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Betaine mediated synthesis of annulated dihydrofurans from oxobis(methylthio)ketene acetals and N-butyl-N'-methyl ethane-1,2-diamine as precursors via NHC elimination

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1. General information

All reactions were carried out under a nitrogen atmosphere with dry, freshly distilled solvent under anhydrous condition. Progress of reactions was monitored by Thin Layer Chromatography (TLC). NMR spectra were recorded in $CDCl_3$ at 300 and 200 MHz (based on availability of instruments) 75 and 50 MHz (for ^{13}C) respectively. Chemical shifts are reported in d(ppm) relative to TMS (^{1}H) or $CDCl_3$ (^{13}C) as internal standards. Integrals are in accordance with assignments; coupling constants are given in Hz. ^{1}H- ^{1}H COSY, HSQC and HMBC methods used to confirm the NMR peak assignments. Yields refer to quantities obtained after chromatography.

2. X-ray Crystallographic Data

The crystal data of 13g: $C_{27}H_{24}O_3$, *M* = 396.46, Monoclinic, P2 1 /c, *a* = 18.7438(12) Å, *b* =5.9398(4), Å, *c* = 19.1345(14) Å, ß= 92.094(6)°, *V* = 2128.9(3) Å 3 , *Z* = 4, *Dx* = 1.237 gcm $^{-3}$, μ(Mo-Ka) = 0.079 mm $^{-1}$, *F(*000) = 840.0, rectangular block, colorless, size = 0.48 x 0.46 x 0.44 mm, 9703 reflections measured (*Rint* = 0.0739 (2947), wR2 = 0.1987(5710) for all data, conventional *R1* = 0.0739 for 2947 Fo > 4σ(Fo) and 0.1987 for all 5710 data, *S* = 1.022 for all data and 265 parameters.

Single-crystal X-ray data, space group, unit-cell dimensions and intensity data for **13g** were collected with an Oxford Diffraction X-calibur CCD diffractometer using graphite monochromated Mo Karadiation (*λ*= 0.71073 Å). The structures were solved by direct methods

using SHELXS-97 and refined on *F* 2 by full-matrix least-squares technique using SHELXL-97. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were geometrically fixed with thermal parameters equivalent to 1.2 times that of the atom to which they are bonded. Diagrams for all complexes were prepared using ORTEP. CCDC (deposit No: 892304) contains the supplementary crystallographic data. Cambridge Crystallographic Data Center,12 Union Road, Cambridge,CB21EZ, U. K; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

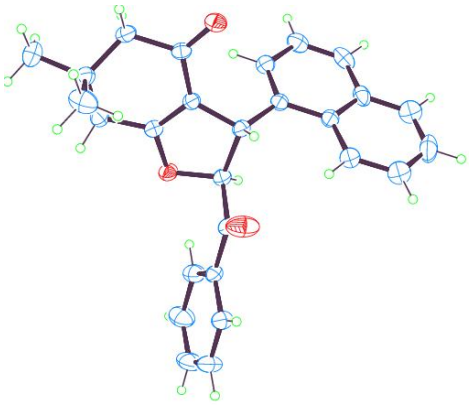


Fig 1. ORTEP diagram of 9g

3. Characteristic representation of Betaine

Our studies aimed at introducing new dogma in *N*-heterocyclic carbene catalysis via betaine[1], a novel nucleophilic intermediates which can be explored for their nucleophilicity and high reactivity towards electrophiles as cycloaddition partners. Betaines of Pseudo-cross-conjugated mesomeric type (Fig 2; I-IV) are isoconjugate with even non-alternant hydrocarbon dianions categorised as heterocyclic mesomeric betaines[2]. Characteristic & systematic dipole types can be dissected from the resonance structures (Fig 2; V). Nodal positions of the HOMO of the anionic building block (Fig 2; VI) & charge distributions according to valence bond theory (Fig 2, VII) within limits also can be represented. The anionic part of the betaine is joined by union bonds

("*u*") to the cationic part via unstarred positions of the isoconjugated hydrocarbon equivalent (Fig 2; X).

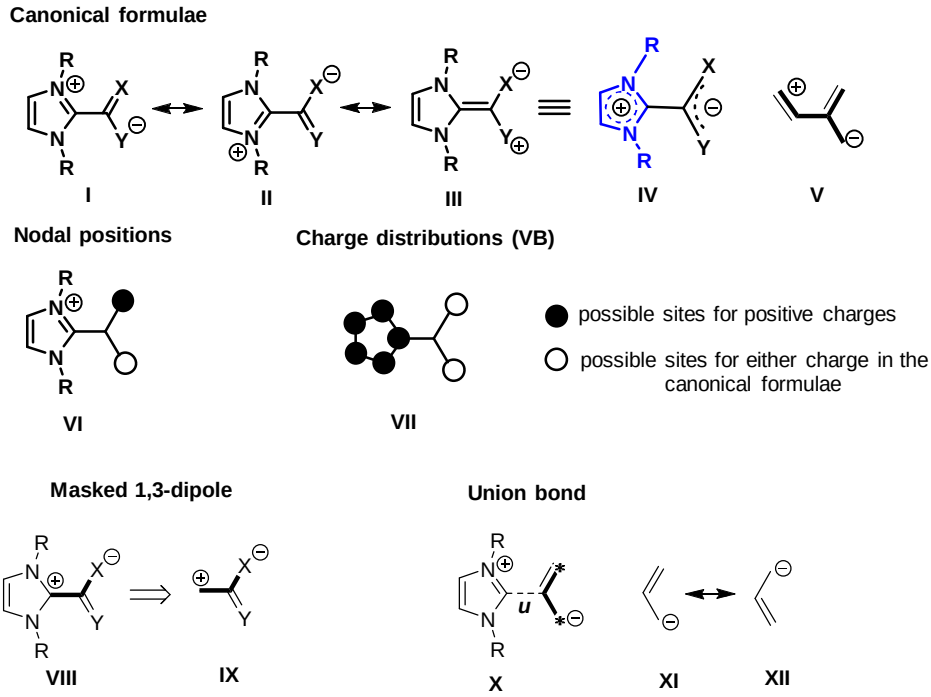


Fig 2. Characteristic representation of Betaine

4. Representative one pot procedure for the synthesis of 9a-q, 11a-h, 13a-k:

NaH (10 mol%) was added to a solution of bis(methylthio)-1-phenylprop-2-en-1-ones (1 mmol), N-butyl-N'-methylethane-1,2-diamine (1 mmol) in THF under N_2 atmosphere. The mixture was stirred for one hr at refluxing condition, followed by the addition of α-ylidene-ß-diketone (1.0 mmol). The reaction mixture was stirred at refluxing condition for completion of 8 h until consumption of starting enone as checked by TLC on various time interval. After completion of the reaction was checked by TLC, the solvent was evaporated in a rotatory evaporator and the residue was extracted with ethyl acetate (3×10 mL) and water. The extracted solution was dried over anhydrous sodium sulphate and concentrated in vacuo. The crude

product was subjected to chromatography on a silica gel column with a hexane-ethyl acetate mixture to afford dihydrofuran derivatives **9a-q, 11a-h, 13a-k** in good to excellent yield.

5. Spectroscopic characterization of all synthesized compounds (9a-p, 11a-g, 13a-j)

2-Benzoyl-3-(3-nitrophenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9a): m.p: 145- 150°C; 87% (0.31 g) as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.13 (t, *J* = 7.9 Hz, 2H, ArH), 7.86 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.66-7.45 (m, 5H, ArH), 5.85 (d, *J* = 5.1 Hz, 1H, CH), 4.68 (d, *J* = 4.4 Hz, 1H, CH), 2.72 (s, 2H, CH_2), 2.34-2.32 (m, 2H, CH_2), 2.16-2.12 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 194.2, 192.2, 148.6, 143.1, 134.4, 134.0, 133.2, 129.9, 129.0, 122.6, 122.1, 115.5, 90.9, 47.8, 36.6, 23.8, 21.6; IR(KBr): 1685 cm^{-1}; MS (ESI+) *m/z*: $[M+H]^+$ 364.1; analysis (calcd., found for $C_{21}H_{17}NO_5$): C (69.41, 69.26), H (4.72, 4.65), N (3.85, 3.79).

2-Benzoyl-3-(4-methoxyphenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9b) : m. p:115-120°C; 82% (0.29 g) as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 7.3Hz, 2H, ArH), 7.62 (t, *J* = 7.1Hz, 1H, Ar-H), 7.47 (t, *J* = 7.7Hz, 2H, ArH), 7.16 (d, *J* = 8.5Hz, 2H, ArH), 6.89 (d, *J* = 8.6Hz, 2H, ArH), 5.83 (d, *J* = 4.6Hz, 1H, CH), 4.36 (d, *J* = 3.8Hz, 1H, CH), 3.79 (s, 3H, OCH_3), 2.70 (s, 2H, CH_2), 2.34-2.29 (m, 2H, CH_2), 2.12 2.08 (m, 2H, CH_2); ^{13}C NMR (50MHz, $CDCl_3$) δ = 194.5, 193.1, 177.3, 159.1, 134.2, 133.4, 129.0, 128.5, 116.7, 114.5, 91.8, 55.4, 48.5, 36.9, 29.8, 24.0, 21.8; IR(KBr): 1687 cm^{-1}; MS (ESI+) *m/z:* 349.1 [M+H]+; analysis (calcd., found for $C_{22}H_{20}O_4$): C (75.84, 75.85), H (5.79, 5.70).

2-Benzoyl-3-(4-chlorophenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9c) : m.p:160-165°C; 89% (0.31 g) as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 7.6Hz, 2H, ArH), 7.63 (t, *J* = 7.0Hz, 1H, Ar-H), 7.47 (t, *J* = 7.2Hz, 2H, ArH), 7.31 (d, *J* = 7.6Hz, 2H, ArH), 7.17 (d, *J* = 7.8Hz, 2H, ArH), 5.81 (d, *J* = 4.6Hz, 1H, CH), 4.43 (d, *J* = 3.6Hz, 1H, CH), 2.69 (s, 2H, CH_2), 2.33-2.29 (m, 2H, CH_2), 2.14-2.12 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 194.06, 192.48, 177.38, 139.59, 134.13, 133.12, 128.98, 128.80, 128.65, 115.92, 91.12, 48.01, 36.55, 23.70, 21.53; IR(KBr): 1685 cm^{-1}; MS (ESI+) *m/z:* 353.1[M+H]+; analysis (calcd., found for $C_{21}H_{17}ClO_3$): C (71.49, 71.55), H (4.86, 4.81).

2-Benzoyl-3-(biphenyl-4-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9d) : m. p :155-158°C; 88% (0.35 g) as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 7.4Hz, 2H, ArH), 7.63 (t, *J* = 7.3Hz, 1H, Ar-H), 7.47-7.32 (m, 7H, ArH), 7.16 (d, *J* = 8.5Hz, 2H, ArH), 6.96 (d, *J* = 8.5Hz, 2H, ArH), 5.83 (d, *J* = 4.6Hz, 1H, CH), 4.37 (d, *J* = 4.0Hz, 1H, CH), 2.70 (s, 2H, CH_2), 2.34-2.30 (m, 2H, CH_2), 2.12-2.08 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 194.4, 193.0, 177.3, 158.3, 137.0, 134.2, 133.6, 133.3, 129.0, 129.0, 128.7, 128.5, 128.1, 127.6, 116.6, 115.4, 91.8, 70.1, 48.4, 36.8, 23.9, 21.8; IR(KBr): 1684 cm^{-1}; MS (ESI+) *m/z:* 395.2 [M+H]+; analysis (calcd., found for $C_{27}H_{22}O_3$): C(82.21, 82.25), H(5.62, 5.60).

2-Benzoyl-6,6-dimethyl-3-propyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9e) : m.p: 94-96°C; 90% (0.28 g) as White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 7.3Hz, 2H, ArH), 7.64 (t, *J* = 7.3Hz, 1H, Ar-H), 7.52 (t, *J* = 7.7Hz, 2H, Ar-H), 5.63 (d, *J* = 4.3Hz, 1H, CH), 3.43 (s, 1H, CH), 2.50-2.33 (m, 2H, CH_2), 2.22 (s, 2H, CH_2), 1.88-1.63 (m, 2H, CH), 1.42-1.30 (m, 2H, CH_2), 1.12 (s, 6H, 2xCH_3), 0.95 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ

= 193.4, 194.1, 176.2, 133.8, 128.8, 128.7, 88.8, 51.2, 42.9, 37.5, 35.2, 34.1, 28.9, 28.3, 19.4, 14.1; IR(KBr): 1685 cm^{-1}; MS (ESI+) *m/z:* 313.2[M+H]+; analysis (calcd., found for $C_{20}H_{24}O_3$): C(76.89, 76.67), H(7.74, 7.65).

2-(4-Bromobenzoyl)-3-(2,5-dimethoxyphenyl)-6,6-dimethyl-2,3,6,7-tetrahydrobenzofuran-4 (5H)-one (9f): m. p:147-150°C; 84% (0.41 g) as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 8.5Hz, 2H, ArH), 7.59 (d, *J* = 8.4Hz, 2H, Ar-H), 6.76 (s, 2H, ArH), 6.66 (s, 1H, ArH), 5.72 (d, *J*= 5.1Hz, 1H, CH), 4.81 (d, *J*= 4.4Hz, 1H, CH), 3.72 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 2.57-2.43 (m, 2H, CH_2), 2.25 (m, 2H, CH_2),1.19 (s, 3H, CH_3), 1.15 (s, 3H, CH_3); ^{13}C NMR (50MHz, $CDCl_3$) δ = 193.7, 192.4, 176.8, 153.8, 150.9, 132.8, 132.0, 129.2, 115.0, 113.5, 112.7, 111.9, 90.2, 55.7, 51.3, 43.1, 37.8, 34.3, 29.2, 28.4; IR(KBr): 1686 cm^{-1}; MS (ESI+) *m/z:* 485.1 [M+H]+; analysis (calcd., found for $C_{25}H_{25}BrO_5$) : C (61.86, 61.88), H (5.19, 5.11).

2-Benzoyl-6,6-dimethyl-3-(naphthalen-2-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9g): m.p:175-179°C; 89% (0.35 g) as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.94- 7.77 (m, 5H, ArH), 7.59-7.32 (m, 7H, Ar-H), 5.86 (s, 1H, CH), 5.45 (s, 1H, CH), 2.56 (s, 2H, CH_2), 2.27 (m, 2H, CH_2), 1.22 (s, 3H, CH_3), 1.17 (s, 3H, CH_3); ^{13}C NMR (50MHz, $CDCl_3$) δ = 193.7, 193.0, 176.0, 134.2, 133.8, 131.3, 129.4, 128.9, 128.3, 126.4, 125.9, 125.7, 123.4, 115.2, 91.5, 51.4, 37.9, 34.4, 29.2, 28.7; IR(KBr): 1684 cm^{-1}; MS (ESI+) *m/z:* 397.1; [M+H]+; analysis (calcd. found for $C_{27}H_{24}O_3$): C (81.79, 81.81), H (6.10, 6.14).

2-(4-Bromobenzoyl)-6,6-dimethyl-3-(thiophen-2-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9h): m. p:145-150°C; 85% (0.37 g) as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 8.5Hz, 2H, ArH), 7.65 (d, *J* = 8.4Hz, 2H, Ar-H), 7.23 (d, *J* = 4.8Hz, 1H, ArH), 6.98 (dd, *J* = 3.4, 4.5Hz, 2H, ArH), 5.84 (d, *J* = 4.2Hz, 1H, CH), 4.78 (s, 1H, CH), 2.61-2.46 (m, 2H,

CH $_2$), 2.24 (m, 2H, CH $_2$), 1.19 (s, 3H, CH_3), 1.15 (s, 3H, CH_3); ^{13}C NMR (50MHz, $CDCl_3$) δ = 193.4,191.6, 176.4, 144.7, 132.4, 132.0, 130.5, 129.8, 127.4, 125.3, 124.9, 114.5, 91.4, 51.2, 43.8, 37.7, 34.3, 29.2, 28.2; IR(KBr): 1687 cm^{-1}; MS (ESI+) *m/z:* 431.0 $[M+H]^+$; analysis (calcd., found for $C_{21}H_{19}BrO_3S$): C(58.47, 58.41), H (4.44, 4.46).

2-Benzoyl-3- ferrocenyl -2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9i): m. p:120-125°C; 88% (0.39 g) as yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.4Hz, 2H, ArH), 7.67-7.52 (m, 3H, Ar-H), 6.07 (d, *J* = 3.6Hz, 1H, CH), 4.47 (d, *J* = 3.3Hz, 1H, CH), 4.26 (s, 1H, Fc-H), 4.27-4.10 (m, 8H, Fc-H), 2.58-2.56 (m, 2H, CH_2), 2.43-2.26 (m, 2H, CH_2), 2.10-2.01 (m, 2H, CH_2); ^{13}C NMR (50MHz, $CDCl_3$) δ = 194.5, 193.8, 176.1, 134.4, 134.1, 129.2, 129.0, 117.0, 90.5, 90.1, 68.7, 68.0, 66.6, 41.4, 37.0, 24.0, 21.6; IR(KBr): 1695 cm^{-1}; MS (ESI+) *m/z:* 427.1 $[M+H]^+$; analysis (calcd., found for $C_{25}H_{22}FeO_3$): C(70.44, 70.24), H (5.20, 5.29).

3- Ferrocenyl, 2-(4-methoxybenzoyl)- 2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9j): m.p:160-165°C; 85% (0.40 g) as yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 8.9Hz, 2H, ArH), 7.02 (d, *J* = 8.8Hz, 2H, Ar-H), 6.02 (d, *J* = 4.0Hz, 1H, CH), 4.49 (d, *J* = 3.7Hz, 1H, CH), 4.26-4.10 (m, 9H, Fc-H), 3.90 (s, 3H, OCH_3), 2.56-2.52 (m, 2H, CH_2), 2.41- 2.30 (m, 2H, CH_2), 2.09-2.03 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 194.5, 191.9, 176.1, 164.3, 131.6, 121.2, 117.1, 114.3, 90.3, 68.6, 68.0, 67.9, 66.5, 55.7, 41.2, 36.9, 24.0, 21.6; IR(KBr): 1690 cm^{-1}; MS (ESI+) *m/z:* 457.1 $[M+H]^+$; analysis (calcd., found for $C_{26}H_{24}FeO_4$): C (68.44, 68.30), H (5.30, 5.39).

2-(4-Bromobenzoyl)-3- ferrocenyl-2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9k):

m.p:150-155°C; 81% (0.42 g) as yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 8.5Hz, 2H, ArH), 7.70 (d, *J* = 8.5Hz, 2H, Ar-H), 5.98 (d, *J* = 3.9Hz, 1H, CH), 4.50 (d, *J* = 3.3Hz, 1H, CH), 4.25 (s, 1H, Fc-H), 4.16-4.10 (m, 8H, Fc-H), 2.53 (s, 2H, CH_2), 2.44-2.25 (m, 2H, CH_2), 2.08-1.95 (m, 2H, CH_2); ^{13}C NMR (50MHz, $CDCl_3$) δ = 194.4, 192.9, 175.7, 133.1, 132.3, 130.7, 129.4, 117.0, 90.6, 89.9, 68.6, 68.0, 66.4, 41.6, 36.9, 23.9, 21.5; IR(KBr): 1696 cm^{-1}; MS (ESI+) *m/z:* 505.2 $[M+H]^+$ analysis (calcd., found for $C_{25}H_{21}FeO_3Br$): C(59.44, 59.31), H(4.19, 4.29).

2-(Biphenylcarbonyl)-3-ferrocenyl-2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9i):

m.p:170-175°C; 78% (0.40 g) as yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.3Hz, 2H, ArH), 7.78 (d, *J* = 8.3Hz, 2H, Ar-H), 7.66 (d, *J* = 6.9Hz, 2H, Ar-H), 7.51-7.39 (m, 3H, Ar-H), 6.09 (d, *J* = 3.7Hz, 1H, CH), 4.52 (d, *J* = 3.5Hz, 1H, CH), 4.29 (s, 1H, Fc-H), 4.17-4.11 (m, 8H, Fc-H), 2.59-2.55 (m, 2H, CH_2), 2.39-2.32 (m, 2H, CH_2), 2.10-2.04 (m, 2H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 194.6, 193.3, 176.1, 146.8, 139.7, 133.0, 129.8, 129.1, 128.6, 127.6, 127.4, 117.1, 90.6, 90.1, 68.7, 68.0, 67.9, 66.6, 41.3, 37.0, 24.0, 21.6; IR(KBr): 1698 cm^{-1}; MS (ESI+) *m/z:* 503.2 $[M+H]^+$; analysis (calcd., found for $C_{31}H_{26}FeO_3$): C (74.11, 74.25), H (5.22, 5.13).

2-Benzoyl-6,6-dimethyl -3-ferrocenyl- 2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9m): m. p :120-123°C; 80% (0.38 g) as yellow solid; ^{1}H NMR (300MHz, $CDCl_3$) δ = 8.06 (d, *J* = 7.3Hz, 2H, ArH), 7.65 (d, *J* = 7.4Hz, 1H, Ar-H), 7.56 (d, *J* = 7.3Hz, 2H, Ar-H), 6.08 (s, 1H, CH), 4.40 (s, 1H, CH), 4.20-4.12 (m, 9H, Fc-H) 2.51-2.36 (m, 2H, CH_2), 2.24 (s, 2H, CH_2), 1.16 (s, 3H, CH_3), 1.12 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 193.8, 193.0, 175.4, 134.3, 134.0, 129.0, 128.9, 115.2, 91.2, 90.4, 68.7, 68.6, 67.9, 67.8, 67.6, 66.6, 51.4, 41.4, 37.8, 34.1, 29.0,

28.3; IR(KBr): 1690 cm^{-1}; MS (ESI+) *m/z:* 455.3 $[M+H]^+$; analysis (calcd., found for $C_{27}H_{26}FeO_3$): C(71.38, 71.45), H(5.77, 5.66).

6, 6-Dimethyl-3-ferrocenyl-2-(4-methoxybenzoyl)-2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9n): m. p:124-128°C; 87% (0.43 g) as yellow solid; yield: ^1H NMR (300 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 8.8Hz, 2H, ArH), 7.03 (d, *J* = 8.8Hz, 2H, Ar-H), 6.05 (d, *J* = 3.7Hz, 1H, CH), 4.43 (d, *J* = 2.6Hz, 1H, CH), 4.20-4.09 (m, 9H, Fc-H), 3.90 (s, 3H, OCH_3), 2.50- 2.36 (m, 2H, CH_2), 2.24 (s, 2H), 1.15 (s, 3H, CH_3), 1.12 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 193.9, 192,1, 175.5, 164.3, 131.5, 127.2, 115.4, 114.3, 91.2, 90.5, 68.7, 67.9, 67.8, 66.7, 55.7, 51.5, 41.4, 37.9, 34.1, 29.1, 28.3; IR(KBr): 1699 cm^{-1}; MS (ESI+) *m/z:* 485.0 $[M+H]^+$ analysis (calcd., found for $C_{28}H_{28}FeO_4$) : C(69.43, 69.23), H(5.83, 5.78).

2-(4-Bromobenzoyl)-6, 6-dimethyl-3-ferrocenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9o) : m. p : 115-125°C; 74% (0.41 g) as yellow solid; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 8.6Hz, 2H, ArH), 7.70 (d, *J* = 8.6Hz, 2H, Ar-H), 6.00 (d, *J* = 3.8Hz, 1H, CH), 4.44 (d, *J* = 3.3Hz, 1H, CH), 4.18-4.07 (m, 9H, Fc-H), 2.41 (s, 2H, CH_2), 2.23 (s, 2H, CH_2), 1.15 (s, 3H, CH_3), 1.11 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 193.9, 193.0, 175.1, 133.1, 132.4, 130.6, 129.4, 115.4, 91.4, 90.3, 68.7, 68.0, 67.7, 66.6, 51.4, 41.3, 37.8, 34.2, 29.0, 28.3; IR(KBr): 1698 cm^{-1}; MS (ESI+) *m/z:* 533.1 $[M+H]^+$; analysis (calcd., found for $C_{27}H_{25}FeO_3Br$): C (60.82, 60.62), H (4.73, 4.63).

2-(Biphenylcarbonyl)-6, 6-dimethyl-3-ferrocenyl-2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9p): m. p : 125-130°C; 79% (0.43 g) as Yellow solid; ^1H NMR (300MHz, $CDCl_3$) δ = 8.15 (d, *J* = 8.2Hz, 2H, Ar-H), 7.77 (d, *J* = 8.3Hz, 2H, ArH), 7.66 (d, *J* = 6.9Hz, 2H, ArH), 7.51-7.42

(m, 3H, ArH), 6.11 (d, *J* = 3.6Hz, 1H, CH), 4.46 (s, 1H, CH), 4.23-4.11 (m, 9H), 2.52-2.38 (m, 2H, CH_2), 2.25 (s, 2H, CH_2), 1.16 (s, 3H, CH_3), 1.13 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 193.8, 193.3, 175.4, 146.7, 139.6, 132.9, 129.7, 129.1, 128.6, 127.6, 127.4, 115.3, 91.4, 90.4, 68.7, 67.9, 67.8, 67.7, 66.7, 51.4, 41.5, 37.8, 34.1, 29.0, 28.3; IR(KBr): 1692 cm^{-1}; MS (ESI+) *m/z:* 531.1 $[M+H]^+$; analysis (calcd., found for $C_{33}H_{30}FeO_3$): C (74.72, 74.52), H (5.70, 5.79).

3-(4-chlorophenyl)-6,6-dimethyl-2-(4-nitrobenzoyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (9q): m.p:120-122°C; 74% (0.31 g) as pale yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 8.56 Hz, 2H), 8.03 (t, *J* = 7.94 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.92 Hz, 2H), 7.35 (d, *J* = 8.52 Hz, 2H), 6.58 (d, *J* = 4.0 Hz, 1H), 5.71 (d, *J* = 4.1 Hz, 1H), 2.56 (s, 2H), 2.27 (s, 2H), 1.22 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 20.12, 28.67, 29.12, 38.81, 42.98, 51.36, 91.51, 114.67, 122.63, 128.23, 128.70, 128.95, 129.63, 130.96, 132.44, 138.44, 138.63, 139.28, 147.03, 194.08, 194.80; IR(KBr): 1686 cm^{-1}; MS (ESI+) *m/z:* 426.1 $[M+H]^+$; analysis (calcd., found for $C_{23}H_{20}ClNO_5$): C (64.87, 64.88), H (4.73, 4.71).

2-Benzoyl-3-isopropyl-2H-furo[3,2-c]chromen-4(3H)-one (11a) : m. p: 98-100°C; 93% (0.31 g) as white solid. ^1H NMR (300 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 7.3Hz, 2H, Ar-H), 7.69- 7.51 (m, 4H, ArH), 7.39 (d, *J* = 8.3Hz, 1H, ArH), 7.30 (t, *J* = 7.3Hz, 2H, ArH), 5.94 (d, *J* = 4.6Hz, 1H, CH), 3.90 (t, *J* = 3.9Hz, 1H, CH), 2.54-2.46 (m, 1H, CH), 1.01-0.98 (m, 6H, 2xCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 193.7, 166.2, 160.1, 155.0, 134.1, 133.9, 132.6, 129.1, 128.9, 124.0, 122.8, 116.8, 112.0, 103.8, 86.6, 49.0, 29.3, 19.9, 18.1; IR(KBr): 1689, 1702 cm^{-1}; MS (ESI+) *m/z:* 335.1 $[M+H]^+$ analysis (calcd., found for $C_{21}H_{18}O_4$): C(75.43, 75.40), H (5.43, 5.49).

2-(4-Methoxybenzoyl)-3-phenyl-2H-furo[3,2-c]chromen-4(3H)-one (11b): m.p : 175-180ºC; 80% (0.31 g) as white solid; ^{1}H NMR (300 MHz, $CDCl_3$,) δ = 7.89 (t, *J* = 8.9Hz, 3H, Ar-H), 7.62 (t, *J* = 7.1Hz, 1H, ArH), 7.40-7.32 (m, 7H, ArH), 6.97 (d, *J* = 8.8Hz, 2H, ArH), 6.13 (d, *J* = 4.9Hz, 1H, CH), 4.81(d, *J* = 4.9Hz, 1H, CH), 3.89 (s, 3H, OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$,) δ = 190.7, 166.6, 164.6, 159.5, 155.5, 139.8, 133.0, 131.6, 130.2, 129.3, 128.2, 127.7, 126.1, 124.2, 123.3, 117.1, 114.4, 112.3, 105.5, 92.6, 55.7, 49.6; IR(KBr): 1682, 1705 cm^{-1}; MS (ESI+) *m/z:* 399.1 $[M+H]^+$; analysis (calcd., found for $C_{25}H_{18}O_5$) : C (75.37, 75.45), H (4.55, 4.39).

3-(2,4-Dichlorophenyl)-2-(4-methoxybenzoyl)-2H-furo[3,2-c]chromen-4(3H)-one (11c) : m.p:150-154°C; 86% (0.40 g) as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 8.8Hz, 2H, Ar-H), 7.76 (d, *J* = 6.8Hz, 1H, ArH), 7.63-7.58 (m, 1H, ArH), 7.42 (d, *J* = 8.4Hz, 2H, ArH), 7.34-7.18 (m, 3H, ArH), 6.99 (d, *J* = 8.8Hz, 2H, ArH), 6.07 (d, *J* = 5.1Hz, 1H, CH), 5.45 (d, *J* = 5.0Hz, 1H, CH), 3.90 (s, 3H, OCH_3);^{13}C NMR (50 MHz, $CDCl_3$) δ = 189.6, 166.8, 164.6, 159.1, 155.4, 135.7, 134.4, 134.3, 133.1, 131.6, 130.4, 130.0, 127.9, 126.5, 124.2, 123.1, 117.1, 114.3, 112.0, 103.9, 90.6, 55.6, 45.3; IR(KBr): 1683, 1704 cm^{-1}; MS (ESI+) *m/z:* 467.1 $[M+H]^+$; analysis (calcd., found for $C_{25}H_{16}Cl_2O_5$): C (64.26, 64.32), H (3.45, 3.22).

2-Benzoyl-3-ferrocenyl-2H-furo [3, 2-c] chromen-4(3H)-one (11d): m.p:155-160°C; 80% (0.39 g) as yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 7.2Hz, 2H, Ar-H), 7.71 (t, *J* = 7.5Hz, 2H, ArH), 7.61-7.54 (m, 3H, ArH), 7.38 (d, *J* = 8.2Hz, 1H, ArH), 7.30 (d, *J* = 7.9Hz, 1H, ArH), 6.35 (d, *J* = 4.0Hz, 1H, CH), 4.87 (d, *J* = 3.9Hz, 1H, CH), 4.36 (s, 1H, Fc-H), 4.24-4.11 (m, 8H, Fc-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 193.0, 165.1, 159.7, 155.2, 134.4, 134.2,

132.8, 129.3, 129.1, 124.1, 123.0, 117.0, 112.3, 106.0, 91.7, 88.6, 68.8, 68.4, 68.2, 68.2, 66.2, 42.2; IR(KBr): 1689, 1712 cm^{-1}; MS (ESI+) *m/z:* 477.5 [M+H]+; analysis (calcd., found for $C_{28}H_{20}FeO_4$) : C (70.61, 70.51), H (4.23, 4.43).

3-Ferrocenyl, 2-(4-methoxybenzoyl) - 2H-furo [3, 2-c] chromen-4(3H)-one (11e):

m.p:150-155°C; 75% (0.39 g) as yellow solid; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.6Hz, 2H, Ar-H), 7.71 (d, *J* = 7.6Hz, 1H, ArH), 7.58 (t, *J* = 7.5Hz, 1H, ArH), 7.38 (d, *J* = 8.3Hz, 1H, ArH), 7.29 (d, *J* = 7.9Hz, 1H, ArH), 7.06 (d, *J* = 8.6Hz, 2H, ArH), 6.31 (d, *J* = 3.9Hz, 1H, CH), 4.89 (d, *J* = 3.9Hz, 1H, CH), 4.36 (s, 1H, Fc-H), 4.23-4.11 (m, 8H, Fc-H), 3.92 (s, 3H, OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 191.2, 165.1, 164.6,159.8, 155.2, 132.7, 131.8, 127.1, 124.1, 123.0, 117.0, 114.4, 112.4, 106.0, 91.5, 88.7, 68.8, 68.4, 68.3, 66.2, 55.8, 42.1; IR(KBr): 1698, 1710 cm^{-1}; MS (ESI+) *m/z:* 507.1 $[M+H]^+$; analysis (calcd., found for $C_{29}H_{22}FeO_5$) : C(68.79, 68.85), H (4.38, 4.25).

2-(4-Bromobenzoyl)-3- ferrocenyl-2H-furo [3,2-c]chromen-4(3H)-one (11f): m.p :125-130°C; 82% (0.47 g) as yellow solid; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 8.5Hz, 2H, Ar-H), 7.74-7.66 (m, 3H, ArH), 7.59 (t, *J* = 7.1Hz, 1H, ArH), 7.38 (d, *J* = 8.2Hz, 1H, ArH), 7.30 (d, *J* = 7.5Hz, 1H, ArH), 6.27 (d, *J* = 4.0Hz, 1H, CH), 4.89 (d, *J* = 3.9Hz, 1H, CH), 4.35 (s, 1H, Fc-H), 4.22-4.11 (m, 8H, Fc-H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 192.2, 164.8, 159.6, 155.2, 132.9, 132.5, 130.9, 129.9, 124.2, 122.9, 117.1, 112.2, 106.0, 91.8, 88.4, 68.9, 68.5, 68.3, 66.1, 42.0; IR(KBr): 1695, 1708 cm^{-1}; MS (ESI+) *m/z:* 556.1 $[M+H]^+$; analysis (calcd., found for $C_{28}H_{19}FeO_4Br$): C (60.57, 60.76), H (3.45, 3.33).

2-(Biphenylcarbonyl)-3-ferrocenyl-2H-furo [3, 2-c] chromen-4(3H)-one (11g): m. p :115-120°C; 71% (0.40 g) as yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.31Hz, 2H, Ar-H), 7.82 (d, *J* = 8.3Hz, 2H, ArH), 7.74-7.66 (m, 3H, ArH), 7.59-7.36 (m, 4H, ArH), 7.30 (d, *J* = 7.50Hz, 2H, ArH), 6.38 (d, *J* = 4.0Hz, 1H, CH), 4.91 (d, *J* = 3.9Hz, 1H, CH), 4.38 (s, 1H, Fc-H), 4.26-4.13 (m, 8H, Fc-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 192.5, 165.1, 155.3, 147.1, 139.6, 132.8, 132.8, 130.0, 129.2, 128.7, 127.7, 127.5, 124.1, 123.0, 117.1, 112.4, 106.0, 91.8, 88.7, 68.9, 68.5, 68.3, 66.3, 42.2; IR(KBr): 1685, 1702 cm^{-1}; MS (ESI+) *m/z:* 553.2 $[M+H]^+$; analysis (calcd., found for $C_{34}H_{24}FeO_4$): C (73.93, 73.79), H (4.38, 4.54)

4-(3-(4-chlorophenyl)-4-oxo-2,3-dihydro-4H-furo[3,2-c]chromene-2-carbonyl)benzonitrile (11h): m.p:148-150°C; 71% (0.30 g) as dirty white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77-7.94 (m, 5H), 7.57 (t, *J* = 8.8 Hz, 1H), 7.25-7.47 (m, 6H), 5.87 (d, *J* = 4.5 Hz, 1H), 4.85 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 44.39, 92.60, 105.46, 112.13, 120.65, 121.58, 123.62, 128.05, 129.24, 129.35, 129.86, 129.94, 130.61, 132.03, 133.35, 136.12, 136.87, 137.41, 139.54, 139.57, 140.25, 148.13, 163.61, 166.51, 197.20; IR(KBr): 1684, 1703 cm^{-1}; MS (ESI+) *m/z:* 428.1 $[M+H]^+$; analysis (calcd., found for $C_{25}H_{14}ClNO_4$): C (70.18, 70.20), H (3.30, 3.28).

2-(4-Bromobenzoyl)-6-methyl-3-phenyl-2H-furo[3,2-c]pyran-4(3H)-one (13a): m. p: 152-155°C; 90% (0.37g) as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.9Hz, 2H, Ar-H), 7.63 (d, *J* = 7.1Hz, 2H, ArH), 7.37 (d, *J* = 7.3Hz, 3H, ArH), 7.25 (d, *J* = 8.8Hz, 2H, ArH), 6.14 (s 1H, CH), 5.93 (d, *J* = 4.8Hz, 1H, CH), 4.63 (d, *J* = 4.6Hz, 1H, CH), 2.29 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) d= 191.5, 170.9, 166.8, 160.7, 139.7, 132.4, 130.5, 129.3, 128.2, 127.5, 102.5, 95.5, 92.2, 48.3, 20.6; IR(KBr): 1686, 1705 cm^{-1}; MS (ESI+) *m/z:* 411.0 $[M+H]^+$; analysis (calcd., found for $C_{21}H_{15}BrO_4$) : C (61.33, 61.38), H (3.68, 3.60)

2-Benzoyl-3-(4-fluorophenyl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one (13b): m.p:135-140°C; 89% (0.31 g) as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 7.1Hz, 2H, Ar-H), 7.64 (d, *J* = 6.5Hz, 1H, ArH), 7.51 (d, *J* = 7.4Hz, 2H, ArH), 7.24 (dd, *J* = 5.4Hz, 2H, ArH), 7.08 (m, 2H, ArH), 6.16 (s, 1H, CH), 5.96 (d, *J* = 4.9Hz, 1H, CH), 4.63 (d, *J* = 4.7Hz, 1H, CH), 2.30 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) d= 192.3, 171.1, 166.9, 164.9, 160.8, 160.0, 135.6, 134.5, 133.2, 129.3, 129.1, 116.4, 116.0, 102.4, 95.6, 92.3, 47.7, 20.6; IR(KBr): 1683, 1706 cm^{-1}; MS (ESI+) *m/z:* 351.1 $[M+H]^+$; analysis (calcd., found for $C_{21}H_{15}FO_4$) : C (71.99, 71.91), H (4.32, 4.38).

3-(4-Chlorophenyl)-2-(4-methoxybenzoyl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one (13c): m.p:147-150°C; 85% (0.34 g) as white solid; H NMR (300 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.6Hz, 2H, Ar-H), 7.35 (d, *J* = 8.4Hz, 2H, ArH), 7.20 (d, *J* = 8.4Hz, 2H, ArH), 6.95 (d, *J* = 8.9Hz, 2H, Ar-H), 6.15 (s, 1H, CH), 5.90 (d, *J* = 5.0Hz, 1H, CH), 4.62 (d, *J* = 4.8Hz, 1H, CH), 3.88 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 190.6, 171.2, 166.9, 164.6, 160.8, 138.5, 133.9, 131.5, 129.4, 129.0, 126.0, 114.8, 102.2, 95.6, 91.9, 55.7, 48.0, 20.7; IR(KBr): 1685, 1705 cm^{-1}; MS (ESI+) *m/z:* 397.1 $[M+H]^+$. analysis (calcd., found for $C_{22}H_{17}ClO_5$): C (66.59, 4.32), H (66.54, 4.28).

2-(Biphenylcarbonyl)-6-methyl-3-phenyl-2H-furo[3,2-c]pyran-4(3H)-one (13d): m.p:155-160°C; 87% (0.35 g) as white solid; H NMR (300 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 8.3Hz, 2H, Ar-H), 7.64 (d, *J* = 8.2Hz, 2H, ArH), 7.56 (d, *J* = 6.9Hz, 2H, ArH), 7.43-7.34 (m, 3H, ArH), 7.29 (s, 2H, Ar-H), 7.18 (t, *J* = 7.9Hz, 3H, ArH), 6.09 (s, 1H, CH), 5.90 (d, *J* = 5.0Hz, 1H, CH), 4.60 (d, *J* = 4.8Hz, 1H, CH), 2.23 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ =191.8, 171.2, 167.0,

160.8, 147.2, 139.4, 138.4, 134.0, 131.8, 129.7, 129.5, 129.2, 129.0, 128.8, 127.7, 127.4, 102.3, 95.6, 92.2, 47.9, 20.7; IR(KBr): 1684, 1704 cm^{-1}; MS (ESI+) *m/z:* 443.1 $[M+H]^+$; analysis (calcd., found for $C_{27}H_{20}O_4$): C, 79.40; H, 4.94; Found: C, 79.45; H, 4.97. C (79.40, 79.45), H (4.94, 4.97).

2-(Biphenylcarbonyl)-3-(furan-2-yl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one (13e): m.p:125-130°C; 91% (0.36 g) as white solid; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 8.3Hz, 2H, ArH), 7.74 (d, *J* = 8.3Hz, 2H, Ar-H), 7.65 (d, *J* = 7.0Hz, 2H, ArH), 7.51-7.43 (m, 4H, ArH), 6.38 (s, 1H, ArH), 6.31 (d, *J* = 2.8Hz, 1H, ArH), 6.20 (d, *J* = 4.6Hz, 1H, CH), 6.14 (s, 1H, CH), 4.86 (d, *J* = 4.4Hz, 1H, CH), 2.30 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 191.6, 171.6, 167.0, 160.8, 151.3, 147.2, 142.8, 139.5, 131.8, 129.8, 129.1, 128.7, 127.7, 127.4, 111.0, 108.2, 99.6, 95.7, 88.9, 41.9, 20.7; IR(KBr): 1689, 1703 cm^{-1}; MS (ESI^+) *m/z:* 399.1 $[M+H]^+$; analysis (calcd., found for $C_{25}H_{18}O_5$): C (75.37, 75.39), H (4.55, 4.50).

2-(Biphenylcarbonyl)-3-ferrocenyl 6-methyl- 2H-furo [3, 2-c]pyran -4(3H)-one (13f): m. p:175-180°C; 81% (0.43 g) as yellow solid; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 8.4Hz, 2H, Ar-H), 7.70 (d, *J* = 8.3Hz, 2H, ArH), 7.58 (t, *J* = 6.8Hz, 2H, ArH), 7.43-7.33 (m, 3H, ArH), 6.11 (d, *J* = 3.8Hz, 1H, CH), 5.96 (s, 1H, CH), 4.61 (d, *J* = 3.7Hz, 1H, CH), 4.22- 4.05 (m, 9H, Fc-H), 2.18 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 192.7, 170.2, 166.3, 161.3, 147.0, 139.6, 132.7, 129.9, 129.2, 128.7, 127.7, 127.4, 103.0, 95.6, 91.4, 89.1, 68.9, 68.4, 68.1, 67.7, 66.4, 41.3, 20.6; IR(KBr): 1688, 1704 cm^{-1}; MS (ESI+) *m/z:* 516.1 $[M+H]^+$; analysis (calcd., found for $C_{31}H_{24}FeO_4$): C (72.11, 72.24), H (4.68, 4.58).

2-Benzoyl-3-ferrocenyl 6-methyl- -2H-furo [3, 2-c]pyran-4(3H)-one (13g): m. p :165-

170°C; 78% (0.33 g) as yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.08 (d, *J*= 7.5Hz, 2H, Ar-H), 7.69 (t, *J*= 7.0Hz, 1H, ArH), 7.58 (t, *J*= 7.6Hz, 2H, ArH), 6.16 (d, *J*= 3.6Hz, 1H, CH), 6.04 (s, 1H, CH), 4.64 (d, *J*= 3.4Hz ,1H, CH), 4.27-4.11 (m, 9H, Fc-H), 2.27 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 193.2, 170.2, 166.3, 161.3, 134.3, 134.1, 129.2, 129.1, 102.9, 95.5, 91.3, 89.0, 68.8, 68.3, 68.1, 67.6, 66.4, 41.3, 20.6; IR(KBr): 1689, 1705 cm^{-1}; MS (ESI+) *m/z:* 441.1 $[M+H]^+$; analysis (calcd., found for $C_{25}H_{20}FeO_4$): C (68.20, 68.29), H (4.58, 4.68).

3-Ferrocenyl-2-(4-methoxybenzoyl) - 6-methyl- 2H-furo [3,2-c]pyran-4(3H)-one (13h): m. p : 155-160°C; 86% (0.41 g) as yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 8.8Hz, 2H, Ar-H), 7.03 (d, *J* = 8.8Hz, 2H, ArH), 6.12 (d, *J* = 3.8Hz, 1H, CH), 6.03 (s, 1H, CH), 4.65 (d, *J* = 3.6Hz, 1H, CH), 4.28-4.11 (m, 9H, Fc-H), 3.91 (s, 3H, OCH_3), 2.27 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 191.4, 170.2, 166.2, 164.5, 161.4, 131.6, 126.9, 114.4, 103.1, 95.6, 91.1, 89.1, 68.8, 68.3, 68.0, 67.7, 66.4, 55.7, 41.2, 20.6; IR(KBr): 1691, 1708 cm^{-1}; MS (ESI+) *m/z:* 471.8 $[M+H]^+$; analysis (calcd., found for $C_{26}H_{22}FeO_5$): C (66.40, 66.28), H (4.72, 4.69).

2-(4-Bromobenzoyl)- 3-ferrocenyl 6-methyl- -2H-furo[3,2-c]pyran-4(3H)-one (13i): m. p: 142-145°C; 82% (0.44 g) as yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 8.5Hz, 2H, Ar-H), 7.71 (d, *J* = 8.4Hz, 2H, ArH), 6.08 (d, *J* = 3.9Hz, 1H, CH), 6.01 (s, 1H, CH), 4.67 (d, *J* = 3.7Hz, 1H, CH), 4.26 (s, 1H, Fc-H), 4.21-4.12 (m, 8H, Fc-H), 2.27 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 192.3, 169.8, 166.3, 161.0, 132.8, 132.4, 130.7, 129.6, 102.8, 95.4, 91.3, 89.6, 69.6, 69.2, 68.8, 68.5, 67.0, 41.0, 20.6; IR(KBr): 1695, 1706 cm^{-1}; MS (ESI+) *m/z:* 519.2 [M+H]+ analysis (calcd., found for $C_{25}H_{19}FeO_4Br$) : C (57.84, 57.75), H (3.69, 3.78).

2-(4-Methoxybenzoyl)-6-methyl-3-(naphthalen-1-yl)-2H-furo[3,2-c]pyran-4(3H)-one

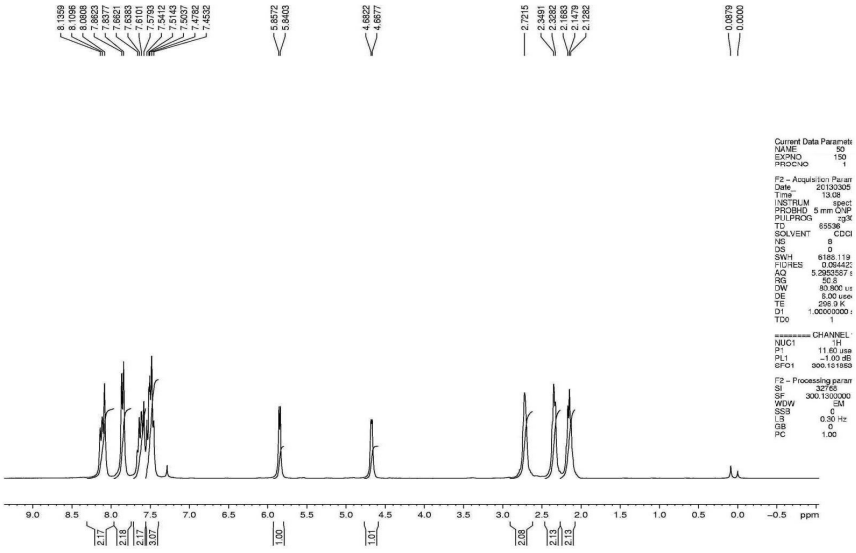
(13j): m.p:160-165°C; 83% (0.34 g) as white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.0Hz, 1H, Ar-H), 7.86-7.79 (m, 4H, ArH), 7.47-7.41 (m, 3H, ArH), 7.33 (d, *J* = 6.9Hz, 1H, ArH), 6.87 (d, *J* = 8.8Hz, 2H, Ar-H), 6.12 (s, 1H, CH), 5.90 (s, 1H, CH), 5.73 (s, 1H, CH), 3.84 (s, 3H, OCH_3), 2.30 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ =190.8, 170.9, 166.5, 164.5, 161.0, 135.9, 134.2, 131.9, 131.3, 129.0, 128.5, 126.6, 125.9, 125.7, 123.2, 114.1, 102.3, 95.5, 91.8, 60.4, 55.6, 42.6, 20.6, 14.2; IR(KBr): 1692, 1700 cm^{-1}; MS (ESI+) *m/z:* 413.1 $[M+H]^+$; analysis (calcd., found for $C_{26}H_{20}O_5$) : C (75.72, 75.78), H (4.89, 4.85).

3-(4-chlorophenyl)-6-methyl-2-(4-nitrobenzoyl)-2,3-dihydro-4H-furo[3,2-c]pyran-4-one

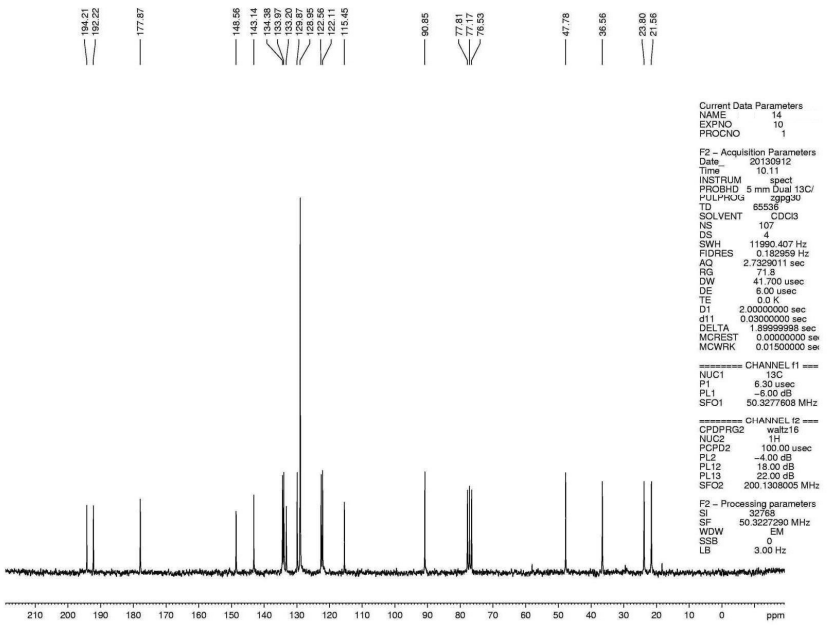
(13k): m.p:150-152°C; 78% (0.32 g) as yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.9 Hz, 1H), 7.00-7.08 (m, 3H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.16 (s, 1H), 5.94 (d, *J* = 4.4 Hz, 1H), 4.62 (d, *J* = 4.8 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 20.71, 39.36, 43.49, 92.03, 95.69, 102.26, 115.96, 123.16, 128.09, 128.29, 128.81, 129.25, 129.56, 132.76, 135.61, 139.14, 148.06, 162.79, 164.21, 171.18, 196.79; IR(KBr): 1684, 1707 cm^{-1}; MS (ESI+) *m/z:* 412.6 $[M+H]^+$; analysis (calcd., found for $C_{21}H_{14}ClNO_6$): C (61.25, 61.23), H (3.43, 3.45).

2-(1-butyl-3-methylimidazolidin-2-ylidene)-1-phenylethan-1-one(4): obtained as viscous pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.42-8.46 (m, 3H), 8.25-8.27 (m, 2H), 5.23 (s, 1H), 3.58-3.62 (m, 2H), 3.39-3.43 (m, 2H), 3.09 (t, *J* = 7.47 Hz, 2H), 2.87 (s, 3H), 1.76-1.83 (m, 2H), 1.26-1.36 (m, 2H), 0.90 (t, *J* = 7.36 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.08, 19.10, 31.62, 35.90, 45.26, 46.96, 49.24, 75.23, 127.35, 129.61, 137.85, 145.65, 167.03, 183.45; IR(KBr): 2918, 2858, 1603, 1545 cm^{-1}; MS (ESI+) *m/z:* 258.1 [M].

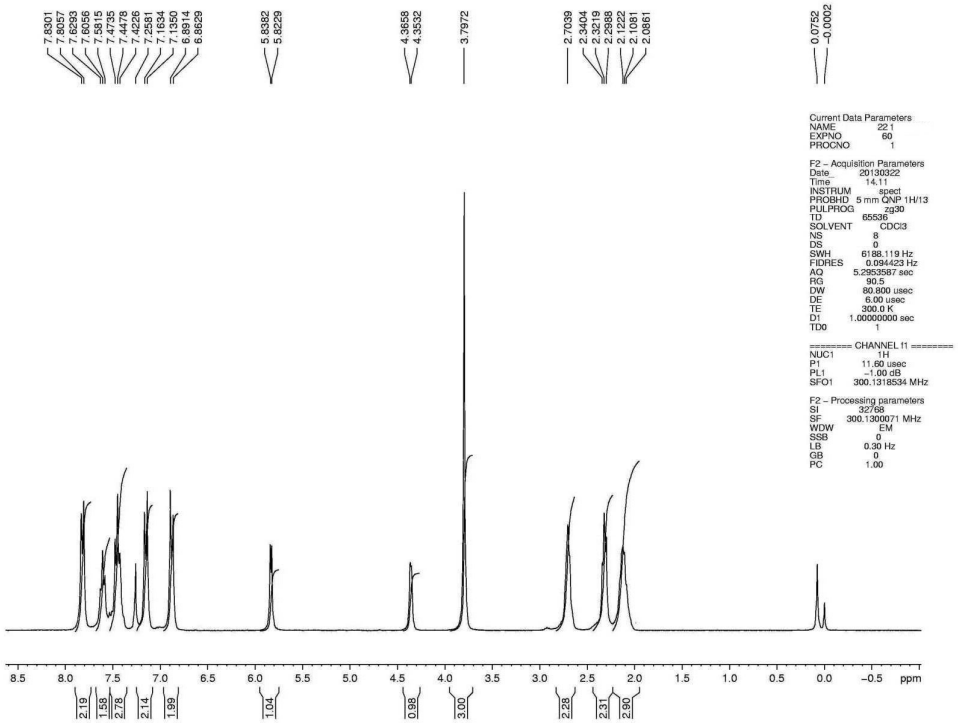
6. Spectral charts of all synthesized compounds(9a-q, 11a-h, 13a-k,4)



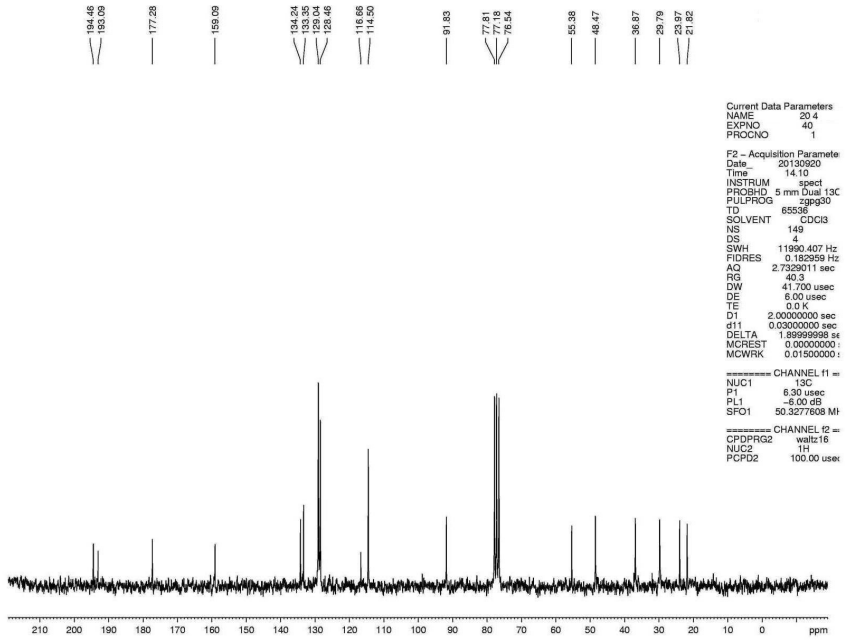
^{1}H spectra of 2-benzoyl-3-(3-nitrophenyl)-2, 3, 6,7-tetrahydrobenzofuran-4(5H)-one (9a)



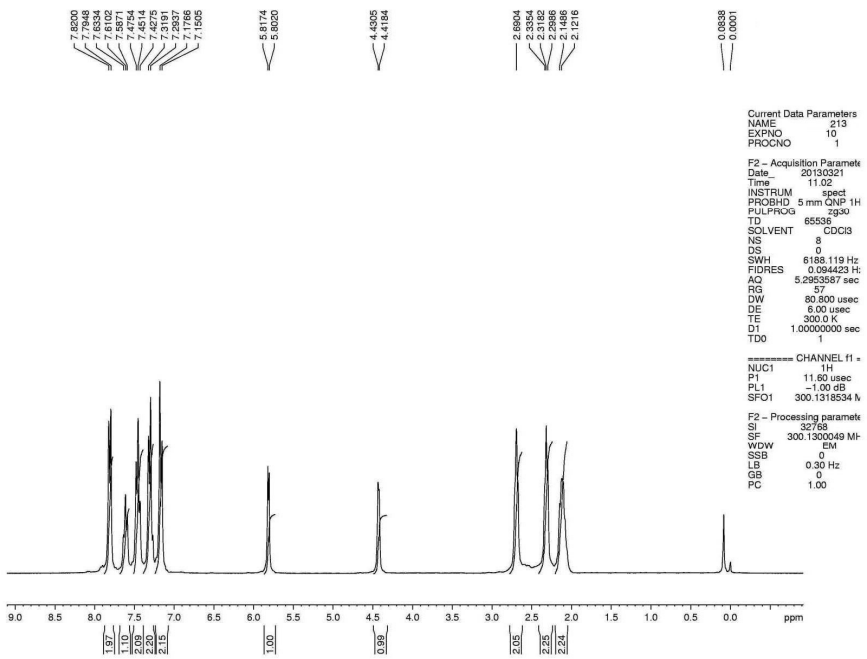
^{13}C spectra of 2-benzoyl-3-(3-nitrophenyl)-2, 3, 6,7-tetrahydrobenzofuran-4(5H)-one (9a)



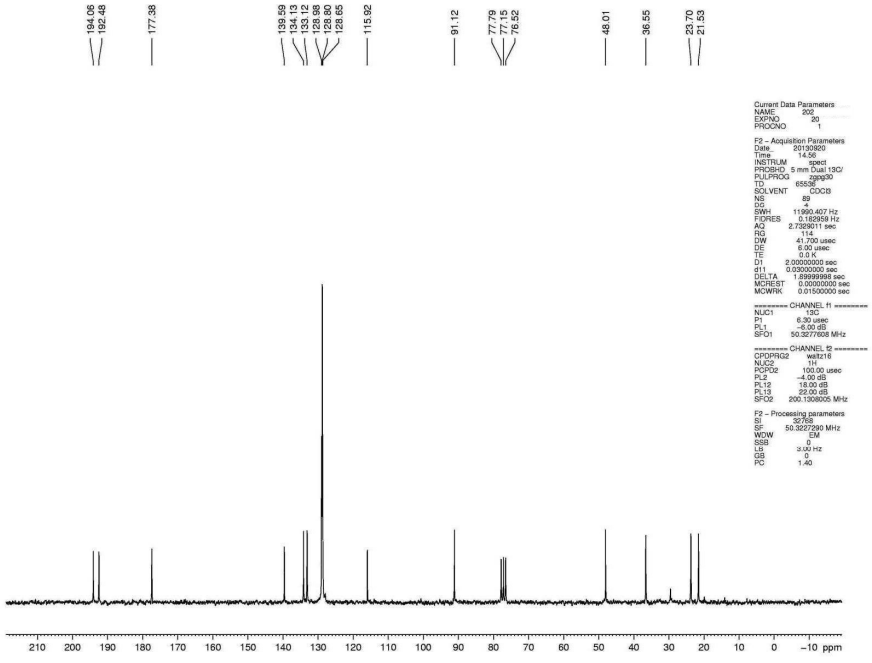
[1]H spectra of 2-benzoyl-3-(4-methoxyphenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9b)



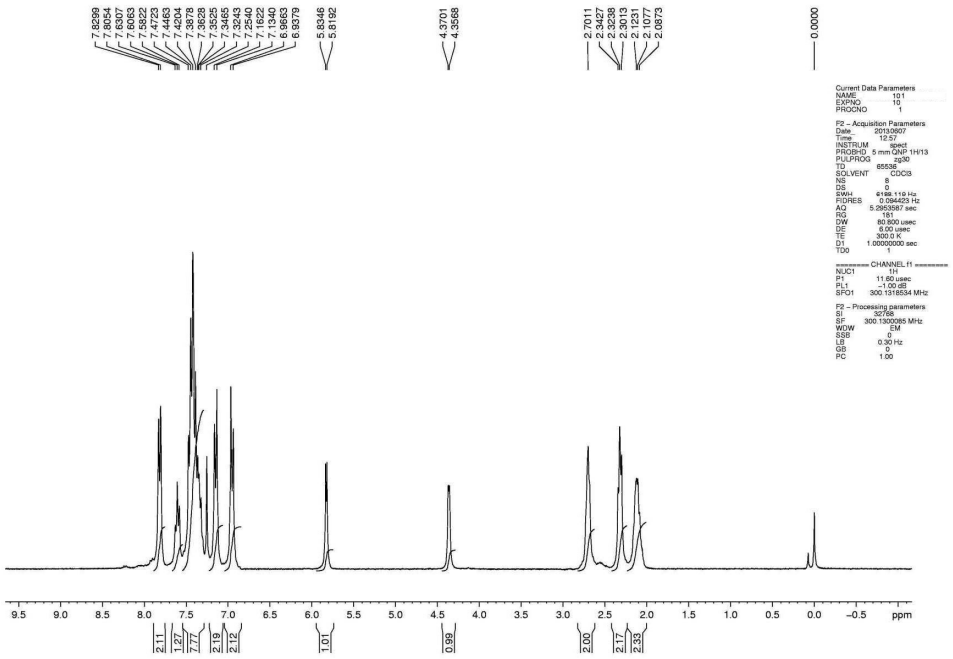
[13] C spectra of 2-benzoyl-3-(4-methoxyphenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9b)



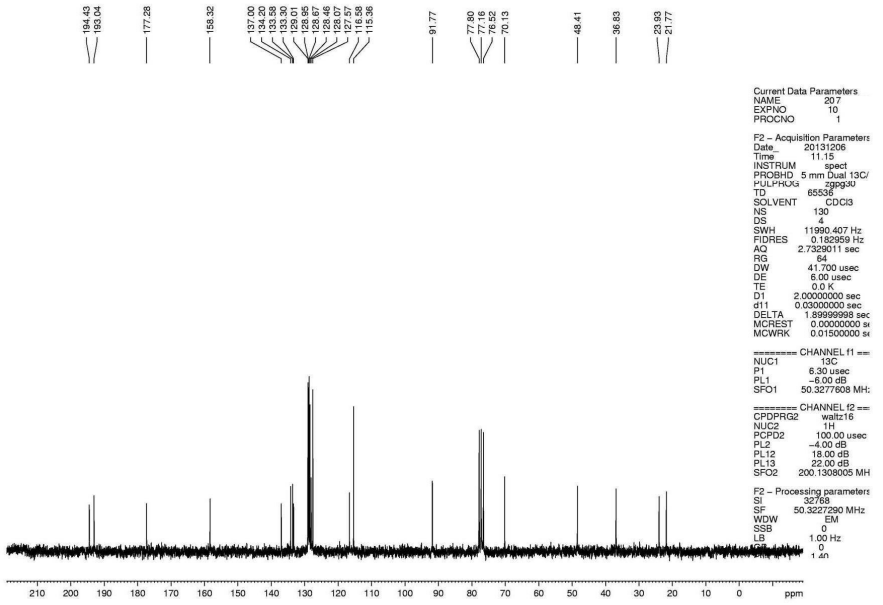
^{1}H spectra of 2-benzoyl-3-(4-chlorophenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9c)



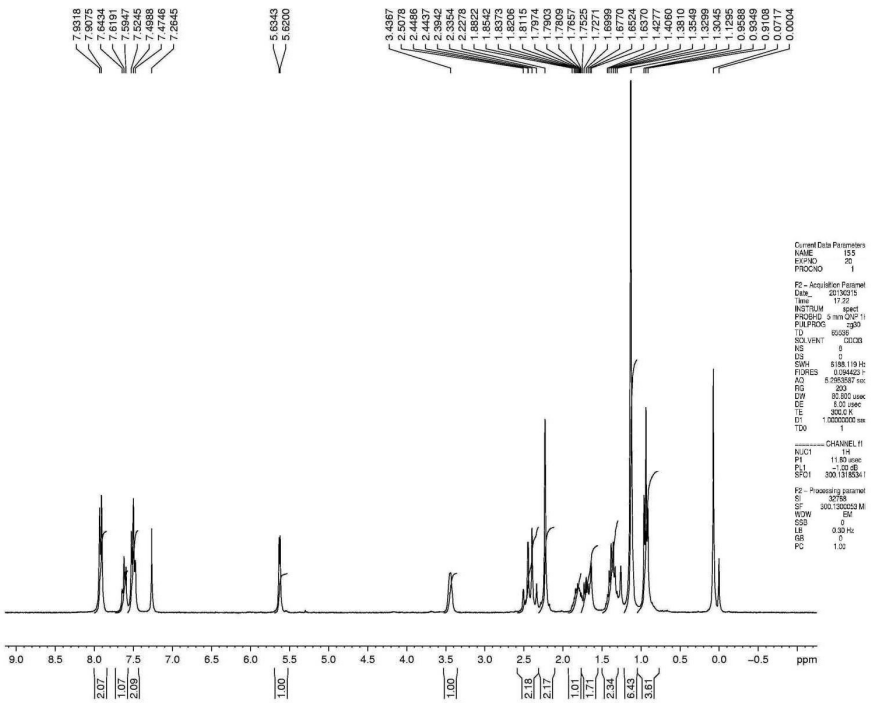
^{13}C spectra of 2-benzoyl-3-(4-chlorophenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9c)



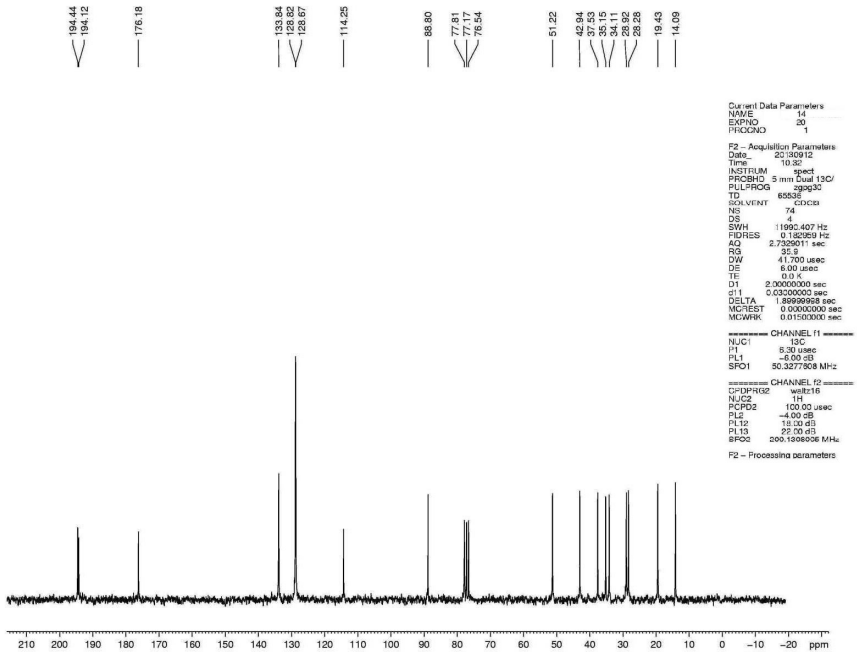
^{1}H spectra of 2-benzoyl-3-(biphenyl-4-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)- one (9d)



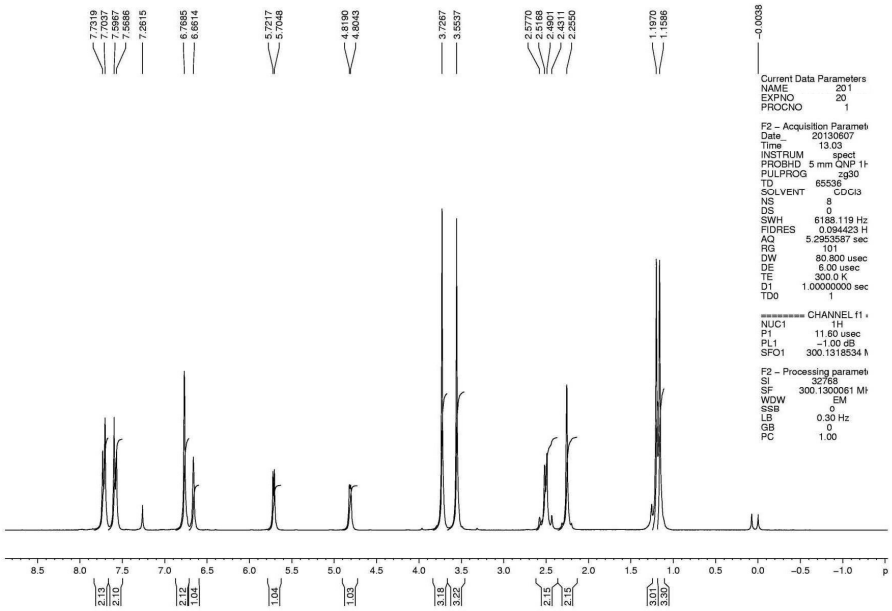
^{13}C spectra of 2-benzoyl-3-(biphenyl-4-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)- one (9d)



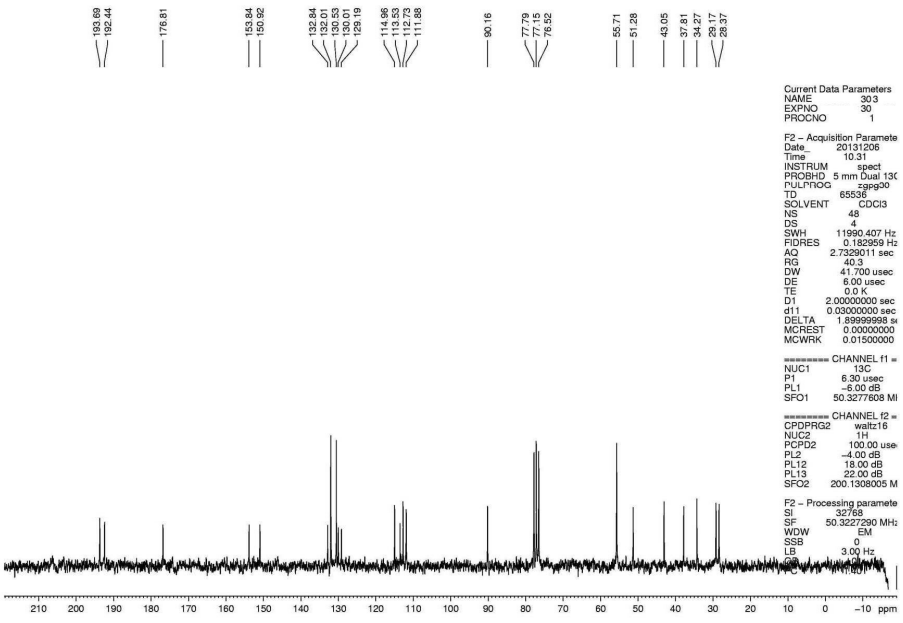
^{1}H spectra of 2-benzoyl-6,6-dimethyl-3-propyl-2,3,6,7-tetrahydrobenzofuran- 4(5H)-one (9e)



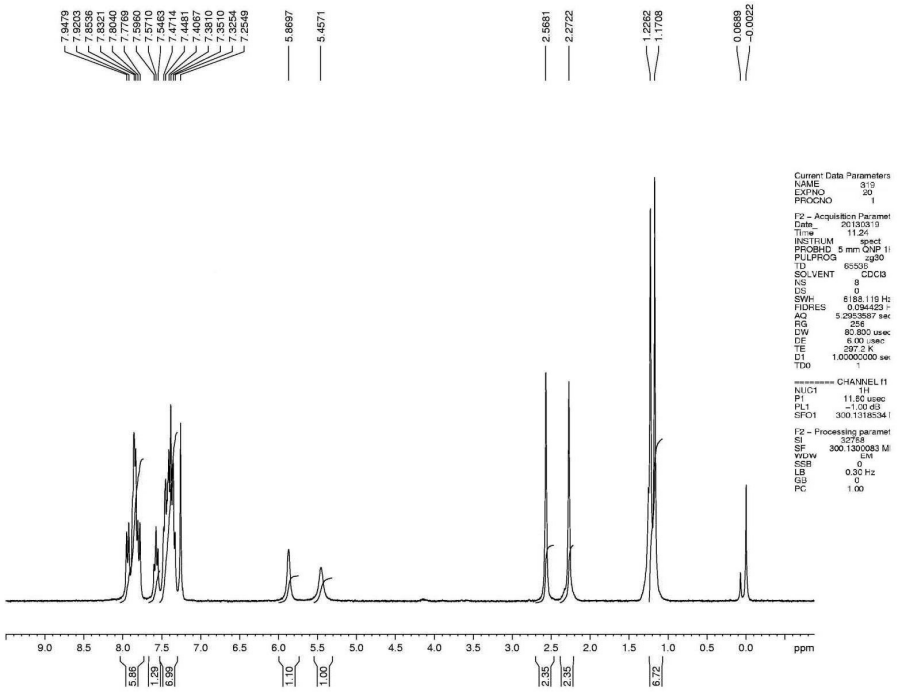
^{13}C spectra of 2-benzoyl-6,6-dimethyl-3-propyl-2,3,6,7-tetrahydrobenzofuran- 4(5H)-one (9e)



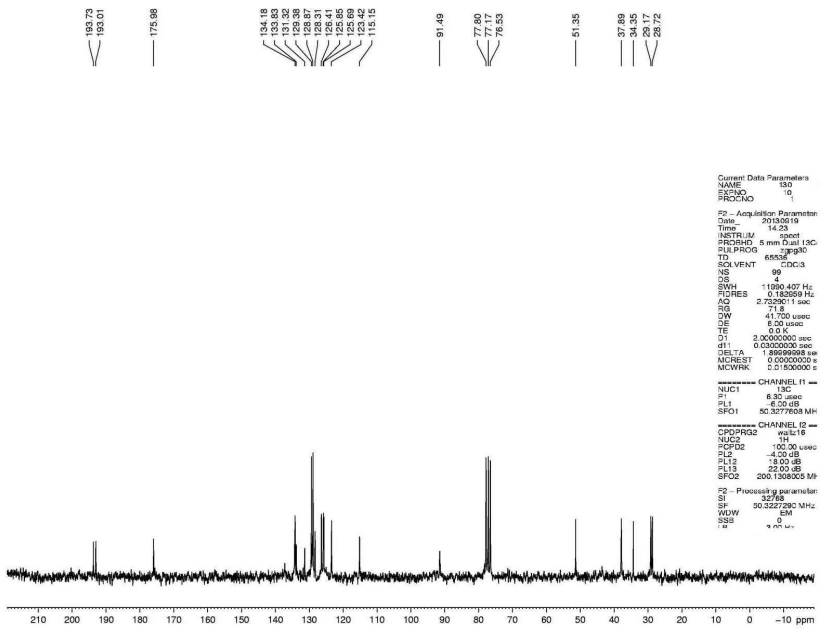
^{1}H spectra of 2-(4-bromobenzoyl)-3-(2, 5-dimethoxyphenyl)-6, 6-dimethyl- 2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9f)



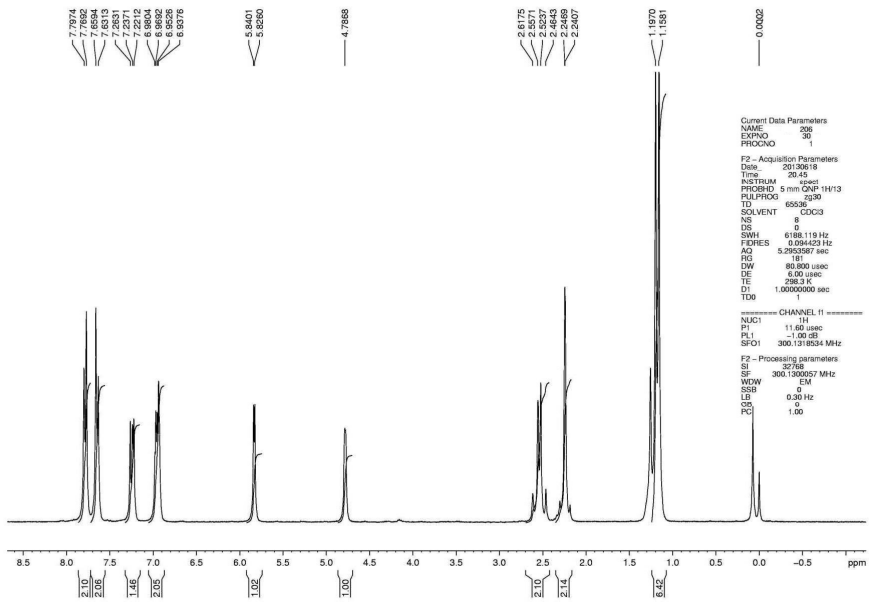
^{13}C spectra of 2-(4-bromobenzoyl)-3-(2, 5-dimethoxyphenyl)-6, 6-dimethyl- 2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9f)



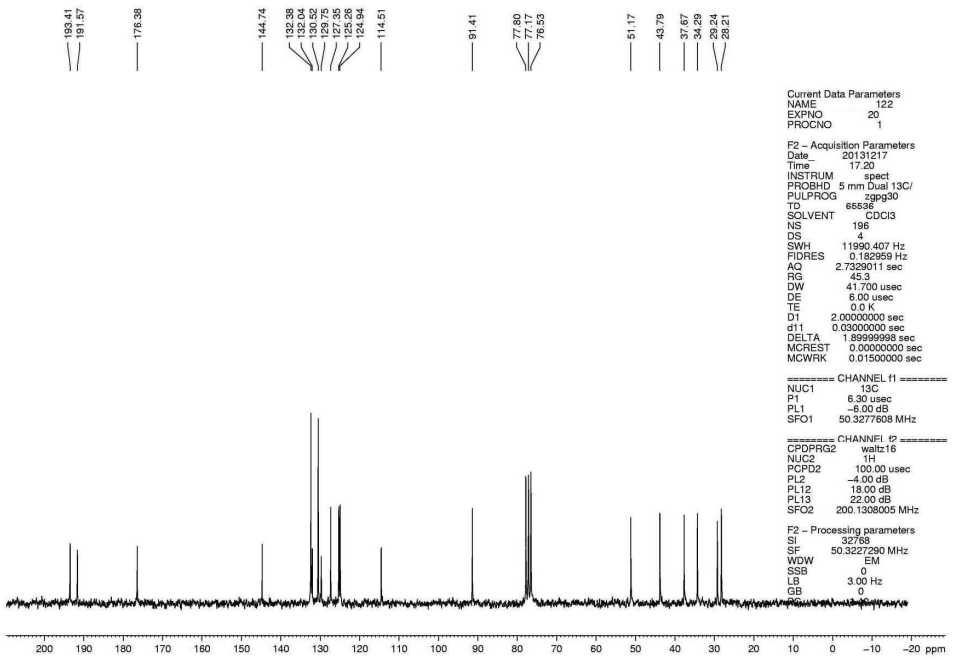
^{1}H spectra of 2-benzoyl-6,6-dimethyl-3-(naphthalen-2-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9g)



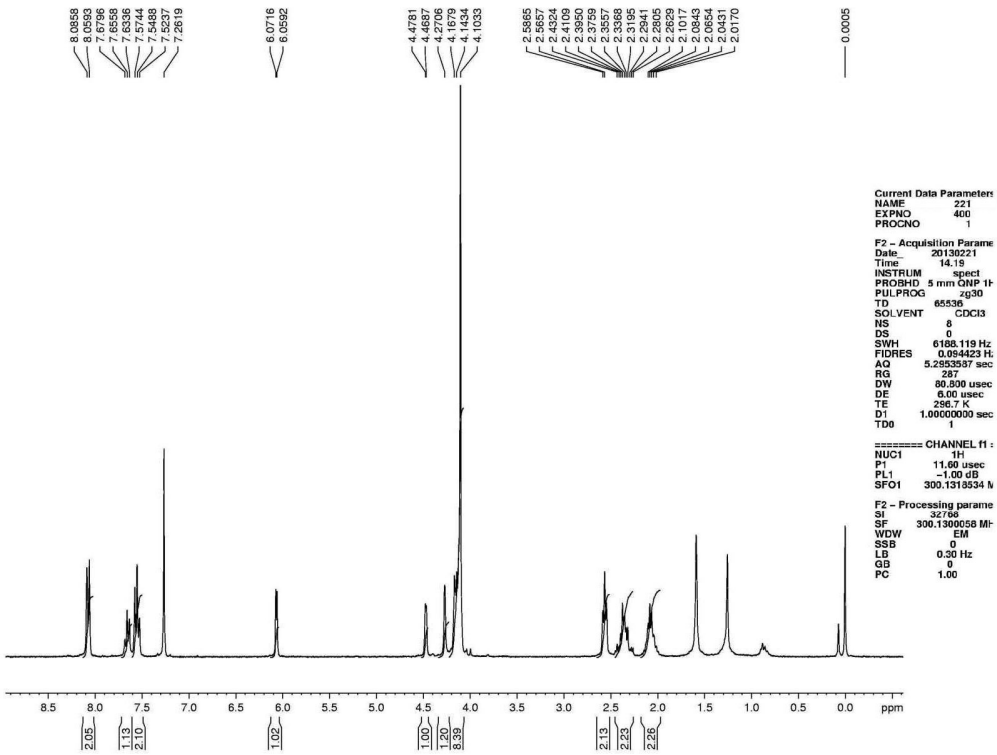
^{13}C spectra of 2-benzoyl-6,6-dimethyl-3-(naphthalen-2-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9g)



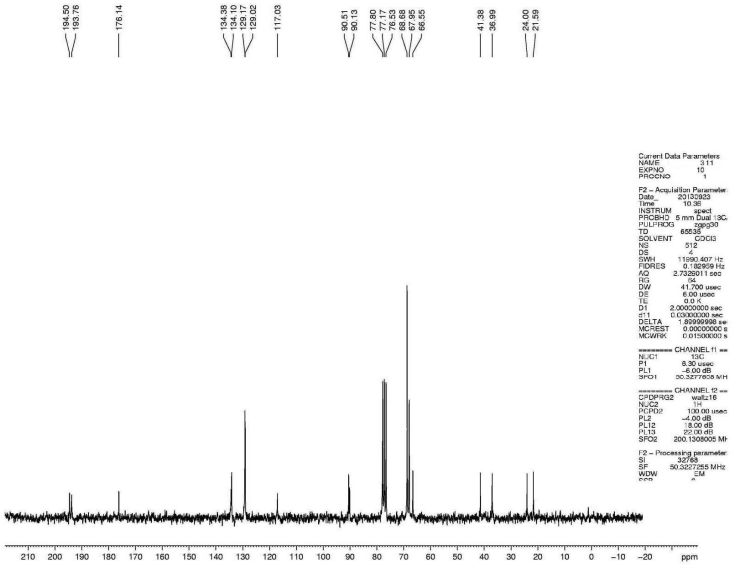
^{1}H spectra of 2-(4-bromobenzoyl)-6,6-dimethyl-3-(thiophen-2-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one(9h)



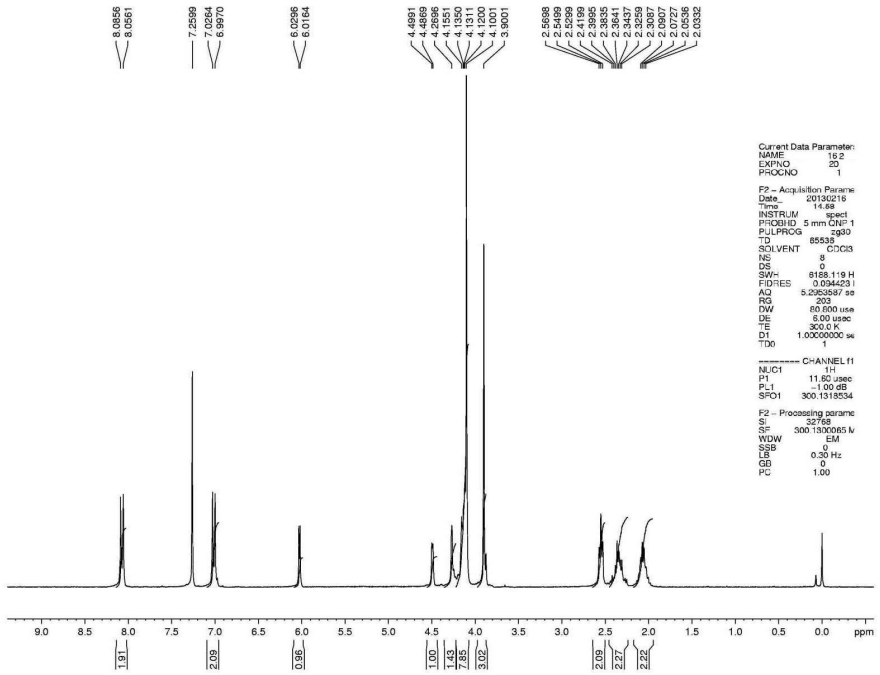
^{13}C spectra of 2-(4-bromobenzoyl)-6,6-dimethyl-3-(thiophen-2-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one(9h)



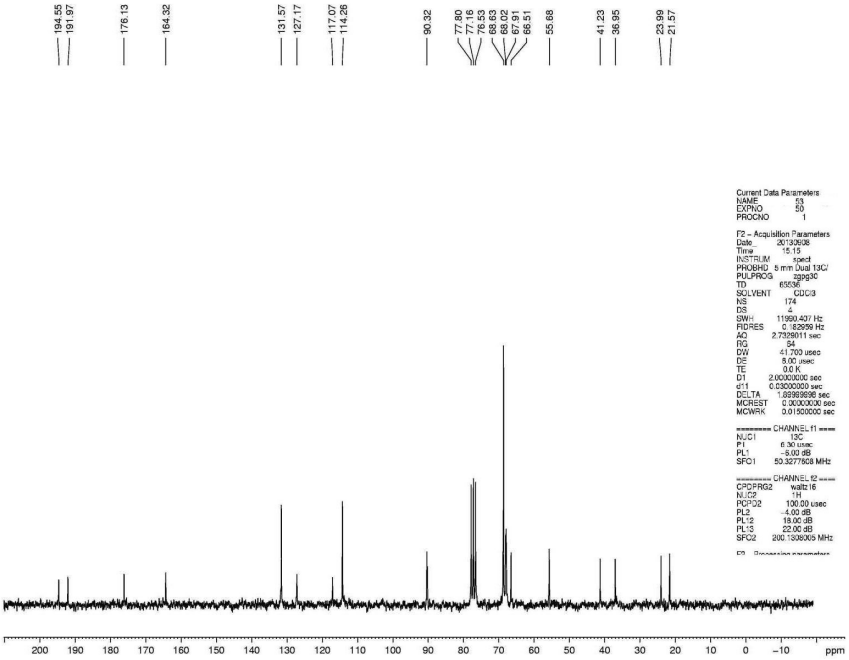
[1]H spectra of 2-benzoyl-3- ferrocenyl -2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9i)



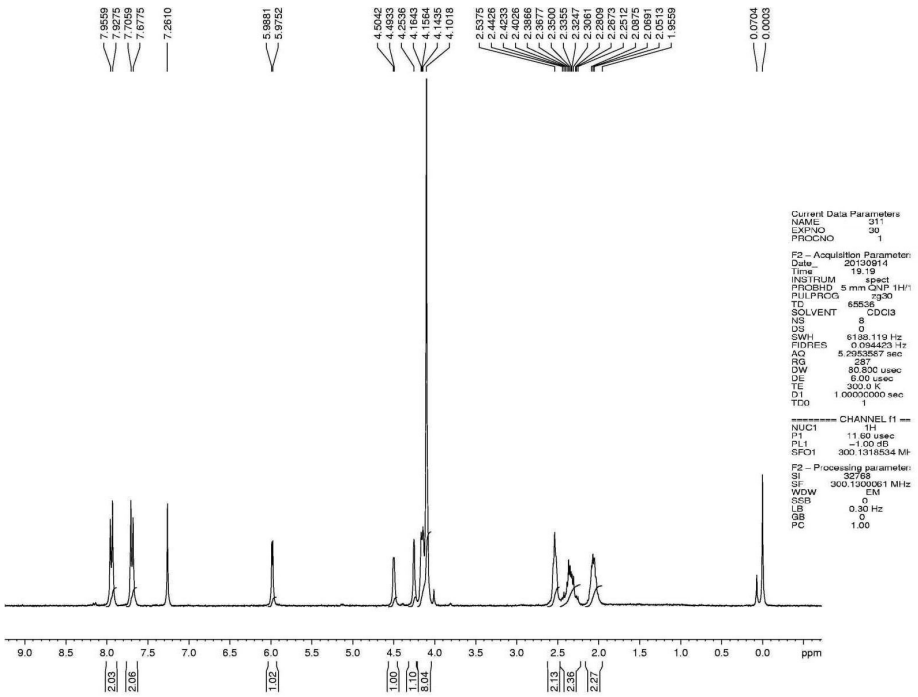
13^{C} spectra of 2-benzoyl-3- ferrocenyl -2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9i)



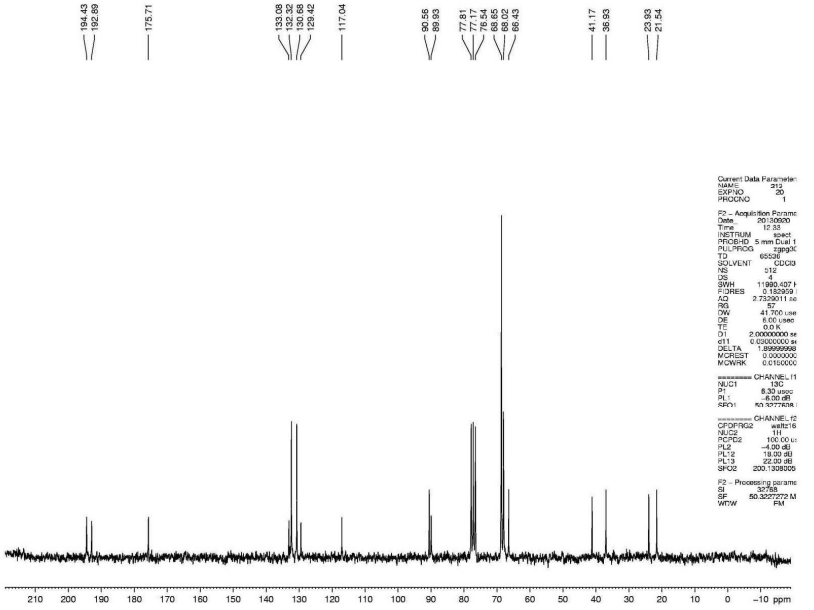
[1]H spectra of 3- ferrocenyl, 2-(4-methoxybenzoyl)-2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9j)



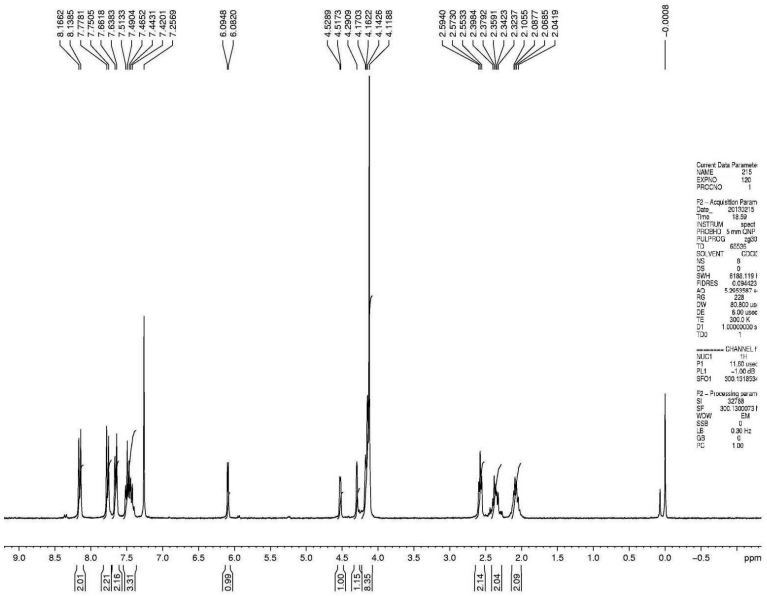
[13]C spectra of 3- ferrocenyl, 2-(4-methoxybenzoyl)-2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9j)



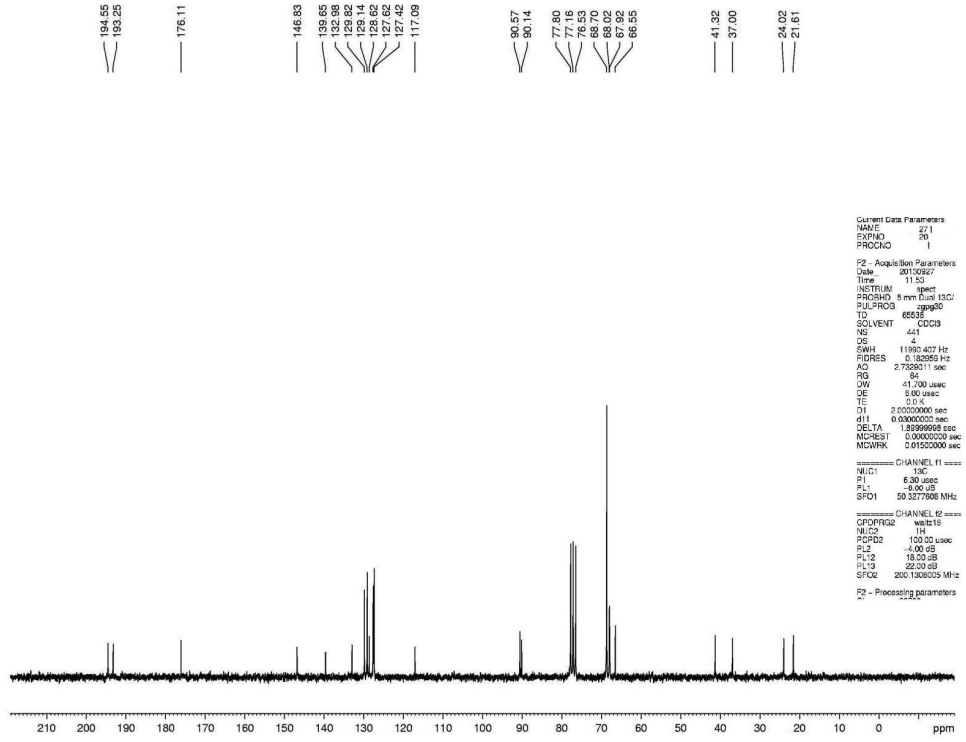
^{1}H spectra of 2-(4-bromobenzoyl)-3- ferrocenyl-2, 3, 6, 7-tetrahydrobenzofuran4(5H)-one (9k)



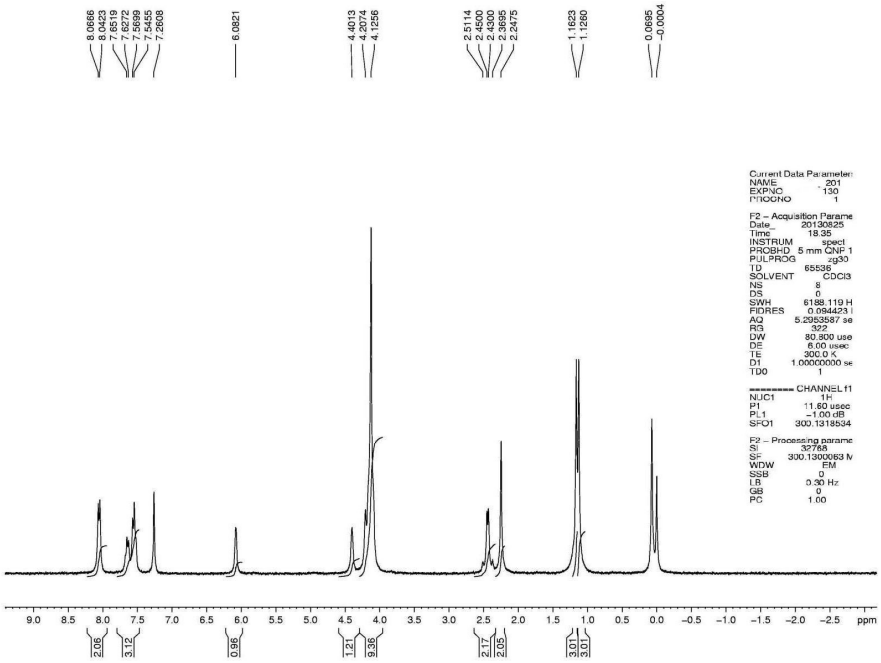
^{13}C spectra of 2-(4-bromobenzoyl)-3- ferrocenyl-2, 3, 6, 7-tetrahydrobenzofuran4(5H)-one (9k)



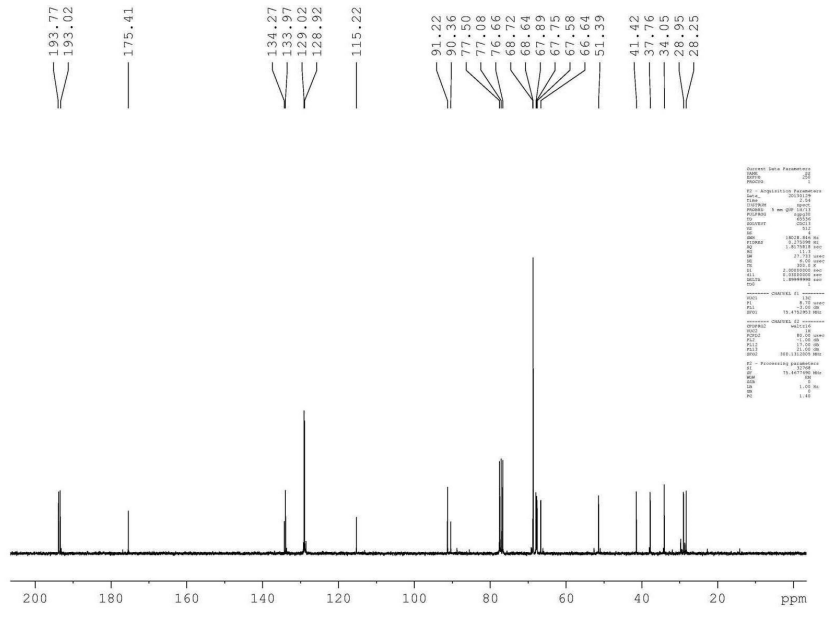
^{1}H spectra 2-(biphenylcarbonyl)-3-ferrocenyl-2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9l)



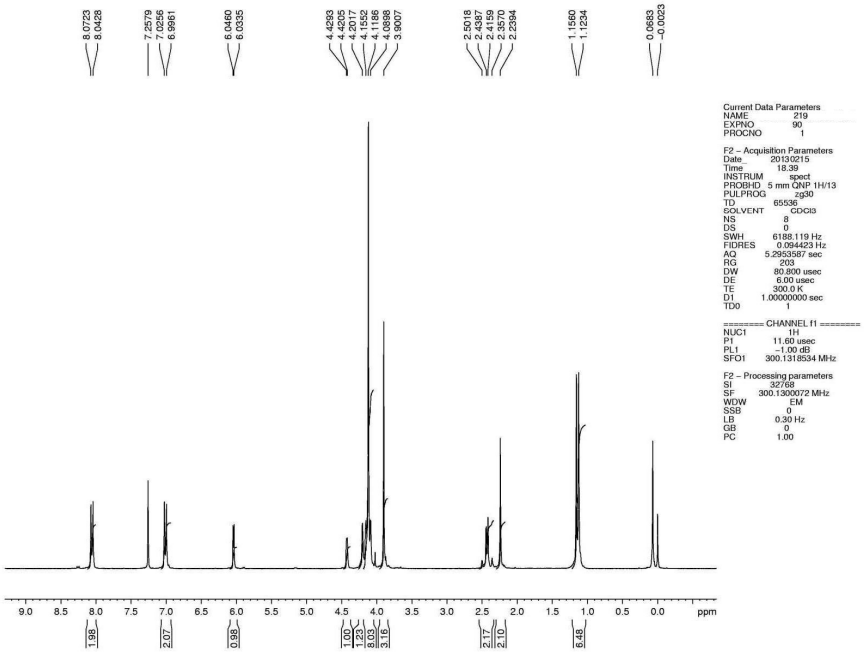
^{13}C spectra 2-(biphenylcarbonyl)-3-ferrocenyl-2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9l)



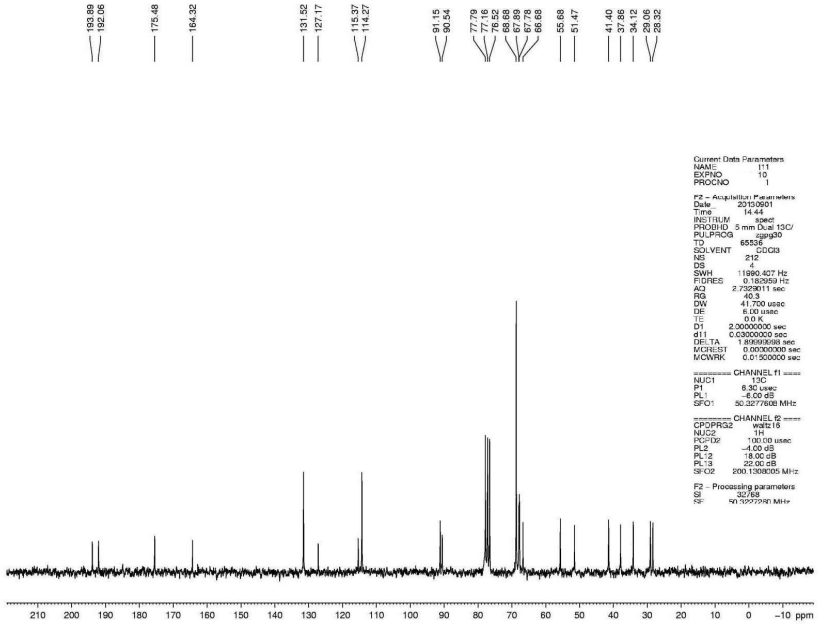
^{1}H spectra of 2-benzoyl-6,6-dimethyl-3-ferrocenyl-2,3,6,7-tetrahydrobenzofuran4(5H)-one (9m):



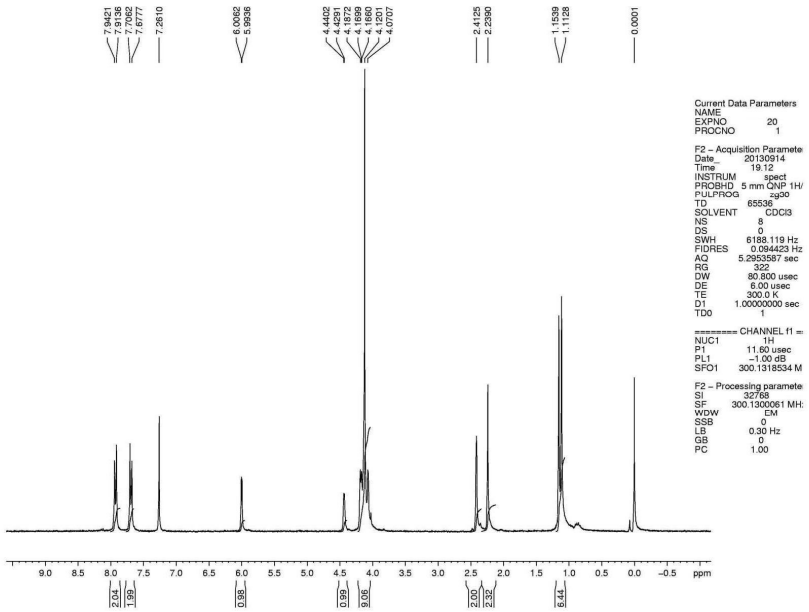
^{13}C spectra of 2-benzoyl-6,6-dimethyl-3-ferrocenyl-2,3,6,7-tetrahydrobenzofuran4(5H)-one (9m):



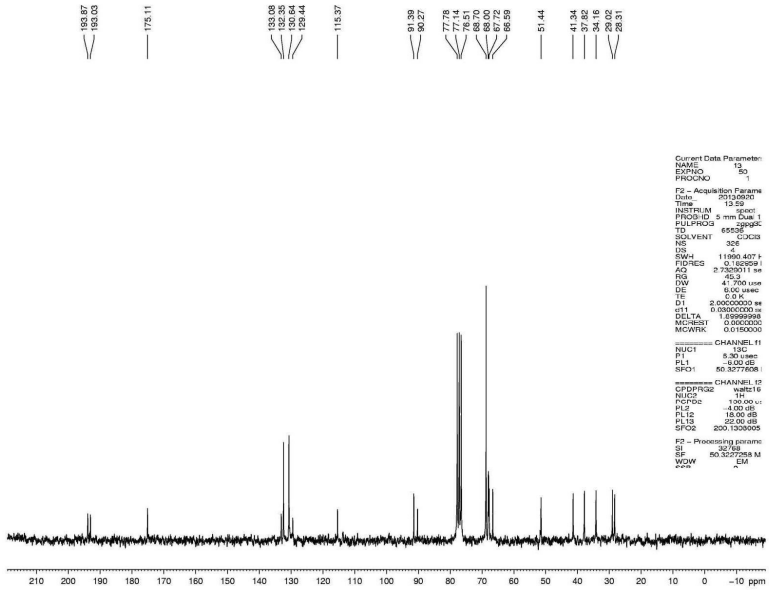
^{1}H spectra of 6, 6-dimethyl-3-ferrocenyl-2-(4-methoxybenzoyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9n)



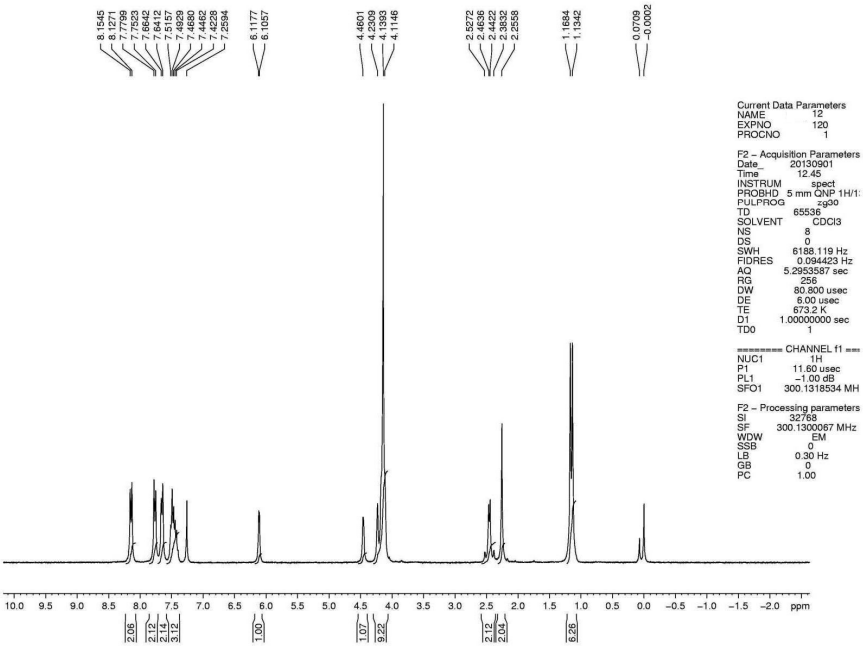
^{13}C spectra of 6, 6-dimethyl-3-ferrocenyl-2-(4-methoxybenzoyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (9n)



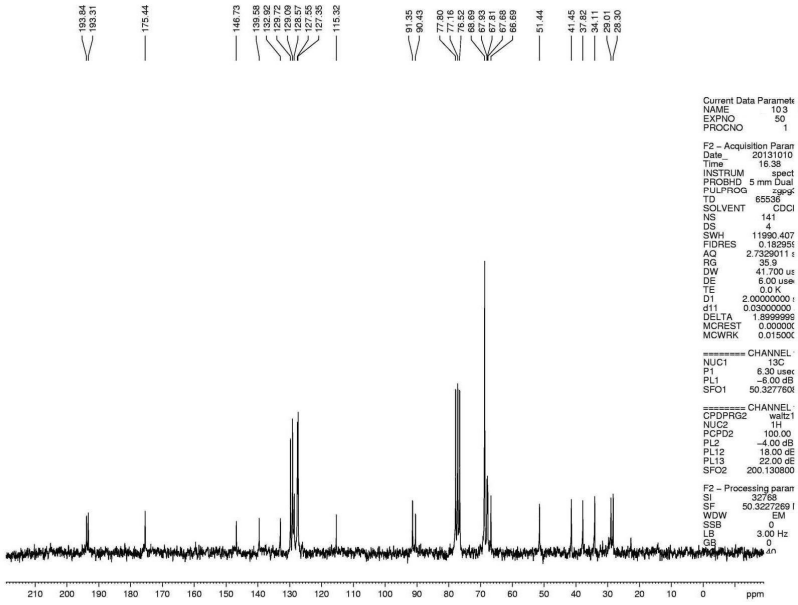
^{1}H spectra of 2-(4-bromobenzoyl)-6, 6-dimethyl-3-ferrocenyl-2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9o)



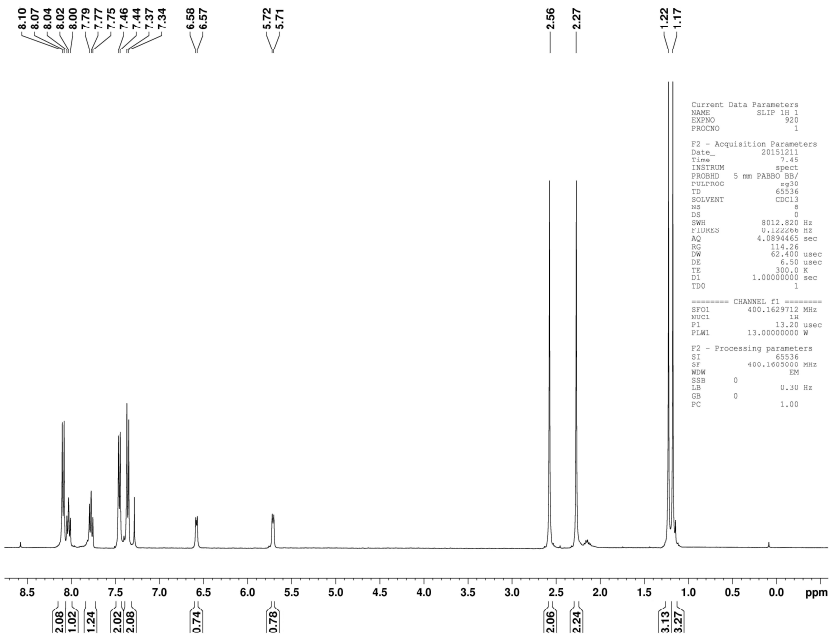
^{13}C spectra of 2-(4-bromobenzoyl)-6, 6-dimethyl-3-ferrocenyl-2, 3, 6, 7-tetrahydrobenzofuran-4(5H)-one (9o)



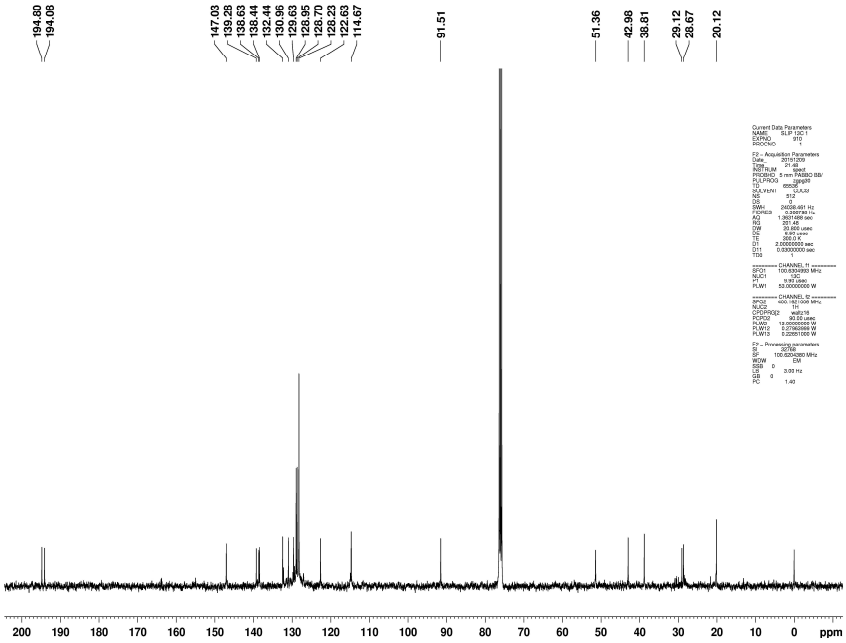
^{1}H spectra of 2-(biphenylcarbonyl)-6,6-dimethyl-3-ferrocenyl-2,3,6,7- tetrahydrobenzofuran-4(5H)-one (9p)



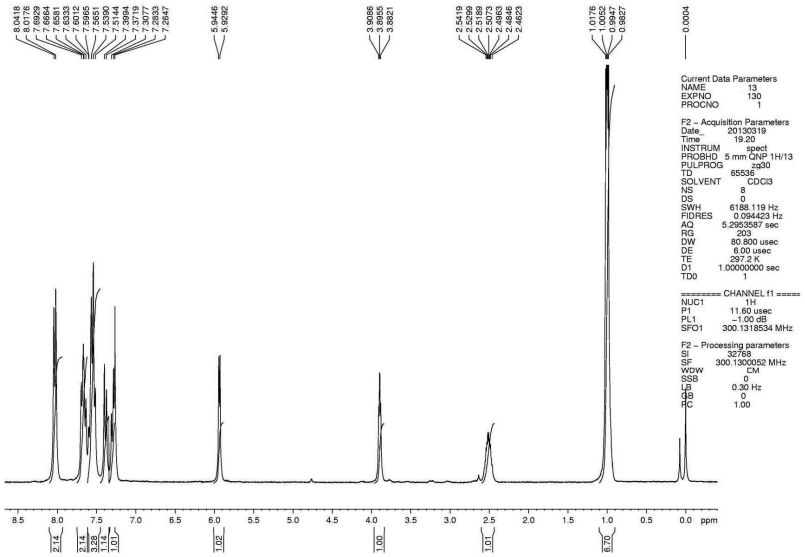
^{13}C spectra of 2-(biphenylcarbonyl)-6,6-dimethyl-3-ferrocenyl-2,3,6,7- tetrahydrobenzofuran-4(5H)-one (9p)



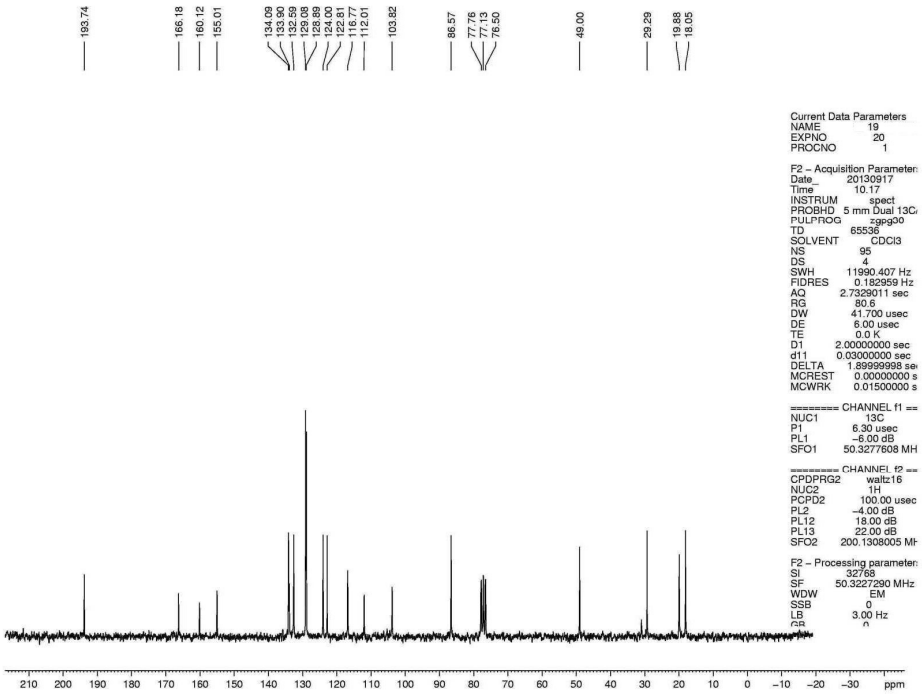
^{1}H spectra of 3-(4-chlorophenyl)-6,6-dimethyl-2-(4-nitrobenzoyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (9q)



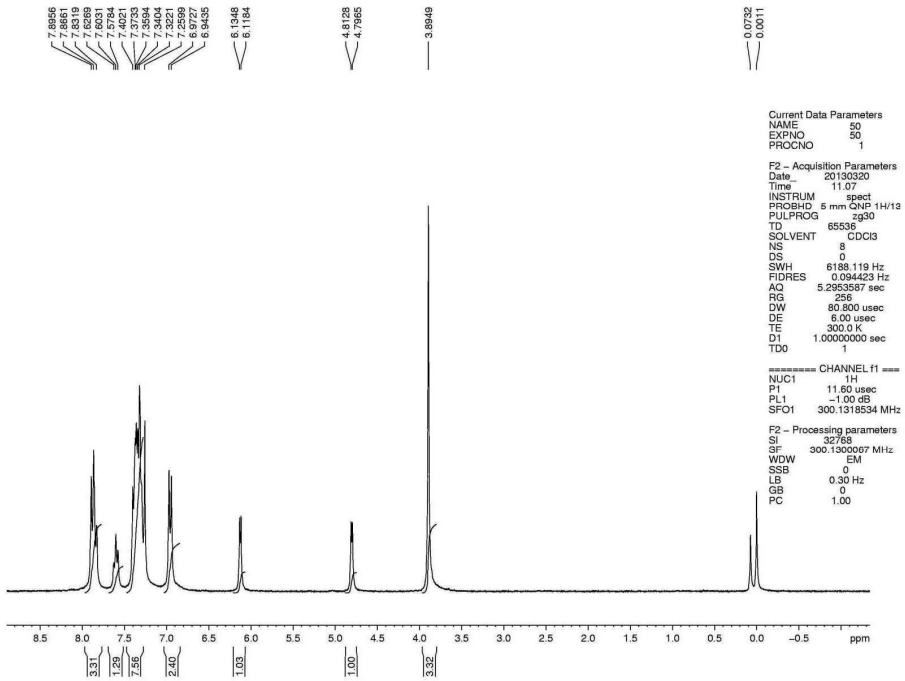
^{13}C spectra of 3-(4-chlorophenyl)-6,6-dimethyl-2-(4-nitrobenzoyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (9q)



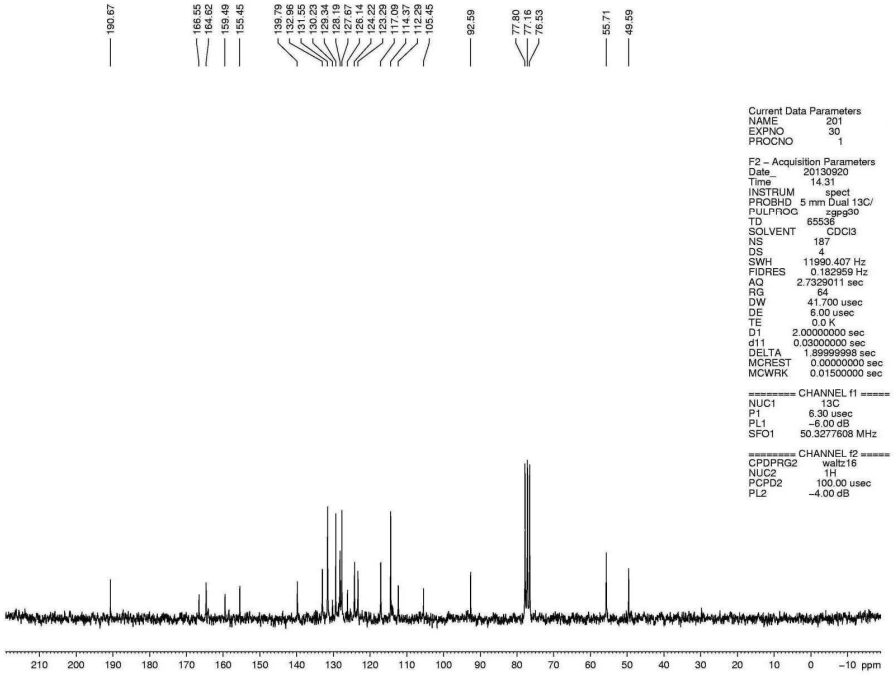
^{1}H spectra of 2-benzoyl-3-isopropyl-2H-furo[3,2-c]chromen-4(3H)-one (11a):



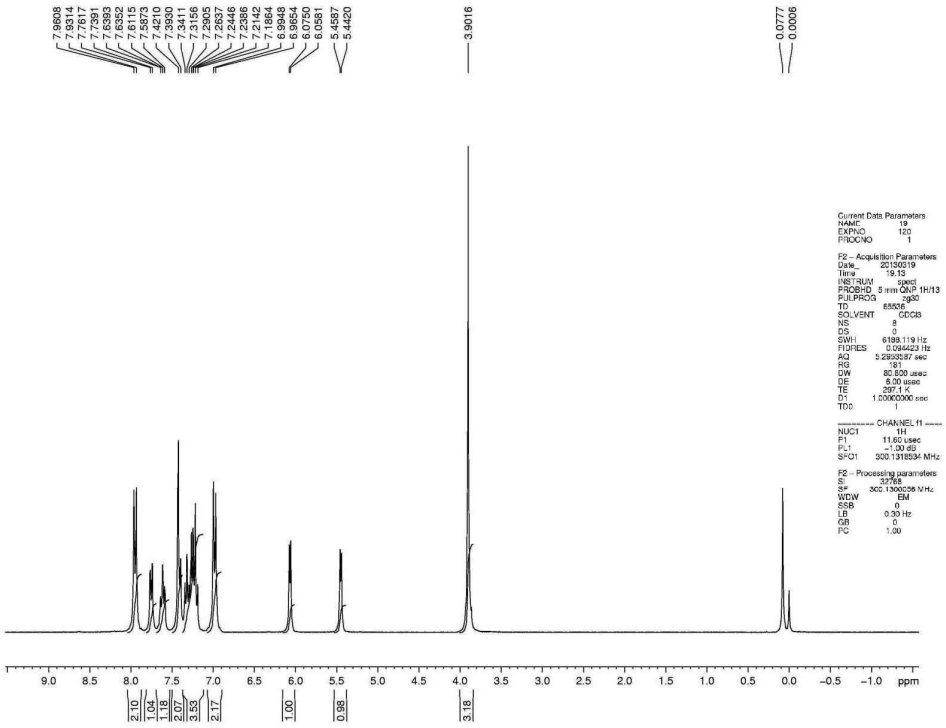
^{13}C spectra of 2-benzoyl-3-isopropyl-2H-furo[3,2-c]chromen-4(3H)-one (11a):



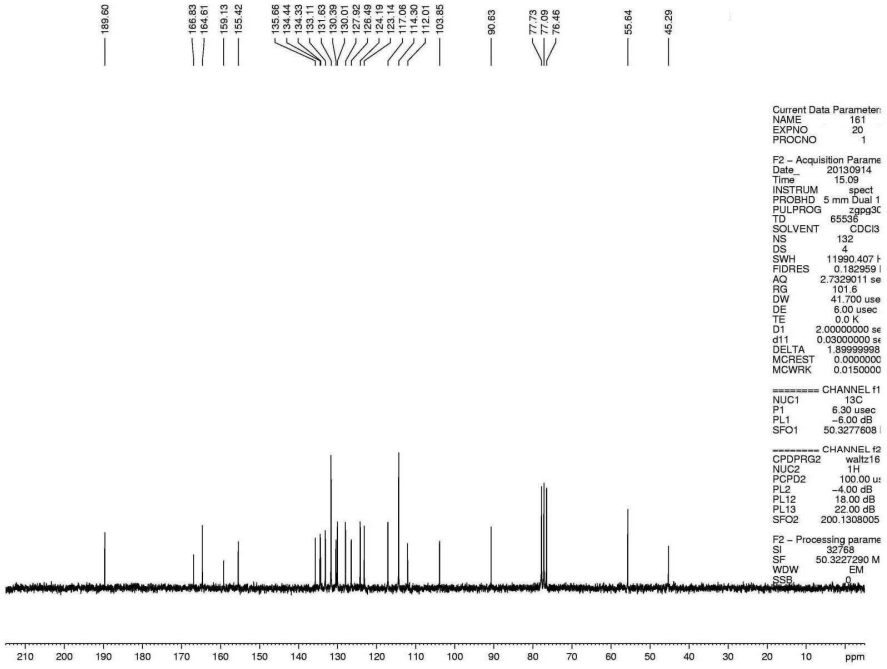
[1]H spectra of 2-(4-methoxybenzoyl)-3-phenyl-2H-furo[3,2-c]chromen-4(3H)-one (11b)



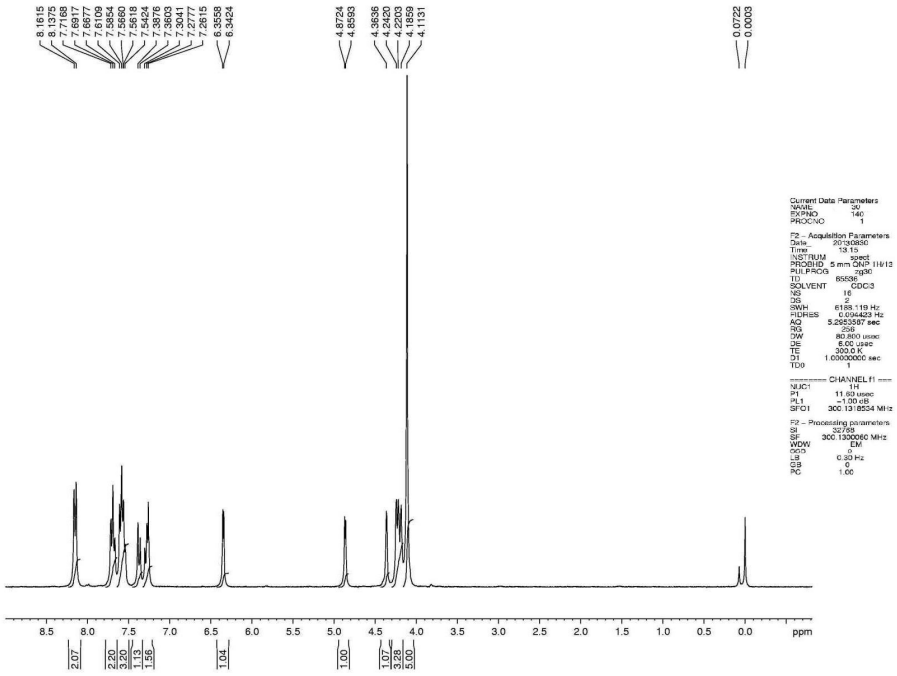
13C spectra of 2-(4-methoxybenzoyl)-3-phenyl-2H-furo[3,2-c]chromen-4(3H)-one (11b)



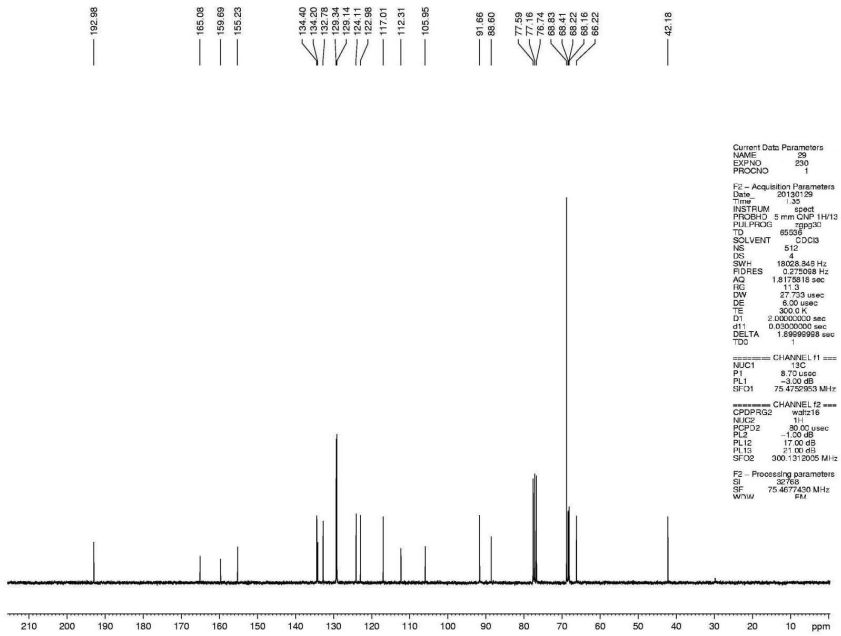
[1]H spectra of 3-(2,4-dichlorophenyl)-2-(4-methoxybenzoyl)-2H-furo[3,2- c]chromen-4(3H)-one (11c)



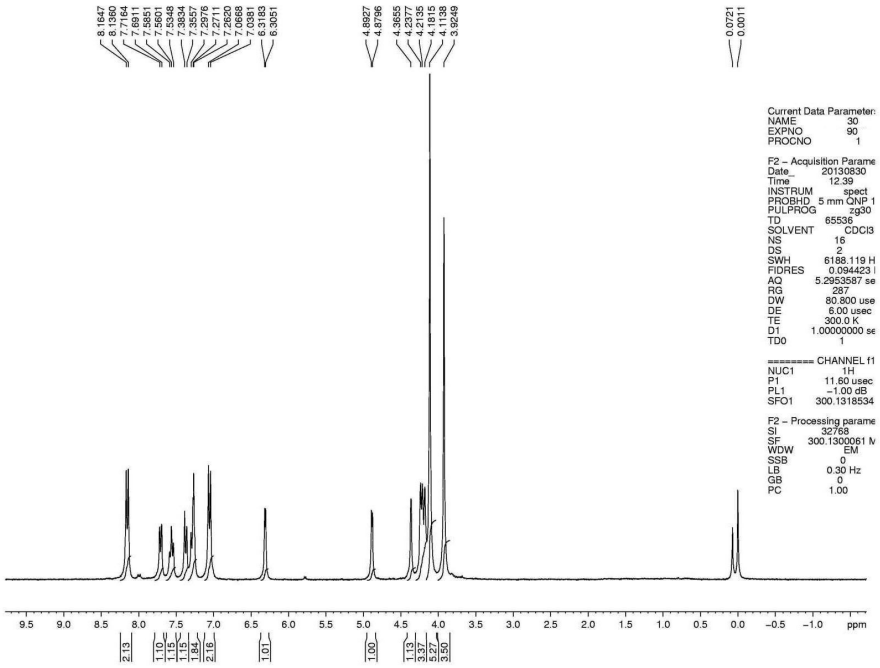
[13]C spectra of 3-(2,4-dichlorophenyl)-2-(4-methoxybenzoyl)-2H-furo[3,2- c]chromen-4(3H)-one (11c)



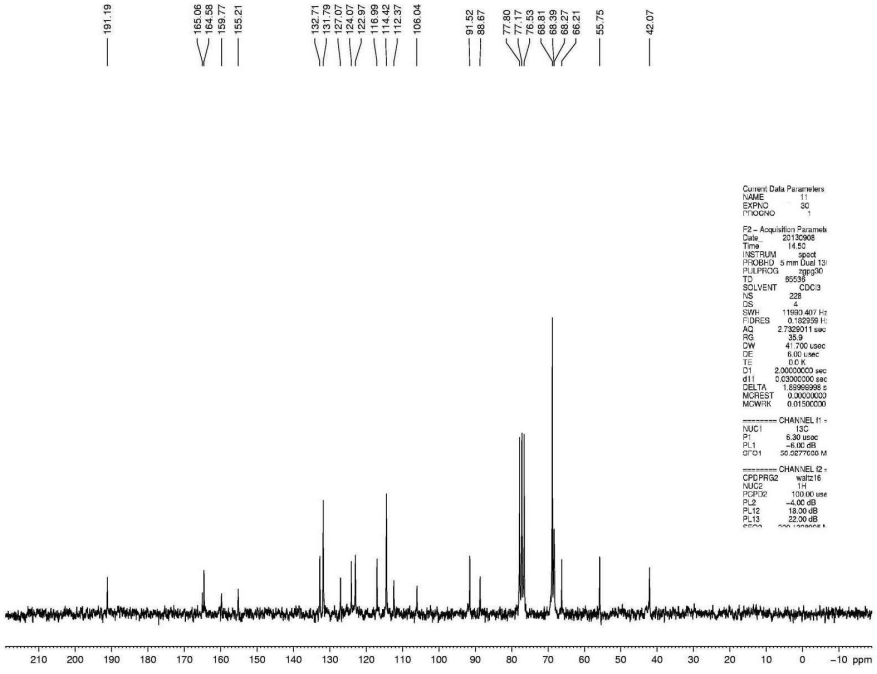
[1]H spectra of 2-benzoyl-3-ferrocenyl-2H-furo[3,2-c]chromen-4(3H)-one (11d)



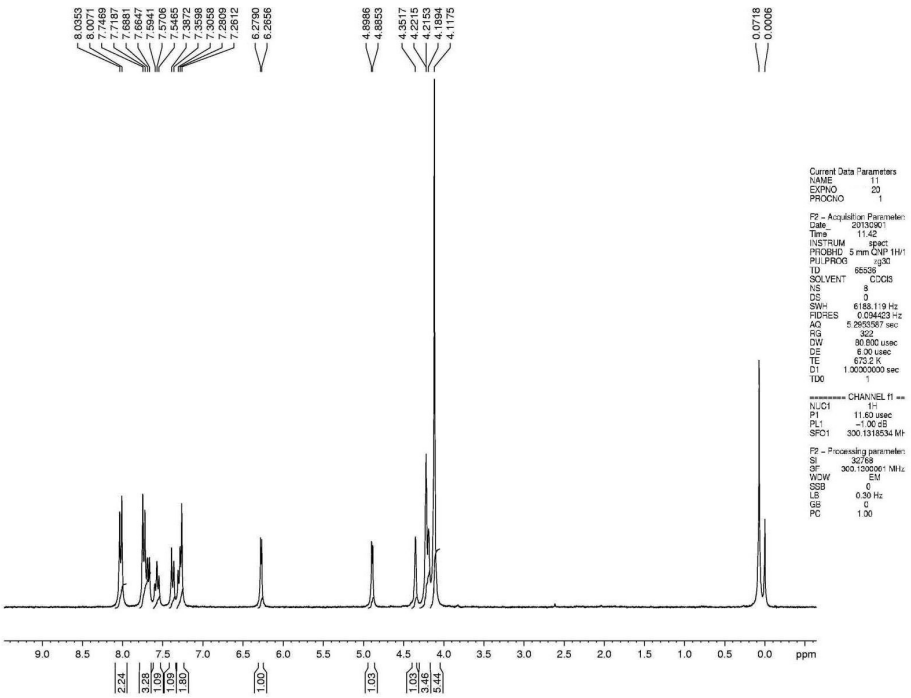
[13]C spectra of 2-benzoyl-3-ferrocenyl-2H-furo[3,2-c]chromen-4(3H)-one (11d)



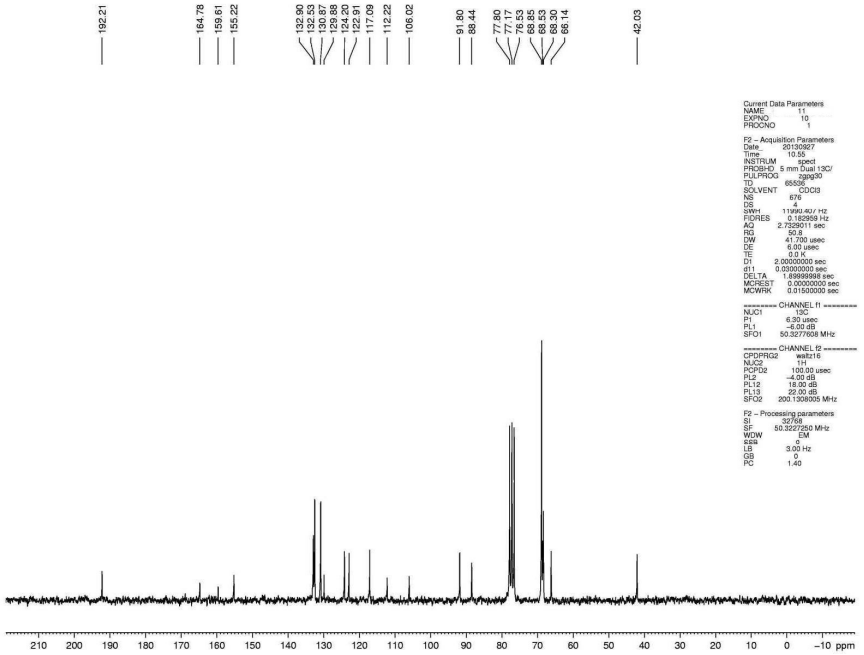
^{1}H spectra of 3- ferrocenyl-2-(4-methoxybenzoyl)-2H-furo[3,2-c]chromen-4(3H)- one (11e)



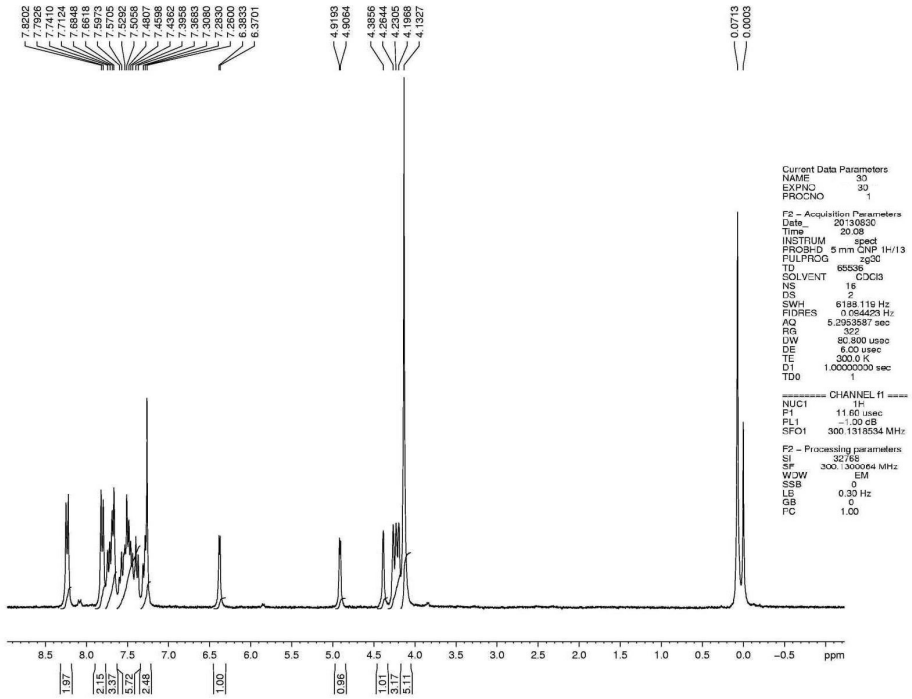
^{13}C spectra of 3- ferrocenyl-2-(4-methoxybenzoyl)-2H-furo[3,2-c]chromen-4(3H)- one (11e)



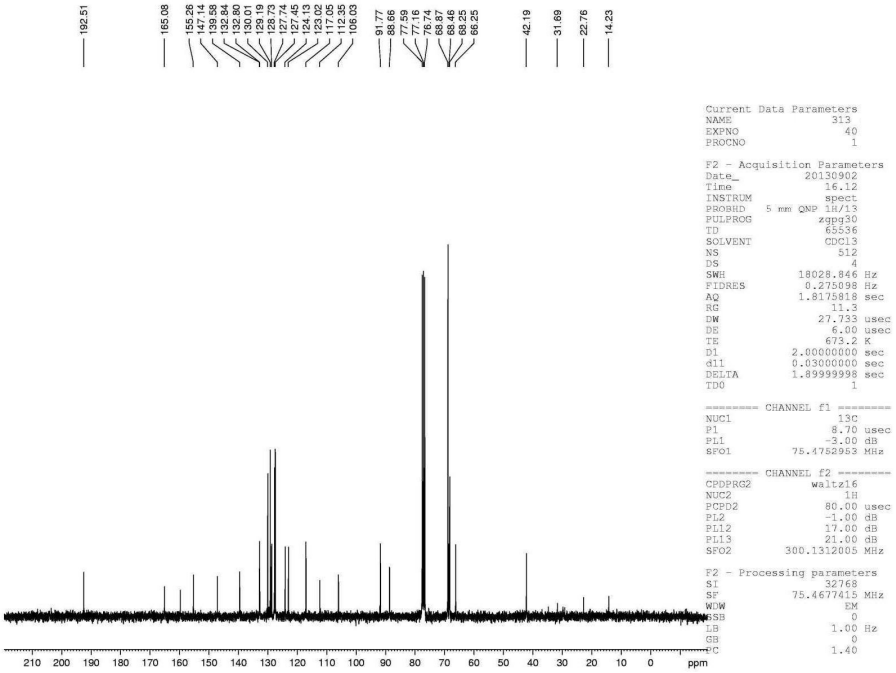
[1]H spectra of 2-(4-bromobenzoyl)-3- ferrocenyl-2H-furo[3,2-c]chromen-4(3H)- one(11f)



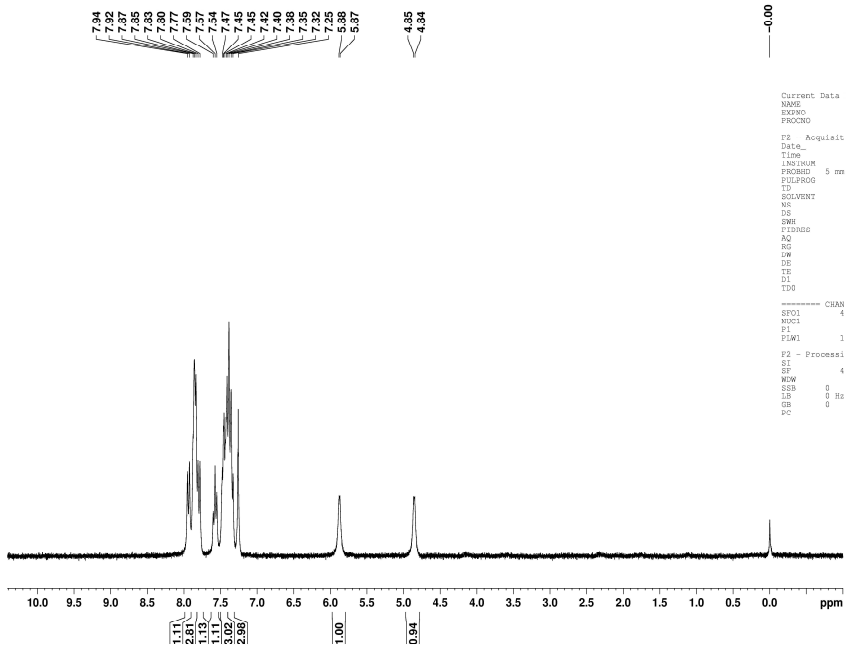
[13] C spectra of 2-(4-bromobenzoyl)-3- ferrocenyl-2H-furo[3,2-c]chromen-4(3H)- one(11f)



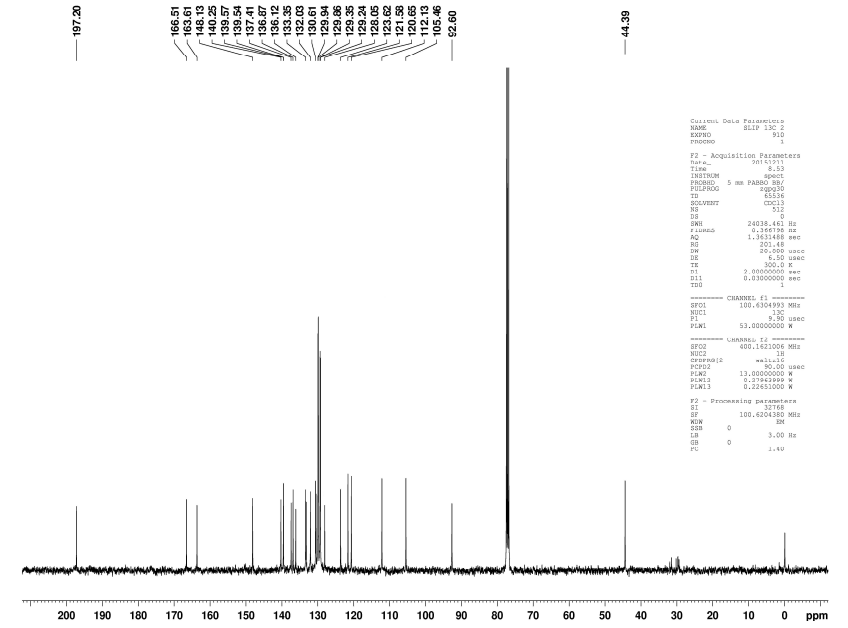
^{1}H spectra of 2-(biphenylcarbonyl)-3-ferrocenyl-2H-furo[3,2-c]chromen-4(3H)-one (11g)



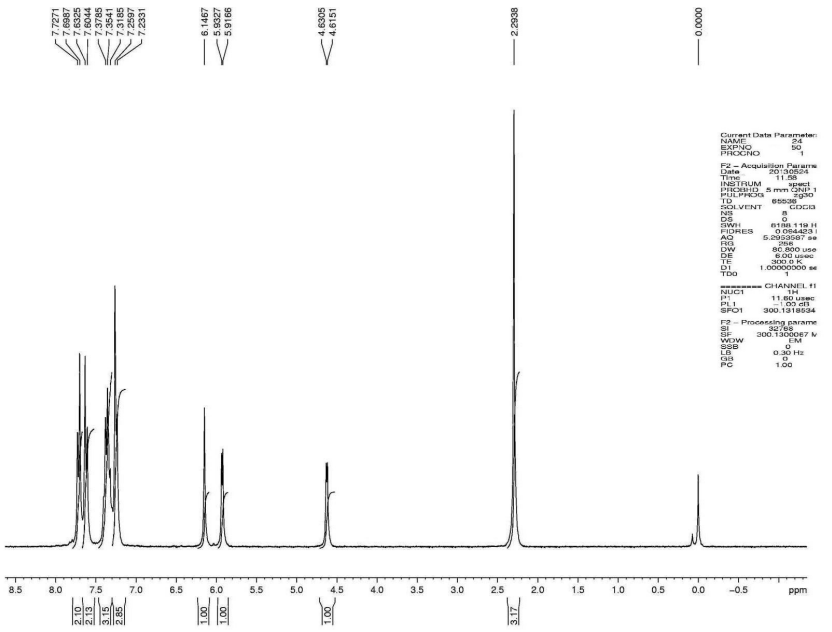
^{13}C spectra of 2-(biphenylcarbonyl)-3-ferrocenyl-2H-furo[3,2-c]chromen-4(3H)-one (11g)



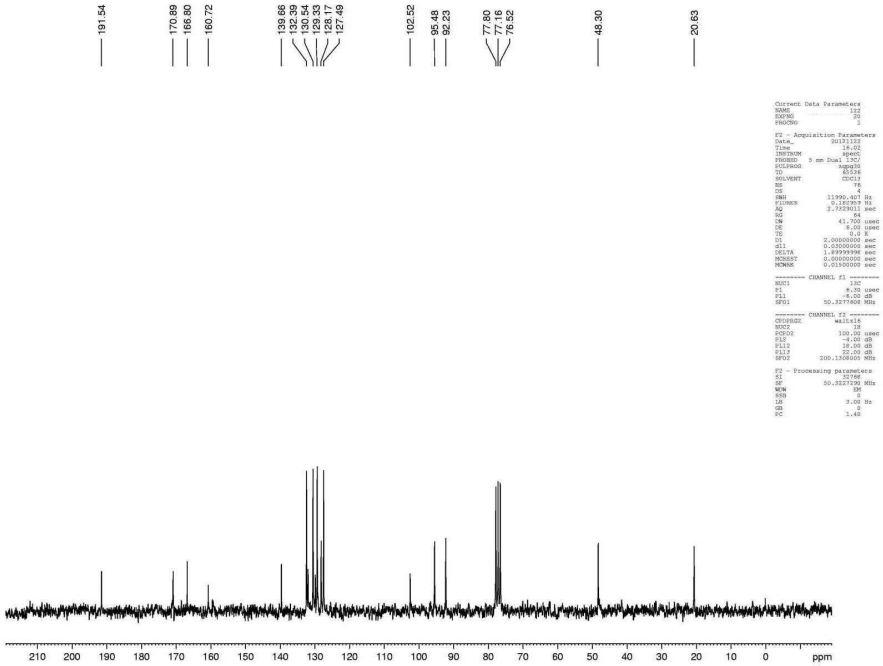
^{1}H spectra of 4-(3-(4-chlorophenyl)-4-oxo-2,3-dihydro-4H-furo[3,2-c]chromene-2-carbonyl)benzonitrile (11h)



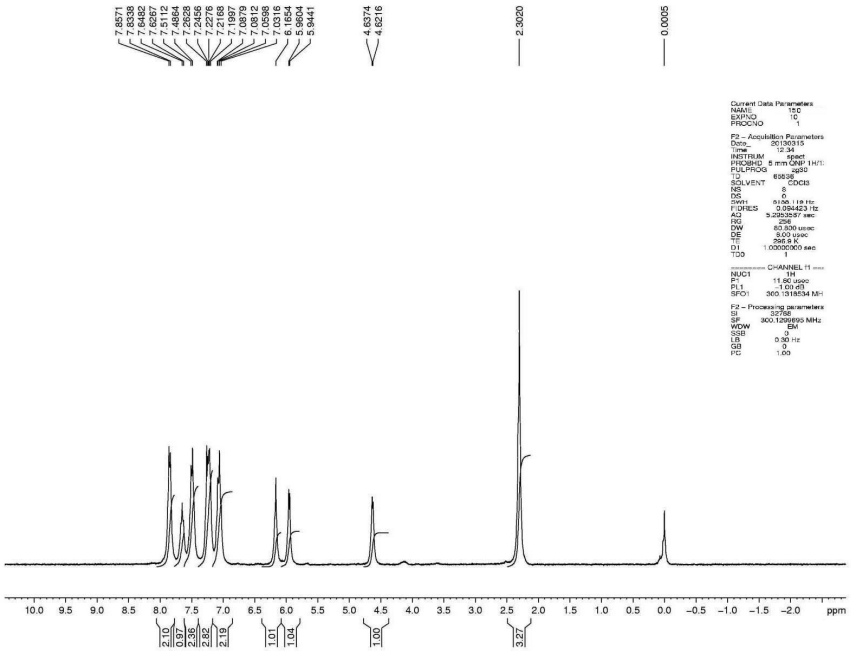
^{13}C spectra of 4-(3-(4-chlorophenyl)-4-oxo-2,3-dihydro-4H-furo[3,2-c]chromene-2-carbonyl)benzonitrile (11h)



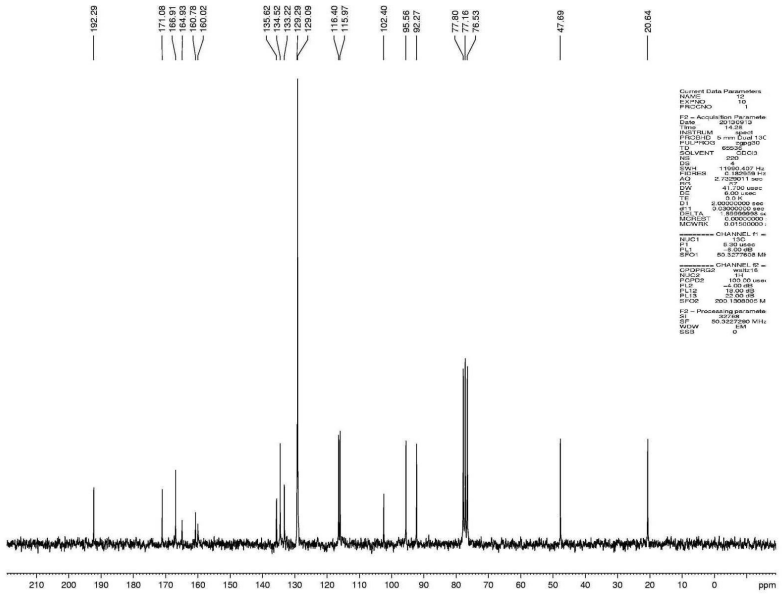
[1]H spectra of 2-(4-bromobenzoyl)-6-methyl-3-phenyl-2H-furo[3,2-c]pyran-4(3H)-one (13a)



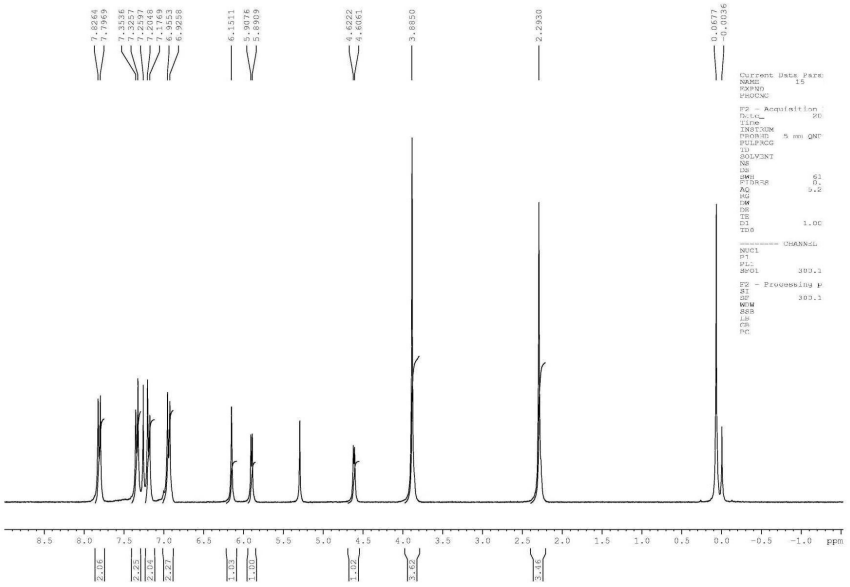
[13]C spectra of 2-(4-bromobenzoyl)-6-methyl-3-phenyl-2H-furo[3,2-c]pyran-4(3H)- one (13a)



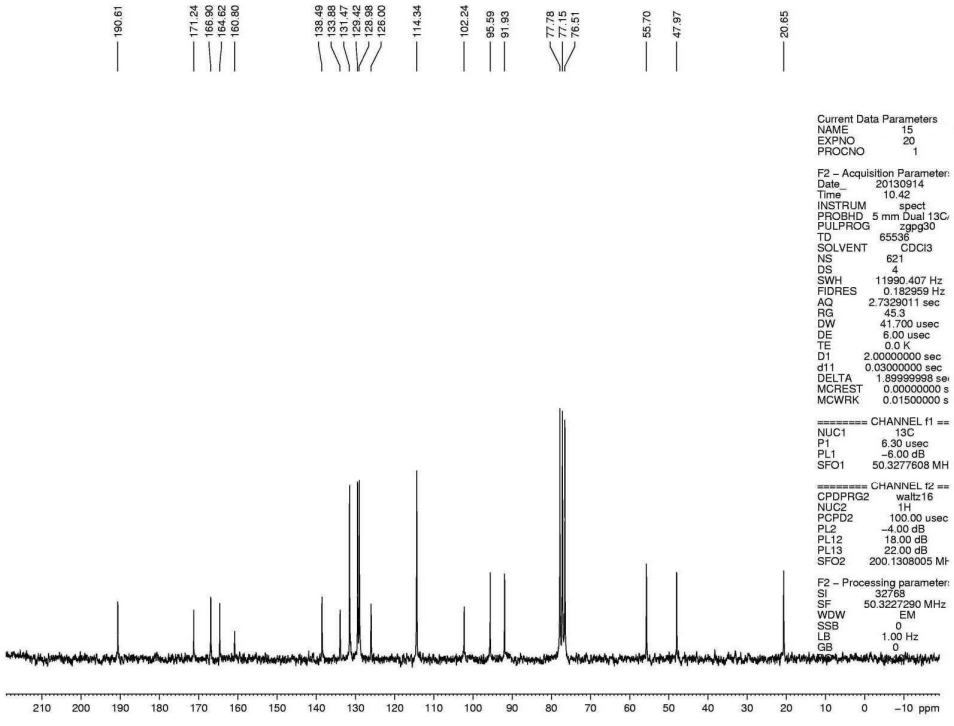
[1]H spectra of 2-benzoyl-3-(4-fluorophenyl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one (13b)



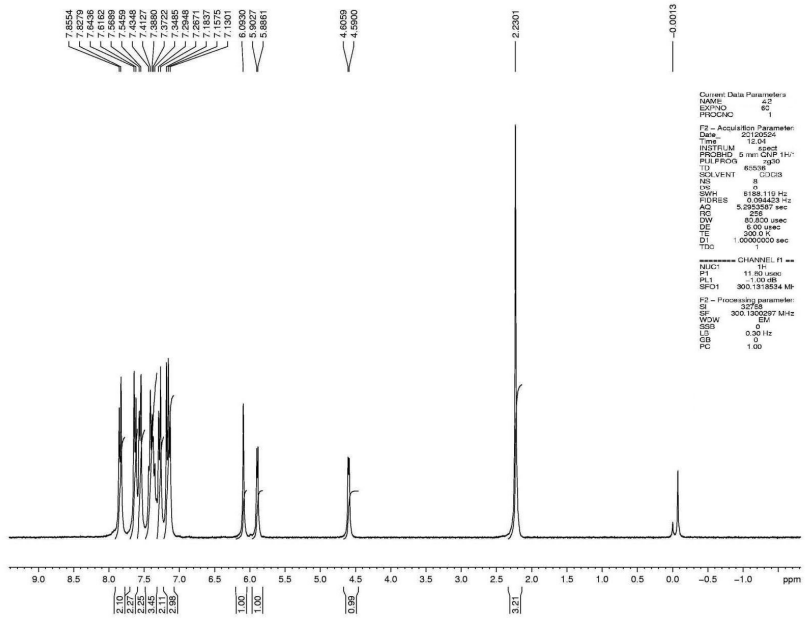
[13] C spectra of 2-benzoyl-3-(4-fluorophenyl)-6-methyl-2H-furo[3,2-c]pyran-4(3H)-one (13b)



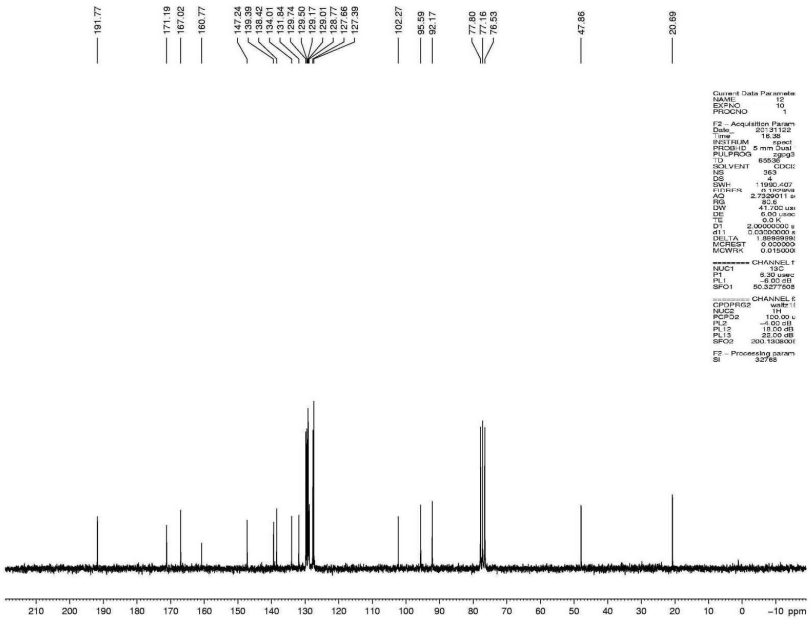
^{1}H spectra of 3-(4-chlorophenyl)-2-(4-methoxybenzoyl)-6-methyl-2H-furo[3,2- c]pyran-4(3H)-one (13c)



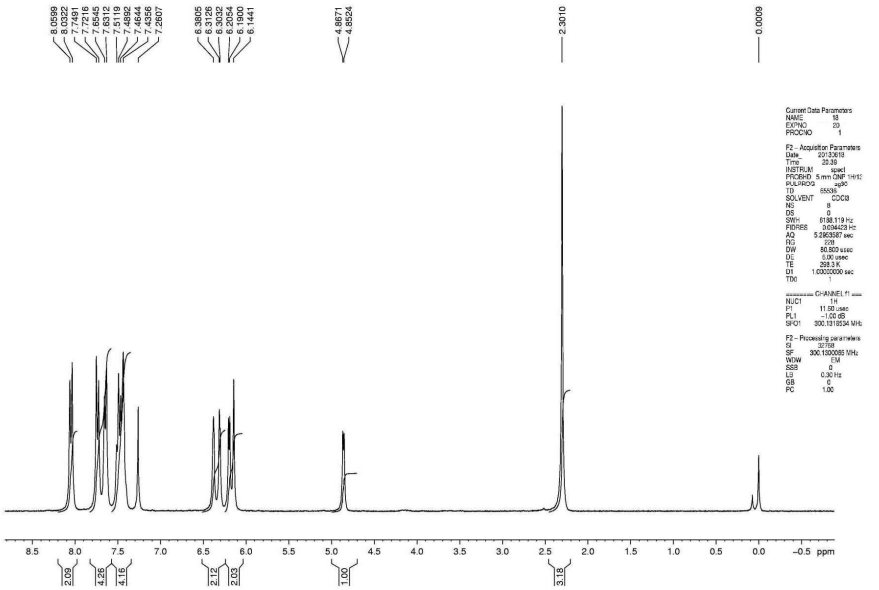
^{13}C spectra of 3-(4-chlorophenyl)-2-(4-methoxybenzoyl)-6-methyl-2H-furo[3,2- c]pyran-4(3H)-one (13c)



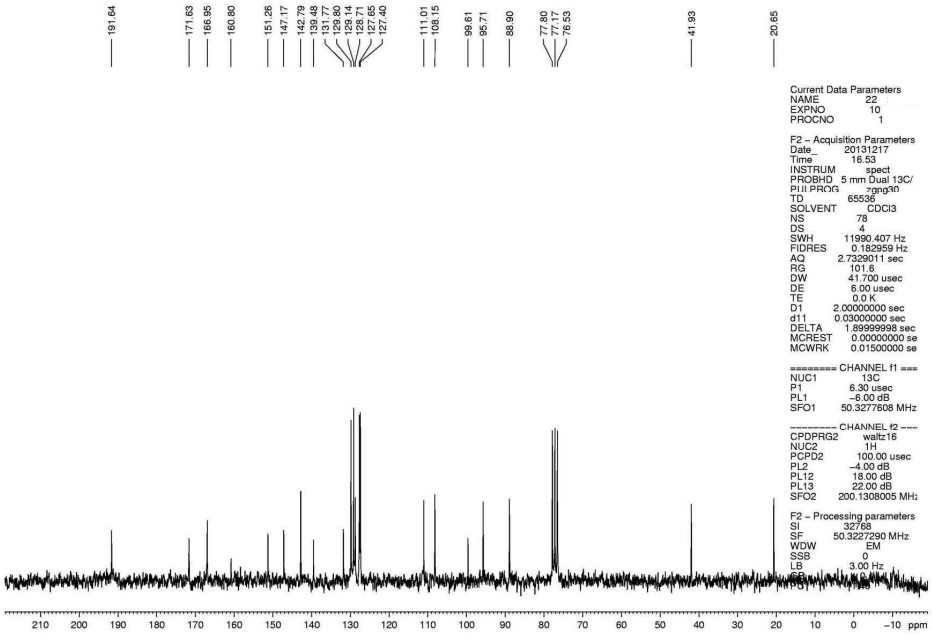
^{1}H spectra of 2-(biphenylcarbonyl)-6-methyl-3-phenyl-2H-furo[3,2-c]pyran- 4(3H)-one (13d)



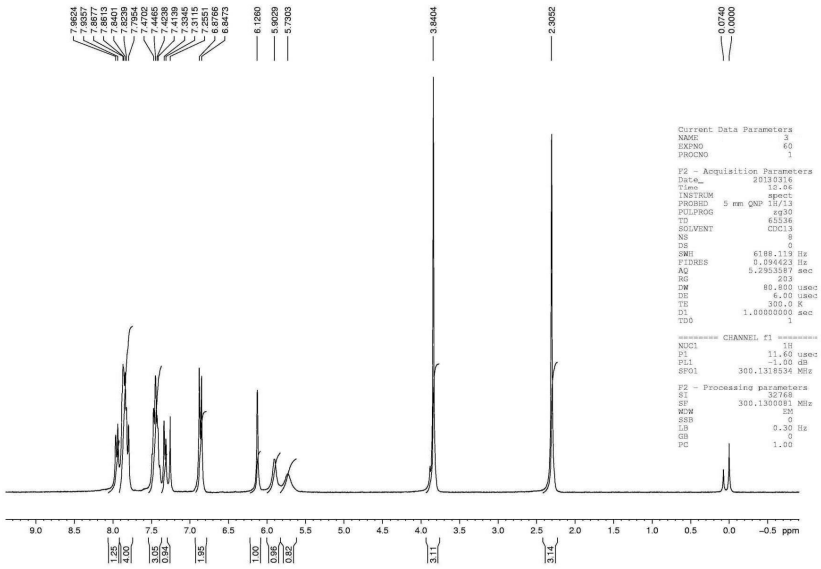
^{13}C spectra of 2-(biphenylcarbonyl)-6-methyl-3-phenyl-2H-furo[3,2-c]pyran- 4(3H)-one (13d)



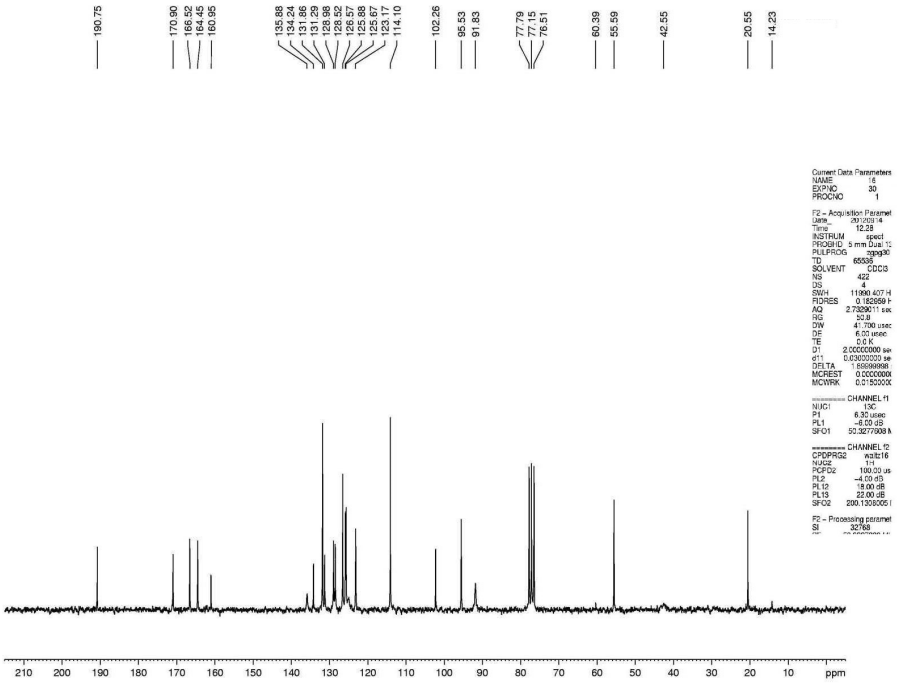
[1]H spectra of 2-(biphenylcarbonyl)-3-(furan-2-yl)-6-methyl-2H-furo[3,2-c]pyran- 4(3H)-one (13e)



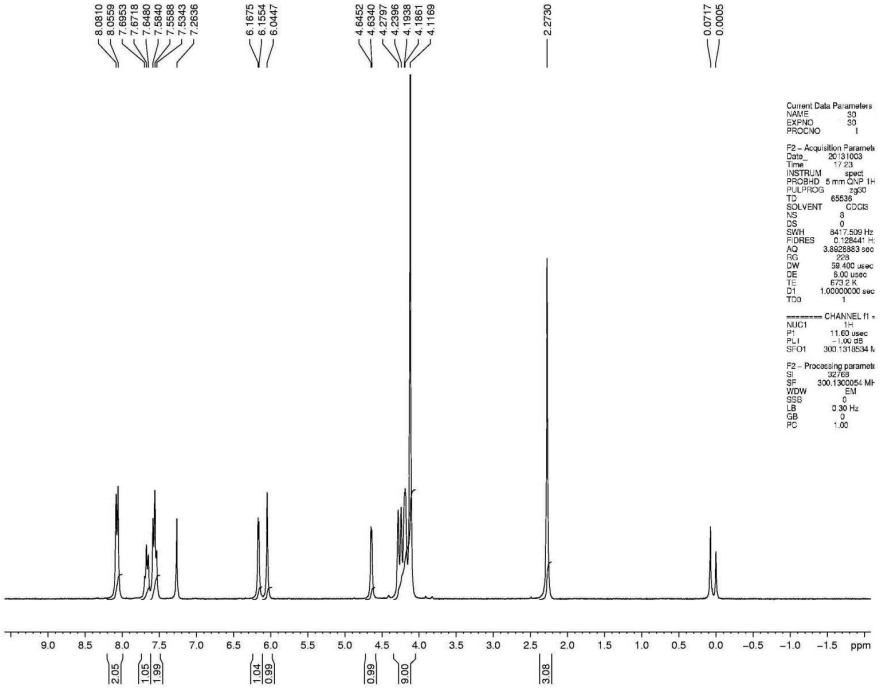
[13] C spectra of 2-(biphenylcarbonyl)-3-(furan-2-yl)-6-methyl-2H-furo[3,2-c]pyran- 4(3H)-one (13e)



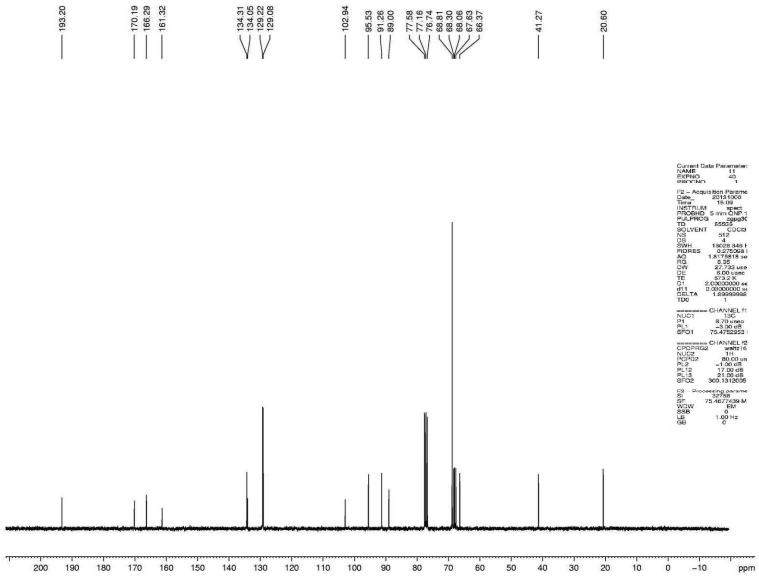
^{1}H spectra of 2-(4-methoxybenzoyl)-6-methyl-3-(naphthalen-1-yl)-2H-furo[3,2-c]pyran-4(3H)-one (13f)



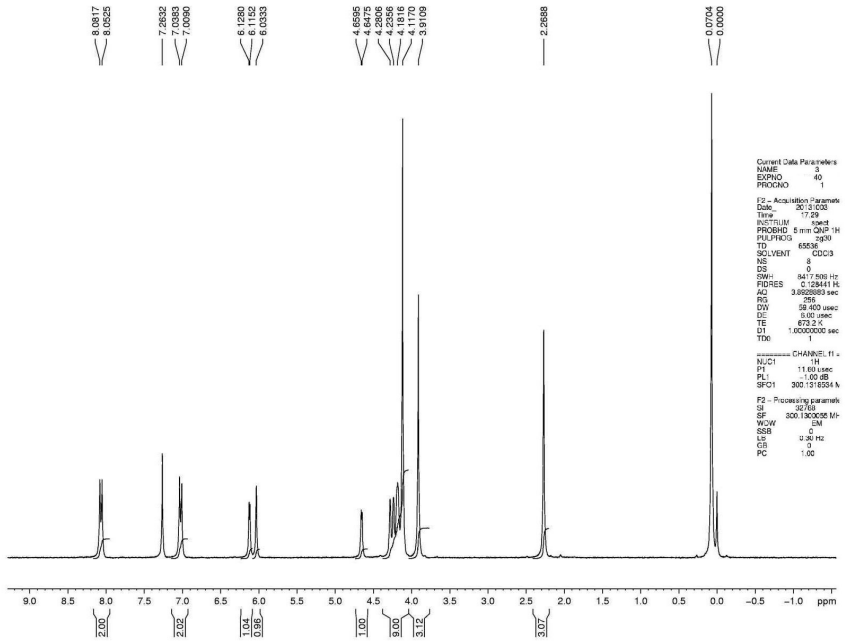
^{13}C spectra of 2-(4-methoxybenzoyl)-6-methyl-3-(naphthalen-1-yl)-2H-furo[3,2-c]pyran-4(3H)-one (13f)



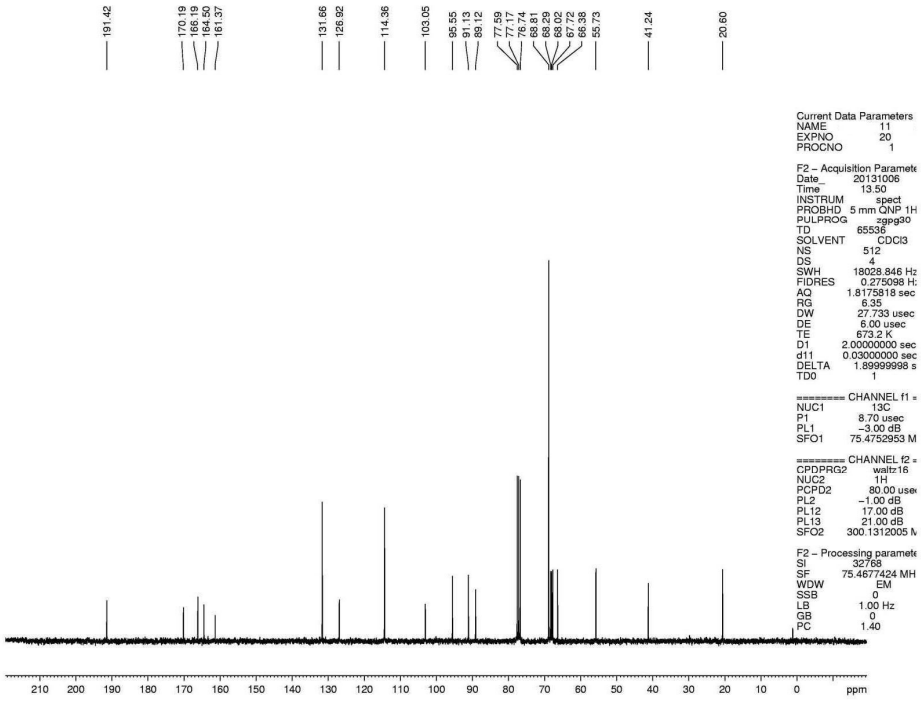
[1]H spectra of 2-benzoyl-3-ferrocenyl -6-methyl- -2H-furo [3, 2-c]pyran-4(3H)-one (13g)



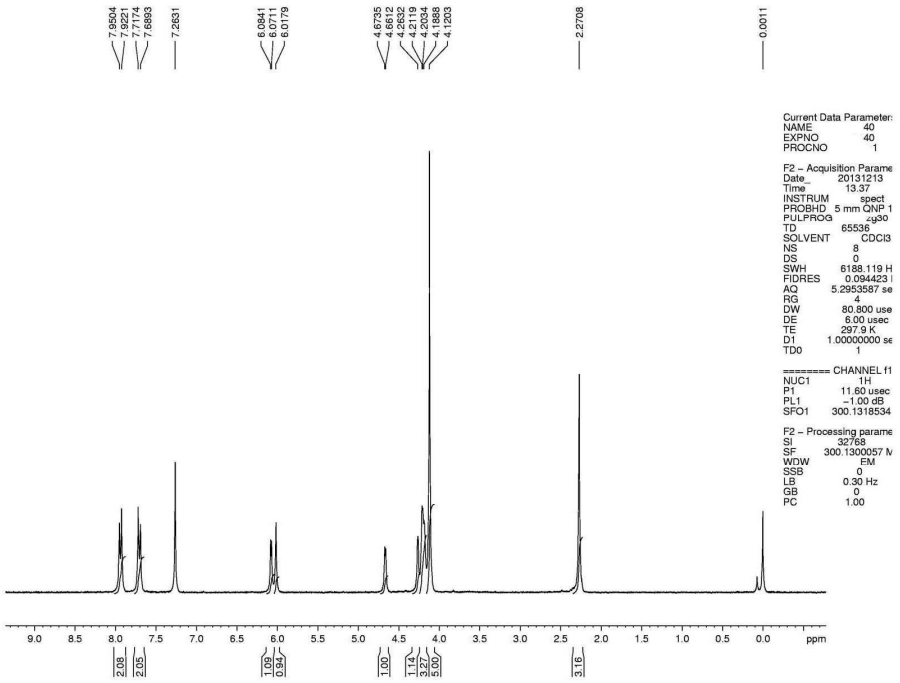
[13] C spectra of 2-benzoyl-3-ferrocenyl -6-methyl- -2H-furo [3, 2-c]pyran-4(3H)-one (13g)



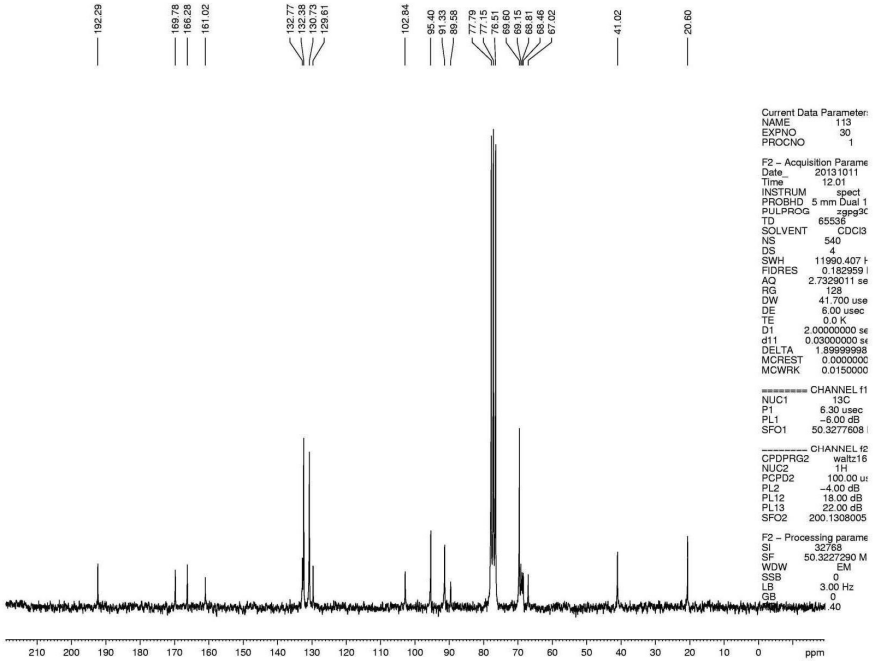
^{1}H spectra of 3-ferrocenyl-2-(4-methoxybenzoyl)-6-methyl- -2H-furo[3,2-c]pyran-4(3H)-one (13h)



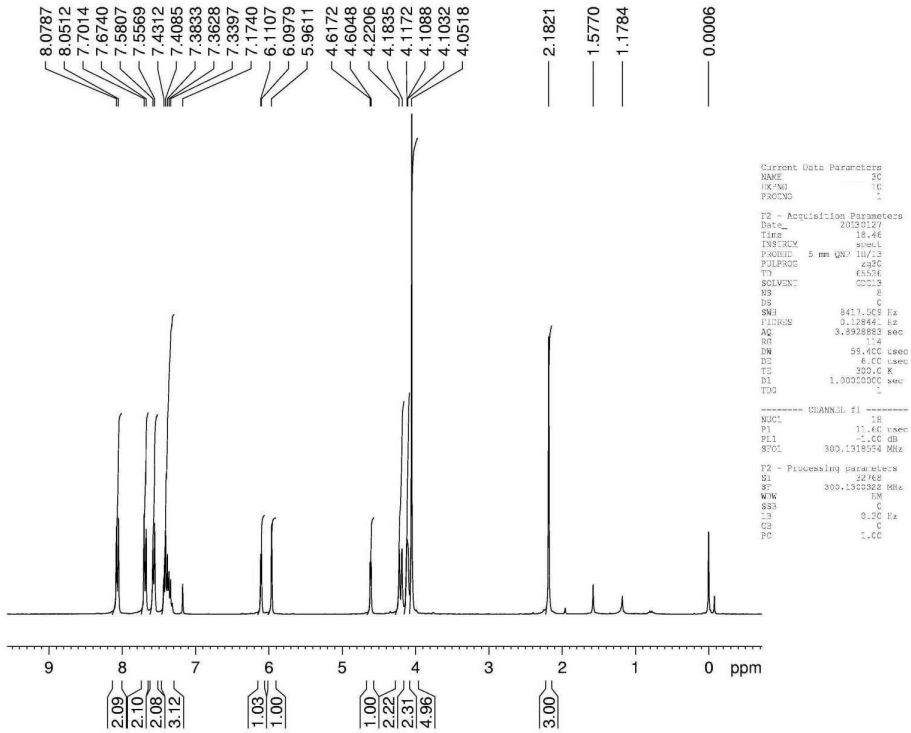
^{13}C spectra of 3-ferrocenyl-2-(4-methoxybenzoyl)-6-methyl- -2H-furo[3,2-c]pyran-4(3H)-one (13h)



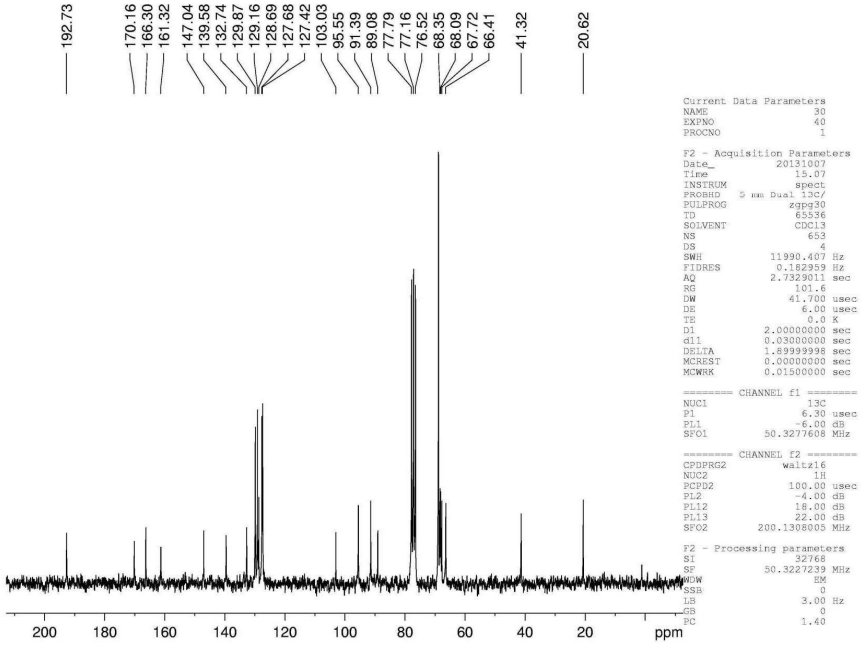
[1]H spectra of 2-(4-bromobenzoyl)-3-ferrocenyl-6-methyl- 2H-furo[3,2-c]pyran-4(3H)-one (13i)



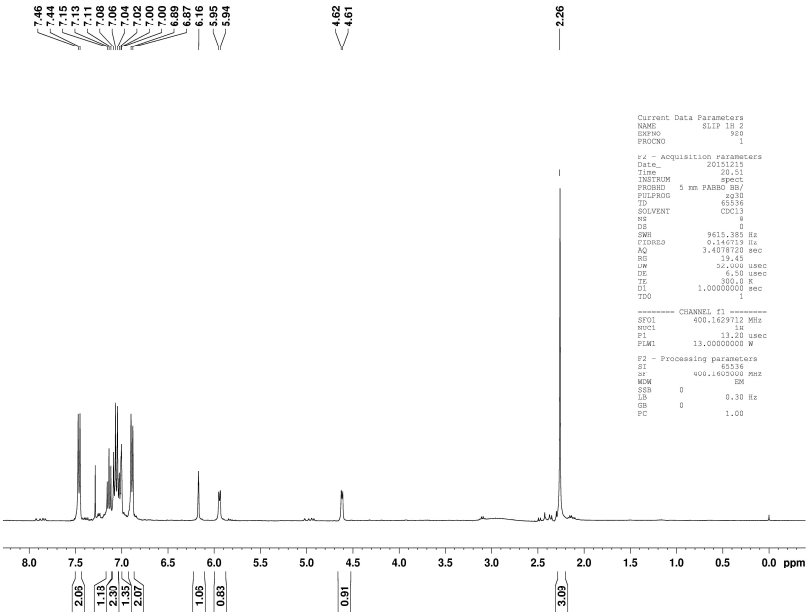
[13]C spectra of 2-(4-bromobenzoyl)-3-ferrocenyl-6-methyl- 2H-furo[3,2-c]pyran-4(3H)-one (13i)



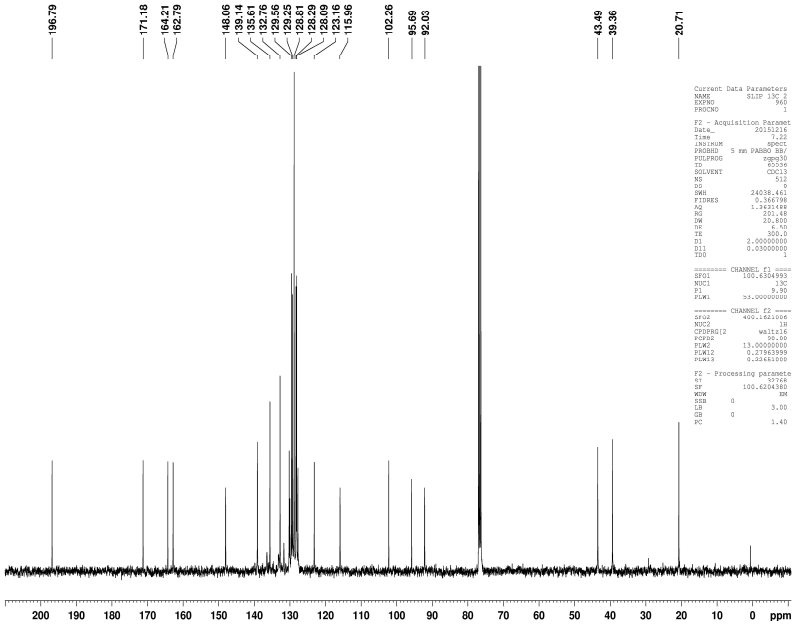
[1]H spectra of 2-(biphenylcarbonyl)-3-ferrocenyl-6-methyl-2H-furo[3,2-c]pyran4(3H)-one (13j)



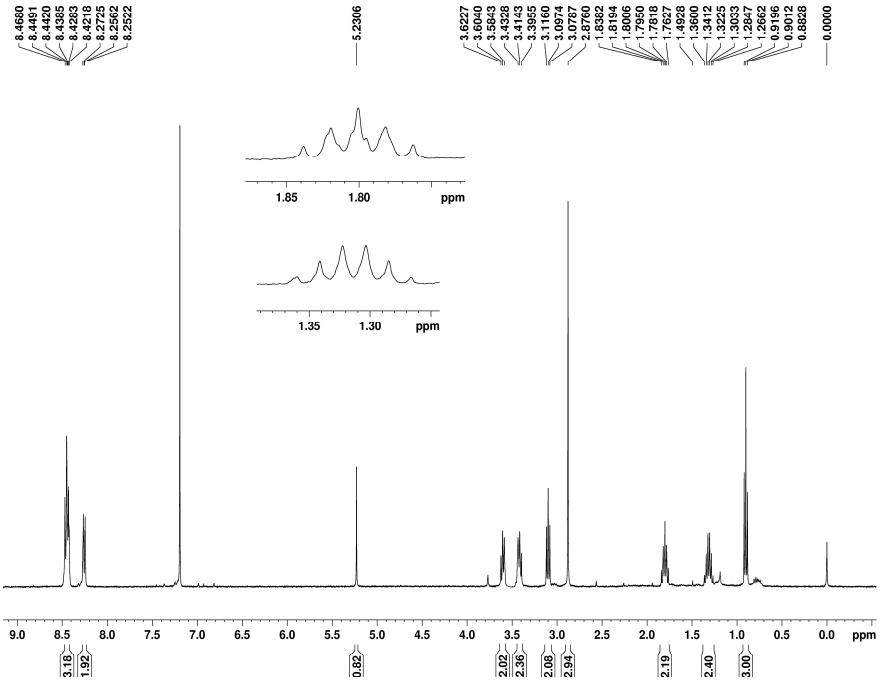
[13]C spectra of 2-(biphenylcarbonyl)-3-ferrocenyl-6-methyl-2H-furo[3,2-c]pyran4(3H)-one (13j)



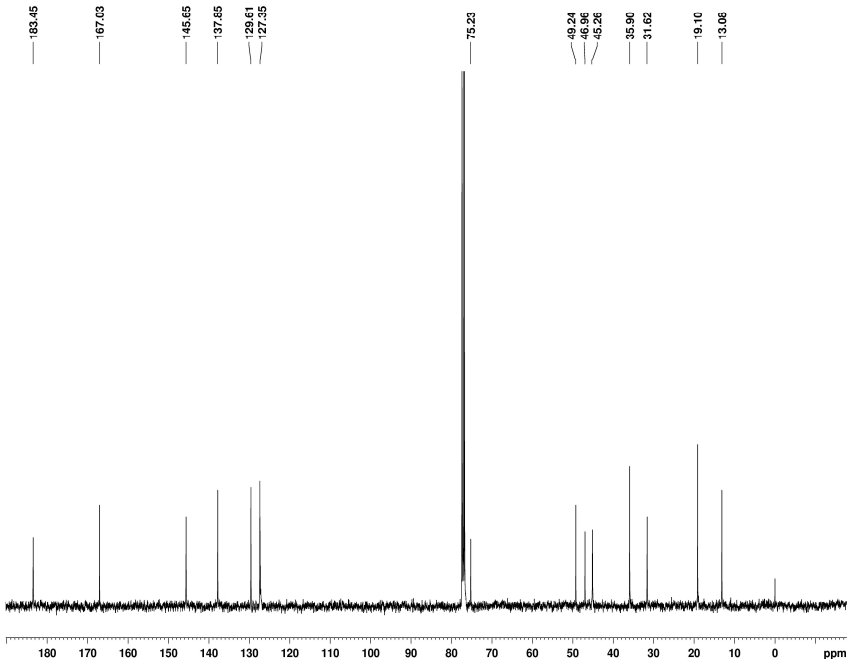
^{1}H spectra of 3-(4-chlorophenyl)-6-methyl-2-(4-nitrobenzoyl)-2,3-dihydro-4H-furo[3,2-c]pyran-4-one (13k)



^{13}C spectra of 3-(4-chlorophenyl)-6-methyl-2-(4-nitrobenzoyl)-2,3-dihydro-4H-furo[3,2-c]pyran-4-one (13k):



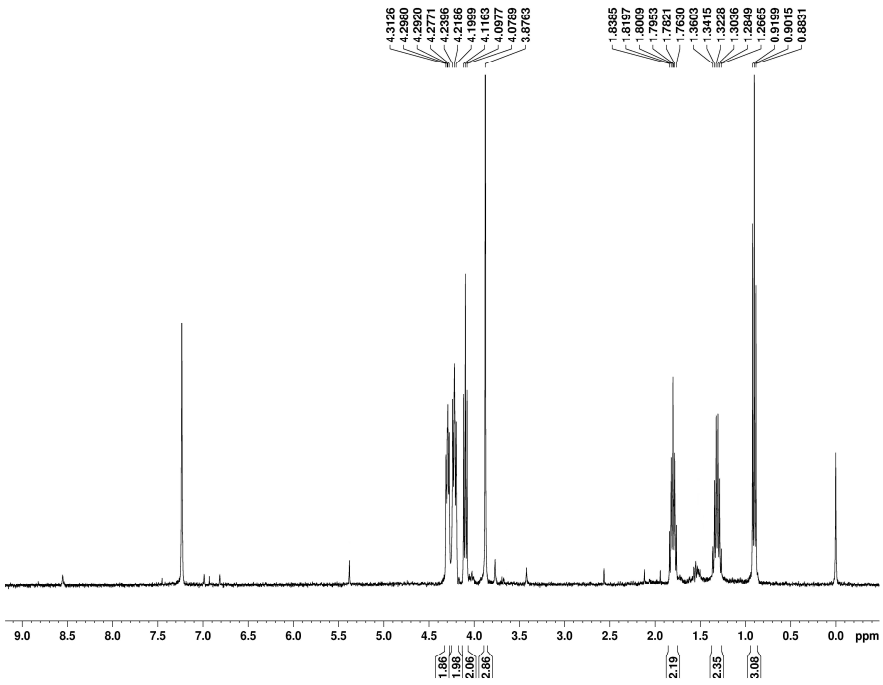
^{1}H spectra of 2-(1-butyl-3-methylimidazolidin-2-ylidene)-1-phenylethan-1-one (4)



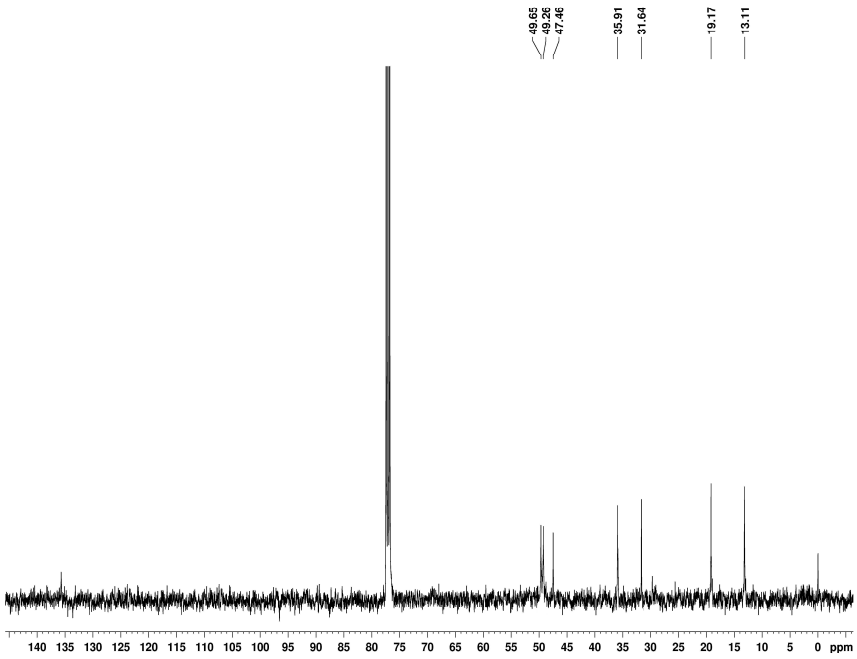
^{13}C spectra of 2-(1-butyl-3-methylimidazolidin-2-ylidene)-1-phenylethan-1-one (4)

7. Mechanistic Experiment: Trapping of carbene as 1-butyl-3-methyl-4,5-dihydro-1H-imidazol-2-ylidene borane complex using BH_3.THF[3]

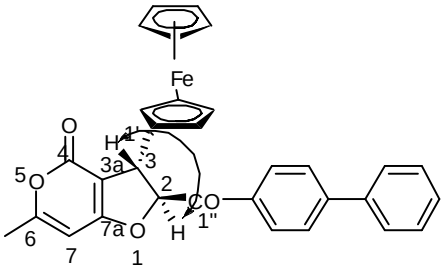
Following the representative one pot procedure, after completion, the reaction mixture was slowly cooled to r.t.. Then resulting supernatant suspension was transferred into other round bottom flask having bar magnet, in N_2 atmosphere. The suspension was further cooled to -78°C followed by drop by drop addition of BH_3.THF(1M). The resulting mixture was stirred overnight and warmed slowly to r.t.. The complex formation was purified by column chromatography, obtained as gummy solid (less stable in nature); IR (KBr): 2913, 2348, 1428, 1365, 734; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.19-4.31 (m, 4H), 4.09 (d, *J* = 7.4 Hz, 2H), 3.87 (s, 3H), 1.76-1.83 (m, 2H), 1.27-1.36 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.11, 19.17, 31.64, 35.91, 47.46, 49.26, 49.65.

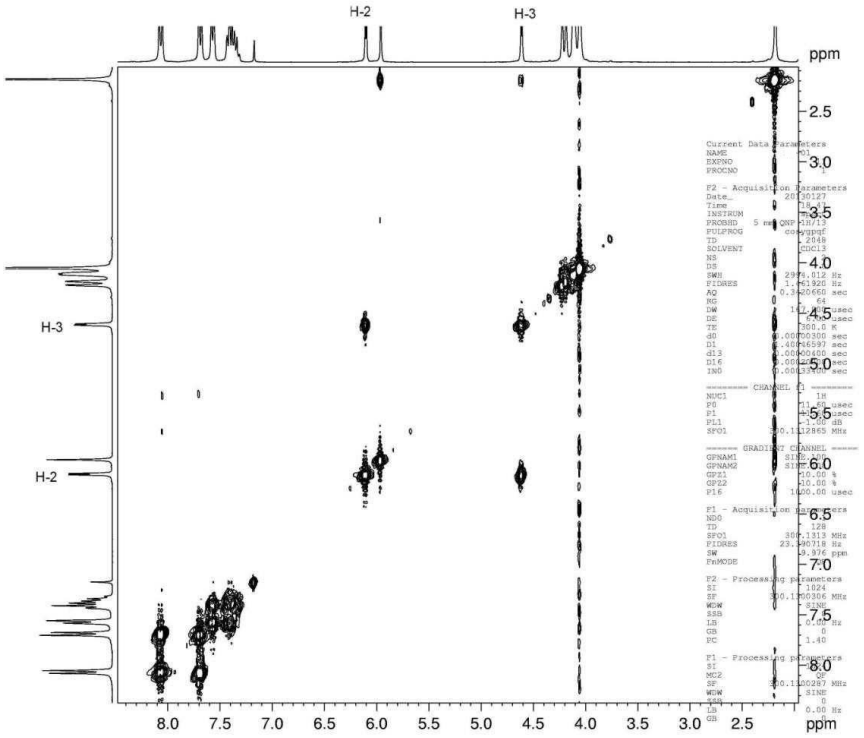


^{1}H spectra of 1-butyl-3-methyl-4,5-dihydro-1H-imidazol-2-ylidene borane complex

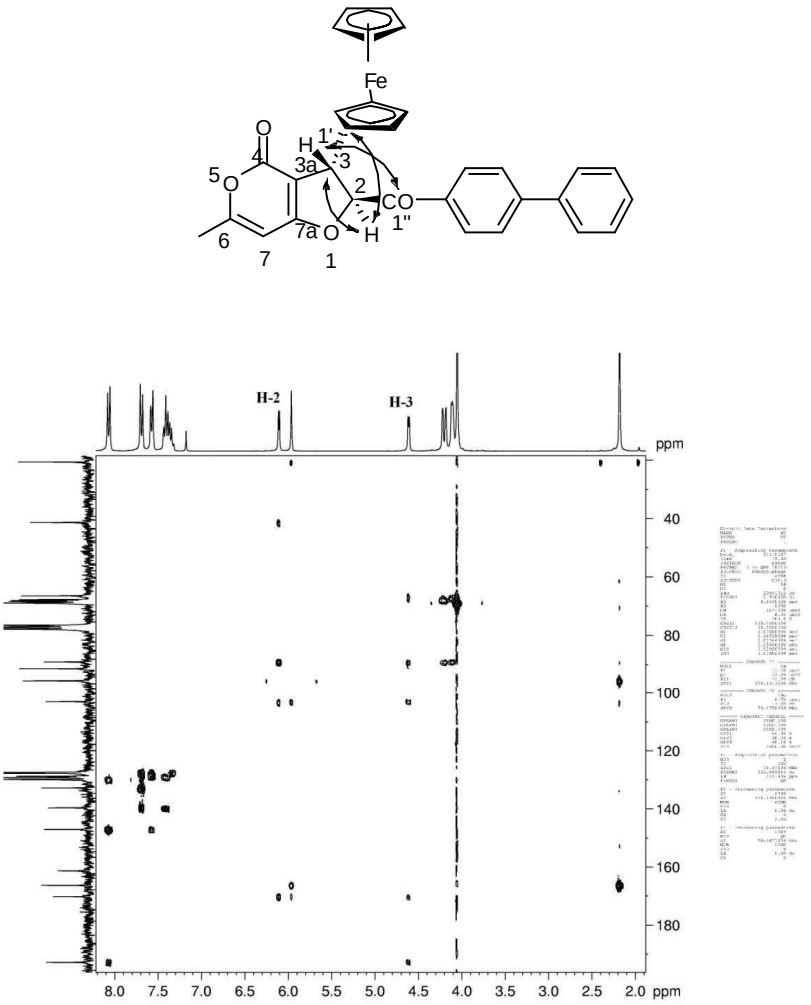


^{13}C spectra of 1-butyl-3-methyl-4,5-dihydro-1H-imidazol-2-ylidene borane complex

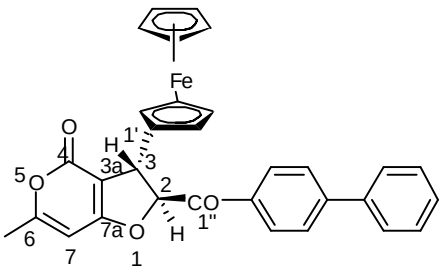


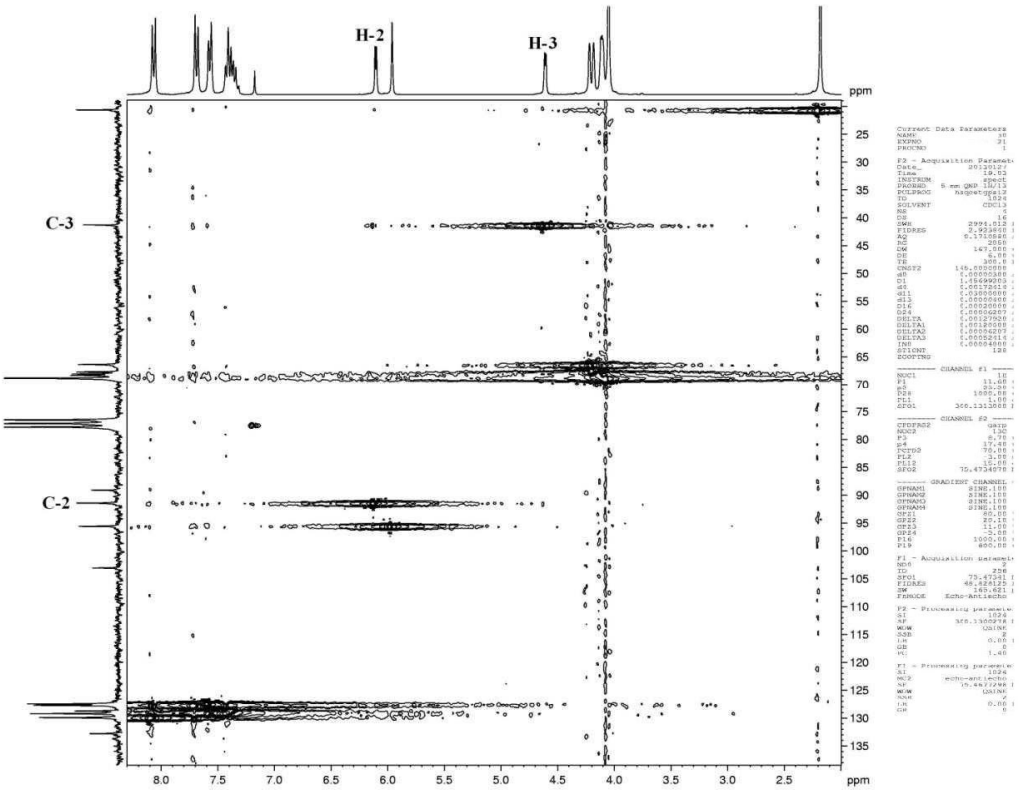


COSY spectra of 2-(biphenylcarbonyl)-3-ferrocenyl 6-methyl- -2H-furo[3,2-c]pyran-4(3H)-one: (13j)



HMBC spectra of 2-(biphenylcarbonyl)-3-ferrocenyl 6-methyl- -2H-furo[3,2-c]pyran-4(3H)-one (13j):





HSQC spectra of 2-(biphenylcarbonyl)-3-ferrocenyl 6-methyl- -2H-furo [3,2-c]pyran-4(3H)-one (13 j) :

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