Electronic Supplementary Information

A new copper-based metal-organic framework as a promising heterogeneous catalyst for chemo- and regio-selective enamination of β-ketoesters

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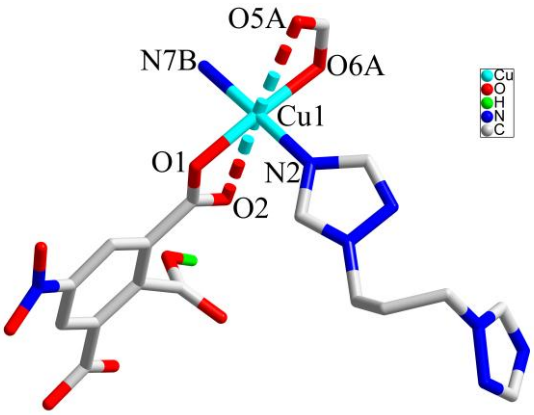


Fig. S1 Coordination environment of the Cu(II) ion in $\mathbf{A_1}$. Symmetry codes for A : 3/2 – *x*, 2 – *y*, 1/2 + *z*; B: 1 – *x*, 1/2 + *y*, 3/2 – *z*.

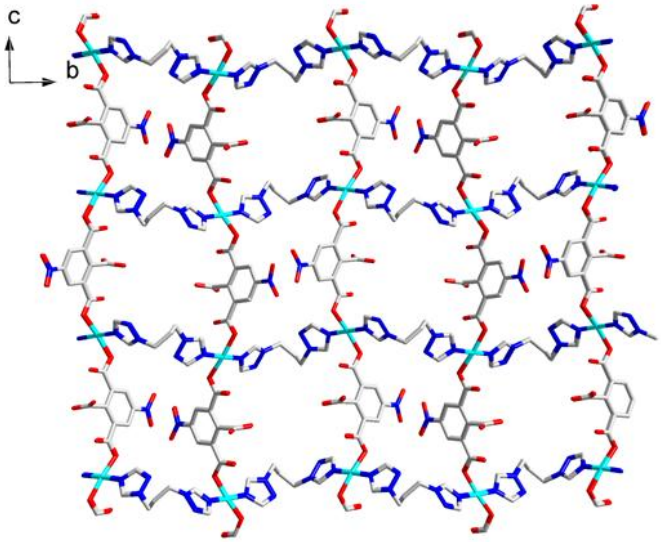
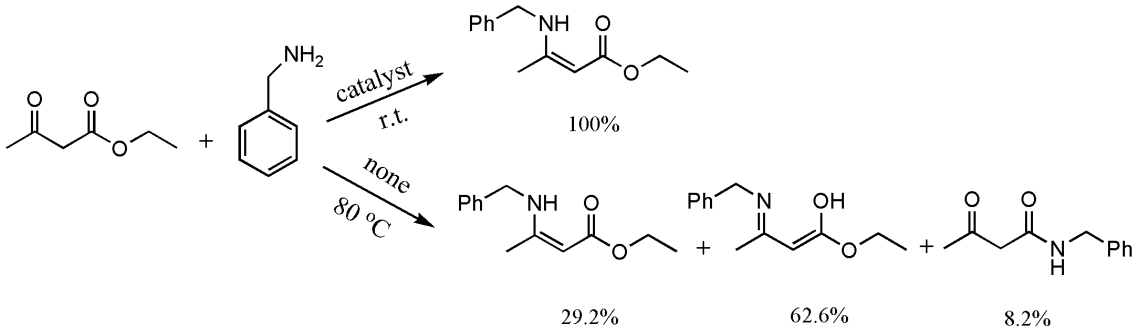


Fig. S2 Perspective view of the 3-D coordination network of $\mathbf{A_1}$. Free water molecules are omitted for clarity.



Scheme S1

Table S1 Synthesis of different β-enaminoesters in the presence of various catalysts

Product	Catalyst	Catalyst load	Time	Yield(%)	Ref.
1	$InBr_3$	1 mol. %	10 min	94	9a
1	A_1	5 mol. %	0.5 h	97	
2	$Sc(OTf)_3$	5 mol. %	1 h	95	9b
2	$InBr_3$	1 mol. %	50 min	98	9a
2	$MgSO_4$, $Zn(OAc)_2{\cdot}2H_2O$	Mg: 10 mol. % Zn: 5 mol. %	2 day	57	9c
2	A_1	5 mol. %	1 h	93	
3	$Sc(OTf)_3$	5 mol. %	2 h	93	9b
3	A_1	5 mol. %	2 h	92	
4	$InBr_3$	1 mol. %	1.5h	92	9a
4	A_1	5 mol. %	2h	92	
6	$Sc(OTf)_3$	5 mol. %	2.5 h	90	9b
6	$InBr_3$	1 mol. %	45 min	93	9a
6	A_1	5 mol. %	1 h	94	
7	$InBr_3$	1 mol. %	40 min	95	9a
7	A_1	5 mol. %	1 h	95	
8	$InBr_3$	1 mol. %	8 h	80	9a
8	A_1	5 mol. %	1 h	94	
11	$InBr_3$	1 mol. %	15 min	95	9a
11	A_1	5 mol. %	2 h	95	

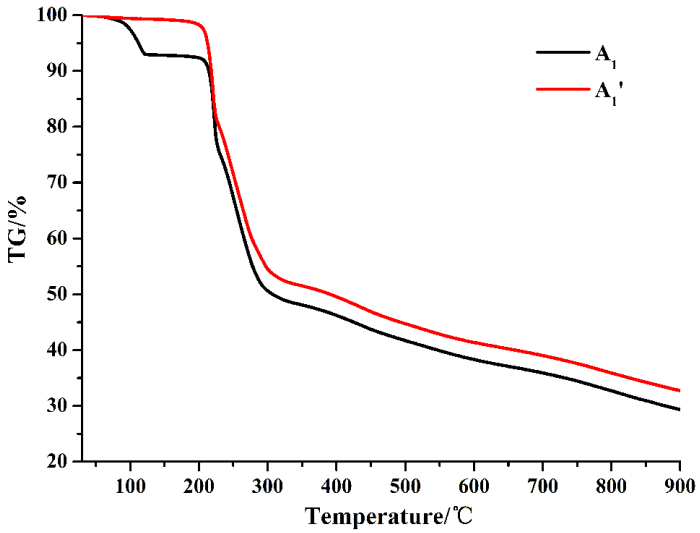


Fig. S3. TGA curves of complexes $\mathbf{A_1}$ and $\mathbf{A_1}$'.

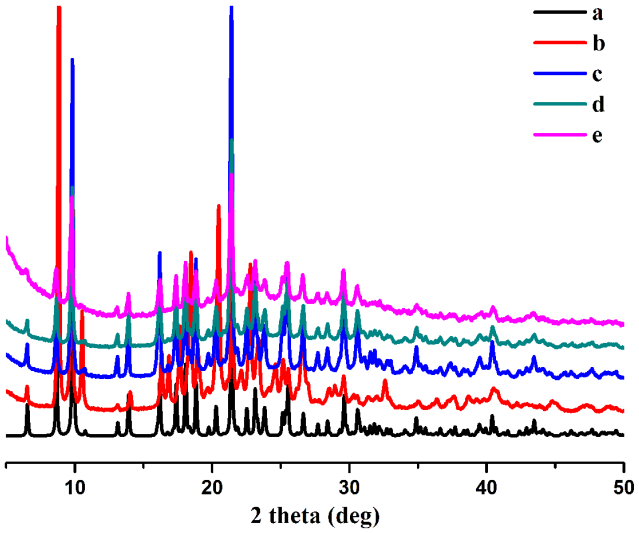


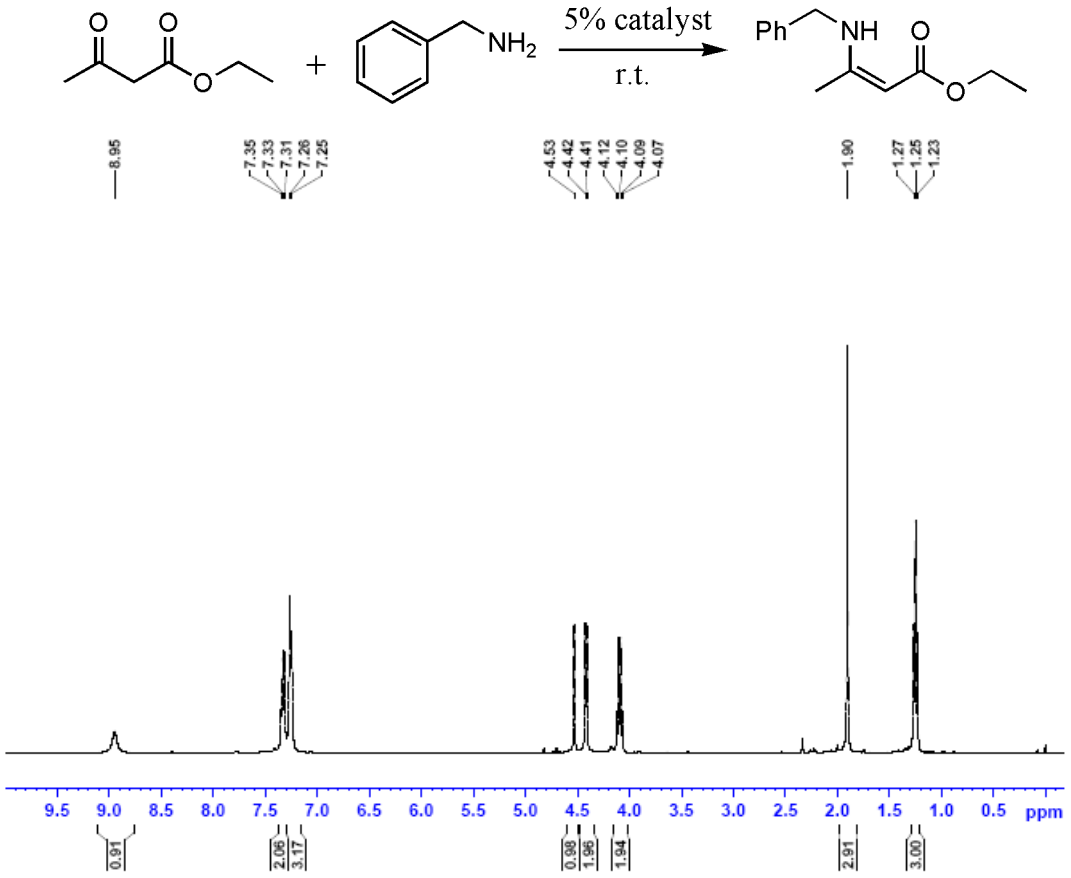
Fig. S4. PXRD patterns of $\mathbf{A_1}$: (a) the simulated pattern; (b) dehydrated solid obtained on heating at 120 °C for 4 h under vacuum; (c) after the first recycling; (d) after the second recycling; (e) after the third recycling.

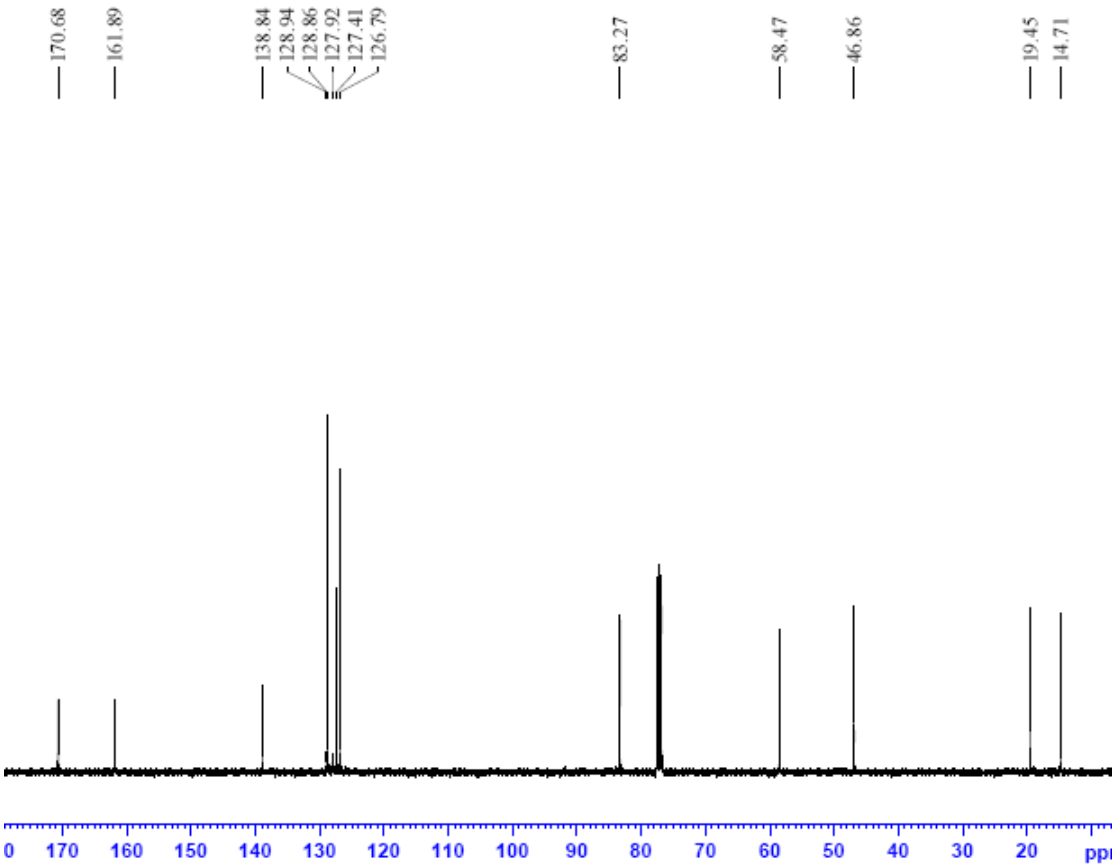
NMR data

^{1}H and ^{13}C NMR spectra were recorded on a Varian UNITY/NOVA 400 NMR spectrameter using $CDCl_3$ as solvent at room temperature. Chemical shifts are given in δ relative to TMS. The coupling constants J are given Hz.

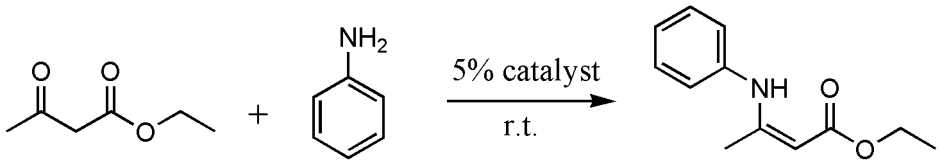
Compound **1**

Yellowish oil. ^{1}H NMR δ: 1.25 (t, J = 8.0 Hz, 3H), 1.90 (s, 3H), 4.07 (q, J = 8.0 Hz, 2H), 4.41 (d, J = 4 Hz), 4.53 (s, 1H), 7.25–7.33 (m, 5H), 8.95 (br s, 1H, NH); ^{13}C NMR δ: 14.71 (CH_3), 19.45 (CH_3), 46.86 (CH_2), 58.47 (OCH_3), 83.27 (=CH), 126.79 (CH arom), 127.41 (CH arom), 127.92 (CH arom), 128.86 (CH arom), 128.94 (CH arom), 138.84 (C arom), 161.89 (=C–NH), 170.68 (C=O).

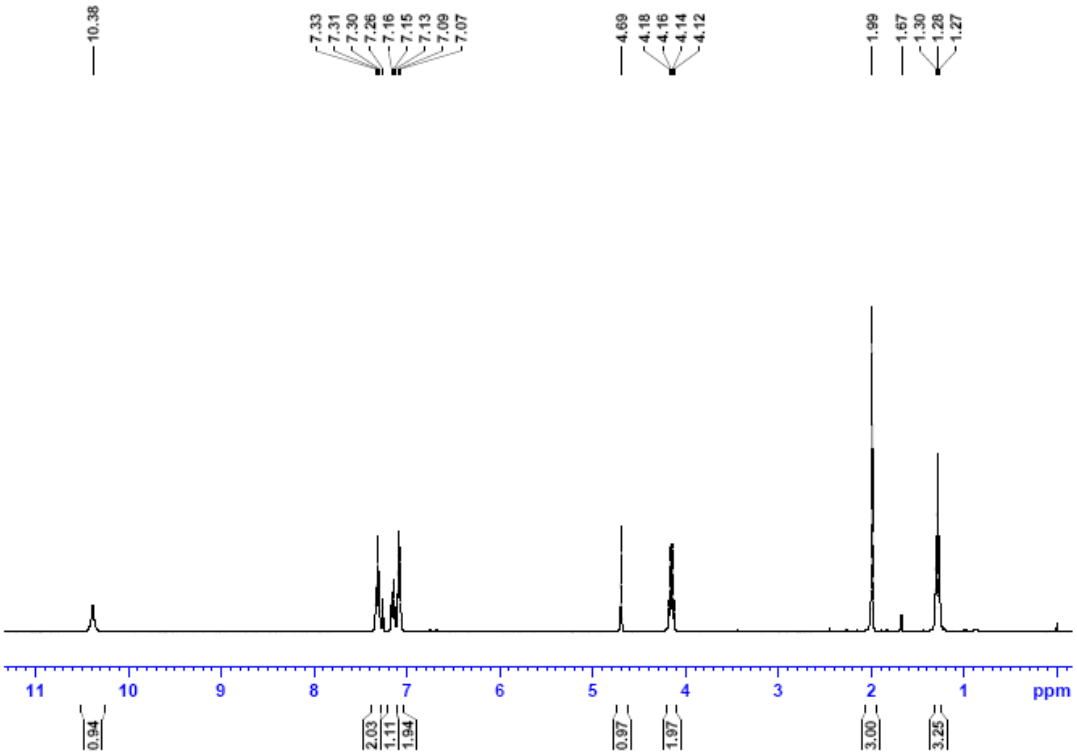


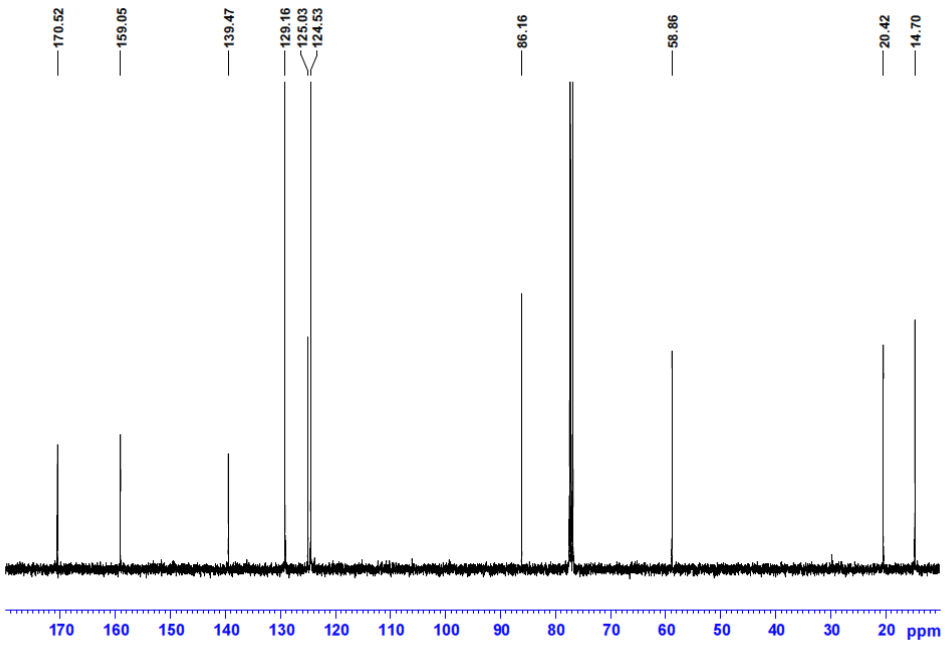


Compound **2**

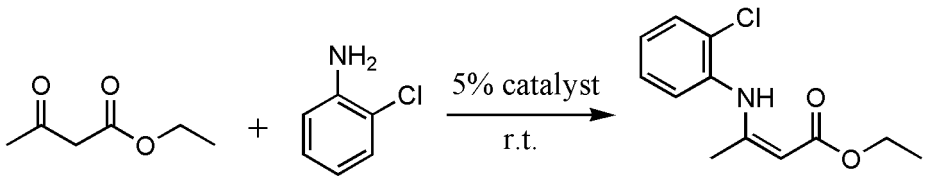


Yellowish oil. ^{1}H NMR δ: 1.27 (t, J = 8.0 Hz, 3H), 1.99 (s, 3H), 4.12 (q, J = 8.0 Hz, 2H), 4.69 (s, 1H), 7.07–7.16 (m, 3H), 7.26–7.33 (m, 2H), 10.38 (br s, 1H, NH); ^{13}C NMR δ: 14.70 (CH_3), 20.42 (CH_3), 58.86 (OCH_2), 86.16 (=CH), 124.53 (CH arom), 125.03 (CH arom), 129.16 (CH arom), 139.43 (C arom), 159.05 (=C–NH), 170.52 (C=O).

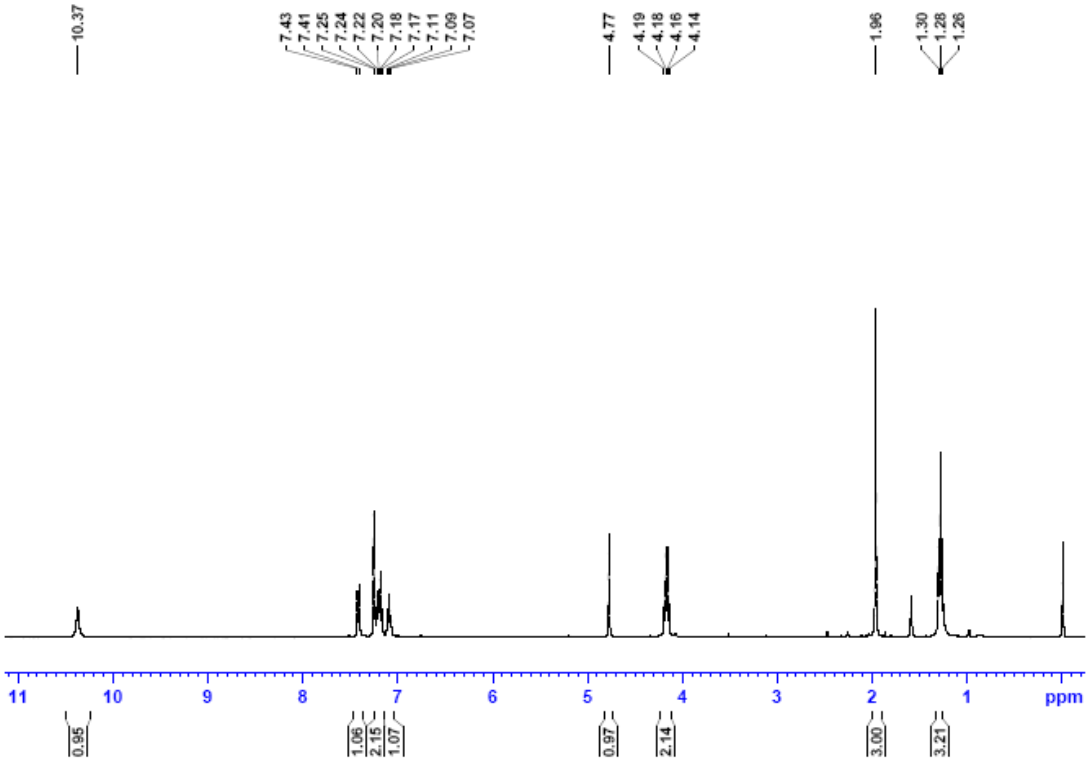


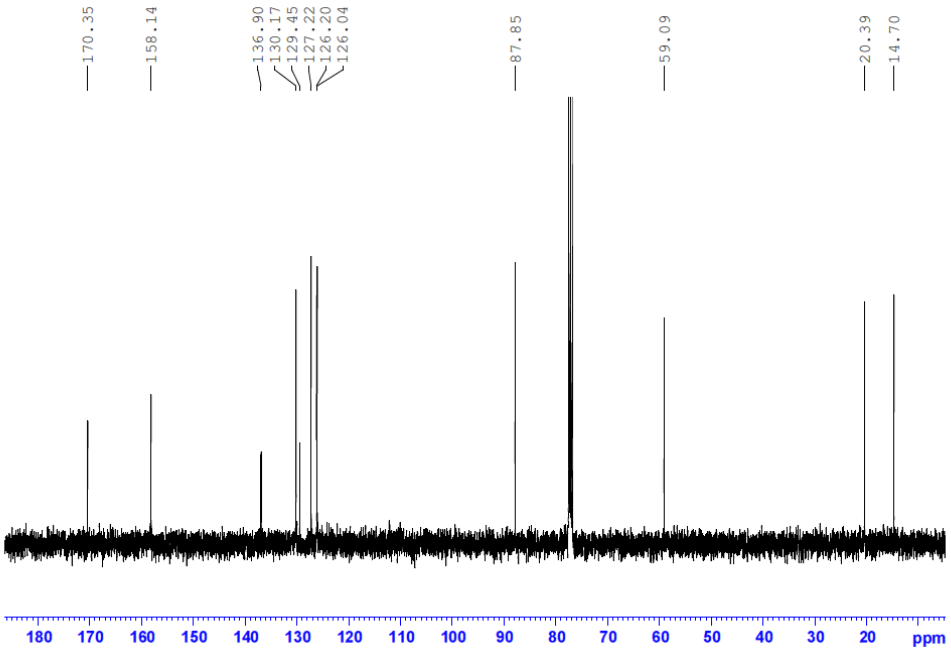


Compound **3**



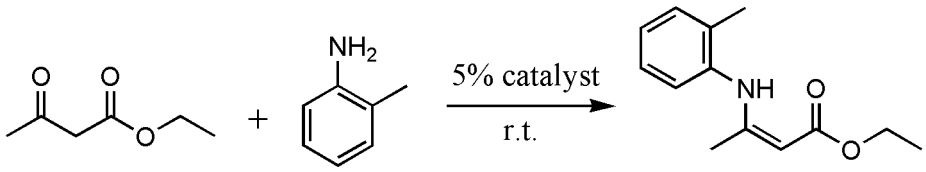
Yellowish oil. ^{1}H NMR δ: 1.26 (t, J = 8.0 Hz, 3H), 1.96 (s, 3H), 4.14 (q, J = 8.0 Hz, 2H), 4.77 (s, 1H), 7.07–7.25 (m, 3H), 7.41 (d, J = 8.0 Hz, 1H), 10.37 (br s, 1H, NH); ^{13}C NMR δ: 14.70 (CH_3), 20.39 (CH_3), 59.09 (OCH_2), 87.85 (=CH), 126.04 (CH arom), 126.20 (CH arom), 127.22 (CH arom), 129.45 (CH, arom), 130.17 (C, arom), 136.90 (C arom), 158.14 (=C–NH), 170.35 (C=O).

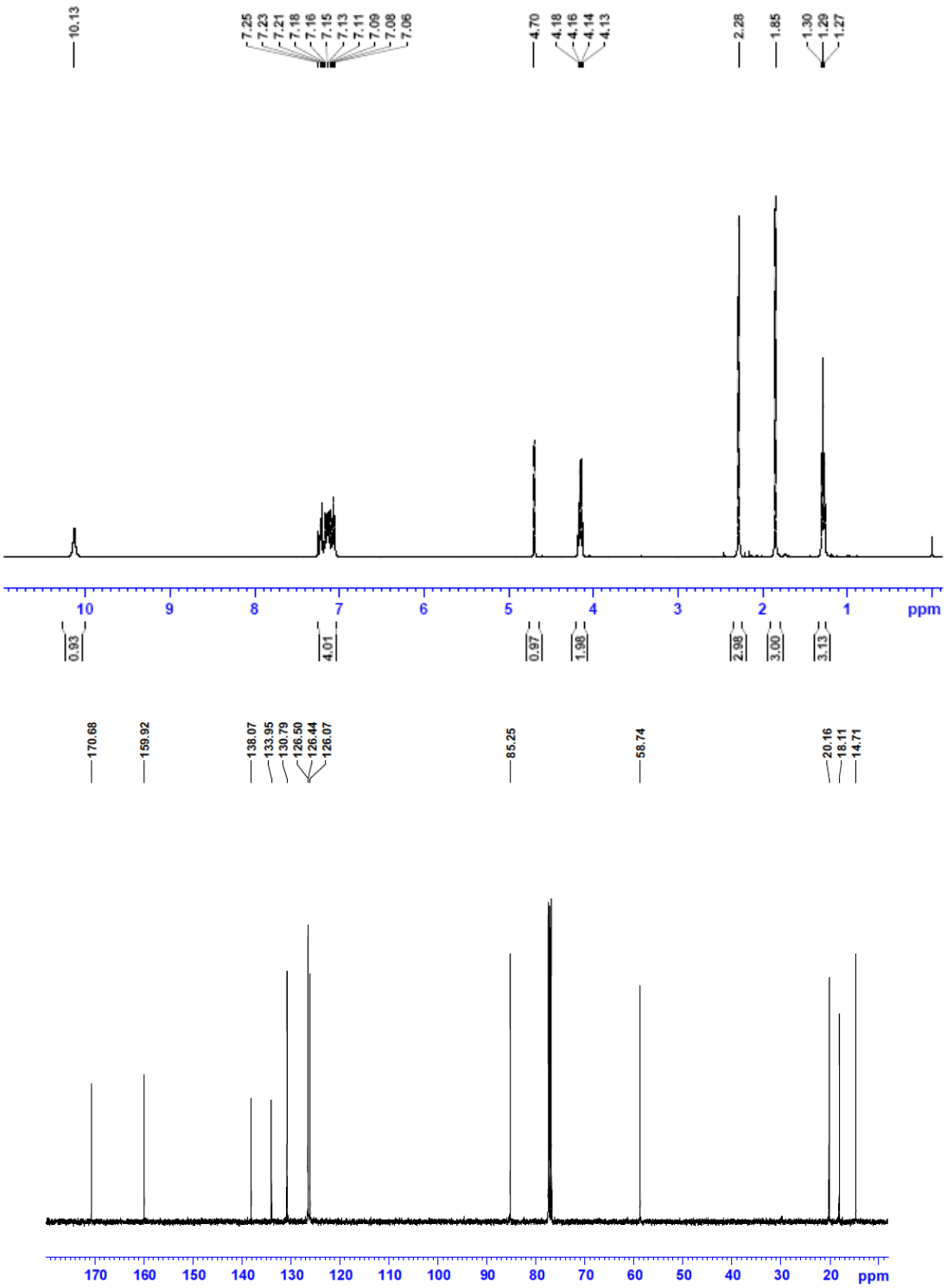




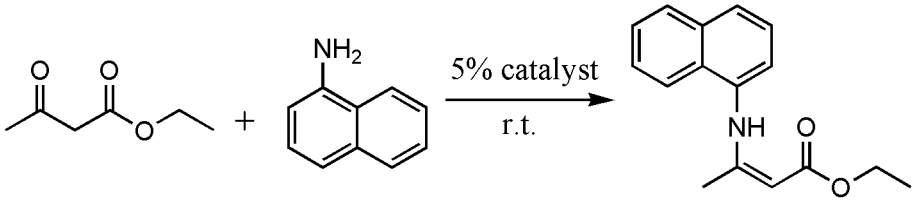
Compound **4**

Yellowish oil. ^{1}H NMR δ: 1.27 (t, J = 8.0 Hz, 3H), 1.85 (s, 3H), 2.28 (s, 3H), 4.13 (q, J = 8.0 Hz, 2H), 4.70 (s, 1H), 7.06–7.25 (m, 4H), 10.13 (br s, 1H, NH); ^{13}C NMR δ: 14.71 (CH_3), 18.11 (CH_3 arom), 20.16 (CH_3), 58.74 (OCH_2), 85.25 (=CH), 126.07 (CH arom), 126.44 (CH arom), 126.50 (CH arom), 130.79 (CH arom), 133.95 (C arom), 138.07 (C arom), 159.92 (=C–NH), 170.68 (C=O).

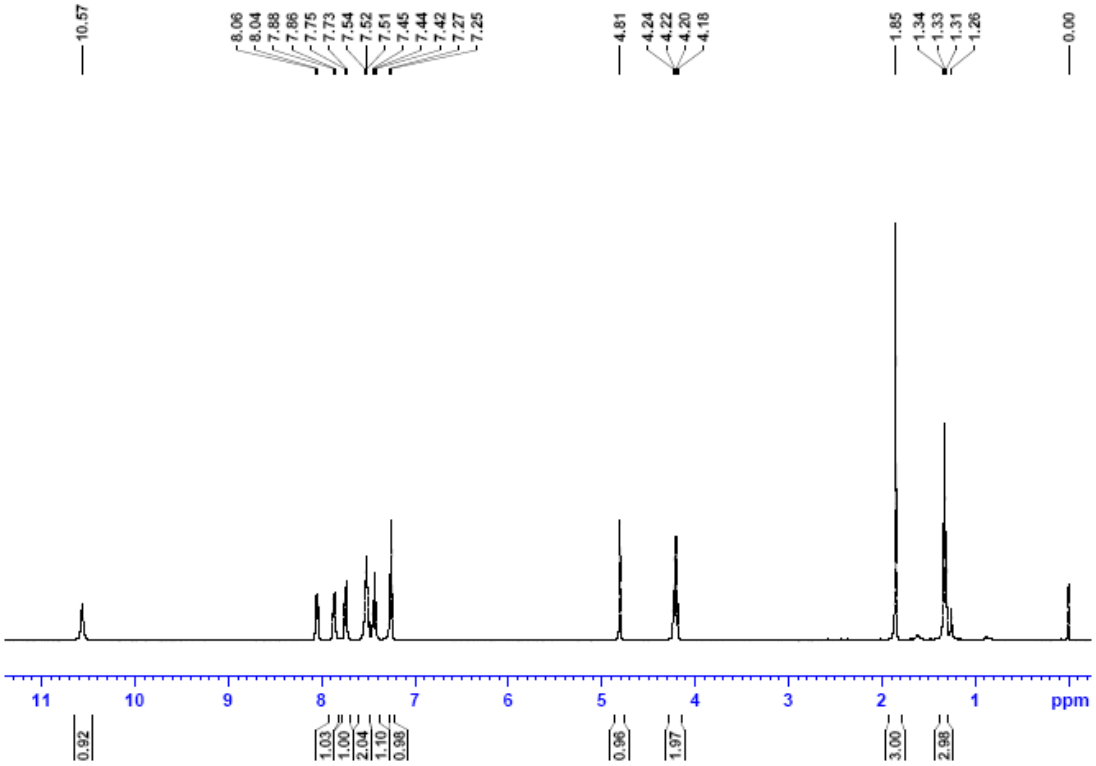


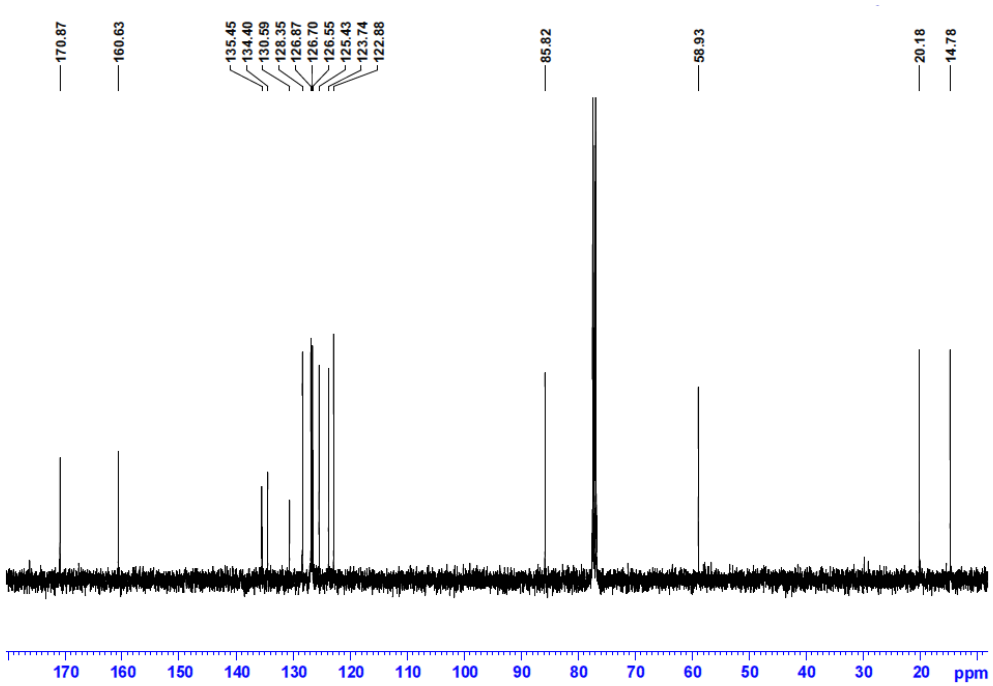


Compound **5**

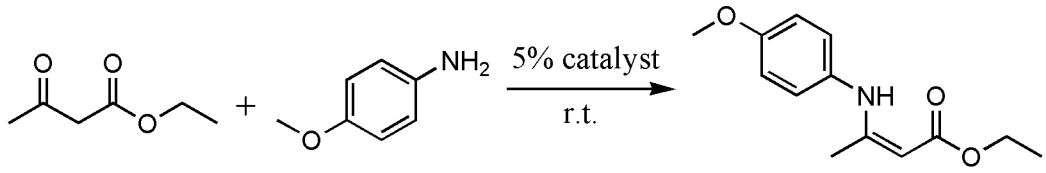


Pale yellow solid. ^{1}H NMR δ: 1.31 (t, J = 8.0 Hz, 3H), 1.85 (s, 3H), 4.16 (q, J = 8.0 Hz, 2H), 4.81 (s, 1H), 7.25–8.06 (m, 7H), 10.57 (br s, 1H, NH); ^{13}C NMR δ: 14.78 (CH_3), 20.16 (CH_3), 58.93 (OCH_2), 85.82 (=CH), 122.88 (CH naph), 123.74 (CH naph), 125.43 (CH naph), 126.55 (CH naph), 126.70 (CH naph), 126.87(CH naph),128.35 (CH naph), 130.59 (C naph), 134.40 (C naph), 135.45 (C naph), 160.63 (=C–NH), 170.87 (C=O).

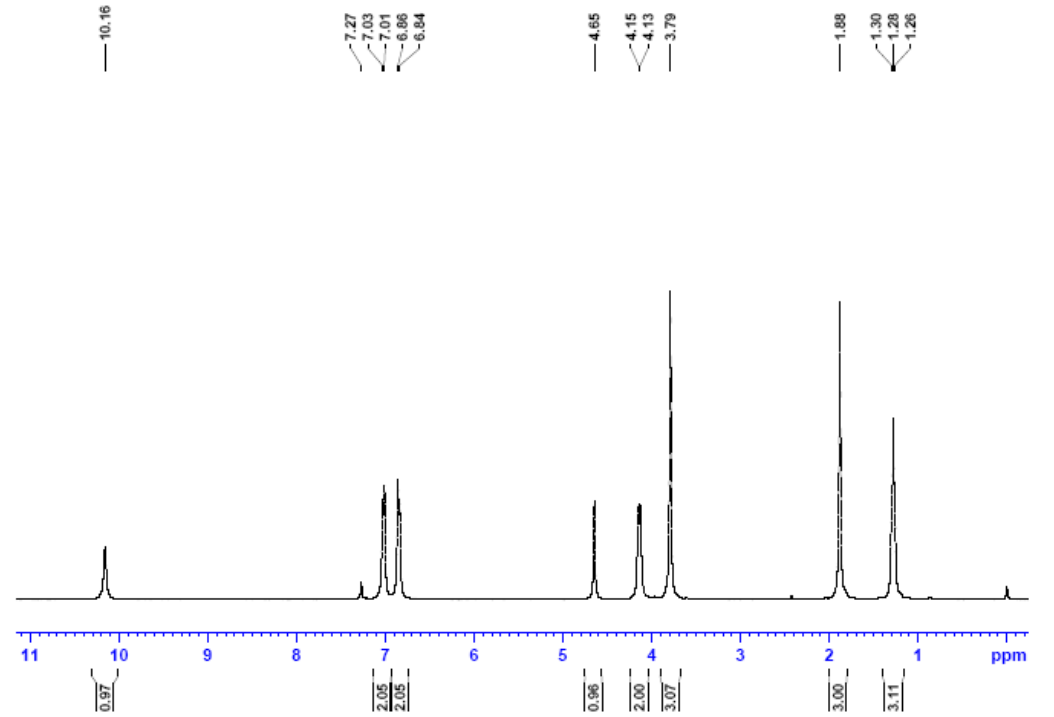


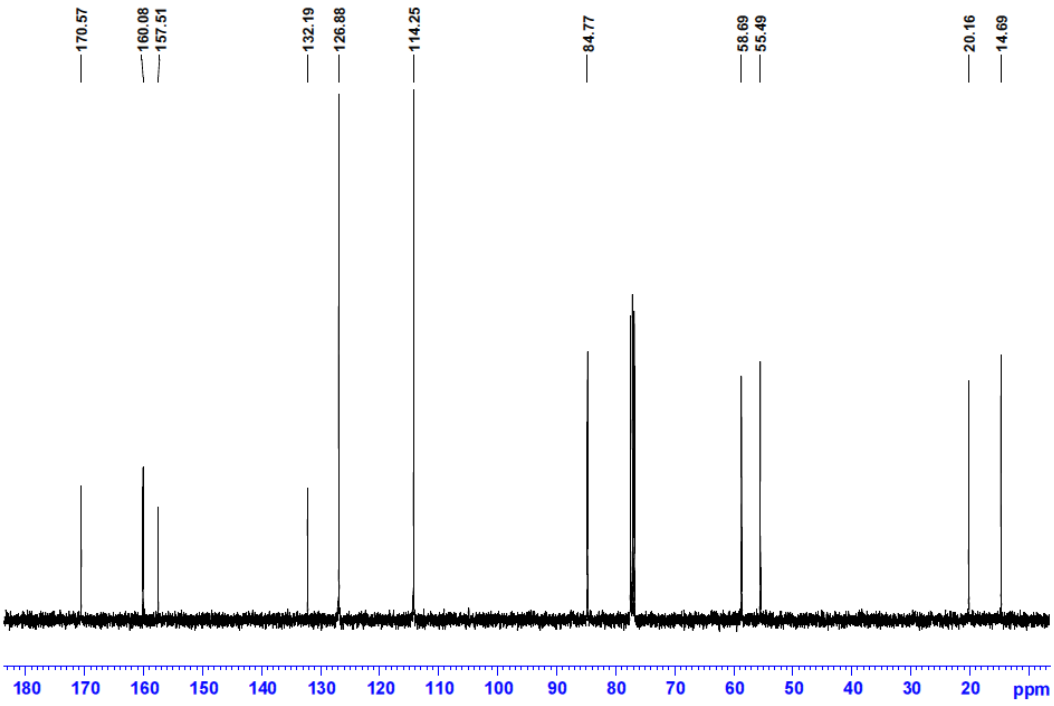


Compound **6**

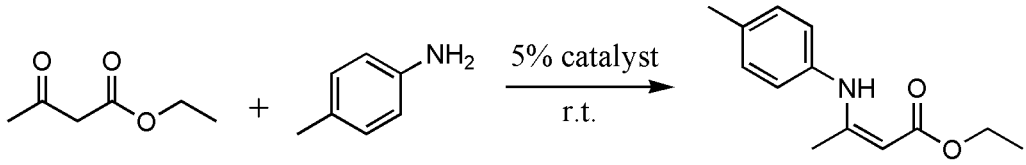


Pale yellow solid. ^{1}H NMR δ: 1.26 (t, J = 8.0 Hz, 3H), 1.88 (s, 3H), 3.79 (s, 3H), 4.13 (d, J = 8.0 Hz, 2H), 4.65 (s, 1H), 6.54 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 10.16 (br s, 1H, NH); ^{13}C NMR δ: 14.69 (CH_3), 20.16 (CH_3), 55.49 (OCH_3), 58.69 (OCH_2), 84.77 (=CH), 114.25 (CH arom), 126.88 (CH arom), 132.19 (CH arom), 157.51 (C arom), 160.08(=C–NH), 170.57 (C=O).

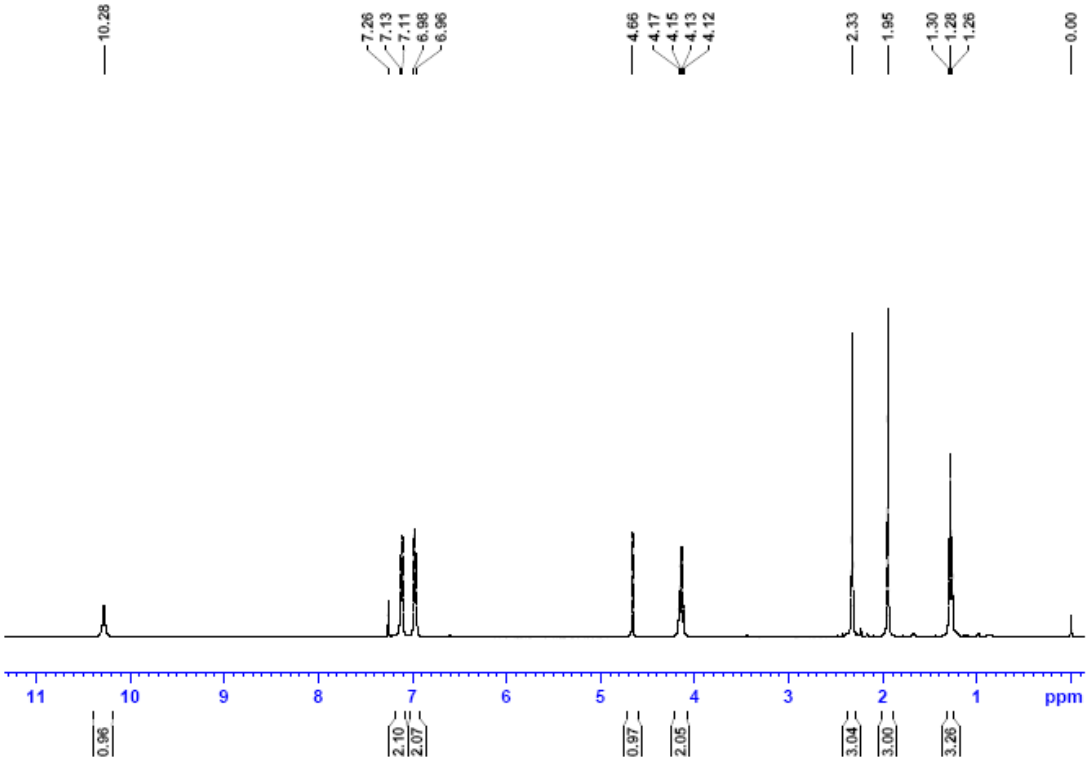


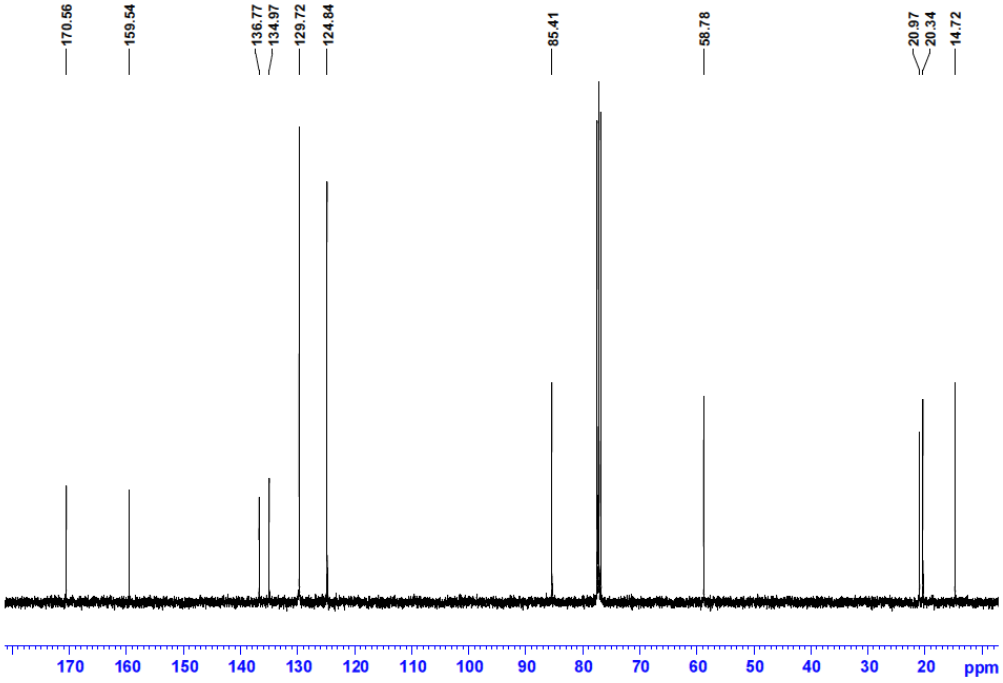


Compound **7**



Yellowish oil. ^{1}H NMR δ: 1.26 (t, J = 8.0 Hz, 3H), 1.95 (s, 3H), 2.33 (s, 3H), 4.12 (q, J = 8.0 Hz, 2H), 4.66 (s, 1H), 6.96 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 10.28 (br s, 1H, NH); ^{13}C NMR δ: 14.72 (CH_3), 20.34 (CH_3), 20.97 (CH_3), 58.78 (OCH_2), 85.41 (=CH), 124.84 (CH arom), 129.72 (CH arom), 134.97 (CH arom), 136.77 (C arom), 159.64 (=C–NH), 170.58 (C=O).





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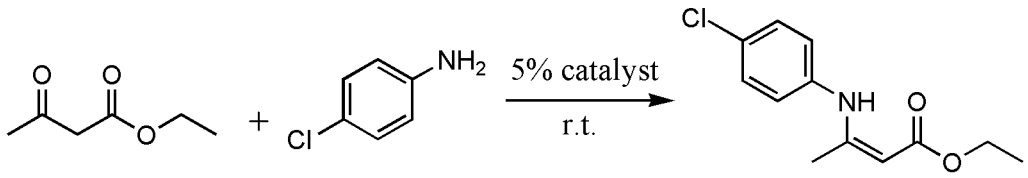
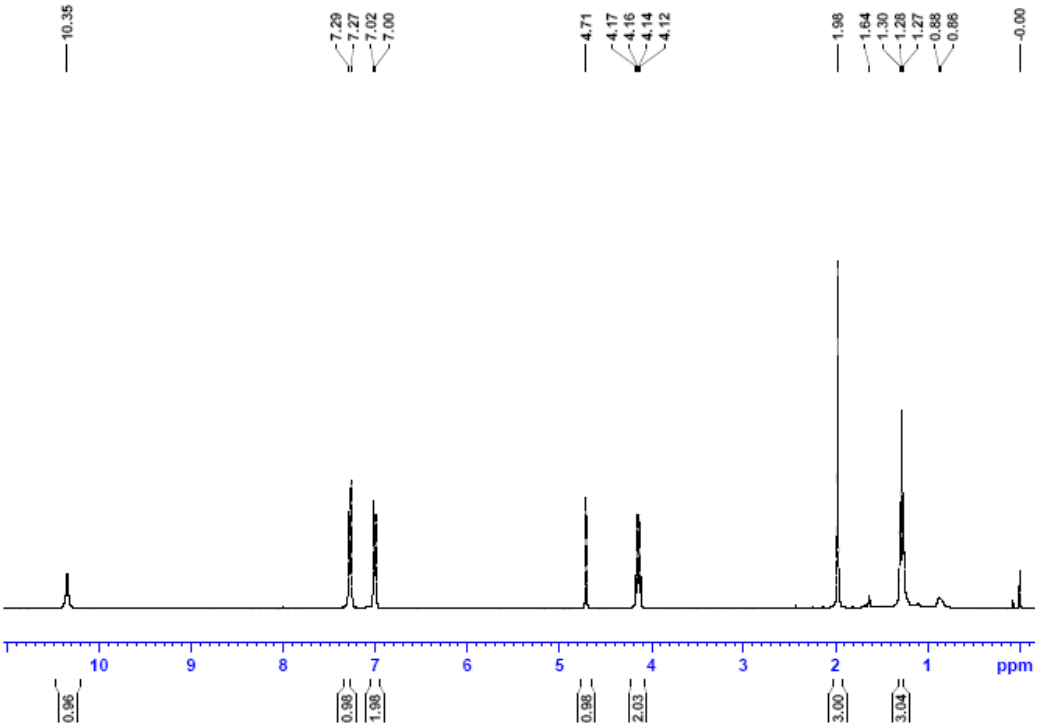
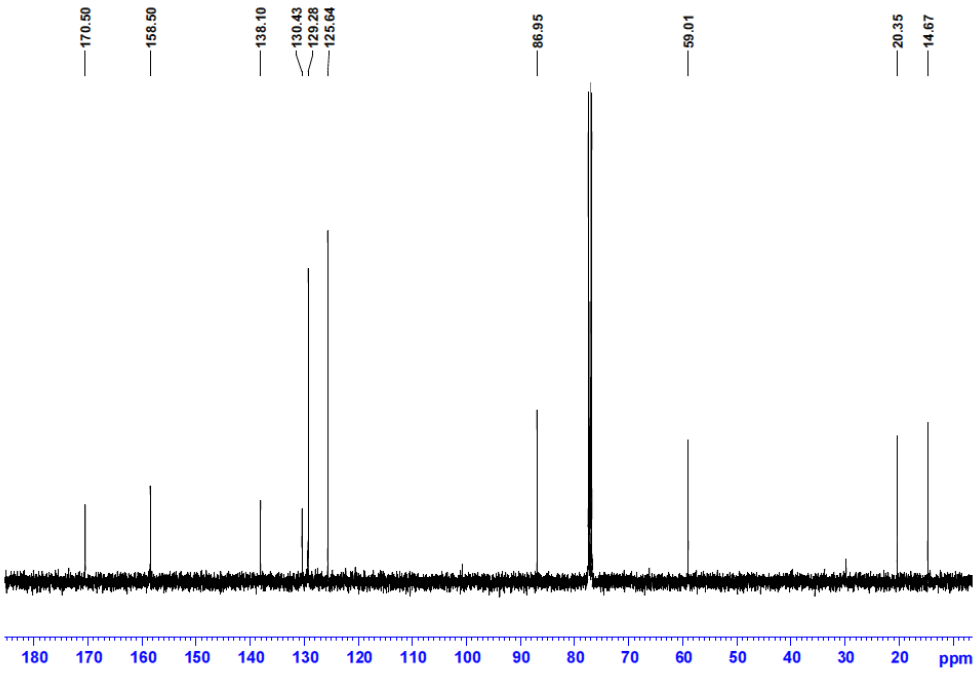
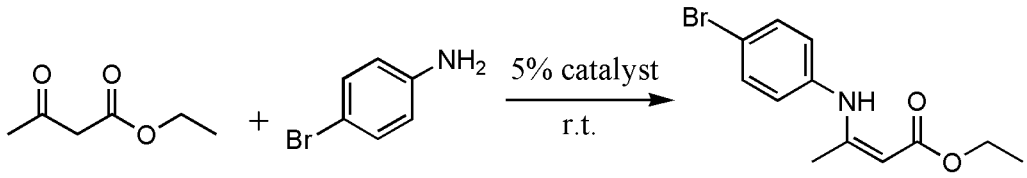


Pale yellow solid. ^{1}H NMR δ: 1.27 (t, J = 8.0 Hz, 3H), 1.99 (s, 3H), 4.12 (q, J = 8.0 Hz, 2H), 4.71 (s, 1H), 7.00 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 10.35 (br s, 1H, NH); ^{13}C NMR δ: 14.67 (CH_3), 20.36 (CH_3), 59.01 (OCH_2), 86.95 (=CH), 125.64 (CH arom), 129.23 (CH arom), 130.43 (CH arom), 138.10 (C arom), 158.50 (=C–NH), 170.50 (C=O).

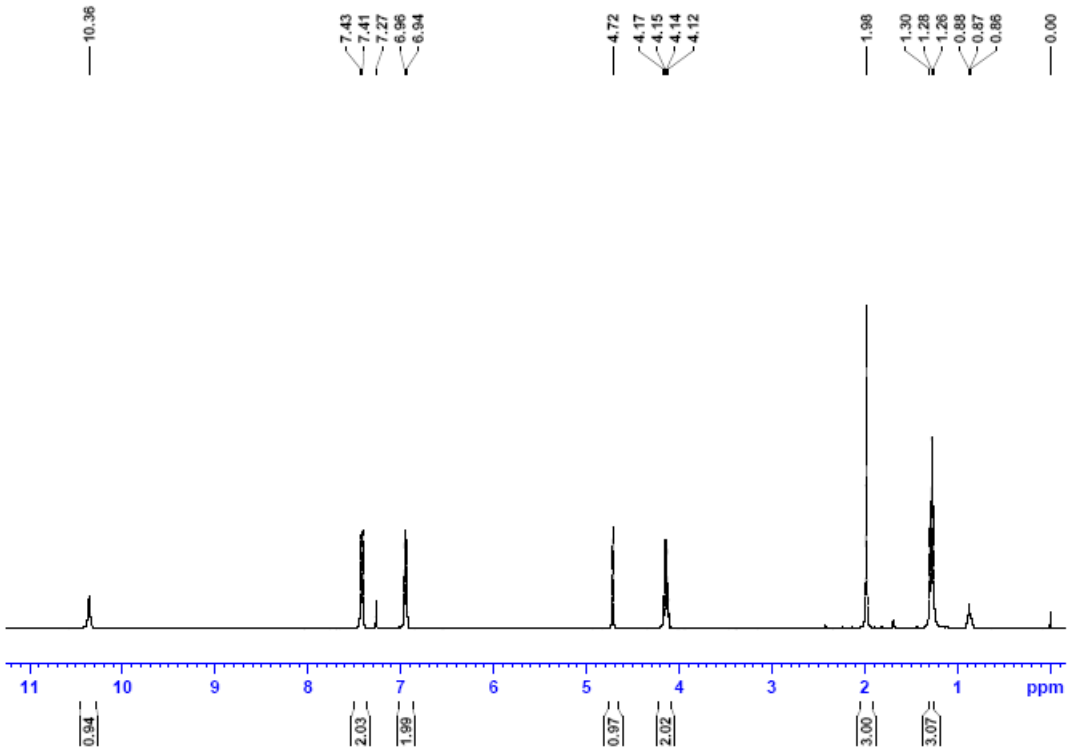


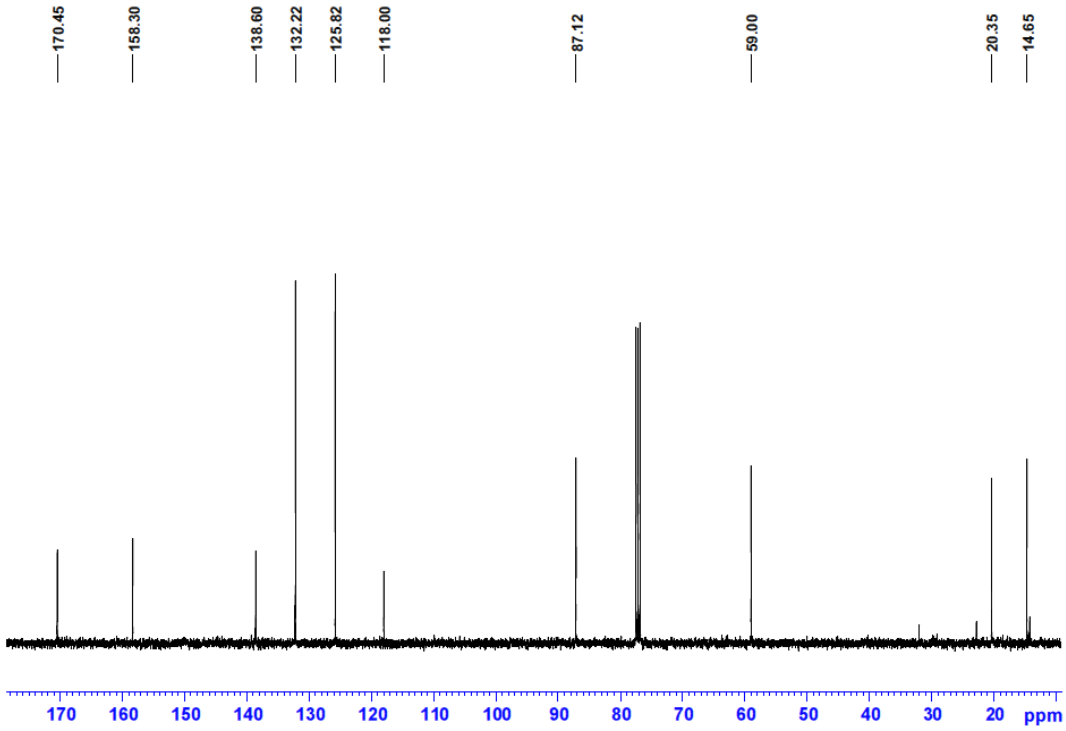


Compound **9**

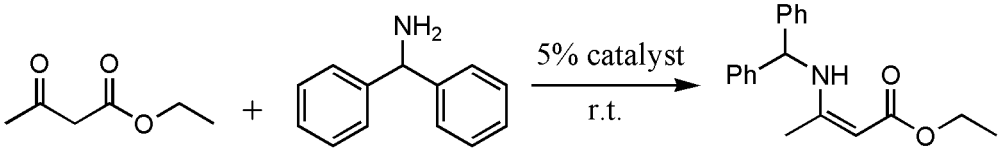


Pale yellow solid. ^{1}H NMR δ: 1.26 (t, J = 8.0 Hz, 3H), 1.98 (s, 3H), 4.12 (q, J = 8.0 Hz, 2H), 4.72 (s, 1H), 6.94 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 10.36 (br s, 1H, NH); ^{13}C NMR δ: 14.65 (CH_3), 20.35 (CH_3), 59.00 (OCH_2), 87.12 (=CH), 118.00 (CH arom), 125.82 (CH arom), 132.22 (CH arom), 138.60 (C arom), 158.30 (=C–NH), 170.45 (C=O).

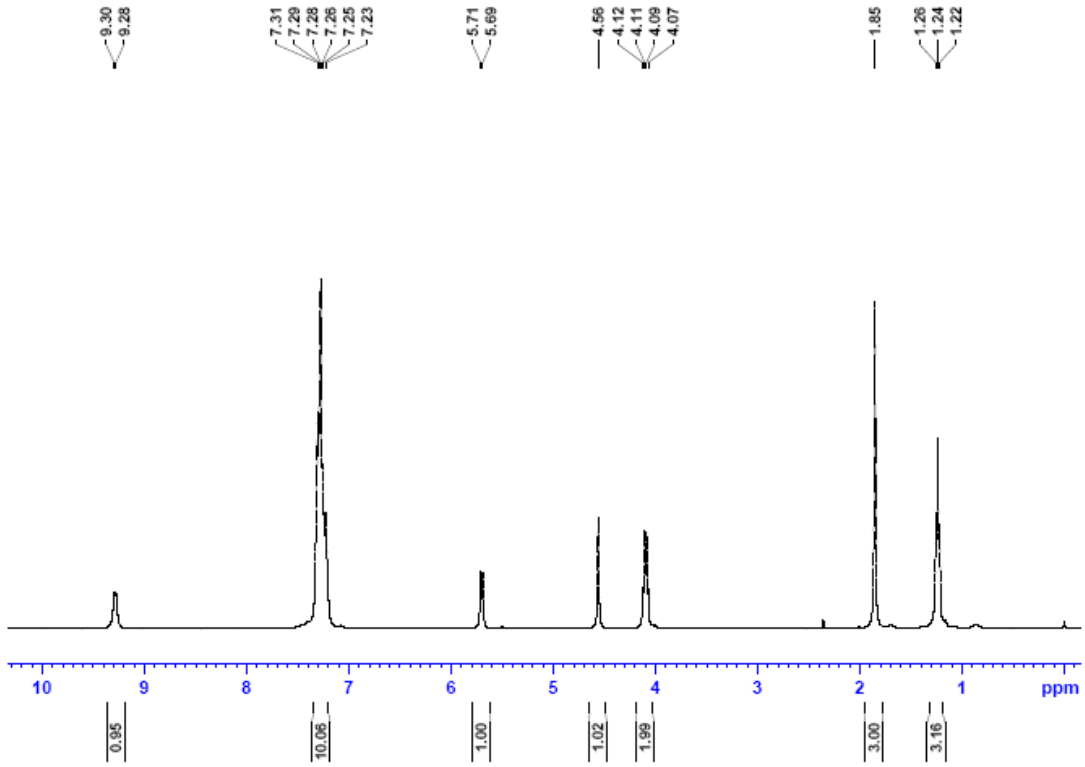


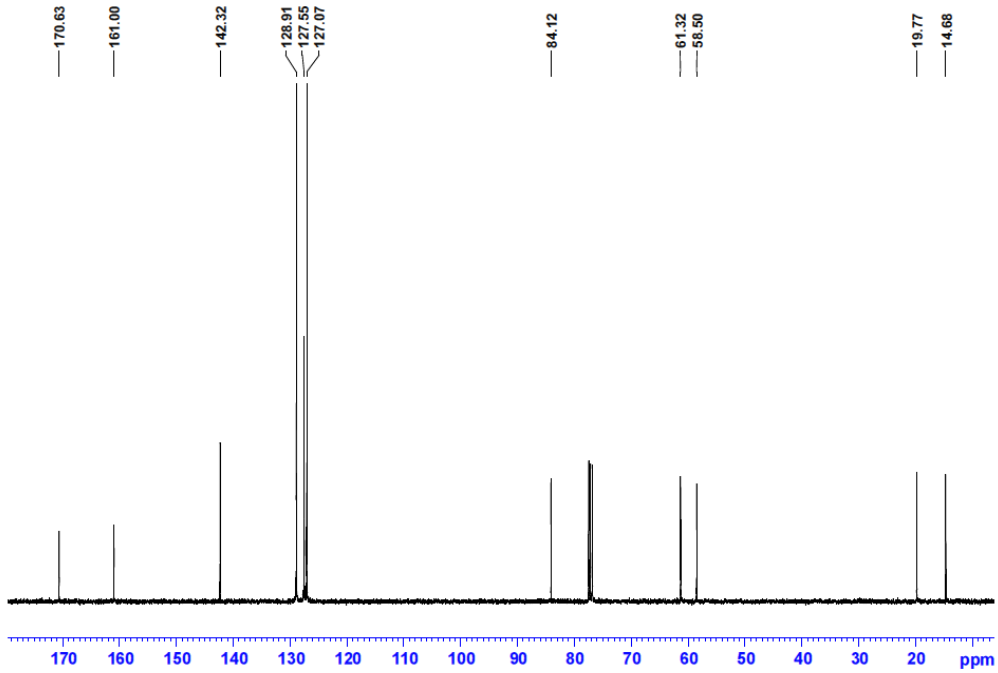


Compound **10**

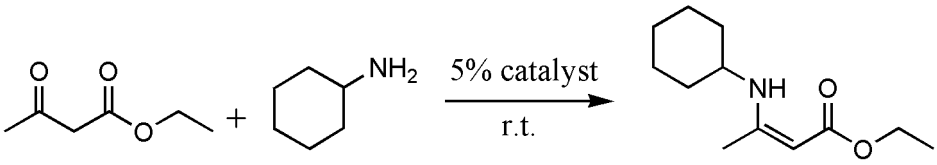


Pale yellow solid. ^{1}H NMR δ: 1.22 (t, J = 8.0 Hz, 3H), 1.85 (s, 3H), 4.07 (q, J = 8.0 Hz, 2H), 4.56 (s, 1H), 5.69 (d, J = 8.0 Hz, 1H), 7.23–7.31 (m, 10H), 9.28 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ: 14.68 (CH_3), 19.77 (CH_3), 58.50 (OCH_2), 61.32 (CH), 84.12 (=CH), 127.07 (CH arom), 127.55 (CH arom), 128.91 (CH arom), 142.32 (C arom), 161.00 (=C–NH), 170.63 (C=O).





Compound **11**



Yellowish oil. ^{1}H NMR δ: 1.23–1.93 (m, 16H), 3.30 (s, 1H), 4.06 (q, J = 8.0 Hz, 2H), 4.39 (s, 1H), 8.64 (br s, 1H, NH); ^{13}C NMR δ: 14.82 (CH_3), 19.37 (CH_3), 24.82 (CH_2), 25.52 (CH_2), 34.42 (CH_2), 51.57 (CH), 58.30 (OCH_2), 81.75 (=CH), 160.98 (=C–NH), 170.75 (C=O).