

Sequential Pd(II)-Pd(0) Catalysis for the Rapid Synthesis of Coumarins.

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Experimental.

Materials. All reagents were used as received. Aryl alkynoates (**1**) were readily prepared in 60-90% yield according to the literature method.¹ NMR spectra were referenced to residual protio solvent signals. Structural assignments are based on ¹H, ¹³C, DEPT-135, and HMQC spectroscopies.

General procedure for catalytic hydroarylation.

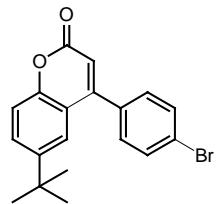
The aryl alkynoate **1** (0.28 mmol), Pd(OAc)₂ (0.014 mmol), and 3:1 TFA/DCM (1 mL) were mixed in a reaction tube and stirred at room temperature for 1-6 h. Stirring continued until complete disappearance of the starting material was observed by ¹H NMR spectroscopy. The solvent was removed under vacuum and the product was purified by column chromatography on silica gel using CH₂Cl₂ as the eluent.

General procedure for the Suzuki coupling reactions.

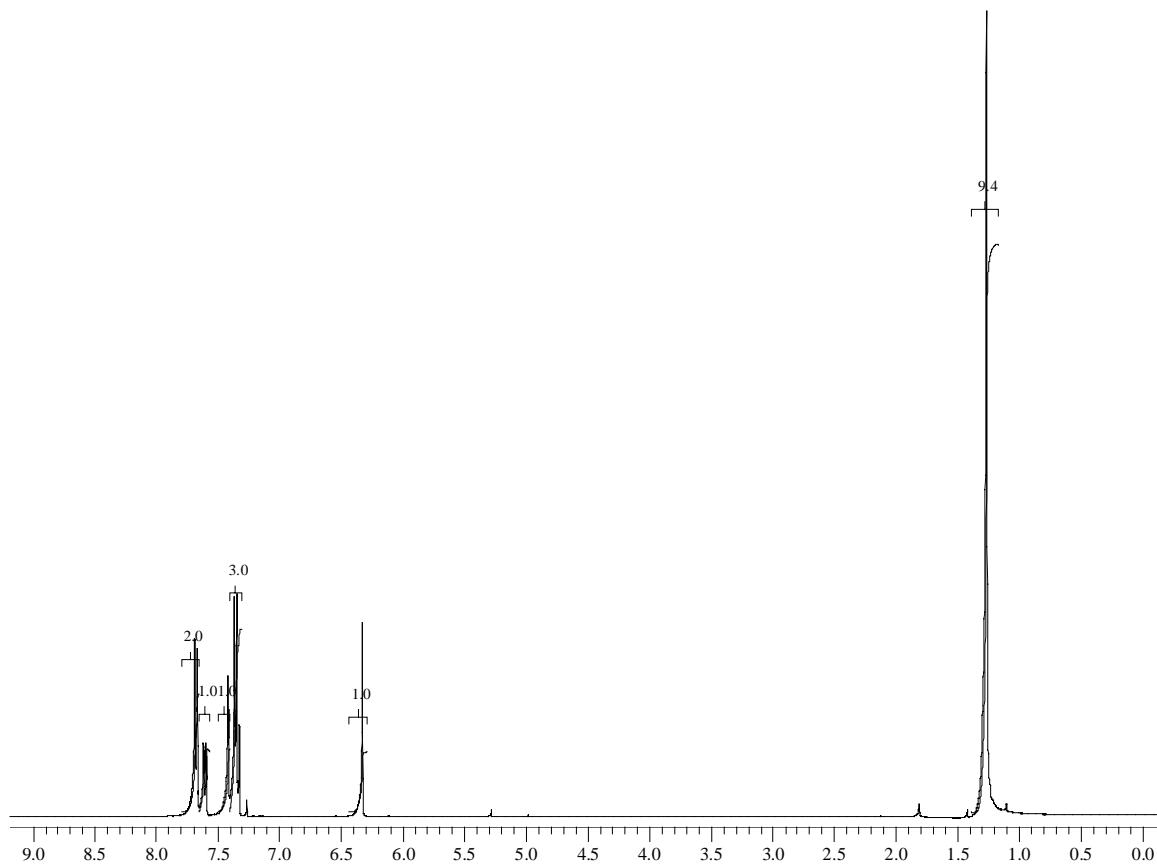
Under a N₂ atmosphere, THF (1 mL) was added to bromophenylcoumarin **2** (0.28 mmol), Pd(OAc)₂ (0.0028 mmol), arylboronic acid (0.42 mmol), KF (0.84 mmol), and 2-(dicyclohexylphosphino)biphenyl (0.056 mmol). The reaction mixture was stirred at room temperature for 16-40 h. The solvent was removed under vacuum and the crude mixture was purified by column chromatography on silica gel using CH₂Cl₂ as the eluent.

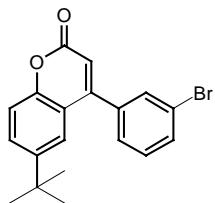
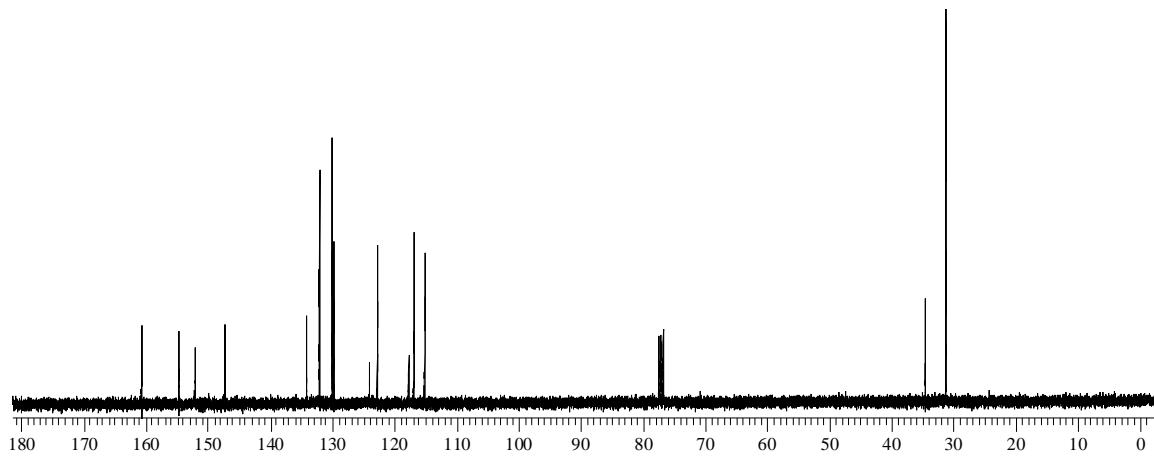
General procedure for the sequential hydroarylation/Suzuki coupling.

The aryl alkynoate (0.14 mmol), Pd(OAc)₂ (0.007 mmol), and 3:1 TFA/DCM (0.5 mL) were mixed in a reaction tube and stirred at room temperature for 1-6 hrs. The solvent was removed under vacuum and arylboronic acid (0.21 mmol), KF (0.42 mmol) and 2-(dicyclohexylphosphino)biphenyl (0.014 mmol) were added under an inert atmosphere (N₂ or Ar). THF (1 mL) was added and the reaction mixture was heated at 50 °C for 16 h. The solvent was removed under vacuum and the crude mixture was purified by column chromatography on silica gel using CH₂Cl₂ as the eluent.

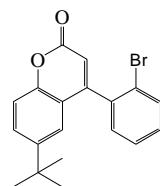
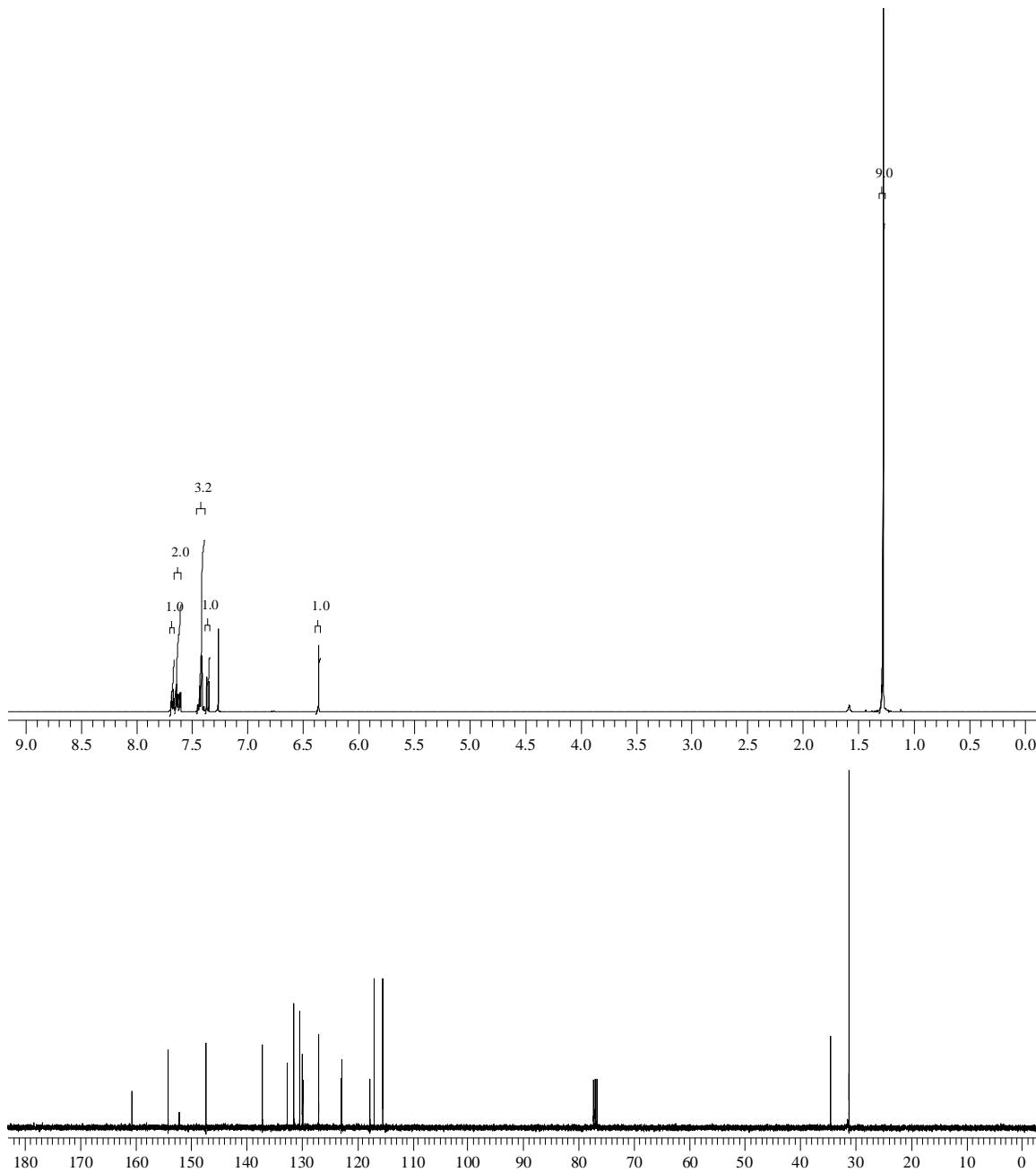


4-(4-Bromophenyl)-6-*tert*-butyl-2*H*-chromen-2-one (2a**).** ^1H NMR (CDCl_3): δ 7.67 (d, 2H, *PhBr*, $J = 8.8$ Hz); 7.60 (dd, 1H, $^t\text{BuPh}$, $J = 8.8$ and 2.3 Hz); 7.41 (d, 1H, $^t\text{BuPh}$, $J = 2.3$ Hz); 7.35 (d, 2H, *PhBr*, $J = 8.8$ Hz); 7.33 (d, 1H, $^t\text{BuPh}$, $J = 8.8$ Hz); 6.33 (s, 1H, CHCO); 1.26 (s, 9H, ^tBu). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.6 (CO), Ph ring and C=C (154.6, 152.1, 147.3, 134.1, 132.1, 129.9, 129.7, 124.1, 122.7, 117.7, 116.9, 115.1), ^tBu (34.5, 31.2). ν_{max} (NaCl)/cm⁻¹: 3055, 1722, 1616, 1570, 1489, 1256, 1184, 1128, 1013. HR-MS: C₁₉H₁₈BrO₂ Calcd. 357.0490 (M+1); found: 357.0498.



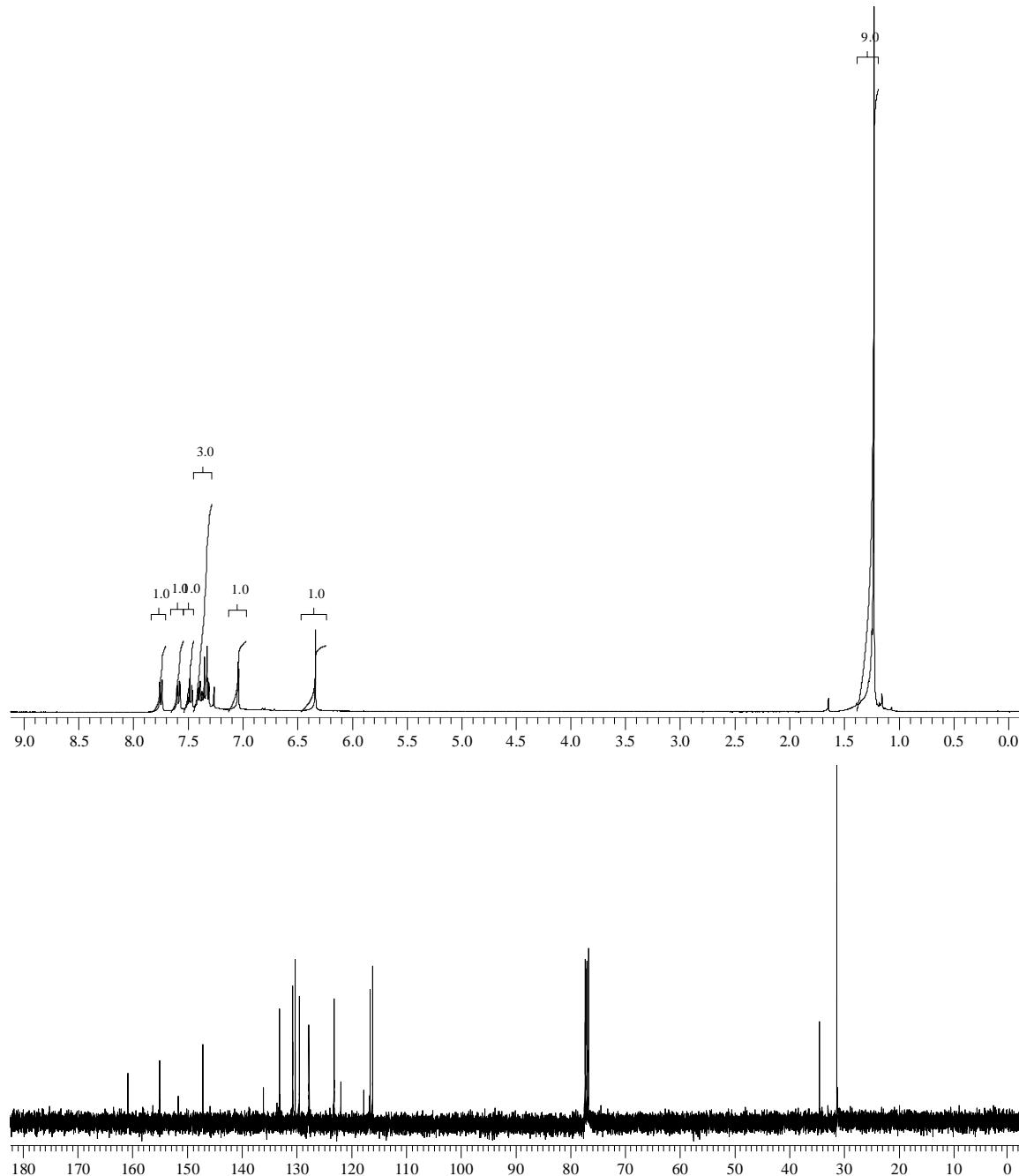


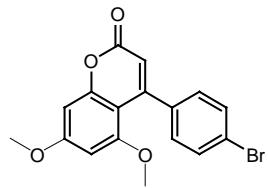
4-(3-Bromophenyl)-6-*tert*-butyl-2*H*-chromen-2-one (2b**).** ^1H NMR (CDCl_3): δ 7.68 (dt, 1H, *PhBr*, $J = 7.0$ and 2.0 Hz); 7.64 (m, 1H, *PhBr*); 7.62 (dd, 1H, $^t\text{BuPh}$, $J = 8.8$ and 2.3 Hz); 7.43 (t, 1H, *PhBr*, $J = 7.6$ Hz); 7.39-7.42 (m, 2H, $^t\text{BuPh}$ and *PhBr*); 7.36 (d, 1H, $^t\text{BuPh}$, $J = 8.8$ Hz); 6.36(s, 1H, CHCO); 1.28 (s, 9H, ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 160.6 (CO), Ph ring and C=C (154.1, 152.1, 147.3, 132.6, 131.3, 130.3, 129.8, 127.0, 122.9, 122.7, 117.7, 116.9, 115.3), ^tBu (34.6, 31.2). ν_{max} (NaCl)/cm $^{-1}$: 3055, 1724, 1616, 1568, 1558, 1489, 1473, 1369, 1186, 1130. HR-MS: $\text{C}_{19}\text{H}_{18}\text{BrO}_2$ Calcd. 357.0490 ($M+1$); found: 357.0488.



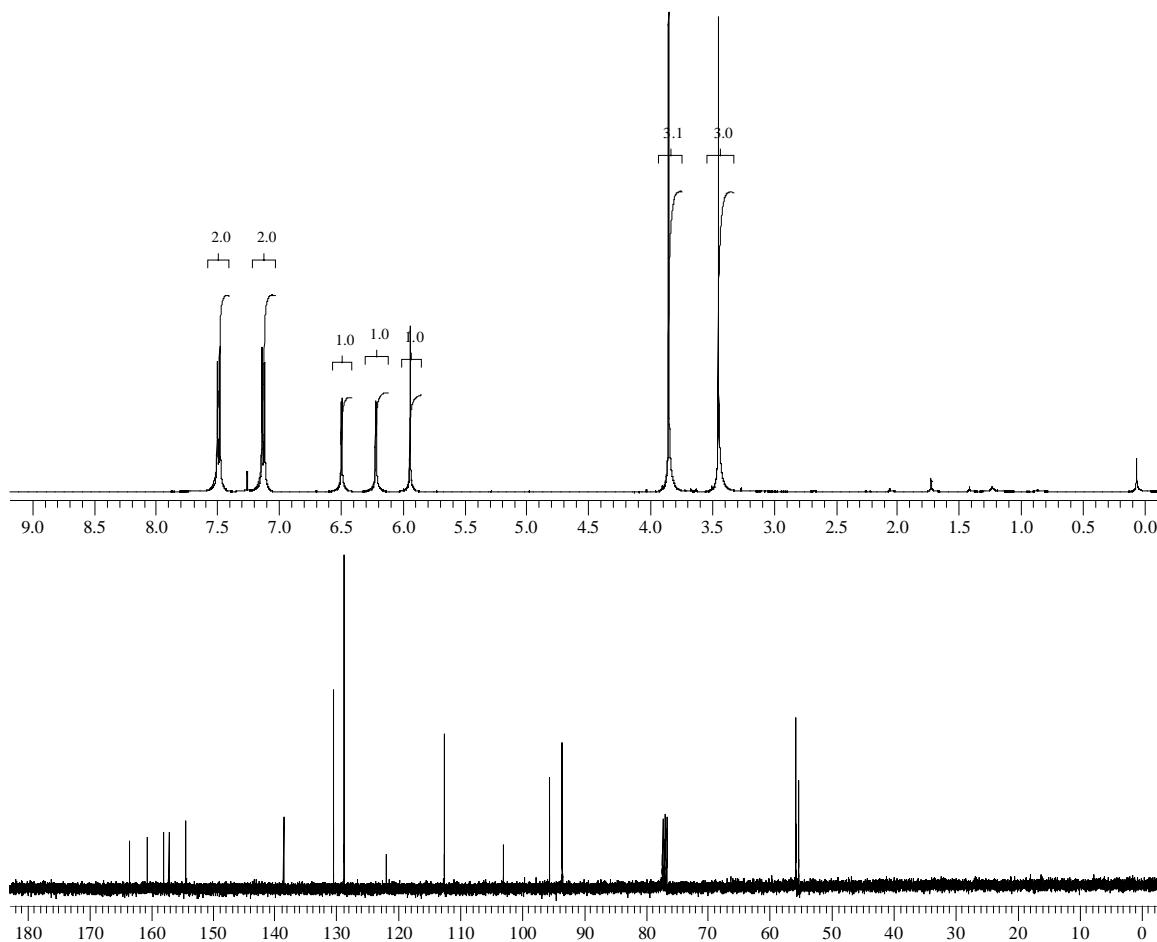
4-(2-Bromophenyl)-6-*tert*-butyl-2*H*-chromen-2-one (2c**).** ^1H NMR (CDCl_3): δ 7.75 (d, 1H, *PhBr*, $J = 7.9$ Hz); 7.59 (dd, 1H, $^1\text{BuPh}$, $J = 8.5$ and 2.3 Hz); 7.48 (t, 1H, *PhBr*, $J = 7.6$ Hz); 7.40 (d, 1H, *PhBr*, $J = 7.6$ Hz); 7.30-7.35 (m, 2H, *PhBr*, 1H; $^1\text{BuPh}$, 1H); 7.04

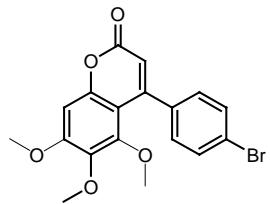
(d, 1H, $t\text{BuPh}$, $J = 2.3$ Hz); 6.33 (s, 1H, CHCO); 1.26 (s, 9H, $t\text{Bu}$). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.9 (CO), Ph ring and C=C (155.1, 151.7, 147.2, 136.2, 133.2, 130.7, 130.2, 129.5, 127.7, 123.2, 121.9, 117.8, 116.6, 116.1), $t\text{Bu}$ (34.4, 31.2). ν_{max} (NaCl)/cm⁻¹: 3055, 1722, 1615, 1570, 1472, 1369, 1184, 1132, 1030. HR-MS: C₁₈H₁₈O₂Br Calcd. 357.0490 (M+1); found: 357.0482.



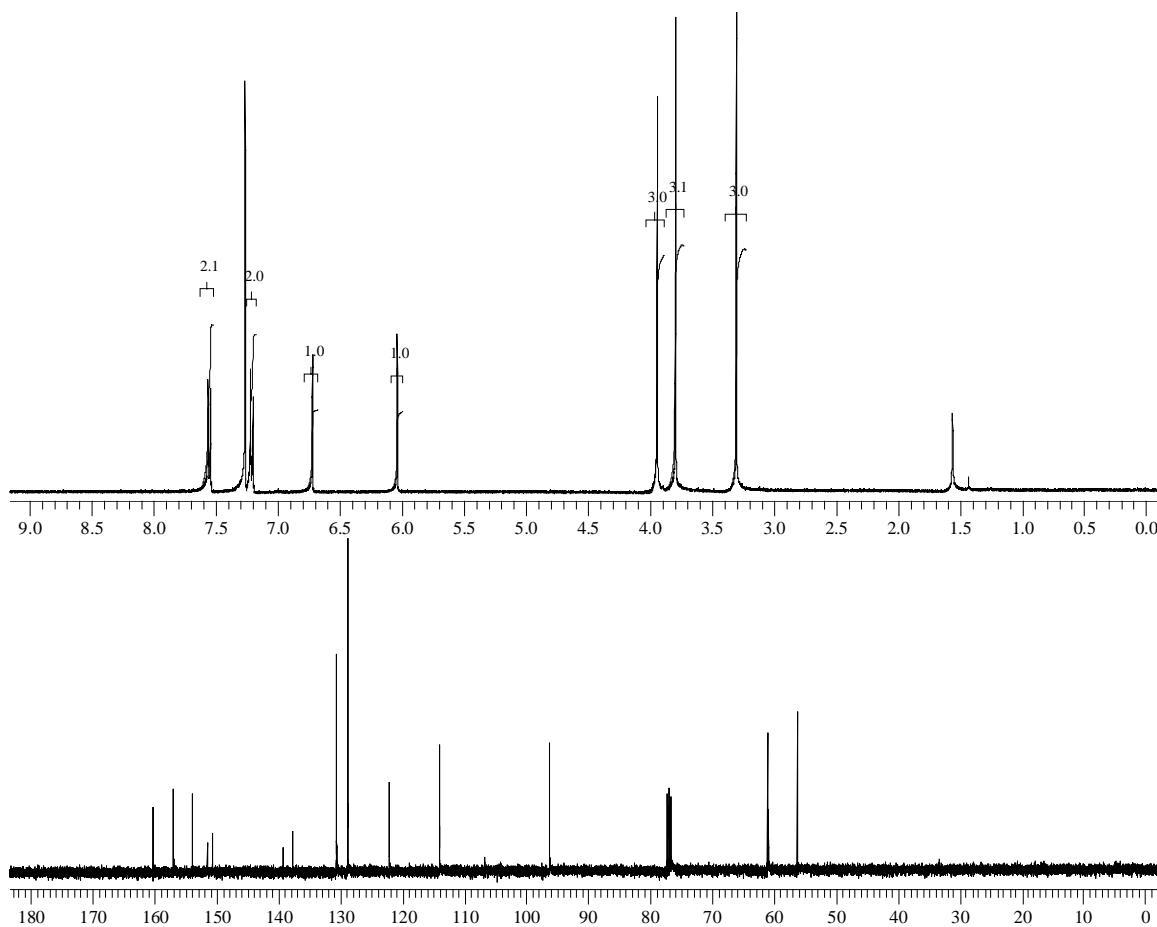


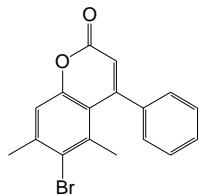
4-(4-Bromophenyl)-5,7-dimethoxy-2H-chromen-2-one (2d). ^1H NMR (CDCl_3): δ 7.49 (d, 2H, PhBr, $J = 8.2$ Hz); 7.13 (d, 2H, PhBr, $J = 8.2$ Hz); 6.49 (d, 1H, PhOCH_3 , $J = 2.0$ Hz); 6.22 (d, 1H, PhOCH_3 , $J = 2.4$ Hz); 5.94 (s, 1H, CHCO); 3.85 (s, 3H, PhOCH_3); 3.45 (s, 3H, PhOCH_3). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.5 (CO), Ph ring and C=C (163.5, 158.0, 157.1, 154.3, 138.6, 130.5, 128.8, 122.0 112.6, 103.0, 95.6, 93.5), PhOCH_3 (55.7, 55.3). ν_{max} (NaCl)/cm $^{-1}$: 3057, 1718, 1614, 1599, 1497, 1465, 1354, 1207, 1159, 1113, 1053, 1012. HR-MS: $\text{C}_{17}\text{H}_{14}\text{O}_4\text{Br}$ Calcd. 361.0075 ($\text{M}+1$); found: 361.0084.



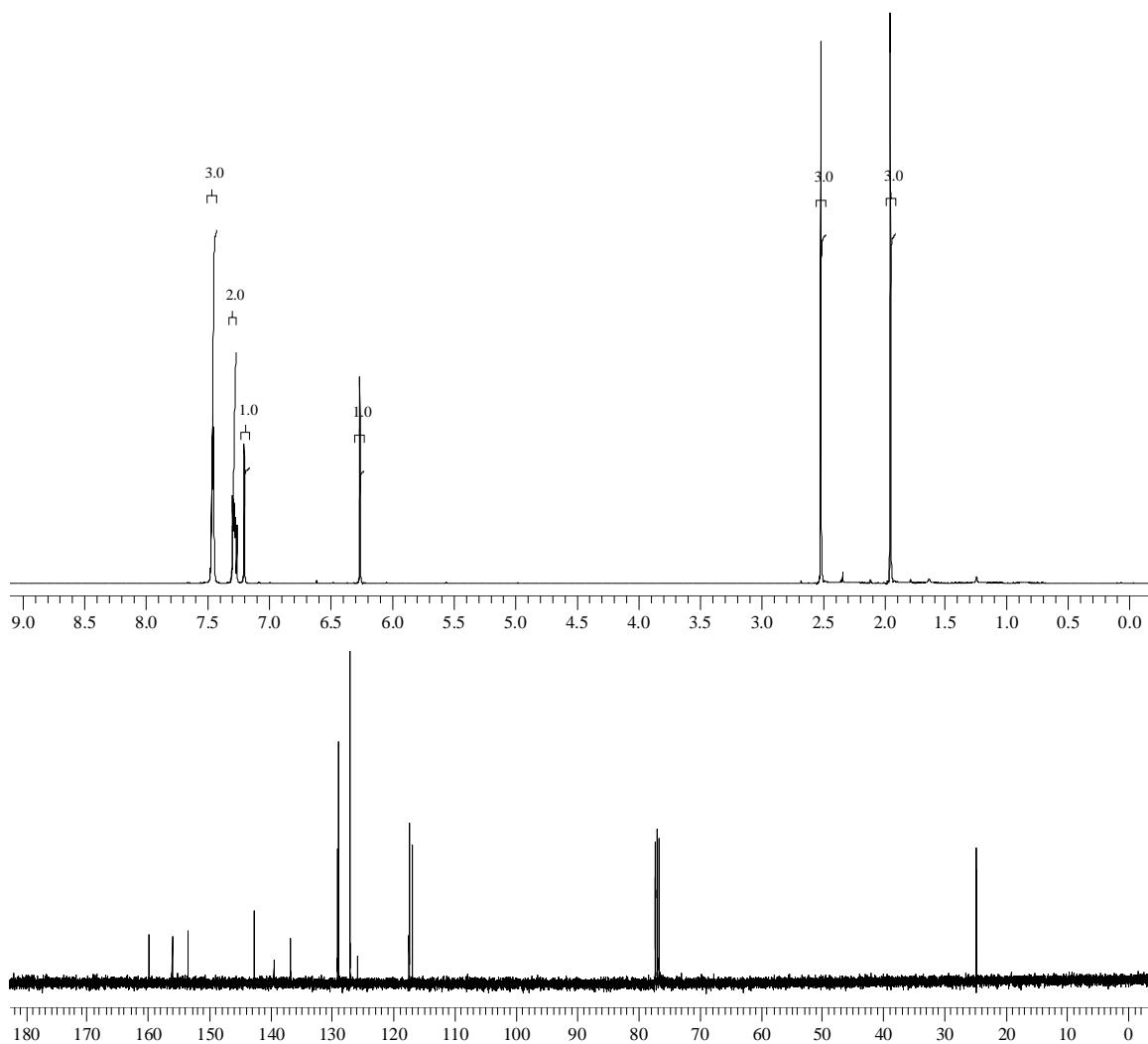


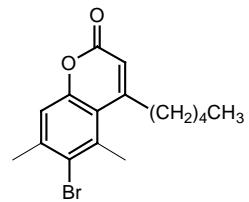
4-(4-Bromophenyl)-5,6,7-trimethoxy-2H-chromen-2-one (2e). ^1H NMR (CDCl_3): δ 7.55 (d, 2H, *PhBr*, $J = 8.5$ Hz); 7.21 (d, 2H, *PhBr*, $J = 8.5$ Hz); 6.72 (s, 1H, *PhOCH₃*); 6.04 (s, 1H, CHCO); 3.94 (s, 3H, *PhOCH₃*); 3.39 (s, 3H, *PhOCH₃*); 3.30 (s, 3H, *PhOCH₃*). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.3 (CO), Ph ring and C=C (157.0, 154.0, 151.6, 150.8, 139.3, 137.8, 130.6, 128.9, 122.1, 114.0, 106.7, 96.2), *PhOCH₃* (61.02, 60.96, 56.2). ν_{max} (NaCl)/cm⁻¹: 3058, 1722, 1605, 1549, 1489, 1458, 1410, 1364, 1200, 1132, 1101, 1036. HR-MS: C₁₈H₁₆O₅Br Calcd. 391.0181 (M+1); found: 391.0176.



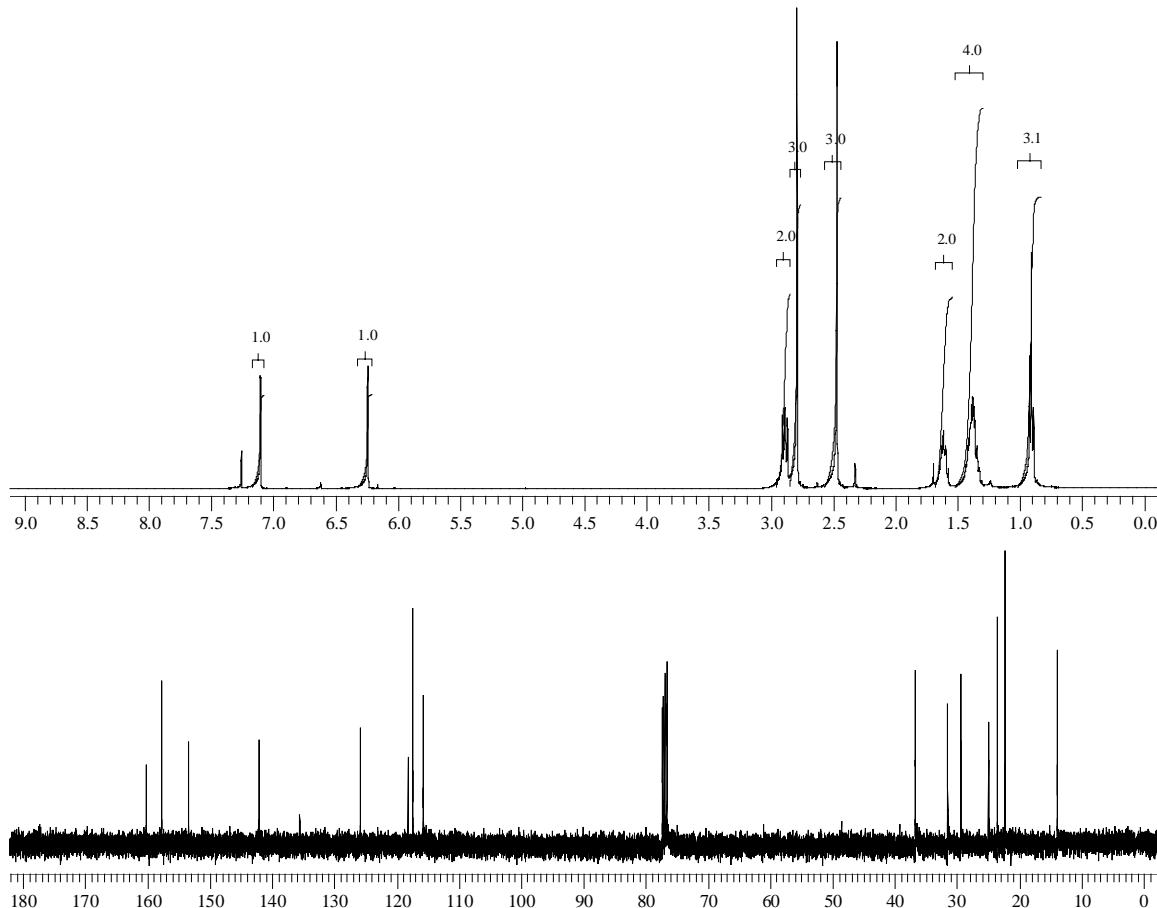


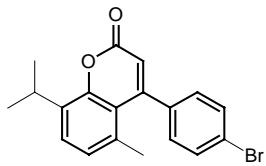
6-Bromo-5,7-dimethyl-4-phenyl-2H-chromen-2-one (2f).² ^1H NMR (CDCl_3): δ 7.45-7.47 (m, 3H, $\text{PhC}=\text{CH}$); 7.27-7.30 (m, 2H, $\text{PhC}=\text{CH}$); 7.20 (s, 1H, PhCH_3); 7.05 (dd, 2H, PhPhO , $J = 6.7$ and 1.5 Hz); 6.26 (s, 1H, CHCO); 2.51 (s, 3H, PhCH_3); 1.95 (s, 3H, PhCH_3). $^{13}\text{C}\{\text{H}\}$ NMR: δ 159.9 (CO), Ph ring and C=C (156.1, 153.6, 142.7, 139.5, 136.8, 129.1, 128.9, 127.1, 125.8, 117.41, 117.39, 116.9), PhCH_3 (24.8, 24.7).



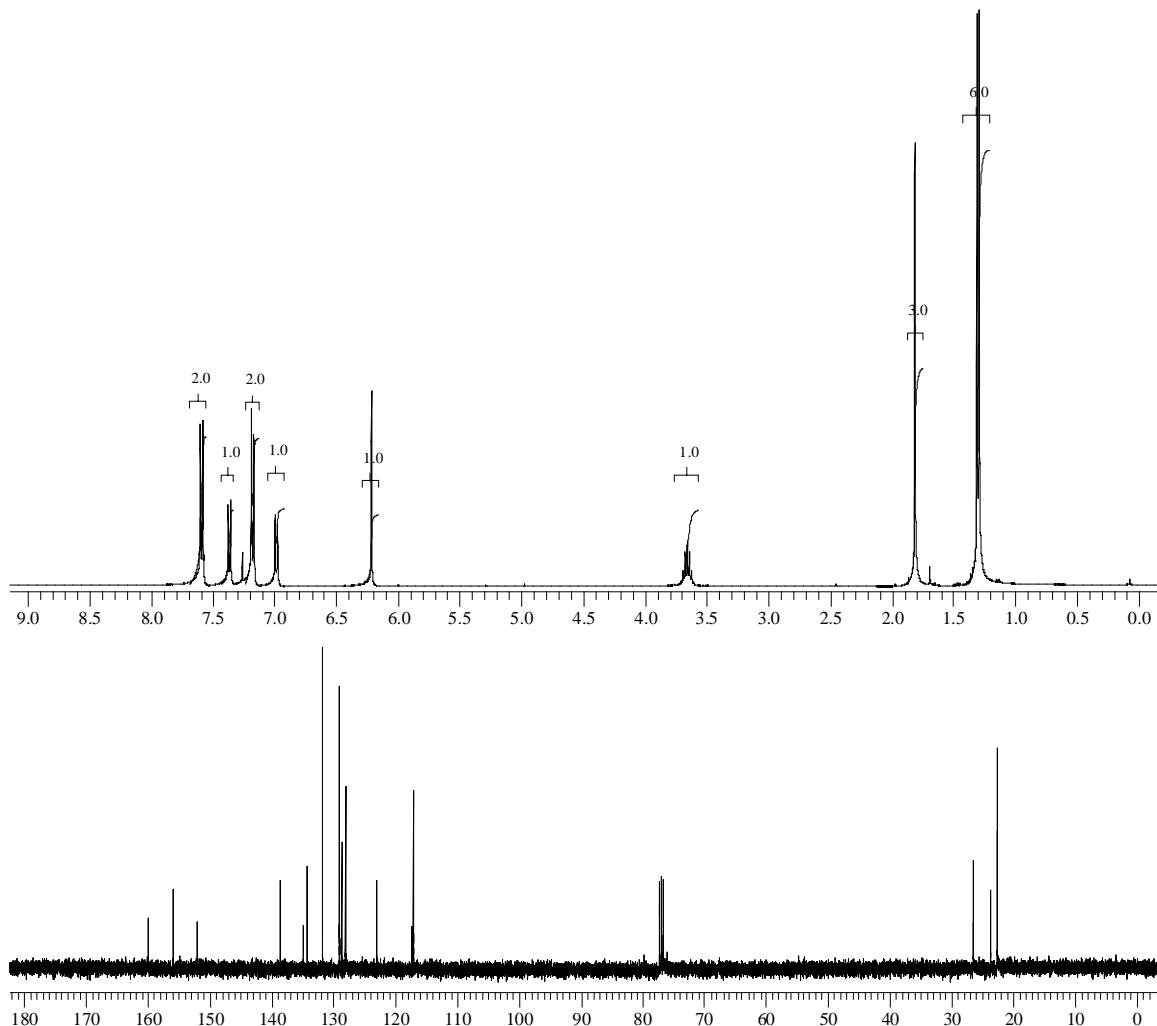


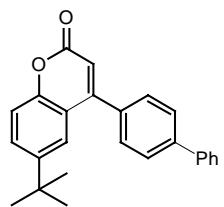
6-Bromo-5,7-dimethyl-4-pentyl-2H-chromen-2-one (2g). ^1H NMR (CDCl_3): δ 7.11 (s, 1H, Ph); 6.24 (s, 1H, CHCO); 2.89 (t, 2H, $\text{CH}=\text{CCH}_2$, $J = 7.9$ Hz); 2.79 (s, 3H, PhCH_3); 2.47 (s, 3H, PhCH_3); 1.58-1.65 (m, 2H, $\text{CH}=\text{CCH}_2\text{CH}_2$); 1.31-1.44 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_3$); 0.91 (t, 3H, CH_2CH_3 , $J = 7.0$ Hz). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.2 (CO), Ph ring and C=C (157.7, 153.4, 142.1, 135.6, 125.9, 118.2, 117.4, 115.7), 36.7 (CCH_2), 31.5 (CCH_2CH_2), 29.4 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 25.0(CH_2CH_3), 23.6 (PhCH_3), 22.4 (PhCH_3), 13.9 (CH_2CH_3). ν_{max} (NaCl)/cm $^{-1}$: 3058, 1724, 1599, 1535, 1448, 1427, 1380, 1356, 1230, 1178, 1105, 1041. HR-MS: $\text{C}_{16}\text{H}_{20}\text{O}_2\text{Br}$ Calcd. 323.0647 ($\text{M}+\text{H}$); found: 323.0647.



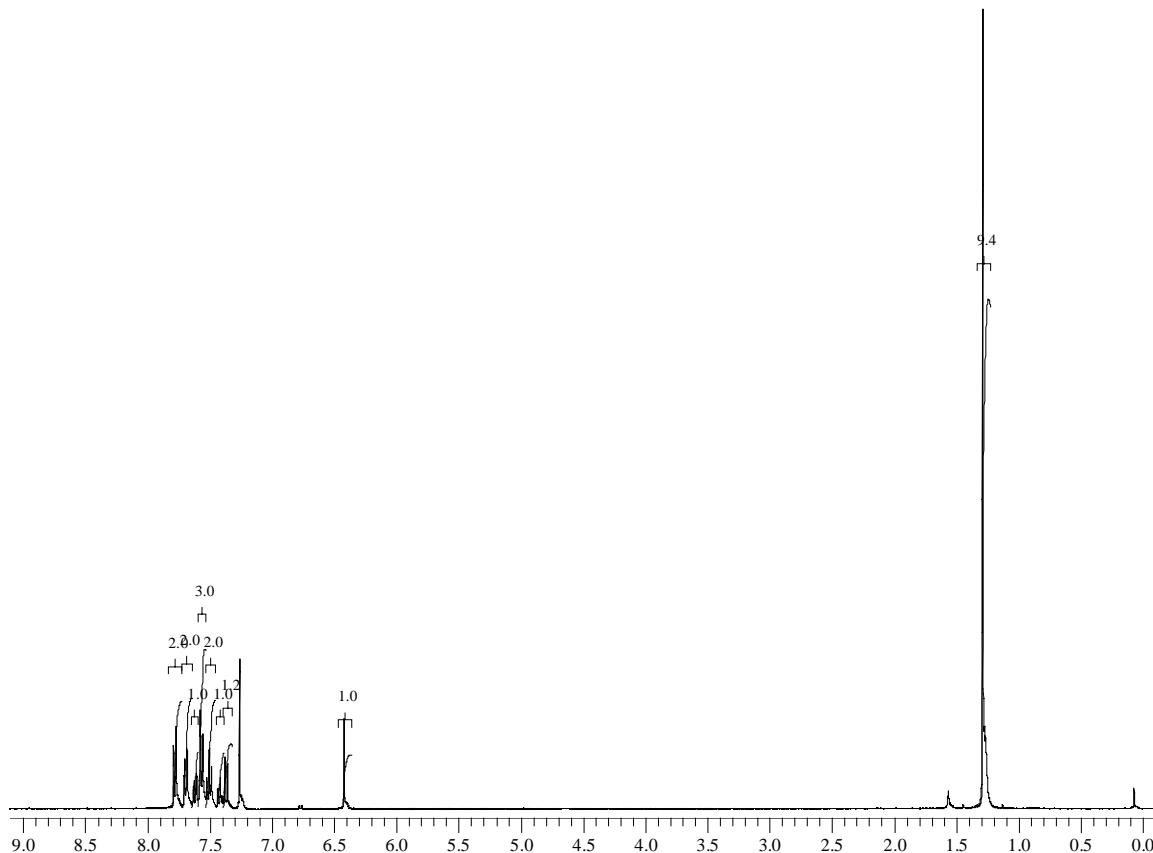


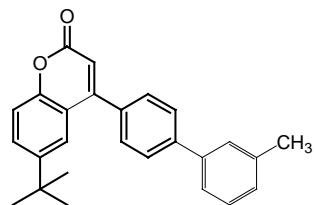
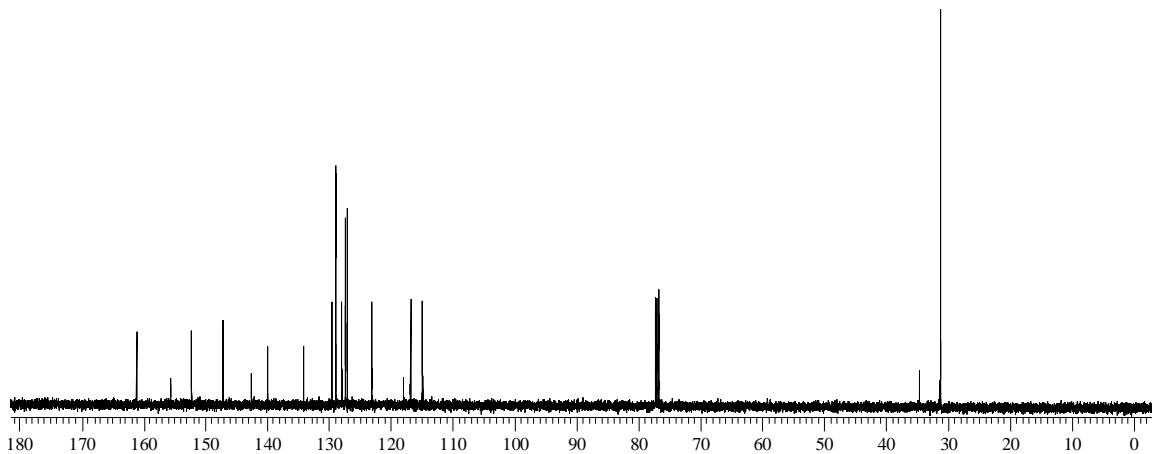
4-(4-Bromophenyl)-8-isopropyl-5-methyl-2H-chromen-2-one (2h). ^1H NMR (CDCl_3): δ 7.59 (d, 2H, *PhBr*, $J = 8.2$ Hz); 7.37 (d, 1H, *PhO*, $J = 7.6$ Hz); 7.18 (d, 2H, *PhBr*, $J = 8.2$ Hz); 6.99 (d, 1H, *PhO*, $J = 7.6$ Hz); 6.22 (s, 1H, *CHCO*); 3.62-3.69 (m, 1H, *CHCH₃*); 1.82 (s, 3H, *PhCH₃*); 1.30 (d, 6H, *CHCH₃*, $J = 6.7$ Hz). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.0 (CO), Ph ring and C=C (155.9, 152.1, 138.7, 134.9, 134.3, 131.8, 129.0, 128.7, 128.1, 123.0, 117.3, 117.1), *CHCH₃* (26.5, 22.7), 23.7 (*PhCH₃*). ν_{max} (NaCl)/cm⁻¹: 3055, 1720, 1578, 1489, 1447, 1416, 1196, 1051, 1015. HR-MS: C₁₉H₁₈O₂Br Calcd. 357.0490 (M+1); found: 357.0502.



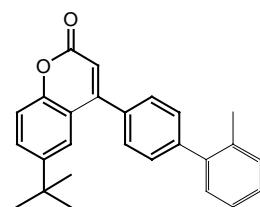
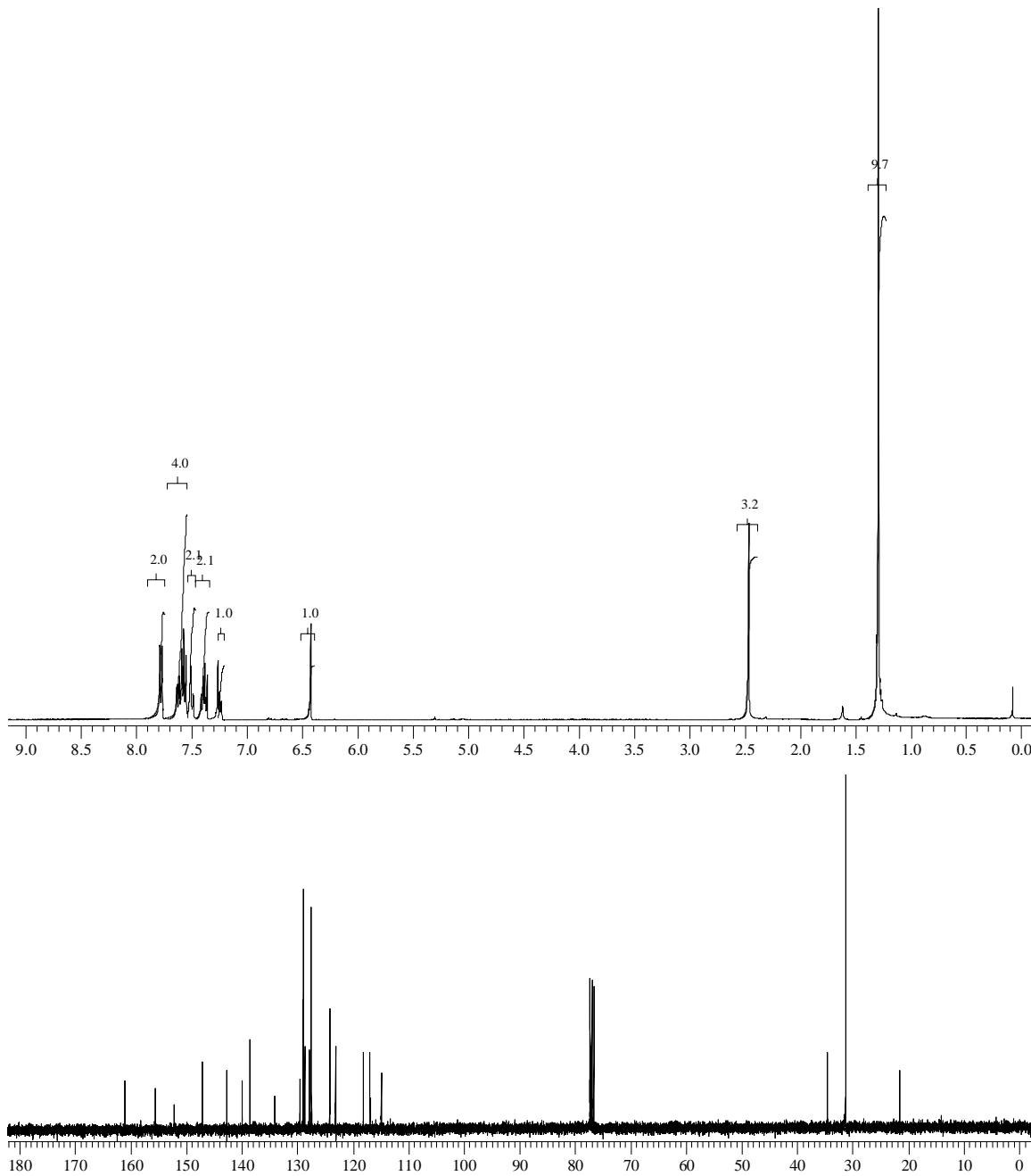


6-*tert*-Butyl-4-(4-biphenyl)-2*H*-chromen-2-one (3a). ^1H NMR (CDCl_3): δ 7.77 (d, 2H, PhPhC, $J = 8.2$ Hz); 7.69 (d, 2H, PhPhC, $J = 7.3$ Hz); 7.62 (dd, 1H, $'\text{BuPh}$, $J = 8.8$ and 2.3 Hz); 7.58 (s, 1H, $'\text{BuPh}$); 7.57 (d, 2H, PhPhC, $J = 8.2$ Hz); 7.51 (t, 2H, PhPhC, $J = 7.6$ Hz); 7.42 (t, 1H, PhPhC, $J = 7.6$ Hz); 7.37 (d, 1H, $'\text{BuPh}$, $J = 8.8$ Hz); 6.42 (s, 1H, CHCO); 1.29 (s, 9H, $'\text{Bu}$). $^{13}\text{C}\{\text{H}\}$ NMR: δ 161.1 (CO), Ph ring and C=C (155.6, 152.2, 147.2, 142.5, 139.9, 134.1, 129.5, 128.95, 128.94, 127.9, 127.4, 127.1, 123.1, 118.1, 116.9, 114.9), $'\text{Bu}$ (34.6, 31.3). ν_{max} (NaCl)/cm $^{-1}$: 3055, 1720, 1614, 1570, 1489, 1369, 1256, 1186, 1130. HR-MS: $\text{C}_{25}\text{H}_{23}\text{O}_2$ Calcd. 355.1698 ($\text{M}+1$); found: 355.1709.



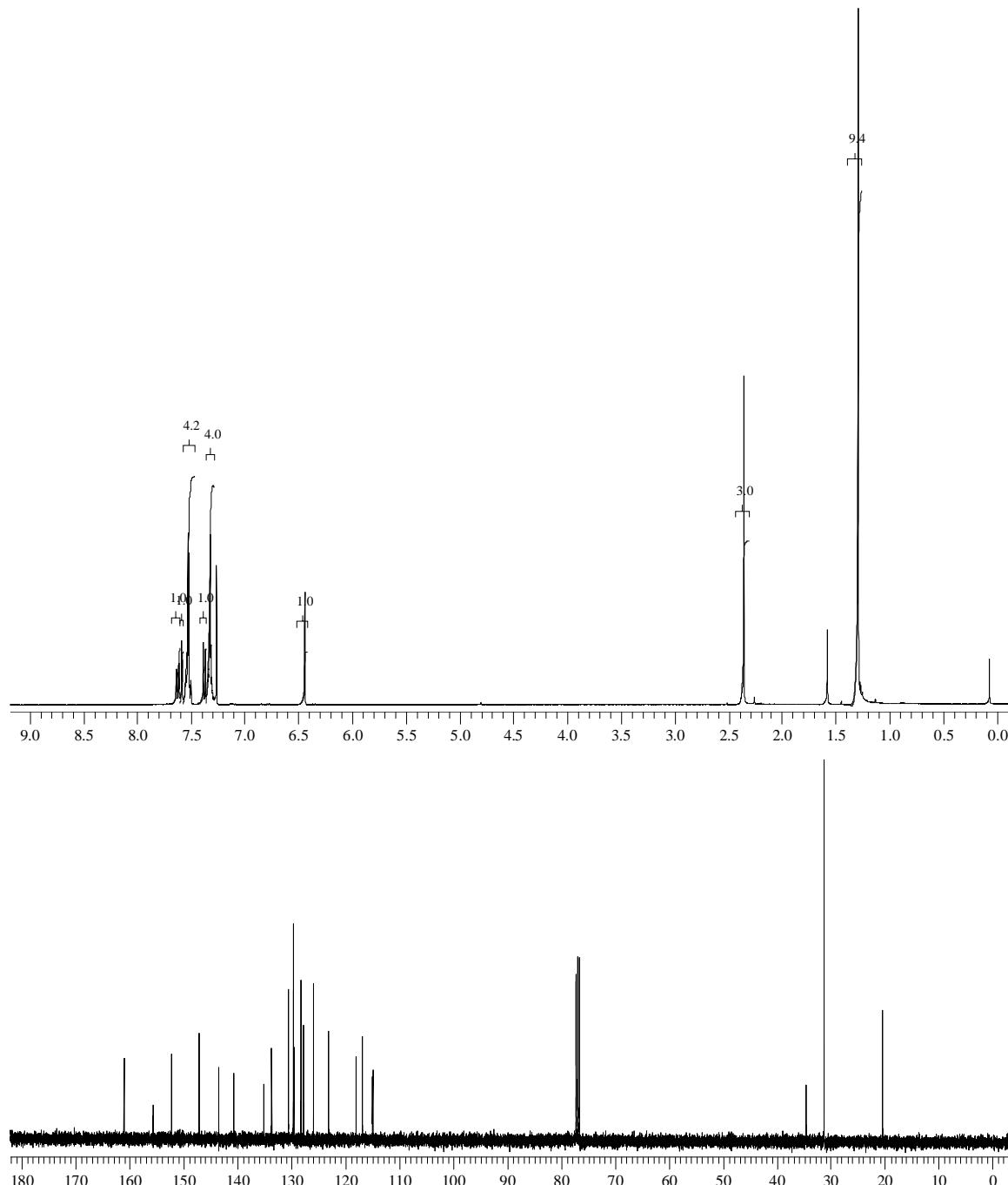


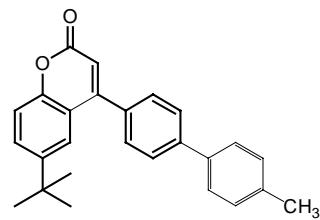
6-*tert*-Butyl-4-(4-*m*-tolylphenyl)-2*H*-chromen-2-one (3b). ^1H NMR (CDCl_3): δ 7.77 (d, 2H, *PhPhCH*₃, *J* = 8.5 Hz); 7.62 (dd, 1H, *tBuPh*, *J* = 8.8 and 2.3 Hz); 7.58 (d, 1H, *tBuPh*, *J* = 2.3 Hz); 7.56 (d, 2H, *PhPhCH*₃, *J* = 8.5 Hz); 7.51 (s, 1H, *PhCH*₃); 7.49 (d, br, 1H, *PhCH*₃, *J* = 7.6 Hz); 7.39 (t, 1H, *PhCH*₃, *J* = 7.3 Hz); 7.37 (d, 1H, *tBuPh*, *J* = 8.8 Hz); 7.24 (d, 1H, *PhCH*₃, *J* = 7.3 Hz); 6.42 (s, 1H, CHCO); 2.46 (s, 3H, *PhCH*₃); 1.29 (s, 9H, *tBu*). $^{13}\text{C}\{\text{H}\}$ NMR: δ 161.1 (CO), Ph ring and C=C (155.6, 152.2, 147.2, 142.7, 139.9, 138.6, 134.1, 129.53, 129.52, 128.91, 128.87, 128.7, 127.9, 124.2, 123.2, 118.1, 116.9, 114.9), *tBu* (34.6, 31.3), 21.5 (*PhCH*₃). ν_{max} (NaCl)/cm⁻¹: 1062, 1720, 1614, 1570, 1486, 1371, 1186, 1130. HR-MS: C₂₆H₂₅O₂ Calcd. 369.1855 (M+1); found: 369.1846.



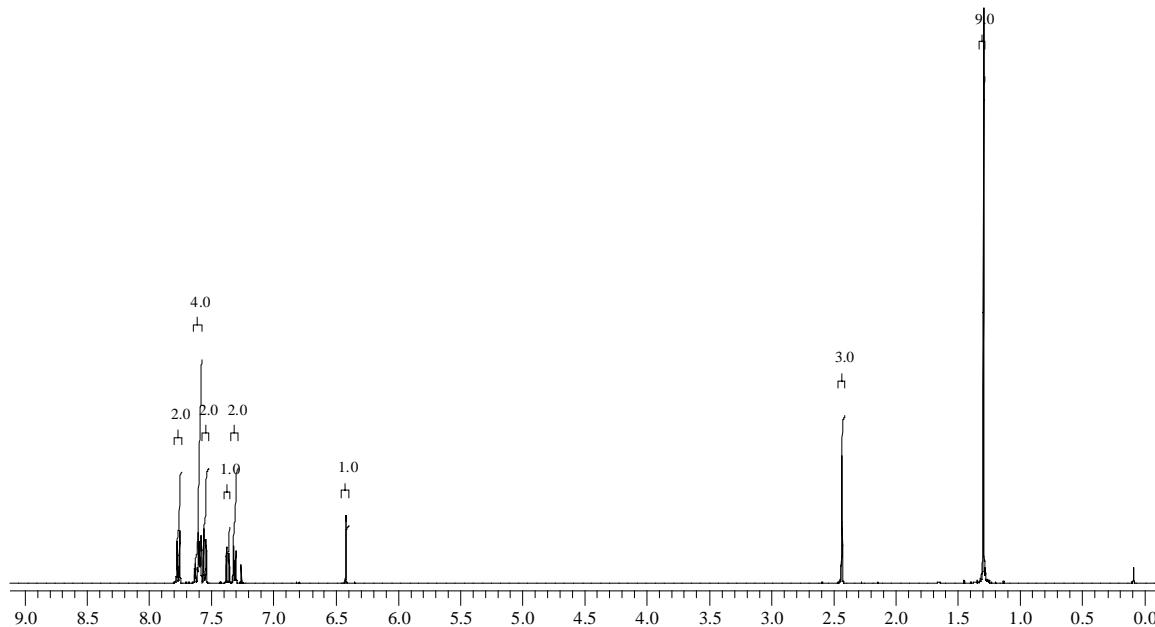
6-*tert*-Butyl-4-(4-*o*-tolylphenyl)-2*H*-chromen-2-one (3c**).** ^1H NMR (CDCl_3): δ 7.62 (dd, 1H, $^3\text{J}_{\text{H,H}} = 8.8$ and 2.3 Hz); 7.58 (d, 1H, $^3\text{J}_{\text{H,H}} = 2.3$ Hz); 7.50-7.55 (m, 4H,

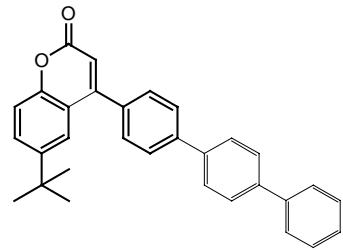
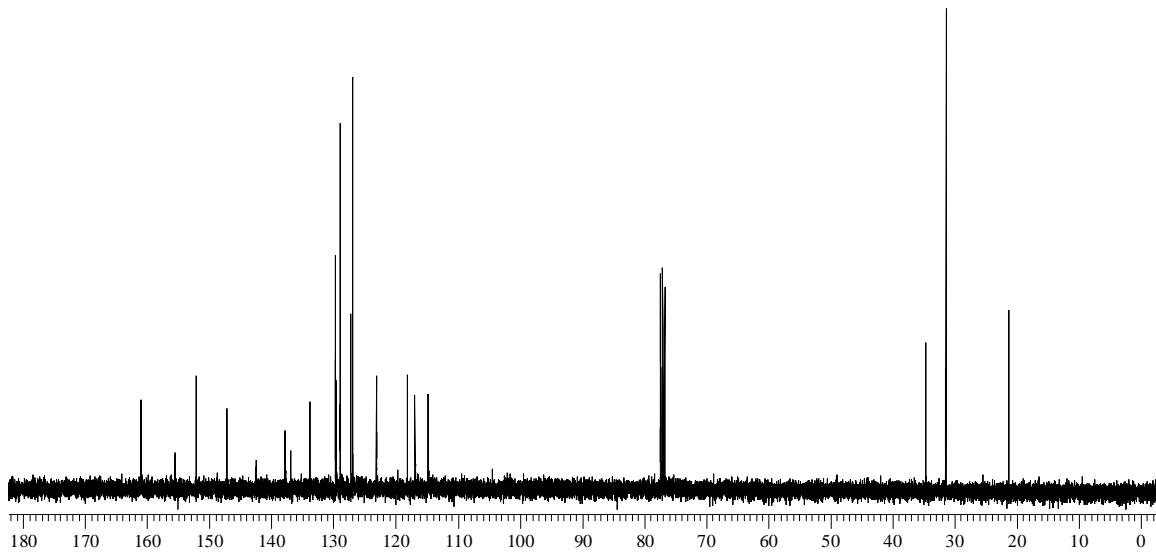
PhPhCH₃); 7.37 (d, 1H, ^tBu*Ph*, *J* = 8.8 Hz); 7.30-7.34 (m, 4H, *PhPhCH₃*); 6.44 (s, 1H, CHCO); 2.36 (s, 3H, PhCH₃); 1.29 (s, 9H, ^tBu). ¹³C{¹H} NMR: δ 161.1 (CO), Ph ring and C=C (155.7, 152.2, 147.2, 143.4, 140.7, 135.2, 133.7, 130.5, 129.7, 129.6, 129.55, 128.3, 127.7, 125.9, 123.1, 118.1, 116.9, 114.9), ^tBu (34.6, 31.3), 20.5 (PhCH₃). ν_{max} (NaCl)/cm⁻¹: 3058, 1720, 1616, 1570, 1485, 1369, 1186, 1130. HR-MS: C₂₆H₂₅O₂ Calcd. 369.1855 (M+1); found: 369.1867.



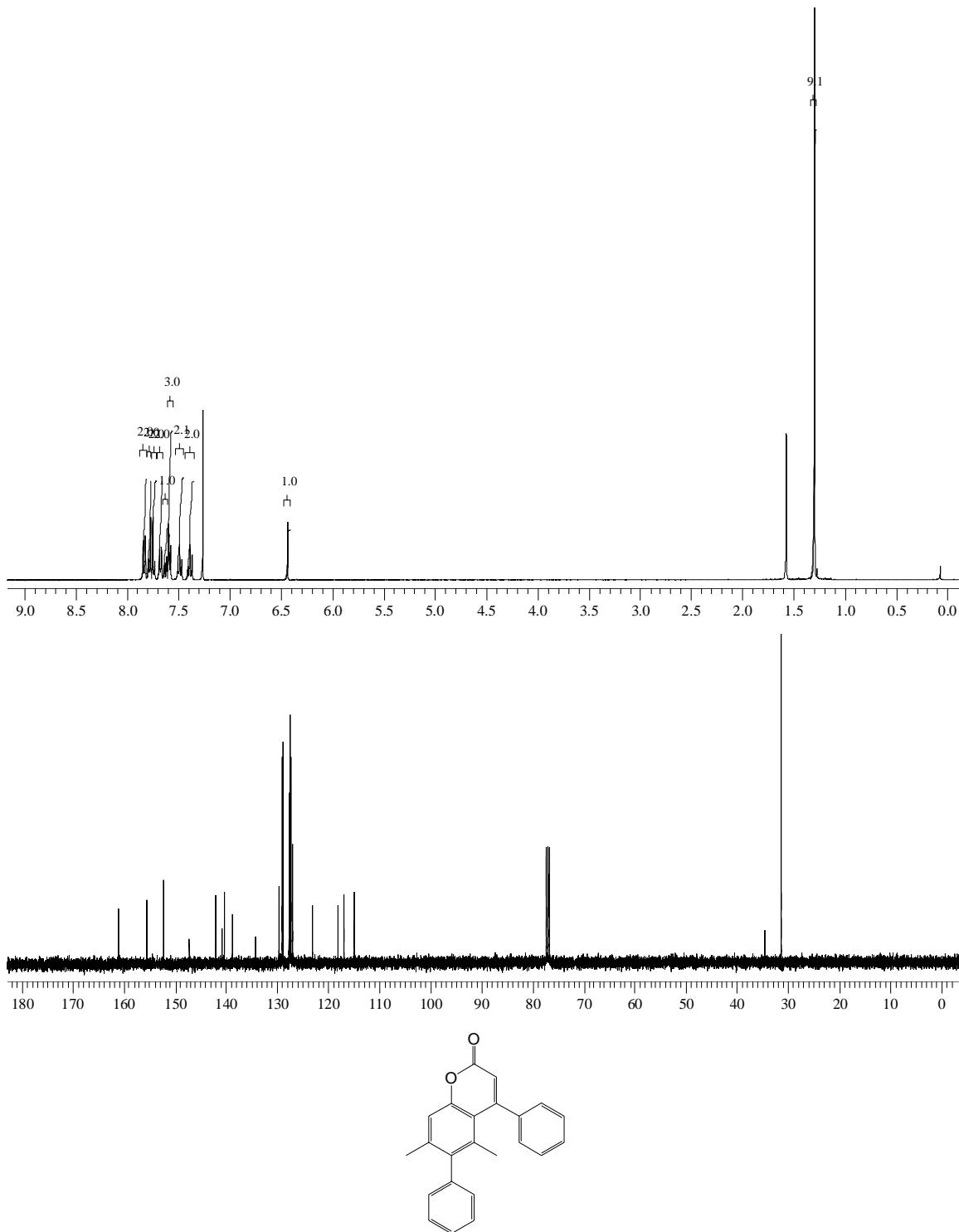


6-*tert*-Butyl-4-(4-*p*-tolylphenyl)-2*H*-chromen-2-one (3d). ^1H NMR (CDCl_3): δ 7.77 (d, 2H, $Ph\text{PhCH}_3$, $J = 8.2$ Hz); 7.62 (dd, 1H, $^t\text{BuPh}$, $J = 8.8$ and 2.3 Hz); 7.60 (d, 1H, $^t\text{BuPh}$, $J = 2.3$ Hz); 7.59 (d, 2H, $Ph\text{CH}_3$, $J = 8.5$ Hz); 7.56 (d, 2H, $Ph\text{PhCH}_3$, $J = 8.2$ Hz); 7.37 (d, 1H, $^t\text{BuPh}$, $J = 8.8$ Hz); 7.31 (d, 2H, $Ph\text{CH}_3$, $J = 8.5$ Hz); 6.42 (s, 1H, CHCO); 2.43 (s, 3H, $Ph\text{CH}_3$); 1.29 (s, 9H, ^tBu). $^{13}\text{C}\{\text{H}\}$ NMR: δ 161.1 (CO), Ph ring and C=C (155.6, 152.2, 147.2, 142.5, 137.8, 137.0, 133.8, 129.7, 129.5, 128.9, 127.2, 126.9, 123.2, 118.1, 116.9, 114.8), ^tBu (34.6, 31.3), 21.1 ($Ph\text{CH}_3$). ν_{max} (NaCl)/ cm^{-1} : 3055, 1720, 1614, 1570, 1499, 1489, 1371, 1186, 1130. HR-MS: $\text{C}_{26}\text{H}_{25}\text{O}_2$ Calcd. 369.1855 ($M+1$); found: 369.1851.



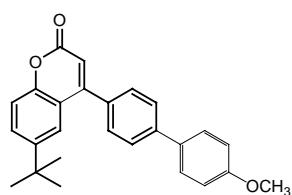
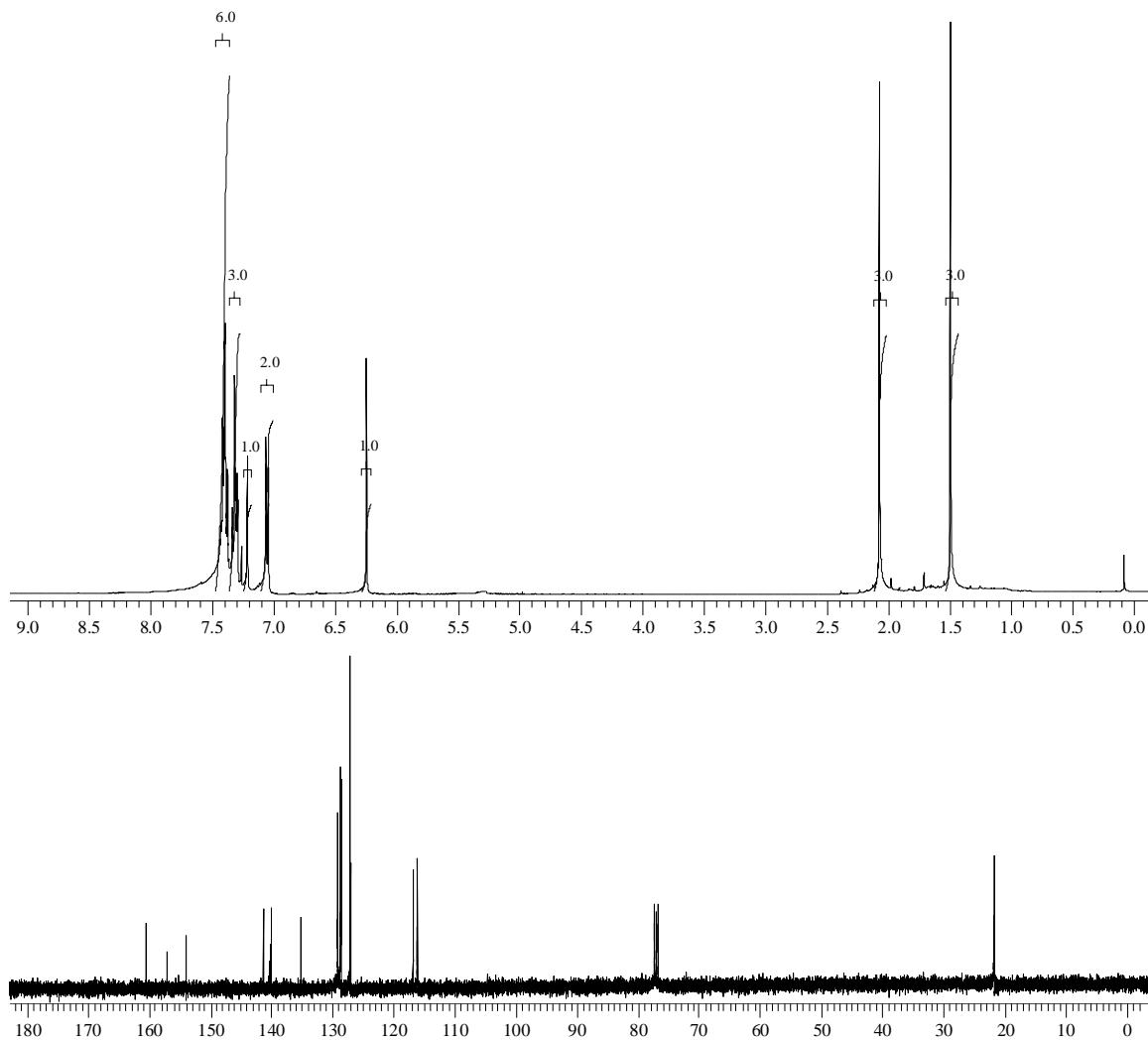


6-*tert*-Butyl-4-(4-terphenyl)-2*H*-chromen-2-one (3e**).** ^1H NMR (CDCl_3): δ 7.83 (d, 2H, PhPhPhC, $J = 8.5$ Hz); 7.78 (d, 2H, PhPhC, $J = 8.2$ Hz); 7.74 (d, 2H, PhPhPhC, $J = 8.5$ Hz); 7.67 (d, 2H, PhPhPhC, $J = 7.3$ Hz); 7.62 (dd, 1H, $'\text{BuPh}$, $J = 8.8$ and 2.3 Hz); 7.60 (s, 1H, $'\text{BuPh}$); 7.59 (d, 2H, PhPhC, $J = 8.2$ Hz); 7.49 (t, 2H, PhPhPhC, $J = 7.3$ Hz); 7.39 (t, 1H, PhPhPhC, $J = 7.3$ Hz); 7.38 (d, 1H, $'\text{BuPh}$, $J = 8.8$ Hz); 6.43 (s, 1H, CHCO); 1.30 (s, 9H, $'\text{Bu}$). $^{13}\text{C}\{\text{H}\}$ NMR: δ 161.1 (CO), Ph ring and C=C (155.5, 152.2, 147.2, 142.0, 140.8, 140.4, 138.7, 134.2, 129.6, 129.0, 128.8, 127.7, 127.52, 127.47, 127.3, 127.0, 123.1, 118.1, 116.9, 114.9), $'\text{Bu}$ (34.6, 31.3). ν_{max} (NaCl)/cm⁻¹: 3055, 1722, 1614, 1570, 1485, 1371, 1184, 1130. HR-MS: $\text{C}_{31}\text{H}_{27}\text{O}_2$ Calcd. 431.2011 (M+1); found: 431.2015.



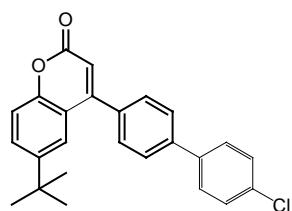
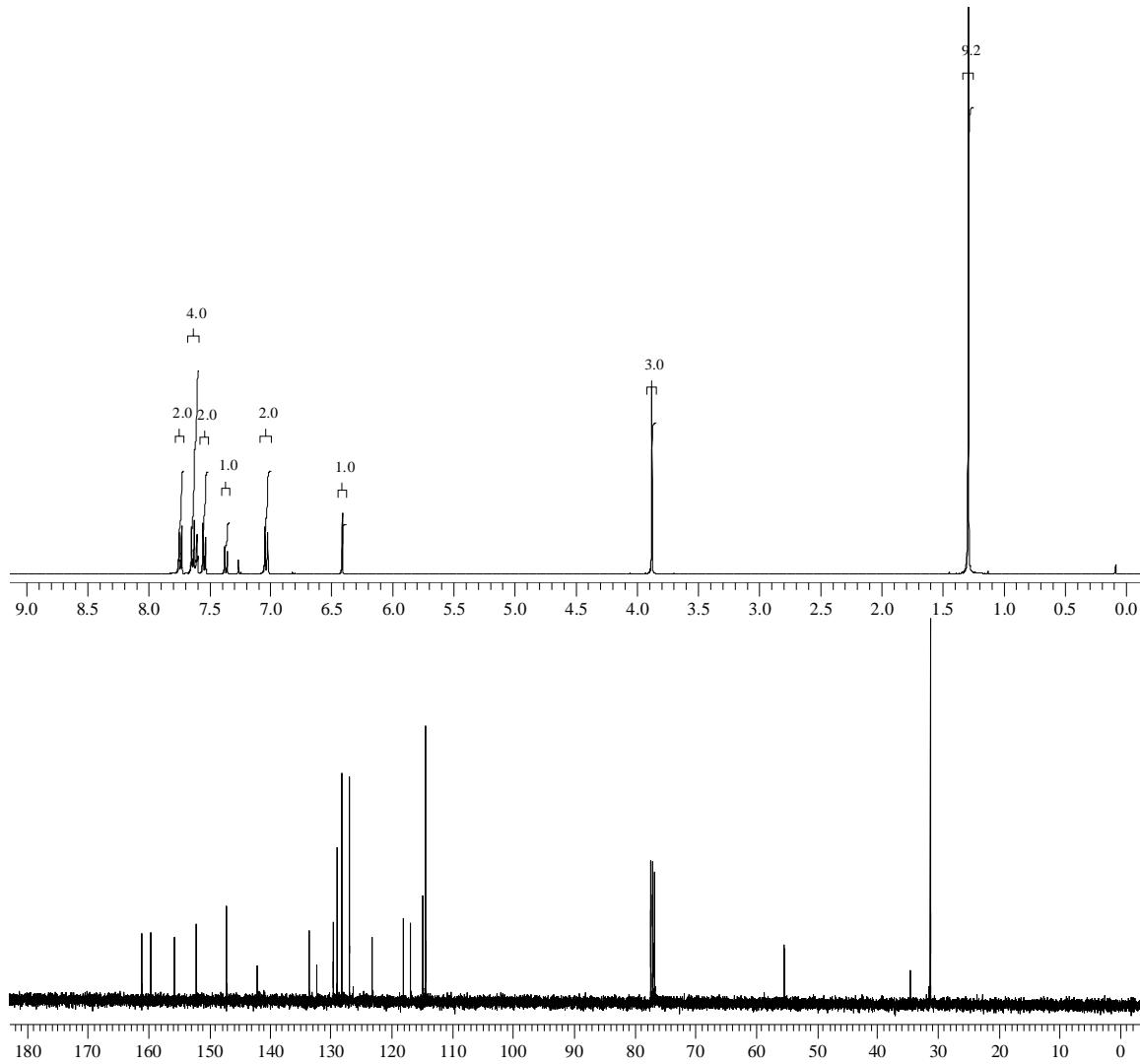
5,7-Dimethyl-4,6-diphenyl-2H-chromen-2-one (3f). ^1H NMR (CDCl_3): δ 7.38-7.44 (m, 6H, $\text{PhC}=\text{CH}$, PhPhO); 7.29-7.34 (m, 3H, $\text{PhC}=\text{CH}$, PhPhO); 7.21 (s, 1H, PhCH_3); 7.05 (dd, 2H, PhPhO , $J = 6.7$ and 1.5 Hz); 6.24 (s, 1H, CHCO); 2.07 (s, 3H, PhCH_3); 1.50 (s, 3H, PhCH_3). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.5 (CO), Ph ring and C=C (157.0, 154.0, 141.3, 140.4,

140.2, 140.0, 135.2, 129.1, 128.7, 128.6, 127.1, 127.0, 116.8, 116.1, 116.0), PhCH₃ (21.8, 21.7). ν_{max} (NaCl)/cm⁻¹: 3055, 1722, 1602, 1541, 1357, 1269, 1211, 1179, 1120, 1070. HR-MS: C₂₃H₁₉O₂ Calcd. 327.1385 (M+1); found: 327.1385.



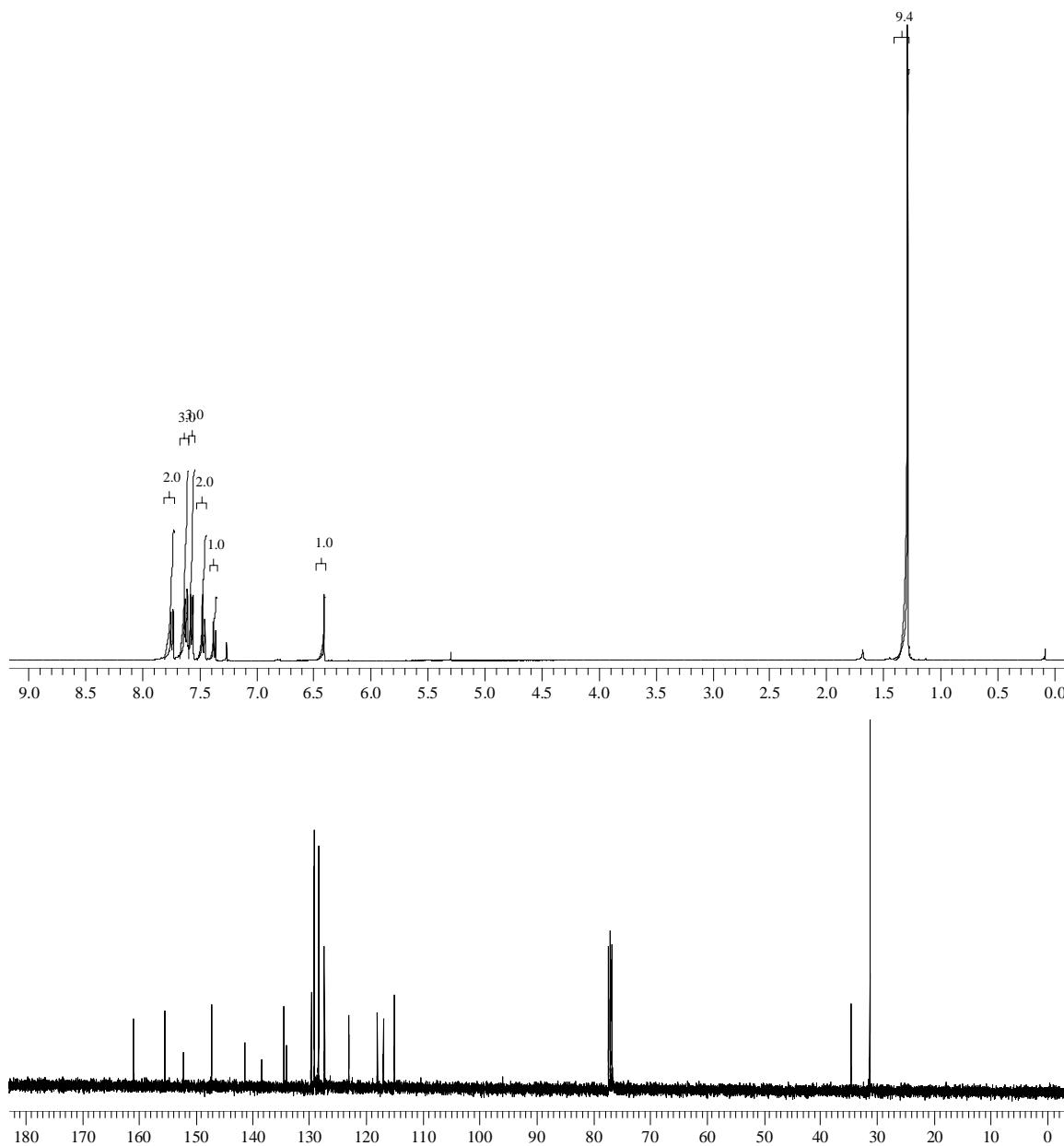
6-*tert*-Butyl-4-(4-p-methoxybiphenyl)-2*H*-chromen-2-one (3g). ¹H NMR (CDCl₃): δ 7.74 (d, 2H, PhPhOCH₃, J = 8.3 Hz); 7.63 (d, 2H, PhOCH₃, J = 8.8 Hz); 7.60-7.64 (m, 2H, ^tBuPh); 7.54 (d, 2H, PhPhOCH₃, J = 8.3 Hz); 7.37 (d, 1H, ^tBuPh, J = 8.5 Hz); 7.03 (d, 2H, PhOCH₃, J = 8.8 Hz); 6.41 (s, 1H, CHCO); 3.88 (s, 3H, OCH₃); 1.29 (s, 9H, ^tBu).

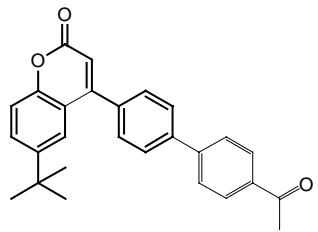
$^{13}\text{C}\{\text{H}\}$ NMR: δ 161.1 (CO), Ph ring and C=C (159.6, 155.7, 152.2, 147.2, 142.1, 133.5, 132.3, 129.5, 129.0, 128.2, 126.9, 123.2, 118.1, 116.9, 114.8, 114.4), 55.3 (OCH_3), ^3Bu (34.6, 31.3). ν_{max} (NaCl)/cm⁻¹: 3055, 1720, 1609, 1568, 1499, 1371, 1250, 1178, 1040. HR-MS: $\text{C}_{26}\text{H}_{25}\text{O}_3$ Calcd. 385.1804 (M+1); found: 385.1800.



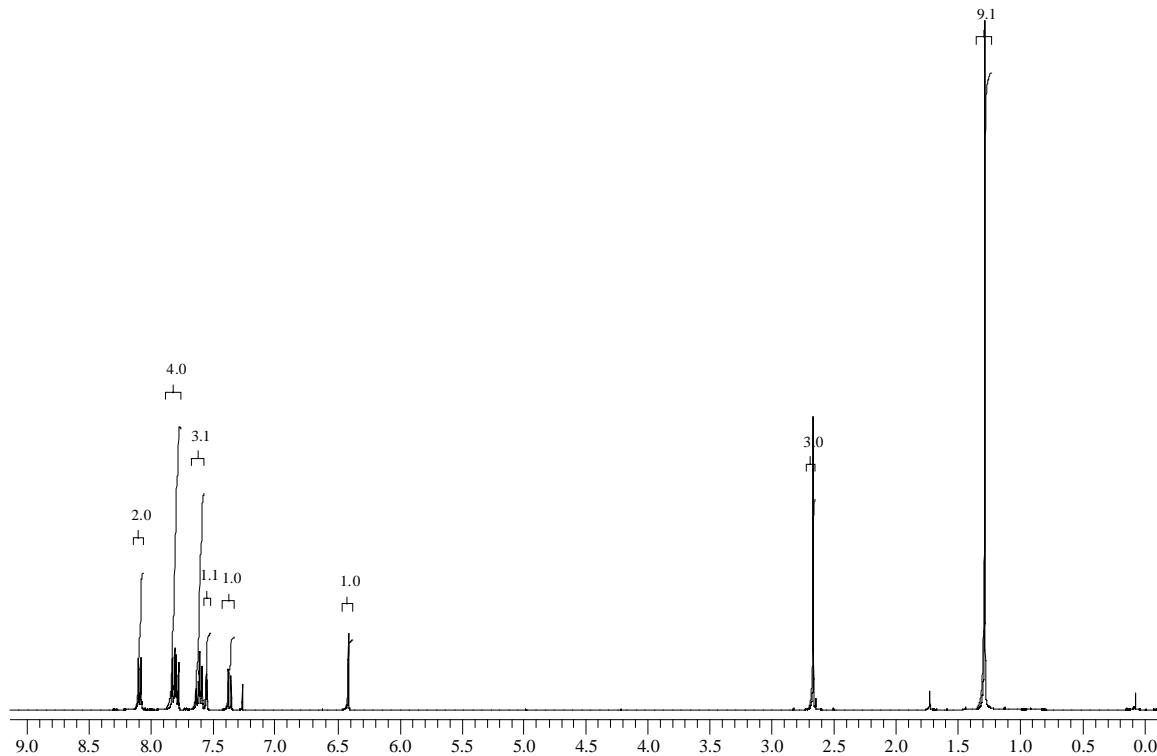
6-tert-Butyl-4-(4-p-chlorobiphenyl)-2H-chromen-2-one (3h). ^1H NMR (CDCl_3): δ 7.74 (d, 2H, PhPhC, $J = 8.5$ Hz); 7.62 (d, 2H, PhCl, $J = 8.5$ Hz); 7.62 (dd, 1H, $^3\text{BuPh}$, $J = 8.8$

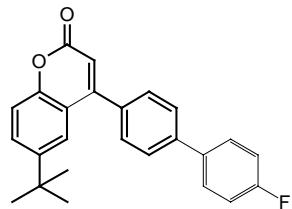
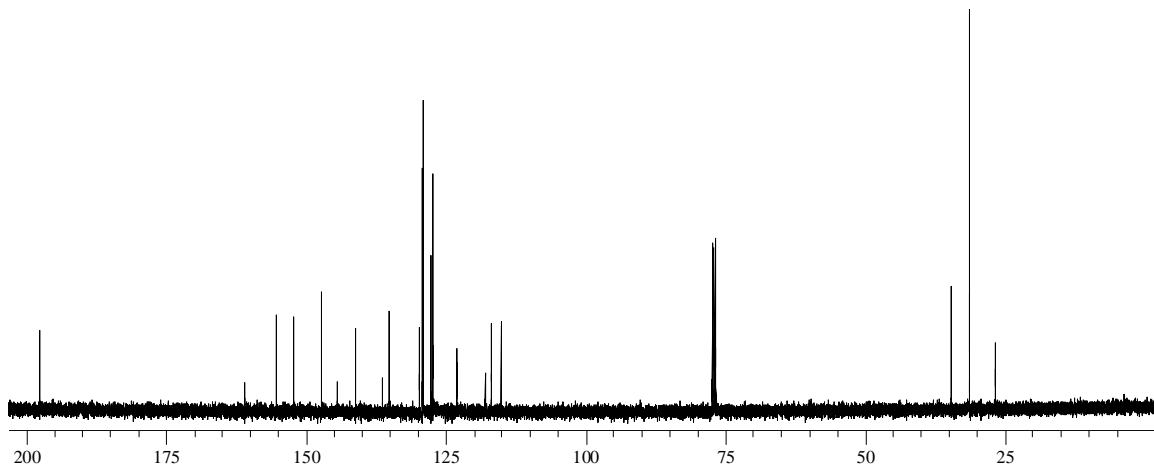
and 2.3 Hz); 7.57 (d, 2H, PhPhC, J = 8.5 Hz); 7.56 (s, 1H, $'\text{BuPh}$); 7.46 (d, 2H, PhCl, J = 8.5 Hz); 7.37 (d, 1H, $'\text{BuPh}$, J = 8.8 Hz); 6.41 (s, 1H, CHCO); 1.29 (s, 9H, $'\text{Bu}$). $^{13}\text{C}\{\text{H}\}$ NMR: δ 161.0 (CO), Ph ring and C=C (155.4, 152.2, 147.3, 141.3, 138.4, 134.5, 134.1, 129.6, 129.11, 129.07, 128.4, 127.3, 123.0, 118.0, 116.9, 115.0), $'\text{Bu}$ (34.6, 31.3). ν_{max} (NaCl)/cm $^{-1}$: 3055, 1720, 1616, 1568, 1558, 1485, 1371, 1184, 1130, 1095. HR-MS: C₂₅H₂₂ClO₂ Calcd. 389.1308 (M+1); found: 389.1306.



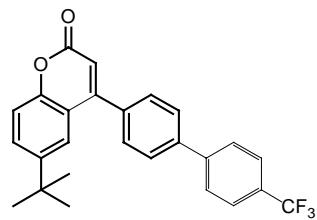
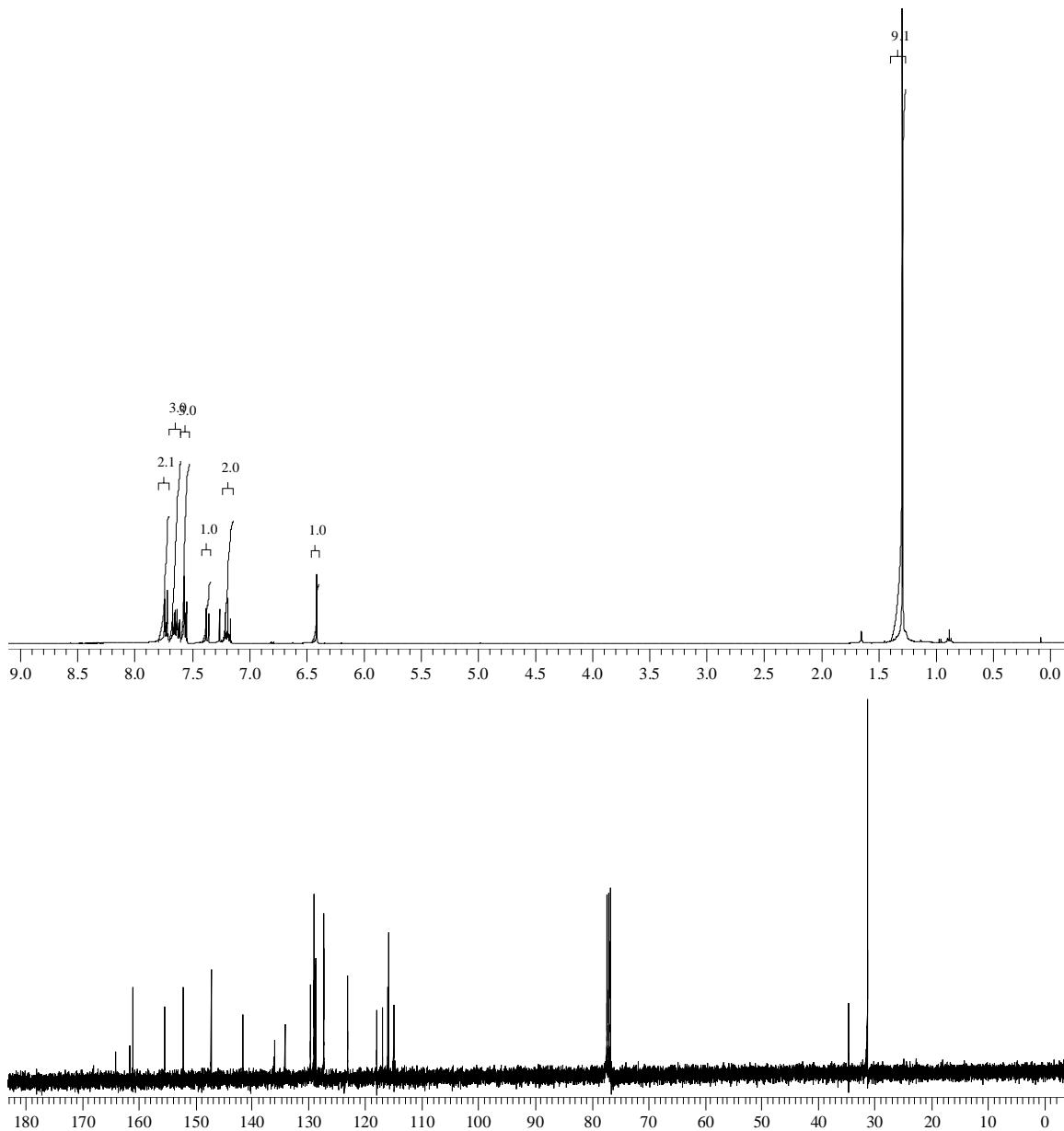


4-(4-p-Acetyl biphenyl)-6-tert-butyl-2H-chromen-2-one (3i). ^1H NMR (CDCl_3): δ 8.09 (d, 2H, PhCOCH_3 , $J = 8.5$ Hz); 7.82 (d, 2H, PhPhC , $J = 8.5$ Hz); 7.79 (d, 2H, PhCOCH_3 , $J = 8.5$ Hz); 7.62 (dd, 1H, $^3\text{BuPh}$, $J = 8.8$ and 2.3 Hz); 7.60 (d, 2H, PhPhC , $J = 8.5$ Hz); 7.55 (d, 1H, $^3\text{BuPh}$, $J = 2.3$ Hz); 7.36 (d, 1H, $^3\text{BuPh}$, $J = 8.8$ Hz); 6.41 (s, 1H, CHCO); 2.67 (s, 3H, COCH_3), 1.29 (s, 9H, ^3Bu). $^{13}\text{C}\{\text{H}\}$ NMR: δ 197.6 (COCH_3), 160.9 (CO_2), Ph ring and C=C (155.3, 152.2, 147.3, 144.4, 141.2, 136.3, 135.2, 129.6, 129.1, 129.0, 127.6, 127.3, 123.0, 118.0, 116.9, 115.1), ^3Bu (34.6, 31.3), 26.7 (COCH_3). ν_{max} (NaCl)/ cm^{-1} : 3058, 1722, 1684, 1605, 1570, 1369, 1360, 1258, 1184. HR-MS: $\text{C}_{27}\text{H}_{25}\text{O}_3$ Calcd. 397.1804 ($\text{M}+1$); found: 397.1799.



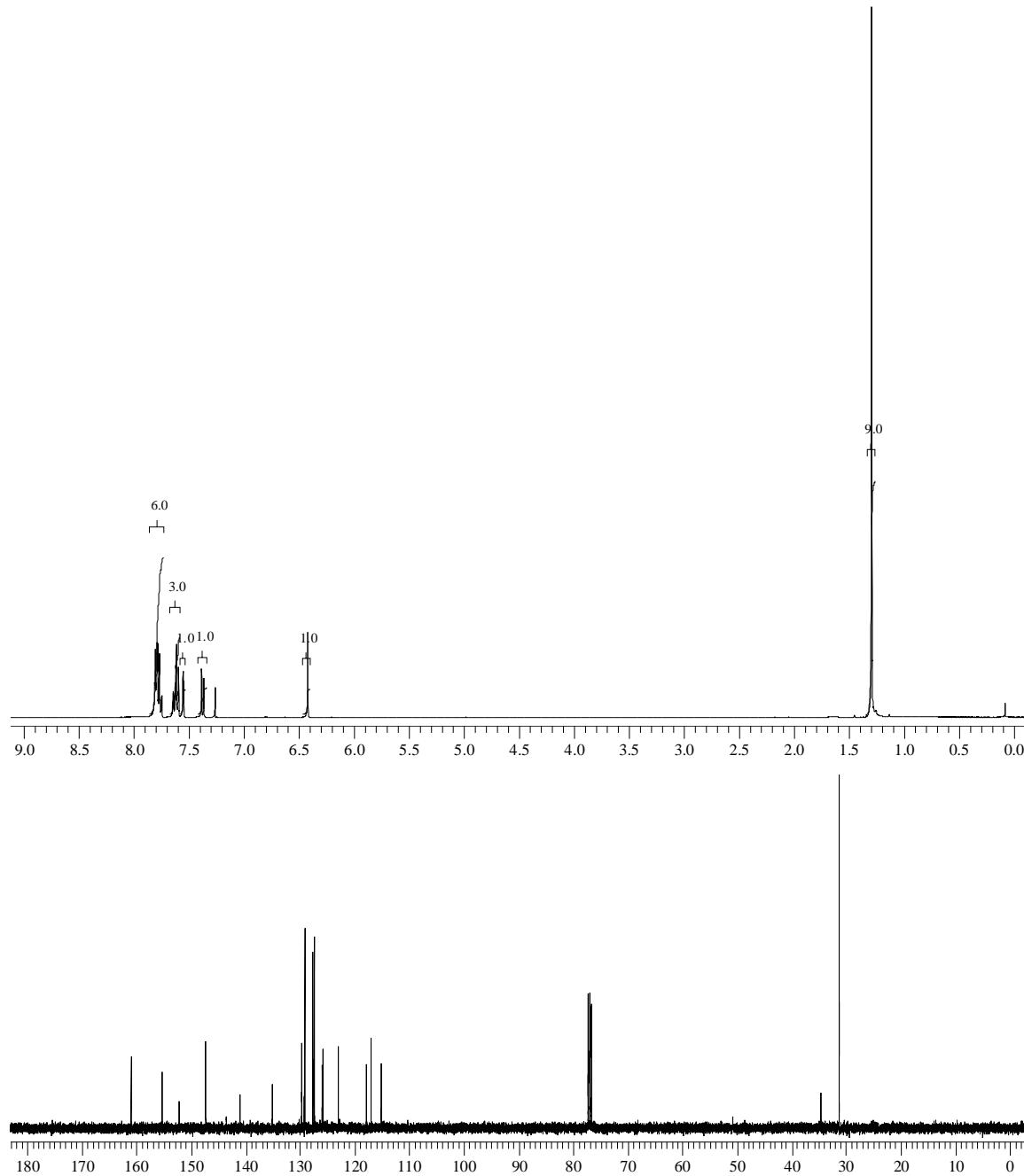


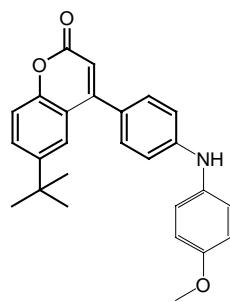
6-*tert*-Butyl-4-(4-*p*-fluorobiphenyl)-2*H*-chromen-2-one (3j**).** ^1H NMR (CDCl_3): δ 7.73 (d, 2H, PhPhC, $J = 8.5$ Hz); 7.65 (dd, 2H, PhF, $J = 9.1$ and 5.3 Hz); 7.62 (dd, 1H, $^1\text{BuPh}$, $J = 8.8$ and 2.3 Hz); 7.57 (d, 1H, $^1\text{BuPh}$, $J = 2.3$ Hz); 7.56 (d, 2H, PhPhC, $J = 8.5$ Hz); 7.37 (d, 1H, $^1\text{BuPh}$, $J = 8.8$ Hz); 7.19 (t, 2H, PhF, $J = 8.8$ Hz); 6.41 (s, 1H, CHCO); 1.29 (s, 9H, ^1Bu). $^{13}\text{C}\{\text{H}\}$ NMR: δ 161.1 (CO), Ph ring and C=C (164.0, 161.6, 155.5, 152.2, 147.2, 141.6, 136.1, 134.2, 129.6, 129.0, 128.8, 127.3, 123.1, 118.1, 116.9, 116.0, 115.8, 115.0), ^1Bu (34.6, 31.3). ν_{max} (NaCl)/cm⁻¹: 3055, 1720, 1614, 1605, 1570, 1499, 1371, 1184, 1159, 1130. HR-MS: $\text{C}_{25}\text{H}_{22}\text{O}_2\text{F}$ Calcd. 373.1604 ($\text{M}+1$); found: 373.1595.



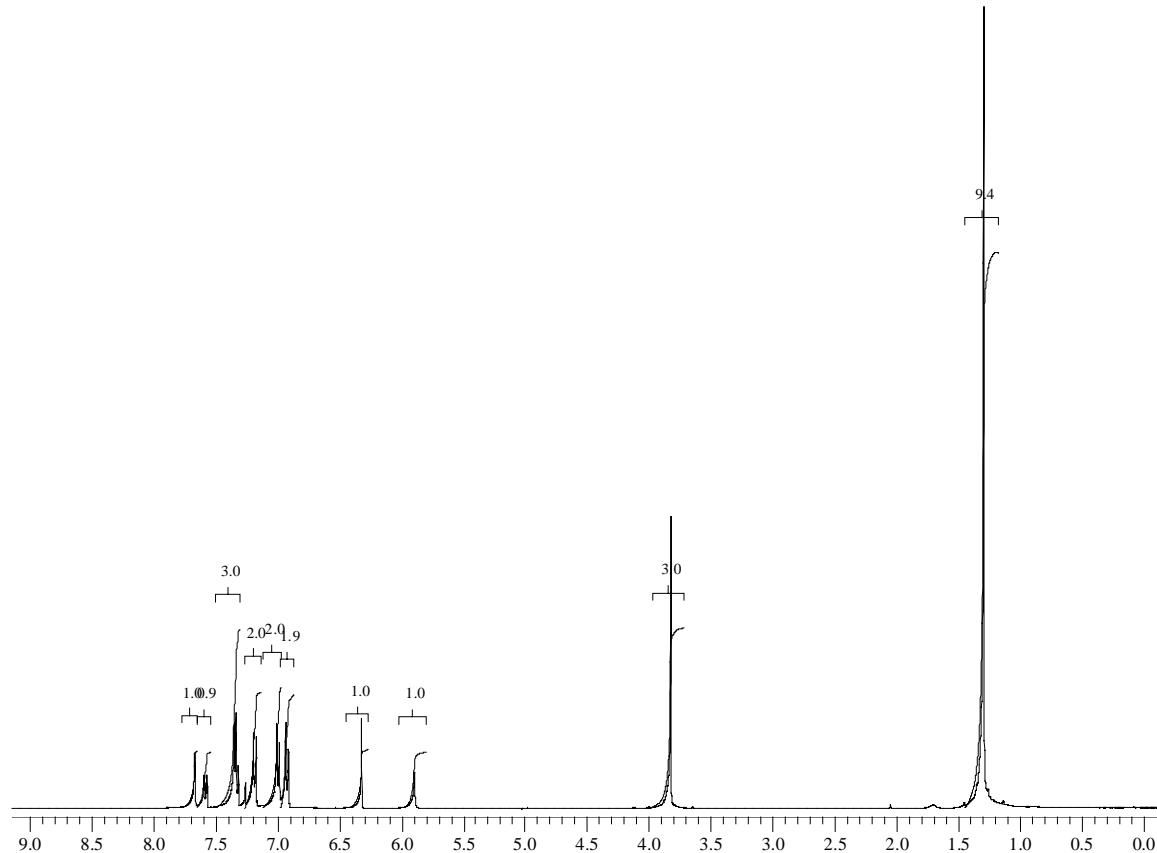
6-tert-Butyl-4-(4-p-trifluoromethylbiphenyl)-2H-chromen-2-one (3k). ¹H NMR (CDCl₃): δ 7.80 (d, 2H, PhCF₃, *J* = 8.5 Hz); 7.79 (d, 2H, PhPhC, *J* = 8.5 Hz); 7.76 (d, 2H, PhCF₃, *J* = 8.5 Hz); 7.63 (dd, 1H, ³BuPh, *J* = 8.8 and 2.3 Hz); 7.60 (d, 2H, PhPhC, *J* =

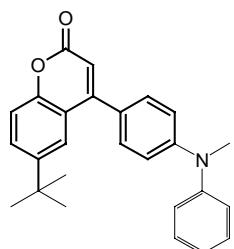
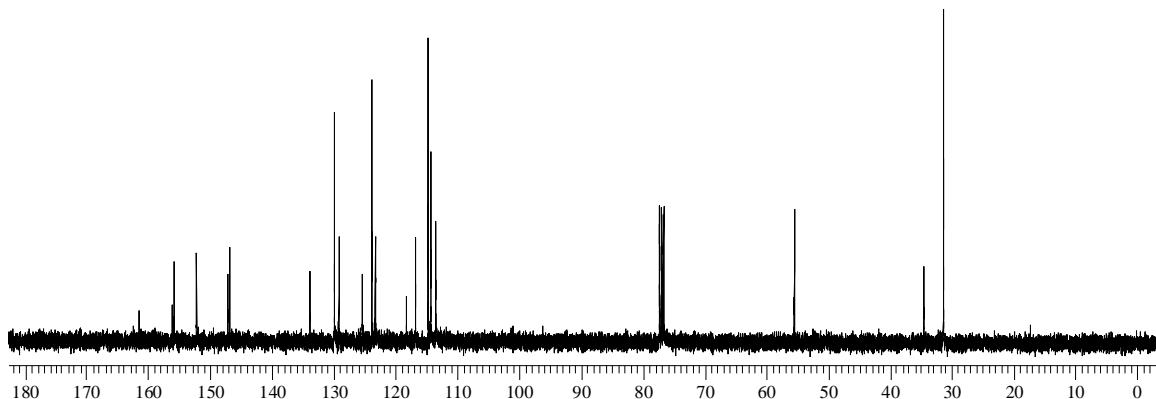
8.5 Hz); 7.55 (d, 1H, $^t\text{BuPh}$, $J = 2.3$ Hz); 7.37 (d, 1H, $^t\text{BuPh}$, $J = 8.8$ Hz); 6.42 (s, 1H, CHCO); 1.29 (s, 9H, ^tBu). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.9 (CO), Ph ring and C=C (155.2, 152.2, 147.3, 143.5, 141.0, 135.2, 129.7, 129.2, 127.7, 127.5, 125.96, 125.92, 125.88, 125.85, 123.0, 118.0, 117.0, 115.1), ^tBu (34.6, 31.3). ν_{max} (NaCl)/cm $^{-1}$: 3059, 1718, 1703, 1616, 1464, 1396, 1326, 1128, 1070, 1020. HR-MS: C₂₆H₂₂O₂F₃ Calcd. 423.1572 (M+1); found: 423.1568.



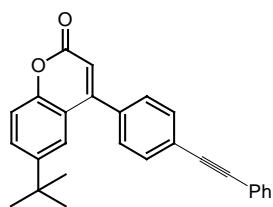
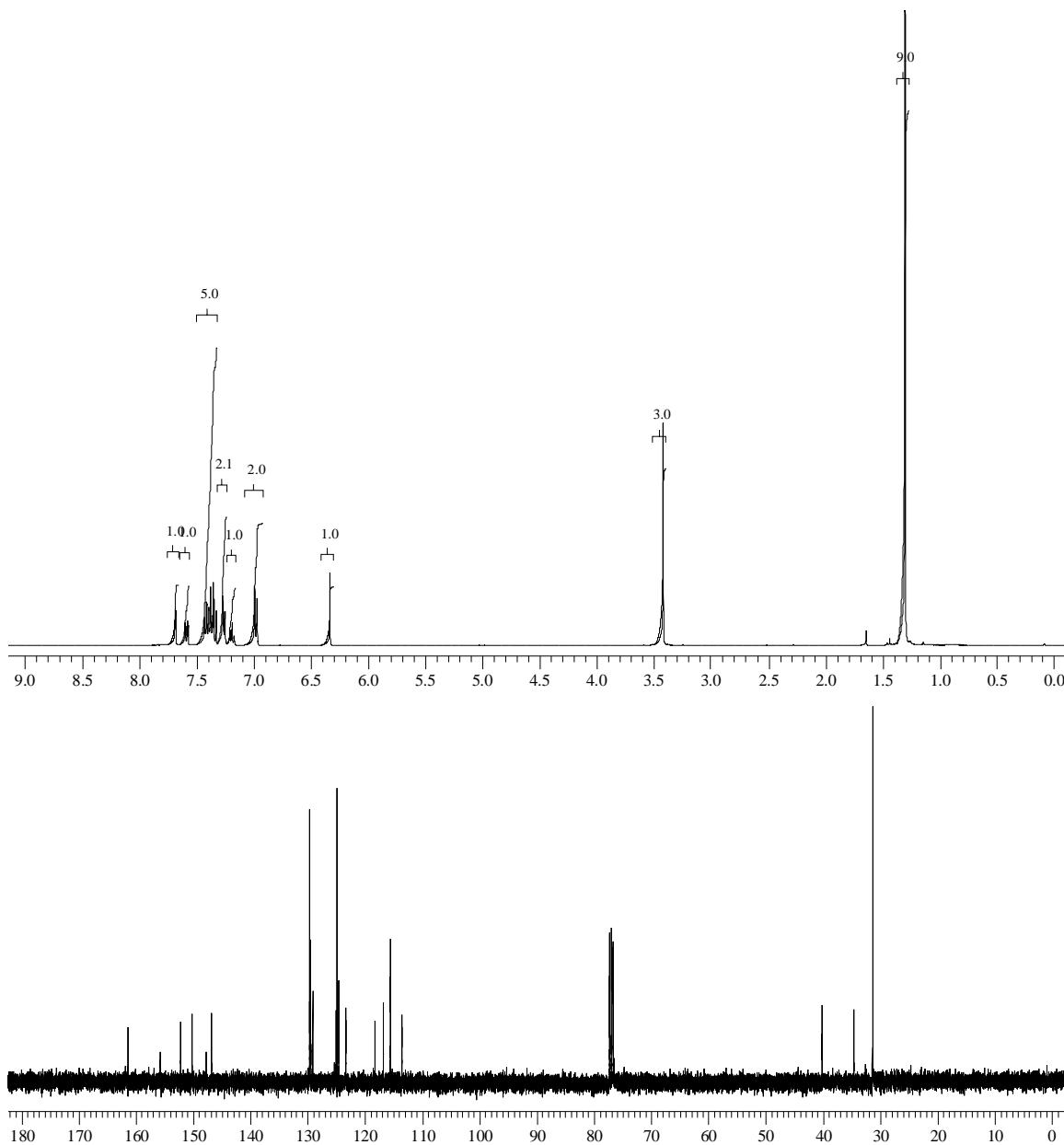


6-*tert*-Butyl-4-(4-p-methoxyanilinophenyl)-2*H*-chromen-2-one (3l). ^1H NMR (CDCl_3): δ 7.67 (d, 1H, $'\text{BuPh}$, $J = 2.3$ Hz); 7.58 (dd, 1H, $'\text{BuPh}$, $J = 8.5$ and 2.3 Hz); 7.34 (d, 2H, NHPhC , $J = 8.5$ Hz); 7.32 (d, 1H, $'\text{BuPh}$, $J = 8.5$ Hz); 7.18 (d, 2H, PhOCH_3 , $J = 8.8$ Hz); 6.99 (d, 2H, NHPhC , $J = 8.5$ Hz); 6.92 (d, 2H, PhOCH_3 , $J = 8.8$ Hz); 6.32 (s, 1H, CHCO); 5.89 (s, br, 1H, NH), 3.82 (s, 3H, OCH_3), 1.29 (s, 9H, $'\text{Bu}$). $^{13}\text{C}\{\text{H}\}$ NMR: δ 161.5 (CO), Ph ring and C=C (156.1, 155.8, 152.2, 147.2, 146.9, 134.0, 129.9, 129.2, 125.4, 123.8, 123.3, 118.3, 116.8, 114.7, 114.3, 113.5), 55.5 (OCH_3), $'\text{Bu}$ (34.6, 31.3). ν_{max} (NaCl)/cm⁻¹: 3424, 3055, 1717, 1705, 1606, 1510, 1369, 1186, 1036. HR-MS: $\text{C}_{26}\text{H}_{26}\text{NO}_3$ Calcd. 400.1913 ($\text{M}+1$); found: 400.1929.



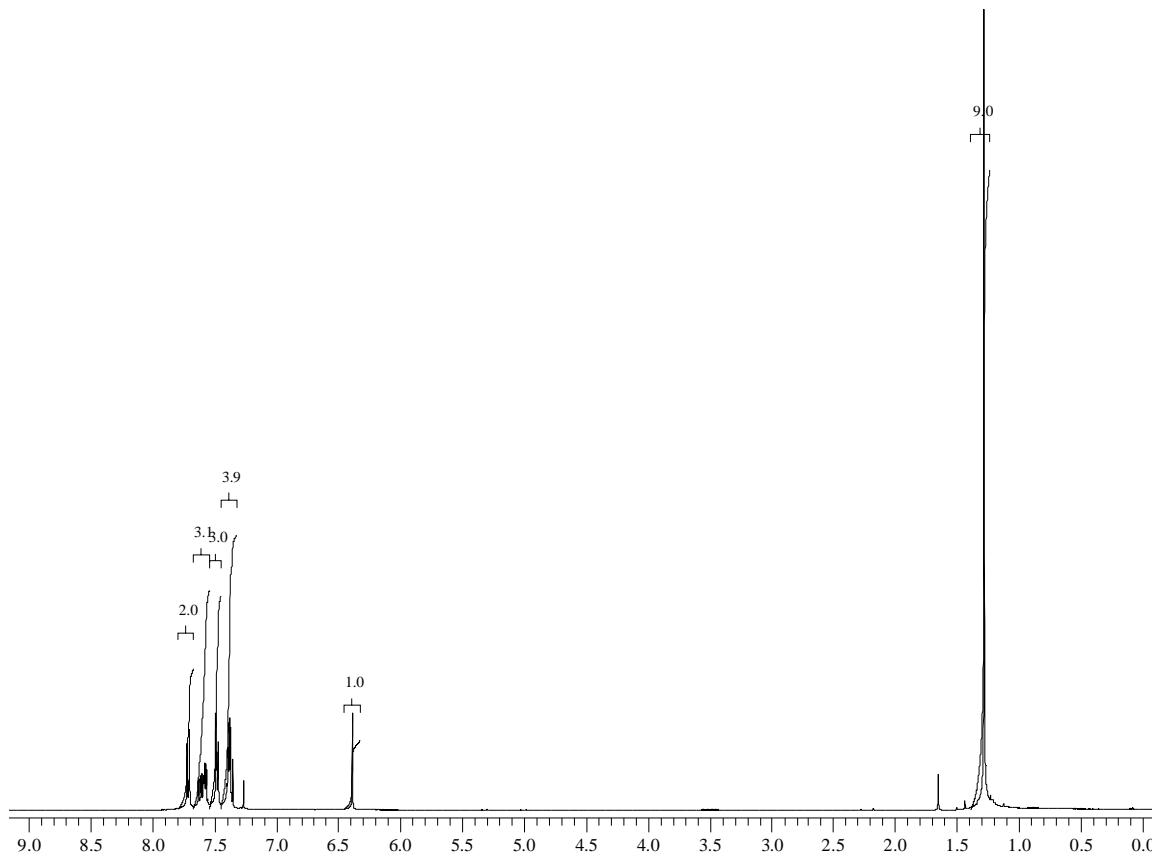


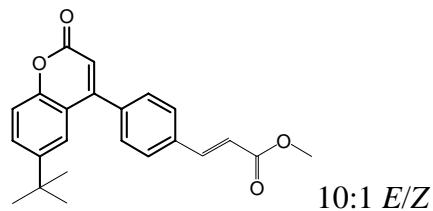
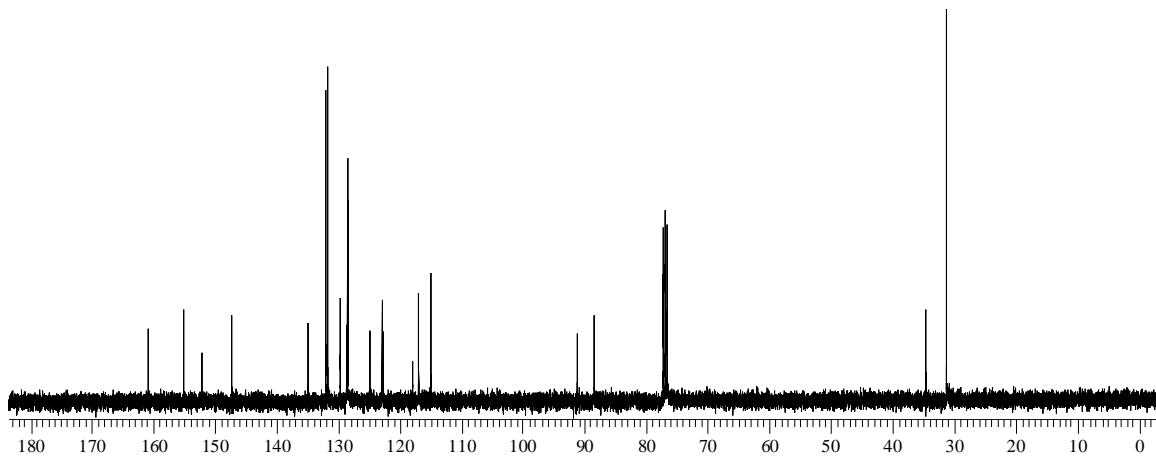
6-*tert*-Butyl-4-(4-N-methylanilinophenyl)-2*H*-chromen-2-one (3m). ^1H NMR (CDCl_3): δ 7.68 (d, 1H, $'\text{BuPh}$, $J = 2.3$ Hz); 7.58 (dd, 1H, $'\text{BuPh}$, $J = 8.8$ and 2.3 Hz); 7.41 (t, 2H, PhNPhC=CH , $J = 7.6$ Hz); 7.36 (d, 2H, PhC=CH , $J = 8.8$ Hz); 7.26 (dt, 2H, PhNPhC=CH , $J = 7.3$ and 2.6 Hz); 7.34 (d, 1H, $'\text{BuPh}$, $J = 8.8$ Hz); 7.19 (t, 1H, PhNPhC=CH , $J = 7.3$ Hz); 6.98 (d, 2H, PhC=CH , $J = 8.8$ Hz); 6.33 (s, 1H, CHCO); 3.42 (s, 3H, NCH_3), 3.82 (s, 3H, OCH_3), 1.30 (s, 9H, $'\text{Bu}$). $^{13}\text{C}\{\text{H}\}$ NMR: δ 161.5 (CO), Ph ring and C=C (155.8, 152.3, 150.2, 147.8, 146.9, 129.7, 129.6, 129.2, 125.0, 124.9, 124.6, 123.3, 118.3, 116.8, 115.6, 113.5), 40.2 (NCH₃), $'\text{Bu}$ (34.6, 31.3). ν_{max} (NaCl)/cm⁻¹: 3058, 1717, 1705, 1610, 1591, 1614, 1495, 1369, 1354, 1193, 1130. HR-MS: $\text{C}_{26}\text{H}_{26}\text{NO}_2$ Calcd. 384.1964 ($\text{M}+1$); found: 384.1956.



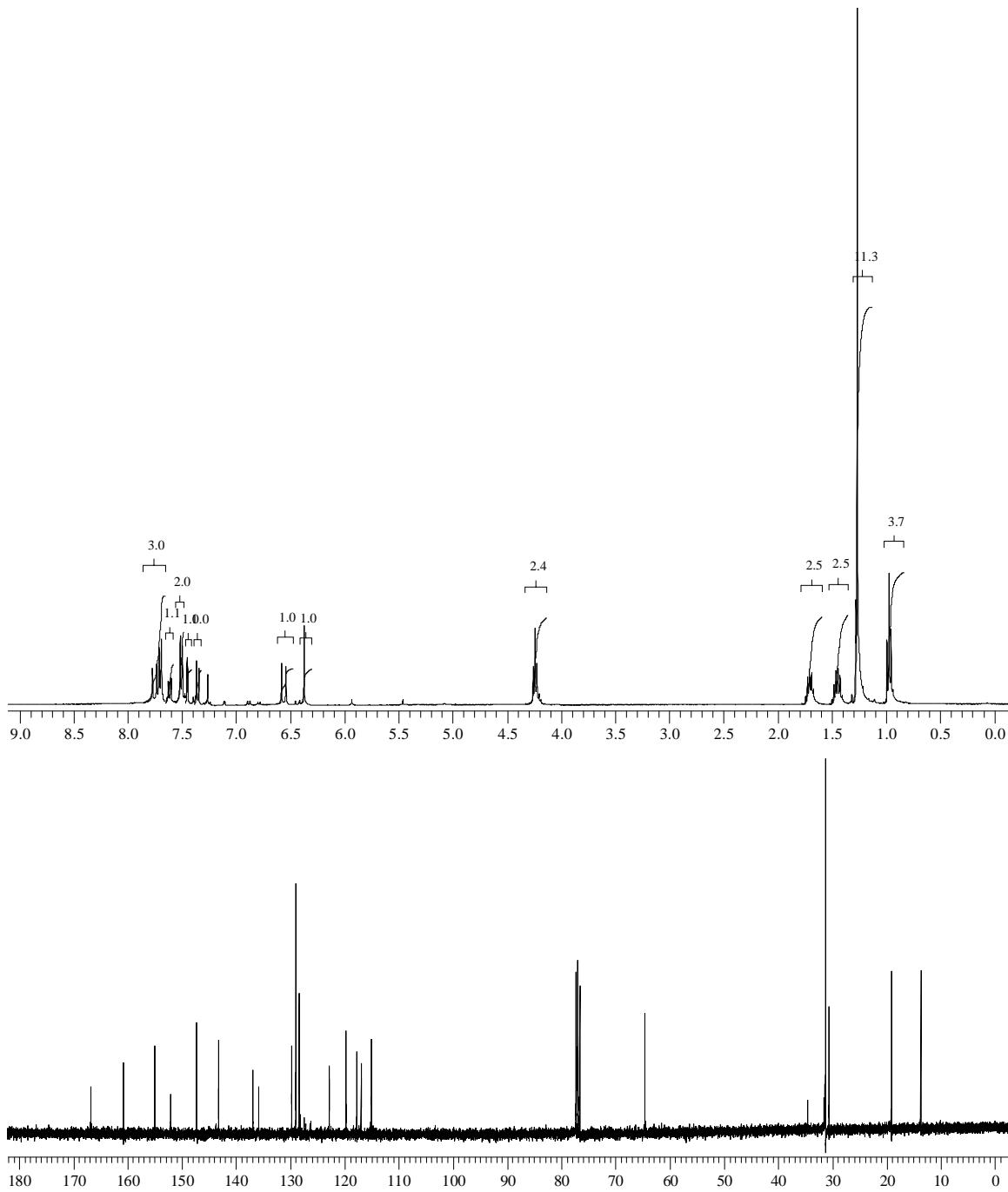
6-*tert*-Butyl-4-(4-*p*-phenylacetylenylphenyl)-2*H*-chromen-2-one (3n). ^1H NMR (CDCl_3): δ 7.71 (d, 2H, $\text{PhC}=\text{CH}$, $J = 8.2$ Hz); 7.62 (dd, 1H, $^3\text{J}_{\text{Ph}} = 8.8$ and 2.3 Hz); 7.58 (dd, 2H, $\text{PhC}\equiv\text{C}$, $J = 7.6$ and 2.0 Hz); 7.49 (d, 1H, $^3\text{J}_{\text{Ph}} = 2.3$ Hz); 7.48 (d, 2H,

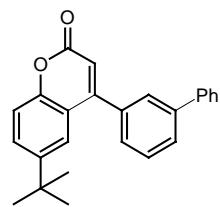
PhC=CH, $J = 8.2$ Hz); 7.37-7.40 (m, 3H, *PhC≡C*); 7.36 (d, 1H, *tBuPh*, $J = 8.8$ Hz); 6.39 (s, 1H, CHCO); 1.28 (s, 9H, *tBu*). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.9 (CO), Ph ring and C=C (155.2, 152.2, 147.3, 135.0, 132.0, 131.7, 129.7, 128.7, 128.5, 128.4, 124.9, 122.9, 122.7, 117.9, 116.9, 115.0), C≡C (91.3, 88.4), *tBu* (34.6, 31.2). ν_{max} (NaCl)/cm⁻¹: 3055, 1720, 1614, 1570, 1510, 1371, 1186, 1018. HR-MS: C₂₇H₂₃O₂ Calcd. 379.1698 (M+1); found: 379.1701.



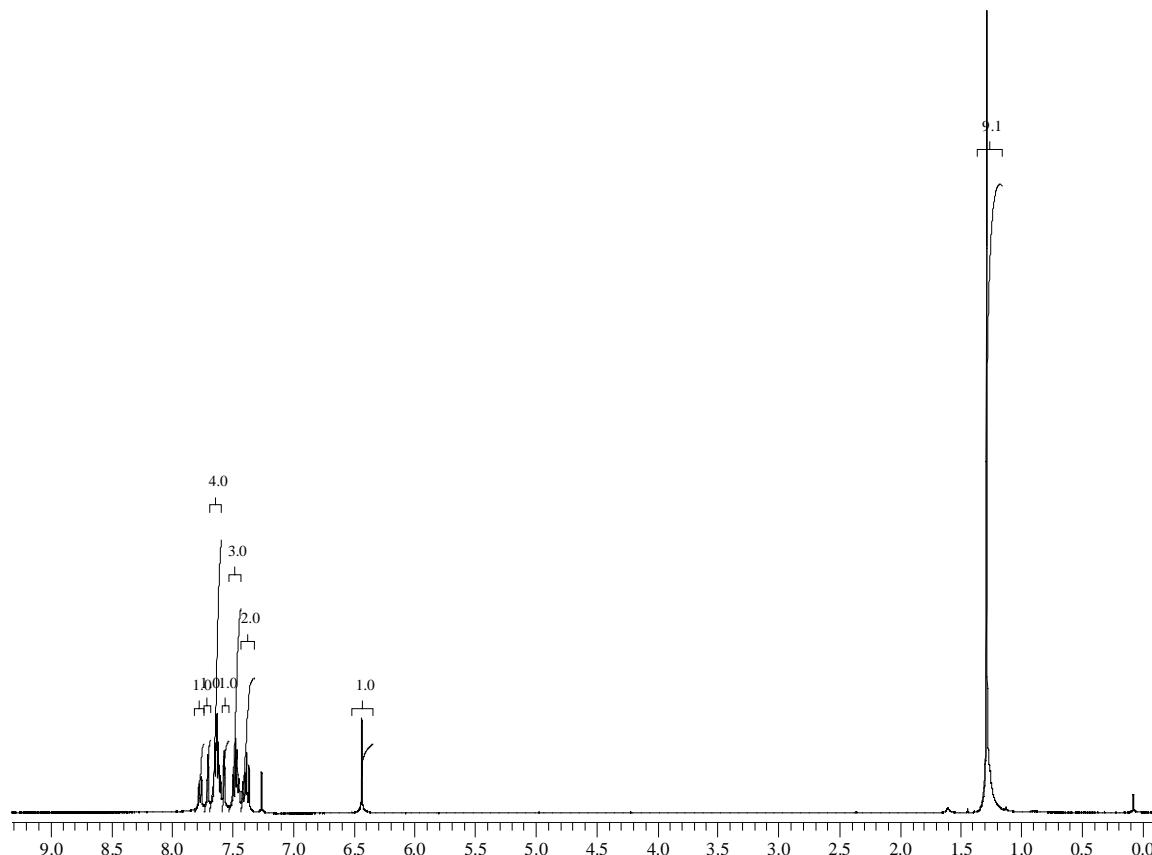


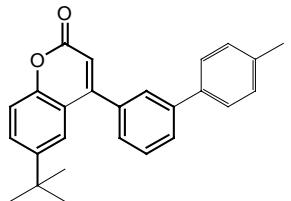
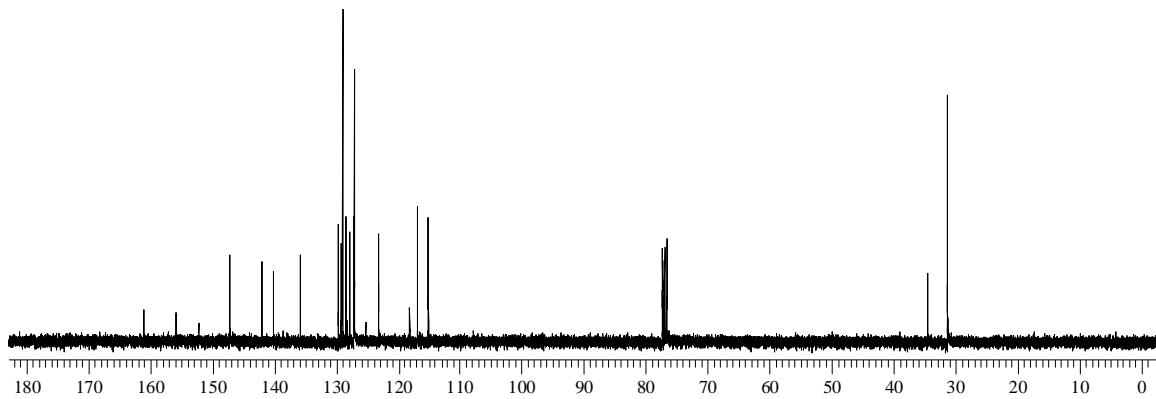
(*E*)-butyl-3-(4-(6-*tert*-butyl-2-oxo-2*H*-chromen-4-yl)phenyl)acrylate (**3o**). ^1H NMR (CDCl_3): δ 7.75 (d, 1H, $\text{CH}=\text{CHCO}_2$, $J = 16.1$ Hz); 7.70 (d, 2H, $\text{PhCH}=\text{CH}$, $J = 8.0$ Hz); 7.61 (dd, 1H, $'\text{BuPh}$, $J = 8.8$ and 2.3 Hz); 7.51(d, 2H, $\text{PhCH}=\text{CH}$, $J = 8.0$ Hz); 7.45 (d, 1H, $'\text{BuPh}$, $J = 2.3$ Hz); 7.36 (d, 1H, $'\text{BuPh}$, $J = 8.8$ Hz); 6.56 (d, 1H, $\text{CH}=\text{CHCO}_2$, $J = 16.1$ Hz); 6.37 (s, 1H, CHCOPh); 4.24 (t, 2H, OCH_2 , $J = 6.6$ Hz); 1.67-1.75 (m, 2H, OCH_2CH_2); 1.41-1.50 (m, 2H, CH_2CH_3); 1.27 (s, 9H, $'\text{Bu}$), 0.98 (t, 3H, CH_2CH_3 , $J = 7.6$ Hz); $.^{13}\text{C}\{\text{H}\}$ NMR: δ CO_2 (166.7, 160.9), Ph ring and C=C (155.0, 152.2, 147.3, 143.2, 136.9, 135.8, 129.7, 129.0, 128.4, 122.9, 119.8, 117.8, 116.9, 115.1), $\text{O}(\text{CH}_2)_3\text{CH}_3$ (64.6, 30.7, 19.2, 13.7), $'\text{Bu}$ (34.5, 31.2). ν_{max} (NaCl)/cm $^{-1}$: 3055, 1720, 1637, 1614, 1568, 1371, 1312, 1205, 1178, 1128. HR-MS: $\text{C}_{26}\text{H}_{29}\text{O}_4$ Calcd. 405.2066 ($\text{M}+1$); found: 405.2070.



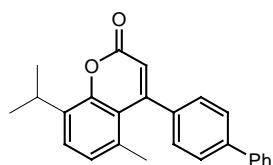
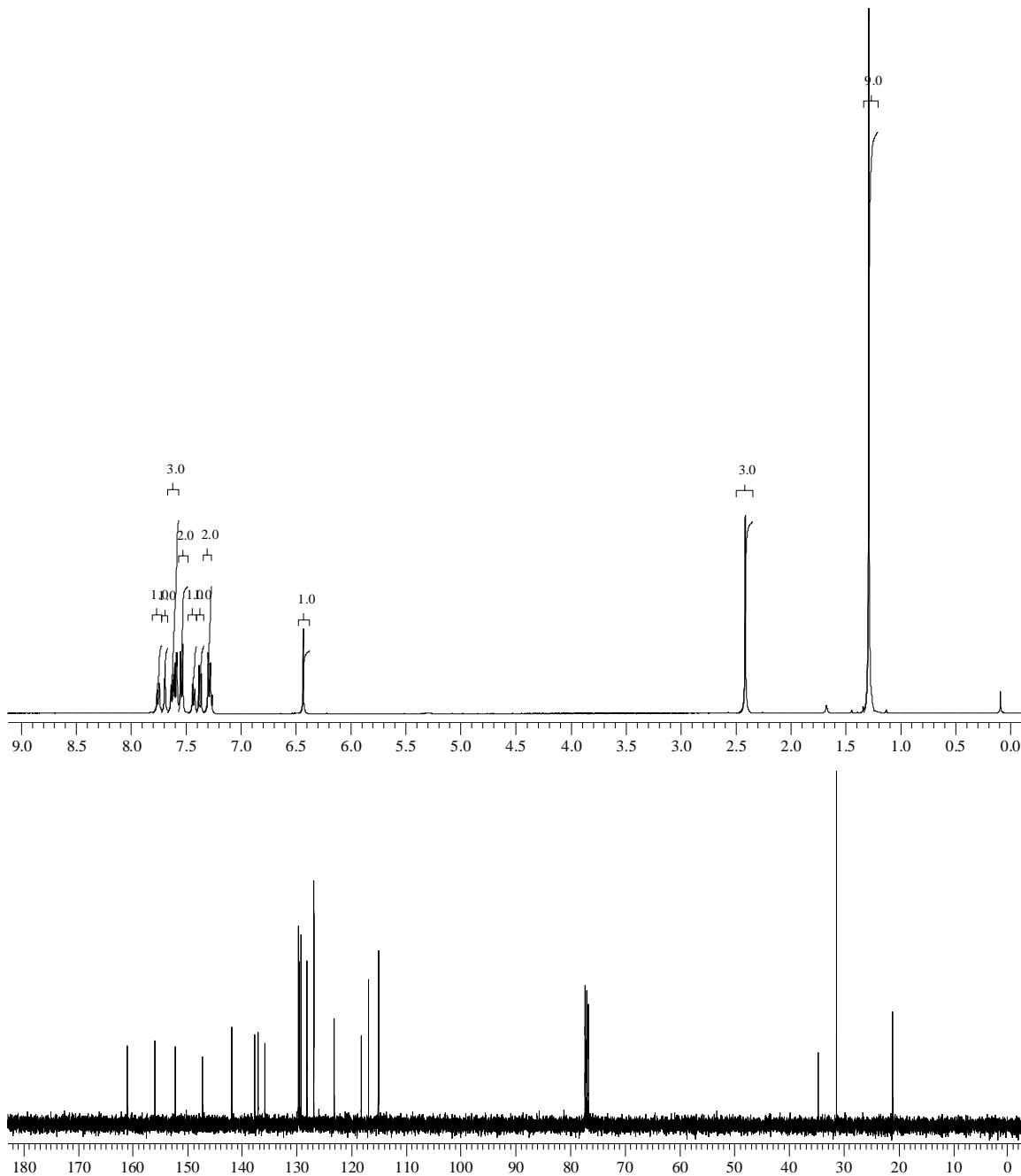


4-(3-Biphenyl)-6-*tert*-butyl-2*H*-chromen-2-one (3p). ^1H NMR (CDCl_3): δ 7.77 (d, 1H, PhPhC , $J = 7.9$ Hz); 7.70 (s, 1H, PhPhC); 7.60-7.65 (m, 4H, $^3\text{BuPh}$, 1H; PhPhC , 1H; PhPhC , 2H); 7.57 (d, 1H, $^3\text{BuPh}$, $J = 2.0$ Hz); 7.48 (t, 2H, PhPhC , $J = 7.6$ Hz); 7.46 (t, 1H, PhPhC , $J = 7.6$ Hz); 7.40 (t, 1H, PhPhC , $J = 7.6$ Hz); 7.37 (d, 1H, $^3\text{BuPh}$, $J = 8.8$ Hz); 6.43 (s, 1H, CHCO); 1.28 (s, 9H, ^3Bu). $^{13}\text{C}\{\text{H}\}$ NMR: δ 161.0 (CO), Ph ring and C=C (155.8, 152.2, 147.2, 141.9, 140.0, 135.8, 129.6, 129.2, 128.9, 128.4, 127.8, 127.2, 127.14, 127.07, 123.1, 118.1, 116.9, 115.1), ^3Bu (34.6, 31.3). ν_{max} (NaCl)/cm⁻¹: 3058, 1722, 1616, 1566, 1479, 1369, 1184, 1128. HR-MS: $\text{C}_{25}\text{H}_{23}\text{O}_2$ Calcd. 355.1698 ($\text{M}+1$); found: 355.1695.



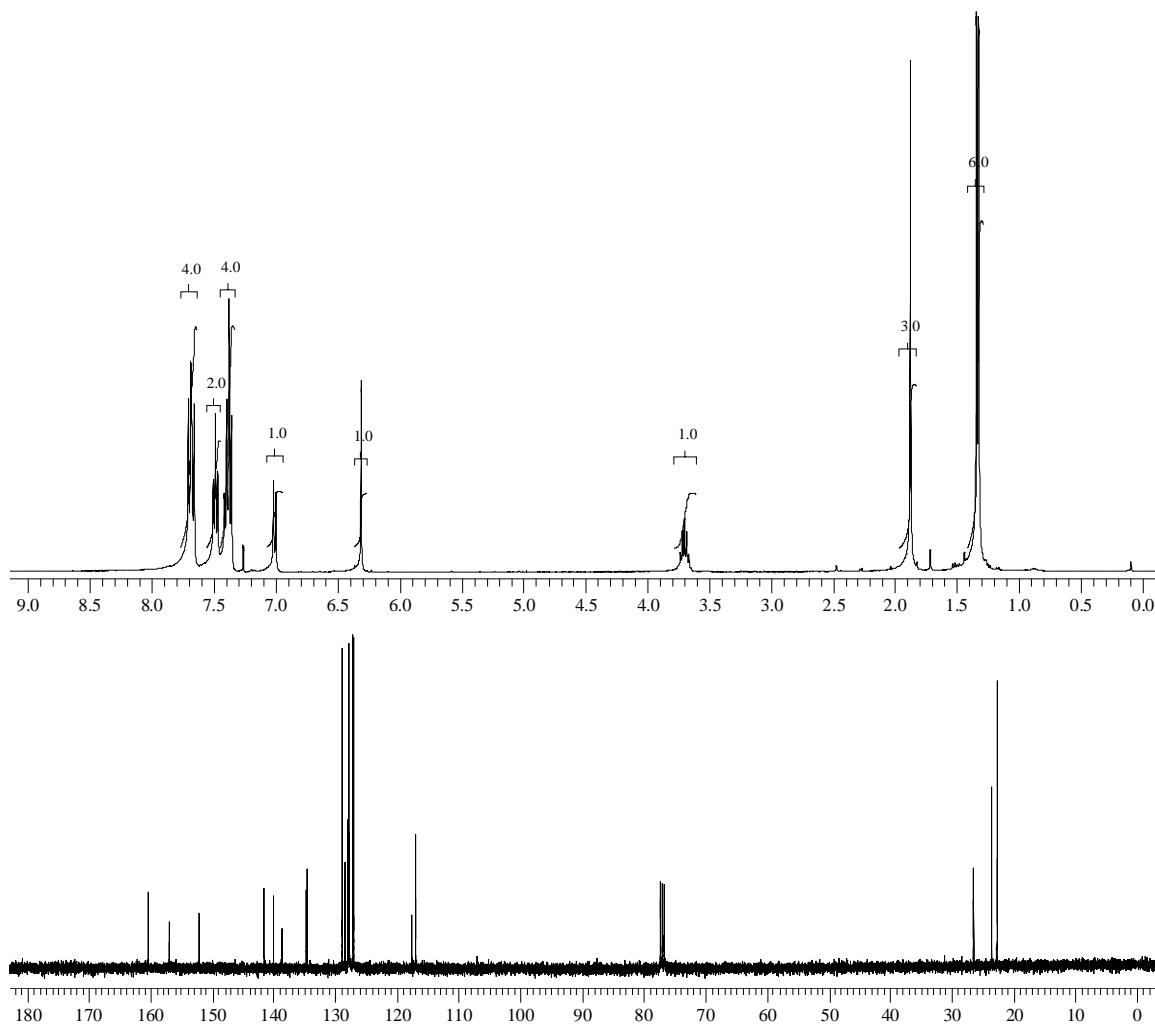


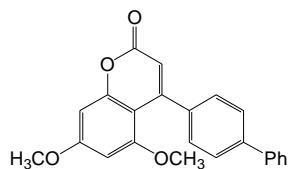
6-*tert*-Butyl-4-(3-*p*-tolylphenyl)-2*H*-chromen-2-one (3q). ^1H NMR (CDCl_3): δ 7.75 (d, 1H, *PhPhCH*₃, *J* = 7.9 Hz); 7.69 (s, 1H, *PhPhCH*₃); 7.60-7.64 (m, 2H, ^tBu*Ph*, 1H; *PhPhCH*₃, 1H); 7.58 (d, 1H, ^tBu*Ph*, *J* = 1.8 Hz); 7.54 (d, 2H, *PhCH*₃, *J* = 8.0 Hz); 7.43 (d, 1H, *PhPhCH*₃, *J* = 7.6 Hz); 7.37 (d, 1H, ^tBu*Ph*, *J* = 8.8 Hz); 7.29 (d, 2H, *PhCH*₃, *J* = 8.0 Hz); 6.43 (s, 1H, CHCO); 2.41 (s, 3H, *PhCH*₃); 1.29 (s, 9H, ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 161.1 (CO), Ph ring and C=C (155.9, 152.2, 147.2, 141.8, 137.7, 137.1, 135.8, 129.7, 129.5, 129.2, 128.2, 126.91, 126.87, 123.2, 118.2, 116.9, 115.0), ^tBu (34.6, 31.3), 21.1 (*PhCH*₃). ν_{max} (NaCl)/cm⁻¹: 3058, 1720, 1616, 1568, 1481, 1369, 1184, 1130. HR-MS: C₂₆H₂₅O₂ Calcd. 369.1855 (M+1); found: 369.1856.



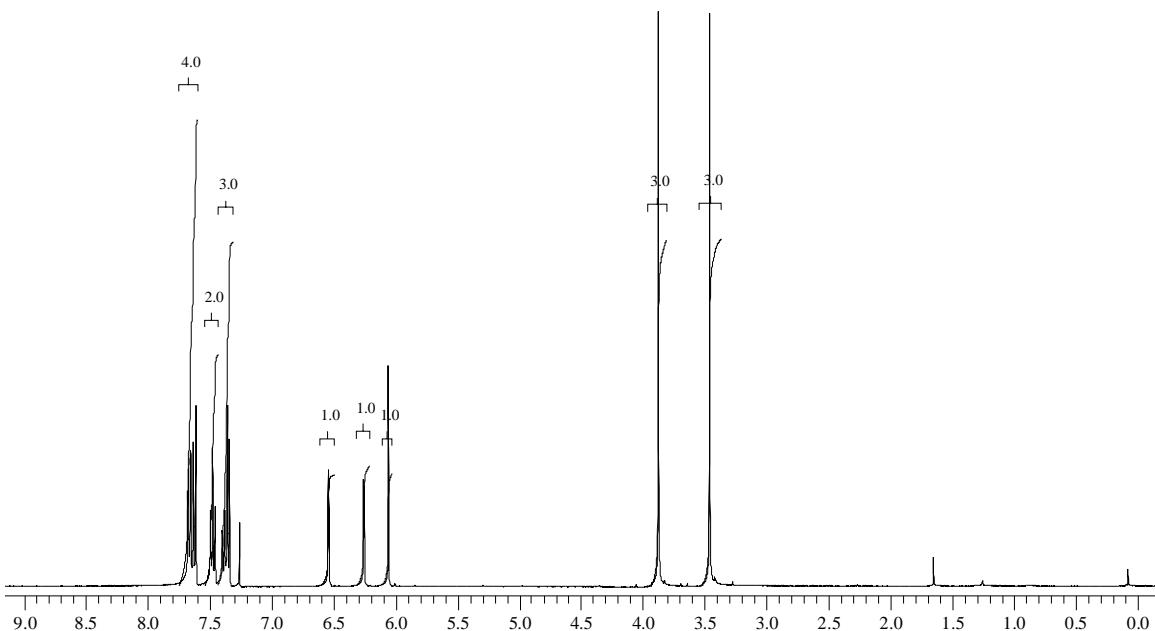
4-(4-Biphenyl)-8-isopropyl-5-methyl-2*H*-chromen-2-one (3r). ^1H NMR (CDCl_3): δ 7.69 (d, 2H, $\text{PhPhC}=\text{CH}$, $J = 7.6$ Hz); 7.67 (d, 2H, $\text{PhPhC}=\text{CH}$, $J = 8.2$ Hz); 7.49 (t, 2H,

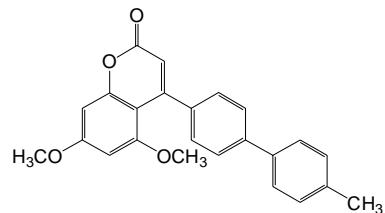
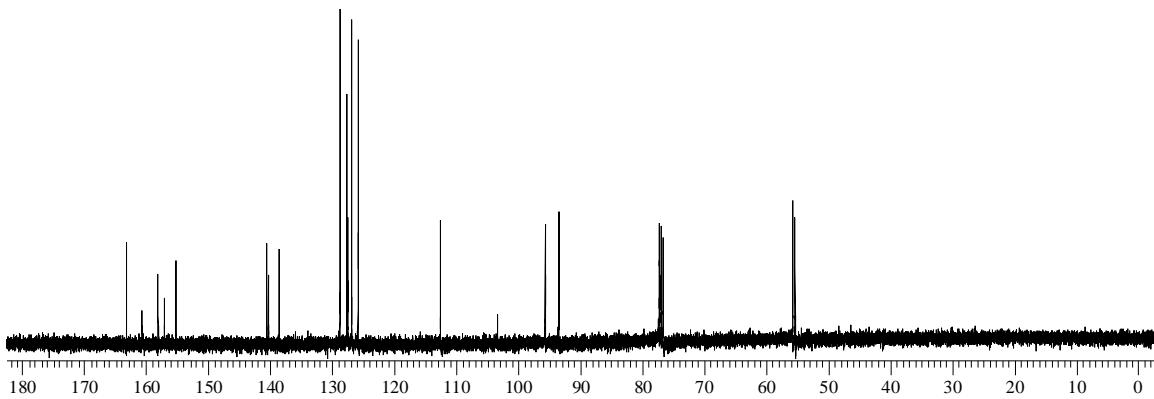
PhPhC=CH, $J = 7.3$ Hz); 7.36-7.42 (m, 4H, *PhPhC=CH*, 2H; *PhPhC=CH*, 1H; PhO, 1H); 7.01 (d, 1H, PhO, $J = 7.9$ Hz); 6.31 (s, 1H, CHCO); 3.66-3.73 (m, 1H, CHCH₃); 1.88 (s, 3H, PhCH₃); 1.33 (d, 6H, CHCH₃, $J = 6.7$ Hz). ¹³C{¹H} NMR: δ 160.3 (CO), Ph ring and C=C (156.9, 152.1, 141.5, 140.0, 138.7, 134.8, 134.6, 128.9, 128.4, 128.0, 127.8, 127.7, 127.1, 127.0, 117.6, 116.9), CHCH₃ (26.5, 22.7), 23.7 (PhCH₃). ν_{max} (NaCl)/cm⁻¹: 3055, 1720, 1614, 1580, 1487, 1447, 1415, 1385, 1346, 1196, 1051. HR-MS: C₂₅H₂₃O₂ Calcd. 355.1698 (M+H); found: 355.1683.



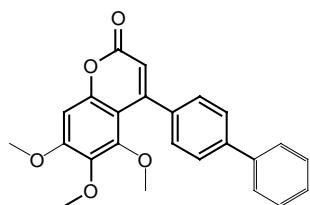
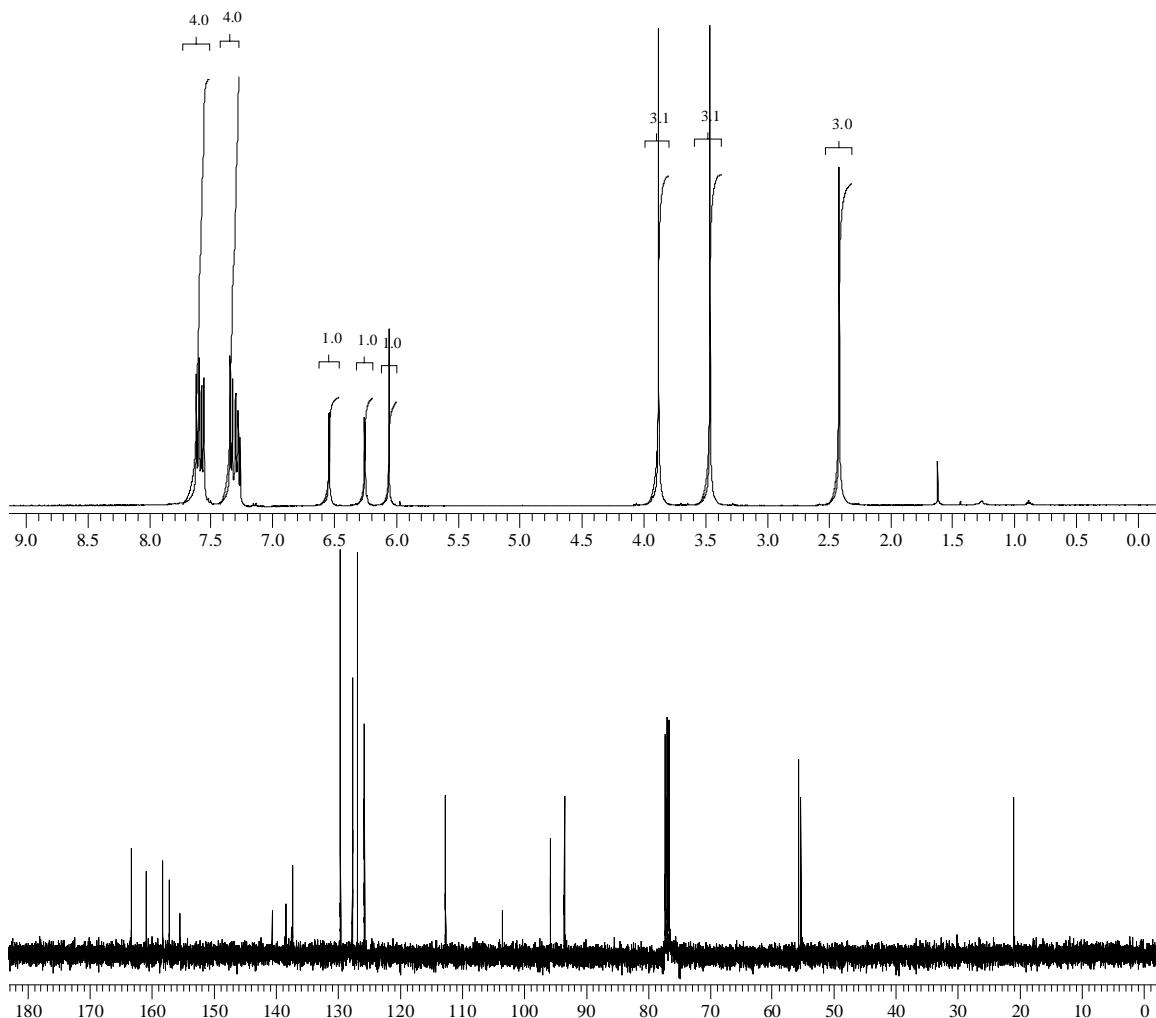


4-(4-Biphenyl)-5,7-dimethoxy-2H-chromen-2-one (3s). ^1H NMR (CDCl_3): δ 7.67 (d, 2H, *PhPhC*, $J = 7.3$ Hz); 7.62 (d, 2H, *PhPhC*, $J = 8.0$ Hz); 7.48 (t, 2H, *PhPhC*, $J = 7.3$ Hz); 7.38 (t, 1H, *PhPhC*, $J = 7.3$ Hz); 7.35 (d, 2H, *PhPhC*, $J = 8.0$ Hz); 6.54 (d, 1H, *PhOCH₃*, $J = 2.4$ Hz); 6.25 (d, 1H, *PhOCH₃*, $J = 2.4$ Hz); 6.06 (s, 1H, CHCO); 3.88 (s, 3H, *PhOCH₃*); 3.46 (s, 3H, *PhOCH₃*). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.8 (CO), Ph ring and C=C (163.3, 158.1, 157.1, 155.3, 140.6, 138.6, 128.8, 127.7, 127.5, 127.0, 125.9, 112.6, 103.4, 95.7, 93.5), PhOCH₃ (55.7, 55.3). ν_{max} (NaCl)/cm⁻¹: 3055, 1718, 1616, 1597, 1493, 1466, 1420, 1354, 1224, 1207, 1159, 1113, 1053. HR-MS: C₂₃H₁₉O₄ Calcd. 359.1283 (M+1); found: 359.1303.



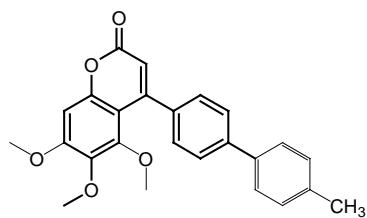
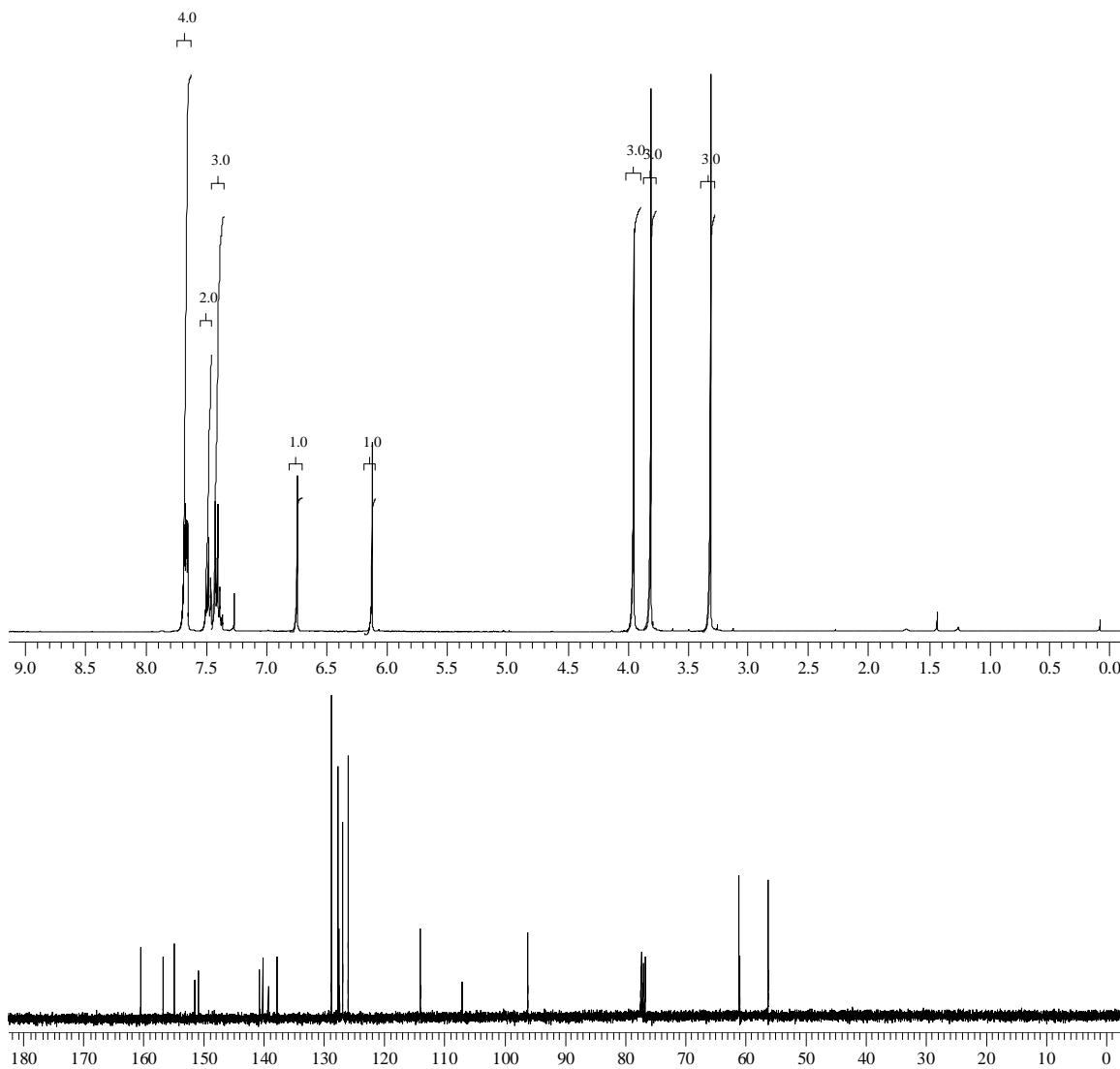


5,7-Dimethoxy-4-(4-p-tolylphenyl)-2H-chromen-2-one (3t). ^1H NMR (CDCl_3): δ 7.61 (d, 2H, $Ph\text{PhCH}_3$, $J = 8.2$ Hz); 7.57 (d, 2H, $Ph\text{PhCH}_3$, $J = 8.2$ Hz); 7.33 (d, 2H, $Ph\text{PhCH}_3$, $J = 8.2$ Hz); 7.29 (d, 2H, $Ph\text{PhCH}_3$, $J = 8.2$ Hz); 6.54 (d, 1H, $Ph\text{OCH}_3$, $J = 2.3$ Hz); 6.25 (d, 1H, $Ph\text{OCH}_3$, $J = 2.3$ Hz); 6.06 (s, 1H, CHCO); 3.88 (s, 3H, $Ph\text{OCH}_3$); 3.46 (s, 3H, $Ph\text{OCH}_3$); 2.42 (s, 3H, $Ph\text{CH}_3$). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.9 (CO), Ph ring and C=C (163.3, 158.2, 157.2, 155.4, 140.6, 138.4, 137.5, 137.4, 129.6, 127.7, 126.8, 125.7, 112.6, 103.5, 95.8, 93.5), $Ph\text{OCH}_3$ (55.8, 55.4). ν_{max} (NaCl)/cm $^{-1}$: 3055, 1718, 1614, 1597, 1498, 1464, 1354, 1225, 1208, 1159, 1113, 1053. HR-MS: $\text{C}_{24}\text{H}_{21}\text{O}_4$ Calcd. 373.1440 ($M+1$); found: 373.1419.



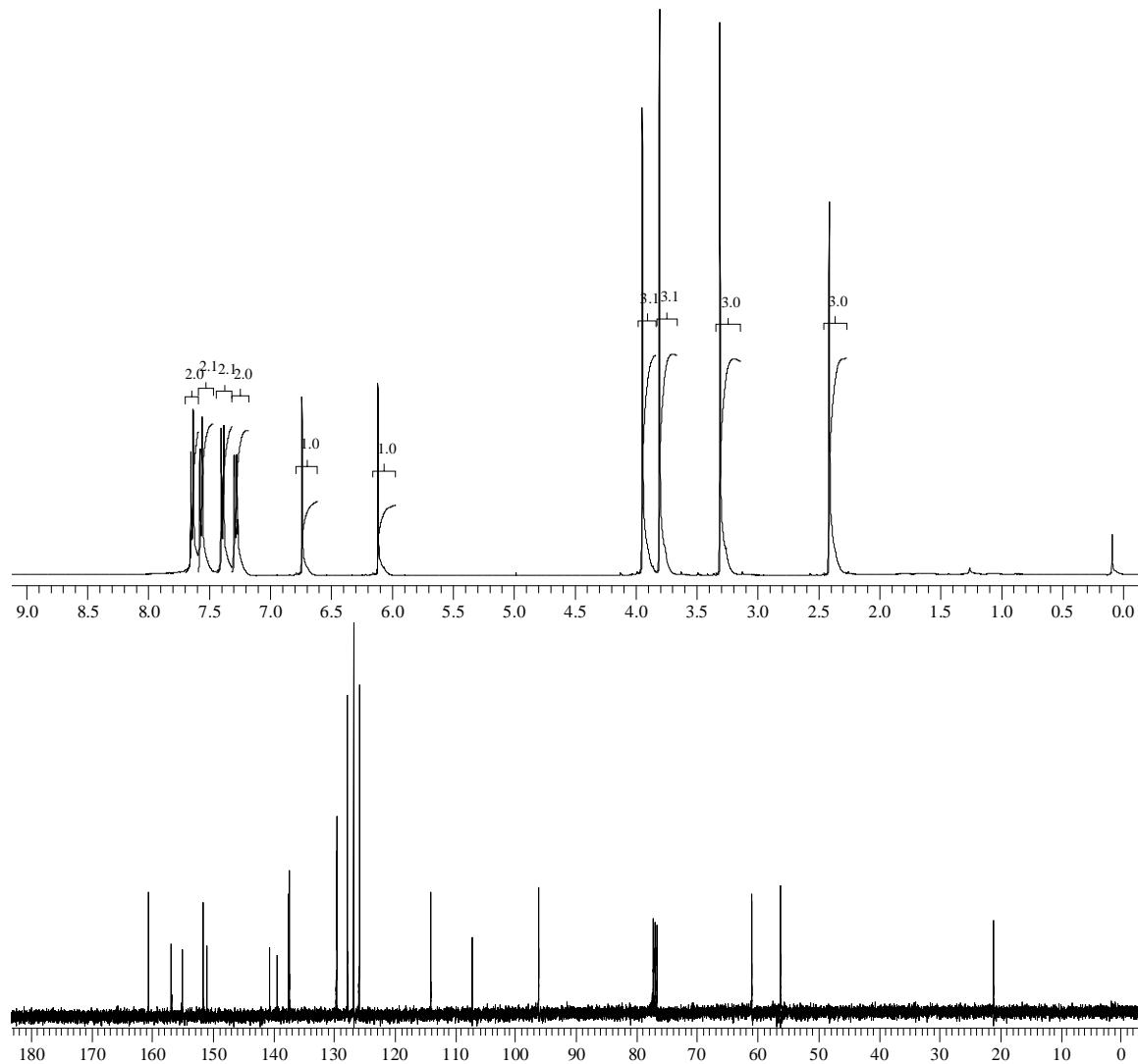
4-(4-Biphenyl)-5,6,7-trimethoxy-2*H*-chromen-2-one (3u**).** ^1H NMR (CDCl_3): δ 7.67 (d, 2H, *PhPhC*, $J = 7.3$ Hz); 7.66 (d, 2H, *PhPhC*, $J = 8.2$ Hz); 7.48 (t, 2H, *PhPhC*, $J = 7.3$ Hz); 7.41 (d, 2H, *PhPhC*, $J = 8.2$ Hz); 7.38 (t, 1H, *PhPhC*, $J = 7.3$ Hz); 6.74 (s, 1H, *PhO*); 6.12 (s, 1H, *CHCO*); 3.95 (s, 3H, *PhOCH_3*); 3.81 (s, 3H, *PhOCH_3*); 3.31 (s, 3H, *PhOCH_3*). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.5 (CO), Ph ring and C=C (156.8, 155.0, 151.6, 151.0, 140.7, 140.3, 139.3, 137.8, 128.8, 127.7, 127.5, 126.9, 126.0, 114.0, 107.1, 96.2), *PhOCH_3* (61.02,

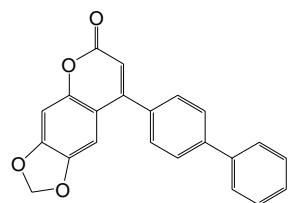
60.96, 56.2). ν_{max} (NaCl)/cm⁻¹: 3055, 1720, 1603, 1549, 1489, 1458, 1408, 1364, 1200, 1132, 1101, 1036. HR-MS: C₂₄H₂₁O₅ Calcd. 389.1389 (M+1); found: 389.1374.



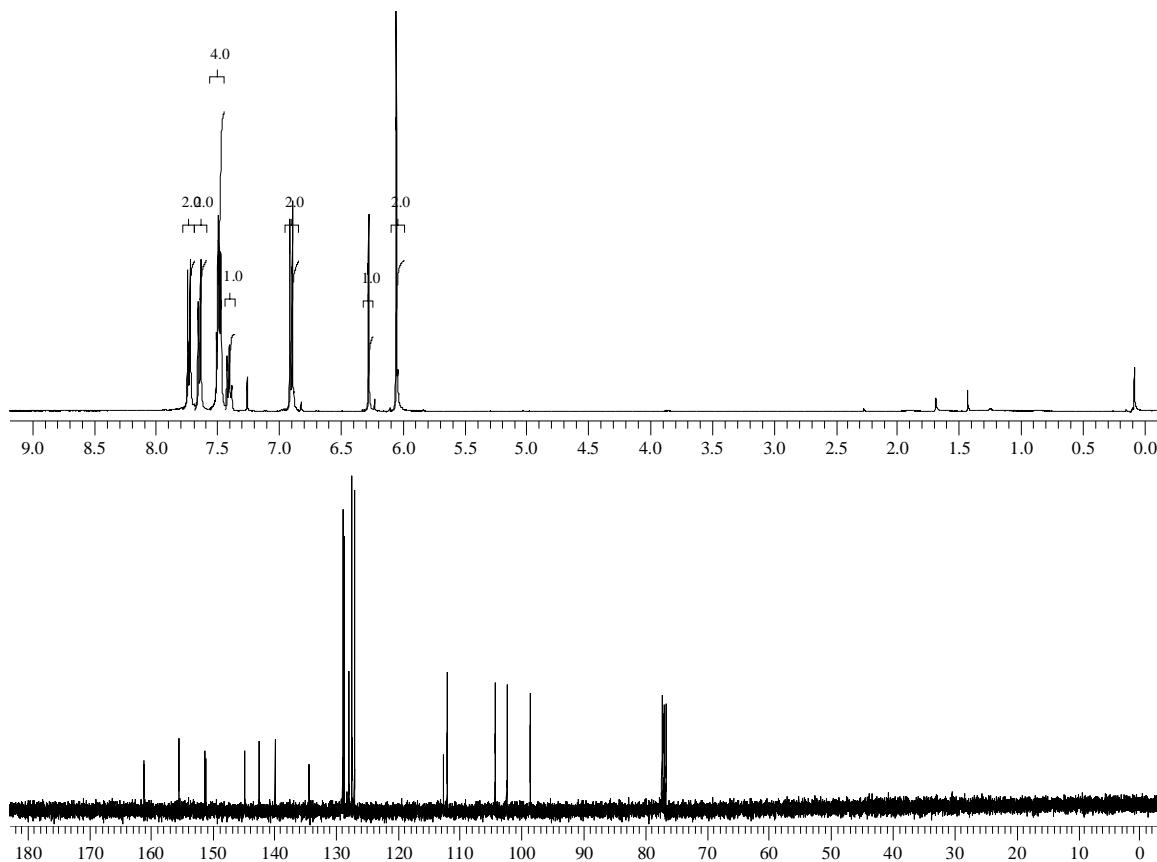
4-(4-p-Tolylphenyl)-5,6,7-trimethoxy-2H-chromen-2-one (3v). ¹H NMR (CDCl₃): δ 7.64 (d, 2H, PhPhCH₃, J = 8.0 Hz); 7.57 (d, 2H, PhCH₃, J = 7.9 Hz); 7.39 (d, 2H, PhPhCH₃, J = 8.0 Hz); 7.28 (d, 2H, PhCH₃, J = 7.9 Hz); 6.73 (s, 1H, PhO); 6.11 (s, 1H, CHCO); 3.94 (s, 3H, PhOCH₃); 3.81 (s, 3H, PhOCH₃); 3.31 (s, 3H, PhOCH₃); 2.41 (s,

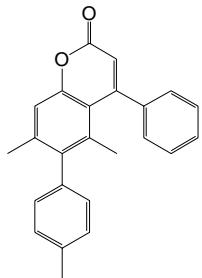
3H, PhCH₃). ¹³C{¹H} NMR: δ 160.6 (CO), Ph ring and C=C (156.8, 155.1, 151.7, 151.0, 140.7, 139.3, 137.5, 137.4, 129.5, 127.7, 126.8, 125.8, 114.0, 107.1, 96.2), PhOCH₃ (61.02, 60.96, 56.2), 21.1 (PhCH₃). ν_{max} (NaCl)/cm⁻¹: 3061, 1718, 1605, 1491, 1460, 1408, 1364, 1200, 1101, 1018. HR-MS: C₂₅H₂₃O₅ Calcd. 403.1545 (M+1); found: 403.1536.



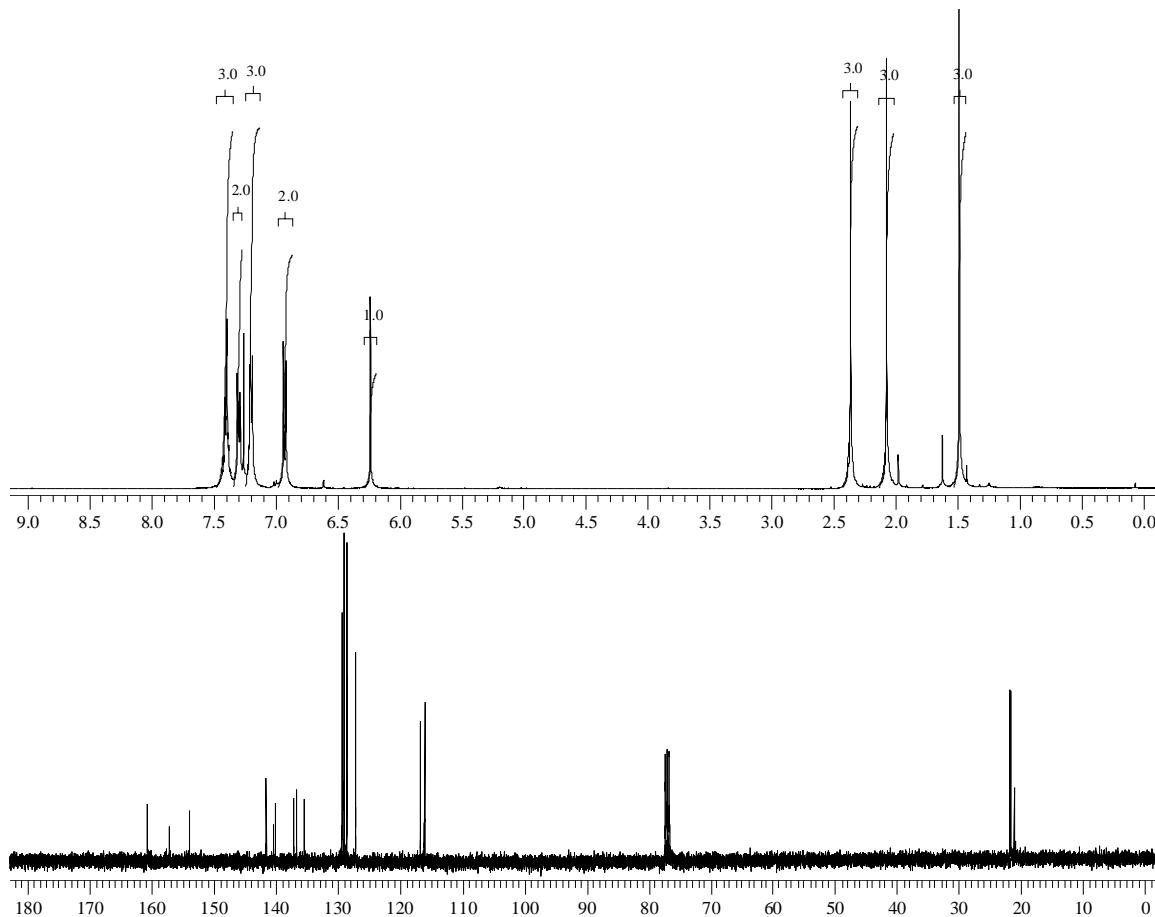


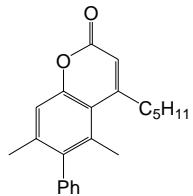
8-(4-Biphenyl)-6H-[1,3]dioxolo[4,5-g]chromen-6-one (3w). ^1H NMR (CDCl_3): δ 7.73 (d, 2H, *PhPhC*, $J = 7.3$ Hz); 7.65 (d, 2H, *PhPhC*, $J = 8.0$ Hz); 7.49 (t, 2H, *PhPhC*, $J = 7.3$ Hz); 7.48 (d, 2H, *PhPhC*, $J = 8.0$ Hz); 7.41 (t, 1H, *PhPhC*, $J = 7.3$ Hz); 6.91 (s, 1H, *PhO*); 6.90 (s, 1H, *PhO*); 6.28 (s, 1H, *CHCO*); 6.04-6.06 (m, 2H, *OCH_2O*). $^{13}\text{C}\{\text{H}\}$ NMR: δ 161.1 (CO), Ph ring and C=C (155.5, 151.3, 151.1, 144.8, 142.5, 139.9, 134.4, 128.9, 128.7, 127.9, 127.5, 127.1, 112.7, 112.0, 104.3, 98.5), 102.3 (*OCH_2O*). ν_{max} (NaCl)/ cm^{-1} : 3055, 1717, 1634, 1576, 1504, 1485, 1445, 1406, 1389, 1334, 1209, 1138, 1040. HR-MS: $\text{C}_{22}\text{H}_{15}\text{O}_4$ Calcd. 343.0970 ($\text{M}+1$); found: 343.0945.



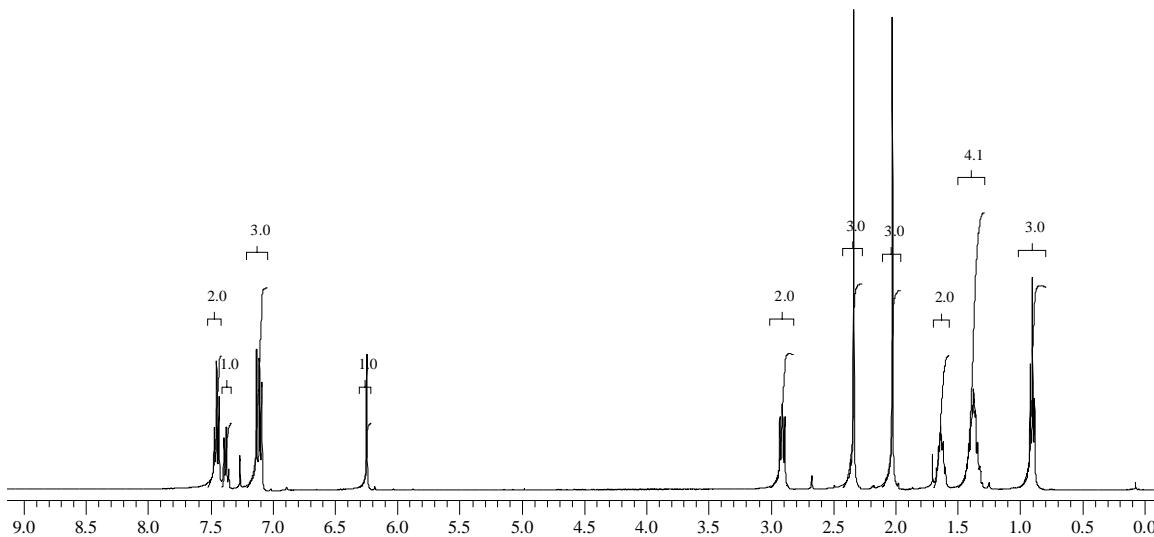


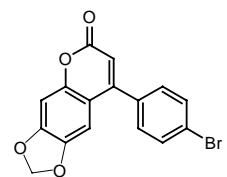
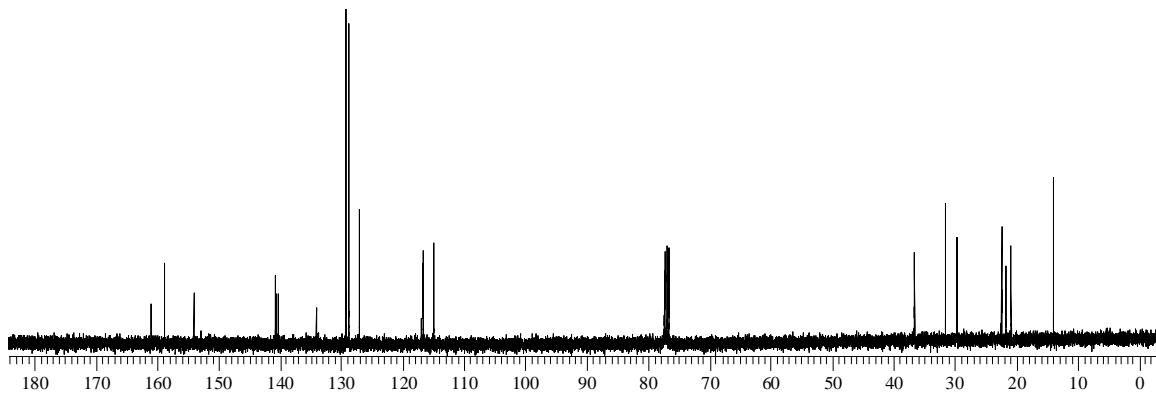
5,7-Dimethyl-4-phenyl-6-p-tolyl-2H-chromen-2-one (3x). ^1H NMR (CDCl_3): δ 7.37-7.44 (m, 3H, $\text{PhC}=\text{CH}$); 7.30 (dd, 2H, $\text{PhC}=\text{CH}$, $J = 7.6$ and 2.6 Hz); 7.20 (s, 1H, PhO); 7.19 (d, 2H, PhCH_3 , $J = 7.9$ Hz); 6.93 (d, 2H, PhCH_3 , $J = 7.9$ Hz); 6.24 (s, 1H, CHCO); 2.37 (s, 3H, PhPhCH_3); 2.08 (s, 3H, OPhCH_3); 1.49 (s, 3H, OPhCH_3). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.6 (CO), Ph ring and C=C (157.1, 153.9, 141.5, 140.4, 140.1, 137.1, 136.6, 135.4, 129.4, 129.0, 128.59, 128.57, 127.2, 116.7, 116.1, 116.0), OPhCH₃ (21.8, 21.7), 21.2 (OPhPhCH₃). ν_{max} (NaCl)/cm⁻¹: 3058, 1720, 1599, 1541, 1536, 1211, 1176, 1069. HR-MS: C₂₄H₂₁O₂ Calcd. 341.1542 (M+1); found: 341.1530.



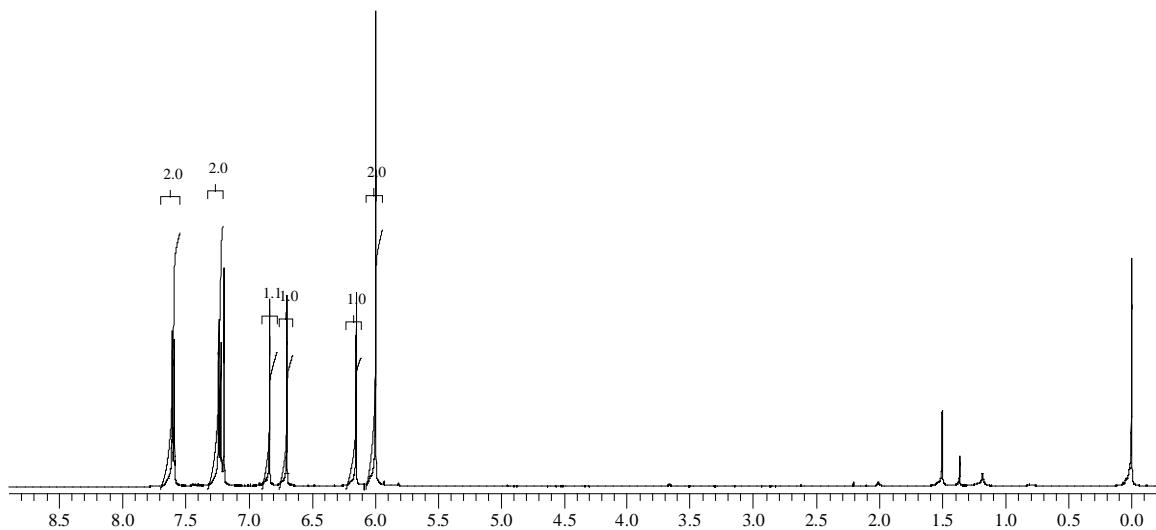


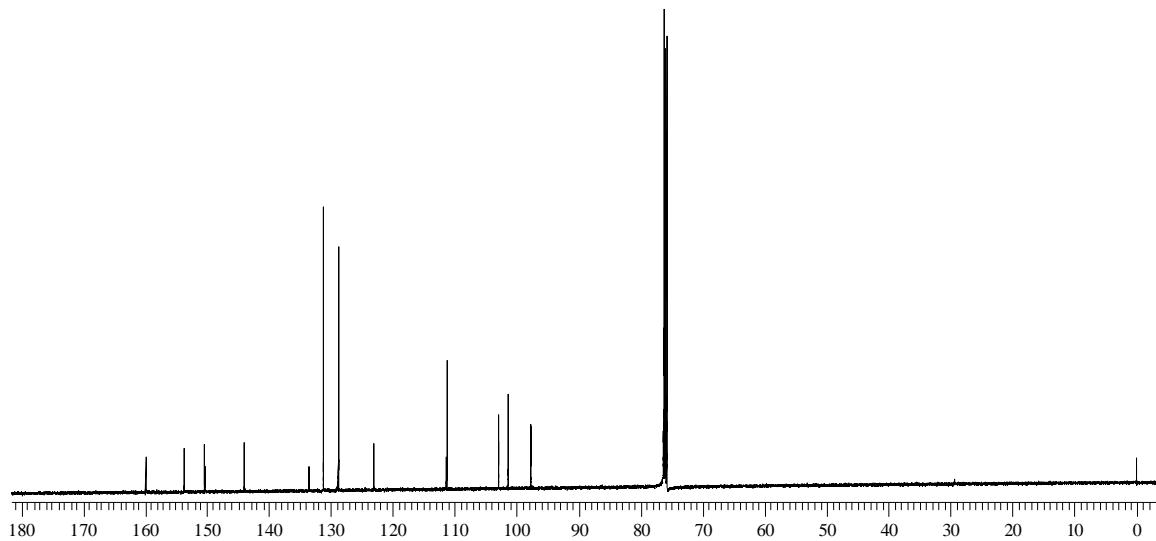
5,7-Dimethyl-4-pentyl-6-phenyl-2H-chromen-2-one (3y). ^1H NMR (CDCl_3): δ 7.45 (t, 2H, *PhPhO*, $J = 7.6$ Hz); 7.37 (t, 1H, *PhPhO*, $J = 7.6$ Hz); 7.13 (s, 1H, *PhPhO*); 7.10 (d, 2H, *PhPhO*, $J = 7.6$ Hz); 6.24 (s, 1H, CHCO); 2.90 (t, 2H, $\text{CH}=\text{CCH}_2$, $J = 7.9$ Hz); 2.33 (s, 3H, PhCH_3); 2.02 (s, 3H, PhCH_3); 1.59-1.67 (m, 2H, $\text{CH}=\text{CCH}_2\text{CH}_2$); 1.30-1.42 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_3$); 0.90 (t, 3H, CH_2CH_3 , $J = 7.3$ Hz). $^{13}\text{C}\{\text{H}\}$ NMR: δ 160.9 (CO), Ph ring and C=C (158.8, 154.0, 140.7, 140.6, 140.3, 134.1, 129.2, 128.8, 127.1, 117.0, 116.6, 115.0), 36.5 (CCH_2), 31.5 (CCH_2CH_2), 29.6 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 22.4 (CH_2CH_3), 21.7 (PhCH_3), 20.9 (PhCH_3), 13.9 (CH_2CH_3). ν_{max} (NaCl)/ cm^{-1} : 3055, 1718, 1605, 1546, 1070. HR-MS: $\text{C}_{22}\text{H}_{24}\text{O}_2\text{Na}$ Calcd. 343.1674 ($\text{M}+\text{Na}$); found: 343.1670.





8-(4-Bromophenyl)-6H-[1,3]dioxolo[4,5-g]chromen-6-one. ^1H NMR (CDCl_3): δ 7.59 (d, 2H, PhBr, $J = 8.8$ Hz); 7.23 (d, 2H, PhBr, $J = 8.8$ Hz); 6.83 (s, 1H, PhO); 6.69 (s, 1H, PhO); 6.15 (s, 1H, CHCO); 5.99 (s, 2H, OCH_2O). $^{13}\text{C}\{\text{H}\}$ NMR: δ 159.9 (CO), Ph ring and C=C (153.6, 150.4, 150.3, 144.0, 133.5, 131.2, 128.8, 123.0, 111.4, 111.3, 103.0, 97.7), 101.4 (OCH_2O). ν_{max} (NaCl)/ cm^{-1} : 3055, 1724, 1633, 1575, 1559, 1504, 1485, 1447, 1375, 1136, 1040. HR-MS: $\text{C}_{16}\text{H}_{10}\text{O}_4\text{Br}$ Calcd. 344.9762 ($\text{M}+\text{H}$); found: 344.9750.





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² (a) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science*, **2000**, 287, 1992-1995. (b) Jia, C.; Piao, D.; Kitamura, T.; Fujiwara, Y. *J. Org. Chem.* **2000**, 65, 7516-7522.