Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

Synthesis of Palladium based MOF *via* an effective post-synthetic modification approach and its catalytic activity towards Heck type coupling reactions

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Experimental section:

Materials. All the reagents and solvents for synthesis were purchased from commercial sources and used as supplied without further purification. $Cu(ClO_4)_2 \cdot 6H_2O$, 4-methylpyridine, hydrazine hydrate, dibromomethane, and all the phenylhydrazines were obtained from the Sigma-Aldrich Chemical Co. India. Pypz ligand was obtained by the previously reported method.[1]

Physical Measurements.

Thermogravimetric analysis was recorded on a Perkin-Elmer TGA 4000 instrument in the temperature range of 30‑700 °C under N_2 flow with a heating rate of 10 °C min^{-1}. IR spectrum of the Cu-MOF and Pd-MOF were recorded on a Perkin-Elmer FT-IR Spectrum BX using the KBr pellets in the region 4000-400 cm^{-1}. Elemental analysis was carried out on an Elementar vario Micro Cube Elemental Analyzer. PXRD patterns were measured on a PANalytical EMPYRIAN instrument by using Cu-Kα radiation. XPS has been done with an ESCA Lab spectrometer having Al kα X-ray source (hν = 1486.6 eV) operating at 150 W using a Physical Electronics 04-548 dual Mg/Al anode and in a UHV system with a base pressure of $\leq 5 \times 10{-}9$ Torr. ICP-MS data were obtained with an Agilent 7700x ICP-MS and analyzed using NexION 300X - Perkin Elmer. Samples were diluted in a 5% HNO3 matrix and analyzed with a ^{159}Tb internal standard against a six-point standard curve over the range from 0.1 ppb to 1000 ppb. Data collection was performed in Spectrum Mode with five replicates per sample and 100 sweeps per replicate.

Sorption measurements

Gas adsorption measurements were performed by using BelSorp-max (BEL Japan) automatic volumetric adsorption instrument. All the gases were used ultra-pure research-grade (99.99%). Before every measurement samples were pretreated for 12 h at 423 K under 10^{-2}KPa continuous vacuum using BelPrepvac II and purged with N_2 on cooling.

Single crystal X-ray diffraction

Single crystal data for Cu-MOF was collected on a Bruker APEX II diffractometer equipped with a graphite monochromator and Mo-Kα (λ = 0.71073 Å, 296 K) radiation. Data collections were performed using φ and ω scan. Non-hydrogen atoms are located from the difference Fourier maps, were refined anisotropically by full-matrix least-squares on F^2, using SHELXS-97.[2] All hydrogen atoms were included in the calculated positions and refined isotropically using a riding model. Determinations of the crystal system, orientation matrix, and cell dimensions were performed according to the established procedures. Lorentz polarization and multi-scan absorption correction were applied. All calculations were carried out using SHELXL 97,[3] PLATON 99,[4] and WinGXsystemVer-1.64.[5] Data collection and structure refinement parameters and crystallographic data in Table S4, and selected bond lengths and bond angles for Cu-MOF is given Table S5.

NMR measurements

^{1}H and ^{13}C NMR spectra were recorded on 400 spectrometers with ^{13}C operating frequencies of 100, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent ($CDCl_3$) signal (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Data for ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

Synthesis of Cu-MOF: Pypz (0.1 mmol, 35 mg) and $Cu(ClO_4)_2{\cdot}6H_2O$ (0.1 mmol, 37 mg) were dissolved separately in 10 mL of methanol and H_2O solution, respectively. Three milliliters of the pypz solution was slowly and carefully layered above 3 mL of metal solution in a narrow glass tube using 2 mL of buffer (1:1 H_2O and MeOH) solution. Blue color block-shaped single crystals were obtained from the junction of the layers after one month. The crystals were separated and washed with MeOH and air-dried (yield: 55%). Elemental analysis: Anal. Calcd. For C42H44Cl2CuN12O8 (%): C, 51.5; H, 4.5; N, 17.1 Found (%): C, 52.1; H, 4.1; N, 15.8

Synthesis of Pd-MOF: Crystals or powder of Cu-MOF (30 mg) were immersed in 5 mL of diethyl formamide (DEF) solution of $[Pd(CH_3CN)_2Cl_2]$ (20 mg) and the mixture was slowly stirred at room temperature for 12 h under N_2 atmospere. Anal. Calcd. For $[Pd_2(pypz)_4(Cl)_2]_nCl_2{\cdot}2n(DEF)$; C94H110Cl4Pd2N26O2 (%): C, 56.7; H, 5.5; N, 18.2, Found (%): C, 57.9; H, 5.3; N, 18.5

General Procedure for Pd-MOF catalyzed C-C bond formation of arylhydrazines with olefins: A 10 mL round bottomed flask equipped with a magnetic stirring bar was charged with arylhydrazine (0.1 mmol), **Pd-MOF** (3 mol %), *tert*-butyl acrylate (0.15 mmol) and 0.1M HCl (0.2 mmol) an in MeOH (2 mL). The flask was stirred at 60 ^{o}C in the air for 8-12 h and judged by TLC. The reaction mixture was cooled to room temperature, the solvent was removed under the reduced pressure, and the residue was purified through column chromatography on silica gel.

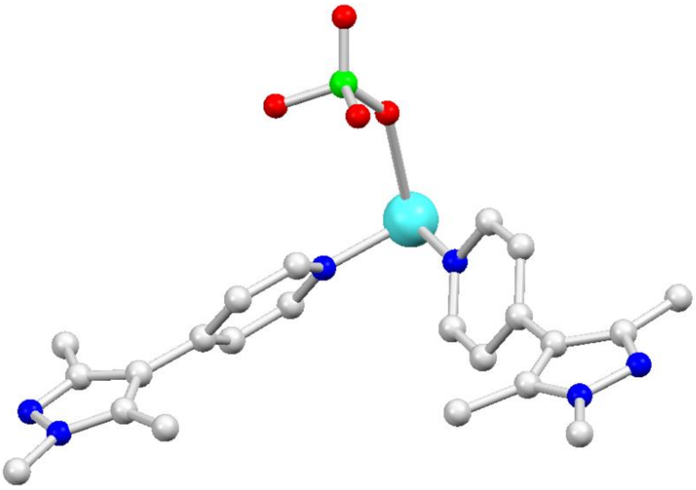


Figure S1. The asymmetric unit of Cu-MOF. Color code: carbon (gray), nitrogen (blue), oxygen (red), chlorine (green) and Copper (cyan). (Hydrogen atoms and water molecules are omitted for clarity). (The structure was proposed by Mercury software using CIF file).

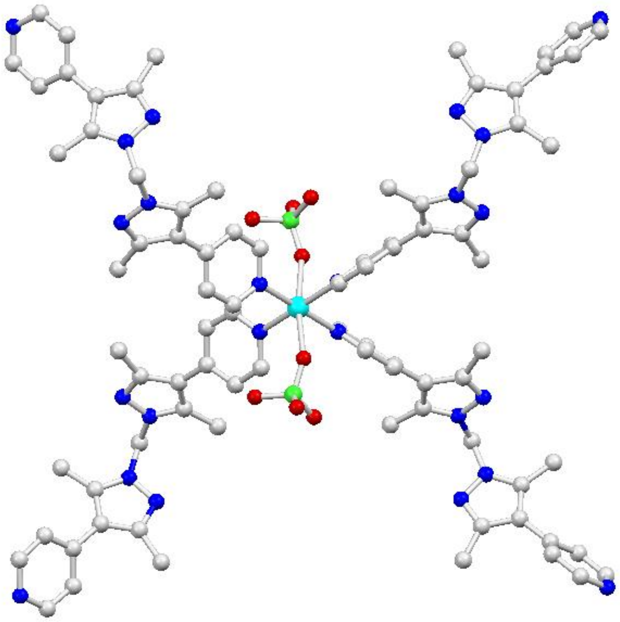


Figure S2. The coordination environment around Cu ion in Cu-MOF. (The structure was proposed by Mercury software using CIF file).

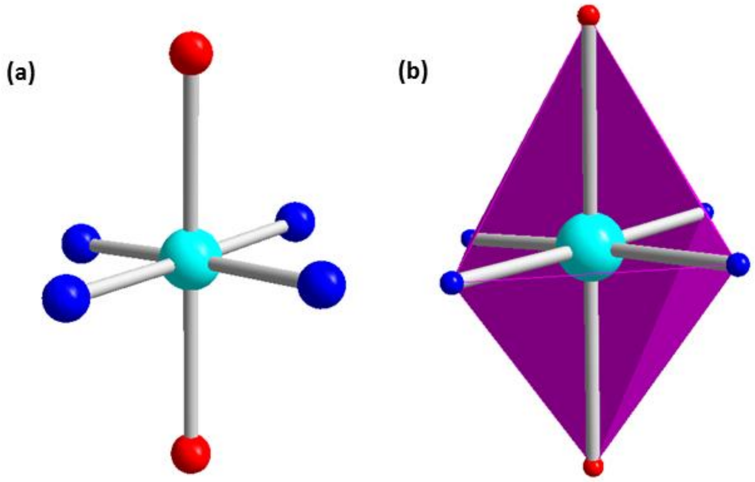


Figure S3. (a) Distorted octahedral geometry around the Cu ions in Cu-MOF (b) its polyhedral view of Cu-MOF. (The structure was proposed by Diamond software using CIF file).

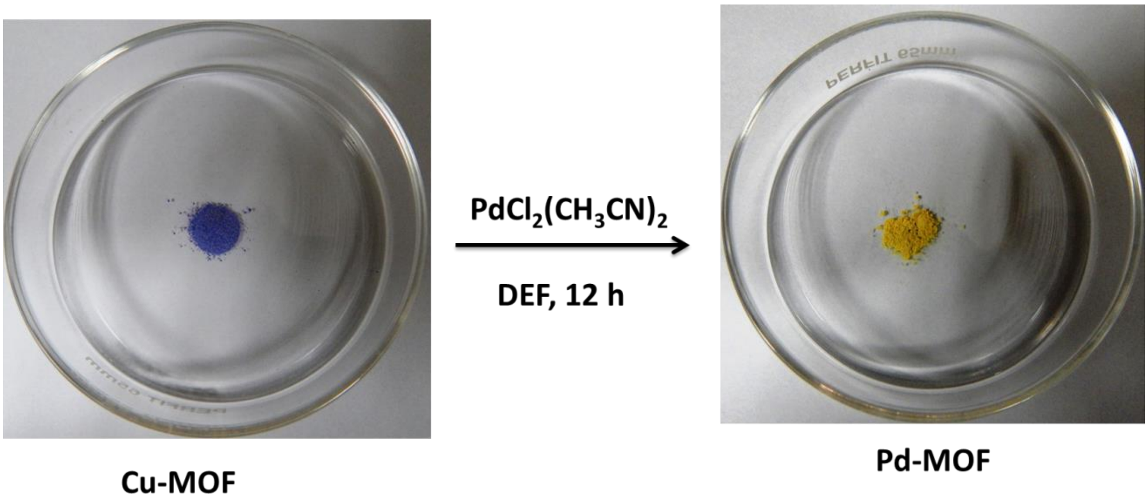


Figure S4. Photographs were taken before and after Palladium loading.

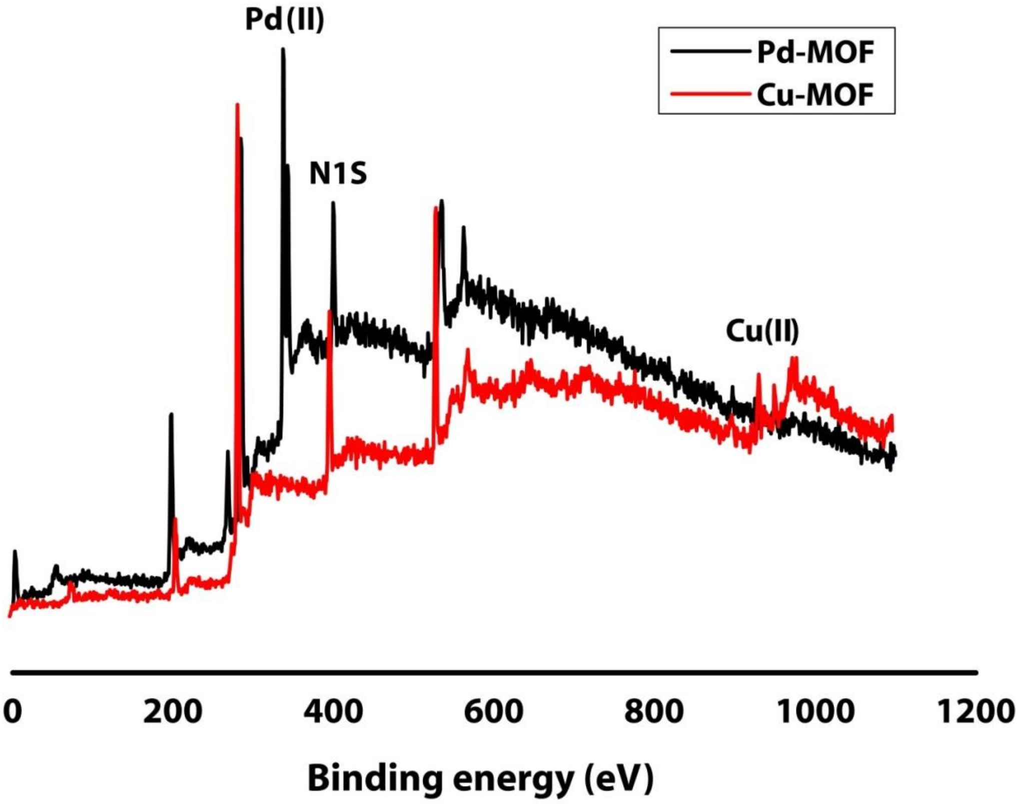


Figure S5. A complete survey of XPS spectrum of Cu-MOF and **Pd-MOF**.

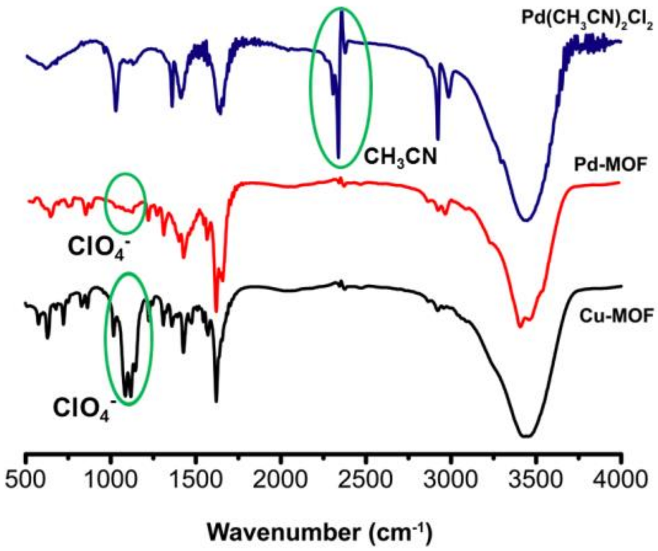


Figure S6. FTIR spectra of Cu-MOF and **Pd-MOF**. The band for perchlorate anion in the corresponding compounds is shown by circles.

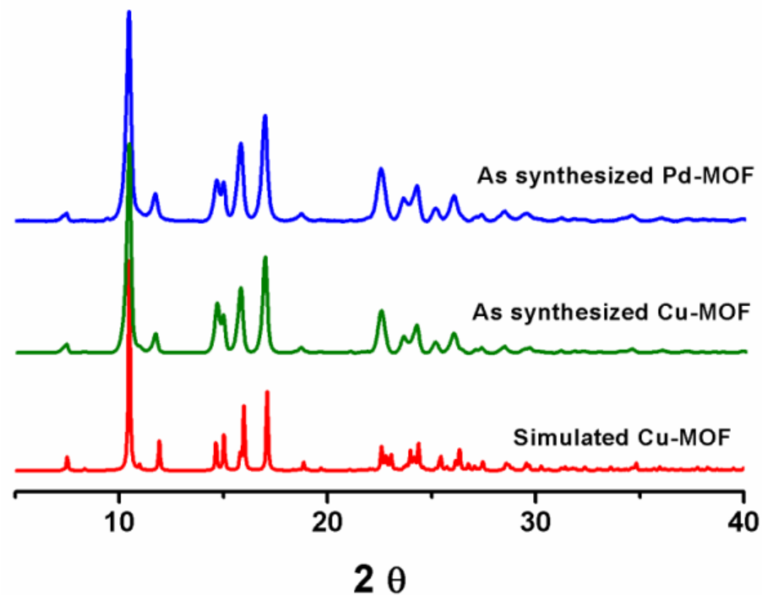


Figure S7. PXRD patterns of Cu-MOF and **Pd-MOF**.

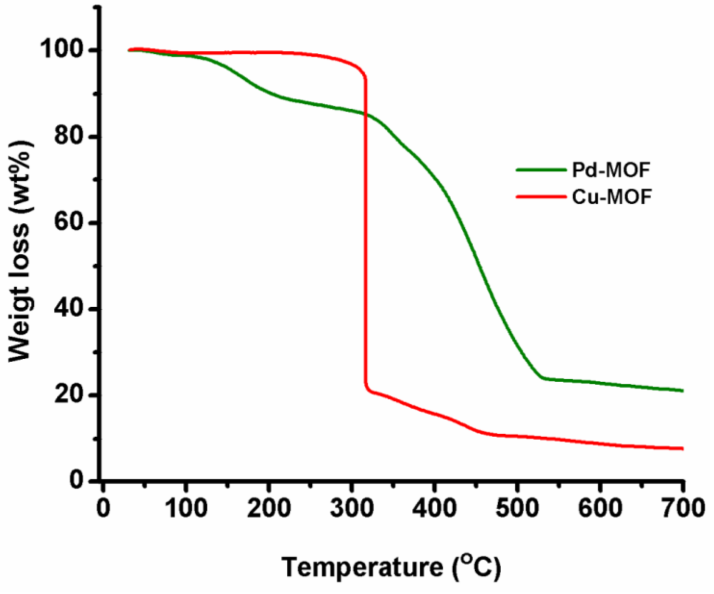


Figure S8. TG Analysis of Cu-MOF and **Pd-MOF**.

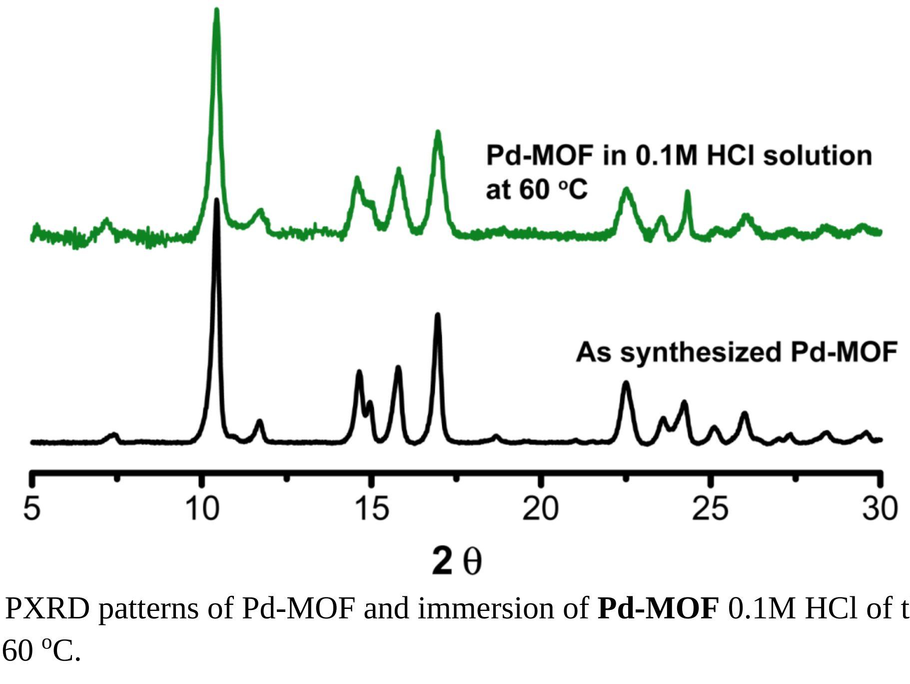


Figure S9. PXRD patterns of Pd-MOF and immersion of **Pd-MOF** 0.1M HCl of the MeOH solution at 60 °C.

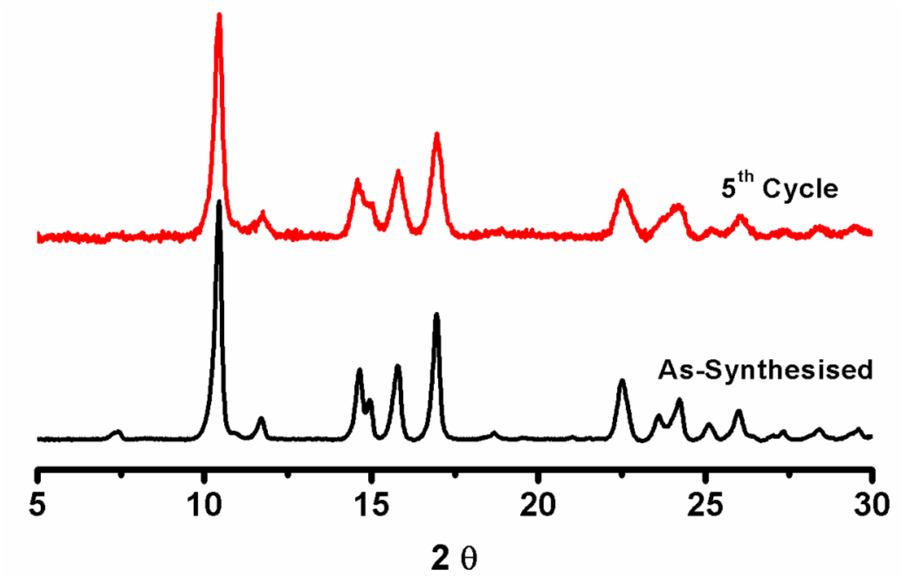


Figure S10. PXRD patterns of the fresh and reused catalyst of **Pd-MOF**.

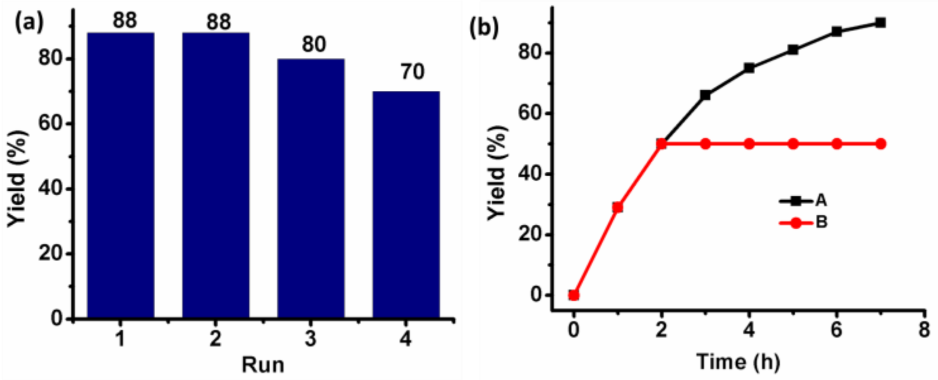


Figure S11. (a) The kinetic profiles in four consecutive reaction cycles employing **Pd-MOF** as the catalyst. (b) The leaching test (filtration test) indicated no contribution from the homogeneous catalysis of the active species (A) in the presence of **Pd-MOF**. (B) The catalyst filtration (after 2 hours).

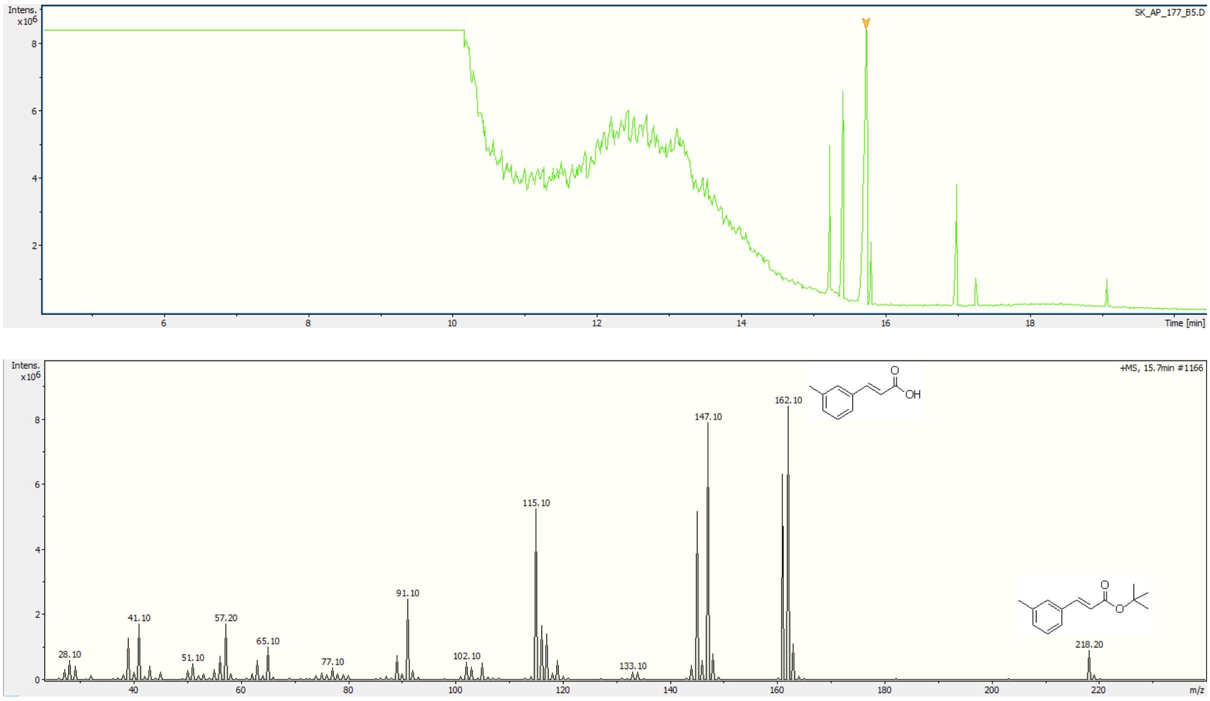


Figure S12. GC-MS plot for the catalysis reaction taking m-tolylphenylhydrazine as the substrate (entry 3, Table 1, main text).

Table S1. Solvent screening by using **Pd-MOF** as catalyst and phenylhydrazine and *tert*-butyl acrylate as a model substrates.

Entry	**Solvent**	**Time(hrs)**	**Yield**
1	EtOH	8	65
2	CH_2Cl_2	8	60
3	Toluene	8	65
4	DMSO	8	12
5	DMF	8	10
6	THF	8	15
7	MeOH	8	88

Table S2. Screening test on catalyst loading.

Entry	Amount of catalst	Solvent	Time	Yield
1	1 mol%	MeOH	8	40
2	2 mol%	MeOH	8	65
3	3 mol%	MeOH	8	88
4	4 mol%	MeOH	8	88
5	5 mol%	MeOH	8	88

Table S3 Crystallographic data for Cu-MOF.

CCDC	1479570
Formula	C42H44Cl2CuN12O8
weight (g/mol)	979.34
Crystal shape	Block
Colour	Blue
Size	0.46×0.34×0.25
Crystal system	Orthorhombic
Space group	*P cca*
Cell length a (Å)	23.562(3)
Cell length b (Å)	24.173(4)
Cell length c (Å)	8.2570(11)
Cell angle alpha (°)	90
Cell angle beta (°)	90
Cell angle gamma (°)	90
Cell volume V ($Å^3$)	4702.9(12)
Cell formula units Z	4
Temperature (K)	140
λ (Mo Kα) (Å)	0.71073
μ (mm^{-1})	0.641
Dc ($g\ cm^{-3}$)	1.383
crystal_F_000	2028.0
Measured reflections	4174
Unique reflections	3232
$R_1[I>2\sigma(I)]$[a]	0.0674
$R_w[I>2\sigma(I)]$[b]	25.065

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o$, [b] $R_w=[\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$

Table S4. Selected bond angles and bond length of Cu-MOF.

Bond length		**Bond angles**	
Cu1-N5	2.012(4)	N5-Cu1-N15	89.4(14)
Cu1-N15	2.027(4)	N5-Cu1-O2	96.7
Cu1-O2	2.524	N5-Cu1-O2	88.5
		N5-Cu1-N5	92.0(2)
		N5-Cu1-N15	177.5(16)
		N5-Cu1-O2	89.3
		N15-Cu1-O2	85.4
		N15-Cu-N15	89.2(2)
		O2-Cu1-O2	172.6
		O2-Cu1-N5	96.7

The symmetry employed for this shelxl refinement

_space_group_symop_operation_xyz

'x, y, z'

'-x+1/2, -y, z'

'x+1/2, -y, -z+1/2'

'-x, y, -z+1/2'

'-x, -y, -z'

'x-1/2, y, -z'

'-x-1/2, y, z-1/2'

'x, -y, z-1/2'

Table S5. Atomic coordinates and equivalent isotropic displacement parameters (A^2) for Cu-MOF.

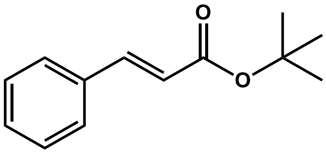
Atom	**x**	**y**	**z**	**U$_{iso}$**	**Occupancy**
Cu1	0.0000	0.25959(3)	0.25	0.0237(2)	1
Cl3	0.11698(8)	0.26906(8)	0.9451(2)	0.0607(5)	1
O1	0.1584(3)	0.2382(5)	1.0295(13)	0.200(5)	1
O2	0.06463(17)	0.25281(17)	1.0070(7)	0.0616(13)	1
O3	0.1271(3)	0.2645(3)	0.7877(7)	0.112(3)	1
O4	0.1234(3)	0.3266(2)	0.9951(8)	0.094(2)	1
N1	0.20179(14)	0.48368(14)	0.7769(4)	0.0183(8)	1
N2	0.16745(15)	0.52434(14)	0.7183(4)	0.0205(8)	1
N5	0.04502(15)	0.31741(14)	0.3692(5)	0.0244(8)	1
N11	0.17022(14)	-0.01765(14)	0.6362(4)	0.0190(8)	1
N12	0.20356(14)	0.02023(14)	0.7131(4)	0.0189(8)	1
N15	0.04628(15)	0.19989(14)	0.3608(5)	0.0230(8)	1
C1	0.10179(18)	0.31650(17)	0.3723(5)	0.0222(9)	1
H1	0.1207	0.2887	0.3161	0.027	1
C2	0.13328(18)	0.35512(17)	0.4553(5)	0.0222(9)	1
H2	0.1727	0.3529	0.454	0.027	1
C3	0.10708(18)	0.39744(17)	0.5410(5)	0.0201(9)	1
C4	0.01915(19)	0.35774(18)	0.4514(6)	0.0296(11)	1
H4	-0.0203	0.3591	0.4505	0.035	1
C5	0.13948(17)	0.44008(17)	0.6284(5)	0.0186(9)	1
C6	0.18721(17)	0.43238(17)	0.7239(5)	0.0183(9)	1
C7	0.12904(16)	0.49784(18)	0.6299(5)	0.0196(9)	1
C8	0.25	0.5	0.8742(7)	0.0212(13)	1
H8A	0.2609	0.4694	0.9434	0.025	0.5
H8B	0.2391	0.5306	0.9434	0.025	0.5
C16	0.08339(19)	0.53000(18)	0.5470(6)	0.0272(10)	1
H16A	0.0493	0.5286	0.6105	0.041	1
H16B	0.0763	0.5143	0.4421	0.041	1
H16C	0.0952	0.5678	0.535	0.041	1
C17	0.21910(19)	0.38176(18)	0.7721(6)	0.0273(10)	1
H17A	0.2564	0.3828	0.7254	0.041	1
H17B	0.1993	0.3496	0.7339	0.041	1
H17C	0.2221	0.3803	0.888	0.041	1
C31	0.18820(18)	0.07328(18)	0.6811(5)	0.0224(10)	1
C32	0.14219(18)	0.06979(17)	0.5775(5)	0.0206(9)	1
C33	0.13274(17)	0.01245(17)	0.5532(5)	0.0195(9)	1
C34	0.08560(19)	-0.01587(19)	0.4642(6)	0.0278(11)	1
H34A	0.0974	-0.0525	0.4341	0.042	1
H34B	0.0764	0.0048	0.3685	0.042	1
H34C	0.0528	-0.0181	0.5328	0.042	1
C39	0.10947(18)	0.11554(17)	0.5049(6)	0.0222(9)	1
C40	0.1013(2)	0.11760(19)	0.3382(6)	0.0273(10)	1
H40	0.1171	0.0905	0.2721	0.033	1
C41	0.08546(19)	0.15770(19)	0.5963(6)	0.0278(10)	1

H41	0.0902	0.1583	0.7081	0.033	1
C42	0.05455(19)	0.19855(18)	0.5208(6)	0.0266(10)	1
H42	0.0387	0.2264	0.5839	0.032	1
C43	0.25	0	0.8110(7)	0.0219(13)	1
H43A	0.2364	-0.0296	0.8801	0.026	0.5
H43B	0.2636	0.0296	0.8801	0.026	0.5
C49	0.0700(2)	0.15966(18)	0.2713(6)	0.0274(10)	1
H49	0.065	0.1603	0.1596	0.033	1
C70	0.04821(18)	0.39744(18)	0.5374(6)	0.0256(10)	1
H70	0.0282	0.4245	0.5935	0.031	1
C76	0.2186(2)	0.12229(19)	0.7496(7)	0.0350(12)	1
H76A	0.2135	0.1232	0.8649	0.052	1
H76B	0.2036	0.1555	0.7027	0.052	1
H76C	0.2584	0.1196	0.7251	0.052	1

NMR data of Biaryl Products.

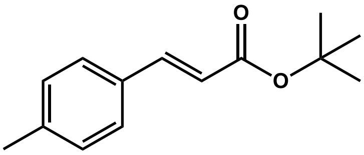
All the products are known compounds and have identical spectroscopic data as that reported.[6]

1. ***tert*-Butyl cinnamate**



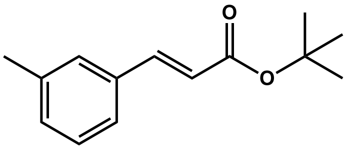
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, 1H), 7.51 (dd, 2H), 7.37– 7.36 (m, 3H), 6.37 (d, 1H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): d 166.3, 143.5, 134.7, 130.0, 128.8, 128.0, 120.2, 80.5, 28.2 ppm.

2. **(*E*)-*tert*-Butyl 3-*p*-tolylacrylate**



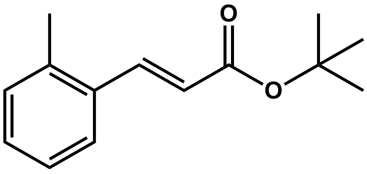
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 1H), 7.40 (d, 2H), 7.17 (d, 2H), 6.32 (d, 1H), 2.36 (s, 3H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): d 166.5, 143.6, 140.3, 132.0, 129.6, 128.0, 119.1, 80.3, 28.2, 21.4 ppm.

3. **(*E*)-*tert*-Butyl 3-*m*-tolylacrylate**



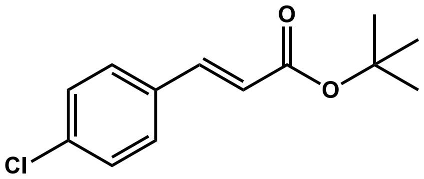
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 1H), 7.31 (d, 2H), 7.25 (d, 1H), 7.17 (d, 1H), 6.35 (d, 1H), 2.36 (s, 3H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): d 166.4, 143.7, 138.4, 134.6, 130.8, 128.7, 128.6, 125.2, 120.0, 80.4, 28.2, 21.3 ppm.

4. **(*E*)-*tert*-Butyl 3-*o*-tolylacrylate**



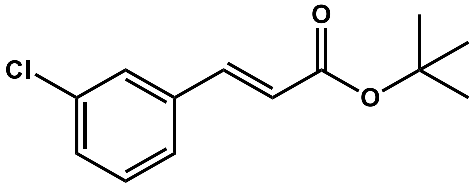
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, 1H), 7.31– 7.15 (m, 4H), 6.29 (d, 1H), 2.43 (s, 3H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): d 166.5, 141.3, 137.5, 133.6, 130.7, 129.7, 126.4, 126.3, 121.1, 80.5, 28.2, 19.8 ppm.

5. (*E*)-*tert*-Butyl 3-(4-chlorophenyl)acrylate



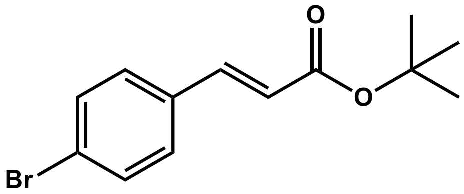
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 1H), 7.31 (d, 2H), 7.25 (d, 1H), 7.17 (d, 1H), 6.35 (d, 1H), 2.36 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): d 166.0, 142.1, 135.8, 133.2, 129.1, 120.8, 80.7, 28.2 ppm.

6. (*E*)-*tert*-Butyl 3-(3-chlorophenyl)acrylate



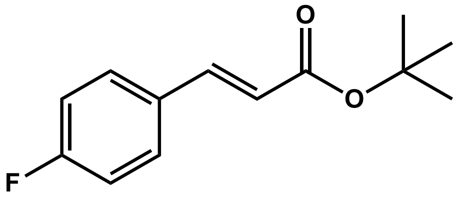
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, 2H), 7.37 (d, 1H), 7.35 – 7.28 (m, 2H), 6.36 (d, 1H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): d 166.0, 142.1, 135.8, 133.2, 129.1, 120.8, 80.7, 28.2 ppm.

7. (*E*)-*tert*-Butyl 3-(4-bromophenyl)acrylate



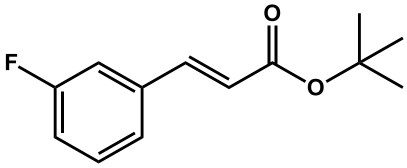
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, 1H), 7.49 (s, 2H), 7.36 (d, 2H), 6.35 (d, 1H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): d 166.0, 142.1, 133.6, 132.1, 129.3, 124.1, 120.9, 80.7, 28.2 ppm.

8. (*E*)-*tert*-Butyl 3-(4-fluorophenyl)acrylate



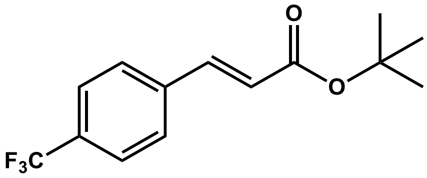
Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 3H), 7.06 (m, 2H), 6.29 (d, 1H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): d 166.2, 163.6 142.2, 130.9 129.8 120.0 115.9 80.6, 28.2 ppm.

9. (*E*)-*tert*-Butyl 3-(4-fluorophenyl)acrylate



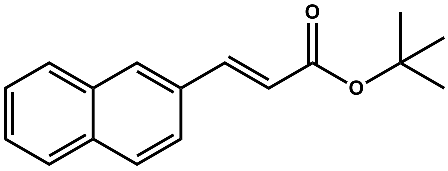
Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, 1H), 7.34 (d, 1H), 7.22 – 7.15 (m, 2H),7.07 (d, 1H) 6.33 (d, 1H), 1.53 (s, 9H). 13C NMR (100 MHz, CDCl3): d 165.0, 143.1,142, 136.8, 130.2, 127.1, 121.8, 80.7, 28.2 ppm.

10. (*E*)-*tert*-buty(E)-tert-butyl 3-(4-(trifluoromethyl)phenyl)acrylate



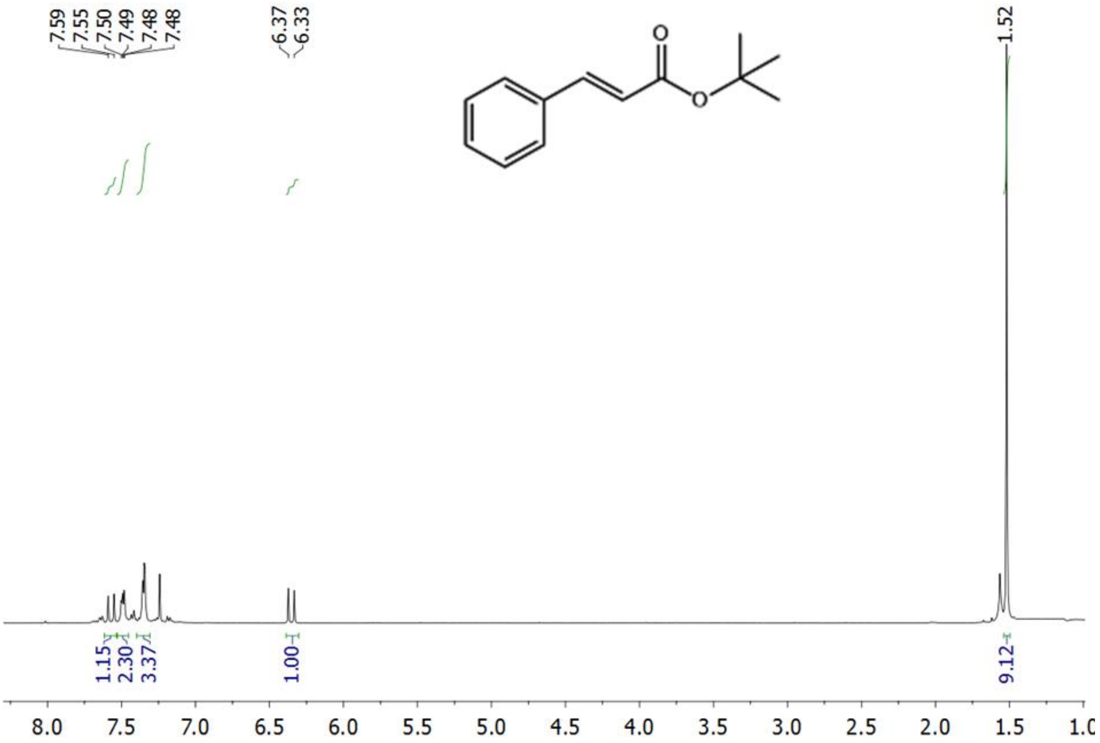
Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): d 7.57-7.63(m, 4H, ArH), 7.59 (d, 1H, CH), 6.43 (d, 1H, CH), 1.54 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz,$CDCl_3$): d 165.7, 141.6, 138.1, 131.5, 128.0, 125.8,123.9, 122.8, 81.0, 28.1 ppm.

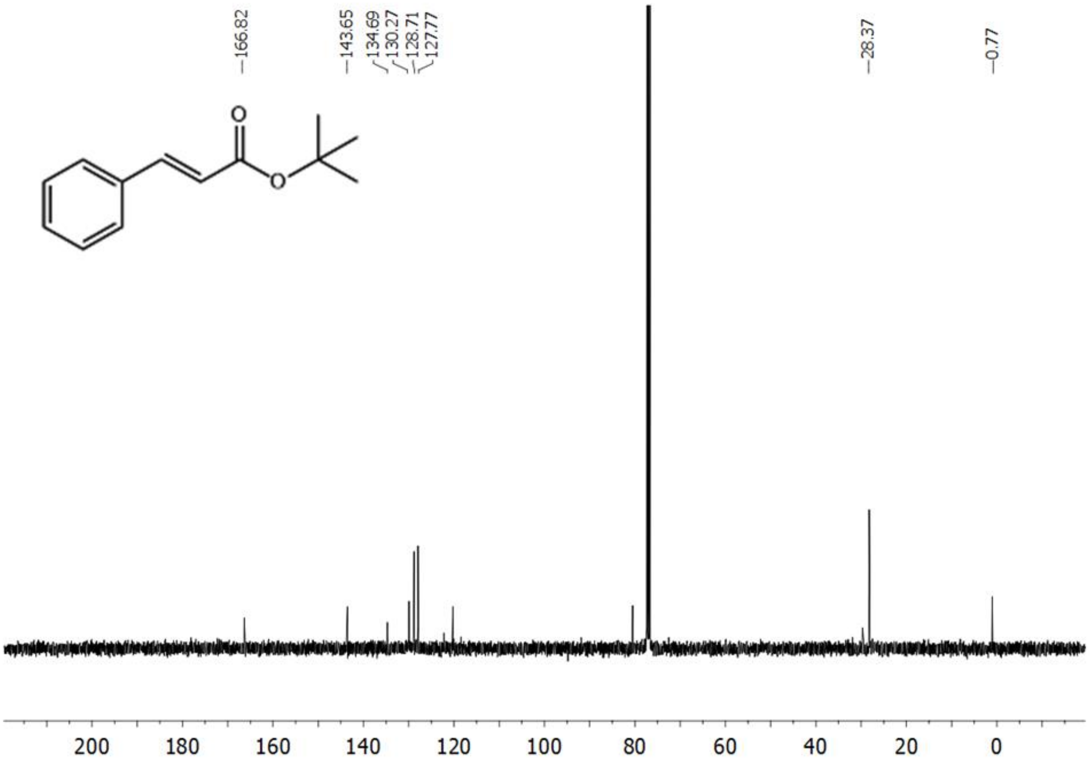
11. (E)-tert-butyl 3-(naphthalen-2-yl)acrylate[2]



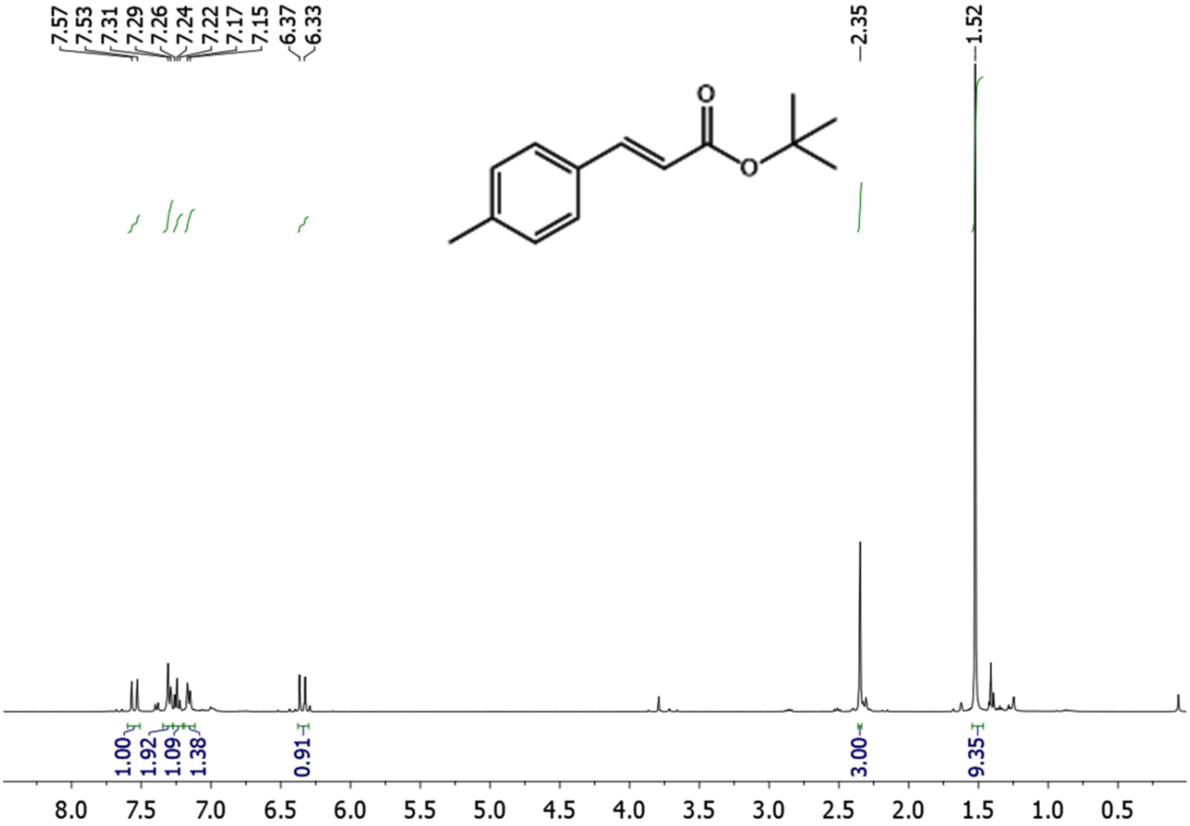
Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): 7.93 (d, J = 19.2 Hz, 1 H), 7.91 (s, 1 H), 7.83–7.86 (m, 1 H), 7.80–7.82 (m, 2 H), 7.77– 7.79 (m, 3 H), 6.59 (d, J = 16.0 Hz, 1 H), 1.46 (s, 9 H). ^{13}C NMR (100 MHz, CDCl3): δ = 166.2, 146.7, 134.9, 133.8, 132.6, 129.7, 128.8, 128.4, 128.4, 126.9, 126.4, 124.3, 121.4, 81.7, 28.4.

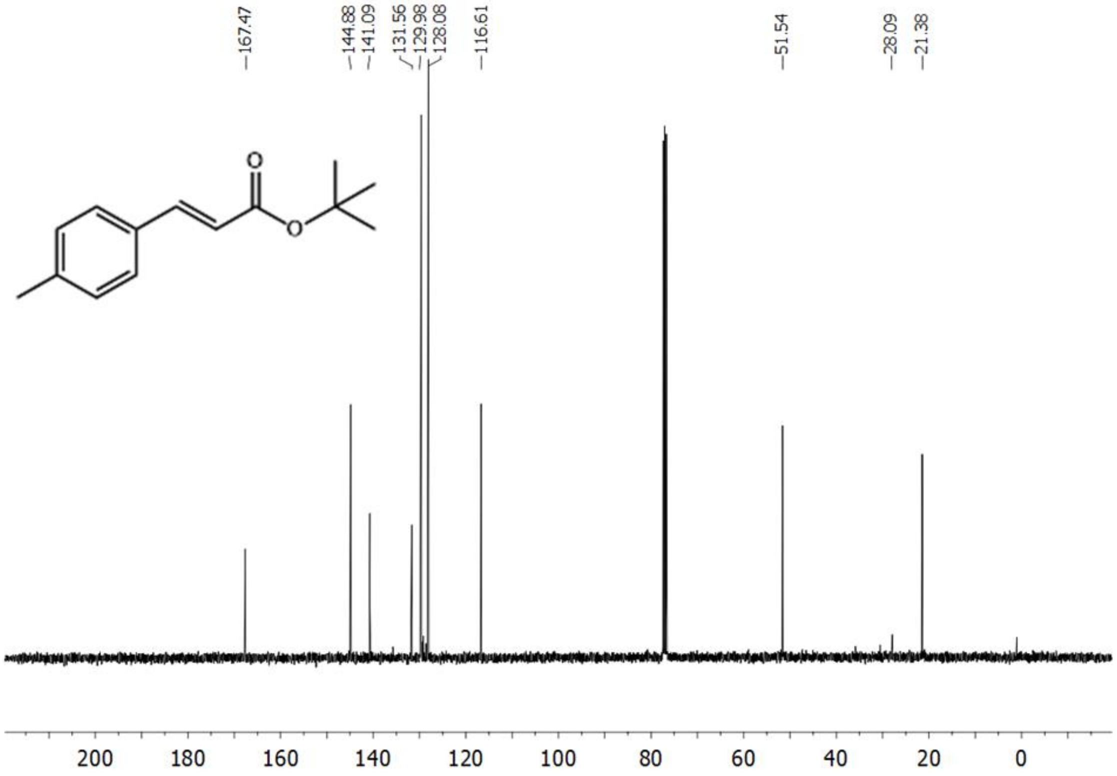
1. *tert*-Butyl cinnamate



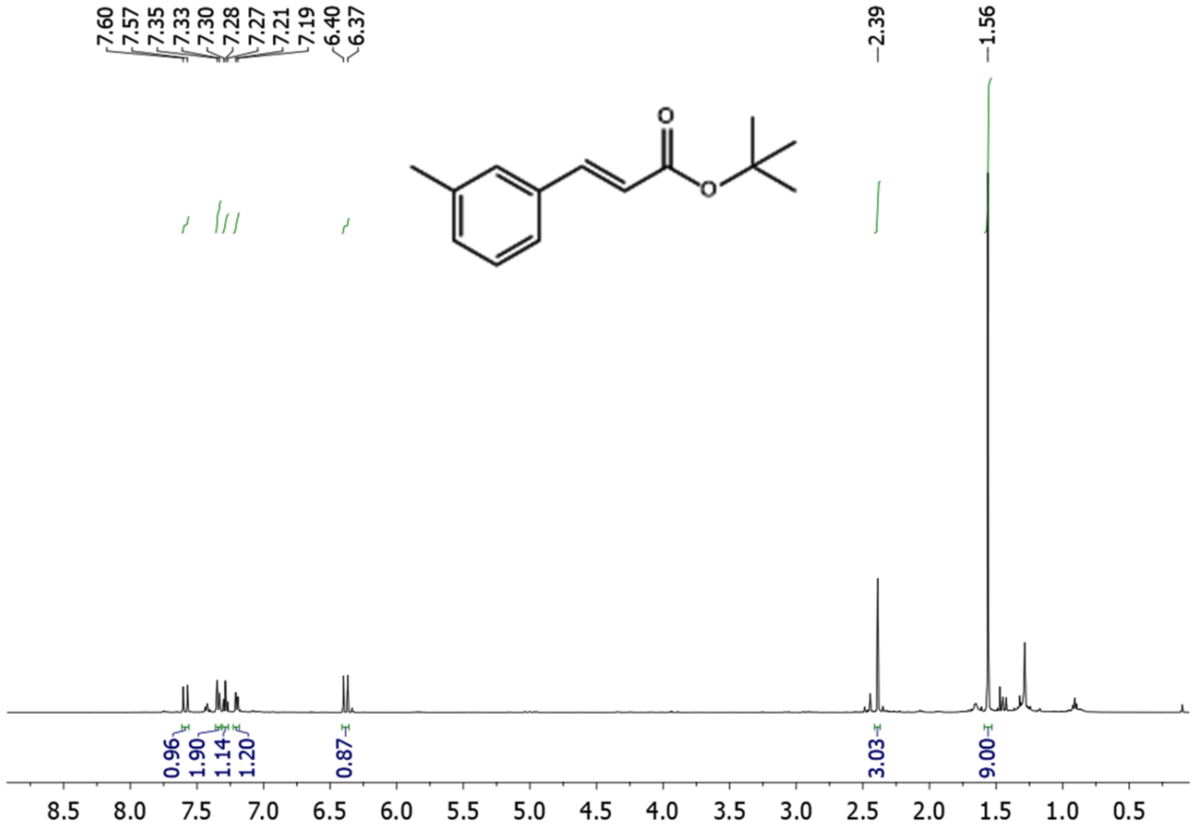


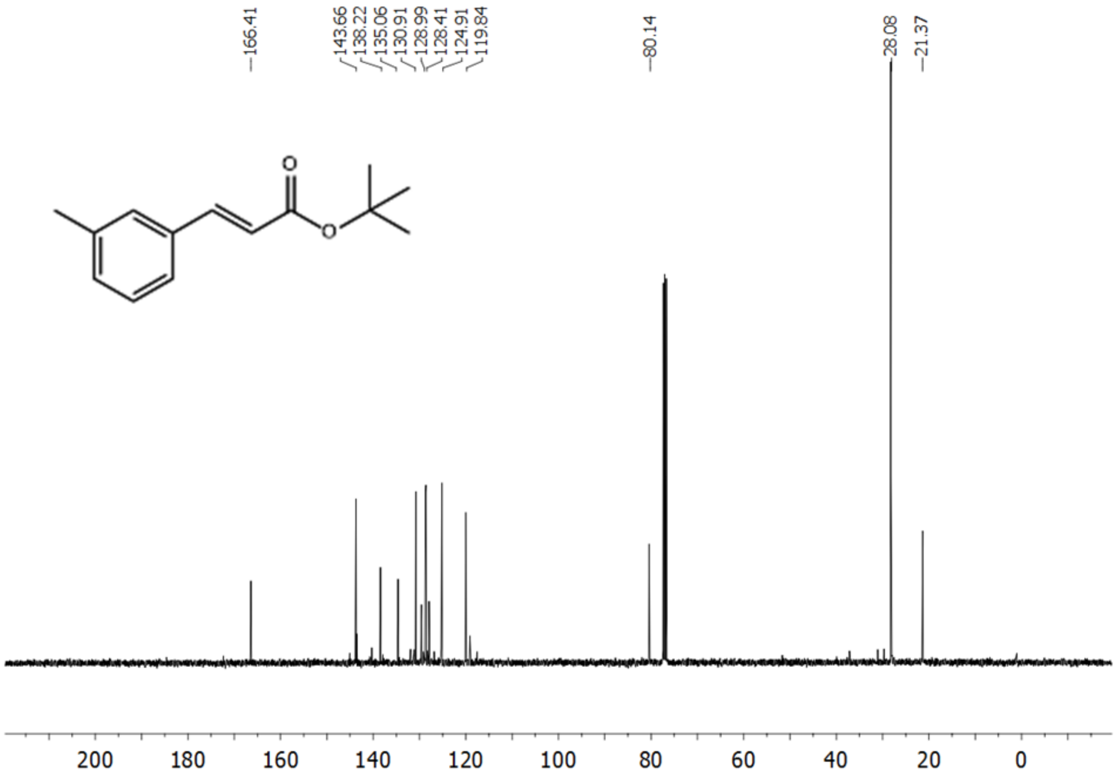
2. (*E*)-*tert*-Butyl 3-*p*-tolylacrylate



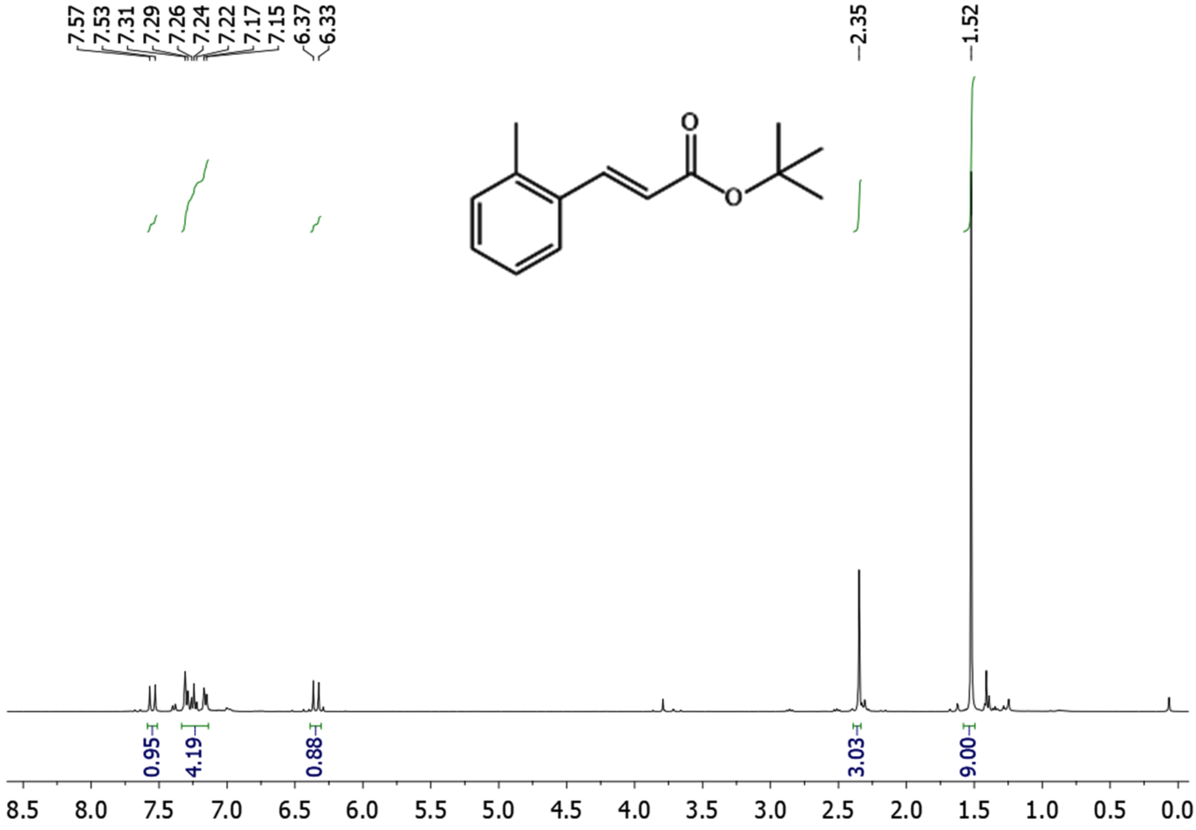


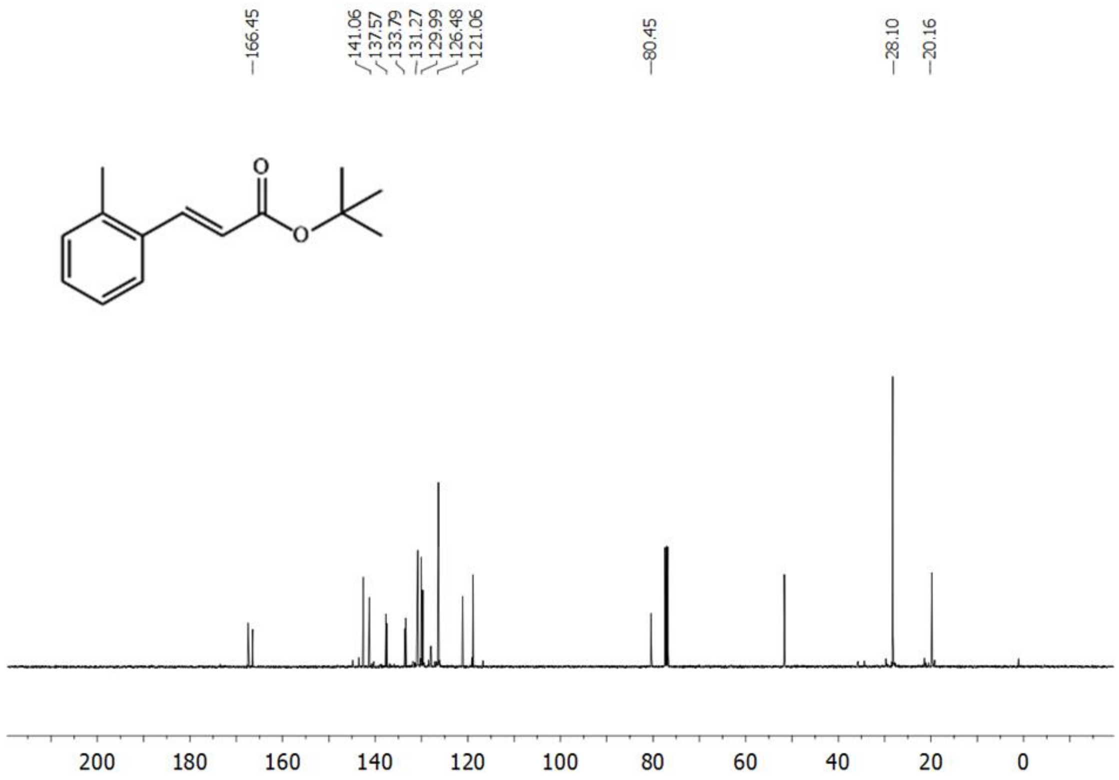
3. (*E*)-*tert*-Butyl 3-*m*-tolylacrylate



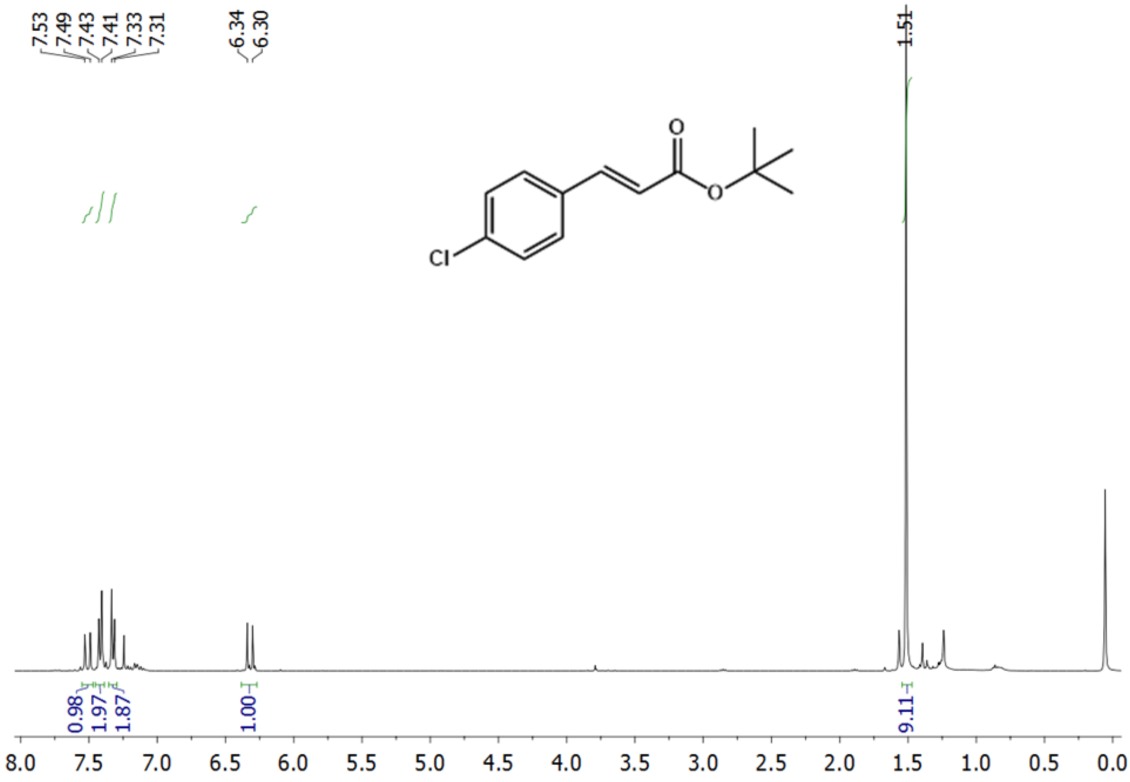


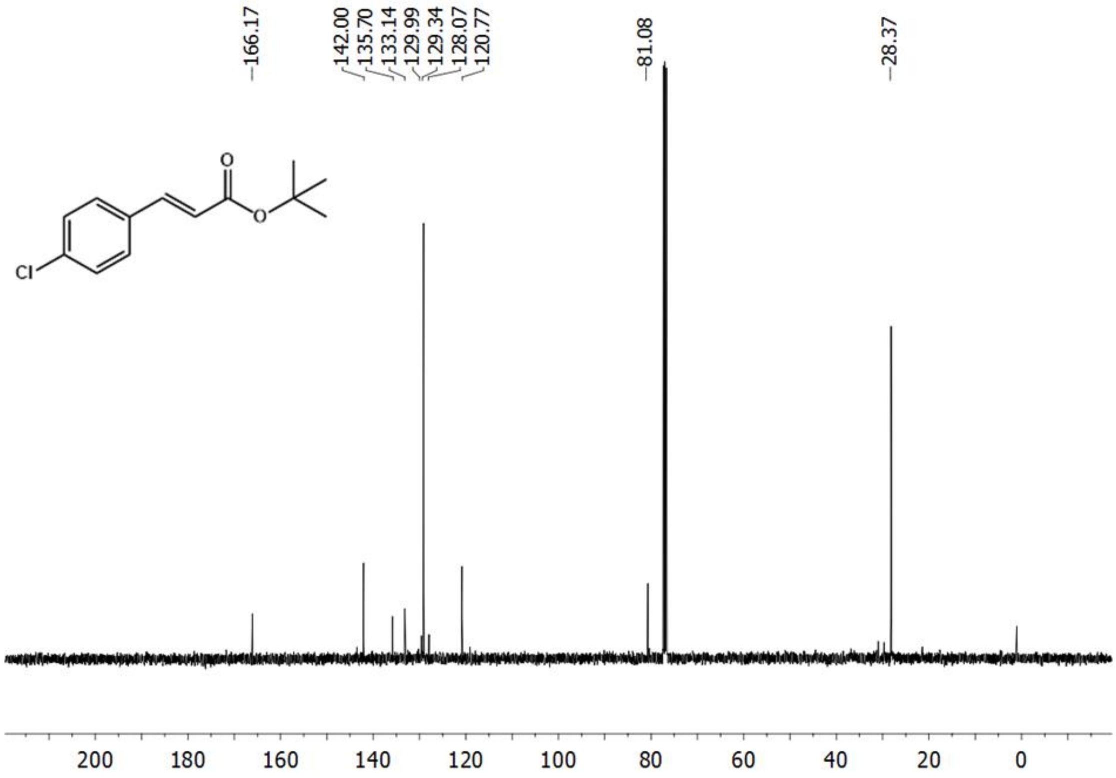
4. (*E*)-*tert*-Butyl 3-*o*-tolylacrylate



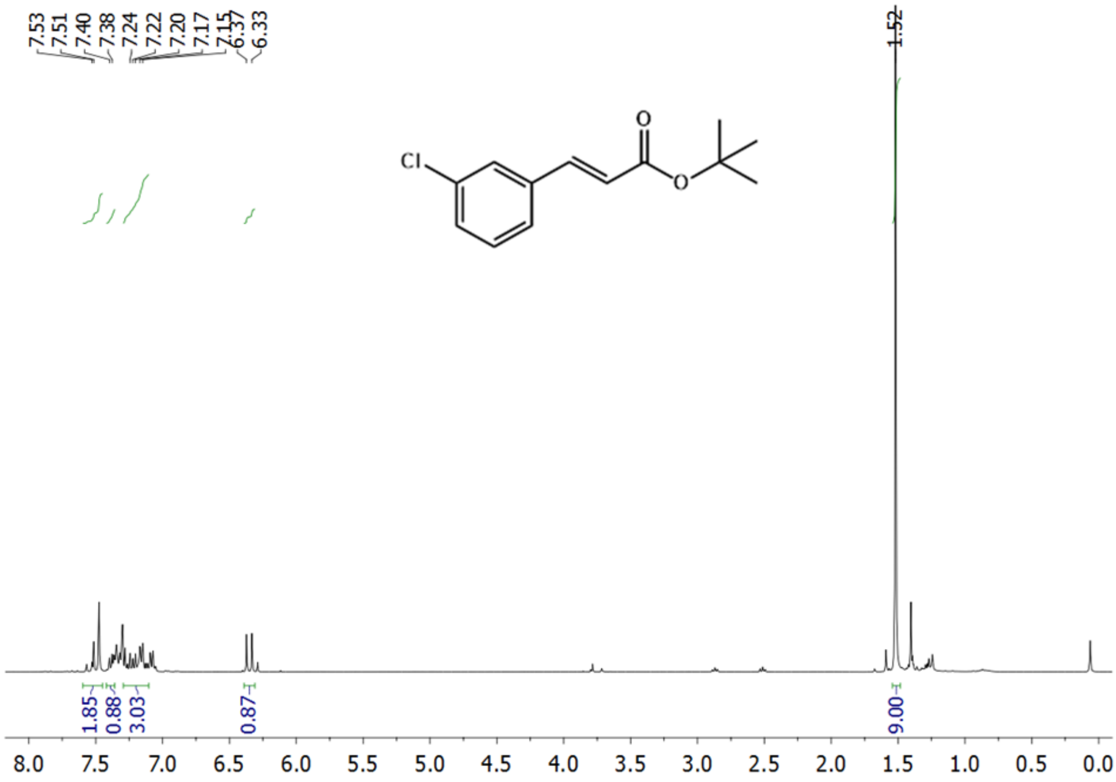


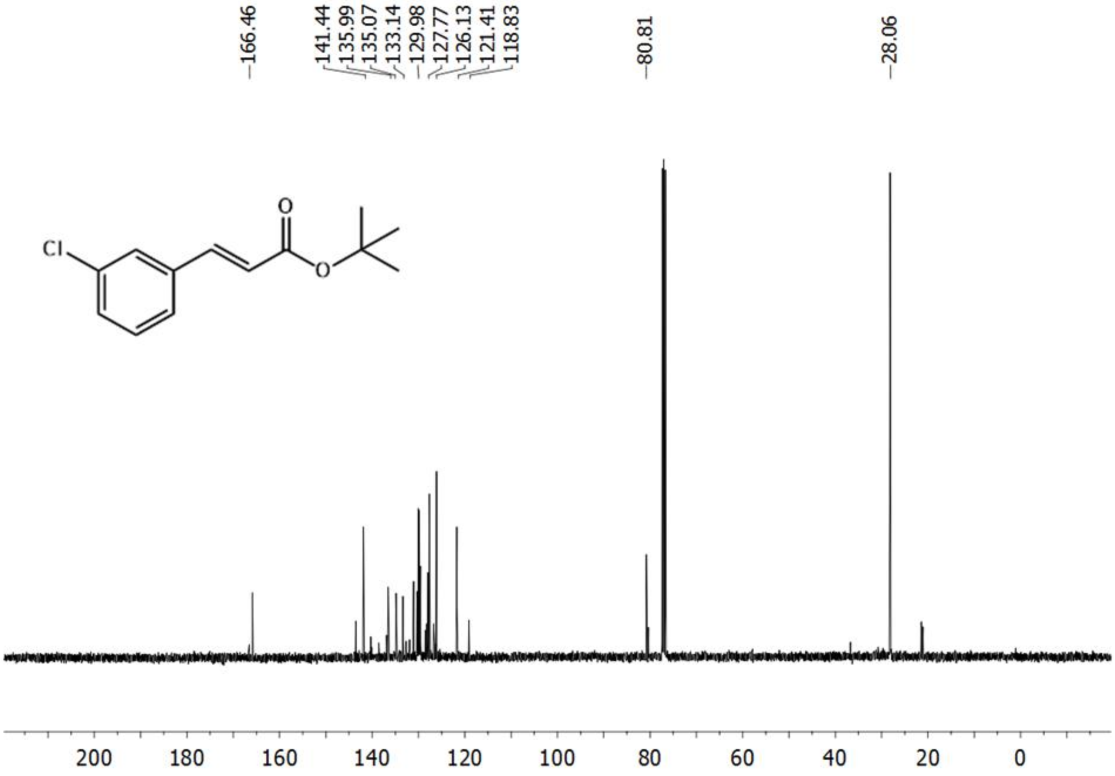
5. (*E*)-*tert*-Butyl 3-(4-chlorophenyl)acrylate



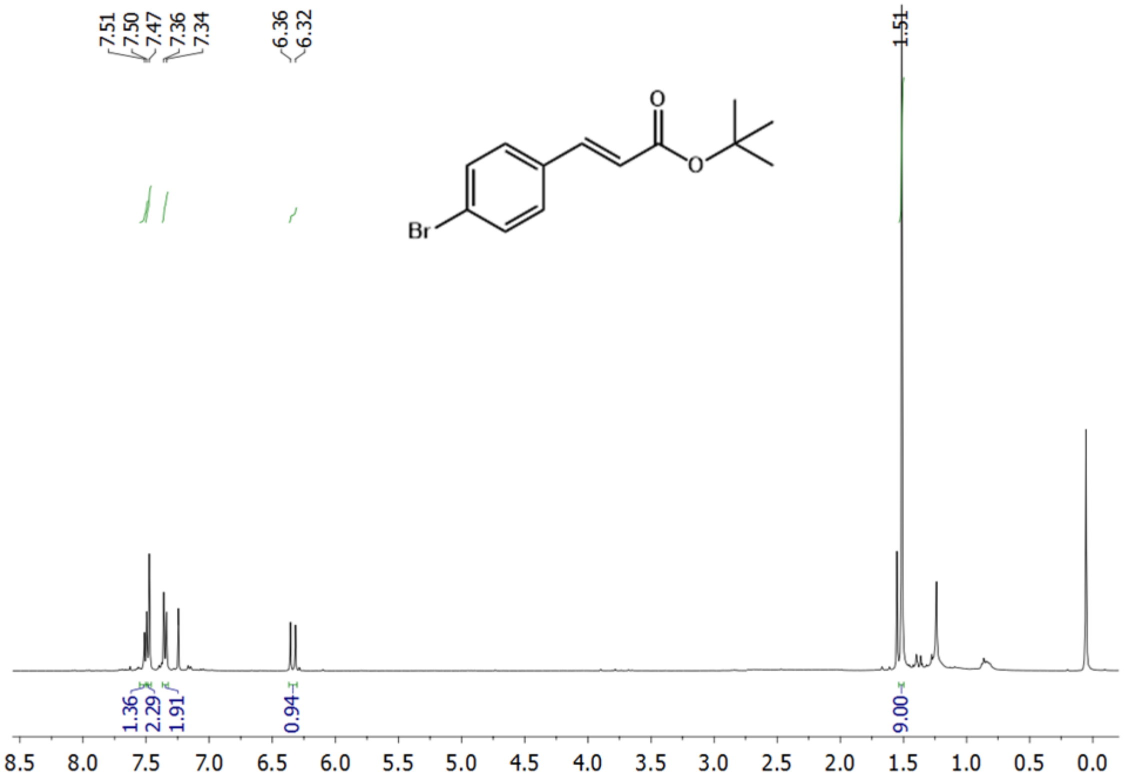


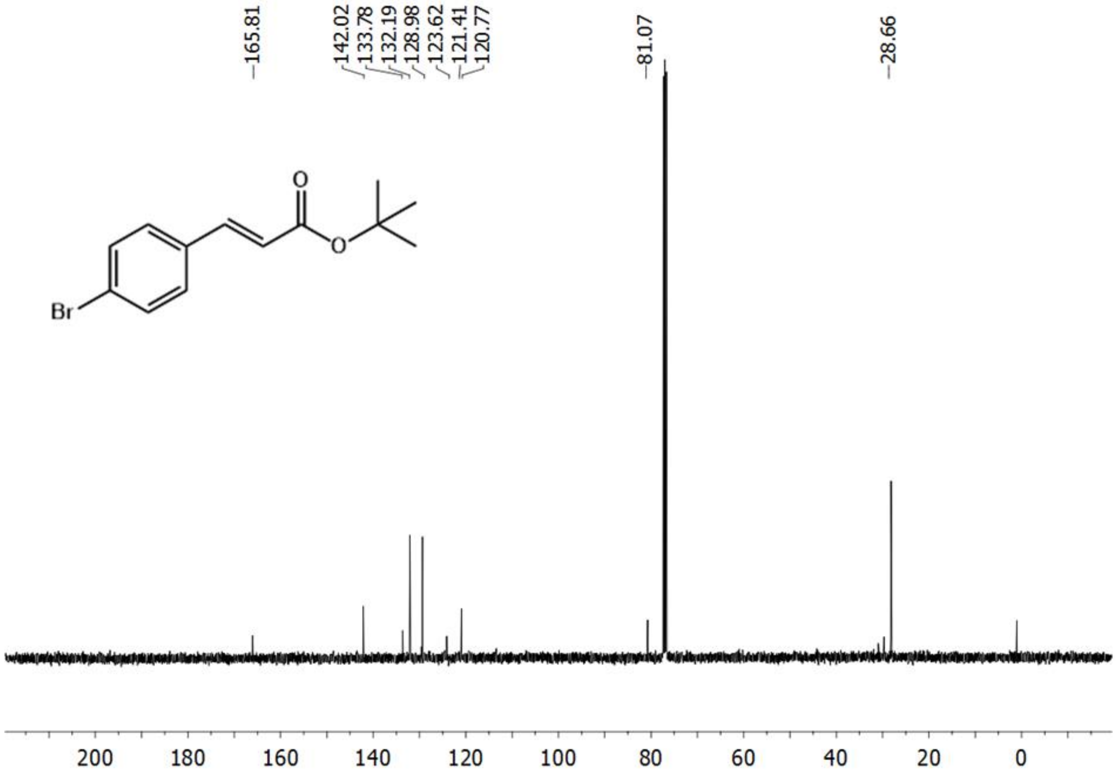
6. (*E*)-*tert*-Butyl 3-(3-chlorophenyl)acrylate



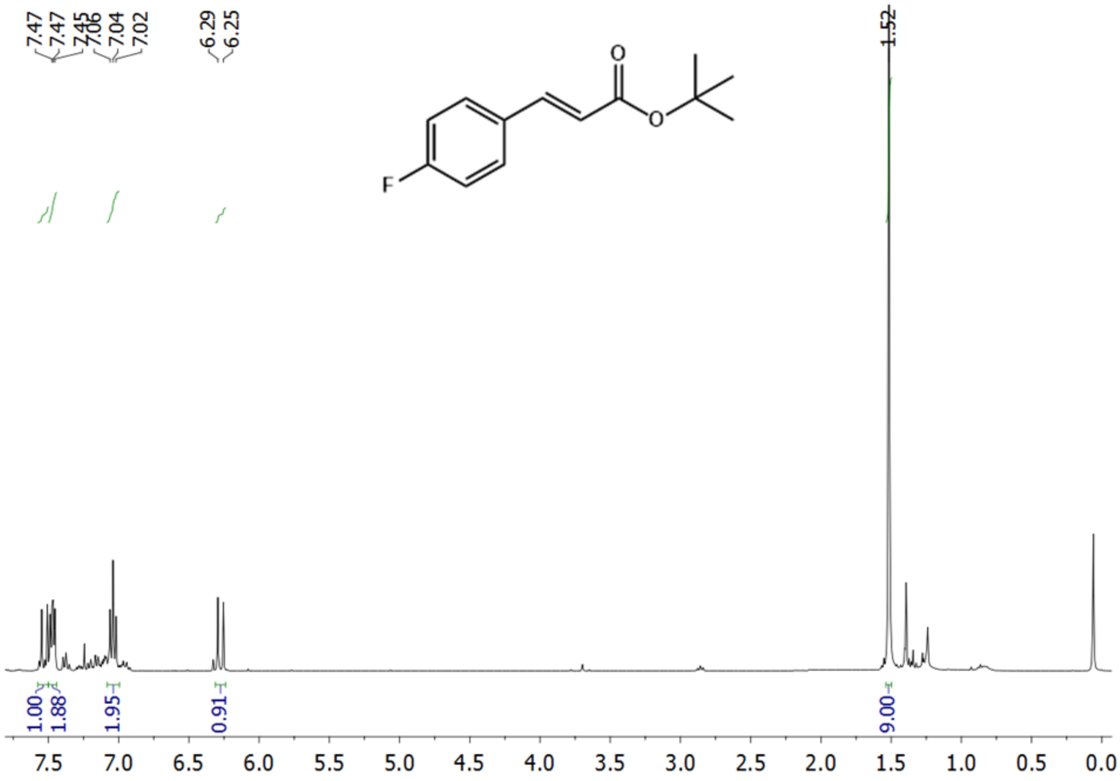


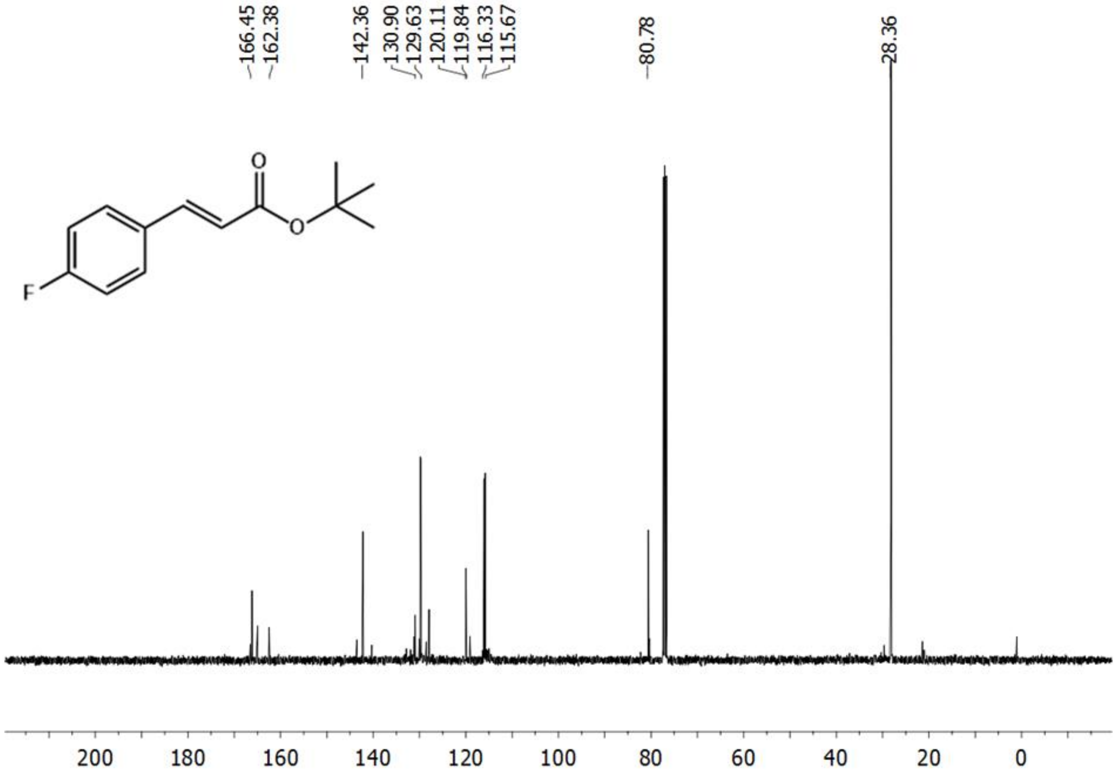
7. (*E*)-*tert*-Butyl 3-(4-bromophenyl)acrylate



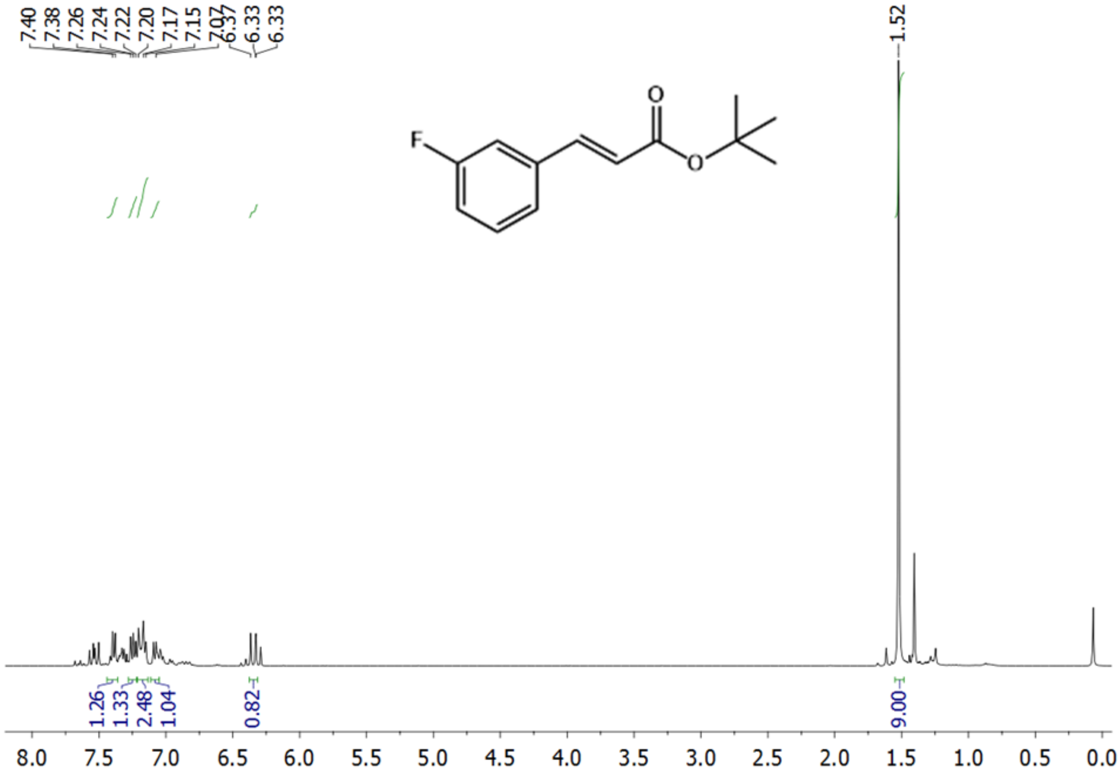


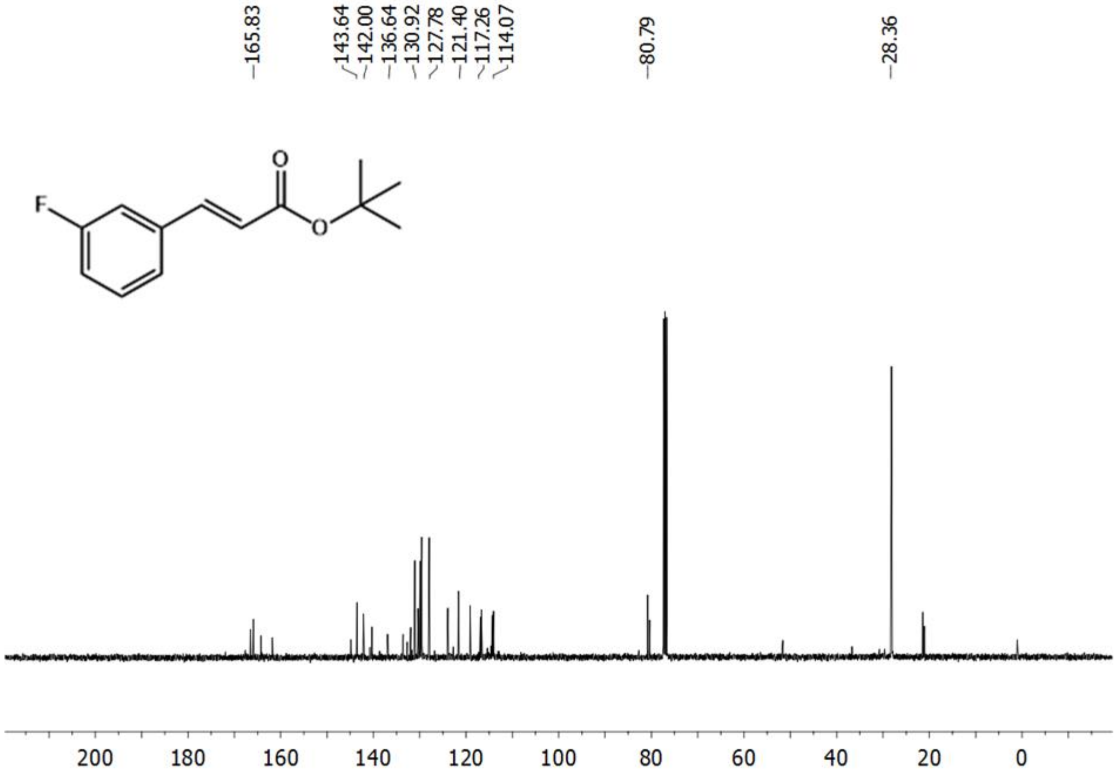
8. (*E*)-*tert*-Butyl 3-(4-fluorophenyl)acrylate



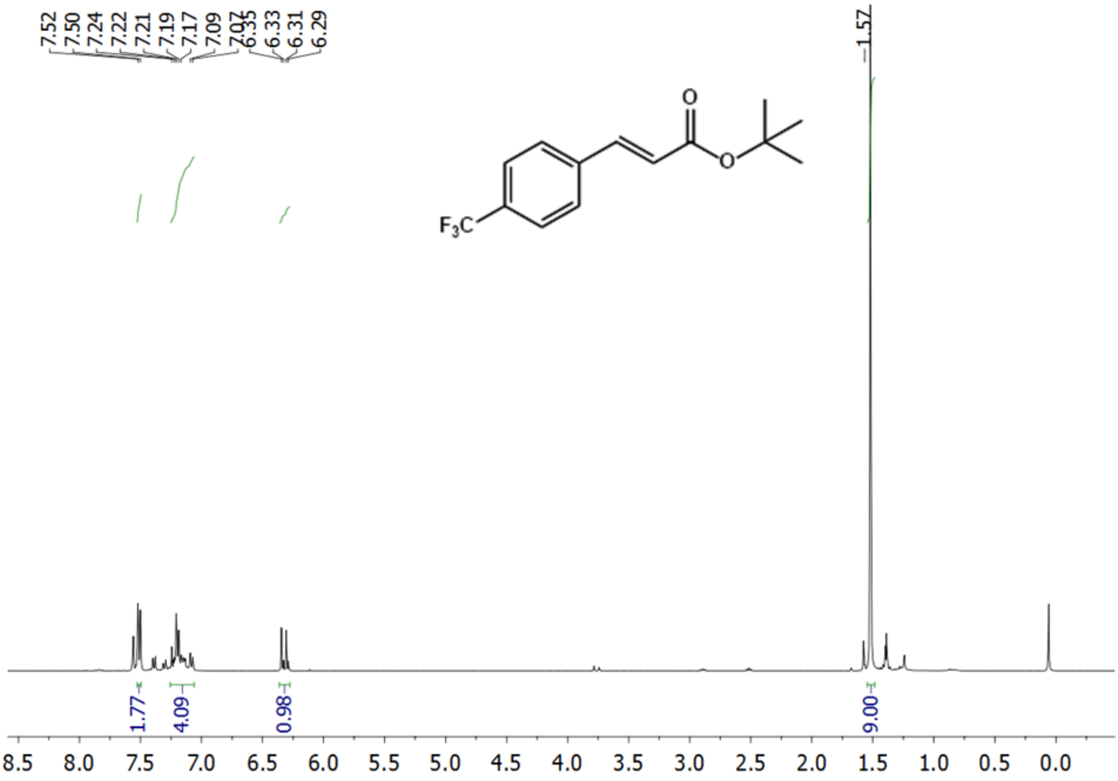


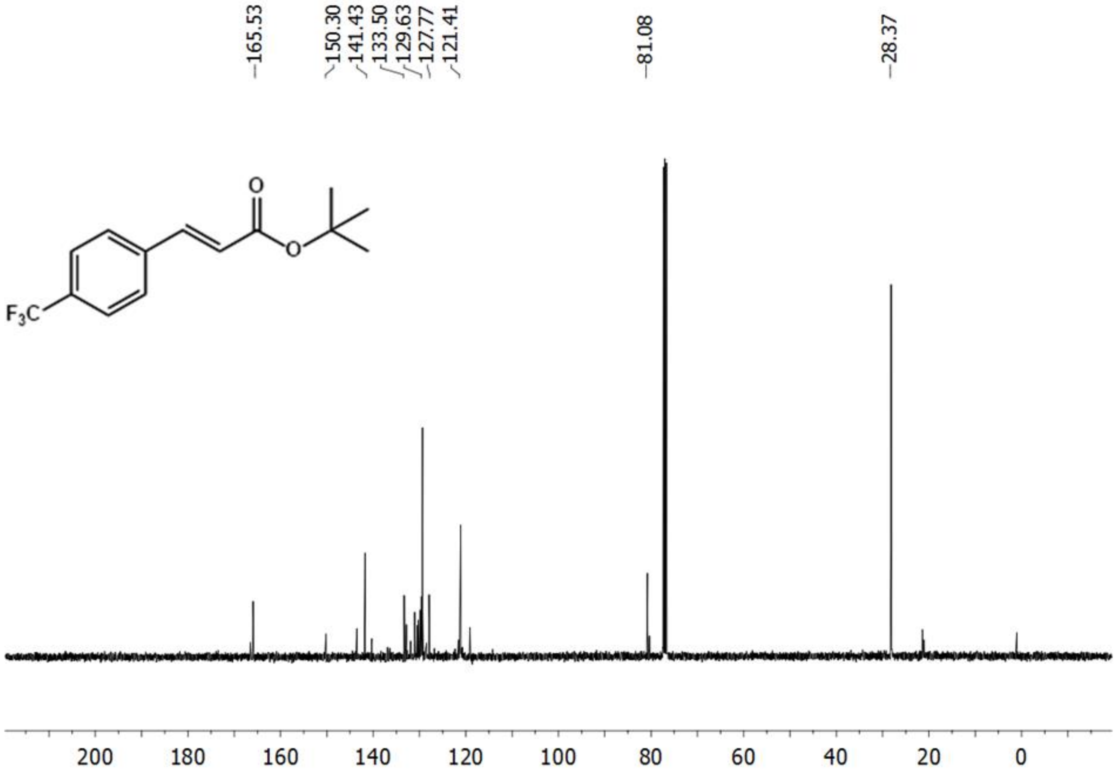
9. (*E*)-*tert*-Butyl 3-(4-fluorophenyl)acrylate



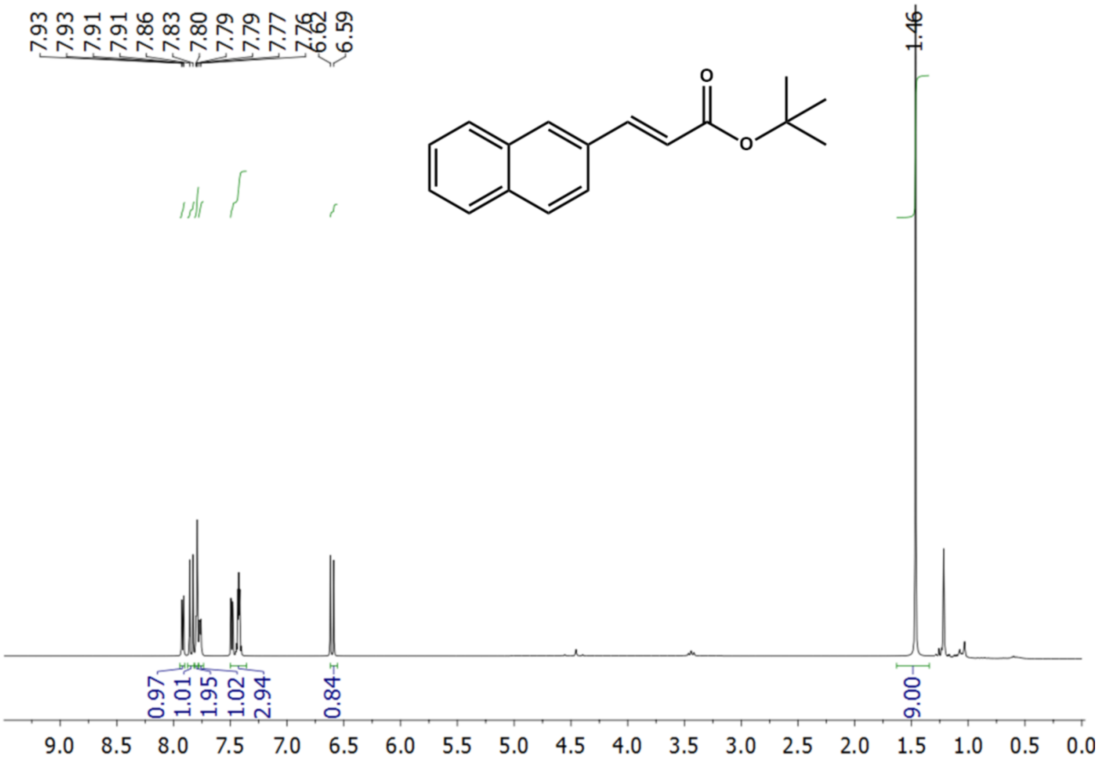


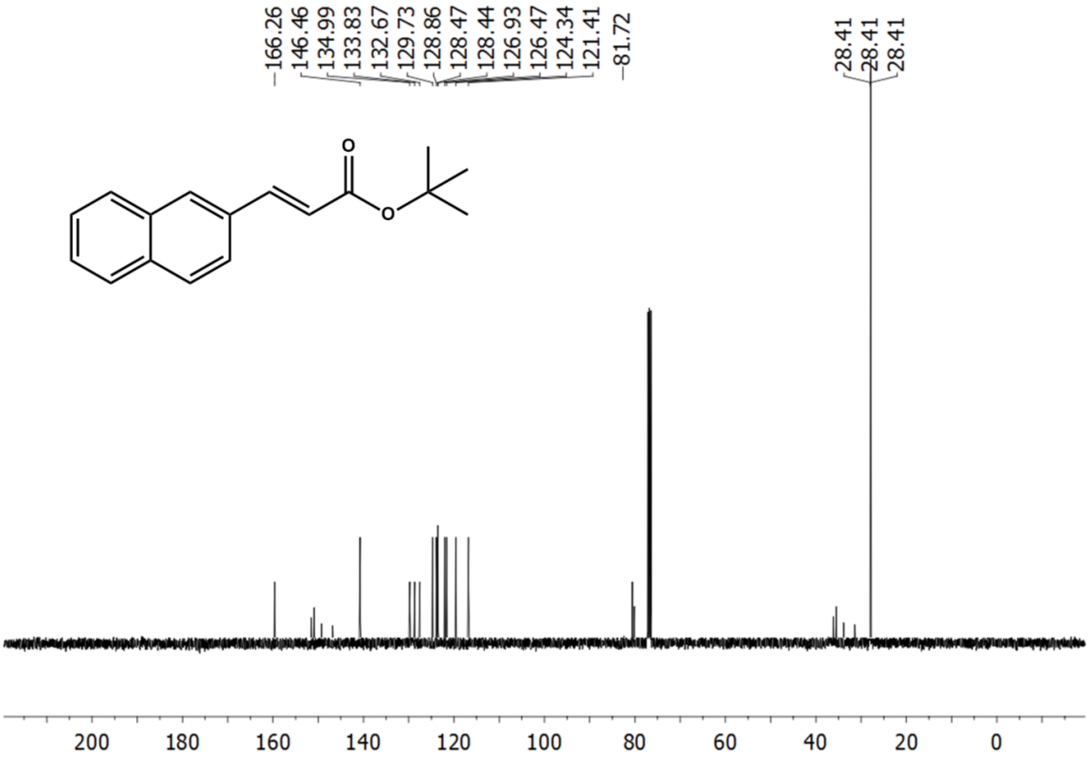
10. (*E*)-*tert*-buty(E)-tert-butyl 3-(4-(trifluoromethyl)phenyl)acrylate





11. (E)-tert-butyl 3-(naphthalen-2-yl)acrylate[2]





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