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Supporting Information

for DOI:

Efficient Strategy for Construction of 6-Carbamoylfulvene-6-carboxylate Skeletons via [3+2] Cycloaddition of 1-Cyanocyclopropane 1-Ester with β-Nitrostyrenes

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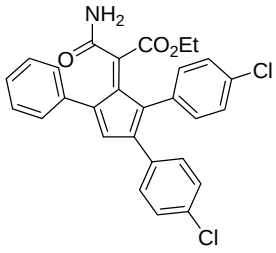
Experimental section

All melting points were determined in a Yanaco melting point apparatus and are uncorrected. IR spectra were recorded in a Nicolet FT-IR 5DX spectrometer. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in a Bruker AV-400 spectrometer with TMS as internal reference in $CDCl_3$ solutions. The *J* values are given in hertz. Only discrete or characteristic signals for the ^{1}H NMR are reported. The MS spectra were obtained on a ZAB-HS mass spectrometer with 70 eV. High-resolution ESI mass spectra were obtained on a UHR-TOF maXis (ESI) mass spectrometer. X-ray crystallographic analysis was performed with a SMART APEX-Ⅱ diffractometer. Flash chromatography was performed on silica gel (230-400 mesh) eluting with ethyl acetate-hexanes mixture. All reactions were monitored by thin layer chromatography (TLC). All reagents and solvents were purchased from commercial sources and purified commonly before used.

General procedure for preparation of 6-carbamoylfulvene-6-carboxylates

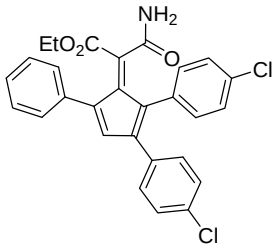
The standard procedure for the synthesis of 6-carbamoylfulvene-6-carboxylates via [3+2] cycloaddition reaction between 1-cyclopropane1-ester and substituted *β*-nitrostyrenes is as follows. To the mixture of 1-cyclopropane1-ester (3 mmol) and substituted *β*-nitrostyrenes (3 mmol) in toluene (15 mL) was added triethylamine (9mmol, 0.909g). The resulting mixture was stirred at 110 ^{o}C for 12 h, and the completion of reaction was confirmed by TLC (Hexanes/EtOAc, 2:1). Subsequently, the solvent was removed by reduced pressure, the residues was added with water (10 mL) and was extracted with dichloromethane (10 mL X 2). The organic phase was washed with water (10 mL) and brine (5 mL), and dried over anhydrate sodium sulfate. After removal of dichloromethane, the crude product was purified by flash chromatography (silica gel, EtOAc/hexanes, 1/8) to give the desirable *Z*-isomer (upper) and *E*-isomer (lower) products, respectively.

(2Z) Ethyl 2-(2,3-bis(4-chlorophenyl)-5-phenylcyclopenta-2,4-dienylidene)-2-carbamoyl-acetate (3a)



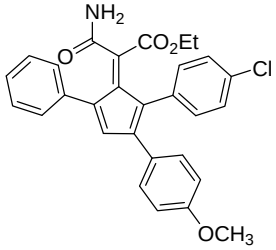
Red solid; m.p.: 223.4-223.7 °C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.38-7.31 (m, 5H), 7.30-7.28 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.66 (s, 1H), 5.43 (s, 1H), 5.03 (s, 1H), 3.76 (q, *J* = 7.2 Hz, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 164.8, 164.3, 145.6, 143.7, 139.7, 135.9, 135.8, 134.0, 133.8, 133.2, 132.8, 132.4, 129.9, 129.6, 128.7, 128.5, 128.4, 128.0, 127.5, 62.3, 13.4; IR (KBr, cm^{-1}) ν: 3414, 3283, 3168, 2996, 1716, 1660, 1609, 1508, 1367, 1254, 1179, 826; MS(EI) (m/z): 490.31 [$(M+1)^+$] (100%); HRMS (ESI) calcd for $C_{28}H_{21}Cl_2NO_3$ [$M+H]^+$ 490.0977; Found 490.0970.

(2E) Ethyl 2-(2,3-bis(4-chlorophenyl)-5-phenylcyclopenta-2,4-dienylidene)-2-carbamoyl-acetate (3a')



Red solid; m.p.: 219.1-219.9 °C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.40 (d, *J* = 6.8 Hz, 2H), 7.37-7.33 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 4H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.71 (s, 1H), 5.49 (s, 1H), 4.99 (s, 1H), 3.45 (q, *J* = 7.2 Hz, 2H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 164.6, 164.5, 145.2, 143.4, 139.3, 136.3, 136.2, 135.8, 134.0, 133.8, 133.1, 132.7, 132.5, 130.2, 129.5, 128.6, 128.5, 128.3, 128.0, 127.7, 62.3, 13.5; IR (KBr, cm^{-1}) ν: 3411, 3280, 3164, 2996, 1717, 1661, 1608, 1509, 1364, 1254, 1173, 828; MS(EI) (m/z): 490.21 [$(M+1)^+$] (100%); HRMS (ESI) calcd for $C_{28}H_{21}Cl_2NO_3$ [$M+H]^+$ 490.0977; Found 490.0968.

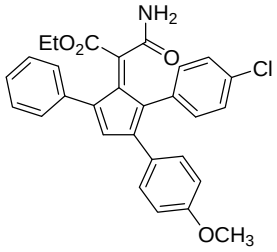
(2Z) Ethyl 2-carbamoyl-2-(2-(4-chlorophenyl)-3-(4-methoxyphenyl)-5-phenylcyclopenta-2,4 -dienylidene)acetate (3b)



Red solid; m.p.: 203.2-204.0 °C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.36-7.33 (m, 4H), 7.31-7.29 (m, 1H), 7.27-7.26 (m, 2H), 7.24-7.22 (m, 2H), 7.07 (d, *J* = 9.2 Hz, 2H), 6.73 (d, *J* = 9.2 Hz, 2H), 6.71 (s, 1H), 5.40 (s, 1H), 5.00 (s, 1H), 3.76 (s, 3H), 3.35 (q, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 165.1, 164.7, 159.5, 146.3, 144.4, 139.5, 136.4, 136.1, 134.6, 133.9, 132.6, 129.8, 128.7, 128.3, 127.9, 127.7, 127.4, 126.7, 113.7, 62.2, 55.2, 13.4; IR (KBr, cm^{-1}) ν: 3415, 3283, 3167, 2998, 1717, 1662, 1608, 1509, 1364, 1255, 1178, 827; MS(EI) (m/z): 486.37 [$(M+1)^+$] (100%); HRMS (ESI) calcd for $C_{29}H_{24}ClNO_4$ [$M+H]^+$ 486.1472; Found 486.1471.

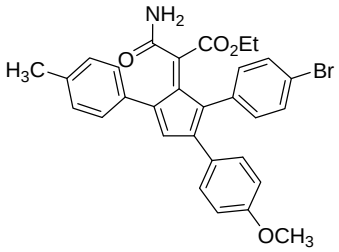
(2E) Ethyl 2-carbamoyl-2-(2-(4-chlorophenyl)-3-(4-methoxyphenyl)-5-phenylcyclopenta-2,4

-dienylidene)acetate (3b')



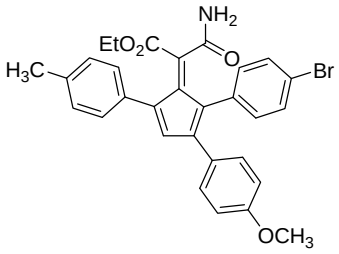
Red solid; m.p.: 220.5-221.3 °C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.40 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.36-7.33 (m, 2H), 7.32-7.29 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 9.2 Hz, 2H), 6.76 (s, 1H), 6.72 (d, *J* = 9.2 Hz, 2H), 5.49 (s, 1H), 4.99 (s, 1H), 3.76 (s, 3H), 3.45 (q, *J* = 7.2 Hz, 2H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 164.9, 159.5, 145.8, 144.1, 139.1, 136.8, 136.1, 134.8, 133.8, 133.4, 132.7, 129.7, 128.6, 128.2, 127.9, 127.6, 126.6, 113.7, 62.1, 55.2, 13.5; IR (KBr, cm^{-1}) ν: 3418, 3284, 3166, 2999, 1718, 1660, 1606, 1508, 1365, 1254, 1177, 835; MS(EI) (m/z): 486.30 [$(M+1)^+$] (100%); HRMS (ESI) calcd for $C_{29}H_{24}ClNO_4$ $[M+H]^+$ 486.1472; Found 486.1472.

(2Z) Ethyl 2-(2-(4-bromophenyl)-3-(4-methoxyphenyl)-5-*p*-tolylcyclopenta-2,4-dienylidene) -2-carbamoylacetate (3c)



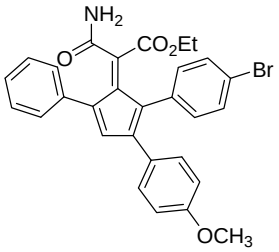
Red solid; m.p.: 214.0-214.6 °C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.41 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 4H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.67 (s, 1H), 5.37 (s, 1H), 4.97 (s, 1H), 3.76 (s, 3H), 3.39 (q, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 165.1, 164.7, 159.5, 146.3, 144.5, 139.5, 137.1, 136.0, 134.5, 133.1, 132.9, 131.3, 129.8, 128.6, 127.5, 126.7, 121.7, 113.7, 62.2, 55.2, 21.2, 13.4; IR (KBr, cm^{-1}) ν: 3421, 3293, 3167, 2995, 1717, 1665, 1618, 1508, 1360, 1254, 1167, 832; MS(EI) (m/z): 544.25 [$(M+1)^+$] (100%); HRMS (ESI) calcd for $C_{30}H_{26}BrNO_4$ $[M+H]^+$ 544.1123; Found 544.1120.

(2E) Ethyl 2-(2-(4-bromophenyl)-3-(4-methoxyphenyl)-5-*p*-tolylcyclopenta-2,4-dienylidene) -2-carbamoylacetate (3c')



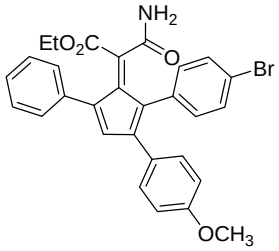
Red solid; m.p.: 208.1-208.7 °C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.45 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 6.0 Hz, 2H), 7.12 (d, *J* = 6.0 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 5.47 (s, 1H), 4.97 (s, 1H), 3.76 (s, 3H), 3.45 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 165.0, 164.9, 159.5, 145.9, 144.1, 139.1, 137.4, 136.4, 134.7, 134.3, 133.1, 131.2, 129.7, 128.7, 128.5, 127.8, 126.7, 121.6, 113.7, 62.1, 55.2, 21.3, 13.5; IR (KBr, cm^{-1}) ν: 3415, 3287, 3169, 2996, 1717, 1663, 1608, 1506, 1364, 1257, 1173, 825; MS(EI) (m/z): 544.36 [$(M+1)^+$] (100%); HRMS (ESI) calcd for $C_{30}H_{26}BrNO_4$ $[M+H]^+$ 544.1123; Found 544.1117.

(2Z) Ethyl 2-(2-(4-bromophenyl)-3-(4-methoxyphenyl)-5-phenylcyclopenta-2,4-dienylidene) -2-carbamoylacetate (3d)



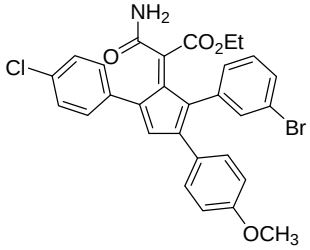
Red solid; m.p.: 212.1-212.9 °C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.42 (d, *J* = 8.4 Hz, 2H), 7.38-7.33 (m, 4H), 7.31-7.28 (m, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.71 (s, 1H), 5.39 (s, 1H), 5.00 (s, 1H), 3.76 (s, 3H), 3.35 (q, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 165.1, 164.7, 159.5, 146.2, 144.4, 139.5, 136.5, 136.1, 134.5, 132.9, 131.3, 131.2, 129.9, 129.7, 128.7, 128.0, 127.7, 127.4, 126.7, 121.7, 113.7, 62.2, 55.2, 13.4; IR (KBr, cm^{-1}) ν: 3414, 3282, 3167, 2996, 1717, 1660, 1608, 1508, 1364, 1254, 1178, 828; MS(EI) (m/z): 530.27 [(M+1)$^+$] (100%); HRMS (ESI) calcd for $C_{29}H_{24}BrNO_4$ [M+H]$^+$ 530.0967; Found 530.0962.

(2E) Ethyl 2-(2-(4-bromophenyl)-3-(4-methoxyphenyl)-5-phenylcyclopenta-2,4-dienylidene) -2-carbamoylacetate (3d')



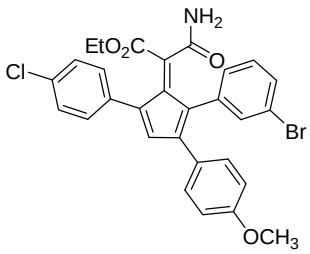
Red solid; m.p.: 230.3-231.1 °C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.45 (d, *J* = 8.4 Hz, 2H), 7.41-7.39 (m, 2H), 7.35-7.30 (m, 3H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.75 (s, 1H), 6.73 (d, *J* = 8.8 Hz, 2H), 5.48 (s, 1H), 4.98 (s, 1H), 3.76 (s, 3H), 3.45 (q, *J* = 6.8 Hz, 2H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 164.9, 159.5, 145.8, 144.1, 139.1, 136.8, 136.1, 134.3, 133.0, 131.2, 129.7, 128.6, 128.0, 127.6, 126.6, 121.6, 113.7, 62.2, 55.2, 13.5; IR (KBr, cm^{-1}) ν: 3414, 3282, 3168, 2996, 1717, 1661, 1608, 1507, 1364, 1254, 1178, 829; MS(EI) (m/z): 530.37 [(M+1)$^+$] (100%); HRMS (ESI) calcd for $C_{29}H_{24}BrNO_4$ [M+H]$^+$ 530.0967; Found 530.0960.

(2Z) Ethyl 2-(2-(3-bromophenyl)-5-(4-chlorophenyl)-3-(4-methoxyphenyl)cyclopenta-2,4-dienylidene) -2-carbamoylacetate (3e)



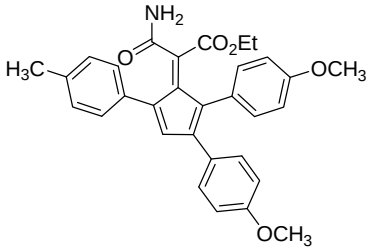
Red solid; m.p.: 192.3-192.9 °C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.35-7.34 (m, 1H), 7.32 (d, *J* = 6.8 Hz, 3H), 7.30-7.28 (m, 3H), 7.13 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.75 (s, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 5.57 (s, 1H), 5.06 (s, 1H), 3.76 (s, 3H), 3.51-3.46 (m, 2H), 1.07 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 164.6, 159.6, 145.4, 144.2, 138.0, 137.2, 137.1, 134.5, 133.8, 133.5, 131.1, 129.9, 129.8, 129.7, 129.4, 128.2, 127.9, 127.6, 126.3, 113.8, 110.0, 62.3, 55.2, 13.5; IR (KBr, cm^{-1}) ν: 3416, 3281, 3165, 2996, 1713, 1662, 1608, 1507, 1363, 1254, 1176, 822; MS(EI) (m/z): 564.50 [(M+1)$^+$] (100%); HRMS (ESI) calcd for $C_{29}H_{23}BrClNO_4$ [M+H]$^+$ 564.0577; Found 564.0571.

(2E) Ethyl 2-(2-(3-bromophenyl)-5-(4-chlorophenyl)-3-(4-methoxyphenyl)cyclopenta-2,4-dienylidene)-2-carbamoylacetate (3e')



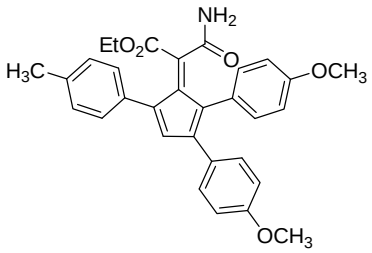
Red solid; m.p.: 212.0-212.9 ^{o}C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.33 (d, *J* = 8.4 Hz, 2H), 7.29-7.26 (m, 4H), 7.24-7.21 (m, 1H), 7.17 (dt, *J* = 7.2, 1.6 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.71 (s, 1H), 5.46 (s, 1H), 5.11 (s, 1H), 3.76 (s, 3H), 3.46 (q, *J* = 7.2 Hz, 2H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 165.0, 164.4, 159.6, 146.0, 144.3, 138.2, 137.2, 136.7, 134.8, 134.5, 133.7, 133.4, 131.1, 130.0, 129.9, 129.6, 129.4, 128.1, 127.8, 127.7, 126.4, 113.8, 62.3, 55.2, 13.9; IR (KBr, cm^{-1}) ν: 3411, 3282, 3167, 2996, 1716, 1660, 1608, 1509, 1364, 1256, 1178, 828; MS(EI) (m/z): 564.18 [$(M+1)^{+}$] (45%); HRMS (ESI) calcd for $C_{29}H_{23}BrClNO_4$ [M+H]$^{+}$ 564.0577; Found 564.0568.

(2Z) Ethyl 2-(2,3-bis(4-methoxyphenyl)-5-*p*-tolylcyclopenta-2,4-dienylidene)-2-carbamoyl--acetate (3f)



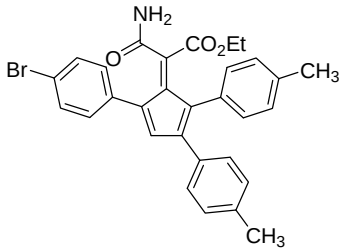
Red solid; m.p.: 194.1-194.6 ^{o}C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.29 (d, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 2H), 6.69 (s, 1H), 5.49 (s, 1H), 4.99 (s, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 3.44 (q, *J* = 6.8 Hz, 2H), 2.35 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 165.3, 165.1, 159.2, 158.9, 146.4, 143.3, 138.5, 137.1, 136.5, 134.5, 133.4, 132.5, 131.1, 129.7, 128.7, 128.4, 127.3, 127.2, 113.6, 113.4, 62.0, 55.2, 55.1, 21.2, 13.5; IR (KBr, cm^{-1}) ν: 3412, 3280, 3168, 2996, 1716, 1660, 1601, 1508, 1362, 1256, 1178, 829; MS(EI) (m/z): 496.46 [$(M+1)^{+}$] (100%); HRMS (ESI) calcd for $C_{31}H_{29}NO_5$ [M+H]$^{+}$ 496.2124; Found 496.2117.

(2E) Ethyl 2-(2,3-bis(4-methoxyphenyl)-5-*p*-tolylcyclopenta-2,4-dienylidene)-2-carbamoyl--acetate (3f')



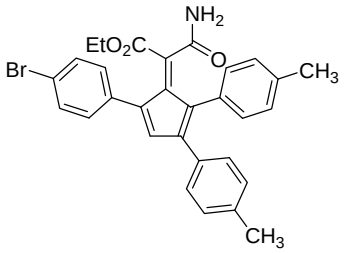
Red solid; m.p.: 193.4-194.2 ^{o}C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.24 (d, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 7.2 Hz, 2H), 6.81 (d, *J* = 7.6 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.69 (s, 1H), 5.32 (s, 1H), 5.05 (s, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 3.38 (q, *J* = 6.8 Hz, 2H), 2.35 (s, 3H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 165.3, 165.2, 159.2, 158.9, 146.9, 143.5, 138.9, 136.9, 136.1, 134.3, 133.4, 132.4, 129.8, 128.6, 128.5, 127.6, 127.2, 113.6, 113.5, 62.0, 55.1, 21.2, 13.4; IR (KBr, cm^{-1}) ν: 3413, 3282, 3167, 2995, 1717, 1660, 1607, 1508, 1363, 1254, 1175, 829; MS(EI) (m/z): 496.33 [$(M+1)^{+}$] (100%); HRMS (ESI) calcd for $C_{31}H_{29}NO_5$ [M+H]$^{+}$ 496.2124; Found 496.2119.

(2Z) Ethyl 2-(5-(4-bromophenyl)-2,3-dip-tolylcyclopenta-2,4-dienylidene)-2-carbamoyl--acetate (3g)



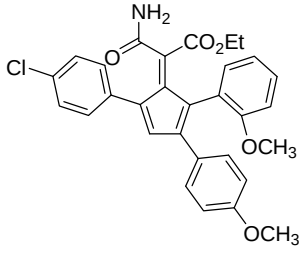
Red solid; m.p.: 225.1-225.8 ^{o}C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.45 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.12-7.10 (m, 4H), 7.01-6.96 (m, 4H), 6.76 (s, 1H), 5.60 (s, 1H), 5.08 (s, 1H), 3.36 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 2.27 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 164.9, 164.8, 145.8, 143.5, 138.0, 137.6, 137.3, 137.2, 135.3, 135.2, 131.7, 131.5, 131.1, 130.9, 130.1, 128.9, 128.7, 128.2, 121.5, 62.1, 21.3, 21.2, 13.4; IR (KBr, cm^{-1}) ν: 3459, 3417, 3282, 3159, 2993, 1733, 1670, 1608, 1478, 1361, 1260, 1136, 1112, 1037, 819; MS(EI) (m/z): 528.16 [$(M+1)^+$] (100%); HRMS (ESI) calcd for $C_{30}H_{26}BrNO_3$ $[M+H]^+$ 528.1174; Found 528.1172.

(2E) Ethyl 2-(5-(4-bromophenyl)-2,3-dip-tolylcyclopenta-2,4-dienylidene)-2-carbamoyl--acetate (3g')



Red solid; m.p.: 228.2-228.9 ^{o}C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.57 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.73 (s, 1H), 5.26 (s, 1H), 4.94 (s, 1H), 3.46 (q, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 2.27 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 164.9, 164.8, 145.8, 143.5, 138.0, 137.6, 137.3, 137.2, 135.3, 135.2, 131.7, 131.5, 131.1, 130.9, 130.1, 128.9, 128.7, 128.2, 121.5, 62.1, 21.3, 21.2, 13.4; IR (KBr, cm^{-1}) ν: 3454, 3418, 3282, 3154, 2992, 1730, 1670, 1605, 1479, 1367, 1260, 1132, 1112, 1034, 818; MS(EI) (m/z): 528.29 [$(M+1)^+$] (100%); HRMS (ESI) calcd for $C_{30}H_{26}BrNO_3$ $[M+H]^+$ 528.1174; Found 528.1173.

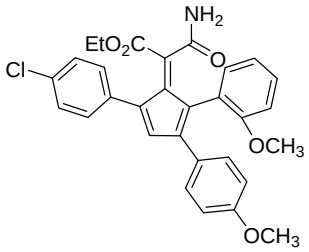
(2Z) Ethyl 2-carbamoyl-2-(5-(4-chlorophenyl)-2-(2-methoxyphenyl)-3-(4-methoxyphenyl) cyclopenta-2,4-dienylidene)acetate (3h)



Red solid; m.p.: 212.6-213.0 ^{o}C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.37-7.35 (m, 2H), 7.30-7.27 (m, 3H), 7.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.09-7.08 (m, 1H), 7.07-7.06 (m, 1H), 6.91 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.89-6.87 (m, 1H), 6.80 (s, 1H), 6.72-6.68 (m, 2H), 5.57 (s, 1H), 5.05 (s, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 3.46-3.23 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 165.2, 164.8, 159.3, 158.6, 145.6, 143.4, 137.7, 137.5, 134.9, 134.1, 133.2, 132.8, 129.8, 129.4, 129.1, 128.1, 127.3, 126.3, 123.9, 120.3, 113.6, 110.8, 61.9, 55.5, 55.1, 13.4; IR (KBr, cm^{-1}) ν: 3460, 3414, 3282, 3153, 2992, 1733, 1670, 1606, 1479, 1366, 1260, 1138, 1112, 1032, 819;

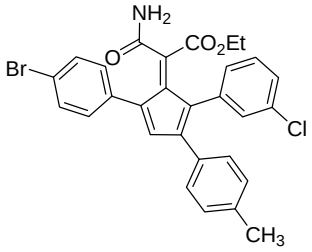
MS(EI) (m/z): 516.82 [$(M+1)^+$] (62%); HRMS (ESI) calcd for $C_{30}H_{26}ClNO_5$ $[M+H]^+$ 516.1578; Found 516.1571.

(2E) Ethyl 2-carbamoyl-2-(5-(4-chlorophenyl)-2-(2-methoxyphenyl)-3-(4-methoxyphenyl) cyclopenta-2,4-dienylidene)acetate (3h')



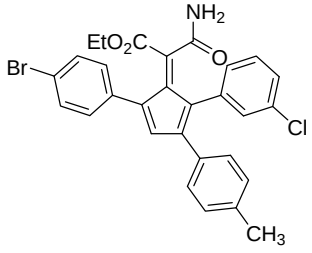
Red solid; m.p.: 200.1-201.0 ^oC (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.34-7.29 (m, 4H), 7.25 (s, 1H), 7.15-7.12 (m, 3H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.78 (s, 1H), 6.71 (d, *J* = 8.8 Hz, 2H), 5.50 (s, 1H), 4.93 (s, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.56-3.38 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 165.2, 164.9, 159.4, 158.6, 146.5, 143.8, 138.1, 136.9, 135.0, 133.8, 133.1, 132.9, 129.9, 129.8, 129.2, 128.1, 127.2, 125.6, 124.3, 120.7, 113.6, 110.9, 62.1, 55.5, 55.2, 13.5; IR (KBr, cm^{-1}) ν: 3461, 3417, 3280, 3159, 2991, 1731, 1665, 1608, 1474, 1361, 1265, 1137, 1114, 1032, 818; MS(EI) (m/z): 516.15 [$(M+1)^+$] (84%); HRMS (ESI) calcd for $C_{30}H_{26}ClNO_5$ $[M+H]^+$ 516.1578; Found 516.1575.

(2Z) Ethyl 2-(5-(4-bromophenyl)-2-(3-chlorophenyl)-3-*p*-tolylcyclopenta-2,4-dienylidene)-2-carbamoylacetate (3i)



Red solid; m.p.: 198.0-198.7 ^oC (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.46 (d, *J* = 8.4 Hz, 2H), 7.34-7.27 (m, 4H), 7.25-7.23 (m, 1H), 7.13 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.03-6.98 (m, 4H), 6.75 (s, 1H), 5.61 (s, 1H), 5.13 (s, 1H), 3.53-3.44 (m, 2H), 2.29 (s, 3H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 164.6, 164.5, 145.3, 144.6, 138.5, 137.9, 137.4, 136.9, 135.4, 134.9, 133.8, 131.1, 131.0, 130.2, 129.6, 129.3, 129.0, 128.9, 128.2, 127.6, 121.8, 62.4, 21.3, 13.5; IR (KBr, cm^{-1}) ν: 3455, 3418, 3282, 3158, 2992, 1734, 1670, 1607, 1479, 1363, 1260, 1138, 1112, 1038, 819; MS(EI) (m/z): 548.15 [$(M+1)^+$] (75%); HRMS (ESI) calcd for $C_{29}H_{23}BrClNO_3$ $[M+H]^+$ 548.0628; Found 548.0625.

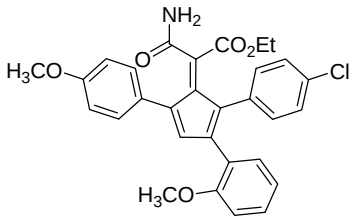
(2E) Ethyl 2-(5-(4-bromophenyl)-2-(3-chlorophenyl)-3-*p*-tolylcyclopenta-2,4-dienylidene)-2-carbamoylacetate (3i')



Red solid; m.p.: 200.5-201.2 ^oC (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.49 (d, *J* = 7.6 Hz, 2H), 7.29-7.28 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.17 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.05-7.00 (m, 4H), 6.72 (s, 1H), 5.50 (s, 1H), 5.23 (s, 1H), 3.47 (q, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 165.0, 164.5, 145.8, 144.8, 138.5, 138.1, 137.0, 136.9, 135.2, 134.9, 133.6, 131.1, 131.0, 129.5, 129.3, 129.0, 128.7, 128.3, 127.8, 121.5, 62.4, 21.3, 13.5; IR (KBr, cm^{-1}) ν: 3462, 3417, 3280, 3159, 2990, 1731, 1672, 1608, 1475, 1361, 1262, 1137, 1110,

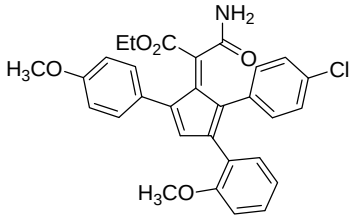
1037, 819; MS(EI) (m/z): 548.60 [$(M+1)^+$] (75%); HRMS (ESI) calcd for $C_{29}H_{23}BrClNO_3$ $[M+H]^+$ 548.0628; Found 548.0622.

(2Z) Ethyl 2-carbamoyl-2-(2-(4-chlorophenyl)-3-(2-methoxyphenyl)-5-(4-methoxyphenyl) cyclopenta-2,4-dienylidene)acetate (3j)



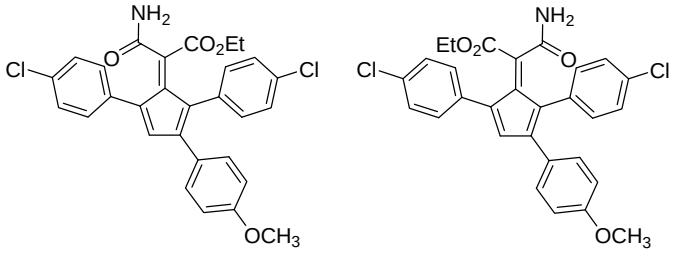
Red solid; m.p.: 177.2-178.0 °C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.27 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.16-7.12 (m, 4H), 6.89 (d, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.74 (d, *J* = 7.2 Hz, 1H), 6.57 (s, 1H), 5.45 (s, 1H), 5.04 (s, 1H), 3.82(s, 3H), 3.70 (s, 3H), 3.47 (q, *J* = 7.2 Hz, 2H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 165.1, 165.0, 159.0, 157.4, 145.6, 144.0, 137.7, 137.6, 134.6, 133.9, 132.9, 131.8, 130.8, 130.7, 130.2, 129.4, 128.5, 127.9, 123.8, 120.3, 113.3, 110.8, 62.2, 55.3, 55.2, 13.5; IR (KBr, cm^{-1}) ν: 3456, 3418, 3282, 3157, 2992, 1734, 1672, 1603, 1479, 1360, 1260, 1138, 1114, 1038, 818; HRMS (ESI) calcd for $C_{30}H_{26}ClNNaO_5[M+Na]^+$ 538.1392; Found 538.1388.

(2E) Ethyl 2-carbamoyl-2-(2-(4-chlorophenyl)-3-(2-methoxyphenyl)-5-(4-methoxyphenyl) cyclopenta-2,4-dienylidene)acetate (3j')



Red solid; m.p.: 196.5-197.1 °C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.33 (d, *J* = 7.2 Hz, 2H), 7.22-7.19 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 7.2 Hz, 2H), 6.74 (d, *J* = 7.2 Hz, 1H), 6.61 (s, 1H), 5.50 (s, 1H), 5.05 (s, 1H), 3.82(s, 3H), 3.69 (s, 3H), 3.43 (q, *J* = 7.2 Hz, 2H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 165.2, 164.9, 159.1, 157.3, 145.3, 143.6, 138.0, 137.1, 134.6, 133.8, 132.8, 132.0, 131.3, 130.7, 139.9, 129.4, 128.5, 127.7, 123.8, 120.2, 113.4, 110.8, 62.1, 55.2, 55.1, 13.5; IR (KBr, cm^{-1}) ν: 3456, 3416, 3282, 3156, 2992, 1735, 1673, 1603, 1477, 1360, 1261, 1139, 1114, 1038, 820; HRMS (ESI) calcd for $C_{30}H_{26}ClNNaO_5[M+Na]^+$ 538.1392; Found 538.1391.

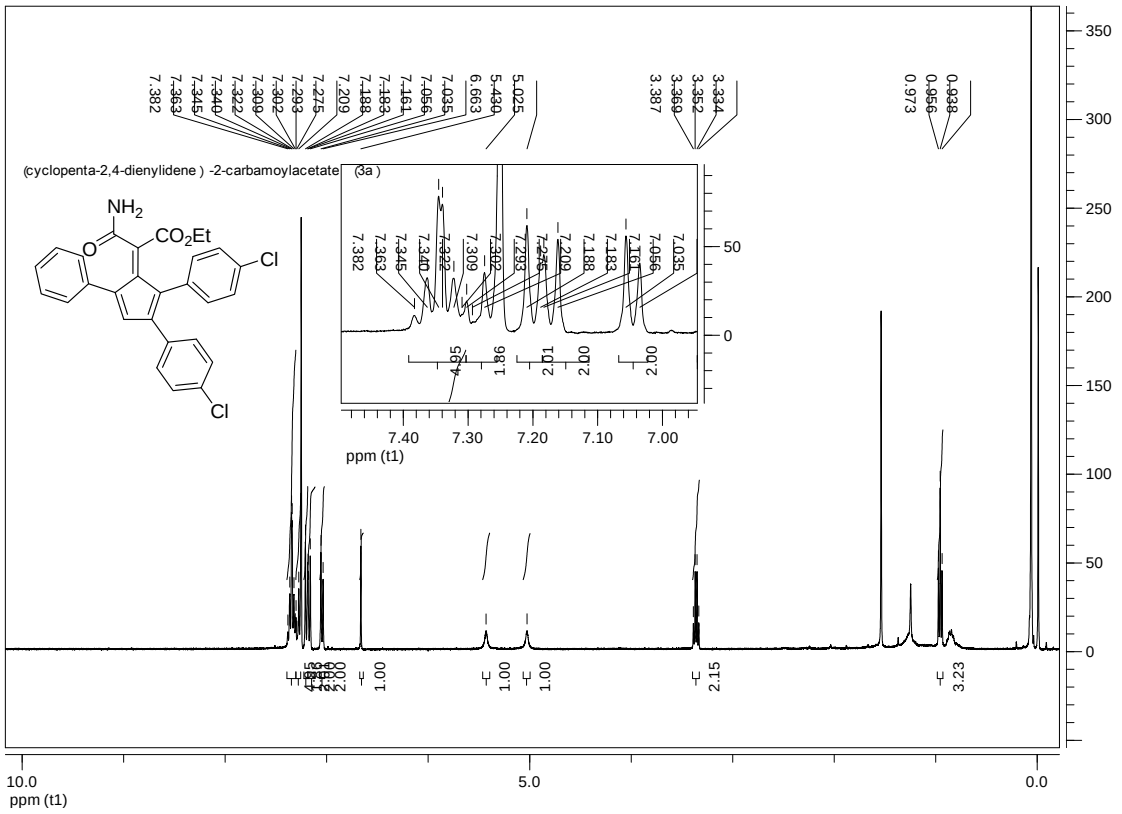
(2E/2Z) Ethyl 2-(2,5-bis(4-chlorophenyl)-3-(4-methoxyphenyl)cyclopenta-2,4-dienylidene)-2-carbamoylacetate (3k/3k')

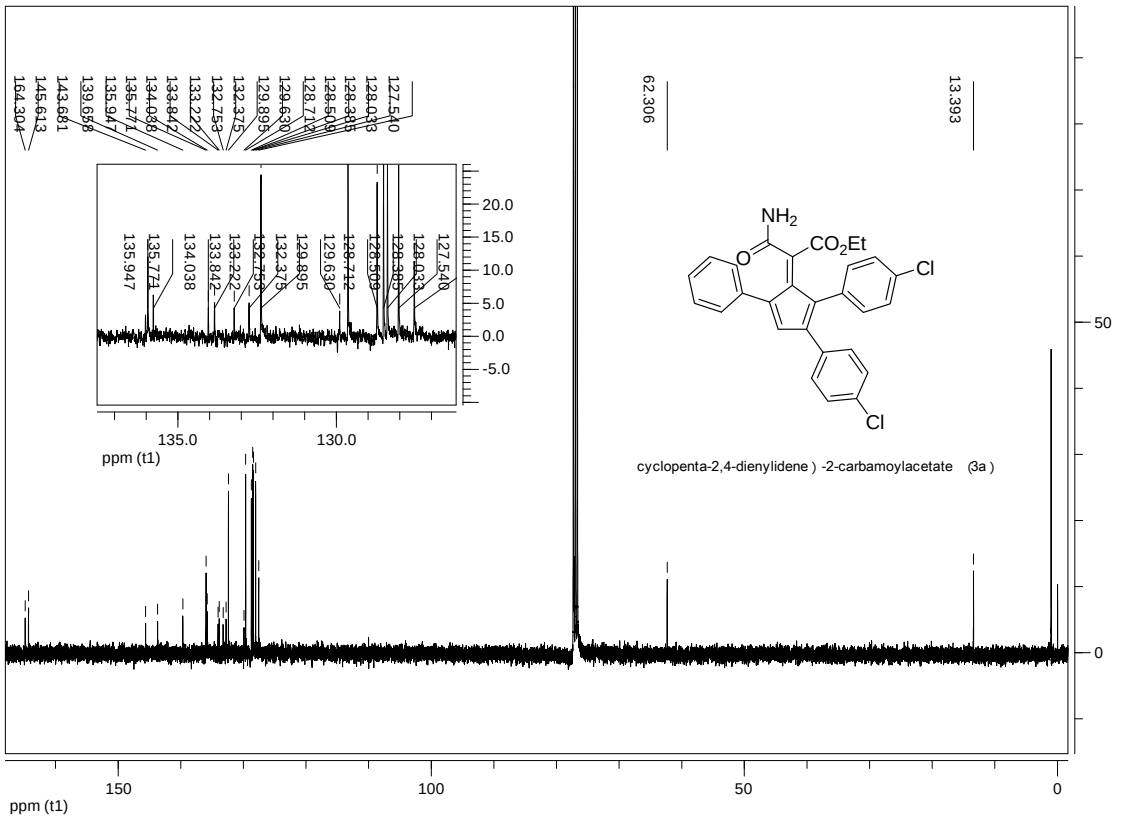


Red solid; m.p.: 219.2-219.9 °C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): (Z/E = 1/1)

7.34-7.26 (m, 5H), 7.25-7.20 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 9.2 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 1H), 6.74-6.71 (m, 3H), 5.60 (s, 0.5H), 5.12 (s, 0.5H), 3.76 (s, 3H), 3.47-3.42 (m, 2H), 1.05-0.99 (m, 3H); (E/Z) 5.41 (s, 0.5H), 5.18 (s, 0.5H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 165.0, 164.8, 164.7, 164.6, 159.6, 159.5, 146.0, 145.5, 144.3, 144.0, 138.2, 137.9, 137.2, 136.8, 134.9, 134.7, 134.6, 133.8, 133.6, 133.5, 133.4, 132.7, 132.6, 130.0, 129.8, 129.7, 128.3, 128.2, 128.1, 127.9, 126.5, 126.4, 113.8, 62.3, 55.2, 13.5, 13.4; IR (KBr, cm^{-1}) ν: 3461, 3418, 3280, 3159, 2992, 1731, 1672, 1618, 1475, 1363, 1262, 1137, 1111, 1038, 819; MS(EI) (m/z): 520.25 [$(M+1)^+$] (100%); HRMS (ESI) calcd for $C_{29}H_{23}Cl_2NO_4$ $[M+H]^+$ 520.1082; Found 520.1080.

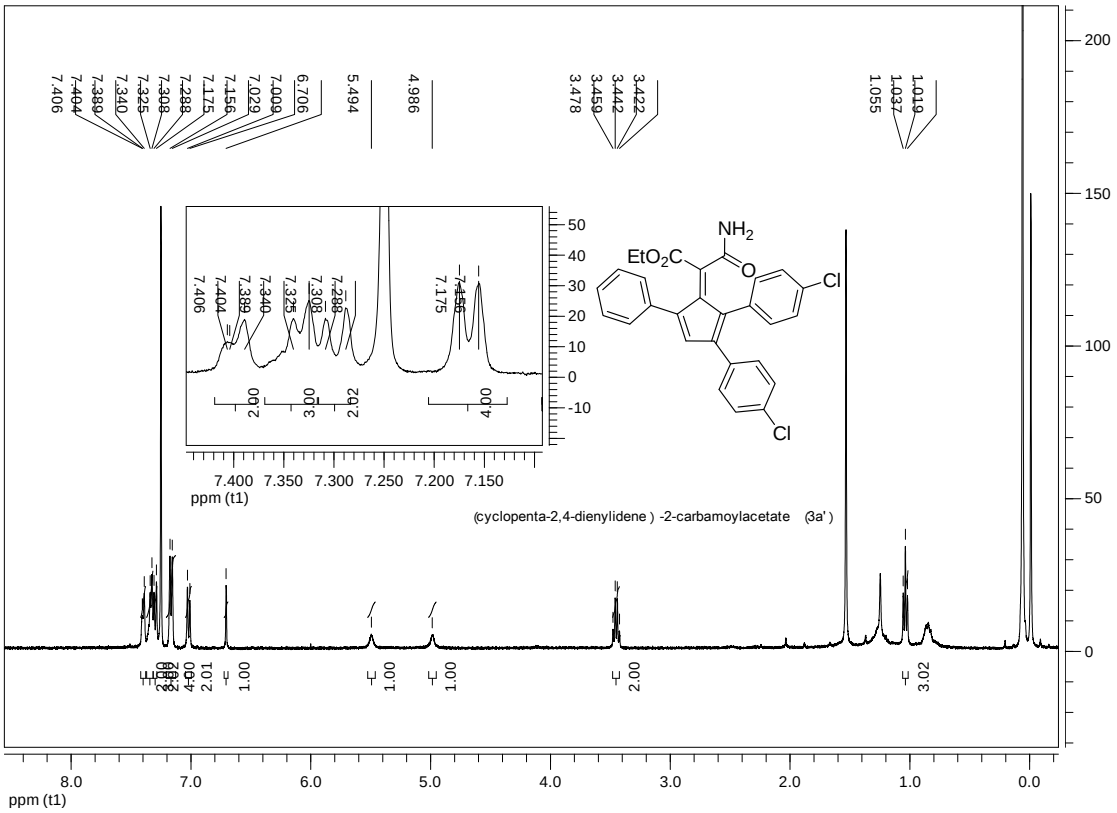
(2Z) Ethyl 2-(2,3-bis(4-chlorophenyl)-5-phenylcyclopenta-2,4-dienylidene)-2-carbamoyl-acetate (3a)

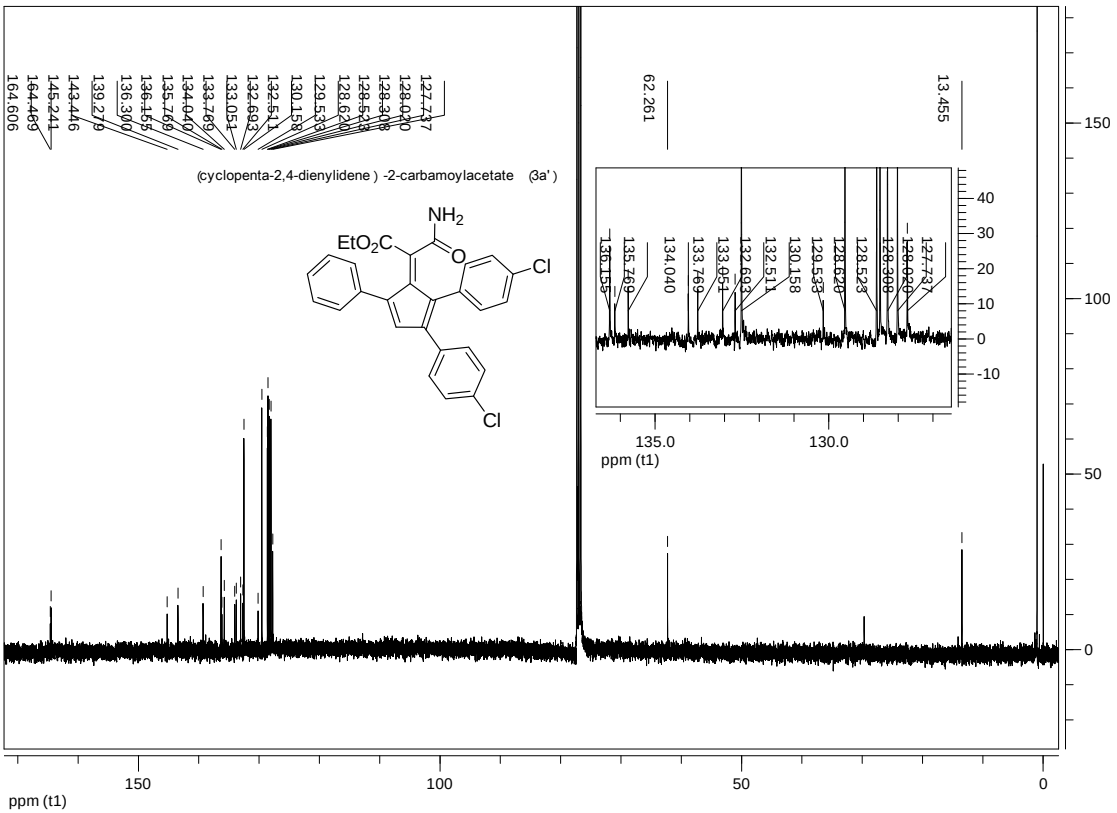




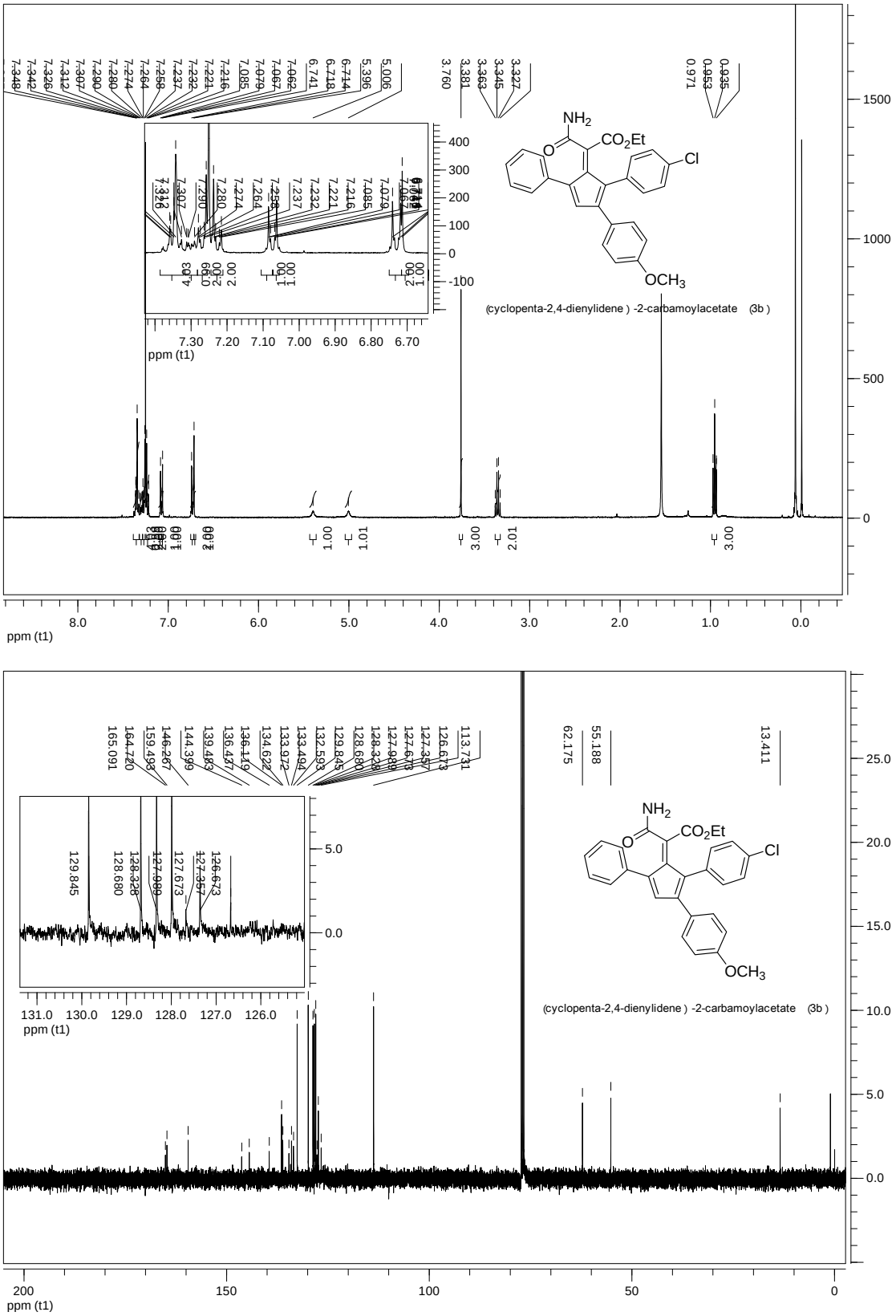
(2E) Ethyl 2-(2,3-bis(4-chlorophenyl)-5-phenylcyclopenta-2,4-dienylidene)-2-carbamoyl-

acetate (3a')

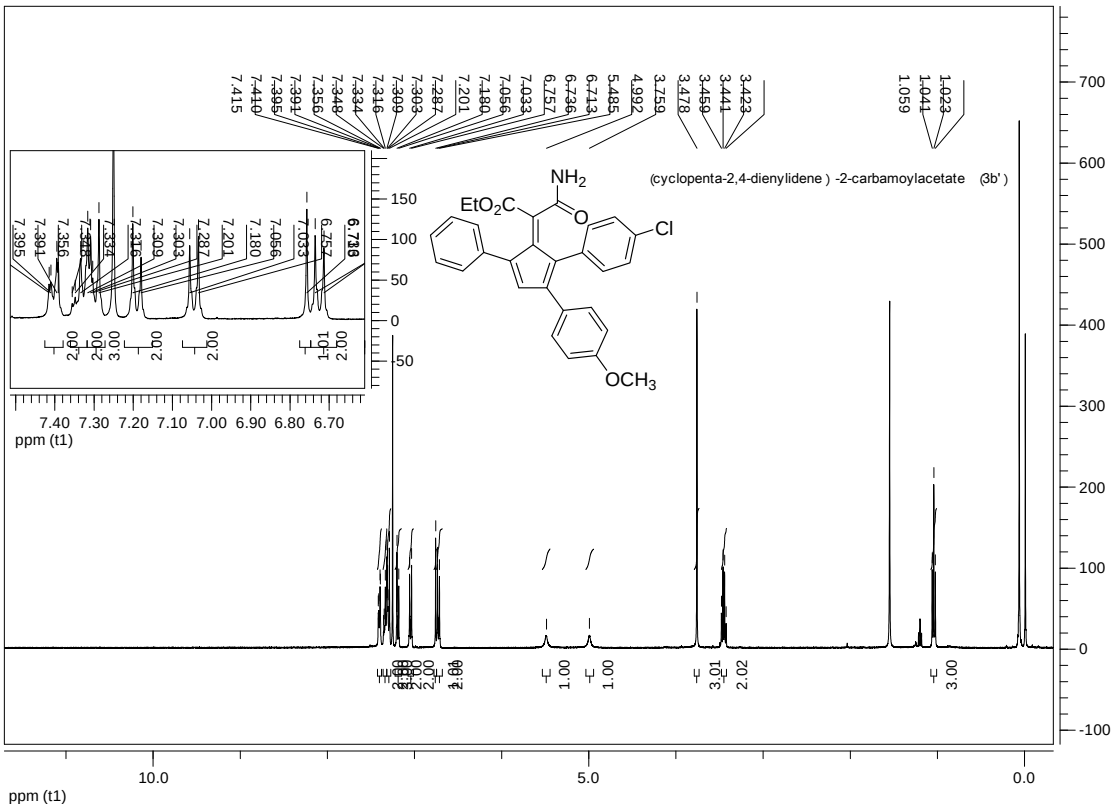


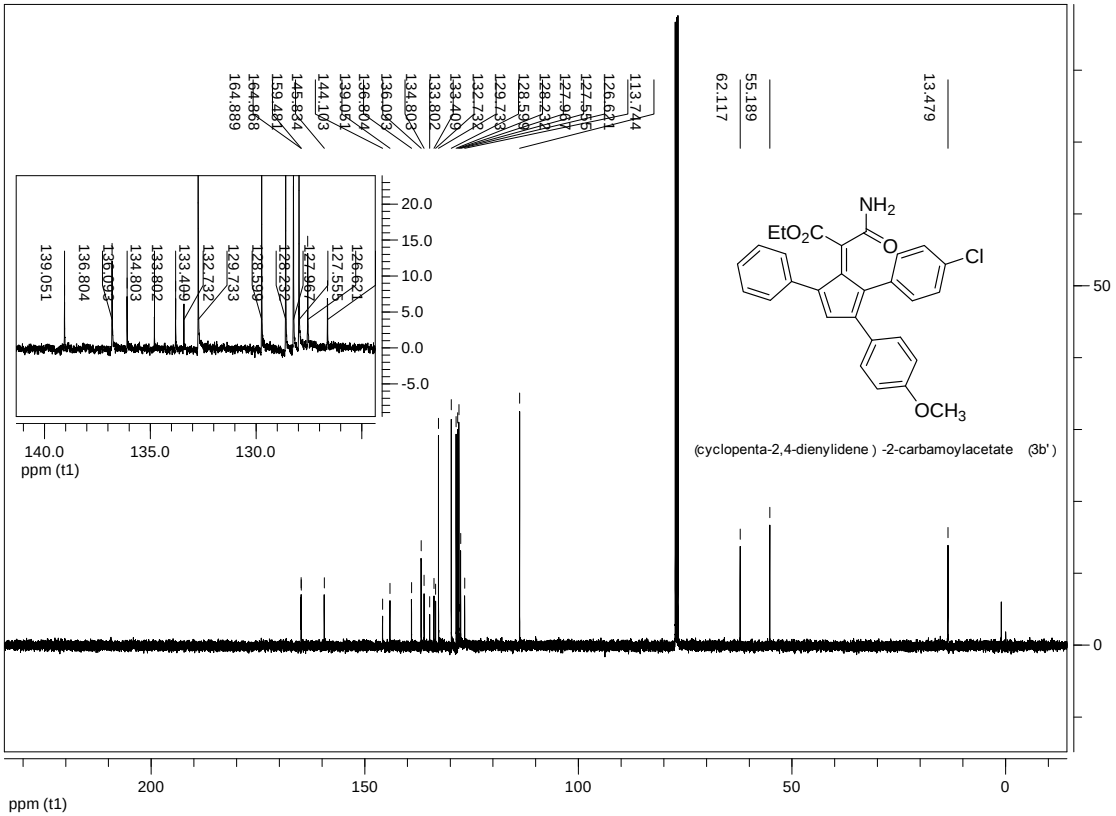


(2Z) Ethyl 2-carbamoyl-2-(2-(4-chlorophenyl)-3-(4-methoxyphenyl)-5-phenylcyclopenta-2,4-dienylidene)acetate (3b)

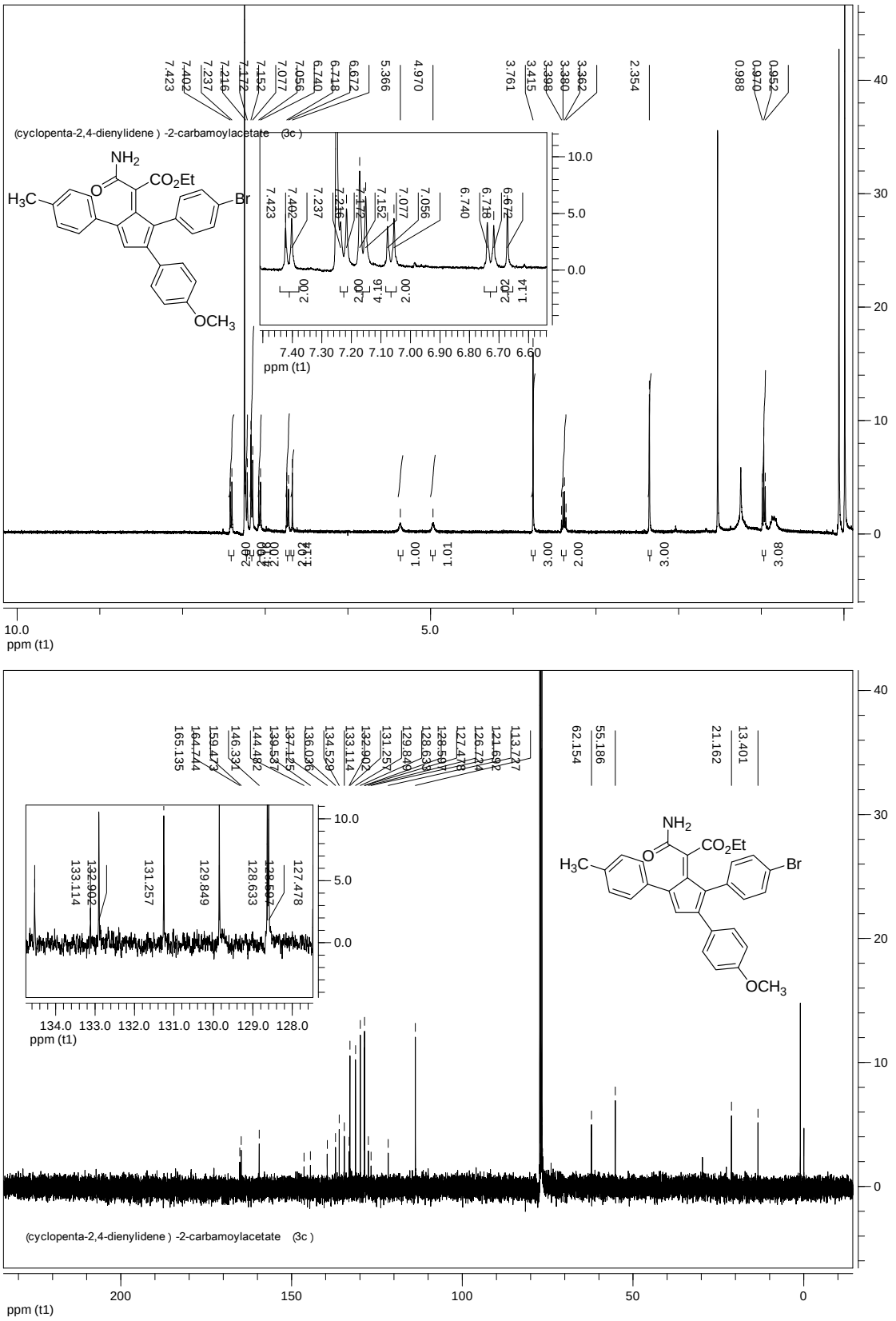


(2E) Ethyl 2-carbamoyl-2-(2-(4-chlorophenyl)-3-(4-methoxyphenyl)-5-phenylcyclopenta-2,4-dienylidene)acetate (3b')

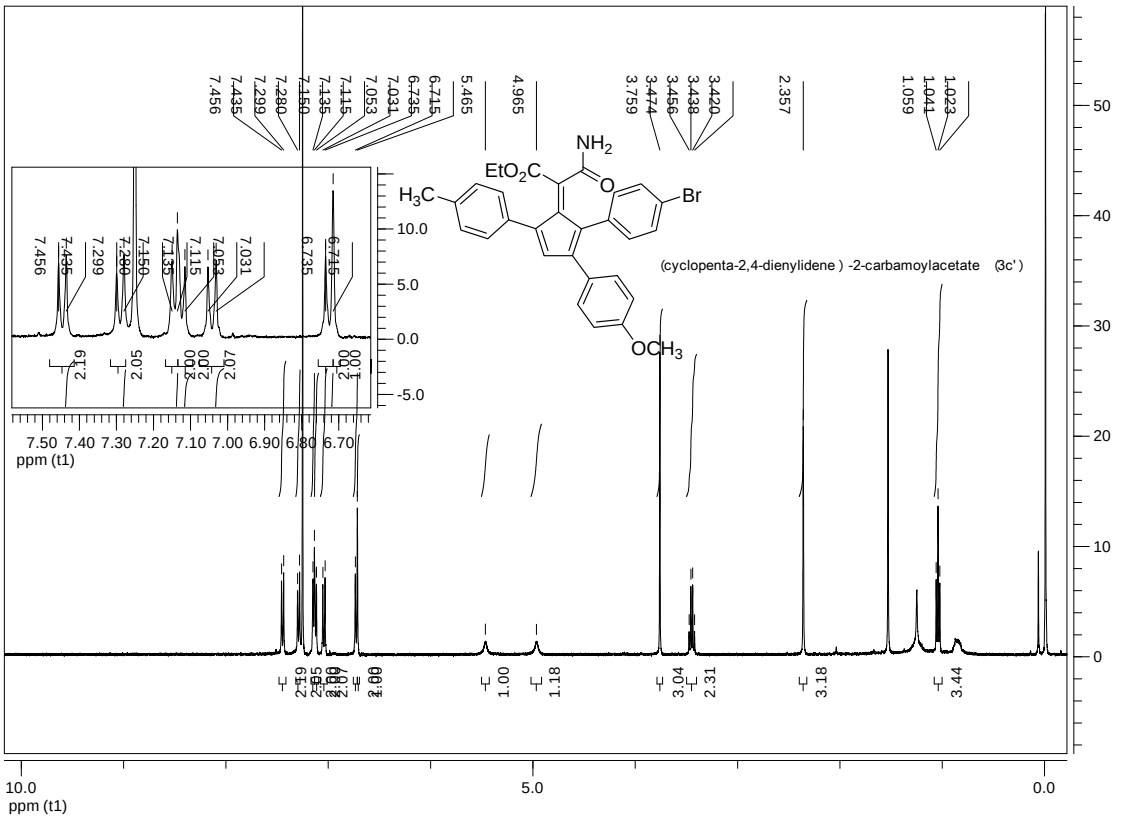


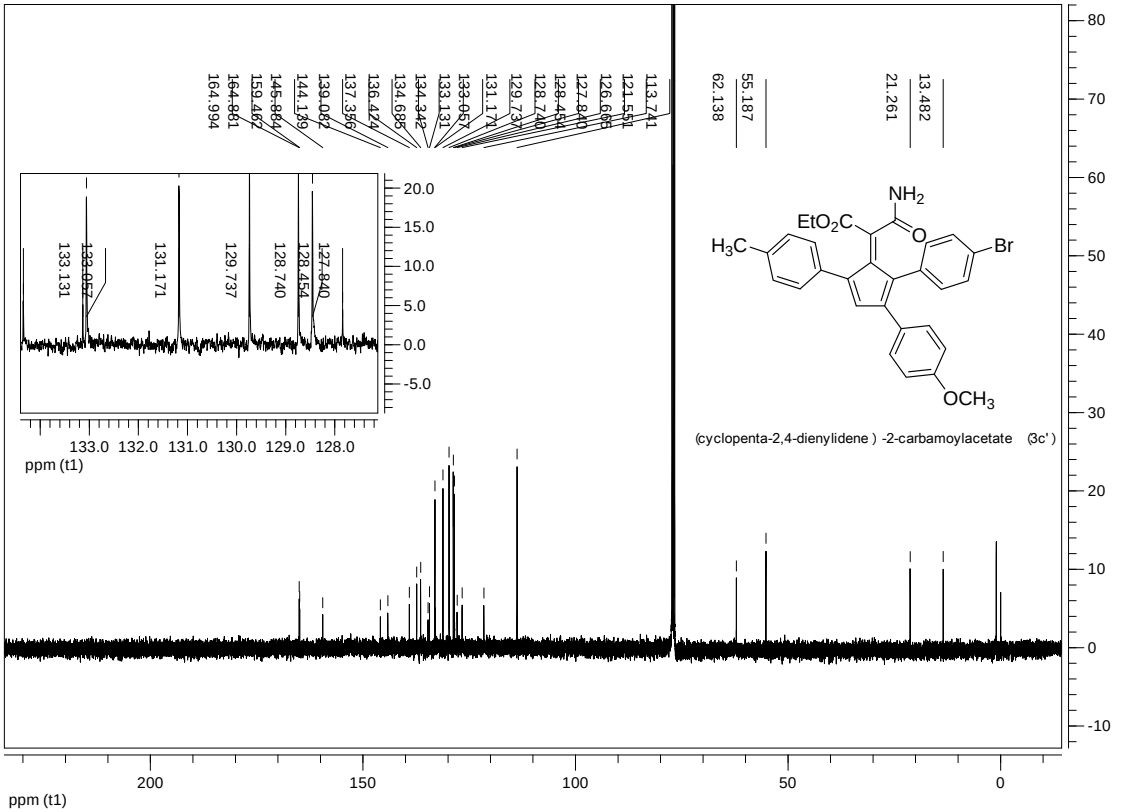


(2Z) Ethyl 2-(2-(4-bromophenyl)-3-(4-methoxyphenyl)-5-*p*-tolylcyclopenta-2,4-dienylidene)-2-carbamoylacetate (3c)

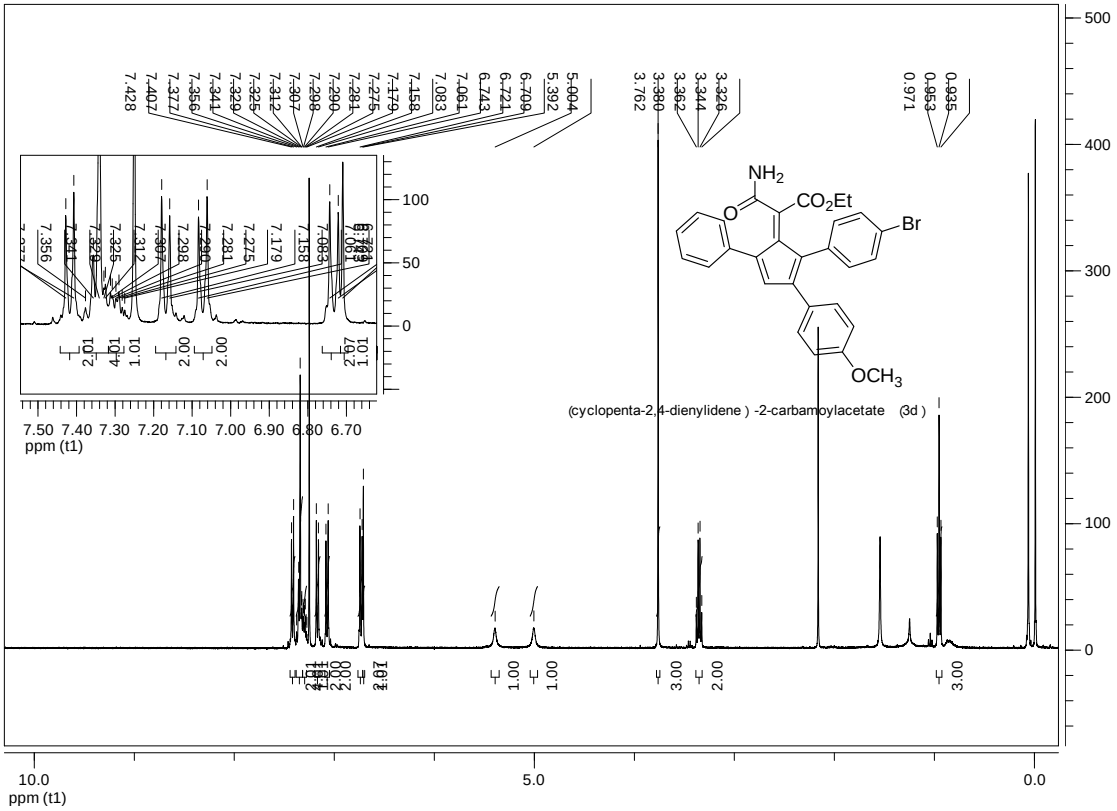


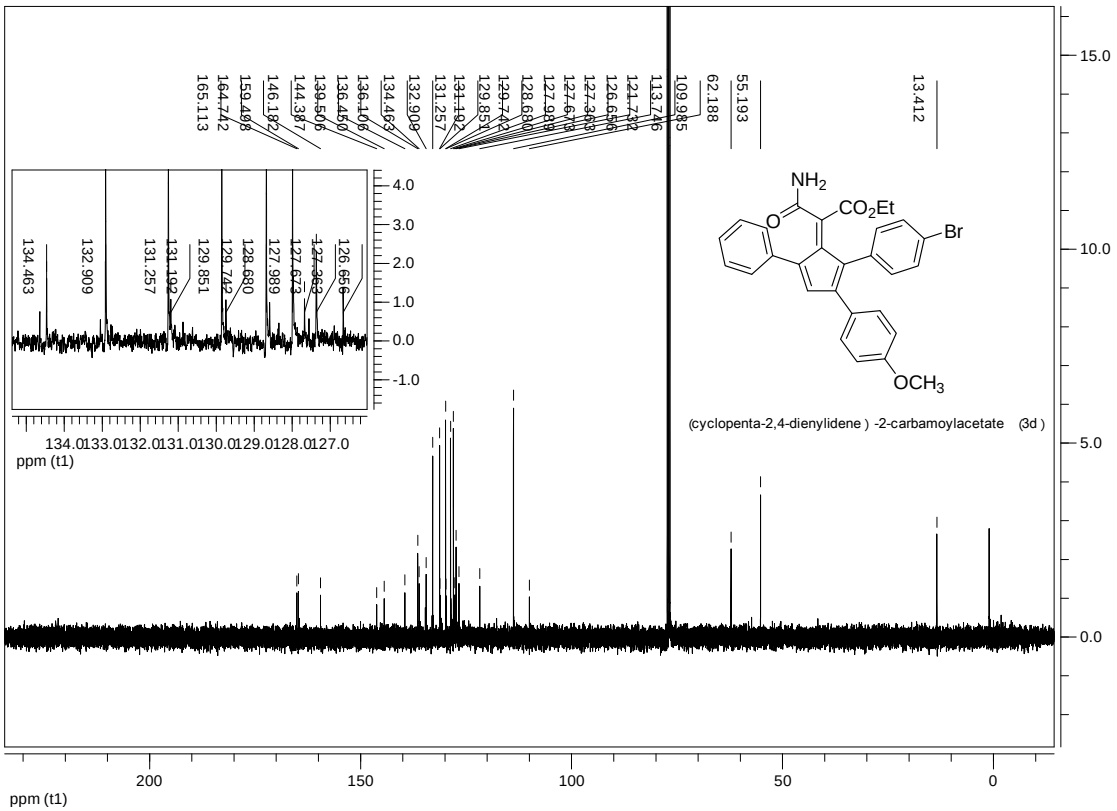
(2E) Ethyl 2-(2-(4-bromophenyl)-3-(4-methoxyphenyl)-5-*p*-tolylcyclopenta-2,4-dienylidene) -2-carbamoylacetate (3c')



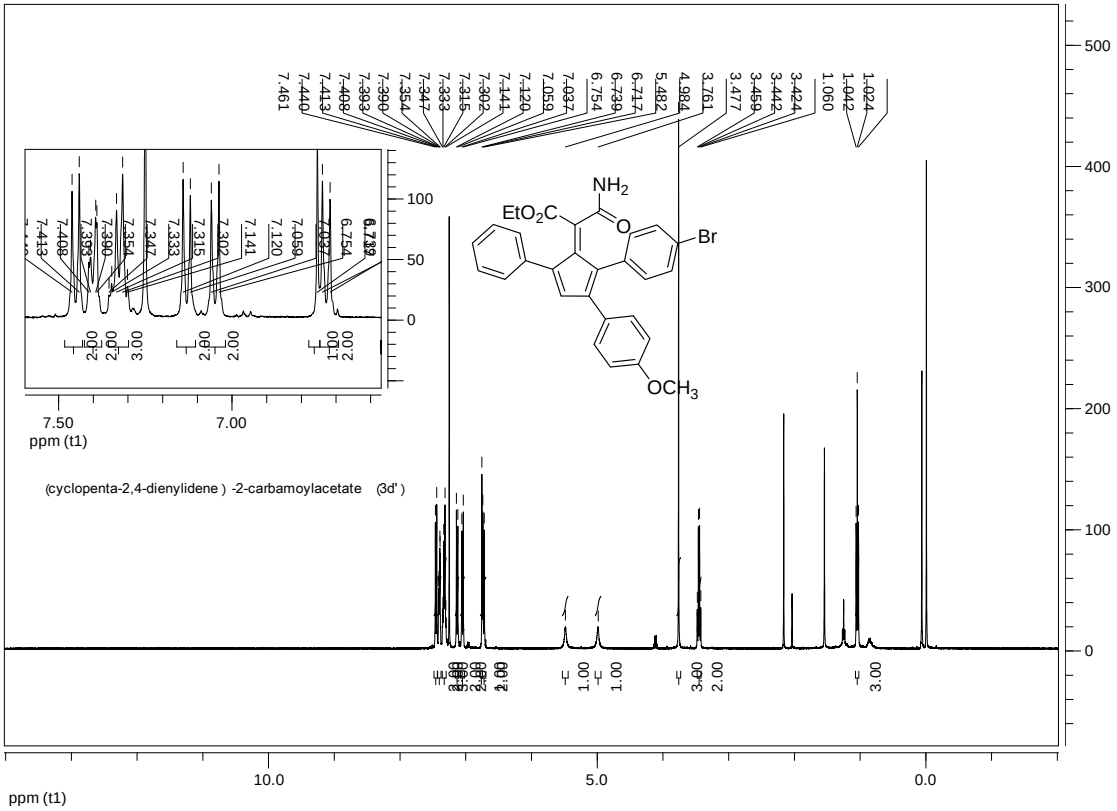


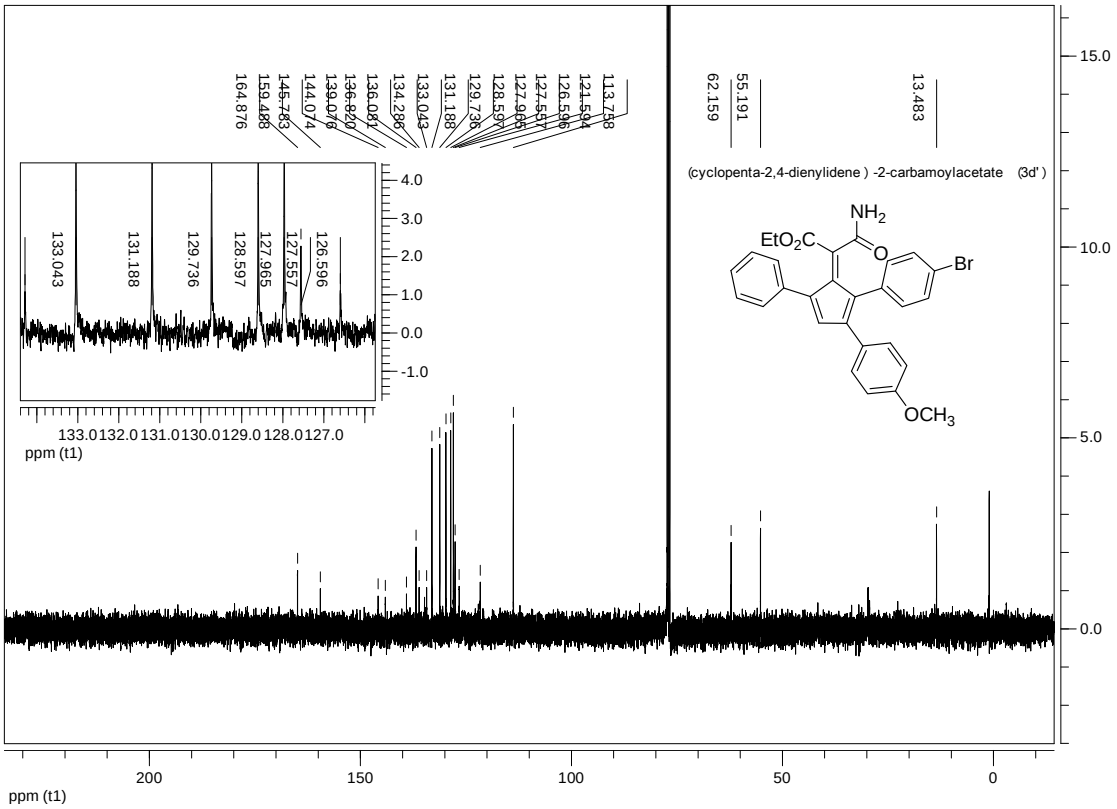
(2Z) Ethyl 2-(2-(4-bromophenyl)-3-(4-methoxyphenyl)-5-phenylcyclopenta-2,4-dienylidene) -2-carbamoylacetate (3d)



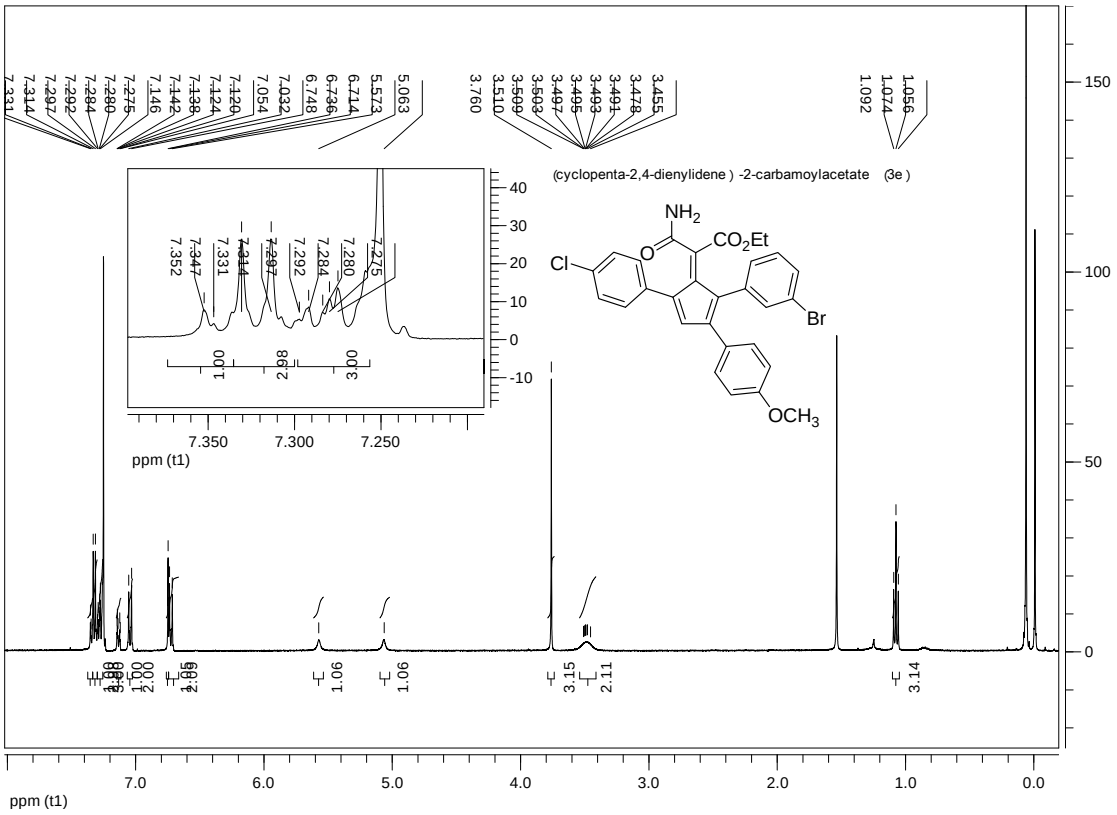


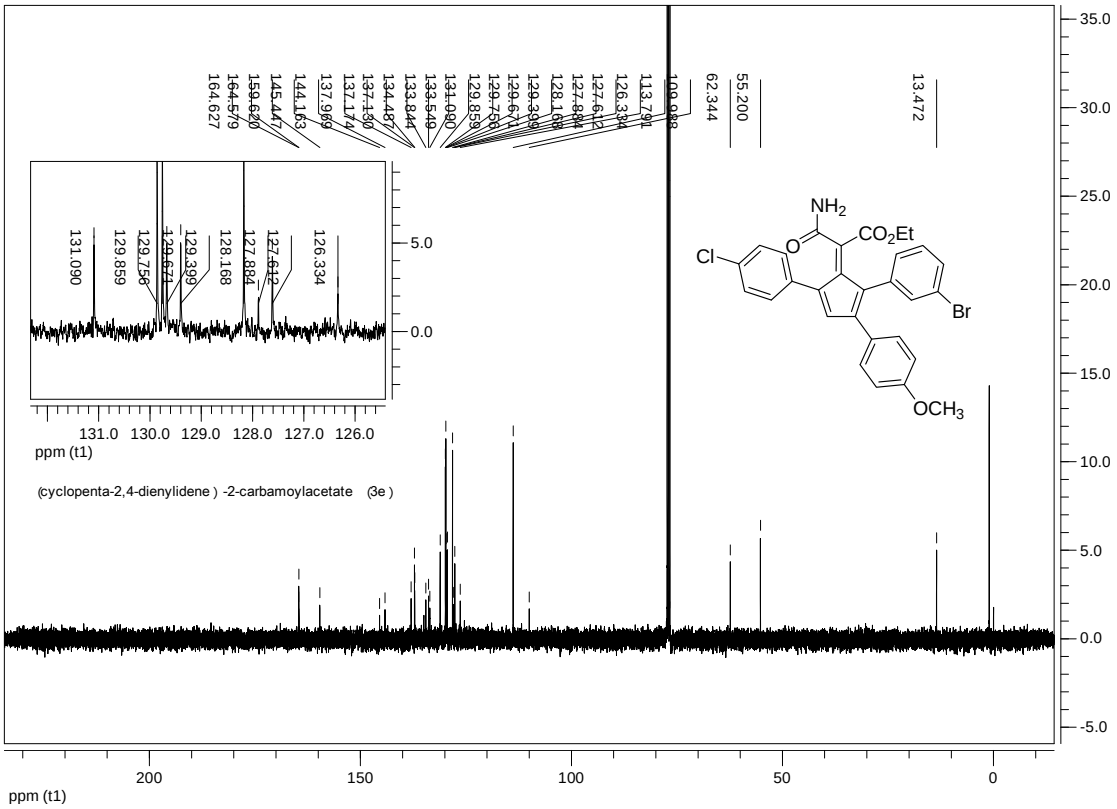
(2E) Ethyl 2-(2-(4-bromophenyl)-3-(4-methoxyphenyl)-5-phenylcyclopenta-2,4-dienylidene) -2-carbamoylacetate (3d')



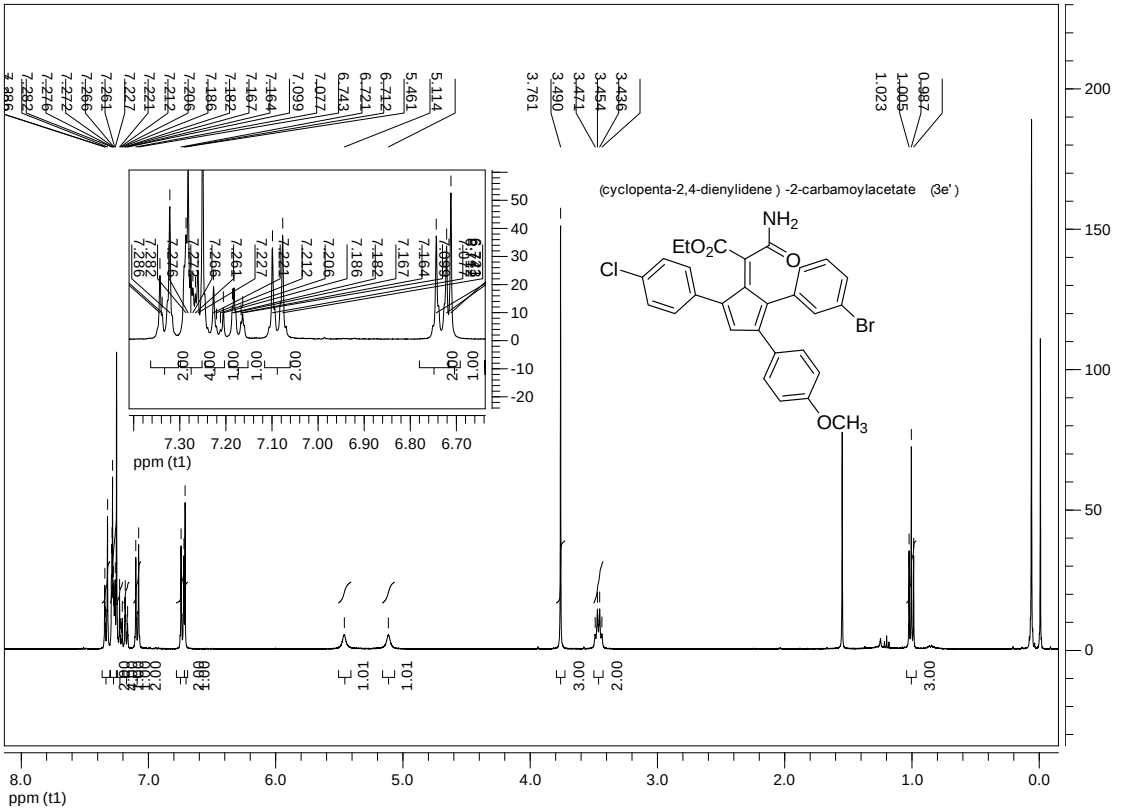


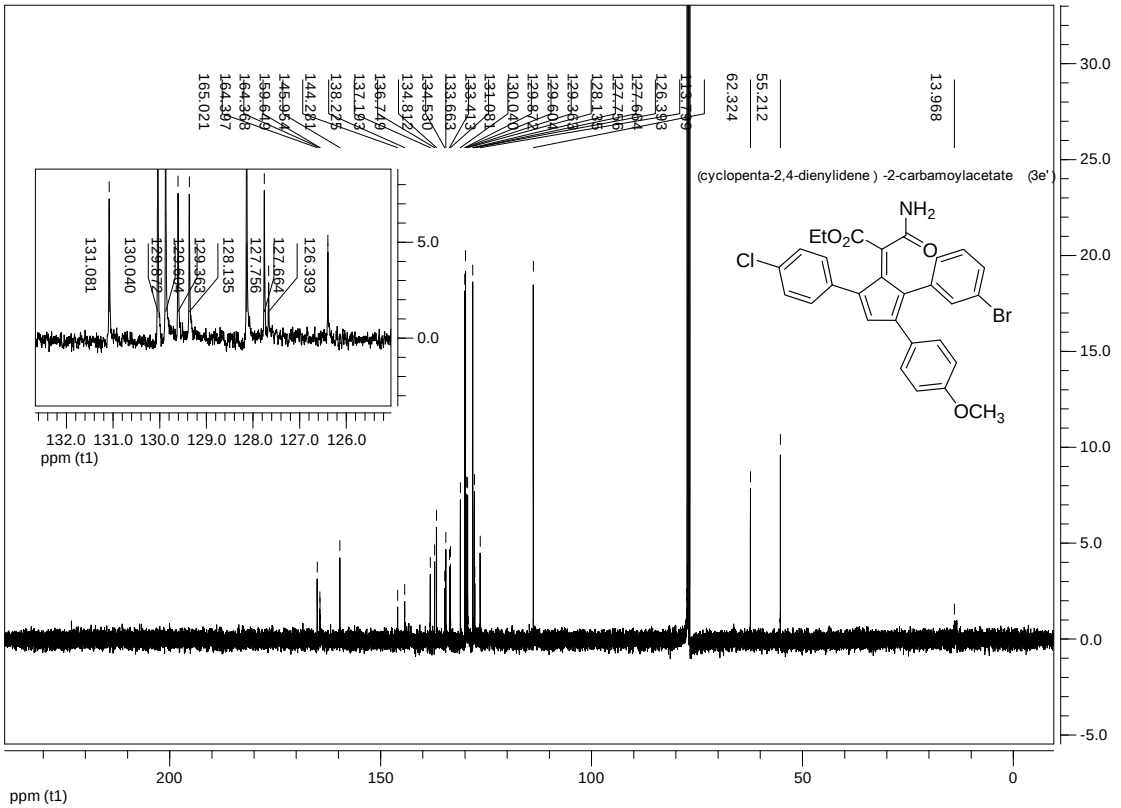
(2Z) Ethyl 2-(2-(3-bromophenyl)-5-(4-chlorophenyl)-3-(4-methoxyphenyl)cyclopenta-2,4-dienylidene) -2-carbamoylacetate (3e)



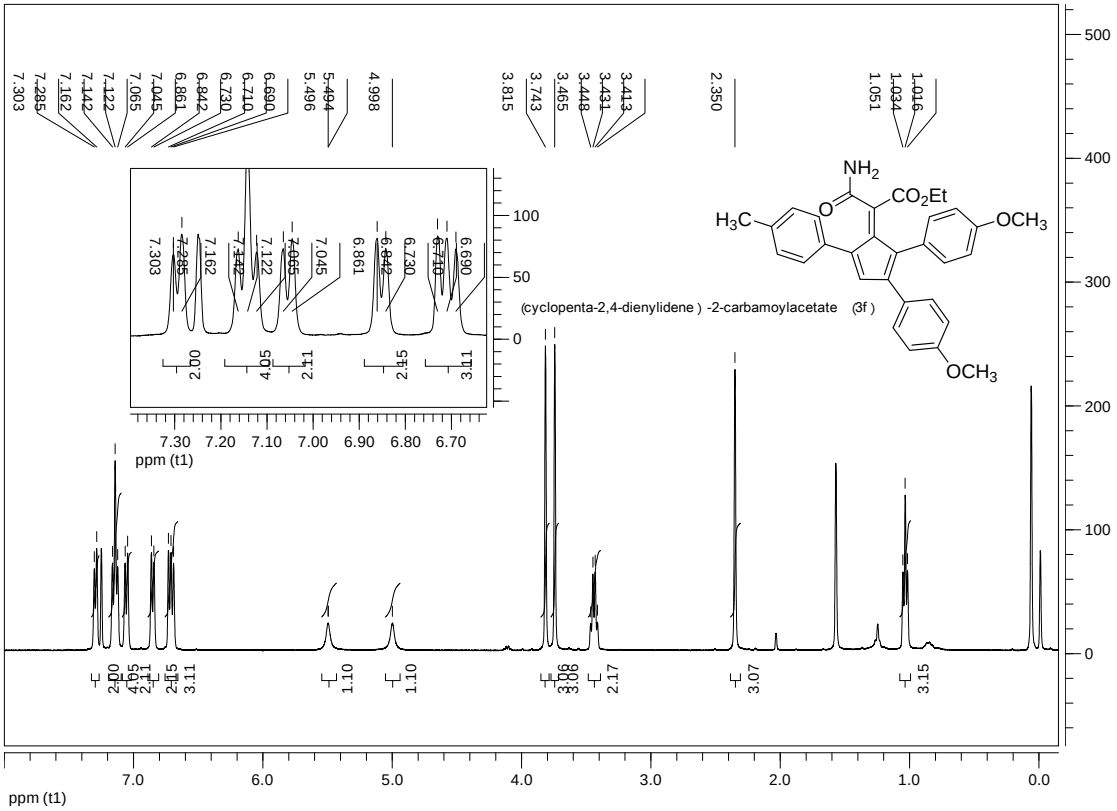


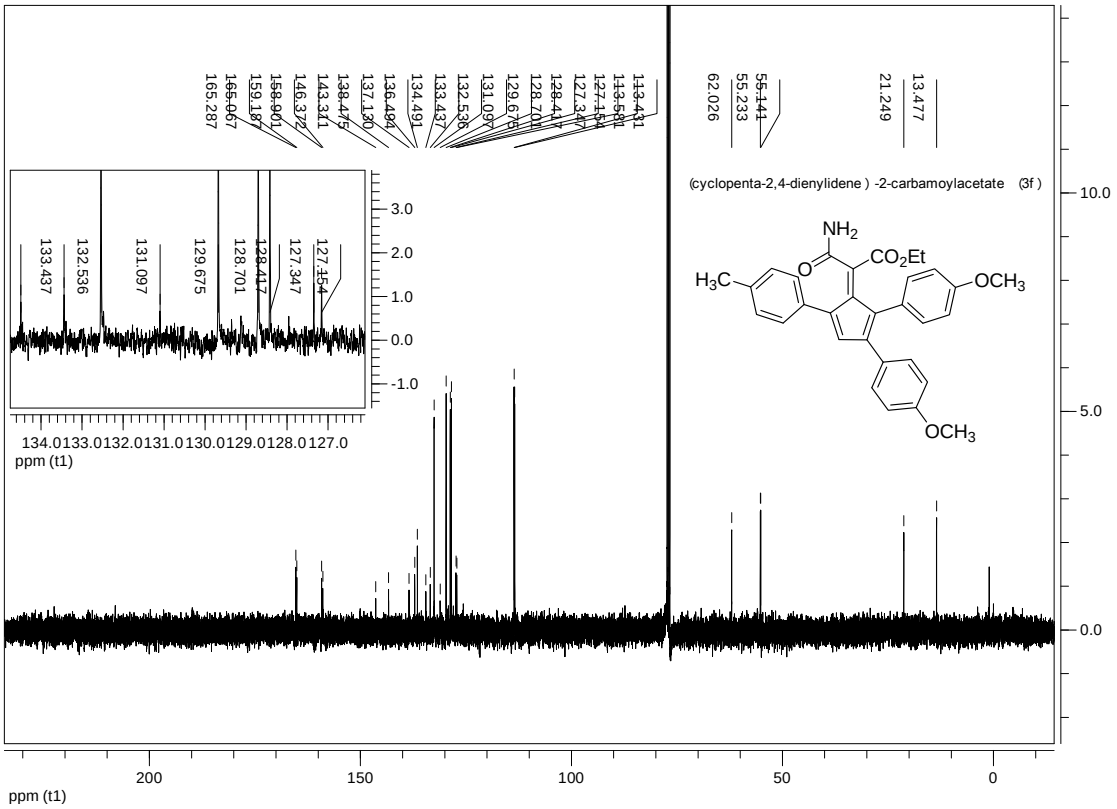
(2E) Ethyl 2-(2-(3-bromophenyl)-5-(4-chlorophenyl)-3-(4-methoxyphenyl)cyclopenta-2,4-dienylidene)-2-carbamoylacetate (3e')



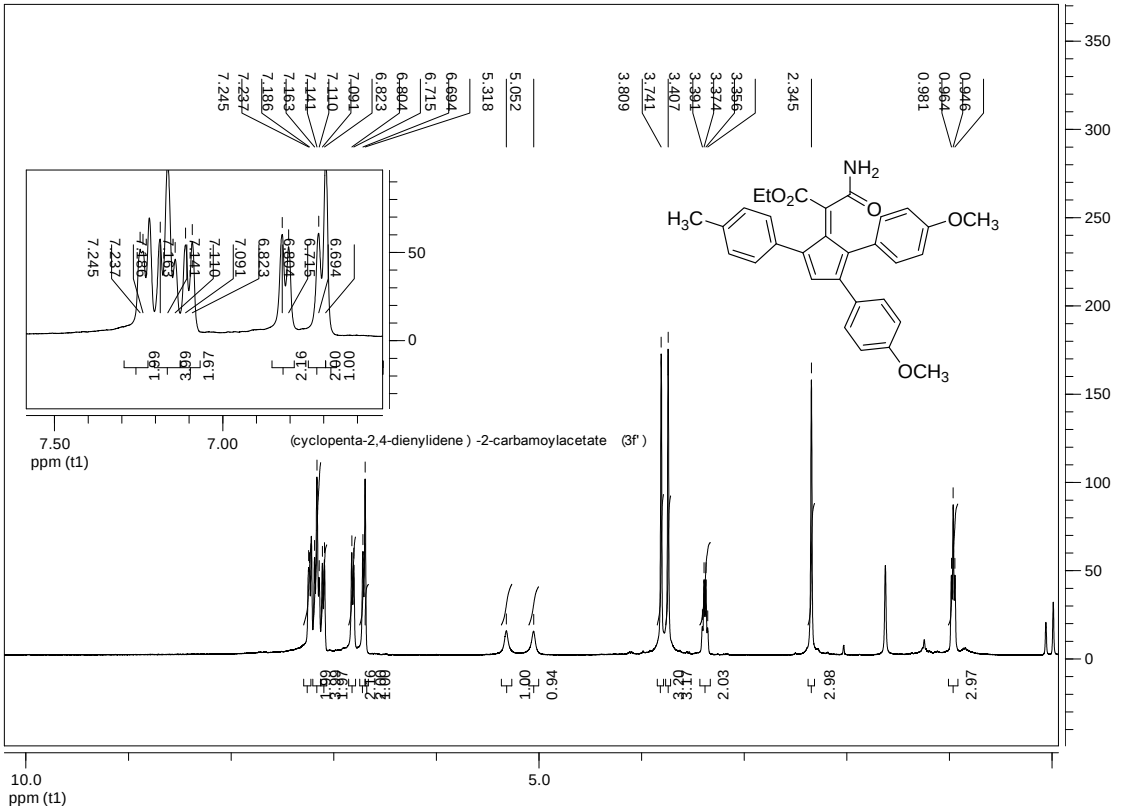


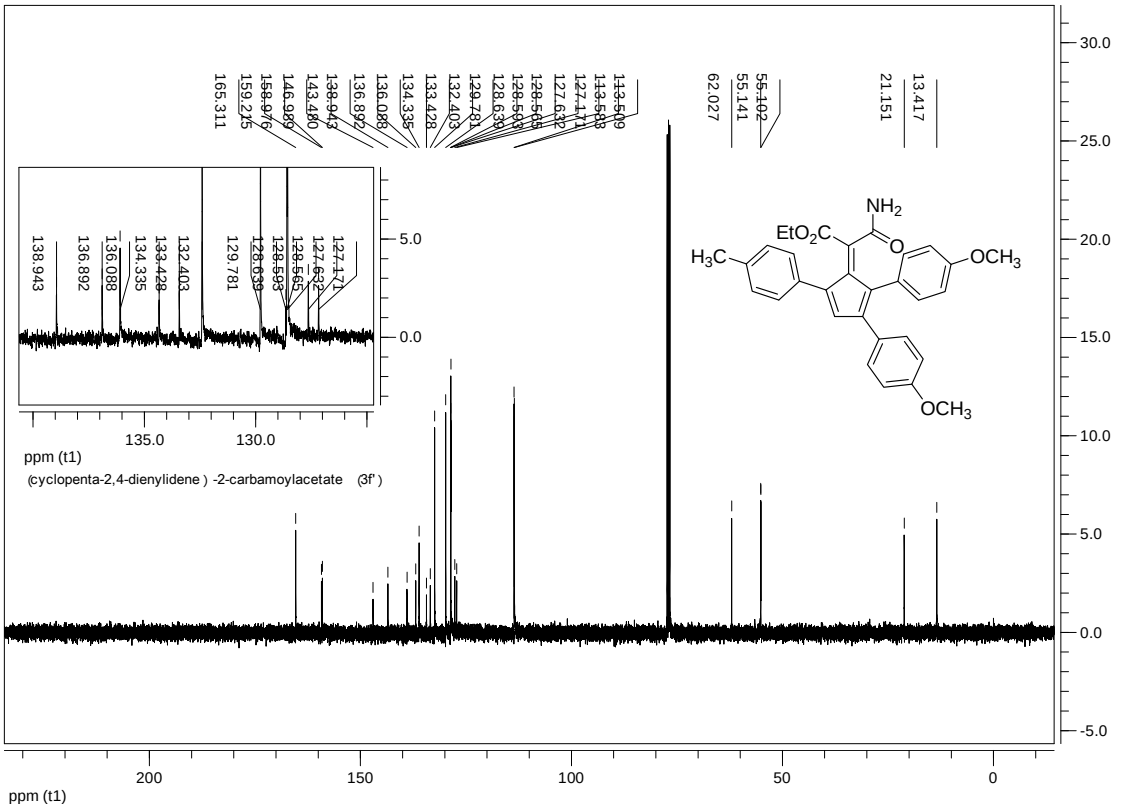
(2Z) Ethyl 2-(2,3-bis(4-methoxyphenyl)-5-*p*-tolylcyclopenta-2,4-dienylidene)-2-carbamoyl-acetate (3f)



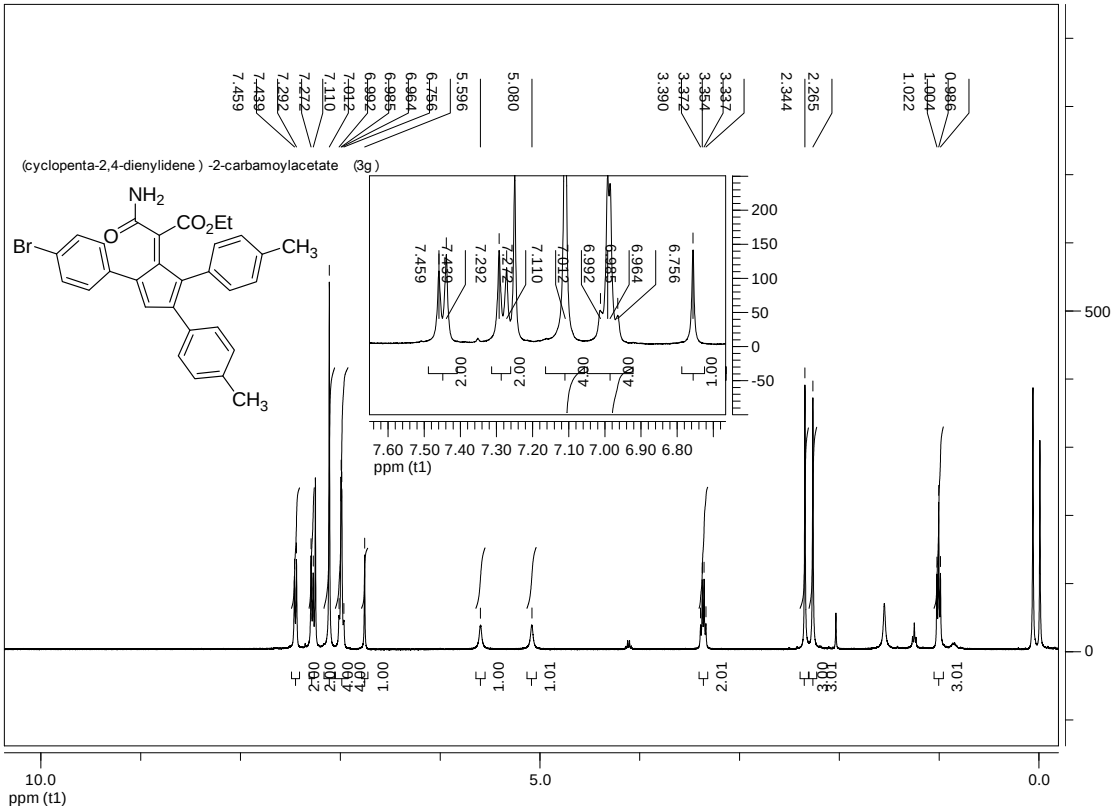


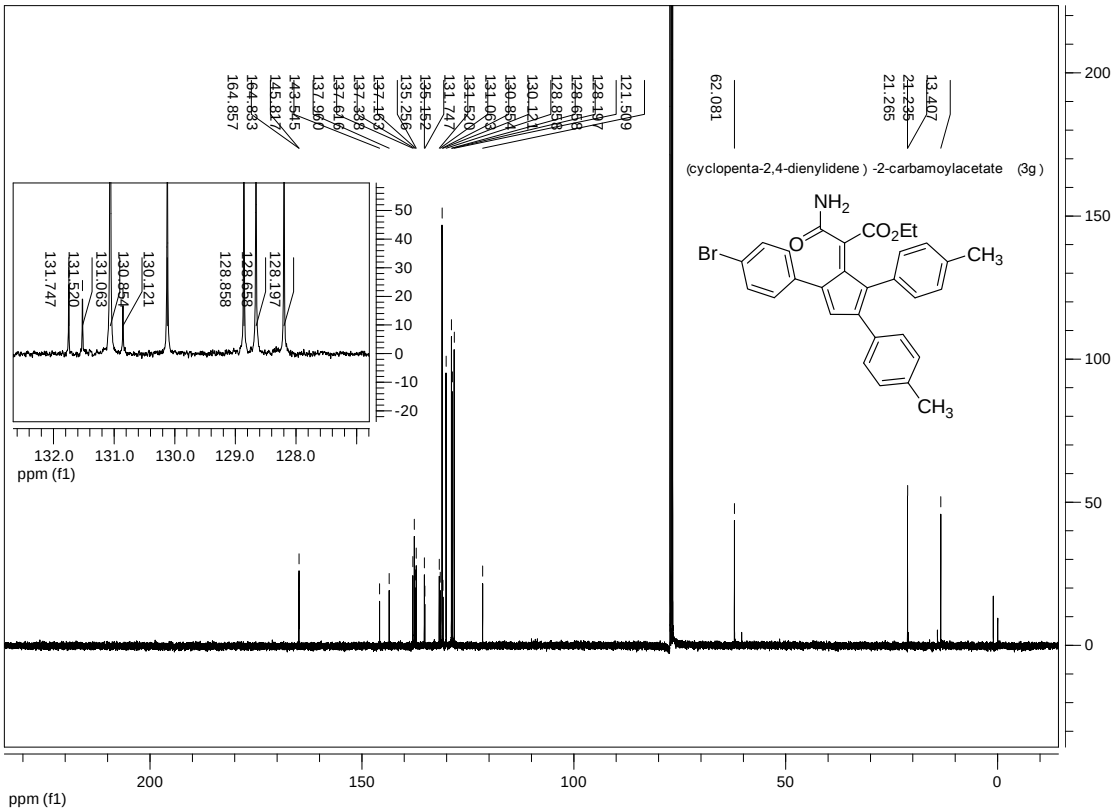
(2E) Ethyl 2-(2,3-bis(4-methoxyphenyl)-5-*p*-tolylcyclopenta-2,4-dienylidene)-2-carbamoyl--acetate (3f')



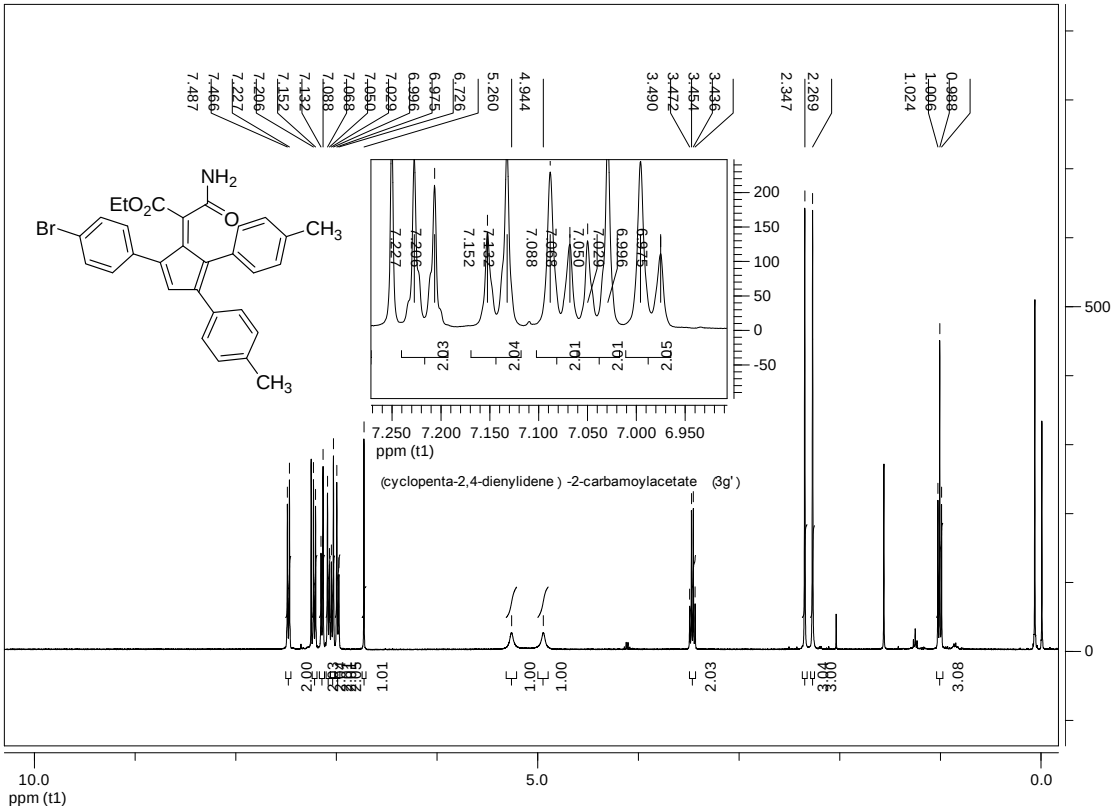


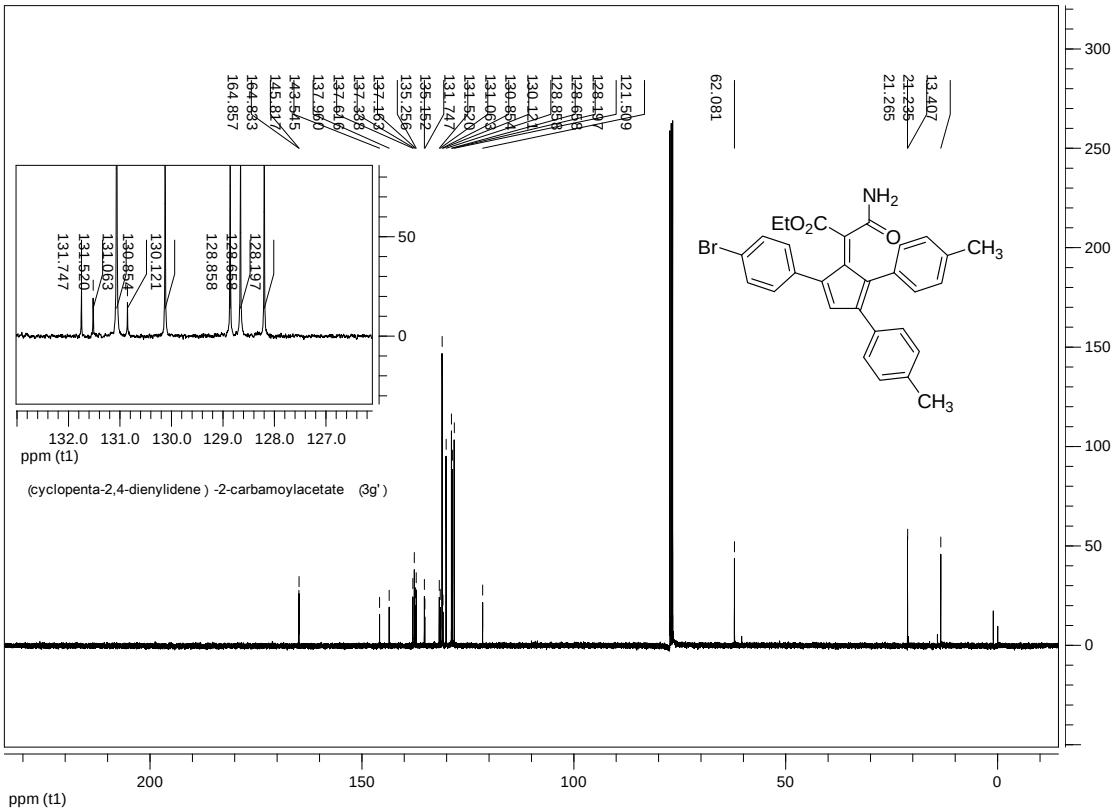
(2Z) Ethyl 2-(5-(4-bromophenyl)-2,3-dip-tolylcyclopenta-2,4-dienylidene)-2-carbamoyl-acetate (3g)



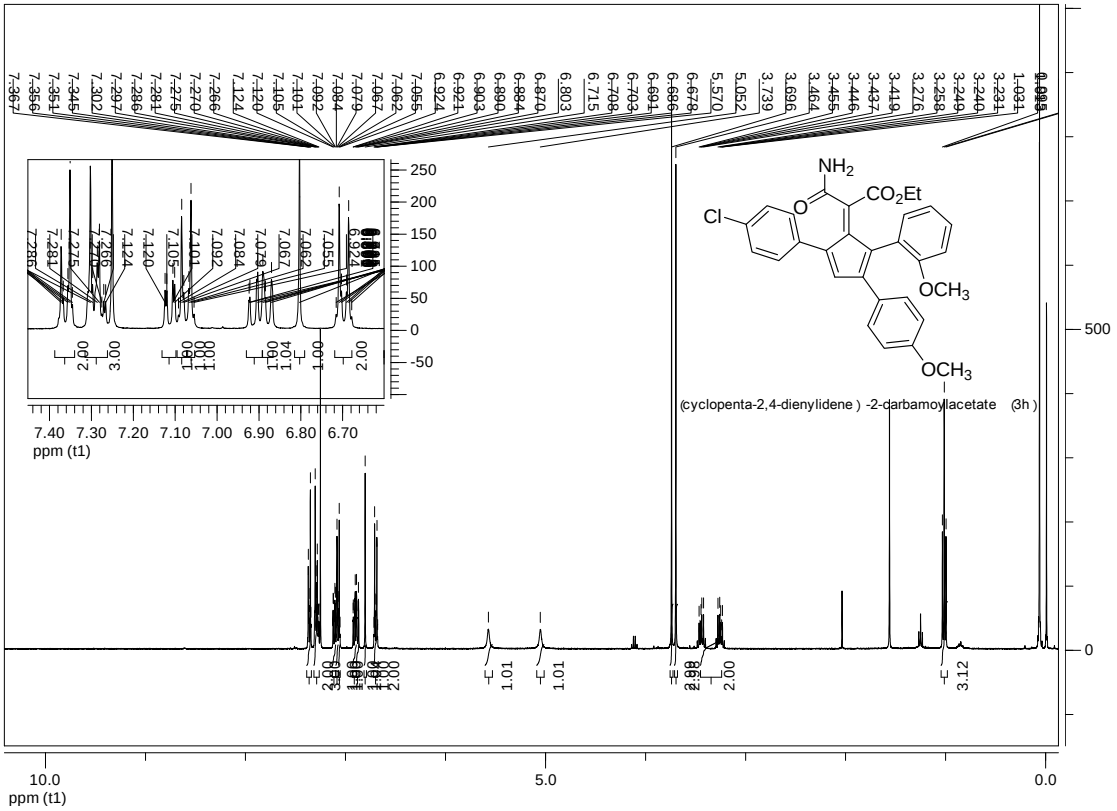


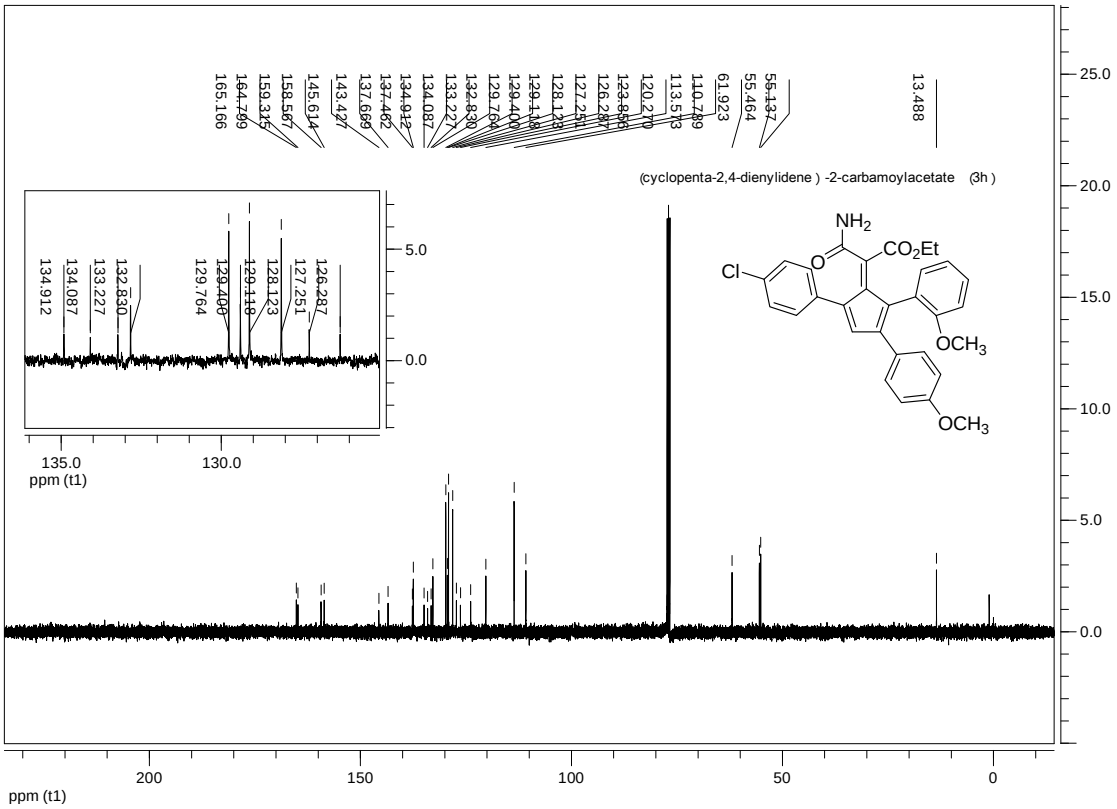
(2E) Ethyl 2-(5-(4-bromophenyl)-2,3-dip-tolylcyclopenta-2,4-dienylidene)-2-carbamoyl-acetate (3g')



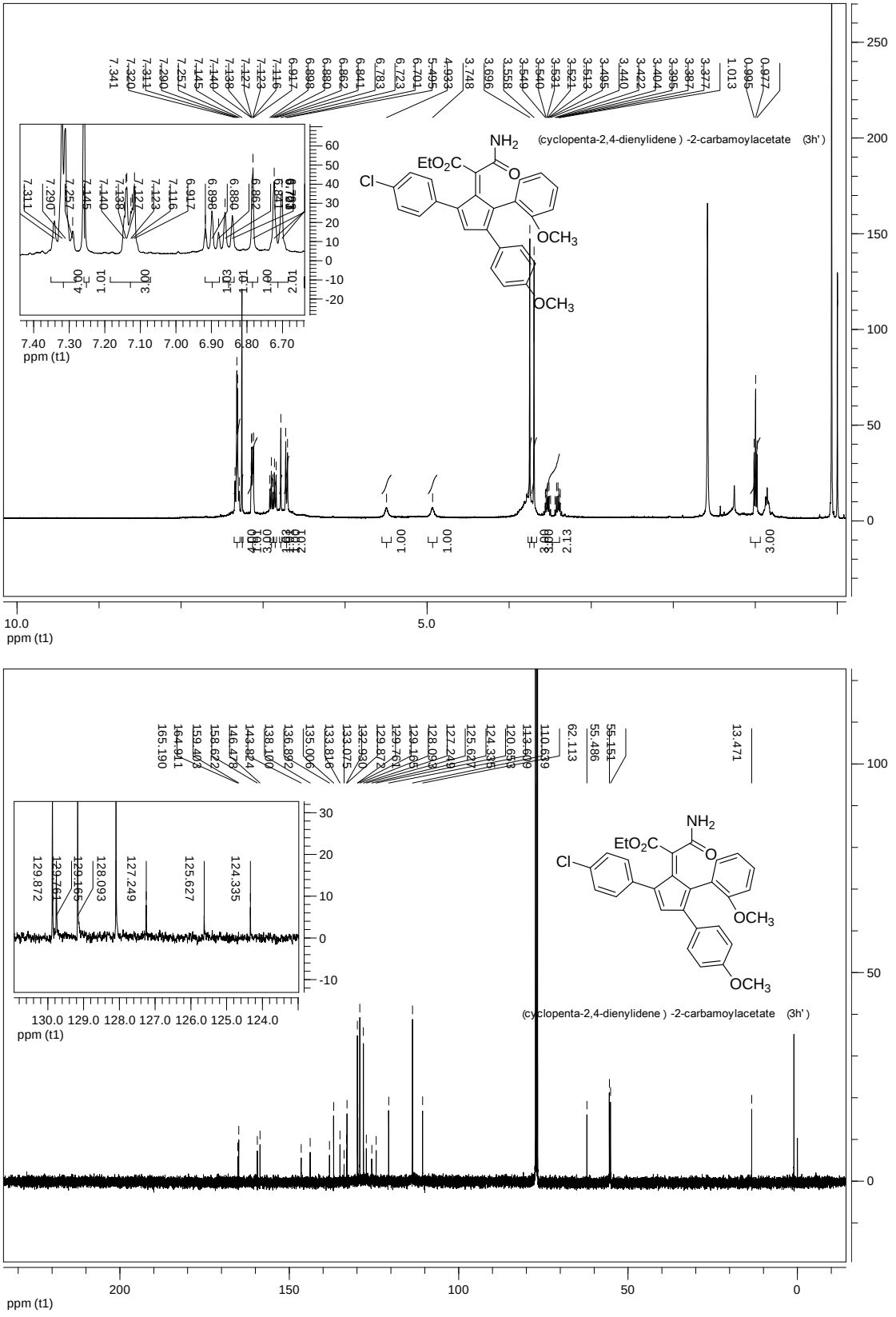


(2Z) Ethyl 2-carbamoyl-2-(5-(4-chlorophenyl)-2-(2-methoxyphenyl)-3-(4-methoxyphenyl) cyclopenta-2,4-dienylidene)acetate (3h)

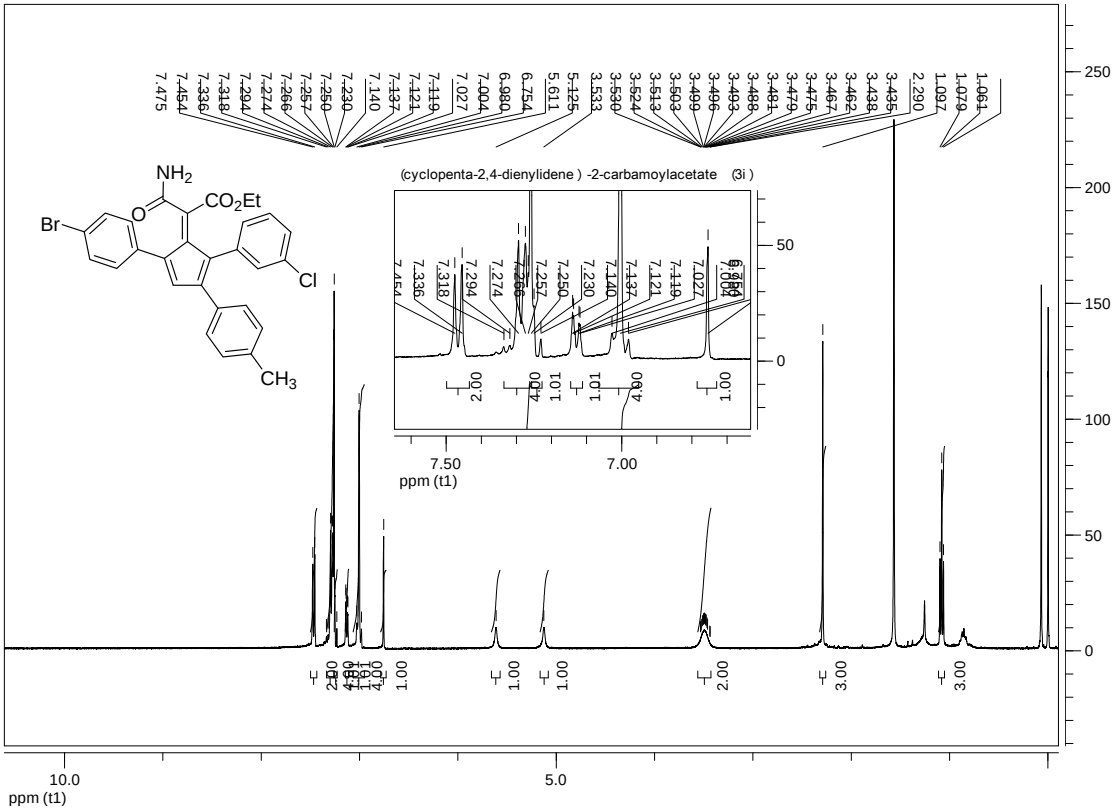


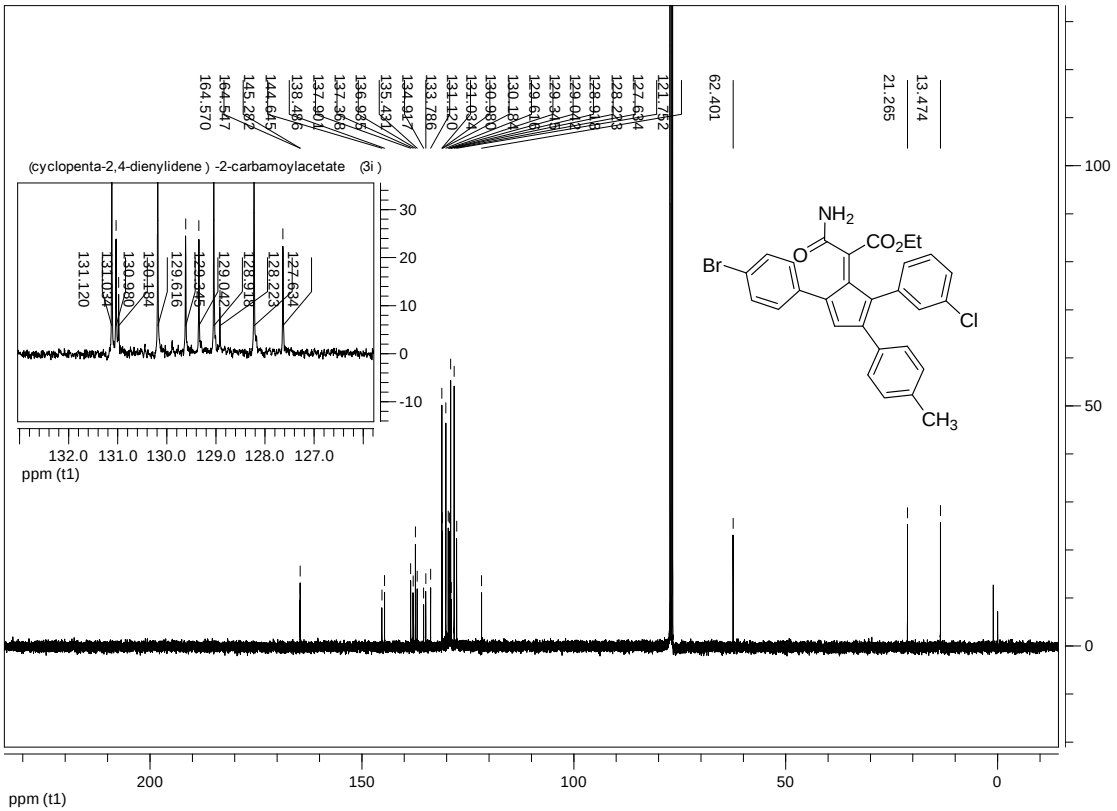


(2E) Ethyl 2-carbamoyl-2-(5-(4-chlorophenyl)-2-(2-methoxyphenyl)-3-(4-methoxyphenyl) cyclopenta-2,4-dienylidene)acetate (3h')

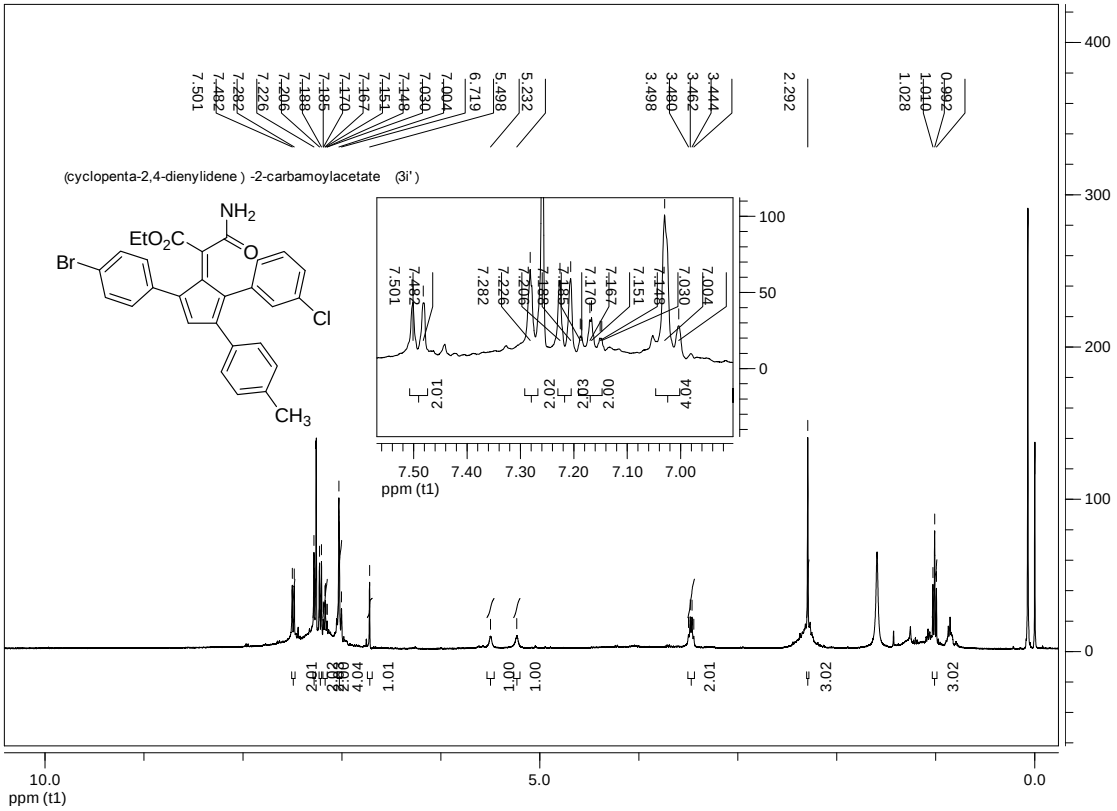


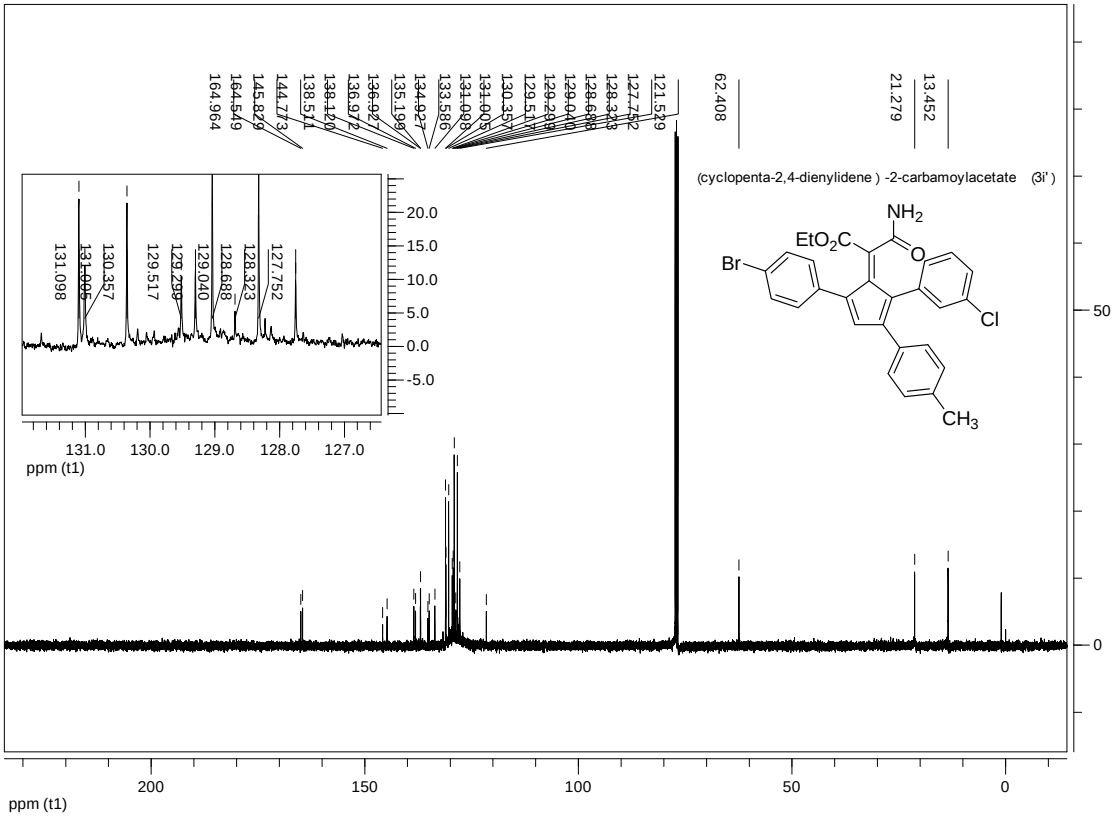
(2Z) Ethyl 2-(5-(4-bromophenyl)-2-(3-chlorophenyl)-3-*p*-tolylcyclopenta-2,4-dienylidene)-2-carbamoylacetate (3i)



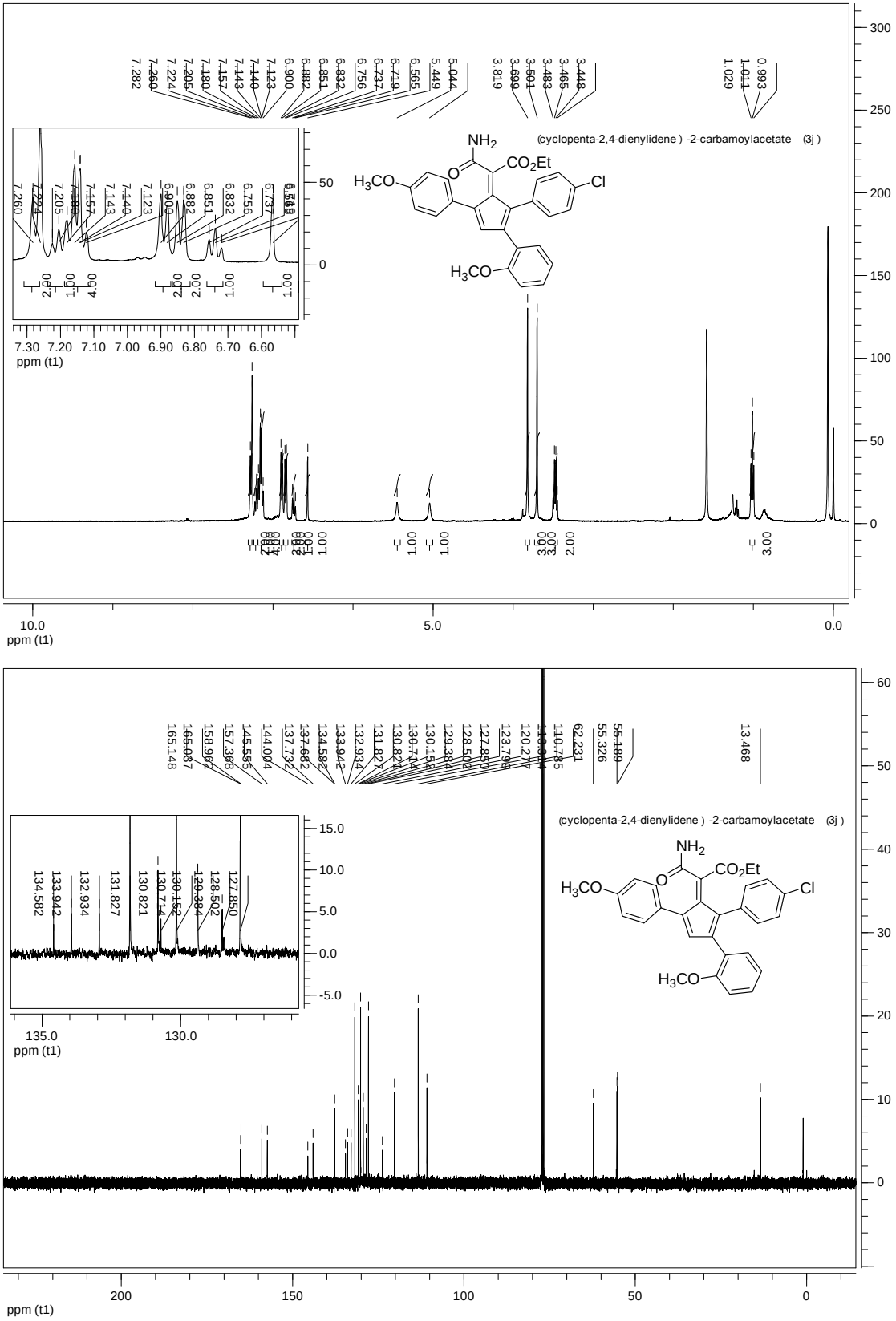


(2E) Ethyl 2-(5-(4-bromophenyl)-2-(3-chlorophenyl)-3-*p*-tolylcyclopenta-2,4-dienylidene)-2-carbamoylacetate (3i')

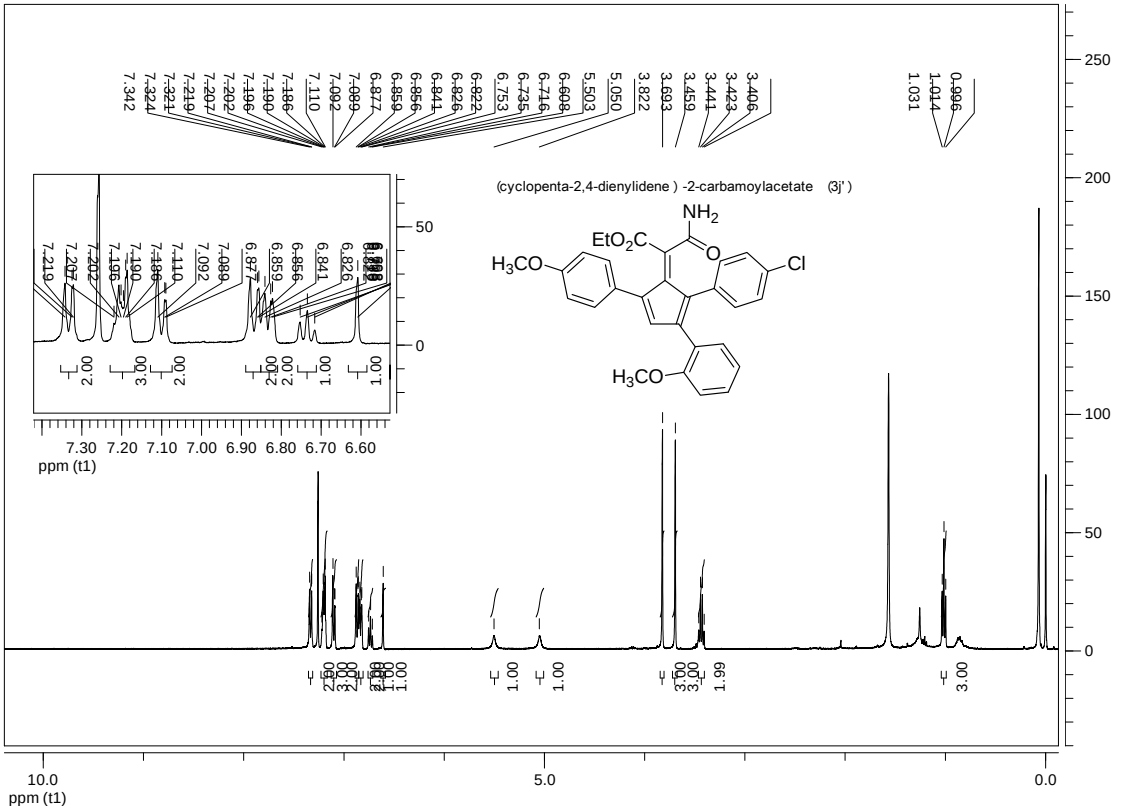


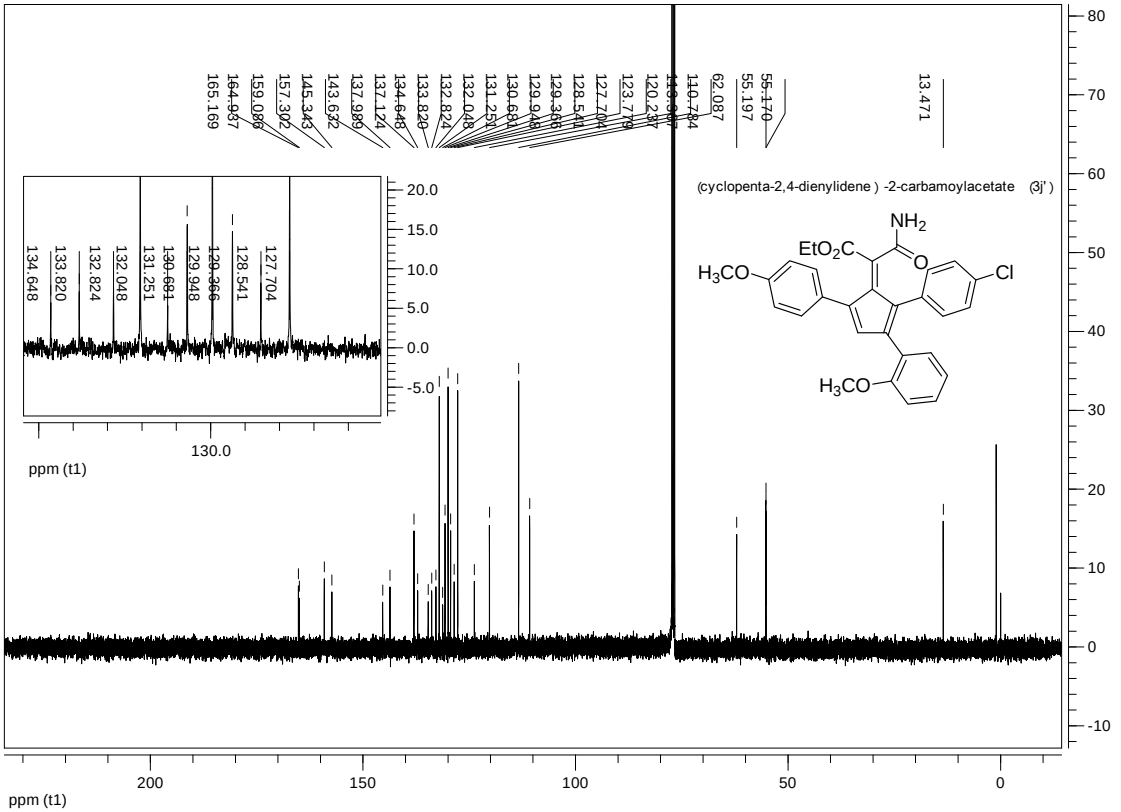


(2Z) Ethyl 2-carbamoyl-2-(2-(4-chlorophenyl)-3-(2-methoxyphenyl)-5-(4-methoxyphenyl) cyclopenta-2,4-dienylidene)acetate (3j)

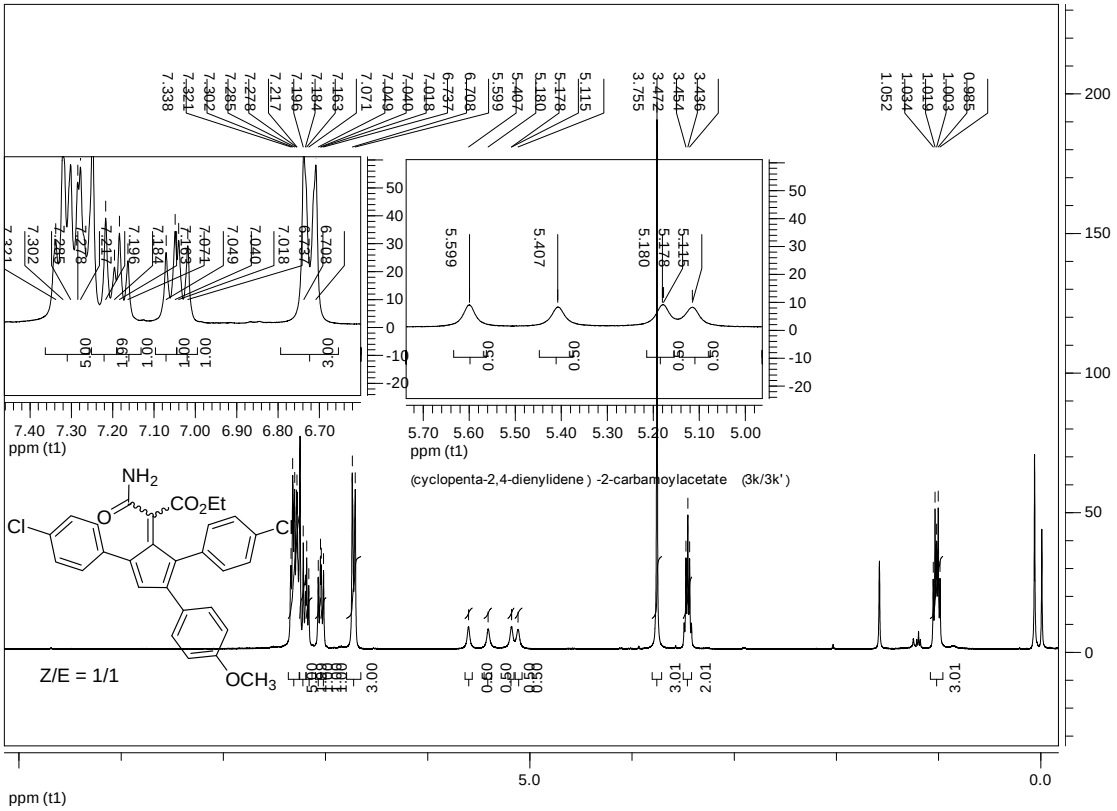


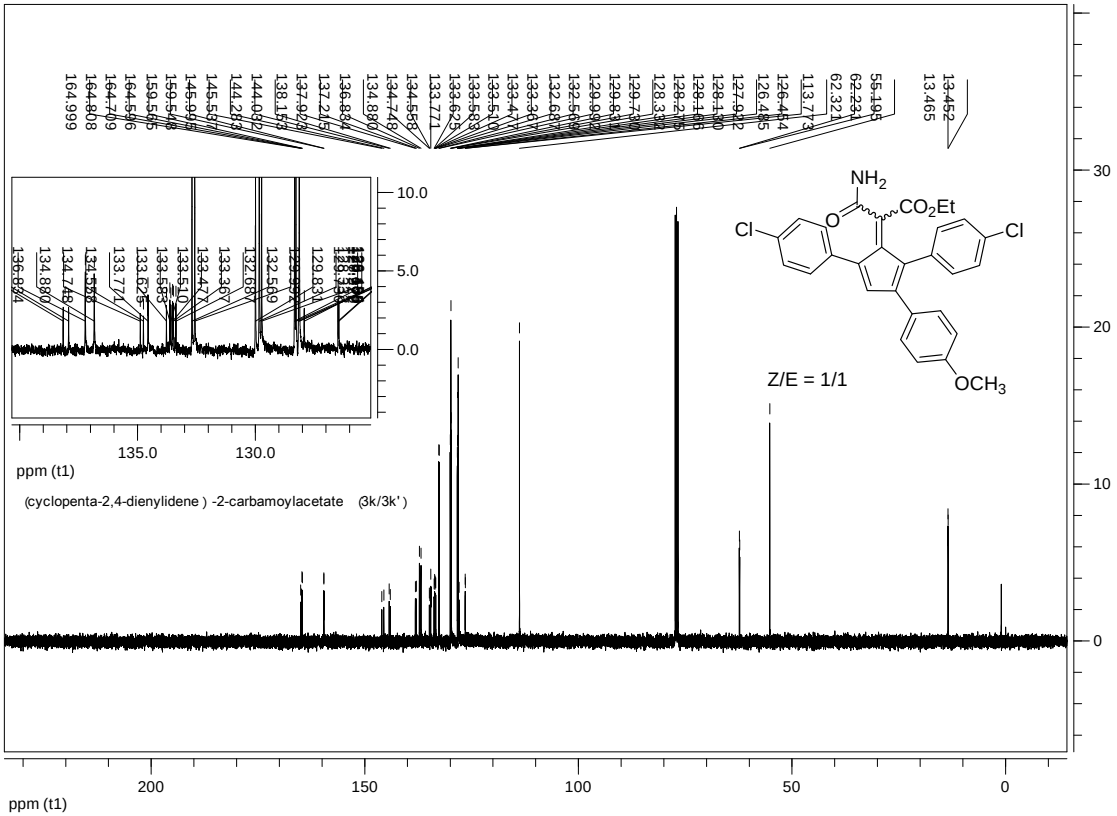
(2E) Ethyl 2-carbamoyl-2-(2-(4-chlorophenyl)-3-(2-methoxyphenyl)-5-(4-methoxyphenyl) cyclopenta-2,4-dienylidene)acetate (3j')





(2E/2Z) Ethyl 2-(2,5-bis(4-chlorophenyl)-3-(4-methoxyphenyl)cyclopenta-2,4-dienylidene)-2-carbamoylacetate (3k/3k')


ppm (t1)
(cyclopenta-2,4-dienylidene) -2-carbamoylacetate (3k/3k')
Z/E = 1/1


ppm (t1)
(cyclopenta-2,4-dienylidene) -2-carbamoylacetate (3k/3k')
Z/E = 1/1

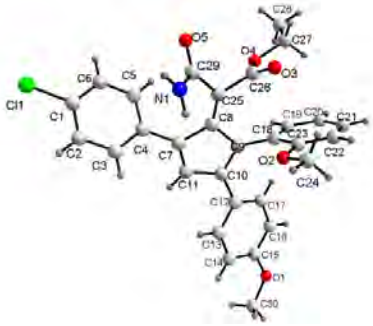


Figure S-1. Molecular structure of fulvene 3h (CCDC 1040541)

Table S-1 Crystal data and structure refinement for 3h

Phase	**3h**
Empirical formula	$\mathbf{C_{30}H_{26}ClNO_5}$
Formula weight	515.97
T/K	293(2) K
Wavelength/nm	0.71073 A
Crystal system	Monoclinic,
Space group	P 21/c
a /Å	19.841(5)
b / Å	14.847(4)
c / Å	8.918(2)
A	90 deg.
β (°)	90.596(6) deg.
Γ	90 deg.
V (Å ^{3})	2626.9(11)
Z	4
F(000)	1080
Crystal size(mm)	0.35 x 0.33 x 0.3
Absorption coefficient (mm^{-1})	0.186
θ range / (°)	2.053- 24.999
Limiting indices	-23<=h<=23, -17<=k<=17, -10<=l<=10
Reflections collected/unique	24139 / 4612 [R(int) = 0.1707]
Completeness to theta	96.9 %
Data/restraints/parameters	4612 / 29 / 348
Refinement method	Full-matrix least-squares on F^2
Final *R* indices[$I>2\sigma(I)$]	R1 = 0.0678, wR2 = 0.0883
R indices (all data)	R1 = 0.2109, wR2 = 0.1094
Goodness-of-fit on F^2	1.059
Largest diff. peak and hole /(e.$Å^{-3}$)	0.196 and -0.208

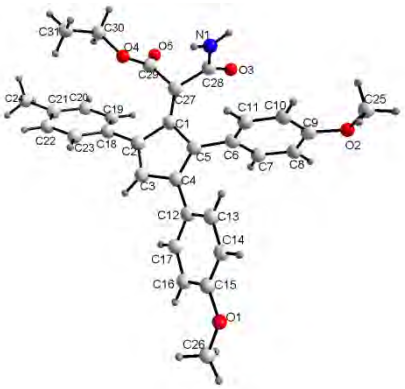


Figure S-2 The Structure of compound 3f' (CCDC 1037660)

Table S-2 Crystal data and structure refinement for 3f'

Phase	**3f'**
Empirical formula	$\mathbf{C_{31}H_{29}NO_5}$
Formula weight	495.55
T/K	296.15
Wavelength/nm	0.71073 A
Crystal system	Triclinic
Space group	P-1
a /Å	5.8328(6)
b / Å	11.8968(14)
c / Å	19.757(2)
A	78.469(4)
β (°)	88.020(4)
Γ	82.246(4)
V (Å ^{3})	1331.0(3)
Z	2
F(000)	524
Crystal size(mm)	0.35 x 0.33 x 0.30
Absorption coefficient (mm^{-1})	0.084
θ range / (°)	1.87 - 24.99
Limiting indices	-6<=h<=6, -14<=k<=14, -23<=l<=23
Reflections collected/unique	24435 / 4654 [R(int) = 0.0410]
Completeness to theta	99.8%
Data/restraints/parameters	4649 / 0 / 346
Refinement method	Full-matrix least-squares on F^2
Final *R* indices[$I>2\sigma(I)$]	R_1 = 0.0476 wR_2 = 0.1320
R indices (all data)	R_1 = 0.0743 wR_2 = 0.1447
Goodness-of-fit on F^2	0.937
Largest diff. peak and hole /(e.Å^{-3})	0.188 and -0.221

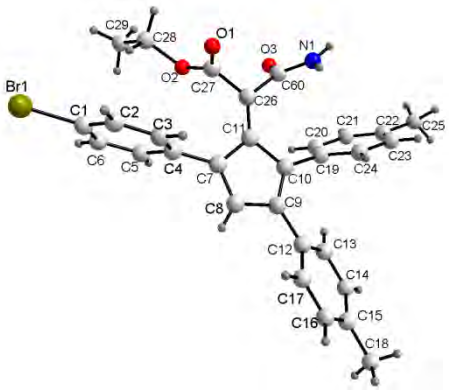


Figure S-3 The Structure of compound 3g'(CCDC 1023075)

Table S-3 Crystal data and structure refinement for 3g'

Phase	**3g'**
Empirical formula	$C_{30}H_{26}BrNO_3$
Formula weight	528.42
T/K	296(2)
Wavelength/nm	0.71073 A
Crystal system	Triclinic
Space group	P-1
a /Å	8.6087(10)
b / Å	12.0564(13)
c / Å	13.9281(15)
A	108.468(3)
β (°)	104.708(3)
Γ	94.122(3)
V (Å ^{3})	1307.8(3)
Z	2
F(000)	544
Crystal size(mm)	0.35×0.33×0.30
Absorption coefficient (mm^{-1})	1.602
θ range / (°)	1.61-27.48
Limiting indices	-11<=h<=11, -15<=k<=15, -18<=l<=18
Reflections collected/unique	19861 / 5999 [R(int) = 0.0359]
Completeness to theta	98.7%
Data/restraints/parameters	4007/0/244
Refinement method	Full-matrix least-squares on F^2
Final *R* indices[$I>2\sigma(I)$]	R_1 = 0.0514 wR_2 = 0.1409
R indices (all data)	R_1 = 0.0933 wR_2 = 0.1672
Goodness-of-fit on F^2	1.042
Largest diff. peak and hole /(e.Å^{-3})	0.259 and -0.710