Supporting information

Magnetically recyclable magnetite-ceria (NanocatFe-Ce) nanocatalysts - Applications in multicomponent reactions under benign conditions

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1. General Methods

All commercial reagents were used as received unless otherwise mentioned. For analytical and preparative thin-layer chromatography, Merck, 0.2 mm and 0.5 mm Kieselgel GF 254 percoated were used, respectively. The spots were visualized using UV light.

The X-ray powder diffraction pattern was obtained using a conventional powder diffractometer RIGAKU, model: MiniFlex™ II benchtop X-ray Diffractometer; X-ray tube: Cu-Kα (30 kV / 15 mA) radiation operating in Bragg-Brentano (θ/2θ) geometry. (Sample preparation: grinding when needed and compression in the sample holder with a flat glass. The sample area in the sample holder is about 2 cm^2).

Transmission electron microscopy (TEM) experiments were performed on a Hitachi H8100 microscope, with a ThermoNoran light elements EDS detector and a CCD camera for image acquisition. The Fe_3O_4-CeO_2 fine powder was placed on carbon stub and the images were recorded at 5-15 kV using LFD detector under low vacuum.

Elemental analysis was done by using ICP-AES (Inductively coupled plasma-atomic emission spectrometer) using a Horiba Jobin-Yvon, France, Ultima, model equipped with a 40.68 MHz RF generator, Czerny-Turner monochromator with 1.00 m (sequential), autosampler AS500 and CMA (concomitant metals analyzer).

Scanning electron microscopy images were acquired using a JEOL JSM7001F FEG-SEM.

Elemental analysis was performed using a light elements EDS detector from Oxford. The Fe_3O_4-CeO_2 powder was spread on a double-sided carbon tape and analyzed using 25kV acceleration voltage.

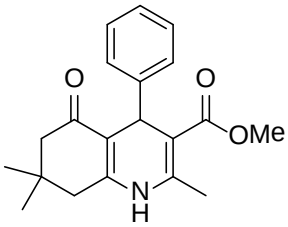
For SIMS, (secondary ion mass spectrometry) positive secondary ion spectra were collected in the mass range of 0 -100 m/z (T=10 min) with an upgraded VG Ionex IX23LS TOF-SIMS set-up based on the Poschenrieder design. A focused liquid Ga^+ gun in pulsed mode (6 kHz) was used as a source of the analytical ions. A beam current in dc mode at 14 keV was ca. 15 nA with a raster size of 300 X 300 μm2. Sample potential was 5 kV. Vacuum during the experiments was maintained in the range of (2-3) $X10^{-9}$ mbar in the analytical chamber.

XPS measurements were performed on VSW XPS system with the Class 100 energy analyzer being a part of an experimental setup assembled for surface investigation. The

spectra were taken in fixed analyzer transmission mode with the pass energy of 22 eV i.e. FAT 22. Fe_3O_4-CeO_2 fine powder was prepared for XPS by pressing on an Indium plate as a matrix in order to reduce the charging problems and providing a mechanical support. For the energy axis calibration Ag(110) and polycrystalline Au samples (previously cleaned by ion sputtering) were used.

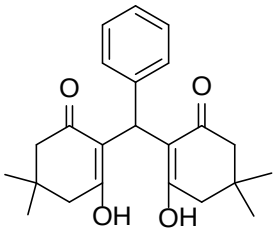
NMR spectra were recorded on a Bruker 400, 5 mm probe at 400 MHz.

2. Characterization of 1,4-dihydropyridines



1a

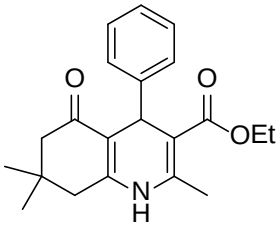
2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid methyl ester (1a).[1] Yield= 93%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.29 (2H, d, *J*= 8.0 Hz, ArH), 7.20 (2H, t, *J*= 8.0 Hz, ArH), 7.10 (1H, t, *J*= 8.0 Hz, ArH), 5.82 (1H, bs, NH), 5.07 (1H, s, CH), 3.61 (3H, s, OCH_3), 2.39 (3H, s, CH_3), 2.21-2.14 (4H, m, CH_2), 1.07 (3H, s, CH_3), 0.93 (3H, s, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 195.6, 168.0, 147.9, 146.9, 143.8, 128.1, 127.9, 126.2, 112.5, 105.9, 51.2, 50.9, 41.4, 36.4, 32.9, 29.6, 27.3, 19.7.



1a'

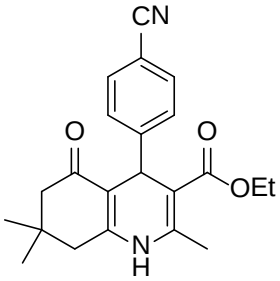
Bis-adduct

2,2'-(phenylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) (1a').[2] Yield= 25%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.24-7.07 (5H, m, ArH), 5.07 (1H, s, CH), 2.46-2.27 (8H, m, CH_2), 1.21 (6H, s, CH_3), 1.08 (6H, s, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 190.5, 189.5, 138.2, 128.3, 126.9, 125.9, 115.7, 47.2, 46.6, 32.9, 31.6, 29.8, 27.6.



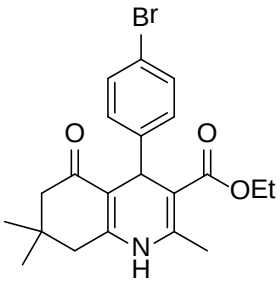
1b

2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (1b).[1,3] Yield= 95%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.27 (2H, d, *J*= 8.0 Hz, ArH), 7.16 (2H, t, *J*= 8.0 Hz, ArH), 7.06 (1H, t, *J*= 8.0 Hz, ArH), 6.07 (1H, bs, NH), 5.02 (1H, s, CH), 4.01 (2H, m, CH_2CH_3), 2.33 (3H, s, CH_3), 2.27-2.10 (4H, m, CH_2), 1.16 (3H, t, *J*= 8.0 Hz, CH_2CH_3), 1.04 (3H, s, CH_3), 0.90 (3H, s, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 195.6, 167.6, 148.3, 147.2, 143.6, 128.1, 128.0, 126.1, 112.3, 106.2, 59.9, 50.9, 41.2, 36.7, 32.8, 29.6, 27.3, 19.5, 14.4.



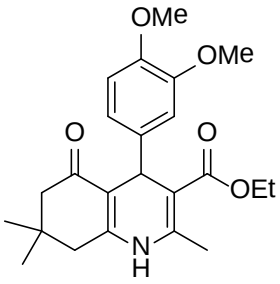
1c

Ethyl 4-(4-cyanophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (1c).[4] Yield= 92%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.49 (2H, d, *J*= 8.0 Hz, ArH), 7.42 (2H, d, *J*= 8.0 Hz, ArH), 6.11 (1H, bs, NH), 5.09 (1H, s, CH), 4.04 (2H, m, CH_2CH_3), 2.39 (3H, s, CH_3), 2.33-2.11 (4H, m, CH_2), 1.16 (3H, t, *J*= 8.0 Hz, CH_2CH_3), 1.07 (3H, s, CH_3), 0.90 (3H, s, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 195.4, 167.0, 152.4, 148.6, 144.4, 1321.0, 129.0, 119.4, 111.4, 109.7, 105.1, 60.2, 50.7, 41.2, 37.4, 29.5, 27.2, 19.6, 14.3.



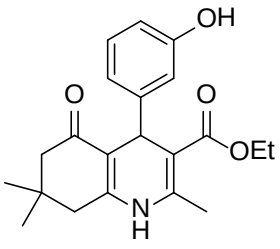
1d

4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (1d).[3] Yield= 90%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.31 (2H, d, *J*= 8.0 Hz, ArH), 7.18 (2H, d, *J*= 8.0 Hz, ArH), 5.97 (1H, bs, NH), 5.01 (1H, s, CH), 4.05 (2H, m, CH_2CH_3), 2.37 (3H, s, CH_3), 2.30-2.12 (4H, m, CH_2), 1.19 (3H, t, *J*= 8.0 Hz, CH_2CH_3), 1.07 (3H, s, CH_3), 0.92 (3H, s, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 195.5, 167.3, 148.1, 146.2, 143.7, 131.1, 130.0, 119.9, 112.0, 105.8, 60.1, 50.8, 41.3, 32.9, 29.6, 27.3, 19.6, 14.4.



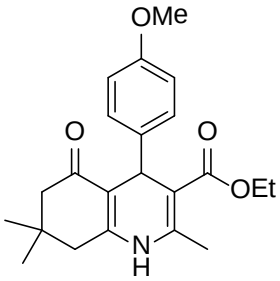
1e

4-(3,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (1e).[5] Yield= 92%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.90 (1H, s, ArH), 6.83 (1H, s, NH), 6.77 (1H, d, *J*= 8.0 Hz, ArH), 6.68 (1H, d, *J*= 8.0 Hz, ArH), 4.99 (1H, s, CH), 4.06 (2H, m, CH_2CH_3), 3.80 (3H, s, OCH_3), 3.77 (3H, s, OCH_3), 2.33 (3H, s, CH_3), 2.27-2.11 (4H, m, CH_2), 1.20 (3H, t, *J*= 8.0 Hz, CH_2CH_3), 1.02 (3H, s, CH_3), 0.92 (3H, s, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 195.90, 167.67, 148.90, 148.33, 147.26, 143.62, 140.25, 119.86, 110.87, 106.06, 59.86, 55.83, 50.87, 40.89, 36.07, 32.67, 29.59, 27.09, 19.30, 14.41.



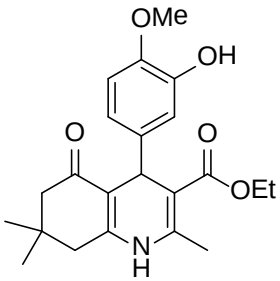
1f

4-(3-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (1f).[6] Yield= 83%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.04 (1H, t, *J*= 8.0 Hz, ArH), 6.85 (2H, m, ArH), 6.59 (1H, d, *J*= 8.0 Hz, ArH), 5.84 (1H, bs, NH), 5.28 (1H, bs, OH), 5.03 (1H, s, CH), 4.09 (2H, m, CH_2CH_3), 2.38 (3H, s, CH_3), 2.22 (4H, m, CH_2), 1.19 (3H, t, *J*= 8.0 Hz, CH_2CH_3), 1.07 (3H, s, CH_3), 0.94 (3H, s, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 193.8, 166.4, 156.0, 148.4, 148.1, 143.6, 127.7, 118.5, 114.2, 111.9, 110.4, 104.1, 58.3, 49.9, 39.4, 35.4, 31.5, 25.9, 17.5, 13.2.



1g

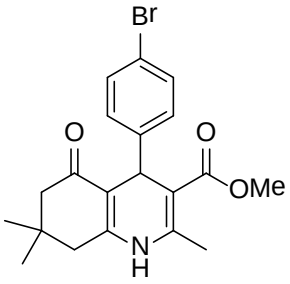
4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (1g).[1,7] Yield= 90%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.20 (2H, d, *J*= 8.0 Hz, ArH), 6.72 (2H, d, *J*= 8.0 Hz, ArH), 6.68 (1H, s, NH), 4.98 (1H, s, CH), 4.04 (2H, m, CH_2CH_3), 3.71 (3H, s, OCH_3), 2.33 (3H, s, CH_3), 2.28-2.10 (4H, m, CH_2), 1.20 (3H, t, *J*= 8.0 Hz, CH_2CH_3), 1.04 (3H, s, CH_3), 0.92 (3H, s, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 195.9, 167.7, 157.9, 148.8, 143.8, 143.6, 139.8, 129.0, 113.3, 112.2, 106.3, 59.9, 55.2, 50.9, 41.0, 35.9, 32.8, 29.6, 27.3, 19.4, 14.4.



1h

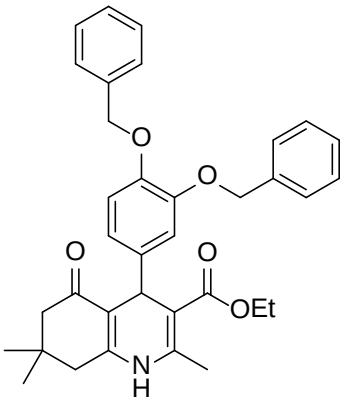
4-(3-hydroxy-4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ester (1h). Yield= 86%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.86 (1H, d, *J*= 8.0 Hz, ArH), 6.82 (1H, s, ArH), 6.68 (1H, d, *J*= 8.0 Hz, ArH), 6.00 (1H, bs, NH), 5.56 (1H, bs, OH), 4.97 (1H, s, CH), 4.07 (2H, q, *J=8.*0, ,

CH$_2$CH$_3$), 3.80 (3H, s, OCH$_3$), 2.34 (3H, s, CH$_3$), 2.28-2.13 (4H, m, CH$_2$), 1.22 (3H, t, *J*= 8.0 Hz, CH$_2$*CH*$_3$), 1.06 (3H, s, CH$_3$), 0.95 (3H, s, CH$_3$). ^{13}C-NMR (CDCl$_3$, 100 MHz) δ (ppm): 195.7, 167.6, 148.0, 145.0, 143.2, 140.7, 120.1, 114.1, 112.4, 110.1, 106.3, 60.0, 56.0, 50.9, 41.3, 36.1, 32.9, 29.5, 27.5, 19.6, 14.4.



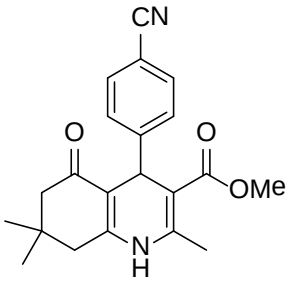
1i

4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid methyl ester (1i).[8] Yield= 92%. ^{1}H-NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.31 (2H, d, *J*= 8.0 Hz, ArH), 7.17 (2H, t, *J*= 8.0 Hz, ArH), 6.73 (1H, bs, NH), 5.01 (1H, s, CH), 3.60 (3H, s, OCH$_3$), 2.34 (3H, s, CH$_3$), 2.30-2.11 (4H, m, CH$_2$), 1.19 (3H, t, *J*= 8.0 Hz, CH$_2$*CH*$_3$), 1.05 (3H, s, CH$_3$), 0.90 (3H, s, CH$_3$). ^{13}C-NMR (CDCl$_3$, 100 MHz) δ (ppm): 195.9, 167.8, 149.2, 146.1, 144.5, 131.1, 129.8, 120.0, 113.5, 111.6, 105.3, 51.2, 50.9, 40.9, 36.3, 32.8, 29.6, 27.2, 19.4.



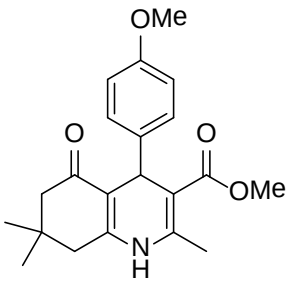
1j

4-(3,4-bis(benzyloxy)phenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxilic acid ethyl ester (1j).[9] Yield= 85%. ^{1}H-NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.42-7.28 (10H, m, PhH), 6.90 (1H, s, ArH), 6.82-6.76 (2H, m, ArH), 6.77 (1H, d, ArH), 5.87 (1H, bs, NH), 5.09 (4H, d, OCH$_2$Ph), 4.96 (1H, s, CH), 4.02 (2H, q, O*CH*$_2$CH$_3$), 2.31 (3H, s, CH$_3$), 2.28-2.11 (4H, m, CH$_2$), 1.15 (3H, t, OCH$_2$*CH*$_3$), 1.05 (3H, s, CH$_3$), 0.90 (3H, s, CH$_3$).



1k

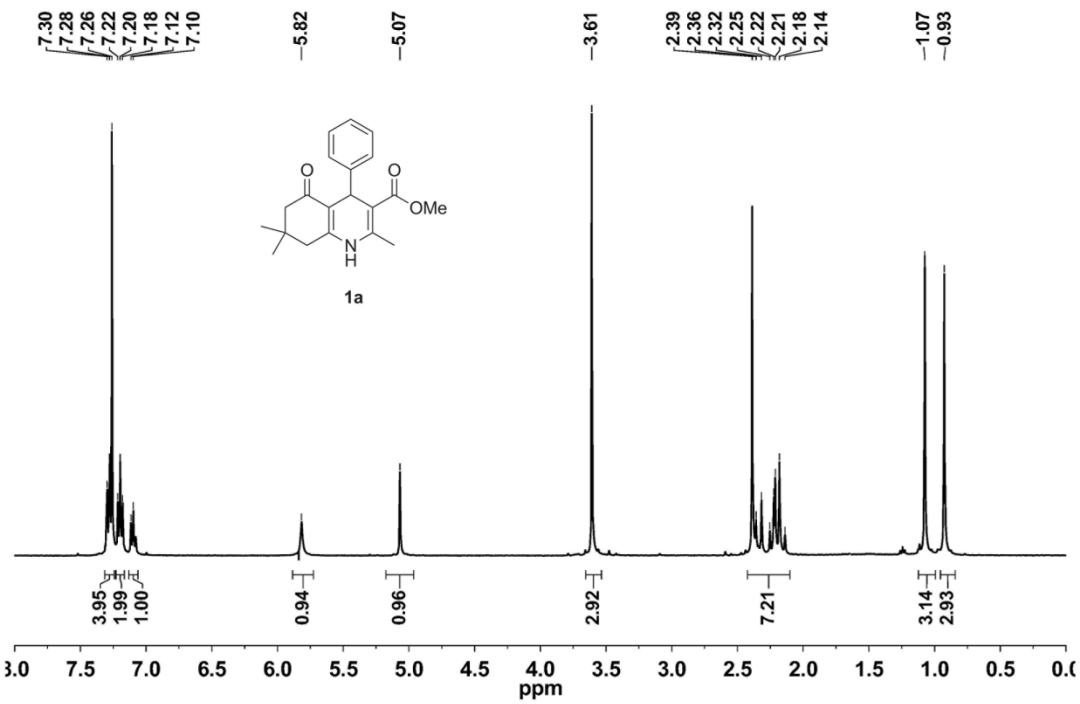
4-(4-cyanophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid methyl ester (1k).[10] Yield= 92%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.49 (2H, d, *J*= 8.0 Hz, ArH), 7.41 (2H, t, *J*= 8.0 Hz, ArH), 6.80 (1H, bs, NH), 5.09 (1H, s, CH), 3.59 (3H, s, OCH_3), 2.33 (3H, s, CH_3), 2.32-2.10 (4H, m, CH_2), 1.06 (3H, s, CH_3), 0.88 (3H, s, CH_3).

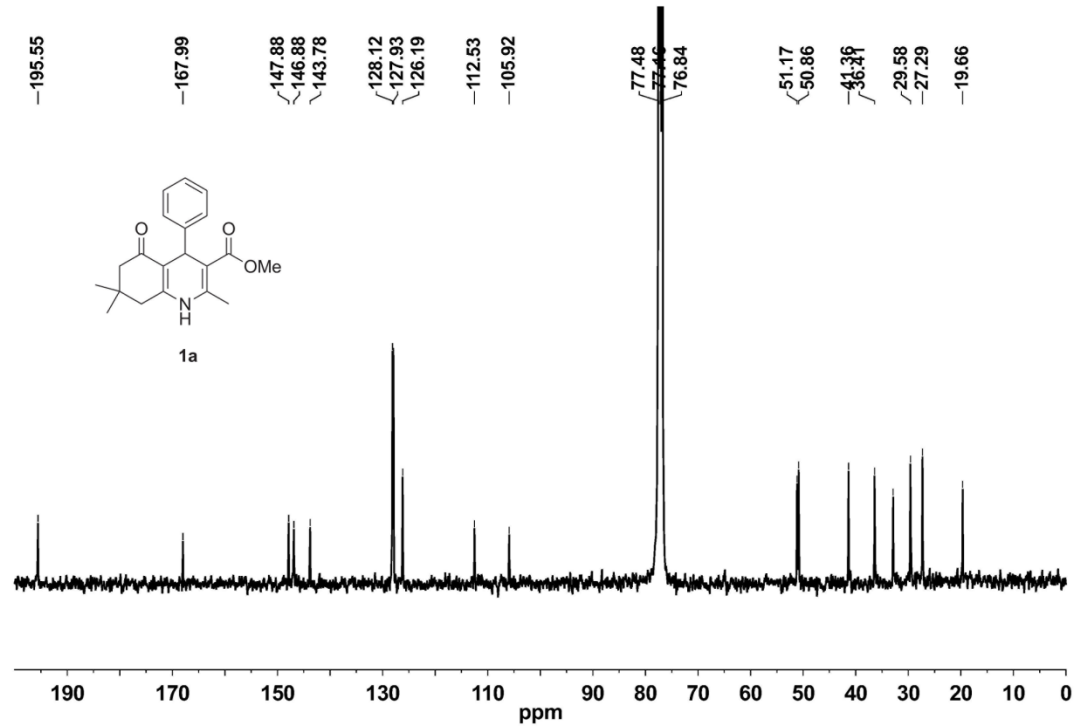


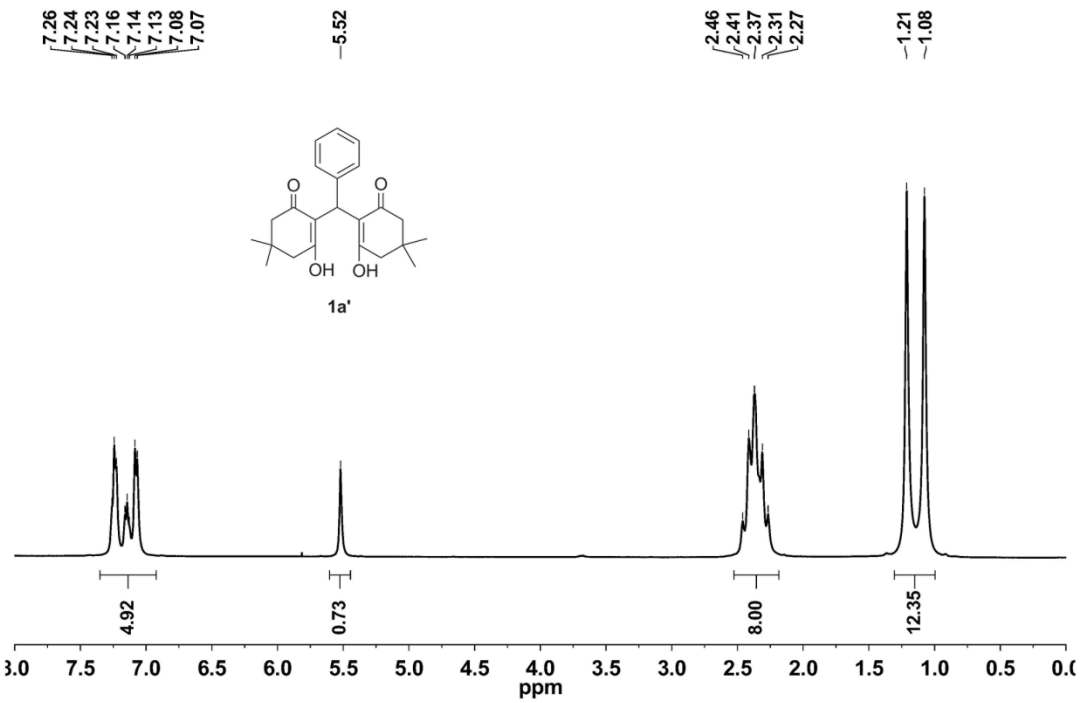
1l

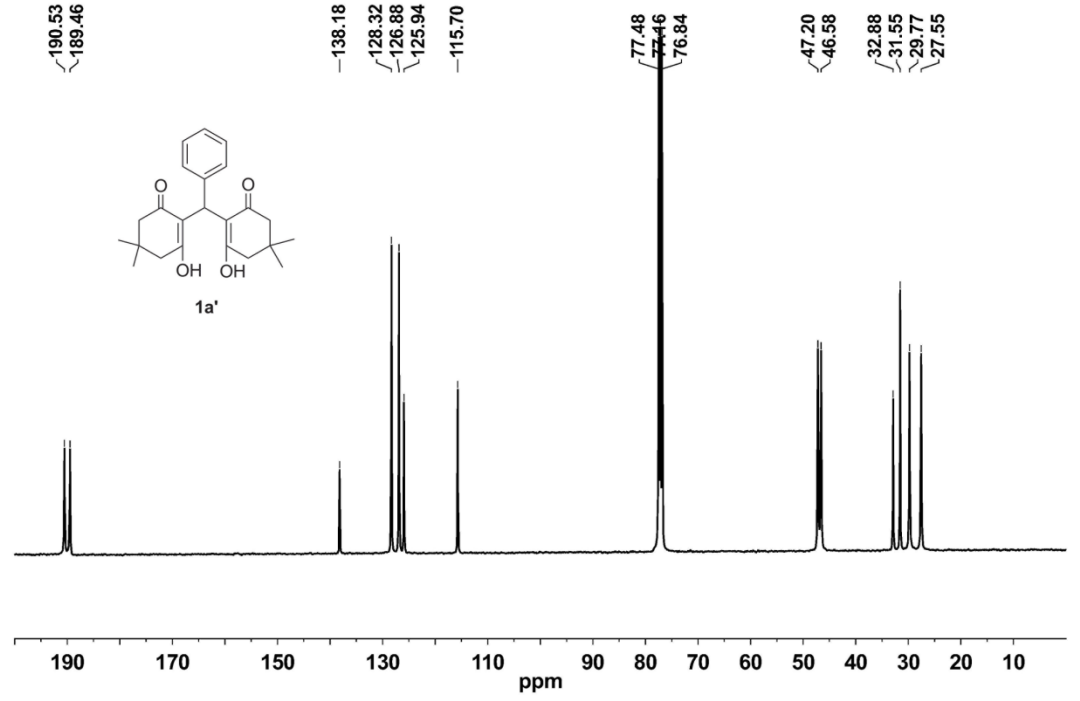
4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid methyl ester (1l).[8] Yield= 95%. ^{1}H-NMR (DMSO-d_6, 400 MHz) δ (ppm): 9.05 (1H, bs, NH), 7.04 (2H, d, *J*= 8.0 Hz, ArH), 6.73 (2H, t, *J*= 8.0 Hz, ArH), 4.79 (1H, s, CH), 3.67 (3H, s, OCH_3), 3.52 (3H, s, OCH_3), 2.41 (1H, d, *J*= 20.0, CH), 2.27 (4H, m, CH+CH_3), 2.16 (1H, d, *J*= 20.0, CH), 1.97 (1H, d, *J*= 16.0, CH), 1.00 (3H, s, CH_3), 0.84 (3H, s, CH_3). ^{13}C-NMR (DMSO-d_6, 100 MHz) δ (ppm): 195.0, 168.1, 157.9, 149.9, 145.6, 140.5, 128.9, 113.8, 110.9, 104.2, 55.5, 51.3, 50.9, 35.4, 32.8, 29.8, 27.1, 18.9.

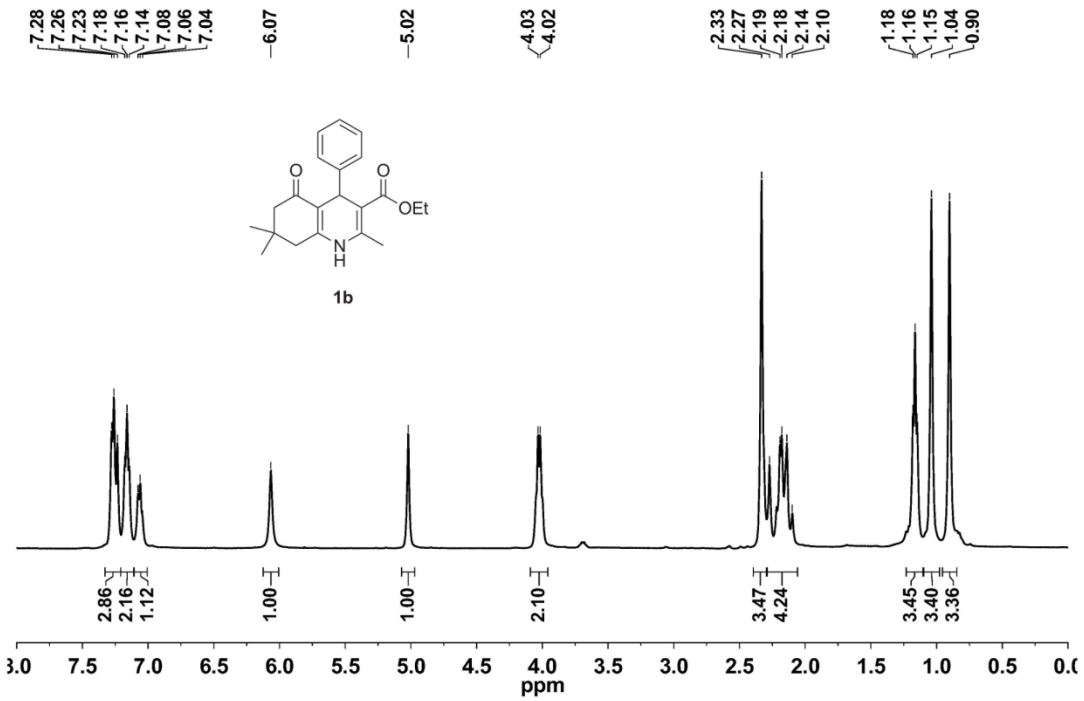
3. ^{1}H NMR and ^{13}C NMR spectra of 1,4-dihydropyridines







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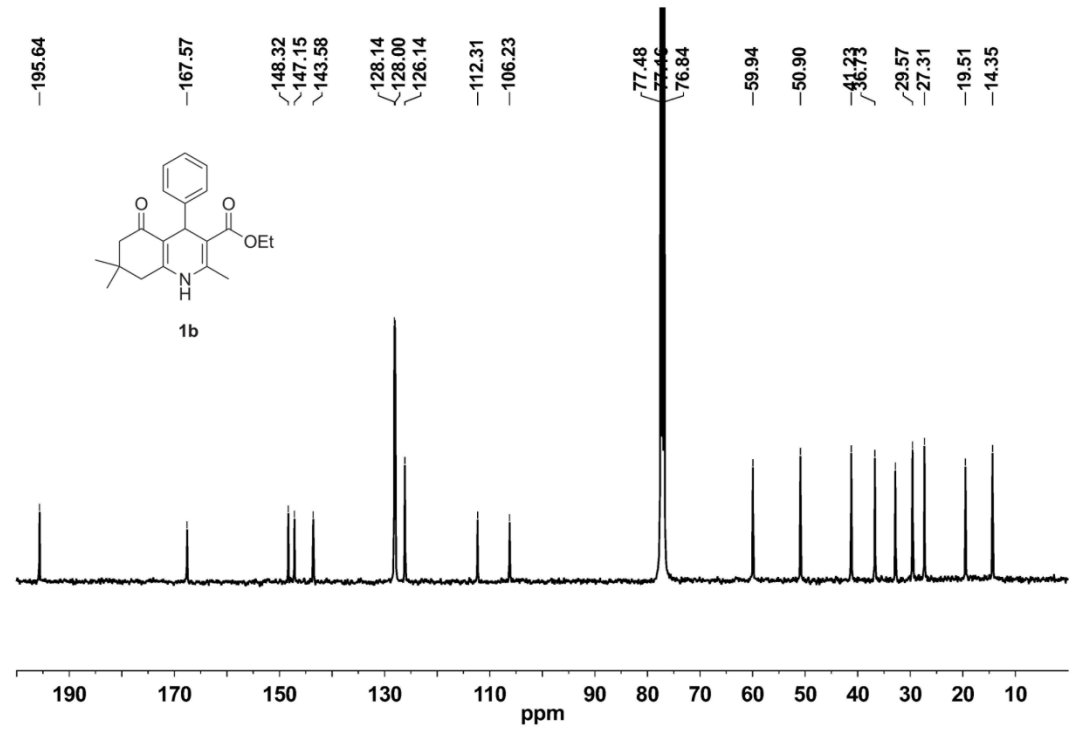
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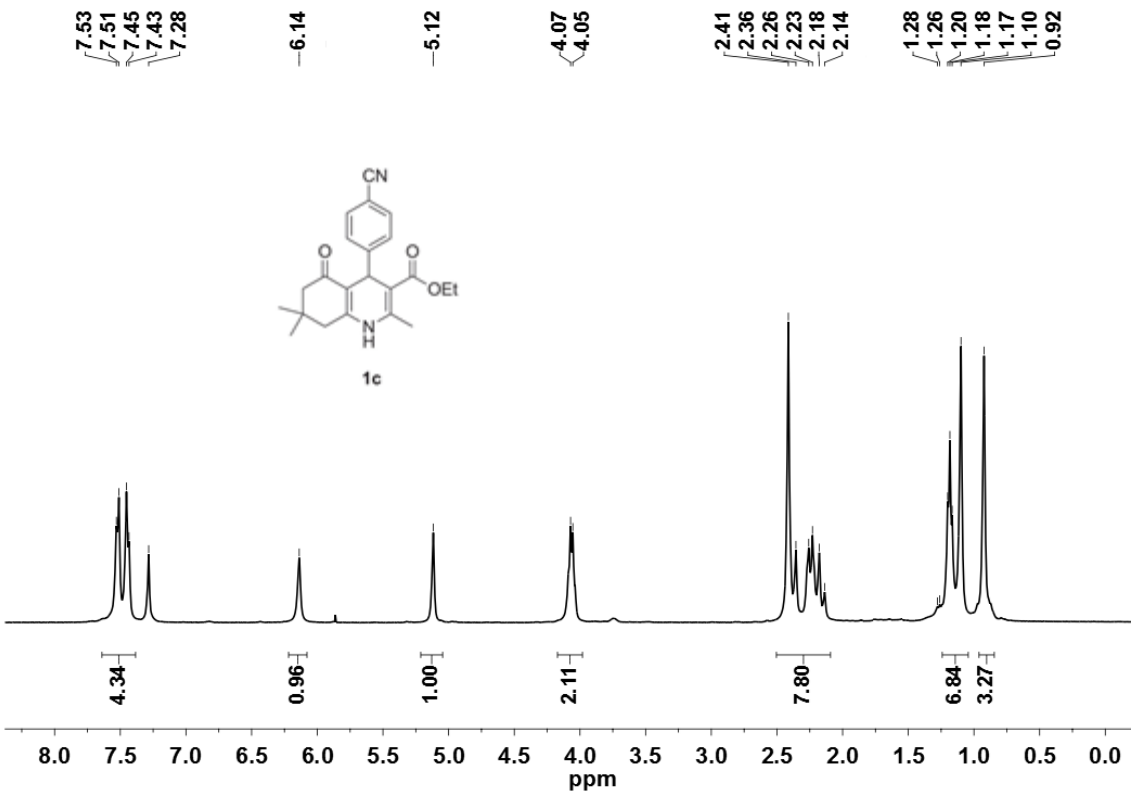
OEt
1b
ppm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4.07
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2.41
2.36
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2.23
2.18
2.14
1.28
1.26
1.20
1.18
1.17
1.10
0.92
CN
O
O
OEt
N
H
1c
4.34
0.96
1.00
2.11
7.80
6.84
3.27
8.0
7.5
7.0
6.5
6.0
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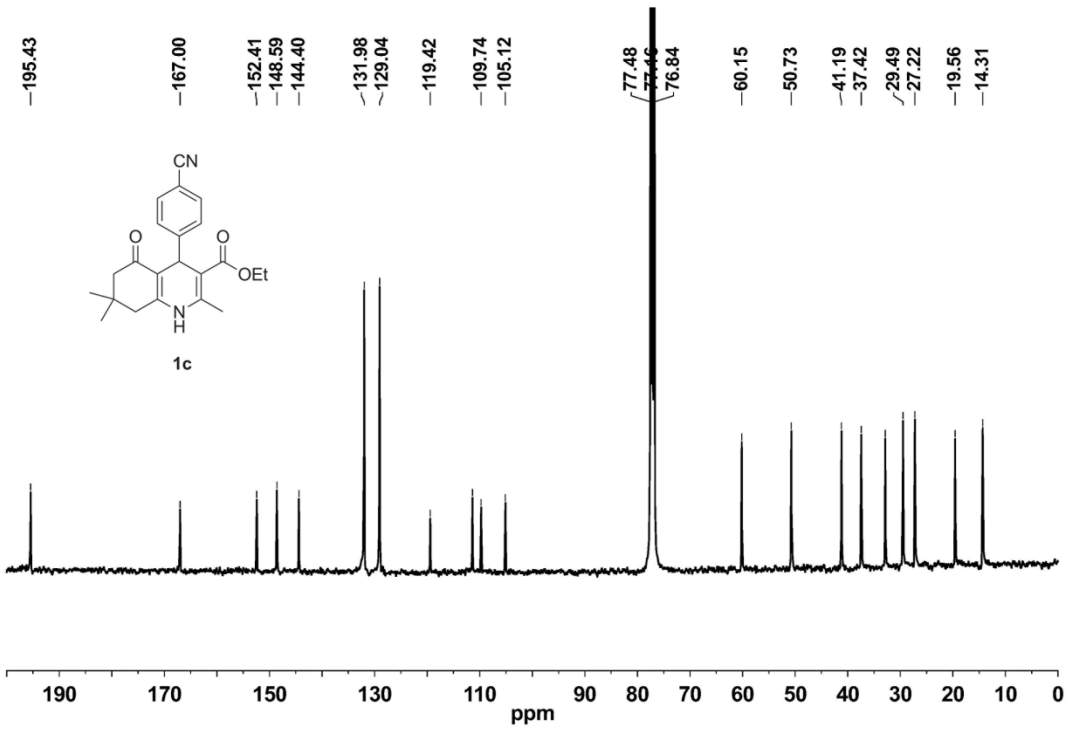
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76.84
60.15
50.73
41.19
37.42
29.49
27.22
19.56
14.31
CN
O
O
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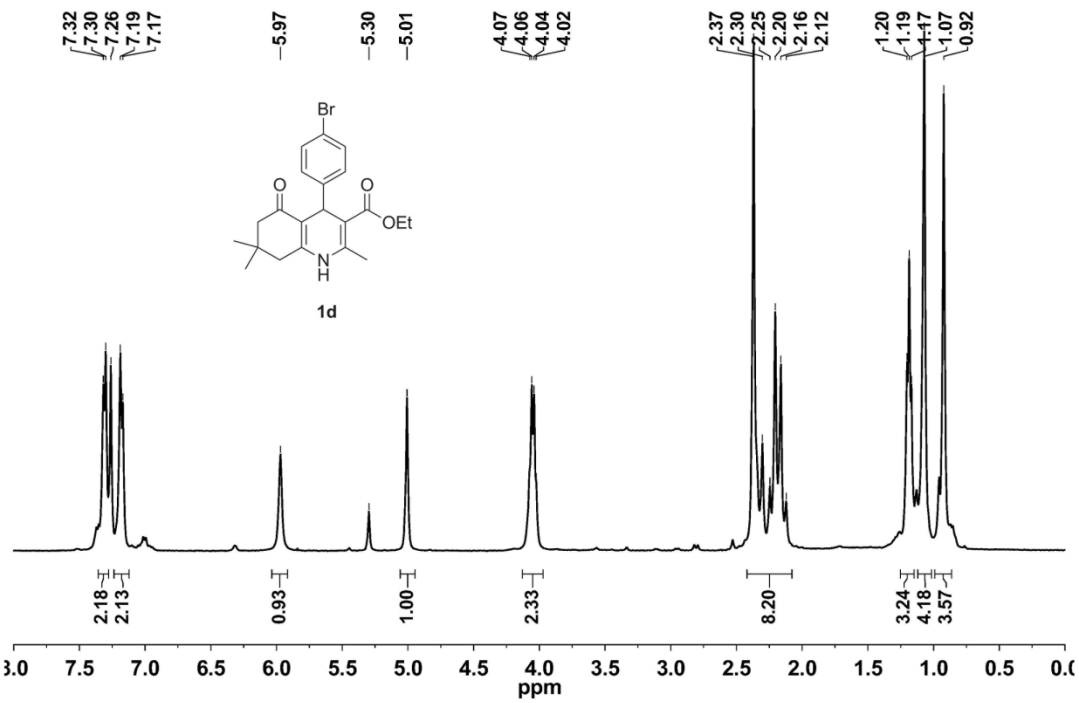

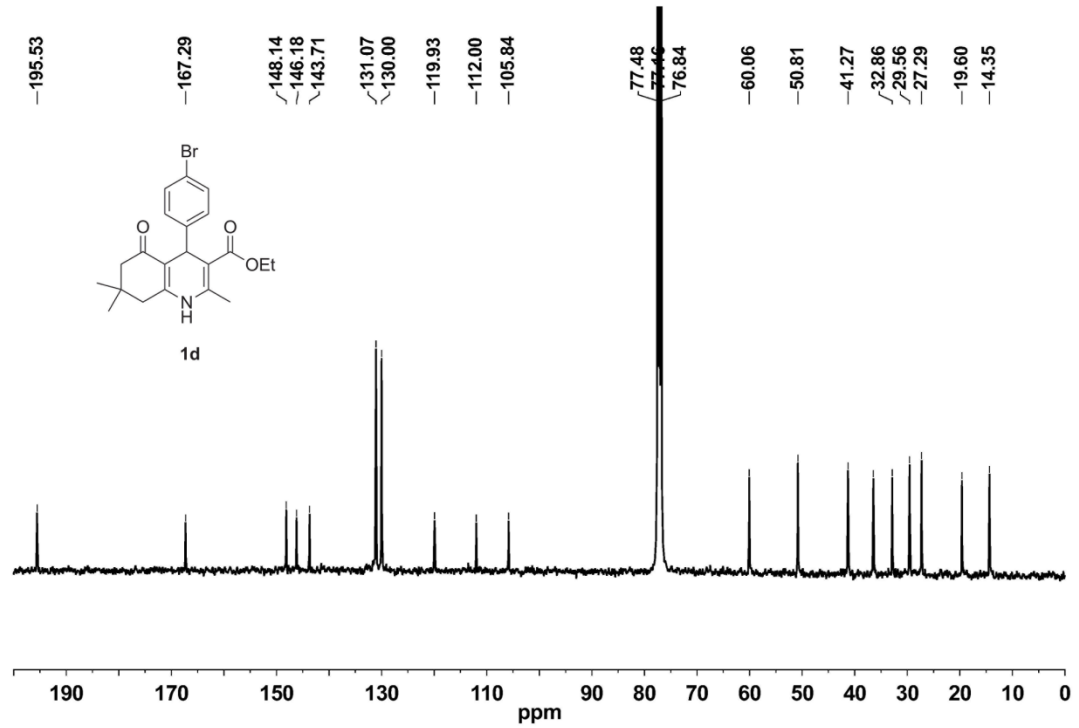

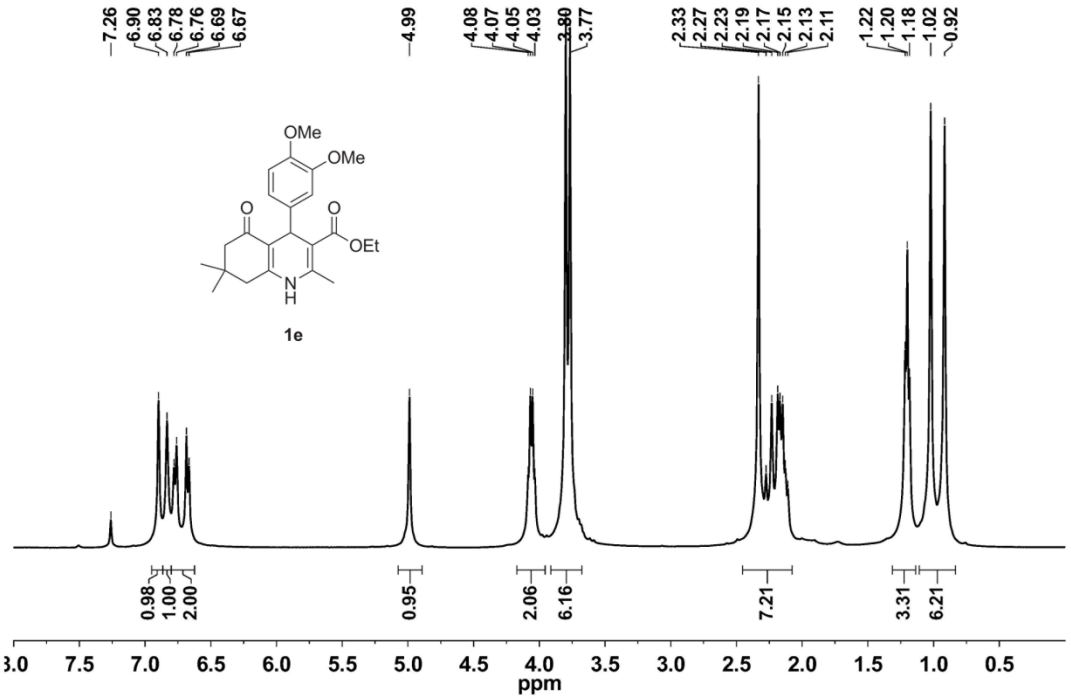

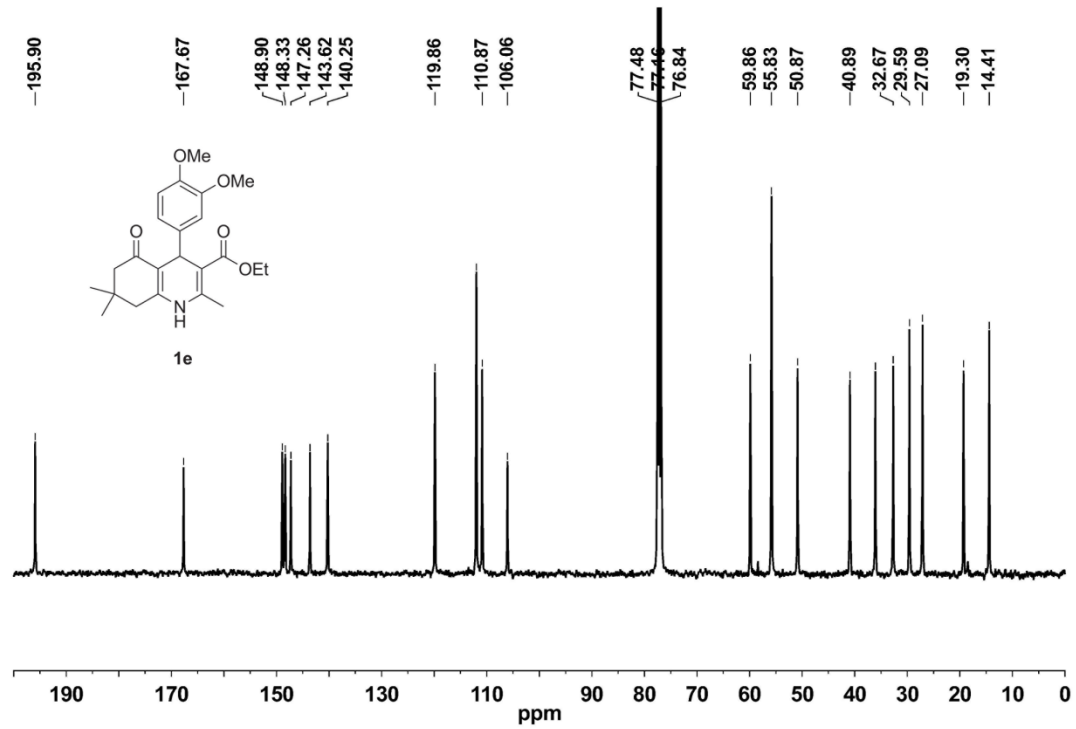

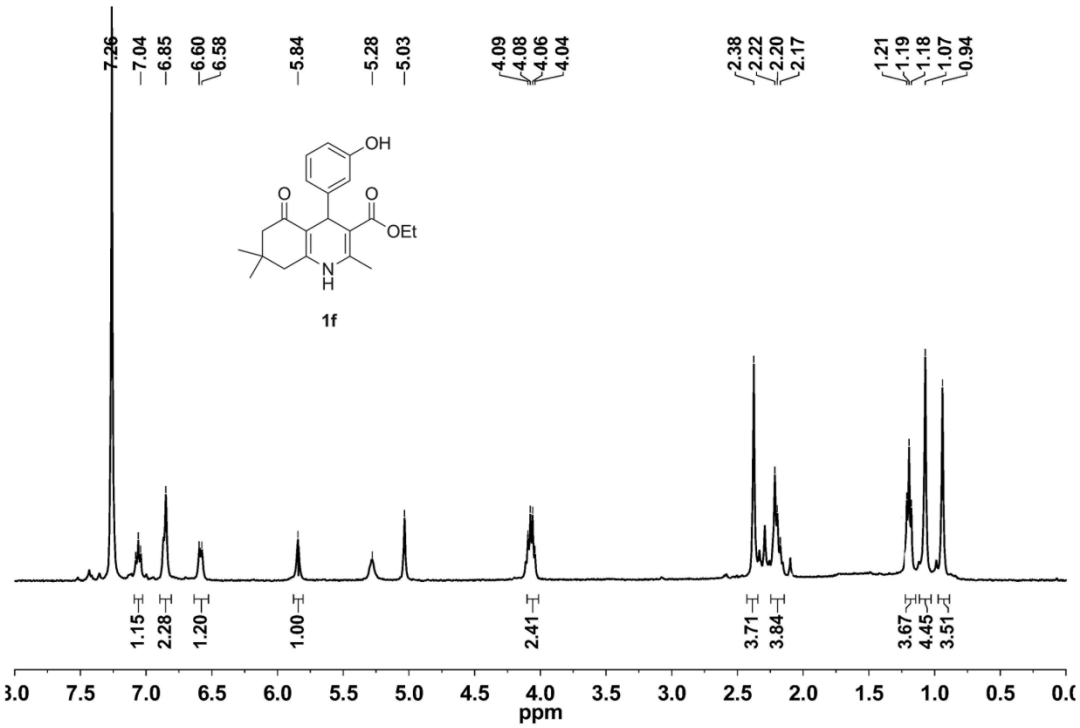

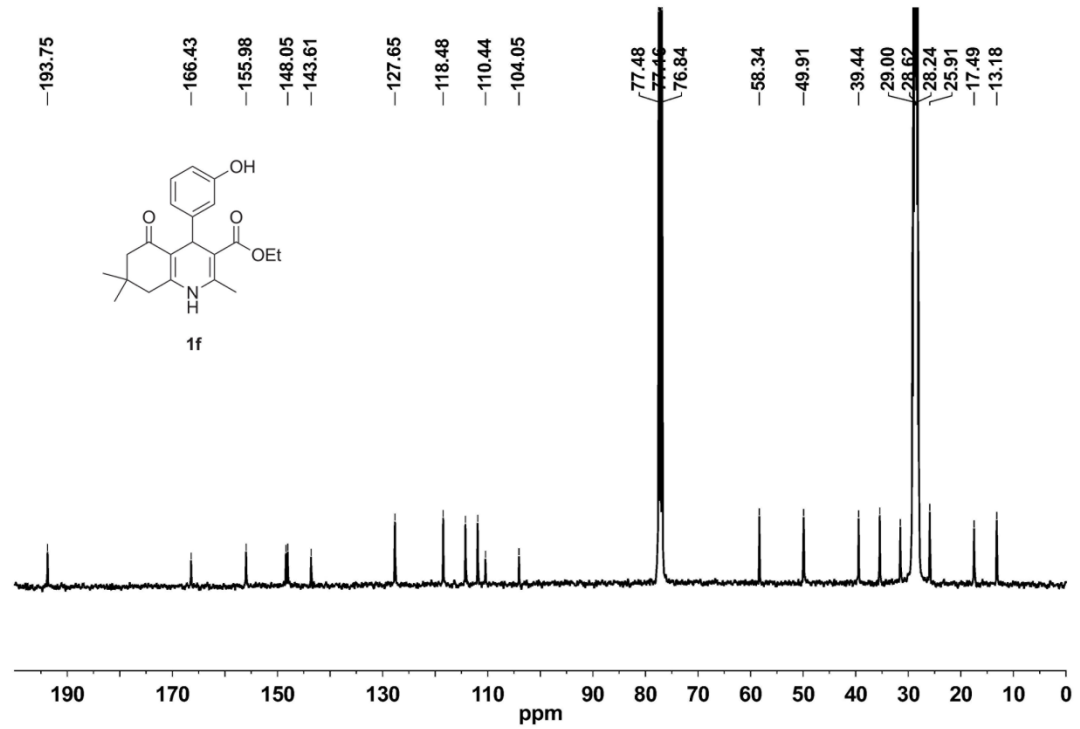

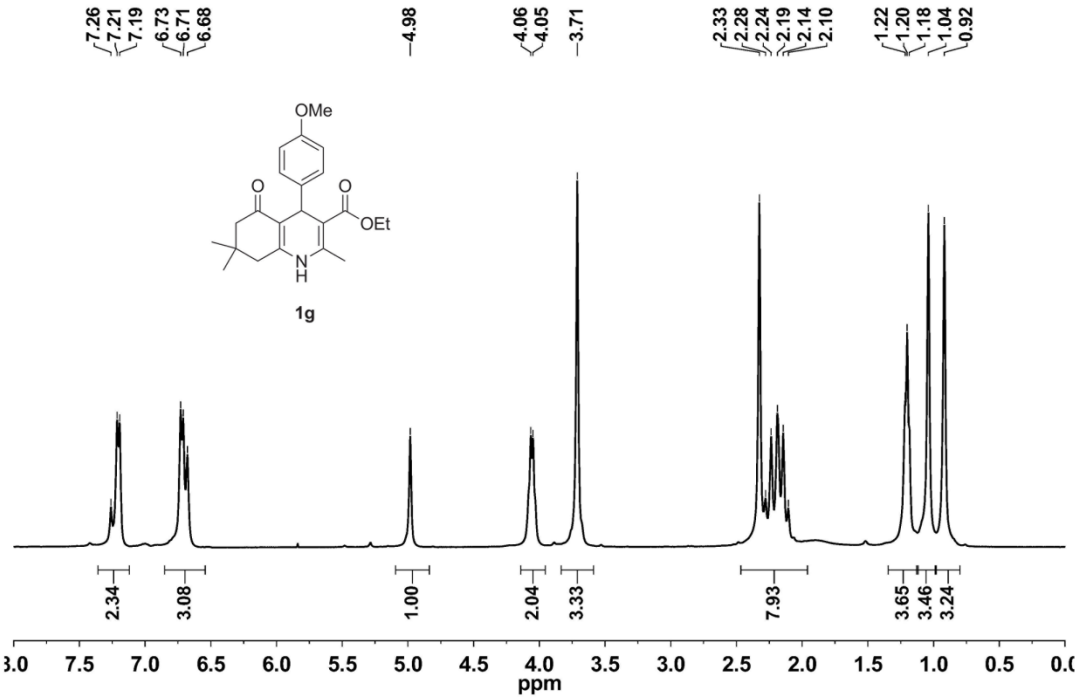

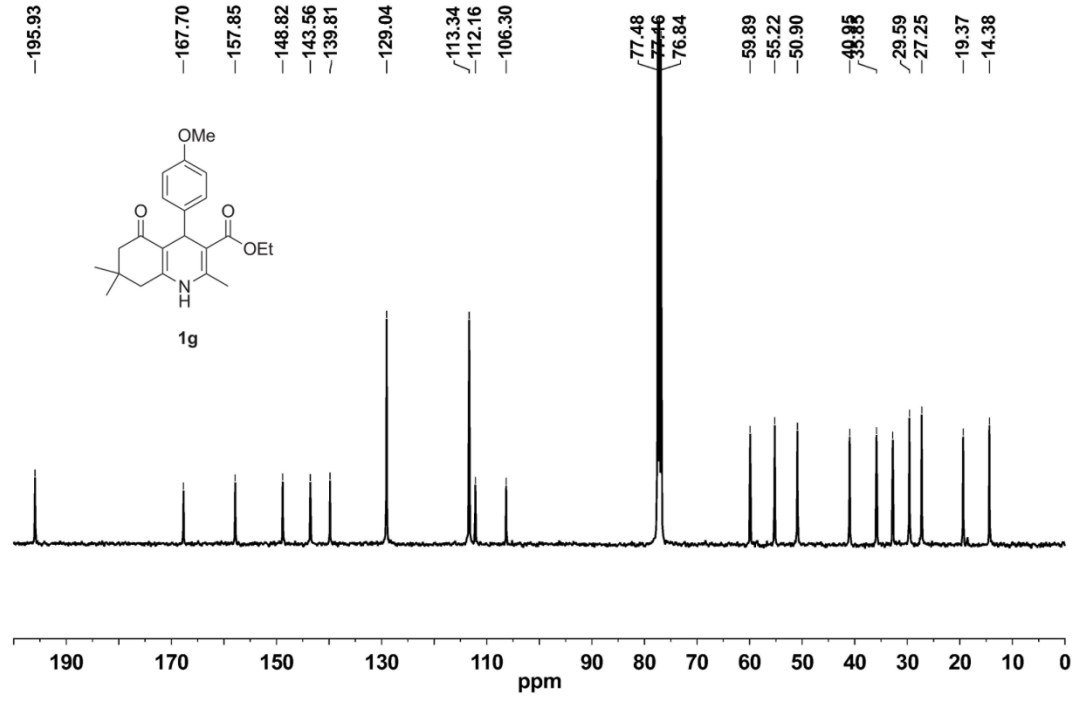

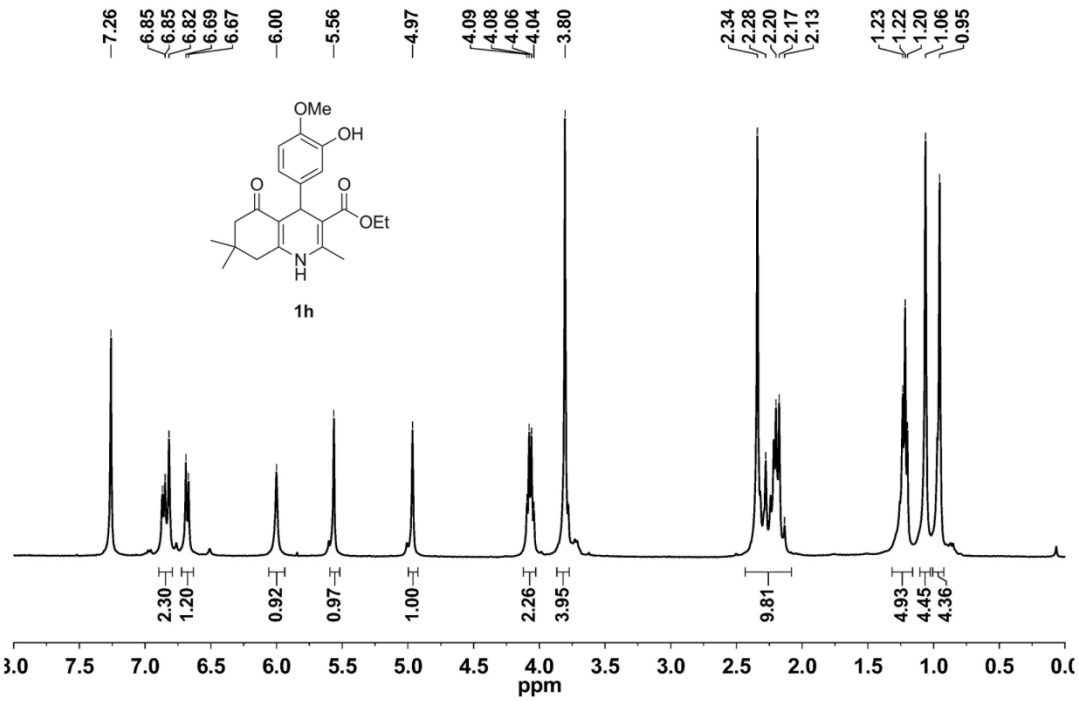

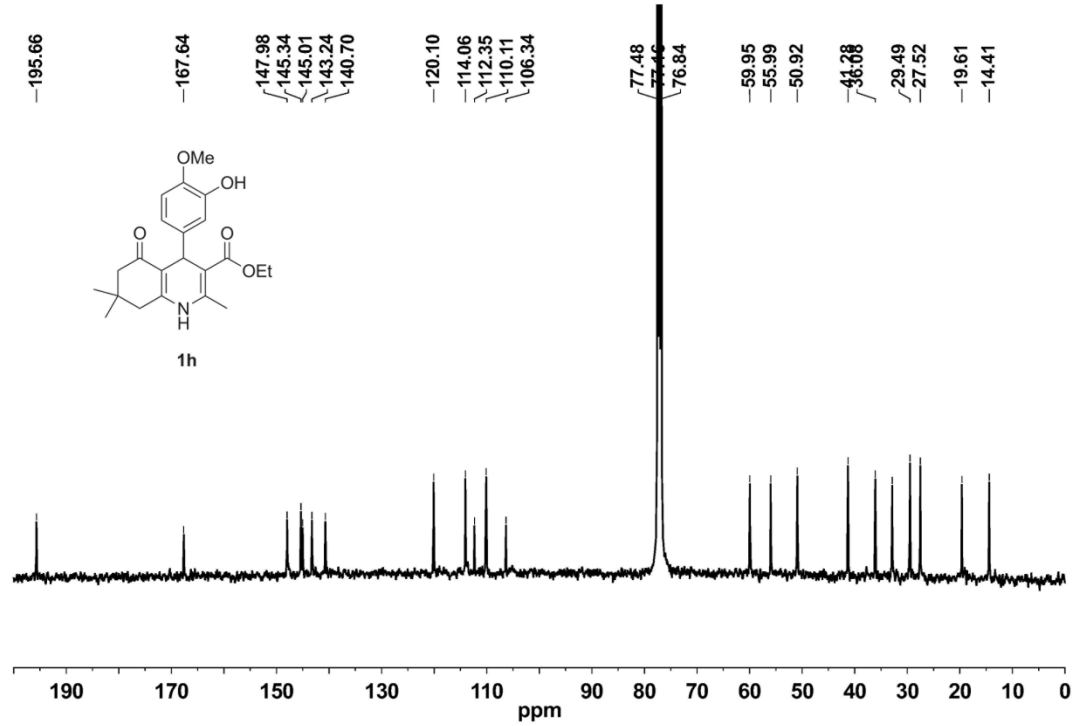

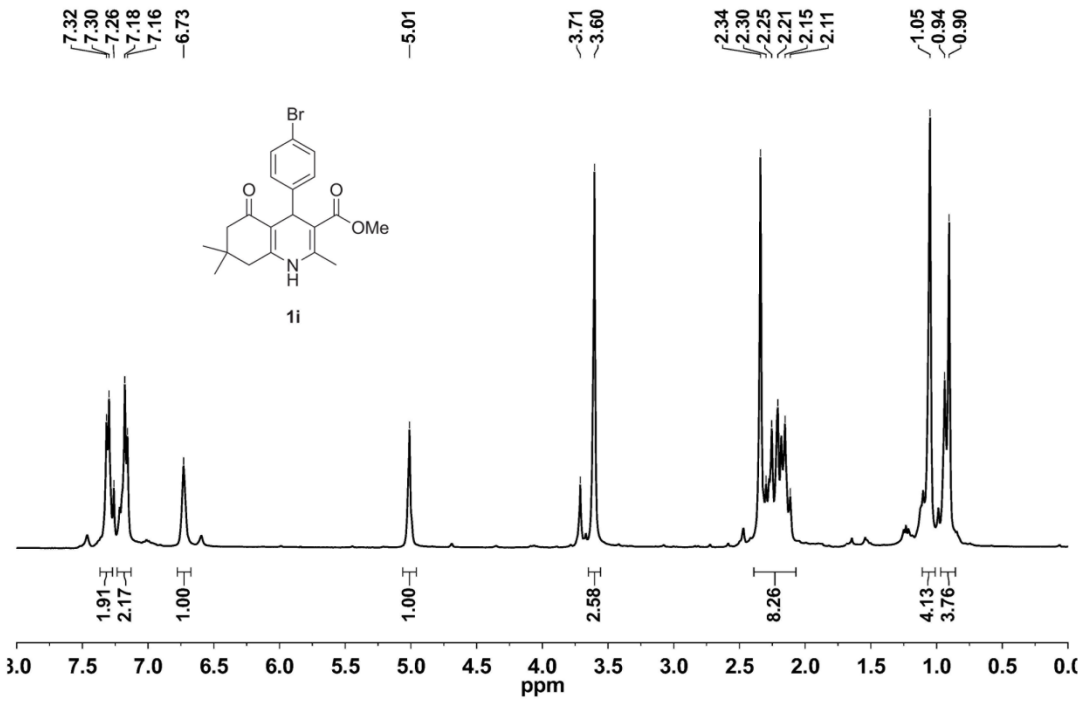
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6.73
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3.71
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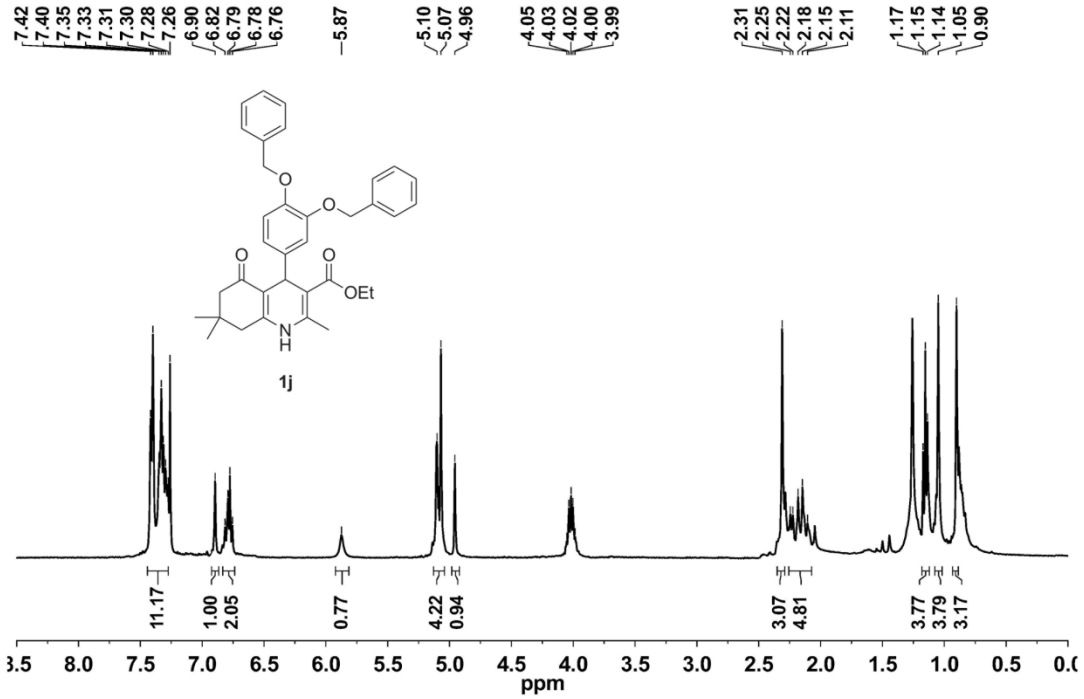
2.34
2.30
2.25
2.21
2.15
2.11
1.05
0.94
0.90
Br
O
O
OMe
N
H
1i
1.91
2.17
1.00
1.00
2.58
8.26
4.13
3.76
ppm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7.30
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7.26
6.90
6.82
6.79
6.78
6.76
5.87
5.10
5.07
4.96
4.05
4.03
4.02
4.00
3.99
2.31
2.25
2.22
2.18
2.15
2.11
1.17
1.15
1.14
1.05
0.90
O
O
O
O
OEt
N
H
1j
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2.05
0.77
4.22
0.94
3.07
4.81
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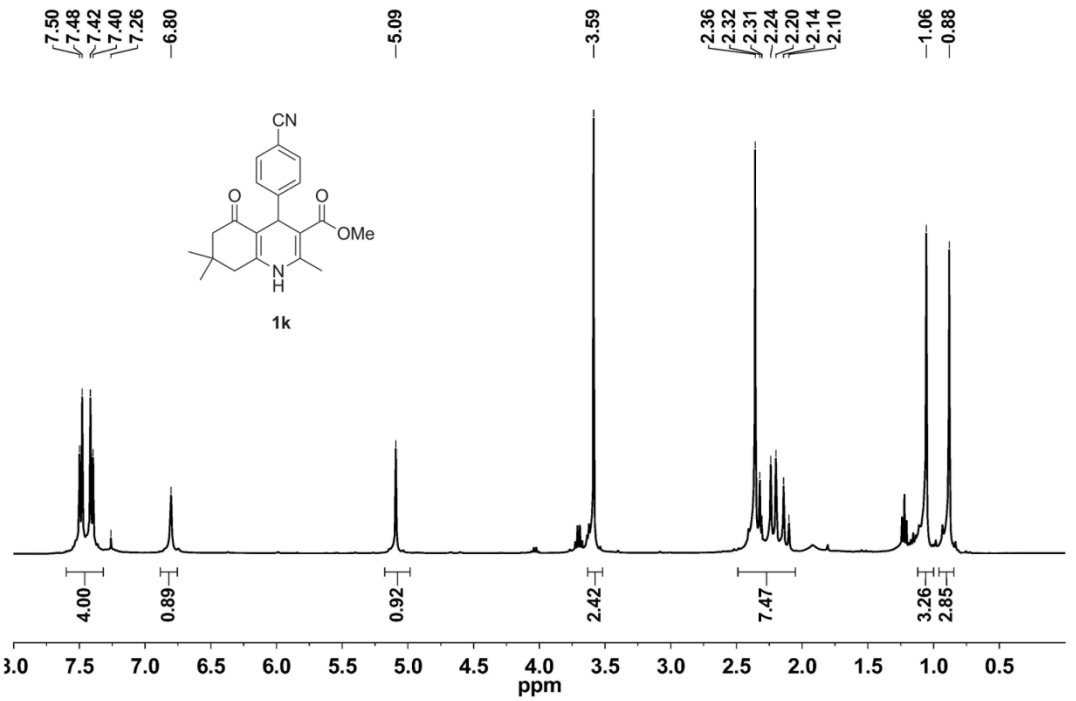
3.79
3.17
ppm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7.26
6.80
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3.59
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2.32
2.31
2.24
2.20
2.14
2.10
1.06
0.88
CN
O
O
OMe
N
H
1k
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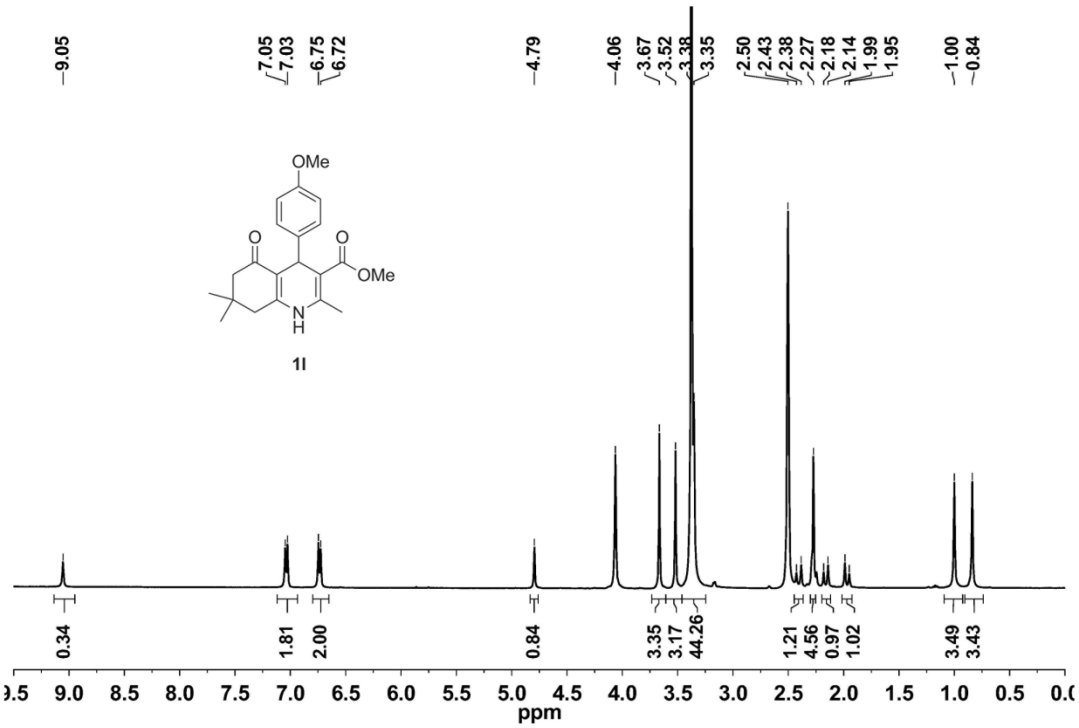
0.92
2.42
7.47
3.26
2.85
ppm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7.03
6.75
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4.06
3.67
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3.38
3.35
2.50
2.43
2.38
2.27
2.18
2.14
1.99
1.95
1.00
0.84
OMe
O
O
OMe
N
H
1l
0.34
1.81
2.00
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3.35
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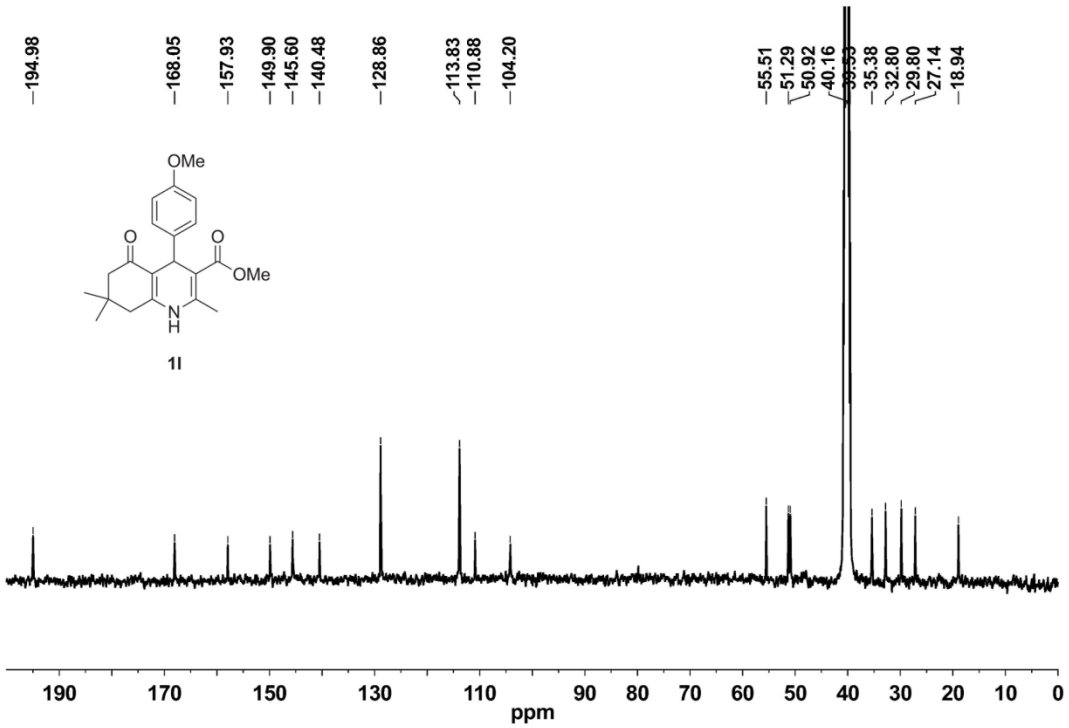
3.49
3.43
ppm



References

[1] a) M. Hong, C. Cai, W.-B. Yi, *J. Fluorine Chem.* **2010**, *131*, 111–114; b) E. Salfrán, M. Suárez, D. Molero, R. Martínez-Álvarez, Y. Verdecia, E. Ochoa, A. Alvarez, C. Seoane, A. Herrera, N. Martín, *Magn. Reson. Chem.* **2006**, *44*, 637–640.

[2] D. B. Ramachary, M. Kishor, *J. Org. Chem.* **2007**, *72*, 5056–5068.

[3] J. L. Donelson, R. A. Gibbs, S. K. De, *J. Mol. Catal. Chem.* **2006**, *256*, 309–311.

[4] B. Das, M. Srilatha, B. Veeranjaneyulu, B. S. Kanth, *Helv. Chim. Acta*, **2011**, *94*, 885–891.

[5] S. R. Cherkupally, R. Mekala, *Chem. Pharm. Bull.* **2008**, *56*, 1002–1004.

[6] G. Song, B. Wang, X. Wu, Y. Kang, L. Yang, *Synth. Commun.* **2005**, *35*, 2875–2880.

[7] L.-M. Wang, J. Sheng, L. Zhang, J.-W. Han, Z.-Y. Fan, H. Tiana, C.-T. Qian, *Tetrahedron*, **2005**, *61*, 1539–1543.

[8] C.X. Yu, D.Q. Shi, Q.Y. Zhuang, S.J. Tu, *Chin. J. Org. Chem.* **2006**, *26*, 263–267.

[9] M. B. Gawande, A. Velhinho, I. D. Nogueira, C. A. A. Ghumman, O. M. N. D. Teodoro, P. S. Branco, *RSC Adv.* **2012**, *2*, 6144–6149.

[10] R. Surasani, D. Kalita, A. V. D. Rao, K. Yarbagi, K. B. Chandrasekhar, *J. Fluorine Chem.* **2012**, *135*, 91–96.