Supporting Information

Photoinduced C–H Heteroarylation of Enamines via Quadruple Cleavage of CF_2Br_2

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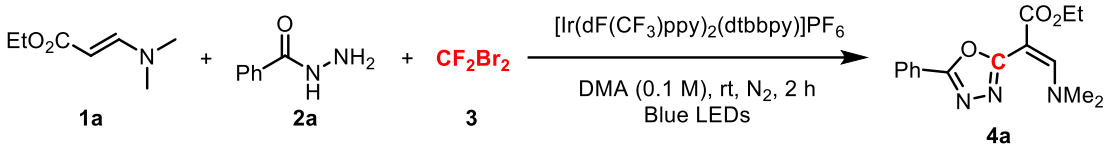
1. General considerations

All ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer (400/100/376 MHz). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Crystallographic data of product **4a** was collected on Bruker SMART APEX II (Mo target, voltage 50 KV, current 30 mA). The chemicals and solvents were purchased from commercial suppliers either Aldrich (USA), or Shanghai Chemical Company (P. R. China). Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2.

2. General procedures for the synthesis of products

2.1 General procedure for the synthesis 4/5 (4a as example)



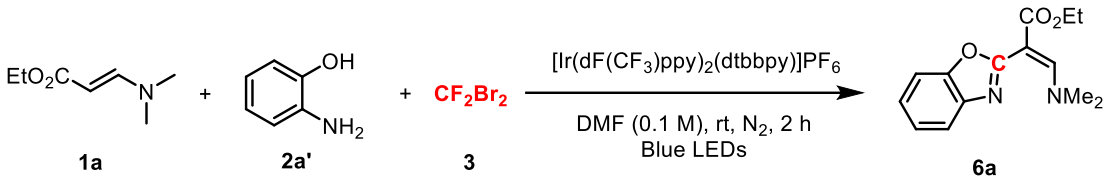
Under nitrogen atmosphere, a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with enaminone (**1a**, 28.6 mg, 0.20 mmol), benzoyl hydrazine (**2a**, 27.2 mg, 0.20 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.48 mg, 0.004 mmol, 2.0 mol%), difluoro-dibromomethane (**3**, 0.60 mmol, prepare 1.0 mg/mL DMA solution of difluoro-dibromomethane and measure 140 μL with a microsyringe), and DMA (2.0 mL). The reaction mixture was stirred under 2×3 W blue LEDs (450–455 nm) at room temperature with stirring for 2 h. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and H_2O. The resulting mixture was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (petroleum ether/ethyl acetate = 3:1, V/V) to give the product **4a** (42.5 mg, 74% yield).

Photoreactor

	Manufacturer: GeAo Chemical Company Model: 2×3 W, blue LEDs Broadband source: λ = 450–455 nm Material of the irradiation vessel: Borosilicate reaction tube Distance from the light source to the irradiation vessel: 3.0 cm No any filters

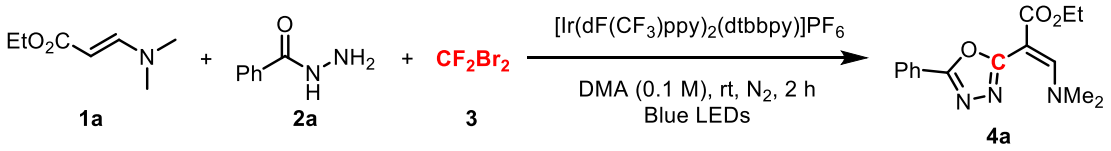
Figure S1. Photoreactor used in this research (2×3 W blue LEDs)

2.2 General procedure for the synthesis 6 (6a as example)



Under nitrogen atmosphere, a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with enaminone (**1a**, 28.6 mg, 0.20 mmol), 2-aminophenol (**2a'**, 21.8 mg, 0.20 mmol), [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.48 mg, 0.004 mmol, 2.0 mol%), difluoro-dibromomethane (**3**, 0.60 mmol, prepare 1.0 mg/mL DMF solution of difluoro-dibromomethane and measure 140 μL with a microsyringe), and DMF (2.0 mL). The reaction mixture was stirred under 2×3 W blue LEDs (450–455 nm) at room temperature with stirring for 2 h. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and H_2O. The resulting mixture was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (petroleum ether/ethyl acetate = 3:1, V/V) to give the product **6a** (29.1 mg, 56% yield).

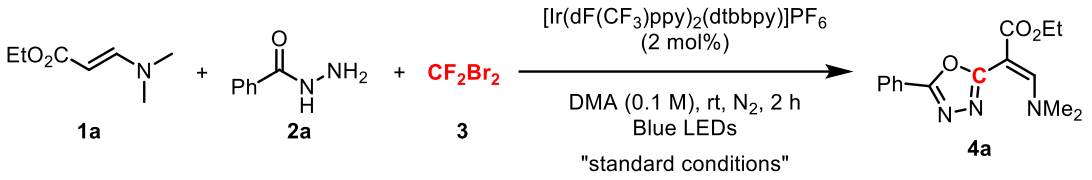
2.3 General procedure for the synthesis 4a in 4.0 mmol scale



Under nitrogen atmosphere, a 200 mL Schlenk bottle equipped with a magnetic stir bar was charged with enaminone (**1a**, 572.8 mg, 4.0 mmol), benzoyl hydrazine (**2a**, 544.6 mg, 4.0 mmol), [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (22.4 mg, 0.02 mmol, 0.5 mol%), difluorodibromomethane (**3**, 12.0 mmol, prepare 1.0 mg/mL DMA solution of difluoro-dibromomethane and measure 2.8 mL with a microsyringe), and DMA (40.0 mL). The reaction mixture was stirred under blue LEDs at room temperature with stirring for 2 h. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and H_2O. The resulting mixture was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and

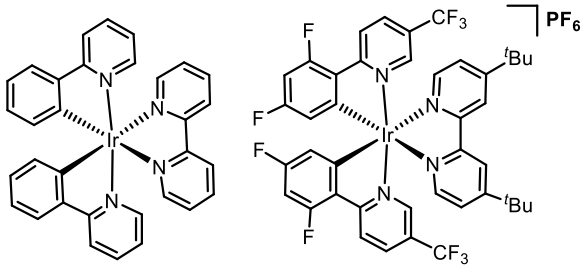
concentrated. The residue was purified with silica gel chromatography (petroleum ether/ethyl acetate = 3:1, V/V) to give the product **4a** (735.0 mg, 64% yield).

3. Optimization reaction conditions



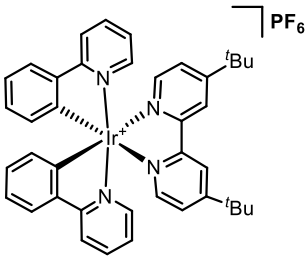
entry	photocatalyst	solvent	additive	the ratio of substrates **1a**:**2a**:**3**	yield of **4a** (%)[b]
1	***PC1***	DMA	–	1:1:3	70
2	***PC2***	**DMA**	–	**1:1:3**	**74**
3	***PC3***	DMA	–	1:1:3	69
4	***PC4***	DMA	–	1:1:3	21
5	***PC5***	DMA	–	1:1:3	55
6	***PC6***	DMA	–	1:1:3	61
7	***PC7***	DMA	–	1:1:3	27
8	***PC8***	DMA	–	1:1:3	20
9	***PC2***	DMSO	–	1:1:3	23
10	***PC2***	DMF	–	1:1:3	47
11	***PC2***	CH_3CN	–	1:1:3	27
12	***PC2***	acetone	–	1:1:3	51
13	***PC2***	1,4-dioxane	–	1:1:3	38
14	***PC2***	TFEA	–	1:1:3	20
15	***PC2***	DMA	–	1:0.8:3	71
16	***PC2***	DMA	–	1:1.5:3	66
17	***PC2***	DMA	–	1:2:3	68
18	***PC2***	DMA	–	1:3:3	63
19	***PC2***	DMA	–	1:1:1	50
20	***PC2***	DMA	–	1:1:2	61
21	***PC2***	DMA	–	1:1:4	69
22	***PC2***	DMA	Na_2CO_3	1:1:3	52
23	***PC2***	DMA	$NaHCO_3$	1:1:3	55
24	***PC2***	DMA	K_3PO_4	1:1:3	52

25	***PC2***	DMA	*t*-BuOK	1:1:3	50
26	***PC2***	DMA	TsOH	1:1:3	43
27	***PC2***	DMA	TFA	1:1:3	40
28	***PC2***	DMA	HCOOH	1:1:3	67
29	–	DMA	–	1:1:3	trace
30[c]	***PC2***	DMA	–	1:1:3	N.D.
31[d]	***PC2***	DMA	–	1:1:3	59
32[e]	***PC2***	DMA	–	1:1:3	29
33[f]	***PC2***	DMA	–	1:1:3	N.D.
34[g]	***PC2***	DMA	–	1:1:3	N.D.
35[h]	***PC2***	DMA	–	1:1:3	N.D.

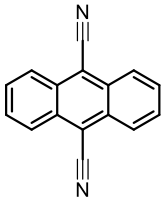


PC1
***fac*-Ir(ppy)$_3$**

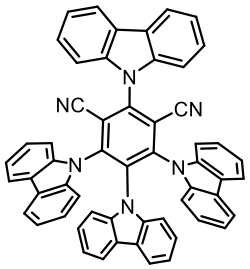
PC2
[Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$



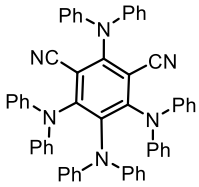
PC3
[Ir(ppy)$_2$(dtbbpy)]PF$_6$



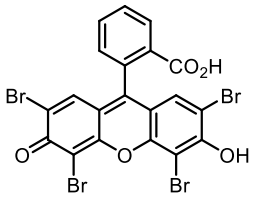
PC4
DCA



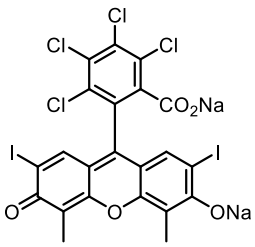
PC5
4CzIPN



PC6
4DPAIPN



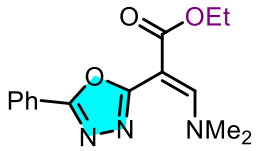
PC7
Eosin Y



PC8
Rose Bengal

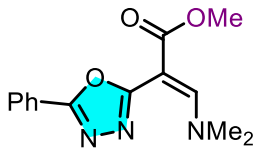
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (amount indicated in this Table), **3** (amount indicated in this Table), photocatalyst (2 mol%), additive (1.0 equiv.) in solvent (2.0 mL), N_2 atmosphere, room temperature, under 2×3 W blue LEDs (450–455 nm) irradiation for 2h. [b]Isolated yield. [c]In the absence of light. [d]Under air atmosphere. [e]$CFBr_3$ instead of CF_2Br_2. [f]CBr_4 instead of CF_2Br_2. [g]CCl_3Br instead of CF_2Br_2. [h] CF_3I instead of CF_2Br_2.

4. Characterization data of products



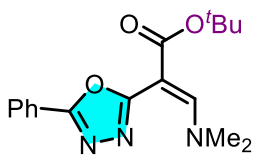
4a

Ethyl (*E*)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 42.5 mg, 74% yield. White solid, melting point: 98.3–99.5 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 2H), 7.80 (s, 1H), 7.49 (d, J = 6.4 Hz, 3H), 4.16 (q, J = 7.2 Hz, 2H), 3.18 (s, 3H), 2.64 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 164.9, 162.0, 154.1, 131.4, 128.9, 126.7, 124.3, 81.6, 60.1, 47.0, 39.7, 14.4. **HRMS (ESI) *m/z***: Calcd for $C_{15}H_{18}N_3O_3^+$ $[M + H]^+$: 288.1343; found: 288.1341.



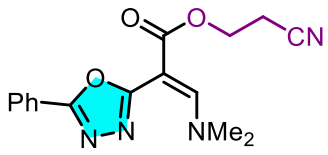
4b

Methyl (*E*)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 37.1 mg, 68% yield. Yellow solid, melting point: 97.8–99.5 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, J = 4.4 Hz, 2H), 7.79 (s, 1H), 7.60–7.30 (m, 3H), 3.66 (s, 3H), 3.16 (s, 3H), 2.60 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 164.9, 161.8, 154.2, 131.4, 128.9, 126.7, 124.2, 81.1, 51.4, 47.2, 39.3. **HRMS (ESI) *m/z***: Calcd for $C_{14}H_{15}N_3NaO_3^+$ $[M + Na]^+$: 296.1006; found: 296.1004.



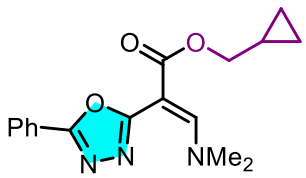
4c

tert*-Butyl (*E*)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate**: 23.6 mg, 41% yield. Yellow solid, melting point: 100.9–102.6 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08–8.00 (m, 2H), 7.70 (s, 1H), 7.51–7.45 (m, 3H), 3.12 (s, 3H), 2.64 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 164.7, 162.3, 153.7, 131.3, 128.9, 126.5, 124.3, 82.9, 79.8, 46.9, 39.6, 28.3. **HRMS (ESI) *m/z: Calcd for $C_{17}H_{21}N_3NaO_3^+$ $[M + Na]^+$: 338.1475; found: 338.1472.



4d

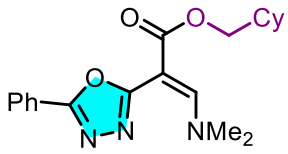
2-cyanoethyl (*E*)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 44.3 mg, 71% yield. Yellow solid, melting point: 95.5–97.7 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.2 Hz, 2H), 7.81 (s, 1H), 7.47 (d, J = 5.6 Hz, 3H), 4.35–4.22 (m, 2H), 3.19 (s, 3H), 2.82–2.53 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 165.1, 161.3, 154.7, 131.5, 128.9, 126.7, 123.9, 117.0, 80.3, 58.3, 47.4, 39.5, 18.1. **HRMS (ESI) *m/z***: Calcd for $C_{16}H_{16}N_4NaO_3^+$ $[M + Na]^+$: 335.1115; found: 335.1110.



4e

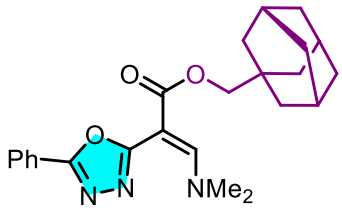
Cyclopropylmethyl (*E*)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl) acrylate: 40.1 mg, 64% yield. Yellow solid, melting point: 116.7–118.7 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 2H), 7.77 (s, 1H), 7.46 (d, J = 6.0 Hz, 3H), 3.92 (d, J = 6.8 Hz, 2H), 3.15 (s, 3H), 2.61 (s, 3H), 1.10–0.97 (m, 1H), 0.46–0.38 (m, 2H), 0.22–0.14 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 164.8, 161.9, 154.0,

131.3, 128.8, 126.5, 124.2, 81.4, 68.4, 47.1, 39.4, 9.8, 2.9. **HRMS (ESI)** ***m/z***: Calcd for $C_{17}H_{19}N_3NaO_3^+$ $[M + Na]^+$: 336.1319; found: 336.1316.



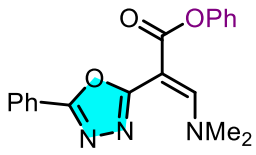
4f

Cyclohexylmethyl (*E*)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl) acrylate: 34.1 mg, 48% yield. Yellow solid, melting point: 100.3–102.4 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10–7.97 (m, 2H), 7.77 (s, 1H), 7.46 (d, J = 6.4 Hz, 3H), 3.89 (d, J = 6.4 Hz, 2H), 3.16 (s, 3H), 2.62 (s, 3H), 1.67–1.47 (m, 6H), 1.17–0.96 (m, 3H), 0.93–0.81 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 164.7, 161.9, 154.0, 131.3, 128.8, 126.5, 124.1, 81.4, 69.1, 47.1, 39.5, 37.1, 29.4, 26.1, 25.5. **HRMS (ESI)** ***m/z***: Calcd for $C_{20}H_{26}N_3O_3^+$ $[M + H]^+$: 356.1969; found: 356.1967.



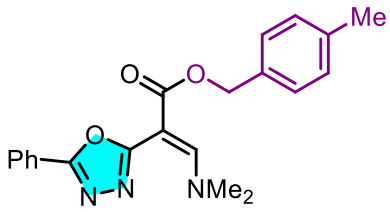
4g

Adamantan-1-ylmethyl (*E*)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl) acrylate: 52.9 mg, 65% yield. Yellow solid, melting point: 162.4–166.7 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12–8.00 (m, 2H), 7.77 (s, 1H), 7.51–7.42 (m, 3H), 3.66 (s, 2H), 3.17 (s, 3H), 2.64 (s, 3H), 1.78 (s, 3H), 1.59–1.51 (m, 3H), 1.47– 1.35 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 164.8, 162.1, 153.9, 131.4, 128.8, 126.6, 124.1, 81.3, 73.6, 47.1, 39.6, 39.1, 36.7, 33.2, 27.8. **HRMS (ESI)** ***m/z***: Calcd for $C_{24}H_{29}N_3NaO_3^+$ $[M + Na]^+$: 430.2101; found: 430.2108.



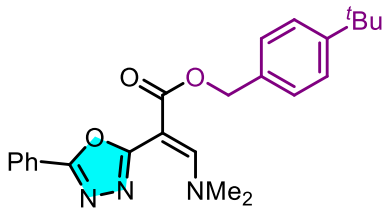
4h

Phenyl (E)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 33.5 mg, 50% yield. Yellow solid, melting point: 101.8–103.5 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13–8.04 (m, 2H), 7.94 (s, 1H), 7.54–7.45 (m, 3H), 7.32 (t, J = 8.0 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 3.22 (s, 3H), 2.68 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 165.2, 161.7, 155.2, 151.1, 131.6, 129.2, 129.1, 126.8, 125.3, 124.2, 121.9, 80.8, 47.6, 39.8. **HRMS (ESI) *m/z***: Calcd for $C_{19}H_{17}N_3NaO_3^+$ $[M + Na]^+$: 358.1162; found: 358.1156.



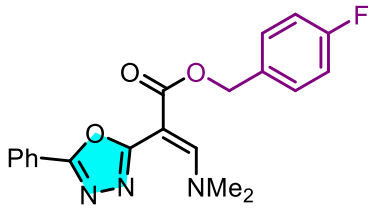
4i

4-Methylbenzyl (*E*)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 33.4 mg, 46% yield. Yellow solid, melting point: 80.7–82.3 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07–7.96 (m, 2H), 7.83 (s, 1H), 7.54–7.45 (m, 3H), 7.19 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 5.15 (s, 2H), 3.18 (s, 3H), 2.65 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 164.8, 161.8, 154.4, 137.4, 133.7, 131.4, 128.95, 128.86, 127.6, 126.7, 124.2, 81.4, 65.6, 47.3, 39.6, 21.1. **HRMS (ESI) *m/z***: Calcd for $C_{21}H_{22}N_3O_3^+$ $[M + H]^+$: 364.1656; found: 364.1655.



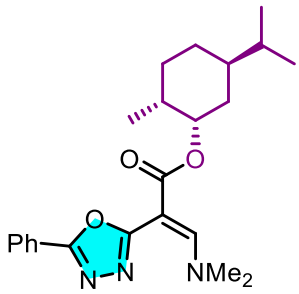
4j

4-(*tert*-Butyl)benzyl (*E*)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl) acrylate: 43.7 mg, 54% yield. Yellow oil (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09–7.97 (m, 2H), 7.83 (s, 1H), 7.53–7.43 (m, 3H), 7.32–7.19 (m, 4H), 5.16 (s, 2H), 3.17 (s, 3H), 2.64 (s, 3H), 1.27 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 164.8, 161.8, 154.3, 150.5, 133.6, 131.3, 128.8, 127.3, 126.6, 125.1, 124.1, 81.2, 65.4, 47.2, 39.6, 34.3, 31.2. **HRMS (ESI) *m/z***: Calcd for $C_{24}H_{28}N_3O_3^+$ $[M + H]^+$: 406.2125; found: 406.2122.



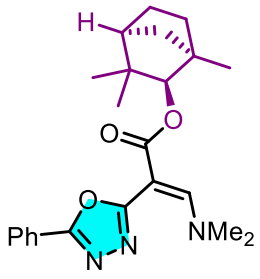
4k

4-Fluorobenzyl (*E*)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 39.6 mg, 54% yield. Yellow oil (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 6.4 Hz, 2H), 7.82 (s, 1H), 7.53–7.44 (m, 3H), 7.29–7.23 (m, 2H), 6.98–6.88 (m, 2H), 5.13 (s, 2H), 3.18 (s, 3H), 2.64 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 164.8, 163.5, 162.2 (d, J = 246.0 Hz), 154.5, 132.5 (d, J = 3.2 Hz), 131.5, 129.4 (d, J = 8.3 Hz), 128.9, 126.6, 124.1, 115.1 (d, J = 21.4 Hz), 81.1, 64.9, 47.4, 39.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ −114.54 (s, 1F). **HRMS (ESI) *m/z***: Calcd for $C_{20}H_{19}FN_3O_3^+$ $[M + H]^+$: 368.1405; found: 368.1403.



4l

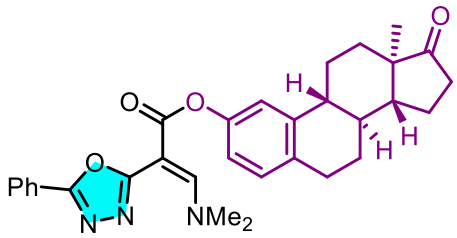
(*1S*,*2R*,*5R*)-5-(*iso*-Propyl)-2-methylcyclohexyl (*E*)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 46.8 mg, 59% yield. Yellow solid, melting point: 124.2–125.3 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07–7.93 (m, 2H), 7.74 (s, 1H), 7.50–7.40 (m, 3H), 4.78–4.59 (m, 1H), 3.13 (s, 3H), 2.60 (s, 3H), 2.01–1.88 (m, 2H), 1.60–1.50 (m, 2H), 1.41 (s, 1H), 1.22–1.12 (m, 1H), 1.02–0.92 (m, 1H), 0.92–0.82 (m, 2H), 0.80 (d, J = 6.4 Hz, 3H), 0.73 (t, J = 7.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 164.6, 161.9, 153.9, 131.3, 128.8, 126.5, 124.1, 81.6, 73.7, 47.1, 46.9, 40.9, 39.5, 34.0, 31.2, 25.9, 23.1, 21.8, 20.6, 16.1. **HRMS (ESI) *m/z***: Calcd for $C_{23}H_{32}N_3O_3^+$ $[M + H]^+$: 398.2438; found: 398.2437.



4m

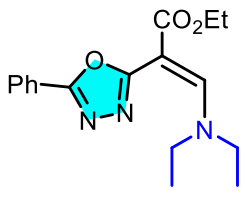
(*1R*,*2R*,*4S*)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl (*E*)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 39.5 mg, 50% yield. White solid, melting point: 127.0–129.1 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11–8.02 (m, 2H), 7.80 (s, 1H), 7.49 (d, J = 6.8 Hz, 3H), 4.41 (s, 1H), 3.18 (s, 3H), 2.66 (s, 3H), 1.63 (s, 1H), 1.56–1.45 (m, 2H), 1.34–1.22 (m, 3H), 1.08 (s, 3H), 0.99 (s, 3H), 0.85–0.80 (m, 1H), 0.80–

0.76 (m, 1H), 0.75 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 164.8, 162.2, 154.0, 131.4, 128.9, 126.6, 124.2, 85.8, 81.4, 48.3, 48.2, 47.2, 41.2, 39.7, 39.6, 29.6, 26.4, 25.7, 20.2, 19.4. **HRMS (ESI)** ***m/z***: Calcd for $C_{23}H_{30}N_3O_3^+$ $[M + H]^+$: 396.2282; found: 396.2281.



4n

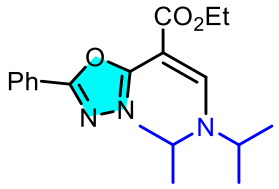
(*8S*,*9R*,*13R*,*14R*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-2-yl (*E*)-3-(dimethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 59.3 mg, 58% yield. Yellow solid, melting point: 195.5–196.8 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 5/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 2H), 7.94 (s, 1H), 7.51 (s, 3H), 7.26 (s, 1H), 6.96–6.76 (m, 2H), 3.26 (s, 3H), 2.88 (s, 3H), 2.71 (s, 3H), 2.38 (s, 2H), 2.05–1.95 (m, 1H), 1.62–1.40 (m, 6H), 1.26 (s, 3H), 0.89 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.9, 166.4, 155.1, 148.9, 137.7, 136.7, 131.5, 129.0, 126.8, 126.1, 124.2, 121.8, 119.0, 80.8, 67.0, 53.4, 50.4, 47.9, 47.5, 44.1, 39.7, 38.0, 35.8, 31.5, 29.6, 29.3, 26.3, 25.7, 21.5, 13.8. **HRMS (ESI)** ***m/z***: Calcd for $C_{31}H_{34}N_3O_4^+$ $[M + H]^+$: 512.2544; found: 512.2542.



4o

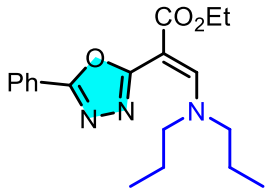
Ethyl (*E*)-3-(diethylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 37.2 mg, 59% yield. White solid, melting point: 73.5–74.8 ºC (Flash column chromatography eluent,

petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11–7.99 (m, 2H), 7.79 (s, 1H), 7.48 (d, J = 6.4 Hz, 3H), 4.13 (q, J = 7.2 Hz, 2H), 3.45–3.23 (m, 2H), 3.21–2.98 (m, 2H), 1.35–1.20 (m, 3H), 1.15 (t, J = 7.2 Hz, 3H), 1.01–0.76 (m, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 164.8, 162.2, 151.8, 131.4, 128.9, 126.6, 124.2, 80.6, 60.0, 52.6, 43.3, 14.7, 14.4, 11.7. **HRMS (ESI)** ***m/z***: Calcd for $C_{17}H_{22}N_3O_3^+$ $[M + H]^+$: 316.1656; found: 316.1654.



4p

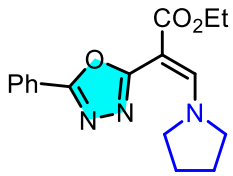
Ethyl (*E*)-3-di(*iso*-propyl)amino-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 46.0 mg, 67% yield. White solid, melting point: 114.5–116.0 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10–7.99 (m, 2H), 7.90 (s, 1H), 7.52–7.43 (m, 3H), 4.11 (q, J = 7.2 Hz, 2H), 3.73– 3.28 (m, 2H), 1.39–1.19 (m, 6H), 1.18–1.12 (m, 4H), 1.11–0.92 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 164.8, 163.0, 148.7, 131.3, 128.9, 126.6, 124.2, 80.2, 59.9, 50.5, 47.1, 23.8, 19.7, 14.3. **HRMS (ESI)** ***m/z***: Calcd for $C_{19}H_{26}N_3O_3^+$ $[M + H]^+$: 344.1969; found: 344.1966.



4q

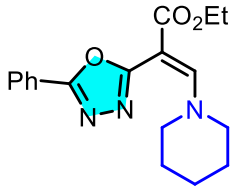
Ethyl (*E*)-3-(dipropylamino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 40.5 mg, 59% yield. Yellow oil (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14–7.98 (m, 2H), 7.79 (s, 1H), 7.50 (d, J = 6.8 Hz, 3H), 4.14 (q, J = 7.2 Hz, 2H), 3.36–3.16 (m, 2H), 3.01–2.87 (m, 2H), 1.75–1.54 (m, 2H), 1.42–1.26 (m, 2H), 1.17 (t, J = 7.2 Hz, 3H), 1.02–0.85 (m,

3H), 0.67–0.45 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 164.9, 162.3, 152.4, 131.4, 128.9, 126.7, 124.3, 80.6, 60.4, 60.1, 50.8, 22.5, 19.8, 14.4, 10.8. **HRMS (ESI)** ***m/z***: Calcd for $C_{19}H_{26}N_3O_3^+$ $[M + H]^+$: 344.1969; found: 344.1965.



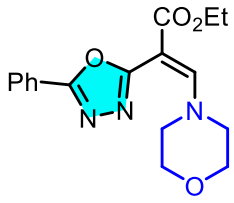
4r

Ethyl (*E*)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)-3-(pyrrolidin-1-yl)acrylate: 40.1 mg, 64% yield. Yellow solid, melting point: 87.0–88.4 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09–8.02 (m, 2H), 7.98 (s, 1H), 7.50–7.45 (m, 3H), 4.15 (q, J = 7.2 Hz, 2H), 3.71–3.52 (m, 2H), 2.98–2.81 (m, 2H), 1.93–1.76 (m, 4H), 1.19 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 164.7, 162.1, 150.3, 131.3, 128.9, 126.6, 124.3, 81.7, 59.9, 54.8, 48.5, 25.8, 24.4, 14.4. **HRMS (ESI)** ***m/z***: Calcd for $C_{17}H_{20}N_3O_3^+$ $[M + H]^+$: 314.1499; found: 314.1496.



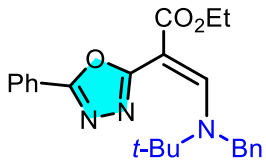
4s

Ethyl (*E*)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)-3-(piperidin-1-yl)acrylate: 32.1 mg, 49% yield. Yellow solid, melting point: 81.2–82.5 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15–7.96 (m, 2H), 7.75 (s, 1H), 7.47 (d, J = 6.4 Hz, 3H), 4.13 (q, J = 7.2 Hz, 2H), 3.66–2.65 (m, 4H), 1.81–1.44 (m, 6H), 1.16 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 164.8, 162.4, 152.9, 131.3, 128.9, 126.6, 124.2, 80.2, 60.0, 56.4, 47.7, 25.8, 25.4, 23.3, 14.3. **HRMS (ESI)** ***m/z***: Calcd for $C_{18}H_{22}N_3O_3^+$ $[M + H]^+$: 328.1656; found: 328.1653.



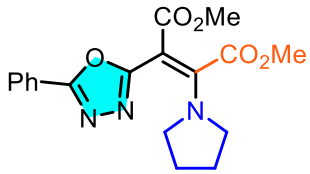
4t

Ethyl (*E*)-3-morpholino-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 44.7 mg, 68% yield. White solid, melting point: 82.6–84.1 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.2 Hz, 2H), 7.74 (s, 1H), 7.48 (d, J = 7.2 Hz, 3H), 4.14 (q, J = 7.2 Hz, 2H), 3.73–3.54 (m, 4H), 3.43–3.00 (m, 4H), 1.17 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 164.9, 161.9, 152.8, 131.5, 128.9, 126.6, 123.9, 82.0, 66.0, 60.3, 50.8, 14.3. **HRMS (ESI)** ***m/z***: Calcd for $C_{17}H_{20}N_3O_4^+$ $[M + H]^+$: 330.1448; found: 330.1446.



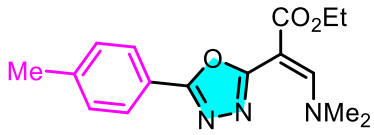
4u

Ethyl (*E*)-3-(benzyl(*tert*-butyl)amino)-2-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylate: 17.8 mg, 22% yield. Yellow oil (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.70–7.61 (m, 2H), 7.41 (dt, J = 23.6, 7.2 Hz, 3H), 6.93 (t, J = 7.6 Hz, 2H), 6.83 (t, J = 7.2 Hz, 1H), 6.72 (d, J = 7.6 Hz, 2H), 4.75 (s, 2H), 4.06 (q, J = 7.2 Hz, 2H), 1.48 (s, 9H), 1.08 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 164.5, 161.7, 147.5, 133.5, 130.9, 128.4, 128.1, 126.7, 126.4, 125.5, 124.2, 82.9, 61.3, 60.0, 48.7, 29.0, 14.3. **HRMS (ESI)** ***m/z***: Calcd for $C_{24}H_{28}N_3O_4^+$ $[M + H]^+$: 406.2125; found: 406.2126.



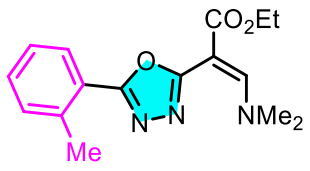
4w

Dimethyl 2-(5-phenyl-1,3,4-oxadiazol-2-yl)-3-(pyrrolidin-1-yl)maleate: 32.1 mg, 45% yield. White solid, melting point: 103.8–105.1 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 6.4 Hz, 2H), 7.52–7.41 (m, 3H), 3.91 (s, 3H), 3.57 (s, 3H), 3.46–2.67 (m, 4H), 1.86–1.70 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 165.0, 164.6, 161.4, 153.9, 131.5, 128.9, 126.6, 123.9, 81.3, 53.0, 51.5, 50.4, 24.9. **HRMS (ESI)** ***m/z***: Calcd for $C_{18}H_{20}N_3O_5^+$ $[M + H]^+$: 358.1397; found: 358.1395.



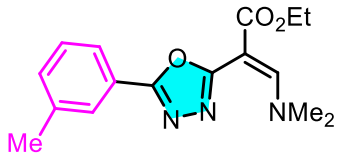
5a

Ethyl (*E*)-3-(dimethylamino)-2-(5-(*p*-tolyl)-1,3,4-oxadiazol-2-yl)acrylate: 36.1 mg, 60% yield. White solid, melting point: 110.5–113.0 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 2H), 7.75 (s, 1H), 7.25 (d, J = 7.6 Hz, 2H), 4.11 (q, J = 6.8 Hz, 2H), 3.13 (s, 3H), 2.58 (s, 3H), 2.36 (s, 3H), 1.15 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 164.9, 161.5, 153.9, 141.8, 129.5, 126.5, 121.4, 81.4, 59.9, 47.1, 39.3, 21.4, 14.3. **HRMS (ESI)** ***m/z***: Calcd for $C_{16}H_{20}N_3O_3^+$ $[M + H]^+$: 302.1499; found: 302.1497.



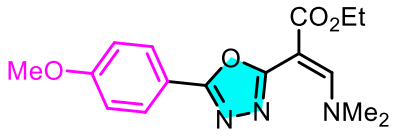
5b

Ethyl (*E*)-3-(dimethylamino)-2-(5-(*o*-tolyl)-1,3,4-oxadiazol-2-yl)acrylate: 37.3 mg, 62% yield. White solid, melting point: 81.1–82.5 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.40–7.35 (m, 1H), 7.34–7.27 (m, 2H), 4.16 (q, J = 7.2 Hz, 2H), 3.16 (s, 3H), 2.84–2.50 (m, 6H), 1.19 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 165.3, 161.5, 154.1, 138.1, 131.6, 130.9, 128.9, 126.0, 123.4, 81.5, 60.1, 47.2, 39.7, 22.0, 14.4. **HRMS (ESI) *m/z***: Calcd for $C_{16}H_{20}N_3O_3^+$ $[M + H]^+$: 302.1499; found: 302.1501.



5c

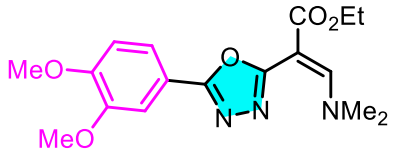
Ethyl (*E*)-3-(dimethylamino)-2-(5-(*m*-tolyl)-1,3,4-oxadiazol-2-yl)acrylate: 40.9 mg, 68% yield. White solid, melting point: 101.7–103.3 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91–7.82 (m, 2H), 7.78 (s, 1H), 7.40–7.28 (m, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.17 (s, 3H), 2.60 (s, 3H), 2.40 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 165.0, 161.8, 154.1, 138.8, 132.2, 128.8, 127.2, 124.1, 123.8, 81.4, 60.1, 47.2, 39.4, 21.2, 14.4. **HRMS (ESI) *m/z***: Calcd for $C_{16}H_{20}N_3O_3^+$ $[M + H]^+$: 302.1499; found: 302.1498.



5d

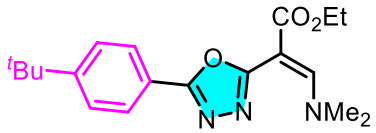
Ethyl (*E*)-3-(dimethylamino)-2-(5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-yl) acrylate: 37.4 mg, 59% yield. Yellow solid, melting point: 120.2–121.8 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.8 Hz, 2H), 7.78 (s, 1H), 6.99 (d, J = 8.8 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 3.13 (s, 3H), 2.63 (s, 3H), 1.19 (t, J = 7.2 Hz,

3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 164.9, 162.1, 161.5, 154.1, 128.5, 116.9, 114.4, 81.8, 60.1, 55.5, 47.1, 39.6, 14.5. **HRMS (ESI)** ***m/z***: Calcd for $C_{16}H_{20}N_3O_4^+$ $[M + H]^+$: 318.1448; found: 318.1452.



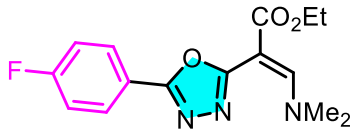
5e

Ethyl (*E*)-2-(5-(3,4-dimethoxyphenyl)-1,3,4-oxadiazol-2-yl)-3-(dimethylamino) acrylate: 40.2 mg, 58% yield. Yellow solid, melting point: 115.5–116.7 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.67–7.53 (m, 2H), 6.94 (d, J = 8.4 Hz, 1H), 4.15 (q, J = 6.8 Hz, 2H), 3.94 (d, J = 6.8 Hz, 6H), 3.16 (s, 3H), 2.63 (s, 3H), 1.19 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 164.9, 161.5, 154.0, 151.7, 149.2, 120.1, 116.9, 111.0, 109.2, 81.6, 60.0, 56.1, 56.0, 47.2, 39.5, 14.4. **HRMS (ESI)** ***m/z***: Calcd for $C_{17}H_{22}N_3O_5^+$ $[M + H]^+$: 348.1554; found: 348.1556.



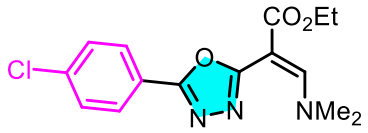
5f

Ethyl (*E*)-2-(5-(4-(*tert*-butyl)phenyl)-1,3,4-oxadiazol-2-yl)-3-(dimethylamino) acrylate: 48.7 mg, 71% yield. Yellow oil (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.77 (s, 1H), 7.49 (d, J = 8.4 Hz, 2H), 4.14 (q, J = 7.2 Hz, 2H), 3.15 (s, 3H), 2.60 (s, 3H), 1.32 (s, 9H), 1.17 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 164.9, 161.6, 154.9, 154.0, 126.5, 125.9, 121.4, 81.5, 60.0, 47.2, 39.3, 34.9, 31.0, 14.3. **HRMS (ESI)** ***m/z***: Calcd for $C_{19}H_{26}N_3O_3^+$ $[M + H]^+$: 344.1969; found: 344.1969.



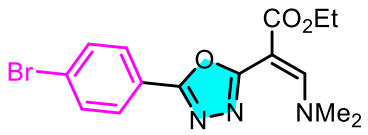
5g

Ethyl (*E*)-3-(dimethylamino)-2-(5-(4-fluorophenyl)-1,3,4-oxadiazol-2-yl)acrylate: 44.5 mg, 73% yield. White solid, melting point: 116.2–117.4 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.79 (s, 1H), 7.17 (t, J = 8.0 Hz, 2H), 4.15 (d, J = 6.8 Hz, 2H), 3.18 (s, 3H), 2.63 (s, 3H), 1.18 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 164.5 (d, J = 251.1 Hz), 164.1, 162.0, 154.1, 128.9 (d, J = 8.8 Hz), 120.6 (d, J = 3.3 Hz), 116.3, 116.1, 81.4, 60.1, 47.3, 39.6, 14.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –107.40 ~ –107.45 (m, 1H). **HRMS (ESI) *m/z***: Calcd for $C_{16}H_{17}FN_3O_3^+$ $[M + H]^+$: 306.1248; found: 306.1249.



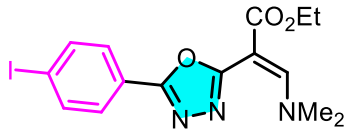
5h

Ethyl (*E*)-2-(5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl)-3-(dimethylamino)acrylate: 41.1 mg, 64% yield. White solid, melting point: 142.7–143.9 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.79 (s, 1H), 7.46 (d, J = 8.4 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.19 (s, 3H), 2.62 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 164.0, 162.1, 154.2, 137.6, 129.3, 127.9, 122.8, 81.3, 60.1, 47.4, 39.6, 14.4. **HRMS (ESI) *m/z***: Calcd for $C_{15}H_{17}ClN_3O_3^+$ $[M + H]^+$: 322.0953; found: 322.0952.



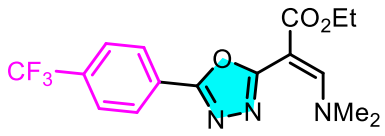
5i

Ethyl (*E*)-2-(5-(4-bromophenyl)-1,3,4-oxadiazol-2-yl)-3-(dimethylamino)acrylate: 41.6 mg, 57% yield. White solid, melting point: 142.9–143.7 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.80 (s, 1H), 7.63 (d, J = 8.4 Hz, 2H), 4.16 (q, J = 7.2 Hz, 2H), 3.19 (s, 3H), 2.63 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 164.2, 162.2, 154.2, 132.3, 128.1, 126.0, 123.2, 81.3, 60.1, 47.3, 39.6, 14.4. **HRMS (ESI) *m/z***: Calcd for $C_{15}H_{17}BrN_3O_3^+$ [M + H]$^+$: 366.0448; found: 366.0449.



5j

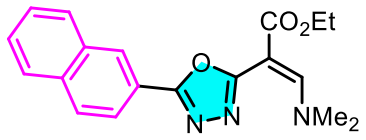
Ethyl (*E*)-3-(dimethylamino)-2-(5-(4-iodophenyl)-1,3,4-oxadiazol-2-yl)acrylate: 46.3 mg, 56% yield. White solid, melting point: 128.8–129.9 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.97 (d, J = 8.4 Hz, 2H), 7.82 (s, 1H), 7.76 (d, J = 8.4 Hz, 2H), 4.05 (q, J = 7.2 Hz, 2H), 3.37 (s, 3H), 3.21 (s, 3H), 1.12 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 166.1, 163.1, 161.6, 153.7, 137.9, 127.5, 122.7, 98.8, 78.9, 58.8, 46.3, 14.0. **HRMS (ESI) *m/z***: Calcd for $C_{15}H_{17}IN_3O_3^+$ [M + H]$^+$: 414.0309; found: 414.0309.



5k

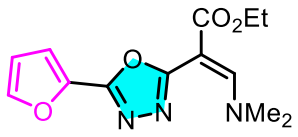
Ethyl (*E*)-3-(dimethylamino)-2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazol -2-yl)acrylate: 44.0 mg, 62% yield. White solid, melting point: 117.7–119.8 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 2H), 7.82 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 3.21 (s, 3H), 2.65 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H). **^{13}C**

NMR (100 MHz, $CDCl_3$) δ 167.4, 163.7, 162.6, 132.9 (q, J = 32.6 Hz), 127.5, 127.0, 126.0 (q, J = 3.6 Hz), 125.0, 122.2, 81.3, 60.2, 47.3, 39.8, 14.4. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –63.05 (s, 3F). **HRMS (ESI)** ***m/z***: Calcd for $C_{16}H_{17}FN_3O_3^+$ $[M + H]^+$: 356.1217; found: 356.1217.



5l

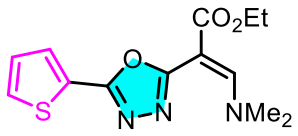
Ethyl (*E*)-3-(dimethylamino)-2-(5-(naphthalen-2-yl)-1,3,4-oxadiazol-2-yl)acrylate: 38.4 mg, 57% yield. Yellow solid, melting point: 98.6–99.9 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.25 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 7.2 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.84 (s, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.61–7.52 (m, 2H), 4.21 (q, J = 7.2 Hz, 2H), 3.16 (s, 3H), 2.71 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 165.1, 161.6, 154.2, 133.8, 132.2, 130.0, 128.6, 128.2, 127.9, 126.5, 126.2, 124.9, 120.9, 81.5, 60.1, 47.3, 39.7, 14.5. **HRMS (ESI)** ***m/z***: Calcd for $C_{19}H_{20}N_3O_3^+$ $[M + H]^+$: 338.1499; found: 338.1500.



5m

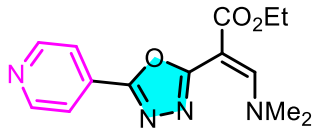
Ethyl (*E*)-3-(dimethylamino)-2-(5-(furan-2-yl)-1,3,4-oxadiazol-2-yl)acrylate: 27.7 mg, 50% yield. Yellow solid, melting point: 70.6–71.8 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.61 (s, 1H), 7.11 (d, J = 3.2 Hz, 1H), 6.61–6.52 (m, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.16 (s, 3H), 2.62 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 161.4, 157.8, 154.3, 145.3, 139.8, 113.5, 112.0, 81.0, 60.1, 47.3, 39.5, 14.3. **HRMS (ESI)** ***m/z***: Calcd for $C_{13}H_{16}N_3O_4^+$ $[M + H]^+$: 278.1135;

found: 278.1139.



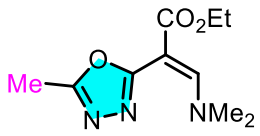
5n

Ethyl (*E*)-3-(dimethylamino)-2-(5-(thiophen-2-yl)-1,3,4-oxadiazol-2-yl)acrylate: 32.2 mg, 55% yield. Yellow solid, melting point: 70.4–71.7 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.73 (d, J = 3.2 Hz, 1H), 7.52 (d, J = 4.8 Hz, 1H), 7.16–7.12 (m, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.17 (s, 3H), 2.64 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 161.4, 161.2, 154.2, 129.7, 129.3, 128.0, 125.7, 81.2, 60.1, 47.2, 39.4, 14.4. **HRMS (ESI) *m/z***: Calcd for $C_{13}H_{16}N_3O_3S^+$ [M + H]$^+$: 294.0907; found: 294.0910.



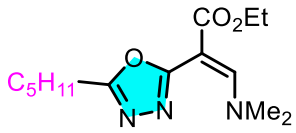
5o

Ethyl (*E*)-3-(dimethylamino)-2-(5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)acrylate: 39.7 mg, 69% yield. Yellow solid, melting point: 102.4–103.8 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 (d, J = 1.2 Hz, 2H), 7.89 (d, J = 5.2 Hz, 2H), 7.81 (s, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.19 (s, 3H), 2.62 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 163.0, 162.9, 154.5, 150.7, 131.3, 120.1, 81.0, 60.2, 47.3, 39.6, 14.4. **HRMS (ESI) *m/z***: Calcd for $C_{14}H_{17}N_4O_3^+$ [M + H]$^+$: 289.1295; found: 289.1297.



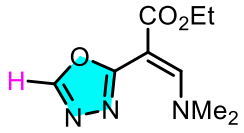
5p

Ethyl (*E*)-3-(dimethylamino)-2-(5-methyl-1,3,4-oxadiazol-2-yl)acrylate: 22.5 mg, 50% yield. Yellow oil (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 4.18–4.09 (m, 2H), 3.09 (s, 3H), 2.72–2.42 (m, 6H), 1.21–1.57 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 164.1, 162.1, 153.9, 81.5, 60.1, 47.2, 39.2, 14.4, 11.2. **HRMS (ESI)** ***m/z***: Calcd for $C_{10}H_{16}N_3O_3^+$ $[M + H]^+$: 226.1186; found: 226.1189.



5q

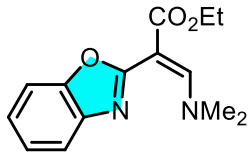
Ethyl (*E*)-3-(dimethylamino)-2-(5-pentyl-1,3,4-oxadiazol-2-yl)acrylate: 38.2 mg, 68% yield. Yellow oil (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 4.07 (q, J = 7.2 Hz, 2H), 3.07 (s, 3H), 2.78 (t, J = 7.6 Hz, 2H), 2.52 (s, 3H), 1.80–1.65 (m, 2H), 1.31–1.26 (m, 4H), 1.12 (t, J = 7.2 Hz, 3H), 0.83 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 167.3, 161.7, 153.7, 81.5, 59.8, 46.9, 39.0, 30.8, 26.1, 25.3, 22.0, 14.2, 13.7. **HRMS (ESI)** ***m/z***: Calcd for $C_{14}H_{24}N_3O_3^+$ $[M + H]^+$: 282.1812; found: 282.1815.



5r

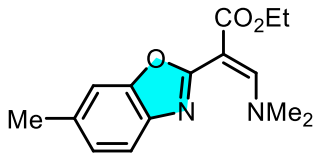
Ethyl (*E*)-3-(dimethylamino)-2-(1,3,4-oxadiazol-2-yl)acrylate: 32.6 mg, 70% yield. Yellow oil (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.75 (s, 1H), 4.10 (q, J = 7.2 Hz,

2H), 3.14 (s, 3H), 2.50 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 162.1, 154.2, 153.3, 80.7, 60.0, 47.1, 39.2, 14.3. **HRMS (ESI) *m/z***: Calcd for $C_9H_{14}N_3O_3^+$ $[M + Na]^+$: 234.0849; found: 234.0849.



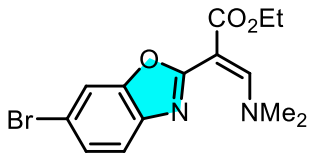
6a

Ethyl (*E*)-2-(benzo[*d*]oxazol-2-yl)-3-(dimethylamino)acrylate: 29.1 mg, 56% yield. Yellow solid, melting point: 102.2–103.4 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.73–7.67 (m, 1H), 7.54–7.48 (m, 1H), 7.34–7.28 (m, 2H), 4.16 (q, J = 7.2 Hz, 2H), 3.10 (s, 3H), 2.58 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 161.1, 154.1, 150.7, 141.4, 124.5, 123.8, 119.7, 110.5, 86.2, 60.0, 47.1, 39.5, 14.4. **HRMS (ESI) *m/z***: Calcd for $C_{14}H_{17}N_2O_3^+$ $[M + H]^+$: 261.1234; found: 261.1233.



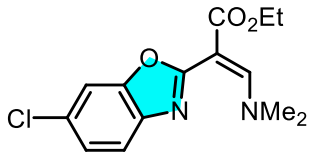
6b

Ethyl (*E*)-3-(dimethylamino)-2-(6-methylbenzo[d]oxazol-2-yl)acrylate: 21.9 mg, 40% yield. Yellow oil (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.30 (s, 1H), 7.09 (d, J = 8.0 Hz, 1H), 4.14 (q, J = 6.8 Hz, 2H), 3.07 (s, 3H), 2.45 (s, 6H), 1.16 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 160.4, 153.9, 150.9, 139.1, 134.8, 125.0, 119.0, 110.6, 86.1, 59.9, 46.8, 39.2, 21.6, 14.3. **HRMS (ESI) *m/z***: Calcd for $C_{15}H_{19}N_2O_3^+$ $[M + H]^+$: 275.1390; found: 275.1388.



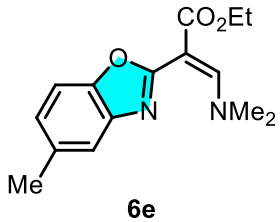
6c

Ethyl (*E*)-2-(6-bromobenzo[d]oxazol-2-yl)-3-(dimethylamino)acrylate: 44.6 mg, 66% yield. White solid, melting point: 76.9–78.3 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.66 (s, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.10 (s, 3H), 2.55 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 161.6, 154.3, 151.1, 140.5, 127.2, 120.5, 117.3, 113.8, 85.6, 60.0, 47.0, 39.6, 14.3. **HRMS (ESI) *m/z***: Calcd for $C_{14}H_{16}BrN_2O_3^+$ $[M + H]^+$: 339.0339; found: 339.0338.



6d

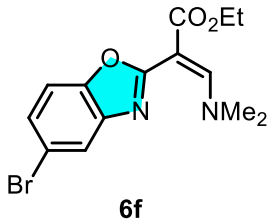
Ethyl (*E*)-2-(6-chlorobenzo[d]oxazol-2-yl)-3-(dimethylamino)acrylate: 18.2 mg, 31% yield. Yellow oil (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.53 (s, 1H), 7.29 (d, J = 8.4 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.13 (s, 3H), 2.58 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 161.9, 154.4, 151.0, 140.2, 130.2, 124.6, 120.2, 111.1, 85.8, 60.2, 47.1, 39.4, 14.4. **HRMS (ESI) *m/z***: Calcd for $C_{14}H_{16}ClN_2O_3^+$ $[M + H]^+$: 295.0844; found: 295.0842.



6e

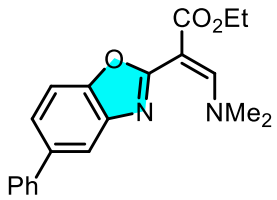
Ethyl (*E*)-3-(dimethylamino)-2-(5-methylbenzo[d]oxazol-2-yl)acrylate: 24.5 mg, 45% yield. Yellow oil (Flash column chromatography eluent, petroleum ether/ethyl

acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.61–7.25 (m, 2H), 7.09 (s, 1H), 4.48–3.82 (m, 2H), 3.09 (s, 3H), 2.43 (s, 6H), 1.41–0.98 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 161.0, 153.9, 148.9, 141.5, 133.6, 125.5, 119.6, 109.8, 86.2, 60.0, 46.8, 39.3, 21.3, 14.3. **HRMS (ESI)** ***m/z***: Calcd for $C_{15}H_{19}N_2O_3^+$ $[M + H]^+$: 275.1390; found: 275.1387.



6f

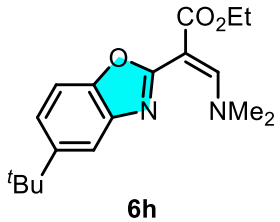
Ethyl (*E*)-2-(5-bromobenzo[d]oxazol-2-yl)-3-(dimethylamino)acrylate: 22.3 mg, 33% yield. White solid, melting point: 77.0–78.6 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 12.8 Hz, 2H), 7.38 (s, 2H), 4.16 (q, J = 6.8 Hz, 2H), 3.14 (s, 3H), 2.57 (s, 3H), 1.19 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 162.4, 154.4, 149.7, 143.0, 127.4, 122.5, 116.6, 111.7, 85.8, 60.1, 47.1, 39.5, 14.4. **HRMS (ESI)** ***m/z***: Calcd for $C_{14}H_{16}BrN_2O_3^+$ $[M + H]^+$: 339.0339; found: 339.0338.



6g

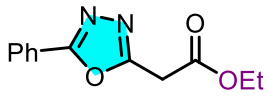
Ethyl (*E*)-3-(dimethylamino)-2-(5-phenylbenzo[d]oxazol-2-yl)acrylate: 28.9 mg, 43% yield. Yellow solid, melting point: 107.5–109.0 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.81 (s, 1H), 7.61 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 8.8 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.12 (s, 3H), 2.61 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 161.7, 154.2, 150.3, 142.0, 141.1, 137.8, 128.7, 127.3, 127.0, 124.0, 118.1,

110.4, 86.1, 60.1, 46.7, 39.6, 14.4. **HRMS (ESI)** ***m/z***: Calcd for $C_{20}H_{21}N_2O_3^+$ [M + H]$^+$: 337.1547; found: 337.1543.



6h

Ethyl (*E*)-2-(5-(*tert*-butyl)benzo[d]oxazol-2-yl)-3-(dimethylamino)acrylate: 31.6 mg, 50% yield. Yellow oil (Flash column chromatography eluent, petroleum ether/ethyl acetate = 3/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77–7.70 (m, 1H), 7.67 (d, J = 7.2 Hz, 1H), 7.44–7.28 (m, 2H), 4.11 (q, J = 6.8 Hz, 2H), 3.05 (s, 3H), 2.54 (s, 3H), 1.33 (s, 9H), 1.19–1.08 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 160.9, 153.8, 148.5, 147.1, 141.1, 122.0, 116.0, 109.4, 86.1, 59.8, 46.7, 39.1, 34.6, 31.5, 14.3. **HRMS (ESI)** ***m/z***: Calcd for $C_{18}H_{25}N_2O_3^+$ [M + H]$^+$: 317.1860; found: 317.1858.



7a, 45%

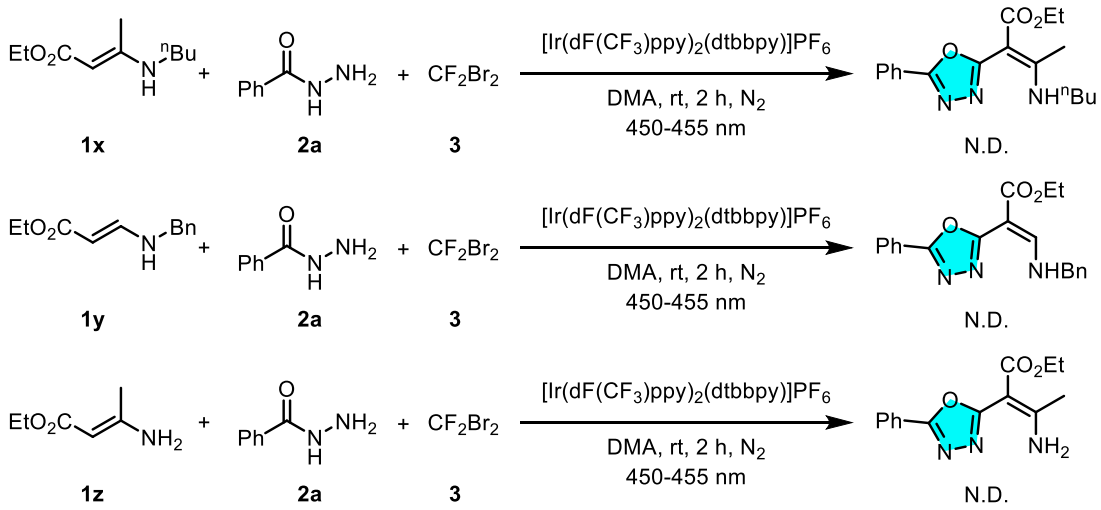
Under nitrogen atmosphere, a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with enaminone (**1a**, 28.6 mg, 0.20 mmol), benzoyl hydrazine (**2a**, 27.2 mg, 0.20 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.48 mg, 0.004 mmol, 2.0 mol%), difluoro-dibromomethane (**3**, 0.60 mmol, prepare 1.0 mg/mL DMA solution of difluoro-dibromomethane and measure 140 μL with a microsyringe), and DMA (2.0 mL). The reaction mixture was stirred under 2×3 W blue LEDs (450–455 nm) at room temperature with stirring for 2 h. After completion of the reaction, added H_2O (0.5 mL), then the reaction mixture was stirred at room temperature with stirring for another 12 h. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and H_2O. The resulting mixture was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and

concentrated. The residue was purified with silica gel chromatography (petroleum ether/ethyl acetate = 30:1, V/V) to give the product **7a** (20.9 mg, 45% yield).

Ethyl 2-(5-phenyl-1,3,4-oxadiazol-2-yl)acetate: 20.9 mg, 45% yield. White solid, melting point: 60.3–61.5 ºC (Flash column chromatography eluent, petroleum ether/ethyl acetate = 30/1, V/V). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11–7.98 (m, 2H), 7.59–7.46 (m, 3H), 4.24 (q, J = 7.2 Hz, 2H), 4.03 (s, 2H), 1.29 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.3, 165.6, 160.3, 131.8, 129.0, 126.9, 123.7, 62.1, 32.0, 14.0. **HRMS (ESI) m/z**: Calcd for $C_{12}H_{13}N_2O_3$ $[M + H]^+$: 233.0921; found: 233.0918.

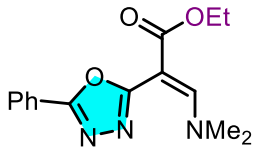
5. Unsuccessful substrates

unsuccessful substrates 1



unsuccessful substrates 2

6. Crystallographic data and molecular structure of 4a (CCDC: 2247417)



4a

General procedure for crystal culture of **4a**: To a test tube (15 mL) with added **4a** (30 mg), dichloromethane (1.0 mL) was added slowly to make it dissolve completely. After it dissolved, a mixture of petroleum ether (2.0 mL) and EtOAc (3.0 mL) was added. Then, the test tube was sealed with a rubber stopper, and connected to air with a syringe needle. Finally, the tube was put in a dry and ventilated place to make the organic solvent to volatilize slowly. After a few days, the crystal of **4a** was obtained. The X-ray crystal structure of **4a** was shown in Figure S2.

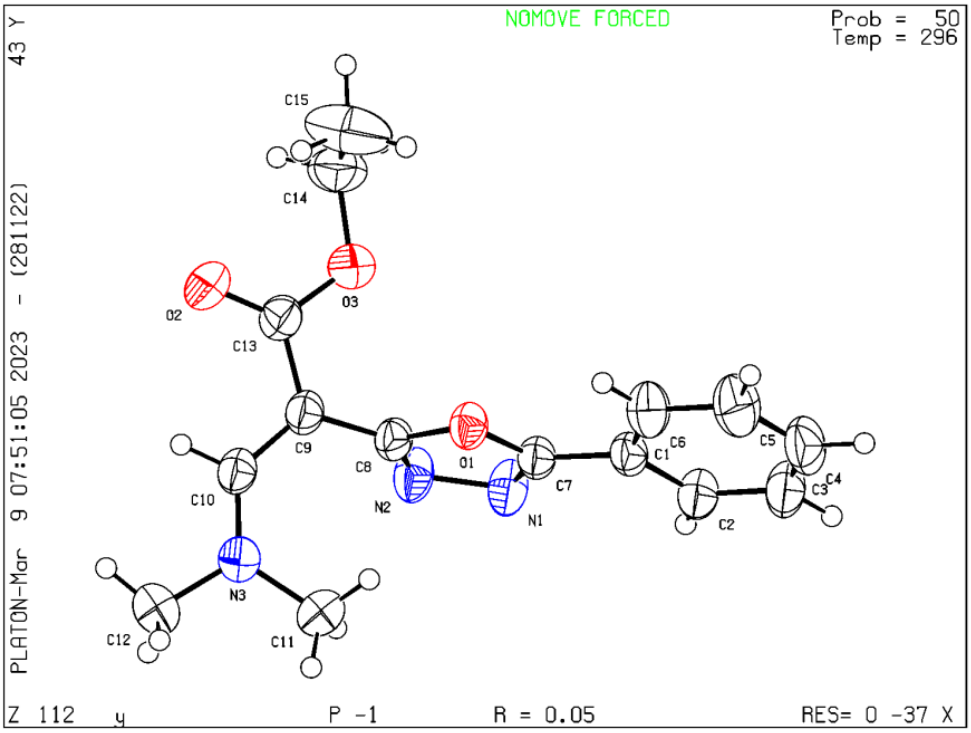


Figure S2 ORTEP diagram of **4a** with thermal displacement parameters drawn at 30% probability.

Datablock: y

Bond precision: C-C = 0.0021 A Wavelength=0.71073

Cell: a=6.9139(16) b=10.160(2) c=11.688(3)
alpha=112.767(3) beta=91.686(3) gamma=91.806(3)
Temperature: 296 K

	Calculated	Reported
Volume	755.9(3)	755.9(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C15 H17 N3 O3	C15 H17 N3 O3
Sum formula	C15 H17 N3 O3	C15 H17 N3 O3
Mr	287.32	287.32
Dx,g cm-3	1.262	1.262
Z	2	2
Mu (mm-1)	0.090	0.090
F000	304.0	304.0
F000'	304.14	
h,k,lmax	10,15,17	10,14,16
Nref	5287	4688
Tmin,Tmax	0.989,0.991	0.665,0.746
Tmin'	0.988	

Correction method= # Reported T Limits: Tmin=0.665 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.887 Theta(max)= 32.079

R(reflections)= 0.0493(3402) wR2(reflections)= 0.1679(4688)

S = 1.045 Npar= 194

7. Control experiment

Under nitrogen atmosphere, a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with enaminone (**1a**, 28.6 mg, 0.20 mmol), benzoyl hydrazine (**2a**, 27.2 mg, 0.20 mmol), TEMPO (62.5 mg, 0.40 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.48 mg, 0.004 mmol, 2.0 mol%), difluoro-dibromomethane (**3**, 0.60 mmol, prepare 1.0 mg/mL DMA solution of difluoro-dibromomethane and measure 140 μL with a microsyringe), and DMA (2.0 mL). The reaction mixture was stirred under 2×3 W blue LEDs (450–455 nm) at room temperature with stirring for 2 h. After completion of the reaction, the reaction mixture was detected by GC-MS (Figure S3). The TEMPO-trapped product **8** was observed during the reaction. This result provided the evidence for support of the proposed mechanism.

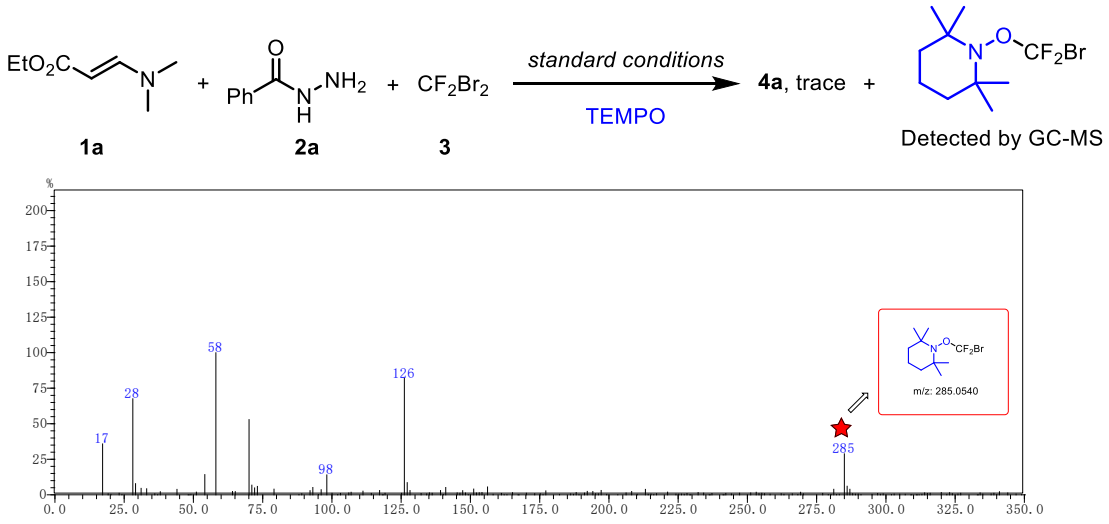
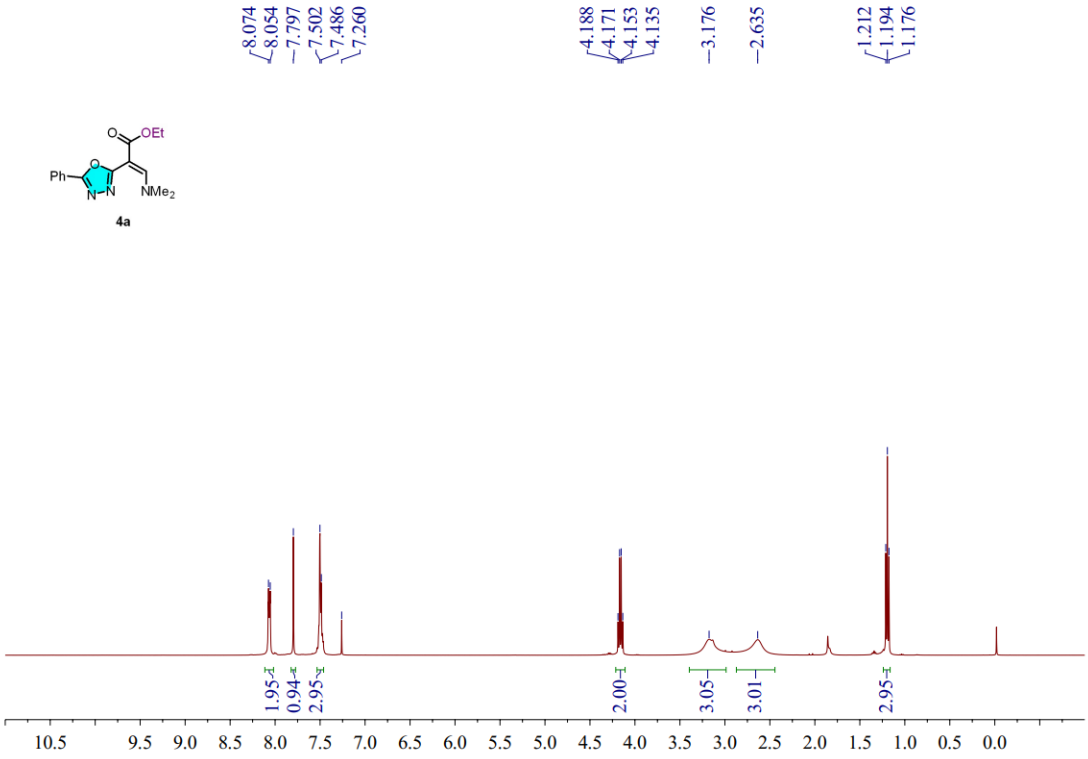
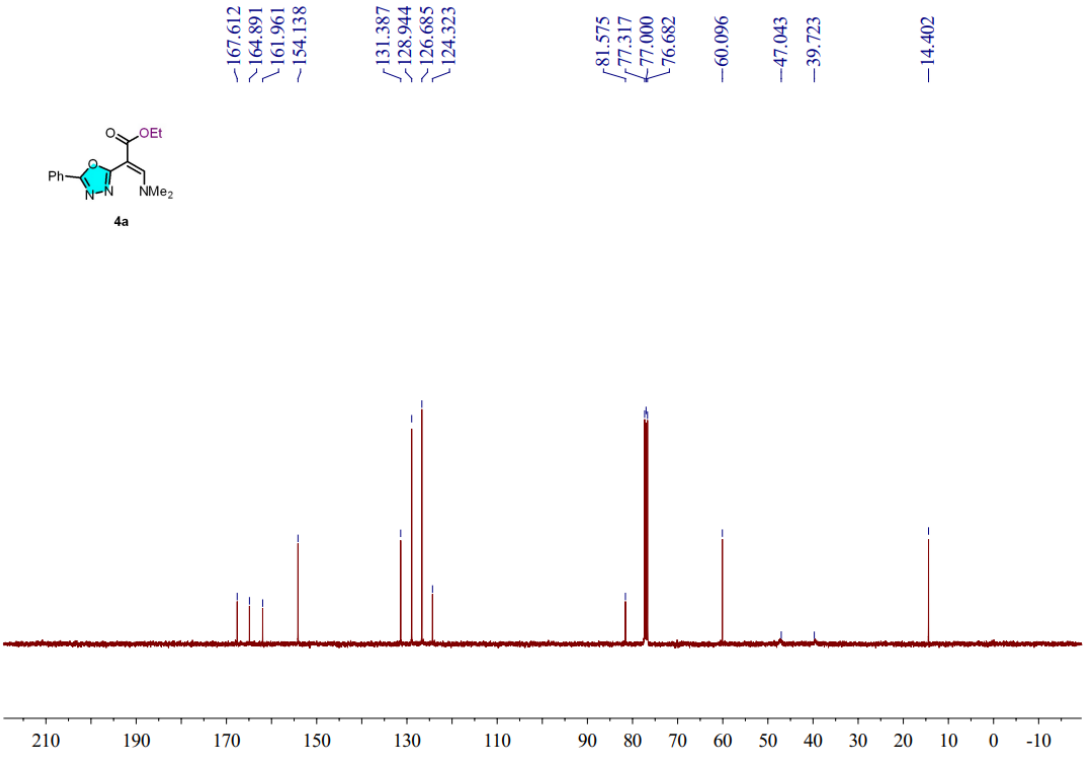


Figure S3 GC-MS analysis of the reaction mixture.

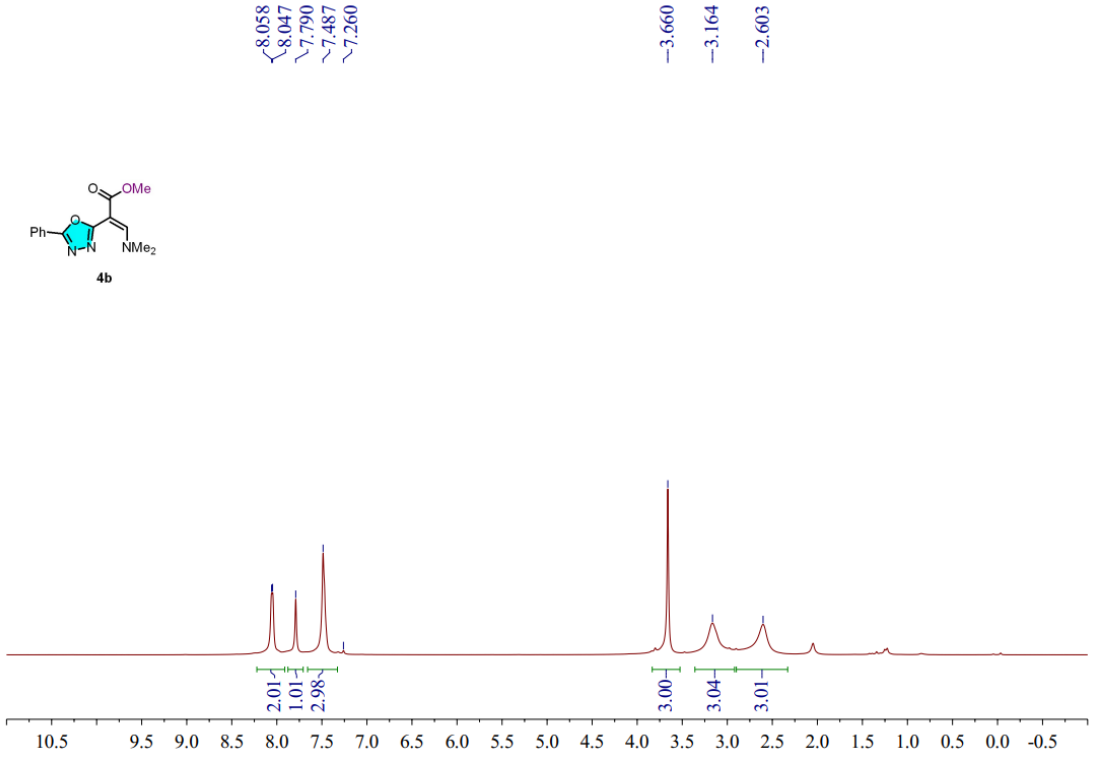
8. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of the products



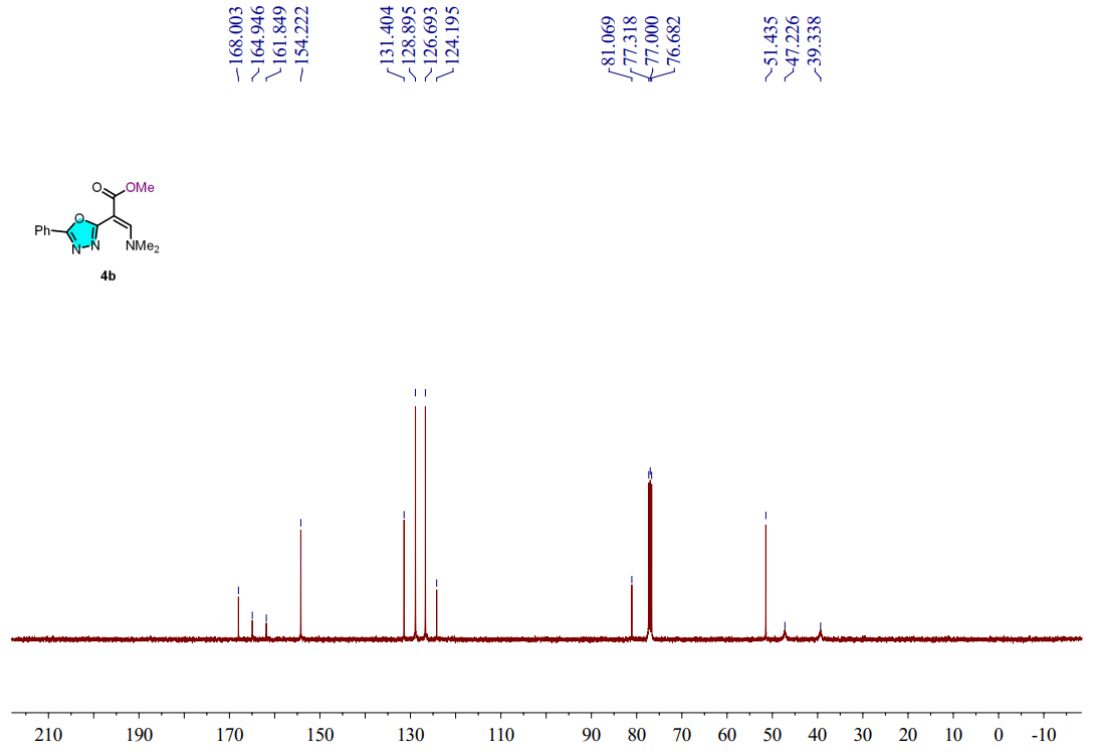
^{1}H NMR Spectrum of Compound **4a** (400 MHz, $CDCl_3$)



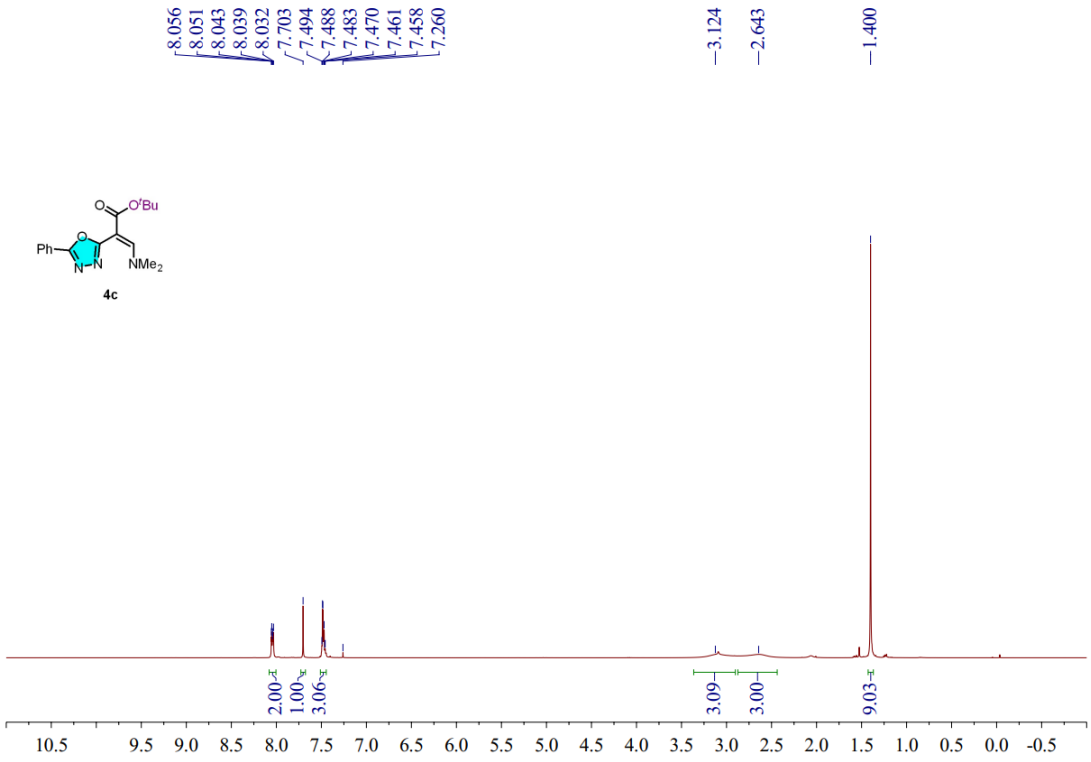
^{13}C{^{1}H} NMR Spectrum of Compound **4a** (100 MHz, $CDCl_3$)



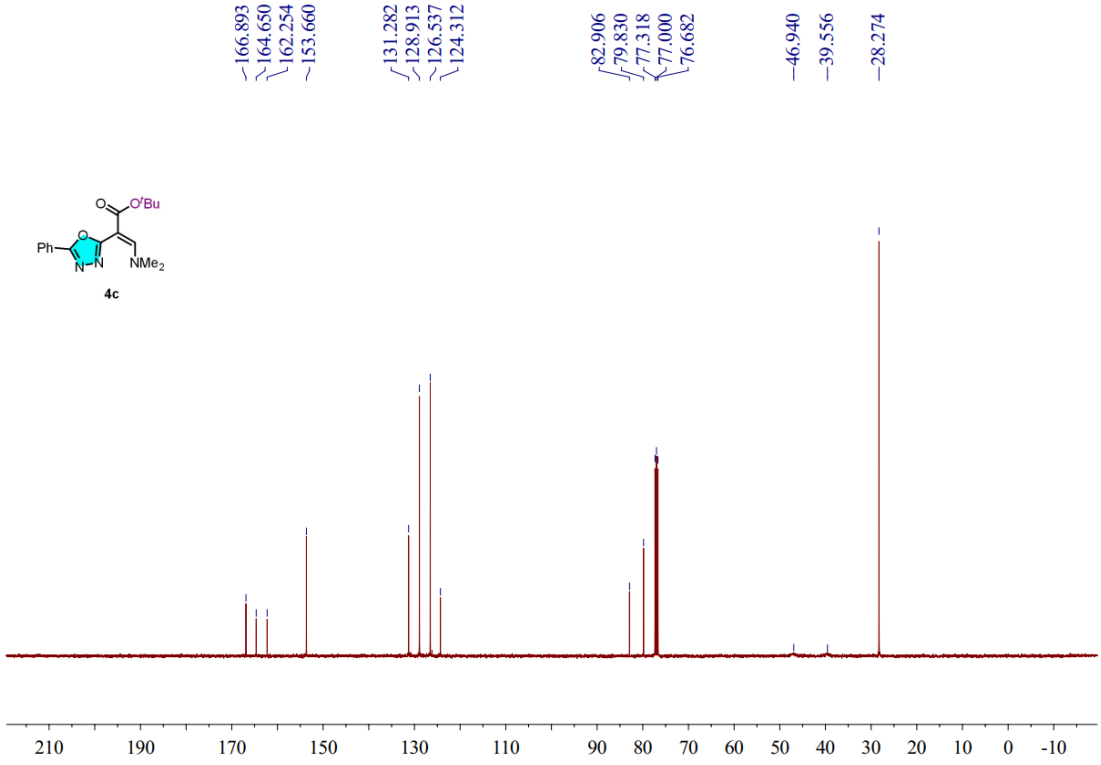
^{1}H NMR Spectrum of Compound **4b** (400 MHz, $CDCl_3$)



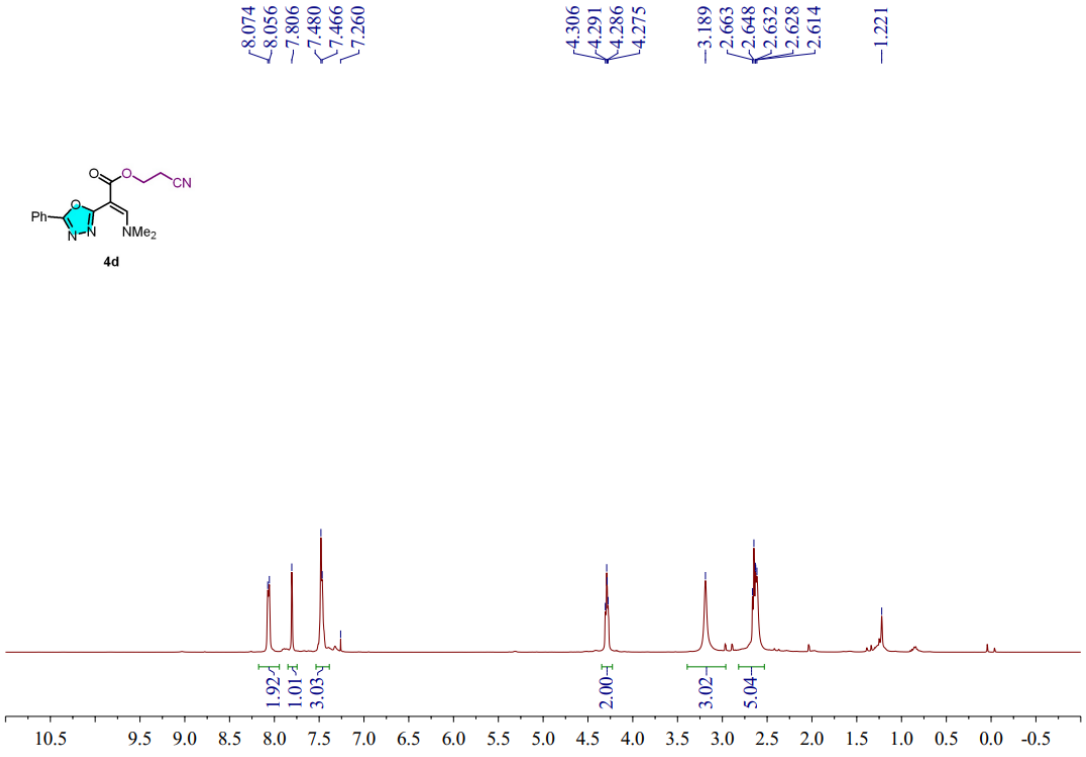
^{13}C{^{1}H} NMR Spectrum of Compound **4b** (100 MHz, $CDCl_3$)



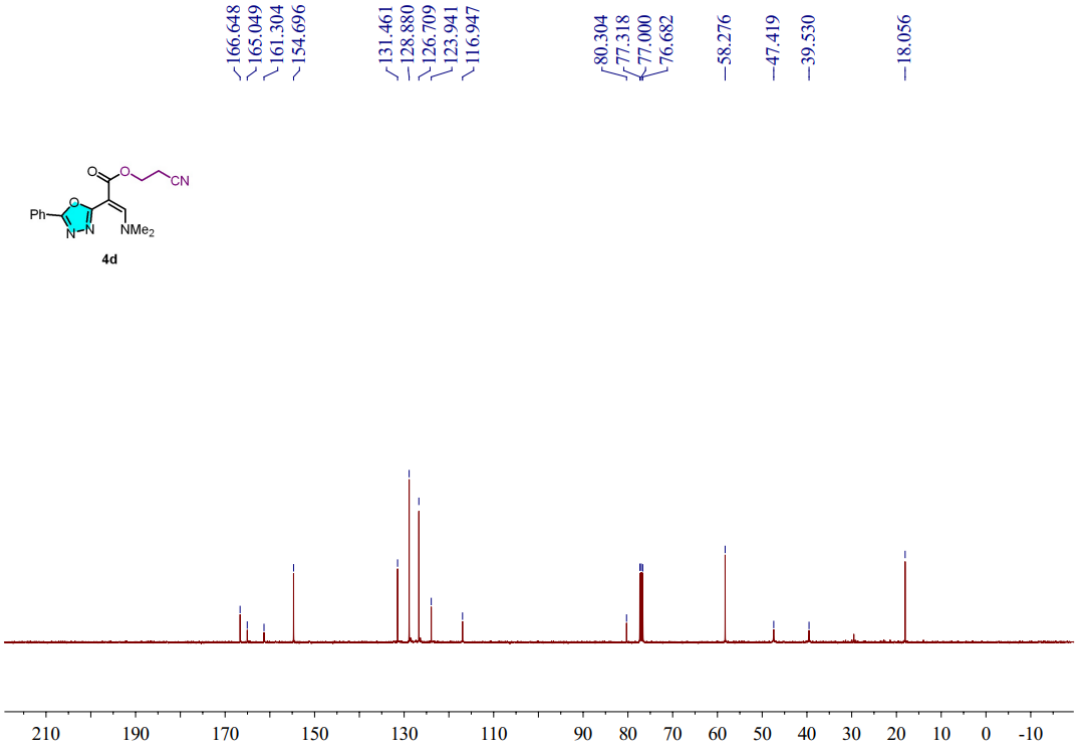
^{1}H NMR Spectrum of Compound **4c** (400 MHz, $CDCl_3$)



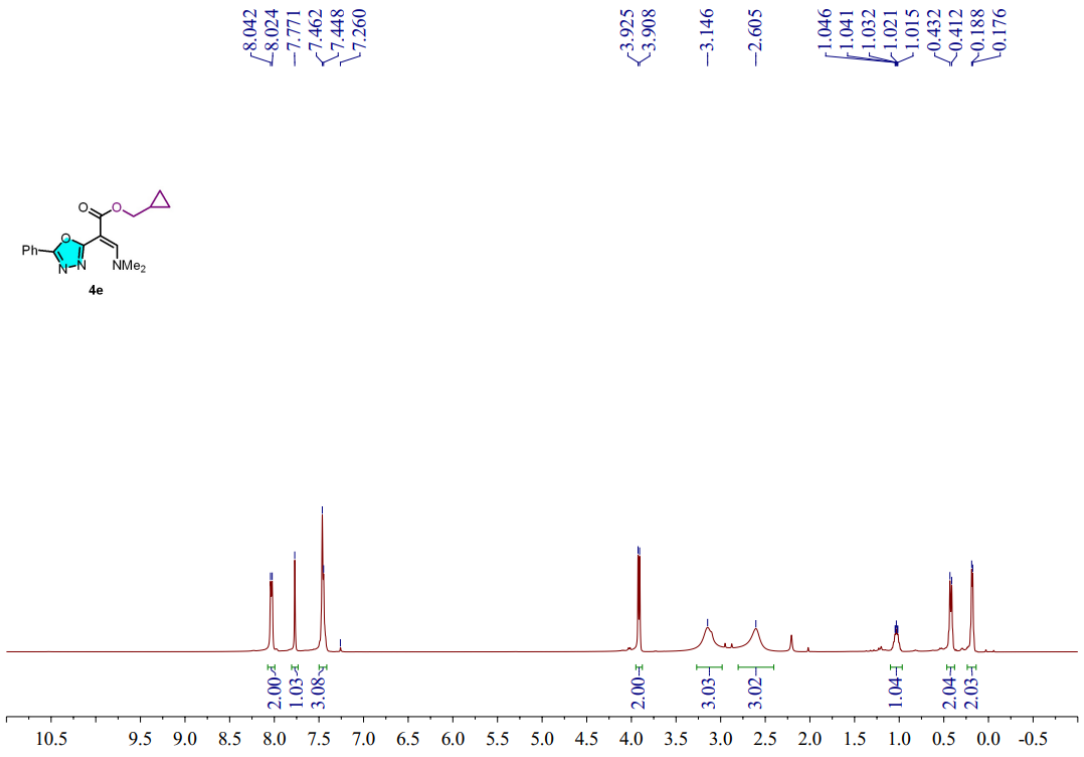
^{13}C{^{1}H} NMR Spectrum of Compound **4c** (100 MHz, $CDCl_3$)



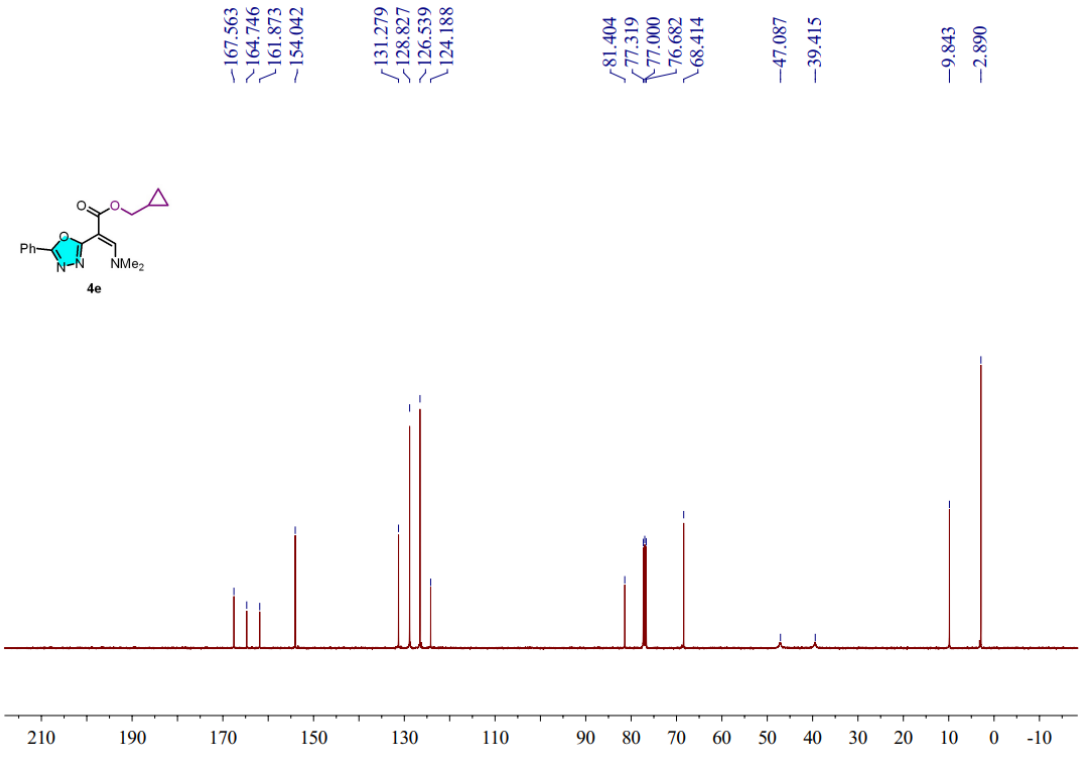
^{1}H NMR Spectrum of Compound **4d** (400 MHz, $CDCl_3$)



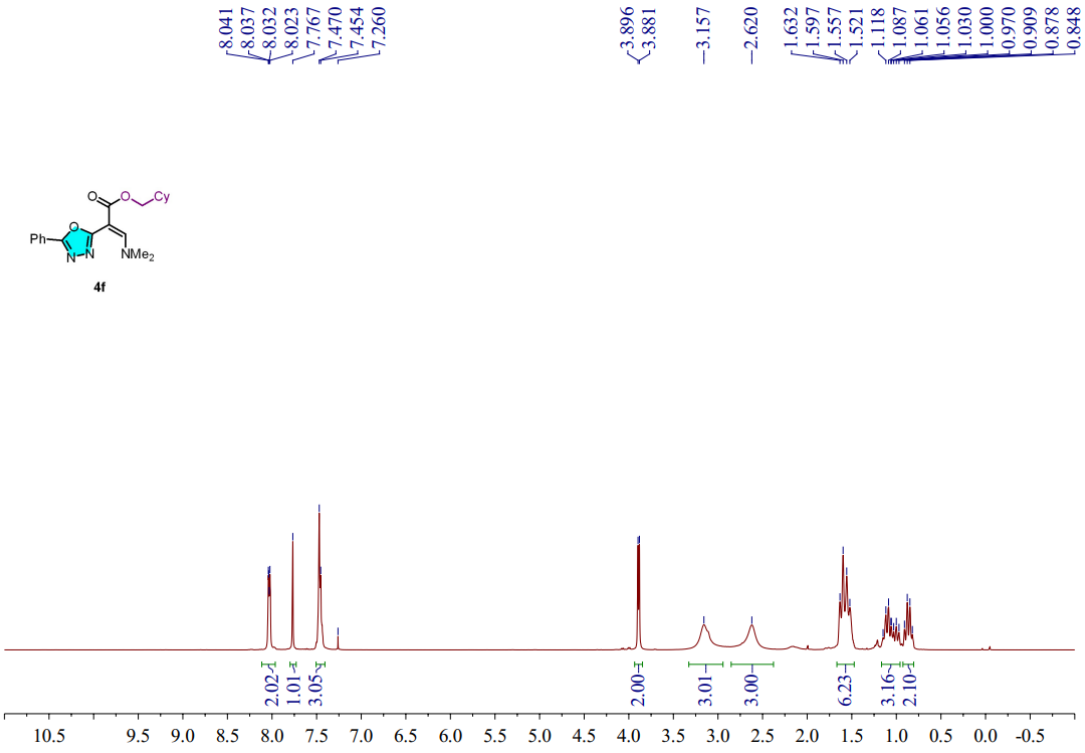
^{13}C{^{1}H} NMR Spectrum of Compound **4d** (100 MHz, $CDCl_3$)



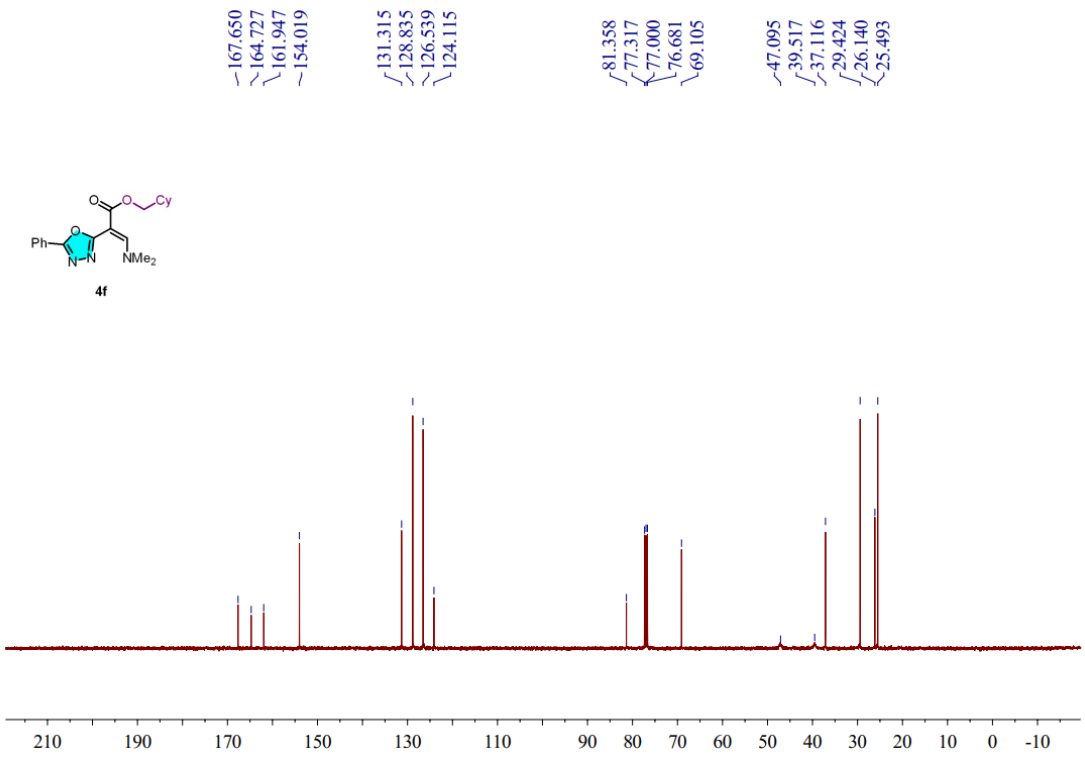
^{1}H NMR Spectrum of Compound **4e** (400 MHz, $CDCl_3$)



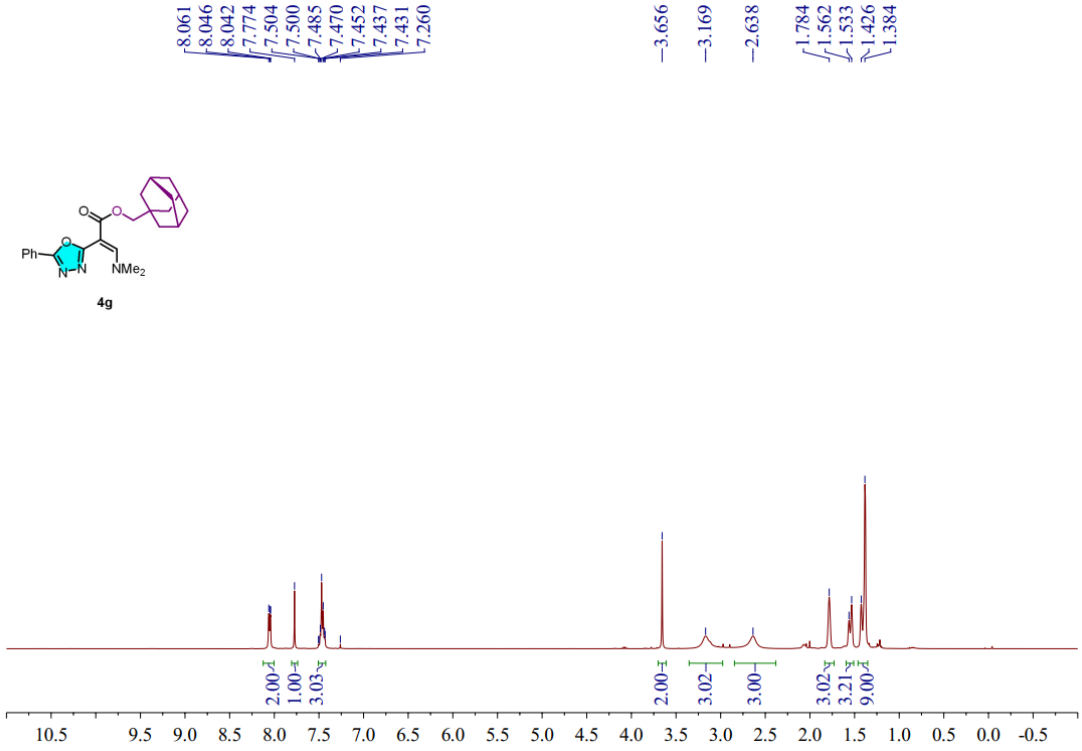
^{13}C{^{1}H} NMR Spectrum of Compound **4e** (100 MHz, $CDCl_3$)



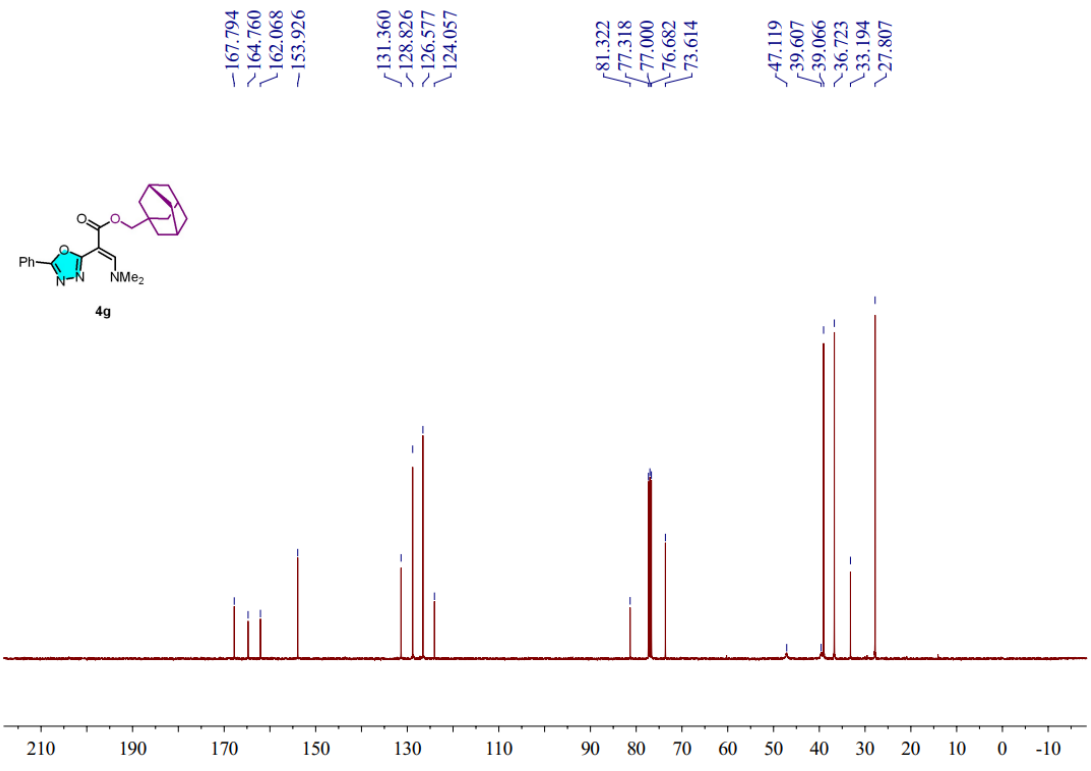
^{1}H NMR Spectrum of Compound **4f** (400 MHz, $CDCl_3$)



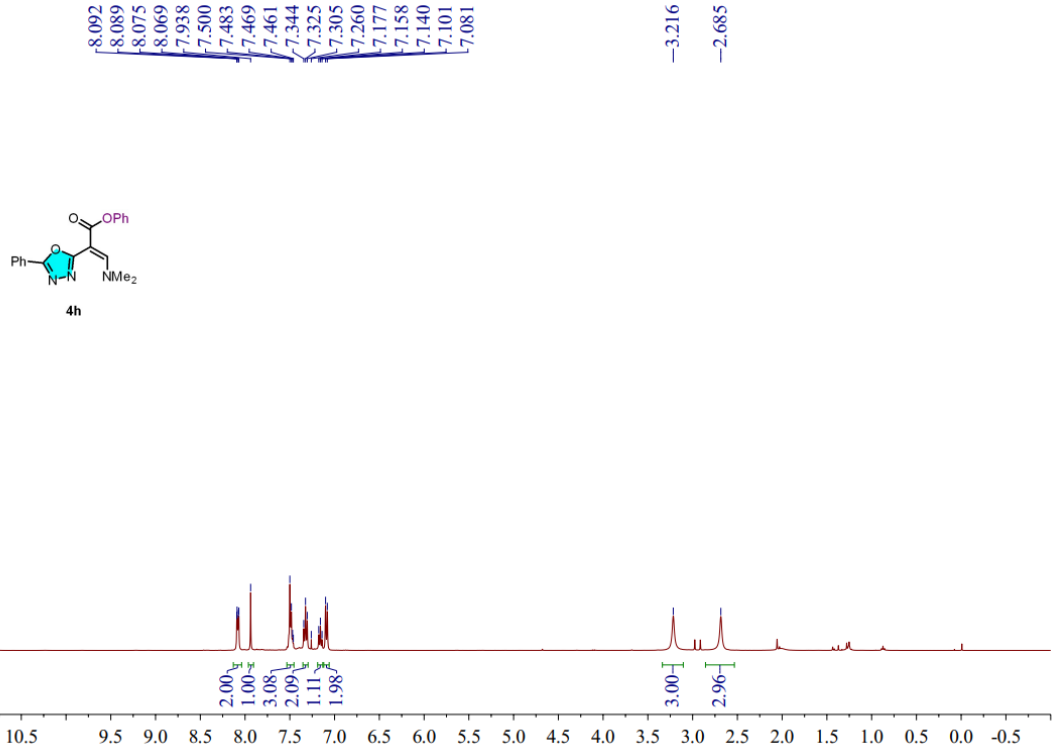
^{13}C{^{1}H} NMR Spectrum of Compound **4f** (100 MHz, $CDCl_3$)



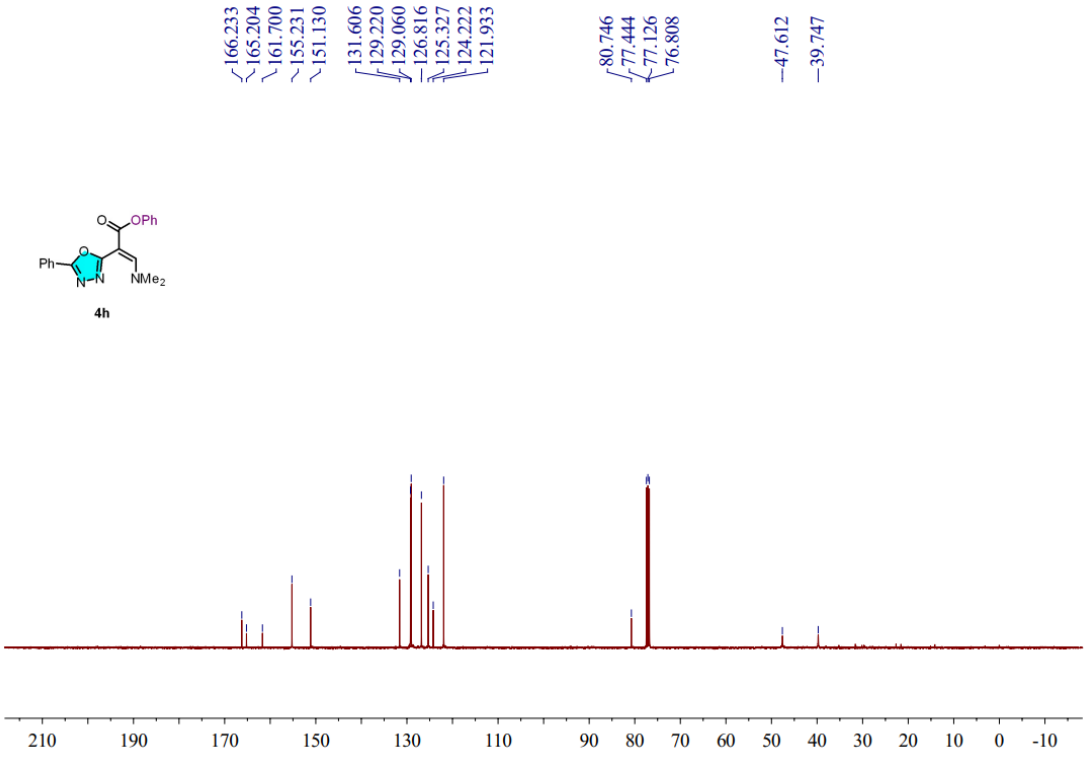
^{1}H NMR Spectrum of Compound **4g** (400 MHz, $CDCl_3$)



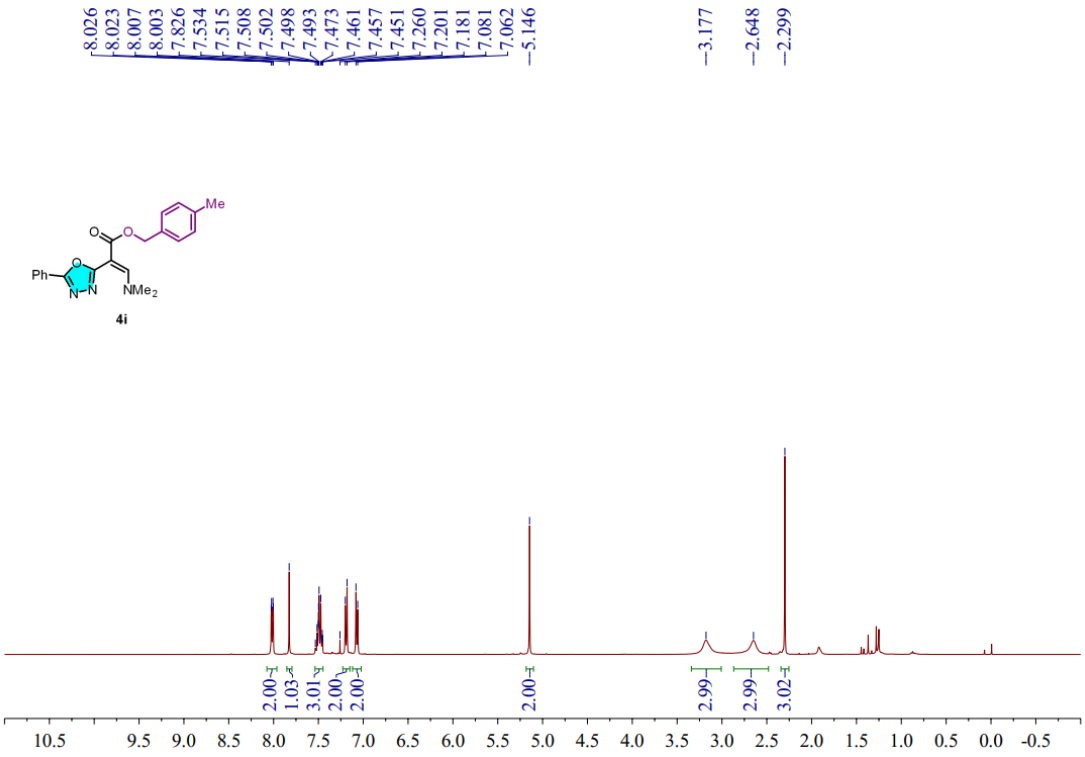
^{13}C{^{1}H} NMR Spectrum of Compound **4g** (100 MHz, $CDCl_3$)



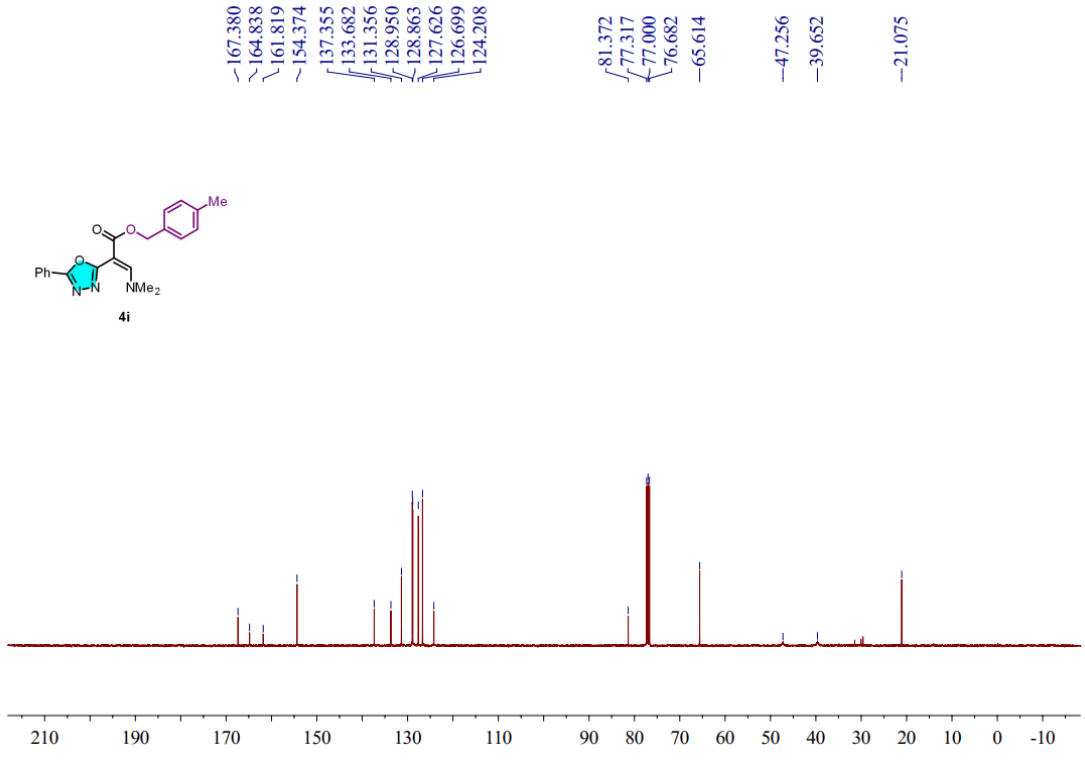
^{1}H NMR Spectrum of Compound **4h** (400 MHz, $CDCl_3$)



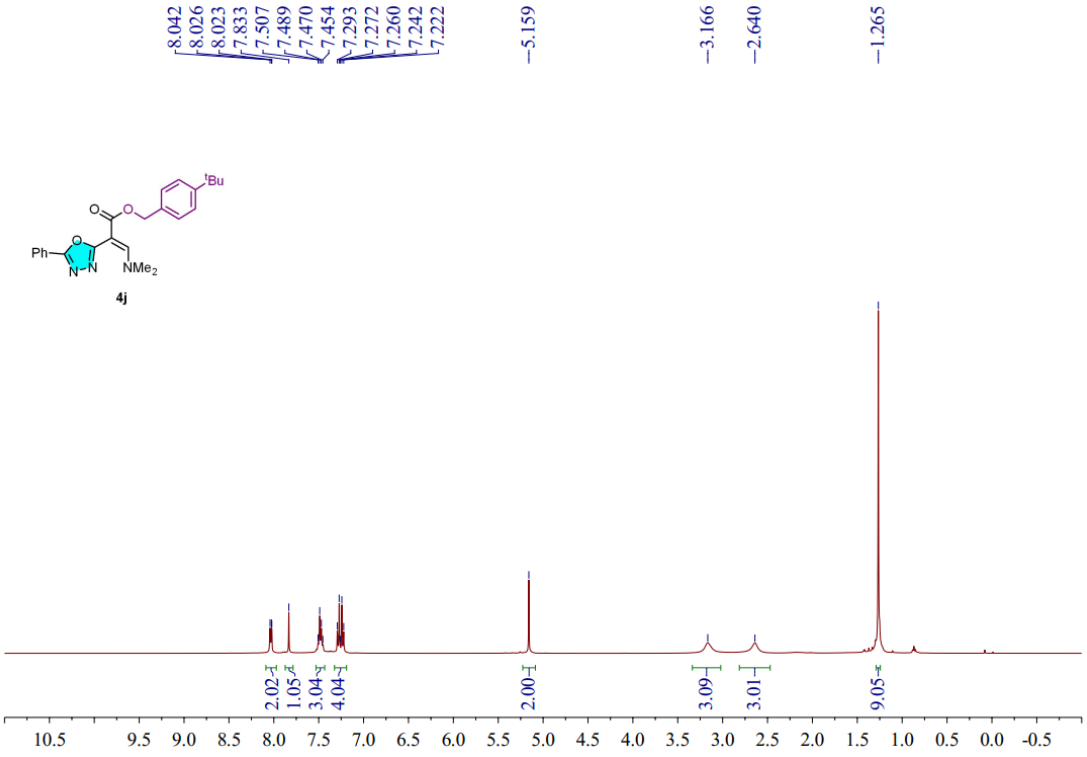
^{13}C{^{1}H} NMR Spectrum of Compound **4h** (100 MHz, $CDCl_3$)



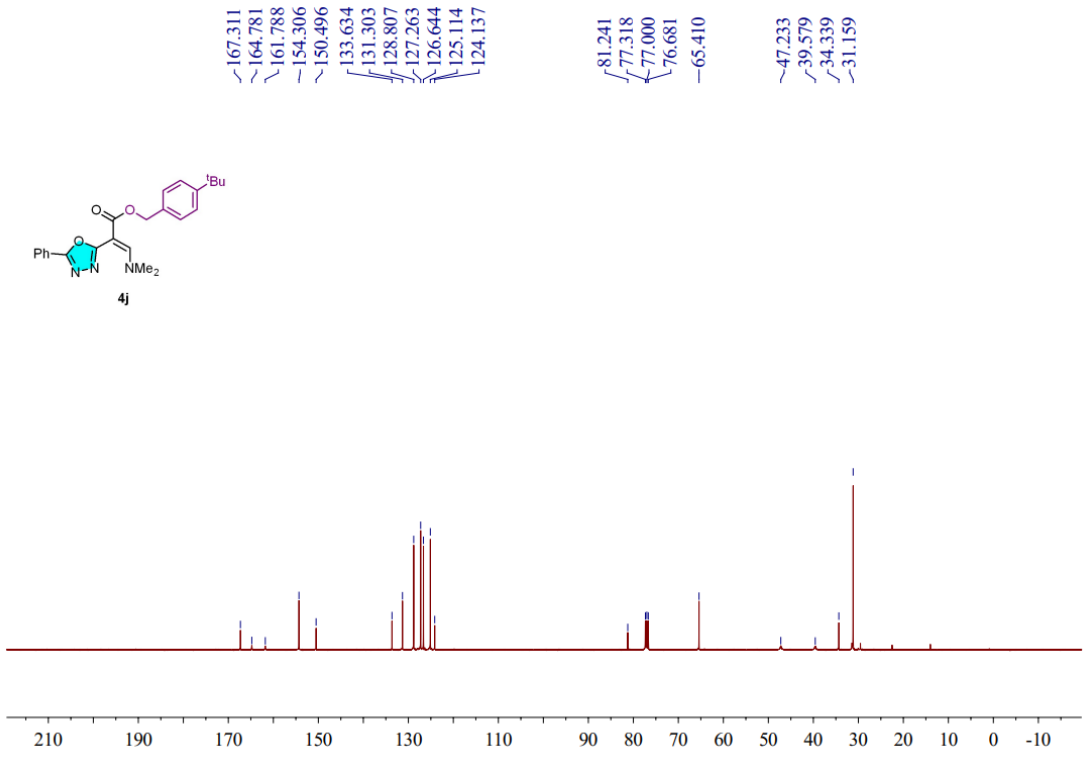
^{1}H NMR Spectrum of Compound **4i** (400 MHz, $CDCl_3$)



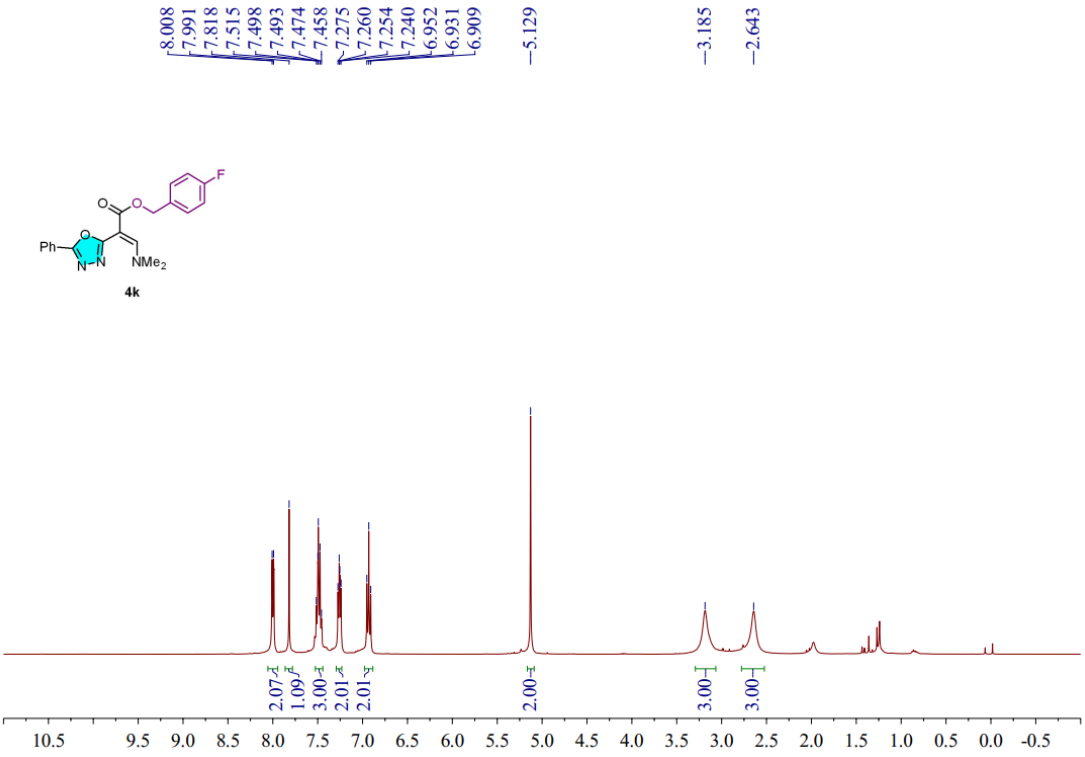
^{13}C{^{1}H} NMR Spectrum of Compound **4i** (100 MHz, $CDCl_3$)



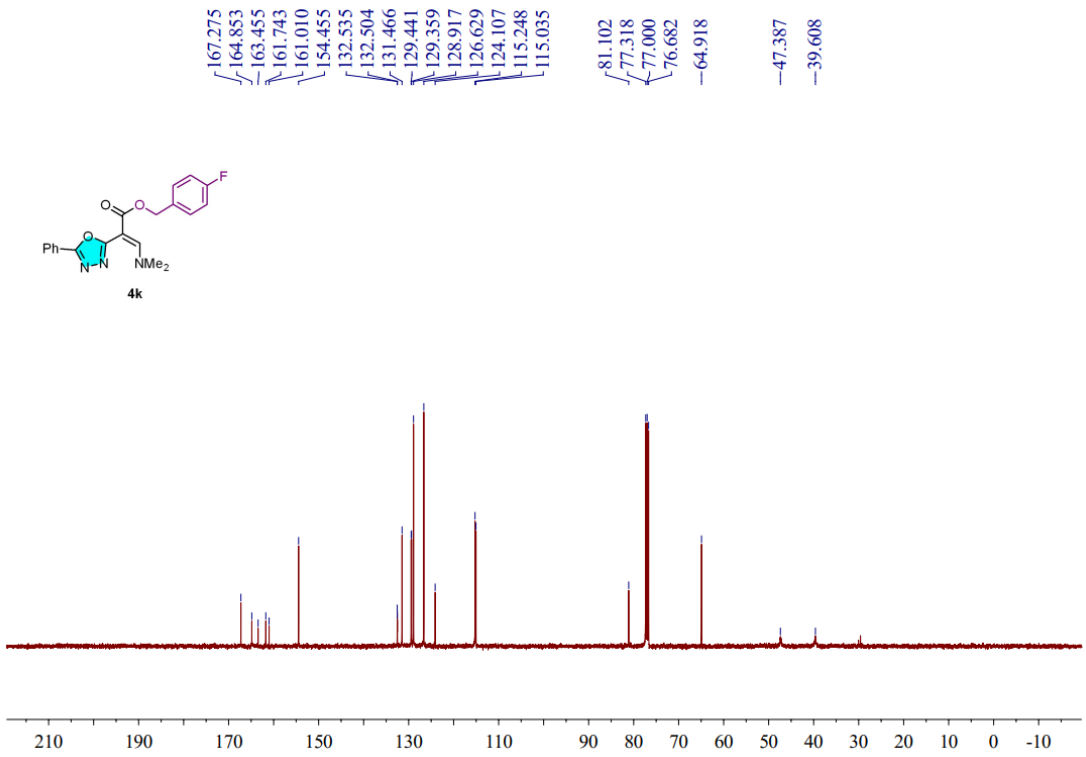
^{1}H NMR Spectrum of Compound **4j** (400 MHz, $CDCl_3$)



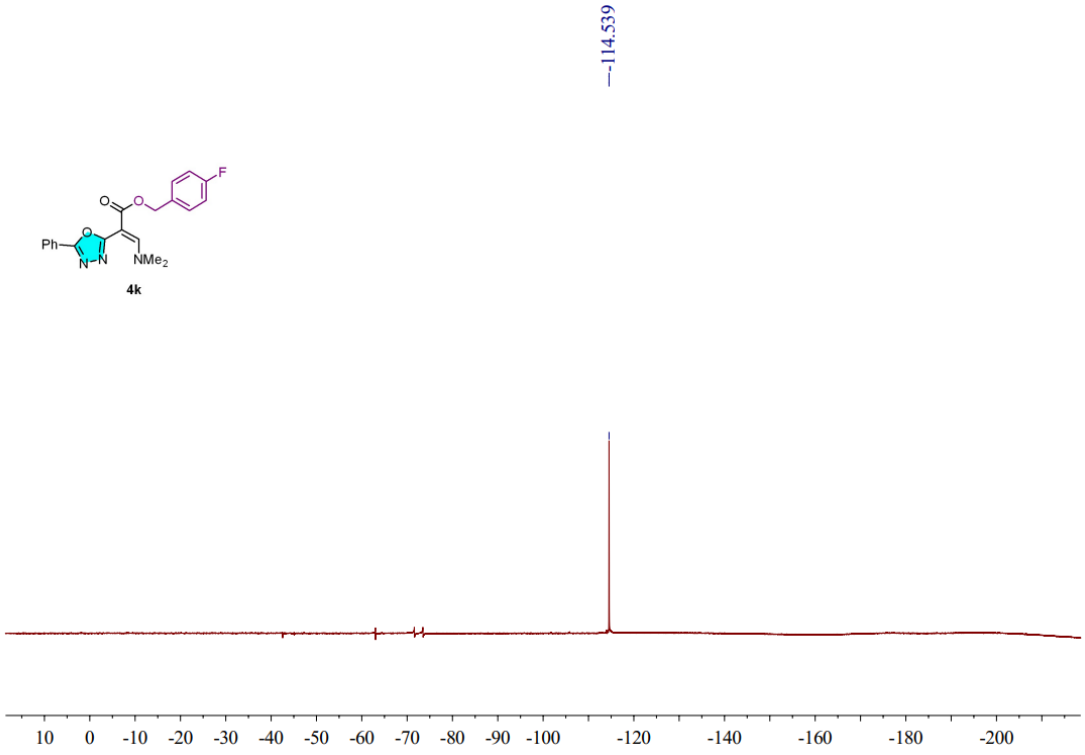
^{13}C{^{1}H} NMR Spectrum of Compound **4j** (100 MHz, $CDCl_3$)



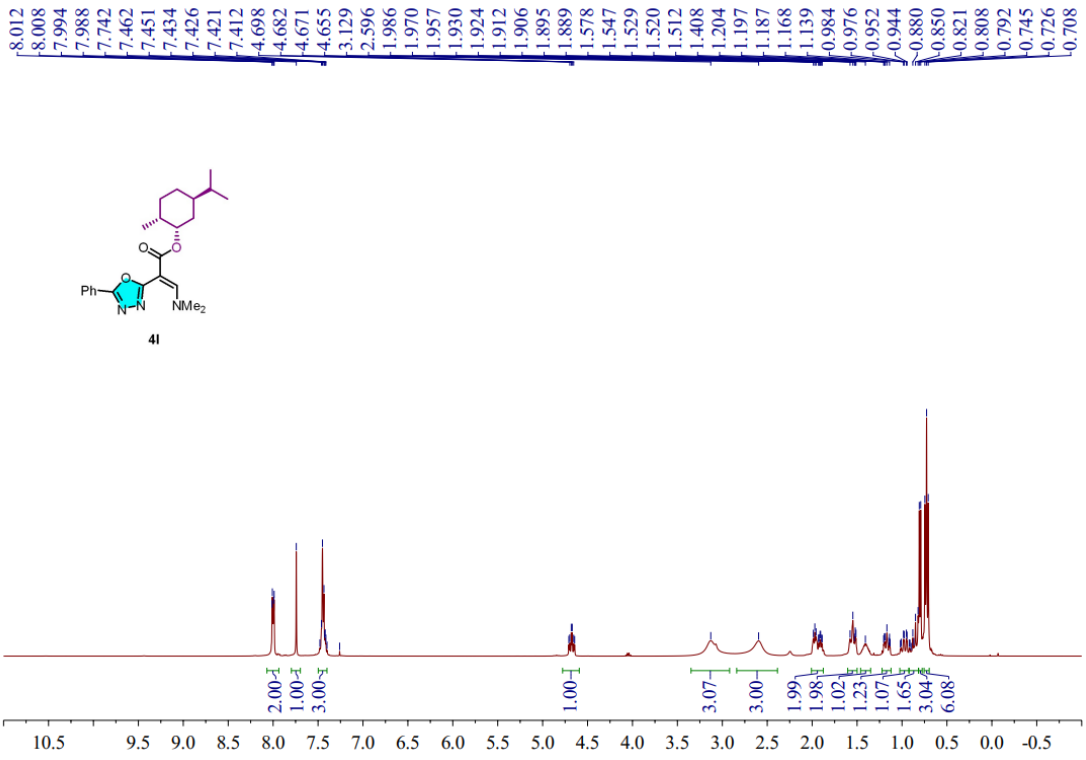
^{1}H NMR Spectrum of Compound **4k** (400 MHz, $CDCl_3$)



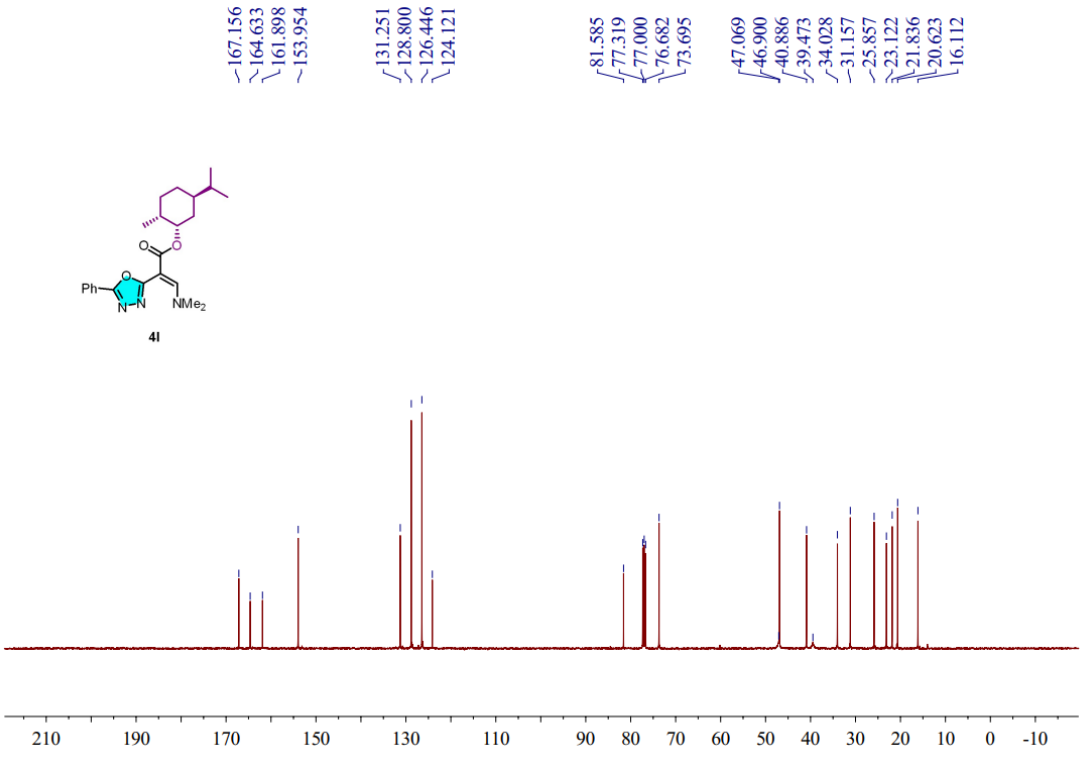
^{13}C{^{1}H} NMR Spectrum of Compound **4k** (100 MHz, $CDCl_3$)



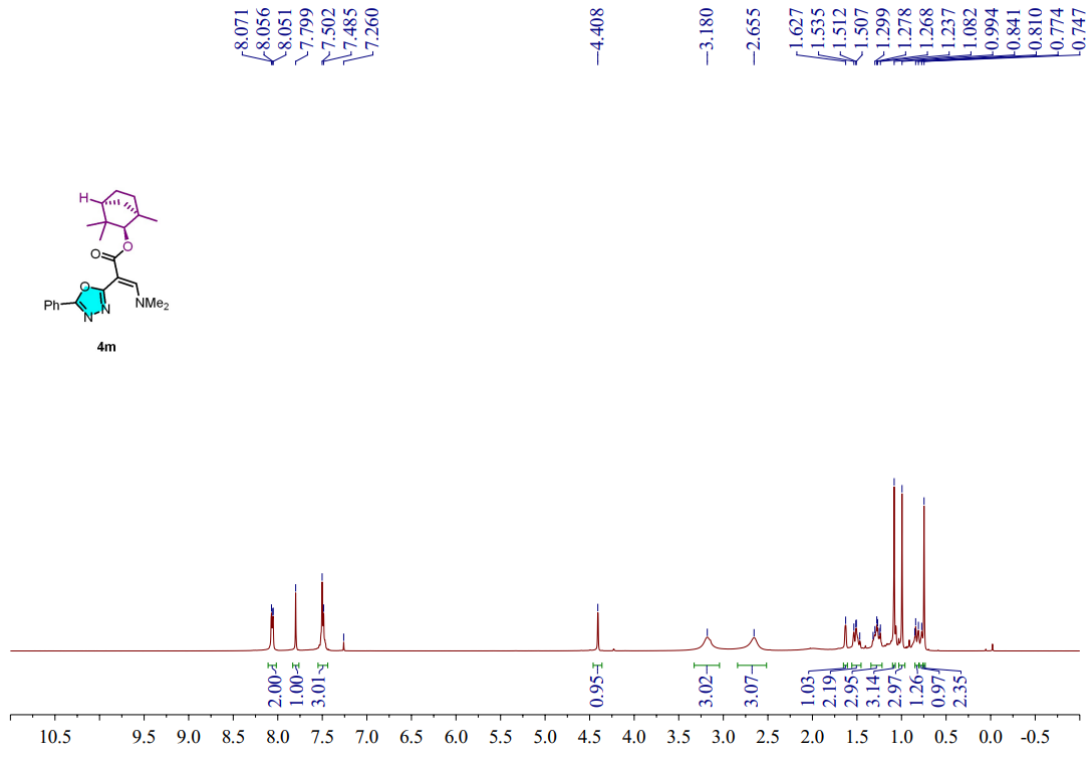
$^{19}F\{^{1}H\}$ NMR Spectrum of Compound **4k** (376 MHz, $CDCl_3$)



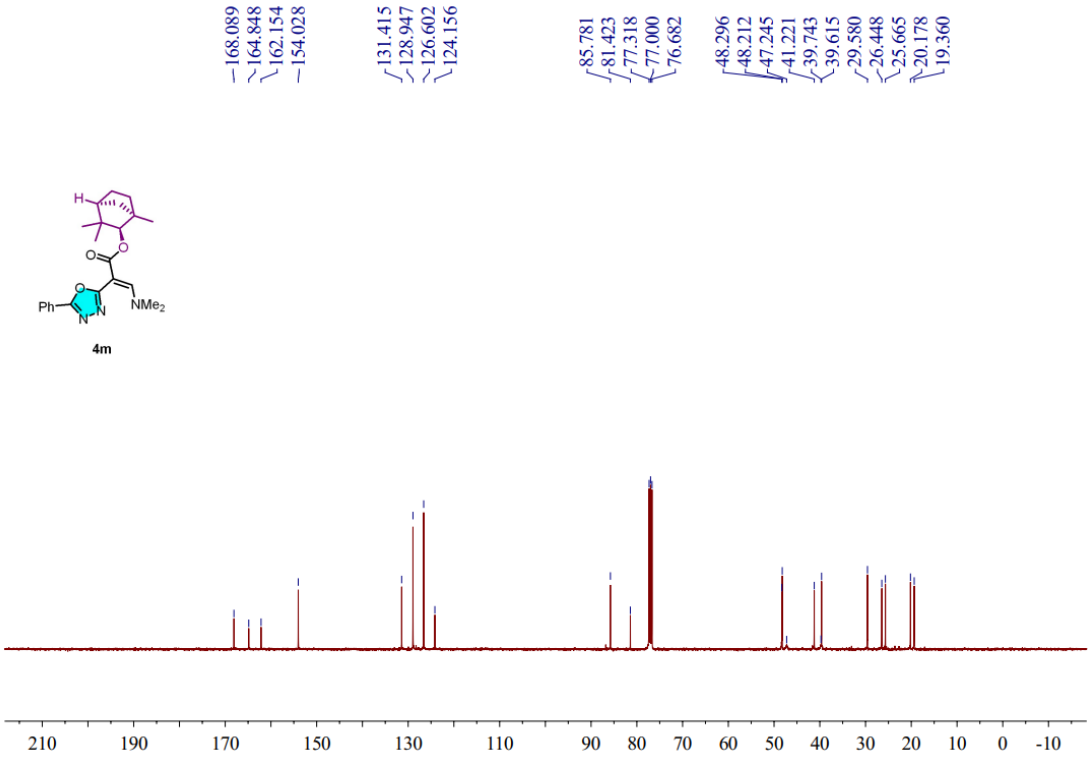
^{1}H NMR Spectrum of Compound **4l** (400 MHz, $CDCl_3$)



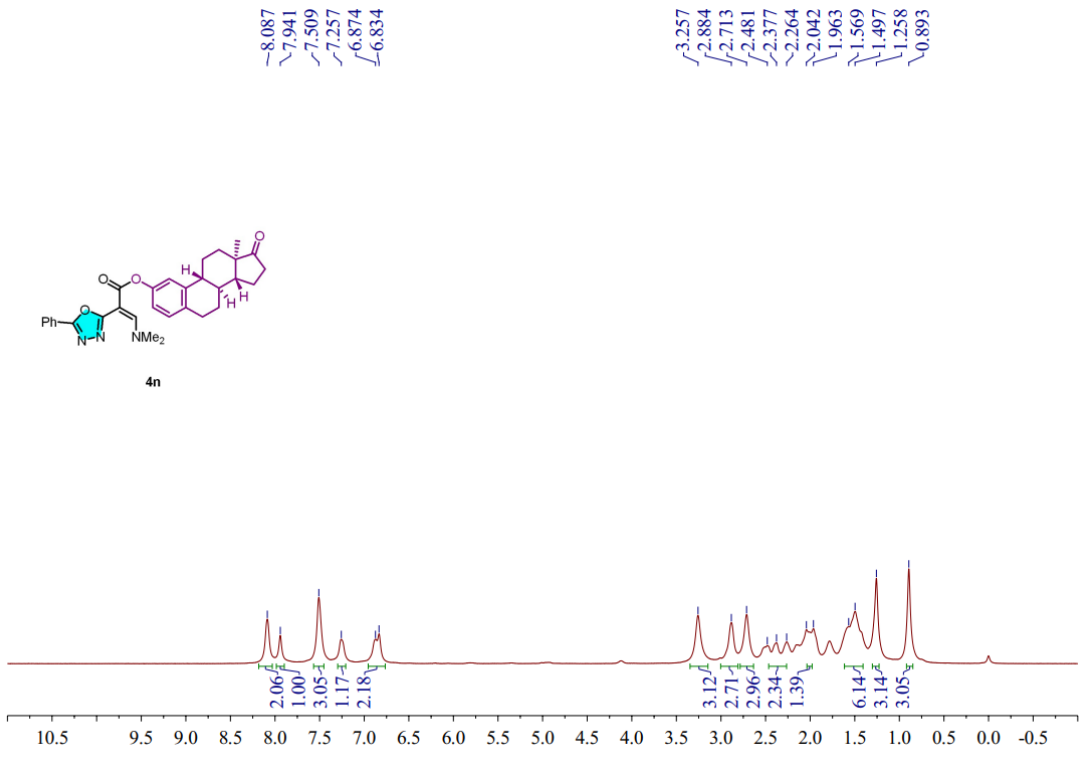
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **4l** (100 MHz, $CDCl_3$)



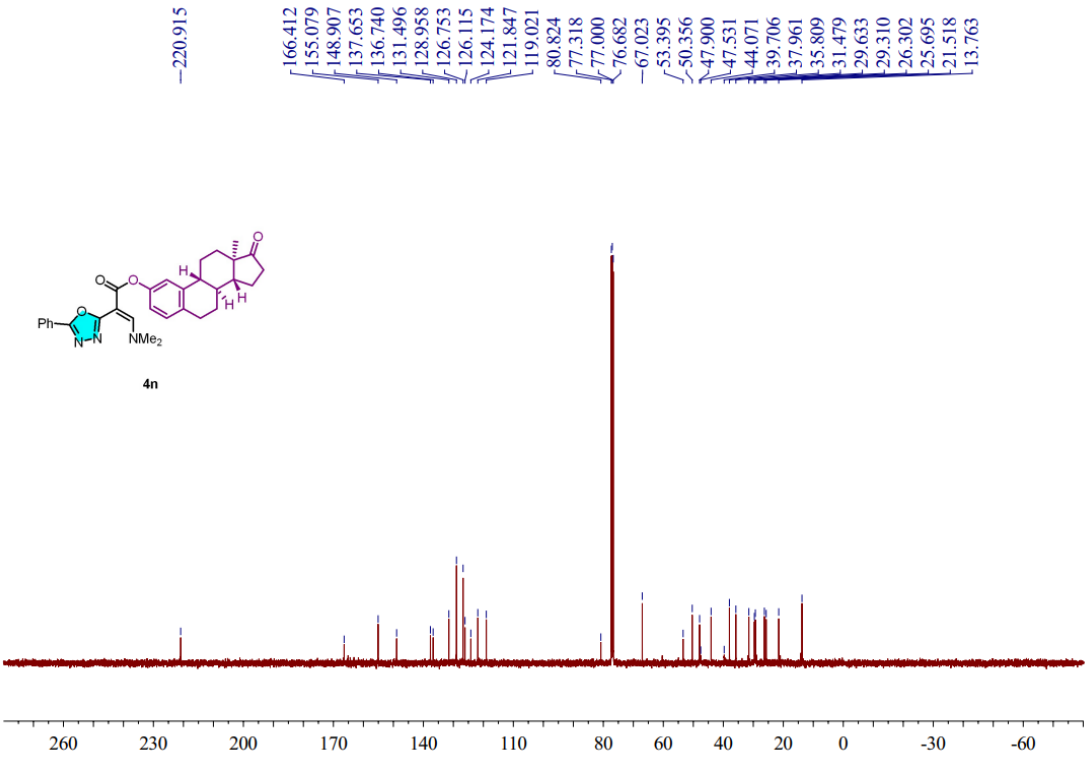
^{1}H NMR Spectrum of Compound **4m** (400 MHz, $CDCl_3$)



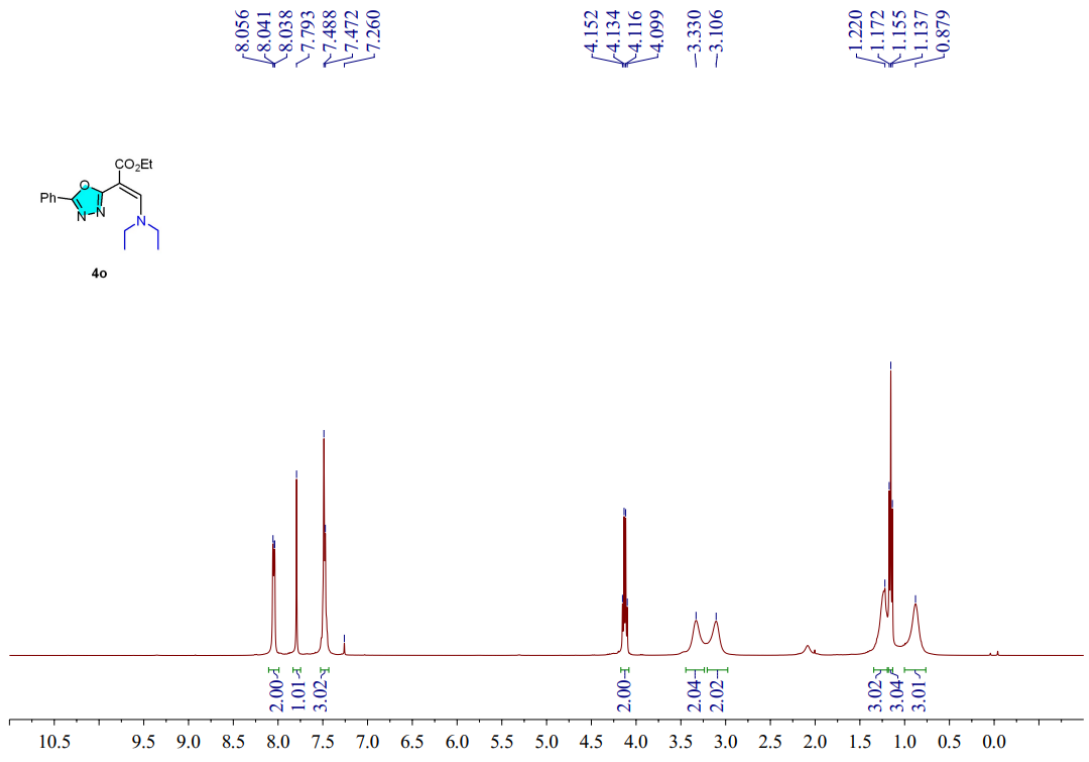
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **4m** (100 MHz, $CDCl_3$)



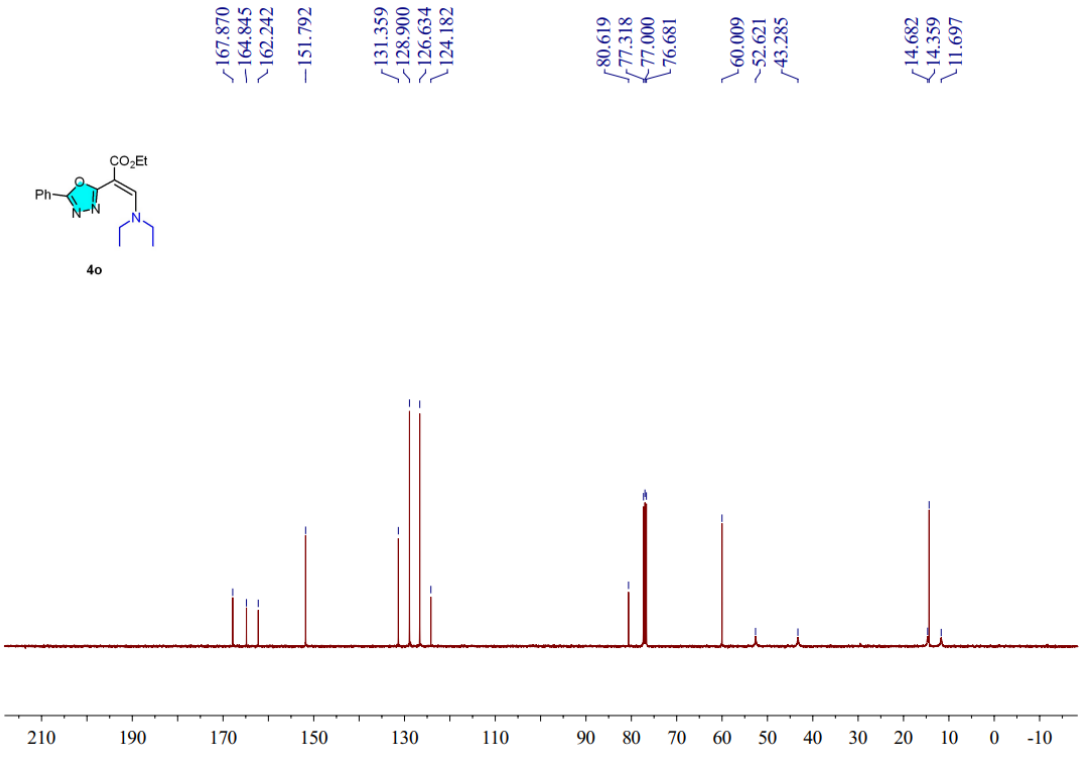
^{1}H NMR Spectrum of Compound **4n** (400 MHz, $CDCl_3$)



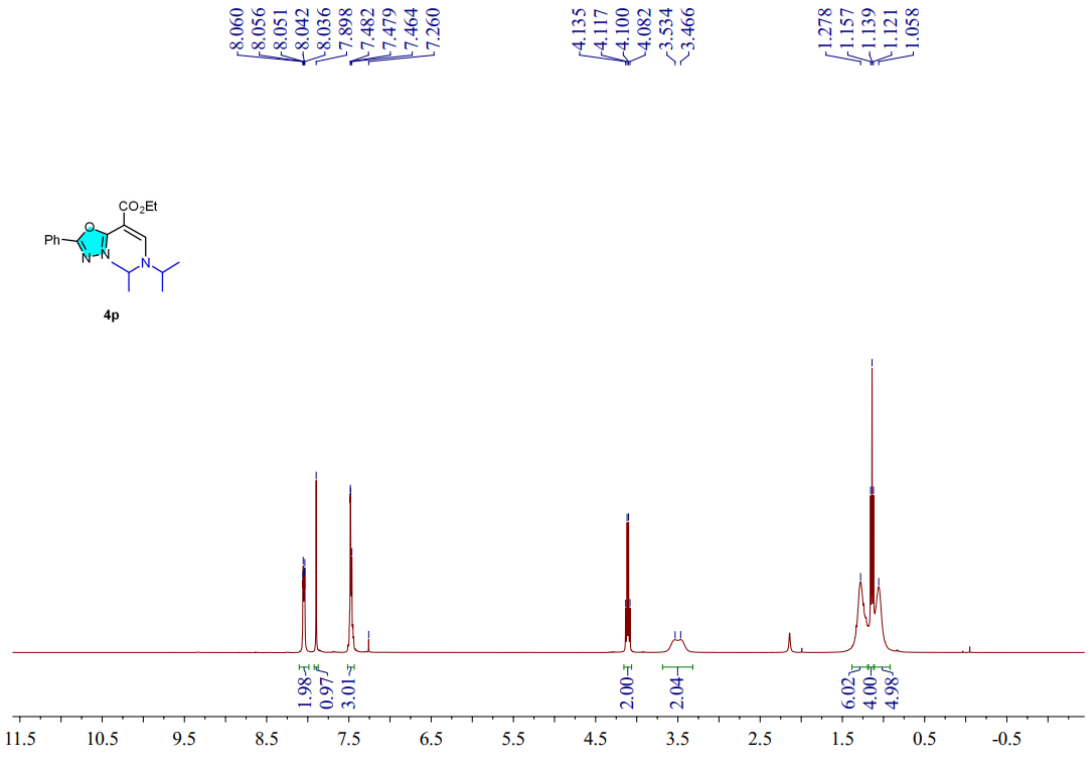
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **4n** (100 MHz, $CDCl_3$)



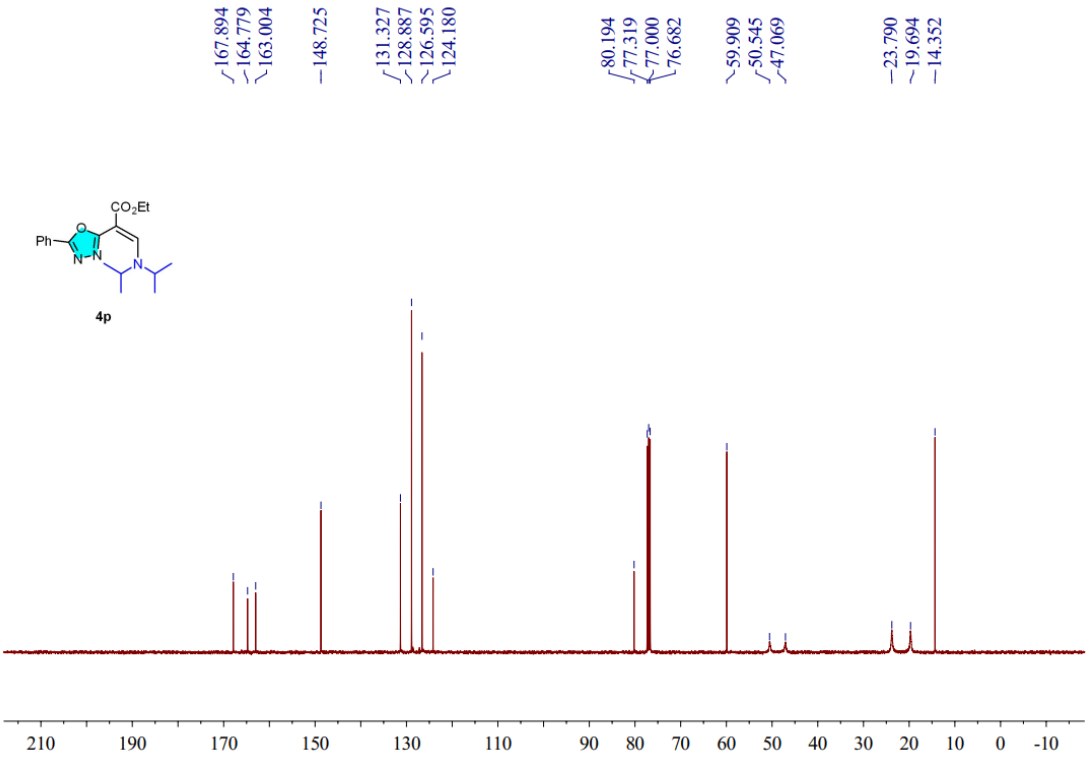
^{1}H NMR Spectrum of Compound **4o** (400 MHz, $CDCl_3$)



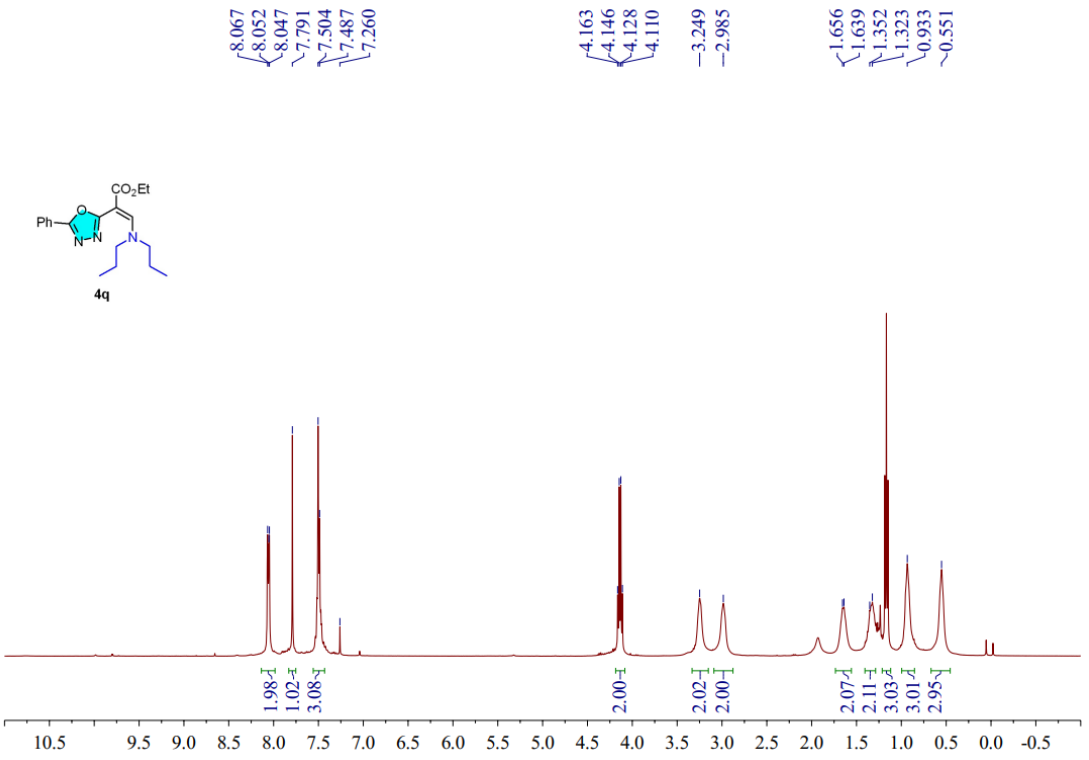
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **4o** (100 MHz, $CDCl_3$)



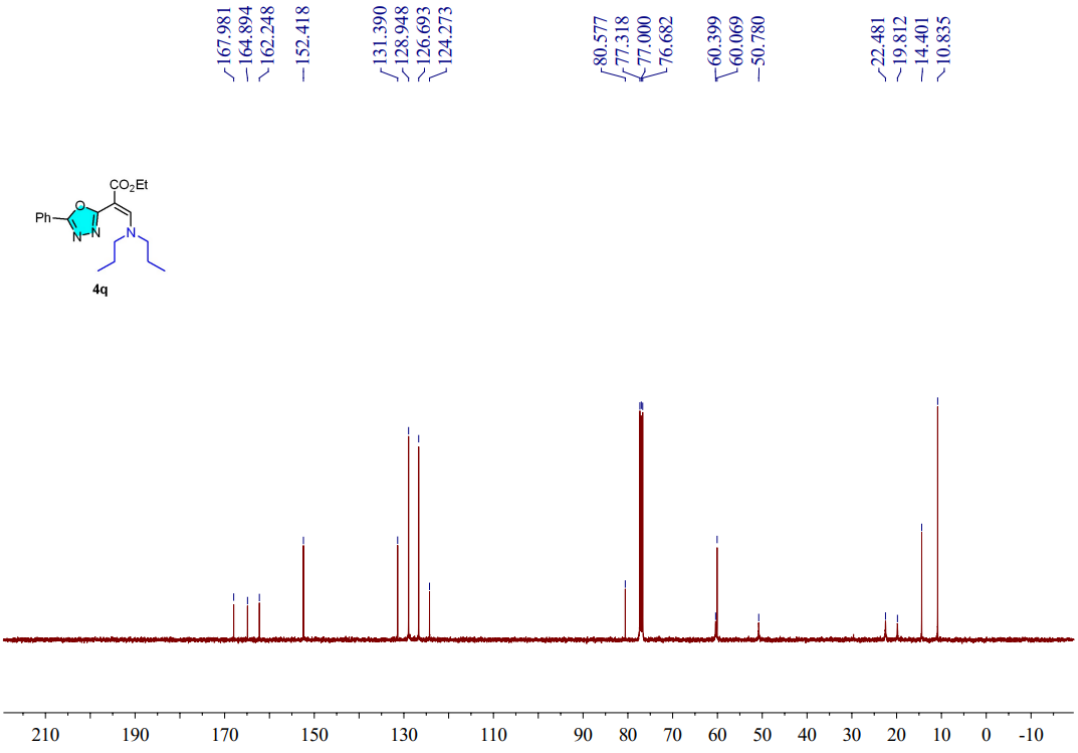
^{1}H NMR Spectrum of Compound **4p** (400 MHz, $CDCl_3$)



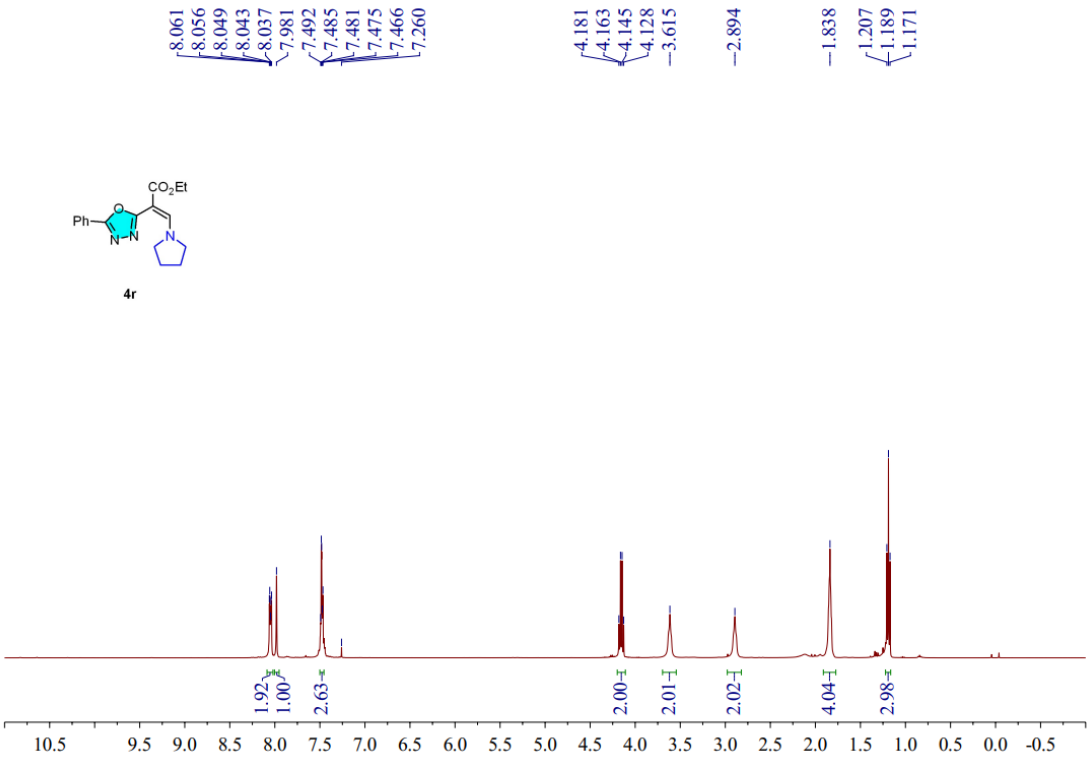
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **4p** (100 MHz, $CDCl_3$)



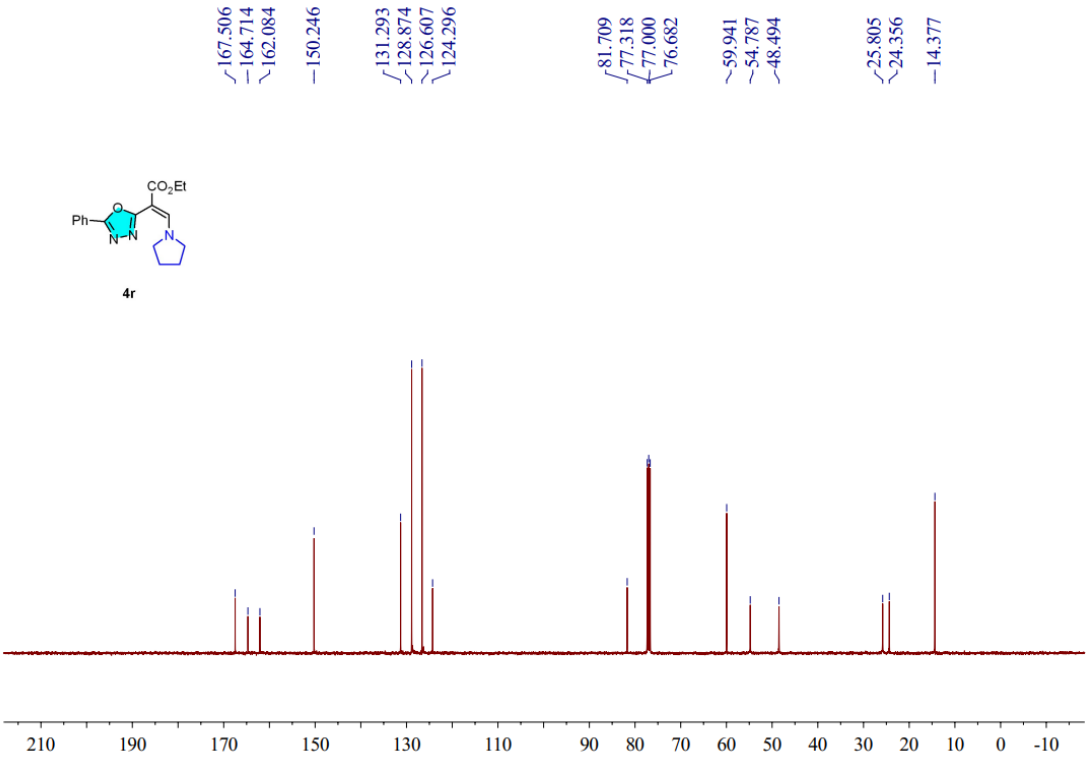
^{1}H NMR Spectrum of Compound **4q** (400 MHz, $CDCl_3$)



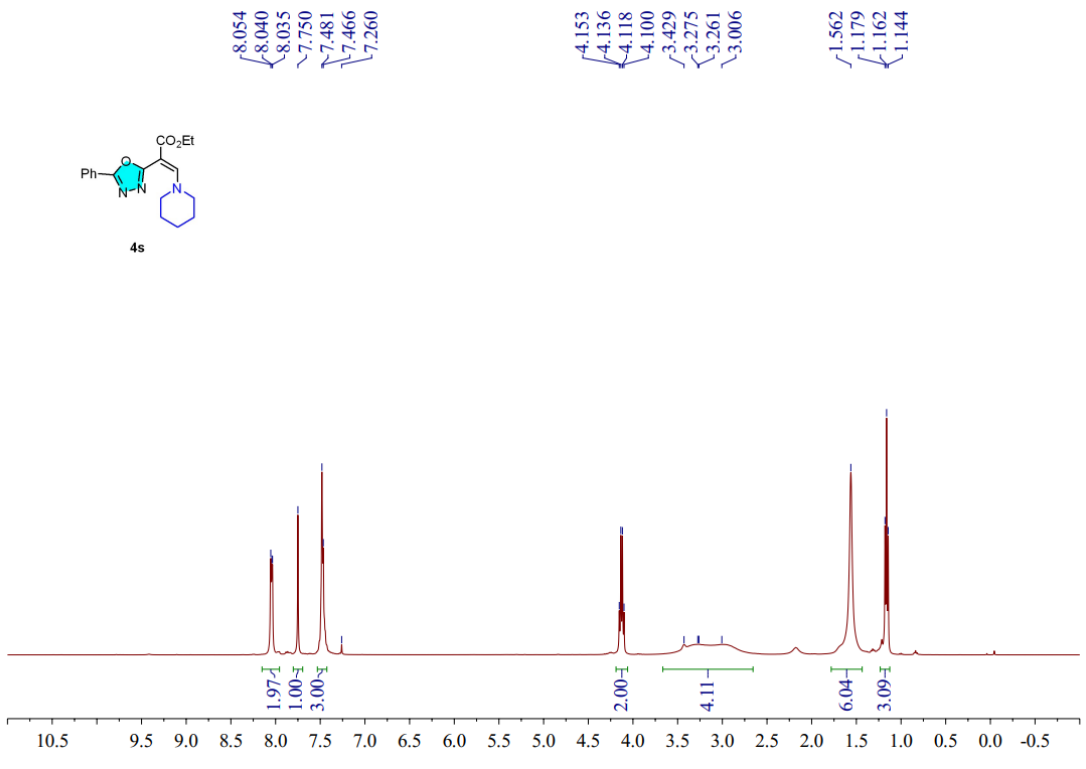
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **4q** (100 MHz, $CDCl_3$)



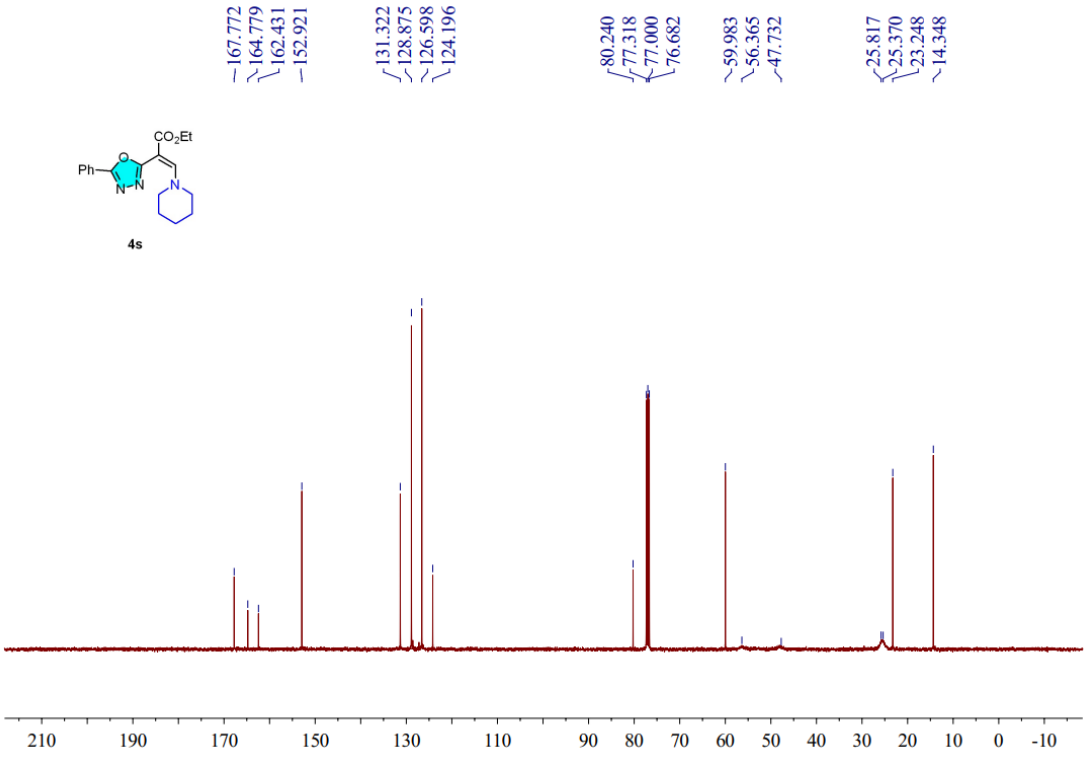
^{1}H NMR Spectrum of Compound **4r** (400 MHz, $CDCl_3$)



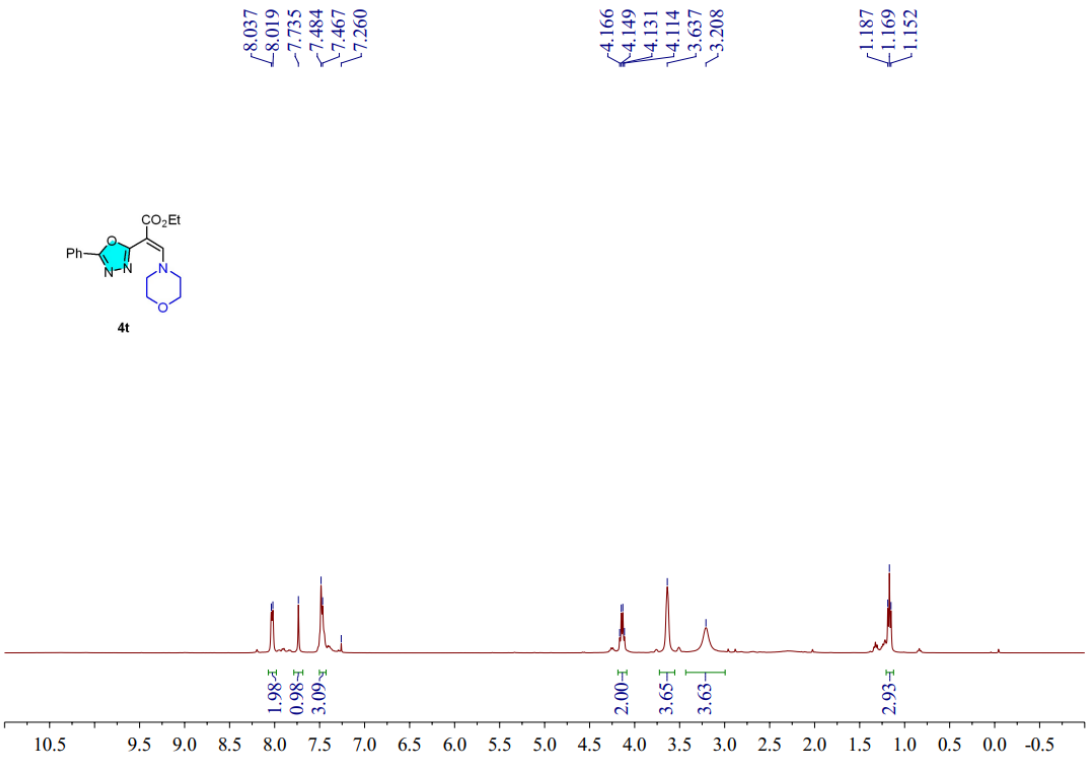
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **4r** (100 MHz, $CDCl_3$)



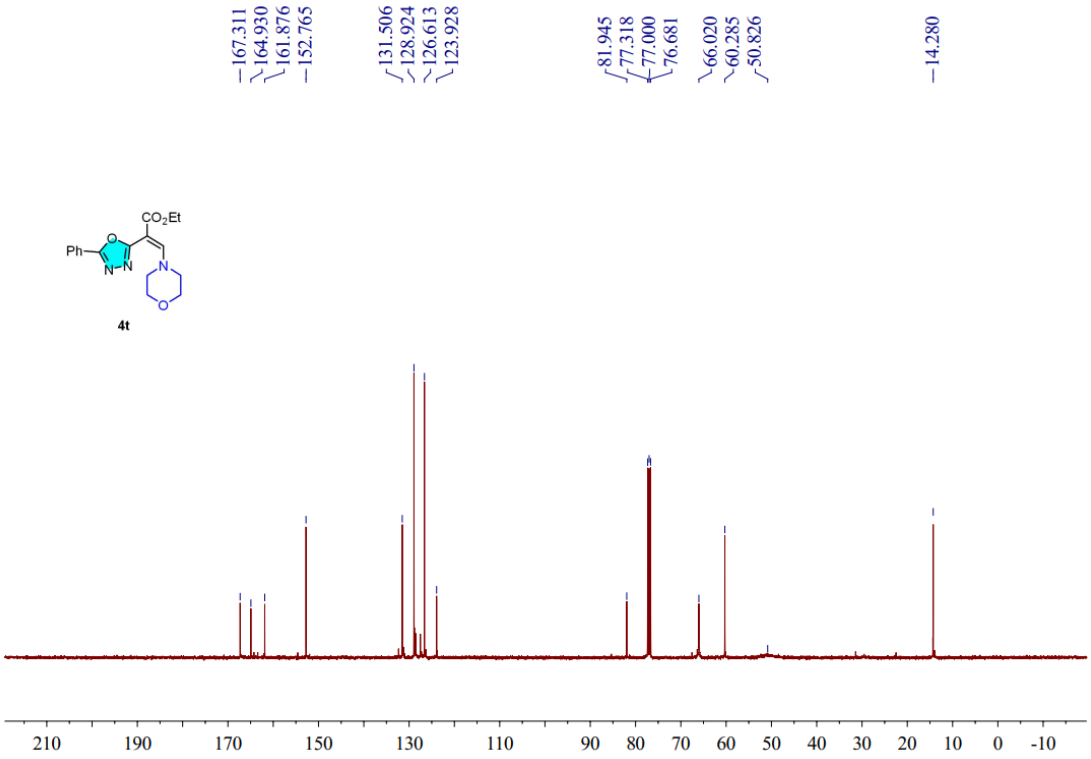
^{1}H NMR Spectrum of Compound **4s** (400 MHz, $CDCl_3$)



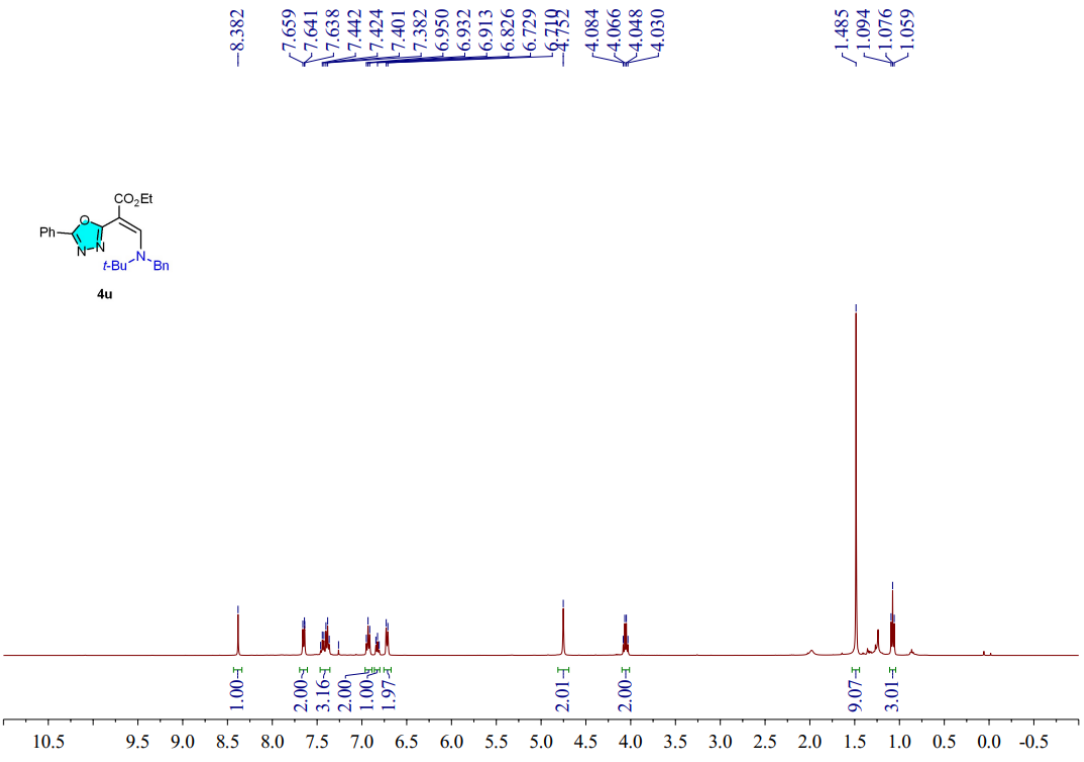
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **4s** (100 MHz, $CDCl_3$)



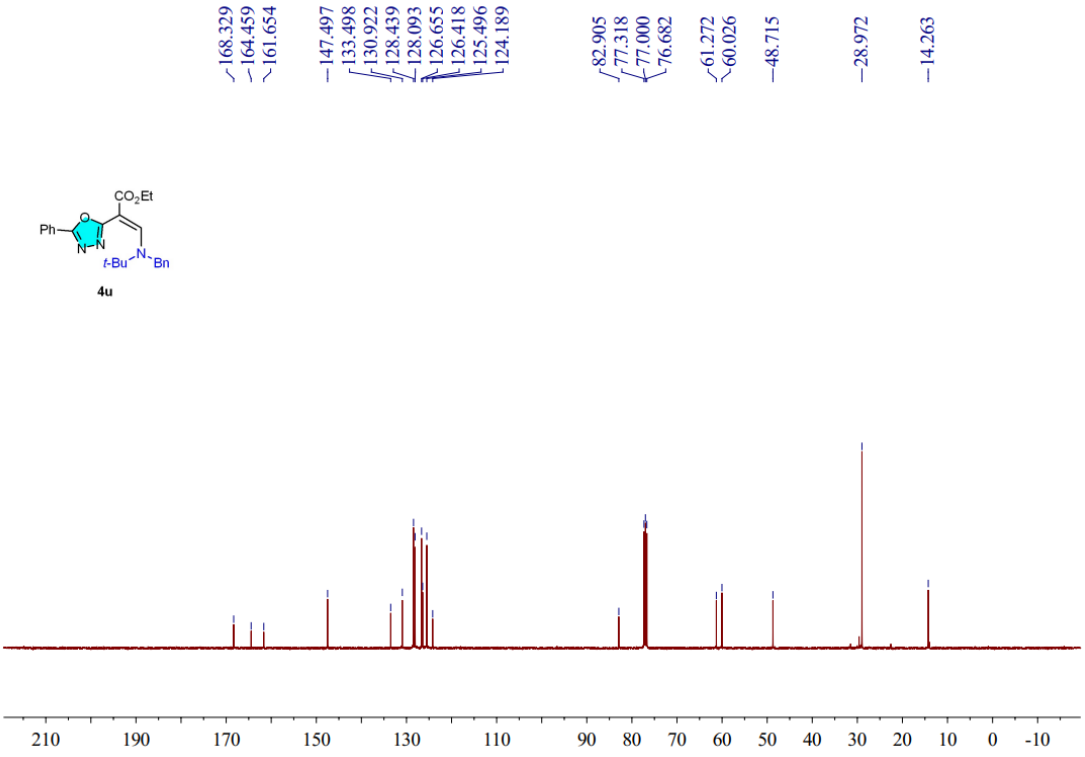
^{1}H NMR Spectrum of Compound **4t** (400 MHz, $CDCl_3$)



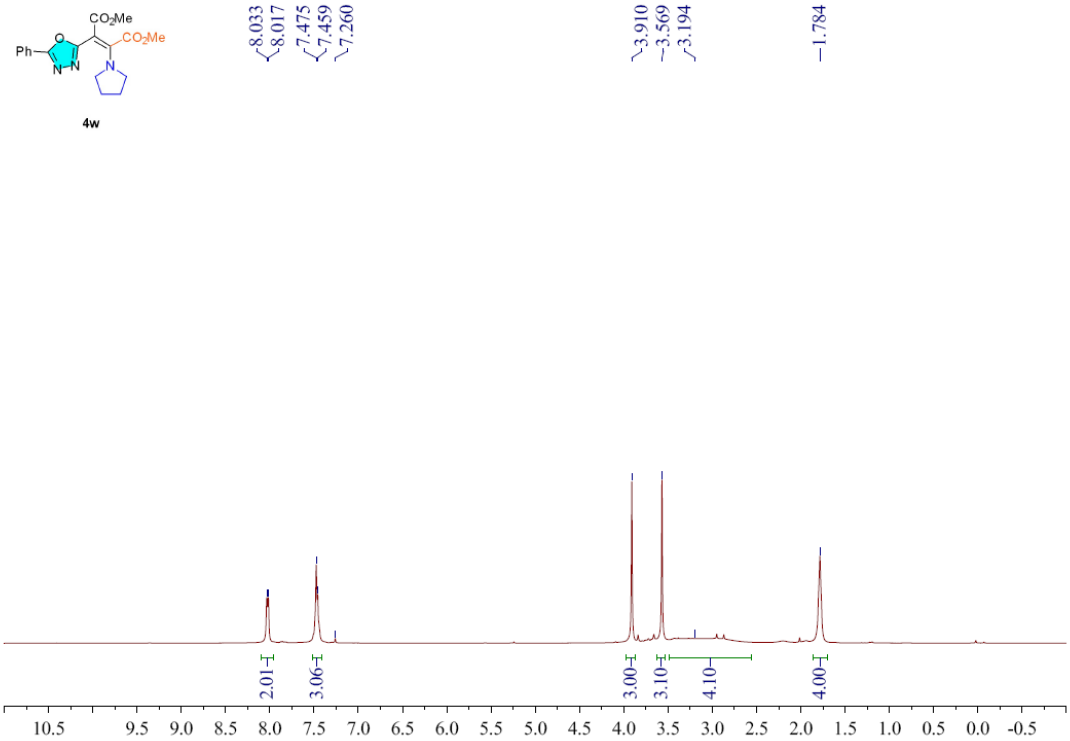
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **4t** (100 MHz, $CDCl_3$)



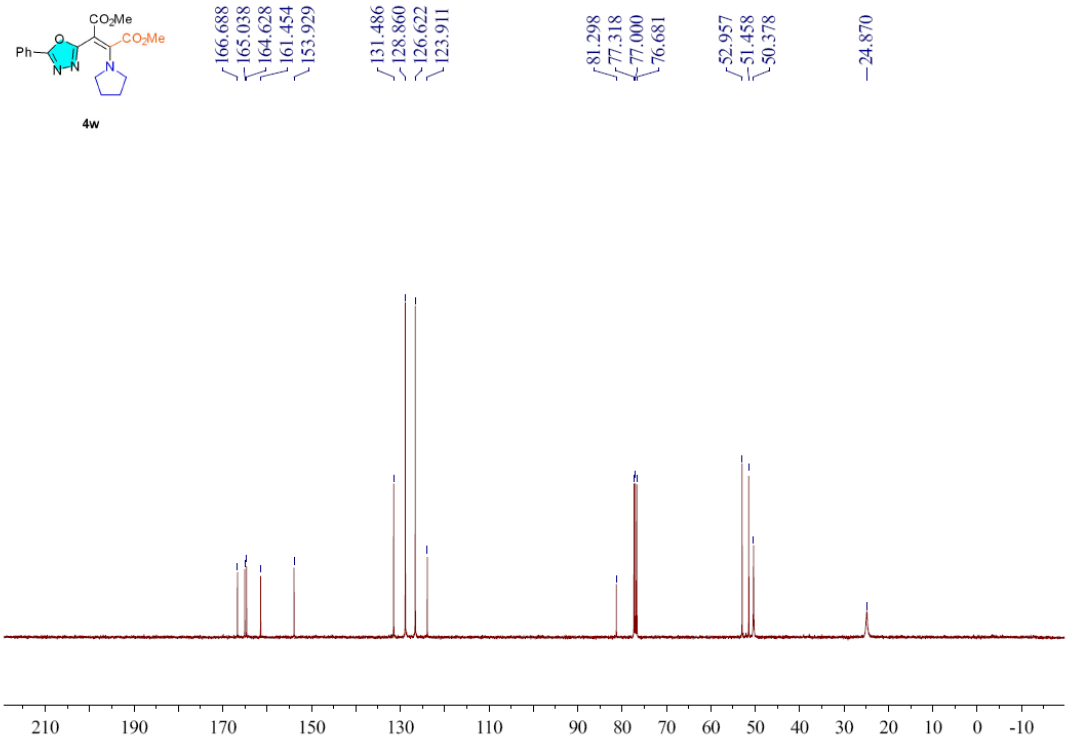
^{1}H NMR Spectrum of Compound **4u** (400 MHz, $CDCl_3$)



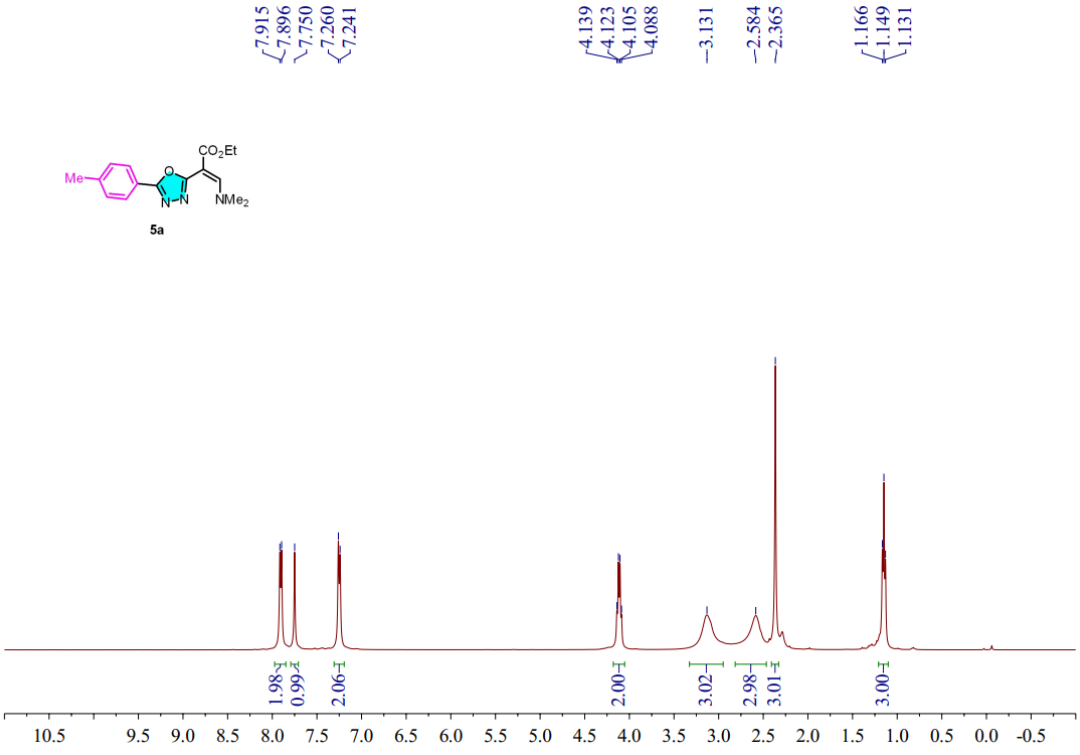
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **4u** (100 MHz, $CDCl_3$)



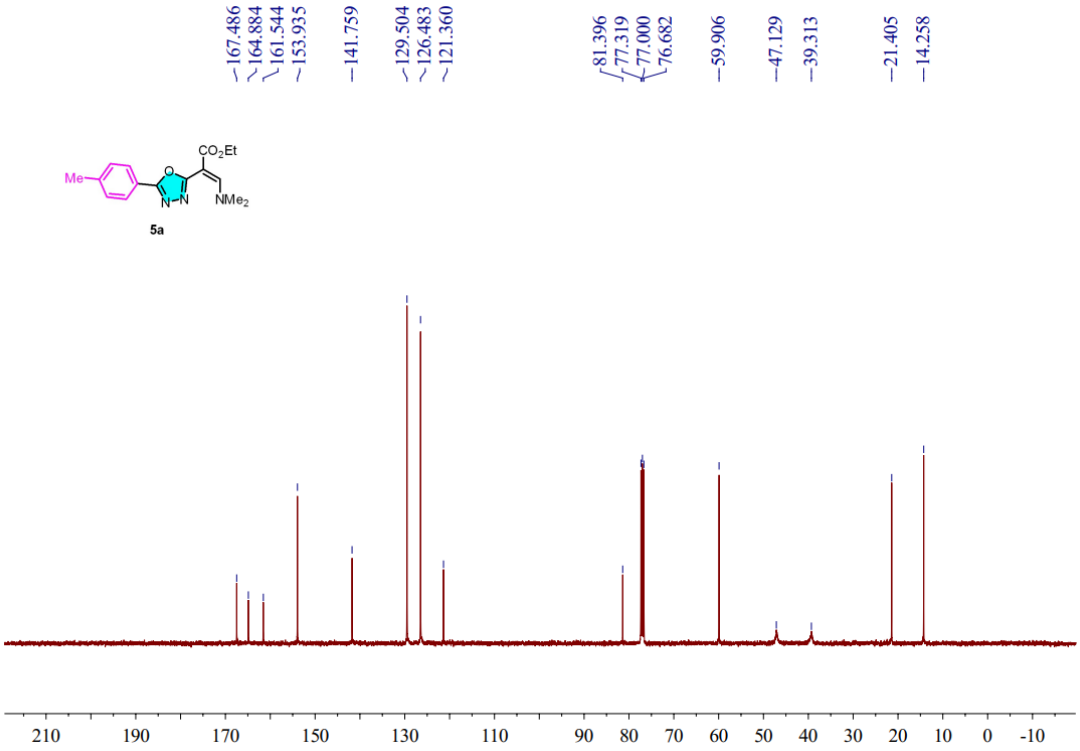
^{1}H NMR Spectrum of Compound **4w** (400 MHz, $CDCl_3$)



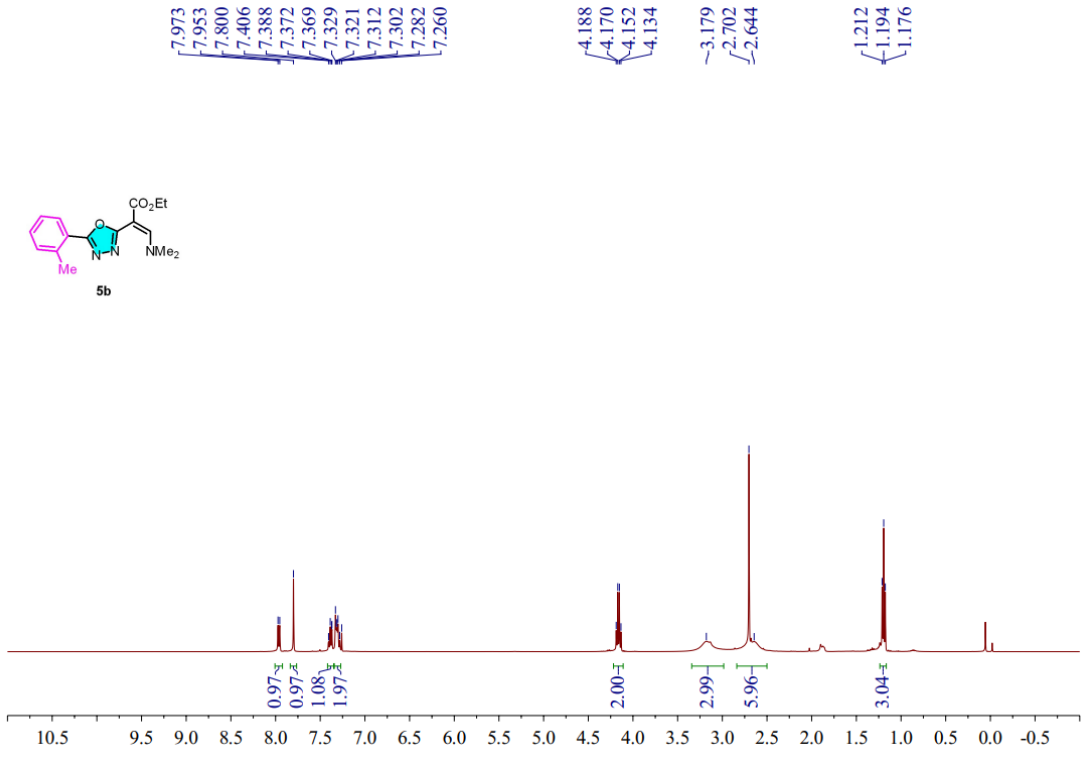
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **4w** (100 MHz, $CDCl_3$)



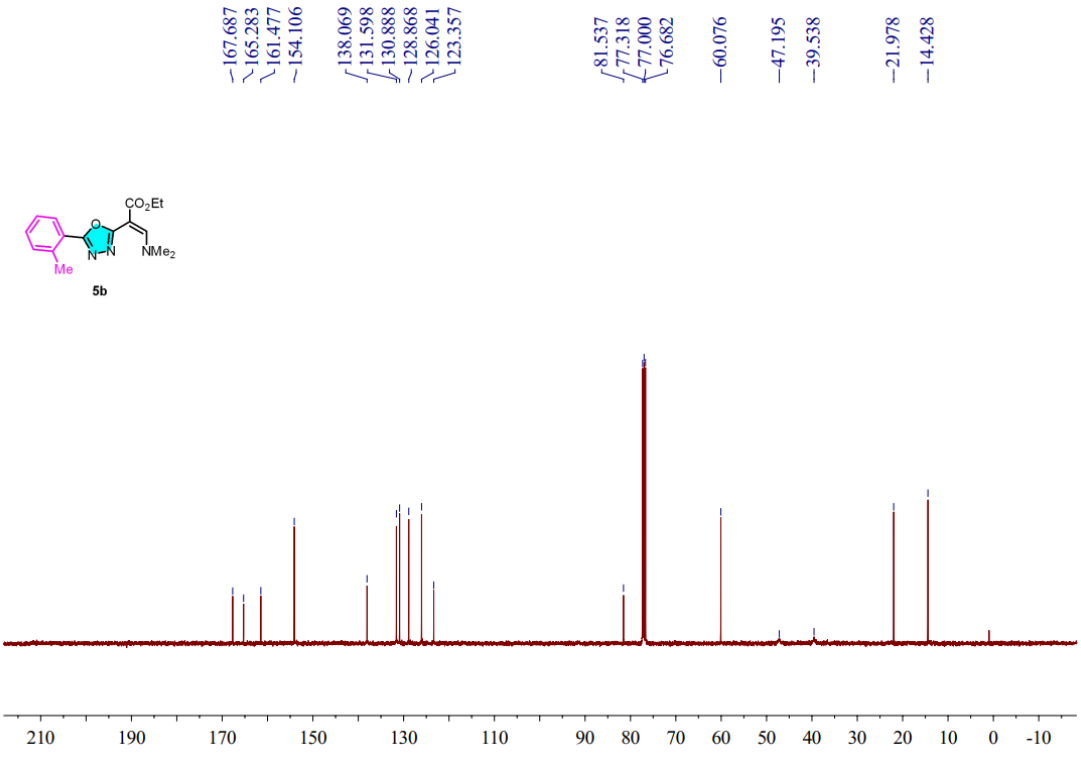
^{1}H NMR Spectrum of Compound **5a** (400 MHz, $CDCl_3$)



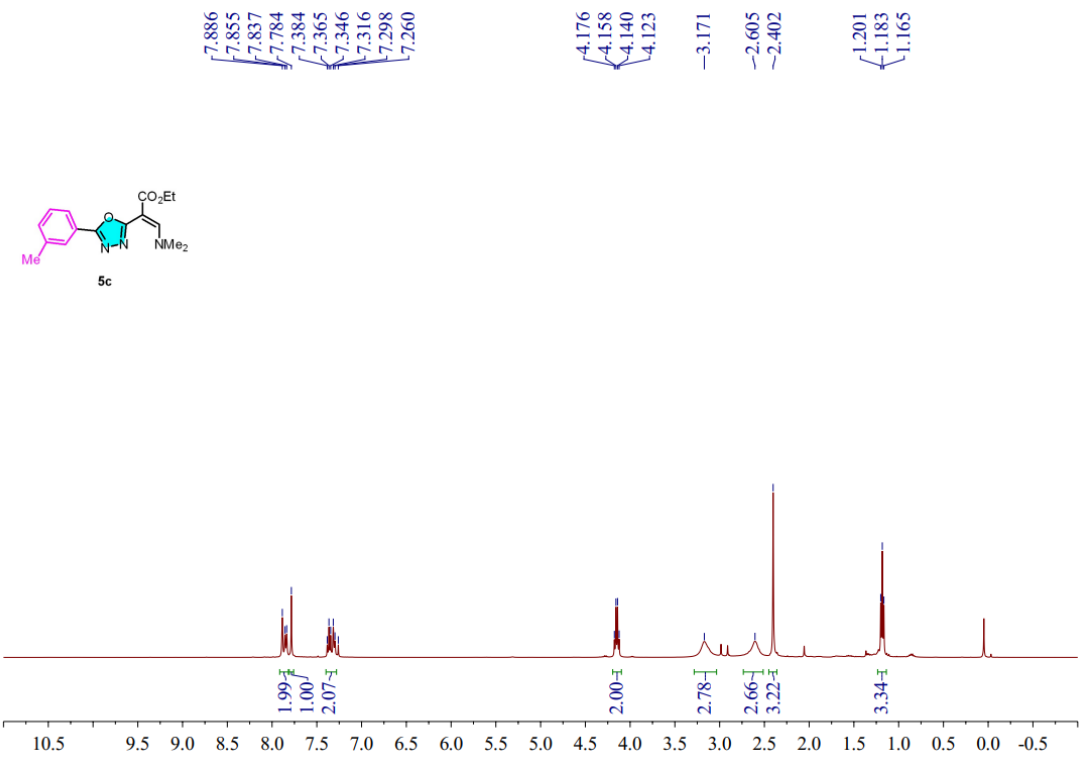
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5a** (100 MHz, $CDCl_3$)



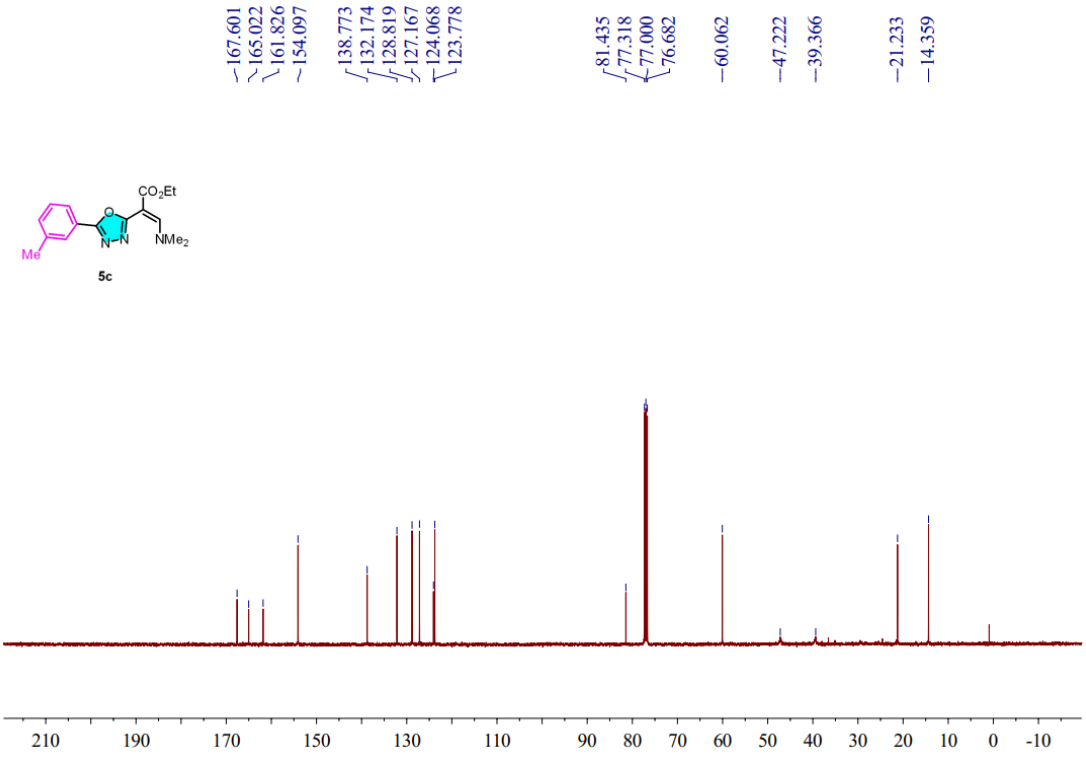
^{1}H NMR Spectrum of Compound **5b** (400 MHz, $CDCl_3$)



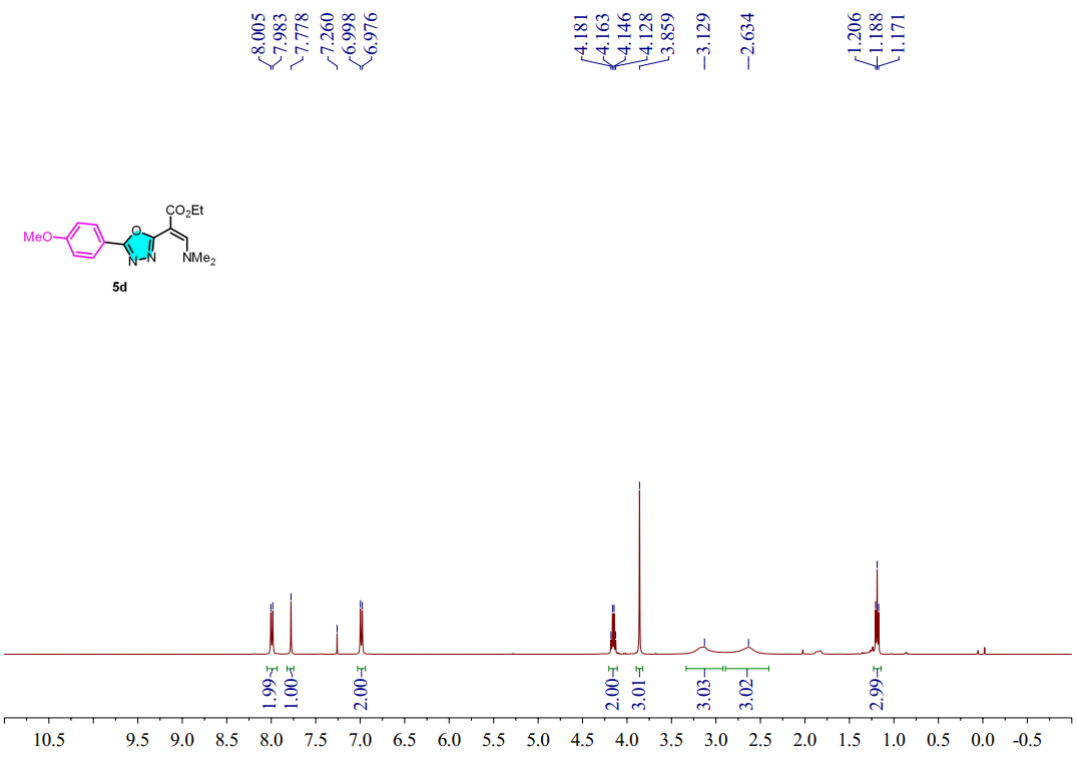
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5b** (100 MHz, $CDCl_3$)



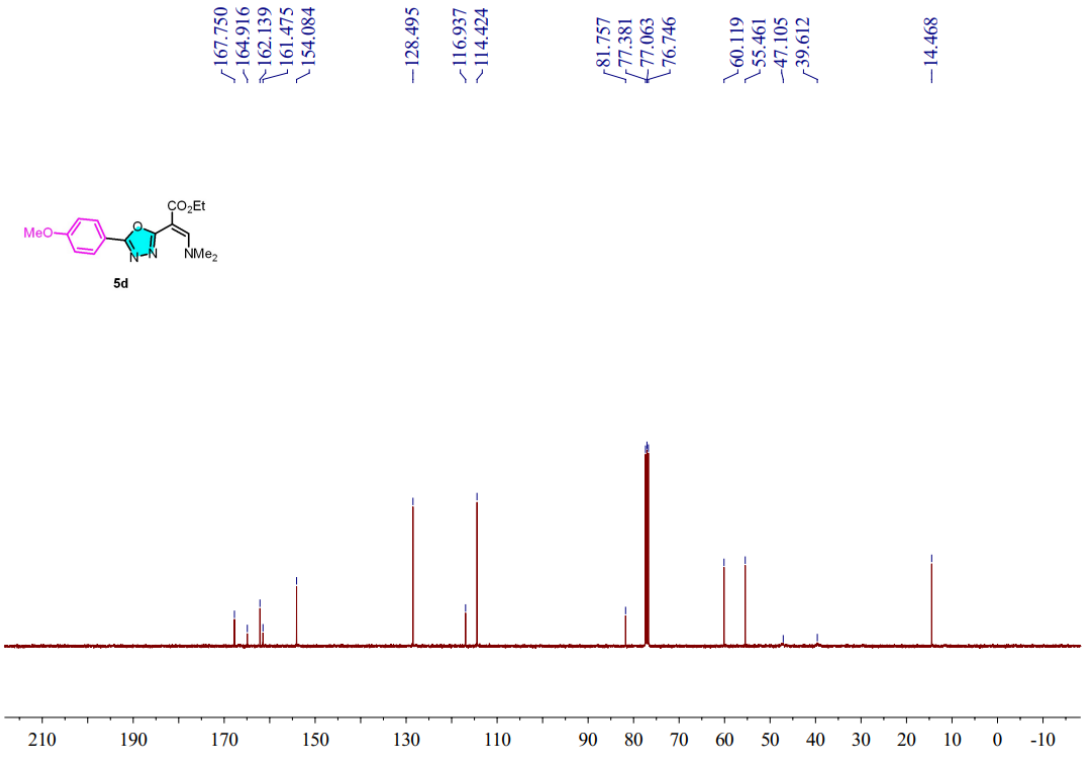
^{1}H NMR Spectrum of Compound **5c** (400 MHz, $CDCl_3$)



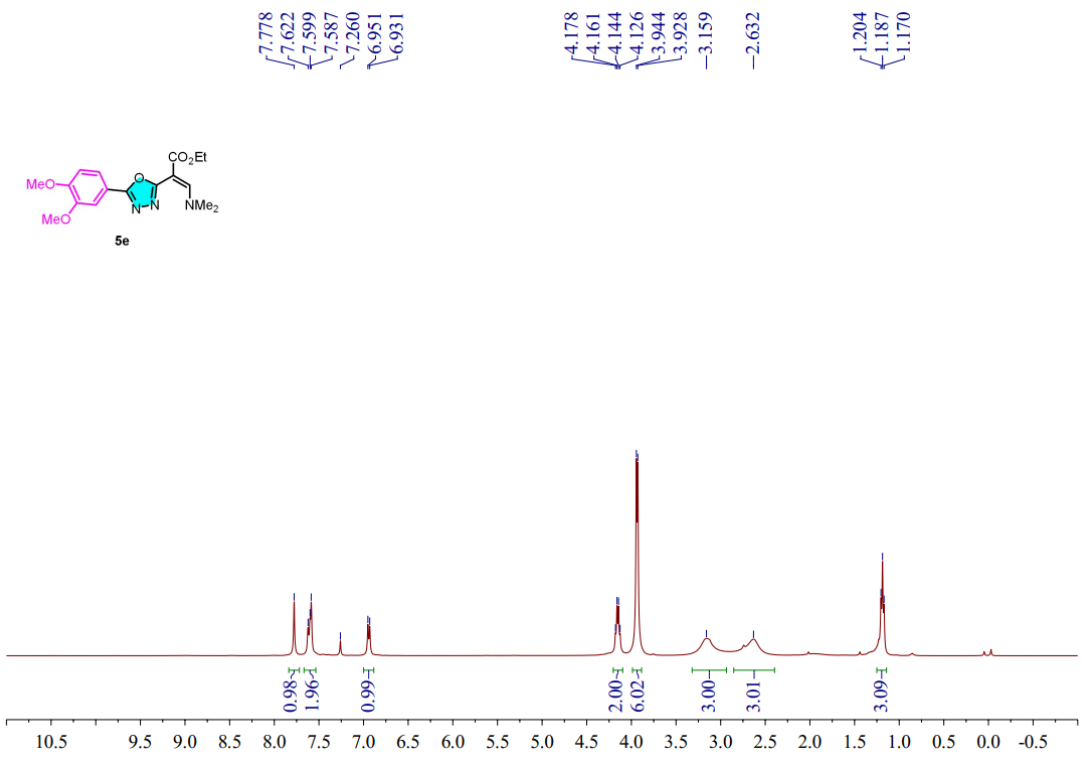
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5c** (100 MHz, $CDCl_3$)



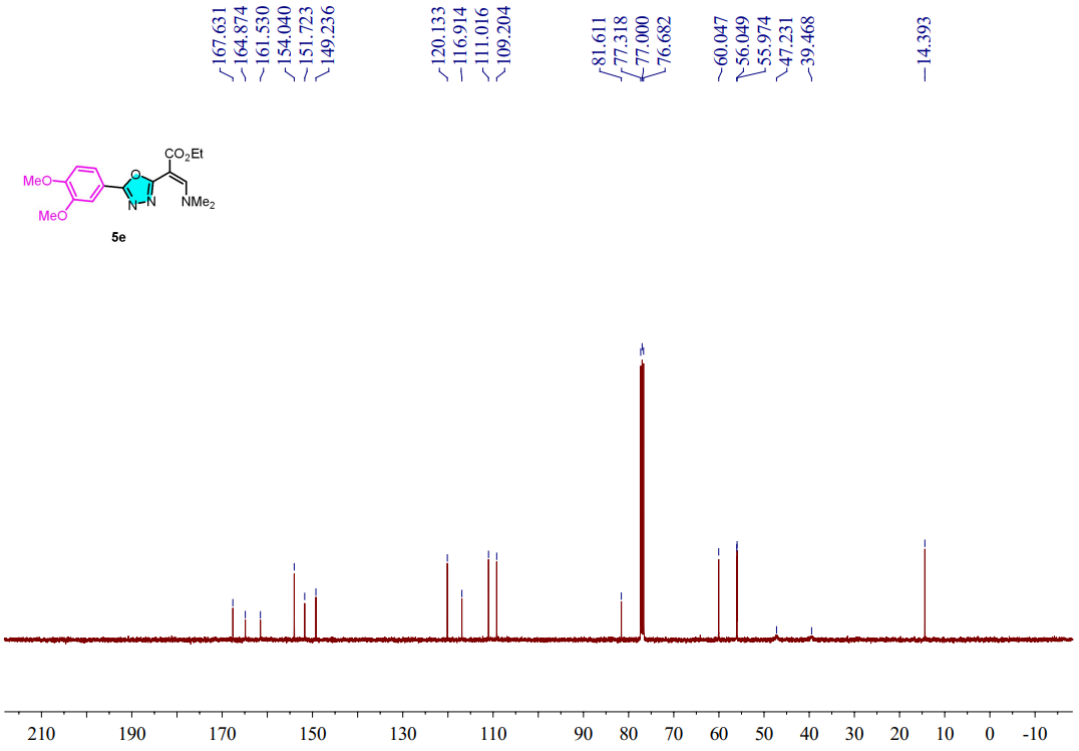
^{1}H NMR Spectrum of Compound **5d** (400 MHz, $CDCl_3$)



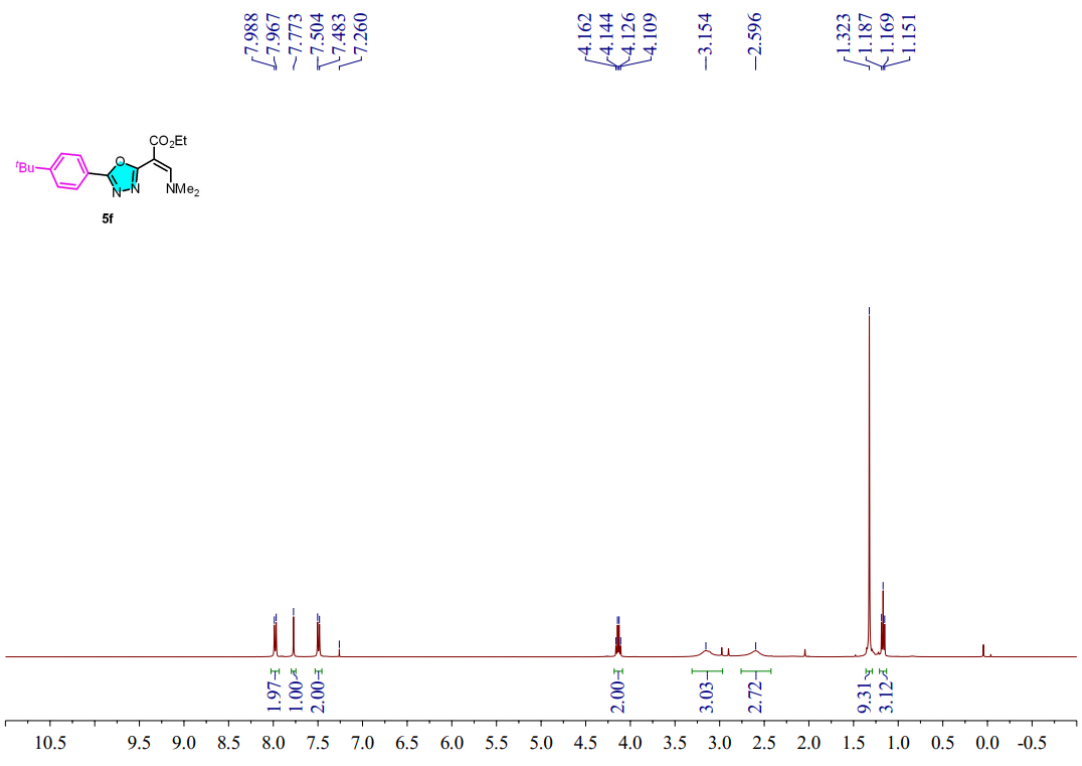
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5d** (100 MHz, $CDCl_3$)



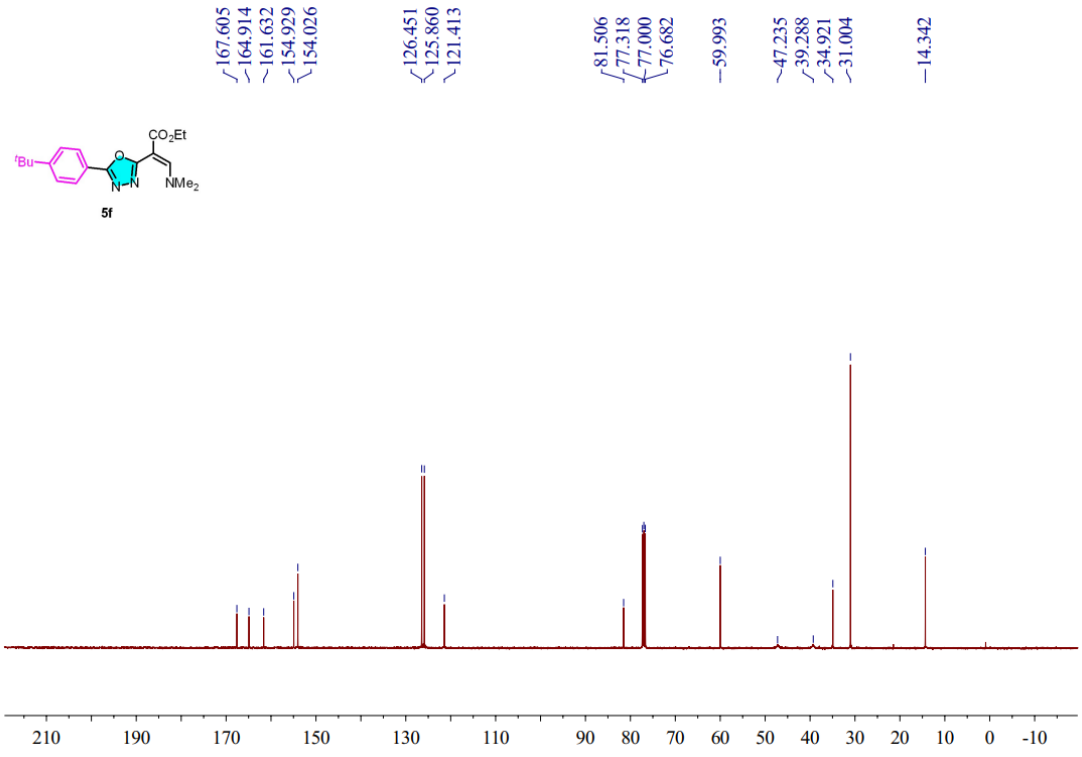
^{1}H NMR Spectrum of Compound **5e** (400 MHz, $CDCl_3$)



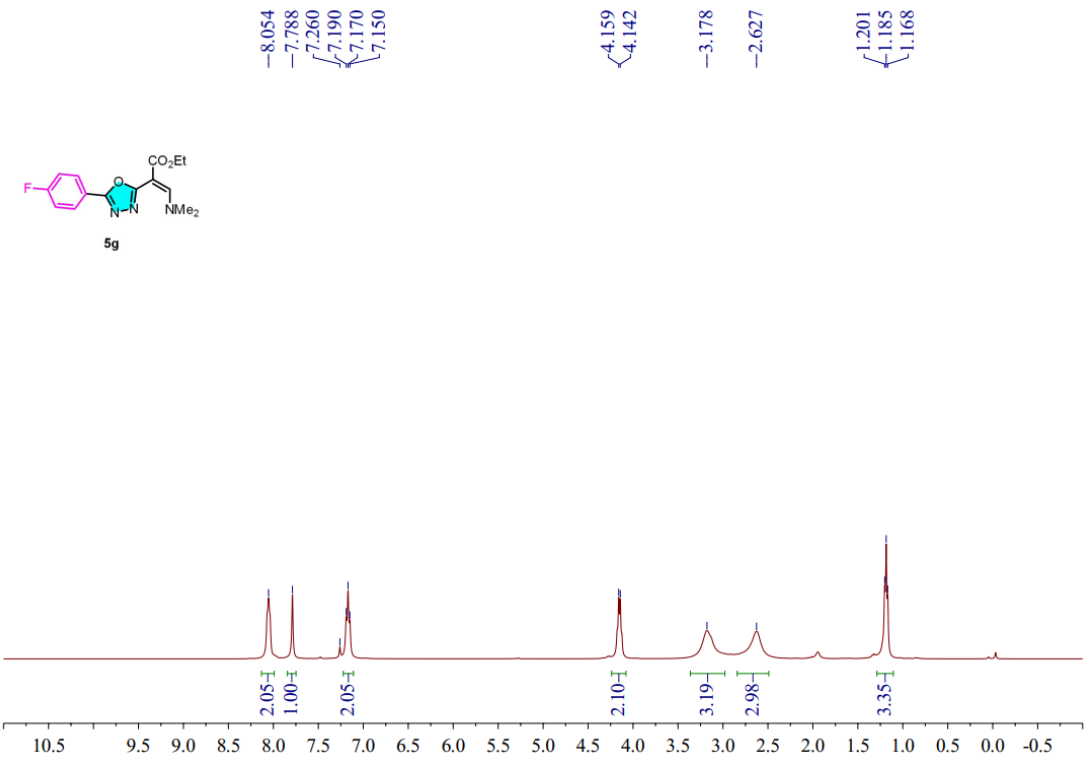
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5e** (100 MHz, $CDCl_3$)



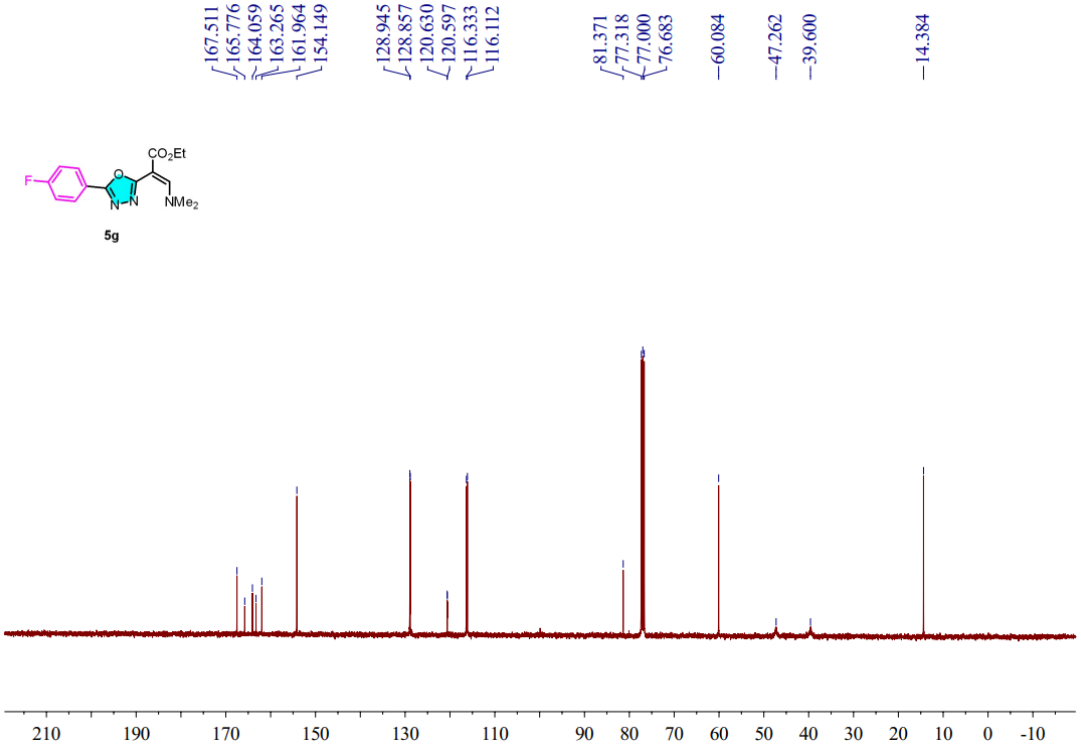
^{1}H NMR Spectrum of Compound **5f** (400 MHz, $CDCl_3$)



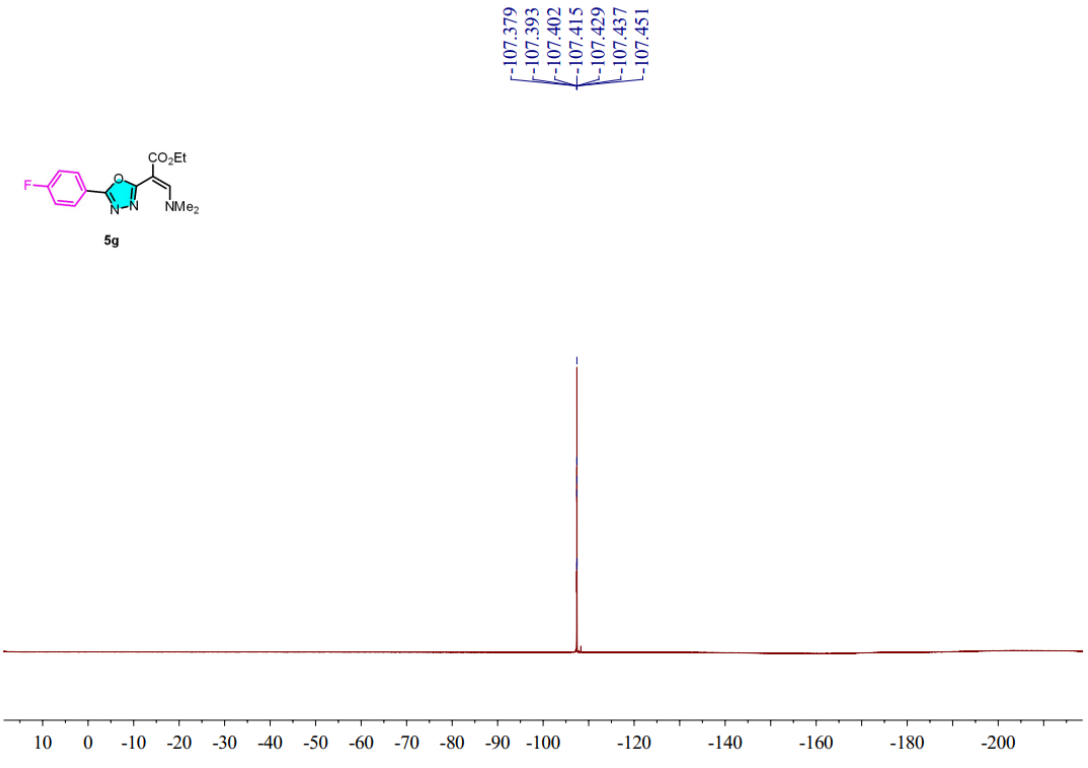
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5f** (100 MHz, $CDCl_3$)



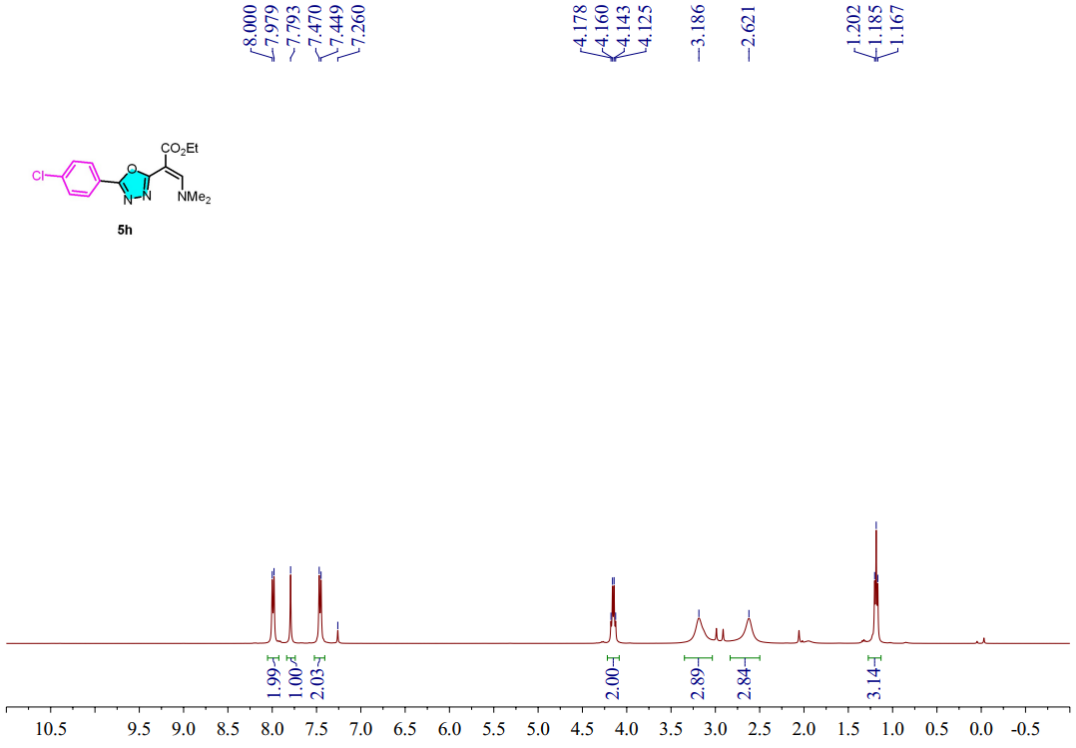
^{1}H NMR Spectrum of Compound **5g** (400 MHz, $CDCl_3$)



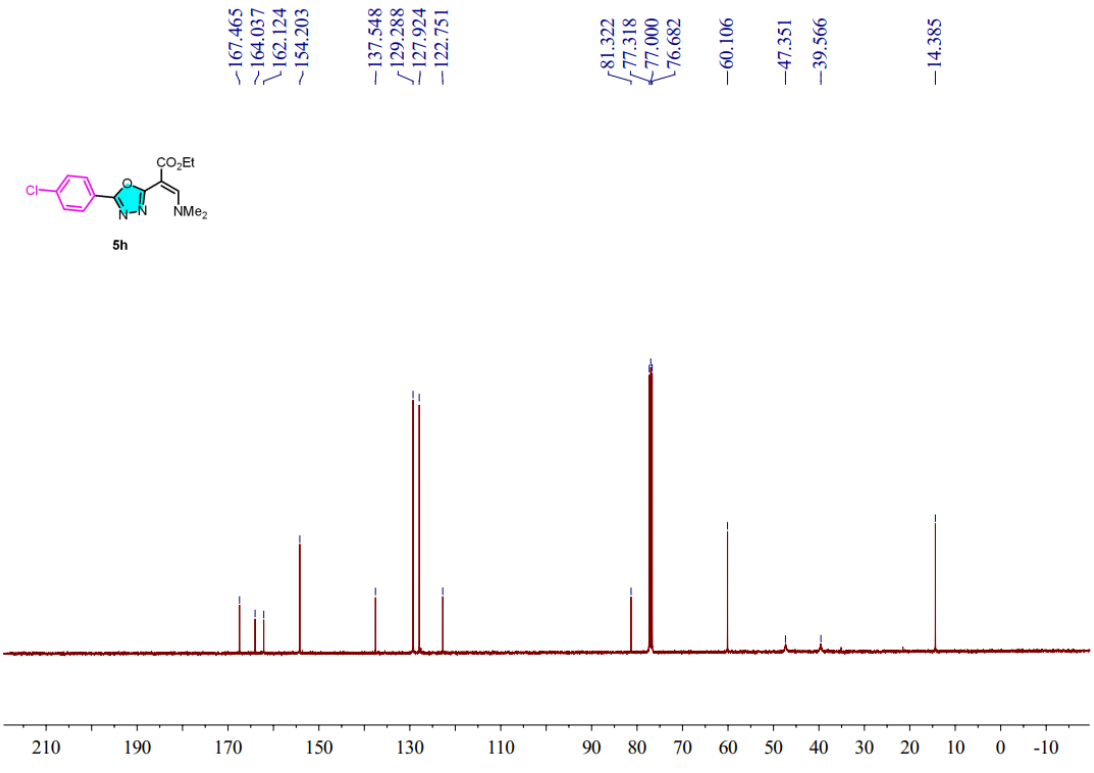
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5g** (100 MHz, $CDCl_3$)



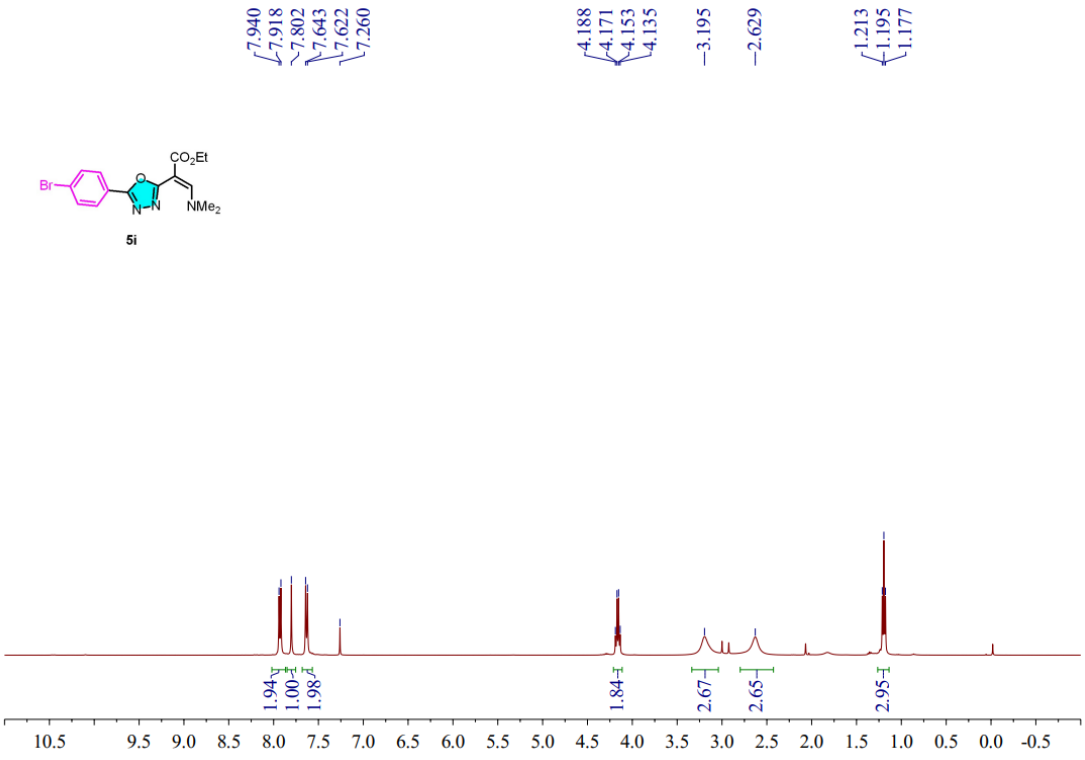
$^{19}F\{^{1}H\}$ NMR Spectrum of Compound **5g** (376 MHz, $CDCl_3$)



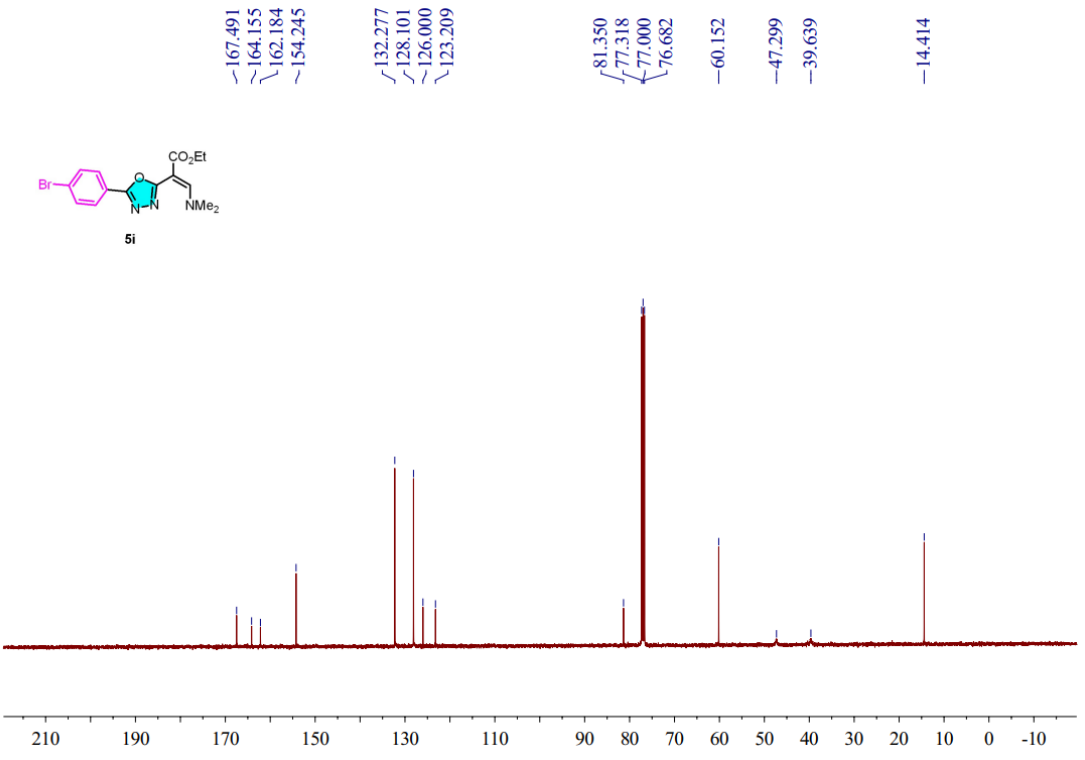
^{1}H NMR Spectrum of Compound **5h** (400 MHz, $CDCl_3$)



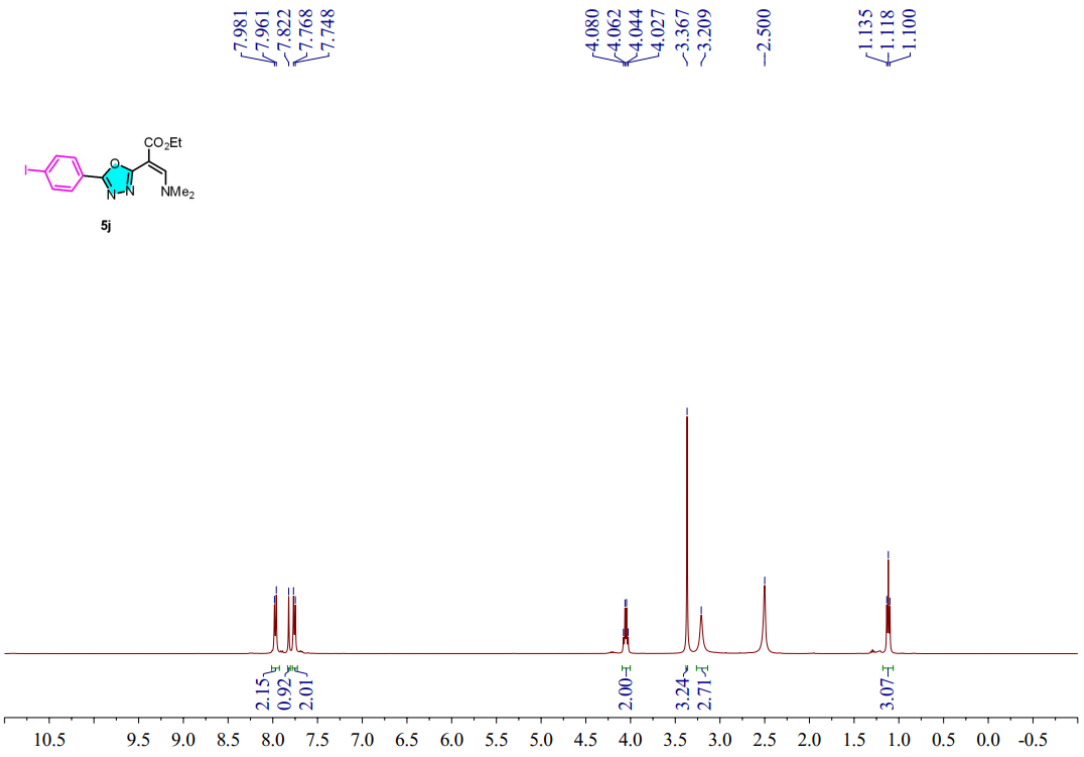
^{13}C{^{1}H} NMR Spectrum of Compound **5h** (100 MHz, $CDCl_3$)



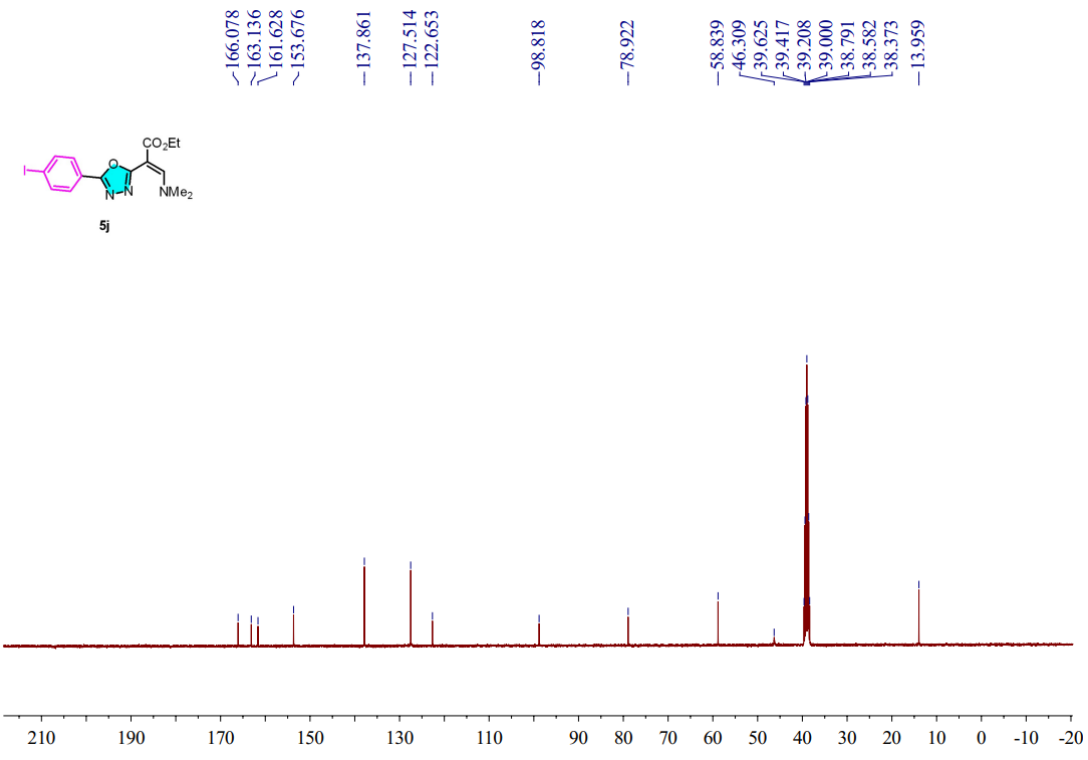
^{1}H NMR Spectrum of Compound **5i** (400 MHz, $CDCl_3$)



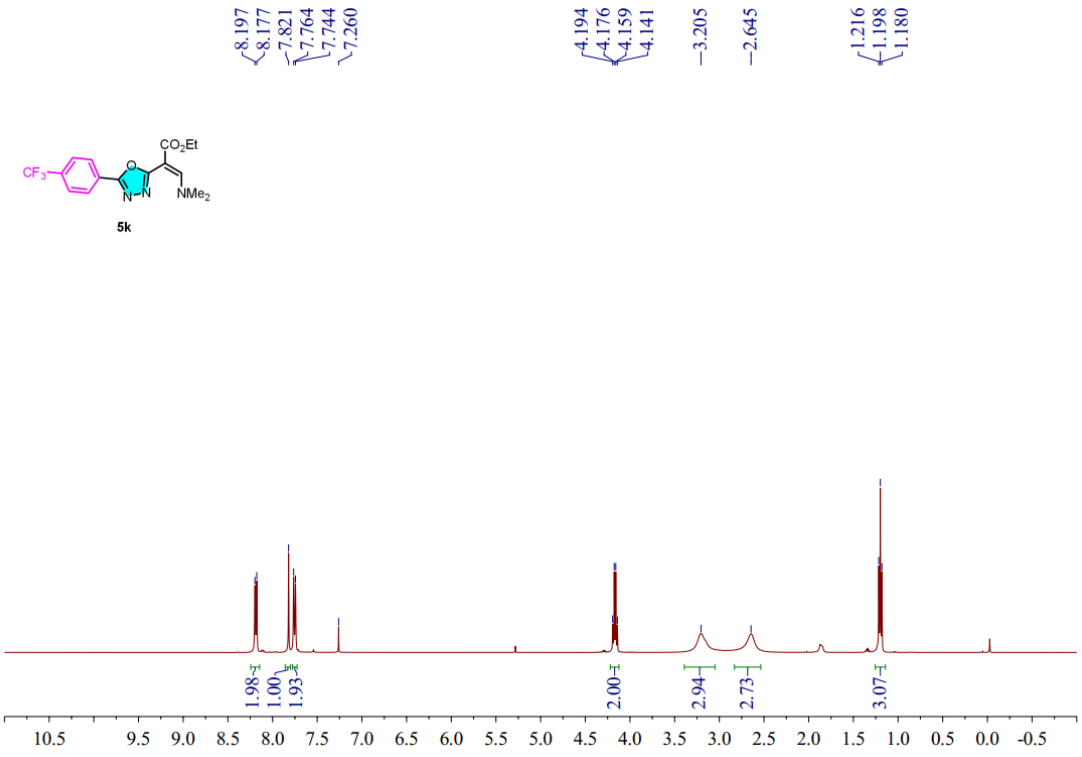
^{13}C{^{1}H} NMR Spectrum of Compound **5i** (100 MHz, $CDCl_3$)



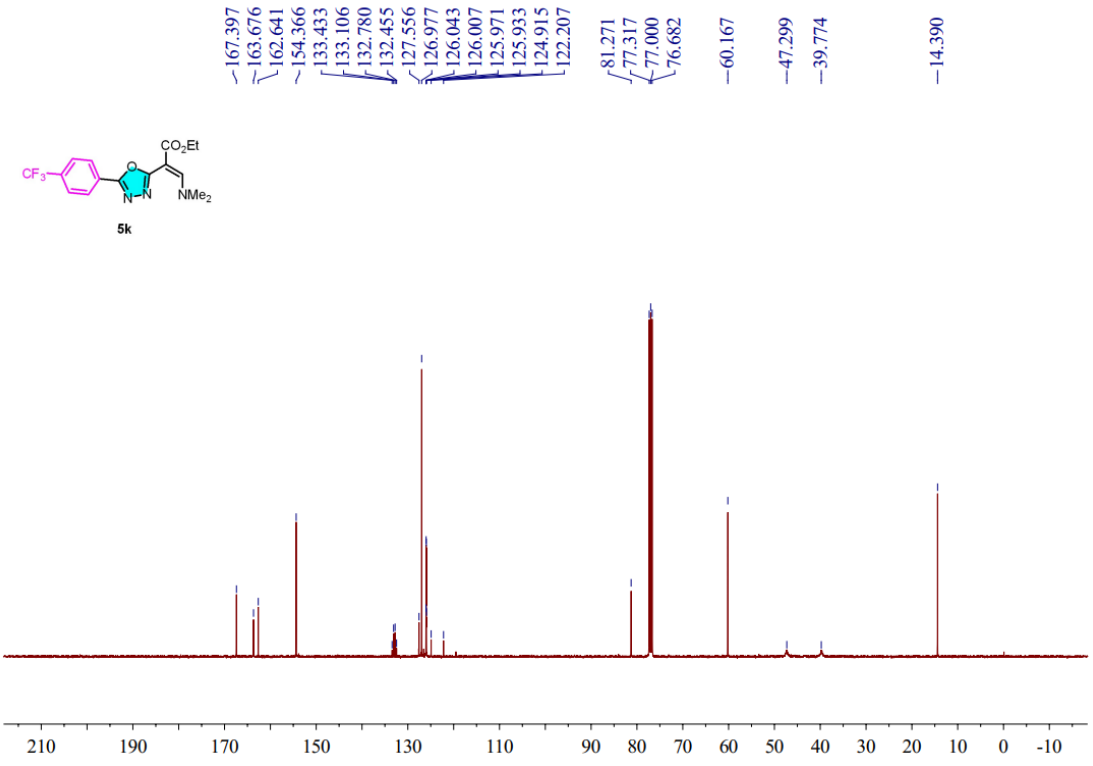
^{1}H NMR Spectrum of Compound **5j** (400 MHz, DMSO-d_6)



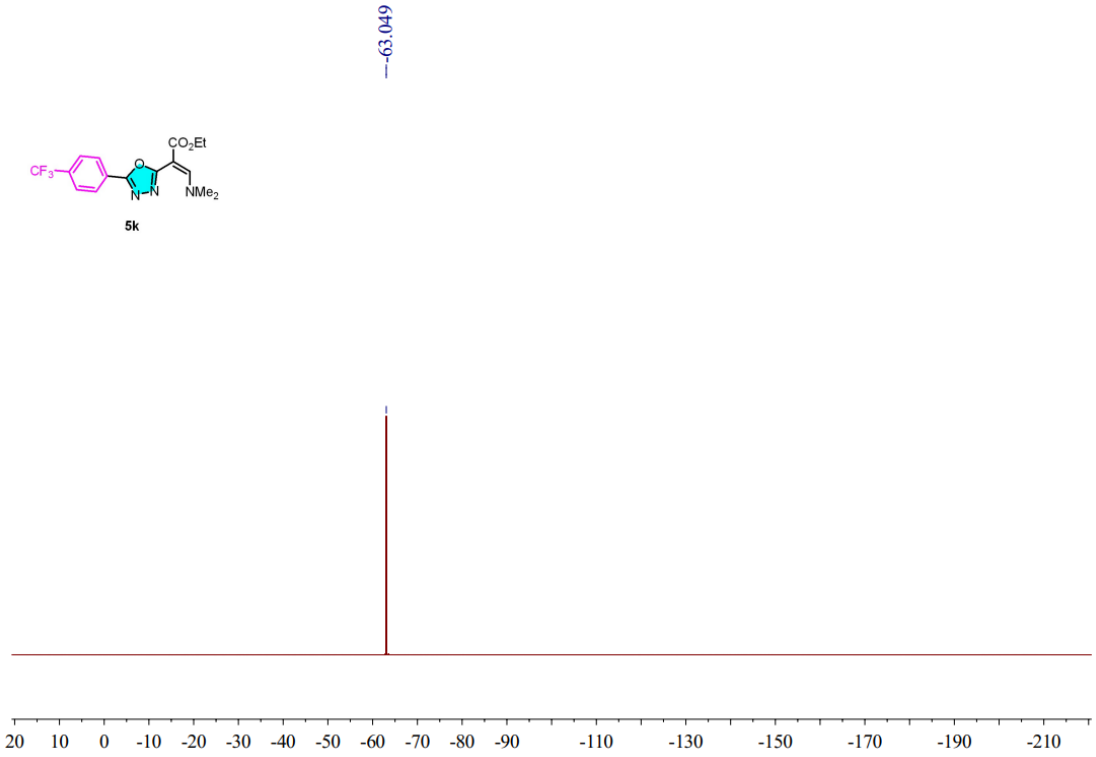
^{13}C{^{1}H} NMR Spectrum of Compound **5j** (100 MHz, DMSO-d_6)



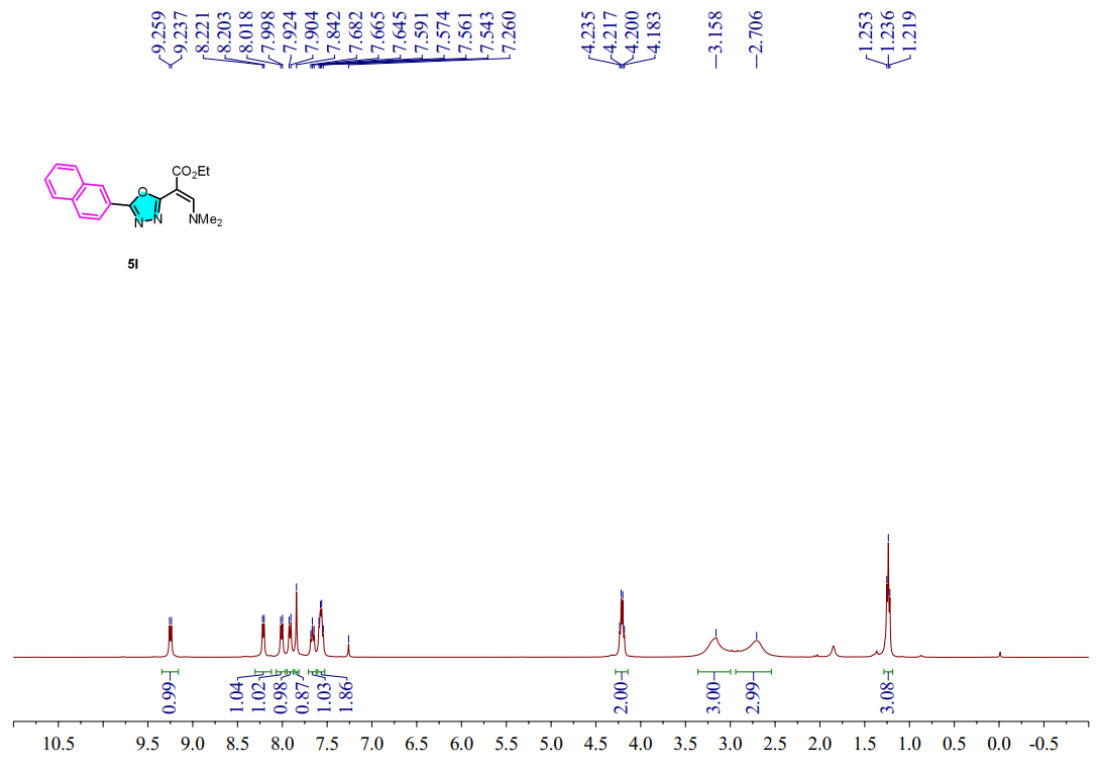
^{1}H NMR Spectrum of Compound **5k** (400 MHz, $CDCl_3$)



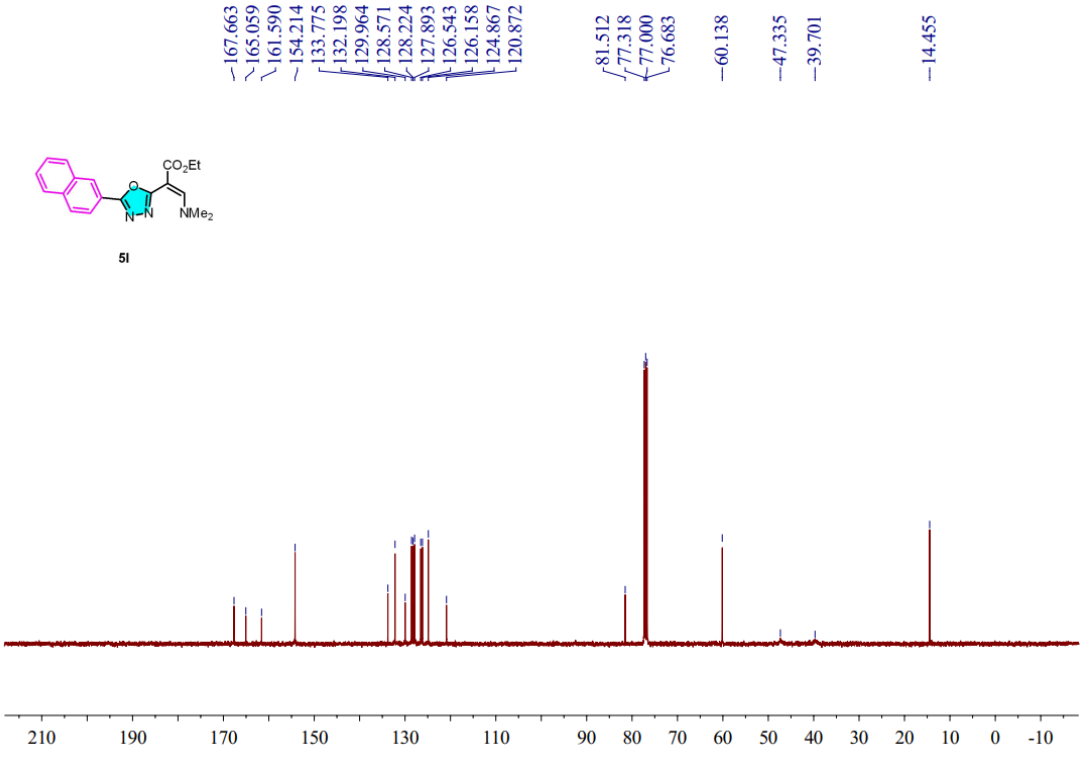
^{13}C{^{1}H} NMR Spectrum of Compound **5k** (100 MHz, $CDCl_3$)



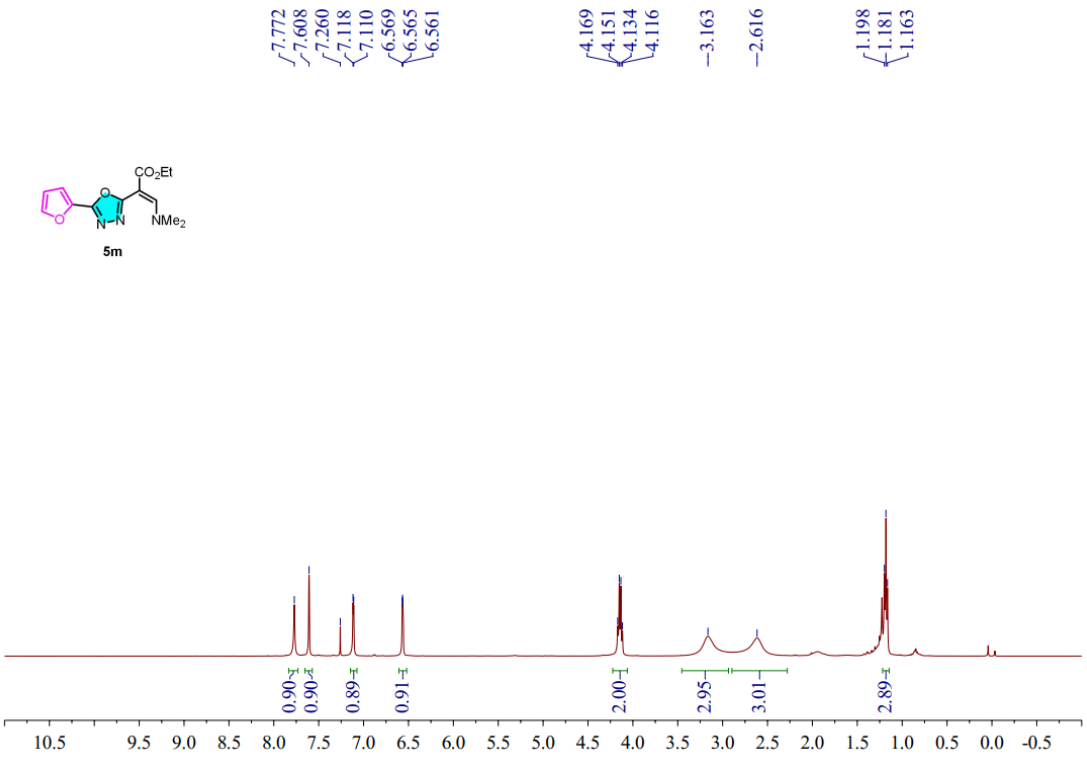
$^{19}F\{^{1}H\}$ NMR Spectrum of Compound **5k** (376 MHz, $CDCl_3$)



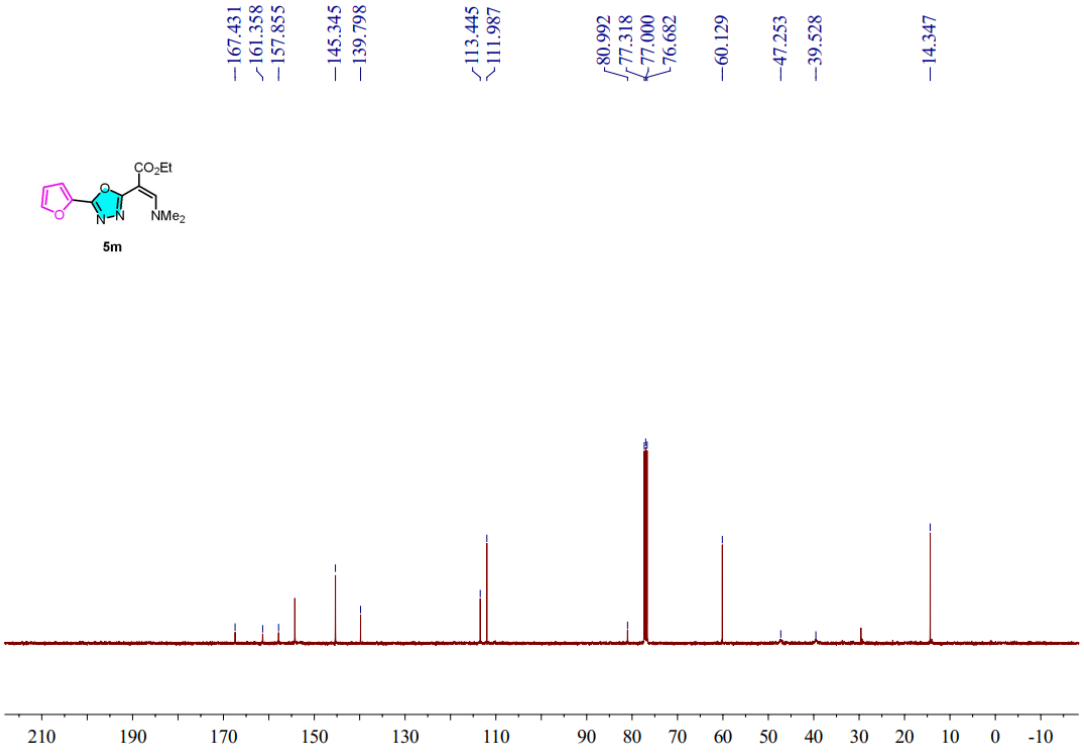
^{1}H NMR Spectrum of Compound **5l** (400 MHz, $CDCl_3$)



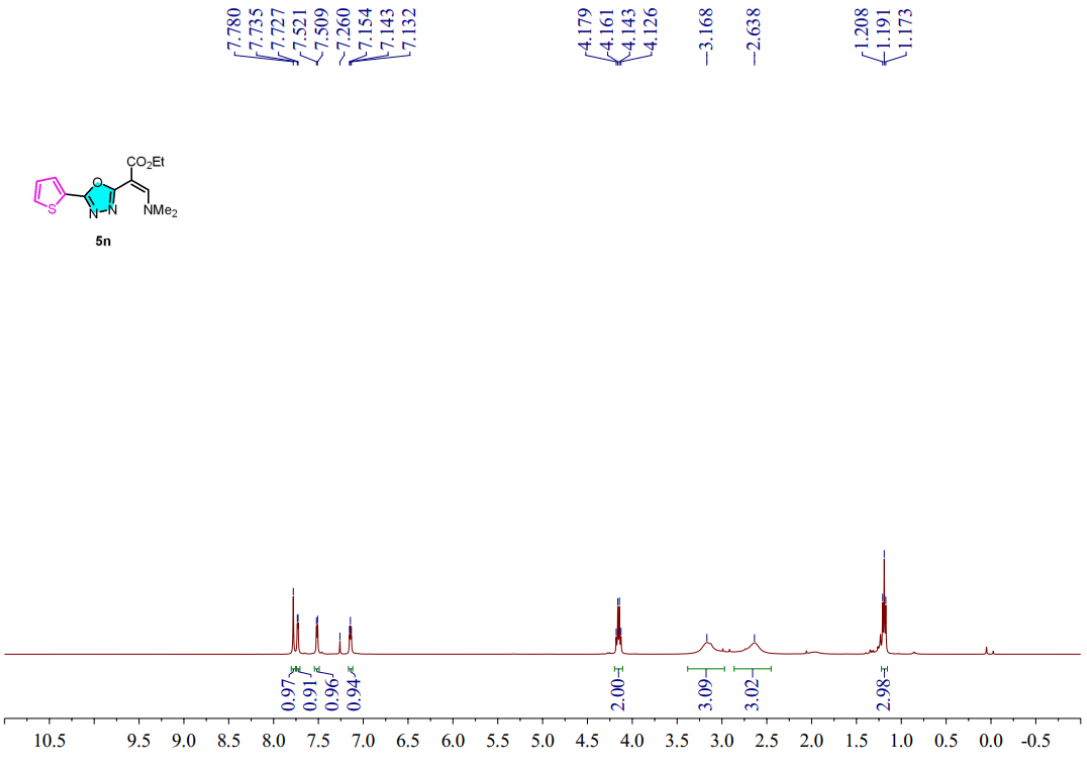
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5l** (100 MHz, $CDCl_3$)



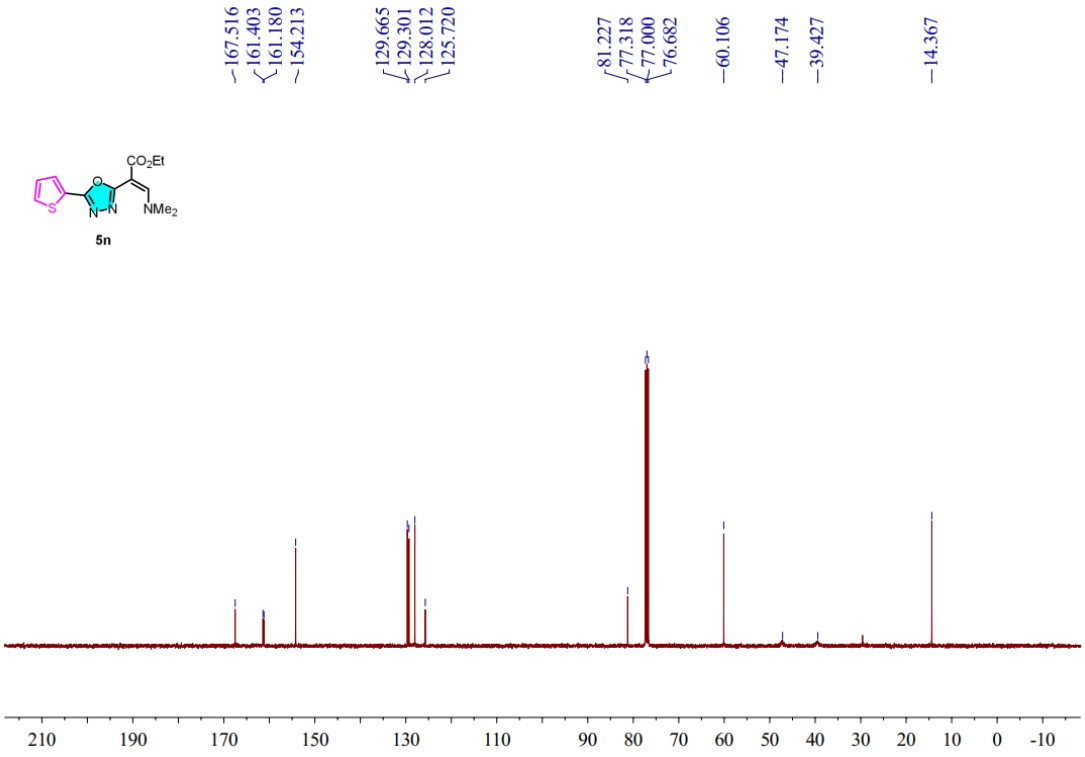
^{1}H NMR Spectrum of Compound **5m** (400 MHz, $CDCl_3$)



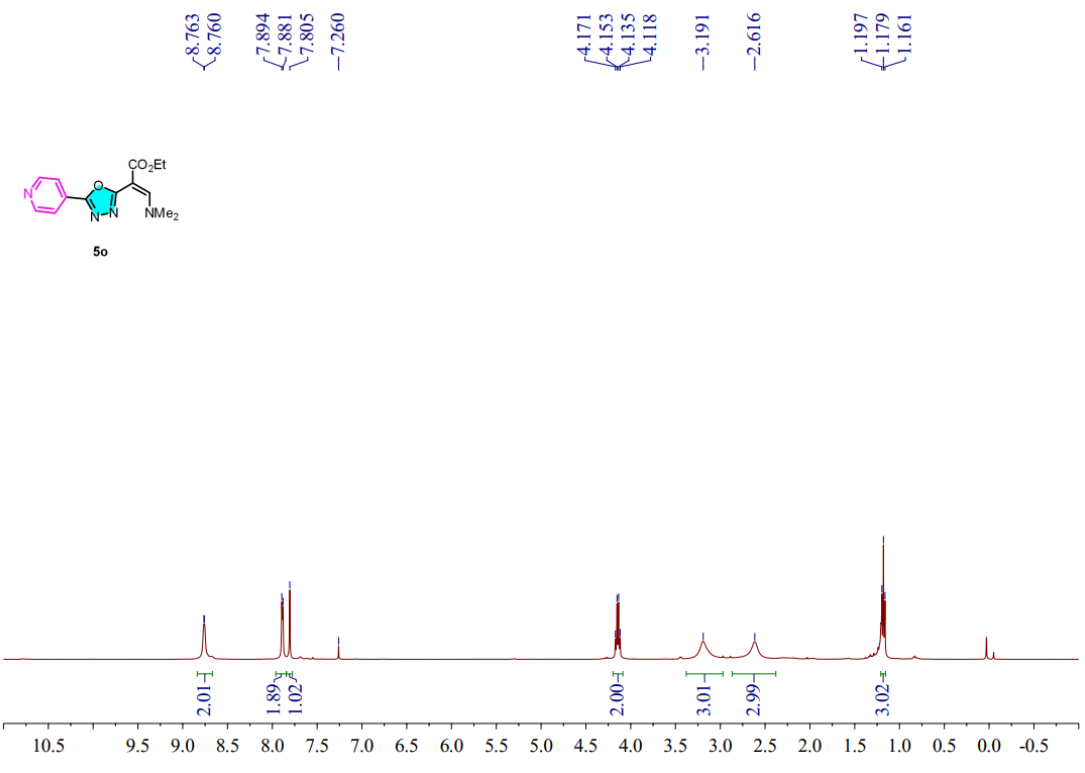
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5m** (100 MHz, $CDCl_3$)



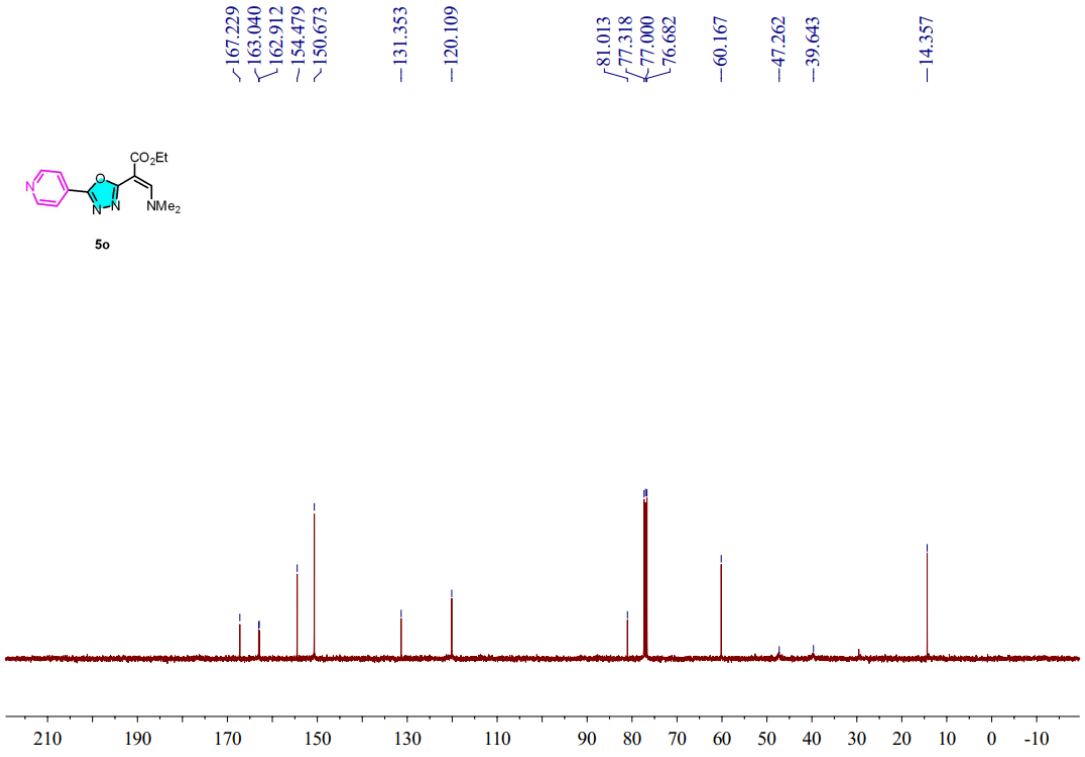
^{1}H NMR Spectrum of Compound **5n** (400 MHz, $CDCl_3$)



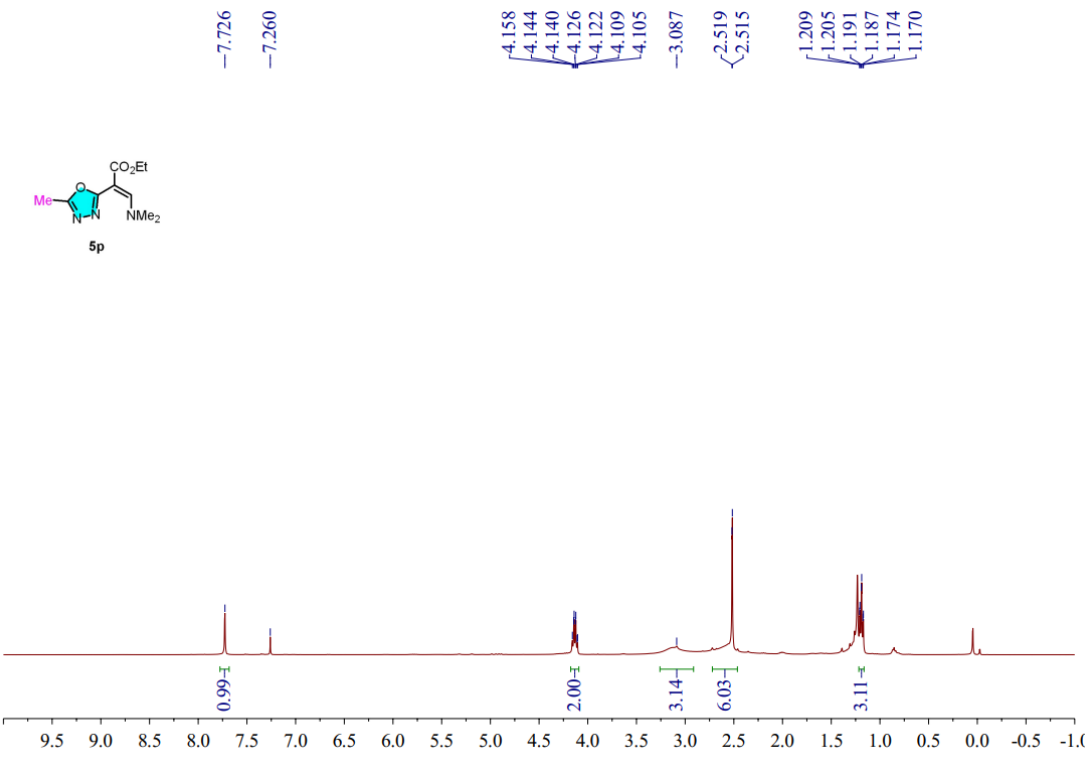
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5n** (100 MHz, $CDCl_3$)



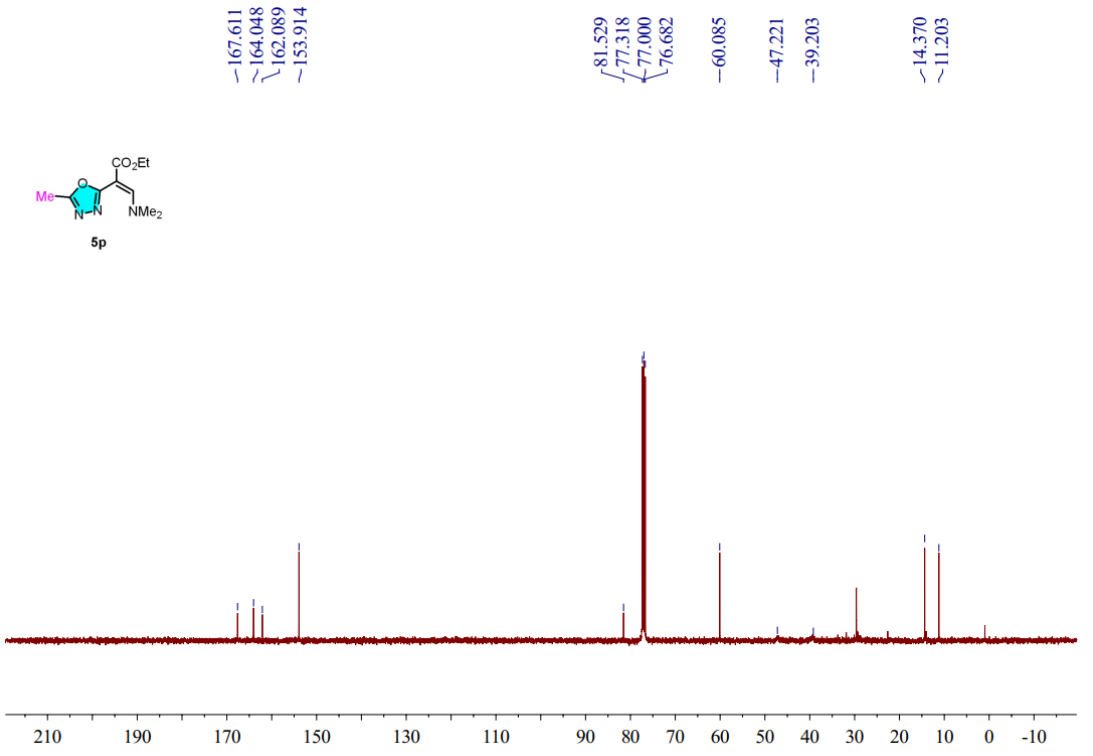
^{1}H NMR Spectrum of Compound **5o** (400 MHz, $CDCl_3$)



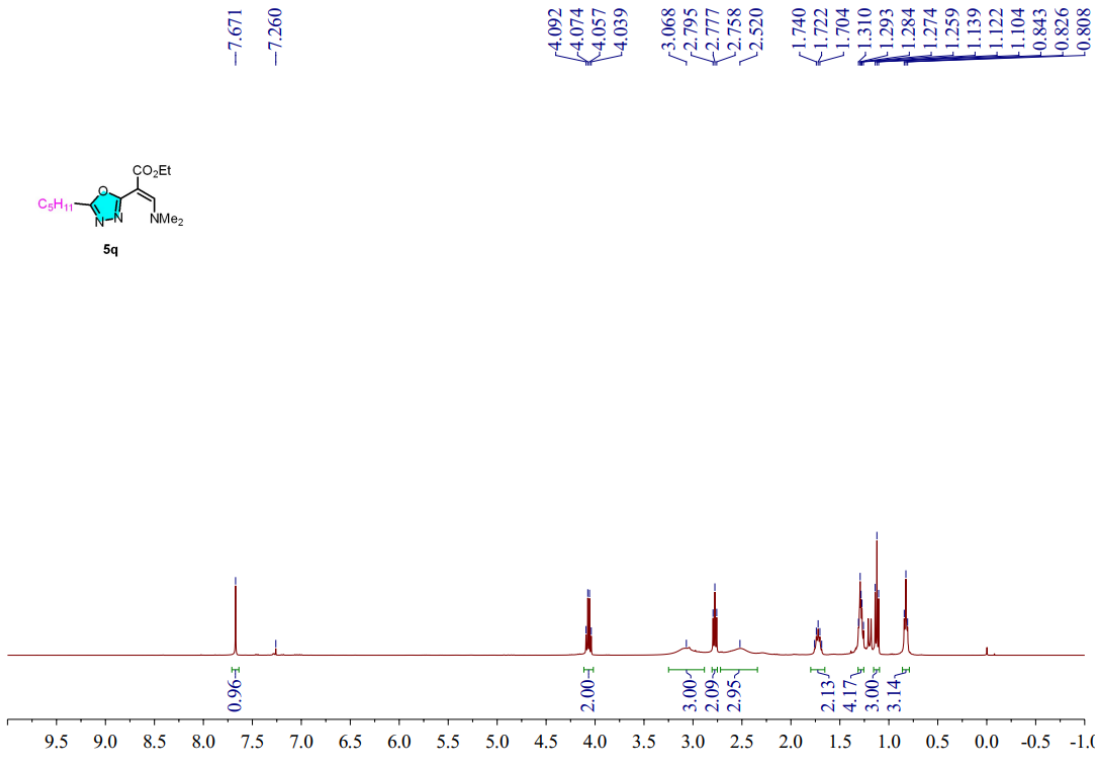
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5o** (100 MHz, $CDCl_3$)



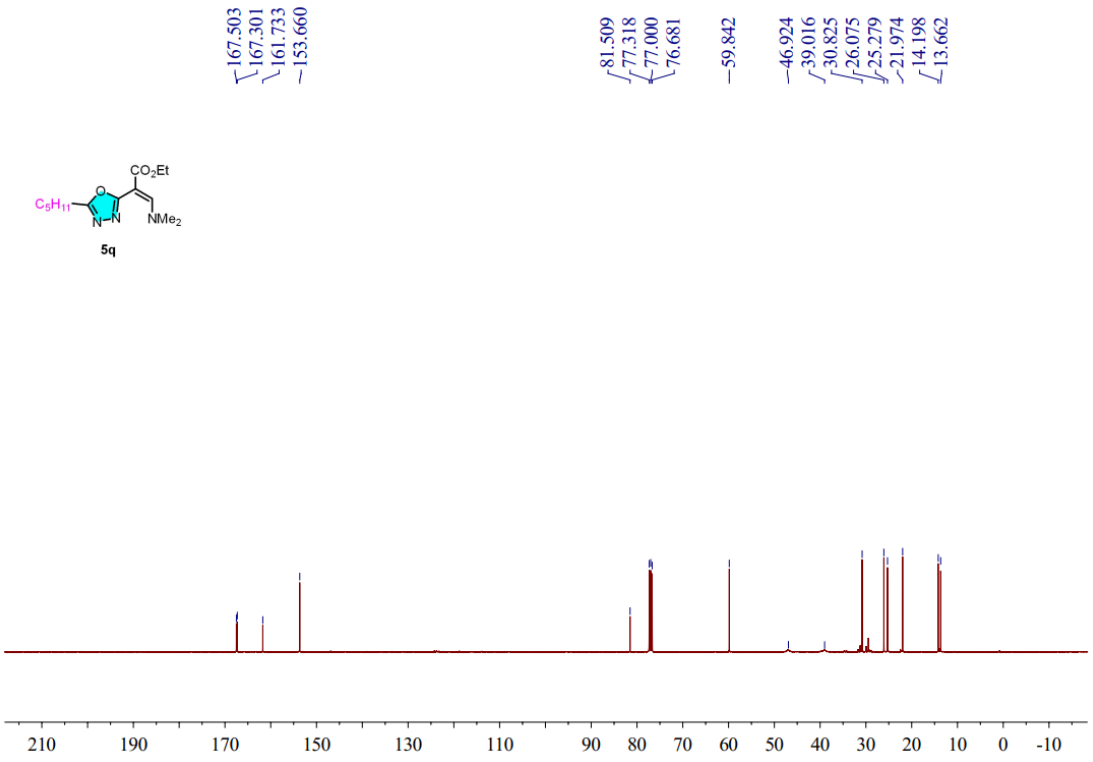
^{1}H NMR Spectrum of Compound **5p** (400 MHz, $CDCl_3$)



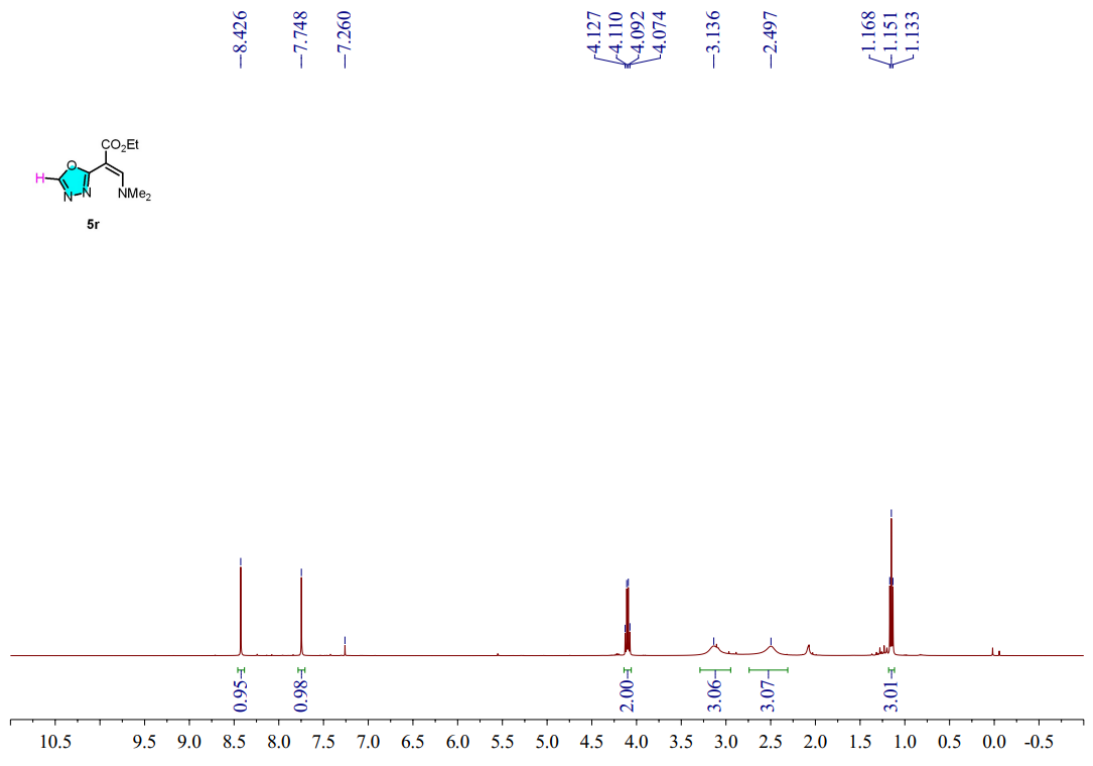
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5p** (100 MHz, $CDCl_3$)



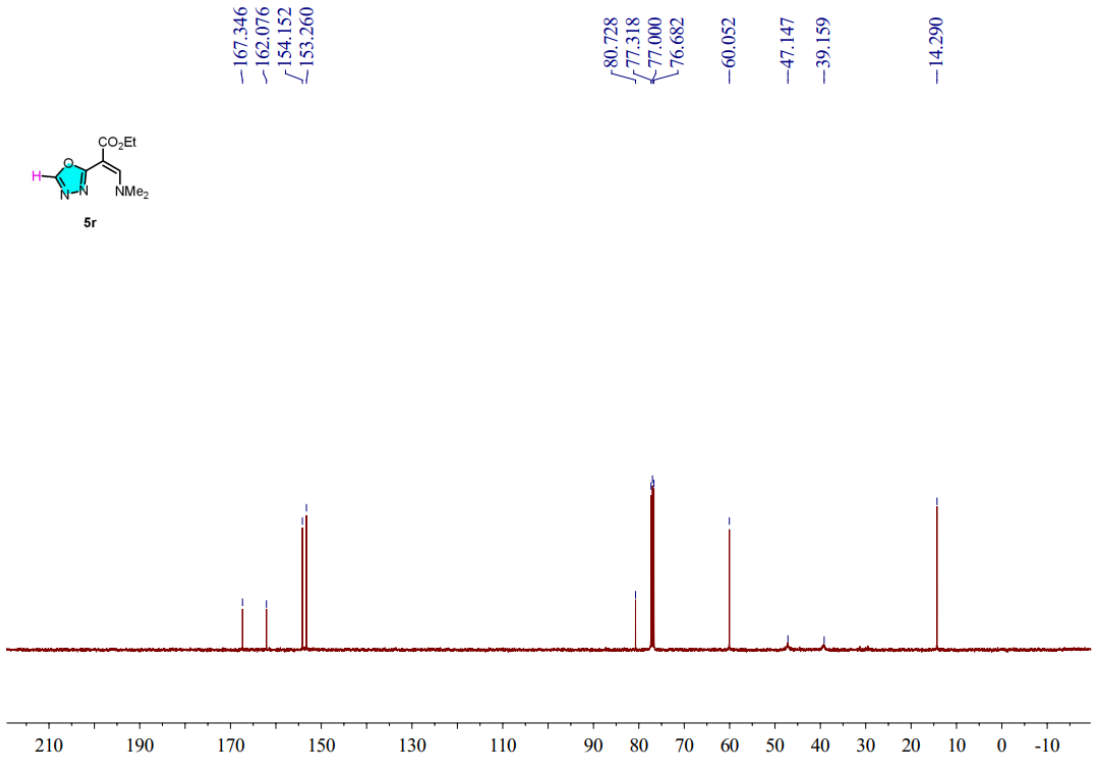
^{1}H NMR Spectrum of Compound **5q** (400 MHz, $CDCl_3$)



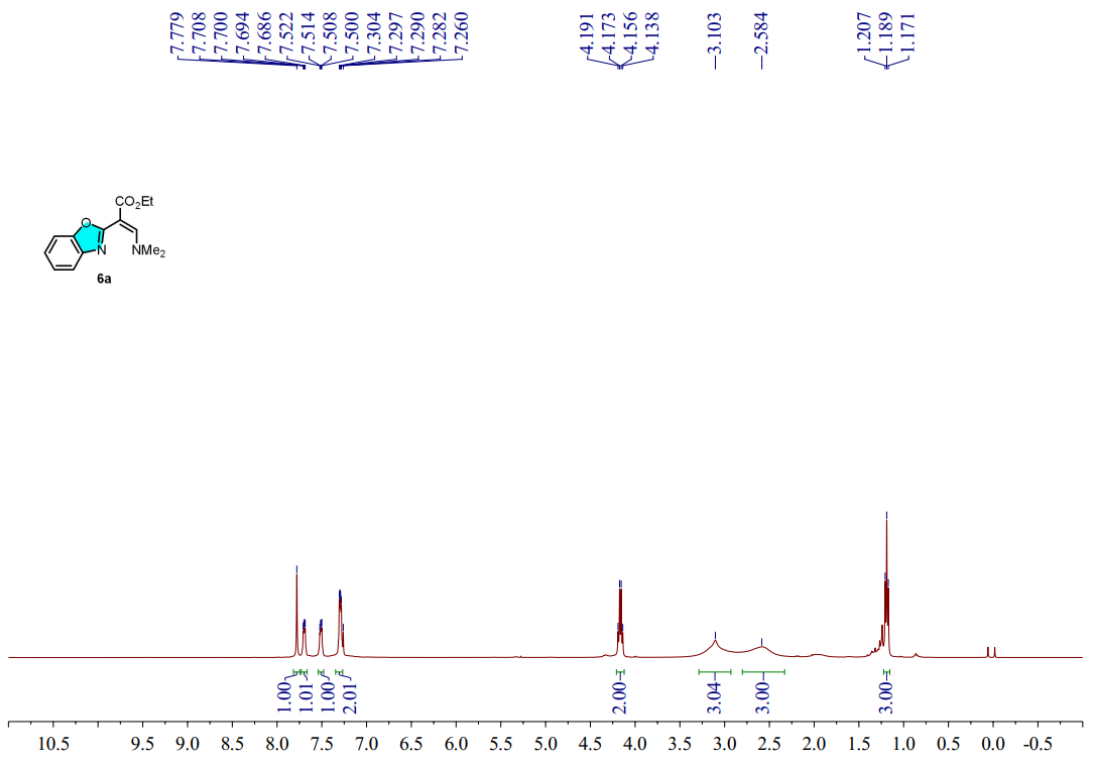
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5q** (100 MHz, $CDCl_3$)



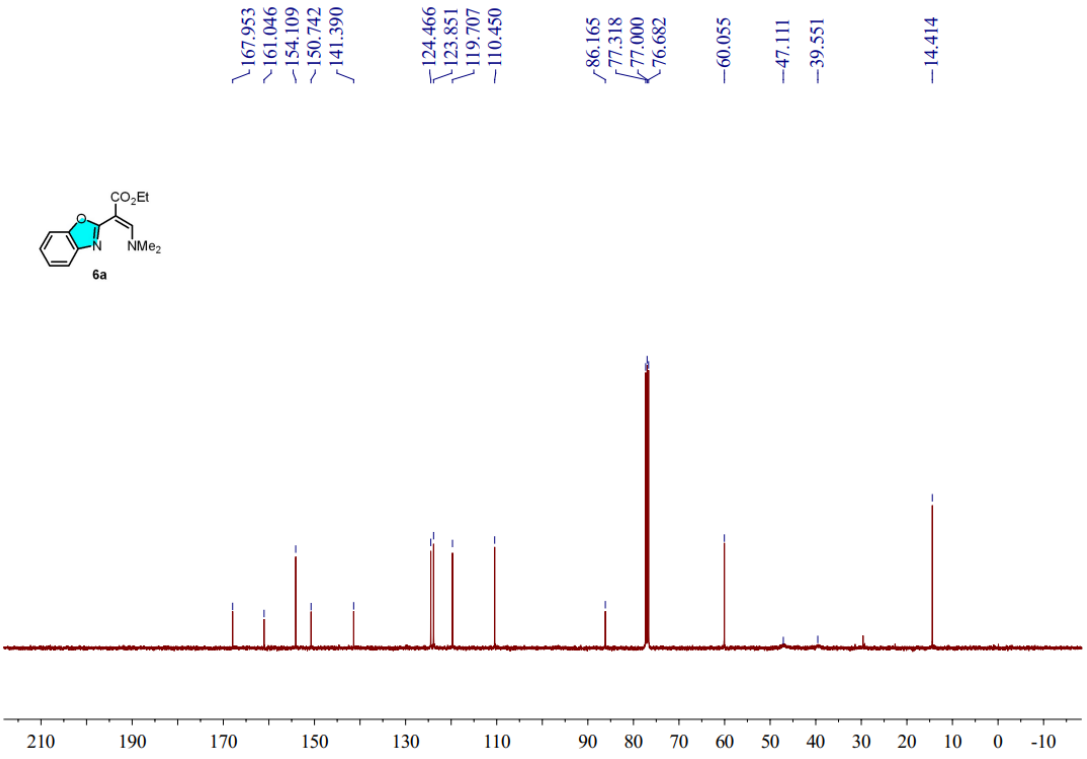
^{1}H NMR Spectrum of Compound **5r** (400 MHz, $CDCl_3$)



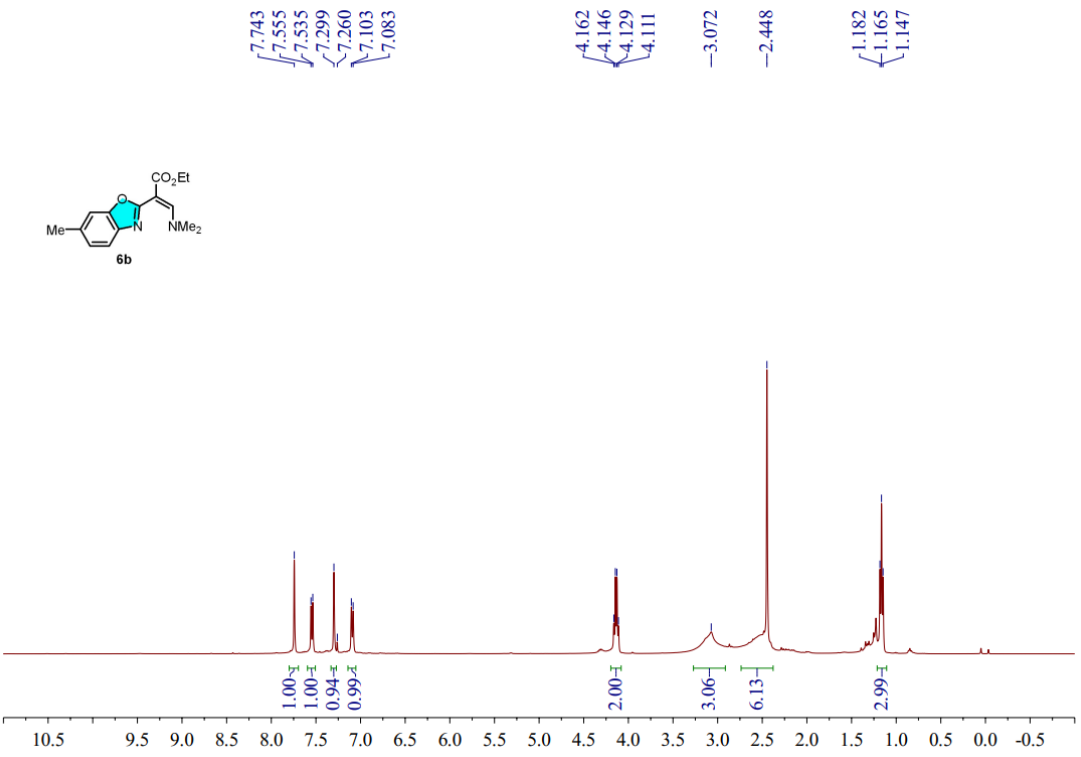
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **5r** (100 MHz, $CDCl_3$)



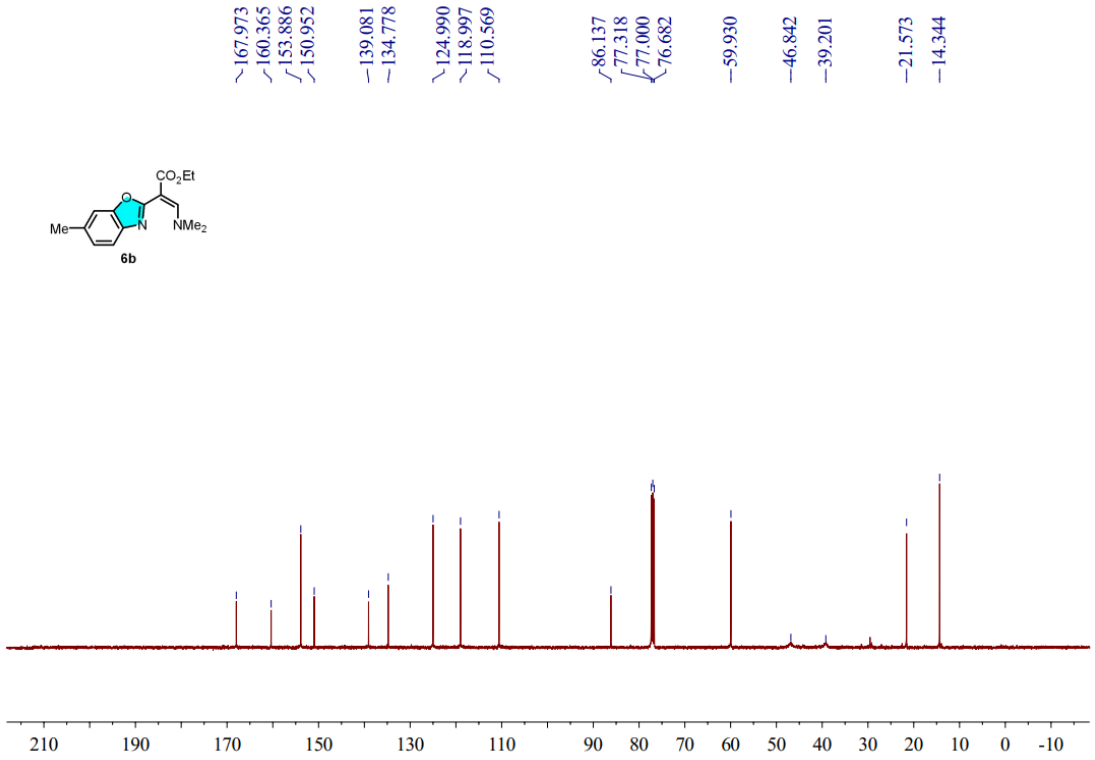
^{1}H NMR Spectrum of Compound **6a** (400 MHz, $CDCl_3$)



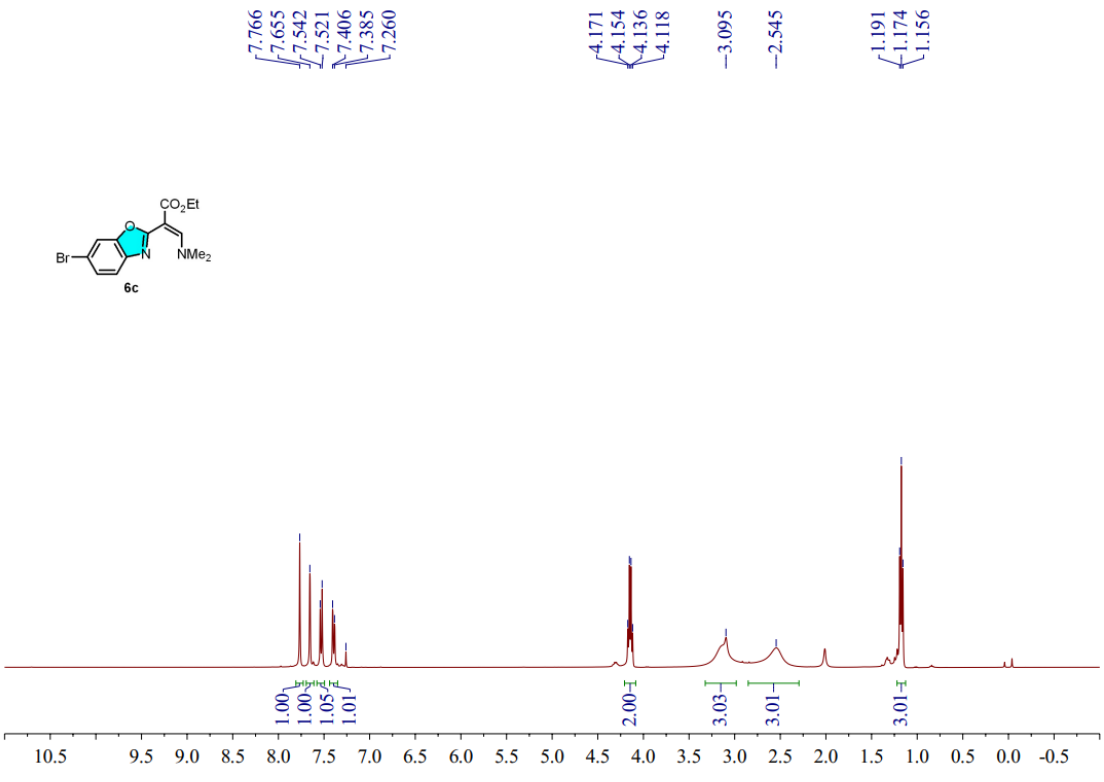
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **6a** (100 MHz, $CDCl_3$)



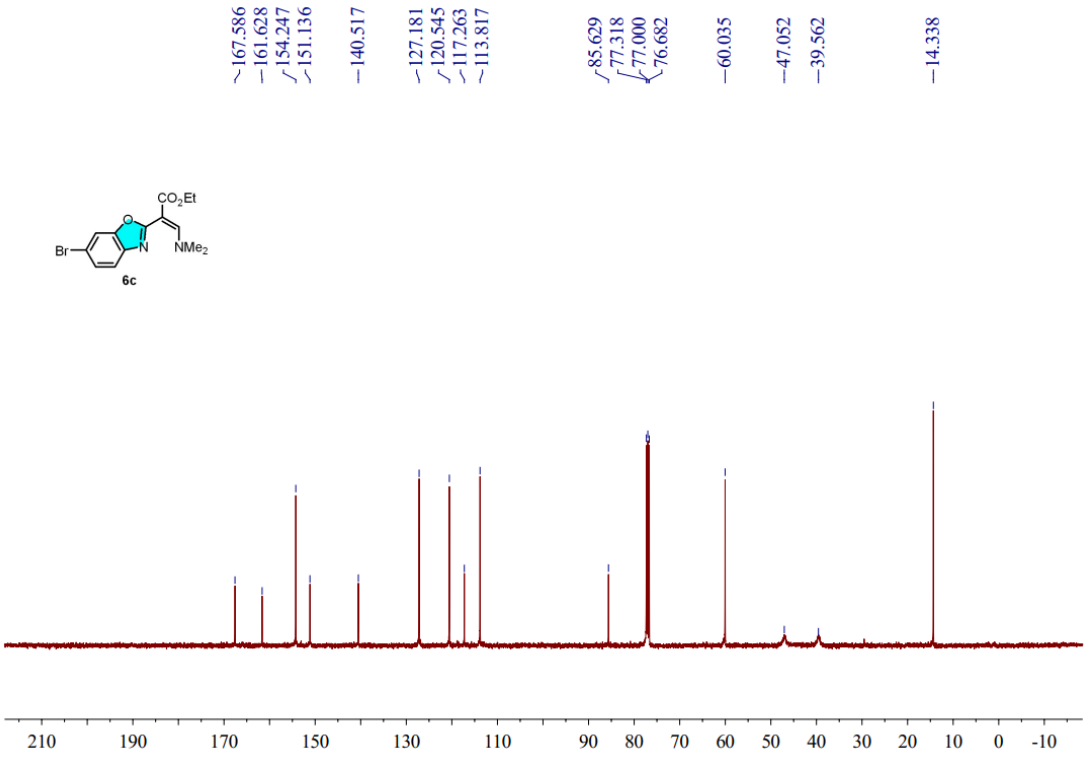
^{1}H NMR Spectrum of Compound **6b** (400 MHz, $CDCl_3$)



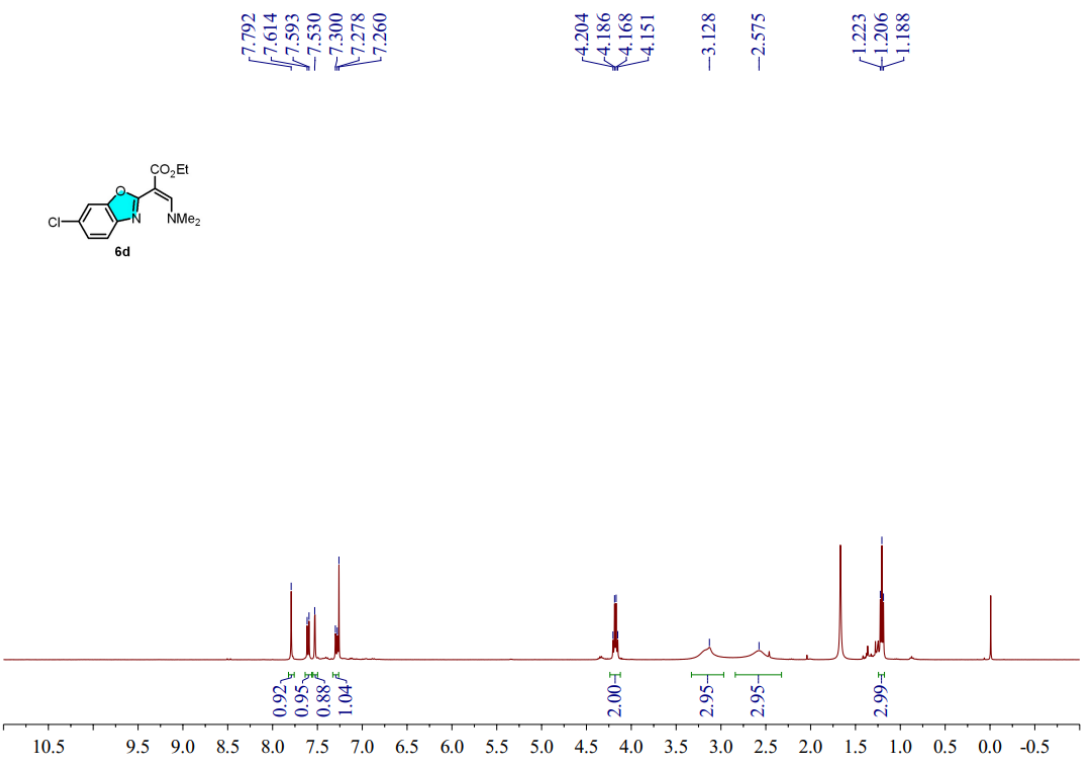
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **6b** (100 MHz, $CDCl_3$)



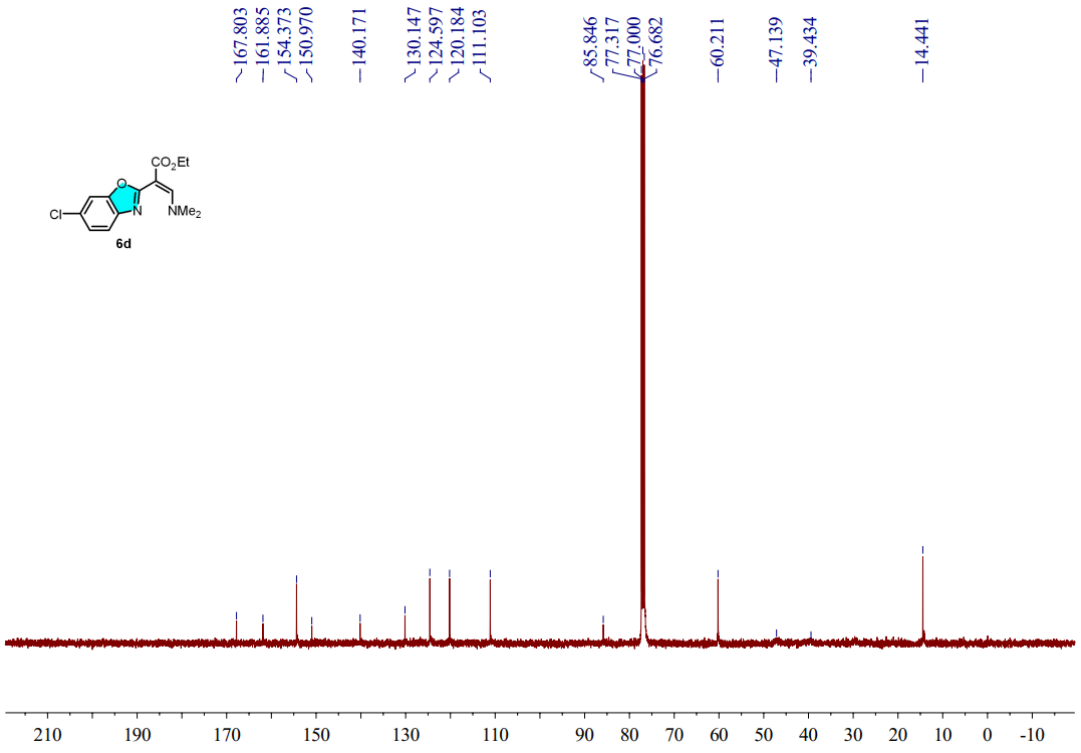
^{1}H NMR Spectrum of Compound **6c** (400 MHz, $CDCl_3$)



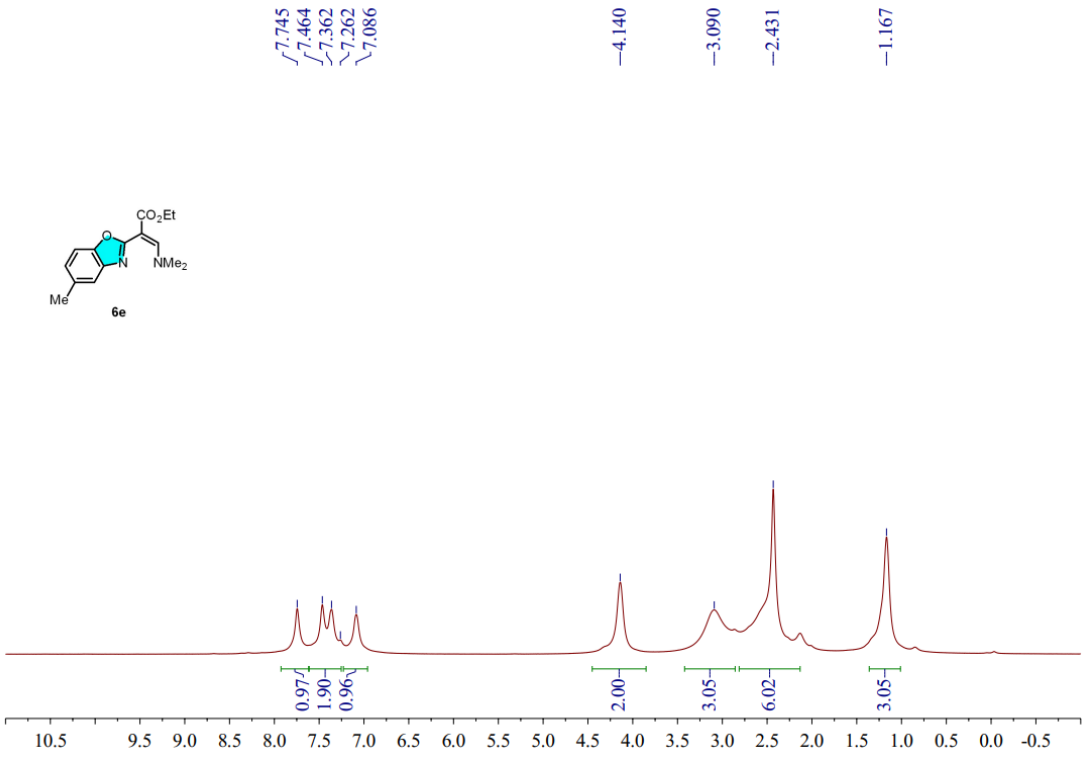
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **6c** (100 MHz, $CDCl_3$)



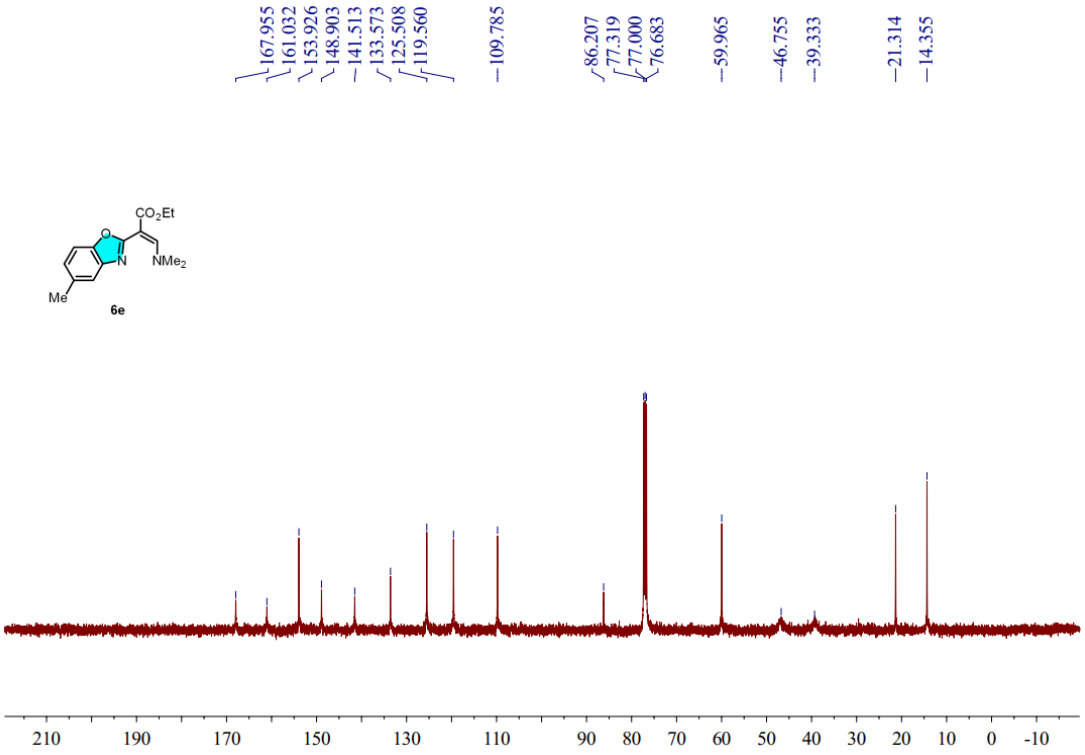
^{1}H NMR Spectrum of Compound **6d** (400 MHz, $CDCl_3$)



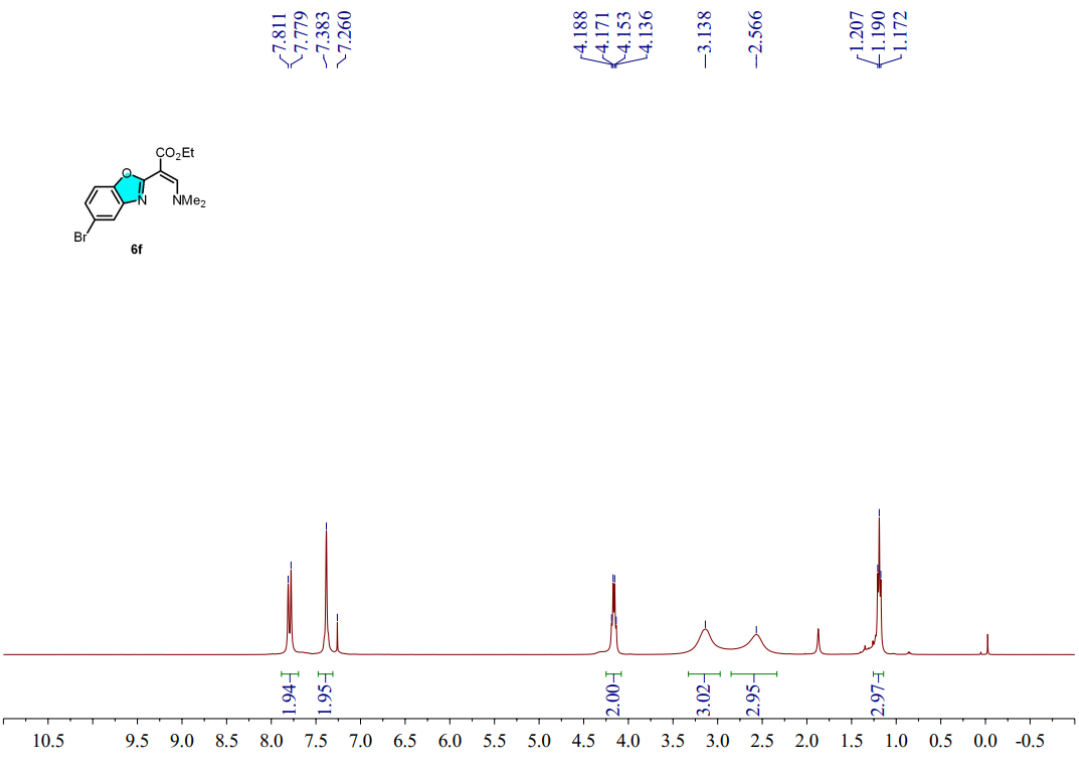
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **6d** (100 MHz, $CDCl_3$)



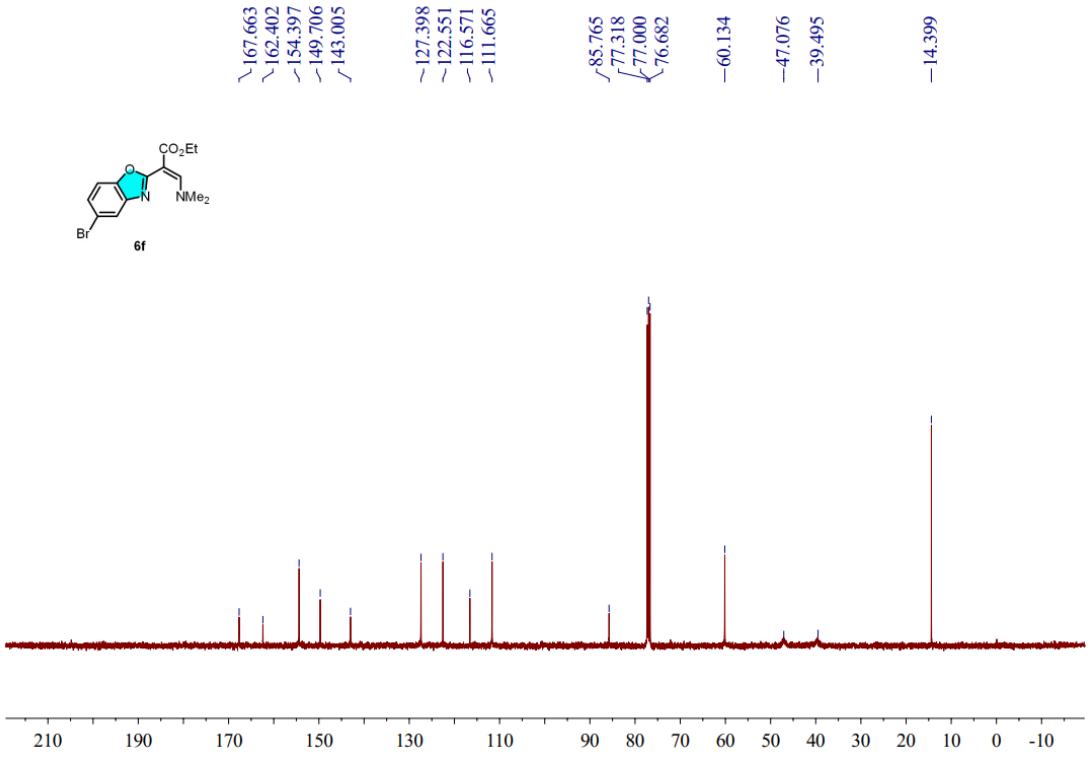
^{1}H NMR Spectrum of Compound **6e** (400 MHz, $CDCl_3$)



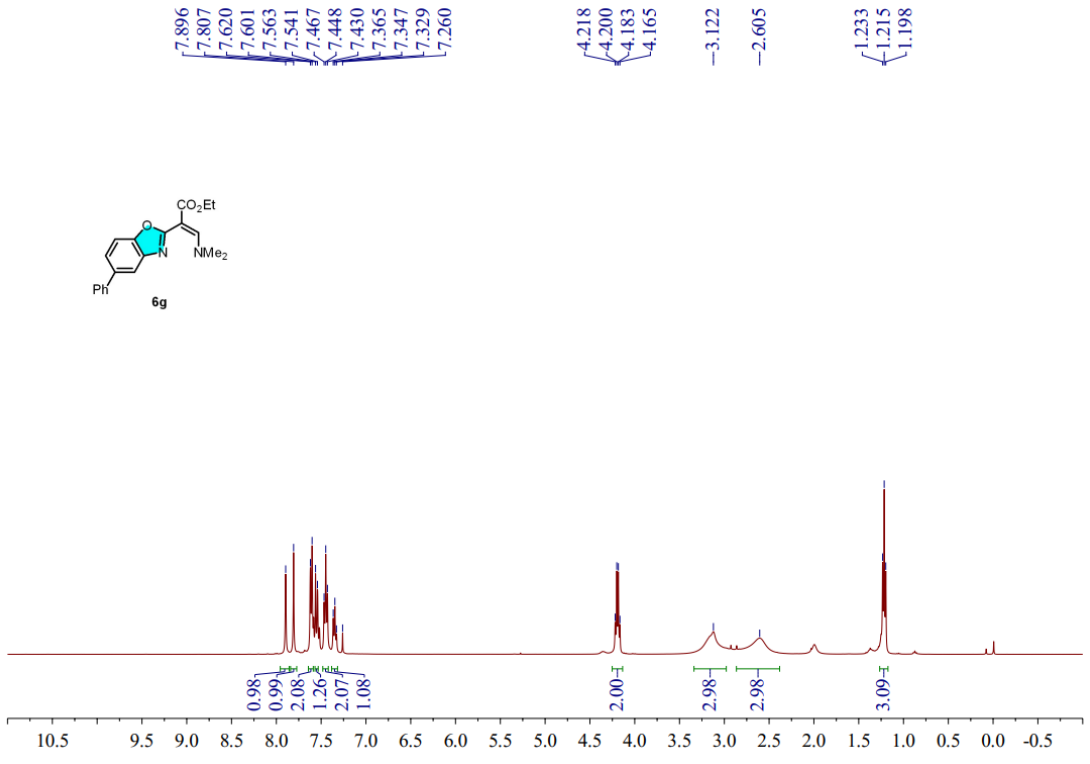
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **6e** (100 MHz, $CDCl_3$)



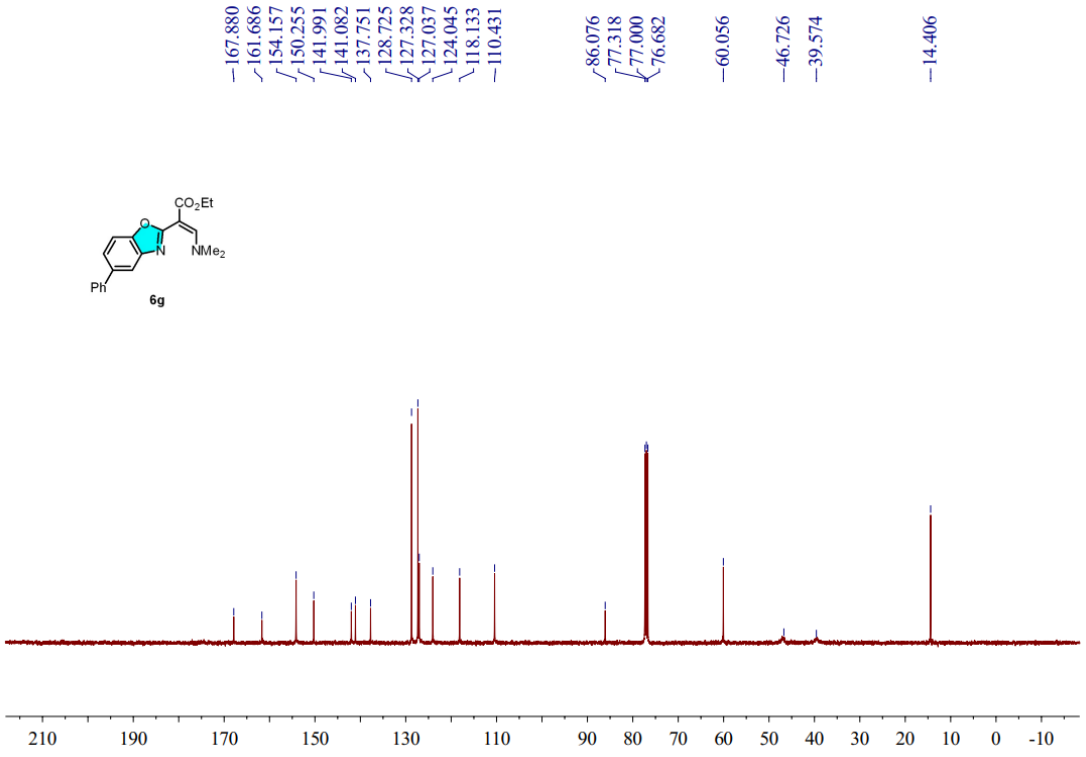
^{1}H NMR Spectrum of Compound **6f** (400 MHz, $CDCl_3$)



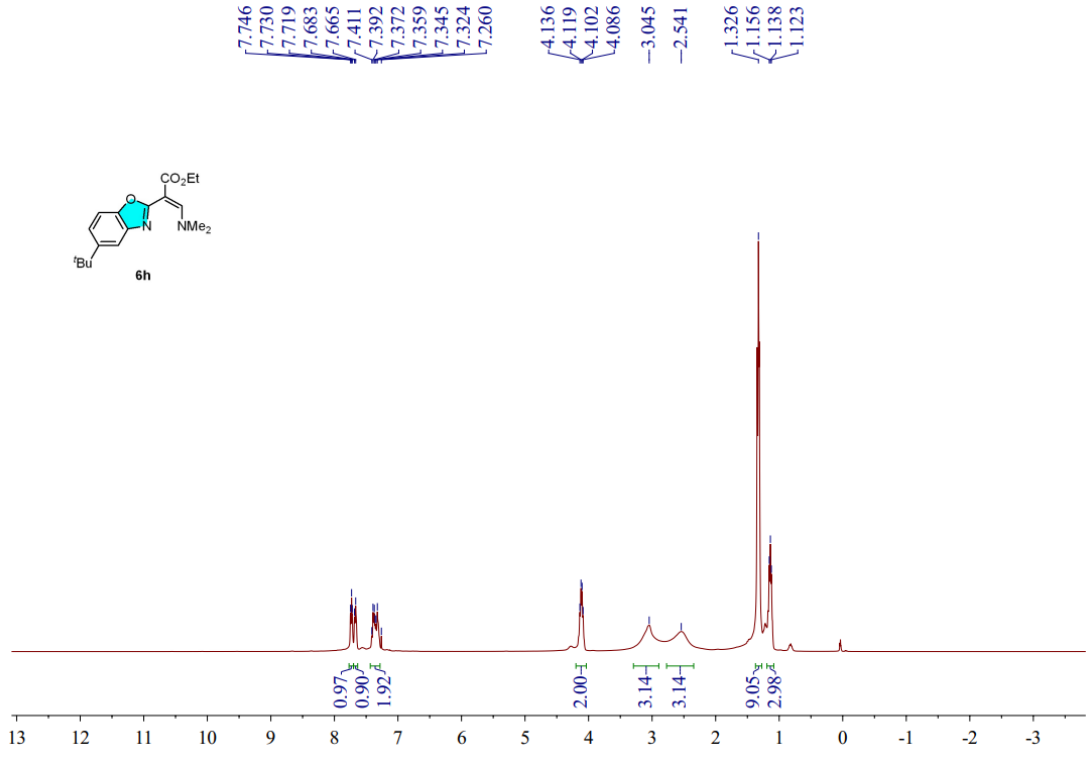
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **6f** (100 MHz, $CDCl_3$)



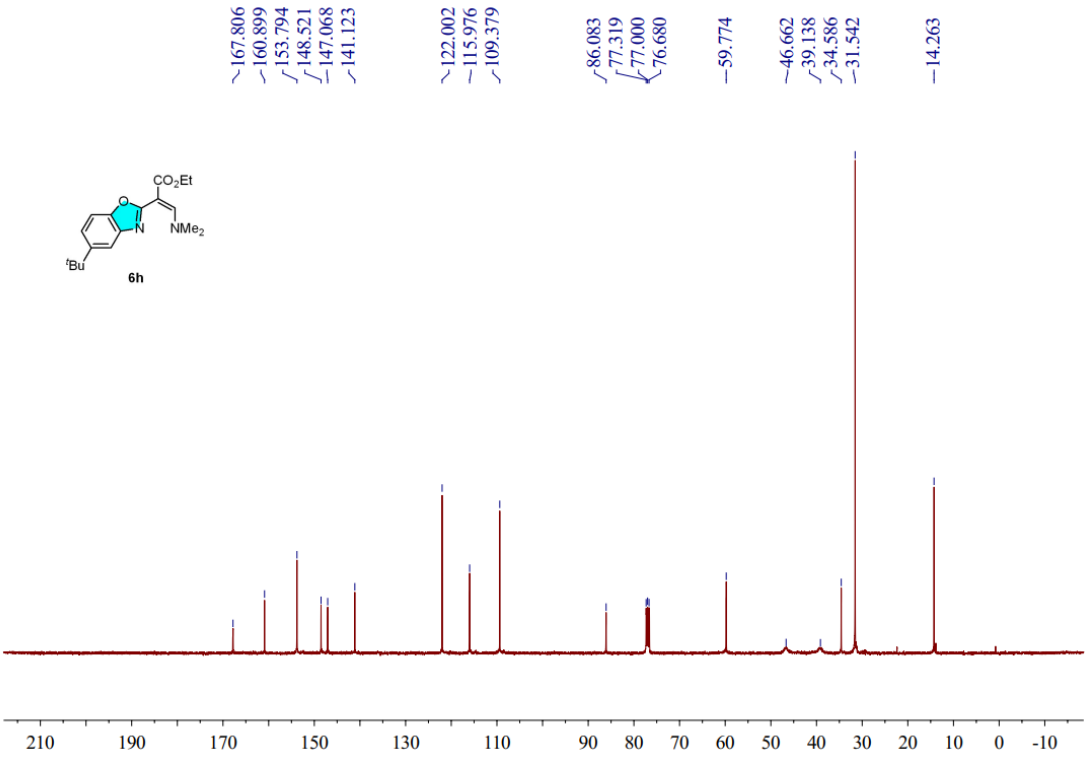
^{1}H NMR Spectrum of Compound **6g** (400 MHz, $CDCl_3$)



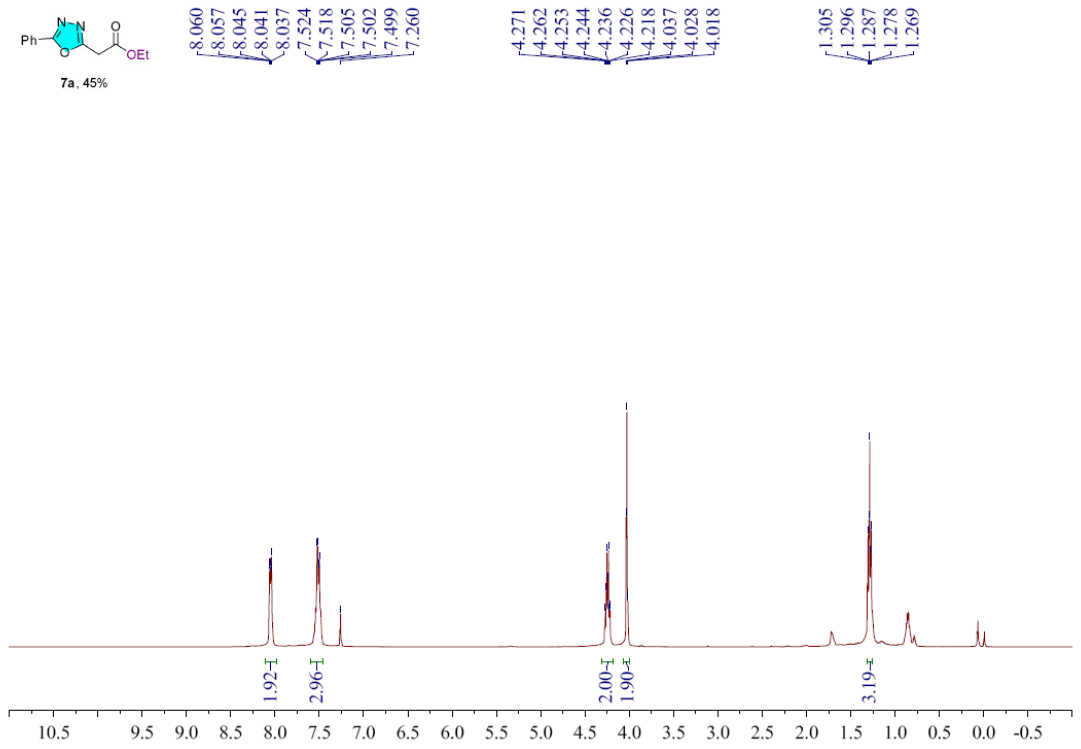
$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **6g** (100 MHz, $CDCl_3$)



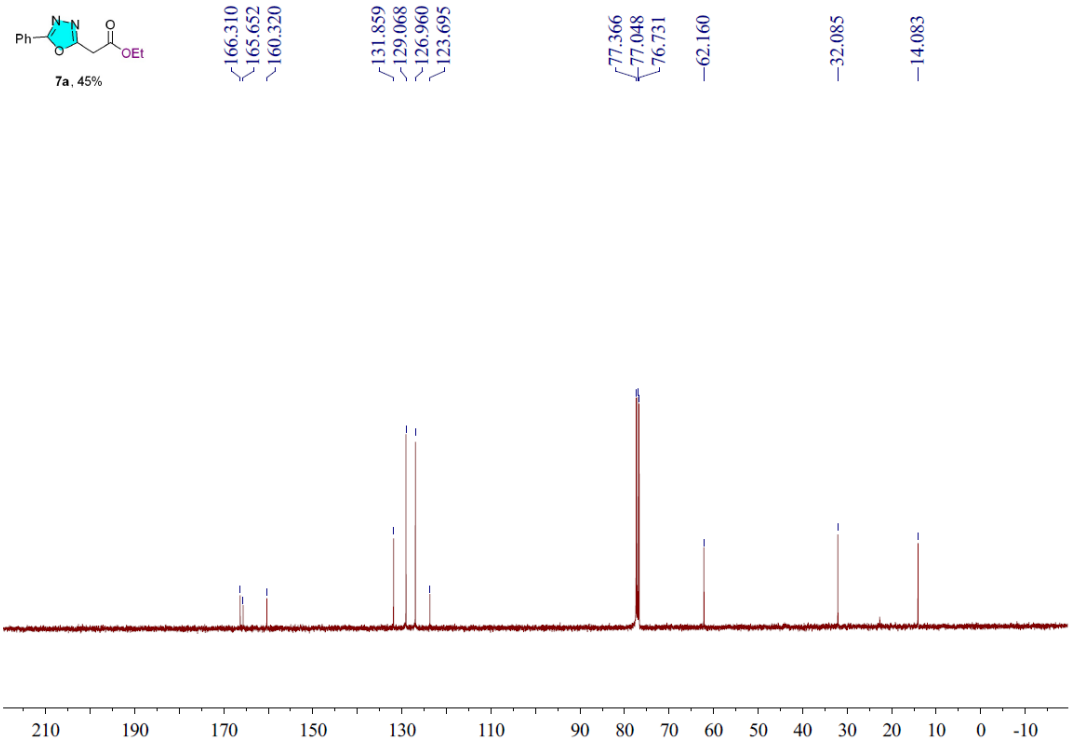
^{1}H NMR Spectrum of Compound **6h** (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **6h** (100 MHz, $CDCl_3$)



^{1}H NMR Spectrum of Compound **7a** (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR Spectrum of Compound **7a** (100 MHz, $CDCl_3$)