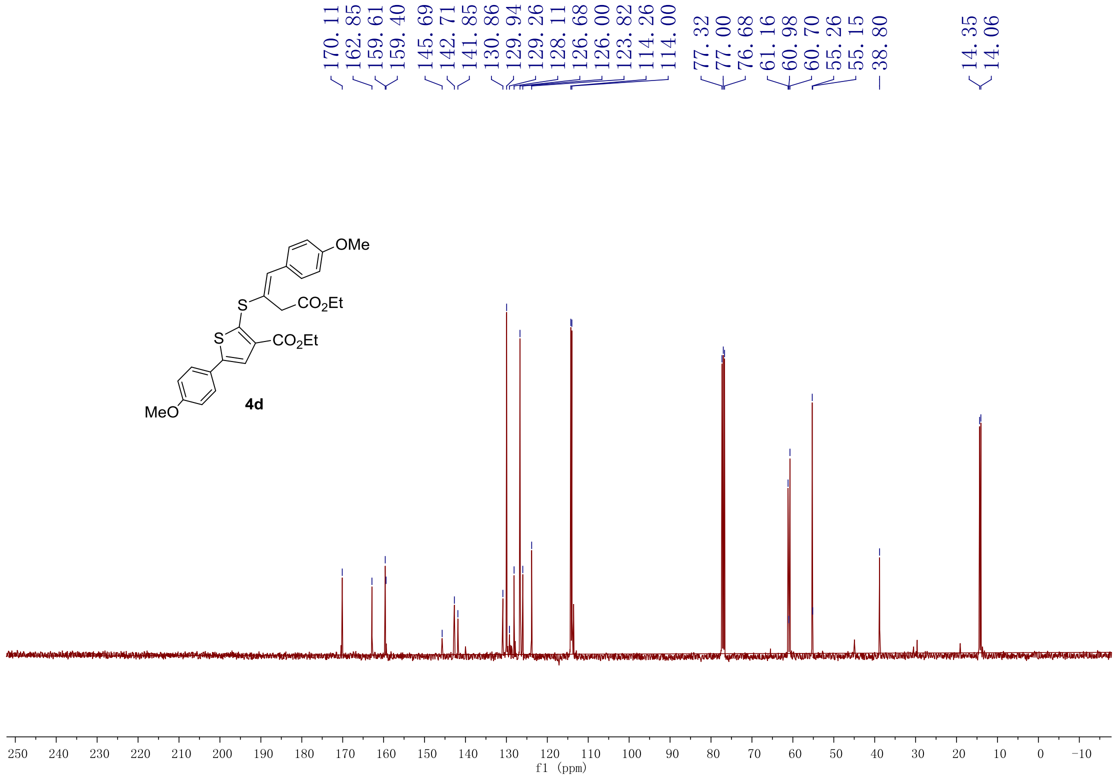


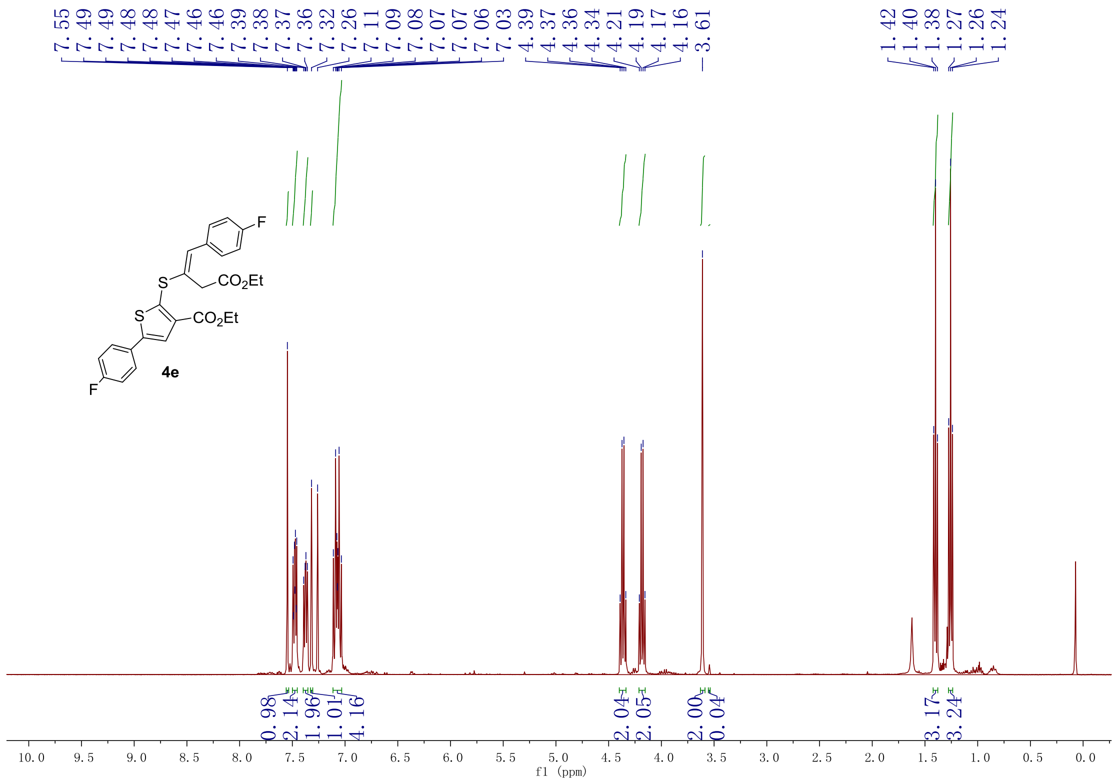
7.59
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.39
7.37
7.35
7.33
7.26
4.40
4.38
4.37
4.35
4.22
4.21
4.19
4.17
3.69
1.43
1.41
1.40
1.34
1.33
1.29
1.27
1.25
t-Bu
S
CO2Et
S
CO2Et
t-Bu
4c
0.99
4.33
3.20
2.31
2.09
2.09
2.00
0.03
3.36
9.39
9.36
3.67
f1 (ppm)

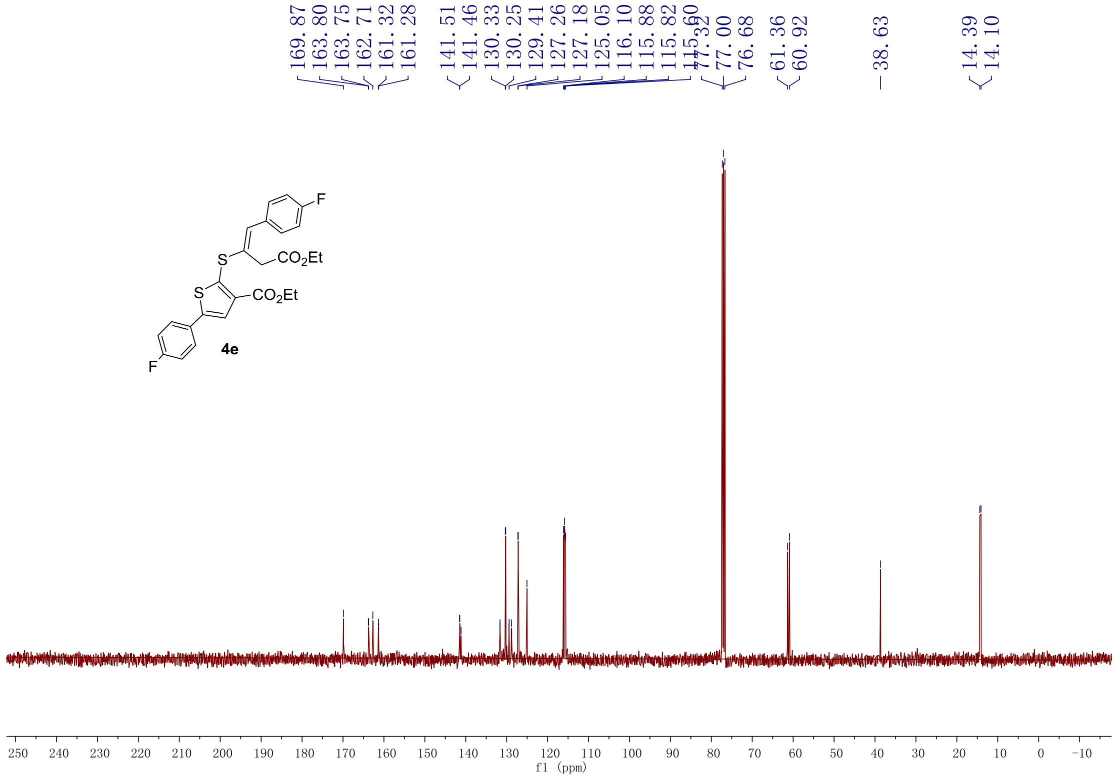


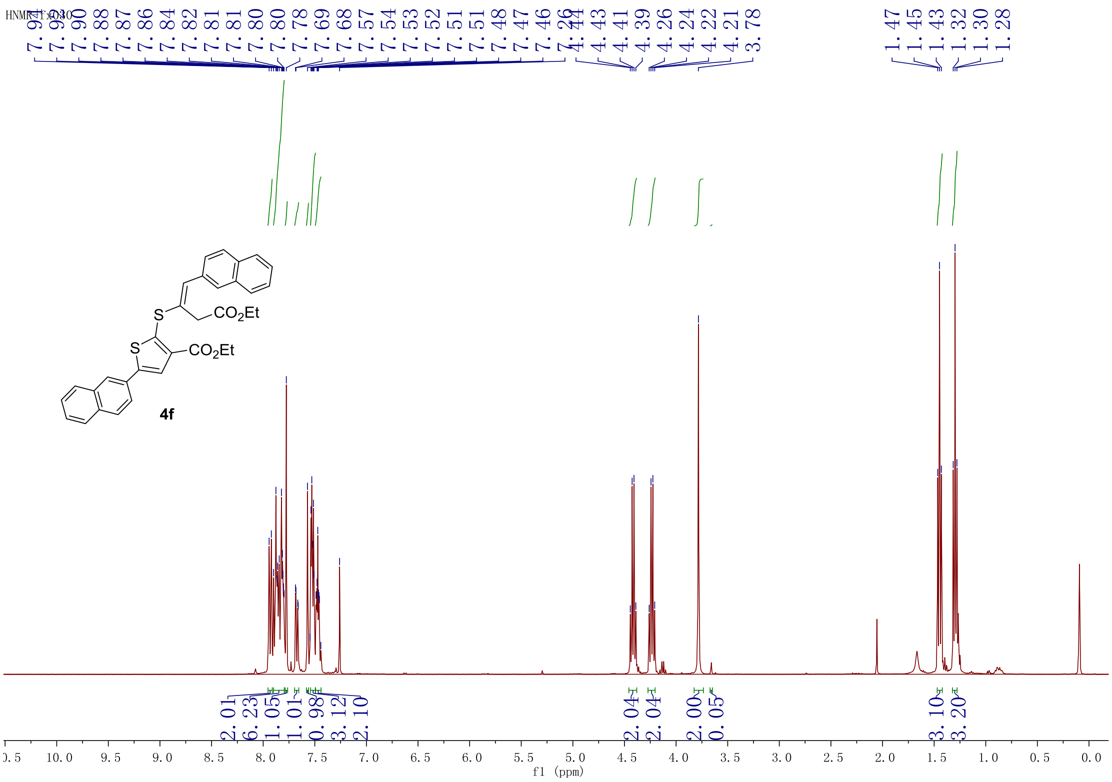
170.08
162.91
151.53
151.08
146.31
143.08
141.96
132.75
130.43
129.35
128.29
127.84
125.84
125.58
125.15
124.52
77.32
77.00
76.68
61.21
60.78
38.88
34.68
34.60
31.19
14.41
14.11
t-Bu
S
CO2Et
S
CO2Et
t-Bu
4c
f1 (ppm)

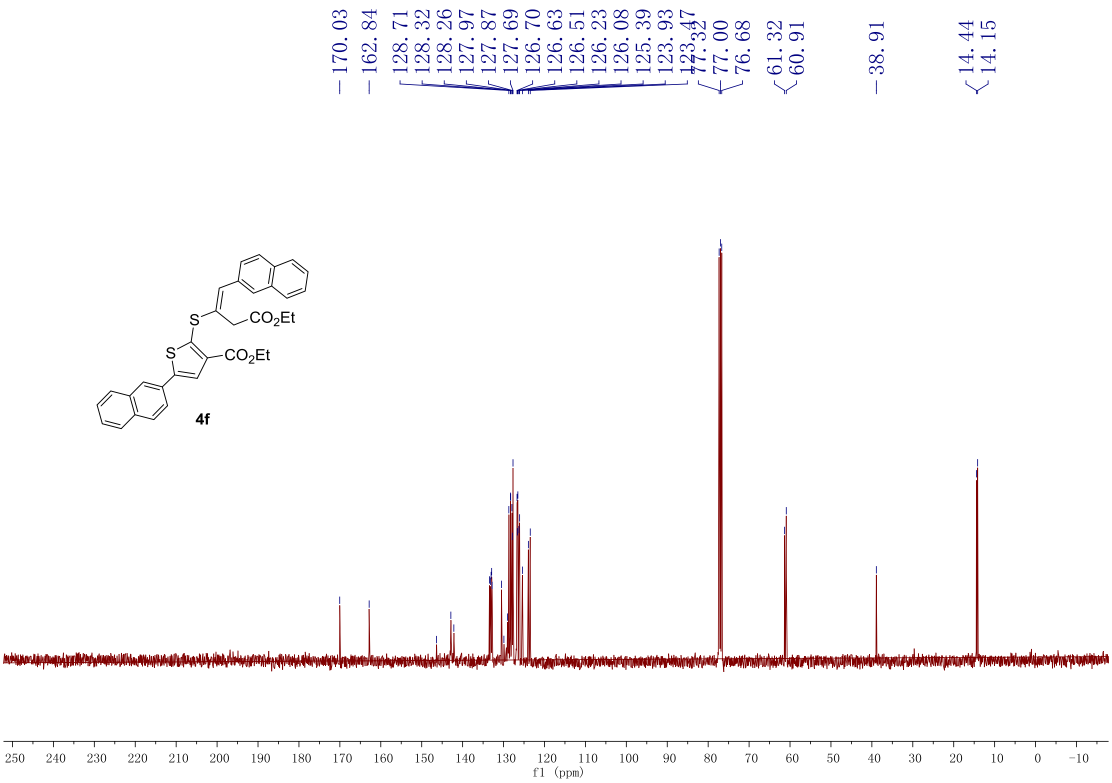

7.50
7.44
7.42
7.36
7.34
7.32
7.26
6.94
6.92
6.89
6.87
4.39
4.37
4.35
4.33
4.21
4.19
4.17
4.16
3.83
3.81
3.79
3.66
3.66
1.42
1.40
1.38
1.28
1.26
1.24
OMe
S
CO2Et
S
CO2Et
MeO
4d
0.97
0.08
2.02
1.99
0.98
2.06
2.29
2.15
2.15
3.00
3.25
0.25
2.00
0.12
3.28
3.85
f1 (ppm)

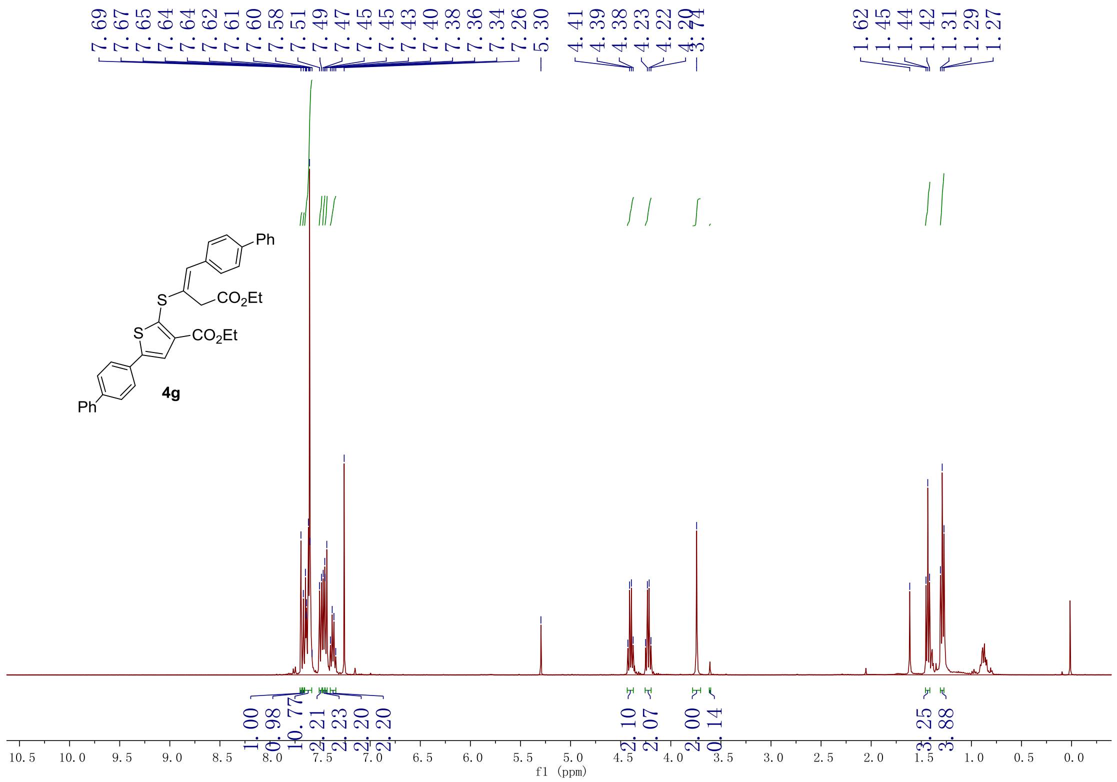

170.11
162.85
159.61
159.40
145.69
142.71
141.85
130.86
129.94
129.26
128.11
126.68
126.00
123.82
114.26
114.00
77.32
77.00
76.68
61.16
60.98
60.70
55.26
55.15
38.80
14.35
14.06
OMe
S
CO2Et
S
CO2Et
MeO
4d
f1 (ppm)

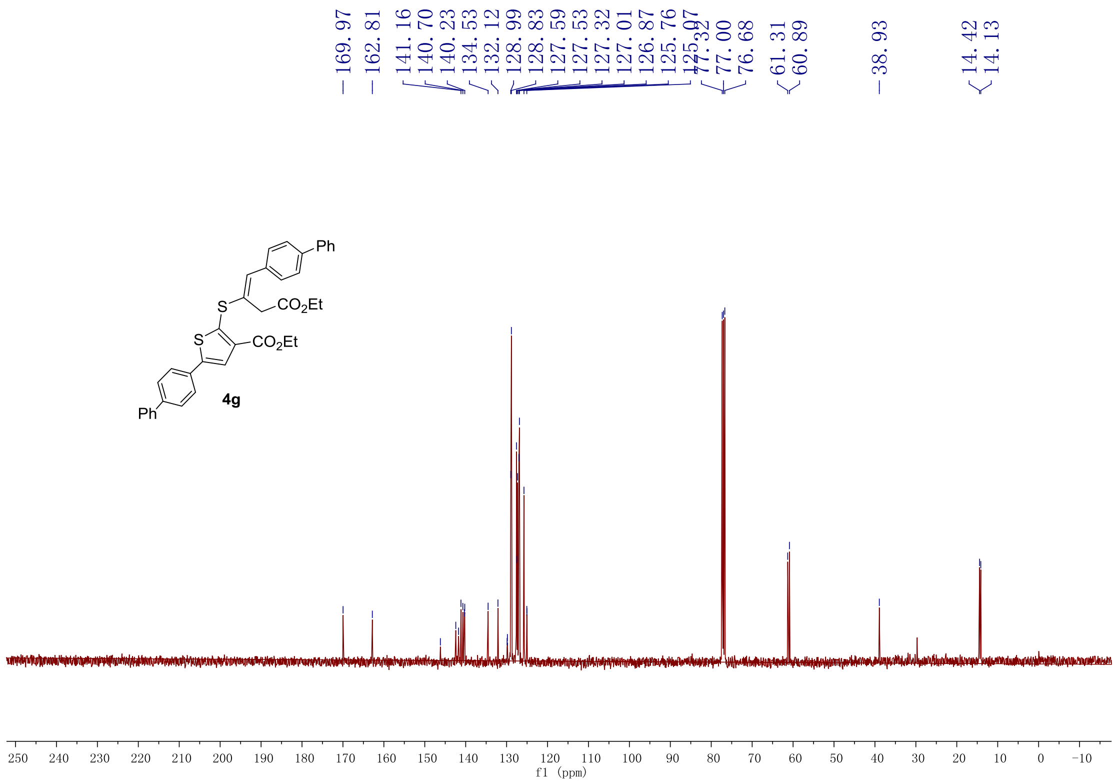


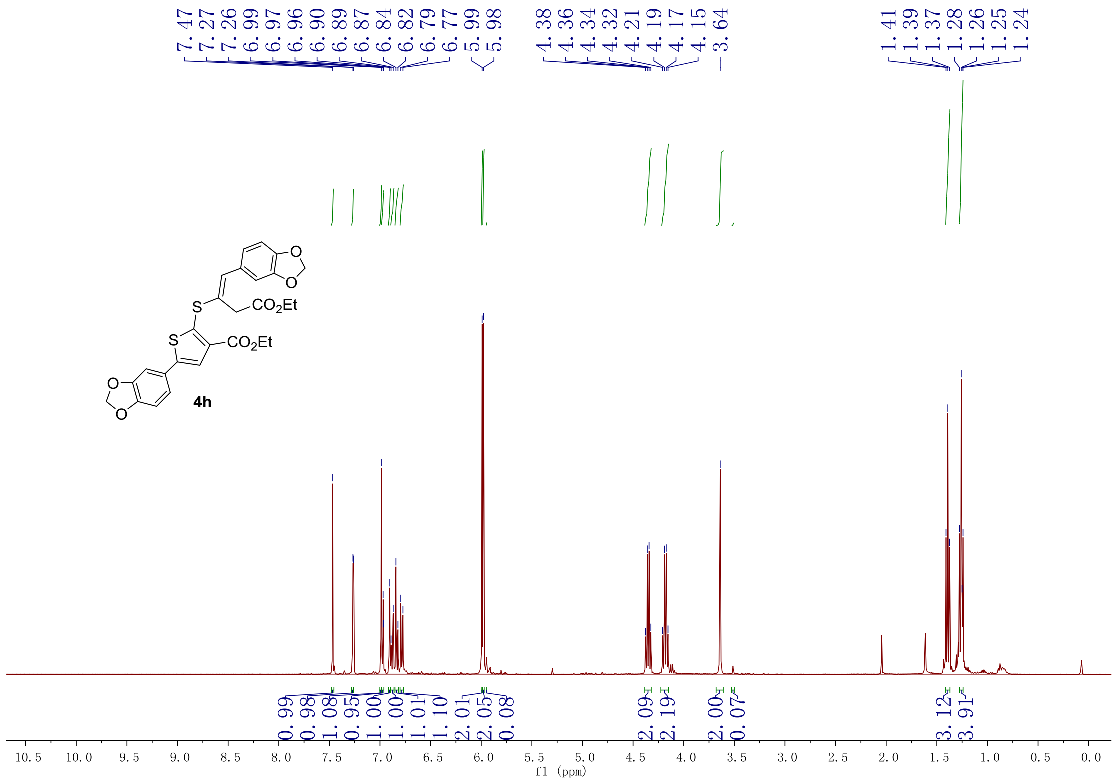


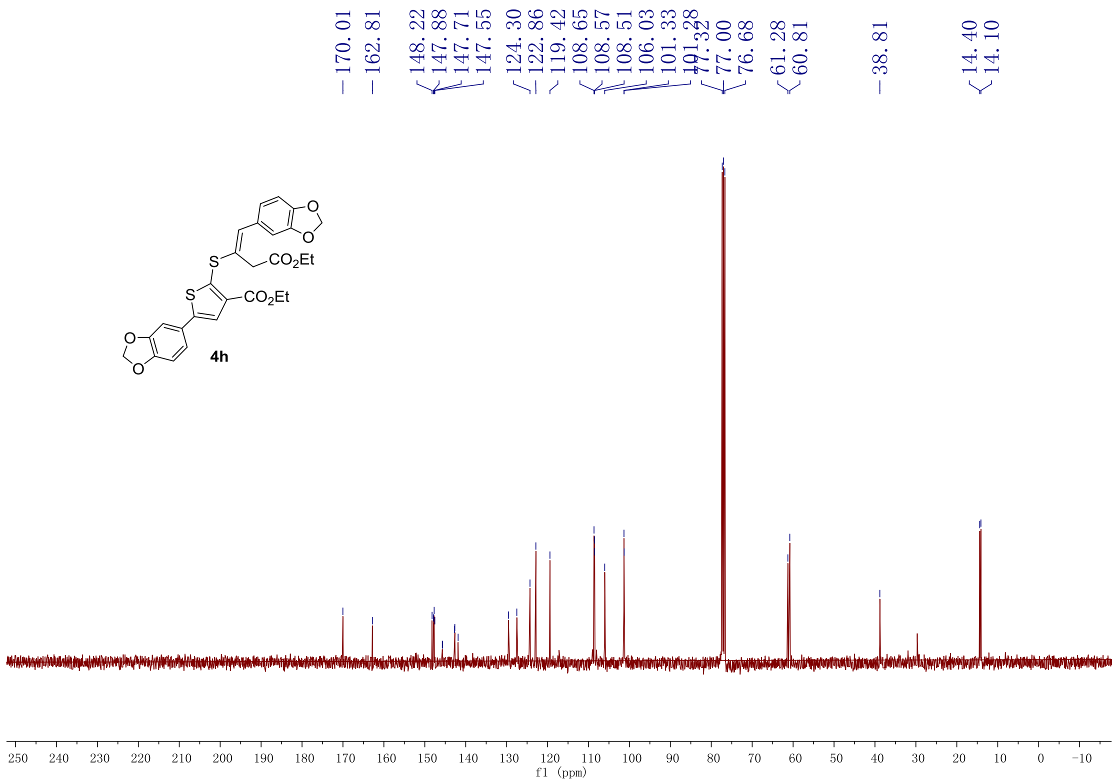


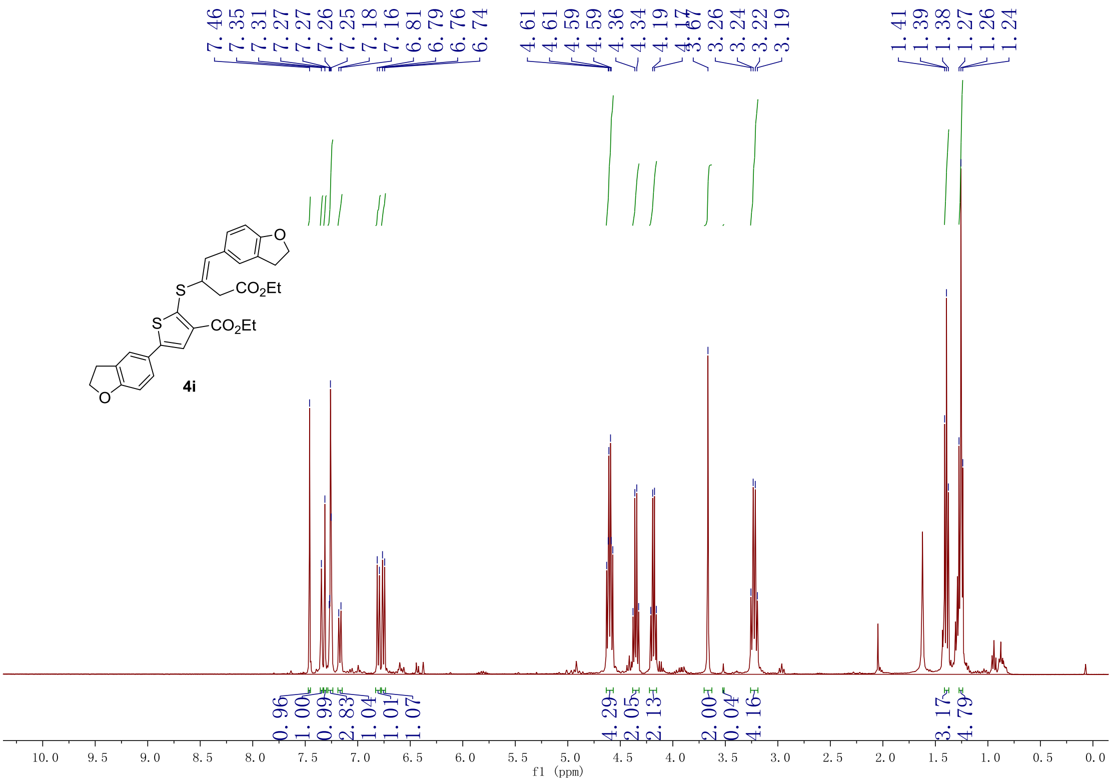


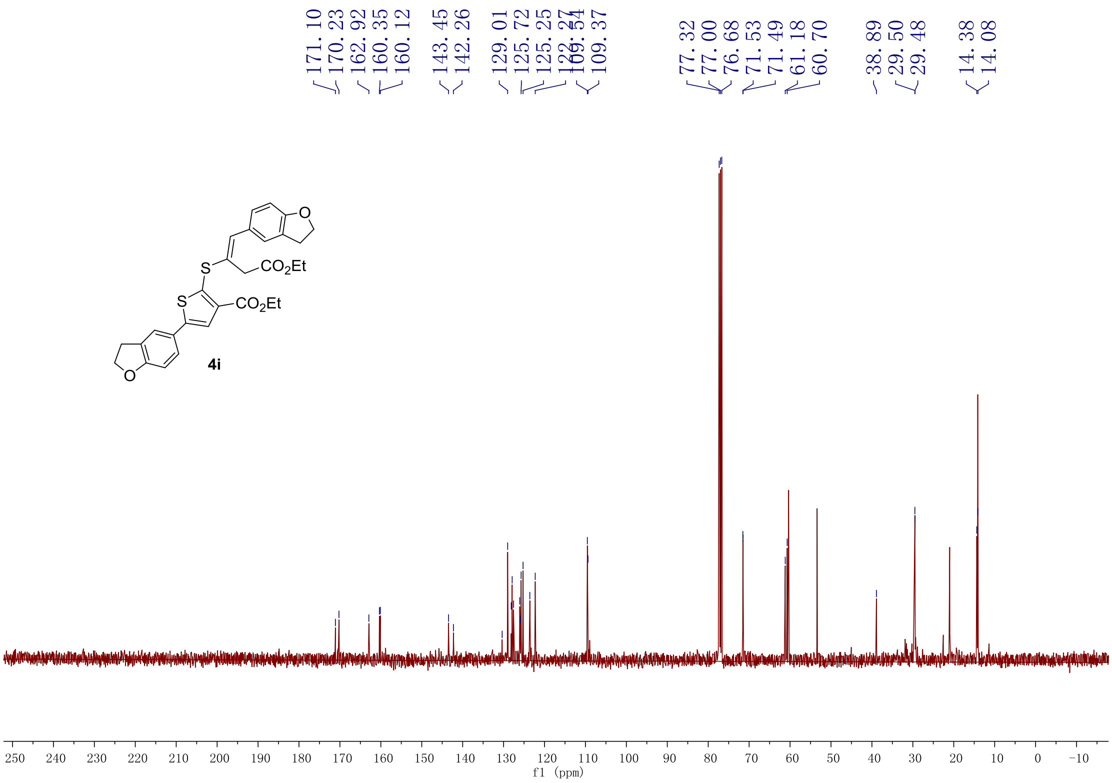


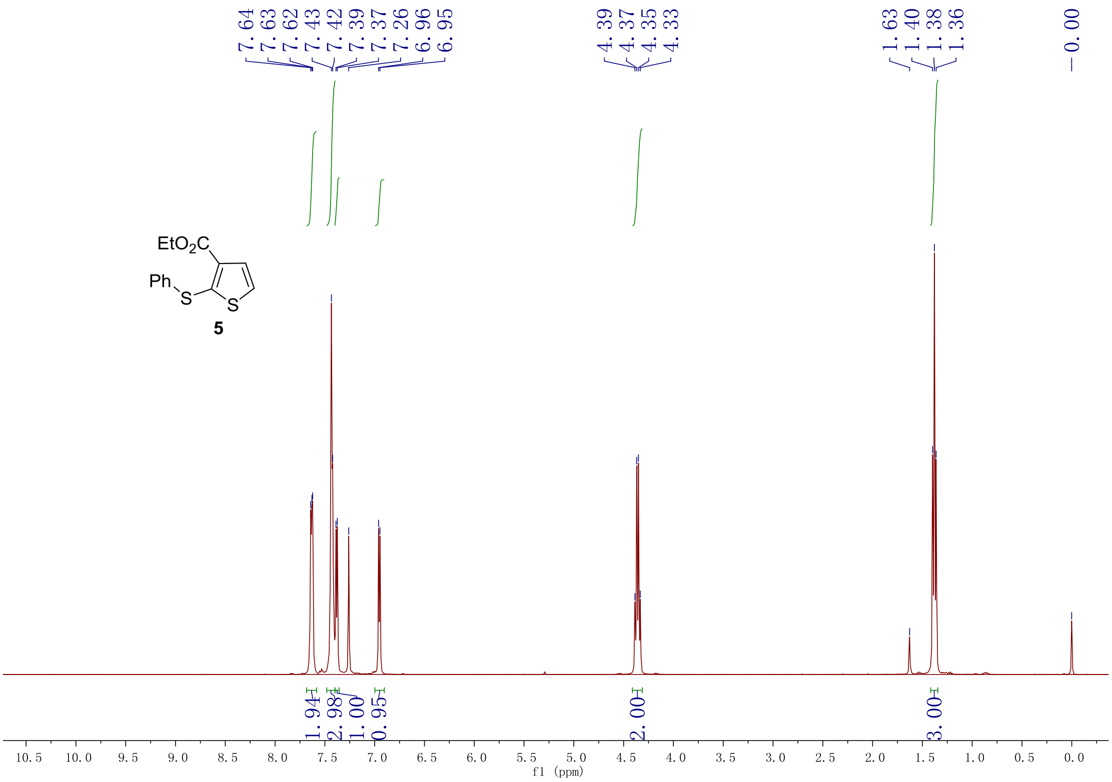


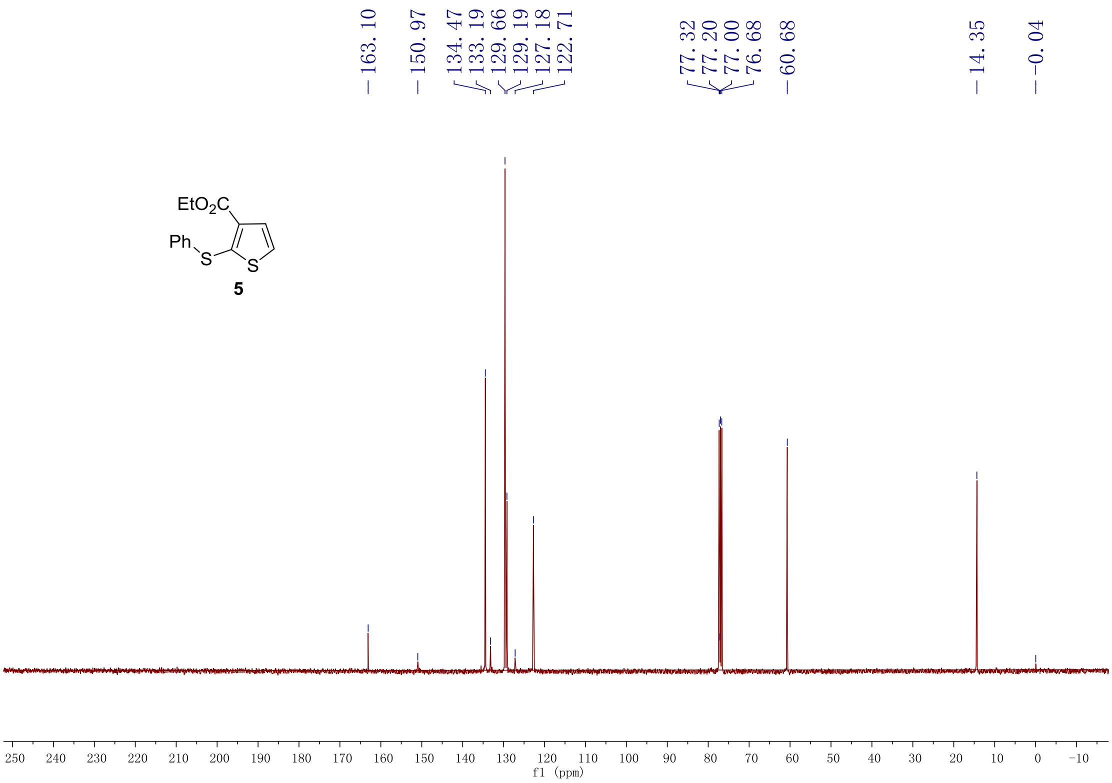

7.47 7.27 7.26 6.99 6.97 6.96 6.90 6.89 6.87 6.84 6.82 6.79 6.77 5.99 5.98
4.38 4.36 4.34 4.32 4.21 4.19 4.17 4.15 3.64
1.41 1.39 1.37 1.28 1.26 1.25 1.24
S
CO2Et
S
CO2Et
O
O
O
O
4h
0.99 0.98 1.08 0.95 1.00 1.00 1.01 1.10 2.01 2.05 0.08
2.09 2.19
2.00 0.07
3.12 3.91
f1 (ppm)

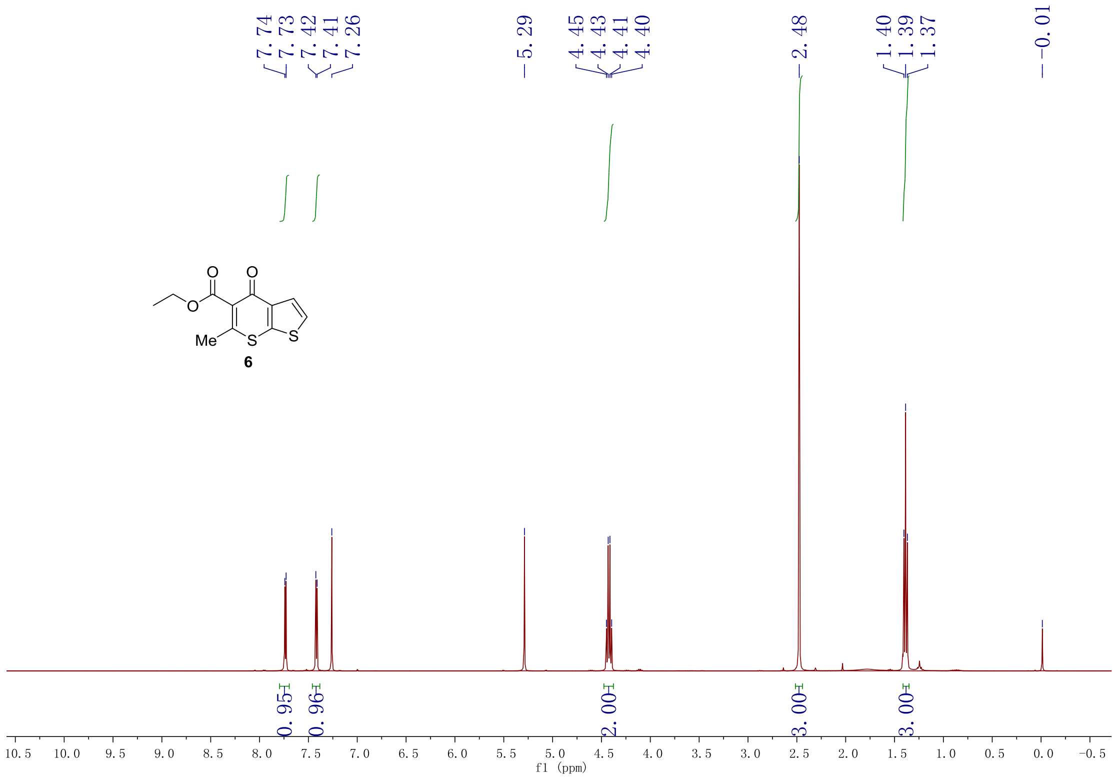

170.01 162.81
148.22 147.88 147.71 147.55
124.30 122.86 119.42 108.65 108.57 108.51 106.03 101.33 101.28 77.32 77.00 76.68
61.28 60.81
38.81
14.40 14.10
S
CO2Et
S
CO2Et
O
O
O
O
4h
f1 (ppm)

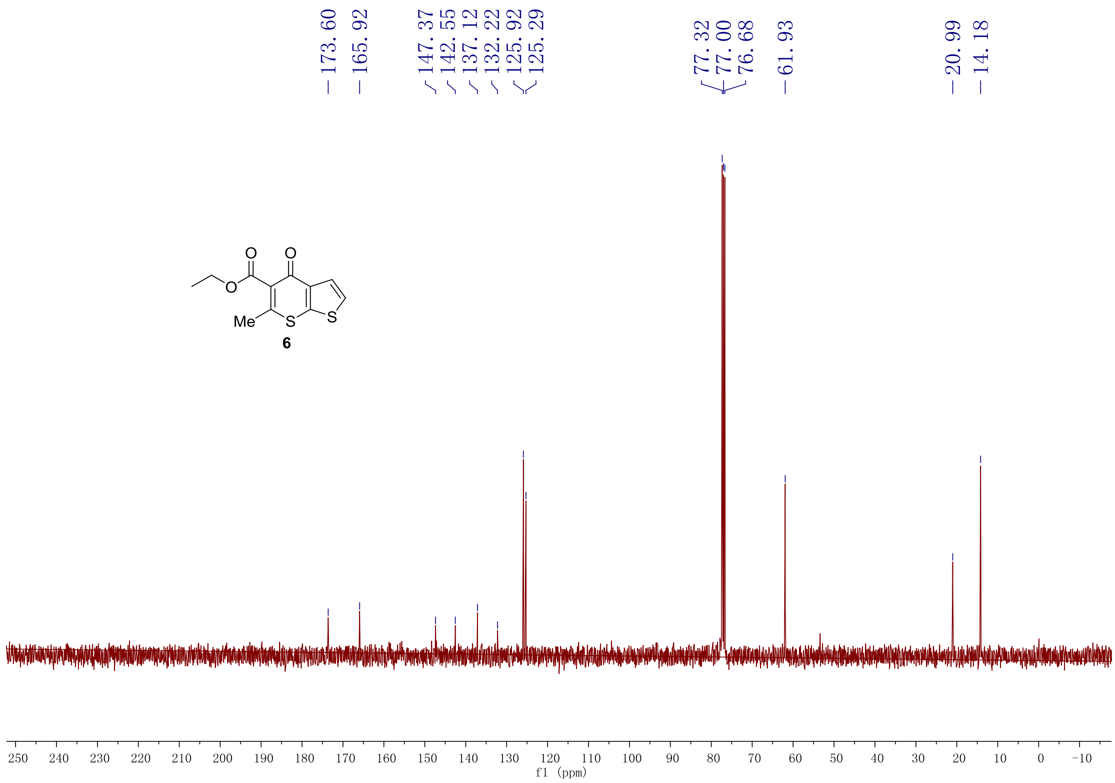

7.46
7.35
7.31
7.27
7.27
7.26
7.25
7.18
7.16
6.81
6.79
6.76
6.74
4.61
4.61
4.59
4.59
4.36
4.34
4.19
4.17
3.67
3.26
3.24
3.22
3.19
1.41
1.39
1.38
1.27
1.26
1.24
S
CO2Et
S
CO2Et
O
O
4i
0.96
1.00
0.99
2.83
1.04
1.01
1.07
4.29
2.05
2.13
2.00
0.04
4.16
3.17
4.79
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

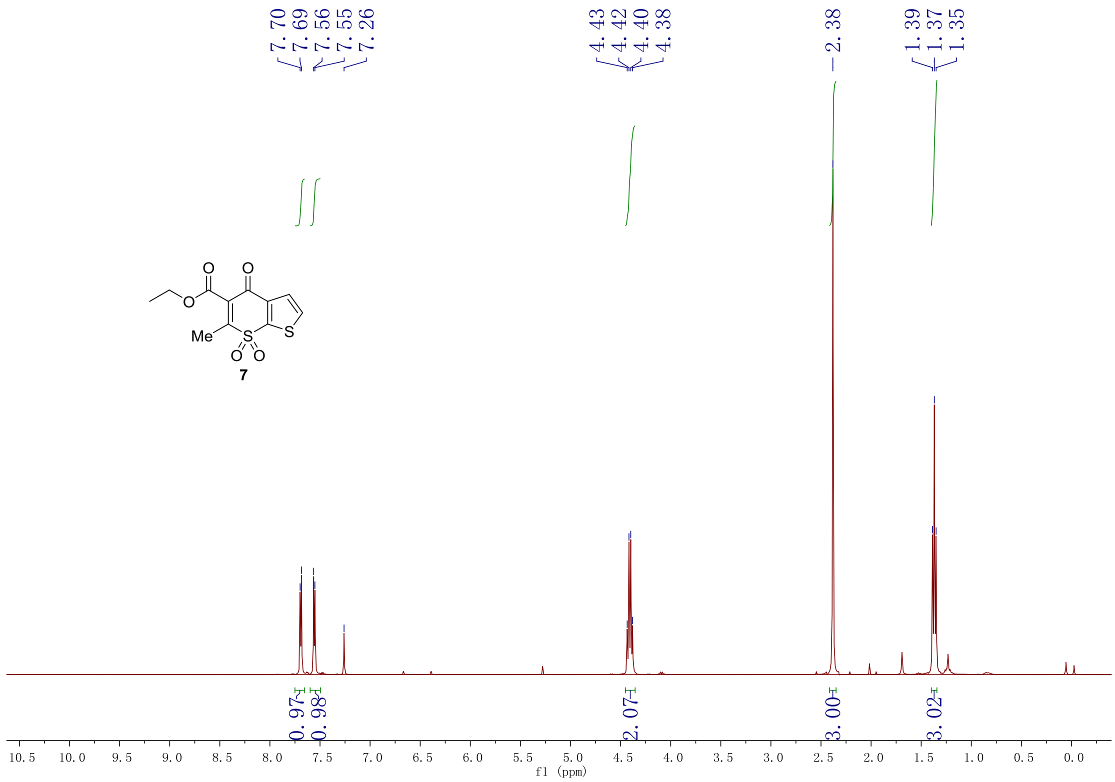

171.10
170.23
162.92
160.35
160.12
143.45
142.26
129.01
125.72
125.25
122.27
109.54
109.37
77.32
77.00
76.68
71.53
71.49
61.18
60.70
38.89
29.50
29.48
14.38
14.08
S
CO2Et
S
CO2Et
O
O
4i
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

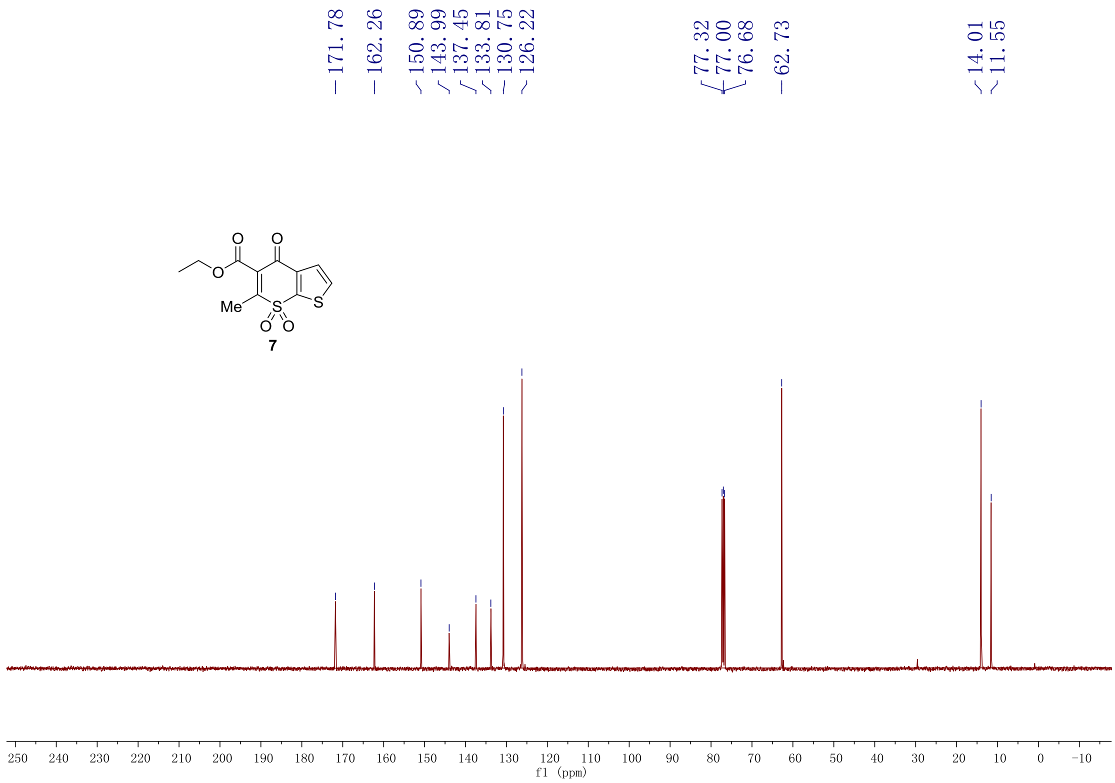

7.64
7.63
7.62
7.43
7.42
7.39
7.37
7.26
6.96
6.95
4.39
4.37
4.35
4.33
1.63
1.40
1.38
1.36
0.00
EtO2C
Ph
S
S
5
1.94
2.98
1.00
0.95
2.00
3.00
f1 (ppm)

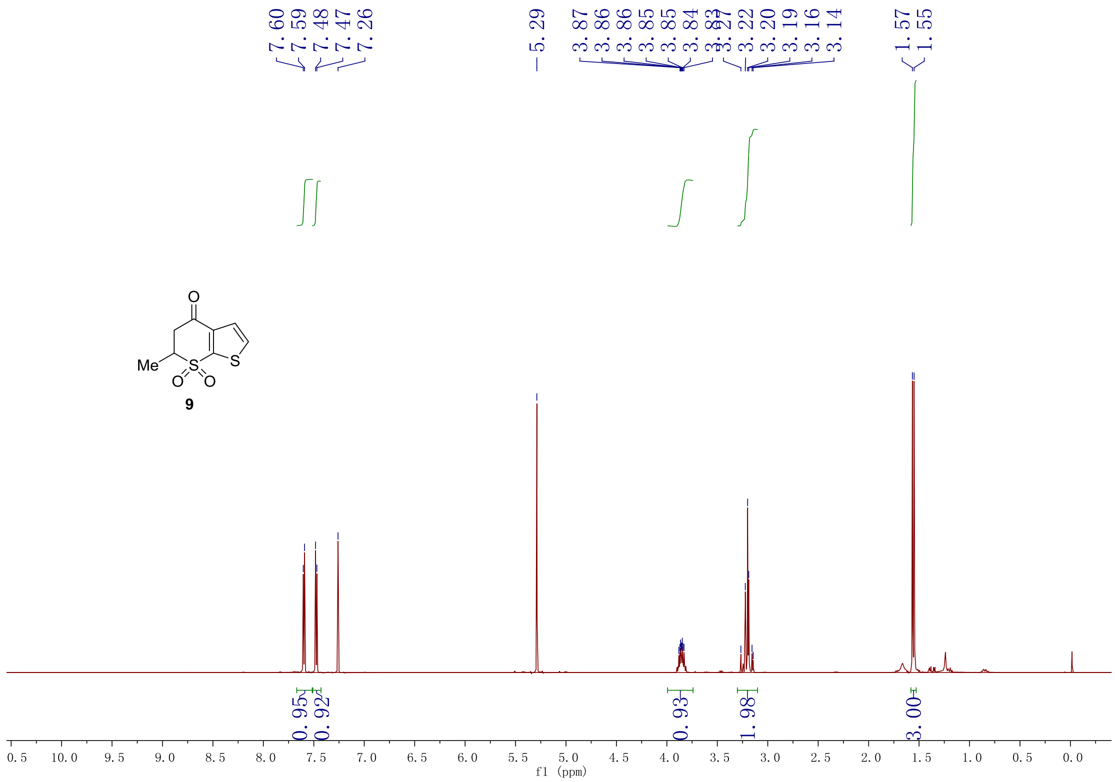

163.10
150.97
134.47
133.19
129.66
129.19
127.18
122.71
77.32
77.20
77.00
76.68
60.68
14.35
-0.04
EtO2C
Ph
S
S
5
f1 (ppm)


7.74
7.73
7.42
7.41
7.26
5.29
4.45
4.43
4.41
4.40
2.48
1.40
1.39
1.37
-0.01
O
O
O
Me
S
S
6
0.95
0.96
2.00
3.00
3.00
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)

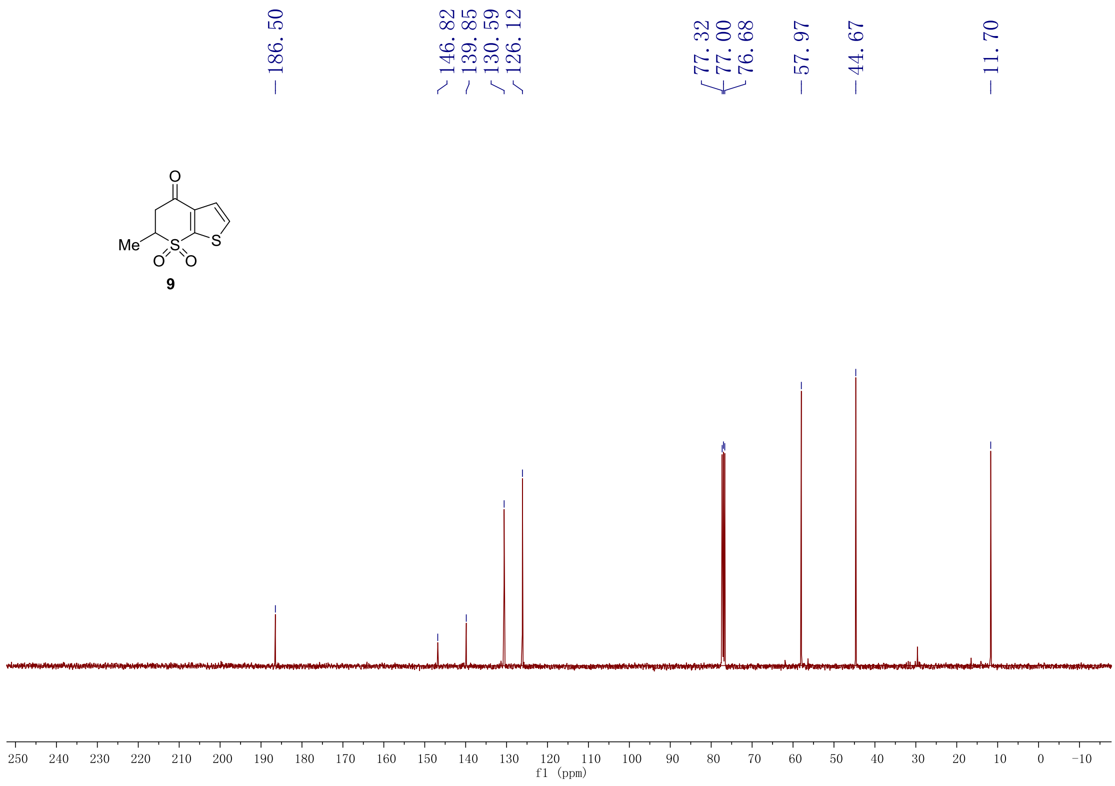

173.60
165.92
147.37
142.55
137.12
132.22
125.92
125.29
77.32
77.00
76.68
61.93
20.99
14.18
O
O
O
Me
S
S
6
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.70
7.69
7.56
7.55
7.26
4.43
4.42
4.40
4.38
2.38
1.39
1.37
1.35
O
O
O
Me
S
S
O O
7
0.97
0.98
2.07
3.00
3.02
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
f1 (ppm)

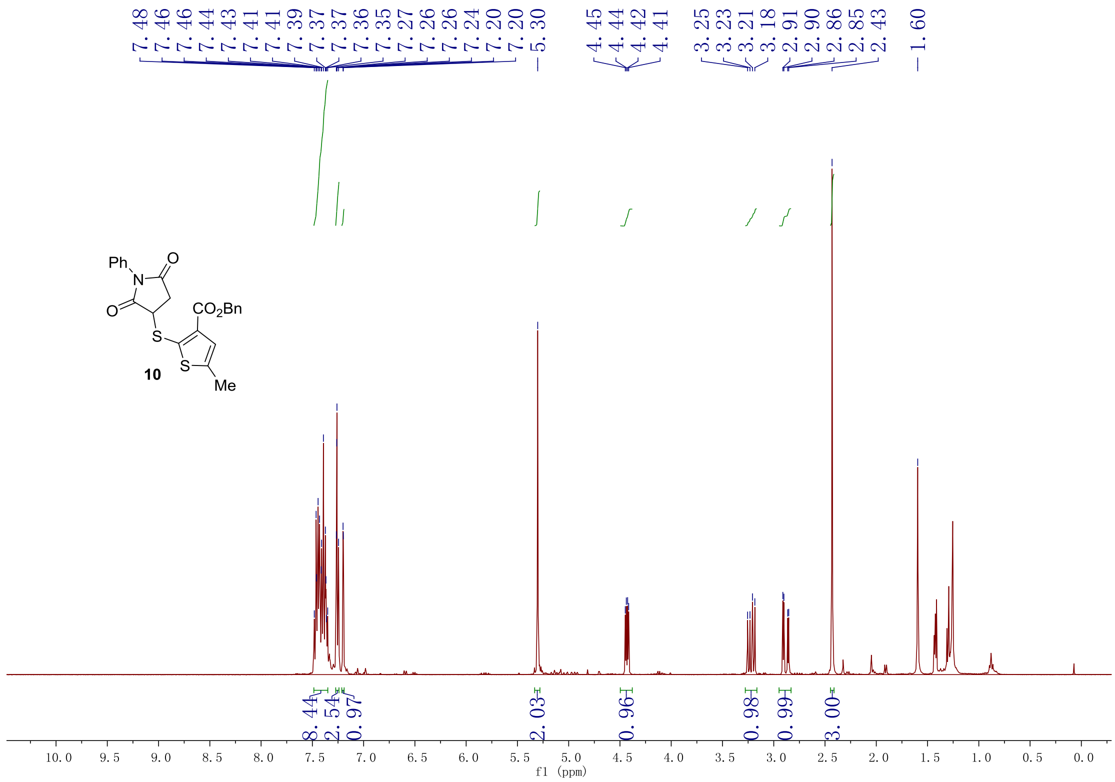

171.78
162.26
150.89
143.99
137.45
133.81
130.75
126.22
77.32
77.00
76.68
62.73
14.01
11.55
O
O
O
Me
S
S
O O
7
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

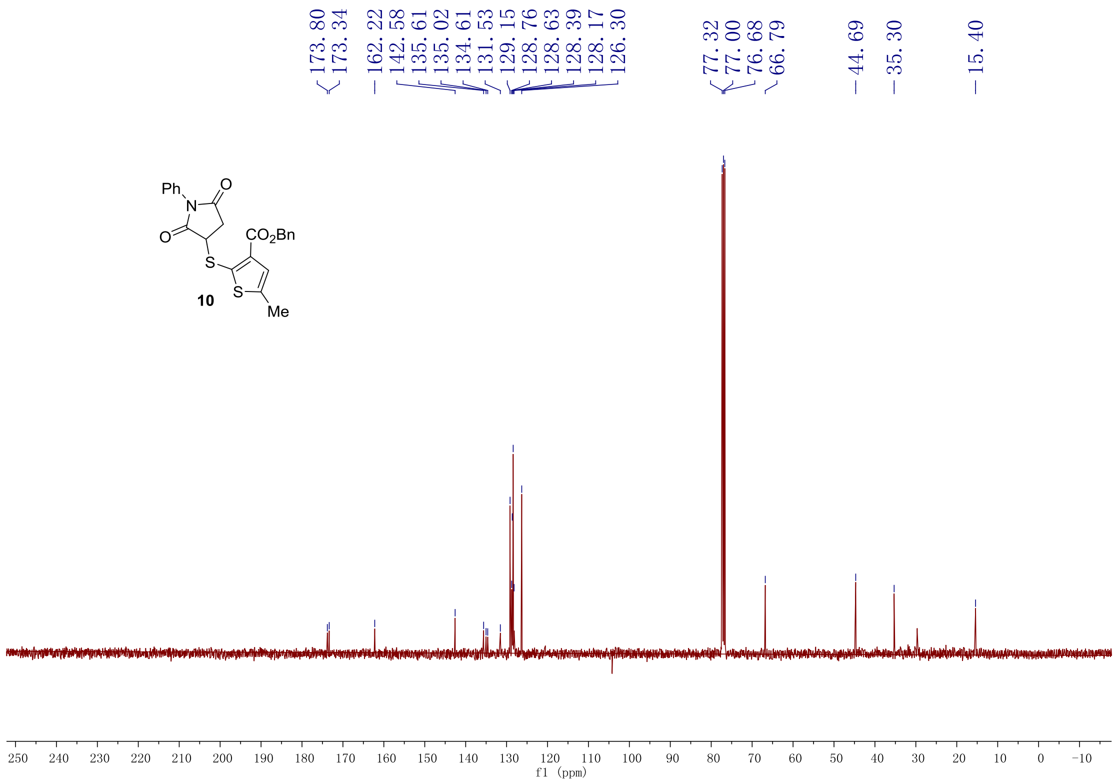


7.60
7.59
7.48
7.47
7.26
5.29
3.87
3.86
3.86
3.85
3.85
3.84
3.83
3.27
3.22
3.20
3.19
3.16
3.14
1.57
1.55
O
Me
S
S
O
O
9
0.95
0.92
0.93
1.98
3.00
f1 (ppm)



186.50
146.82
139.85
130.59
126.12
77.32
77.00
76.68
57.97
44.67
11.70
O
Me
S
S
O
O
9
f1 (ppm)


7.48 7.46 7.46 7.44 7.43 7.41 7.41 7.39 7.37 7.37 7.36 7.35 7.27 7.26 7.26 7.24 7.20 7.20
5.30
4.45 4.44 4.42 4.41
3.25 3.23 3.21 3.18 2.91 2.90 2.86 2.85 2.43
1.60
Ph
N
O
O
CO2Bn
S
S
Me
10
8.44 2.54 0.97 2.03 0.96 0.98 0.99 3.00
f1 (ppm)


173.80 173.34
162.22 142.58 135.61 135.02 134.61 131.53 129.15 128.76 128.63 128.39 128.17 126.30
77.32 77.00 76.68 66.79
44.69
35.30
15.40
Ph
N
O
O
CO2Bn
S
S
Me
10
f1 (ppm)