Green Chemistry

Electronic Supplementary Information associated with the paper

Enolate ion as a synthon in biocatalytic synthesis of 3,4-dihydro-2(1H)-quinoxalinones and 3,4-dihydro-1,4-benzoxazin-2-ones: lemon juice as an alternative to hazardous solvents and catalysts

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1. Graphical representation of *E*-factor

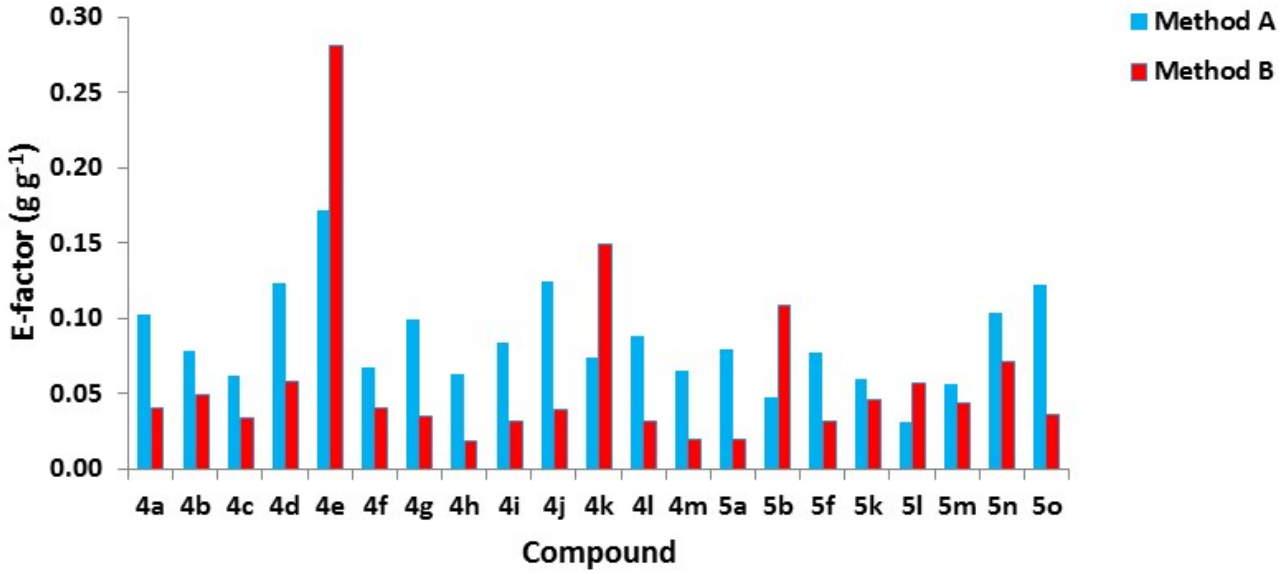
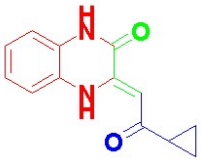


Fig S1. Graphical representation of *E*-factor (g g^{-1}) for two green methods

2. ^{1}H and ^{13}C NMR spectrums of 4a-m

3,4-dihydro-3-(2-oxo-2-cyclopropylethylidene)-2(1H)-quinoxalinone (4a)



Orange powder; yield: 85 (94)%; mp = 257°C; IR (KBr): ν 3438, 3413, 2964, 1681, 1613, 1574, 1390 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 0.83-1.08 (m, 4H, 2×CH_2), 1.99-2.11 (m, 1H, CH), 6.22 (s, 1H, CH), 7.03-7.09 (t, 3H, CH_{Ar}), 7.31-7.42 (m, 1H, CH_{Ar}), 11.86 (br. s, 1H, NH), 12.99 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 10.1, 20.9, 93.0, 115.4, 115.9, 123.4, 123.7, 124.4, 126.3, 142.7, 155.9, 199.4 ppm; ESI-MS: m/z (%) = 228 $[M]^{+}$. Calcd for $C_{13}H_{12}N_2O_2$ (%): C 68.41, H 5.30, N 12.27; found: C 68.30, H 5.38, N 12.20.

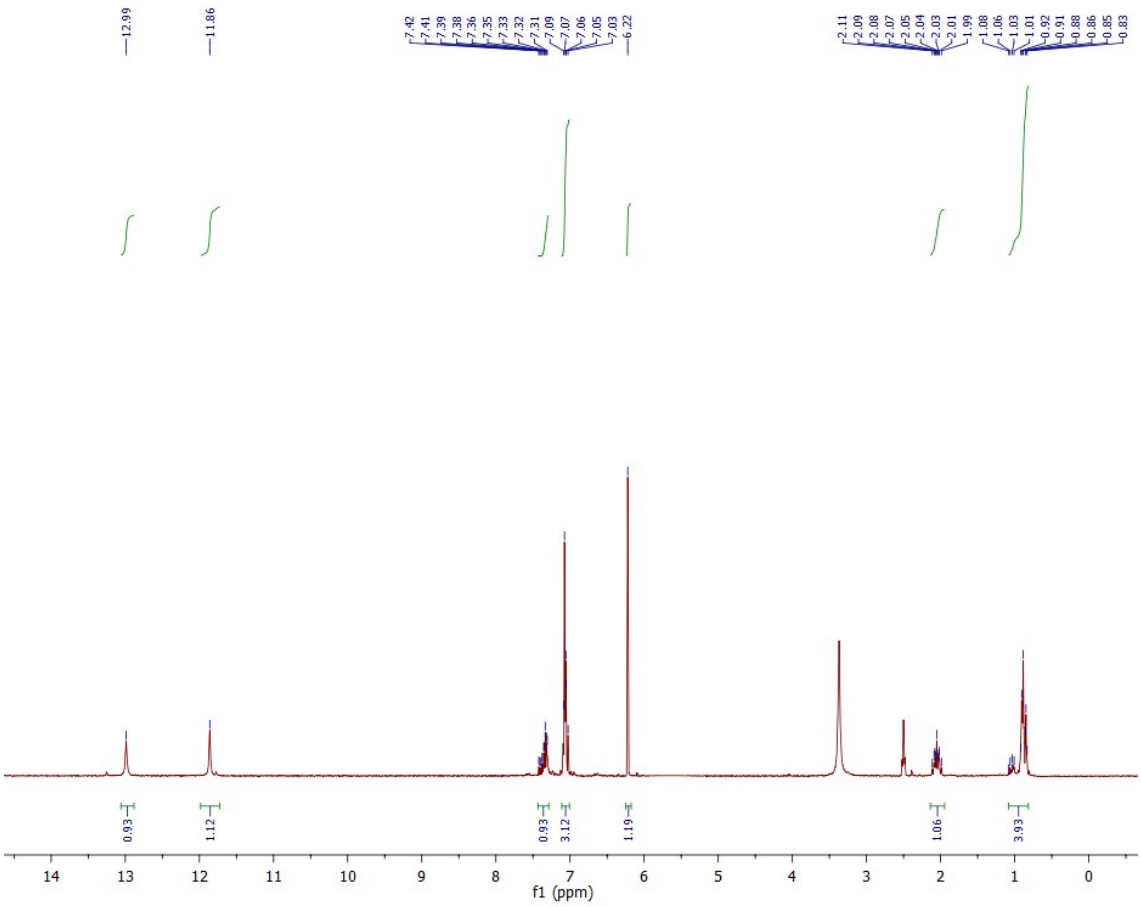


Fig. S2 ^{1}H NMR spectrum of **4a**

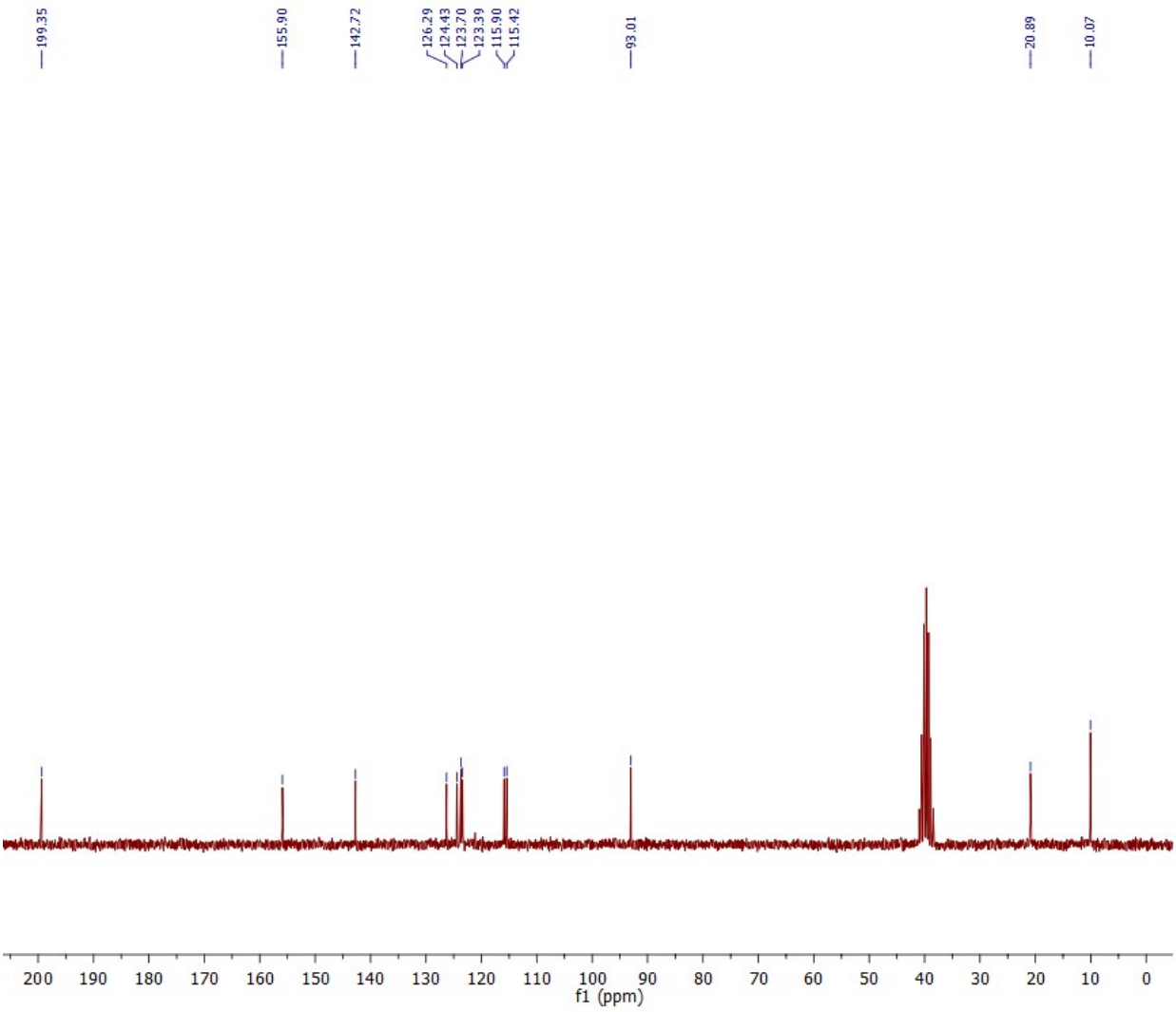
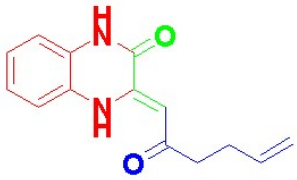


Fig. S3 ^{13}C NMR spectrum of 4**a**

3,4-dihydro-3-(2-oxo-hex-5-enylidene)-2(1H)-quinoxalinone (4b)



Brown crystals; yield: 89 (93)%; mp = 212˚C; IR (KBr): ν 3438, 2961, 1673, 1614, 1577, 1380 cm^{-1} ; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 2.32-2.49 (m, 2H, CH_2), 2.50-2.55 (m, 2H, CH_2), 4.91-5.00 (m, 2H, CH_2), 5.76-5.90 (m, 1H, CH), 6.05 (s, 1H, CH), 6.93-7.07 (m, 3H, CH_{Ar}), 7.09-7.40 (m, 1H, CH_{Ar}), 11.87 (br. s, 1H, NH), 12.95 (br. s, 1H, NH) ppm; $_{13}C$ NMR (50 MHz, DMSO-d_6): δ = 29.0, 41.2, 92.9, 115.3, 115.5, 116.2, 123.6, 123.8, 124.4, 126.4, 138.0, 143.6, 155.9, 199.3 ppm; ESI-MS: m/z (%) = 265 $[M + Na]^+$; Anal. Calcd. for $C_{14}H_{14}N_2O_2$ (%): C 69.41, H 5.82, N 11.56; found: C 69.28, H 5.87, N 11.51.

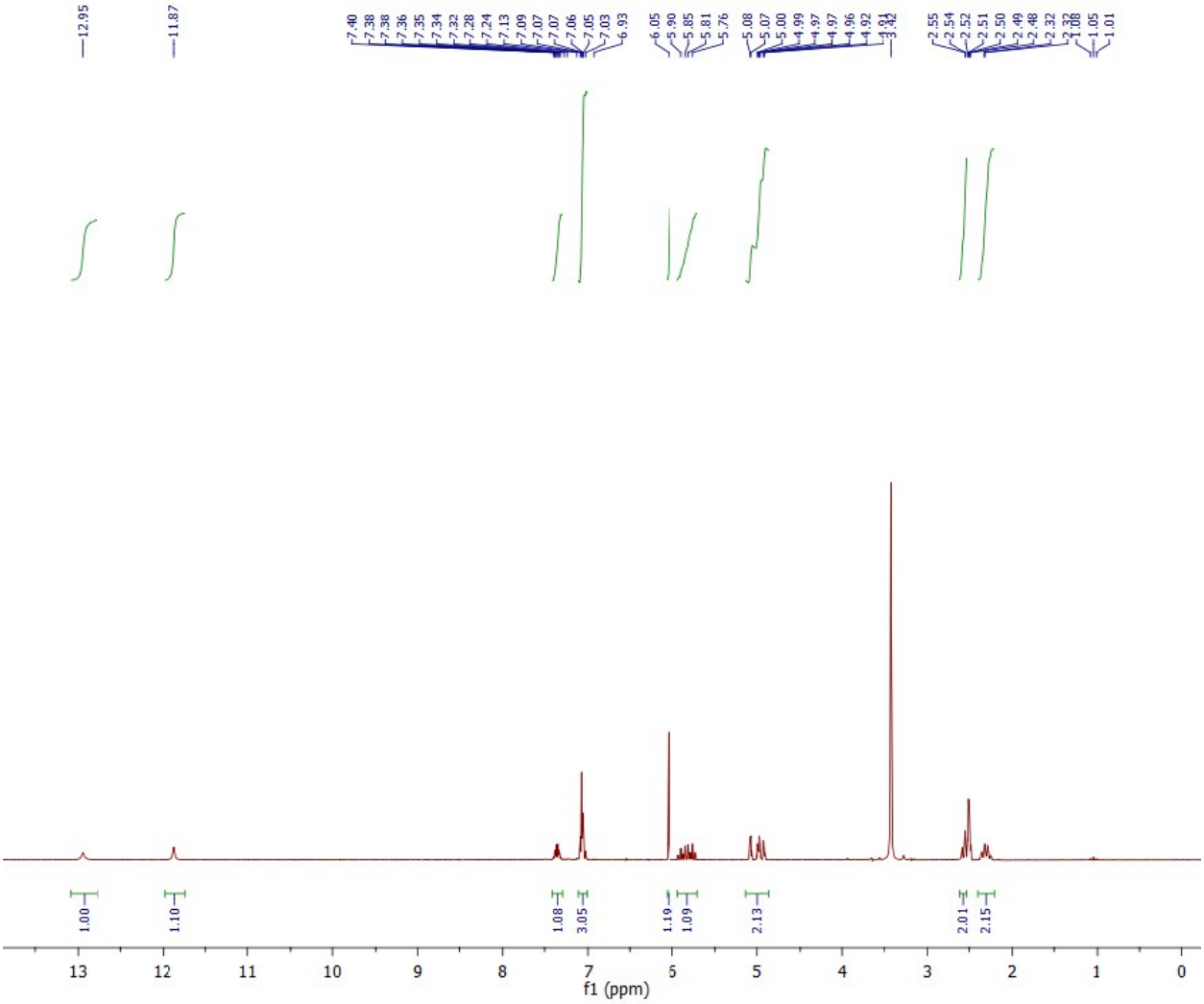


Fig. S4 ^{1}H NMR spectrum of **4b**

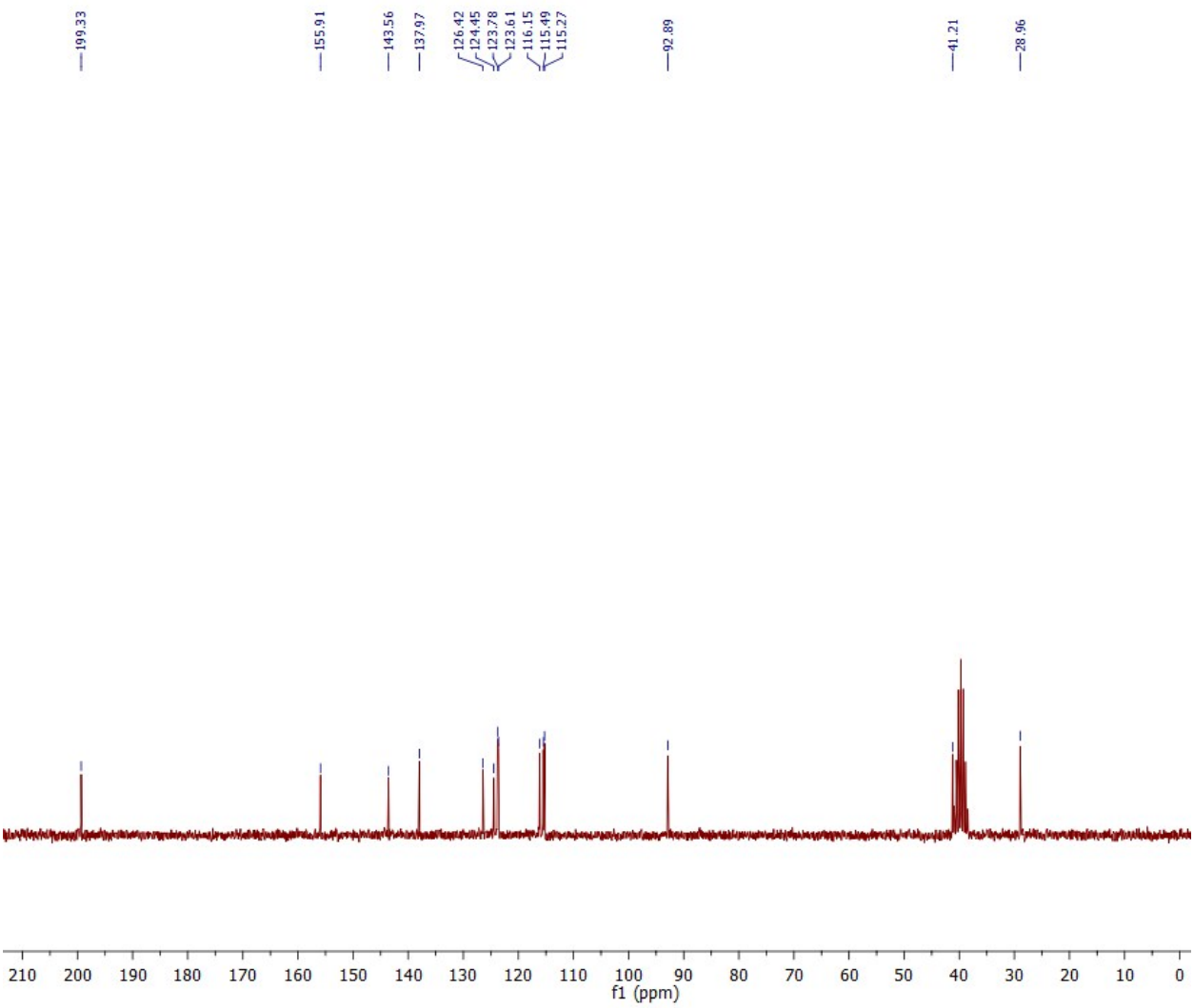
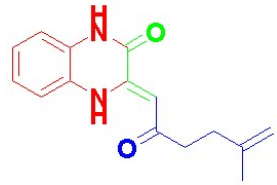


Fig. S5 ^{13}C NMR spectrum of **4b**

3,4-dihydro-3-(5-methyl-2-oxo-hex-5-enylidene)-2(1H)-quinoxalinone (4c)



Orange powder; yield: 91 (95)%; mp > 300˚C; IR (KBr): ν 3412, 2963, 2854, 1667, 1612, 1568, 1460, 1380 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 1.71 (s, 3H, CH_3), 2.24-2.31 (m, 2H, CH_2), 2.57-2.64 (m, 2H, CH_2), 4.69 (s, 2H, CH_2), 6.08 (s, 1H, CH), 7.04-7.10 (m, 3H, CH_{Ar}), 7.37-7.42 (m, 1H, CH_{Ar}), 11.88 (br. s, 1H, NH), 12.96 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 22.6, 32.7, 40.3, 92.8, 110.4, 115.4, 116.1, 123.6, 123.7, 124.4, 126.4, 143.5, 144.7, 155.9, 199.5 ppm; ESI-MS: m/z (%) = 256 $[M]^{+}$; Anal. Calcd for $C_{15}H_{16}N_2O_2$ (%): C 70.29, H 6.29, N 10.93; found: C 70.41, H 6.39, N 10.97.

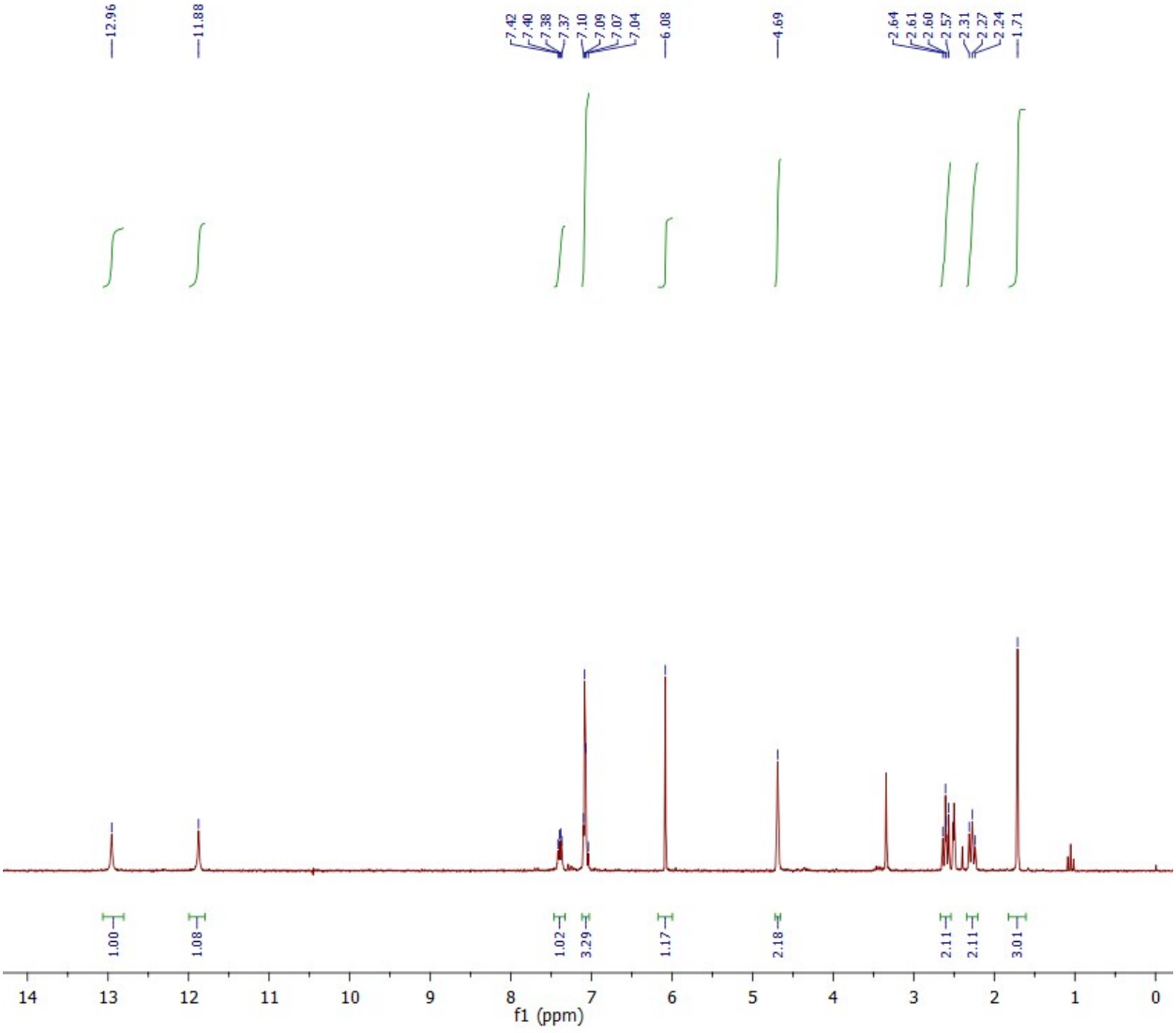


Fig. S6 ^{1}H NMR spectrum of **4c**

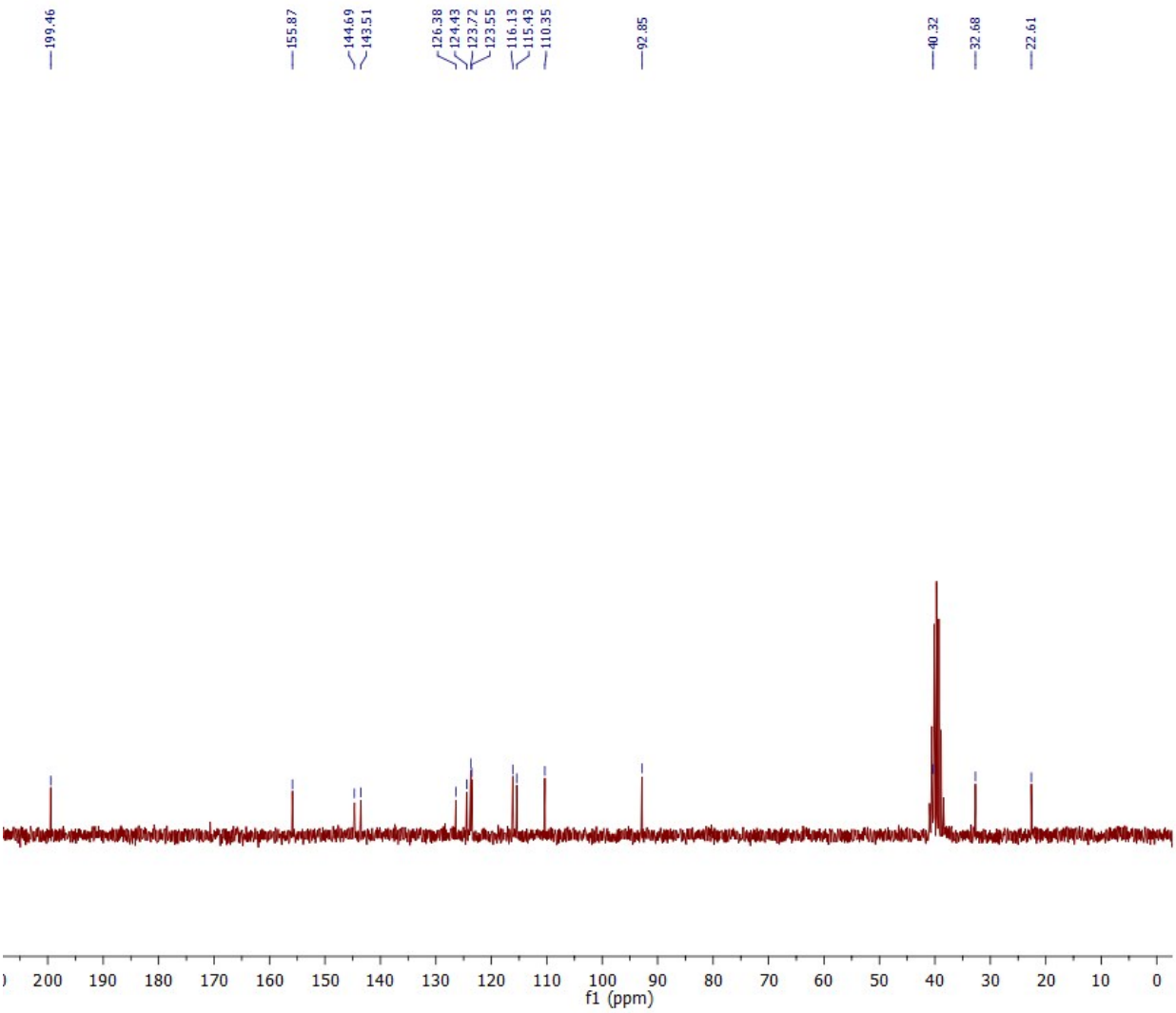
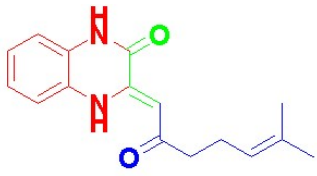


Fig. S7 ^{13}C NMR spectrum of **4c**

3,4-dihydro-3-(6-methyl-2-oxo-hept-5-enylidene)-2(1H)-quinoxalinone (4d)



Brown crystals; yield: 83 (92)%; mp = 215°C; IR (KBr): ν 3438, 2966, 1681, 1627, 1614, 1580, 1387 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 1.58-1.63 (d, 6H, 2×CH_3), 2.22-2.30 (t, 2H, CH_2), 2.40-2.44 (d, 2H, CH_2), 5.07-5.14 (t, 1H, CH), 6.05 (s, 1H, CH), 7.07-7.10 (d, 3H, CH_{Ar}), 7.37-7.42 (m, 1H, CH_{Ar}), 11.87 (br. s, 1H, NH), 12.98 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 17.7, 23.7, 25.6, 42.3, 92.9, 115.4, 116.1, 123.5, 123.7, 124.5, 126.4, 131.5, 143.4, 155.9, 199.7 ppm; ESI-MS: m/z (%) = 271 $[M + H]^+$; Anal. Calcd. for $C_{16}H_{18}N_2O_2$ (%): C 71.09, H 6.71, N 10.36; found: C 71.20, H 6.64, N 10.41.

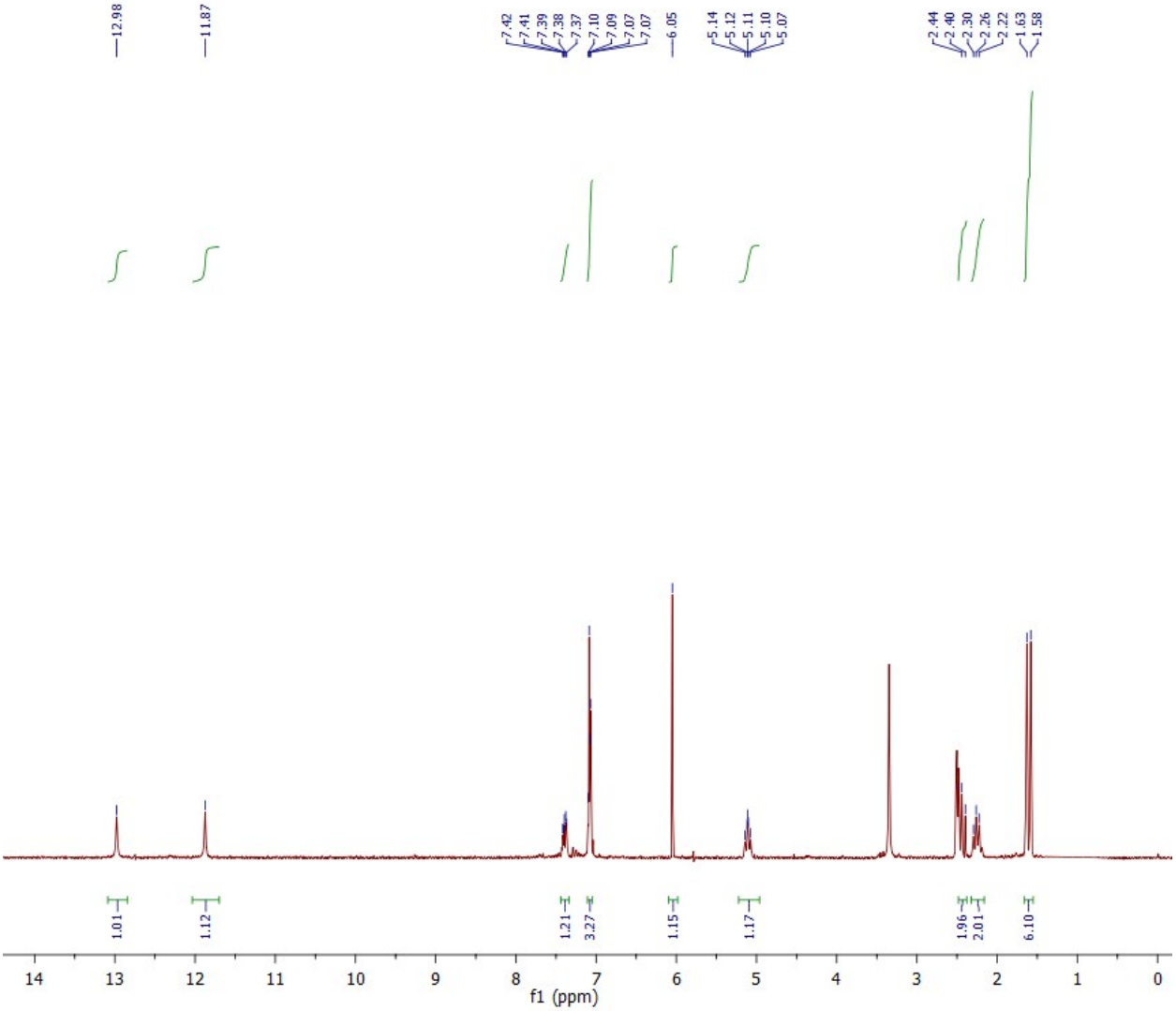


Fig. S8 ^{1}H NMR spectrum of **4d**

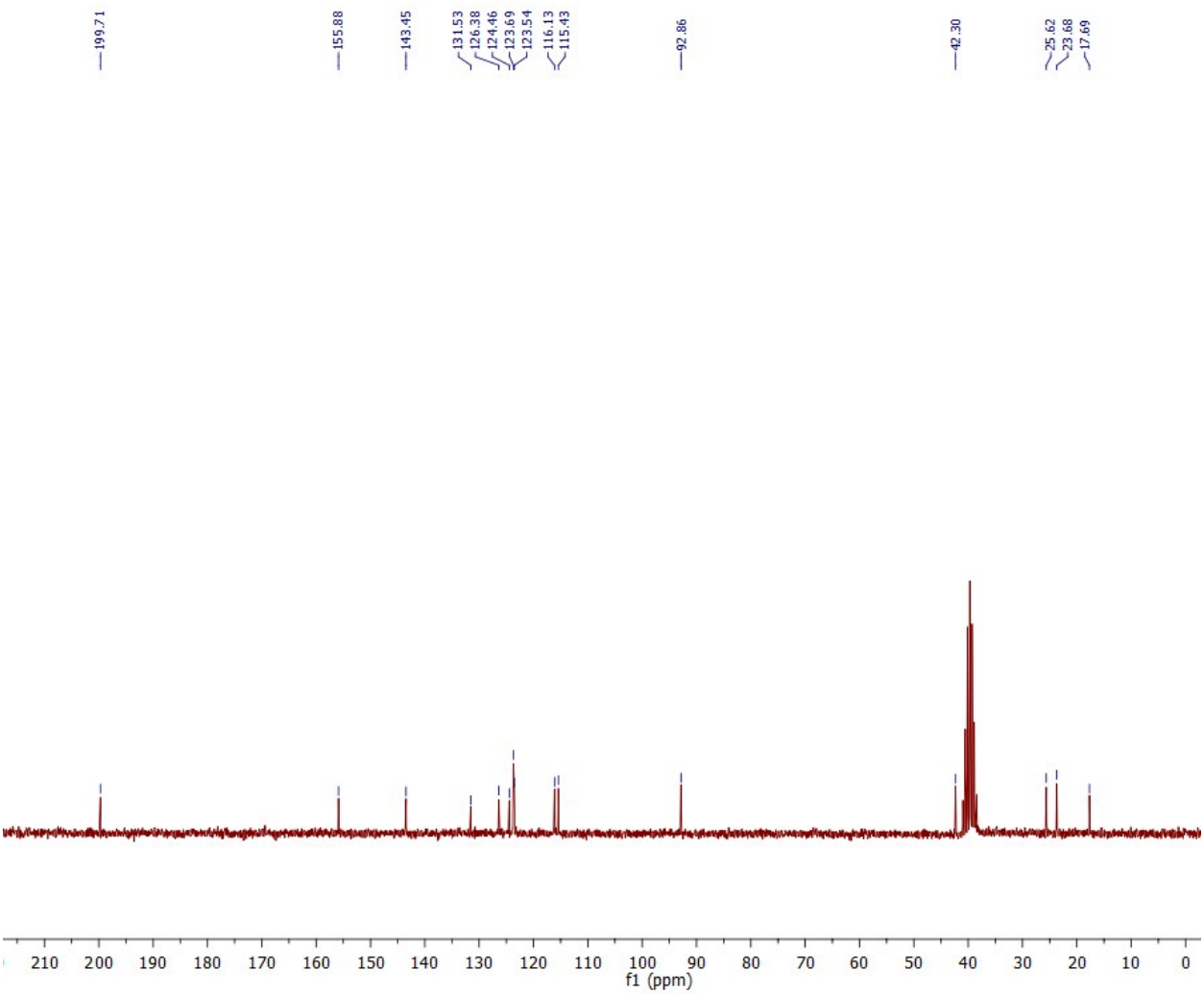
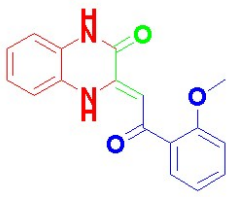


Fig. S9 ^{13}C NMR spectrum of **4d**

3,4-dihydro-3-[2-oxo-2-(2-methoxyphenyl)ethylidene]-2(1H)-quinoxalinone (4e)



Orange powder; yield: 78 (64)%; mp = 278-279˚C; IR (KBr): ν 3436, 2984, 2840, 1683, 1592, 1371, 1241, 1169 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 3.87 (s, 3H, OCH_3), 6.82 (s, 1H, CH), 7.10-7.17 (q, 4H, CH_{Ar}), 7.44-7.49 (m, 3H, CH_{Ar}), 7.52-7.68 (m, 1H, CH_{Ar}), 11.96 (br. s, 1H, NH), 13.53 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 56.0, 95.2, 112.6, 115.5, 116.6, 120.7, 123.9, 124.0, 124.5, 126.9, 129.3, 129.8, 132.8, 144.7, 156.1, 157.6, 189.3 ppm; ESI-MS: m/z (%) = 294 $[M]^+$; Anal. Calcd. for $C_{17}H_{14}N_2O_3$ (%): C 69.38, H 4.79, N 9.52; found: C 69.45, H 4.81, N 9.47.

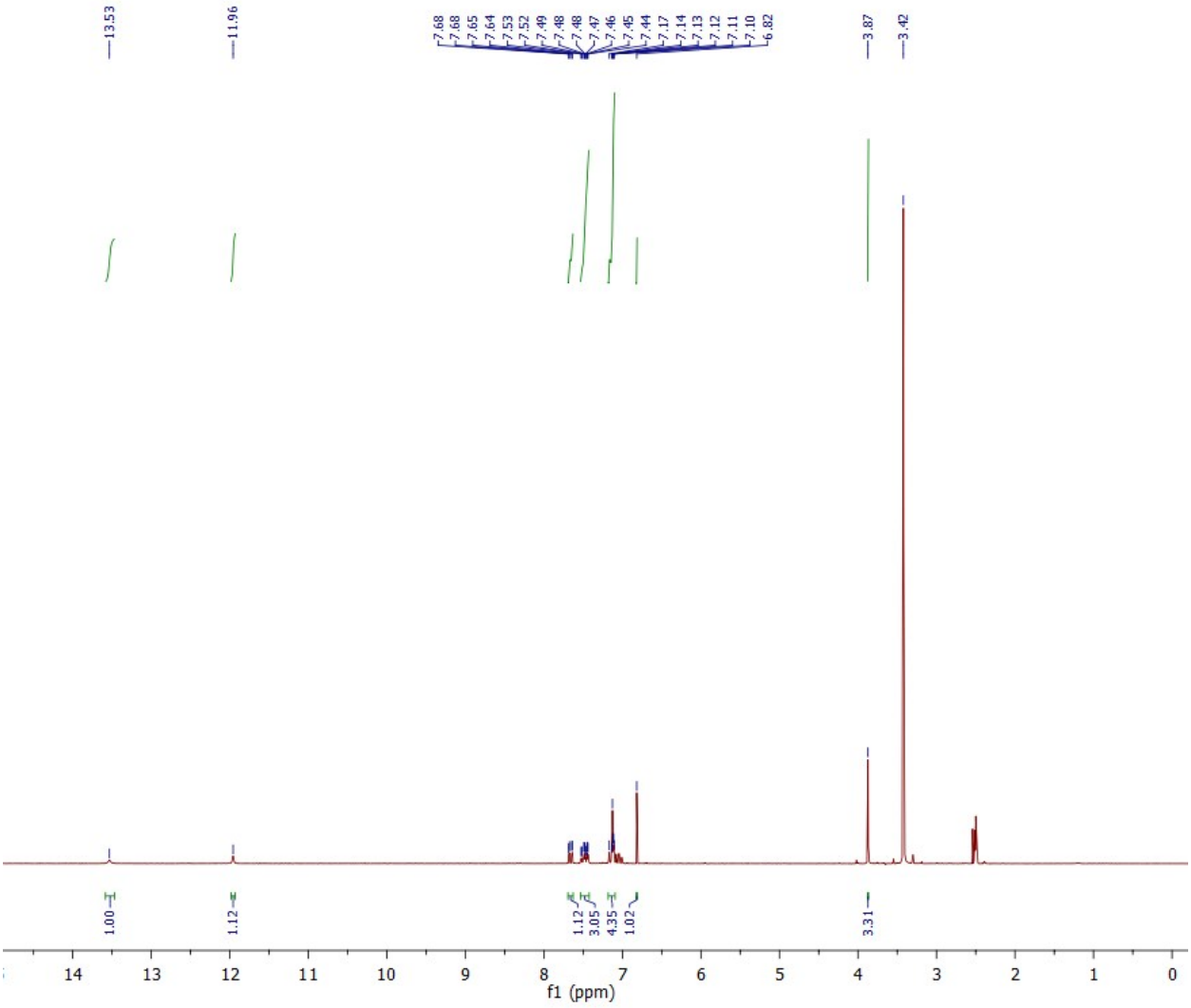


Fig. S10 ^{1}H NMR spectrum of **4e**

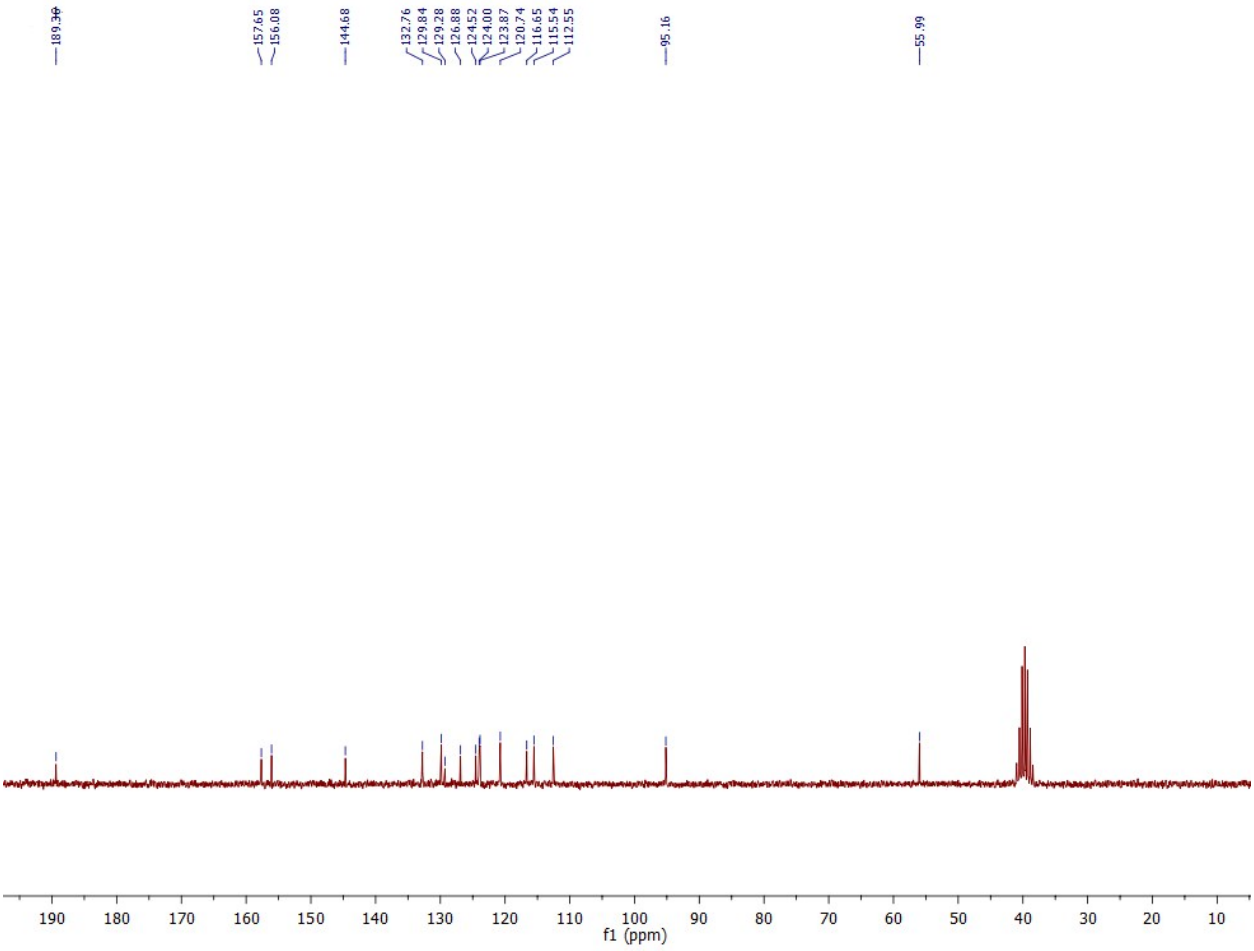
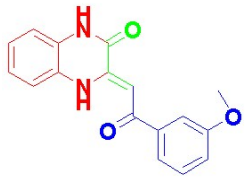


Fig. S11 ^{13}C NMR spectrum of **4e**

3,4-dihydro-3-[2-oxo-2-(3-methoxyphenyl)ethylidene]-2(1H)-quinoxalinone (4f)



Yellow powder; yield: 90 (94)%; mp = 263°C; IR (KBr): ν 3435, 3052, 2924, 1686, 1604, 1587, 1379 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 3.82 (s, 3H, OCH_3), 6.77 (s, 1H, CH), 7.12-7.14 (d, 4H, CH_{Ar}), 7.38-7.57 (m, 4H, CH_{Ar}), 12.04 (br. s, 1H, NH), 13.67 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 55.4, 89.4, 111.8, 115.5, 116.7, 118.0, 119.6, 123.8, 124.2, 124.2, 126.9, 130.0, 140.3, 145.8, 155.8, 159.7, 188.2 ppm; ESI-MS: m/z (%) = 317 $[M + Na]^+$; Anal. Calcd. for $C_{17}H_{14}N_2O_3$ (%): C 69.38, H 4.79, N 9.52; found: C 69.27, H 4.85, N 9.50.

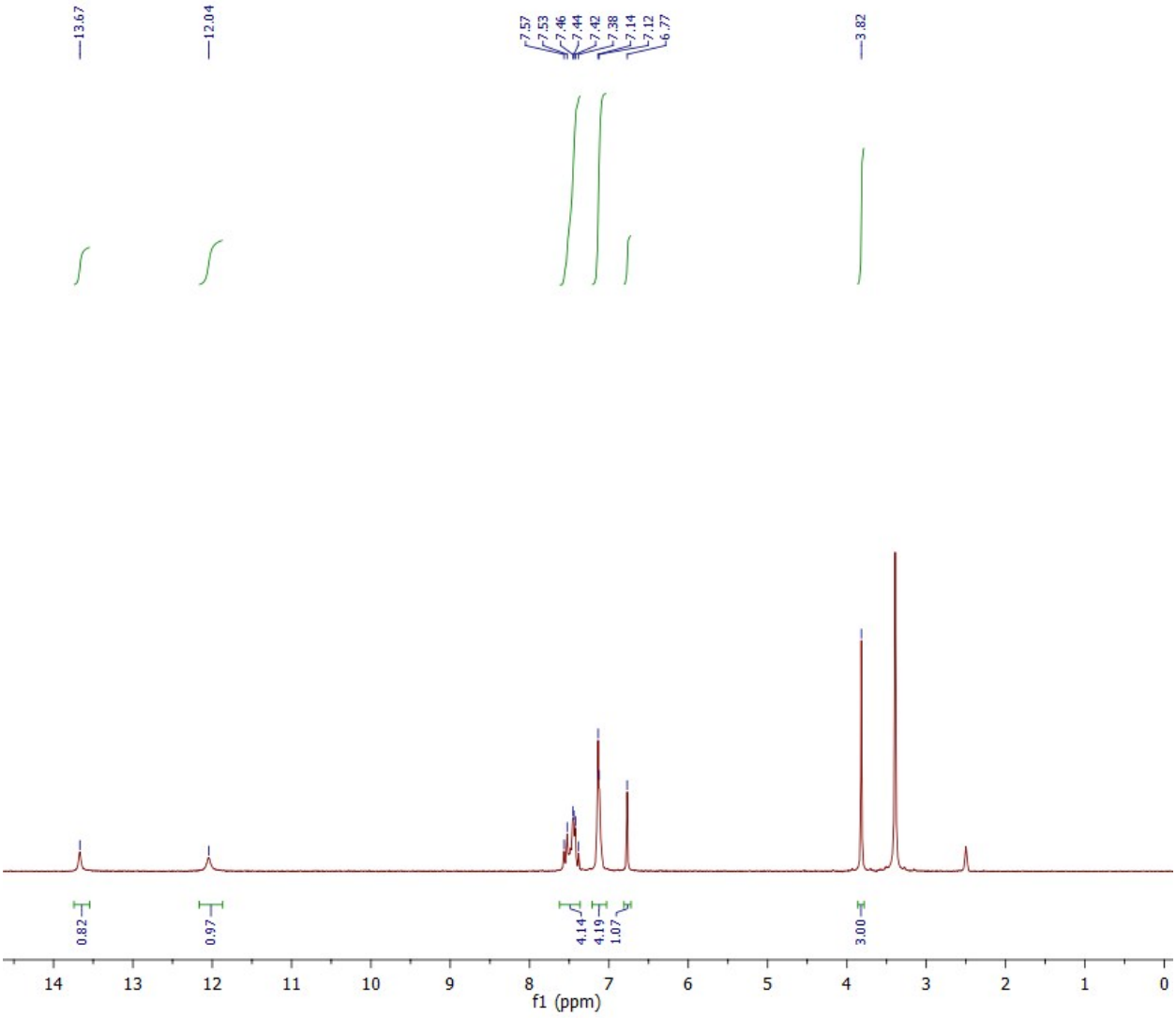


Fig. S12 ^{1}H NMR spectrum of **4f**

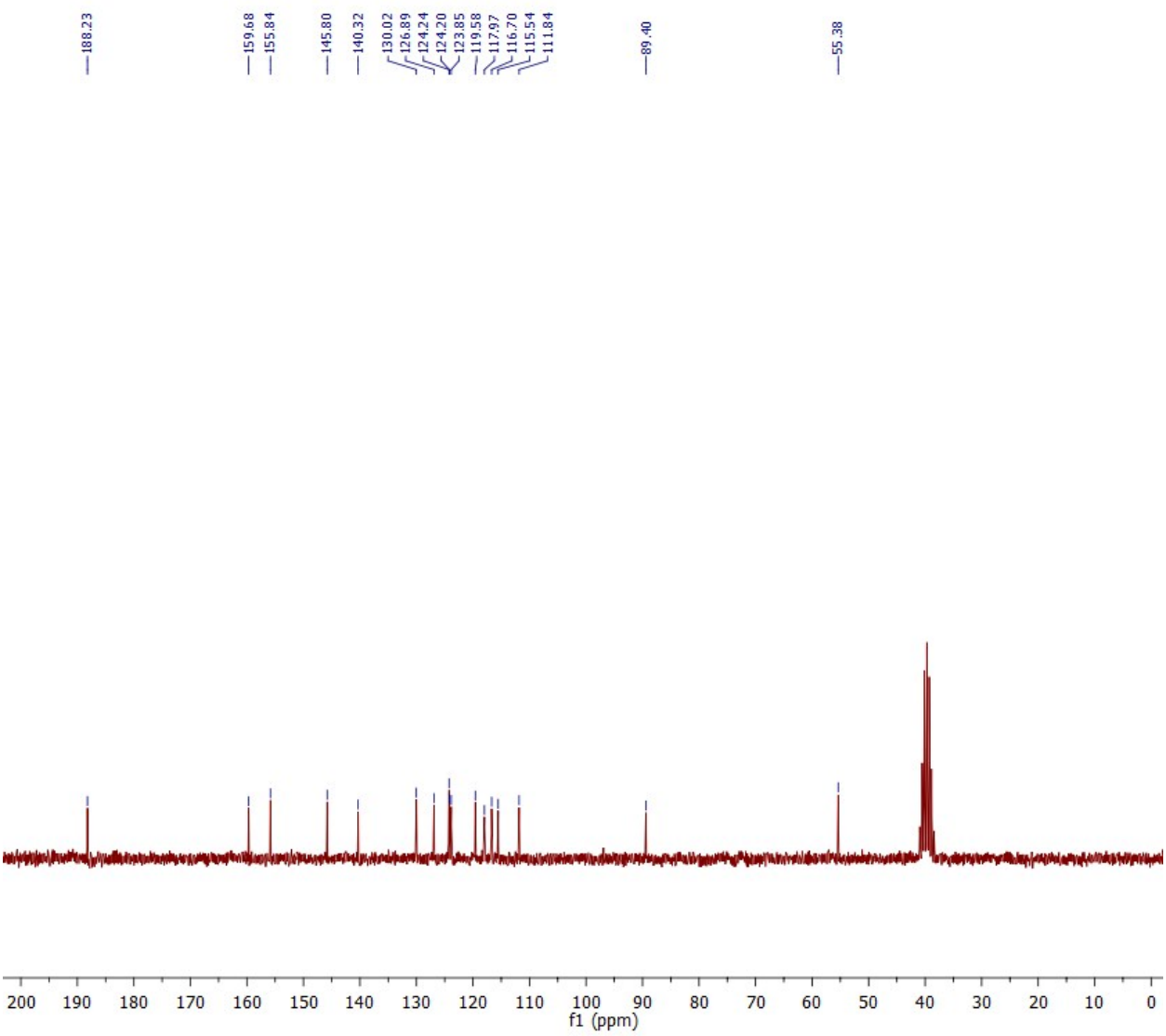
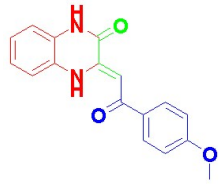


Fig. S13 ^{13}C NMR spectrum of **4f**

3,4-dihydro-3-[2-oxo-2-(4-methoxyphenyl)ethylidene]-2(1H)-quinoxalinone (4g)



Orange powder; yield: 86 (95)%; mp = 241˚C; IR (KBr): ν 3437, 2965, 2842, 1681, 1597, 1373, 1246, 1172 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 3.82 (s, 3H, OCH_3), 6.76 (s, 1H, CH), 6.99-7.13 (m, 5H, CH_{Ar}), 7.38-7.46 (m, 1H, CH_{Ar}), 7.90-7.98 (m, 2H, CH_{Ar}), 11.96 (br. s, 1H, NH), 13.57 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 55.6, 89.2, 114.2, 115.6, 116.4, 123.9, 124.5, 126.7, 129.4, 131.6, 145.2, 156.1, 162.6, 188.0 ppm; ESI-MS: m/z (%) = 294 $[M]^+$; Anal. Calcd. for $C_{17}H_{14}N_2O_3$ (%): C 69.38, H 4.79, N 9.52; found: C 69.49, H 4.75, N 9.47.

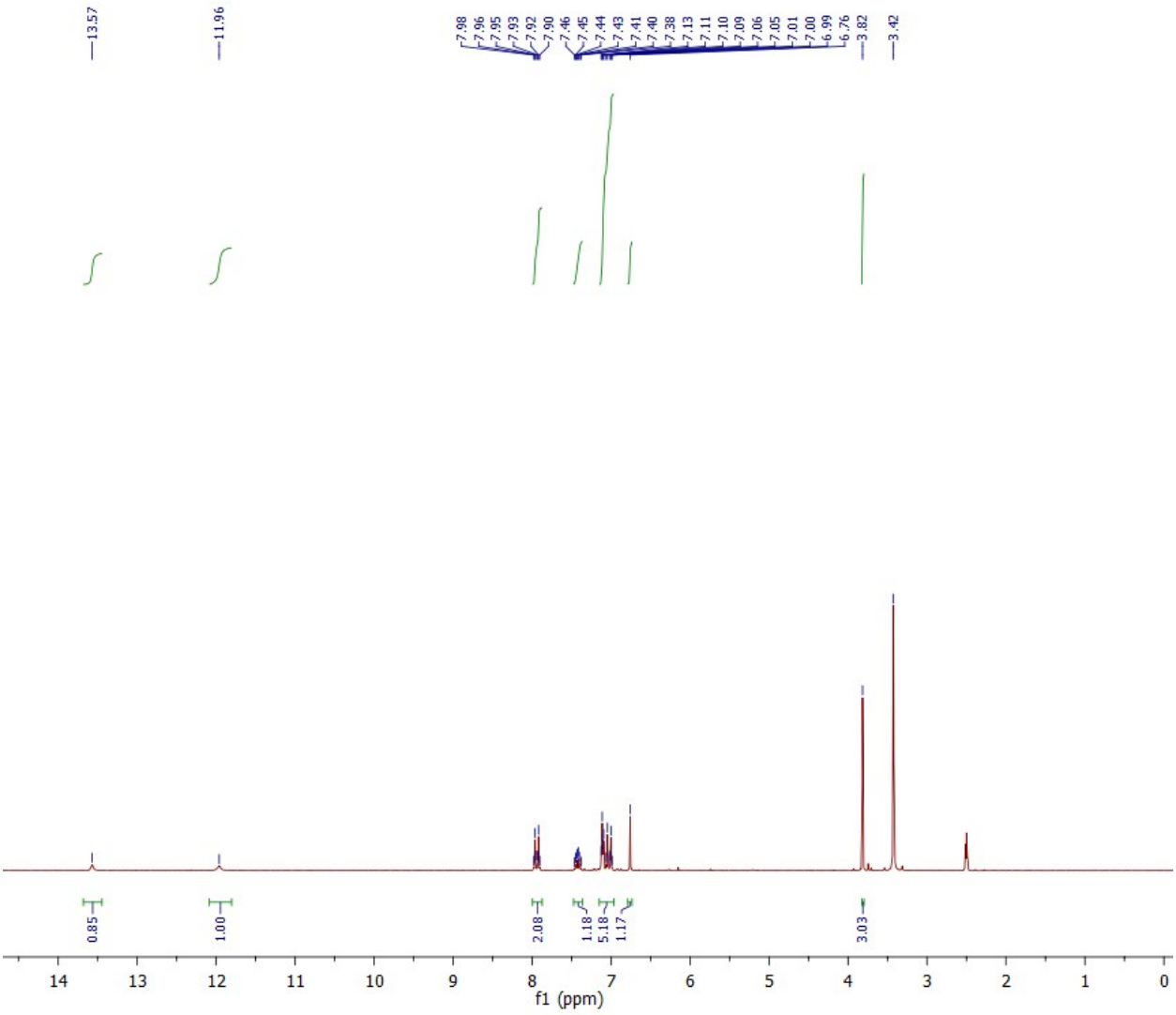


Fig. S14 ^{1}H NMR spectrum of **4g**

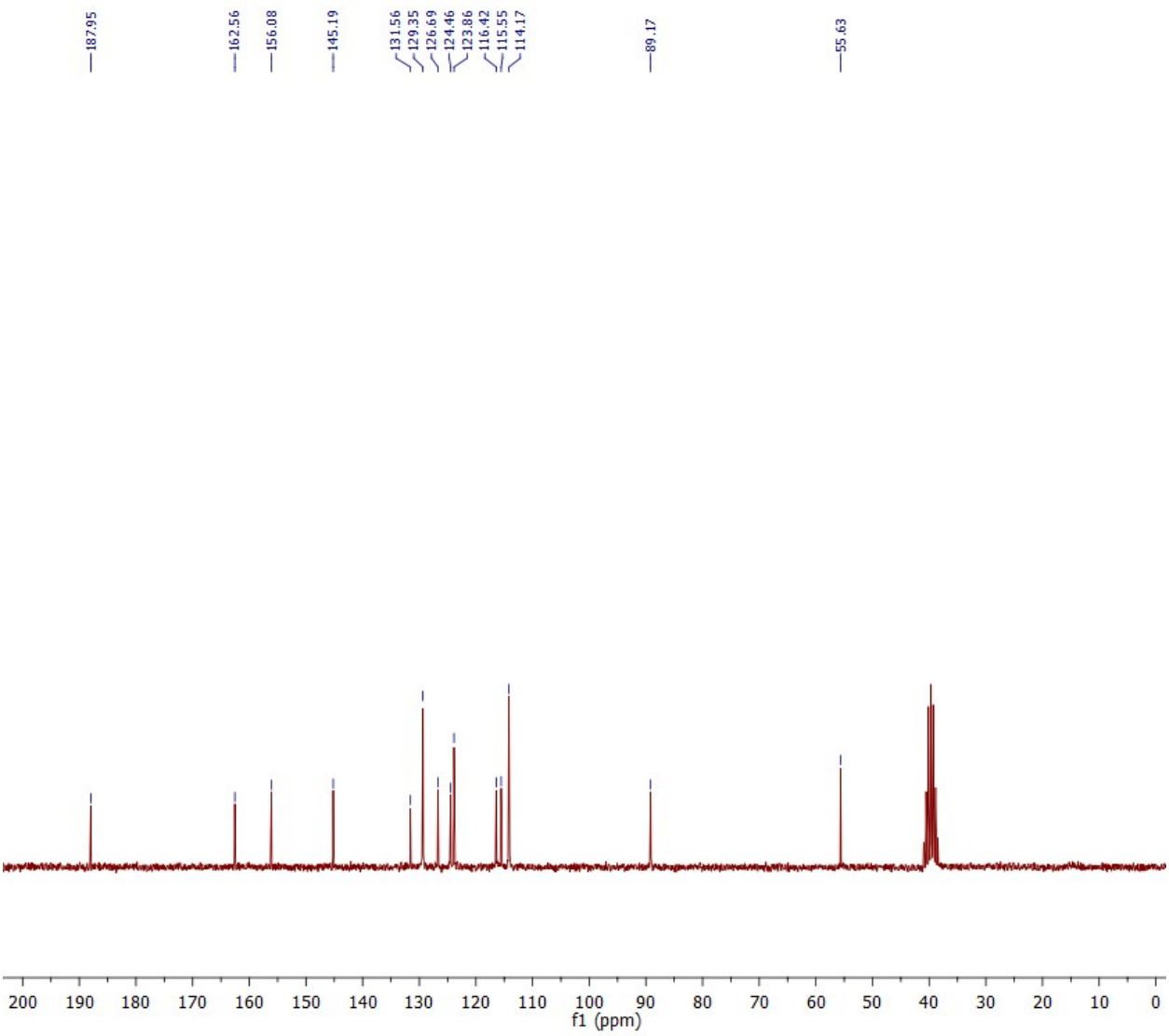
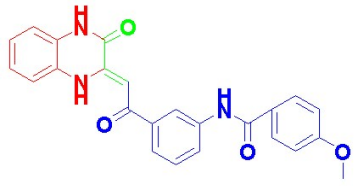


Fig. S15 ^{13}C NMR spectrum of **4g**

3,4-dihydro-3-[2-(3-(N-4-methoxybenzoyl)phenyl)-2-oxo-ethylidene]-2(1H)-quinoxalinone (4h)



Yellow powder; yield: 90 (97)%; mp = 297˚C; IR (KBr): ν 3412, 3359, 3285, 2964, 1683, 1650, 1607, 1594, 1378, 1255, 1214 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 3.85 (s, 3H, OCH_3), 6.85 (s, 1H, CH), 7.46-7.54 (t, 5H, CH_{Ar}), 7.68-7.72 (m, 3H, CH_{Ar}), 7.99-8.08 (m, 3H, CH_{Ar}), 8.46 (s, 1H, CH_{Ar}), 10.32 (br. s, 1H, NH), 12.10 (br. s, 1H, NH), 13.67 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 55.6, 89.3, 113.8, 115.6, 116.7, 119.0, 122.1, 123.6, 123.8, 124.2, 124.3, 126.9, 129.2, 129.8, 139.2, 140.0, 145.8, 155.9, 162.2, 165.2, 188.4 ppm; ESI-MS: m/z (%) = 414 $[M + H]^+$; Anal. Calcd. for $C_{24}H_{19}N_3O_4$ (%): C 69.72, H 4.63, N 10.16; found: C 69.64, H 4.74, N 10.15.

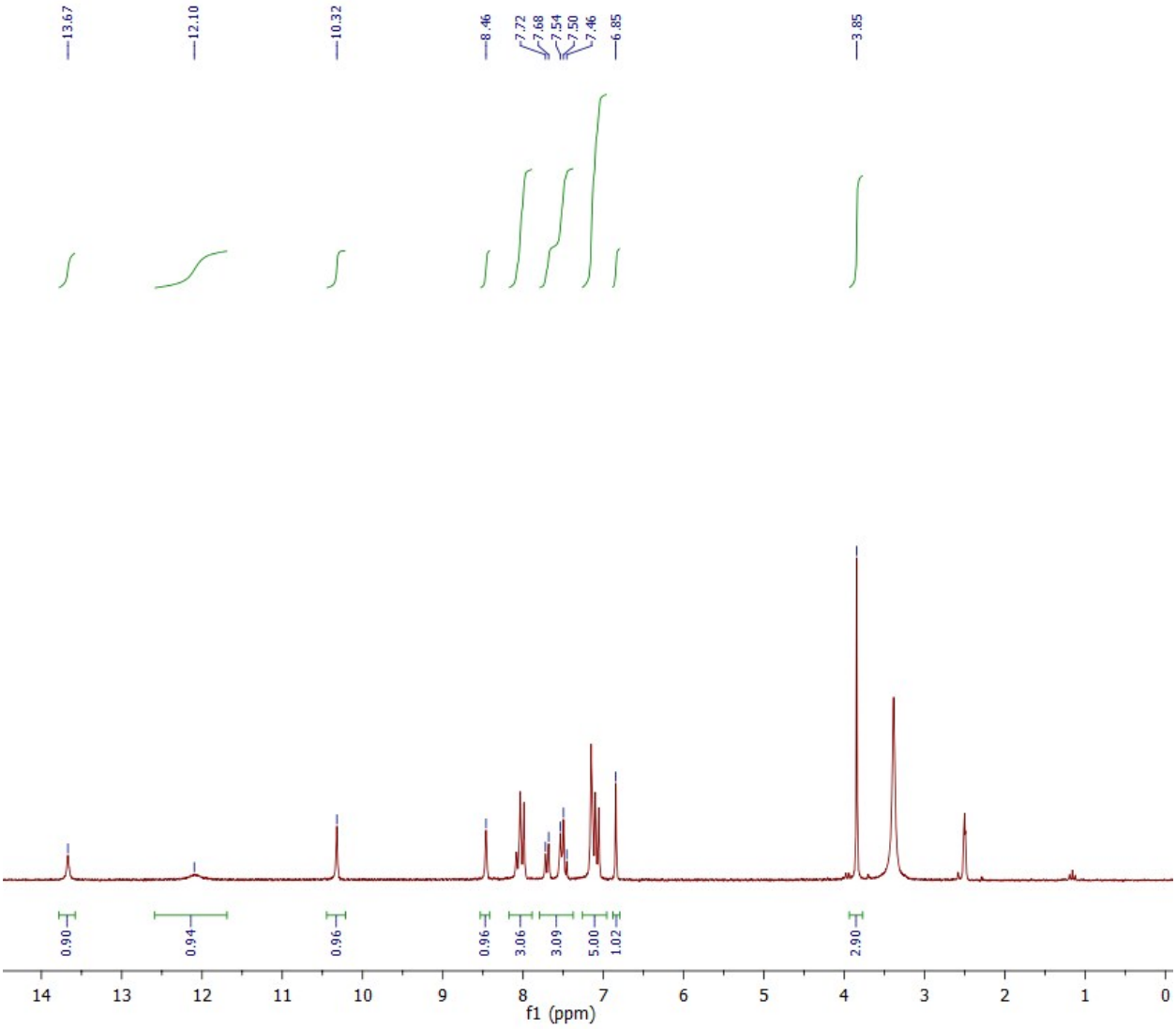


Fig. S16 ^{1}H NMR spectrum of **4h**

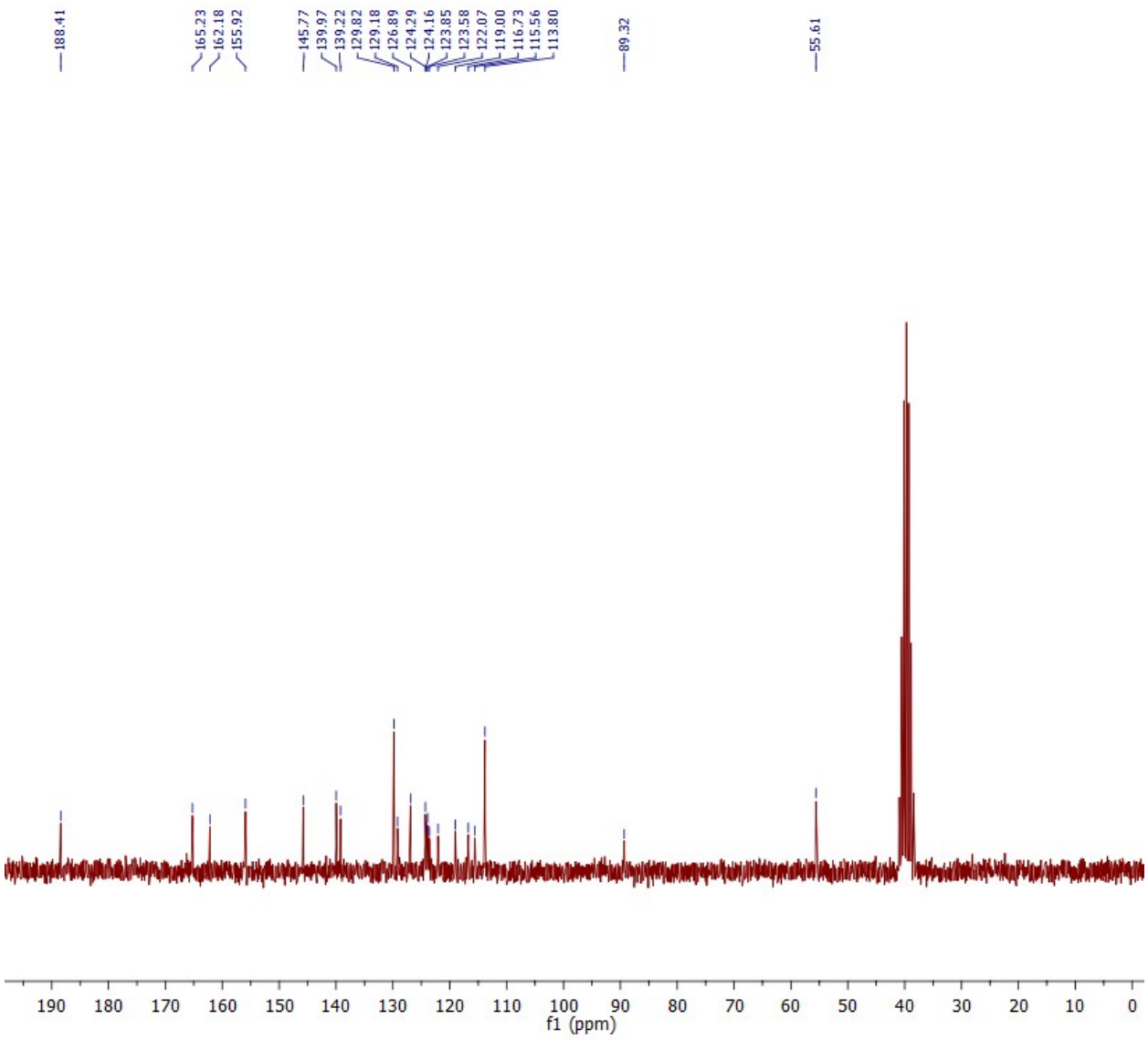
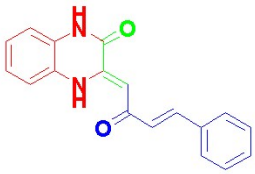


Fig. S17 ^{13}C NMR spectrum of **4h**

3,4-dihydro-3-(2-oxo-4-phenyl-but-3-enylidene)-2(1H)-quinoxalinone (4i)



Orange powder; yield: 87 (95)%; mp = 247°C; IR (KBr): ν 3437, 2876, 1675, 1606, 1576, 1378 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 6.37 (s, 1H, CH), 7.12-7.16 (m, 4H, CH_{Ar}), 7.38-7.48 (m, 5H, CH_{Ar}), 7.69-7.74 (m, 2H, CH), 12.02 (br. s, 1H, NH), 13.84 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 94.6, 115.5, 117.4, 123.8, 124.9, 127.2, 128.0, 128.3, 129.0, 135.2, 138.6, 146.3, 155.7, 185.5 ppm; ESI-MS: m/z (%) = 290 $[M]^+$; Anal. Calcd. for $C_{18}H_{14}N_2O_2$ (%): C 74.47, H 4.86, N 9.65; found: C 74.33, H 4.80, N 9.64.

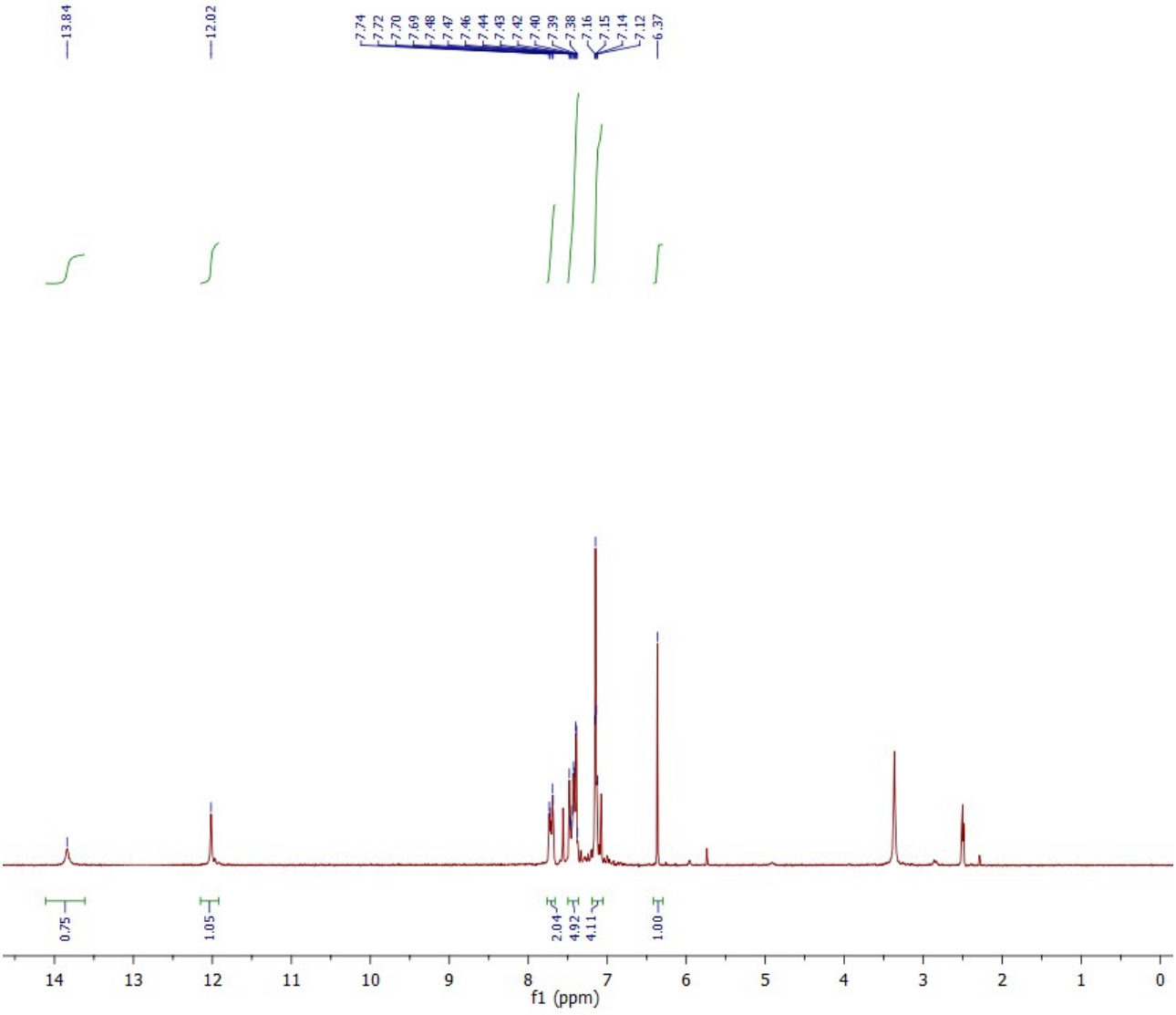


Fig. S18 ^{1}H NMR spectrum of **4i**

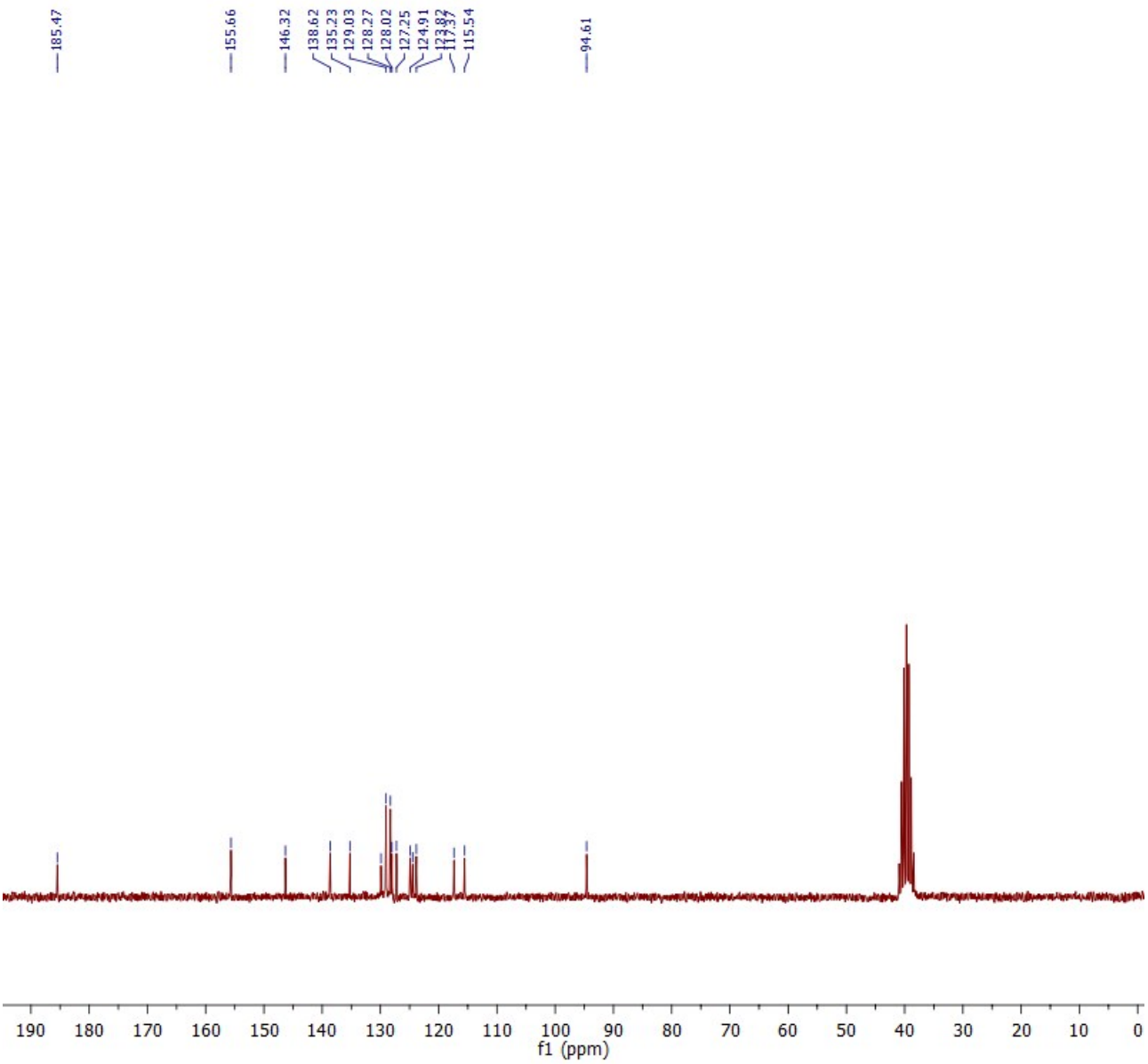
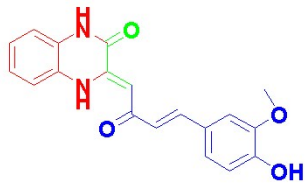


Fig. S19 ^{13}C NMR spectrum of **4i**

3,4-dihydro-3-[2-oxo-4-(4-hydroxy-3-methoxyphenyl)but-3-enylidene]-2(1H)-quinoxalinone (4j)



Yellow powder; yield: 81 (94)%; mp = 211-214°C; IR (KBr): 3561, 2871, 1670, 1611, 1584, 1345 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 3.84 (s, 3H, OCH_3), 6.33 (s, 1H, CH), 6.78-6.82 (d, 1H, CH), 6.95-7.13 (m, 5H, CH_{Ar}), 7.34-7.49 (m, 3H, CH + CH_{Ar}), 9.57 (br. s, 1H, OH), 11.94 (br. s, 1H, NH), 13.73 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 55.8, 94.6, 111.2, 115.5, 115.8, 116.9, 123.2, 123.8, 124.1, 125.0, 125.2, 126.8, 127.0, 139.6, 145.5, 148.1, 149.1, 155.8, 186.6 ppm; ESI-MS: m/z (%) = 337 $[M + H]^+$; Anal. Calcd. for $C_{19}H_{16}N_2O_4$ (%): C 67.85, H 4.79, N 8.33; found: C 67.90, H 4.68, N 8.24.

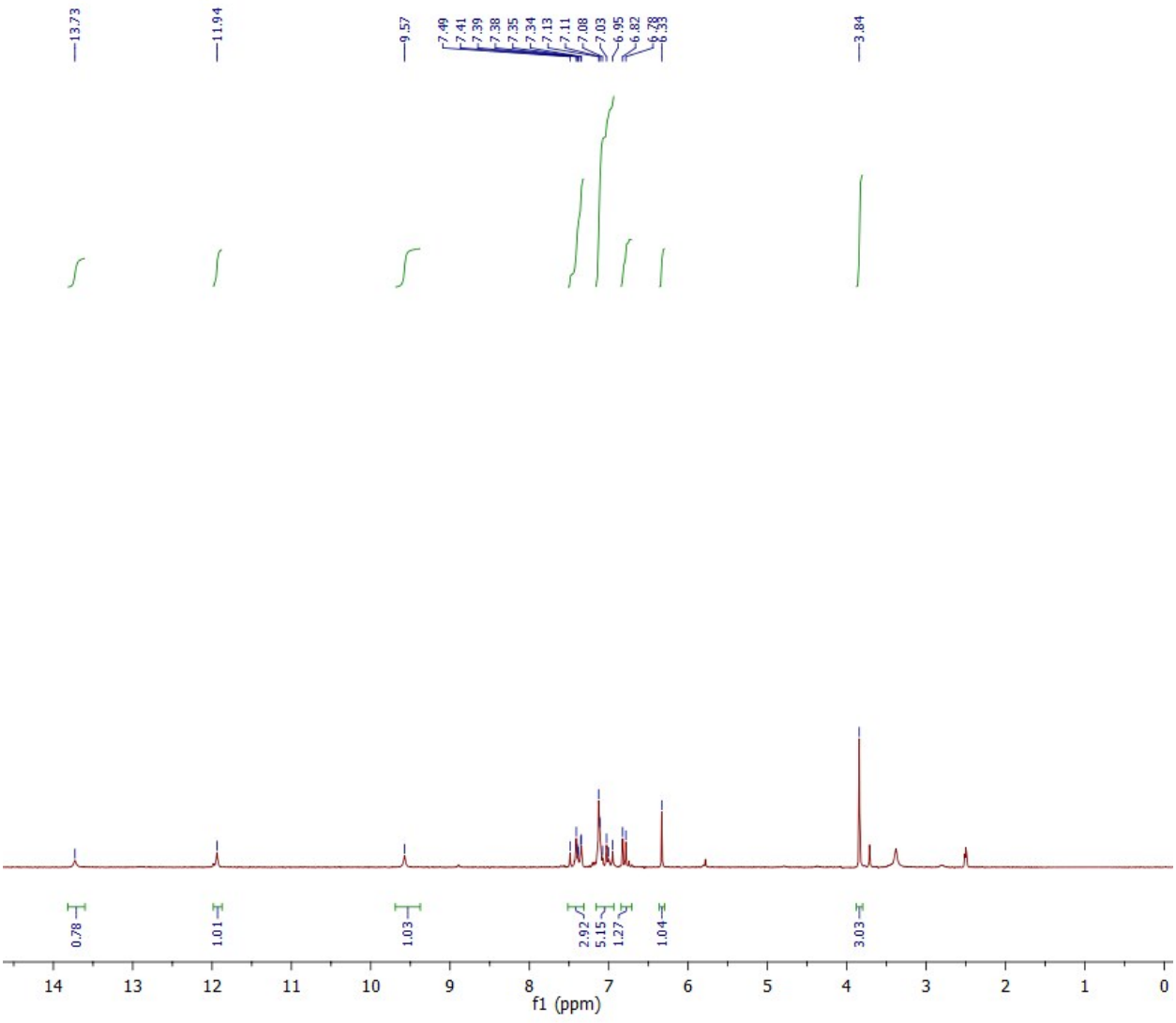


Fig. S20 ^{1}H NMR spectrum of **4j**

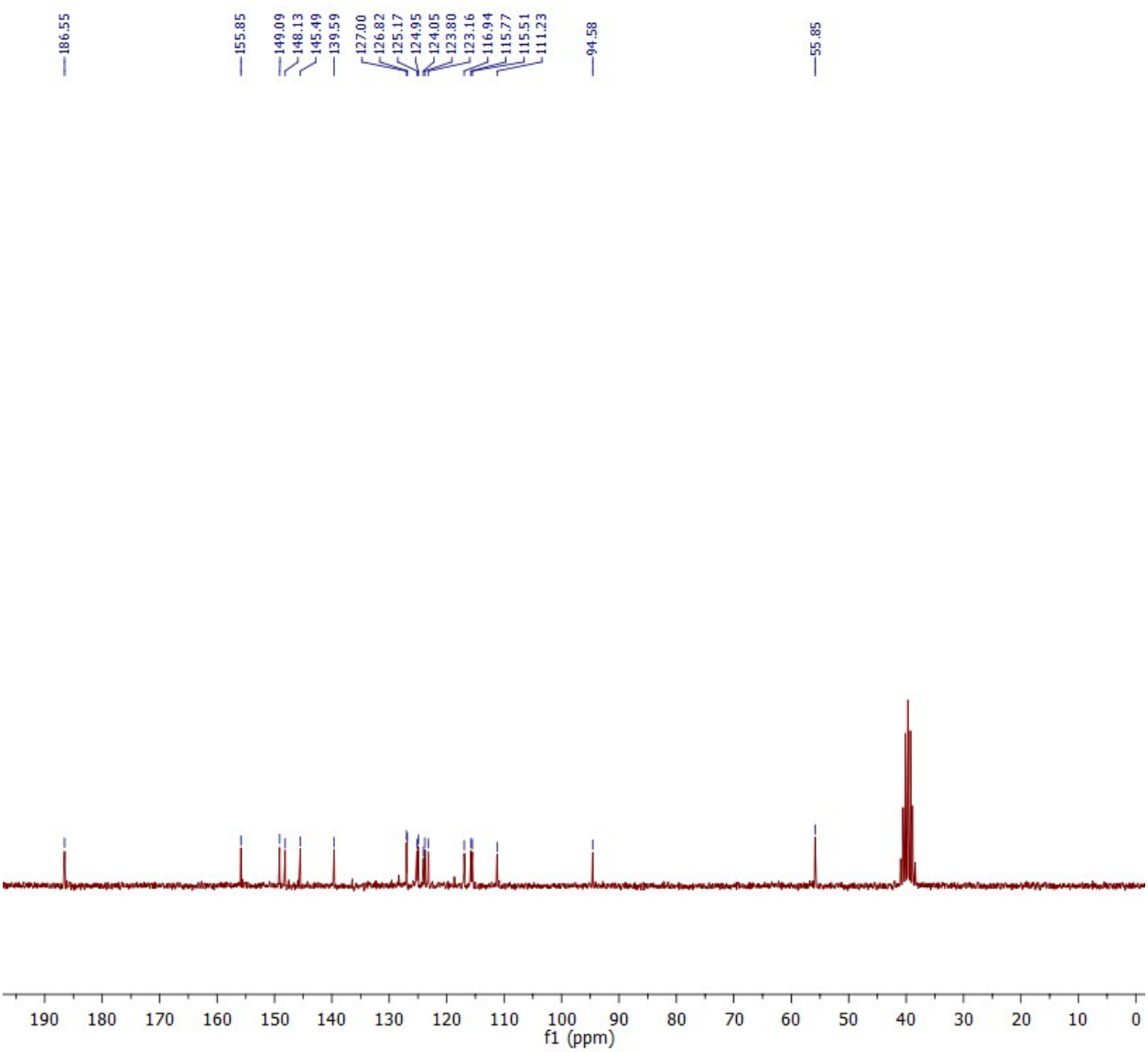
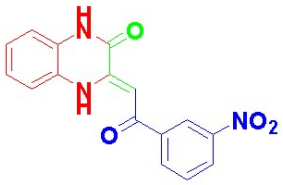


Fig. S21 ^{13}C NMR spectrum of **4j**

3,4-dihydro-3-[2-oxo-2-(3-nitrophenyl)ethylidene]-2(1H)-quinoxalinone (4k)



Orange powder; yield: 89 (78)%; mp > 300°C; IR (KBr): ν 3438, 3170, 2928, 1701, 1689, 1605, 1531, 1347 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 6.83 (s, 1H, CH), 7.16 (s, 3H, CH_{Ar}), 7.55 (s, 1H, CH_{Ar}), 7.76-7.84 (t, 1H, CH_{Ar}), 8.37-8.63 (d + s, 3H, CH_{Ar}), 12.16 (br. s, 1H, NH), 13.68 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 89.0, 115.6, 117.1, 121.5, 124.0, 124.8, 126.3, 127.2, 130.8, 133.3, 140.1, 146.7, 148.4, 155.6, 185.6 ppm; ESI-MS: m/z (%) = 308 $[M - H]^+$; Anal. Calcd. for $C_{16}H_{11}N_3O_4$ (%): C 62.14, H 3.58, N 13.59; found: C 62.21, H 3.64, N 13.60.

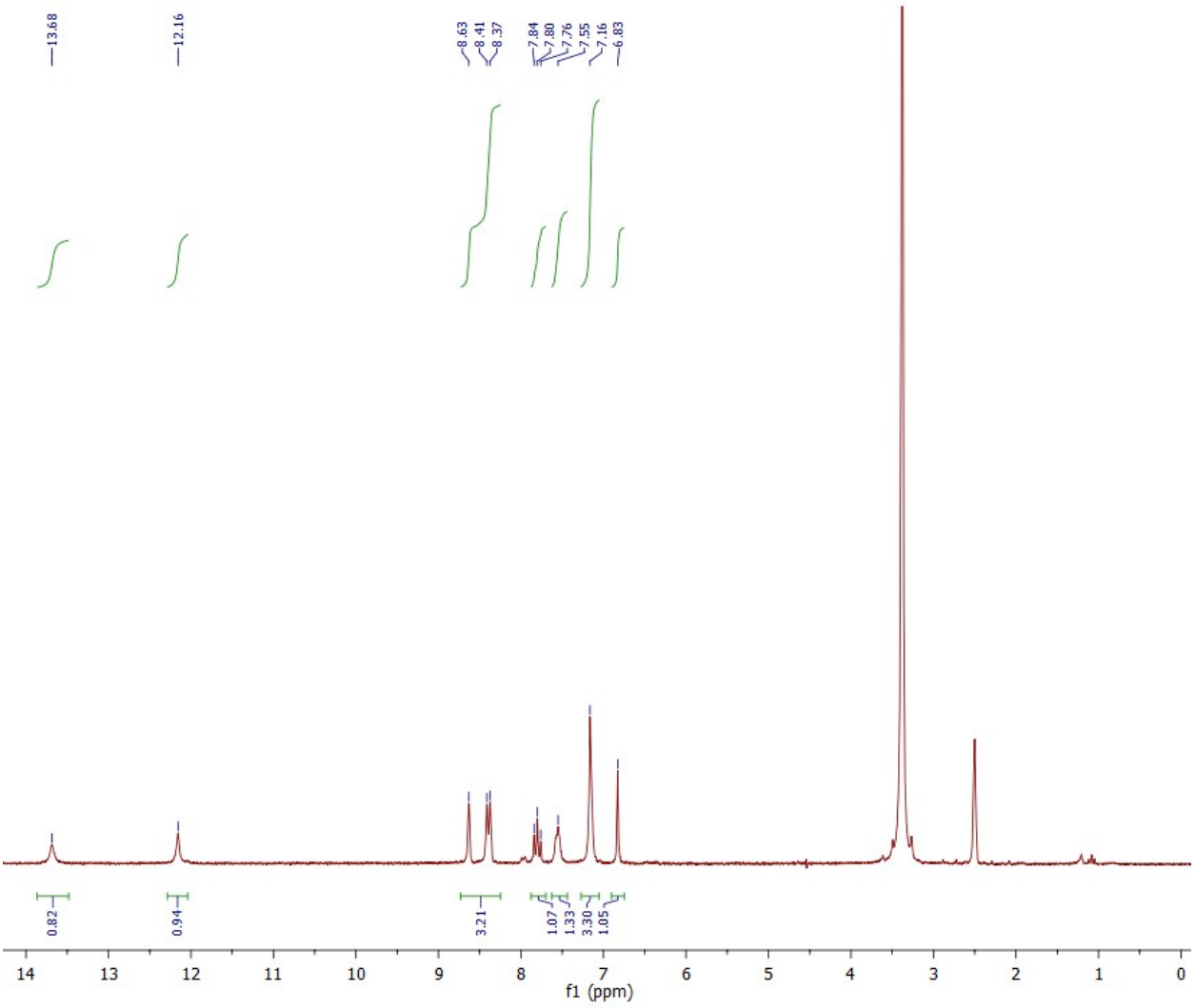


Fig. S22 ^{1}H NMR spectrum of **4k**

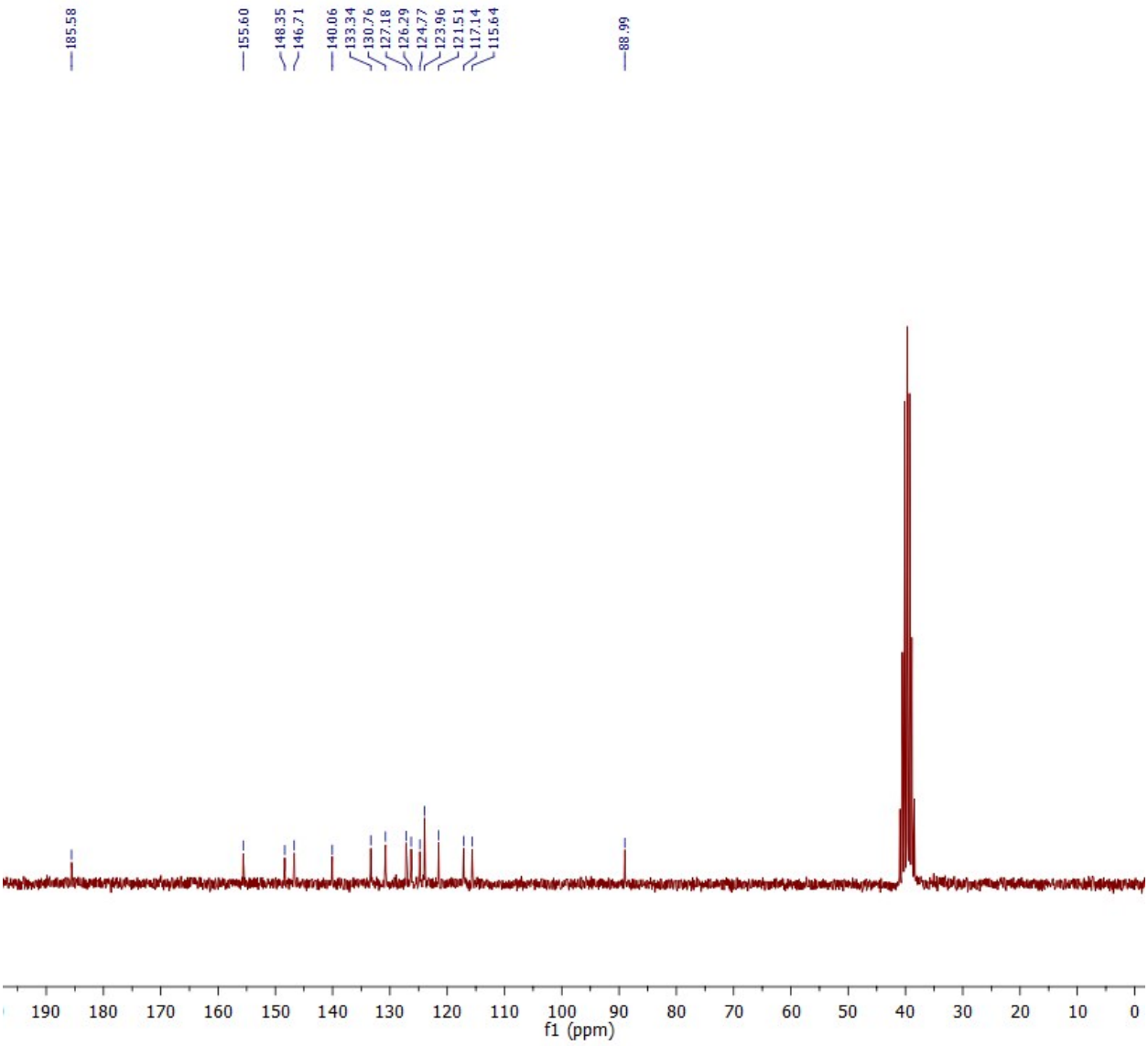
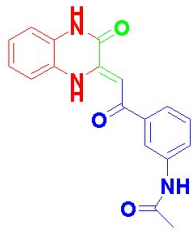


Fig. S23 ^{13}C NMR spectrum of **4k**

3,4-dihydro-3-[2-oxo-2-(3-N-acetylphenyl)ethylidene]-2(1H)-quinoxalinone (4l)



Yellow powder; yield: 86 (95)%; mp > 300°C; IR (KBr): ν 3438, 3253, 3191, 2925, 1676, 1663, 1607, 1554, 1378 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6): δ = 2.08 (s, 3H, CH_3), 6.79 (s, 1H, CH), 7.14-7.83 (m, 7H, CH_{Ar}), 8.25 (s, 1H, CH_{Ar}), 10.16 (br. s, 1H, NH), 12.06 (br. s, 1H, NH), 13.62 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 24.2, 89.3, 115.5, 116.7, 117.7, 121.7, 122.3, 123.8, 124.3, 126.9, 128.3, 129.3, 139.3, 139.9, 145.7, 155.9, 168.7, 188.4 ppm; ESI-MS: m/z (%) = 322 $[M + H]^+$; Anal. Calcd. for $C_{18}H_{15}N_3O_3$ (%): C 67.28, H 4.70, N 13.08; found: C 67.45, H 4.78, N 13.05.

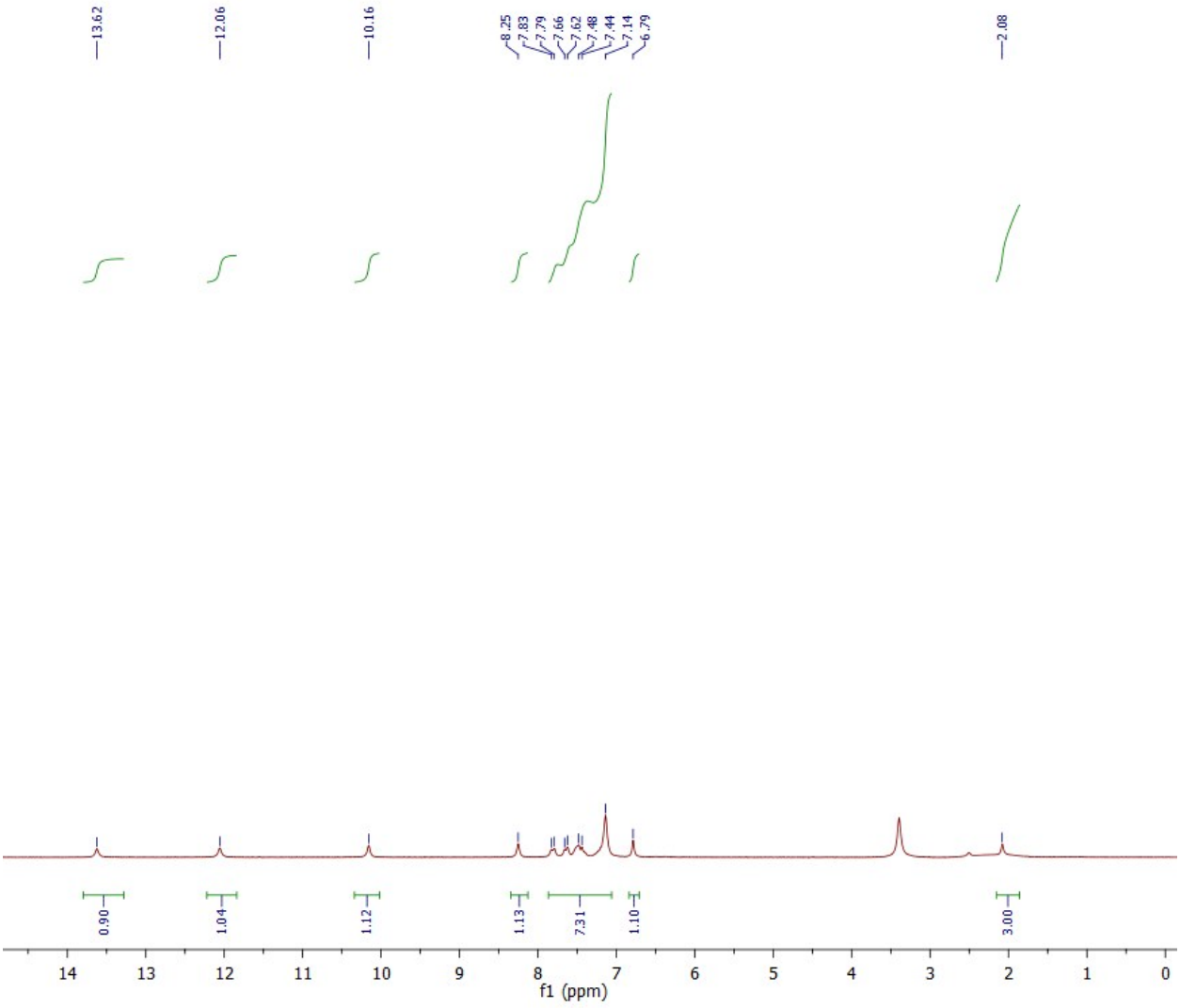


Fig. S24 ^1H NMR spectrum of **4l**

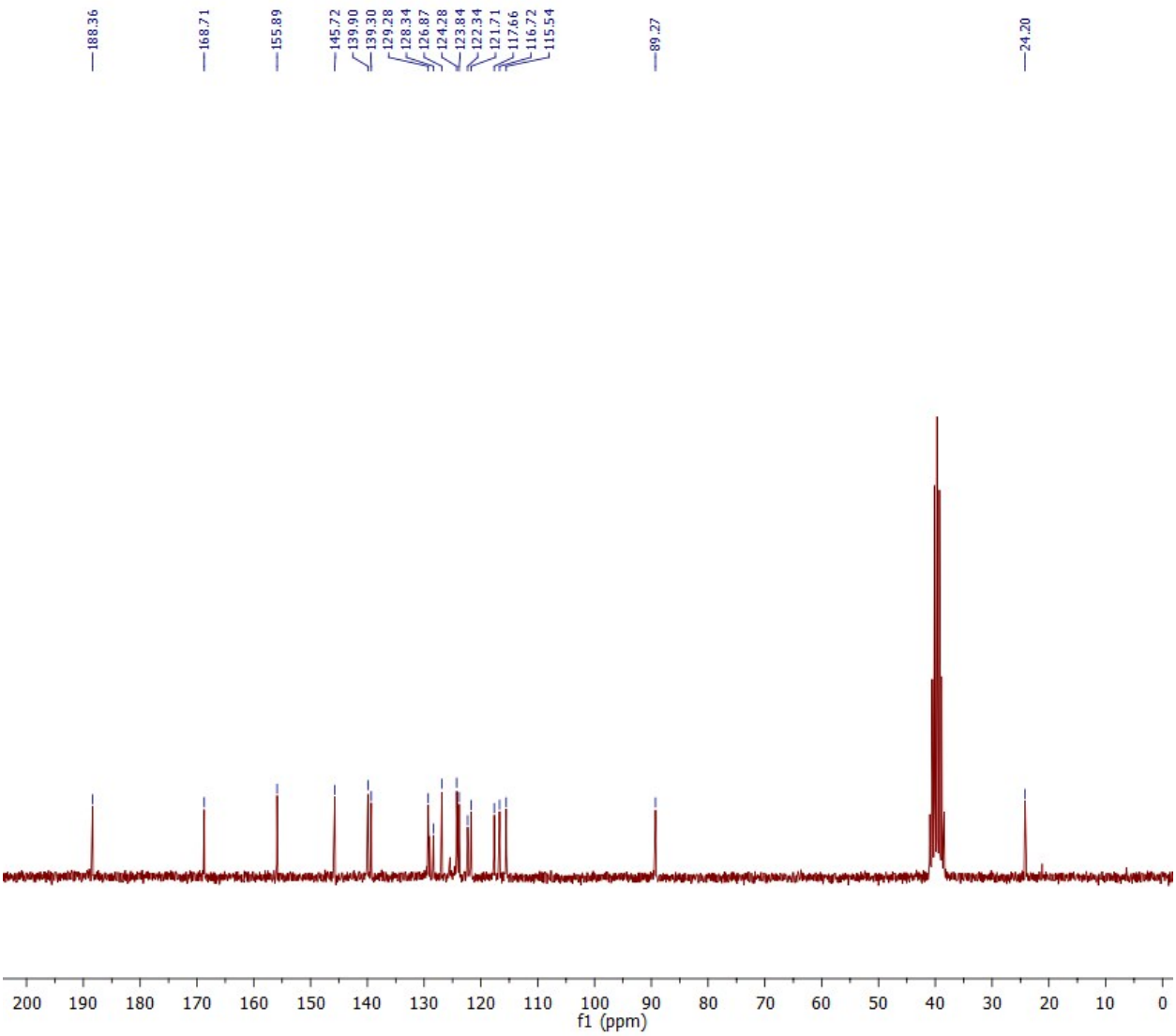
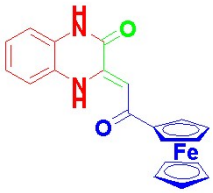


Fig. S25 ^{13}C NMR spectrum of **4l**

3,4-dihydro-3-(2-oxo-2-ferrocenylethylidene)-2(1H)-quinoxalinone (4m)



Red crystals; yield 90 (97)%; mp > 300°C; IR (KBr): ν 3437, 3413, 2855, 1681, 1611, 1561, 1378 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 4.17 (s, 5H, CH_{Fc}), 4.54 (s, 2H, CH_{Fc}), 4.83 (s, 2H, CH_{Fc}), 6.35 (s, 1H, CH), 7.08-7.35 (d, 4H, CH_{Ar}), 11.89 (br. s, 1H, NH), 13.26 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 68.6, 69.7, 71.7, 81.7, 91.2, 115.3, 115.8, 123.1, 123.6, 124.6, 126.2, 142.9, 156.1, 193.6 ppm; ESI-MS: m/z (%) = 372 $[M]^+$; Anal. Calcd. for $C_{20}H_{16}N_2O_2Fe$ (%): C 64.54, H 4.33, N 7.53; found: C 64.60, H 4.41, N 7.47.

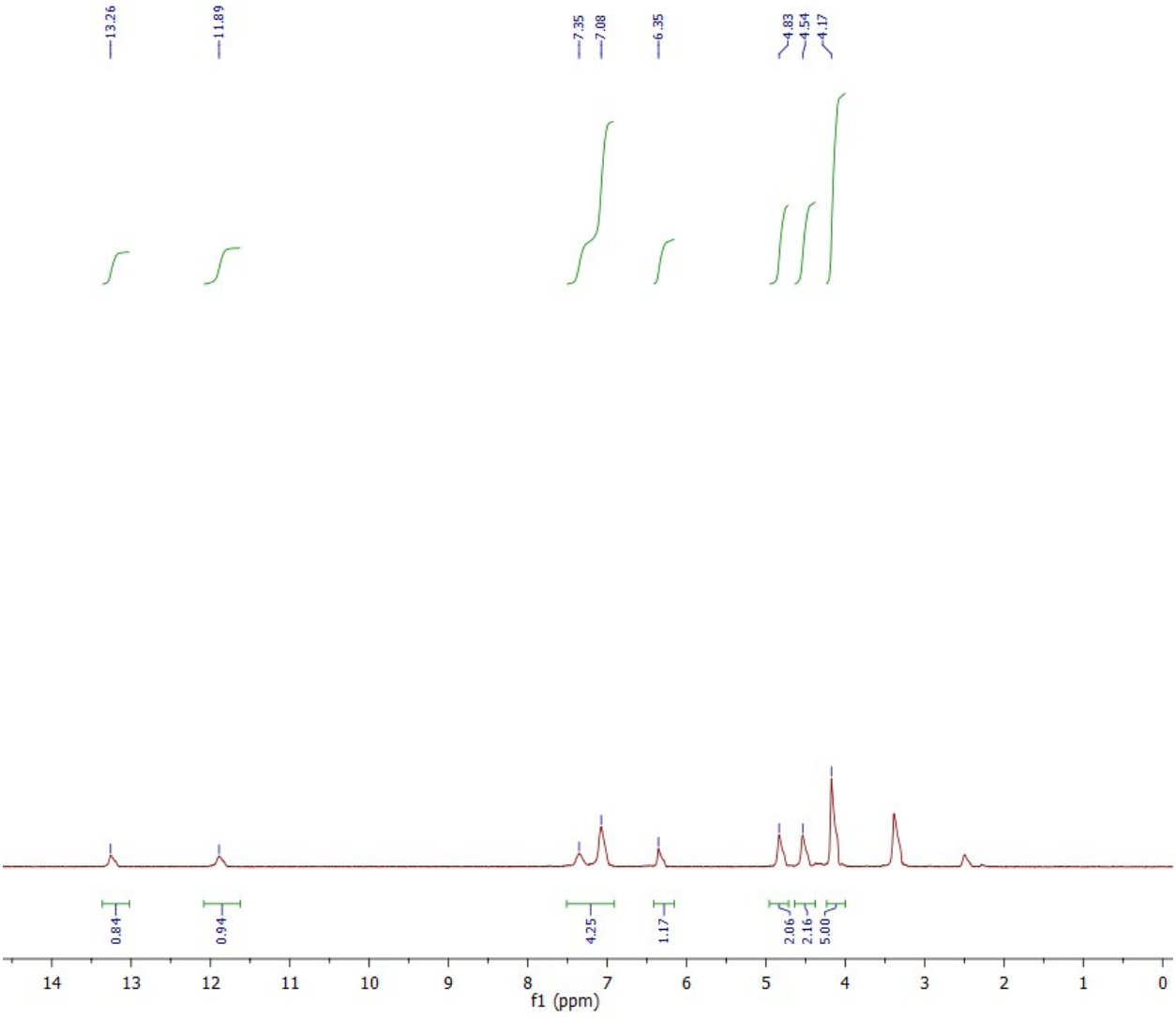


Fig. S26 ^{1}H NMR spectrum of **4m**

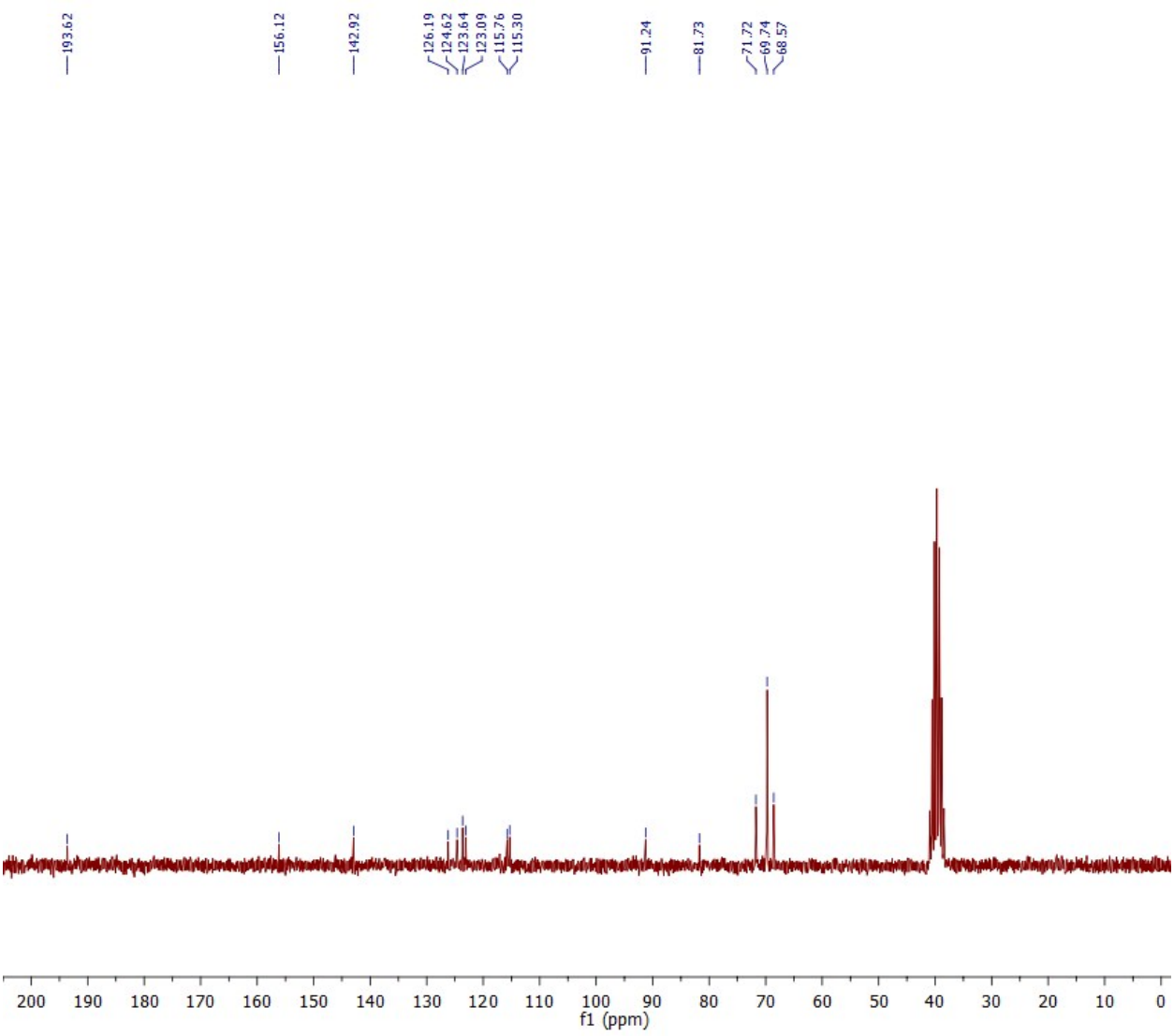
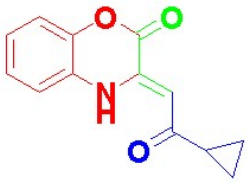


Fig. S27 ^{13}C NMR spectrum of **4m**

3. ^{1}H and ^{13}C NMR spectrums of 5a, 5b, 5f, 5k-o

3,4-dihydro-3-(2-oxo-2-cyclopropylethylidene)-1,4-benzoxazin-2-one (5a)



Yellow powder; yield: 88 (97)%; mp = 189°C; IR (KBr): ν 3483, 3060, 1756, 1627, 1597, 1570, 1388 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.97-1.14 (m, 4H, 2×CH_2), 1.94-2.06 (m, 1H, CH), 6.44 (s, 1H, CH), 6.95-7.27 (m, 4H, CH_{Ar}), 12.45 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.3, 21.9, 97.9, 115.4, 117.0, 123.3, 123.9, 125.7, 136.4, 140.8, 156.2, 202.0 ppm; ESI-MS: m/z (%) = 252 $[M + Na]^+$; Anal. Calcd. for $C_{13}H_{11}NO_3$ (%): C 68.11, H 4.84, N 6.11; found: C 68. 24, H 4.91, N 6.15.

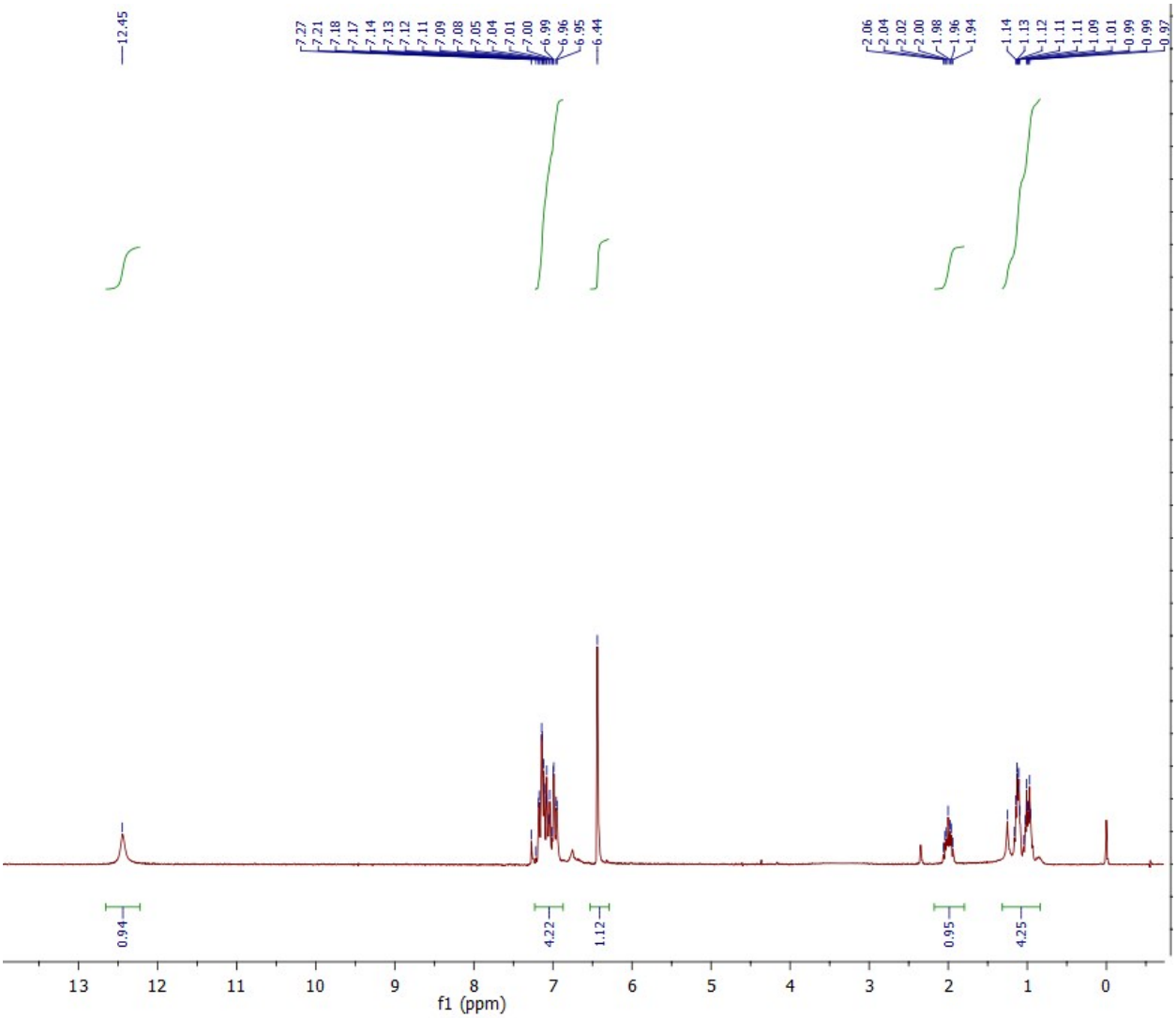


Fig. S28 ^{1}H NMR spectrum of **5a**

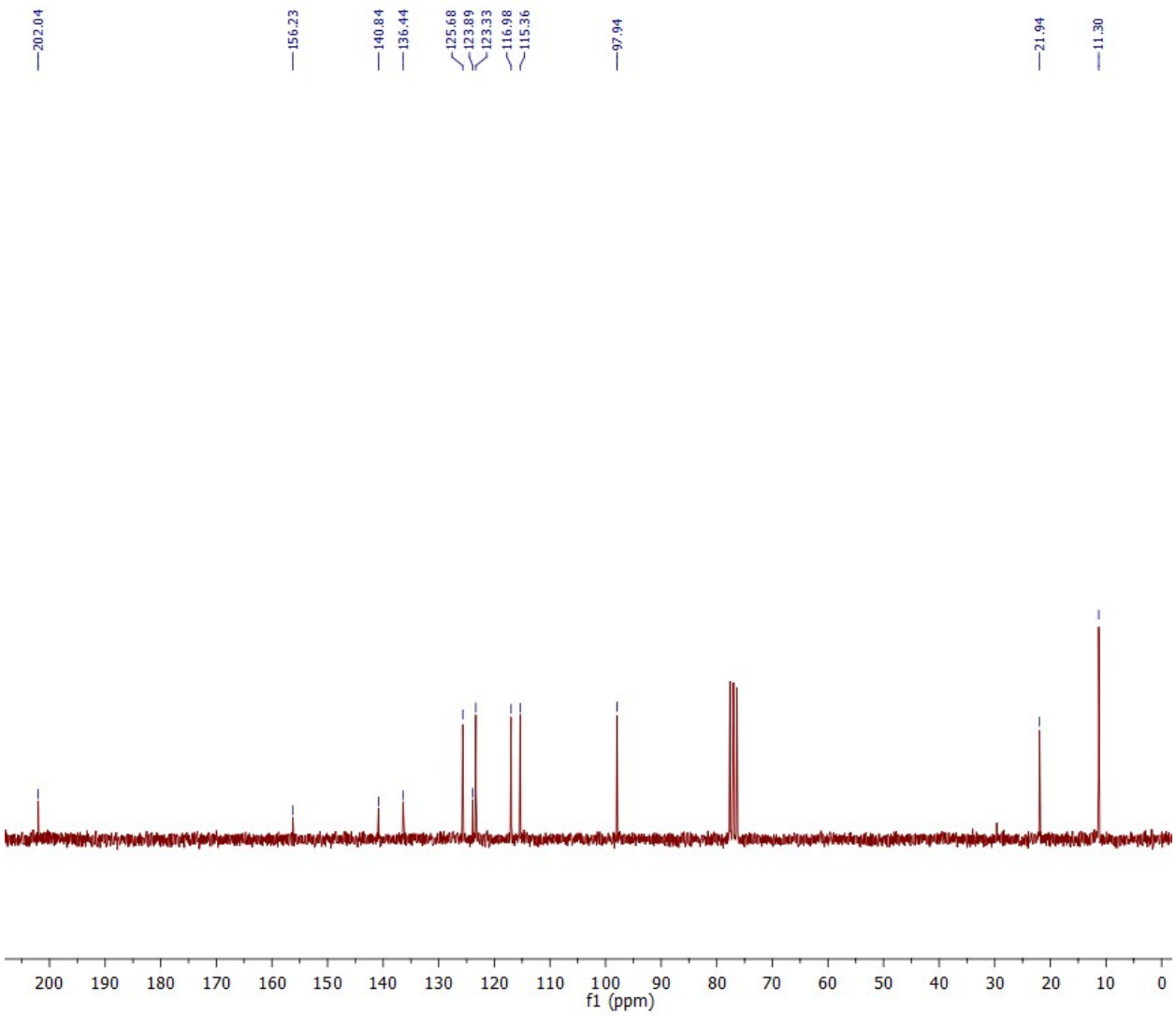
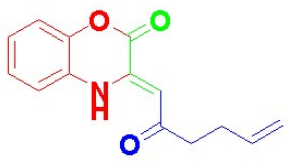


Fig. S29 ^{13}C NMR spectrum of **5a**

3,4-dihydro-3-(2-oxo-hex-5-enylidene)-1,4-benzoxazin-2-one (5b)



Yellow crystals; yield: 93 (84)%; mp = 100° C; IR (KBr): ν 3491, 3061, 2854, 1758, 1638, 1583, 1571, 1499, 1361 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.37-2.47 (q, 2H, CH_2), 2.63-2.70 (t, 2H, CH_2), 4.99-5.12 (m, 2H, CH_2), 5.79-5.93 (m, 1H, CH), 6.32 (s, 1H, CH), 7.00-7.27 (m, 4H, CH_{Ar}), 12.46 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.8, 42.2, 97.6, 115.4, 115.6, 117.0, 126.6, 123.8, 125.7, 136.9, 137.4, 141.0, 156.1, 201.9 ppm; ESI-MS: m/z (%) = 243 $[M]^+$ Anal. Calcd. for $C_{14}H_{13}NO_3$ (%): C 69.12, H 5.39, N 5.76; found: C 69.26, H 5.41, N 5.69.

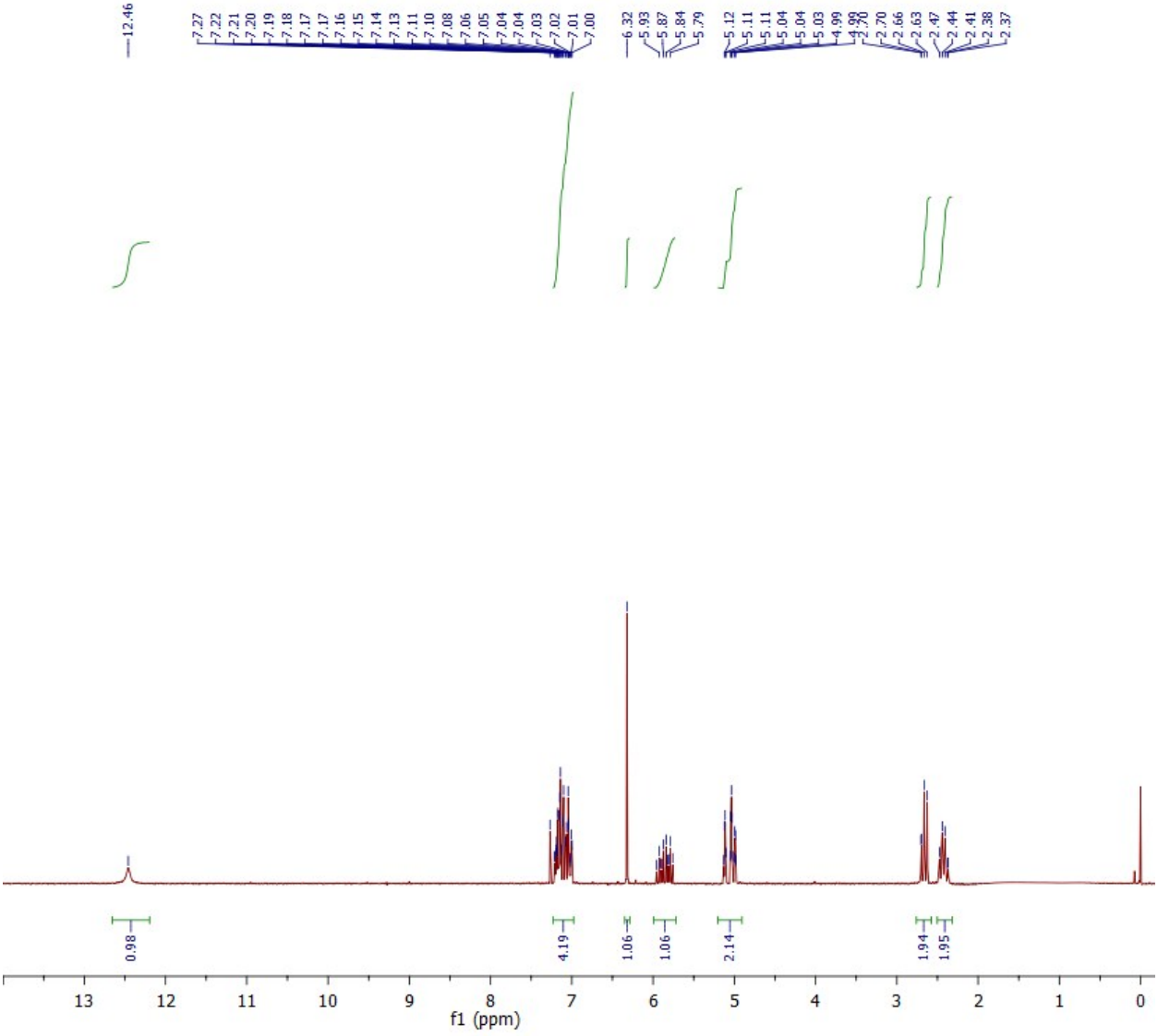


Fig. S30 ^{1}H NMR spectrum of **5b**

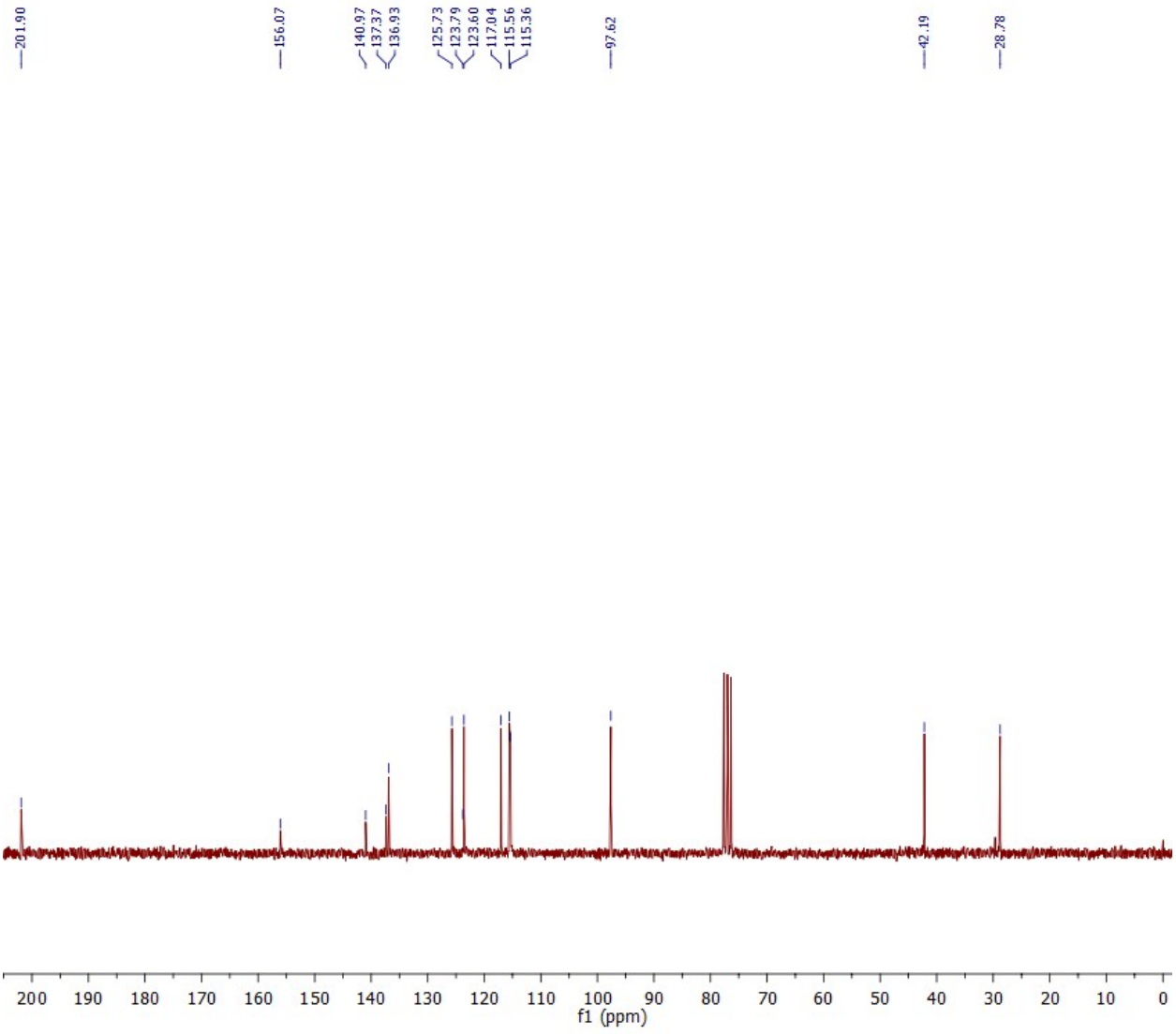
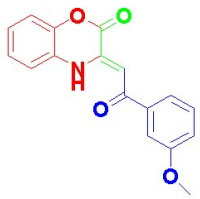


Fig. S31 ^{13}C NMR spectrum of **5b**

3,4-dihydro-3-[2-oxo-2-(3-methoxyphenyl)ethylidene]-1,4-benzoxazin-2-one (5f)



Yellow powder; yield: 88 (95)%; mp = 151°C; IR (KBr): ν 3852, 3491, 3060, 2918, 1758, 1621, 1601, 1585, 1348 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.87 (s, 3H, OCH_3), 7.01-7.56 (m, 9H, CH + CH_{Ar}), 13.04 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.4, 94.7, 111.9, 115.9, 117.1, 119.1, 120.2, 123.7, 123.9, 125.8, 129.6, 139.0, 139.6, 141.2, 156.1, 160.0, 191.1 ppm; ESI-MS: m/z (%) = 296 $[M + H]^+$; Anal. Calcd. for $C_{17}H_{13}NO_4$ (%): C 69.15, H 4.44, N 4.74; found: C 69.20, H 4.59, N 4.68.

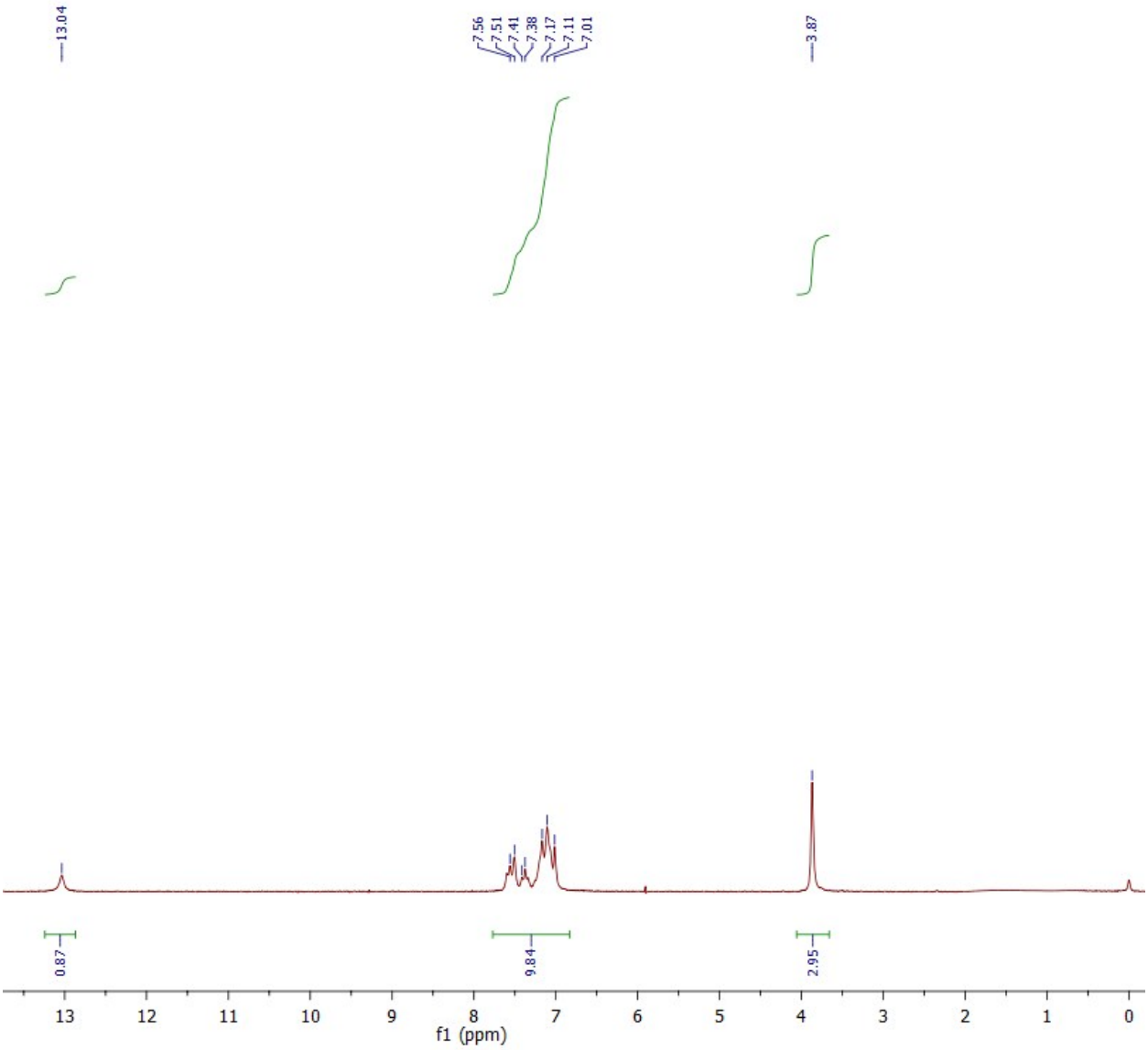


Fig. S32 ^{1}H NMR spectrum of **5f**

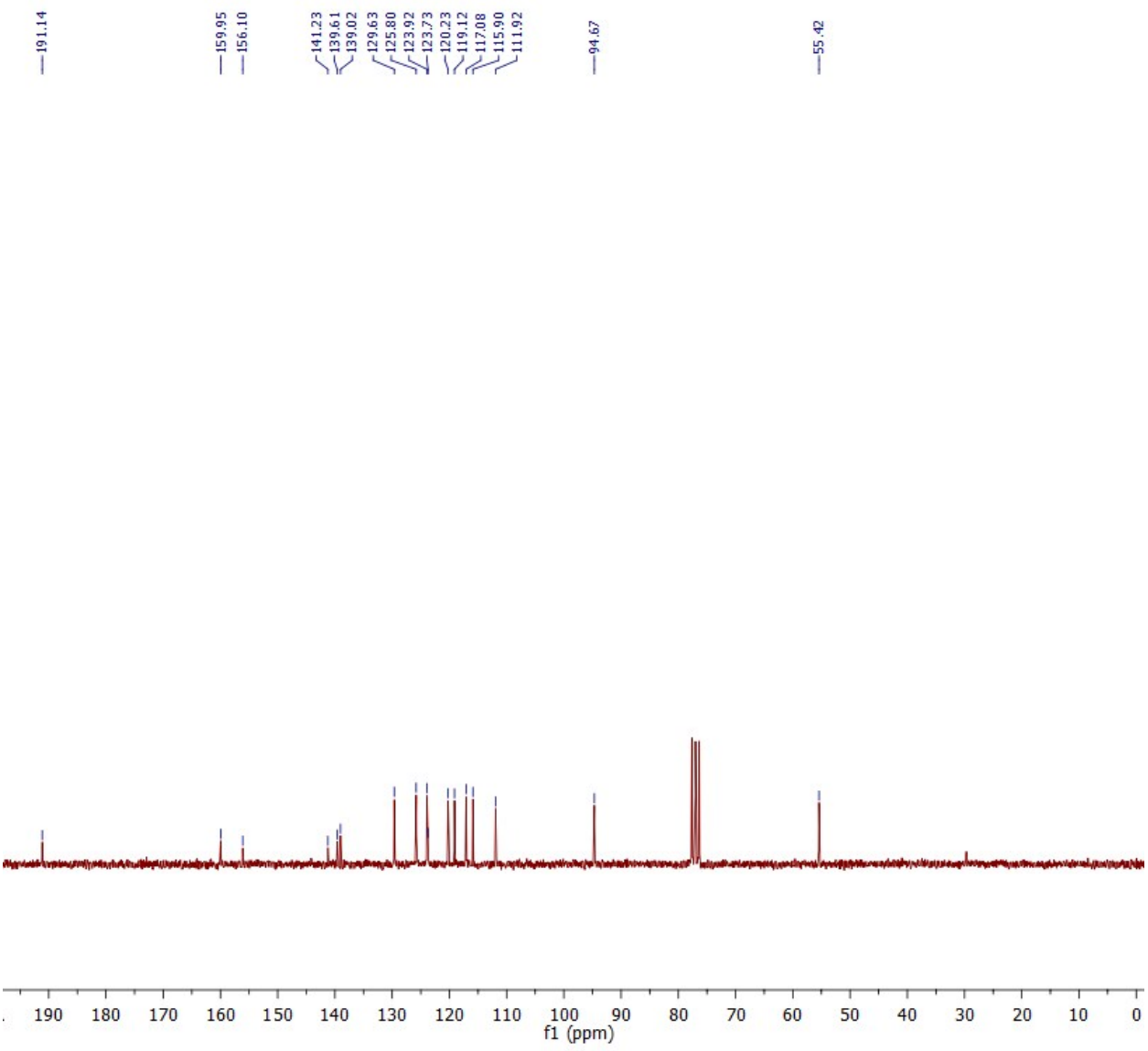
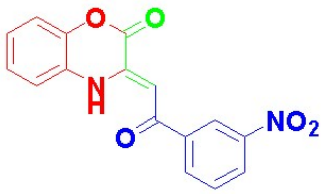


Fig. S33 ^{13}C NMR spectrum of **5f**

3,4-dihydro-3-[2-oxo-2-(3-nitrophenyl)ethylidene]-1,4-benzoxazin-2-one (5k)



Orange crystals; yield: 91 (93)%; mp = 228°C; IR (KBr): ν 3490, 3101, 2918, 1751, 1625, 1615, 1587, 1348 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.07 (s, 1H, CH), 7.21-7.24 (m, 3H, CH_{Ar}), 7.71-7.75 (m, 1H, CH_{Ar}), 8.31-8.44 (m, 3H, CH_{Ar}), 8.84-8.86 (m, 1H, CH_{Ar}), 13.17 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.7, 93.7, 116.4, 117.3, 122.6, 123.4, 124.8, 126.0, 126.7, 129.8, 133.0, 139.7, 140.3, 141.6, 188.4 ppm; ESI-MS: m/z (%) = 310 $[M]^+$; Anal. Calcd. for $C_{16}H_{10}N_2O_5$ (%): C 61.94, H 3.25, N 9.03; found: C 62.11, H 3.31, N 8.97.

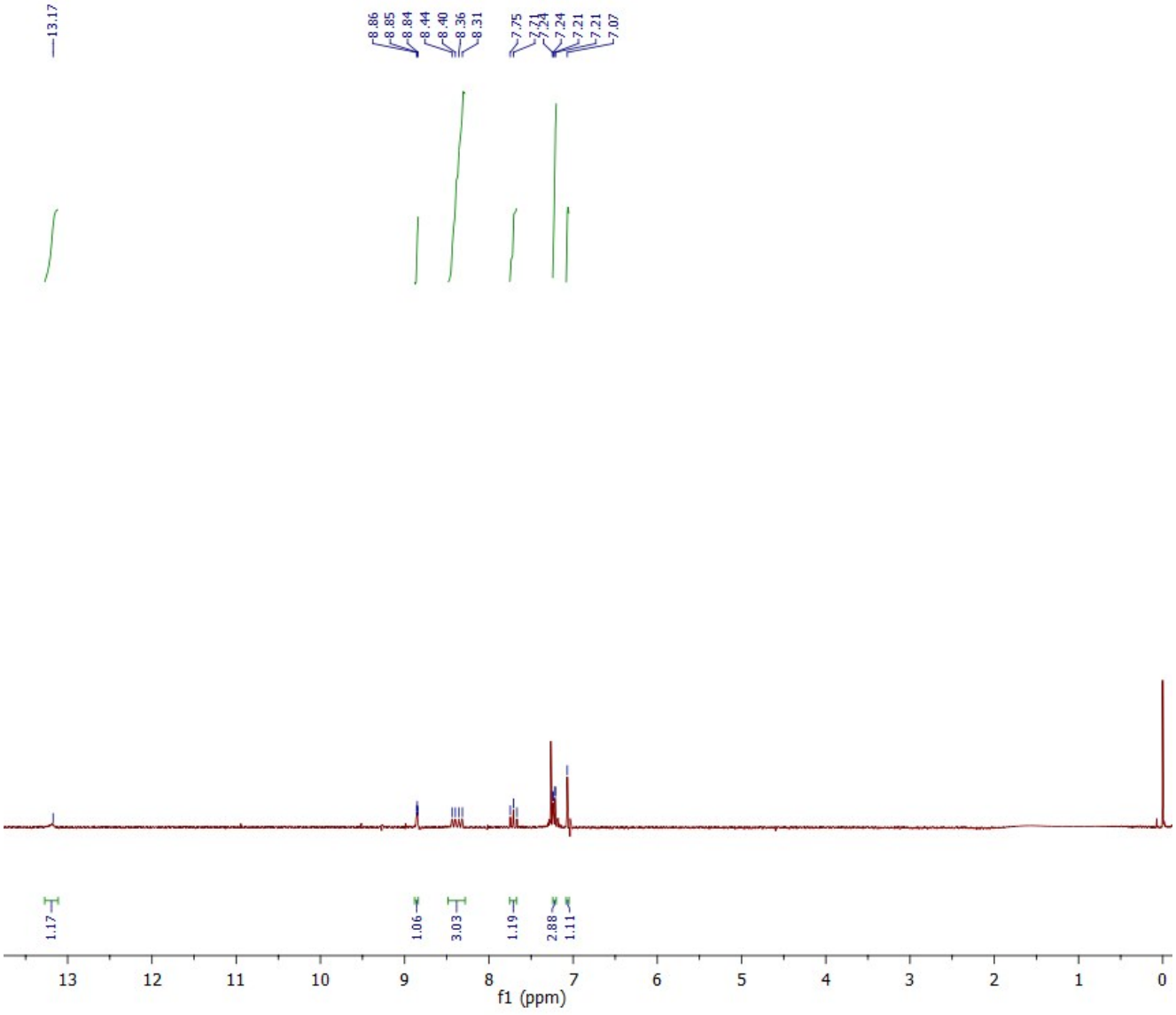


Fig. S34 ^{1}H NMR spectrum of **5k**

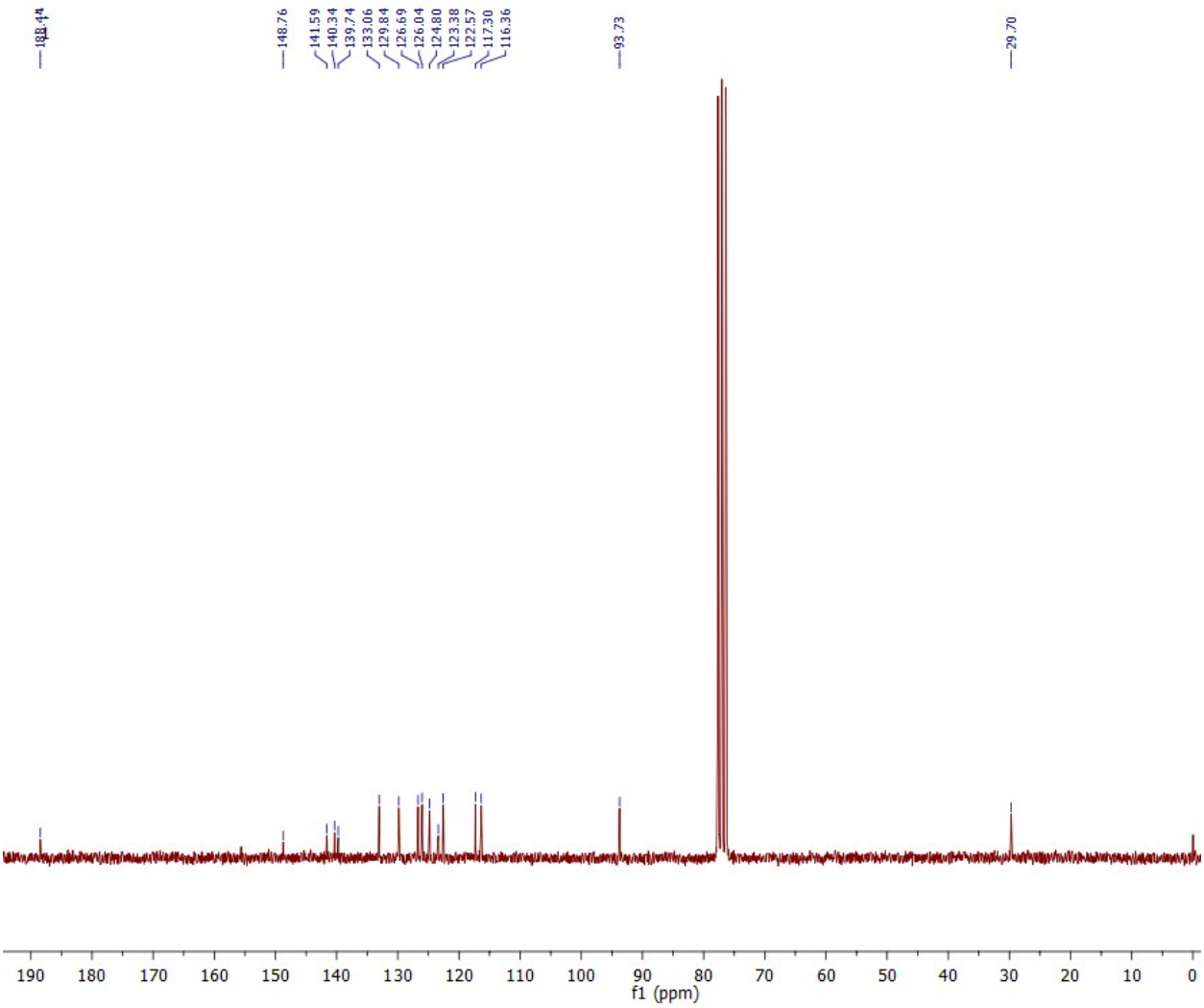
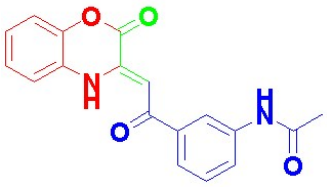


Fig. S35 ^{13}C NMR spectrum of **5k**

3,4-dihydro-3-[2-oxo-2-(3-N-acetylphenyl)ethylidene]-1,4-benzoxazin-2-one (5l)



Yellow powder; yield: 95 (91)%; mp = 235°C; IR (KBr): ν 3484, 3288, 3091, 2853, 1754, 1672, 1630, 1599, 1553, 1351 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 2.07 (s, 3H, CH_3), 6.81 (s, 1H, CH), 7.11-7.84 (m, 7H, CH_{Ar}), 8.24 (s, 1H, CH_{Ar}), 10.16 (br. s, 1H, NH), 12.76 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 24.2, 92.7, 116.6, 117.0, 117.7, 121.9, 122.8, 123.8, 124.1, 125.5, 129.4, 138.8, 140.0, 140.1, 141.3, 156.2, 168.8, 189.4 ppm; ESI-MS: m/z (%) = 322 $[M]^+$; Anal. Calcd. for $C_{18}H_{14}N_2O_4$ (%): C 67.08, H 4.38, N 8.69; found: C 67.15, H 4.31, 8.70.

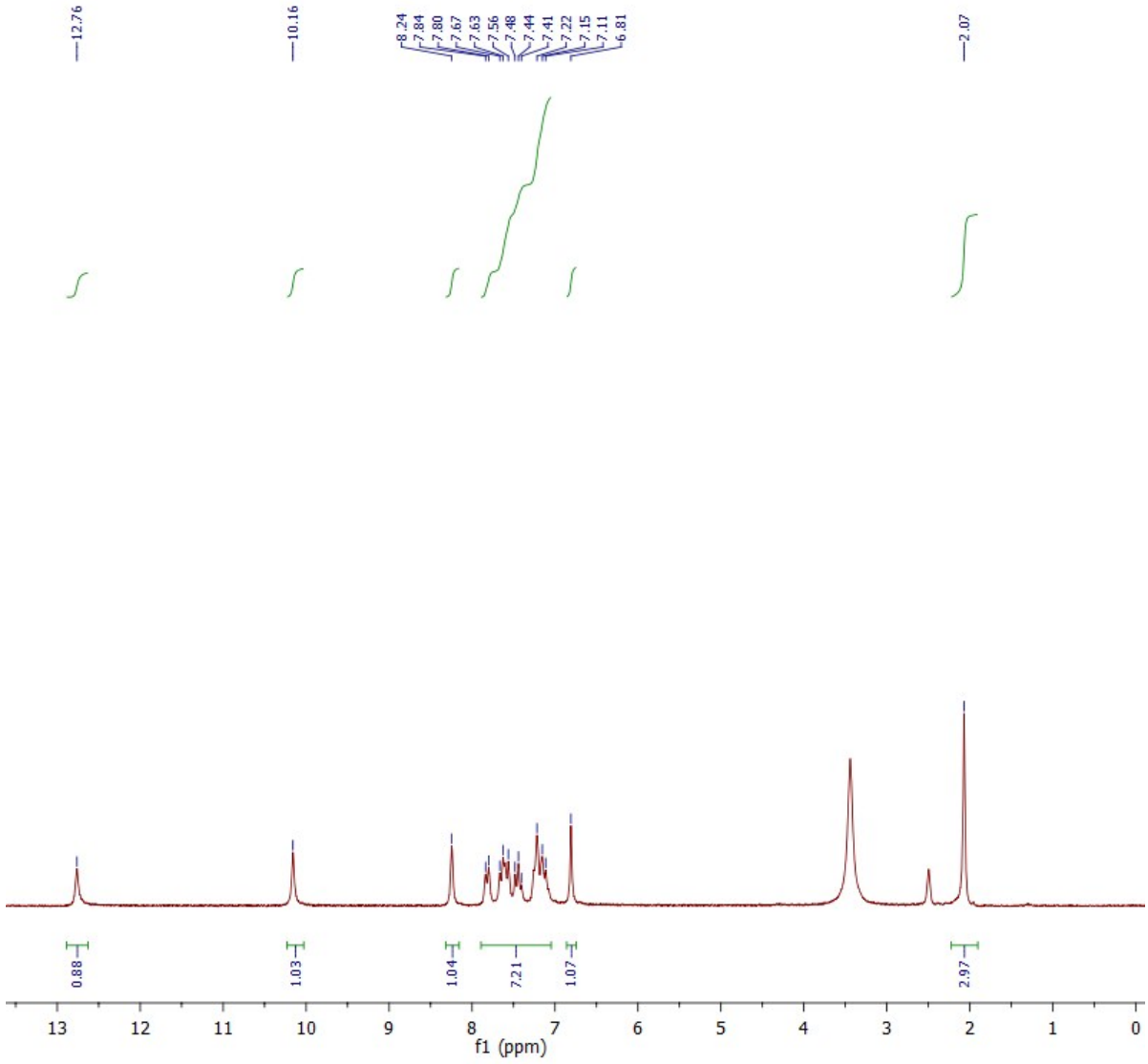


Fig. S36 ^{1}H NMR spectrum of **5l**

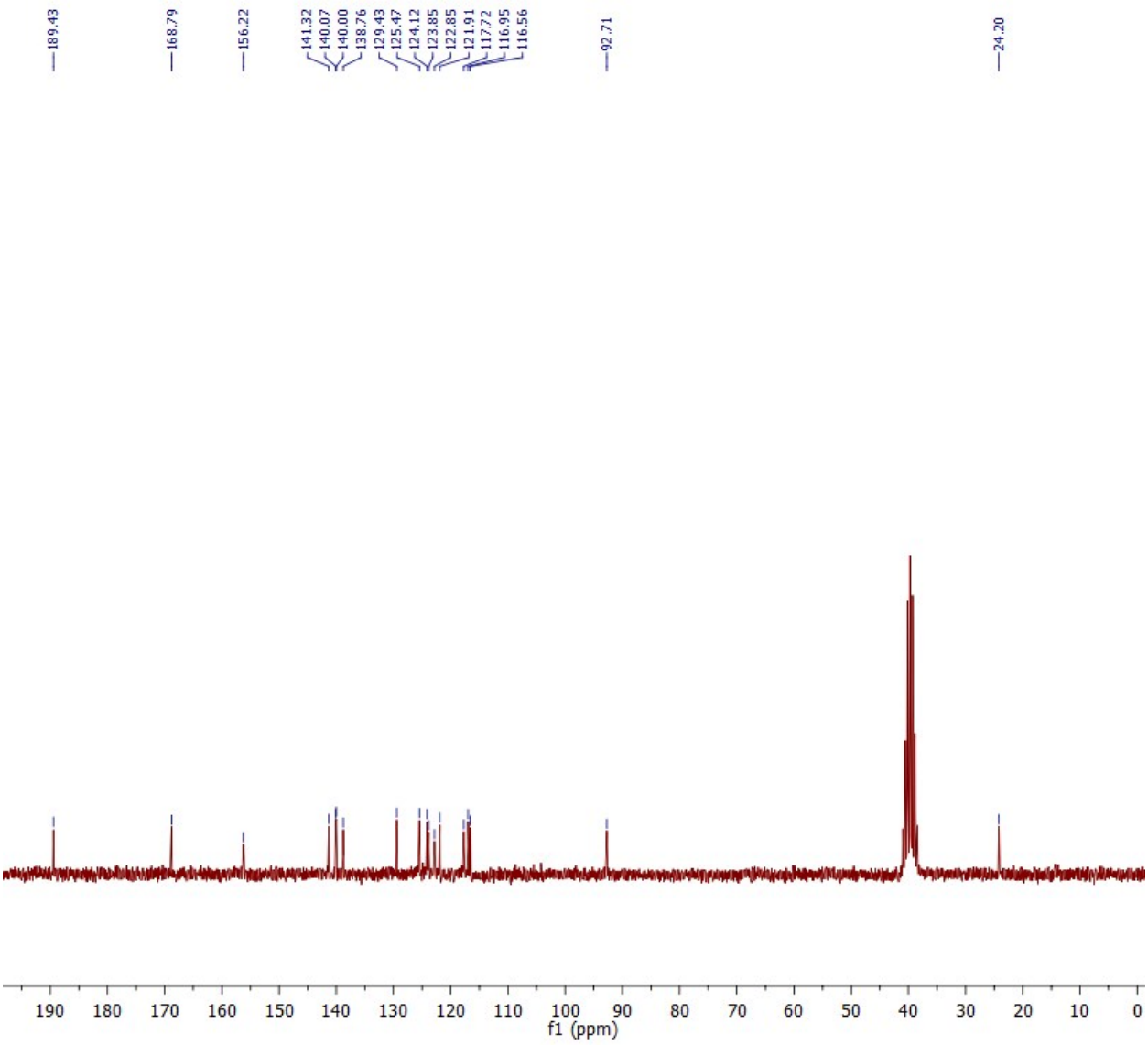
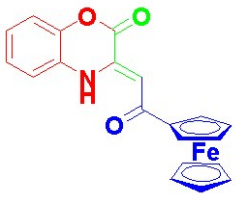


Fig. S37 ^{13}C NMR spectrum of **5l**

3,4-dihydro-3-(2-oxo-2-ferrocenylethylidene)-1,4-benzoxazin-2-one (5m)



Red crystals; yield: 91 (93)%; mp = 223˚C; IR (KBr): ν 3853, 3750, 3491, 3081, 2918, 1760, 1629, 1596, 1375 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.21 (s, 5H, CH_{Fc}), 4.57-4.59 (d, 2H, CH_{Fc}), 4.87-4.89 (t, 2H, CH_{Fc}), 6.55 (s, 1H, CH), 6.99-7.26 (m, 4H, CH_{Ar}), 12.68 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 69.1, 70.2, 72.7, 80.9, 96.6, 115.4, 117.0, 123.1, 124.2, 125.7, 136.5, 140.8, 156.7, 196.2 ppm; ESI-MS: m/z (%) = 374 $[M + H]^+$; Anal. Calcd. for $C_{20}H_{15}NO_3Fe$ (%): C 64.37, H 4.05, N 3.75; found: C 64.30, H 3.92, N 3.78.

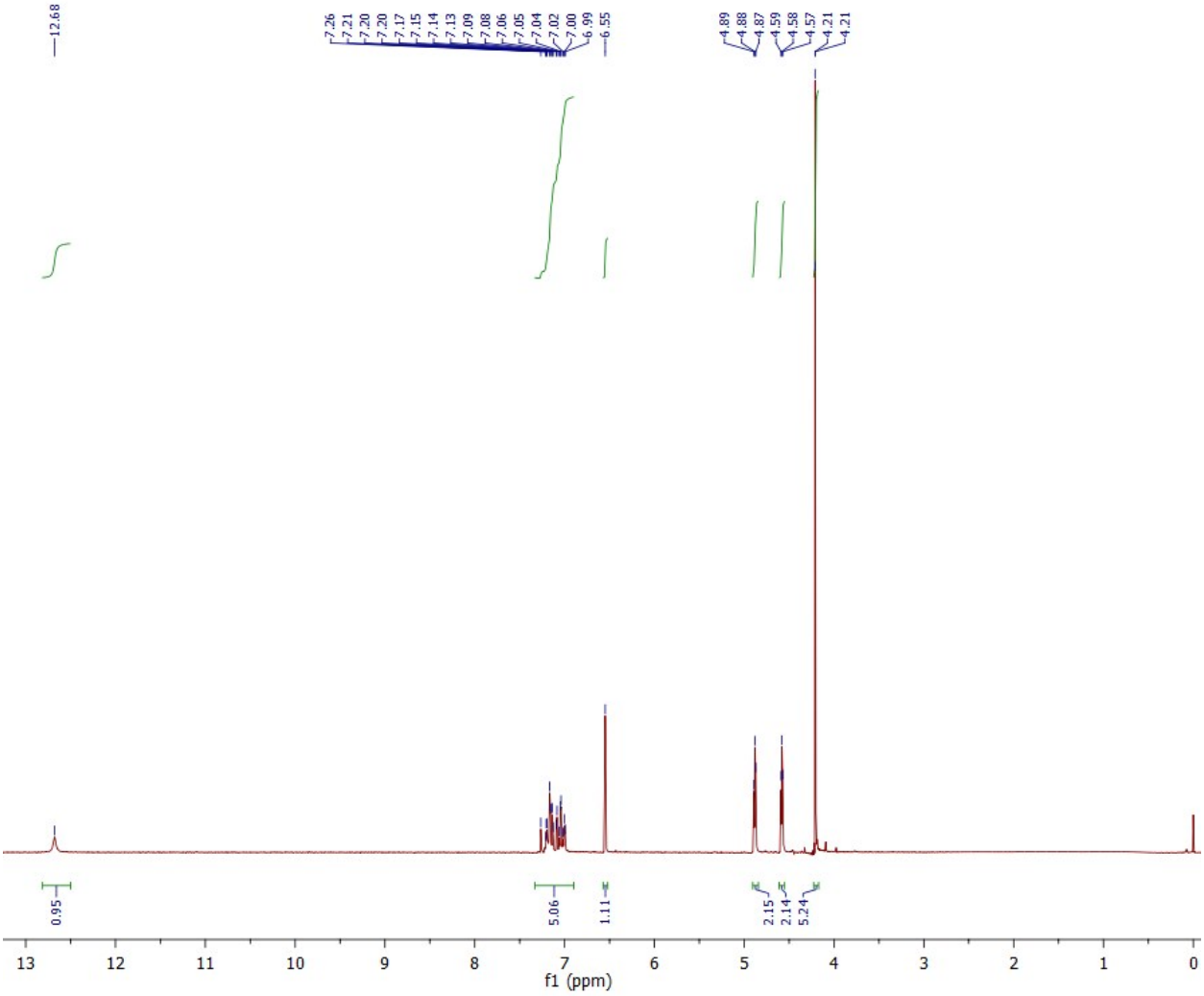


Fig. S38 ^{1}H NMR spectrum of **5m**

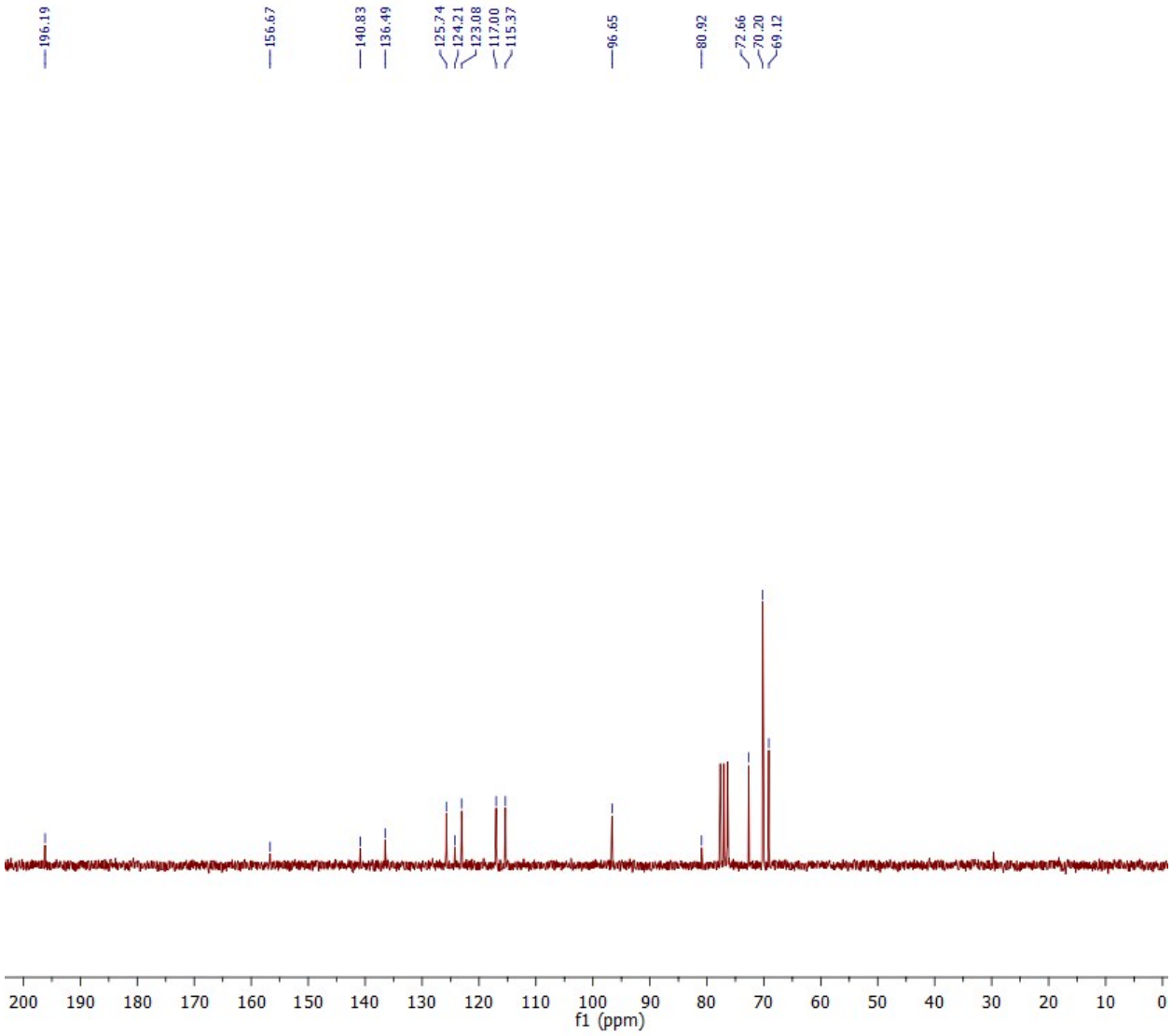
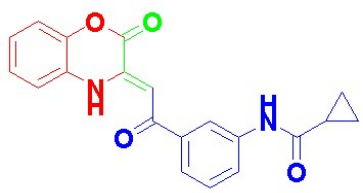


Fig. S39 ^{13}C NMR spectrum of **5m**

3,4-dihydro-3-[2-oxo-2-(3-N-cyclopropanoylphenyl)ethylidene]-1,4-benzoxazin-2-one (5n)



Yellow powder; yield: 84 (89)%; mp = 264°C; IR (KBr): ν 3486, 3259, 3061, 2921, 1760, 1651, 1618, 1599, 1560, 1348 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6): δ = 0.84 (s, 4H, CH_2), 1.78 (m, 1H, CH), 6.81 (s, 1H, CH), 7.16-7.81 (m, 7H, CH_{Ar}), 8.27 (s, 1H, CH_{Ar}), 10.42 (br. s, 1H, NH), 12.76 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, DMSO-d_6): δ = 7.5, 14.8, 92.7, 116.6, 117.0, 117.7, 121.8, 122.8, 123.9, 124.1, 125.5, 129.5, 138.8, 140.0, 140.1, 156.2, 172.1, 189.4 ppm; ESI-MS: m/z (%) = 348 $[M]^+$; Anal. Calcd. for $C_{20}H_{16}N_2O_4$ (%): C 68.96, H 4.63, N 8.04; found: C 68.90, H 4.75, N 8.01.

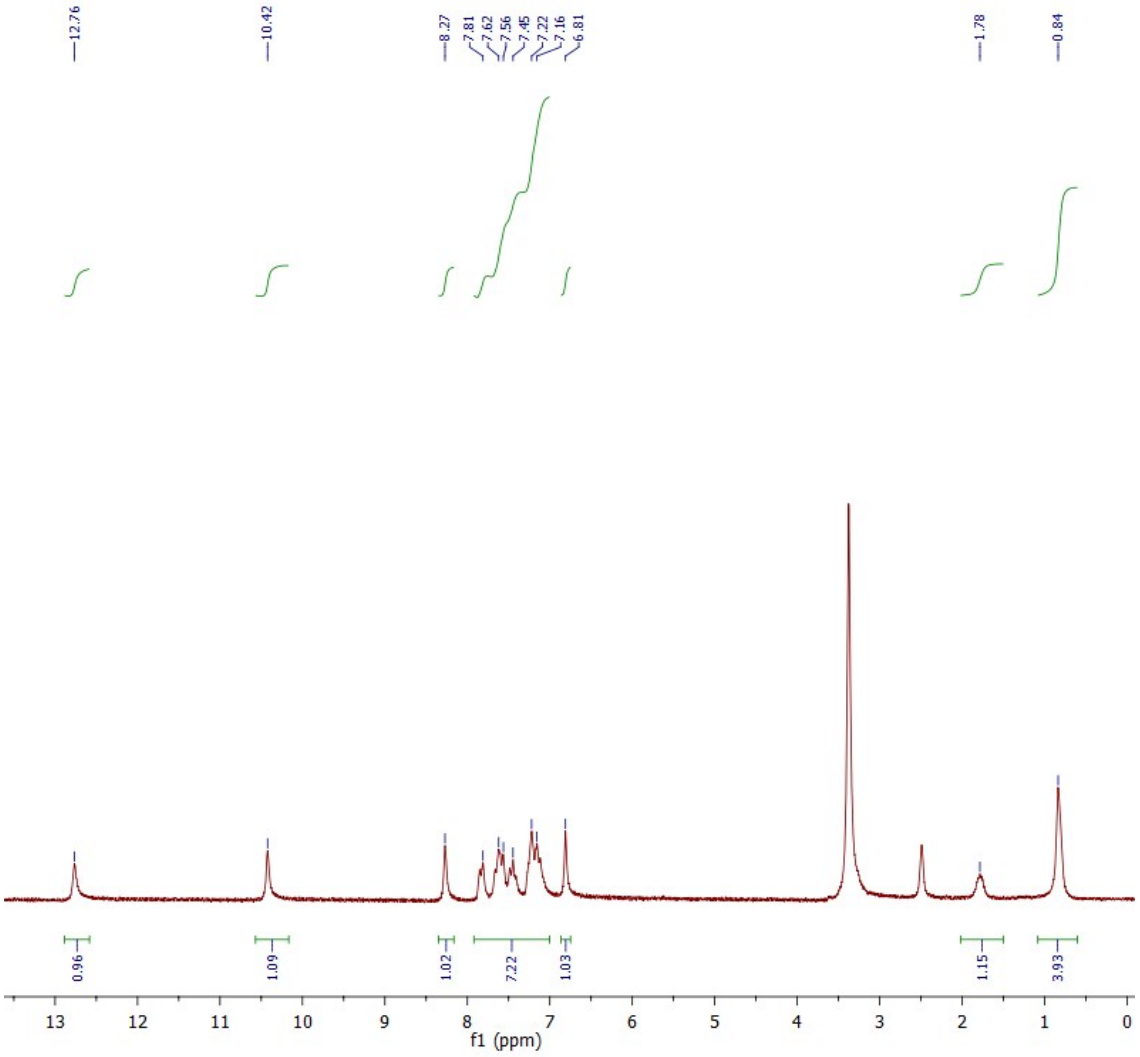


Fig. S40 ^{1}H NMR spectrum of **5n**

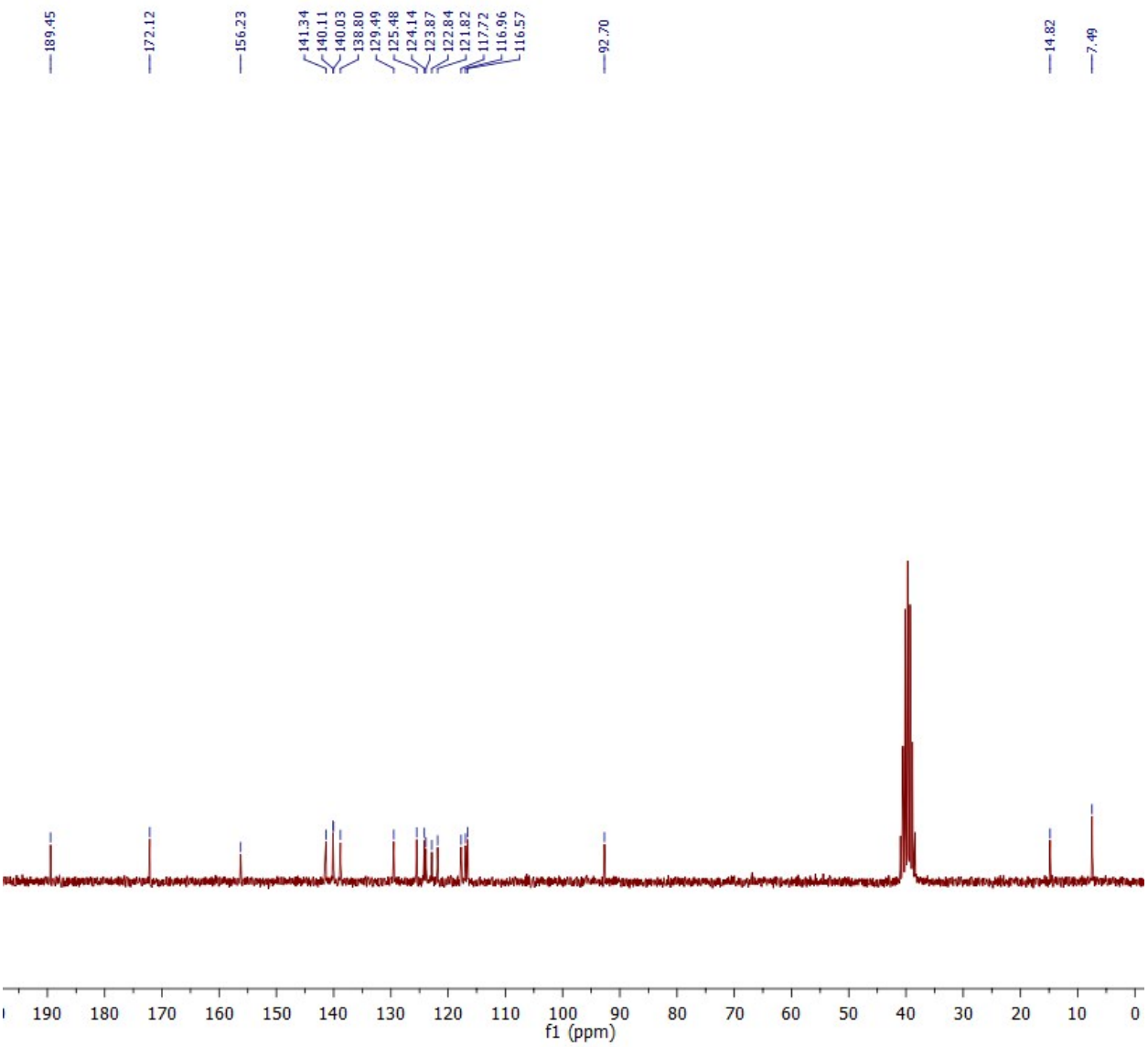
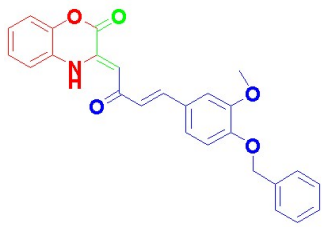


Fig. S41 ^{13}C NMR spectrum of **5n**

3,4-dihydro-3-[2-oxo-4-(4-benzyloxy-3-methoxyphenyl)but-3-enylidene]-1,4-benzoxazin-2-one (5o)



Orange powder; yield: 80 (94)%; mp = 188°C; IR (KBr): ν 3750, 3061, 2955, 1751, 1613, 1595, 1341 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.94 (s, 3H, OCH_3), 5.19 (s, 2H, OCH_2), 6.53-7.60 (m, 15H, CH_{Ar}), 12.99 (br. s, 1H, NH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.0, 70.8, 98.4, 113.5, 116.1, 117.0, 122.9, 123.8, 125.3, 125.7, 127.2, 128.0, 128.6, 136.5, 138.6, 141.3, 141.6, 149.8, 150.5, 156.1, 189.3 ppm; ESI-MS: m/z (%) = 450 $[M + Na]^+$; Anal. Calcd. for $C_{26}H_{21}NO_5$ (%): C 73.06, H 4.95, N 3.28; found: C 73.19, H 4.91, N 3.32.

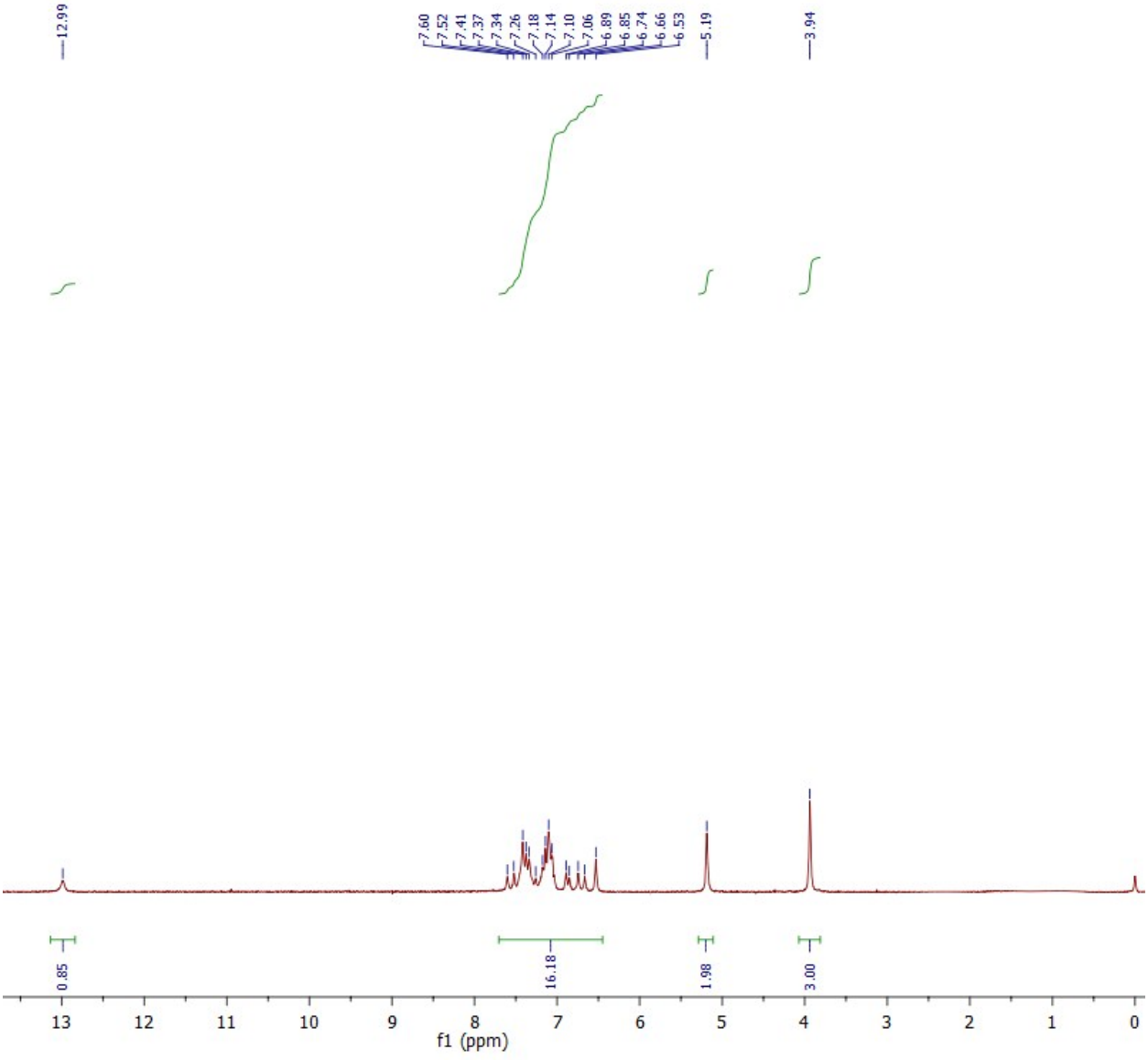


Fig. S42 ^{1}H NMR spectrum of **5o**

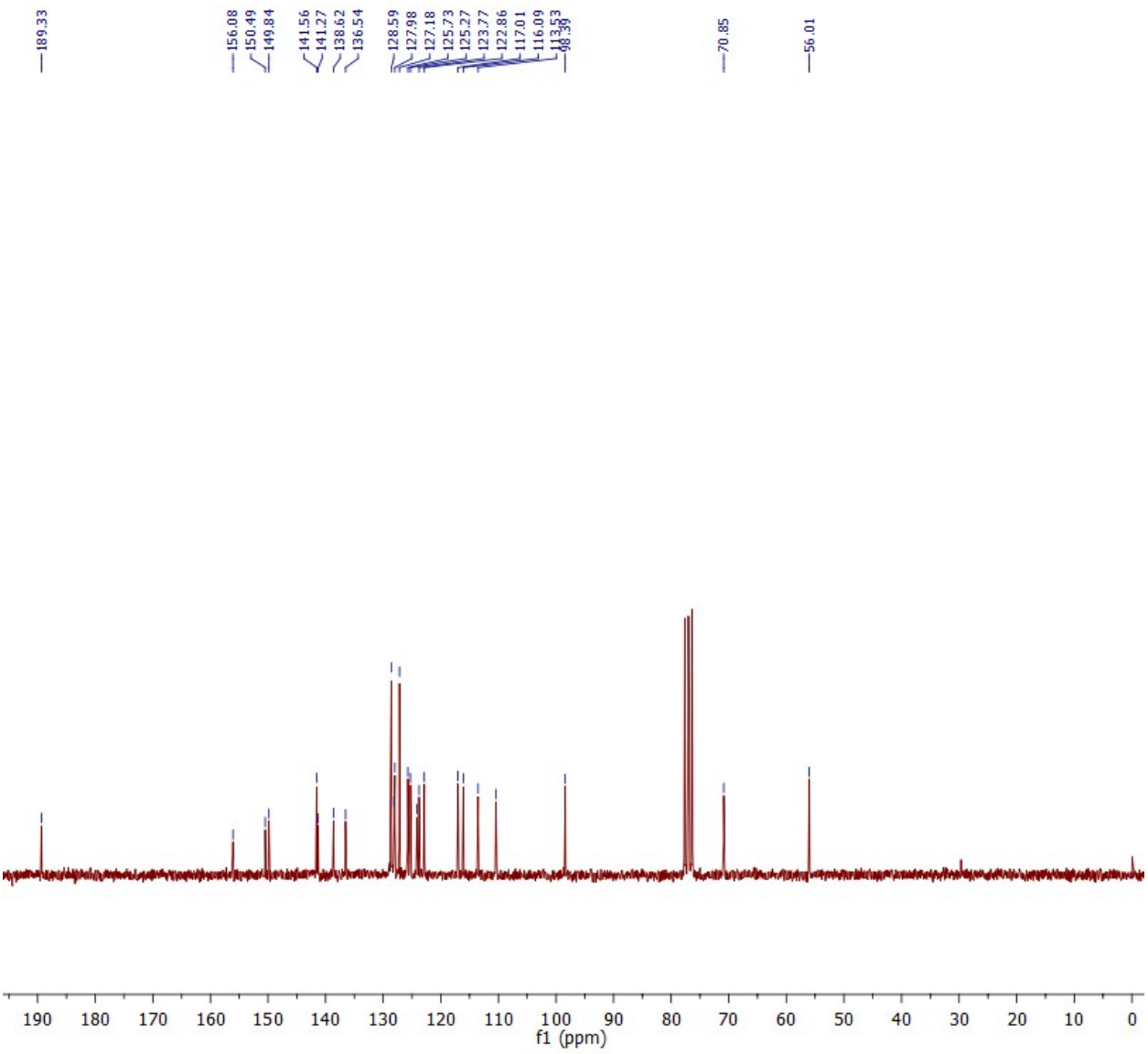


Fig. S43 ^{13}C NMR spectrum of **5o**

4. Crystallographic data of 5b

Table S1. Selected bond lengths (Å) in crystal structure of the compound **5b**

O1−C1	1.352(2)
O1−C8	1.385(2)
O2−C1	1.193(2)
O3−C10	1.238(2)
N1−C2	1.357(2)
N1−C3	1.382(2)
C1−C2	1.494(2)
C2−C9	1.351(2)
C3−C8	1.386(2)
C9−C10	1.444(2)
C10−C11	1.493(2)
C11−C12	1.526(2)
C12−C13	1.473(2)
C13−C14	1.287(3)

Table S2 Crystallographic data for the compound **5b**

Empirical formula	$C_{14}\ H_{13}\ N\ O_3$
Formula weight	243.25
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a	14.2032(8) Å
b	4.6426(3) Å
c	18.5046(10) Å
β	99.389(6)°
Volume	1203.84(12) $Å^3$
Z	4
Density (calculated)	1.342 Mg/m^3
Absorption coefficient (μ)	0.095 mm^{-1}
Crystal size	0.30 x 0.18 x 0.17 mm
Crystal color and shape	yellow, prismatic
θ range for data collection	2.91 to 29.00°
Index ranges	−19<=h<=11, −6<=k<=5, −23<=l<=23
Reflections collected	4778
Independent reflections	2717 [R(int) = 0.0190]
Completeness to θ = 26.00°	99.9 %
Data / restraints / parameters	2717 / 0 / 167
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.0951
R indices (all data)	R1 = 0.0845, wR2 = 0.1153
Largest diff. peak and hole	0.127 and −0.156 $eÅ^{-3}$

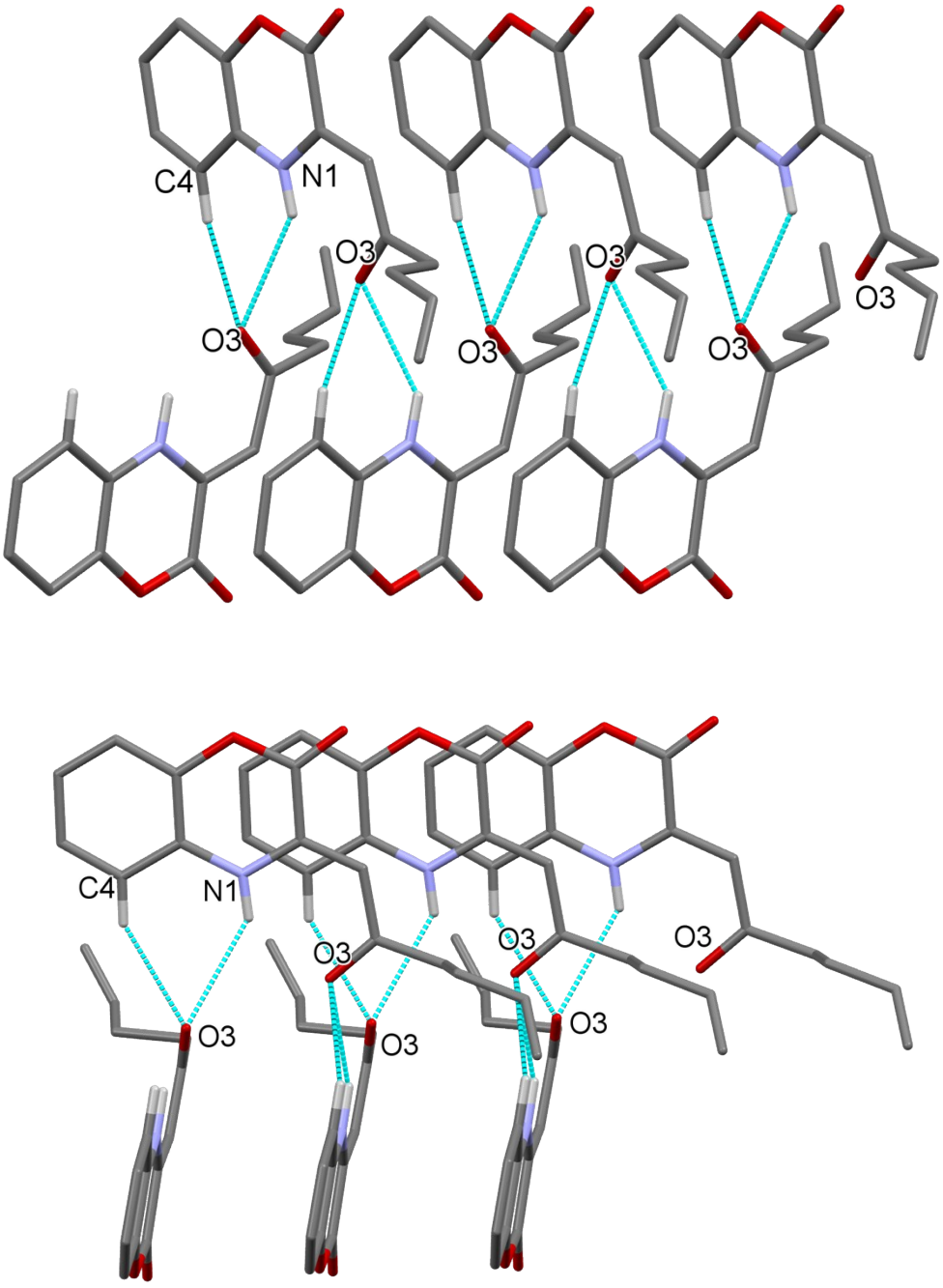


Fig. S44 Formation of double chain in the crystal packing of **5b**. The double chain is shown in two projections where bottom figure illustrates the parallel stacking of rings. The N1−H…O3^{i} and C4−H…O3^{i} [symmetry code: (i) −x+0.5, y−0.5, −z+1.5] intermolecular hydrogen bonds are shown by dotted blue lines. H atoms which are not involved in hydrogen bonds are omitted for clarity.

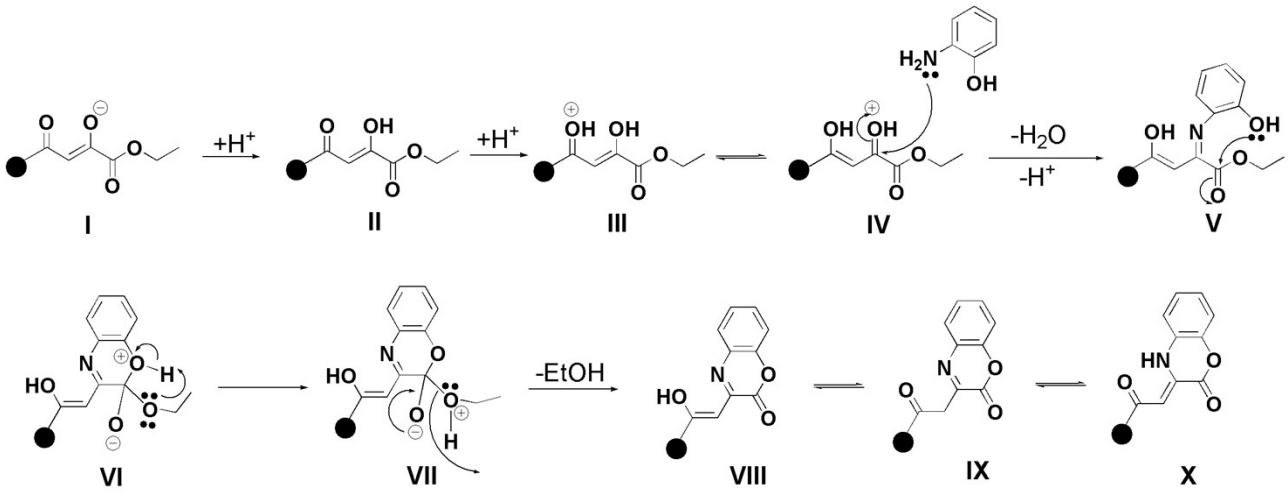


Fig. S45 Proposed mechanism for formation of 3,4-dihydro-1,4-benzoxazin-2-ones