Supporting Information

Phosphine-Catalyzed α-Umpolung Addition of Nucleophile to δ-Acetoxy Allenoate

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1. General Information

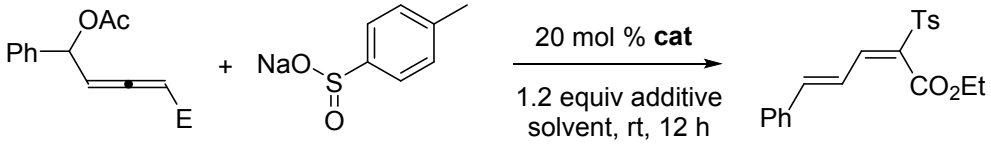
Unless otherwise noted, all reagents were obtained commercially and used without further purification.

NMR Spectroscopy: ^{1}H and ^{13}C spectra are recorded on the Bruker AVANCE spectrometer, operating at 400 MHz (300 MHz or 500 MHz) for ^{1}H 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: 7.26 ppm) for ^{1}H 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[a]



1a (E = CO_2Et) **2a** (1.2 equiv) **3aa**

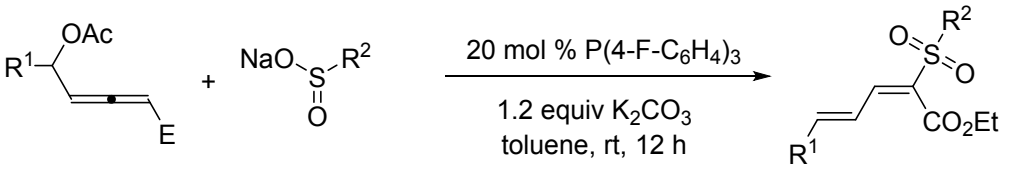
entry	Cat.	Solvent	additive	yield (%)[C]
1	PPh_3	EtOH	---[b]	<5
2	PPh_3	toluene	---[b]	29
3	PPh_3	toluene	TBAB	35
4	PPh_3	toluene	Na_2CO_3	64
5	PPh_3	toluene	K_2CO_3	86
6	PPh_3	toluene	CS_2CO_3	69
7	PPh_3	toluene	Et_3N	58
8	PPh_3	toluene	NaOH	40
7	PPh_2Me	toluene	K_2CO_3	66
8	$PPhMe_2$	toluene	K_2CO_3	43
9	PMe_3	toluene	K_2CO_3	30
10	$P(4\text{-}F\text{-}C_6H_4)_3$	toluene	K_2CO_3	92
11	$P(4\text{-}F\text{-}C_6H_4)_3$	DCM	K_2CO_3	15
12	$P(4\text{-}F\text{-}C_6H_4)_3$	THF	K_2CO_3	<5
13	$P(4\text{-}F\text{-}C_6H_4)_3$	Dioxane	K_2CO_3	10
14	$P(4\text{-}F\text{-}C_6H_4)_3$	Acetone	K_2CO_3	43
15	$P(4\text{-}F\text{-}C_6H_4)_3$	MeCN	K_2CO_3	63
16	$P(4\text{-}F\text{-}C_6H_4)_3$	DMF	K_2CO_3	<5
17	---[b]	toluene	K_2CO_3	N.D

[a]Reaction conditions:to the solution of 2a (0.22 mmol), cat (0.04 mmol), the indicated additive (0.22 mmol) in the indicated solvent (1.5 mL) was added the solution of 1a (0.2 mmol) in the same solvent (1.5 mL) at room temperature.

[b]No additive or cat was added.

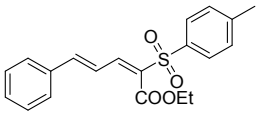
[c]Isolated yield.

3. Syntheis of products 3



1 (E = CO_2Et) **2** (1.2 equiv) **3**

General Procedure: To a 25 mL flask was added catalysts P(4-F-C_6H_4)$_3$ (0.04 mmol, 12.6 mg), K_2CO_3 (0.24 mmol, 33.2 mg), **2** (0.24 mmol), and toluene (1.5 mL). A solution of **1** (0.20 mmol) in toluene (1.5 mL) was slowly added to the mixture at room temperature. 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.

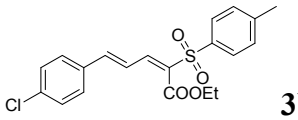


3aa, Yield = 92%, 65.3 mg, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 11.6 Hz, 1H), 7.83-7.86 (m, 3H), 7.53-7.51 (m, 2H), 7.36-7.35 (m, 3H), 7.28-7.22 (m, 3H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 161.73, 150.30, 149.68, 144.17, 137.81, 135.26, 130.77, 130.67, 129.37, 129.06, 128.56, 128.43, 123.00, 61.66, 21.66, 13.98.

HRMS (ESI): Calcd for $C_{20}H_{20}O_4S$ (M+Na^+) 379.0975, found 379.0977.

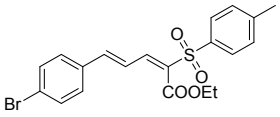


3ba, Yield = 74%, 57.6 mg, colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, *J* = 11.4 Hz, 1H), 7.89-7.76 (m, 3H), 7.50 (d, *J* = 9.6 Hz, 2H), 7.37 (d, *J* = 8.4Hz, 2H), 7.31(d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 15.2Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 161.74, 149.95, 147.95, 144.33, 137.78, 136.74, 133.85, 131.29, 129.58, 129.47, 129.43, 128.67, 123.58, 61.82, 21.75, 14.03.

HRMS (ESI): Calcd for $C_{20}H_{19}ClO_4S$ (M+Na^+) 413.0585, found 413.0588.



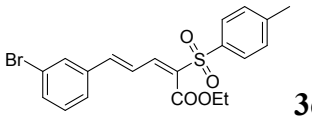
3ca, Yield = 73%, 63.5 mg, white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 11.6 Hz, 1H), 7.85-7.78 (m, 3H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 15.2

Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz): δ 161.65, 149.84, 147.94, 144.27, 137.65, 134.17, 132.30, 131.26, 129.69, 129.30, 128.58, 125.06, 123.56, 61.75, 21.67, 13.95.

HRMS (ESI): Calcd for $C_{20}H_{19}BrO_4S$ ($M+Na^+$) 457.0080, found 457.0081.

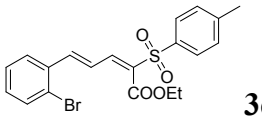


3da, Yield = 83%, 72.1 mg, white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 11.6 Hz, 1H), 7.84-7.77 (m, 3H), 7.68 (s, 1H), 7.51-7.45 (m, 2H), 7.32-7.24 (m, 3H), 7.18 (d, *J* = 15.6 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 161.58, 149.49, 147.39, 144.34, 137.56, 137.32, 133.39, 131.80, 130.91, 130.53, 129.42, 128.62, 126.97, 124.23, 123.19, 61.83, 21.69, 13.95.

HRMS (ESI): Calcd for $C_{20}H_{19}BrO_4S$ ($M+Na^+$) 457.0080, found 457.0084.

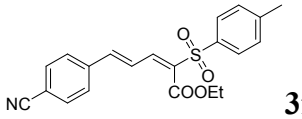


3ea, Yield = 81%, 70.4 mg, white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 10.8 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 11.2 Hz, 1H), 7.71-7.61 (m, 3H), 7.35-7.29 (m, 3H), 7.25-7.20 (m, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 161.61, 149.63, 147.24, 144.31, 137.59, 134.95, 133.61, 131.90, 131.54, 129.40, 128.64, 127.96, 127.82, 125.72, 125.19, 61.78, 21.67, 13.94.

HRMS (ESI): Calcd for $C_{20}H_{19}BrO_4S$ ($M+Na^+$) 457.0080, found 457.0078.

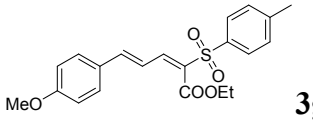


3fa, Yield = 66%, 50.3 mg, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 11.2 Hz, 1H), 7.92-7.79 (m, 3H), 7.71-7.61 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 16.0 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 161.50, 148.60, 146.14, 144.60, 139.50, 137.40, 133.34, 132.79, 129.53, 128.74, 128.60, 126.21, 118.44, 113.51, 62.03, 21.75, 14.00.

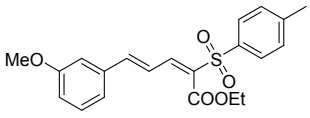
HRMS (ESI): Calcd for $C_{21}H_{19}NO_4S$ ($M+Na^+$) 404.0927, found 404.0928.



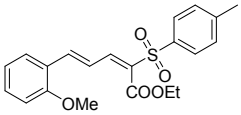
3ga, Yield = 94%, 72.3 mg, yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, *J* = 11.4 Hz, 1H), 7.83-7.69 (m, 2H), 7.52 (d, *J* = 8.4Hz, 2H), 7.83-7.69 (m, 4H), 6.91 (d, *J* = 8.0 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 2.42 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

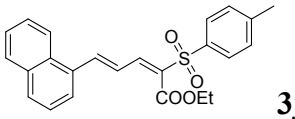
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 161.93, 151.23, 149.56, 143.96, 138.08, 131.75, 130.34, 129.30, 128.77, 128.48, 128.13, 120.90, 114.56, 61.74, 55.49, 21.65, 13.98.
HRMS (ESI): Calcd for $C_{21}H_{22}O_5S$ ($M+H^+$) 387.1261, found 387.1262.



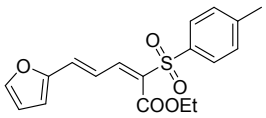
3ha, Yield = 87%, 67.2 mg, slight yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 11.6 Hz, 1H), 7.84-7.77 (m, 3H), 7.32-7.22 (m, 4H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.06 (s, 1H), 6.95 (dd, *J* = 2.0 Hz, *J* = 8.4 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.43 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H).
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 161.70, 159.97, 150.20, 149.58, 144.17, 137.77, 136.62, 130.75, 130.04, 129.37, 128.57, 123.28, 121.17, 116.61, 113.22, 61.66, 55.37, 21.66, 13.96.
HRMS (ESI): Calcd for $C_{21}H_{22}O_5S$ ($M+H^+$) 387.1261, found 387.1260.



3ia, Yield = 92%, 71.0 mg, yellow foam.
^{1}H NMR (400 MHz, DMSO): δ 8.06 (d, *J* = 10.0 Hz, 1H), 7.87-7.80 (m, 2H), 7.77-7.65 (m, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.45-7.40 (m, 3H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.03-6.99 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 2.39 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H).
$^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO): δ 161.33, 158.13, 150.02, 145.16, 143.94, 137.66, 132.34, 129.90, 129.42, 129.19, 127.98, 123.38, 123.09, 120.81, 111.83, 61.34, 55.62, 20.95, 13.64.
HRMS (ESI): Calcd for $C_{21}H_{22}O_5S$ ($M+H^+$) 387.1261, found 387.1258.

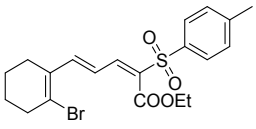


3ja, Yield = 81%, 65.7 mg, yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22-8.11 (m, 3H), 7.93-7.86 (m, 6H), 7.63-7.50 (m, 3H), 7.34-7.31 (m, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H).
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 161.74, 150.27, 146.01, 144.21, 137.80, 133.78, 132.23, 131.35, 131.23, 130.83, 129.40, 128.99, 128.62, 127.25, 126.39, 125.69, 125.55, 125.21, 122.93, 61.72, 21.68, 13.99.
HRMS (ESI): Calcd for $C_{24}H_{22}O_4S$ ($M+H^+$) 407.1312, found 407.1315.



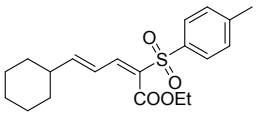
3ka, Yield = 86%, 59.4 mg, rufous liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 12.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.69-7.61 (m, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 15.2 Hz, 1H), 6.68 (d, *J* = 3.2 Hz, 1H), 6.52-6.49 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 161.77, 151.82, 149.64, 145.69, 144.08, 137.87, 134.84, 129.34, 128.63, 128.54, 121.17, 115.85, 112.86, 61.60, 21.66, 13.95.
HRMS (ESI): Calcd for $C_{18}H_{18}O_5S$ ($M+Na^+$) 369.0767, found 369.0768.



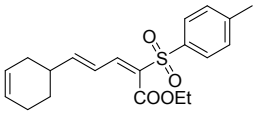
3la, Yield = 68%, 59.4 mg, white foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 11.2 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 15.6 Hz, 1H), 7.32-7.26 (m, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.74 (s, 2H), 2.42 (s, 3H), 2.34 (s, 2H), 1.74 (s, 4H), 1.21 (t, *J* = 7.2 Hz, 3H).
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 161.74, 150.67, 149.40, 144.11, 137.81, 134.66, 132.62, 130.64, 129.33, 128.55, 123.61, 61.57, 38.44, 27.30, 24.29, 21.82, 21.64, 13.91.
HRMS (ESI): Calcd for $C_{20}H_{23}BrO_4S$ ($M+H^+$) 439.0573, found 439.0570.



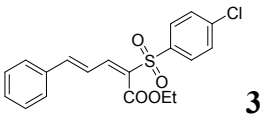
3na, Yield = 49%, 35.4 mg, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 11.6 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.08-7.00 (m, 1H), 6.54 (dd, *J* = 7.2 Hz *J* = 15.2 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 2.21-2.28 (m, 1H), 1.82-1.68 (m, 5H), 1.34-1.27 (m, 2H), 1.24-1.20 (m, 6H).
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 161.70, 160.84, 151.14, 144.02, 137.88, 129.65, 129.30, 128.51, 123.37, 61.53, 41.86, 31.79, 25.87, 25.65, 21.64, 13.92.
HRMS (ESI): Calcd for $C_{20}H_{26}O_4S$ ($M+H^+$) 363.1625, found 363.1628.



3oa, Yield = 51%, 36.9 mg, slight yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 11.2 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.09 (dd, *J* = 11.2 Hz *J* = 15.2 Hz, 1H), 6.60 (dd, *J* = 7.2 Hz *J* = 15.2 Hz, 1H), 5.73-5.65 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.57-2.49 (m, 1H), 2.42 (s, 3H), 2.21-2.15 (m, 1H), 2.10-2.08 (m, 2H), 1.98-1.91 (m, 1H), 1.87-1.83 (m, 1H), 1.54-1.46 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 3H).
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 161.66, 159.62, 150.80, 144.09, 137.80, 129.97, 129.33, 128.53, 127.09, 125.16, 124.00, 61.59, 37.76, 30.19, 27.67, 24.34, 21.65, 13.92.
HRMS (ESI): Calcd for $C_{20}H_{24}O_4S$ ($M+H^+$) 361.1468, found 361.1465.



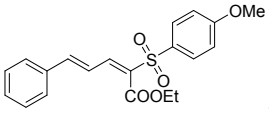
3ab, Yield = 97%, 72.8 mg, colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, *J* = 11.4 Hz, 1H), 7.90-7.80 (m, 3H), 7.59-

7.55 (m, 2H), 7.51-7.47 (m, 2H), 7.42-7.40 (m, 3H),7.32 (d, *J* = 15.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 161.49, 151.14, 150.50, 139.86, 139.35, 135.14, 131.00, 130.04, 129.81, 129.12, 129.04, 128.55, 122.87, 61.82, 14.02.

HRMS (ESI): Calcd for $C_{19}H_{17}ClO_4S$ ($M+Na^+$) 399.0428, found 399.0430.

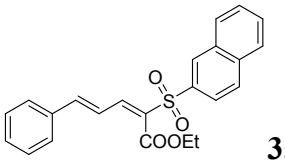


3ac, Yield = 51%, 37.6 mg, slight yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 11.4 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.81 (dd, *J* = 11.6 Hz *J* = 15.6 Hz, 1H), 7.56-7.53 (m, 2H), 7.40-7.38 (m, 3H), 7.26 (d, *J* = 15.6 Hz, 1H), 6.97 (d, *J* = 9.2 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 163.45, 161.81, 149.85, 149.45, 135.30, 132.15, 130.98, 130.88, 130.71, 129.05, 128.39, 123.05, 113.94, 61.66, 55.69, 14.04.

HRMS (ESI): Calcd for $C_{20}H_{20}O_5S$ ($M+Na^+$) 395.0924, found 395.0925.

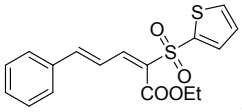


3ad, Yield = 41%, 31.8 mg, yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 11.2 Hz, 1H), 7.99-7.84 (m, 6H), 7.67-7.57 (m, 4H), 7.42-7.40 (m, 3H), 7.34 (d, *J* = 15.6 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 161.65, 150.92, 150.07, 137.61, 135.25, 135.12, 132.07, 130.85, 130.36, 130.30, 129.95, 129.37, 129.08, 128.90, 128.50, 127.97, 127.51, 123.28, 123.04, 61.66, 13.93.

HRMS (ESI): Calcd for $C_{23}H_{20}O_4S$ ($M+Na^+$) 415.0975, found 415.0974.

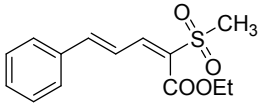


3ae, Yield = 32%, 22.1 mg, yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, *J* = 15.6 Hz, 1H), 7.88-7.82 (m, 1H), 7.78-7.76 (m, 1H), 7.69-7.66 (m, 1H), 7.58-7.54 (m, 2H), 7.41-7.39 (m, 3H), 7.28 (d, *J* = 14.8 Hz, 1H), 7.12-7.09 (m, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 161.67, 150.49, 150.20, 141.98, 135.20, 134.76, 133.89, 130.88, 129.08, 128.77, 128.50, 127.36, 122.99, 61.86, 14.13.

HRMS (ESI): Calcd for $C_{17}H_{16}O_4S_2$ ($M+Na^+$) 371.0382, found 371.0386.

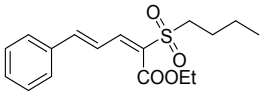


3af, Yield = 86%, 47.9 mg, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.76 (m, 2H), 7.58-7.55 (m, 2H), 7.42-7.40 (m, 3H), 7.27-7.23 (m, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 3.24 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 162.13, 150.55, 150.06, 135.13, 130.89, 129.80, 129.09, 128.45, 122.58, 62.11, 43.48, 14.23.

HRMS (ESI): Calcd for $C_{14}H_{16}O_4S$ ($M+H^+$) 281.0842, found 281.0844.

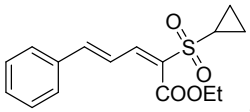


3ag, Yield = 66%, 42.4 mg, colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82-7.62 (m, 2H), 7.56-7.53 (m, 2H), 7.41-7.38 (m, 3H), 7.26-7.20 (m, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.40-3.34 (m, 2H), 1.78-1.69 (m, 2H), 1.49-1.40 (m, 5H), 0.93 (t, *J* = 6.9 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 162.24, 151.06, 149.71, 135.14, 130.84, 129.08, 128.67, 128.41, 122.65, 62.05, 54.50, 24.66, 21.59, 14.23, 13.59.

HRMS (ESI): Calcd for $C_{17}H_{22}O_4S$ ($M+H^+$) 323.1312, found 323.1310.



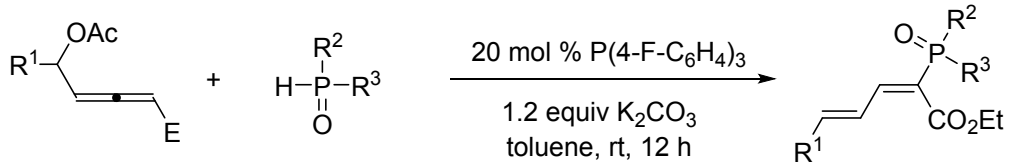
3ah, Yield = 73%, 44.5 mg, colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84-7.68 (m, 2H), 7.55-7.52 (m, 2H), 7.40-7.37 (m, 3H), 7.20 (d, *J* = 14.8 Hz, 1H), 4.42 (q, *J* = 6.9 Hz, 2H), 3.02-2.96 (m, 1H), 1.43 (t, *J* = 6.9 Hz, 3H), 1.28-1.25 (m, 2H), 1.05-1.03 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 162.29, 149.55, 149.37, 135.22, 130.73, 129.79, 129.06, 128.35, 122.72, 61.99, 31.90, 14.27, 6.16.

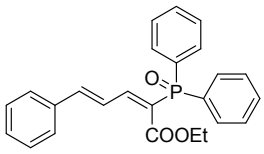
HRMS (ESI): Calcd for $C_{16}H_{18}O_4S$ ($M+Na^+$) 329.0818, found 329.0813.

4. Syntheis of products 5 and 7



1 (E = CO_2Et) **4 or 6** **5 or 7**

General Procedure: To a 25 mL flask was added catalysts P(4-F-C_6H_4)$_3$ (0.04 mmol, 12.6 mg), K_2CO_3 (0.24 mmol, 33.2 mg), **4 or 6** (0.20 mmol, 1.0 equiv), and toluene (1.5 mL). A solution of **1** (0.22 mmol, 1.1 equiv) in toluene (1.5 mL) was slowly added to the mixture at room temperature. 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.



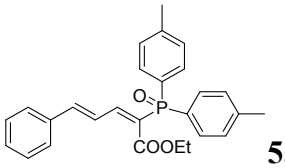
5aa, Yield = 56%, 44.8 mg, slight yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (dd, *J* = 12.0 Hz *J* = 15.2 Hz, 1H), 8.19 (d, *J* = 12.0 Hz, 1H), 7.84-7.78 (m, 4H), 7.55-7.44 (m, 8H), 7.34-7.32 (m, 3H), 7.04 (d, *J* = 15.2 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.48 (d, $J_{C\text{-}P}$ = 13.9 Hz), 158.53 (d, $J_{C\text{-}P}$ = 6.4 Hz), 147.19, 135.73, 133.53 (d, $J_{C\text{-}P}$ = 107.8 Hz), 131.79, 131.69, 130.02, 128.77, 128.40, 128.27, 124.54 (d, $J_{C\text{-}P}$ = 6.0 Hz), 122.65 (d, $J_{C\text{-}P}$ = 98.4 Hz), 61.11, 13.78.

^{31}P{^{1}H} NMR (122 MHz, $CDCl_3$): δ 27.1

HRMS (ESI): Calcd for $C_{25}H_{23}O_3P$ (M+Na^+) 425.1277, found 425.1276.



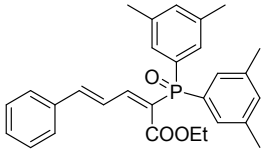
5ab, Yield = 66%, 56.8 mg, slight yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 11.6 Hz *J* = 15.6 Hz, 1H), 7.77 (dd, *J* = 11.6 Hz *J* = 18.0 Hz, 1H), 7.69-7.64 (m, 4H), 7.55-7.52 (m, 2H), 7.39-7.36 (m, 3H), 7.28-7.26 (m, 4H), 7.09 (d, *J* = 15.6 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 6H), 1.02 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.64 (d, $J_{C\text{-}P}$ = 13.4 Hz), 155.52 (d, $J_{C\text{-}P}$ = 6.5 Hz), 146.79, 142.53, 136.08, 132.31 (d, $J_{C\text{-}P}$ = 10.3 Hz), 130.29, 129.41 (d, $J_{C\text{-}P}$ = 110.5 Hz), 129.31, 129.20, 128.39, 124.91 (d, $J_{C\text{-}P}$ = 14.6 Hz), 124.40 (d, $J_{C\text{-}P}$ = 98.5 Hz), 61.14, 21.94, 14.13.

^{31}P{^{1}H} NMR (122 MHz, $CDCl_3$): δ 29.1

HRMS (ESI): Calcd for $C_{27}H_{27}O_3P$ ($M+Na^+$) 453.1590, found 453.1594.



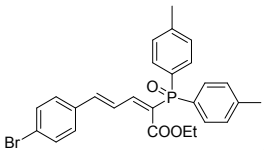
5ac, Yield = 59%, 53.9 mg, slight yellow liquid.

^1H NMR (300 MHz, $CDCl_3$): δ 7.95 (ddd, J = 1.5 Hz J = 10.0 Hz J = 13.8 Hz, 1H), 7.72 (dd, J = 11.4 Hz J = 18.0 Hz, 1H), 7.55-7.51 (m, 2H), 7.41-7.34 (m, 7H), 7.14 (s, 2H), 7.07 (d, J = 15.2 Hz, 1H), 4.09 (q, J = 7.2 Hz, 2H), 2.33 (s, 12H), 1.01 (t, J = 7.2 Hz, 3H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.22 (d, $J_{C\text{-}P}$ = 13.2 Hz), 154.85 (d, $J_{C\text{-}P}$ = 6.5 Hz), 146.08, 137.74 (d, $J_{C\text{-}P}$ = 12.8 Hz), 135.61, 133.34, 131.95 (d, $J_{C\text{-}P}$ = 107.2 Hz), 129.78, 129.28, 128.71, 127.89, 124.28 (d, $J_{C\text{-}P}$ = 97.2 Hz), 124.46 (d, $J_{C\text{-}P}$ = 14.5 Hz), 60.58, 21.17, 13.59.

$^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$): δ 29.5

HRMS (ESI): Calcd for $C_{29}H_{31}O_3P$ ($M+Na^+$) 481.1903, found 481.1906.



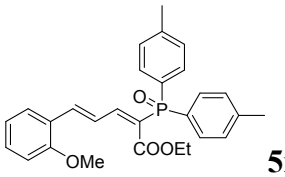
5cb, Yield = 65%, 65.9 mg, yellow foam.

^1H NMR (300 MHz, $CDCl_3$): δ 7.93 (ddd, J = 1.5 Hz J = 11.4 Hz J = 15.3 Hz, 1H), 7.74 (dd, J = 11.4 Hz J = 18.0 Hz, 1H), 7.68-7.61 (m, 4H), 7.51-7.47 (m, 2H), 7.39-7.36 (m, 2H), 7.28-7.24 (m, 4H), 7.01 (d, J = 15.3 Hz, 1H), 4.06 (q, J = 7.2 Hz, 2H), 2.40 (s, 6H), 1.00 (t, J = 7.2 Hz, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 165.25 (d, $J_{C\text{-}P}$ = 13.2 Hz), 154.73 (d, $J_{C\text{-}P}$ = 6.5 Hz), 144.78, 142.29, 134.68, 132.12, 131.98 (d, $J_{C\text{-}P}$ = 10.5 Hz), 129.00 (d, $J_{C\text{-}P}$ = 110.7 Hz), 129.39, 129.17, 125.13 (d, $J_{C\text{-}P}$ = 14.6 Hz), 124.92 (d, $J_{C\text{-}P}$ = 97.6 Hz), 124.15, 60.91, 21.66, 13.80.

$^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$): δ 27.3

HRMS (ESI): Calcd for $C_{27}H_{26}BrO_3P$ ($M+H^+$) 509.0876, found 509.0872.



5ib, Yield = 58%, 53.4 mg, white foam.

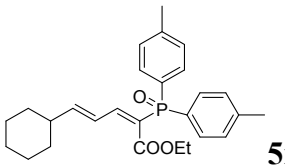
^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, J = 11.6 Hz J = 15.6 Hz, 1H), 7.78 (dd, J = 11.6 Hz J = 18.4 Hz, 1H), 7.69-7.63 (m, 4H), 7.57 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 15.6 Hz, 1H), 7.32-7.24 (m, 3H), 6.94 (t, J = 7.6 Hz, 3H), 6.88 (d, J = 8.4 Hz, 1H), 4.06 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 2.39 (s, 6H), 1.01 (t, J = 7.2 Hz, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 165.48 (d, $J_{C\text{-}P}$ = 13.6 Hz), 158.05, 156.20 (d, $J_{C\text{-}P}$ = 6.8 Hz), 142.08, 141.80, 131.99 (d, $J_{C\text{-}P}$ = 10.4 Hz), 131.32, 129.33 (d, $J_{C\text{-}P}$ = 110.4

Hz), 129.02 (d, $J_{C\text{-}P}$ = 12.8 Hz), 128.07, 124.94 (d, $J_{C\text{-}P}$ = 14.7 Hz), 124.75, 123.00 (d, $J_{C\text{-}P}$ = 99.5 Hz), 120.80, 111.15, 60.72, 55.60, 21.63, 13.85.

$^{31}P\{^{1}H\}$ NMR (122 MHz, $CDCl_3$): δ 27.5

HRMS (ESI): Calcd for $C_{28}H_{29}O_4P$ ($M+H^+$) 461.1876, found 461.1880.



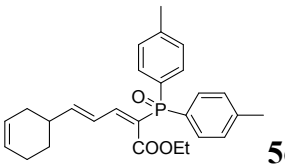
5nb, Yield = 60%, 52.4 mg, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.4 Hz *J* = 12.4 Hz, 4H), 7.55 (dd, *J* = 11.2 Hz *J* = 18.8 Hz, 1H), 7.26-7.22 (m, 4H), 7.13 (dd, *J* = 11.2 Hz *J* = 15.2 Hz, 1H), 6.32 (dd, *J* = 6.8 Hz *J* = 15.2 Hz, 1H), 4.02 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 6H), 2.23-2.14 (m, 1H), 1.78-1.72 (m, 4H), 1.30-1.24 (m, 4H), 1.18-1.12 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 165.41 (d, $J_{C\text{-}P}$ = 13.9 Hz), 157.17, 156.18 (d, $J_{C\text{-}P}$ = 6.8 Hz), 142.11, 132.01, 131.91, 129.27 (d, $J_{C\text{-}P}$ = 110.1 Hz), 129.06, 128.93, 124.69 (d, $J_{C\text{-}P}$ = 14.4 Hz), 122.56 (d, $J_{C\text{-}P}$ = 99.1 Hz), 60.70, 41.52, 31.95, 25.97, 25.73, 21.62, 13.79.

$^{31}P\{^{1}H\}$ NMR (122 MHz, $CDCl_3$): δ 27.3

HRMS (ESI): Calcd for $C_{27}H_{33}O_3P$ ($M+Na^+$) 459.2060, found 459.2055.



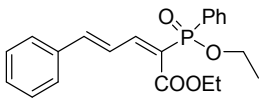
5ob, Yield = 53%, 46.1 mg, colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.0 Hz *J* = 12.0 Hz, 4H), 7.57 (dd, *J* = 11.2 Hz *J* = 18.8 Hz, 1H), 7.26-7.22 (m, 4H), 7.19-7.15 (m, 1H), 6.38 (dd, *J* = 7.2 Hz *J* = 15.2 Hz, 1H), 5.71-5.64 (m, 2H), 4.02 (q, *J* = 7.2 Hz, 2H), 2.54-2.44 (m, 1H), 2.38 (s, 6H), 2.19-2.07 (m, 3H), 1.95-1.80 (m, 3H), 0.98 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 165.38 (d, $J_{C\text{-}P}$ = 13.9 Hz), 155.93, 155.81 (d, $J_{C\text{-}P}$ = 6.2 Hz), 132.02, 131.91, 129.22 (d, $J_{C\text{-}P}$ = 110.6 Hz), 129.07, 128.95, 126.22 (d, $J_{C\text{-}P}$ = 104.2 Hz), 125.25, 60.75, 37.45, 30.37, 27.83, 24.47, 21.64, 13.79.

$^{31}P\{^{1}H\}$ NMR (122 MHz, $CDCl_3$): δ 27.1

HRMS (ESI): Calcd for $C_{27}H_{31}O_3P$ ($M+H^+$) 435.2084, found 435.2082.



7aa, Yield = 54%, 40.1 mg, colorless liquid.

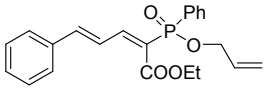
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (dd, *J* = 12.0 Hz *J* = 15.6 Hz, 1H), 8.07 (d, *J* = 12.0 Hz, 1H), 7.89 (dd, *J* = 7.6 Hz *J* = 12.8 Hz, 2H), 7.62-7.59 (m, 2H), 7.53-7.35 (m,

6H), 7.08 (d, J = 15.6 Hz, 1H), 4.23-4.06 (m, 4H), 1.41 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 166.10 (d, $J_{C\text{-}P}$ = 14.5 Hz), 157.74 (d, $J_{C\text{-}P}$ = 5.4 Hz), 147.39, 135.81, 132.55 (d, $J_{C\text{-}P}$ = 144.8 Hz), 131.93 (d, $J_{C\text{-}P}$ = 3.1 Hz), 131.47 (d, $J_{C\text{-}P}$ = 10.6 Hz), 130.07, 128.87, 128.36, 128.19 (d, $J_{C\text{-}P}$ = 13.6 Hz), 124.86 (d, $J_{C\text{-}P}$ = 4.9 Hz), 128.81(d, $J_{C\text{-}P}$ = 128.6 Hz), 61.13, 61.07, 16.58, 14.00.

$^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$): δ 28.8

HRMS (ESI): Calcd for $C_{21}H_{23}O_4P$ ($M+Na^+$) 393.1226, found 393.1225.



7ab, Yield = 81%, 62.2 mg, colorless liquid.

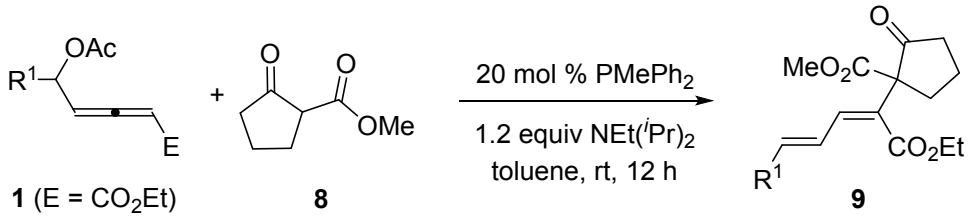
^1H NMR (400 MHz, $CDCl_3$): δ 7.94-7.83 (m, 4H), 7.56-7.50 (m, 3H), 7.47-7.42 (m, 2H), 7.39-7.36 (m, 3H), 7.15 (d, J = 14.4 Hz, 1H), 6.04-5.94 (m, 1H), 5.39 (dd, J = 1.6 Hz J = 17.2 Hz, 1H), 5.25 (dd, J = 1.6 Hz J = 10.4 Hz, 1H), 4.60-4.56 (m, 2H), 4.20-4.10 (m, 2H), 1.16 (t, J = 7.2 Hz, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 163.69 (d, $J_{C\text{-}P}$ = 14.2 Hz), 154.86 (d, $J_{C\text{-}P}$ = 6.8 Hz), 146.06, 134.59, 132.00 (d, $J_{C\text{-}P}$ = 7.2 Hz), 131.04, 130.71 (d, $J_{C\text{-}P}$ = 10.4 Hz), 130.35 (d, $J_{C\text{-}P}$ = 145.4 Hz), 129.11, 127.88, 127.28, 127.12, 123.41 (d, $J_{C\text{-}P}$ = 16.0 Hz), 121.11 (d, $J_{C\text{-}P}$ = 129.2 Hz), 116.79, 64.38 (d, $J_{C\text{-}P}$ = 5.4 Hz), 59.86, 12.94.

$^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$): δ 29.4

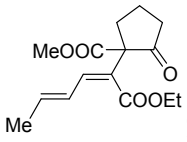
HRMS (ESI): Calcd for $C_{22}H_{23}O_4P$ ($M+H^+$) 383.1407, found 383.1410.

5. Syntheis of products 9



1 (E = CO_2Et) **8** **9**

General Procedure: To a 25 mL flask was added catalysts $PMePh_2$ (0.04 mmol, 8.0 mg), $NEt(^iPr)_2$ (0.24 mmol, 31.0 mg), **8** (0.24 mmol, 1.2 equiv), and toluene (1.5 mL). A solution of **1** (0.20 mmol, 1.0 equiv) in toluene (1.5 mL) was slowly added to the mixture at room temperature. 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.

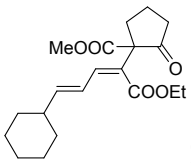


9m, Yield = 80%, 44.8 mg, colorless liquid.

^1H NMR (400 MHz, $CDCl_3$): δ 7.00 (ddd, *J* = 1.6 Hz *J* = 10.8 Hz *J* = 14.8 Hz, 1H), 6.25 (d, *J* = 10.8 Hz, 1H), 6.01 (dd, *J* = 7.2 Hz *J* = 14.8 Hz, 1H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 3H), 2.80-2.74 (m, 1H), 2.44-2.36 (m, 2H), 2.23-2.16 (m, 1H), 2.03-1.88 (m, 2H), 1.83 (dd, *J* = 1.2 Hz *J* = 6.8 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 212.75, 170.76, 166.18, 140.33, 139.96, 128.16, 126.31, 65.33, 60.83, 52.92, 38.37, 35.04, 19.30, 18.76, 14.10.

HRMS (ESI): Calcd for $C_{15}H_{20}O_5$ ($M+Na^+$) 303.1203, found 303.1205.



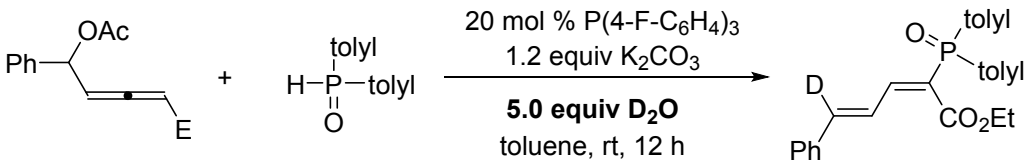
9n, Yield = 66%, 46.0 mg, colorless liquid.

^1H NMR (400 MHz, $CDCl_3$): δ 6.96 (dd, *J* = 11.2 Hz *J* = 15.2 Hz, 1H), 6.25 (d, *J* = 11.2 Hz, 1H), 5.93 (dd, *J* = 7.2 Hz *J* = 15.2 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 3H), 2.79-2.75 (m, 1H), 2.44-2.36 (m, 2H), 2.22-2.17 (m, 1H), 2.09-1.89 (m, 3H), 1.73-1.62 (m, 5H), 1.30-1.26 (m, 5H), 1.16-1.04 (m, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 212.86, 170.60, 166.22, 150.85, 140.98, 126.53, 124.32, 65.42, 60.81, 52.93, 41.18, 38.43, 35.08, 32.30, 26.04, 25.83, 19.34, 14.13.

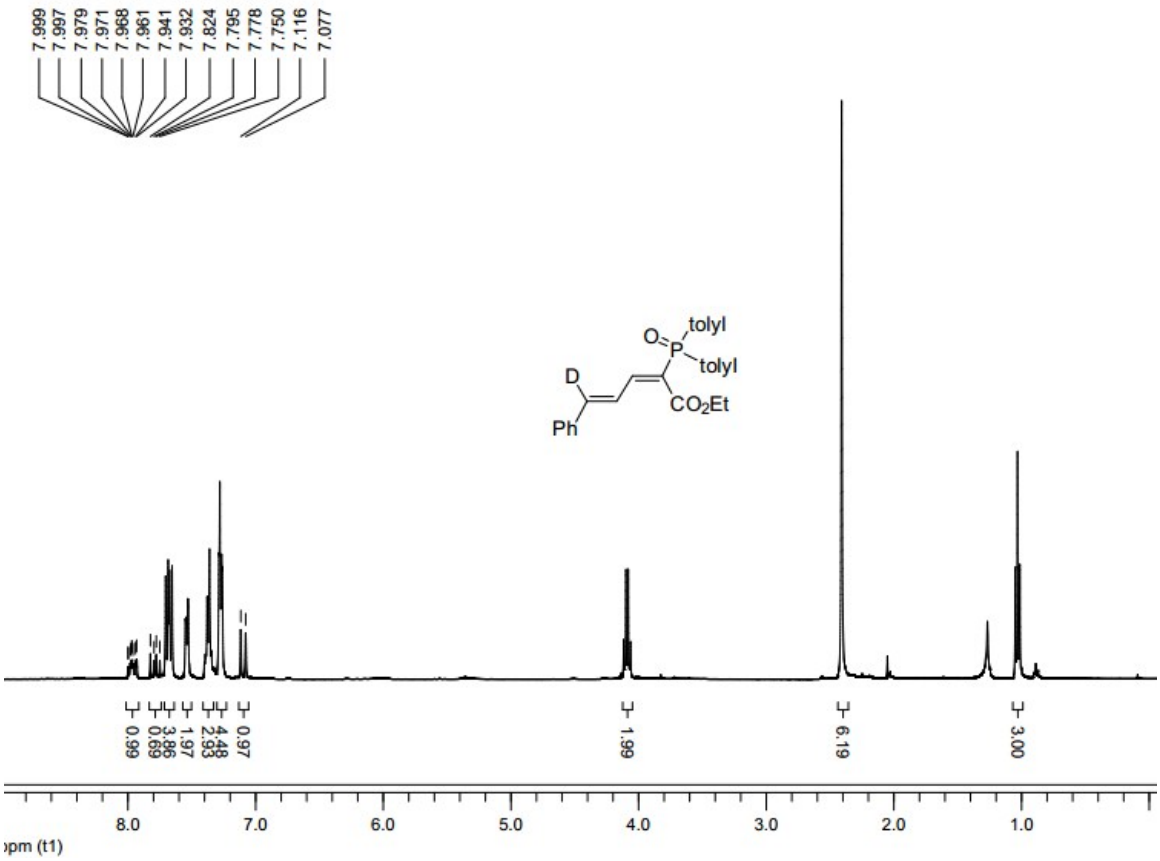
HRMS (ESI): Calcd for $C_{20}H_{28}O_5$ ($M+Na^+$) 371.1829, found 371.1826.

6. Control Experiments



1a (E = CO_2Et) **4b** **5ab-D**

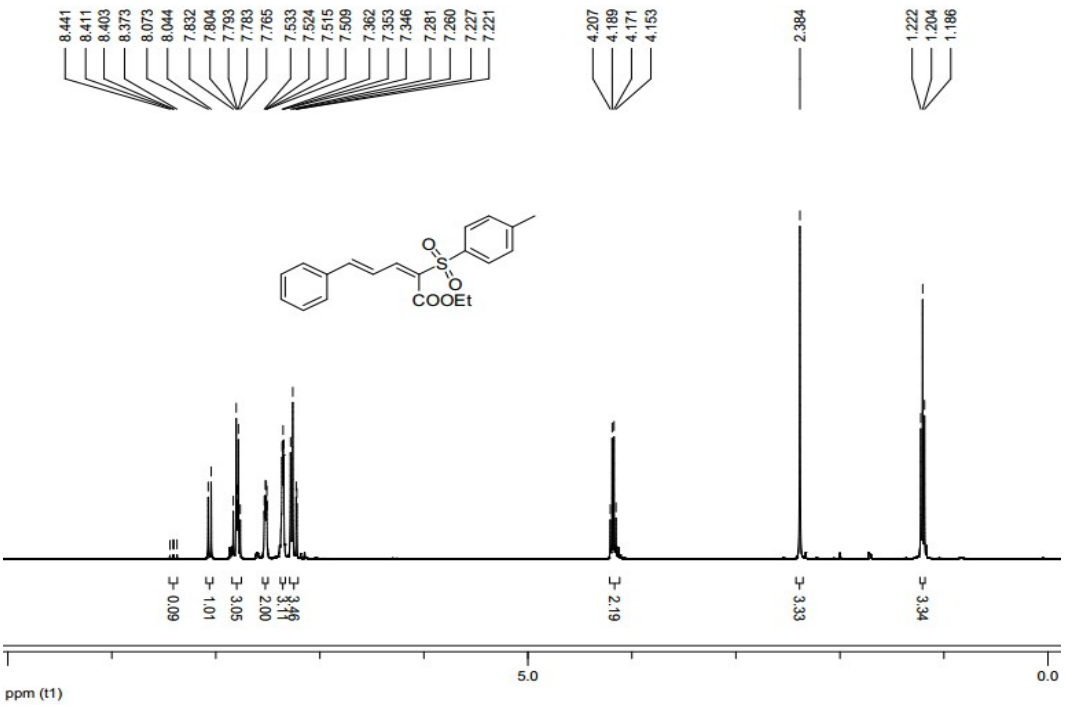
63% yield, **31% D**



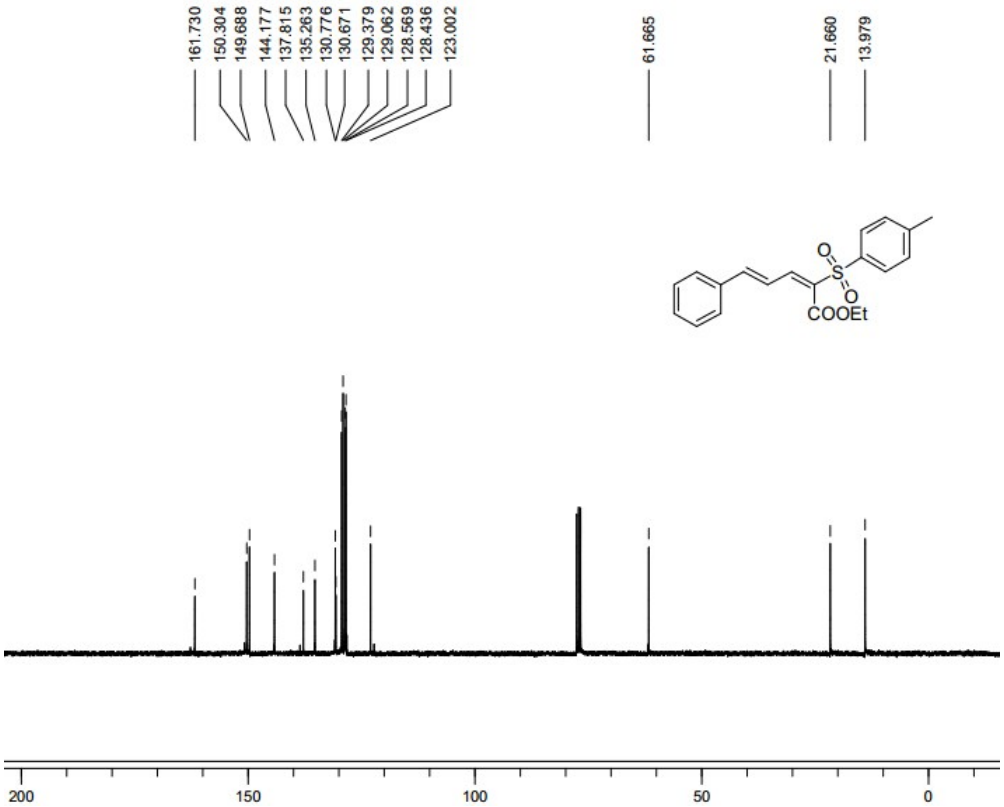
7. The Spectra of Products

3aa

^{1}H-NMR

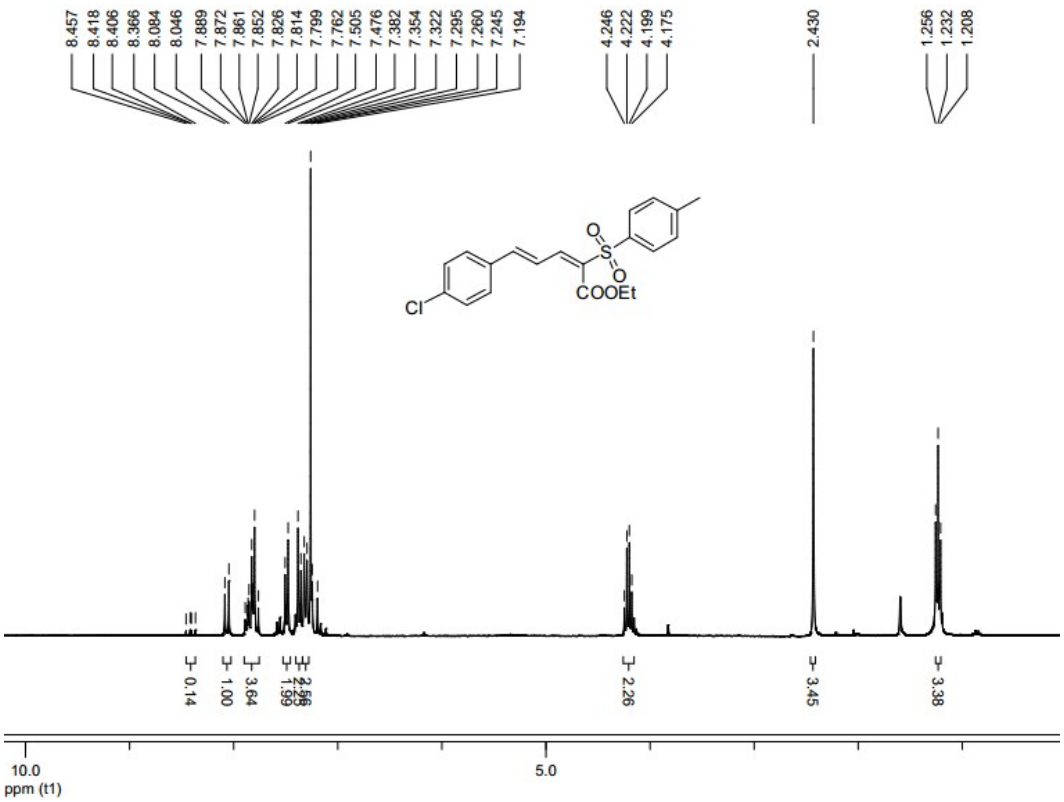


^{13}C{^{1}H}-NMR

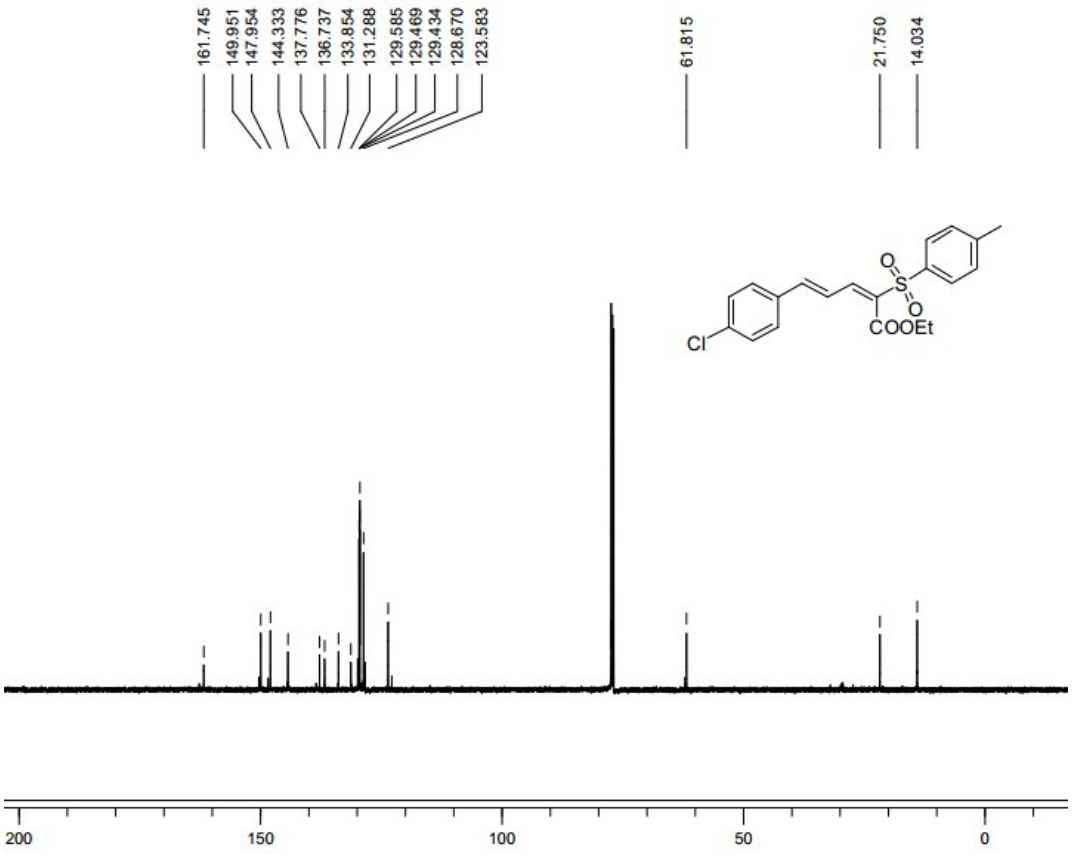


3ba

^{1}H-NMR

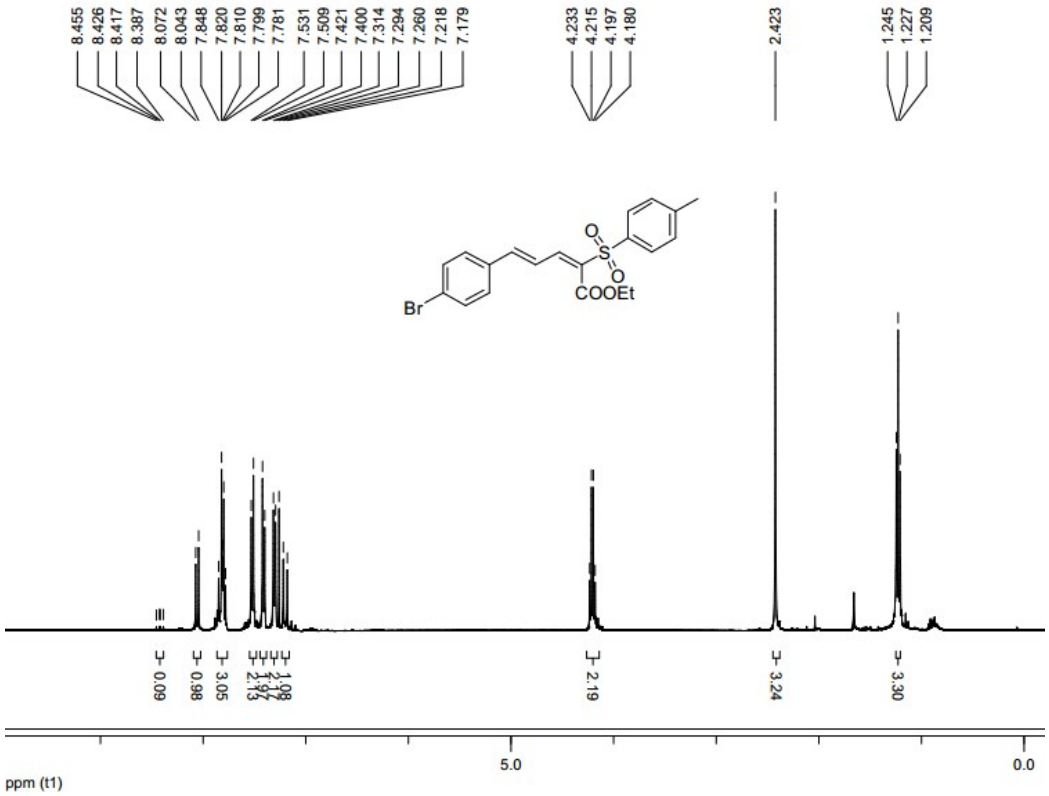


^{13}C{^{1}H}-NMR

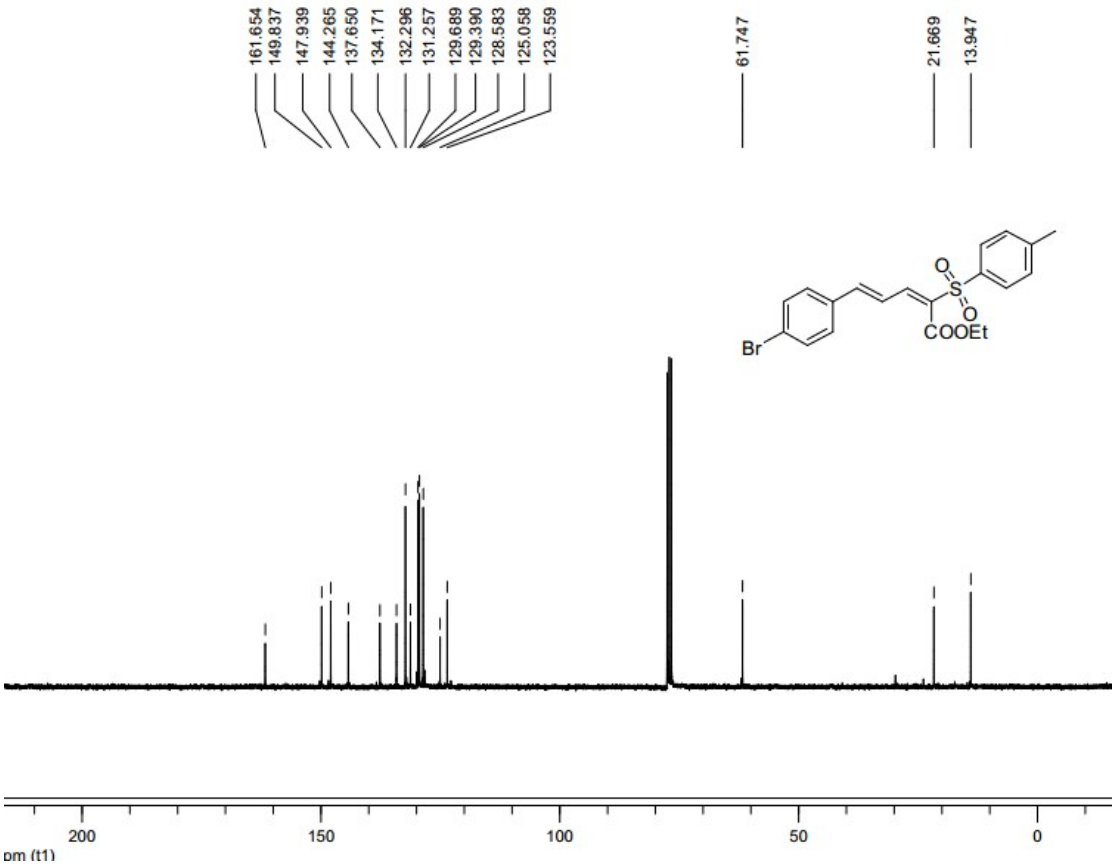


3ca

^{1}H-NMR

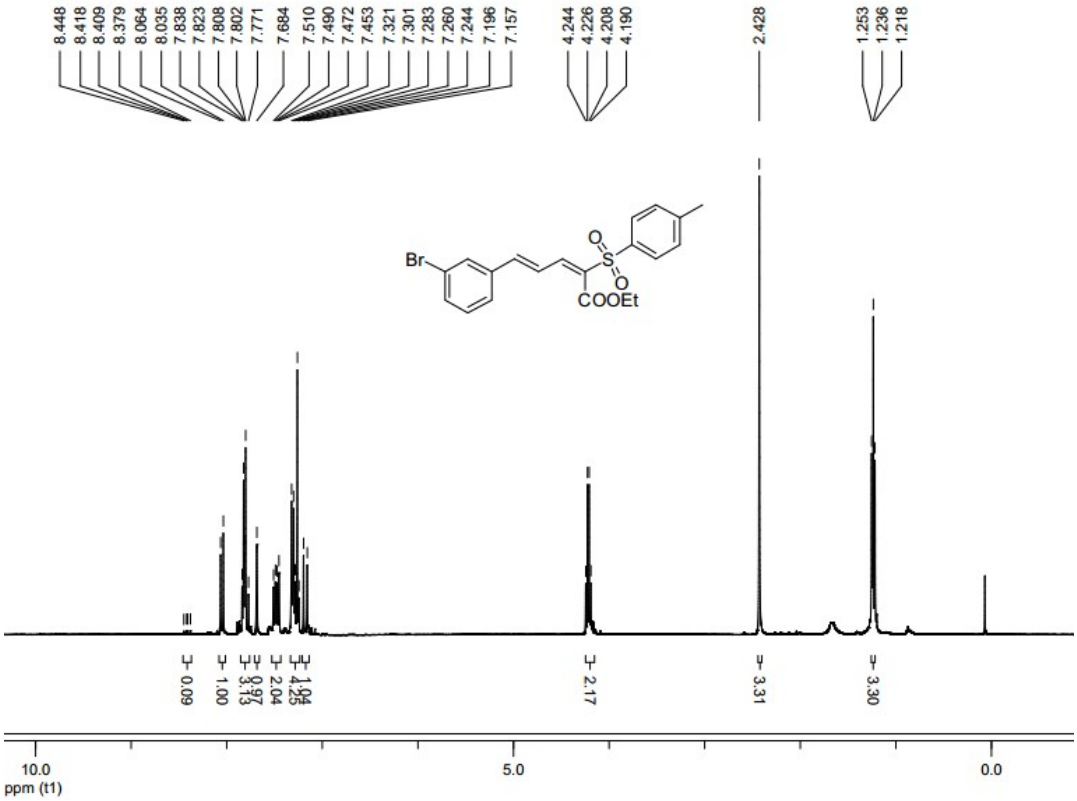


^{13}C{^{1}H}-NMR

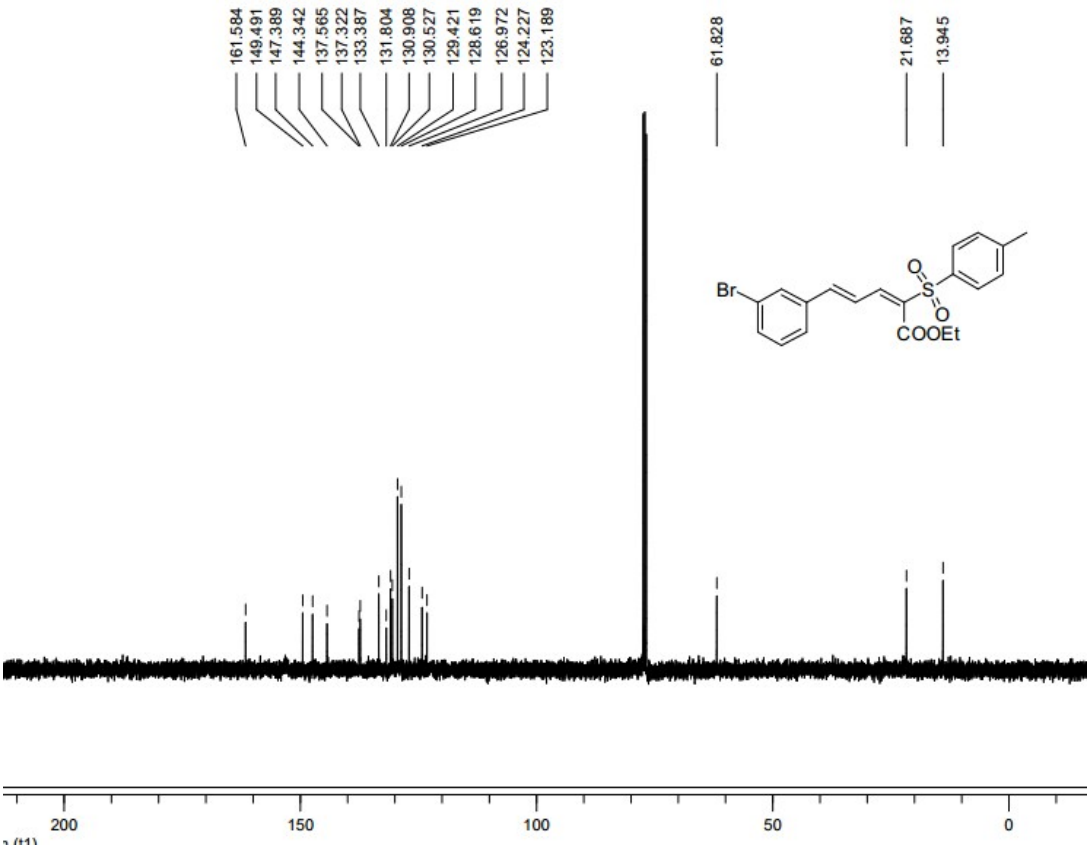


3da

^{1}H-NMR

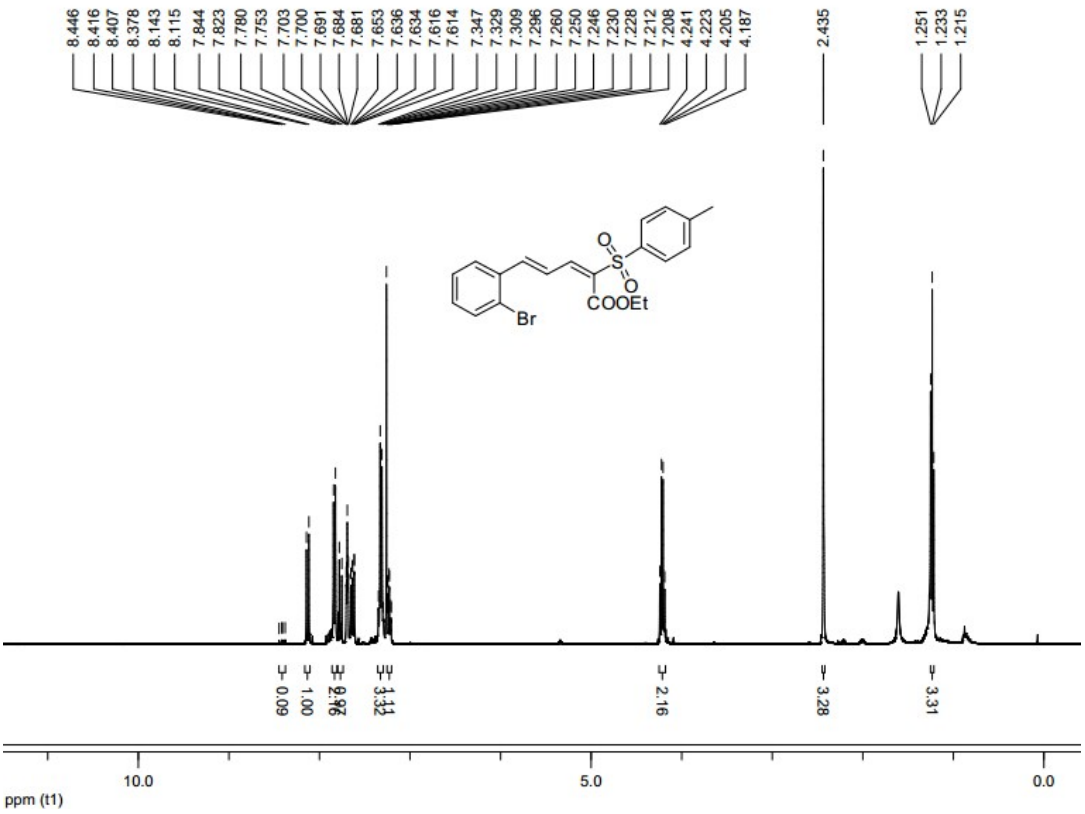


^{13}C{^{1}H}-NMR

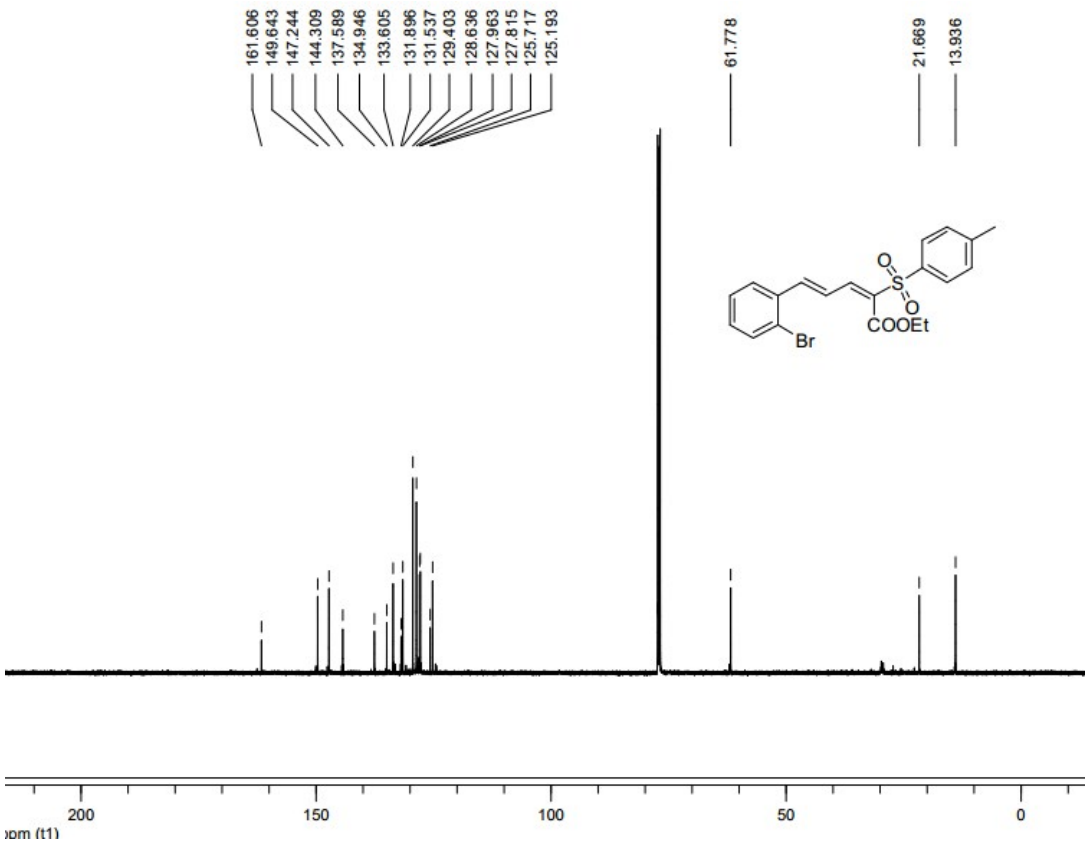


3ea

^{1}H-NMR

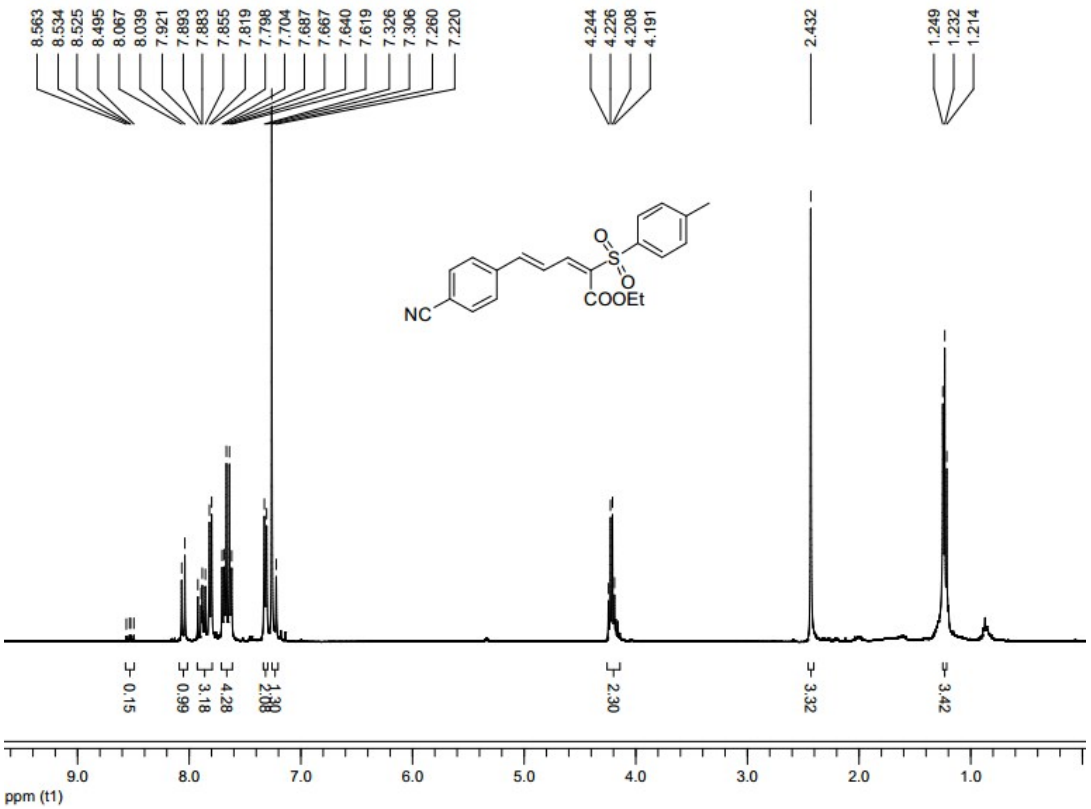


^{13}C{^{1}H}-NMR

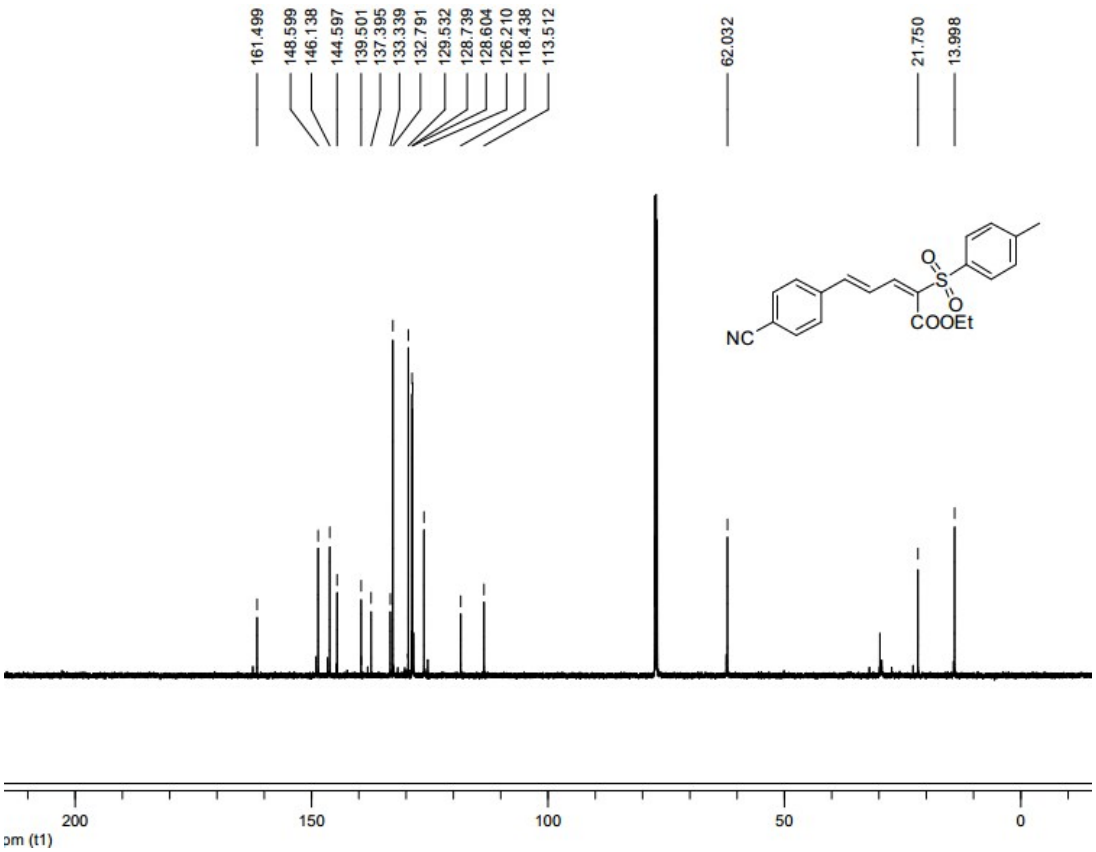


3fa

^{1}H-NMR

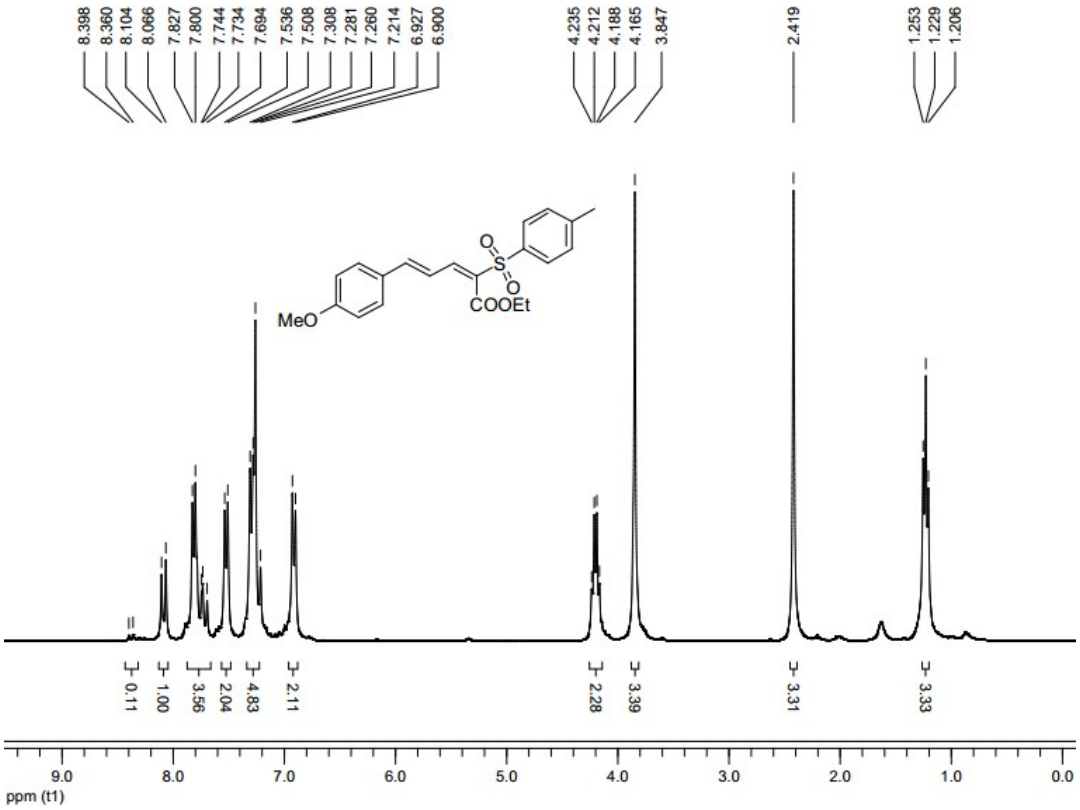


^{13}C{^{1}H}-NMR

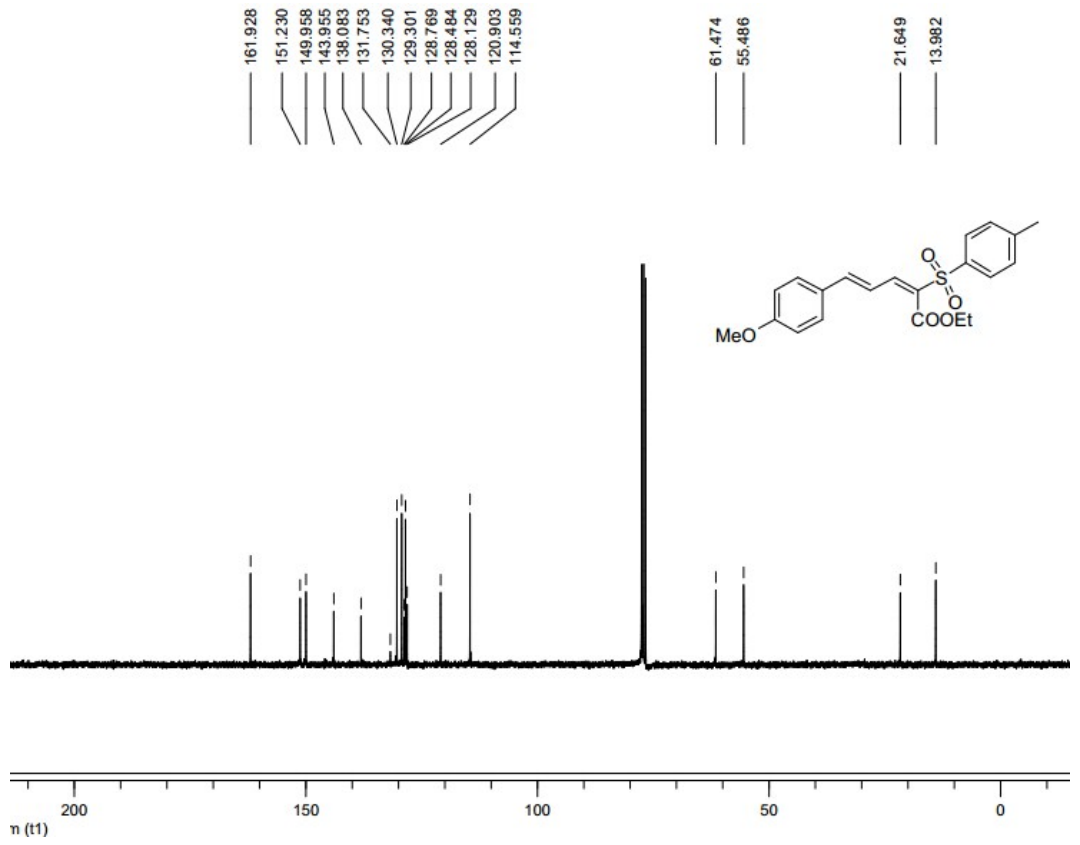


3ga

^{1}H-NMR

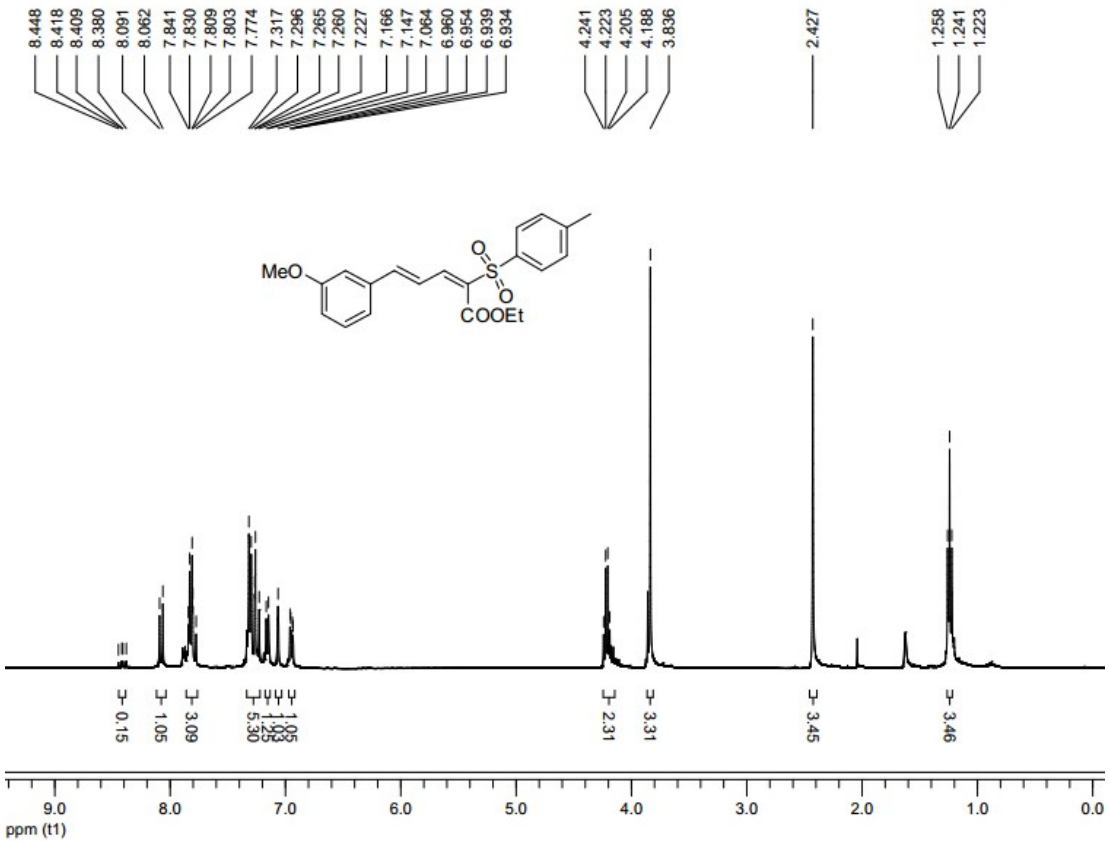


^{13}C{^{1}H}-NMR



3ha

^{1}H-NMR



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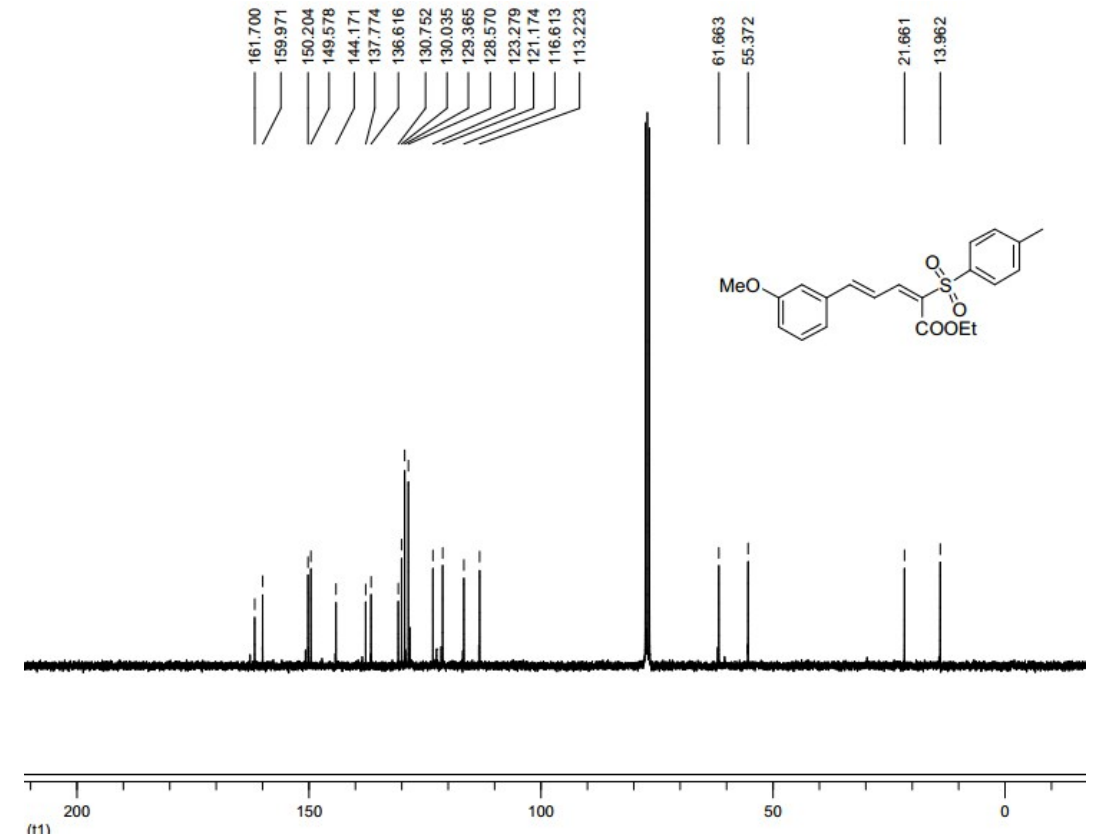
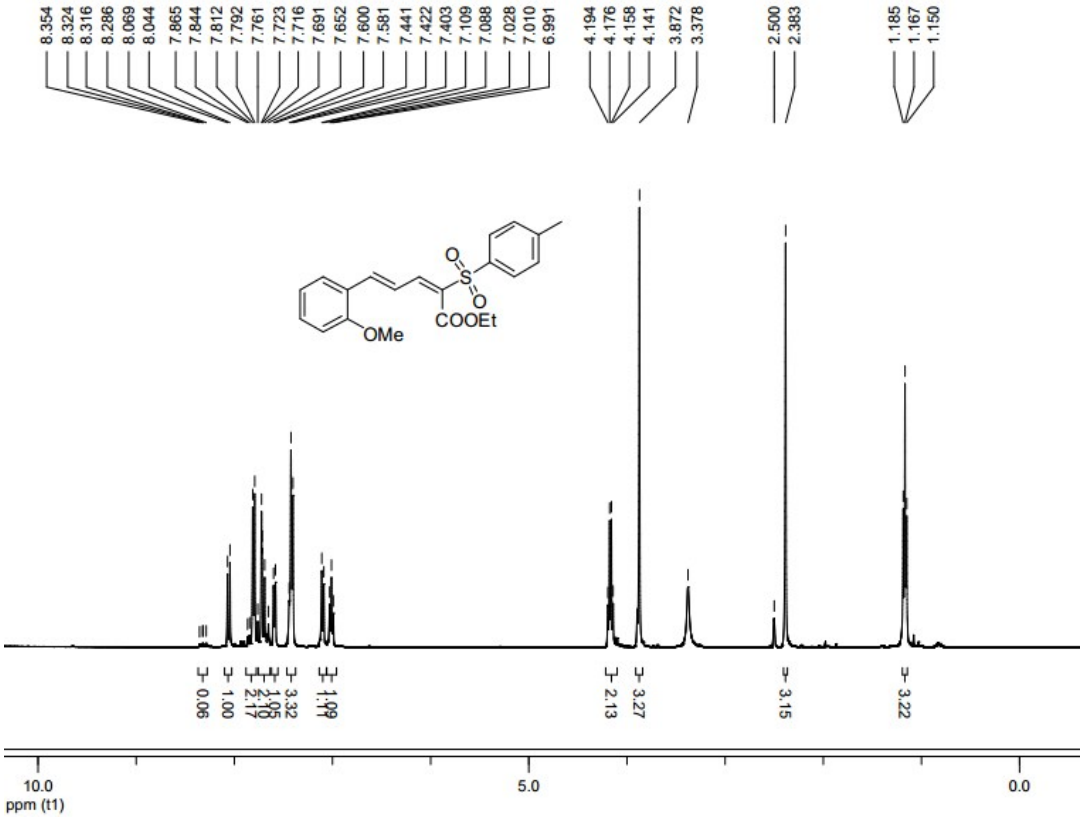


3ia

^{1}H-NMR



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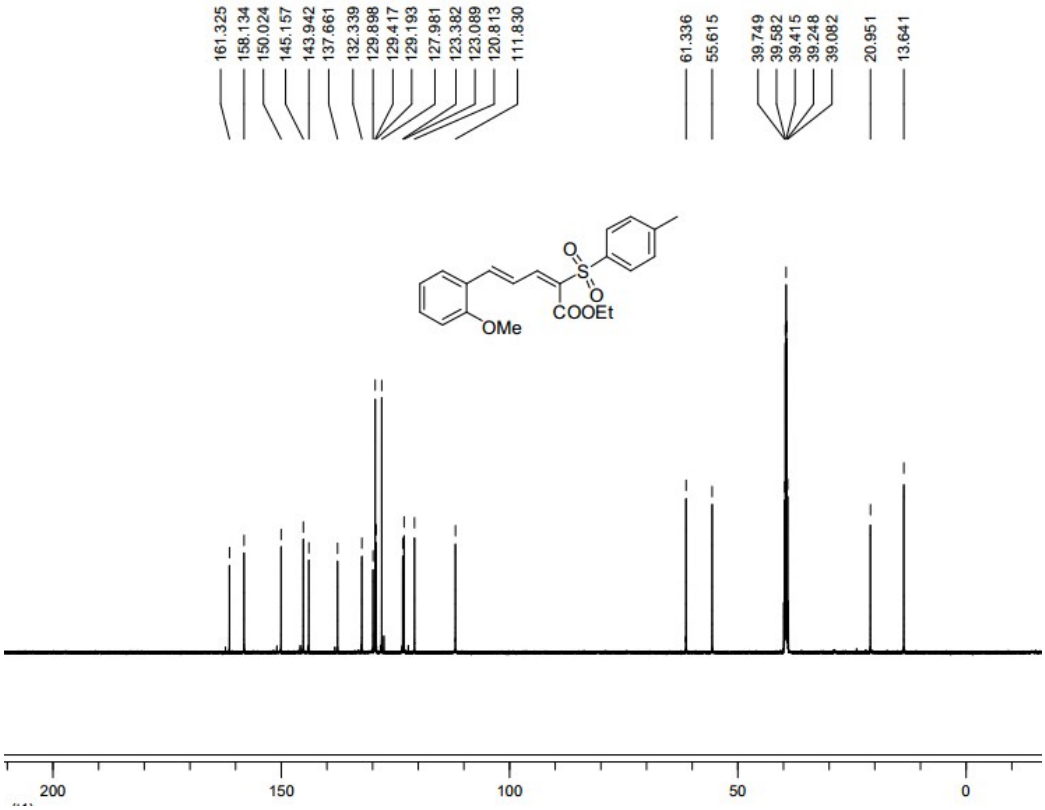

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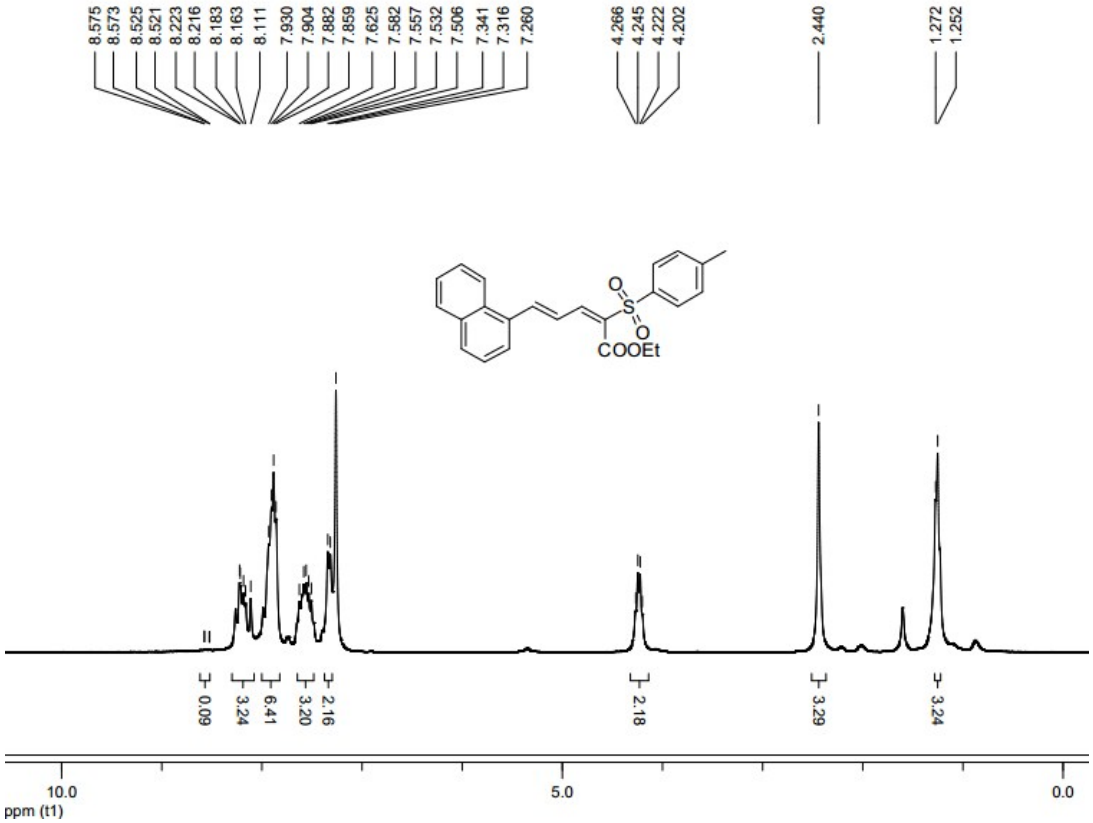
^{1}H-NMR



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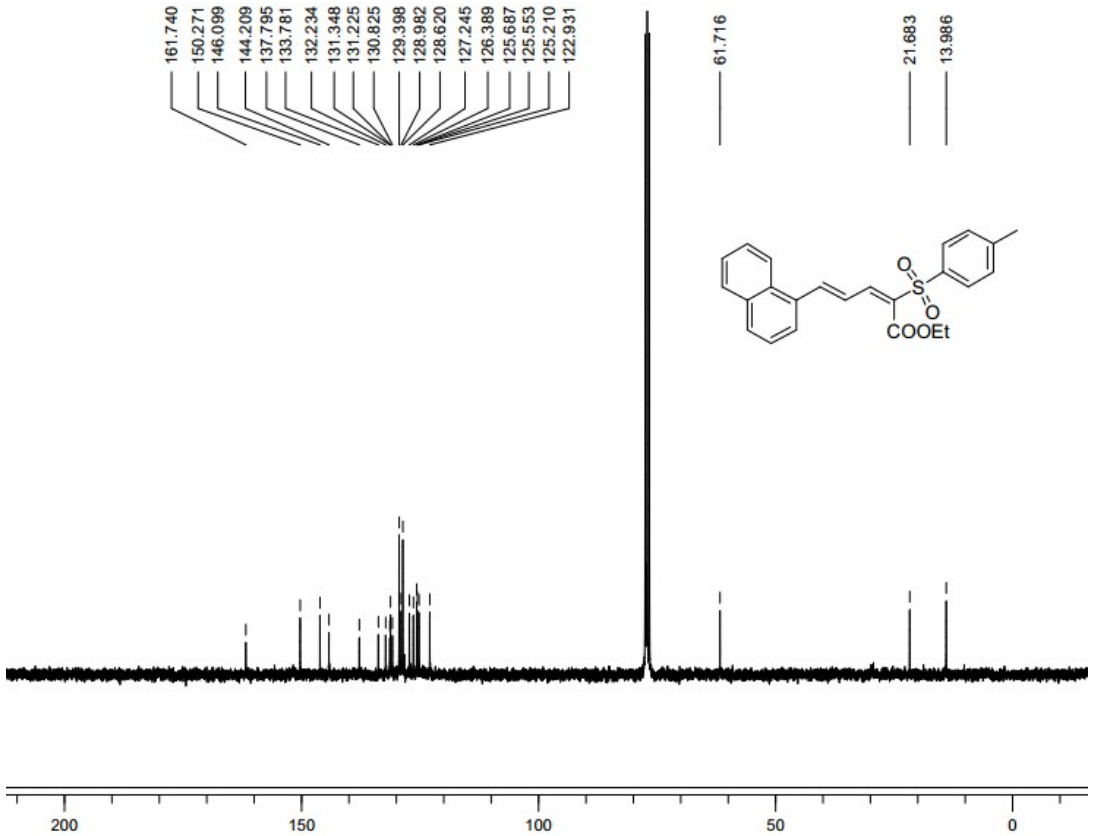

3ka

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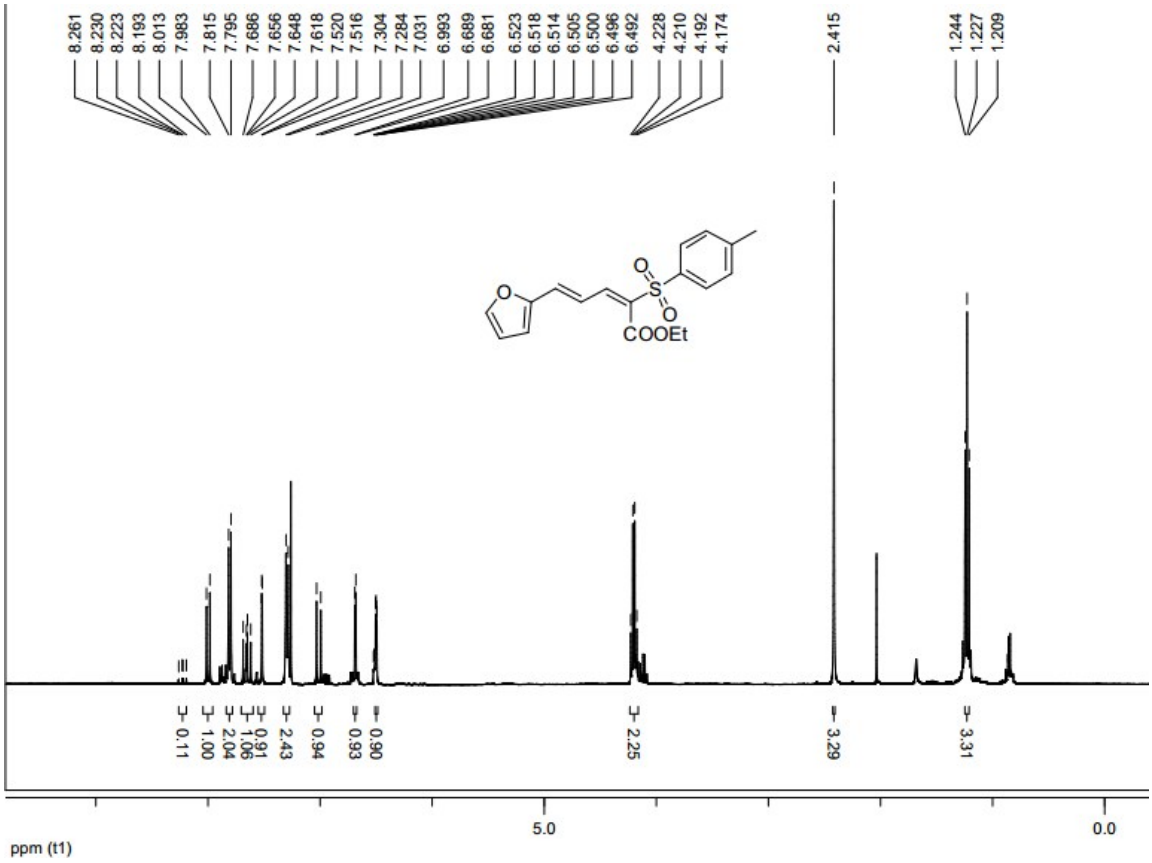

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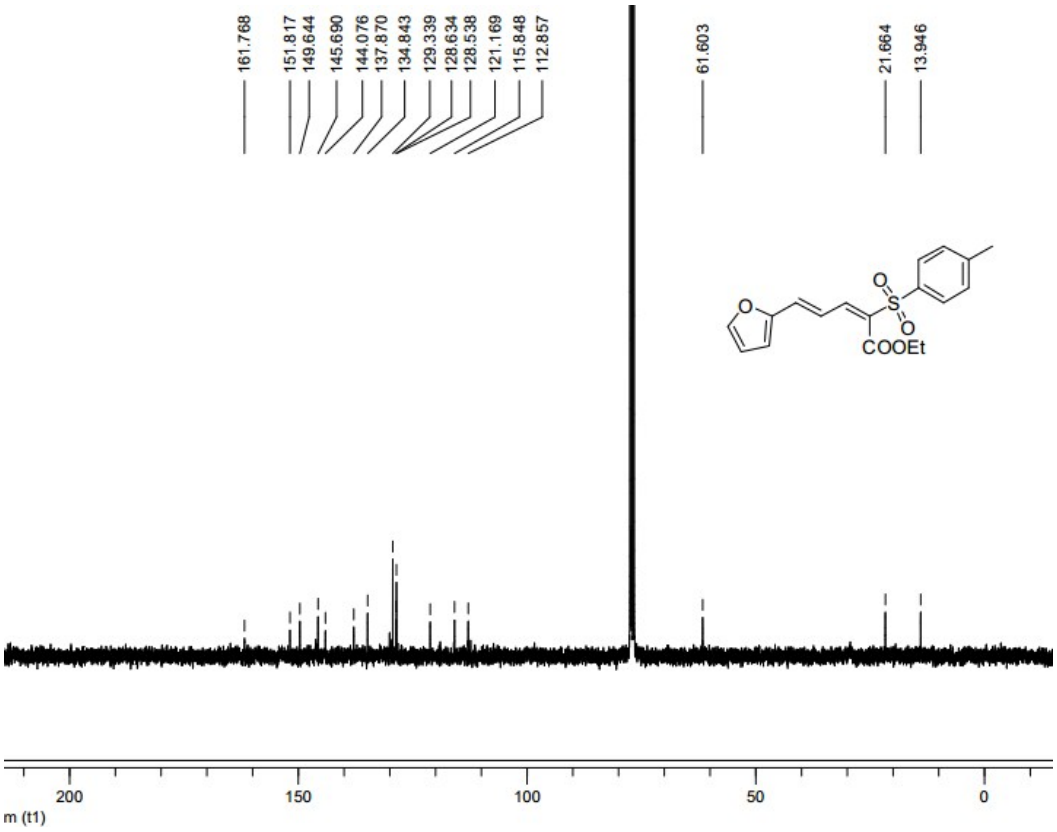
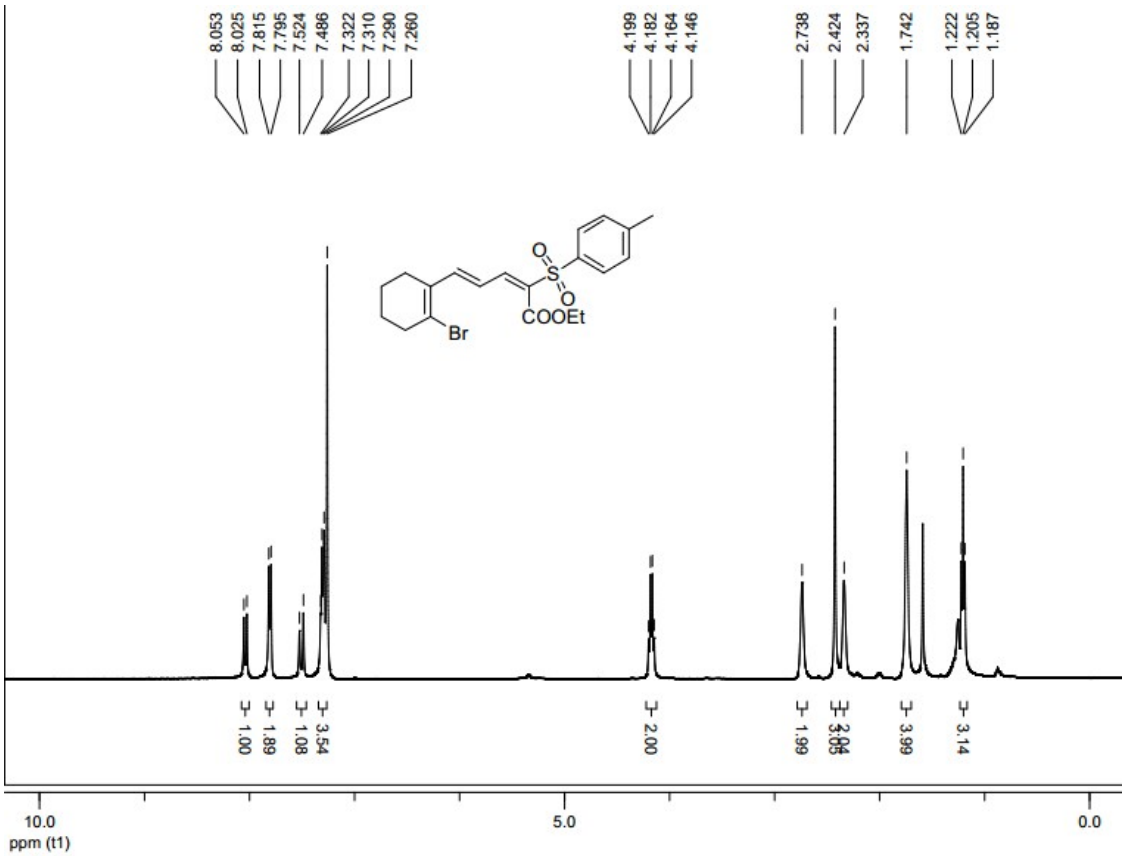


3la

^{1}H-NMR



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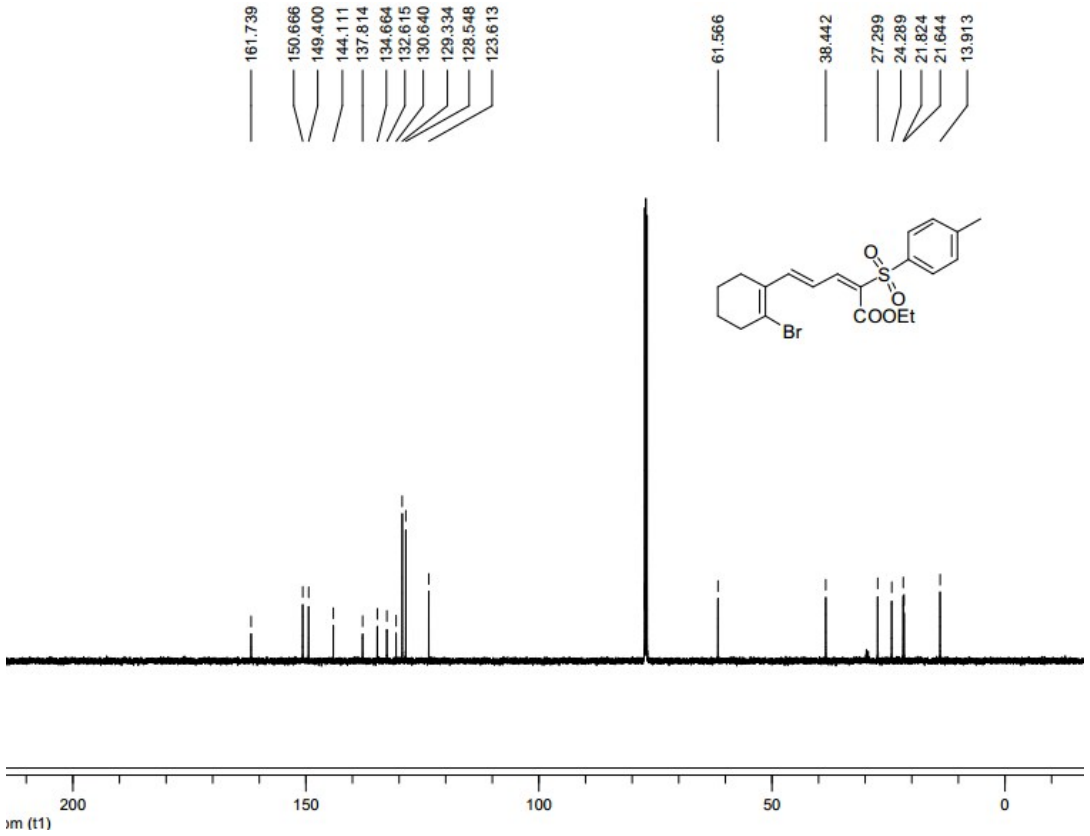
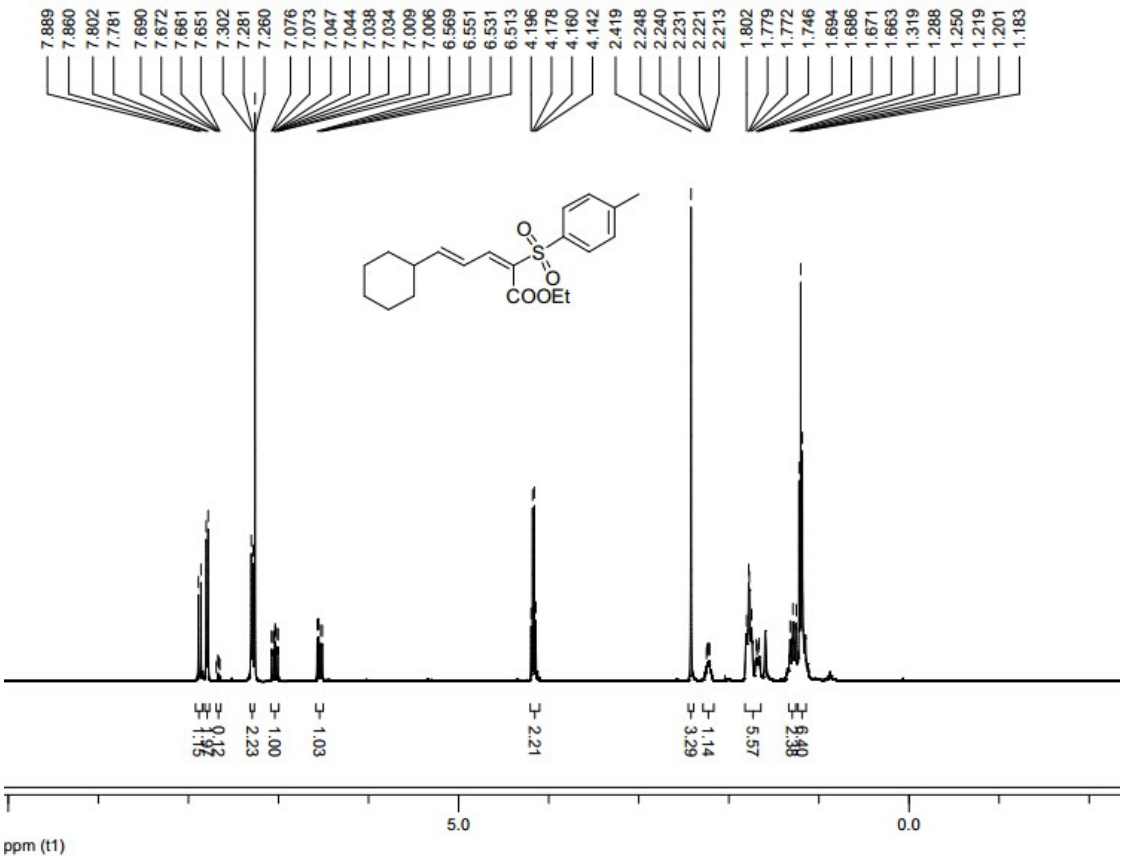


3na

^{1}H-NMR



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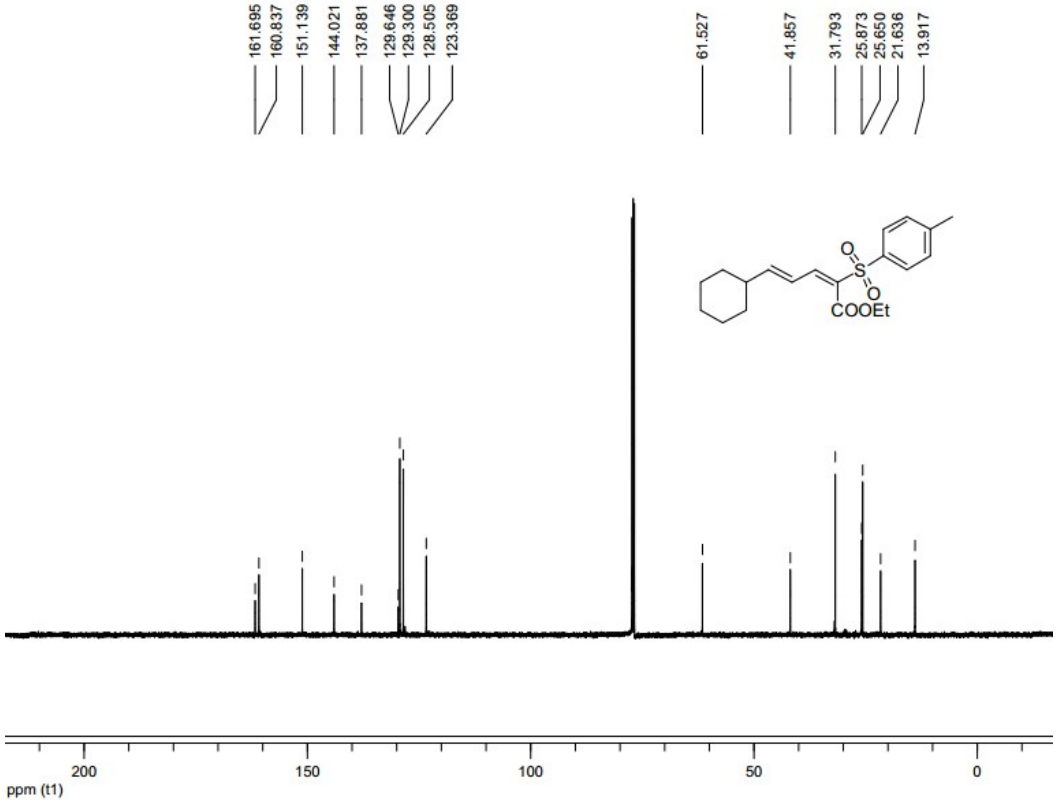

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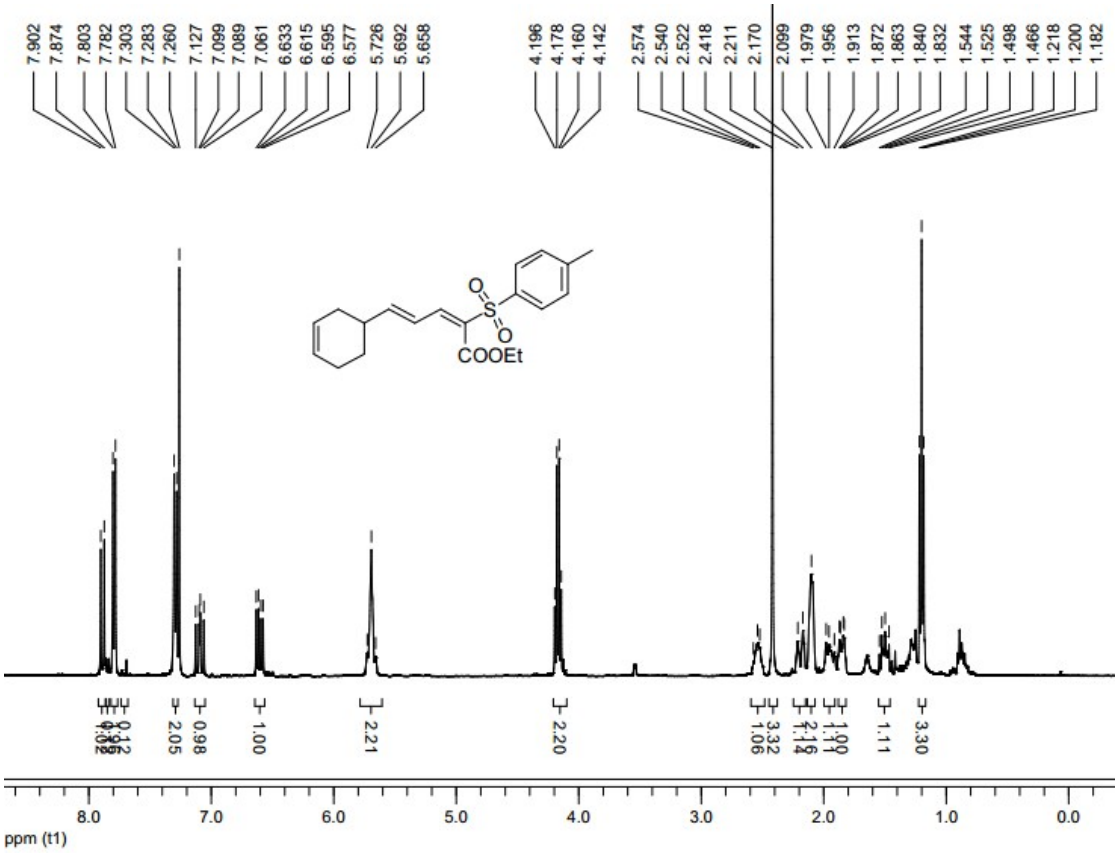

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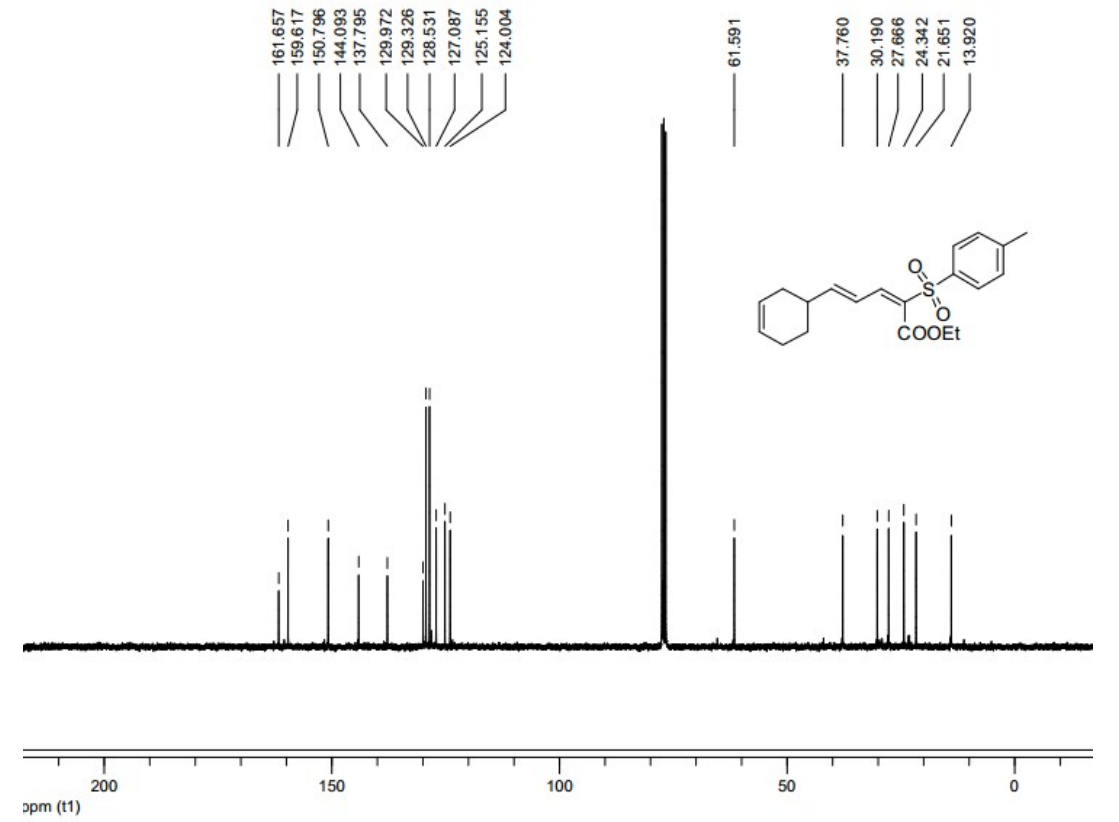
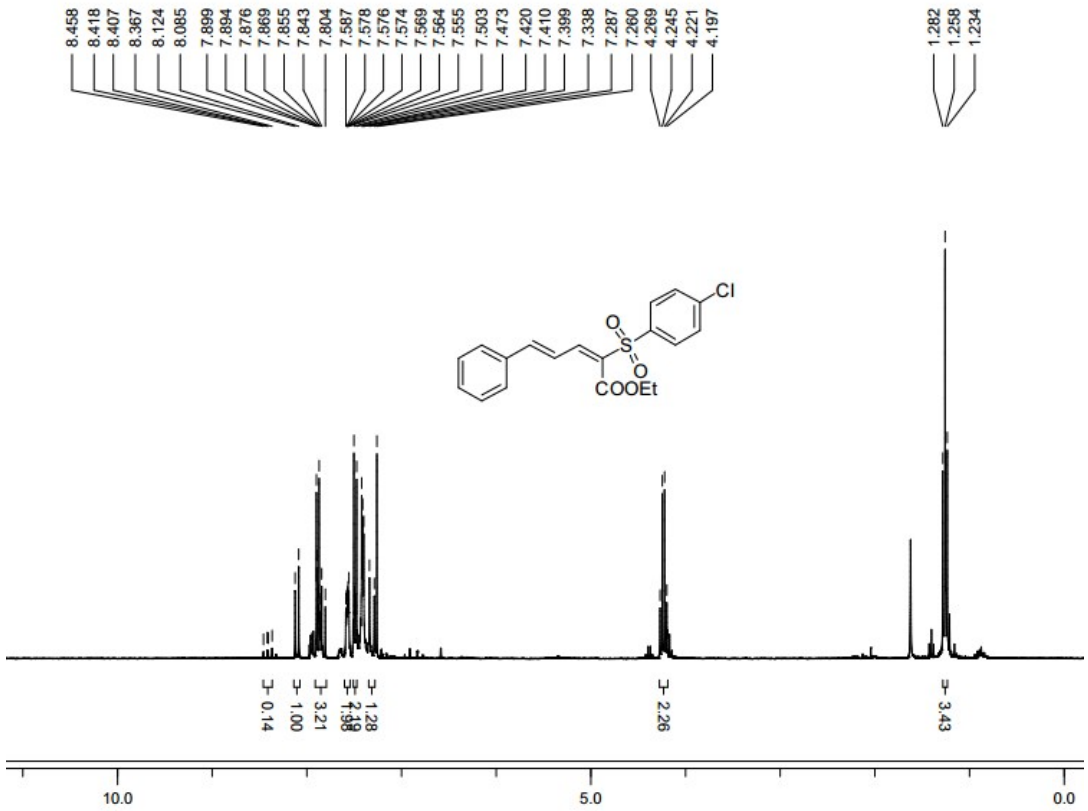


3ab

^{1}H-NMR



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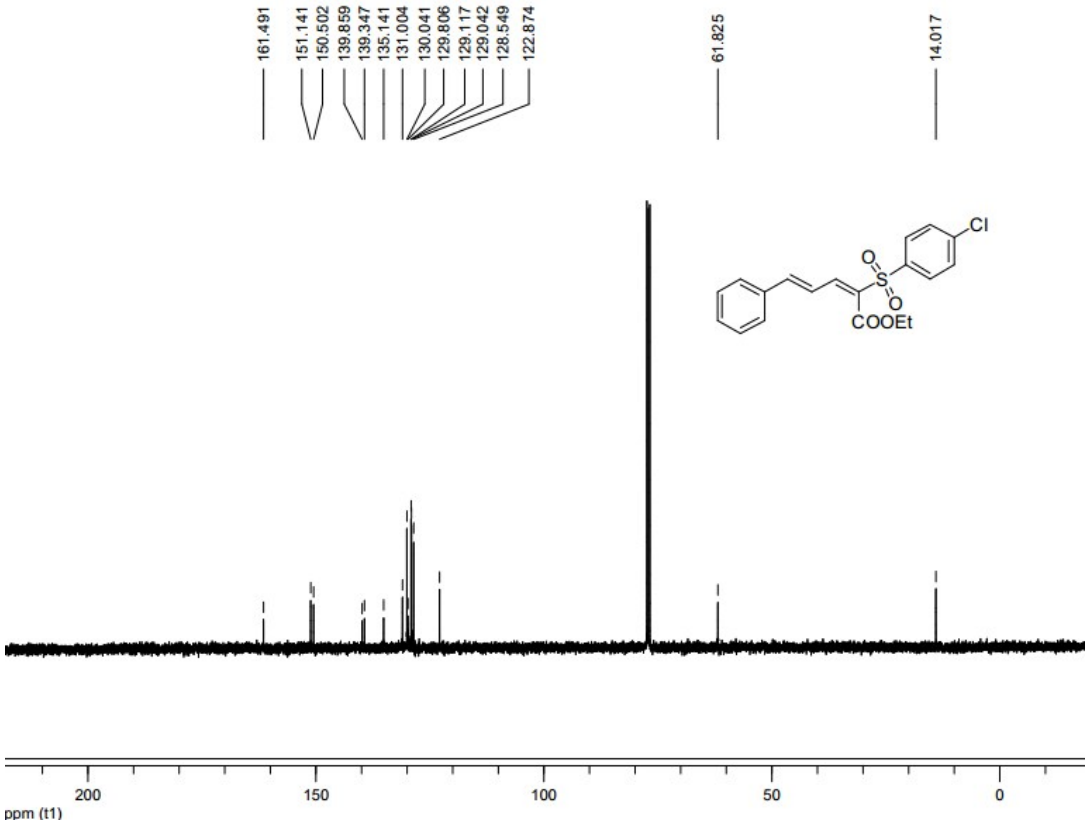
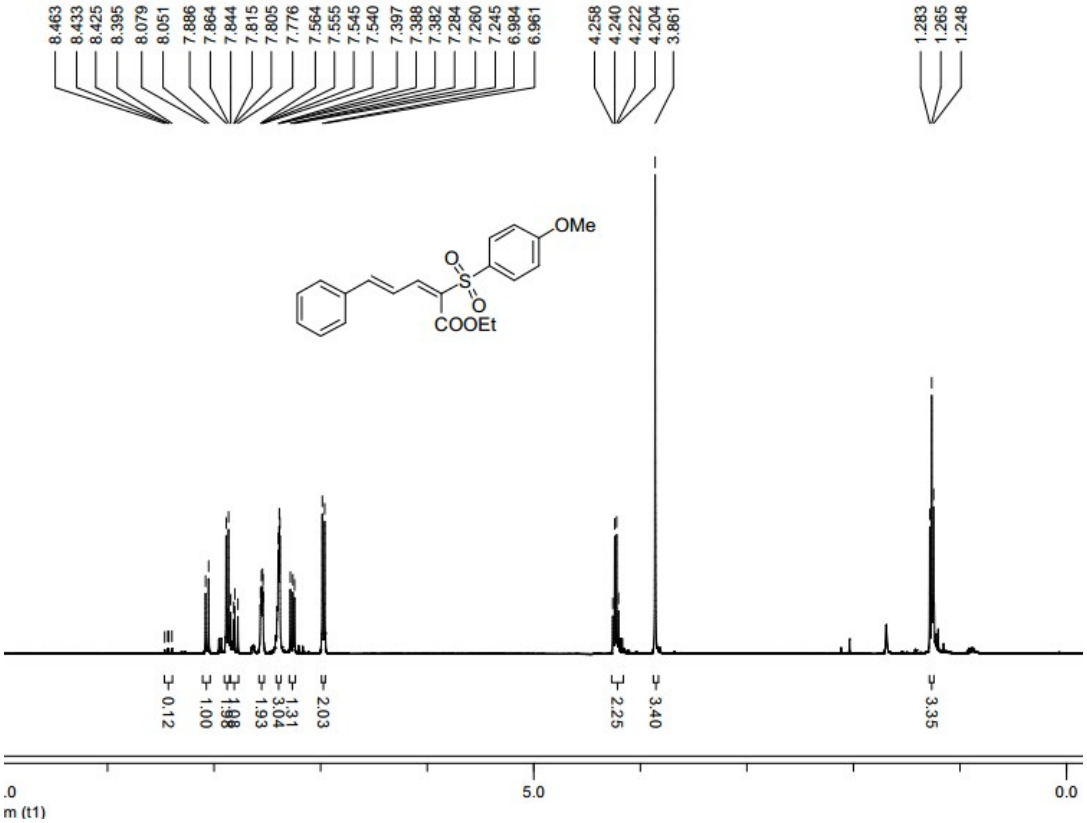


3ac

^{1}H-NMR



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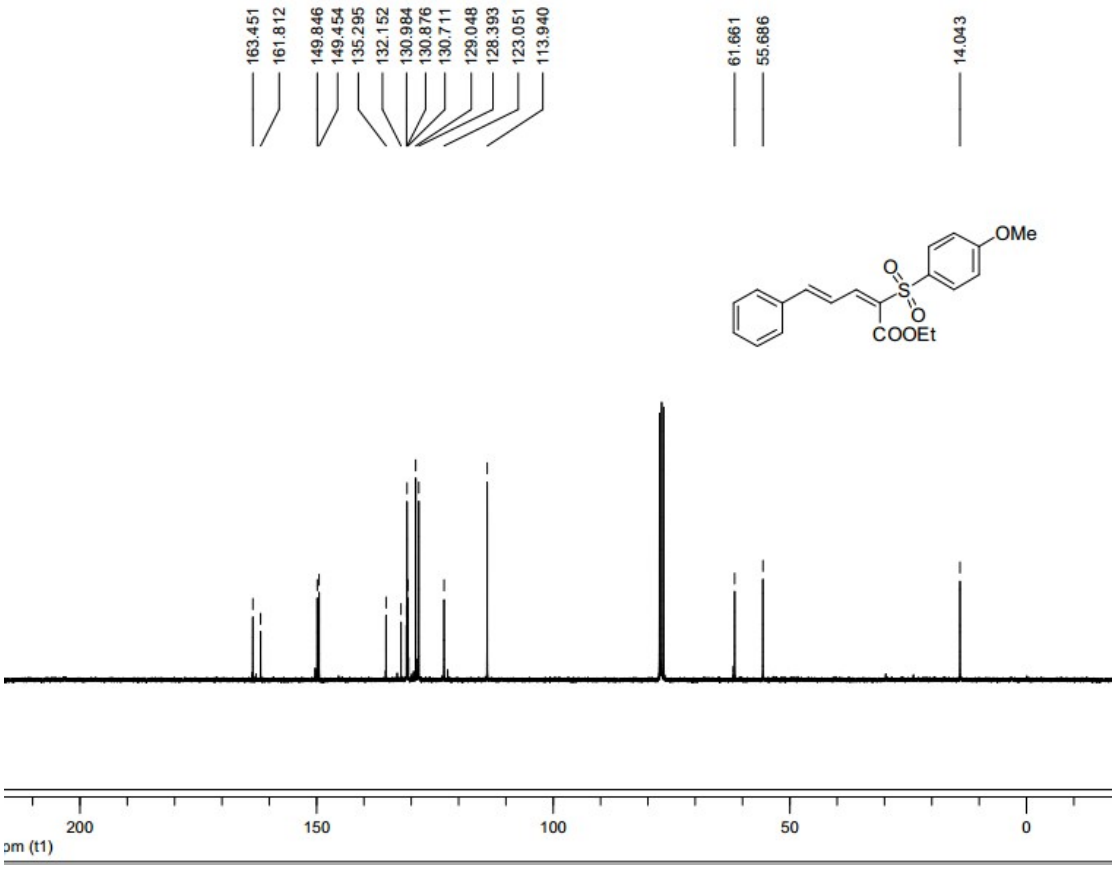
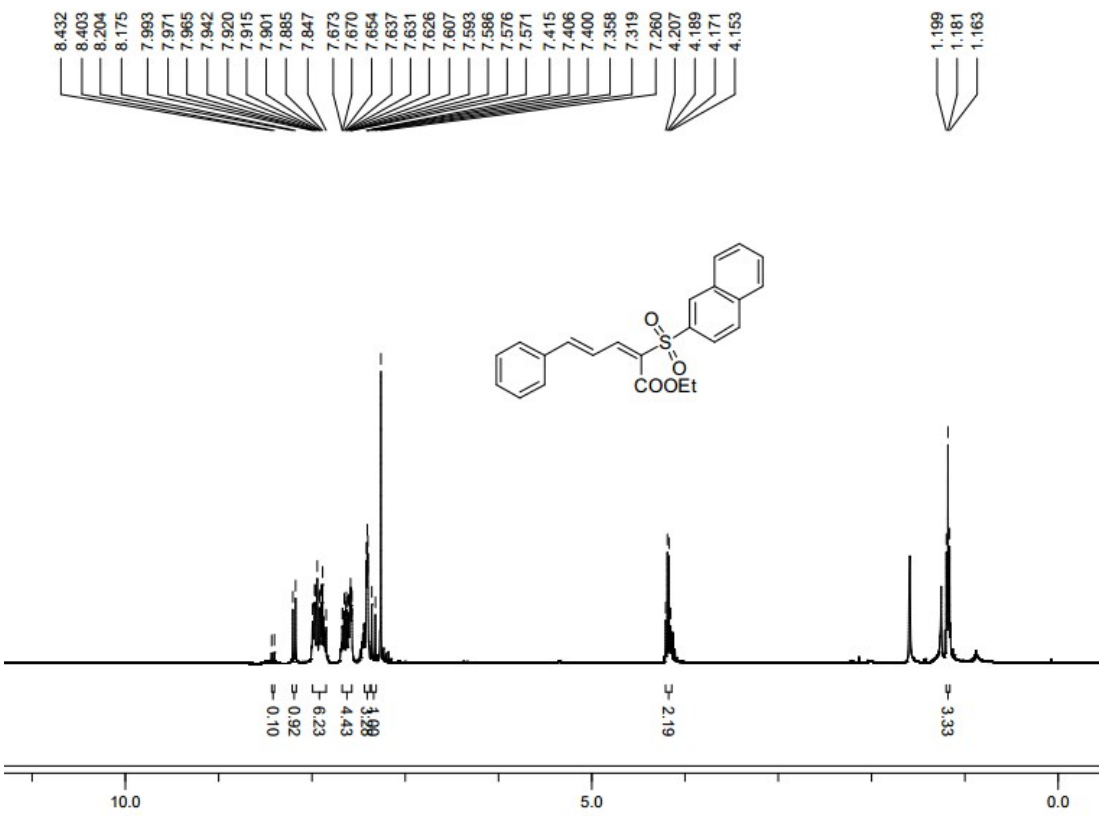
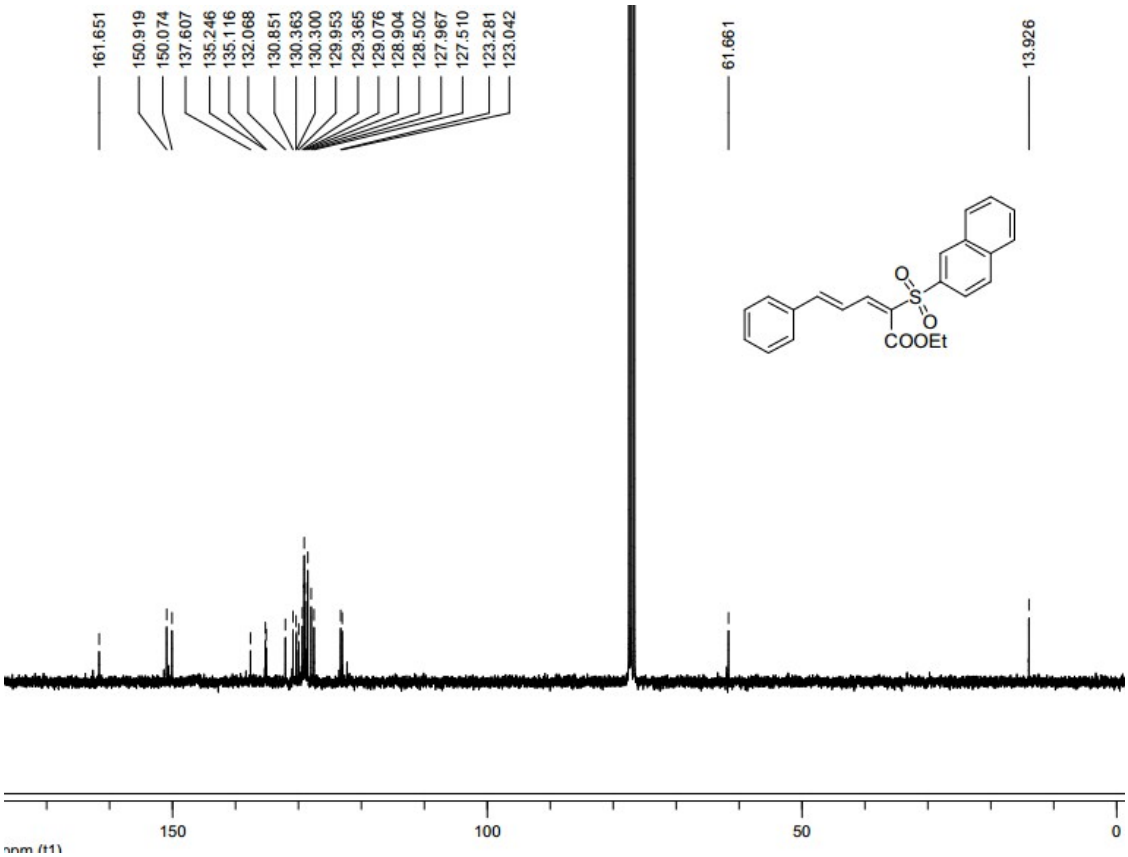


3ad

^{1}H-NMR



^{13}C{^{1}H}-NMR



3ae

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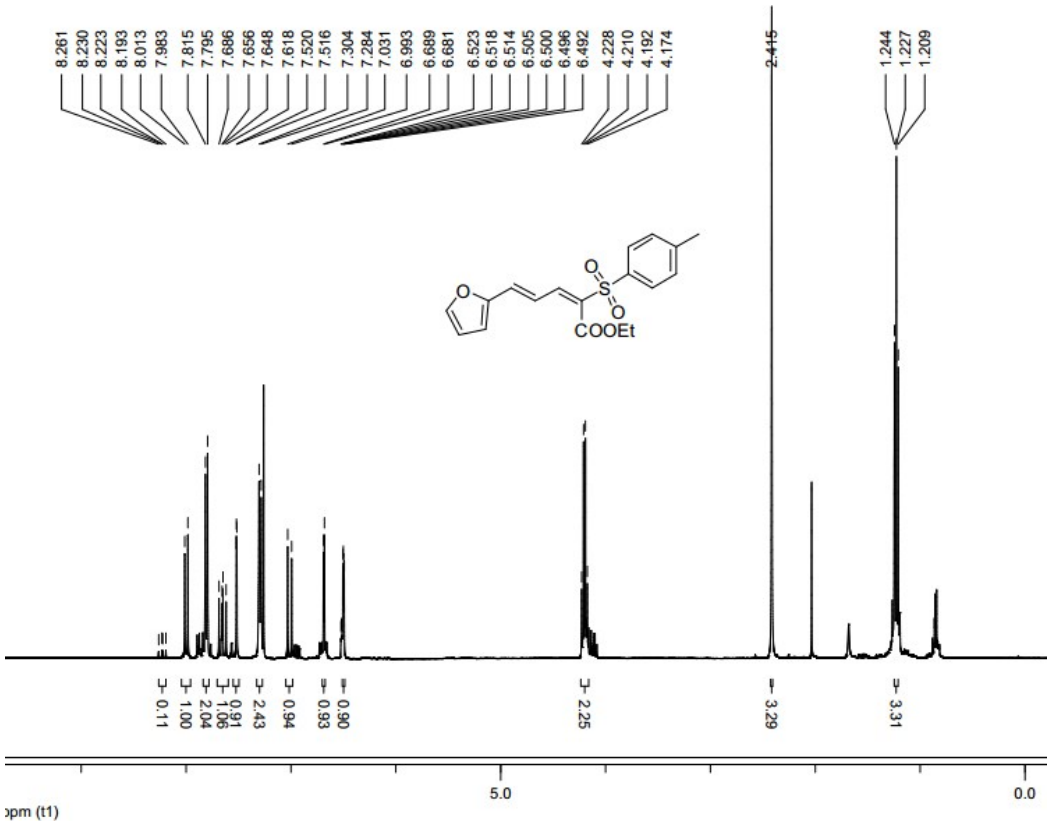
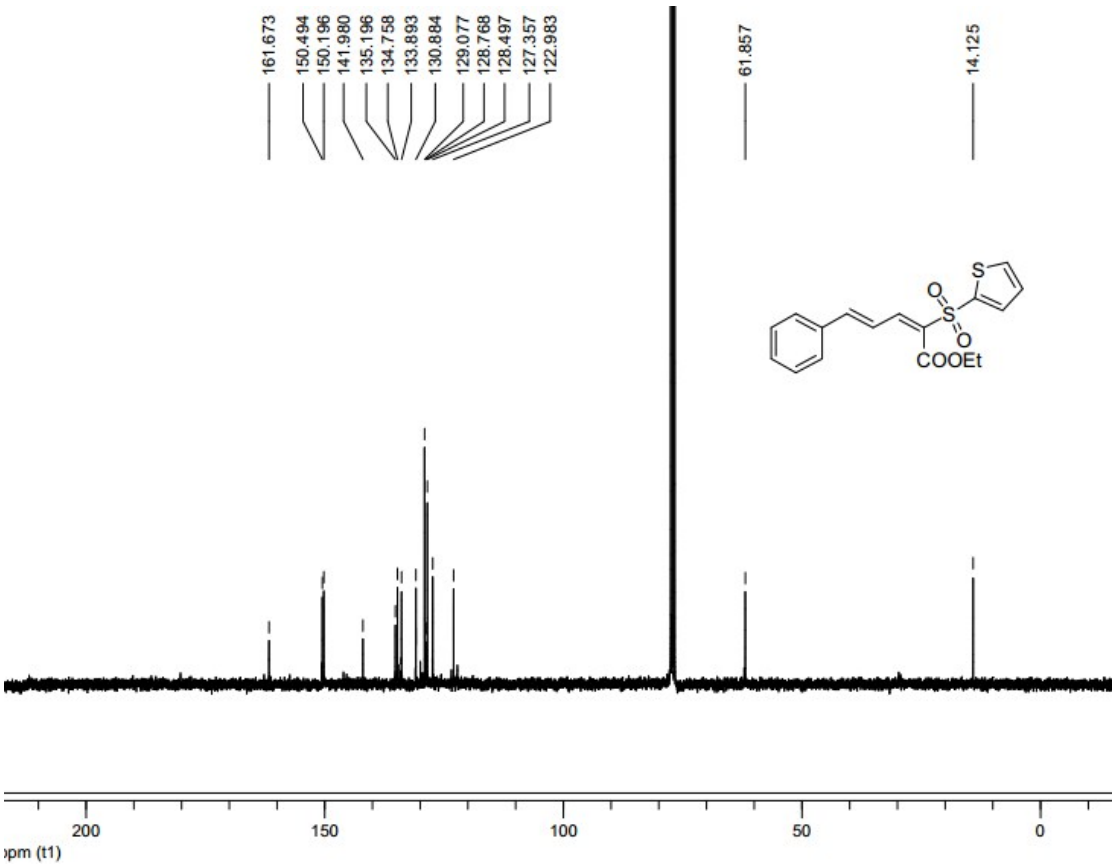
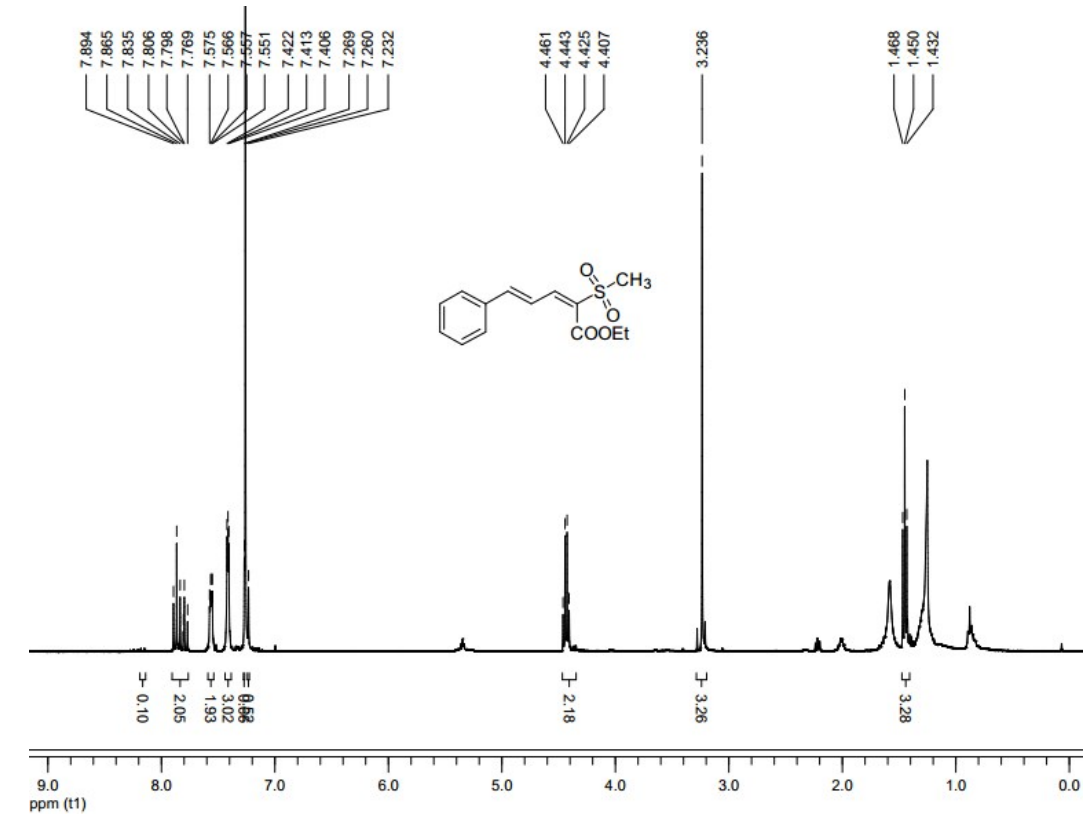


^{13}C{^{1}H}-NMR

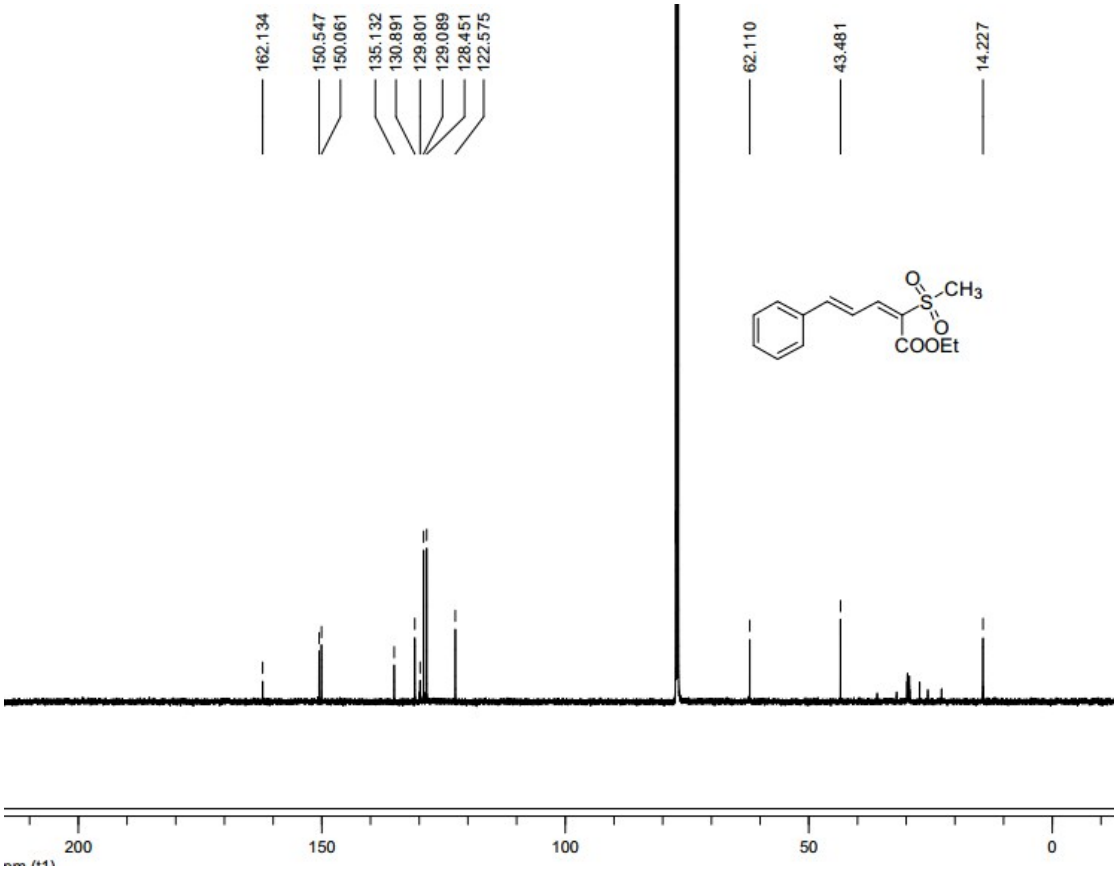


3af

^{1}H-NMR

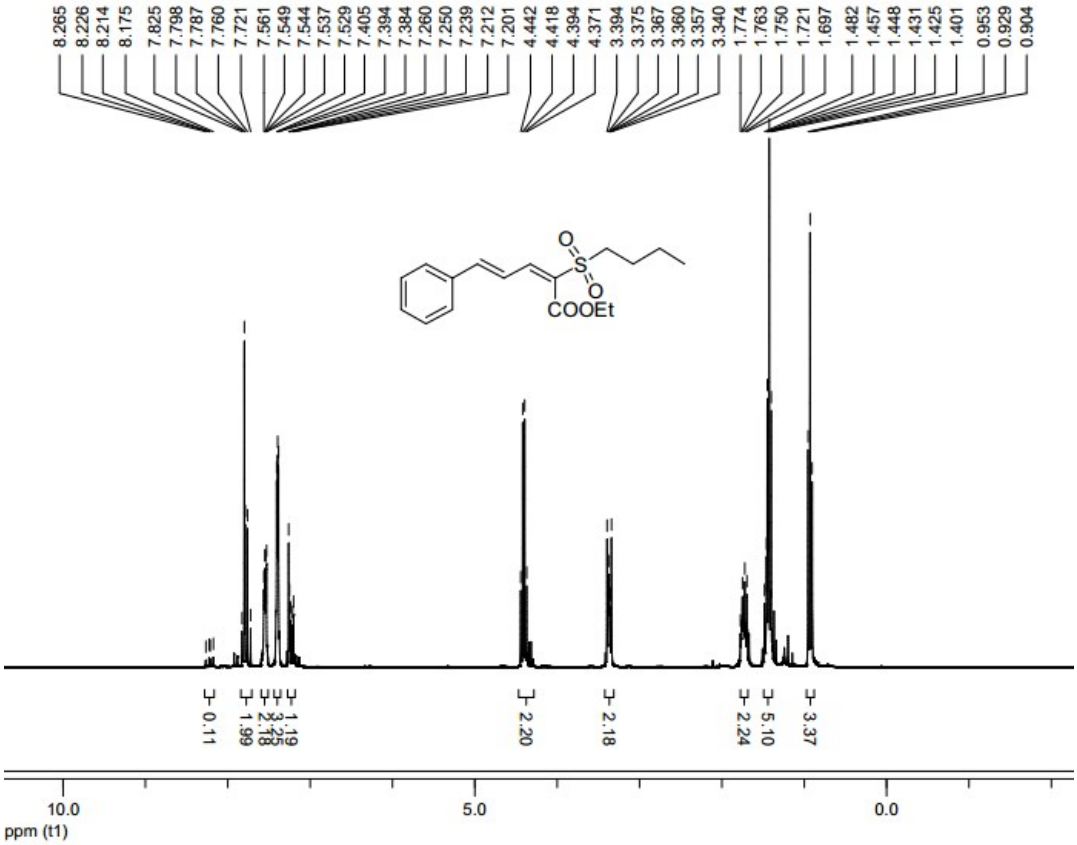


^{13}C{^{1}H}-NMR



3ag

^{1}H-NMR



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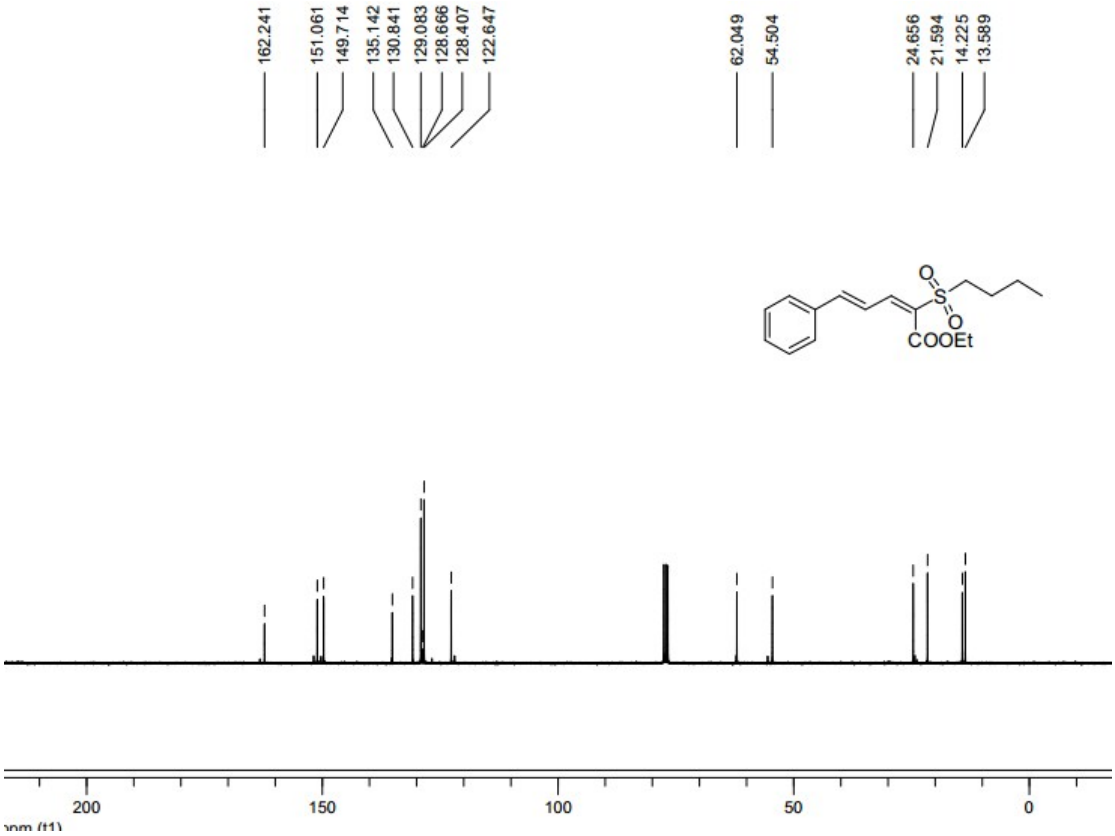
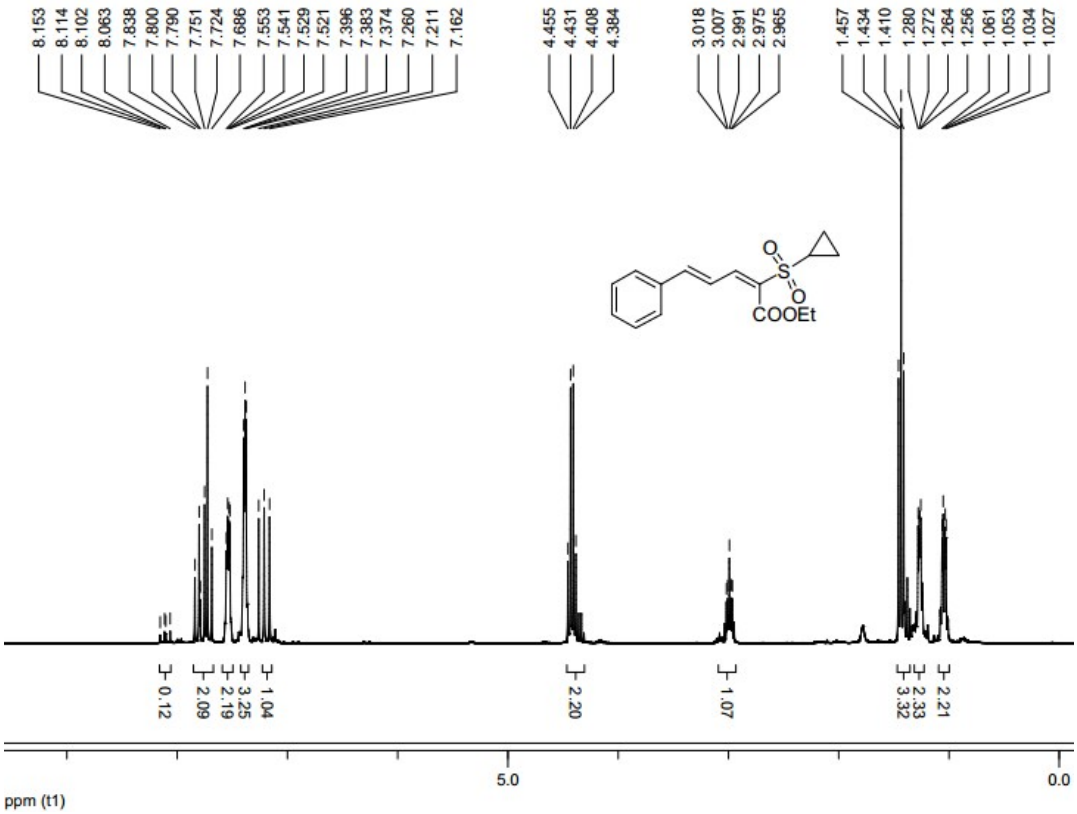
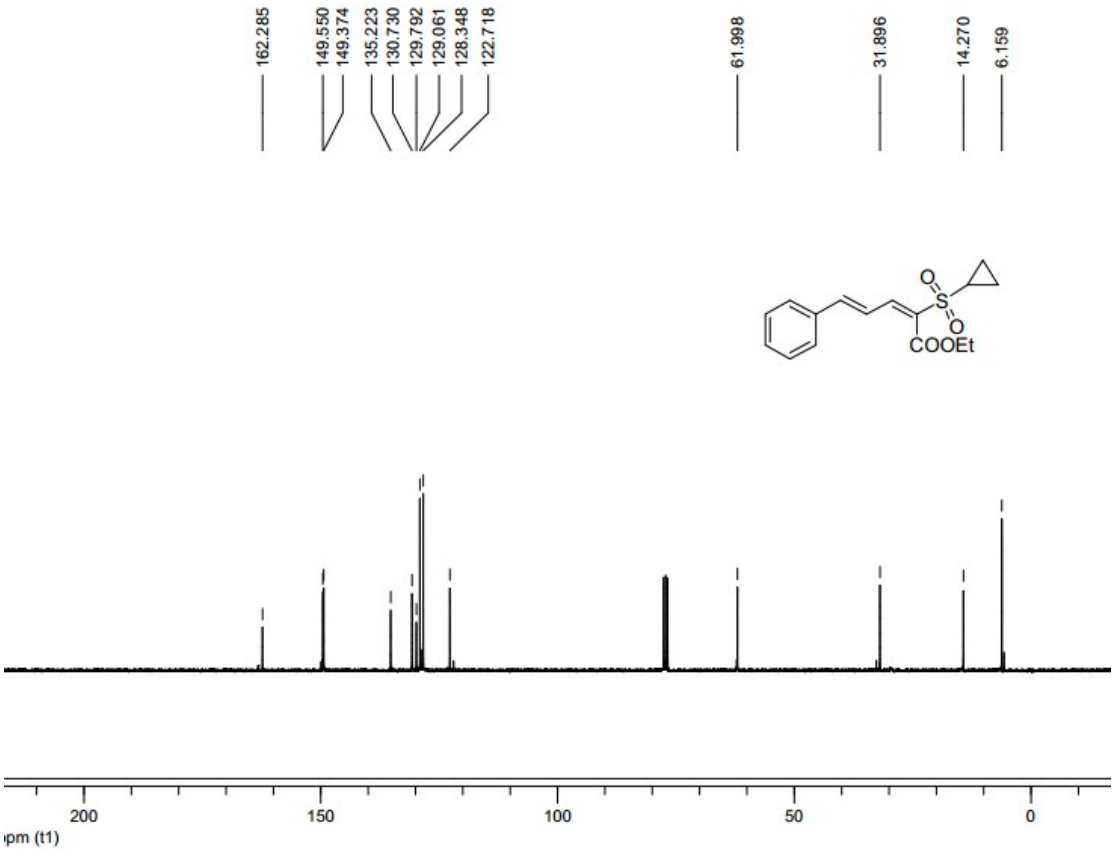


3ah

^{1}H-NMR

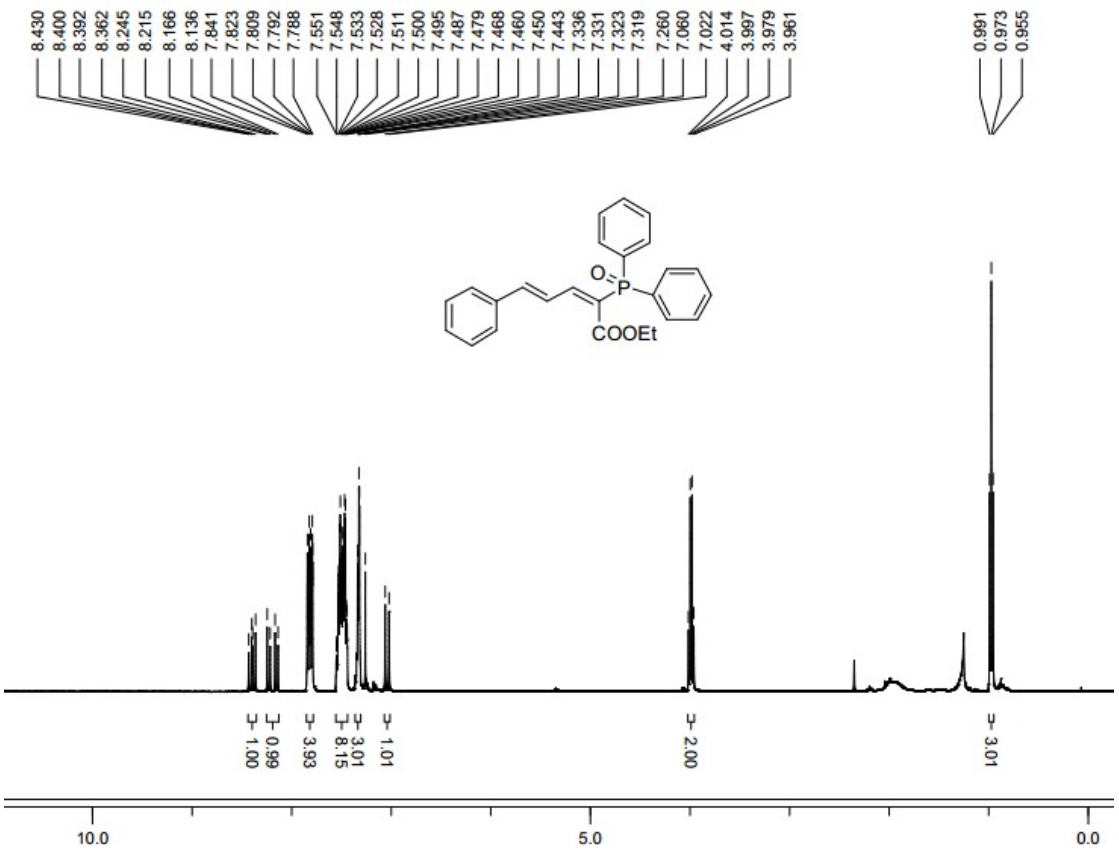


^{13}C{^{1}H}-NMR



5aa

^{1}H-NMR



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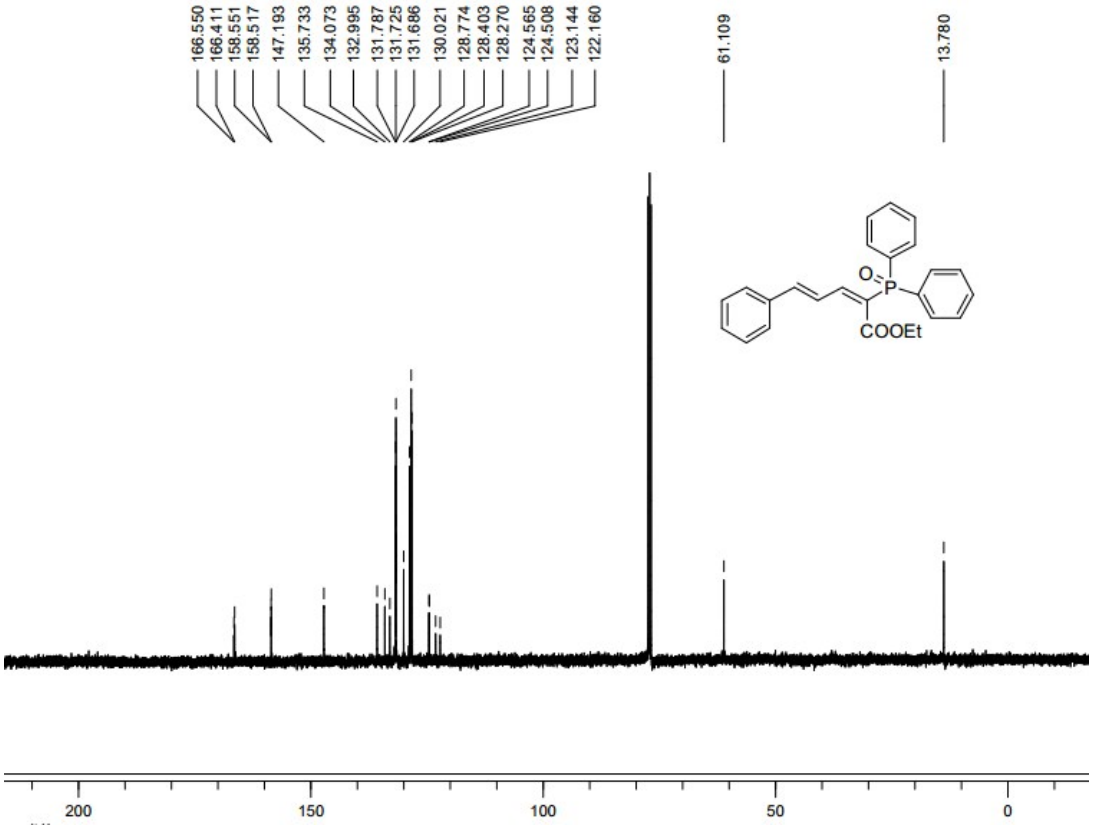
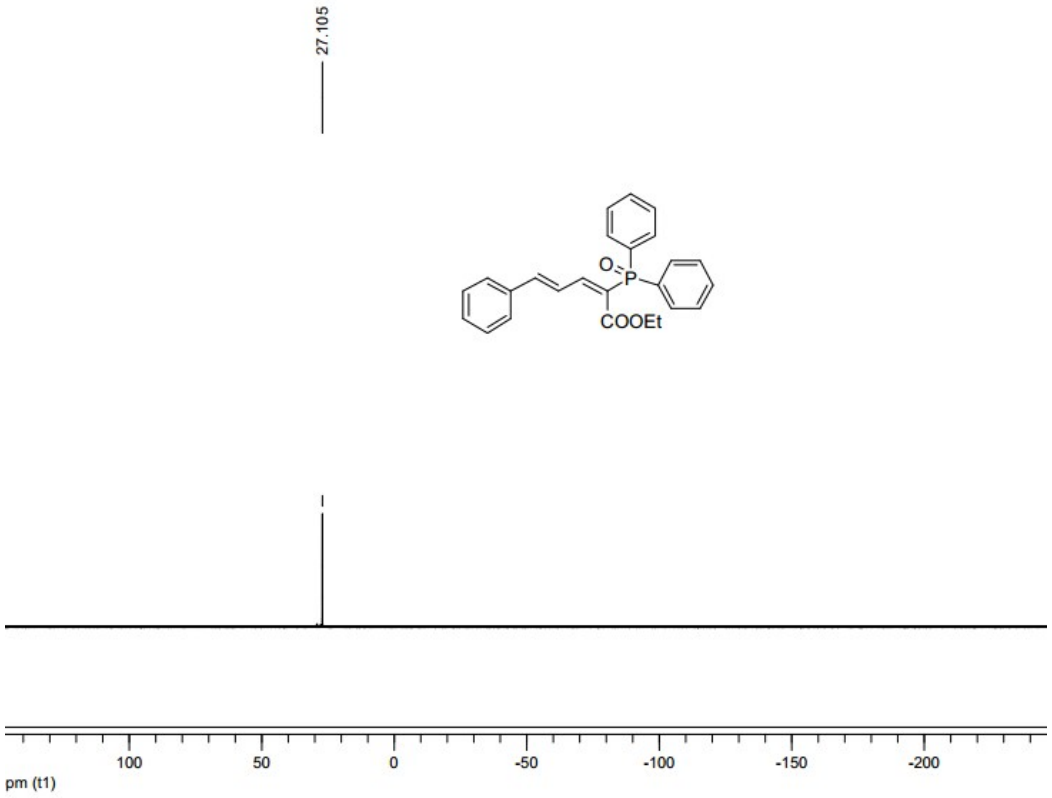
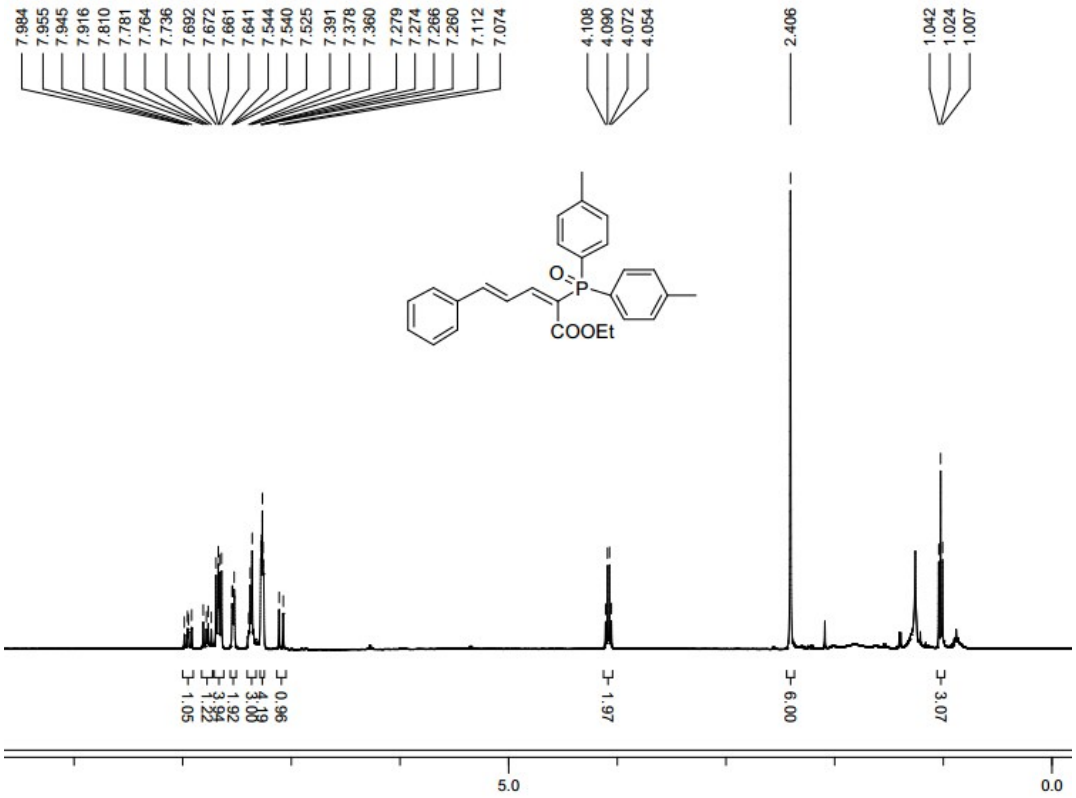


$^{31}P\{^{1}H\}$-NMR



5ab

^{1}H-NMR



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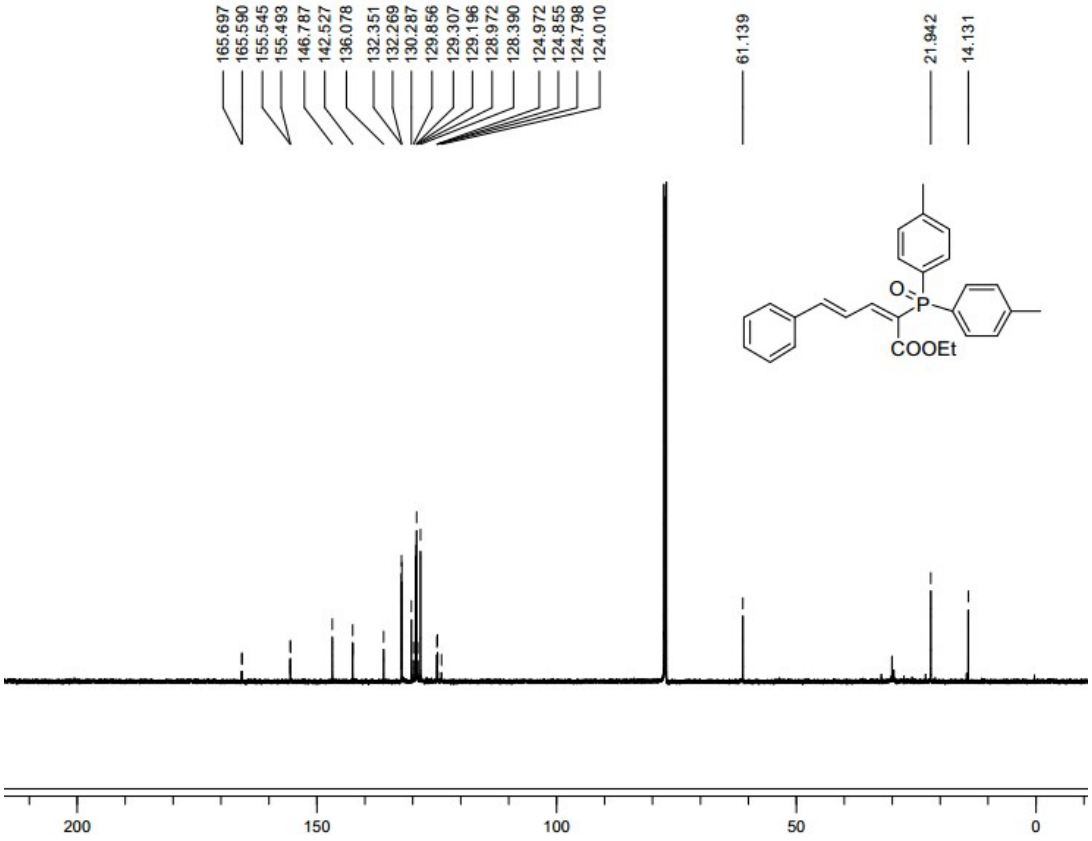
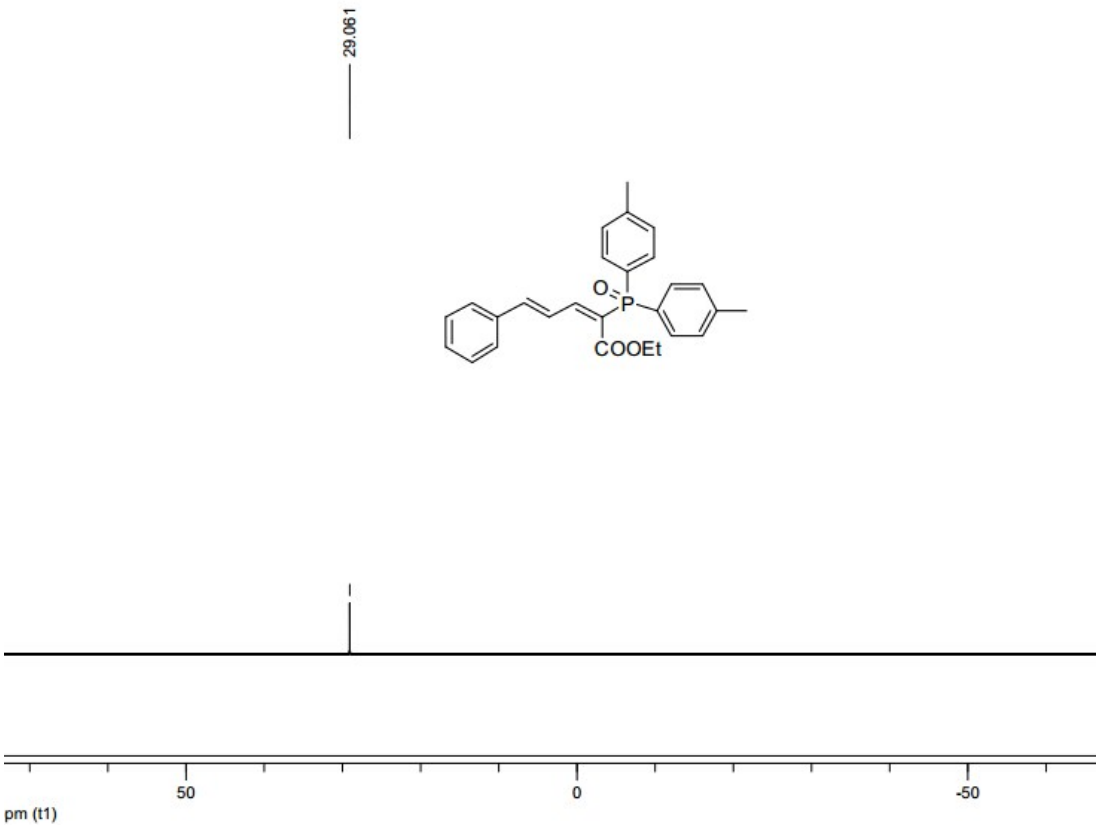


$^{31}P\{^{1}H\}$-NMR



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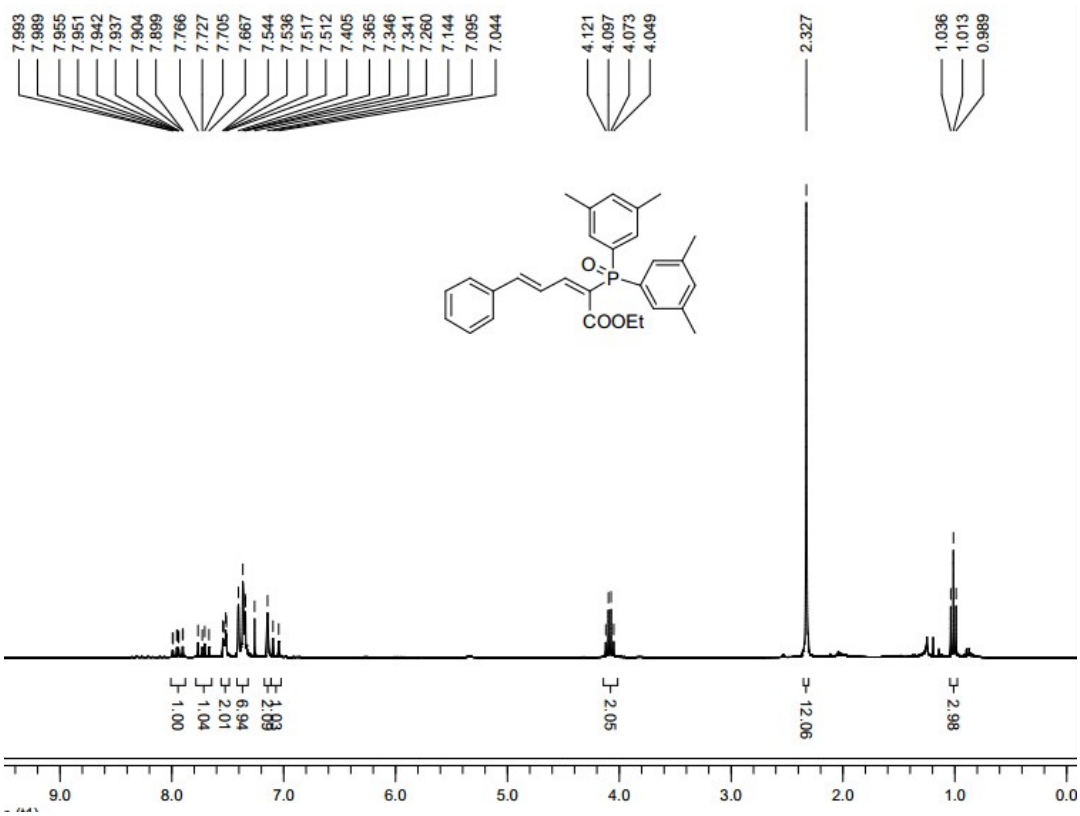
^{1}H-NMR



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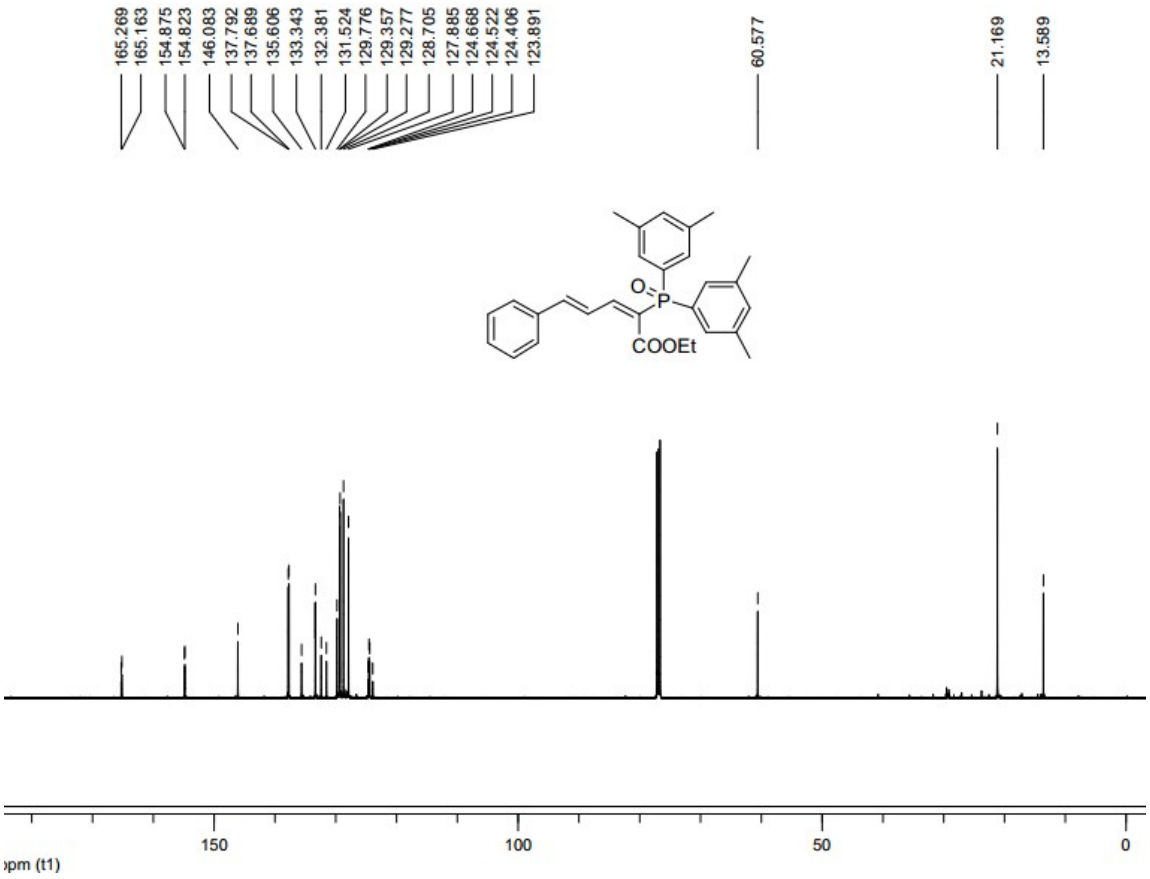

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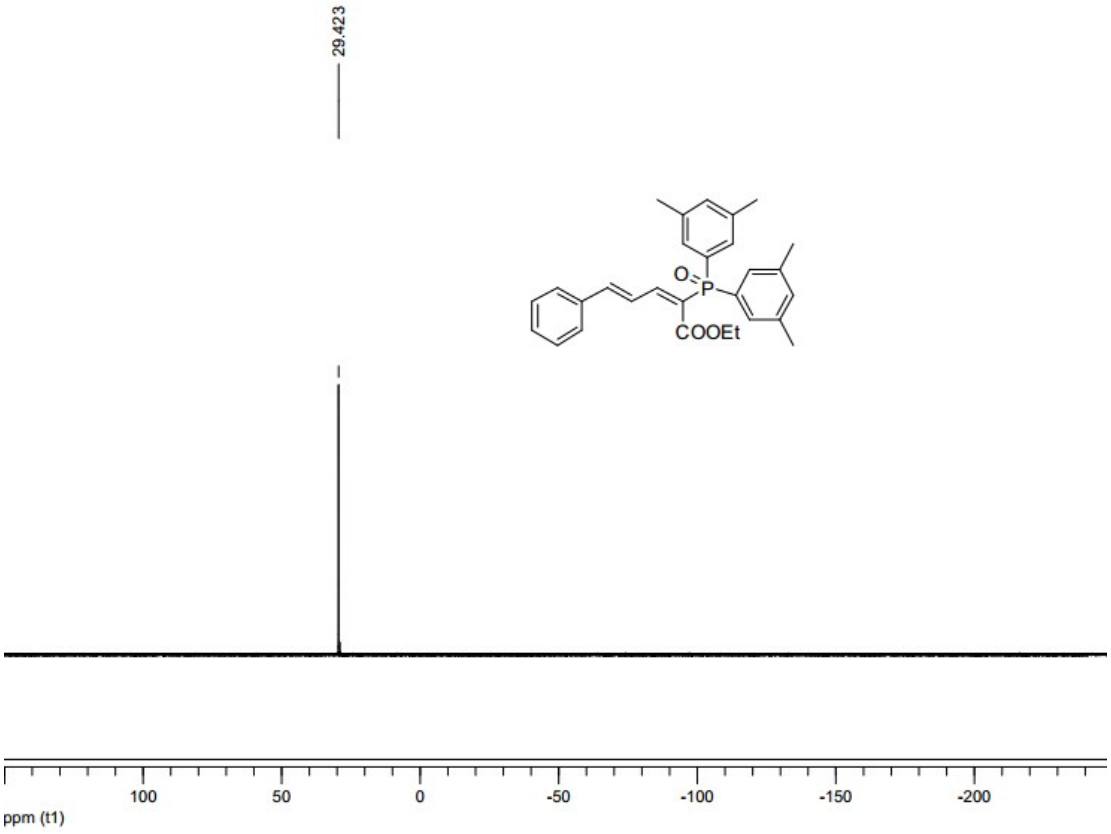

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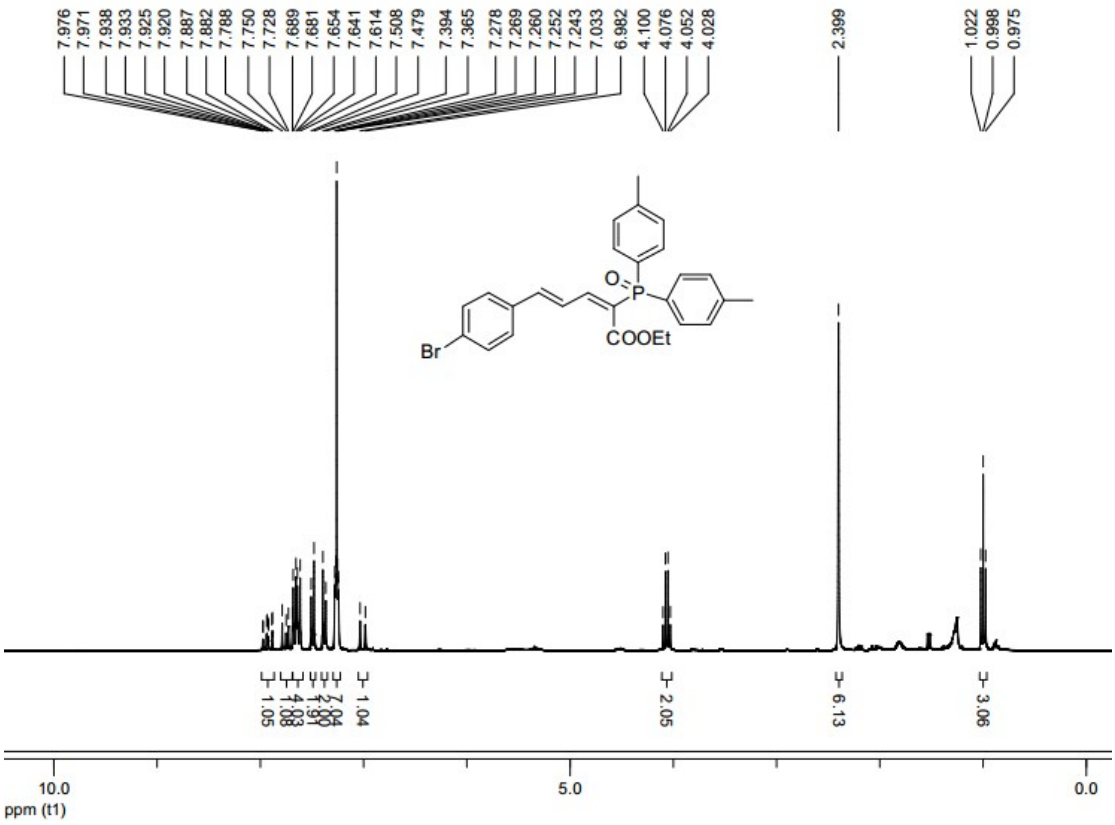

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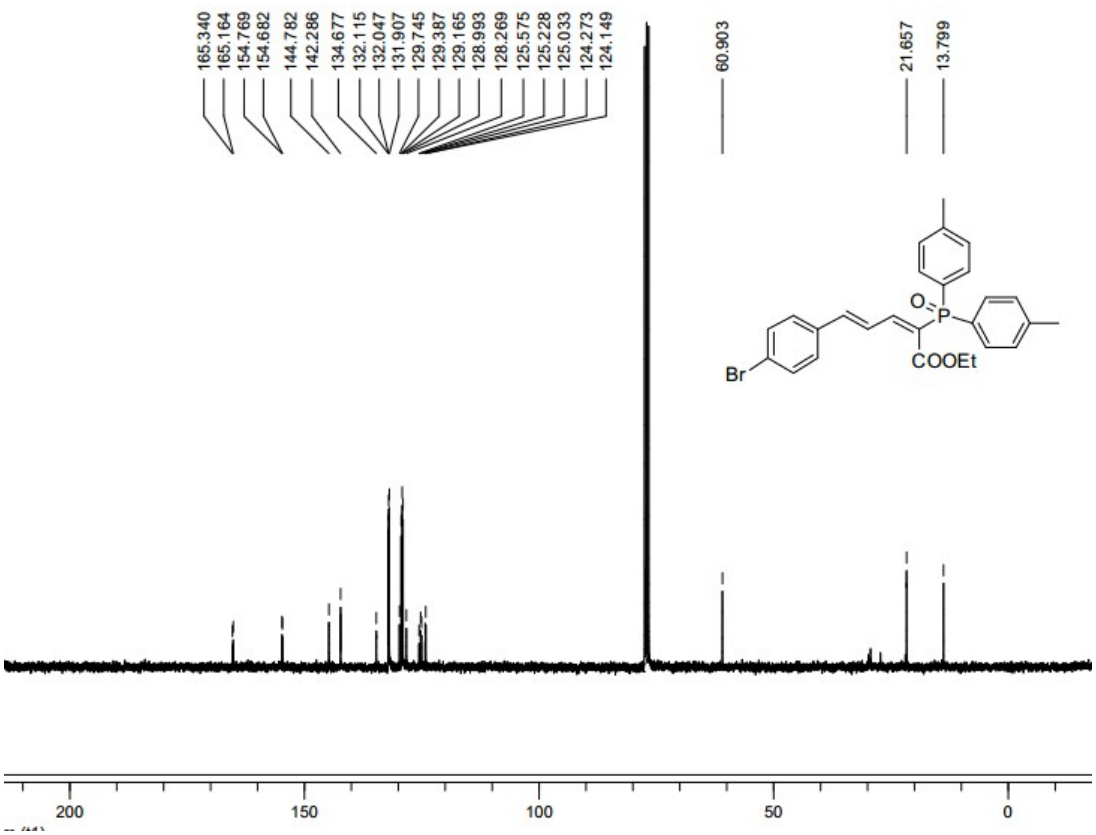
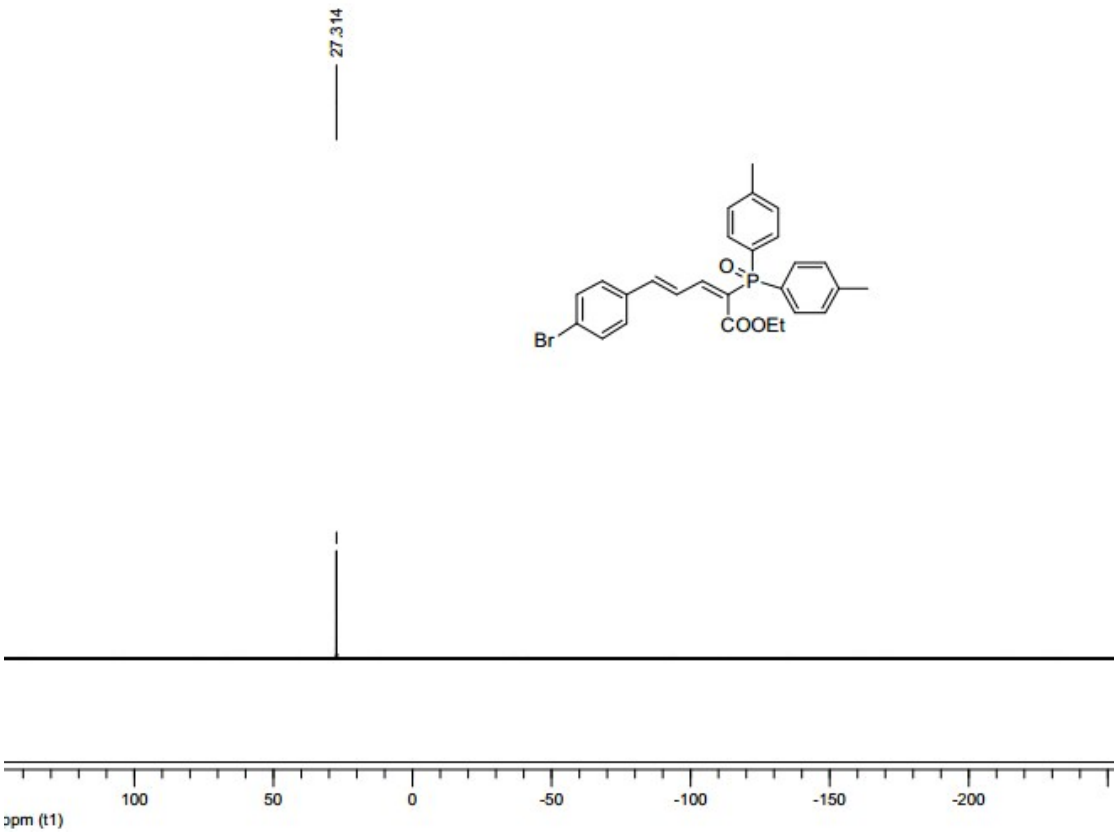
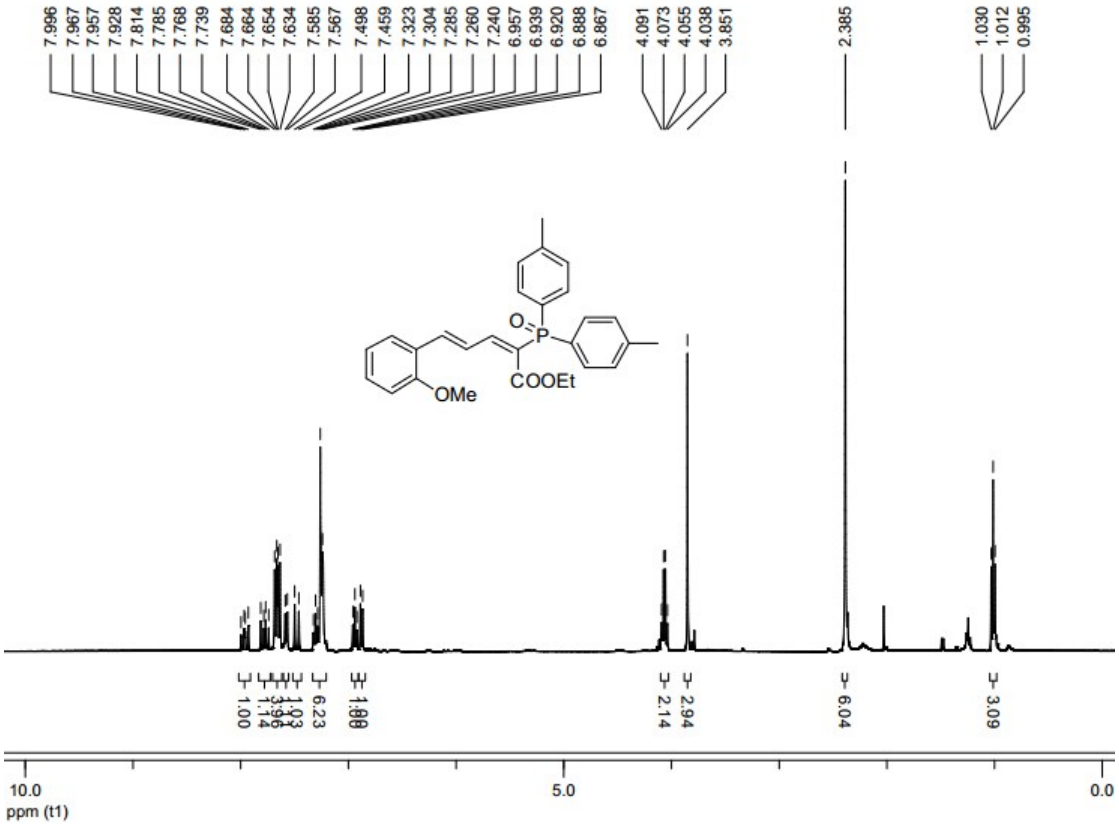


$^{31}P\{^{1}H\}$-NMR



5ib

^{1}H-NMR



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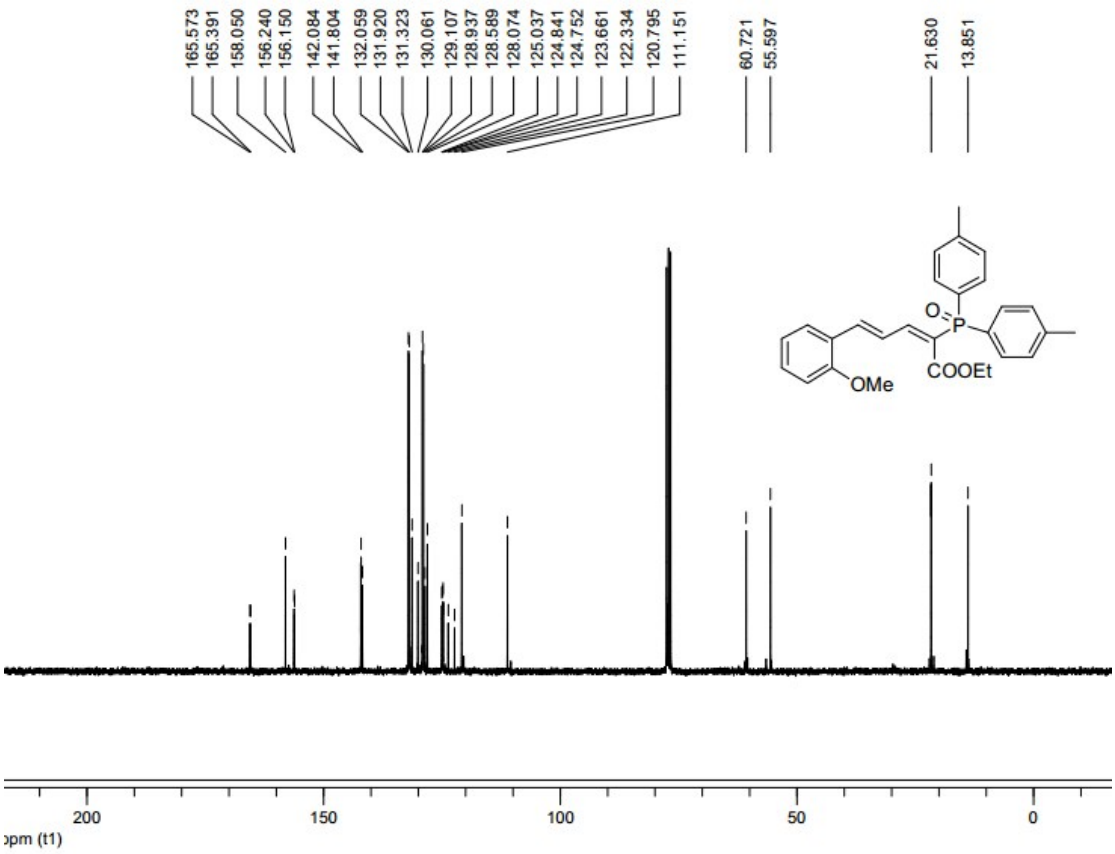

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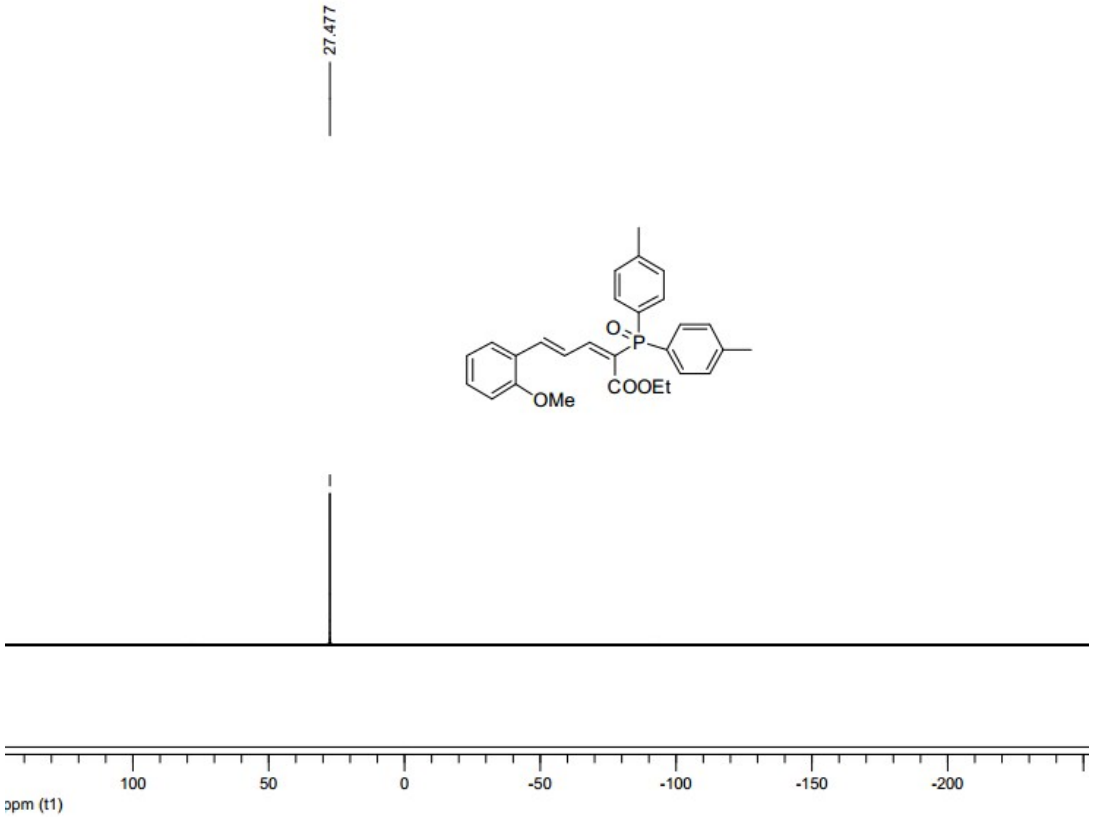

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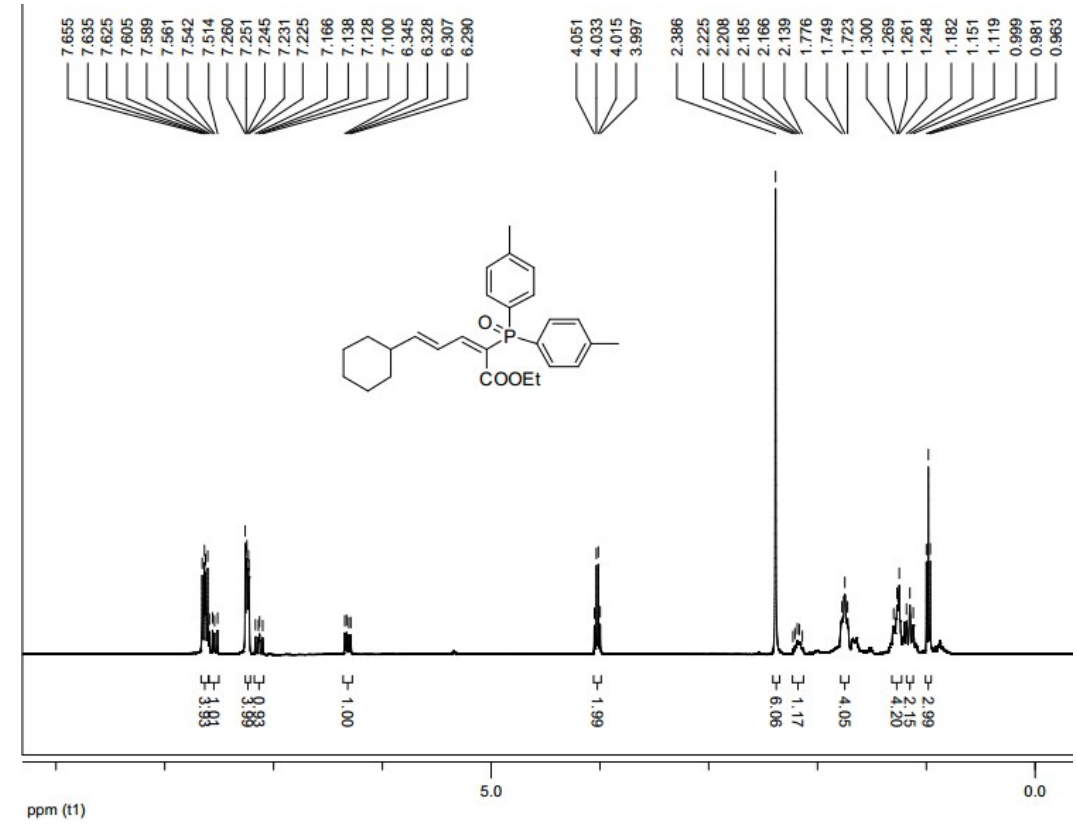
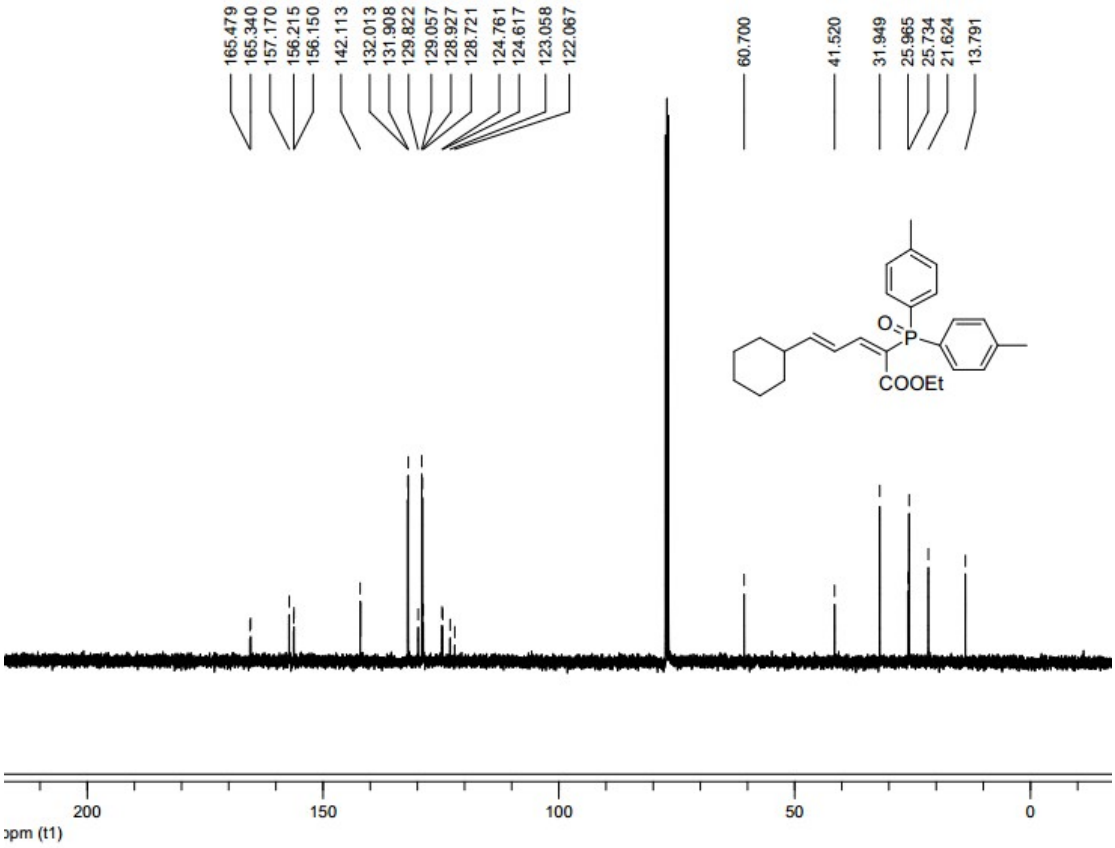
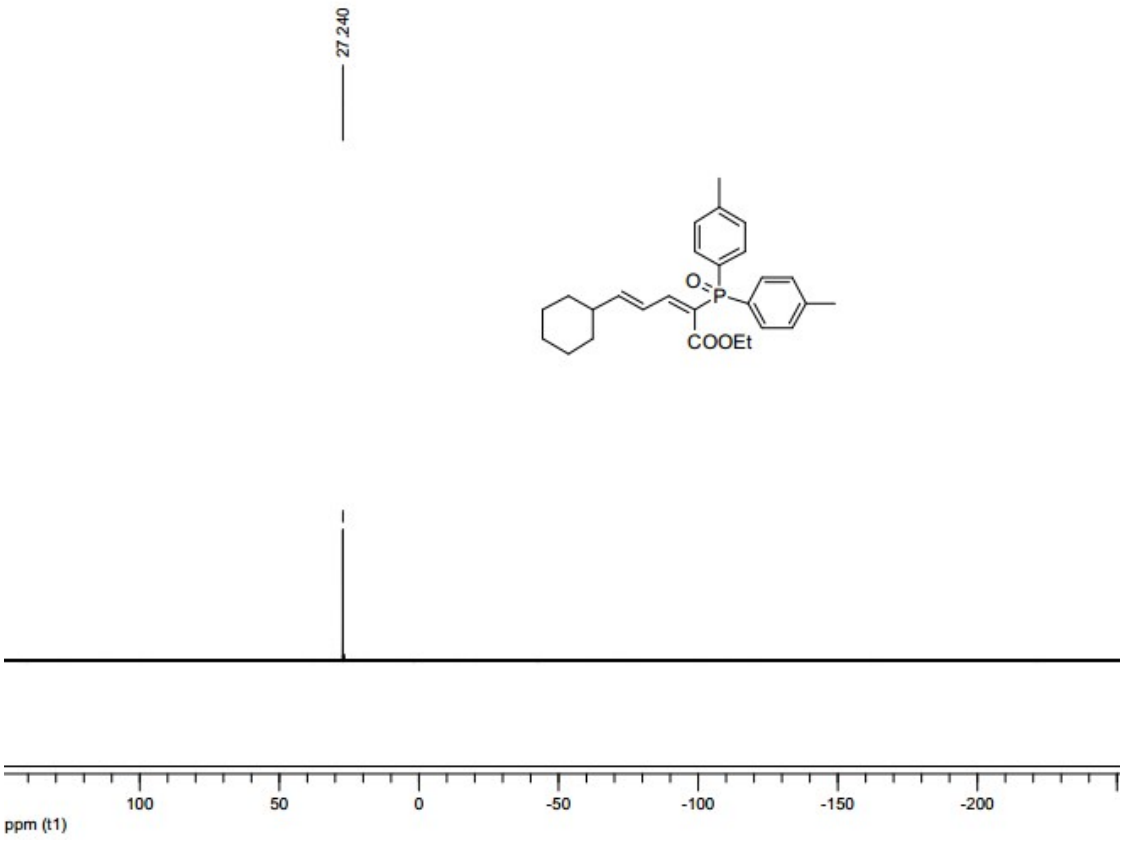


$^{13}C\{^{1}H\}$-NMR

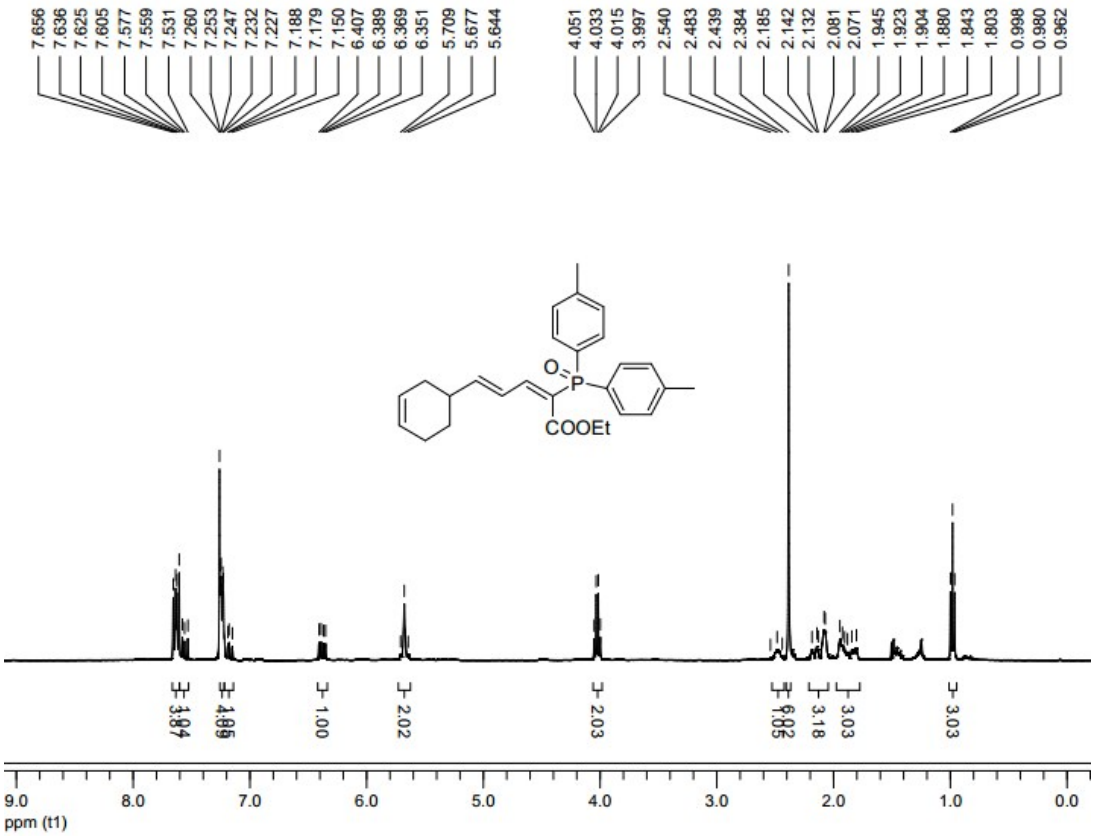


$^{31}P\{^{1}H\}$-NMR

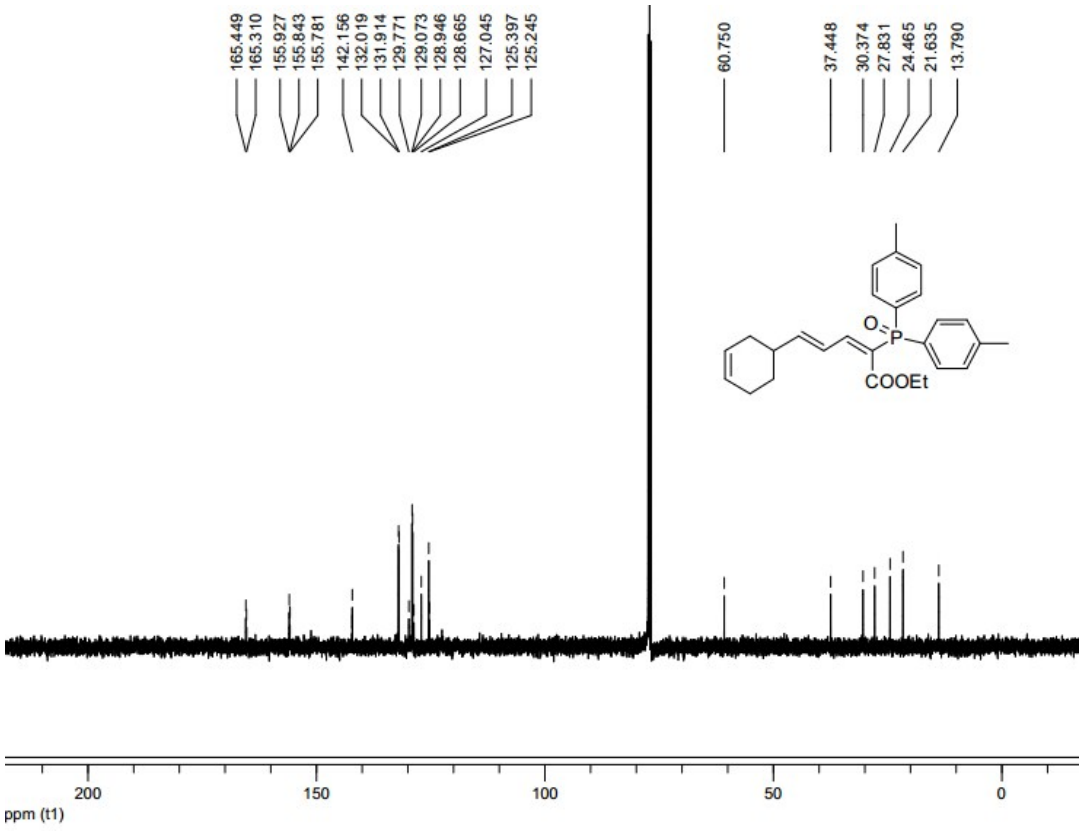


5ob

^{1}H-NMR



^{13}C{^{1}H}-NMR



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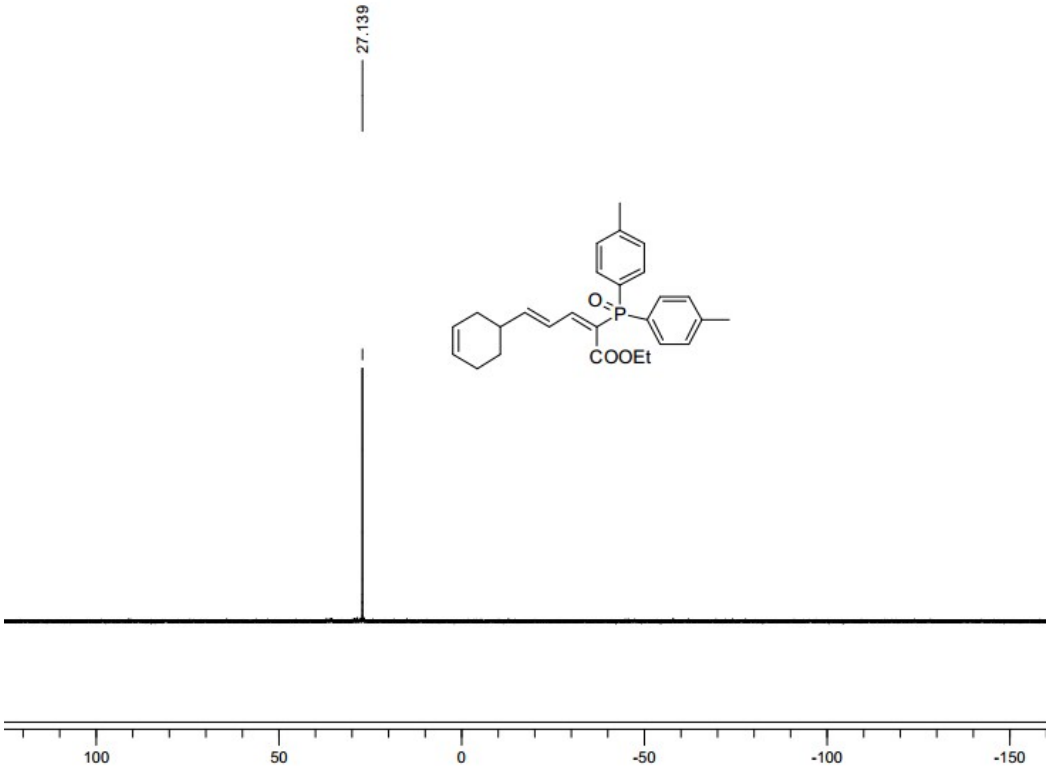
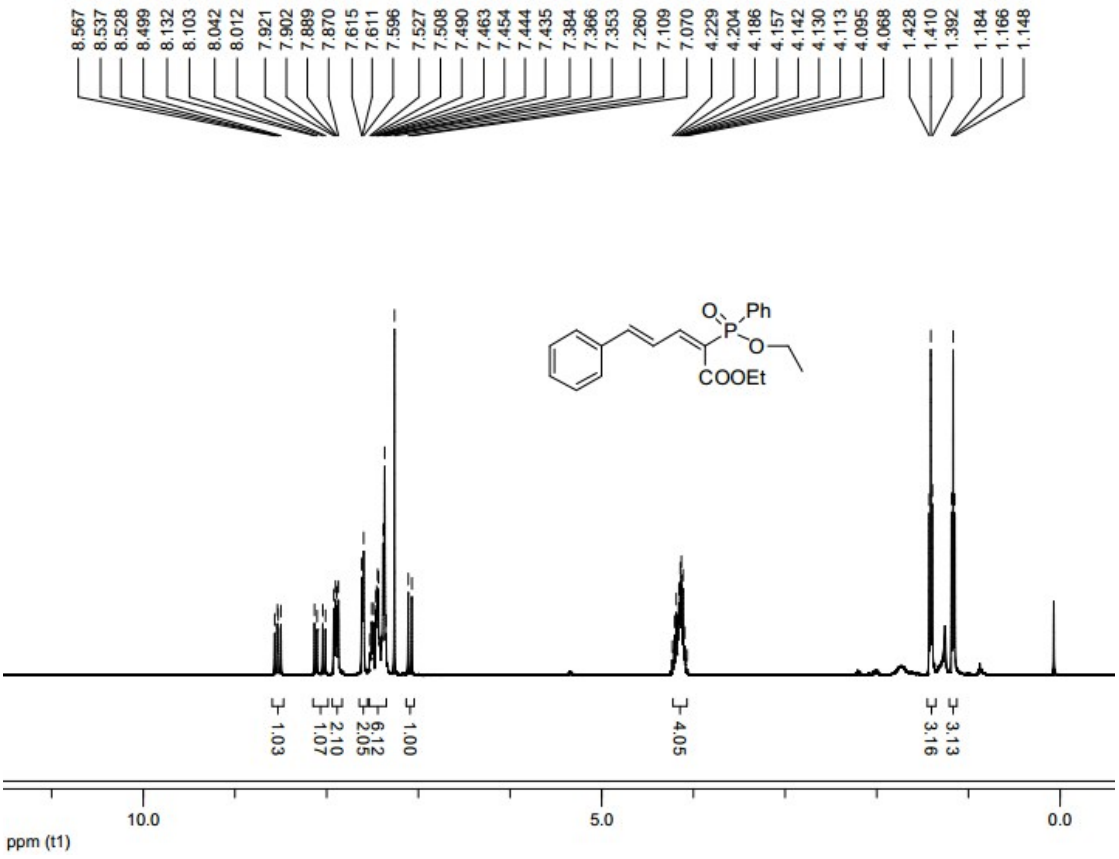
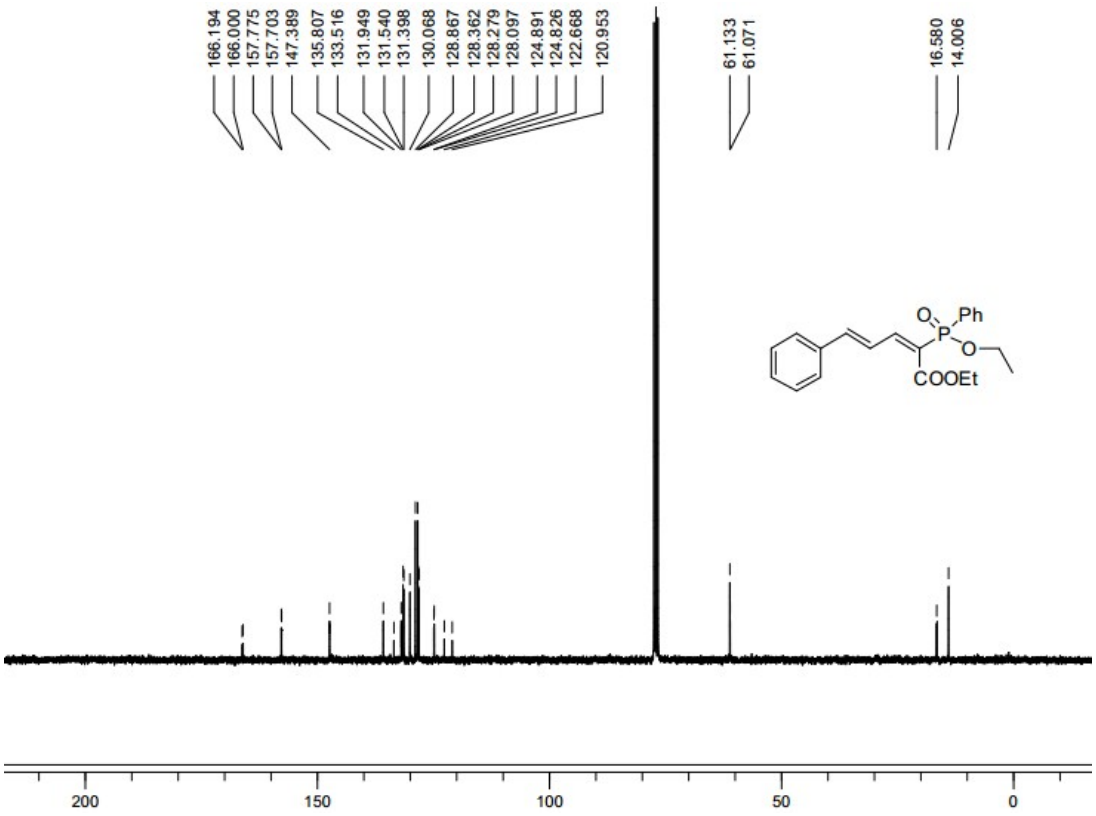


7aa

^{1}H-NMR



$^{13}C\{^{1}H\}$-NMR



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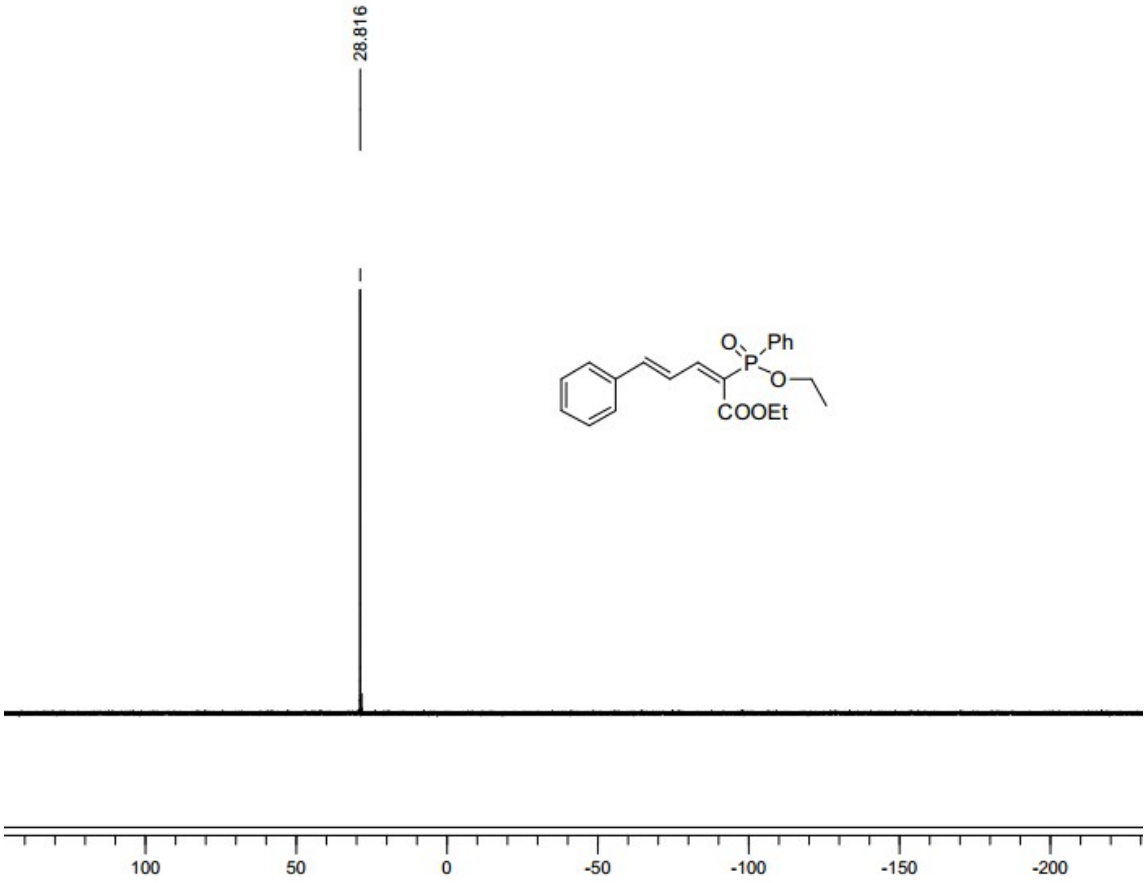
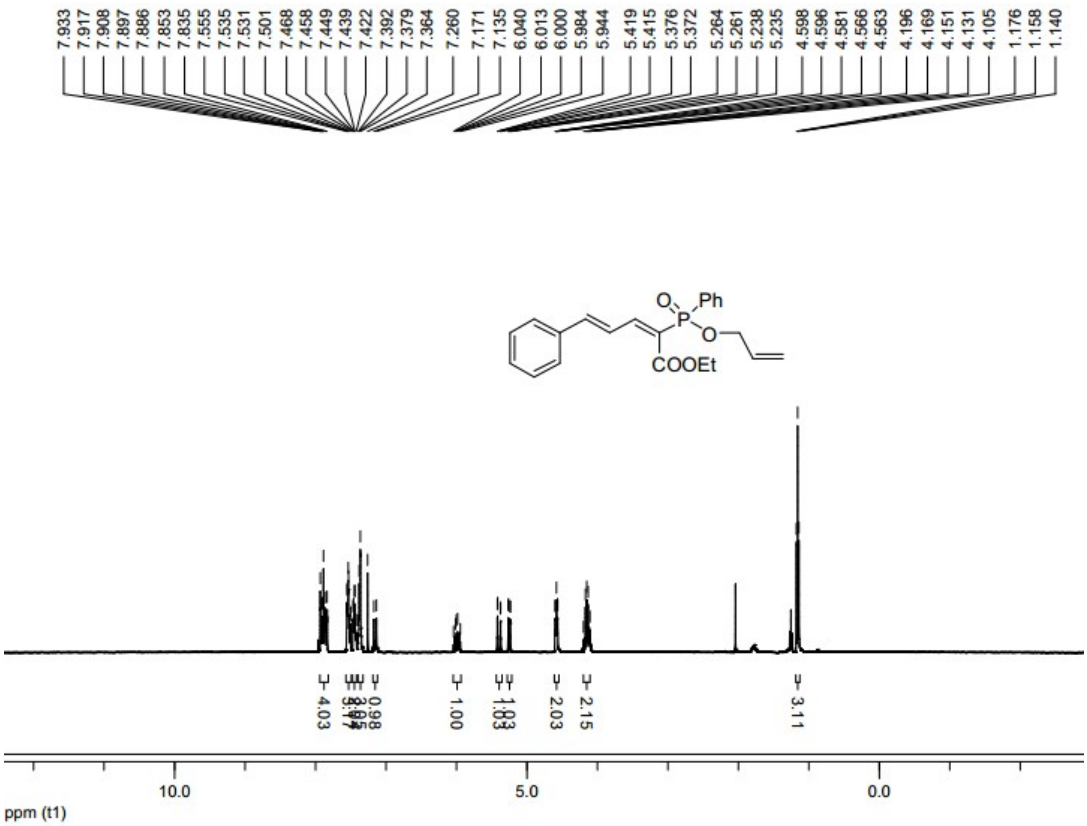


7ab

^{1}H-NMR



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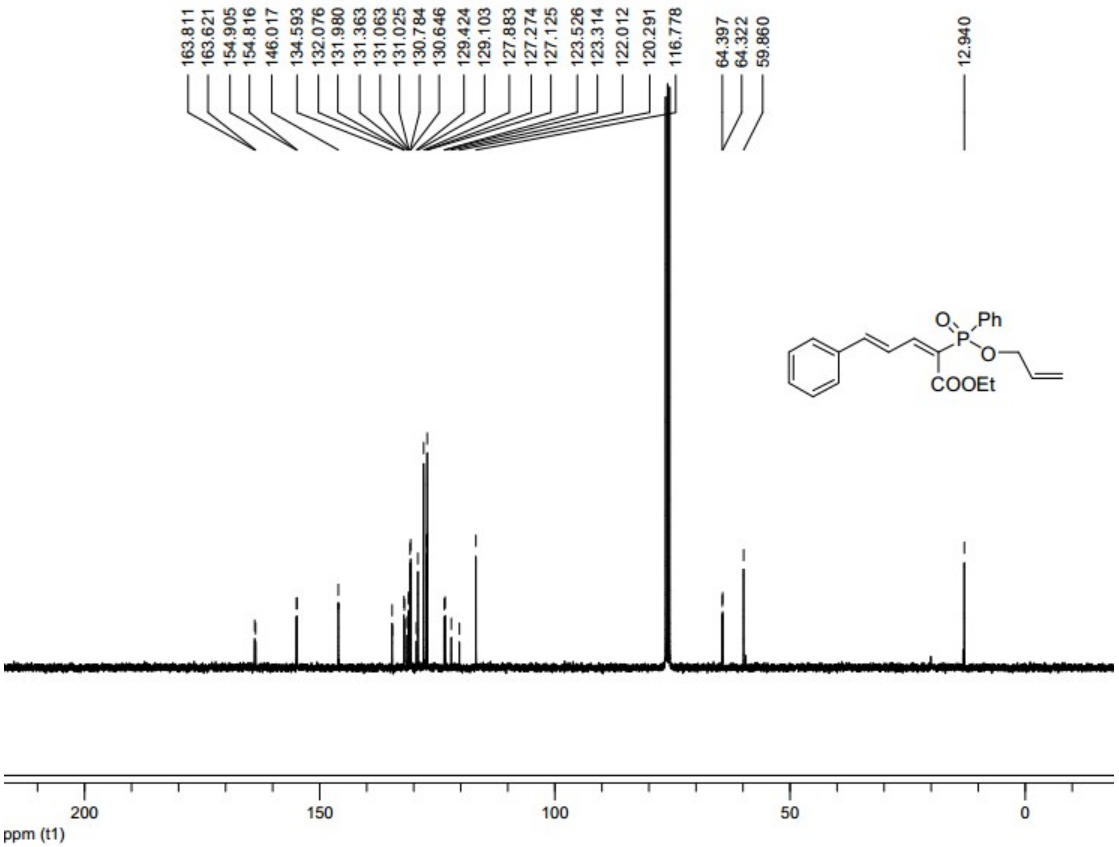

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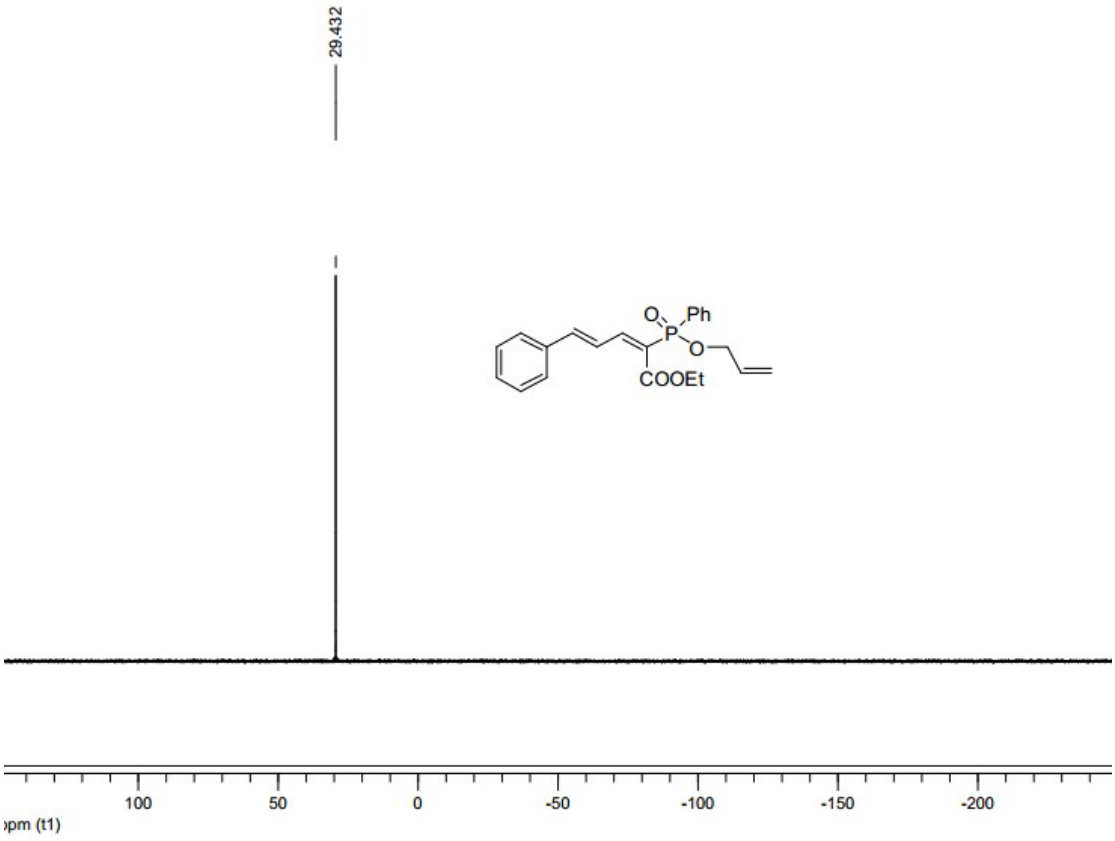
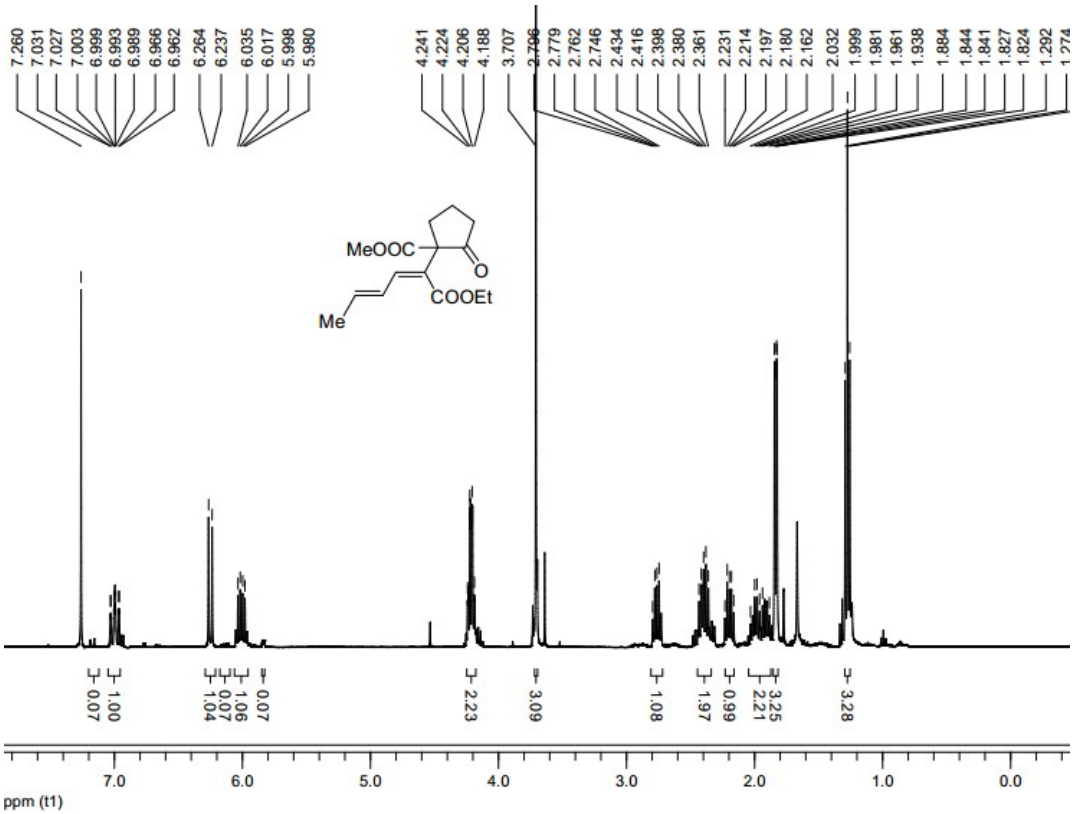


9m

^{1}H-NMR



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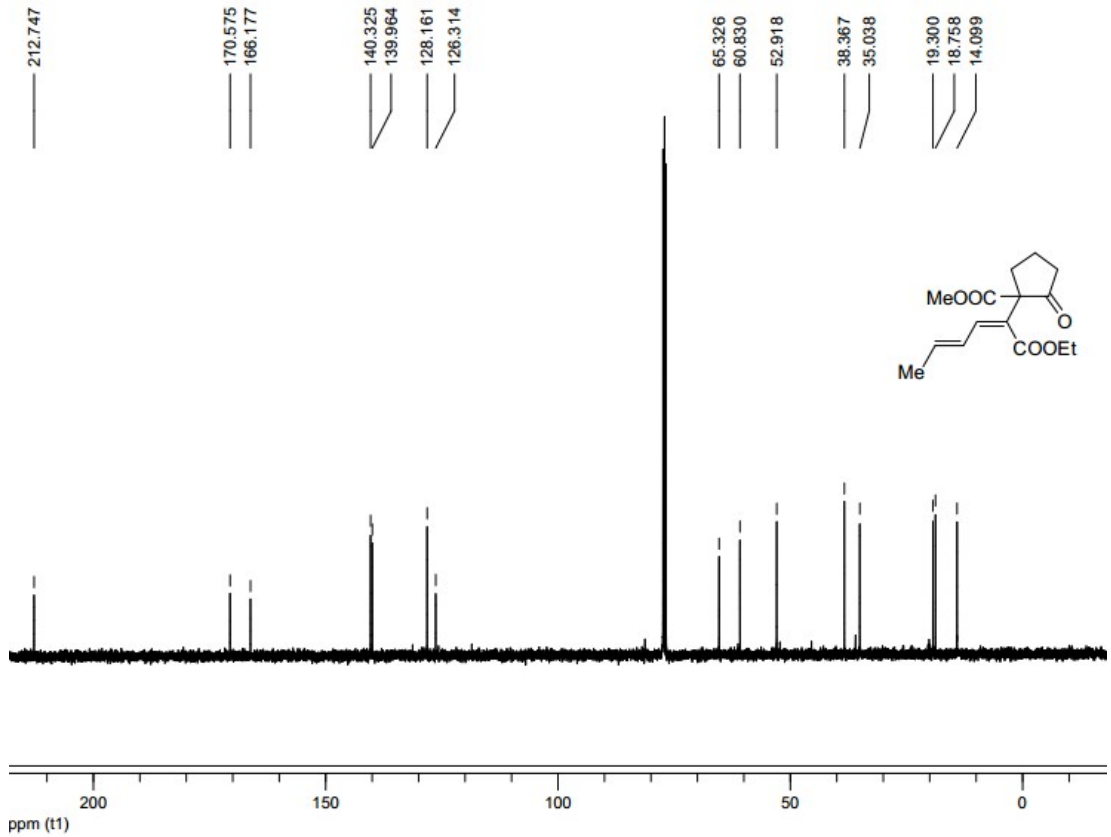
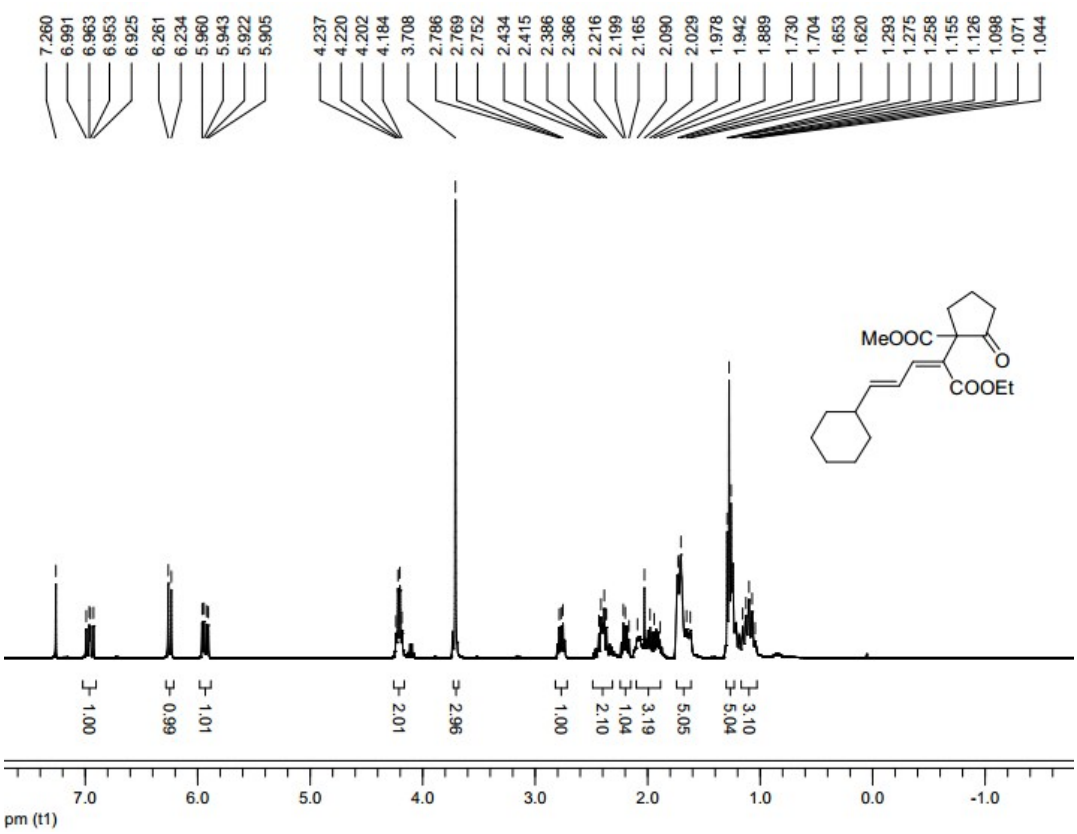
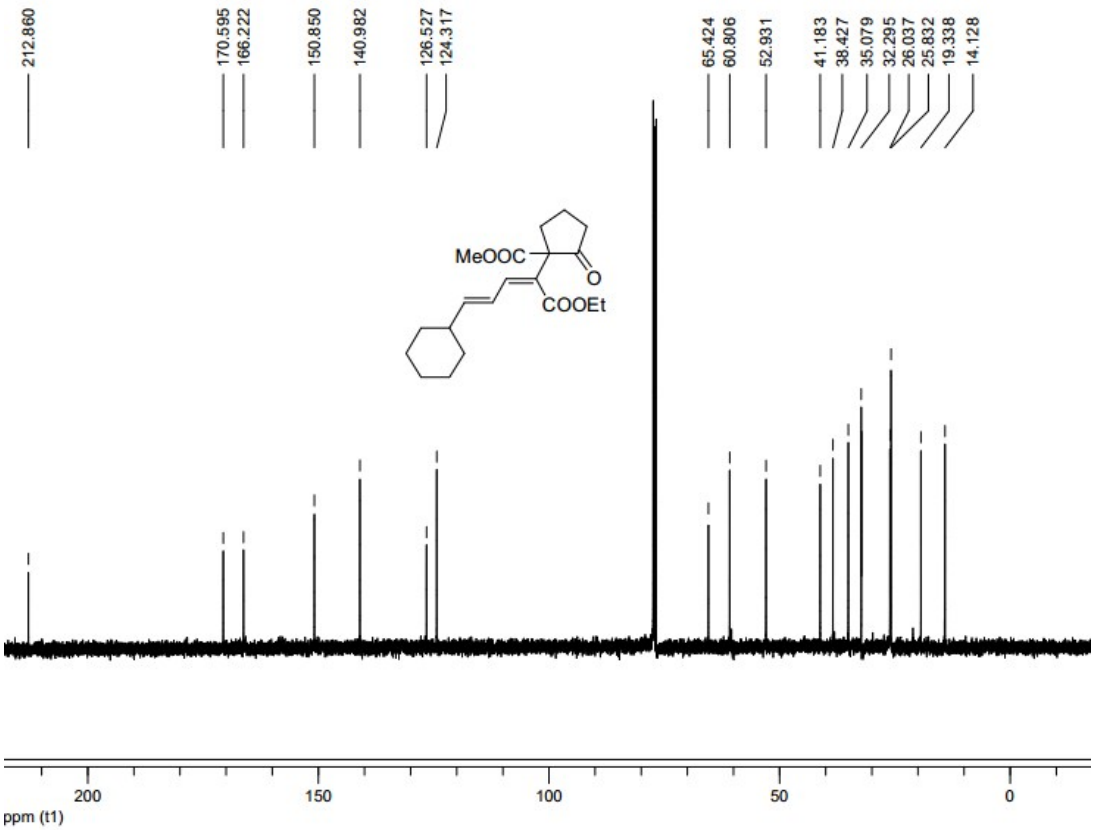


9n

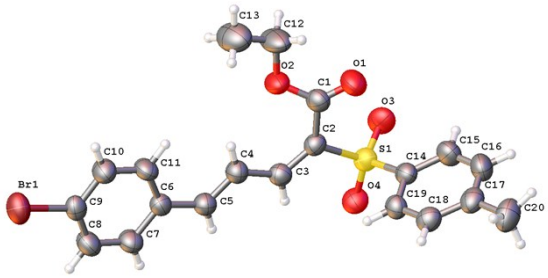
^{1}H-NMR



^{13}C{^{1}H}-NMR



8. X-ray Analysis



Compound 3ca

Single crystals of $C_{20}H_{19}BrO_4S$ were collected on a Bruker D8 Venture diffractometer. The crystal was kept at 303.0 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing, and refined with the ShelXL [3] refinement package using Least Squares minimisation.

[1] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
[2] Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
[3] Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Identification code	mo_d8v17425_0m
Empirical formula	$C_{20}H_{19}BrO_4S$
Formula weight	435.32
Temperature	303.0 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P 1
Unit cell dimensions	a = 7.5123(3) Å = 63.522(10)°. b = 12.1628(6) Å =79.736(10)°. c = 12.1719(4) Å = 89.681(2)°.
Volume	976.11(7) Å3
Z	2
Density (calculated)	1.481 Mg/m^3
Absorption coefficient	2.234 mm^{-1}
F(000)	444
Crystal size	0.15 x 0.1 x 0.08 mm^3
Theta range for data collection	2.765 to 30.514°.
Index ranges	-10<=h<=10, -17<=k<=17, -17<=l<=17
Reflections collected	13882
Independent reflections	5858 [R(int) = 0.0338]
Completeness to theta = 53.594°	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.5261
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5858 / 0 / 237
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.0926

R indices (all data)	R1 = 0.0978, wR2 = 0.1121
Extinction coefficient	n/a
Largest diff. peak and hole	0.288 and -0.422 e.Å^{-3}