Electronic Supplementary Material (ESI) for Polymer Chemistry.

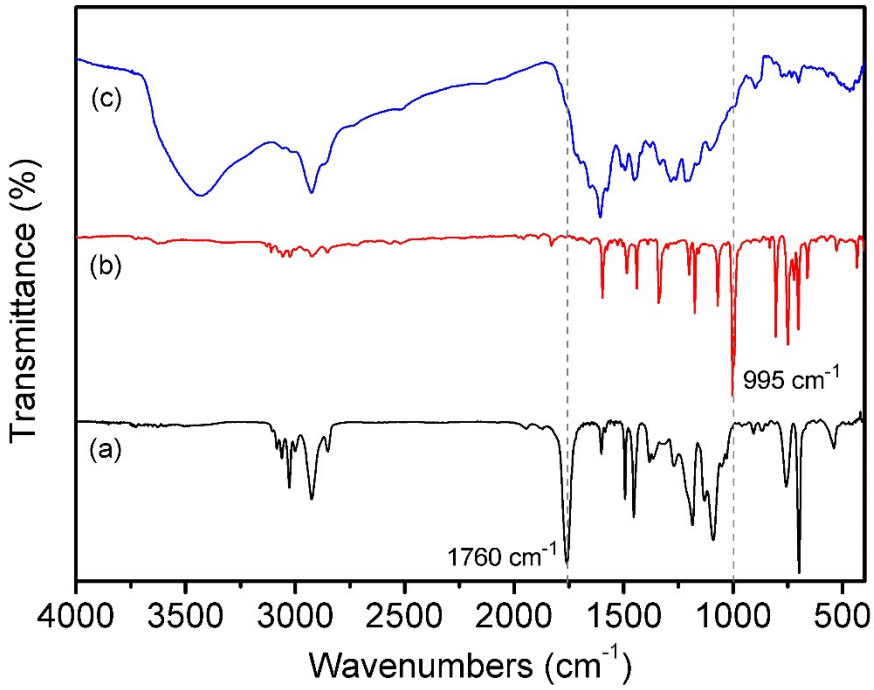


Figure S1. FTIR spectra of (a) PGM-*g*-(PLA-*b*-PS), (b) Fe(TPP)Cl and (c) Fe(TPP)Cl-MONNs.

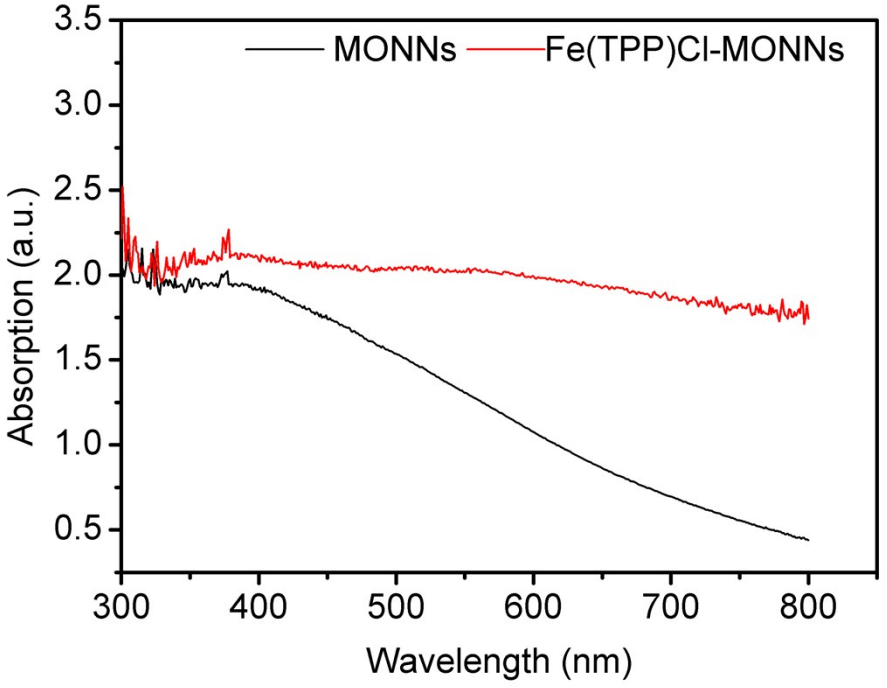


Figure S2. Solid-state diffuse reflectance spectra of Fe(TPP)Cl-MONNs and MONNs.

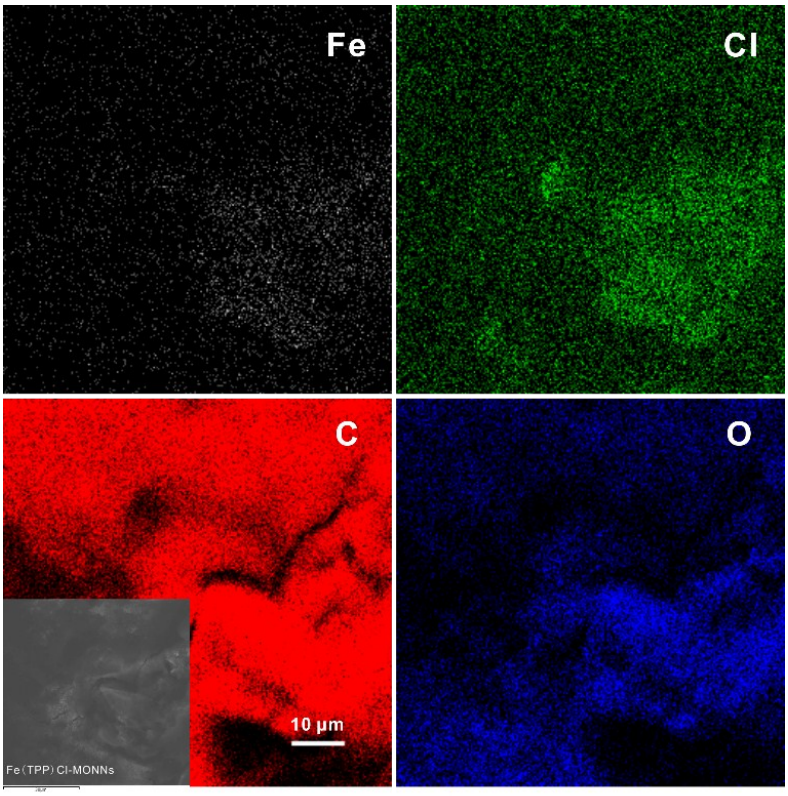


Figure S3. SEM elemental mapping images of Fe(TPP)Cl-MONNs in 10 μm. (Different colors indicate different atoms)

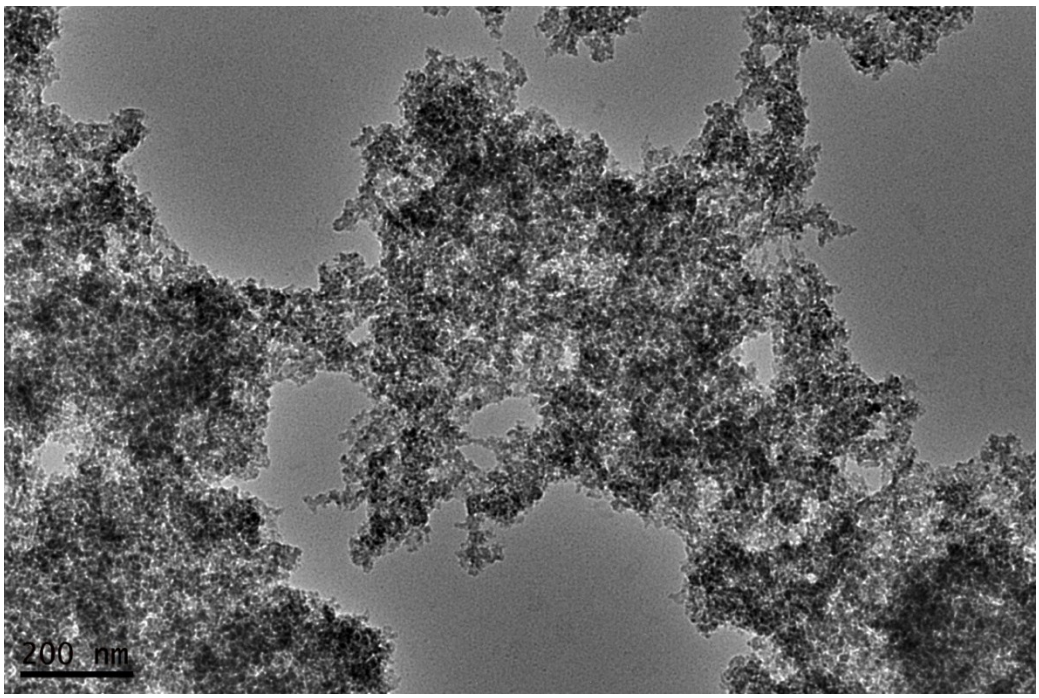


Figure S4. TEM image of the Fe(TPP)Cl-MOPs.

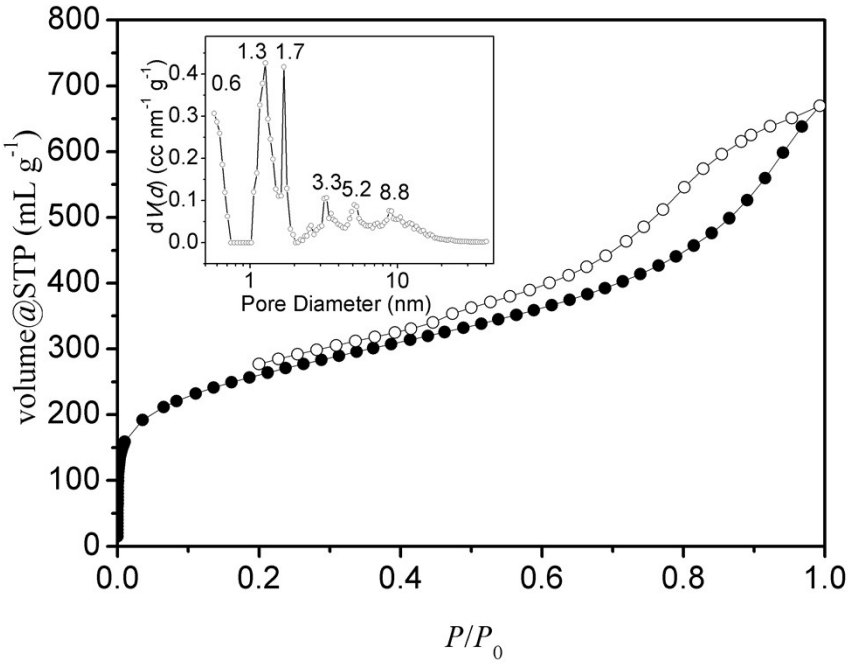


Figure S5. Nitrogen adsorption–desorption isotherms and pore size distribution of Fe(TPP)Cl-MOPs based on DFT method.

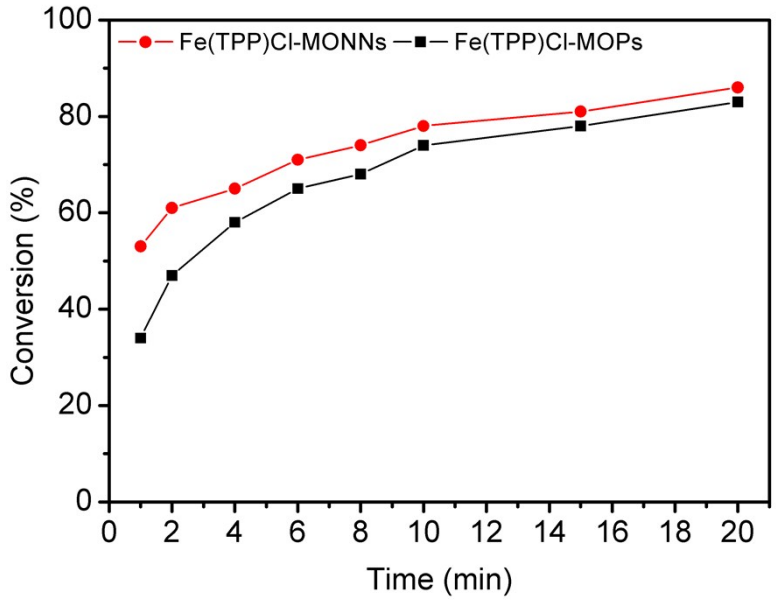


Figure S6. The conversion for N-H insertion reactions catalyzed by Fe(TPP)Cl-MOPs or Fe(TPP)Cl-MONNs at different time. Reaction conditions: *p*-chloroaniline (0.2 mmol), EDA (0.2 mmol) and ethyl ether (5 ml) with catalysts Fe(TPP)Cl-MONNs (4 mg, 1.0 μmol) or Fe(TPP)Cl-MOPs (6 mg, 1.0 μmol) at ambient temperature under N_2.

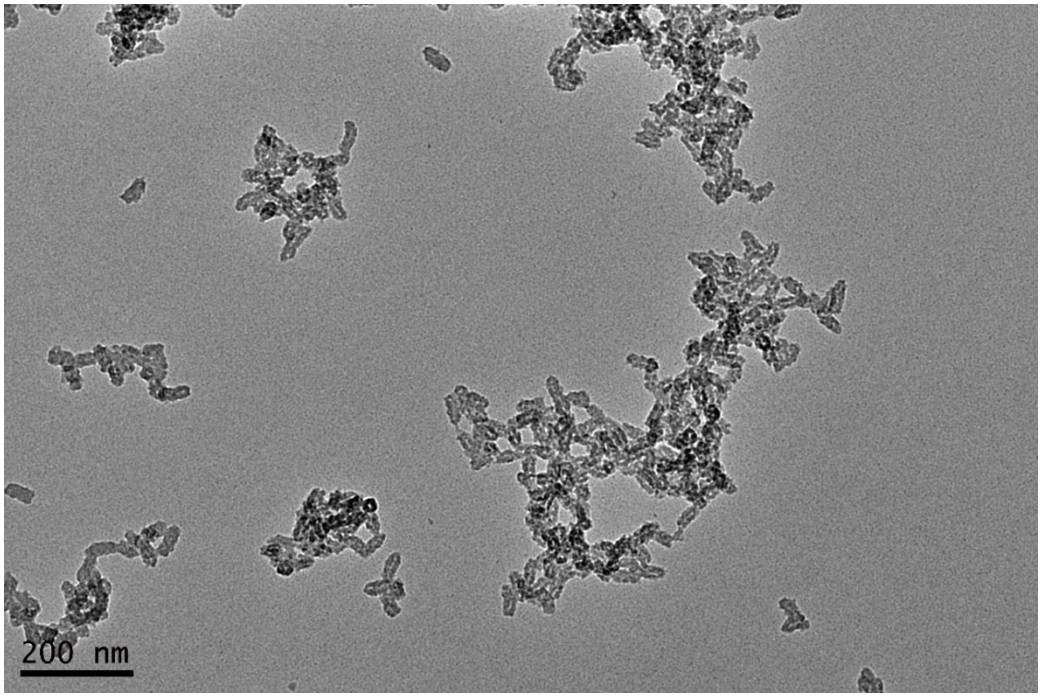


Figure S7. TEM image of the Fe(TPP)Cl-MONNs after recycled.

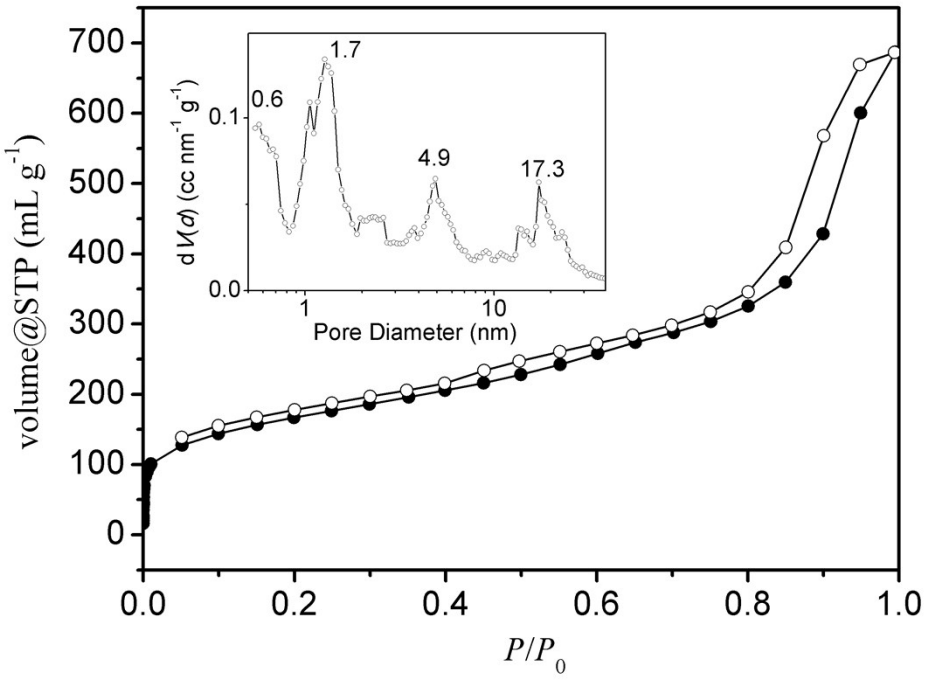


Figure S8. Nitrogen adsorption–desorption isotherms and pore size distribution of Fe(TPP)Cl-MONNs after recycled based on DFT method.

Table S1. Element analysis of MONNs, Fe(TPP)Cl-MONNs and Fe(TPP)Cl-MOPs.

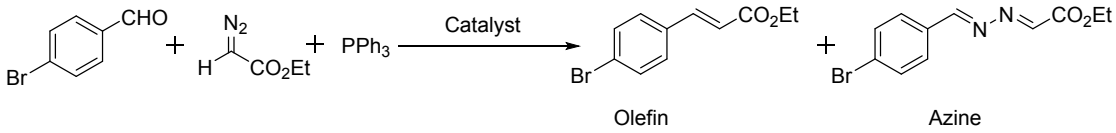
Materials	C [wt %]	H [wt %]	N [wt %]
MONNs	77.83	5.70	0
Fe(TPP)Cl-MONNs	70.51	5.44	1.45
Fe(TPP)Cl-MOPs	76.39	6.006	0.939

Table S2. Porous properties of Fe(TPP)Cl-MONNs catalysts before reaction (1), after 12 runs (2) and Fe(TPP)Cl-MOPs catalysts before reaction (3).

Samples	Pore parameters			
	S_{BET} [a] (m^2g^{-1})	S_{mico} [b] (m^2g^{-1})	S_{meso} [c] (m^2g^{-1})	V_{total} [d] (cm^3g^{-1})
(1)	732	179	553	1.21
(2)	589	138	451	1.06
(3)	890	287	603	1.04

[a] BET specific surface area from N2 adsorption; [b] Microporous surface area calculated from *t-plots*; [c] Mesoporous surface area; [d] Total pore volume (P/P_0=0.995).

Table S3. Olefination of *p*-Bromobenzaldenhyde by Fe(TPP)Cl and Fe(TPP)Cl-MONNs.



Olefin Azine

Entry	Catalyst	Olefin/ Azine	Temp. (°C)	Time (h)	Conversion (%) [a]	E/Z (%) [a]
1	Fe(TPP)Cl	4/96	30	4	50.9	91/9
2	Fe(TPP)Cl	22/78	80	2	99.6	95/5
3	Fe(TPP)Cl-MONNs	94/6	30	4	80.3	95/5
4	Fe(TPP)Cl-MONNs	99/1	80	1	95.9	94/6

[a] determined by GC.

Table S4. Olefination of aldehydes by different catalysts.

Catalyst	S_{BET} (m^2g^{-1})	Benzaldehyde/EDA/PPh3/catalysts	Reaction conditions	Yield	E/Z	Ref.
Ru(TPP)(CO)	-	100/120/120/0.7	toluene, 80°C, 2h, added via syringe	95[a]	93/7	[1]
Fe(TPP)Cl	-	100/120/120/2	toluene, 80°C, 1h, added via syringe	96[a]	96/4	[1]
Iron(II) Porphyrin	-	100/110/200/2	toluene, at ambient temperature, 6h, added dropwise of ethyl diazoacetate	94[a]	96/4	[2]
Basic Mg/La mixed oxide	-	1 mmol/1 mmol[e]/1 mmol /0.1 g	DMF, RT, 14h	92[b]	99/1	[3]
NAP-MgO	-	1 mmol/1 mmol[e]/1 mmol /0.075 g	DMF, RT, 8h	96[a]	99/1	[4]
Myoglobin	-	500/500/500/1	PH=8, $Na_2S_2O_4$, RT	-[c]	99/1	[5]
Iron (II) NHC complexes	-	100/120/200/10	CD_3CN, 70°C, 2h	90[b]	-[f]	[6]
Copper (I) Iodide	-	100/200/120/5	THF, 60°C, 10h, Slow addition of ethyl diazoacetate	94[a]	95/5	[7]
P4VP-1 or P4VP-2[d]	-	100/120/120/1	THF, 60°C, 24h	84[a]	94/6	[8]
rGO/hemin	-	100/120/120/1	toluene, 80°C, 12h	92[a]	88/12	[9]
Fe(TPP)Cl-MONNs[e]	732	100/120/120/2	toluene, 80°C, 2h, added in one portion	**86[a]**	**93/7**	**This work**

[a] Isolated yield. [b] Yield determined by NMR spectroscopy. [c] TON=31. [d] Ru(II)(salen)$(PPh_3)_2$ complexes grafted on poly(4-vinylpyridine).

[e] Fe-porphyrin functionalized microporous organic nanotubes networks.

Table S5. N-H insertion by different catalysts (At room temperature under nitrogen atmosphere unless specified differently).

Catalysts	S_{BET} (m^2g^{-1})	Reaction conditions	Yield (%)	Ref.
Ruthenium porphyrin (Ru(TMP)CO)	-	diethylamine/EDA/catalysts=150/100/1; benzene, 2h, added slowly	81[b]	[10]
Fe(III) corrole or porphyrin	-	aniline/EDA/catalysts=1000/1000/1; diethyl ether, <3min, aerobic, added in one portion	>92[b]	[11]
Tp*Cu	-	aniline/EDA/catalysts =100/100/2; CH_2Cl_2, 20min, added with a syringe pump	95[c]	[12]
Ru(II)-N-heterocyclic carbine (NHC) complex	-	aniline/EDA/catalysts=100/150/1; CH_2Cl_2, 6h, 40°C	98[c]	[13]
$TBPA^{\cdot+}SbCl_6$	-	*p*-chloro-aniline/EDA/catalysts=100/100/10; CH_3NO_2, 14h	86[a]	[14]
Iridium porphyrin ($Ir(TTP)CH_3$)	-	aniline/EDA/catalysts=200/100/0.07; CH_2Cl_2, 2h, -78 to 22 °C	92[b]	[15]
Cytochrome P450-BM3	-	aniline/EDA/Na2S2O4/catalysts=2000/850/1000/1; PH=8, 12h, Ar	68[c]	[16]
Myoglobin (Mb(H64V,V68A))	-	aniline/EDA/Na2S2O4/catalysts=10000/10000/10000/1; PH=8, 12h, RT, Ar	61[c]	[17]
γ-Fe2O3@CuO	-	aniline/EDA/catalysts =100/110/2.4; CH_2Cl_2, 1h, reflux	96[b]	[18]
SBA-15-FeTPP-x	676	piperidine/EDA/catalysts=120/100/2; CH_2Cl_2, 2h	96[b]	[19]
Fe3O4@FePMN[d]	173	aniline/EDA/catalysts =100/100/1; acetone, 20min,	94[a]	[20]
Fe(TPP)Cl-MONNs[e]	732	aniline/EDA/catalysts=100/100/1; ethyl ether, 10 min, added in one portion	**97[b]**	**This work**

[a] Isolated yield. [b] Yield determined by NMR spectroscopy. [c] Yield determined by GC. [d] Fe−porphyrin microporous networks on iron oxide nanoparticles.
[e] Fe-porphyrin functionalized microporous organic nanotubes networks.

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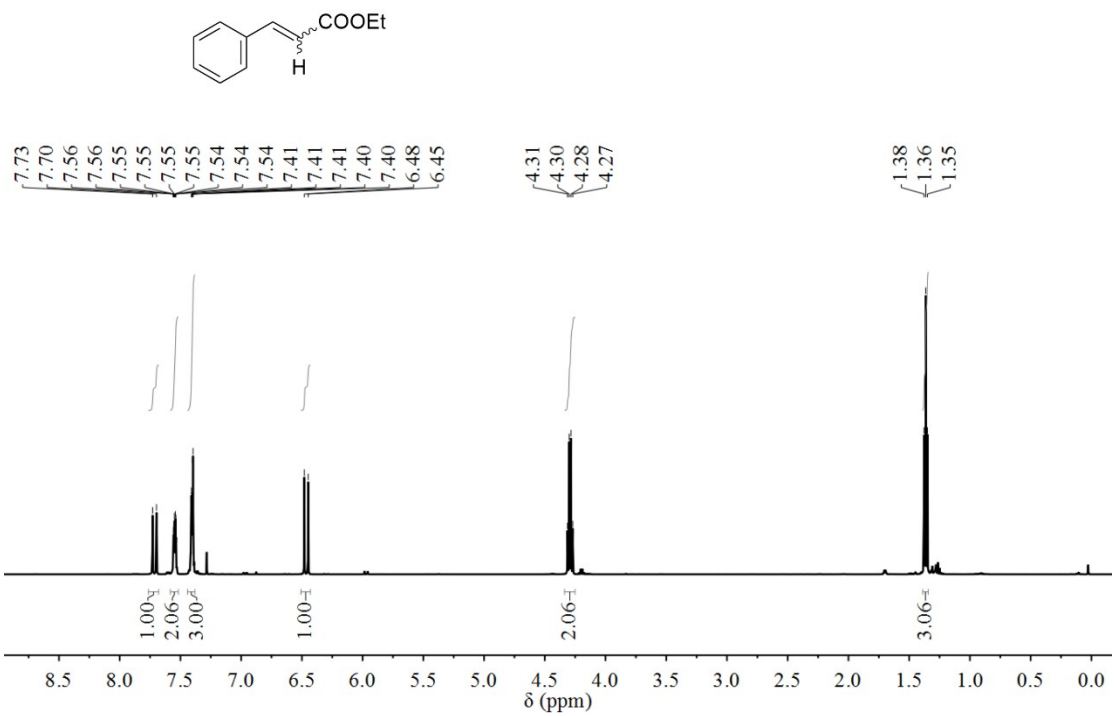
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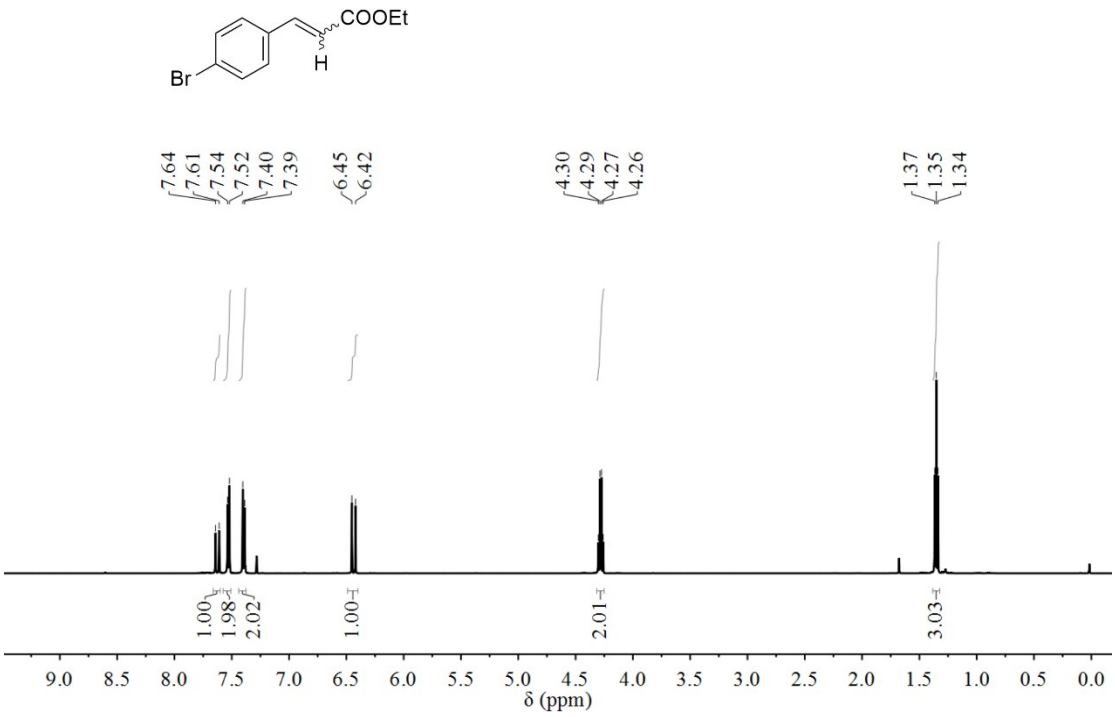
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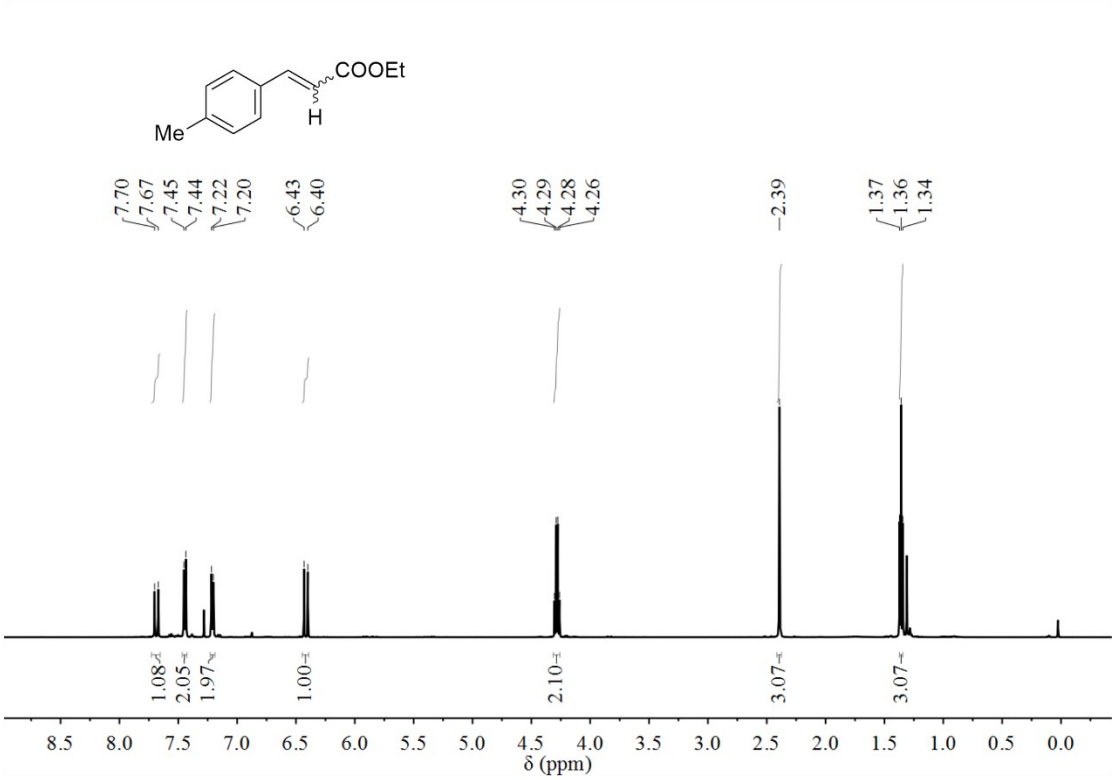
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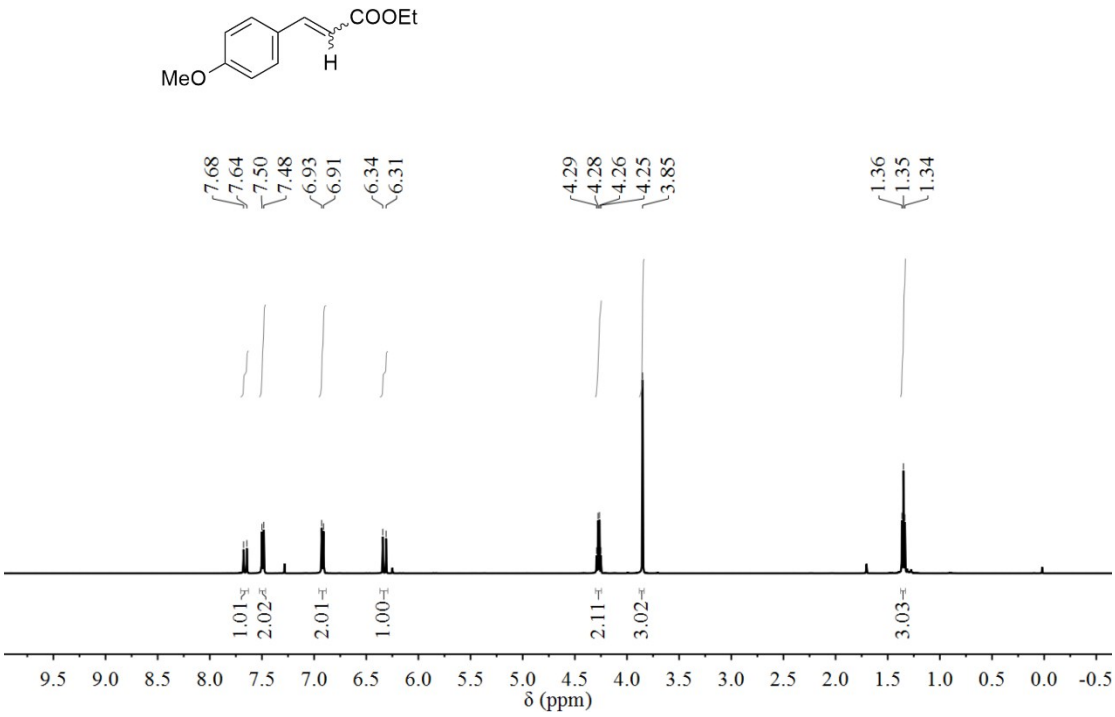
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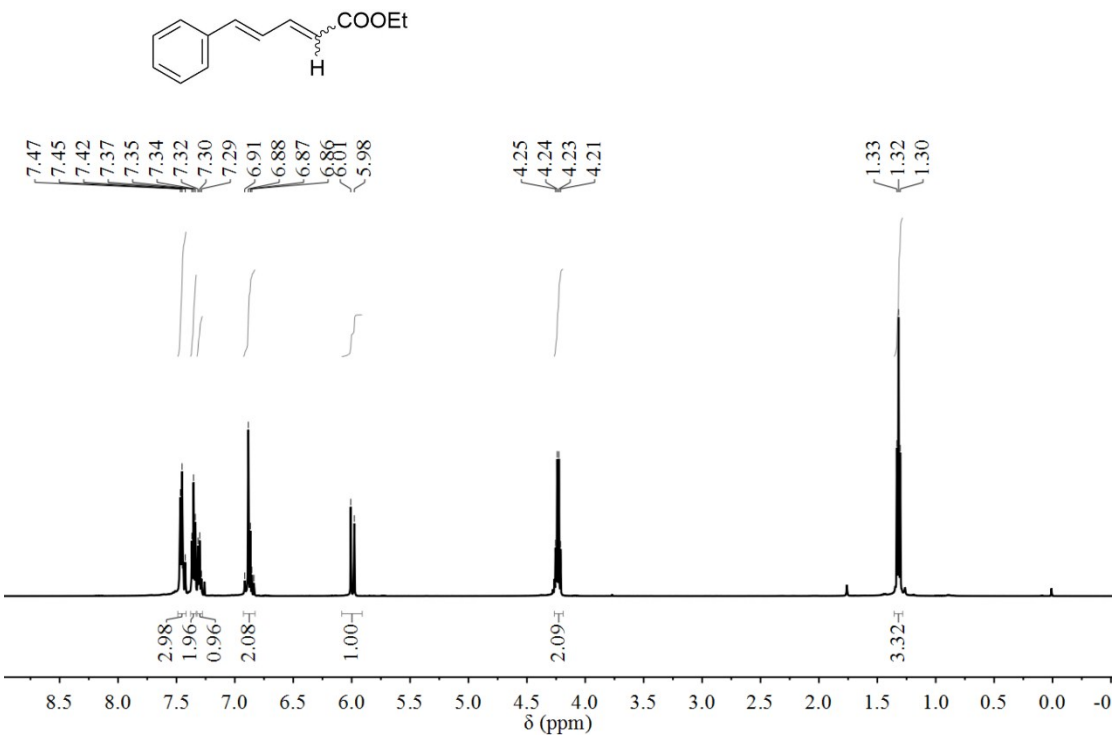
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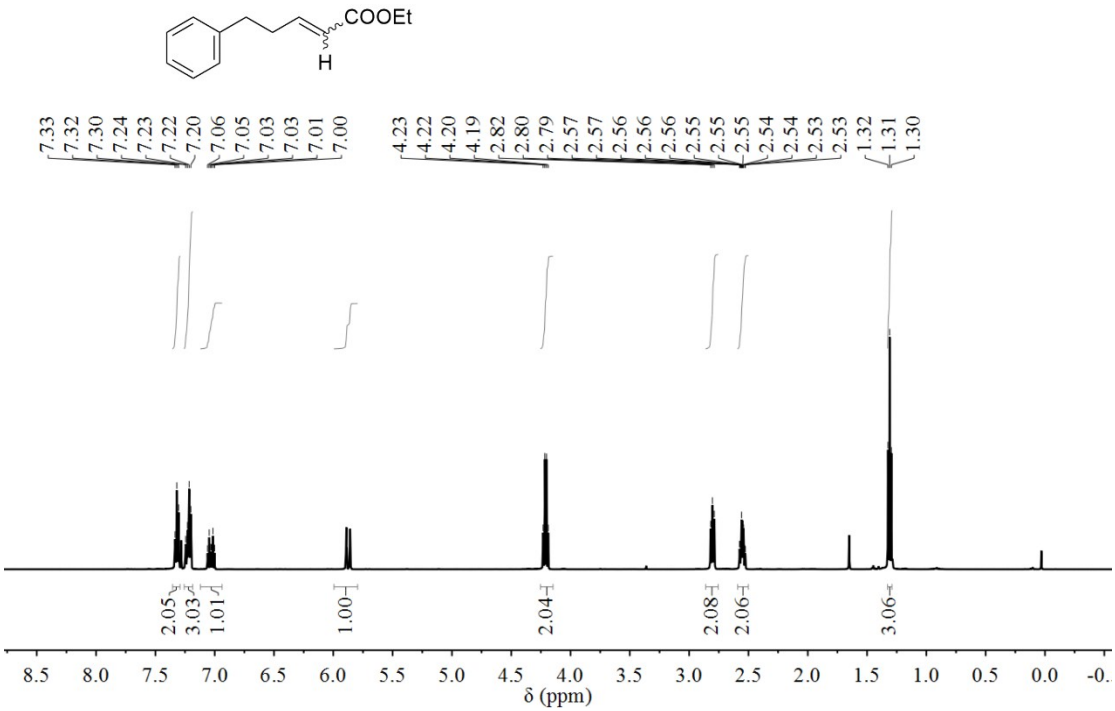
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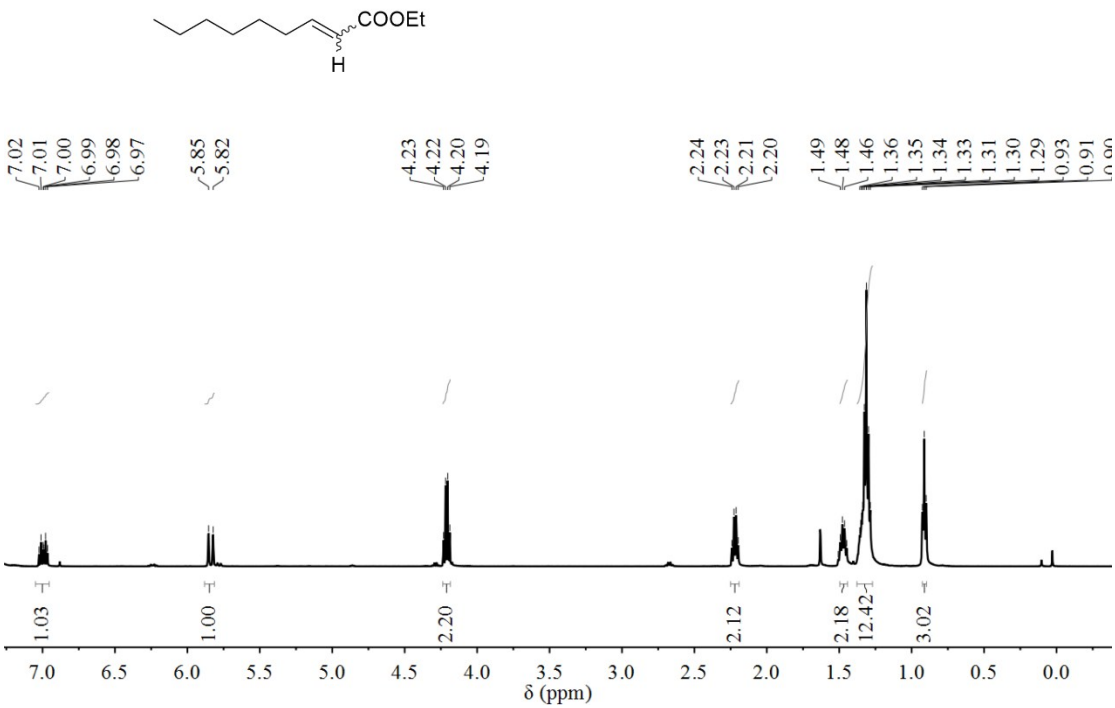
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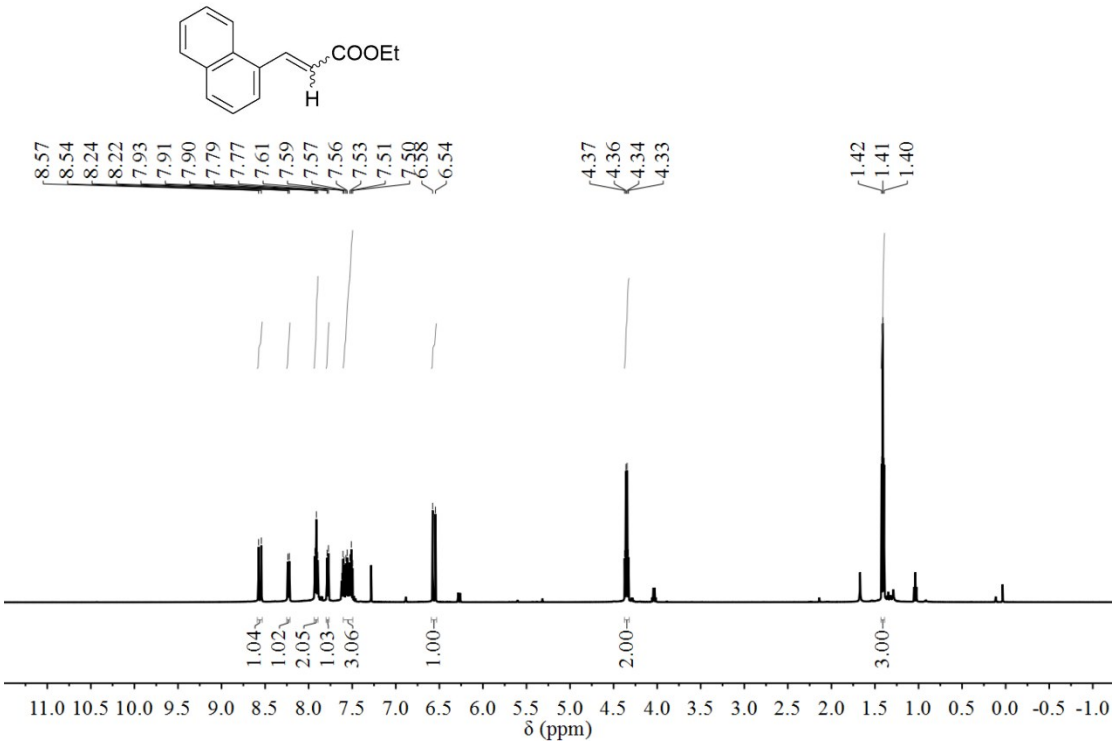
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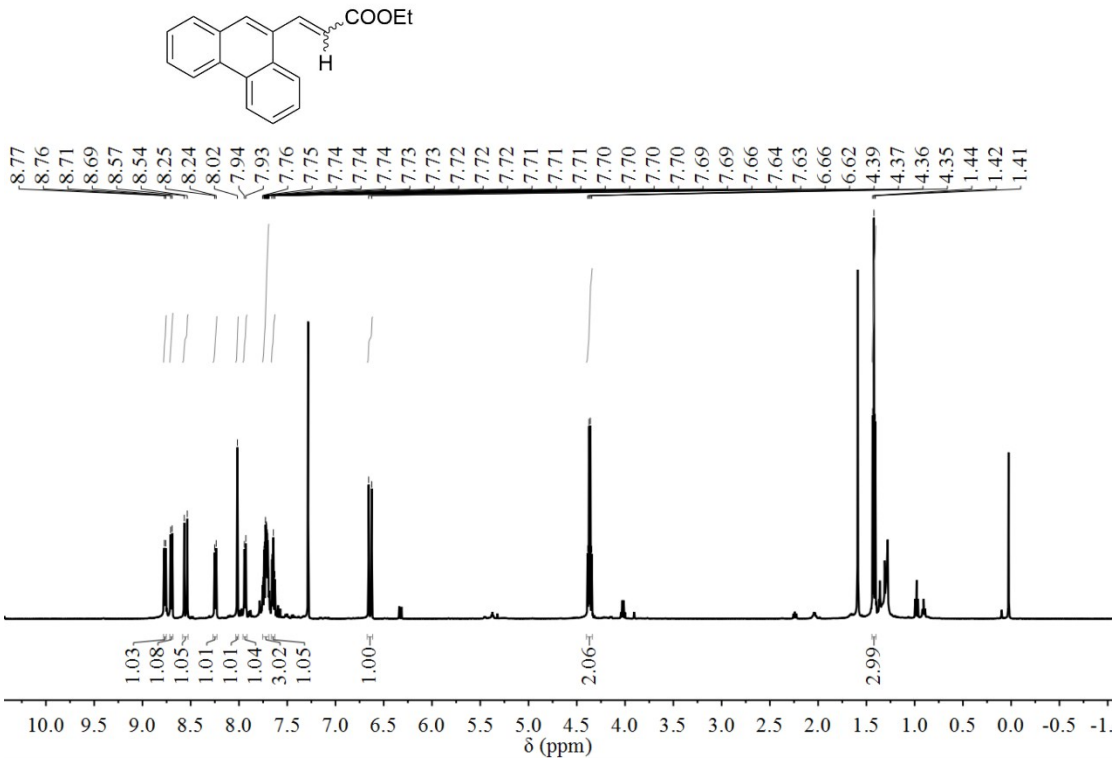
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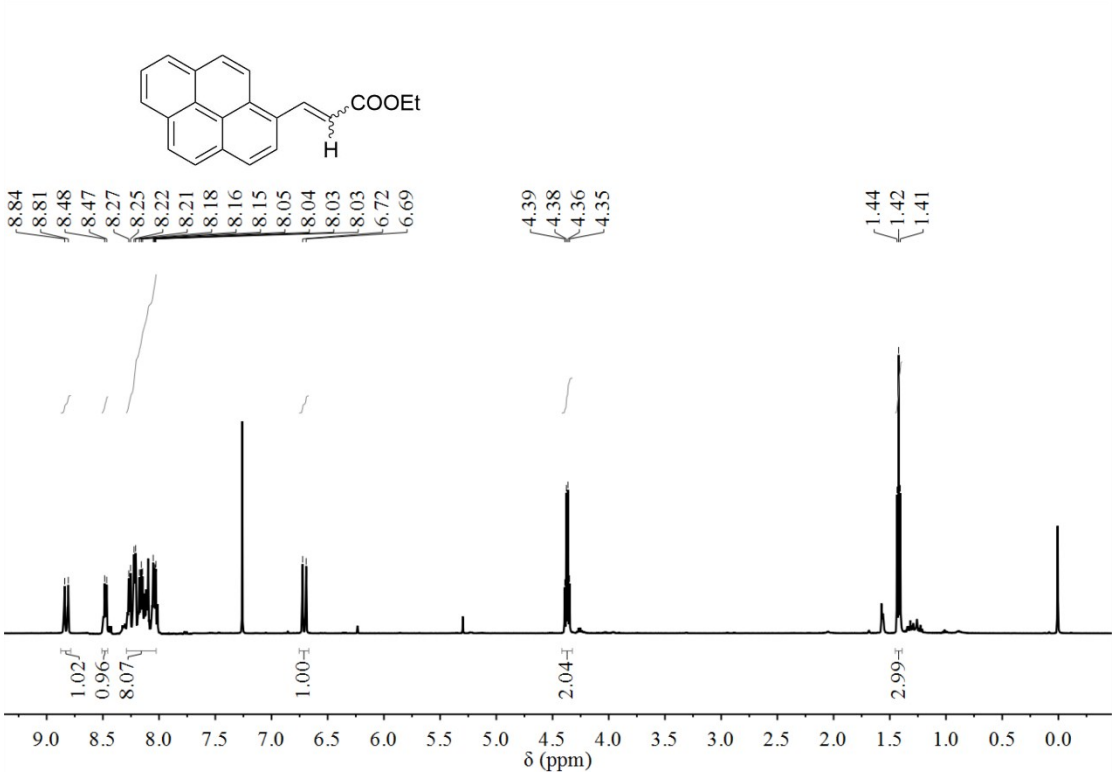
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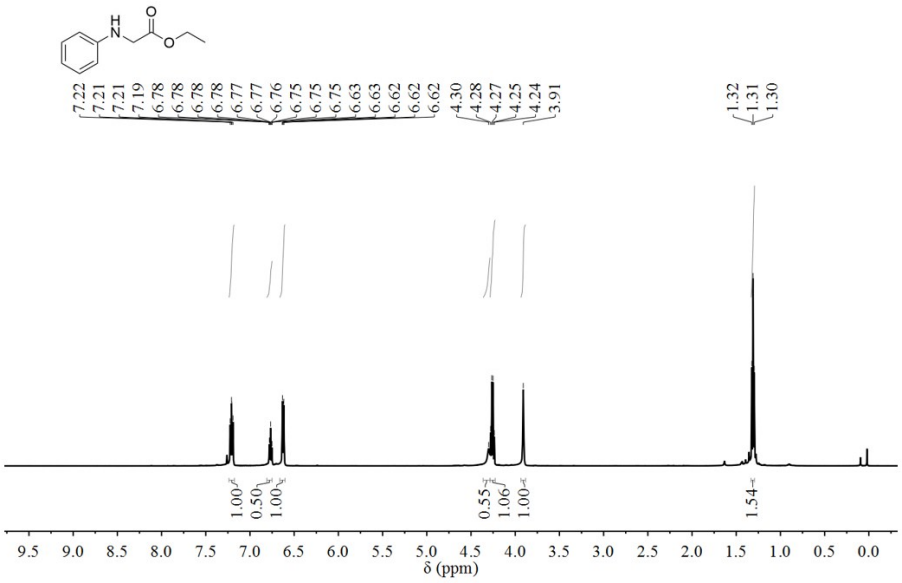
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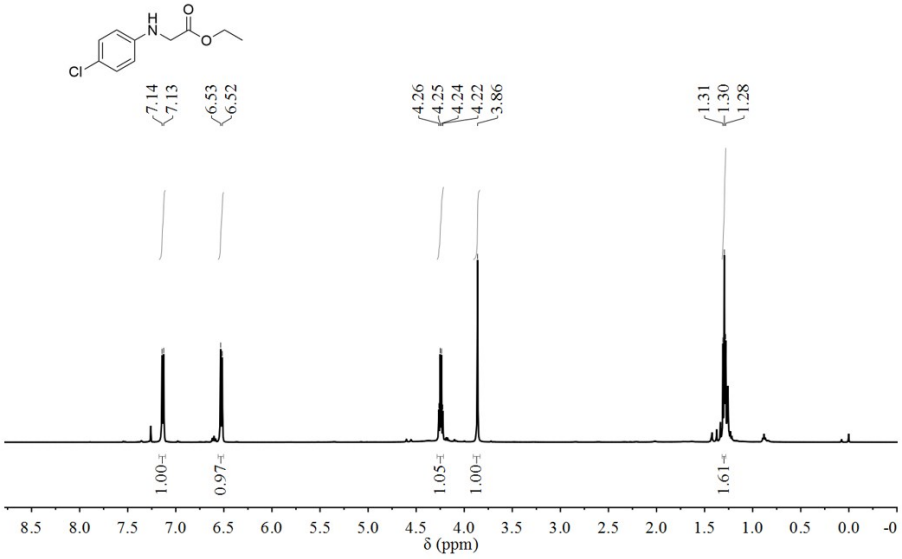
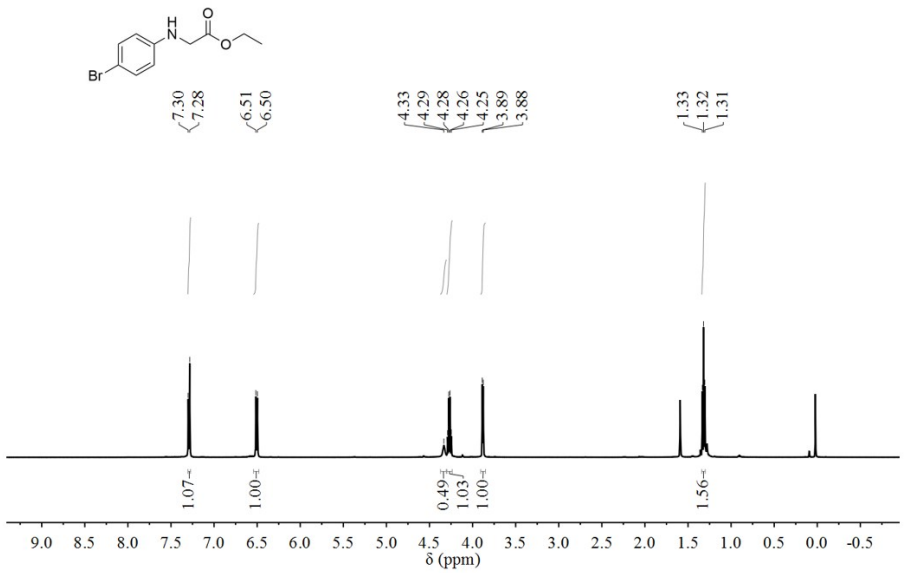
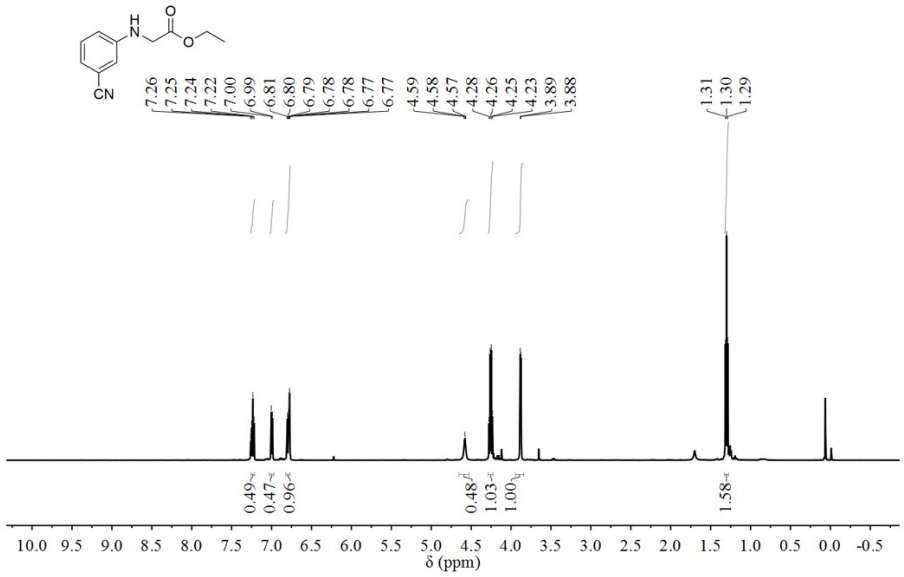
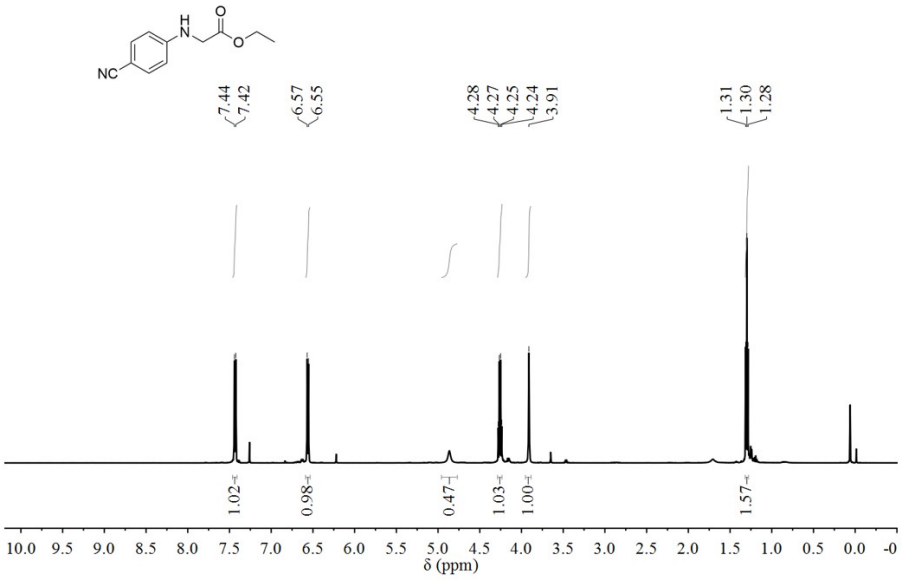
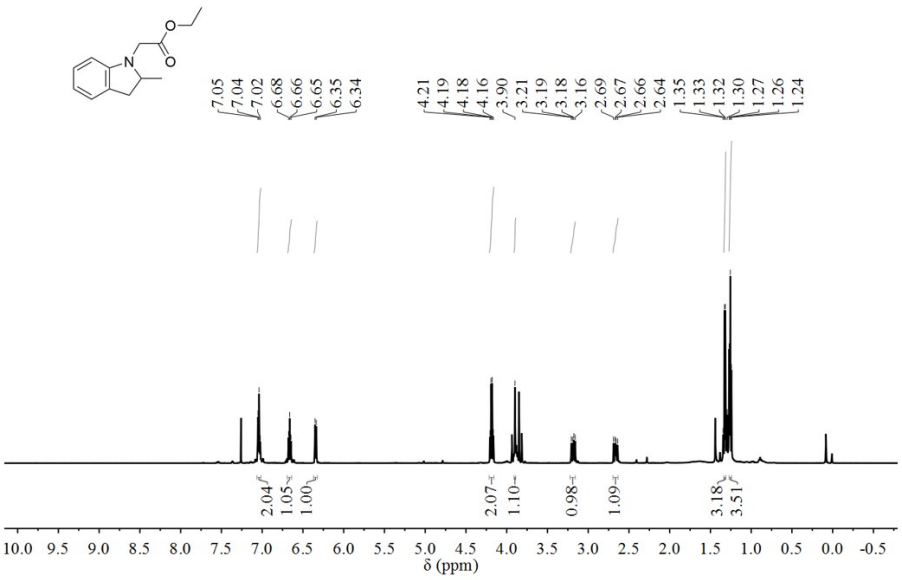
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

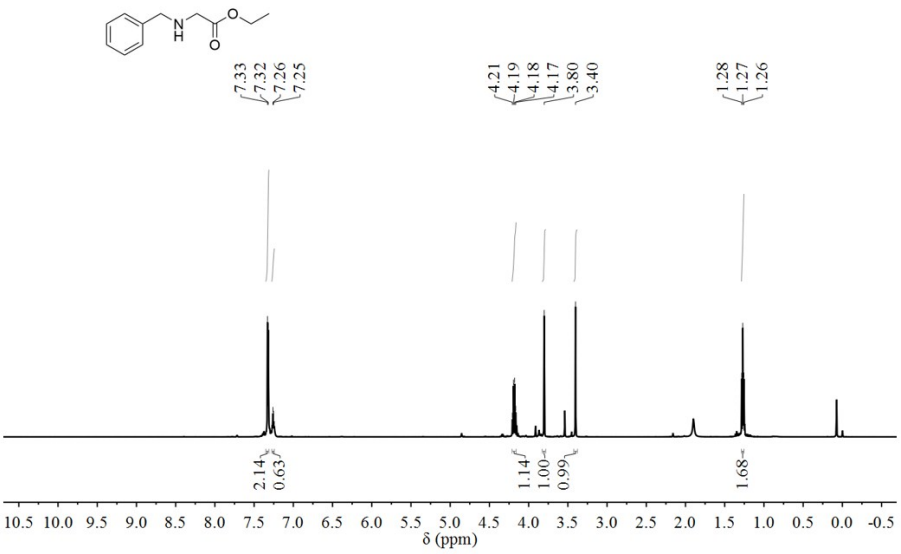

Cl
7.14
7.13
6.53
6.52
4.26
4.25
4.24
4.22
3.86
1.31
1.30
1.28
1.00
0.97
1.05
1.00
1.61
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
δ (ppm)

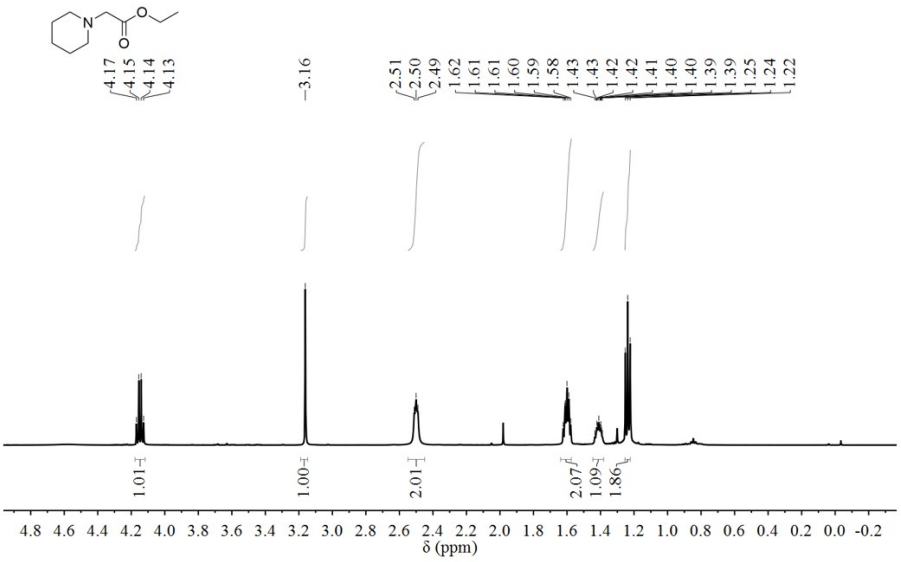

Br
7.30
7.28
6.51
6.50
4.33
4.29
4.28
4.26
4.25
3.89
3.88
1.33
1.32
1.31
1.07
1.00
0.49
1.03
1.00
1.56
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

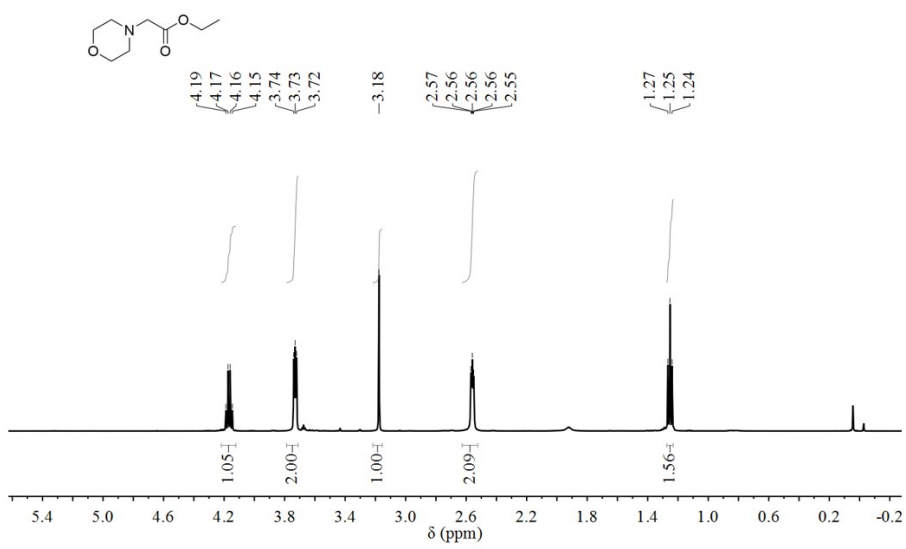

CN
7.26
7.25
7.24
7.22
7.00
6.99
6.81
6.80
6.79
6.78
6.78
6.77
6.77
4.59
4.58
4.57
4.28
4.26
4.25
4.23
3.89
3.88
1.31
1.30
1.29
0.49
0.47
0.96
0.48
1.03
1.00
1.58
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

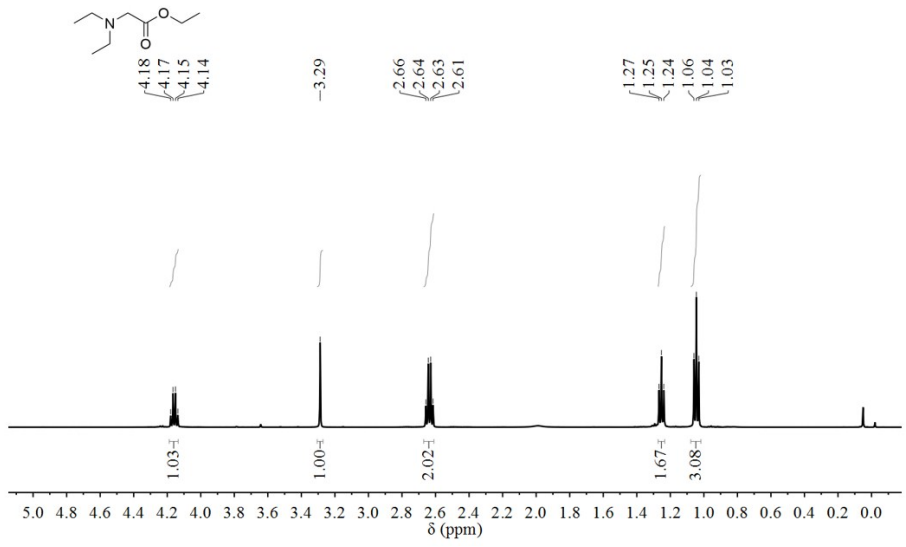

NC
H
N
O
O
7.44
7.42
6.57
6.55
4.28
4.27
4.25
4.24
3.91
1.31
1.30
1.28
1.02
0.98
0.47
1.03
1.00
1.57
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
δ (ppm)

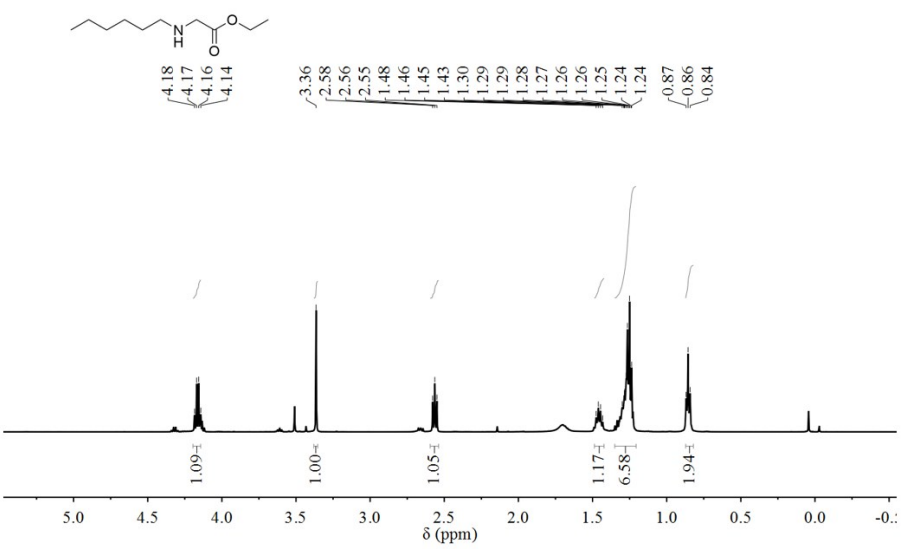

N
O
O
7.05
7.04
7.02
6.68
6.66
6.65
6.35
6.34
4.21
4.19
4.18
4.16
3.90
3.21
3.19
3.18
3.16
2.69
2.67
2.66
2.64
1.35
1.33
1.32
1.30
1.27
1.26
1.24
2.04
1.05
1.00
2.07
1.10
0.98
1.09
3.18
3.51
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

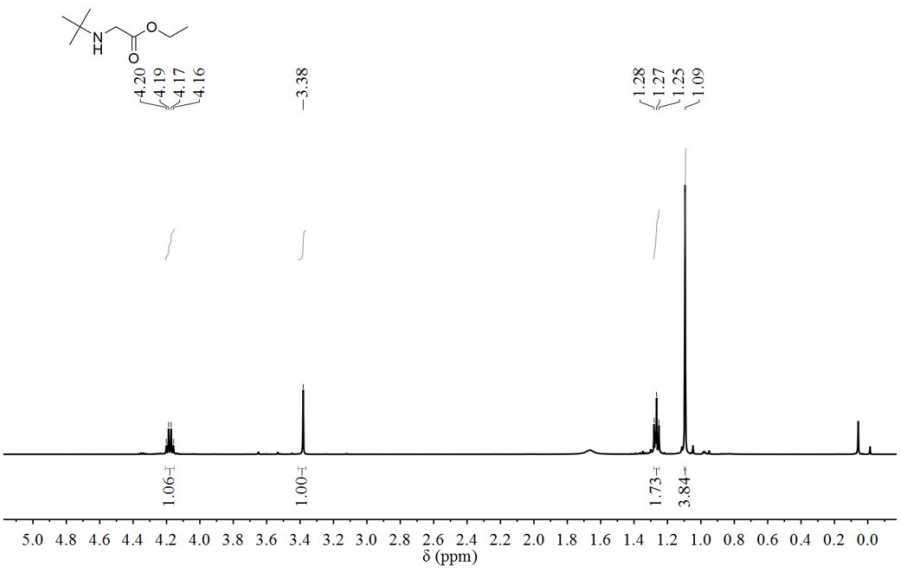

7.33
7.32
7.26
7.25
4.21
4.19
4.18
4.17
3.80
3.40
1.28
1.27
1.26
2.14
0.63
1.14
1.00
0.99
1.68
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)


4.17
4.15
4.14
4.13
3.16
2.51
2.50
2.49
1.62
1.61
1.61
1.60
1.59
1.58
1.43
1.43
1.42
1.42
1.41
1.40
1.40
1.39
1.39
1.25
1.24
1.22
1.01
1.00
2.01
2.07
1.09
1.86
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2
δ (ppm)


4.19
4.17
4.16
4.15
3.74
3.73
3.72
3.18
2.57
2.56
2.56
2.56
2.55
1.27
1.25
1.24
1.05
2.00
1.00
2.09
1.56
5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8 1.4 1.0 0.6 0.2 -0.2
δ (ppm)


4.18
4.17
4.15
4.14
3.29
2.66
2.64
2.63
2.61
1.27
1.25
1.24
1.06
1.04
1.03
1.03
1.00
2.02
1.67
3.08
5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
δ (ppm)


4.18
4.17
4.16
4.14
3.36
2.58
2.56
2.55
1.48
1.46
1.45
1.43
1.30
1.29
1.29
1.28
1.27
1.26
1.26
1.25
1.24
1.24
0.87
0.86
0.84
1.09
1.00
1.05
1.17
6.58
1.94
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


4.20
4.19
4.17
4.16
3.38
1.28
1.27
1.25
1.09
1.06
1.00
1.73
3.84
5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
δ (ppm)