Selective modification of hydroxyl groups in lignin model compounds by ruthenium-catalyzed transfer hydrogenation

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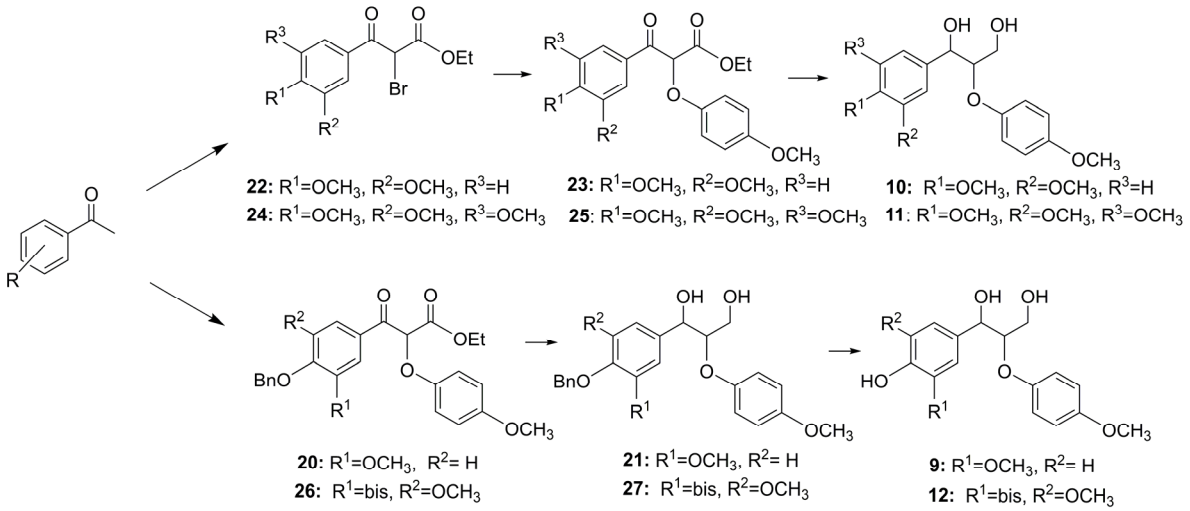
ESI

General considerations

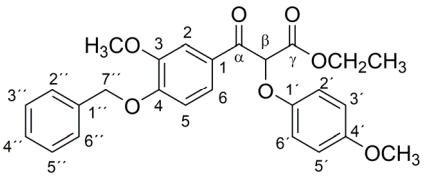
All chemicals were purchased from TCI, ACBR or Sigma-Aldrich and used without further purification unless otherwise indicated. For reactions under protective atmosphere, solvents and liquid reagents used in the experiments involving glass reactors were dried and degassed and stored in a glovebox. The NMR spectra were recorded using 500 and 600 MHz NMR spectrometers. The measured NMR spectra were calibrated against the residual solvent signal as internal standard. The NMR signals assignments were based on 2D NMR (NOESY, DEPT, COSY, HSQC and HMBC). High resolution mass spectroscopy (HRMS) was carried out on a micrOTOF spectrometer (Electrospray (ESI)) with a time of flight (TOF) mass analyzer. The product distribution was monitored by both GC/MS and GC/FID. The GC/MS instrument was equipped with an MS detector (EI), HP-5MS column (30m × 250 µm × 0.25 µm) using He as the carrier gas with the following temperature program: injector 250 °C, oven Tinitial= 50 °C (4 min), rate 10 °C/min, Tfinal=300 °C, hold 5 min; The GC/FID instrument was equipped with HP-1 column (30m × 320 µm × 0.25 µm), and He as the carrier gas, using the following temperature program: injector 220 °C, oven T initial = 50 °C (2 min), rate 10 °C/min, Tfinal = 300 °C, hold 2 min. Flash column chromatography was carried out on automated purification system using pre-packed columns with 20-40 µm particle size.

All intermediates and the lignin model compounds were synthesized from substituted acetophenones according to literature procedures.[1] All new intermediates (**20-27**) from the synthesis of the monomeric compounds were characterized by NMR spectroscopy and high resolution mass spectroscopy. In order to simplify the assignment of the NMR spectra in the experimental descriptions, the atoms in lignin-type compounds were numbered following standard practices for lignin derivatives.[2]



[1] W. G. Forsythe, M. D. Garrett, C. Hardacre, M. Nieuwenhuyzen, G. N. Sheldrake, *Green chem.*, 2013, **15**, 3031-3038.
[2] M. Balakshin, E. Capanema, H. Gracz, H. M. Chang, H. Jameel. *Planta*, 2011, **233**, 1097-1110.

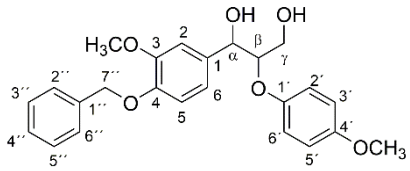
Ethyl 3-(4-(benzyloxy)-3-methoxyphenyl)-2-(4-methoxyphenoxy)-3-oxopropanoate (20)



Ethyl 3-(4-(benzyloxy)-3-methoxyphenyl)-2-bromo-3-oxopropanoate (7.0 g, 0.017 mole) was dissolved in acetone (50 mL) and to this K_2CO_3 (2.5 g, 0.018 mole) and 4-methoxyphenol (2.3 g, 0.018 mole) were added. The reaction mixture was allowed to reflux. After two hours, the reaction mixture was cooled down to room temperature. Water was added to the reaction mixture and the acetone was evaporated under vacuum. The water suspension was extracted with EtOAc (3 x 30 mL). Organic fractions were combined, dried over Na_2SO_4, filtered and evaporated. The resulting oil was purified by flash chromatography (hexane : ethyl acetate) and dried under vacuum. Yield: 3.8 g, 50%.

^{1}H NMR ($CDCl_3$ with 0.05% v/v TMS, 500 MHz): δ_H 7.67 (1H, dd, J=6.6 Hz, 10.5 Hz, H6), 7.57 (1H, d, J=2.1 Hz, H2), 7.33 - 7.37 (2H, m, H2´´ and H6´´), 7.28-7.33 (2H, m, H3´´ and H5´´), 7.22-7.27 (1H, m, H4´´), 6.80 - 6.85 (3H, m, H5, H2´ and H6´), 6.70 – 6.75 (2H, m, H3´and H5´), 5.53 (1H, s, Hβ), 5.15 (2H, s, H7´´), 4.11 - 4.27 (2H, m, $OC\underline{H_2}CH_3\gamma$), 3.85 (3H, s, $OC\underline{H_3}3$), 3.68 (3H, s, $OC\underline{H_3}4'$), 1.15 (3H, t, J=7.5 Hz, $OCH_2C\underline{H_3}\gamma$). ^{13}C NMR ($CDCl_3$, 500 MHz): δ_C 190.05 (Cα), 167.08(Cγ), 155.08 (C4´), 153.40 (C4), 151.09 (C1´), 149.53 (C3), 136.06 (C1´´), 128.72 (C3´´and C5´´), 128.20 (C4´´), 127.23 (C2´´and C6´´), 127.17 (C1), 124.61 (C6) , 116.83 (C2´and C6´), 114.78 (C3´and C5´), 112.14 (C5), 111.82 (C2), 82.34 (Cβ), 70.86 (C7´´), 62.28 ($O\underline{C}H_2CH_3\gamma$), 56.05 ($O\underline{C}H_33$), 55.65 ($O\underline{C}H_34'$), 14.04 ($OCH_2\underline{C}H_3\gamma$). $[M+Na]^+$ calculated 473.1576 found 433.1553.

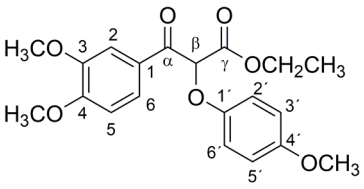
1-(4-(benzyloxy)-3-methoxyphenyl)-2-(4-methoxyphenoxy)propane-1,3-diol (21)



Compound **20** (3.8 g, 8 mmol) was dissolved in a mixture of $CHCl_3$ (6 mL) and MeOH (3 mL). $NaBH_4$ (0.32 g, 8 mmol) was added to the solution in small portions. The reaction mixture was stirred overnight at room temperature. Next, unreacted $NaBH_4$ was quenched with water (5 ml) and the solvents were removed under vacuum. The mixture was extracted with dichloromethane (3 x 10). Organic fractions were combined, dried over Na_2SO_4, filtered and evaporated. The resulting oil was purified by flash chromatography (hexane/ethyl acetate) and dried under vacuum. Yield: 2.2 g, 64%.

^{1}H NMR ($CDCl_3$ with 0.05% v/v TMS, 500 MHz): δ_H 7.32-7.37 (2H, m, H2´´ and H6´´), 7.26-7.32 (2H, m, H3´´ and H5´´), 7.20-7.26 (1H, m, H4´´), 6.87-6.92 (1H, br, H2), 6.75-6.96 (2H, m, H5 and H6), 6.67-6.75 (4H, H2´, H3´, H5´and H6´) 5.03-5.09 (2H, multiple overlapping singlets 7´´ from diastereoisomers), 4.86-4.94 (1H, m, Hα), 4.10-4.17 (1H, m, Hβ), 3.78-3.79 (3H, multiple overlapping singlets OCH_3 from diastereoisomers), 3.71-3.87 (2H, m, $\underline{H_2}\gamma$), 3.65-3.70 (3H, multiple overlapping singlets OCH_3´ from diastereoisomers), 2.75-2.94 (1H, br, OHα), 2.20-2.38 (1H, br, OHβ). ^{13}C NMR ($CDCl_3$, 500 MHz): δ_C 154.80 (C4´), 151.69 (C1´), 149.78 (C3), 147.83 (C4), 137.08 (C1´´), 133.64, 133.59 (C1), 128.56, 128.48 (C3´´ and C5´´), 127.87 (C4´´), 127.27 (C2´´ and C6´´), 118.59 (C6), 118.35, 118.14 (C2´and C6´), 114.83, 114.74 (C3´and C5´), 113.99 (C5), 110.04 (C2), 83.51 (Cβ), 73.87 (Cα), 71.10 (C7´´), 61.40 (Cγ), 56.09 (OCH_33), 55.68 (OCH_34'). $[M+Na]^+$ calculated 433.1627 found 433.1604.

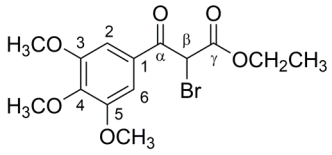
Ethyl 3-(3,4-dimethoxyphenyl)-2-(4-methoxyphenoxy)-3-oxopropanoate (23)



Compound **22** was dissolved in acetone (100 mL) and K_2CO_3 (5.15 g, 0.037 mole) and 4-methoxyphenol (4.62 g, 0.037 mole) were added to this solution. The reaction mixture was allowed to reflux. After two hours, the reaction mixture was allowed to cool down to room temperature. Next, water was added to the reaction mixture and the acetone was evaporated under vacuum. The water suspension was extracted with EtOAc (3 x 30 mL). Organic fractions were combined, dried over Na_2SO_4, filtered and evaporated. The resulting oil was purified by flash chromatography (hexane/ethyl acetate) and dried under vacuum. Yield: 13.8 g, 98%.

^{1}H NMR ($CDCl_3$ with 0.05% v/v TMS, 500 MHz): δ_H 7.71-7.80 (1H, dd, J = 2.15 Hz, 8.61 Hz), 7.54-7.57 (1H, d, J=2.10 Hz), 6.65-6.87 (5H, m), 5.54 (1H, s), 4.17-4.25 (2H, q, J = 7.20 Hz), 3.88 (3H, s), 3.84 (3H, s), 3.68 (3H, s), 1.17 (3H, t, J = 7.18). The obtained NMR spectrum is consistent with the literature.[3]

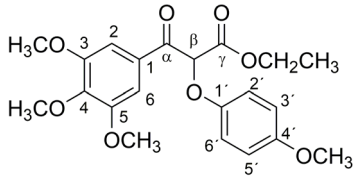
Ethyl 2-bromo-3-oxo-3-(3,4,5-trimethoxyphenyl)propanoate (24)



Ethyl 3-oxo-3-(3,4,5-trimethoxyphenyl)propanoate (2.8 g, 0.01 mole) was dissolved in ethyl acetate (50 mL). To this, Amberlyst 15 (1g) and *N*-bromosuccineimide (2 g, 0.01 mole) were added. The reaction mixture was stirred overnight at 90 °C. Next, the reaction mixture was filtered, washed with saturated Na_2CO_3 (2 x 30 mL) and water (30mL). The organic layer was dried over Na_2SO_4, evaporated and the resulting oil was dried under vacuum. Yield: 3.5 g, 96%.

^{1}H NMR ($CDCl_3$ with 0.05% v/v TMS, 500 MHz): δ_H 7.20 (2H, s, H2 and H6), 5.54 (1H, s, Hβ), 4.18-4.25 (2H, q, J=7.23 Hz, $OC\underline{H}_2CH_3\gamma$), 3.87 (3H, s, $OC\underline{H}_34$), 3.84 (6H, s, $OC\underline{H}_34$ and $OC\underline{H}_35$), 1.17-1.22 (1H, t, J=7.18 Hz, $OCH_2C\underline{H}_3\gamma$). ^{13}C NMR ($CDCl_3$, 500 MHz): 186.86 (Cα), 165.27 (Cγ), 153.17 (C3 and C5), 143.72 (C4), 128.21 (C1), 106.88 (C2 and C6), 63.37 ($O\underline{C}H_2CH_3\gamma$), 61.04 ($O\underline{C}H_34$), 56.37 ($O\underline{C}H_33$ and $O\underline{C}H_35$), 46.61 (Cβ), 13.94 ($OCH_2\underline{C}H_3\gamma$). $[M+Na]^+$ calculated 383.0106 found 383.0081.

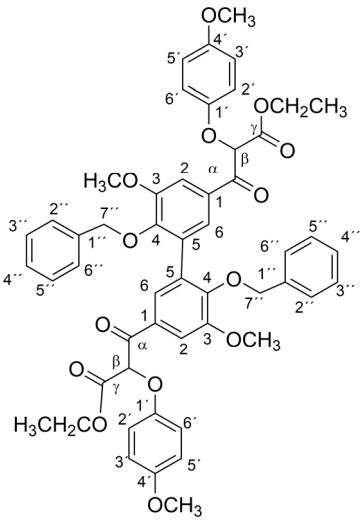
Ethyl 2-(4-methoxyphenoxy)-3-oxo-3-(3,4,5-trimethoxyphenyl)propanoate (25)



Compound **24** (3.5 g, 0.01 mole) was dissolved in acetone (50 mL) and to this K_2CO_3 (1.38 g, 0.01 mole) and 4-methoxyphenol (1.24 g, 0.01 mole) were added. The reaction mixture was allowed to reflux. After two hours, the reaction mixture was allowed to cool down to room temperature. Water was added to the reaction mixture and the acetone was evaporated under vacuum. The water suspension was extracted with EtOAc (3 x 30 mL). The organic fractions were combined, dried over Na_2SO_4, filtered and evaporated. The resulting oil was purified by flash chromatography (hexane/ethyl acetate) and dried under vacuum. ^{1}H NMR-purity 87%. Yield: 2.3 g, 57%.

^{1}H NMR ($CDCl_3$ with 0.05% v/v TMS, 500 MHz): δ_H 7.35 (2H, s, H2 and H6), 6.82-6.88 (2H, m, H2′ and H6′), 6.70-6.77 (2H, m, H3′ and H5′), 5.52 (1H, s, Hβ), 4.18-4.27 (2H, m, $OC\underline{H}_2CH_3\gamma$), 3.86 (3H, s, $OC\underline{H}_34$), 3.81 (6H, s, $OC\underline{H}_33$ and $OC\underline{H}_35$), 3.67 (3H, s, $OC\underline{H}_34'$), 1.17 (3H, m, $OCH_2C\underline{H}_3\gamma$). ^{13}C NMR ($CDCl_3$, 500 MHz): 190.29 (Cα), 166.99 (Cγ), 155.17 (C4′), 153.02 (C3 and C5), 150.99 (C1′), 143.50 (C4), 128.68 (C1), 116.84 (C2′and C6′), 114.82 (C3′and C5′), 107.13 (C2 and C6), 82.75 (Cβ), 62.42 ($O\underline{C}H_2CH_3\gamma$), 60.99 ($O\underline{C}H_34$), 56.24 ($O\underline{C}H_33$ and $O\underline{C}H_35$), 55.64 ($O\underline{C}H_34'$), 14.07 ($OCH_2\underline{C}H_3\gamma$). $[M+Na]^+$ calculated 427.1363 found 427.1332.

5-5-Bis-Ethyl 3-(4-(benzyloxy)-3-methoxyphenyl)-2-(4-methoxyphenoxy)-3-oxopropanoate (26)



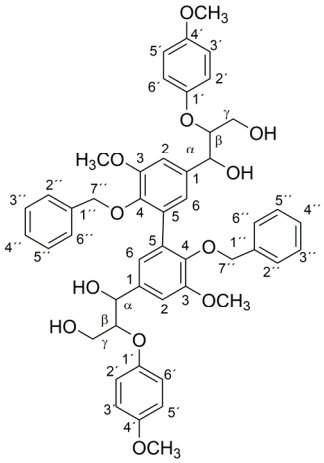
5-5-Bis-Ethyl 3-(4-(benzyloxy)-3-methoxyphenyl)-2-bromo-3-oxopropanoate (4.0 g, 0.005 mole) was dissolved in acetone (50mL) and to this K_2CO_3 (1.22 g, 0.01 mole) and 4-methoxyphenol (1.36 g, 0.01 mole) were added. The reaction mixture was allowed to reflux. After two hours, the reaction mixture was allowed to cool down to room temperature. Water was added to the reaction mixture and the acetone was evaporated under vacuum. The water suspension was extracted with EtOAc (3 x 30 mL). The organic fractions were combined, dried over Na_2SO_4, filtered and evaporated. The resulting oil was purified by flash chromatography (hexane/ethyl acetate) and dried under vacuum. Yield: 4.2 g, 93%.

^{1}H NMR ($CDCl_3$ with 0.05% v/v TMS, 500 MHz): δ_H 7.60-7.75 (2H, m, H2), 7.47-7.59 (2H, m, H6), 6.80 - 7.15 (10H, m, H2′′, H3′′, H4′′ H5′′and H6′′), 6.75-6.83 (4H, m, H2′ and H3′), 6.64-6.72 (4H, m, H3′and H5′), 5.50-5.57 (2H, m, Hβ), 4.75-4.84 (4H, m,

[3] S. G. Yao, M. S. Meier, R. B. Pace III, M. Crocker. RSC advances, 2016, **6**(106), 104742-104753.

H7´´), 4.08 - 4.22 (2H, m, OC<u>H</u>$_2$CH$_3$γ), 3.80-3.93 (6H, m, OC<u>H</u>$_3$3), 3.59-3.68 (6H, m, OC<u>H</u>$_3$4´), 1.06-1.16 (6H, m, OCH$_2$C<u>H</u>$_3$<u>γ</u>). ^{13}C ($CDCl_3$, 500 MHz): δ_C 190.26 (<u>Cα</u>), 166.85(<u>Cγ</u>), 155.11 (C4´), 152.88 (C3), 151.20 (C4), 151.03 (C1´), 137.14 (C1´´), 132.35 (C1), 129.21 (C5), 128.05, 127.84, 127.72 (C2´´, C3´´, C4´´, C5´´ and C6´´), 125.70 (C6), 116.93 (C2´and C6´), 114.78 (C3´and C5´), 112.85 (C2), 82.19 (Cβ), 74.64 (C7´´), 62.32 (O<u>C</u>H$_2$CH$_3$γ), 56.11, 55.45 (O<u>C</u>H$_3$3), 55.61 (O<u>C</u>H$_3$4´), 14.01 (OCH$_2$<u>C</u>H$_3$γ). Based on the NMR spectra, a diastereomeric mixture of products was formed. $[M+Na]^+$ calculated 921.3093 found 921.3123.

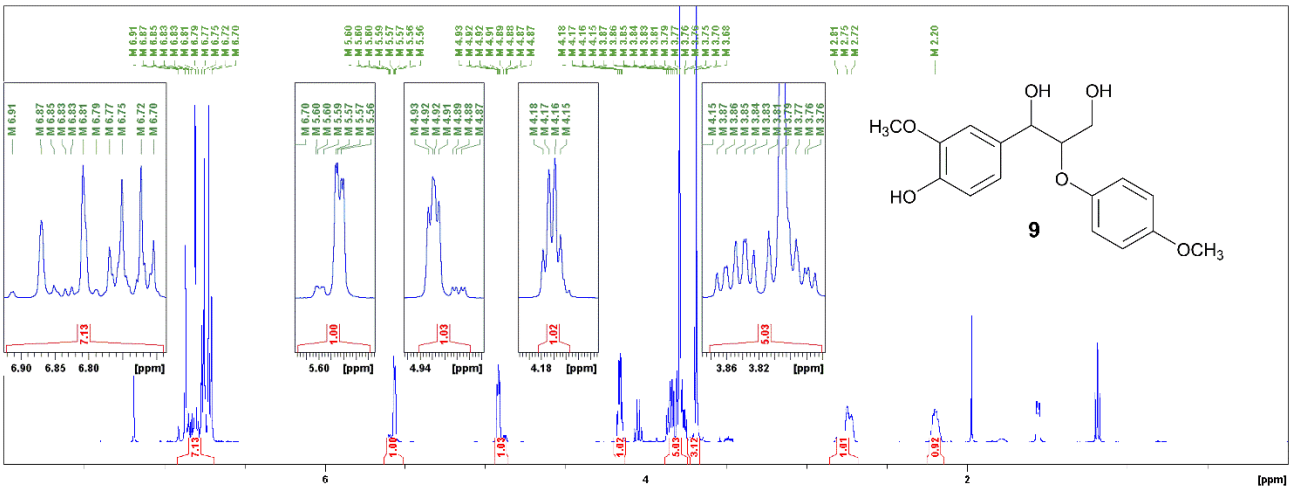
5-5-Bis-1-(4-(benzyloxy)-3-methoxyphenyl)-2-(4-methoxyphenoxy)propane-1,3-diol (27)



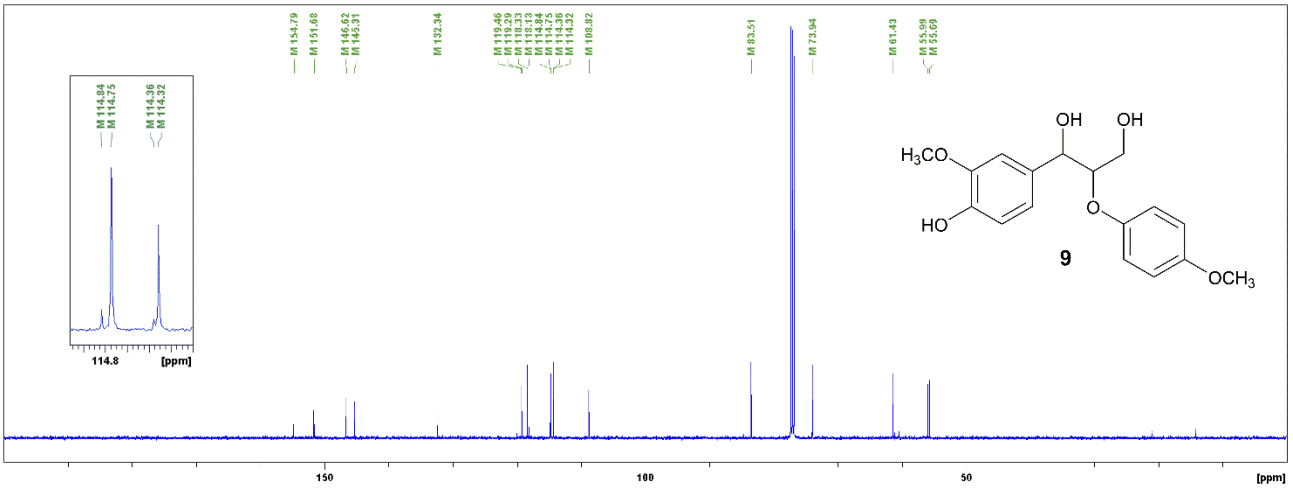
Compound **26** (4.2 g, 0,0047 mole) was dissolved in a mixture of $CHCl_3$ (6mL) and MeOH (3 mL). Next, $NaBH_4$ (0.40 g, 0.010 mole) was added to the solution by small portions. The reaction mixture was stirred overnight at room temperature. Then, unreacted $NaBH_4$ was quenched with water (5 mL) and the solvents were removed under vacuum. The mixture was extracted with dichloromethane (3 x 10 mL). The organic fractions were combined, dried with Na_2SO_4, filtered and evaporated. The resulting oil was purified by flash chromatography (hexane/ethyl acetate) and dried under vacuum. Yield: 1.2 g, 32%.

^{1}H NMR ($CDCl_3$ with 0.05% v/v TMS, 500 MHz): δ_H 6.60 - 7.16 (22H, m, Ar), 4.84-4.92 (2H, m, Hα), 4.63-4.75 (4H, m, H7´´), 4.08 - 4.17 (2H, m, Hβ), 3.57-3.90 (4H, m, <u>H</u>$_2$γ), 3.81-3.83 (6H, m, OC<u>H</u>$_3$3), 3.65-3.69 (6H, m, OC<u>H</u>$_3$4´). ^{13}C ($CDCl_3$, 500 MHz): δ_C 154.69 (C4´), 153.09 (C3), 151.58 (C1´), 145.27 (C4), 137.83 (C1´´), 135.68 (C1), 132.63, 132.69 (C5), 128.03, 127.86, 127.52 (C2´´, C3´´, C4´´, C5´´ and C6´´), 121.39 (C6) 118.25, 118.10 (C2´and C6´), 114.75, 114.78 (C3´and C5´), 109.87 (C2), 83.01 (Cβ), 74.57, 74.52 (C7´´), 73.90 (Cα), 61.37 (Cγ), 56.09 (O<u>C</u>H$_3$3), 55.68 (O<u>C</u>H$_3$4´). Note: According to the spectra, several diastereoisomers are formed. $[M+Na]^+$ calculated 841.3194 found 841.3174.

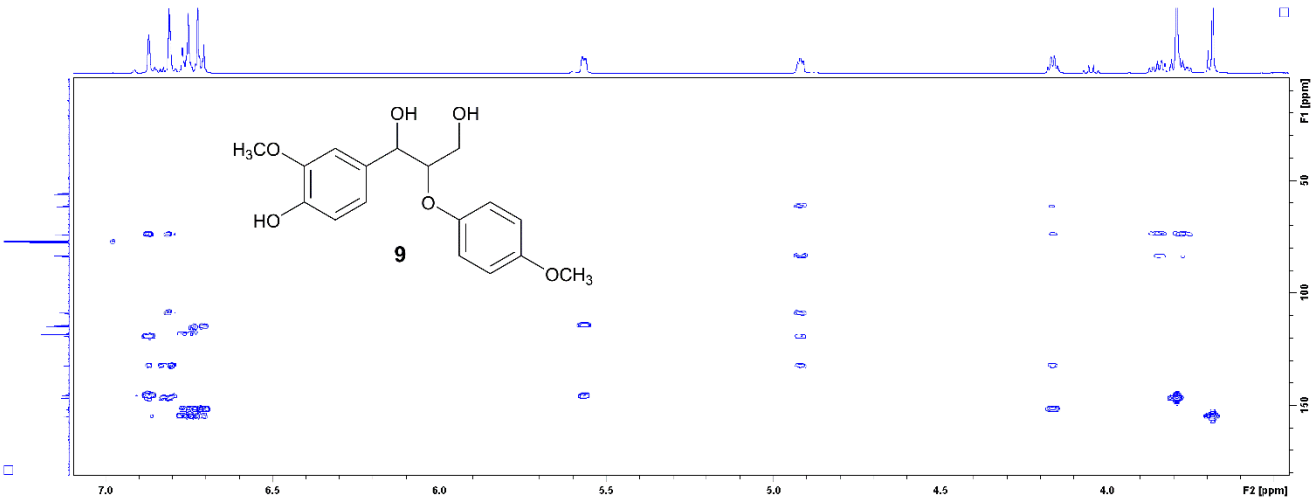
^{1}H NMR spectrum of compound **9**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



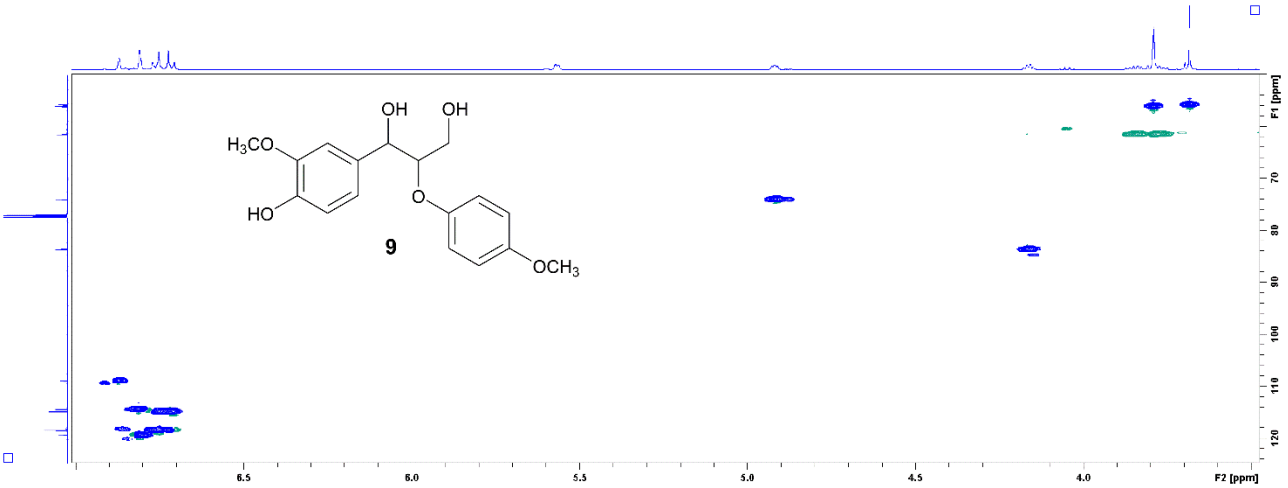
^{13}C NMR spectrum of compound **9**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



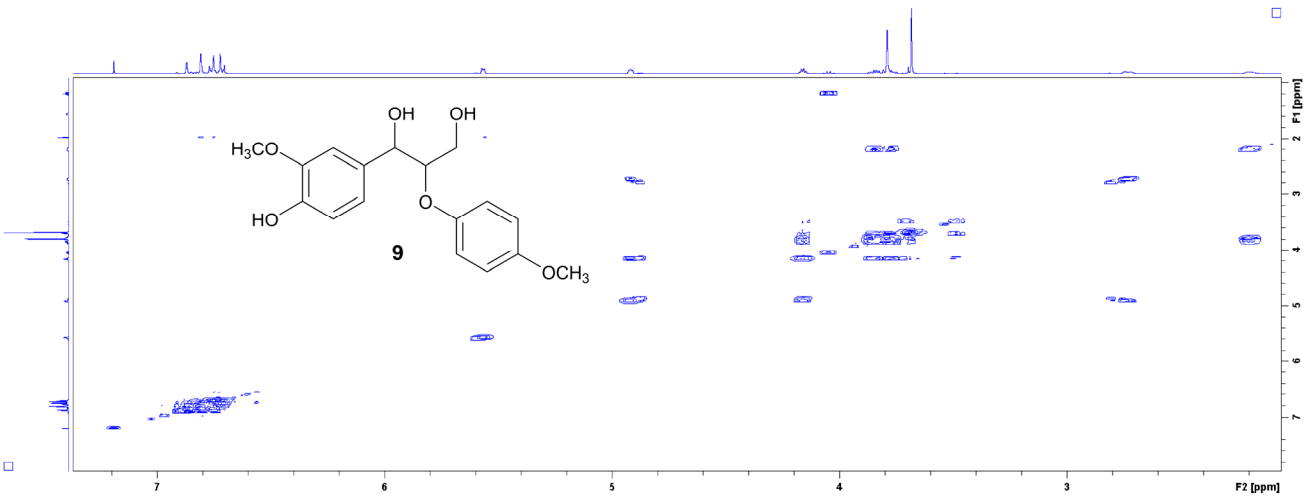
HMBC NMR spectrum of compound **9**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



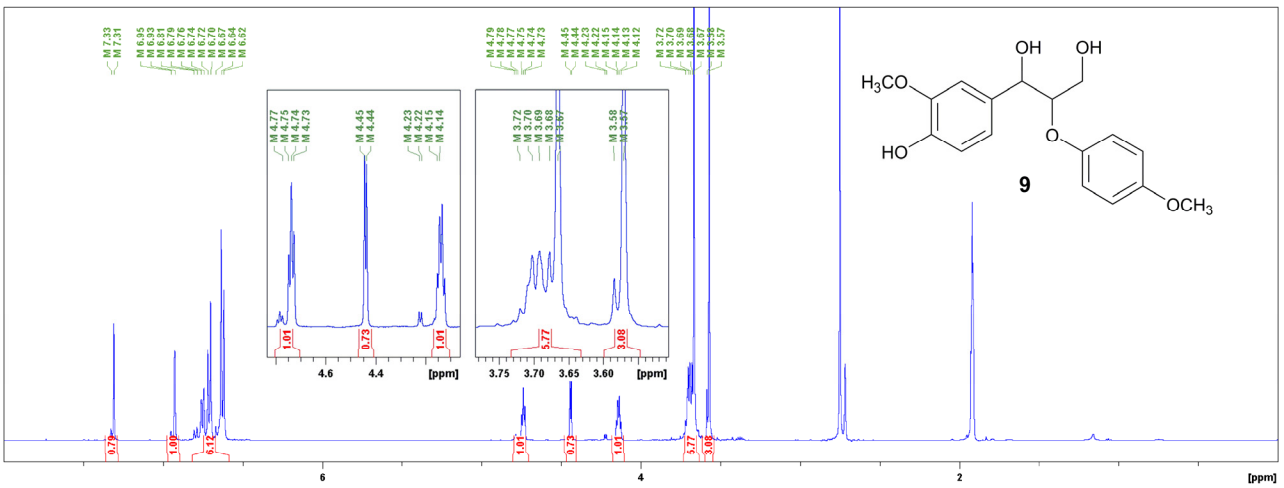
HSQC NMR spectrum of compound **9**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



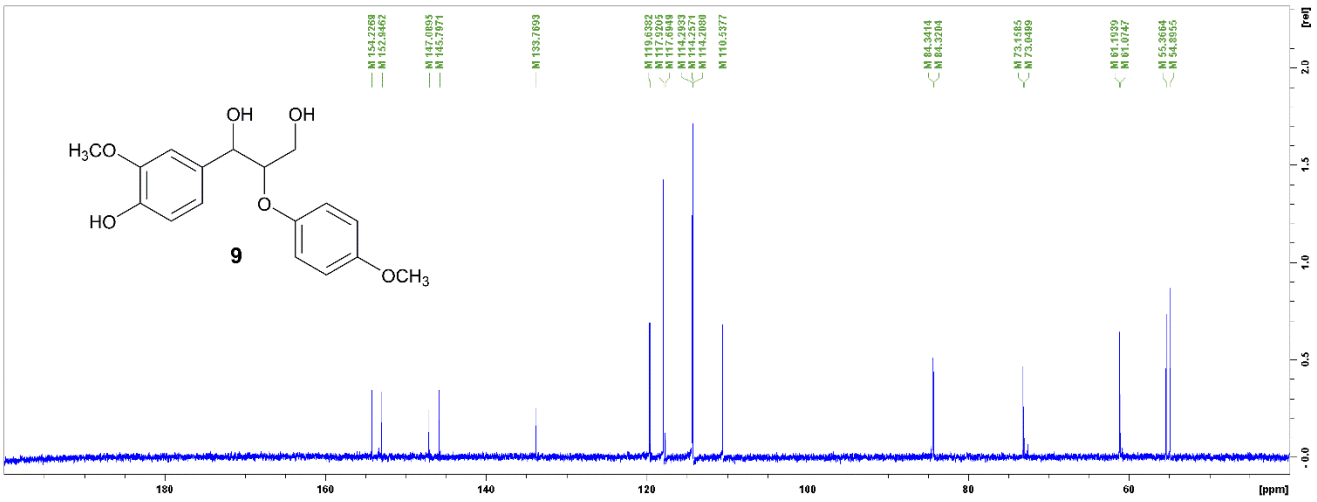
COSY NMR spectrum of compound **9**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



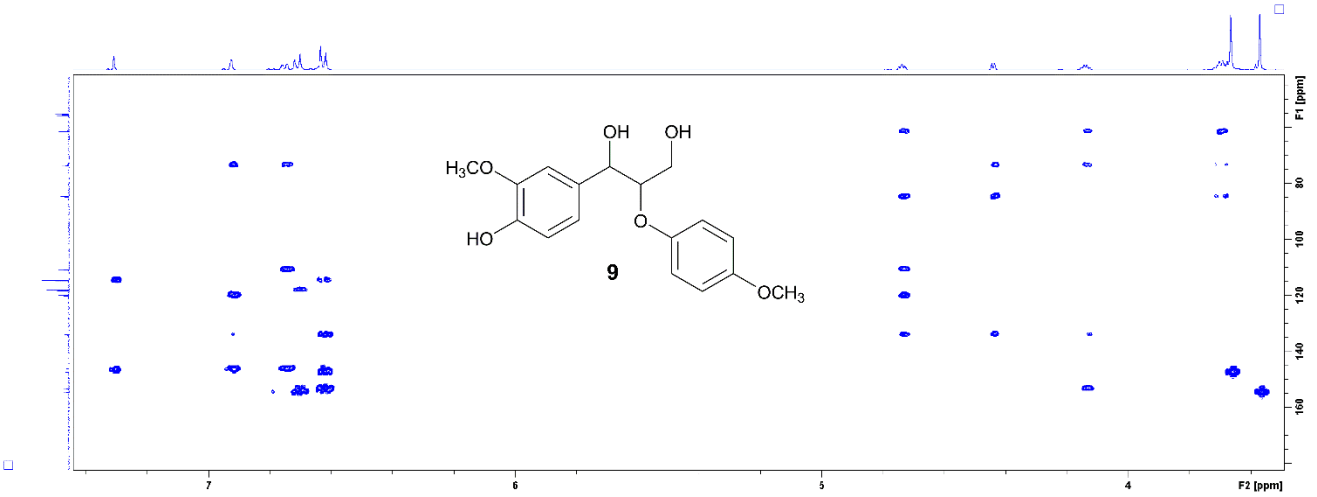
^{1}H NMR spectrum of compound **9**, 298K, acetone-d_6, 500 MHz



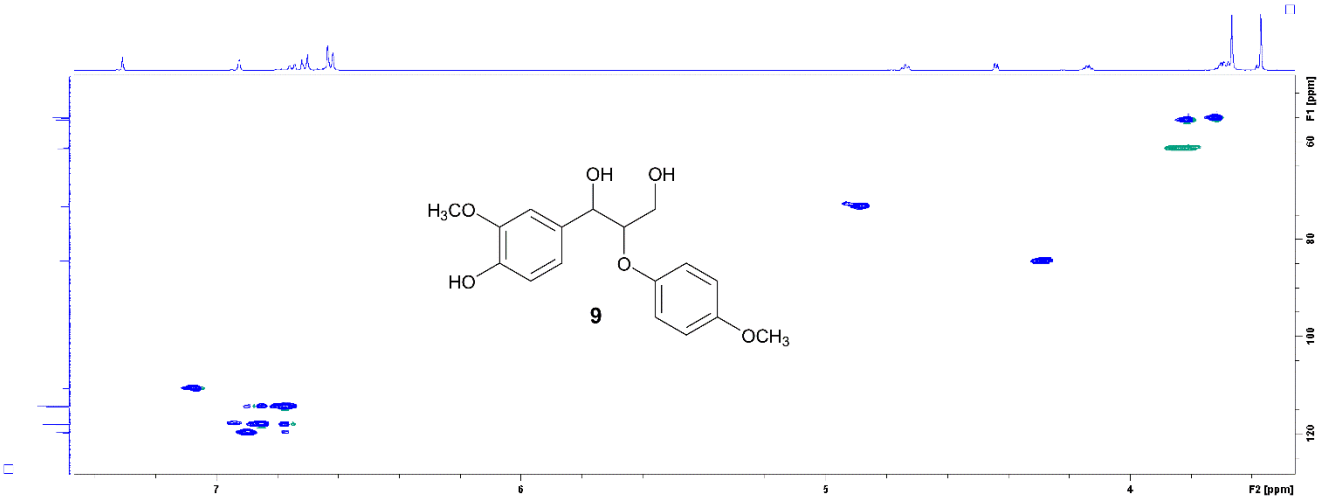
^{13}C NMR spectrum of compound **9**, 298K, acetone-d_6, 500 MHz



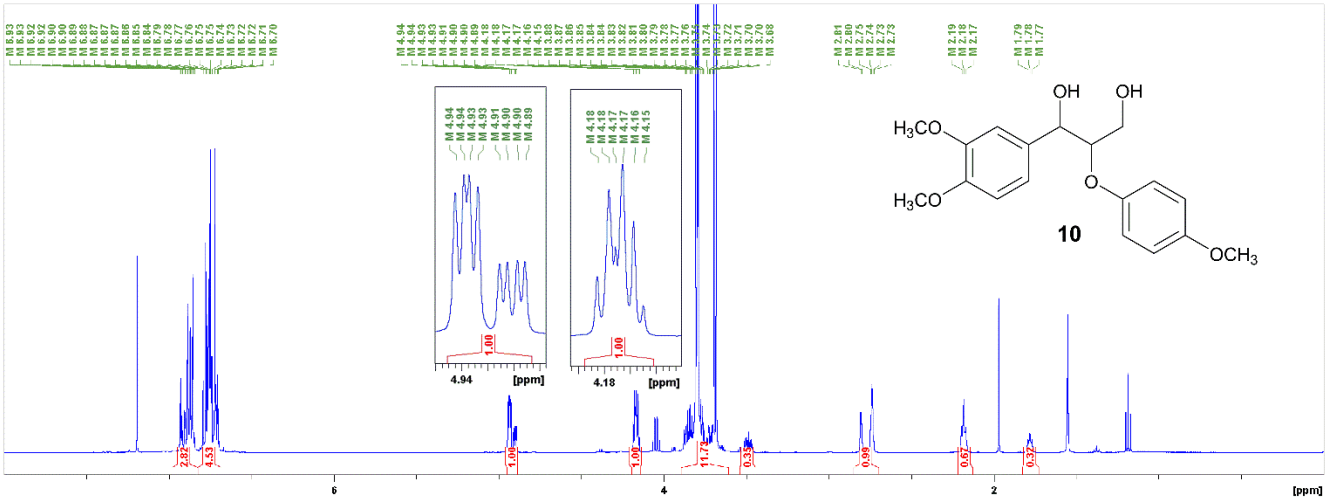
HMBC NMR spectrum of compound **9**, 298K, acetone-d_6, 500 MHz



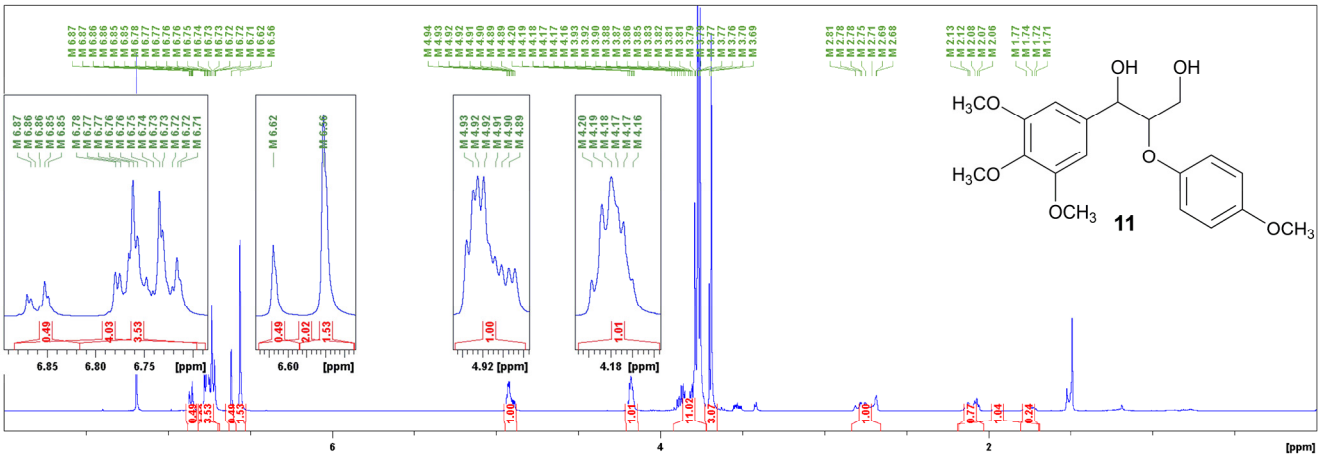
HSQC NMR spectrum of compound **9**, 298K, acetone-d_6, 500 MHz



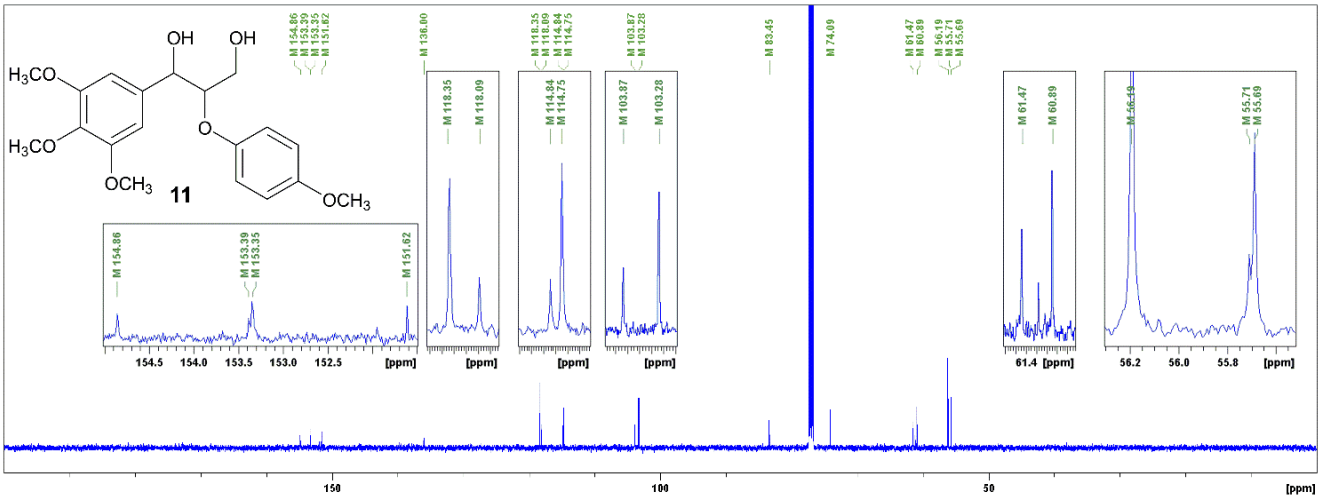
^{1}H NMR spectrum of compound **10**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



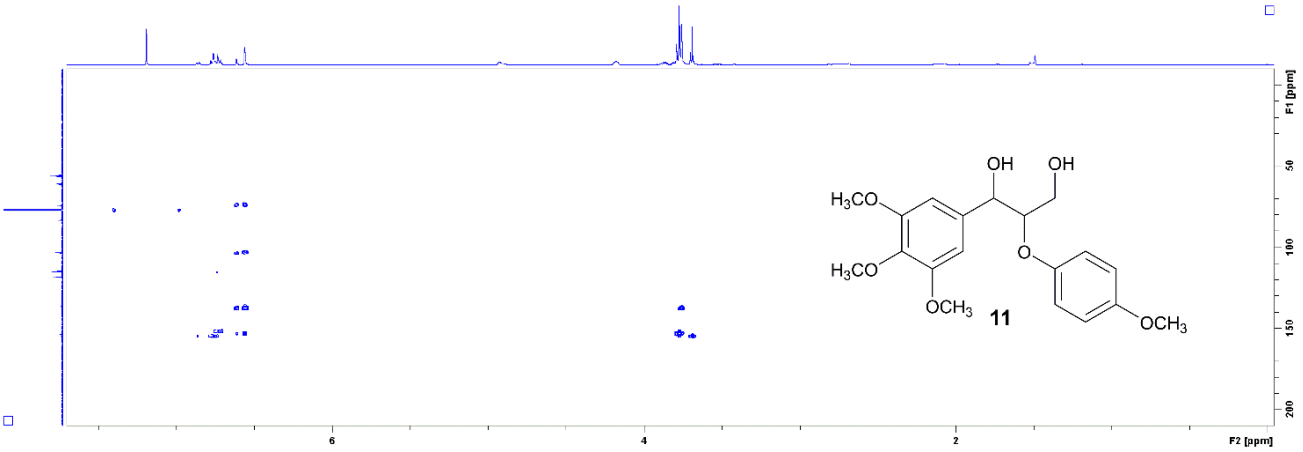
^{1}H NMR spectrum of compound **11**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



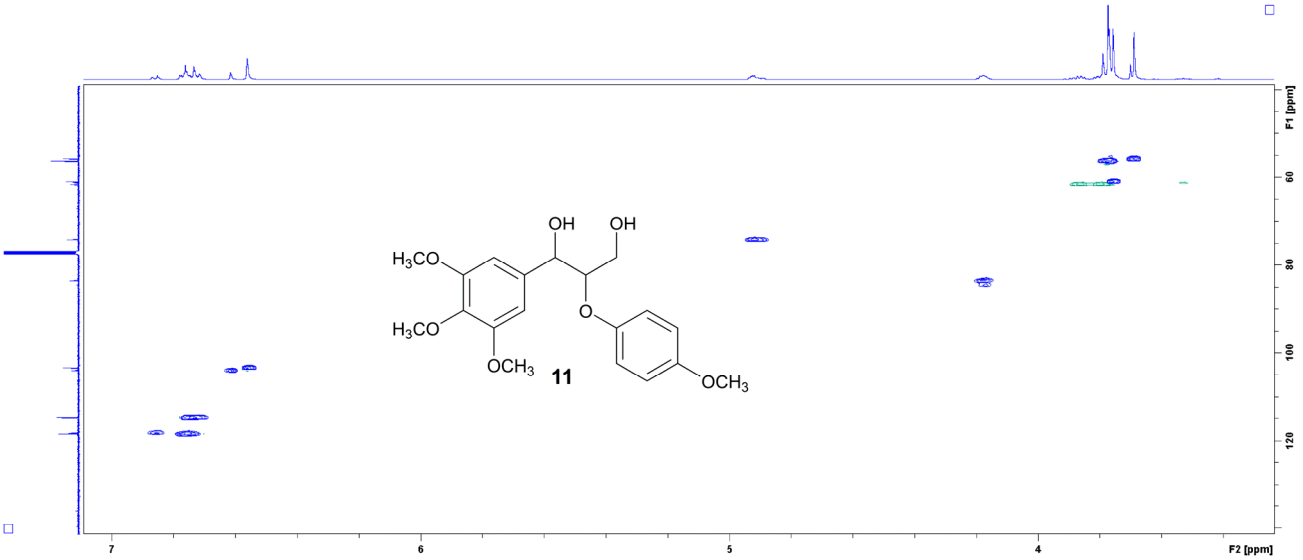
^{13}C NMR spectrum of compound **11**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



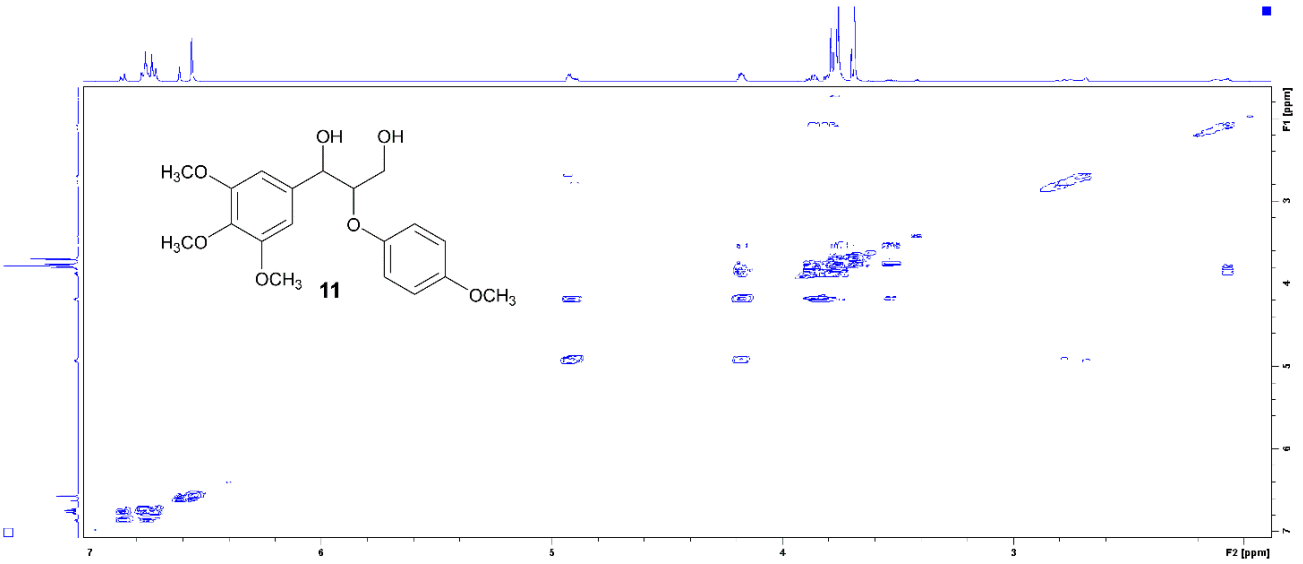
HMBC NMR spectrum of compound **11**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



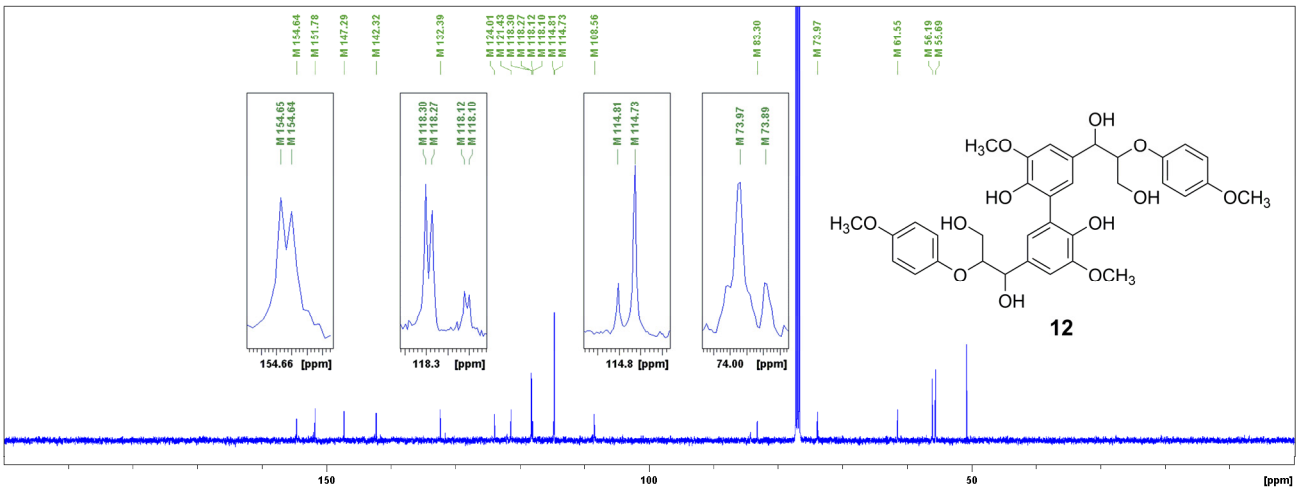
HSQC NMR spectrum of compound **11**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



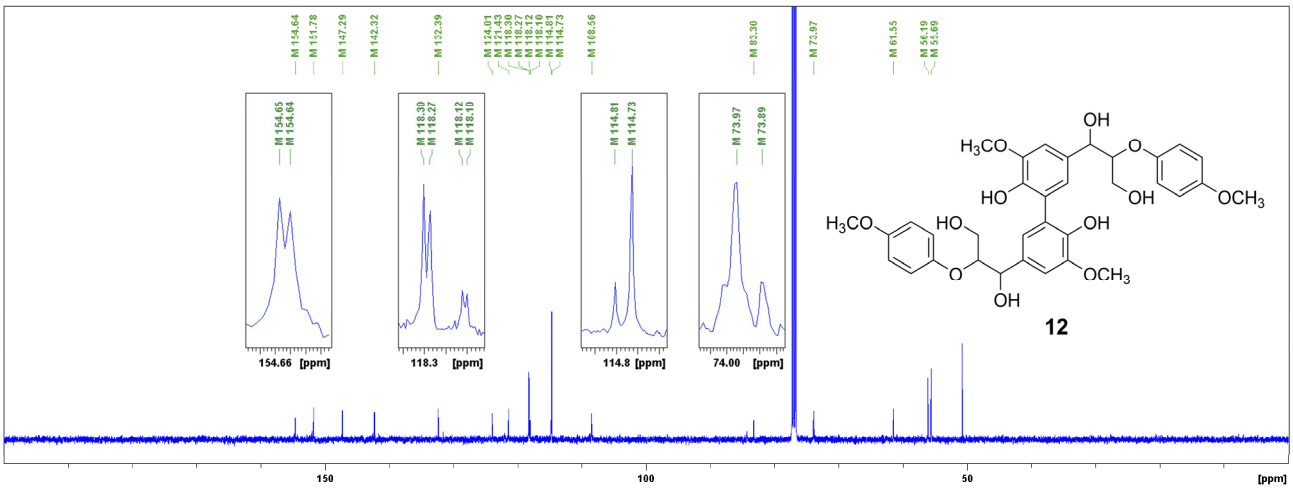
COSY NMR spectrum of compound **11**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



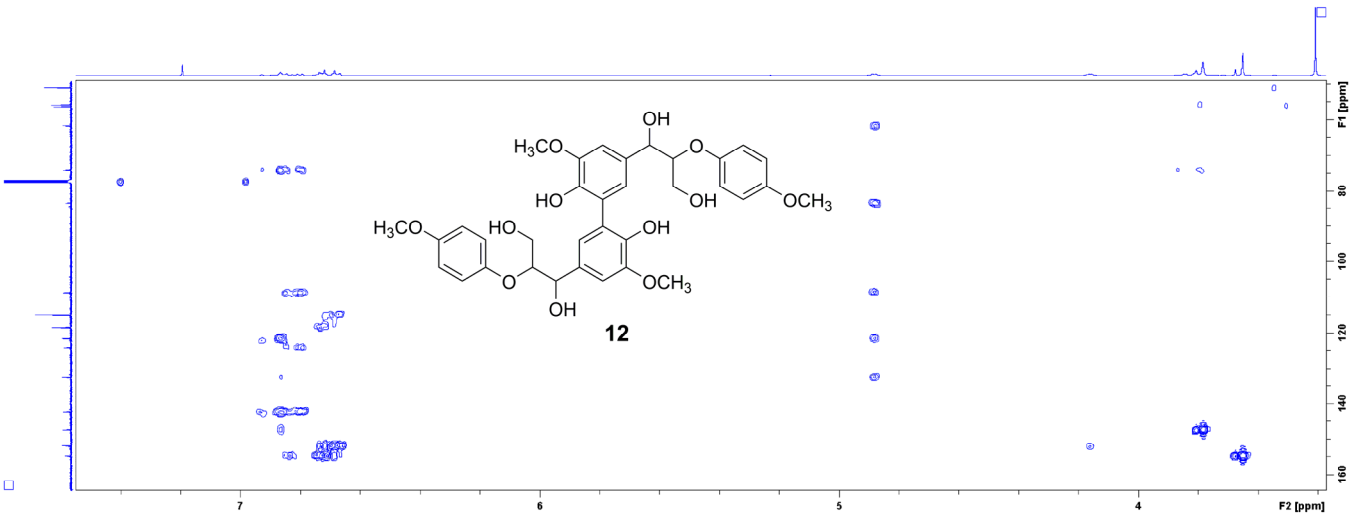
^{1}H NMR spectrum of compound **12**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



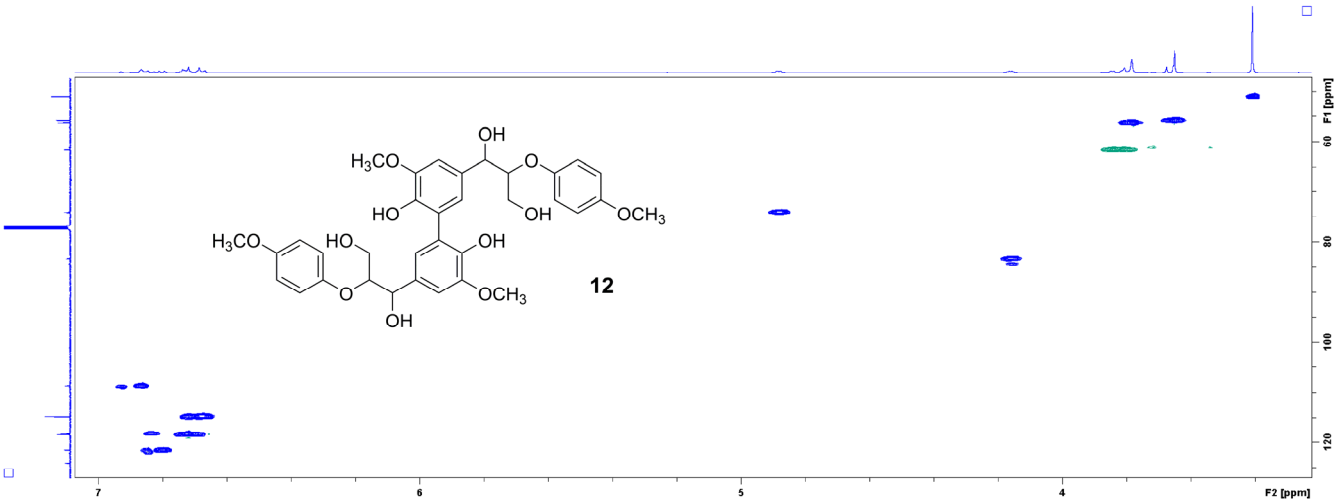
^{13}C NMR spectrum of compound **12**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



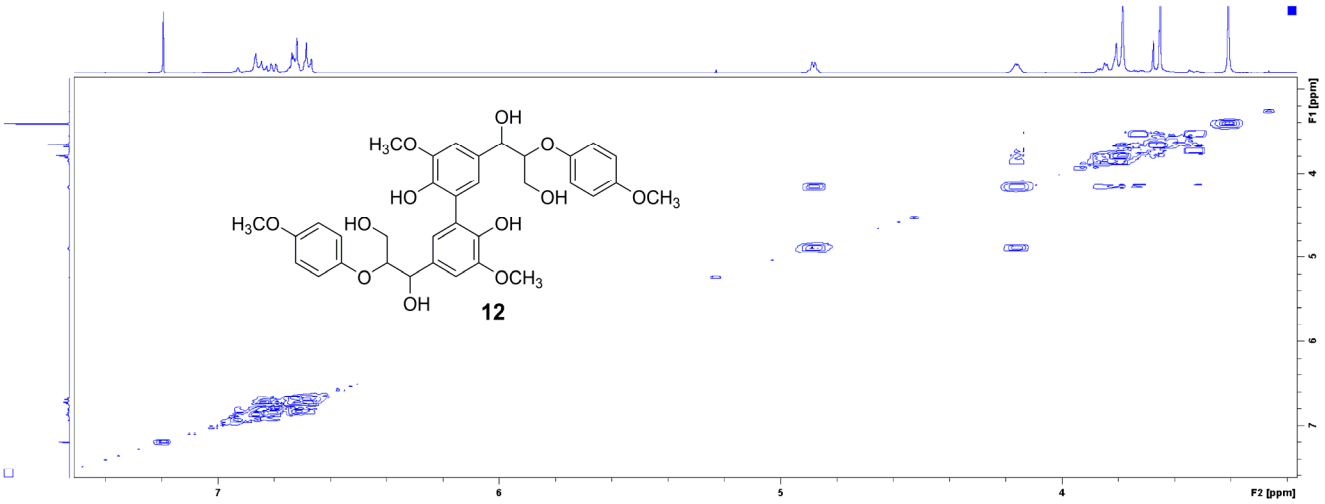
HMBC NMR spectrum of compound **12**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



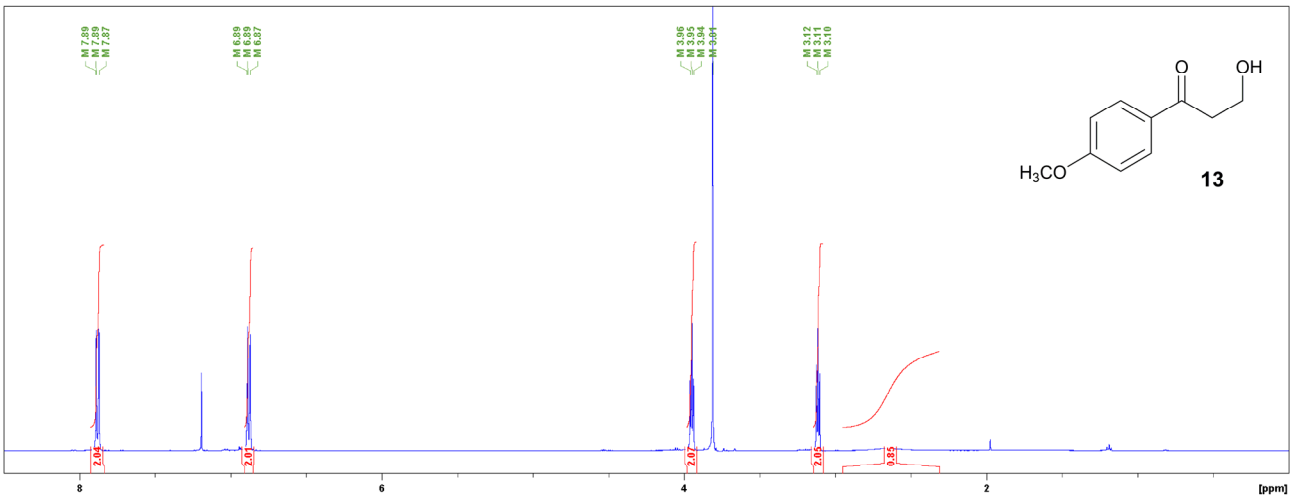
HSQC NMR spectrum of compound **12**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MH



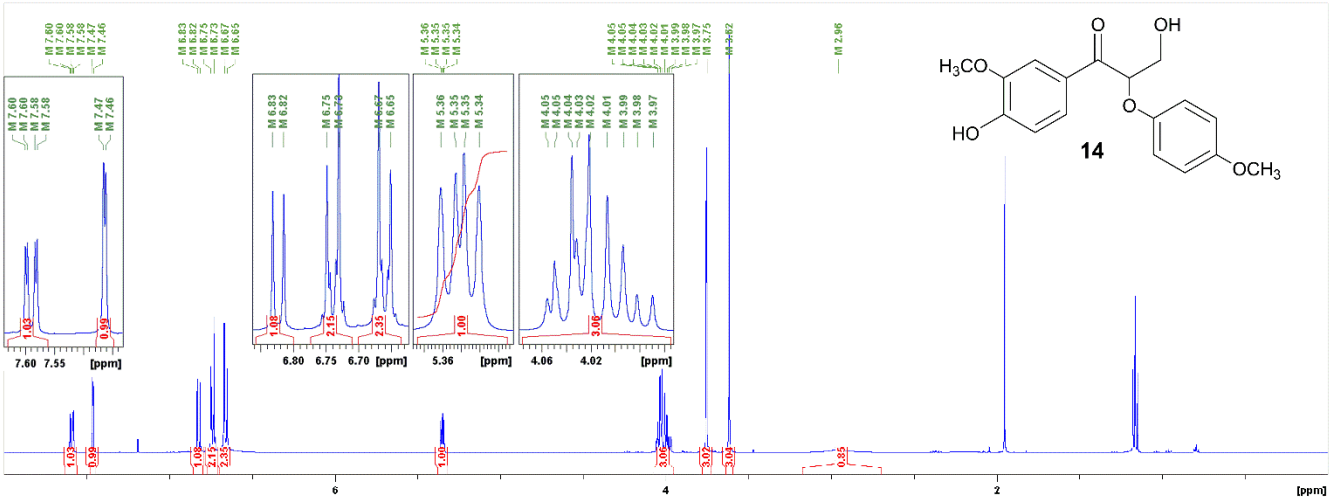
COSY NMR spectrum of compound **12**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



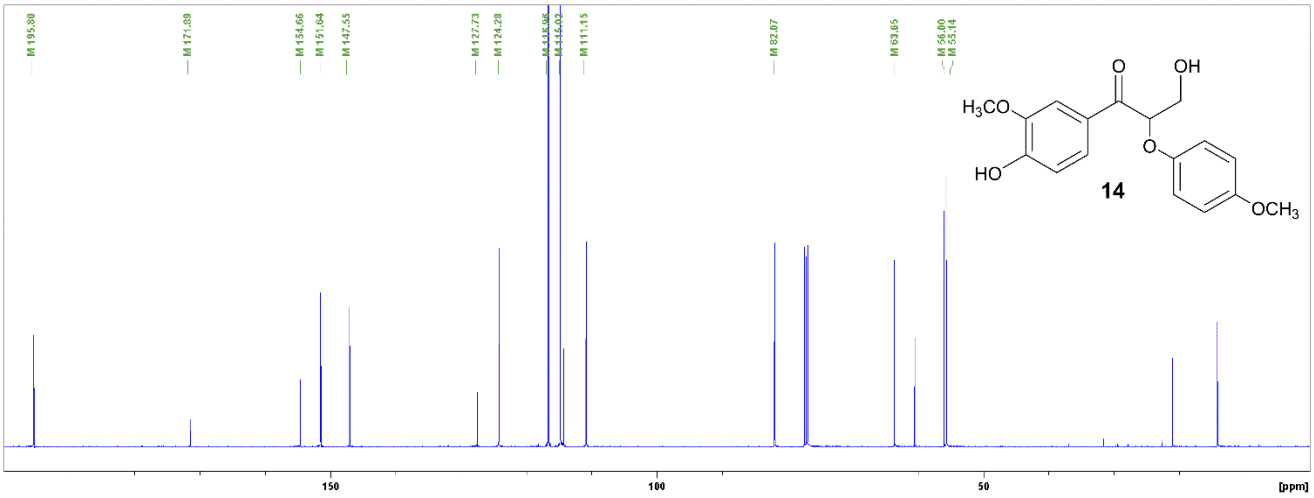
^1H NMR spectrum of compound **13**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



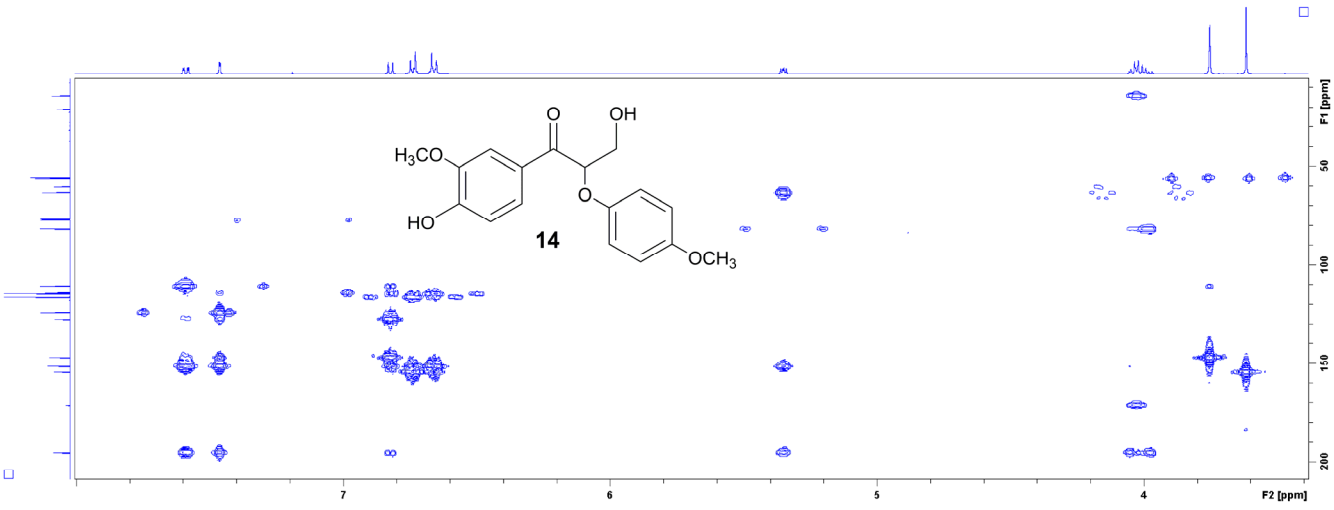
^{1}H NMR spectrum of compound **14**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



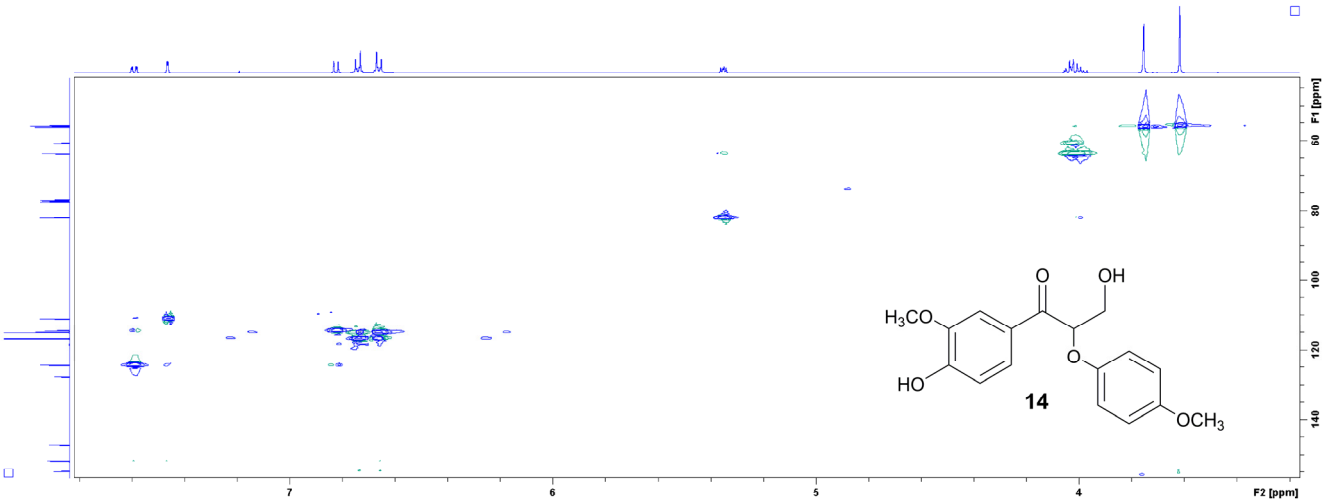
^{13}C NMR spectrum of compound **14**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



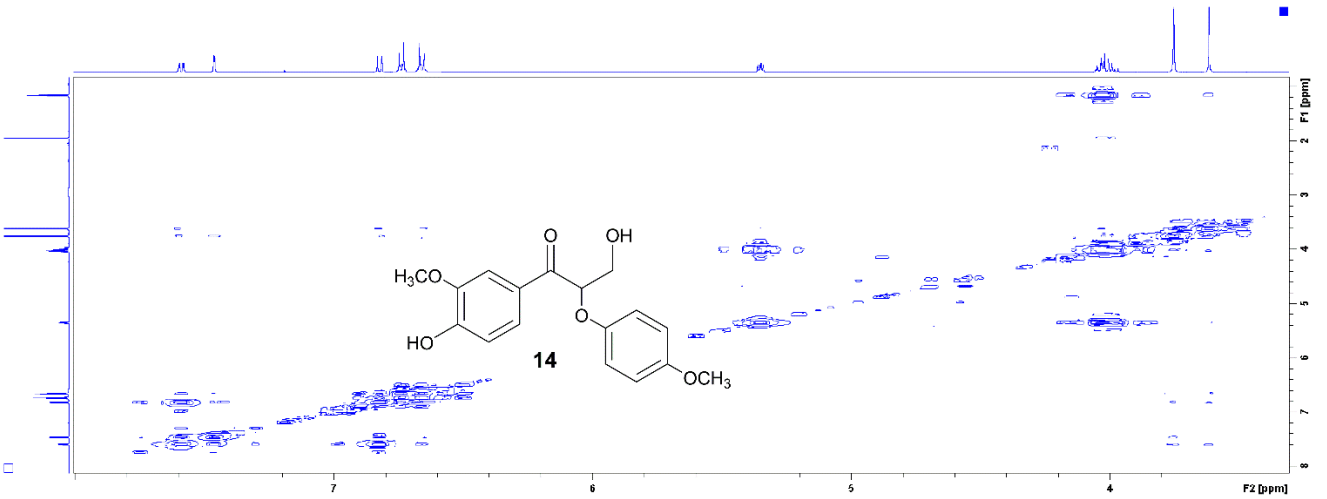
HMBC NMR spectrum of compound **14**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



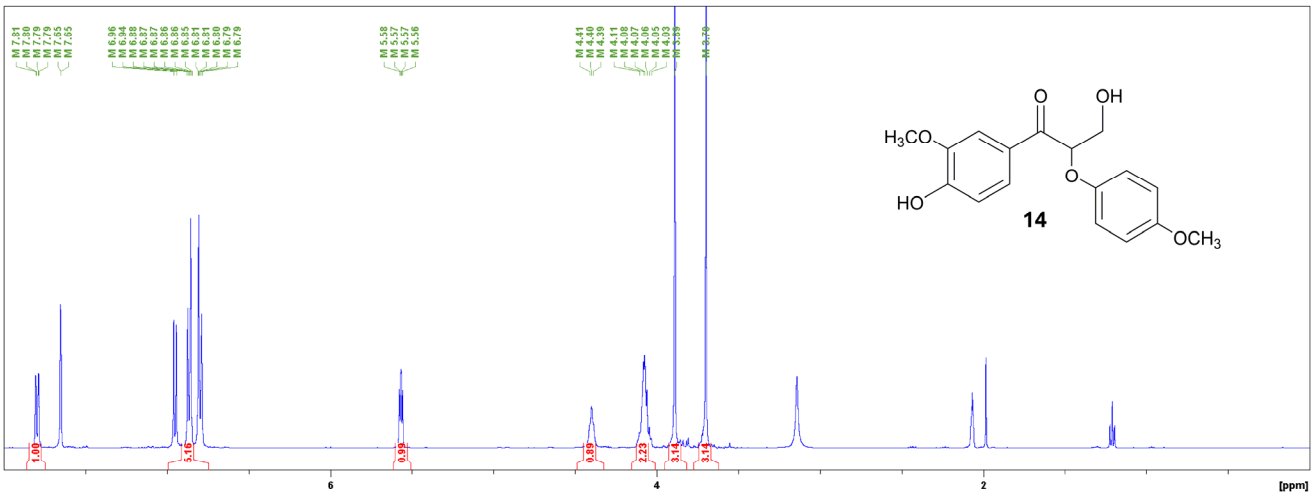
HSQC NMR spectrum of compound **14**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MH



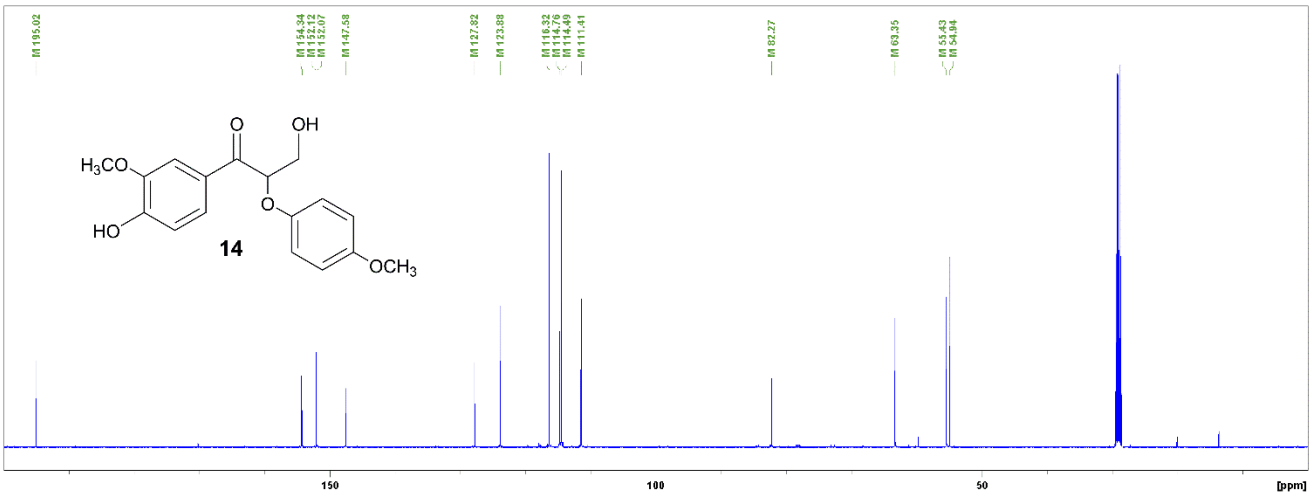
COSY NMR spectrum of compound **14**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



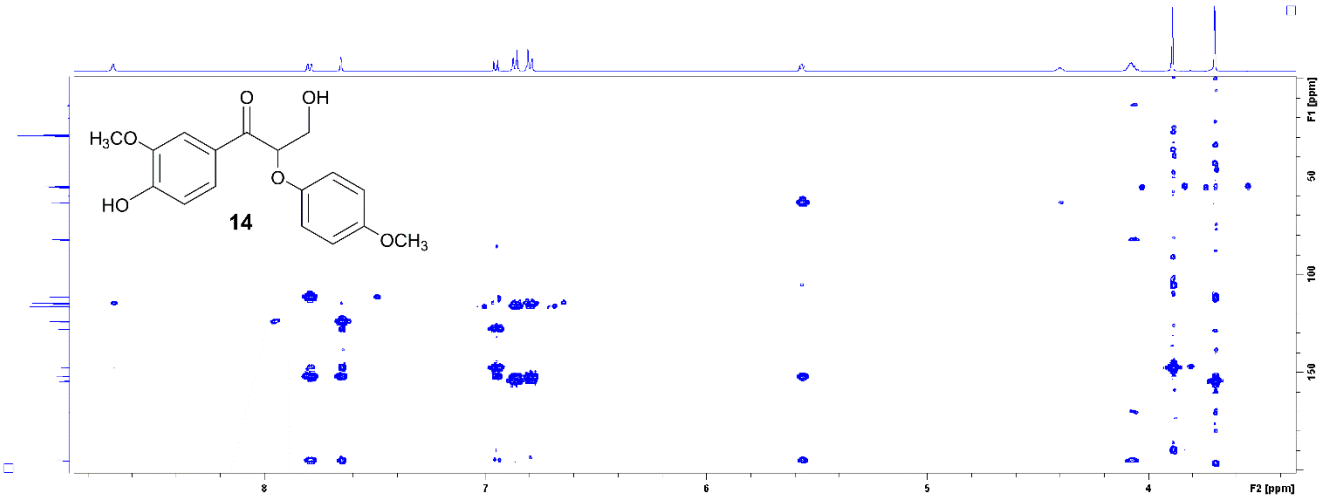
^{1}H NMR spectrum of compound **14**, 298K, acetone-d_6, 500 MHz



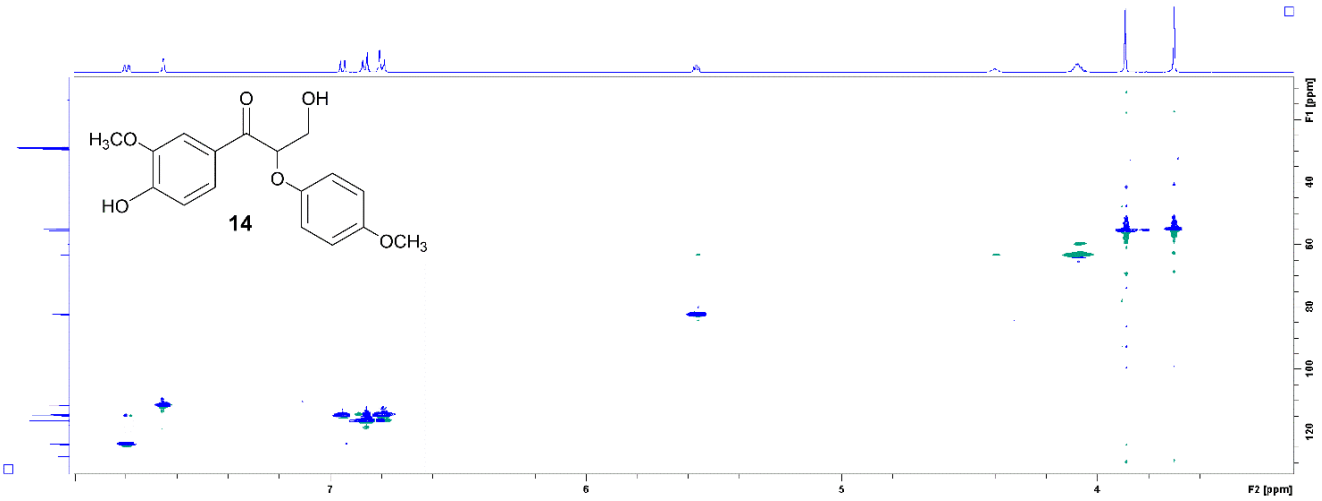
^{13}C NMR spectrum of compound **14**, 298K, acetone-d_6, 500 MHz



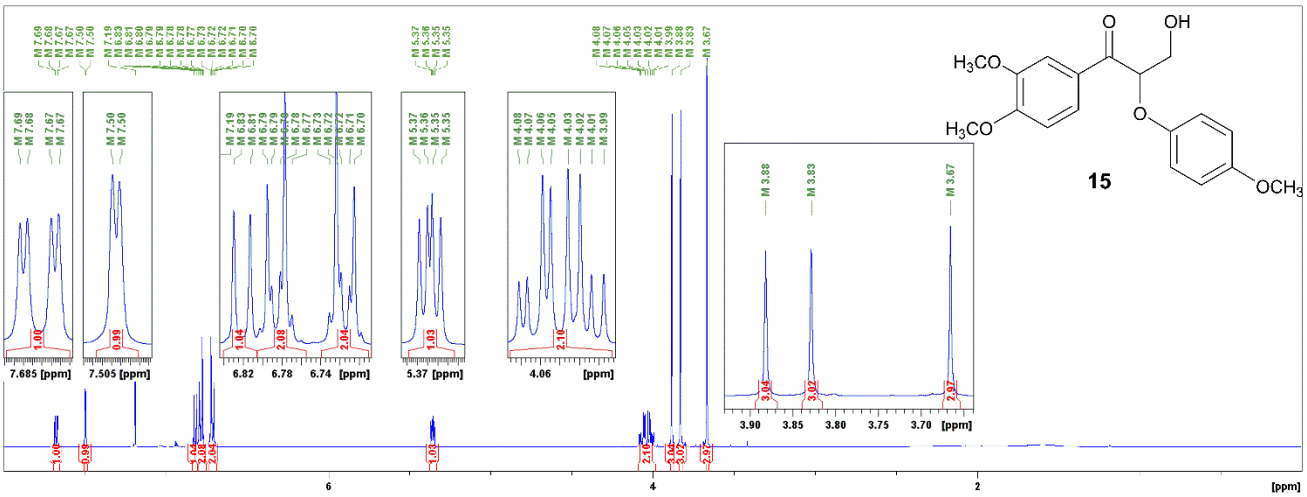
HMBC NMR spectrum of compound **14**, 298K, acetone-d_6, 500 MHz



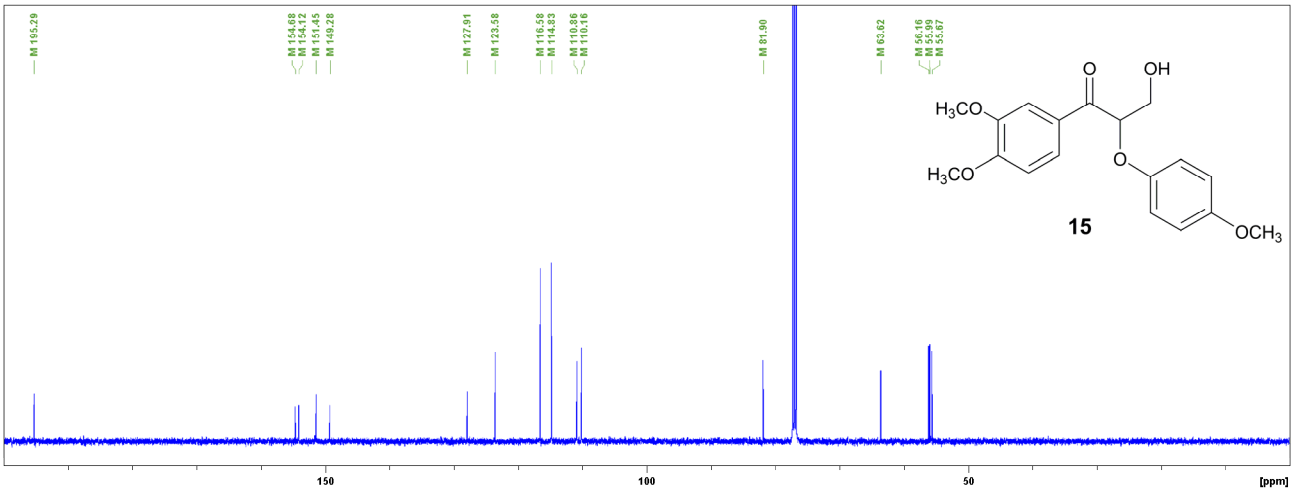
HSQC NMR spectrum of compound **14**, 298K, acetone-d_6, 500 MHz



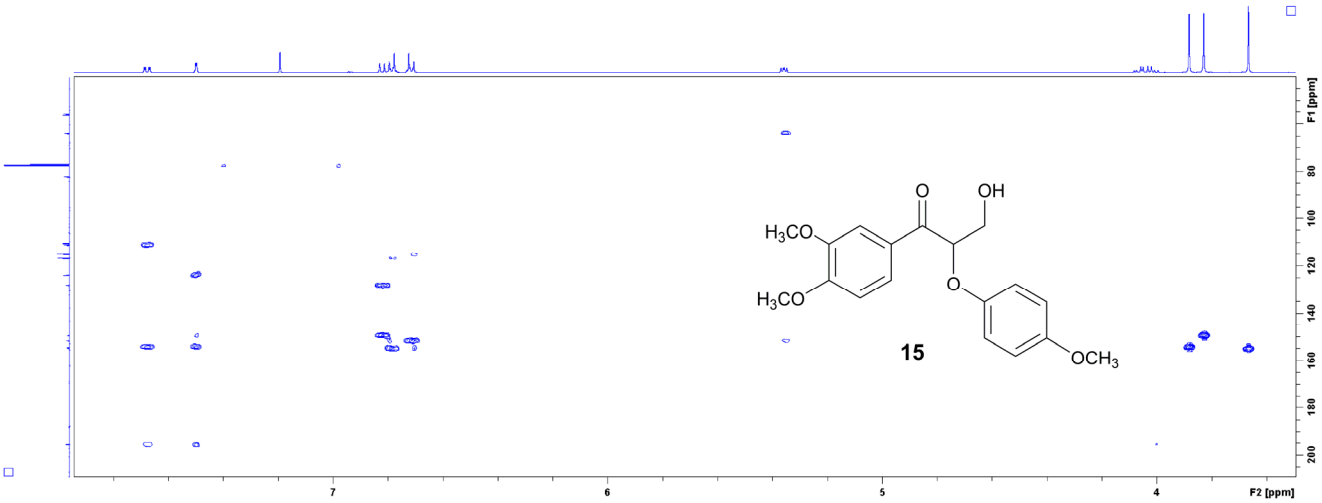
^{1}H NMR spectrum of compound **15**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



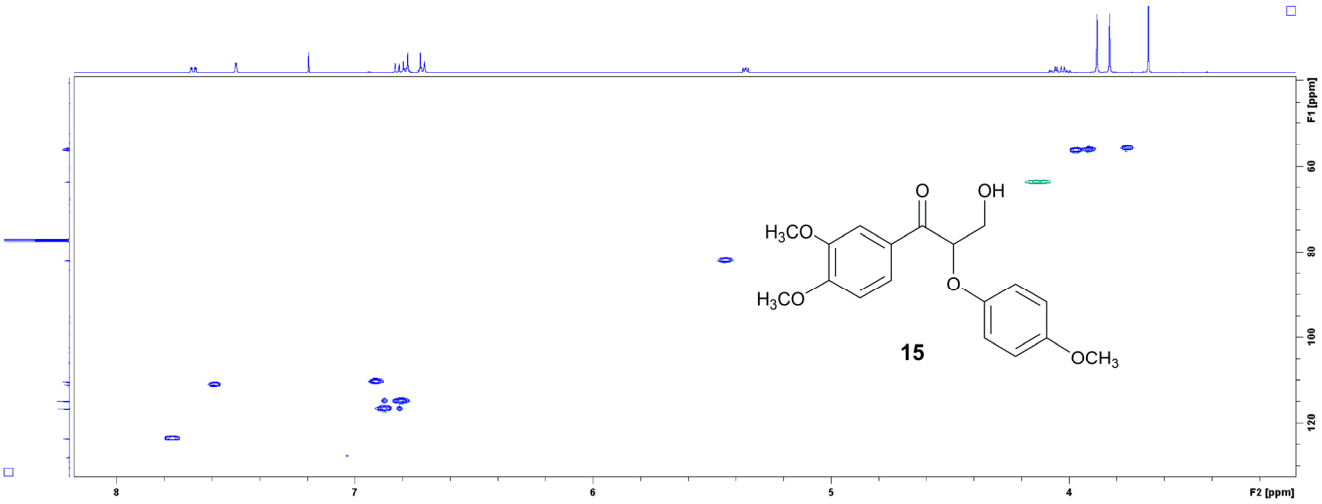
^{13}C NMR spectrum of compound **15**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



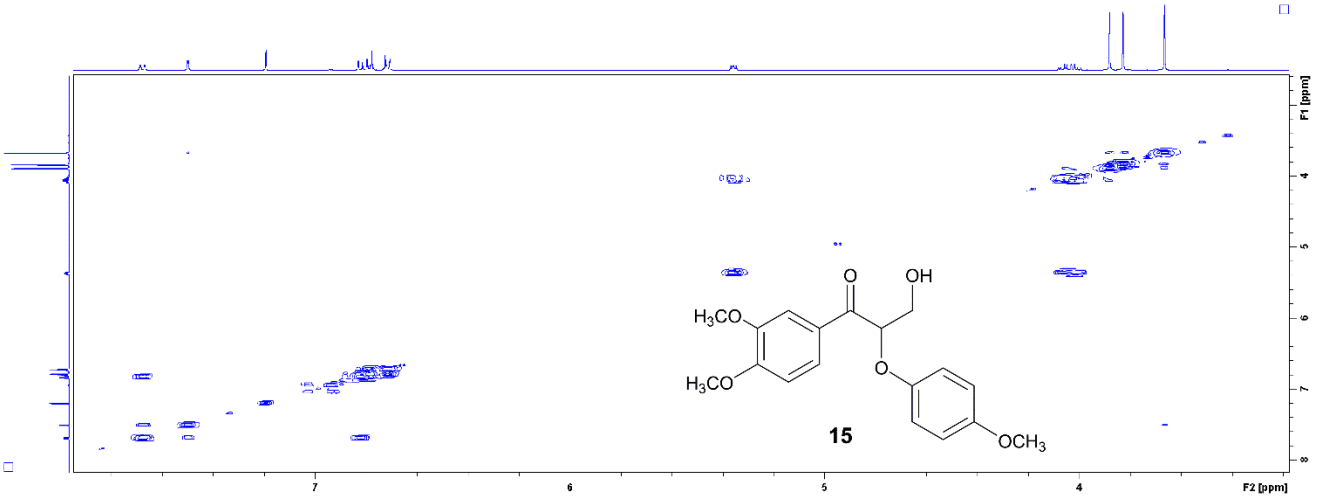
HMBC NMR spectrum of compound **15**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



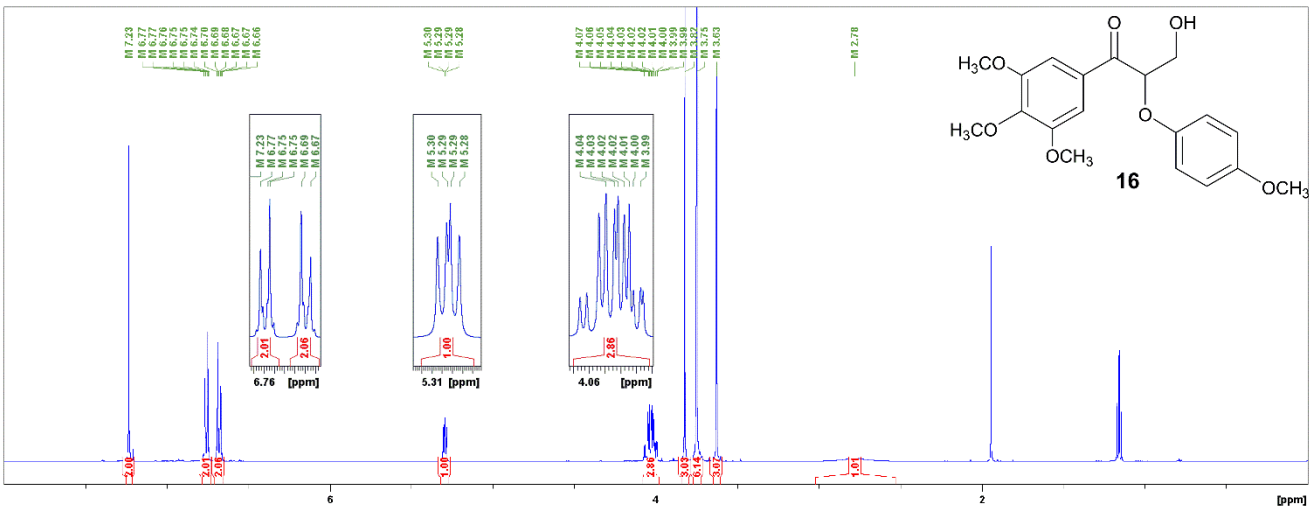
HSQC NMR spectrum of compound **15**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



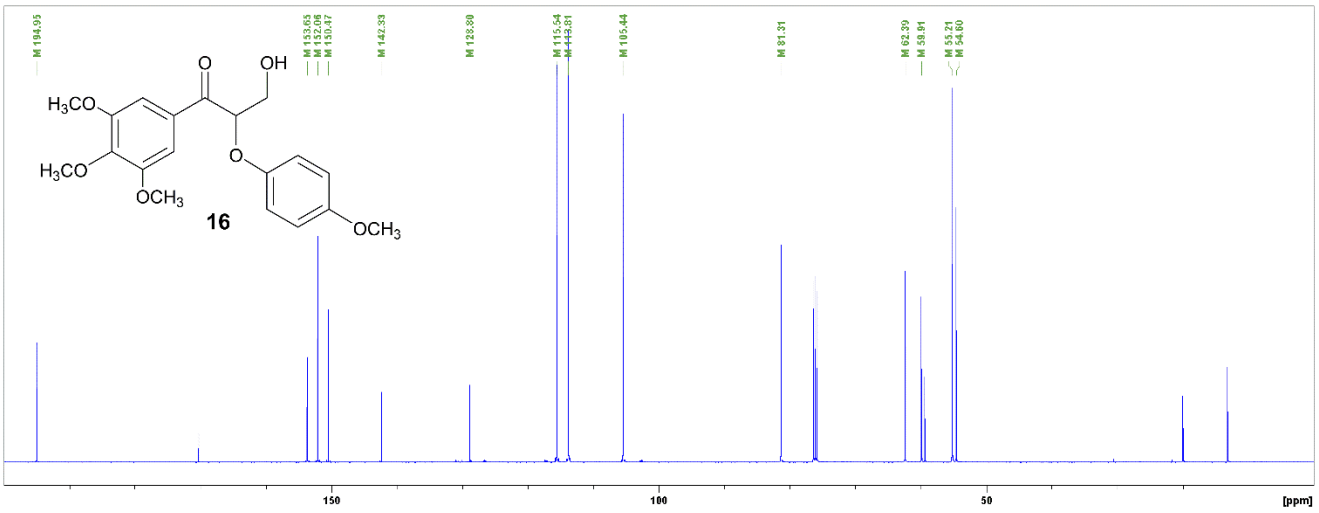
COSY NMR spectrum of compound **15**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



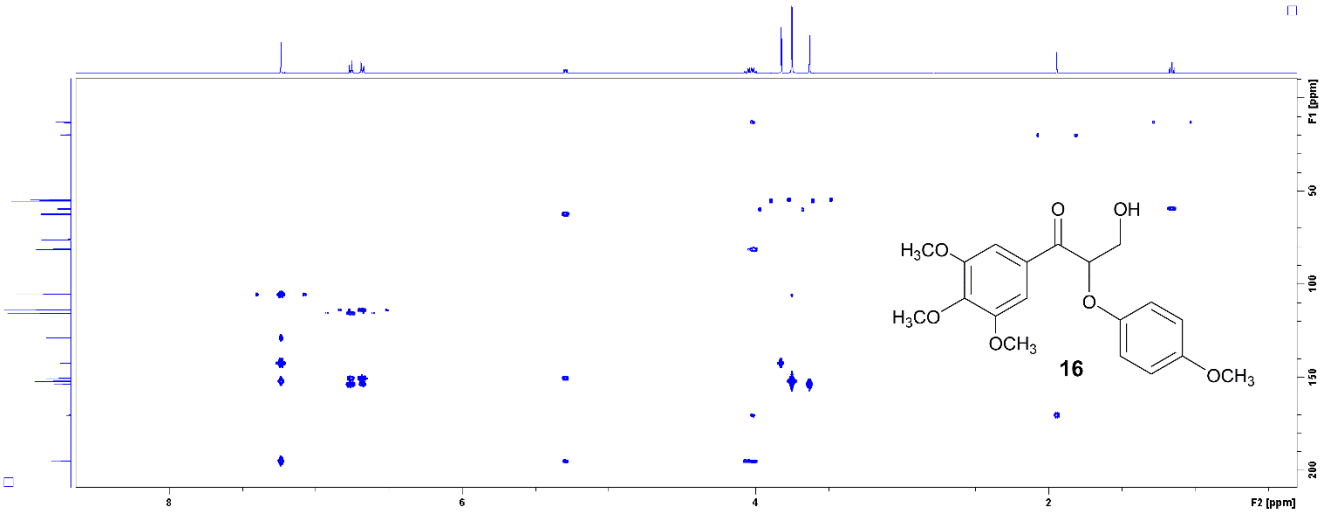
^{1}H NMR spectrum of compound **16**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



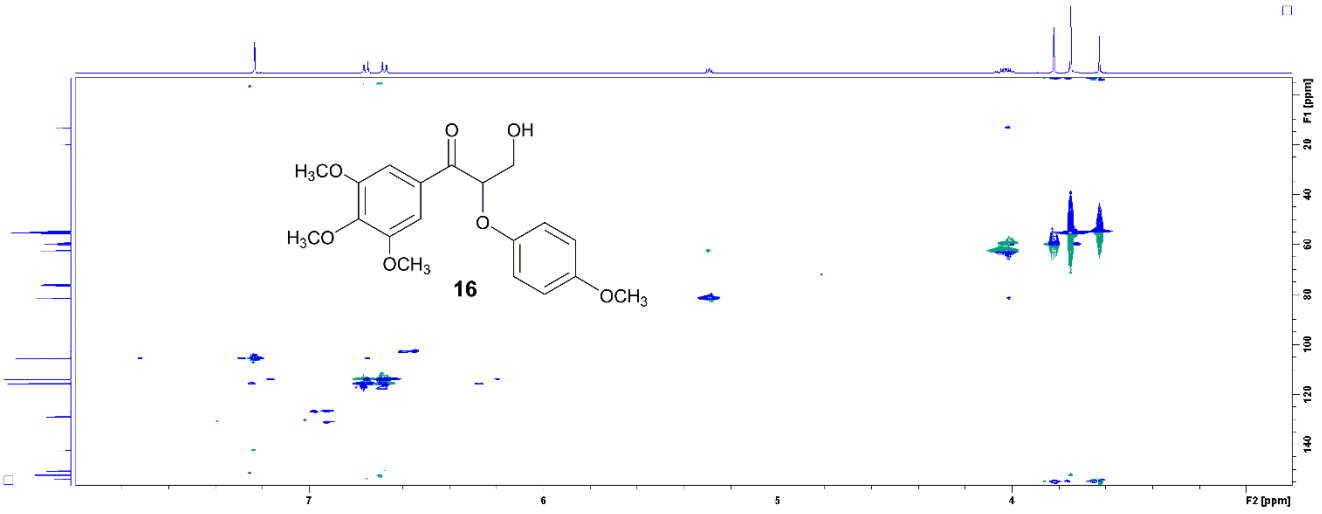
^{13}C NMR spectrum of compound **16**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



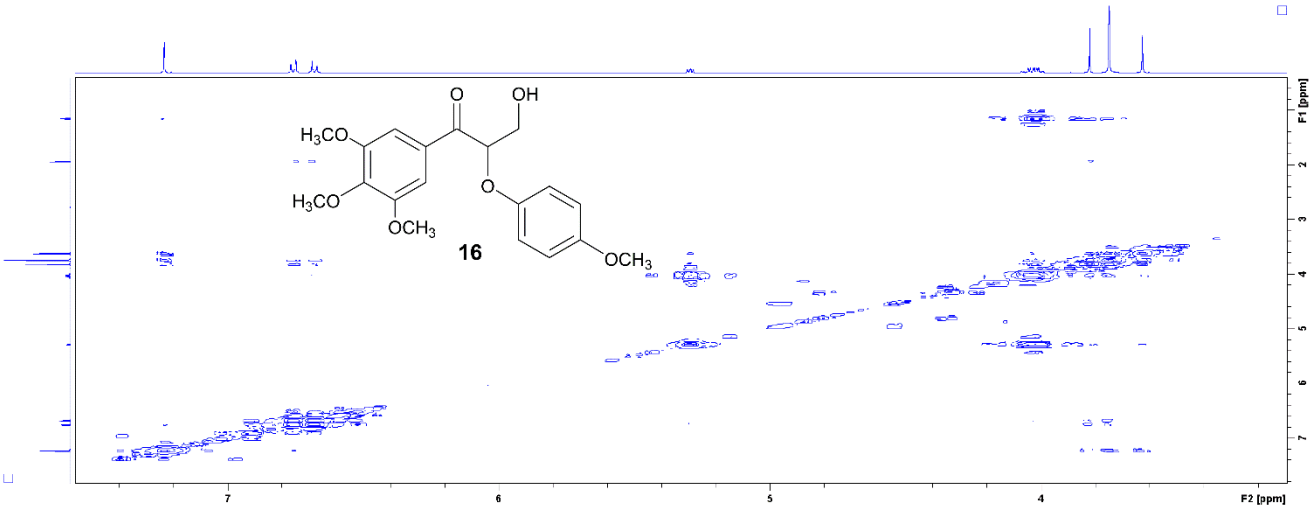
HMBC NMR spectrum of compound **16**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



HSQC NMR spectrum of compound **16**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz

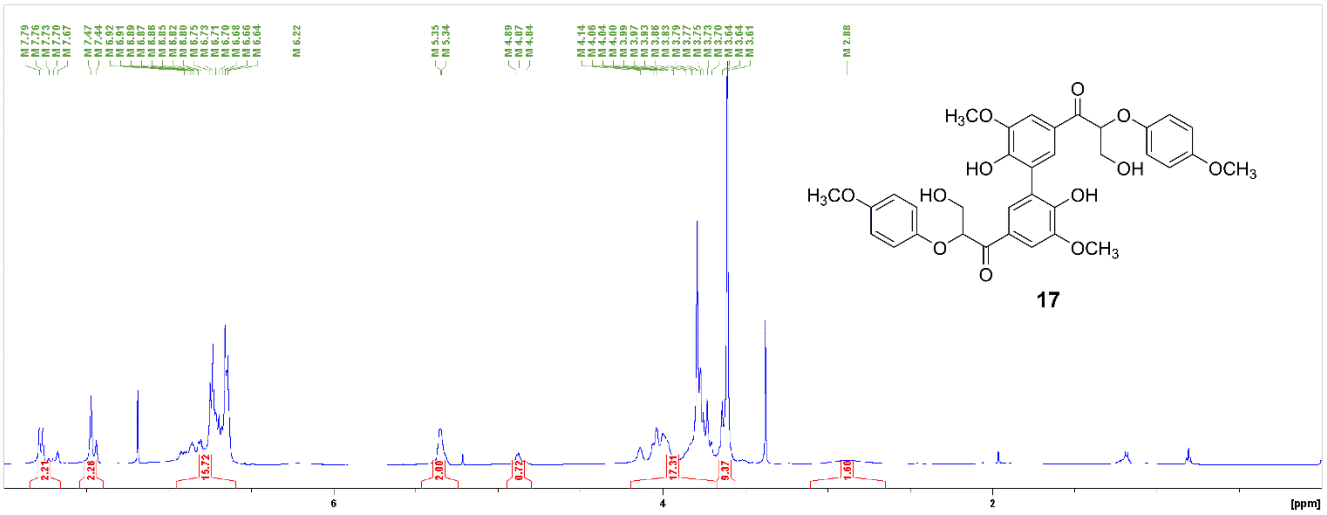


COSY NMR spectrum of compound **16**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



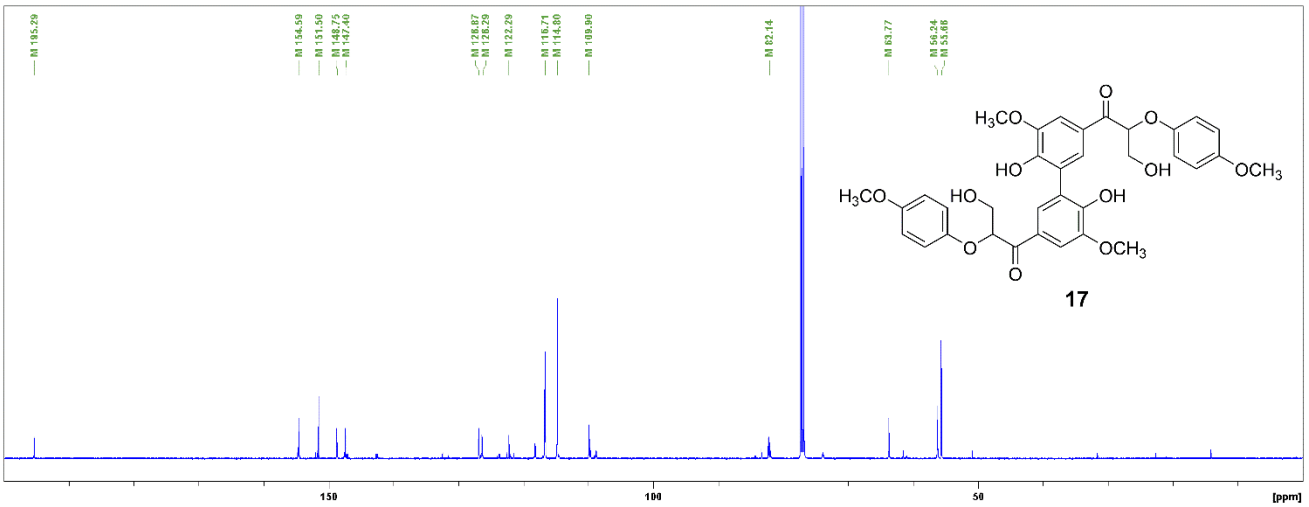
16

^{1}H NMR spectrum of compound **17**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



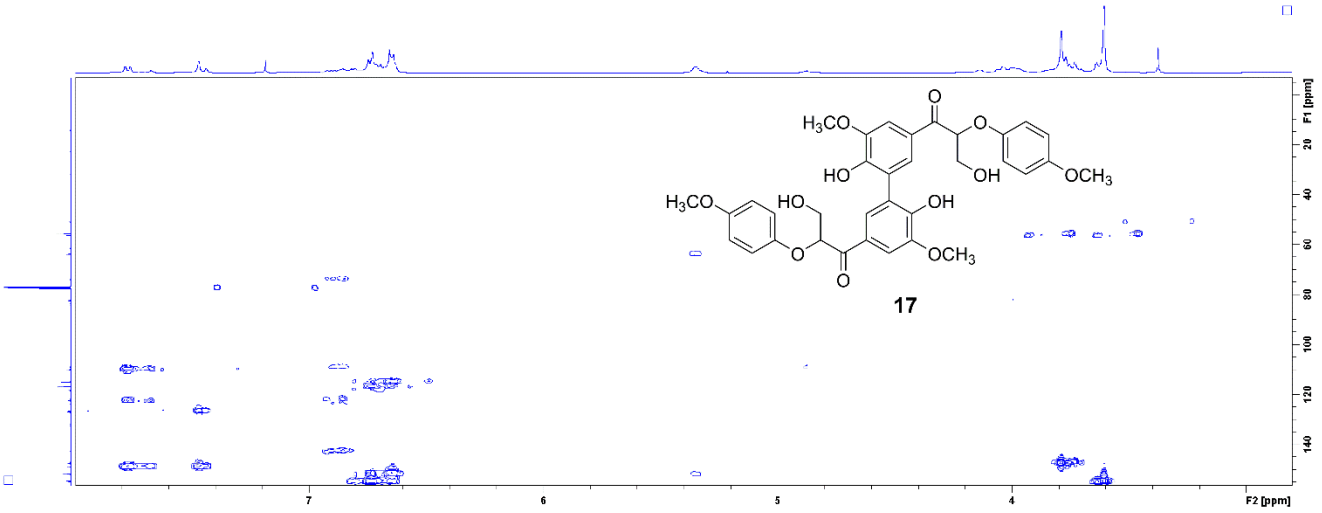
17

^{13}C NMR spectrum of compound **17**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



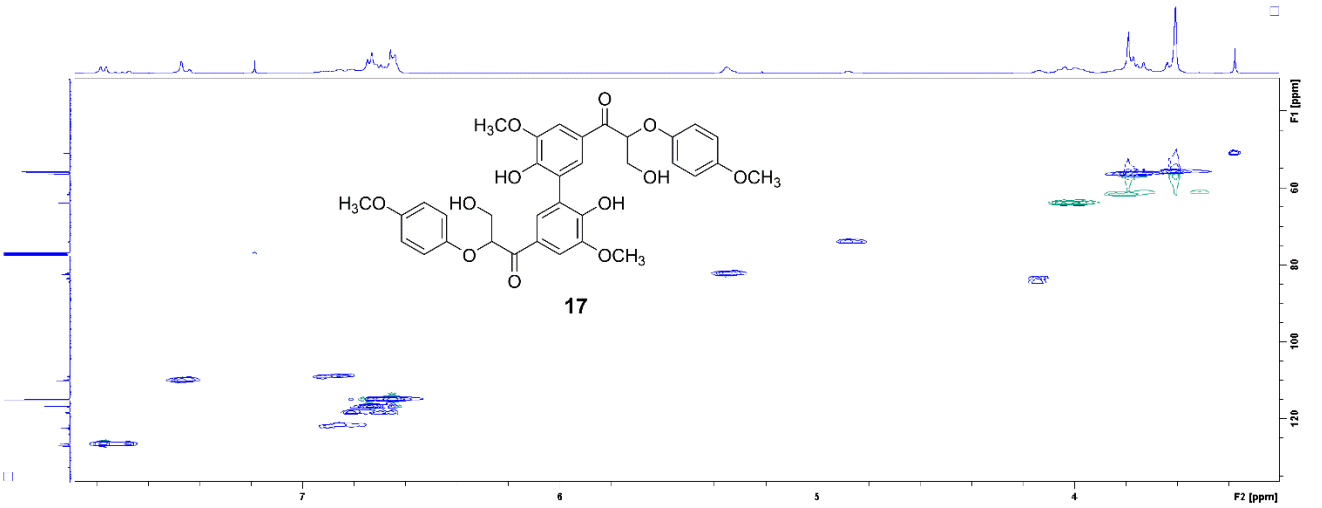
17

HMBC NMR spectrum of compound **17**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



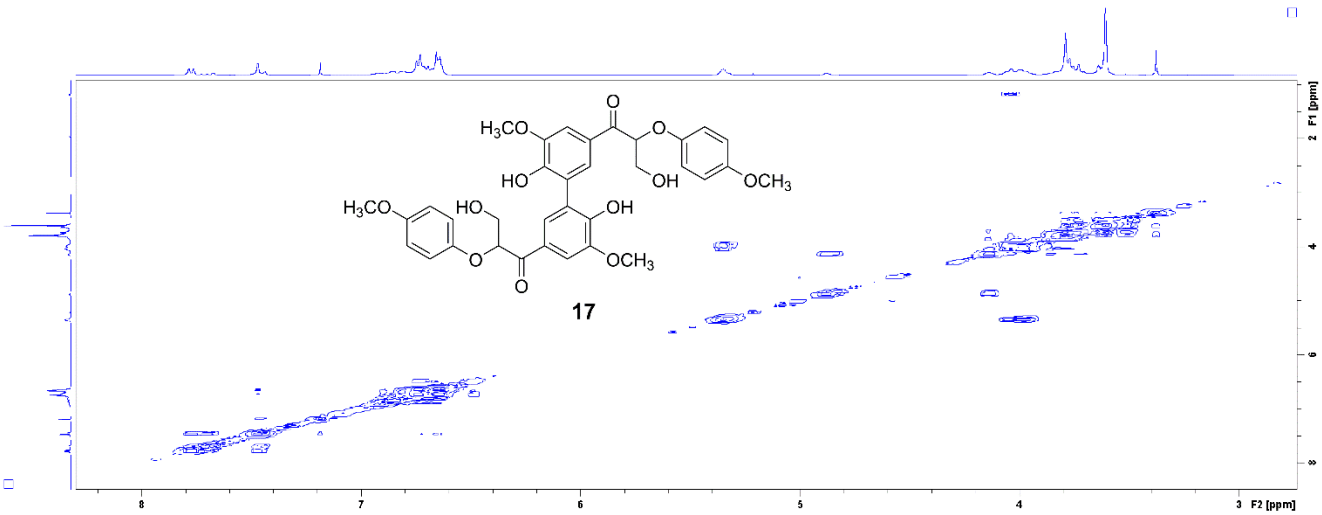
17

HSQC NMR spectrum of compound **17**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



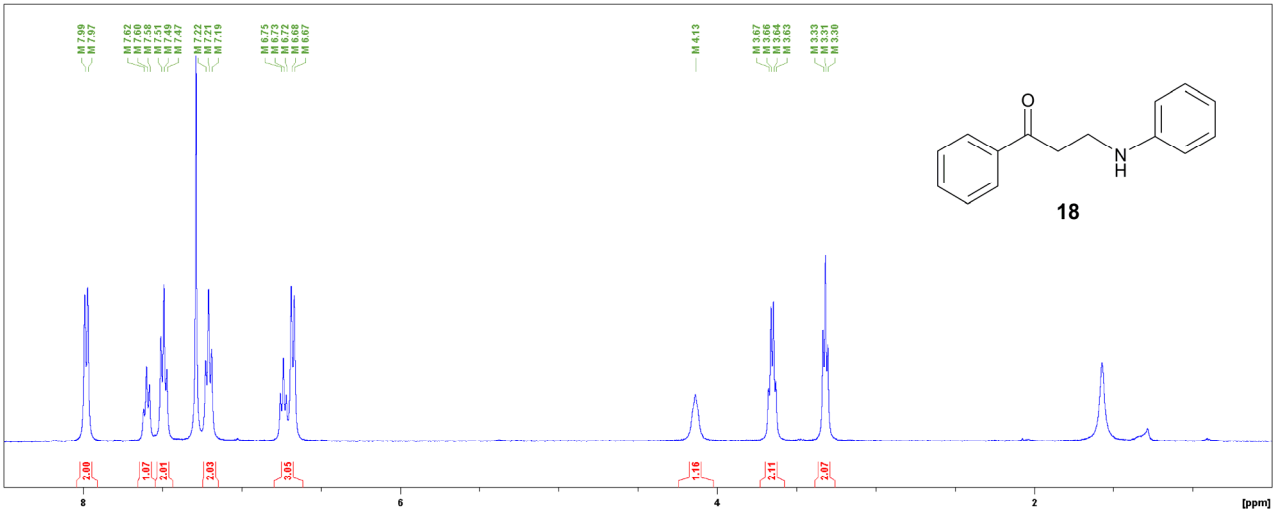
17

COSY NMR spectrum of compound **17**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz

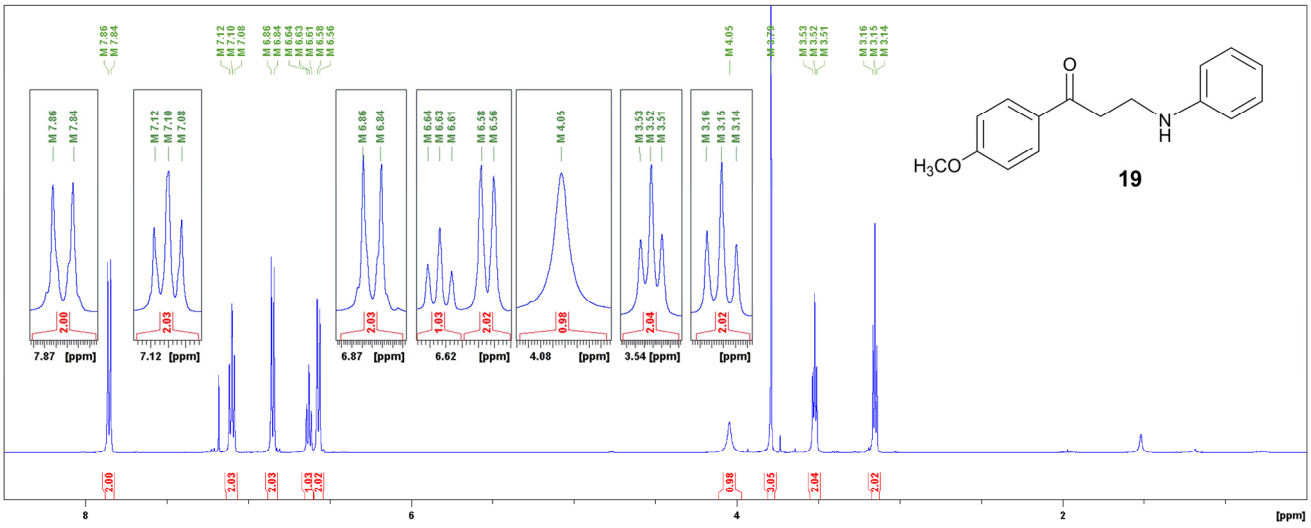


17

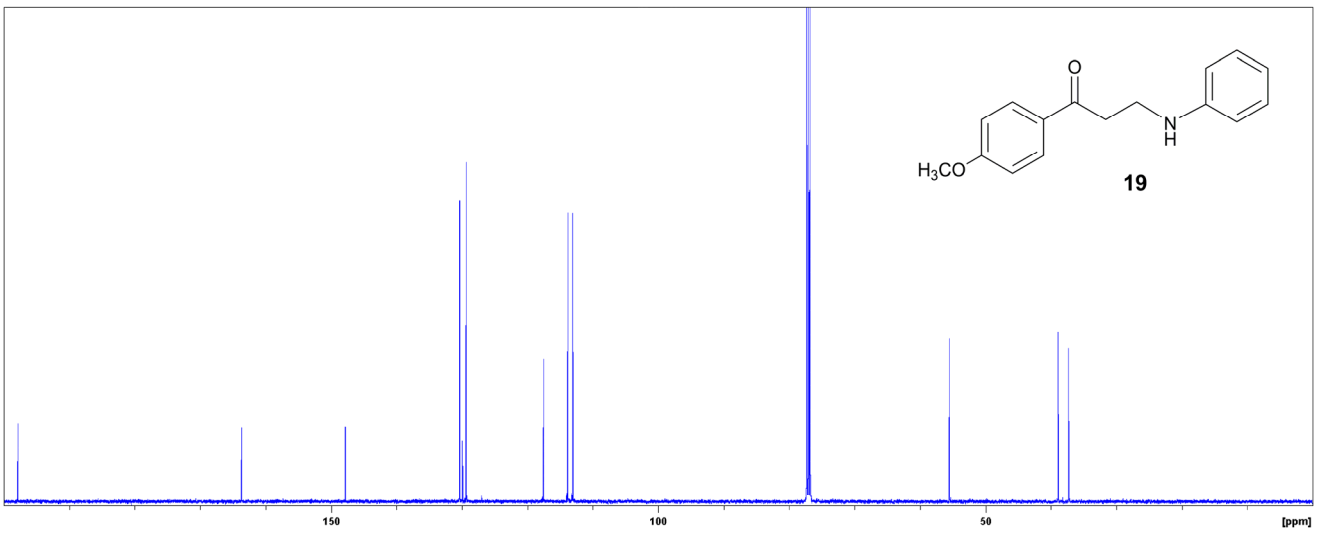
^{1}H NMR spectrum of compound **18**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



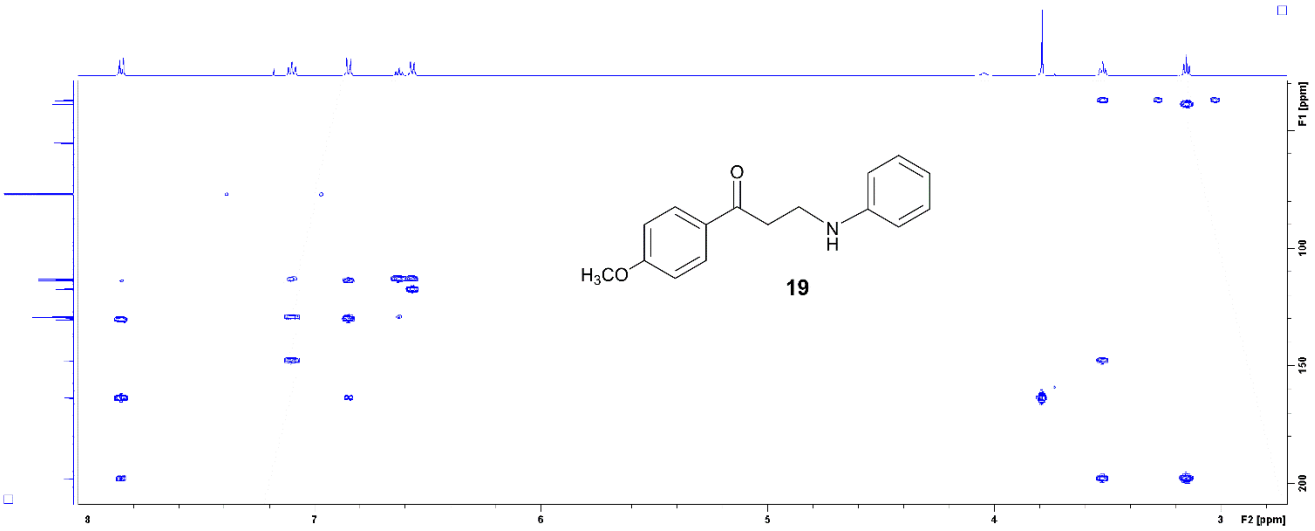
^{1}H NMR spectrum of compound **19**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



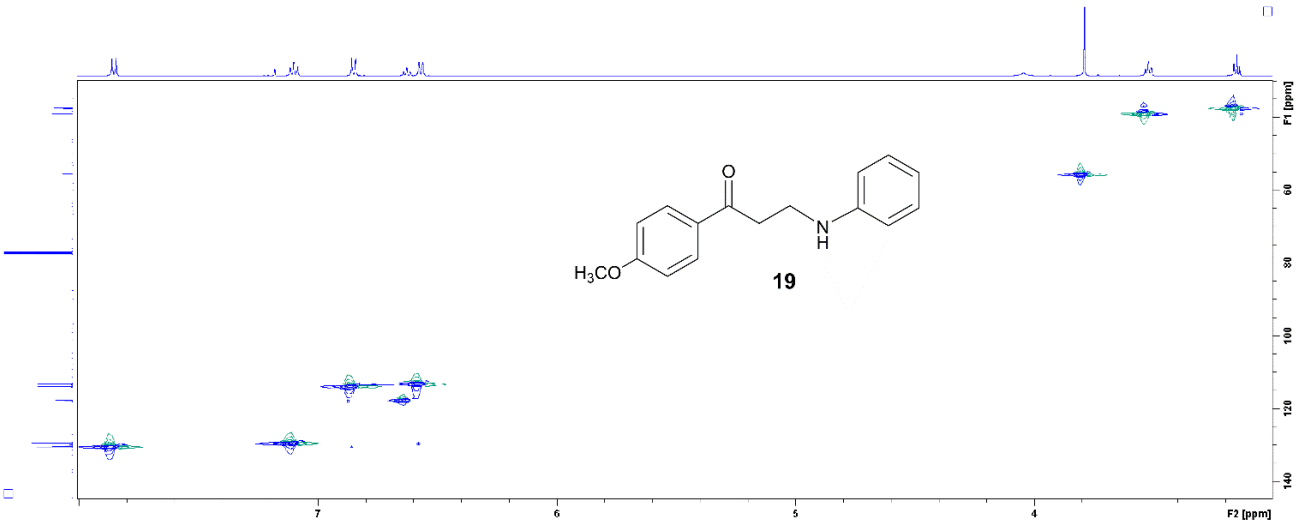
^{13}C NMR spectrum of compound **19**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



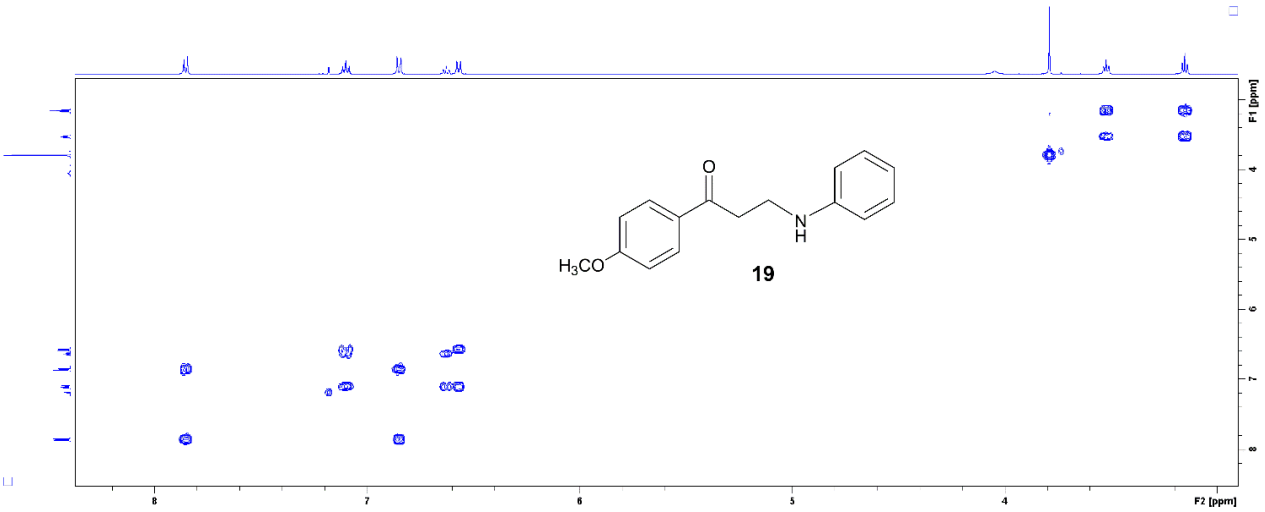
HMBC NMR spectrum of compound **19**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



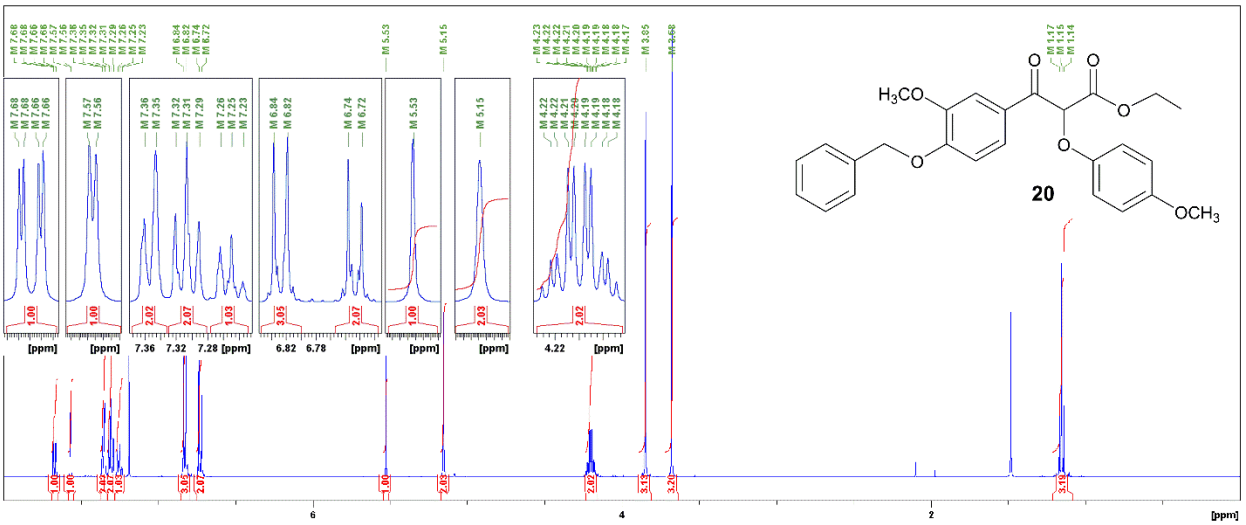
HSQC NMR spectrum of compound **19**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



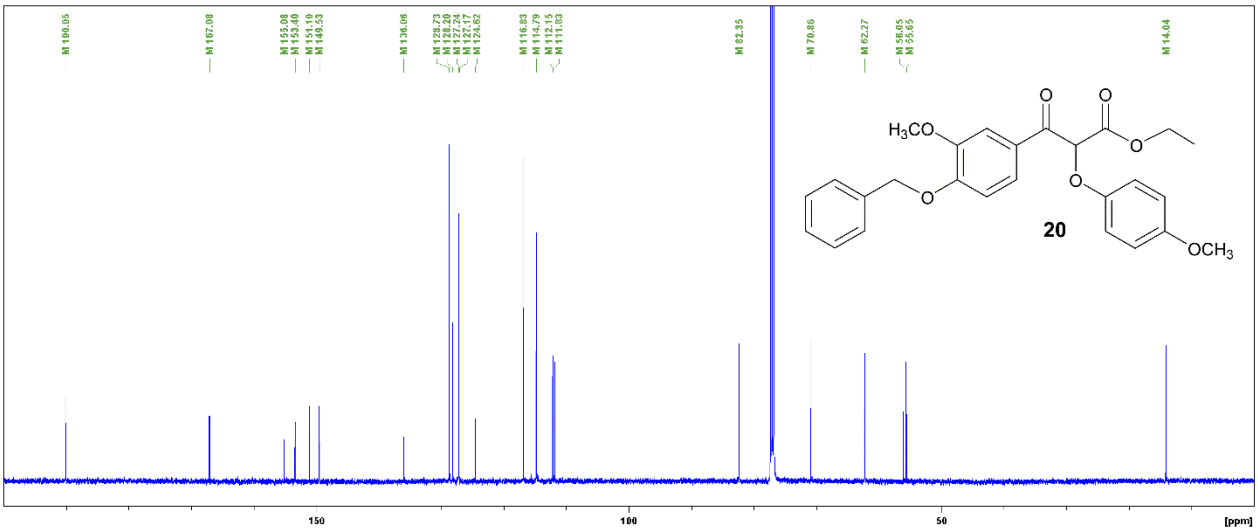
COSY NMR spectrum of compound **19**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



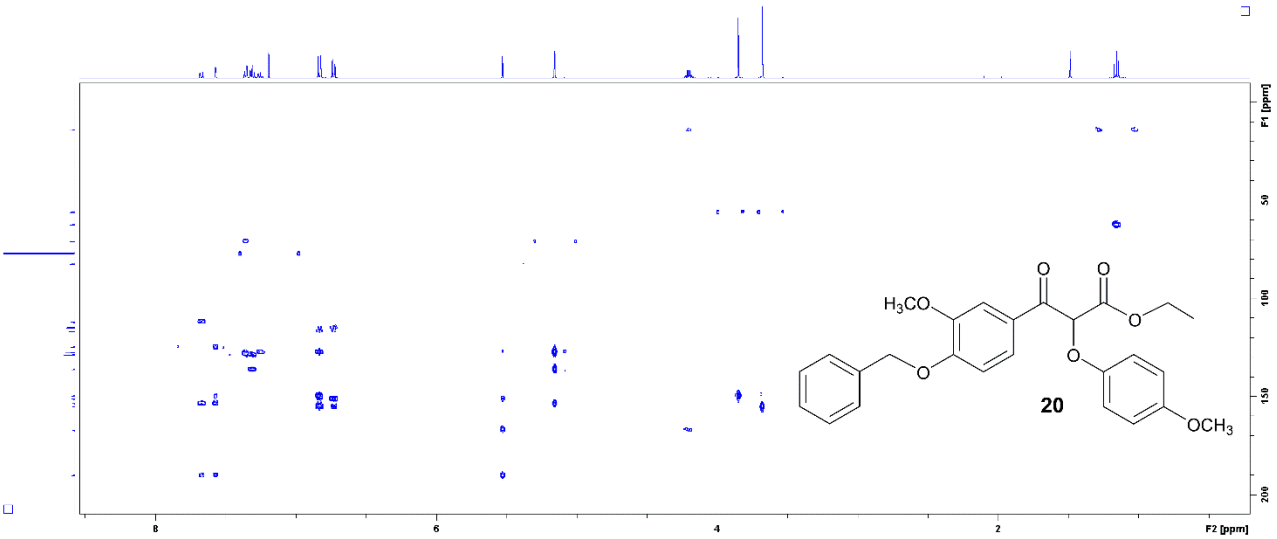
^{1}H NMR spectrum of compound **20**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



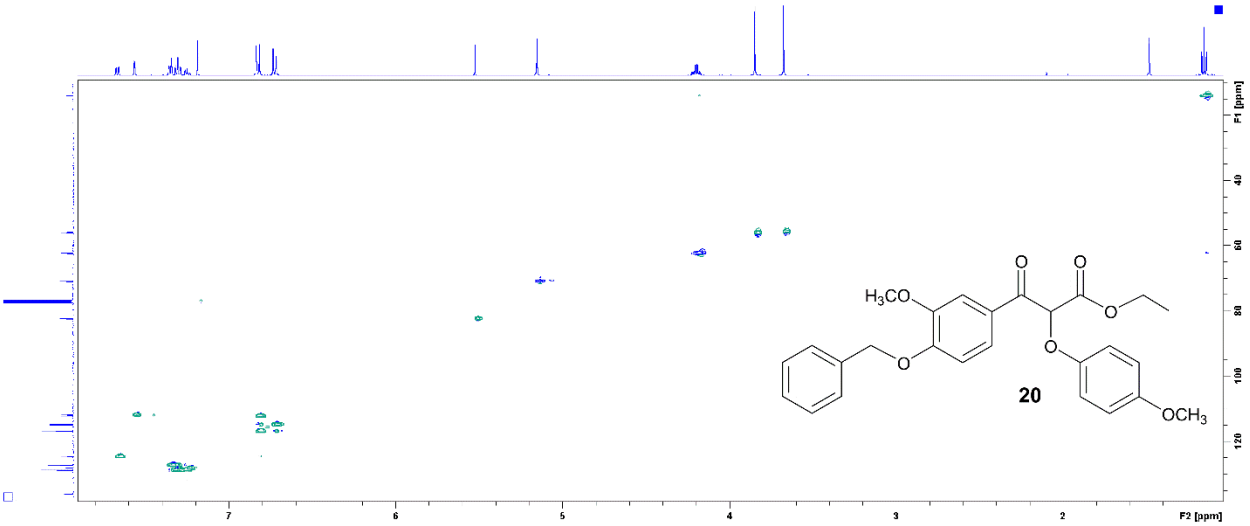
^{13}C NMR spectrum of compound **20**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



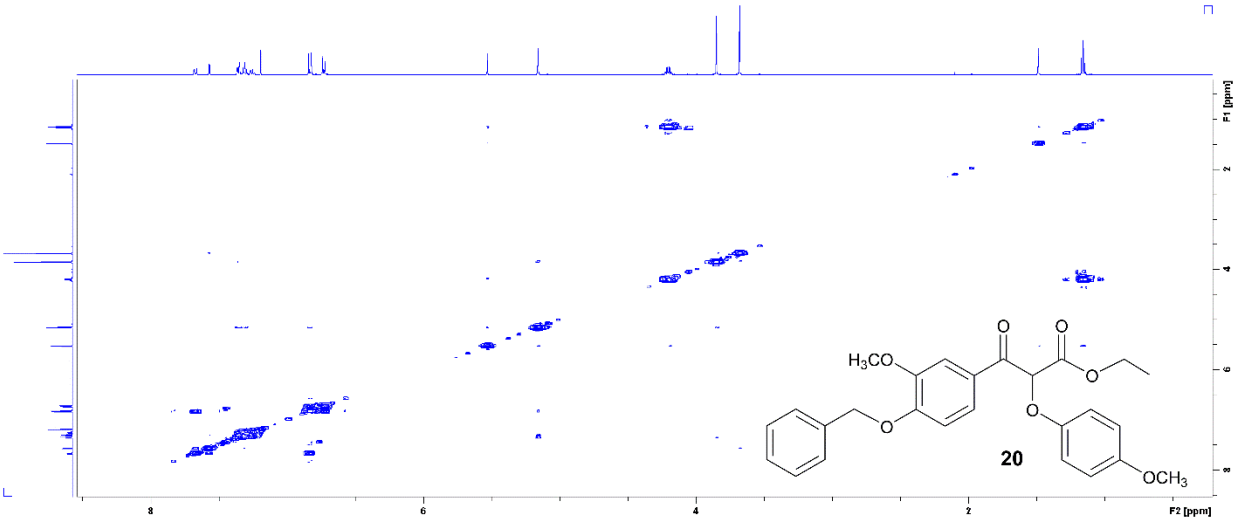
HMBC NMR spectrum of compound **20**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



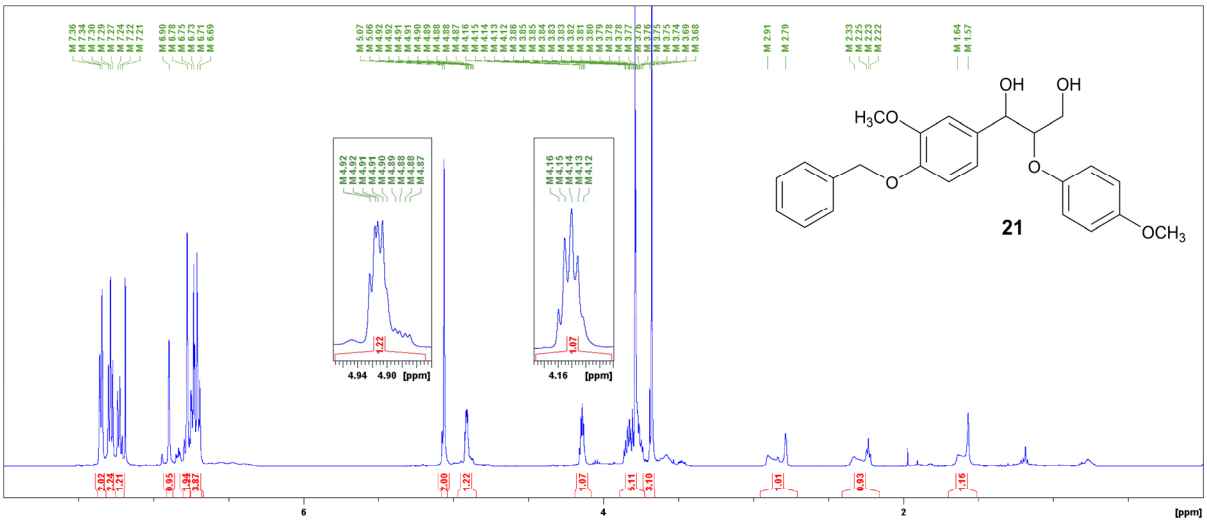
HSQC NMR spectrum of compound **20**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



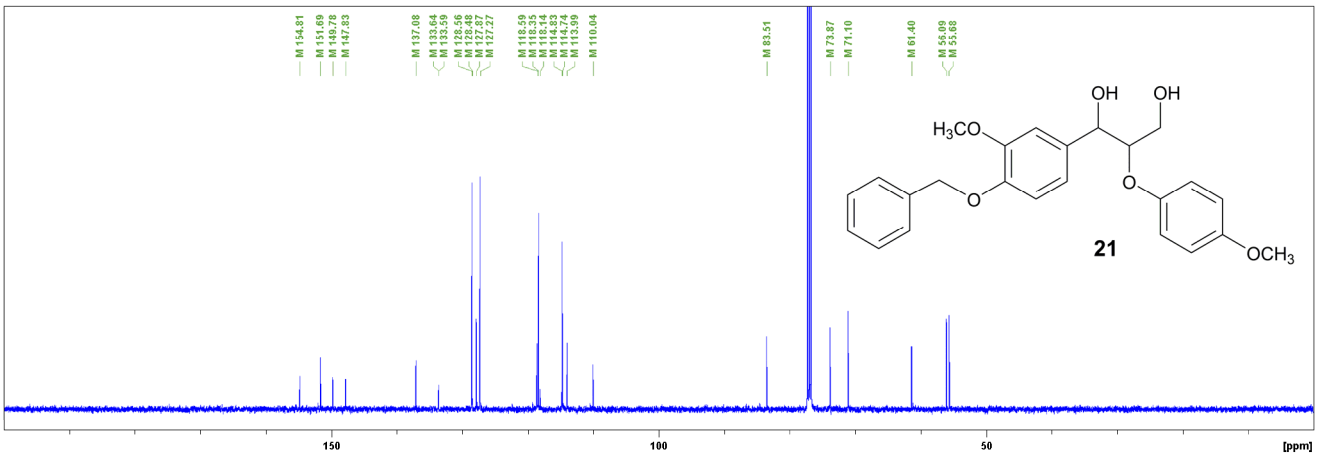
COSY NMR spectrum of compound **20**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



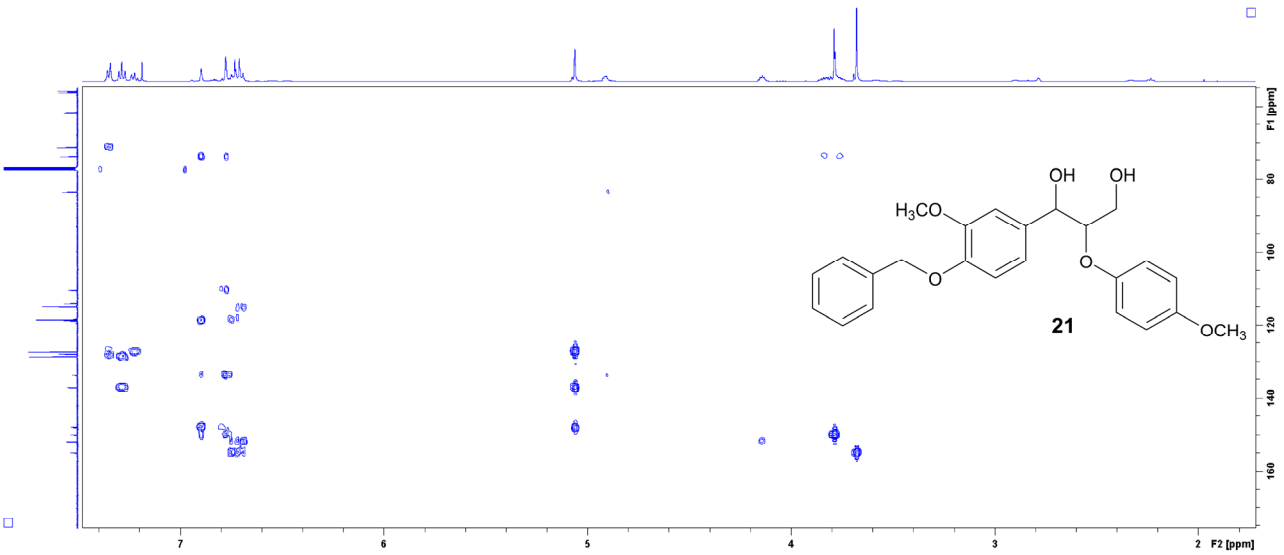
^{1}H NMR spectrum of compound **21**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



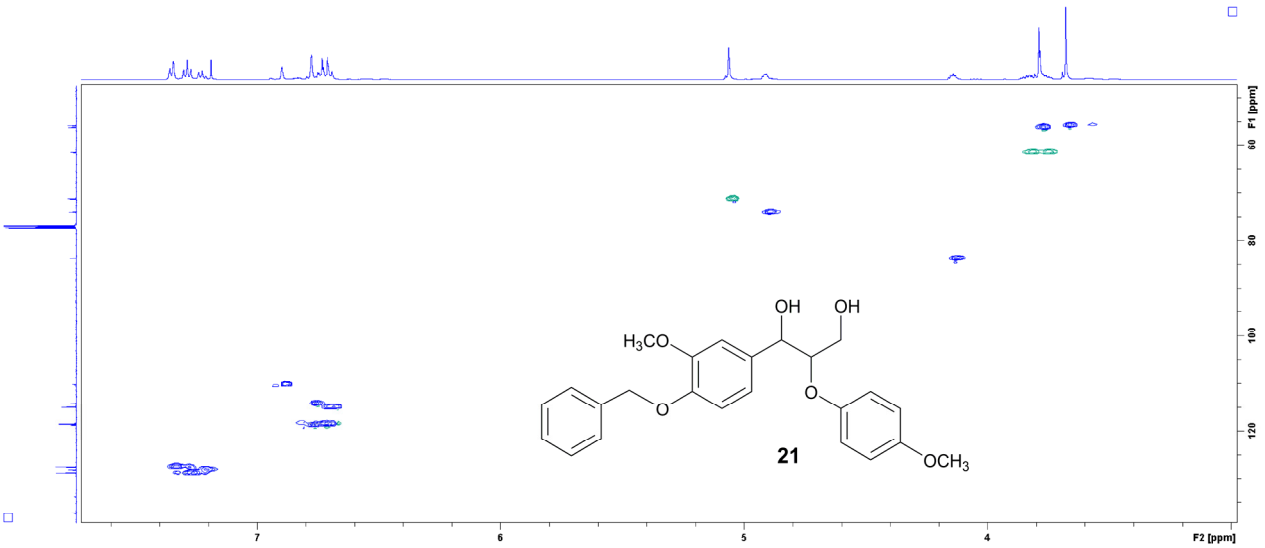
^{13}C NMR spectrum of compound **21**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



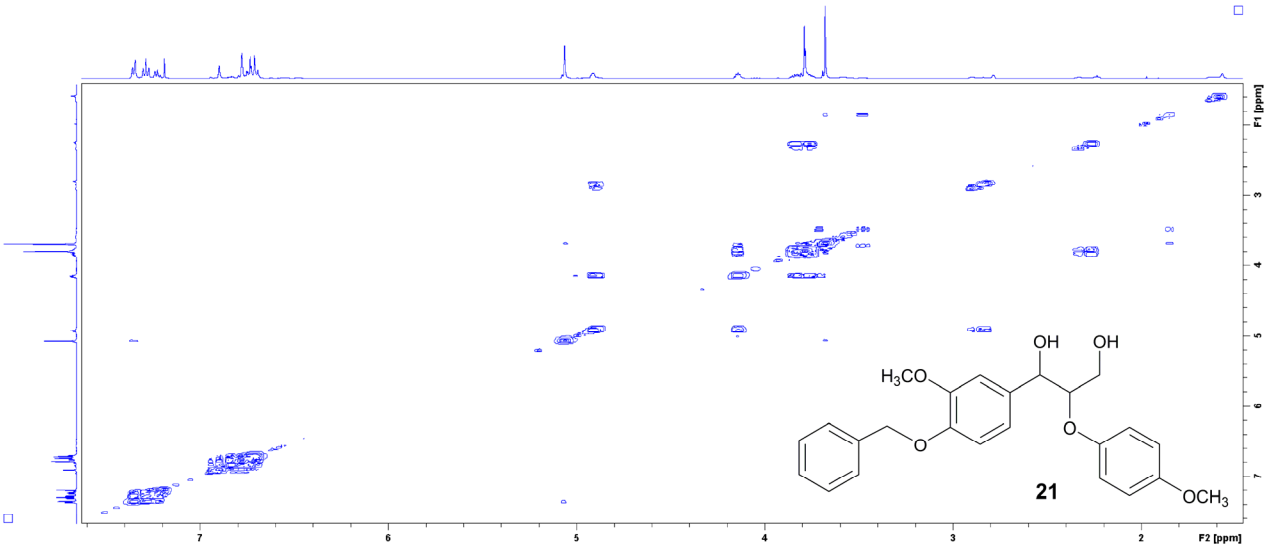
HMBC NMR spectrum of compound **21**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



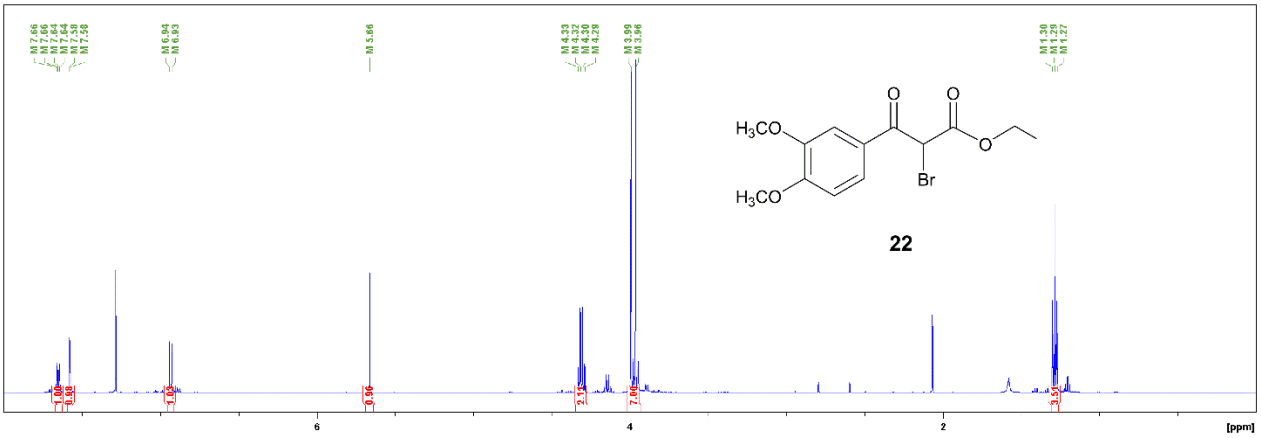
HSQC NMR spectrum of compound **21**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



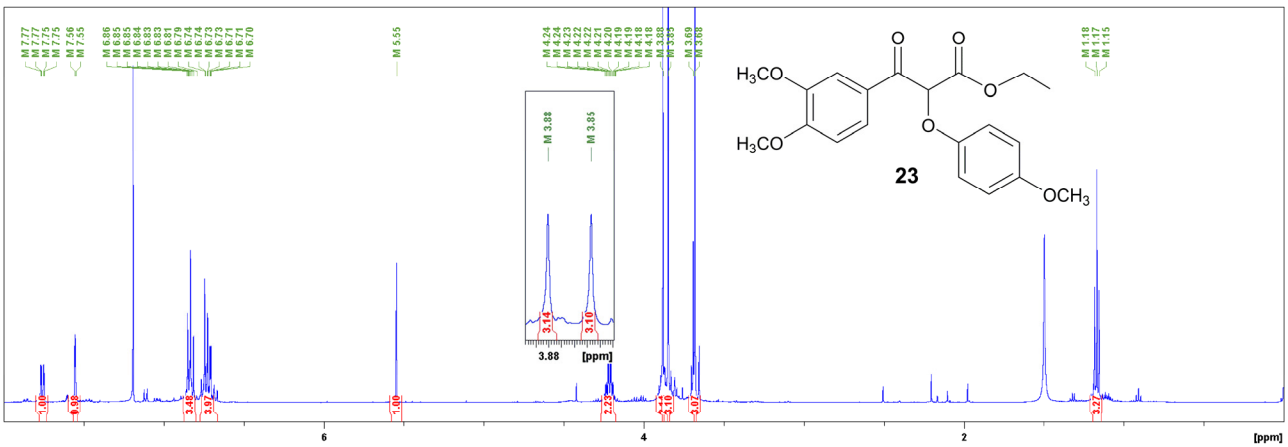
COSY NMR spectrum of compound **21**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



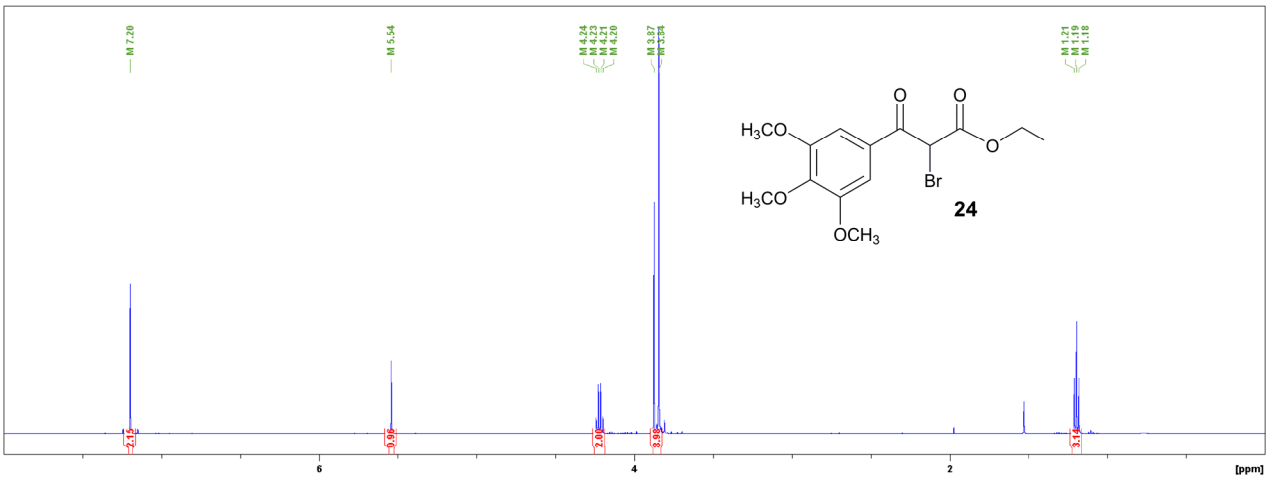
^{1}H NMR spectrum of compound **22**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



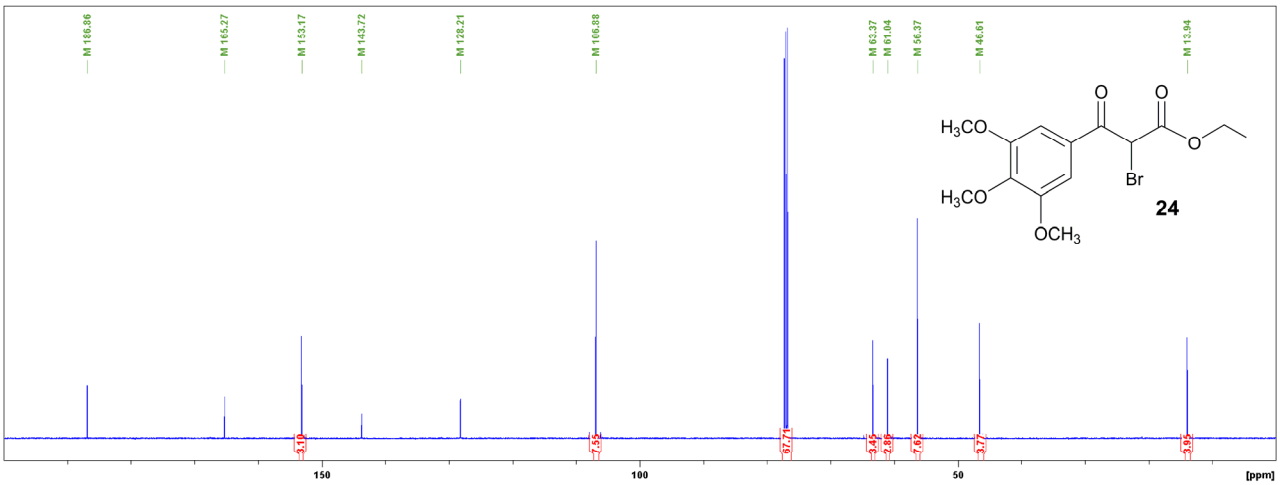
^{1}H NMR spectrum of compound **23**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



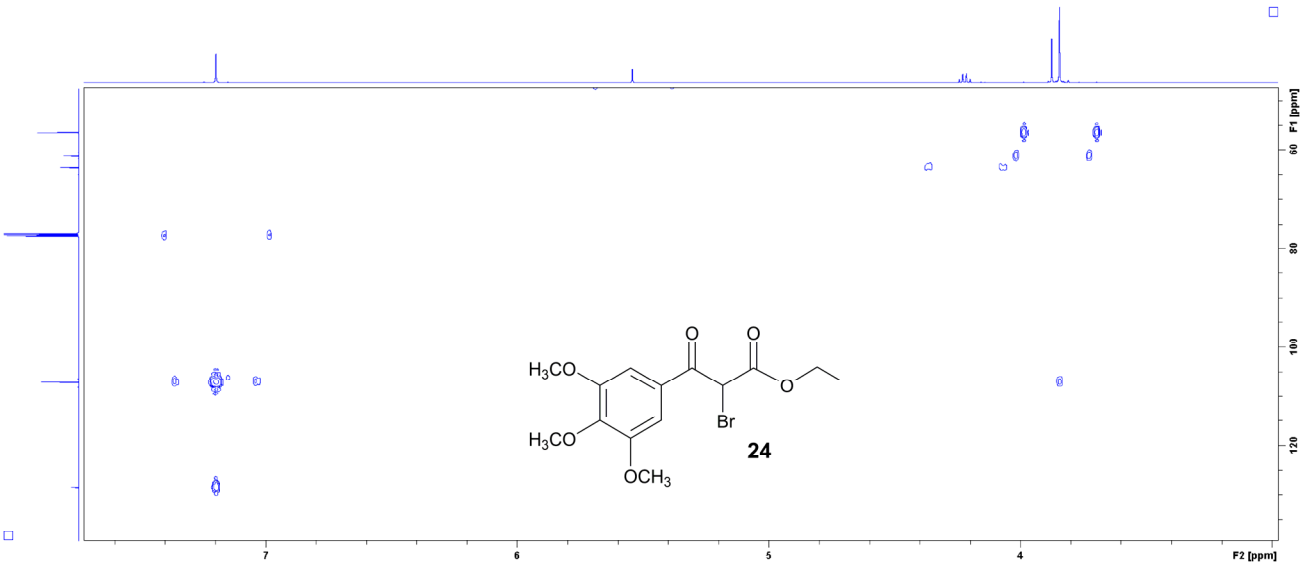
^{1}H NMR spectrum of compound **24**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



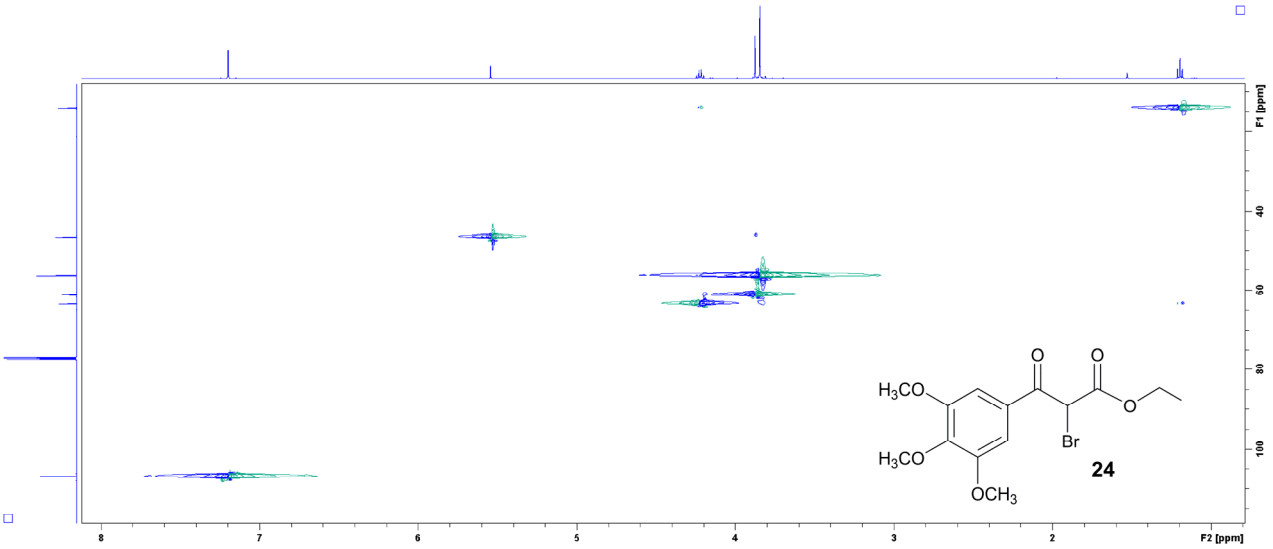
^{13}C NMR spectrum of compound **24**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



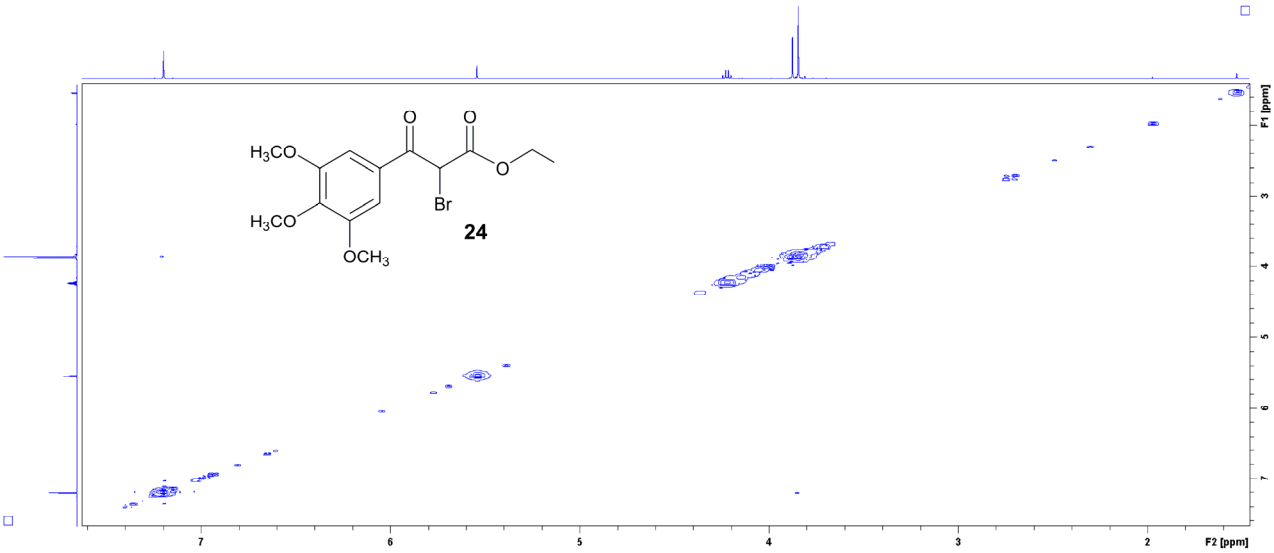
HMBC NMR spectrum of compound **24**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



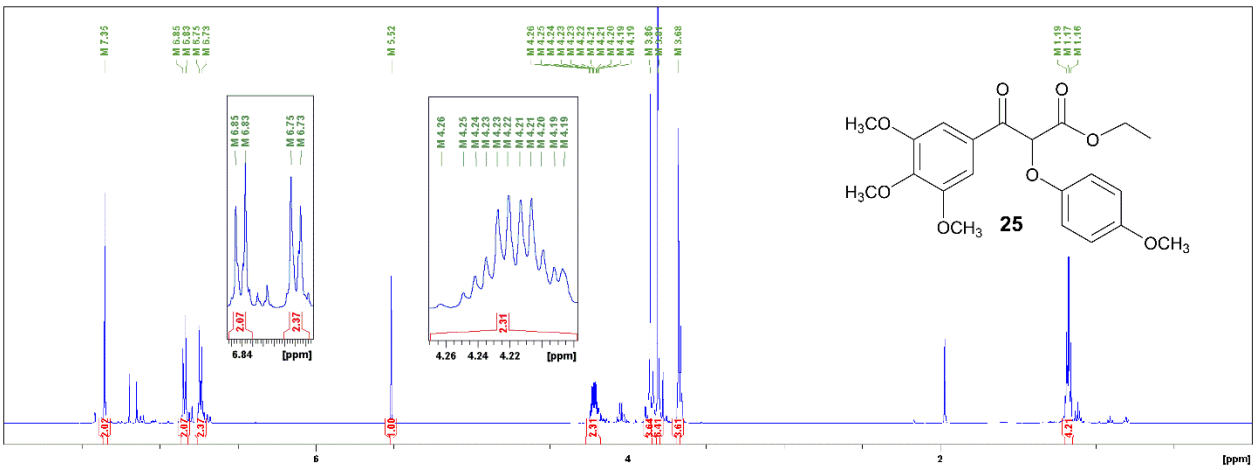
HSQC NMR spectrum of compound **24**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



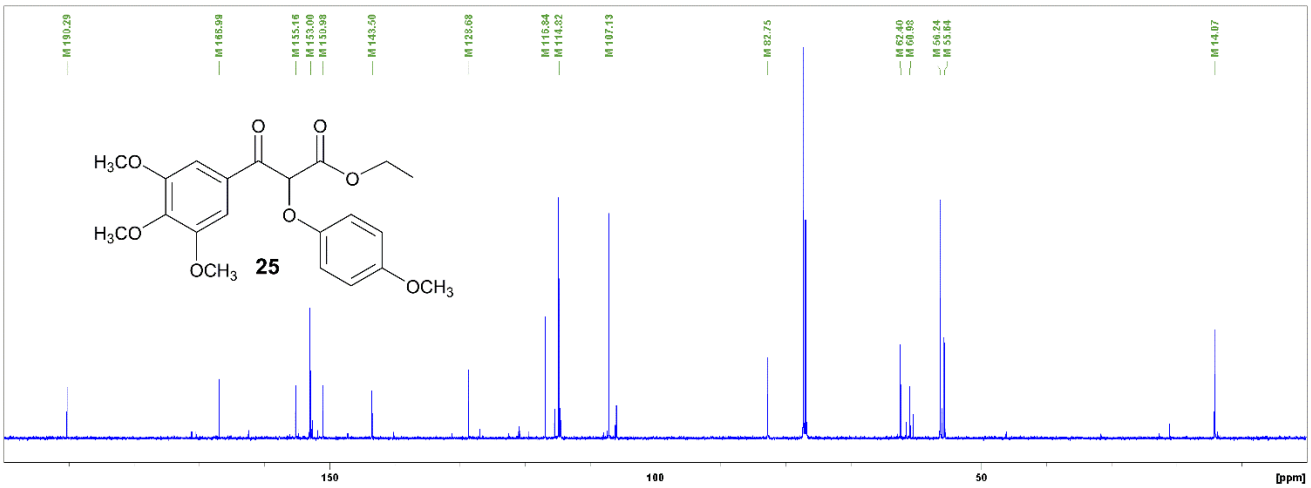
COSY NMR spectrum of compound **24**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



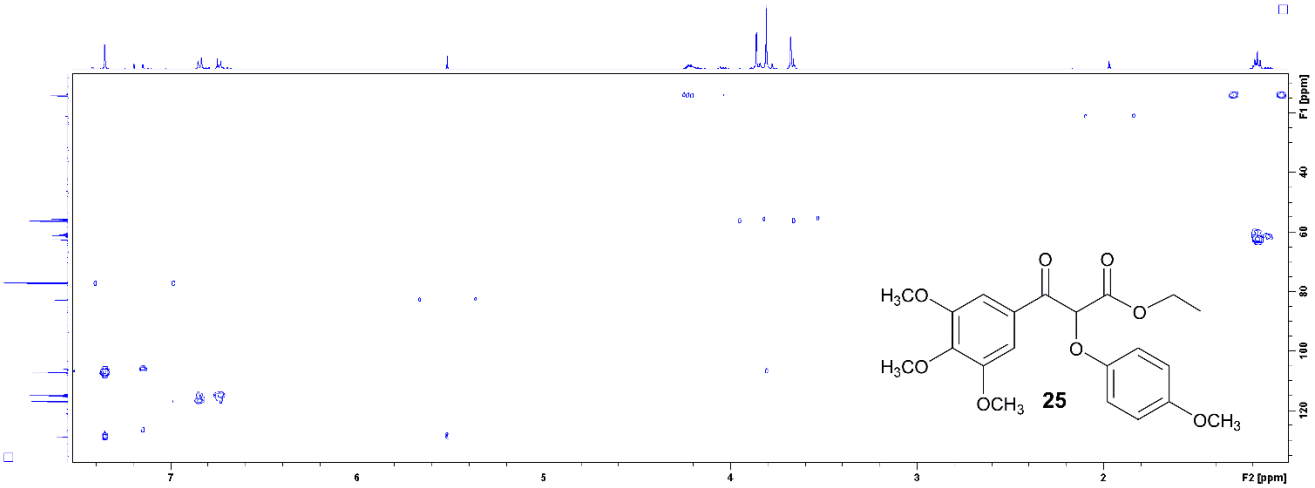
^{1}H NMR spectrum of compound **25**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



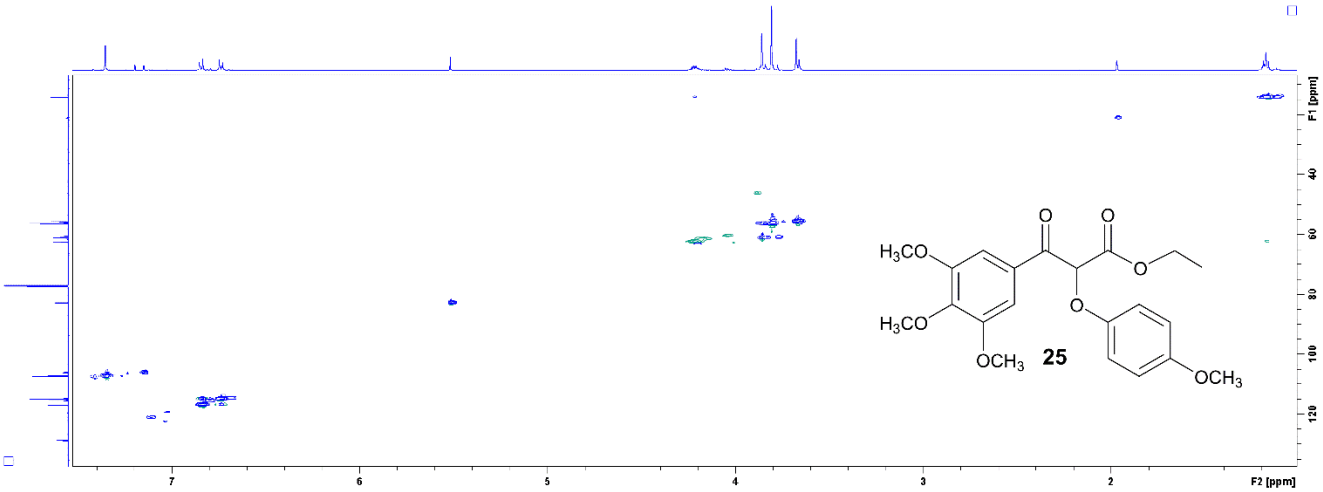
^{13}C NMR spectrum of compound **25**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



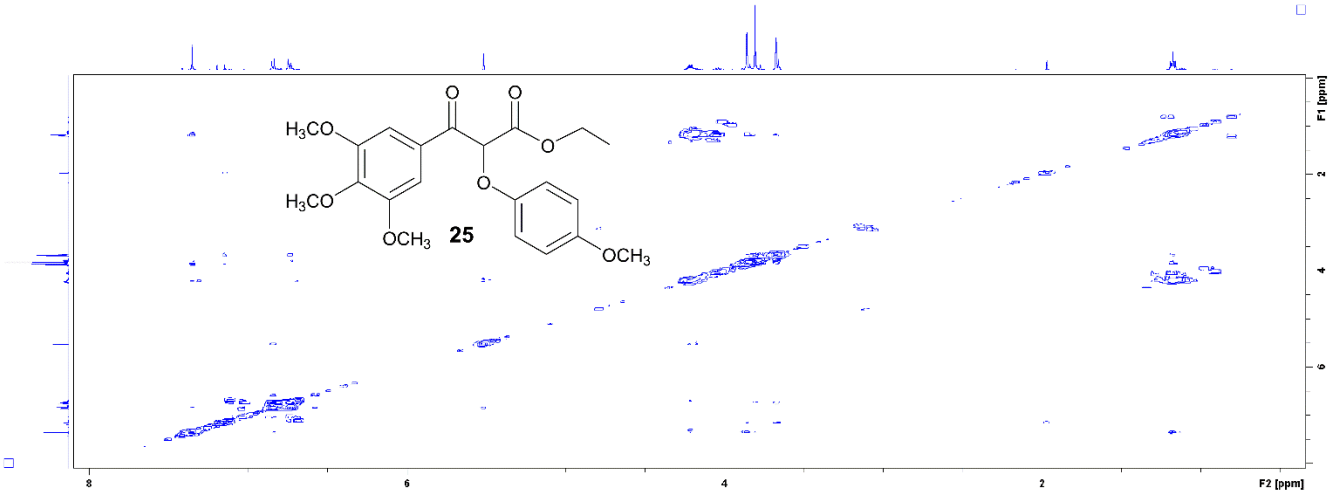
HMBC NMR spectrum of compound **25**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



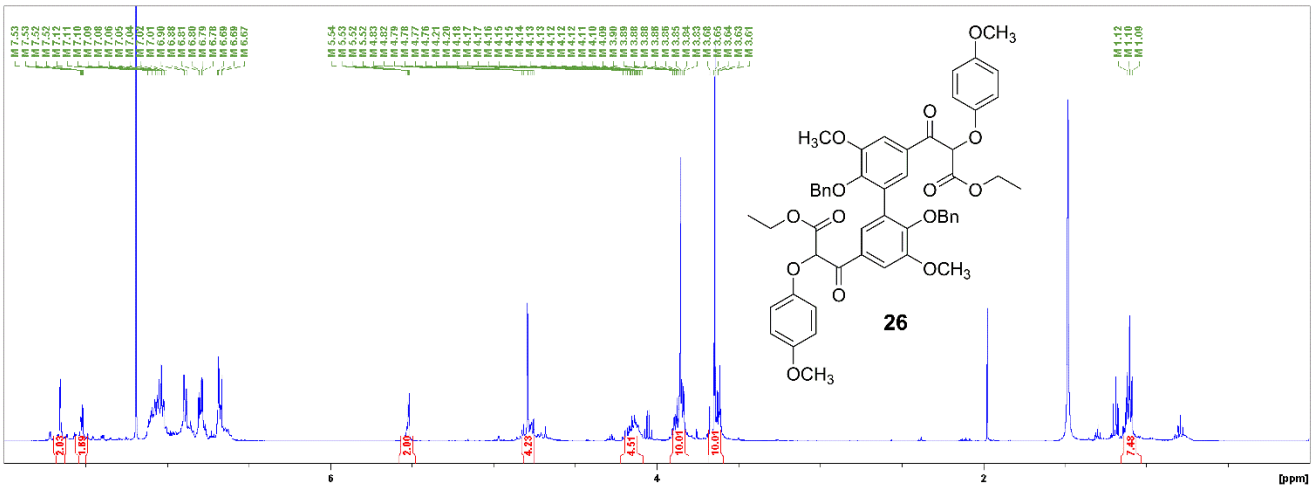
HSQC NMR spectrum of compound **25**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



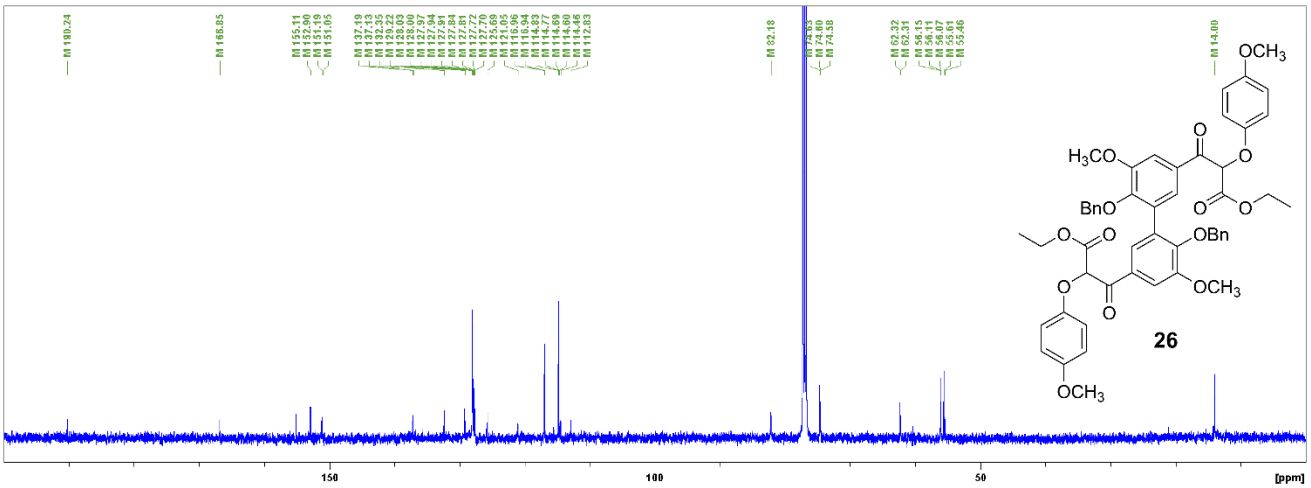
COSY NMR spectrum of compound **25**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



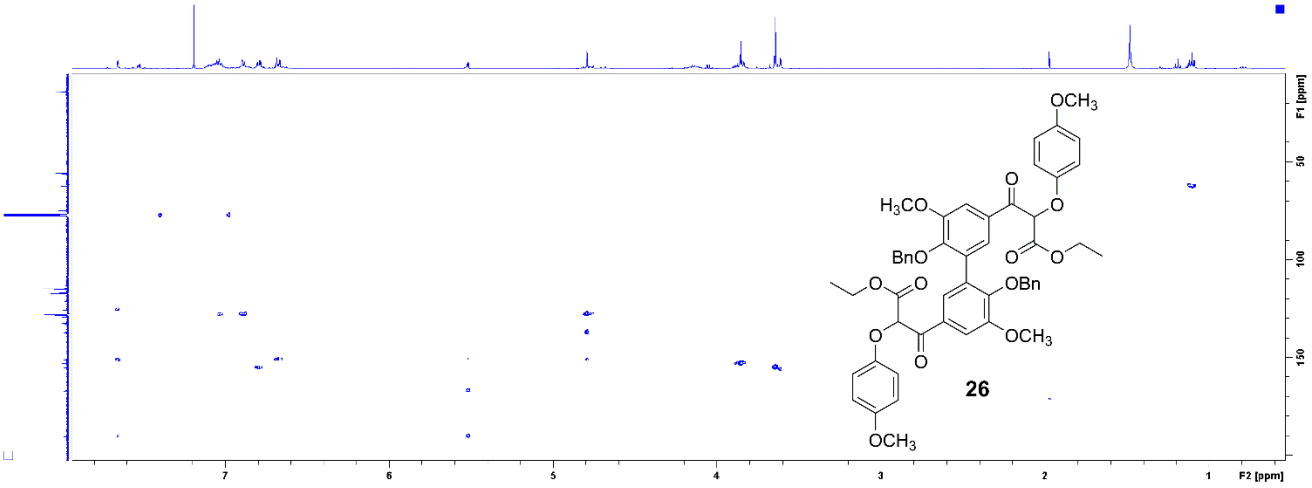
^{1}H NMR spectrum of compound **26**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



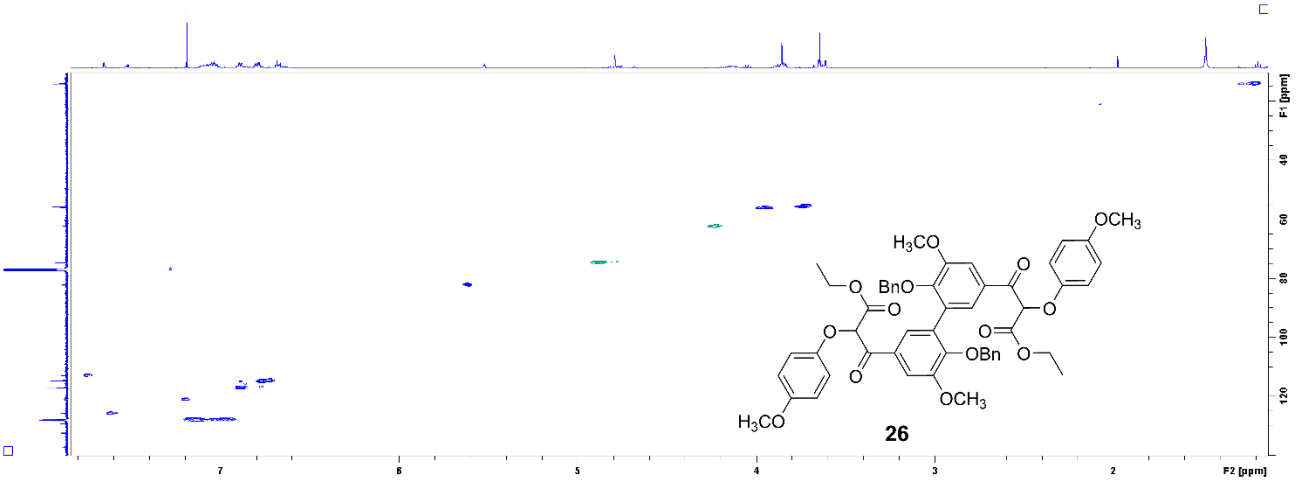
^{13}C NMR spectrum of compound **26**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



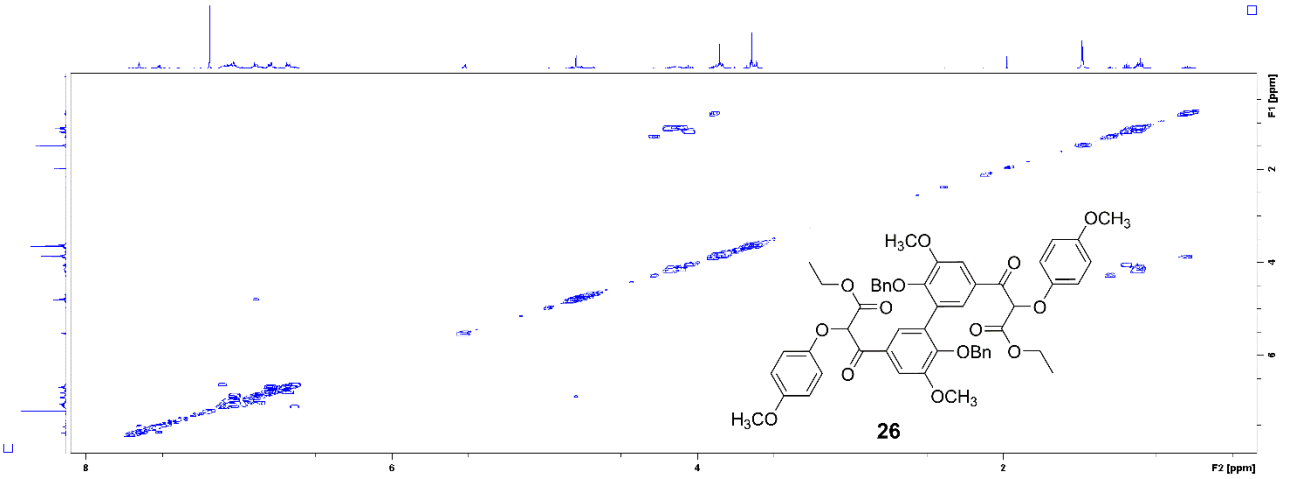
HMBC NMR spectrum of compound **26**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



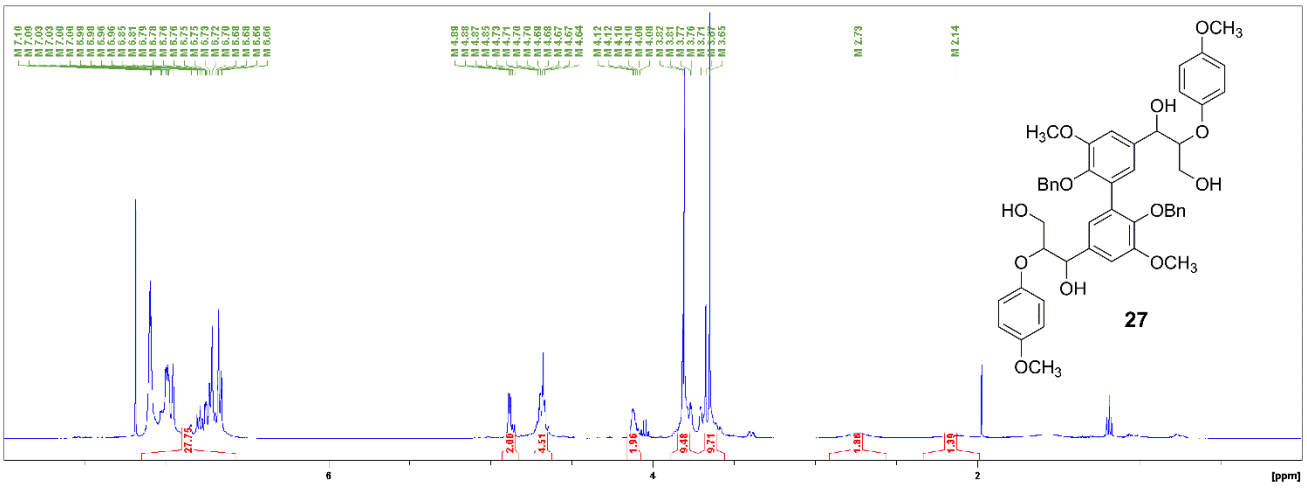
HSQC NMR spectrum of compound **26**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



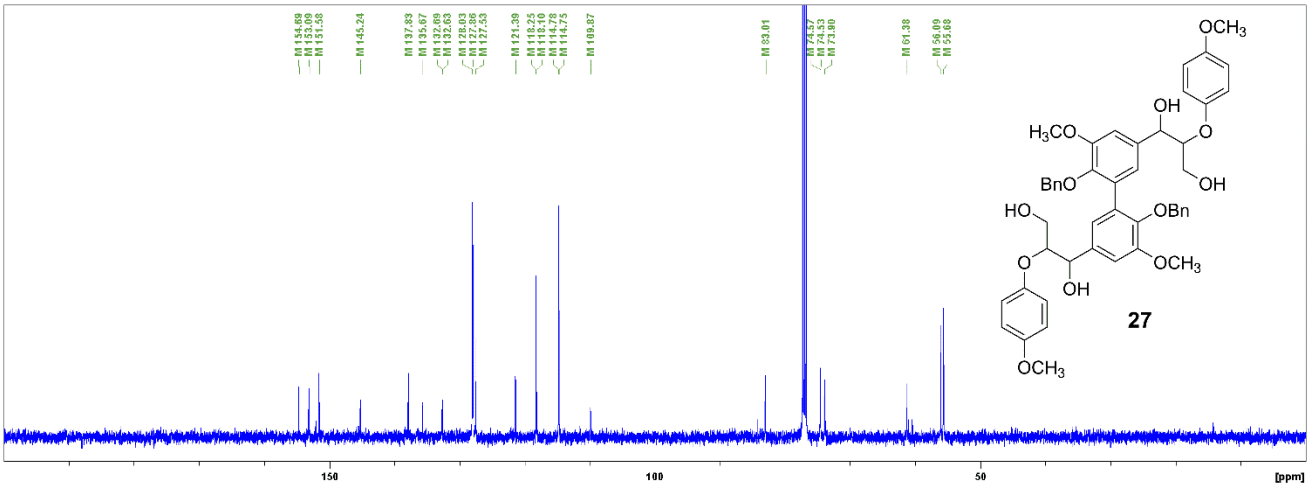
COSY NMR spectrum of compound **26**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



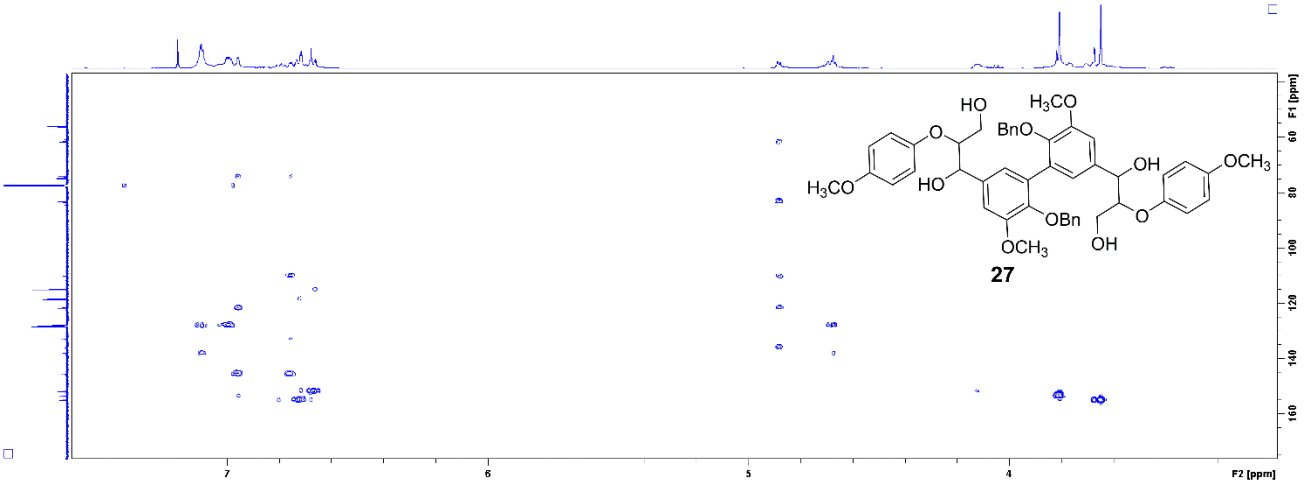
^{1}H NMR spectrum of compound **27**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



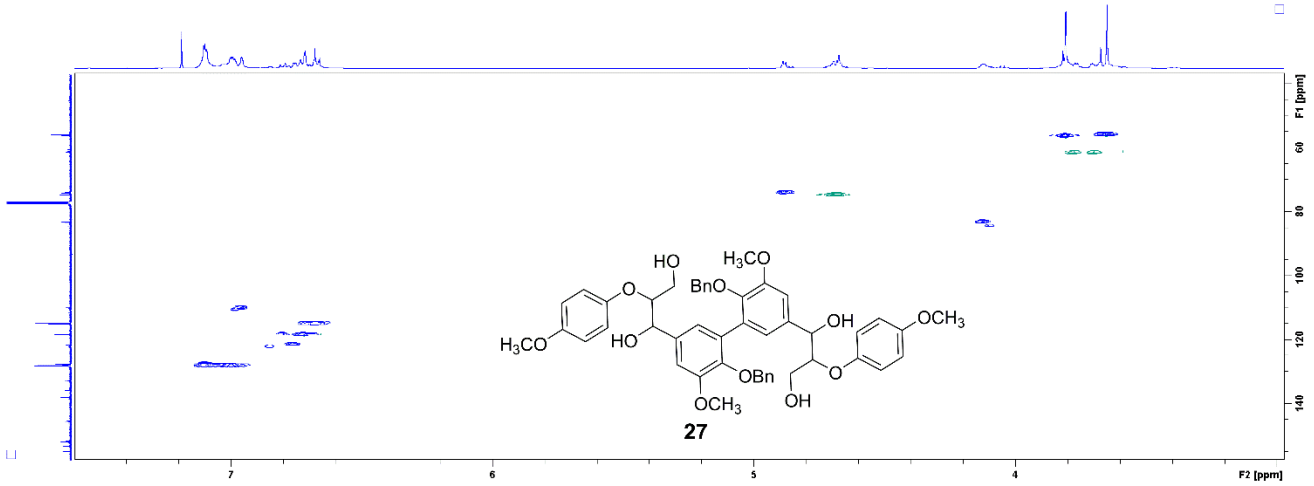
^{13}C NMR spectrum of compound **27**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



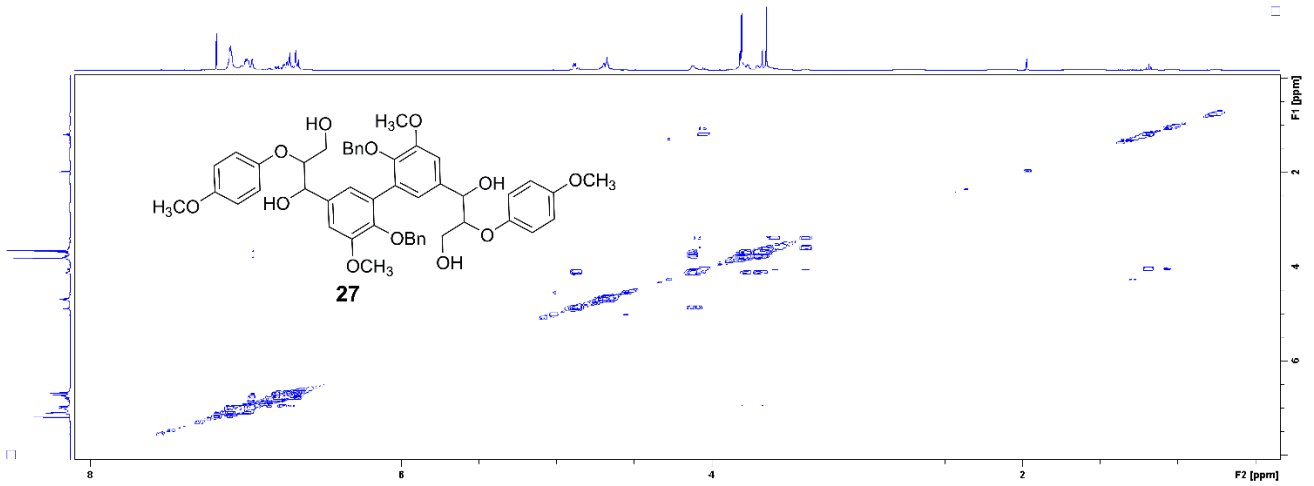
HMBC NMR spectrum of compound **27**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



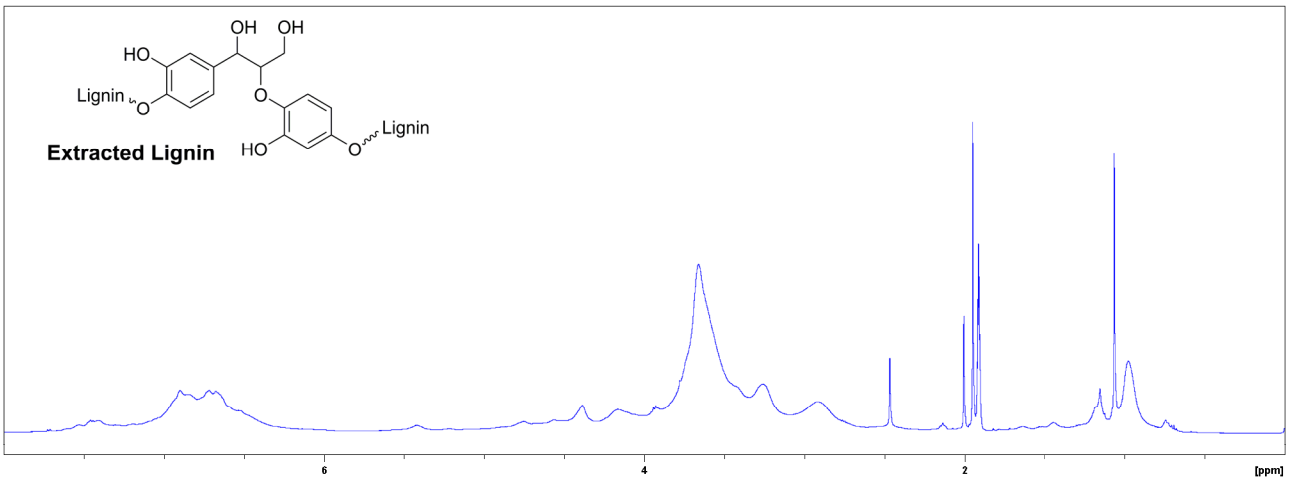
HSQC NMR spectrum of compound **27**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



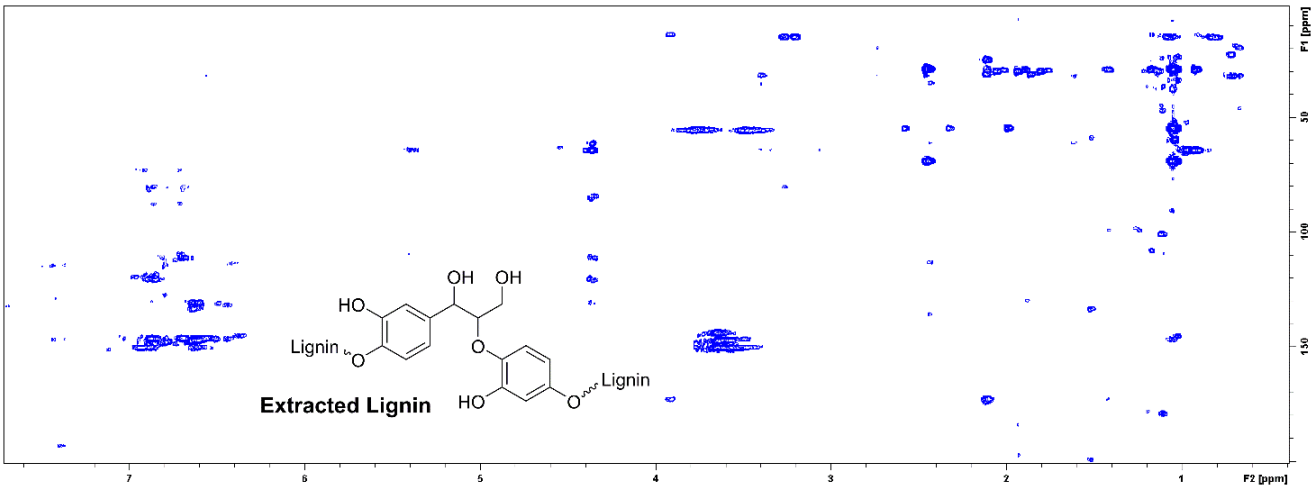
COSY NMR spectrum of compound **27**, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



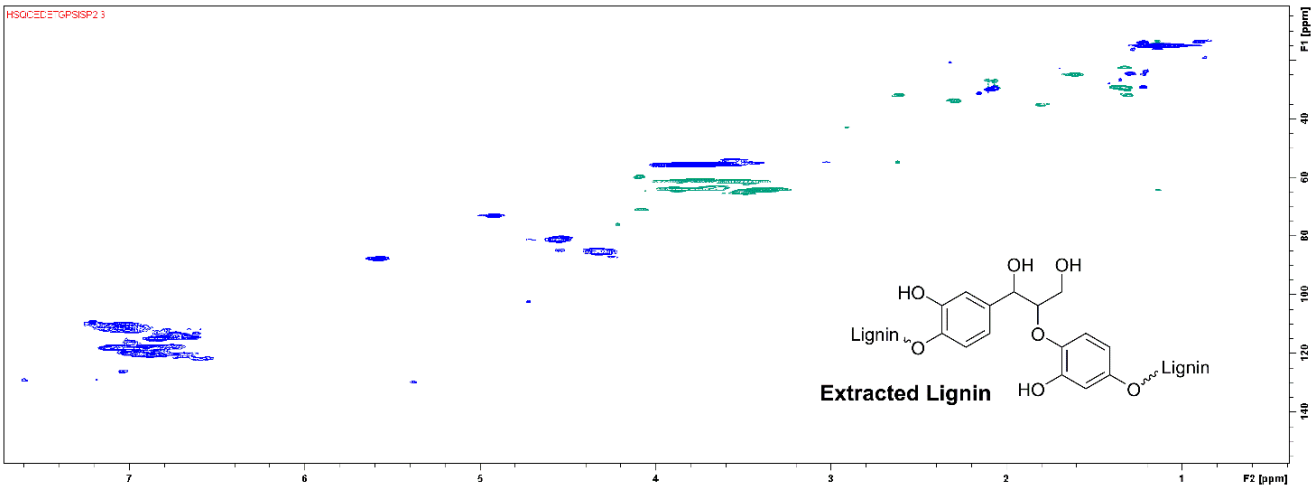
^{1}H NMR spectrum of extracted lignin, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



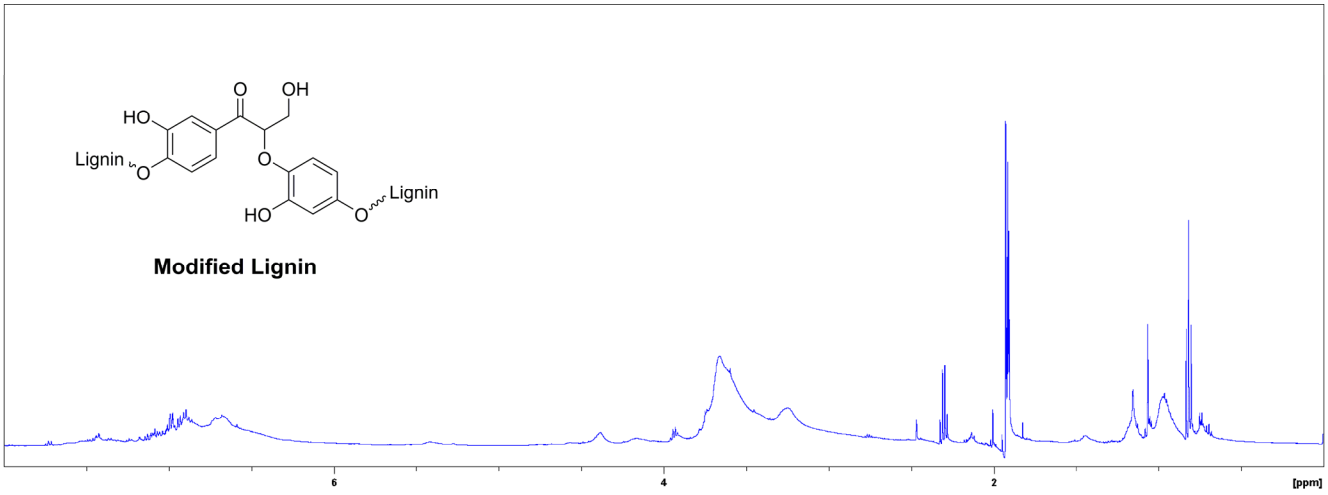
HMBC NMR spectrum of extracted lignin, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



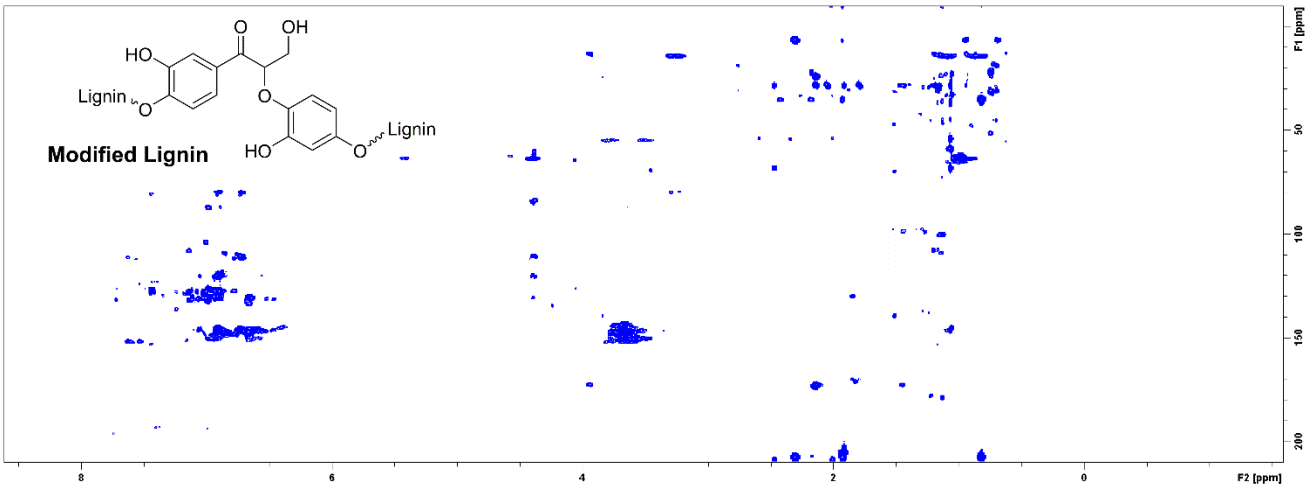
HSQC NMR spectrum of extracted lignin, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



^{1}H NMR spectrum of modified lignin, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



HMBC NMR spectrum of modified lignin, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz



HSQC NMR spectrum of modified lignin, 298K, $CDCl_3$ with 0.05% v/v TMS, 500 MHz