Supporting Information

DMAP-promoted multicomponent reaction of cyanoacetylene, MBH carbonate and water: A facile access to functional quaternary carbon

Ling-Guo Meng,[†] Chun-Tao Li,[†] Jin-Feng Zhang,[†] Guo-Yuan Xiao,[†] Lei Wang[†‡*]

[†] *Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P R China*

[‡] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P R China*

leiwang@chnu.edu.cn

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1. General Remarks

All reactions were conducted under air in oven-dried glassware with magnetic stirring. Dichloromethane was dried and freshly distilled from calcium hydride under nitrogen atmosphere. Chromatographic purification was performed on silica gel (100–200 mesh) and analytical thin layer chromatography (TLC) on silica gel 60-F_{254} (Qindao, China), which was detected by fluorescence. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured with a Bruker AC 400 spectrometer using tetramethylsilane (TMS) as an internal standard. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (*J* are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad singlet). High resolution mass spectra were obtained with a Micromass GCT-TOF mass spectrometer.

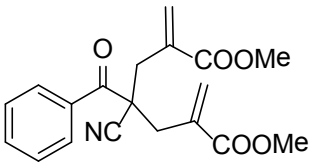
2. General Procedure

General procedure for the multicomponent reaction of cyanoacetylene, MBH carbonate and water promoted by 4-dimethylaminopyridine (DMAP)

To a solution of cyanoacetylene (0.20 mmol), MBH carbonate (0.60 mmol) and water (0.20 mmol) in CH_3CN (2.0 mL), 4-dimethylaminopyridine (DMAP, 0.10 mmol) was added. The mixture was then stirred at room temperature for 72 h. Then the solvent was removed in vacuo and residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to give the desired products.

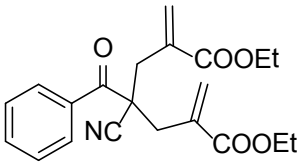
3. Characterization data for compounds 3a–n

Dimethyl 4-benzoyl-4-cyano-2,6-dimethyleneheptanedioate (3a)



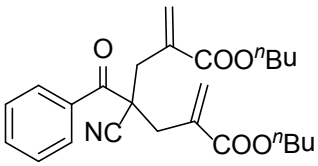
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 6.42 (s, 2H), 5.79 (s, 2H), 3.71 (s, 6H), 3.33 (d, *J* = 14.4 Hz, 2H), 2.99 (d, *J* = 14.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.7, 166.7, 135.2, 134.4, 133.5, 130.6, 129.1, 128.5, 119.8, 52.2, 51.5, 38.2. HRMS (ESI) calcd for $C_{19}H_{20}NO_5$ $(M+H)^+$: 342.1341; Found: 342.1336.

Diethyl 4-benzoyl-4-cyano-2,6-dimethyleneheptanedioate (3b)



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 6.41 (s, 2H), 5.77 (s, 2H), 4.19 (q, *J* = 7.2 Hz, 4H), 3.34 (d, *J* = 14.4 Hz, 2H), 2.98 (d, *J* = 14.4 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 166.1, 135.2, 134.7, 133.4, 130.1, 129.1, 128.3, 119.7, 61.1, 51.4, 38.0, 13.8. HRMS (ESI) calcd for $C_{21}H_{24}NO_5$ $(M+H)^+$: 370.1654; Found: 370.1653.

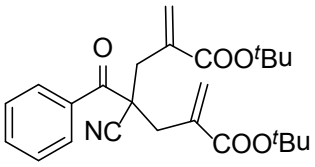
Dibutyl 4-benzoyl-4-cyano-2,6-dimethyleneheptanedioate (3c)



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 6.40 (s, 2H), 5.77 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 4H), 3.33 (d, *J* = 14.4 Hz, 2H), 2.97 (d, *J* = 14.4 Hz, 2H), 1.62–1.56 (m, 4H), 1.39–1.33 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.7, 166.2, 135.1, 134.7, 133.4, 130.0, 129.1, 128.3, 119.7, 65.0, 51.4, 38.0, 30.3, 19.0,

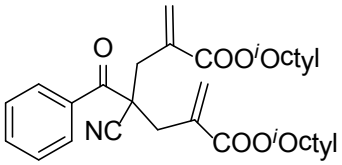
13.5. HRMS (ESI) calcd for $C_{25}H_{32}NO_5$ $(M+H)^+$: 426.2280; Found: 426.2277.

Di-*tert*-butyl 4-benzoyl-4-cyano-2,6-dimethyleneheptanedioate (3d)



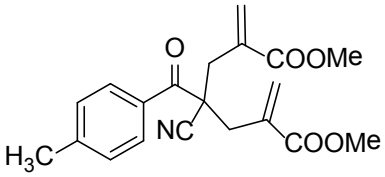
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 6.31 (s, 2H), 5.68 (s, 2H), 3.27 (d, *J* = 14.4 Hz, 2H), 2.92 (d, *J* = 14.4 Hz, 2H), 1.42 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 165.1, 136.1, 135.3, 133.2, 129.3, 129.1, 128.2, 119.9, 81.4, 51.5, 38.1, 27.7. HRMS (ESI) calcd for $C_{25}H_{32}NO_5$ $(M+H)^+$: 426.2280; Found: 426.2281.

Di-*iso*-octyl 4-benzoyl-4-cyano-2,6-dimethyleneheptanedioate (3e)



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 6.39 (s, 2H), 5.78 (s, 2H), 4.08–3.98 (m, 4H), 3.33 (d, *J* = 14.4 Hz, 2H), 2.98 (d, *J* = 14.4 Hz, 2H), 1.64–1.56 (m, 2H), 1.39–1.32 (m, 16H), 0.90 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.7, 166.3, 135.2, 134.7, 133.3, 129.8, 129.1, 128.3, 119.8, 67.6, 67.6, 51.4, 38.5, 38.0, 30.3, 28.7, 23.7, 22.8, 13.8, 10.8. HRMS (ESI) calcd for $C_{33}H_{48}NO_5$ $(M+H)^+$: 538.3532; Found: 538.3534.

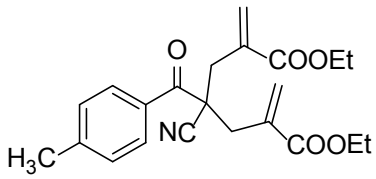
Dimethyl 4-cyano-4-(4-methylbenzoyl)-2,6-dimethyleneheptanedioate (3f)



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 2H), 5.78 (s, 2H), 3.71 (s, 6H), 3.32 (d, *J* = 14.4 Hz, 2H), 2.97

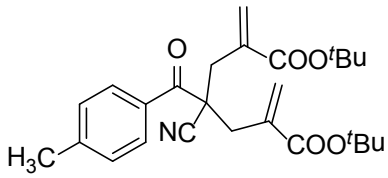
(d, J = 14.4 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9, 166.6, 144.5, 134.4, 132.5, 130.3, 129.2, 129.0, 119.9, 52.0, 51.2, 38.0, 21.5. HRMS (ESI) calcd for $C_{20}H_{22}NO_5$ $(M+H)^+$: 356.1498; Found: 356.1498.

Diethyl 4-cyano-4-(4-methylbenzoyl)-2,6-dimethyleneheptanedioate (3g)



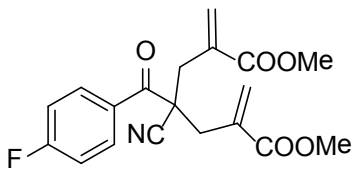
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.40 (s, 2H), 5.76 (s, 2H), 4.19 (q, J = 7.2 Hz, 4H), 3.33 (d, J = 14.4 Hz, 2H), 2.96 (d, J = 14.4 Hz, 2H), 2.41 (s, 3H), 1.27 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9, 166.1, 144.5, 134.7, 132.5, 130.0, 129.3, 129.0, 119.9, 61.1, 51.2, 37.9, 21.5, 13.8. HRMS (ESI) calcd for $C_{22}H_{26}NO_5$ $(M+H)^+$: 384.1811; Found: 384.1812.

Di-*tert*-butyl 4-cyano-4-(4-methylbenzoyl)-2,6-dimethyleneheptanedioate (3h)



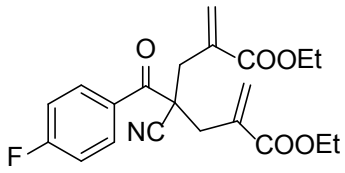
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 6.32 (s, 2H), 5.68 (s, 2H), 3.27 (d, J = 14.4 Hz, 2H), 2.92 (d, J = 14.4 Hz, 2H), 2.40 (s, 3H), 1.44 (t, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3, 165.2, 144.3, 136.1, 132.7, 129.3, 129.2, 128.9, 120.1, 81.3, 51.3, 38.0, 27.7, 21.5. HRMS (ESI) calcd for $C_{26}H_{34}NO_5$ $(M+H)^+$: 440.2437; Found: 440.2438.

Dimethyl 4-cyano-4-(4-fluorobenzoyl)-2,6-dimethyleneheptanedioate (3i)



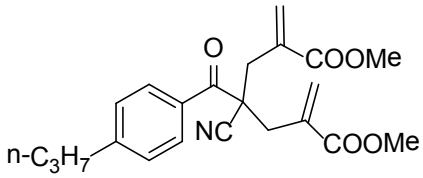
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (dd, *J* = 7.6, 5.2 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 6.41 (s, 2H), 5.79 (s, 2H), 3.71 (s, 6H), 3.32 (d, *J* = 14.4 Hz, 2H), 2.96 (d, *J* = 14.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 166.9 (d, *J* = 255.3 Hz), 166.5, 134.3, 132.0 (d, *J* = 9.3 Hz), 131.5 (d, *J* = 3.1 Hz), 130.4, 119.7, 115.7 (d, *J* = 21.8 Hz), 52.0, 51.2, 38.1. HRMS (ESI) calcd for $C_{19}H_{19}FNO_5$ $(M+H)^+$: 360.1247; Found: 360.1245.

Diethyl 4-cyano-4-(4-fluorobenzoyl)-2,6-dimethyleneheptanedioate (3j)



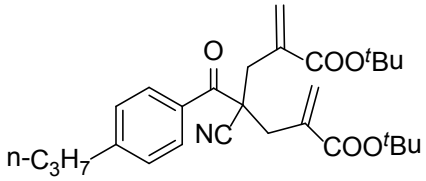
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (dd, *J* = 7.2, 5.6 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.41 (s, 2H), 5.77 (s, 2H), 4.20 (q, *J* = 7.2 Hz, 4H), 3.32 (d, *J* = 14.4 Hz, 2H), 2.96 (d, *J* = 14.4 Hz, 2H), 1.27 (q, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 166.9 (d, *J* = 255.3 Hz), 166.1, 134.6, 132.1 (d, *J* = 9.3 Hz), 131.5 (d, *J* = 3.1 Hz), 130.1, 119.7, 115.6 (d, *J* = 21.8 Hz), 61.2, 51.3, 38.0, 13.8. HRMS (ESI) calcd for $C_{21}H_{23}FNO_5$ $(M+H)^+$: 388.1560; Found: 388.1561.

Dimethyl 4-cyano-2,6-dimethylene-4-(4-propylbenzoyl)heptanedioate (3k)



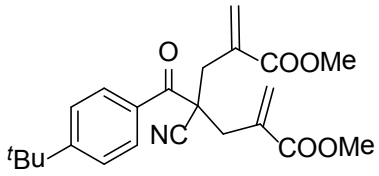
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 2H), 5.78 (s, 2H), 3.71 (s, 6H), 3.33 (d, *J* = 14.4 Hz, 2H), 2.97 (d, *J* = 14.4 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.71–1.62 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9, 166.6, 149.1, 134.4, 132.7, 130.3, 129.3, 128.4, 119.9, 52.0, 51.1, 38.0, 37.9, 23.8, 13.6. HRMS (ESI) calcd for $C_{22}H_{26}NO_5$ $(M+H)^+$: 384.1811; Found: 384.1808.

Di-*tert*-butyl 4-cyano-2,6-dimethylene-4-(4-propylbenzoyl)heptanedioate (3l)



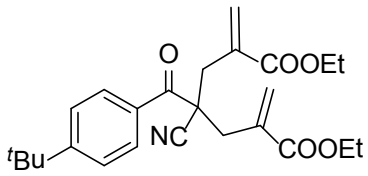
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.32 (s, 2H), 5.68 (s, 2H), 3.28 (d, *J* = 14.4 Hz, 2H), 2.91 (d, *J* = 14.4 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.68–1.59 (m, 2H), 1.43 (s, 18H), 0.95 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.2, 165.2, 148.9, 136.1, 132.8, 129.4, 129.2, 128.3, 120.1, 81.3, 51.3, 38.0, 37.8, 27.7, 23.8, 13.5. HRMS (ESI) calcd for $C_{28}H_{38}NO_5$ $(M+H)^+$: 468.2750; Found: 468.2752.

Dimethyl 4-(4-(*tert*-butyl)benzoyl)-4-cyano-2,6-dimethyleneheptanedioate (3m)



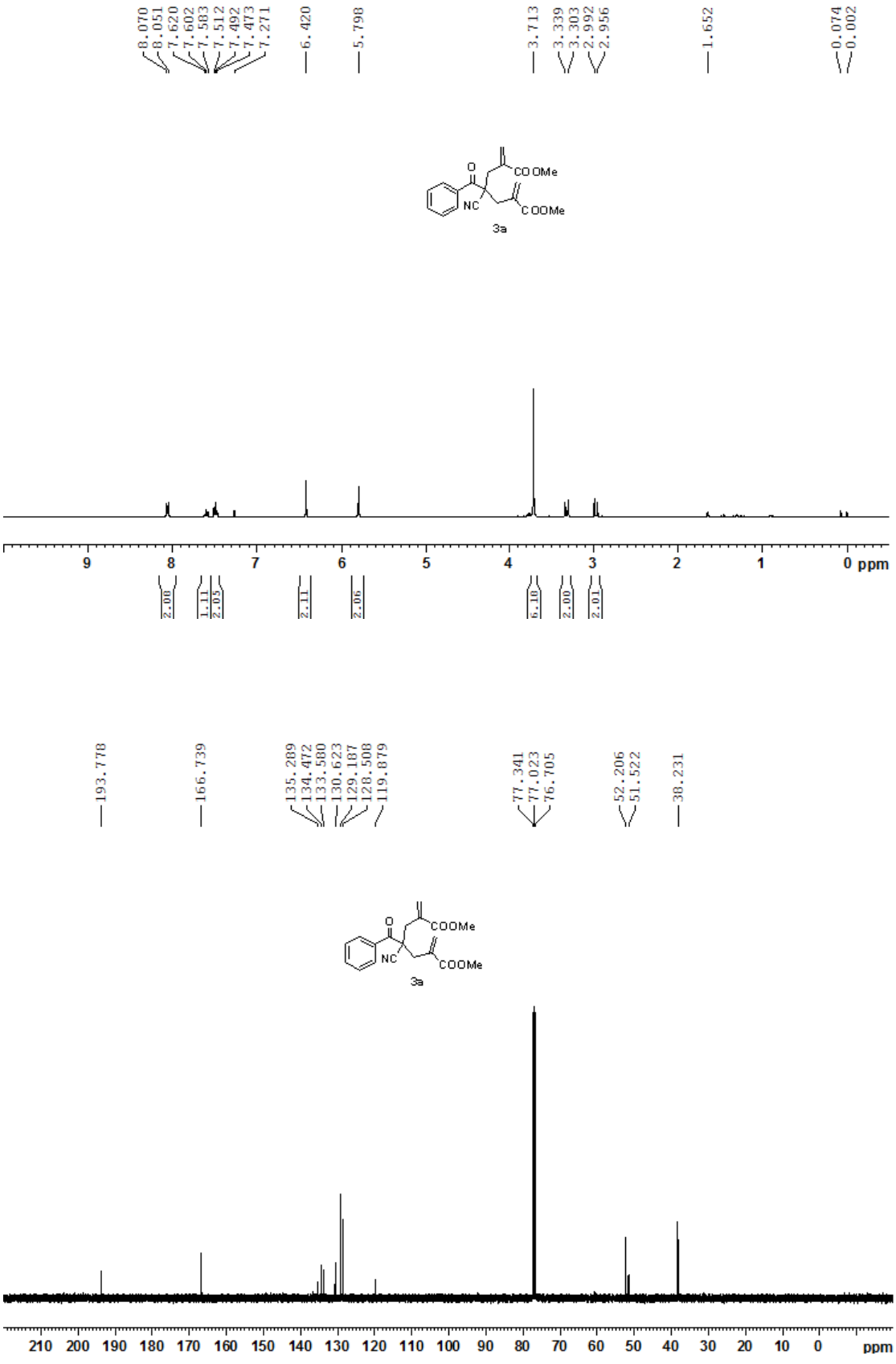
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 2H), 5.78 (s, 2H), 3.72 (s, 6H), 3.34 (d, *J* = 14.4 Hz, 2H), 2.96 (d, *J* = 14.4 Hz, 2H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8, 166.6, 157.4, 134.4, 132.3, 130.3, 129.1, 125.3, 119.9, 52.0, 51.1, 37.9, 35.0, 30.8. HRMS (ESI) calcd for $C_{23}H_{28}NO_5$ $(M+H)^+$: 398.1967; Found: 398.1963.

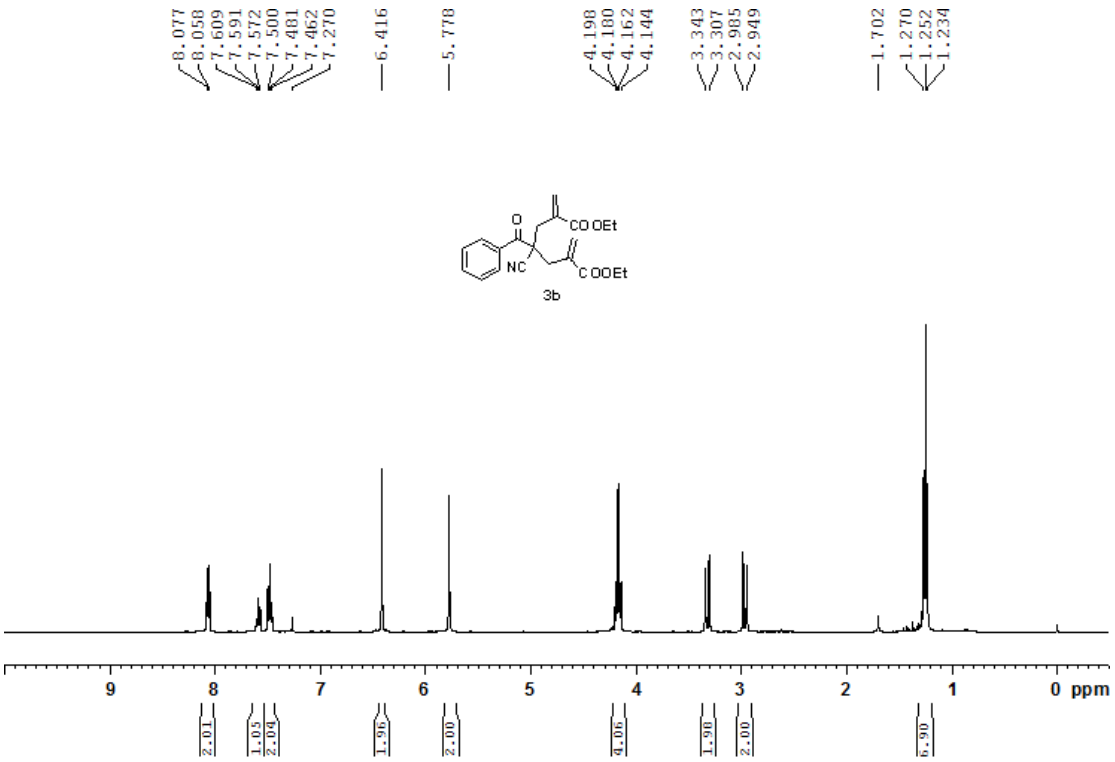
Diethyl 4-(4-(*tert*-butyl)benzoyl)-4-cyano-2,6-dimethyleneheptanedioate (3n)

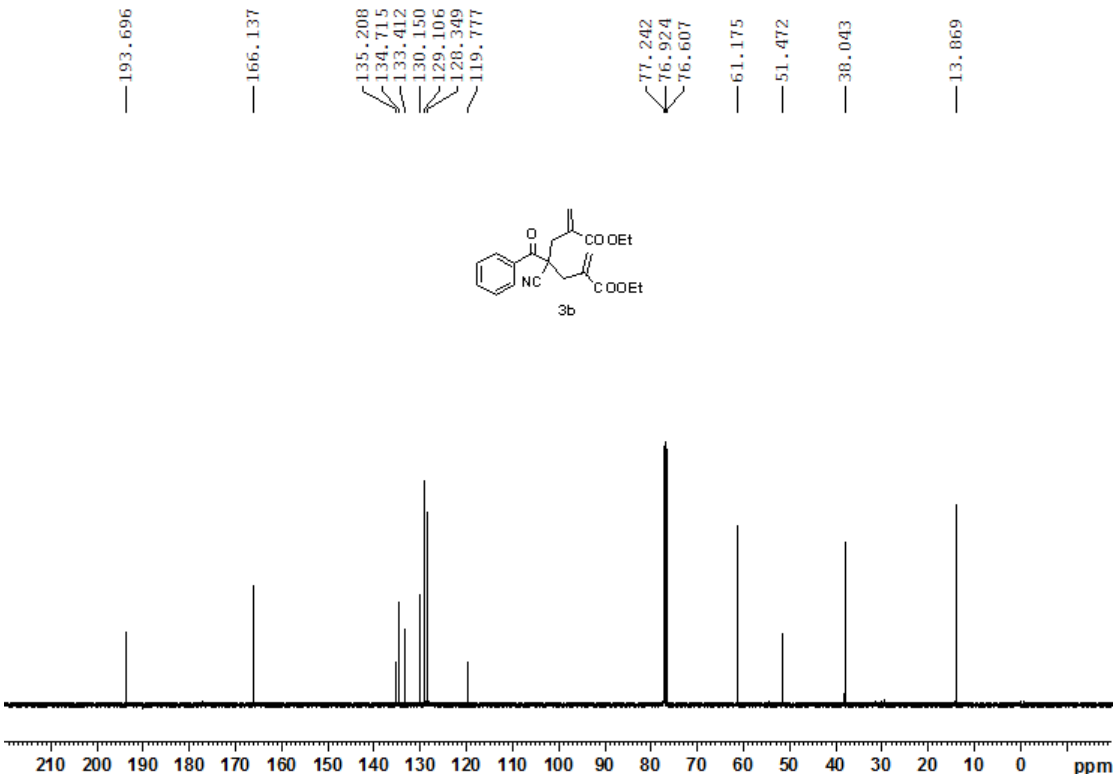


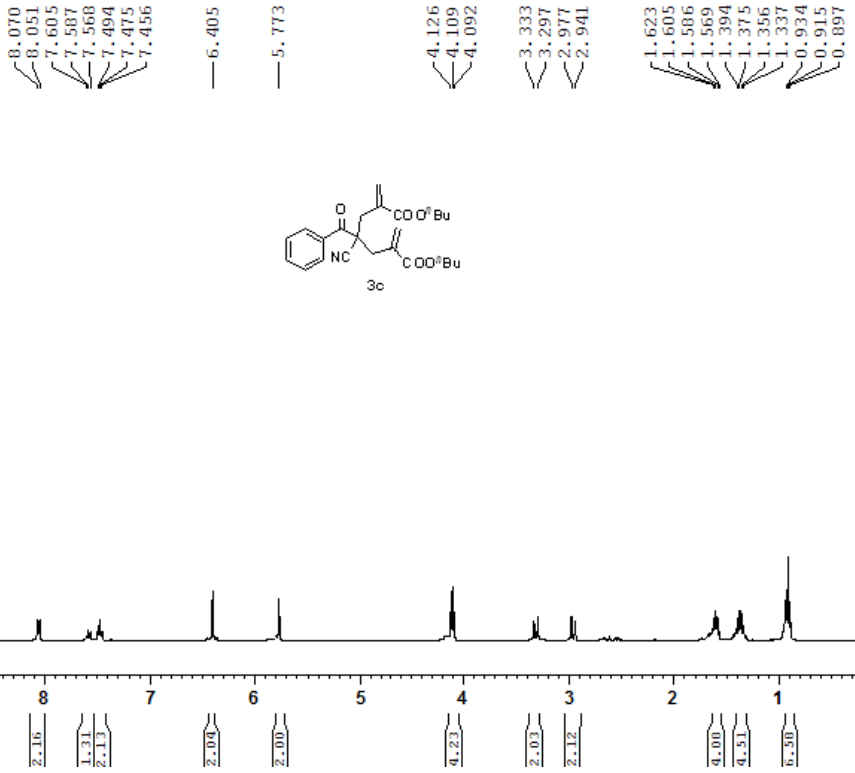
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 6.41 (s, 2H), 5.77 (s, 2H), 4.20 (q, *J* = 7.2 Hz, 4H), 3.34 (d, *J* = 14.4 Hz, 2H), 2.96 (d, *J* = 14.4 Hz, 2H), 1.34 (s, 9H), 1.27 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9, 166.2, 157.4, 134.7, 132.3, 130.0, 129.2, 125.3, 119.9, 61.1, 51.2, 37.9, 35.0, 30.8, 13.8. HRMS (ESI) calcd for $C_{25}H_{32}NO_5$ $(M+H)^+$: 426.2280; Found: 426.2278.

4. Copies of ^{1}H and ^{13}C NMR spectra of compounds 3a–n





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8.051
7.605
7.587
7.568
7.494
7.475
7.456
6.405
5.773
4.126
4.109
4.092
3.333
3.297
2.977
2.941
1.623
1.605
1.586
1.569
1.394
1.375
1.356
1.337
0.934
0.915
0.897
O
NC
COO^{t}Bu
COO^{t}Bu
3c
9
8
7
6
5
4
3
2
1
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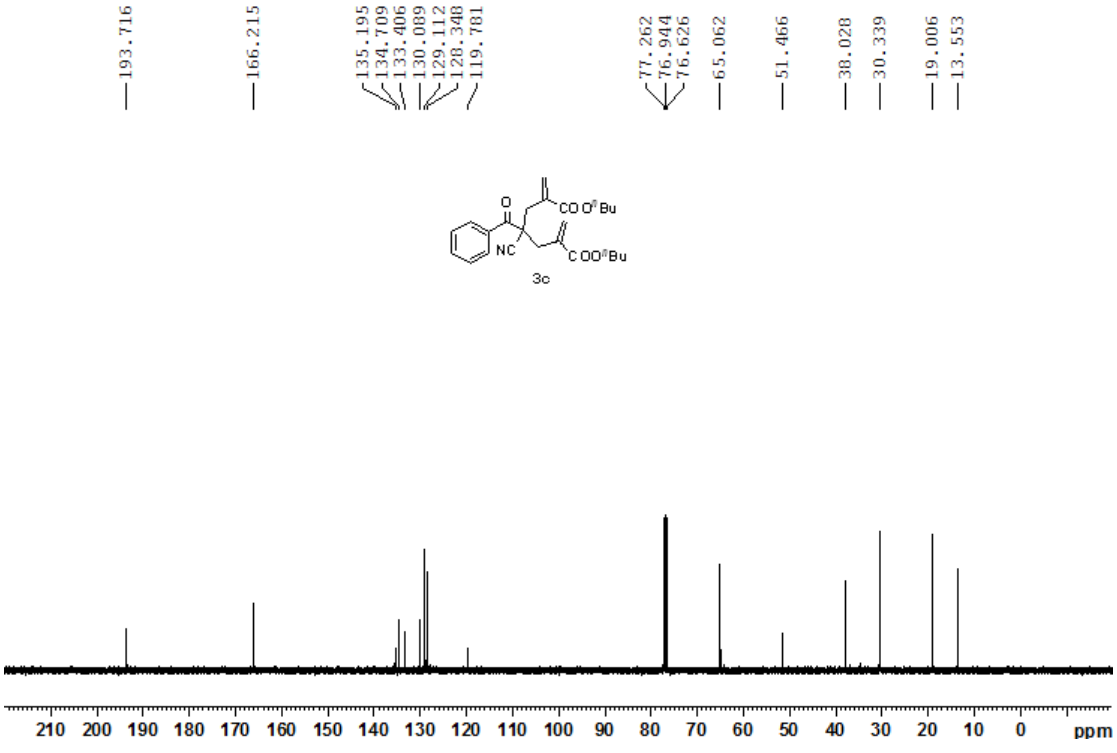
4.23
2.03
2.12
4.00
4.51
6.50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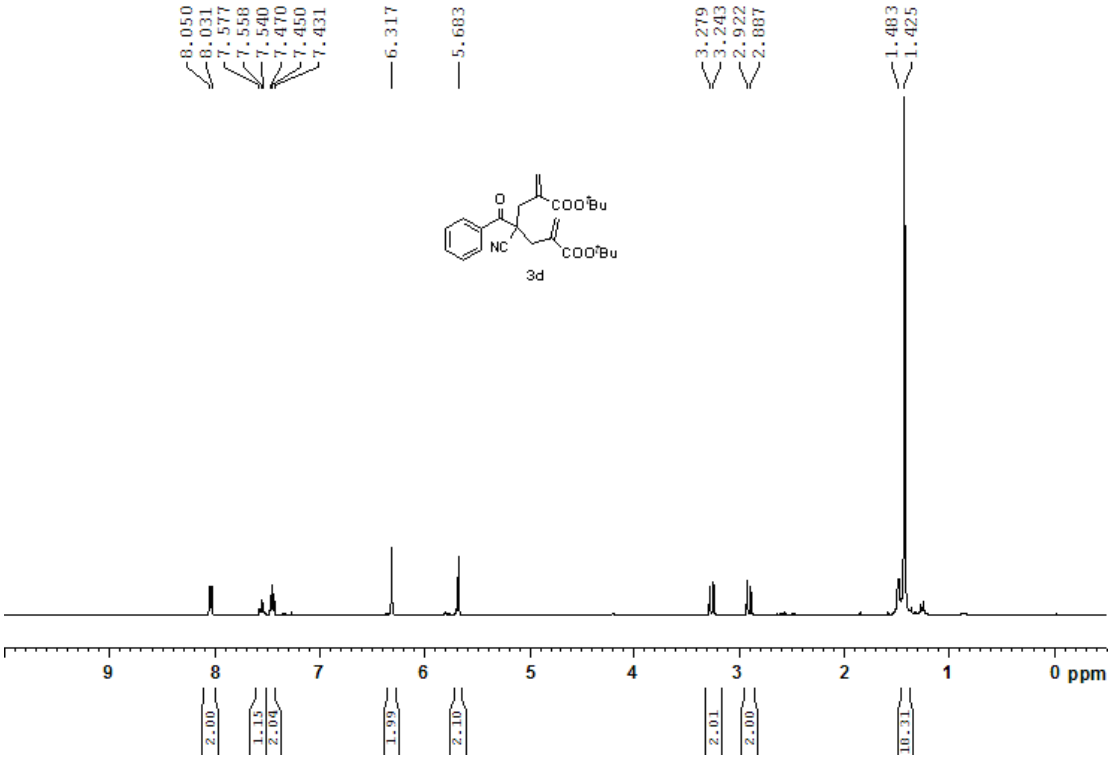
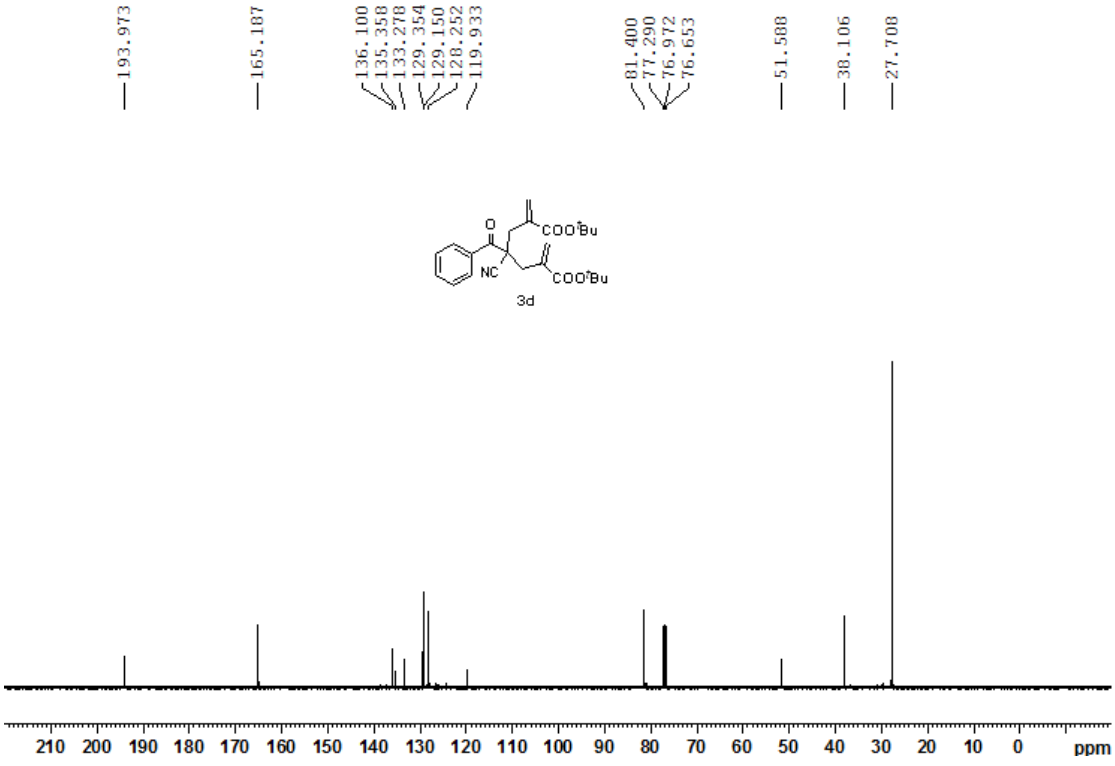
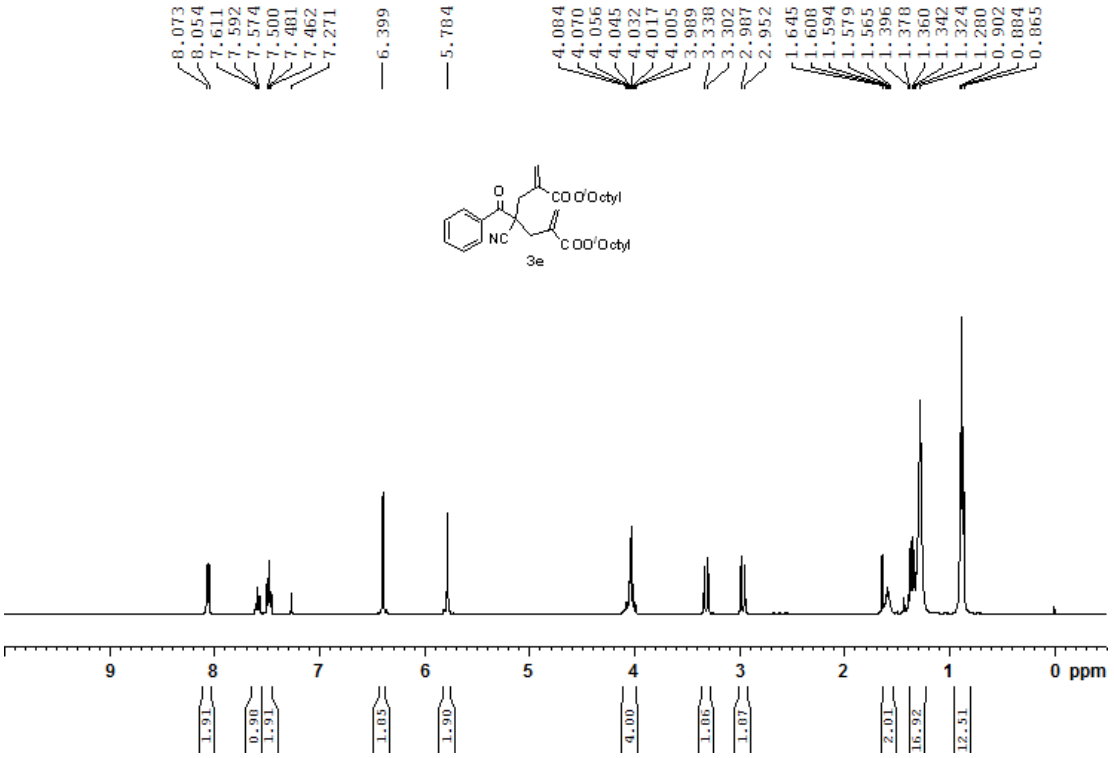
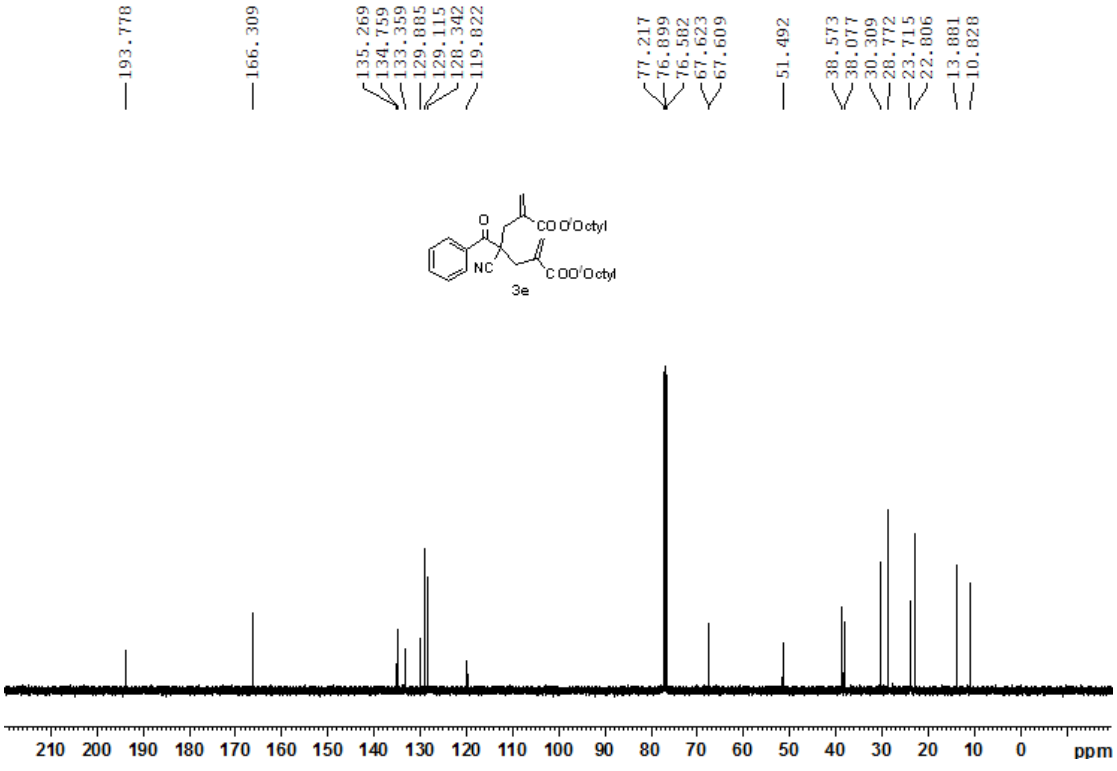
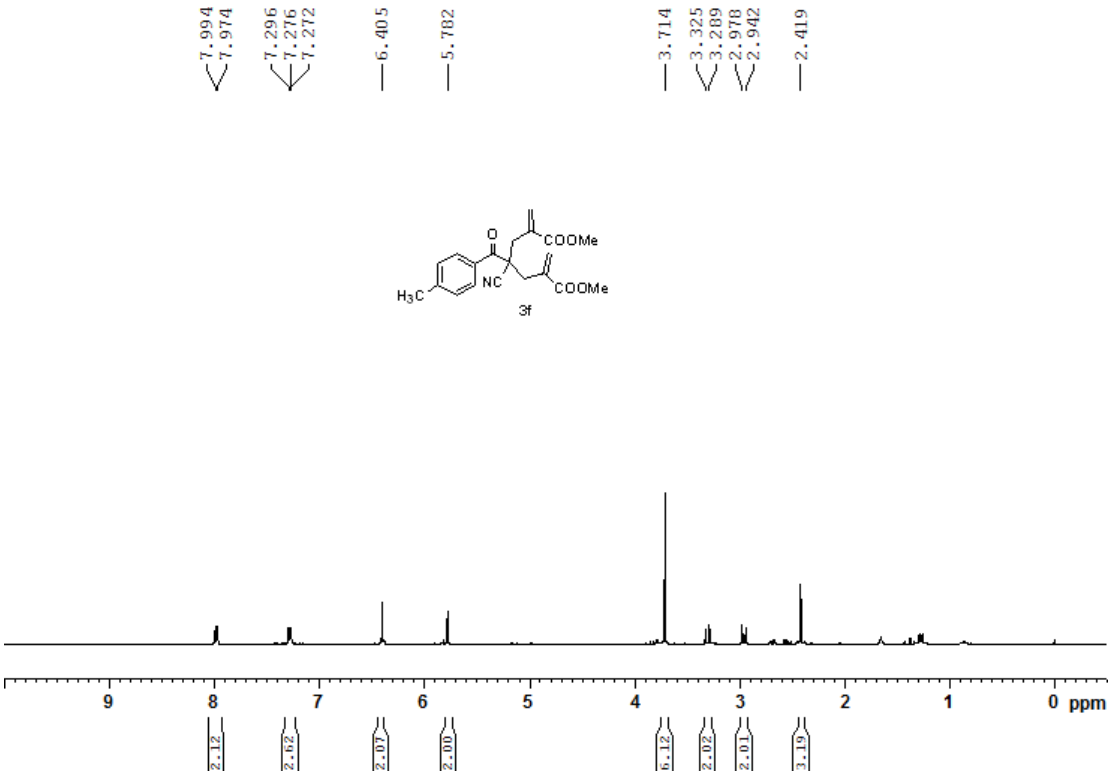
166.215
135.195
134.709
133.406
130.089
129.112
128.348
119.781
77.262
76.944
76.626
65.062
51.466
38.028
30.339
19.006
13.553
O
NC
COO^{t}Bu
COO^{t}Bu
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

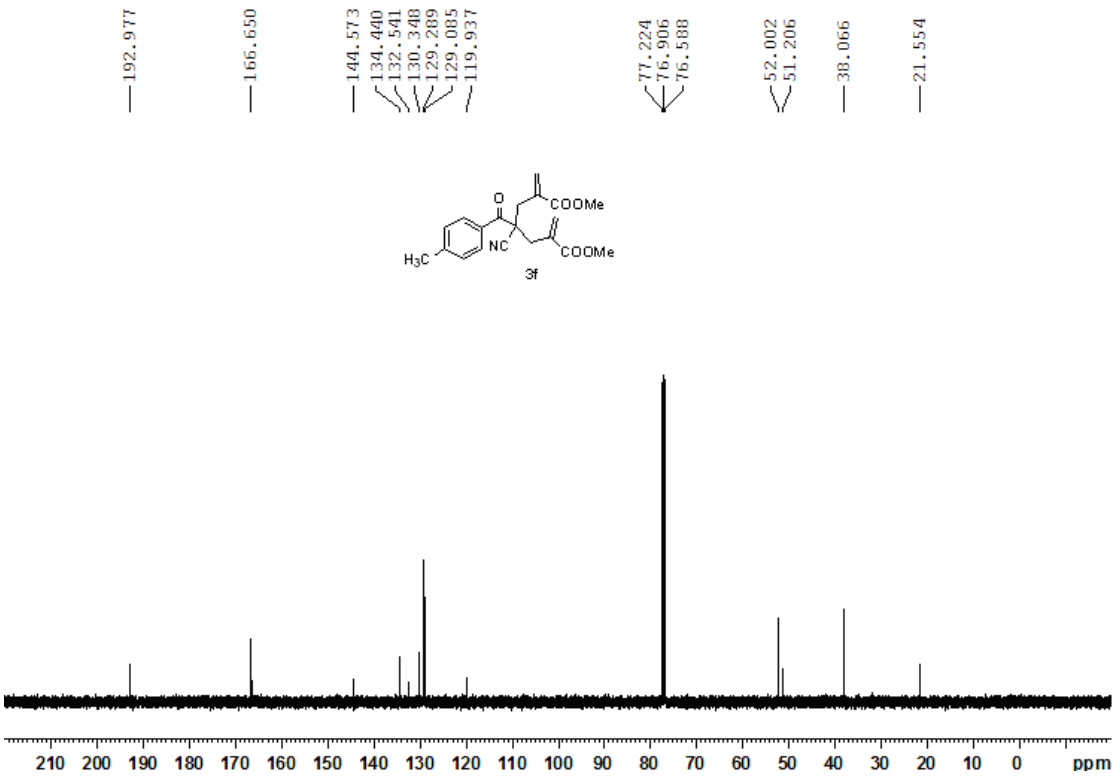


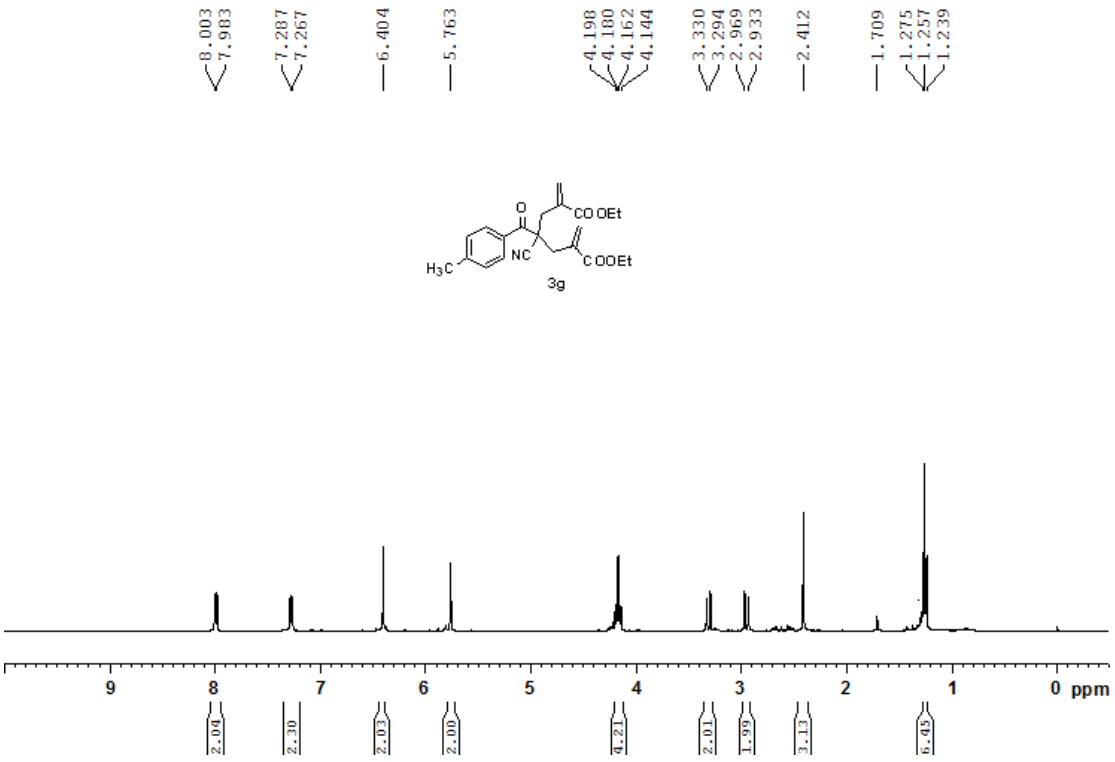


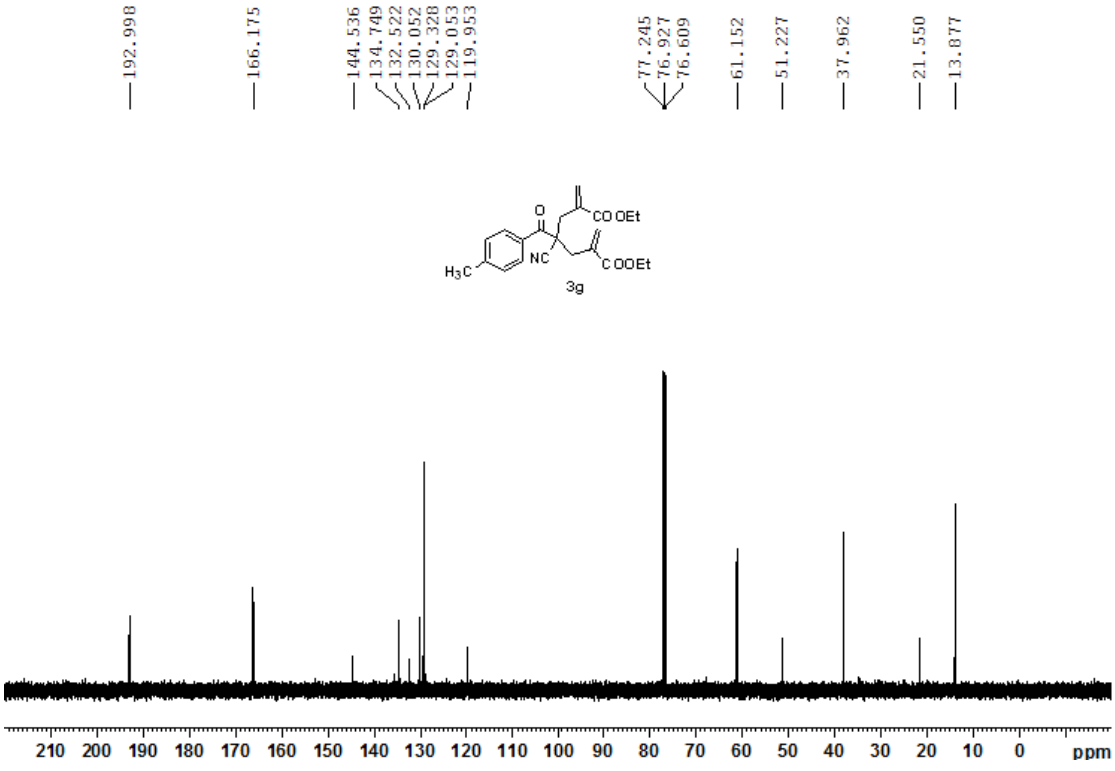


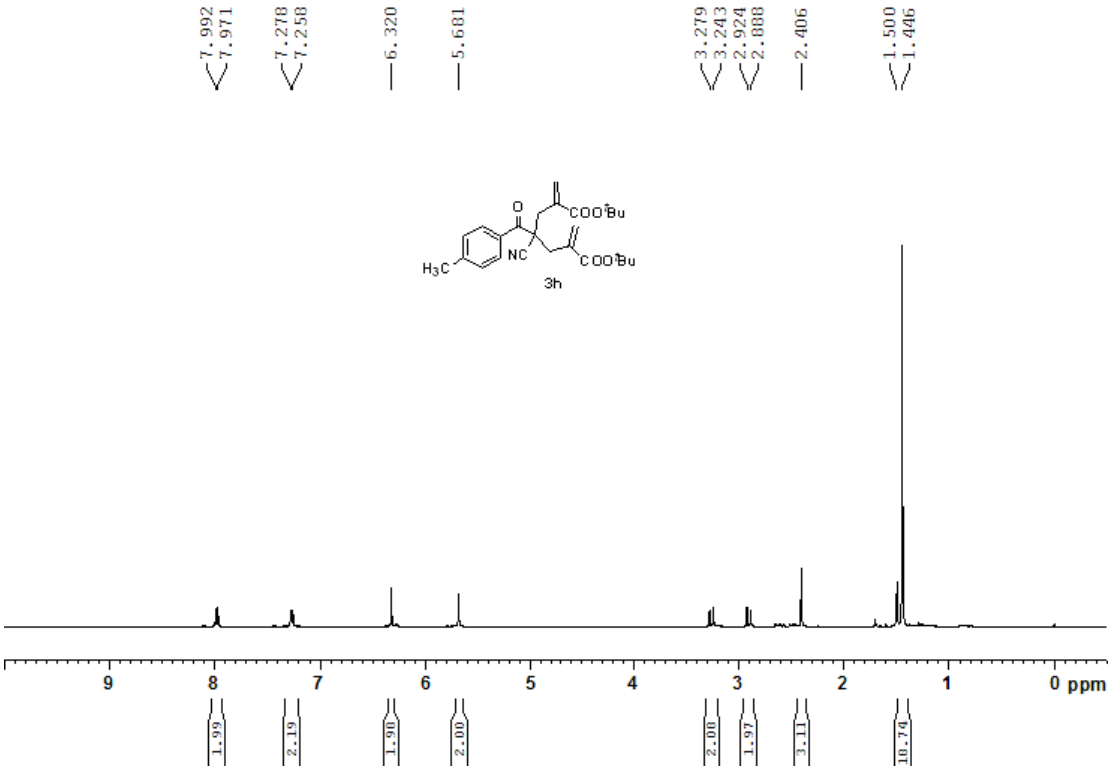


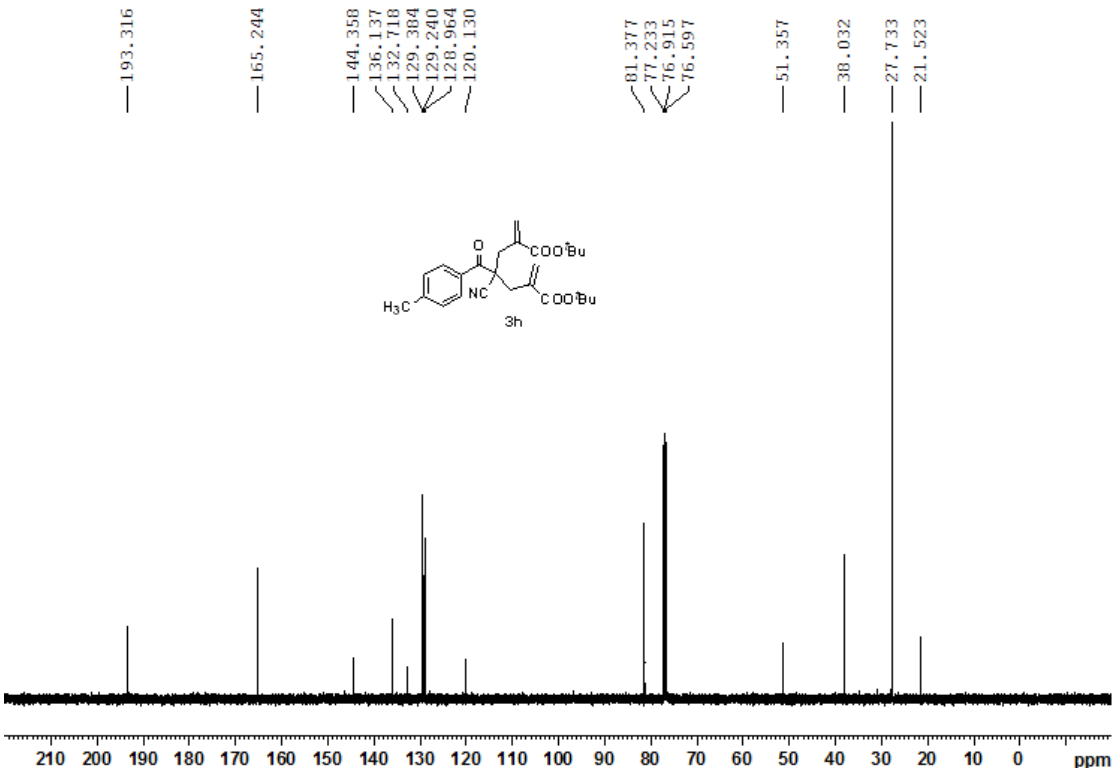


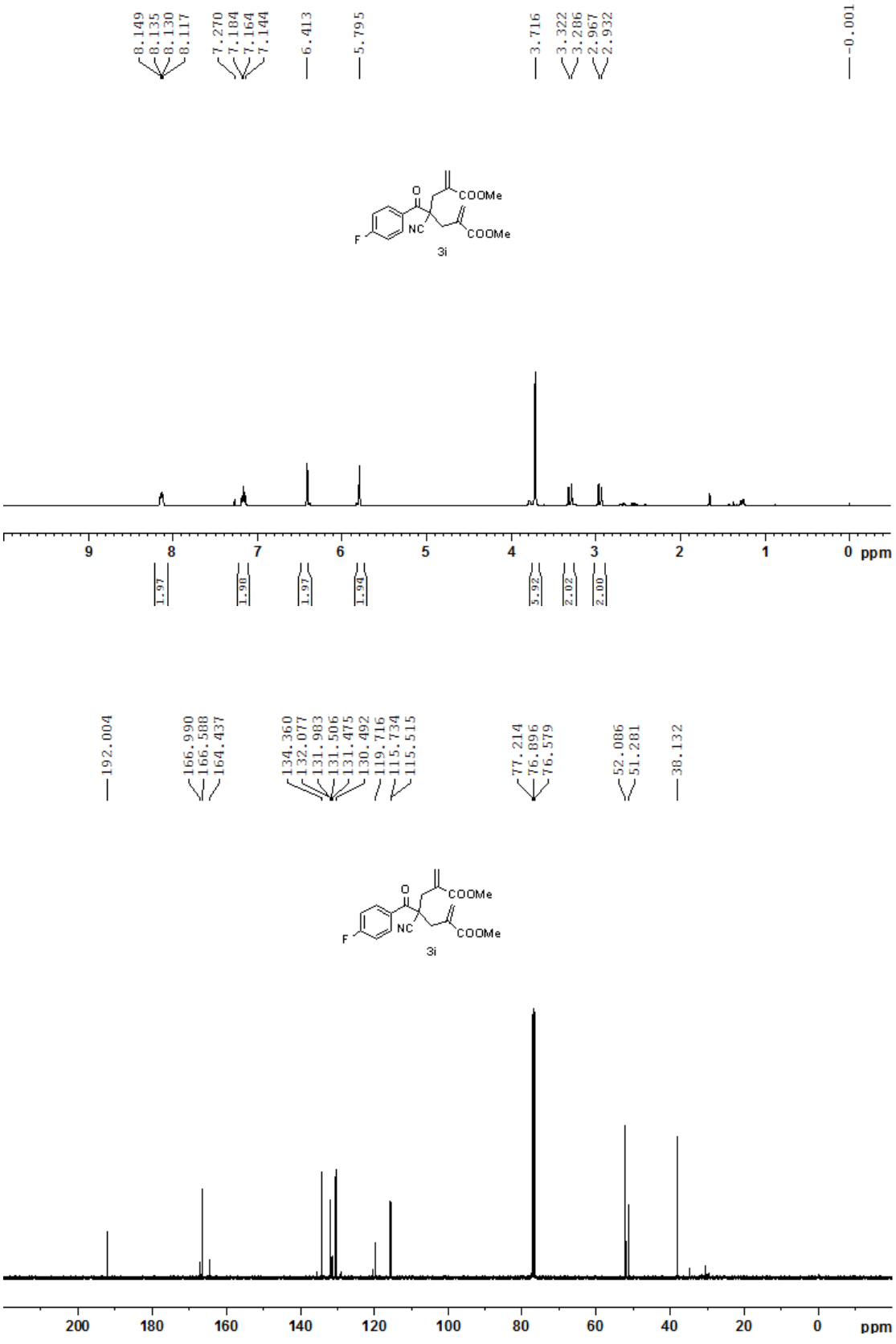


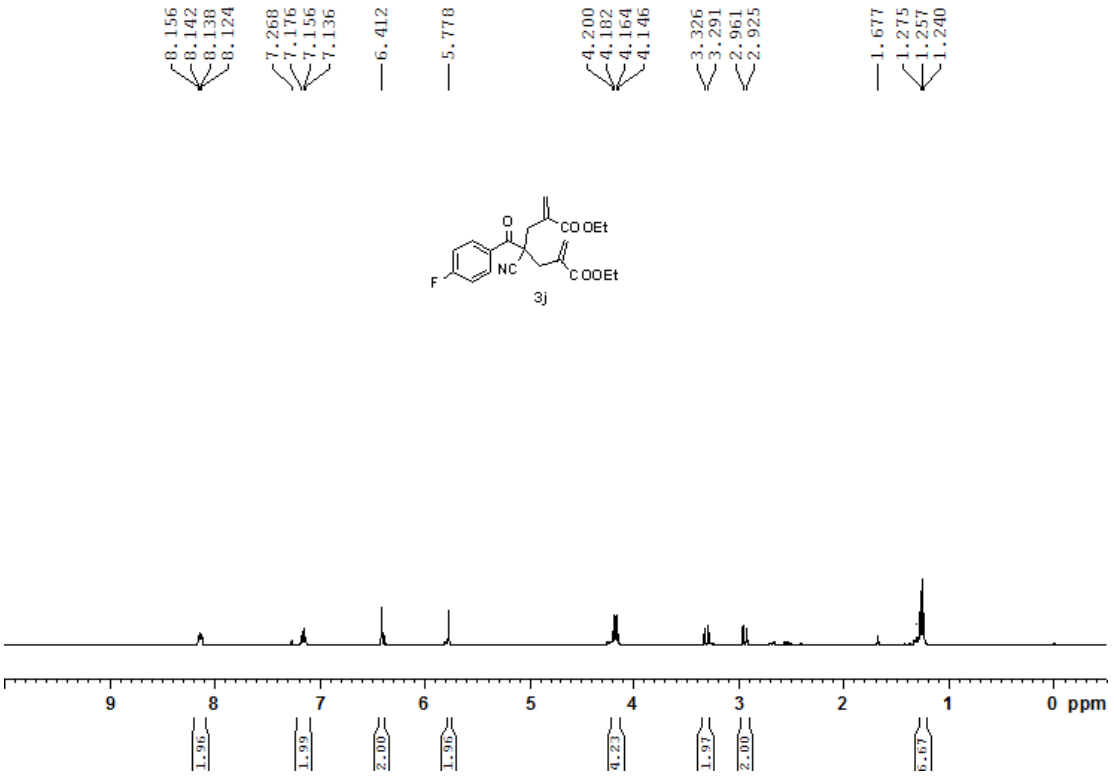








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COOEt
NC
COOEt
F
3j
9
8
7
6
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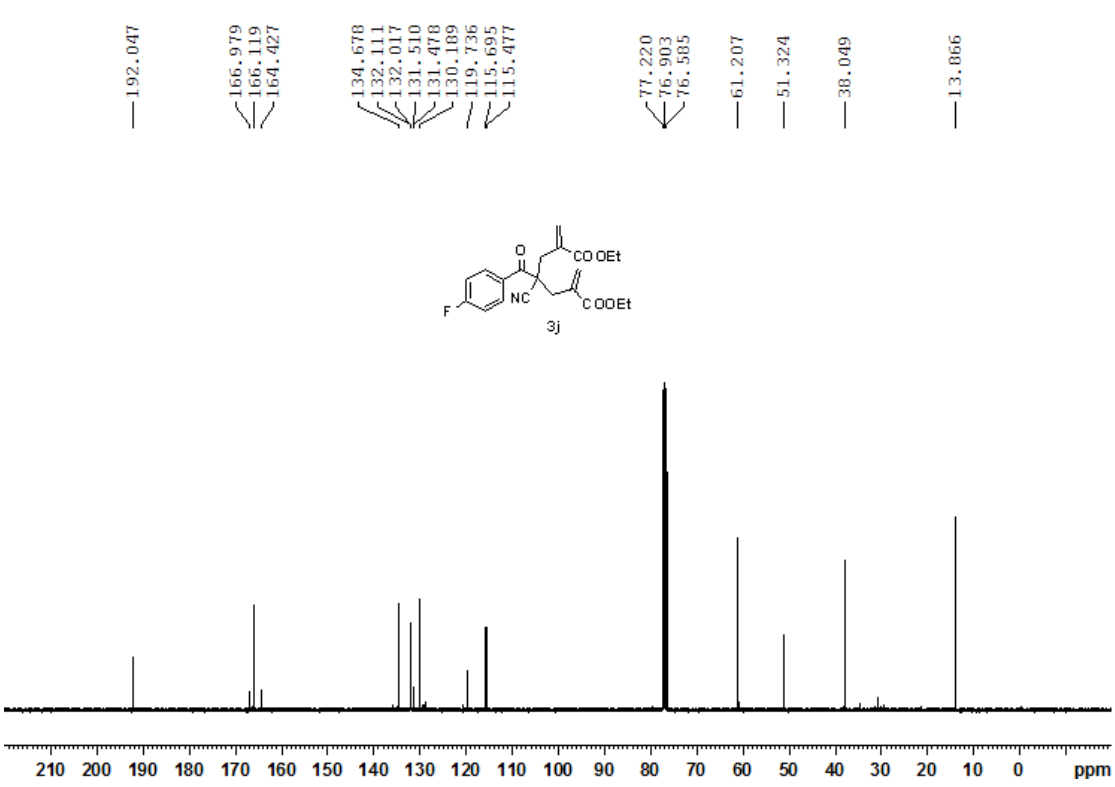
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F
3j
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