

Phosphine-catalysed (4+1) annulations of β' -acetoxy allenolate with β,γ -unsaturated carbonyl compounds

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1. General Information	S2
2. Optimization of Reaction Conditions	S3
3. Synthesis and Data of Products 3	S4
4. Synthesis and Data of Products 4	S14
5. Synthesis and Data of Products 5	S15
6. Synthetic Application	S16
7. NMR Spectrum	S17

1. General Information

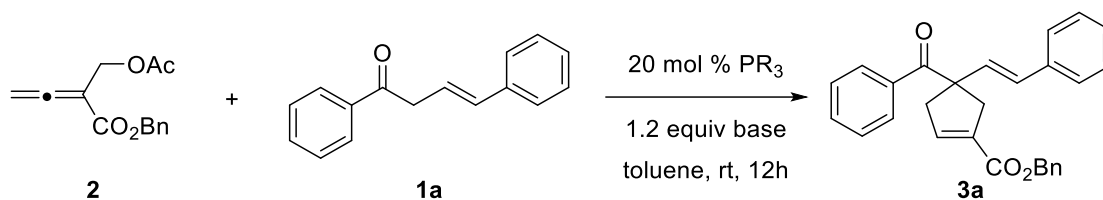
Unless otherwise noted, all reagents were obtained commercially and used without further purification.

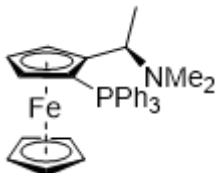
NMR spectroscopy: ^1H and ^{13}C spectra are recorded on the Bruker AVANCE spectrometer, operating at 400 MHz (300 MHz or 500 MHz) for ^1H NMR and 100 MHz (75 MHz or 125 MHz) for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm). Chemical shifts are reported downfield from CDCl_3 (δ : 7.28 ppm) for ^1H NMR. Chemical shifts of ^{13}C NMR are reported in the scale relative to the solvent of CDCl_3 (δ : 77.0 ppm) used as an internal reference. Multiplicities are recorded as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet), brs (broad singlet), qd (quartet of double). Coupling constants are reported in Hertz (Hz).

Mass spectroscopy: Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector.

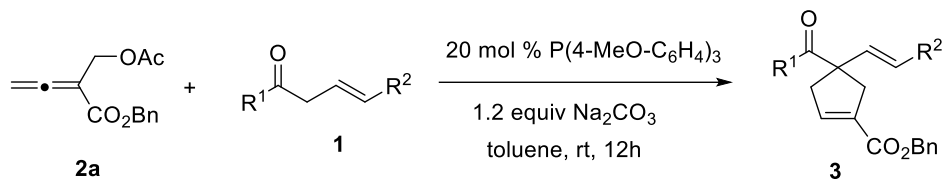
Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM).

2. Optimization of Reaction Conditions

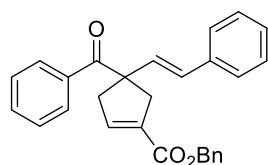


Entry	1a/2a	Cat.	Solvent	Additive	T (°C)	Yield (%) ^b
1	1 : 1.2	P(4-MeOPh) ₃	PhMe	Cs ₂ CO ₃	r.t.	34%
2	1 : 1.2	P-(N-(CH ₃) ₂) ₃	PhMe	Cs ₂ CO ₃	r.t.	22%
3	1 : 1.2	P(4-CH ₃ Ph) ₃	PhMe	Na ₂ CO ₃	r.t.	60%
4	1 : 1.2	P(4-MeOPh) ₃	PhMe	Na ₂ CO ₃	r.t.	71%
5	1 : 1.2	P(4-FPh) ₃	PhMe	Na ₂ CO ₃	r.t.	22%
6	1 : 1.2	P(4-MeOPh) ₃	THF	Na ₂ CO ₃	r.t.	47%
7	1 : 1.2	P(4-MeOPh) ₃	PhMe	Na ₂ CO ₃	60°C	46%
8	1 : 1.2	P(4-MeOPh) ₃	CH ₂ Cl ₂	Na ₂ CO ₃	r.t.	20%
9	1 : 1.2	P(4-MeOPh) ₃	Et ₂ O	Na ₂ CO ₃	r.t.	22%
10	1 : 1.2	PPhMe ₂	PhMe	Na ₂ CO ₃	r.t.	41%
11	1 : 1.2	P(4-MeOPh) ₃	PhMe	Et ₃ N	r.t.	56%
12	1.2 : 1	PPh ₃	PhMe	Na ₂ CO ₃	r.t.	30%
13	1 : 1.2	PPh ₂ Me	PhMe	Na ₂ CO ₃	r.t.	55%
14	1 : 1.2	P(4-MeOPh) ₃	Ph	Na ₂ CO ₃	r.t.	50%
15	1 : 1.2	P(4-MeOPh) ₃	PhMe	Et ₃ N	r.t.	56%
16	1 : 1.2	P(4-MeOPh) ₃	PhMe	K ₂ CO ₃	r.t.	52%
17	1 : 1.2		PhMe	Cs ₂ CO ₃	r.t.	26%
18	1 : 1.2	PPh ₃	THF	Na ₂ CO ₃	r.t.	53%
19	1 : 1.2	P(<i>n</i> -Bu) ₃	PhMe	Na ₂ CO ₃	r.t.	28%

3. Synthesis and Data of Products 3



General Procedure: To a 25 mL flask was added catalyst P(4-MeO-C₆H₄)₃ (0.04 mmol), **1** (0.24 mmol), Na₂CO₃ (0.24 mmol) and toluene (1.5 mL). After the mixture was stirred at rt for five minutes, a solution of **2a** (0.20 mmol) in toluene (1.5 mL) was slowly added. After 12 h, the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give product.



3a: Yield = 71 %, 57.9 mg, yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.96–7.89 (m, 2H), 7.44–7.29 (m, 12H), 7.27–7.20 (m, 1H), 6.80 (s, 1H), 6.66 (d, *J* = 16.4 Hz,

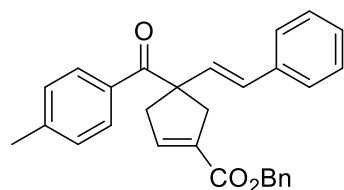
1H), 6.43 (d, *J* = 16.4 Hz, 1H), 5.22 (s, 2H), 3.58 (dq, *J* = 18.8 Hz, *J* = 2.4 Hz, 1H),

3.45 (dq, *J* = 17.2 Hz, *J* = 2.4 Hz, 1H), 3.15 (d, *J* = 17.2 Hz, 1H), 2.87 (d, *J* = 18.8 Hz,

1H).

¹³C NMR (100 MHz, CDCl₃) δ 200.9, 164.3, 141.2, 136.6, 136.0, 135.3, 134.4, 133.3, 132.6, 129.9, 129.8, 128.7, 128.6, 128.4, 128.2, 127.9, 126.4, 66.2, 59.9, 44.5, 42.5.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₈H₂₄O₃ 431.1618, found: 431.1619.



3b: Yield = 77 %, 65.1 mg, yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.87–7.82 (m, 2H),

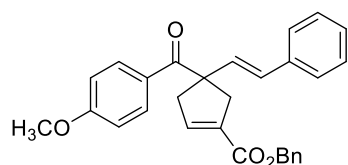
7.40–7.30 (m, 9H), 7.27–7.20 (m, 3H), 6.82–6.78 (m,

1H), 6.65 (d, *J* = 16.4 Hz, 1H), 6.41 (d, *J* = 16.4 Hz, 1H), 5.22 (s, 2H), 3.59 (dq, *J* =

18.8 Hz, $J = 2.4$ Hz, 1H), 3.44 (dq, $J = 17.2$ Hz, $J = 2.4$ Hz, 1H), 3.15 (d, $J = 17.2$ Hz, 1H), 2.86 (d, $J = 18.8$ Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 200.4, 164.4, 143.4, 141.2, 136.6, 136.0, 134.6, 133.3, 132.6, 130.1, 129.6, 129.1, 128.6, 128.6, 128.2, 127.8, 126.3, 66.2, 59.8, 44.6, 42.5, 21.6

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{26}\text{O}_3$ 445.1774, found: 445.1774.



3c: Yield = 81 %, 70.8 mg, yellow oil.

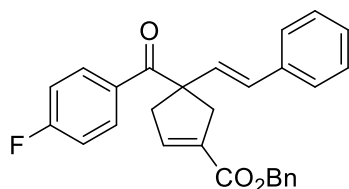
^1H NMR (400 MHz, CDCl_3) δ 8.02–7.90 (m, 2H),

7.40–7.30 (m, 9H), 7.27–7.21 (m, 1H), 6.93–6.86 (m,

2H), 6.82–6.79 (m, 1H), 6.66 (d, $J = 16.4$ Hz, 1H), 6.42 (d, $J = 16.4$ Hz, 1H), 5.22 (s, 2H), 3.86 (s, 3H), 3.61 (dd, $J = 19.2$ Hz, $J = 2.4$ Hz, 1H), 3.46 (dd, $J = 16.8$ Hz, $J = 2.4$ Hz, 1H), 3.15 (d, $J = 16.8$ Hz, 1H), 2.88 (d, $J = 19.2$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 201.1, 164.4, 159.4, 141.3, 136.0, 135.5, 133.3, 132.5, 132.2, 129.9, 129.3, 128.6, 128.4, 128.2, 128.2, 127.5, 114.1, 66.2, 59.8, 55.4, 44.6, 42.5.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{26}\text{O}_4$ 461.1723, found: 461.1725.



3d: Yield = 58 %, 47.6 mg, yellow oil.

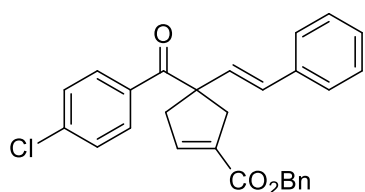
^1H NMR (400 MHz, CDCl_3) δ 7.99 (dd, $J = 5.6$ Hz, $J = 3.2$ Hz, 2H), 7.43–7.29 (m, 10H), 7.27–7.22 (m, 1H),

7.09 (t, $J = 8.6$ Hz, 1H), 6.82–6.77 (m, 1H), 6.64 (d, $J = 16.4$ Hz, 1H), 6.41 (d, $J = 16.4$ Hz, 1H), 5.22 (s, 2H), 3.59 (dq, $J = 18.8$ Hz, $J = 2.4$ Hz, 1H), 3.43 (dq, $J = 16.8$

Hz, $J = 2.4$ Hz, 1H), 3.15 (d, $J = 16.8$ Hz, 1H), 2.86 (d, $J = 18.8$ Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 199.1, 164.3, 141.1, 136.4, 136.0, 134.1, 133.2, 132.7, 132.6, 130.0, 128.7, 128.6, 128.3, 128.2, 128.0, 126.3, 115.4, 66.3, 59.7, 44.5, 42.5.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{23}\text{FO}_3$ 449.1523, found: 449.1526.



3e: Yield = 58 %, 51.7 mg, yellow oil.

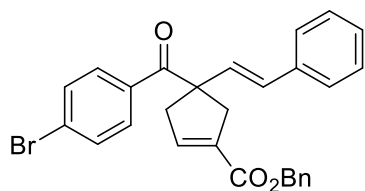
^1H NMR (400 MHz, CDCl_3) δ 7.92-7.86 (m, 2H),

7.42-7.29 (m, 11H), 7.27-7.22 (m, 1H), 6.79 (t, $J = 1.8$

Hz, 1H), 6.62 (d, $J = 16.4$ Hz, 1H), 6.40 (d, $J = 16.4$ Hz, 1H), 5.22 (s, 2H), 3.57 (dq, $J = 18.8$ Hz, $J = 2.4$ Hz, 1H), 3.41 (dq, $J = 17.2$ Hz, $J = 2.4$ Hz, 1H), 3.13 (d, $J = 17.2$ Hz, 1H), 2.85 (d, $J = 18.8$ Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 199.5, 164.2, 141.0, 139.0, 136.3, 135.9, 134.0, 133.5, 133.2, 131.4, 130.1, 128.7, 128.6, 128.3, 128.2, 128.0, 126.3, 66.3, 59.7, 44.4, 42.4.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{23}\text{ClO}_3$ 465.1228, found: 465.1229.



3f: Yield = 62 %, 60.5 mg, yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.85-7.78 (m, 2H),

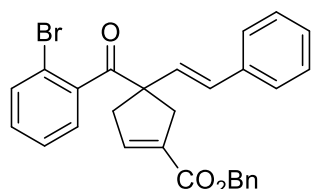
7.59-7.54 (m, 2H), 7.45-7.30 (m, 9H), 7.27-7.22 (m,

1H), 6.81-6.77 (m, 1H), 6.62 (d, $J = 16.4$ Hz, 1H), 6.40 (d, $J = 16.4$ Hz, 1H), 5.22 (s,

2H), 3.57 (dq, $J = 18.8$ Hz, $J = 2.4$ Hz, 1H), 3.41 (dq, $J = 16.8$ Hz, $J = 2.4$ Hz, 1H), 3.13 (d, $J = 16.8$ Hz, 1H), 2.85 (d, $J = 18.8$ Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 199.7, 164.2, 141.0, 136.3, 134.0, 133.2, 131.7, 131.5, 130.2, 128.7, 128.6, 128.3, 128.2, 127.8, 126.3, 66.3, 59.7, 44.4, 42.4.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{23}\text{BrO}_3$ 509.0723, found: 509.0724.



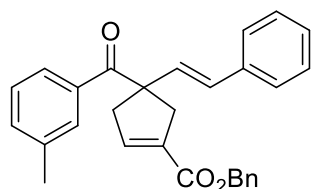
3g: Yield = 50 %, 48.3 mg, yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.63-7.56 (m, 1H), 7.43-7.29 (m, 10H), 7.27-7.23 (m, 3H), 6.80 (t, $J = 1.4$ Hz, 1H), 6.55

(d, $J = 16.4$ Hz, 1H), 6.44 (d, $J = 16.4$ Hz, 1H), 5.22 (s, 2H), 3.44 (dq, $J = 18.4$ Hz, $J = 2.4$ Hz, 1H), 3.37 (dq, $J = 16.4$ Hz, $J = 2.4$ Hz, 1H), 2.99 (d, $J = 16.4$ Hz, $J = 1.6$ Hz, 1H), 2.83 (dd, $J = 18.4$ Hz, $J = 1.6$ Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 205.5, 164.2, 141.3, 141.1, 136.4, 136.0, 133.8, 133.4, 131.3, 131.1, 130.7, 128.7, 128.6, 128.2, 128.2, 128.1, 127.2, 126.9, 126.5, 118.9, 66.2, 62.0, 42.7, 40.6.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{23}\text{BrO}_3$ 509.0723, found: 509.0724.



3h: Yield = 63 %, 53.1 mg, yellow oil.

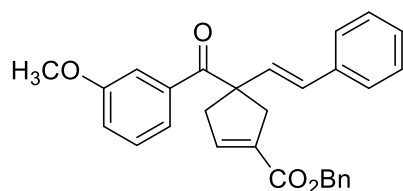
^1H NMR (400 MHz, CDCl_3) δ 7.78-7.69 (m, 2H), 7.42-7.29 (m, 12H), 7.27-7.20 (m, 1H), 6.82-6.78 (m, 1H), 6.65 (d, J

= 16.4 Hz, 1H), 6.44 (d, $J = 16.4$ Hz, 1H), 5.22 (s, 2H), 3.58 (dq, $J = 19.2$ Hz, $J = 2.4$ Hz, 1H), 3.44 (dq, $J = 16.8$ Hz, $J = 2.4$ Hz, 1H), 3.15 (d, $J = 16.8$ Hz, 1H), 2.87 (d, J

= 19.2 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 201.2, 164.4, 141.2, 138.2, 136.6, 136.0, 135.4, 134.5, 133.3, 130.3, 129.7, 128.6, 128.6, 128.2, 128.1, 127.8, 127.1, 126.3, 66.2, 59.9, 44.6, 42.5, 21.5.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{26}\text{O}_3$ 445.1774, found: 445.1775.



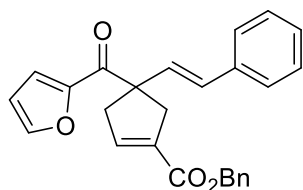
3i: Yield = 74 %, 64.5 mg, colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.53-7.47 (m, 2H),
7.43-7.29 (m, 10H), 7.27-7.21 (m, 1H), 7.10-7.02

(m, 1H), 6.80 (s, 1H), 6.65 (d, J = 16.4 Hz, 1H), 6.44 (d, J = 16.4 Hz, 1H), 5.22 (s, 2H),
3.83 (s, 3H), 3.58 (dd, J = 18.8 Hz, J = 2.4 Hz, 1H), 3.45 (dd, J = 16.8 Hz, J = 2.4 Hz,
1H), 3.15 (d, J = 16.8 Hz, 1H), 2.88 (d, J = 18.8 Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 200.7, 164.3, 159.5, 141.1, 136.7, 136.6, 136.0, 134.3,
133.3, 129.8, 129.3, 128.7, 128.6, 128.2, 127.8, 126.3, 122.4, 118.8, 114.4, 66.2, 59.9,
55.4, 44.5, 42.5.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{26}\text{O}_4$ 461.1723, found: 461.1724.



3j: Yield = 54 %, 43.1 mg, colorless oil.

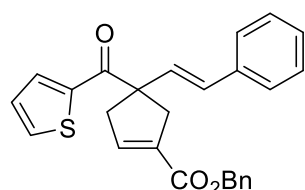
^1H NMR (400 MHz, CDCl_3) δ 7.59-7.56 (m, 1H), 7.45-7.29
(m, 9H), 7.26-7.21 (m, 2H), 6.80 (t, J = 1.8 Hz, 1H), 6.58 (d,

J = 17.6 Hz, 1H), 6.51 (dd, J = 3.6 Hz, J = 2.0 Hz, 1H), 6.45 (d, J = 16.4 Hz, 1H),

5.22 (s, 2H), 3.54 (dq, $J = 18.8$ Hz, $J = 2.4$ Hz, 1H), 3.45 (dq, $J = 16.8$ Hz, $J = 2.4$ Hz, 1H), 3.17 (d, $J = 16.8$ Hz, 1H), 2.89 (d, $J = 18.8$ Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 188.5, 164.4, 151.5, 146.2, 141.2, 136.6, 136.0, 133.3, 133.0, 130.2, 128.6, 128.6, 128.2, 127.8, 126.4, 119.3, 112.1, 66.2, 59.1, 42.6, 41.1.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{22}\text{O}_4$ 421.1410, found: 421.1414.



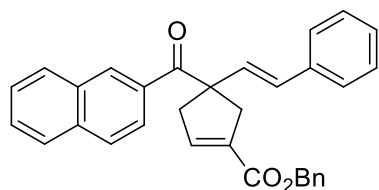
3k: Yield = 65 %, 53.8 mg, yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 3.6$ Hz, 1H), 7.60 (d, $J = 5.2$ Hz, 1H), 7.42-7.29 (m, 9H), 7.27-7.22 (m, 1H),

7.69 (t, $J = 4.4$ Hz, 1H), 6.81 (s, 1H), 6.60 (d, $J = 16.4$ Hz, 1H), 6.50 (d, $J = 16.0$ Hz, 1H), 5.23 (s, 2H), 3.61 (dd, $J = 18.8$ Hz, $J = 2.4$ Hz, 1H), 3.49 (dd, $J = 16.8$ Hz, $J = 2.4$ Hz, 1H), 3.17 (d, $J = 16.8$ Hz, 1H), 2.86 (d, $J = 18.8$ Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 193.1, 164.3, 142.0, 141.0, 136.5, 136.0, 133.6, 133.2, 130.1, 128.7, 128.6, 128.2, 128.2, 128.0, 127.9, 126.4, 66.2, 59.9, 43.7, 42.0.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{22}\text{O}_3\text{S}$ 437.1182, found: 437.1184.



3l: Yield = 61 %, 58.7 mg, yellow oil.

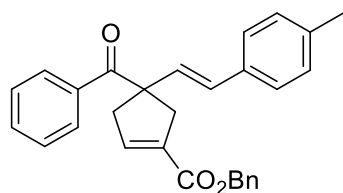
^1H NMR (400 MHz, CDCl_3) δ 8.05-7.90 (m, 2H),

7.89-7.82 (m, 2H), 7.64-7.50 (m, 2H), 7.42-7.29 (m, 10H), 7.27-7.19 (m, 1H), 6.83 (t, $J = 2.0$ Hz, 1H), 6.75 (d, $J = 16.4$ Hz, 1H), 6.50 (d,

$J = 16.0$ Hz, 1H), 5.23 (s, 2H), 3.66 (dq, $J = 18.8$ Hz, $J = 2.4$ Hz, 1H), 3.53 (dq, $J = 16.8$ Hz, $J = 2.4$ Hz, 1H), 3.25 (d, $J = 16.8$ Hz, 1H), 2.94 (d, $J = 18.8$ Hz, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 200.8, 164.3, 141.2, 136.6, 136.0, 135.2, 134.5, 133.3, 132.6, 132.4, 131.5, 129.9, 129.7, 128.7, 128.6, 128.2, 128.0, 127.8, 127.7, 126.7, 126.4, 125.6, 66.2, 60.0, 44.6, 42.6.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{32}\text{H}_{26}\text{O}_3$ 481.1774, found: 481.1775.



3m: Yield = 75 %, 57.8 mg, yellow oil.

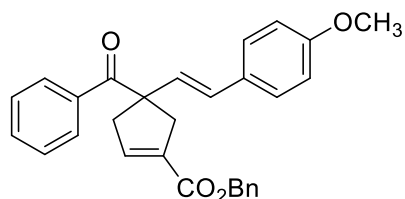
^1H NMR (400 MHz, CDCl_3) δ 7.96–7.91 (m, 2H),

7.55–7.48 (m, 1H), 7.45–7.32 (m, 7H), 7.24 (d, $J = 8.0$

Hz, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 6.82–6.78 (m, 1H), 6.61 (d, $J = 16.4$ Hz, 1H), 6.41 (d, $J = 16.4$ Hz, 1H), 5.22 (s, 2H), 3.58 (dq, $J = 18.8$ Hz, $J = 2.4$ Hz, 1H), 3.44 (dd, $J = 16.8$ Hz, $J = 2.4$ Hz, 1H), 3.15 (d, $J = 16.8$ Hz, 1H), 2.87 (d, $J = 18.8$ Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 219.4, 201.0, 164.4, 141.2, 137.8, 136.0, 135.4, 133.8, 133.3, 132.5, 129.9, 129.3, 128.6, 128.3, 128.2, 126.2, 66.2, 59.8, 44.5, 42.5, 21.2.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{26}\text{O}_3$ 445.1774, found: 445.1774.



3n: Yield = 74 %, 65.0 mg, colorless oil.

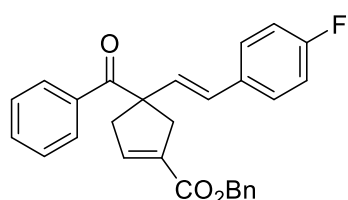
^1H NMR (400 MHz, CDCl_3) δ 7.96–7.91 (m, 2H),

7.54–7.47 (m, 1H), 7.46–7.31 (m, 7H), 7.27 (d, $J =$

8.0 Hz, 2H), 6.85 (d, $J = 8.0$ Hz, 2H), 6.80 (t, $J = 1.6$ Hz, 1H), 6.51 (d, $J = 16.4$ Hz,

¹H), 6.38 (d, *J* = 16.4 Hz, 1H), 5.22 (s, 2H), 3.81 (s, 3H), 3.56 (dq, *J* = 18.8 Hz, *J* = 2.4 Hz, 1H), 3.43 (dq, *J* = 16.8 Hz, *J* = 2.4 Hz, 1H), 3.14 (d, *J* = 16.8 Hz, 1H), 2.86 (d, *J* = 18.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 201.1, 164.4, 159.4, 141.2, 136.0, 135.5, 133.3, 132.5, 132.1, 129.9, 129.3, 128.6, 128.3, 128.2, 127.5, 114.1, 66.2, 59.8, 55.3, 44.6, 42.5.
HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₉H₂₆O₄ 461.1723, found: 461.1723.

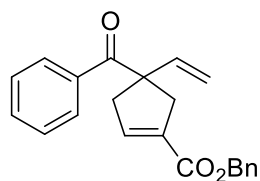


3o: Yield = 45 %, 38.9 mg, yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 7.86-7.80 (m, 2H),
7.46-7.29 (m, 7H), 7.26-7.16 (m, 3H), 6.95-6.85 (m,

2H), 6.73-6.66 (m, 1H), 6.47 (d, *J* = 16.2 Hz, 1H), 6.29 (d, *J* = 16.2 Hz, 1H), 5.12 (s, 2H), 3.48 (dq, *J* = 18.9 Hz, *J* = 2.4 Hz, 1H), 3.45 (dq, *J* = 17.1 Hz, *J* = 2.4 Hz, 1H), 3.09-2.99 (m, 1H), 2.82-2.70 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 200.8, 164.3, 141.1, 136.0, 135.3, 133.3, 132.6, 129.8, 128.7, 128.6, 128.4, 128.2, 127.9, 127.8, 115.7, 115.4, 66.2, 59.8, 44.5, 42.5.
HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₈H₂₃FO₃ 449.1523, found: 449.1525.



3p: Yield = 58 %, 38.3 mg, colorless oil.

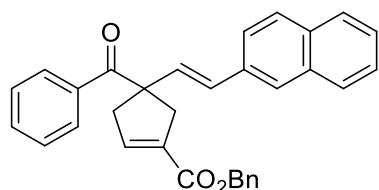
¹H NMR (400 MHz, CDCl₃) δ 7.95-7.88 (m, 2H), 7.56-7.49 (m, 1H), 7.44-7.31 (m, 7H), 6.77-6.73 (m, 1H), 6.28 (dd, *J* = 17.6

Hz, *J* = 10.8 Hz, 1H), 5.21-5.17 (m, 3H), 5.14 (d, *J* = 17.6 Hz, 1H), 3.49 (dq, *J* = 19.2

Hz, $J = 2.4$ Hz, 1H), 3.37 (dq, $J = 16.8$ Hz, $J = 2.4$ Hz, 1H), 3.07 (d, $J = 16.8$ Hz, 1H), 2.85-2.74 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 200.9, 164.3, 142.8, 141.0, 136.0, 135.4, 133.2, 132.5, 129.9, 128.6, 128.3, 128.2, 128.2, 114.7, 66.2, 60.4, 43.9, 41.8.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{20}\text{O}_3$ 355.1305, found: 355.1306.



3q: Yield = 61 %, 56.1 mg, yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 8.07-8.01 (m, 2H),

7.88-7.72 (m, 3H), 7.56-7.34 (m, 13H), 7.16 (d, $J =$

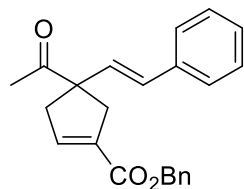
16.0 Hz, 2H) 6.89-6.83 (m, 1H), 6.67 (d, $J = 16.0$ Hz, 1H), 5.24 (s, 2H), 3.81 (s, 3H),

3.69 (dq, $J = 18.8$ Hz, $J = 2.4$ Hz, 1H), 3.55 (dq, $J = 17.2$ Hz, $J = 2.4$ Hz, 1H), 3.26

(d, $J = 17.2$ Hz, 1H), 2.98 (d, $J = 18.8$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 200.8, 164.3, 141.2, 137.9, 136.0, 135.3, 134.5, 133.5, 133.4, 132.7, 131.1, 130.1, 128.6, 128.5, 128.4, 128.2, 128.2, 127.7, 126.2, 125.9, 125.6, 123.8, 123.6, 66.3, 60.2, 44.7, 42.7.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{32}\text{H}_{26}\text{O}_3$ 481.1774, found: 481.1776



3r: Yield = 38 %, 26.5 mg, colorless oil

^1H NMR (400 MHz, CDCl_3) δ 7.41-7.29 (m, 10H), 6.77 (s, 1H),

6.49 (d, $J = 16.0$ Hz, 1H), 6.35 (d, $J = 16.0$ Hz, 1H), 5.22 (s, 2H),

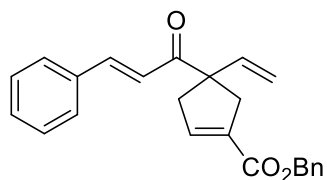
3.30 (dd, $J = 18.4$ Hz, $J = 2.0$ Hz, 1H), 3.23 (dd, $J = 16.8$ Hz, $J = 2.0$ Hz, 1H), 2.96

(dd, $J = 16.8$ Hz, $J = 1.2$ Hz, 1H), 2.70 (dd, $J = 18.4$ Hz, $J = 1.2$ Hz, 1H), 2.24 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 207.3, 164.3, 141.4, 136.4, 136.0, 133.4, 131.7, 130.7,

128.7, 128.6, 128.2, 128.1, 128.0, 126.4, 66.2, 61.8, 41.3, 39.7, 26.3.

HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{23}H_{22}O_3$ 369.1461, found: 369.1463.



3s: Yield = 66 %, 47.5 mg, colorless oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 15.6 Hz, 1H),

7.62-7.52 (m, 2H), 7.44-7.31 (m, 8H), 6.94 (d, J = 15.6

Hz, 1H), 6.77 (t, J = 1.6 Hz, 1H), 6.07 (dd, J = 10.4 Hz, J = 17.2 Hz, 1H), 5.28-7.19

(m, 4H), 3.35 (dq, J = 18.8 Hz, J = 2.4 Hz, 1H), 3.26 (dq, J = 16.8 Hz, J = 2.4 Hz,

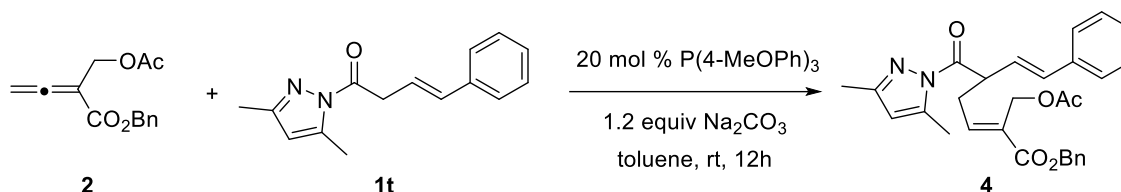
1H), 2.95 (dd, J = 16.8 Hz, J = 1.6 Hz, 1H), 2.67 (dd, J = 1.6 Hz, J = 18.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 164.3, 143.7, 141.5, 140.4, 136.0, 134.6, 133.4,

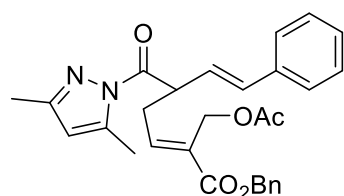
130.6, 128.9, 128.6, 128.5, 128.2, 128.2, 122.2, 115.8, 66.2, 61.0, 40.9, 39.3.

HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{24}H_{22}O_3$ 381.1461, found: 381.1463.

4. Synthesis and Data of Products 4



General Procedure: To a 25 mL flask was added catalyst P(4-MeOPh)₃ (0.04 mmol), **1t** (0.24 mmol), Na₂CO₃ (0.24 mmol) and toluene (1.5 mL). After the mixture was stirred at rt for five minutes, a solution of **2** (0.20 mmol) in toluene (1.5 mL) was slowly added. After 12 h, the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give product.



4: Yield = 30.8 %, 25.8 mg, colorless oil.

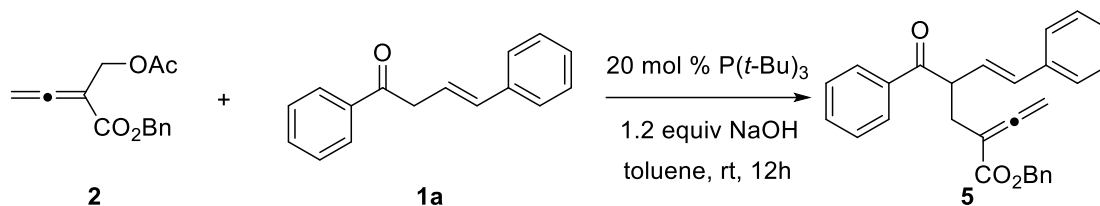
¹H NMR (400 MHz, CDCl₃) δ 7.40-7.30 (m, 10H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 16.0 Hz, 2H), 6.36 (dd, *J* =

16.0 Hz, *J* = 8.8 Hz, 1H), 5.99 (s, 1H), 5.22 (s, 2H), 4.94 (dd, *J* = 20.0 Hz, *J* = 12.0 Hz, 2H), 4.85 (dd, *J* = 15.6 Hz, *J* = 8.4 Hz, 1H), 3.09-2.98 (m, 1H), 2.88-2.74 (m, 1H), 2.55 (s, 1H), 2.26 (s, 3H), 2.01 (s, 3H).

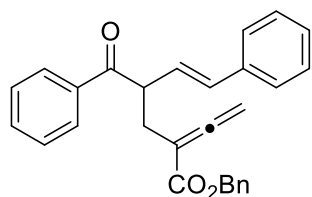
¹³C NMR (100 MHz, CDCl₃) δ 173.0, 170.8, 165.9, 152.4, 145.7, 144.4, 136.6, 136.0, 133.8, 128.9, 128.6, 128.5, 128.2, 128.0, 127.9, 126.5, 126.5, 126.0, 111.8, 66.6, 58.2, 46.5, 31.4, 20.8, 14.6, 13.9.

HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₉H₃₀N₂O₅ 509.2047, found: 509.2048.

5. Synthesis and Data of Products 5



General Procedure: To a 25 mL flask was added catalyst $P(t\text{-Bu})_3$ (0.04 mmol), **1** (0.24 mmol), NaOH (0.24 mmol) and toluene (1.5 mL). After the mixture was stirred at rt for five minutes, a solution of **2a** (0.20 mmol) in toluene (1.5 mL) was slowly added. After 12 h, the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give product.



5: Yield = 69%, 56.4 mg, colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 7.6$ Hz, 2H),

7.60-7.54 (m, 1H), 7.48-7.44 (m, 2H), 7.38-7.20 (m, 10H),

6.50 (d, $J = 16.0$ Hz, 1H), 6.25 (dd, $J = 8.8$ Hz, $J = 16.0$ Hz, 1H), 5.22 (s, 2H), 5.10

(dt, $J = 14.0$ Hz, $J = 2.4$ Hz, 1H), 5.00 (dt, $J = 14.0$ Hz, $J = 2.4$ Hz, 1H), 3.07-2.99 (m,

1H), 2.69-2.61 (m, 1H).

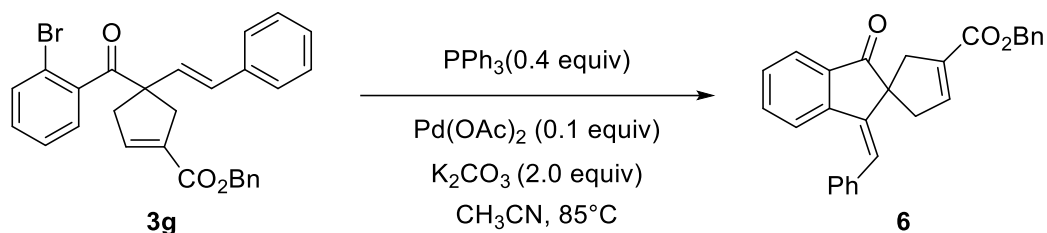
^{13}C NMR (100 MHz, CDCl_3) δ 215.0, 200.0, 166.9, 136.8, 136.6, 136.1, 133.6, 133.2,

128.7, 128.7, 128.6, 128.3, 128.2, 127.9, 127.8, 127.5, 126.4, 97.6, 79.6, 66.7, 49.3,

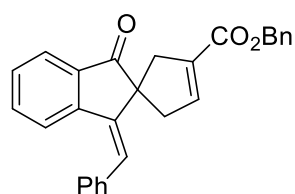
31.6.

HRMS (ESI) m/z : $[M+H]^+$ Calcd for $\text{C}_{28}\text{H}_{24}\text{O}_3$ 431.1618, found: 431.1619.

6. Synthetic Application



General Procedure: To a 25 mL flask was added catalyst PPh_3 (0.08 mmol), $\text{Pd}(\text{OAc})_2$ (0.02 mmol), K_2CO_3 (0.40 mmol) and CH_3CN (1.5 mL). After the mixture was stirred at rt for one minutes, a solution of **3g** (0.20 mmol) in CH_3CN (1.5 mL) was slowly added, then, the solution was heated to 85°C . After 6 h, the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give product **6**.



6: Yield = 73 %, 59.3 mg, yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.72 (dt, J = 8.0 Hz, J = 0.8 Hz, 1H),

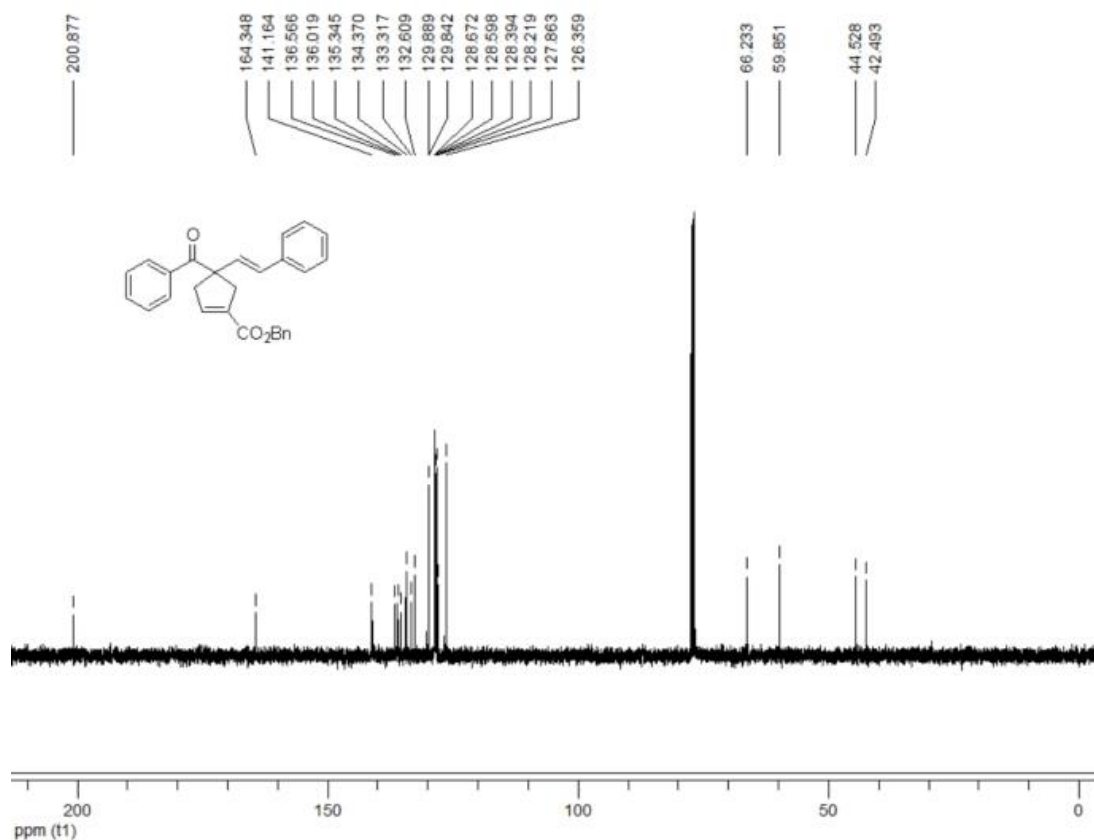
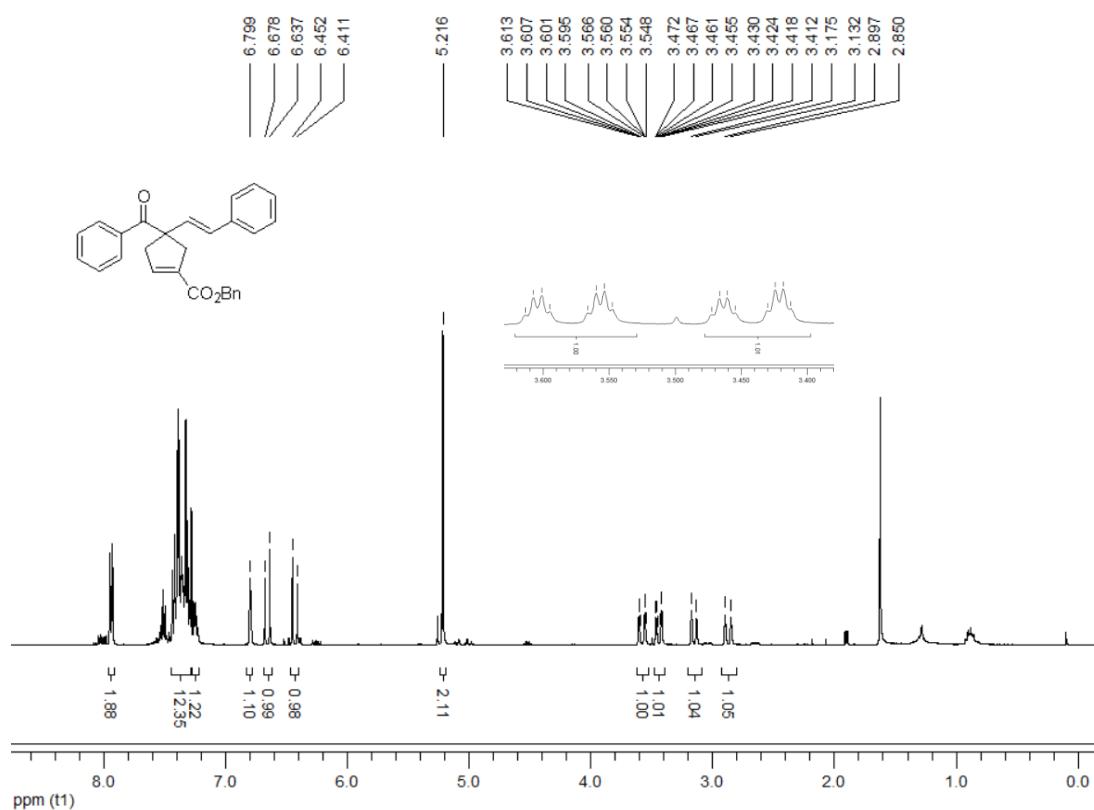
7.49 (t, J = 7.4 Hz, 1H), 7.43-7.29 (m, 8H), 7.27-7.20 (m, 2H), 6.78 (t, J = 2.2 Hz, 1H), 5.21 (dd, J = 14.4 Hz, J = 12.8 Hz, 2H), 3.05 (d, J = 2.4 Hz, 1H), 2.90 (t, J = 2.2 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 219.4, 207.7, 163.9, 150.8, 142.5, 142.3, 136.1, 135.5, 135.4, 134.7, 133.3, 129.3, 129.1, 128.6, 128.4, 128.2, 128.1, 127.8, 124.4, 124.0, 120.7, 66.1, 55.1, 43.0, 42.2.

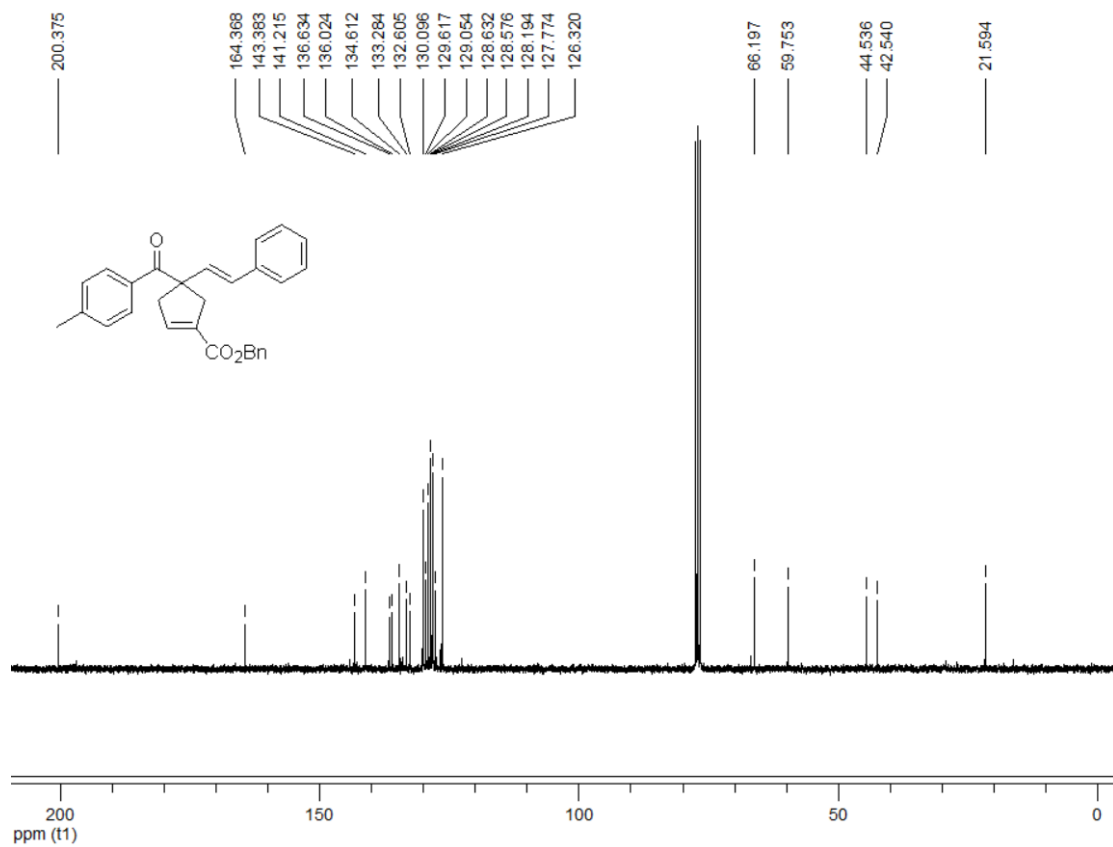
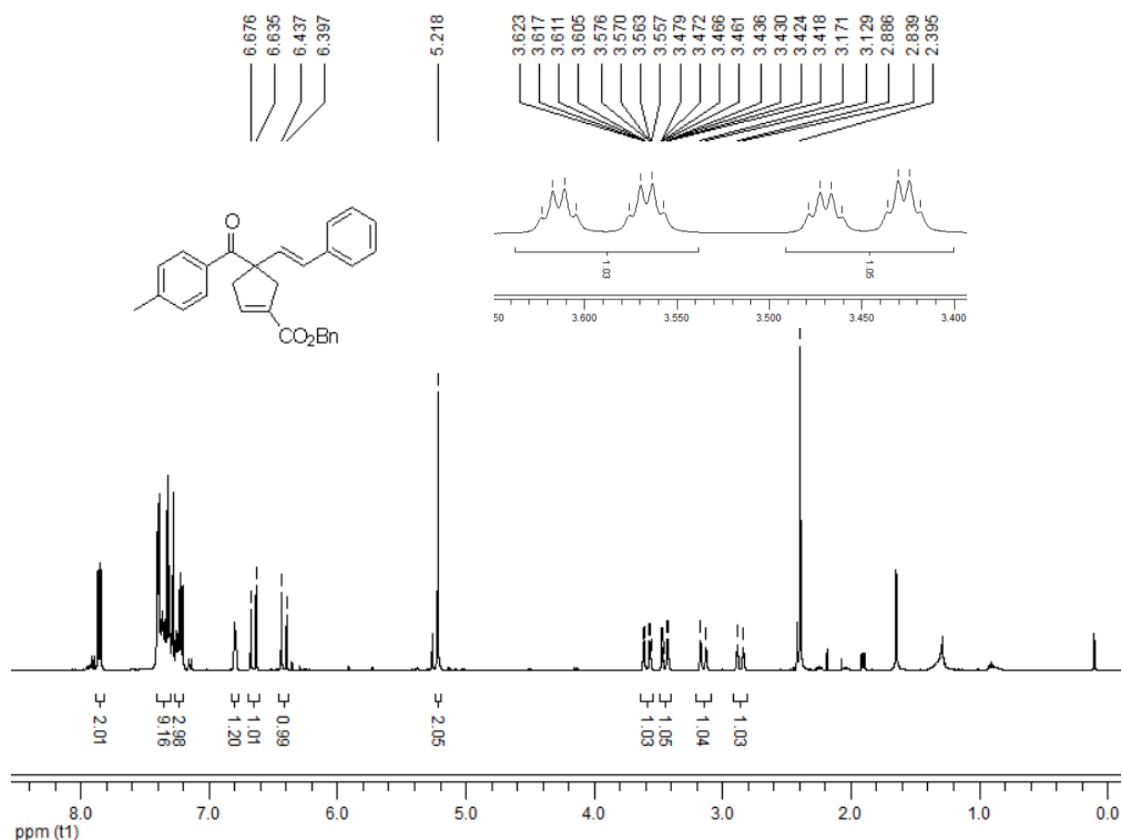
HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{22}\text{O}_3$ 429.1461, found: 429.1463.

7. NMR Spectrum

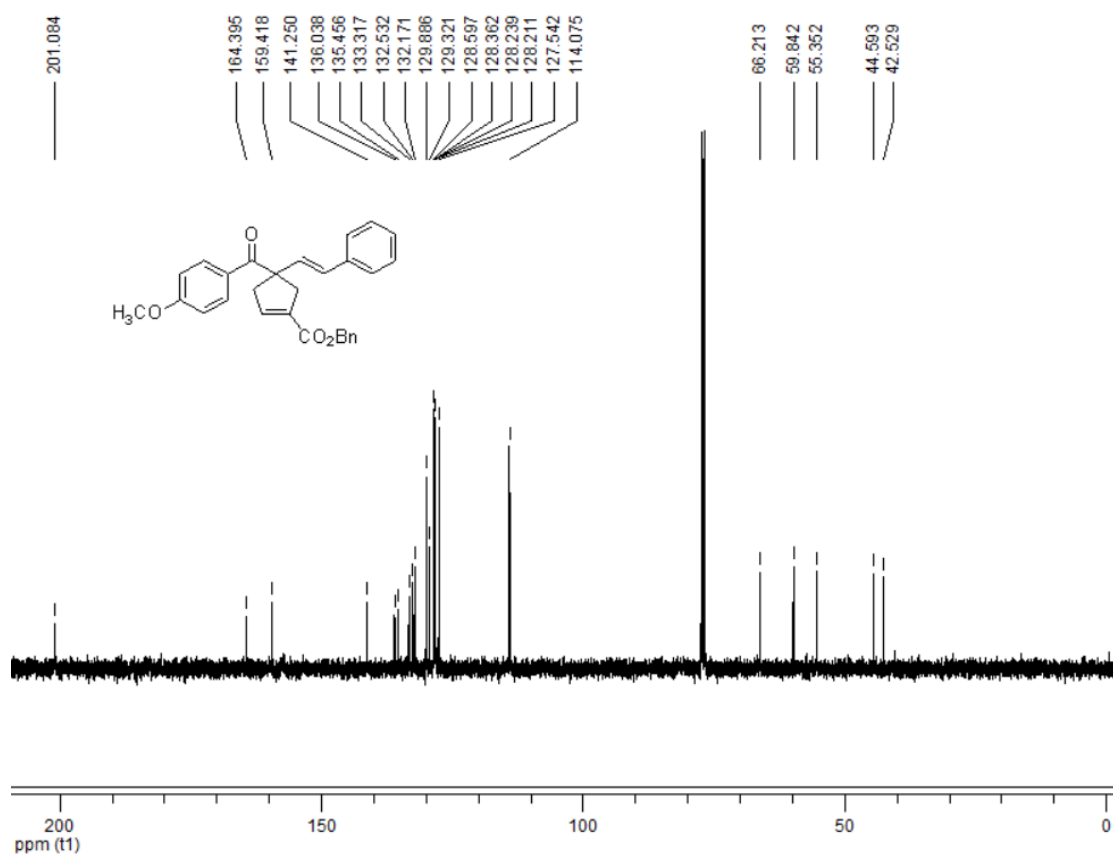
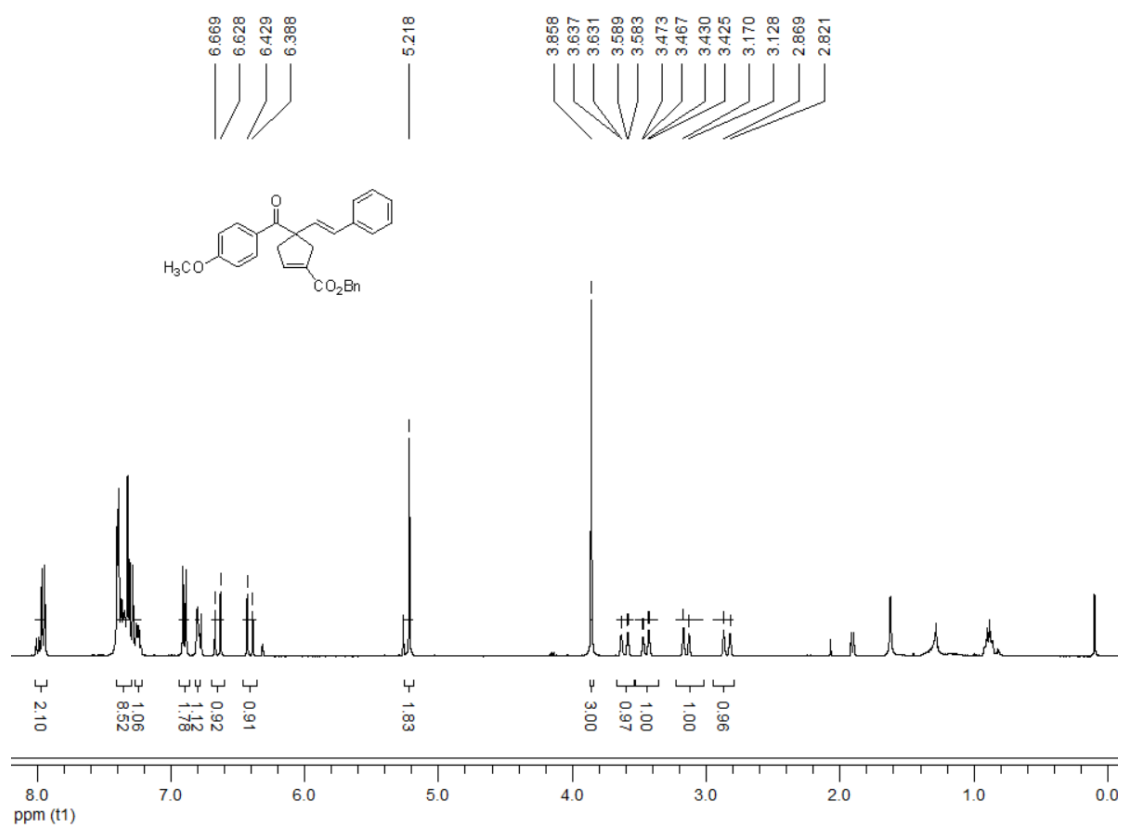
3a



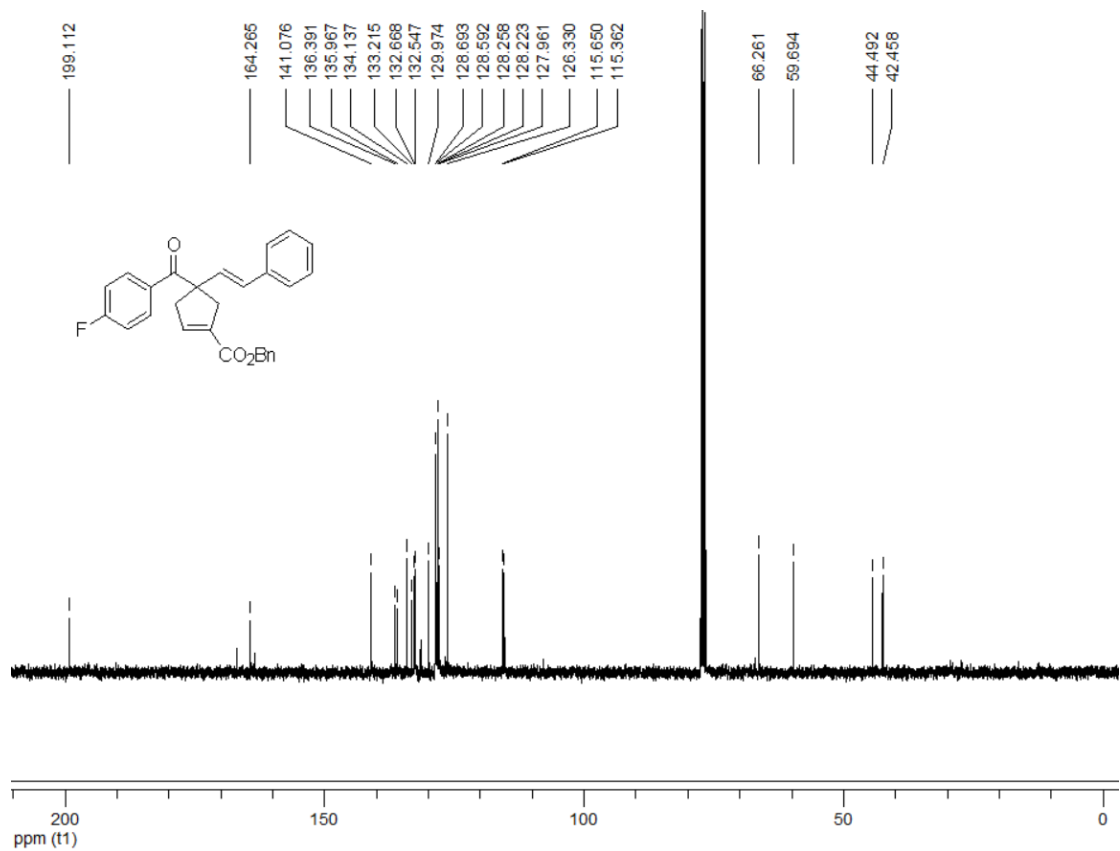
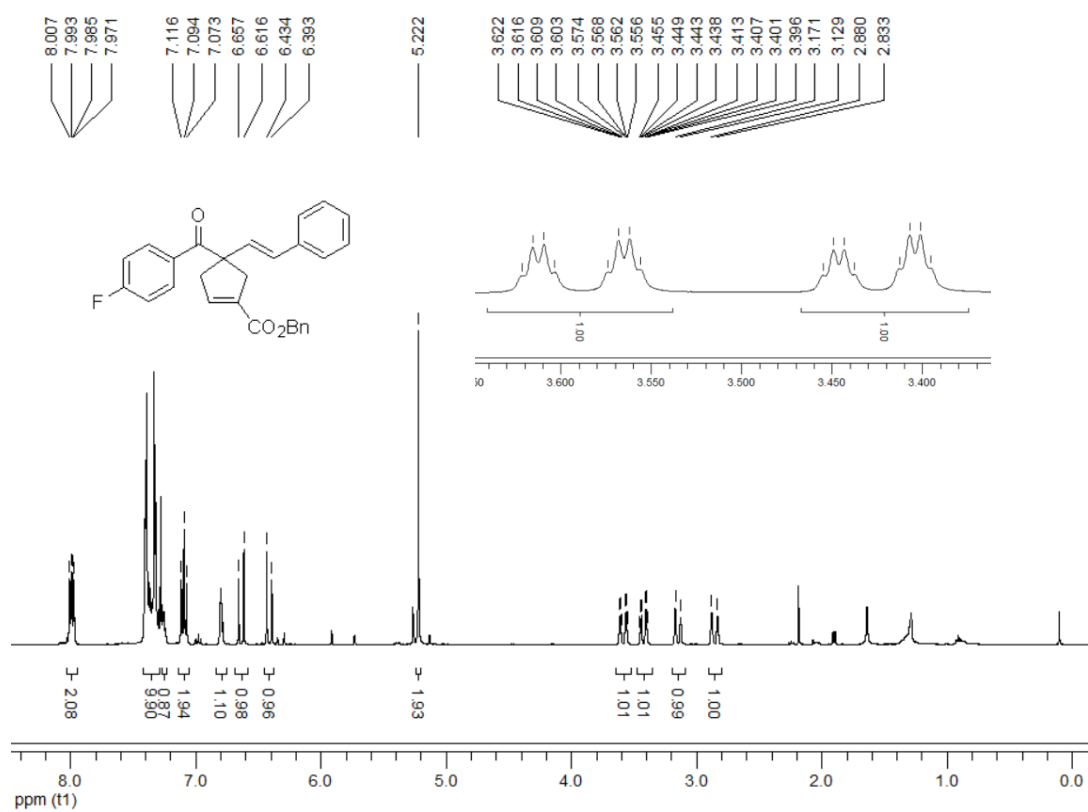
3b



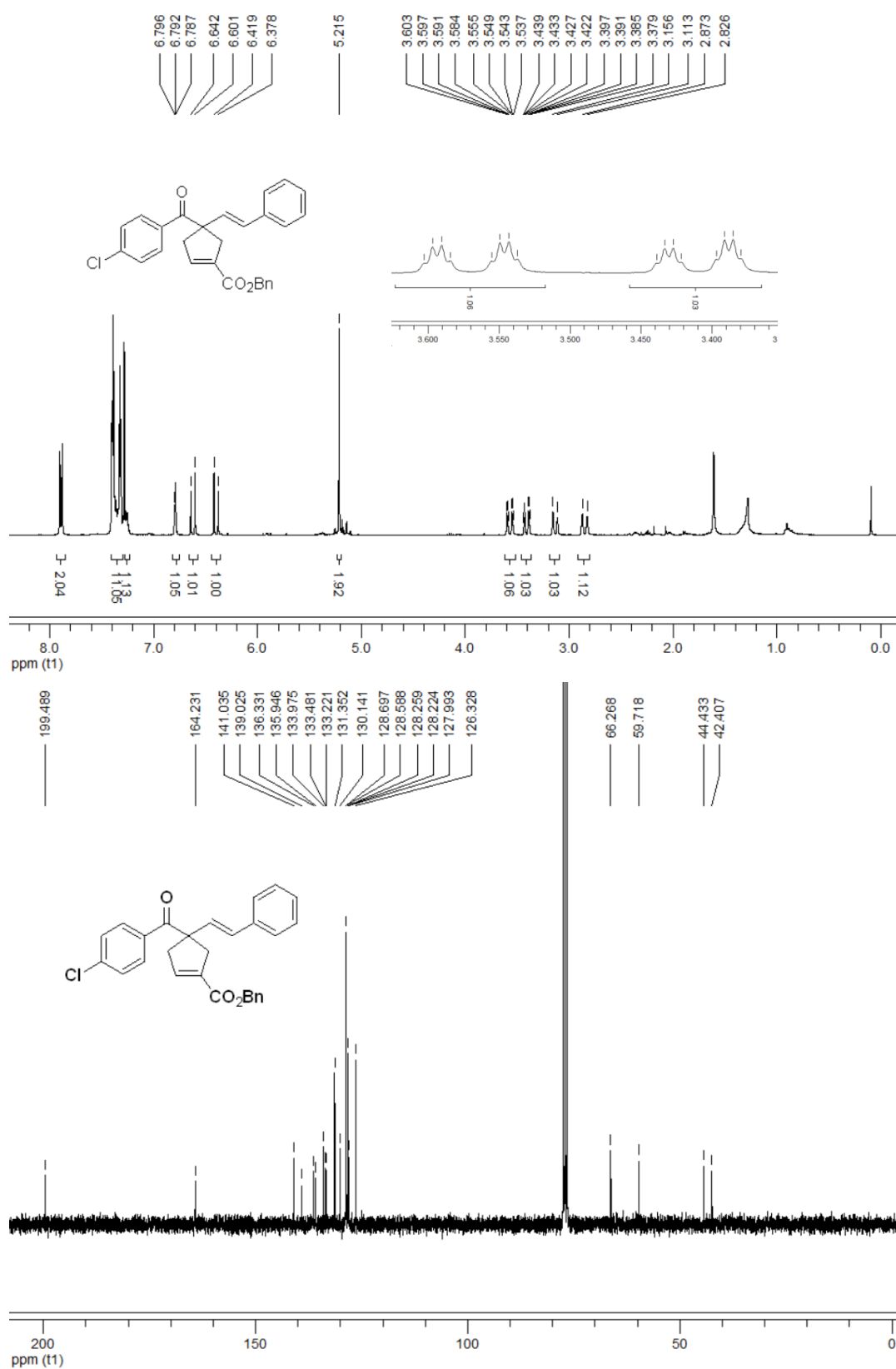
3c



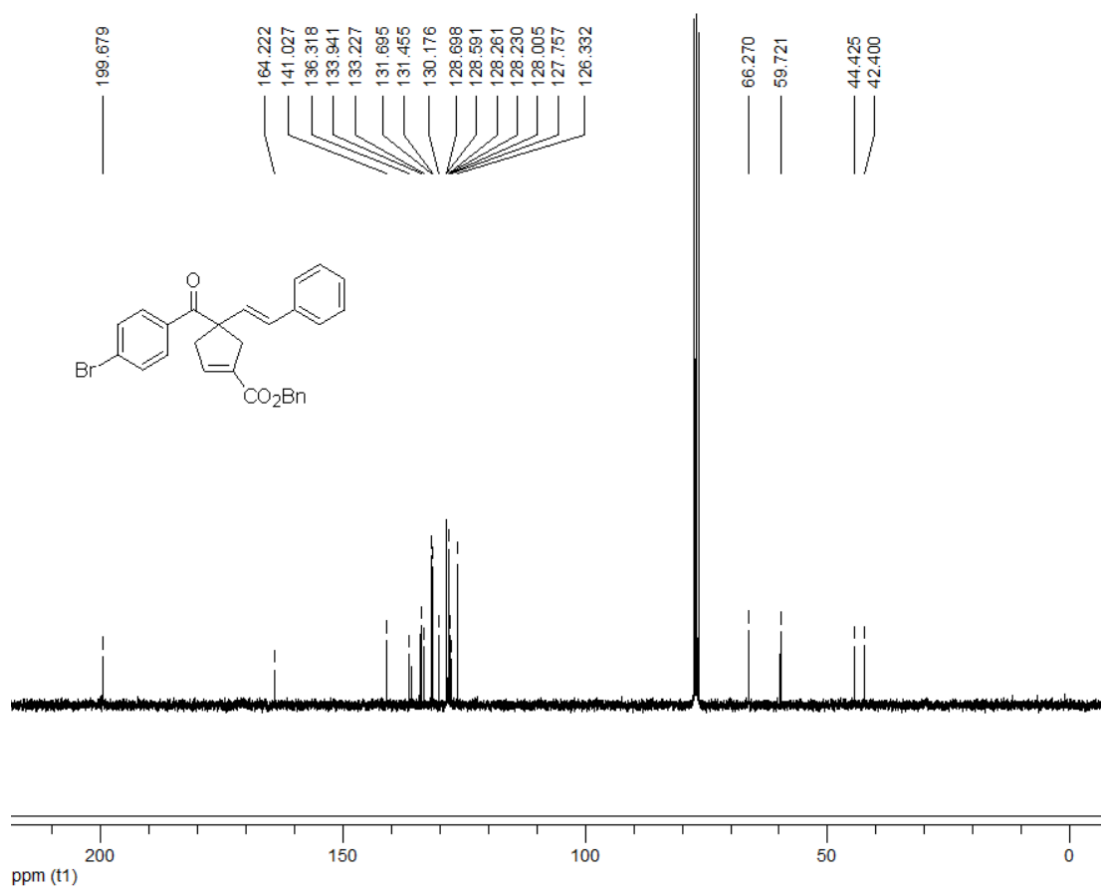
3d



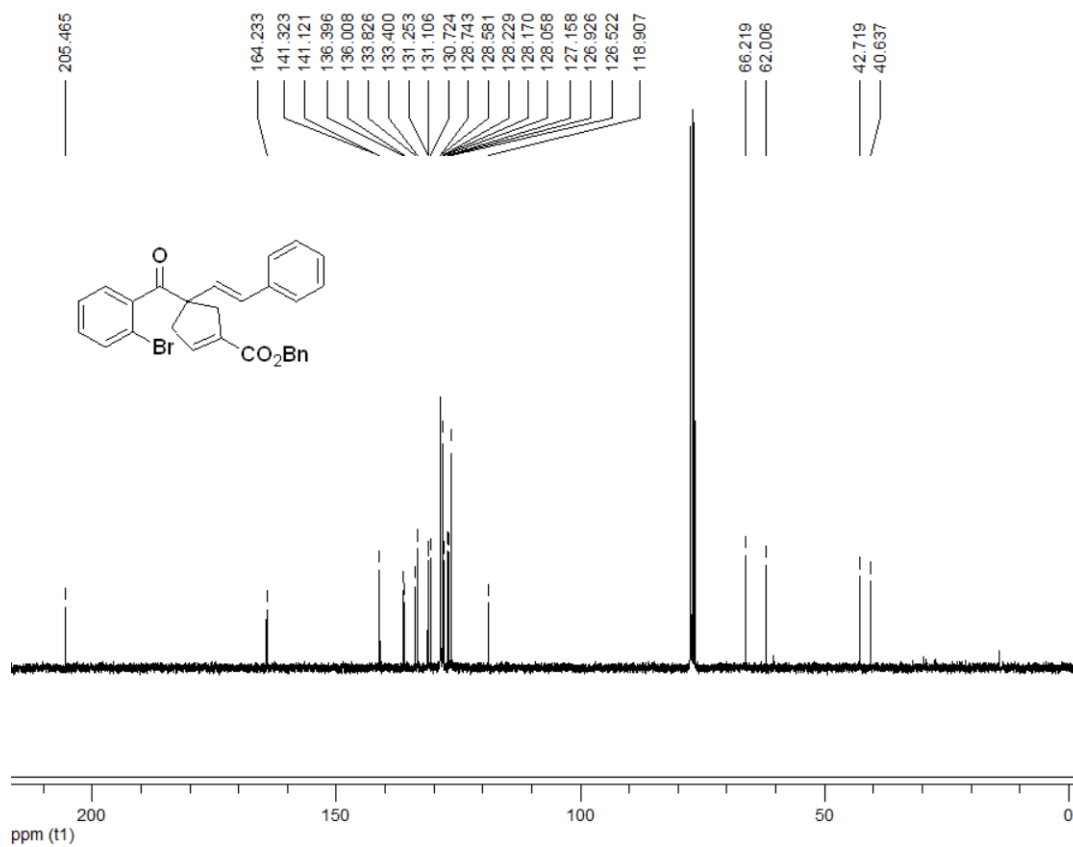
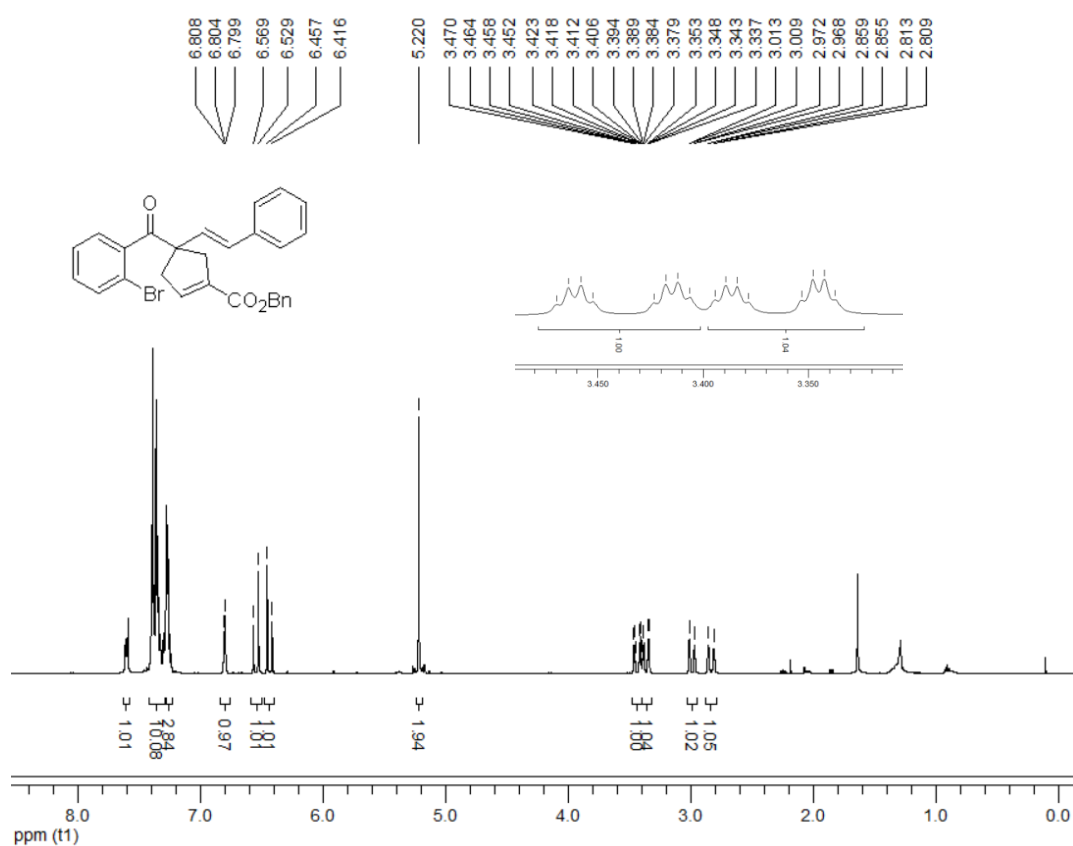
3e



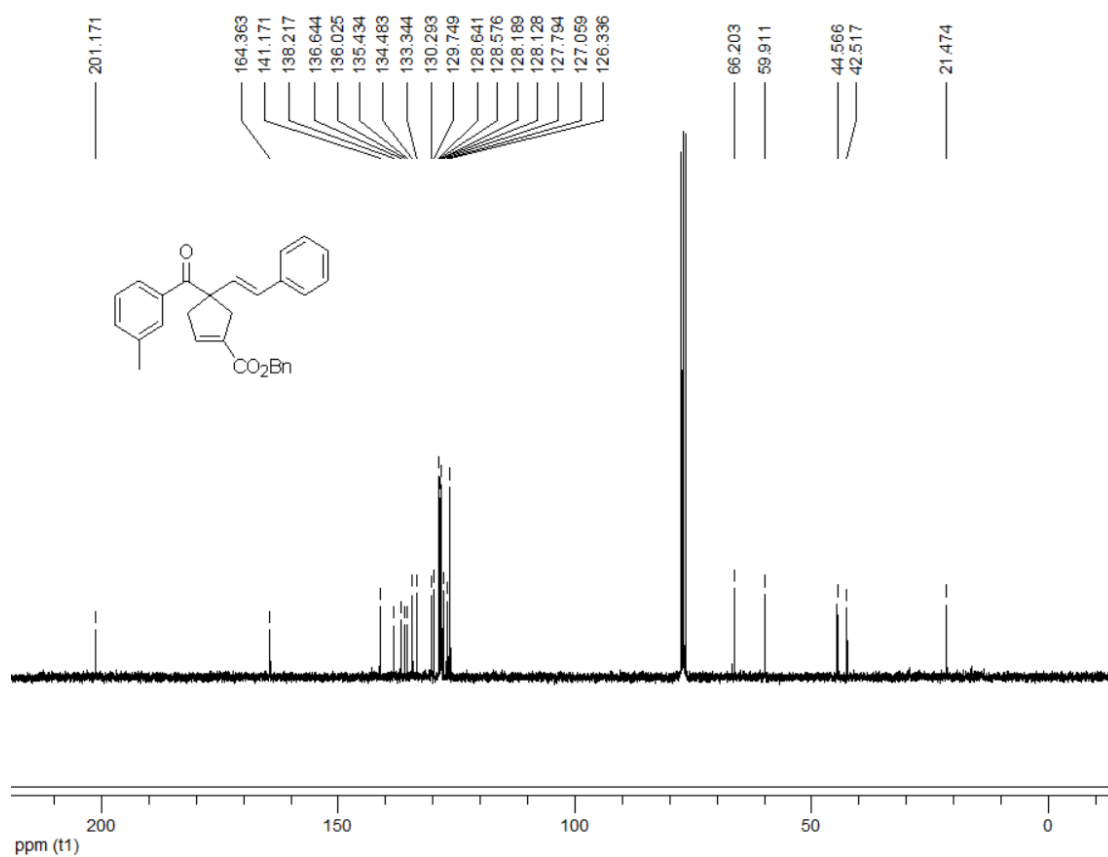
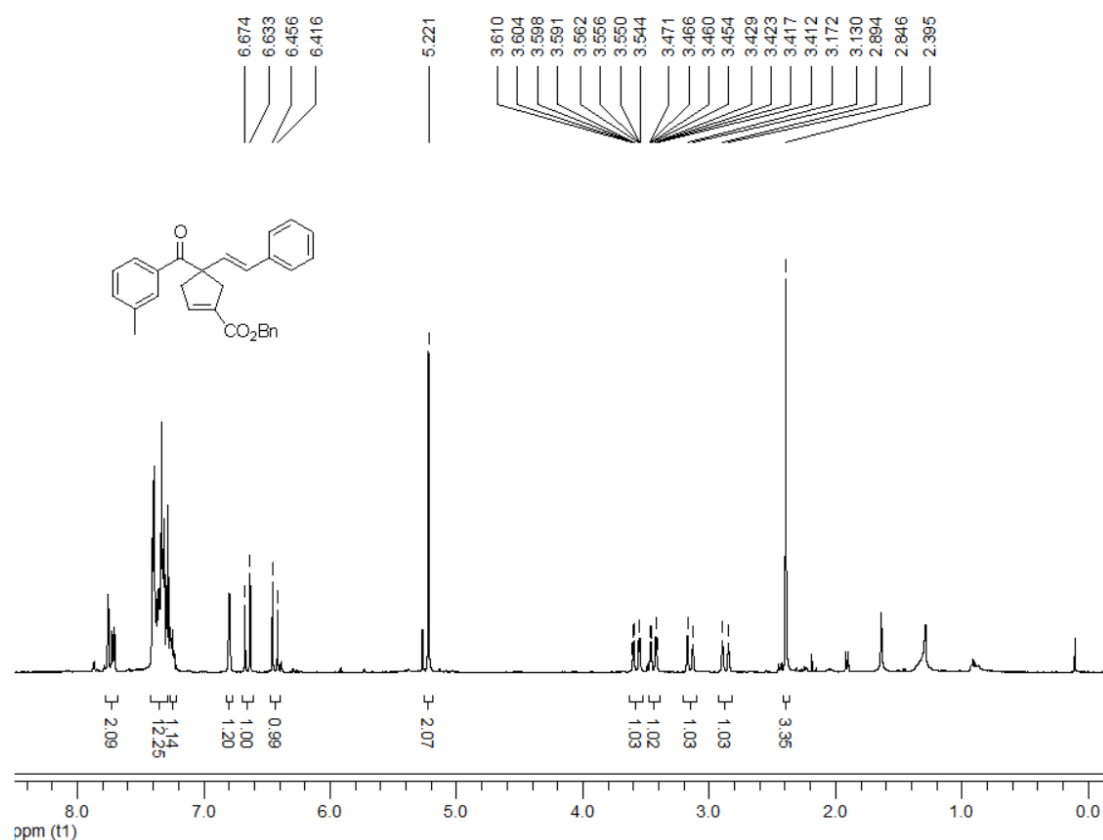
S22



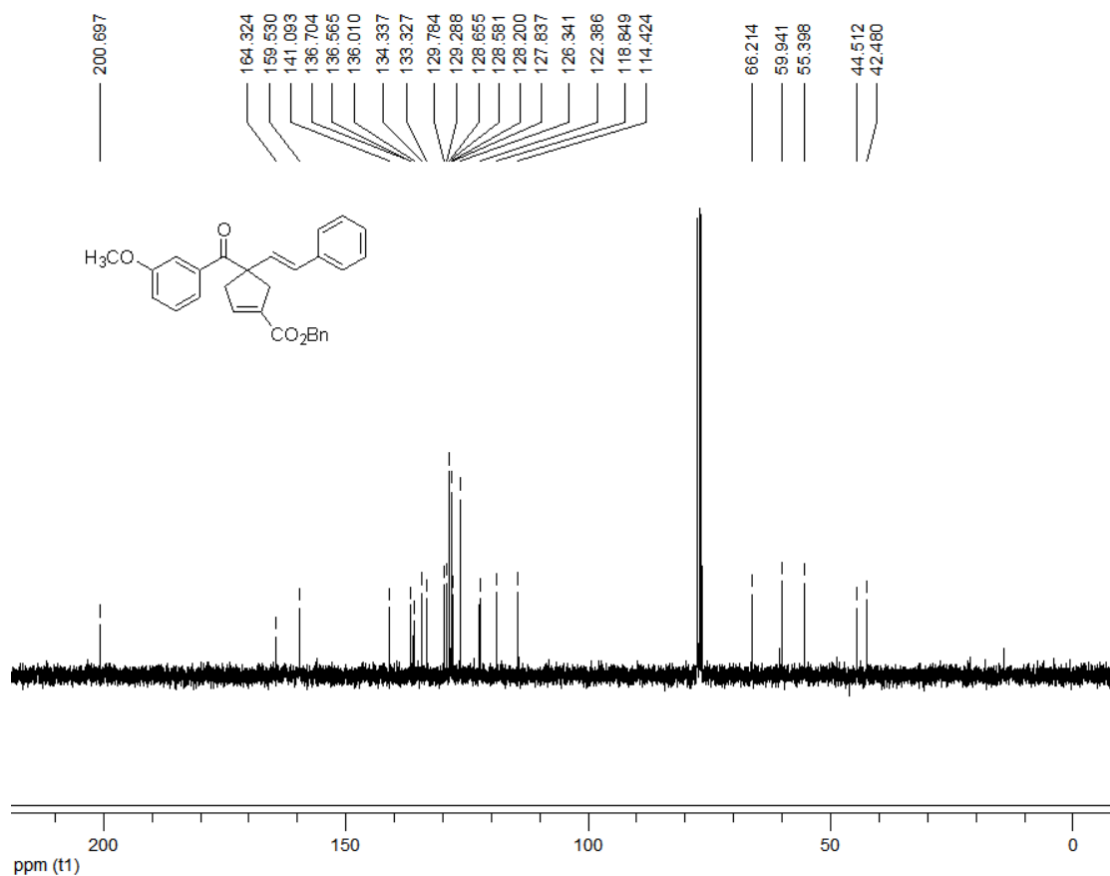
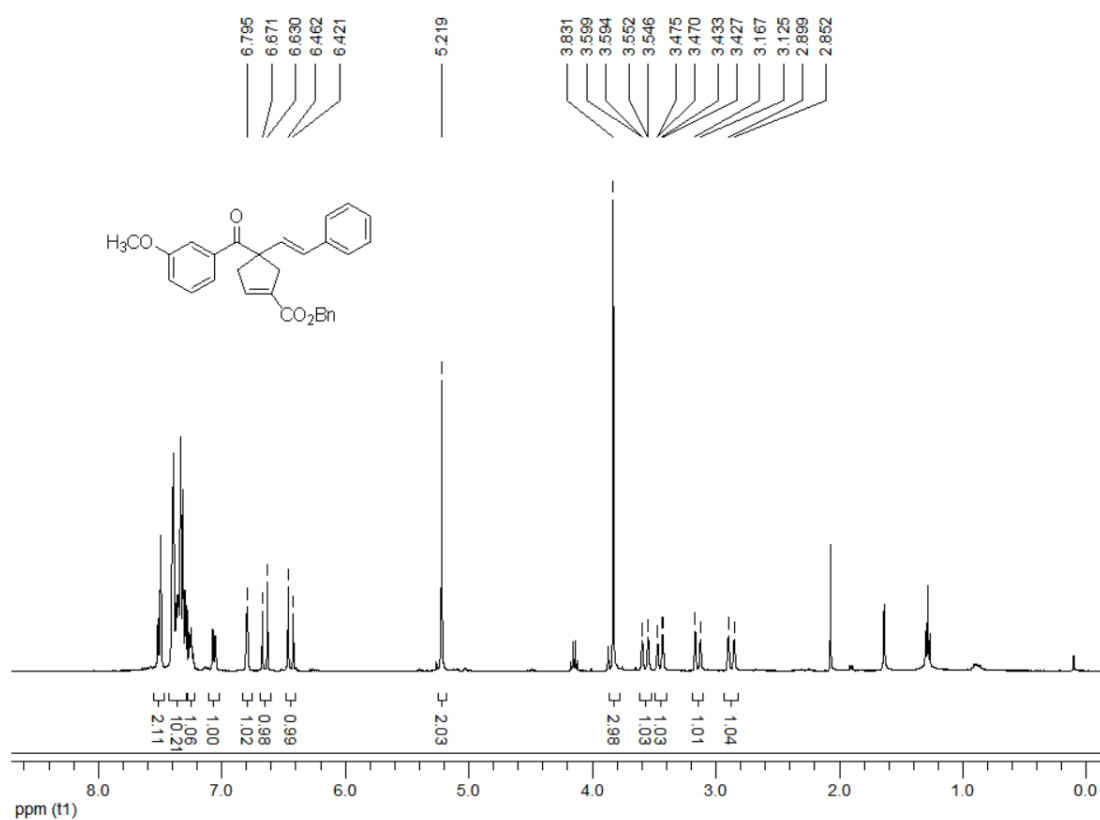
3g



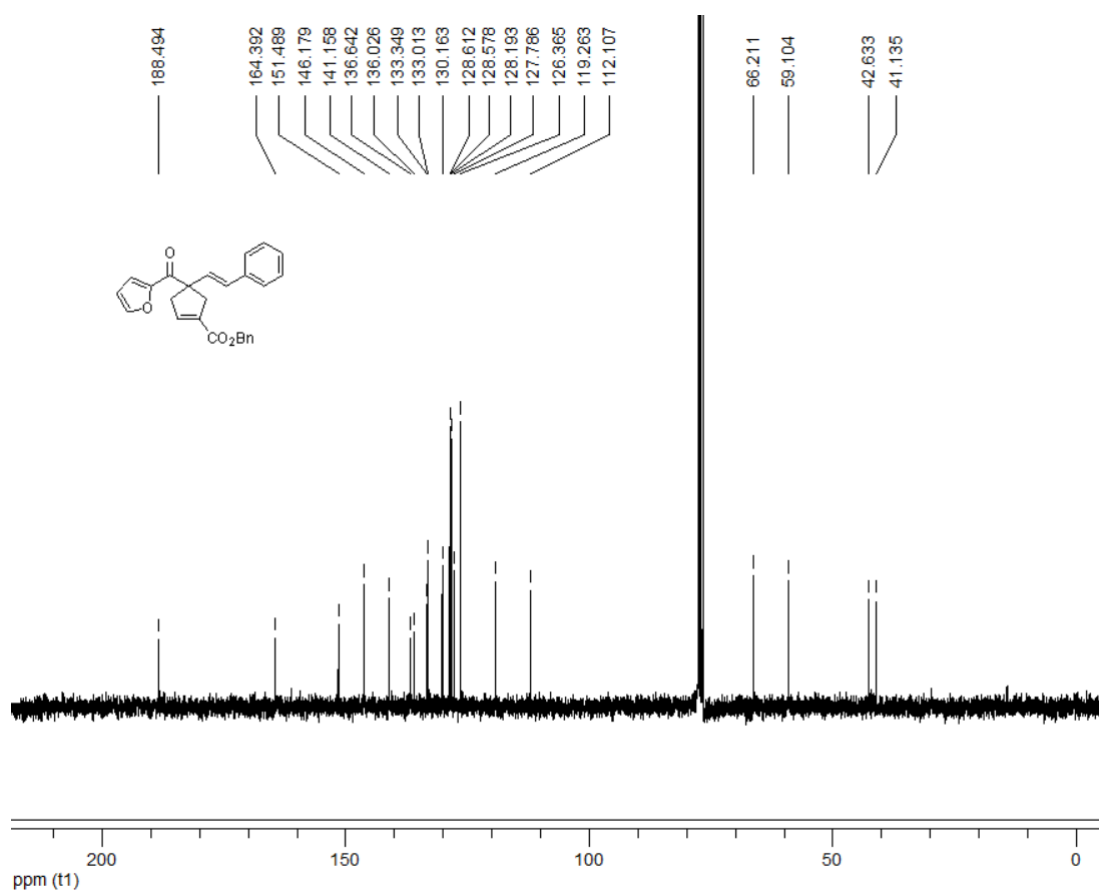
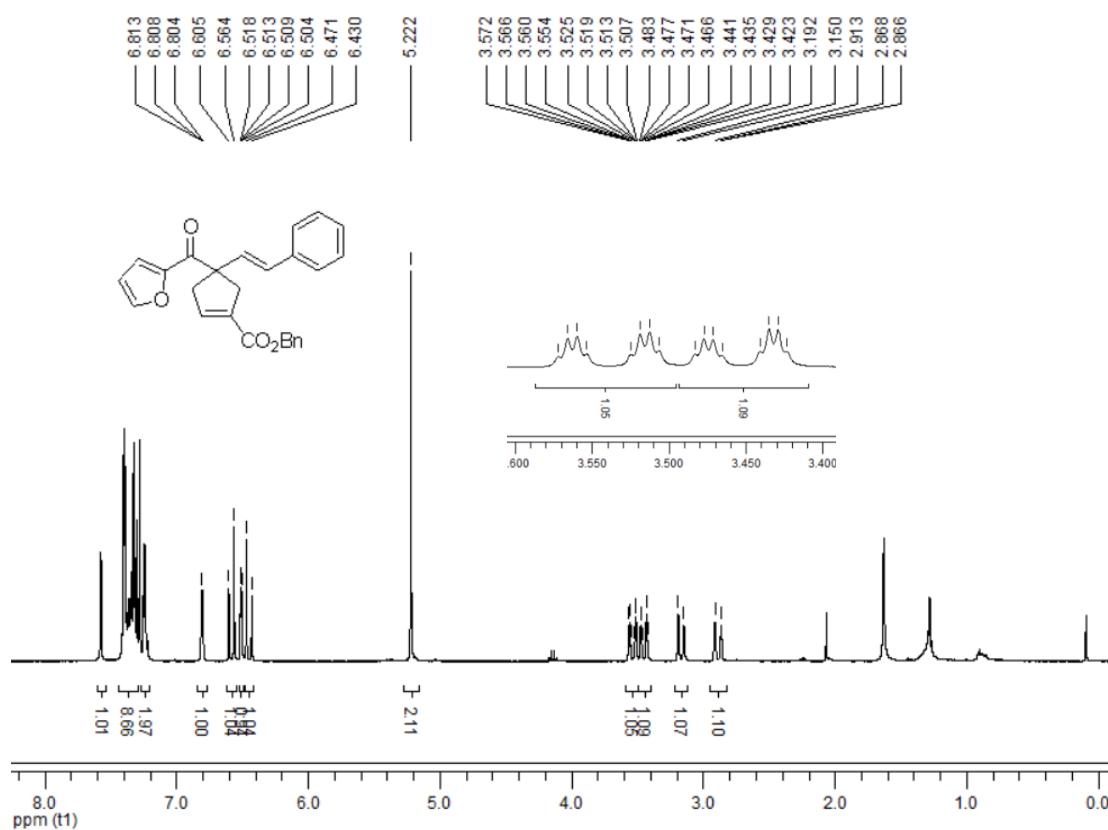
3h



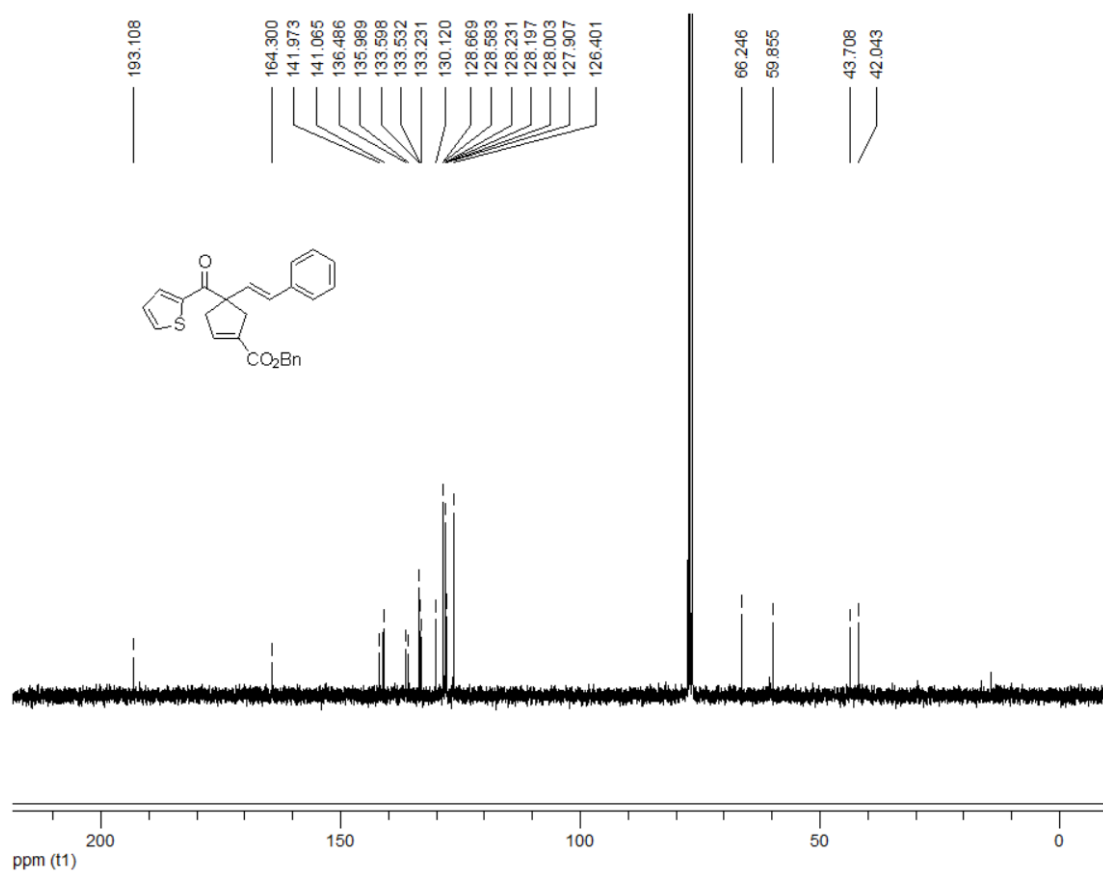
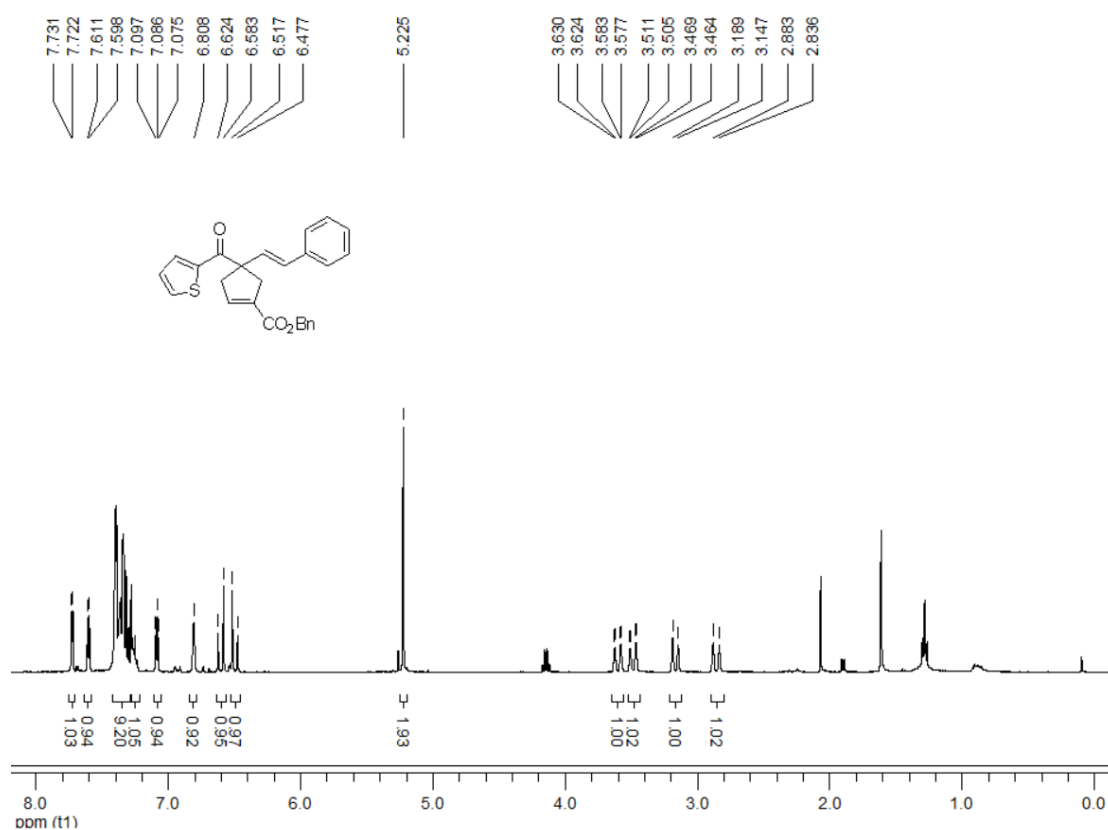
3i



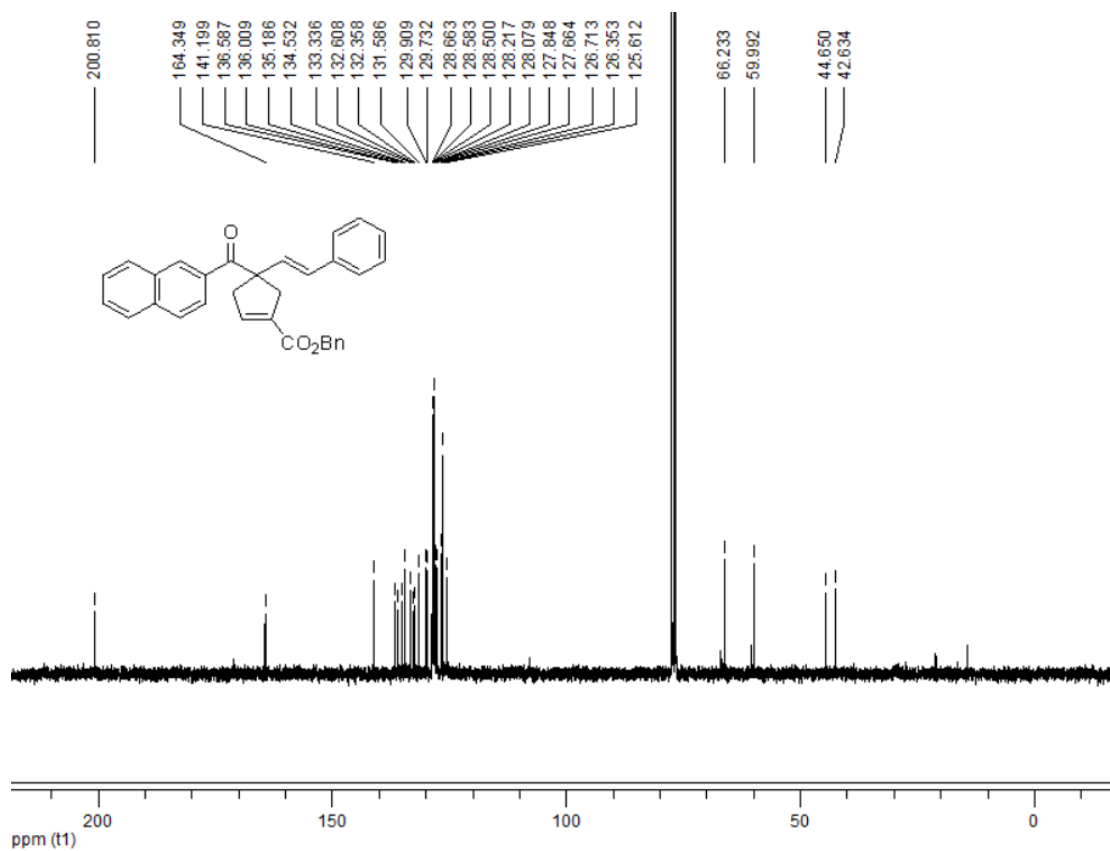
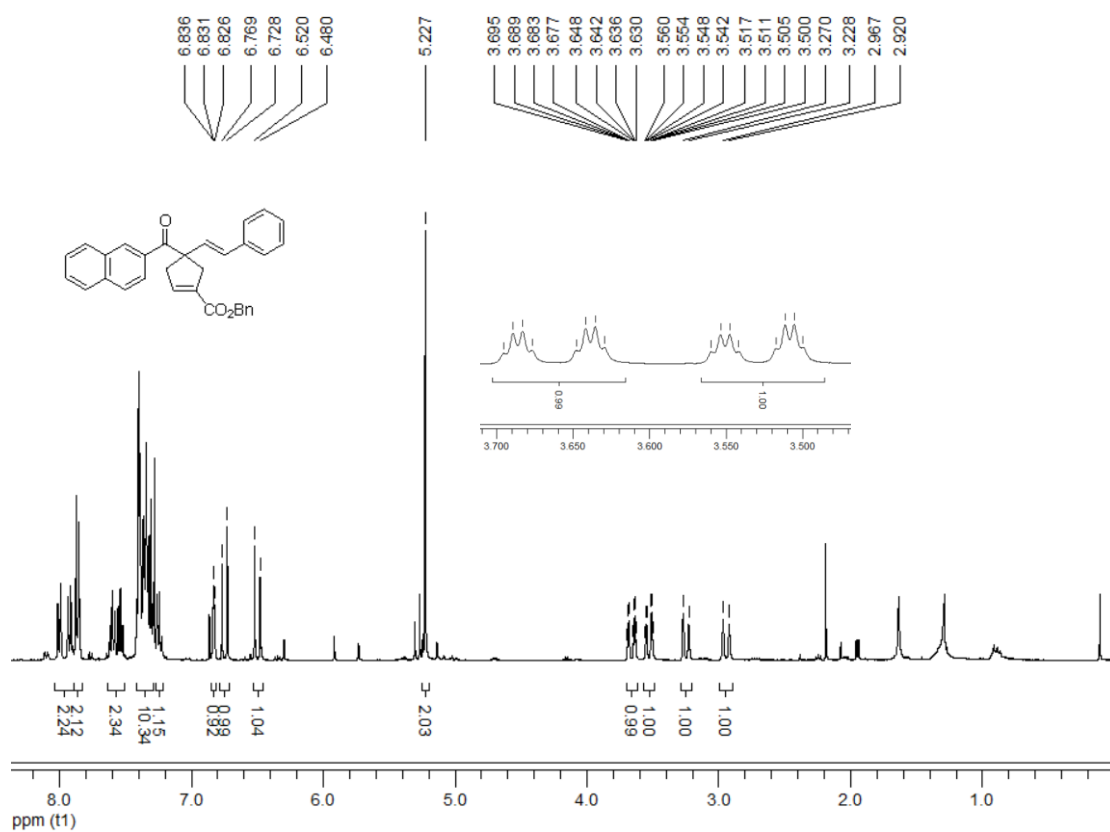
3j



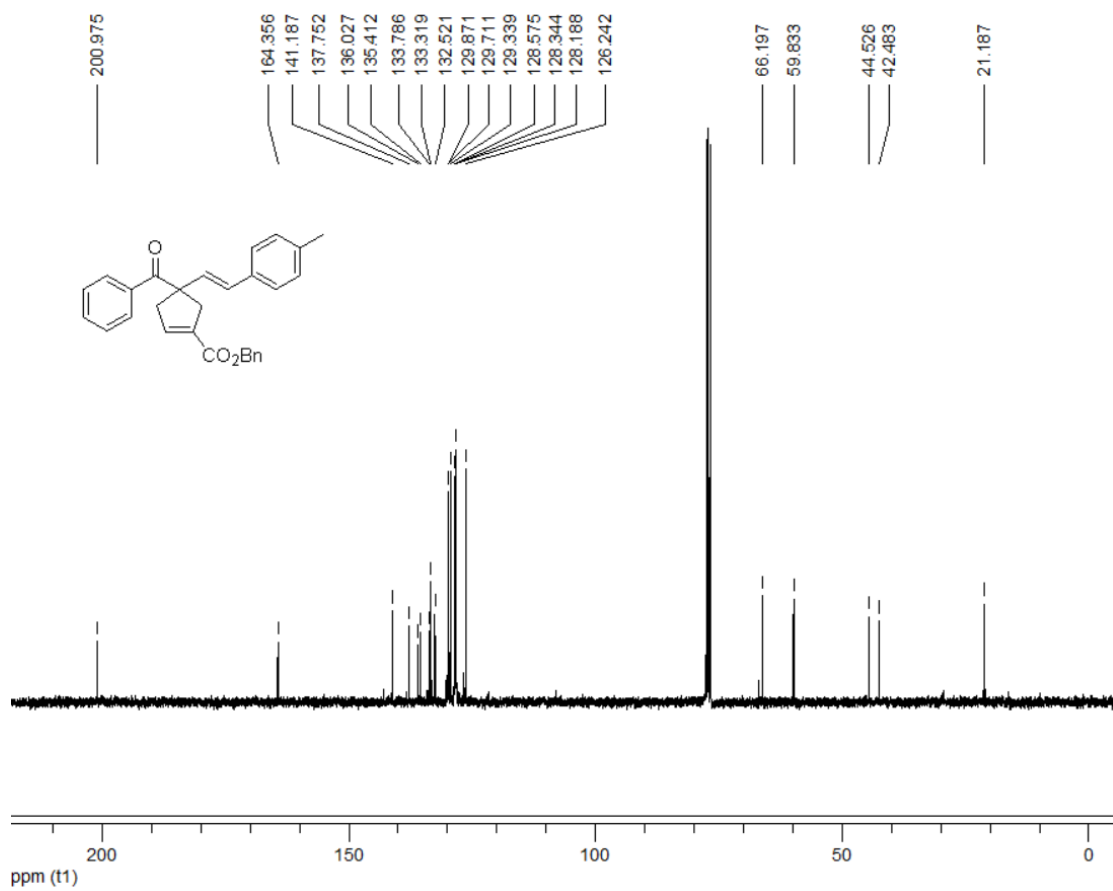
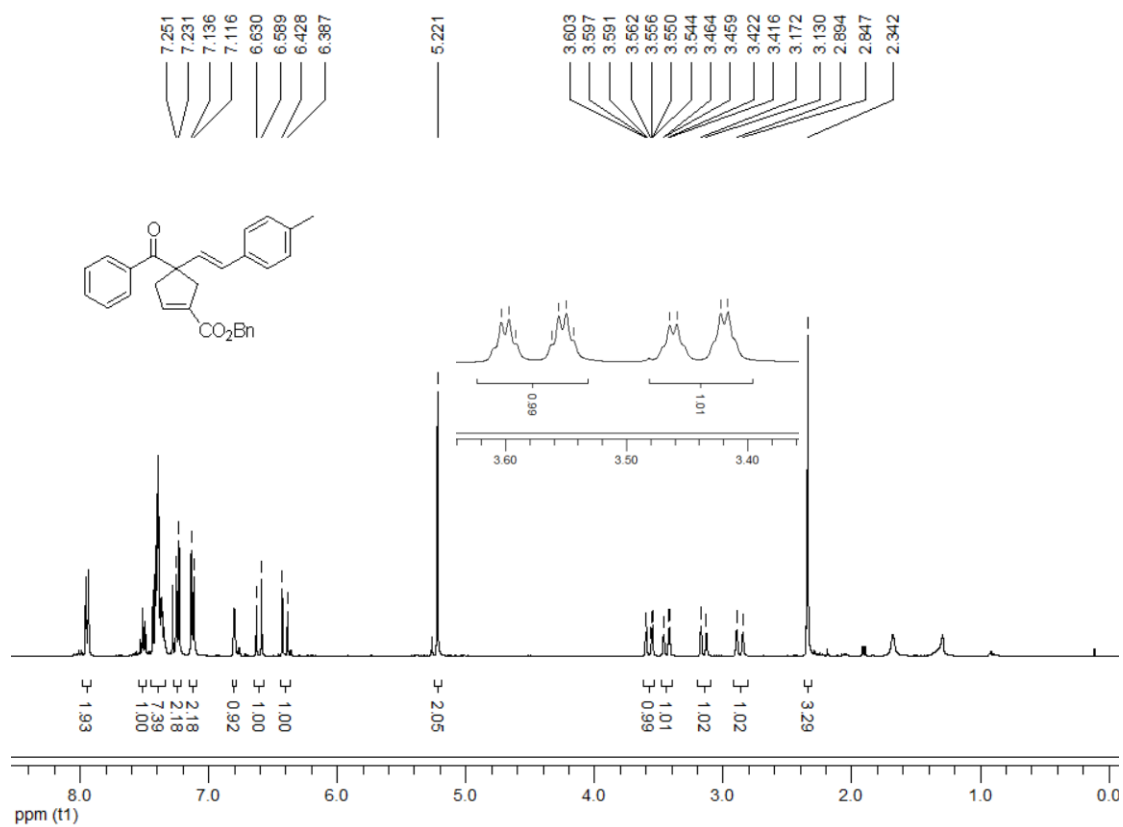
3k



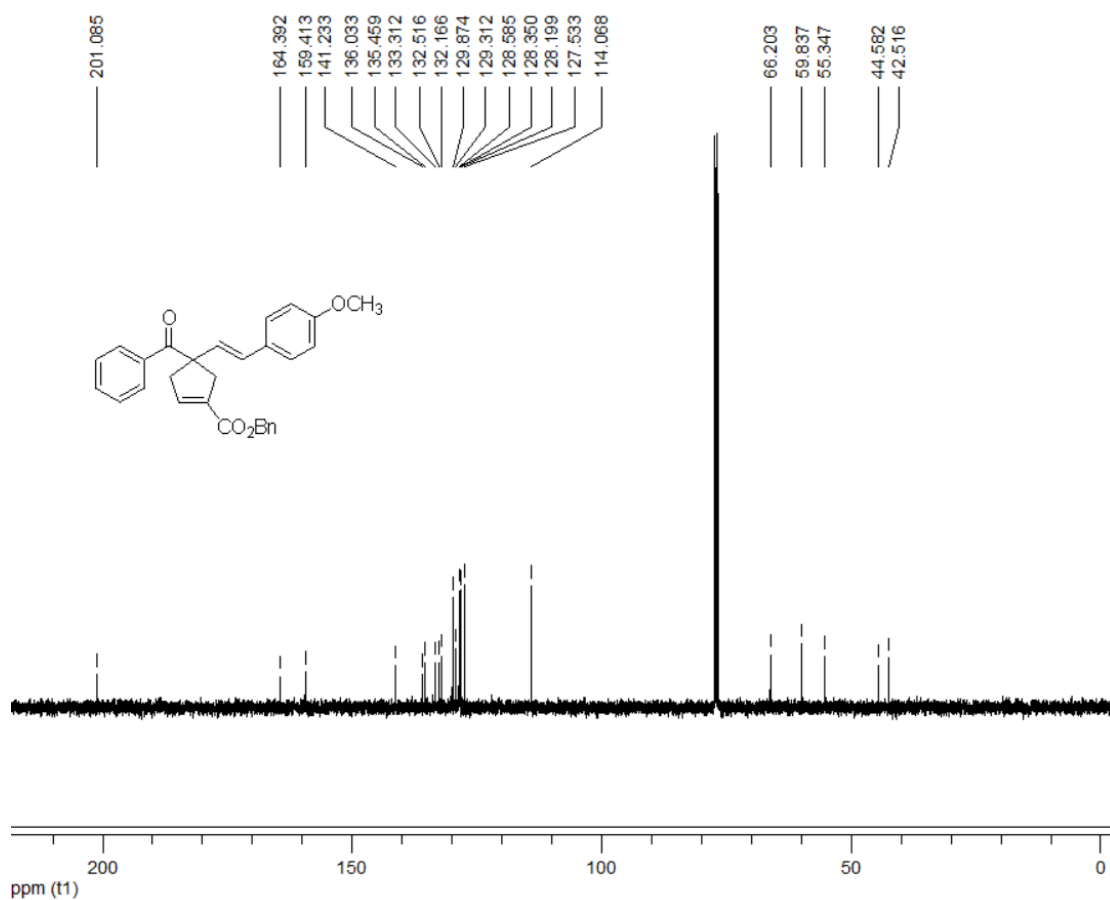
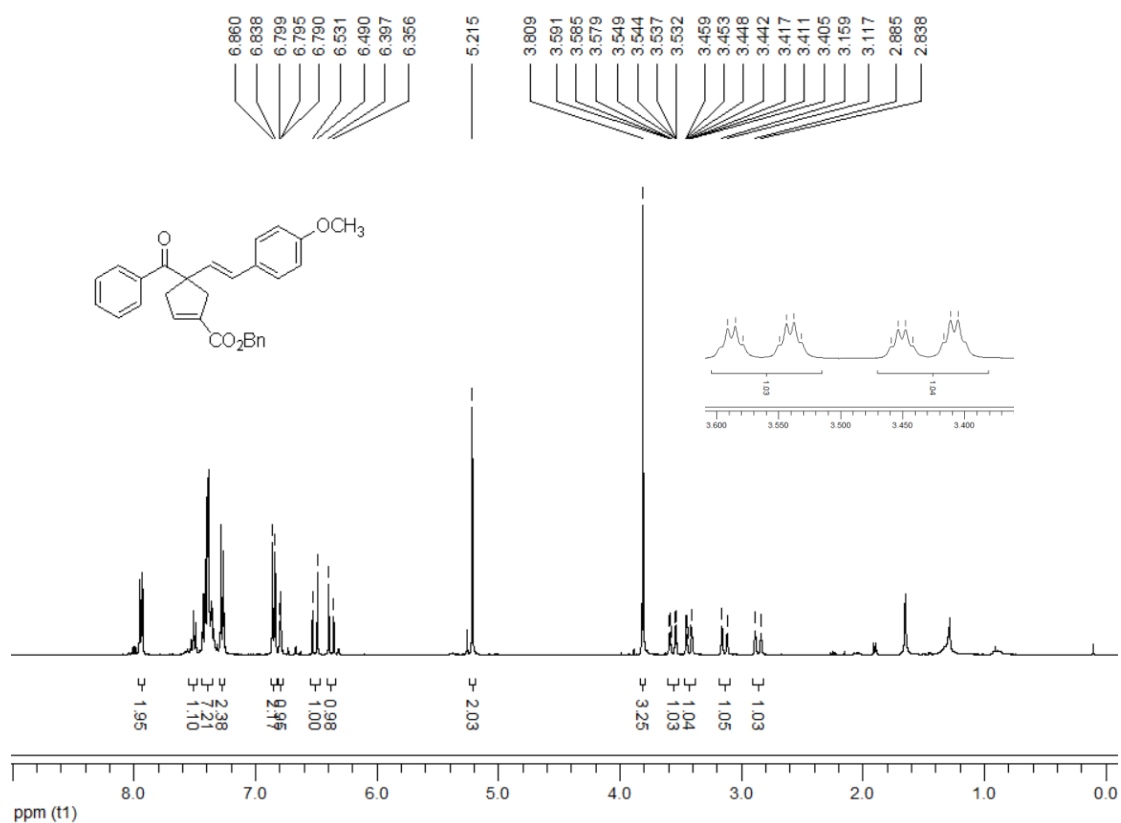
3l



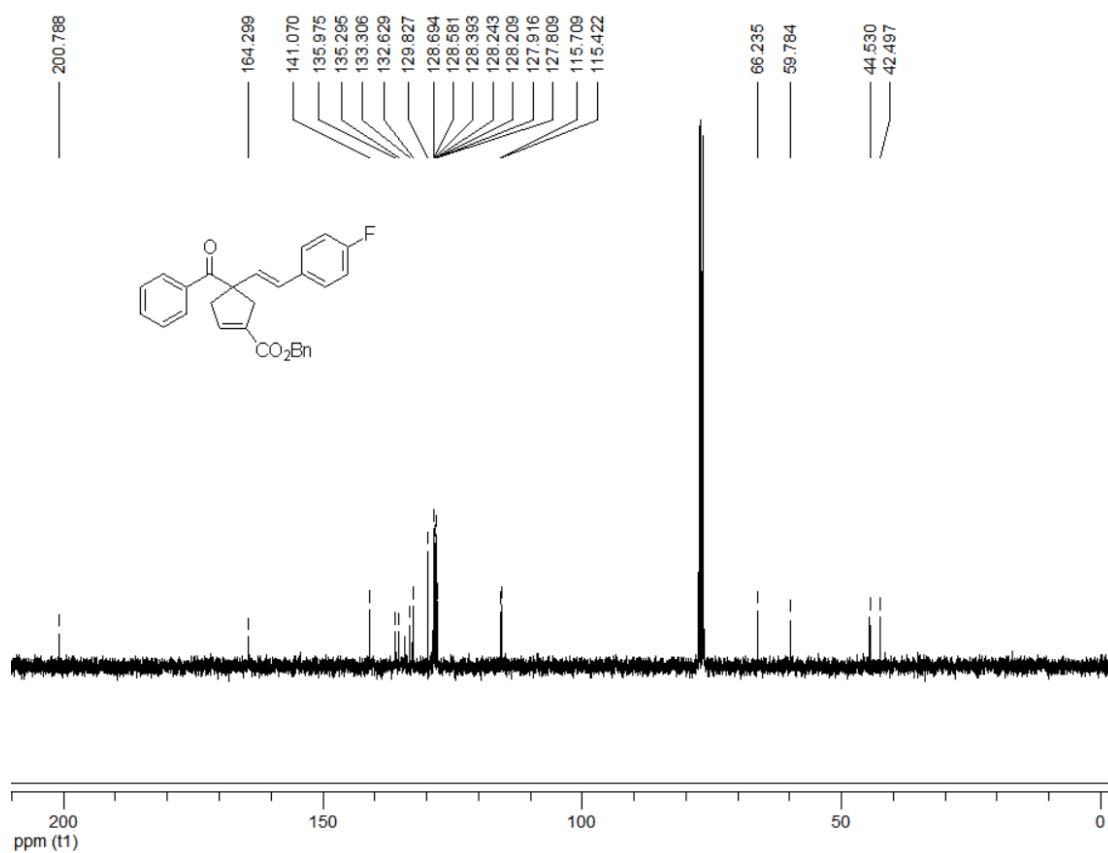
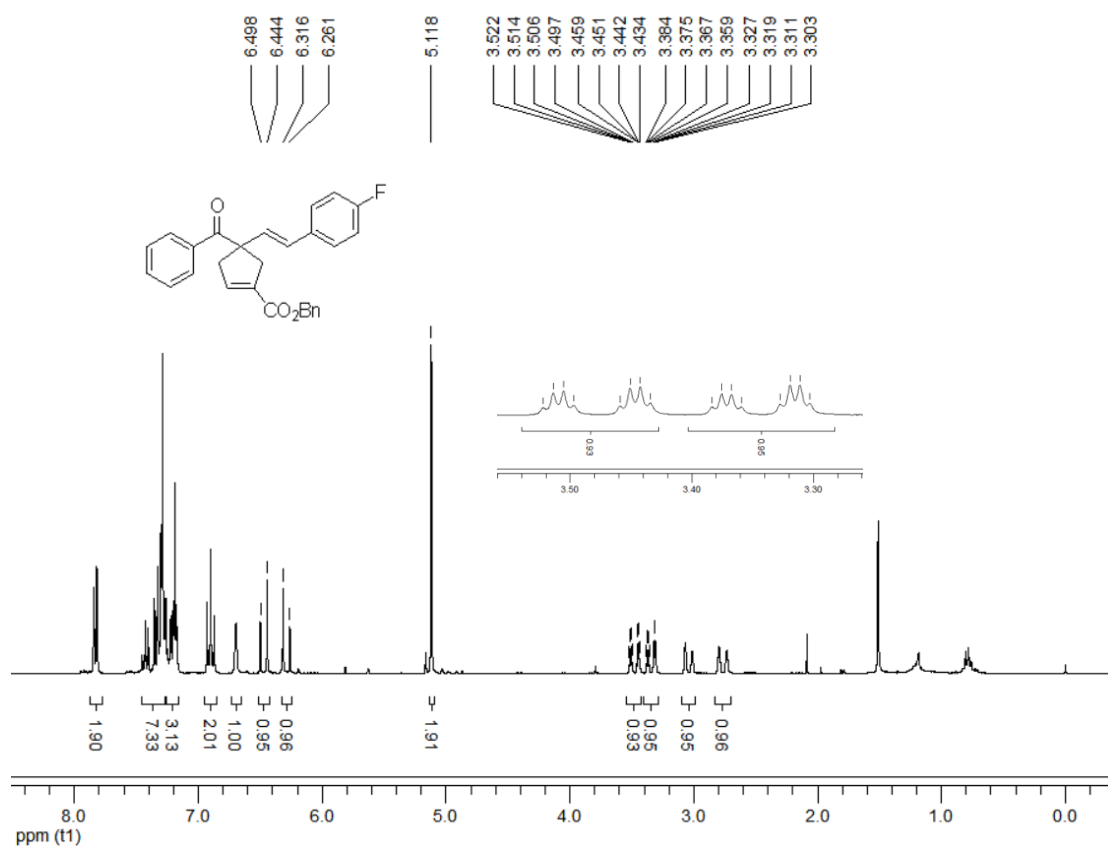
3m



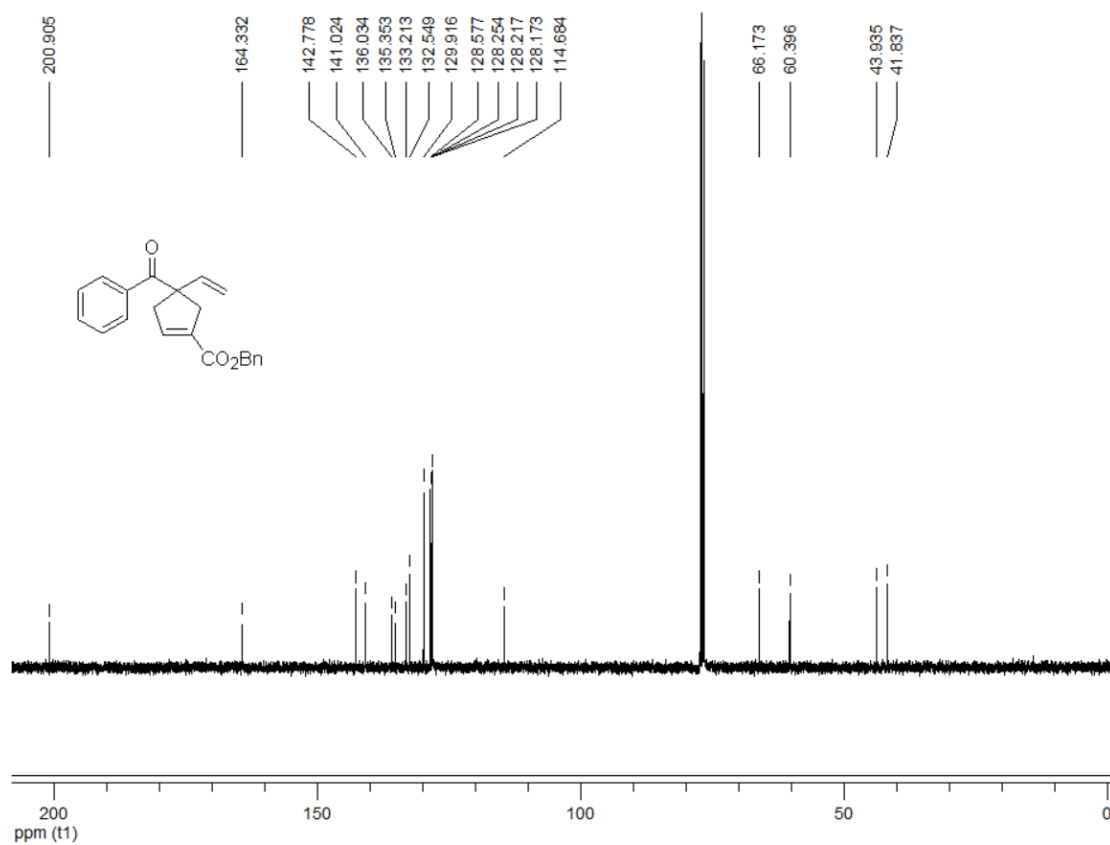
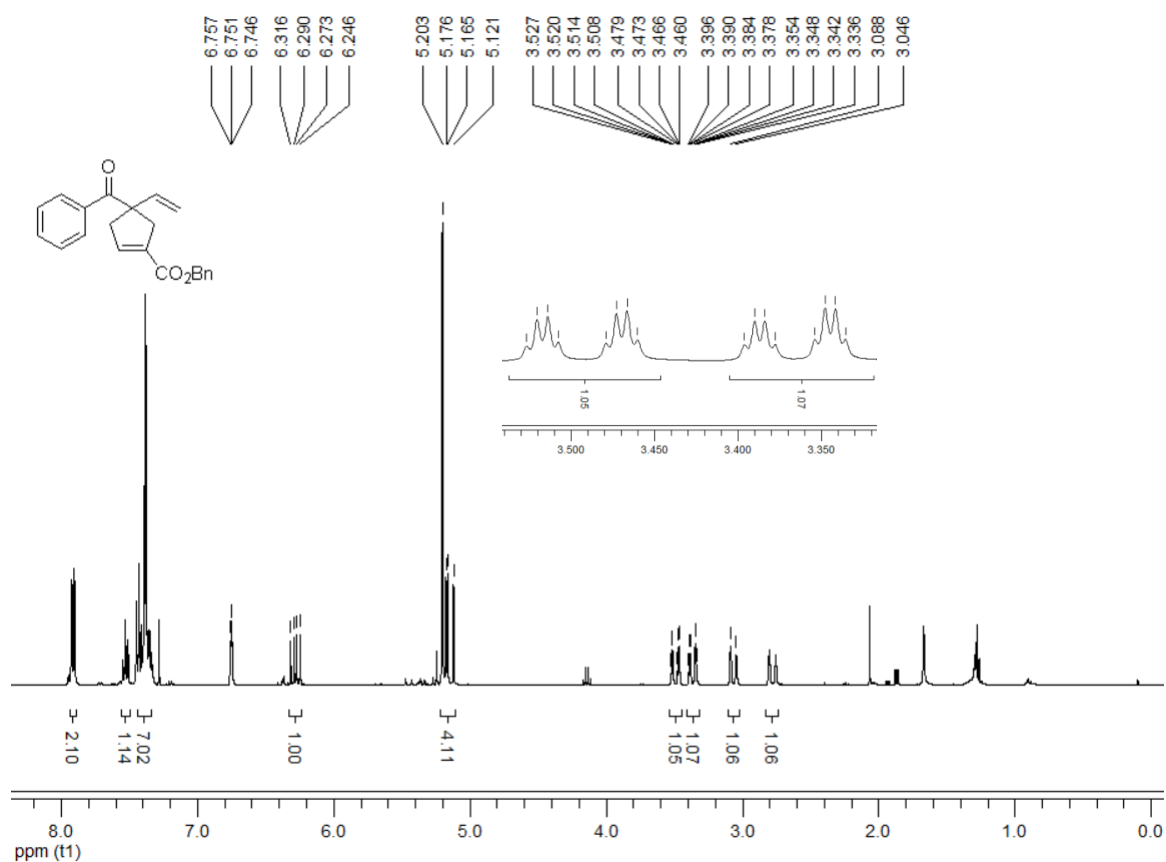
3n



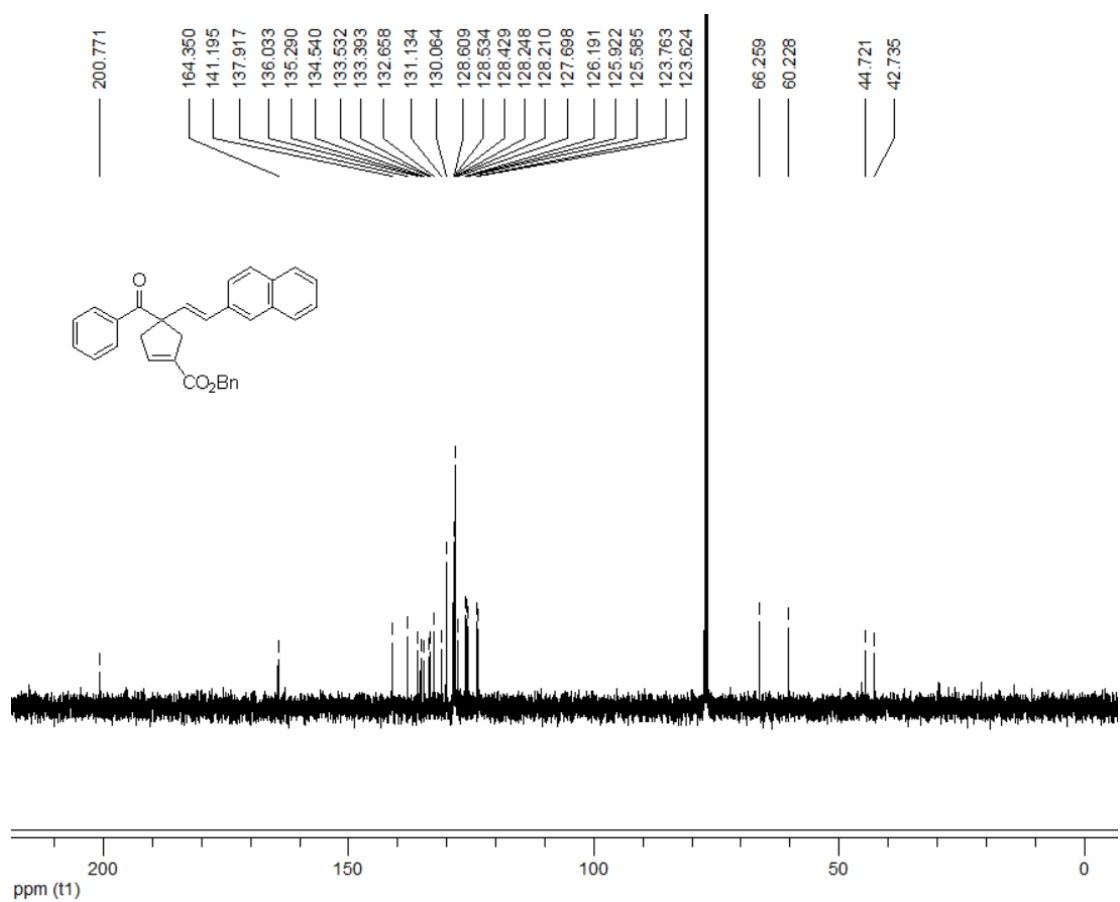
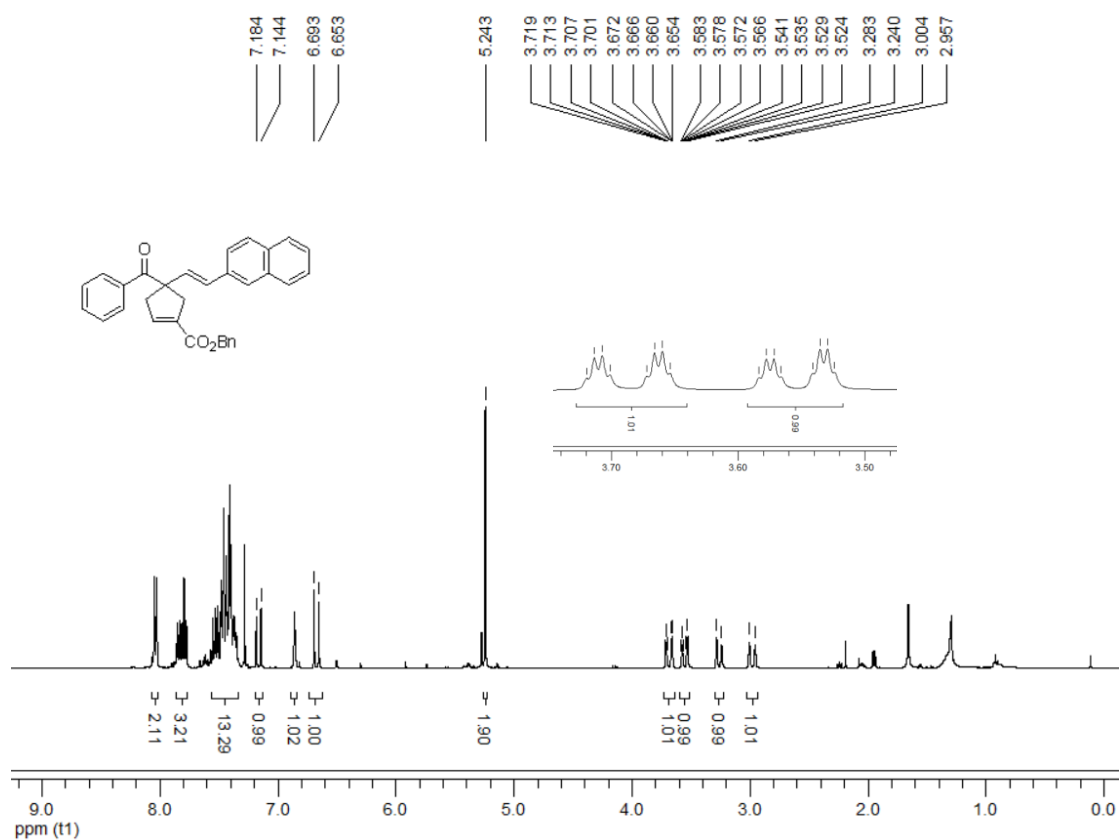
3o



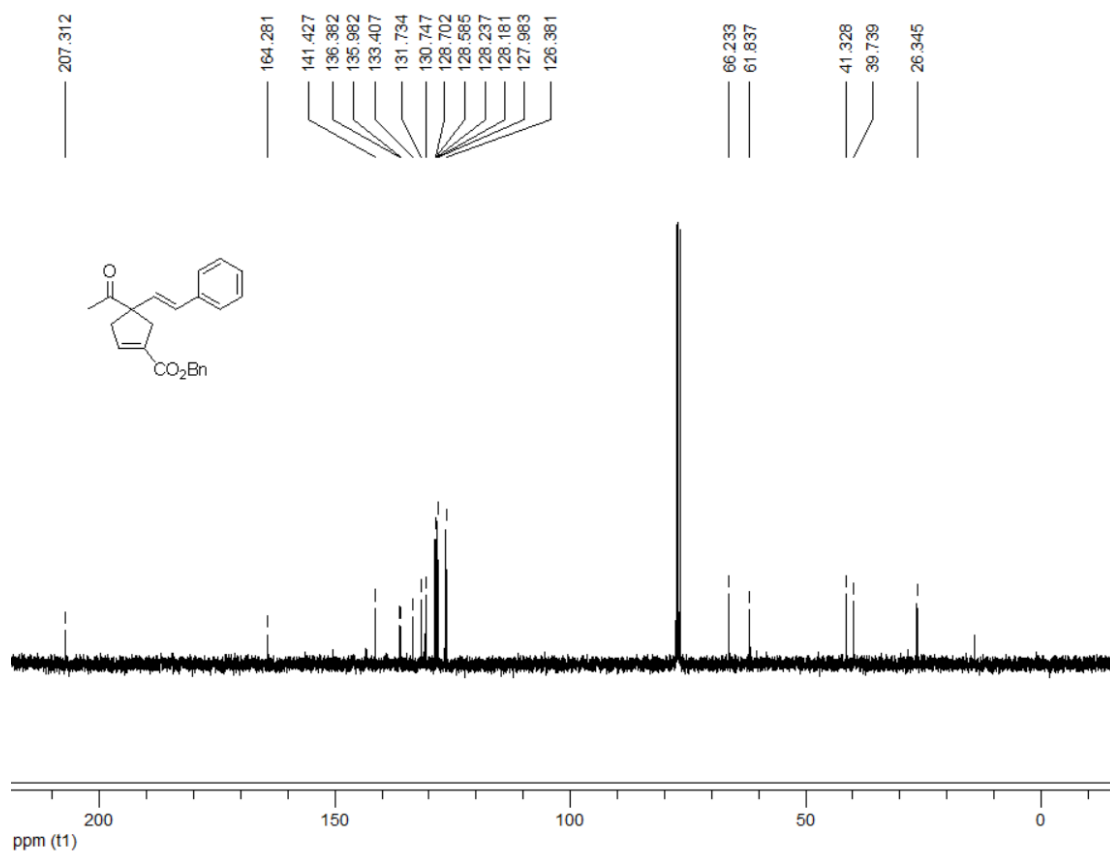
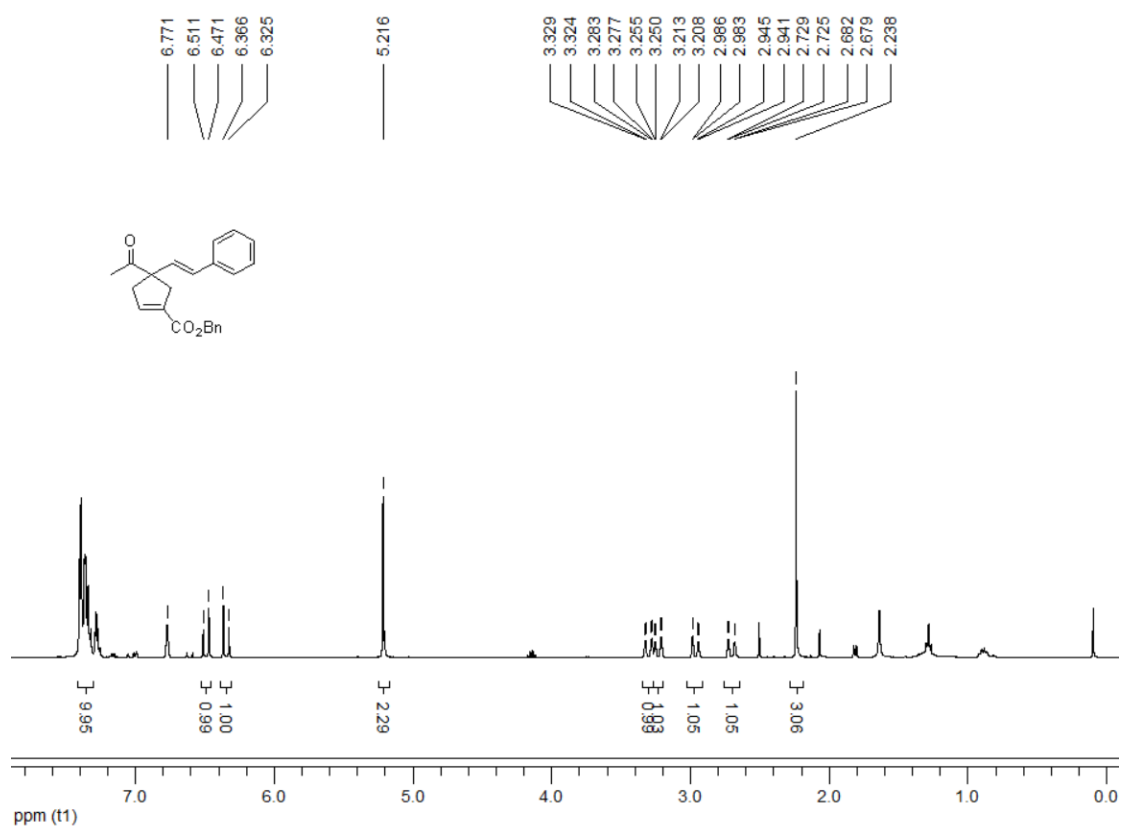
3p



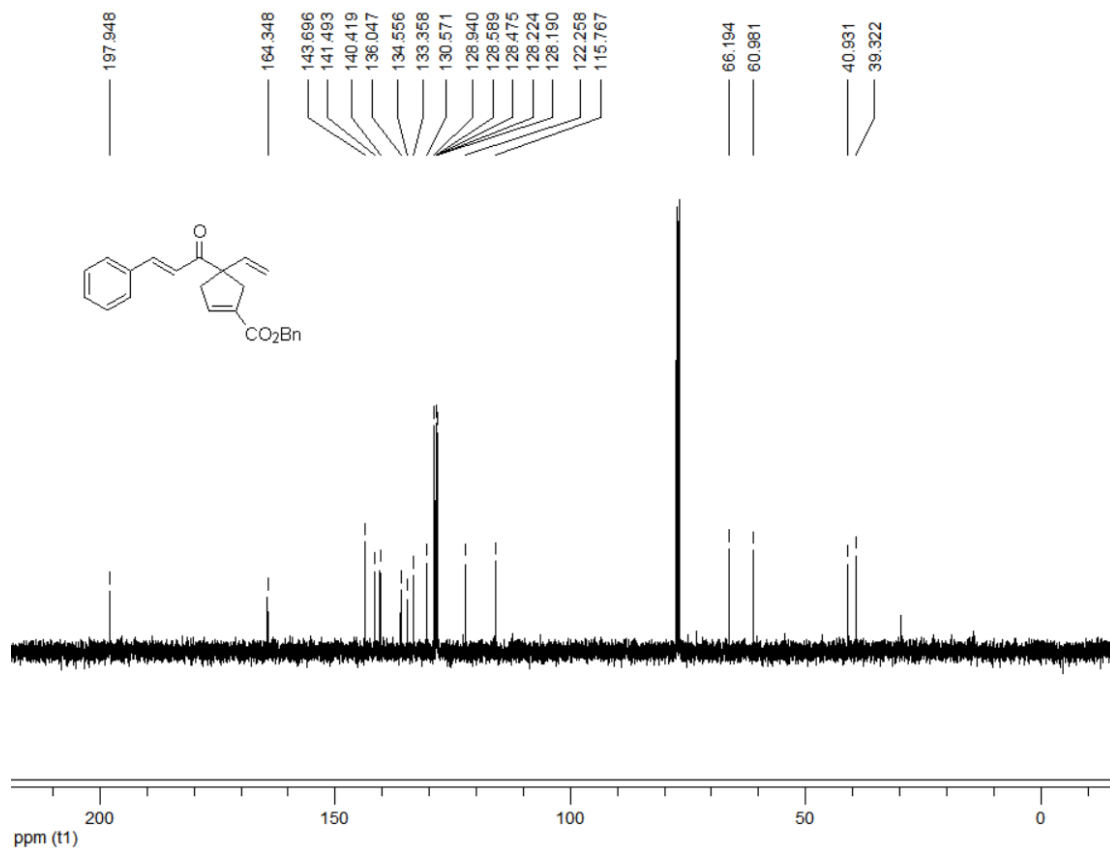
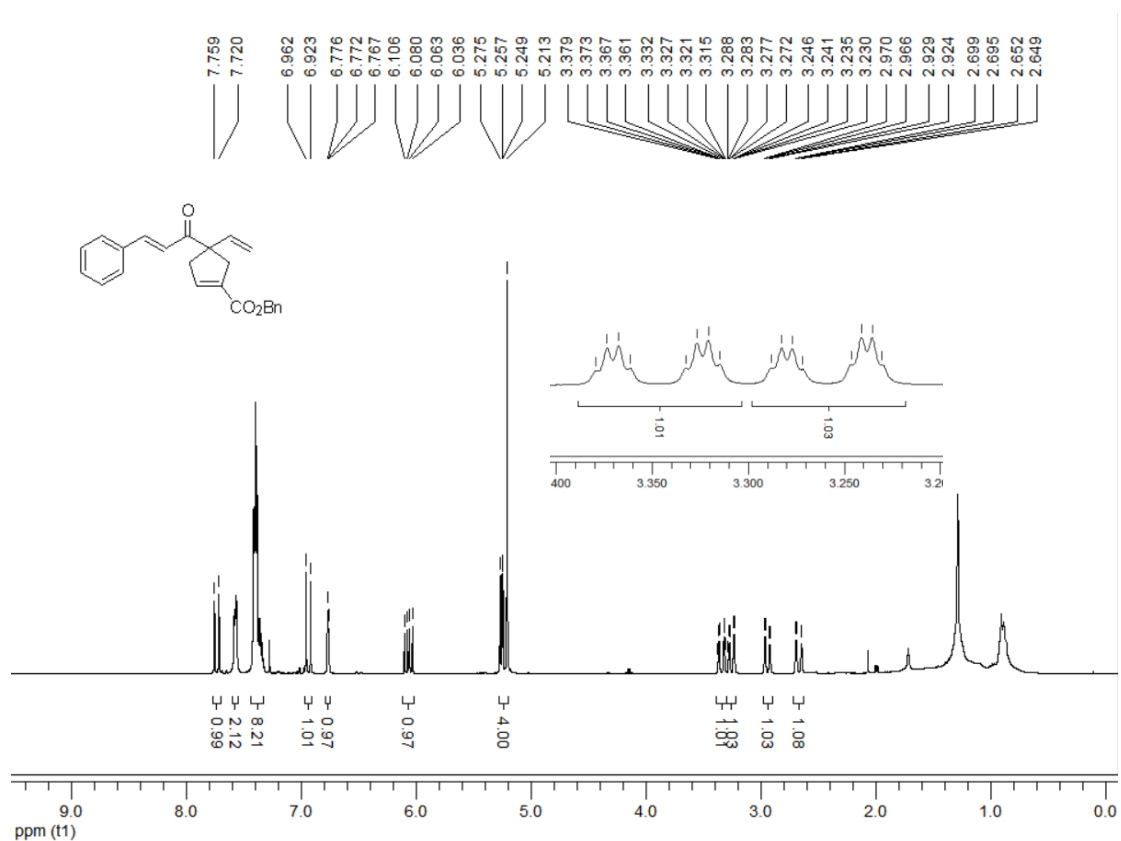
3q

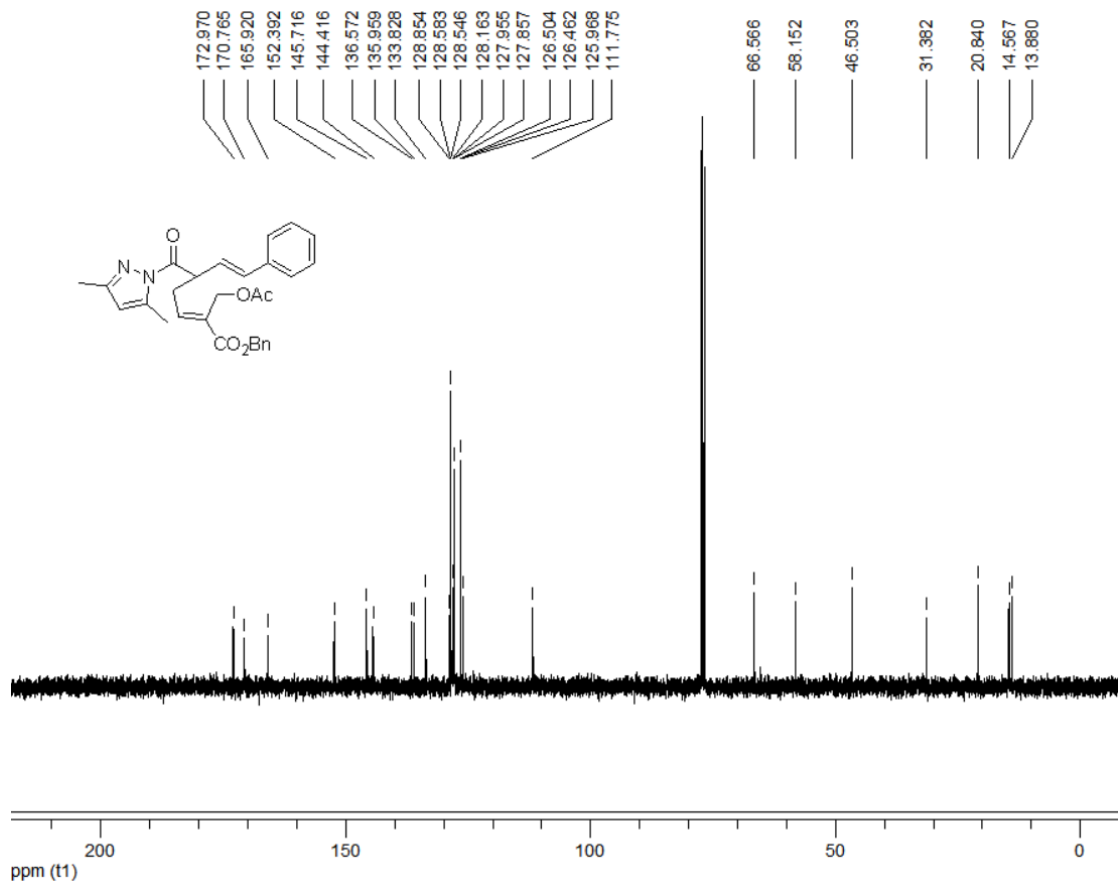
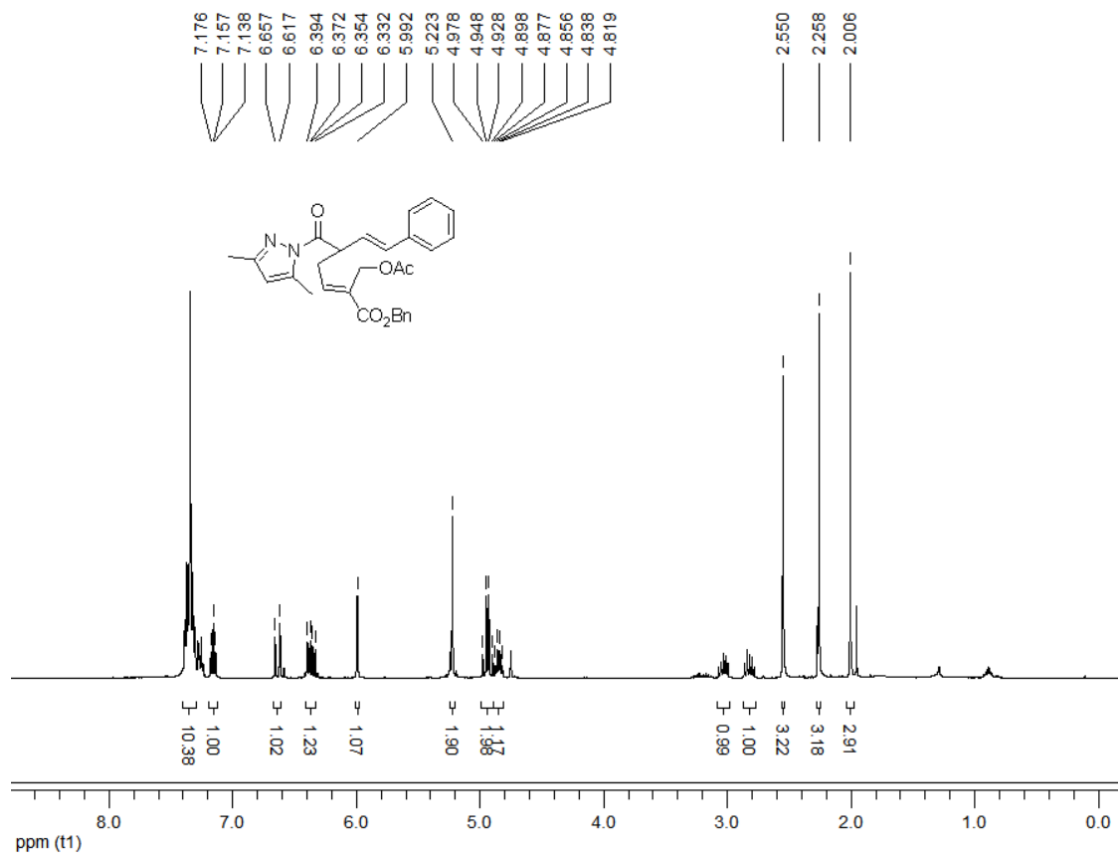


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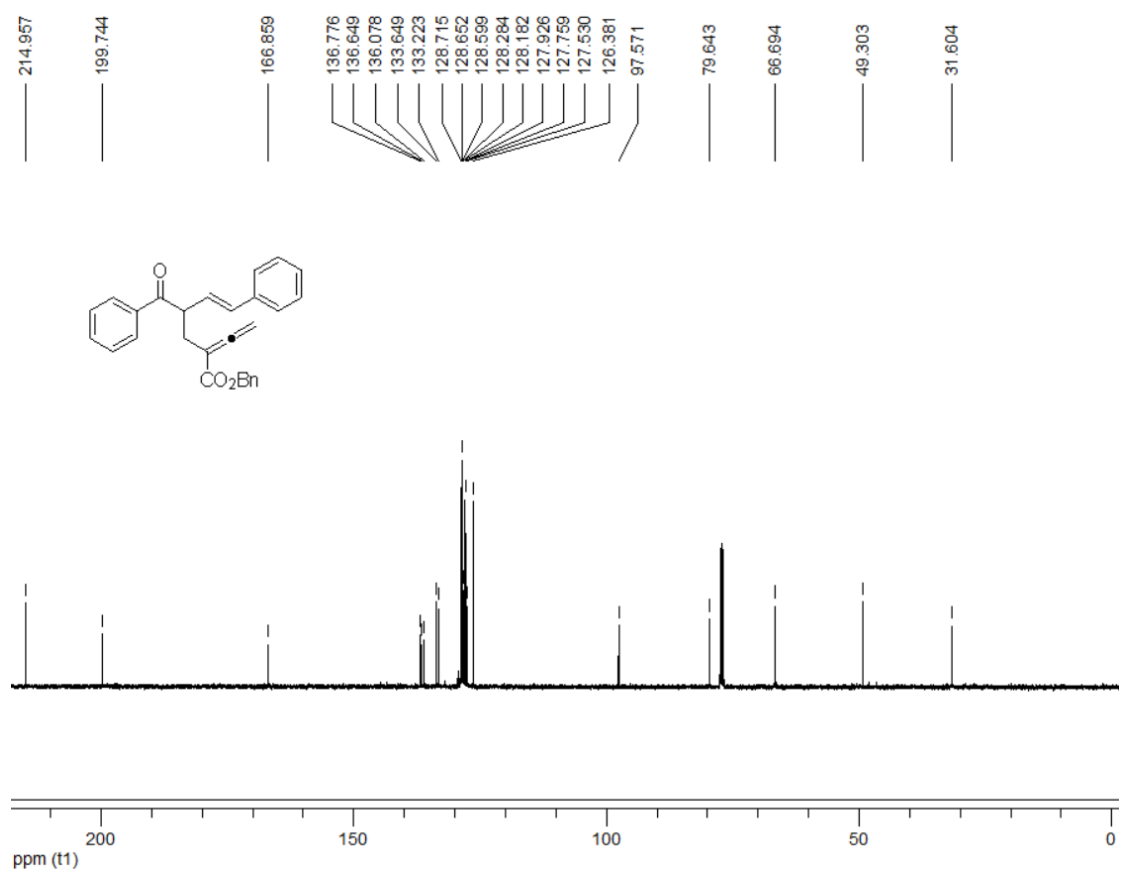
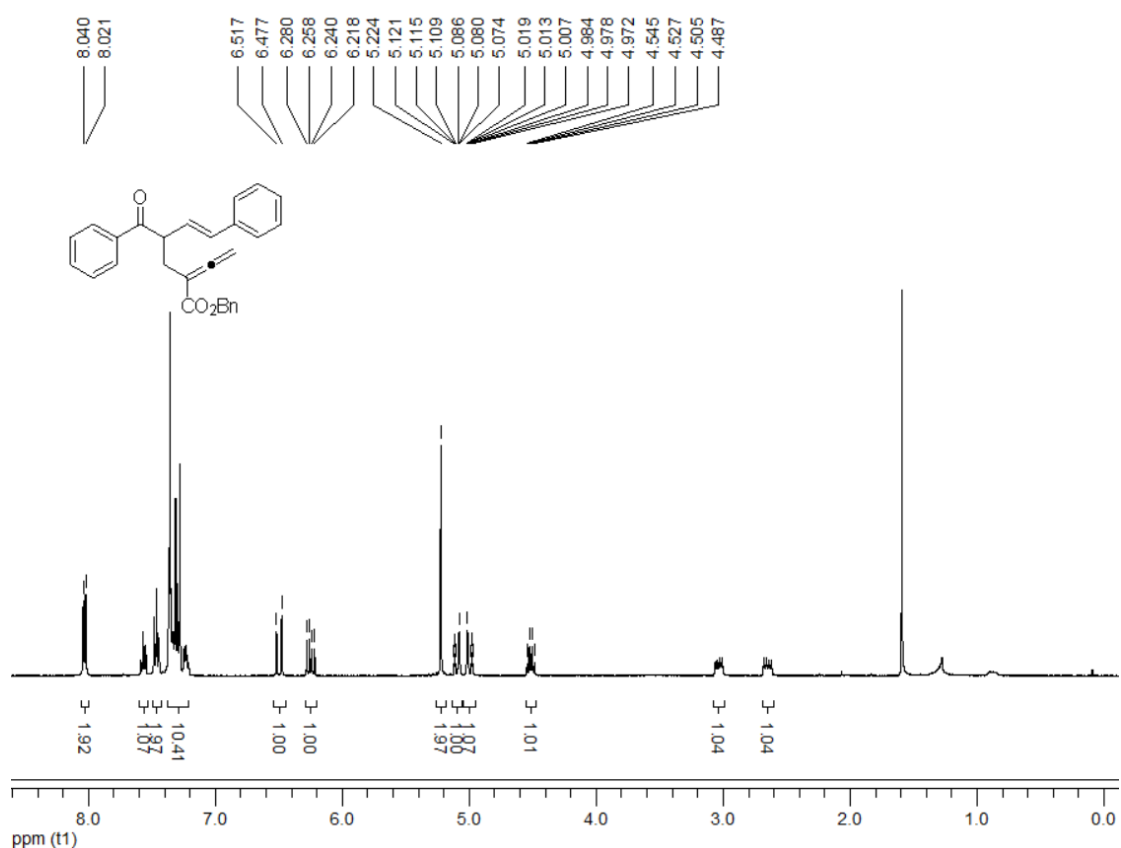


3s





5



6

