Supplementary Information

Recyclable Picolinamide-Derived Ligand-Controlled Branched-Selective Hydroesterification of Alkynes with Alcohols and Phenols

Ding Liu, [a,b] Luyun Zhang, [a,b] Jiaxin Cheng, [a,b] Qiuxiang Wei, [a,b] Zhenhua Jia,* [a,b] Fen-Er Chen* [a,b]

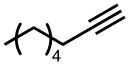
[a] D. Liu, L. Zhang, J. Cheng, Q. Wei, Prof. Dr. Z. Jia* and Prof. Dr. F.-E. Chen*
Department Engineering Center of Catalysis and Synthesis for Chiral Molecules, Department of Chemistry, Fudan University, Shanghai 200433, China.
E-mail: zhenhua_jia@fudan.edu.cn; E-mail: rfchen@fudan.edu.cn
[b] Shanghai Engineering Center of Industrial Asymmetric Catalysis for Chiral Drugs, 200433, Shanghai, China.

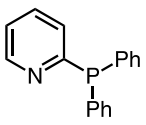
The PDF file includes:

Table of Contents

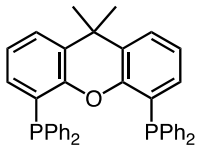
1. Tables and Figures.

Table S1. Selected examples of alkyne esterification reactions with CO.

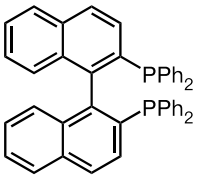
Entry	Representative substrate	Catalyst	Conditions	Selectivity	Ref.
1		$Pd(OAc)_2$ 2-$PyPPh_2$, MsOH	60 ºC 60 bar	99%	Drent **1993** [1]
2		$Pd(OAc)_2$ **S-L1**, MsOH	50 ºC, 40 bar MeOH	>99%	Matteoli **2001** [2]
3		$Pd(OAc)_2$ **S-L2**, TsOH	100 ºC, 60 bar MeOH	86%	Woollins **2002** [3]
4		$Pd(OAc)_2$ **S-L3**, MsOH	50 ºC, 10 bar MeOH	86%	Green **2004** [4]
5		$Pd(OAc)_2$ BINAP, $Al(OTf)_3$	80 ºC, 35 bar MeOH	99%	Williams **2011** [5]
6		$Pd(OAc)_2$ **S-L4**, TsOH	80 ºC, 20 bar (CO/H_2) MeCN	99%	Brüggeller **2012** [6]
7		$Pd(OAc)_2$ **S-L5**, TsOH	60 ºC, 45 bar MeOH	95%	Sparkes **2017** [7]
8		$PdCl_2$ **S-L6**, TsOH	60 ºC, 60 bar MeCN	99%	Li **2018** [8]
9		$Pd(acac)_2$ **S-L7**, TsOH	80 ºC, 40 bar MeOH	95%	Beller **2018** [9]
10		$Pd(OAc)_2$ **L5**, TsOH	25 ºC, 40 bar MeOH	>99%	Our results **2022** [10]
11		$Pd(OAc)_2$ **S-L8**, MsOH	50 ºC, 40 bar MeOH	>99%	Doherty **2006** [11]
12		$Pd(MeCN)_2Cl_2$ **S-L9**, H_2O	110 ºC, 30 bar MeOH/Toluene	95	Liu **2019** [12]



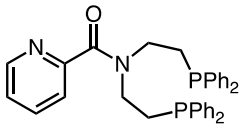
2-PyPPh$_2$



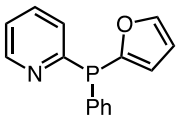
BINAP



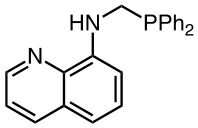
BINAP



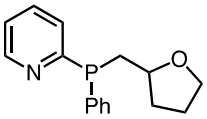
L5



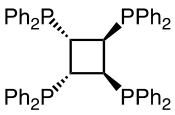
S-L1



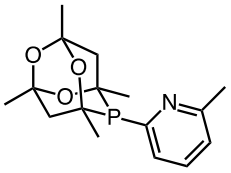
S-L2



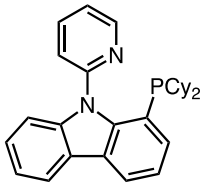
S-L3



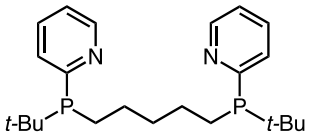
S-L4



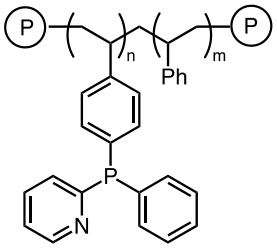
S-L5



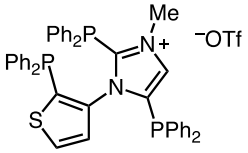
S-L6



S-L7

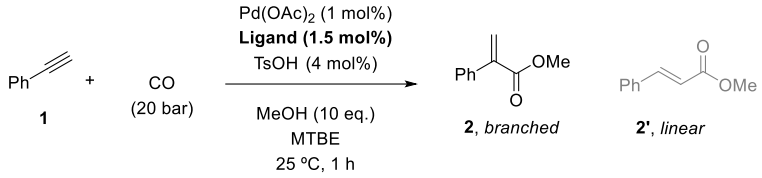


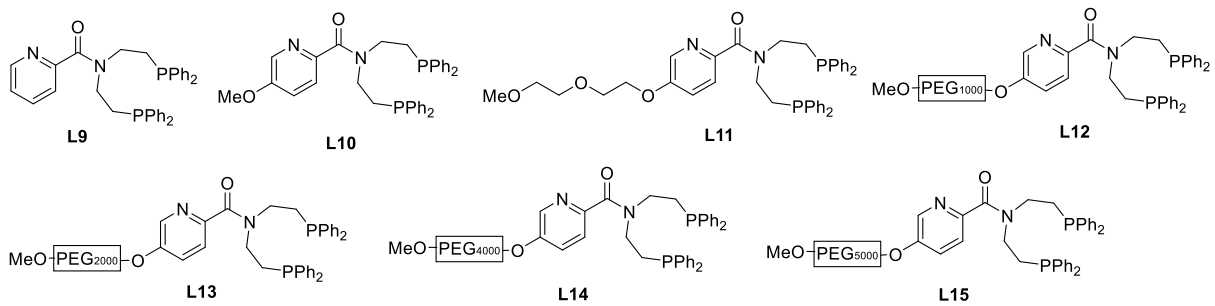
S-L8

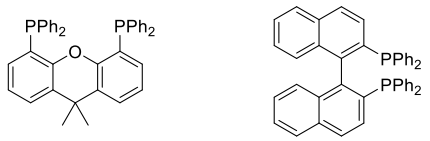


S-L9

Table S2. Ligand Screening.[a]



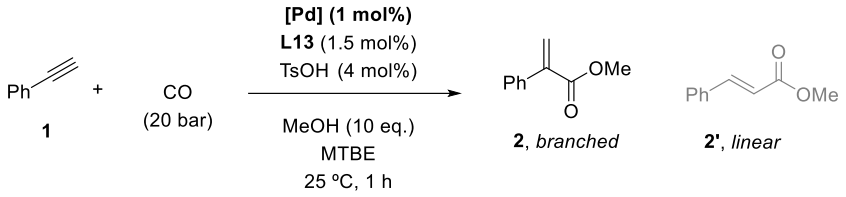




Entry	Ligands	Conversion (%)	Yield (%)	*b/l* ratio (**2 : 2'**)
1	**L9**	66	62	> 99:1
2	**L10**	74	69	> 99:1
3	**L11**	63	55	>99:1
4	**L12**	80	73	> 99:1
5	**L13**	>99	97 (93[b])	> 99:1
6	**L14**	92	86	> 99:1
7	**L15**	82	75	98:2
8	**L16**	N.d.	–	–
9	**L17**	N.d.	–	–
10	**L18**	N.d.	–	–

[a]Reactions were performed with **1** (0.5 mmol) and MeOH (10 eq.) in MTBE (1 mL). The conversions and *b*/*l* ratios were determined with ^{1}H NMR and GC analysis. [b]isolated yield.

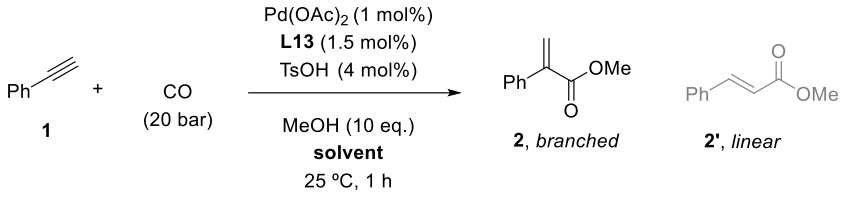
Table S3. Effects of palladium precursors.[a]



Entry	Pd salts	Conv. (%)	*b*/*l* ratio
1	$Pd(MeCN)_2Cl_2$	>99 (90[b])	>99:1
2	$PdCl_2$	85	>99:1
3	$PdBr_2$	35	65:35
4	$Pd_2(dba)_3 \cdot CHCl_3$	<5	n.d.
5	$Pd(TFA)_2$	82	>99:1
6	$Pd(OAc)_2$	>99 (93[b])	>99:1

[a]Reactions were performed with **1** (0.5 mmol) and MeOH (10 eq.) in MTBE (1 mL). The conversions and *b*/*l* ratios were determined with GC analysis, and yields were determined with ^{1}H NMR using tetrachloroethane as an internal standard. [b]Isolated yield.

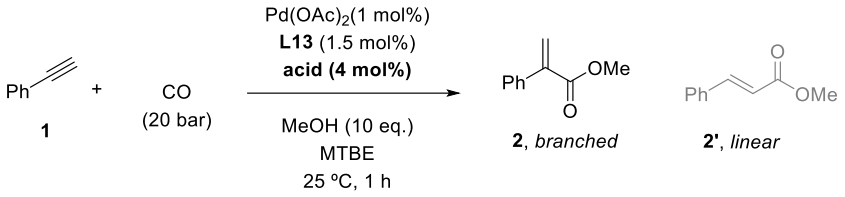
Table S4. Effect of solvents.[a]



Entry	Solvents	Conv. (%)	Yield (%)	*b*/*l* ratio
1	MTBE	>99	95	>99:1
2	$CHCl_3$	>99	94	>99:1
3	2-Me THF	>99	90	>99:1
4	Et_2O	>99	92	>99:1
5	THF	90	84	>99:1
6	EtOAc	92	86	>99:1

[a]Reactions were performed with **1** (0.5 mmol) and MeOH (10 eq.) in solvent (1 mL). The conversions and *b*/*l* ratios were determined with GC analysis, and yields were determined with ^{1}H NMR using tetrachloroethane as an internal standard.

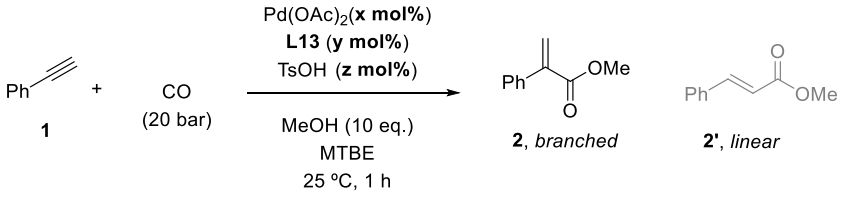
Table S5. Effect of acids.[a]



Entry	Acids	Conv. (%)	*b*/*l* ratio
1	-	n.d.	-
2	TsOH	>99	>99:1
3	MSA	72	>99:1
4	TFA	25	-

[a]Reactions were performed with **1** (0.5 mmol) and MeOH (10 eq.) in MTBE (1 mL). The conversions and *b*/*l* ratios were determined with ^{1}H NMR and GC analysis.

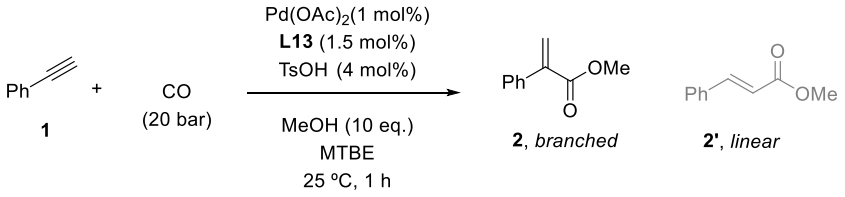
Table S6. Effect of catalyst loading.[a]



Entry	Pd:L:acid	Conv. (%)	*b*/*l* ratio
1	1:1:4	96	>99:1
2	1:1.5:4	>99	>99:1
3	1:2:4	91	>99:1
4	0.5:0.75:2	75	>99:1

[a]Reactions were performed with **1** (0.5 mmol) and MeOH (10 eq.) in MTBE (1 mL). The conversions and *b*/*l* ratios were determined with ^{1}H NMR and GC analysis.

Table S7. Catalyst recycling.[a,b]



Entry	Runs	Conv. (%)	*b*/*l* ratio	Pd leaching[b]
1	1	>95	99:1	< 0.1%
2	2	>95	99:1	< 0.1%
3	3	>95	99:1	< 0.1%
4	4	>95	99:1	< 0.1%
5	5	>95	99:1	< 0.1%
6	6	90	99:1	0.12%

[a]Reactions were performed with **1** (0.5 mmol) and MeOH (10 eq.) in MTBE (1 mL). The conversions and *b*/*l* ratios were determined with ^{1}H NMR and GC analysis. [b]Pd leaching was determined by ICP-MS.

Figure S1. FT-IR spectra of indicated compounds.

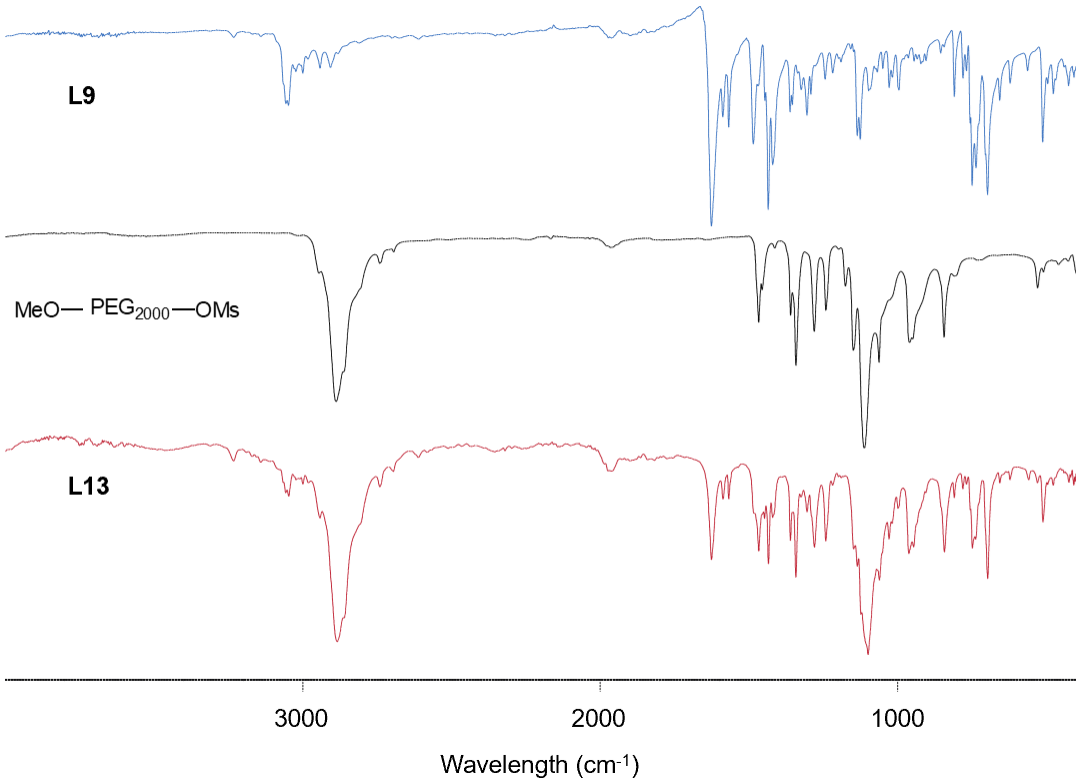


Figure S2. MALDI analysis of indicated compounds.

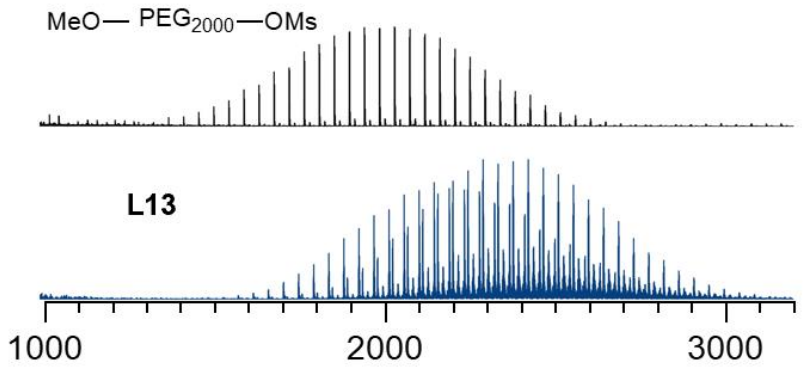
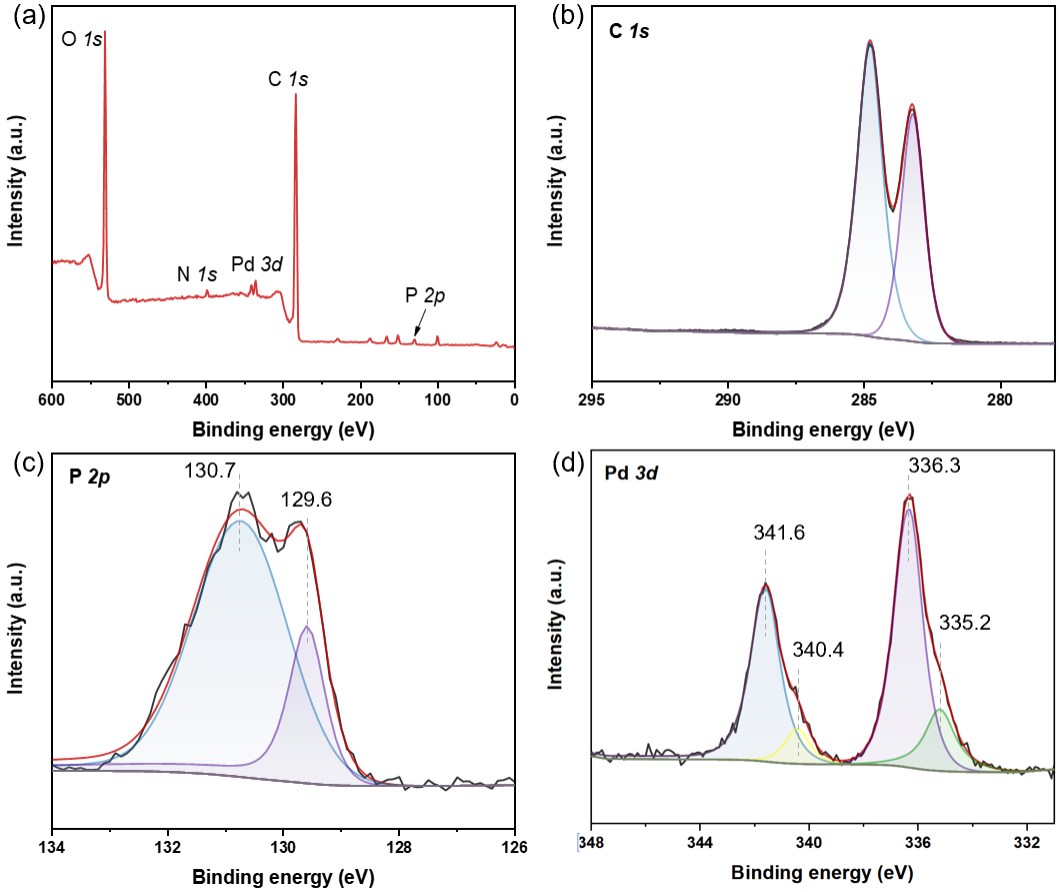
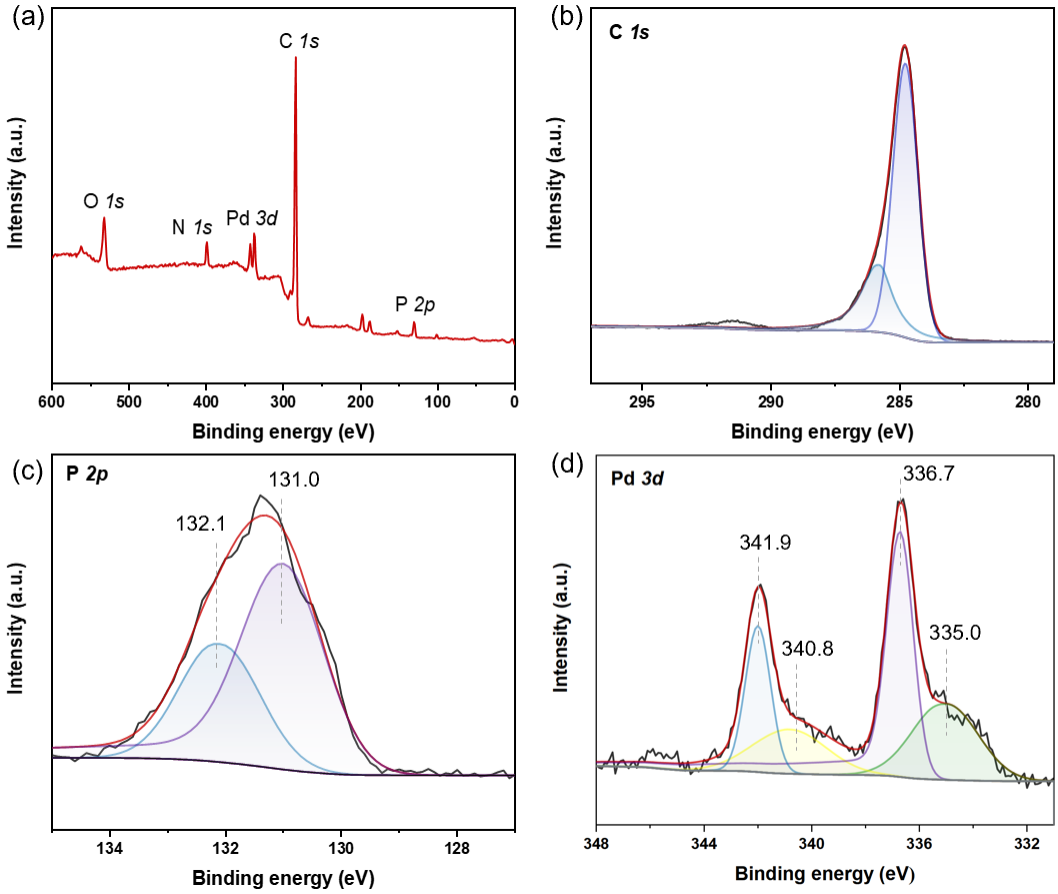


Figure S3. Surface chemical composition and chemical state of Pd/L13.



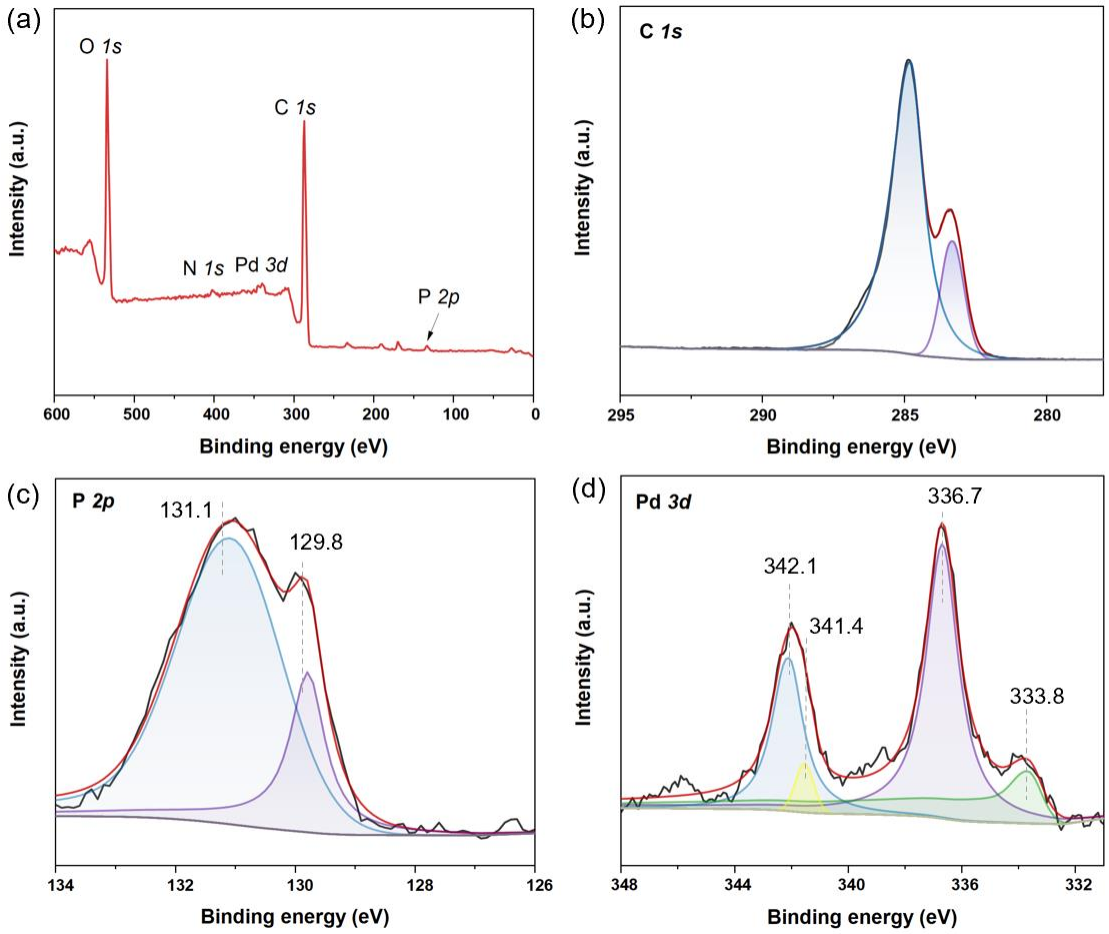
a. XPS survey spectra. b. C *1s* spectra. c. P *2p* spectra. d. Pd *3d* spectra.

Figure S4. Surface chemical composition and chemical state of Pd/L10.



a. XPS survey spectra. b. C *1s* spectra. c. P *2p* spectra. d. Pd *3d* spectra.

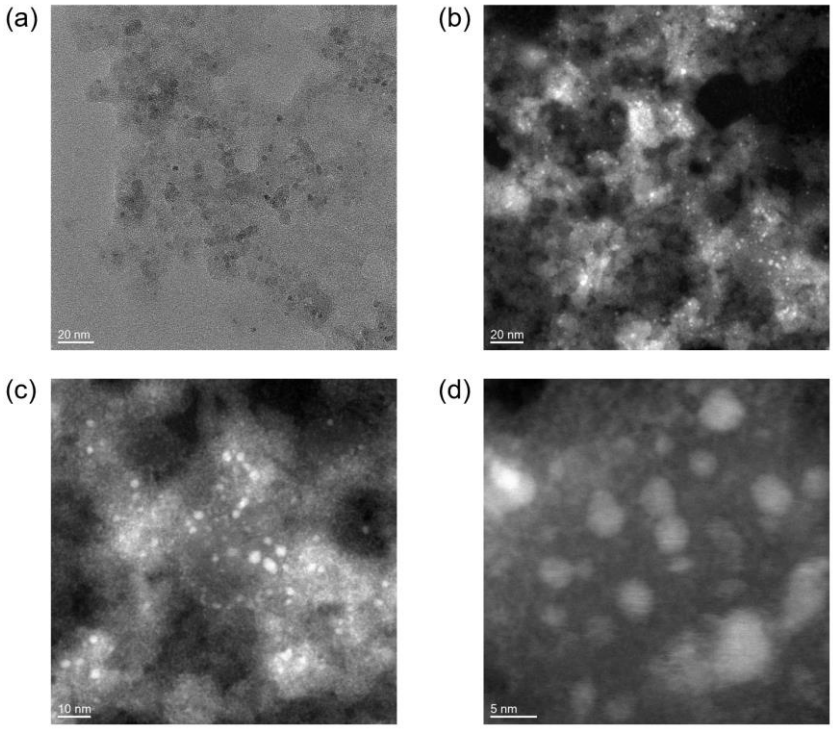
Figure S5. Surface chemical composition and chemical state of Pd/L13 after 5 runs.



a. XPS survey spectra. b. C *1s* spectra. c. P *2p* spectra. d. Pd *3d* spectra.

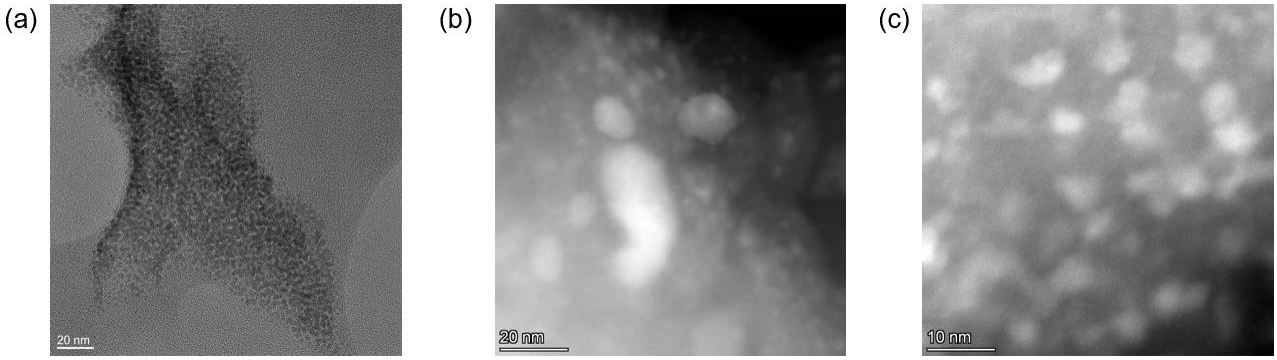
The XPS spectra of the catalyst show consistent major peaks after five cycles, aligning with its robust catalytic performance upon recycling.

Figure S6. TEM images of Pd/L13 complex.



a. TEM image. b-d. HAADF-STEM.

Figure S7. TEM images of Pd/L10 complex.



a. TEM image. b-c. HAADF-STEM.

2. General Procedures

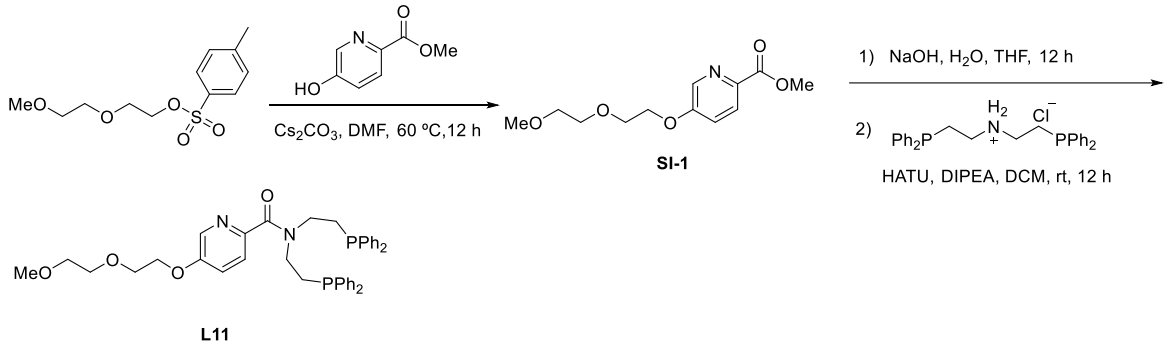
Commercial reagents and solvents were ordered from Aldrich, TCI, and Bidepharm. Reagents and solvents were used as received unless otherwise stated. Where necessary, solvents were purified by passing through columns of alumina using a solvent purification system. Commercially available alkyne substrates were used as received, and other alkynes were prepared according to our previous procedure[10, 13]. Air- and moisture-sensitive synthesis were performed under nitrogen atmosphere with oven-dried glassware. Column chromatography was performed on silica gel (100-200 mesh). Thin-layer chromatography (TLC) was performed on EM reagents 0.25 mm silica 60-F plates.

NMR spectra were recorded with a Bruker AVANCE III (400 MHz) spectrometer. ^{1}H NMR spectra are reported in parts per million on the δ scale, and are referenced from the residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ($CHCl_3$), CD_3OD: δ 3.31 (CHD_2OD), DMSO-d_6: δ 2.50 (DMSO-d_5)). Data are reported as follows: chemical shift [multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant(s) in Hertz, integration]. ^{13}C NMR spectra are reported in parts per million on the δ scale, and are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.16, CD_3OD: δ 49.00, DMSO-d_6: δ 39.52). ^{31}P {^{1}H} NMR spectra are reported in parts per million on the δ scale. Data are reported as follows: chemical shift (assignment). GC-MS analysis was carried out on Agilent 7820A GC system and Angilent 5977B MSD. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF spectrometer with electron spray ionization (ESI). Matrix-assisted laser desorption/ionization time of flight mass spectra (MALDI-TOF-MS) were recorded on ultrafleXtreme. Infrared data (IR) were obtained with a Thermo Fisher Scientific FT-IR. Transmission electron microscopy (TEM) analysis was perforemed at FEI Talos F200X G2. X-ray photoelectron spectra (XPS) were recorded on AXIS Kratos Supra^{+}. The Pd leaching was determined by inductively coupled plasma mass spectrometry (ICP-MS) using Agilent 7800 ICP-MS.

3. Preparation and characterization of PEG-supported ligands

Ligands **L9** and **L10** were prepared according to our previous procedure [10]. Ligand **L16-L18** were commercially available and used without further purification.

Synthesis of L11



2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate (SI-1)

To a solution of 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate (0.48 g, 1.8 mmol) and methyl 5-hydroxypicolinate (0.33 g, 2.2 mmol) in DMF (10 mL), cesium carbonate (0.71 g, 2.2 mmol) was added at 0 ºC under nitrogen atmosphere. The solution was stirred at 60 ºC for 12 h. The mixture was cooled to room temperature and filtered through a pad of Celite. The mixture was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with DCM/MeOH (50:1) as eluent to give **SI-1** (0.30 g, 65% yield).

Physical State: colorless sticky oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 2.9 Hz, 1H), 8.02 (d, *J* = 8.7 Hz, 1H), 7.22 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.21-4.16 (m, 2H), 3.90 (s, 3H), 3.86-3.80 (m, 2H), 3.68-3.61 (m, 2H), 3.53-3.48 (m, 2H), 3.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 157.5, 140.2, 138.6, 126.5, 120.4, 71.8, 70.8, 69.4, 68.0, 59.1, 52.6.

HRMS (ESI): Calcd. for $C_{12}H_{18}NO_5$ $[M+H]^+$: 256.1180, found: 256.1179.

N,N-bis(2-(diphenylphosphaneyl)ethyl)-5-(2-(2-methoxyethoxy)ethoxy)picolinamide (L11)

To a solution of **SI-1** (0.30 g, 1.2 mmol) in THF/H_2O (*v*/*v* = 9/1, 10 mL) sodium hydroxide (0.20 g, 4.8 mmol) was added at room temperature. The reaction was then stirred at room temperature for 12 h. The mixture was filtered through a pad of Celite and concentrated under reduced pressure to afford a colourless solid. The solid was used directly in the next step without further purification.

To a solution of the above solid and bis(2-(diphenylphosphanyl)ethyl)ammonium chloride (0.67 g, 1.4 mmol) in dry DCM (20 mL), HATU (0.45 g, 1.2 mmol) and DIPEA (0.30 g, 2.4 mmol) were added at 0 ºC under nitrogen atmosphere. The mixture was then stirred at room temperature for 12 h. The resulting mixture was diluted with DCM (10 mL). The mixture was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with DCM/MeOH (20:1) as eluent to give **L11** (0.30 g, 58% yield).

Physical State: colourless amorphous solid

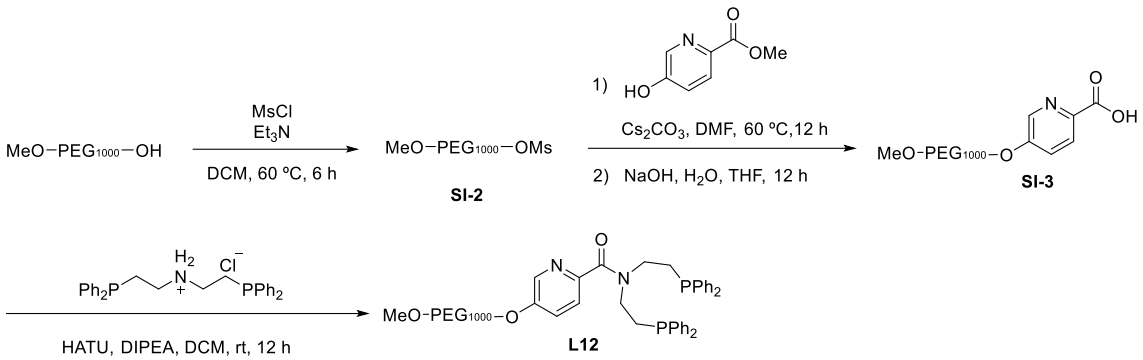
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 2.8 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.51-7.45 (m, 4H), 7.36-7.27 (m, 16H), 7.19 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.23-4.14 (m, 2H), 3.94-3.86 (m, 2H), 3.78-3.71 (m, 2H), 3.62-3.50 (m, 6H), 3.40 (s, 3H), 2.51-2.43 (m, 2H), 2.41-2.31 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 155.4, 146.4, 137.9 (d, *J* = 12.3 Hz), 137.6 (d, *J* = 12.1 Hz), 136.0, 132.8 (d, *J* = 10.4 Hz), 132.6 (d, *J* = 10.5 Hz), 128.8, 128.63, 128.57, 128.5, 124.9, 121.4, 72.0, 70.9, 69.6, 67.9, 59.2, 47.1 (d, *J* = 28.9 Hz), 44.3 (d, *J* = 24.1 Hz), 27.9 (d, *J* = 14.3 Hz), 26.3 (d, *J* = 14.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ -20.57, -20.83.

HRMS (ESI): Calcd. for $C_{39}H_{43}N_2O_4P_2$ $[M+H]^+$: 665.2693, found: 665.2690.

Synthesis of L12



PEG1000-mesylate (SI-2) [14]

To a solution of methoxypolyethylene glycols (MeO-PEG-OH, 4.20 g, 4.0 mmol, M.W. = 1000) and Et_3N (2.20 mL, 16.0 mmol) in dry dichloromethane (50 mL), MsCl (0.94 g, 8.0 mmol) was added at 0 ºC under nitrogen atmosphere. The mixture was then refluxed at 60 ºC for 6 h. The mixture was cooled to room temperature and diluted with DCM (50 mL). The mixture was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was added to cold *tert*-butyl methyl ether (100 mL). The resulting precipitates were collected, washed with cold *tert*-butyl methyl ether (50 mL) and dried to give **SI-2** (3.72 g, 92%).

Physical State: colourless amorphous solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.36-4.26 (m, 2H), 3.72-3.68 (m, 2H), 3.64-3.53 (m, 86H), 3.51-3.45 (m, 2H), 3.31 (s, 3H), 3.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 71.9, 70.6-70.4 (overlapping signals), 69.3, 69.0, 59.0, 37.7.

PEG1000-picolinic acid (SI-3)

To a solution of **SI-2** (3.72 g, 3.7 mmol) and methyl 5-hydroxypicolinate (0.73 g, 4.8 mmol) in DMF (50 mL), cesium carbonate (7.19 g, 22.1 mmol) was added at 0 ºC under nitrogen atmosphere. The mixture was stirred at 60 ºC for 12 h. The mixture was cooled to room temperature and filtered through a pad of Celite. The mixture was concentrated to afford a colourless solid. The solid was used directly in the next step without further purification.

To a solution of the above solid in THF/H_2O (*v*/*v* = 9/1, 80 mL), sodium hydroxide (0.59 g, 14.7 mmol) was added. The reaction was then stirred at room temperature for 12 h. The mixture was filtered through a pad of Celite and concentrated under reduced pressure. The residue was added dropwise to cold *tert*-butyl methyl ether (100 mL). The resulting precipitates were collected, washed with cold *tert*-butyl methyl ether (50 mL) and dried to give **SI-3** (3.36 g, 80%).

Physical State: colourless amorphous solid

^{1}H NMR (400 MHz, MeOD): δ 8.33 (s, 1H), 8.02 (d, *J* = 8.7 Hz, 1H), 7.43 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.30-4.24 (m, 2H), 3.91-3.87 (m, 2H), 3.68-3.61 (m, 86H), 3.58-3.54 (m, 2H), 3.38 (s, 3H).

^{13}C NMR (100 MHz, MeOD): δ 172.3, 157.8, 148.5, 138.2, 126.3, 122.4, 72.6, 71.6, 71.2-70.6 (overlapping signals), 69.3, 59.2.

PEG1000-picolinamide (L12)

To a solution of **SI-3** (3.36 g, 3.0 mmol) and bis(2-(diphenylphosphanyl)ethyl)ammonium chloride (1.81 g, 3.6 mmol) in dry DCM (30 mL), HATU (1.37 g, 3.6 mmol) and DIPEA (0.78 g, 6.0 mmol) were added at 0 ºC under nitrogen atmosphere. The mixture was then stirred at room temperature for 12 h. The resulting mixture was diluted with DCM (50 mL). The mixture was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was added dropwise to cold *tert*-butyl methyl ether (100 mL). The resulting precipitates were collected, washed with cold *tert*-butyl methyl ether (50 mL) and dried to give **L12** (2.77 g, 59%). The catalyst loading of PEG-supported ligand **L12** was calculated as 0.69 mmol/g. The catalyst loading (mmol/g) of PEG-supported ligands was determined using ^{1}H NMR with tetrachloroethane (TCE) as an internal standard. The calculation was performed according to the following equation:

$$Cat.loading = \frac{n_{TCE} \times R_{lig/TCE}}{W_{lig}}$$

Where n_{TCE} represents the molar amount of TCE, $R_{lig/TCE}$ represents the normalized integration ratio of the ligand to TCE, and W_{lig}represents the weight of ligand

Physical State: colourless amorphous solid

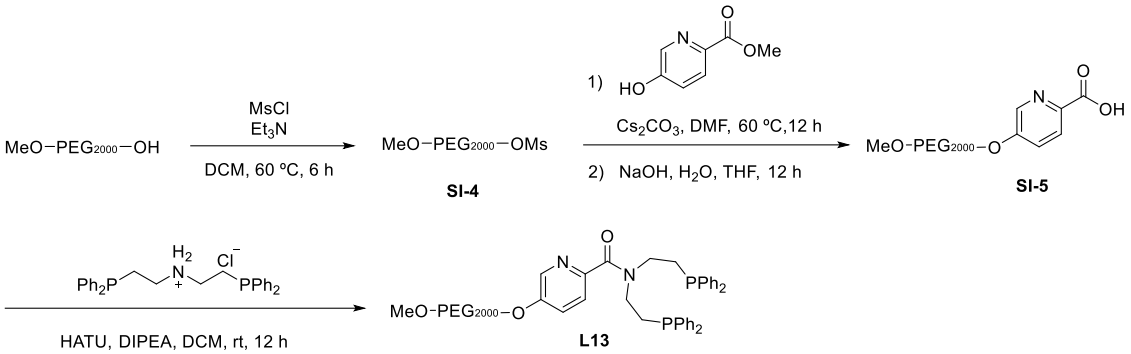
^{1}H NMR (400 MHz, MeOD): δ 7.99 (d, *J* = 2.8 Hz, 1H), 7.51-7.41 (m, 5H), 7.38-7.17 (m, 17H), 4.28-4.18 (m, 2H), 3.93-3.87 (m, 2H), 3.74-3.70 (m, 2H), 3.70-3.55 (m, 84H), 3.55-3.52 (m, 2H), 3.47-3.37 (m, 3H), 3.35 (s, 3H), 2.51-2.40 (m, 2H), 2.33-2.23 (m, 2H).

^{13}C NMR (100 MHz, MeOD): δ 170.4, 157.2, 147.0, 139.3 (d, *J* = 12.6 Hz), 138.7 (d, *J* = 12.4 Hz), 137.6, 133.8 (d, *J* = 10.8 Hz), 133.6 (d, *J* = 10.7 Hz), 129.98, 129.95, 129.74 (d, *J* = 2.5 Hz),

129.67 (d, *J* = 2.6 Hz), 125.5, 122.9, 72.8, 71.7, 71.5, 71.4-71.1 (overlapping signals), 70.5, 69.3, 59.1, 47.9 (d, *J* = 26.6 Hz), 44.8 (d, *J* = 24.7 Hz), 28.5 (d, *J* = 14.5 Hz), 27.2 (d, *J* = 14.2 Hz).

^{31}P NMR (162 MHz, MeOD): δ -21.02, -21.38.

Synthesis of **L13**



PEG2000-mesylate (SI-4) [15]

To a solution of methoxypolyethylene glycols (MeO-PEG-OH, 8.10 g, 4.0 mmol, M.W. = 2000) and Et_3N (2.22 mL, 16.0 mmol) in dry dichloromethane (50 mL), MsCl (0.92g, 8.0 mmol) was added at 0 ºC under nitrogen atmosphere. The solution was then refluxed at 60 ºC for 6 h. The mixture was cooled to room temperature and diluted with DCM (50 mL). The mixture was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was added to cold *tert*-butyl methyl ether (100 mL). The resulting precipitates were collected, washed with cold *tert*-butyl methyl ether (50 mL) and dried to give **SI-4** (7.90 g, 96%).

Physical State: colourless amorphous solid

^{1}H NMR (400 MHz, CDCl3): δ 4.38-4.29 (m, 2H), 3.91-3.76 (m, 2H), 3.75-3.72 (m, 2H), 3.70-3.54 (m, 176H), 3.53-3.39 (m, 4H), 3.34 (s, 3H), 3.05 (s, 3H).

PEG2000-picolinic acid (SI-5)

To a solution of **SI-4** (7.90 g, 3.8 mmol) and methyl 5-hydroxypicolinate (0.76 g, 4.9 mmol) in DMF (50 mL), cesium carbonate (7.42 g, 22.8 mmol) was added at 0 ºC under nitrogen atmosphere. The mixture was stirred at 60 ºC for 12 h. The resulting mixture was cooled to room temperature and filtered through a pad of Celite. The filtrate was concentrated to afford a colourless solid. The solid was used directly in the next step without further purification.

To a solution of the above solid in THF/H_2O (*v*/*v* = 9/1, 80 mL), sodium hydroxide (0.61 g, 15.2 mmol) was added at room temperature. The reaction was then stirred at room temperature for 12

h. The mixture was filtered through a pad of Celite and concentrated under reduced pressure. The residue was added dropwise to cold *tert*-butyl methyl ether (100 mL). The resulting precipitates were collected, washed with cold *tert*-butyl methyl ether (50 mL) and dried to give **SI-5** (7.13 g, 84%).

Physical State: colourless solid

^{1}H NMR (400 MHz, MeOD): δ 8.32 (s, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.41 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.35-4.11 (m, 2H), 3.93-3.85 (m, 2H), 3.83-3.50 (m, 180H), 3.49-3.41 (m, 2H), 3.36 (s, 3H).

^{13}C NMR (100 MHz, MeOD): δ 172.4, 157.7, 148.4, 137.8, 126.1, 122.4, 72.9, 71.7-71.2 (overlapping signals), 70.6, 69.2, 59.1.

PEG2000-picolinamide (L13)

To a solution of **SI-6** (7.13 g, 3.2 mmol) and bis(2-(diphenylphosphanyl)ethyl)ammonium chloride (1.81 g, 3.8 mmol) in dry DCM (30 mL), HATU (1.44 g, 3.8 mmol) and DIPEA (0.83 g, 6.4 mmol) were added at 0 ºC under nitrogen atmosphere. The solution was then stirred at room temperature for 12 h. The resulting mixture was diluted with DCM (50 mL). The mixture was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was added to cold *tert*-butyl methyl ether (100 mL). The resulting precipitates were collected, washed with cold *tert*-butyl methyl ether (50 mL) and dried to give **L13** (5.05 g, 62%). The catalyst loading of PEG-supported ligand **L13** was calculated as 0.41 mmol/g.

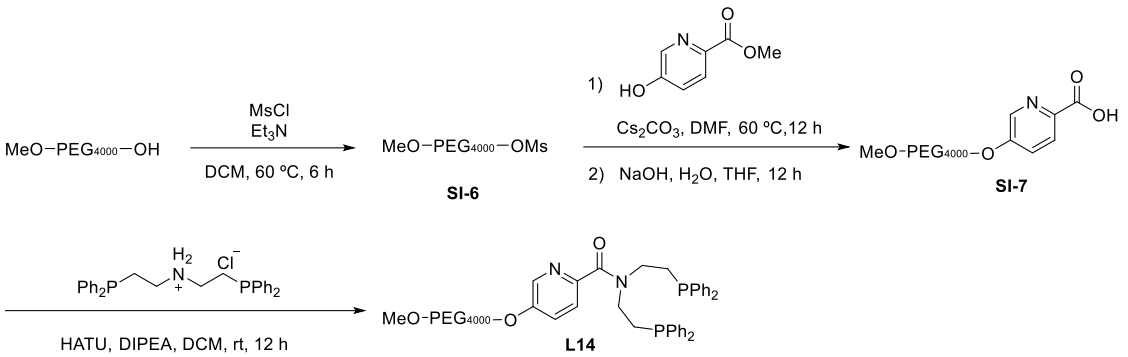
Physical State: colourless amorphous solid

^{1}H NMR (400 MHz, MeOD): δ 8.00 (d, *J* = 2.7 Hz, 1H), 7.51-7.41 (m, 5H), 7.39-7.32 (m, 8H), 7.32-7.18 (m, 9H), 4.29-4.15 (m, 2H), 3.96-3.87 (m, 2H), 3.85-3.77 (m, 2H), 3.74-3.71 (m, 2H), 3.70-3.55 (m, 178H), 3.55-3.52 (m, 2H), 3.46-3.41 (m, 2H), 3.35 (s, 3H), 2.52-2.42 (m, 2H), 2.35-2.24 (m, 2H).

^{13}C NMR (100 MHz, MeOD): δ 170.4, 157.2, 147.0, 139.3 (d, *J* = 12.7 Hz), 138.7 (d, *J* = 12.3 Hz), 137.6, 133.8 (d, *J* = 9.8 Hz), 133.6 (d, *J* = 9.7 Hz), 130.1, 130.0, 129.8, 129.7, 125.6, 122.9, 72.9, 71.8-71.3 (overlapping signals), 70.6, 69.4, 59.1, 47.9 (d, *J* = 26.9 Hz), 44.9 (d, *J* = 24.3 Hz), 28.5 (d, *J* = 15.0 Hz), 27.2 (d, *J* = 14.5 Hz).

^{31}P NMR (162 MHz, MeOD) δ -21.02, -21.46.

Synthesis of **L14**



PEG4000-mesylate (SI-6) [15]

To a solution of methoxypolyethylene glycols (MeO-PEG-OH, 8.35 g, 2.0 mmol, M.W. = 4000) and Et_3N (1.20 mL, 8.0 mmol) in dry dichloromethane (50 mL), MsCl (0.48 g, 4.0 mmol) was added at 0 ºC under nitrogen atmosphere. The mixture was then refluxed at 60 ºC for 6 h. The resulting mixture was cooled to room temperature and diluted with DCM (50 mL). The mixture was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was added to cold *tert*-butyl methyl ether (100 mL). The resulting precipitates were collected, washed with cold *tert*-butyl methyl ether (50 mL) and dried to give **SI-6** (7.90 g, 95%).

Physical State: colourless amorphous solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.33-4.31 (m, 2H), 3.88-3.36 (m, 286H), 3.32 (s, 3H), 3.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 71.9, 70.6-70.5 (overlapping signals), 69.3, 69.0, 59.0, 37.7.

PEG4000-picolinic acid (SI-7)

To a solution of **SI-6** (7.90 g, 1.9 mmol) and methyl 5-hydroxypicolinate (0.38 g, 2.5 mmol) in DMF (50 mL), cesium carbonate (3.71 g, 11.4 mmol) was added at 0 ºC under nitrogen atmosphere. The mixture was stirred at 60 ºC for 12 h. The mixture was cooled to room temperature and filtered through a pad of Celite. The filtrate was concentrated to afford a colourless solid. The solid was used directly in the next step without further purification.

To a solution of the above solid in THF/H_2O (*v*/*v* = 9/1, 80 mL), sodium hydroxide (0.31 g, 7.6 mmol) was added. The reaction was then stirred at room temperature for 12 h. The mixture was filtered through a pad of Celite and concentrated under reduced pressure. The residue was added

dropwise to cold *tert*-butyl methyl ether (100 mL). The resulting precipitates were collected, washed with cold *tert*-butyl methyl ether (50 mL) and dried to give **SI-7** (6.58 g, 76%).

Physical State: colourless solid

^{1}H NMR (400 MHz, MeOD): δ 8.27 (s, 1H), 8.11-7.99 (m, 1H), 7.49-7.32 (m, 1H), 4.99-4.93 (m, 2H), 4.33-4.21 (m, 2H), 3.92-3.44 (m, 284H), 3.36 (s, 3H).

^{13}C NMR (100 MHz, MeOD): δ 172.0, 157.5, 148.9, 138.0, 126.2, 122.1, 73.4, 72.8, 71.7-71.0 (overlapping signals), 70.6, 69.2, 61.9, 59.1.

PEG4000-picolinamide (L14)

To a solution of **SI-7** (6.58 g, 1.4 mmol) and bis(2-(diphenylphosphanyl)ethyl)ammonium chloride (0.83 g, 1.7 mmol) in dry DCM (30 mL), HATU (0.66 g, 1.7 mmol) and DIPEA (0.22 g, 3.4 mmol) were added at 0 ºC under nitrogen atmosphere. The mixture was then stirred at room temperature for 12 h. The resulting mixture was diluted with DCM (50 mL). The mixture was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was added to cold *tert*-butyl methyl ether (100 mL). The resulting precipitates were collected, washed with cold *tert*-butyl methyl ether (50 mL) and dried to give **L14** (3.64 g, 57%). The catalyst loading of PEG-supported ligand **L14** was calculated as 0.22 mmol/g.

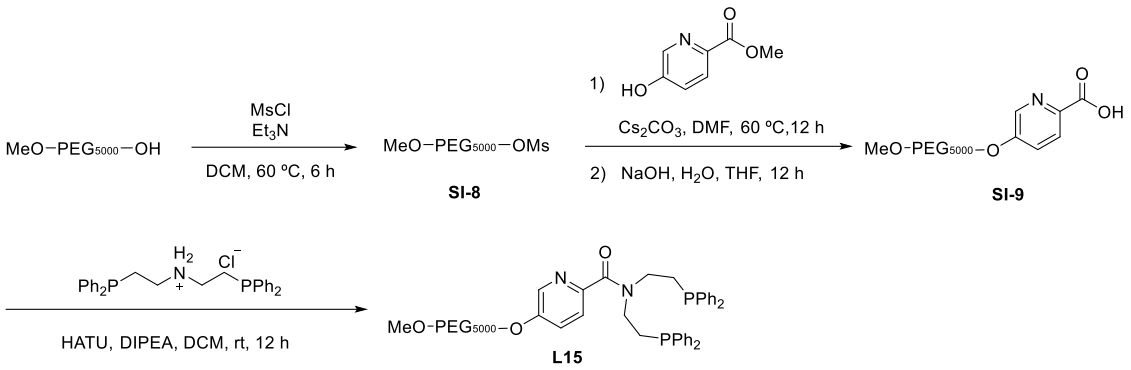
Physical State: colourless amorphous solid

^{1}H NMR (400 MHz, MeOD): δ 8.01-7.99 (m, 1H), 7.48-7.44 (m, 5H), 7.34-7.23 (m, 17H), 4.24-4.22 (m, 2H), 3.90-3.88 (m, 2H), 3.86-3.49 (m, 286H), 3.45-3.42 (m, 2H), 3.35 (s, 3H), 2.49-2.44 (m, 2H), 2.31-2.27 (m, 2H).

^{13}C NMR (100 MHz, MeOD): δ 170.5, 157.2, 147.1, 139.3 (d, *J* = 12.5 Hz), 138.7 (d, *J* = 12.5 Hz), 137.7, 133.8 (d, *J* = 10.9 Hz), 133.6 (d, *J* = 10.9 Hz), 129.99, 129.95, 129.74 (d, *J* = 2.4 Hz), 129.67 (d, *J* = 2.5 Hz), 125.5, 122.9, 72.9, 71.8, 71.6-71.2 (overlapping signals), 70.6, 69.4, 59.1, 48.0 (d, *J* = 25.9 Hz), 44.9 (d, *J* = 24.8 Hz), 28.5 (d, *J* = 14.1 Hz), 27.2 (d, *J* = 14.2 Hz).

^{31}P NMR (162 MHz, MeOD): δ -21.02, -21.37.

Synthesis of **L15**



PEG5000-mesylate (SI-8)

To a solution of methoxypolyethylene glycols (MeO-PEG-OH, 10.45 g, 2.0 mmol, M.W. = 5000) and Et_3N (1.20 mL, 8.0 mmol) in dry DCM (50 mL), MsCl (0.48 g, 4.0 mmol) was added at 0 ºC under nitrogen atmosphere. The mixture was then refluxed at 60 ºC for 6 h. The resulting mixture was cooled to room temperature and diluted with DCM (50 mL). The mixture was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was added to cold *tert*-butyl methyl ether (100 mL). The resulting precipitates were collected, washed with cold *tert*-butyl methyl ether (50 mL) and dried to give **SI-8** (8.55 g, 85%).
Physical State: colourless amorphous solid
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.39-4.35 (m, 2H), 3.82-3.79 (m, 2H), 3.77-3.74 (m, 2H), 3.67-3.60 (m, 504H), 3.55-3.52 (m, 2H), 3.47-3.44 (m, 2H), 3.37 (s, 3H), 3.08 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 71.7, 70.8-70.1 (overlapping signals), 69.1, 68.8, 58.8, 37.5.

PEG5000-picolinic acid (SI-9)

To a solution of **SI-8** (8.50 g, 1.7 mmol) and methyl 5-hydroxypicolinate (0.34 g, 2.3 mmol) in DMF (50 mL), cesium carbonate (4.46 g, 13.7 mmol) was added at 0 ºC under nitrogen atmosphere. The suspension was stirred at 60 ºC for 12 h. The mixture was cooled to room temperature and filtered through a pad of Celite. The mixture was concentrated to afford a colourless solid. The solid was used directly in the next step without further purification.
To a solution of the above solid in THF/H_2O (*v*/*v* = 9/1, 70 mL), sodium hydroxide (0.13 g, 6.8 mmol) was added. The reaction was then stirred at room temperature for 12 h. The mixture was filtered through a pad of Celite and concentrated under reduced pressure. The residue was added

to cold *tert*-butyl methyl ether (100 mL). The resulting precipitates were collected, washed with cold *tert*-butyl methyl ether (50 mL) and dried to give **SI-9** (6.61 g, 75%).

Physical State: colourless amorphous solid

^{1}H NMR (400 MHz, MeOD): δ 8.26 (s, 1H), 8.13-7.97 (m, 1H), 7.49-7.31 (m, 1H), 4.31-4.23 (m, 2H), 3.91-3.86 (m, 2H), 3.84-3.80 (m, 4H), 3.75-3.53 (m, 502H), 3.49-3.44 (m, 4H), 3.36 (s, 3H).

^{13}C NMR (100 MHz, MeOD): δ 170.0, 157.5, 148.8, 137.9, 126.2, 122.2, 73.4, 72.8, 71.7-71.1 (overlapping signals), 70.5, 62.0, 59.1.

PEG5000-picolinamide (L15)

To a solution of **SI-9** (6.60 g, 1.3 mmol) and bis(2-(diphenylphosphanyl)ethyl)ammonium chloride (0.83 g, 1.7 mmol) in dry DCM (30 mL), HATU (0.66 g, 1.7 mmol) and DIPEA (0.22 g, 3.4 mmol) were added at 0 ºC under nitrogen atmosphere. The mixture was then stirred at room temperature for 12 h. The resulting mixture was diluted with DCM (50 mL). The mixture was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was added to cold *tert*-butyl methyl ether (100 mL). The resulting precipitates were collected, washed with cold *tert*-butyl methyl ether (50 mL) and dried to give **L15** (3.64 g, 57%). The catalyst loading of PEG-supported ligand **L15** was calculated as 0.18 mmol/g.

Physical State: colourless amorphous solid

^{1}H NMR (400 MHz, MeOD): δ 8.00 (d, *J* = 2.8 Hz, 1H), 7.72-7.43 (m, 6H), 7.42-7.14 (m, 16H), 4.26-4.21 (m, 2H), 3.95-3.87 (m, 4H), 3.83-3.79 (m, 4H), 3.73-3.53 (m, 504H), 3.48-3.44 (m, 4H), 3.36 (s, 3H), 2.52-2.42 (m, 2H), 2.37-2.24 (m, 2H).

^{13}C NMR (100 MHz, MeOD): δ 170.2, 157.1, 147.0, 139.2 (d, *J* = 12.7 Hz), 138.7 (d, *J* = 12.6 Hz), 137.5, 133.7 (d, *J* = 10.9 Hz), 133.6 (d, *J* = 11.1 Hz), 130.1, 129.9, 129.74 (d, *J* = 4.1 Hz), 129.67 (d, *J* = 4.3 Hz), 125.6, 122.8, 72.8, 71.7, 71.7-71.1 (overlapping signals), 70.5, 69.3, 59.1, 47.8 (d, *J* = 26.7 Hz), 44.8 (d, *J* = 25.0 Hz), 28.5 (d, *J* = 14.4 Hz), 27.1 (d, *J* = 14.2 Hz).

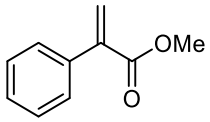
^{31}P NMR (162 MHz, MeOD): δ -21.10, -21.42.

4. General procedure for Pd-catalyzed hydroesterification of alkynes

A 10 mL reaction tube with a Teflon-coated stirring bar was charged with $Pd(OAc)_2$ (1.2 mg, 1.0 mol%), **L13** (18.4 mg, 1.5 mol%), TsOH (3.4 mg, 4.0 mol%), and nucleophile (10 eq, 5.0 mmol) in MTBE (1.0 mL). Alkyne (0.5 mmol) was added to the mixture. The tube was placed into a 300-mL stainless steel Parr autoclave (WP-MSAR-250A) equipped with an insert suitable for 4 reaction vials for conducting parallel reactions. The autoclave was purged three times with 20 bar of nitrogen and then pressurized with 20 bar of carbon monoxide. The reaction mixture was allowed to stir (800 rpm) at 25℃ for 1 h, and the pressure was carefully released. The reaction mixture was centrifugated and an aliquot of the supernatant was analyzed with GC to determine the conversions and *b/l* ratios. The supernatant was concentrated under reduced pressure, and yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The pure product was isolated by column chromatography on silica gel.

5. Characterization data of α,β-unsaturated carboxylic esters

methyl 2-phenylacrylate (2)



75.1 mg, 93% yield.

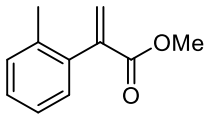
Physical State: light yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.32 (m, 5H), 6.38 (d, *J* = 1.3 Hz, 1H), 5.90 (d, *J* = 1.3 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 141.4, 136.8, 128.4, 128.3, 128.2, 127.0, 52.3.

HRMS (ESI): Calcd. for $C_{10}H_{11}O_2$ $[M+H]^+$: 163.0754, found: 163.0753.

methyl 2-(o-tolyl)acrylate (3)



73.4 mg, 84% yield.

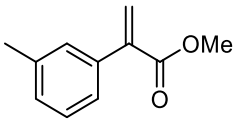
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.15 (m, 1H), 7.15-7.09 (m, 2H), 7.09-7.03 (m, 1H), 6.44 (d, *J* = 1.6 Hz, 1H), 5.64 (d, *J* = 1.7 Hz, 1H), 3.68 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 141.7, 137.2, 136.2, 130.0, 129.6, 128.9, 128.3, 125.8, 52.4, 19.9.

HRMS (ESI): Calcd. for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0910, found: 177.0911.

methyl 2-(m-tolyl)acrylate (4)



72.5 mg, 82% yield.

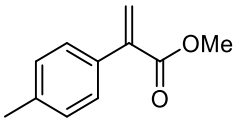
Physical State: colorless oil

^{1}H NMR (400 MHz, MeOD): δ 7.26-7.08 (m, 4H), 6.30-6.22 (m, 1H), 5.95-5.81 (m, 1H), 3.79 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, MeOD): δ 168.9, 143.0, 138.8, 138.0, 129.9, 129.8, 129.0, 126.8, 126.4, 52.6, 21.4.

HRMS (ESI): Calcd. for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0910, found: 177.0912.

methyl 2-(p-tolyl)acrylate (5)



72.0 mg, 82% yield.

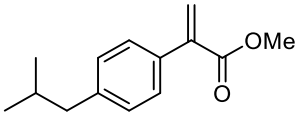
Physical State: light yellow oil

^{1}H NMR (400 MHz, MeOD): δ 7.28 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.24 (s, 1H), 5.88 (s, 1H), 3.78 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, MeOD): δ 169.0, 142.7, 139.2, 135.1, 129.7, 129.1, 126.2, 52.6, 21.2.

HRMS (ESI): Calcd. for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0910, found: 177.0909.

methyl 2-(4-isobutylphenyl)acrylate (6)



93.3 mg, 85% yield.

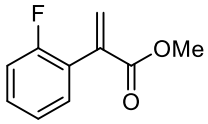
Physical State: light yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.32 (d, *J* = 1.3 Hz, 1H), 5.89 (d, *J* = 1.3 Hz, 1H), 3.83 (s, 3H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.95-1.83 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 142.0, 141.3, 134.1, 129.0, 128.1, 126.2, 52.3, 45.3, 30.3, 22.5.

HRMS (ESI): Calcd. for $C_{14}H_{19}O_2$ $[M+H]^+$: 219.1380, found: 219.1377.

methyl 2-(2-fluorophenyl)acrylate (7)



81.9 mg, 91% yield.

Physical State: light yellow oil

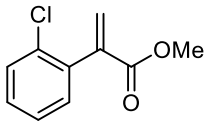
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.27 (m, 2H), 7.20-7.03 (m, 2H), 6.54 (d, *J* = 1.2 Hz, 1H), 5.91 (d, *J* = 1.3 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 161.2, 158.8, 136.6, 130.9 (d, *J* = 3.3 Hz), 130.2 (d, *J* = 8.2 Hz), 129.5 (d, *J* = 1.4 Hz), 124.1 (d, *J* = 3.6 Hz), 115.6 (d, *J* = 21.8 Hz), 52.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -113.76.

HRMS (ESI): Calcd. for $C_{10}H_{10}FO_2$ $[M+H]^+$: 181.0659, found: 181.0661.

methyl 2-(2-chlorophenyl)acrylate (8)



77.0 mg, 78% yield.

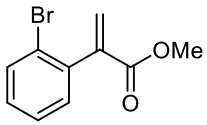
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.39 (m, 1H), 7.34-7.27 (m, 3H), 6.55 (d, *J* = 1.3 Hz, 1H), 5.81 (d, *J* = 1.3 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 140.3, 136.6, 133.4, 131.0, 129.6, 129.4, 129.3, 126.9, 52.5.

HRMS (ESI): Calcd. for $C_{10}H_{10}ClO_2$ $[M+H]^+$: 197.0364, found: 197.0362.

methyl 2-(2-bromophenyl)acrylate (9)



102.6 mg, 85% yield.

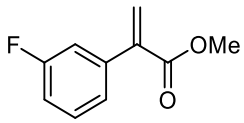
Physical State: light yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.55 (m, 1H), 7.41-7.33 (m, 1H), 7.31-7.19 (m, 2H), 6.55 (d, *J* = 1.3 Hz, 1H), 5.79 (d, *J* = 1.3 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 141.9, 138.7, 132.6, 131.0, 129.7, 129.3, 127.5, 123.4, 52.5.

HRMS (ESI): Calcd. for $C_{10}H_{10}BrO_2$ $[M+H]^+$: 240.9859, found: 240.9861.

methyl 2-(3-fluorophenyl)acrylate (10)



79.6 mg, 88% yield.

Physical State: colorless oil

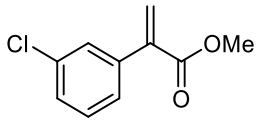
^{1}H NMR (400 MHz, MeOD): δ 7.42-7.30 (m, 1H), 7.26-7.13 (m, 2H), 7.12-7.02 (m, 1H), 6.37 (d, *J* = 1.0 Hz, 1H), 5.99 (d, *J* = 1.0 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (100 MHz, MeOD): δ 168.2, 163.8 (d, *J* = 243.8 Hz), 141.6 (d, *J* = 2.3 Hz), 140.3 (d, *J* = 8.2 Hz), 130.9 (d, *J* = 8.4 Hz), 128.3, 125.2 (d, *J* = 2.9 Hz), 116.2 (d, *J* = 23.0 Hz), 115.9 (d, *J* = 21.3 Hz), 52.7.

^{19}F NMR (376 MHz, MeOD): δ -111.81.

HRMS (ESI): Calcd. for $C_{10}H_{10}FO_2$ $[M+H]^+$: 181.0659, found: 181.0662.

methyl 2-(3-chlorophenyl)acrylate (11)



81.3 mg, 83% yield.

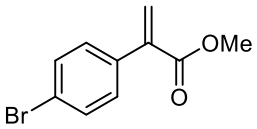
Physical State: light yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.39 (m, 1H), 7.35-7.27 (m, 3H), 6.41 (d, *J* = 1.1 Hz, 1H), 5.92 (d, *J* = 1.1 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 140.2, 138.5, 134.1, 129.5, 128.6, 128.4, 128.1, 126.7, 52.5.

HRMS (ESI): Calcd. for $C_{10}H_{10}ClO_2$ $[M+H]^+$: 197.0364, found: 197.0366.

methyl 2-(4-bromophenyl)acrylate (12)



102.8 mg, 85% yield.

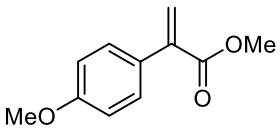
Physical State: light yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.41 (m, 2H), 7.32-7.26 (m, 2H), 6.39 (d, *J* = 1.1 Hz, 1H), 5.90 (d, *J* = 1.1 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 140.3, 135.7, 131.4, 130.1, 127.6, 122.6, 52.5.

HRMS (ESI): Calcd. for $C_{10}H_{10}BrO_2$ $[M+H]^+$: 240.9859, found: 240.9856.

methyl 2-(4-methoxyphenyl)acrylate (13)



82.9 mg, 86% yield.

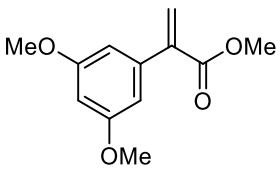
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.27 (d, *J* = 1.2 Hz, 1H), 5.83 (d, *J* = 1.3 Hz, 1H), 3.87-3.77 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 159.7, 140.7, 129.6, 129.2, 125.4, 113.6, 55.3, 52.2.

HRMS (ESI): Calcd. for $C_{11}H_{13}O_3$ $[M+H]^+$: 193.0859, found: 193.0857.

methyl 2-(3,5-dimethoxyphenyl)acrylate (14)



96.6 mg, 87% yield.

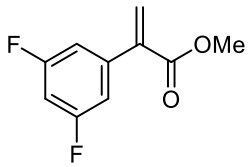
Physical State: light yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.60-6.52 (m, 2H), 6.49-6.42 (m, 1H), 6.34 (d, *J* = 1.3 Hz, 1H), 5.89 (d, *J* = 1.3 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 160.5, 141.3, 138.6, 127.1, 106.6, 100.3, 55.4, 52.3.

HRMS (ESI): Calcd. for $C_{12}H_{15}O_4$ $[M+H]^+$: 223.0965, found: 223.0964.

methyl 2-(3,5-difluorophenyl)acrylate (15)



82.5 mg, 83% yield.

Physical State: light yellow oil

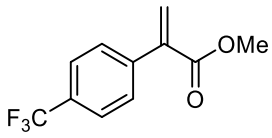
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02-6.91 (m, 2H), 6.83-6.70 (m, 1H), 6.44 (s, 1H), 5.95 (s, 1H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 163.9 (d, *J* = 13.0 Hz), 161.5 (d, *J* = 13.0 Hz), 139.7 (t, *J* = 10.0 Hz), 139.4 (t, *J* = 2.6 Hz), 111.7-111.4 (m, 2C), 103.7 (t, *J* = 25.4 Hz), 52.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -110.20.

HRMS (ESI): Calcd. for $C_{10}H_9F_2O_2$ $[M+H]^+$: 199.0565, found: 199.0562.

methyl 2-(4-(trifluoromethyl)phenyl)acrylate (16)



91.7 mg, 80% yield.

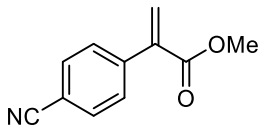
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 6.48 (d, *J* = 1.0 Hz, 1H), 5.96 (d, *J* = 1.0 Hz, 1H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 140.4, 140.3, 130.3 (q, *J* = 32.4 Hz), 128.9, 128.7, 125.2 (q, *J* = 3.9 Hz), 124.2 (q, *J* = 272.0 Hz), 52.5.

HRMS (ESI): Calcd. for $C_{11}H_{10}F_3O_2$ $[M+H]^+$: 231.0627, found: 231.0626.

methyl 2-(4-cyanophenyl)acrylate (17)



67.3 mg, 72% yield.

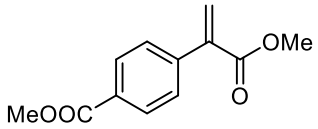
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 6.50 (s, 1H), 5.98 (s, 1H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 141.3, 139.9, 132.0, 129.4, 129.2, 118.7, 112.0, 52.6.

HRMS (ESI): Calcd. for $C_{11}H_{10}NO_2$ $[M+H]^+$: 188.0706, found: 188.0707.

methyl 4-(3-methoxy-3-oxoprop-1-en-2-yl)benzoate (18)



87.6 mg, 80% yield.

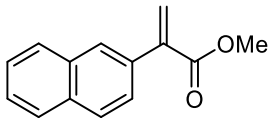
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 6.43 (d, *J* = 1.1 Hz, 1H), 5.95 (d, *J* = 1.1 Hz, 1H), 3.90 (s, 3H), 3.81 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 166.7, 141.2, 140.6, 129.8, 129.4, 128.4, 128.4, 52.4, 52.2.

HRMS (ESI): Calcd. for $C_{12}H_{13}O_4$ $[M+H]^+$: 221.0808, found: 221.0812.

methyl 2-(naphthalen-2-yl)acrylate (19)



84.1 mg, 79% yield.

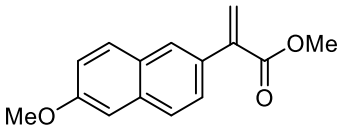
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.94 (m, 1H), 7.91-7.82 (m, 3H), 7.60-7.49 (m, 3H), 6.49 (d, *J* = 1.2 Hz, 1H), 6.06 (d, *J* = 1.2 Hz, 1H), 3.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 141.3, 134.2, 133.2, 133.1, 128.4, 127.7, 127.7, 127.6, 127.4, 126.5, 126.4, 126.2, 52.4.

HRMS (ESI): Calcd. for $C_{14}H_{13}O_2$ $[M+H]^+$: 213.0910, found: 213.0906.

methyl 2-(6-methoxynaphthalen-2-yl)acrylate (20)



100.9 mg, 83% yield.

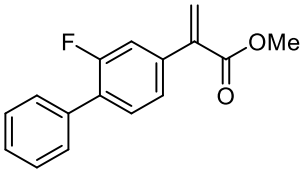
Physical State: colourless solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.81 (m, 1H), 7.77-7.68 (m, 2H), 7.53-7.47 (m, 1H), 7.18-7.11 (m, 2H), 6.40 (d, *J* = 1.2 Hz, 1H), 5.99 (d, *J* = 1.2 Hz, 1H), 3.93 (s, 3H), 3.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 158.2, 141.4, 134.4, 132.0, 129.9, 128.6, 127.4, 126.7, 126.60, 126.56, 119.2, 105.7, 55.4, 52.4.

HRMS (ESI): Calcd. for $C_{15}H_{15}O_3$ $[M+H]^+$: 243.1016, found: 243.1017.

methyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)acrylate (21)



108.4 mg, 85% yield.

Physical State: light yellow oil

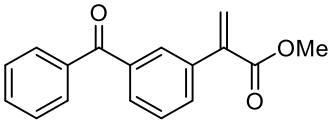
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.55 (m, 2H), 7.53-7.43 (m, 3H), 7.43-7.37 (m, 1H), 7.35-7.28 (m, 2H), 6.51-6.41 (m, 1H), 6.06-5.95 (m, 1H), 3.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 159.3 (d, *J* = 247.7 Hz), 139.9 (d, *J* = 2.0 Hz), 137.6 (d, *J* = 8.3 Hz), 135.4 (d, *J* = 1.4 Hz), 130.4 (d, *J* = 4.0 Hz), 129.0 (d, *J* = 3.0 Hz), 128.9 (d, *J* = 13.7 Hz), 128.6, 127.9, 127.7, 124.3 (d, *J* = 3.4 Hz), 116.2 (d, *J* = 24.4 Hz), 52.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -118.10.

HRMS (ESI): Calcd. for $C_{16}H_{14}FO_2$ $[M+H]^+$: 257.0972, found: 257.0968.

methyl 2-(3-benzoylphenyl)acrylate (22)



109.5 mg, 80% yield.

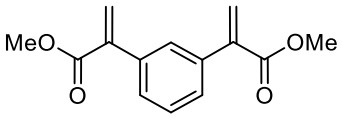
Physical State: light yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.79 (m, 3H), 7.78-7.74 (m, 1H), 7.66-7.62 (m, 1H), 7.61-7.55 (m, 1H), 7.51-7.44 (m, 3H), 6.44 (d, *J* = 1.1 Hz, 1H), 5.96 (d, *J* = 1.1 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 166.8, 140.4, 137.5, 137.4, 137.0, 132.6, 132.4, 130.2, 130.0, 129.9, 128.4, 128.2, 52.4.

HRMS (ESI): Calcd. for $C_{17}H_{15}O_3$ $[M+H]^+$: 267.1016, found: 267.1013.

dimethyl 2,2'-(1,3-phenylene)diacrylate (23)



98.7 mg, 80% yield.

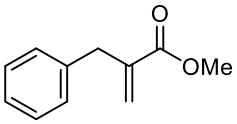
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.44 (m, 1H), 7.42-7.29 (m, 3H), 6.38 (d, *J* = 1.3 Hz, 2H), 5.92 (d, *J* = 1.3 Hz, 2H), 3.81 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 141.0, 136.6, 128.4, 128.2, 127.9, 127.4, 52.2.

HRMS (ESI): Calcd. for $C_{14}H_{15}O_4$ $[M+H]^+$: 247.0965, found: 247.0963.

methyl 2-benzylacrylate (24)



75.1 mg, 85% yield.

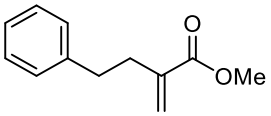
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.17 (m, 2H), 7.17-7.06 (m, 3H), 6.30-6.07 (m, 1H), 5.49-5.31 (m, 1H), 3.65 (s, 3H), 3.56 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 140.2, 138.8, 129.2, 128.5, 126.5, 126.4, 52.0, 38.2.

HRMS (ESI): Calcd. for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0910, found: 177.0909.

methyl 2-methylene-4-phenylbutanoate (25)



89.3 mg, 88% yield.

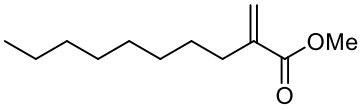
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.27 (m, 2H), 7.23-7.13 (m, 3H), 6.17 (d, *J* = 1.4 Hz, 1H), 5.55-5.45 (m, 1H), 3.77 (s, 3H), 2.86-2.76 (m, 2H), 2.67-2.56 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 141.5, 139.9, 128.6, 128.4, 126.1, 125.5, 51.9, 35.0, 34.0.

HRMS (ESI): Calcd. for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1067, found: 191.1064.

methyl 2-methylenedecanoate (26)



86.5 mg, 87% yield.

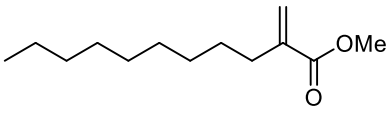
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.17-6.09 (m, 1H), 5.54-5.47 (m, 1H), 3.74 (s, 3H), 2.35-2.22 (m, 2H), 1.49-1.39 (m, 2H), 1.31-1.22 (m, 10H), 0.92-0.82 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 140.9, 124.6, 53.6, 51.9, 32.0, 29.5, 29.4, 29.4, 28.5, 22.8, 14.2.

HRMS (ESI): Calcd. for $C_{12}H_{23}O_2$ $[M+H]^+$: 199.1693, found: 199.1691.

methyl 2-methyleneundecanoate (27)



87.6 mg, 82% yield.

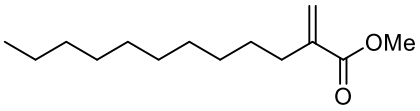
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.24-6.02 (m, 1H), 5.67-5.45 (m, 1H), 3.75 (s, 3H), 2.40-2.17 (m, 2H), 1.51-1.38 (m, 2H), 1.35-1.19 (m, 12H), 0.93-0.81 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 141.0, 124.6, 51.9, 32.0, 29.7, 29.6, 29.5, 29.4, 28.5, 22.8, 14.3.

HRMS (ESI): Calcd. for $C_{13}H_{25}O_2$ $[M+H]^+$: 213.1849, found: 213.1852.

methyl 2-methylenedodecanoate (28)



99.7 mg, 88% yield.

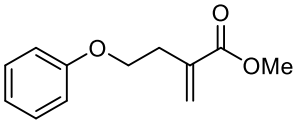
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.23-6.06 (m, 1H), 5.62-5.44 (m, 1H), 3.75 (s, 3H), 2.29 (t, *J* = 7.6 Hz, 2H), 1.50-1.40 (m, 2H), 1.31-1.22 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 141.0, 124.6, 51.9, 32.1, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 28.5, 22.8, 14.3.

HRMS (ESI): Calcd. for $C_{14}H_{27}O_2$ $[M+H]^+$: 227.2006, found: 227.2003.

methyl 2-methylene-4-phenoxybutanoate (31)



80.1 mg, 78% yield.

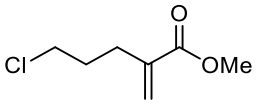
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.24 (m, 2H), 7.00-6.90 (m, 3H), 6.32 (d, *J* = 1.3 Hz, 1H), 5.76 (d, *J* = 1.3 Hz, 1H), 4.14 (t, *J* = 6.6 Hz, 2H), 3.80 (s, 3H), 2.83 (t, *J* = 6.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 158.8, 136.7, 129.6, 127.6, 120.9, 114.7, 114.7, 66.2, 52.1, 32.1.

HRMS (ESI): Calcd. for $C_{12}H_{15}O_3$ $[M+H]^+$: 207.1016, found: 207.1015.

methyl 5-chloro-2-methylenepentanoate (32)



70.6 mg, 87% yield.

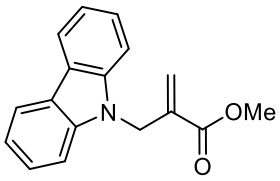
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29-6.16 (m, 1H), 5.71-5.50 (m, 1H), 3.75 (s, 3H), 2.45 (t, *J* = 7.5 Hz, 2H), 2.34 (t, *J* = 7.1 Hz, 2H), 1.85 (p, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 138.4, 126.7, 119.4, 52.1, 31.1, 24.3, 16.6.

HRMS (ESI): Calcd. for $C_7H_{12}ClO_2$ $[M+H]^+$: 163.0520, found: 163.0521.

methyl 2-((9*H*-carbazol-9-yl)methyl)acrylate (33)



99.8 mg, 75% yield.

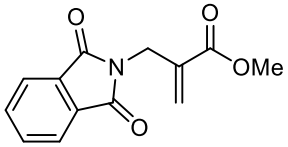
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 7.6 Hz, 2H), 7.56-7.45 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.34-7.26 (m, 2H), 6.28-6.20 (m, 1H), 5.26-5.16 (m, 2H), 5.10-5.05 (m, 1H), 3.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 140.4, 134.8, 126.0, 125.8, 123.2, 120.5, 119.5, 108.9, 52.3, 43.5.

HRMS (ESI): Calcd. for $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1176, found: 266.1174.

methyl 2-((1,3-dioxoisoindolin-2-yl)methyl)acrylate (34)



97.3 mg, 79% yield.

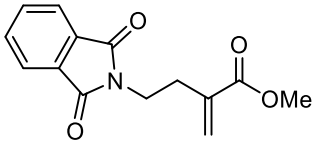
Physical State: colourless solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.81 (m, 2H), 7.76-7.68 (m, 2H), 6.34-6.23 (m, 1H), 5.64-5.49 (m, 1H), 4.53 (s, 2H), 3.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 165.8, 134.4, 134.2, 132.0, 126.1, 123.5, 52.2, 38.3.

HRMS (ESI): Calcd. for $C_{13}H_{12}NO_4$ $[M+H]^+$: 246.0761, found: 246.0762.

methyl 4-(1,3-dioxoisoindolin-2-yl)-2-methylenebutanoate (35)



105.9 mg, 82% yield.

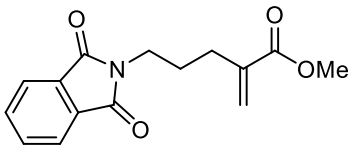
Physical State: colourless solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.35 (m, 2H), 7.30-7.22 (m, 2H), 5.71 (d, *J* = 1.3 Hz, 1H), 5.10 (d, *J* = 1.4 Hz, 1H), 3.46 (t, *J* = 6.7 Hz, 2H), 3.34 (s, 3H), 2.27 (t, *J* = 6.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 166.9, 137.2, 134.0, 132.1, 127.5, 123.3, 52.1, 36.9, 31.5.

HRMS (ESI): Calcd. for $C_{14}H_{14}NO_4$ $[M+H]^+$: 260.0917, found: 260.0918.

methyl 5-(1,3-dioxoisoindolin-2-yl)-2-methylenepentanoate (36)



115.4 mg, 85% yield.

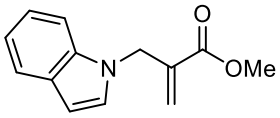
Physical State: colourless solid

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.76 (m, 2H), 7.71-7.63 (m, 2H), 6.18-6.10 (m, 1H), 5.62-5.53 (m, 1H), 3.69 (s, 3H), 3.68-3.63 (m, 2H), 2.33 (t, *J* = 7.8 Hz, 2H), 1.90-1.75 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 167.4, 139.3, 134.0, 132.2, 125.5, 123.2, 51.9, 37.5, 29.2, 27.2.

HRMS (ESI): Calcd. for $C_{15}H_{16}NO_4$ $[M+H]^+$: 274.1074, found: 274.1071.

methyl 2-((1*H*-indol-1-yl)methyl)acrylate (37)



88.7 mg, 82% yield.

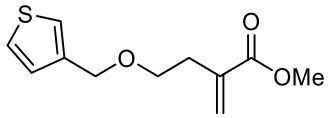
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.61 (m, 1H), 7.32-7.27 (m, 1H), 7.25-7.19 (m, 1H), 7.17-7.10 (m, 2H), 6.56 (d, *J* = 3.2 Hz, 1H), 6.33-6.21 (m, 1H), 5.18 (s, 1H), 5.01 (s, 2H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 136.4, 136.1, 128.7, 128.5, 126.3, 121.9, 121.1, 119.7, 109.6, 102.0, 52.2, 46.9.

HRMS (ESI): Calcd. for $C_{13}H_{14}NO_2$ $[M+H]^+$: 216.1019, found: 216.1022.

methyl 2-methylene-4-(thiophen-3-ylmethoxy)butanoate (38)



85.3 mg, 75% yield.

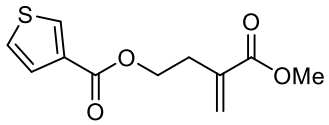
Physical State: yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (m, 1H), 7.20-7.13 (m, 1H), 7.06-7.01 (m, 1H), 6.24-6.19 (m, 1H), 5.69-5.61 (m, 1H), 4.51 (s, 2H), 3.74 (s, 3H), 3.60 (t, *J* = 6.6 Hz, 2H), 2.62 (t, *J* = 6.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 139.6, 137.4, 127.4, 126.8, 126.0, 122.7, 68.6, 68.2, 51.9, 32.4.

HRMS (ESI): Calcd. for $C_{11}H_{15}O_3S$ $[M+H]^+$: 227.0736, found: 227.0734.

3-(methoxycarbonyl)but-3-en-1-yl thiophene-3-carboxylate (39)



88.0 mg, 73% yield.

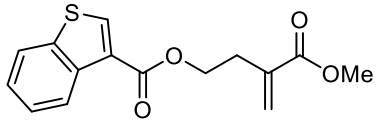
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.00 (m, 1H), 7.52-7.46 (m, 1H), 7.34-7.27 (m, 1H), 6.31-6.23 (m, 1H), 5.73-5.60 (m, 1H), 4.42 (t, *J* = 6.5 Hz, 2H), 3.77 (s, 3H), 2.77 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 162.7, 136.7, 133.8, 132.8, 128.0, 127.6, 126.1, 63.1, 52.2, 31.7.

HRMS (ESI): Calcd. for $C_{11}H_{13}O_4S$ $[M+H]^+$: 241.0529, found: 241.0527.

3-(methoxycarbonyl)but-3-en-1-yl benzo[14]thiophene-3-carboxylate (40)



110.8 mg, 76% yield.

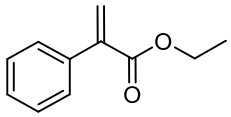
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 8.2 Hz, 1H), 8.37 (s, 1H), 7.91-7.79 (m, 1H), 7.56-7.47 (m, 1H), 7.46-7.39 (m, 1H), 6.32 (s, 1H), 5.78-5.71 (m, 1H), 4.54 (t, *J* = 6.5 Hz, 2H), 3.80 (s, 3H), 2.86 (t, *J* = 6.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 162.7, 140.1, 136.8 (m), 127.6, 127.2, 125.5, 125.1, 124.8, 122.6, 63.1, 52.2, 31.7.

HRMS (ESI): Calcd. for $C_{15}H_{15}O_4S$ $[M+H]^+$: 291.0686, found: 291.0685.

ethyl 2-phenylacrylate (41)



79.5 mg, 93% yield.

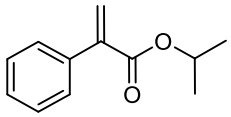
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.41 (m, 2H), 7.40-7.31 (m, 3H), 6.36 (d, *J* = 1.3 Hz, 1H), 5.90 (d, *J* = 1.3 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 141.7, 136.9, 128.4, 128.23, 128.19, 126.6, 61.2, 14.3.

HRMS (ESI): Calcd. for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0910, found: 177.0908.

isopropyl 2-phenylacrylate (42)



86.8 mg, 89% yield.

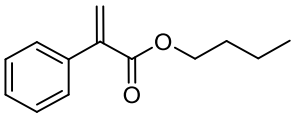
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.40 (m, 2H), 7.40-7.30 (m, 3H), 6.32 (d, *J* = 1.3 Hz, 1H), 5.88 (d, *J* = 1.3 Hz, 1H), 5.23-5.10 (m, 1H), 1.32 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 142.0, 137.0, 128.4, 128.16, 128.15, 126.2, 68.7, 21.9.

HRMS (ESI): Calcd. for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1067, found: 191.1069.

propyl 2-phenylacrylate (43)[16]



87.1 mg, 85% yield.

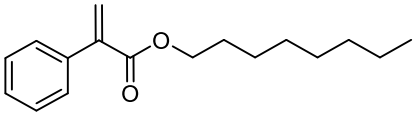
Physical State: yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.28 (m, 5H), 6.35 (d, *J* = 1.3 Hz, 1H), 5.89 (d, *J* = 1.3 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 1.81 – 1.64 (m, 2H), 1.51-1.37 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 141.7, 136.9, 128.4, 128.2, 128.1, 126.5, 65.1, 30.7, 19.3, 13.8.

HRMS (ESI): Calcd. for $C_{13}H_{17}O_2$ $[M+H]^+$: 205.1223, found: 205.1226.

octyl 2-phenylacrylate (44)



107.2 mg, 82% yield.

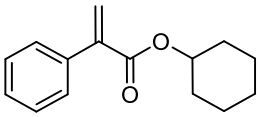
Physical State: yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.28 (m, 5H), 6.35 (d, *J* = 1.3 Hz, 1H), 5.89 (d, *J* = 1.3 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 1.81-1.63 (m, 2H), 1.51-1.18 (m, 11H), 1.03-0.80 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 141.7, 136.9, 128.4, 128.2, 128.1, 126.5, 65.4, 31.8, 29.3, 28.6, 26.0, 22.7, 14.2.

HRMS (ESI): Calcd. for $C_{17}H_{25}O_2$ $[M+H]^+$: 261.1849, found: 261.1851.

cyclohexyl 2-phenylacrylate (45)



97.5 mg, 85% yield.

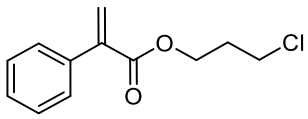
Physical State: yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.30 (m, 5H), 6.33 (d, *J* = 1.3 Hz, 1H), 5.87 (d, *J* = 1.3 Hz, 1H), 5.03-4.87 (m, 1H), 2.05-1.84 (m, 2H), 1.80-1.66 (m, 2H), 1.57-1.25 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 142.0, 137.0, 128.4, 128.1, 126.2, 73.4, 31.6, 25.5, 23.7.

HRMS (ESI): Calcd. for $C_{15}H_{19}O_2$ $[M+H]^+$: 231.1380, found: 231.1382.

3-chloropropyl 2-phenylacrylate (46)



96.2 mg, 86% yield.

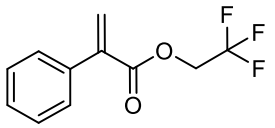
Physical State: yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.31 (m, 5H), 6.37 (d, *J* = 1.2 Hz, 1H), 5.91 (d, *J* = 1.2 Hz, 1H), 4.39 (t, *J* = 6.1 Hz, 2H), 3.62 (t, *J* = 6.4 Hz, 2H), 2.24-2.11 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 141.3, 136.6, 128.31, 128.28, 128.2, 127.1, 61.8, 41.3, 31.6.

HRMS (ESI): Calcd. for $C_{12}H_{14}ClO_2$ $[M+H]^+$: 225.0677, found: 225.0676.

2,2,2-trifluoroethyl 2-phenylacrylate (47)



94.2 mg, 84% yield.

Physical State: yellow oil

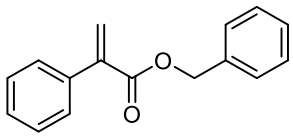
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.32 (m, 5H), 6.58-6.44 (m, 1H), 6.12-6.00 (m, 1H), 4.72-4.55 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 139.9, 136.0, 129.0, 128.7, 128.5, 128.4, 123.2 (q, *J* = 277.4 Hz), 60.9 (q, *J* = 36.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.40.

HRMS (ESI): Calcd. for $C_{11}H_{10}F_3O_2$ $[M+H]^+$: 231.0627, found: 231.0624.

benzyl 2-phenylacrylate (48)[16]



77.0 mg, 65% yield.

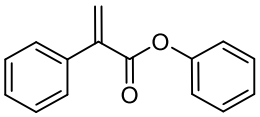
Physical State: yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.29 (m, 11H), 6.41 (d, *J* = 1.2 Hz, 1H), 5.93 (d, *J* = 1.2 Hz, 1H), 5.29 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 141.3, 136.7, 136.0, 128.6, 128.4, 128.3, 128.22, 128.18, 127.2, 66.9.

HRMS (ESI): Calcd. for $C_{16}H_{15}O_2$ $[M+H]^+$: 239.1067, found: 239.1069.

phenyl 2-phenylacrylate (49)[16]



99.0 mg, 81% yield.

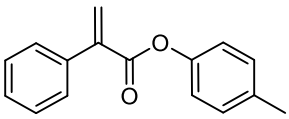
Physical State: colorless oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.54 (m, 2H), 7.49-7.40 (m, 5H), 7.34-7.27 (m, 1H), 7.25-7.20 (m, 2H), 6.66 (d, *J* = 1.1 Hz, 1H), 6.14 (d, *J* = 1.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 151.0, 140.9, 136.4, 129.6, 128.6, 128.5, 128.3, 126.0, 121.7. (one signal of aromatic carbon is missing).

HRMS (ESI): Calcd. for $C_{15}H_{13}O_2$ $[M+H]^+$: 225.0910, found: 225.0909.

***p*-tolyl 2-phenylacrylate (50)**



104.3 mg, 88% yield.

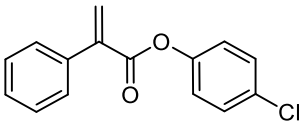
Physical State: yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.50 (m, 2H), 7.47-7.33 (m, 3H), 7.25-7.17 (m, 2H), 7.12-7.04 (m, 2H), 6.61 (d, *J* = 1.1 Hz, 1H), 6.09 (d, *J* = 1.1 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 148.7, 141.0, 136.4, 135.6, 130.0, 128.44, 128.41, 128.29, 128.25, 121.3, 20.9.

HRMS (ESI): Calcd. for $C_{16}H_{15}O_2$ $[M+H]^+$: 239.1067, found: 239.1066.

4-chlorophenyl 2-phenylacrylate (51)



101.0 mg, 78% yield.

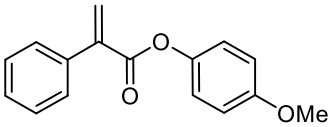
Physical State: yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.47 (m, 2H), 7.43-7.34 (m, 5H), 7.16-7.10 (m, 2H), 6.61 (d, *J* = 1.0 Hz, 1H), 6.10 (d, *J* = 1.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 149.4, 140.6, 136.2, 131.4, 129.6, 129.0, 128.6, 128.4, 128.3, 123.1.

HRMS (ESI): Calcd. for $C_{15}H_{12}ClO_2$ $[M+H]^+$: 259.0520, found: 259.0525.

4-methoxyphenyl 2-phenylacrylate (52)



116.3 mg, 92% yield.

Physical State: yellow oil

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.47 (m, 2H), 7.46-7.32 (m, 3H), 7.19-7.03 (m, 2H), 6.99-6.83 (m, 2H), 6.60 (d, *J* = 1.1 Hz, 1H), 6.08 (d, *J* = 1.1 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 157.4, 144.4, 140.9, 136.4, 128.44,128.43, 128.33, 128.26, 122.4, 114.5, 55.7.

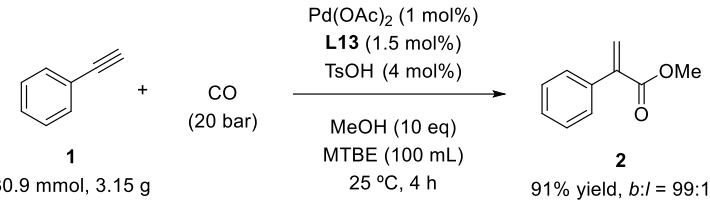
HRMS (ESI): Calcd. for $C_{16}H_{15}O_3$ $[M+H]^+$: 255.1016, found: 255.1010.

6. Catalyst recycling.

A 10 mL reaction tube with a Teflon-coated stirring bar was charged with $Pd(OAc)_2$ (1.2 mg, 1.0 mol%), **L13** (18.4 mg, 1.5 mol%), TsOH (3.4 mg, 4.0 mol%), and methanol (0.2 mL, 5 mmol) in MTBE (1.0 mL). Phenylacetylene (51.0 mg, 0.5 mmol) was added to the mixture. The tube was placed into a 300-mL stainless steel Parr autoclave (WP-MSAR-250A). The autoclave was purged three times with 20 bar of nitrogen and then pressurized with 20 bar of carbon monoxide. The reaction mixture was allowed to stir (800 rpm) at 25℃ for 1 h, and the pressure was carefully released. The reaction mixture was centrifugated and an aliquot the supernatant was analyzed with GC to determine the conversions and *b/l* ratios. The supernatant was concentrated under reduced

pressure, and yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The solid obtained after centrifuge was washed with cold *tert*-butyl methyl ether (5.0 mL × 3), dried under reduced pressure, and used in the next cycle with the same condition and procedure.

7. Gram scale synthesis of methyl 2-phenylacrylate.



A 250 mL reaction tube with a Teflon-coated stirring bar was charged with $Pd(OAc)_2$ (69.2 mg, 1.0 mol%), **L5** (1.18 g, 1.5 mol%), TsOH (0.21 g, 4.0 mol%), and MeOH (9.93 g, 12.5 mL, 0.31 mol) in MTBE (100.0 mL). Phenylacetylene (3.15 g, 30.9 mmol) was added to the mixture. The tube was placed into a 500-mL stainless steel Parr autoclave (YZPR-500). The autoclave was purged three times with 20 bar of nitrogen and then pressurized with 20 bar of carbon monoxide. The reaction mixture was allowed to stir (800 rpm) at 25℃ for 4 h, and the pressure was carefully released. The reaction mixture was centrifugated and an aliquot of the supernatant was analyzed with GC to determine the conversions and *b/l* ratios. The supernatant was concentrated under reduced pressure, and yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The residue was purified by flash column chromatography on silica gel with *n*-hexane/ethyl acetate = 20:1 as eluent to give **2** (4.56 g, 91% yield, *b*:*l* = 99:1).

8. References

[1] E. Drent, P. Arnoldy, P. H. M. Budzelaar, *J. Organomet. Chem.* **1993**, *455*, 247-253.

[2] A. Scrivanti, V. Beghetto, E. Campagna, U. Matteoli, *J. Mol. Catal. A: Chem.* **2001**, *168*, 75-80.

[3] M. L. Clarke, D. J. Cole-Hamilton, D. F. Foster, A. M. Z. Slawin, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **2002**, 1618-1624.

[4] M. J. Green, K. J. Cavell, P. G. Edwards, R. P. Tooze, B. W. Skelton, A. H. White, *Dalton Trans.* **2004**, 3251-3260.

[5] D. B. G. Williams, M. L. Shaw, T. Hughes, *Organometallics* **2011**, *30*, 4968-4973.

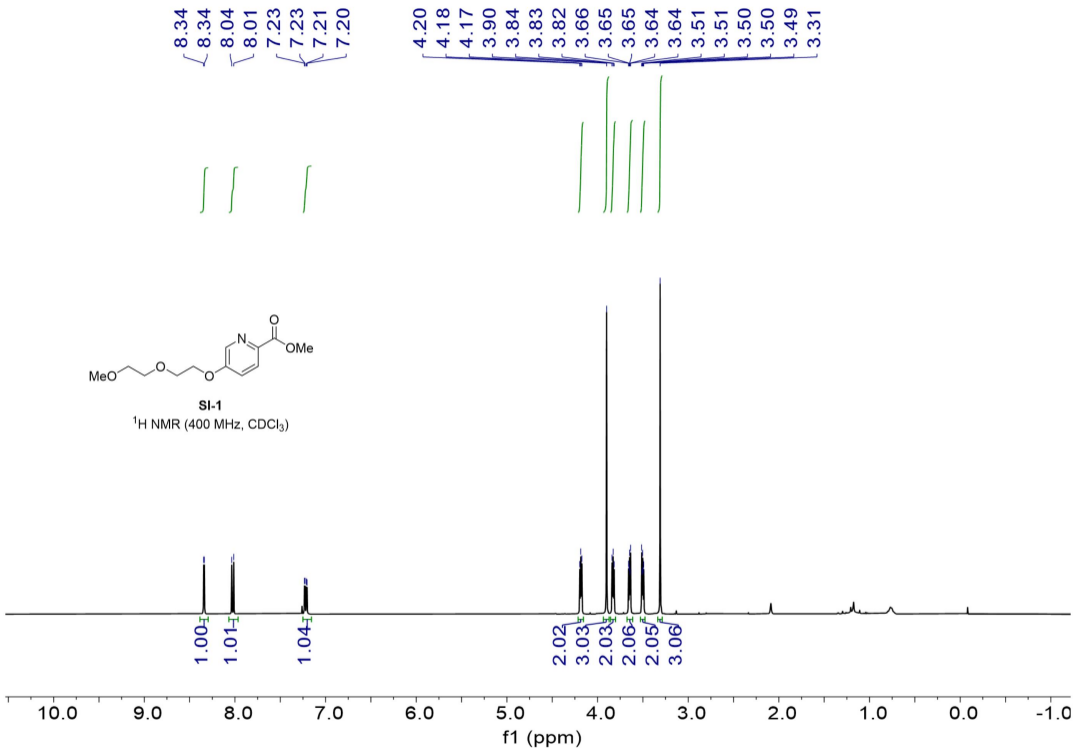
[6] W. Oberhauser, A. Ienco, F. Vizza, B. Trettenbrein, D. Oberhuber, C. Strabler, T. Ortner, P. Brüggeller, *Organometallics* **2012**, *31*, 4832-4837.

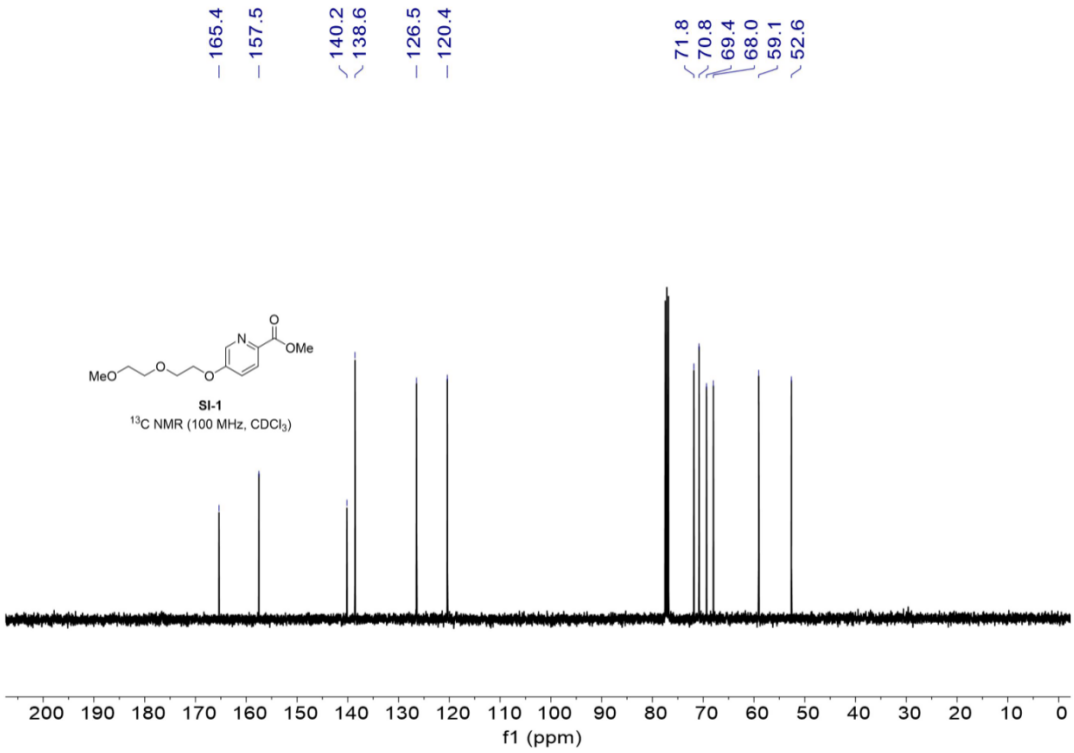
[7] T. A. Shuttleworth, A. M. Miles-Hobbs, P. G. Pringle, H. A. Sparkes, *Dalton Trans.* **2017**, *46*, 125-137.

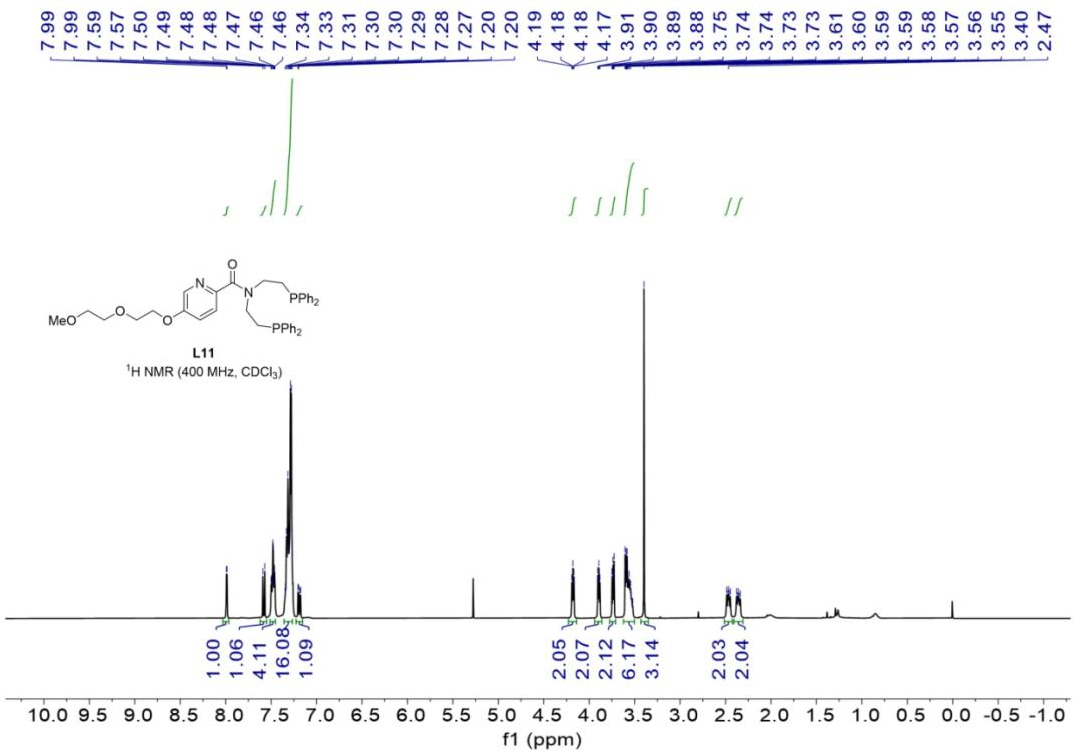
[8] H. Qi, Z. Huang, M. Wang, P. Yang, C.-X. Du, S.-W. Chen, Y. Li, *J. Catal.* **2018**, *363*, 63-

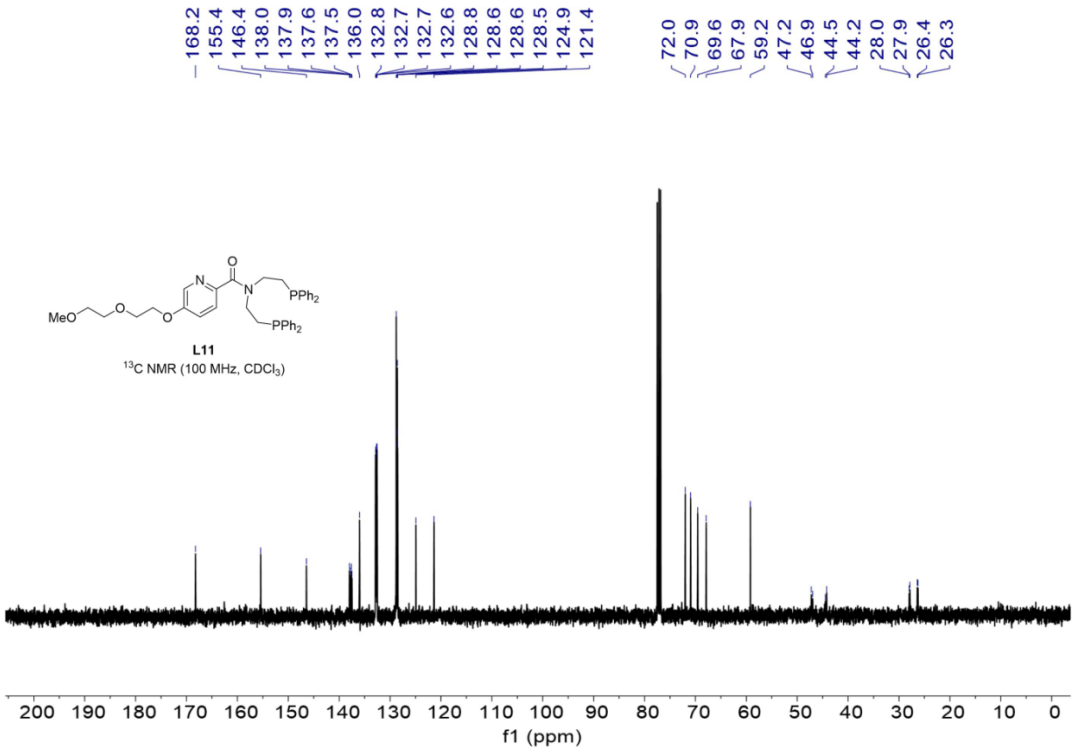
68.
[9] J. Liu, K. Dong, R. Franke, H. Neumann, R. Jackstell, M. Beller, *J. Am. Chem. Soc.* **2018**, *140*, 10282-10288.
[10] D. Liu, M. Ke, T. Ru, Y. Ning, F.-E. Chen, *Chem. Commun.* **2022**, *58*, 1041-1044.
[11] S. Doherty, J. G. Knight, M. Betham, *Chem. Commun.* **2006**, 88-90.
[12] D. Yang, L. Liu, D.-L. Wang, Y. Lu, X.-L. Zhao, Y. Liu, *J. Catal.* **2019**, *371*, 236-244.
[13] D. Liu, T. Ru, Z. Deng, L. Zhang, Y. Ning, F.-E. Chen, *ACS Catal.* **2023**, *13*, 12868-12876.
[14] A. Fishman, M. E. Farrah, J.-H. Zhong, S. Paramanantham, C. Carrera, E. Lee-Ruff, *J. Org. Chem.* **2003**, *68*, 9843-9846.
[15] Y. Xia, Y. Ning, M. Liu, F.-E. Chen, *J. Catal.* **2023**, *417*, 35-40.
[16] J. Liu, H. Li, R. Dühren, J. Liu, A. Spannenberg, R. Franke, R. Jackstell, M. Beller, *Angew. Chem., Int. Ed.* **2017**, *56*, 11976-11980.

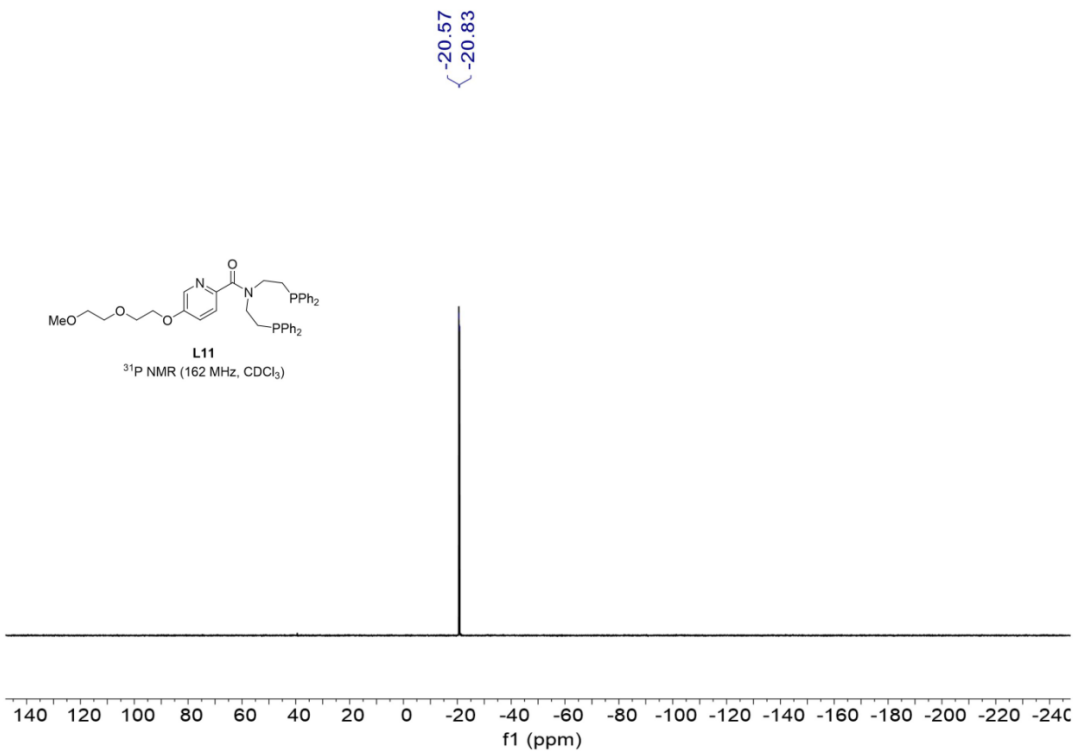
9. NMR spectra

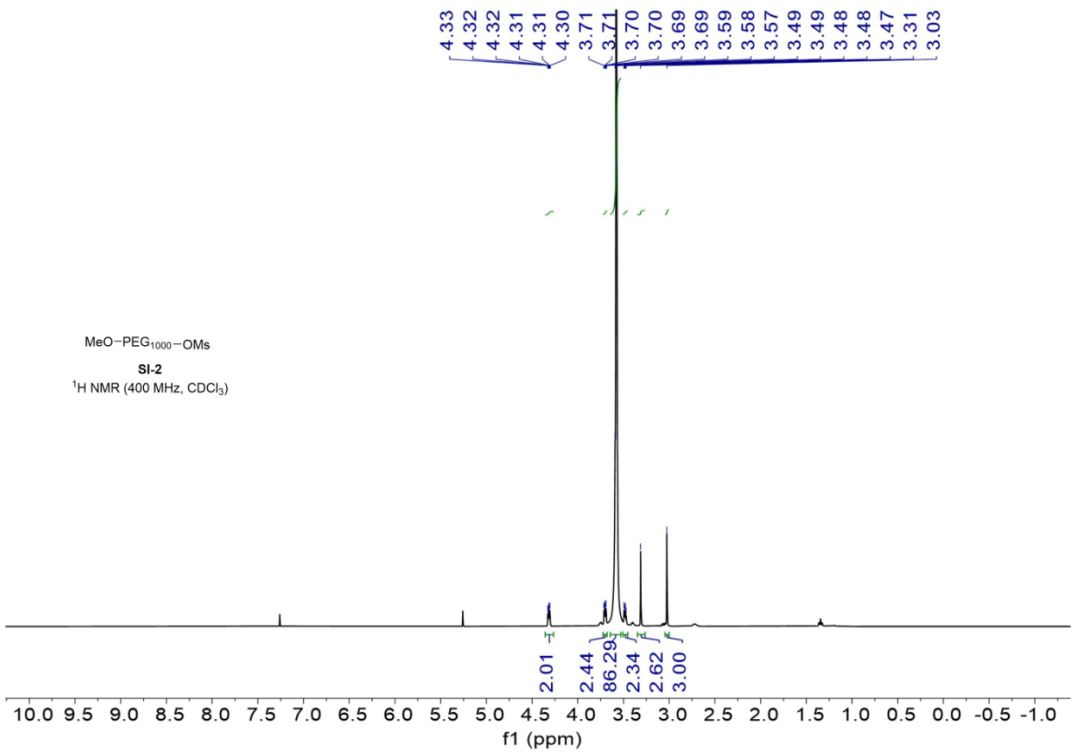


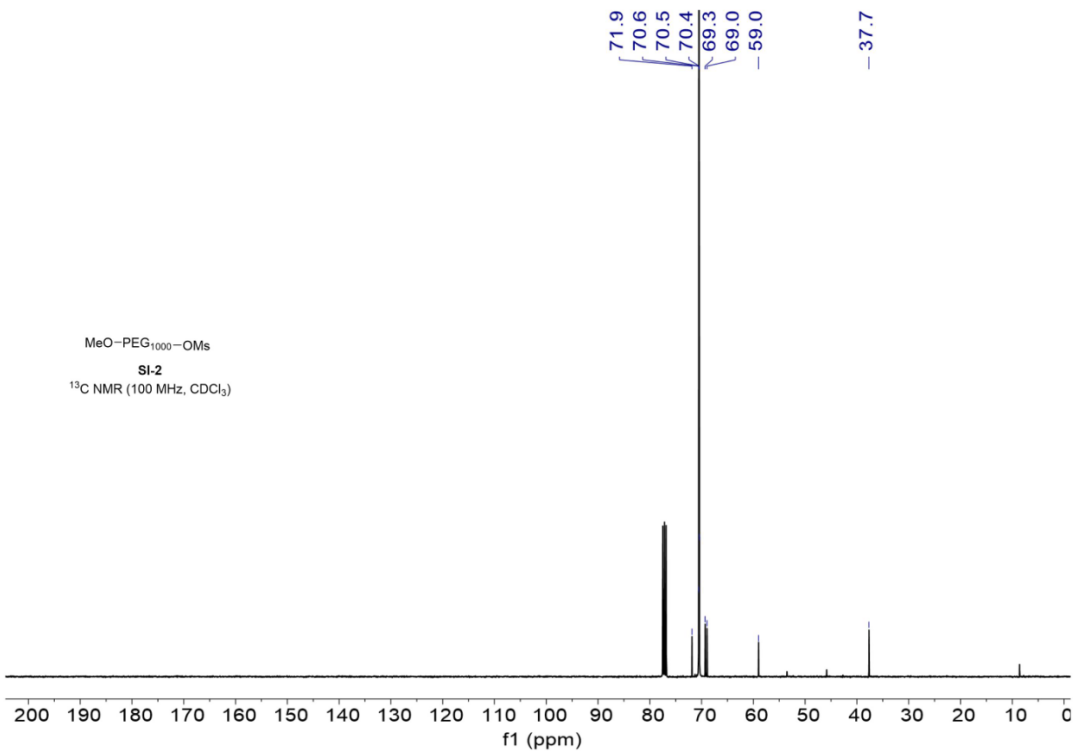


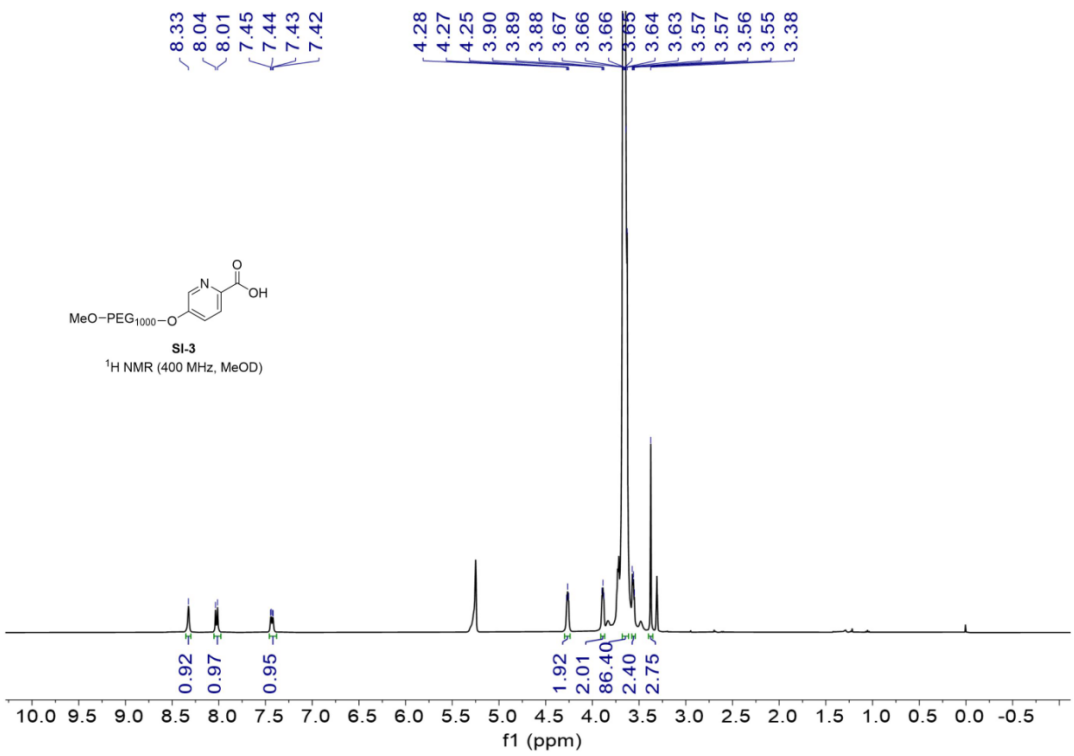

7.99 7.99 7.59 7.57 7.50 7.49 7.48 7.48 7.47 7.46 7.46 7.34 7.33 7.31 7.30 7.30 7.29 7.28 7.27 7.20 7.20 4.19 4.18 4.18 4.17 3.91 3.90 3.89 3.88 3.75 3.74 3.74 3.73 3.73 3.61 3.60 3.59 3.59 3.58 3.57 3.56 3.55 3.40 2.47
MeO
PPh2
PPh2
L11
1H NMR (400 MHz, CDCl3)
1.00 1.06 4.11 16.08 1.09 2.05 2.07 2.12 6.17 3.14 2.03 2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

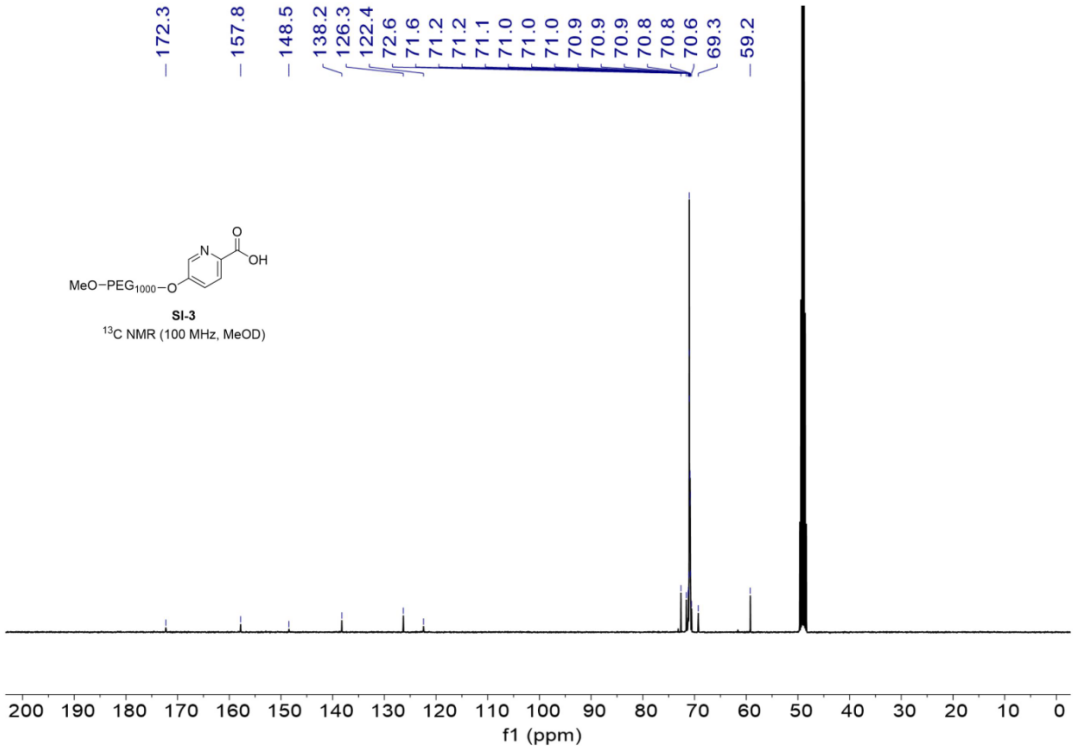

168.2 155.4 146.4 138.0 137.9 137.6 137.5 136.0 132.8 132.7 132.7 132.6 128.8 128.6 128.6 128.5 124.9 121.4
72.0 70.9 69.6 67.9 59.2 47.2 46.9 44.5 44.2 28.0 27.9 26.4 26.3
MeO
PPh2
PPh2
L11
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

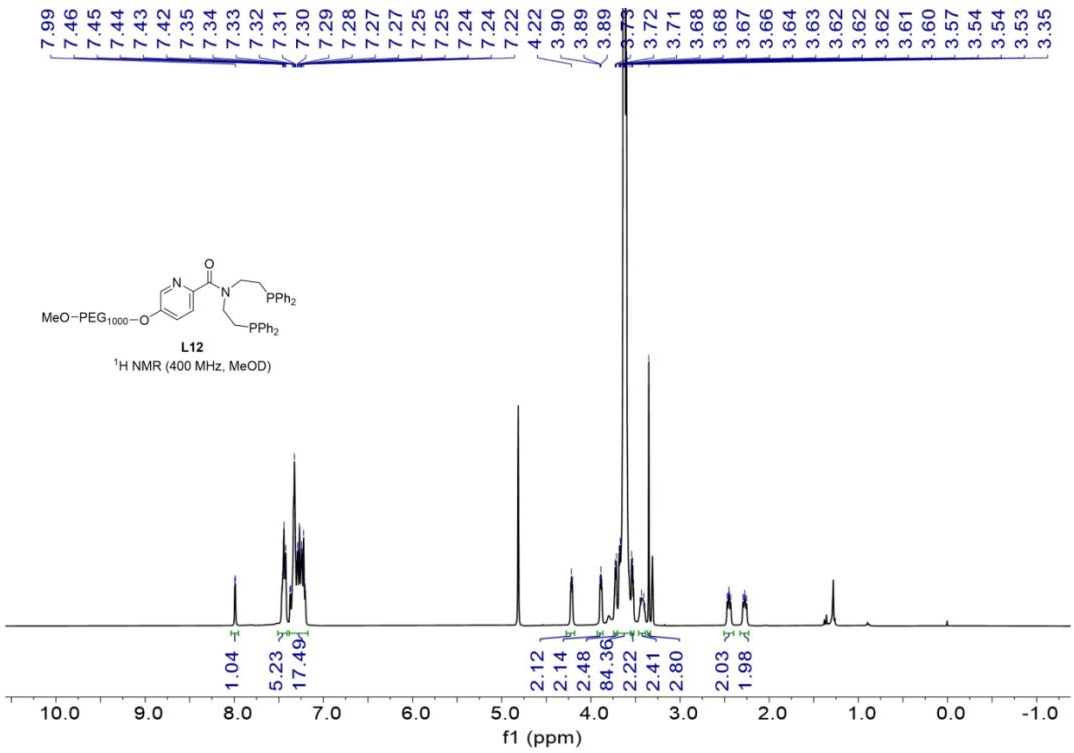

-20.57
-20.83
MeO
O
O
N
O
N
PPh2
PPh2
L11
31P NMR (162 MHz, CDCl3)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

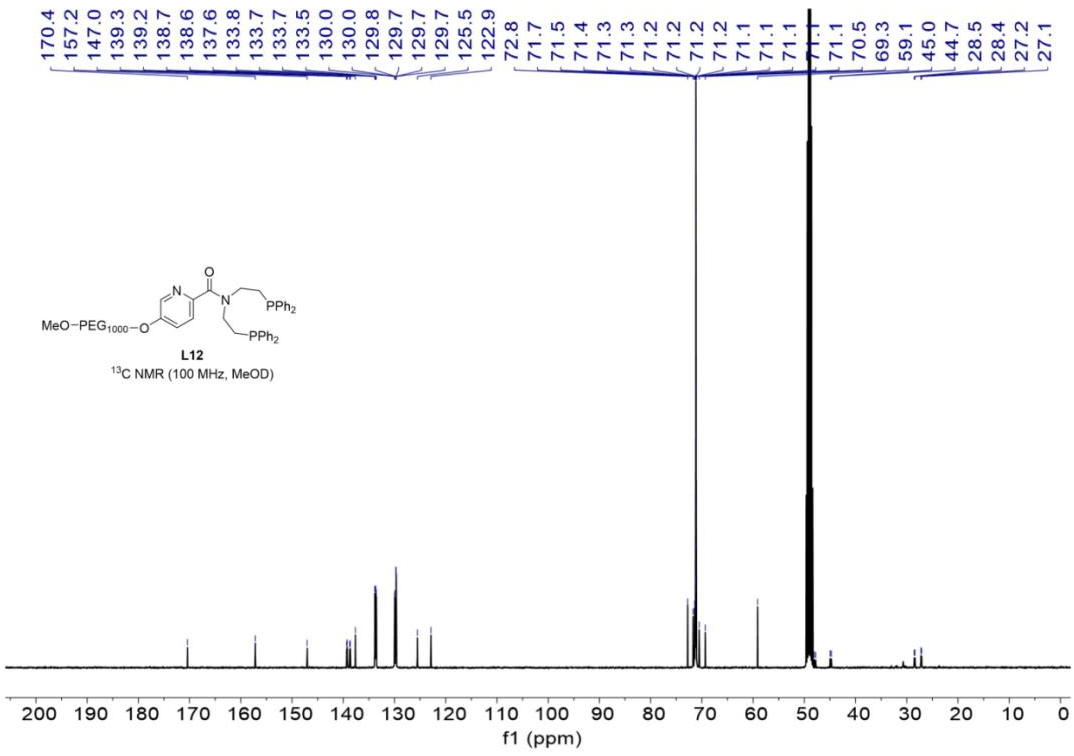

4.33
4.32
4.32
4.31
4.31
4.30
3.71
3.71
3.70
3.70
3.69
3.69
3.59
3.58
3.57
3.49
3.49
3.48
3.48
3.47
3.31
3.03
MeO−PEG1000−OMs
SI-2
1H NMR (400 MHz, CDCl3)
2.01
2.44
86.29
2.34
2.62
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

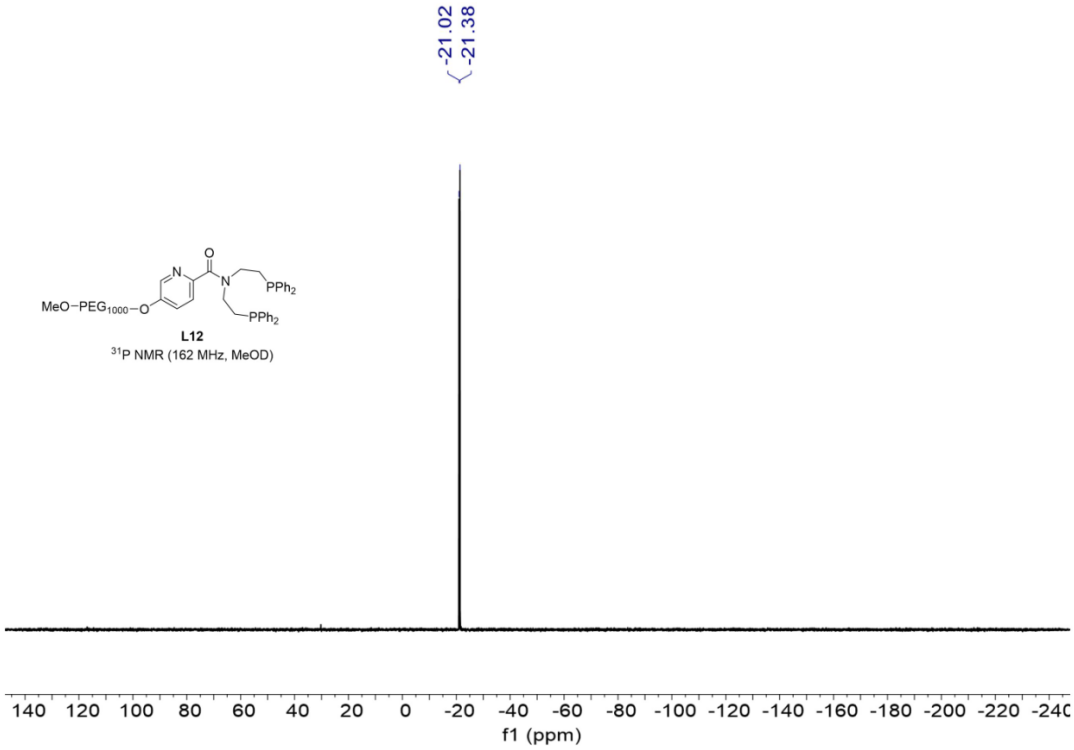

71.9
70.6
70.5
70.4
69.3
69.0
59.0
37.7
MeO−PEG1000−OMs
SI-2
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

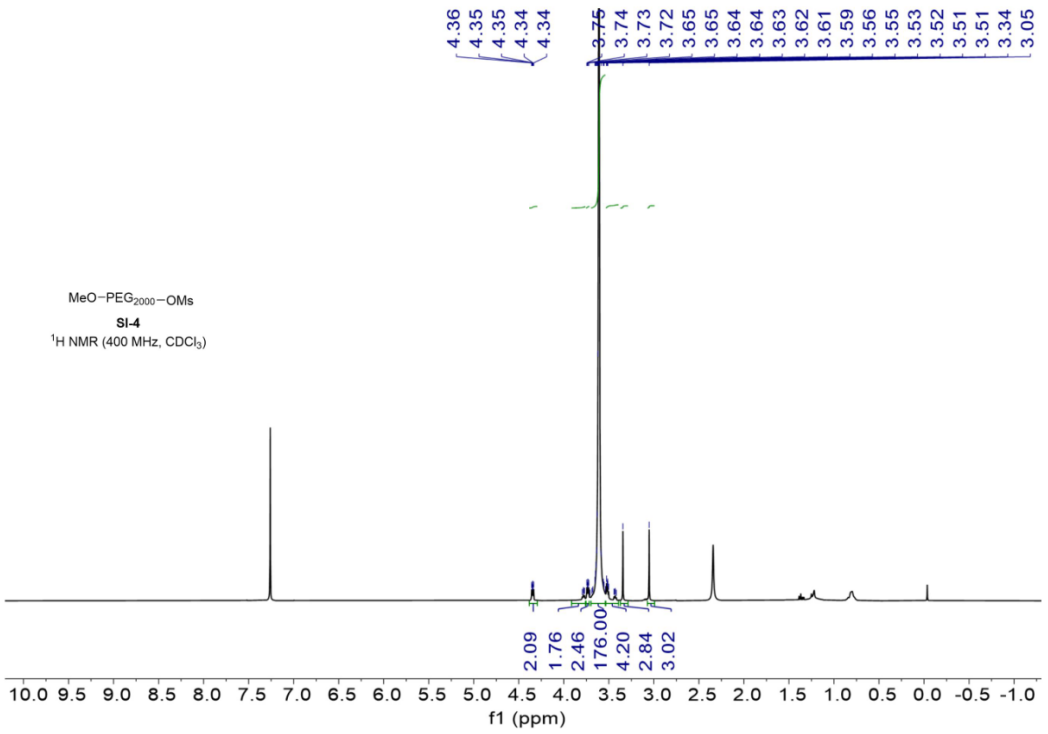

8.33
8.04
8.01
7.45
7.44
7.43
7.42
4.28
4.27
4.25
3.90
3.89
3.88
3.67
3.66
3.66
3.65
3.64
3.63
3.57
3.57
3.56
3.55
3.38
N
O
OH
MeO−PEG1000−O
SI-3
1H NMR (400 MHz, MeOD)
0.92
0.97
0.95
1.92
2.01
86.40
2.40
2.75
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

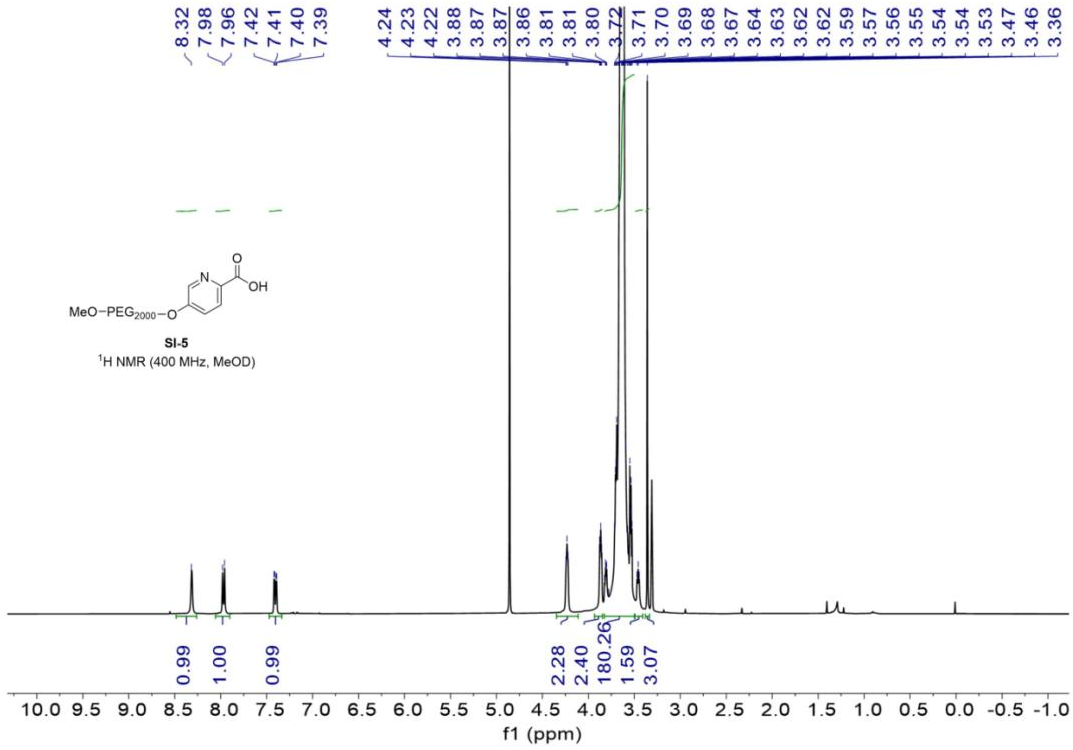

172.3
157.8
148.5
138.2
126.3
122.4
72.6
71.6
71.2
71.2
71.1
71.0
71.0
71.0
70.9
70.9
70.9
70.8
70.8
70.6
69.3
59.2
MeO−PEG1000−O
SI-3
13C NMR (100 MHz, MeOD)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

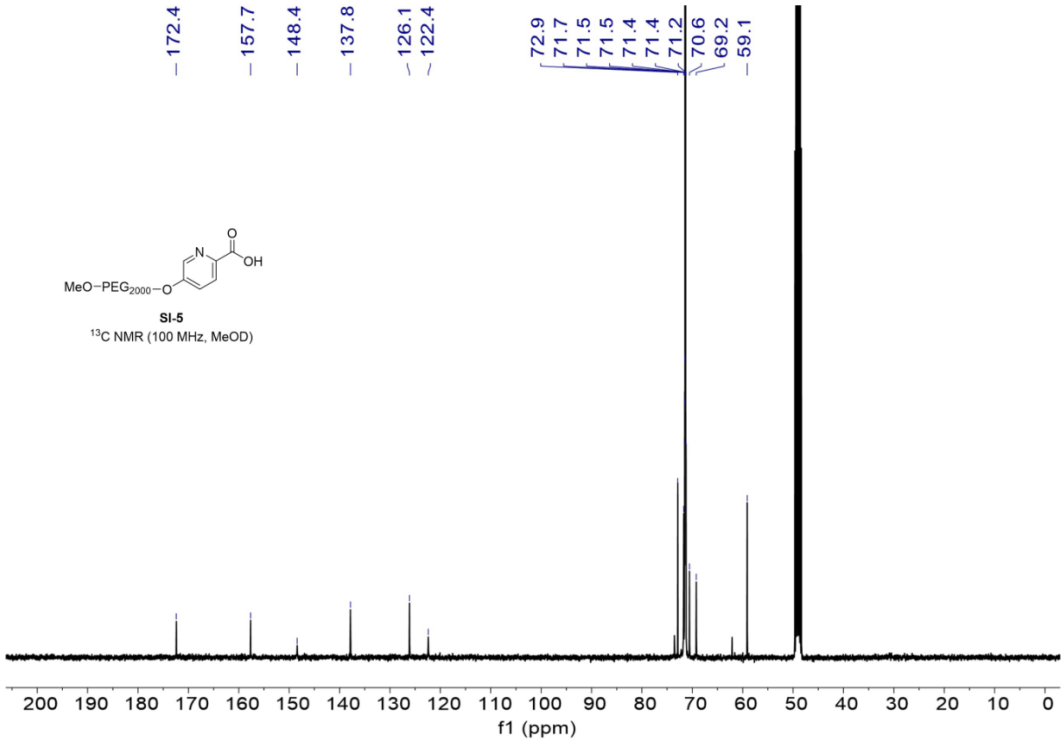

7.99
7.46
7.45
7.44
7.43
7.42
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.27
7.25
7.25
7.24
7.24
7.22
4.22
3.90
3.89
3.89
3.73
3.72
3.71
3.68
3.68
3.67
3.66
3.64
3.63
3.62
3.62
3.62
3.61
3.60
3.57
3.54
3.54
3.53
3.35
MeO−PEG1000−O
PPh2
PPh2
L12
1H NMR (400 MHz, MeOD)
1.04
5.23
17.49
2.12
2.14
2.48
84.36
2.22
2.41
2.80
2.03
1.98
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

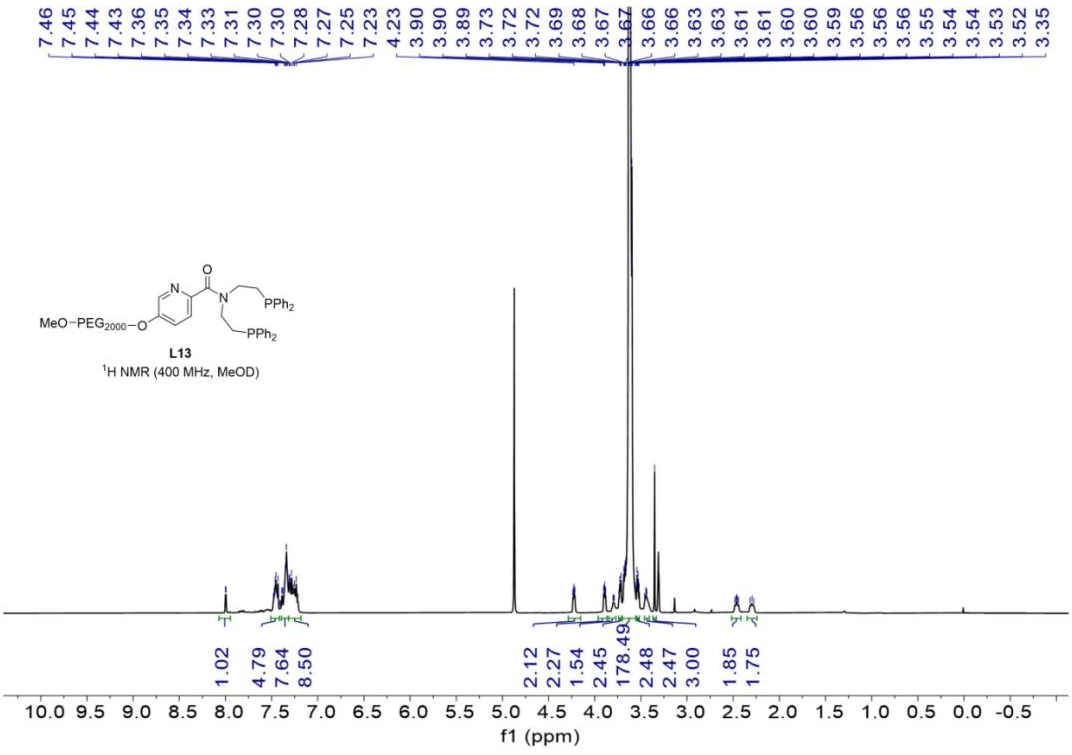

170.4
157.2
147.0
139.3
139.2
138.7
138.6
137.6
133.8
133.7
133.7
133.5
130.0
130.0
129.8
129.7
129.7
129.7
125.5
122.9
72.8
71.7
71.5
71.4
71.3
71.3
71.2
71.2
71.2
71.2
71.1
71.1
71.1
71.1
70.5
69.3
59.1
45.0
44.7
28.5
28.4
27.2
27.1
MeO−PEG1000−O
PPh2
PPh2
L12
13C NMR (100 MHz, MeOD)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

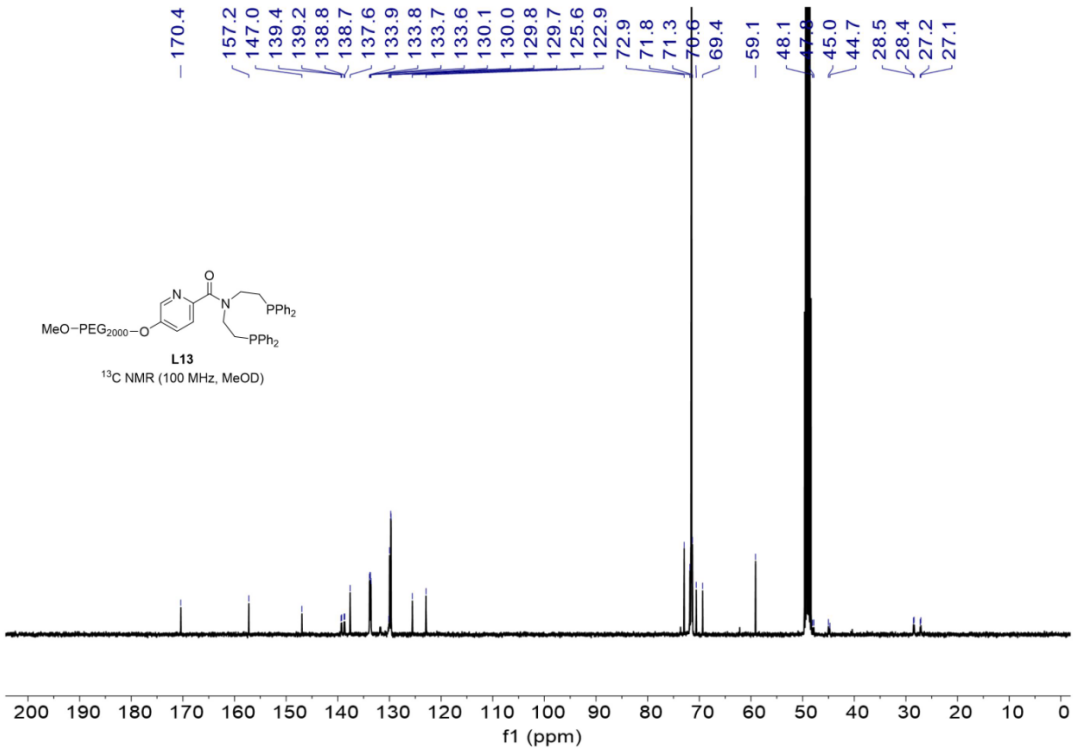

-21.02
-21.38
MeO−PEG1000−O
PPh2
PPh2
L12
31P NMR (162 MHz, MeOD)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

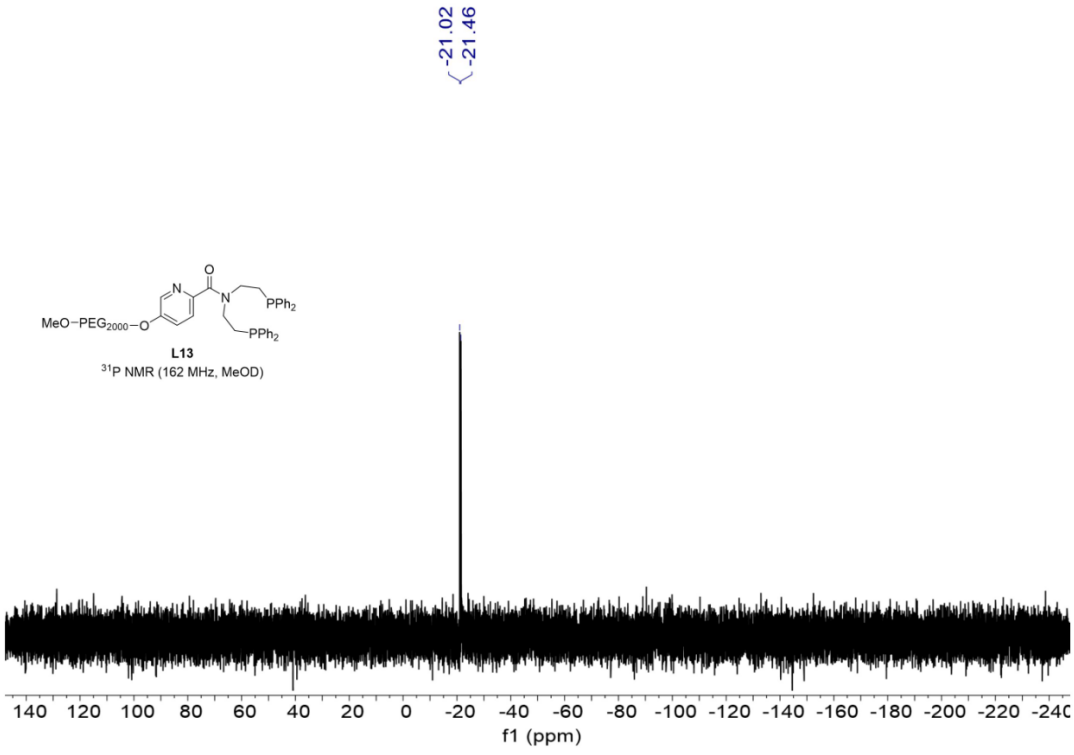

4.36
4.35
4.35
4.34
4.34
3.75
3.74
3.73
3.72
3.65
3.65
3.64
3.64
3.63
3.62
3.61
3.59
3.56
3.55
3.53
3.52
3.51
3.51
3.34
3.05
MeO−PEG2000−OMs
SI-4
1H NMR (400 MHz, CDCl3)
2.09
1.76
2.46
176.00
4.20
2.84
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

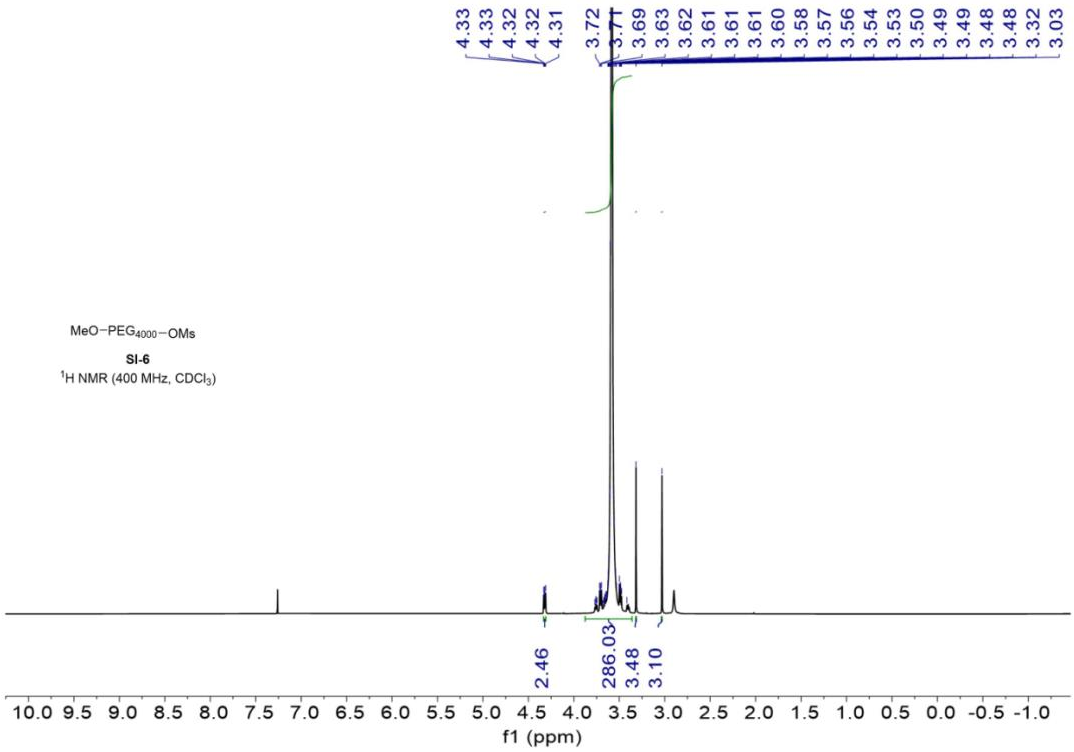

8.32
7.98
7.96
7.42
7.41
7.40
7.39
4.24
4.23
4.22
3.88
3.87
3.87
3.86
3.81
3.81
3.80
3.72
3.71
3.70
3.69
3.68
3.67
3.64
3.63
3.62
3.59
3.57
3.56
3.55
3.54
3.54
3.53
3.47
3.46
3.36
N
O
OH
MeO−PEG2000−O
SI-5
1H NMR (400 MHz, MeOD)
0.99
1.00
0.99
2.28
2.40
180.26
1.59
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

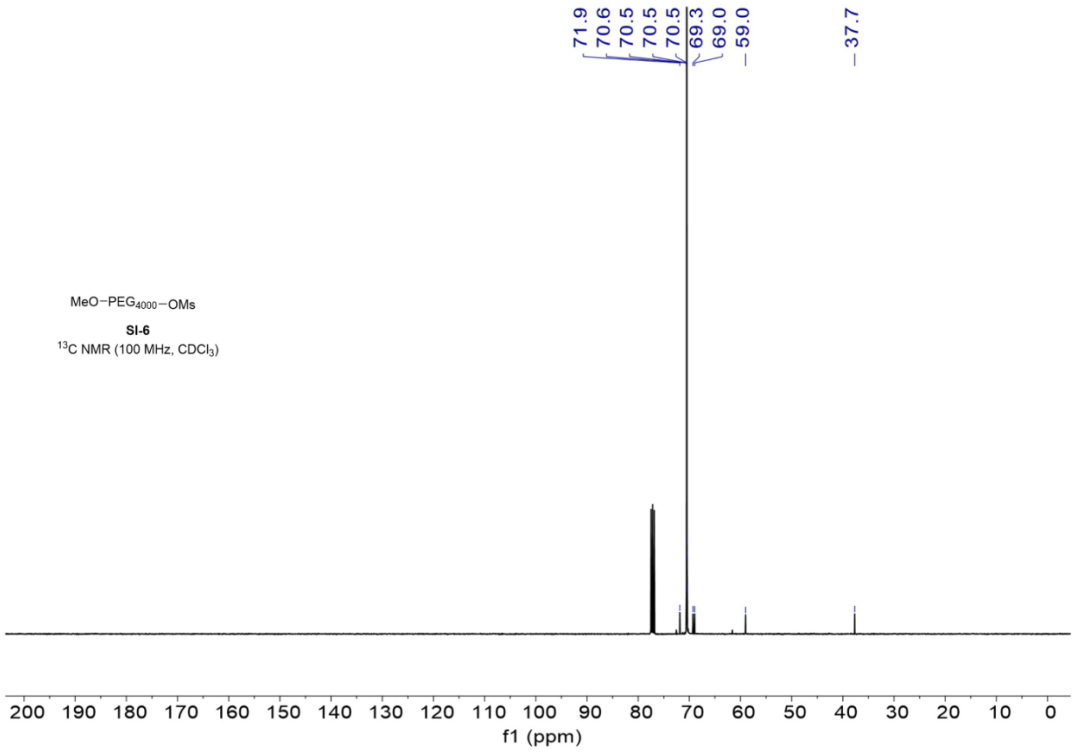

172.4
157.7
148.4
137.8
126.1
122.4
72.9
71.7
71.5
71.5
71.4
71.4
71.2
70.6
69.2
59.1
MeO−PEG2000−O
OH
SI-5
13C NMR (100 MHz, MeOD)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

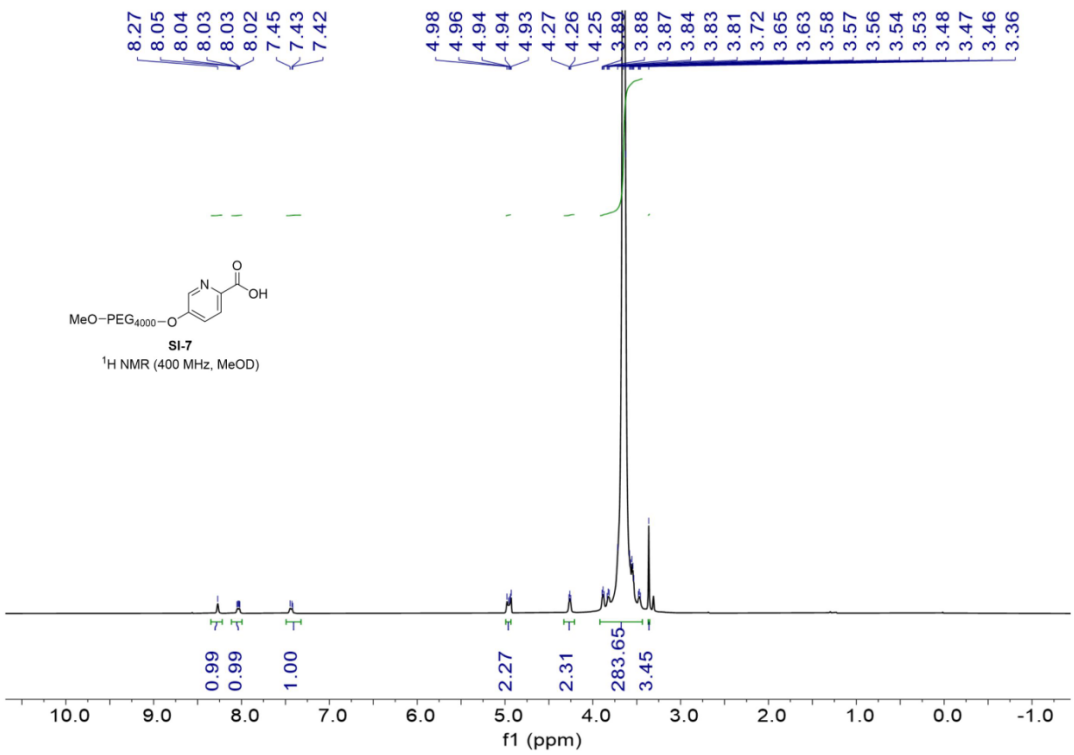

7.46
7.45
7.44
7.43
7.36
7.35
7.34
7.33
7.31
7.30
7.30
7.28
7.27
7.25
7.23
4.23
3.90
3.90
3.89
3.73
3.72
3.72
3.69
3.68
3.67
3.67
3.66
3.66
3.63
3.63
3.61
3.61
3.60
3.60
3.59
3.56
3.56
3.56
3.55
3.54
3.54
3.53
3.52
3.35
MeO−PEG2000−O
PPh2
PPh2
L13
1H NMR (400 MHz, MeOD)
1.02
4.79
7.64
8.50
2.12
2.27
1.54
2.45
178.49
2.48
2.47
3.00
1.85
1.75
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

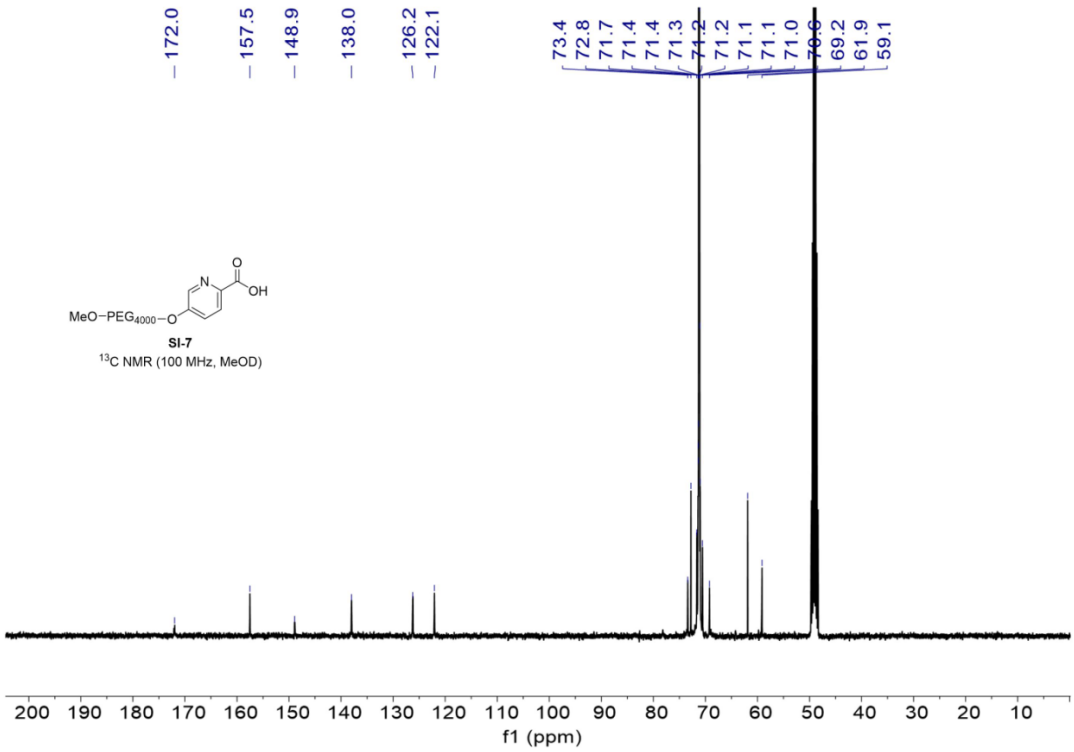

170.4
157.2
147.0
139.4
139.2
138.8
138.7
137.6
133.9
133.8
133.7
133.6
130.1
130.0
129.8
129.7
125.6
122.9
72.9
71.8
71.3
70.6
69.4
59.1
48.1
47.8
45.0
44.7
28.5
28.4
27.2
27.1
MeO−PEG2000−O
PPh2
PPh2
L13
13C NMR (100 MHz, MeOD)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

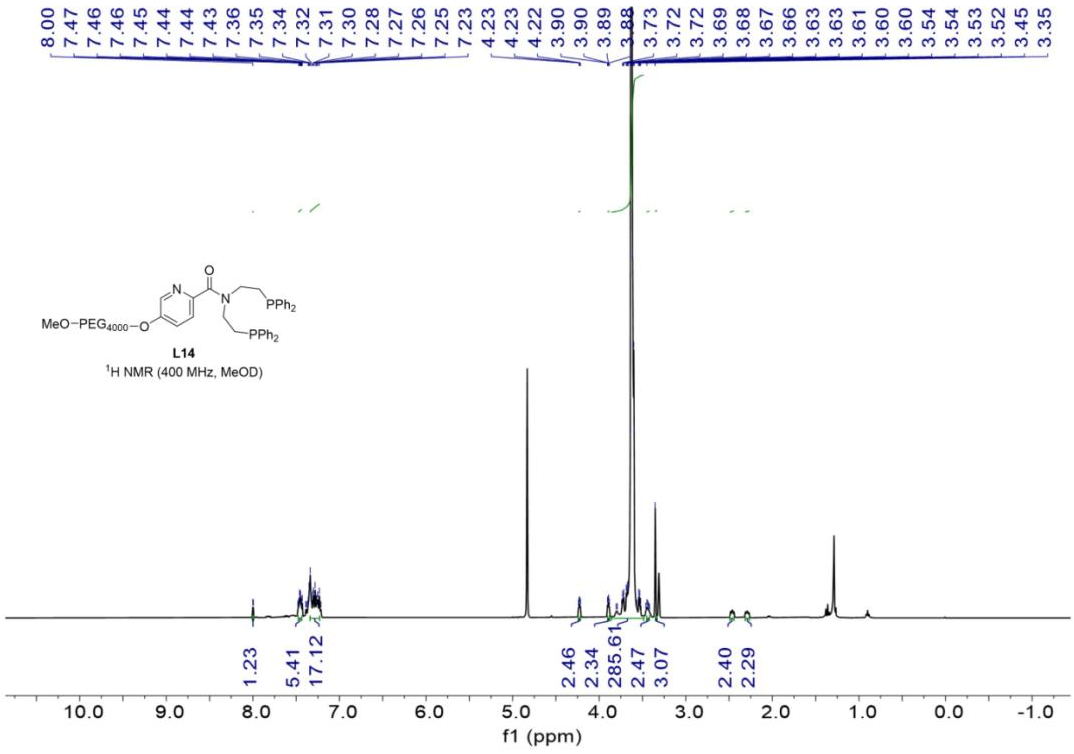

-21.02
-21.46
MeO−PEG2000−O
PPh2
PPh2
L13
31P NMR (162 MHz, MeOD)
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

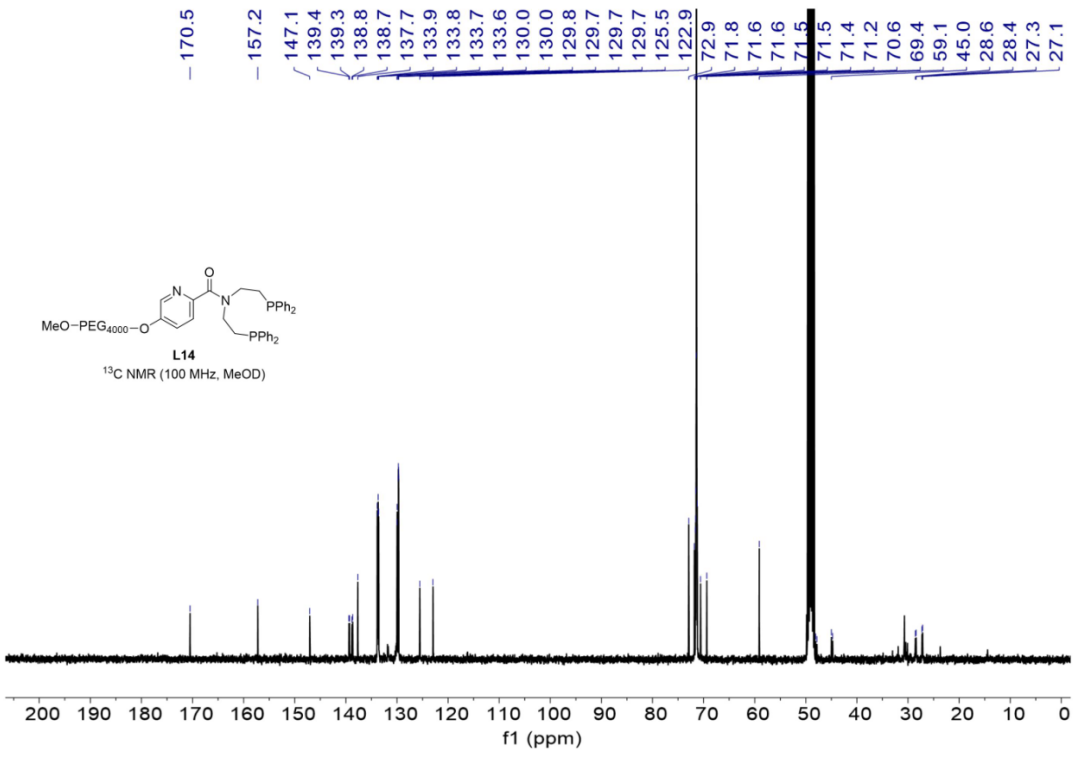

4.33
4.33
4.32
4.32
4.31
3.72
3.71
3.69
3.63
3.62
3.61
3.61
3.61
3.60
3.58
3.57
3.56
3.54
3.53
3.50
3.49
3.49
3.48
3.48
3.32
3.03
MeO−PEG4000−OMs
SI-6
1H NMR (400 MHz, CDCl3)
2.46
286.03
3.48
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

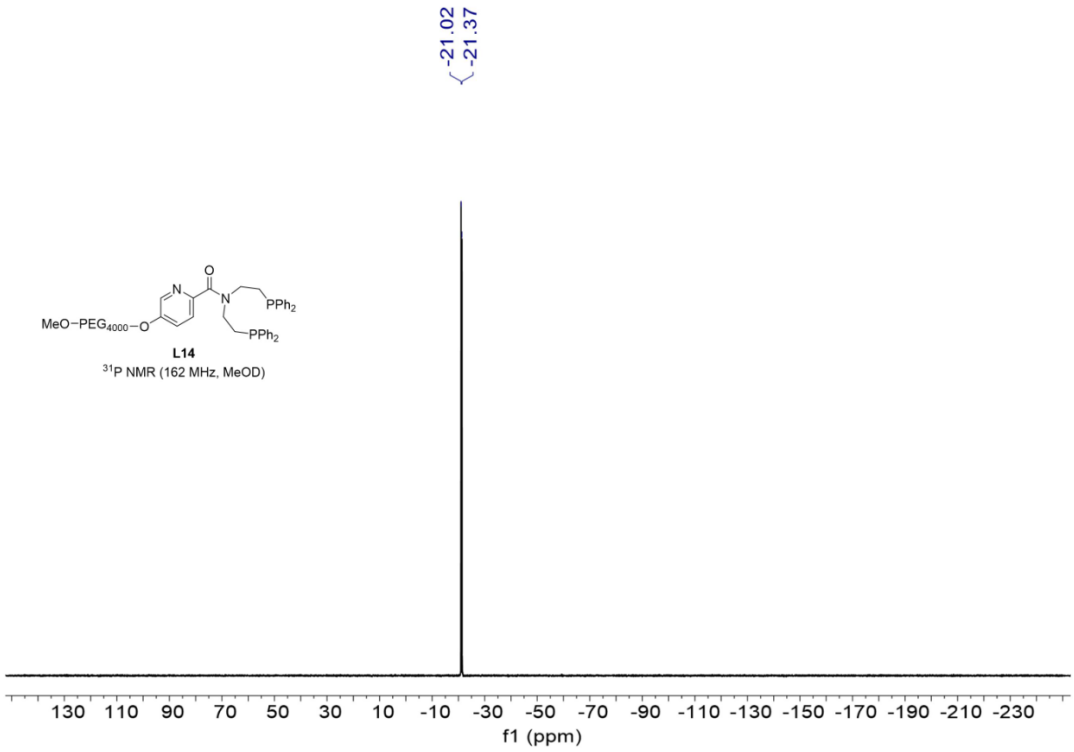

71.9
70.6
70.5
70.5
70.5
69.3
69.0
59.0
37.7
MeO−PEG4000−OMs
SI-6
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

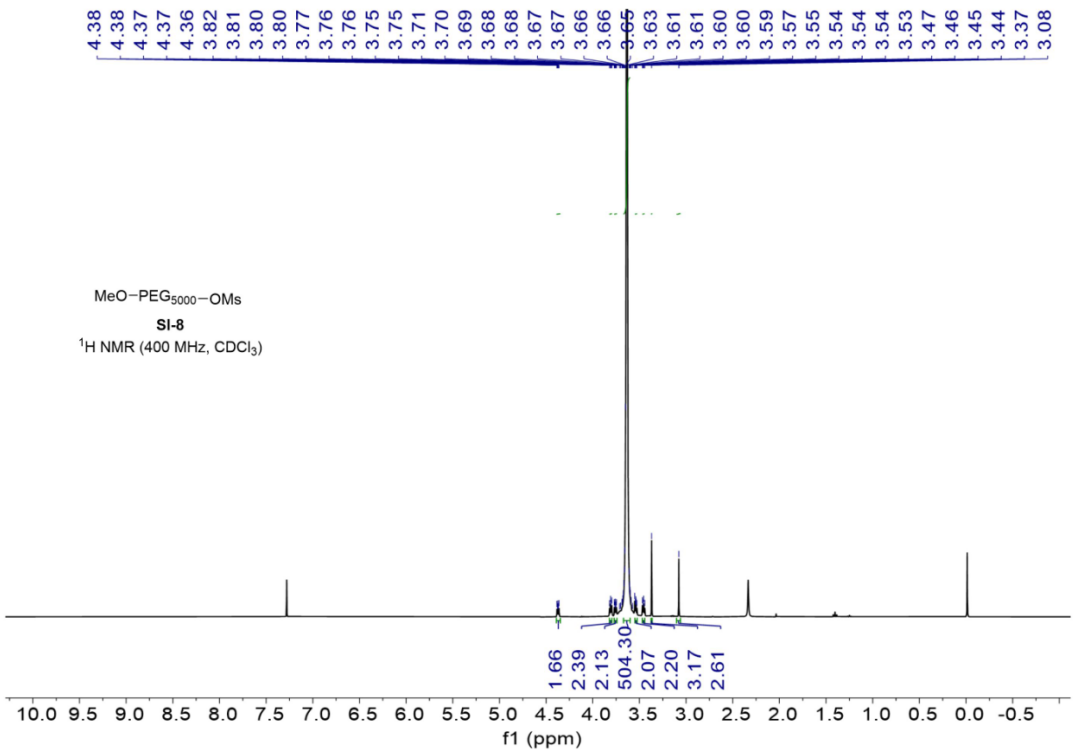

8.27
8.05
8.04
8.03
8.03
8.02
7.45
7.43
7.42
4.98
4.96
4.94
4.94
4.93
4.27
4.26
4.25
3.89
3.88
3.87
3.84
3.83
3.81
3.72
3.65
3.63
3.58
3.57
3.56
3.54
3.53
3.48
3.47
3.46
3.36
MeO−PEG4000−O
OH
N
O
SI-7
1H NMR (400 MHz, MeOD)
0.99
0.99
1.00
2.27
2.31
283.65
3.45
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

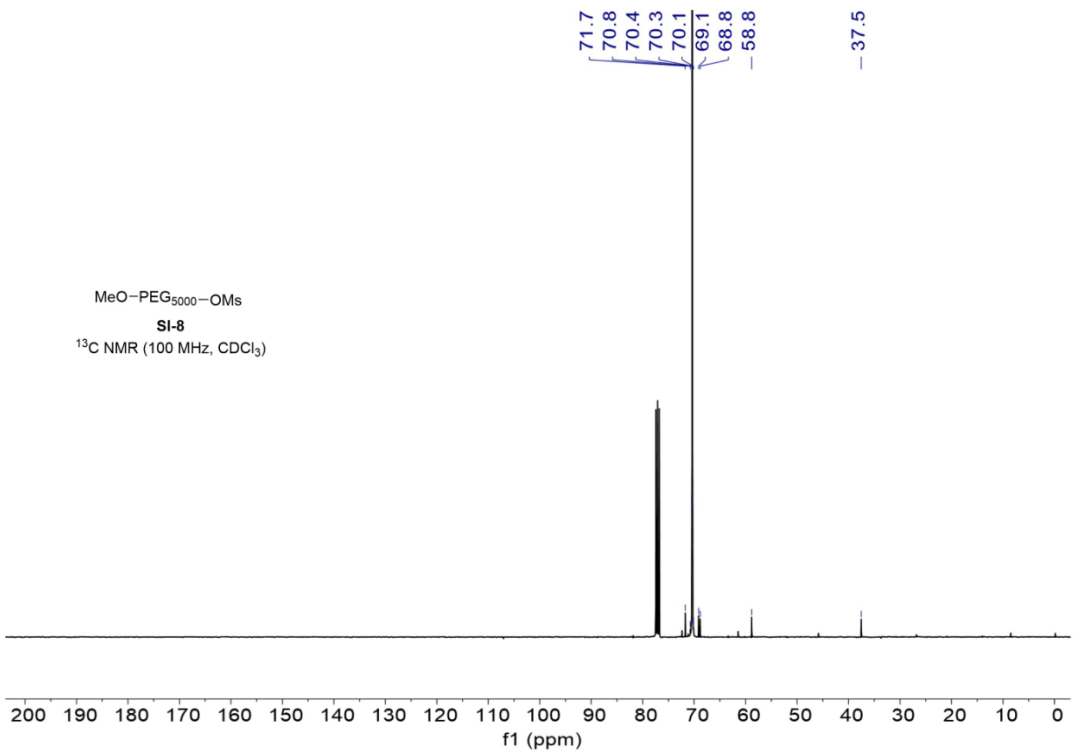

172.0
157.5
148.9
138.0
126.2
122.1
73.4
72.8
71.7
71.4
71.4
71.3
71.2
71.2
71.1
71.1
71.0
70.6
69.2
61.9
59.1
MeO−PEG4000−O
OH
N
O
SI-7
13C NMR (100 MHz, MeOD)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

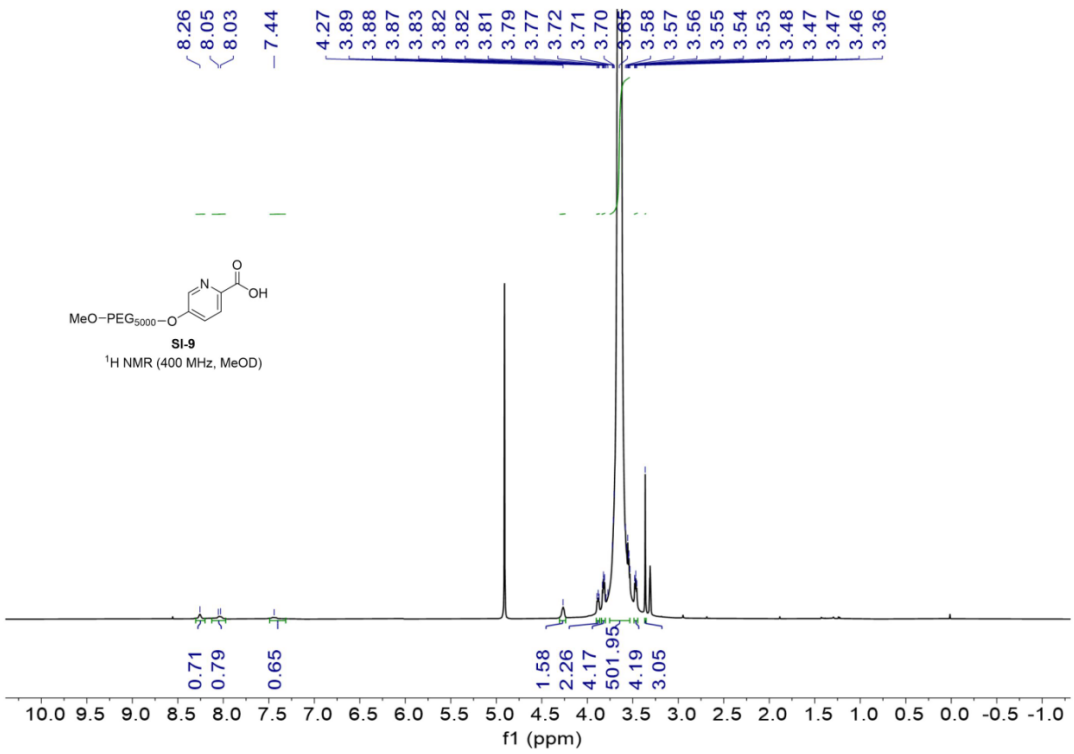

8.00 7.47 7.46 7.46 7.45 7.44 7.44 7.43 7.36 7.35 7.34 7.32 7.31 7.30 7.28 7.27 7.26 7.25 7.23 4.23 4.22 4.22 3.90 3.90 3.89 3.88 3.73 3.72 3.72 3.69 3.68 3.67 3.66 3.63 3.63 3.61 3.60 3.60 3.54 3.54 3.53 3.52 3.45 3.35
MeO−PEG4000−O
PPh2
PPh2
L14
1H NMR (400 MHz, MeOD)
1.23 5.41 17.12 2.46 2.34 285.61 2.47 3.07 2.40 2.29
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

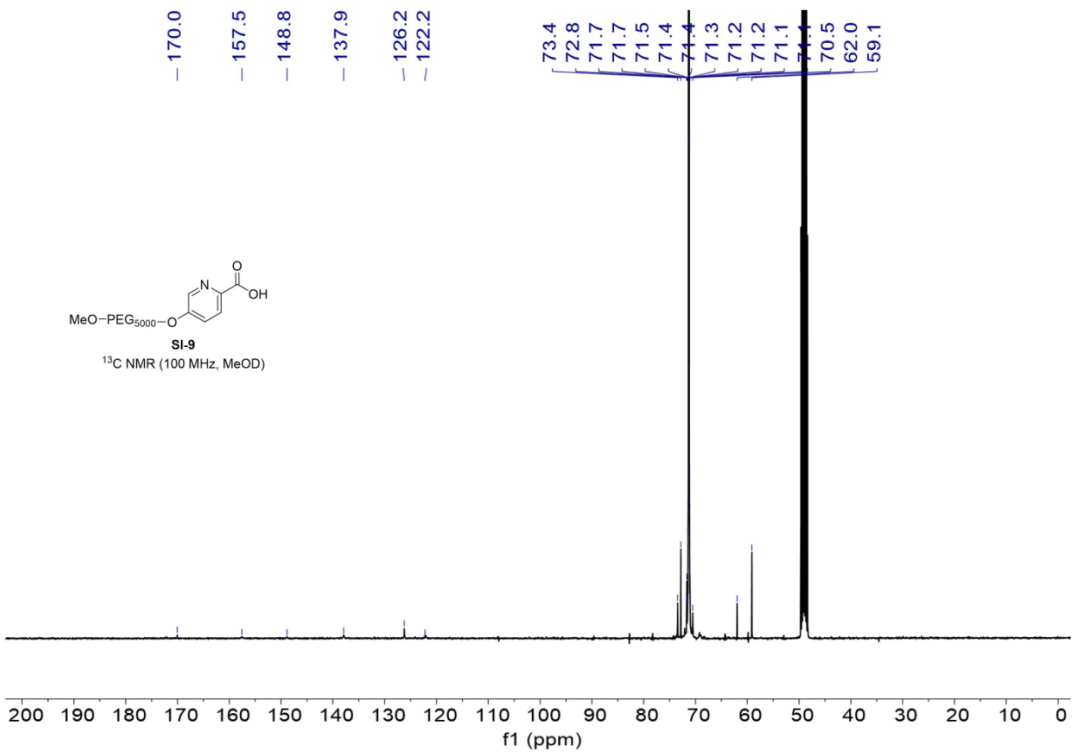

170.5 157.2 147.1 139.4 139.3 138.8 138.7 137.7 133.9 133.8 133.7 133.6 130.0 130.0 129.8 129.7 129.7 129.7 125.5 122.9 72.9 71.8 71.6 71.6 71.5 71.5 71.4 71.2 70.6 69.4 59.1 45.0 28.6 28.4 27.3 27.1
MeO−PEG4000−O
PPh2
PPh2
L14
13C NMR (100 MHz, MeOD)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

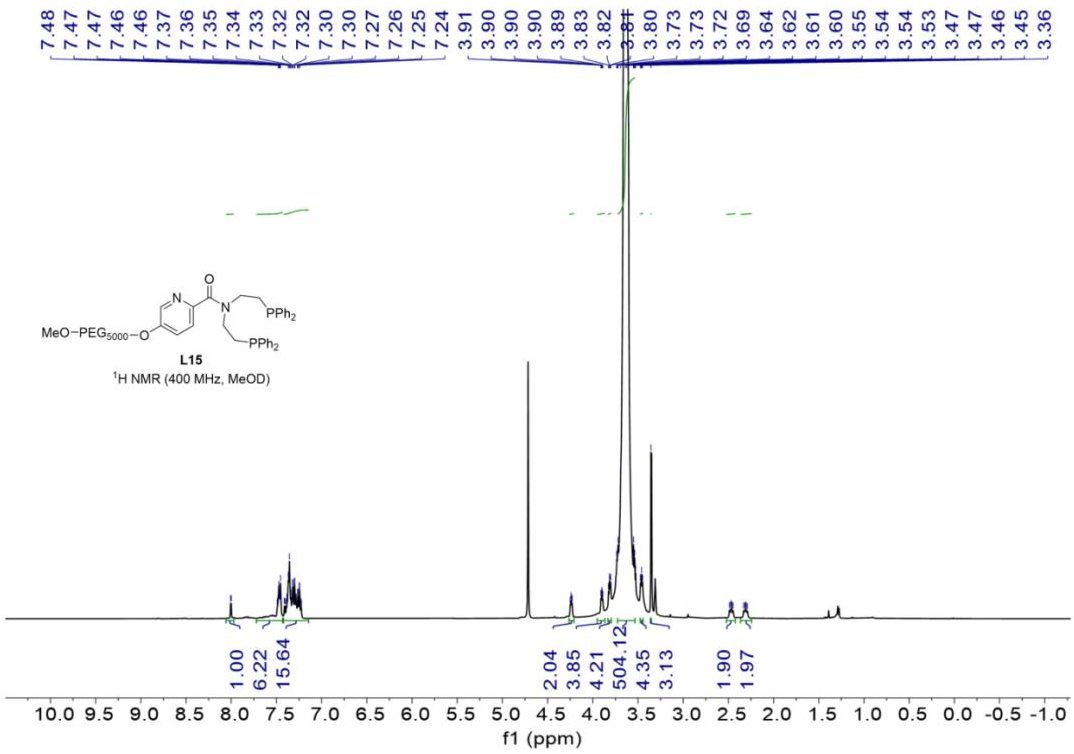

-21.02
-21.37
MeO−PEG4000−O
PPh2
PPh2
L14
31P NMR (162 MHz, MeOD)
130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

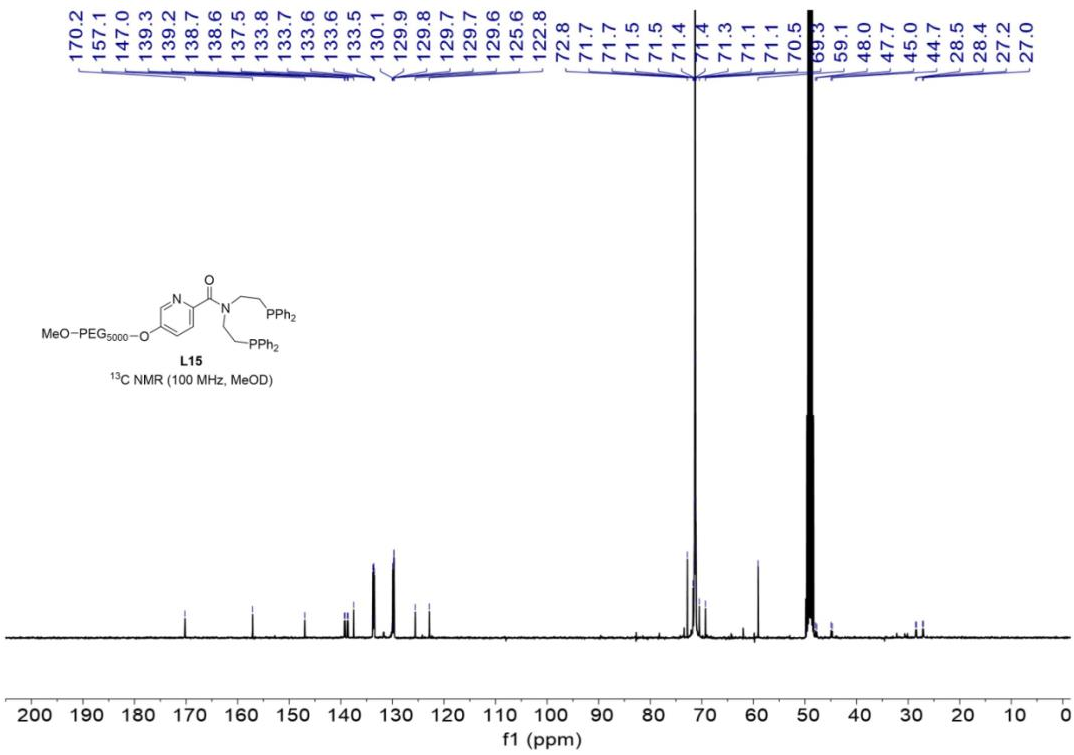

4.38 4.38 4.37 4.37 4.36 3.82 3.81 3.80 3.80 3.77 3.76 3.76 3.75 3.75 3.71 3.70 3.69 3.68 3.68 3.67 3.67 3.66 3.66 3.65 3.63 3.61 3.61 3.60 3.60 3.59 3.57 3.55 3.54 3.54 3.54 3.53 3.47 3.46 3.45 3.44 3.37 3.08
MeO−PEG5000−OMs
SI-8
1H NMR (400 MHz, CDCl3)
1.66 2.39 2.13 504.30 2.07 2.20 3.17 2.61
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

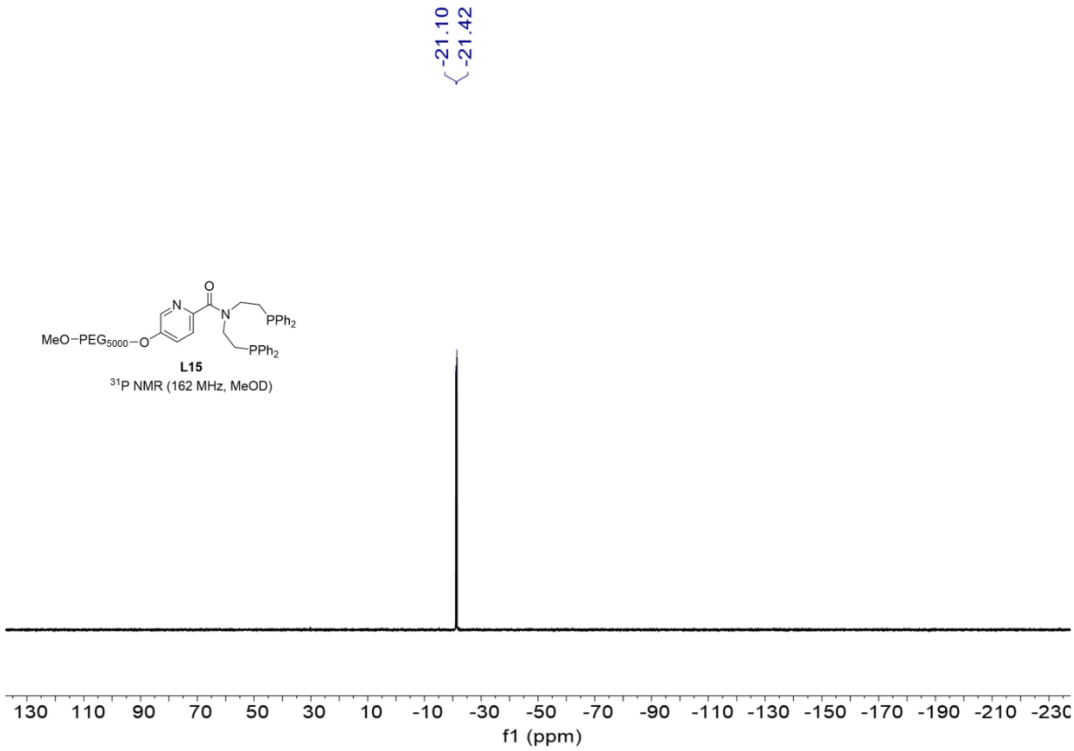

71.7
70.8
70.4
70.3
70.1
69.1
68.8
58.8
37.5
MeO−PEG5000−OMs
SI-8
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

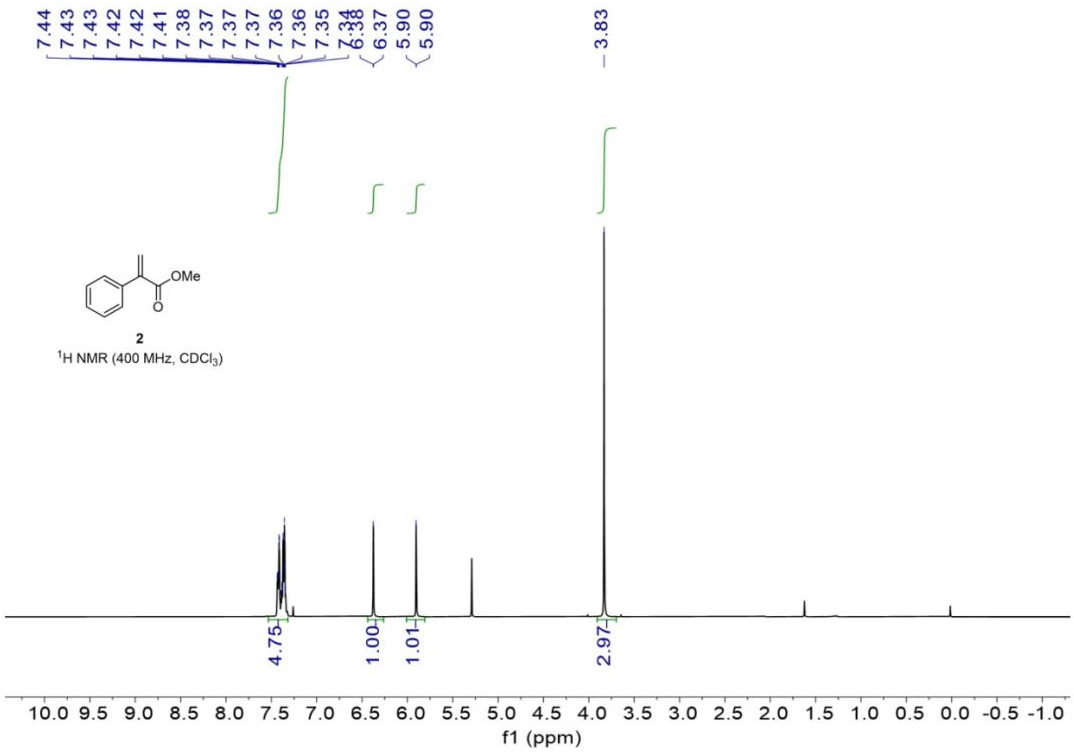

8.26
8.05
8.03
7.44
4.27
3.89
3.88
3.87
3.83
3.82
3.82
3.81
3.79
3.77
3.72
3.71
3.70
3.65
3.58
3.57
3.56
3.55
3.54
3.53
3.48
3.47
3.47
3.46
3.36
MeO−PEG5000−O
OH
SI-9
1H NMR (400 MHz, MeOD)
0.71
0.79
0.65
1.58
2.26
4.17
501.95
4.19
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


170.0
157.5
148.8
137.9
126.2
122.2
73.4
72.8
71.7
71.7
71.5
71.4
71.4
71.3
71.2
71.2
71.1
70.5
62.0
59.1
MeO−PEG5000−O
N
O
OH
SI-9
13C NMR (100 MHz, MeOD)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.48
7.47
7.47
7.46
7.46
7.37
7.36
7.35
7.34
7.33
7.32
7.32
7.30
7.30
7.27
7.26
7.25
7.24
3.91
3.90
3.90
3.90
3.89
3.83
3.82
3.81
3.80
3.73
3.73
3.72
3.69
3.64
3.62
3.61
3.60
3.55
3.54
3.54
3.53
3.47
3.47
3.46
3.45
3.36
MeO−PEG5000−O
N
O
N
PPh2
PPh2
L15
1H NMR (400 MHz, MeOD)
1.00
6.22
15.64
2.04
3.85
4.21
504.12
4.35
3.13
1.90
1.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

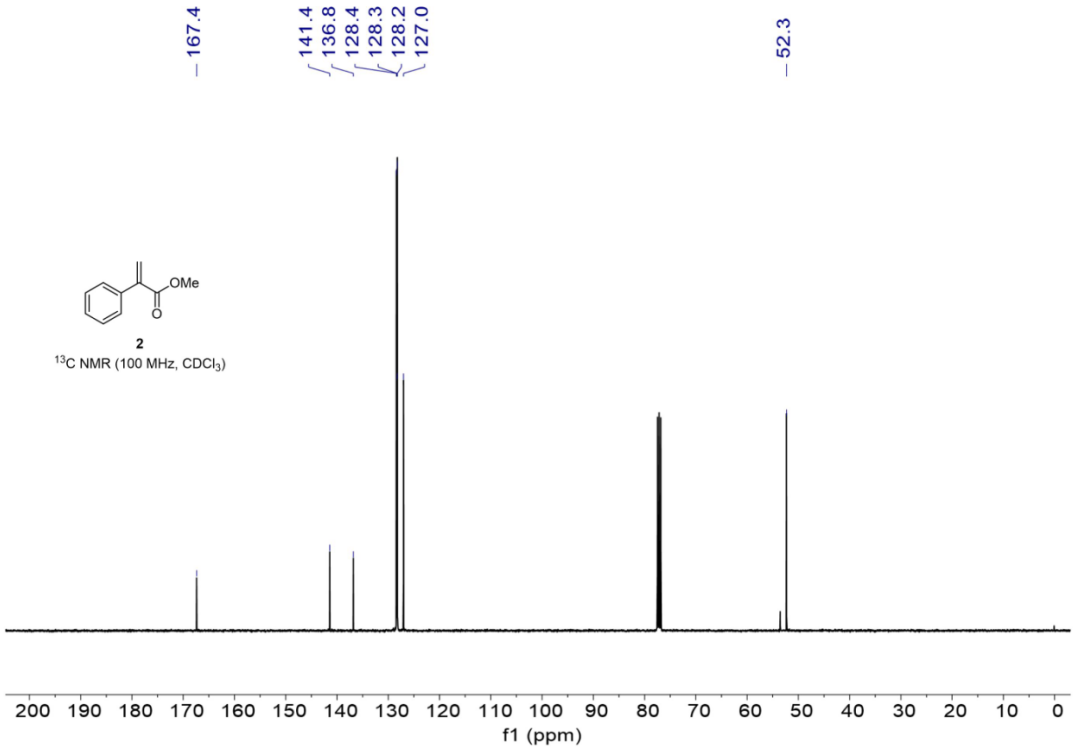

170.2
157.1
147.0
139.3
139.2
138.7
138.6
137.5
133.8
133.7
133.6
133.6
133.5
130.1
129.9
129.8
129.7
129.7
129.6
125.6
122.8
72.8
71.7
71.7
71.5
71.5
71.4
71.4
71.3
71.1
71.1
70.5
69.3
59.1
48.0
47.7
45.0
44.7
28.5
28.4
27.2
27.0
MeO−PEG5000−O
PPh2
PPh2
L15
13C NMR (100 MHz, MeOD)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-21.10
-21.42
MeO−PEG5000−O
PPh2
PPh2
L15
31P NMR (162 MHz, MeOD)
130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)



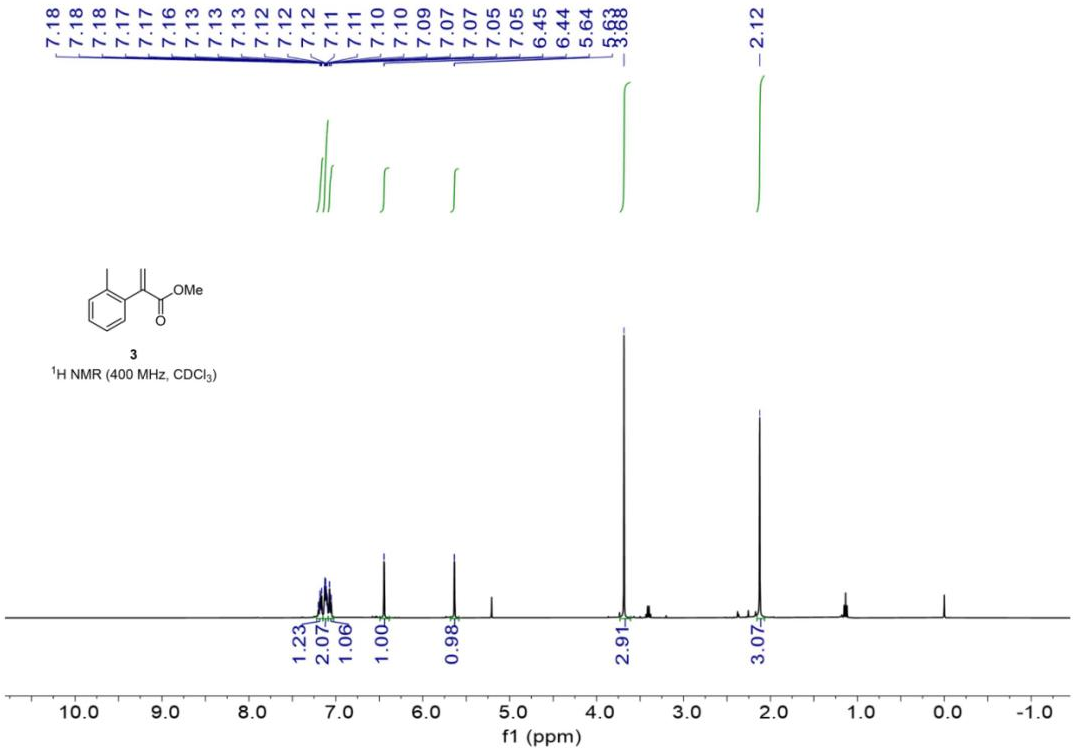
2

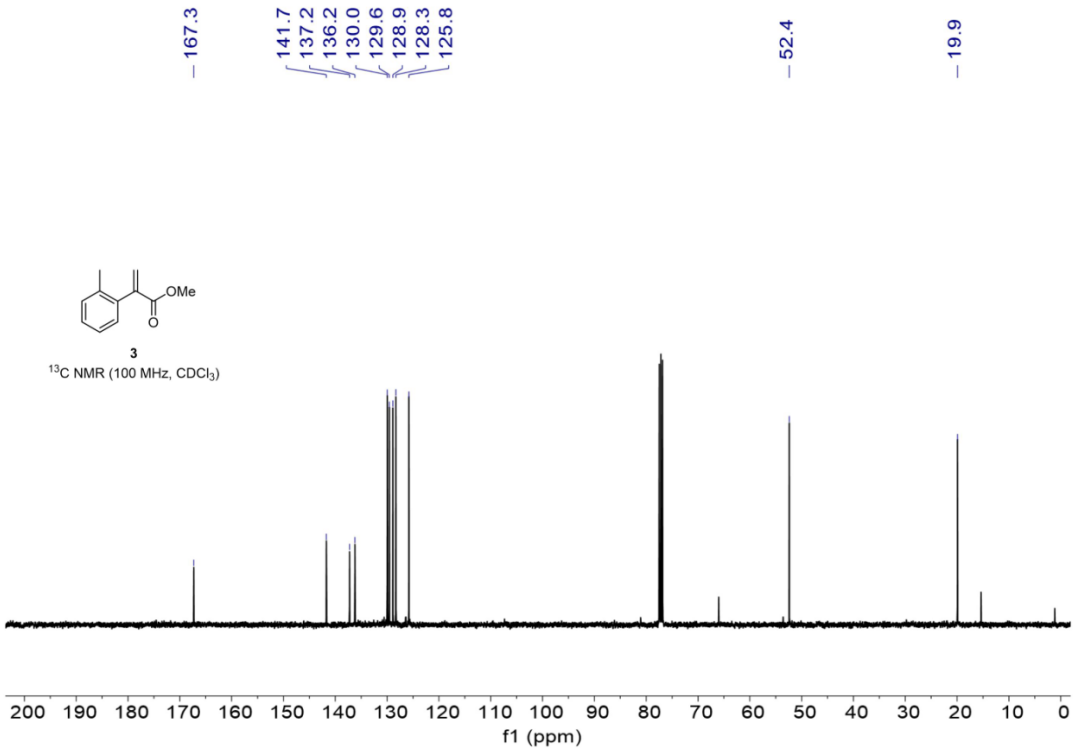
^{1}H NMR (400 MHz, $CDCl_3$)

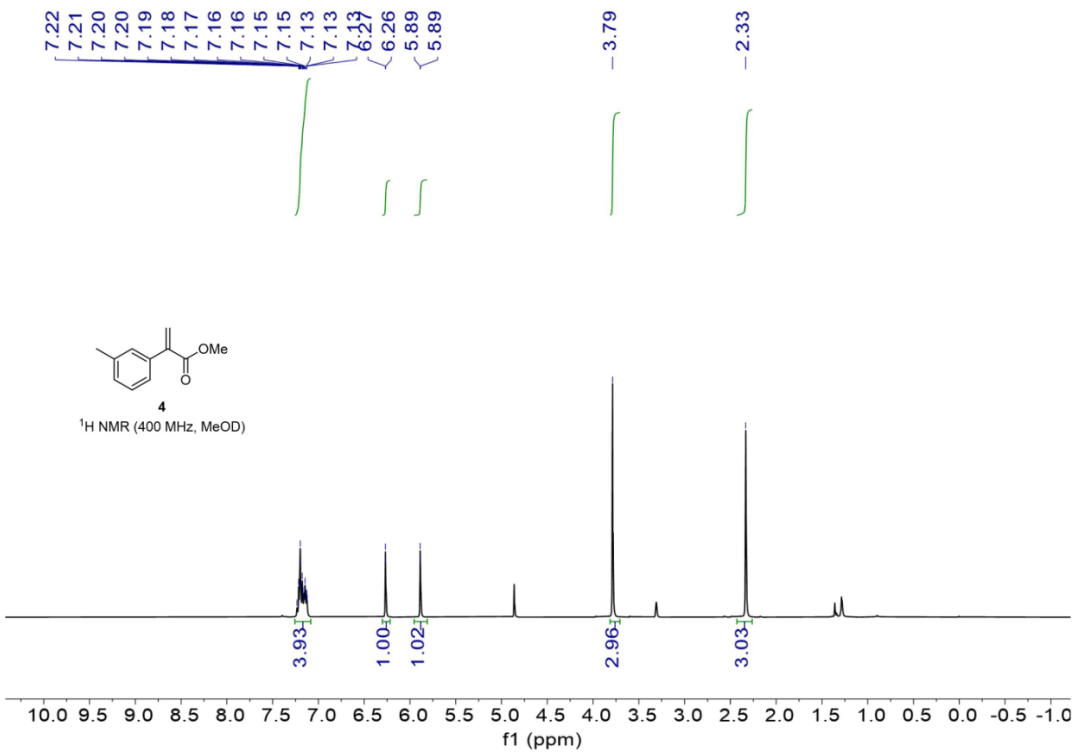


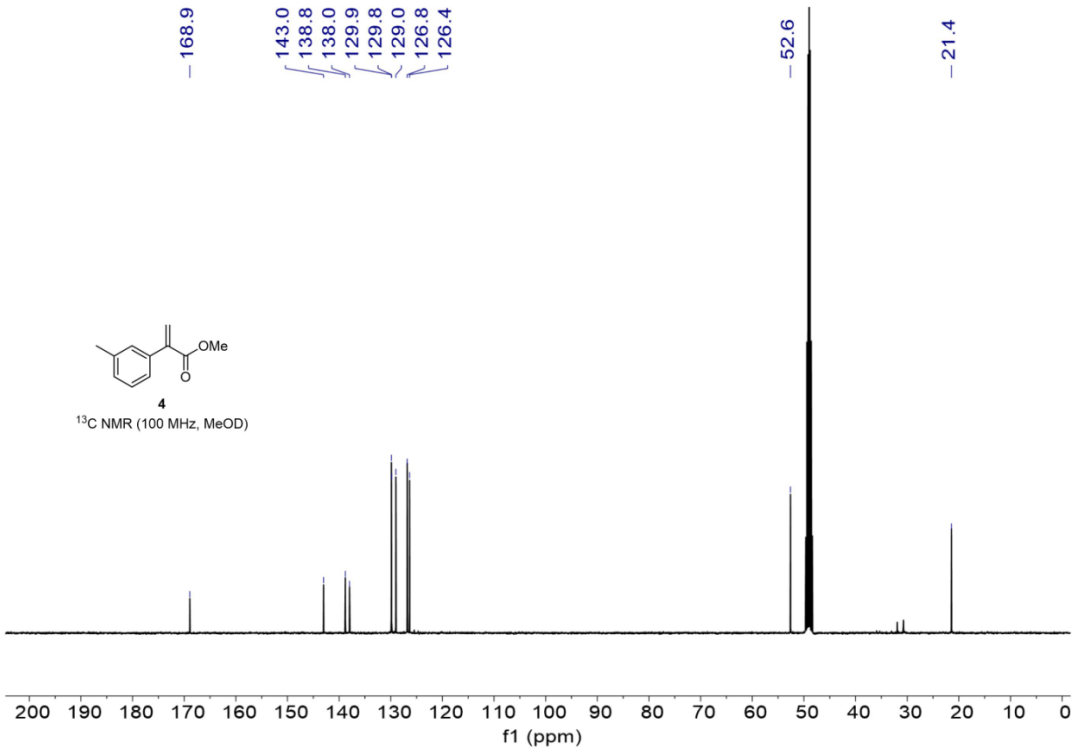
2

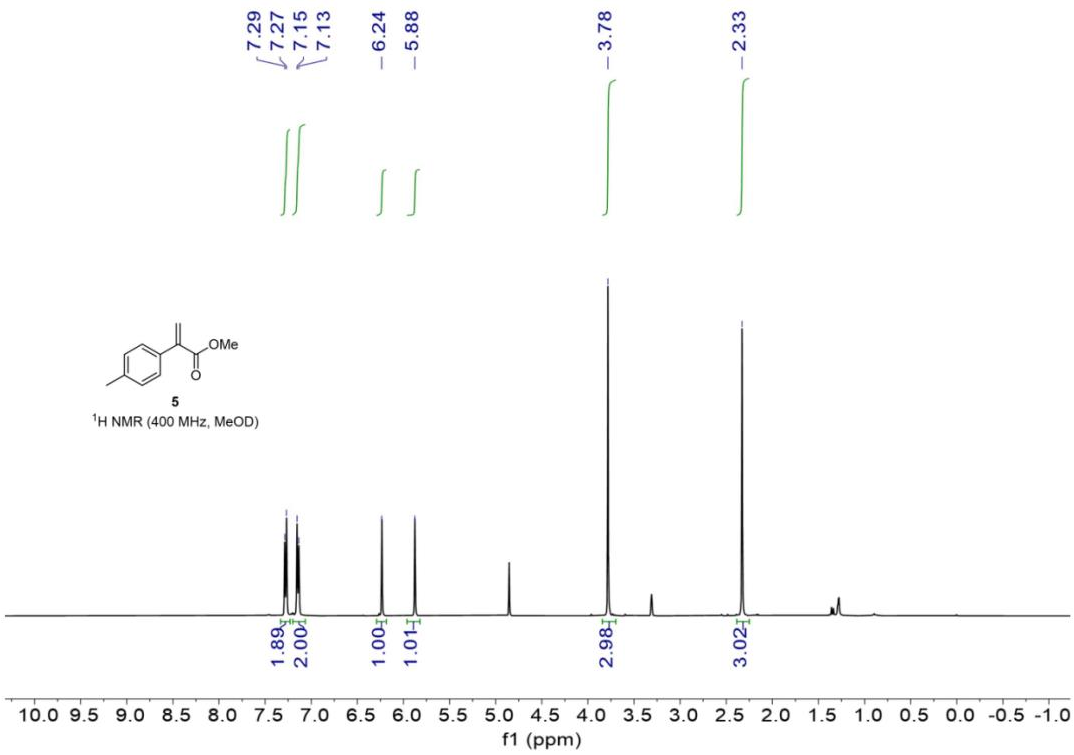
^{13}C NMR (100 MHz, $CDCl_3$)

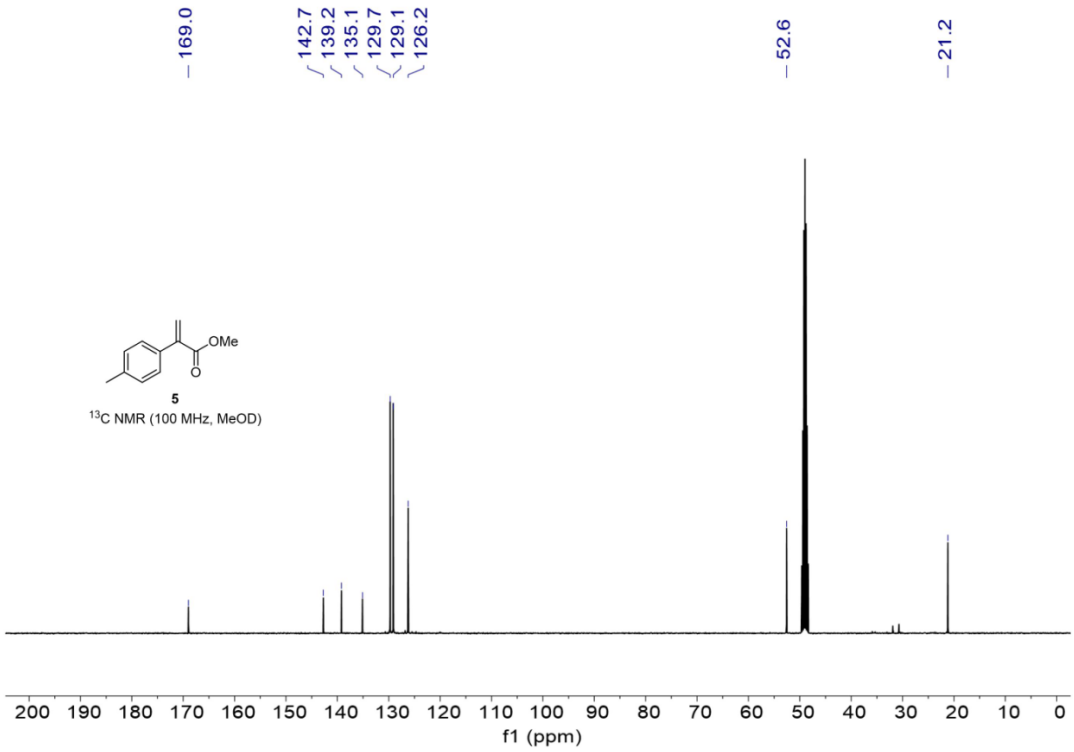

7.18
7.18
7.18
7.17
7.17
7.16
7.13
7.13
7.13
7.12
7.12
7.12
7.11
7.11
7.10
7.10
7.09
7.07
7.07
7.05
7.05
6.45
6.44
5.64
3.88
2.12
OMe
O
3
1H NMR (400 MHz, CDCl3)
1.23
2.07
1.06
1.00
0.98
2.91
3.07
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

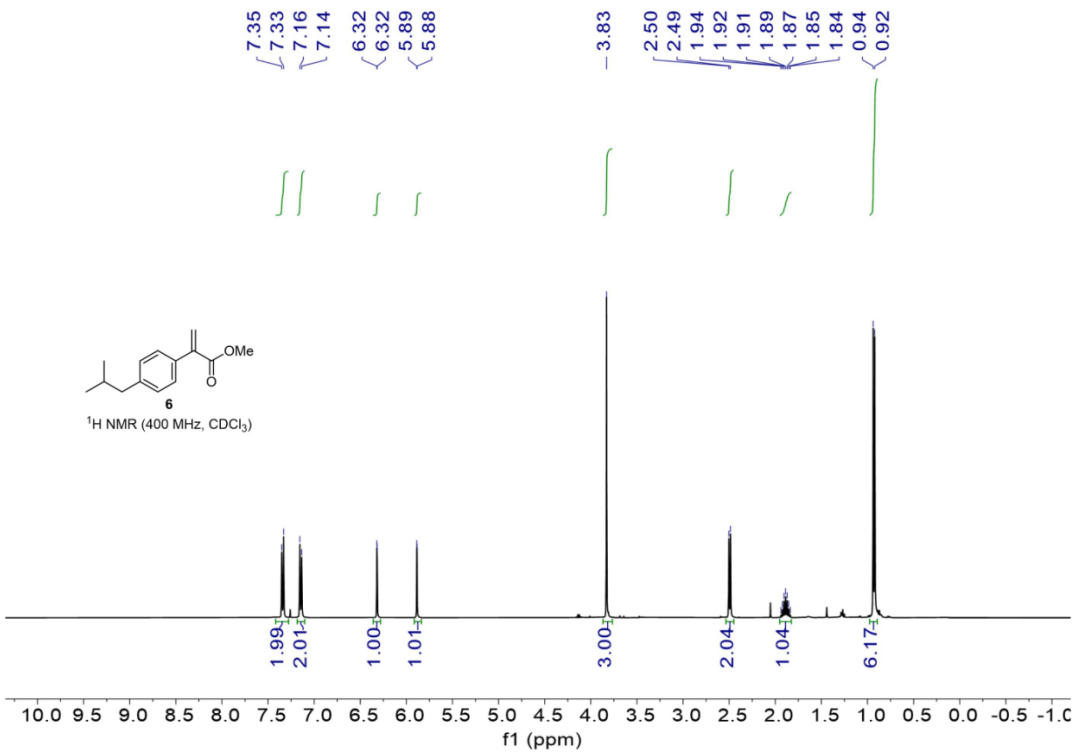

167.3
141.7
137.2
136.2
130.0
129.6
128.9
128.3
125.8
52.4
19.9
OMe
O
3
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

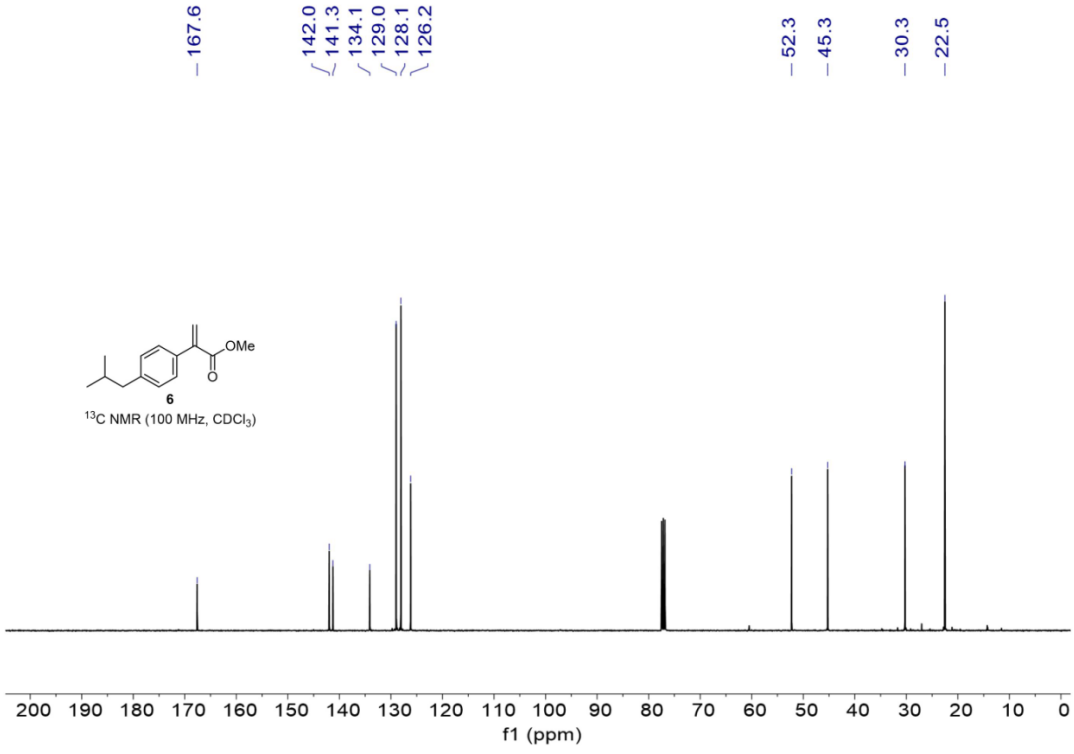

7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.16
7.16
7.15
7.15
7.13
7.13
6.27
6.26
5.89
5.89
3.79
2.33
OMe
O
4
1H NMR (400 MHz, MeOD)
3.93
1.00
1.02
2.96
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

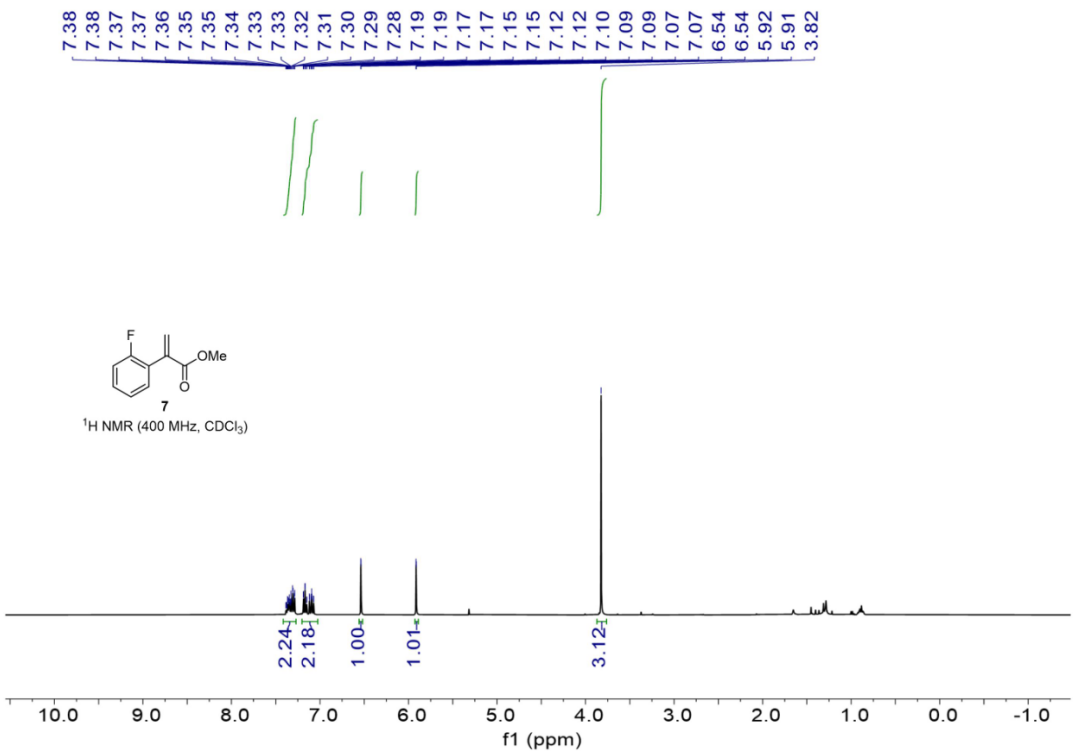

168.9
143.0
138.8
138.0
129.9
129.8
129.0
126.8
126.4
52.6
21.4
OMe
O
4
13C NMR (100 MHz, MeOD)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

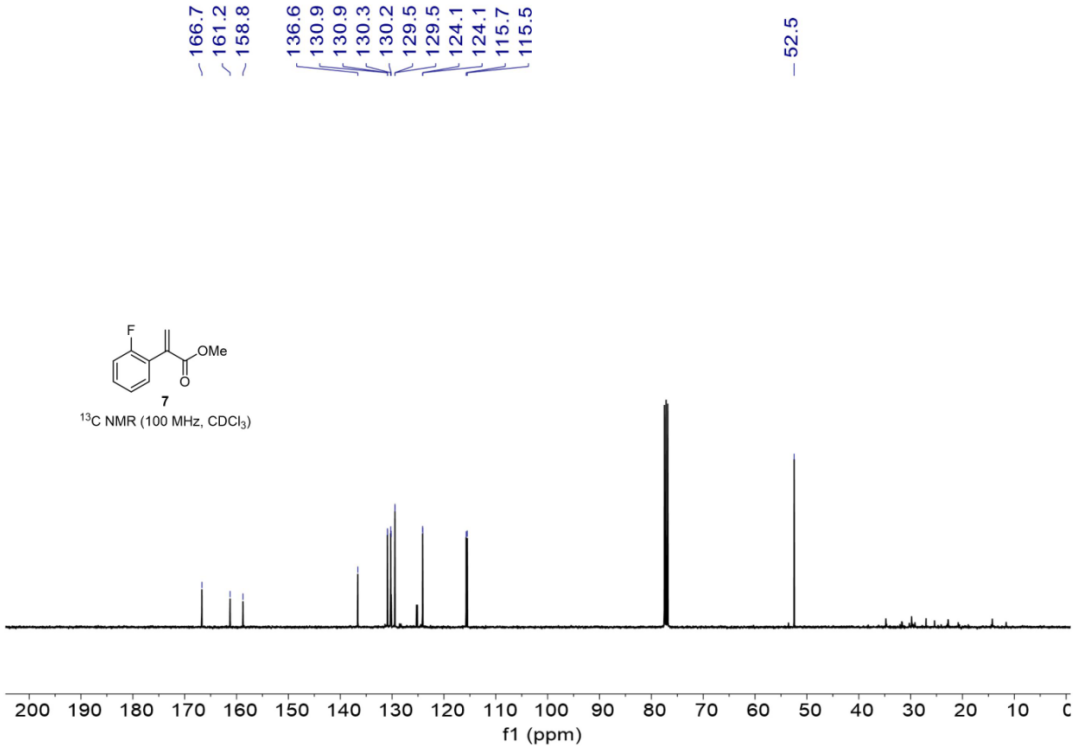

7.29
7.27
7.15
7.13
6.24
5.88
3.78
2.33
OMe
O
5
1H NMR (400 MHz, MeOD)
1.89
2.00
1.00
1.01
2.98
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

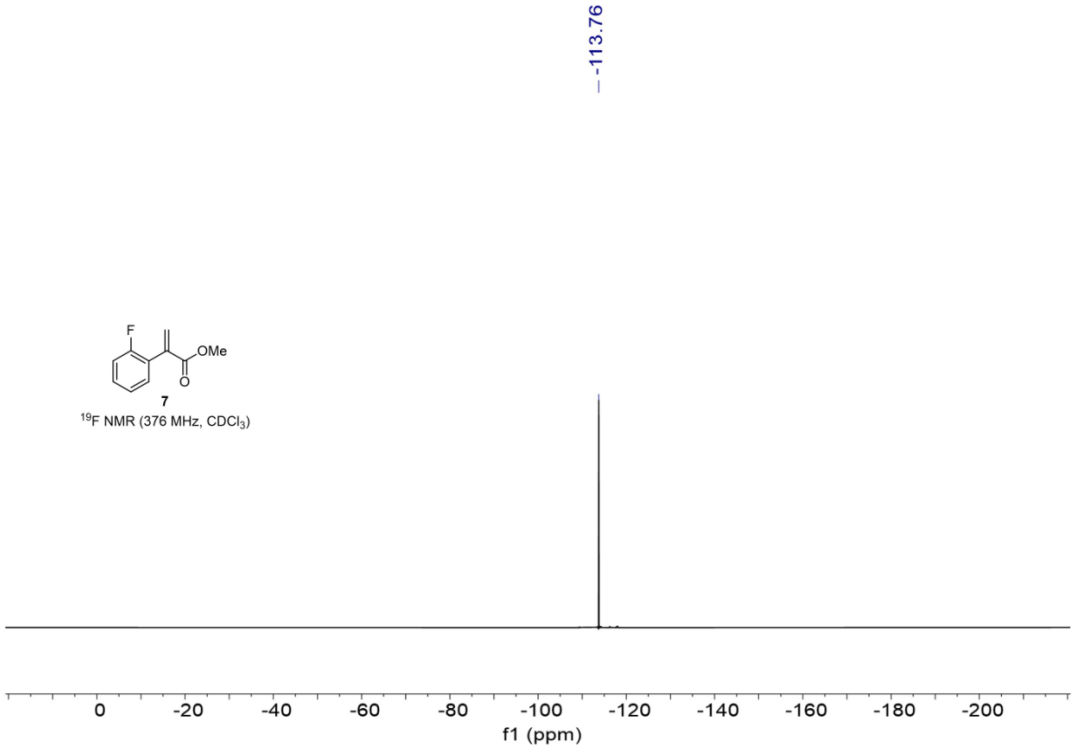

169.0
142.7
139.2
135.1
129.7
129.1
126.2
52.6
21.2
OMe
O
5
13C NMR (100 MHz, MeOD)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

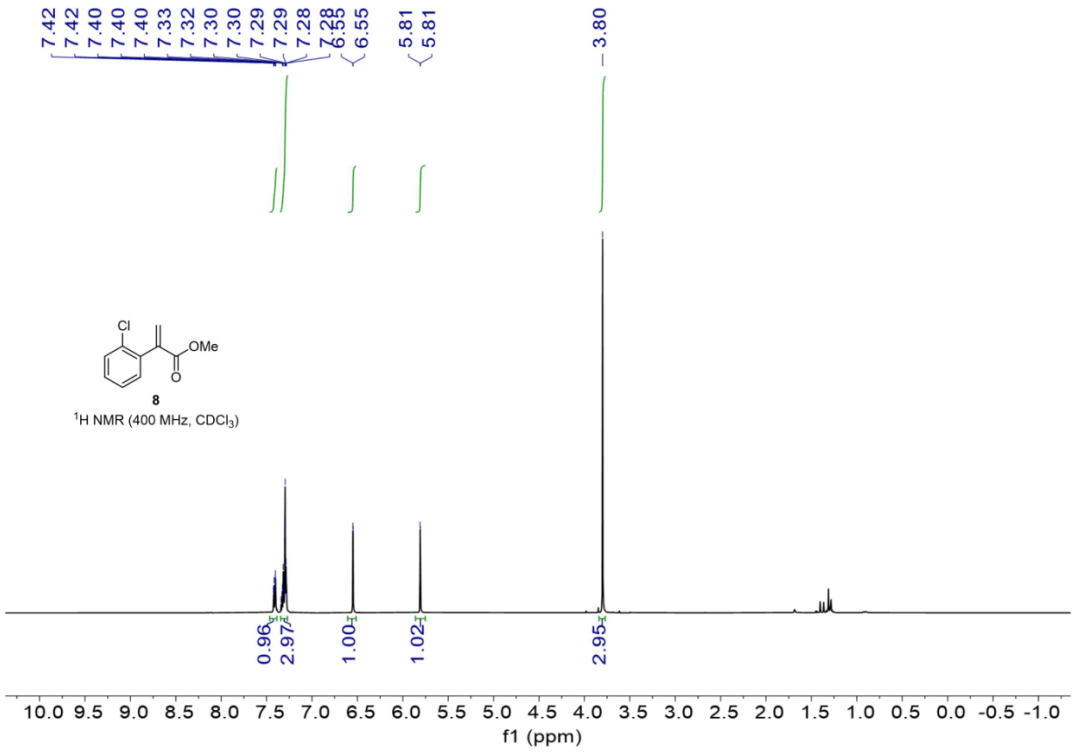

7.35
7.33
7.16
7.14
6.32
6.32
5.89
5.88
3.83
2.50
2.49
1.94
1.92
1.91
1.89
1.87
1.85
1.84
0.94
0.92
OMe
O
6
1H NMR (400 MHz, CDCl3)
1.99
2.01
1.00
1.01
3.00
2.04
1.04
6.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

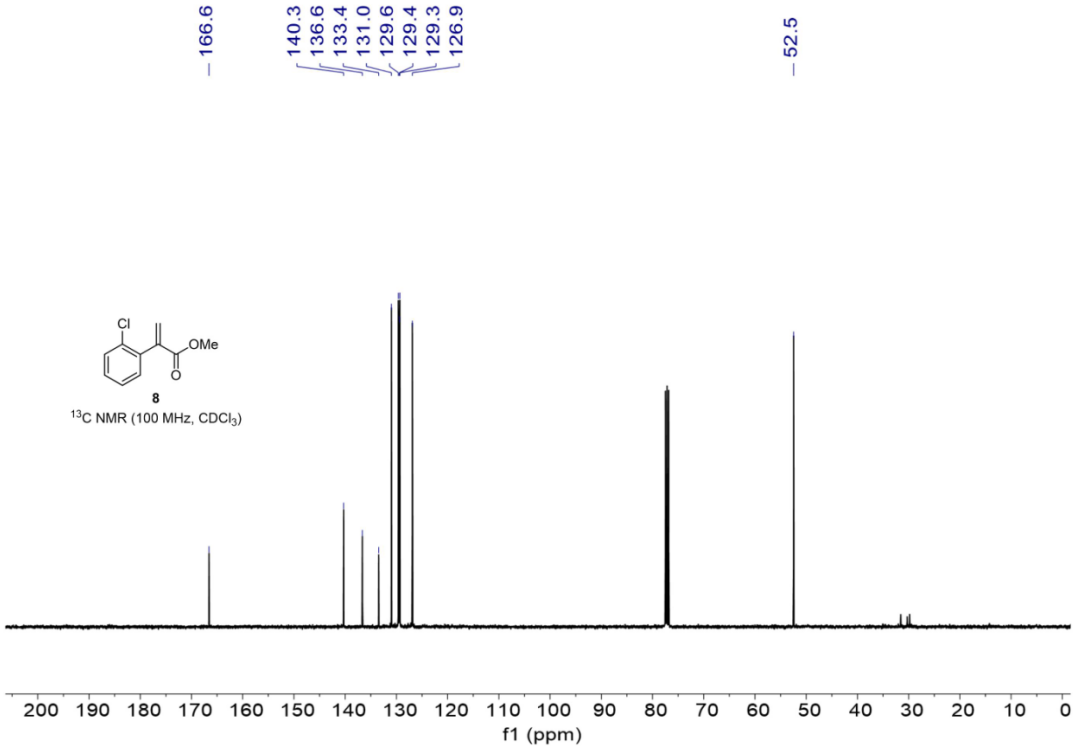

167.6
142.0
141.3
134.1
129.0
128.1
126.2
52.3
45.3
30.3
22.5
OMe
O
6
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

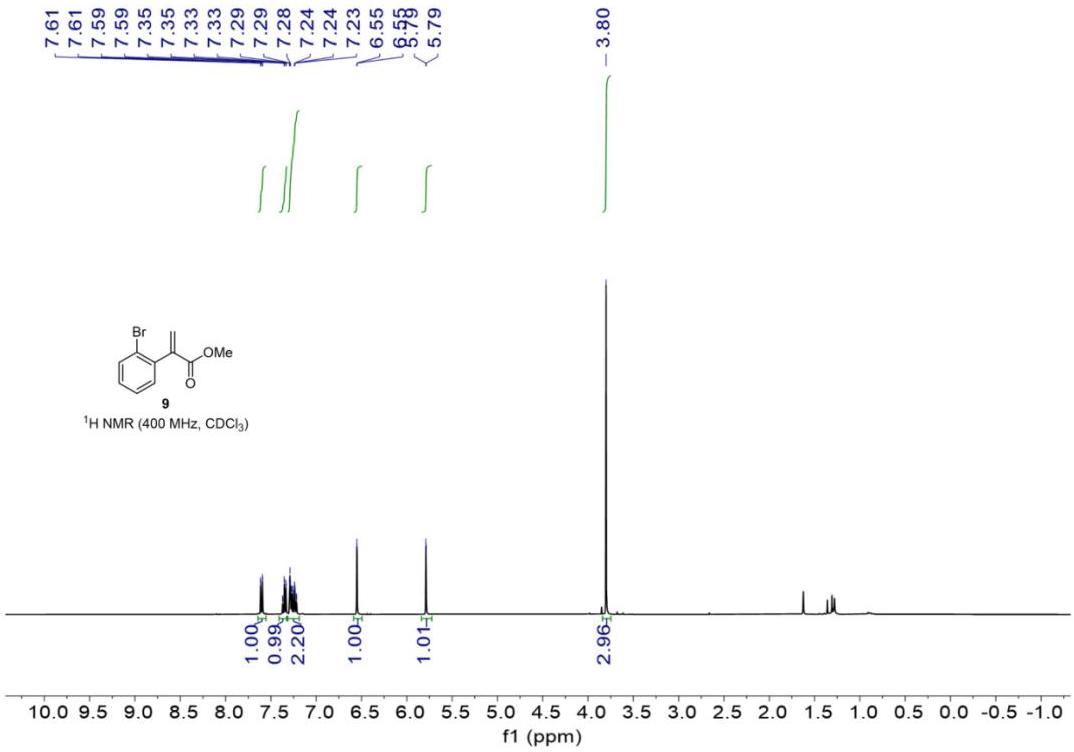

7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.28
7.19
7.19
7.17
7.17
7.15
7.15
7.12
7.12
7.10
7.09
7.09
7.07
7.07
6.54
6.54
5.92
5.91
3.82
F
OMe
O
7
1H NMR (400 MHz, CDCl3)
2.24
2.18
1.00
1.01
3.12
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

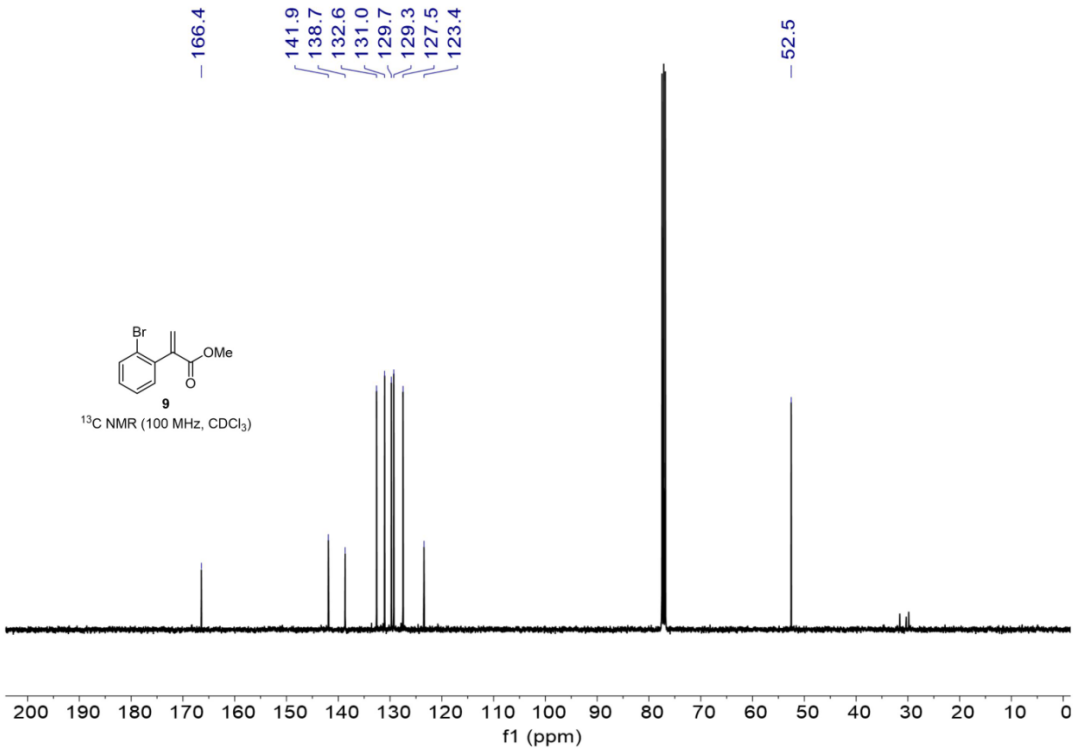

166.7
161.2
158.8
136.6
130.9
130.9
130.3
130.2
129.5
129.5
124.1
124.1
115.7
115.5
52.5
F
OMe
O
7
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

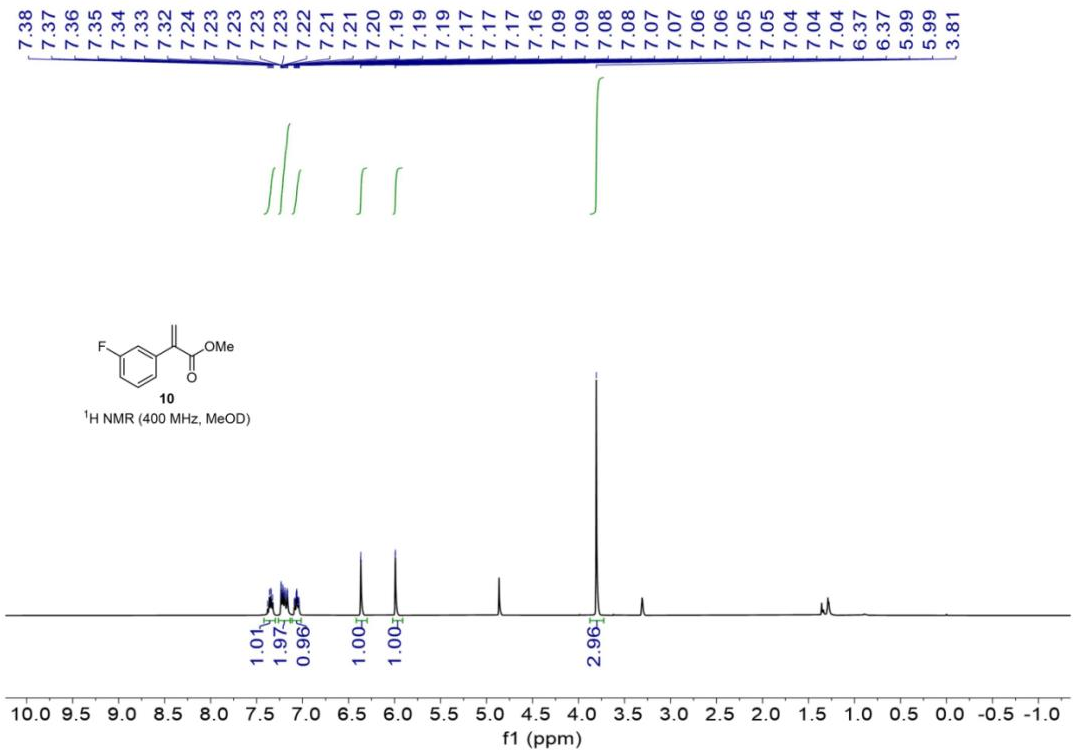

-113.76
F
OMe
O
7
^{19}F NMR (376 MHz, CDCl$_3$)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

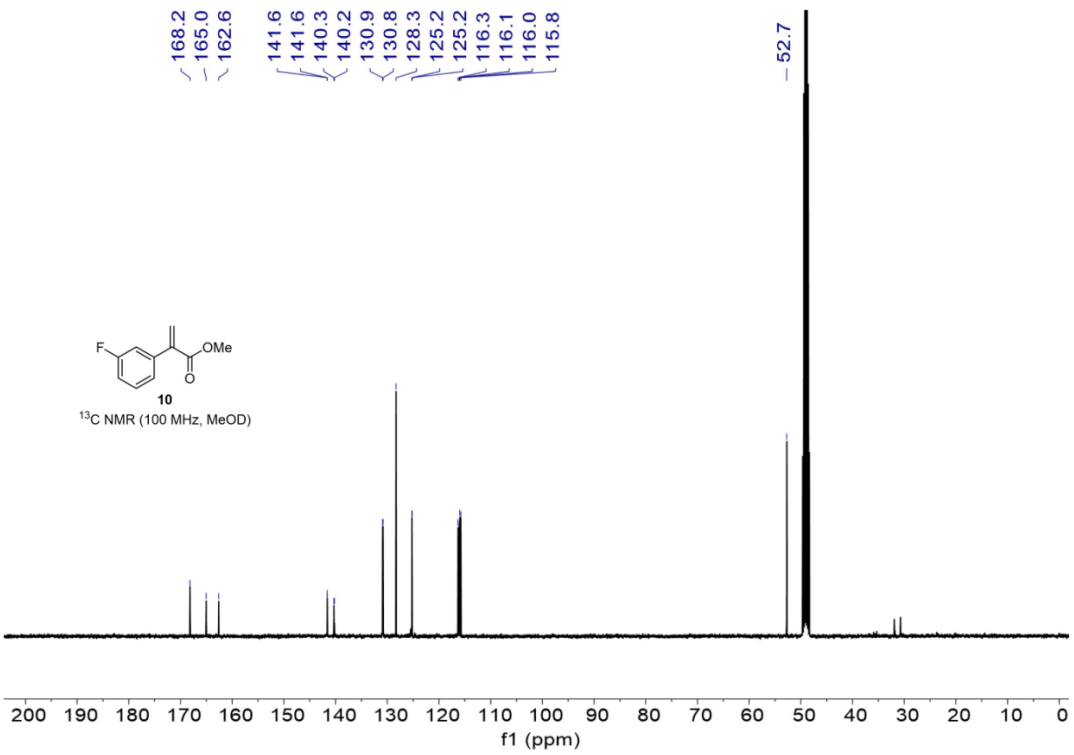

7.42
7.42
7.40
7.40
7.40
7.33
7.32
7.30
7.30
7.29
7.29
7.28
6.55
6.55
5.81
5.81
3.80
Cl
OMe
O
8
^{1}H NMR (400 MHz, CDCl$_3$)
0.96
2.97
1.00
1.02
2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

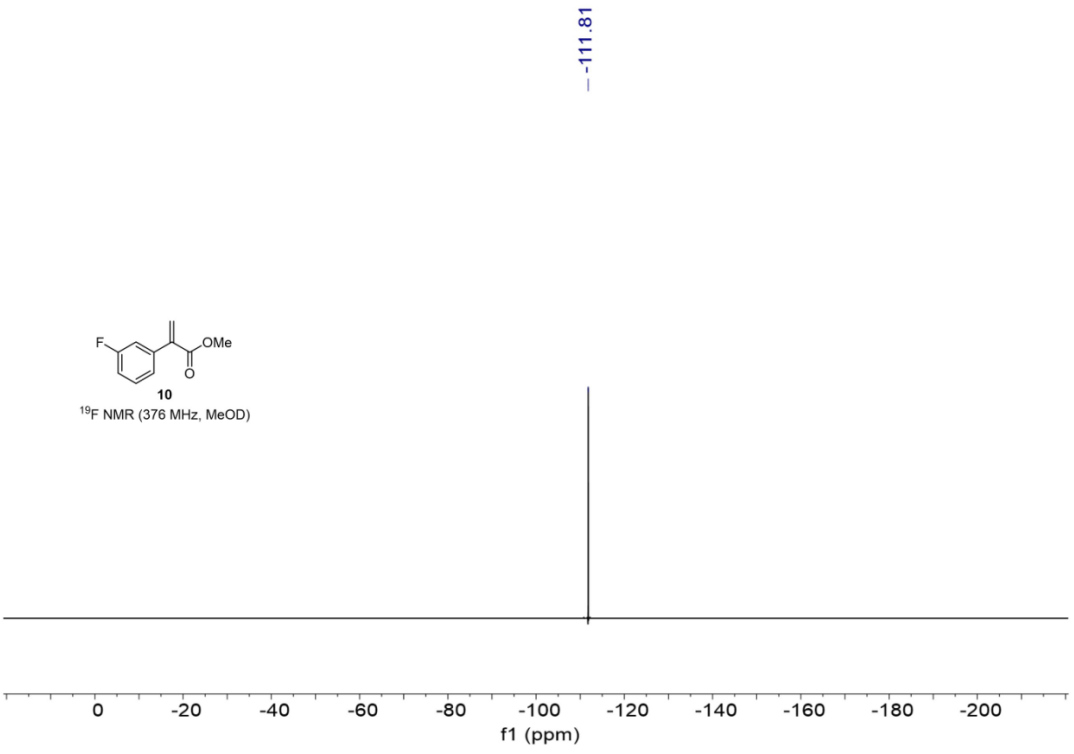

166.6
140.3
136.6
133.4
131.0
129.6
129.4
129.3
126.9
52.5
Cl
OMe
O
8
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

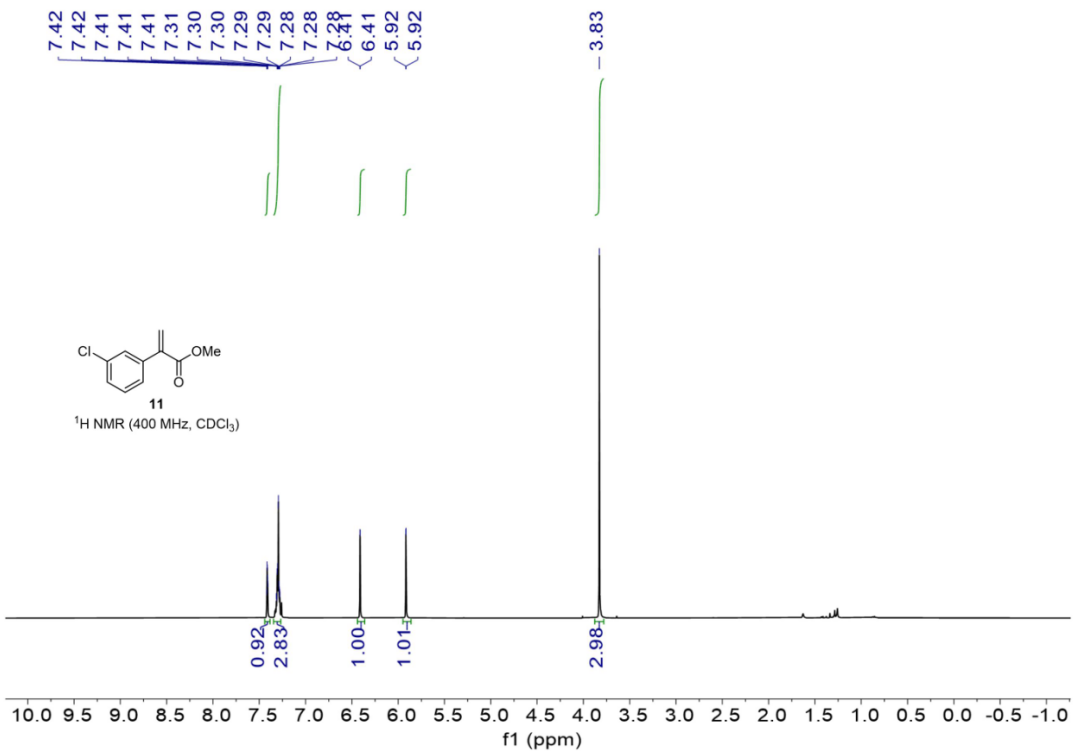

7.61
7.61
7.59
7.59
7.35
7.35
7.33
7.33
7.29
7.29
7.28
7.24
7.24
7.23
6.55
5.79
5.79
3.80
Br
OMe
O
9
1H NMR (400 MHz, CDCl3)
1.00
0.99
2.20
1.00
1.01
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

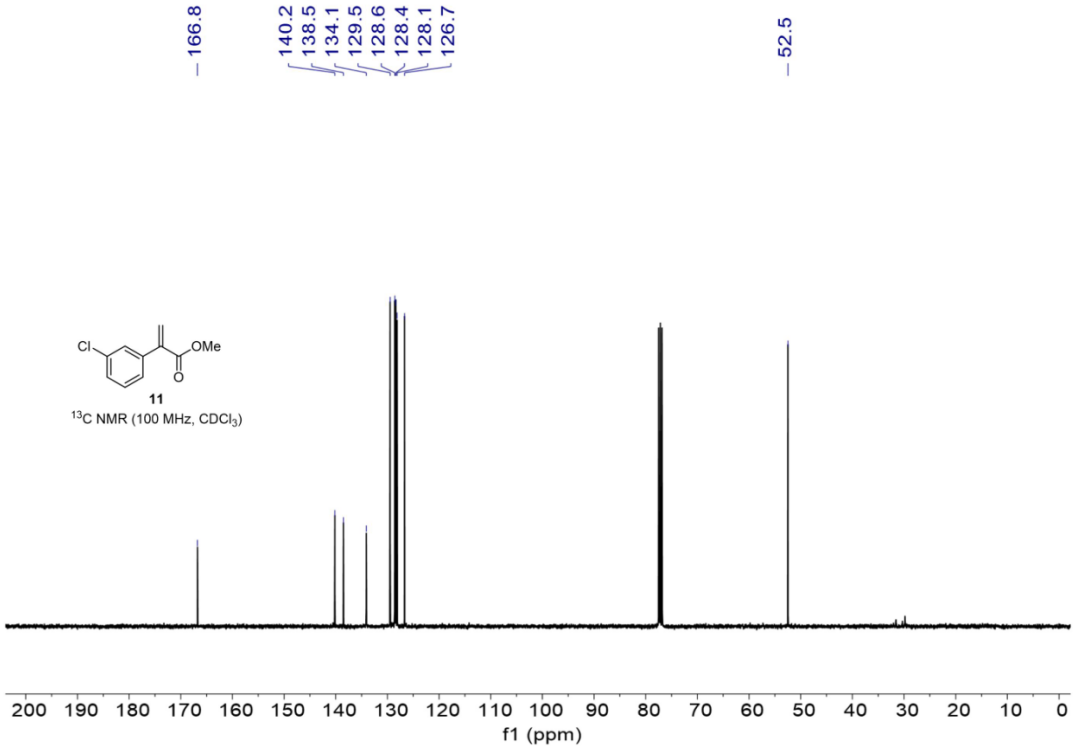

166.4
141.9
138.7
132.6
131.0
129.7
129.3
127.5
123.4
52.5
Br
OMe
O
9
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

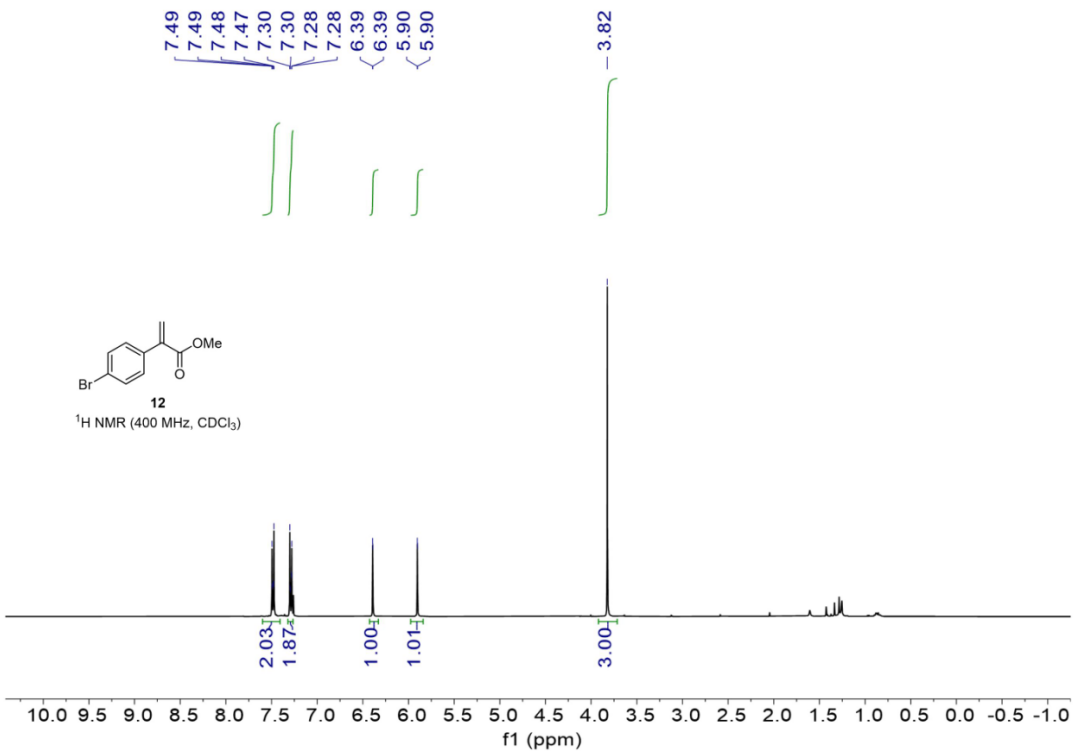

7.38 7.37 7.36 7.35 7.34 7.33 7.32 7.24 7.23 7.23 7.23 7.23 7.22 7.21 7.21 7.20 7.19 7.19 7.19 7.17 7.17 7.17 7.16 7.09 7.09 7.08 7.08 7.07 7.07 7.06 7.06 7.05 7.05 7.04 7.04 7.04 6.37 6.37 5.99 5.99 3.81
F
OMe
O
10
1H NMR (400 MHz, MeOD)
1.01
1.97
0.96
1.00
1.00
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

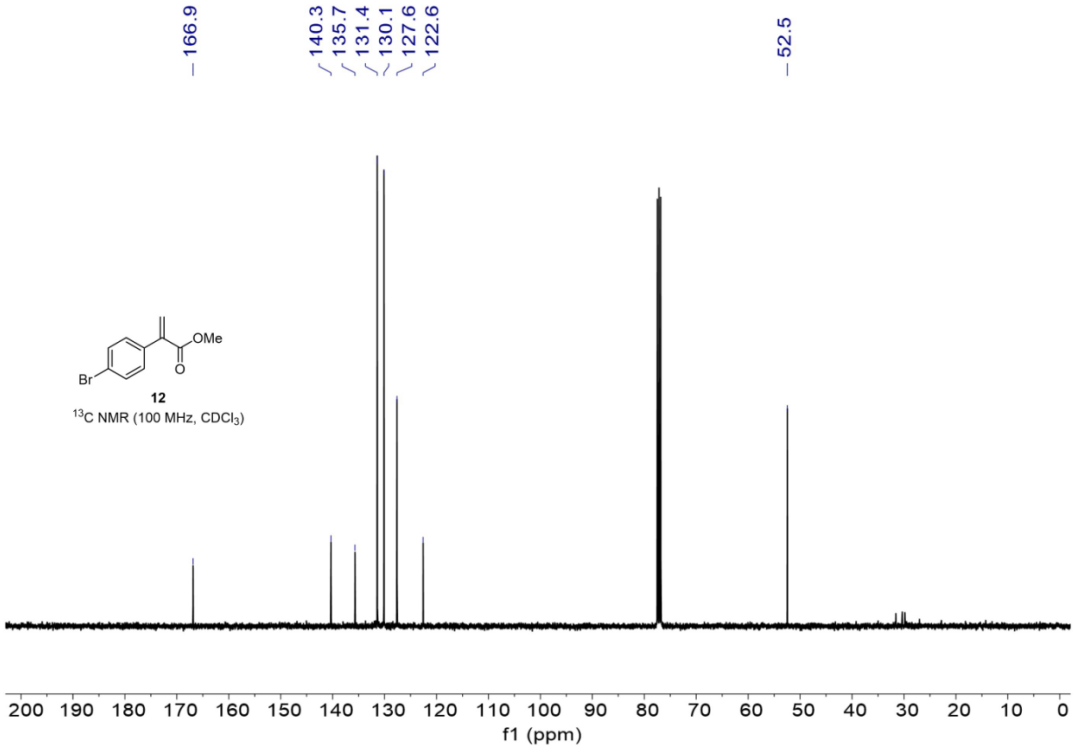

168.2
165.0
162.6
141.6
141.6
140.3
140.2
130.9
130.8
128.3
125.2
125.2
116.3
116.1
116.0
115.8
52.7
F
OMe
O
10
13C NMR (100 MHz, MeOD)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

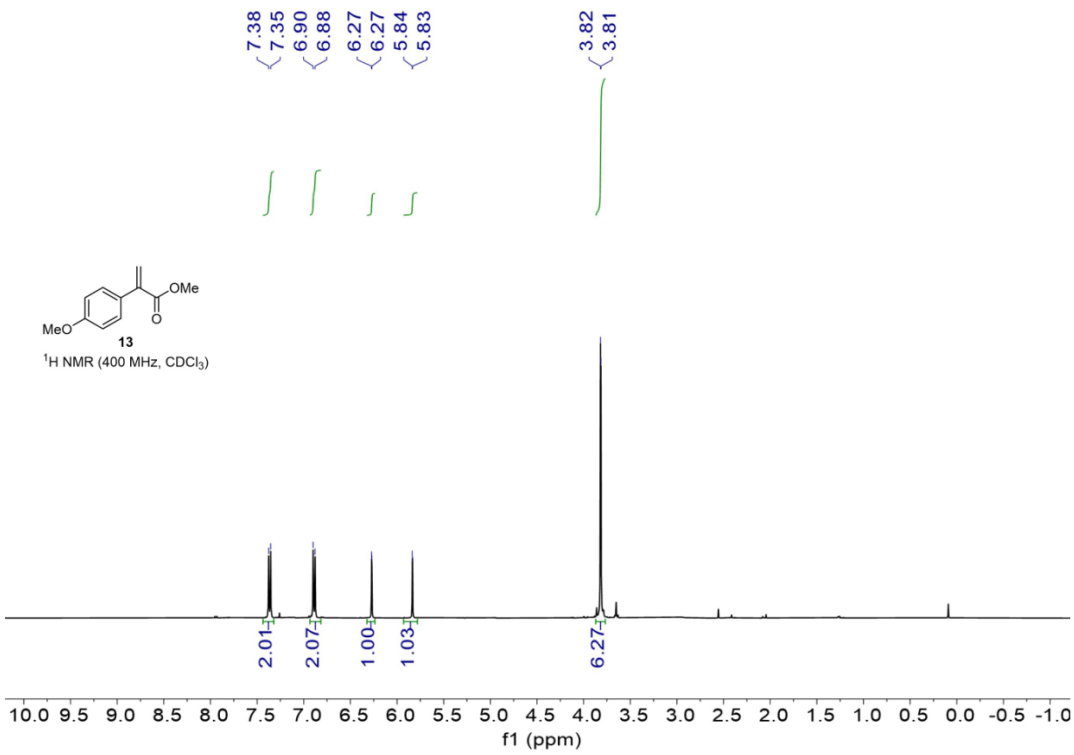

-111.81
F
OMe
O
10
19F NMR (376 MHz, MeOD)
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

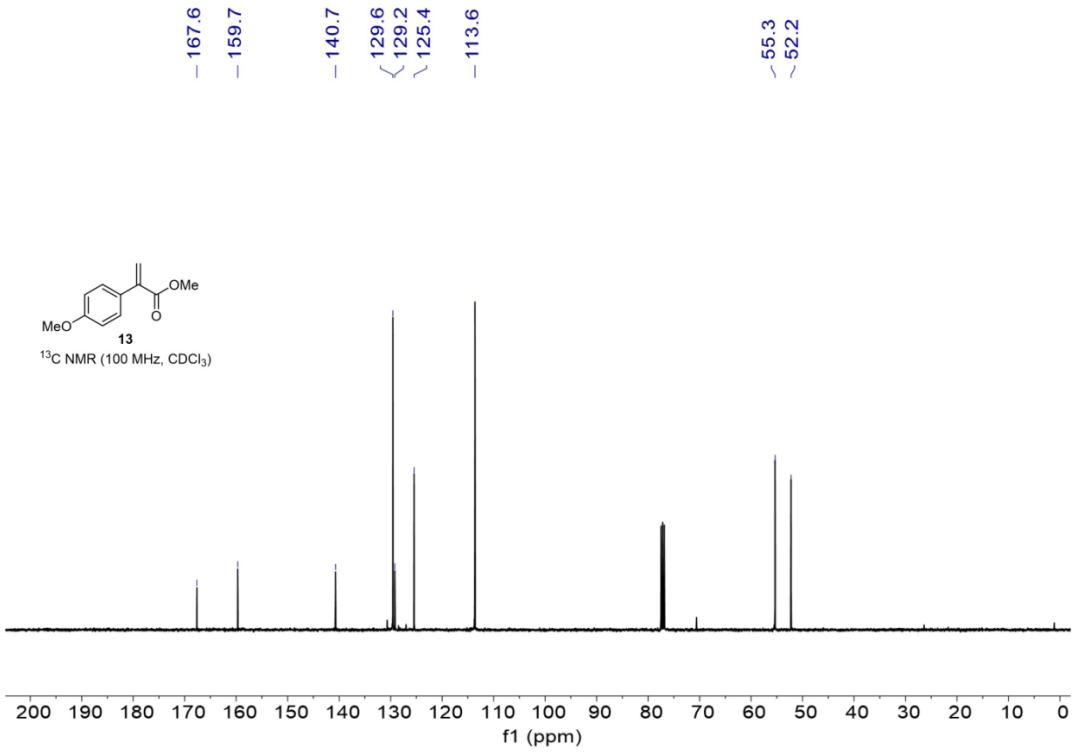

7.42
7.42
7.41
7.41
7.41
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.28
6.41
6.41
5.92
5.92
3.83
Cl
OMe
O
11
^{1}H NMR (400 MHz, $CDCl_3$)
0.92
2.83
1.00
1.01
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

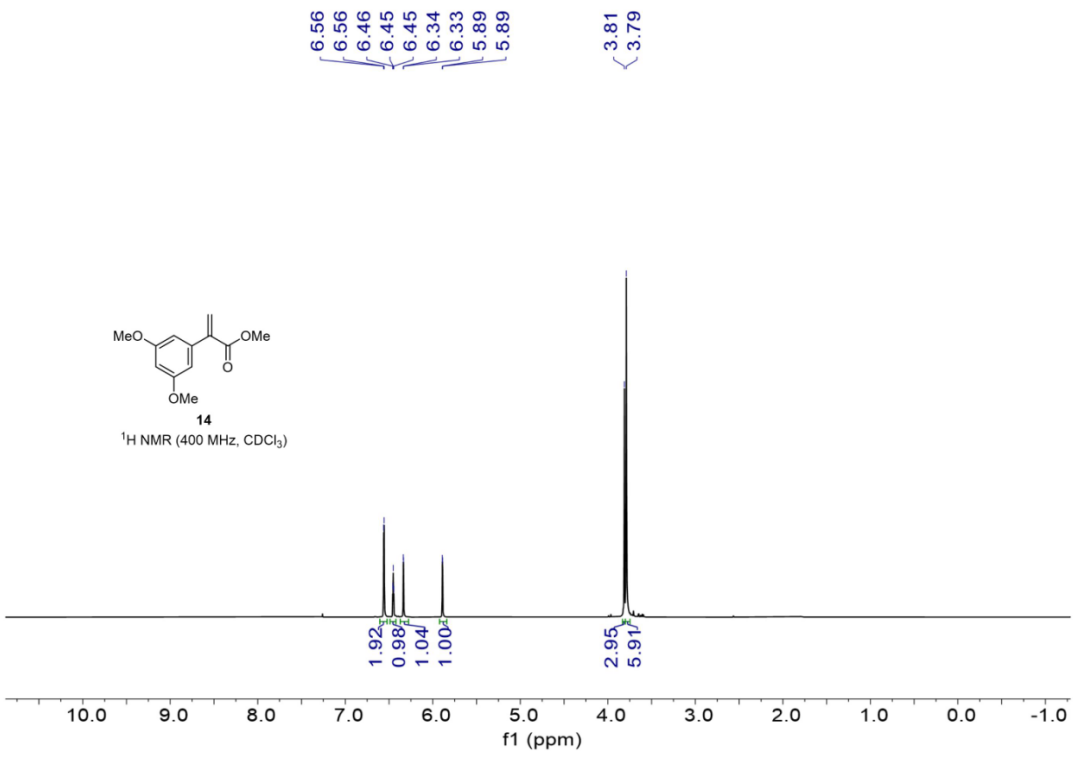

166.8
140.2
138.5
134.1
129.5
128.6
128.4
128.1
126.7
52.5
Cl
OMe
O
11
^{13}C NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

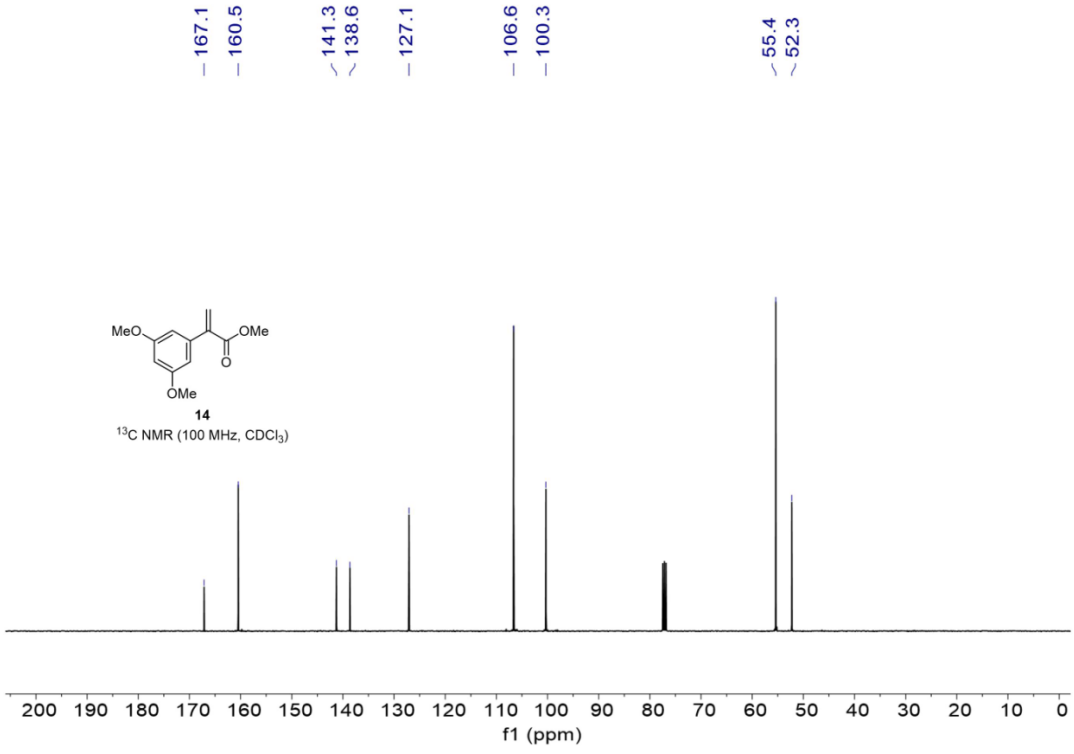

7.49
7.49
7.48
7.47
7.30
7.30
7.28
7.28
6.39
6.39
5.90
5.90
3.82
OMe
O
Br
12
1H NMR (400 MHz, CDCl3)
2.03
1.87
1.00
1.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

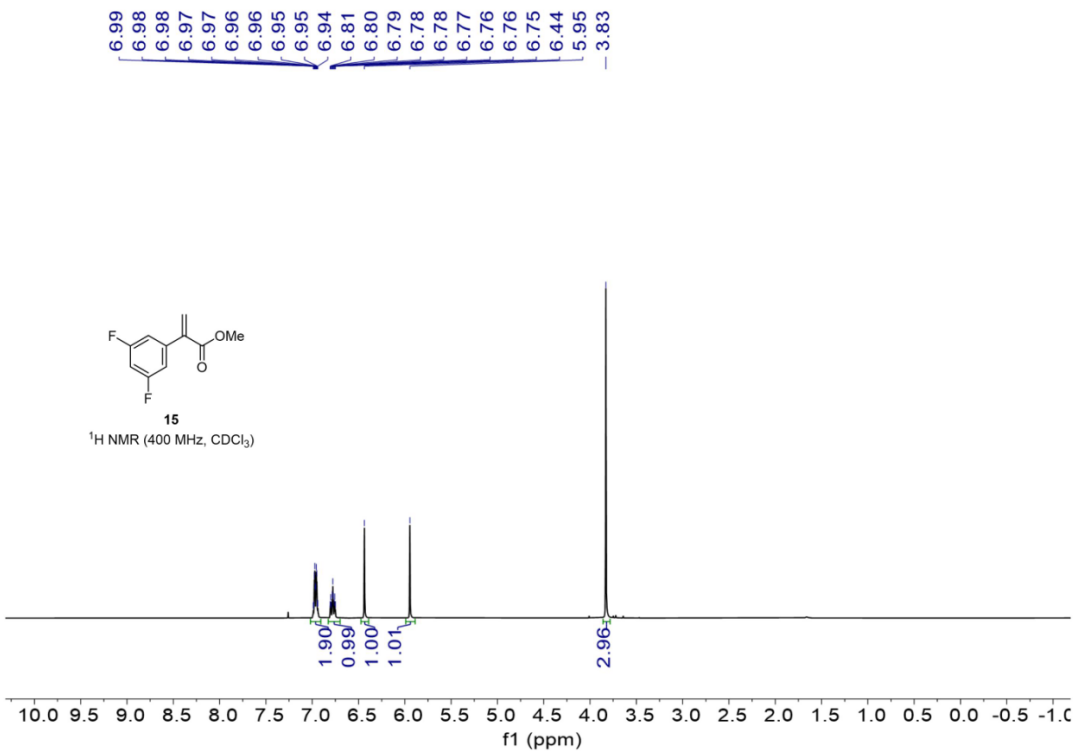

166.9
140.3
135.7
131.4
130.1
127.6
122.6
52.5
OMe
O
Br
12
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

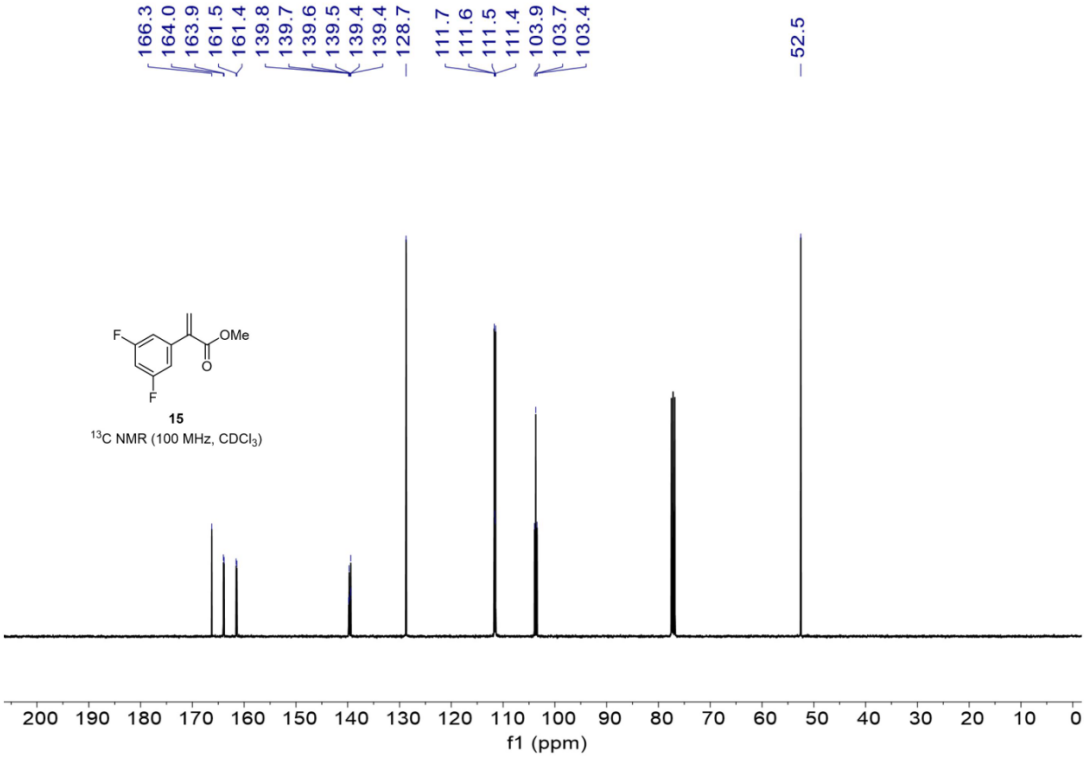

7.38
7.35
6.90
6.88
6.27
6.27
5.84
5.83
3.82
3.81
OMe
MeO
O
13
^{1}H NMR (400 MHz, CDCl$_3$)
2.01
2.07
1.00
1.03
6.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

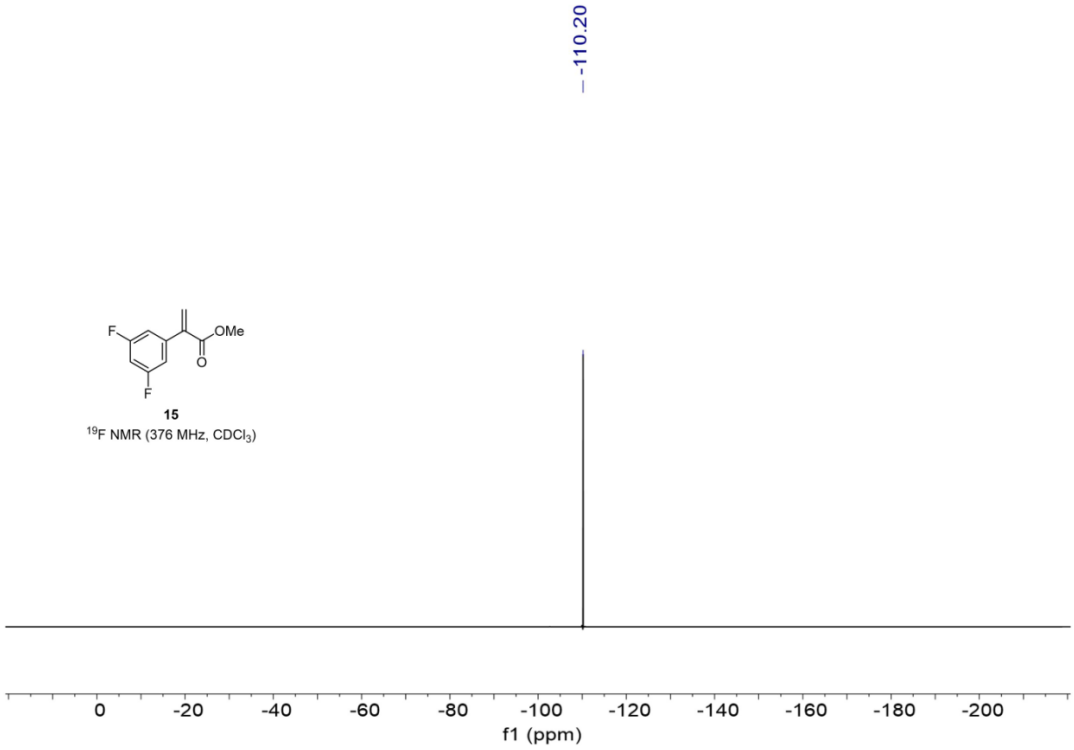

167.6
159.7
140.7
129.6
129.2
125.4
113.6
55.3
52.2
OMe
MeO
O
13
^{13}C NMR (100 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

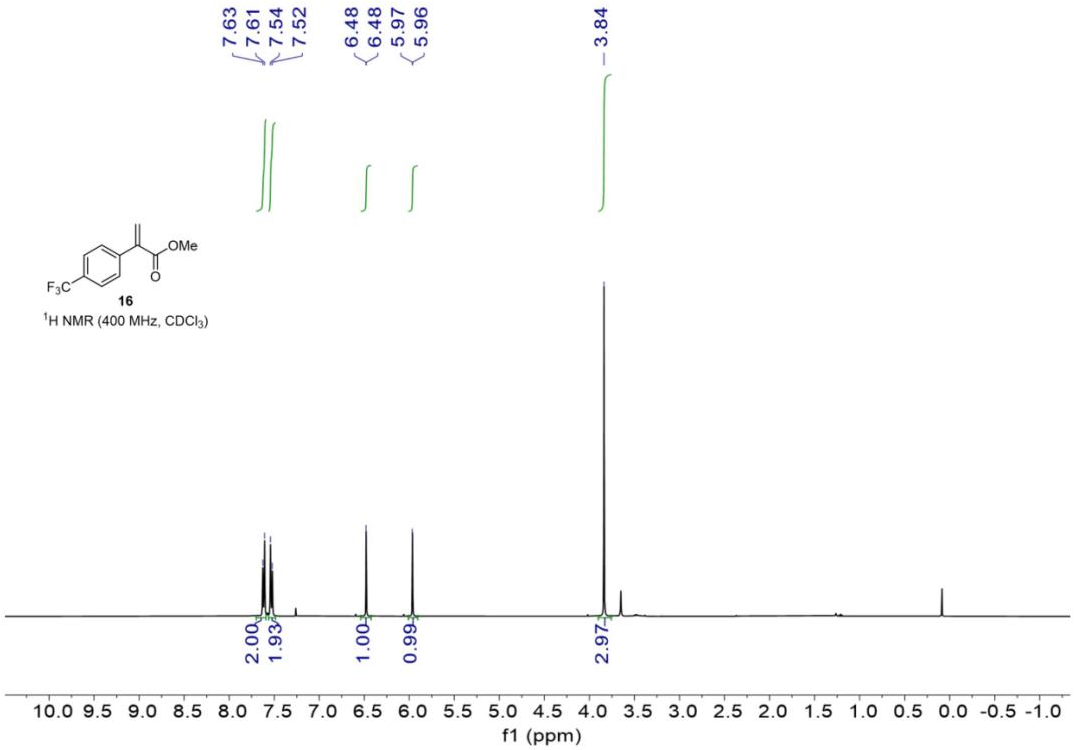

6.56
6.56
6.46
6.45
6.45
6.34
6.33
5.89
5.89
3.81
3.79
MeO
OMe
O
OMe
14
1H NMR (400 MHz, CDCl3)
1.92
0.98
1.04
1.00
2.95
5.91
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

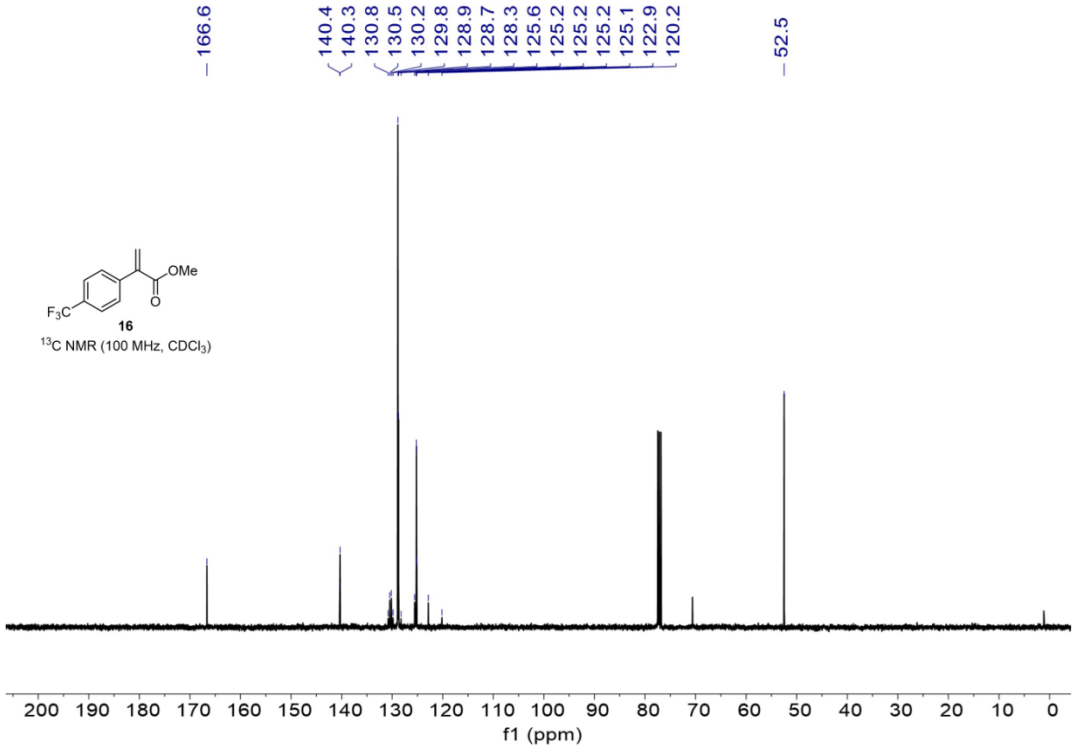

167.1
160.5
141.3
138.6
127.1
106.6
100.3
55.4
52.3
MeO
OMe
O
OMe
14
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

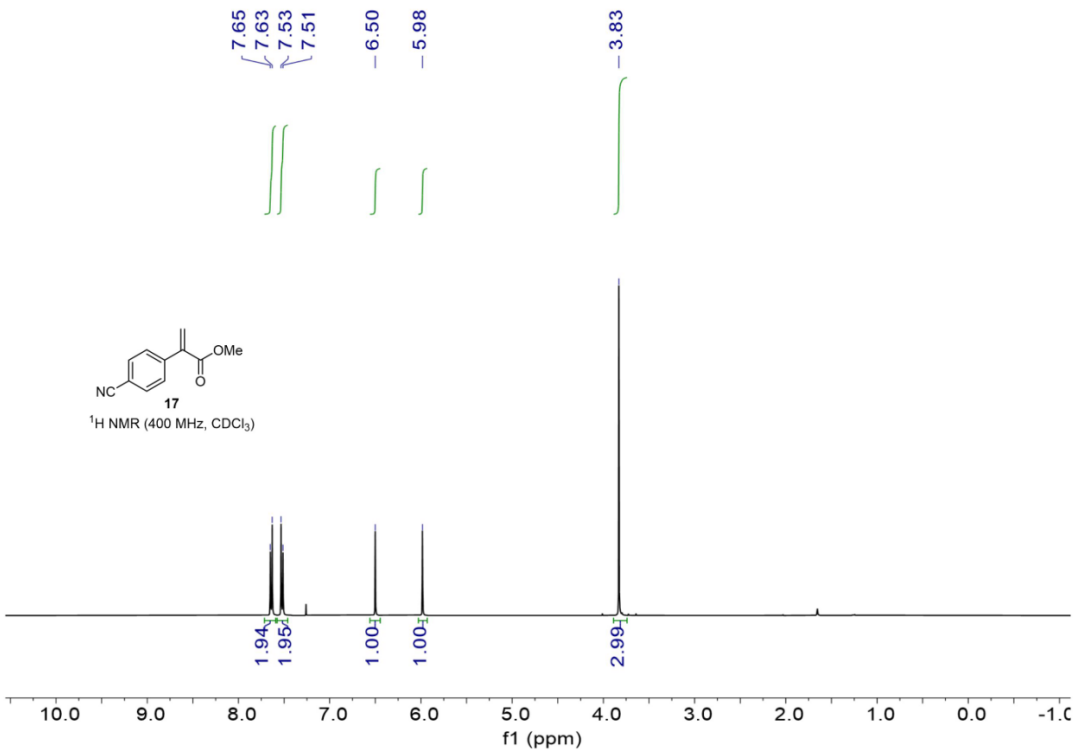

6.99
6.98
6.98
6.97
6.97
6.96
6.96
6.95
6.95
6.94
6.81
6.80
6.79
6.78
6.78
6.77
6.76
6.76
6.75
6.44
5.95
3.83
F
OMe
O
F
15
1H NMR (400 MHz, CDCl3)
1.90
0.99
1.00
1.01
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

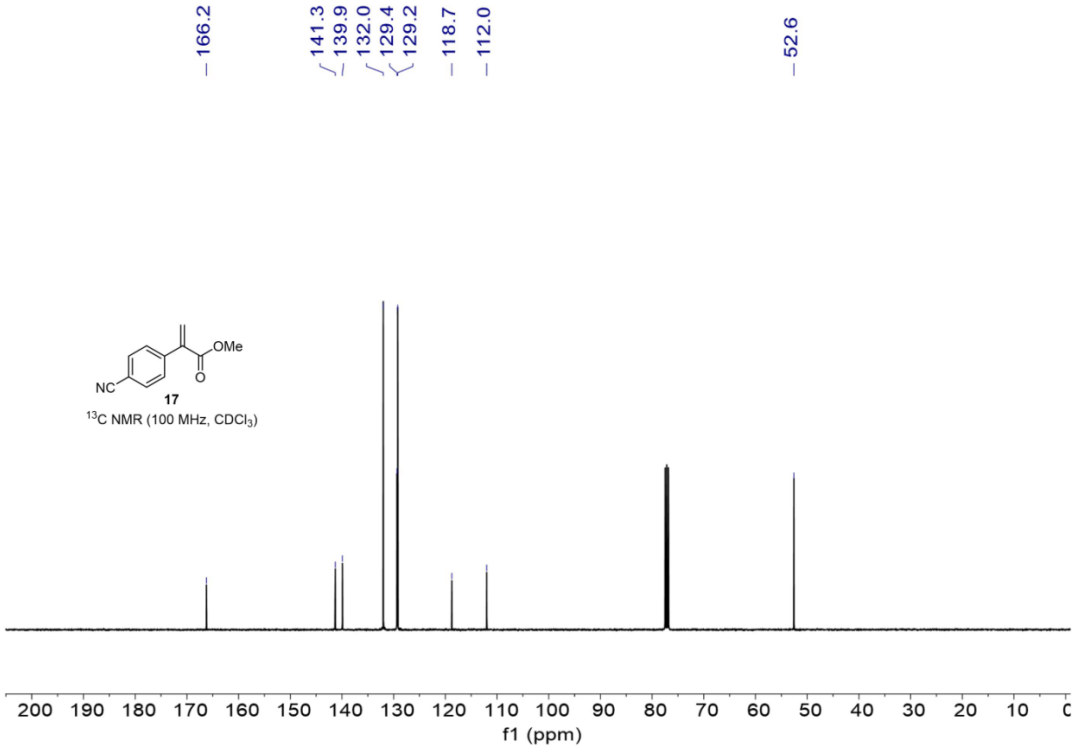

166.3
164.0
163.9
161.5
161.4
139.8
139.7
139.6
139.5
139.4
139.4
128.7
111.7
111.6
111.5
111.4
103.9
103.7
103.4
52.5
F
OMe
O
F
15
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

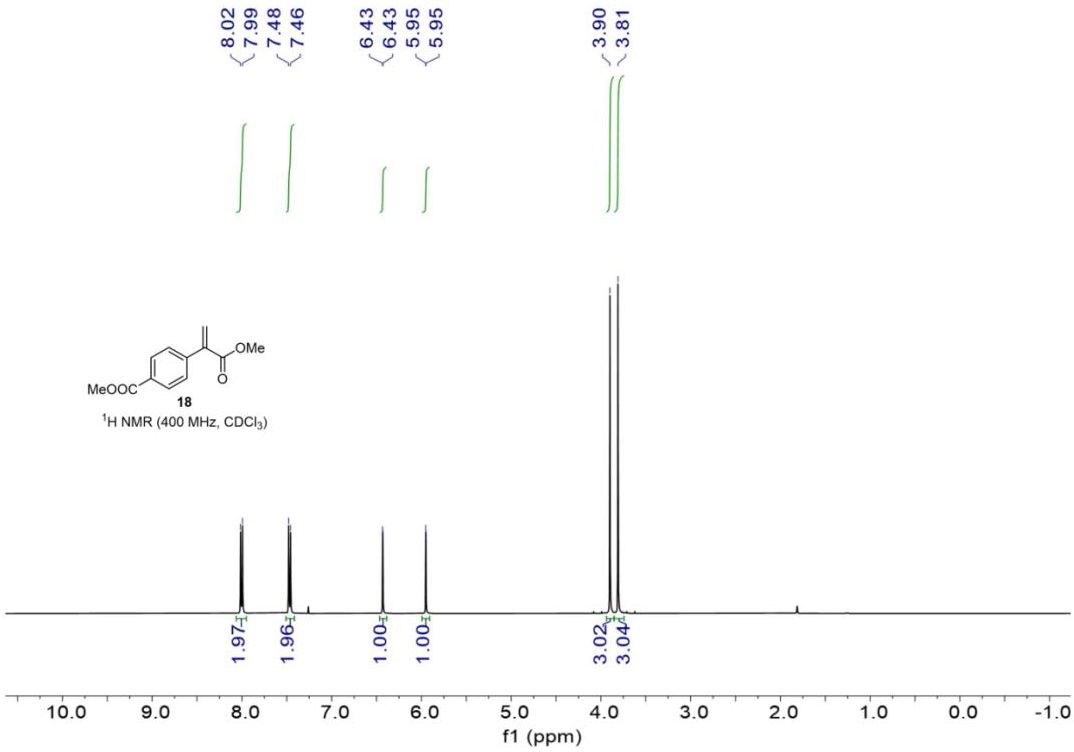

-110.20
F
OMe
O
F
15
^{19}F NMR (376 MHz, $CDCl_3$)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

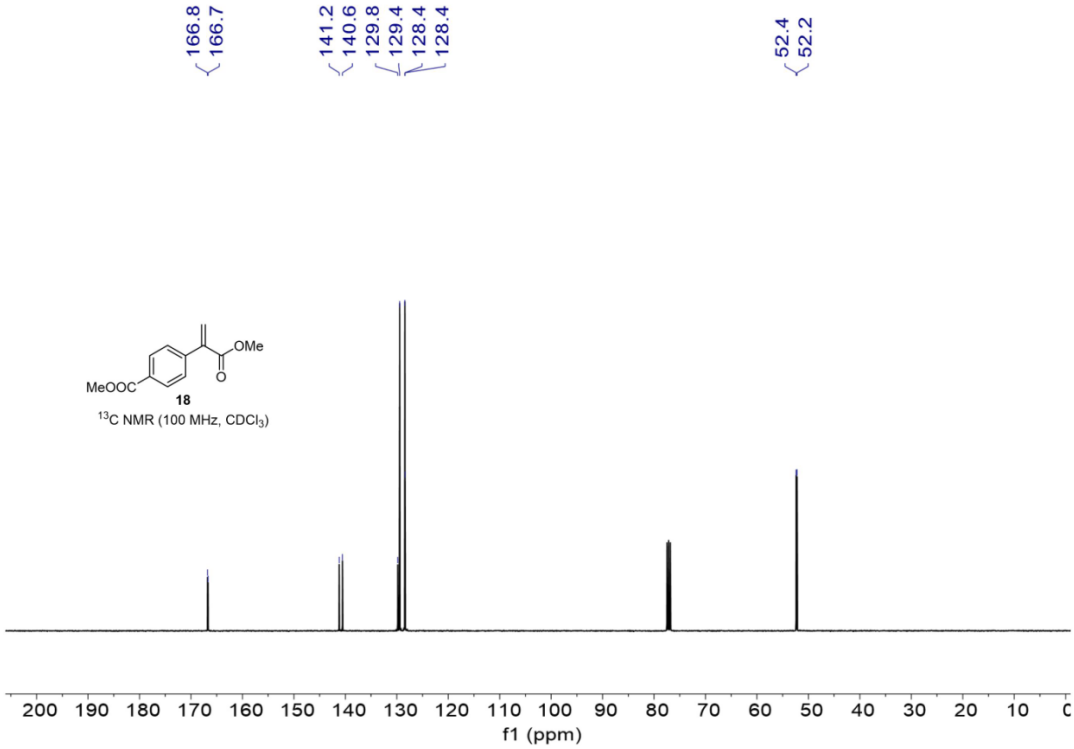

7.63
7.61
7.54
7.52
6.48
6.48
5.97
5.96
3.84
OMe
O
F_3C
16
^{1}H NMR (400 MHz, $CDCl_3$)
2.00
1.93
1.00
0.99
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

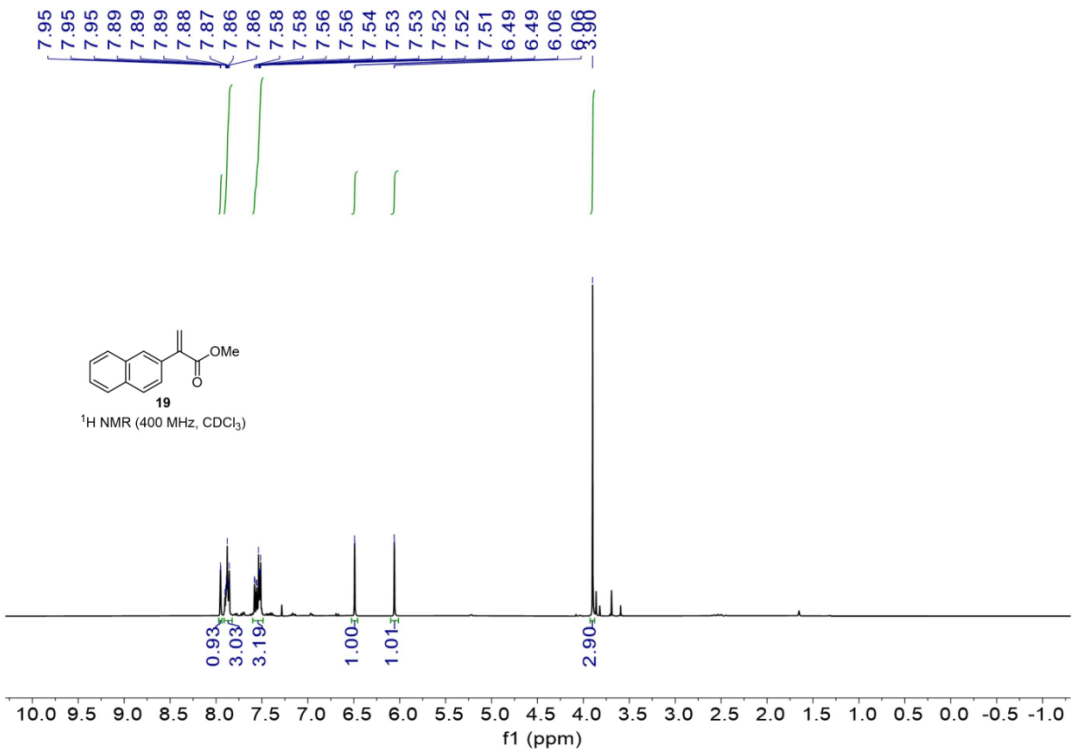

166.6
140.4
140.3
130.8
130.5
130.2
129.8
128.9
128.7
128.3
125.6
125.2
125.2
125.2
125.1
122.9
120.2
52.5
OMe
O
F3C
16
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

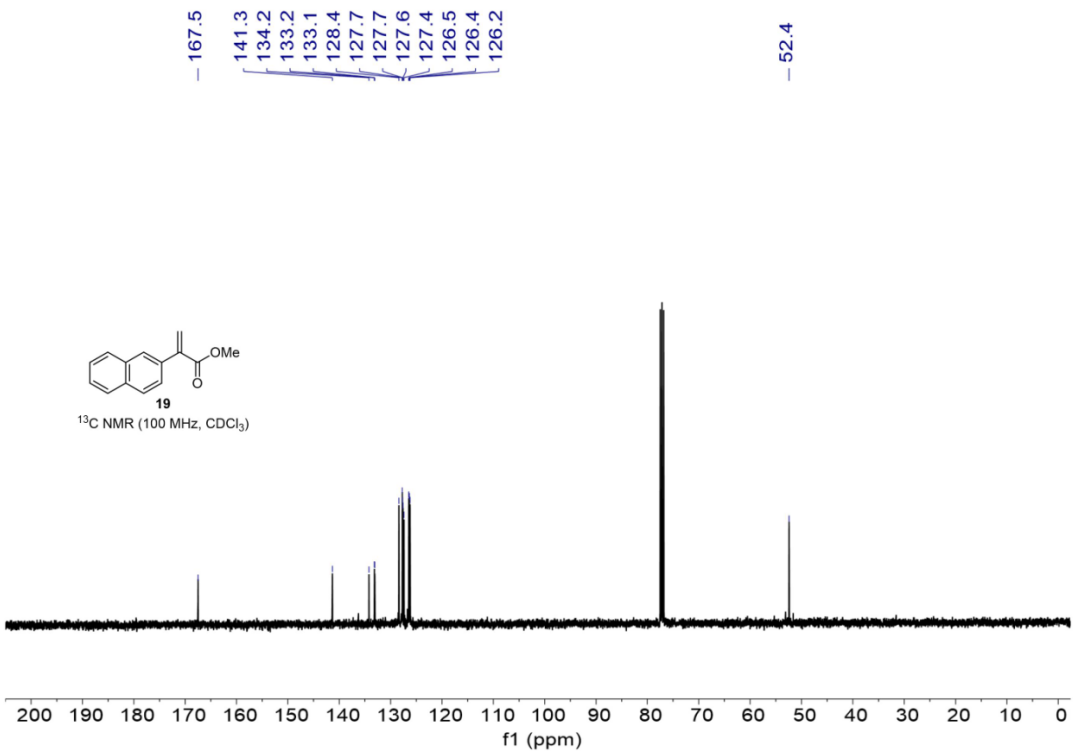

7.65
7.63
7.53
7.51
6.50
5.98
3.83
OMe
O
NC
17
1H NMR (400 MHz, CDCl3)
1.94
1.95
1.00
1.00
2.99
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

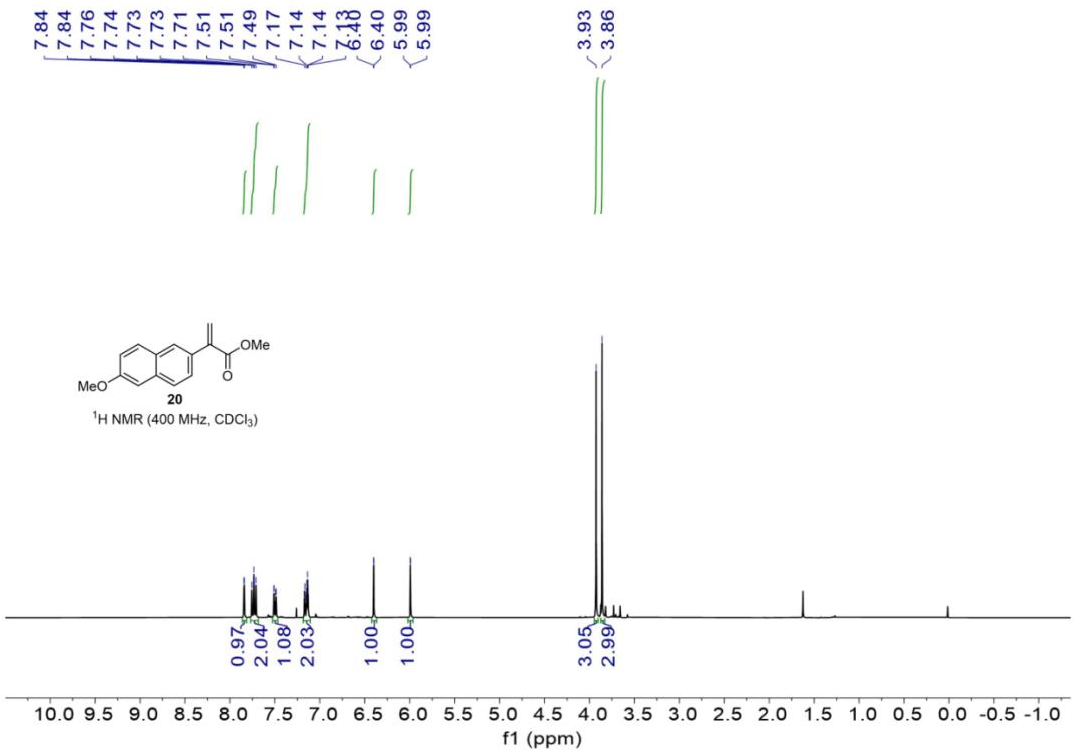

166.2
141.3
139.9
132.0
129.4
129.2
118.7
112.0
52.6
OMe
O
NC
17
^{13}C NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

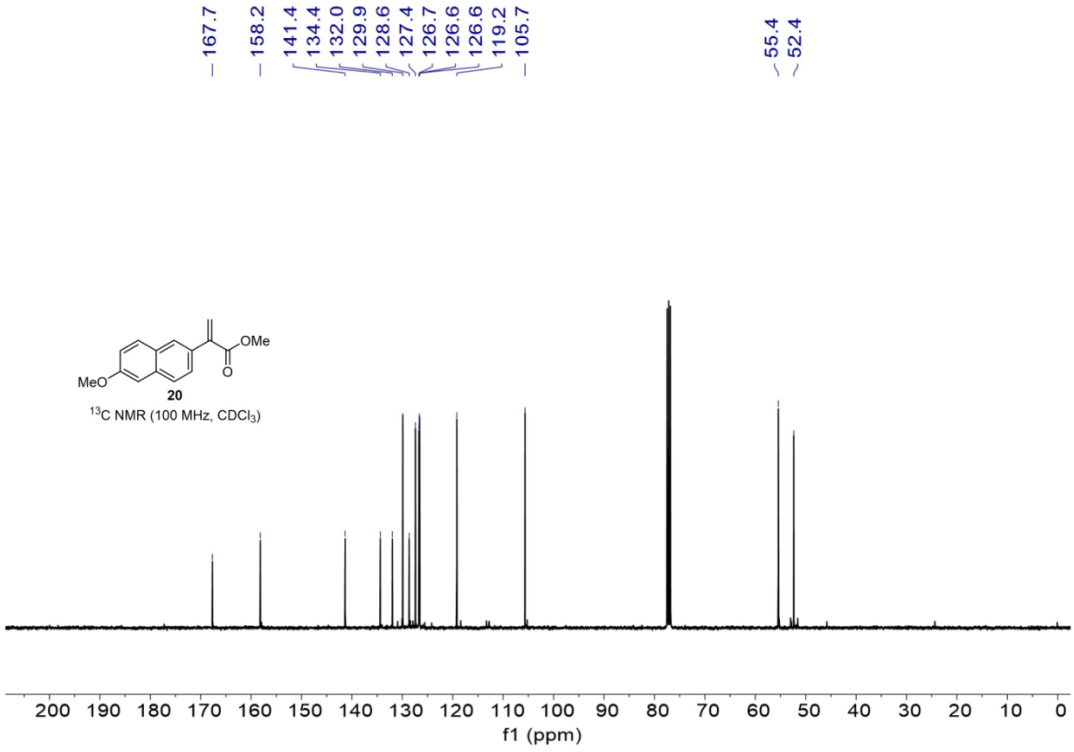

8.02
7.99
7.48
7.46
6.43
6.43
5.95
5.95
3.90
3.81
OMe
O
MeOOC
18
^{1}H NMR (400 MHz, $CDCl_3$)
1.97
1.96
1.00
1.00
3.02
3.04
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

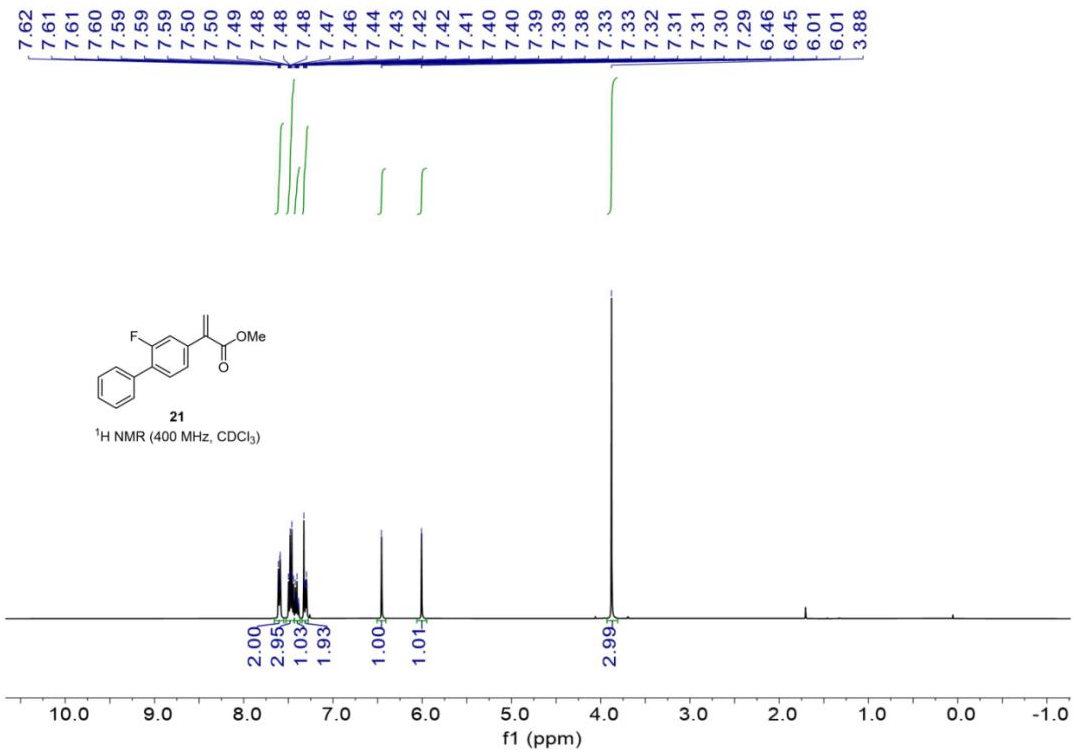

166.8
166.7
141.2
140.6
129.8
129.4
128.4
128.4
52.4
52.2
OMe
O
MeOOC
18
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

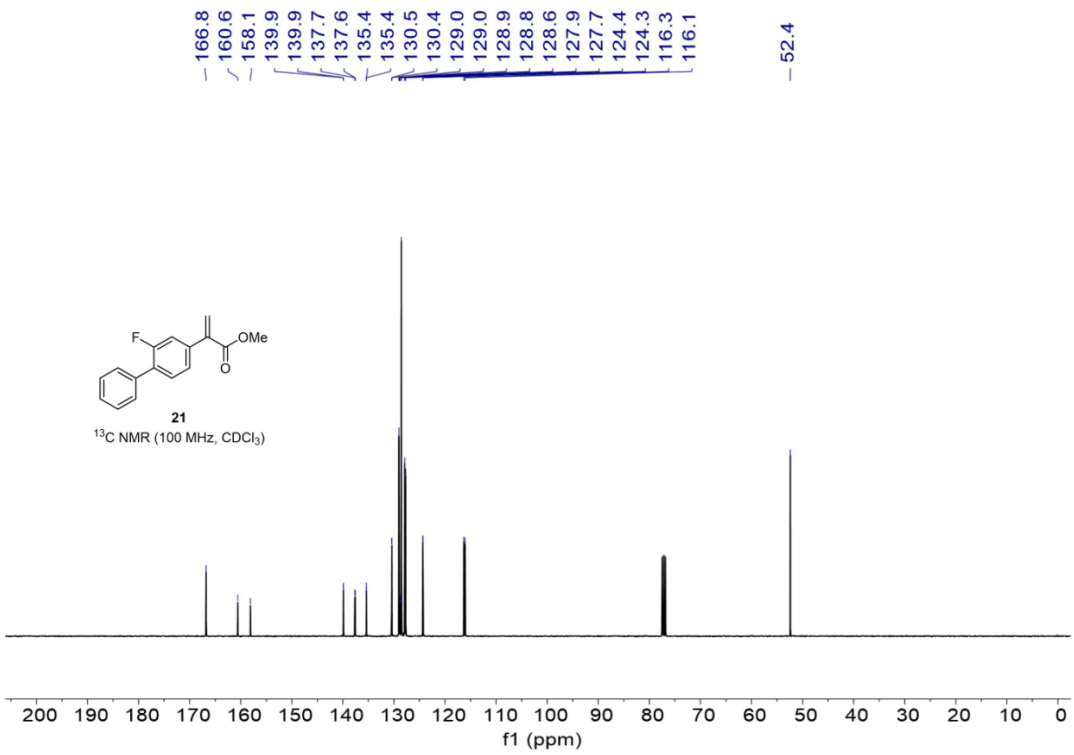

7.95
7.95
7.95
7.89
7.89
7.89
7.88
7.87
7.86
7.86
7.58
7.58
7.56
7.56
7.54
7.53
7.53
7.52
7.52
7.51
6.49
6.49
6.06
6.06
3.90
OMe
O
19
1H NMR (400 MHz, CDCl3)
0.93
3.03
3.19
1.00
1.01
2.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

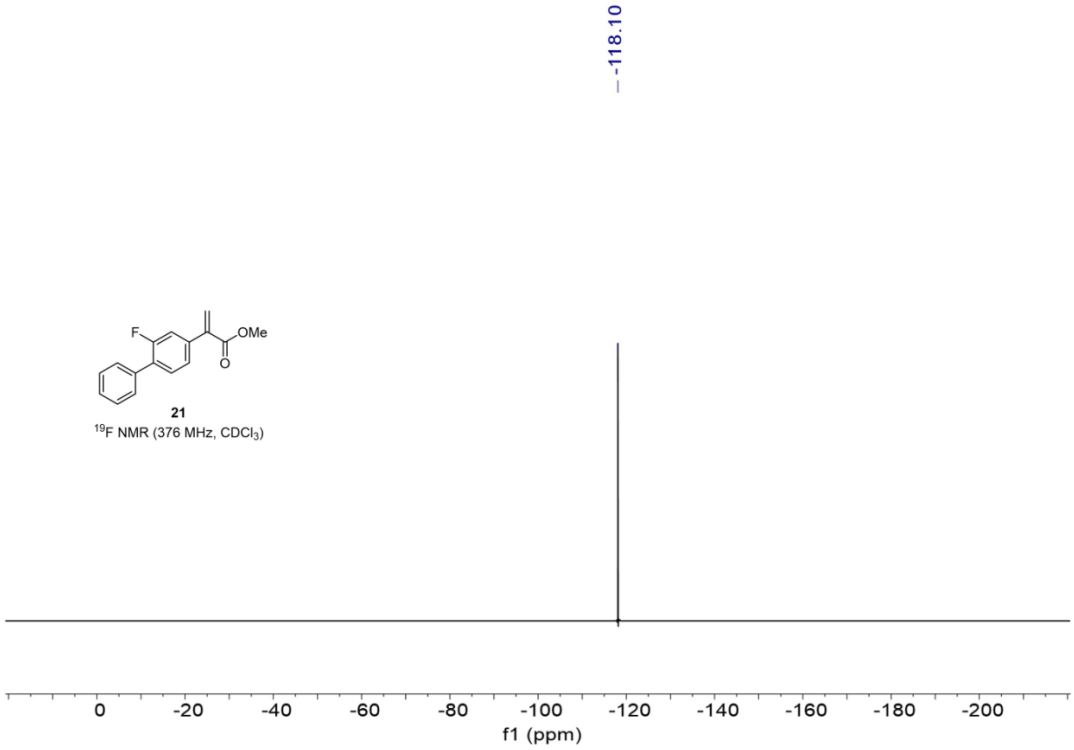

167.5
141.3
134.2
133.2
133.1
128.4
127.7
127.7
127.6
127.4
126.5
126.4
126.2
52.4
OMe
O
19
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

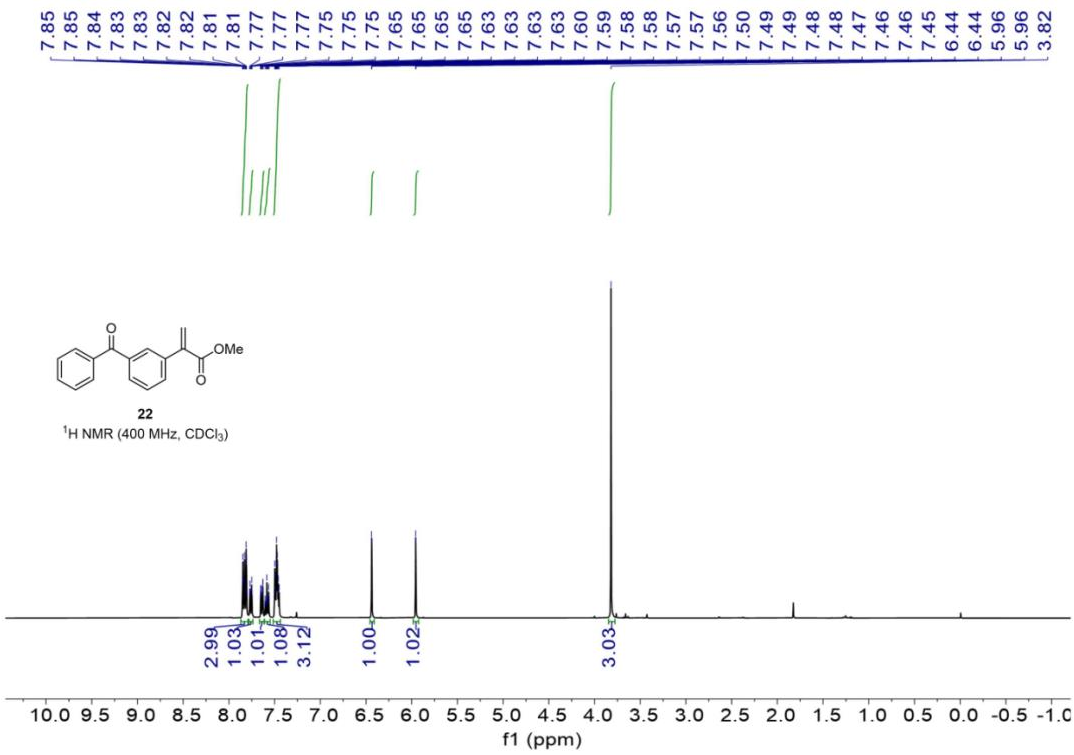

7.84
7.84
7.76
7.74
7.73
7.73
7.71
7.51
7.51
7.49
7.17
7.14
7.14
7.13
6.40
6.40
5.99
5.99
3.93
3.86
OMe
MeO
O
20
1H NMR (400 MHz, CDCl3)
0.97
2.04
1.08
2.03
1.00
1.00
3.05
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

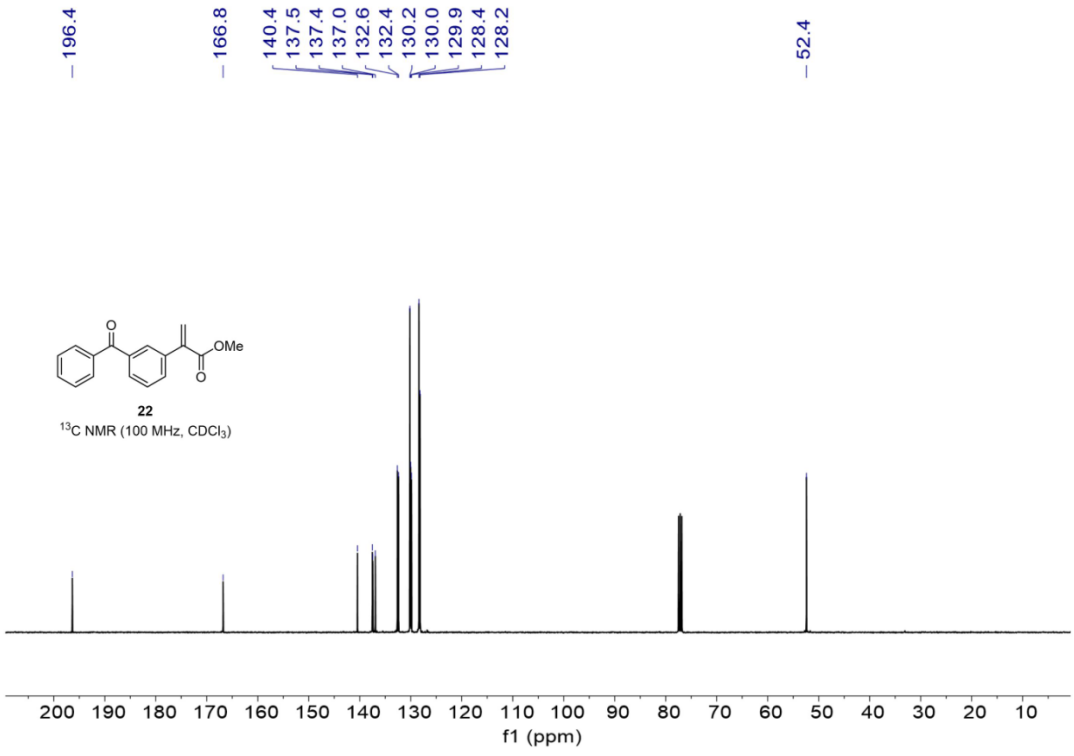

167.7
158.2
141.4
134.4
132.0
129.9
128.6
127.4
126.7
126.6
126.6
119.2
105.7
55.4
52.4
OMe
O
MeO
20
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

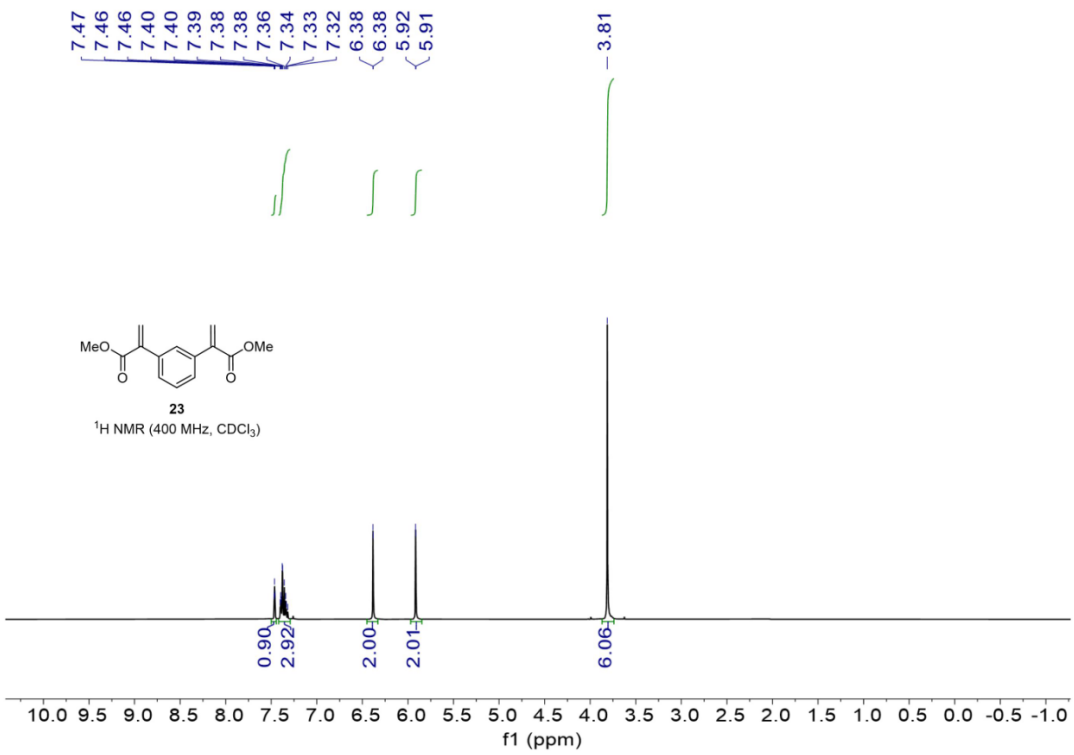

7.62
7.61
7.61
7.60
7.59
7.59
7.59
7.50
7.50
7.49
7.48
7.48
7.48
7.47
7.46
7.44
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.33
7.33
7.32
7.31
7.31
7.30
7.29
6.46
6.45
6.01
6.01
3.88
F
OMe
O
21
1H NMR (400 MHz, CDCl3)
2.00
2.95
1.03
1.93
1.00
1.01
2.99
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

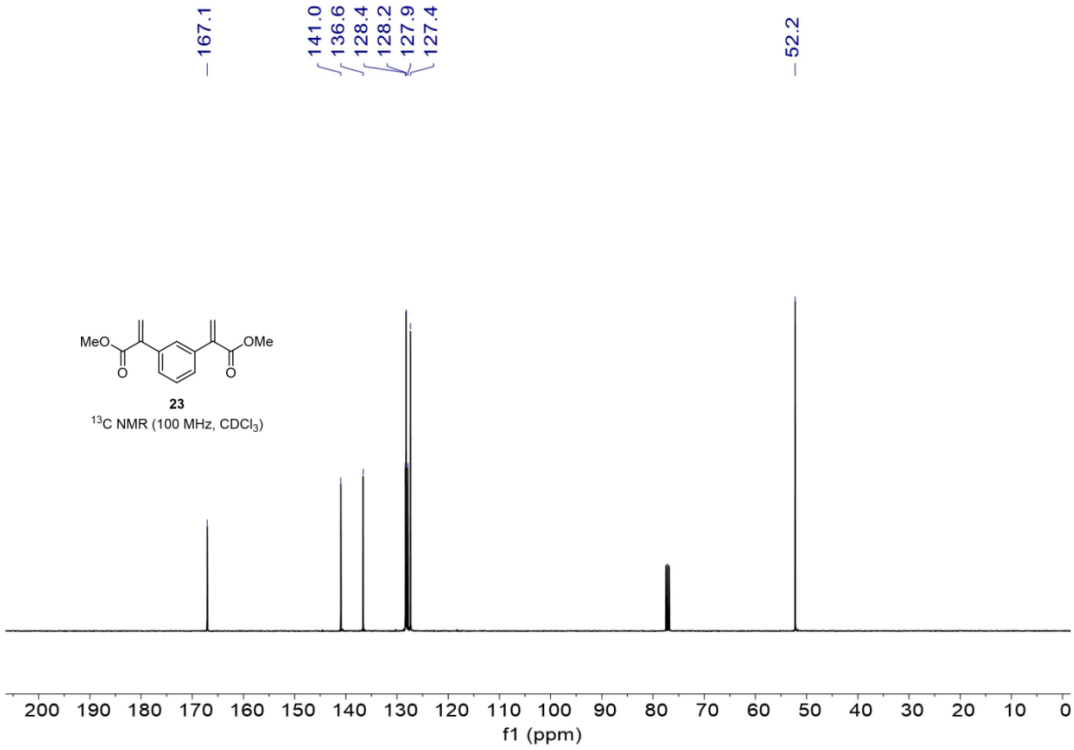

166.8
160.6
158.1
139.9
139.9
137.7
137.6
135.4
135.4
130.5
130.4
129.0
129.0
128.9
128.8
128.6
127.9
127.7
124.4
124.3
116.3
116.1
52.4
F
OMe
O
21
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

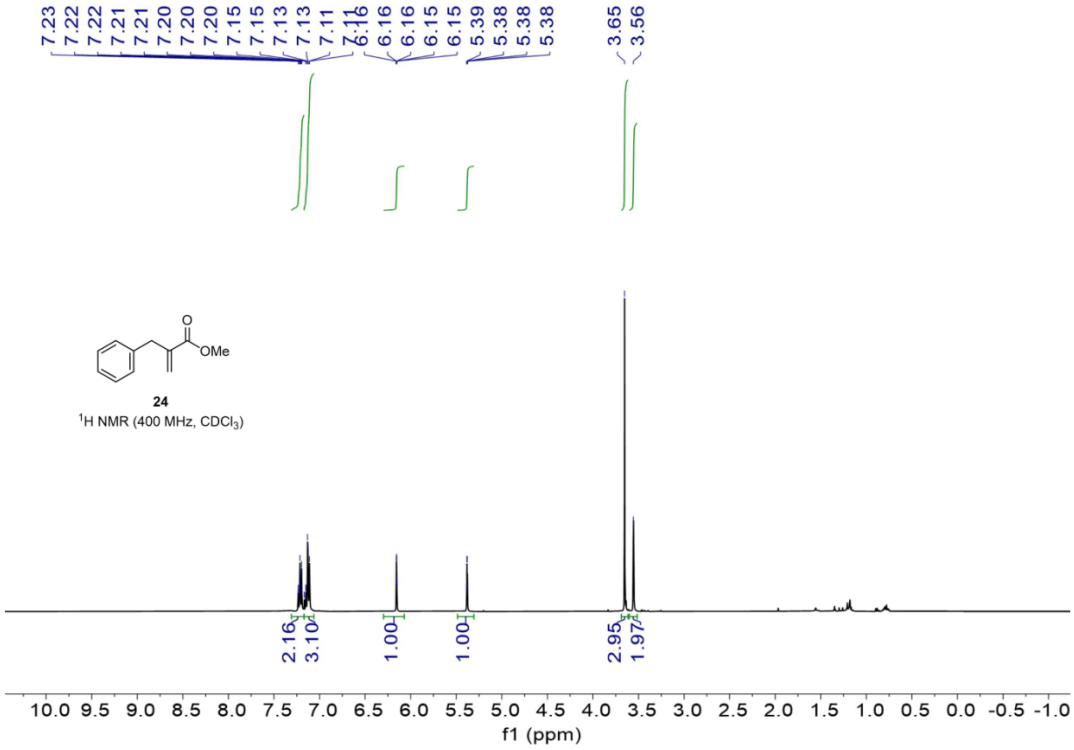

-118.10
F
OMe
O
21
19F NMR (376 MHz, CDCl3)
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

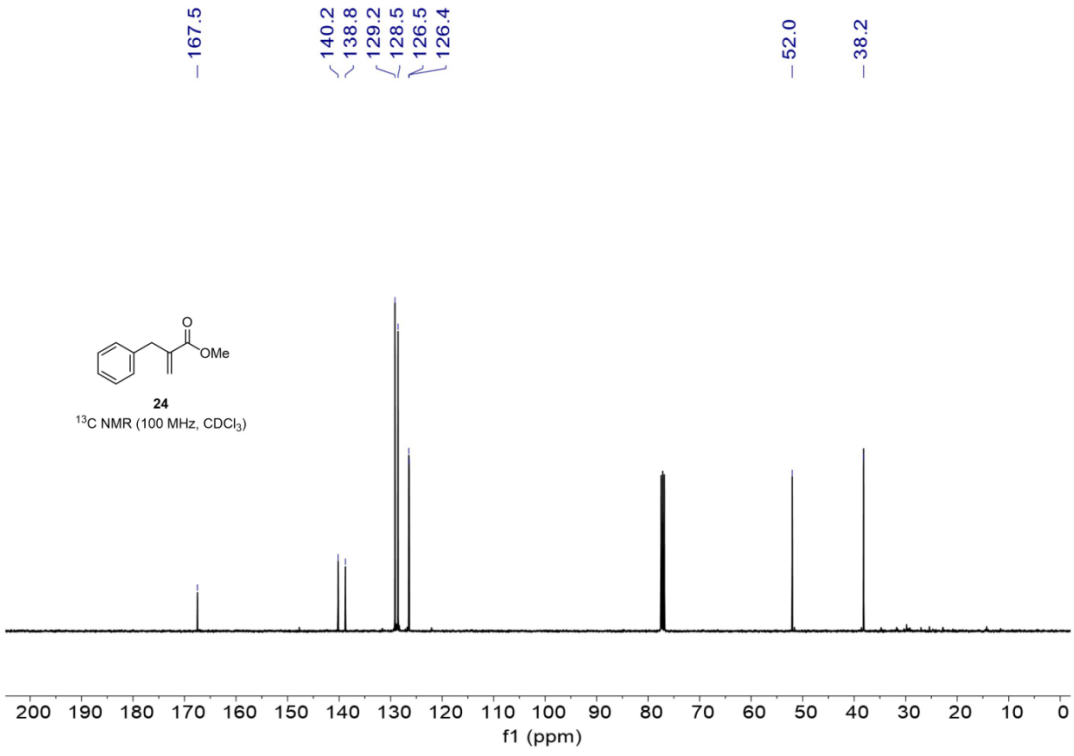

7.85 7.85 7.84 7.83 7.83 7.82 7.82 7.81 7.81 7.77 7.77 7.77 7.75 7.75 7.75 7.65 7.65 7.65 7.65 7.63 7.63 7.63 7.63 7.60 7.59 7.58 7.58 7.57 7.57 7.56 7.50 7.49 7.49 7.48 7.48 7.47 7.46 7.46 7.45 6.44 6.44 5.96 5.96 3.82
O
OMe
O
22
1H NMR (400 MHz, CDCl3)
2.99 1.03 1.01 1.08 3.12 1.00 1.02 3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

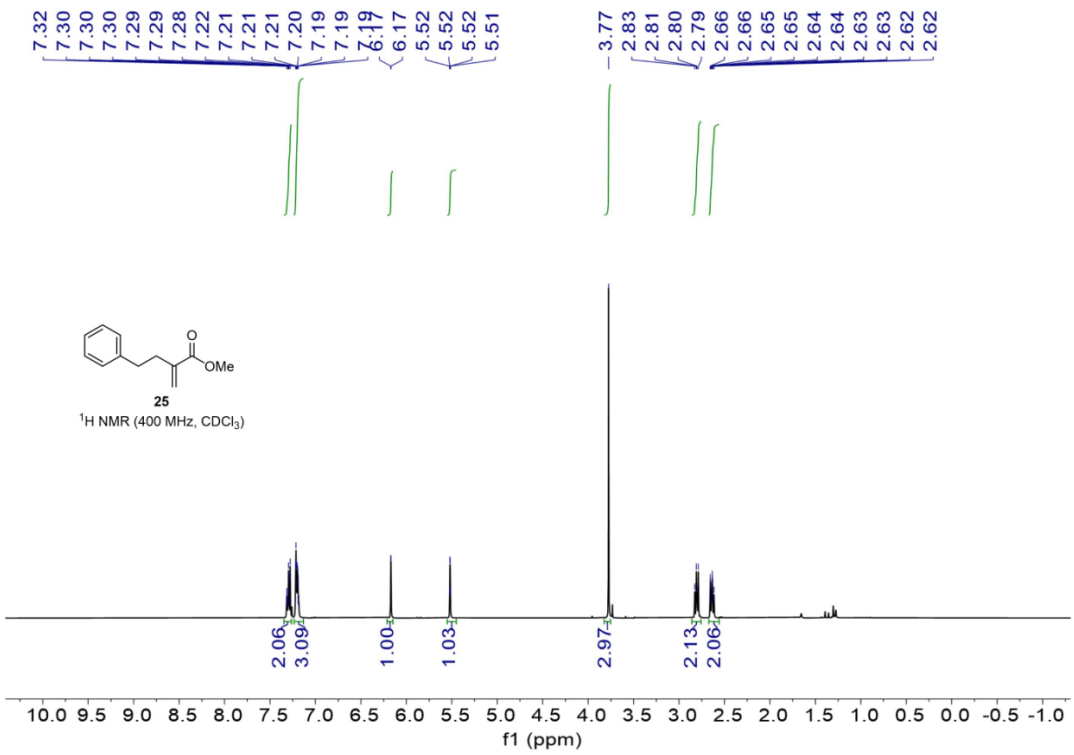

196.4
166.8
140.4 137.5 137.4 137.0 132.6 132.4 130.2 130.0 129.9 128.4 128.2
52.4
O
OMe
O
22
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

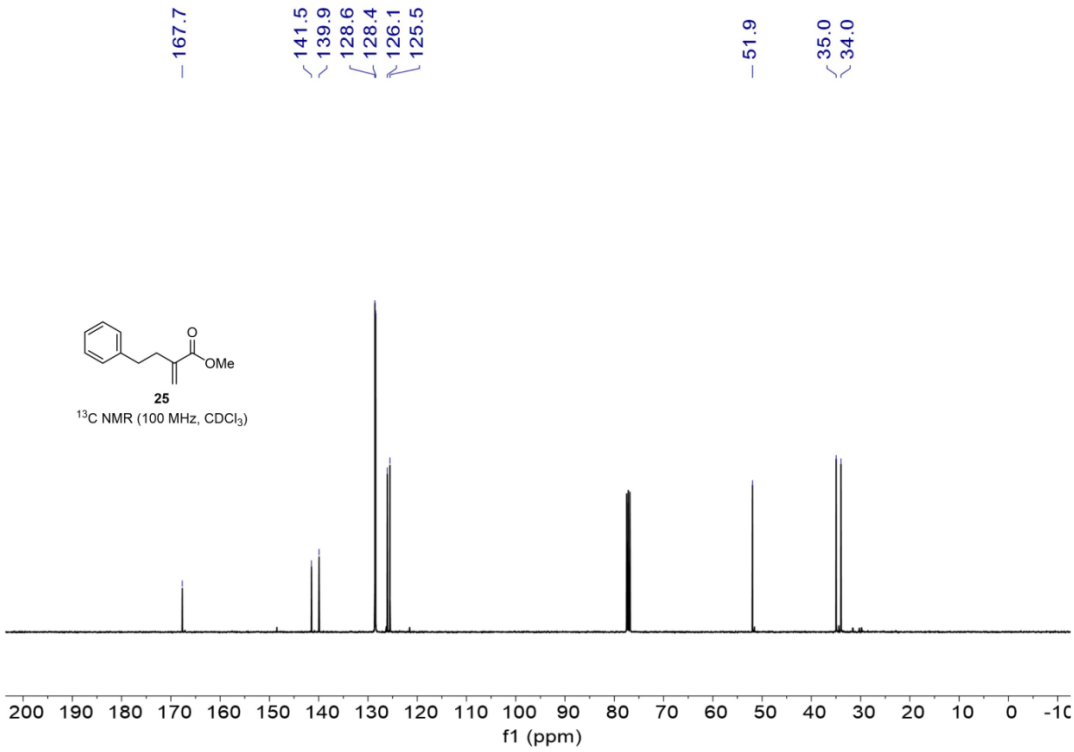

7.47
7.46
7.46
7.40
7.40
7.39
7.38
7.38
7.36
7.34
7.33
7.32
6.38
6.38
5.92
5.91
3.81
MeO
OMe
O
O
O
O
23
1H NMR (400 MHz, CDCl3)
0.90
2.92
2.00
2.01
6.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

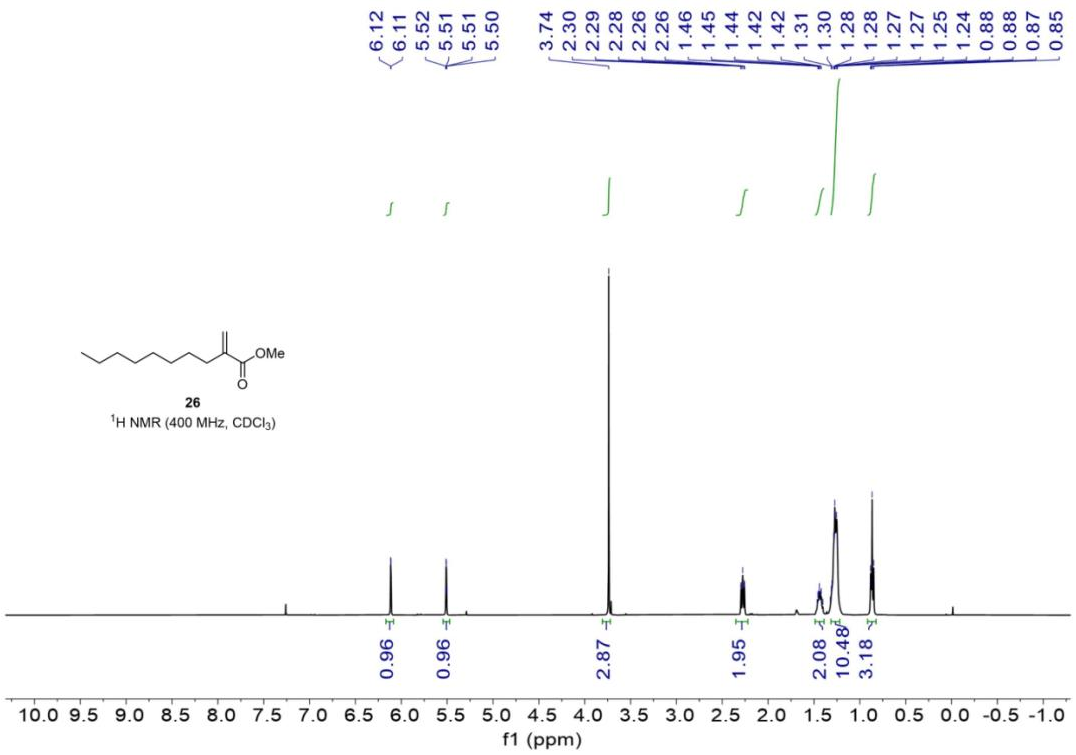

167.1
141.0
136.6
128.4
128.2
127.9
127.4
52.2
MeO
OMe
O
O
O
O
23
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.20
7.15
7.15
7.13
7.13
7.11
7.11
6.16
6.16
6.16
6.15
6.15
5.39
5.38
5.38
5.38
3.65
3.56
OMe
24
1H NMR (400 MHz, CDCl3)
2.16
3.10
1.00
1.00
2.95
1.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.5
140.2
138.8
129.2
128.5
126.5
126.4
52.0
38.2
OMe
24
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

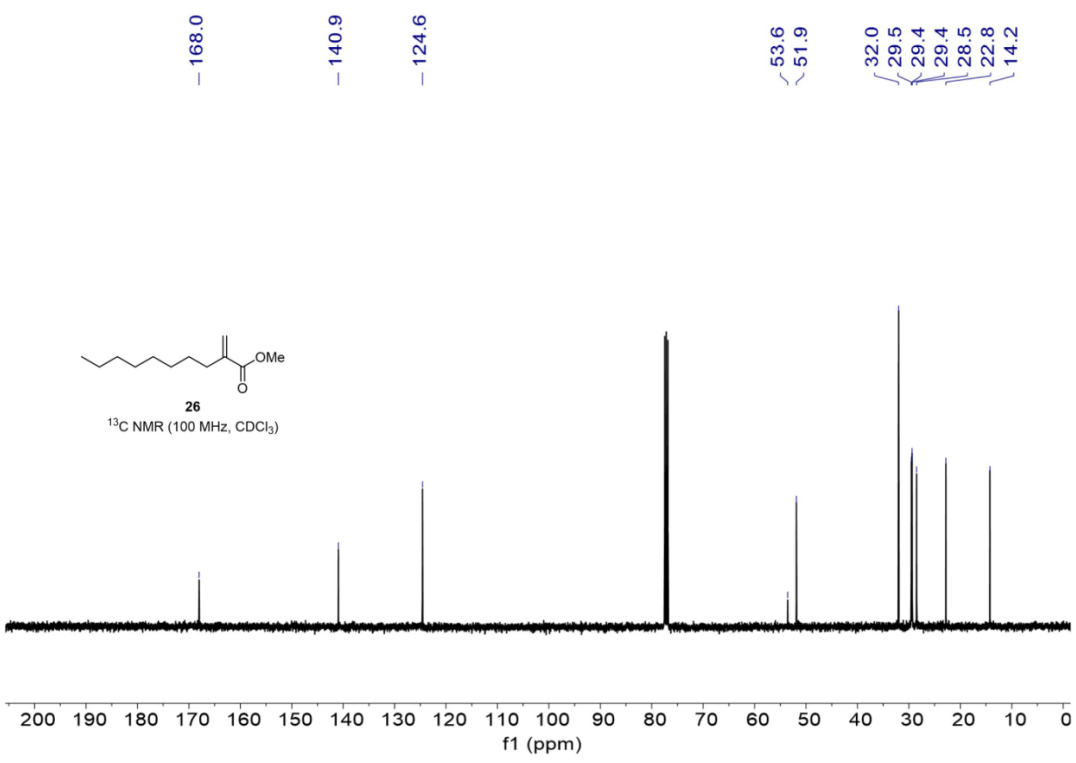

7.32
7.30
7.30
7.30
7.29
7.29
7.28
7.22
7.21
7.21
7.21
7.20
7.19
7.19
6.17
5.52
5.52
5.52
5.51
3.77
2.83
2.81
2.80
2.79
2.66
2.66
2.65
2.65
2.64
2.64
2.63
2.63
2.62
2.62
OMe
25
1H NMR (400 MHz, CDCl3)
2.06
3.09
1.00
1.03
2.97
2.13
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.7
141.5
139.9
128.6
128.4
126.1
125.5
51.9
35.0
34.0
OMe
25
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



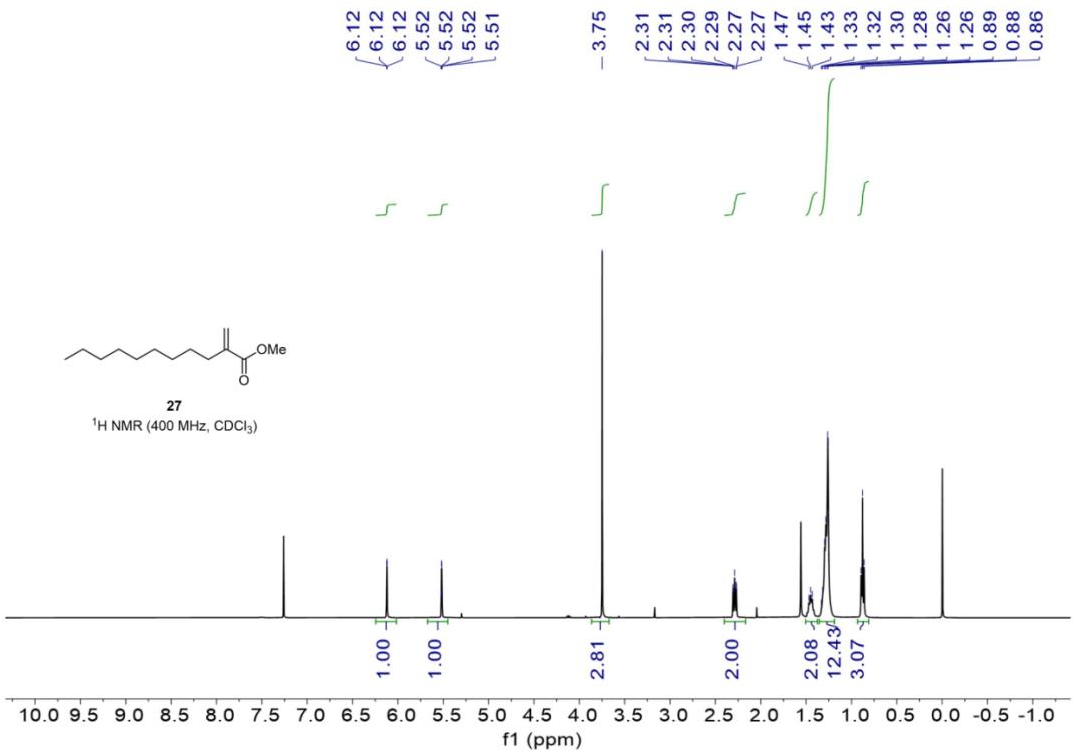
26

^{1}H NMR (400 MHz, $CDCl_3$)

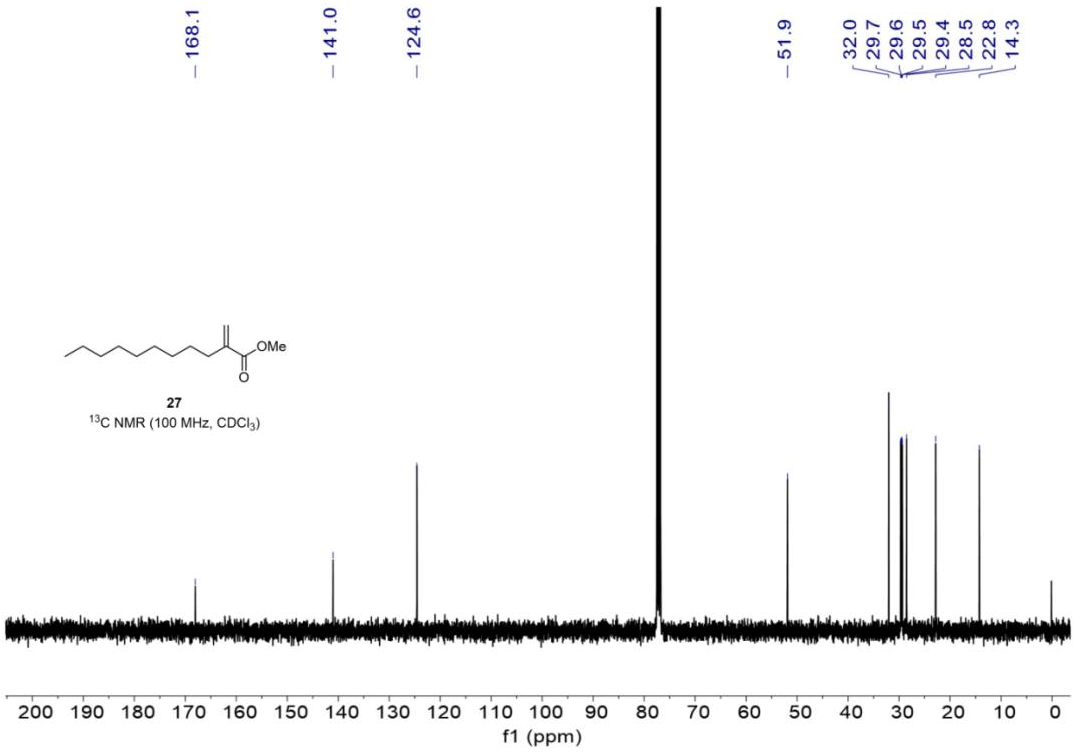


26

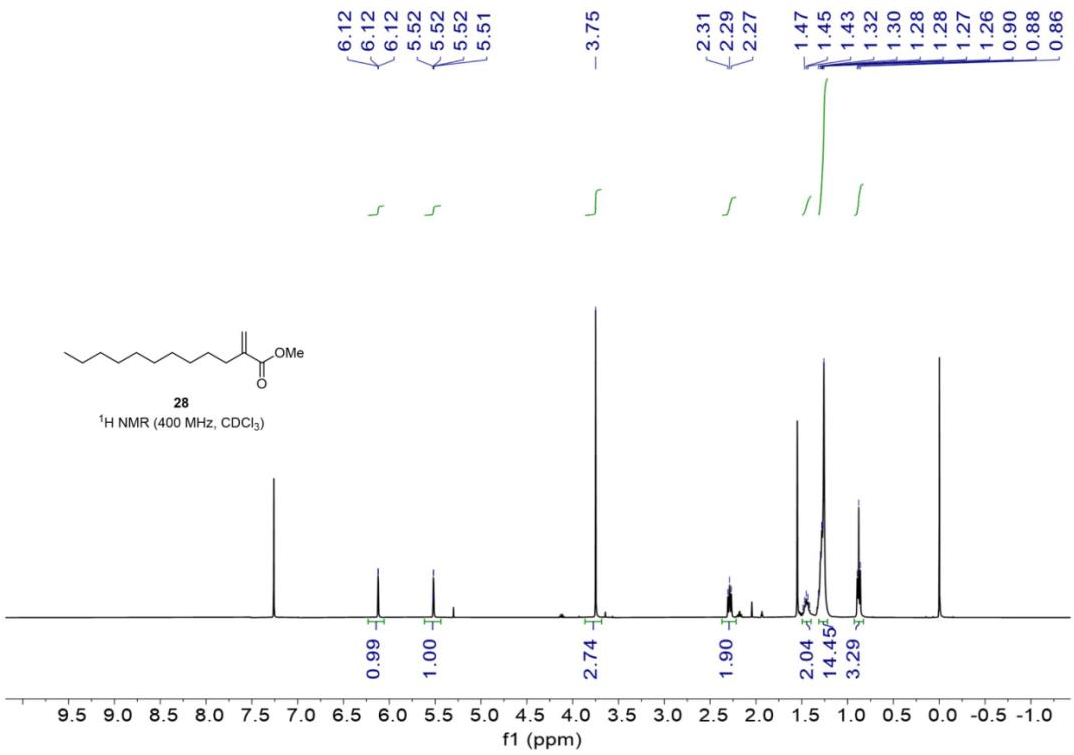
^{13}C NMR (100 MHz, $CDCl_3$)

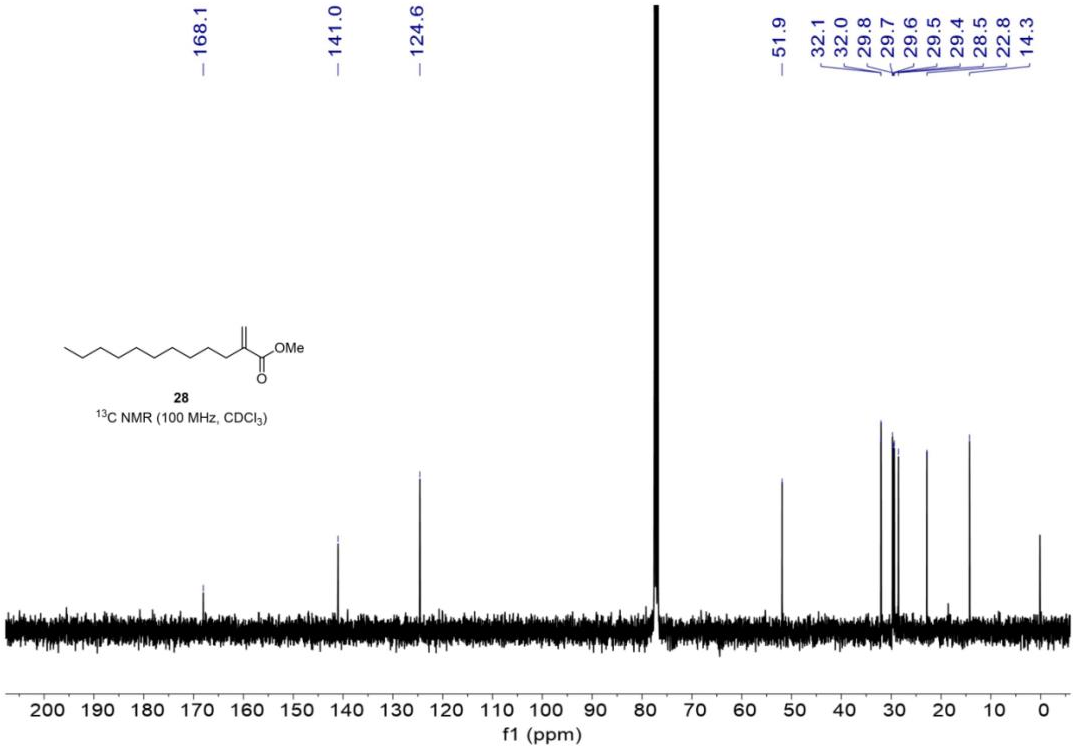


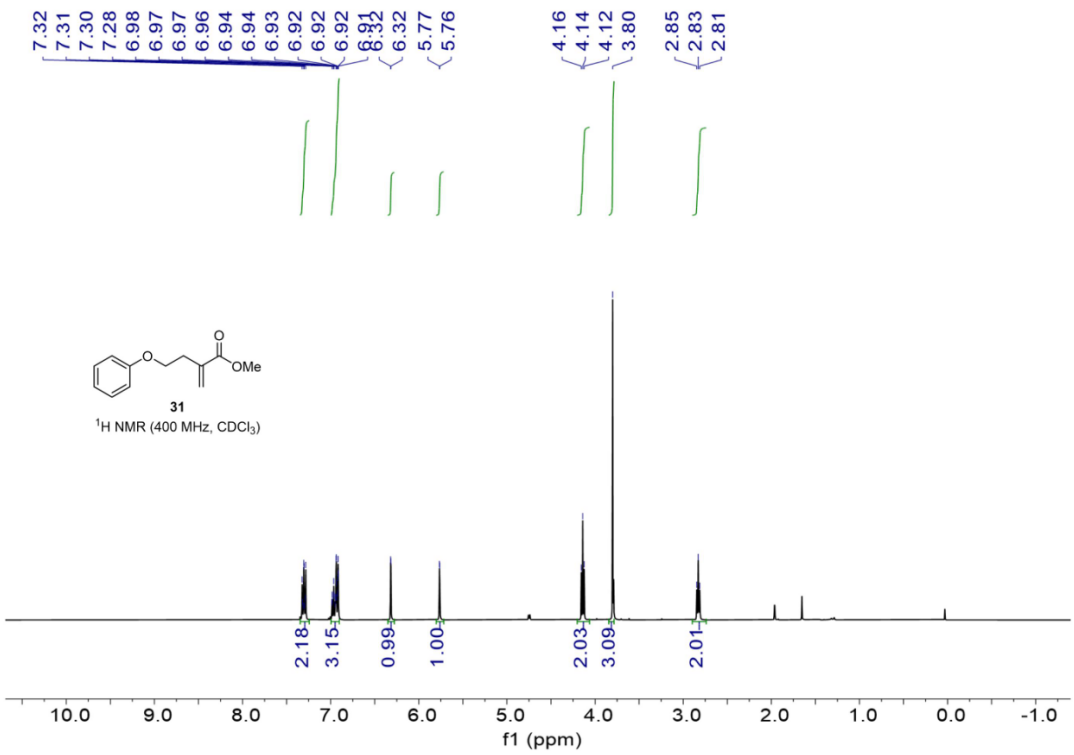
27
^{1}H NMR (400 MHz, $CDCl_3$)

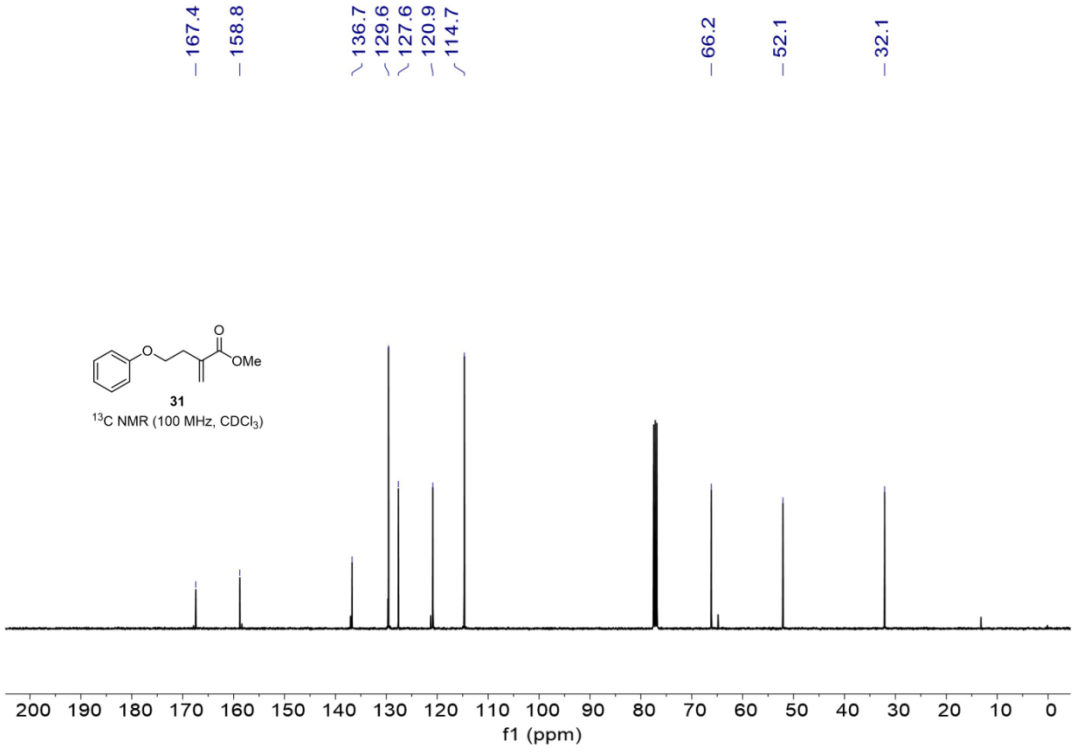


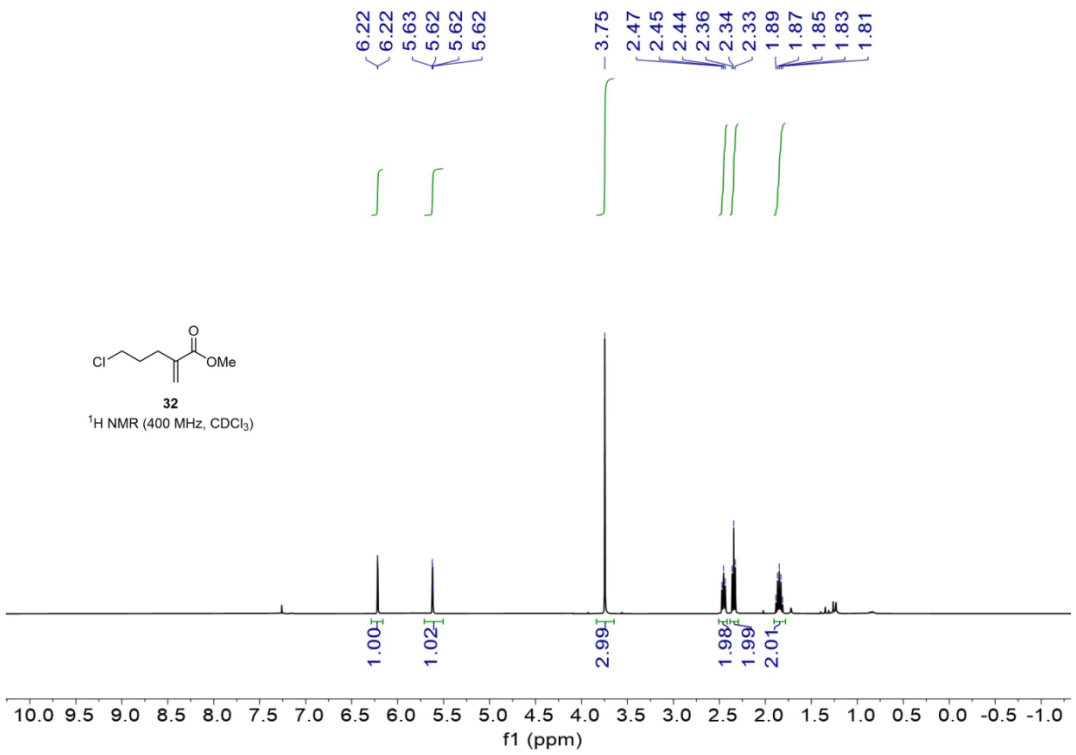
27
^{13}C NMR (100 MHz, $CDCl_3$)

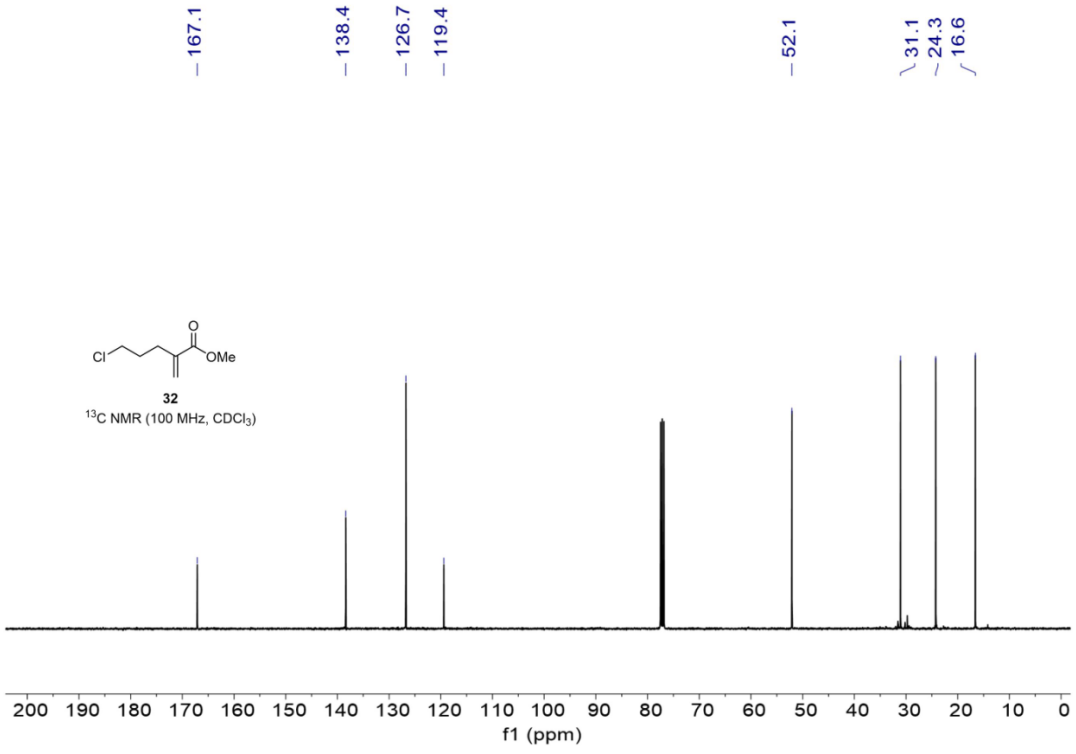

6.12
6.12
6.12
5.52
5.52
5.52
5.51
3.75
2.31
2.29
2.27
1.47
1.45
1.43
1.32
1.30
1.28
1.28
1.27
1.26
0.90
0.88
0.86
OMe
O
28
^{1}H NMR (400 MHz, $CDCl_3$)
0.99
1.00
2.74
1.90
2.04
14.45
3.29
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

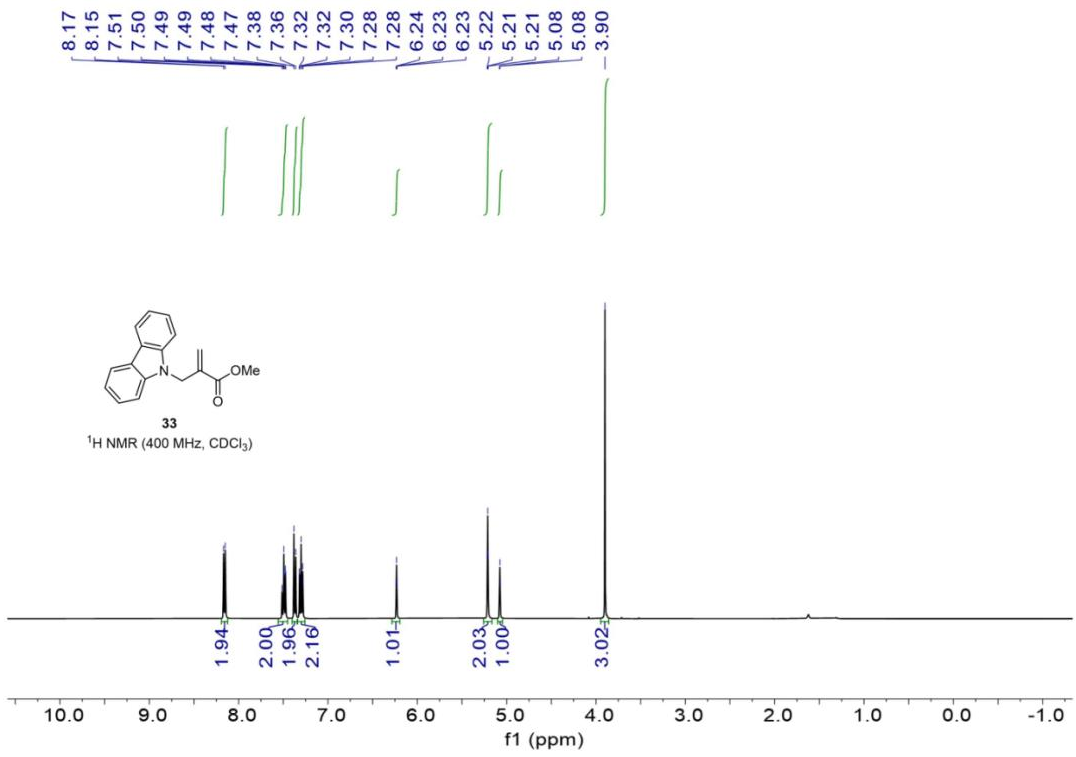

168.1
141.0
124.6
51.9
32.1
32.0
29.8
29.7
29.6
29.5
29.4
28.5
22.8
14.3
OMe
O
28
^{13}C NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.32
7.31
7.30
7.28
6.98
6.97
6.97
6.96
6.94
6.94
6.93
6.92
6.92
6.92
6.91
6.32
5.77
5.76
4.16
4.14
4.12
3.80
2.85
2.83
2.81
OMe
31
1H NMR (400 MHz, CDCl3)
2.18
3.15
0.99
1.00
2.03
3.09
2.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


167.4
158.8
136.7
129.6
127.6
120.9
114.7
66.2
52.1
32.1
OMe
31
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

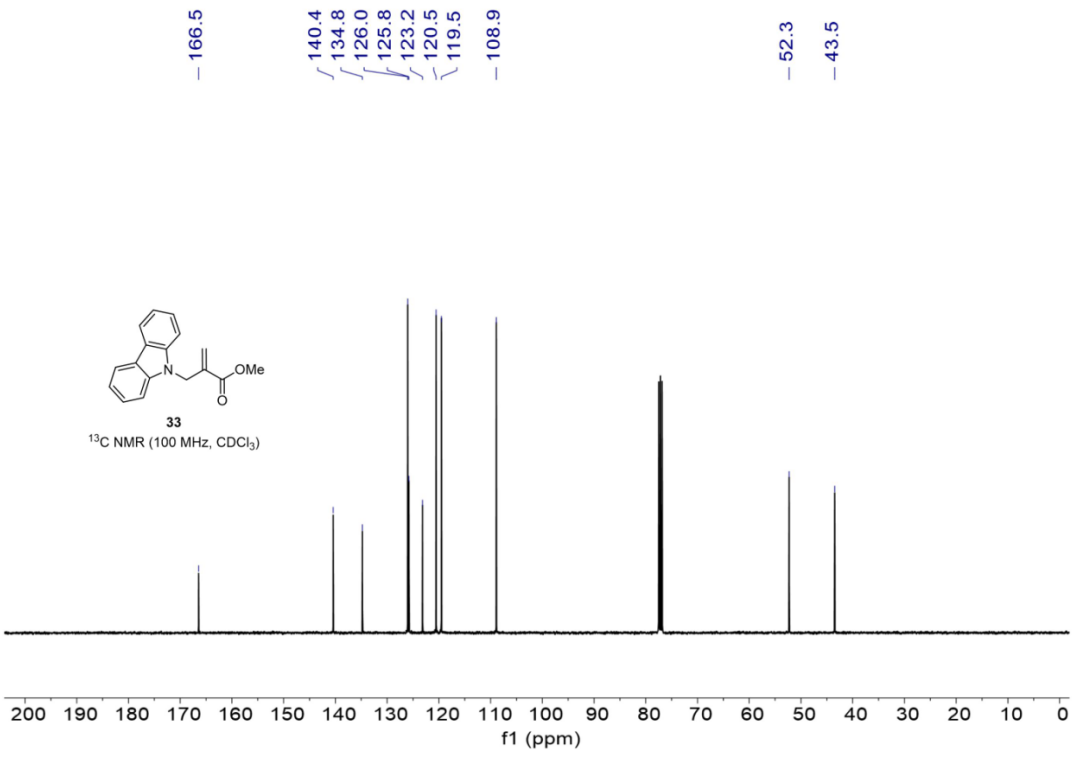

6.22
6.22
5.63
5.62
5.62
5.62
3.75
2.47
2.45
2.44
2.36
2.34
2.33
1.89
1.87
1.85
1.83
1.81
Cl
O
OMe
32
1H NMR (400 MHz, CDCl3)
1.00
1.02
2.99
1.98
1.99
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.1
138.4
126.7
119.4
52.1
31.1
24.3
16.6
Cl
O
OMe
32
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



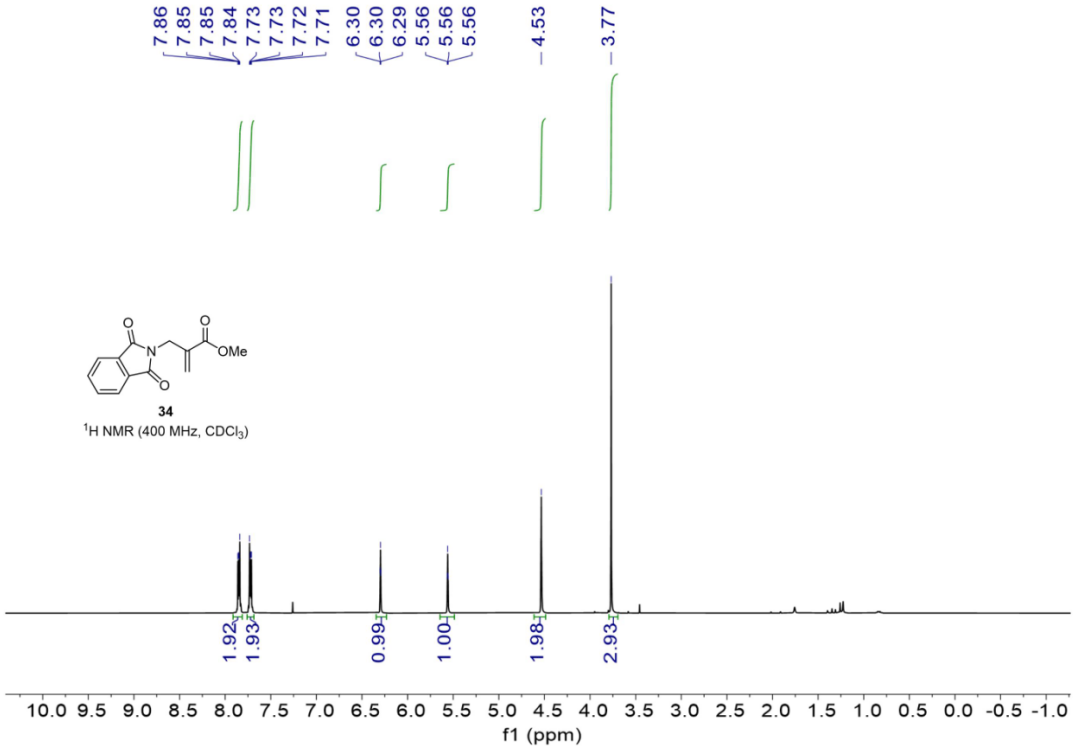
33

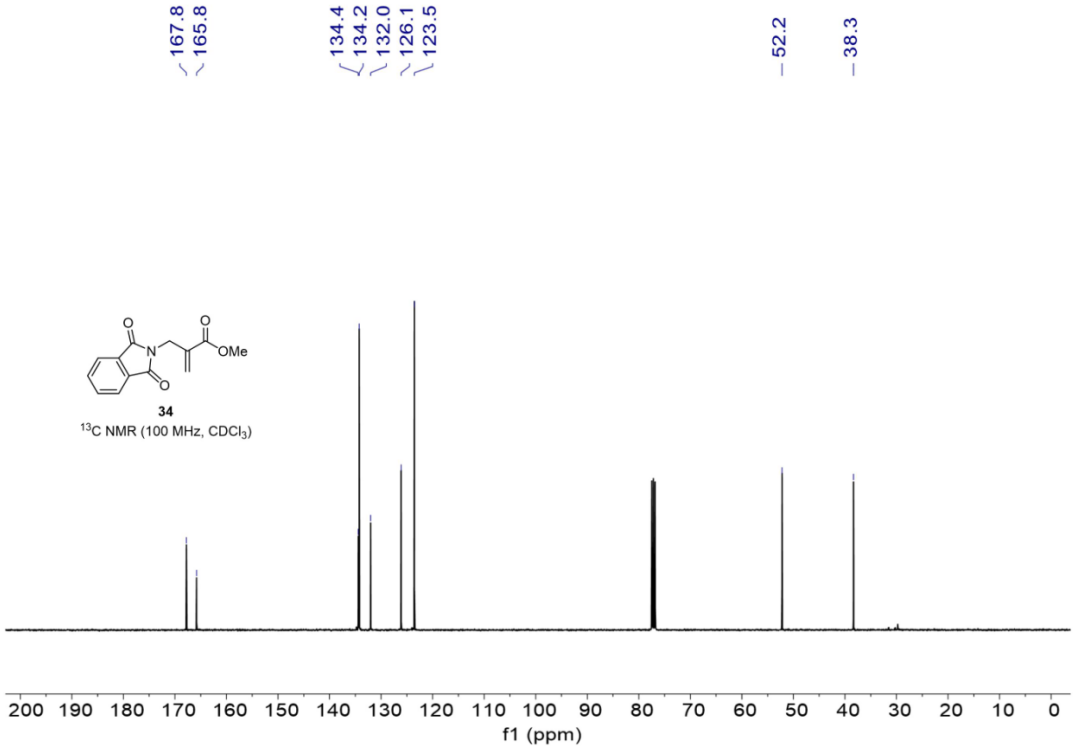
^{1}H NMR (400 MHz, $CDCl_3$)

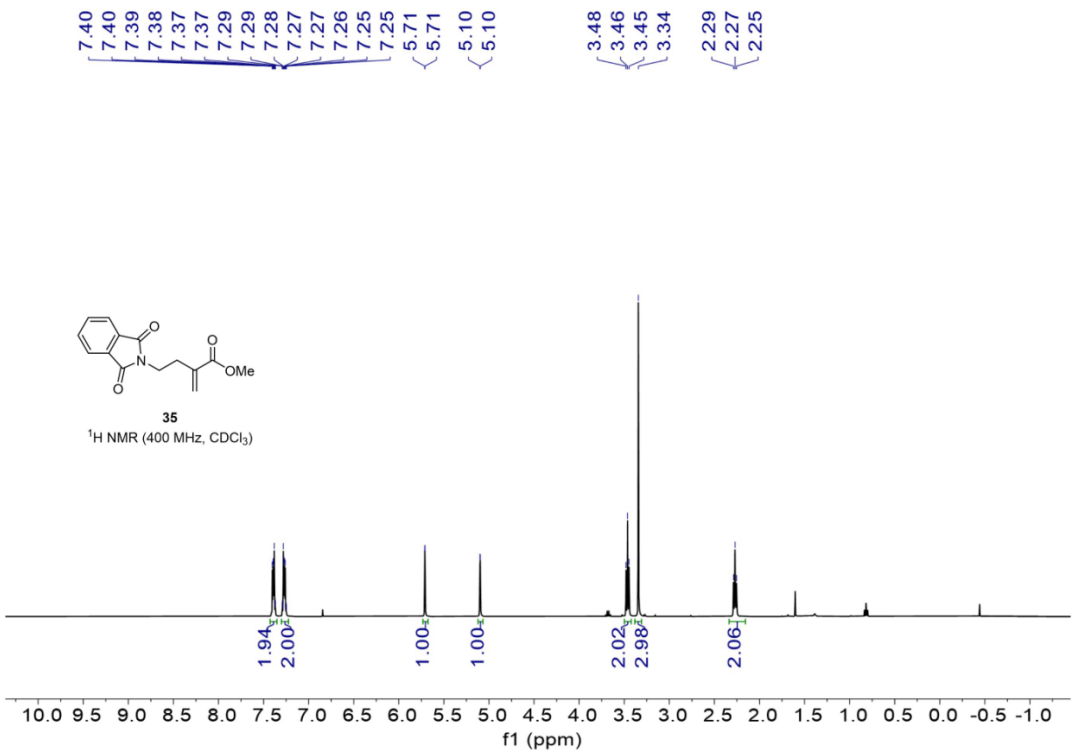


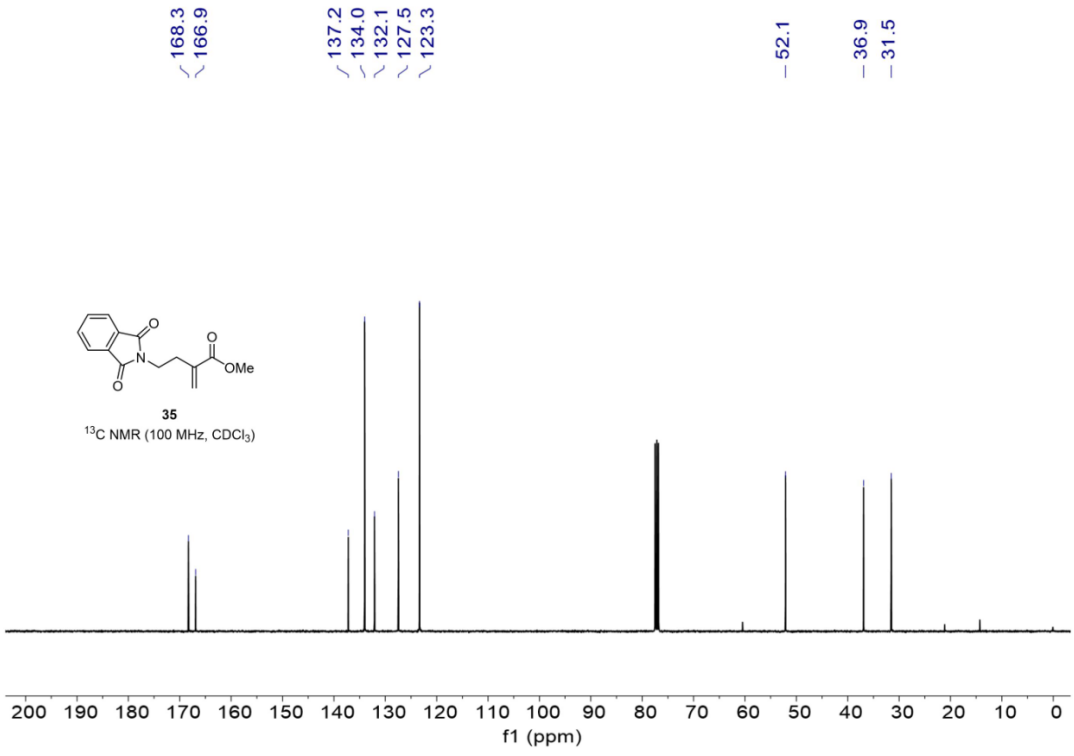
33

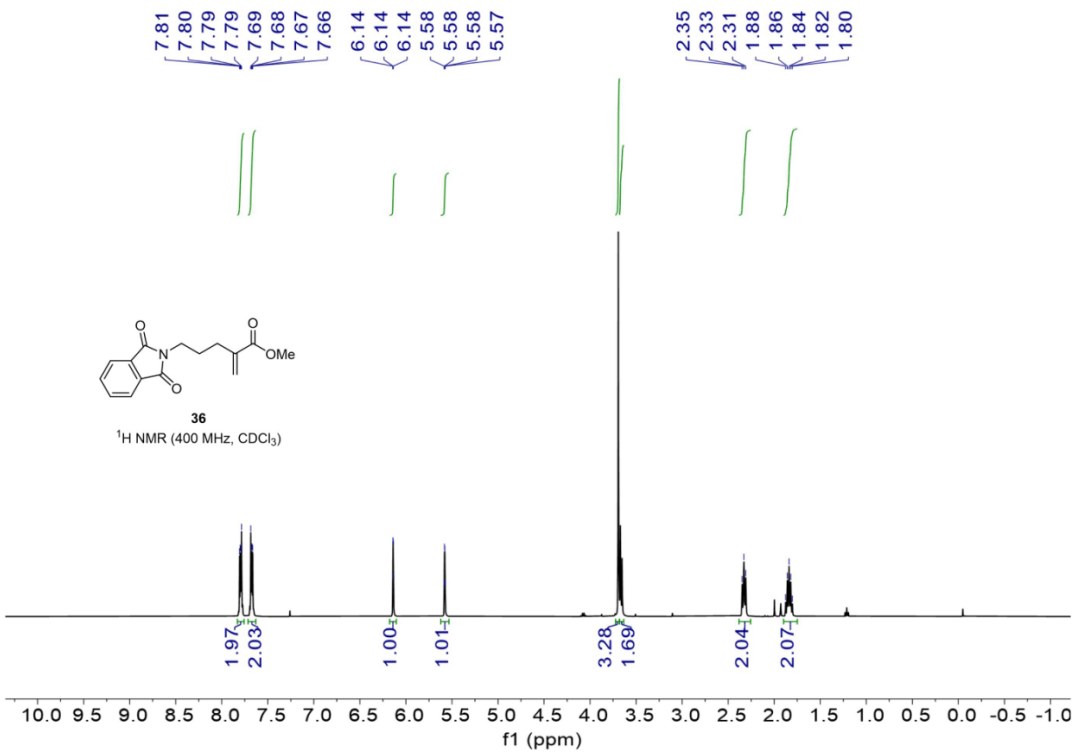
^{13}C NMR (100 MHz, $CDCl_3$)


7.86
7.85
7.85
7.84
7.73
7.73
7.72
7.71
6.30
6.30
6.29
5.56
5.56
5.56
4.53
3.77
OMe
34
1H NMR (400 MHz, CDCl3)
1.92
1.93
0.99
1.00
1.98
2.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.8
165.8
134.4
134.2
132.0
126.1
123.5
52.2
38.3
OMe
34
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

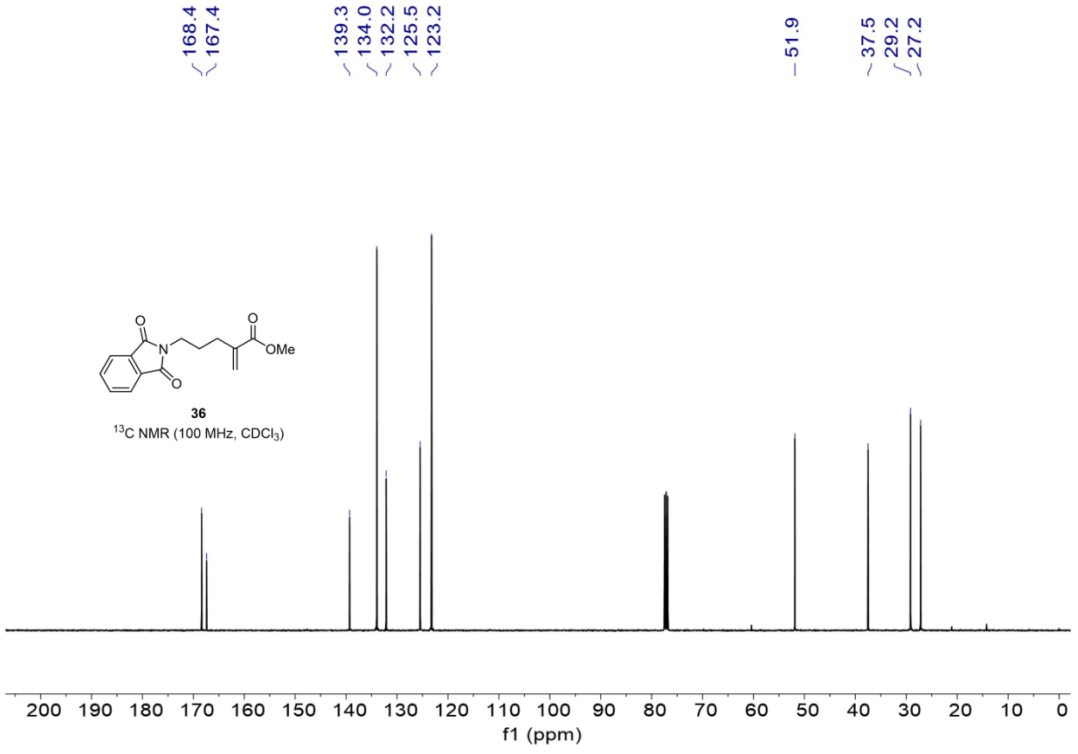

7.40
7.40
7.39
7.38
7.37
7.37
7.29
7.29
7.28
7.27
7.27
7.26
7.25
7.25
5.71
5.71
5.10
5.10
3.48
3.46
3.45
3.34
2.29
2.27
2.25
OMe
35
1H NMR (400 MHz, CDCl3)
1.94
2.00
1.00
1.00
2.02
2.98
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


168.3
166.9
137.2
134.0
132.1
127.5
123.3
52.1
36.9
31.5
OMe
35
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



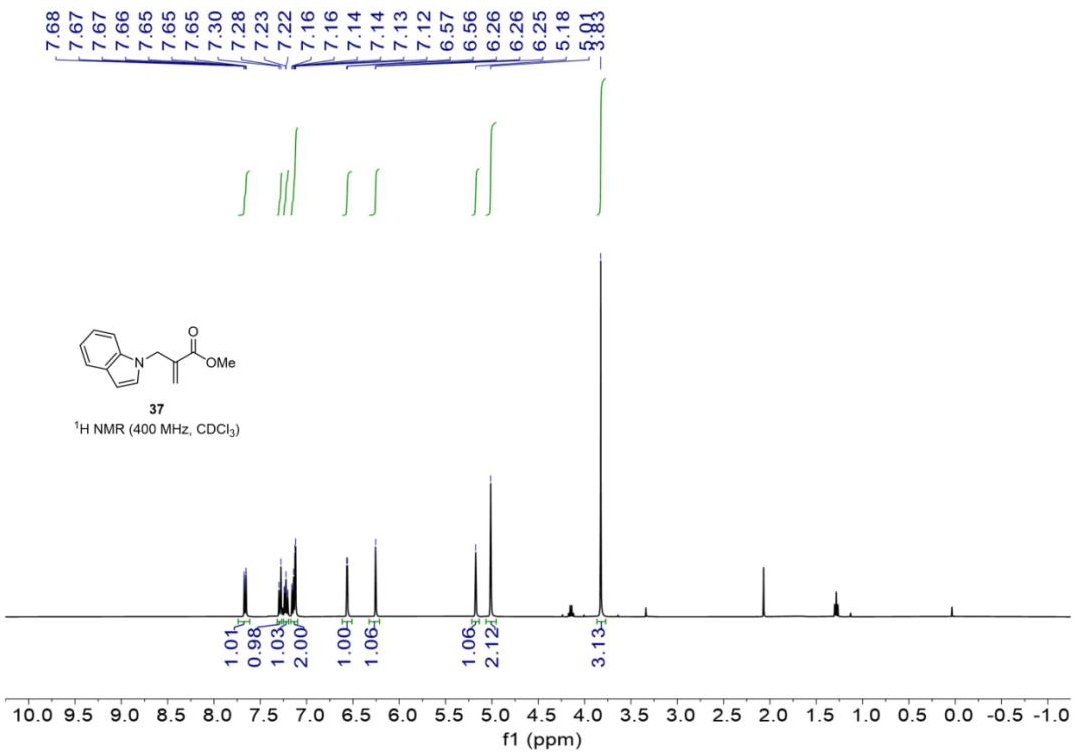
36

^{1}H NMR (400 MHz, $CDCl_3$)



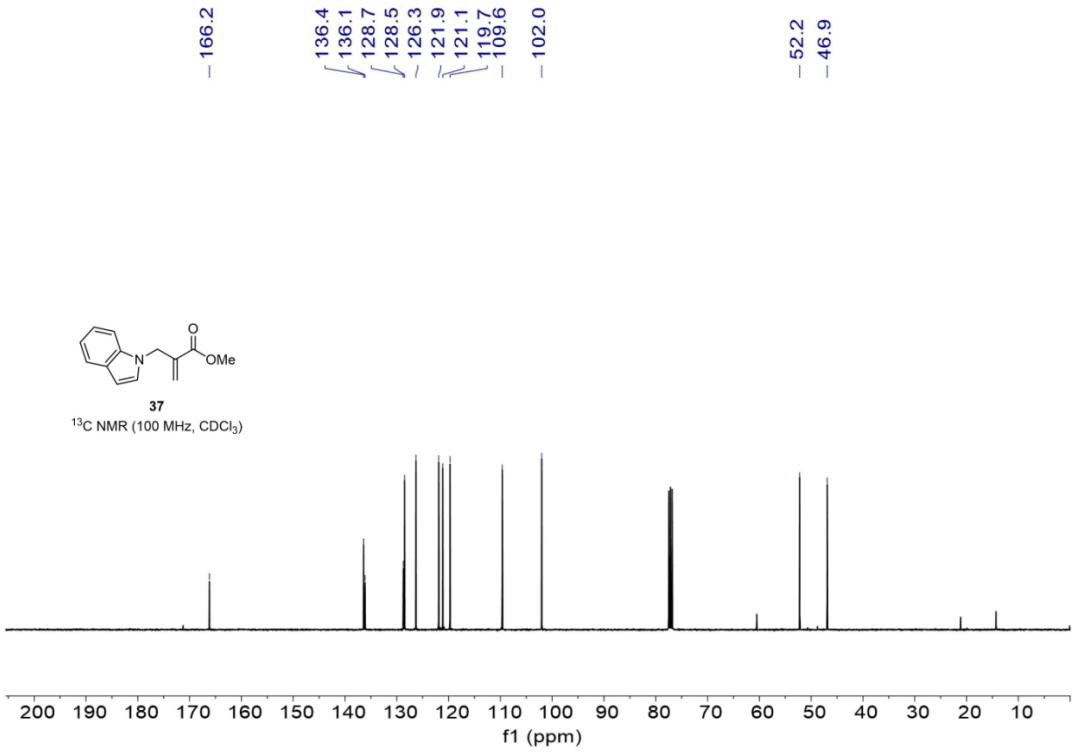
36

^{13}C NMR (100 MHz, $CDCl_3$)



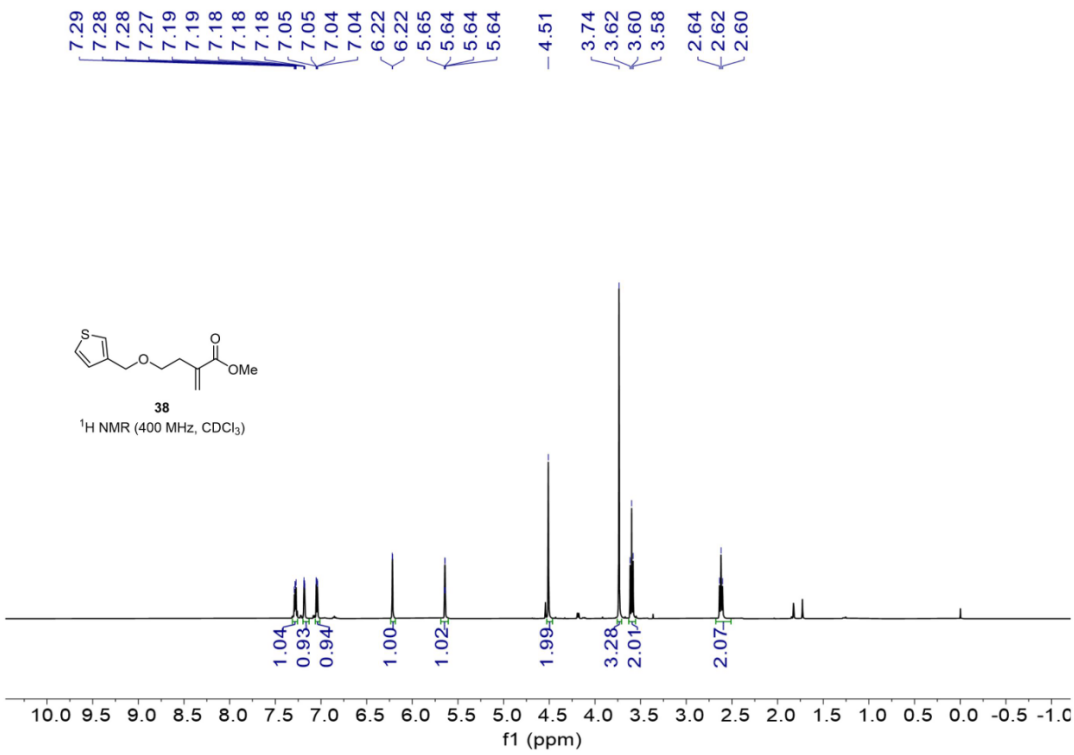
37

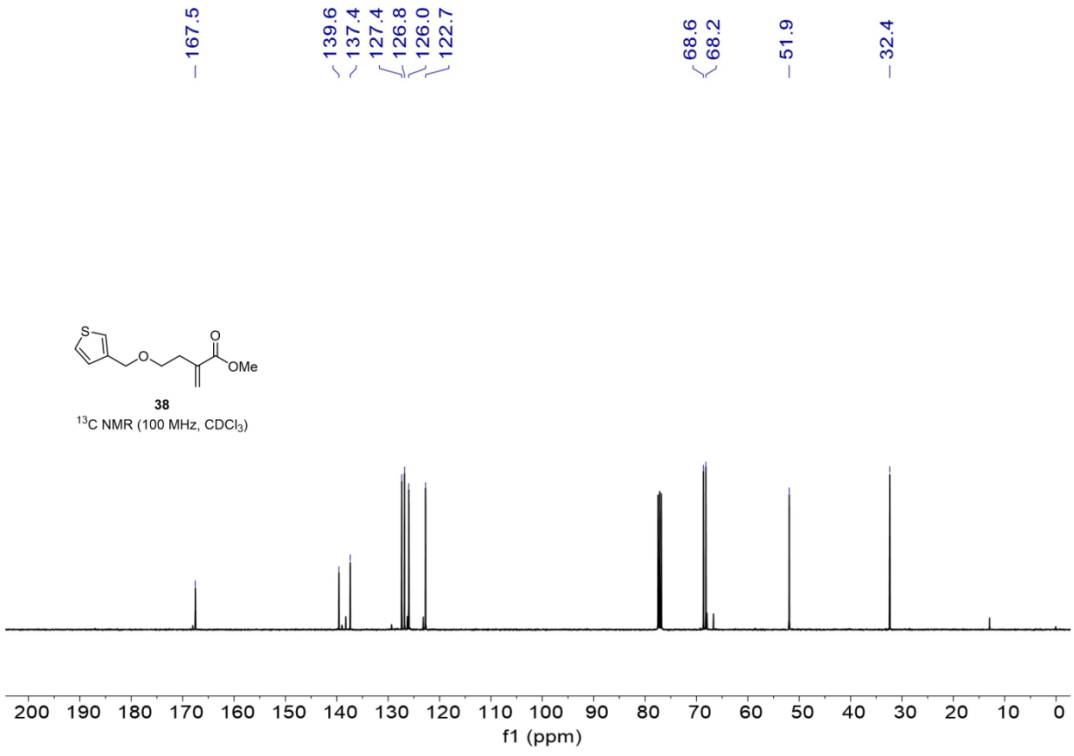
^{1}H NMR (400 MHz, $CDCl_3$)

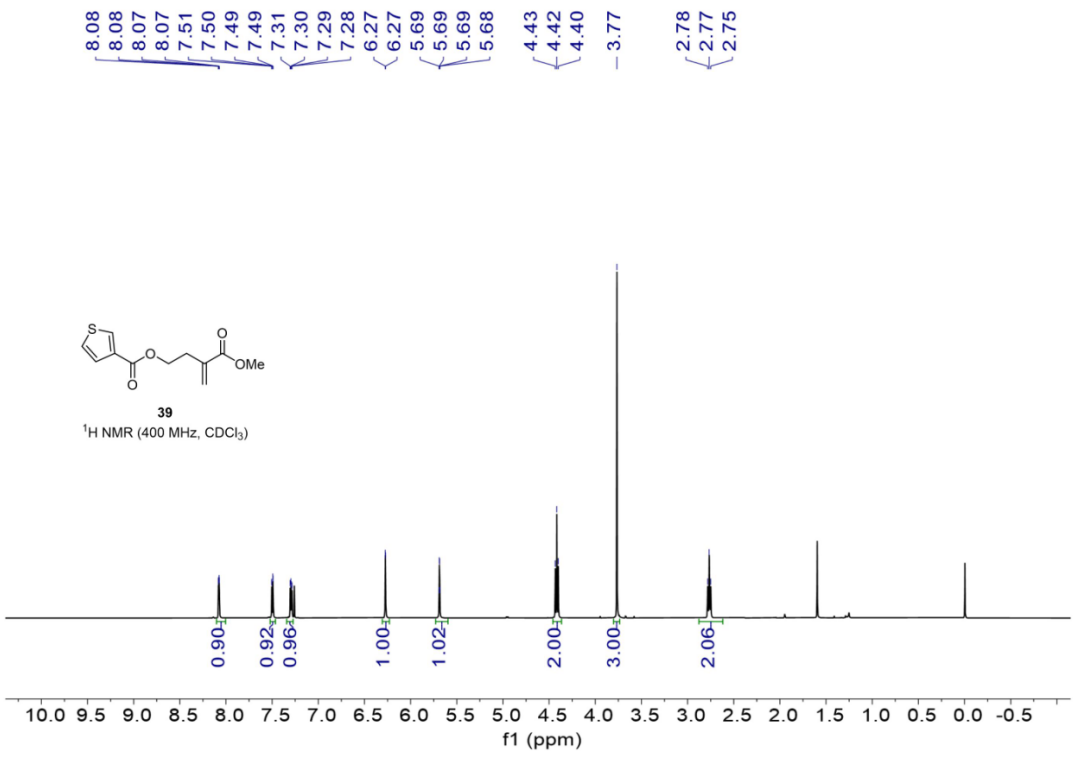


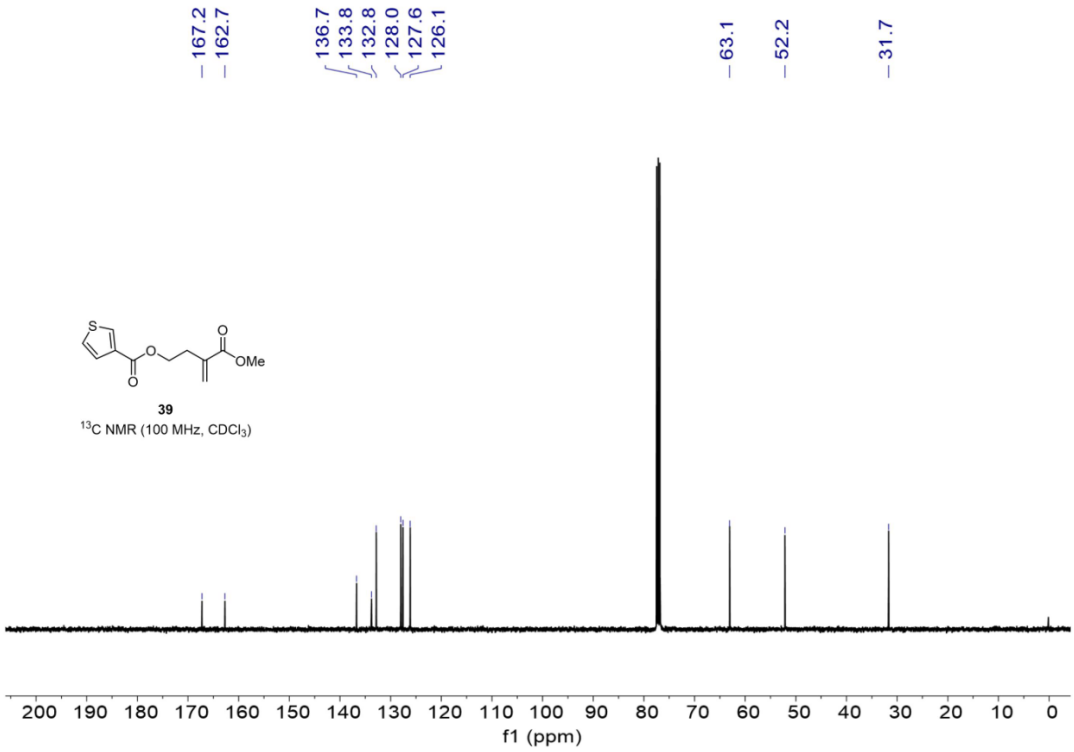
37

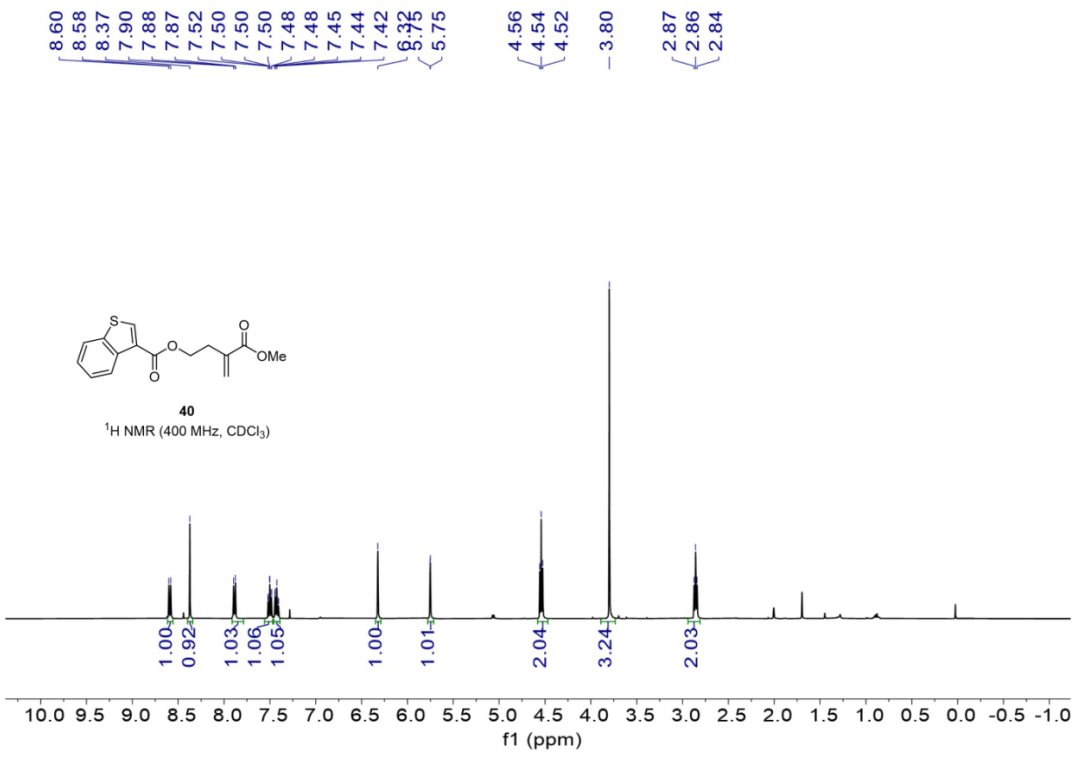
^{13}C NMR (100 MHz, $CDCl_3$)

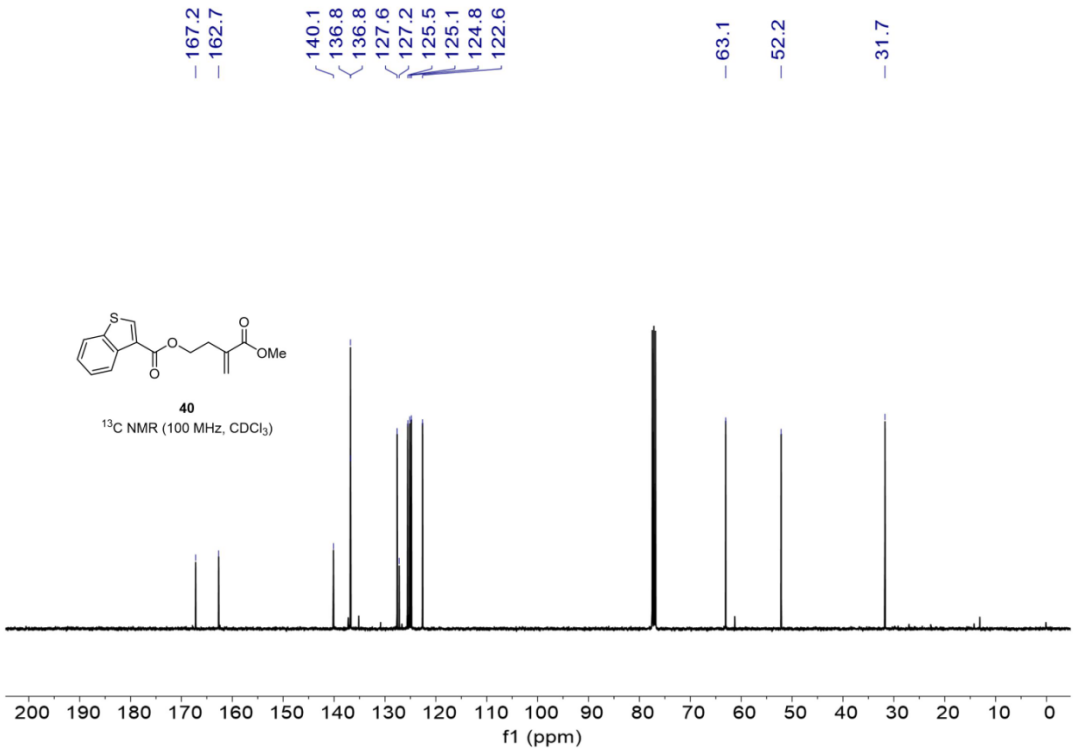

7.29
7.28
7.28
7.27
7.19
7.19
7.18
7.18
7.18
7.05
7.05
7.04
7.04
6.22
6.22
5.65
5.64
5.64
5.64
4.51
3.74
3.62
3.60
3.58
2.64
2.62
2.60
S
O
O
OMe
38
1H NMR (400 MHz, CDCl3)
1.04
0.93
0.94
1.00
1.02
1.99
3.28
2.01
2.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

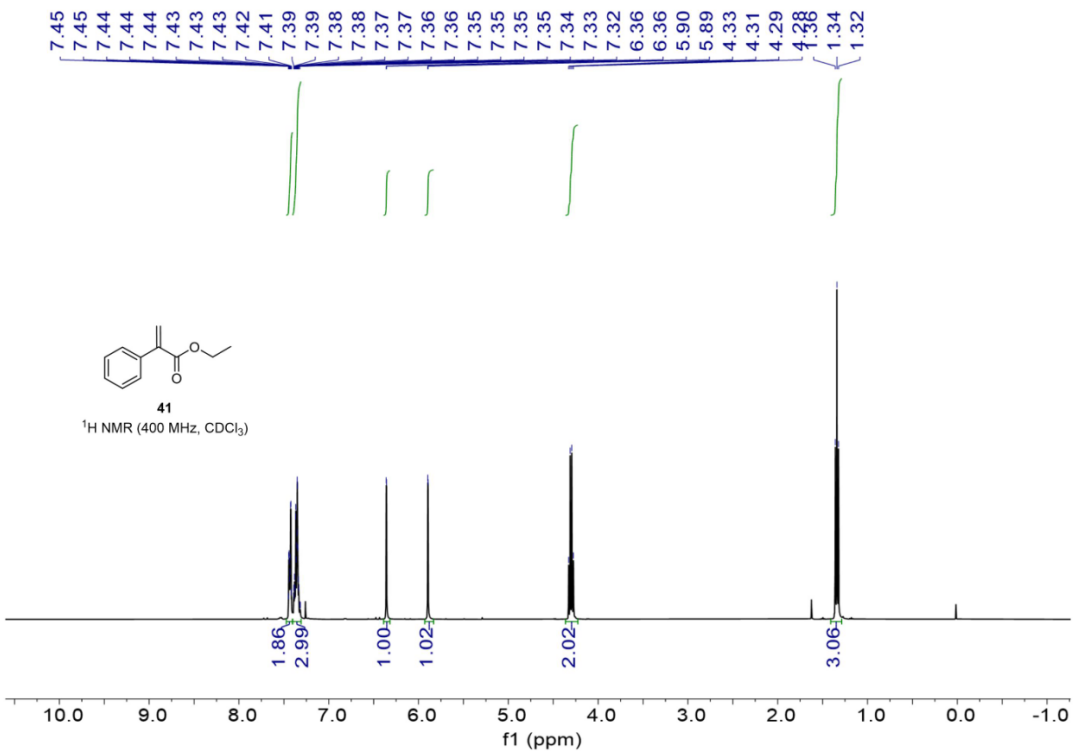

167.5
139.6
137.4
127.4
126.8
126.0
122.7
68.6
68.2
51.9
32.4
S
O
O
OMe
38
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

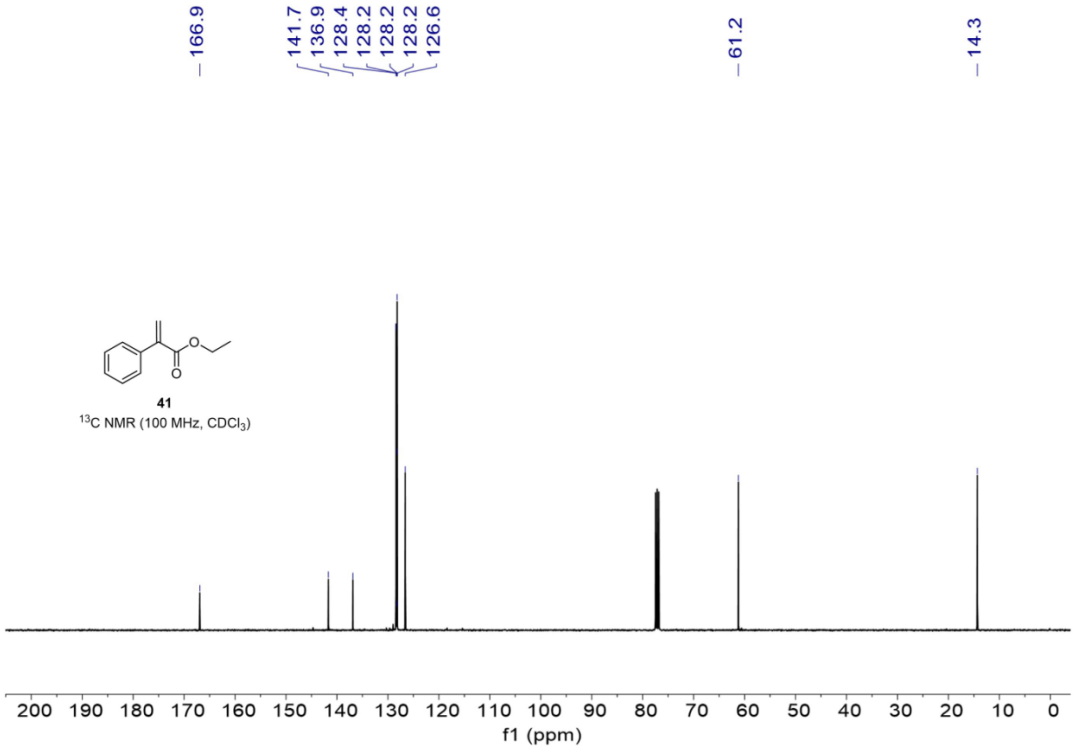

8.08
8.08
8.07
8.07
7.51
7.50
7.49
7.49
7.31
7.30
7.29
7.28
6.27
6.27
5.69
5.69
5.69
5.68
4.43
4.42
4.40
3.77
2.78
2.77
2.75
S
O
O
O
OMe
39
1H NMR (400 MHz, CDCl3)
0.90
0.92
0.96
1.00
1.02
2.00
3.00
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

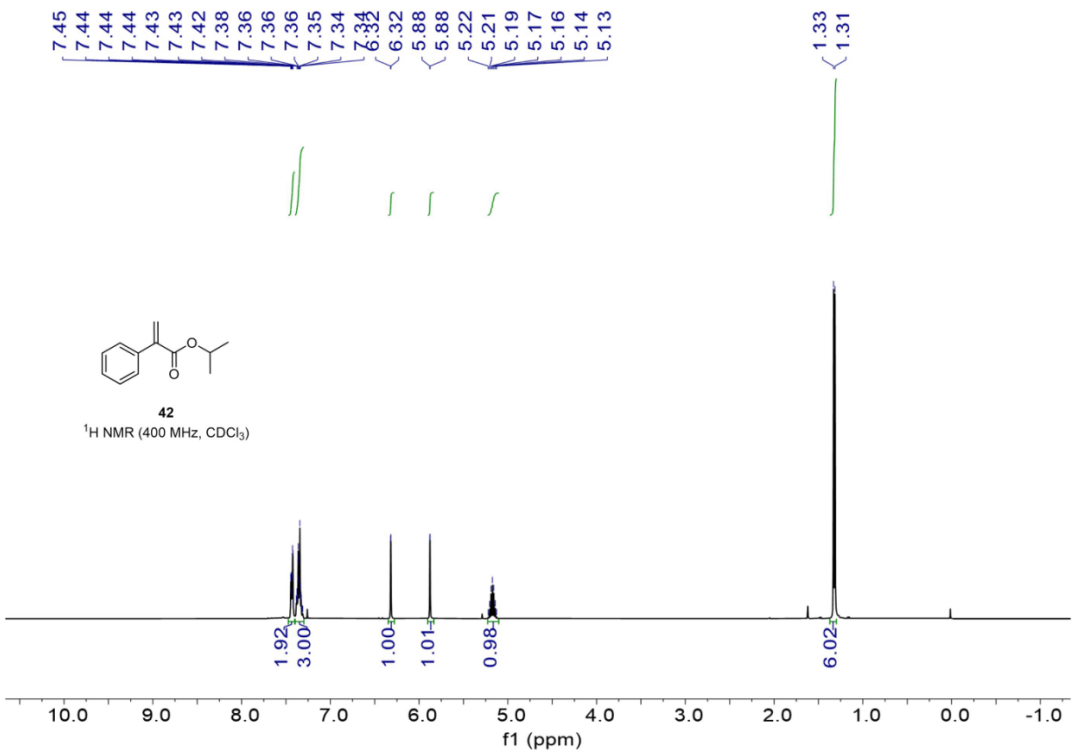

167.2
162.7
136.7
133.8
132.8
128.0
127.6
126.1
63.1
52.2
31.7
S
O
O
O
OMe
39
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.60
8.58
8.37
7.90
7.88
7.87
7.52
7.50
7.50
7.50
7.48
7.48
7.45
7.44
7.42
6.32
5.75
5.75
4.56
4.54
4.52
3.80
2.87
2.86
2.84
S
O
O
O
OMe
40
1H NMR (400 MHz, CDCl3)
1.00
0.92
1.03
1.06
1.05
1.00
1.01
2.04
3.24
2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.2
162.7
140.1
136.8
136.8
127.6
127.2
125.5
125.1
124.8
122.6
63.1
52.2
31.7
S
O
O
O
OMe
40
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

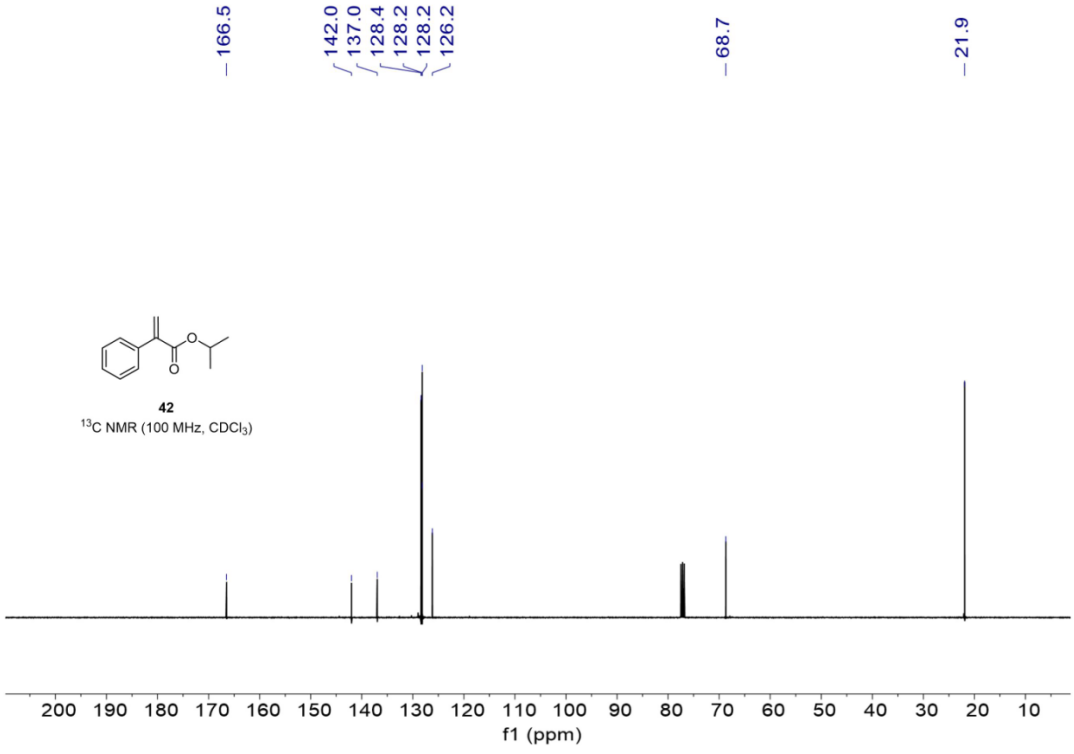

7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.41 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.35 7.34 7.33 7.32 6.36 6.36 5.90 5.89 4.33 4.31 4.29 1.36 1.34 1.32
41
1H NMR (400 MHz, CDCl3)
1.86 2.99 1.00 1.02 2.02 3.06
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)


166.9
141.7 136.9 128.4 128.2 128.2 128.2 126.6
61.2
14.3
41
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



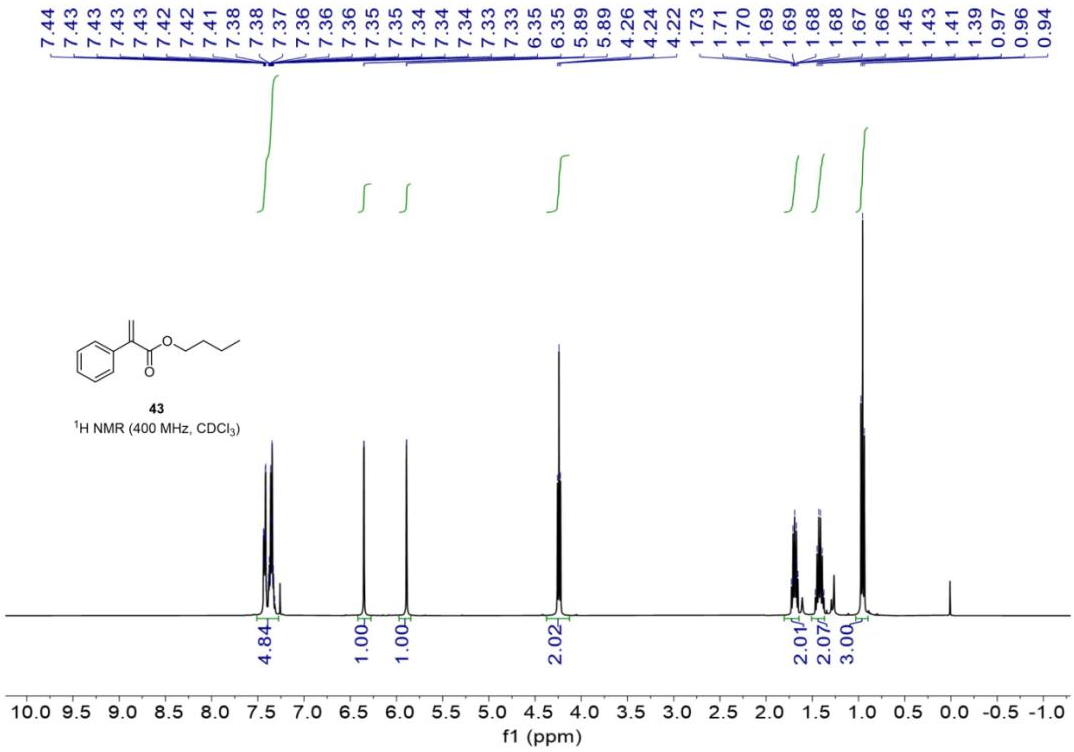
42

^{1}H NMR (400 MHz, $CDCl_3$)

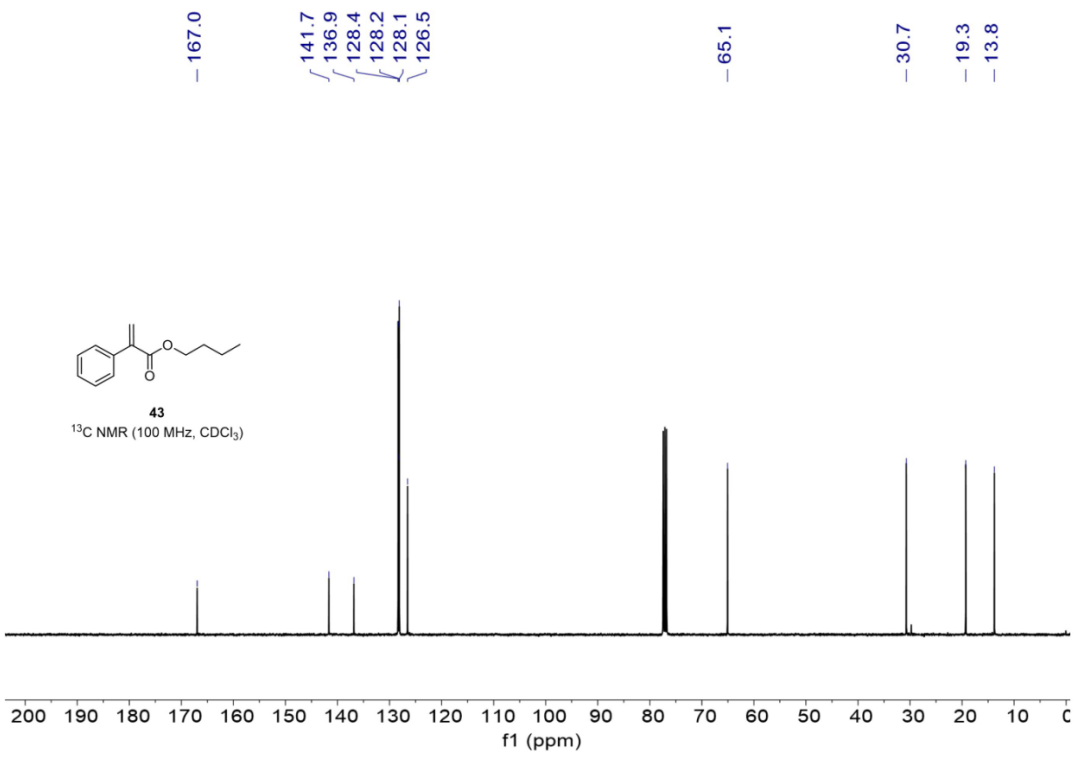


42

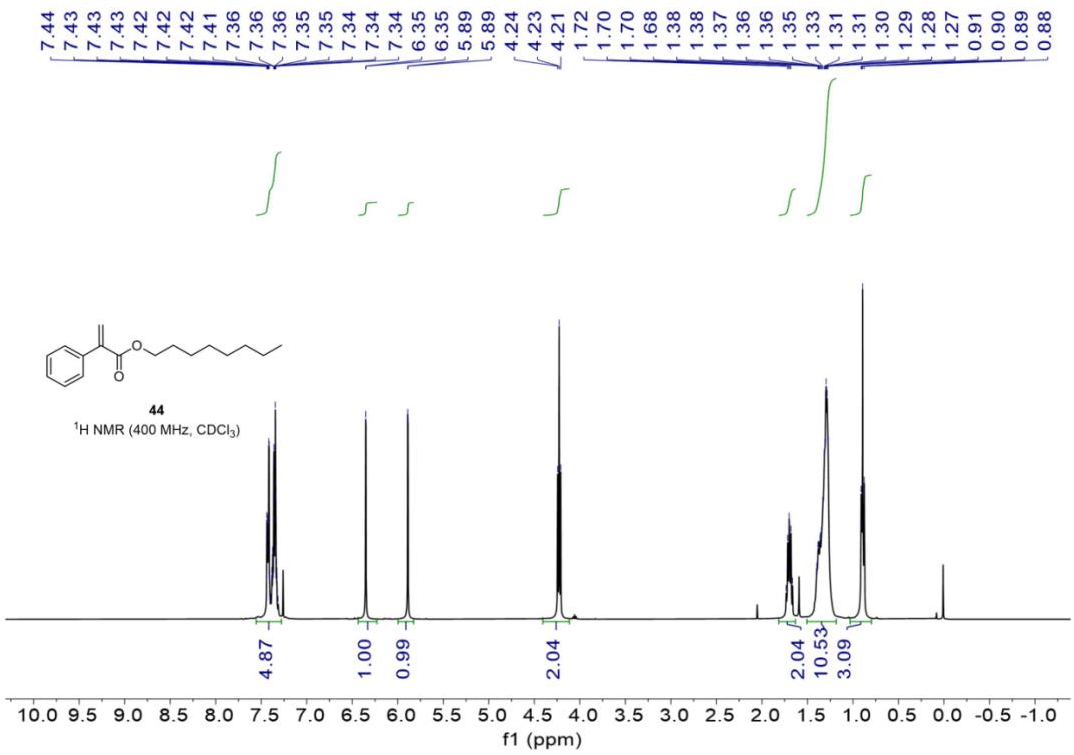
^{13}C NMR (100 MHz, $CDCl_3$)

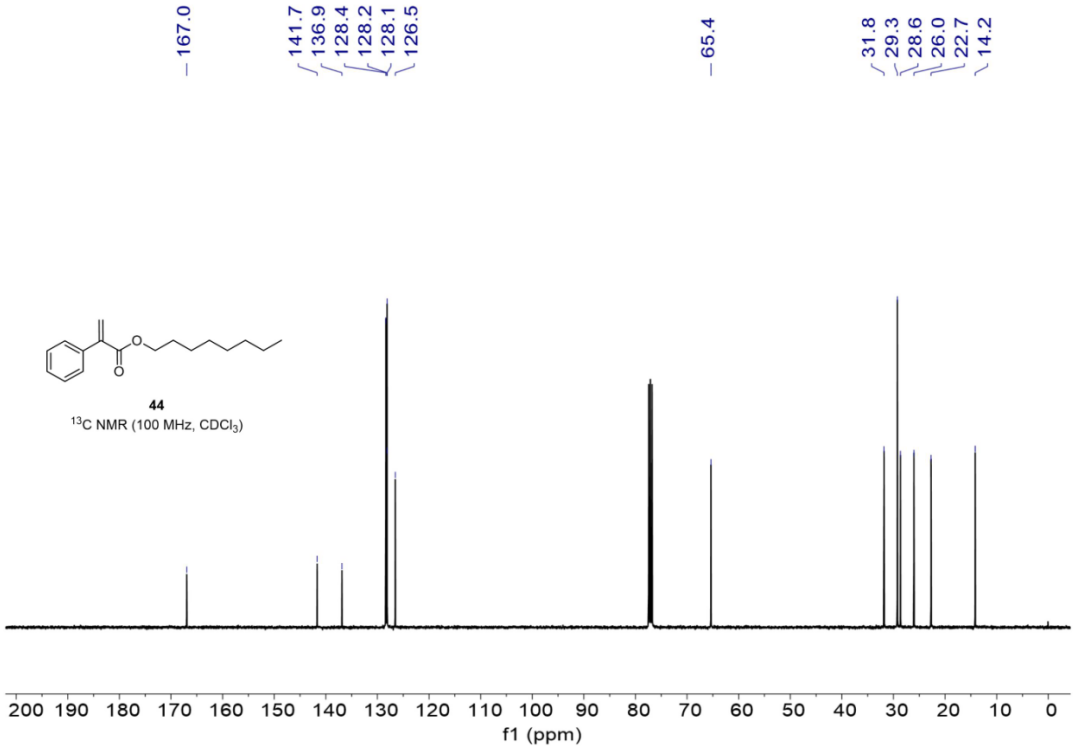


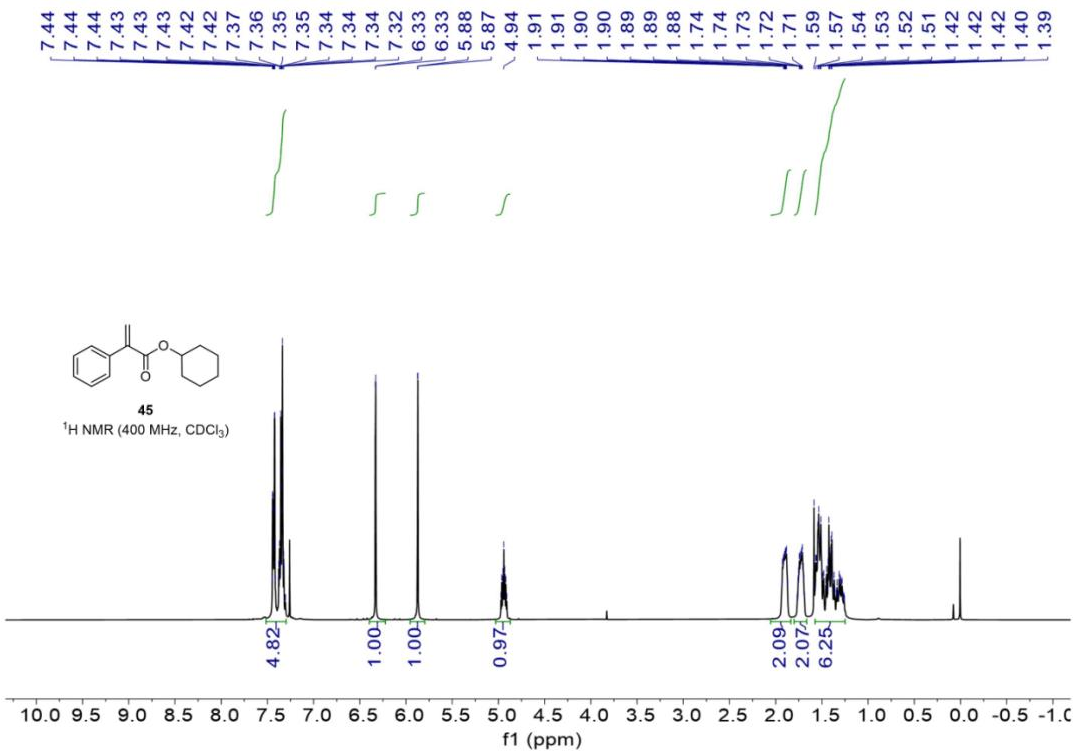
43
^{1}H NMR (400 MHz, $CDCl_3$)

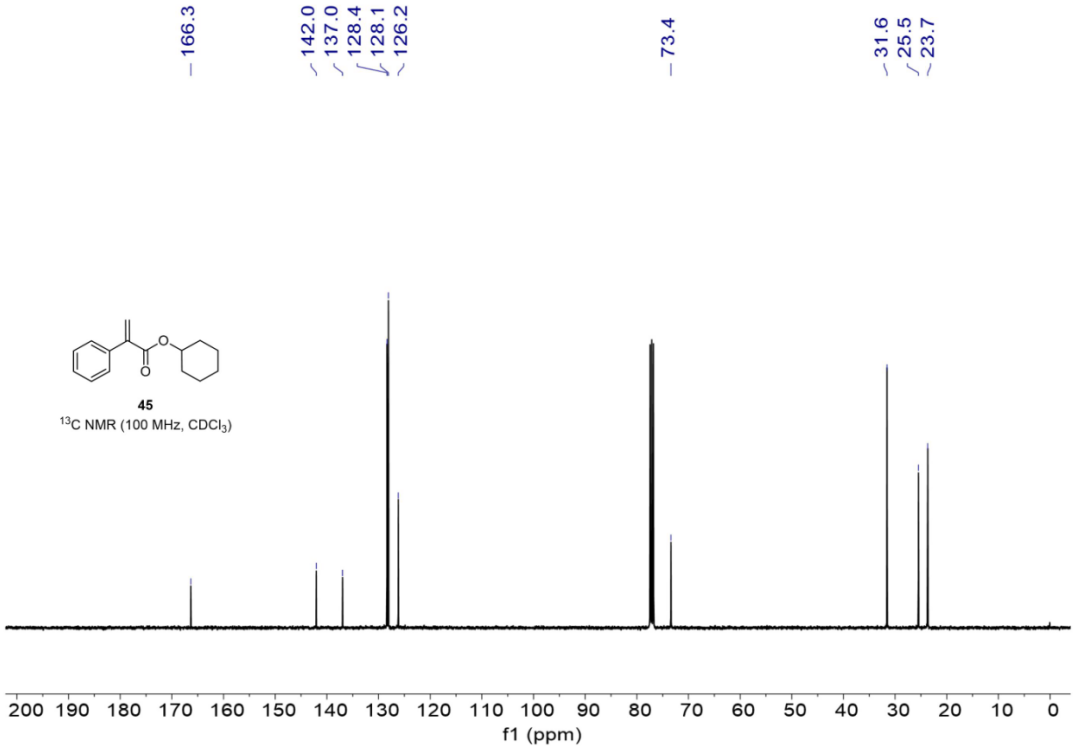


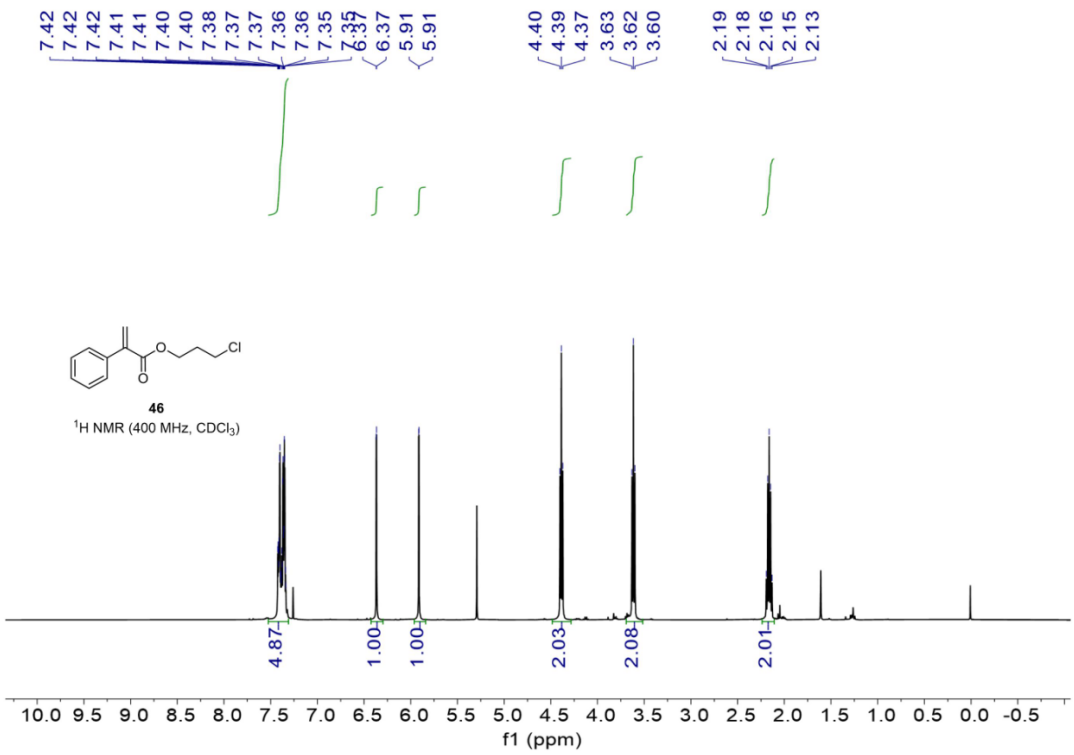
43
^{13}C NMR (100 MHz, $CDCl_3$)

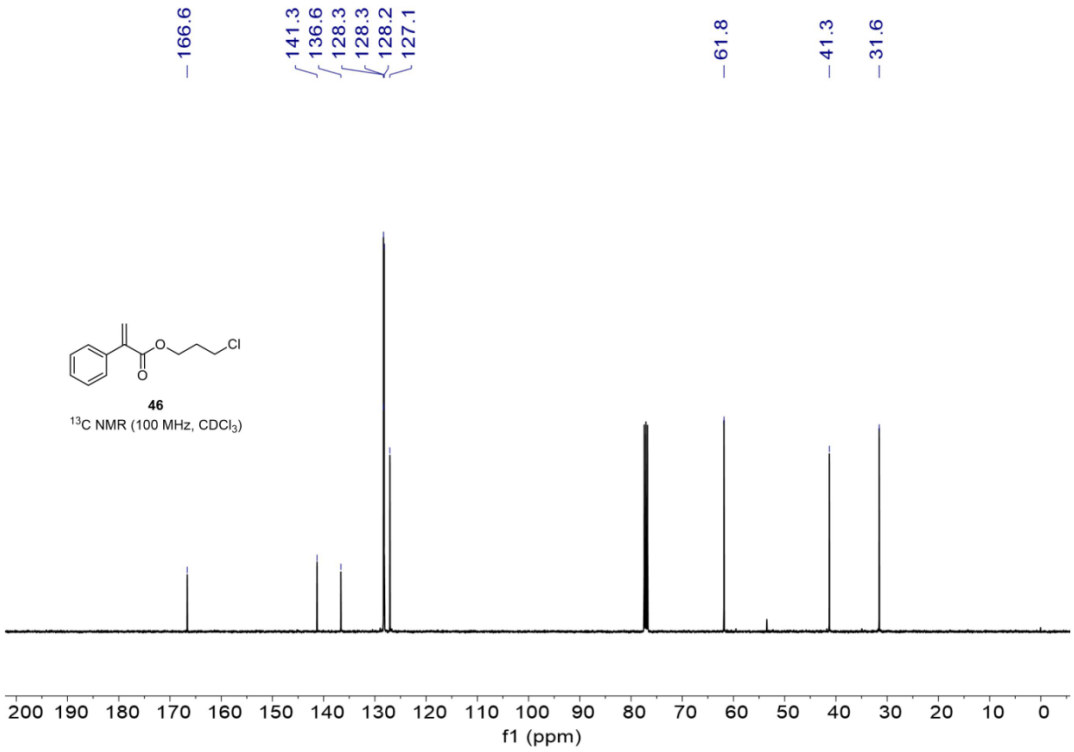

7.44 7.43 7.43 7.43 7.42 7.42 7.42 7.41 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.34 6.35 6.35 5.89 5.89 4.24 4.23 4.21 1.72 1.70 1.70 1.68 1.38 1.38 1.37 1.36 1.36 1.35 1.33 1.31 1.31 1.30 1.29 1.28 1.27 0.91 0.90 0.89 0.88
44
^{1}H NMR (400 MHz, $CDCl_3$)
4.87 1.00 0.99 2.04 2.04 10.53 3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

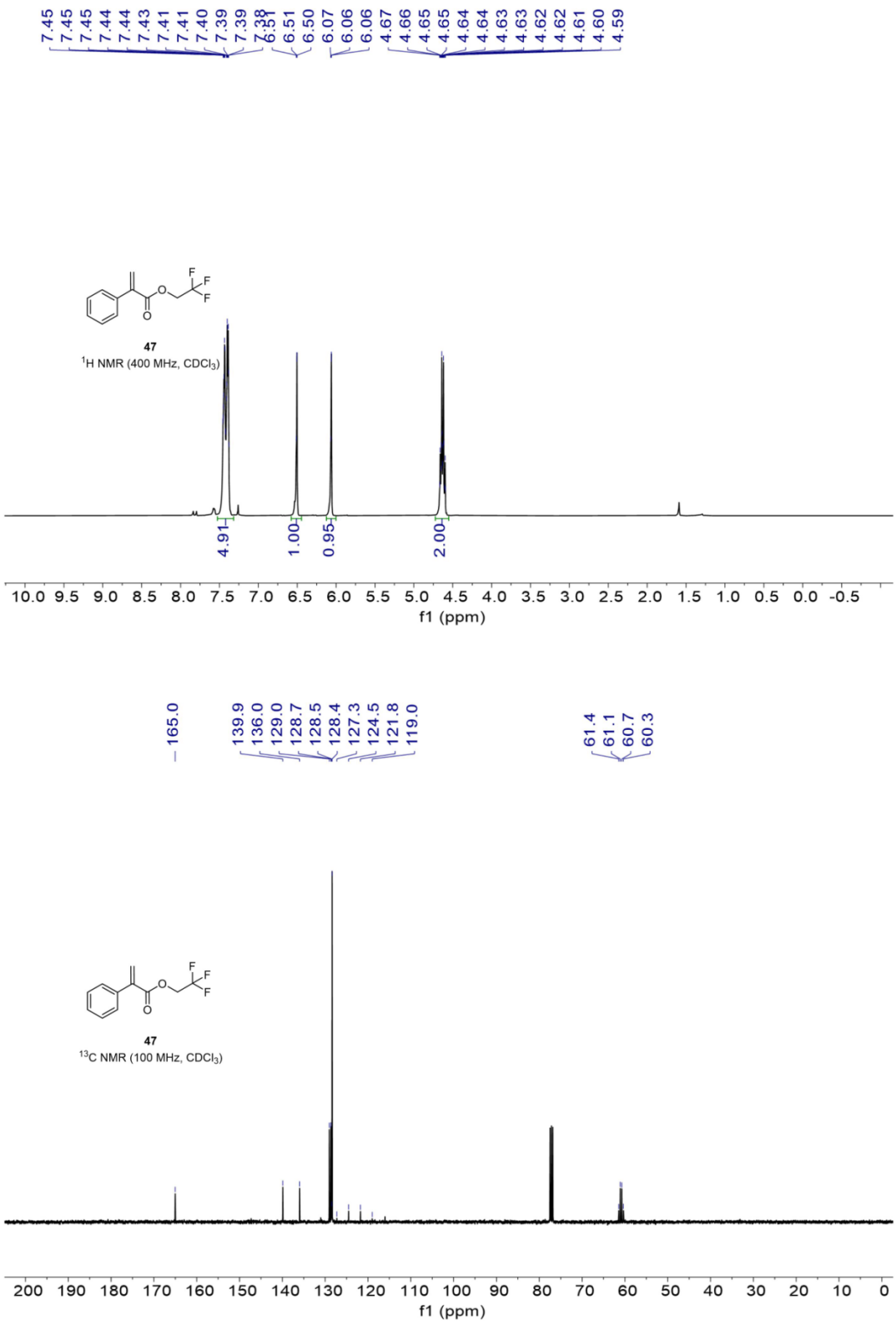

167.0
141.7 136.9 128.4 128.2 128.1 126.5
65.4
31.8 29.3 28.6 26.0 22.7 14.2
44
^{13}C NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

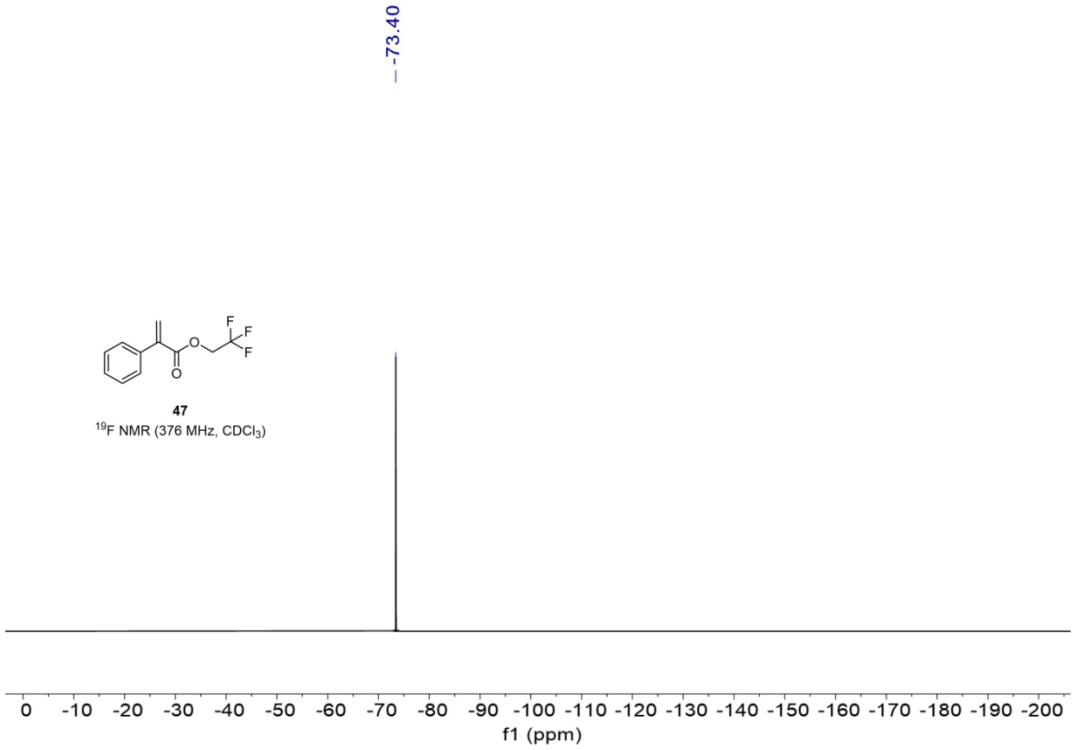

7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.37 7.36 7.35 7.35 7.34 7.34 7.34 7.32 6.33 6.33 5.88 5.87 4.94 1.91 1.91 1.90 1.90 1.89 1.89 1.88 1.74 1.74 1.73 1.72 1.71 1.59 1.57 1.54 1.53 1.52 1.51 1.42 1.42 1.42 1.40 1.39
45
^{1}H NMR (400 MHz, $CDCl_3$)
4.82 1.00 1.00 0.97 2.09 2.07 6.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.3
142.0 137.0 128.4 128.1 126.2
73.4
31.6 25.5 23.7
45
^{13}C NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.38
7.37
7.37
7.36
7.36
7.35
7.35
6.37
6.37
5.91
5.91
4.40
4.39
4.37
3.63
3.62
3.60
2.19
2.18
2.16
2.15
2.13
Cl
O
O
46
^{1}H NMR (400 MHz, $CDCl_3$)
4.87
1.00
1.00
2.03
2.08
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

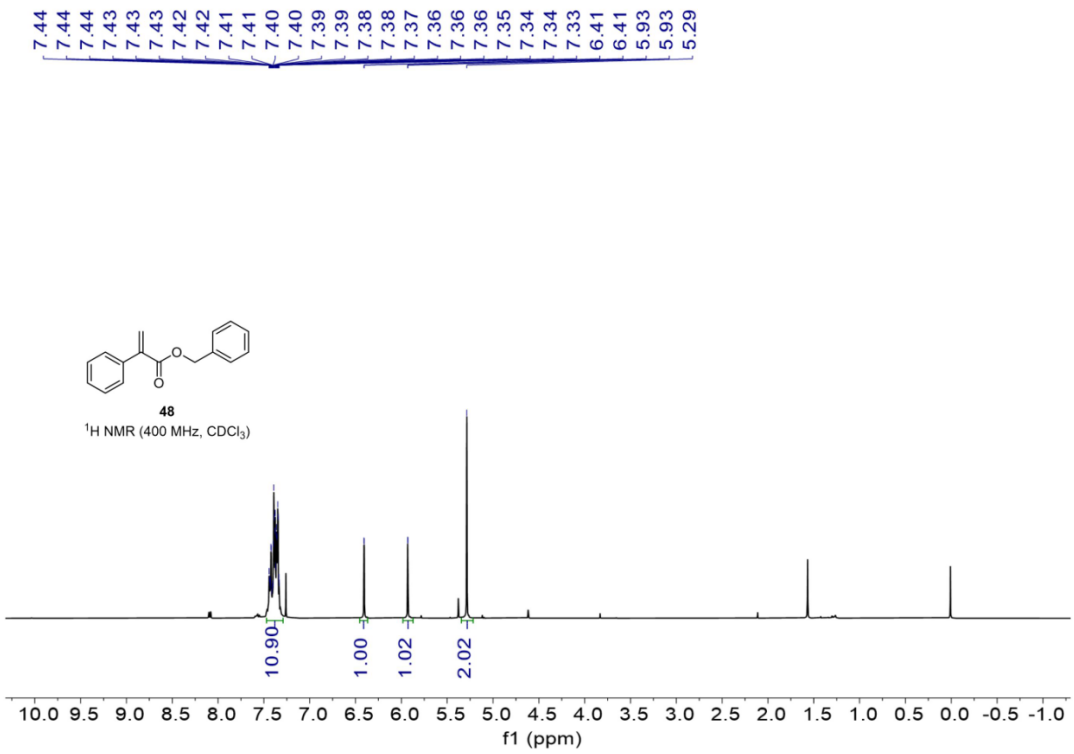

166.6
141.3
136.6
128.3
128.3
128.2
127.1
61.8
41.3
31.6
Cl
O
O
46
^{13}C NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.45
7.45
7.45
7.44
7.44
7.43
7.41
7.41
7.40
7.39
7.39
7.38
6.51
6.50
6.07
6.06
6.06
4.67
4.66
4.65
4.65
4.64
4.64
4.63
4.63
4.62
4.62
4.61
4.60
4.59
47
1H NMR (400 MHz, CDCl3)
4.91
1.00
0.95
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
165.0
139.9
136.0
129.0
128.7
128.5
128.4
127.3
124.5
121.8
119.0
61.4
61.1
60.7
60.3
47
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



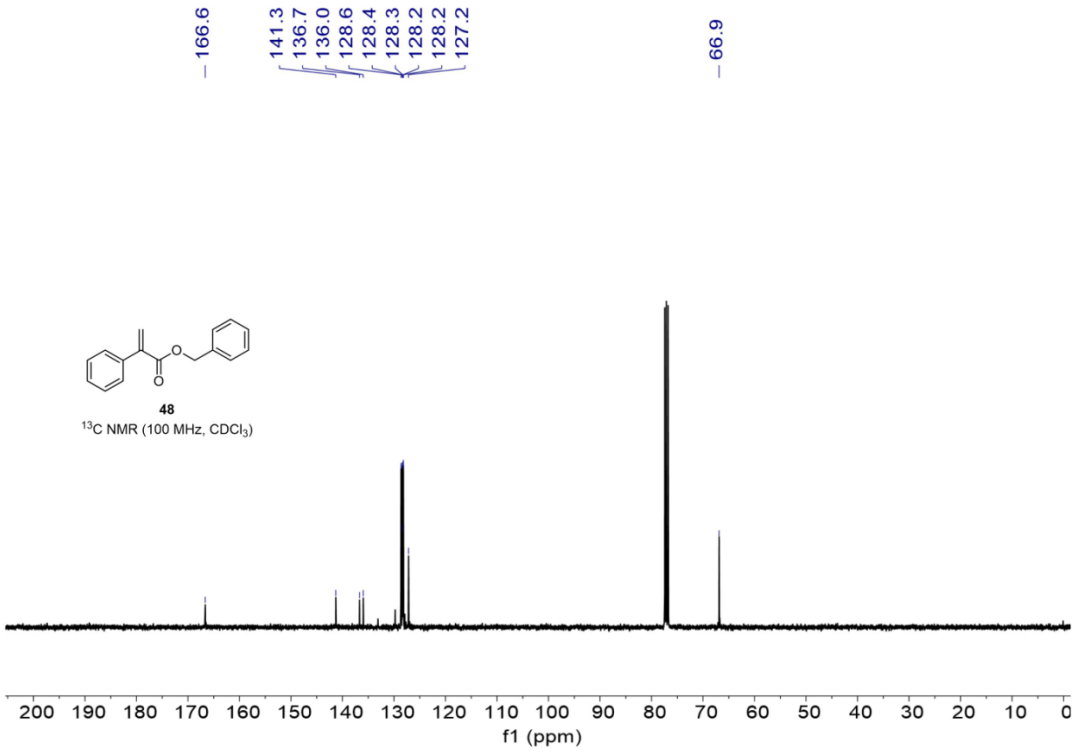
47

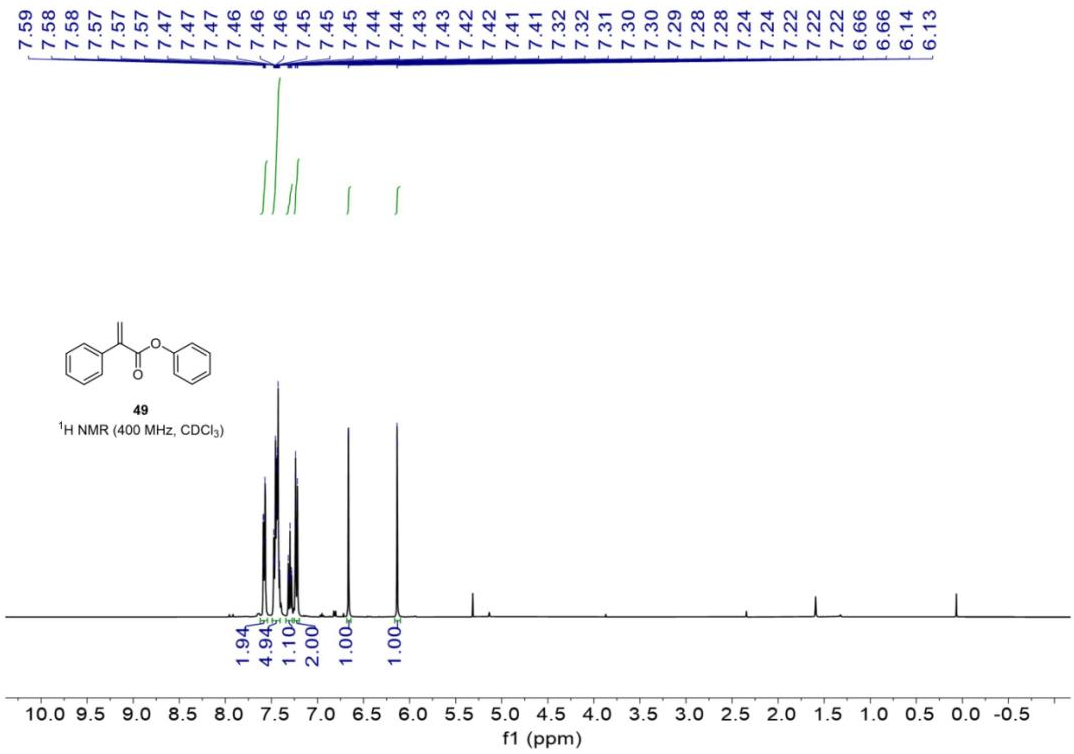
^{19}F NMR (376 MHz, $CDCl_3$)

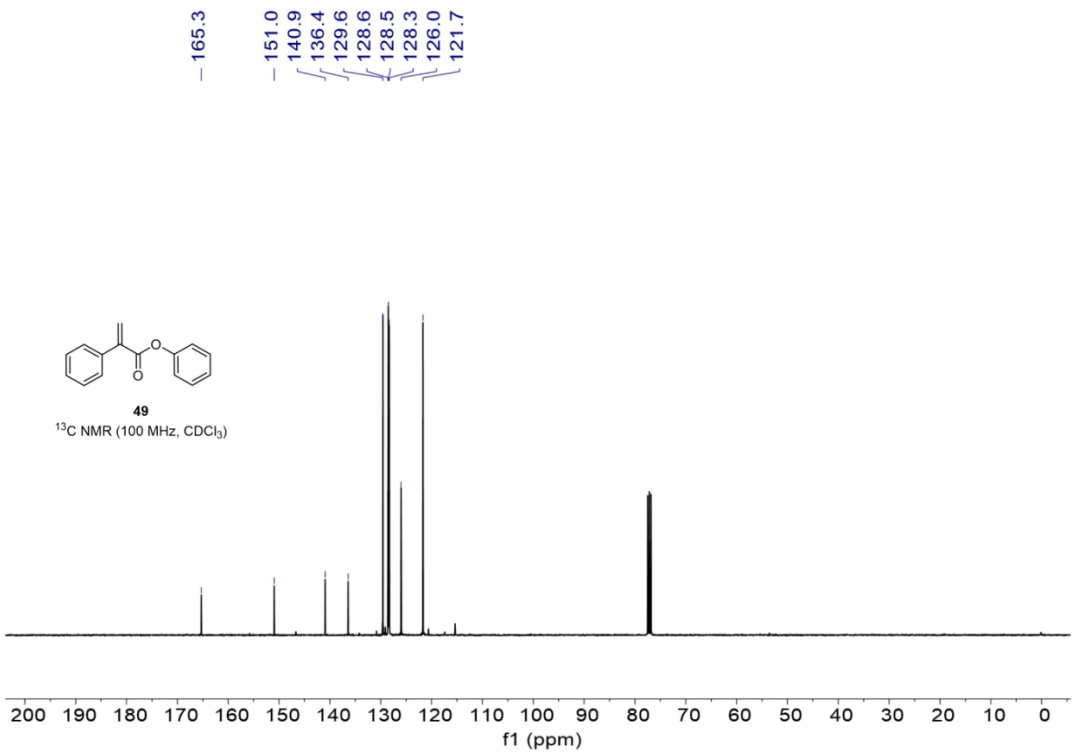


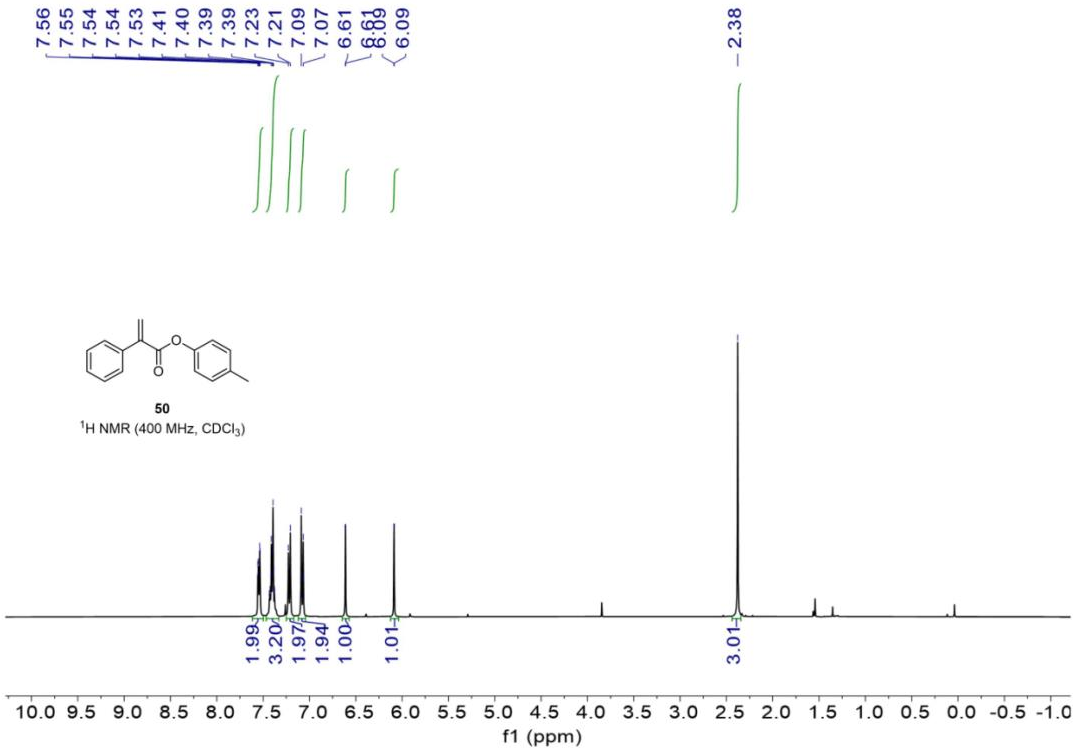
48

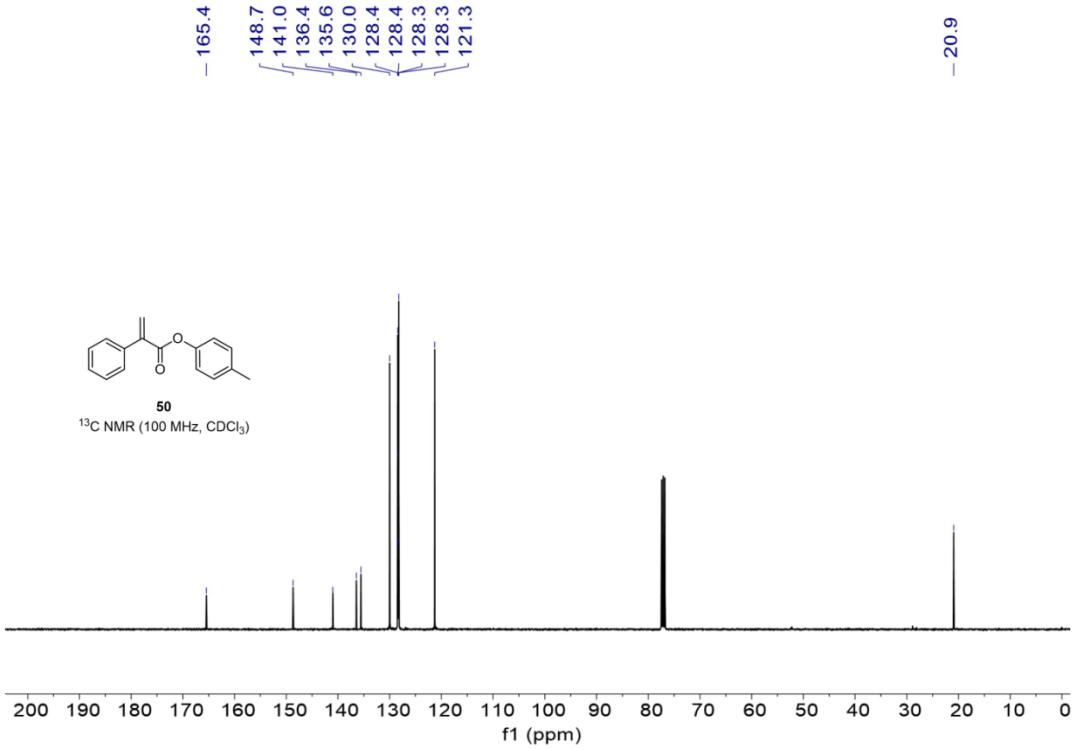
^{1}H NMR (400 MHz, $CDCl_3$)

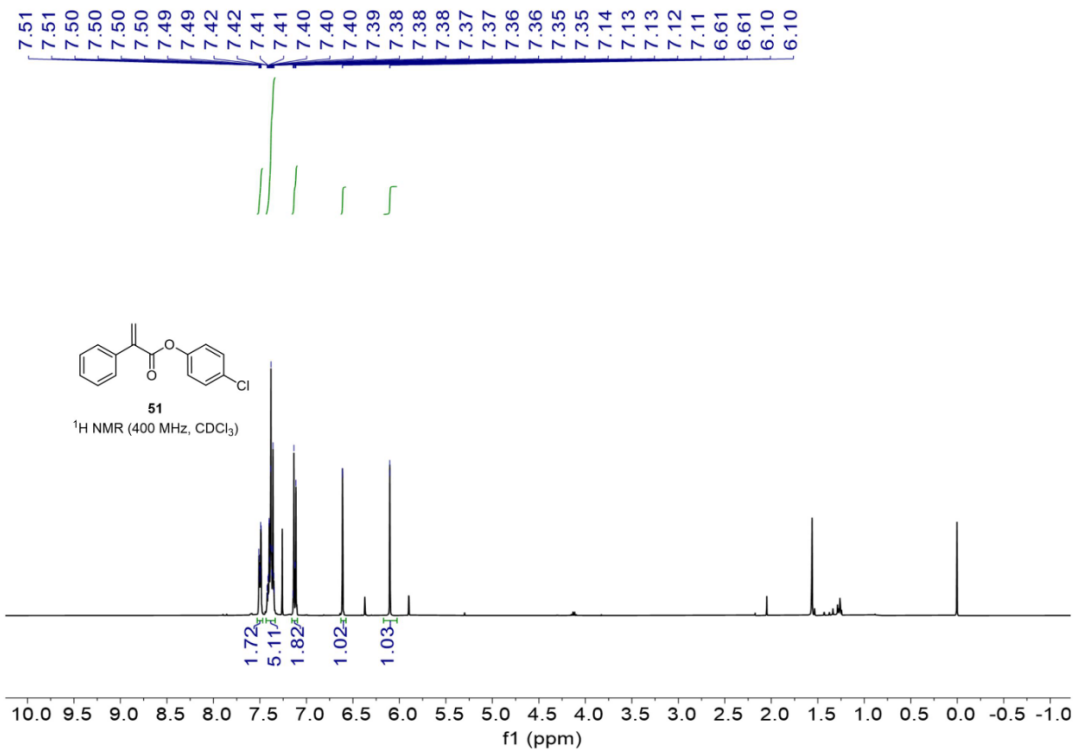

166.6
141.3
136.7
136.0
128.6
128.4
128.3
128.2
128.2
127.2
66.9
48
^{13}C NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

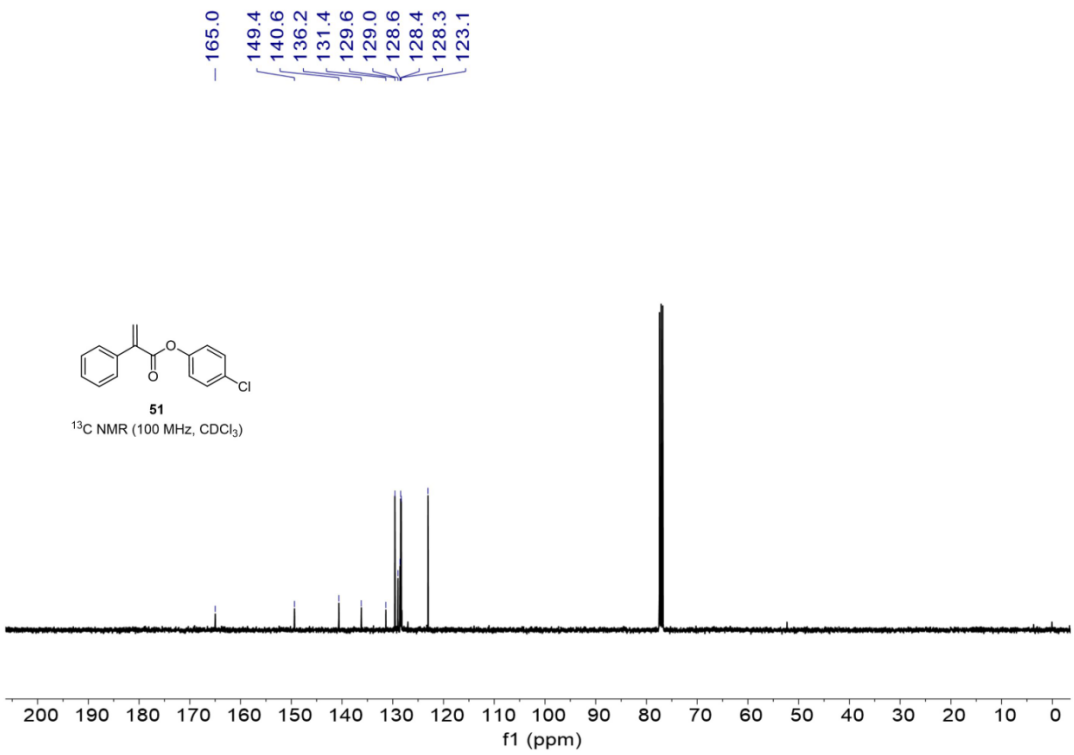

7.59
7.58
7.58
7.57
7.57
7.57
7.47
7.47
7.47
7.46
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.24
7.24
7.22
7.22
7.22
6.66
6.66
6.14
6.13
49
^{1}H NMR (400 MHz, $CDCl_3$)
1.94
4.94
1.10
2.00
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

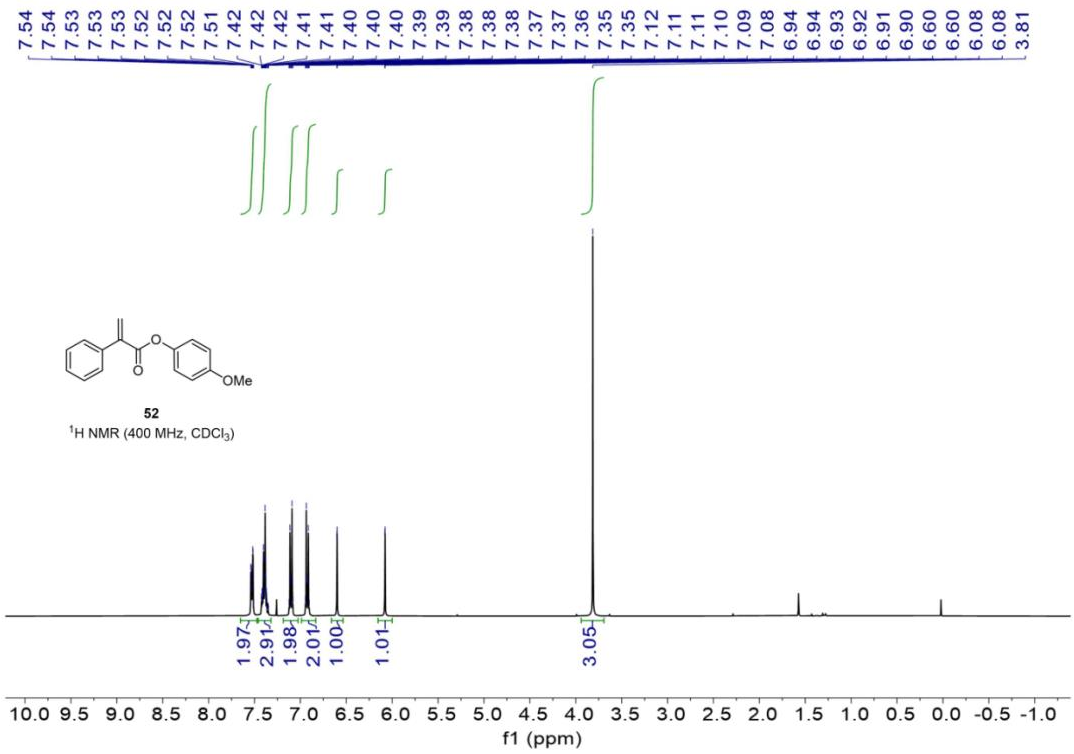

165.3
151.0
140.9
136.4
129.6
128.6
128.5
128.3
126.0
121.7
49
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

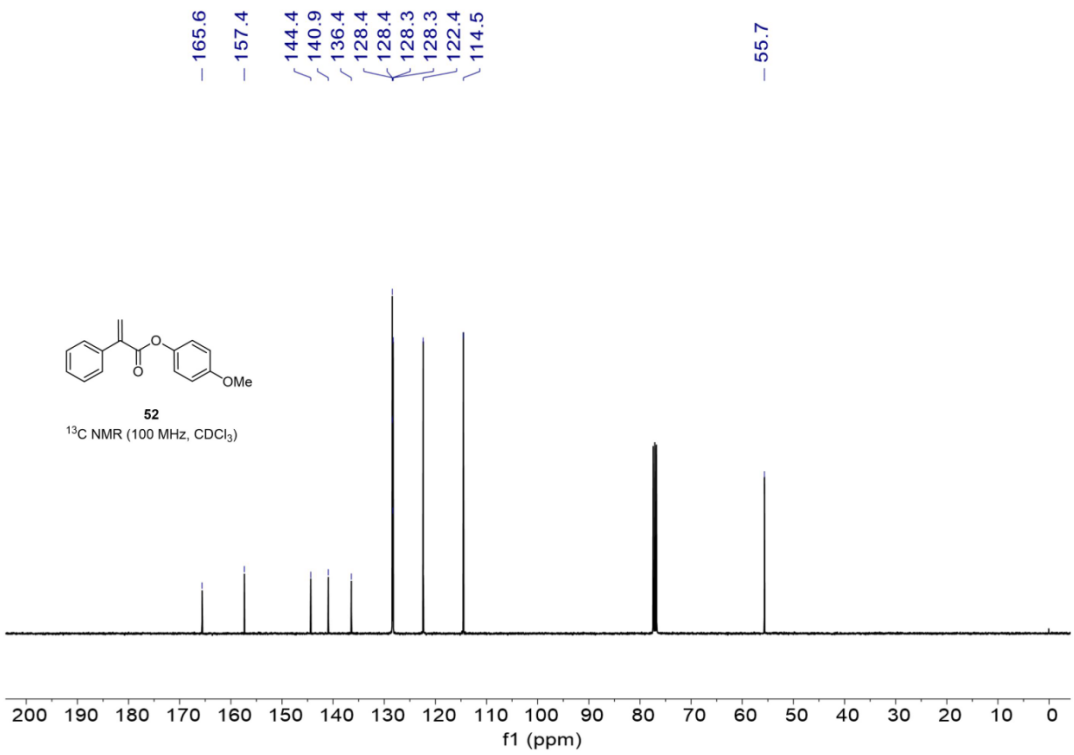

7.56
7.55
7.54
7.54
7.53
7.41
7.40
7.39
7.39
7.23
7.21
7.09
7.07
6.61
6.09
2.38
50
1H NMR (400 MHz, CDCl3)
1.99
3.20
1.97
1.94
1.00
1.01
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


165.4
148.7
141.0
136.4
135.6
130.0
128.4
128.4
128.3
128.3
121.3
20.9
50
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.51
7.51
7.50
7.50
7.50
7.50
7.49
7.49
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.14
7.13
7.13
7.12
7.11
6.61
6.61
6.10
6.10
Cl
51
1H NMR (400 MHz, CDCl3)
1.72
5.11
1.82
1.02
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


165.0
149.4
140.6
136.2
131.4
129.6
129.0
128.6
128.4
128.3
123.1
Cl
51
^{13}C NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.54 7.54 7.53 7.53 7.53 7.52 7.52 7.52 7.51 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.12 7.11 7.11 7.10 7.09 7.08 6.94 6.94 6.93 6.92 6.91 6.90 6.60 6.60 6.08 6.08 3.81
OMe
52
^{1}H NMR (400 MHz, $CDCl_3$)
1.97 2.91 1.98 2.01 1.00 1.01 3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


165.6
157.4
144.4
140.9
136.4
128.4
128.4
128.3
128.3
122.4
114.5
55.7
OMe
O
O
52
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)