Supporting Information

Biomimetic Total Synthesis of Horsfiequinone B Enabled by a Friedel-Crafts Alkylation-Type Non-homodimerization

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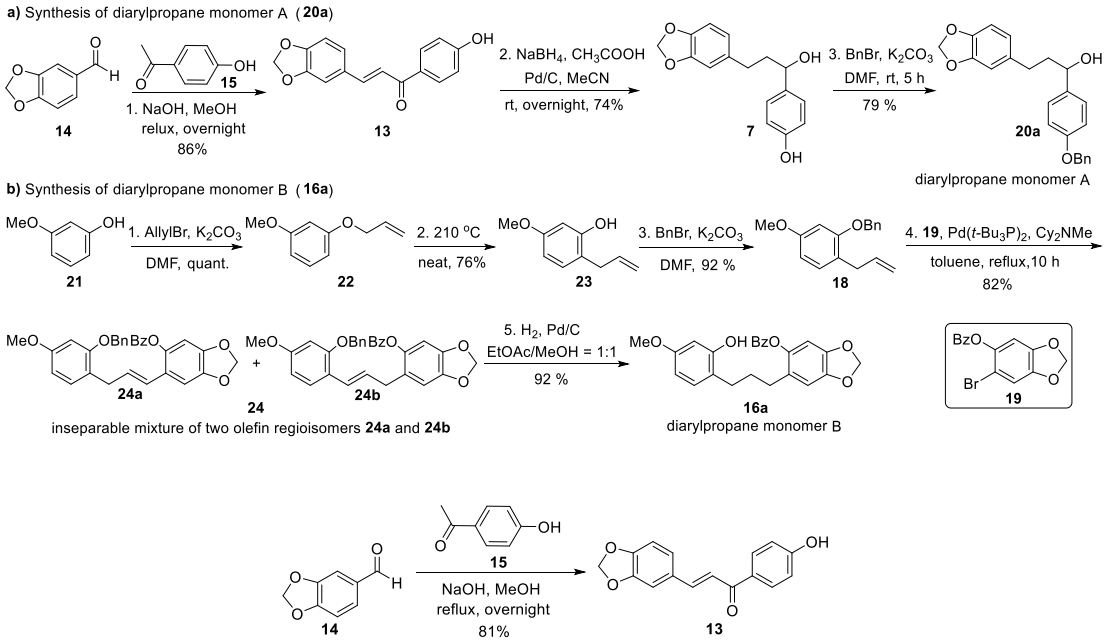
1. General Information

All reactions were conducted in oven-dried round-bottom flasks under argon atmosphere. Toluene was freshly distilled with Na. Methylene chloride (CH_2Cl_2) was freshly distilled with CaH_2. All reagents were used from commercial sources without further purification, unless otherwise noted. The silica gel (200-300 meshes, Qingdao Marine Chemical Inc., Qingdao, China) was used for column chromatography. Thin layer chromatographies (TLC) were carried out on GF plates (0.25 mm layer thickness, Qingdao Marine Chemical Inc., Qingdao, China). Visualization of the developed chromatogram was performed by ultraviolet light (254 nm, if applicable) or by phosphomolybdic acid (50 g/L) in ethanol following heating as developing agents. Yields reported were for isolated, spectroscopically pure compounds, unless otherwise noted.

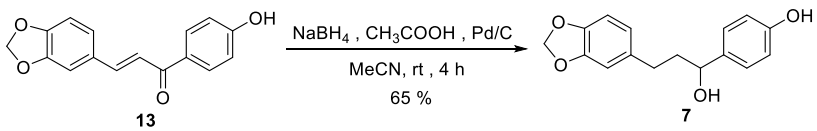
^{1}H and ^{13}C NMR spectras were recorded on AM-500 MHz and ADVANCE III 600 MHz spectrometers (Bruker, Germany) at ambient temperature. The residue solvent protons (^{1}H) or the solvent carbons (^{13}C) were used as internal standards. ^{1}H NMR data were presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant (Hz), integration). Chemical shifts (δ) were given in ppm with reference to solvent signals [^{1}H NMR: $CDCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.16)]. The following abbreviations are used in reporting NMR data: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, m = multiplet. HRMS (ESI) was taken on Agilent UPLC-Q-TOF G6530 (Agilent Technologies, USA) and Thermo Scientific Orbitrap Exploris120 spectrometer (Thermo Fisher Scientific, USA).

2. Experimental Procedure and Characterization Data

Scheme S1. Synthesis of diarylpropane monomer A (**20a**) and B (**16a**)

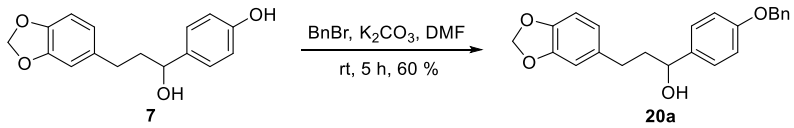


(E)-3-(benzo[d][1,3]dioxol-5-yl)-1-(4-hydroxyphenyl)prop-2-en-1-one (13). To solution of 4-hydroxyacetophenone **15** (4.3 g, 28.64 mmol, 1.1 eq.) and piperonyl aldehyde **14** (3.54 g, 26.03 mmol. 1 eq.) in MeOH (AR, 120 mL) was added NaOH (4.16 g, 104.12 mmol, 4 eq.) at the room temperature. Then the mixture was heated to reflux for overnight. The reaction was adjusted to pH = 7 with 1 N HCl at 0 ^{o}C. The resulting mixture was extracted with EtOAc (5 × 150 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 6:1) to yield product **13** (6.0 g, 86%) as a yellow amorphous powder. **^{1}H NMR** (500 MHz, acetone-d_6) δ 8.09 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 15.5 Hz, 1H), 7.68 (d, J = 15.5 Hz, 1H), 7.46 (d, J = 1.7 Hz, 1H), 7.26 (dd, J = 8.1, 1.6 Hz, 1H), 6.96 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.0 Hz, 1H), 6.08 (s, 2H); **^{13}C NMR** (125 MHz, acetone-d_6) δ 187.9, 162.6, 150.6, 149.4, 143.6, 131.8, 131.3, 130.8, 126.0, 120.9, 116.1, 109.3, 107.4, 102.6. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{13}O_4$ $[M+H]^+$: 269.0808, found: 269.0806.



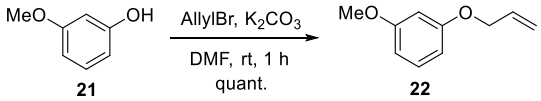
4-(3-(benzo[d][1,3]dioxol-5-yl)-1-hydroxypropyl)phenol (7). To a solution of **13** (2.8 g, 4.1 mmol, 1 eq.) in MeCN (AR, 40 mL) was added acetic acid (1.2 mL, 20.9 mmol, 2 eq.) and $NaBH_4$ (1.98 g, 52.2 mmol, 5 eq.) and Pd/C (280 mg, 10% wt) at room temperature. The mixture was stirred for overnight at the same temperature. The resulting mixture was quenched by adding a saturated NH_4Cl aqueous solution at 0 ^{o}C. The mixture was filtrated though a short pad of celite and the filter cake was washed

with ethyl acetate, then the combined organic layers were washed with saturated $NaHCO_3$ aqueous solution and brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/DCM/EtOAc = 4:1:1) to yield product **7** (2.1 g, 74%) as a white amorphous powder. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.70 (d, *J* = 1.7 Hz, 1H), 6.65 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.94 (s, 2H), 4.64 (t, *J* = 6.5 Hz, 1H), 2.69 – 2.56 (m, 2H), 2.14 – 2.07 (m, 1H), 2.00 - 1.93 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.2, 147.7, 145.8, 137.0, 135.8, 127.6, 121.3, 115.5, 109.1, 108.3, 100.9, 73.5, 40.7, 32.0. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{15}O_4$ $[M-H]^-$: 271.0976, found: 271.0971.



7 **20a**

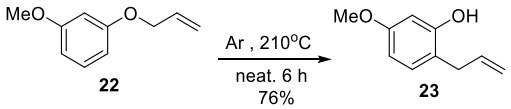
3-(benzo[d][1,3]dioxol-5-yl)-1-(4-(benzyloxy)phenyl)propan-1-ol (20a). To a solution of **7** (2.4 g, 8.82 mmol, 1 eq.) in DMF (AR, 10 mL) was added BnBr (1.47 mL, 12.4 mmol, 1.4 eq.) and K_2CO_3 (2.2 g, 15.9 mmol, 1.8 eq.) at room temperature. Then the mixture was stirred for 5 h at the same temperature. The resulting mixture was diluted by added water. The resulting mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (5 × 10 mL), dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 8 : 1) to yield product **20a** (2.53 g , 79%) as a colorless, viscous oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.68 (s, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 5.91 (s, 2H), 5.07 (s, 2H), 4.63 – 4.60 (m, 1H), 2.67 – 2.54 (m, 2H), 2.12 – 2.05 (m, 1H), 1.99 – 1.92 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.5, 147.7, 145.8, 137.1, 137.1, 135.8, 128.7, 128.1, 127.6, 127.3, 121.3, 115.0, 109.1, 108.3, 100.9, 73.5, 70.2, 40.7, 32.0. **HR-ESI-MS** (m/z): calculated for $C_{23}H_{22}O_4Na$ $[M+Na]^+$: 385.1410, found: 385.1408.



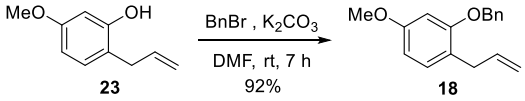
21 **22**

1-(allyloxy)-3-methoxybenzene (22). To a solution of 3-methoxyphenol **21** (3.72 g, 30 mmol) in DMF (AR, 50 mL) was added allyl bromide (3.37 mL, 39 mmol) and K_2CO_3 (8.28 g, 60 mmol) at room temperature. Then the mixture was stirred for 1 h at the same temperature. The resulting mixture was diluted with water. The resulting mixture was extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 100 : 1) to yield product **22** (4.90 g, quant.) as a colorless, viscous oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (t, *J* = 8.1 Hz, 1H), 6.54 – 6.49 (m, 3H), 6.10 – 6.03 (m, 1H),

5.42 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.29 (dd, *J* = 10.6, 1.5 Hz, 1H), 4.53 (d, *J* = 5.3 Hz, 2H), 3.79 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.0, 160.0, 133.4, 130.0, 117.8, 107.0, 106.6, 101.4, 69.0, 55.4. **HR-ESI-MS** (m/z): calculated for $C_{10}H_{13}O_2$ $[M+H]^+$: 165.0910, found: 165.0906.

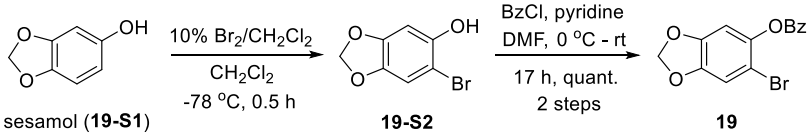


2-allyl-5-methoxyphenol (23). Compound **22** (1.97 g, 12.03 mmol) was connected to an Ar balloon, and was stirred for 6 h at 210°C. Then the mixture was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 10 : 1) to yield product **23** (1.50 g, 76%) as a colorless, viscous oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.3 Hz, 1H), 6.46 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.42 (d, *J* = 2.5 Hz, 1H), 6.05 – 5.97 (m, 1H), 5.17 (dq, *J* = 7.9, 1.7 Hz, 1H), 5.14 (t, *J* = 1.6 Hz, 1H), 5.10 – 5.08 (m, 1H), 3.77 (s, 3H), 3.35 (d, *J* = 6.3 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.8, 155.2, 136.9, 131.0, 117.5, 116.4, 106.5, 102.2, 55.5, 34.7. **HR-ESI-MS** (m/z): calculated for $C_{10}H_{13}O_2$ $[M+H]^+$: 165.0910, found: 165.0906.



1-allyl-2-(benzyloxy)-4-methoxybenzene (18). To a solution of **23** (2.67 g, 16.3 mmol, 1 eq.) in DMF (AR, 20 mL) was added BnBr (3.09 mL, 26 mmol, 1.6 eq) and K_2CO_3 (3.37 g, 24.4 mmol, 1.5 eq) at room temperature. Then the mixture was stirred for 7 h at the same temperature. The resulting mixture was diluted with water and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/DCM = 60 : 1) to yield product **18** (3.80 g , 92%) as a colorless, viscous oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.47 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.04 – 5.97 (m, 1H), 5.08 – 5.02 (m, 4H), 3.78 (s, 3H), 3.39 (d, *J* = 6.6 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.4, 157.3, 137.5, 137.4, 130.2, 128.6, 127.9, 127.3, 121.5, 115.2, 104.6, 100.0, 70.1, 55.5, 34.0. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{19}O_2$ $[M+H]^+$: 255.1380, found: 255.1379.

Preparation of 6-bromobenzo[d][1,3]dioxol-5-yl benzoate (19).

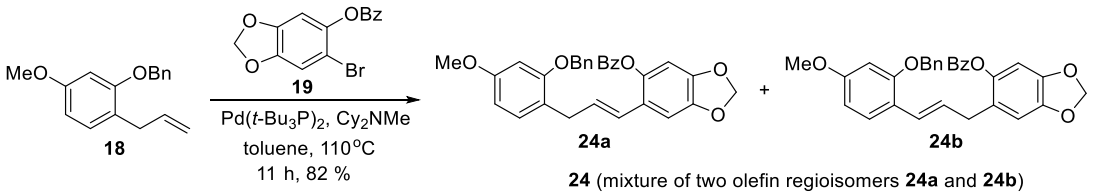


To a solution of sesamol (**19-S1**) (2.76 g, 20 mmol) in CH_2Cl_2 (30 mL) was added Br_2/CH_2Cl_2 (10% in CH_2Cl_2, 8.7 mL, 17 mmol) dropwise at -78 °C. Then the mixture was stirred for 0.5 h at the same temperature. The resulting mixture was quenched by added a saturated $Na_2S_2O_3$ solution, and extracted with EtOAc (3 × 50

mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue (4.3 g, brown amorphous powder) was used in next step without further purification due to instability of **19-S2**.

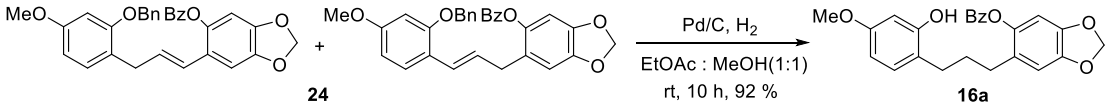
To a solution of **19-S2** (4.3 g) in DMF (20 mL) was added pyridine (4.82 mL, 60 mmol) and BzCl (3.53 mL, 30 mmol) at 0 ^{o}C. Then the mixture was stirred for 17 h at room temperature. The resulting mixture was quenched by adding saturated $NaHCO_3$ solution, The resulting mixture was extracted with EtOAc (5 × 30 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/acetone= 100 : 1) to yield product **19** (5.03 g, quant.).

6-bromobenzo[d][1,3]dioxol-5-yl benzoate (19). white amorphous powder. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.06 (s, 1H), 6.79 (s, 1H), 6.03 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.7, 147.8, 146.4, 142.6, 134.0, 130.5, 129.1, 128.8, 112.2, 106.7, 105.2, 102.5. **HR-ESI-MS** (m/z): calculated for $C_{14}H_{10}O_4Br$ $[M+H]^+$: 320.9757, found: 320.9763.



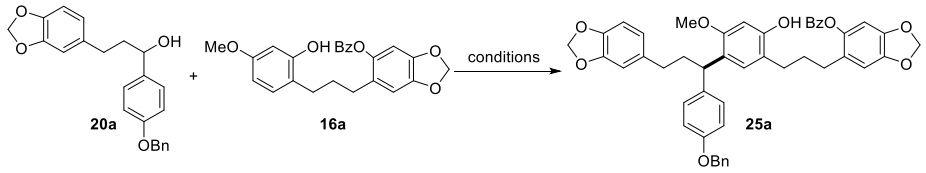
24 (mixture of two olefin regioisomers **24a** and **24b**)

Mixture of two olefin regioisomers (E)-6-(3-(2-(benzyloxy)-4-methoxyphenyl)prop-1-en-1-yl)benzo[d][1,3]dioxol-5-yl benzoate (24a) and (E)-6-(3-(2-(benzyloxy)-4-methoxyphenyl)allyl)benzo[d][1,3]dioxol-5-yl benzoate (24b) (24). To solution of $Pd(t\text{-}Bu_3P)_2$ (442 mg, 0.87 mmol, 0.05 eq) and aryl bromide **19** (5.56g, 17.3 mmol, 1 eq) in degassed toluene (10 mL) was added solution of olefin **18** (6.6g, 26 mmol, 1.5 eq) and Cy_2NMe (4.06 mL, 19 mmol, 1.1 eq) in toluene (15 mL) at room temperature. Then the mixture was stirred for 11 h at 110 ^{o}C. The resulting mixture was concentrated in vacuo and the residue was purified by silica gel flash column chromatography (petroleum ether/acetone = 60 : 1) to yield product **24** (7.03 g, 82 %, mixture of two olefin regioisomers **24a** and **24b**) as a yellow, viscous oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.8 Hz,, 1.32H), 8.11 (d, *J* = 7.5 Hz, 0.66H), 7.63 (t, *J* = 7.5 Hz, 0.33H), 7.59 (t, *J* = 7.4 Hz, 0.66H), 7.49 – 7.44 (m, 2H), 7.38 – 7.29 (m, 6H), 7.00 (d, *J* = 9.6 Hz, 0.66H), 6.79 (s, 0.66H), 6.69 (s, 1H), 6.66 (s, 0.33H), 6.64 (s, 0.33H), 6.46 (s, 1H), 6.45 – 6.43 (m, 0.66H), 6.36 – 6.33 (m, 0.66H), 6.24 (dt, *J* = 15.6, 6.6 Hz, 0.33H), 6.15 (dt, *J* = 15.6, 6.6 Hz, 0.66H), 5.97 (s, 2H), 5.02 (s, 1.32H), 4.97 (s, 0.66H), 3.77 (s, 2H), 3.73 (s, 1H), 3.43 (d, *J* = 6.6 Hz, 0.66H), 3.38 (d, *J* = 6.6 Hz, 1.32H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.5, 165.3, 160.1, 159.4, 157.3, 156.7, 147.1, 146.5, 146.0, 145.7, 142.8, 142.1, 137.3, 137.1, 133.7, 130.4, 130.32, 130.27, 129.5, 128.72, 128.69, 128.67, 128.0, 127.9, 127.5, 127.3, 126.3, 126.1, 125.6, 123.9, 123.4, 121.1, 120.0, 109.5, 105.4, 105.1, 104.5, 104.1, 104.0, 101.8, 101.7, 100.1, 100.0, 70.4, 70.1, 55.5, 55.4, 34.2, 33.1. **HR-ESI-MS** (m/z): calculated for $C_{31}H_{26}O_6K$ $[M+K]^+$: 533.1361, found: 533.1354.



6-(3-(2-hydroxy-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (16a). To a solution of **24** (4.20 g, 8.5 mmol) in EtOAc/MeOH (1:1, 20 mL) was added Pd/C (420 mg, 10% wt). Then the mixture was connected to a H_2 balloon and stirred for 20 h at room temperature. After consumption of the starting materials, the mixture was filtrated through a short pad of celite, and the filter cake was washed with ethyl acetate, then the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 8 : 1) to yield product **16a** (3.07 g, 92 %) as a yellow, viscous oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.4 Hz, 1.5 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.77 (s, 1H), 6.68 (s, 1H), 6.35 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.29 (d, *J* = 2.5 Hz, 1H), 5.99 (s, 2H), 4.83 (s, 1H), 3.74 (s, 3H), 2.57 – 2.51 (m, 4H), 1.89 – 1.83 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.8, 159.1, 154.4, 146.3, 145.7, 142.8, 133.8, 130.5, 130.3, 129.5, 128.8, 127.0, 120.2, 109.2, 106.0, 104.2, 102.0, 101.7, 55.4, 30.4, 29.9, 28.9. **HR-ESI-MS** (m/z): calculated for $C_{24}H_{22}O_6Cl$ $[M+Cl]^-$: 441.1110, found: 441.1110.

Table S1. Optimization of Friedel-Crafts alkylation type non-homodimerization conditions[a]



Entry	Acid (0.1 eq)	Solvent	Temperature	Yield (%)[b]
1	H_3PO_4	CH_2Cl_2	0 ℃	NR
2	CF_3COOH	CH_2Cl_2	0 ℃	5
3	(-)-CSA	CH_2Cl_2	0 ℃	37
4	TsOH	CH_2Cl_2	0 ℃	53
5	MsOH	CH_2Cl_2	0 ℃	56
6	TfOH	CH_2Cl_2	0 ℃	79
7	Tf_2NH	CH_2Cl_2	0 ℃	91
8	Tf_2NH	CH_2Cl_2	25 ℃	76
9	Tf_2NH	THF	0 ℃	17
10	Tf_2NH	CH_3CN	0 ℃	75
11	Tf_2NH	DMF	0 ℃	NR[c]

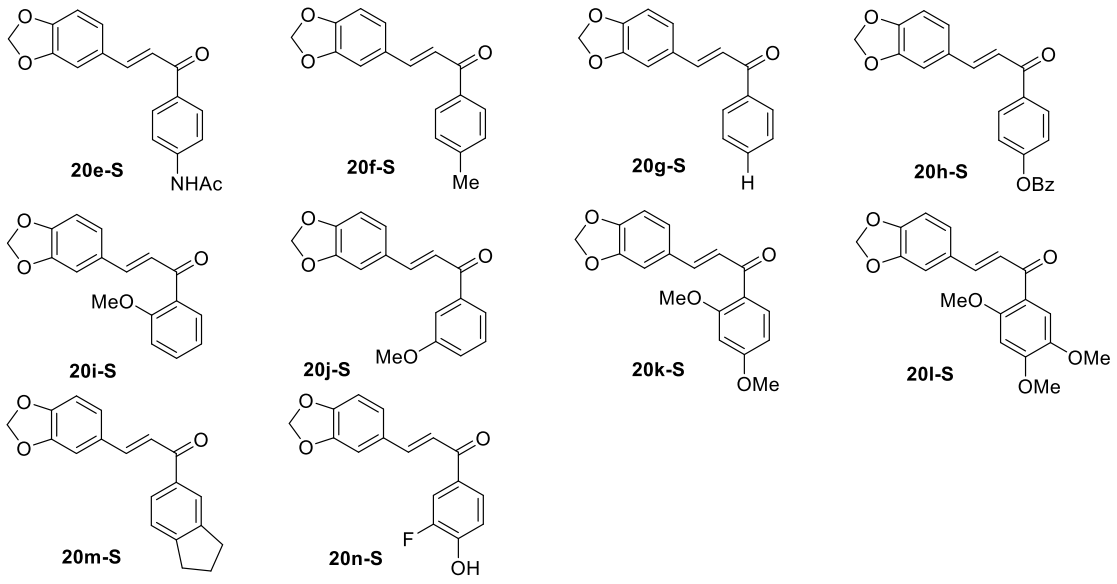
[a] Unless otherwise noted, all of the reactions were performed in dry solvent (1 mL) with **20a** (0.15 mmol) and **16a** (0.15 mmol) at 0 ℃ for 6 h. [b] Isolated yield. [c] NR: no reaction.

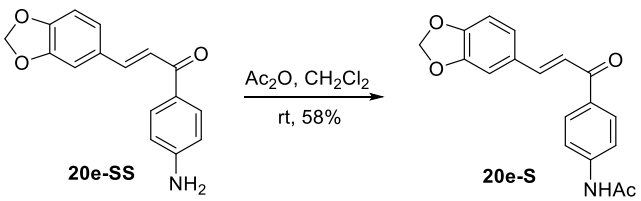
General procedure for Table S1.

6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-(benzyloxy)phenyl)propyl)-2-hydroxy-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25a). To solution

of **20a** (0.15 mmol, 1 eq) and **16a** (0.15 mmol, 1 eq) in CH_2Cl_2 (5 mL) was added acid (0.015 mmol, 0.1 eq) dropwise at 0 ^oC. Then the mixture was stirred for 6 h at the same temperature. The mixture was quenched by adding saturated $NaHCO_3$ solution at 0 ^oC, The resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 4 : 1) to yield product **25a** as a yellow, viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.1 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.47 (d, J = 7.8 Hz, 2H), 7.43 (d, J = 4.2 Hz, 1H), 7.41 (s, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.32 (d, J = 7.0 Hz, 1H), 7.13 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 6.86 (s, 1H), 6.73 (s, 1H), 6.70 (d, J = 7.9 Hz, 1H), 6.66 (s, 1H), 6.62 (d, J = 1.6 Hz, 1H), 6.55 (dd, J = 7.9, 1.7 Hz, 1H), 6.22 (s, 1H), 5.96 (s, 2H), 5.90 (s, 2H), 5.01 (s, 2H), 4.17 (t, J = 7.8 Hz, 1H), 3.66 (s, 3H), 2.54 (t, J = 7.6 Hz, 2H), 2.49 -2.42 (m, 4H), 2.20 – 2.14 (m, 2H), 1.85 – 1.77 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 157.0, 156.2, 152.3, 147.5, 146.2, 145.7, 145.5, 142.7, 137.7, 137.4, 133.8, 130.3, 129.3, 129.0, 128.8, 128.7, 128.0, 127.6, 126.9, 125.7, 121.2, 118.9, 114.6, 109.3, 109.1, 108.1, 104.1, 101.7, 100.8, 99.5, 70.1, 55.6, 41.6, 37.5, 34.1, 30.5, 30.1, 29.2. **HR-ESI-MS** (m/z): calculated for $C_{47}H_{46}O_9N$ $[M+NH_4]^+$: 768.3167, found: 768.3163.

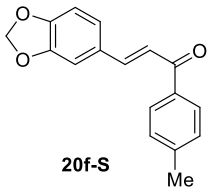
General procedure for the preparation of *α,β*-unsaturated ketones [(20e-S) – (20o-S)]





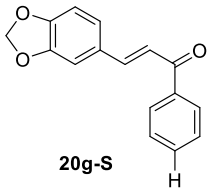
(E)-N-(4-(3-(benzo[d][1,3]dioxol-5-yl)acryloyl)phenyl)acetamide (20e-S). To a

solution of **20e-SS** (230 mg, 0.86 mmol) in CH_2Cl_2 (6 mL) was added Ac_2O (121 μL, 1.29 mmol) at room temperature. Then the mixture was stirred for 3 h at the same temperature. The resulting mixture was quenched by adding aqueous $NaHCO_3$ solution. The resulting mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The resulting mixture was filtered and concentrated in vacuo, and purified by silica gel flash column chromatography (petroleum ether/DCM/EtOAc = 2:1:1) to yield product **20e-S** (154 mg , 58%) as a yellow amorphous powder. **^{1}H NMR** (400 MHz, $CDCl_3$) 8.01 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 15.5 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.47 (s, 1H), 7.37 (d, *J* = 15.5 Hz, 1H), 7.17 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.0, 168.6, 150.0, 148.6, 144.6, 142.1, 134.2, 130.0, 129.5, 125.3, 119.9, 119.1, 108.8, 106.8, 101.8, 25.0. **HR-ESI-MS** (m/z): calculated for $C_{18}H_{16}O_4N$ $[M+H]^+$: 310.1074, found: 310.1072.



20f-S

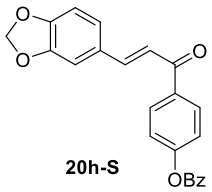
(E)-3-(benzo[d][1,3]dioxol-5-yl)-1-(p-tolyl)prop-2-en-1-one (20f-S). Yellow amorphous powder. 73 % yield (583 mg). R_f = 0.50 (petroleum ether/EtOAc = 5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 15.6 Hz, 1H), 7.37 (d, *J* = 15.6 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 1.7 Hz, 1H), 7.12 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 149.9, 148.5, 144.4, 143.6, 135.9, 129.6, 129.4, 128.7, 125.3, 120.2, 108.8, 106.8, 101.8, 21.8. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{15}O_3$ $[M+H]^+$: 267.1016, found: 267.1021.



20g-S

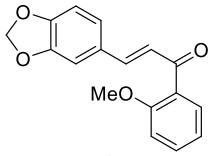
(E)-3-(benzo[d][1,3]dioxol-5-yl)-1-phenylprop-2-en-1-one (20g-S). Yellow amorphous powder. 87 % yield (169 mg). R_f = 0.60 (petroleum ether / Acetone = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.3 Hz, 2H), 7.74 (d, *J* = 15.6 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.37 (d, *J* = 15.6 Hz, 1H), 7.17 (s, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ190.6, 150.1, 148.6, 144.8, 138.5, 132.8, 129.5, 128.7, 128.6, 125.4, 120.2, 108.8, 106.8, 101.8. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{13}O_3$ $[M+H]^+$: 253.0859, found: 253.0859.

Note: the reaction was conducted under room temperature.



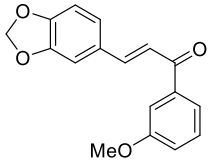
20h-S

(E)-4-(3-(benzo[d][1,3]dioxol-5-yl)acryloyl)phenyl benzoate (20h-S). Yellow amorphous powder. Quant. (220 mg). R_f = 0.70 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.1 Hz, 2H), 8.10 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 15.5 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.36 (m, 3H), 7.18 (d, *J* = 1.7 Hz, 1H), 7.14 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 189.3, 164.8, 154.5, 150.1, 148.6, 145.1, 136.2, 134.0, 130.4, 130.2, 129.4, 129.3, 128.8, 125.5, 122.1, 120.0, 108.8, 106.8, 101.8. **HR-ESI-MS** (m/z): calculated for $C_{23}H_{17}O_5$ $[M+H]^+$: 373.1071, found: 373.1067.



20i-S

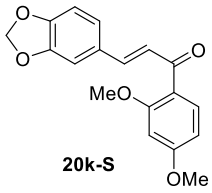
(E)-3-(benzo[d][1,3]dioxol-5-yl)-1-(2-methoxyphenyl)prop-2-en-1-one (**20i-S**). Yellow amorphous powder. 89% yield (752 mg). R_f = 0.50 (petroleum ether / Acetone = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.54 (d, *J* = 15.8 Hz, 1H), 7.46 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H), 7.20 (d, *J* = 15.8 Hz, 1H), 7.10 (d, *J* = 1.7 Hz, 1H), 7.07 – 7.00 (m, 2H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.00 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ192.9, 158.0, 149.7, 148.4, 143.2, 132.8, 130.3, 129.6, 129.4, 125.3, 125.1, 120.7, 111.7, 108.6, 106.7, 101.6, 55.8. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{15}O_4$ $[M+H]^+$: 283.0965, found: 283.0958.



20j-S

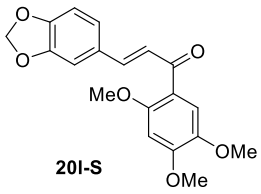
(E)-3-(benzo[d][1,3]dioxol-5-yl)-1-(3-methoxyphenyl)prop-2-en-1-one (20j-S). Yellow amorphous powder. 93% yield (789 mg). R_f = 0.50 (petroleum ether / EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 15.6 Hz, 1H), 7.57 (s, 1H), 7.54 – 7.52 (m, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 15.6 Hz, 1H), 7.17 (d, *J* = 1.6 Hz, 1H), 7.12 (dd, *J* = 8.1, 2.1 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H), 3.88 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 160.0, 150.0,

148.5, 144.8, 139.9, 129.6, 129.4, 125.4, 121.1, 120.2, 119.3, 112.9, 108.8, 106.8, 101.8, 55.6. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{15}O_4$ $[M+H]^+$: 283.0965, found: 283.0968.



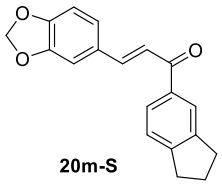
20k-S

(E)-3-(benzo[d][1,3]dioxol-5-yl)-1-(2,4-dimethoxyphenyl)prop-2-en-1-one (20k-S). Yellow amorphous powder. 81% yield (760 mg). R_f = 0.50 (petroleum ether/Acetone = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.6 Hz, 1H), 7.60 (d, J = 15.7 Hz, 1H), 7.35 (d, J = 15.7 Hz, 1H), 7.11 (d, J = 1.6 Hz, 1H), 7.07 (dd, J = 8.0, 1.7 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.56 (dd, J = 8.6, 2.3 Hz, 1H), 6.49 (d, J = 2.3 Hz, 1H), 6.00 (s, 2H), 3.90 (s, 3H), 3.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.4, 164.1, 160.3, 149.5, 148.3, 142.0, 132.9, 130.0, 125.4, 124.9, 122.4, 108.7, 106.7, 105.2, 101.6, 98.7, 55.9, 55.7. **HR-ESI-MS** (m/z): calculated for $C_{18}H_{17}O_5$ $[M+H]^+$: 313.1071, found: 313.1074.



20l-S

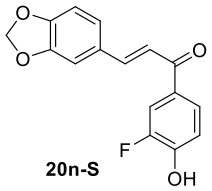
(E)-3-(benzo[d][1,3]dioxol-5-yl)-1-(2,4,5-trimethoxyphenyl)prop-2-en-1-one (20l-S). Yellow amorphous powder. 86% yield (118 mg). R_f = 0.30 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 15.6 Hz, 1H), 7.47 (d, J = 15.6 Hz, 1H), 7.37 (s, 1H), 7.13 (s, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.54 (s, 1H), 6.01 (s, 2H), 3.96 (s, 3H), 3.92 (s, 3H), 3.89 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.9, 154.9, 153.6, 149.5, 148.4, 143.5, 142.0, 130.2, 125.5, 125.0, 120.8, 113.3, 108.7, 106.7, 101.6, 97.2, 57.0, 56.5, 56.3. **HR-ESI-MS** (m/z): calculated for $C_{19}H_{19}O_6$ $[M+H]^+$: 343.1176, found: 343.1175.



20m-S

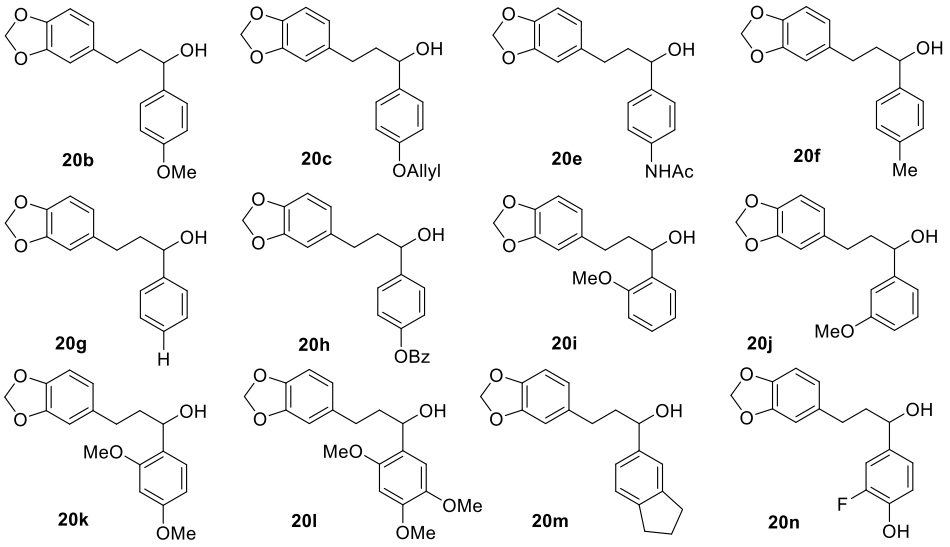
(E)-3-(benzo[d][1,3]dioxol-5-yl)-1-(2,3-dihydro-1H-inden-5-yl)prop-2-en-1-one (20m-S). Yellow amorphous powder. 63% yield (554 mg). R_f = 0.50 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 15.6 Hz, 1H), 7.38 (d, J = 15.6 Hz, 1H), 7.33 (d, J = 7.7 Hz, 1H), 7.18 (s, 1H), 7.12 (d, J = 7.8 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 6.03 (s, 2H), 3.00 - 2.96 (m, 4H), 2.17 – 2.10 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.5, 150.0,

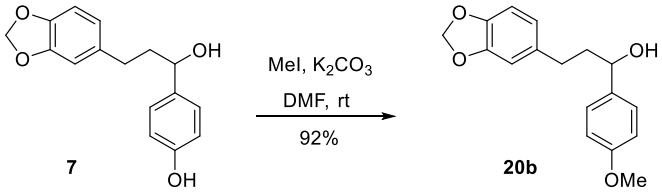
149.9, 148.5, 145.0, 144.2, 137.0, 129.7, 127.1, 125.2, 124.5, 120.6, 108.8, 106.8, 101.7, 33.2, 32.8, 25.5. **HR-ESI-MS** (m/z): calculated for $C_{19}H_{17}O_3$ $[M+H]^+$: 293.1172, found: 293.1176.



(E)-3-(benzo[d][1,3]dioxol-5-yl)-1-(3-fluoro-4-hydroxyphenyl)prop-2-en-1-one (20n-S). Yellow amorphous powder. 87 % yield (751 mg). R_f = 0.30 (petroleum ether/EtOAc = 4:1). **^{1}H NMR** (400 MHz, CD_3OD) δ 7.88 – 7.79 (m, 2H), 7.70 (d, J = 15.5 Hz, 1H), 7.59 (d, J = 15.5 Hz, 1H), 7.37 (s, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.03 (t, J = 8.6 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.03 (s, 2H); **^{13}C NMR** (100 MHz, CD_3OD) δ189.6, 153.9, 151.5, 150.0, 145.7, 131.5 (d, $J_{C\text{-}F}$ = 5 Hz), 130.8, 127.4 (d, $J_{C\text{-}F}$ = 3 Hz), 126.8, 120.3, 118.5 (d, $J_{C\text{-}F}$ = 3 Hz), 117.4(d, $J_{C\text{-}F}$ = 19 Hz), 109.5, 107.8, 103.1; **^{19}F NMR** (376 MHz, CD_3OD) δ -136.04. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{12}O_4F$ $[M+H]^+$: 287.0714, found: 287.0713.

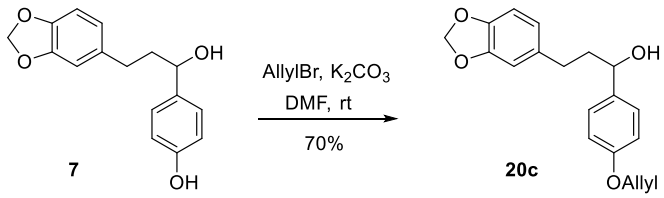
General Procedure for the Preparation of Diarylpropanes A (20b –20n)



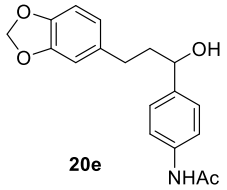


3-(benzo[d][1,3]dioxol-5-yl)-1-(4-methoxyphenyl)propan-1-ol (20b). To a solution of **7** (136 mg, 0.5 mmol) in DMF (AR, 2 mL) was added MeI (87 μL, 0.6 mmol) and

K_2CO_3 (103.5 mg, 0.75 mmol) at room temperature. Then the mixture was stirred for 1 h at the same temperature. The resulting mixture was diluted with water and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 80 : 1) to yield product **20b** (132 mg , 92%) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.68 (s, 1H), 6.64 (s, 1H), 5.91 (s, 2H), 4.62 (t, *J* = 6.7 Hz, 1H), 3.81 (s, 3H), 2.68 – 2.53 (m, 2H), 2.13 - 2.04 (m, 1H), 2.02 – 1.90 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 147.7, 145.7, 136.8, 135.8, 127.3, 121.3, 114.0, 109.0, 108.3, 100.9, 73.5, 55.4, 40.7, 32.0. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{19}O_4$ $[M+H]^+$: 287.1278, found: 287.1273.

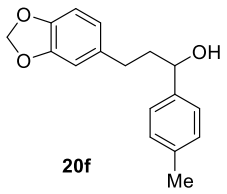


1-(4-(allyloxy)phenyl)-3-(benzo[d][1,3]dioxol-5-yl)propan-1-ol (20c). To a solution of **7** (136 mg, 0.5 mmol) in DMF (AR, 2 mL) was added AllylBr (52 μL, 0.6 mmol) and K_2CO_3 (103.5 mg, 0.75 mmol) in order at room temperature. Then the mixture was stirred for 2 h at the same temperature. The resulting mixture was quenched by added water. The resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The resulting mixture was filtered and concentrated in vacuo, and purified by silica gel flash column chromatography (petroleum ether/EtOAc = 80 : 1) to yield product **20c** (110 mg , 70%) as a yellow sticky amorphous powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.7 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.11 - 6.01 (m, 1H), 5.91 (s, 2H), 5.42 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.29 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.61 (dd, *J* = 7.7, 5.6 Hz, 1H), 4.54 (dt, *J* = 5.4, 1.6 Hz, 2H), 2.71 – 2.50 (m, 2H), 2.13 – 2.02 (m, 1H), 2.01 – 1.90 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 147.7, 145.7, 137.0, 135.8, 133.4, 127.3, 121.2, 117.8, 114.8, 109.0, 108.3, 100.9, 73.4, 69.0, 40.7, 32.0. **HR-ESI-MS** (m/z): calculated for $C_{19}H_{20}O_4Na$ $[M+Na]^+$: 335.1254, found: 335.1255.



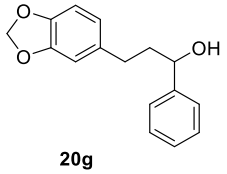
N-(4-(3-(benzo[d][1,3]dioxol-5-yl)-1-hydroxypropyl)phenyl)acetamide (20e). White amorphous powder. 61% yield (105 mg). R_f = 0.30 (petroleum ether/EtOAc = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.6 Hz,

2H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.67 (d, *J* = 1.7 Hz, 1H), 6.62 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (s, 2H), 4.62 (dd, *J* = 7.8, 5.4 Hz, 1H), 2.67 – 2.53 (m, 2H), 2.17 (s, 3H), 2.10 – 2.01 (m, 1H), 1.97 – 1.89 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 168.5, 147.7, 145.7, 140.6, 137.3, 135.6, 126.7, 121.3, 120.1, 109.0, 108.3, 100.9, 73.4, 40.8, 31.9, 29.8, 24.7. **HR-ESI-MS** (m/z): calculated for $C_{18}H_{18}O_4N$ $[M-H]^-$: 312.1241, found: 312.1245.



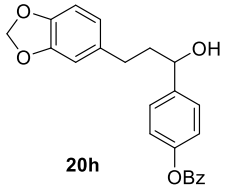
20f

3-(benzo[d][1,3]dioxol-5-yl)-1-(p-tolyl)propan-1-ol (20f). White amorphous powder. 61% yield (250 mg). R_f = 0.50 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 1.7 Hz, 1H), 6.64 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (s, 2H), 4.63 (dd, *J* = 7.8, 5.4 Hz, 1H), 2.68 – 2.55 (m, 2H), 2.35 (s, 3H), 2.12 – 2.04 (m, 1H), 2.00 – 1.93 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.8, 145.8, 141.8, 137.5, 135.9, 129.4, 126.0, 121.3, 109.1, 108.3, 100.9, 73.8, 40.8, 32.0, 21.2. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{18}O_3Na$ $[M+Na]^+$: 293.1148, found: 293.1146.



20g

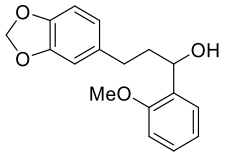
3-(benzo[d][1,3]dioxol-5-yl)-1-phenylpropan-1-ol (20g). White amorphous powder. 91 % yield (89 mg). R_f = 0.60 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 4H), 7.31 – 7.27 (m, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 1.7 Hz, 1H), 6.64 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (s, 2H), 4.67 (dd, *J* = 7.9, 5.4 Hz, 1H), 2.70 – 2.57 (m, 2H), 2.12 – 2.05 (m, 1H), 2.01 - 1.94 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.8, 145.9, 144.8, 135.8, 128.7, 127.8, 126.1, 121.3, 109.1, 108.3, 100.9, 73.9, 40.9, 32.0. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{17}O_3$ $[M+H]^+$: 257.1172, found: 257.1168.



20h

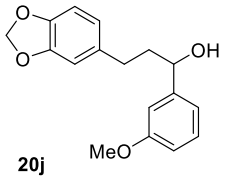
4-(3-(benzo[d][1,3]dioxol-5-yl)-1-hydroxypropyl)phenyl benzoate (20h). White amorphous powder. 42 % yield (140 mg). R_f = 0.40 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.21 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.70 (s, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 5.92 (s, 2H), 4.76 – 4.66 (m, 1H),

2.75 – 2.58 (m, 2H), 2.15 – 1.96 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ165.4, 150.4, 147.7, 145.8, 142.4, 135.6, 133.8, 130.3, 129.6, 128.7, 127.2, 121.9, 121.3, 109.0, 108.3, 100.9, 73.3, 40.9, 31.9. **HR-ESI-MS** (m/z): calculated for $C_{23}H_{20}O_5Na$ $[M+Na]^+$: 399.1203, found: 399.1198.



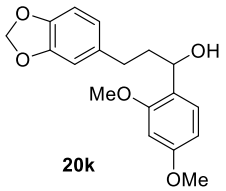
20i

3-(benzo[d][1,3]dioxol-5-yl)-1-(2-methoxyphenyl)propan-1-ol (20i). White amorphous powder. 81 % yield (625 mg). R_f = 0.50 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.6, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 2H), 6.66 (d, *J* = 7.9 Hz, 1H), 5.91 (s, 2H), 4.87 (t, *J* = 6.5 Hz, 1H), 3.85 (s, 3H), 2.75 (ddd, *J* = 15.0, 9.7, 5.8 Hz, 1H), 2.63 (q, *J* = 8.5, 6.9 Hz, 2H), 2.16 – 1.99 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7, 147.6, 145.6, 136.1, 132.4, 128.5, 127.1, 121.3, 120.9, 110.7, 109.1, 108.2, 100.8, 70.6, 55.4, 39.0, 32.2. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{18}O_4Na$ $[M+Na]^+$: 309.1097, found: 309.1091.



20j

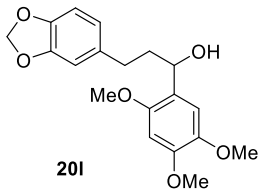
3-(benzo[d][1,3]dioxol-5-yl)-1-(3-methoxyphenyl)propan-1-ol (20j). White amorphous powder. 83% yield (648 mg). R_f = 0.50 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 1H), 6.94 – 6.90 (m, 2H), 6.82 (ddd, *J* = 8.3, 2.5, 1.1 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 1.6 Hz, 1H), 6.64 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.91 (s, 2H), 4.65 (dd, *J* = 7.9, 5.2 Hz, 1H), 3.81 (s, 3H), 2.72 – 2.52 (m, 2H), 2.11 – 1.92 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.9, 147.7, 146.4, 145.7, 135.7, 129.7, 121.3, 118.3, 113.2, 111.5, 109.0, 108.3, 100.9, 73.8, 55.4, 40.8, 31.9. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{18}O_4Na$ $[M+Na]^+$: 309.1097, found: 309.1090.



20k

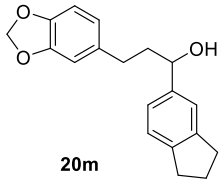
3-(benzo[d][1,3]dioxol-5-yl)-1-(2,4-dimethoxyphenyl)propan-1-ol (20k). White amorphous powder. 63 % yield (462 mg). R_f = 0.40 (petroleum ether / Acetone = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.3 Hz, 1H), 6.75 – 6.69 (m, 2H), 6.65 (d, *J* = 7.9 Hz, 1H), 6.47 (d, *J* = 7.3 Hz, 2H), 5.91 (s, 2H), 4.86 – 4.74 (m, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 2.72 (ddd, *J* = 15.0, 9.9, 5.7 Hz, 1H), 2.59 (ddd, *J* = 14.0, 9.6, 6.6

Hz, 1H), 2.18 – 1.90 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.2, 157.8, 147.6, 145.6, 136.2, 127.7, 124.9, 121.2, 109.1, 108.2, 104.2, 100.8, 98.8, 70.1, 55.5, 55.4, 39.0, 32.3. **HR-ESI-MS** (m/z): calculated for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1203, found: 339.1195.



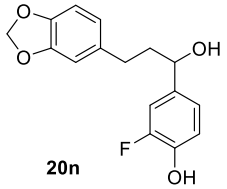
20l

3-(benzo[d][1,3]dioxol-5-yl)-1-(2,4,5-trimethoxyphenyl)propan-1-ol (20l). White amorphous powder. 53% yield (200 mg). R_f = 0.30 (petroleum ether/EtOAc = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.73 – 6.71 (m, 2H), 6.65 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.52 (s, 1H), 5.91 (s, 2H), 4.88 – 4.83 (m, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 2.76 – 2.69 (m, 1H), 2.64 – 2.56 (m, 1H), 2.13 – 1.95 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.8, 148.8, 147.6, 145.7, 143.2, 136.1, 124.0, 121.3, 111.1, 109.1, 108.2, 100.9, 97.6, 69.9, 56.7, 56.4, 56.3, 39.4, 32.2. **HR-ESI-MS** (m/z): calculated for $C_{19}H_{22}O_6Na$ $[M+Na]^+$: 369.1309, found: 369.1304.



20m

3-(benzo[d][1,3]dioxol-5-yl)-1-(2,3-dihydro-1H-inden-5-yl)propan-1-ol (20m). White amorphous powder. 57% yield (190 mg). R_f = 0.50 (petroleum ether/Acetone = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.71 – 6.69 (m, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 5.92 (s, 2H), 4.63 (dd, *J* = 7.6, 5.6 Hz, 1H), 2.90 (t, *J* = 7.4 Hz, 4H), 2.72 – 2.55 (m, 2H), 2.12 – 2.05 (m, 3H), 2.02 – 1.92 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.6, 145.7, 144.8, 143.9, 142.7, 135.9, 124.5, 124.1, 122.0, 121.3, 109.0, 108.2, 100.9, 74.0, 40.8, 32.9, 32.7, 32.0, 25.6. **HR-ESI-MS** (m/z): calculated for $C_{19}H_{20}O_3Na$ $[M+Na]^+$: 319.1305, found: 319.1314.

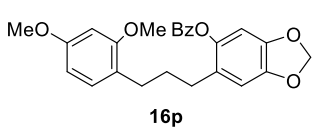


20n

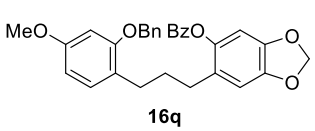
4-(3-(benzo[d][1,3]dioxol-5-yl)-1-hydroxypropyl)-2-fluorophenol (20n). White amorphous powder. 60 % yield (157 mg). R_f = 0.30 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 7.05 (m, 1H), 6.96 (d, *J* = 7.4 Hz, 2H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.67 (d, *J* = 1.6 Hz, 1H), 6.62 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.92 (s, 2H), 4.59 (dd, *J* = 7.8, 5.4 Hz, 1H), 2.69 – 2.51 (m, 2H), 2.10 – 1.98 (m, 1H), 1.95 – 1.88

(m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.3, 149.9, 147.7, 145.8, 143.0 (d, $J_{C\text{-}F}$ = 14 Hz), 137.7 (d, $J_{C\text{-}F}$ = 5 Hz), 135.5, 122.5 (d, $J_{C\text{-}F}$ = 3 Hz), 121.3, 117.3, 113.3 (d, $J_{C\text{-}F}$ = 18 Hz), 109.0, 108.3, 100.9, 73.1, 40.7, 31.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 140.1. **HR-ESI-MS** (m/z): $C_{16}H_{14}O_4F$ $[M\text{-}H]^-$: 289.0882, found: 289.0877.

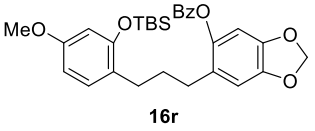
Procedure for the Preparation of Diarylpropanes B (16p – 16t)



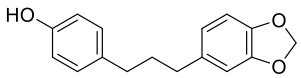
16p



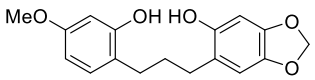
16q



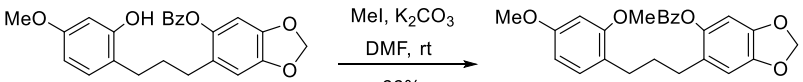
16r



16s

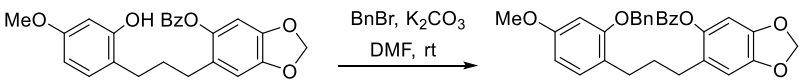


16t



16a **16p**

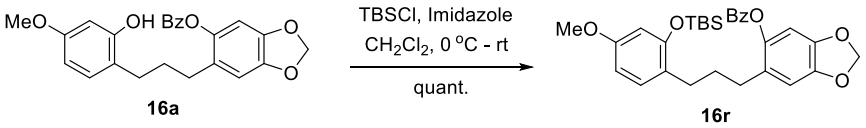
6-(3-(2,4-dimethoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (16p). To a solution of **16a** (132 mg, 0.33 mmol) in DMF (AR, 1 mL) was added MeI (25 μL, 0.4 mmol) and K_2CO_3 (69 mg, 0.5 mmol) in order at room temperature. Then the mixture was stirred for 2 h at the same temperature. The resulting mixture was quenched by added water. The resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The resulting mixture was filtered and concentrated in vacuo, and purified by silica gel flash column chromatography (petroleum ether/EtOAc = 50 : 1) to yield product **16p** (91 mg , 66%) as a colourless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 6.93 (d, J = 8.1 Hz, 1H), 6.76 (s, 1H), 6.66 (s, 1H), 6.35 (d, J = 2.4 Hz, 1H), 6.30 (dd, J = 8.2, 2.4 Hz, 1H), 5.97 (s, 2H), 3.75 (s, 3H), 3.69 (s, 3H), 2.55 – 2.48 (m, 4H), 1.85 – 1.77 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 159.2, 158.5, 146.1, 145.7, 142.8, 133.7, 130.4, 130.1, 129.7, 128.8, 127.5, 123.0, 109.3, 104.2, 103.8, 101.7, 98.6, 55.5, 55.4, 30.6, 30.1, 29.5.**HR-ESI-MS** (m/z): calculated for $C_{25}H_{25}O_6$ $[M+H]^+$: 421.1646, found: 421.1654.



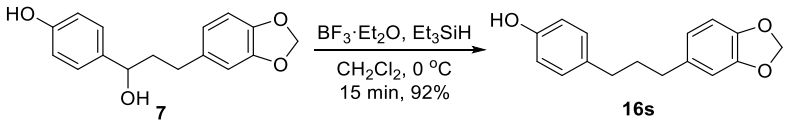
16a **16q**

6-(3-(2-(benzyloxy)-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (16q). To a solution of **16a** (100 mg, 0.25 mmol) in DMF (AR, 1 mL) was added BnBr (43.6 μL, 0.35 mmol) and K_2CO_3 (65.6 mg, 0.48 mmol) at room temperature. Then the mixture was stirred for 1 h at the same temperature. The resulting mixture was quenched by added water. The resulting mixture was extracted with EtOAc (3 ×

10 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The resulting mixture was filtered and concentrated in vacuo, and purified by silica gel flash column chromatography (petroleum ether/EtOAc = 30 : 1) to yield product **16q** (120 mg , 98%) as a colorless viscous oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.4 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.33 (m, 4H), 7.29 (t, *J* = 6.8 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.72 (s, 1H), 6.66 (s, 1H), 6.42 (d, *J* = 2.0 Hz, 1H), 6.32 (dd, *J* = 8.2, 2.2 Hz, 1H), 5.96 (s, 2H), 4.96 (s, 2H), 3.73 (s, 3H), 2.61 (t, *J* = 7.4 Hz, 2H), 2.53 – 2.47 (t, *J* = 7.4 Hz, 2H), 1.86 (p, *J* = 7.7 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.5, 159.0, 157.4, 146.1, 145.6, 142.7, 137.4, 133.6, 130.24, 130.17, 129.5, 128.7, 128.6, 127.8, 127.4, 127.1, 123.2, 109.2, 104.3, 104.1, 101.6, 99.9, 69.9, 55.4, 30.7, 30.0, 29.4. **HR-ESI-MS** (m/z): calculated for $C_{31}H_{28}O_6K$ $[M+K]^+$: 535.1517, found: 535.1520.

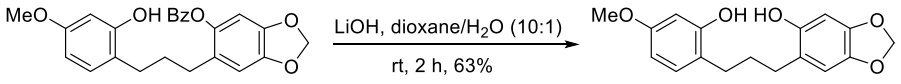


6-(3-(2-((tert-butyldimethylsilyl)oxy)-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (16r). To a solution of **16a** (100 mg, 0.26 mmol) in CH_2Cl_2 (2 mL) was added imidazole (44 mg , 0.4 mmol) and TBSCl (59 mg, 0.2 mmol) in order at 0 ^oC. Then the mixture was stirred for 5 h at the room temperature. The resulting mixture was quenched by added water at 0 ^oC. The resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The resulting mixture was filtered and concentrated in vacuo, and purified by silica gel flash column chromatography (petroleum ether/EtOAc = 15 : 1) to yield product **16r** (132 mg , quant.) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.26 (s, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.72 (s, 1H), 6.66 (s, 1H), 6.34 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.30 (d, *J* = 2.5 Hz, 1H), 5.97 (s, 2H), 3.72 (s, 3H), 2.52 – 2.45 (m, 4H), 1.81 (p, *J* = 7.8 Hz, 2H), 0.94 (s, 9H), 0.17 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 158.6, 154.3, 146.1, 145.6, 142.7, 133.7, 130.3, 129.6, 128.7, 127.3, 125.1, 109.2, 105.7, 105.5, 104.1, 101.6, 55.3, 31.0, 30.0, 29.5, 25.9, 18.3, -4.1. **HR-ESI-MS** (m/z): calculated for $C_{30}H_{37}O_6Si$ $[M+H]^+$: 521.2354, found: 521.2355.



4-(3-(benzo[d][1,3]dioxol-5-yl)propyl)phenol (16s). To a solution of **7** (150 mg, 0.55 mmol) in CH_2Cl_2 (5 mL) was added BF_3 ŁEt_2O (142 μL, 1.1 mmol) and Et_3SiH (131 μL, 0.83 mmol) at 0 ^oC. Then the mixture was stirred for 15 min at the same temperature. The resulting mixture was quenched by adding saturated $NaHCO_3$ solution at 0 ^oC. The resulting mixture was extracted with EtOAc (3 × 10 mL). The

combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The resulting mixture was filtered and concentrated in vacuo, and purified by silica gel flash column chromatography (petroleum ether/EtOAc = 6 : 1) to yield product **16s** (130 mg , 92%) as a White amorphous powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (d, J = 8.5 Hz, 2H), 6.76 (d, J = 8.5 Hz, 2H), 6.73 (d, J = 7.9 Hz, 1H), 6.68 (d, J = 1.6 Hz, 1H), 6.62 (dd, J = 7.9, 1.7 Hz, 1H), 5.92 (s, 2H), 4.75 (s, 1H), 2.58 – 2.54 (m, 4H), 1.95 – 1.80 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.7, 147.7, 145.6, 136.4, 134.6, 129.6, 121.3, 115.3, 109.0, 108.2, 100.8, 35.2, 34.5, 33.6. **HR-ESI-MS** (m/z): calculated for $C_{16}H_{17}O_3$ $[M+H]^+$: 257.1172, found: 257.1172.



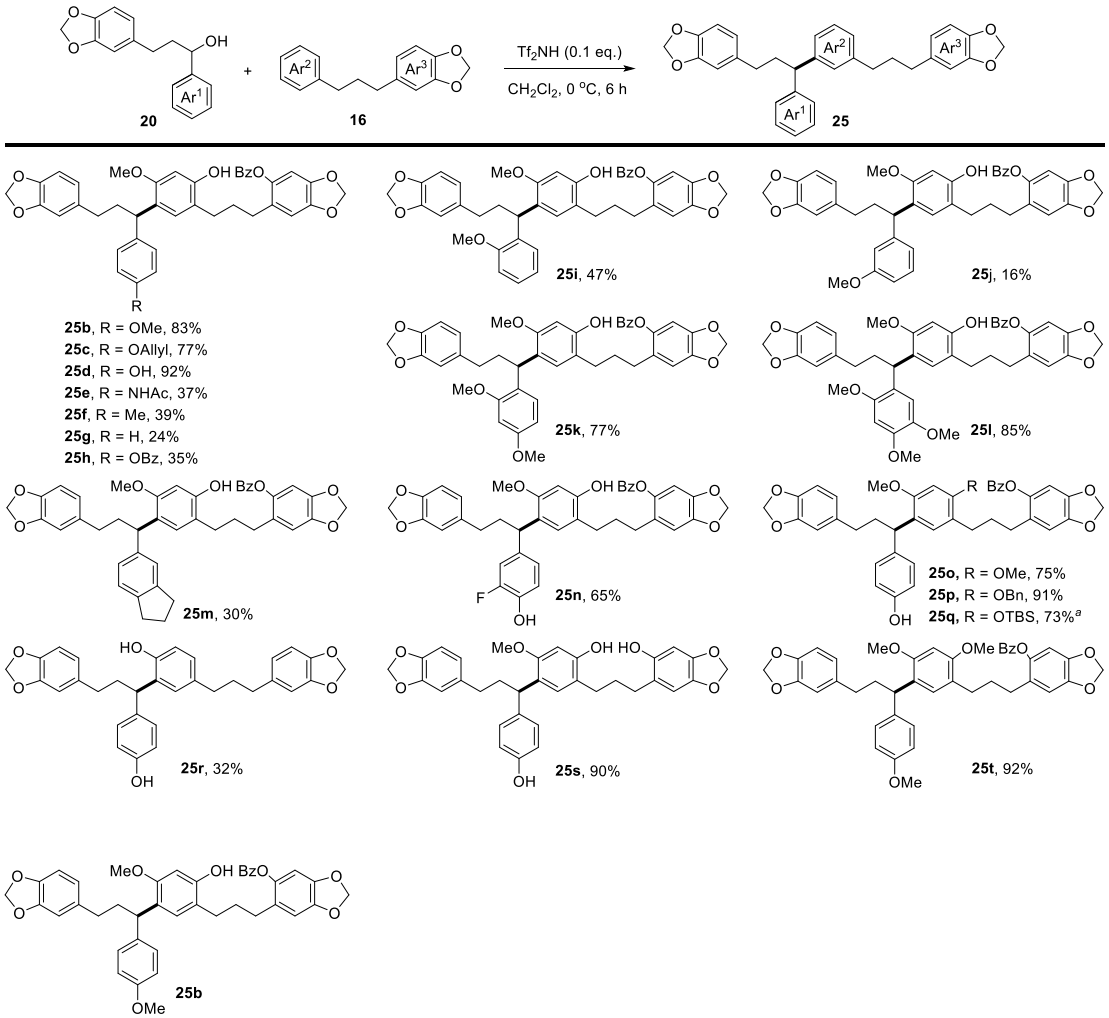
16a **16t**

6-(3-(2-hydroxy-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-ol (16t). To a solution of **16a** (406 mg, 1 mmol) in dioxane/H_2O (10:1) (5.5 mL) was added LiOH (48 mg, 2 mmol) at the room temperature. Then the mixture was stirred for 2 h at the same temperature. The resulting mixture was quenched by adding 1 N HCl to adjust PH = 7 at 0 ^{o}C. The resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The resulting mixture was filtered and concentrated in vacuo, and purified by silica gel flash column chromatography (petroleum ether/EtOAc = 4 : 1) to yield product **16t** (190 mg , 63 %.) as a White amorphous powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 (d, J = 8.3 Hz, 1H), 6.61 (s, 1H), 6.45 (dd, J = 8.4, 2.5 Hz, 1H), 6.39 (s, 1H), 6.37 (d, J = 2.5 Hz, 1H), 5.87 (s, 2H), 3.76 (s, 3H), 2.57 (dt, J = 17.9, 7.6 Hz, 4H), 1.88 (p, J = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 154.4, 147.9, 146.2, 141.6, 130.8, 120.4, 120.1, 109.4, 106.3, 102.0, 101.1, 98.4, 55.5, 30.4, 29.4, 28.9. **HR-ESI-MS** (m/z): calculated for $C_{17}H_{18}O_5Na$ $[M+Na]^+$: 325.1046, found: 325.1046.

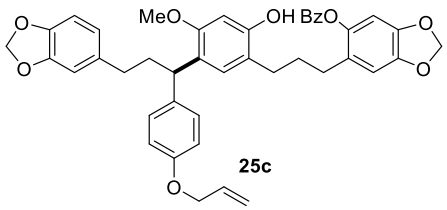
General Procedure for Brønsted Acid-catalyzed Friedel-Crafts Type non-Homodimerization

To solution of **20** (0.15 mmol, 1 eq) and **16** (0.15 mmol, 1 eq) in CH_2Cl_2 (5 mL) was added acid (0.015 mmol, 0.1 eq) dropwise at 0 ^{o}C. Then the mixture was stirred for 6 h at the same temperature. The mixture was quenched by adding saturated $NaHCO_3$ solution at 0 ^{o}C, The resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography to yield product **25**.

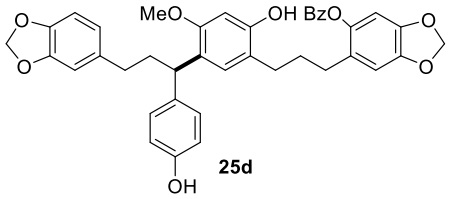
Table S1. Substrate scope of non-homodimerization



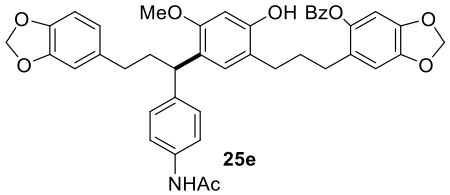
6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-methoxyphenyl)propyl)-2-hydroxy-4-m e-thoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25b): white amorphous powder. 83 % yield (84 mg). R_f = 0.50 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.17 – 7.10 (m, 2H), 6.86 (s, 1H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.73 (s, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.66 (s, 1H), 6.62 (s, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 6.22 (s, 1H), 5.96 (s, 2H), 5.90 (s, 2H), 4.79 (s, 1H), 4.17 (t, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.49 – 2.43 (m, 4H), 2.17 (q, *J* = 7.8 Hz, 2H), 1.81 (p, *J* = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 157.6, 156.2, 152.3, 147.5, 146.2, 145.7, 145.5, 142.7, 137.4, 136.6, 133.8, 130.3, 129.3, 129.0, 128.7, 126.9, 125.7, 121.2, 119.0, 113.6, 109.3, 109.1, 108.1, 104.1, 101.7, 100.8, 99.5, 55.6, 55.3, 41.7, 37.5, 34.1, 30.5, 30.1, 29.2. **HR-ESI-MS** (m/z): calculated for $C_{41}H_{37}O_9$ $[M-H]^-$: 673.2443, found: 673.2449.



6-(3-(5-(1-(4-(allyloxy)phenyl)-3-(benzo[d][1,3]dioxol-5-yl)propyl)-2-hydroxy-4-methoxyphe-nyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25c): yellow, viscous oil. 77 % yield (81 mg). R_f=0.50 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.1 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.85 (s, 1H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.73 (s, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.66 (s, 1H), 6.62 (s, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 6.22 (s, 1H), 6.10 – 6.00 (m, 1H), 5.96 (s, 2H), 5.90 (s, 2H), 5.40 (d, *J* = 17.3 Hz, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 4.49 (d, *J* = 5.3 Hz, 2H), 4.17 (t, *J* = 7.7 Hz, 1H), 3.65 (s, 3H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.49 – 2.42 (m, 4H), 2.17 (q, *J* = 7.8 Hz, 2H), 1.81 (p, *J* = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 156.7, 156.2, 152.3, 147.5, 146.2, 145.7, 145.5, 142.7, 137.6, 136.6, 133.8, 133.7, 130.2, 129.3, 129.0, 128.8, 126.9, 125.7, 121.2, 119.0, 117.6, 114.5, 109.3, 109.1, 108.1, 104.1, 101.7, 100.8, 99.5, 68.9, 55.6, 41.7, 37.5, 34.1, 30.5, 30.1, 29.2. **HR-ESI-MS** (m/z): calculated for $C_{43}H_{39}O_9$ $[M-H]^-$: 699.2600, found: 699.2608.

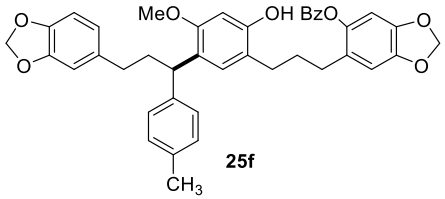


6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-hydroxyphenyl)propyl)-2-hydroxy-4-methoxyphen- yl) propyl)benzo[d][1,3]dioxol-5-yl benzoate (25d): yellow, viscous oil. 92% yield (91 mg). R_f = 0.40 (petroleum ether / Acetone = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.83 (s, 1H), 6.69 (d, *J* = 7.9 Hz, 4H), 6.65 (s, 1H), 6.61 (d, *J* = 1.2 Hz, 1H), 6.54 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.21 (s, 1H), 5.93 (s, 2H), 5.90 (s, 2H), 4.15 (t, *J* = 7.8 Hz, 1H), 3.63 (s, 3H), 2.52 (t, *J* = 7.5 Hz, 2H), 2.48 – 2.42 (m, 4H), 2.18 – 2.13 (m, 2H), 1.80 (p, *J* = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 156.2, 153.6, 152.3, 147.5, 146.2, 145.7, 145.5, 142.7, 137.5, 136.6, 133.8, 130.3, 129.3, 129.2, 128.8, 126.9, 125.8, 121.2, 119.0, 115.1, 109.3, 109.1, 108.1, 104.1, 101.7, 100.8, 99.6, 55.6, 41.7, 37.4, 34.1, 30.5, 30.0, 29.2. **HR-ESI-MS** (m/z): calculated for $C_{40}H_{40}O_9N$ $[M+NH_4]^+$: 678.2698, found: 678.2703.



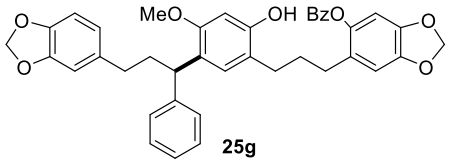
6-(3-(5-(1-(4-acetamidophenyl)-3-(benzo[d][1,3]dioxol-5-yl)propyl)-2-hydroxy-4-

methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25e): white amorphous powder. 37 % yield (39 mg). R_f=0.30 (DCM / EtOAc = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.22 (s, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.82 (s, 1H), 6.69 (d, *J* = 8.1 Hz, 2H), 6.65 (s, 1H), 6.60 (s, 1H), 6.53 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.21 (s, 1H), 5.94 (s, 2H), 5.89 (s, 2H), 4.16 (t, *J* = 7.8 Hz, 1H), 3.58 (s, 3H), 2.53 – 2.41 (m, 6H), 2.19 – 2.14 (m, 2H), 2.12 (s, 3H), 1.80 (p, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.6, 165.9, 156.2, 152.7, 147.5, 146.2, 145.6, 142.7, 141.6, 136.5, 135.5, 133.8, 130.2, 129.4, 128.8, 128.6, 127.0, 125.0, 121.2, 120.0, 119.1, 109.3, 109.1, 108.2, 104.1, 101.7, 100.8, 99.5, 55.5, 42.0, 37.1, 34.1, 30.5, 30.1, 29.3, 24.6. **HR-ESI-MS** (m/z): calculated for $C_{42}H_{40}O_9N$ $[M+H]^+$: 702.2698, found: 702.2691.



25f

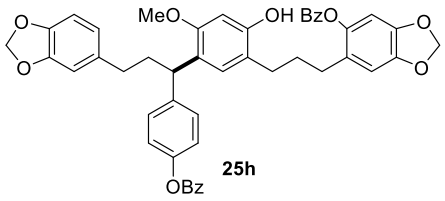
6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(p-tolyl)propyl)-2-hydroxy-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25f): colorless, viscous oil. 39 % yield (39 mg). R_f=0.30 (petroleum ether/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.1 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.87 (s, 1H), 6.72 (s, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 6.66 (s, 1H), 6.61 (d, *J* = 1.4 Hz, 1H), 6.55 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.22 (s, 1H), 5.97 (s, 2H), 5.90 (s, 2H), 4.19 (t, *J* = 7.6 Hz, 1H), 3.66 (s, 3H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.48 – 2.42 (m, 4H), 2.28 (s, 3H), 2.21 – 2.15 (m, 2H), 1.81 (p, *J* = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 156.2, 152.3, 147.5, 146.3, 145.7, 145.5, 142.8, 142.2, 136.6, 135.2, 133.8, 130.3, 129.4, 129.0, 128.8, 128.8, 128.0, 126.9, 125.6, 121.2, 118.9, 109.3, 109.1, 108.1, 104.2, 101.7, 100.8, 99.5, 55.6, 42.0, 37.4, 34.2, 30.5, 30.1, 29.2, 21.1. **HR-ESI-MS** (m/z): calculated for $C_{41}H_{37}O_8$ $[M-H]^-$: 657.2494, found: 657.2490.



25g

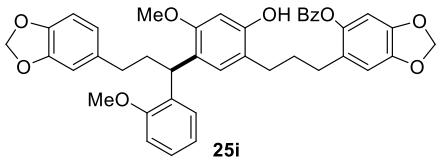
6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-phenylpropyl)-2-hydroxy-4-methoxyphenyl)propyl) benzo[d][1,3]dioxol-5-yl benzoate (25g): white amorphous powder. 24 % yield (23 mg). R_f=0.50 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.17 (m, 5H), 6.87 (s, 1H), 6.72 (s, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 6.65 (s, 1H), 6.61 (s, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 6.22 (s, 1H), 5.97 (s, 2H), 5.90 (s, 2H), 4.21 (t, *J* = 7.7 Hz, 1H), 3.66 (s, 3H), 2.53 (t, *J* = 7.5 Hz, 2H), 2.47 – 2.42 (m, 4H), 2.20 (q, *J* = 7.8 Hz, 2H), 1.80 (p, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 156.3, 152.4, 147.5, 146.3, 145.7, 145.5, 145.3, 142.8, 136.5, 133.8, 130.3, 129.3, 128.9, 128.8,

128.3, 128.2, 126.9, 125.8, 125.4, 121.2, 118.9, 109.4, 109.1, 108.2, 104.2, 101.7, 100.8, 99.5, 55.6, 42.5, 37.3, 34.1, 30.5, 30.1, 29.2. **HR-ESI-MS** (m/z): calculated for $C_{40}H_{35}O_8$ [M-H]$^-$: 643.2337, found: 643.2336.



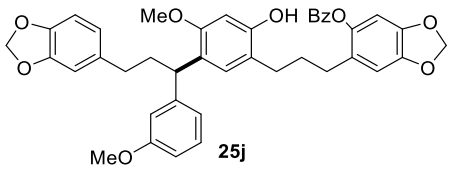
25h

6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-(benzoyloxy)phenyl)propyl)-2-hydroxy-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25h): white amorphous powder. 35 % yield (40 mg). R_f=0.30 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 – 8.13 (m, 4H), 7.64 – 7.60 (m, 2H), 7.52 – 7.45 (m, 4H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.88 (s, 1H), 6.74 (s, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.65 (s, 1H), 6.62 (s, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 6.23 (s, 1H), 5.96 (s, 2H), 5.91 (s, 2H), 4.23 (t, *J* = 7.7 Hz, 1H), 3.66 (s, 3H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.49 – 2.44 (m, 4H), 2.21 (q, *J* = 7.8 Hz, 2H), 1.82 (p, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 165.4, 156.3, 152.5, 148.9, 147.6, 146.3, 145.7, 145.6, 143.0, 142.8, 136.4, 133.8, 133.6, 130.3, 129.8, 129.4, 129.1, 128.8, 128.7, 126.9, 125.0, 121.3, 119.0, 109.4, 109.1, 108.2, 104.2, 101.7, 100.8, 99.5, 55.6, 42.0, 37.3, 34.1, 30.5, 30.1, 29.2. **HR-ESI-MS** (m/z): calculated for $C_{47}H_{39}O_{10}$ [M-H]$^-$: 763.2549, found: 763.2553.



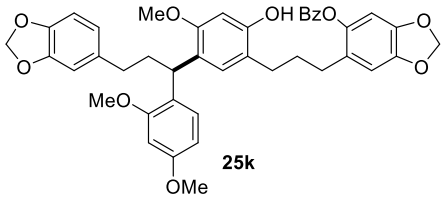
25i

6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(2-methoxyphenyl)propyl)-2-hydroxy-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25i): white amorphous powder. 47% yield (47 mg). R_f=0.30 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.16 – 7.12 (m, 2H), 6.88 (s, 1H), 6.86 (d, *J* = 6.9 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.72 (s, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.66 (s, 1H), 6.63 (s, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.21 (s, 1H), 5.97 (s, 2H), 5.89 (s, 2H), 4.59 (d, *J* = 7.7 Hz, 1H), 3.75 (s, 3H), 3.64 (s, 3H), 2.53 (t, *J* = 7.7 Hz, 2H), 2.48 – 2.44 (m, 4H), 2.20 – 2.13 (m, 2H), 1.81 (p, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 157.5, 156.7, 152.2, 147.4, 146.2, 145.7, 145.4, 142.7, 137.0, 133.8, 133.5, 130.3, 129.8, 129.3, 128.8, 128.4, 126.9, 126.8, 124.9, 121.2, 120.4, 118.5, 110.9, 109.3, 109.1, 108.1, 104.1, 101.7, 100.7, 99.6, 55.8, 55.7, 36.6, 36.5, 34.3, 30.6, 30.0, 29.2. **HR-ESI-MS** (m/z): calculated for $C_{41}H_{42}O_9N$ [M+NH_4]$^+$: 692.2854, found: 692.2849.



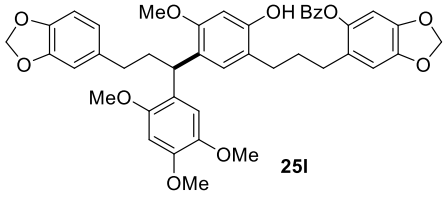
25j

6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(3-methoxyphenyl)propyl)-2-hydroxy-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25j): white amorphous powder. 16% yield (16 mg). R_f=0.40 (petroleum ether/Acetone = 2:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 6.7 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.9 Hz, 1H), 6.87 (s, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.79 (t, *J* = 2.1 Hz, 1H), 6.72 (s, 1H), 6.70 – 6.67 (m, 2H), 6.66 (s, 1H), 6.61 (d, *J* = 1.6 Hz, 1H), 6.54 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.22 (s, 1H), 5.97 (s, 2H), 5.90 (s, 2H), 4.20 (t, *J* = 7.7 Hz, 1H), 3.75 (s, 3H), 3.66 (s, 3H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.48 – 2.43 (m, 4H), 2.21 – 2.16 (m, 2H), 1.81 (p, *J* = 7.7 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.8, 159.7, 156.5, 152.5, 147.7, 147.2, 146.4, 145.8, 145.7, 143.0, 136.6, 133.7, 130.3, 129.6, 129.2, 129.1, 128.8, 127.0, 125.5, 121.3, 120.7, 119.2, 114.5, 111.0, 109.3, 109.1, 108.2, 104.2, 101.7, 100.8, 99.8, 55.7, 55.3, 42.7, 37.3, 34.2, 30.6, 30.1, 29.3. **HR-ESI-MS** (m/z): calculated for $C_{41}H_{42}O_9N$ $[M+NH_4]^+$: 692.2854, found: 692.2847.



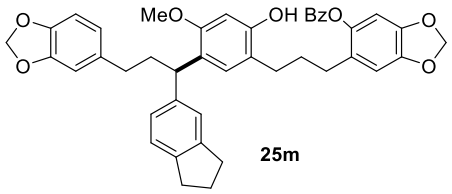
25k

6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(2,4-dimethoxyphenyl)propyl)-2-hydroxy-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25k): white amorphous powder. 77% yield (82 mg). R_f=0.30 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.13 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 9.1 Hz, 1H), 6.86 (s, 1H), 6.73 (s, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 6.66 (s, 1H), 6.63 (d, *J* = 1.6 Hz, 1H), 6.56 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.42 (s, 1H), 6.41 (d, *J* = 3.1 Hz, 1H), 6.21 (s, 1H), 5.97 (s, 2H), 5.89 (s, 2H), 4.73 (s, 1H), 4.50 (t, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.64 (s, 3H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.50 – 2.38 (m, 4H), 2.13 (dtd, *J* = 14.1, 7.5, 6.5, 3.7 Hz, 2H), 1.81 (p, *J* = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 165.9, 158.8, 158.3, 156.5, 152.1, 147.4, 146.2, 145.6, 145.4, 142.7, 137.0, 133.8, 130.2, 129.7, 129.3, 128.8, 127.0, 125.9, 125.2, 121.1, 118.5, 109.3, 109.1, 108.1, 104.1, 103.9, 101.7, 100.7, 99.6, 98.8, 55.8, 55.6, 55.4, 36.7, 36.0, 34.3, 30.6, 30.0, 29.2. **HR-ESI-MS** (m/z): calculated for $C_{42}H_{44}O_{10}N$ $[M+ NH_4]^+$: 722.2960, found: 722.2956.



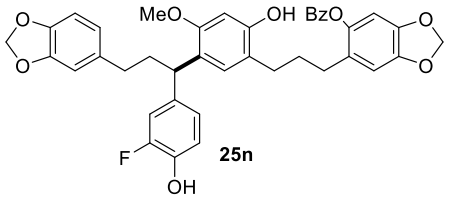
25l

6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(2,4,5-trimethoxyphenyl)propyl)-2-hydrox y-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25l): white amorphous powder. 85% yield (94 mg). R_f=0.30 (petroleum ether / Acetonie = 1.5 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.8 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 6.89 (s, 1H), 6.75 (s, 1H), 6.72 (s, 1H), 6.69 (d, J = 7.9 Hz, 1H), 6.65 (s, 1H), 6.63 (s, 1H), 6.55 (d, J = 7.9 Hz, 1H), 6.48 (s, 1H), 6.21 (s, 1H), 5.96 (s, 2H), 5.89 (s, 2H), 4.50 (t, J = 7.7 Hz, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 3.64 (s, 3H), 2.53 (t, J = 7.6 Hz, 2H), 2.58 – 2.43 (m, 4H), 2.15 (q, J = 8.0 Hz, 2H), 1.80 (p, J = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 156.5, 152.3, 151.7, 147.6, 147.5, 146.2, 145.7, 145.4, 142.9, 142.7, 136.9, 133.8, 130.2, 129.7, 129.3, 128.7, 126.9, 125.3, 125.0, 121.2, 118.6, 113.0, 109.3, 109.1, 108.1, 104.1, 101.7, 100.8, 99.6, 98.5, 57.1, 56.8, 56.2, 55.7, 36.7, 36.7, 34.3, 30.7, 30.0, 29.2. **HR-ESI-MS** (m/z): calculated for $C_{43}H_{46}O_{11}N$ $[M+ NH_4]^+$: 752.3065, found: 752.3056.



25m

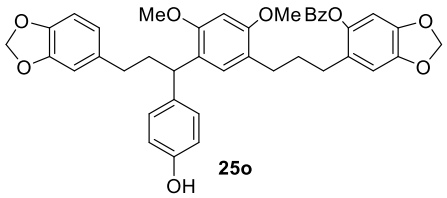
6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(2,3-dihydro-1H-inden-5-yl)propyl)-2-hyd roxy-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25m): Colourless, viscous oil. 30% (31 mg). R_f = 0.30 (petroleum ether/EtOAc = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, J = 7.8 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 7.8 Hz, 1H), 6.89 (s, 1H), 6.73 (s, 1H), 6.69 (d, J = 7.9 Hz, 1H), 6.66 (s, 1H), 6.61 (d, J = 1.6 Hz, 1H), 6.55 (dd, J = 7.9, 1.7 Hz, 1H), 6.22 (s, 1H), 5.97 (s, 2H), 5.90 (s, 2H), 4.21 (t, J = 7.8 Hz, 1H), 3.68 (s, 3H), 2.83 (t, J = 7.4 Hz, 4H), 2.54 (t, J = 7.5 Hz, 2H), 2.49 – 2.42 (m, 4H), 2.18 (q, J = 7.8 Hz, 2H), 2.01 (p, J = 7.4 Hz, 2H), 1.81 (p, J = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) 165.9, 156.3, 152.3, 147.5, 146.3, 145.7, 145.5, 144.2, 143.2, 142.8, 141.7, 136.7, 133.8, 130.3, 129.4, 128.9, 128.8, 126.9, 125.9, 125.7, 124.0, 121.2, 118.9, 109.3, 109.1, 108.1, 104.2, 101.7, 100.8, 99.5, 55.7, 42.2, 37.7, 34.2, 33.0, 32.6, 30.5, 30.1, 29.2, 25.6. **HR-ESI-MS** (m/z): calculated for $C_{43}H_{44}O_8N$ $[M+NH_4]^+$: 702.3061, found: 702.3054.



25n

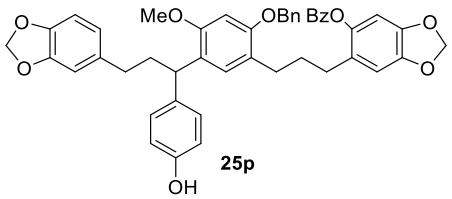
6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(3-fluoro-4-hydroxyphenyl)propyl)-2-hydr oxy-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25n): white amorphous powder. 65% (66 mg). R_f=0.40 (petroleum ether/Acetone = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.10 (m, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 6.91 (d, J = 12.6 Hz, 1H), 6.86 (s, 1H), 6.85 (d, J = 7.6, 1H), 6.82 (s, 1H),

6.72 (s, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.66 (s, 1H), 6.60 (s, 1H), 6.54 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.23 (s, 1H), 5.95 (s, 2H), 5.90 (s, 2H), 4.12 (t, *J* = 7.8 Hz, 1H), 3.65 (s, 3H), 2.56 – 2.52 (t, *J* = 7.5 Hz, 2H), 2.49 – 2.41 (m, 4H), 2.18 – 2.11 (m, 2H), 1.81 (p, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 165.9, 156.2, 152.6, 152.0, 149.7, 147.6, 146.3, 145.6 (d, J_{C-F} = 8 Hz), 142.7, 141.3 (d, J_{C-F} = 14 Hz), 138.6 (d, J_{C-F} = 5 Hz), 136.3, 133.8, 130.3, 129.3, 128.8, 128.7, 126.8, 125.0, 124.2 (d, J_{C-F} = 3 Hz), 121.2, 119.1, 116.8, 115.1 (d, J_{C-F} = 17 Hz), 109.3, 109.0, 108.2, 104.1, 101.7, 100.8, 99.6, 55.6, 41.7, 37.2, 34.0, 30.5, 30.1, 29.2; **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* -141.0. **HR-ESI-MS** (m/z): calculated for $C_{40}H_{39}O_9NF$ $[M+NH_4]^+$: 696.2603, found: 696.2595.



25o

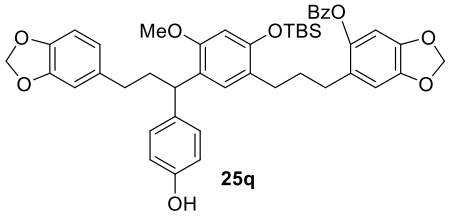
6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-hydroxyphenyl)propyl)-2,4-dimethoxyp heny- l)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25o): white amorphous powder. 75% (76 mg). R_f=0.40 (petroleum ether/Acetone = 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.13 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.57 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.89 (s, 1H), 6.73 – 6.69 (m, 4H), 6.67 (s, 1H), 6.63 (s, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 5.96 (s, 2H), 5.90 (s, 2H), 4.18 (t, *J* = 7.8 Hz, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 2.59 – 2.39 (m, 6H), 2.18 (q, *J* = 7.8 Hz, 2H), 1.79 (p, *J* = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 165.5, 156.3, 156.1, 153.6, 147.5, 146.0, 145.5, 145.5, 142.7, 137.6, 136.6, 133.6, 130.2, 129.5, 129.2, 128.7, 128.6, 127.4, 125.0, 122.1, 121.2, 115.1, 109.3, 109.1, 108.1, 104.1, 101.6, 100.8, 95.6, 55.9, 55.5, 41.6, 37.4, 34.1, 30.8, 30.1, 29.7. **HR-ESI-MS** (m/z): calculated for $C_{41}H_{42}O_9N$ $[M+NH_4]^+$: 692.2854, found: 692.2851.



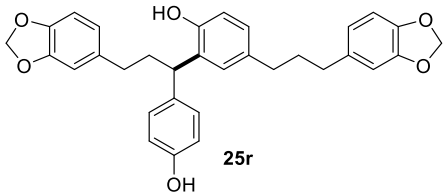
25p

6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-hydroxyphenyl)propyl)-2-(benzyloxy)-4 -methoxy-phenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25p): yellow, viscous oil. 91 % yield (103 mg). R_f = 0.50 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.28 (m, 5H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.91 (s, 1H), 6.74 – 6.67 (m, 4H), 6.65 (s, 1H), 6.62 (d, *J* = 1.6 Hz, 1H), 6.55 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.35 (s, 1H), 5.95 (s, 2H), 5.90 (s, 2H), 4.95 (s, 2H), 4.18 (t, *J* = 7.8 Hz, 1H), 3.67 (s, 3H), 2.59 (t, *J* = 7.5 Hz, 2H), 2.51 – 2.42 (m, 4H), 2.17 (q, *J* = 7.9 Hz, 2H), 1.83 (p, *J* = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 156.0, 155.5, 153.6, 147.5, 146.1, 145.6, 145.5, 142.7, 137.6, 136.6, 133.6, 130.2, 129.5, 129.2, 128.8, 128.7, 128.6, 127.8, 127.4,

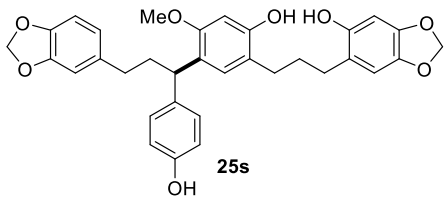
127.1, 125.5, 122.5, 121.2, 115.1, 109.3, 109.1, 108.2, 104.1, 101.6, 100.8, 97.1, 70.3, 55.8, 41.7, 37.4, 34.1, 30.9, 30.1, 29.8. **HR-ESI-MS** (m/z): calculated for $C_{47}H_{43}O_9$ $[M+H]^+$: 751.2902, found: 751.2899.



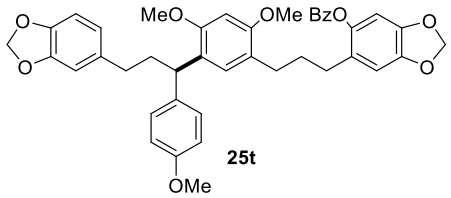
6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-hydroxyphenyl)propyl)-2-((tert-butyldim-ethyllsilyl)oxy)-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25q): yellow, viscous oil. 73 % yield (85 mg). R_f = 0.30 (petroleum ether / EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.86 (s, 1H), 6.72 (s, 1H), 6.70 (d, *J* = 2.6 Hz, 1H), 6.69 (s, 2H), 6.66 (s, 1H), 6.61 (s, 1H), 6.55 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.22 (s, 1H), 5.96 (s, 2H), 5.90 (s, 2H), 4.15 (t, *J* = 7.8 Hz, 1H), 3.66 (s, 3H), 2.50 – 2.42 (m, 6H), 2.19 – 2.13 (m, 2H), 1.78 (p, *J* = 7.8 Hz, 2H), 0.93 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 155.7, 153.6, 152.1, 147.5, 146.1, 145.6, 145.5, 142.7, 137.6, 136.6, 133.6, 130.2, 129.5, 129.3, 128.7, 128.7, 127.3, 126.0, 124.0, 121.2, 115.1, 109.3, 109.1, 108.1, 104.1, 102.6, 101.6, 100.8, 55.6, 41.8, 37.5, 34.1, 31.2, 30.2, 29.8, 25.8, 18.3, -4.0. **HR-ESI-MS** (m/z): calculated for $C_{46}H_{50}O_9SiNa$ $[M+Na]^+$: 797.3116, found: 797.3115.



2-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-hydroxyphenyl)propyl)-4-(3-(benzo[d][1,3]dioxol-5-yl)propyl)phenol (25r) : white amorphous powder. 32% yield (25 mg). R_f=0.30 (petroleum ether/EtOAc = 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 7.4 Hz, 2H), 7.04 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.77 – 6.71 (m, 4H), 6.66 (d, *J* = 8.2 Hz, 3H), 6.61 (d, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H, 5.92 (s, 4H), 4.10 (t, *J* = 7.7 Hz, 1H), 2.58 – 2.49 (m, 6H), 2.36 – 2.18 (m, 2H), 1.87 (p, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 151.5, 147.6, 147.6, 145.7, 145.6, 136.4, 136.2, 136.2, 134.7, 130.9, 129.3, 128.0, 127.3, 121.3, 121.3, 116.1, 115.6, 109.0, 108.3, 108.2, 100.9, 100.8, 43.0, 37.0, 35.2, 34.8, 33.9, 33.7; **HR-ESI-MS** (m/z): calculated for $C_{32}H_{34}O_6N$ $[M+NH_4]^+$: 528.2381, found: 528.2374.

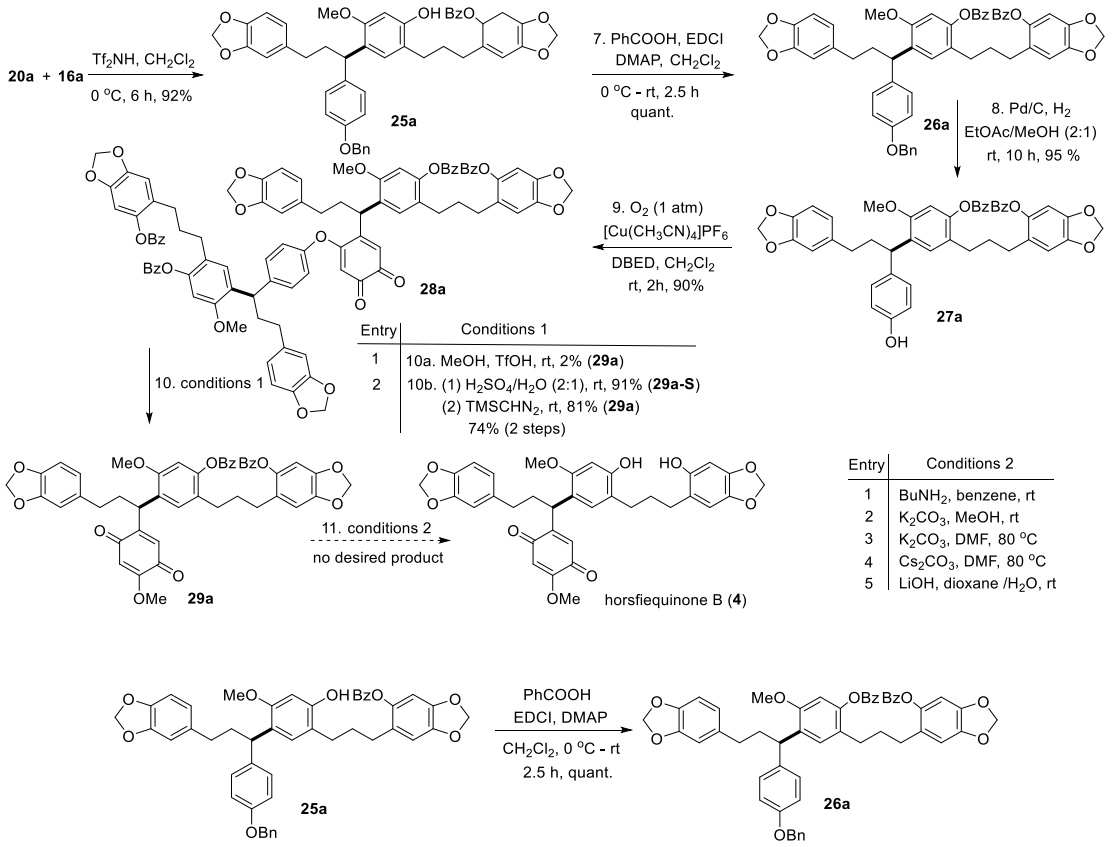


4-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-hydroxy-5-(3-(6-hydroxybenzo[d][1,3]dioxol-5-yl)propyl)-2-methoxyphenyl)propyl)phenyl benzoate (25s): white amorphous powder. 90% (76 mg). R_f=0.50 (petroleum ether/EtOAc = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.4 Hz, 2H), 7.06 (s, 1H), 6.73 – 6.65 (m, 4H), 6.62 (s, 1H), 6.59 (d, J = 7.9 Hz, 1H), 6.44 (d, J = 3.3 Hz, 2H), 5.92 (s, 2H), 5.83 (s, 2H), 4.18 (t, J = 7.8 Hz, 1H), 3.67 (s, 3H), 2.66 – 2.57 (m, 4H), 2.45 (t, J = 7.7 Hz, 2H), 2.27 – 2.16 (m, 2H), 1.85 (p, J = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7, 156.1, 154.5, 150.1, 148.4, 146.6, 146.4, 141.2, 137.4, 137.4, 129.7, 129.5, 125.0, 122.0, 121.5, 120.9, 115.6, 110.1, 109.6, 108.7, 101.6, 101.4, 99.9, 98.4, 55.7, 42.2, 38.5, 34.8, 31.5, 30.5, 30.1. **HR-ESI-MS** (m/z): calculated for $C_{33}H_{36}O_8N$ $[M+NH_4]^+$: 574.2435, found: 574.2433.

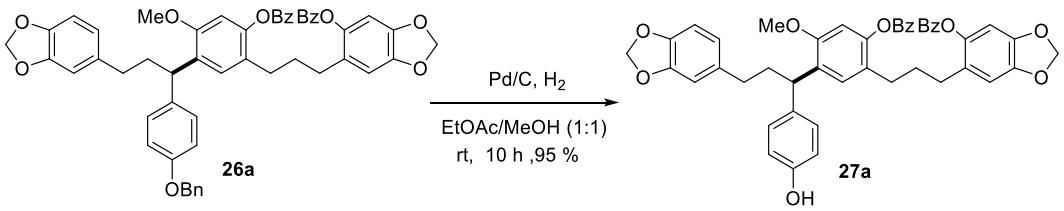


6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-methoxyphenyl)propyl)-2,4-dimethoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl benzoate (25t): yellow, viscous oil. 92 % yield (95 mg). R_f=0.50 (petroleum ether / DCM / EtOAc = 3 : 1: 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.10 (m, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.90 (s, 1H), 6.79 (d, J = 8.6 Hz, 2H), 6.75 (s, 1H), 6.70 (d, J = 7.9 Hz, 1H), 6.67 (s, 1H), 6.62 (d, J = 1.6 Hz, 1H), 6.55 (dd, J = 7.9, 1.7 Hz, 1H), 6.30 (s, 1H), 5.97 (s, 2H), 5.90 (s, 2H), 4.19 (t, J = 7.8 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.69 (s, 3H), 2.51 (td, J = 9.4, 8.3, 5.7 Hz, 4H), 2.45 (dd, J = 9.4, 6.2 Hz, 2H), 2.18 (q, J = 7.8 Hz, 2H), 1.79 (p, J = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 157.6, 156.3, 156.1, 147.5, 146.0, 145.5, 145.5, 142.7, 137.5, 136.6, 133.6, 130.2, 129.5, 129.0, 128.7, 128.6, 127.4, 125.0, 122.1, 121.2, 113.6, 109.2, 109.1, 108.1, 104.1, 101.6, 100.8, 95.6, 55.9, 55.4, 55.3, 41.6, 37.5, 34.2, 30.8, 30.2, 29.8. **HR-ESI-MS** (m/z): calculated for $C_{42}H_{40}O_9Na$ $[M+Na]^+$: 711.2565, found: 711.2565.

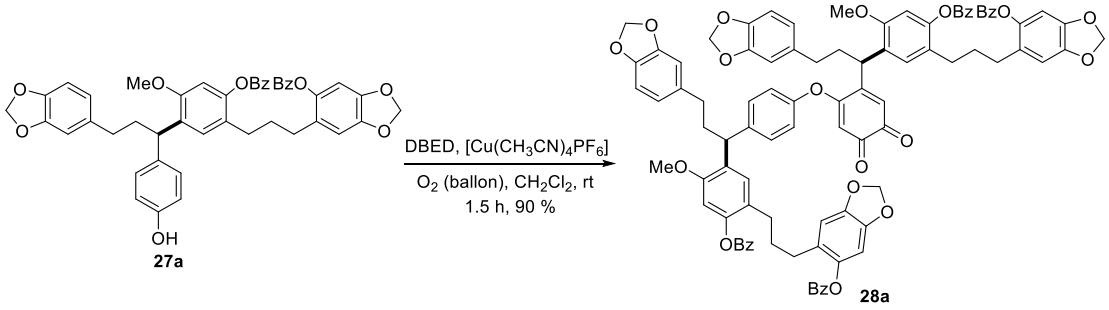
Scheme S2. Synthesis of benzoylhorsfiequinone B (**29a**)



4-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-(benzyloxy)phenyl)propyl)-2-(3-(6-(benzoyloxy)benzo[d][1,3]dioxol-5-yl)propyl)-5-methoxyphenyl benzoate (26a). To solution of **25a** (1.14 g, 1.52 mmol, 1 eq.) and benzoic acid (298 mg, 2.44 mmol, 1.6 eq.) in CH_2Cl_2 (5 mL) were added EDCI (584 mg, 3.04 mmol, 2 eq.) and DMAP (298 mg, 2.44 mmol, 1.6 eq.) at 0 ^oC. Then the mixture was stirred for 2.5 h at room temperature. The resulting mixture was diluted with water and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 6 : 1) to yield product **26a** (1.42 g, quant.) as a yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.3 Hz, 2H), 8.06 (d, *J* = 7.3 Hz, 2H), 7.65 – 7.55 (m, 2H), 7.50 – 7.35 (m, 8H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.05 (s, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.65 – 6.64 (m, 2H), 6.59 - 6.55 (m, 3H), 5.92 (s, 4H), 5.03 (s, 2H), 4.26 (t, *J* = 7.7 Hz, 1H), 3.71 (s, 3H), 2.50 – 2.44 (m, 6H), 2.26 – 2.20 (m, 2H), 1.82 (p, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 165.2, 157.1, 155.8, 147.7, 147.6, 146.1, 145.6, 145.5, 142.6, 137.4, 136.9, 136.4, 133.6, 131.4, 130.2, 129.5, 129.4, 129.2, 128.8, 128.7, 128.7, 128.0, 127.7, 126.8, 125.2, 121.3, 114.7, 109.2, 109.1, 108.2, 105.4, 104.1, 101.6, 100.8, 70.1, 55.7, 42.0, 37.3, 34.1, 31.1, 29.9, 29.5. **HR-ESI-MS** (m/z): calculated for $C_{54}H_{50}O_{10}N$ $[M+NH_4]^+$: 872.3429, found: 872.3424.

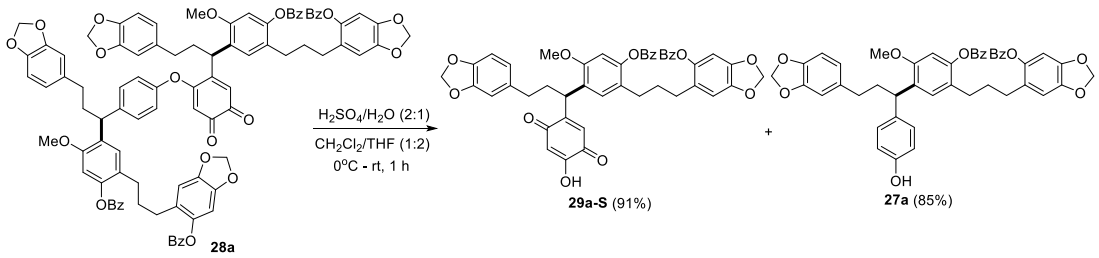


4-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-hydroxyphenyl)propyl)-2-(3-(6-(benzoyloxy)benzo[d][1,3]dioxol-5-yl)propyl)-5-methoxyphenyl benzoate (27a). To a solution of **26a** (1.40 g, 1.64 mmol) in EtOAc : MeOH (1:1, 10 mL) was added Pd/C (140 mg, 10% wt). Then the mixture was connected to a H_2 balloon and stirred for 10 h at room temperature. After consumption of the starting material, the mixture was filtered through a short pad of celite, and the filter cake was washed with ethyl acetate, the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 3 : 1) to yield product **27a** (1.19 g, 95 %) as a white amorphous powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.2 Hz, 2H), 8.05 (d, *J* = 8.2 Hz, 2H), 7.64 – 7.56 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.02 (s, 1H), 6.73 – 6.70 (m, 3H), 6.63 (d, *J* = 6.8 Hz, 2H), 6.57 – 6.54 (t, *J* = 5.8 Hz, 3H), 5.91 (s, 4H), 4.23 (t, *J* = 7.7 Hz, 1H), 3.70 (s, 3H), 2.49 – 2.42 (m, 6H), 2.23 – 2.18 (m, 2H), 1.81 (p, *J* = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 165.3, 155.8, 153.8, 147.6, 147.5, 146.1, 145.6, 145.5, 142.6, 136.6, 136.4, 133.6, 131.5, 130.2, 129.5, 129.4, 129.3, 128.9, 128.7, 126.8, 125.2, 121.3, 115.2, 109.3, 109.1, 108.2, 105.4, 104.0, 101.6, 100.8, 55.7, 42.0, 37.2, 34.1, 31.1, 29.9, 29.5. **HR-ESI-MS** (m/z): calculated for $C_{47}H_{44}O_{10}N$ $[M+NH_4]^+$: 782.2960, found: 782.2955.

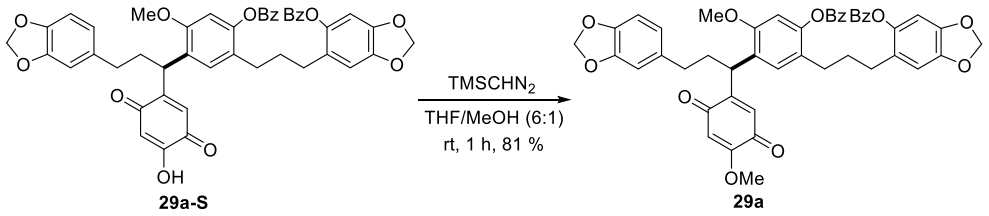


4-(-3-(benzo[d][1,3]dioxol-5-yl)-1-(4-((6-(-3-(benzo[d][1,3]dioxol-5-yl)-1-(4-(benzoyloxy)-5-(3-(6-(benzoyloxy)benzo[d][1,3]dioxol-5-yl)propyl)-2-methoxyphenyl)propyl)-3,4-dioxocyclohexa-1,5-dien-1-yl)oxy)phenyl)propyl)-2-(3-(6-(benzoyloxy)benzo[d][1,3]dioxol-5-yl)propyl)-5-methoxyphenyl benzoate. (28a). To solution of $[Cu(CH_3CN)PF_6]$ (7.5 mg, 0.02 mmol, 10 mol %) and DBED (5 µL, 0.024 mmol, 12 mol %) in DCM (1 mL) under Ar atmosphere, the resulting catalyst system (pink solution) was stirred for 15 min at room temperature, after which time a solution of phenol **27a** (153 mg, 0.20 mmol) in DCM (1 mL) was added to the aforementioned catalyst system solution and stirred for 1 min at room temperature, then the resulting solution was vented three times to remove Ar under a O_2 balloon and a dramatic color change was observed, resulting in a blackish/brown reaction mixture, and stirred for

1.5 h. Then the mixture was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 2.5 : 1) to yield product **28a** (138 mg, 90%) as a orange amorphous powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 8H), 7.64 – 7.56 (m, 4H), 7.50 – 7.39 (m, 8H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 3.2 Hz, 1H), 7.05 (s, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.73 – 6.68 (m, 2H), 6.65 – 6.62 (m, 5H), 6.59 – 6.54 (m, 5H), 6.28 (s, 1H), 5.92 (s, 2H), 5.90 (s, 4H), 5.86 (s, 1H), 5.82 (d, *J* = 4.2 Hz, 1H), 5.46 (s, 1H), 4.58 (t, *J* = 7.1 Hz, 1H), 4.29 (t, *J* = 7.6 Hz, 1H), 3.70 (s, 6H), 2.65 – 2.56 (m, 2H), 2.51 – 2.44 (m, 10H), 2.28 – 2.17 (m, 4H), 1.88 – 1.78 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.6, 179.0, 169.2, 165.4, 165.2, 165.1, 156.1, 155.9, 155.3, 150.2, 148.8, 148.0, 147.7, 147.6, 146.2, 146.1, 145.9, 145.7, 145.5, 143.63, 143.60, 142.6, 135.9, 135.3, 133.8, 133.7, 133.6, 130.2, 130.0, 129.4, 129.3, 129.2, 128.8, 128.72, 128.68, 127.2, 126.7, 126.5, 126.4, 125.9, 125.5, 121.28, 121.25, 120.6, 109.2, 109.1, 109.0, 108.9, 108.3, 108.2, 106.1, 106.0, 105.6, 104.0, 101.6, 100.91, 100.86, 55.9, 55.7, 42.3, 37.6, 37.0, 35.3, 33.9, 33.7, 31.1, 29.95, 29.90, 29.6, 29.5. **HR-ESI-MS** (m/z): calculated for $C_{95}H_{77}O_{23}$ $[M+HCOO]^-$: 1585.4861, found: 1585.4860.

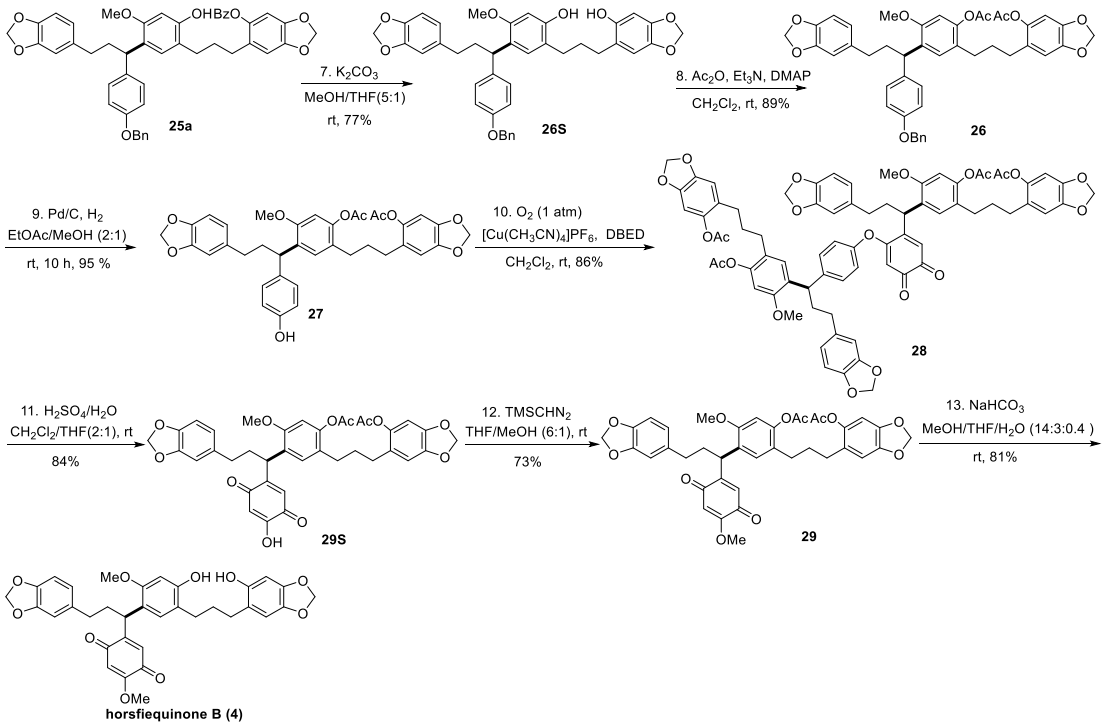


4-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-hydroxy-3,6-dioxocyclohexa-1,4-dien-1-yl)propyl)-2-(3-(6-(benzoyloxy)benzo[d][1,3]dioxol-5-yl)propyl)-5-methoxyphenyl benzoate (29a-S). To a solution of **28a** (100 mg, 0.065 mmol, 1 eq) in CH_2Cl_2/THF (1:2, 1.8 mL) was added H_2SO_4/H_2O (104 μL, 2:1, v/v) dropwise at 0 ^oC. Then the reaction mixture was stirred for 1 h at room temperature. Then the mixture was adjusted to PH = 2 with a saturated $NaHCO_3$ solution at 0 ^oC. The resulting mixture was extracted with CH_2Cl_2 (6 × 10 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (DCM/MeOH = 40 : 1) to yield product **29a-S** (47 mg, 91%) as a orange amorphous powder and phenol **27a** (42 mg, 85%) amorphous powder, respectively. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (t, *J* = 8.8 Hz, 4H), 7.65 – 7.57 (m, 2H), 7.49 – 7.41 (m, 4H), 7.06 (s, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 6.65 (s, 1H), 6.62 (s, 1H), 6.59 (s, 1H), 6.56 – 6.53 (m, 2H), 6.45 (s, 1H), 6.06 (s, 1H), 5.92 (s, 2H), 5.90 (s, 2H), 4.46 (t, *J* = 7.5 Hz, 1H), 3.71 (s, 3H), 2.54 – 2.45 (m, 6H), 2.15 – 2.07 (m, 2H), 1.84 (p, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.0, 184.0, 165.4, 165.1, 156.1, 155.3, 154.1, 148.6, 147.7, 146.2, 145.8, 145.5, 142.6, 135.5, 133.8, 133.7, 130.2, 129.9, 129.34, 129.28, 128.8, 128.7, 128.1, 126.6, 126.3, 125.6, 121.3, 109.2, 109.0, 108.4, 108.3, 105.8, 104.1, 101.6, 100.9, 55.7, 37.4, 35.2, 34.0, 31.1, 30.0, 29.5. **HR-ESI-MS** (m/z): calculated for $C_{47}H_{42}O_{12}N$ $[M+NH_4]^+$: 812.2702, found: 812.2695.

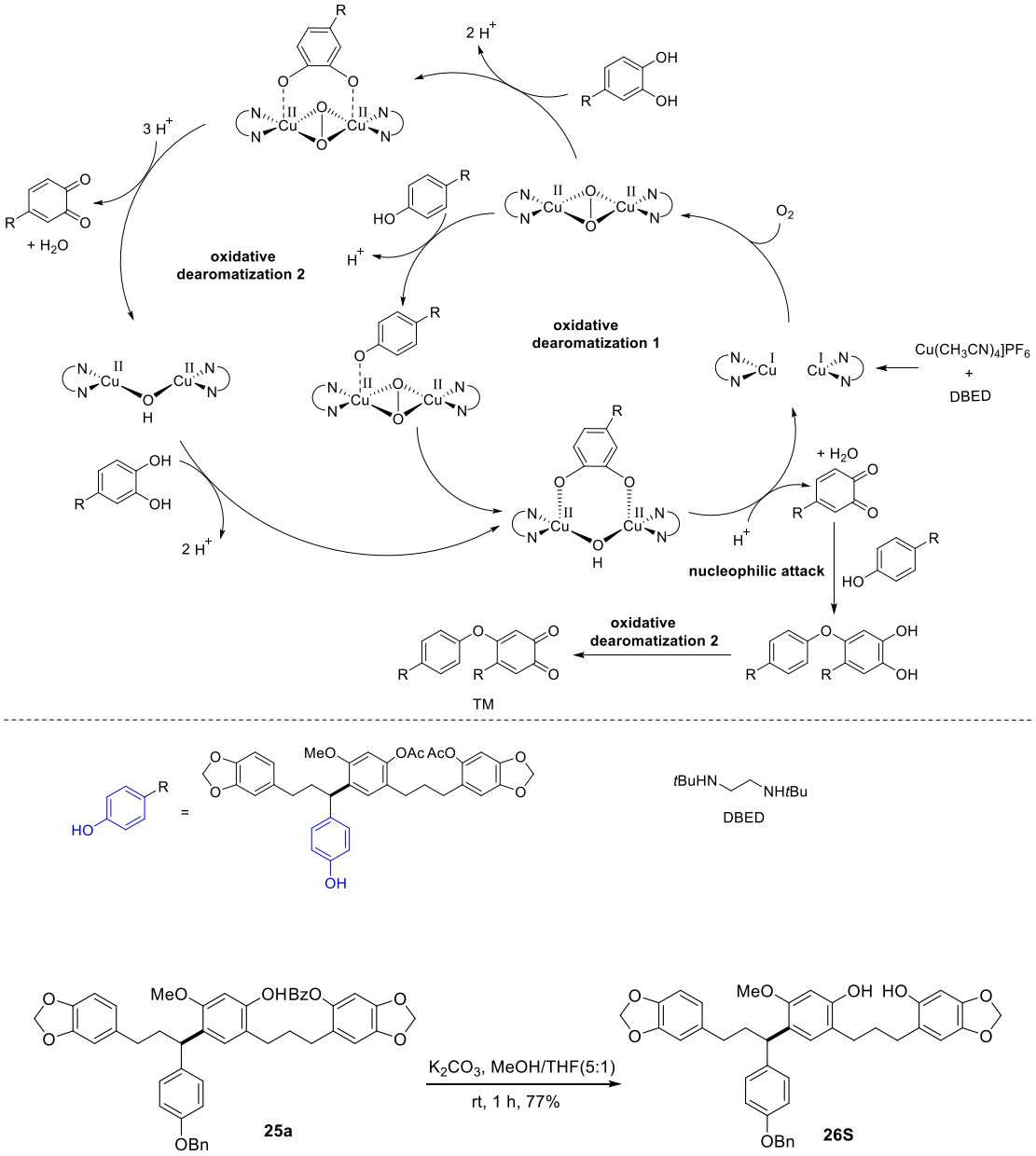


4-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-methoxy-3,6-dioxocyclohexa-1,4-dien-1-yl)propyl)-2-(3-(6-(benzoyloxy)benzo[d][1,3]dioxol-5-yl)propyl)-5-methoxyphenyl benzoate. (29a). To a solution of **29a-S** (75 mg, 0.094 mmol, 1 eq.) in THF/MeOH (2.1 mL, 6:1, v/v) was added $TMSCHN_2$ (94.3 μL, 2 M in hexanes) dropwise at room temperature. Then the mixture was stirred for 1 h at the same temperature. The resulting mixture was concentrated and purified by silica gel flash column chromatography (petroleum ether/EtOAc = 2 : 1) to yield product **29a** (61.6 mg, 81%) as a orange amorphous powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.0, 7.6 Hz, 4H), 7.64 – 7.57 (m, 2H), 7.49 – 7.41 (m, 4H), 7.06 (s, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.65 (s, 1H), 6.62 (s, 1H), 6.58 (s, 1H), 6.55 (d, *J* = 6.8 Hz, 2H), 6.42 (s, 1H), 5.91 (s, 2H), 5.90 (s, 2H), 5.88 (s, 1H), 4.42 (t, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 2.53 – 2.44 (m, 6H), 2.15 – 2.08 (m, 2H), 1.83 (p, *J* = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.8, 182.9, 165.4, 165.1, 158.3, 156.2, 152.4, 148.5, 147.7, 146.1, 145.8, 145.5, 142.6, 135.6, 133.72, 133.67, 130.6, 130.2, 130.0, 129.4, 129.3, 128.75, 128.72, 126.7, 126.4, 125.6, 121.3, 109.3, 109.0, 108.3, 108.0, 105.8, 104.1, 101.6, 100.9, 56.3, 55.7, 37.2, 35.0, 34.0, 31.1, 30.0, 29.5. **HR-ESI-MS** (m/z): calculated for $C_{48}H_{44}O_{12}N$ $[M+NH_4]^+$: 826.2858, found: 826.2864.

Scheme S3. Total synthesis of horsfiequinone B (**4**)

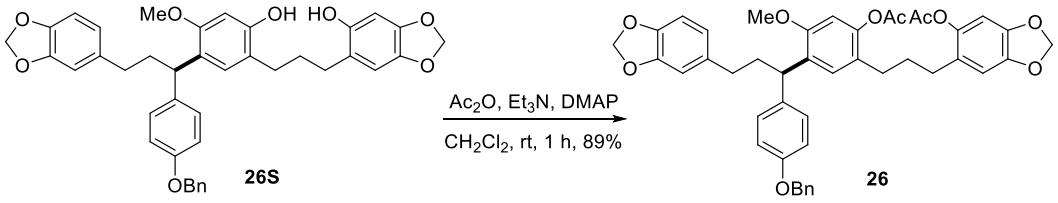


Scheme S4. Proposed mechanism of oxidation of phenol **27** to **28**[1, 2]

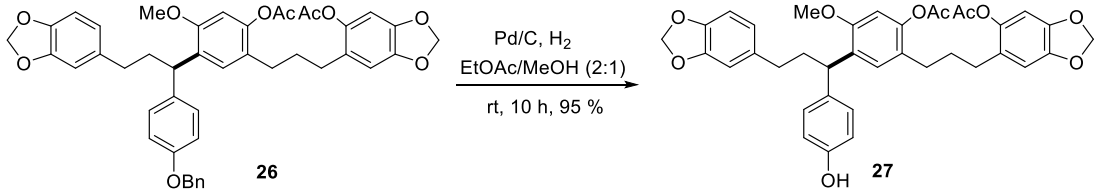


6-(3-(5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-(benzyloxy)phenyl)propyl)-2-hydroxy-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-ol (26S). To a solution of **25a** (3.36 g, 4.48 mmol, 1 eq) in MeOH/THF (24 mL, 5:1, v/v) was added K_2CO_3 (741 mg, 5.37 mmol, 1.2 eq) at room temperature. Then the mixture was stirred for 1 h at the same temperature. The resulting mixture was filtered through a pad of celite and concentrated. The residue was purified by silica gel flash column chromatography (petroleum ether/DCM/EtOAc = 6:1:1) to yield product **26S** (2.23 g, 77 %) as a white amorphous powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 6.4 Hz, 1H), 7.18 (dd, *J* = 8.6, 2.5 Hz, 2H), 6.96 (s, 1H), 6.90 (d, *J* = 7.8 Hz, 2H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.65 (s, 1H), 6.61 (s, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 6.37 (s, 1H), 6.30 (s, 1H), 5.91 (s, 2H), 5.86 (s, 2H), 5.02 (s, 2H), 4.23 (t, *J* = 7.3 Hz, 1H), 3.65 (s, 3H), 2.60 – 2.53 (m, 4H), 2.50 -2.46 (m, 2H), 2.26 – 2.19

(m, 2H), 1.87 (t, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0, 156.2, 152.2, 147.8, 147.5, 146.1, 145.5, 141.5, 137.8, 137.3, 136.6, 129.0, 128.6, 128.0, 127.7, 125.9, 121.3, 120.2, 119.4, 114.6, 109.5, 109.1, 108.2, 101.0, 100.8, 99.7, 98.4, 70.2, 55.7, 41.7, 37.5, 34.1, 30.7, 29.4, 29.0. **HR-ESI-MS** (m/z): calculated for $C_{40}H_{42}O_8N$ $[M+NH_4]^+$: 664.2905, found: 664.2908.

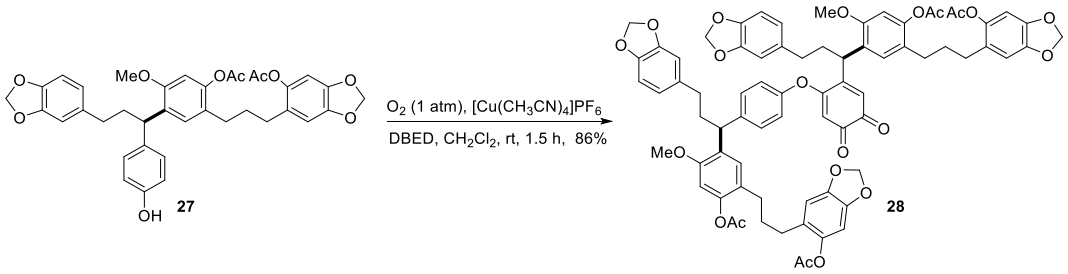


6-(3-(2-acetoxy-5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-(benzyloxy)phenyl)propyl)-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl acetate (26). To a solution of **26S** (2.00 g, 3.1 mmol, 1 eq.) in CH_2Cl_2 (10 mL) was added Ac_2O (0.87 mL, 9.27 mmol, 3 eq.), DMAP (37.7 mg, 0.31 mmol, 0.1 eq) and Et_3N (2.14mL, 15.45 mmol, 5 eq) at 0 ^oC. Then the mixture was stirred for 1 h at room temperature. The resulting mixture was concentrated and purified by silica gel flash column chromatography (petroleum ether/DCM/EtOAc = 8 : 1 : 1) to yield product **26** (2.01 g, 89%) as a colorless, viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 7.1 Hz, 1H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.04 (s, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.67 (s, 1H), 6.64 (s, 1H), 6.57 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.54 (s, 1H), 6.51 (s, 1H), 5.94 (s, 2H), 5.91 (s, 2H), 5.03 (s, 2H), 4.27 (t, *J* = 7.7 Hz, 1H), 3.73 (s, 3H), 2.51 – 2.39 (m, 6H), 2.27 – 2.21 (m, 6H), 2.15 (s, 3H), 1.75 (p, *J* = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 169.6, 157.2, 155.8, 147.6, 147.5, 146.1, 145.6, 145.5, 142.6, 137.3, 136.8, 136.4, 131.5, 129.2, 128.8, 128.7, 128.0, 127.6, 126.7, 125.1, 121.2, 114.7, 109.1, 109.0, 108.2, 105.4, 104.0, 101.6, 100.8, 70.1, 55.7, 42.0, 37.3, 34.1, 30.7, 29.8, 29.5, 21.0, 20.7. **HR-ESI-MS** (m/z): calculated for $C_{44}H_{46}O_{10}N$ $[M+NH_4]^+$: 748.3116, found: 748.3110.

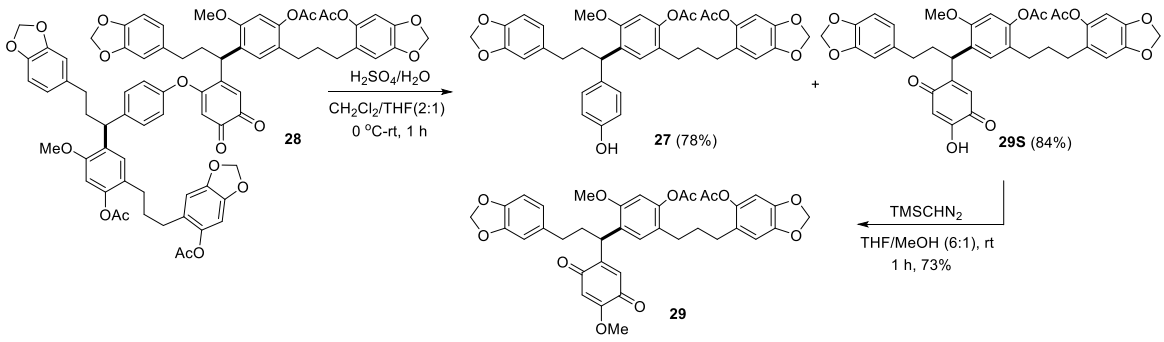


6-(3-(2-acetoxy-5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-hydroxyphenyl)propyl)-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl acetate (27). To a solution of **26** (1.20 g, 1.64 mmol, 1 eq) in EtOAc/MeOH (2 : 1, 12 mL) was added Pd/C (120 mg, 10% wt). Then the mixture was connected to a H_2 balloon and stirred for 10 h at room temperature. After consumption of the starting material, the mixture was filtrated through a short pad of celite, the filter cake was washed with ethyl acetate, and the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (petroleum ether / EtOAc = 3 : 1) to yield product **27** (1.00 g, 95 %)

as a white amorphous powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.2 Hz, 2H), 7.00 (s, 1H), 6.73 – 6.69 (m, 3H), 6.63 (d, *J* = 6.0 Hz, 2H), 6.55 (d, *J* = 7.9 Hz, 1H), 6.52 (s, 1H), 6.50 (s, 1H), 5.93 (s, 2H), 5.90 (s, 2H), 4.23 (t, *J* = 7.6 Hz, 1H), 3.71 (s, 3H), 2.49 – 2.36 (m, 6H), 2.24 (s, 3H), 2.22 – 2.18 (m, 2H), 2.13 (s, 3H), 1.72 (p, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 169.7, 155.8, 153.8, 147.6, 147.5, 146.1, 145.6, 145.6, 142.6, 136.6, 136.4, 131.6, 129.4, 128.9, 126.7, 125.1, 121.2, 115.3, 109.2, 109.1, 108.2, 105.4, 104.0, 101.6, 100.8, 55.8, 42.0, 37.2, 34.1, 30.7, 29.8, 29.5, 21.0, 20.8. **HR-ESI-MS** (m/z): calculated for $C_{37}H_{40}O_{10}N$ $[M+NH_4]^+$: 658.2647, found: 658.2643.

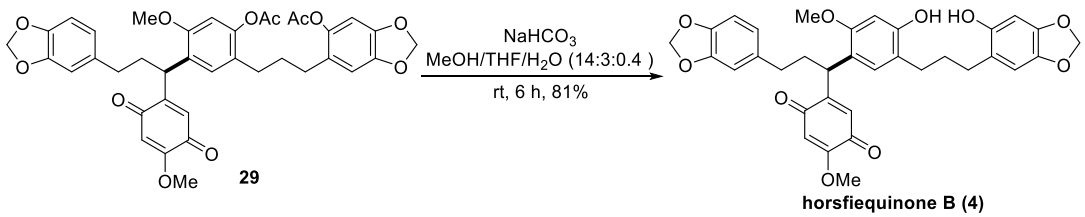


6-(3-(2-acetoxy-5-(1-(4-((6-(1-(4-acetoxy-5-(3-(6-acetoxybenzo[d][1,3]dioxol-5-yl)propyl)-2-methoxyphenyl)-3-(benzo[d][1,3]dioxol-5-yl)propyl)-3,4-dioxocyclohexa-1,5-dien-1-yl)oxy)phenyl)-3-(benzo[d][1,3]dioxol-5-yl)propyl)-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl acetate (28). To solution of $[Cu(CH_3CN)PF_6]$ (18.7 mg, 0.05 mmol, 10 mol %) and DBED (13 μL, 0.06 mmol, 12 mol %) in DCM (1 mL) under Ar atmosphere, the resulting catalyst system (pink solution) was stirred for 15 min, after which time a solution of phenol **27** (319 mg, 0.50 mmol) in DCM (1 mL) was added to the aforementioned catalyst system solution and stirred for 1 min at room temperature, then the resulting solution was vented three times to remove Ar under a O_2 balloon and a dramatic color change was observed, resulting in a blackish/brown reaction mixture and stirred for 1.5 h. Then the mixture was concentrated and purified by silica gel flash column chromatography (petroleum ether/EtOAc = 1.5 : 1) to yield product **28** (277 mg, 86 %) as a orange amorphous powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 5.4 Hz, 1H), 7.01 (s, 1H), 6.74 – 6.69 (m, 4H), 6.66 (d, *J* = 8.4 Hz, 2H), 6.64 – 6.62 (m, 2H), 6.58 – 6.53 (m, 6H), 6.28 (s, 1H), 5.92 (s, 4H), 5.91 (s, 2H), 5.86 (d, *J* = 1.4 Hz, 1H), 5.82 (dd, *J* = 3.0, 1.4 Hz, 1H), 5.43 (s, 1H), 4.58 (t, *J* = 7.2 Hz, 1H), 4.29 (t, *J* = 7.7 Hz, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 2.64 – 2.56 (m, 2H), 2.49 – 2.39 (m, 10H), 2.27 – 2.18 (m, 13H), 2.16 (s, 3H), 1.80 – 1.70 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.6, 178.9, 169.8, 169.6, 169.4, 169.1, 156.1, 155.9, 155.2, 150.3, 148.6, 147.9, 147.7, 147.6, 146.19, 146.16, 145.9, 145.7, 145.6, 143.6, 143.5, 142.60, 142.57, 135.9, 135.2, 130.18, 130.15, 129.9, 129.29, 129.28, 128.74, 128.68, 127.2, 126.5, 126.3, 125.8, 125.3, 121.25, 121.23, 120.6, 109.10, 109.05, 109.0, 108.9, 108.3, 108.2, 106.1, 105.9, 105.5, 104.01, 103.98, 101.6, 100.90, 100.86, 55.9, 55.7, 42.3, 37.5, 37.04, 37.01, 35.3, 33.9, 33.6, 30.7, 29.8, 29.5, 29.4, 20.94, 20.91, 20.85, 20.8. **HR-ESI-MS** (m/z): calculated for $C_{74}H_{68}O_{21}K$ $[M+K]^+$: 1331.3885, found: 1331.3895.



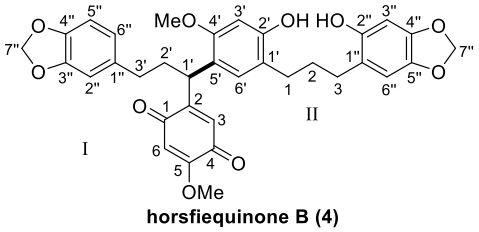
6-(3-(2-acetoxy-5-(3-(benzo[d][1,3]dioxol-5-yl)-1-(4-methoxy-3,6-dioxocyclohexa-1,4-dien-1-yl)propyl)-4-methoxyphenyl)propyl)benzo[d][1,3]dioxol-5-yl acetate (28). To a solution of **28** (1138 mg, 0.88 mmol, 1 eq.) in CH_2Cl_2/THF (1:2.5, 18 mL, v/v) was added H_2SO_4/H_2O (1.17 mL, 2:1, v/v) at 0 °C. Then the reaction mixture was stirred for 1 h at the room temperature. The mixture was adjusted PH to 1-2 by a saturated $NaHCO_3$ solution at 0 °C, The resulting mixture was extracted with CH_2Cl_2 (6 × 10 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (DCM/MeOH = 40 : 1) to yield phenol **27** (474 mg, 78%) as white amorphous powder and the desired product **29S** (496 mg, 84%) as a orange amorphous powder, respectively. **29S** was used directly in the next step without further structural characterization, due to the proper of instability.

To a solution of **29S** (496 mg, 0.74 mmol, 1 eq) in THF/MeOH (3.5 mL, 6:1, v/v) was added $TMSCHN_2$ (0.74 mL, 2 M in hexane) at room temperature. Then the mixture was stirred for 1 h at the same temperature. The resulting mixture was concentrated and purified by silica gel flash column chromatography (petroleum ether/EtOAc = 2: 1) to yield product **29** (370 mg, 73%) as a orange amorphous powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 (s, 1H), 6.70 (s, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 1.7 Hz, 1H), 6.55 (dd, *J* = 7.6, 1.6Hz, 1H), 6.53 (s, 1H), 6.52 (s, 1H), 6.42 (s, 1H), 5.94 (s, 2H), 5.90 (s, 2H), 5.88 (s, 1H), 4.43 (t, *J* = 7.5 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 2.52 – 2.40 (m, 6H), 2.24 (s, 3H), 2.21 (s, 3H), 2.14 – 2.07 (m, 2H), 1.74 (p, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.8, 182.9, 169.9, 169.5, 158.3, 156.1, 152.4, 148.3, 147.6, 146.1, 145.8, 145.6, 142.5, 135.6, 130.6, 129.9, 126.5, 125.4, 121.2, 109.2, 108.9, 108.3, 108.0, 105.7, 104.0, 101.7, 100.9, 56.4, 55.8, 37.0, 35.1, 34.0, 30.7, 29.4, 21.0, 20.9. **HR-ESI-MS** (m/z): calculated for $C_{38}H_{37}O_{12}$ $[M+H]^+$: 685.2280, found: 685.2280.



Horsfiequinone B (4). To a solution of **29** (107 mg, 0.16 mmol, 1 eq) in MeOH/THF/H_2O (13.92 mL, 14:3:0.4, v/v) was added $NaHCO_3$ (118 mg, 1.44 mmol, 9 eq) at room temperature. Then the mixture was stirred for 2 h at the same temperature. The resulting mixture was diluted with H_2O (5 mL), adjusted to pH = 5 with 0.1 N HCl, and extracted with EtOAc (3×20 mL). The combined organic layers was dried with Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel flash column chromatography (DCM/MeOH = 100 : 1) to yield product horsfiequinone B (**4**, 78 mg, 81 %) as a orange amorphous powder. **^{1}H NMR** (600 MHz, acetone-d_6) δ 7.10 (s, 1H), 6.73 (dd, *J* = 7.8, 1.8 Hz, 2H), 6.67 (s, 1H), 6.64 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.53 (s, 1H), 6.47 (s, 1H), 6.41 (d, *J* = 1.6 Hz, 1H), 5.99 (s, 1H), 5.95 (s, 2H), 5.87 (s, 2H), 4.44 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.84 (s, 3H), 3.73 (s, 3H), 2.71 – 2.62 (m, 4H), 2.60 – 2.50 (m, 2H), 2.21 – 2.12 (m, 2H), 1.93 – 1.88 (m, 2H); ^{13}C NMR (150 MHz, acetone-d_6) δ 186.7, 182.1, 158.5, 156.3, 154.5, 152.7, 149.2, 147.6, 145.8, 145.7, 140.4, 136.0, 130.1, 129.7, 121.2, 120.6, 120.3, 119.5, 109.3, 108.7, 107.9, 107.6, 100.7, 100.6, 99.4, 97.5, 55.7, 54.9, 36.1, 35.1, 33.7, 30.7, 29.6, 29.1. **HR-ESI-MS** (m/z): calculated for $C_{34}H_{33}O_{10}$ $[M+H]^+$: 601.2068, found: 601.2072.

3. NMR Comparison of Synthetic and Natural Horsfiequinone B (4)



horsfiequinone B (4)

Table S3. ^{1}H NMR data comparison of synthetic and natural horsfiequinone B (**4**) in acetone-d_6

position	Natural horsfiequinone B [a] (500 MHz in acetone-d_6)	Synthetic horsfiequinone B [b] (600 MHz in acetone-d_6)	$\Delta\delta$ ($\delta_{Synthetic}$ - $\delta_{Natural}$)
Moiety I			
3	6.41 (s)	6.41 (d, 1.6)	0
6	5.99 (s)	5.99 (s)	0
1′	4.44 (t, 7.5)	4.44 (dd, 8.4, 8.4)	0
2′	2.13 (m)	2.21 – 2.12 (m)	-
3′	2.53 (m)	2.60 – 2.50 (m)	-
2′′	6.73 (d, 1.0)	6.73 (d, 1.8)	0
5′′	6.73 (d, 8.0)	6.73 (d, 7.8)	0
6′′	6.64 (dd, 8.0, 1.0)	6.64 (dd, 7.8, 1.8)	0
7′′	5.95 (s)	5.95 (s)	0
5-OCH_3	3.83 (s)	3.84 (s)	0.01
Moiety II			
1	2.64 (m) [c]	2.71 – 2.62 (m, 4H)	-
2	1.89 (m)	1.93 – 1.88 (m, 2H)	-
3	2.64 (m) [c]	2.71 – 2.62 (m, 4H)	-
3′	6.53 (s)	6.53 (s)	0
6′	7.09 (s)	7.10 (s)	0.01
3′′	6.47 (s)	6.47 (s)	0
6′′	6.66 (s)	6.67 (s)	0.01
7′′	5.87 (s)	5.87 (s)	0
4′-OCH_3	3.73 (s)	3.73 (s)	0

[a] The chemical shifts referenced to acetone-d_6 at 2.090 ppm. [b] Chemical shifts referenced to acetone-d_6 at 2.090 ppm. [c] In the literature, the chemical shifts of hydrogen at C1 and C3 of the moiety II were assigned as 2.55 (m) and 2.55 (m) respectively, actually, which should be assigned as 2.64 (m) and 2.64 (m) respectively according to the ^{1}H NMR and HSQC spectra of natural horsfiequinone B.[3]

Table S4. ^{13}C NMR data comparison of synthetic and natural horsfiequinone B (**4**) in acetone-d_6

position	Natural horsfiequinone B [a] (500 MHz in acetone-d_6)	Synthetic horsfiequinone B [b] (600 MHz in acetone-d_6)	$\Delta\delta$ ($\delta_{Synthetic}$ - $\delta_{Natural}$)
Moiety I			
1	186.7	186.7	0
2	152.8	152.7	-0.1
3	130.1	130.1	0
4	182.2	182.1	-0.1
5	158.5	158.5	0
6	107.6	107.6	0
1′	36.1	36.1	0
2′	35.1	35.1	0
3′	33.7	33.7	0
1″	136.0	136.0	0
2″	108.7	108.7	0
3″	147.6	147.6	0
4″	145.8	145.8	0
5″	107.9	107.9	0
6″	121.2	121.2	0
7″	100.7	100.7	0
5-OCH_3	55.7	55.7	0
Moiety II			
1	29.5 [c]	29.6	0.1
2	30.6	30.7	0.1
3	29.0	29.1 [d]	0.1
1′	120.3	120.3	0
2′	154.6	154.5	-0.1
3′	99.5	99.4	-0.1
4′	156.3	156.3	0
5′	119.4	119.5	0.1
6′	129.7	129.7	0
1″	120.7	120.6	-0.1
2″	149.3	149.2	-0.1
3″	97.6	97.5	-0.1
4″	140.3	140.4	0.1
5″	145.7	145.7	0
6″	109.3	109.3	0
7″	100.5	100.6	0.1
4′-OCH_3	54.9	54.9	0

[a] The chemical shifts referenced to acetone-d_6 at 28.97 ppm. [b] Chemical shifts referenced to acetone-d_6 at 28.97 ppm. [c] In the literature, the chemical shift of C1 of the moiety II was assigned as 29.1, actually, which should be assigned as 29.5 according to the ^{13}C NMR and HSQC spectra of natural horsfiequinone B.[3] [d] The chemical shift of C3 was assigned as 29.1 according to the HSQC spectrum of synthetic horsfiequinone B (**4**).

4. Reference

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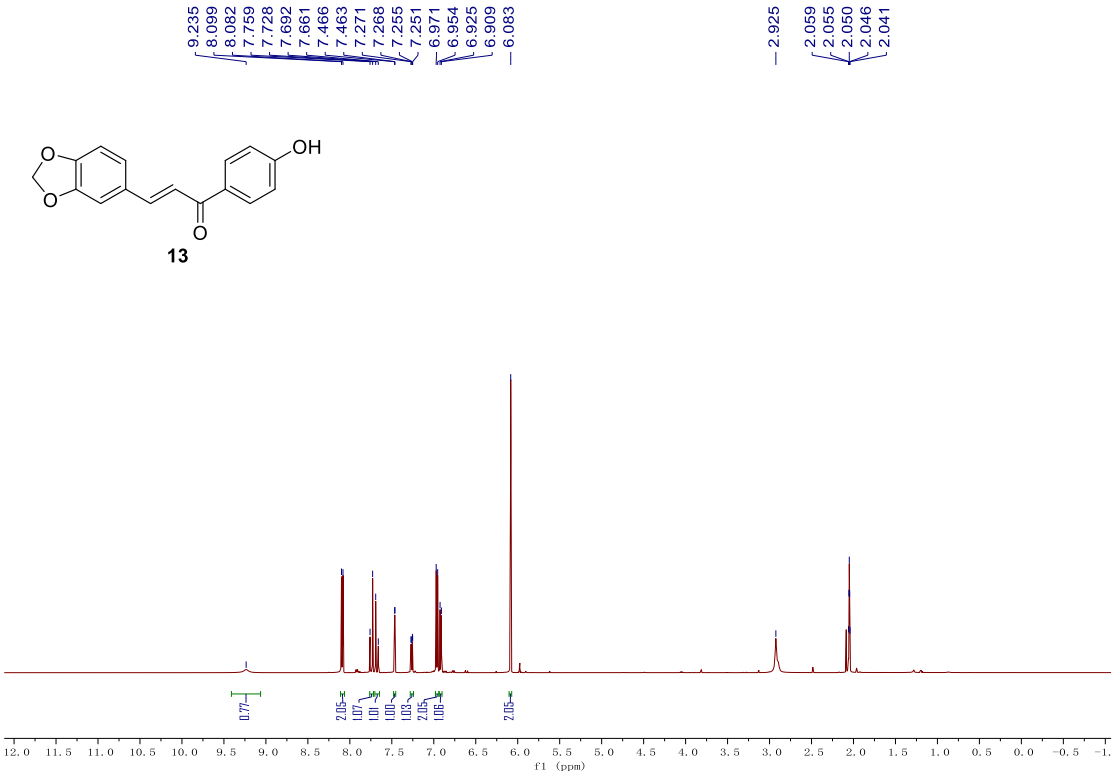
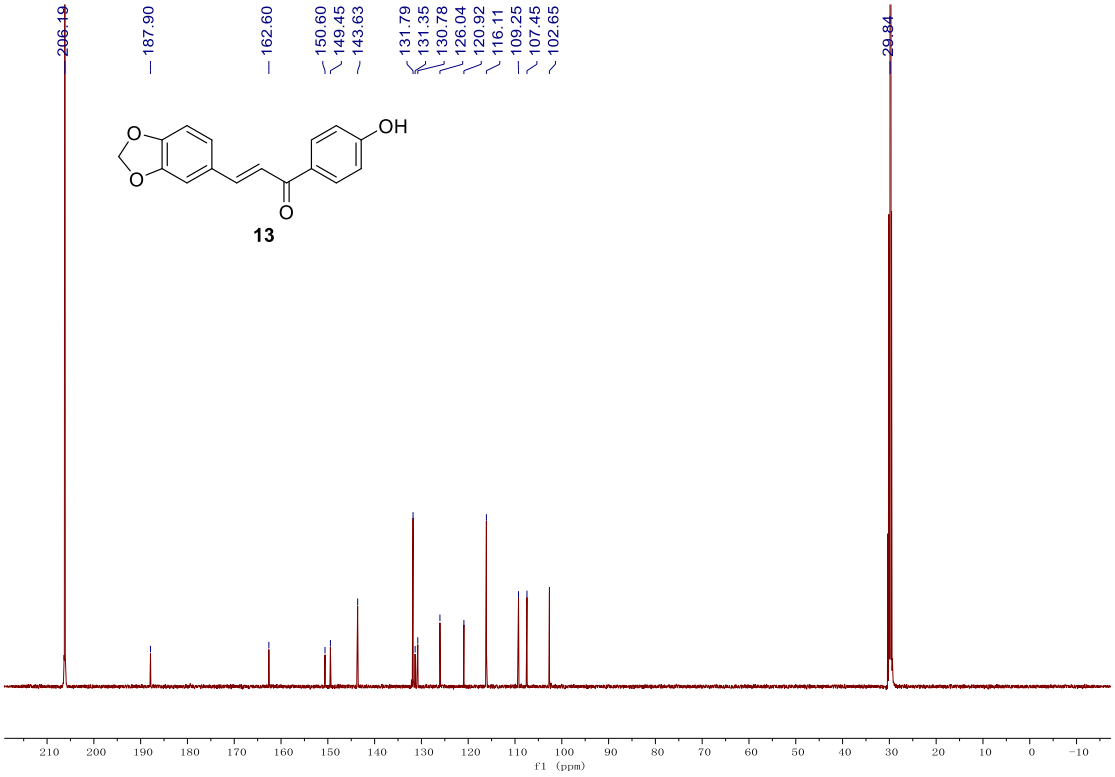
2 K. V. N. Esguerra, Y. Fall and J.-P. Lumb, A Biomimetic Catalytic Aerobic Functionalization of Phenols, *Angew. Chem. Int. Ed.*, 2014, **53**, 5877.
3 Q. Ma, K. Min, H.-L. Li, J.-H. Jiang, Y. Liu, R. Zhan, Y.-G. Chen, Horsfiequinones A-F, Dimeric Diarylpropanoids from Horsfieldia tetratepala., *Planta Medica*, 2014, **80**, 688.

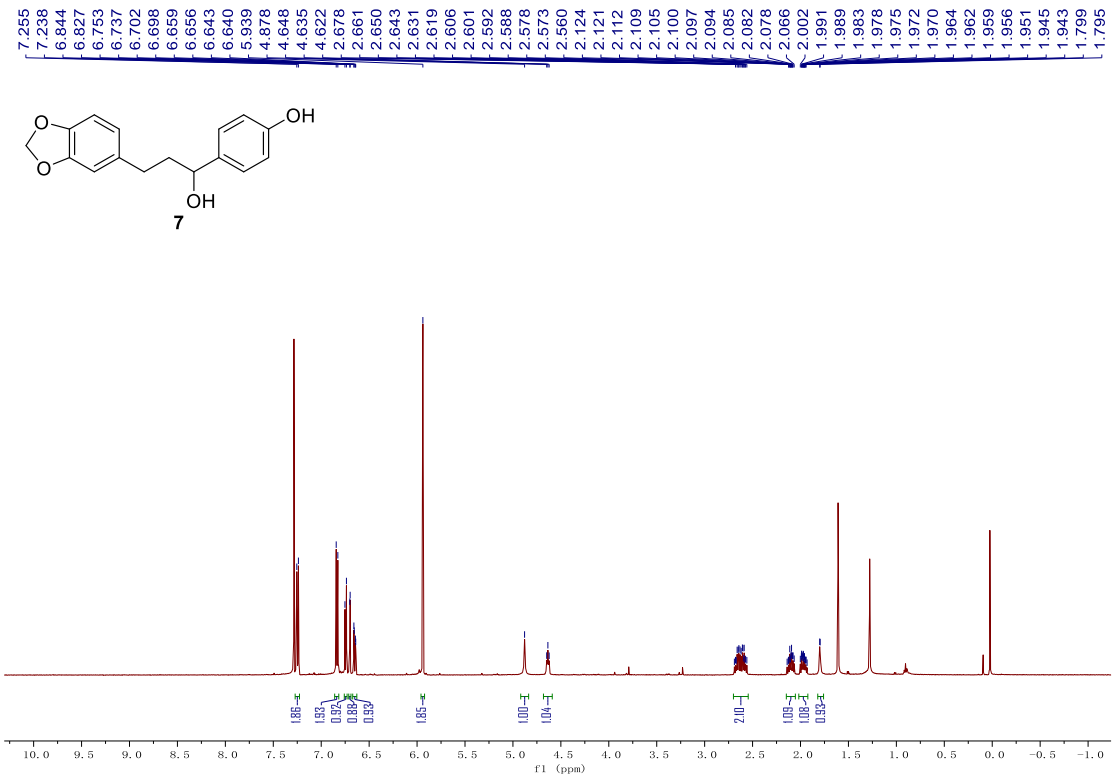
5. NMR Spectra Copies of Synthetic Compounds



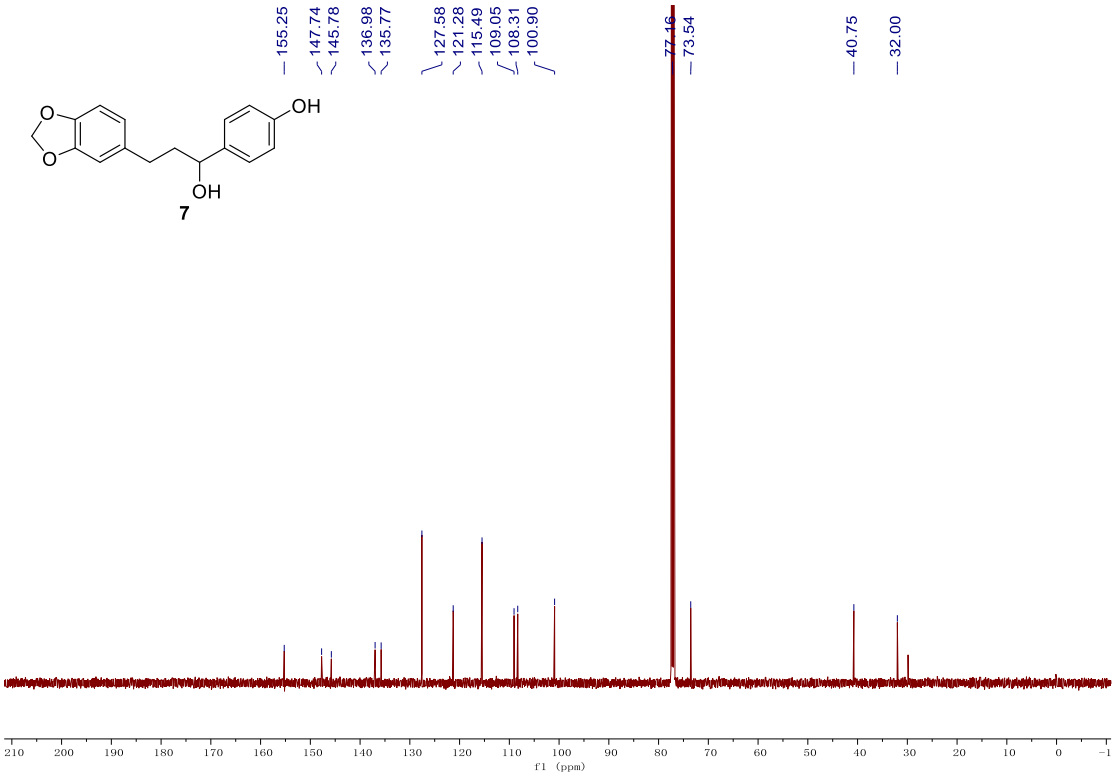
^{1}H NMR spectrum (500 MHz, acetone-d_6) of compound **13**



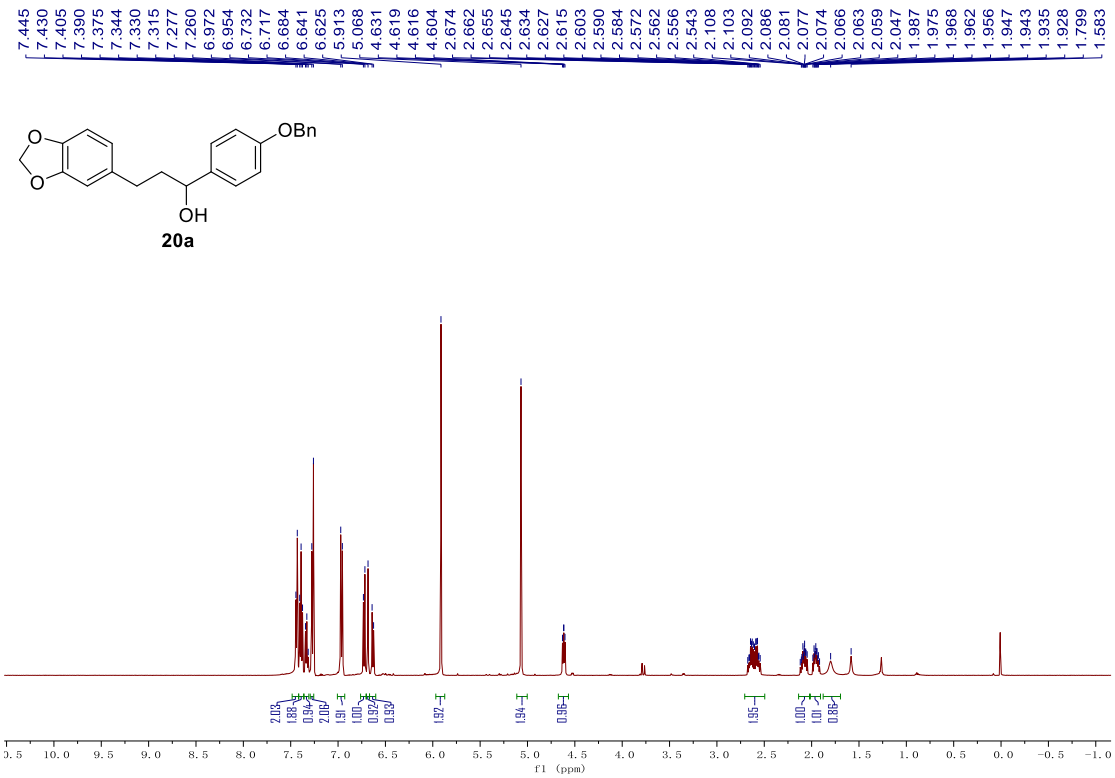
^{13}C NMR spectrum (125 MHz, acetone-d_6) of compound **13**



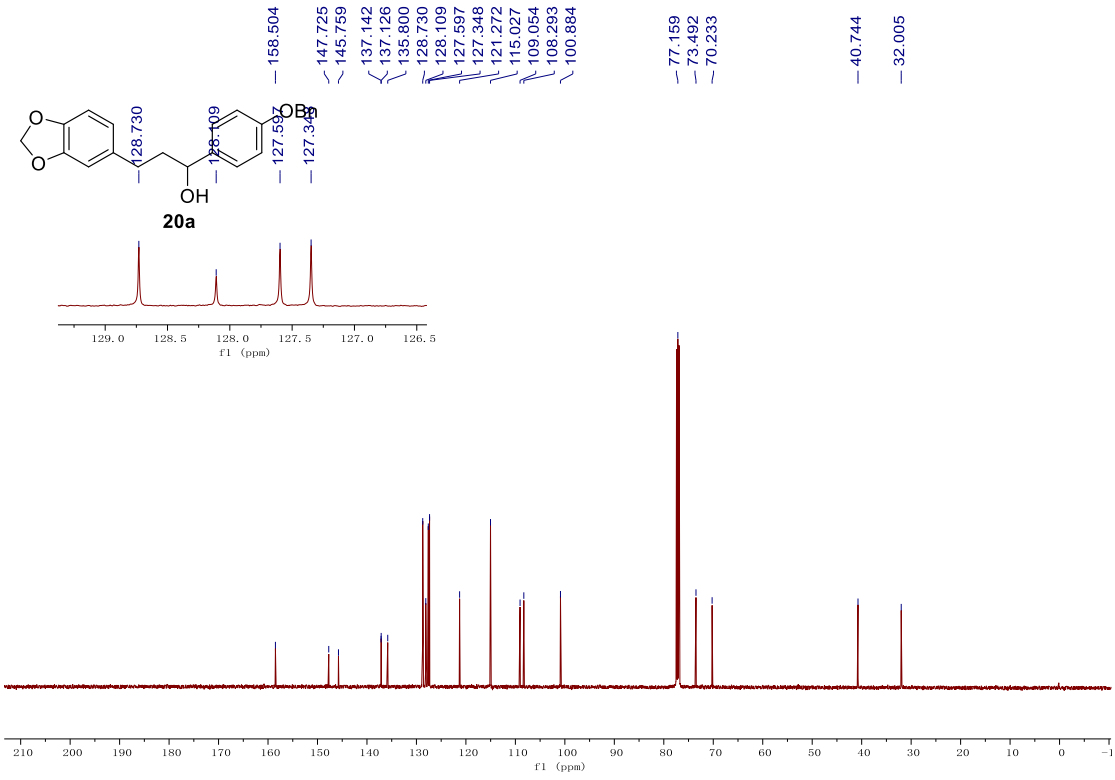
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **7**



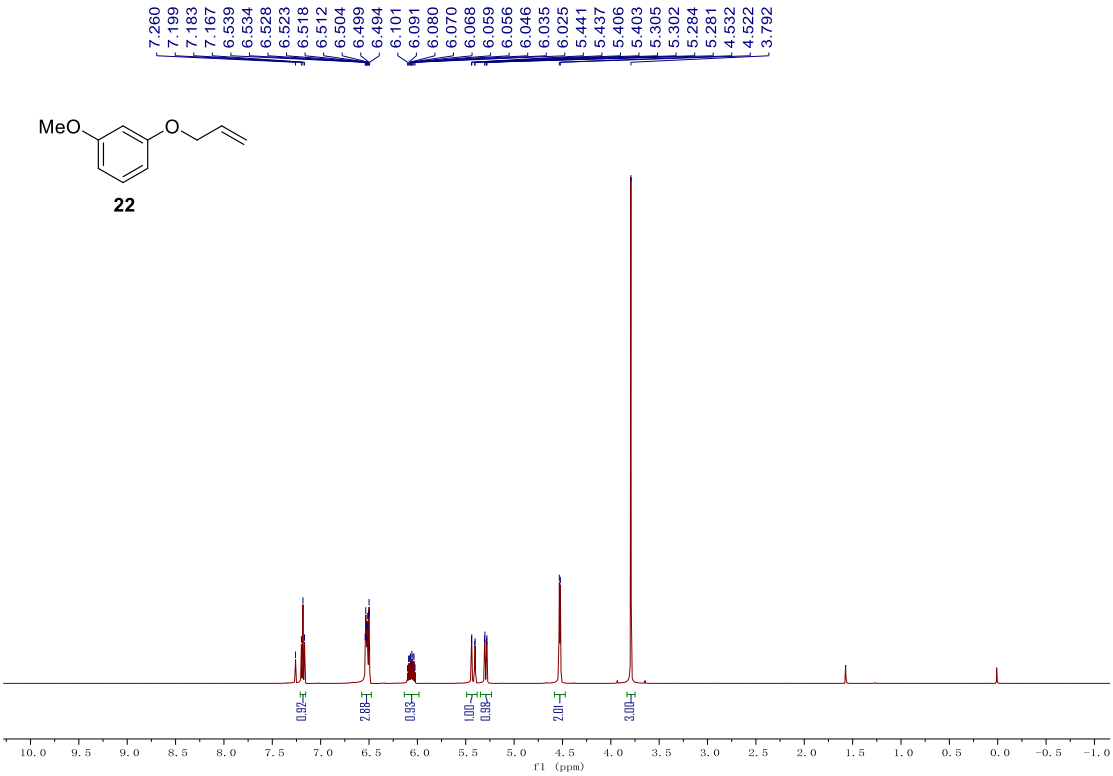
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **7**



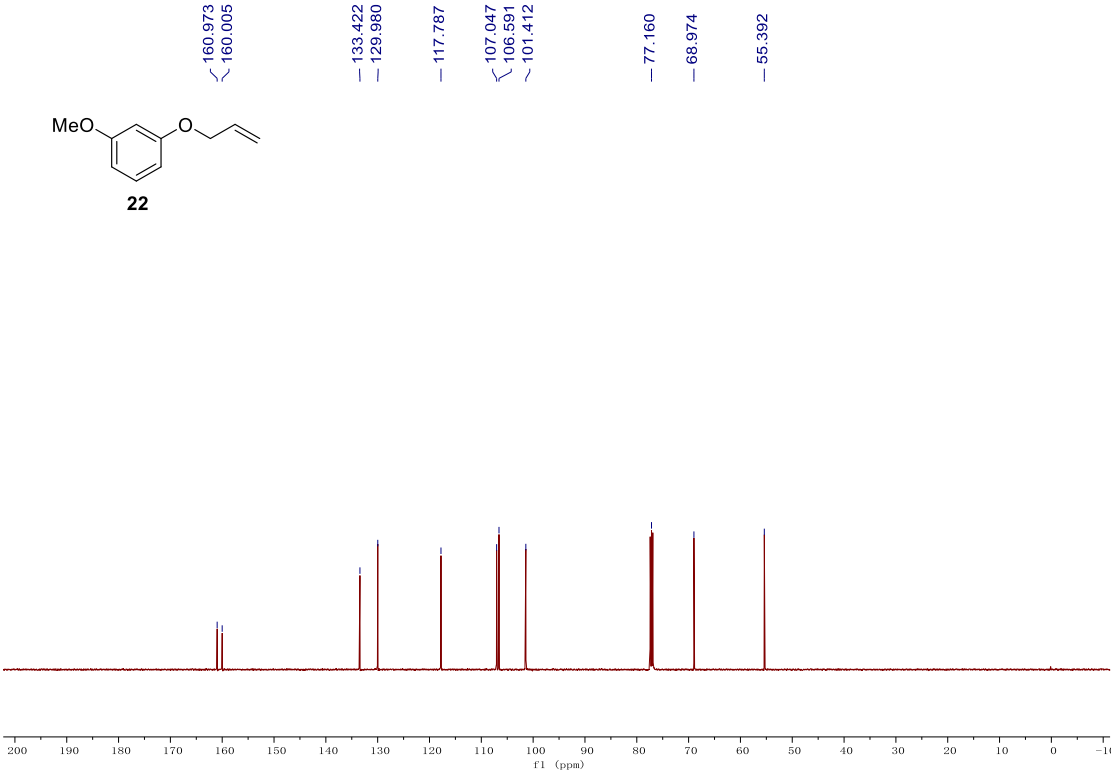
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **20a**



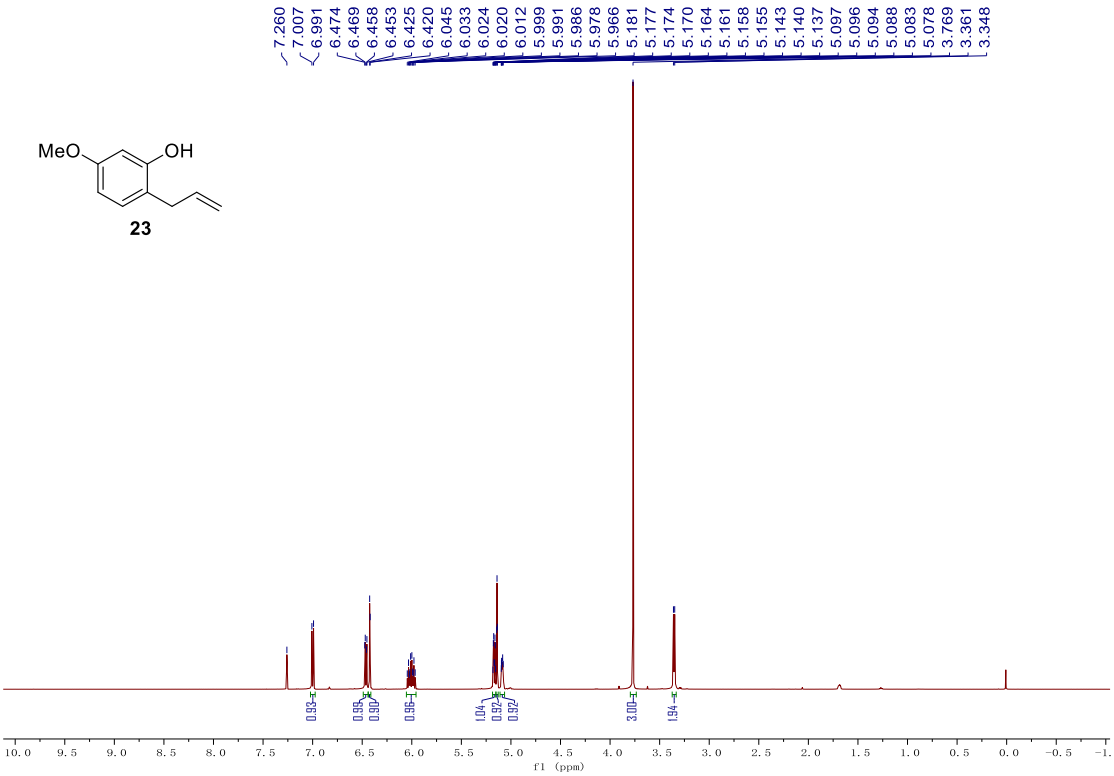
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **20a**



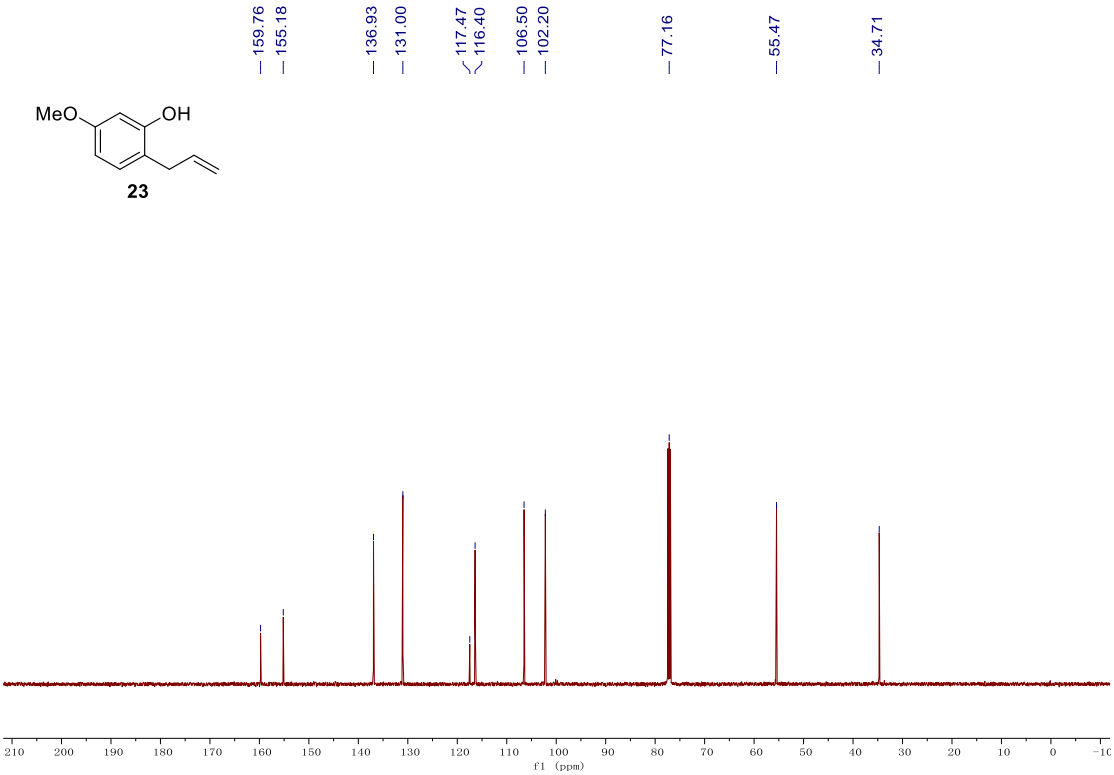
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **22**



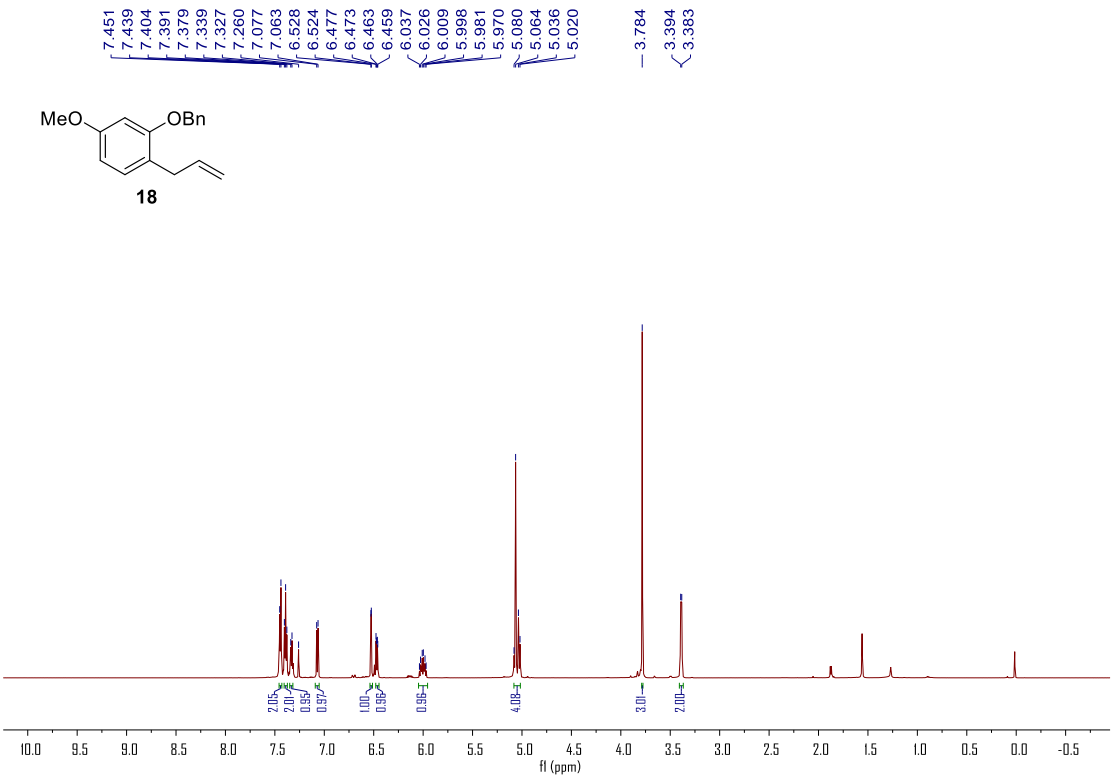
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **22**



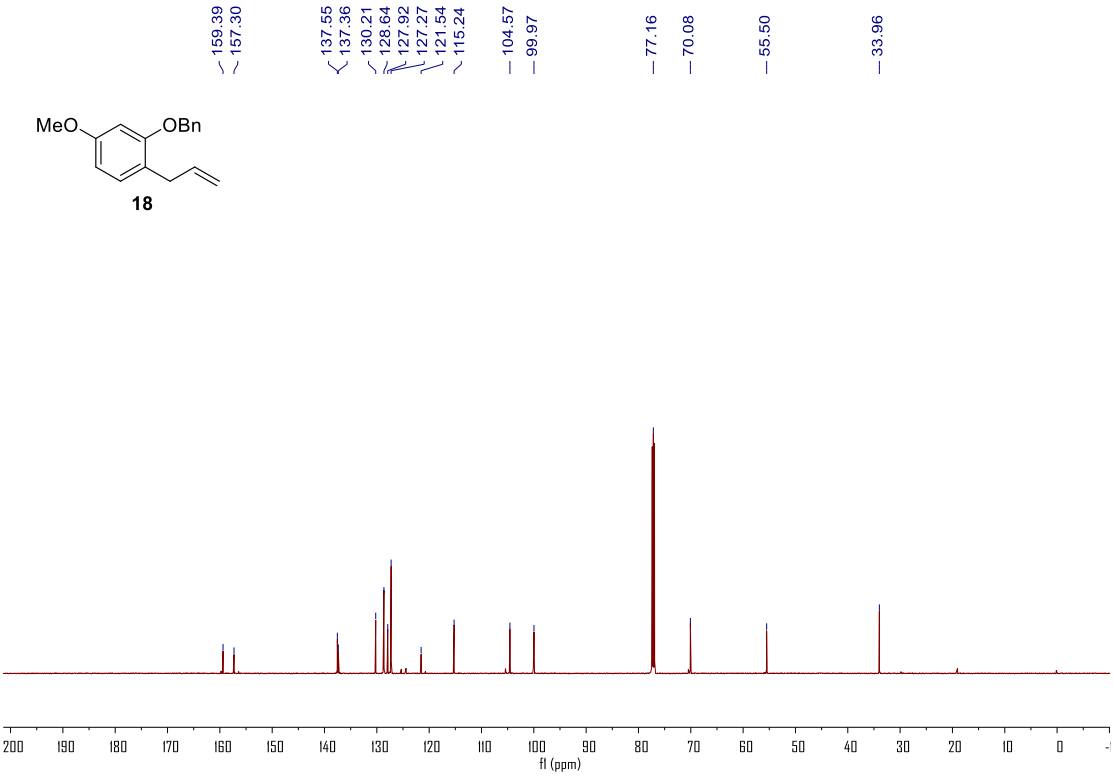
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **23**



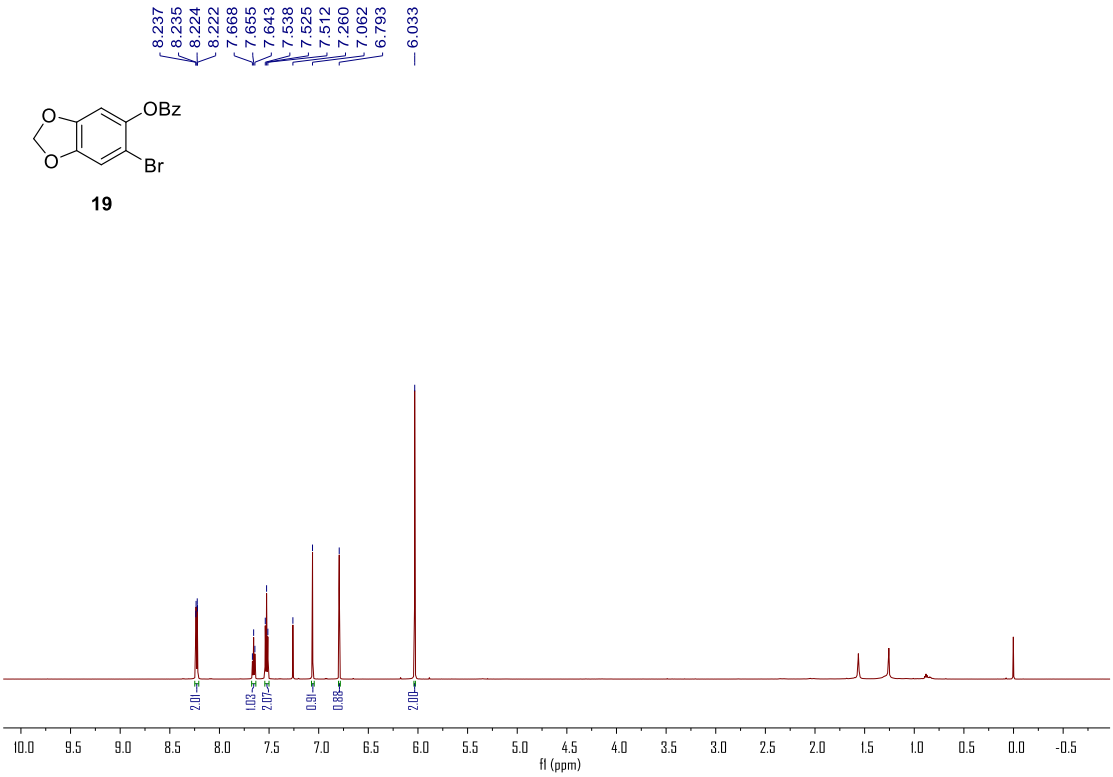
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **23**



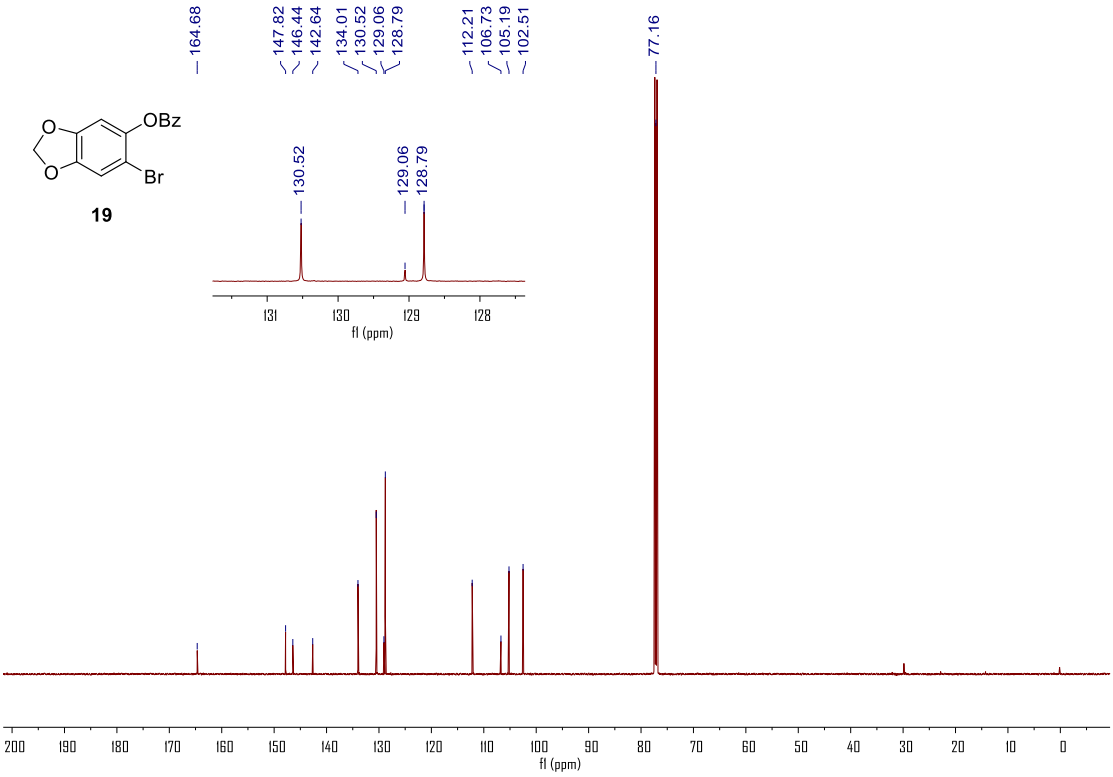
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **18**



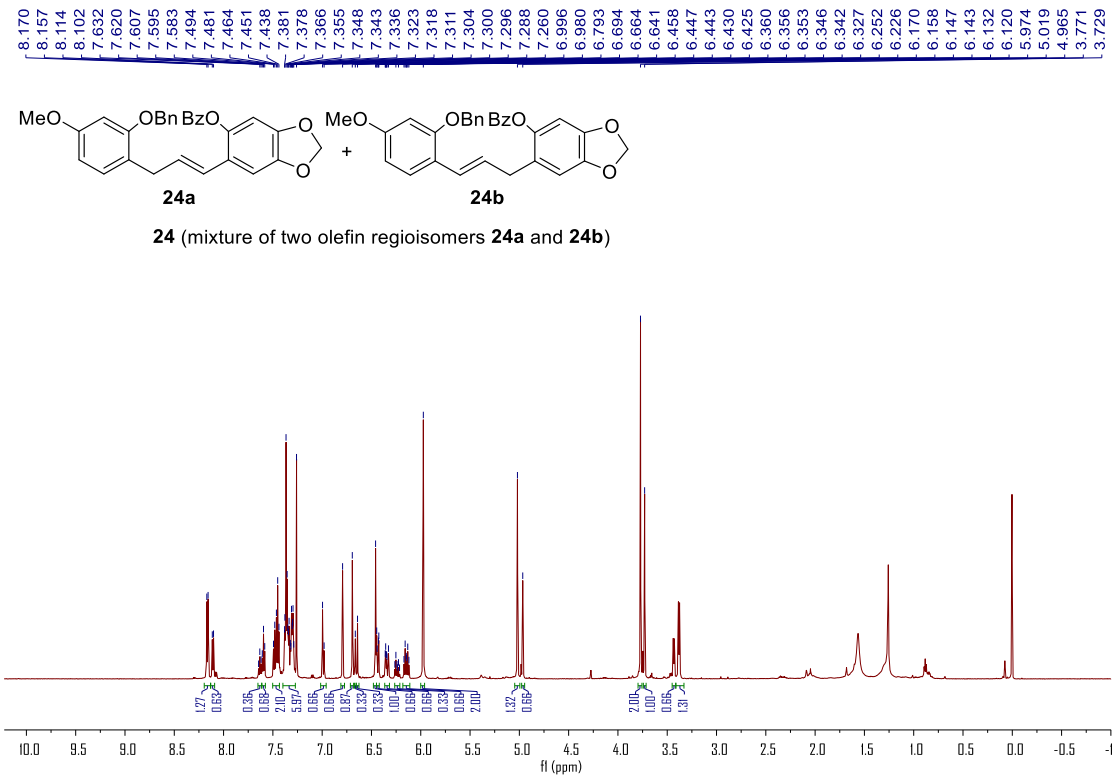
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **18**



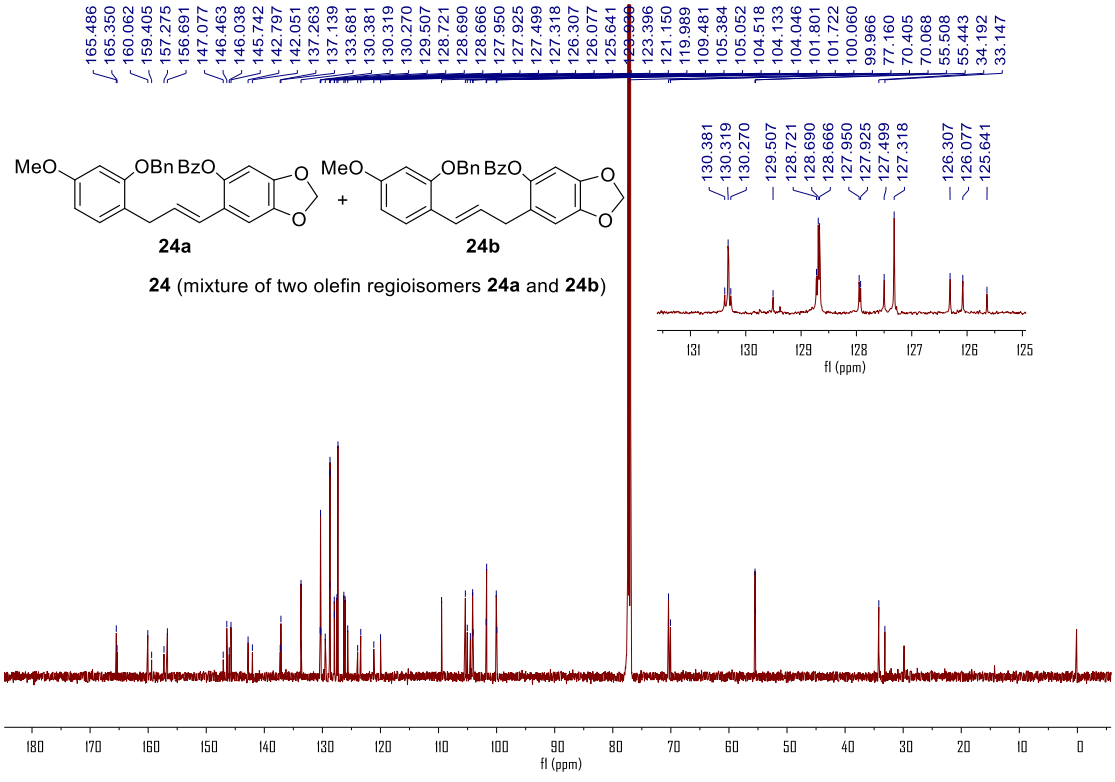
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **19**



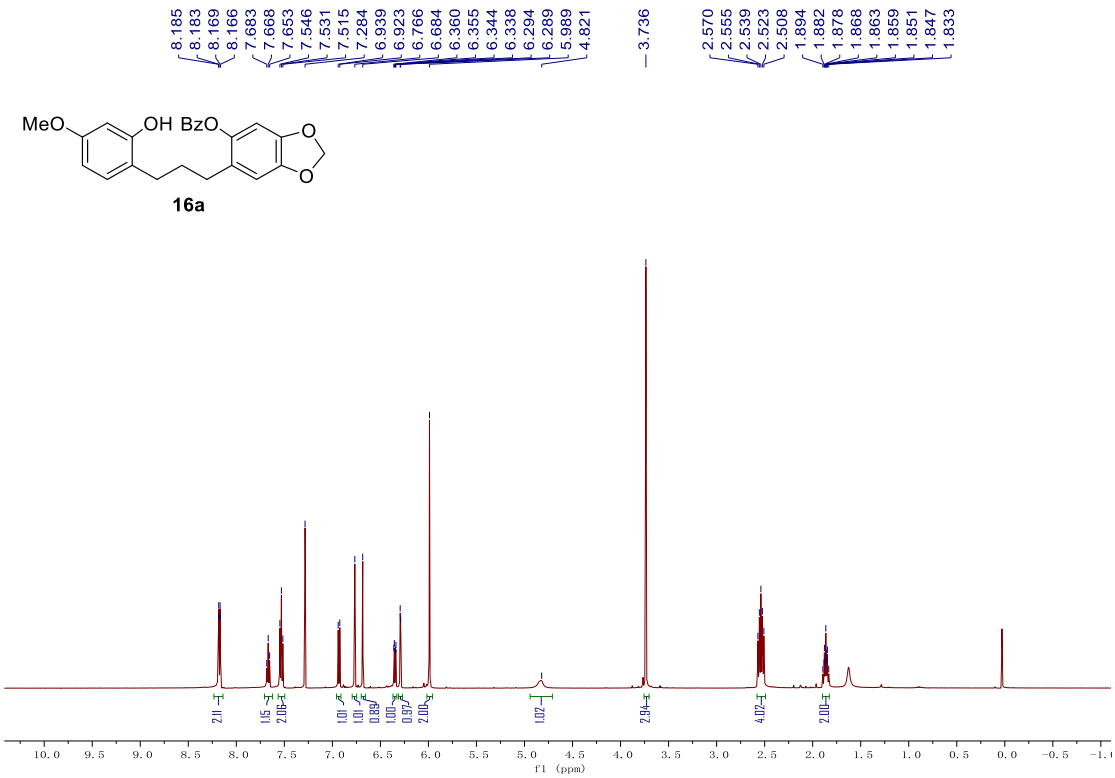
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **19**



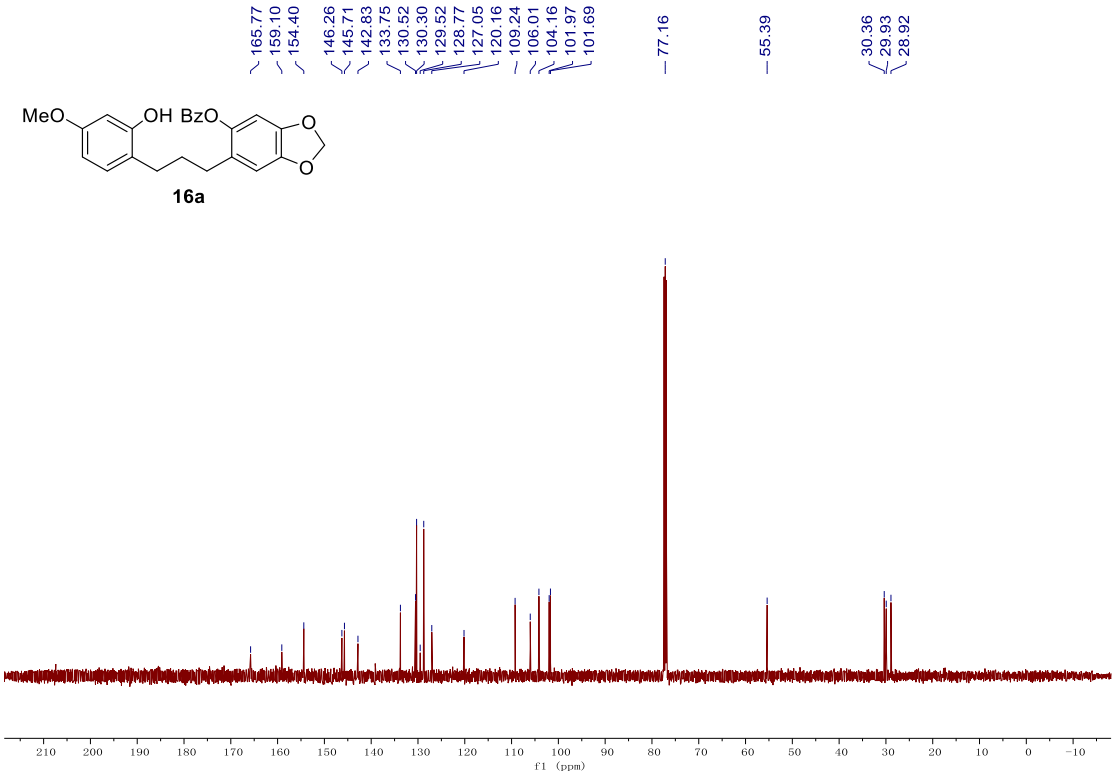
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **24**



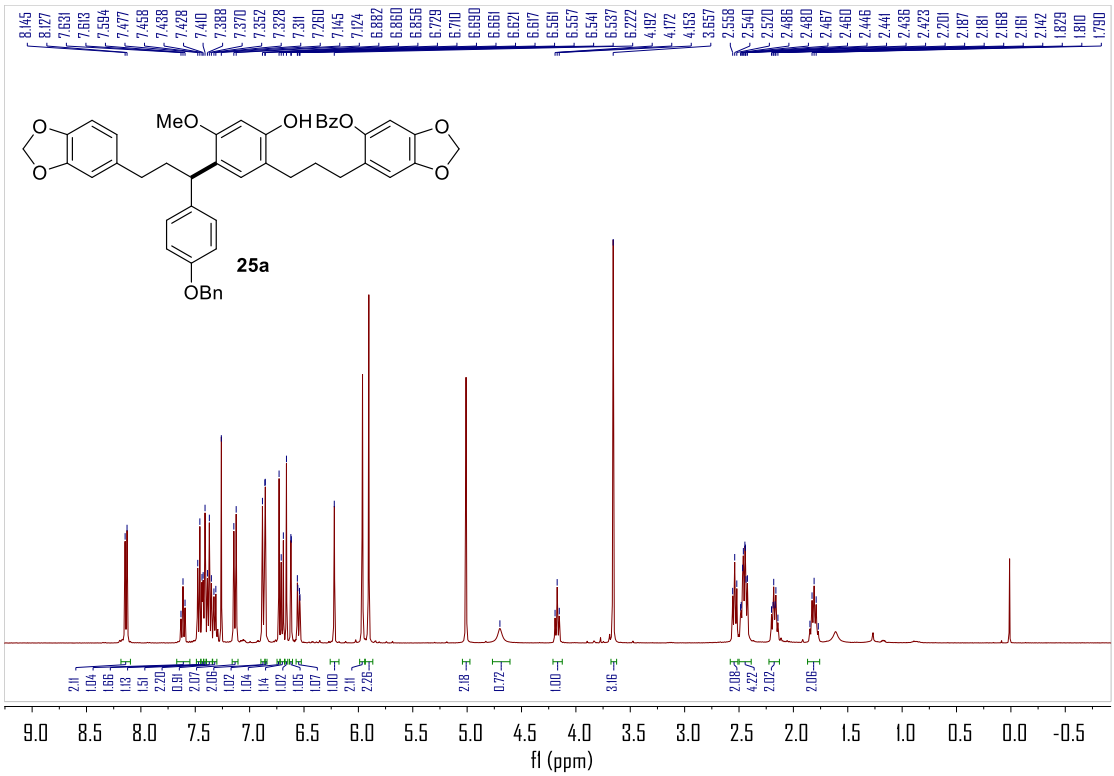
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **24**



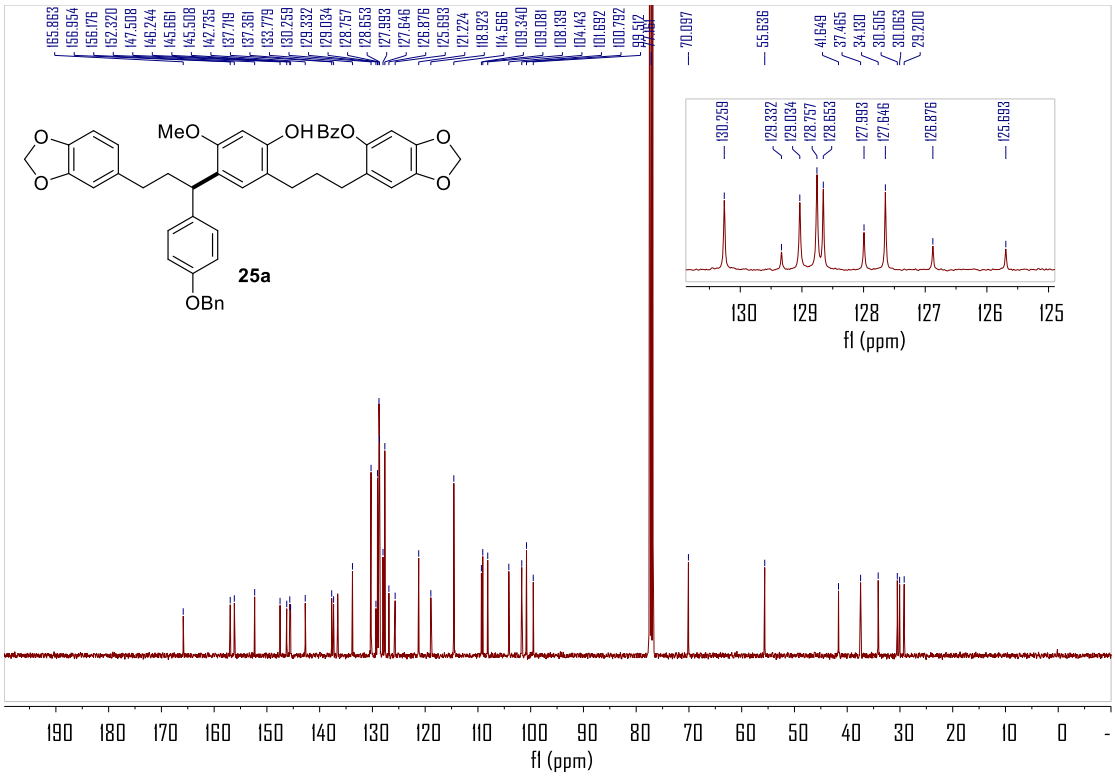
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **16a**



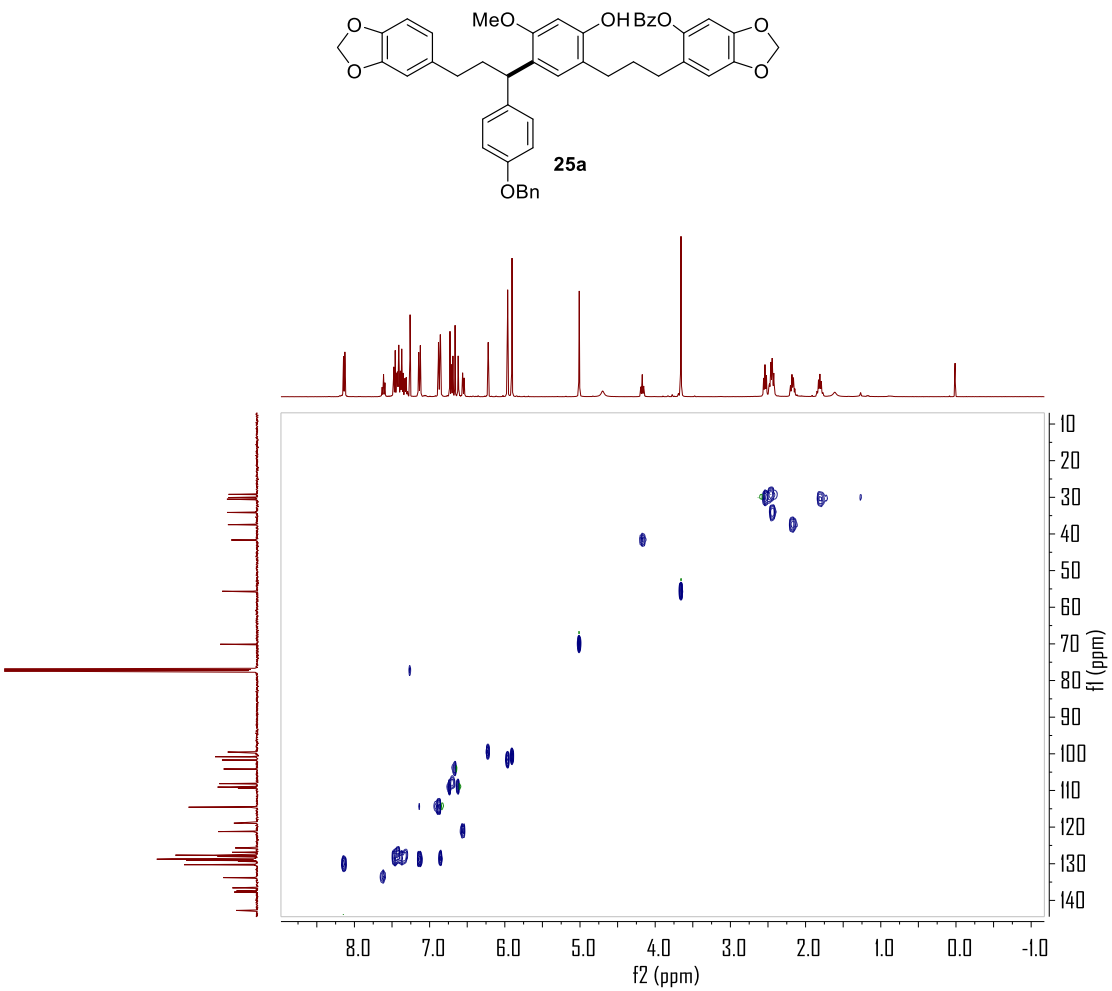
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **16a**



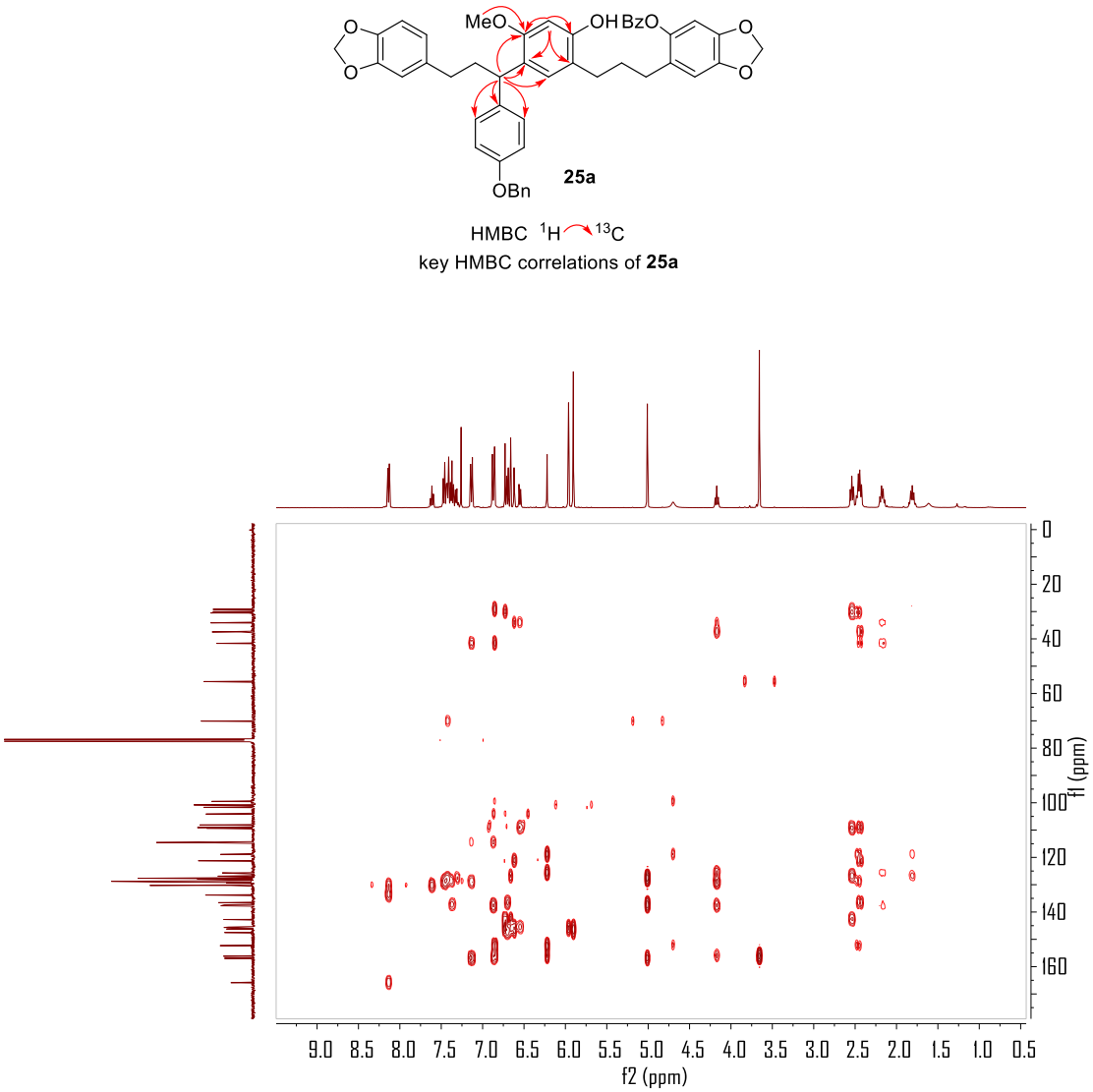
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25a**



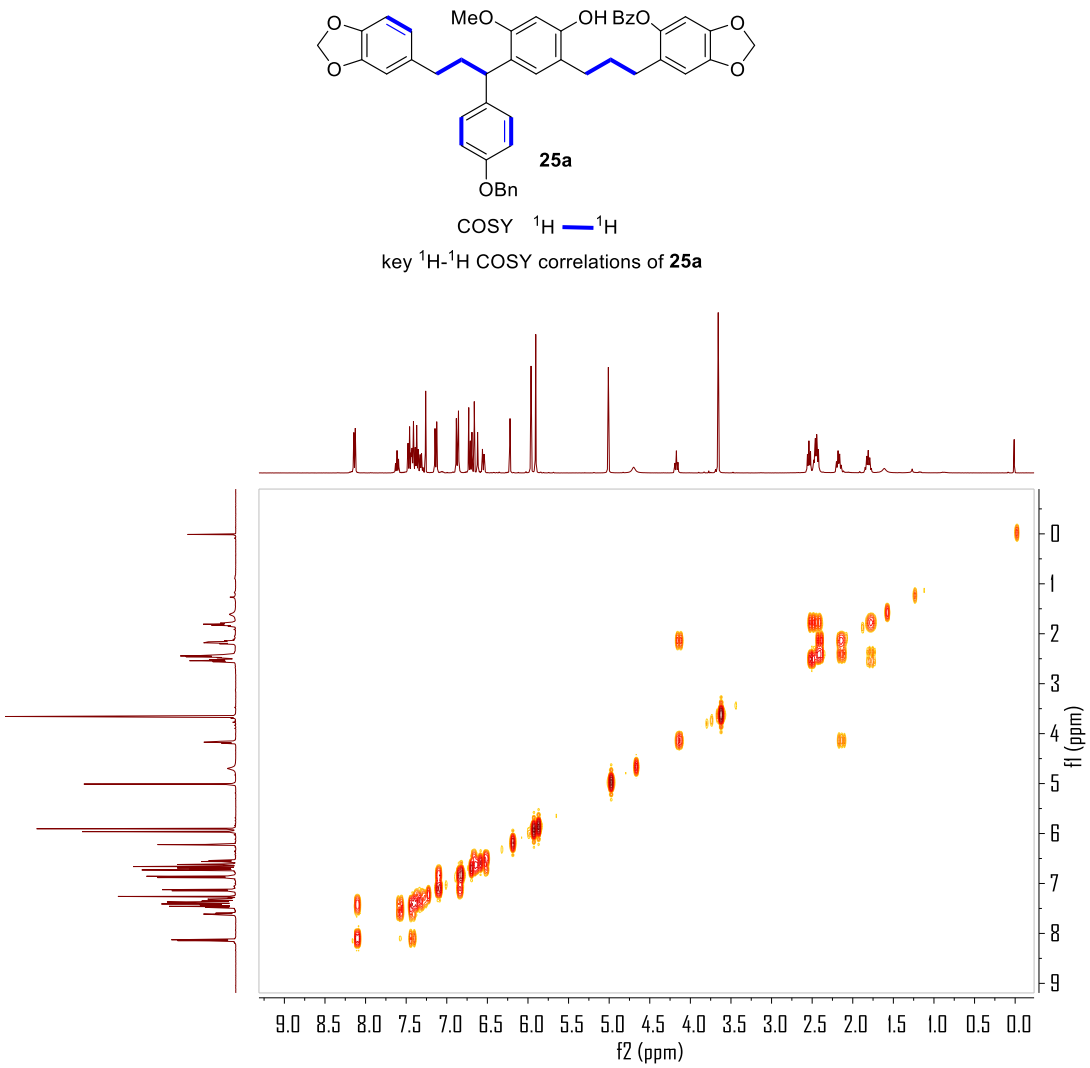
^{13}C NMR (100 MHz, $CDCl_3$) of compound **25a**



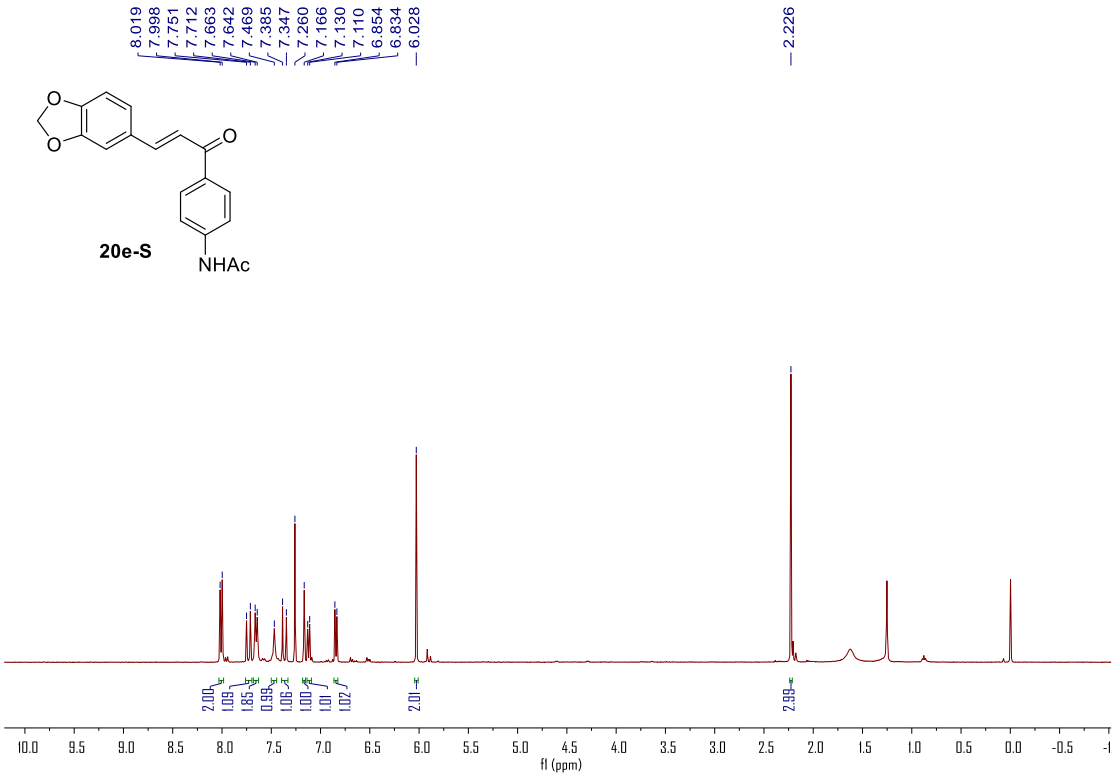
HSQC spectrum (400 MHz, $CDCl_3$)of compound **25a**



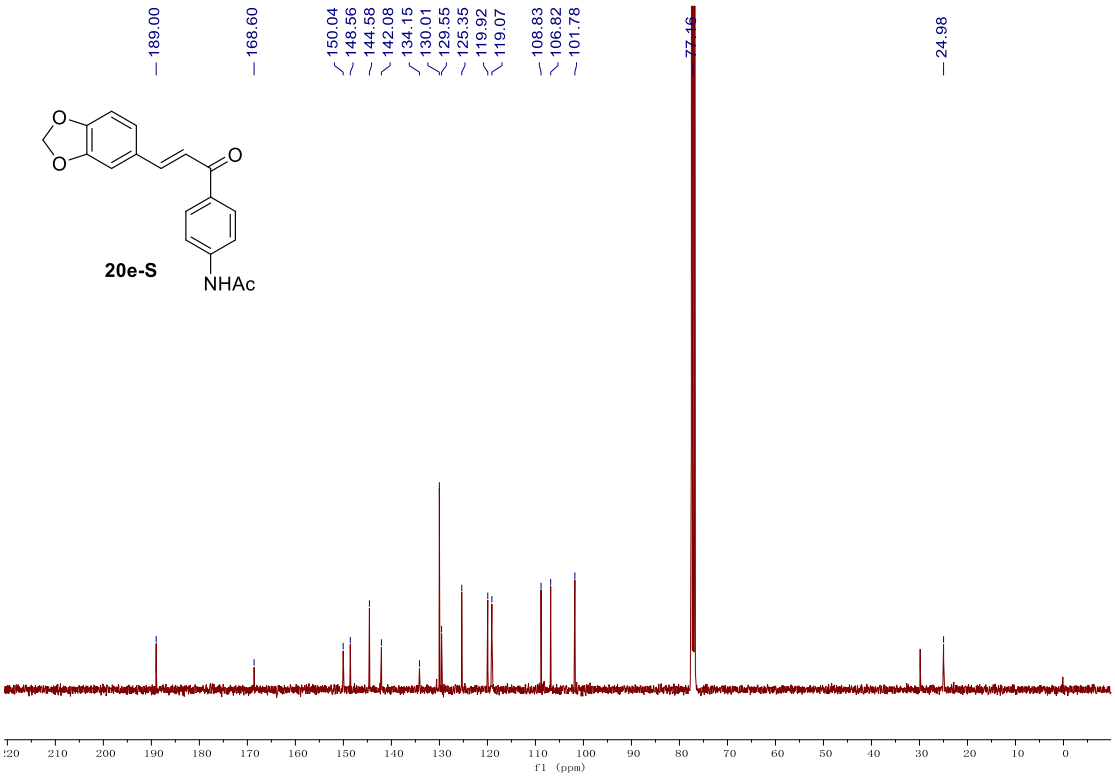
HMBC spectrum (400 MHz, $CDCl_3$) of compound **25a**



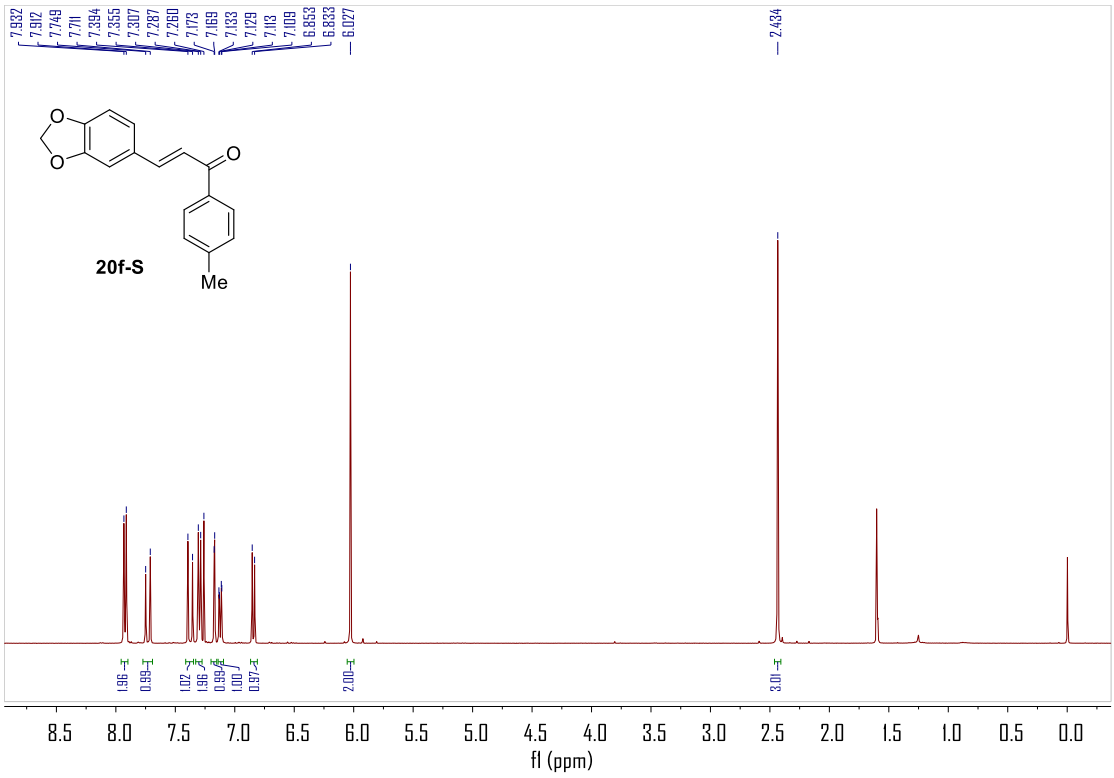
^{1}H-^{1}H COSY spectrum (400 MHz, $CDCl_3$) of compound **25a**



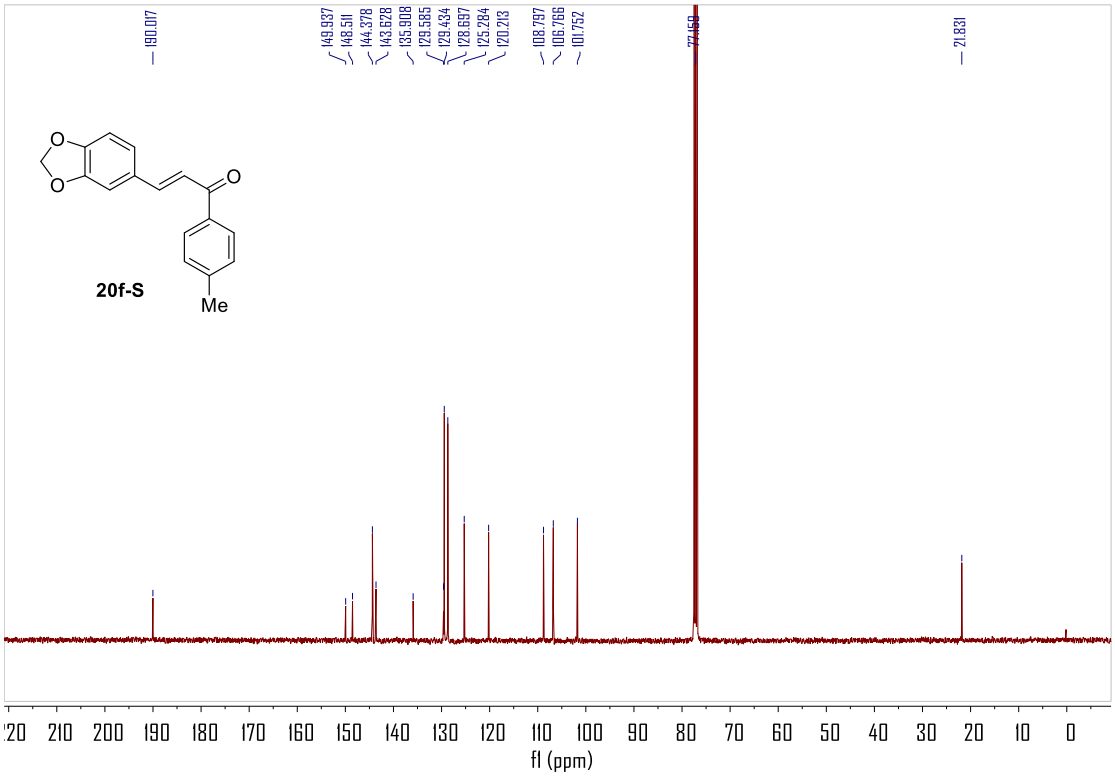
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20e-S**



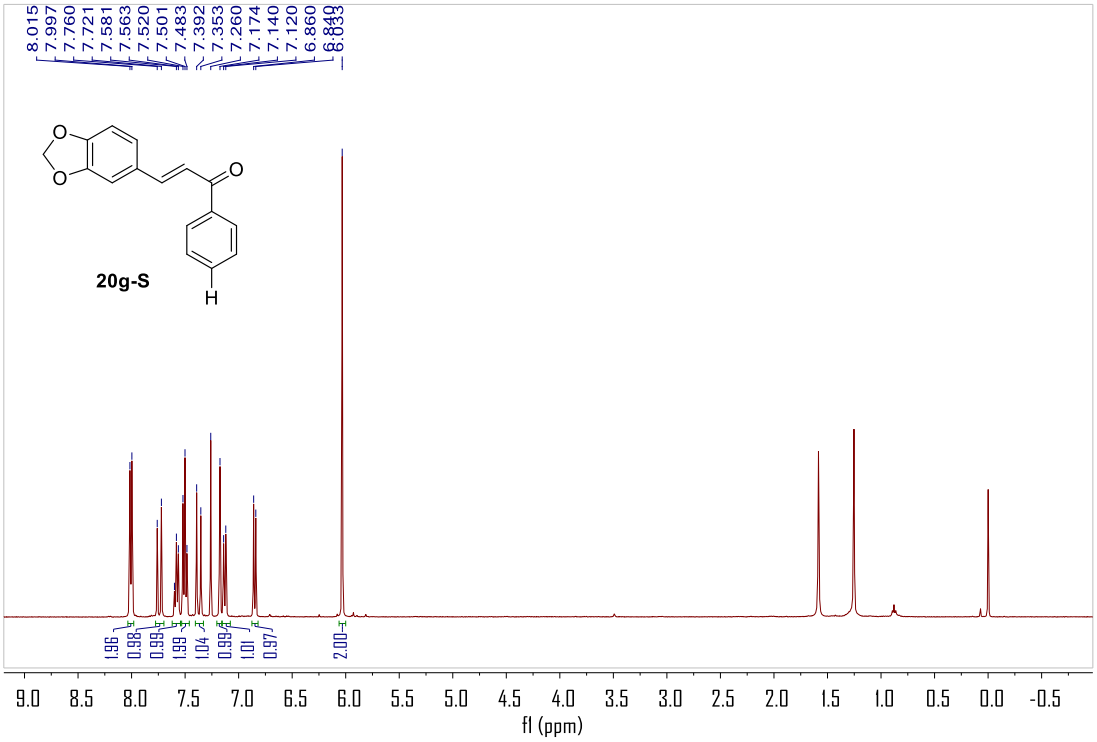
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20e-S**



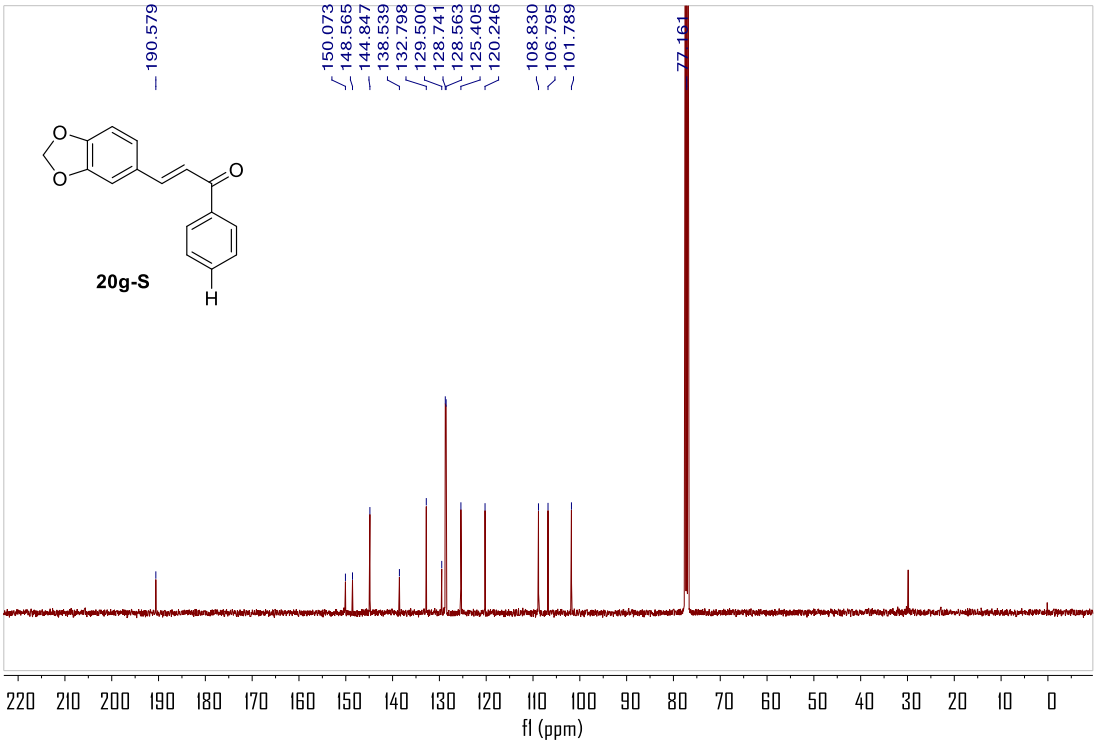
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20f-S**



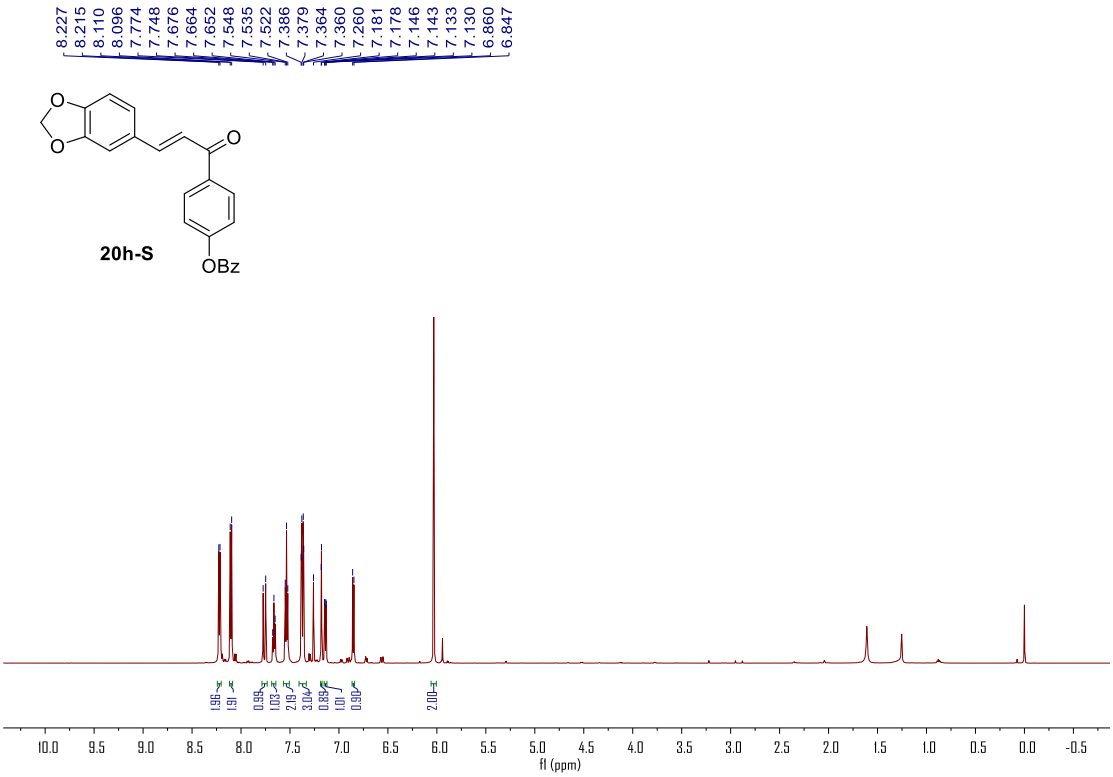
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20f-S**



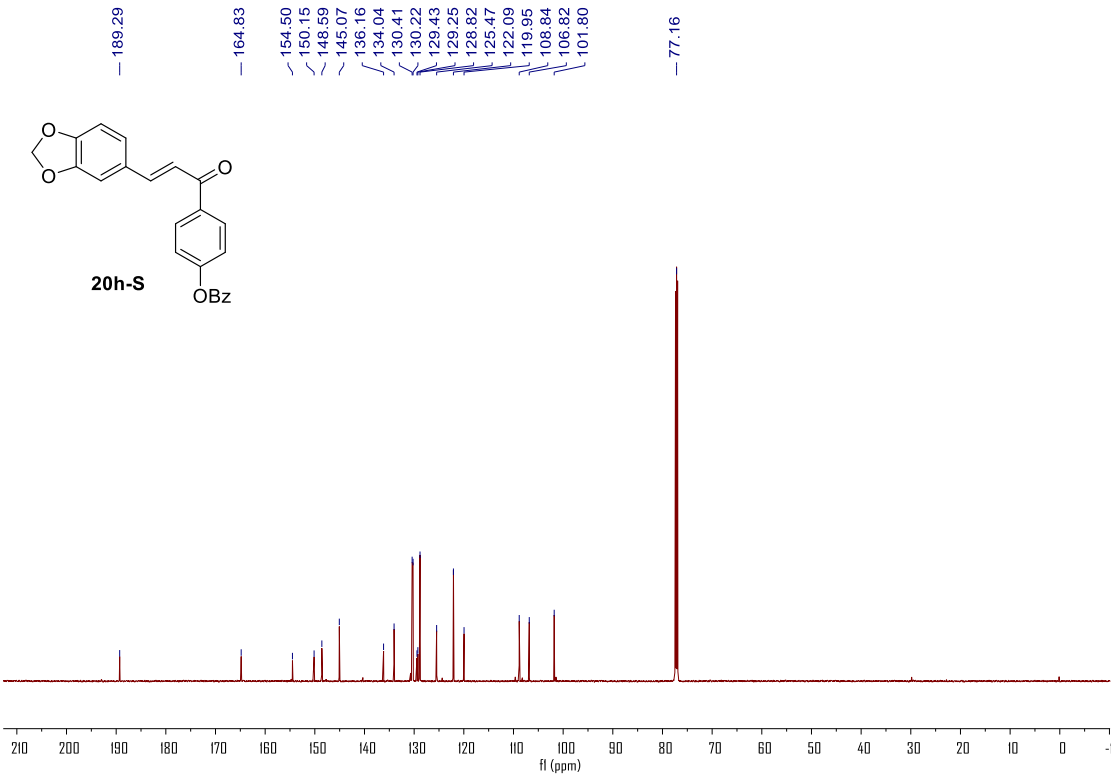
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20g-S**



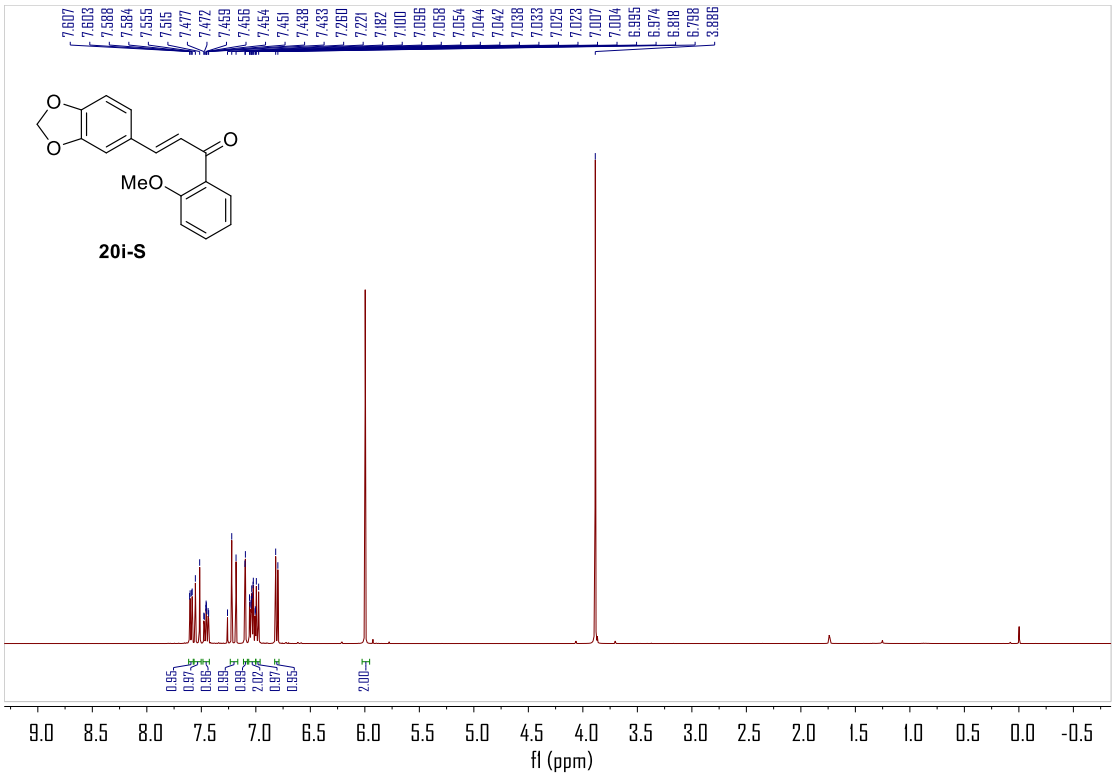
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20g-S**



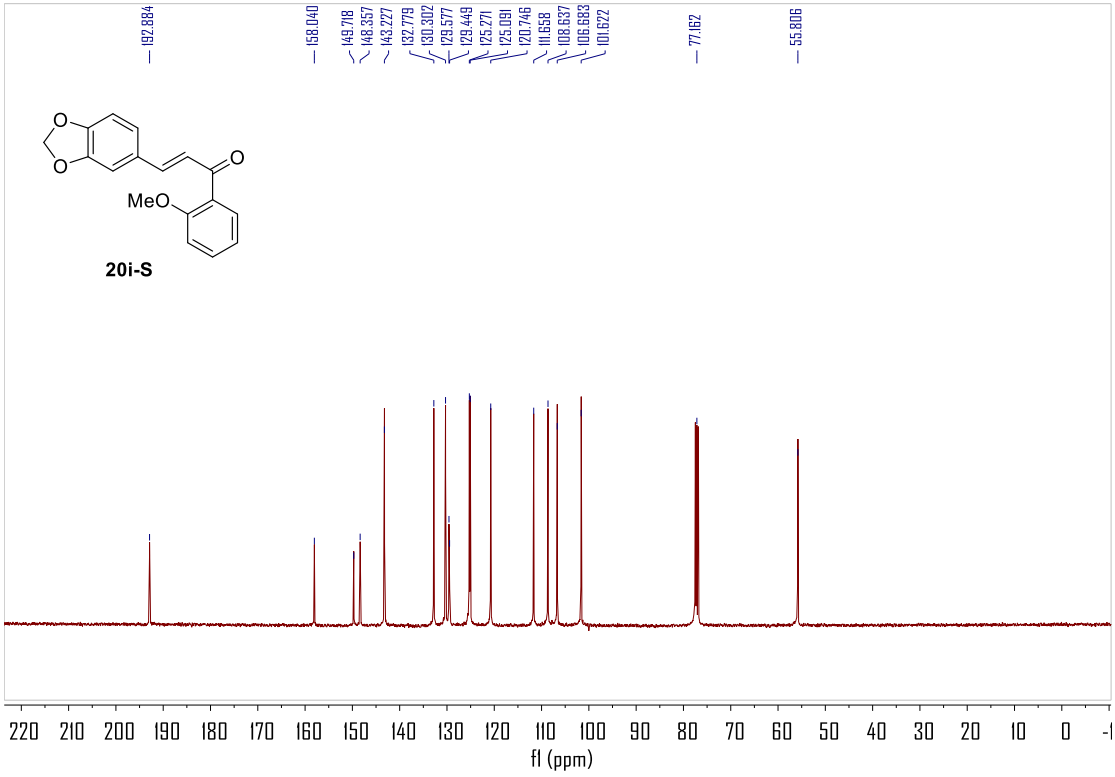
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **20h-S**



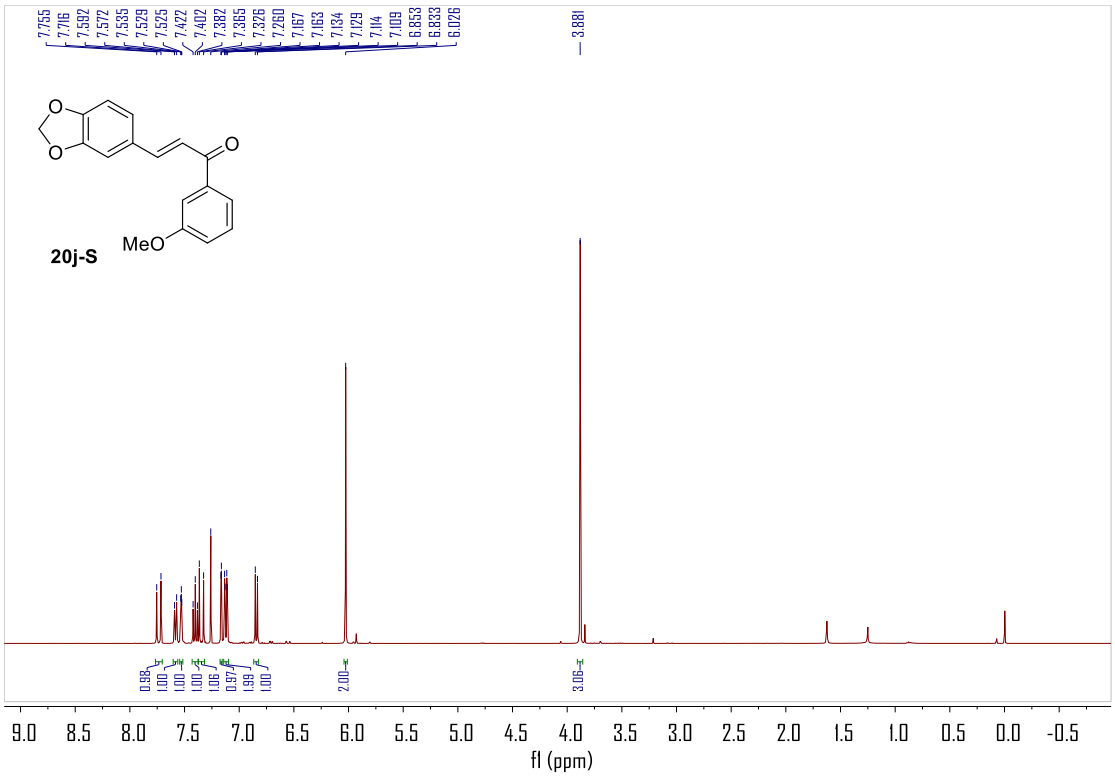
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **20h-S**



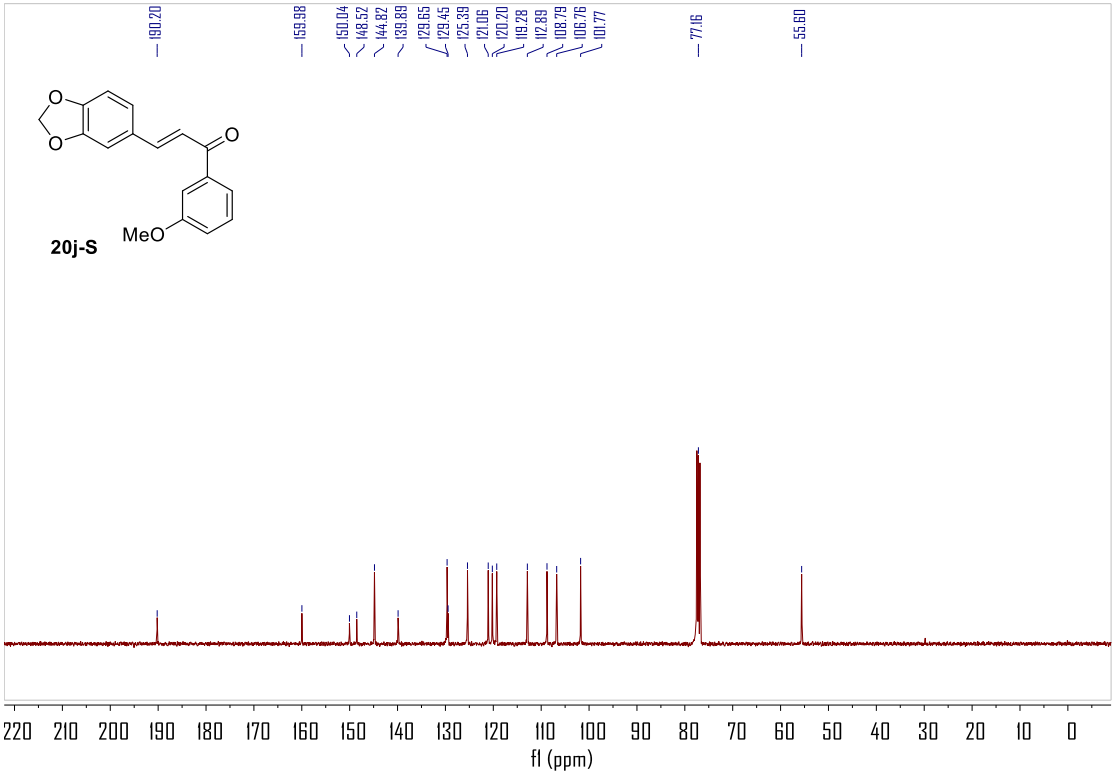
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20i-S**



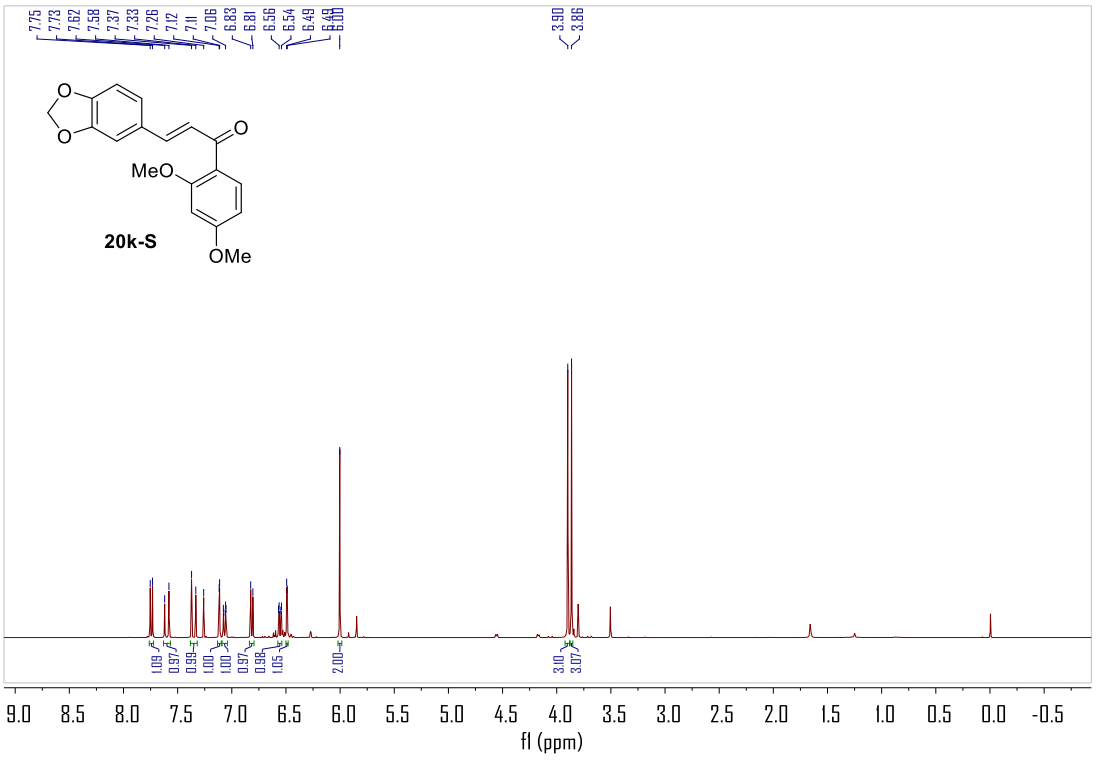
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20i-S**



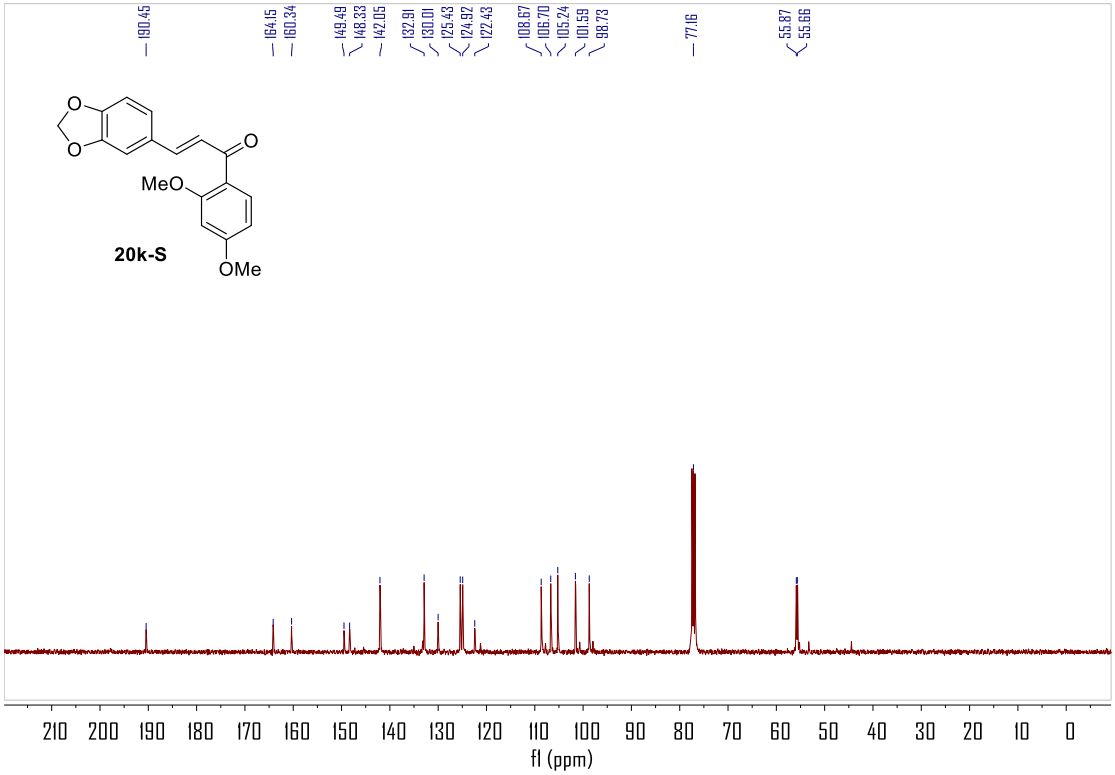
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20j-S**



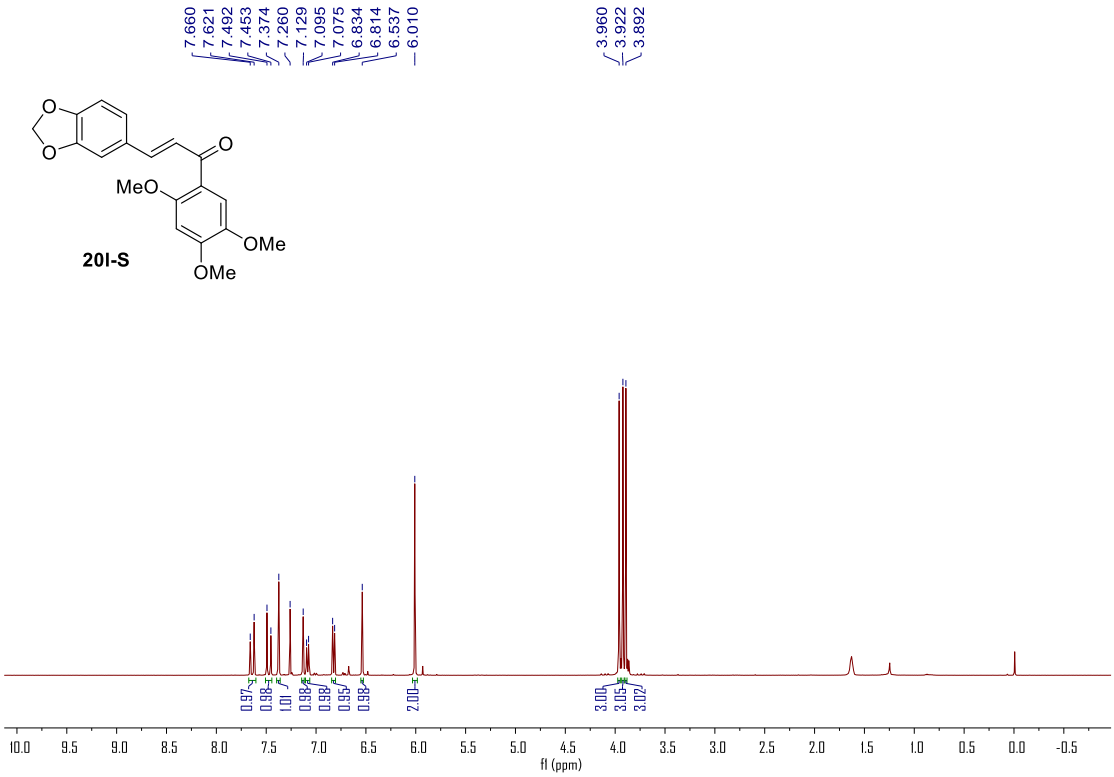
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20j-S**



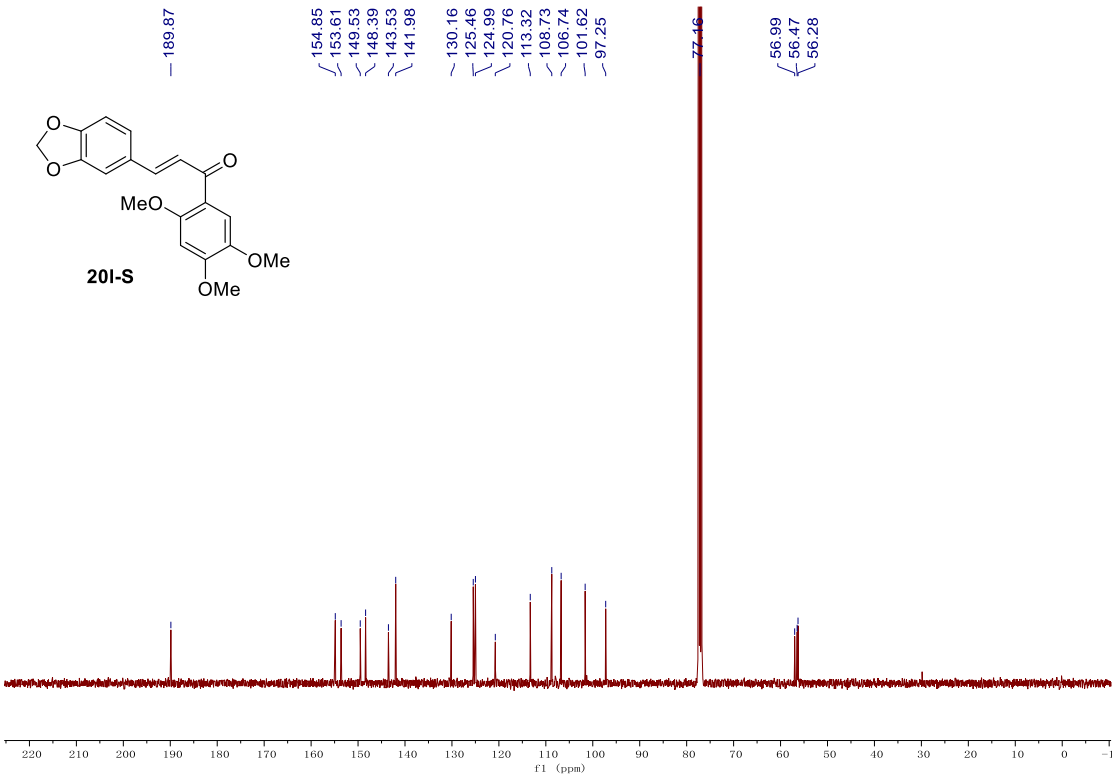
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20k-S**



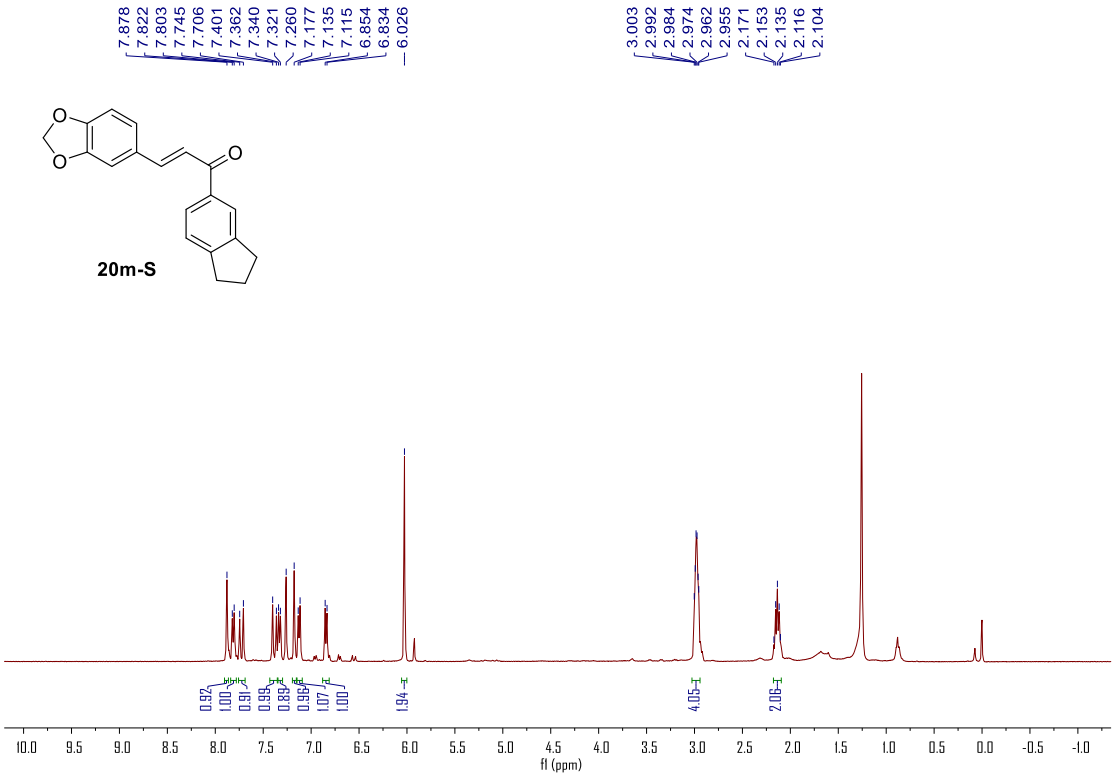
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20k-S**



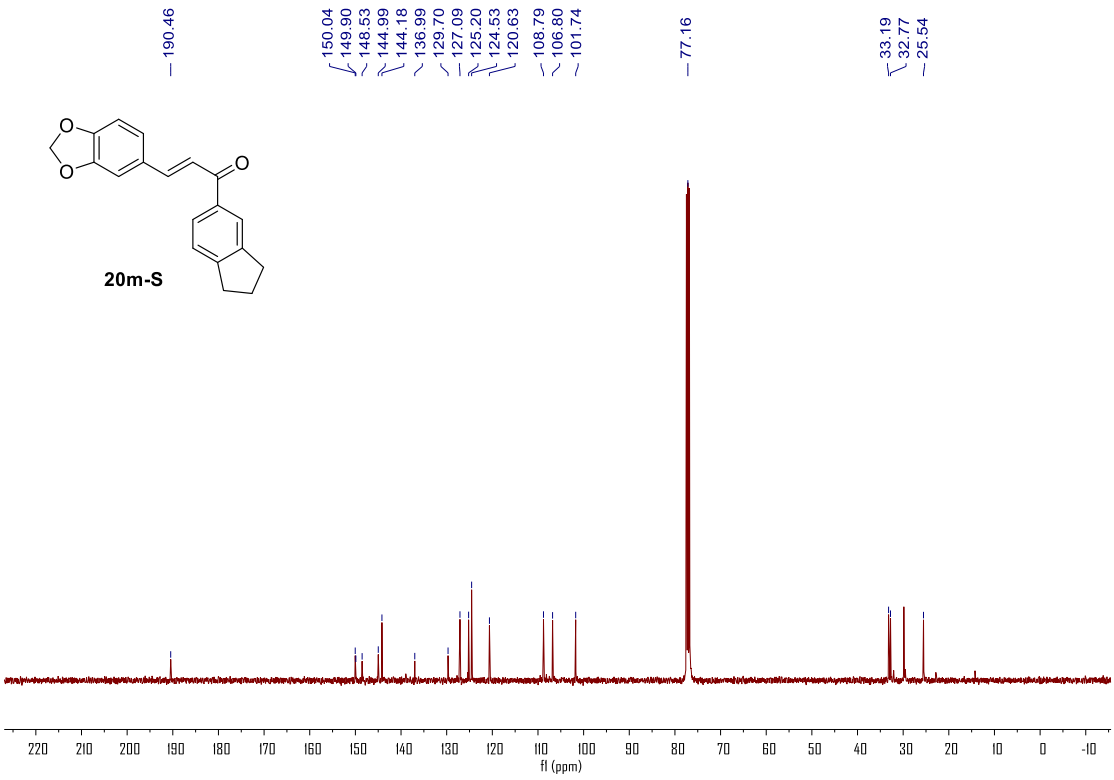
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20l-S**



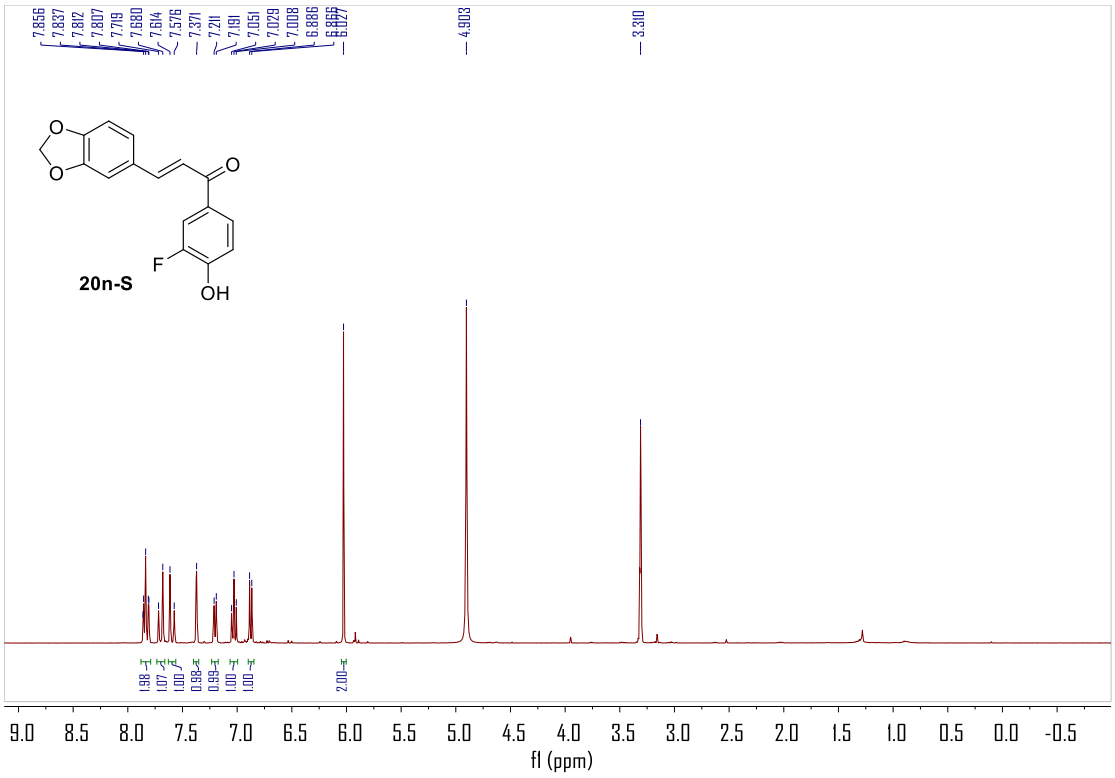
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20l-S**



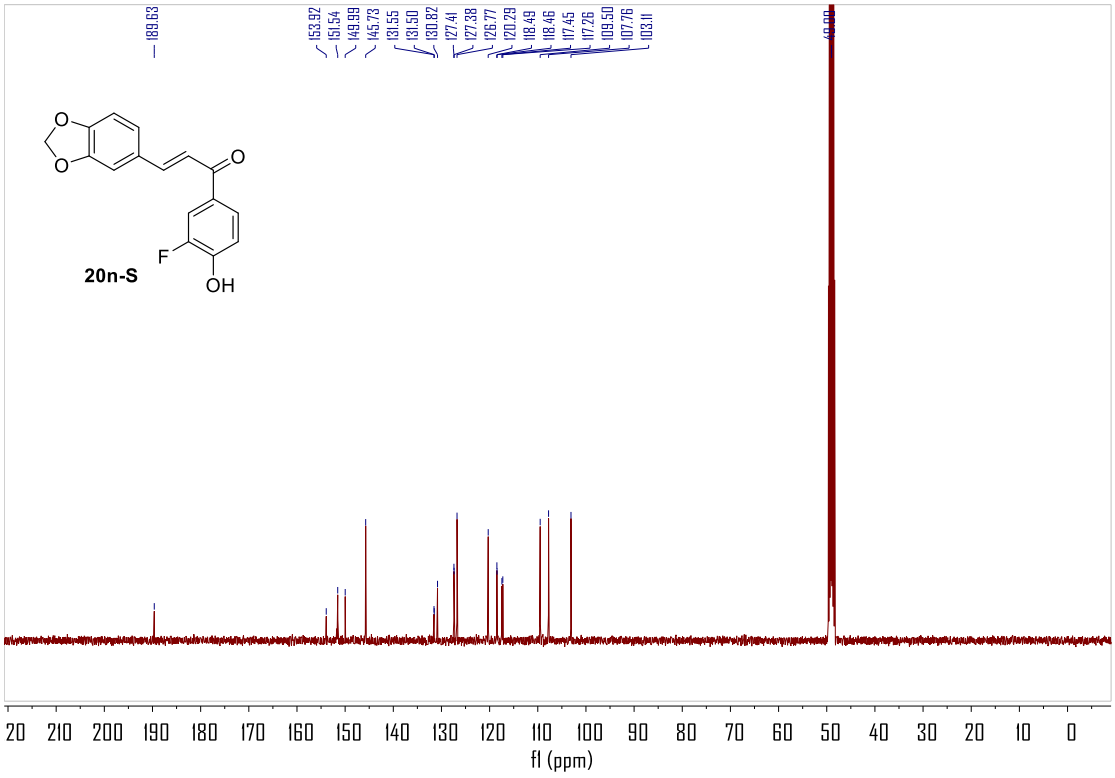
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20m-S**



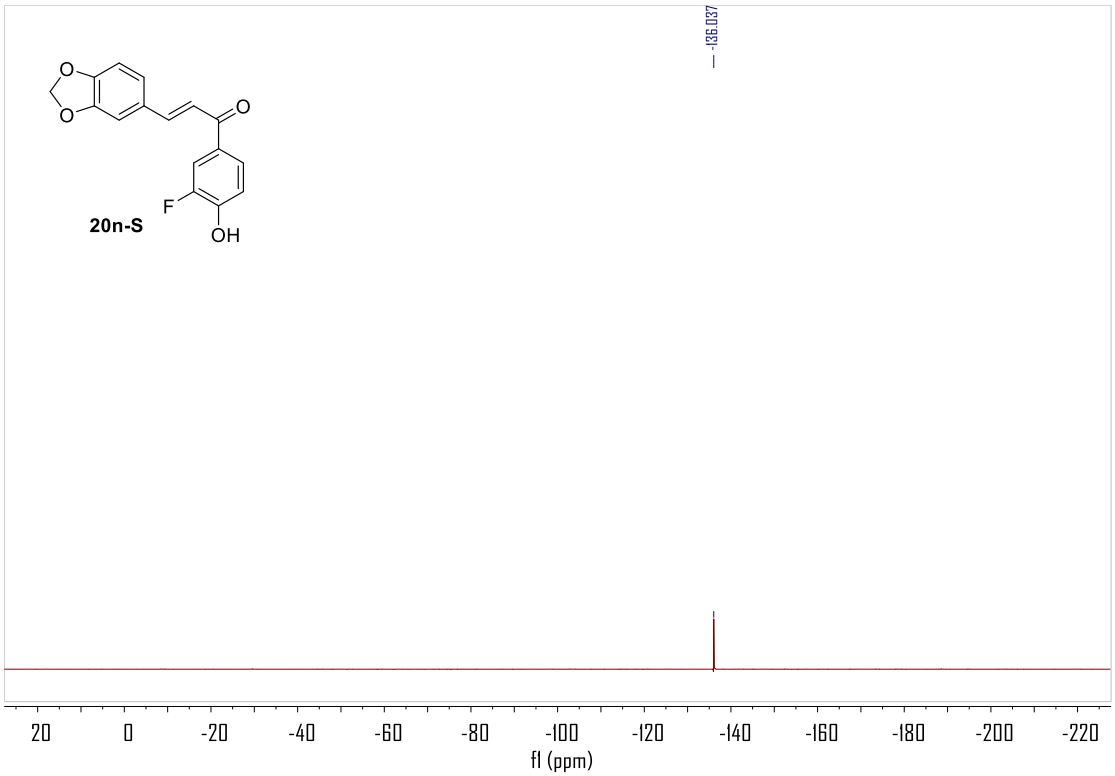
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20m-S**



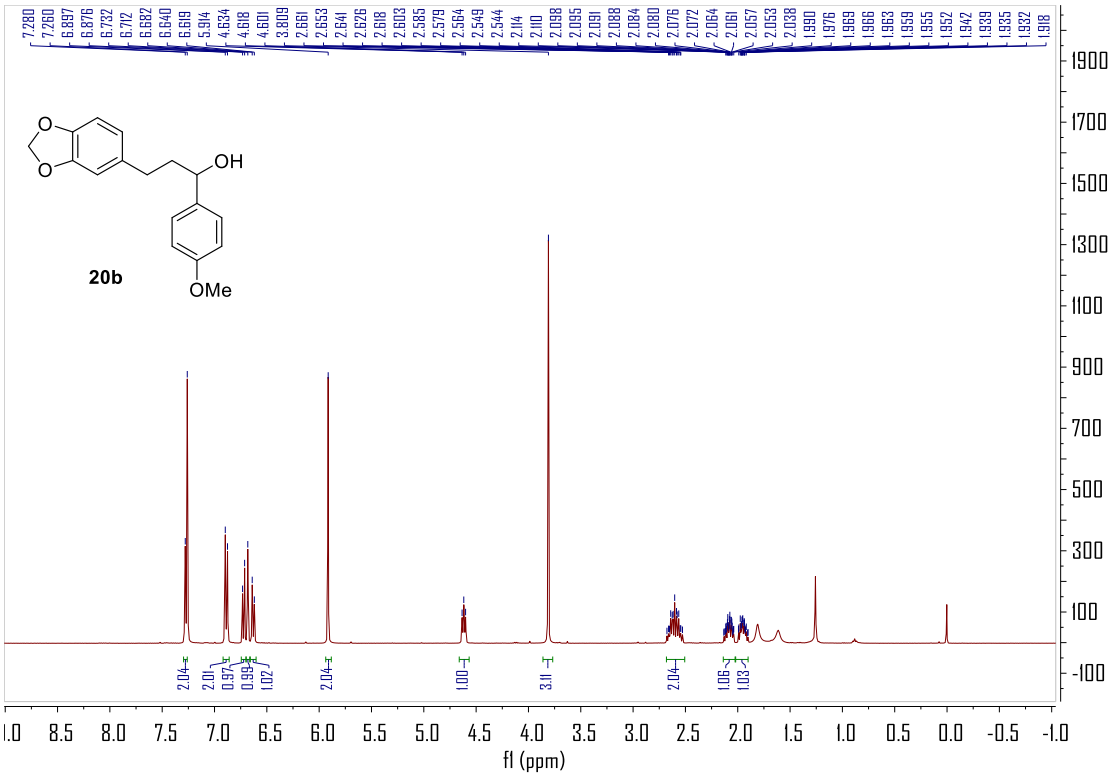
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20n-S**



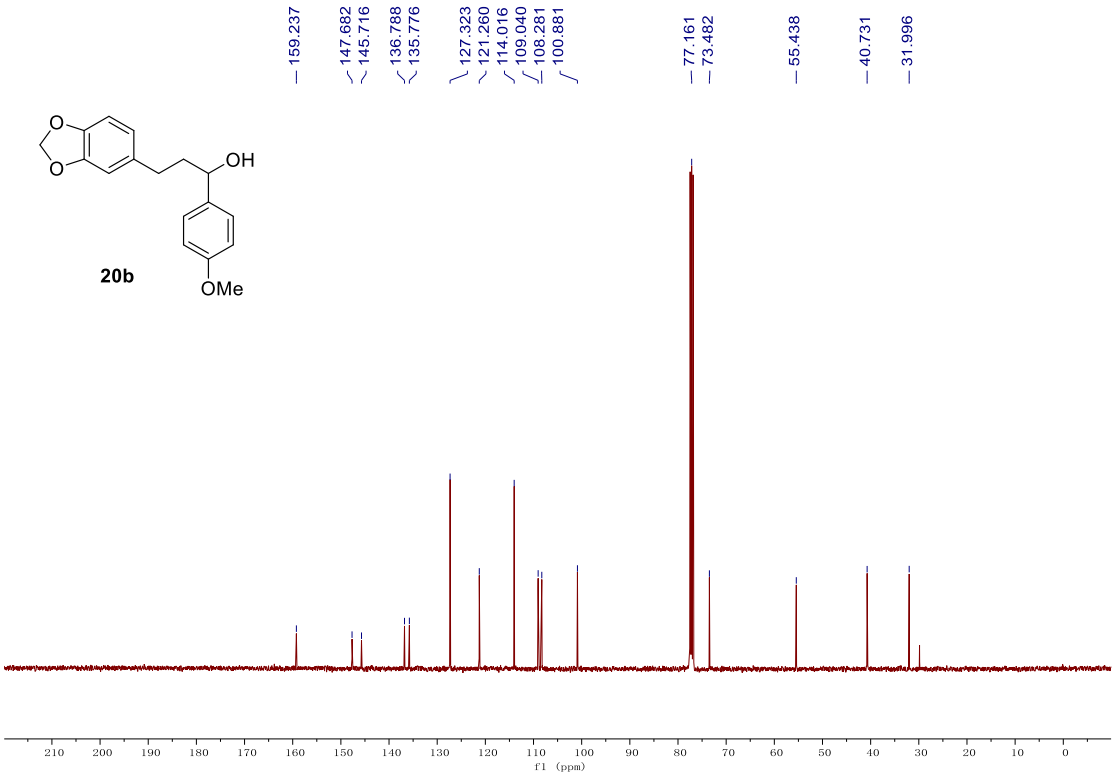
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20n-S**



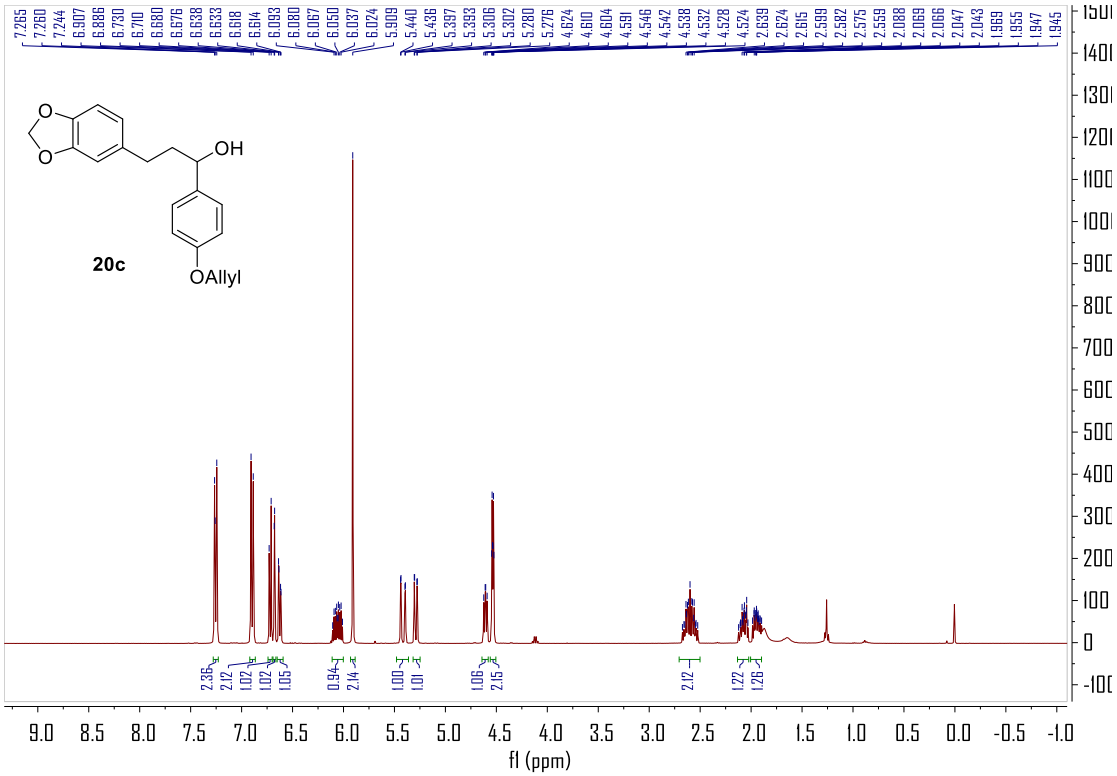
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **20n-S**



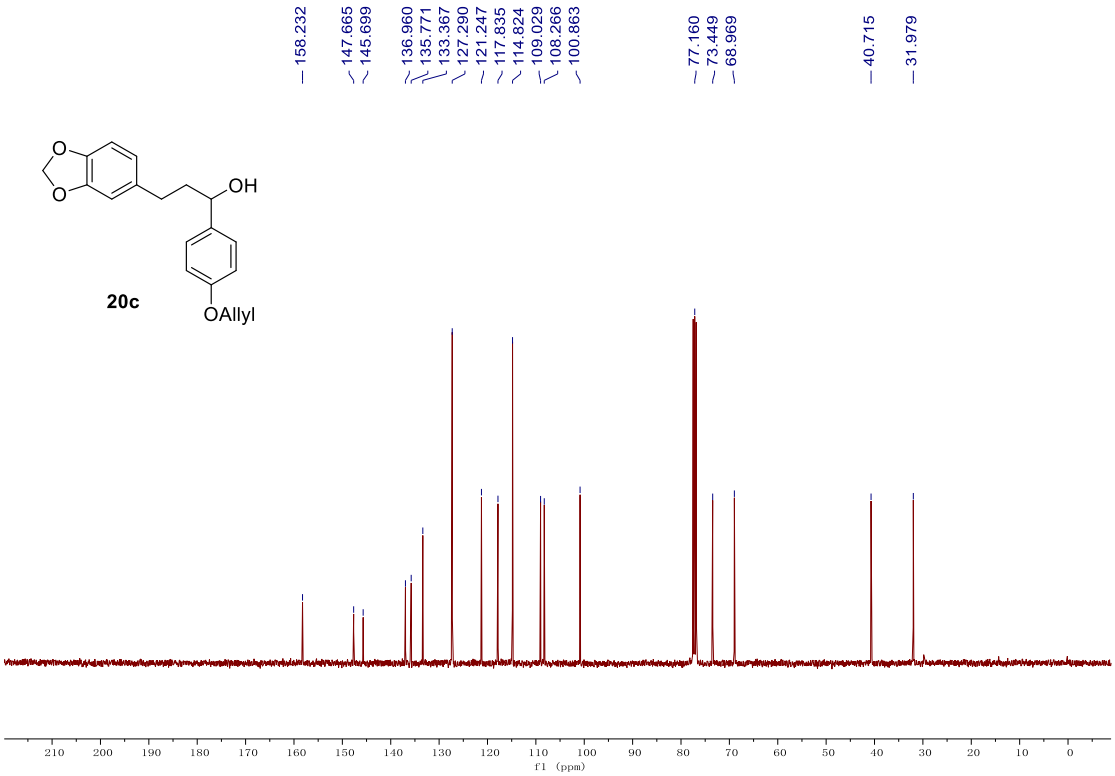
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20b**



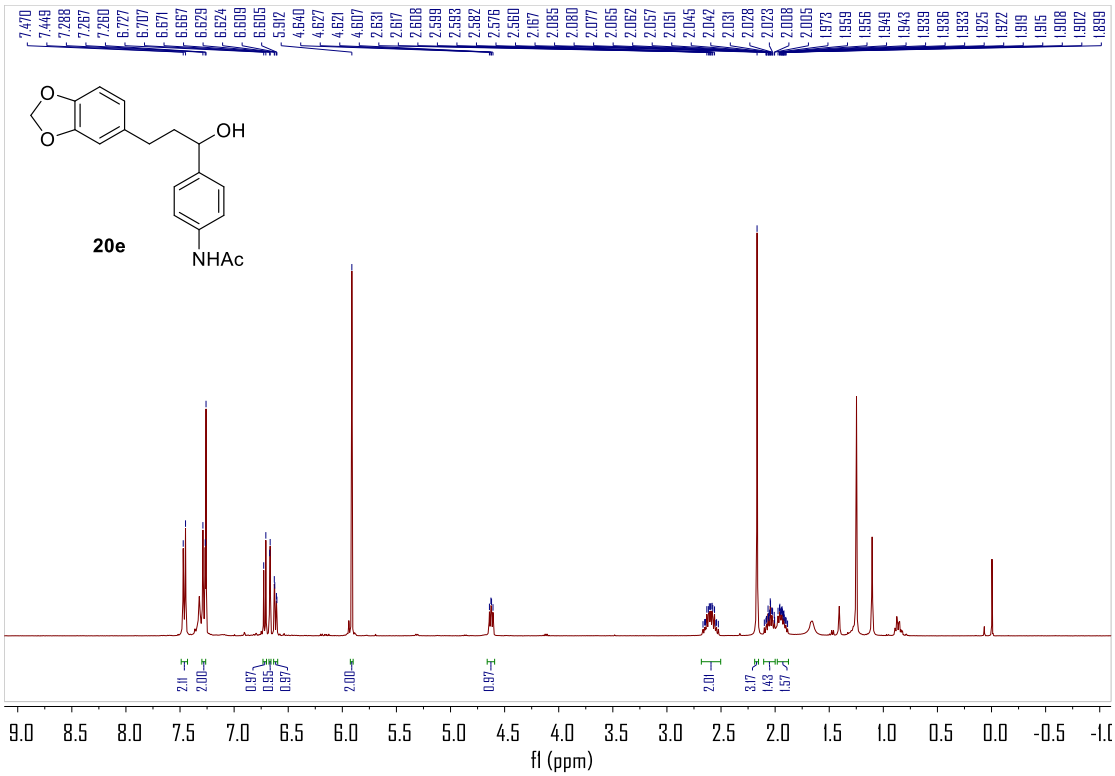
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20b**



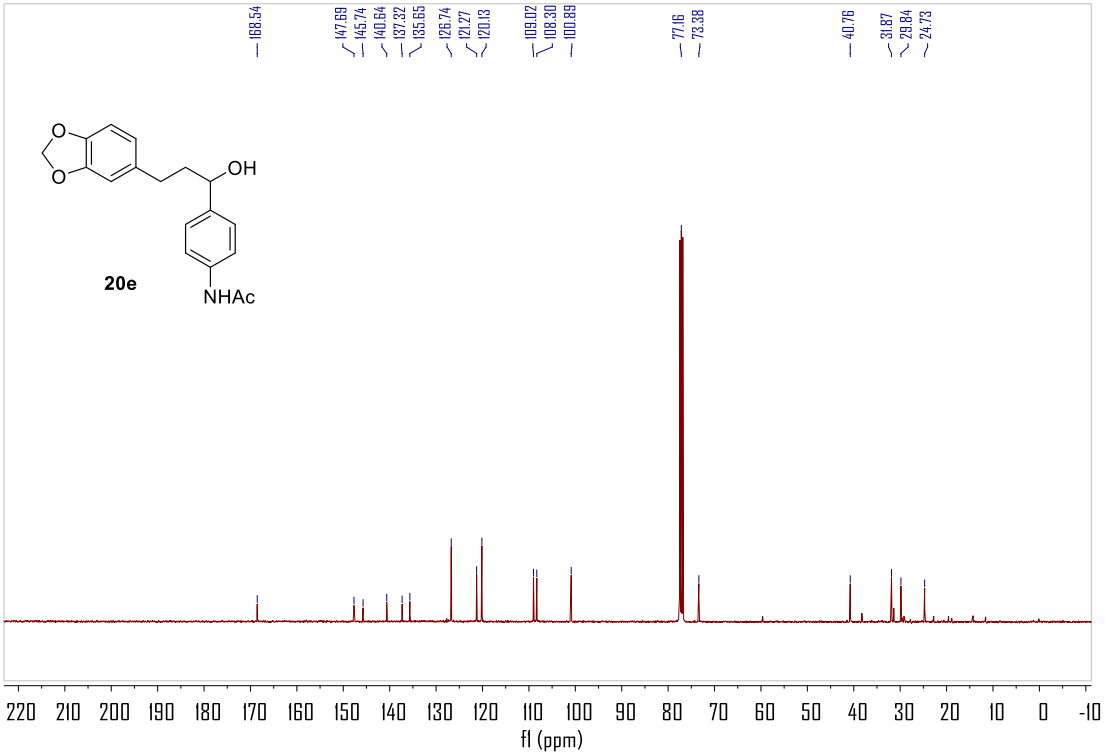
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20c**



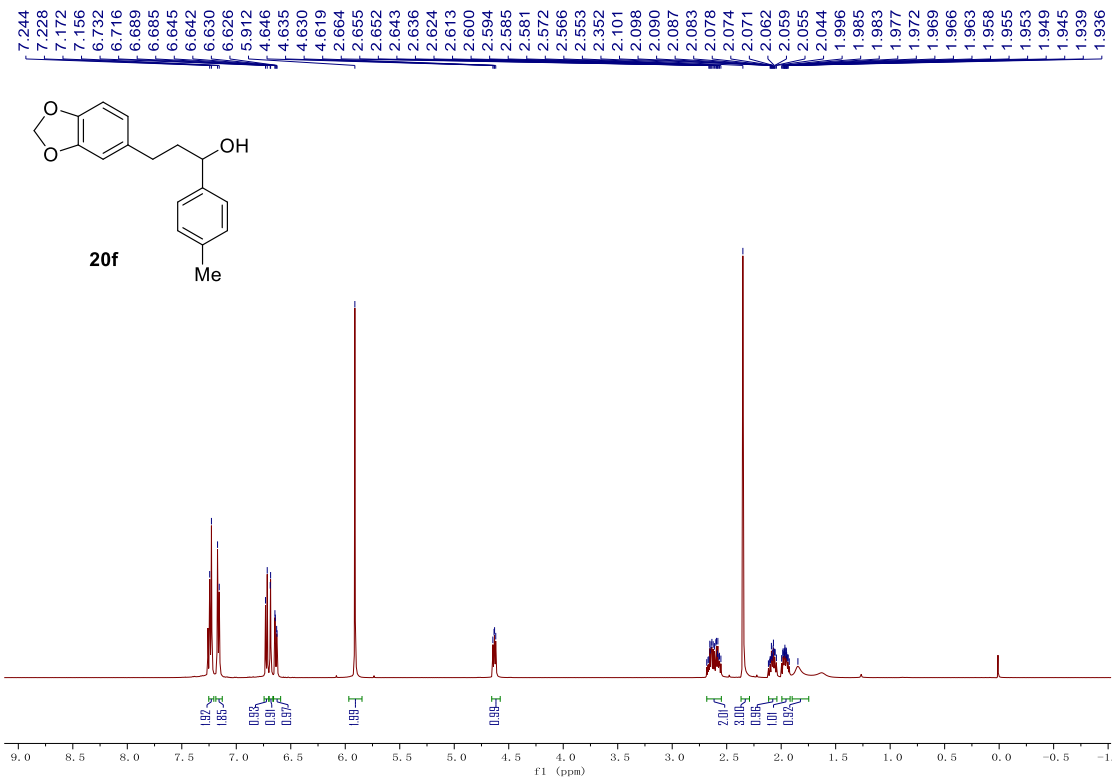
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20c**



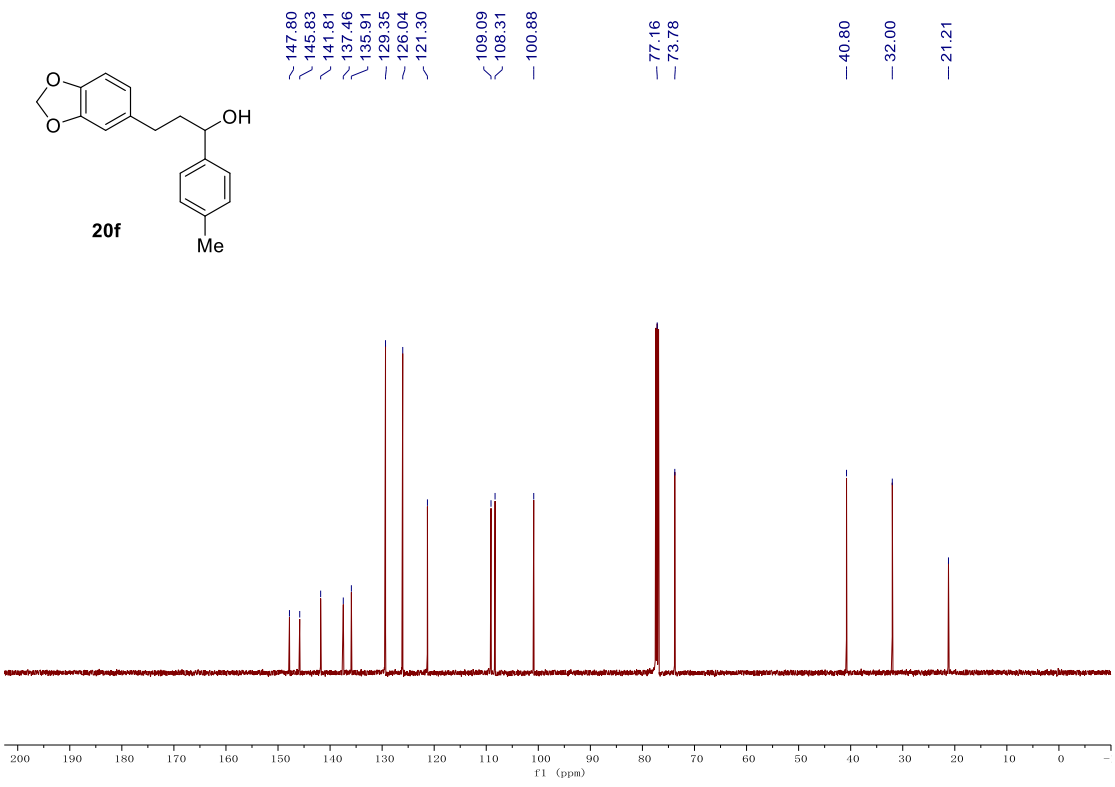
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20e**



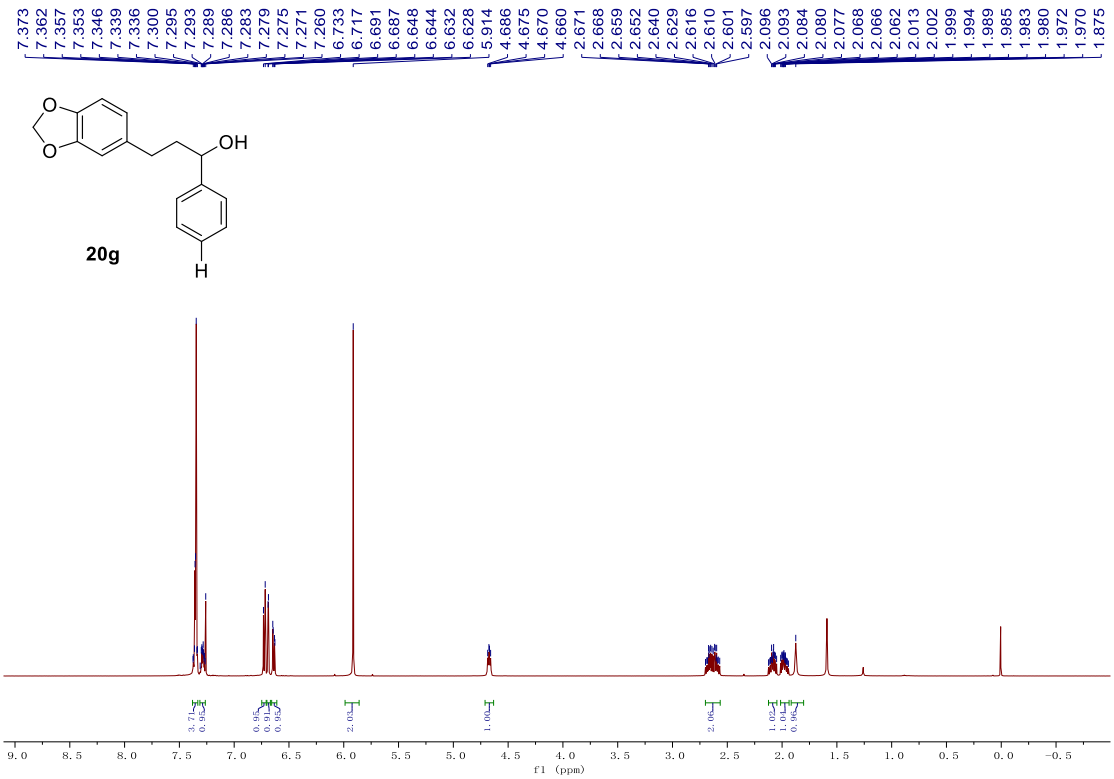
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20e**



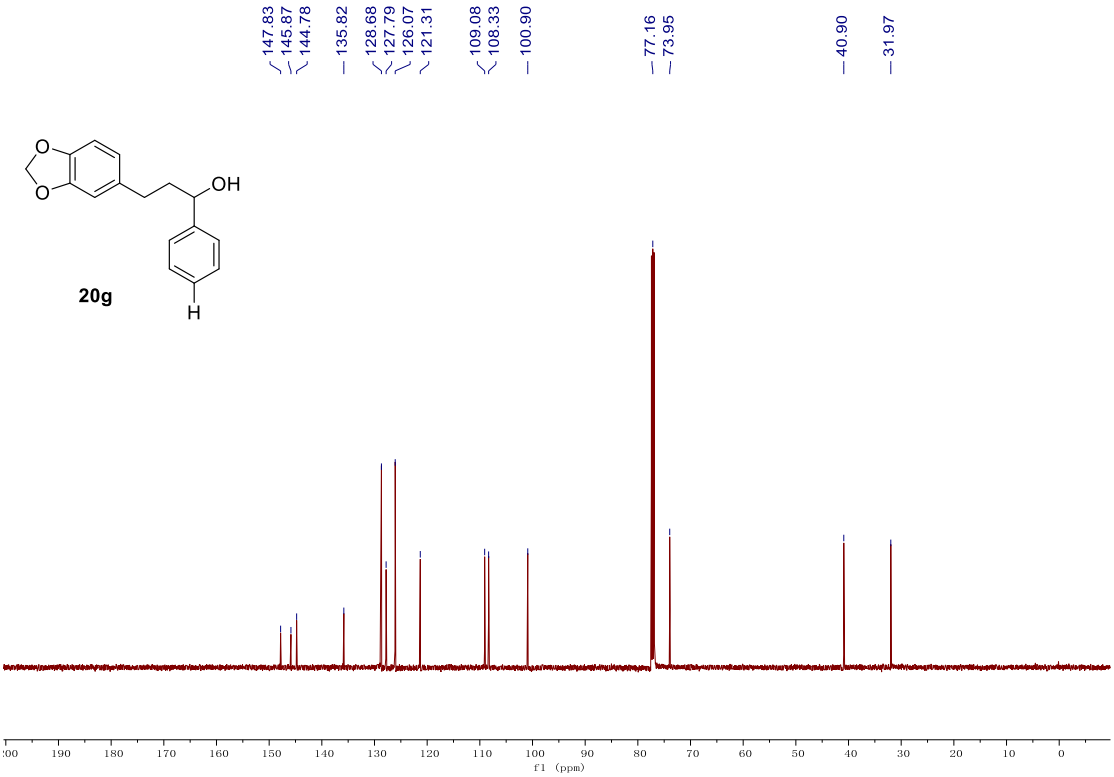
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **20f**



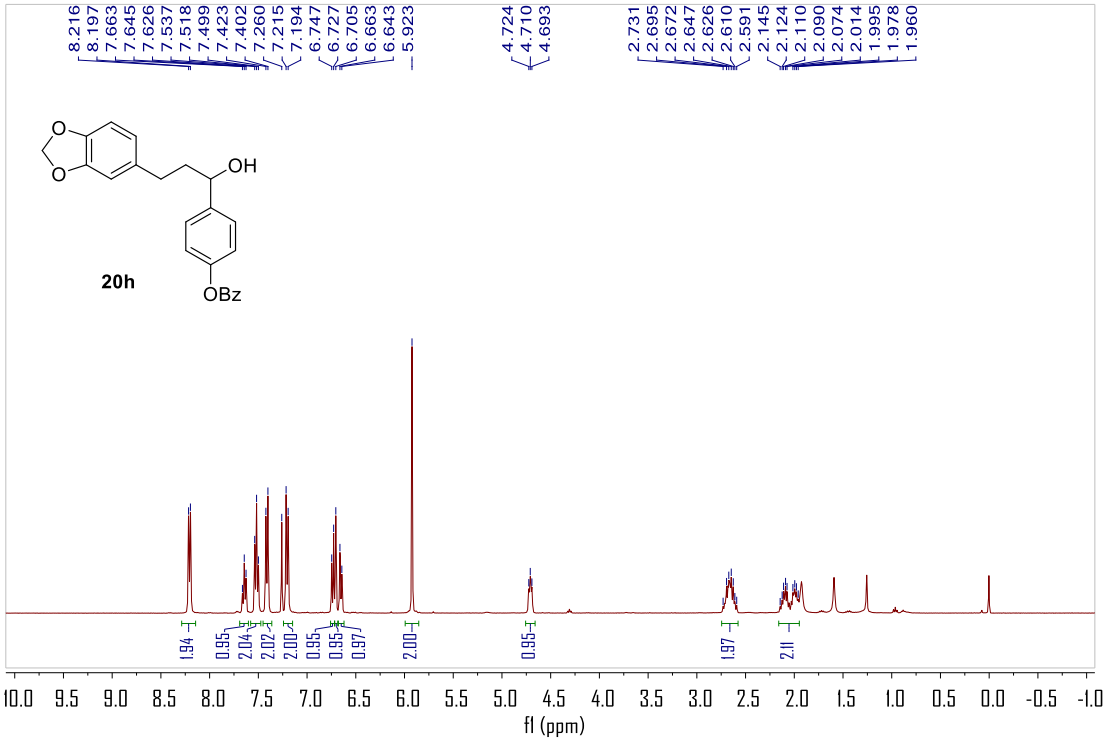
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **20f**



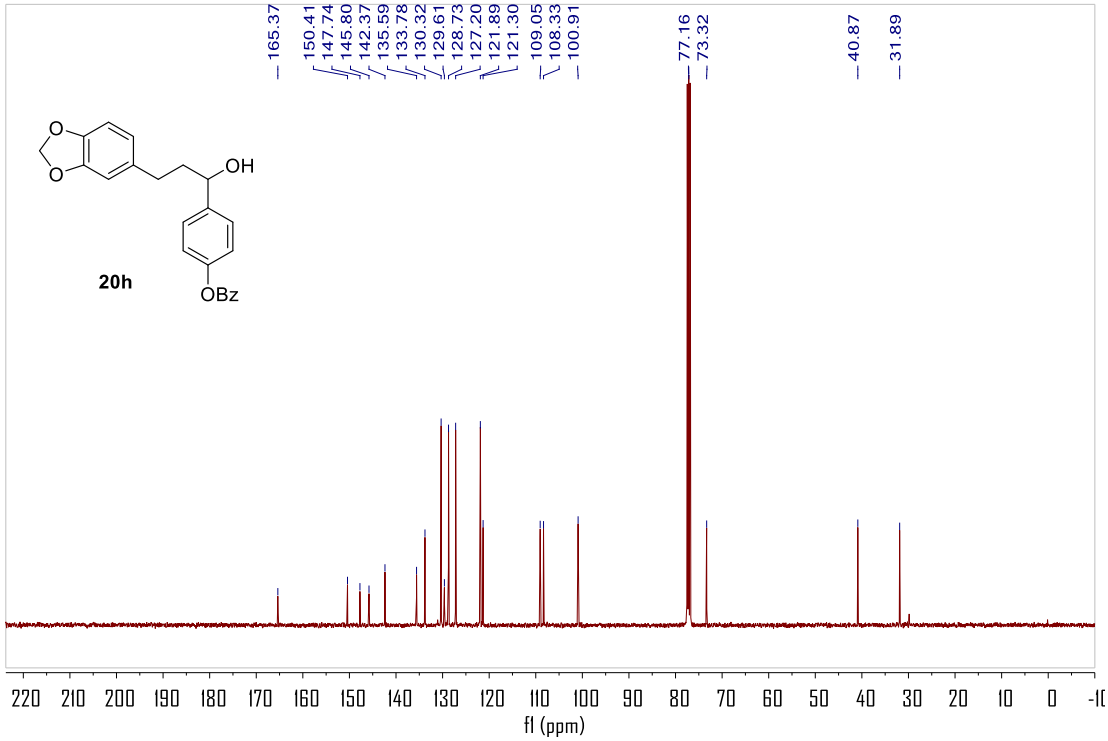
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **20g**



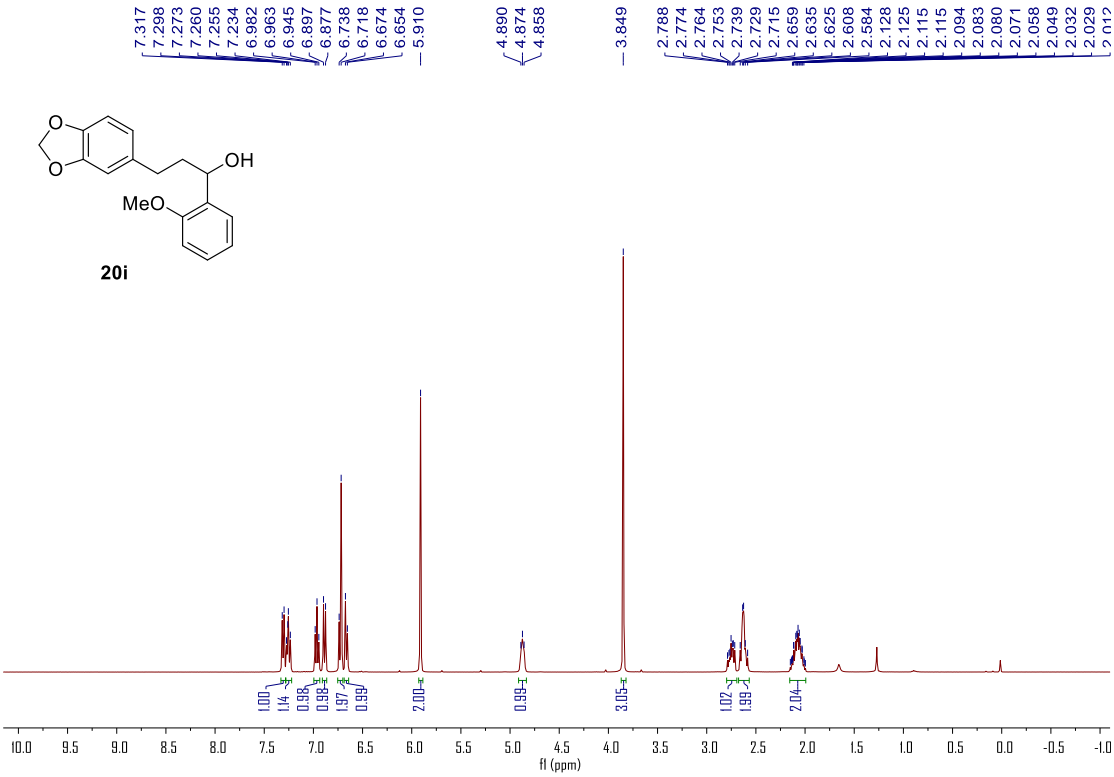
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **20g**



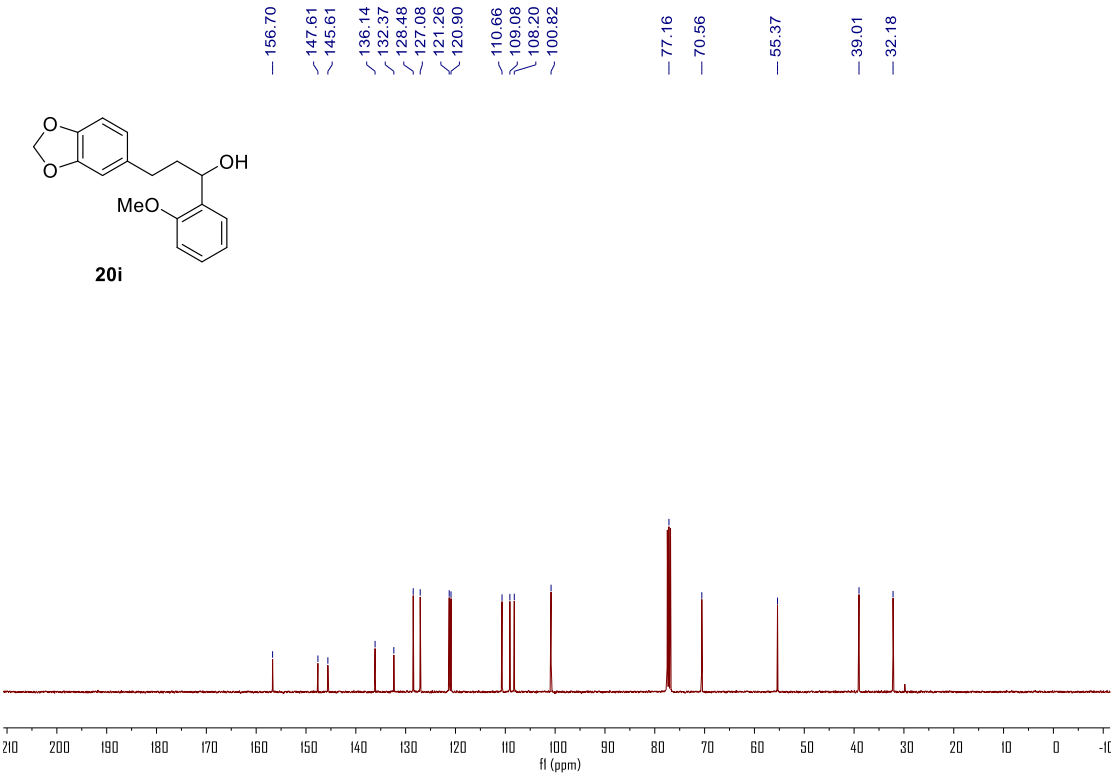
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20h**



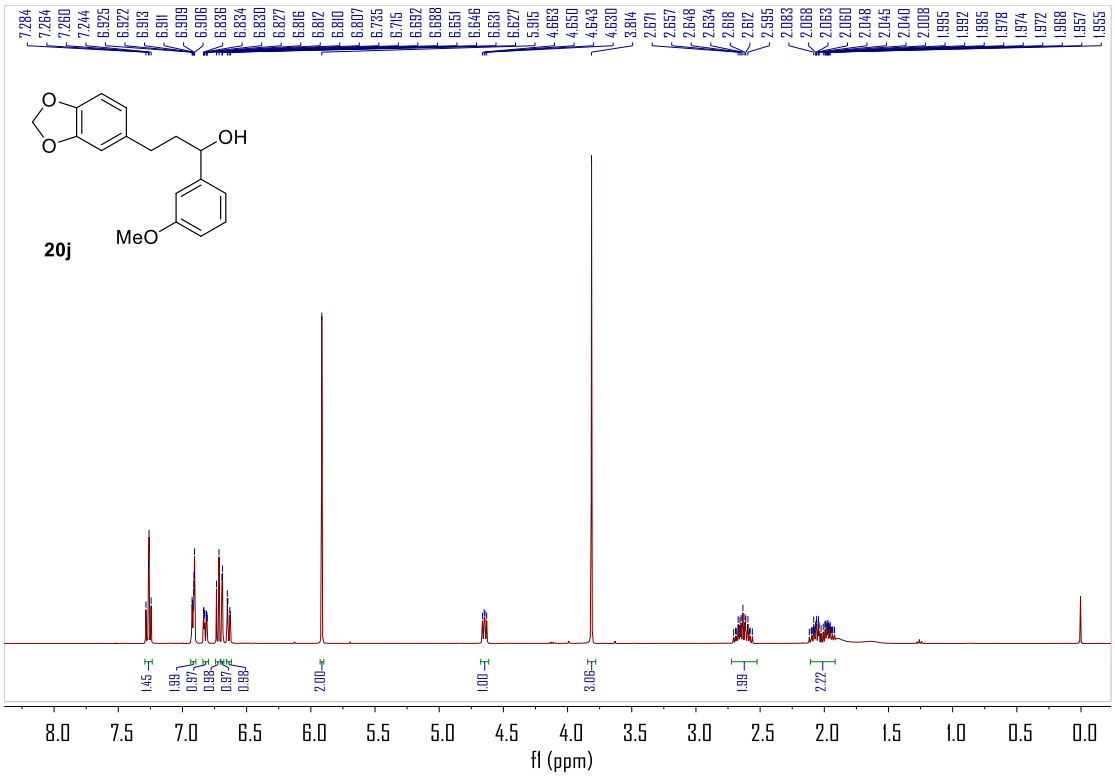
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20h**



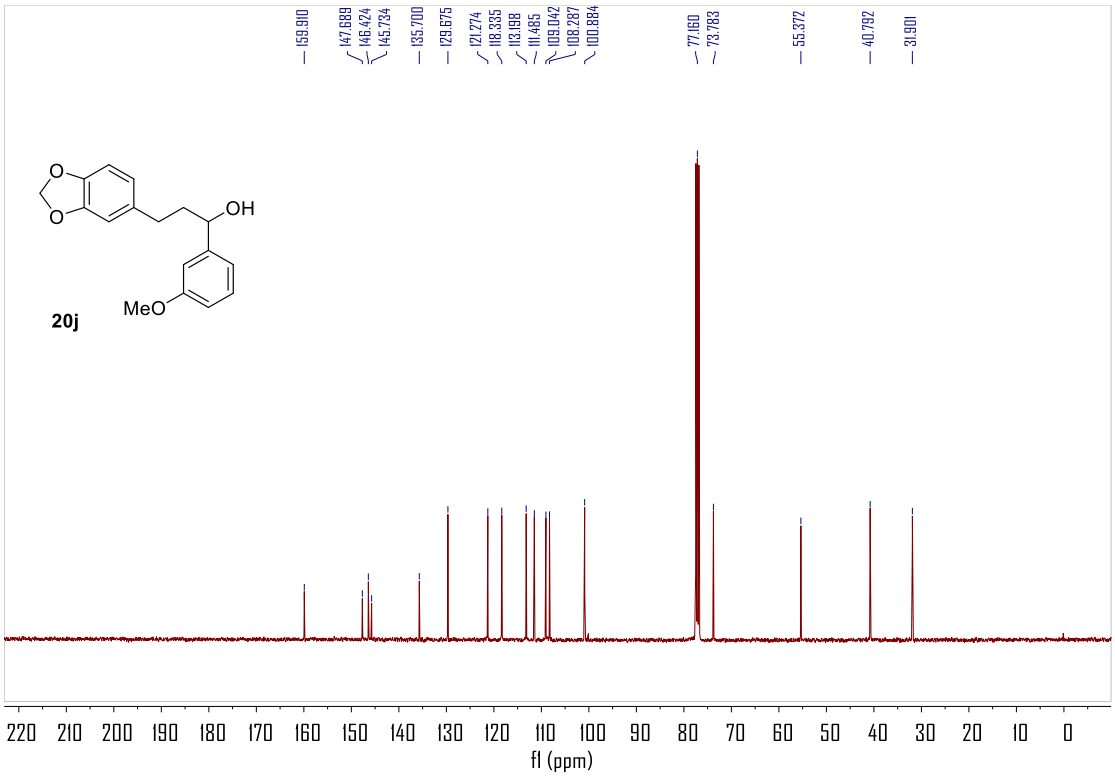
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20i**



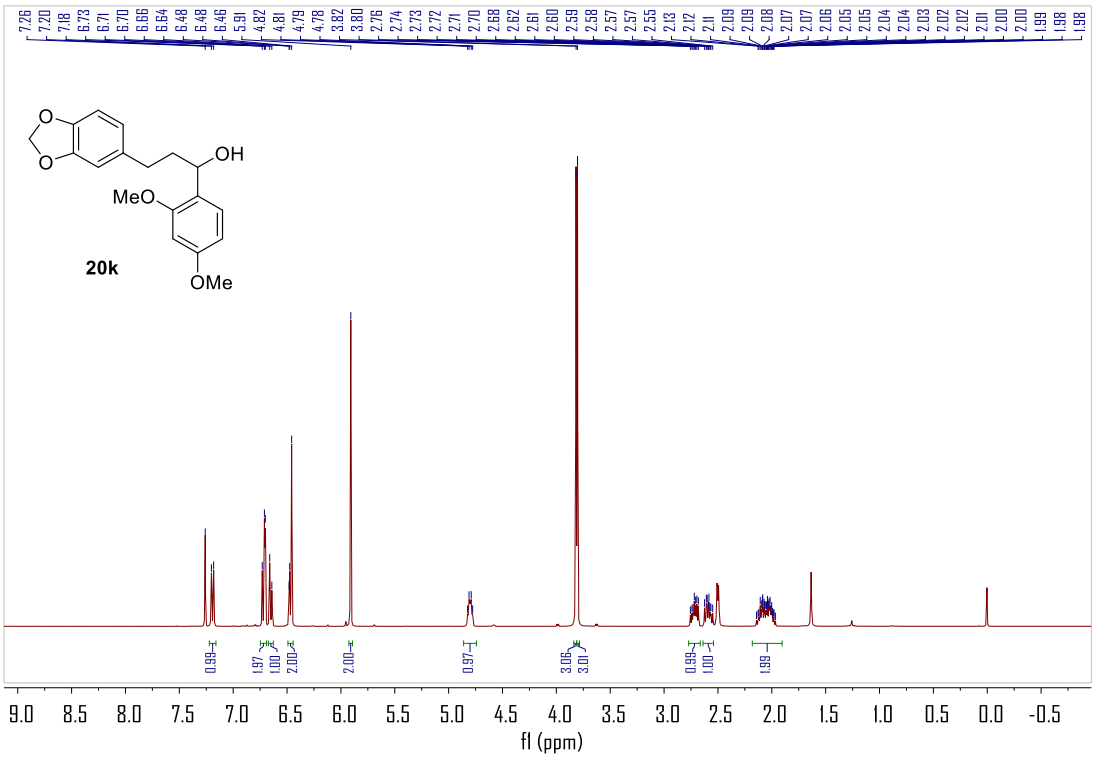
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20i**



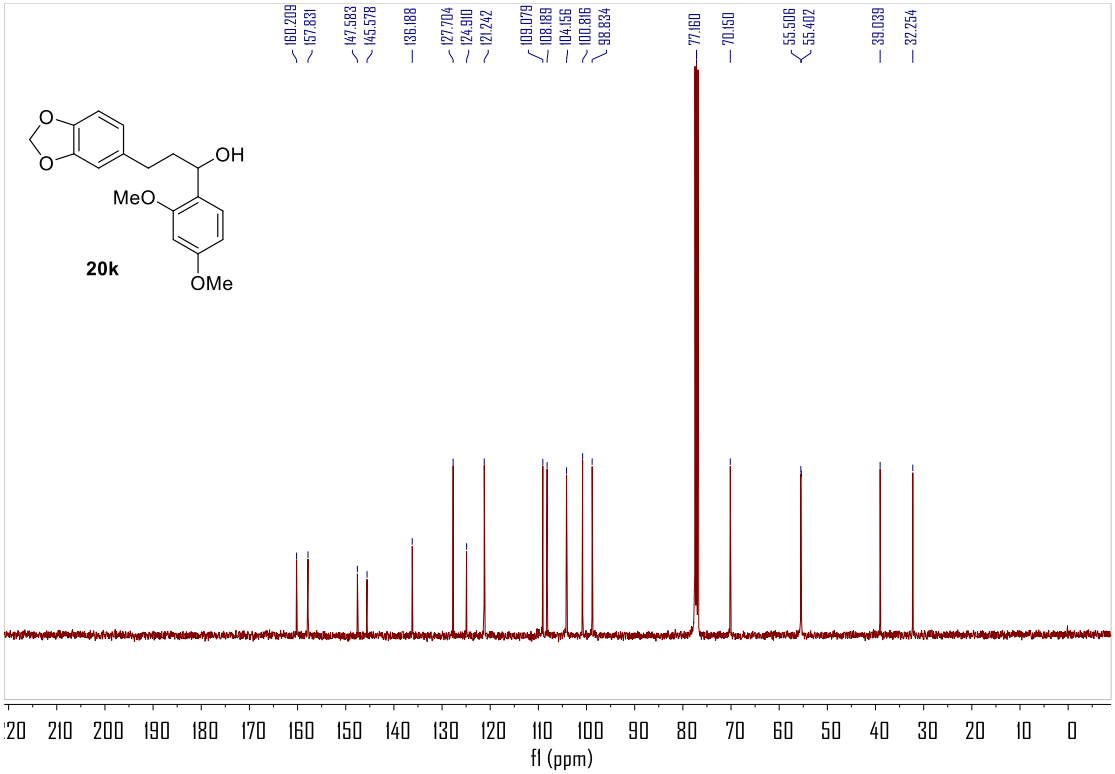
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20j**



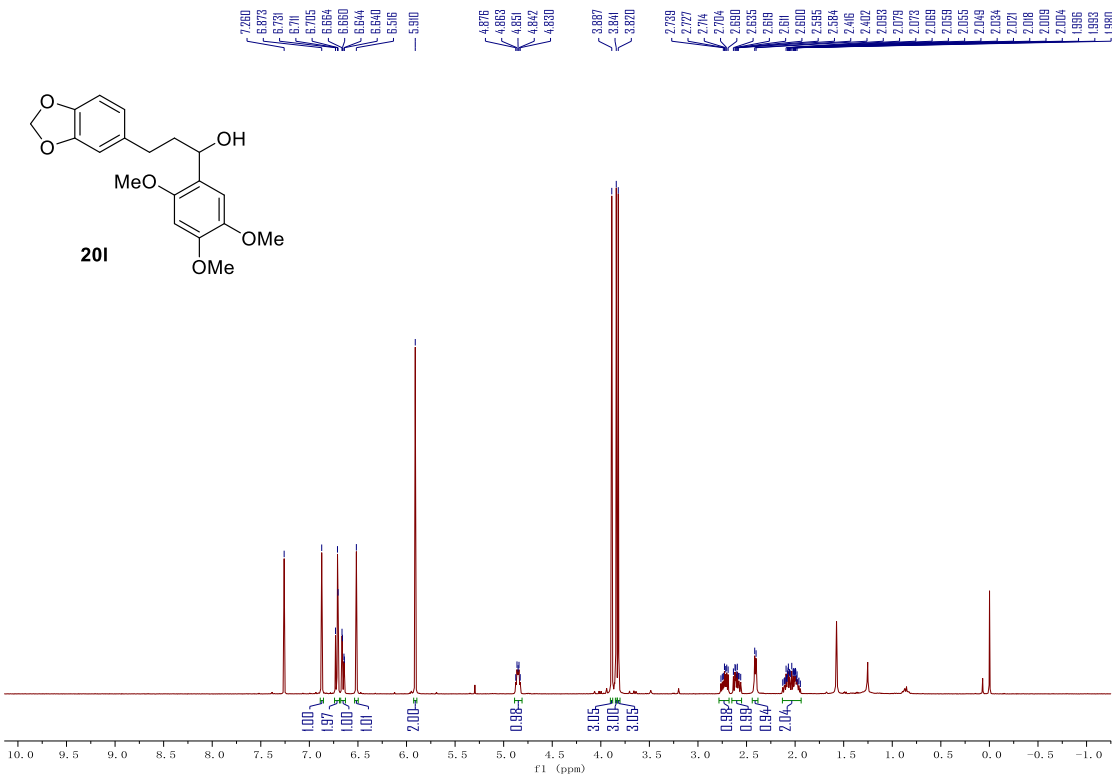
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20j**



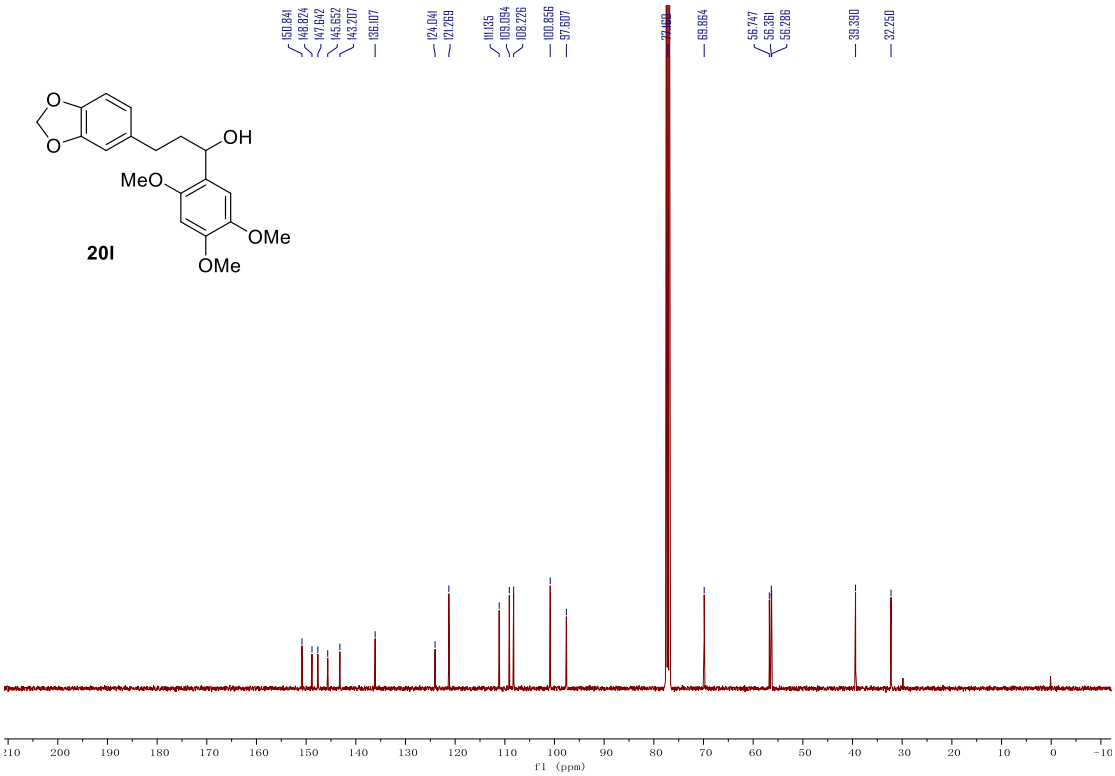
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20k**



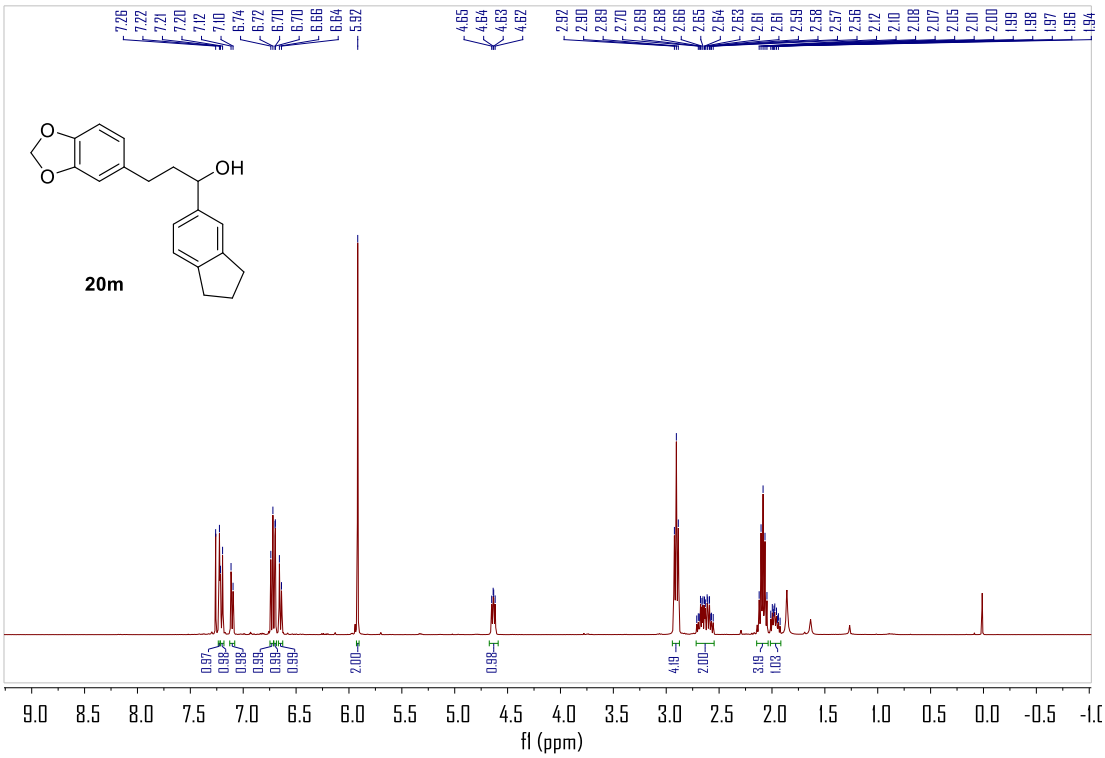
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20k**



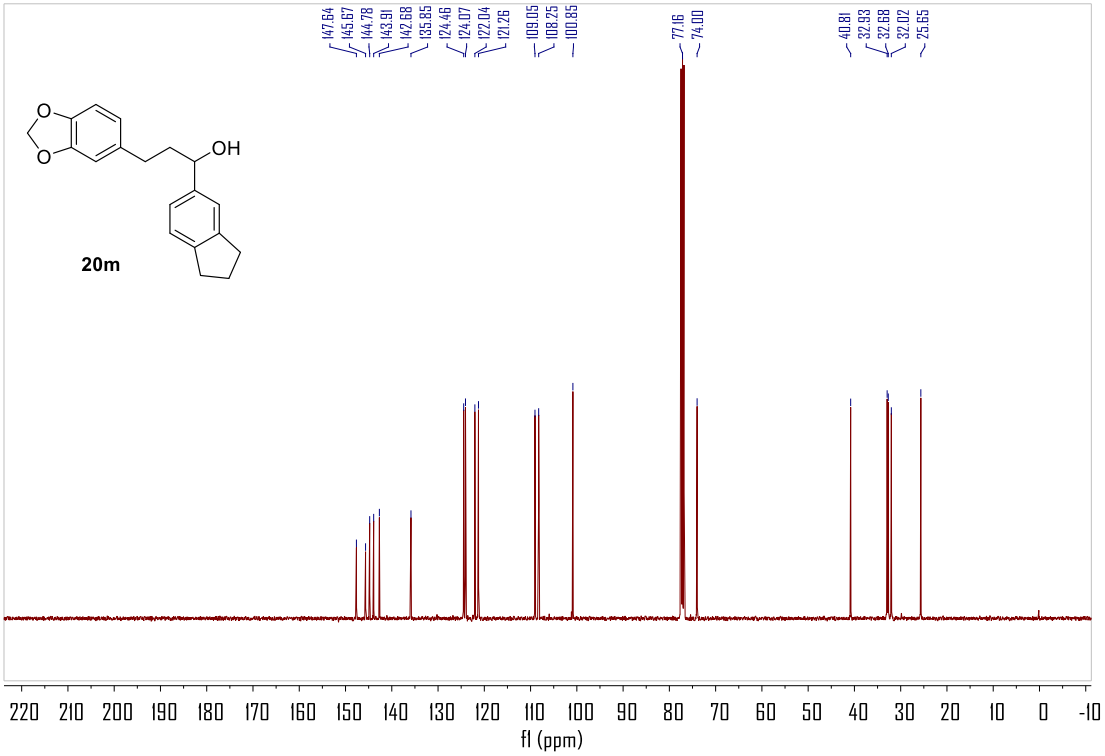
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20l**



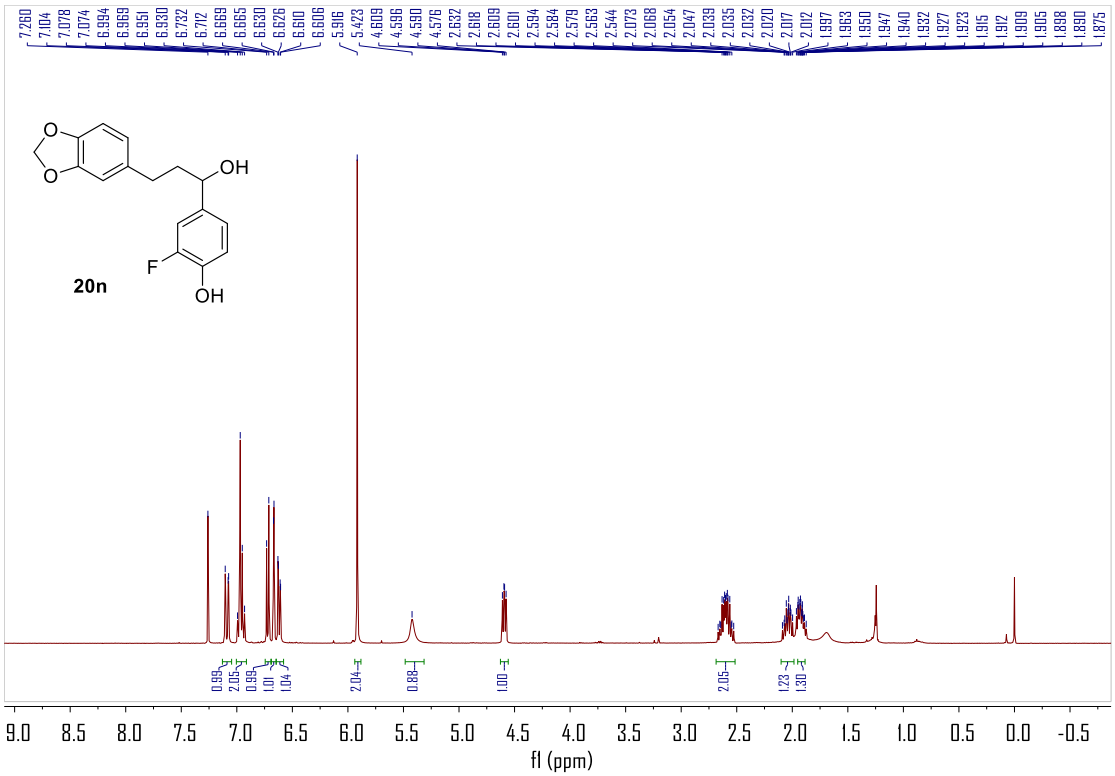
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20l**



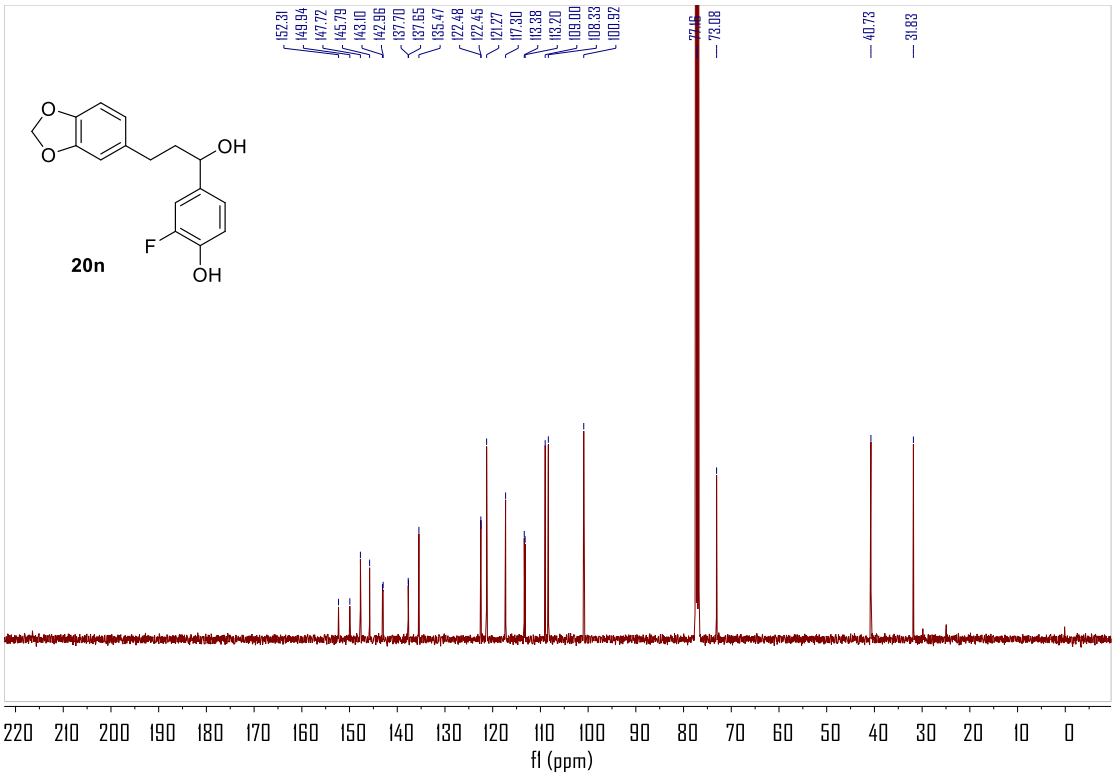
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20m**



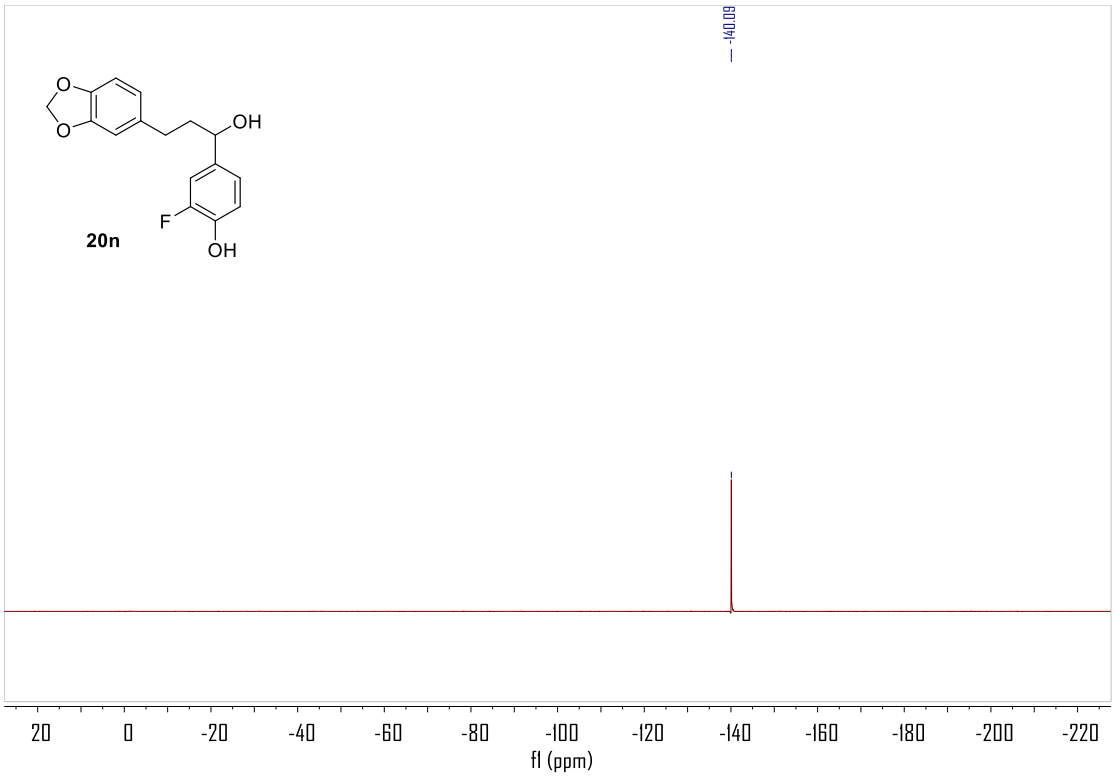
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20m**



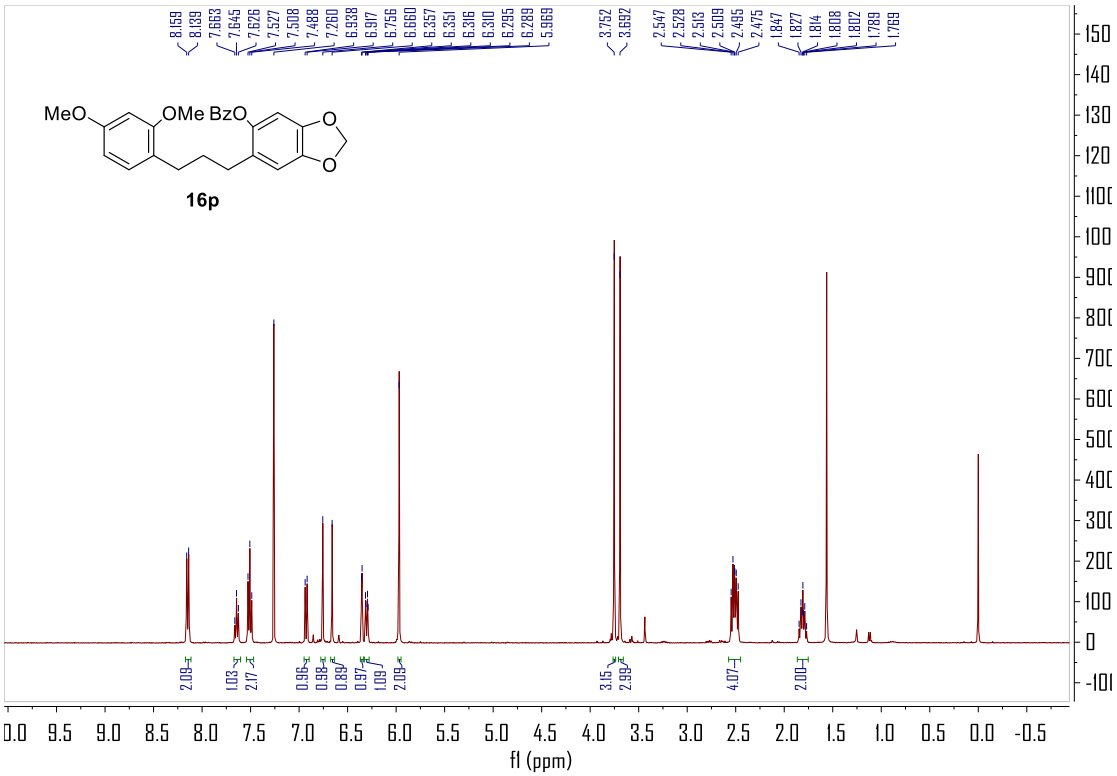
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **20n**



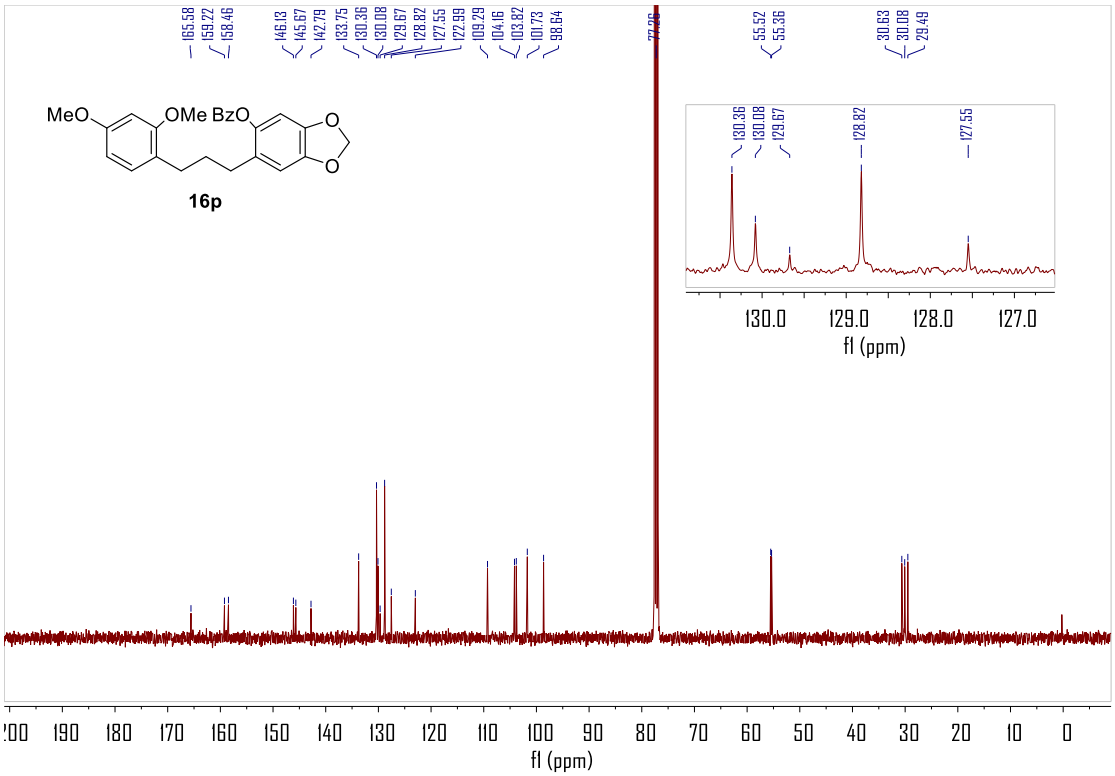
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **20n**



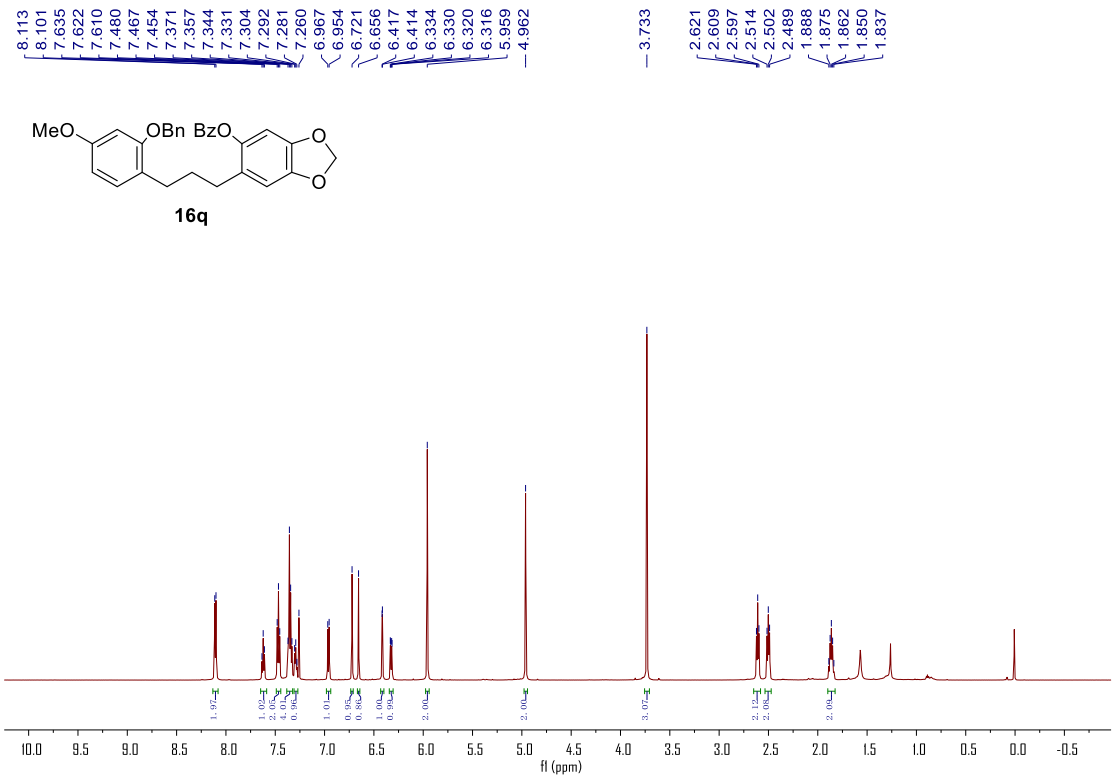
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **20n**



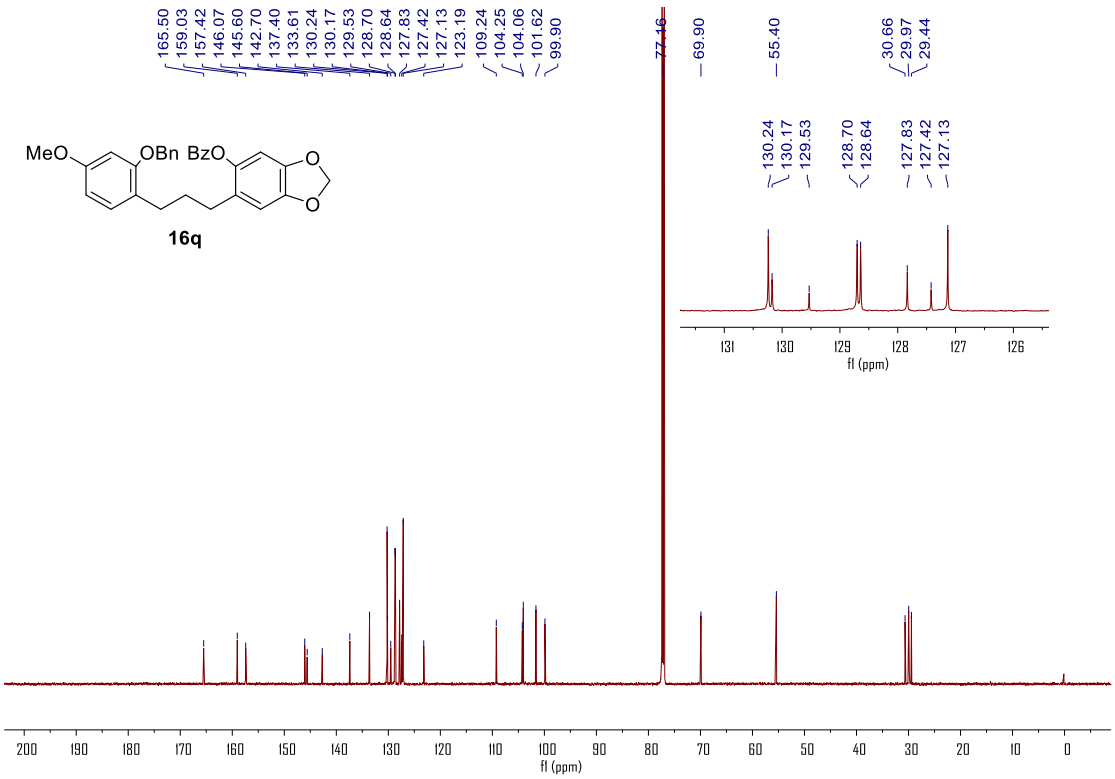
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **16p**



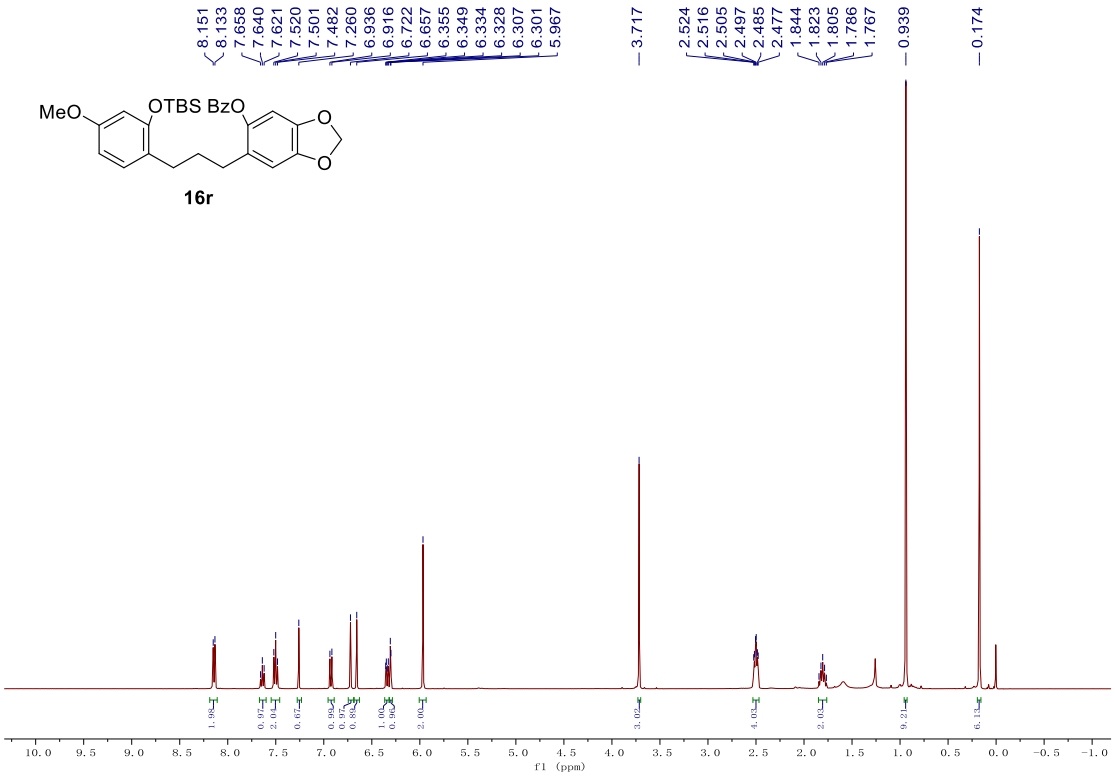
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **16p**



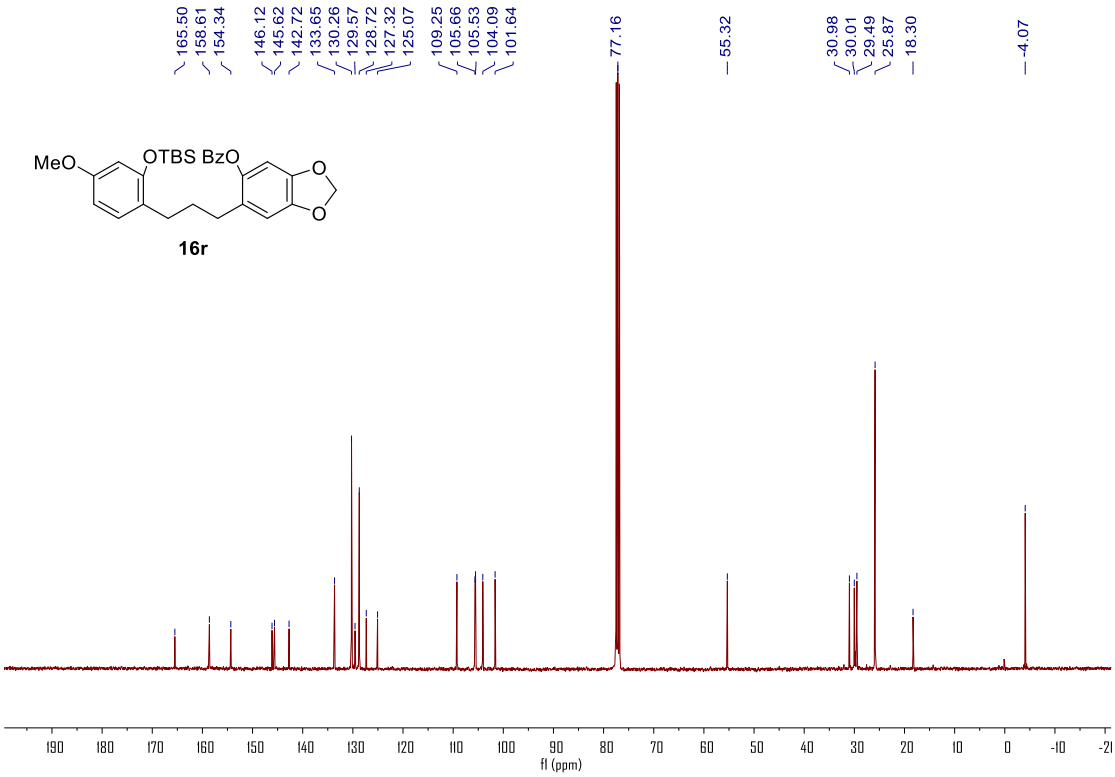
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **16q**



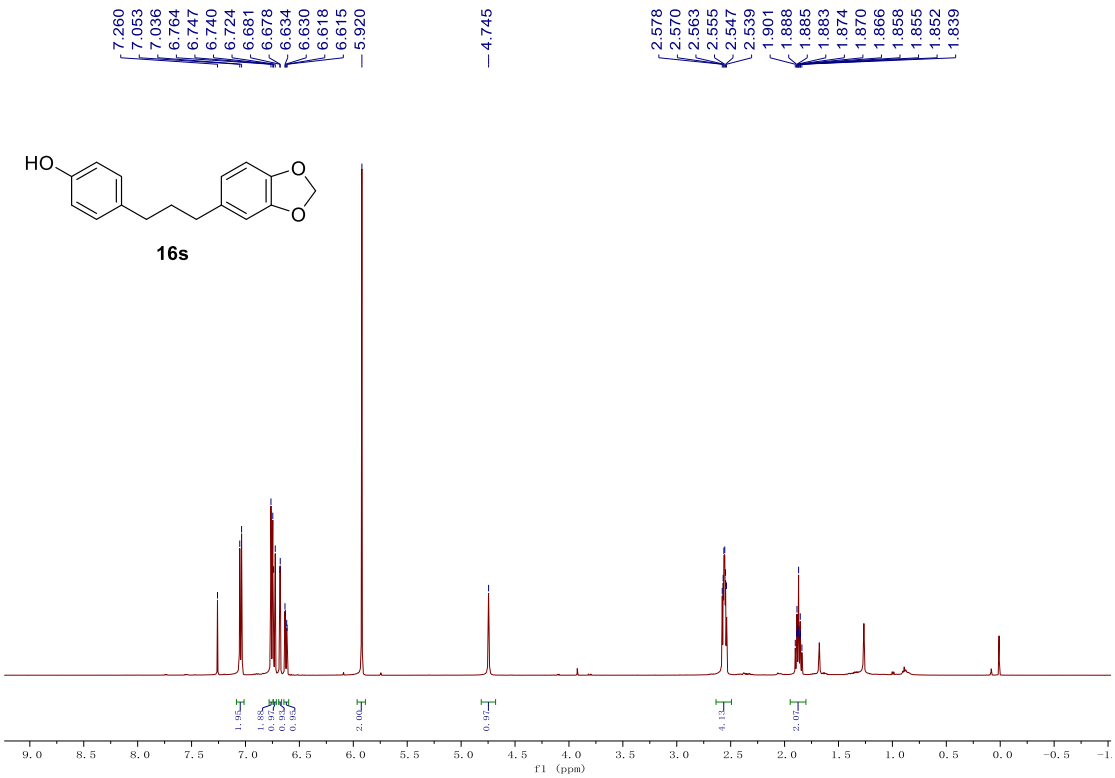
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound **16q**



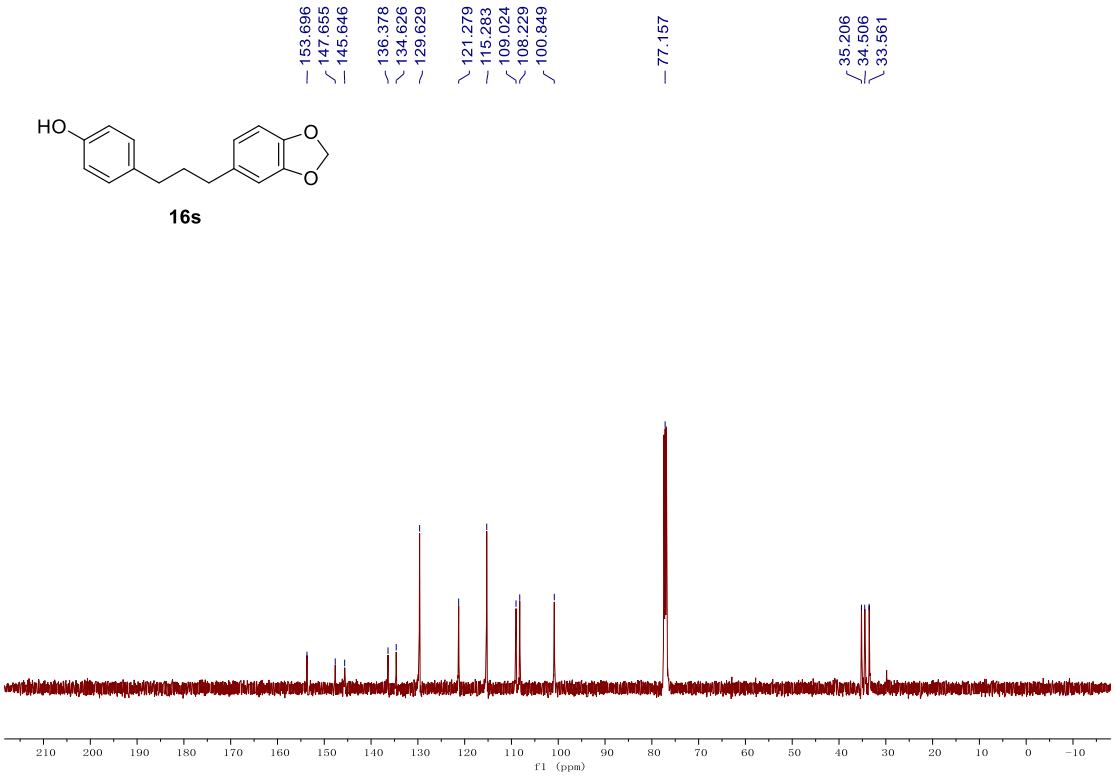
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **16r**



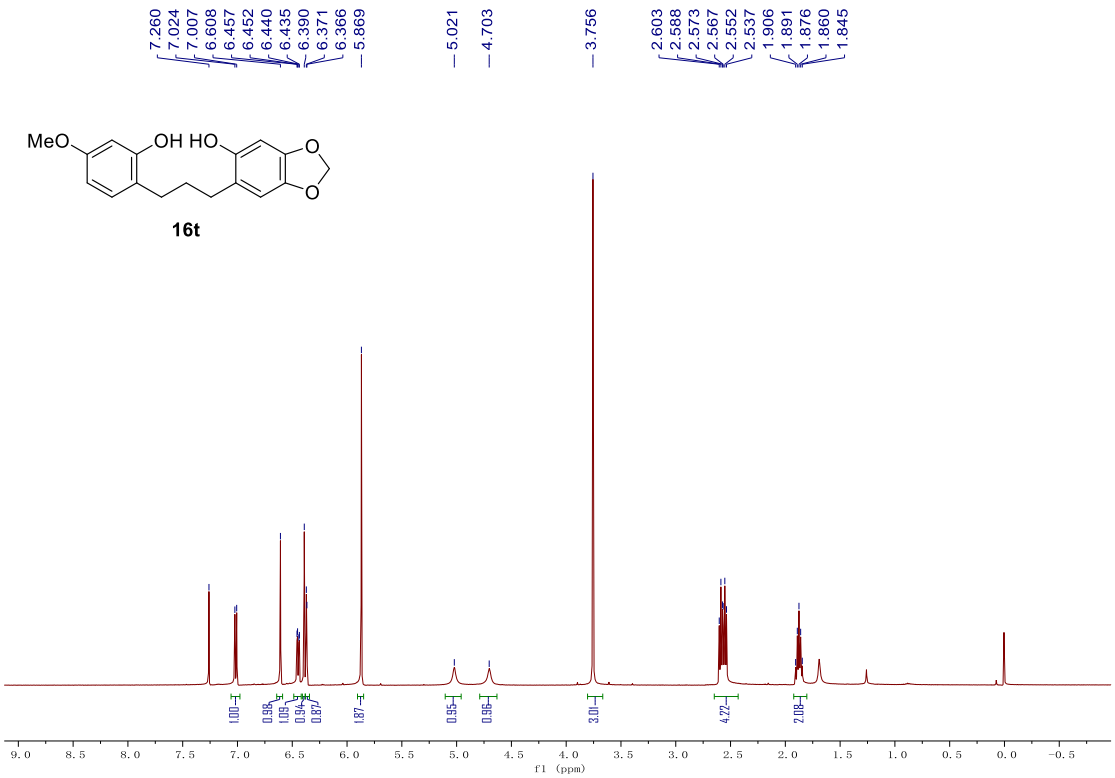
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **16r**



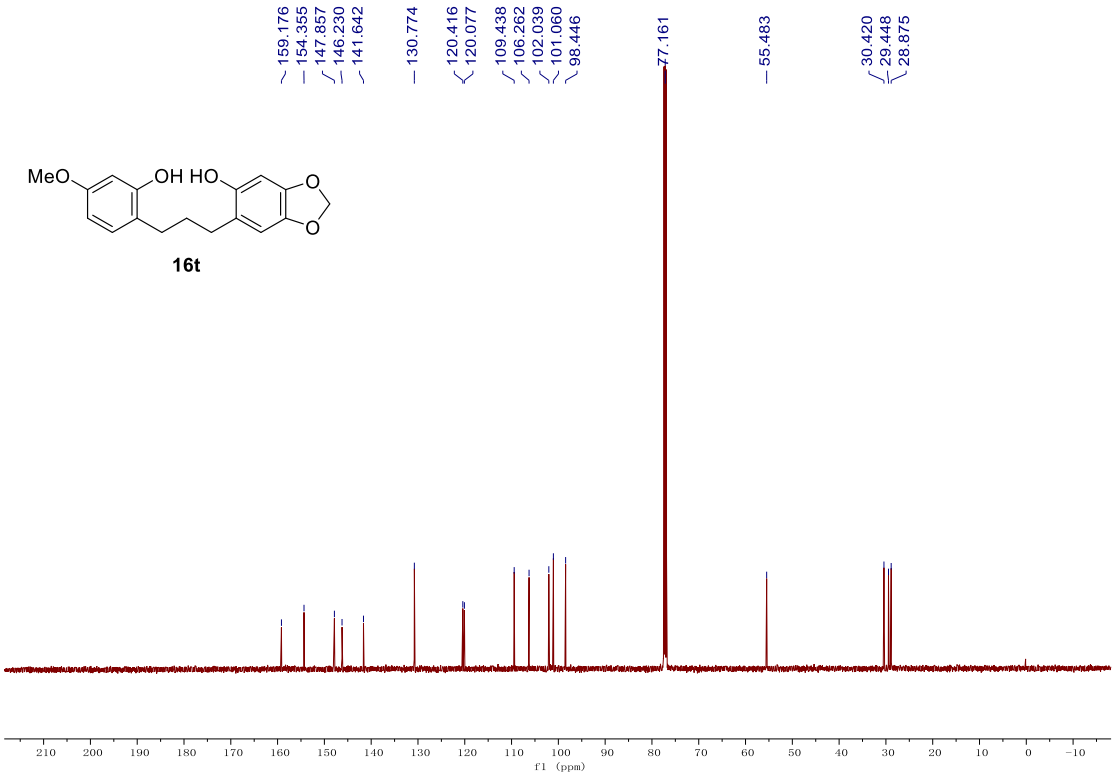
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **16s**



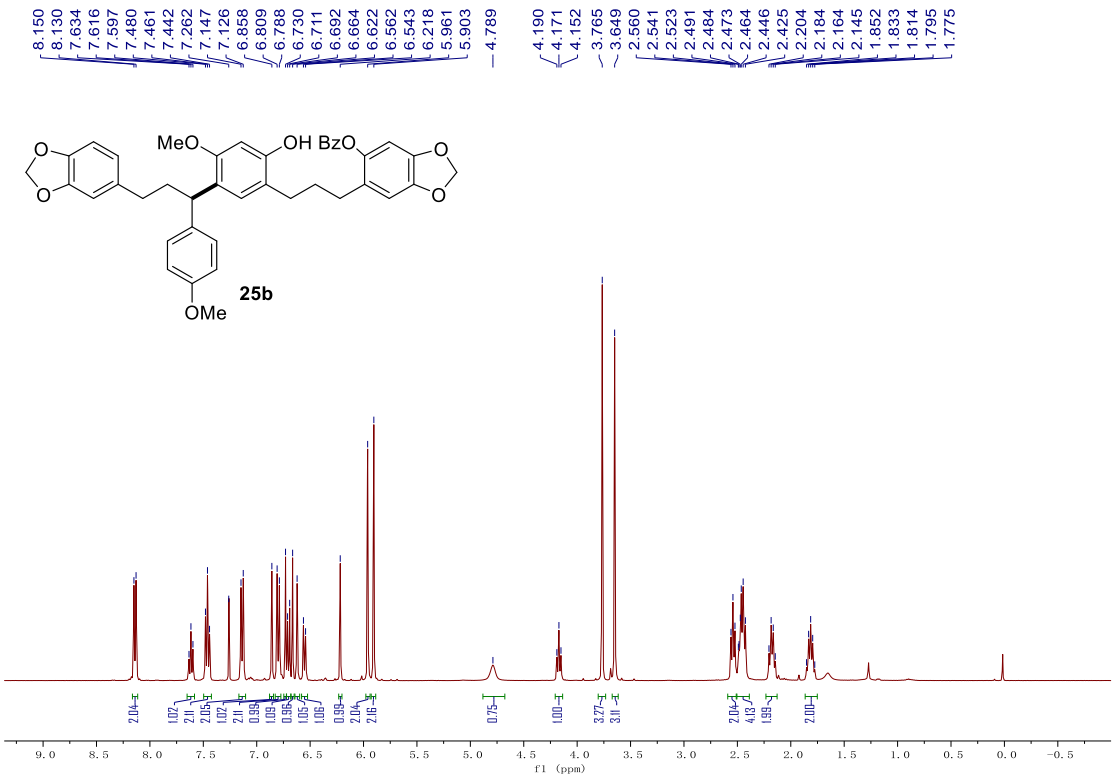
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **16s**



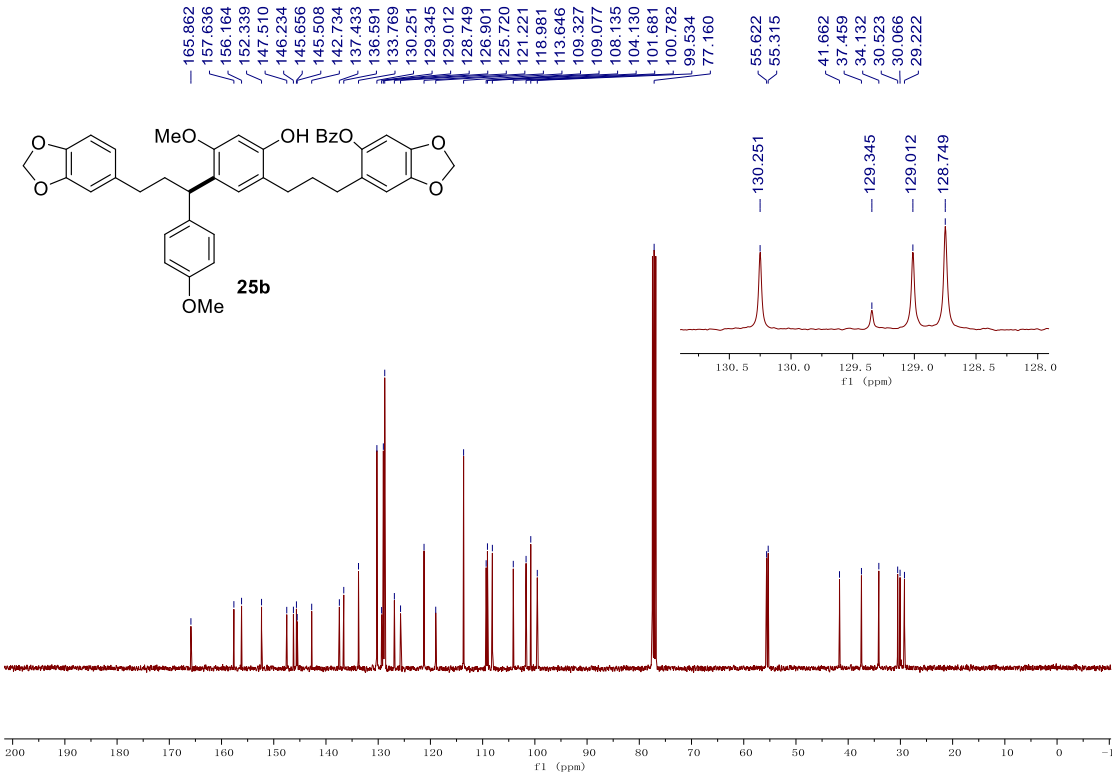
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **16t**



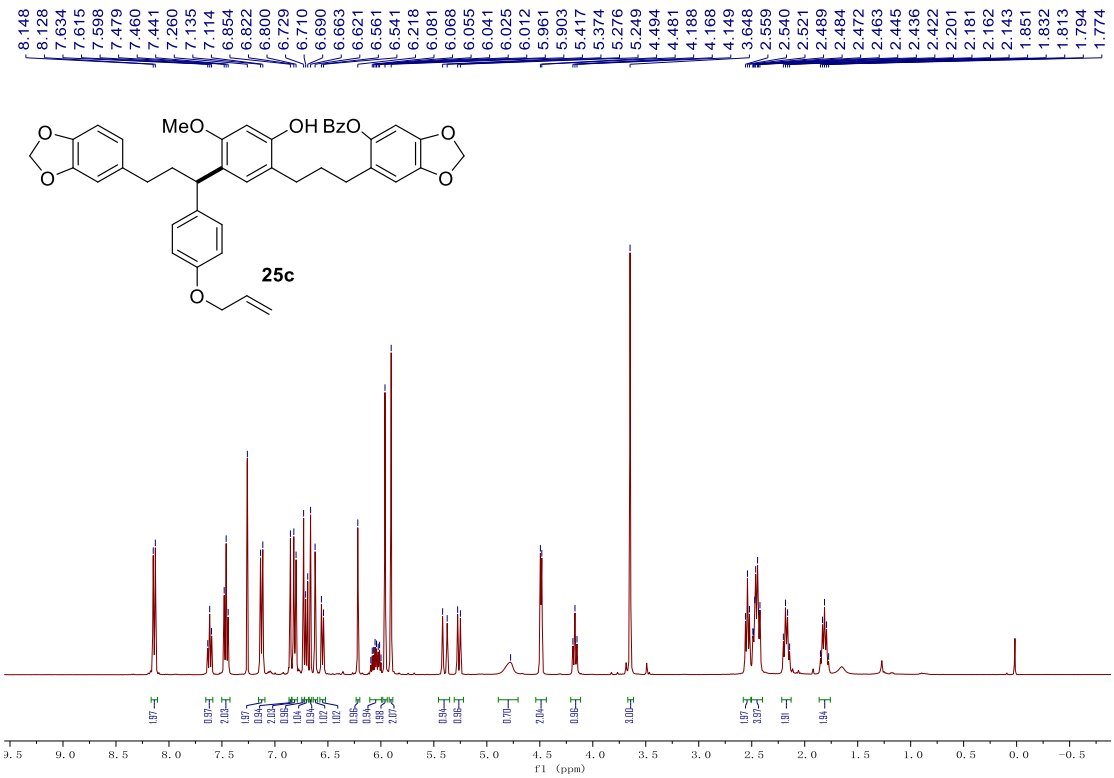
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **16t**



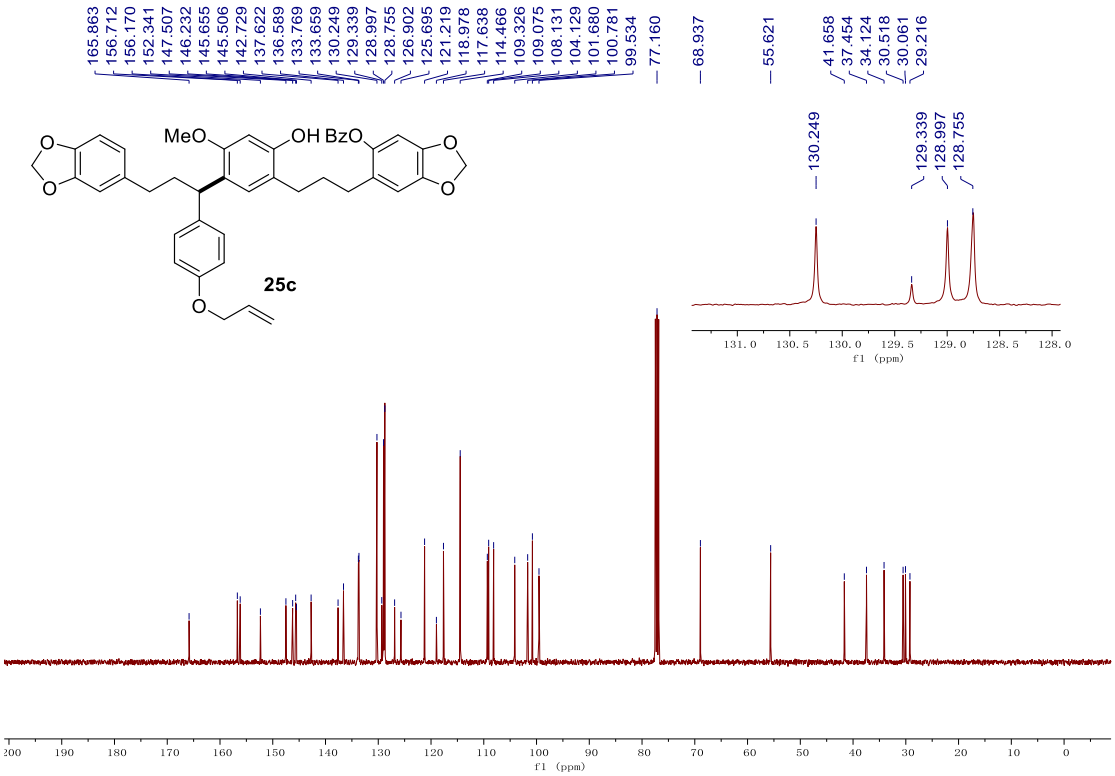
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25b**



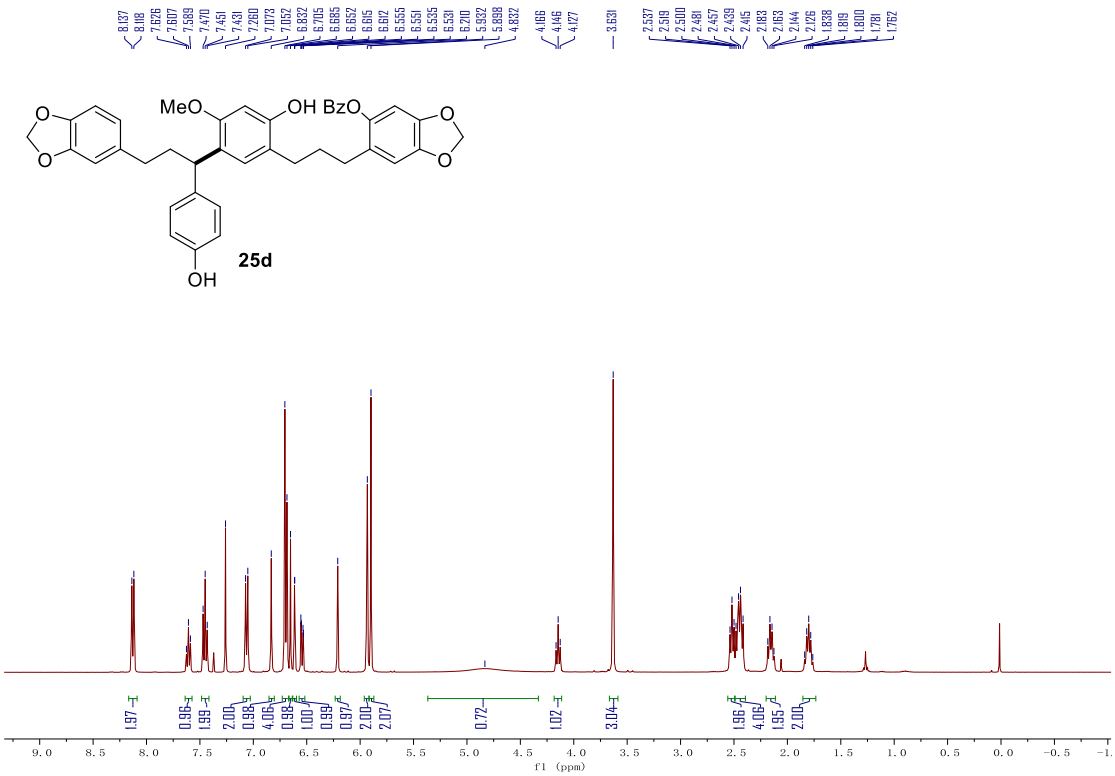
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25b**



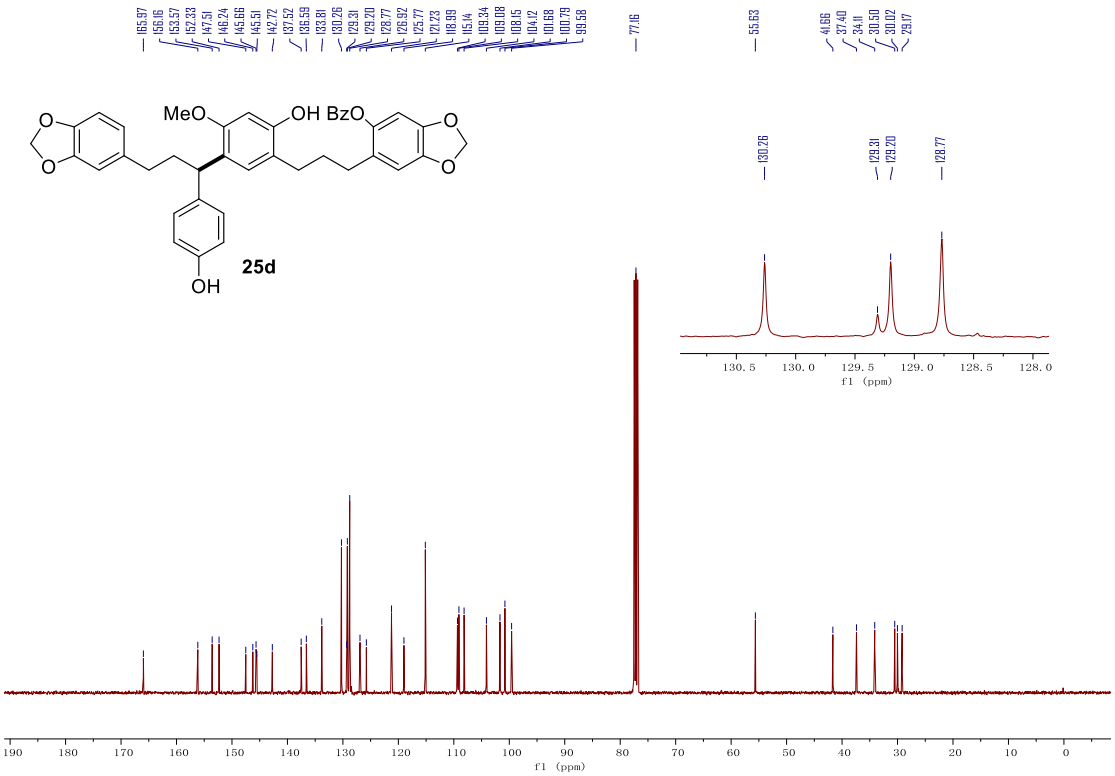
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25c**



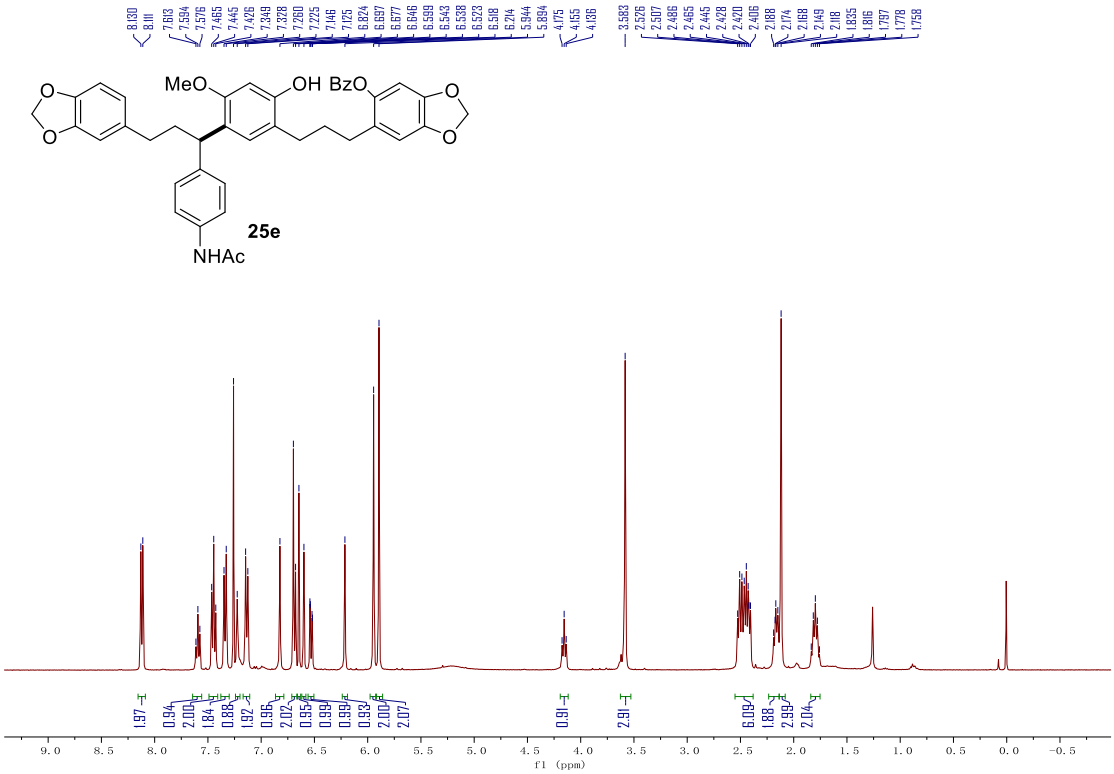
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25c**



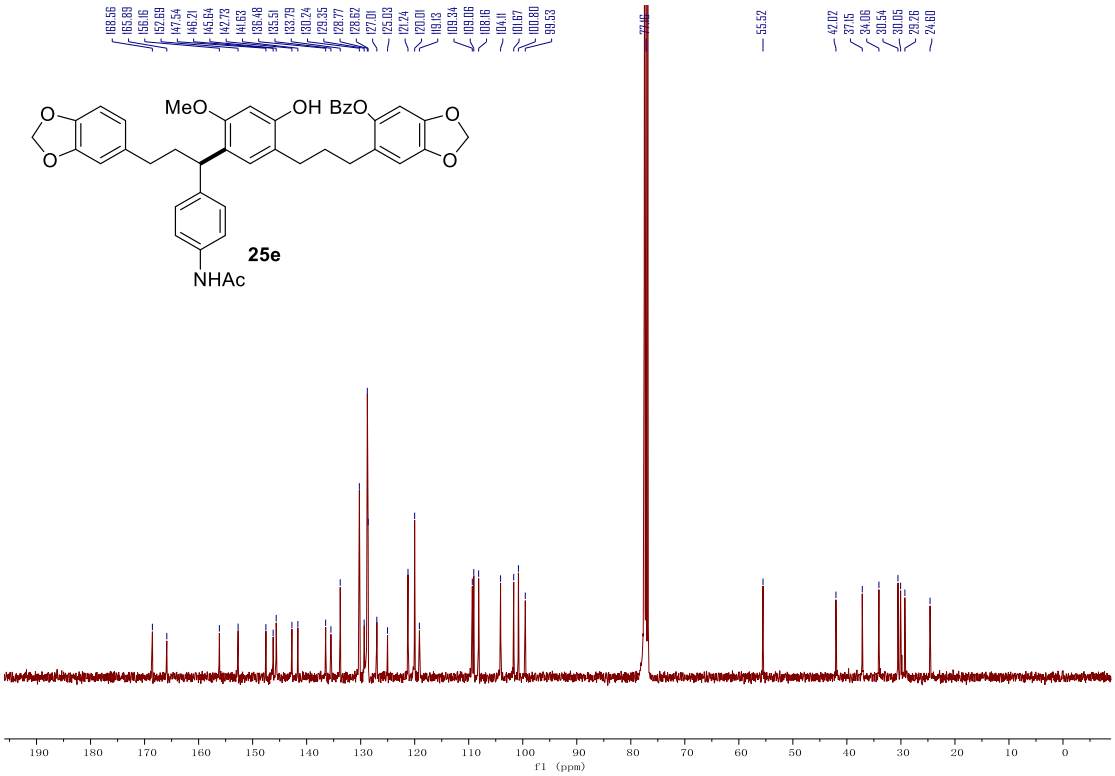
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25d**



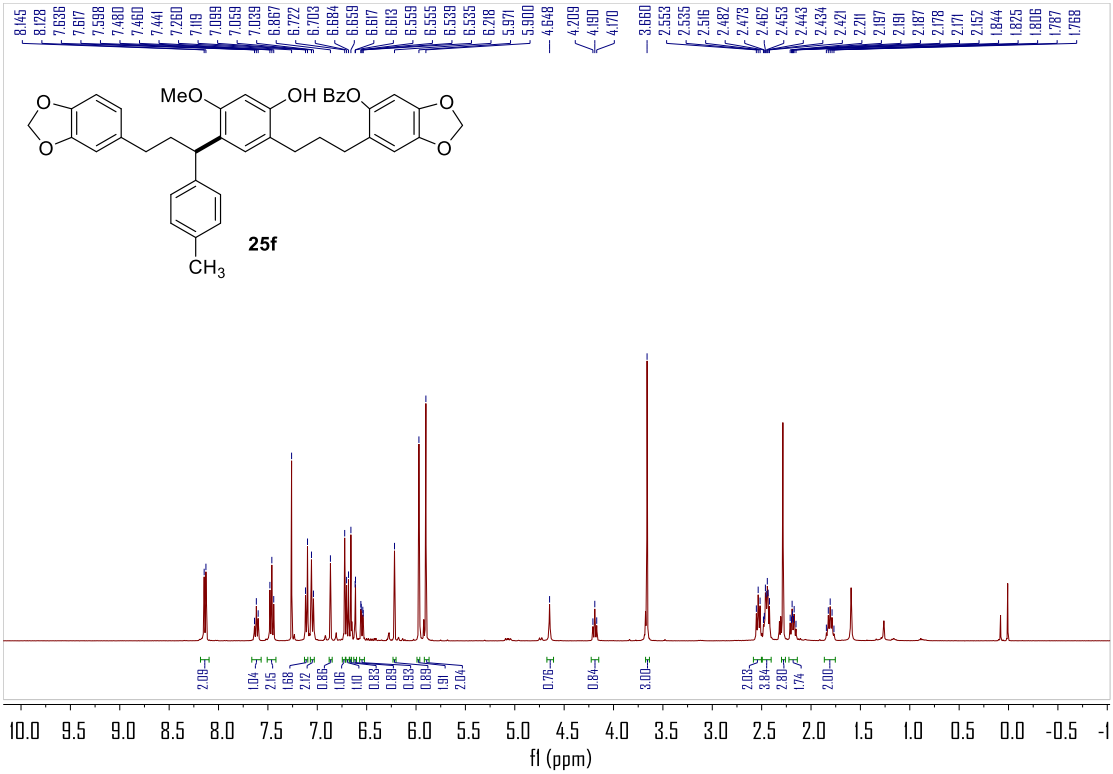
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25d**



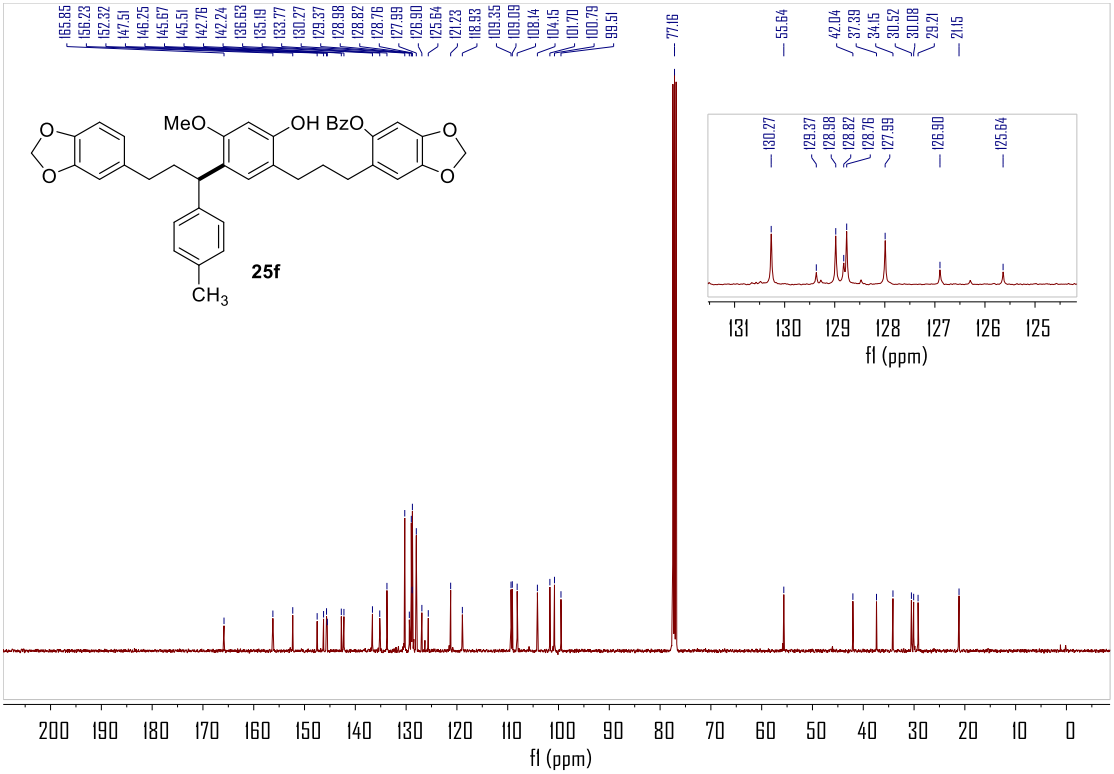
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25e**



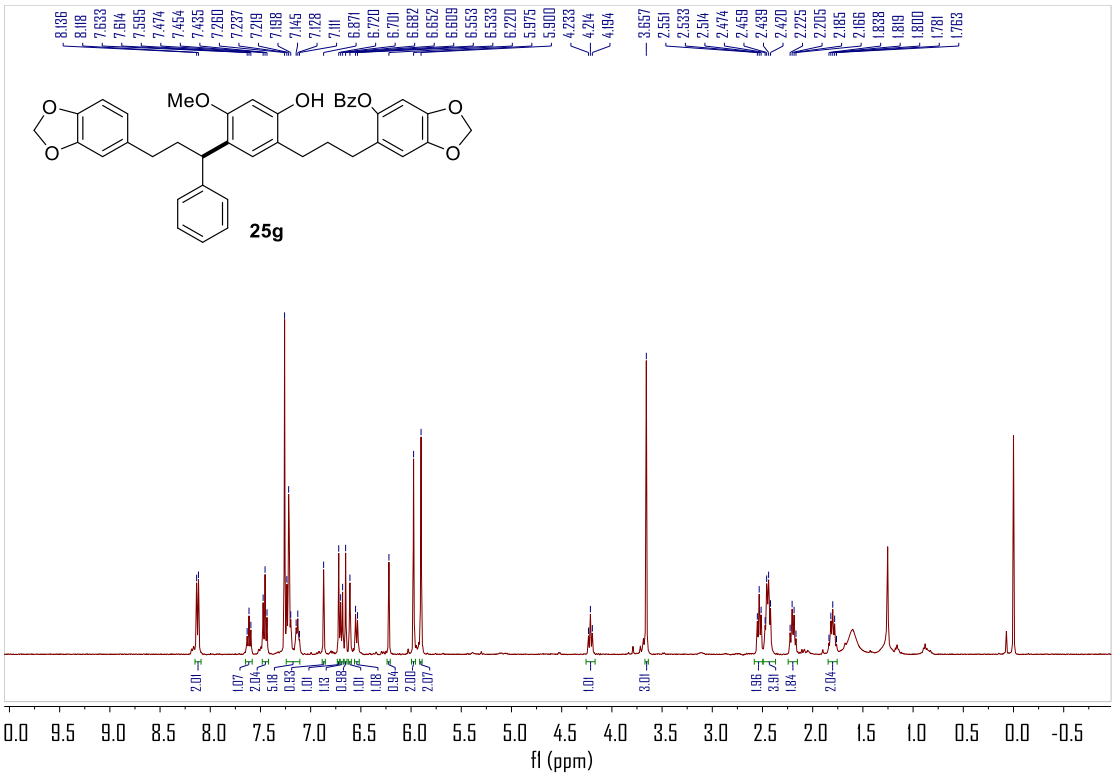
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25e**



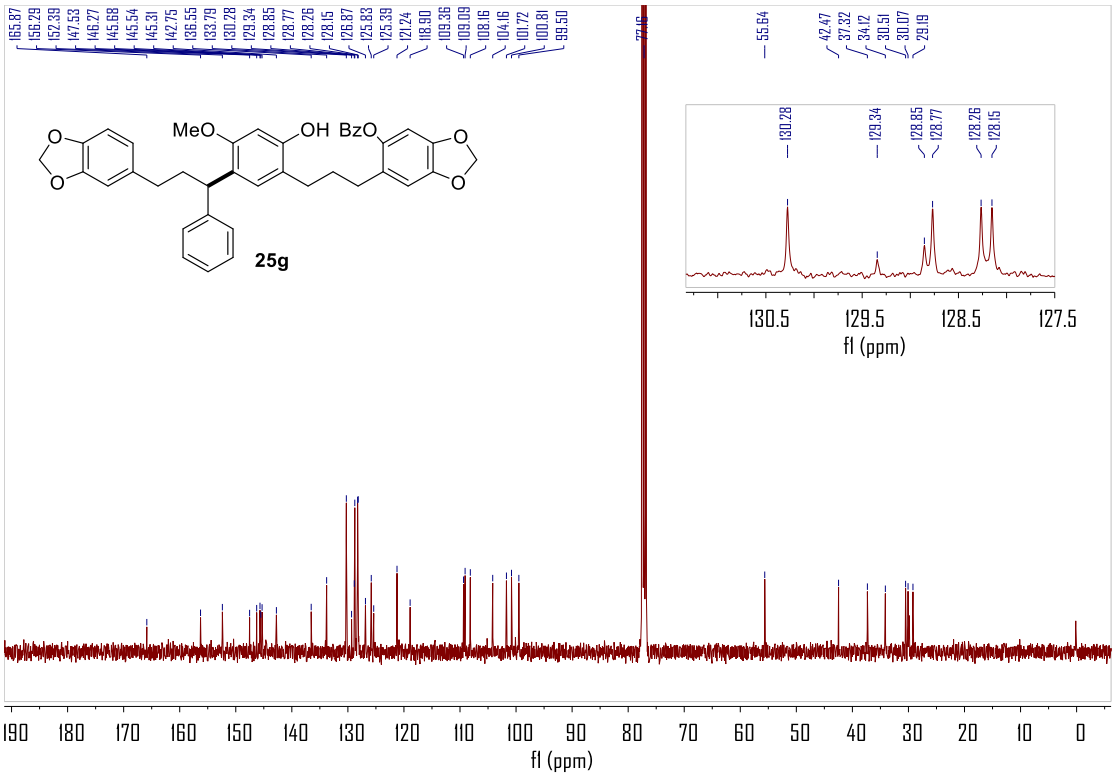
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25f**



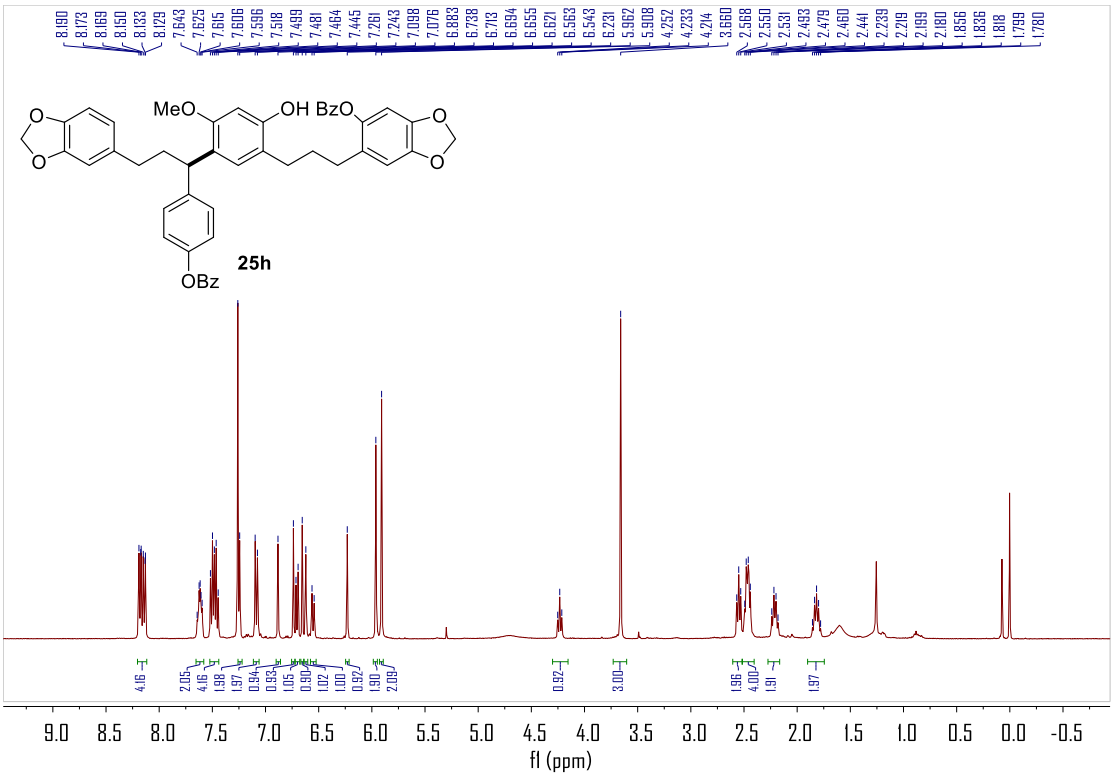
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25f**



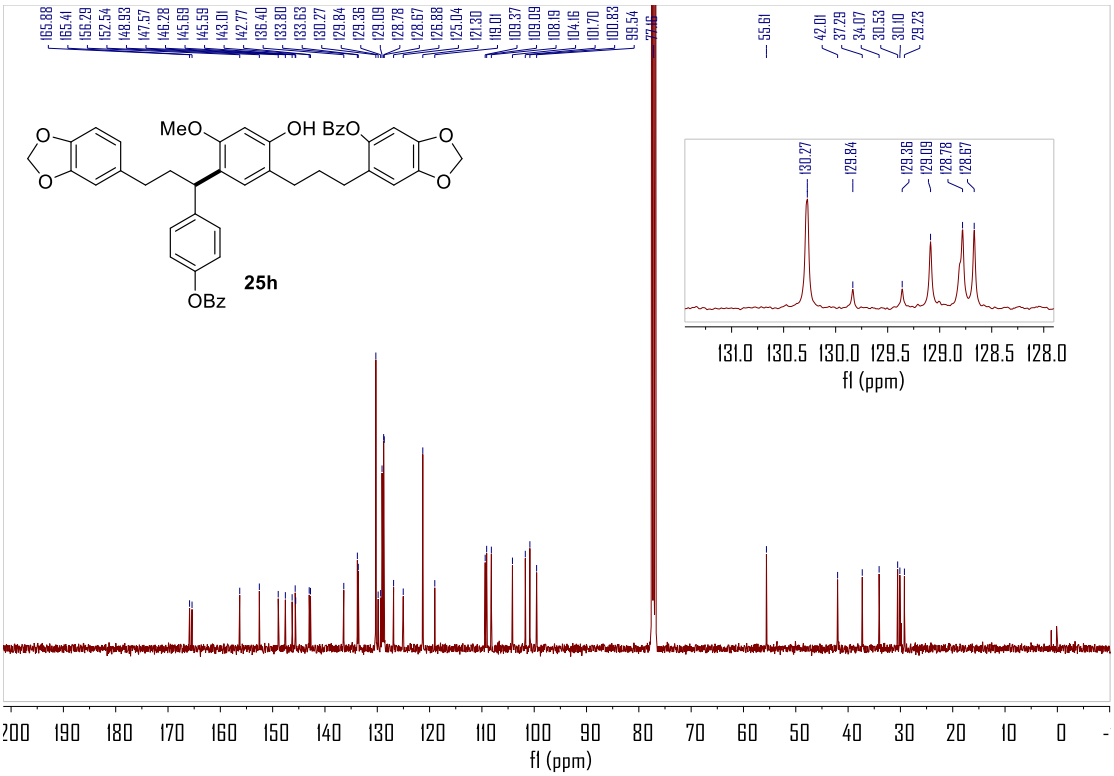
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25g**



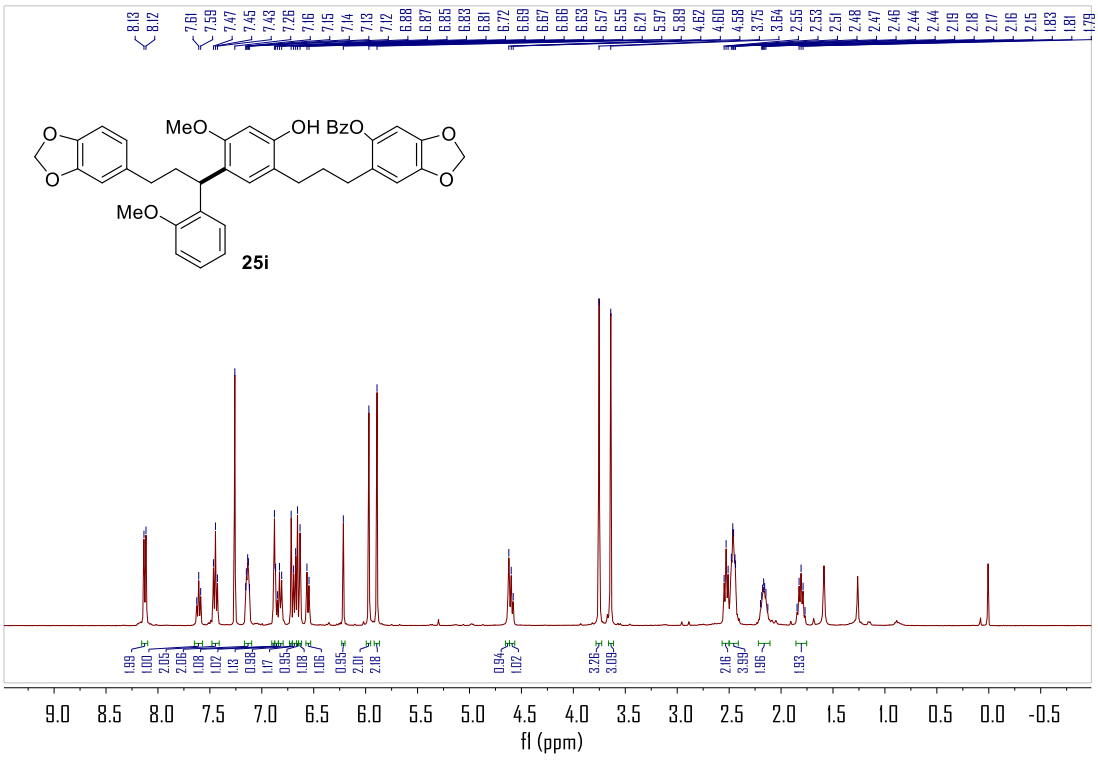
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25g**



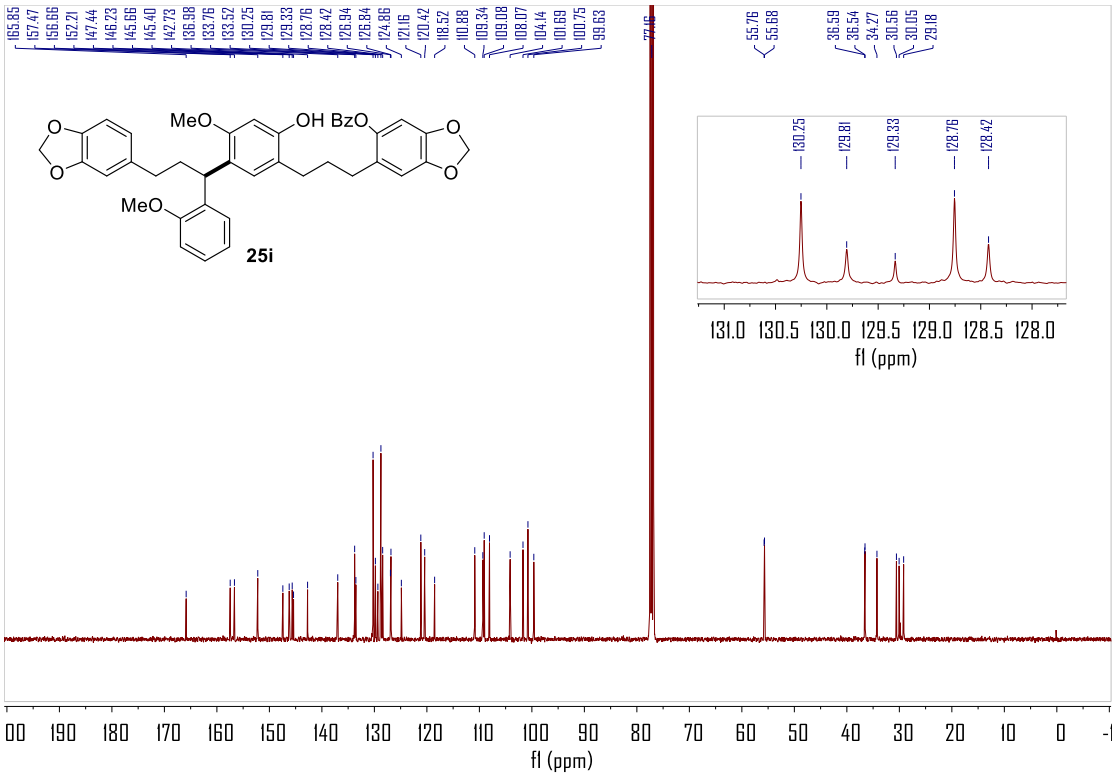
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25h**



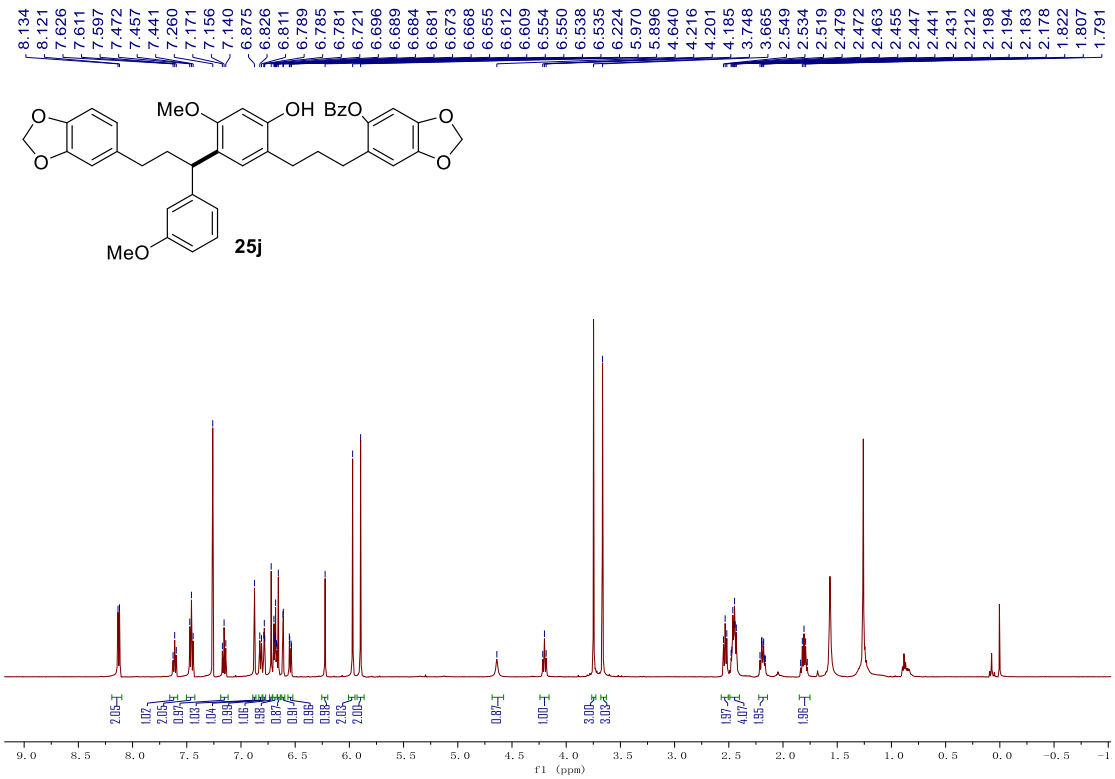
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25h**



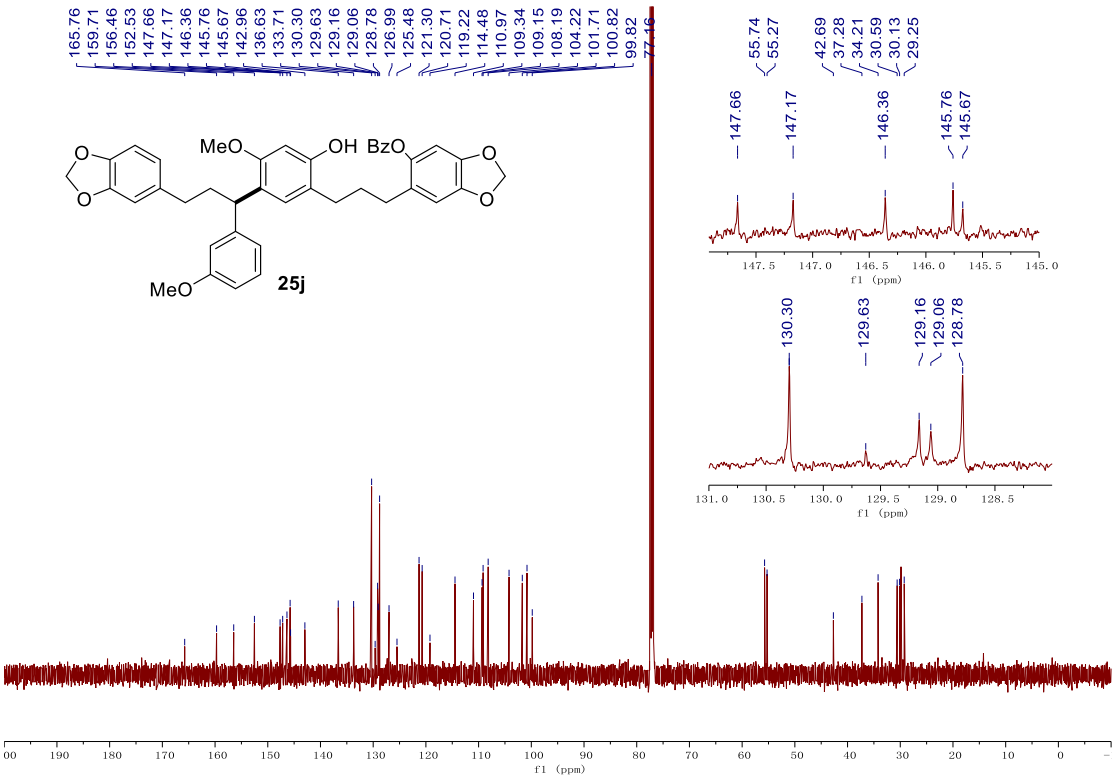
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25i**



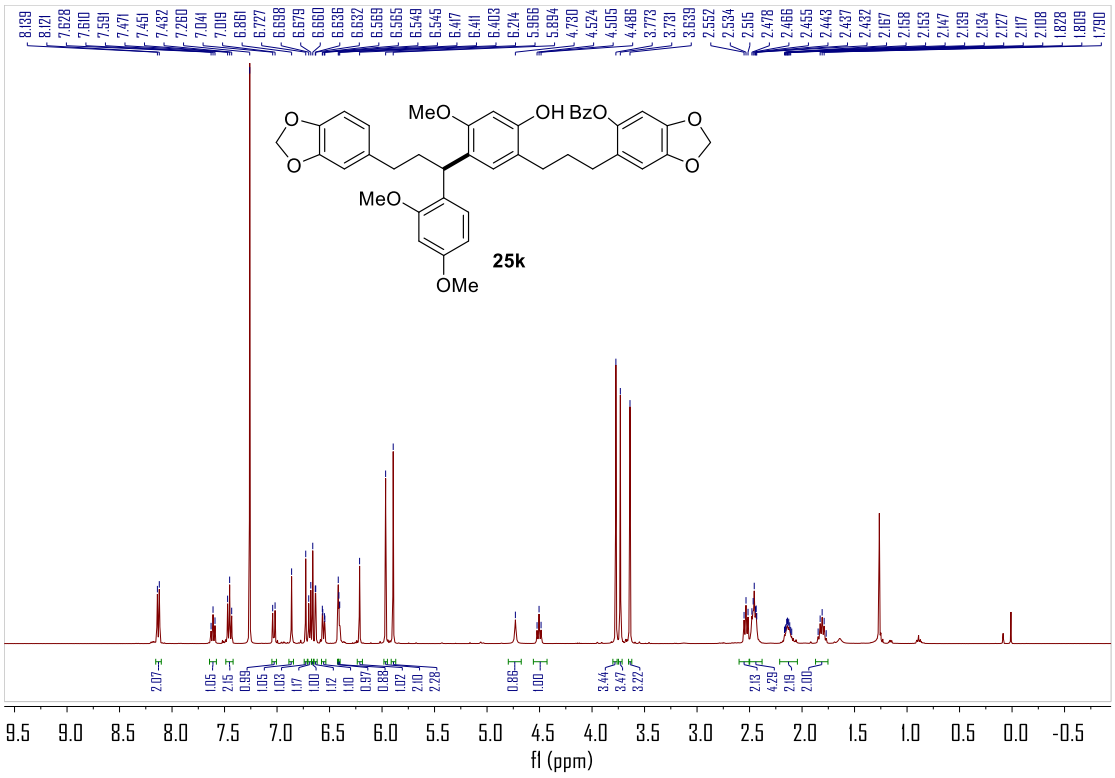
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25i**



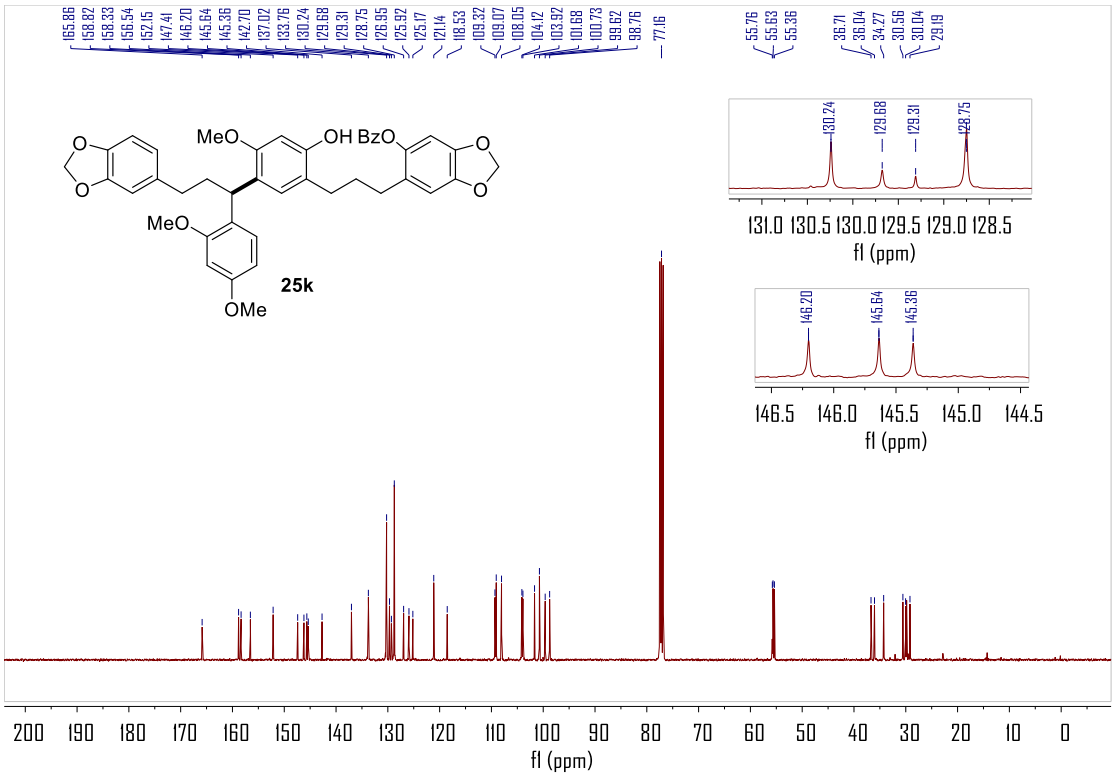
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **25j**



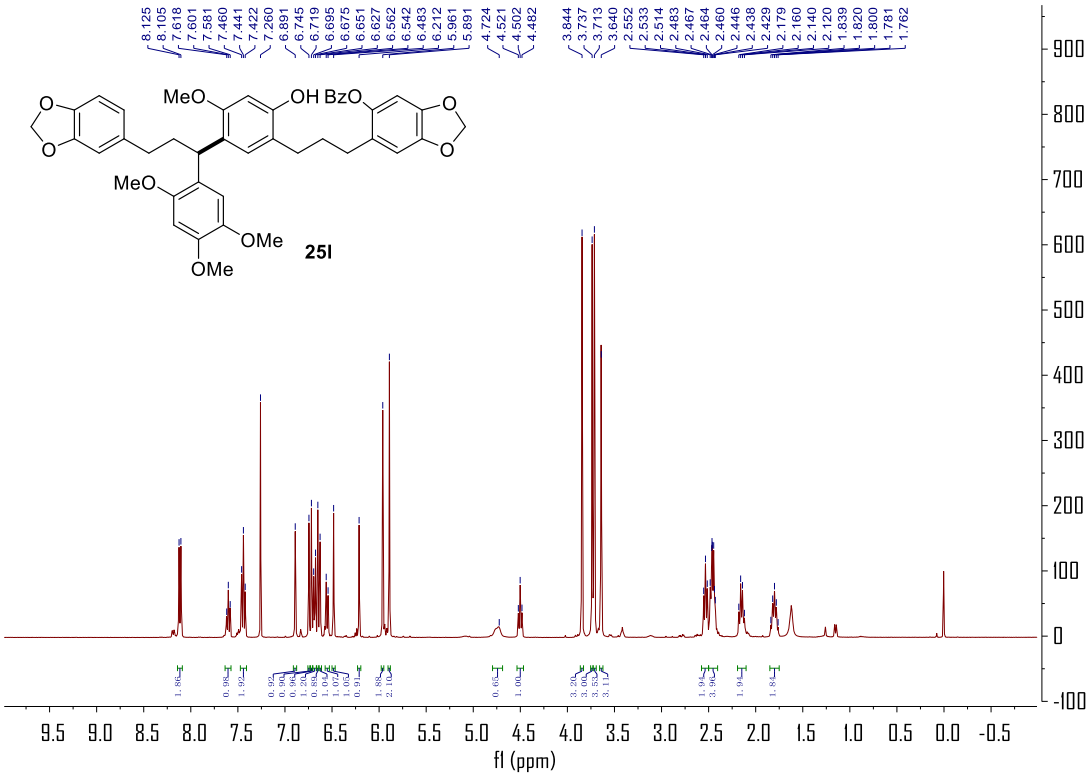
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **25j**



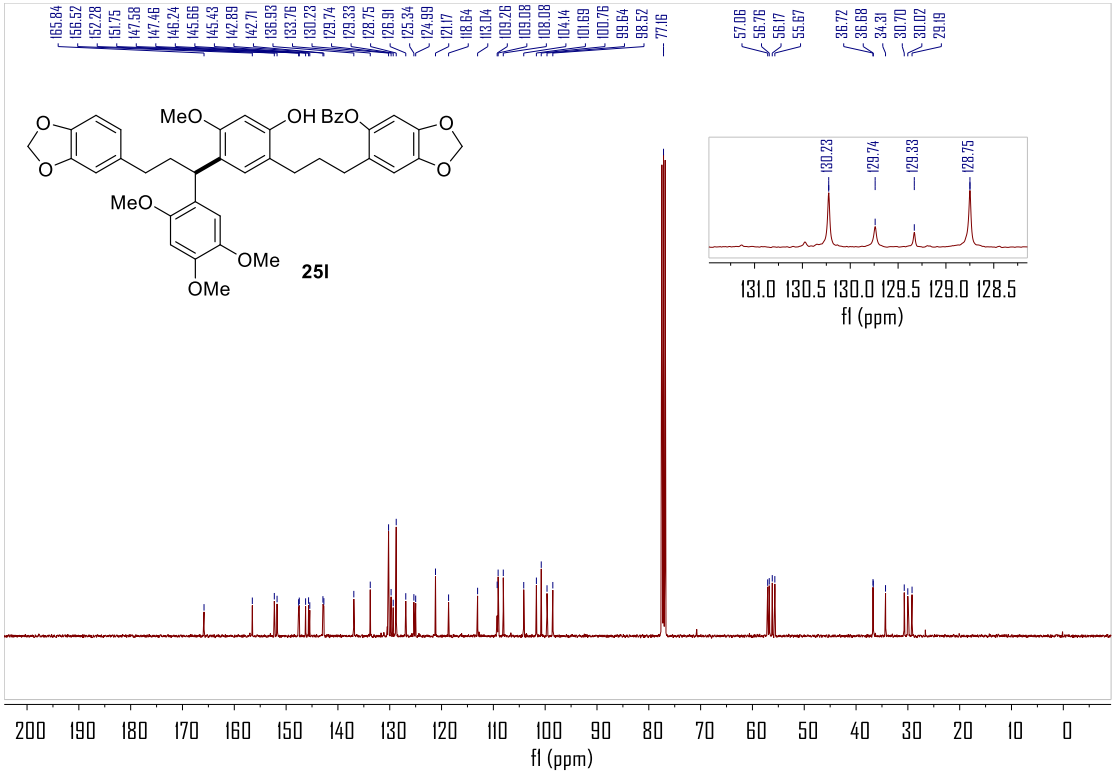
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25k**



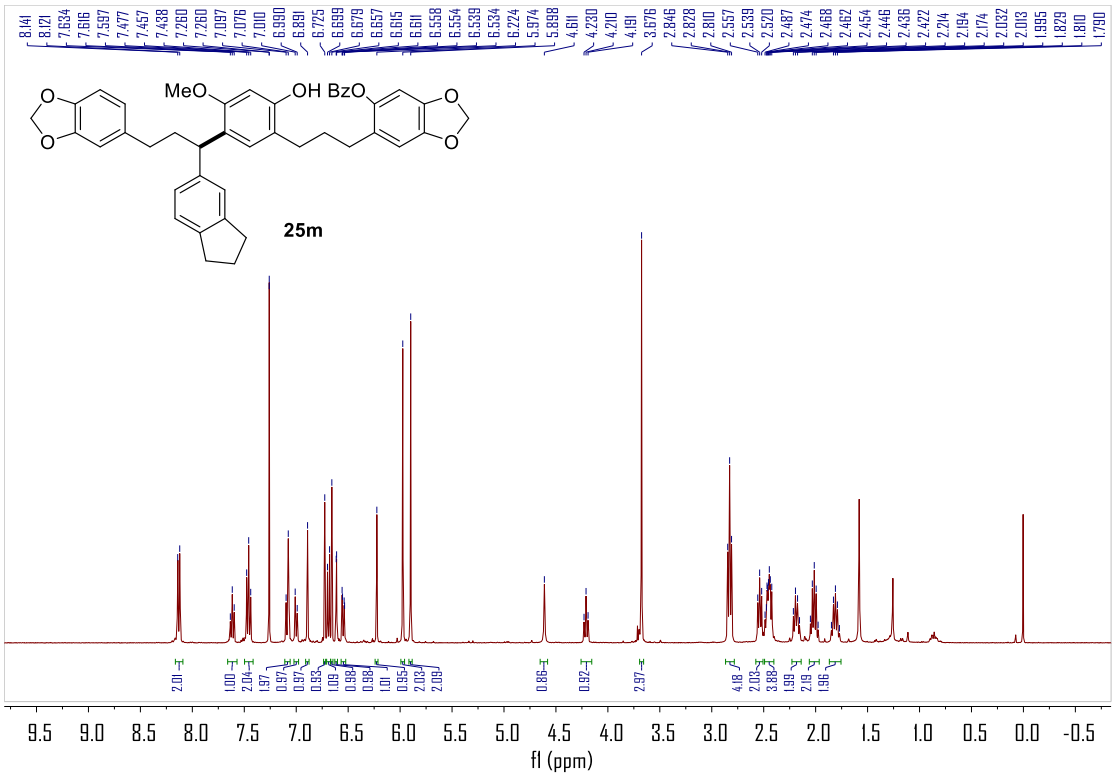
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25k**



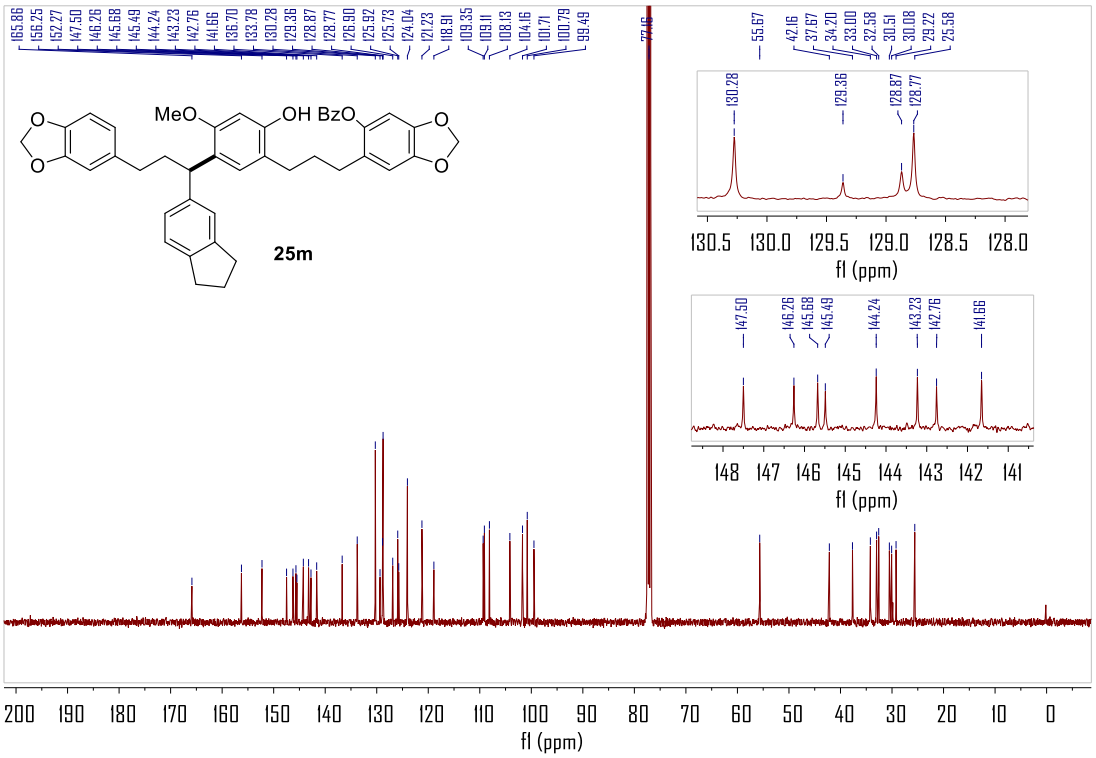
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25l**



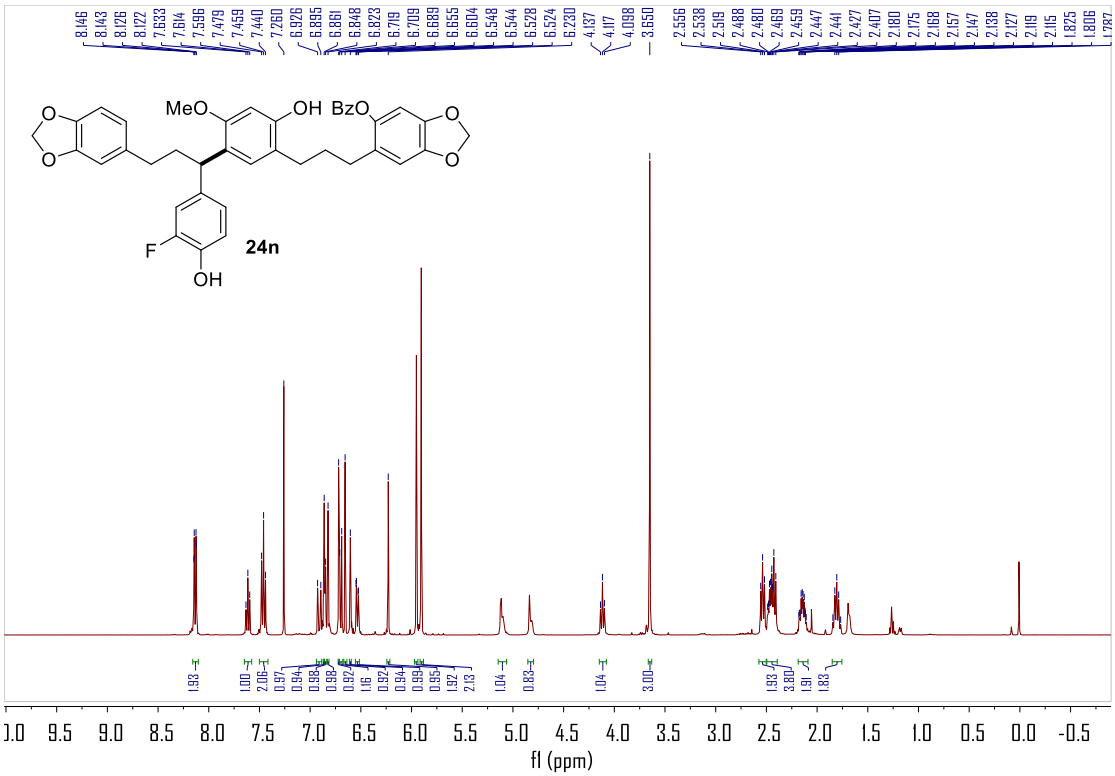
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25l**



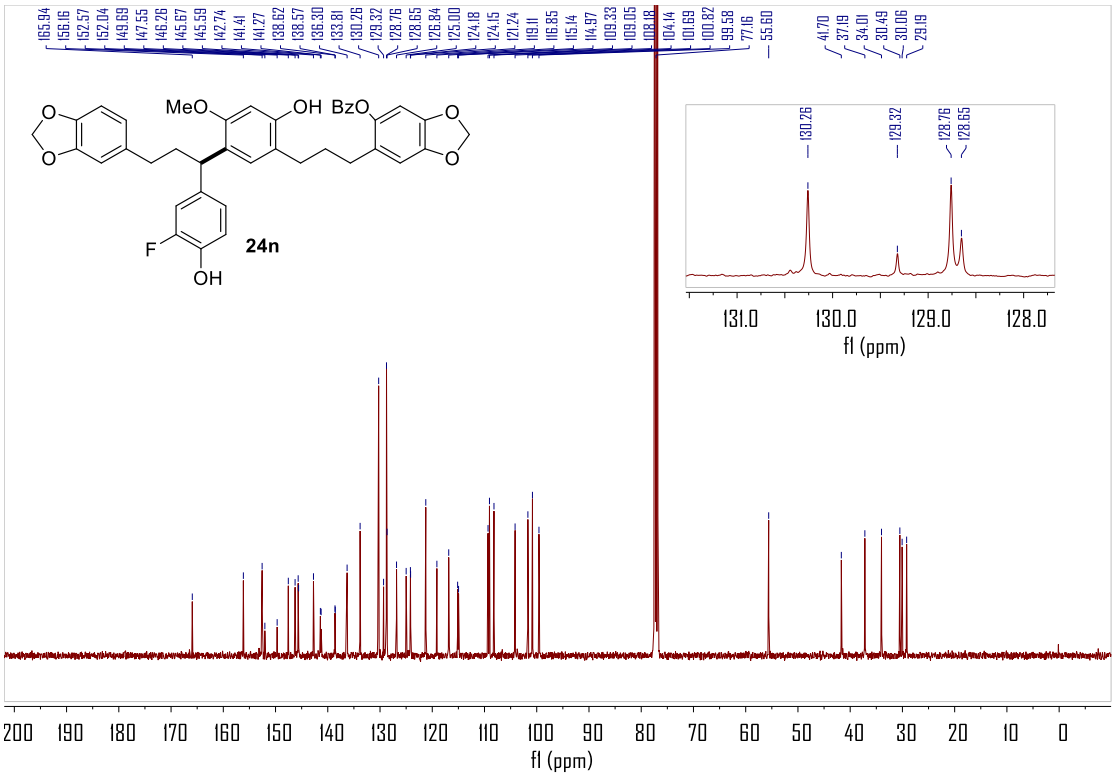
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25m**



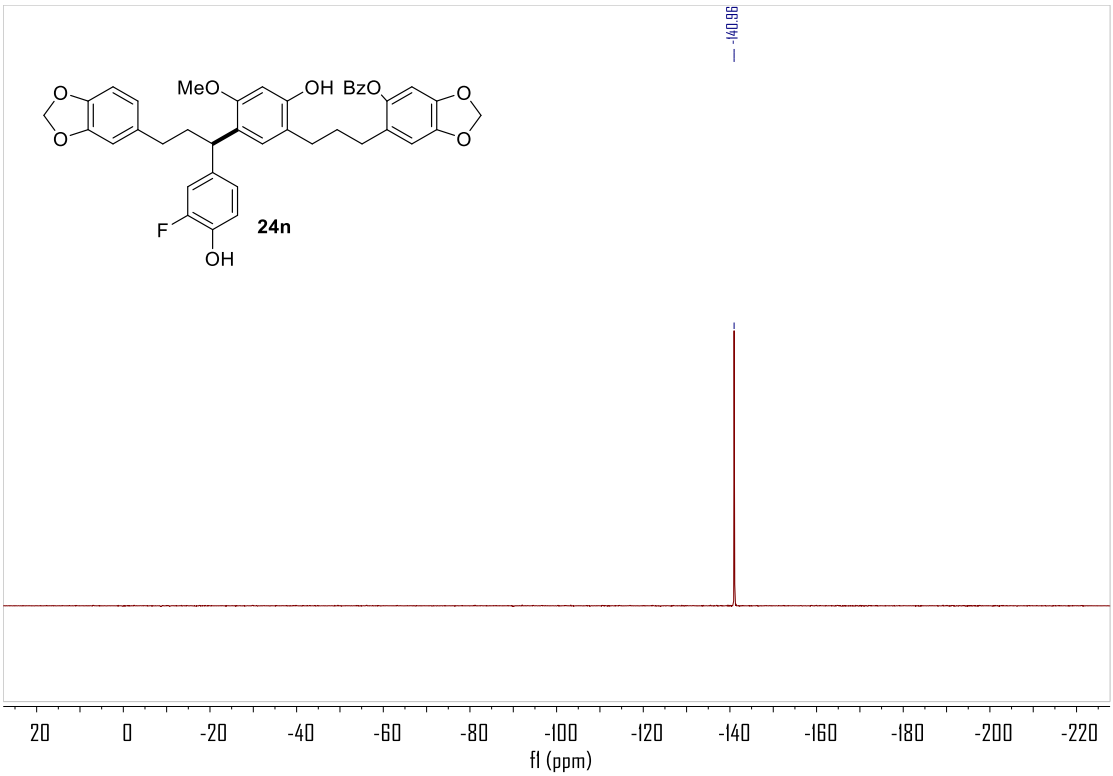
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25m**



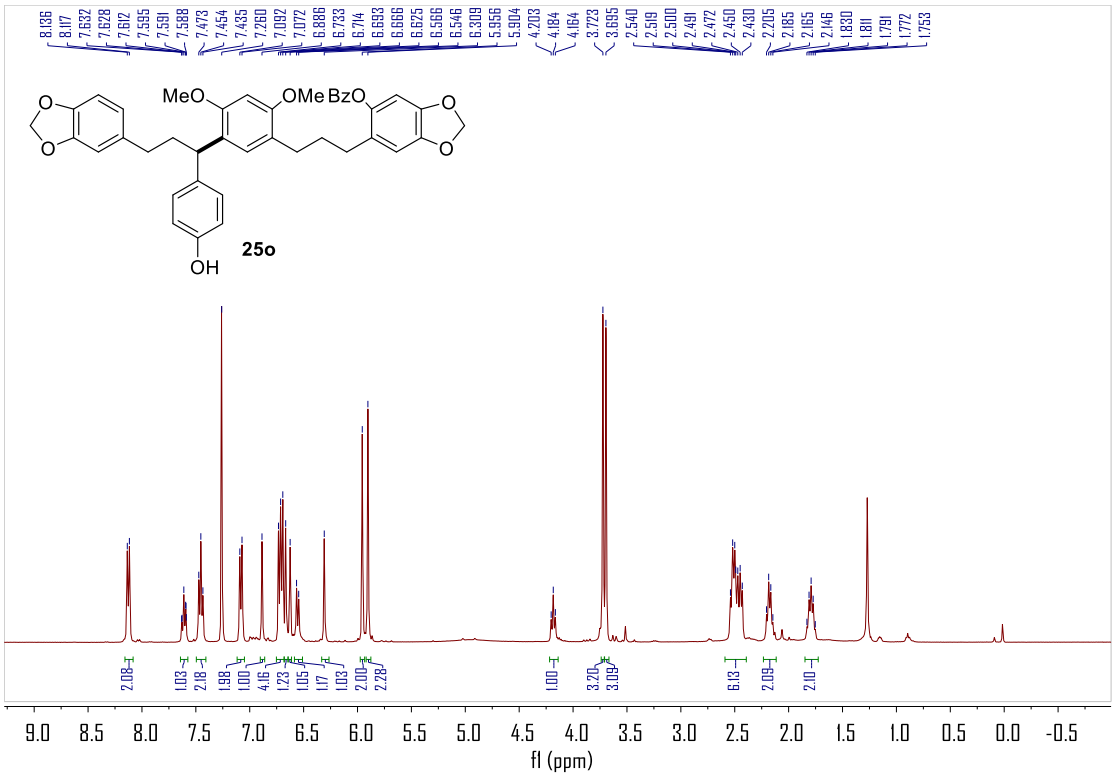
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25n**



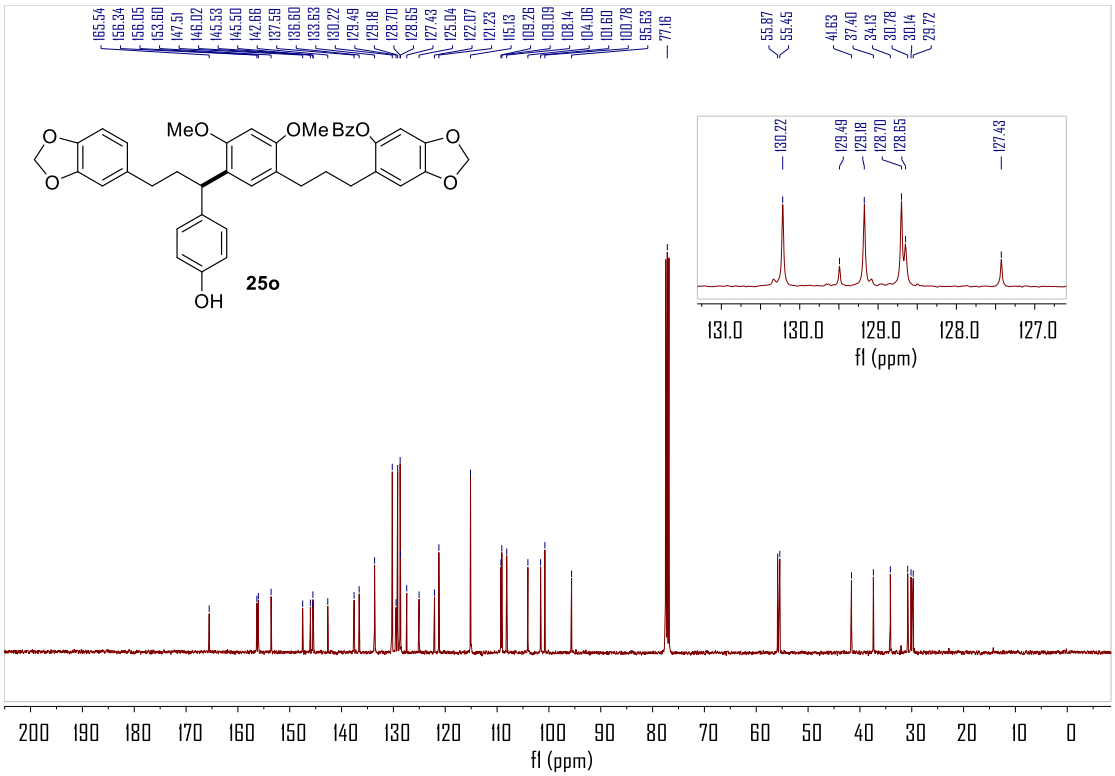
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25n**



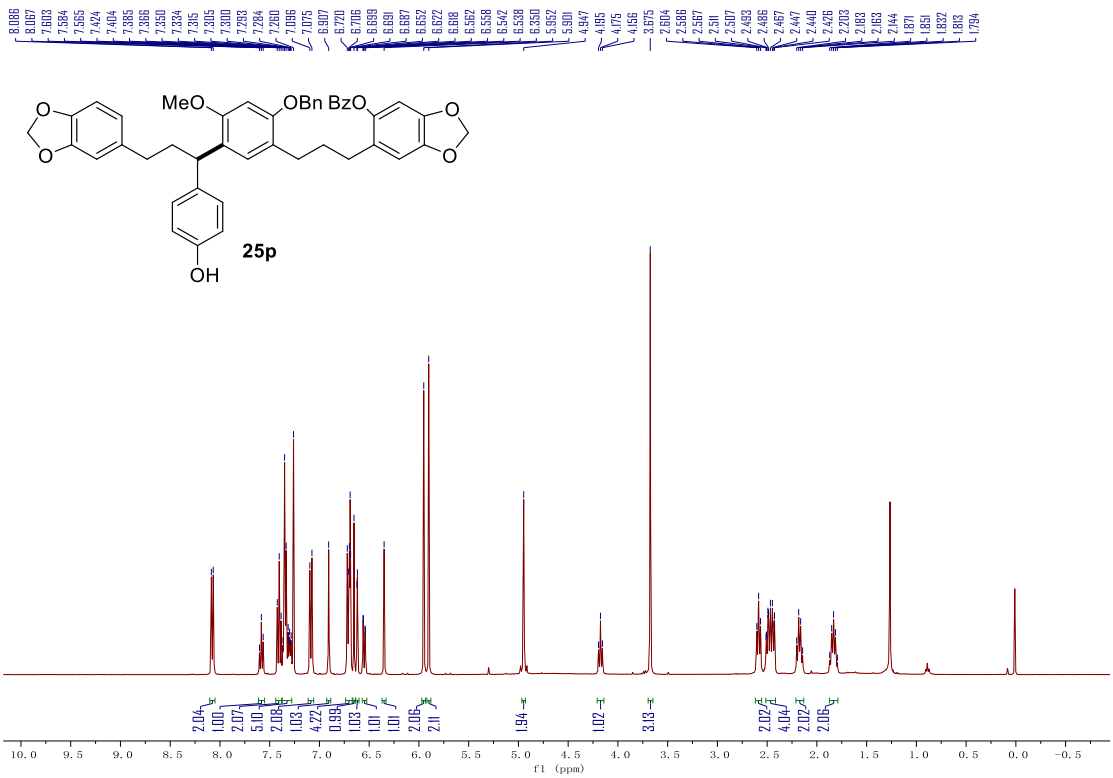
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **25n**



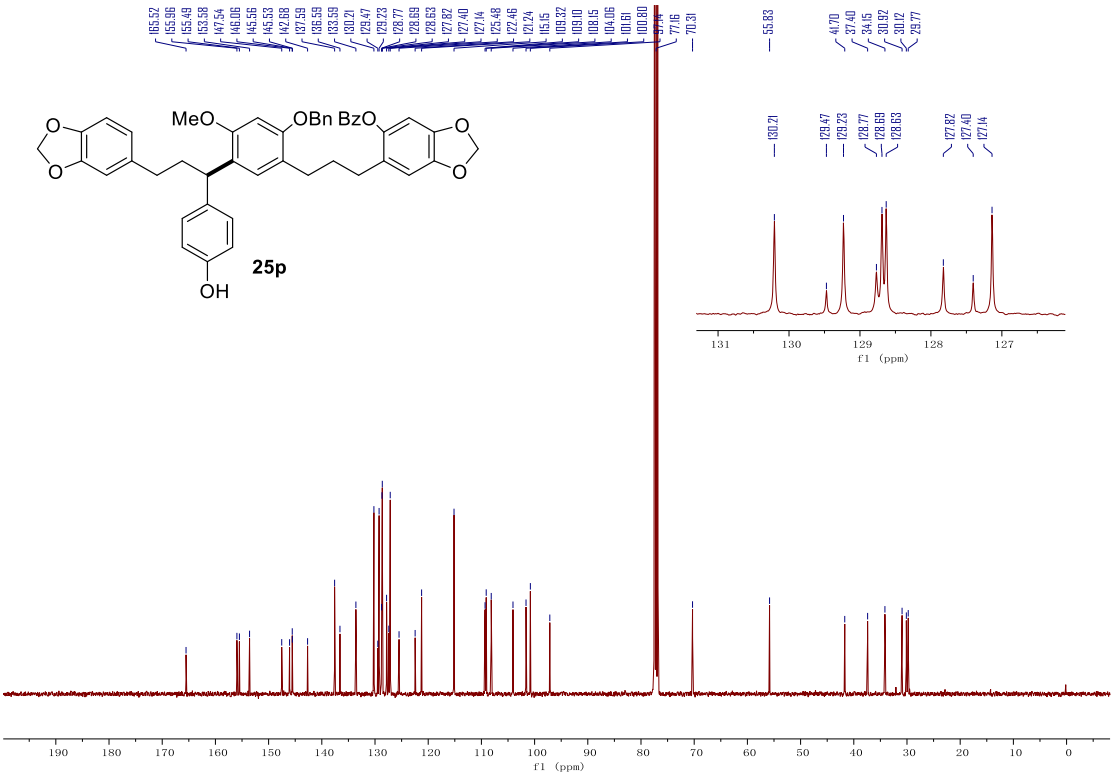
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25o**



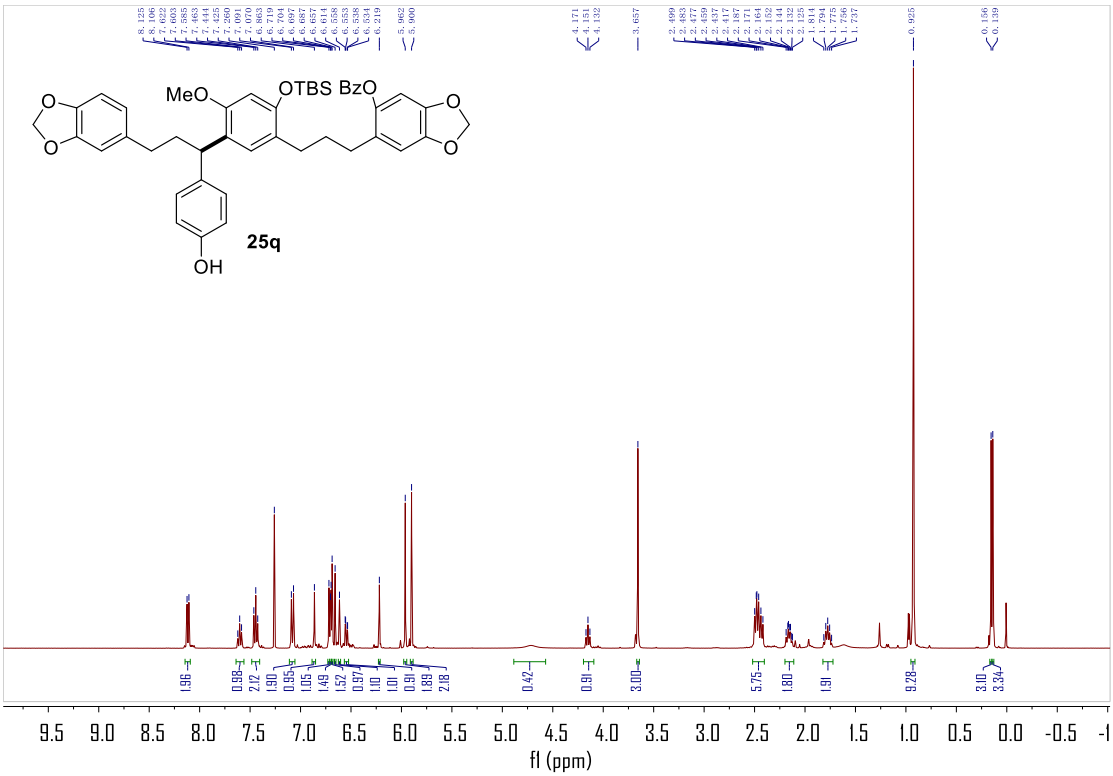
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25o**



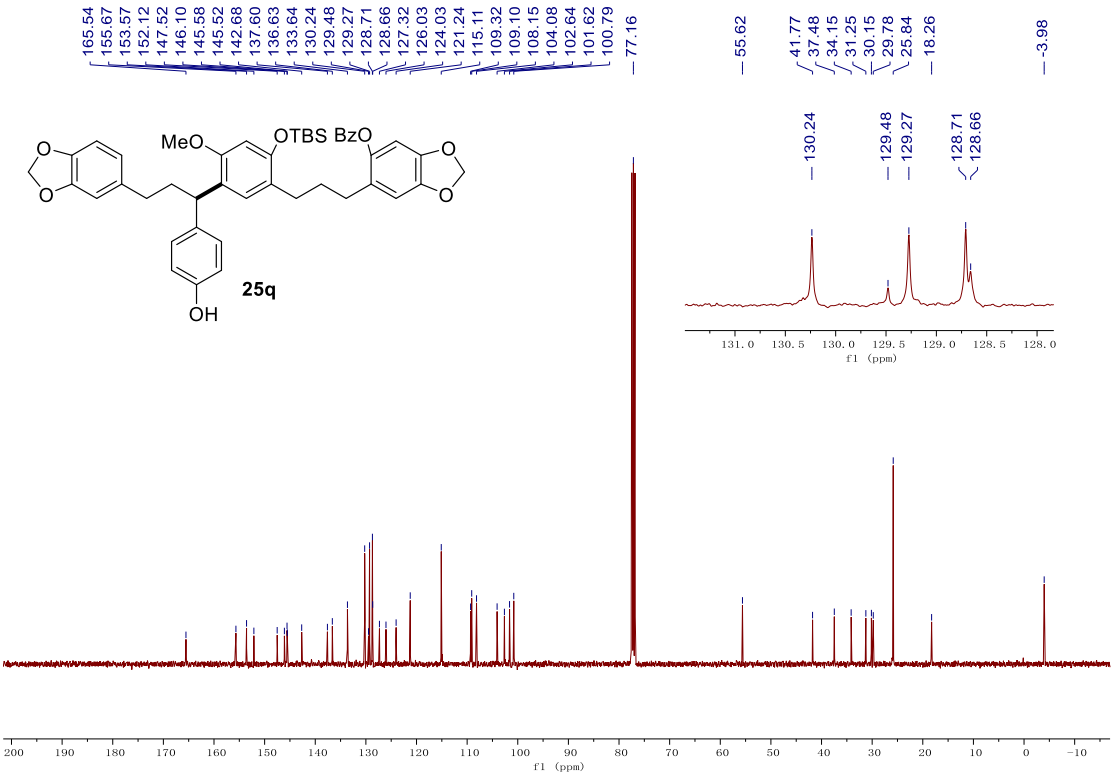
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25p**



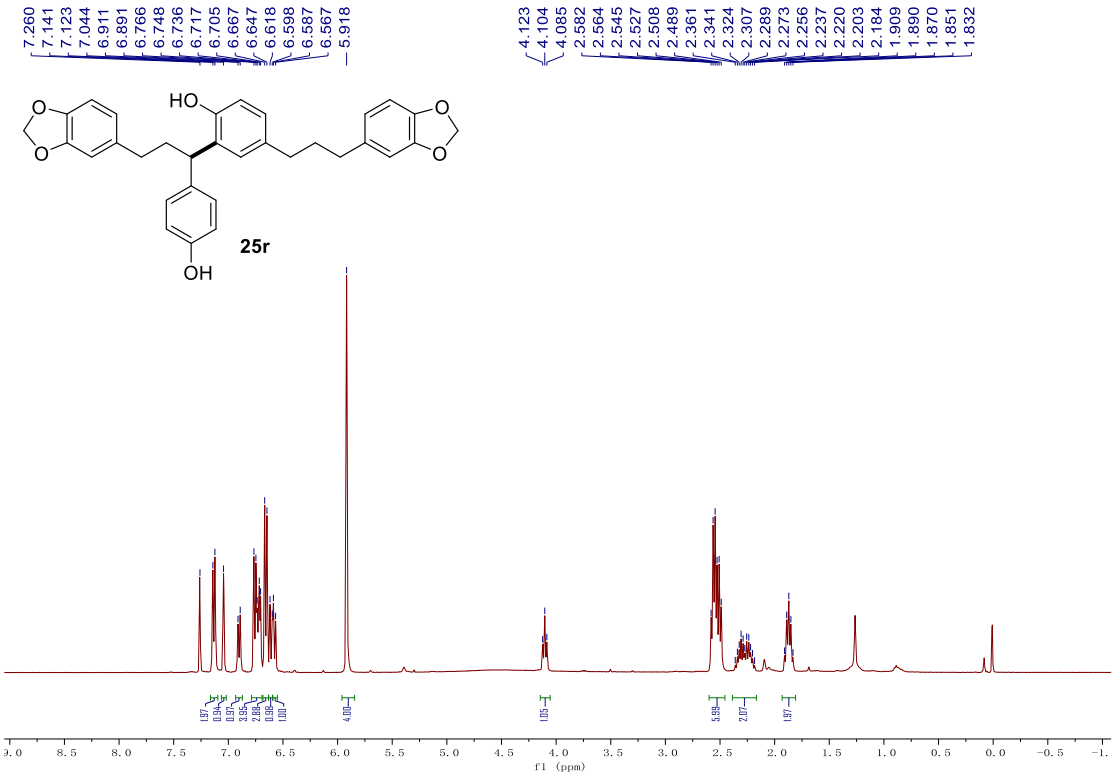
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25p**



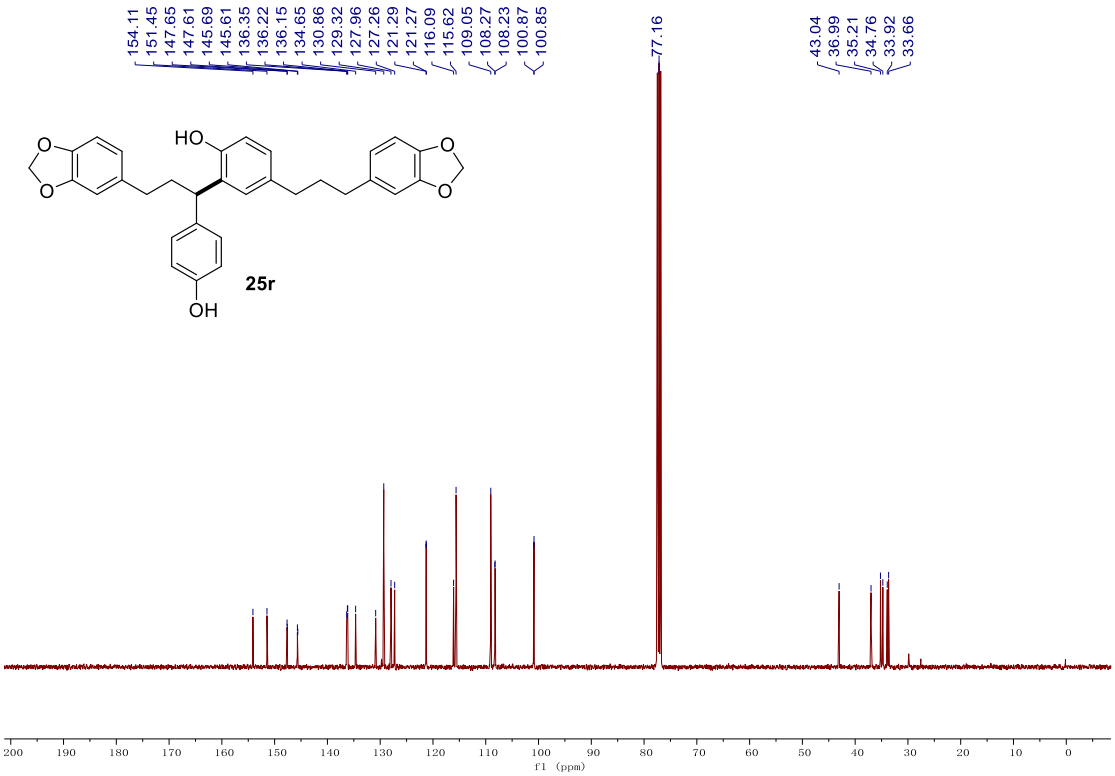
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25q**



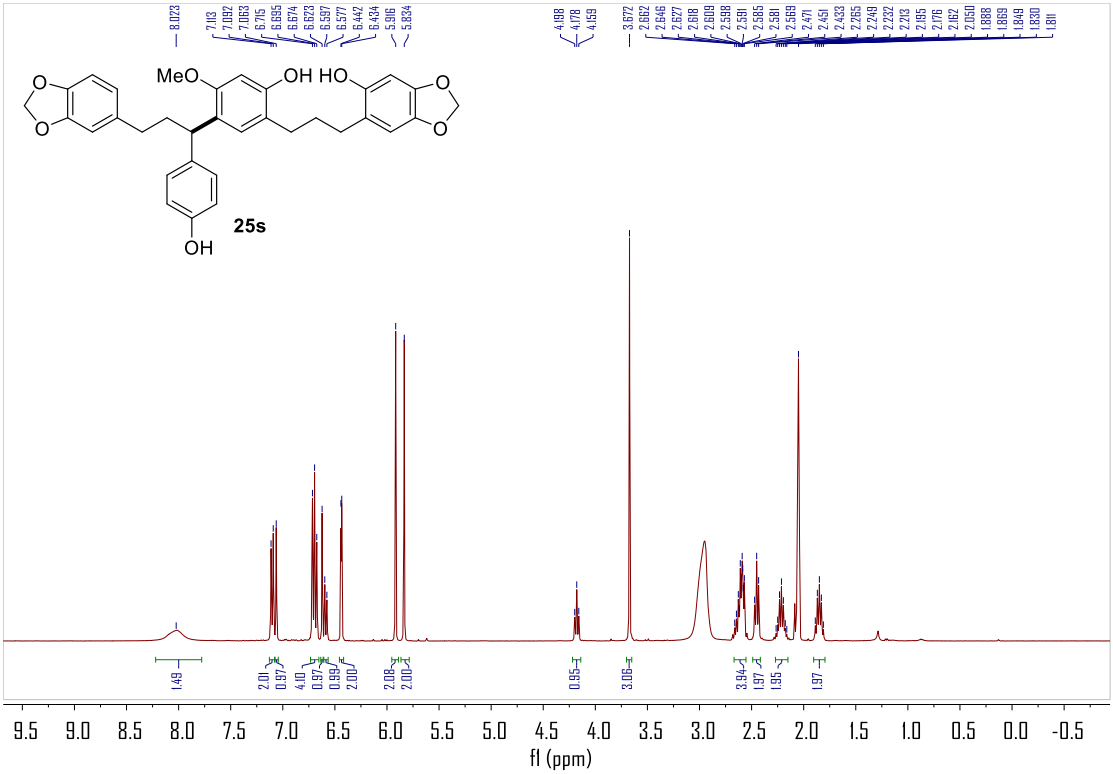
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25q**



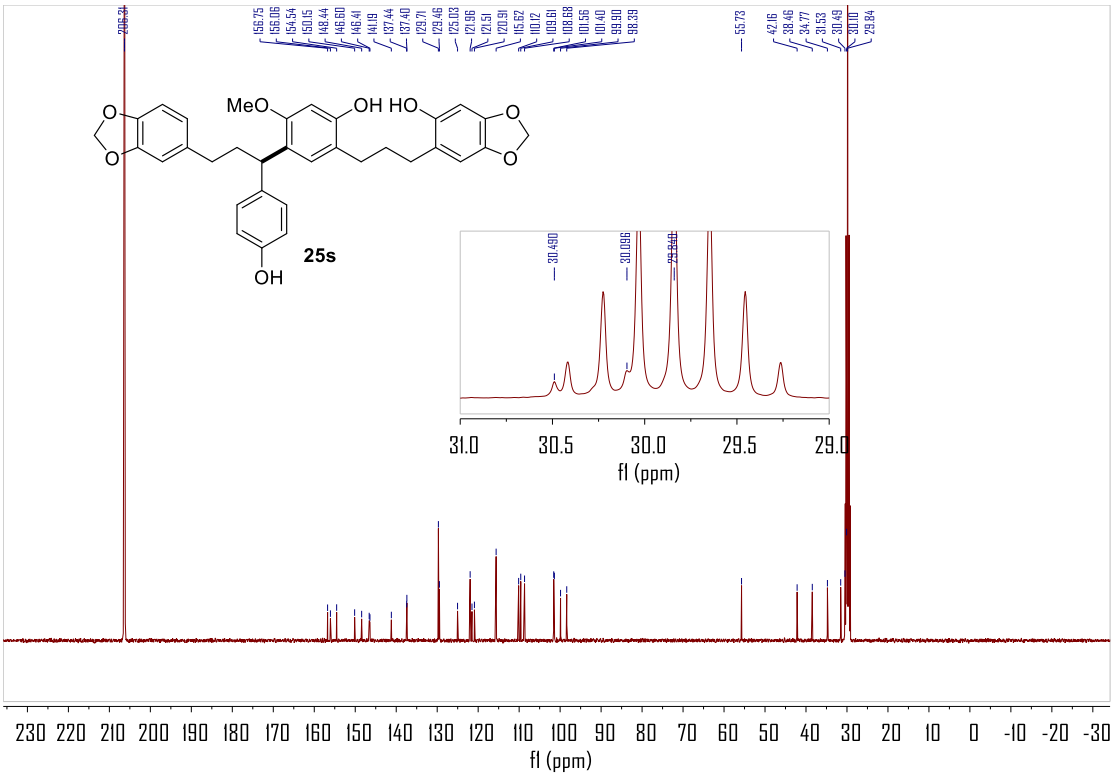
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25r**



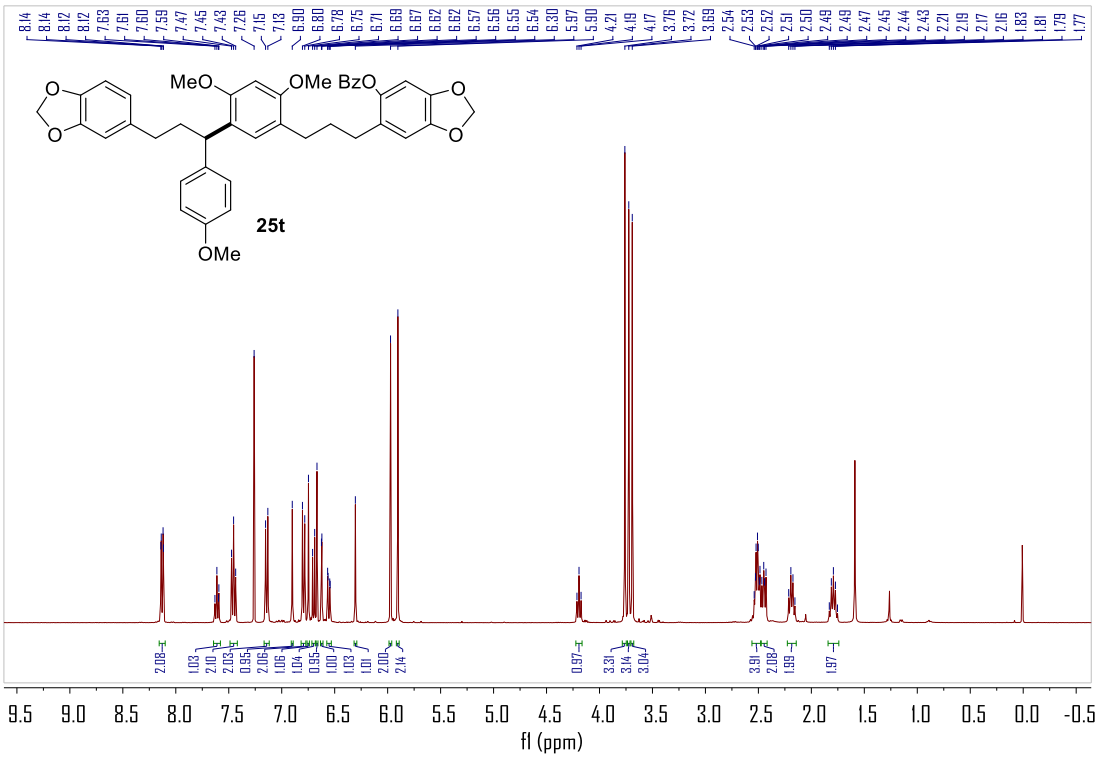
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25r**



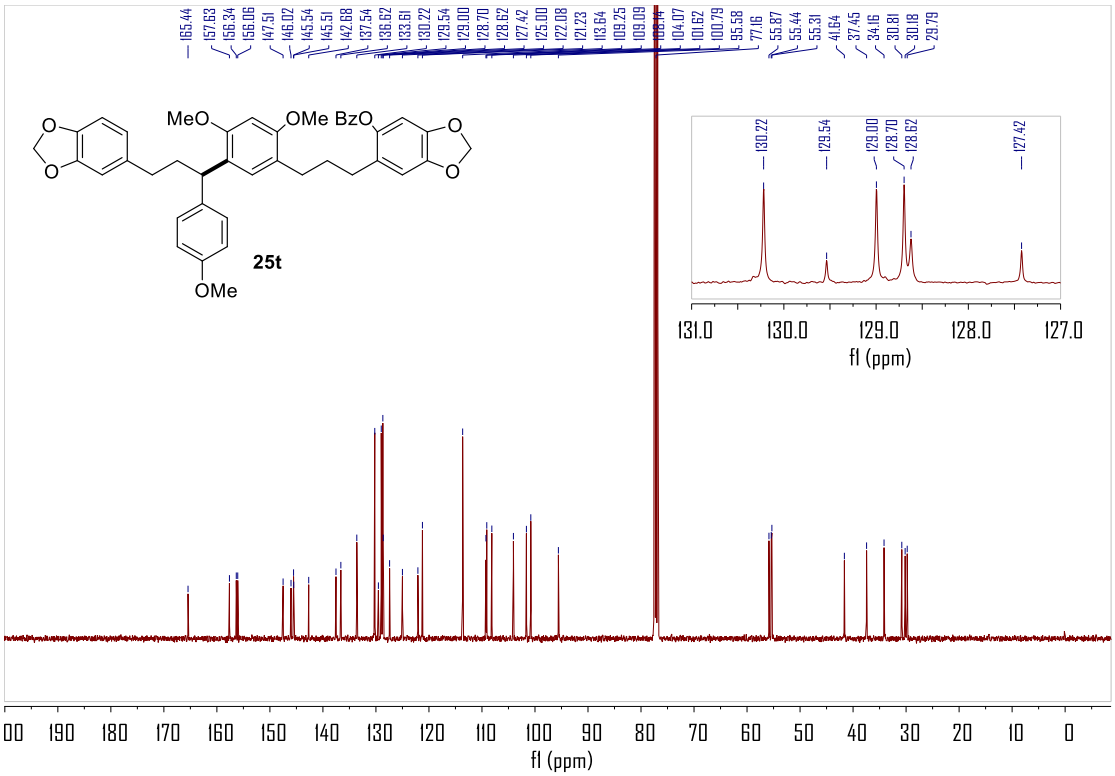
^{1}H NMR spectrum (400 MHz, acetone-d_6) of compound **25s**



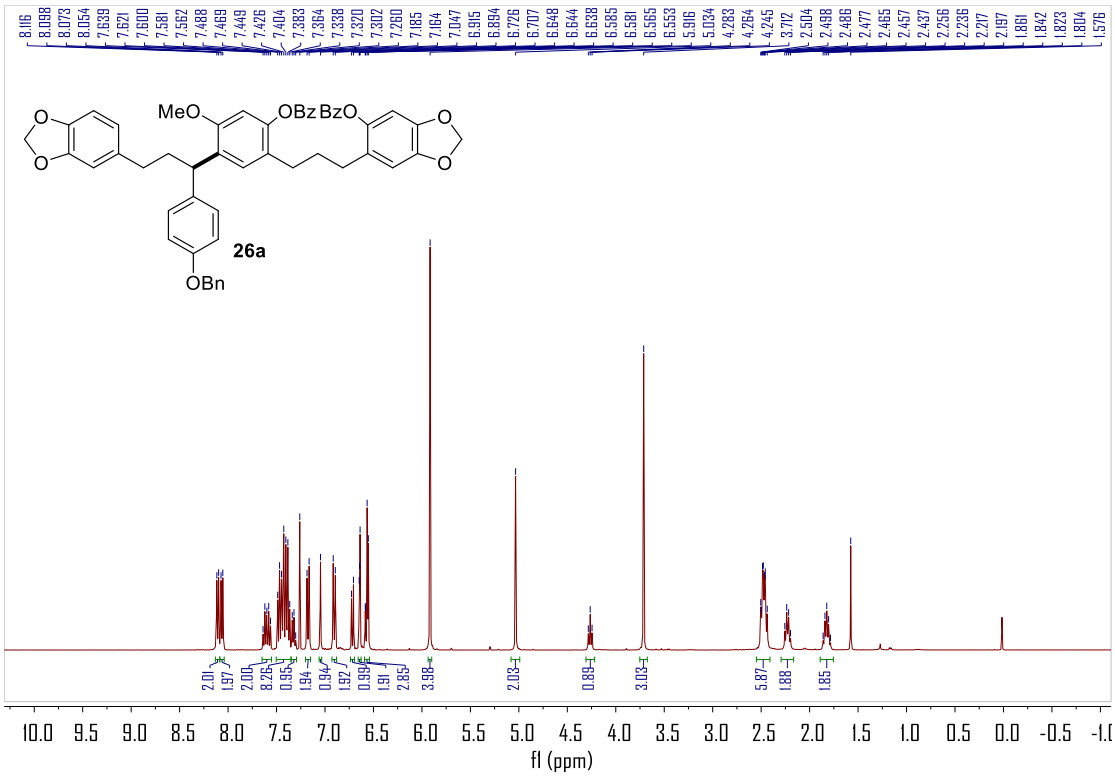
^{13}C NMR spectrum (100 MHz, acetone-d_6) of compound **25s**



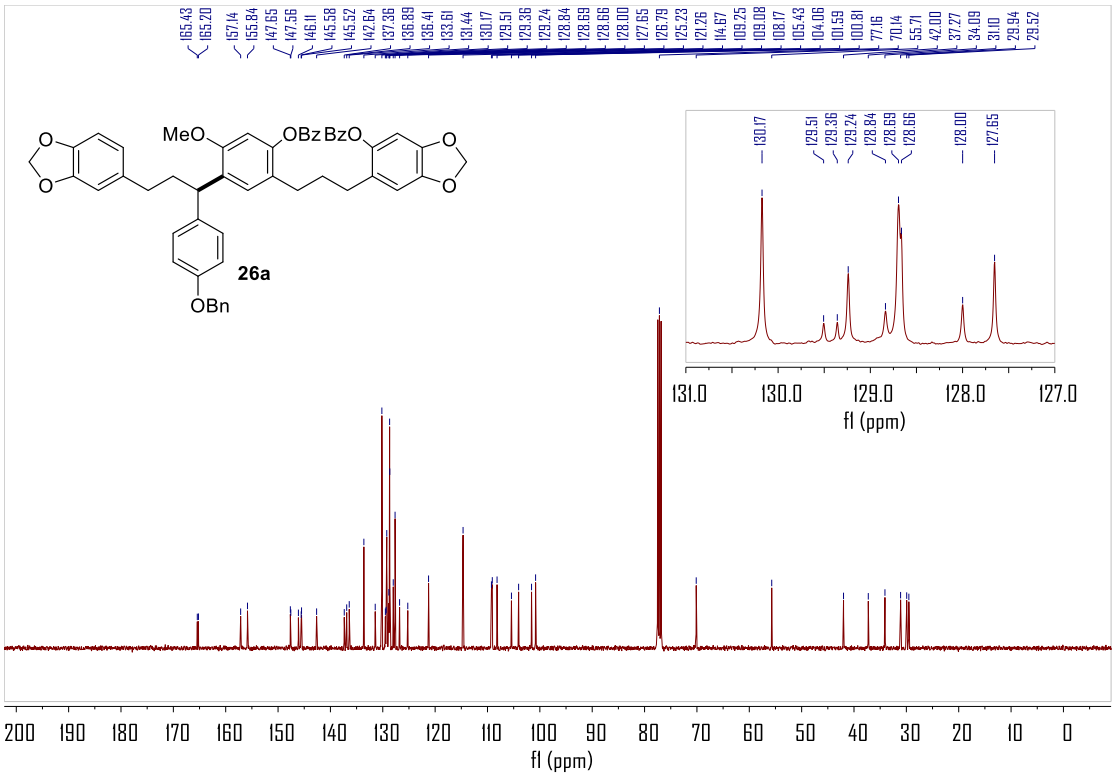
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **25t**



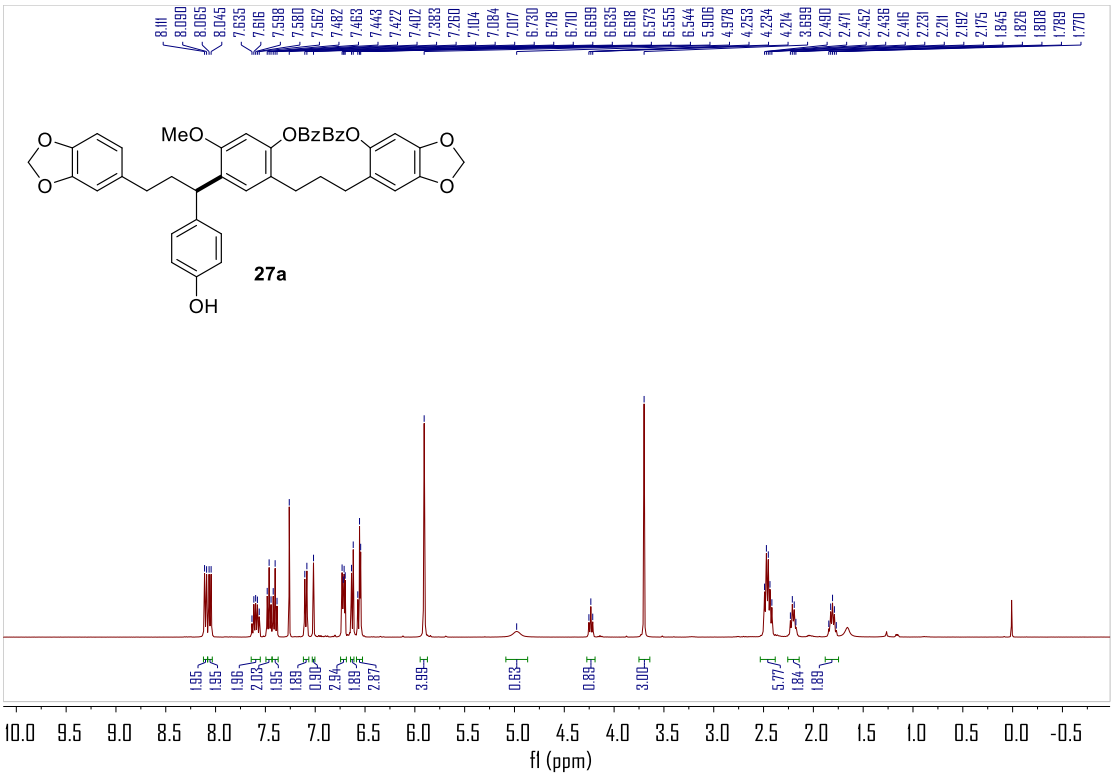
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **25t**



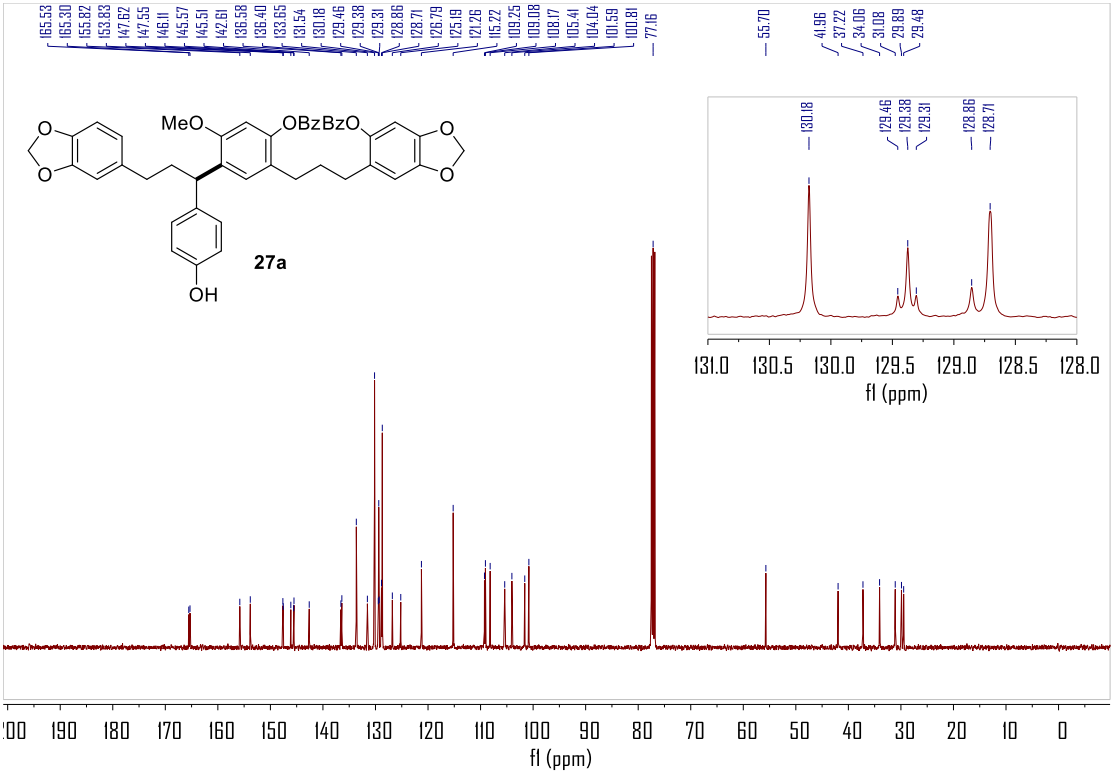
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **26a**



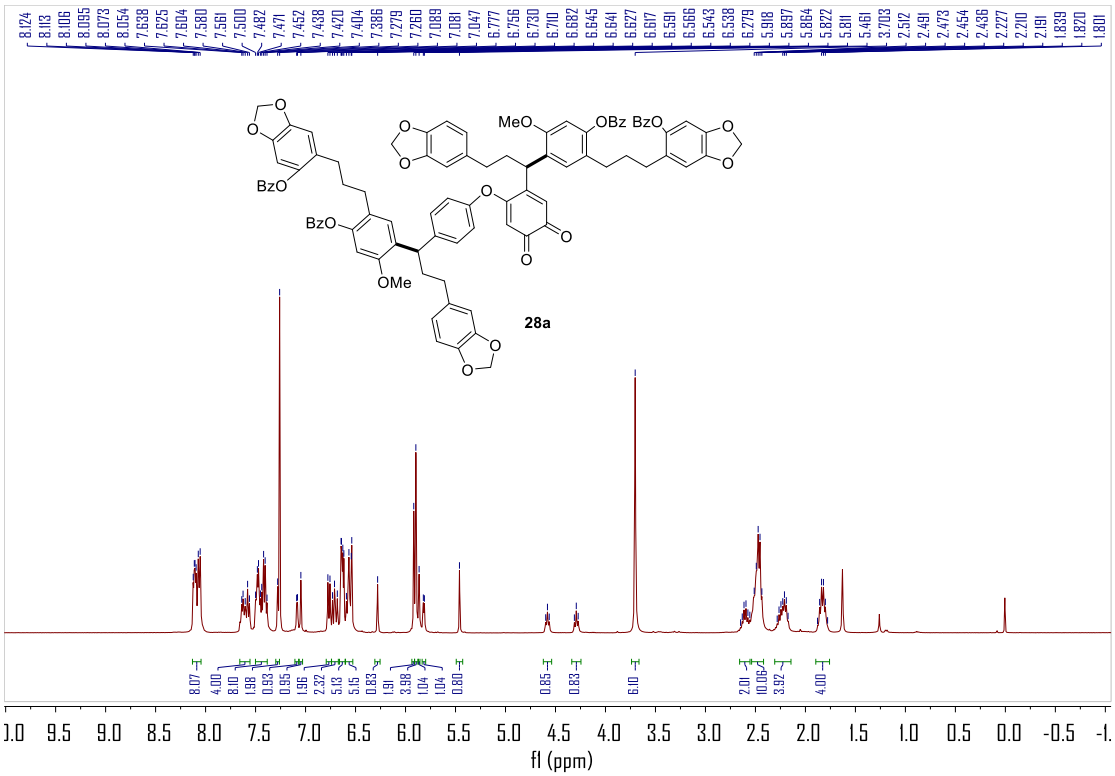
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **26a**



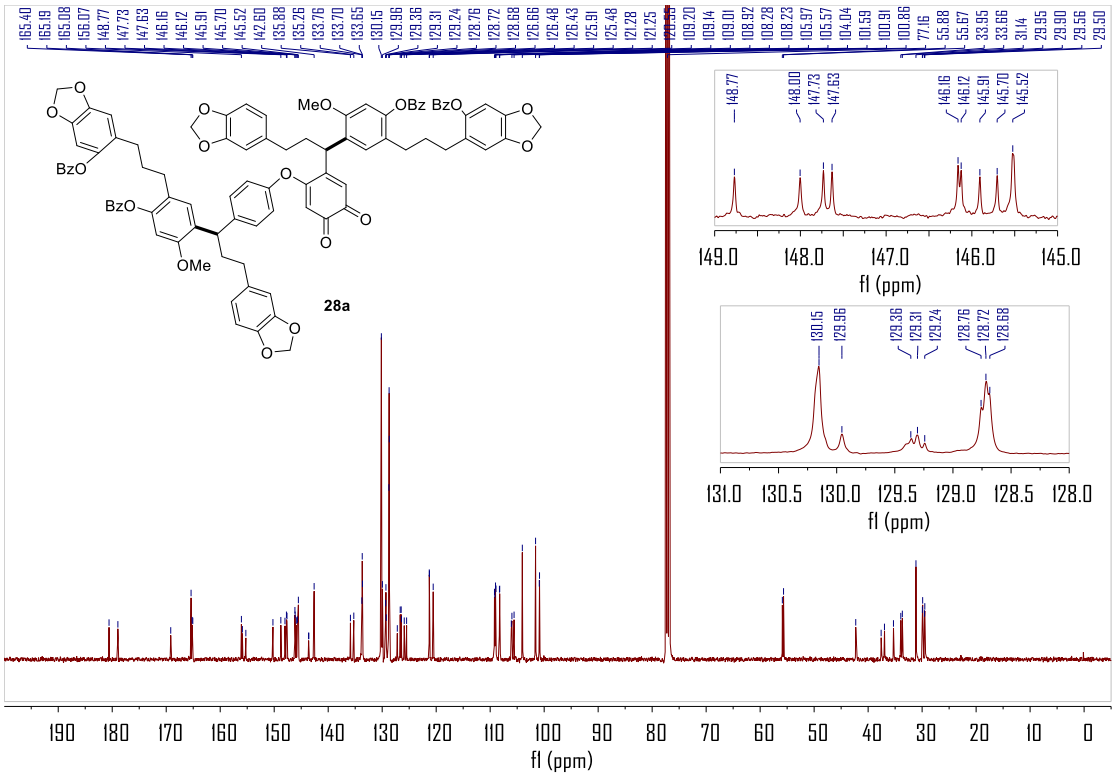
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **27**



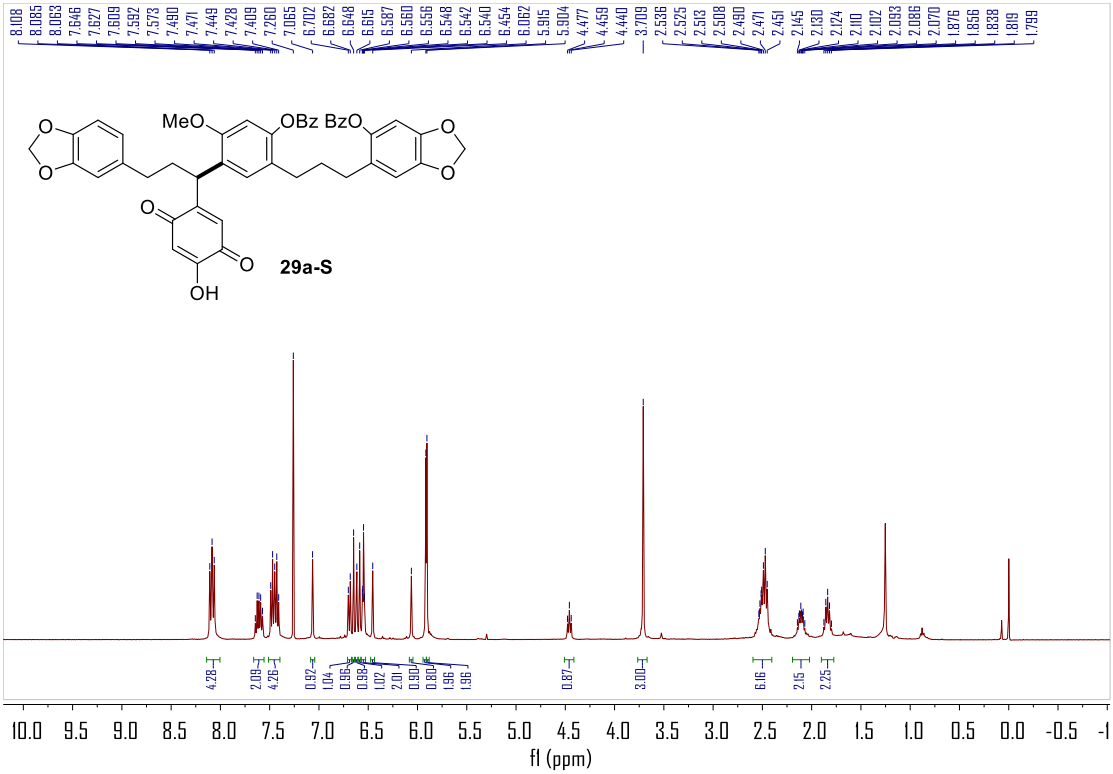
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **27**



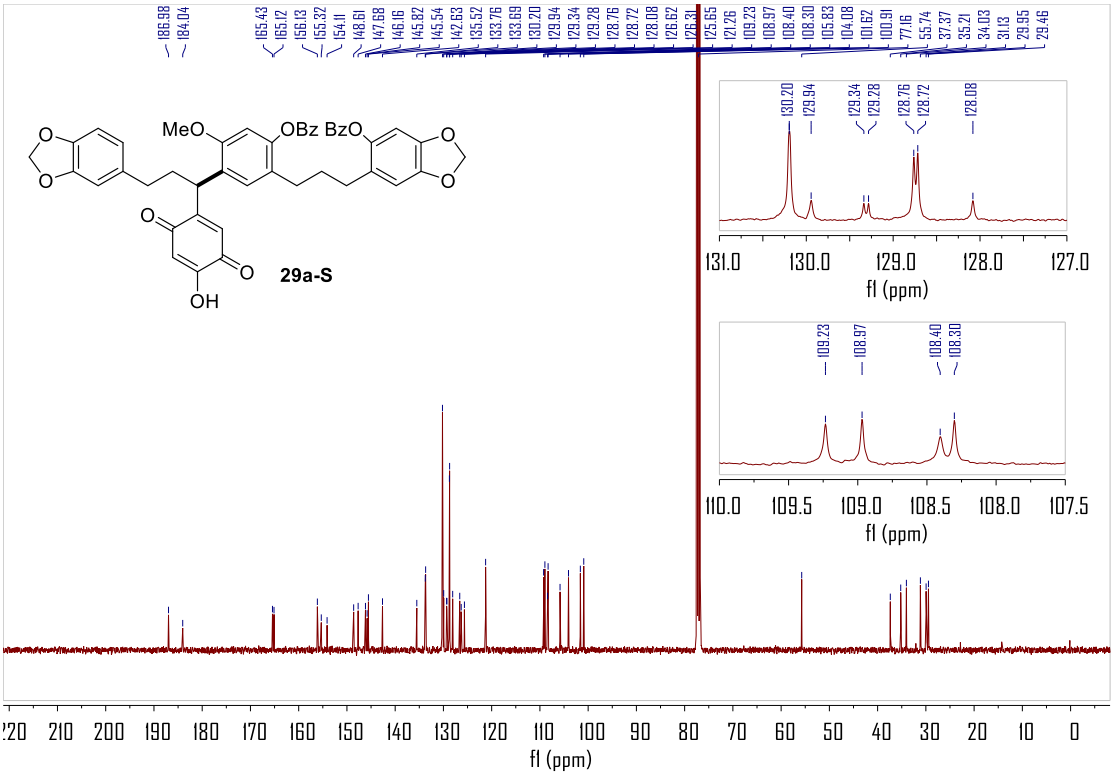
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **28a**



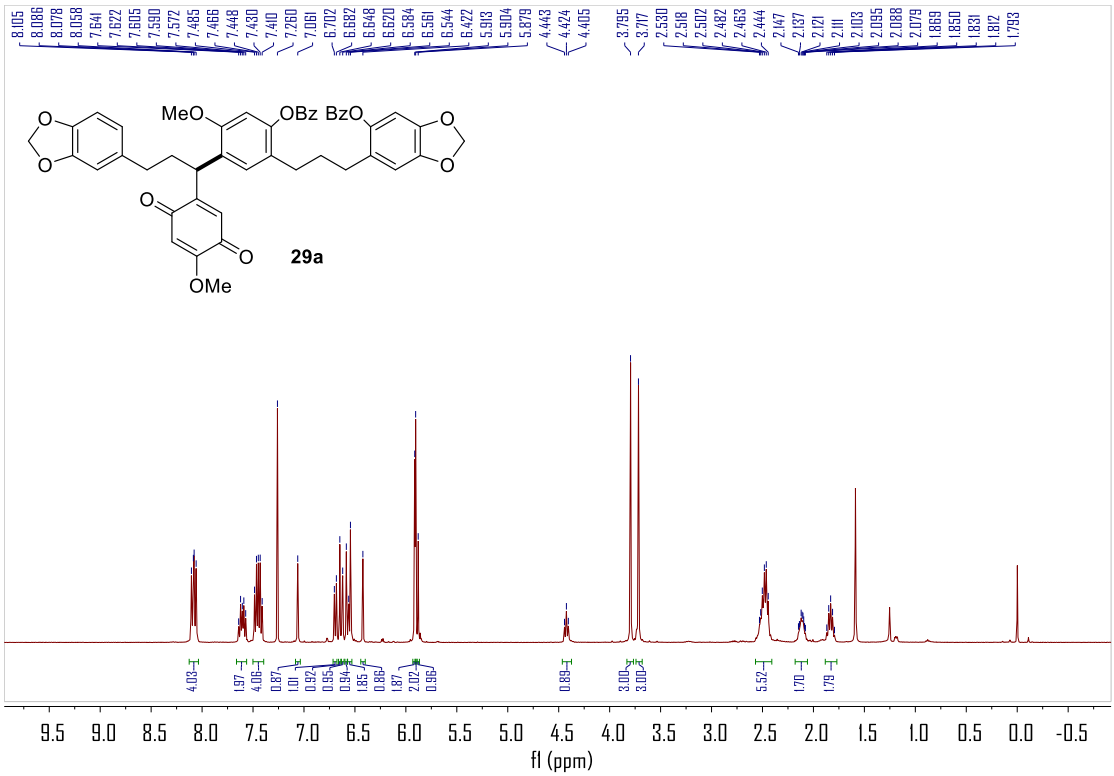
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **28a**



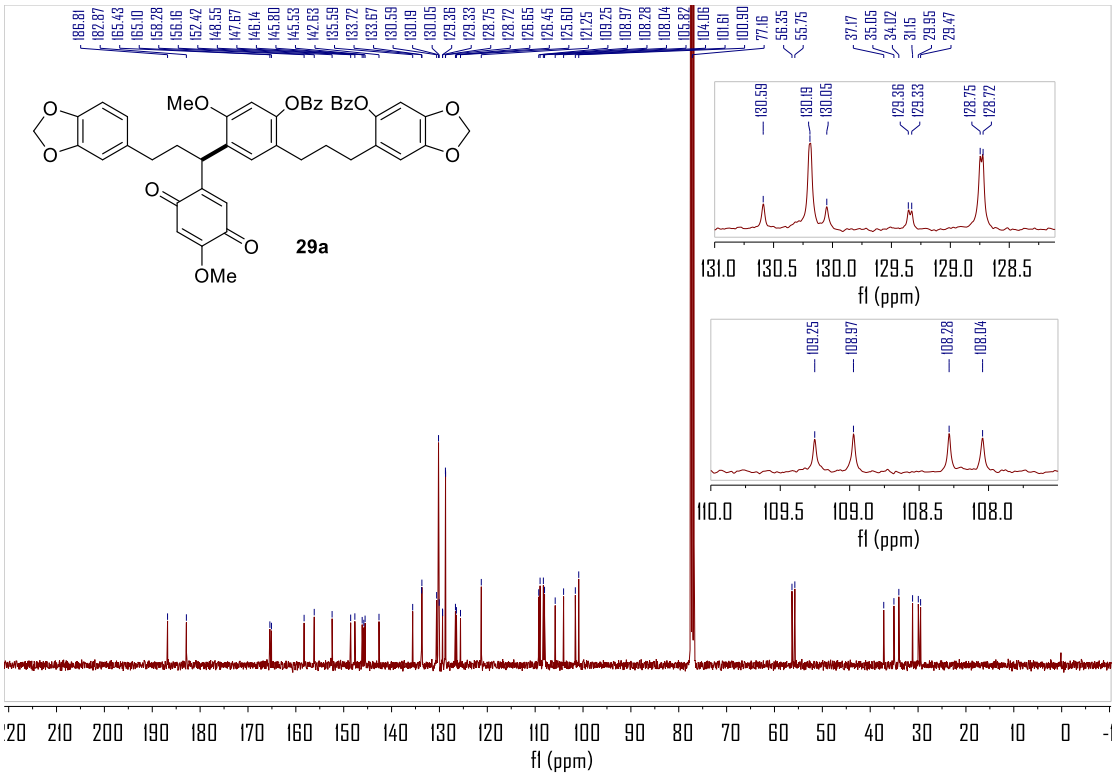
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **29a-S**



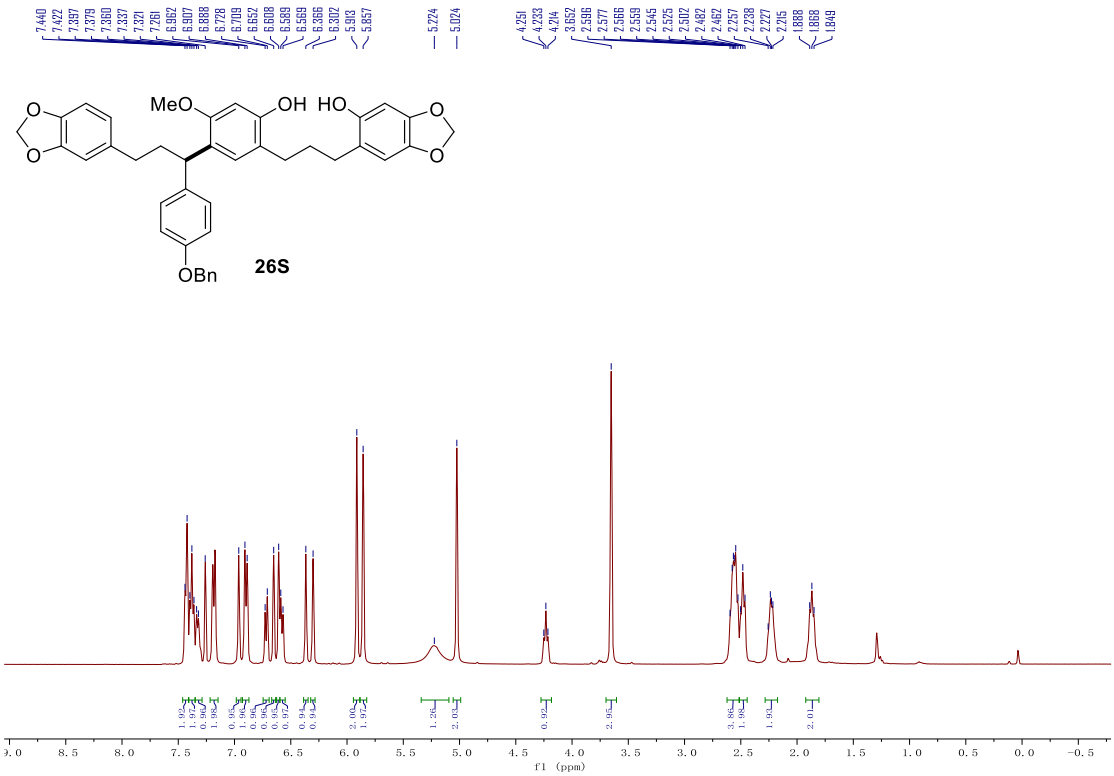
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **29a-S**



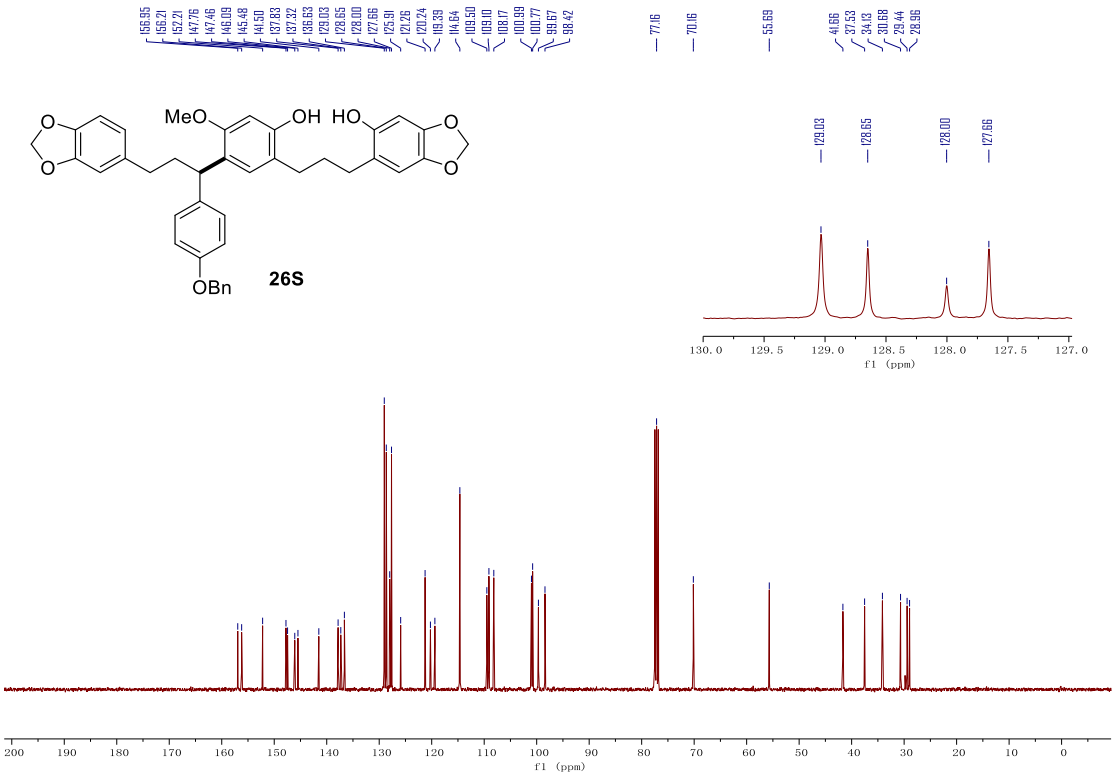
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **29a**



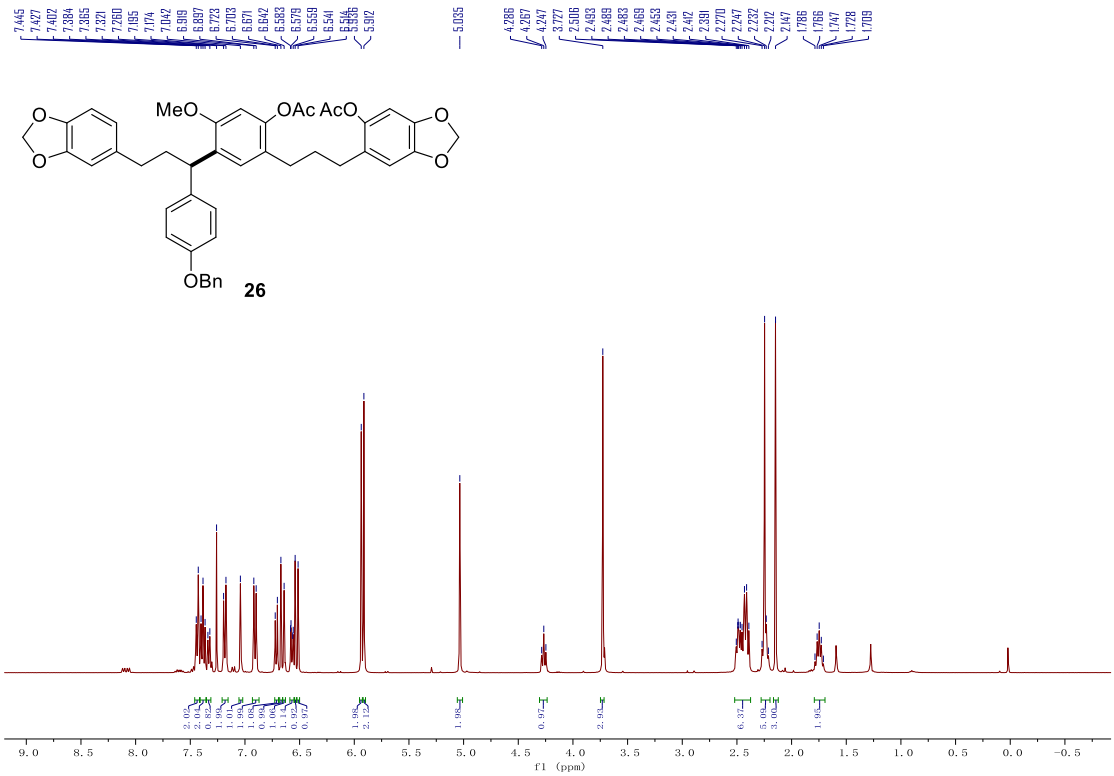
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **29a**



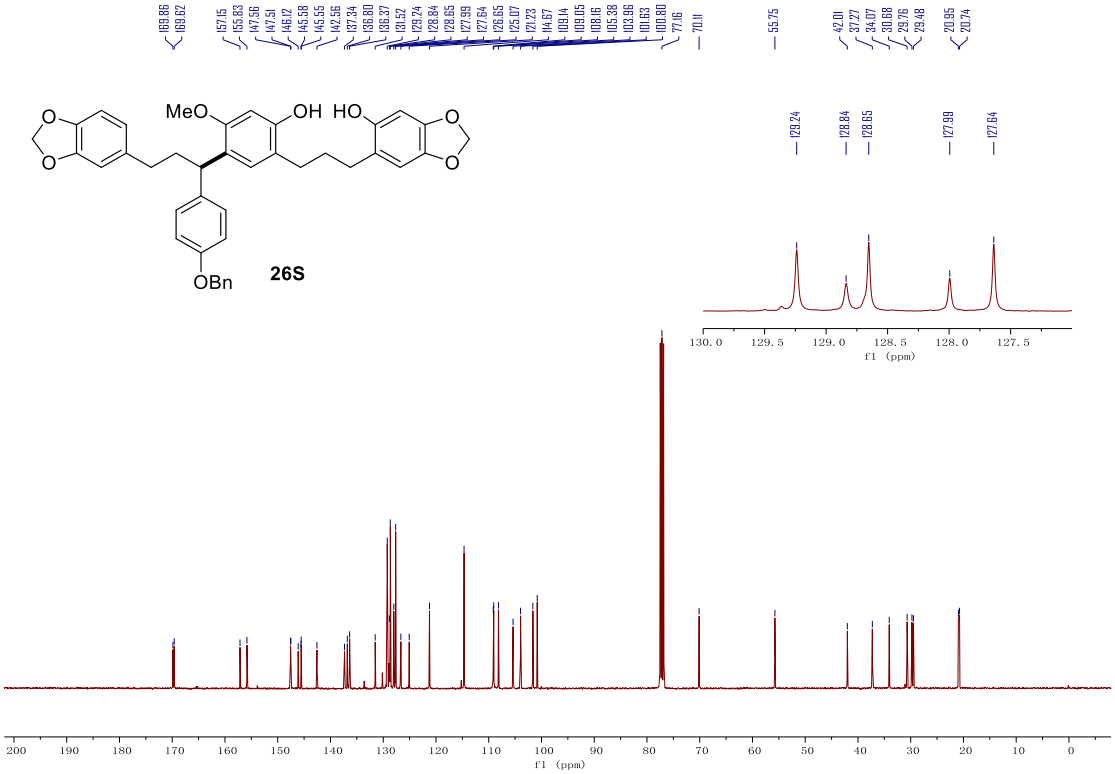
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **26S**



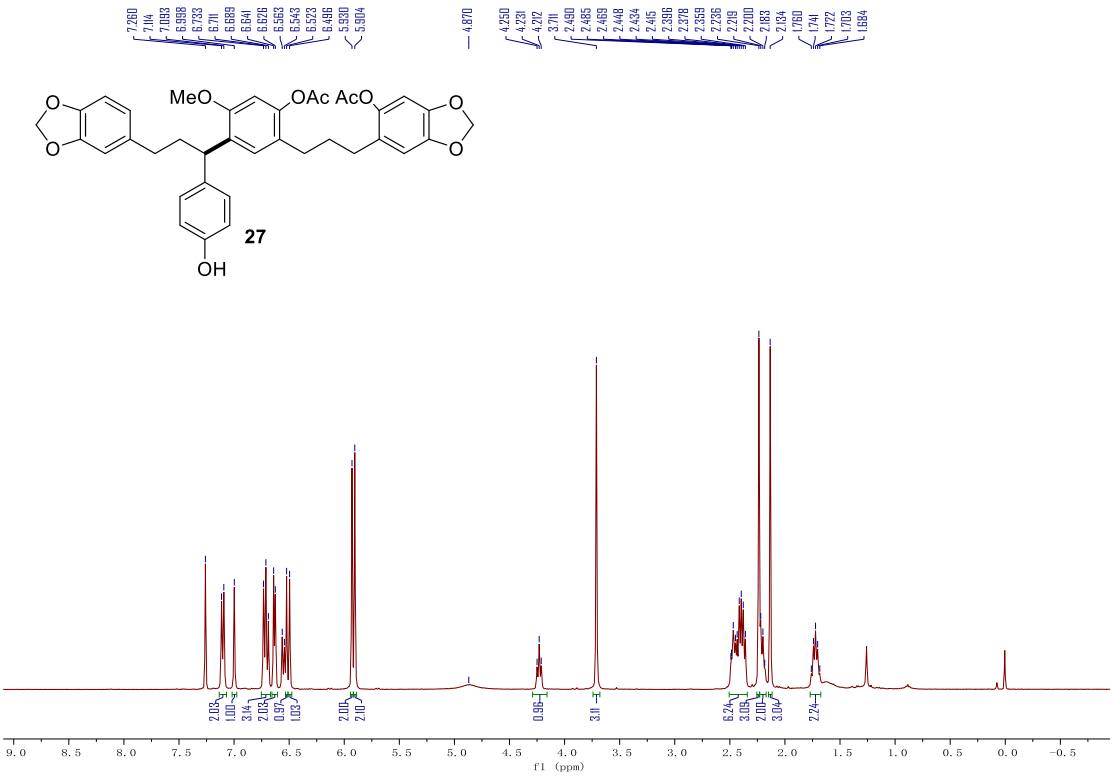
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **26S**



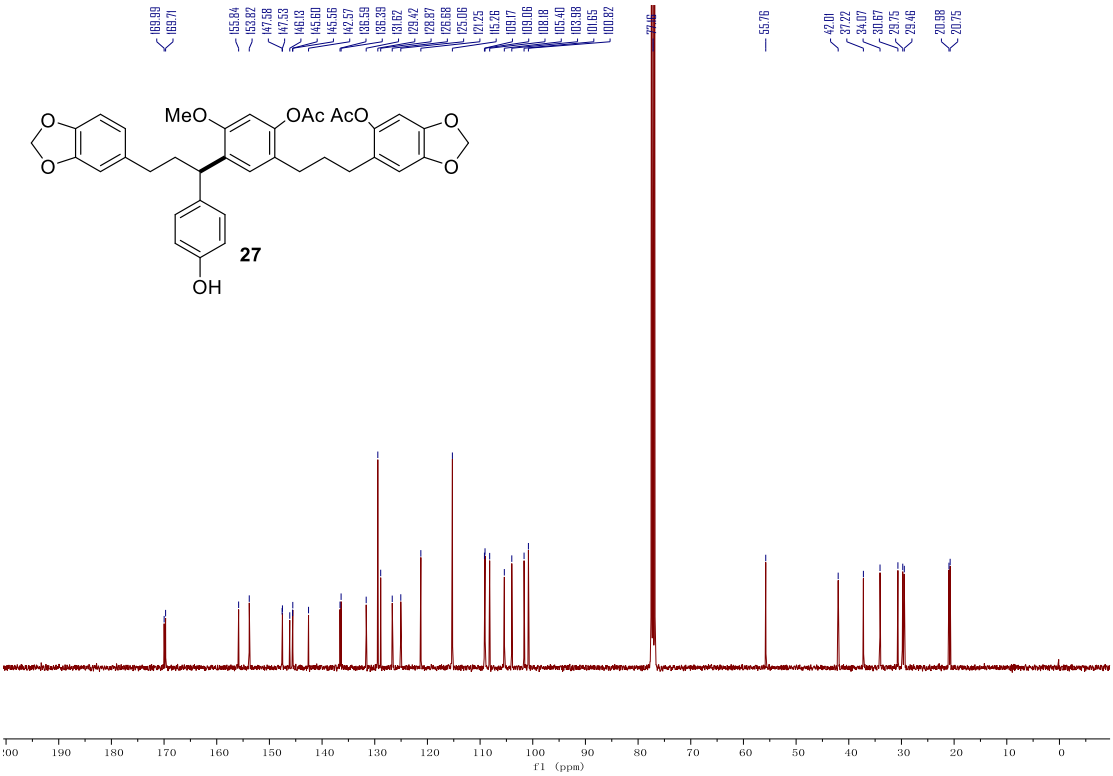
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **26**



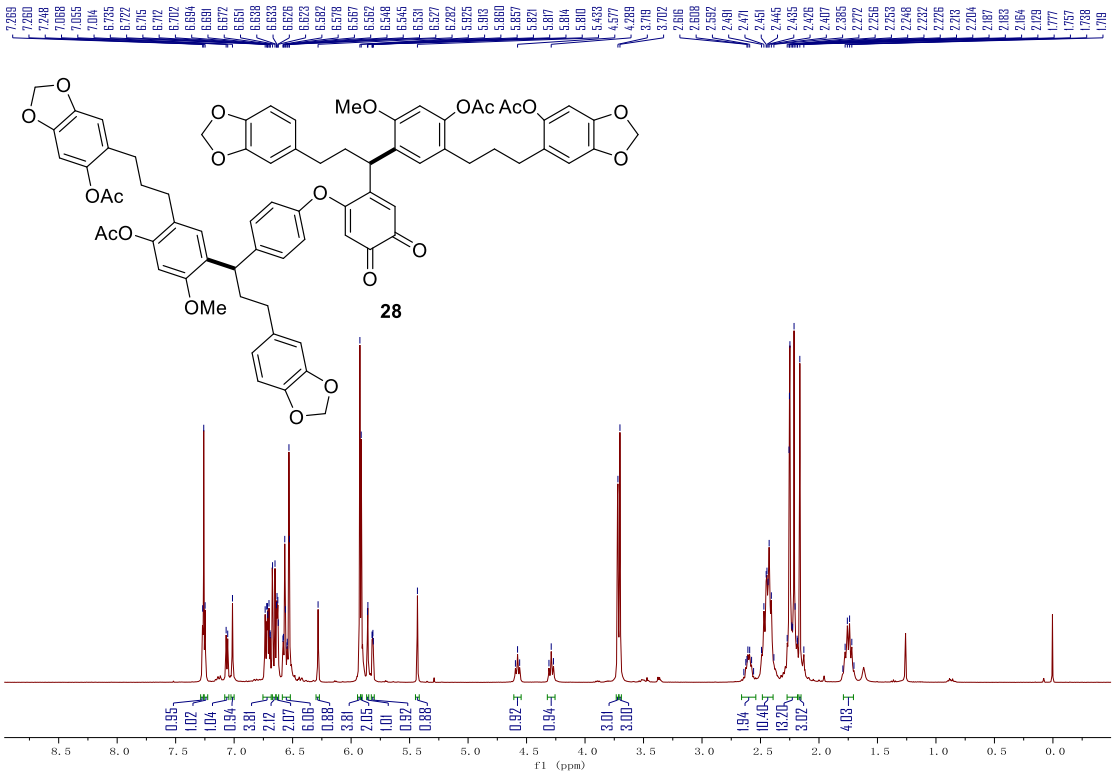
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **26**



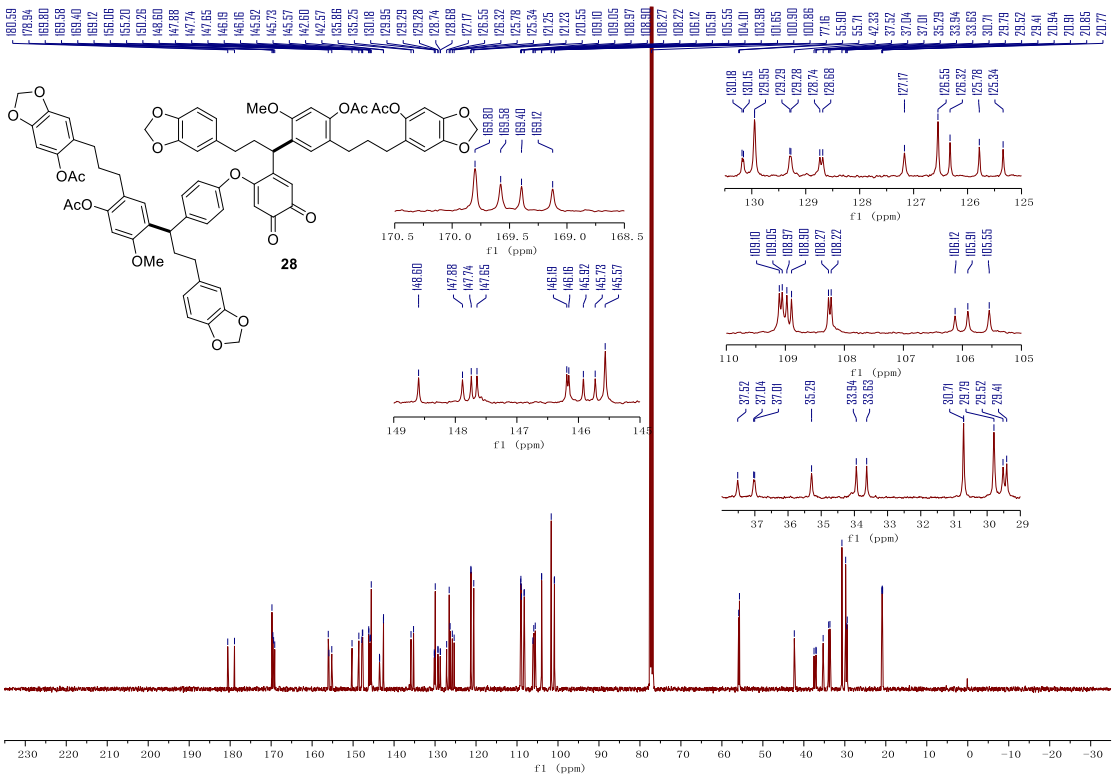
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **27**



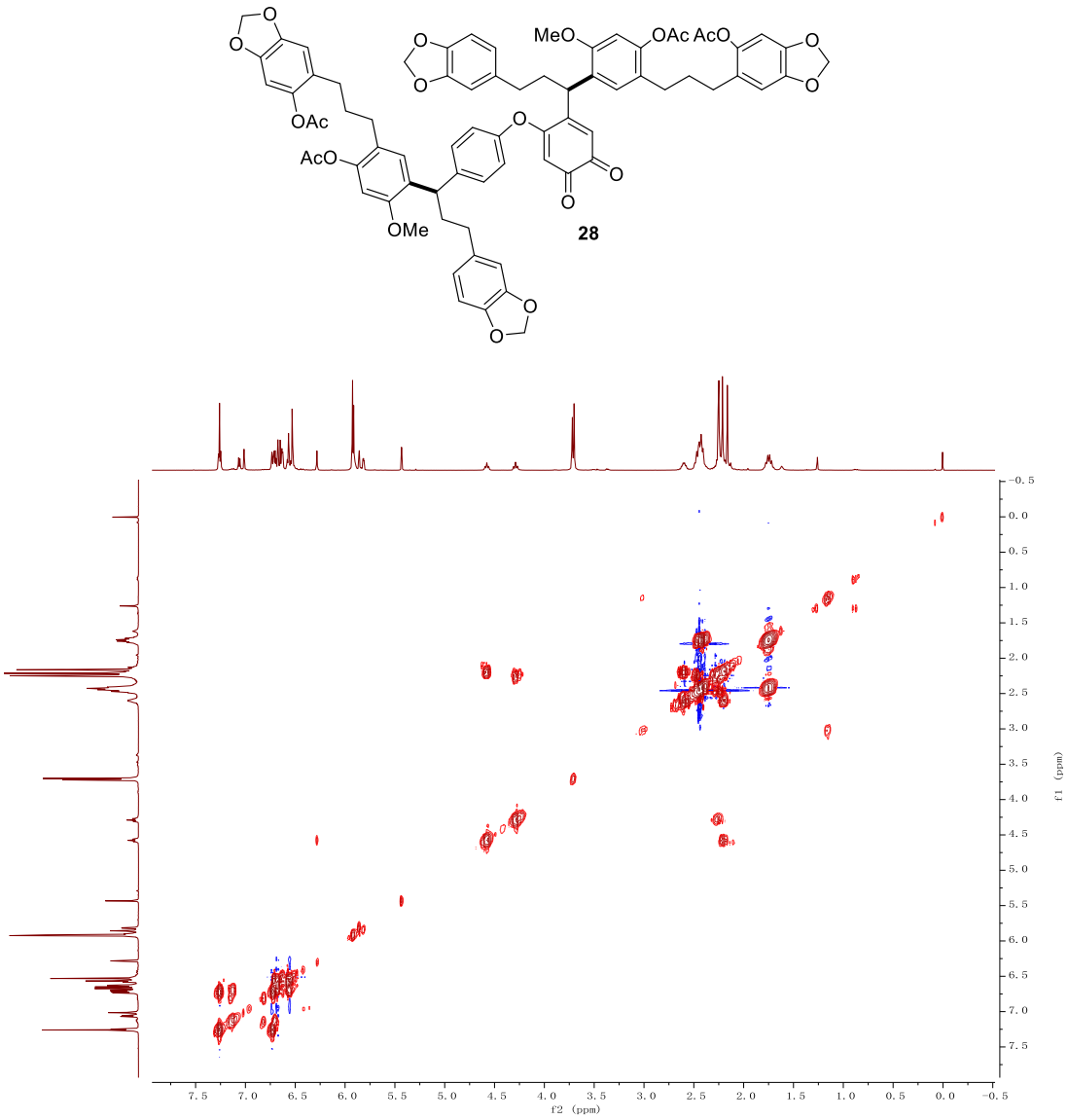
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **27**



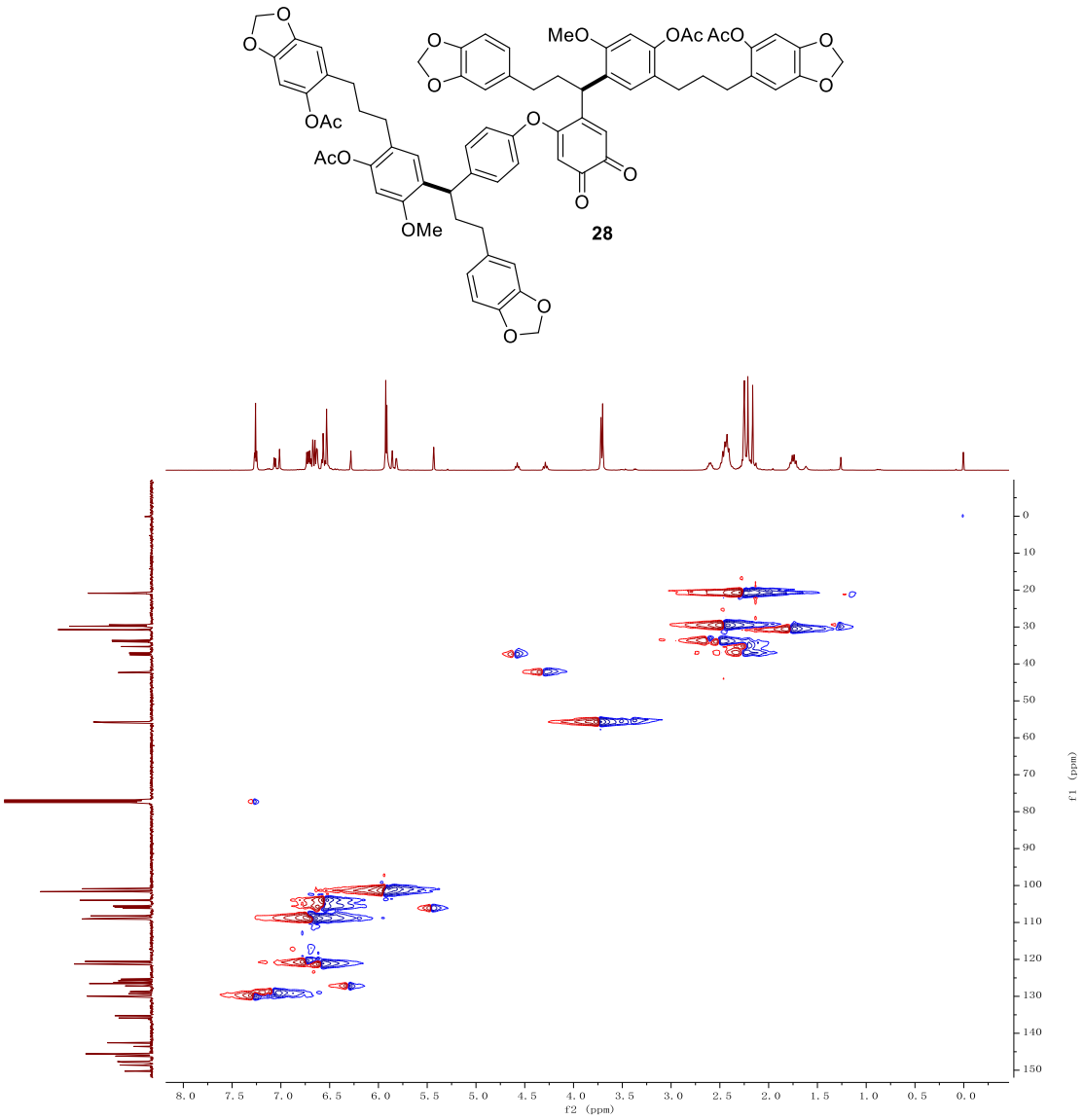
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **28**



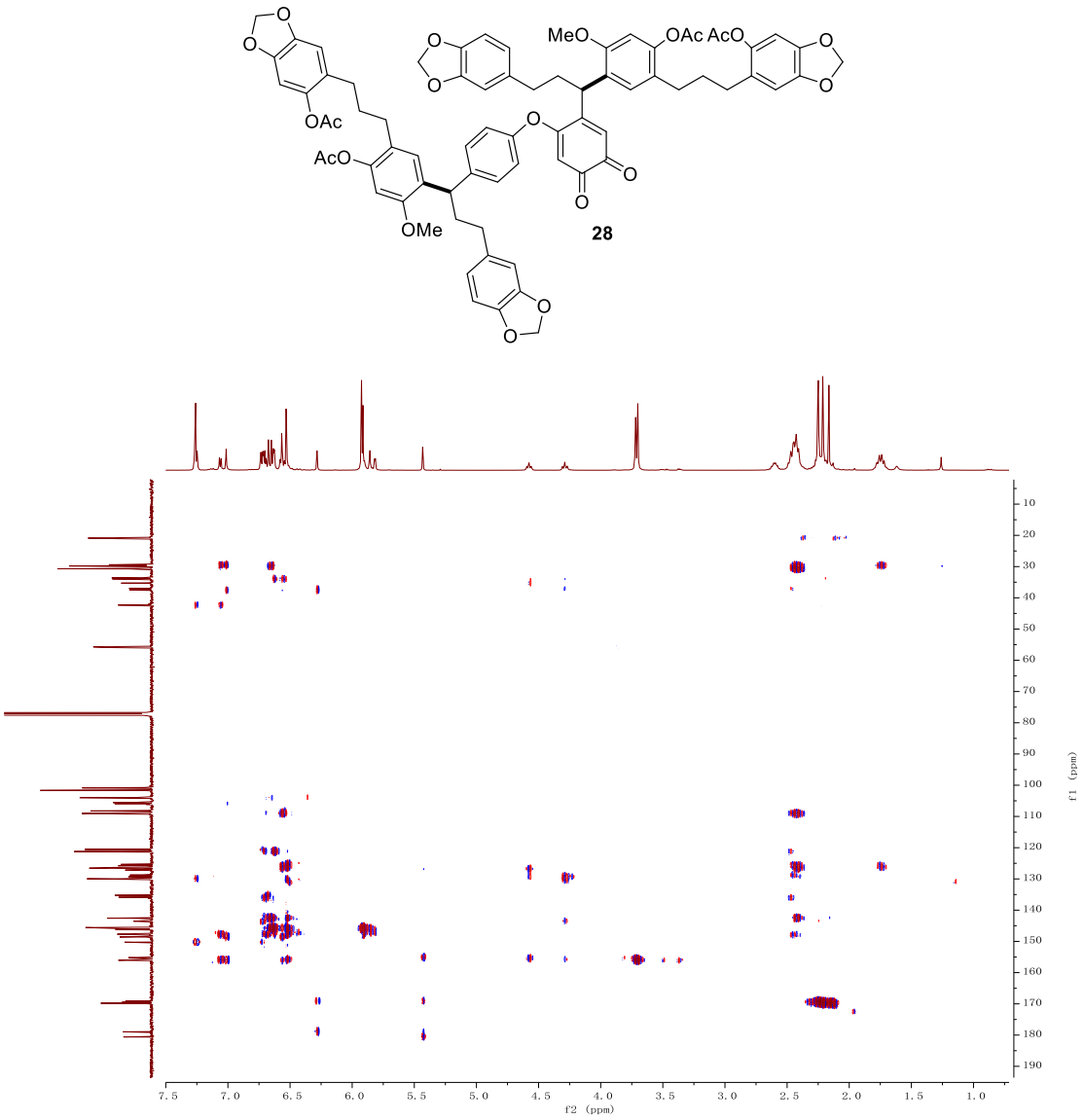
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **28**



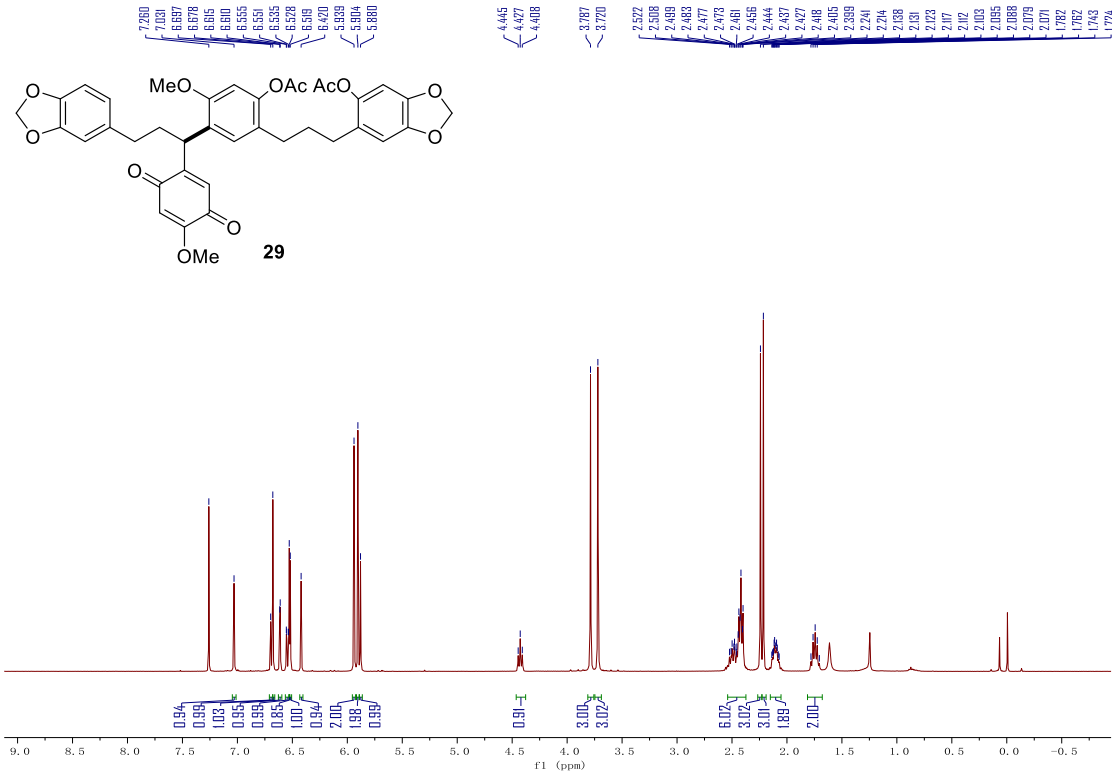
^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$) of **28**



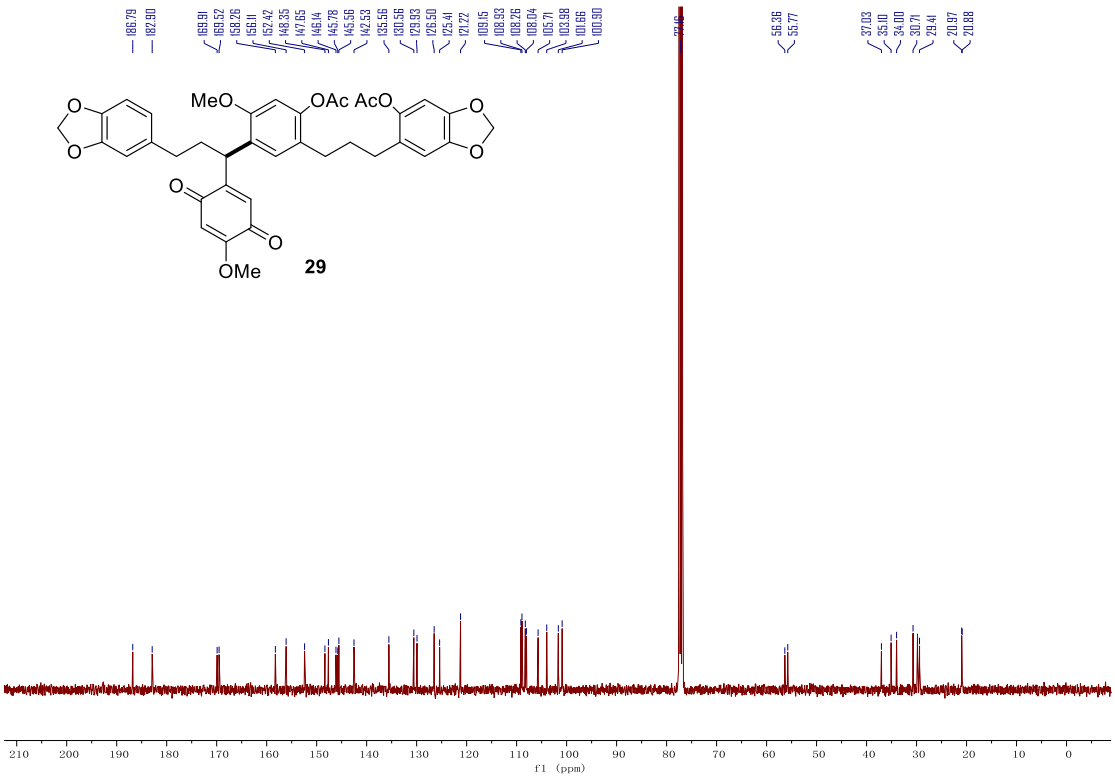
HSQC spectrum (500 MHz, $CDCl_3$) of **28**



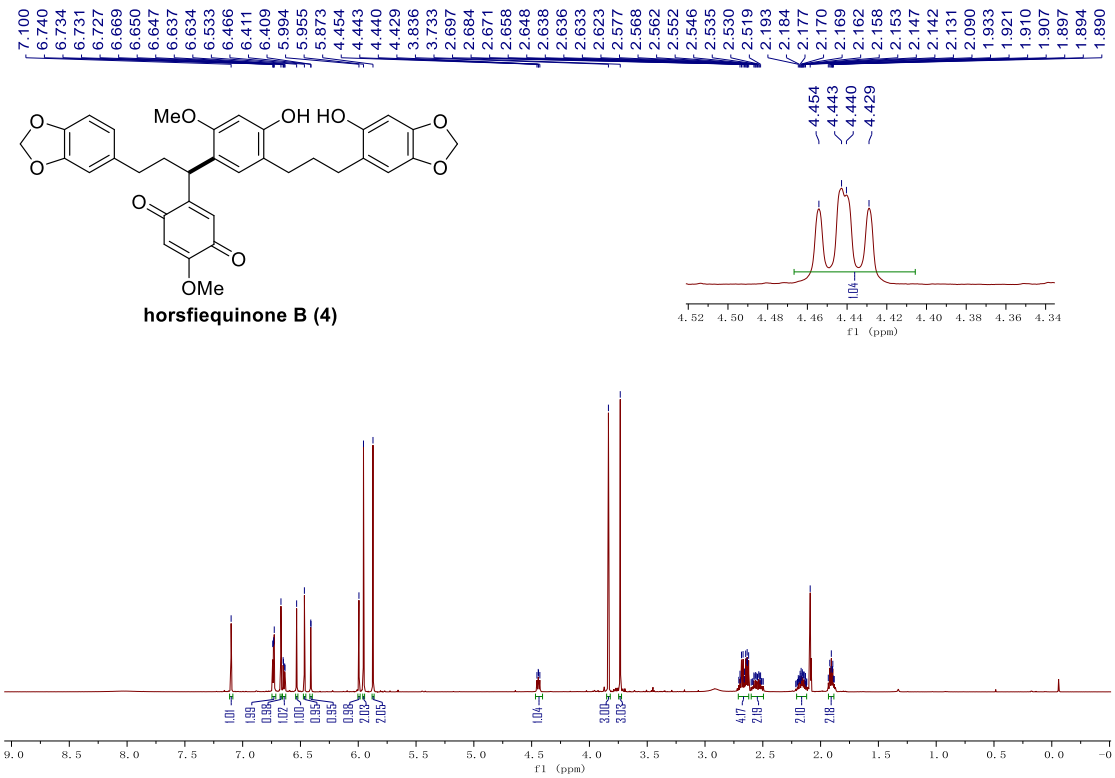
HMBC spectrum (500 MHz, $CDCl_3$) of **28**



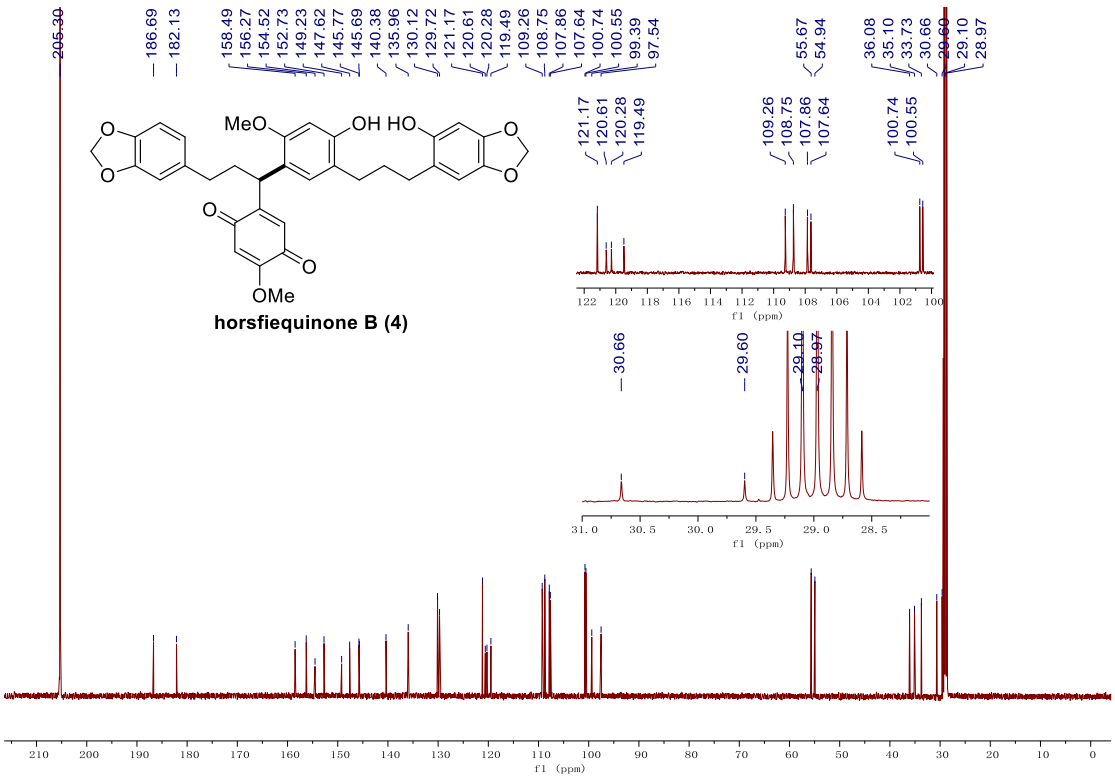
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **29**



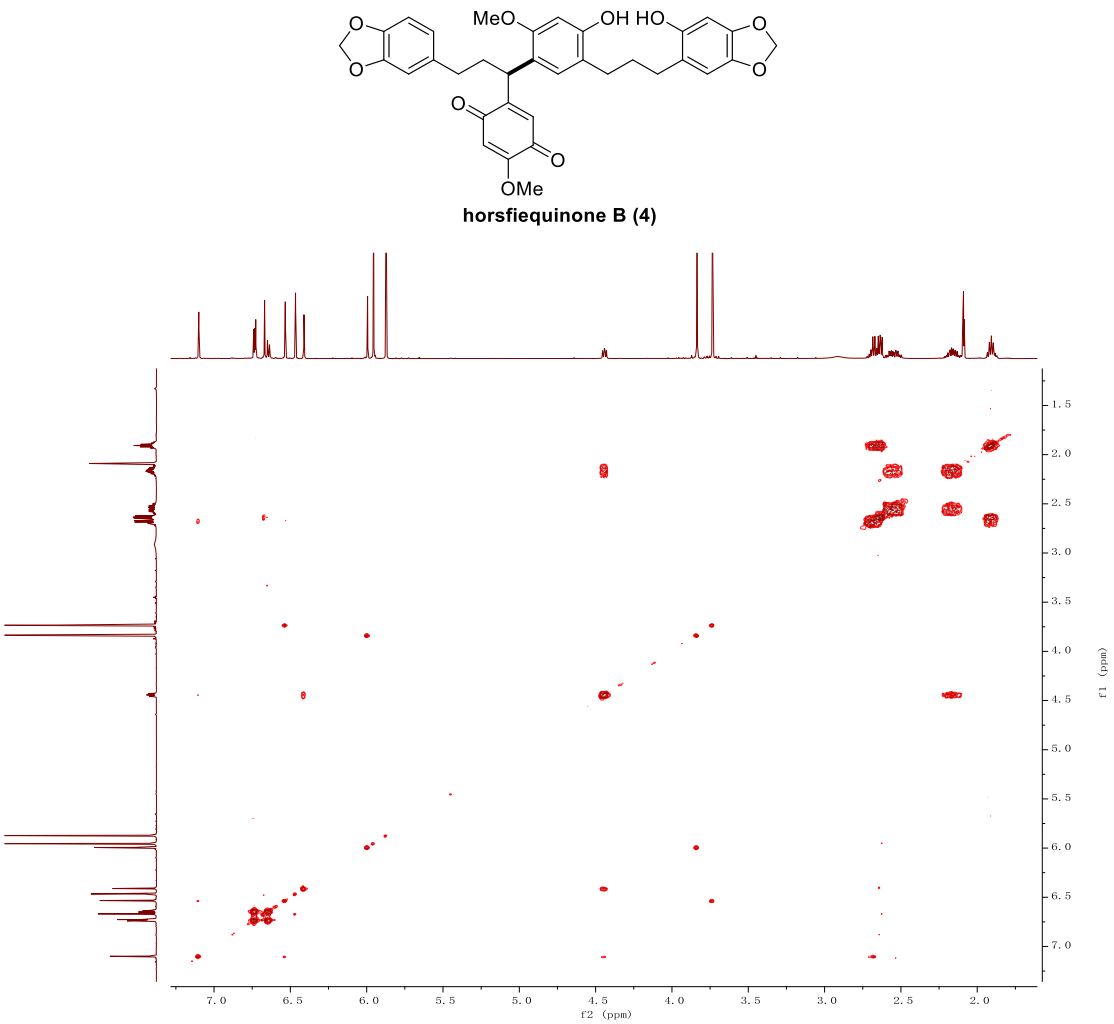
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **29**



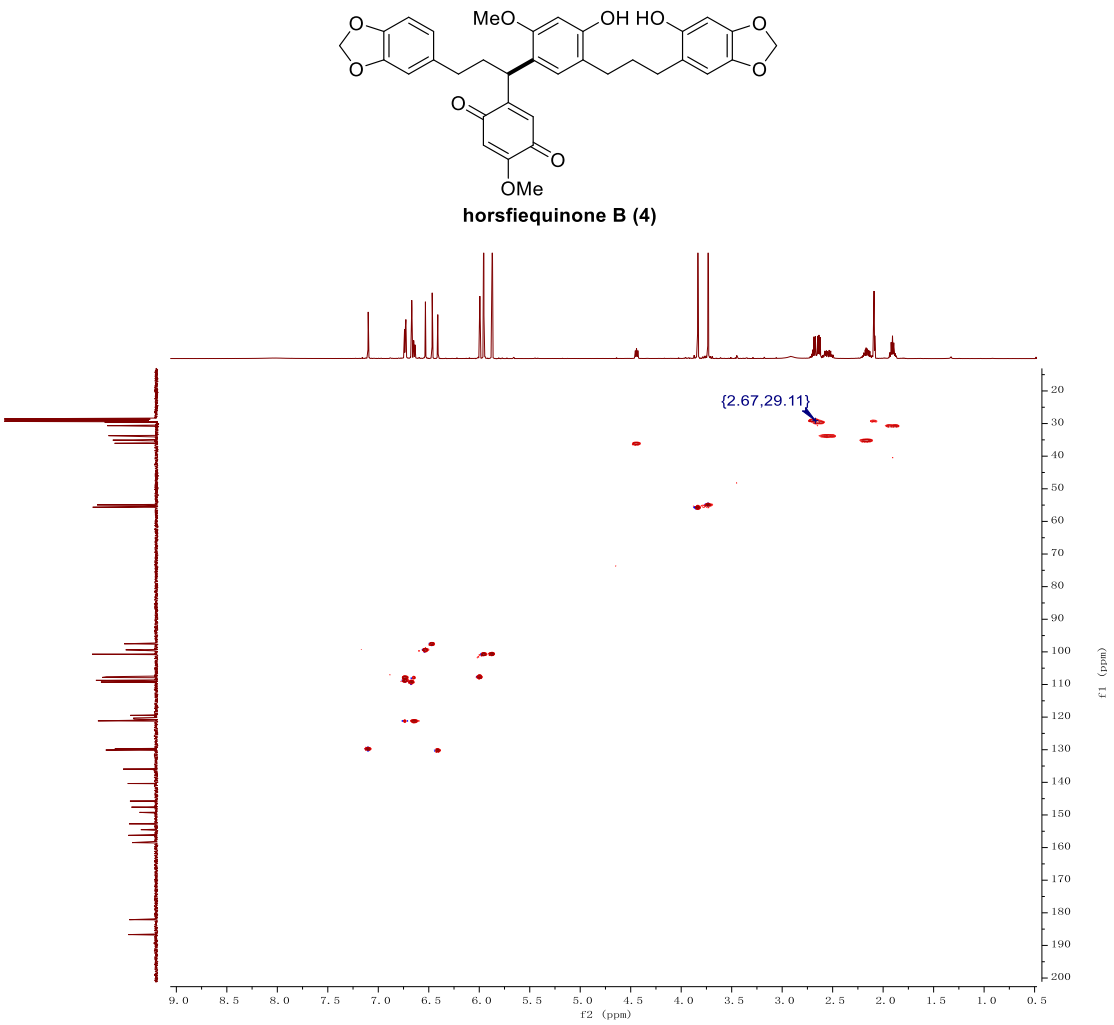
^{1}H NMR spectrum (600 MHz, acetone-d_6) of synthetic horsfiequinone B (**4**)



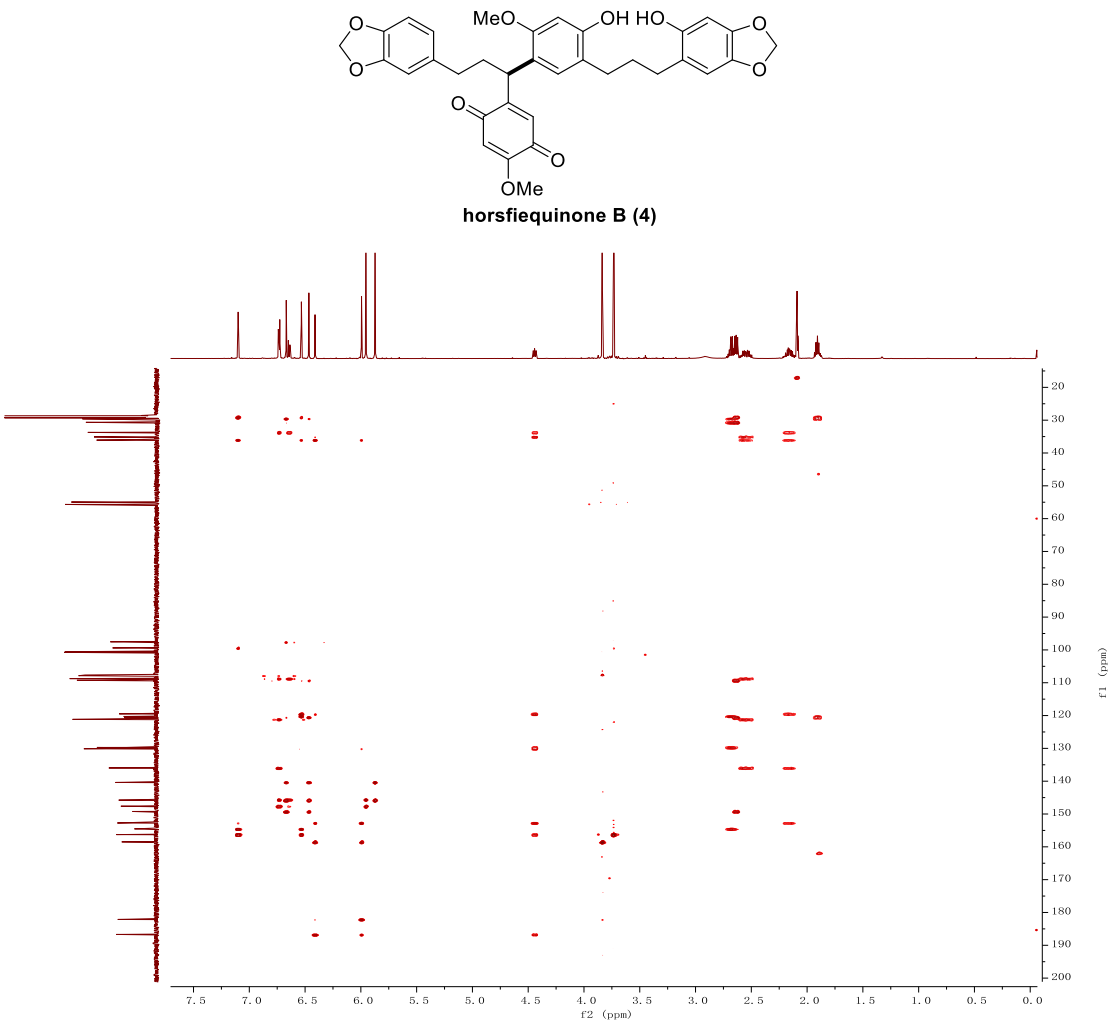
^{13}C NMR spectrum (150 MHz, acetone-d_6) of synthetic horsfiequinone B (**4**)



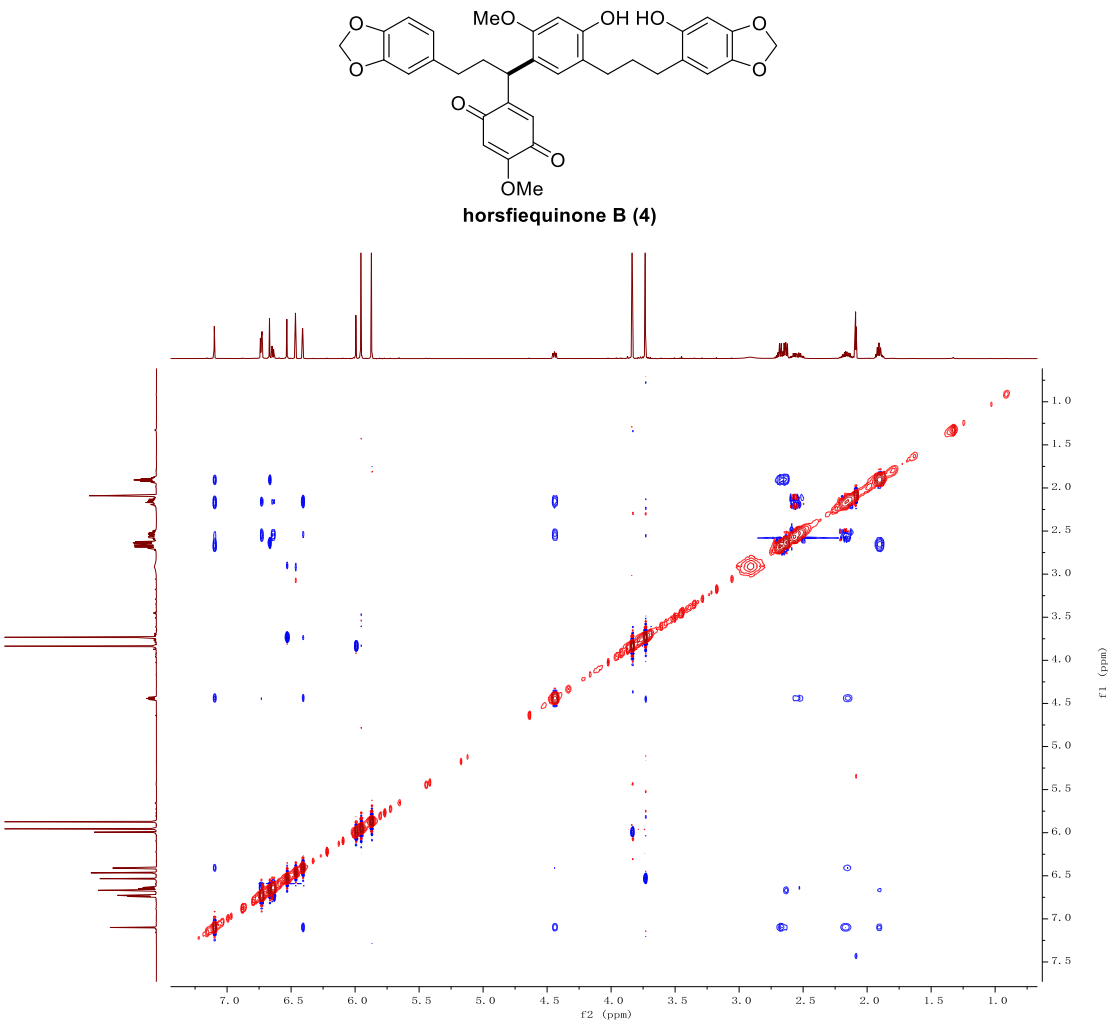
^{1}H-^{1}H COSY spectrum (600 MHz, acetone-d_6) of synthetic horsfiequinone B (**4**)



HSQC spectrum (600 MHz, acetone-d_6) of synthetic horsfiequinone B (**4**)



HMBC spectrum (600 MHz, acetone-d_6) of synthetic horsfiequinone B (**4**)



NOESY spectrum (600 MHz, acetone-d_6) of synthetic horsfiequinone B (**4**)