Supporting Information

for

Expedient Stereoselective Synthesis of Multi-substituted Functionalized Allylic Boronates from Morita−Baylis−Hillman Alcohols

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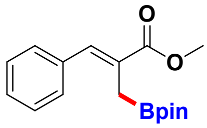
I. General Methods

Unless otherwise noted, otherwise noted, all reagents were obtained from commercial suppliers and were used without further purification. ^{1}H, ^{13}C spectra were recorded in $CDCl_3$ on a Bruker AVIII-500M spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. Column chromatography was performed using silica gel (200-300 mesh).

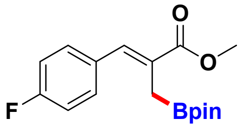
General Optimization Procedure: To a reaction tube equipped with a stir bar, 60.9 mg of B_2pin_2 (0.24 mmol), 7.2mg $Cu(OTf)_2$ (0.02 mmol) and base (0.02 mmol) were added. Next, 0.2 mmol of Morita−Baylis−Hillman alcohols and solvent (2ml) was added via syringe, then sealed the reaction tube. The mixture was stired at room tempreture for about 10h. After the reaction was finished, the mixture was washed with water and extracted with ethyl acetate, repeat three times. The combined organic layer was evaporated under reduced pressure, and the product was purified by column chromatography.

II. Analytic data of products



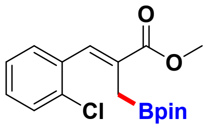
2a: 89%

Methyl(E)-3-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2a): shallow yellow oil (89%, 53.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.40 (qd, J = 8.2, 4.0 Hz, 4H), 7.32 (ddd, J = 6.9, 4.0, 1.7 Hz, 1H), 3.82 (s, 3H), 2.16 (s, 2H), 1.26 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.11 (s), 137.58 (s), 136.22 (s), 130.14 (s), 129.37 (s), 128.30 (s), 128.03 (s), 83.46 (s), 52.02 (s), 24.69 (s).



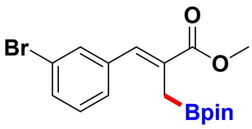
2b: 70%

Methyl(E)-3-(4-fluorophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2b): shallow yellow oil (70%, 44.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.38 (dd, J = 8.5, 5.6 Hz, 2H), 7.06 (t, J = 8.7 Hz, 2H), 3.80 (s, 3H), 2.11 (s, 2H), 1.24 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.94 (s), 162.31 (d, J = 248.5 Hz), 136.39 (s), 132.23 (d, J = 3.3 Hz), 131.16 (d, J = 8.1 Hz), 130.05 (s), 115.34 (d, J = 21.5 Hz), 83.51 (s), 52.04 (s), 24.67 (s).



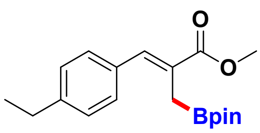
2c: 78%

methyl(E)-3-(2-chlorophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2c): shallow yellow oil (78%, 52.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.41 (dd, J = 5.4, 3.9 Hz, 2H), 7.28 – 7.23 (m, 2H), 3.82 (s, 3H), 2.01 (s, 2H), 1.25 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.53 (s), 134.66 (d, J = 11.2 Hz), 134.10 (s), 131.99 (s), 130.44 (s), 129.49 (s), 129.25 (s), 126.39 (s), 83.51 (s), 52.11 (s), 24.67 (s).



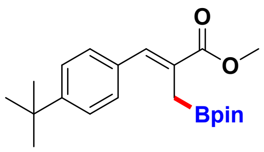
2d: 80%

Methyl(E)-3-(3-bromophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2d): shallow yellow oil (80%, 61.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 1.8 Hz, 2H), 7.44 (d, J = 7.9 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 3.81 (s, 3H), 2.11 (s, 2H), 1.27 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.68 (s), 138.30 (s), 135.84 (s), 132.04 (s), 131.60 (s), 130.91 (s), 129.85 (s), 127.89 (s), 122.42 (s), 83.64 (s), 52.15 (s), 24.71 (s).



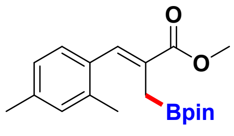
2e: 88%

Methyl(E)-3-(4-ethylphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2e): shallow yellow oil (88%, 58.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 3.81 (s, 3H), 2.67 (q, J = 7.6 Hz, 2H), 2.18 (s, 2H), 1.27 – 1.23 (m, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.23 (s), 144.39 (s), 137.66 (s), 133.57 (s), 129.52 (s), 129.29 (s), 127.83 (s), 83.41 (s), 51.96 (s), 28.69 (s), 24.69 (s), 15.43 (s).



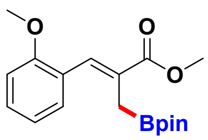
2f: 88%

Methyl(E)-3-(4-(tert-butyl)phenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2f): shallow yellow oil (88%, 63.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.41 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 3.81 (s, 3H), 2.19 (s, 2H), 1.35 (s, 9H), 1.25 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.25 (s), 151.23 (s), 137.56 (s), 133.34 (s), 129.32 (d, J = 7.0 Hz), 125.26 (s), 83.40 (s), 51.97 (s), 34.69 (s), 31.25 (s), 24.71 (s).



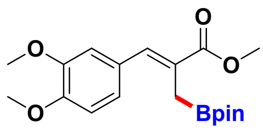
2g: 92%

Methyl(E)-3-(2,4-dimethylphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2g): shallow yellow oil (92%, 59.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.20 (d, J = 7.7 Hz, 1H), 7.05 – 7.00 (m, 2H), 3.82 (s, 3H), 2.34 (s, 3H), 2.28 (s, 3H), 2.00 (s, 2H), 1.25 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.05 (s), 137.82 (s), 137.11 (s), 136.87 (s), 132.53 (s), 130.77 (s), 130.11 (s), 128.74 (s), 126.18 (s), 83.36 (s), 51.93 (s), 24.67 (s), 21.17 (s), 19.88 (s).



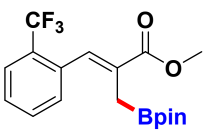
2h: 98%

Methyl(E)-3-(2-methoxyphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (h): shallow yellow oil (98%, 65.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.31 – 7.25 (m, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 8.3 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.07 (s, 2H), 1.24 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.98 (s), 157.47 (s), 133.74 (s), 130.02 (d, J = 5.0 Hz), 129.60 (s), 125.12 (s), 120.07 (s), 110.42 (s), 83.34 (s), 55.37 (s), 51.88 (s), 24.68 (s).



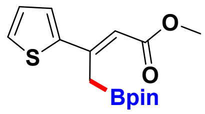
2i: 86%

Methyl(E)-3-(3,4-dimethoxyphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2i): shallow yellow oil (86%, 62.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.03 – 6.99 (m, 2H), 6.88 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.80 (s, 3H), 2.19 (s, 2H), 1.24 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.26 (s), 148.98 (s), 148.54 (s), 137.54 (s), 128.95 (s), 128.31 (s), 122.74 (s), 112.48 (s), 110.85 (s), 83.45 (s), 55.85 (d, J = 6.9 Hz), 51.99 (s), 24.70 (s).



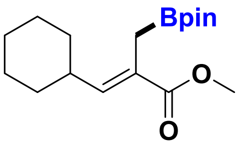
2j: 94%

Methyl(E)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-(2-(trifluoromethyl)phenyl)acrylate (2j): shallow yellow oil (94%, 69.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 3.81 (s, 3H), 1.90 (s, 2H), 1.24 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.25 (s), 135.06 (d, J = 1.8 Hz), 134.11 (s), 132.82 (s), 131.44 (s), 130.54 (s), 128.62 (q, J = 30.1 Hz), 127.77 (s), 125.82 (q, J = 5.3 Hz), 123.94 (q, J = 273.8 Hz), 83.48 (s), 52.06 (s), 24.61 (s).



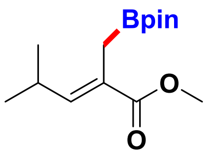
2k: 98%

Methyl(E)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(thiophen-2-yl)but-2-enoate (2k): shallow yellow oil (98%, 63.4 mg); [1]H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 3.81 (s, 3H), 2.67 (q, J = 7.6 Hz, 2H), 2.18 (s, 2H), 1.27 – 1.23 (m, 15H). [13]C NMR (126 MHz, $CDCl_3$) δ 168.96 (s), 139.24 (s), 131.35 (s), 130.14 (s), 128.23 (s), 127.20 (s), 126.74 (s), 83.51 (s), 52.05 (s), 24.70 (s).



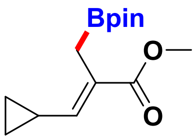
2m: 75%

Methyl(E)-3-cyclohexyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate (2m): shallow yellow oil (75%, 46.2 mg); [1]H NMR (500 MHz, $CDCl_3$) δ 6.56 (d, J = 9.6 Hz, 1H), 3.70 (s, 3H), 2.24 (dddd, J = 14.5, 11.0, 7.3, 3.7 Hz, 1H), 1.86 (s, 2H), 1.75 – 1.70 (m, 2H), 1.69 – 1.64 (m, 2H), 1.34 – 1.14 (m, 19H). [13]C NMR (126 MHz, $CDCl_3$) δ 168.98 (s), 146.14 (s), 127.06 (s), 83.27 (s), 51.64 (s), 37.99 (s), 31.87 (s), 25.89 (s), 25.62 (s), 24.67 (s).



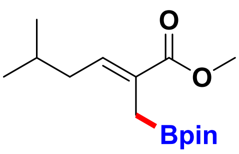
2n: 87%

Methyl(E)-4-methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pent-2-enoate (2n): shallow yellow oil (87%, 46.6 mg); [1]H NMR (500 MHz, $CDCl_3$) δ 6.54 (d, J = 9.7 Hz, 1H), 3.70 (s, 3H), 2.57 (ddt, J = 13.3, 9.7, 6.6 Hz, 1H), 1.85 (s, 2H), 1.22 (s, 12H), 1.02 (s, 3H), 1.01 (s, 3H). [13]C NMR (126 MHz, $CDCl_3$) δ 168.85 (s), 147.50 (s), 126.84 (s), 83.24 (s), 51.60 (s), 28.15 (s), 24.65 (s), 21.97 (s).



2o: 95%

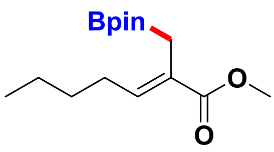
Methyl(E)-3-cyclopropyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2o): shallow yellow oil (95%, 50.5 mg); [1]H NMR (500 MHz, $CDCl_3$) δ 6.09 (d, J = 10.5 Hz, 1H), 3.67 (s, 3H), 1.94 (s, 2H), 1.60 – 1.50 (m, 1H), 1.22 (s, 12H), 0.92 – 0.87 (m, 2H), 0.59 – 0.54 (m, 2H). [13]C NMR (126 MHz, $CDCl_3$) δ 168.42 (s), 146.04 (s), 126.39 (s), 83.20 (s), 51.50 (s), 24.66 (s), 11.74 (s), 8.33 (s).



2p: 99%

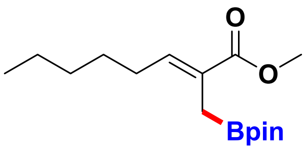
Methyl(E)-5-methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)hex-2-enoate (2p): shallow yellow oil (99%, 55.8 mg); [1]H NMR (500 MHz, $CDCl_3$) δ 6.74 (t, J = 7.5 Hz, 1H), 3.70 (s, 3H), 2.03 (t, J = 7.2 Hz, 2H), 1.83 (s, 2H), 1.73 (dp, J = 13.3, 6.7 Hz, 1H), 1.21 (d, J = 0.6 Hz, 12H), 0.91

(d, J = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.58 (s), 139.99 (s), 129.47 (s), 83.18 (s), 51.56 (s), 37.93 (s), 28.27 (s), 24.65 (s), 22.50 (s).



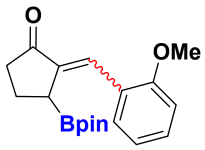
2q: 89%

Methyl(E)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)hept-2-enoate (2q): shallow yellow oil (89%, 50.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (t, J = 7.4 Hz, 1H), 3.71 (s, 3H), 2.15 (q, J = 7.4 Hz, 2H), 1.85 (s, 2H), 1.45 – 1.39 (m, 2H), 1.34 (dd, J = 15.1, 7.2 Hz, 2H), 1.23 (s, 12H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.65 (s), 141.24 (s), 128.88 (s), 83.24 (s), 51.59 (s), 30.72 (s), 28.56 (s), 24.67 (s), 22.41 (s), 13.89 (s).



2r: 97%

Methyl(E)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)oct-2-enoate (2r): shallow yellow oil (97%, 57.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (t, J = 7.4 Hz, 1H), 3.70 (s, 3H), 2.14 (q, J = 7.4 Hz, 2H), 1.84 (s, 2H), 1.47 – 1.40 (m, 2H), 1.32 – 1.28 (m, 4H), 1.22 (s, 13H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.70 (s), 141.37 (s), 128.86 (s), 83.27 (s), 51.64 (s), 31.55 (s), 28.86 (s), 28.30 (s), 24.69 (s), 22.53 (s), 14.02 (s).



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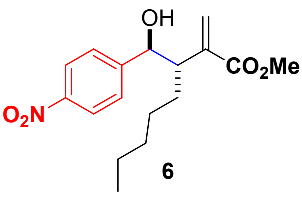
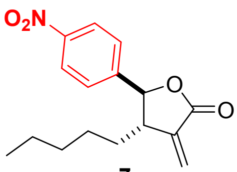
2-(2-methoxybenzylidene)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentan-1-one (4): shallow yellow oil (83%, 54.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (ddd, J = 22.7, 7.6, 1.4 Hz, 1H), 7.20 – 7.14 (m, 1H), 6.91 (tt, J = 7.6, 3.8 Hz, 1H), 6.77 (t, J = 7.9 Hz, 1H), 5.29 (dd, J = 161.0, 5.6 Hz, 1H), 3.76 (d, J = 11.2 Hz, 3H), 2.71 (ddd, J = 19.6, 11.4, 5.6 Hz, 1H), 2.39 – 2.13 (m, 2H), 1.79 – 1.43 (m, 2H), 0.95 (dd, J = 22.7, 9.7 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.31 (s), 131.19 (s), 129.78 (s), 128.49 (s), 128.24 (s), 127.96 (s), 126.77 (s), 120.78 (s), 120.50 (s), 110.34 (s), 109.84 (s), 83.24 (s), 68.98 (s), 57.11 (s), 55.07 (s), 39.30 (s), 24.55 (s).

Methyl -3-(hydroxy(4-nitrophenyl)methyl)-2-methyleneoctanoate (6): shallow yellow oil (90%, 57.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, J = 8.7 Hz, 1H), 8.18 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.7 Hz, 1H), 6.40 (d, J = 2.1 Hz, 1H), 6.30 (s, 1H), 5.49 (s, 1H), 4.98 (d, J = 4.0 Hz, 1H), 3.80 (s, 3H), 2.94 (dt, J = 10.9, 4.0 Hz, 1H), 1.60 – 1.43 (m, 2H), 1.24 – 1.09 (m, 6H), 0.82 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.56 (s), 150.21 (s), 147.08 (s), 139.88 (s), 127.83 (s), 127.26 (s), 123.21 (s), 75.43 (s), 52.37 (s), 49.63 (s), 31.64 (s), 26.99 (s), 26.58 (s), 22.43 (s), 13.96 (s).



6
90% yield
dr =10:1



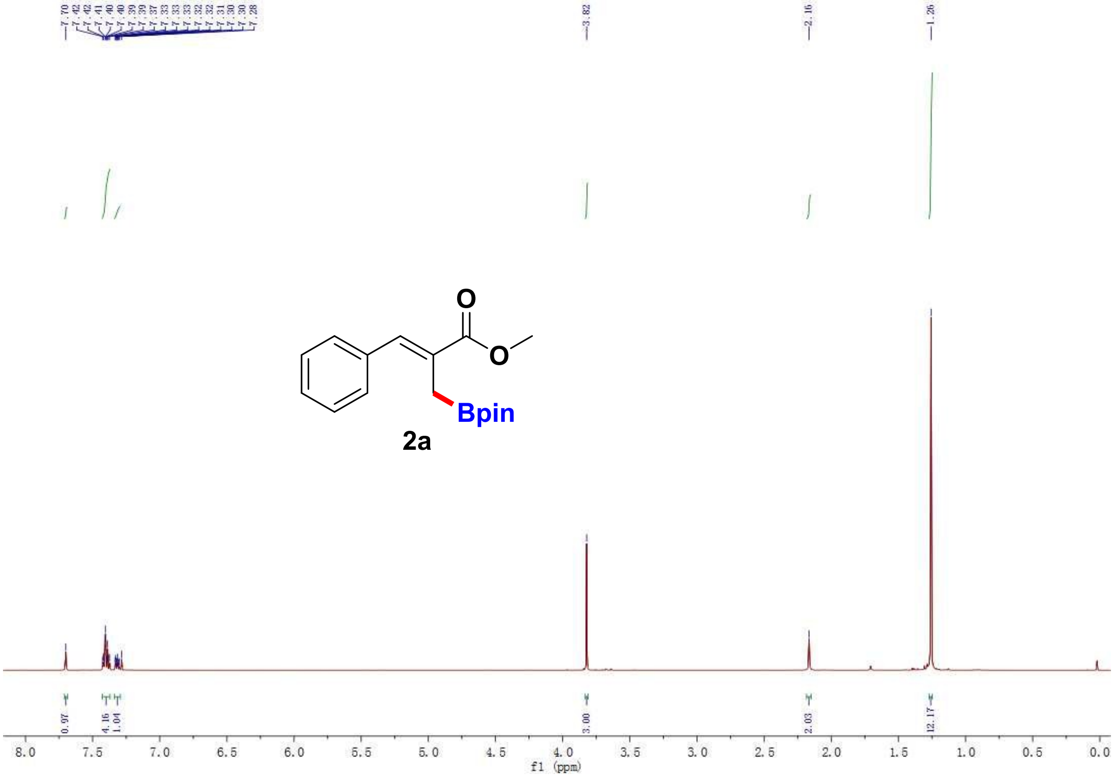
7
82% yield
dr =10:1

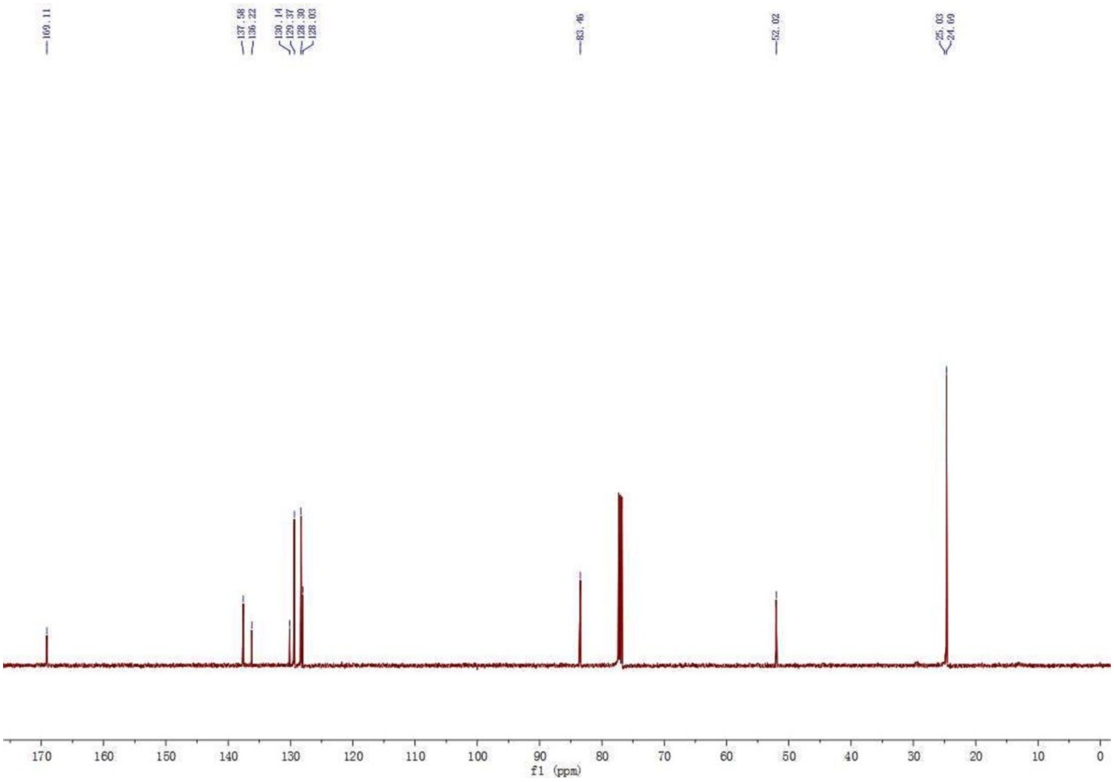
3-methylene-5-(4-nitrophenyl)-4-pentyldihydrofuran-2(3H)-one (7): shallow yellow oil (82%, 44.0 mg); ^{1}H NMR

(500 MHz, $CDCl_3$) δ 8.27 (d, J = 8.7 Hz, 1H), 8.18 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.7 Hz, 1H), 6.40 (d, J = 2.1 Hz, 1H), 6.30 (s, 1H), 5.49 (s, 1H), 4.98 (d, J = 4.0 Hz, 1H), 2.94 (dt, J = 10.9, 4.0 Hz, 1H), 1.60 – 1.43 (m, 2H), 1.24 – 1.09 (m, 6H), 0.82 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.56 (s), 150.21 (s), 147.08 (s), 139.88 (s), 127.83 (s), 127.26 (s), 123.21 (s), 75.43 (s), 52.37 (s), 49.63 (s), 31.64 (s), 26.99 (s), 26.58 (s), 22.43 (s), 13.96 (s).

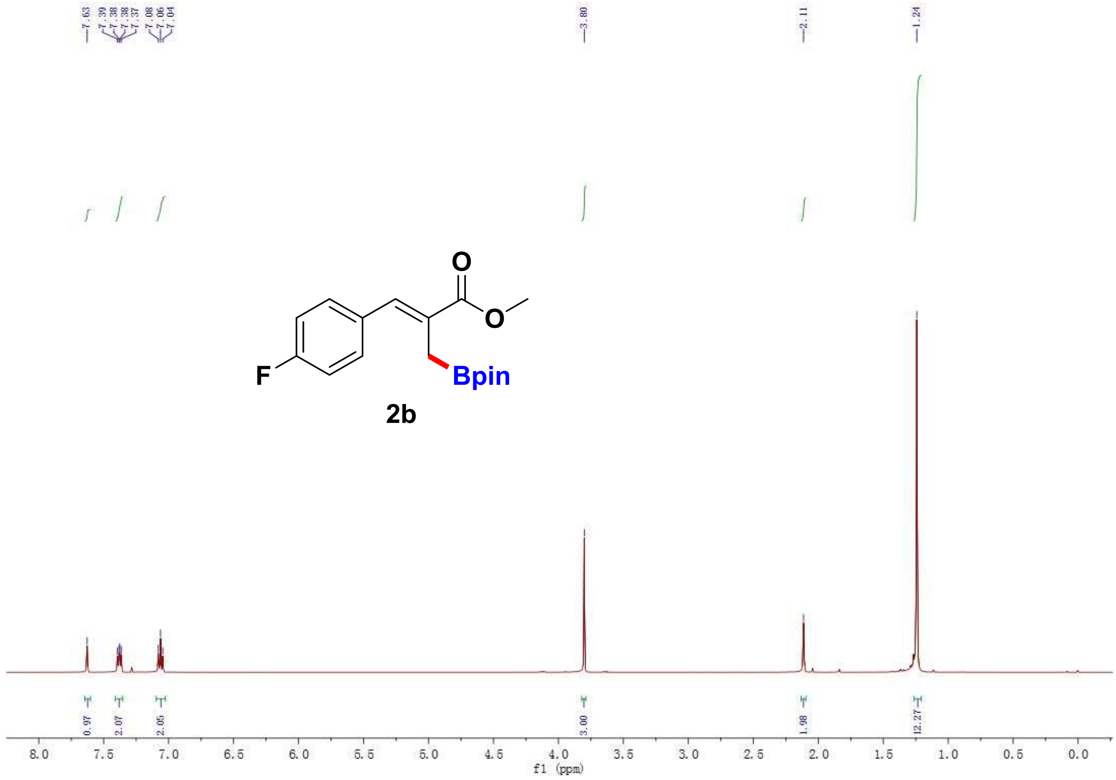
III. ^{1}H and ^{13}C NMR spectra of products

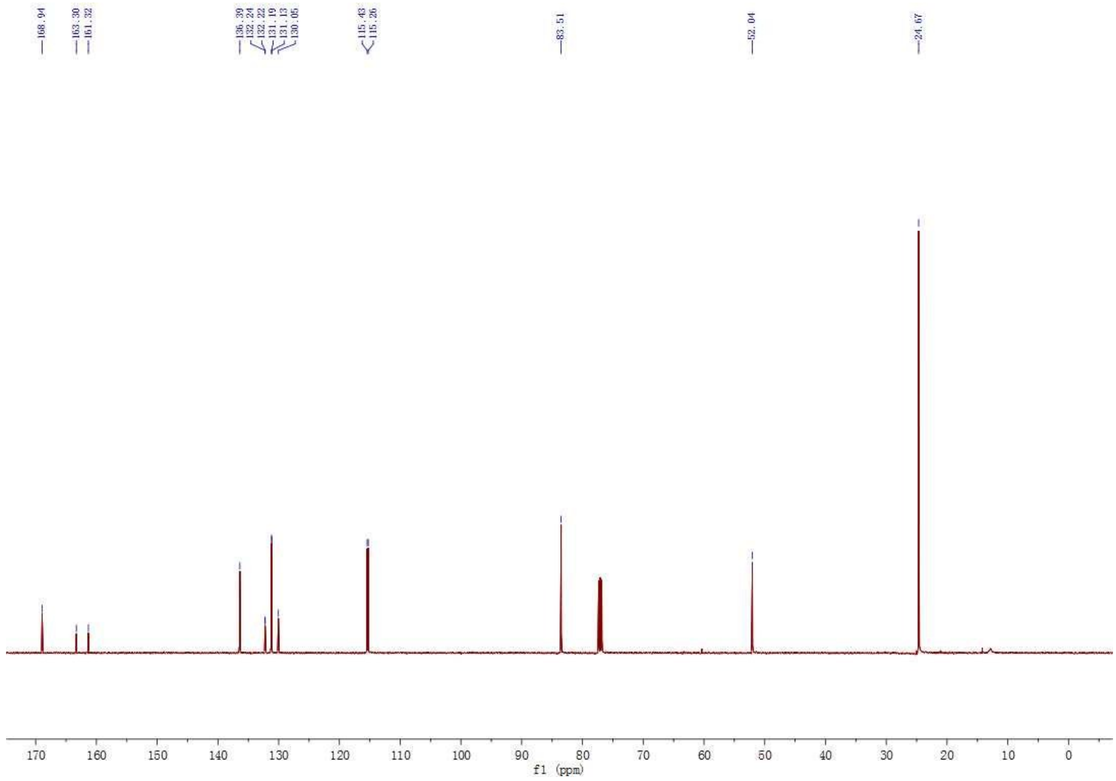
^{1}H NMR and ^{13}C NMR of **2a**



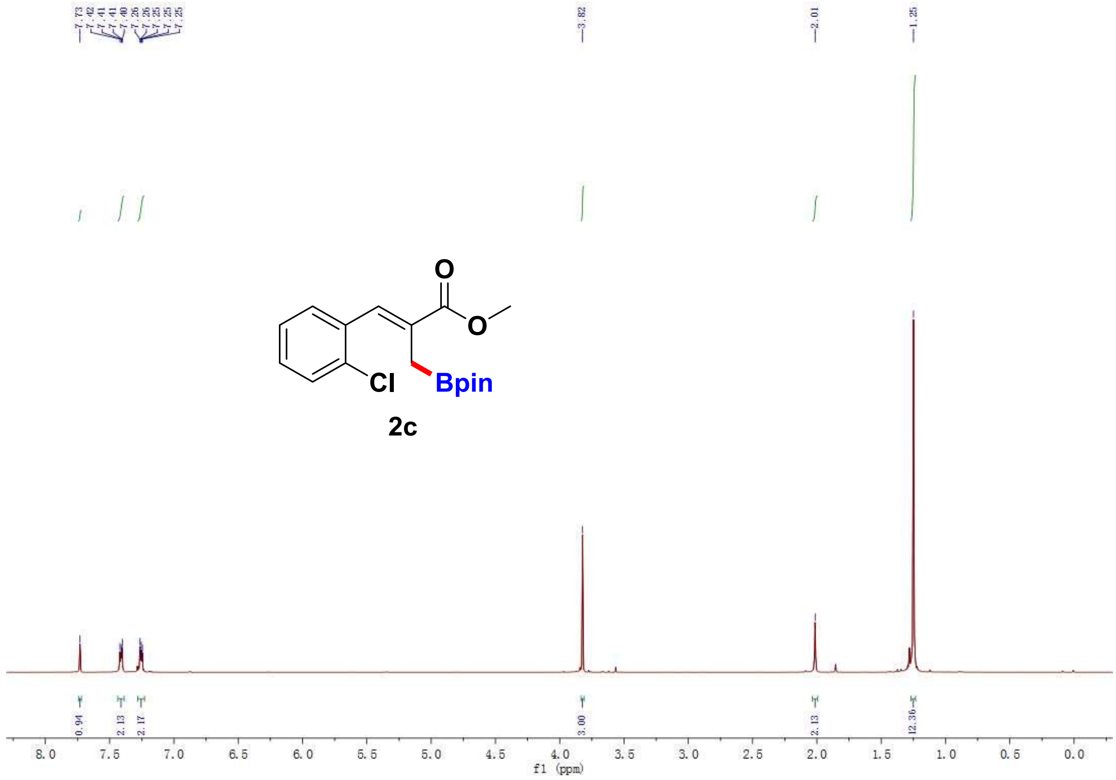


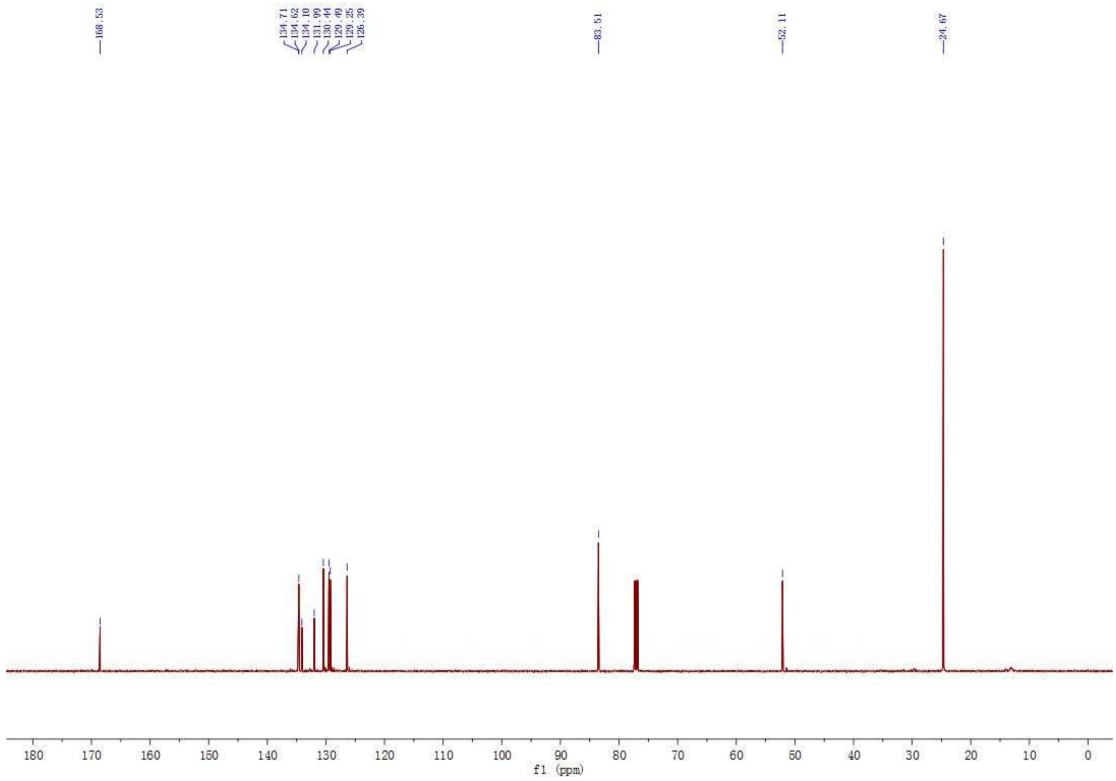
^{1}H NMR and ^{13}C NMR of **2b**



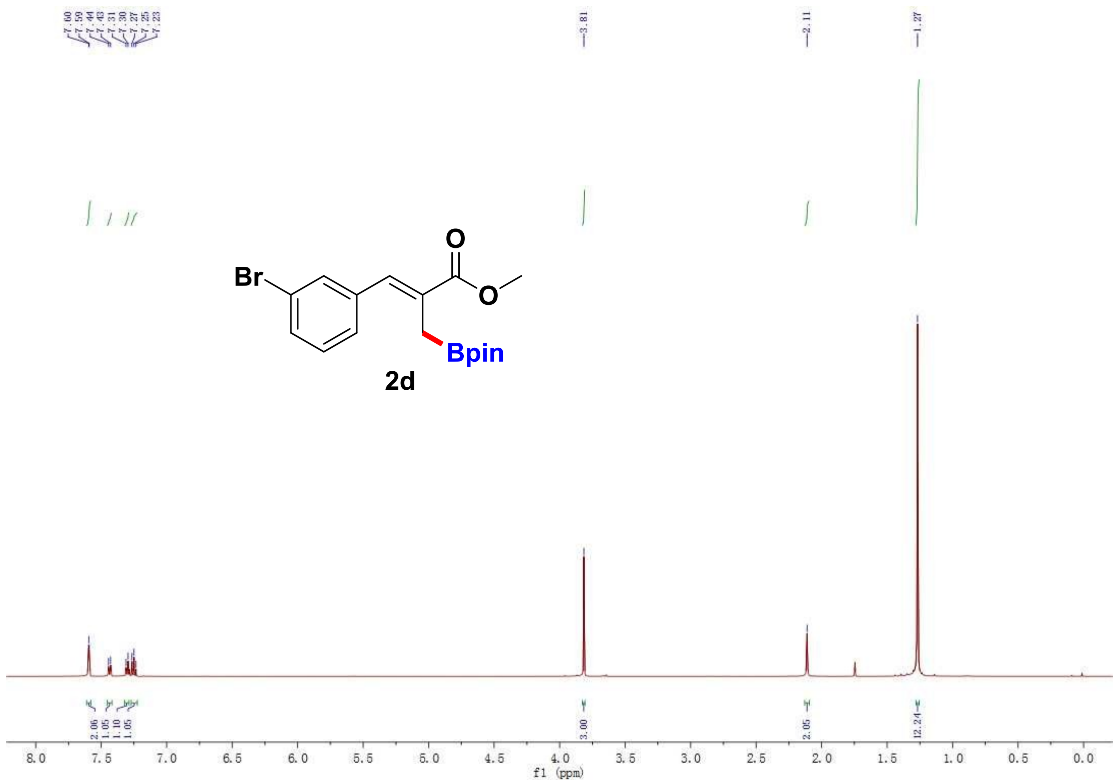


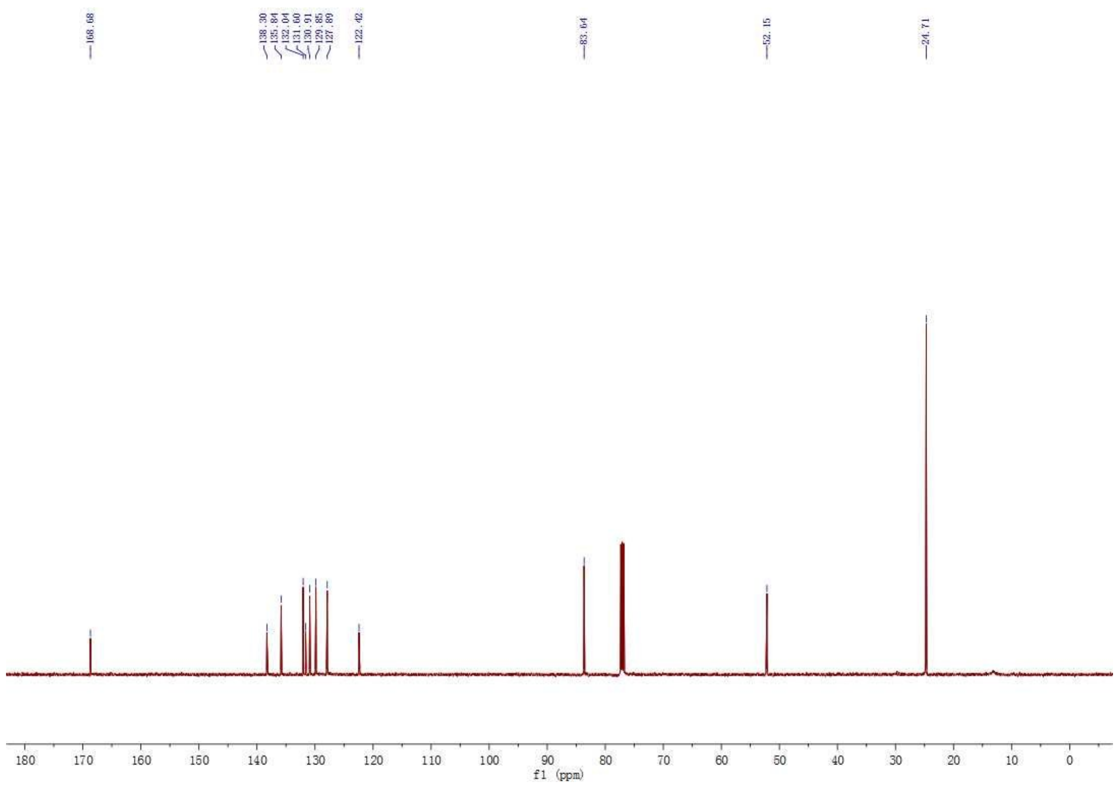
^{1}H NMR and ^{13}C NMR of **2c**



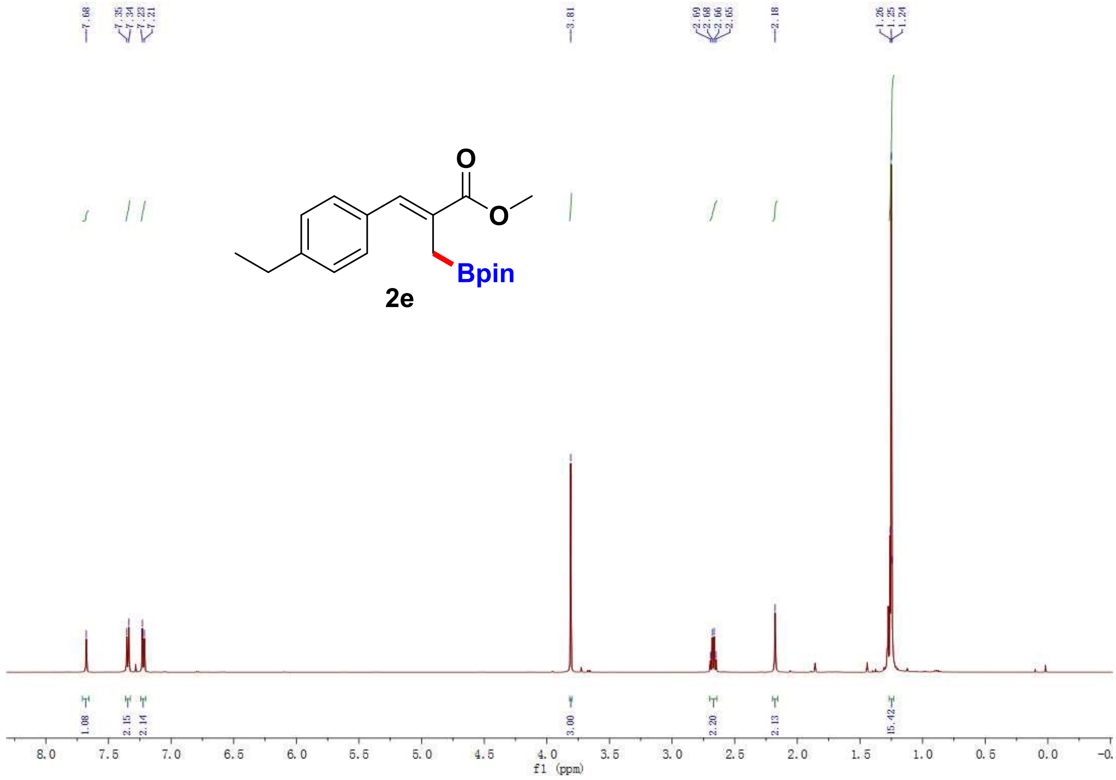


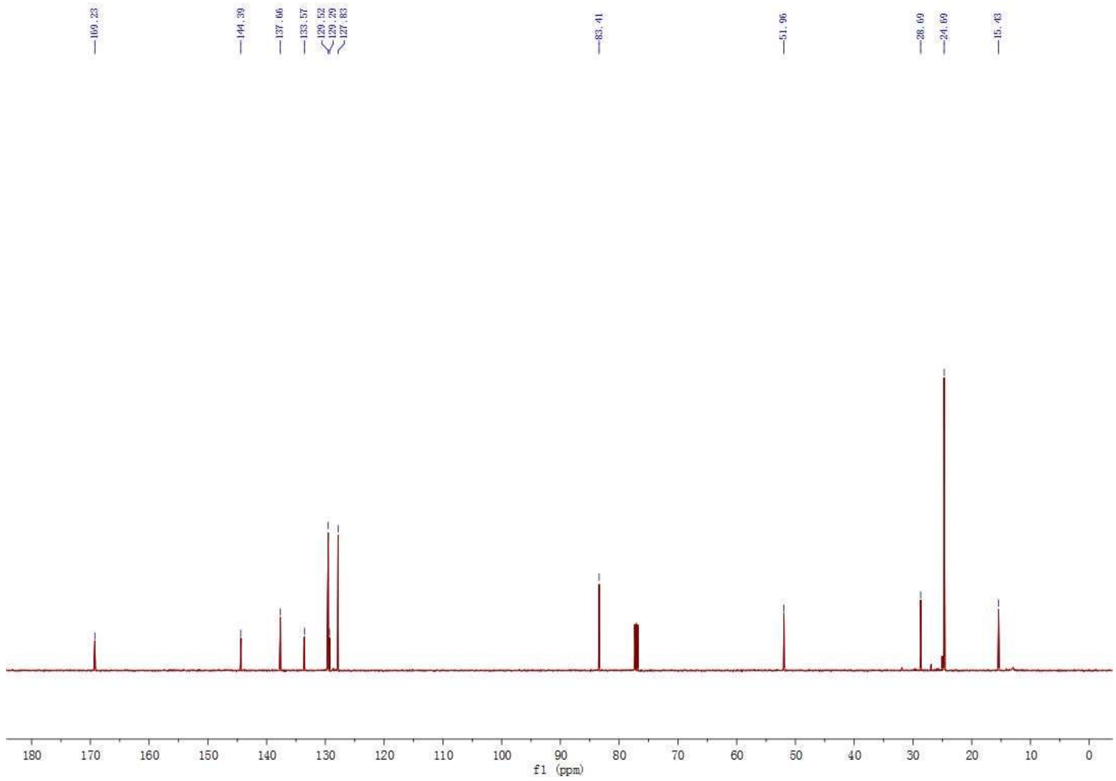
^{1}H NMR and ^{13}C NMR of **2d**



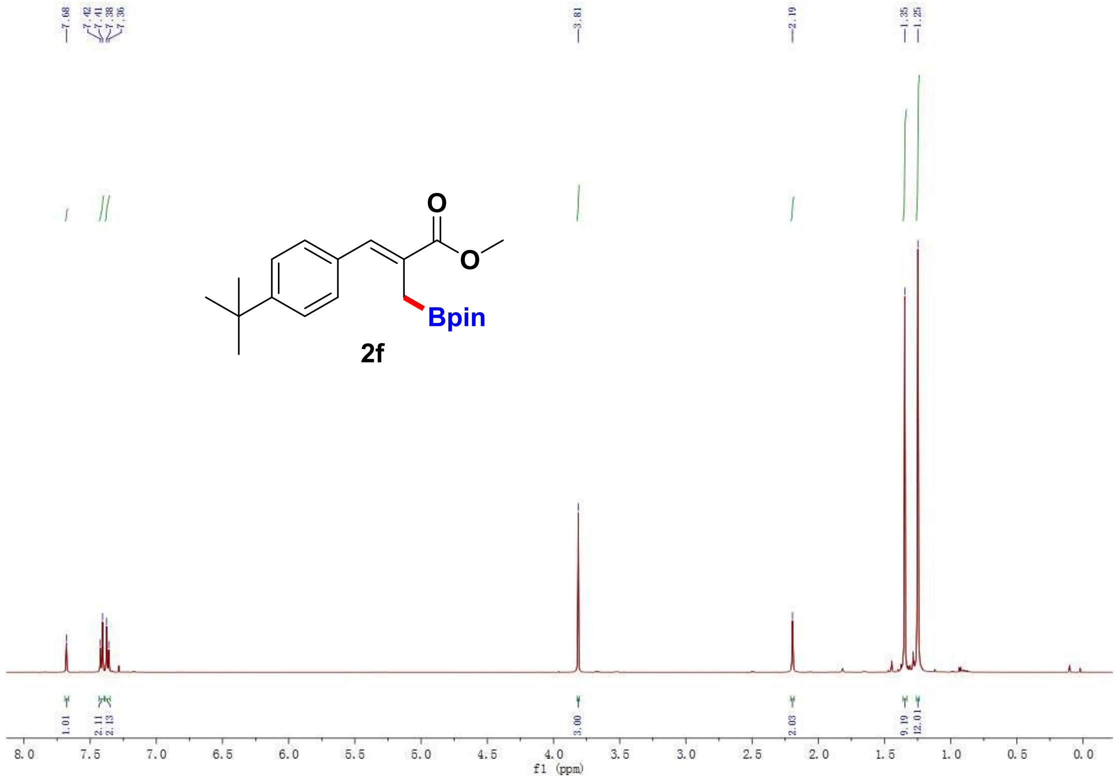


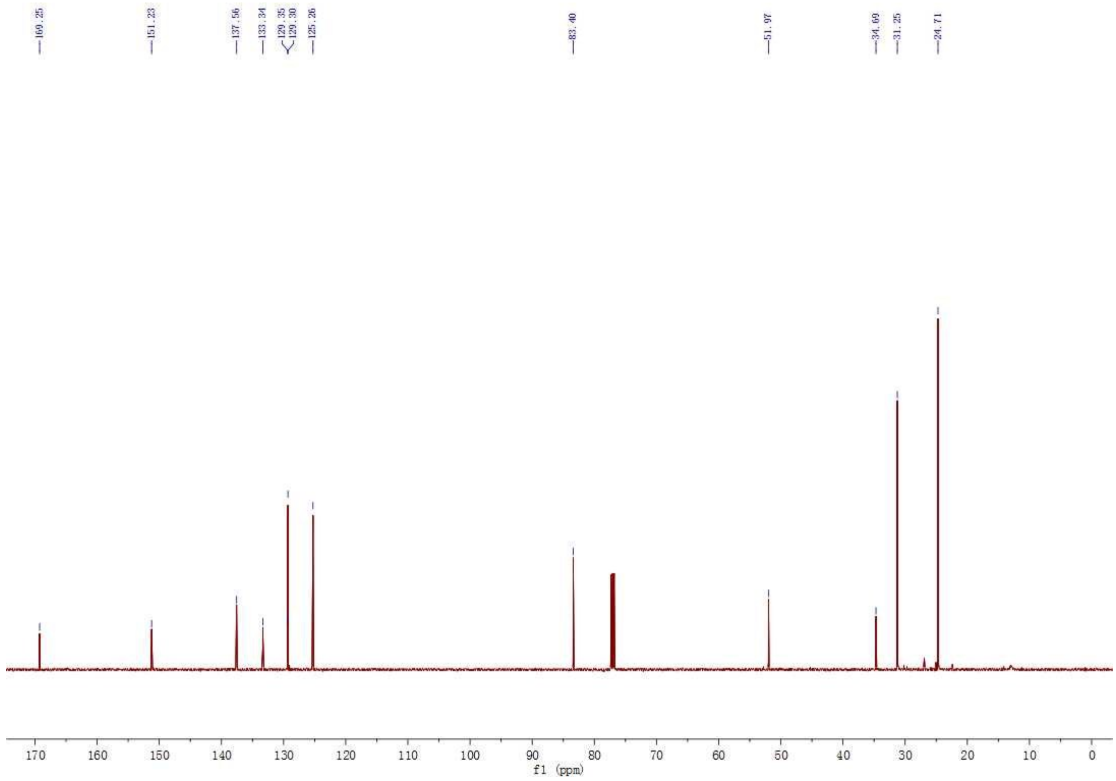
[1]H NMR and [13]C NMR of **2e**



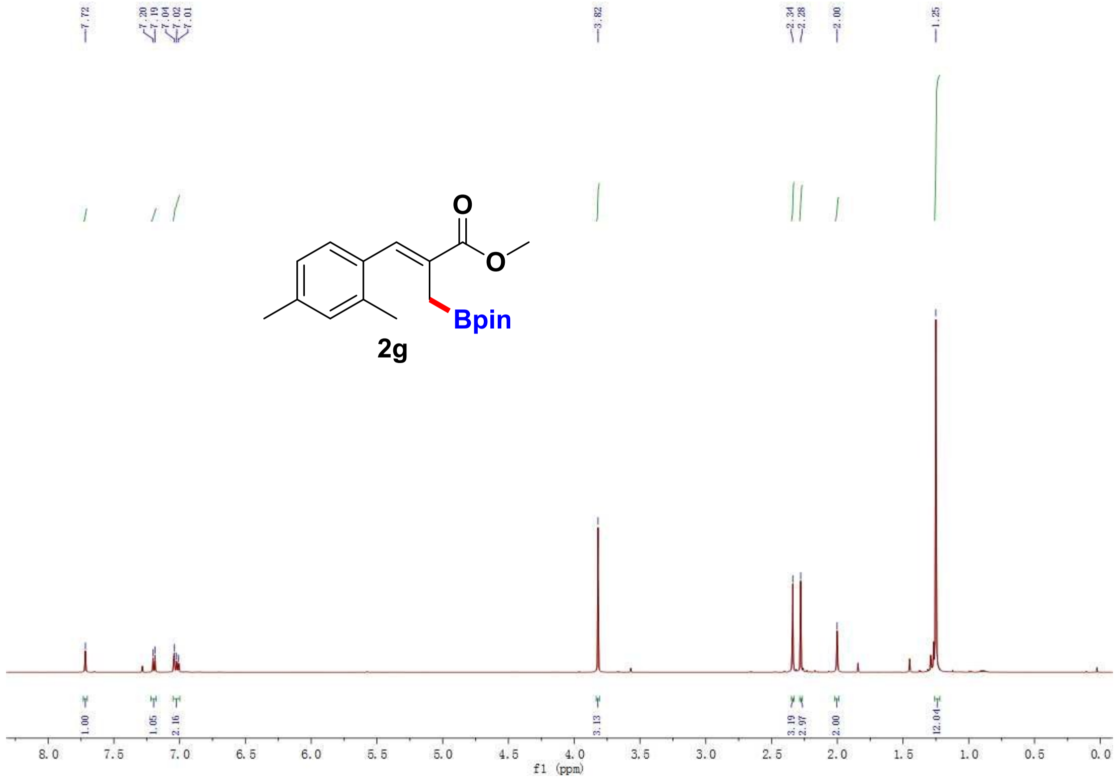


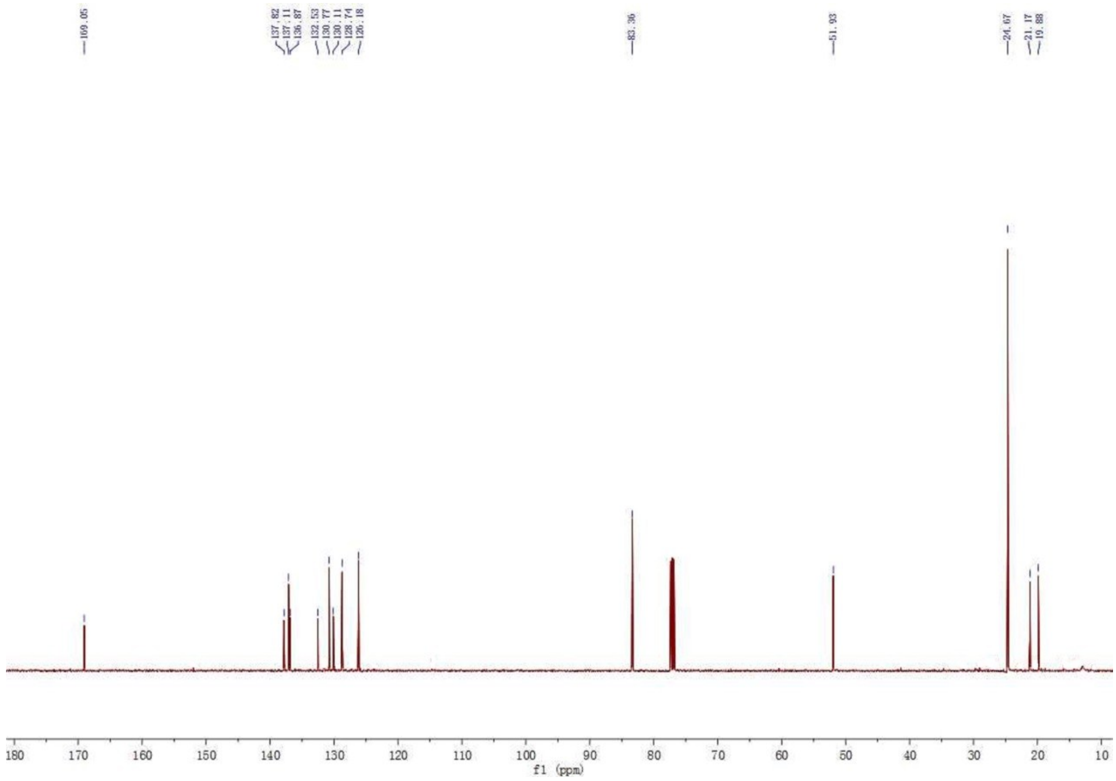
^{1}H NMR and ^{13}C NMR of **2f**



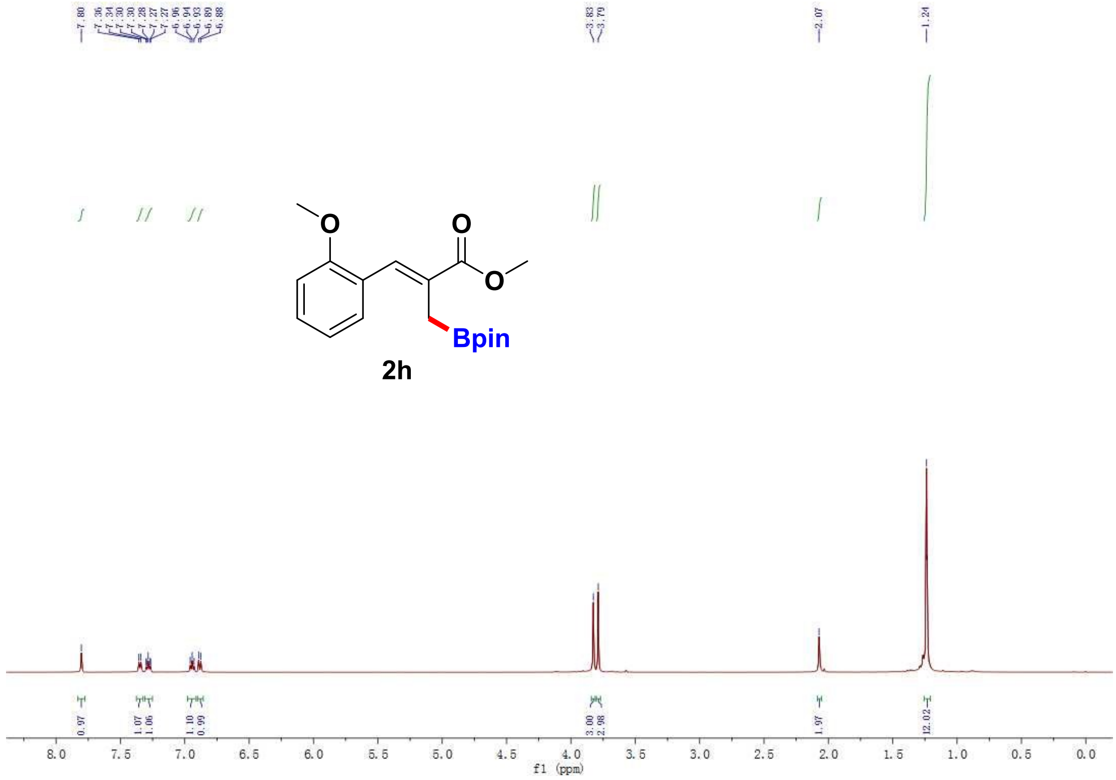


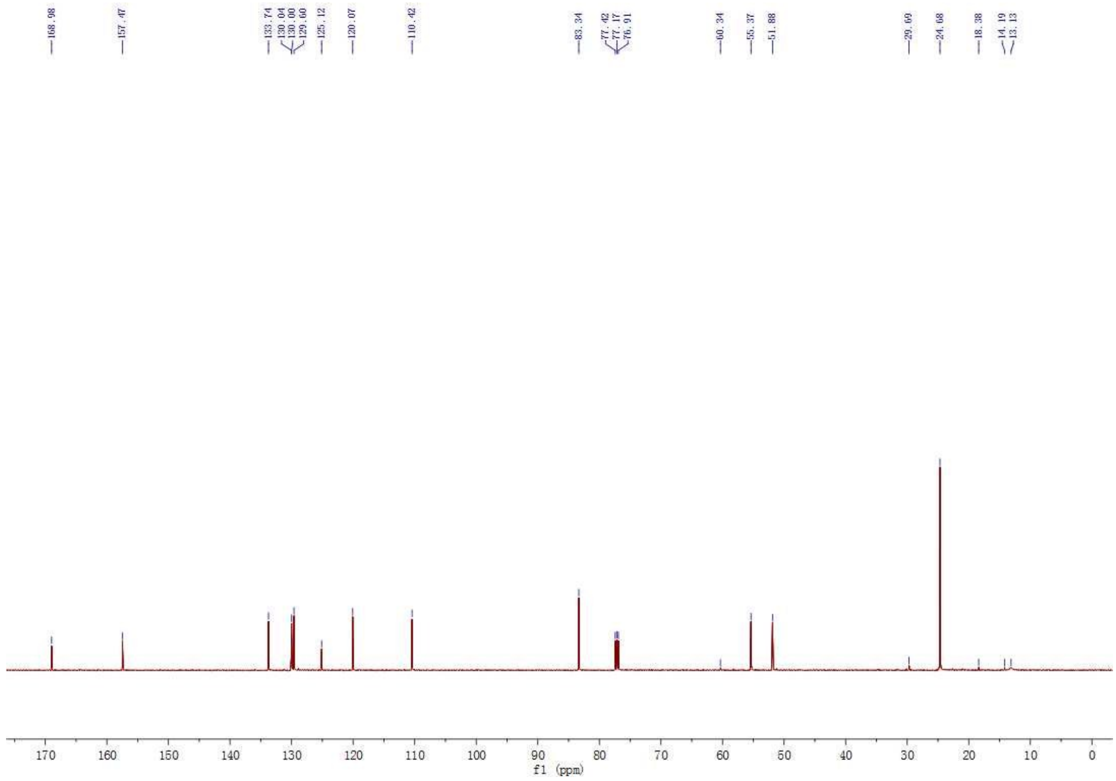
[1]H NMR and [13]C NMR of **2g**



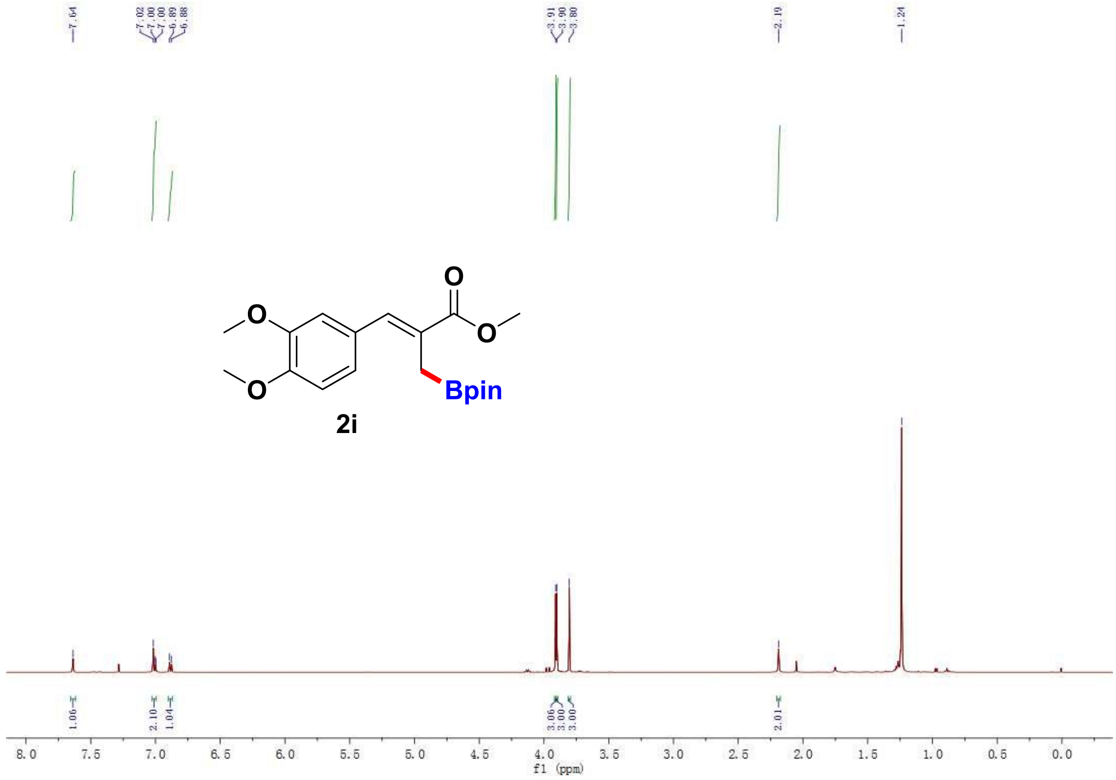


[1]H NMR and [13]C NMR of **2h**

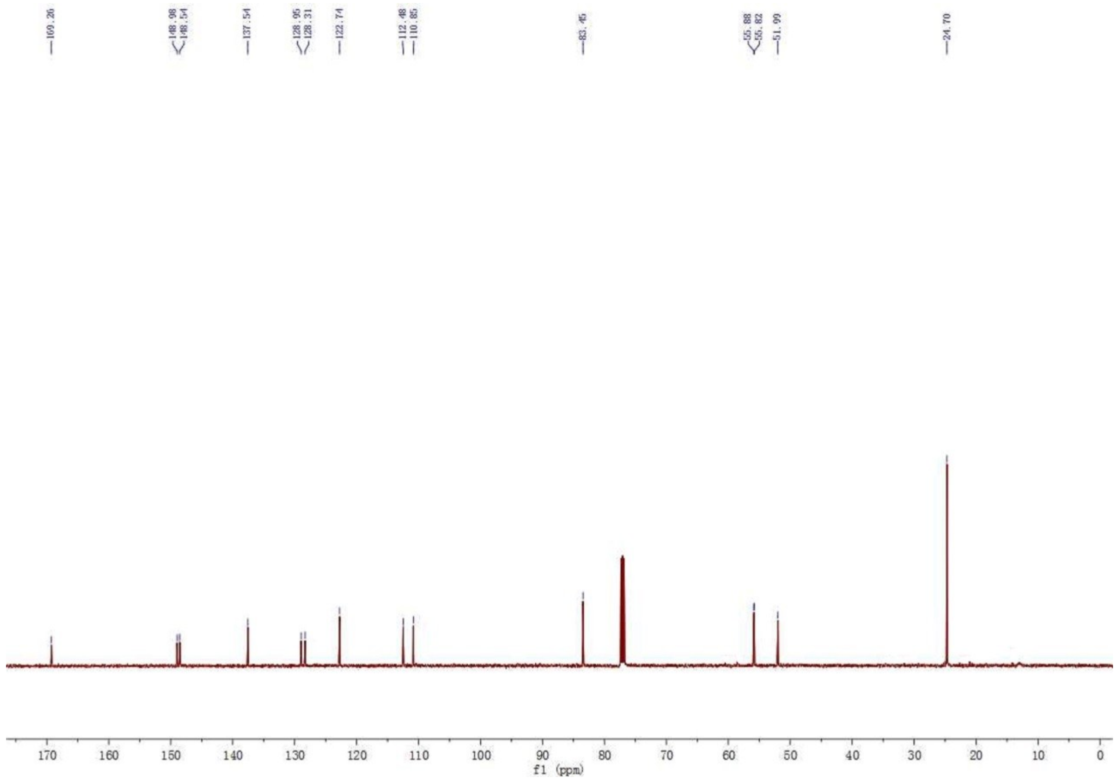




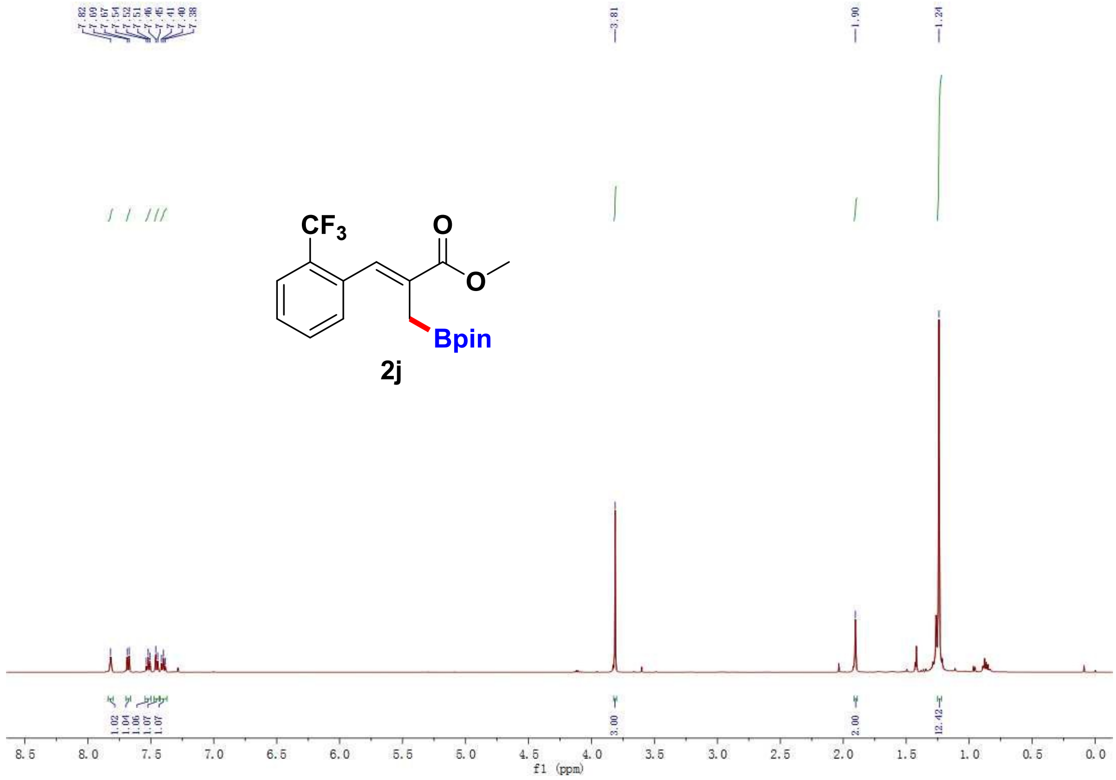
^{1}H NMR and ^{13}C NMR of **2i**

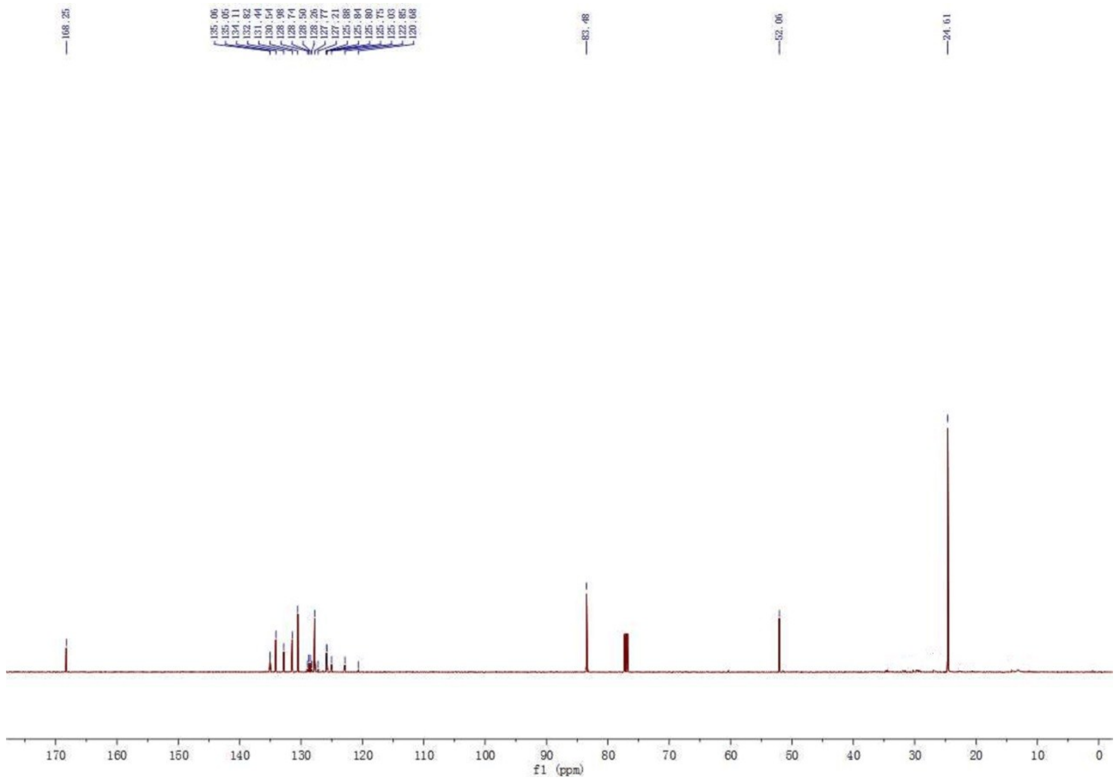


2i

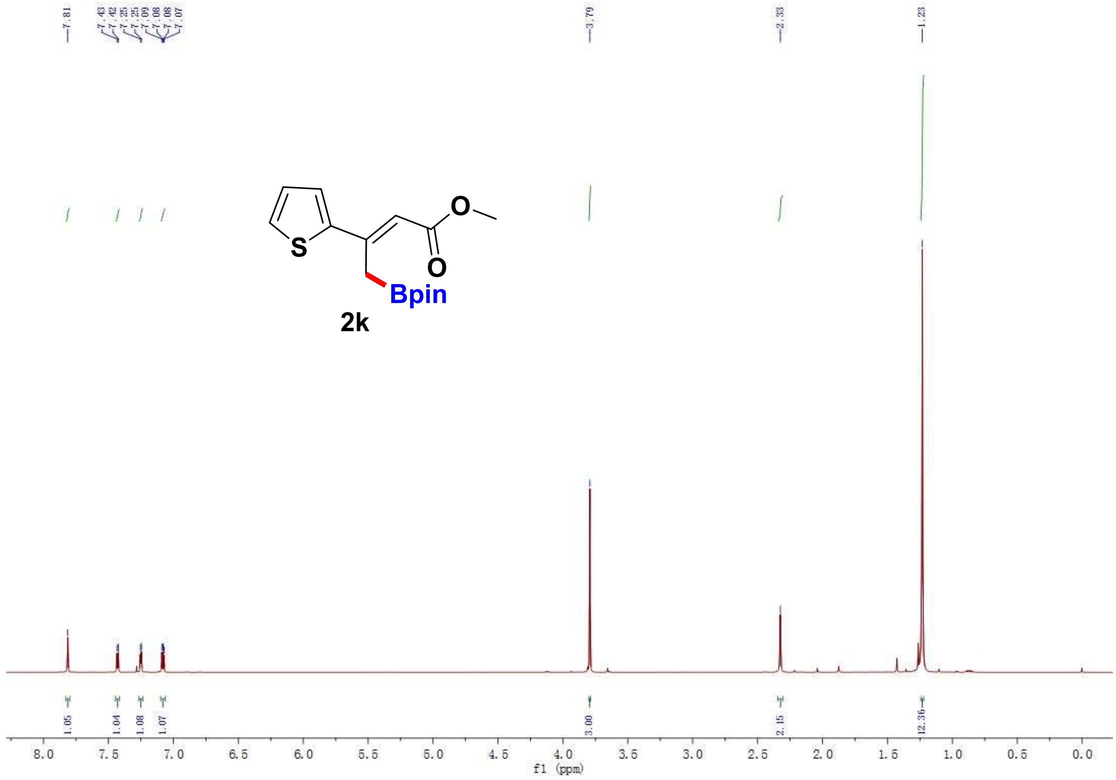


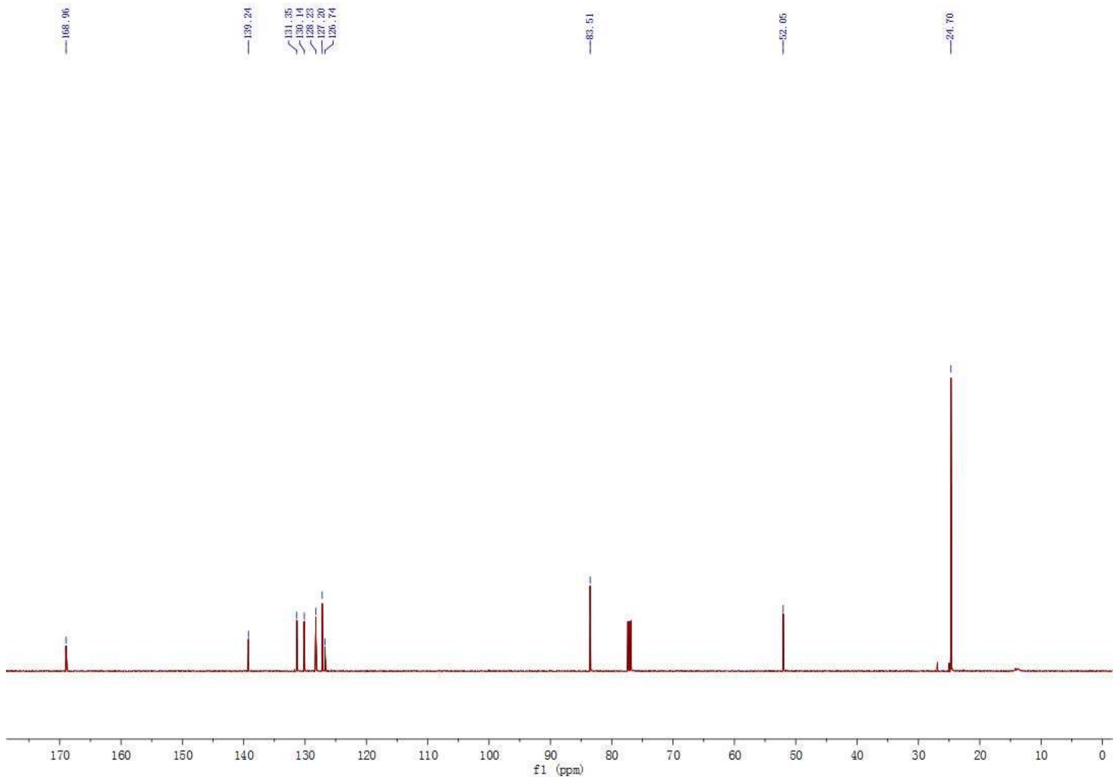
^{1}H NMR and ^{13}C NMR of **2j**



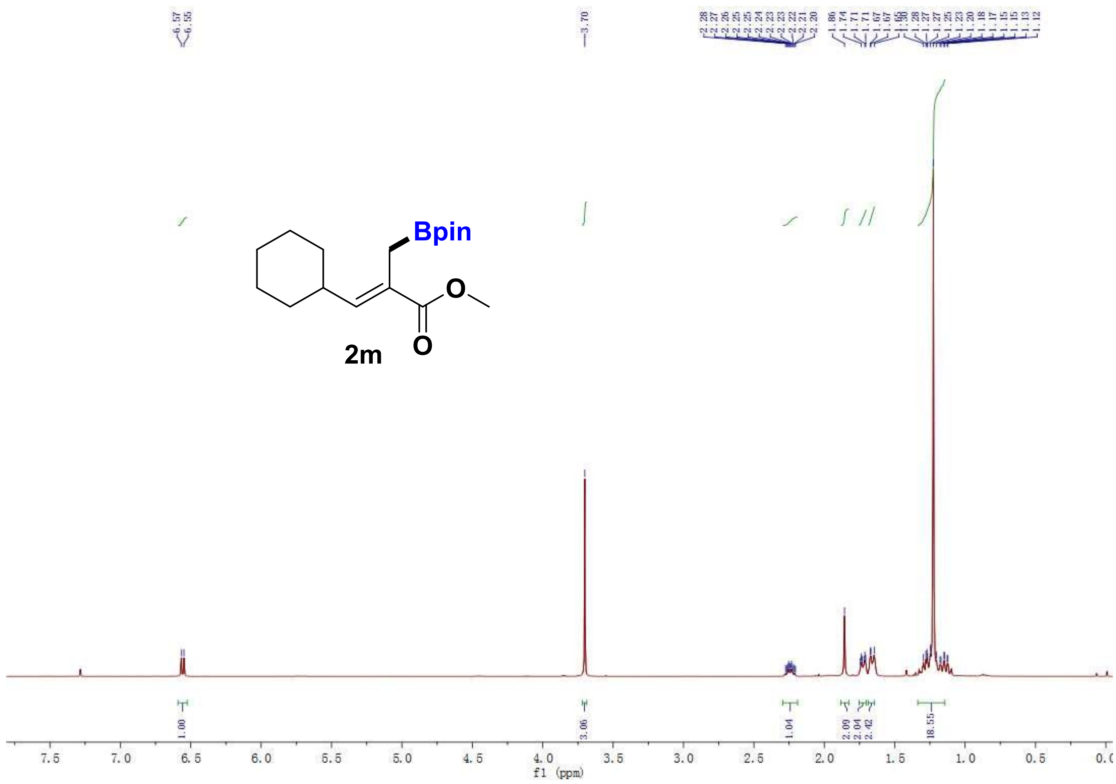


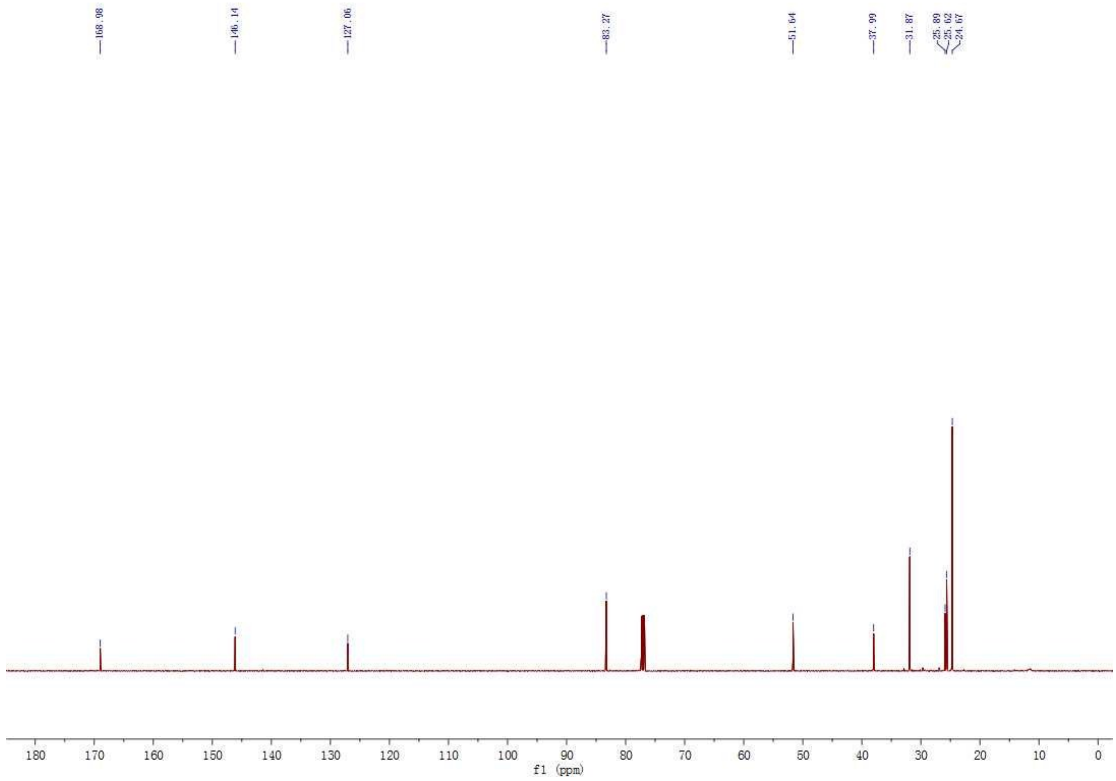
[1]H NMR and [13]C NMR of **2k**



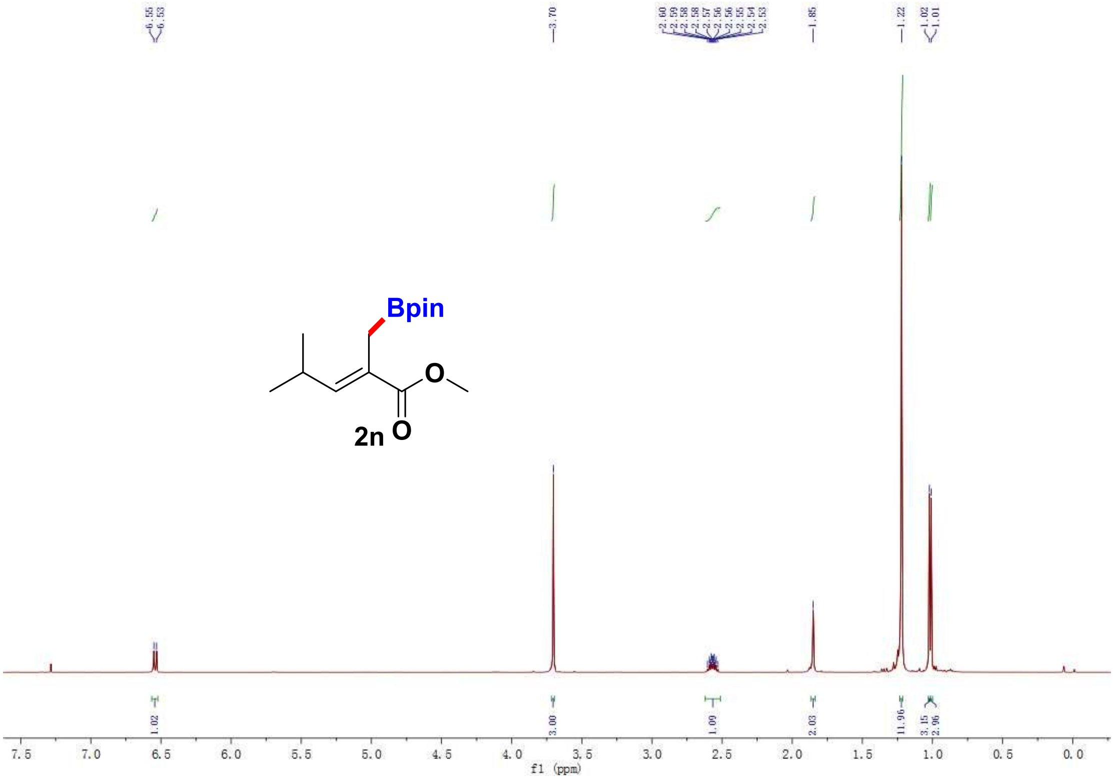


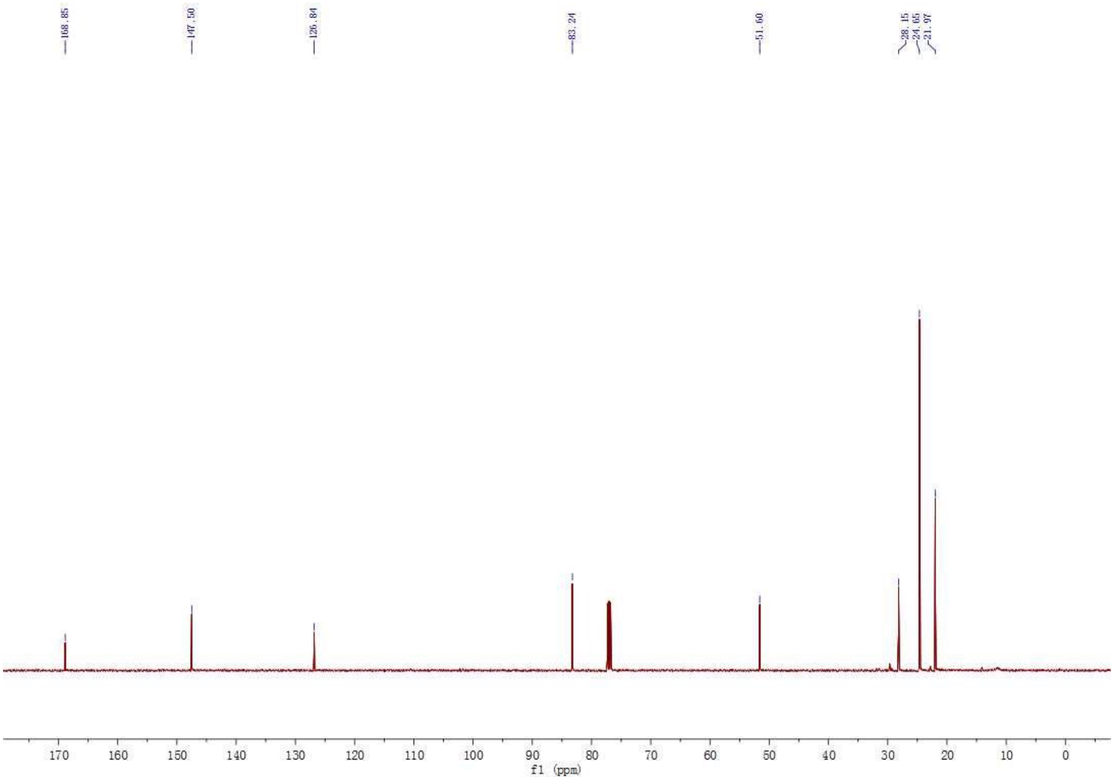
^{1}H NMR and ^{13}C NMR of **2m**



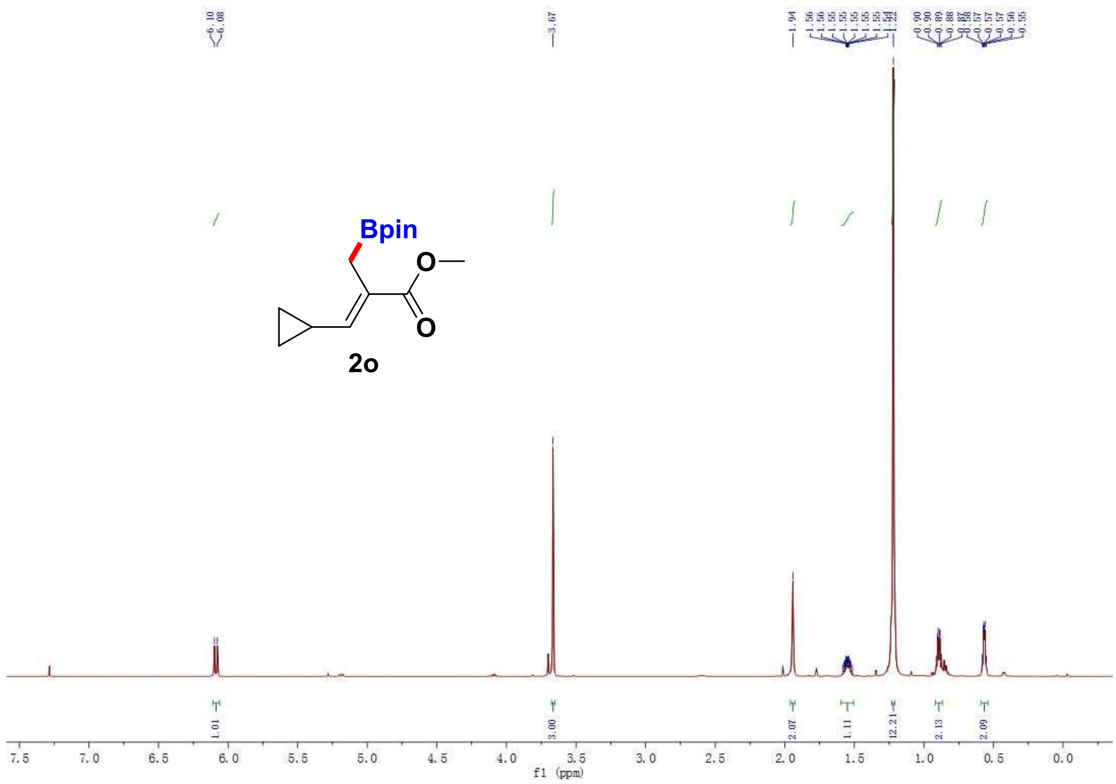


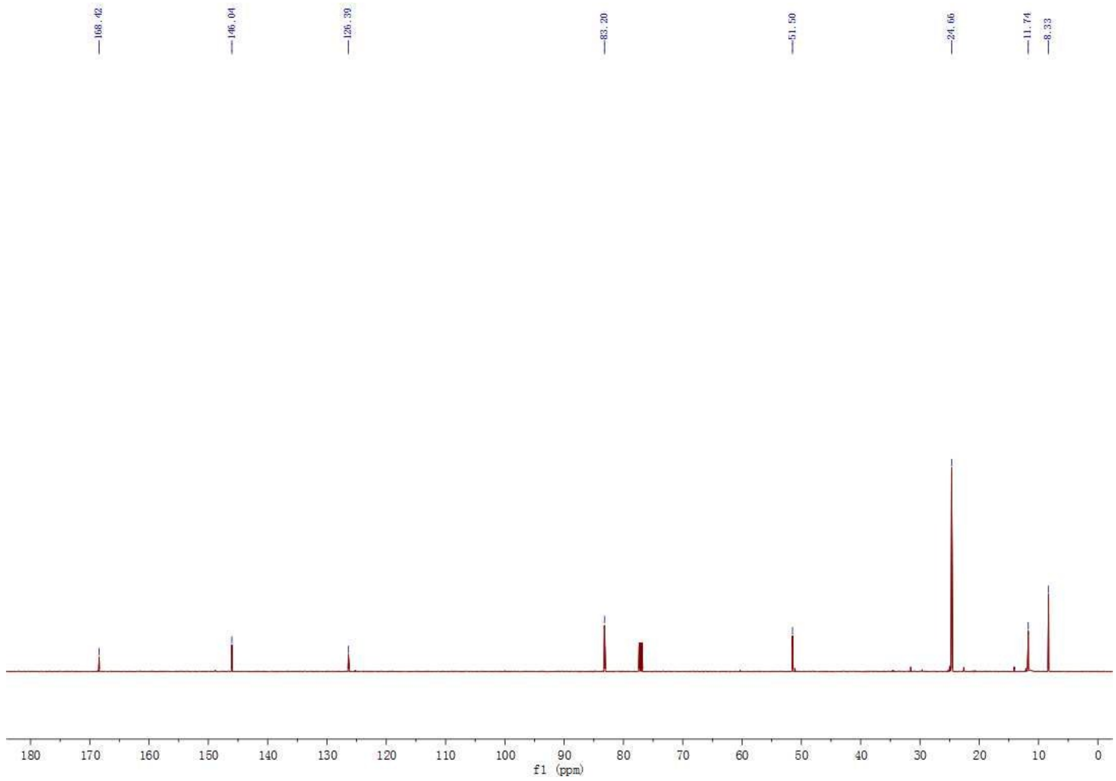
[1]H NMR and [13]C NMR of **2mn**



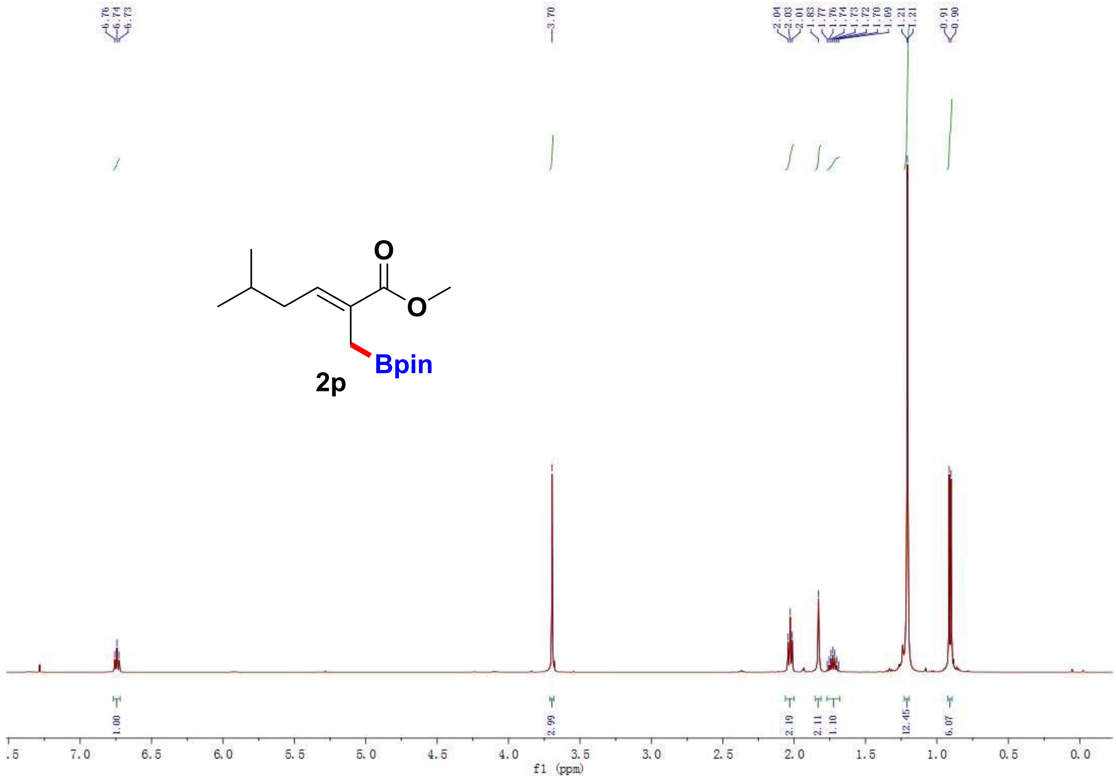


^1H NMR and ^{13}C NMR of **2o**

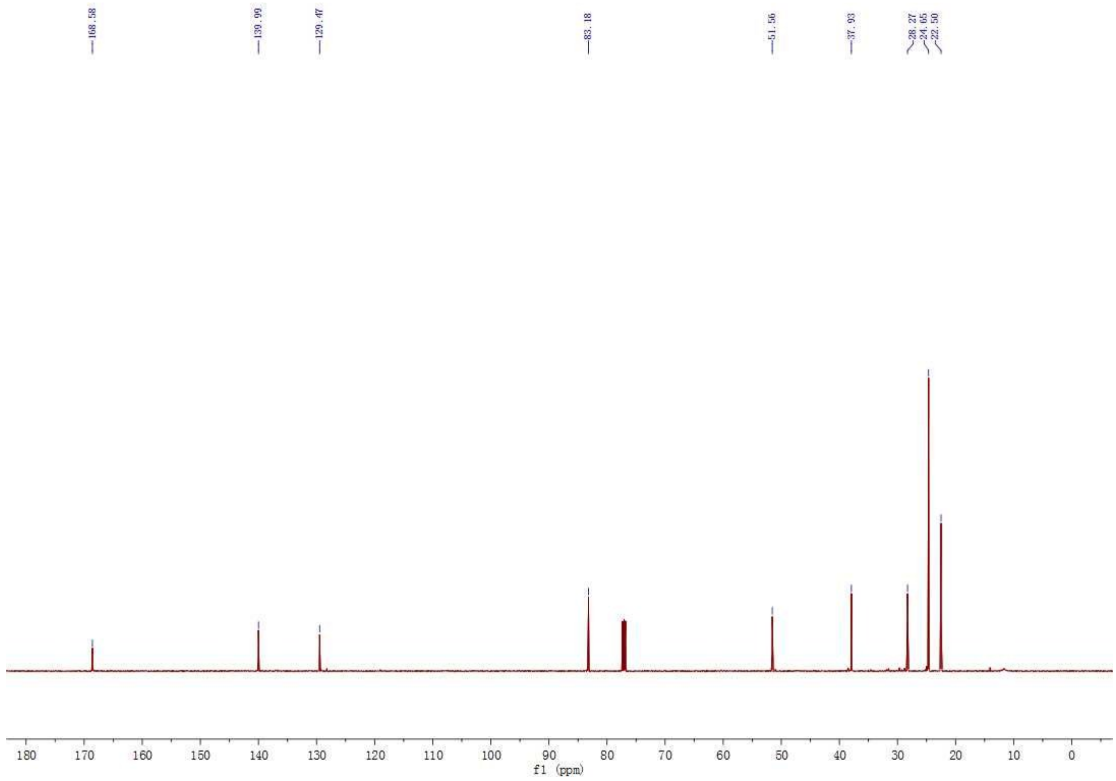




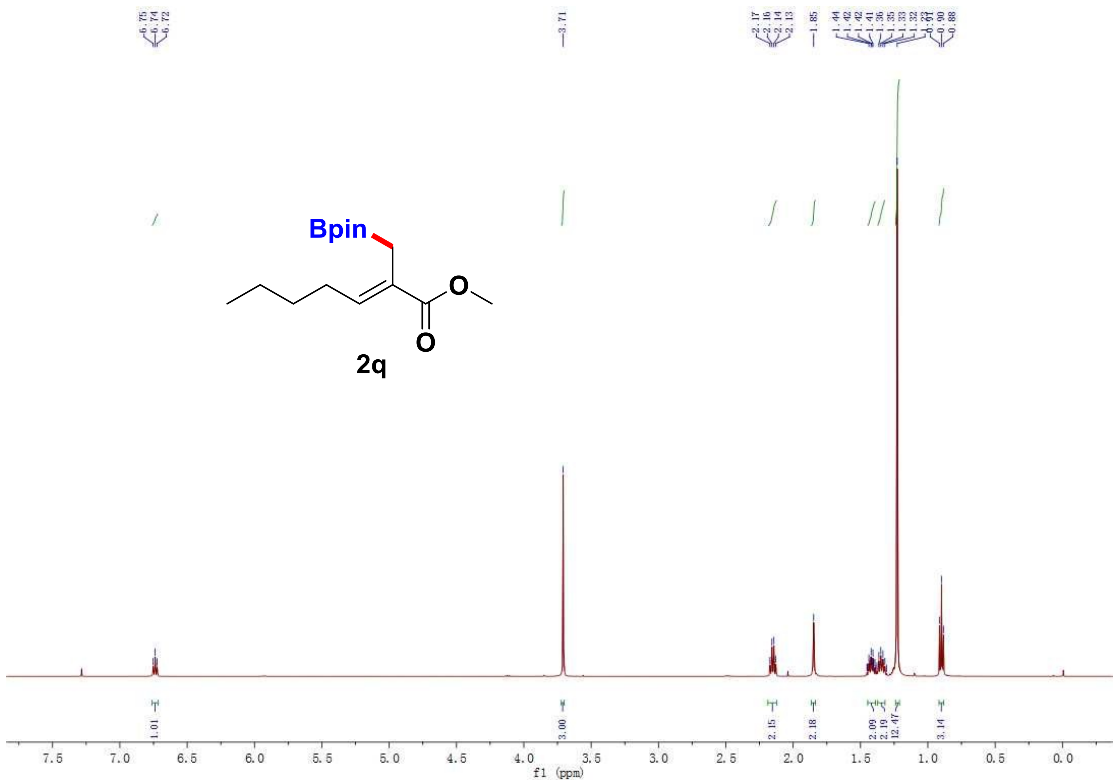
^{1}H NMR and ^{13}C NMR of **2p**

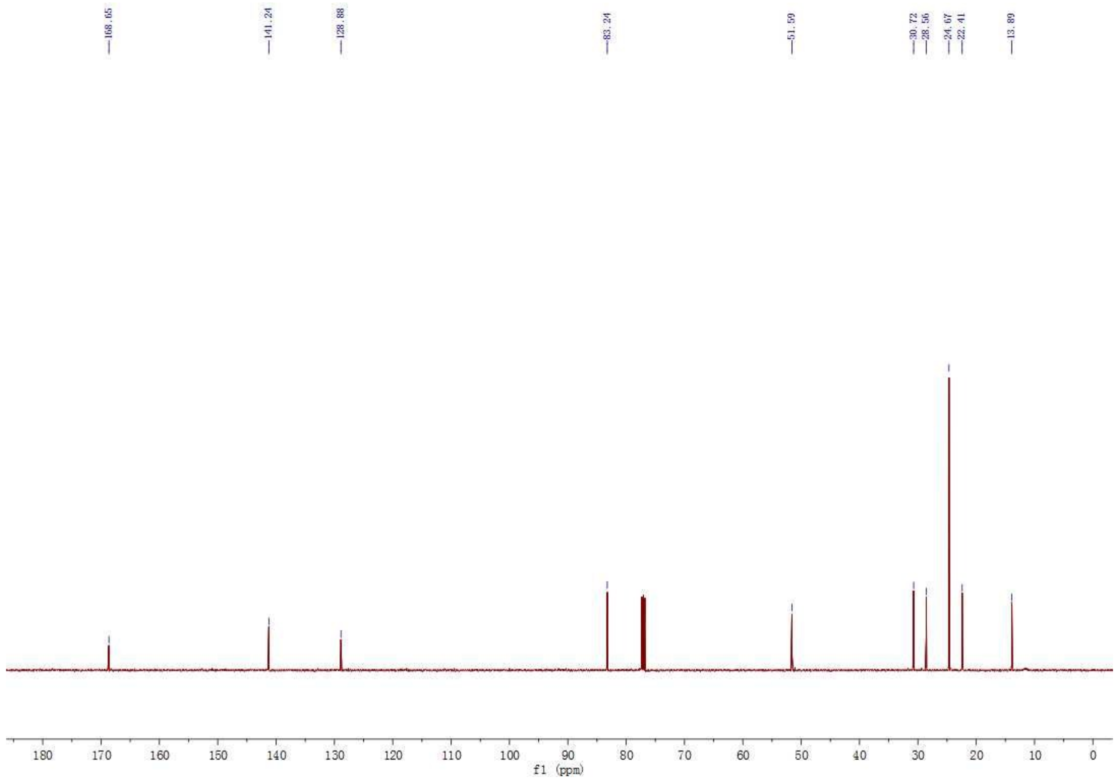


2p

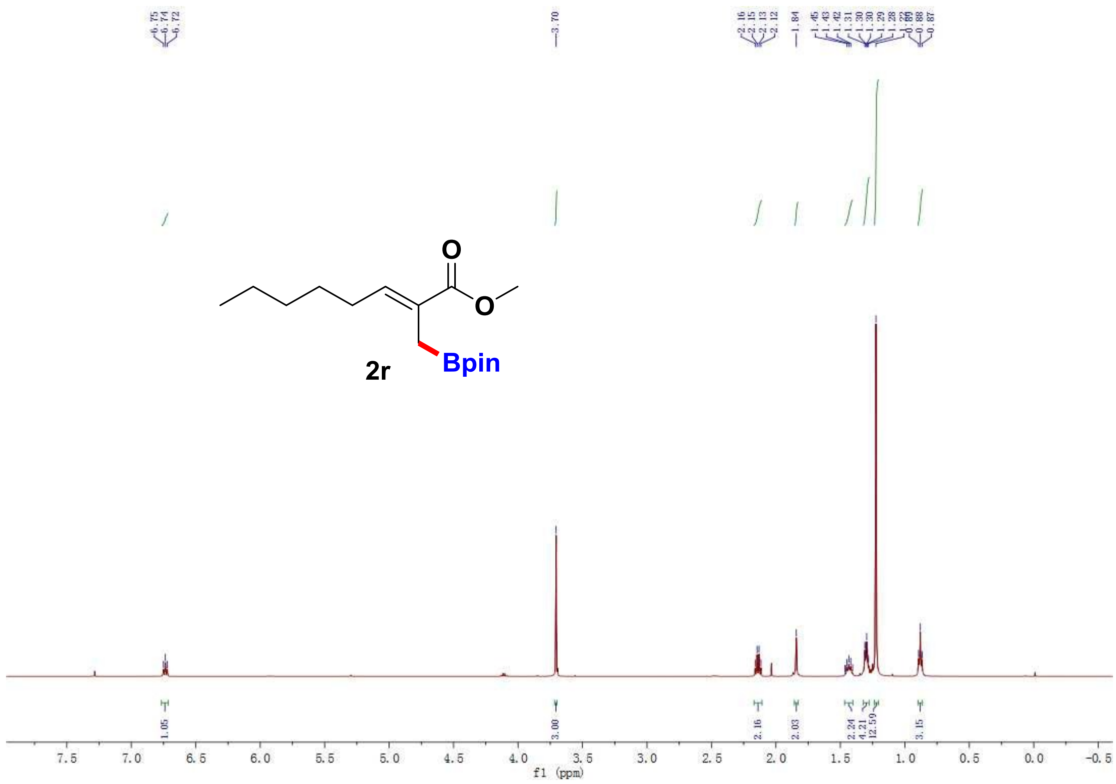


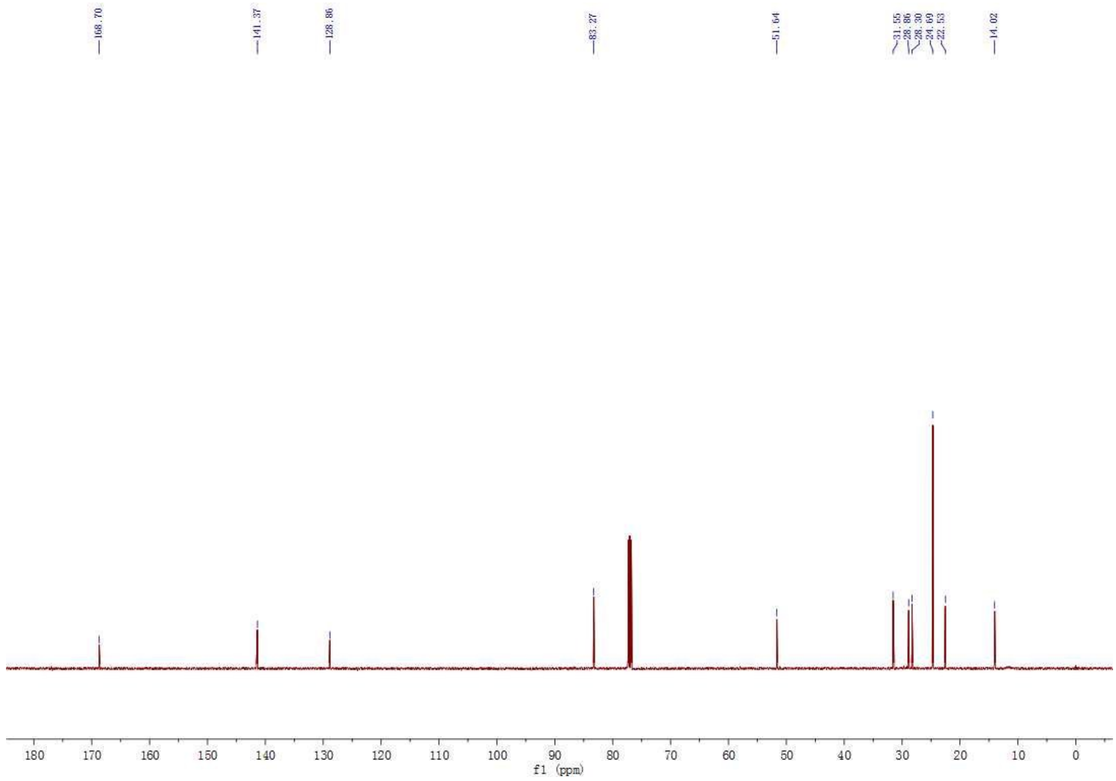
[1]H NMR and [13]C NMR of **2q**



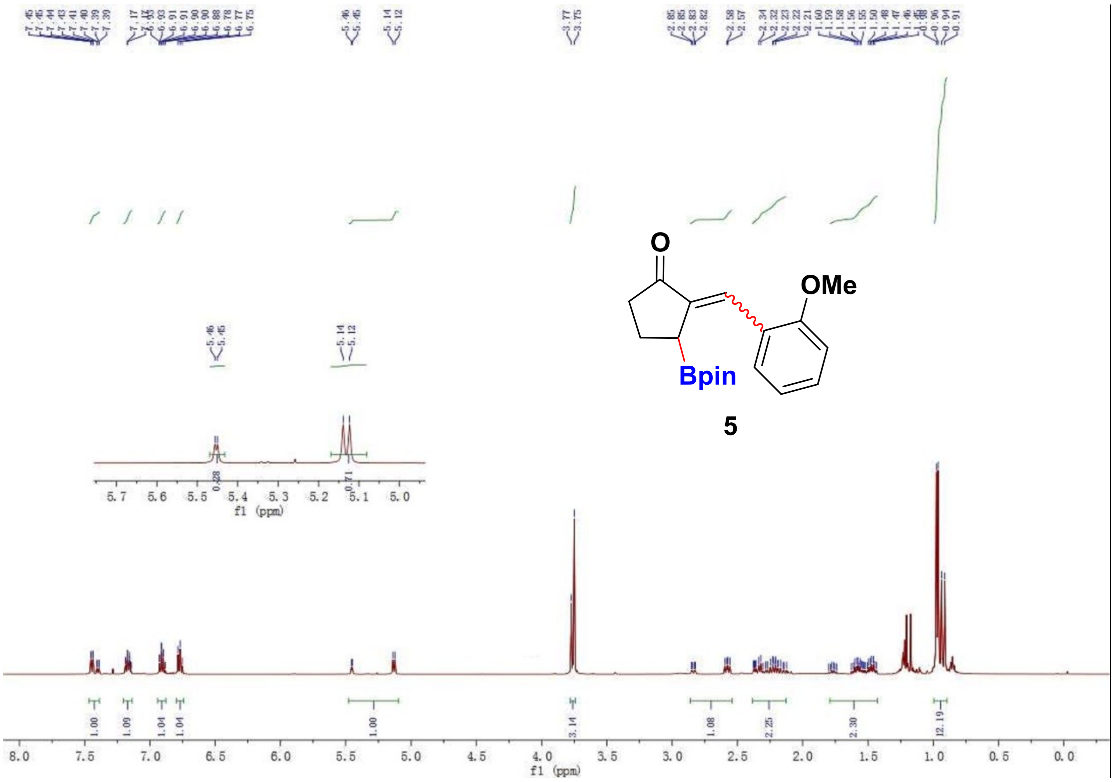


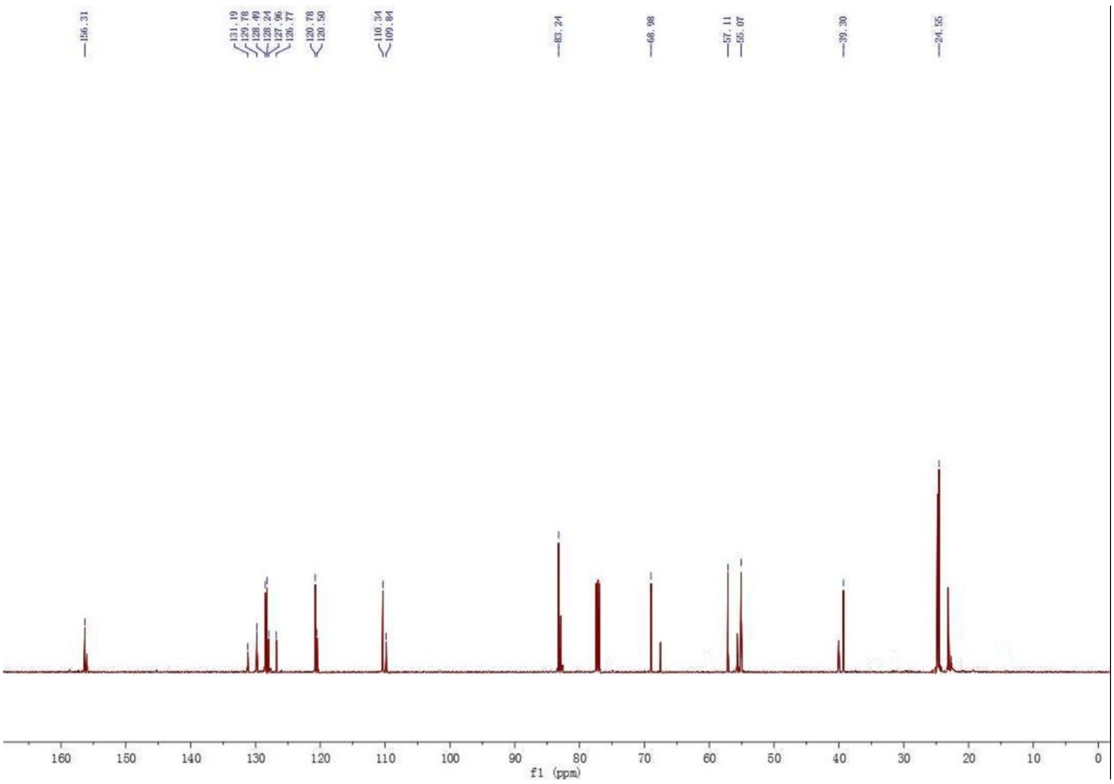
[1]H NMR and [13]C NMR of **2r**



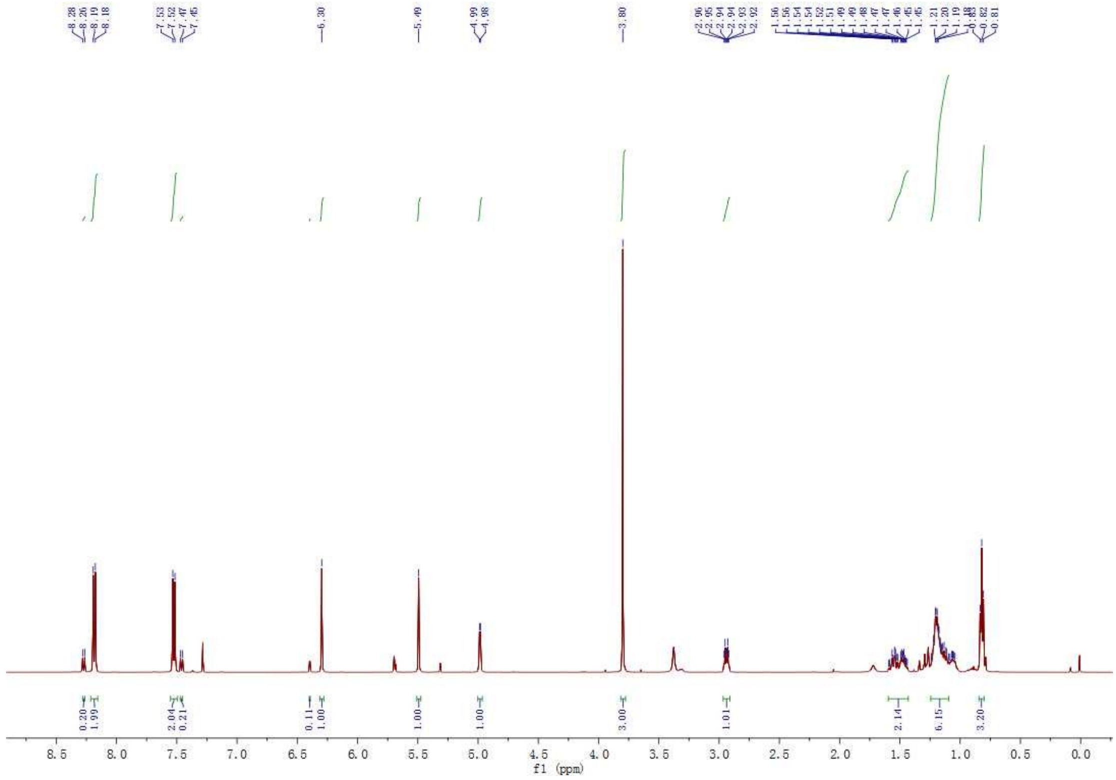


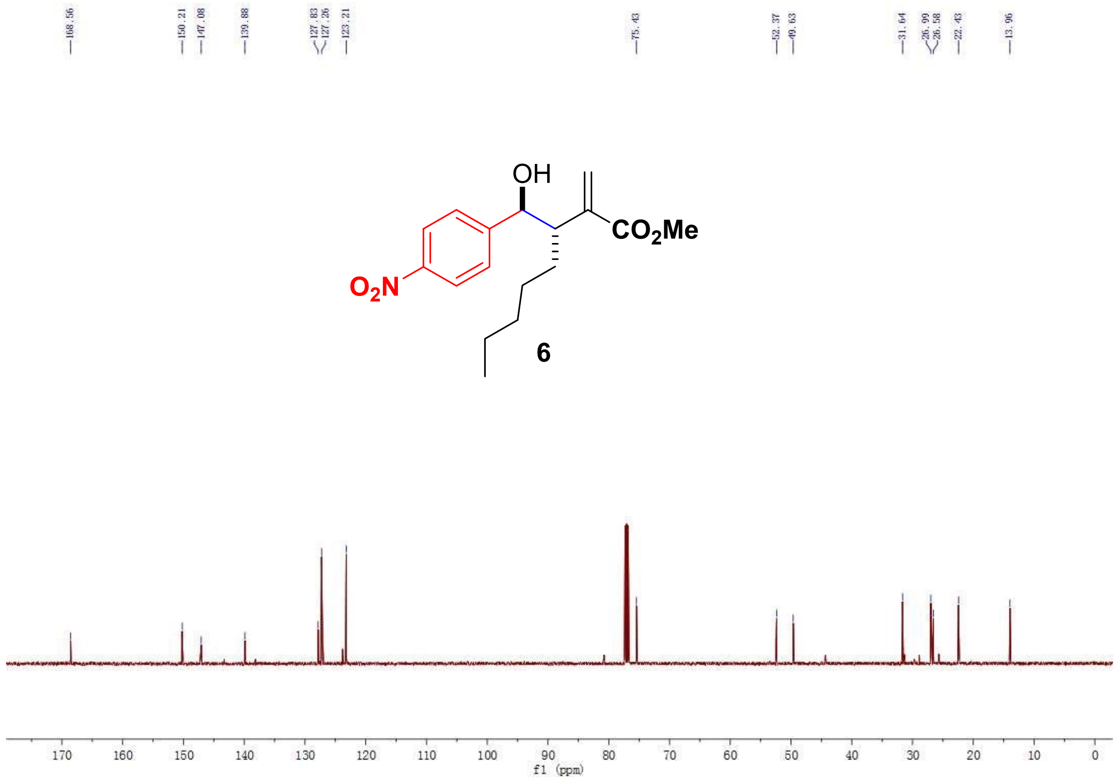
^{1}H NMR and ^{13}C NMR of **5**



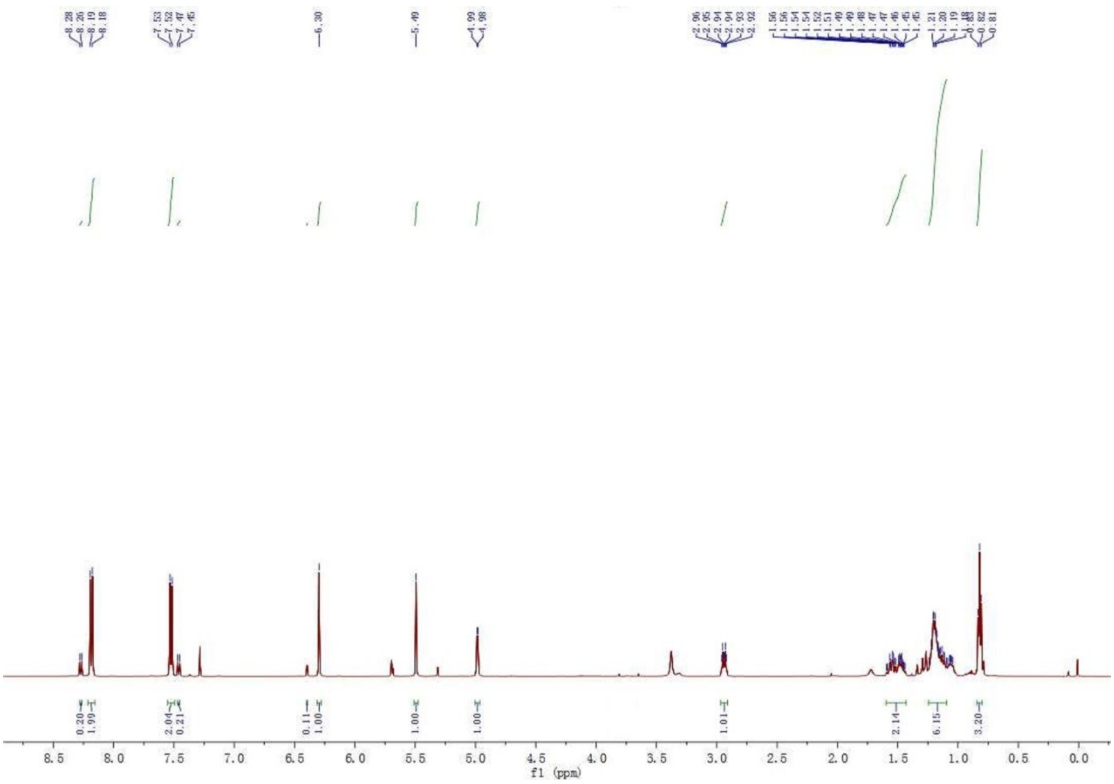


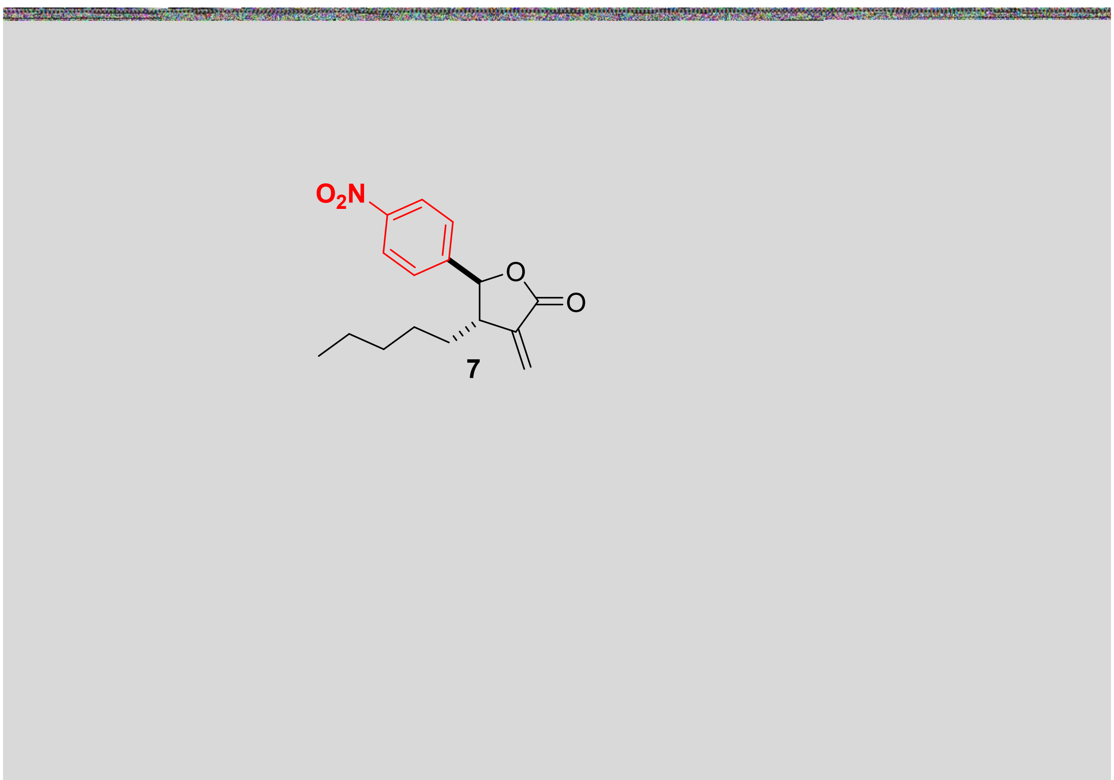
^{1}H NMR and ^{13}C NMR of **6**





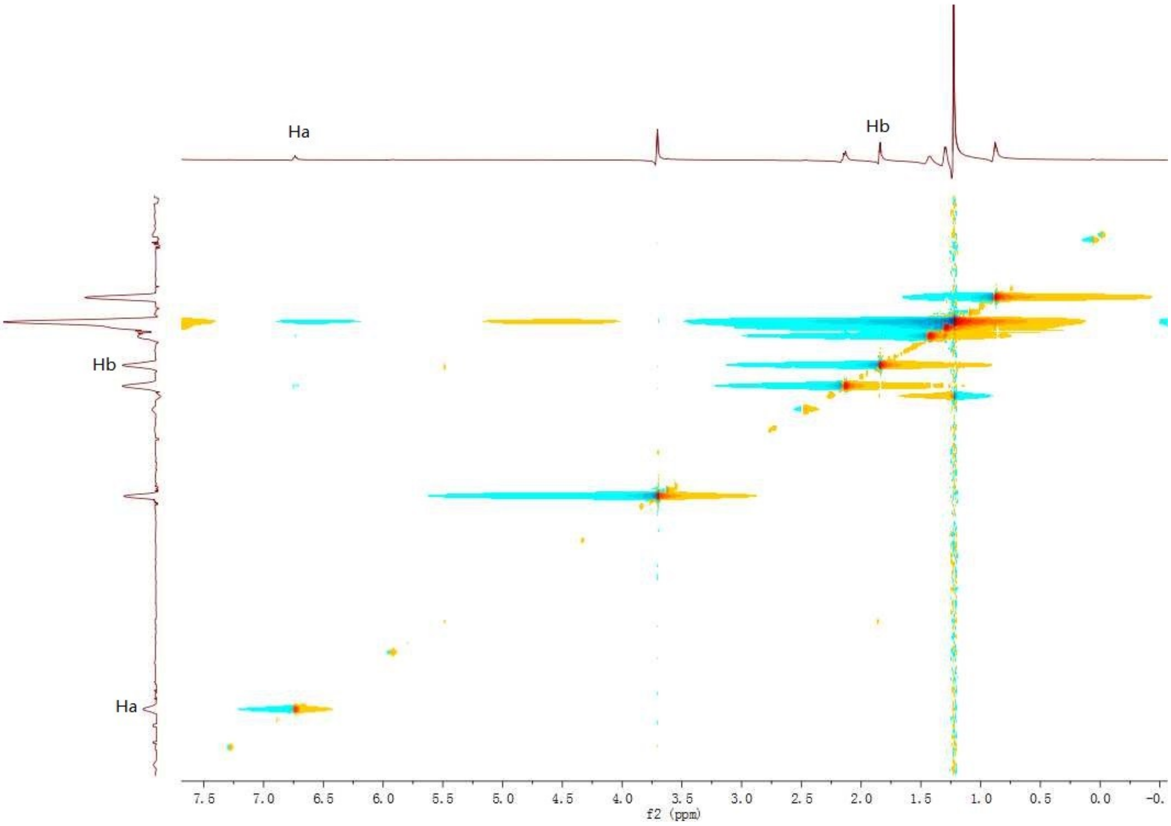
^{1}H NMR and ^{13}C NMR of **7**

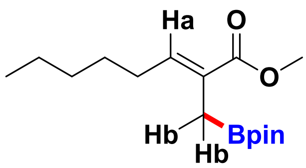




IV. **Determination of the stereochemistry of** 2r

According to the NOESY spectrum of **2r**, there is no correspondence between H_a and H_b, so it can be determined that **2r** was *E*-selectivity.





V. **Determination of the stereochemistry of 5**

The distance between H_a and H_b in E-configuration was more large than in ***Z***-configuration, so from the coupling constants of H_a and H_b, we could determined that the ratio of ***E***-5 and ***Z***-5 was about 7:3.