

Supporting Information

Nickel-catalyzed Alkoxy carbonylation of Aryl Iodides with 1 atm CO

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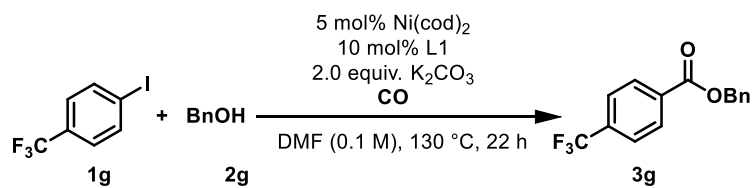
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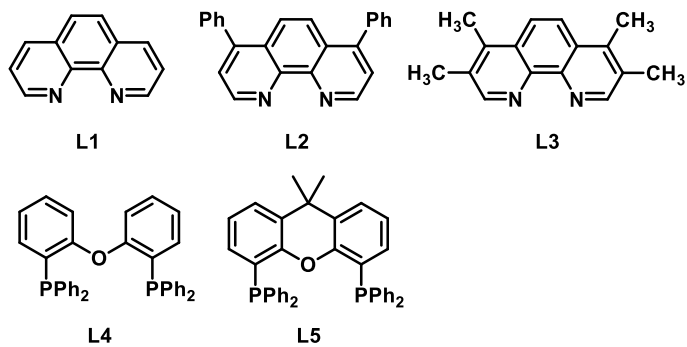
General Information

All catalytic reactions were carried out using oven dried glassware unless otherwise stated. Ni(cod)₂ (CAS 1295-35-8) was purchased from Sinocompound; 1,10-Phenanthroline (CAS 66-71-7) was purchased from 9dingchem; DPEphos(CAS 166330-10-5) was purchased from TCI; K₂CO₃(CAS 584-08-7) was purchased from 9dingchem; Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.20 mm Huanghai silica gel plates (HSGF 254) using UV light as the visualizing agent. All new compounds were characterized by means of GC, ¹H NMR, ¹³C NMR, ¹⁹F NMR and HRMS. GC analysis was performed on Agilent Technologies 7820A GC system. GC runs were performed with the following method: inlet temperature 100 °C; column temperature 100 °C for 1 min, then 50 °C/min to 250 °C, then 250 °C for 6 min. NMR spectra were recorded using a Bruker AVANCE III 400 MHz NMR spectrometer and can be found at the end of the paper. High-resolution mass spectra (HRMS) were recorded on Waters Xevo G2 TOF MS (ESI), JEOL AccuTOF LC-plus 4G (**3d**, **3s**, **3q**) and Agilent Technologies 7250 GCQTOF(**3h**). All ¹H NMR data are reported in δ units, parts per million (ppm), and were calibrated relative to the signals for residual chloroform (7.26 ppm) in deuteriochloroform (CDCl₃). All ¹³C NMR data are reported in ppm relative to CDCl₃ (77.16 ppm). ¹⁹F NMR was recorded on a Bruker AVANCE III 400 NMR spectrometer (CFC₃ as an external standard and low field is positive) and were obtained with ¹H decoupling. The following abbreviations or combinations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet.

Detailed optimization of 4-CF₃C₆H₄I^a

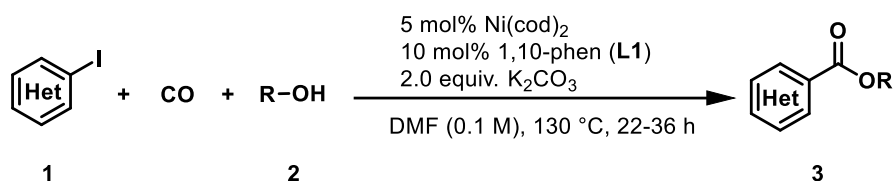


Entry	Ligand	Solvent	3a(%) ^b
1	L1	DMF	10%
2	L2	DMF	14%
3	L3	DMF	6%
4	L4	DMF	62%(57%) ^c
5	L5	DMF	47%
6	L1	DMSO	3%
7	L4	DMSO	-
8	L4	DMA	22%



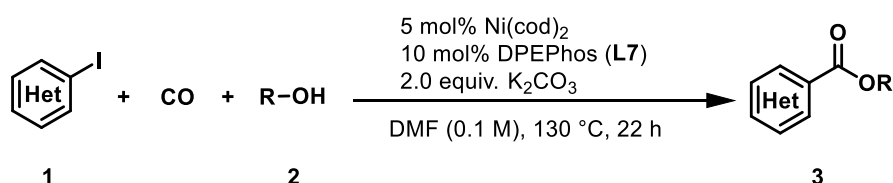
^aReaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), Ni(cod)₂ (0.01 mmol), **L** (0.02 mmol) and **CO** (1 atm) in the indicate solvent (2.0 mL) at 130 °C for 22 h. ^bDetermined by GC analysis with dodecane as the internal standard. ^cIsolated yield.

General Procedure A for Nickel-catalyzed Alkoxy carbonylation Reaction of Aryl Iodides with 1 atm CO:



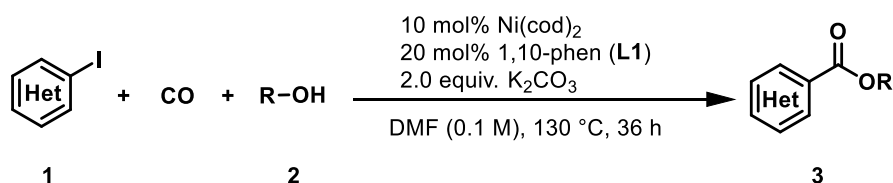
To an oven-dried 30 mL reaction tube, aryl iodide (1.0 equiv. 0.20 mmol), K₂CO₃ (2.0 equiv. 0.40 mmol, 55.3 mg), 1,10-Phenanthroline (10 mol%, 0.02 mmol, 3.6 mg) were added. Then the tube was transferred into glovebox and Ni(cod)₂ (5 mol%, 0.01 mmol, 2.8 mg) was added. The tube was evacuated and backfilled with CO. DMF (2.0 mL) and alcohol (1.5 equiv. 0.30 mmol) were added in sequence. The reaction was stirred at 130 °C for 22 h, then the reaction was quenched with saturated aqueous solution of NH₄Cl. The mixture was extracted with ethyl acetate and washed with water for 3 times respectively. The combined organic layer was dried over Na₂SO₄, filtered and then concentrated under reduced pressure to give the crude residual, which was purified by flash column chromatography (SiO₂) to yield the product 3.

General Procedure B for Nickel-catalyzed Alkoxy carbonylation Reaction of Aryl Iodides with 1 atm CO:



To an oven-dried 30 mL reaction tube, aryl iodide (1.0 equiv. 0.20 mmol), K₂CO₃ (2.0 equiv. 0.40 mmol, 55.3 mg), DPEphos (10 mol%, 0.02 mmol, 10.8 mg) were added. Then the tube was transferred into glovebox and Ni(cod)₂ (5 mol%, 0.01 mmol, 2.8 mg) was added. The tube was evacuated and equipped with a CO balloon. DMF (2.0 mL) and alcohol (1.5 equiv. 0.30 mmol) were added in sequence. The reaction was stirred at 130 °C for 22 h, then the reaction was quenched with saturated aqueous solution of NH₄Cl. The mixture was extracted with ethyl acetate for 3 times, and washed with water for 3 times. The combined organic layer was dried over Na₂SO₄, filtered and then concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO₂) to yield the product 3.

General procedure C for Nickel-catalyzed alkoxy carbonylation reaction of aryl iodides with 1 atm CO:

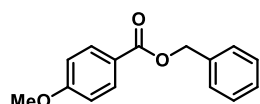


To an oven-dried 30 mL reaction tube, aryl iodide (1.0 equiv. 0.20 mmol), K₂CO₃ (2.0 equiv. 0.40 mmol, 55.3 mg), 1,10-Phenanthroline (20 mol%, 0.04 mmol, 7.2 mg) were added. Then the tube was transferred into glovebox and Ni(cod)₂ (10 mol%, 0.02 mmol, 5.6 mg) was added. The tube was evacuated and equipped with a CO balloon. DMF (2.0 mL) and alcohol (1.5 equiv. 0.30 mmol) were added in sequence. The reaction was

stirred at 130 °C for 36 h, then the reaction was quenched with saturated aqueous solution of NH₄Cl. The mixture was extracted with ethyl acetate for 3 times, and washed with water for 3 times. The combined organic layer was dried over Na₂SO₄, filtered and then concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO₂) to yield the product **3**.

Characterization data of products:

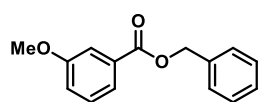
Benzyl 4-methoxybenzoate (**3a**)



General procedure A was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3a** as a light-yellow oil (38.8 mg, 80%). $R_f = 0.30$ (PE/EtOAc = 20/1); **¹H NMR** (400 MHz, CDCl₃): δ 8.06–8.02 (m, 2H), 7.45(d, $J = 7.2$ Hz, 2H), 7.41–7.34 (m, 3H), 6.94–6.90 (m, 2H), 5.34 (s, 2H), 3.86 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 166.3, 163.5, 136.4, 131.9, 128.7, 128.3, 128.2, 122.6, 113.7, 66.5, 55.5;

The spectral data are consistent with those reported in the literature.¹

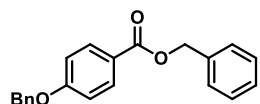
Benzyl 3-methoxybenzoate (**3b**)



General procedure A was followed on 0.2 mmol scale with 36 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3b** as a light-yellow oil (27.1 mg, 56%). $R_f = 0.44$ (PE/EtOAc = 20/1); **¹H NMR** (400 MHz, CDCl₃): δ 7.68 (d, $J = 8.0$ Hz, 1H), 7.60 (dd, $J = 2.8, 1.2$ Hz, 1H), 7.47–7.45 (m, 2H), 7.42–7.33 (m, 4H), 7.11 (dd, $J = 8.4, 2.0$ Hz, 1H), 5.37 (s, 2H), 3.85 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 166.5, 159.7, 136.1, 131.5, 129.5, 128.7, 128.4, 128.3, 122.2, 119.6, 114.3, 66.9, 55.6;

The spectral data are consistent with those reported in the literature.²

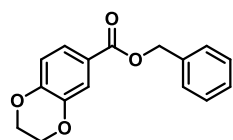
Benzyl 4-(benzyloxy) benzoate (**3c**)



General procedure A was followed on 0.2 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 30/1) afforded **3c** as a white solid (45.1 mg, 71%). $R_f = 0.40$ (PE/EtOAc = 30/1); **¹H NMR** (400 MHz, CDCl₃): δ 8.05 (d, $J = 8.8$ Hz, 2H), 7.47–7.33 (m, 10H), 7.00 (d, $J = 8.8$ Hz, 2H), 5.35 (s, 2H), 5.12 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃): 166.3, 162.7, 136.4, 136.3, 131.9, 128.8, 128.7, 128.3, 128.3, 128.2, 127.6, 122.8, 114.6, 70.2, 66.5;

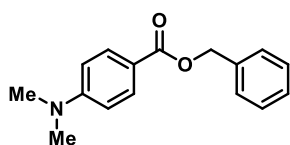
The spectral data are consistent with those reported in the literature.³

Benzyl 2,3-dihydrobenzo [1,4] dioxine-6-carboxylate (**3d**)



General procedure A was followed on 0.2 mmol scale with 36 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3d** as a yellow oil (38.5 mg, 71%). $R_f = 0.32$ (PE/EtOAc = 20/1); **¹H NMR** (400 MHz, CDCl₃): δ 7.61–7.59 (m, 2H), 7.45–7.43 (m, 2H), 7.40–7.32 (m, 3H), 6.90–6.87 (m, 1H), 5.33 (s, 2H), 4.31–4.25 (m, 4H); **¹³C NMR** (100 MHz, CDCl₃): δ 166.0, 148.0, 143.3, 136.3, 128.7, 128.2, 128.2, 123.7, 123.5, 119.2, 117.2, 66.6, 64.7, 64.2; **HRMS (ESI)**: [M+Na]⁺ Calcd for C₁₆H₁₄O₄Na⁺: 293.0784; found: 293.0791.

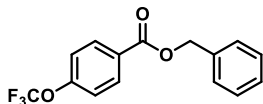
Benzyl 4-(dimethylamino) benzoate (**3e**)



General procedure A was followed on 0.2 mmol scale with 36 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3e** as a white solid (33.4 mg, 65%). $R_f = 0.22$ (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.99-7.95 (m, 2H), 7.47-7.45 (m, 2H), 7.41-7.37 (m, 2H), 7.35-7.31 (m, 1H), 6.67-6.63 (m, 2H), 5.34 (s, 2H), 3.04 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.9, 153.5, 136.9, 131.5, 128.6, 128.1, 128.0, 116.9, 110.8, 66.0, 40.1;

The spectral data are consistent with those reported in the literature.⁴

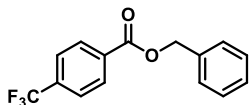
Benzyl 4-(trifluoromethoxy) benzoate (**3f**)



General procedure B was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3f** as a light-yellow oil (37.0 mg, 63%). $R_f = 0.56$ (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.11 (d, $J = 8.4$ Hz, 2H), 7.44-7.34 (m, 5H), 7.25 (d, $J = 8.0$ Hz, 2H), 5.36 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 165.4, 152.8 (q, $J_{\text{C-F}} = 1.4$ Hz), 135.9, 131.8, 128.8, 128.6, 128.5, 128.4, 120.4, 120.4 (q, $J_{\text{C-F}} = 257.2$ Hz), 67.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -57.6.

The spectral data are consistent with those reported in the literature.⁵

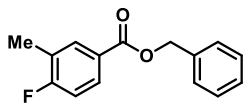
Benzyl 4-(trifluoromethyl) benzoate (**3g**)



General procedure B was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3g** as a yellow oil (32.1 mg, 57%). $R_f = 0.67$ (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.19 (d, $J = 8.0$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H), 7.47-7.35 (m, 5H), 5.40 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 165.4, 135.7, 134.7 (q, $J_{\text{C-F}} = 32.6$ Hz), 133.5, 130.3, 128.8, 128.6, 128.5, 125.6 (q, $J_{\text{C-F}} = 3.7$ Hz), 123.8 (q, $J_{\text{C-F}} = 271.4$ Hz), 67.4. $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -63.1.

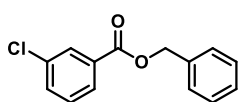
The spectral data are consistent with those reported in the literature.¹

Benzyl 4-fluoro-3-methylbenzoate (**3h**)



General procedure B was followed on 0.2 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 50/1) afforded **3h** as a colorless oil (28.8 mg, 59%). $R_f = 0.66$ (PE/EtOAc = 50/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.95-7.90 (m, 2H), 7.46-7.34 (m, 5H), 7.04 (t, $J = 8.8$ Hz, 1H), 5.35 (s, 2H), 2.31 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 165.9, 164.5 (d, $J_{\text{C-F}} = 251.0$ Hz), 136.1, 133.5 (d, $J_{\text{C-F}} = 6.4$ Hz), 129.7 (d, $J_{\text{C-F}} = 9.4$ Hz), 128.8, 128.4, 128.4, 126.1 (d, $J_{\text{C-F}} = 3.3$ Hz), 125.3 (d, $J_{\text{C-F}} = 18.0$ Hz), 115.3 (d, $J_{\text{C-F}} = 23.1$ Hz), 66.9, 14.6 (d, $J_{\text{C-F}} = 3.5$ Hz). $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -109.8. **HRMS (EI)**: Calcd for $\text{C}_{15}\text{H}_{13}\text{FO}_2$: 244.0894; found: 244.0889.

Benzyl 3-chlorobenzoate (**3i**)

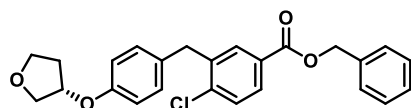


General procedure B was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 50/1~20/1) afforded **3i** as a light-yellow oil (28.8 mg, 59%). $R_f = 0.7$ (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3):

δ 8.05 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.46–7.34 (m, 6H), 5.37 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.4, 135.8, 134.7, 133.2, 132.0, 129.9, 129.9, 128.8, 128.6, 128.4, 128.0, 67.2.

The spectral data are consistent with those reported in the literature.²

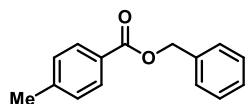
Benzyl (S)-4-chloro-3-((tetrahydrofuran-3-yl) oxy) benzyl benzoate (3j)



General procedure B was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1~5/1) afforded **3j** as a yellow oil (61.6 mg, 73%). R_f = 0.39 (PE/EtOAc = 5/1); ^1H NMR (400 MHz, CDCl_3): δ 7.89 (d, J = 2.0 Hz,

1H), 7.86 (dd, J = 8.4, 2.4 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.40–7.34 (m, 5H), 7.09 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 5.33 (s, 2H), 4.90–4.86 (m, 1H), 4.07 (s, 2H), 4.00–3.94 (m, 3H), 3.89 (td, J = 8.0, 4.8 Hz, 1H), 2.23–2.11 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.8, 156.1, 139.5, 135.9, 132.3, 131.2, 130.1, 129.9, 128.9, 128.7, 128.7, 128.4, 128.3, 127.1, 115.5, 77.4, 73.2, 67.3, 67.0, 38.4, 33.1 HRMS (ESI): $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{23}\text{ClO}_4\text{Na}^+$: 445.1177; found: 445.1168.

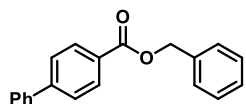
Benzyl 4-methylbenzoate (3k)



General procedure A was followed on 0.2 mmol scale with 36 h and purification by flash column chromatography on silica gel (PE/EtOAc = 50/1~30/1) afforded **3k** as a light-yellow oil (31.6 mg, 70%). R_f = 0.57 (PE/EtOAc = 30/1); ^1H NMR (400 MHz, CDCl_3): δ 7.98 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 7.2 Hz, 2H), 7.41–7.33 (m, 3H), 7.24 (d, J = 8.4 Hz, 2H), 5.36 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.7, 143.9, 136.3, 129.9, 129.2, 128.7, 128.3, 128.3, 127.5, 66.5, 21.8.

The spectral data are consistent with those reported in the literature.¹

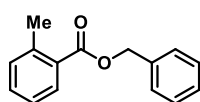
Benzyl (1,1'-biphenyl)-4-carboxylate (3l)



General procedure A was followed on 0.2 mmol scale with 36 h and purification by flash column chromatography on silica gel (PE/EtOAc = 30/1~20/1) afforded **3l** as a white solid (34.9 mg, 61%). R_f = 0.56 (PE/EtOAc = 20/1); ^1H NMR (400 MHz, CDCl_3): δ 8.15 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.49–7.45 (m, 4H), 7.43–7.34 (m, 4H), 5.40 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): 166.5, 145.9, 140.1, 136.2, 130.4, 129.1, 129.0, 128.7, 128.4, 128.3, 128.3, 127.4, 127.2, 66.8.

The spectral data are consistent with those reported in the literature.⁶

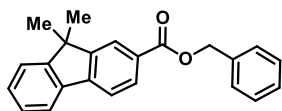
Benzyl 2-methylbenzoate (3m)



General procedure C was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 50/1~20/1) afforded **3m** as a light-yellow solid (24.5 mg, 54%). R_f = 0.66 (PE/EtOAc = 20/1); ^1H NMR (400 MHz, CDCl_3): δ 7.96 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 2H), 7.41–7.32 (m, 4H), 7.24 (t, J = 7.6 Hz, 2H), 5.35 (s, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.5, 140.5, 136.3, 132.2, 131.8, 130.8, 129.6, 128.7, 128.3, 125.9, 66.6, 21.9.

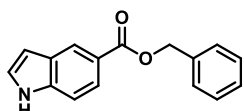
The spectral data are consistent with those reported in the literature.¹

Benzyl 9,9-dimethyl-9H-fluorene-2-carboxylate (3n)



General procedure B was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3n** as a light-yellow oil (44.1 mg, 67%). R_f = 0.48 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.16 (s, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.80–7.76 (m, 2H), 7.51–7.47 (m, 3H), 7.44–7.35 (m, 5H), 5.42 (s, 2H), 1.52 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.9, 154.8, 153.7, 144.2, 138.1, 136.4, 129.3, 128.8, 128.7, 128.6, 128.4, 128.4, 127.3, 124.2, 122.9, 121.0, 119.8, 66.8, 47.1, 27.0; **HRMS (ESI)**: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_2\text{Na}^+$: 351.1356; found: 351.1346.

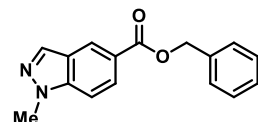
Benzyl 1H-indole-5-carboxylate (**3o**)



General procedure A was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 10/1~5/1) afforded **3o** as a yellow solid (30.8 mg, 61%). R_f = 0.53 (PE/EtOAc = 5/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.46 (s, 2H), 7.95 (dd, J = 8.8, 1.6 Hz, 1H), 7.48 (d, J = 7.2 Hz, 2H), 7.41–7.38 (m, 3H), 7.36–7.32 (m, 1H), 7.25 (s, 1H), 6.64 (s, 1H), 5.40 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 167.7, 138.6, 136.7, 128.7, 128.2, 127.6, 126.1, 125.7, 124.1, 123.7, 122.0, 110.9, 104.1, 66.5;

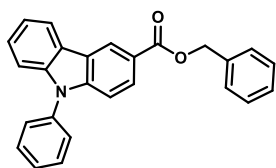
The spectral data are consistent with those reported in the literature.⁷

Benzyl 1-methyl-1H-indazole-5-carboxylate (**3p**)



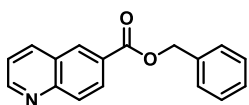
General procedure A was followed on 0.2 mmol scale with 36 h and purification by flash column chromatography on silica gel (PE/EtOAc = 5/1) afforded **3p** as a white solid (43.7 mg, 82%). R_f = 0.46 (PE/EtOAc = 5/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.55 (s, 1H), 8.10 (dd, J = 8.8, 1.2 Hz, 1H), 8.08 (s, 1H), 7.48 (d, J = 6.8 Hz, 2H), 7.43–7.36 (m, 4H), 5.40 (s, 2H), 4.10 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.8, 141.7, 136.3, 134.7, 128.7, 128.4, 128.3, 127.3, 124.9, 123.8, 122.8, 108.8, 66.8, 35.8; **HRMS (ESI)**: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}_2^+$: 267.1128; found: 267.1120.

Benzyl 9-phenyl-9H-carbazole-2-carboxylate (**3q**)



General procedure A was followed on 0.2 mmol scale with 36 h and purification by flash column chromatography on silica gel (PE/EtOAc = 30/1~20/1) afforded **3q** as a yellow gel-like oil (56.2mg, 75%). R_f = 0.50 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.92 (d, J = 1.2 Hz, 1H), 8.20 (d, J = 7.6 Hz, 1H), 8.17 (dd, J = 8.4, 1.6 Hz, 1H), 7.65–7.62 (m, 2H), 7.67–7.45 (m, 5H), 7.48–7.33 (m, 7H), 5.46 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 167.3, 143.7, 141.8, 137.1, 136.6, 130.2, 128.7, 128.3, 128.3, 128.2, 127.8, 127.3, 126.8, 123.4, 123.3, 123.1, 121.8, 121.0, 120.8, 110.3, 109.5, 66.7; **HRMS (ESI)**: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{19}\text{NO}_2\text{Na}^+$: 400.1308; found: 400.1313.

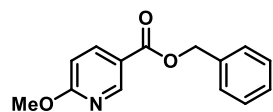
Benzyl quinoline-6-carboxylate (**3r**)



General procedure B was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 5/1) afforded **3r** as a yellow oil (28.9 mg, 55%). R_f = 0.26 (PE/EtOAc = 5/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.00 (s, 1H), 8.62 (s, 1H), 8.34 (dd, J = 8.8, 1.6 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.51–7.35 (m, 6H), 5.44 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.1, 152.7, 150.2, 137.5, 135.9, 131.3, 130.4, 129.9, 129.1, 128.8, 128.6, 128.5, 128.2, 122.0, 67.3;

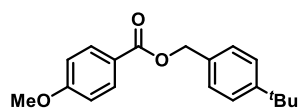
The spectral data are consistent with those reported in the literature.⁸

Benzyl 6-methoxynicotinate(3s)



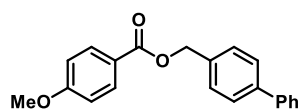
General procedure C was followed on 0.2 mmol scale with 36 h and purification by flash column chromatography on silica gel (PE/EtOAc = 30/1~20/1) afforded **3s** as a light-yellow solid (25.7 mg, 53%). $R_f = 0.41$ (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.89 (d, $J = 2.4$ Hz, 1H), 8.17 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.45–7.33 (m, 5H), 6.76 (d, $J = 8.8$ Hz, 1H), 5.36 (s, 2H), 4.00 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 167.0, 165.4, 150.4, 139.7, 136.0, 128.8, 128.5, 128.3, 119.7, 110.8, 66.7, 54.2; **HRMS (ESI)**: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_3^+$: 244.0968; found: 244.0968.

4-(Tert-butyl) benzyl 4-methoxybenzoate (3t)



General procedure A was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3t** as a yellow oil (37.8 mg, 63%). $R_f = 0.40$ (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.05–8.02 (m, 2H), 7.43–7.37 (m, 4H), 6.93–6.89 (m, 2H), 5.31 (s, 2H), 3.86 (s, 3H), 1.33 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.4, 163.5, 151.3, 133.4, 131.9, 128.2, 125.6, 122.8, 113.7, 66.4, 55.6, 34.7, 31.5; **HRMS (ESI)**: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_3\text{Na}^+$: 321.1461; found: 321.1453.

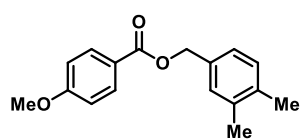
[1,1'-Biphenyl]-4-ylmethyl 4-methoxybenzoate (3u)



General procedure A was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3u** as a brown solid (46.6 mg, 73%). $R_f = 0.38$ (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.07–8.04 (m, 2H), 7.62–7.59 (m, 4H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.38–7.34 (m, 1H), 6.94–6.91 (m, 2H), 5.38 (s, 2H), 3.86 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.4, 163.6, 141.2, 140.8, 135.4, 131.9, 128.9, 128.7, 127.5, 127.4, 127.3, 122.6, 113.8, 66.3, 55.5.

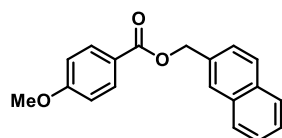
The spectral data are consistent with those reported in the literature.⁹

3,4-Dimethylbenzyl 4-methoxybenzoate (3v)



General procedure A was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3v** as a yellow oil (40.5 mg, 75%). $R_f = 0.54$ (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.02 (d, $J = 8.8$ Hz, 2H), 7.21 (s, 1H), 7.19 (d, $J = 8.4$ Hz, 1H), 7.15 (d, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 8.8$ Hz, 2H), 5.27 (s, 2H), 3.85 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.4, 163.5, 136.9, 136.8, 133.8, 131.9, 129.9, 129.8, 126.0, 122.8, 113.7, 66.6, 55.6, 19.9, 19.7; **HRMS (ESI)**: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{Na}^+$: 293.1148; found: 293.1140.

Naphthalen-2-ylmethyl 4-methoxybenzoate (3w)

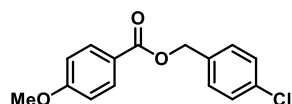


General procedure A was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3w** as a light-yellow solid (39.0 mg, 67%). $R_f = 0.38$ (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.08–8.06 (m, 2H), 7.91 (s, 1H), 7.89–7.85 (m, 3H), 7.56 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.53–7.48 (m, 2H); 6.94–6.91 (m, 2H); 5.51 (s, 2H); 3.85 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3):

δ 166.4, 163.6, 133.9, 133.4, 133.2, 131.9, 128.5, 128.1, 127.9, 127.4, 126.4, 126.4, 126.0, 122.7, 113.8, 66.7, 55.6.

The spectral data are consistent with those reported in the literature.¹⁰

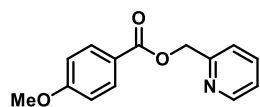
4-Chlorobenzyl 4-methoxybenzoate (**3x**)



General procedure A was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 30/1~20/1) afforded **3x** as a white solid (32.9 mg, 60%). R_f = 0.32 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.04–8.00 (m, 2H), 7.39–7.34 (m, 4H), 6.94–6.90 (m, 2H), 5.30 (s, 2H), 3.86 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.2, 163.7, 134.9, 134.1, 131.9, 129.6, 128.9, 122.4, 113.8, 65.7, 55.6;

The spectral data are consistent with those reported in the literature.¹¹

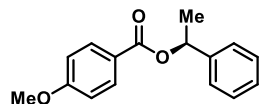
Pyridin-2-ylmethyl 4-methoxybenzoate (**3y**)



General procedure C was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 10/1~5/1) afforded **3y** as a light-yellow solid (39.0 mg, 80%). R_f = 0.29 (PE/EtOAc = 5/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.61 (d, J = 4.4 Hz, 1H), 8.09–8.06 (m, 2H), 7.71 (td, J = 7.6, 1.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.24 (dd, J = 7.2, 2.0 Hz, 1H), 6.95–6.92 (m, 2H), 5.46 (s, 2H), 3.87 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.1, 163.7, 156.4, 149.5, 136.9, 132.0, 122.9, 122.3, 121.8, 113.8, 67.0, 55.5;

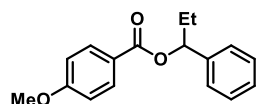
The spectral data are consistent with those reported in the literature.¹²

(*R*)-1-Phenylethyl 4-methoxybenzoate (**3z**)



General procedure A was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3z** as a yellow oil (36.5 mg, 71%). R_f = 0.31 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.06–8.02 (m, 2H), 7.45–7.43 (m, 2H), 7.39–7.35 (m, 2H), 7.31–7.27 (m, 1H), 6.94–6.90 (m, 2H), 6.11 (q, J = 6.4 Hz, 1H), 3.86 (s, 3H), 1.66 (d, J = 6.8 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 165.7, 163.5, 142.2, 131.8, 128.7, 127.9, 126.2, 123.1, 113.7, 72.7, 55.6, 22.6; **HRMS (ESI)**: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{Na}^+$: 279.0992; found: 279.0984.

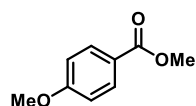
1-Phenylpropyl 4-methoxybenzoate (**3aa**)



General procedure A was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 50/1~30/1) afforded **3aa** as a yellow oil (26.0 mg, 48%). R_f = 0.68 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.07–8.03 (m, 2H), 7.42–7.40 (m, 2H), 7.37–7.33 (m, 2H), 7.30–7.26 (m, 1H), 6.94–6.91 (m, 2H), 5.89 (t, J = 6.8 Hz, 1H), 3.86 (s, 3H), 2.11–2.01 (m, 1H), 1.99–1.89 (m, 1H), 0.96 (t, J = 6.8 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 165.8, 163.5, 141.0, 131.8, 128.5, 127.9, 126.6, 123.1, 113.7, 77.6, 55.6, 29.8, 10.1;

The spectral data are consistent with those reported in the literature.¹³

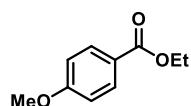
Methyl 4-methoxybenzoate (**3ab**)



General procedure A was followed on 0.2 mmol scale with 36 h by using 20 equivalents of methanol as nucleophile and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3ab** as a white solid (19.8 mg, 60%). R_f = 0.53 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.00–7.98 (m, 2H), 6.94–6.90 (m, 2H), 3.89 (s, 3H), 3.86 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 167.0, 163.5, 131.7, 122.7, 113.7, 55.5, 52.0;

The spectral data are consistent with those reported in the literature.⁹

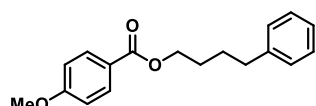
Ethyl 4-methoxybenzoate (**3ac**)



General procedure A was followed on 0.2 mmol scale with 36 h by using 20 equivalents of ethanol as nucleophile and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3ac** as a colorless liquid (28.7 mg, 80%). R_f = 0.43 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.01–7.98 (m, 2H), 6.93–6.89 (m, 2H), 4.34 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.5, 163.4, 131.7, 123.1, 113.7, 60.8, 55.5, 14.5.

The spectral data are consistent with those reported in the literature.¹⁴

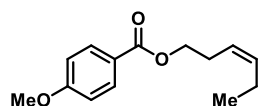
4-Phenylbutyl 4-methoxybenzoate (**3ad**)



General procedure A was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 30/1~20/1) afforded **3ad** as a light-yellow oil (32.6 mg, 57%). R_f = 0.35 (PE/EtOAc = 20/1);

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.01–7.97 (m, 2H), 7.31–7.27 (m, 2H), 7.21–7.17 (m, 3H), 6.93–6.90 (m, 2H), 4.31 (t, J = 5.6 Hz, 2H), 3.86 (s, 3H), 2.69 (t, J = 2.8 Hz, 2H), 1.79 (quin, J = 3.2 Hz, 4H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.6, 163.4, 142.2, 131.7, 128.5, 128.5, 126.0, 123.0, 113.7, 64.7, 55.5, 35.6, 28.5, 28.0. **HRMS (ESI)**: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_3\text{Na}^+$: 307.1305; found: 307.1296.

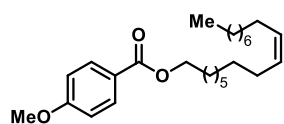
(Z)-Hex-3-en-1-yl 4-methoxybenzoate (**3ae**)



General procedure A was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3ae** as a light-yellow oil (30.7 mg, 66%). R_f = 0.53 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.01–7.97 (m, 2H), 6.93–6.89 (m, 2H), 5.56–5.49 (m, 1H), 5.44–5.36 (m, 1H), 4.28 (t, J = 7.2 Hz, 2H), 3.85 (s, 3H), 2.50 (q, J = 6.8 Hz, 2H), 2.09 (quin, J = 7.2 Hz, 2H), 0.97 (t, J = 7.2 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.5, 163.4, 134.7, 131.7, 124.0, 122.9, 113.7, 64.3, 55.5, 27.0, 20.8, 14.4;

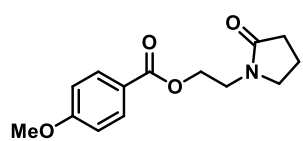
The spectral data are consistent with those reported in the literature.¹⁵

(Z)-Octadec-9-en-1-yl 4-methoxybenzoate (**3af**)



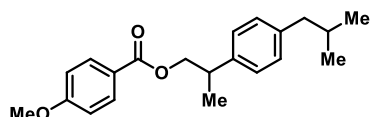
General procedure A was followed on 0.2 mmol scale with 36 h and purification by flash column chromatography on silica gel (PE/EtOAc = 100/1~50/1) afforded **3af** as a yellow oil (43.7 mg, 53%). R_f = 0.32 (PE/EtOAc = 50/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.01–7.98 (m, 2H), 6.93–6.90 (m, 2H), 5.36–5.33 (m, 2H), 4.28 (t, J = 6.4 Hz, 2H), 3.86 (s, 3H), 2.01 (q, J = 6.0 Hz, 2H), 1.75 (quin, J = 7.2 Hz, 2H), 1.47–1.26 (m, 24H), 0.88 (t, J = 7.2 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.6, 163.4, 131.7, 130.1, 130.0, 123.3, 123.1, 113.7, 65.0, 55.5, 32.0, 29.9, 29.9, 29.7, 29.6, 29.5, 29.4, 29.4, 28.9, 27.3, 27.3, 26.2, 22.8, 14.2. **HRMS (ESI)**: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{42}\text{O}_3\text{Na}^+$: 425.3026; found: 425.3029.

2-(2-Oxopyrrolidin-1-yl) ethyl 4-methoxybenzoate (3ag)



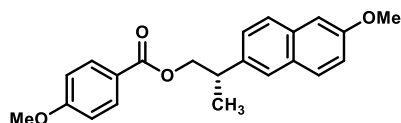
General procedure A was followed on 0.2 mmol scale with 36 h and purification by flash column chromatography on silica gel (PE/EtOAc = 1/1) afforded **3ag** as a yellow oil (34.8 mg, 66%). R_f = 0.23 (PE/EtOAc = 1/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.00–7.96 (m, 2H), 6.94–6.91 (m, 2H), 4.42 (t, J = 5.2 Hz, 2H), 3.86 (s, 3H), 3.68 (t, J = 5.2 Hz, 2H), 3.51 (t, J = 6.8 Hz, 2H), 2.39 (t, J = 8.0 Hz, 2H), 2.03 (quin, J = 7.6 Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 175.5, 166.2, 163.6, 131.8, 122.3, 113.9, 62.3, 55.6, 48.1, 41.9, 30.9, 18.2; **HRMS (ESI)**: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4\text{Na}^+$: 286.1050; found: 286.1044.

2-(4-Isobutylphenyl) propyl 4-methoxybenzoate (3ah)



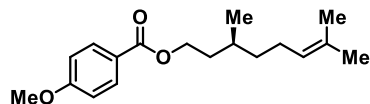
General procedure A was followed on 0.2 mmol scale with 22 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3ah** as a light-yellow oil (37.5 mg, 58%). R_f = 0.54 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.94 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 9.2 Hz, 2H), 4.38 (dd, J = 10.8, 6.8 Hz, 1H), 4.32 (dd, J = 10.8, 6.8 Hz, 1H), 3.85 (s, 3H), 3.21 (sext, J = 7.6 Hz, 1H), 2.45 (d, J = 7.2 Hz, 2H), 1.90–1.80 (m, 1H), 1.38 (d, J = 6.8 Hz, 3H), 0.90 (d, J = 6.8 Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.4, 163.4, 140.6, 140.1, 131.7, 129.3, 127.2, 122.9, 113.7, 69.9, 55.5, 45.2, 38.8, 30.3, 22.5, 22.5, 18.2. **HRMS (ESI)**: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{26}\text{O}_3\text{Na}^+$: 349.1774; found: 349.1768.

(S)-2-(6-Methoxynaphthalen-2-yl) propyl 4-methoxybenzoate (3ai)



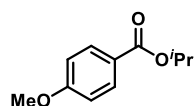
General procedure A was followed on 0.2 mmol scale with 36 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3ai** as a white solid (47.1 mg, 67%). R_f = 0.27 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.96–7.92 (m, 2H), 7.71 (dd, J = 8.4, 4.8 Hz, 2H), 7.66 (s, 1H), 7.40 (dd, J = 8.4, 1.2 Hz, 1H), 7.15–7.13 (m, 2H), 6.90–6.87 (m, 2H), 4.48 (dd, J = 10.8, 6.8 Hz, 1H), 4.42 (dd, J = 10.8, 6.8 Hz, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.37 (sext, J = 7.2 Hz, 1H), 1.46 (d, J = 7.2 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.4, 163.4, 157.6, 138.6, 133.6, 131.7, 129.3, 129.2, 127.1, 126.6, 125.7, 122.9, 119.0, 113.7, 105.7, 69.8, 55.5, 55.4, 39.2, 18.3; **HRMS (ESI)**: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{22}\text{O}_4\text{Na}^+$: 373.1410; found: 373.1403.

(S)-3,7-Dimethyloct-6-en-1-yl 4-methoxybenzoate (3aj)



General procedure A was followed on 0.2 mmol scale with 36 h and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3aj** as a yellow oil (39.5 mg, 68%). R_f = 0.47 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.01–7.97 (m, 2H), 6.93–6.90 (m, 2H), 5.10 (tt, J = 6.8, 1.2 Hz, 1H), 4.37–4.28 (m, 2H), 3.86 (s, 3H), 2.08–1.93 (m, 2H), 1.84–1.76 (m, 1H), 1.67 (s, 3H), 1.66–1.62 (m, 1H), 1.60 (s, 3H), 1.59–1.52 (m, 1H), 1.44–1.36 (m, 1H), 1.28–1.18 (m, 1H), 0.96 (d, J = 6.8 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.6, 163.4, 131.7, 131.5, 124.7, 123.1, 113.7, 63.3, 55.5, 37.1, 35.7, 29.7, 25.8, 25.5, 19.6, 17.8. **HRMS (ESI)**: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_3\text{Na}^+$: 313.1774; found: 313.1767.

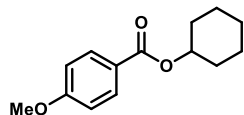
Isopropyl 4-methoxybenzoate (3ak)



General procedure A was followed on 0.2 mmol scale with 36 h by using 20 equivalents of ethanol as nucleophile and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3ak** as a colorless liquid (30.9 mg, 80%). $R_f = 0.39$ (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.99 (d, $J = 8.4$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 5.22 (sept, $J = 6.4$ Hz, 1H), 3.85 (s, 3H), 1.35 (d, $J = 6.4$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.0, 163.3, 131.6, 123.5, 113.6, 68.1, 55.5, 22.1.

The spectral data are consistent with those reported in the literature.¹³

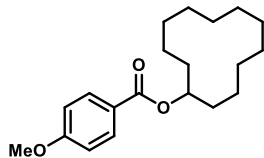
Cyclohexyl 4-methoxybenzoate (3al)



General procedure C was followed on 0.2 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3al** as a yellow oil (19.3 mg, 41%). $R_f = 0.59$ (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.02–7.98 (m, 2H), 6.63–6.89 (m, 2H), 5.03–4.96 (m, 1H), 3.86 (s, 3H), 1.95–1.91 (m, 2H), 1.81–1.77 (m, 2H), 1.62–1.53 (m, 4H), 1.49–1.25 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 165.9, 163.3, 131.7, 123.6, 113.6, 72.8, 55.5, 31.8, 25.6, 23.8;

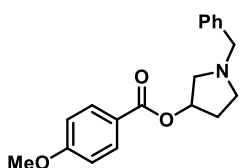
The spectral data are consistent with those reported in the literature.¹⁵

Cyclododecyl 4-methoxybenzoate (3am)



General procedure C was followed on 0.2 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 50/1~20/1) afforded **3am** as a yellow solid (33.3 mg, 52%). $R_f = 0.77$ (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): 8.01–7.97 (m, 2H), 6.92–6.89 (m, 2H), 5.26–5.20 (m, 1H), 3.85 (s, 3H), 1.86–1.77 (m, 2H), 1.67–1.59 (m, 2H), 1.45–1.33 (m, 18H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.2, 163.3, 131.6, 123.5, 113.6, 72.6, 55.5, 29.2, 24.3, 24.3, 24.1, 23.5, 23.3, 21.0; **HRMS (ESI)**: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_3^+\text{Na}$: 341.2087; found: 341.2080.

1-Benzylpyrrolidin-3-yl 4-methoxybenzoate (3an)

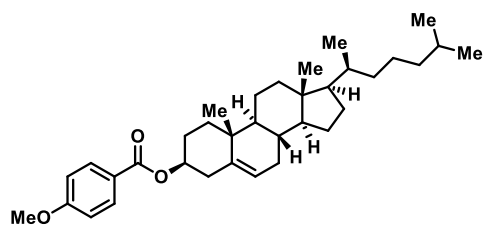


General procedure C was followed on 0.2 mmol scale with 36 h and purification by flash column chromatography on silica gel (PE/EtOAc = 5/1) afforded **3an** as a yellow oil (34.4 mg, 55%). $R_f = 0.27$ (PE/EtOAc = 5/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.00–7.96 (m, 2H), 7.37–7.24 (m, 5H), 6.93–6.88 (m, 2H), 5.42–5.37 (m, 1H), 3.85 (s, 3H), 3.71 (dd, $J = 28.8, 12.8$ Hz, 2H), 3.01 (dd, $J = 11.2, 6.4$ Hz, 1H), 2.88–2.82 (m, 1H), 2.79 (dd, $J = 11.2, 3.2$ Hz, 1H), 2.61 (q, $J = 7.6$ Hz, 1H), 2.41–2.32 (m, 1H), 2.06–1.98 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.3, 163.5, 138.1, 131.8, 129.1, 128.5, 127.4, 122.7, 113.7, 74.3, 60.3, 59.9, 55.5, 52.8, 32.1; **HRMS (ESI)**: $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_3^+$: 312.1594; found: 312.1586.

(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((S)-6-methylheptan-2-yl)

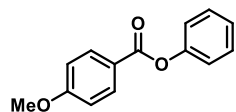
2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl methoxybenzoate (3ao)

4-



General procedure C was followed on 0.2 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3ao** as a white solid (49.6 mg, 48%). R_f = 0.33 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.00–7.98 (m, 2H), 6.92–6.89 (m, 2H), 5.41 (d, J = 4.0 Hz, 1H), 4.87–4.79 (m, 1H), 3.86 (s, 3H), 2.45 (d, J = 8.0 Hz, 2H), 2.04–1.67 (m, 6H), 1.55–1.09 (m, 16H), 1.06 (s, 3H), 1.04–0.95 (m, 4H), 0.92 (d, J = 6.4 Hz, 3H), 0.87 (dd, J = 6.4, 1.6 Hz, 6H), 0.69 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 165.9, 163.3, 139.9, 131.7, 123.4, 122.8, 113.6, 74.4, 56.8, 56.3, 55.5, 50.2, 42.2, 39.9, 39.6, 38.4, 37.2, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.1, 28.1, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0. **HRMS (ESI)**: $[\text{M}+\text{K}]^+$ Calcd for $\text{C}_{35}\text{H}_{52}\text{O}_3\text{K}^+$: 559.3548; found: 559.3543.

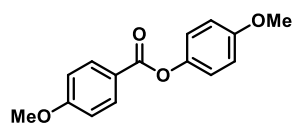
Phenyl 4-methoxybenzoate (**3ap**)



General procedure A was followed on 0.2 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3ap** as a white solid (19.5 mg, 43%). R_f = 0.35 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.17 (d, J = 8.8 Hz, 2H), 7.43 (t, J = 8.0 Hz, 2H), 7.26 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 7.6 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 165.1, 164.0, 151.2, 142.1, 132.4, 129.6, 125.9, 121.9, 114.0, 55.7;

The spectral data are consistent with those reported in the literature.⁹

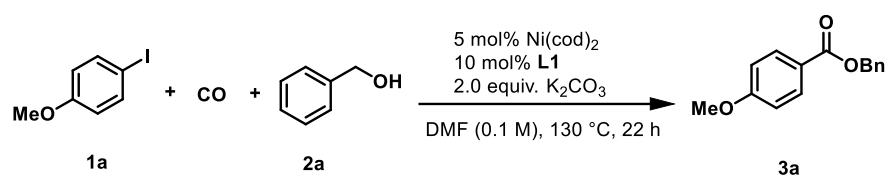
4-Methoxyphenyl 4-methoxybenzoate (**3aq**)



General procedure A was followed on 0.2 mmol scale and purification by flash column chromatography on silica gel (PE/EtOAc = 20/1) afforded **3aq** as light-yellow solid (24.1 mg, 47%). R_f = 0.23 (PE/EtOAc = 20/1); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.16–8.13 (m, 2H), 7.14–7.10 (m, 2H), 7.00–6.98 (d, J = 9.2 Hz, 2H), 6.95–6.91 (m, 2H), 3.90 (s, 3H), 3.82 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 165.4, 164.0, 157.4, 144.7, 132.4, 122.7, 122.1, 114.6, 113.9, 55.8, 55.7;

The spectral data are consistent with those reported in the literature.¹⁶

Procedure for Synthesis of the 3a on a 1.0 mmol-scale



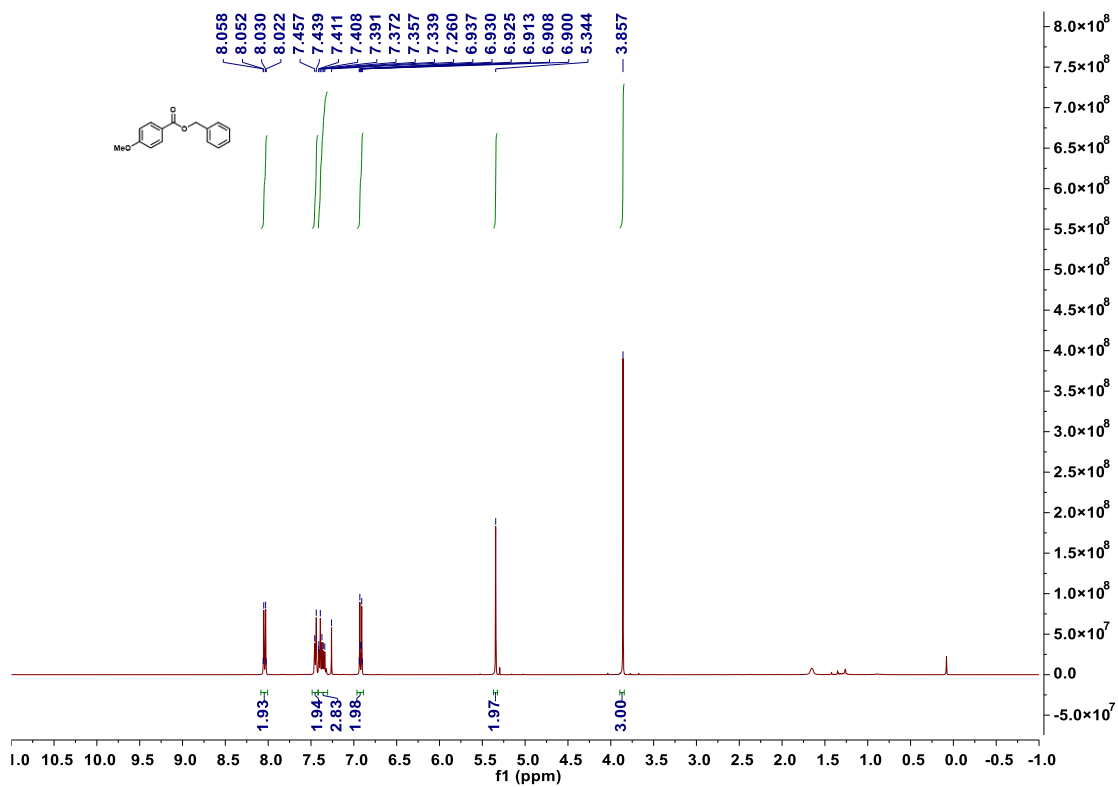
To an oven-dried 25 mL Schlenk tube, 4-iodoanisole (1.0 equiv. 1.0 mmol, 234.0 mg), K₂CO₃ (2.0 equiv. 2.0 mmol, 276.4 mg), L1 (10 mol%, 0.1 mmol, 18.0 mg) were added. Then the tube was transferred into glovebox and Ni(cod)₂ (5 mol%, 0.05 mmol, 13.8 mg) was added. The tube was evacuated and equipped with a CO balloon. DMF (10 mL) and benzyl alcohol (1.5 equiv. 1.5 mmol, 155 μL) were added in sequence and the mixture was stirred at 130 °C for 22 h. Then the reaction was quenched with saturated aqueous solution of NH₄Cl. The mixture was extracted with ethyl acetate for 3 times, and washed with water for 3 times. The combined organic layer was dried over Na₂SO₄, filtered and then concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO₂, PE/EA = 30/1~20/1) to yield the product **3a** (159.8 mg, 66%) as light-yellow oil.

References

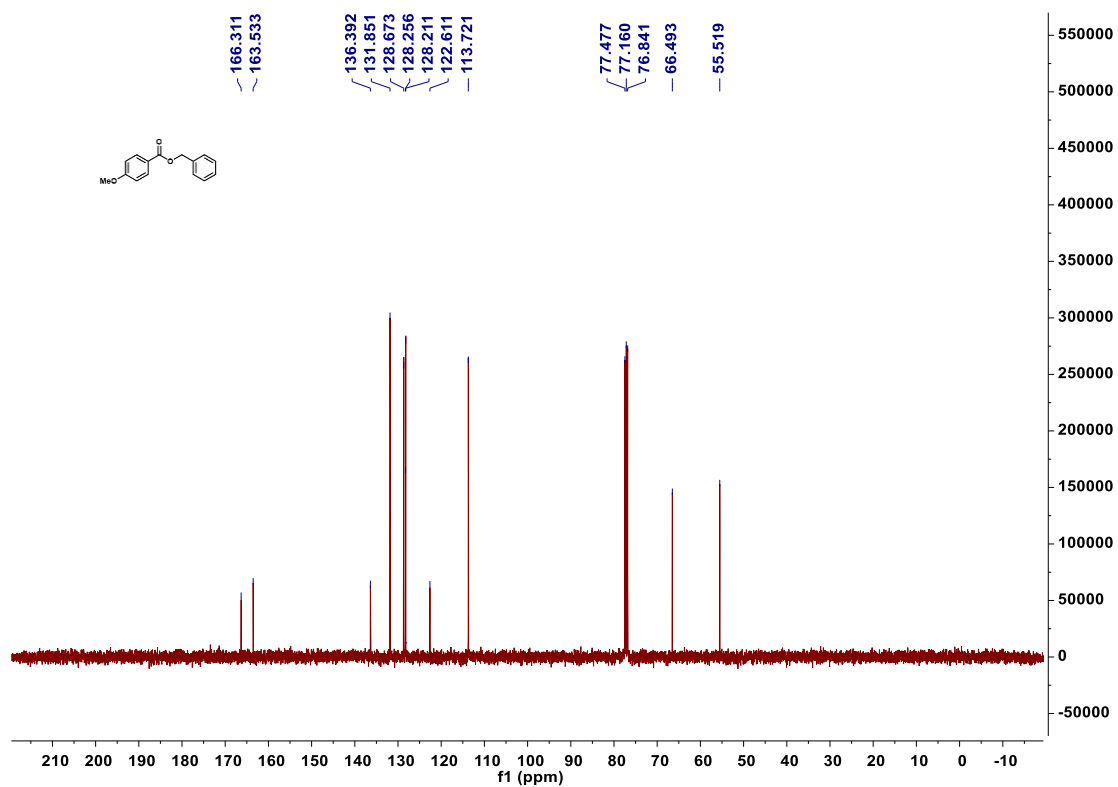
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NMR Spectrum

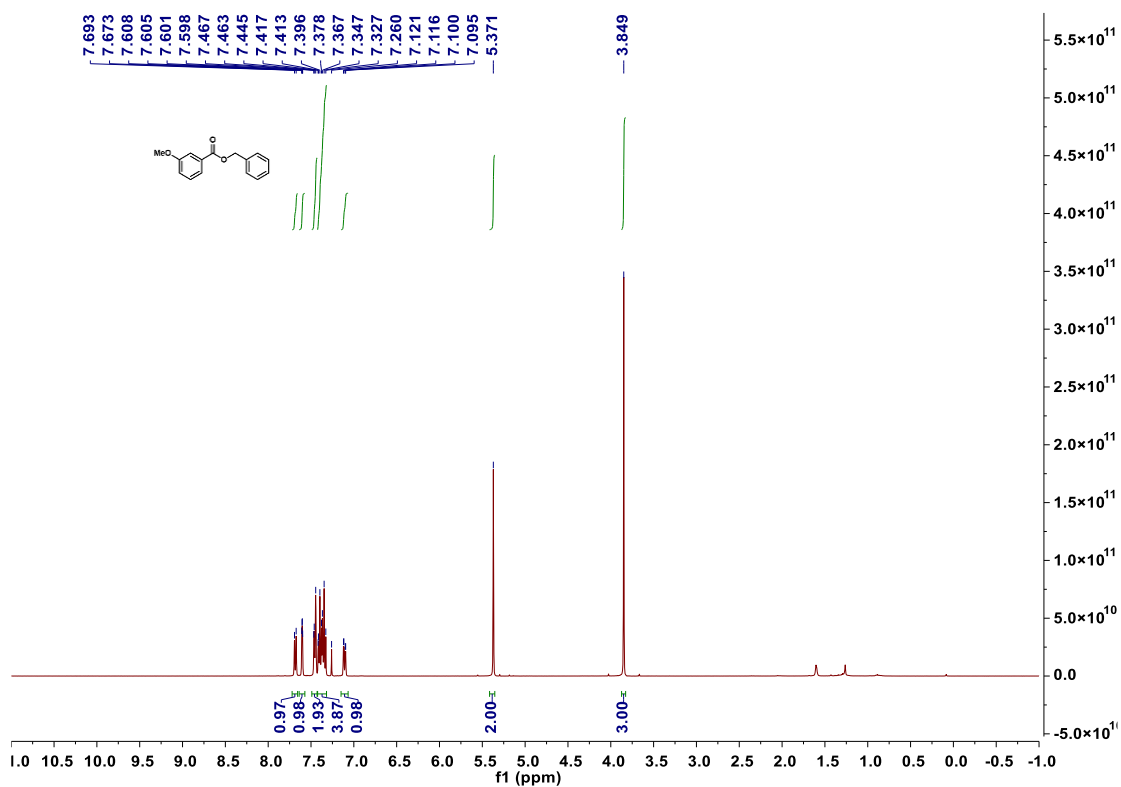
¹H NMR-spectrum (400 MHz, CDCl₃) of 3a



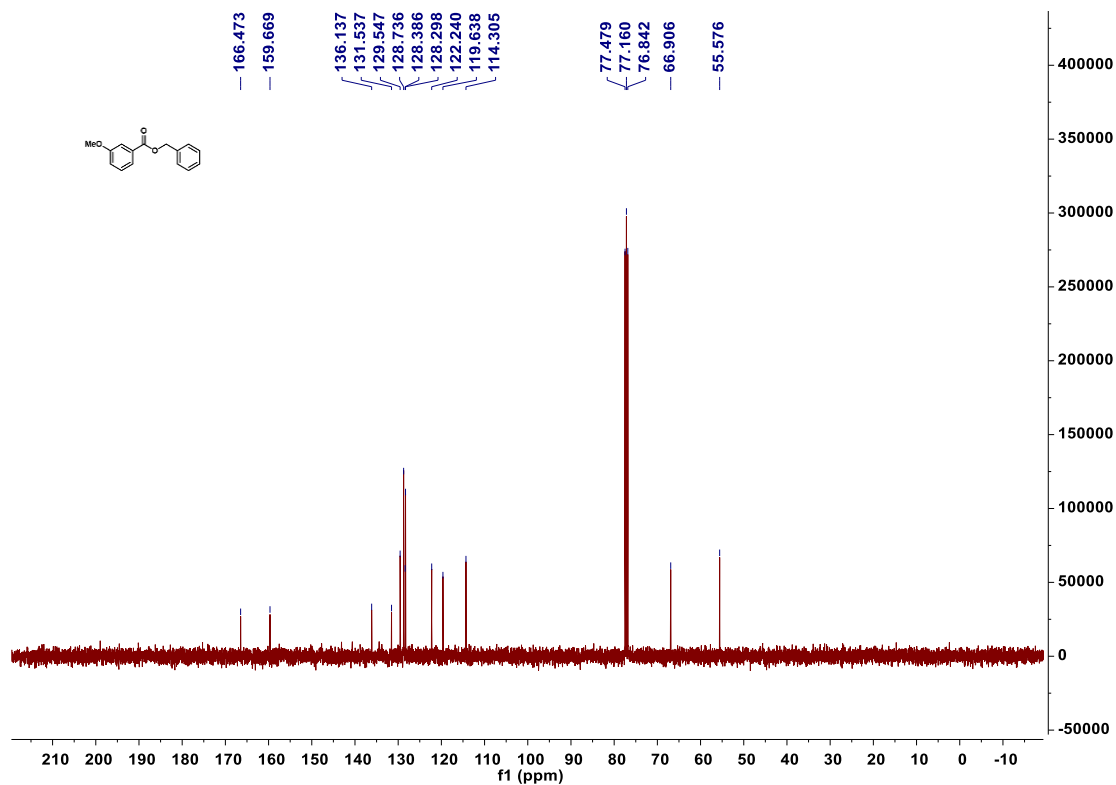
¹³C NMR-spectrum (100 MHz, CDCl₃) of 3a



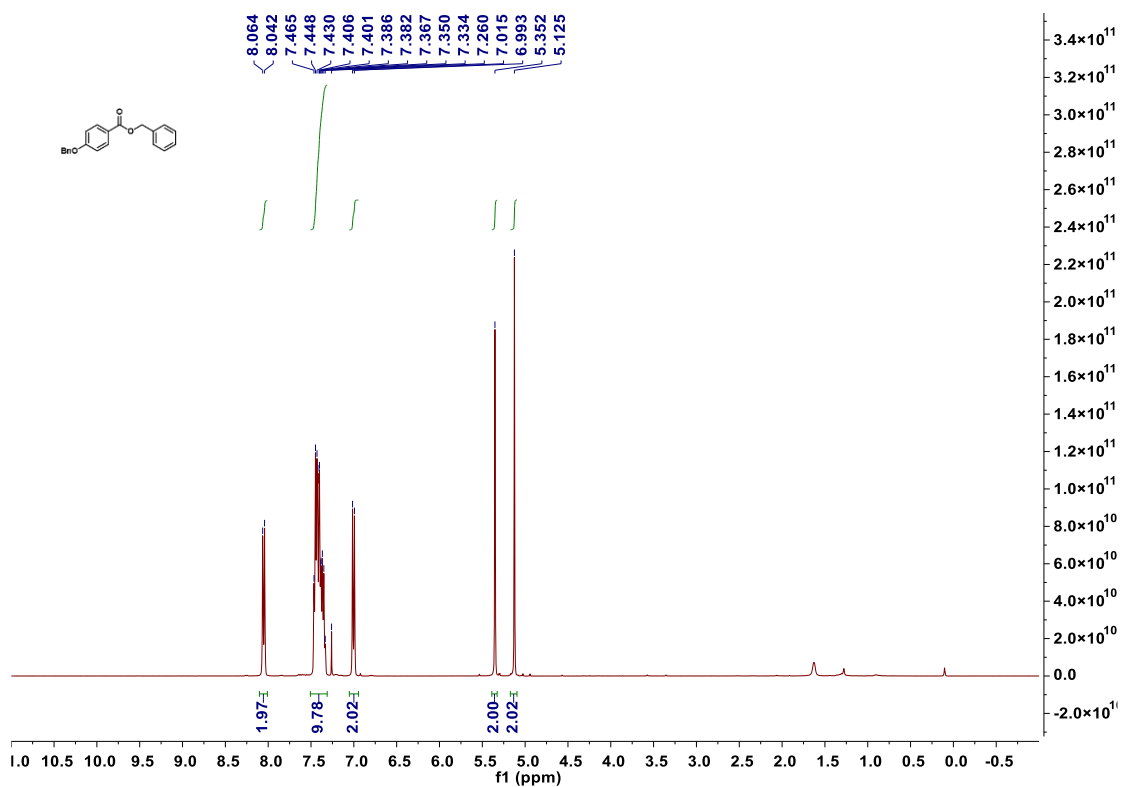
¹H NMR-spectrum (400 MHz, CDCl₃) of **3b**



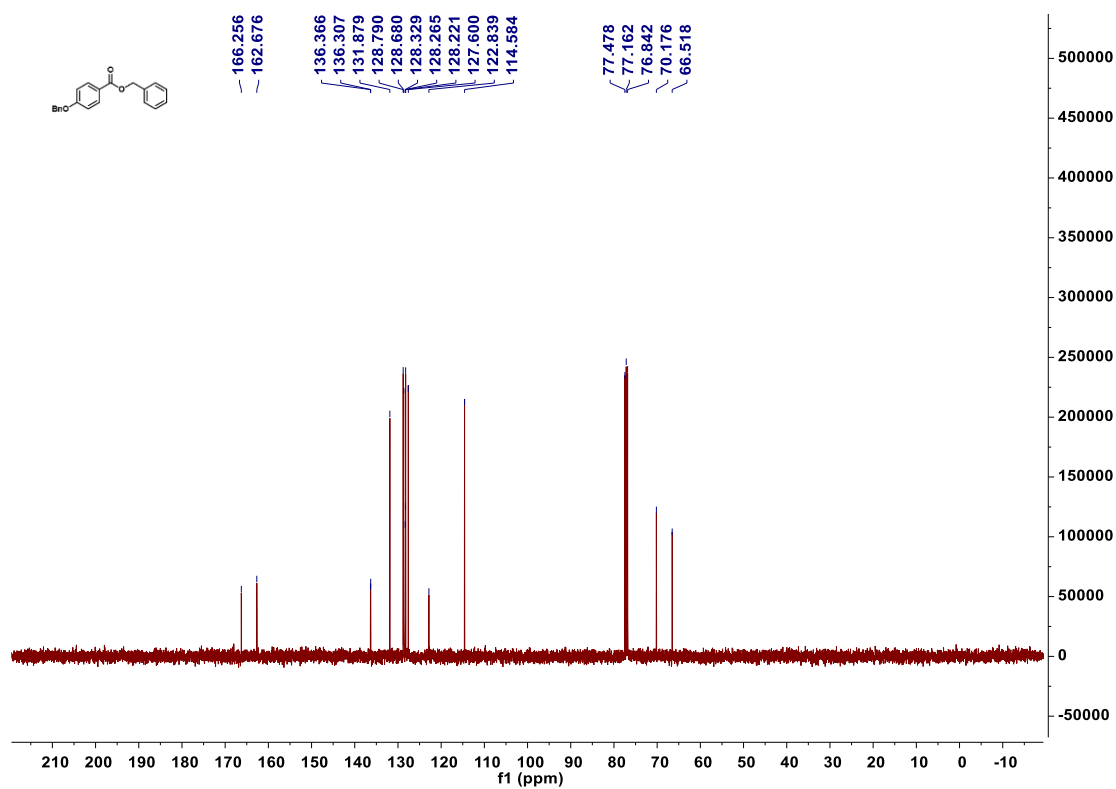
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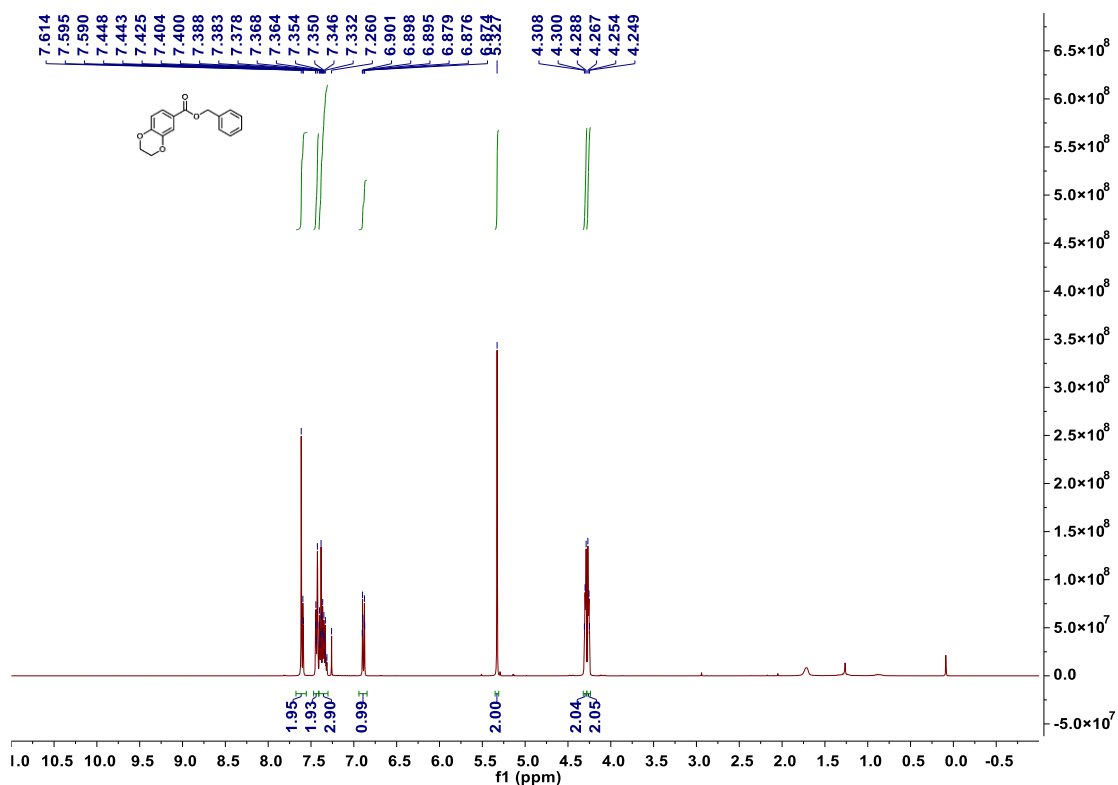
¹H NMR-spectrum (400 MHz, CDCl₃) of **3c**



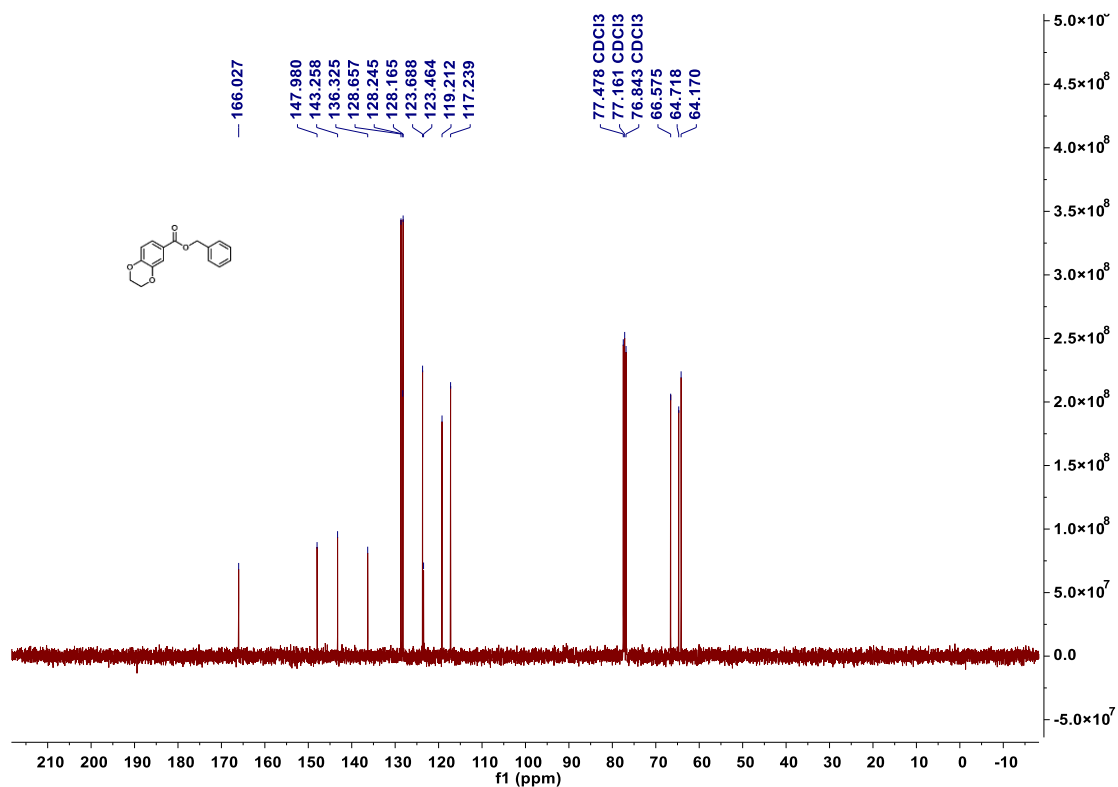
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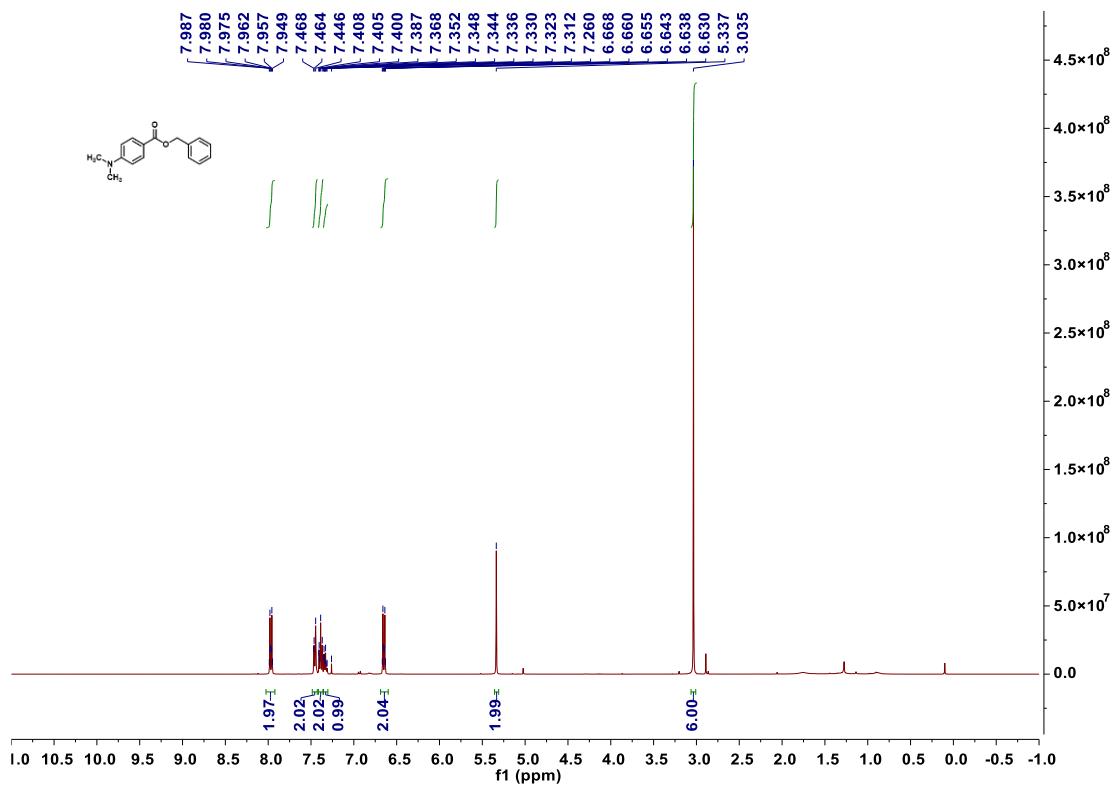
¹H NMR-spectrum (400 MHz, CDCl₃) of **3d**



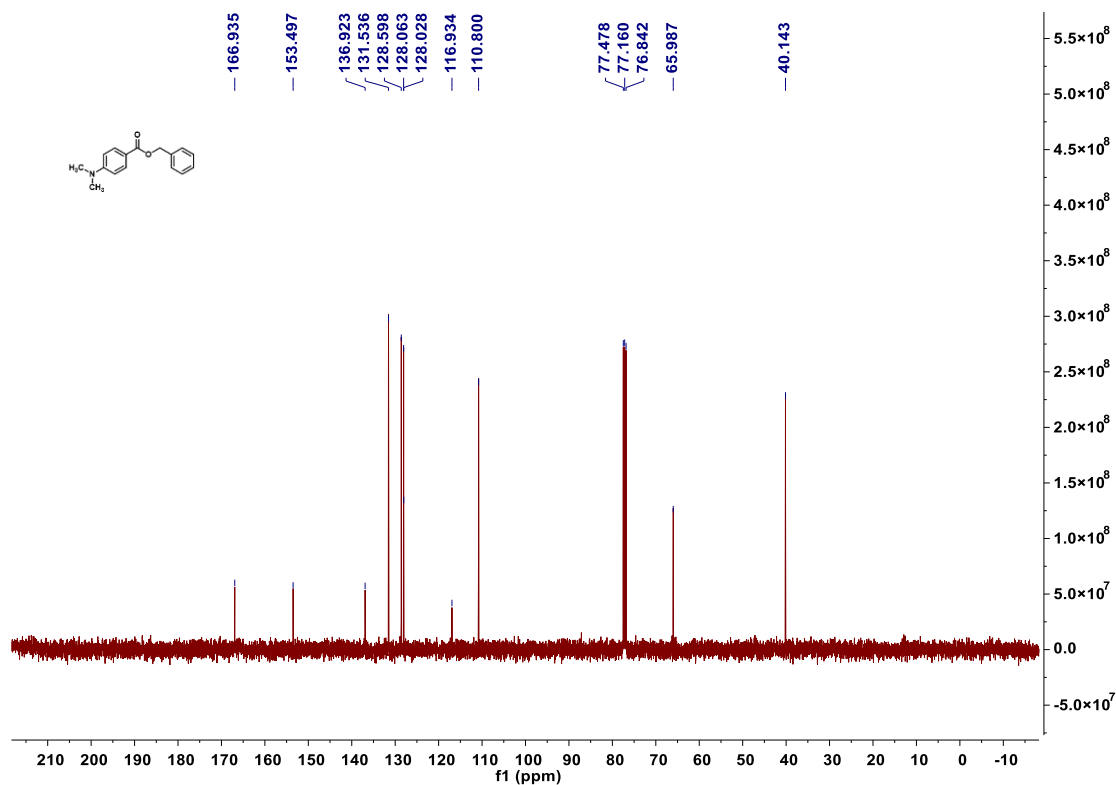
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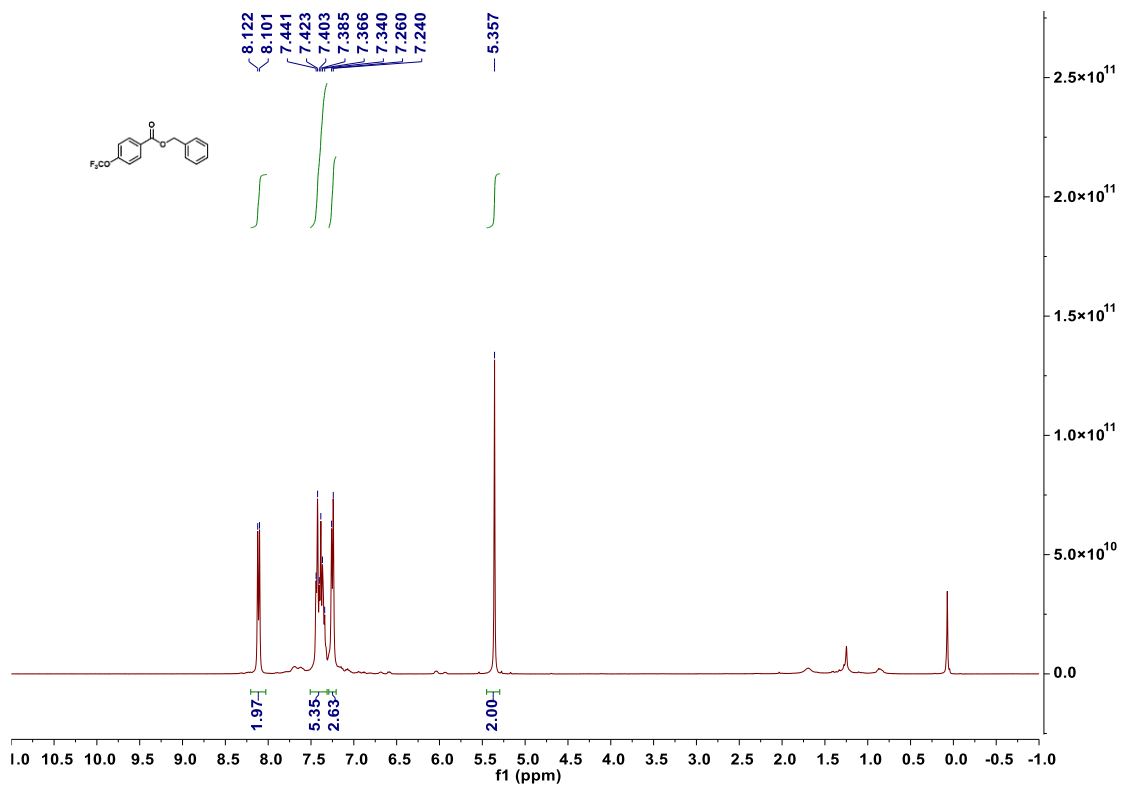
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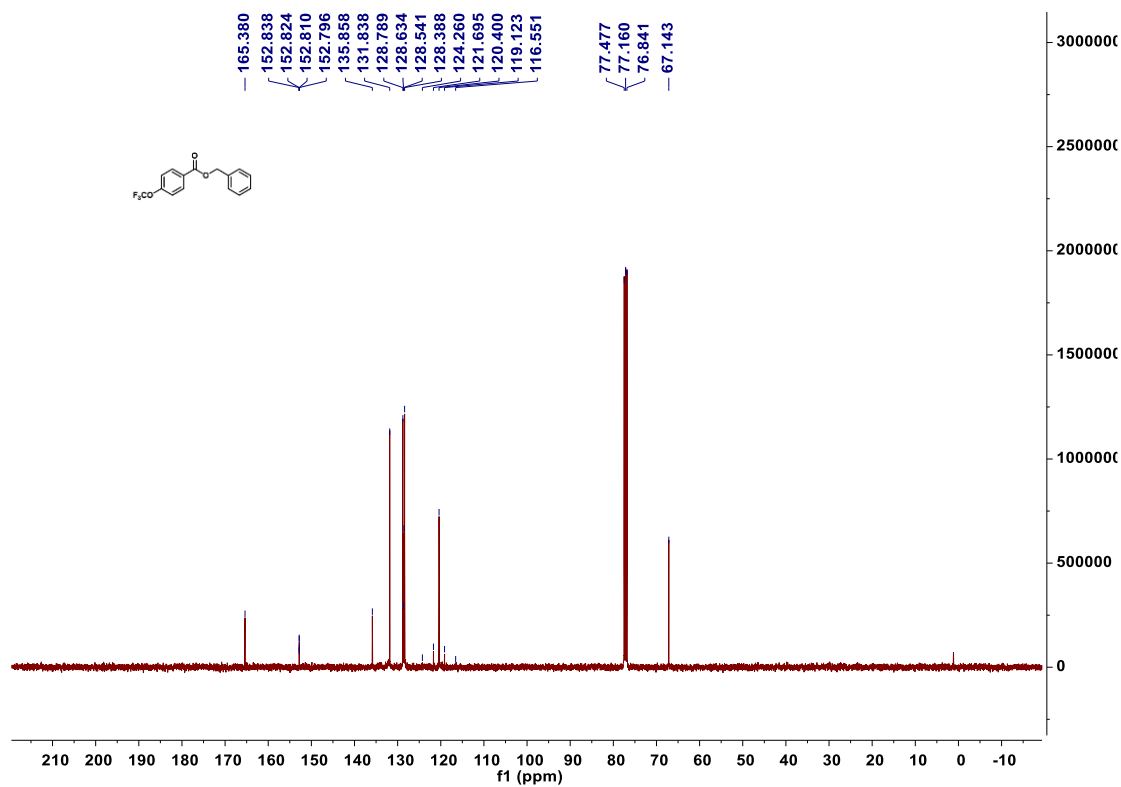
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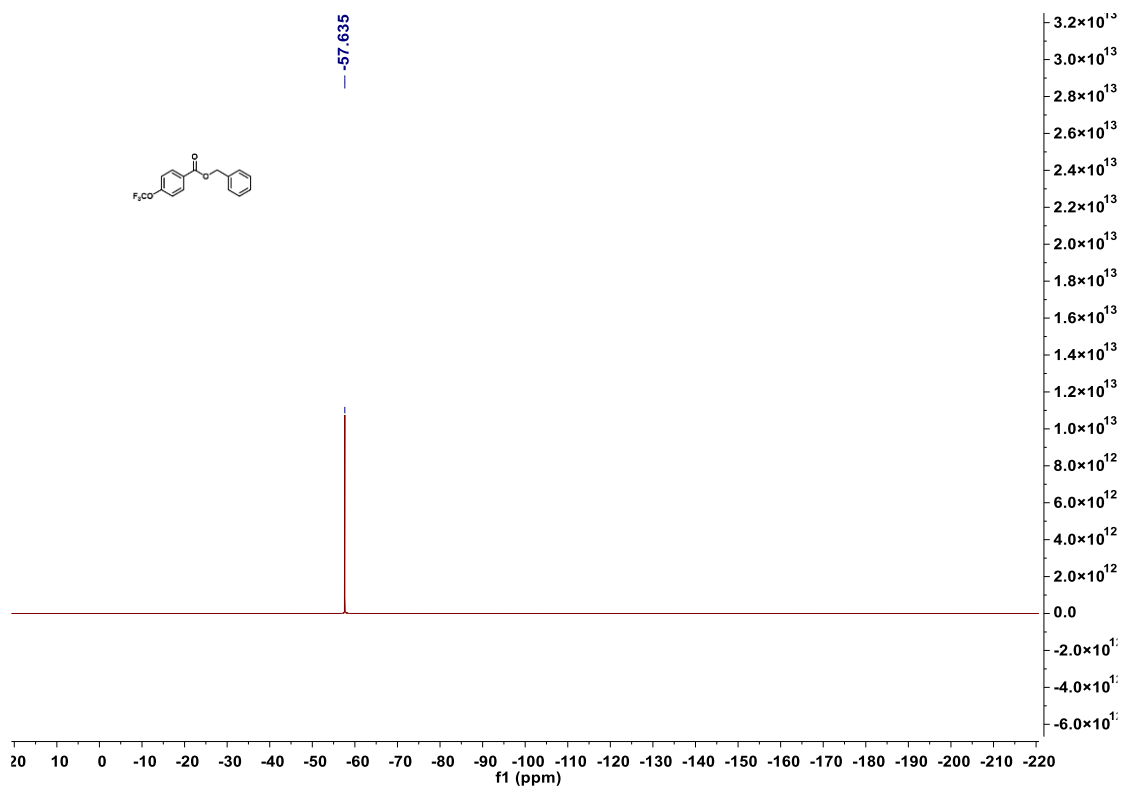
¹H NMR-spectrum (400 MHz, CDCl₃) of **3f**



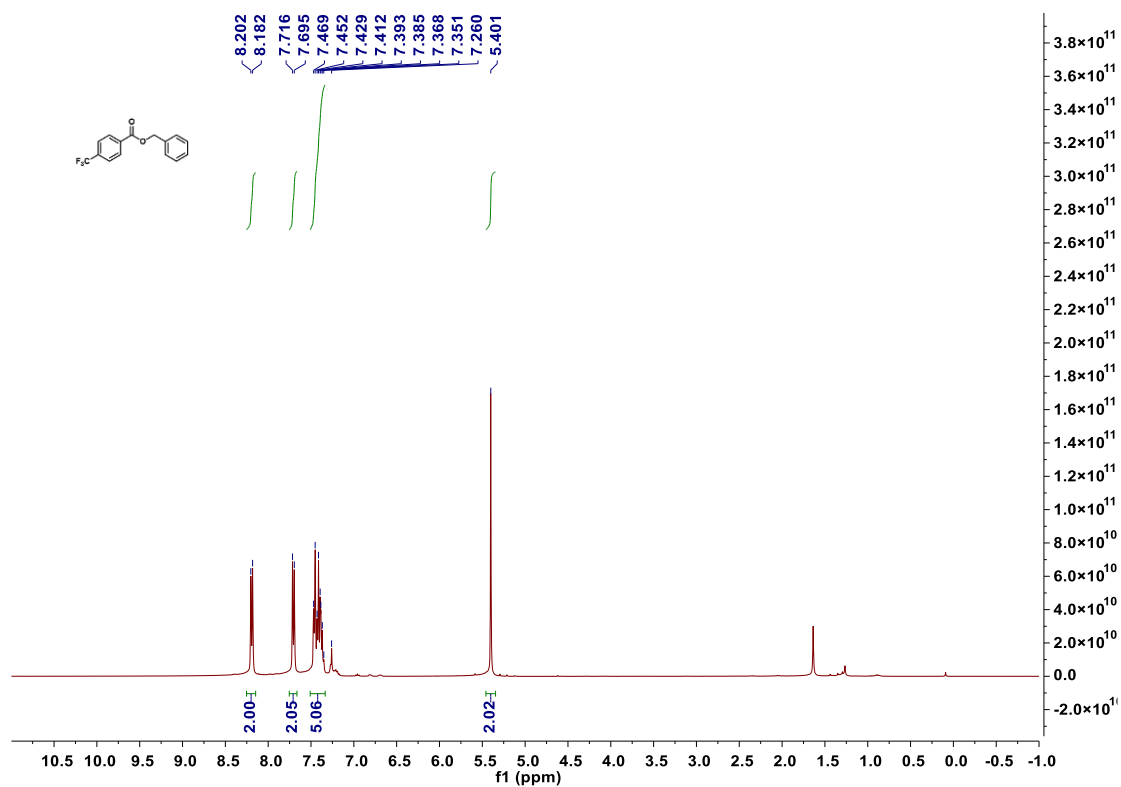
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3f**



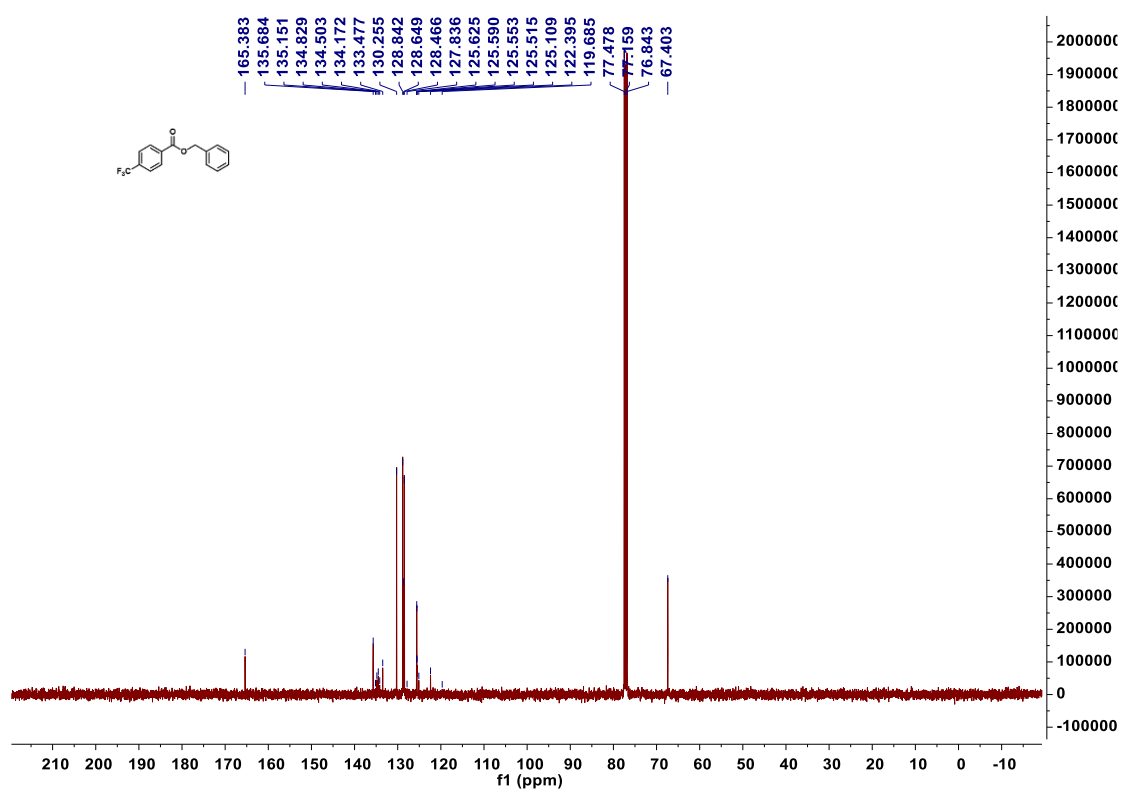
¹⁹F NMR-spectrum (376 MHz, CDCl₃) of **3f**



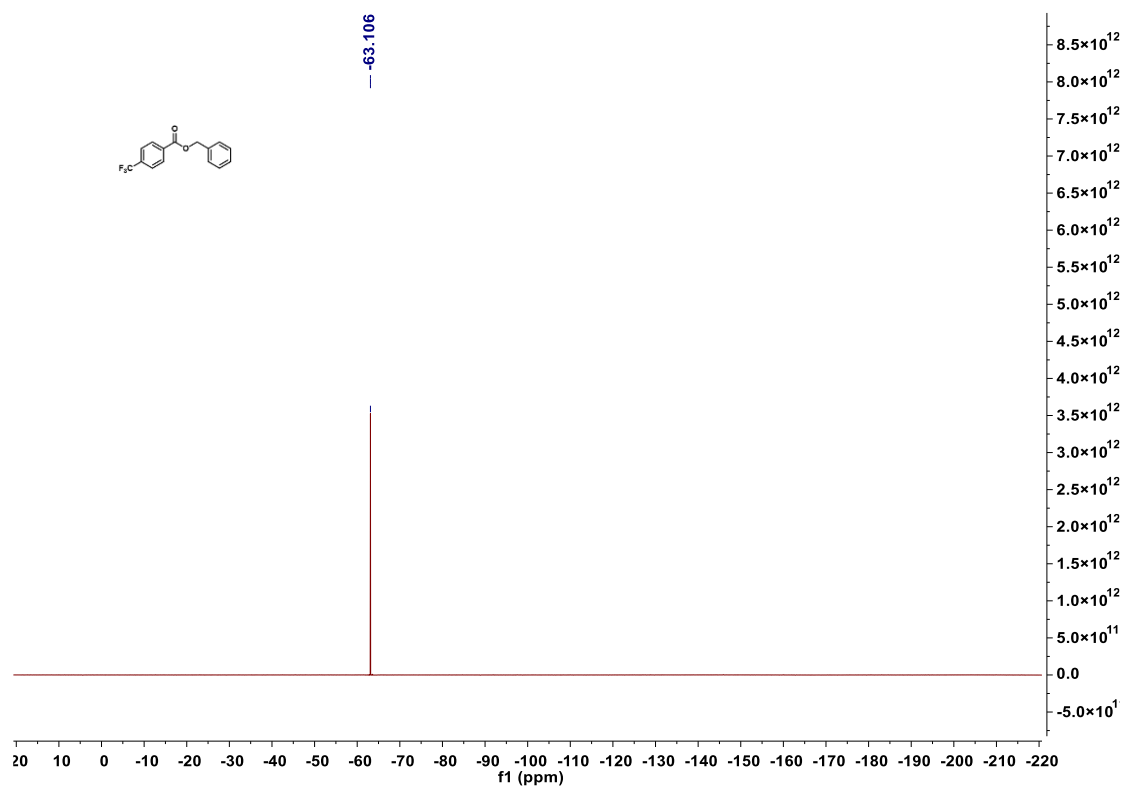
¹H NMR-spectrum (400 MHz, CDCl₃) of **3g**



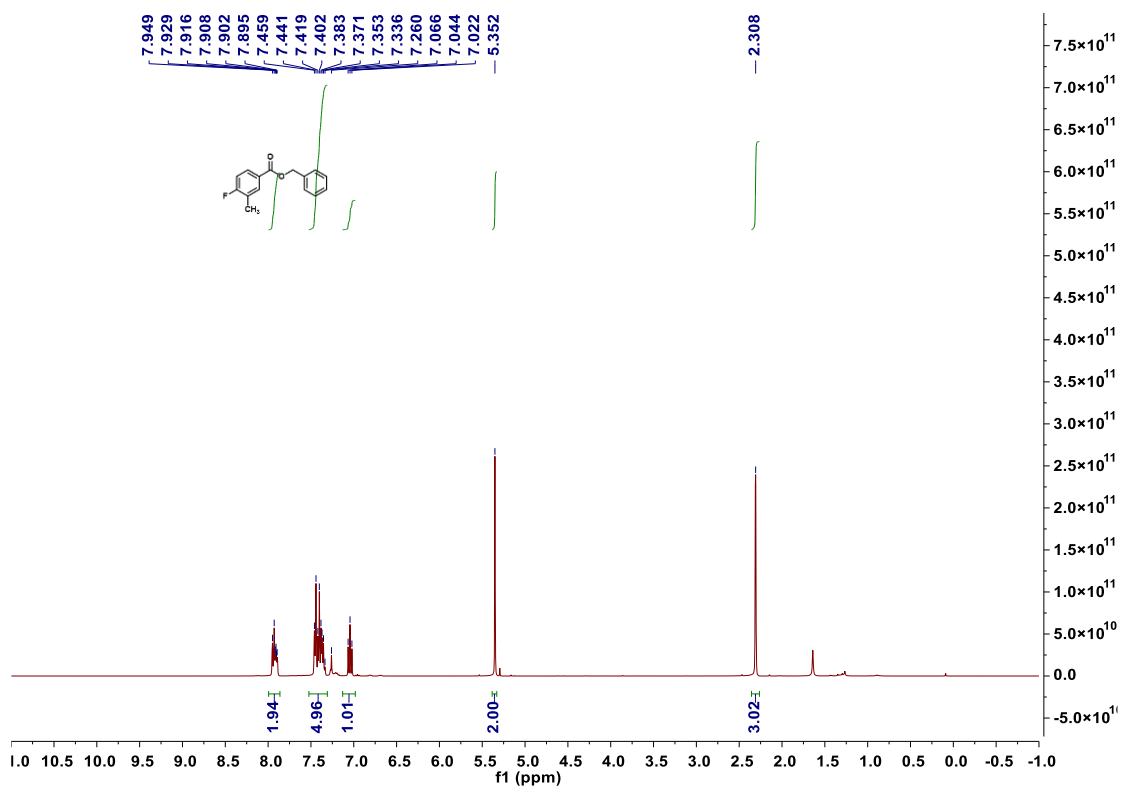
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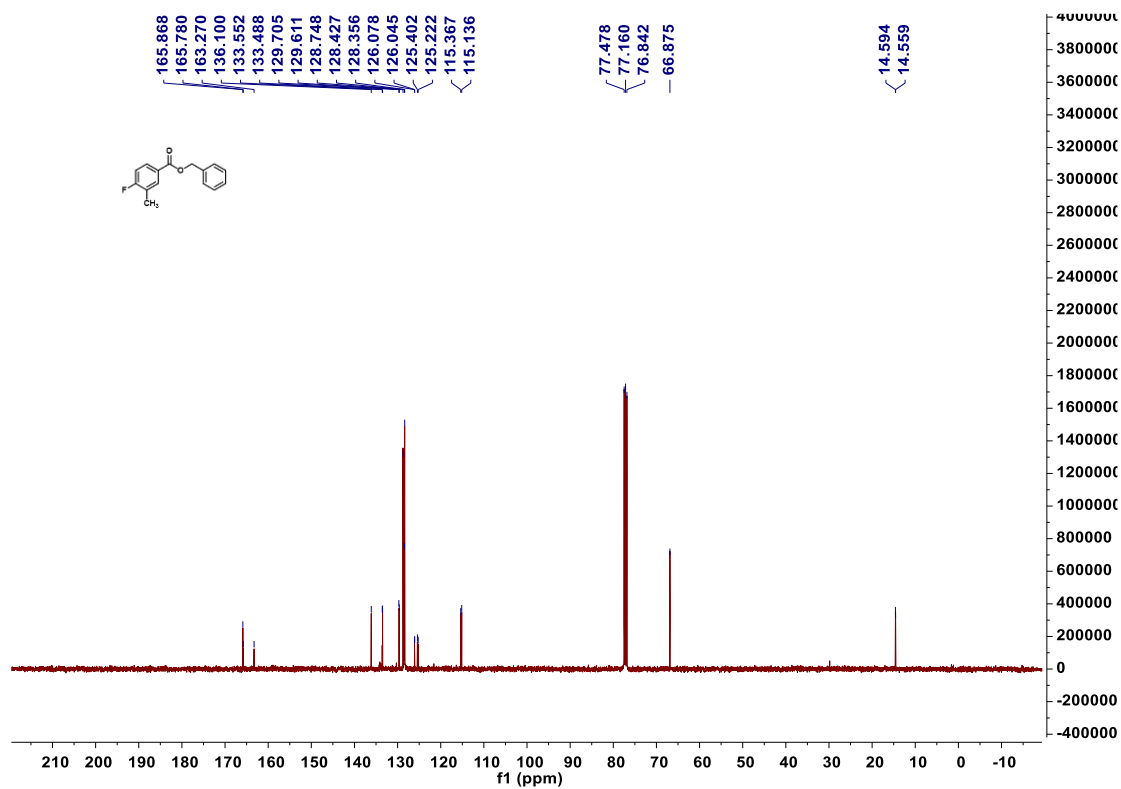
¹⁹F NMR-spectrum (376 MHz, CDCl₃) of 3g



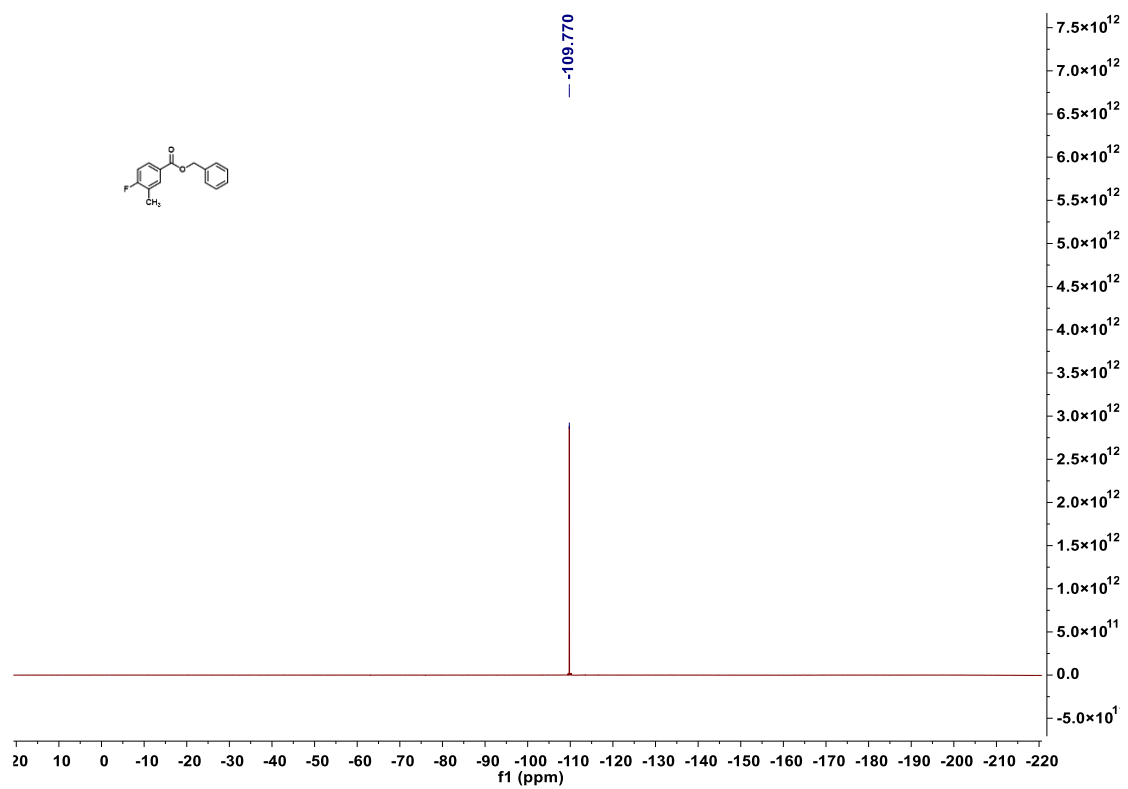
¹H NMR-spectrum (400 MHz, CDCl₃) of **3h**



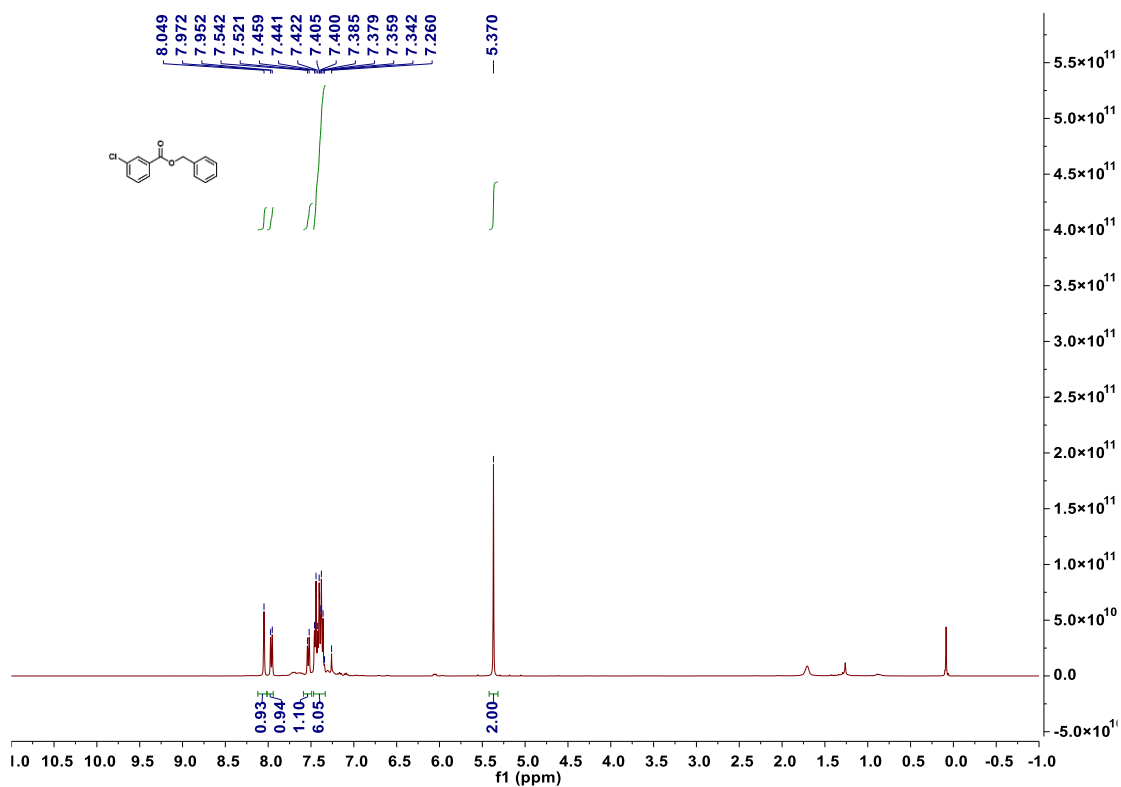
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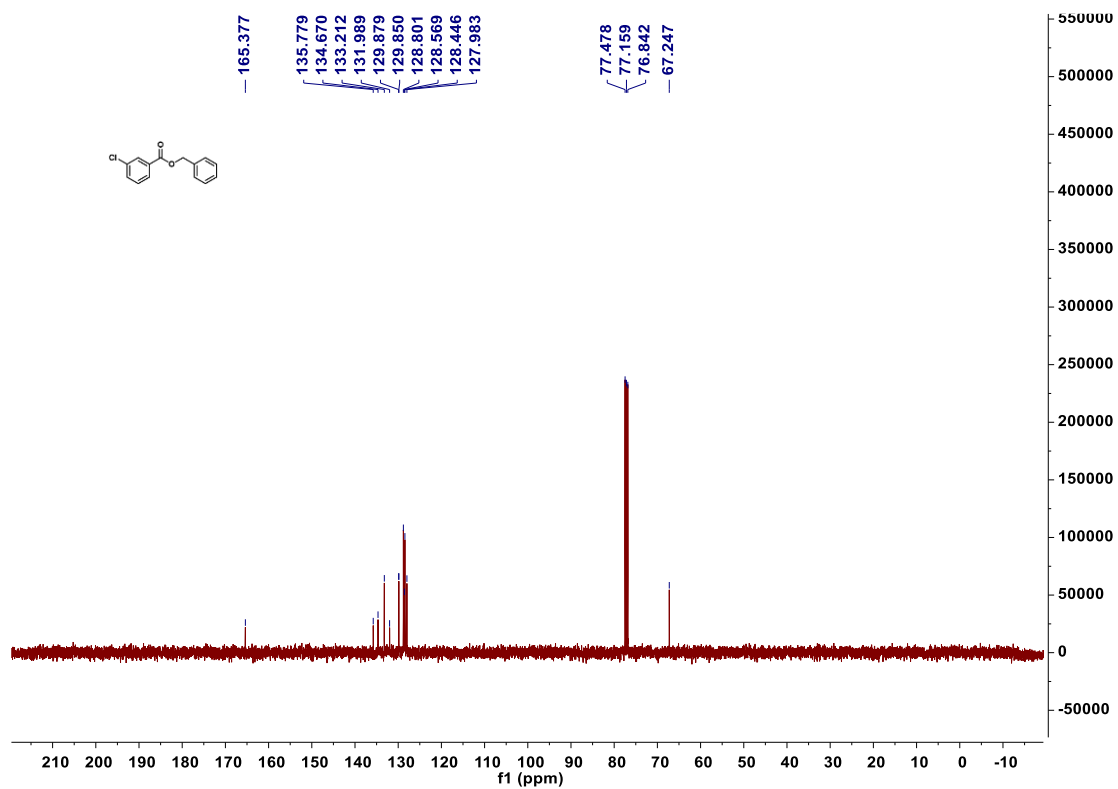
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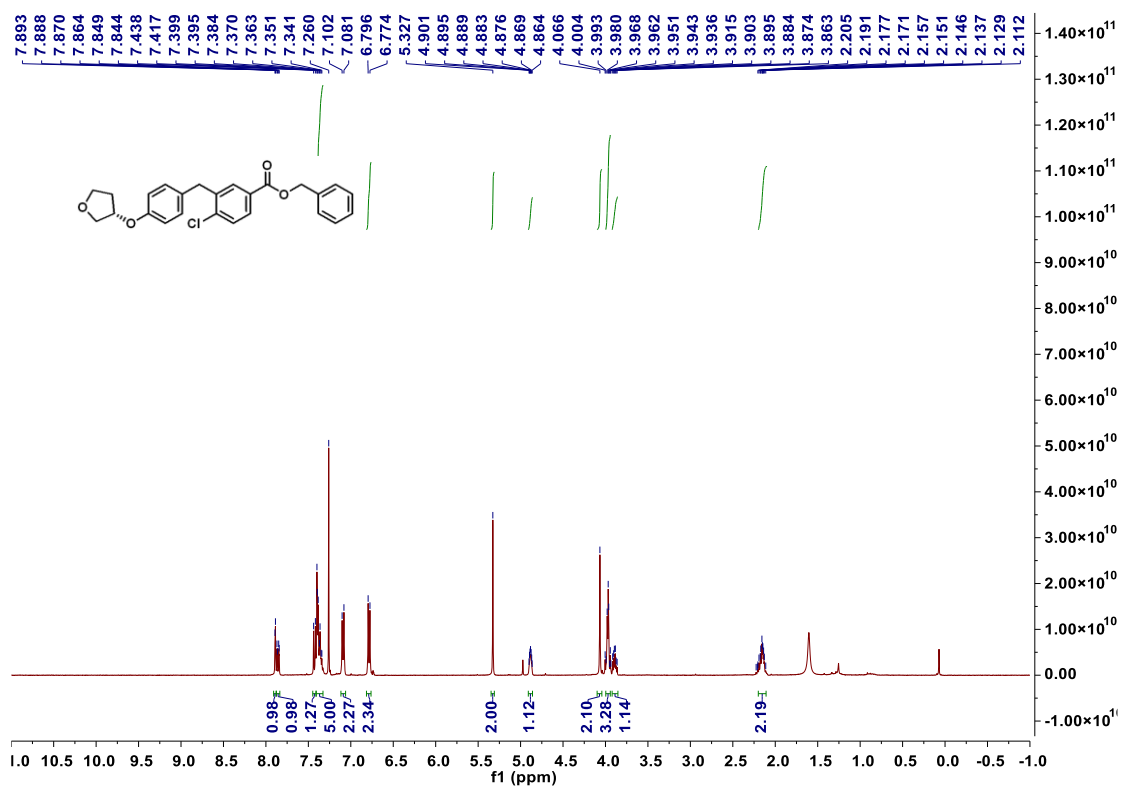
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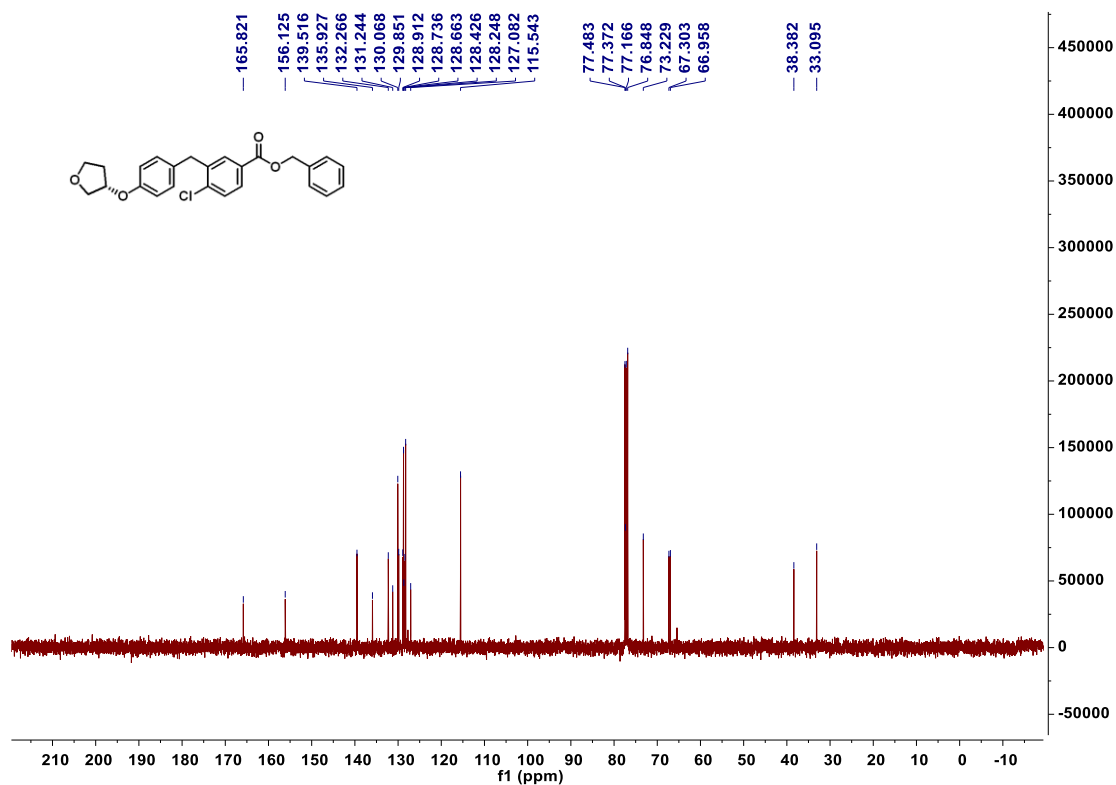
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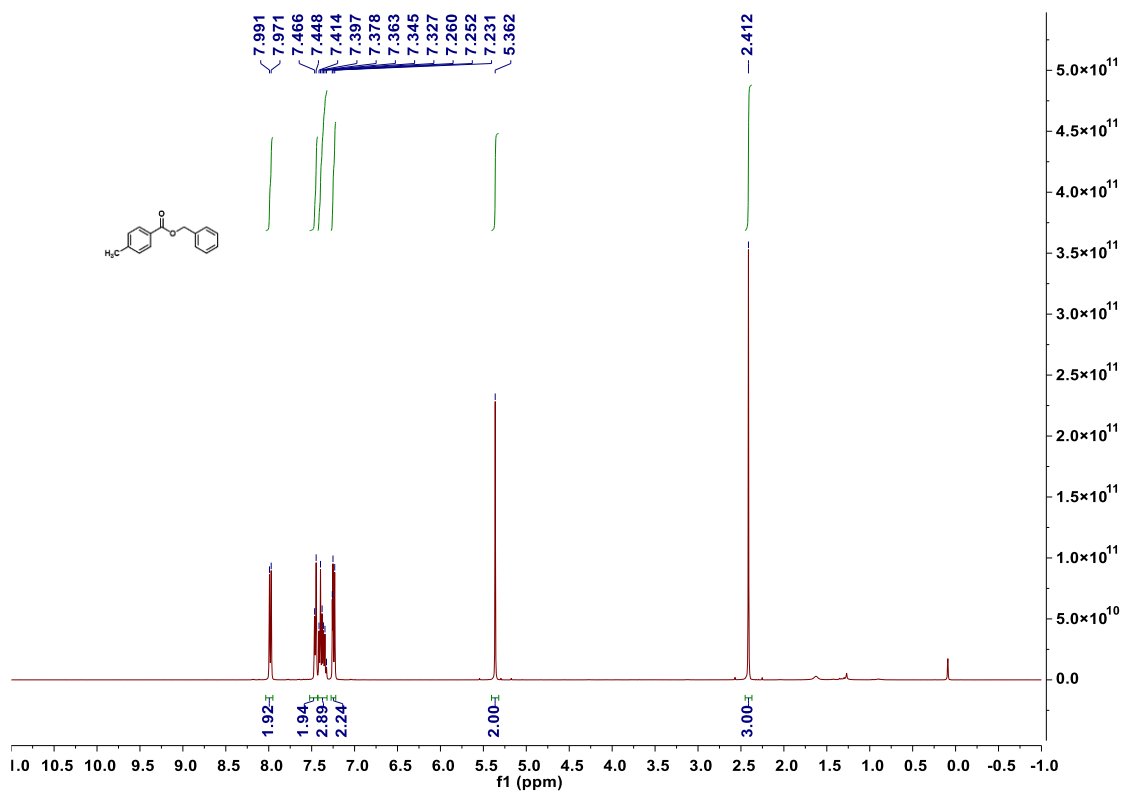
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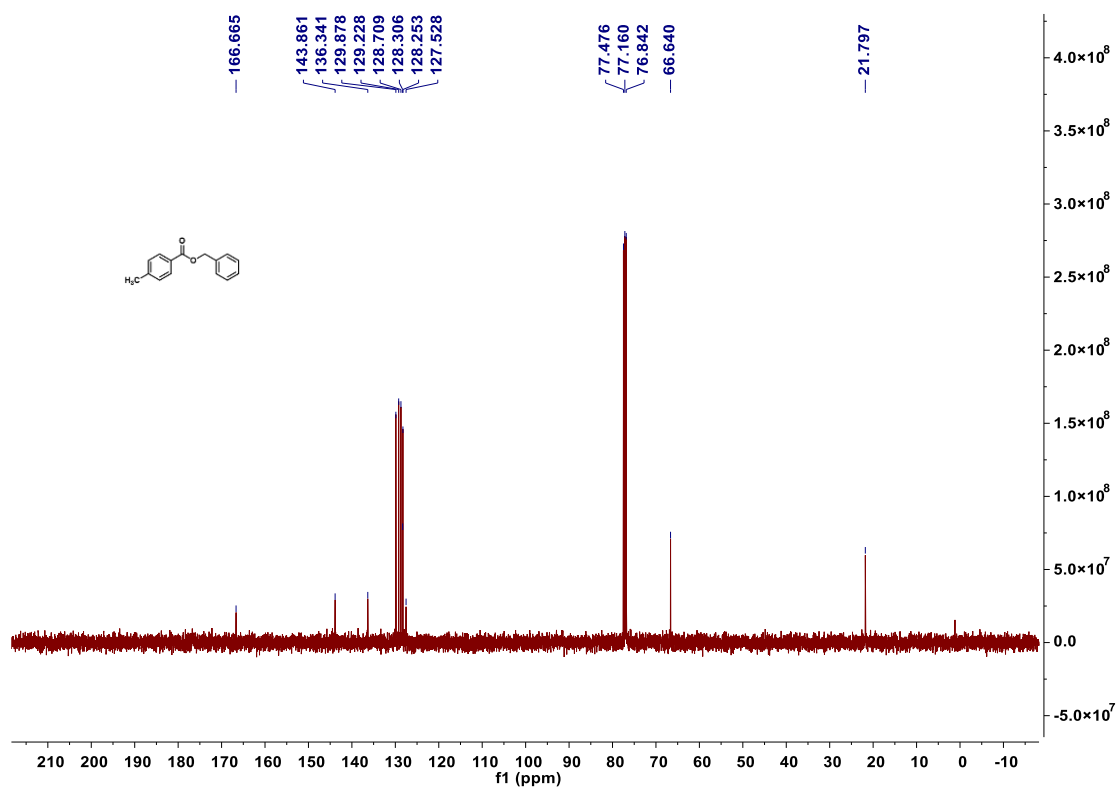
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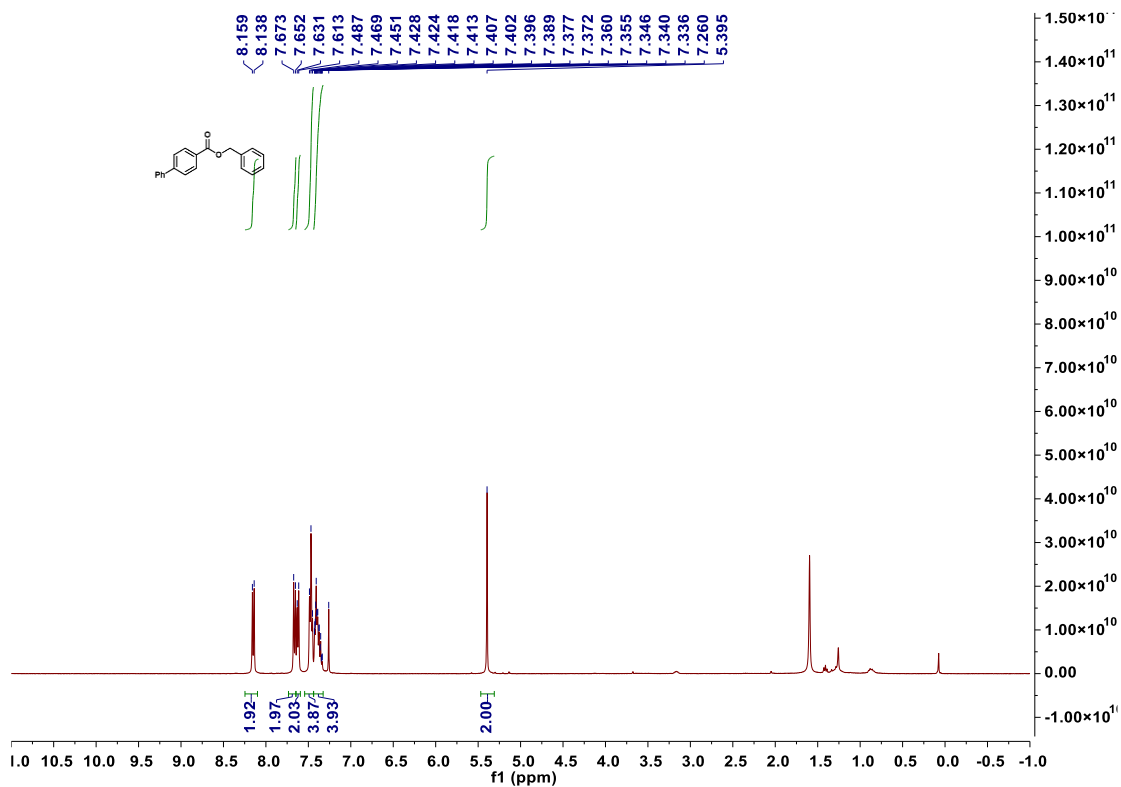
¹H NMR-spectrum (400 MHz, CDCl₃) of **3k**



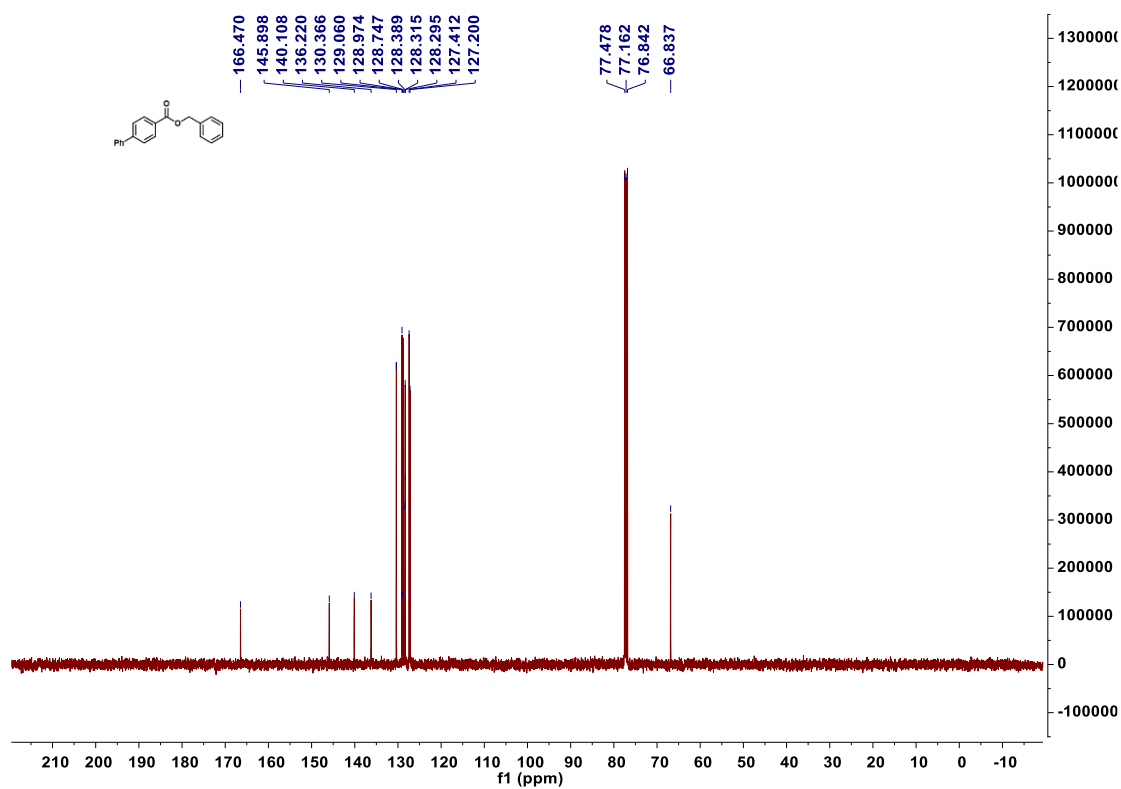
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3k**



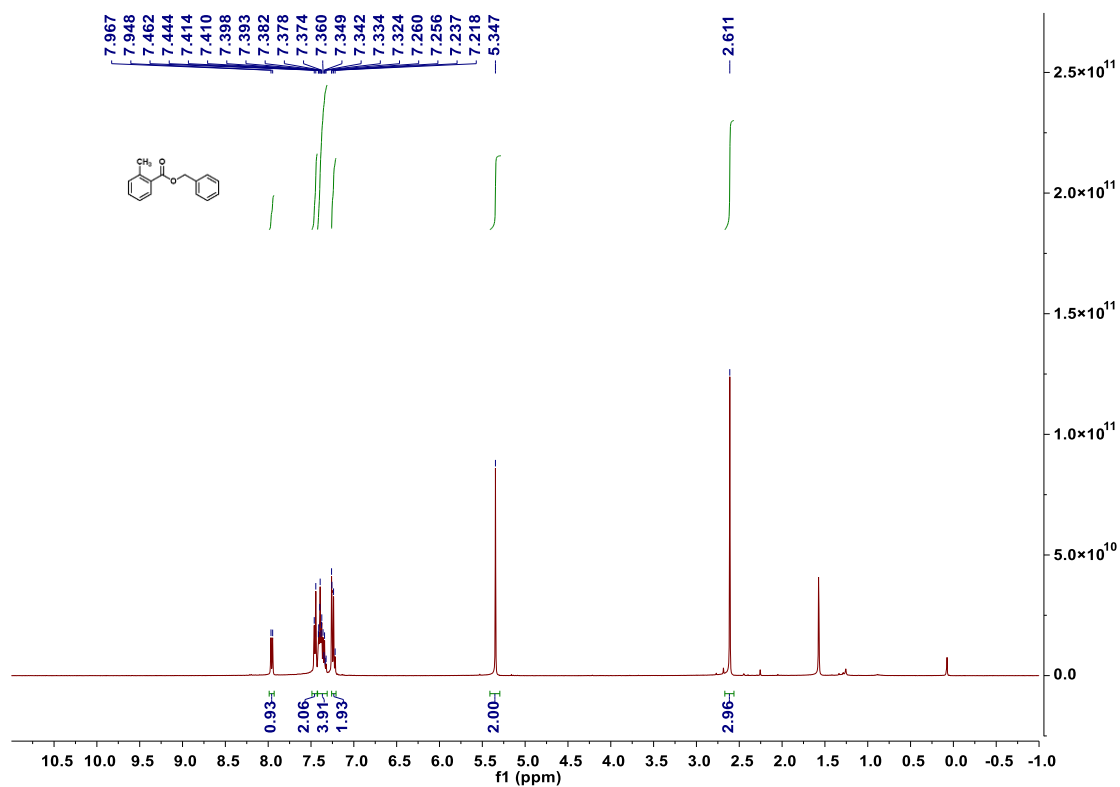
¹H NMR-spectrum (400 MHz, CDCl₃) of 31



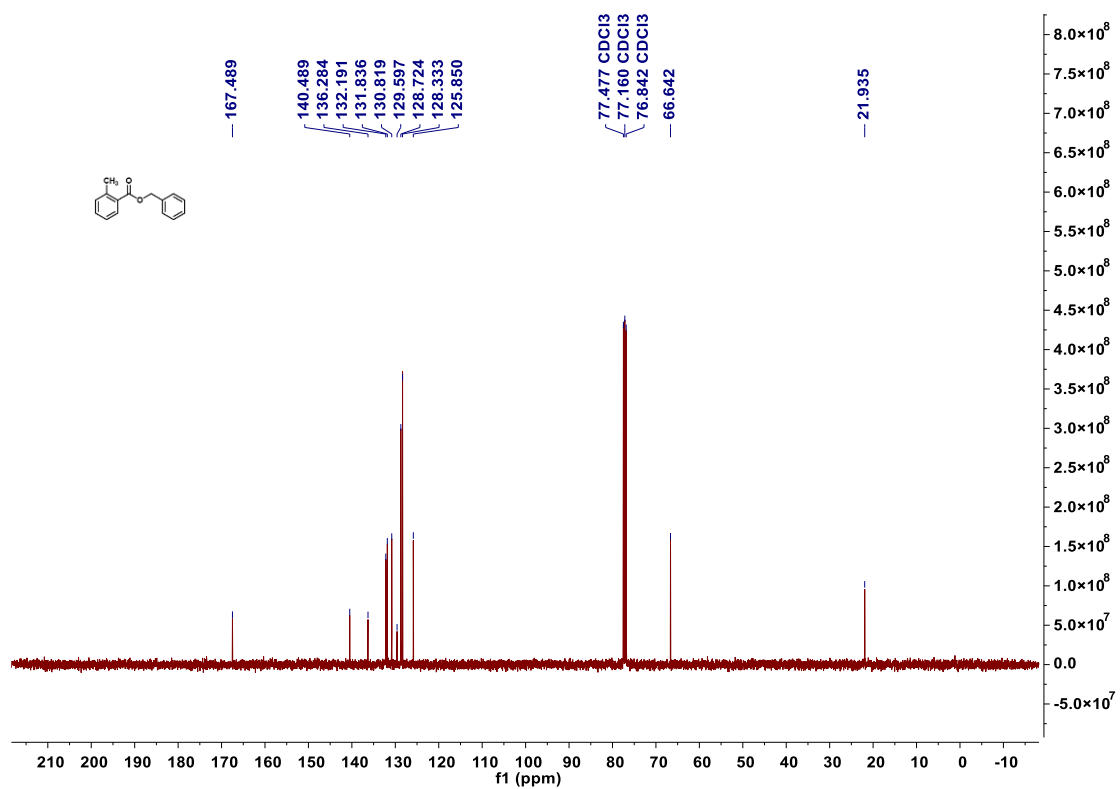
¹³C NMR-spectrum (100 MHz, CDCl₃) of 31



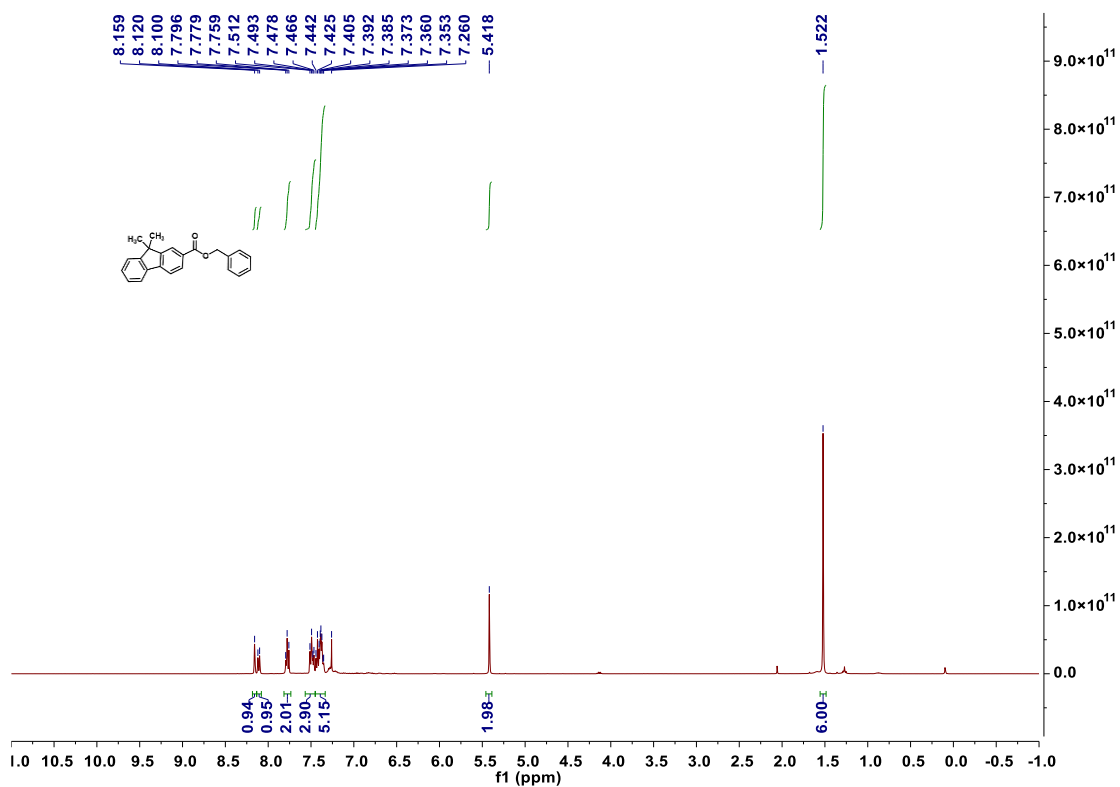
¹H NMR-spectrum (400 MHz, CDCl₃) of **3m**



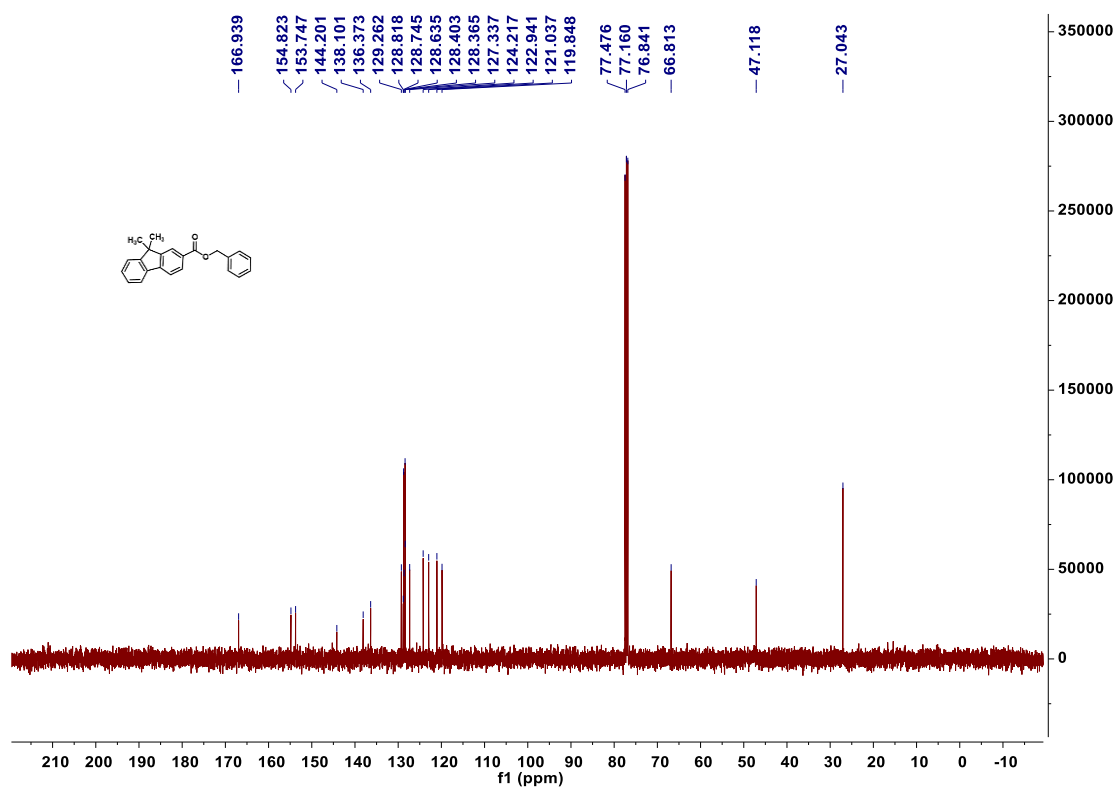
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3m**



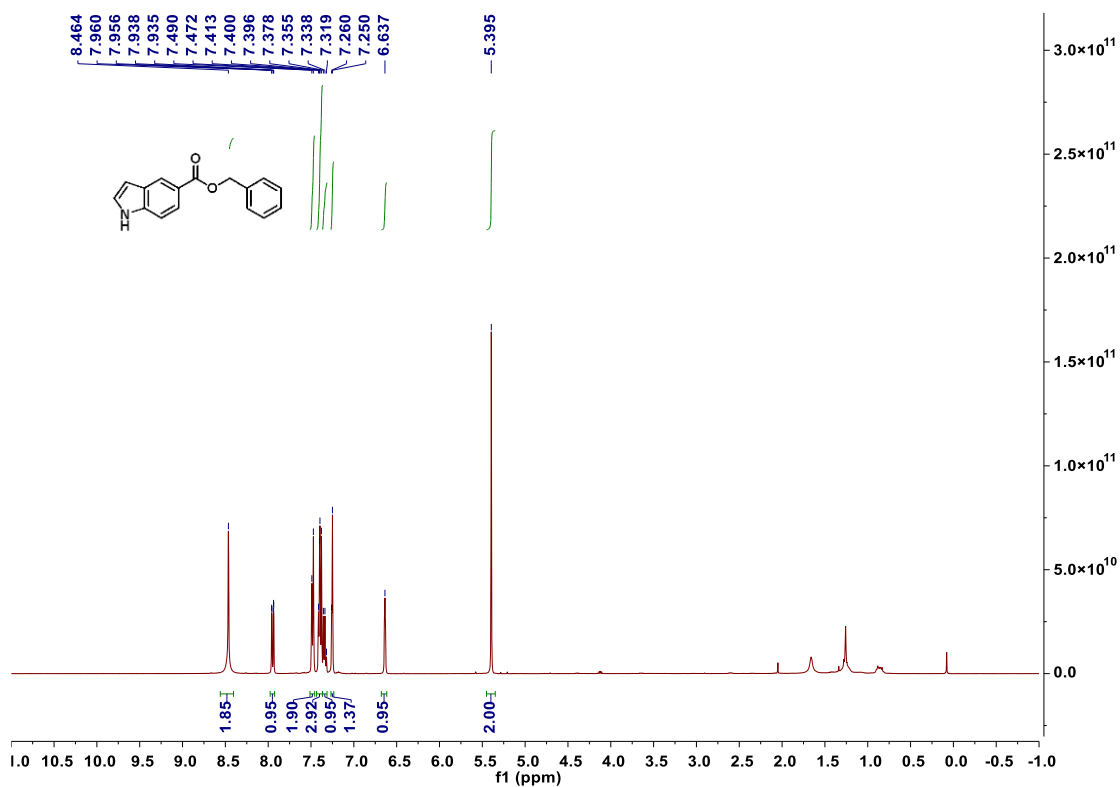
¹H NMR-spectrum (400 MHz, CDCl₃) of **3n**



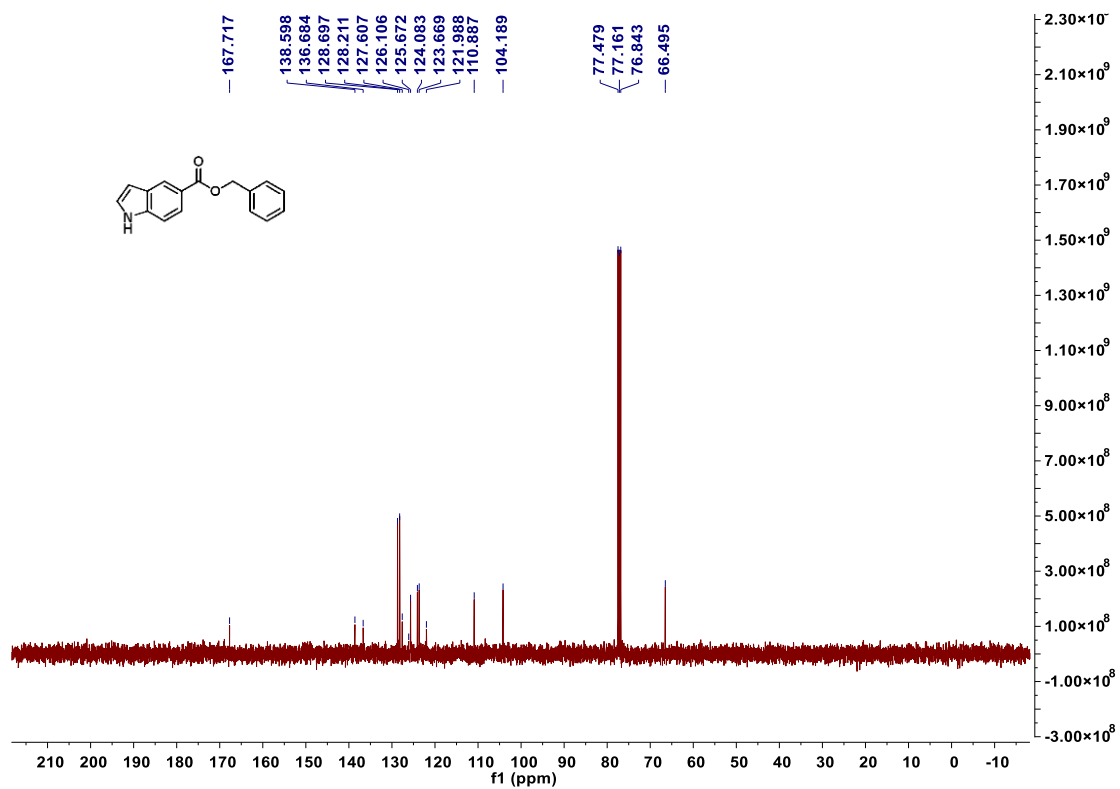
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3n**



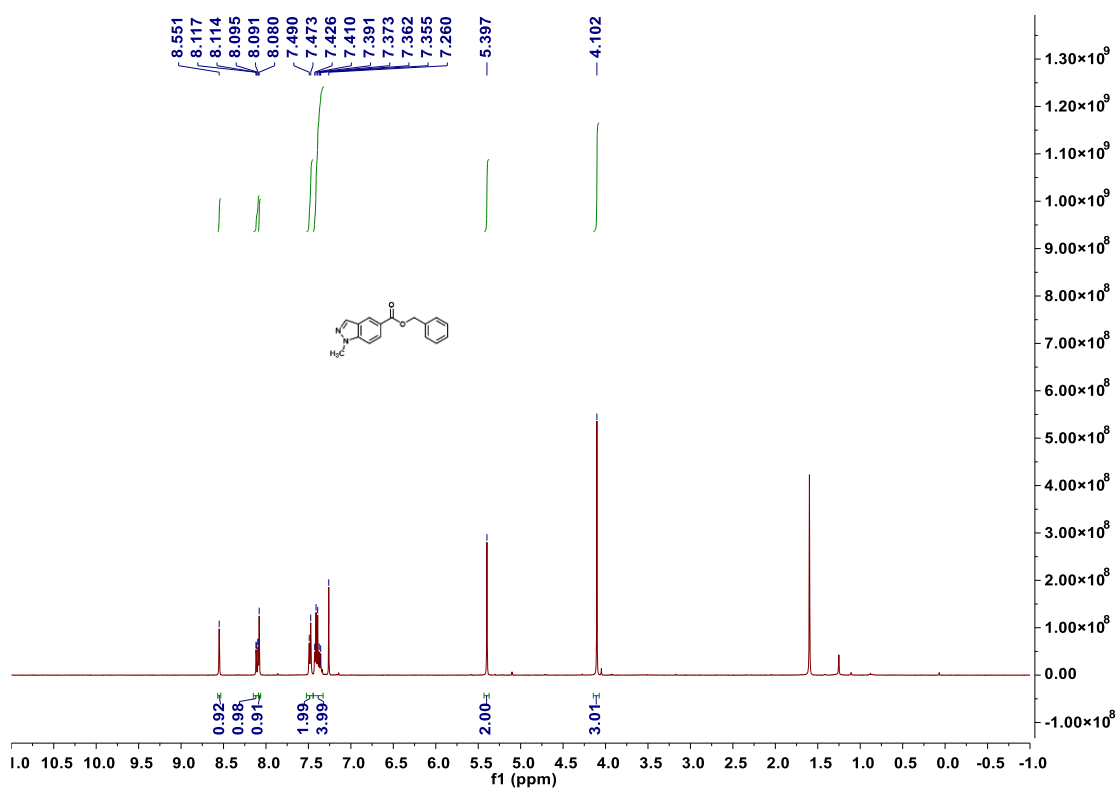
¹H NMR-spectrum (400 MHz, CDCl₃) of **3o**



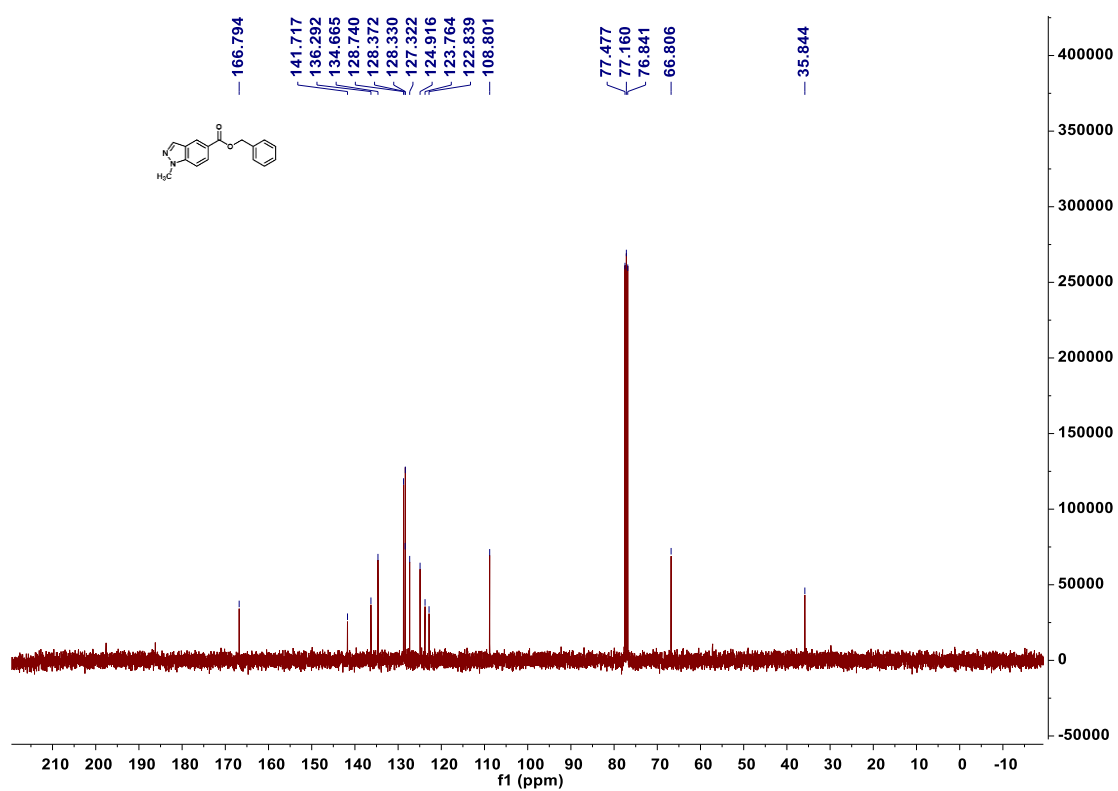
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3o**



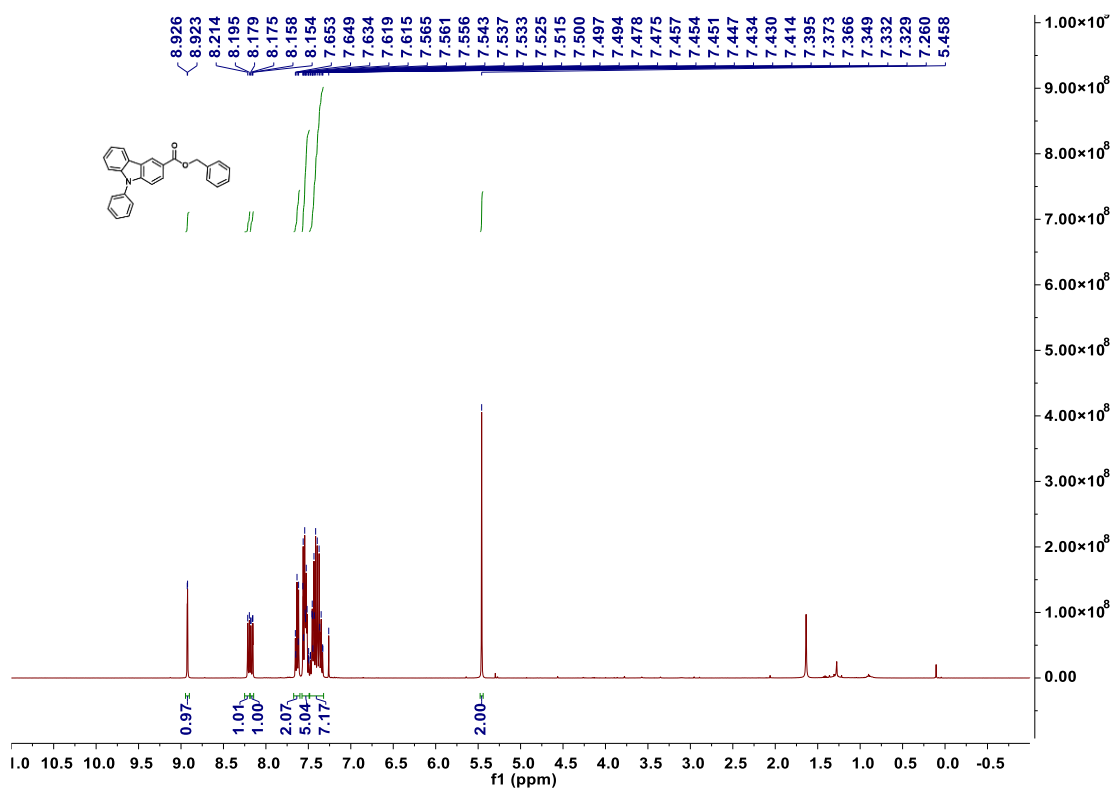
¹H NMR-spectrum (400 MHz, CDCl₃) of **3p**



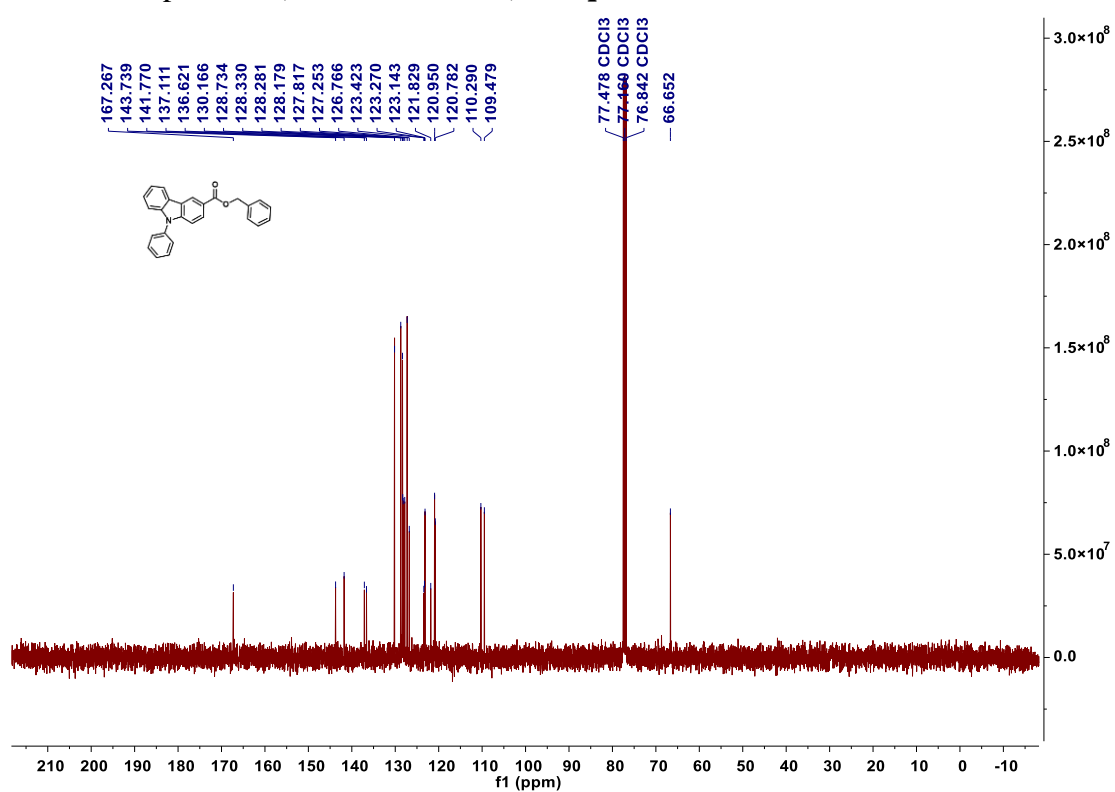
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3p**



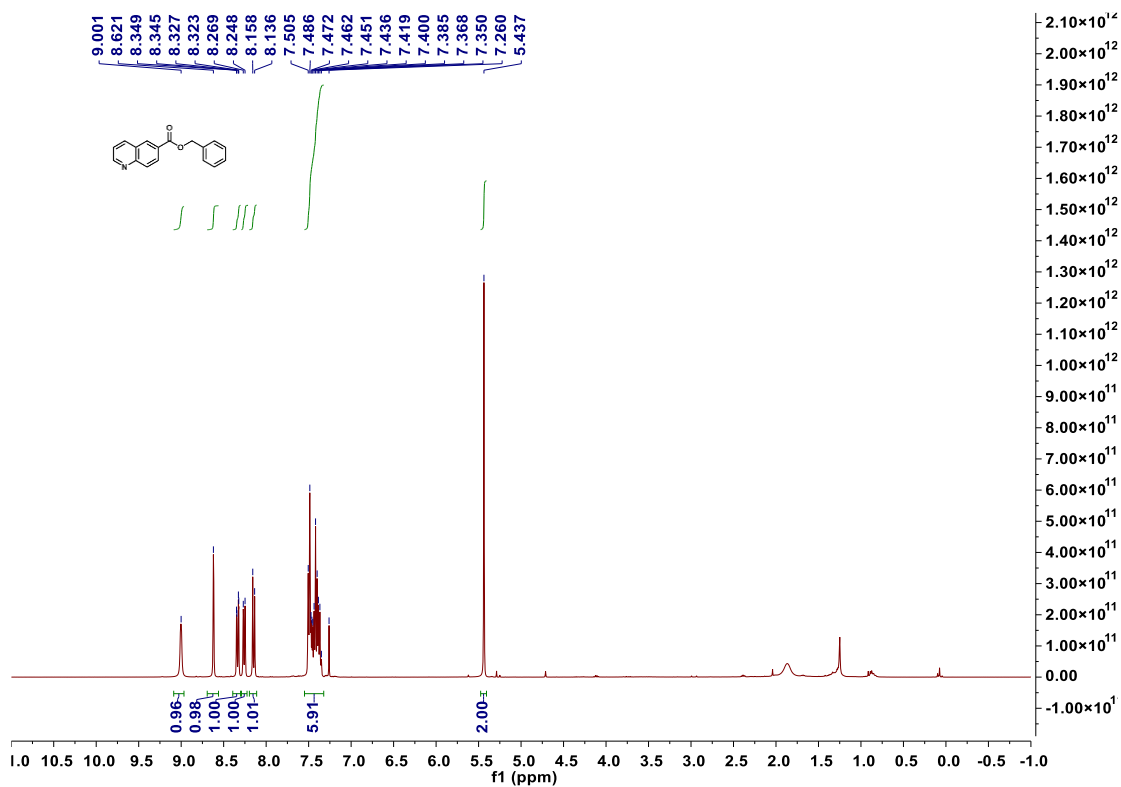
¹H NMR-spectrum (400 MHz, CDCl₃) of **3q**



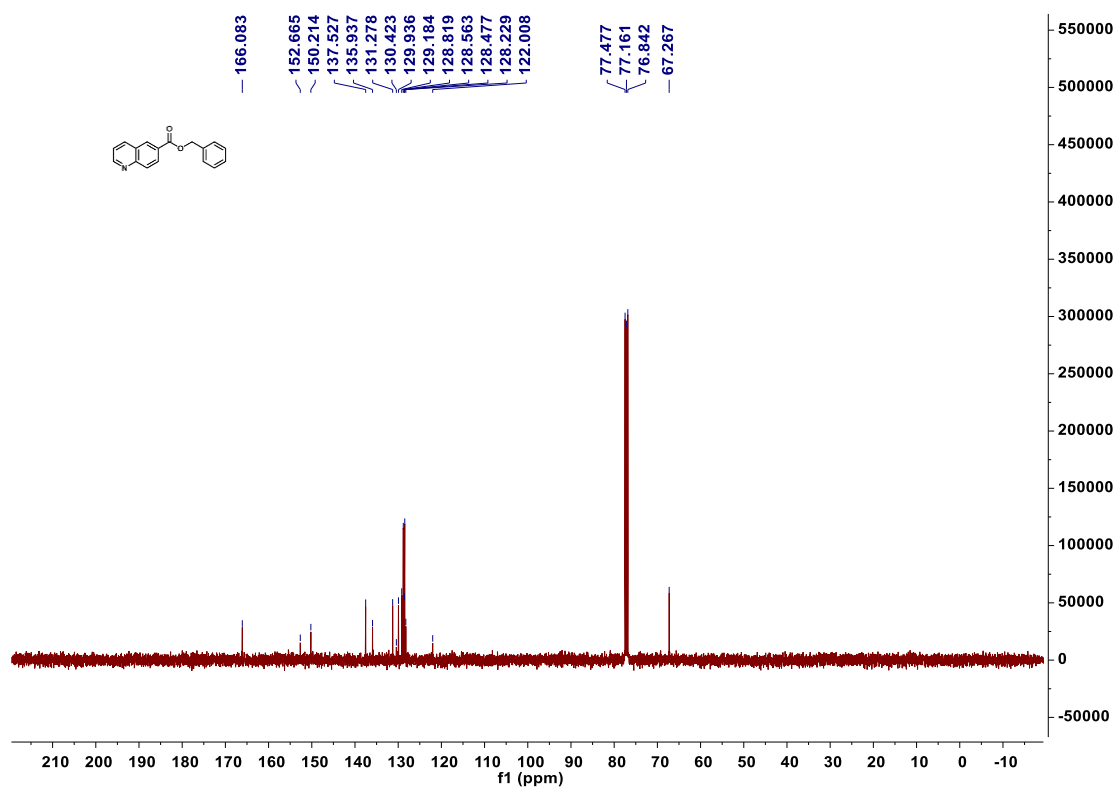
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3q**



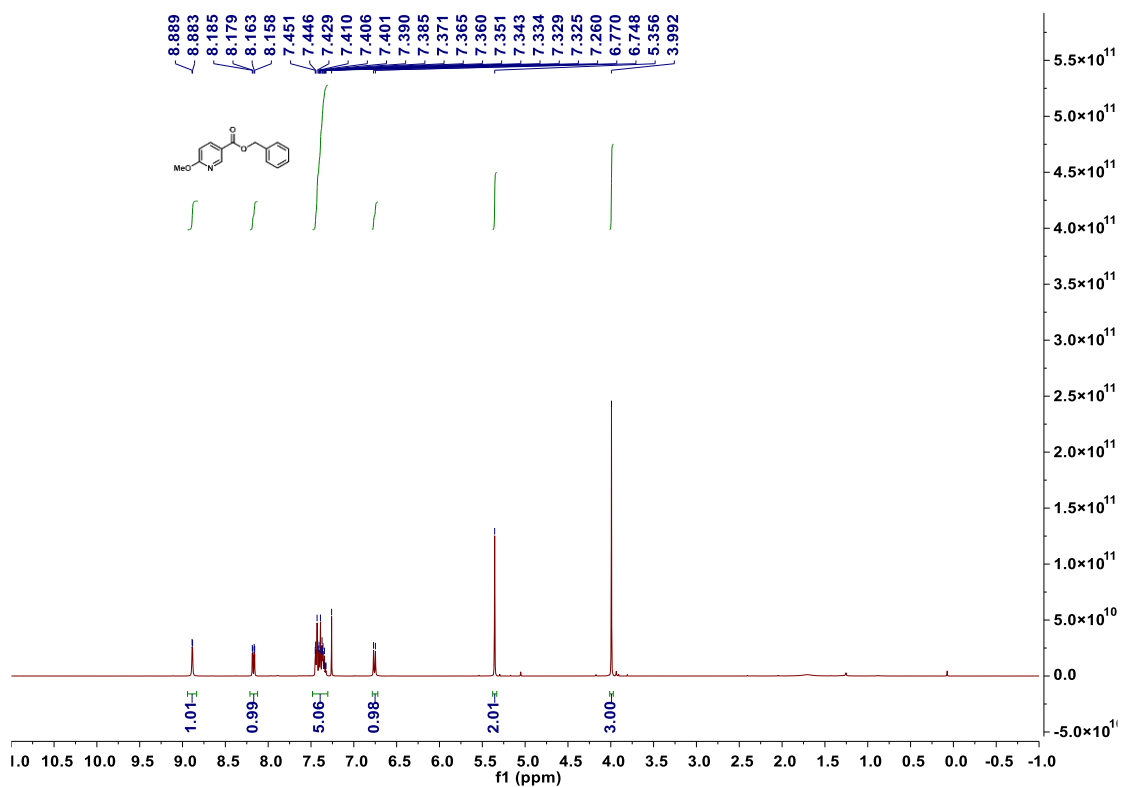
¹H NMR-spectrum (400 MHz, CDCl₃) of **3r**



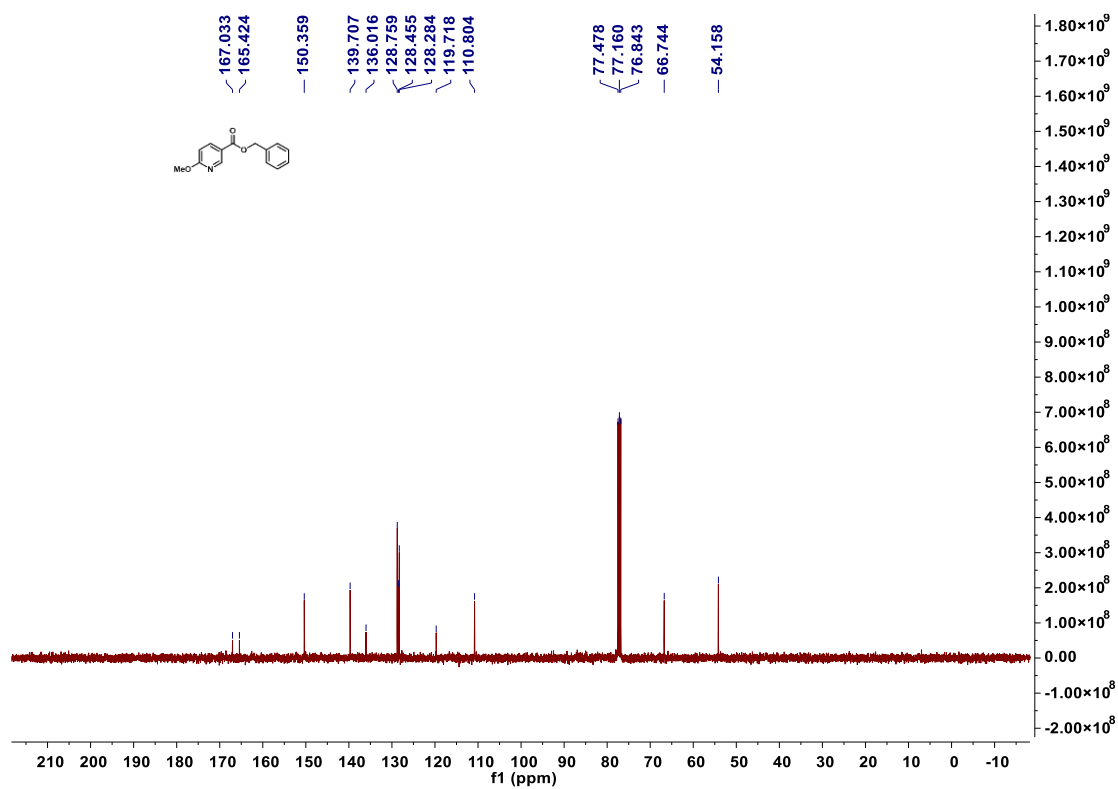
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3r**



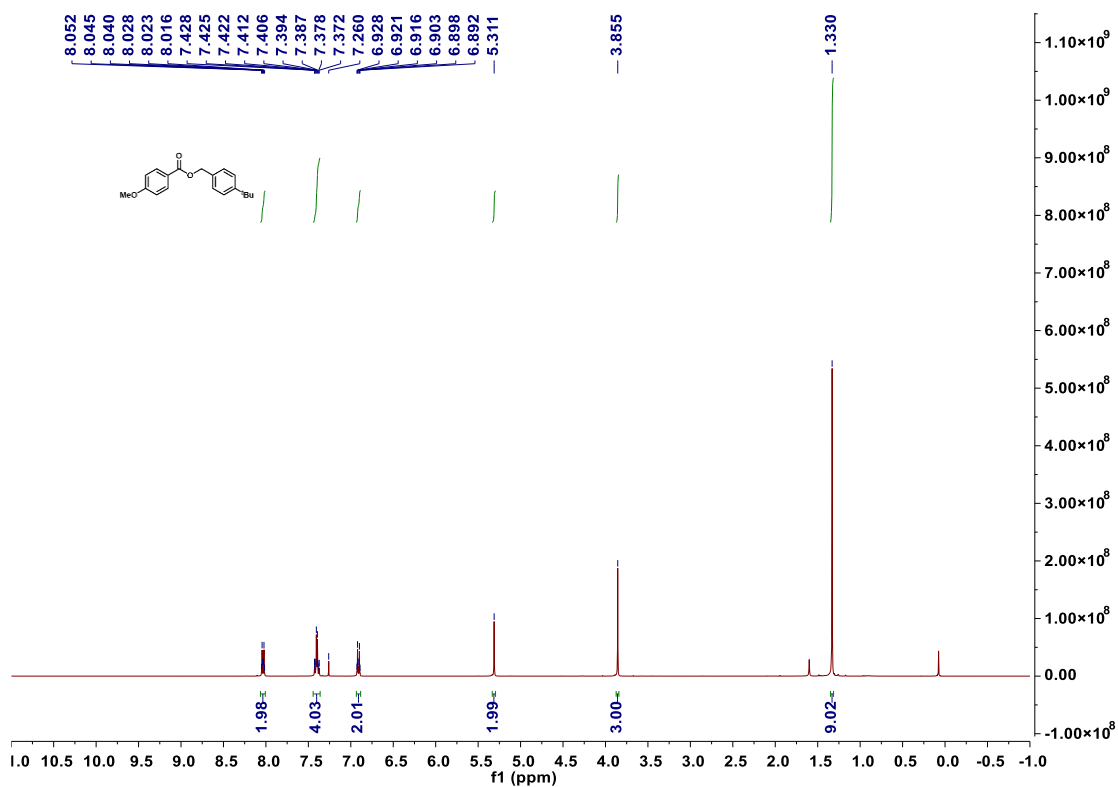
¹H NMR-spectrum (400 MHz, CDCl₃) of 3s



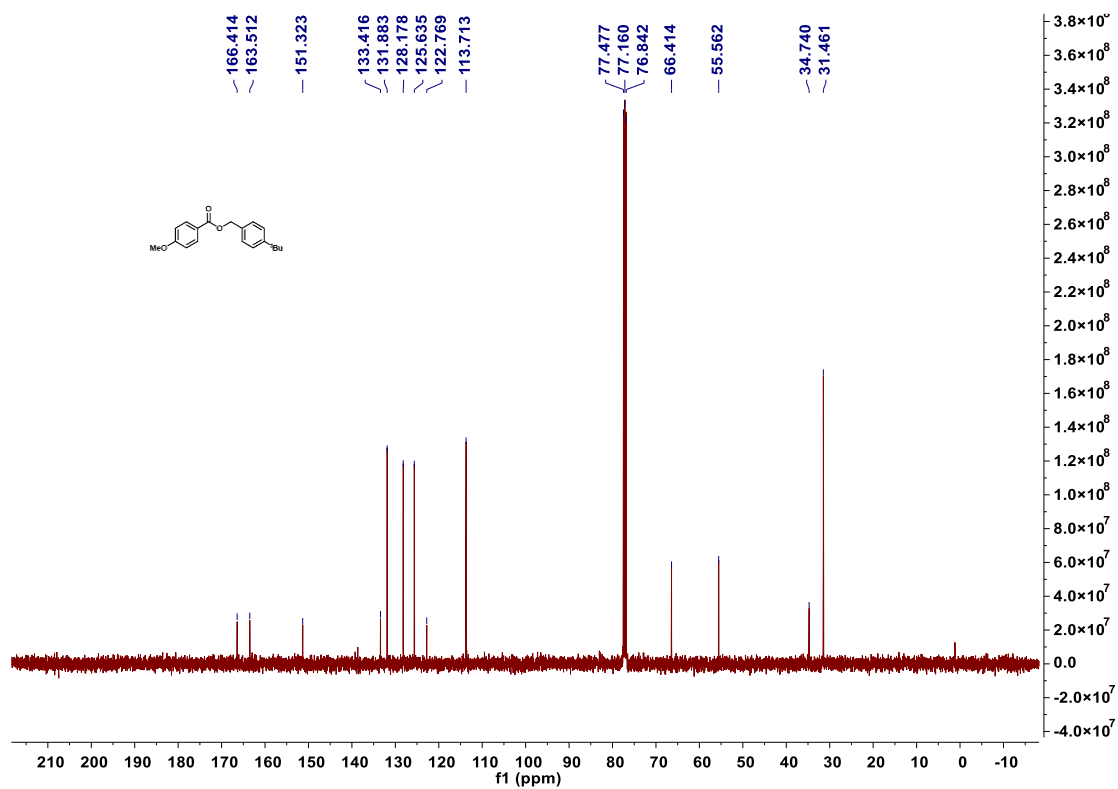
¹³C NMR-spectrum (100 MHz, CDCl₃) of 3s



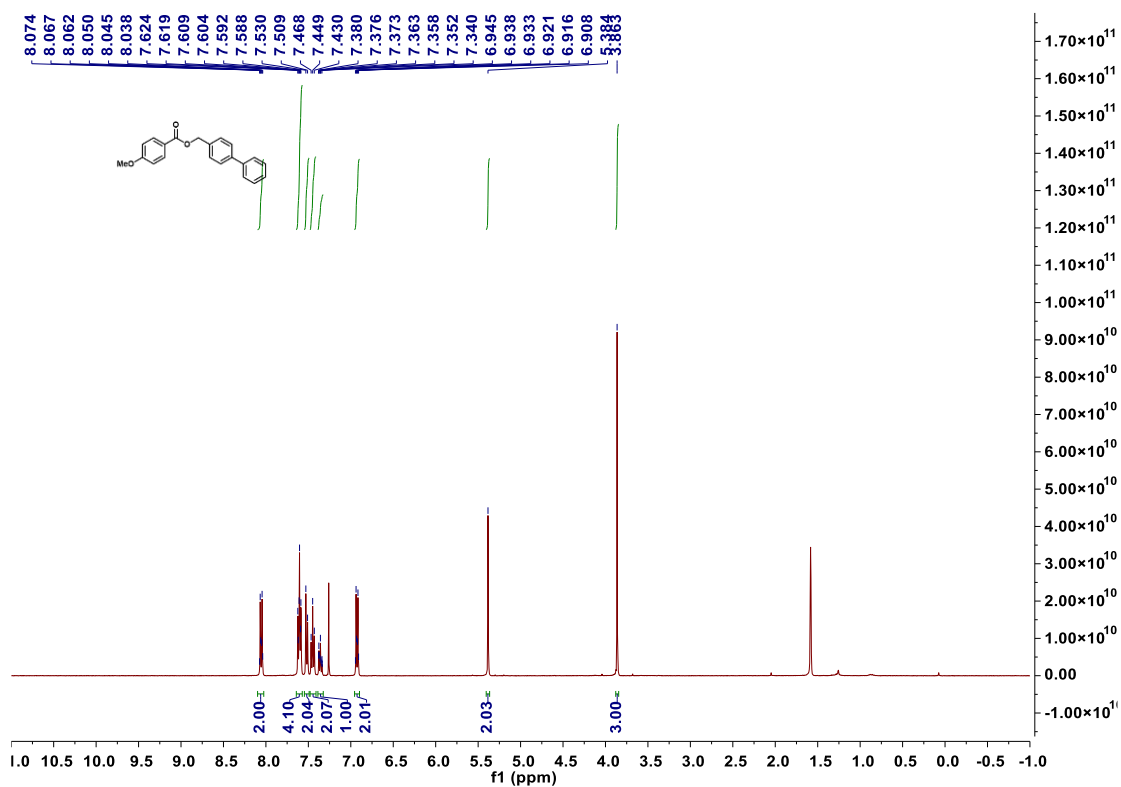
¹H NMR-spectrum (400 MHz, CDCl₃) of 3t



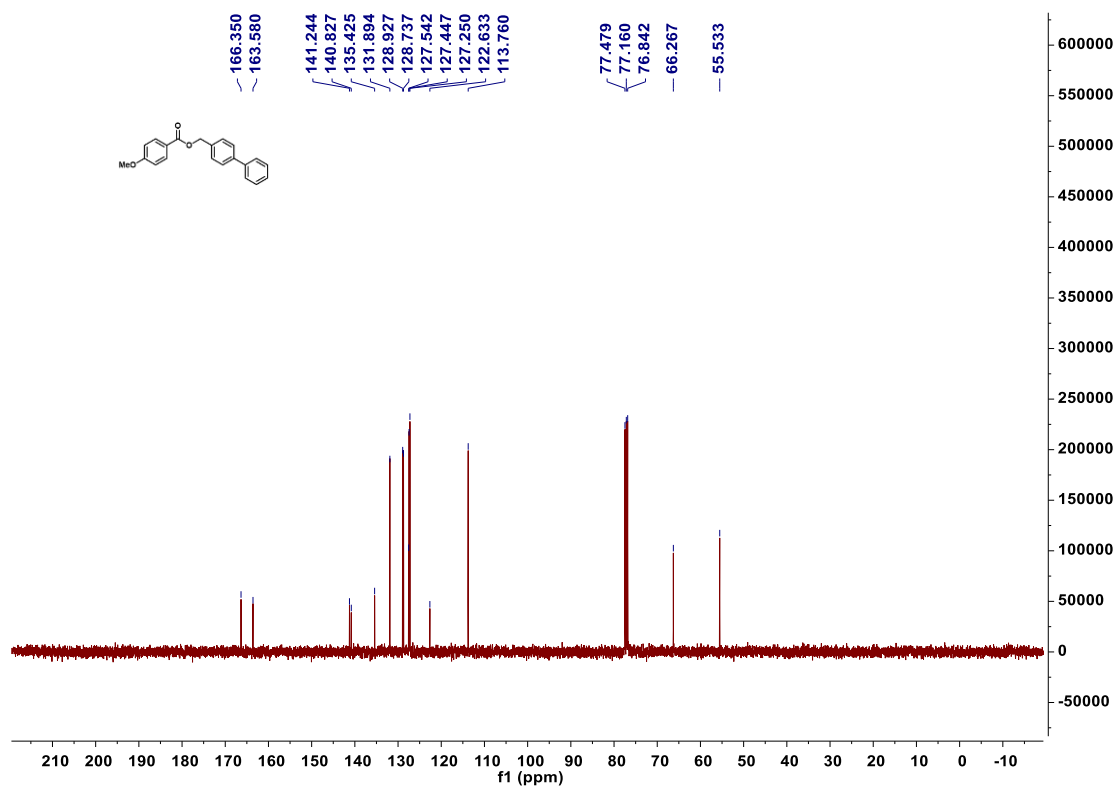
¹³C NMR-spectrum (100 MHz, CDCl₃) of 3t



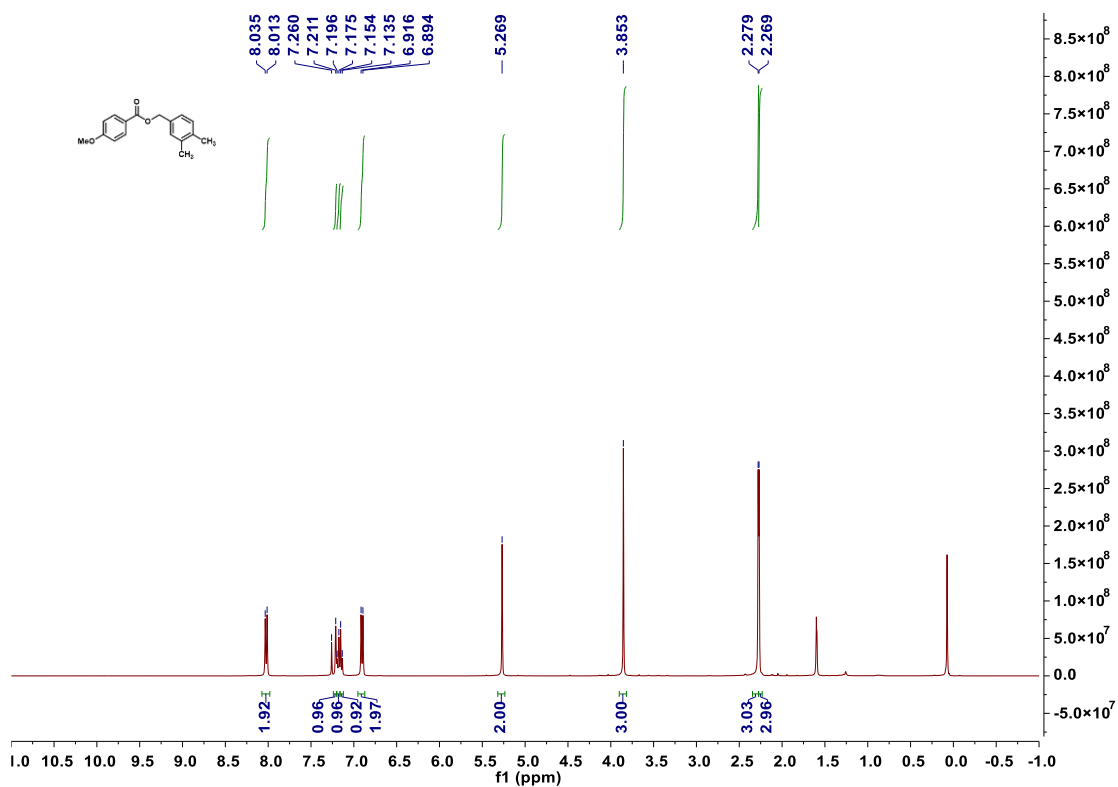
¹H NMR-spectrum (400 MHz, CDCl₃) of **3u**



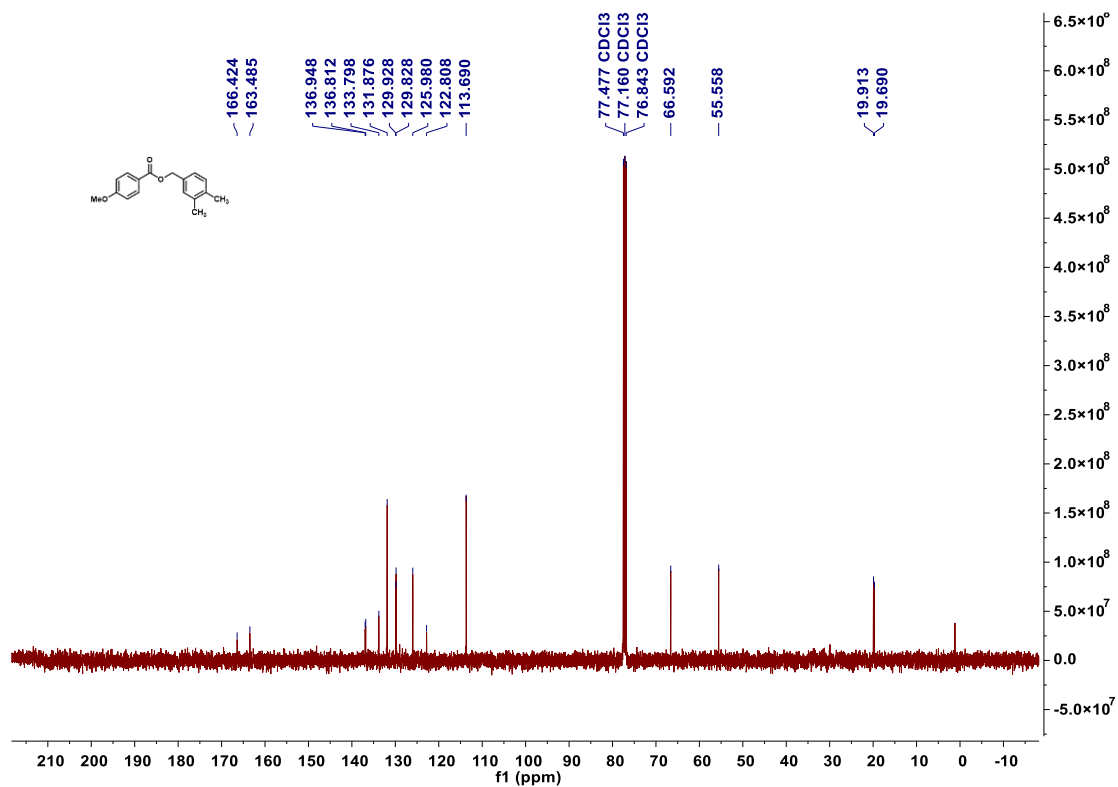
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3u**



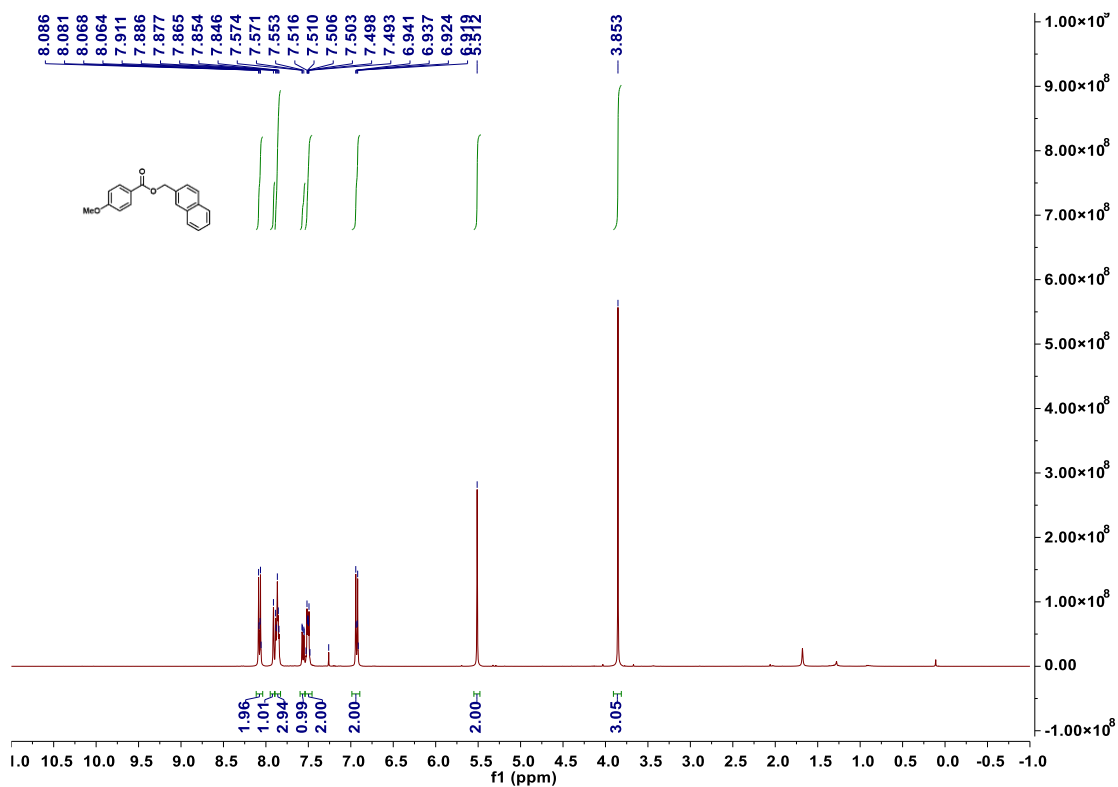
¹H NMR-spectrum (400 MHz, CDCl₃) of **3v**



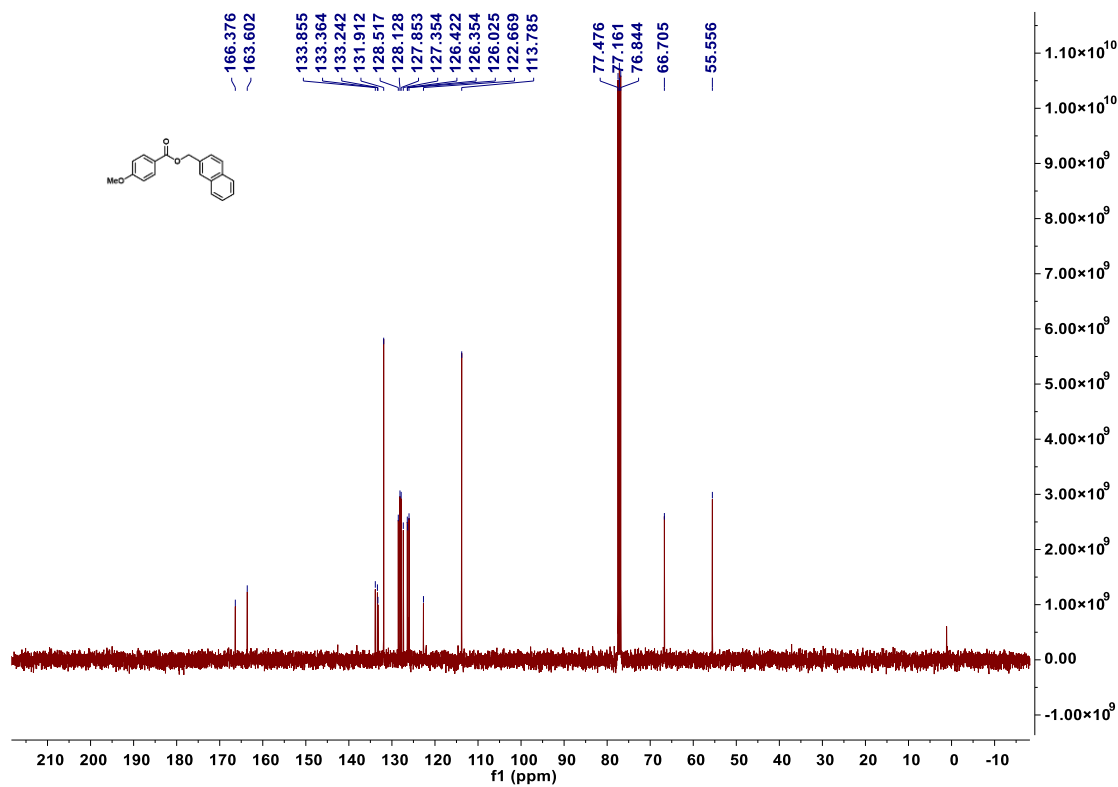
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3v**



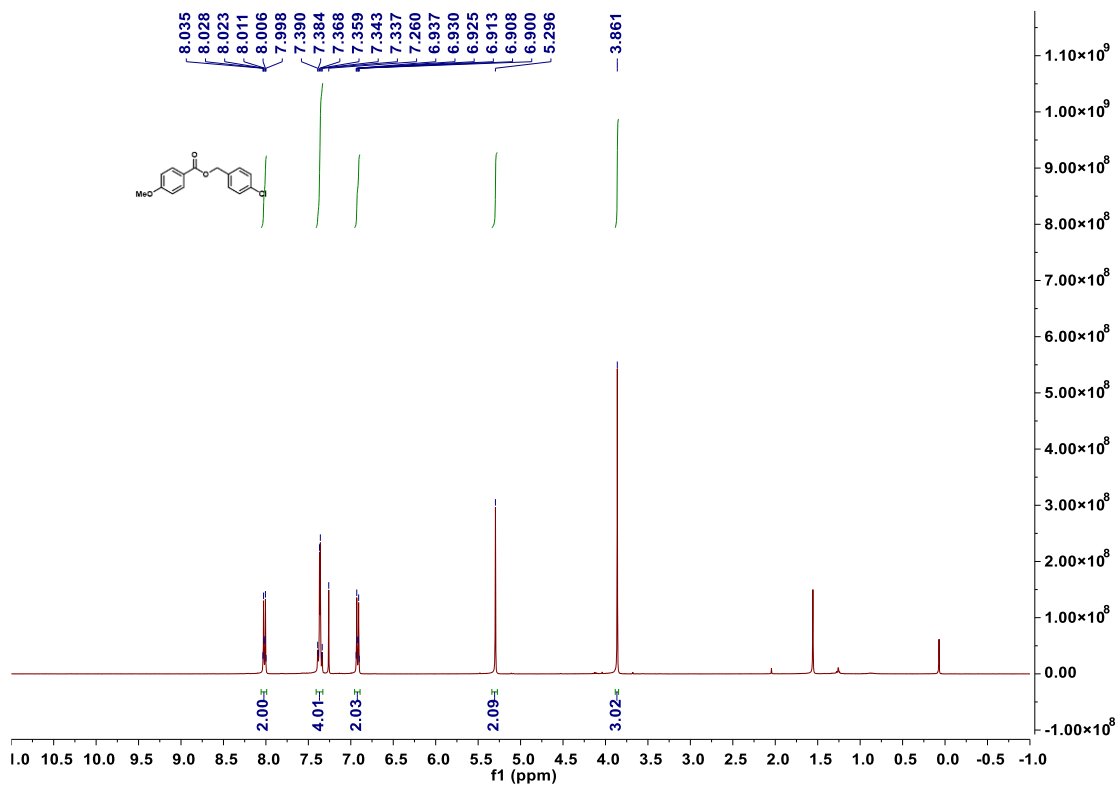
¹H NMR-spectrum (400 MHz, CDCl₃) of 3w



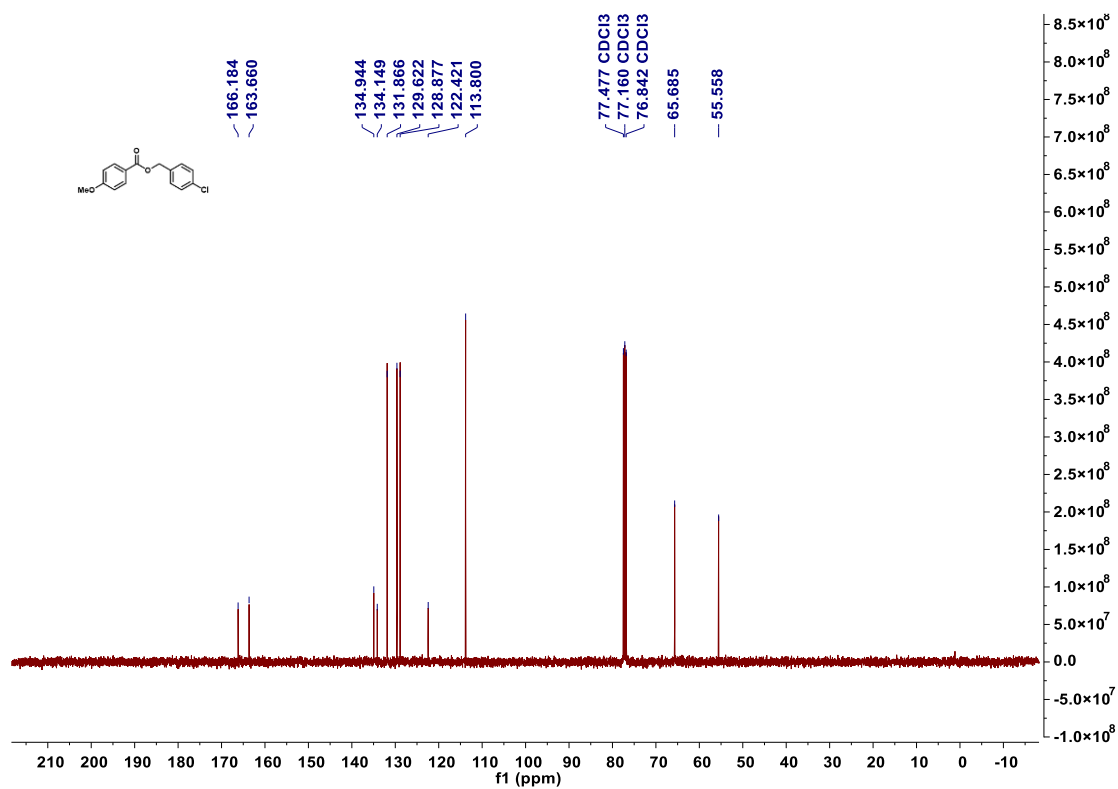
¹³C NMR-spectrum (100 MHz, CDCl₃) of 3w



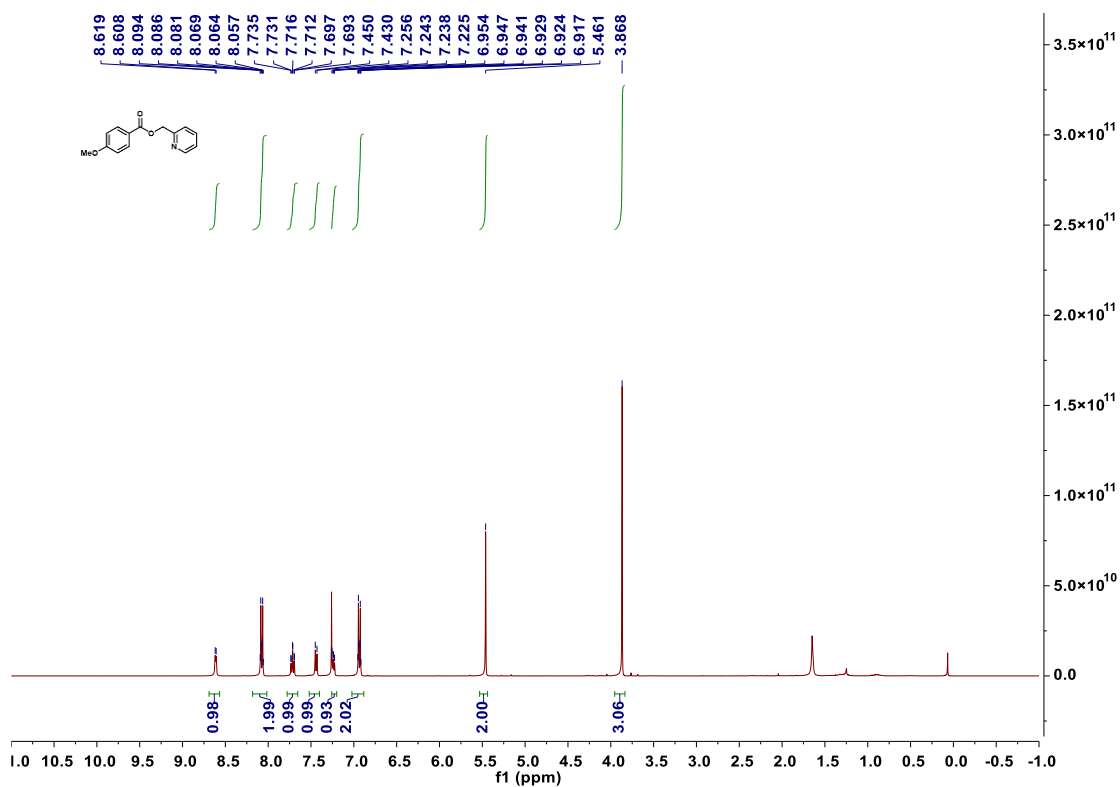
¹H NMR-spectrum (400 MHz, CDCl₃) of 3x



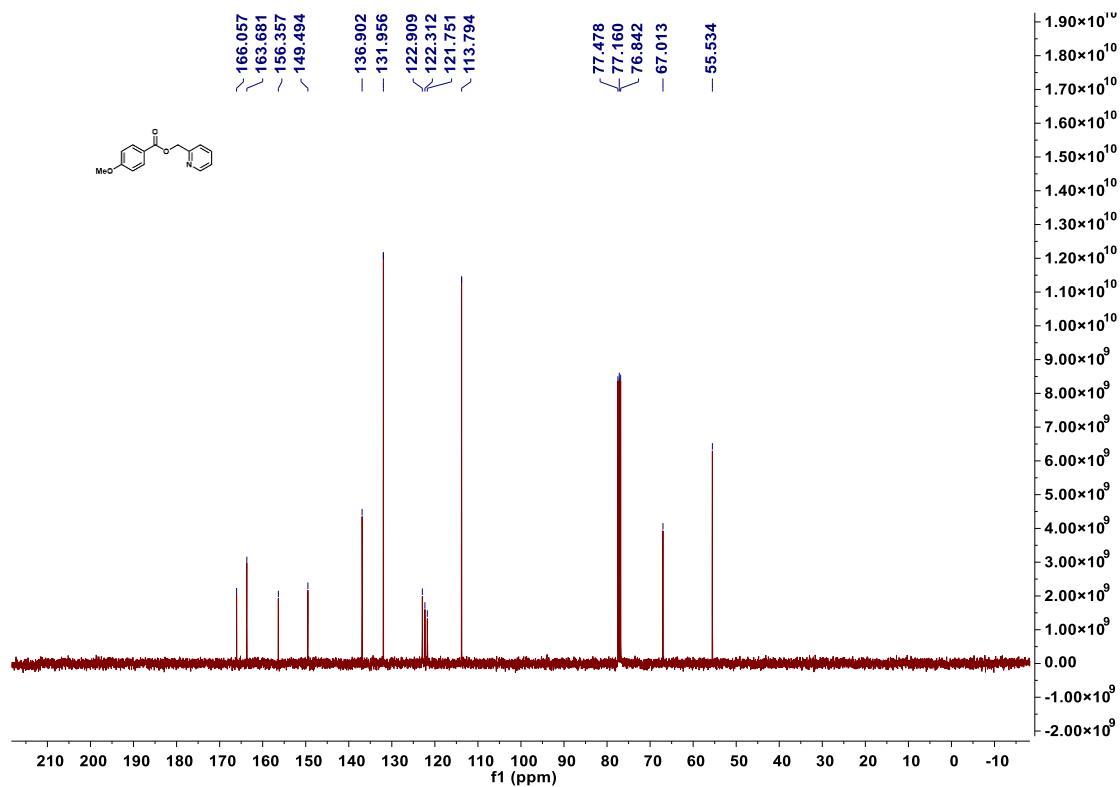
¹³C NMR-spectrum (100 MHz, CDCl₃) of 3x



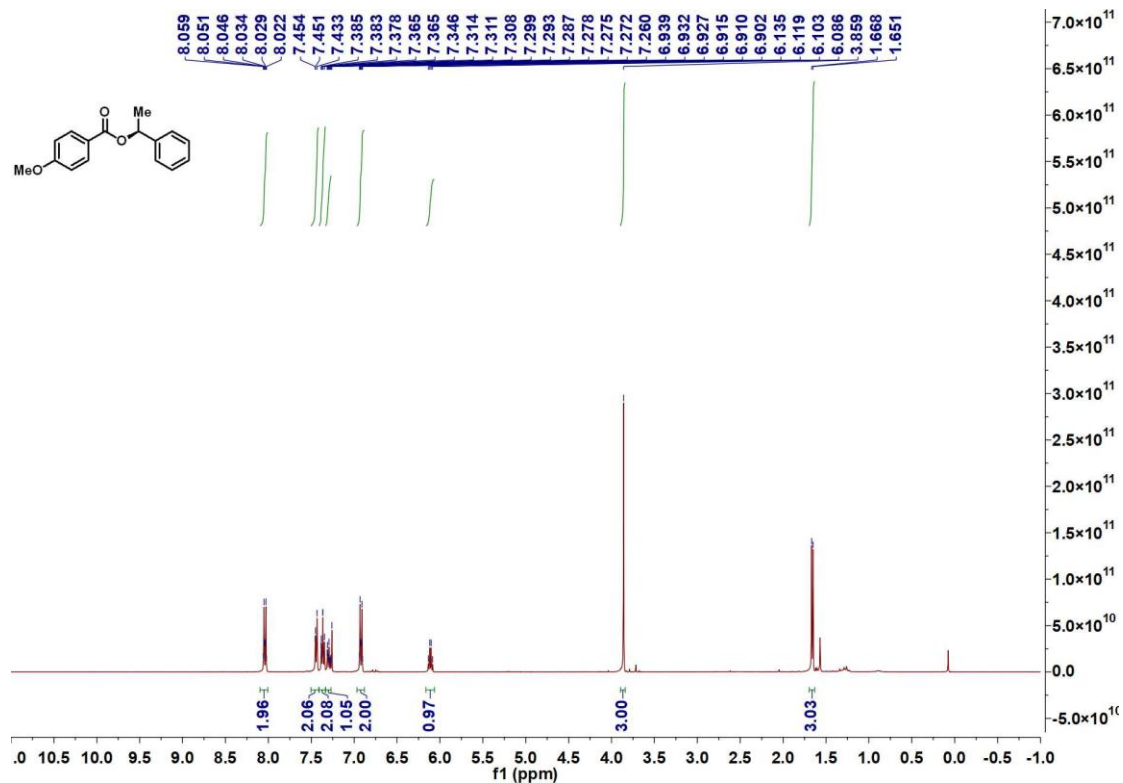
¹H NMR-spectrum (400 MHz, CDCl₃) of **3y**



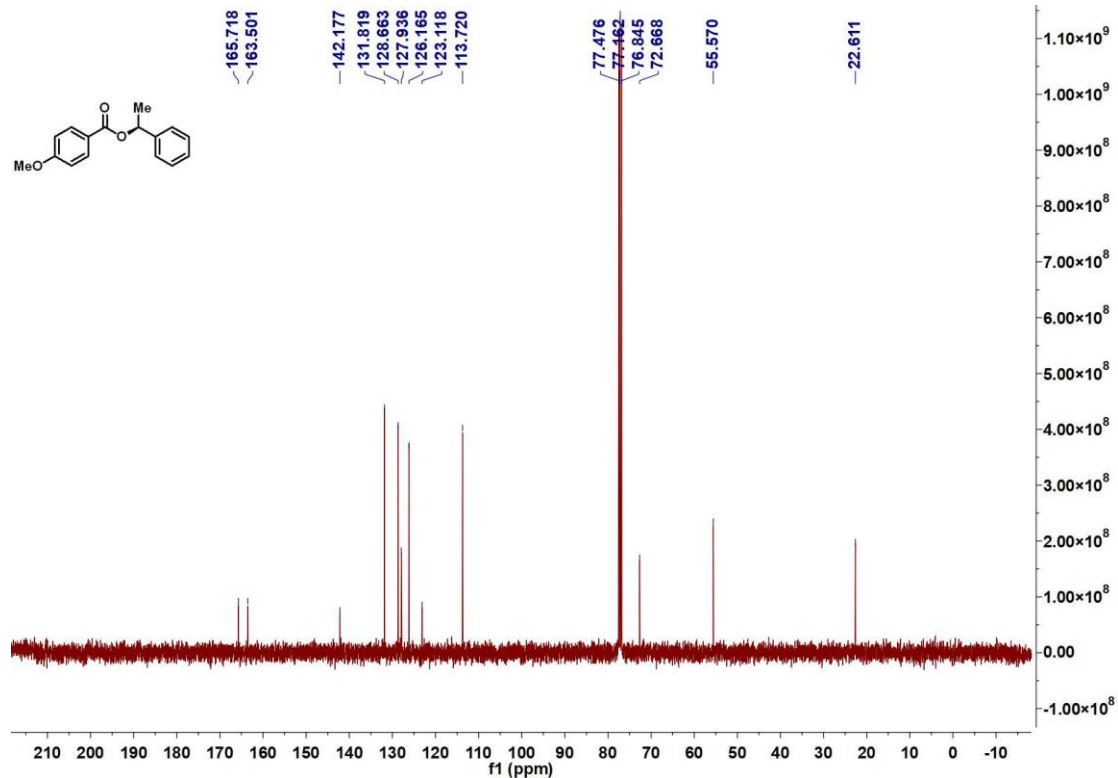
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3y**



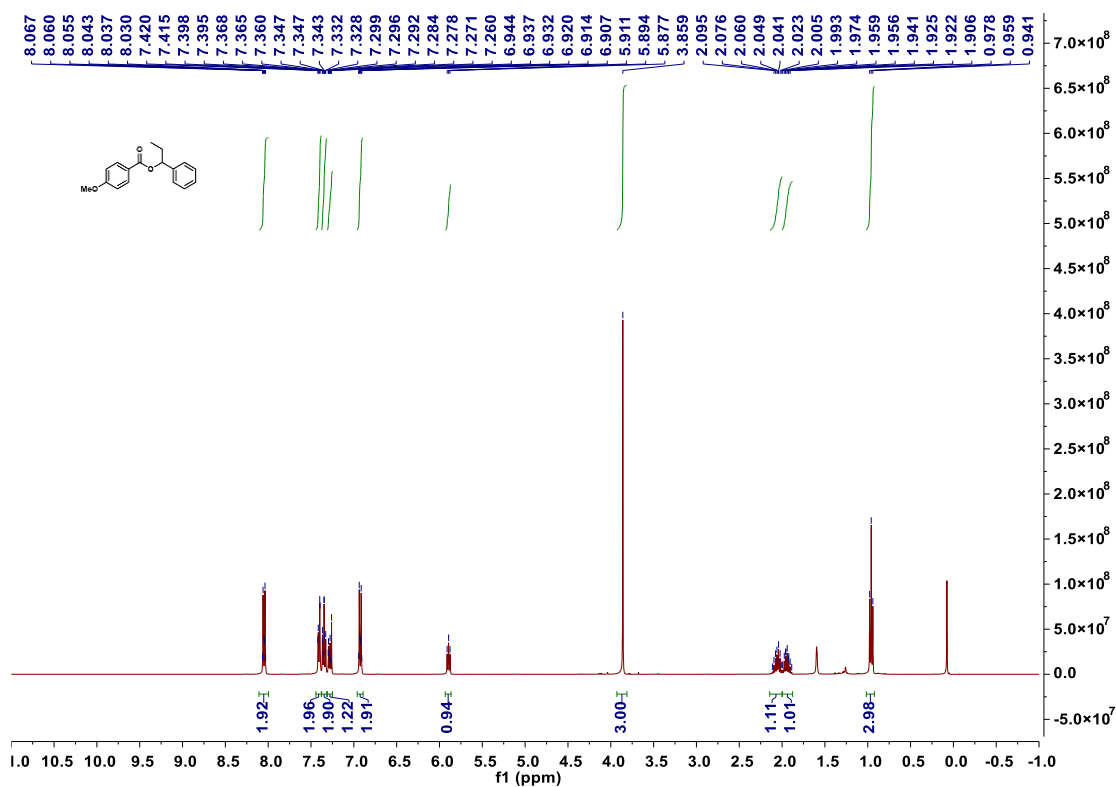
¹H NMR-spectrum (400 MHz, CDCl₃) of **3z**



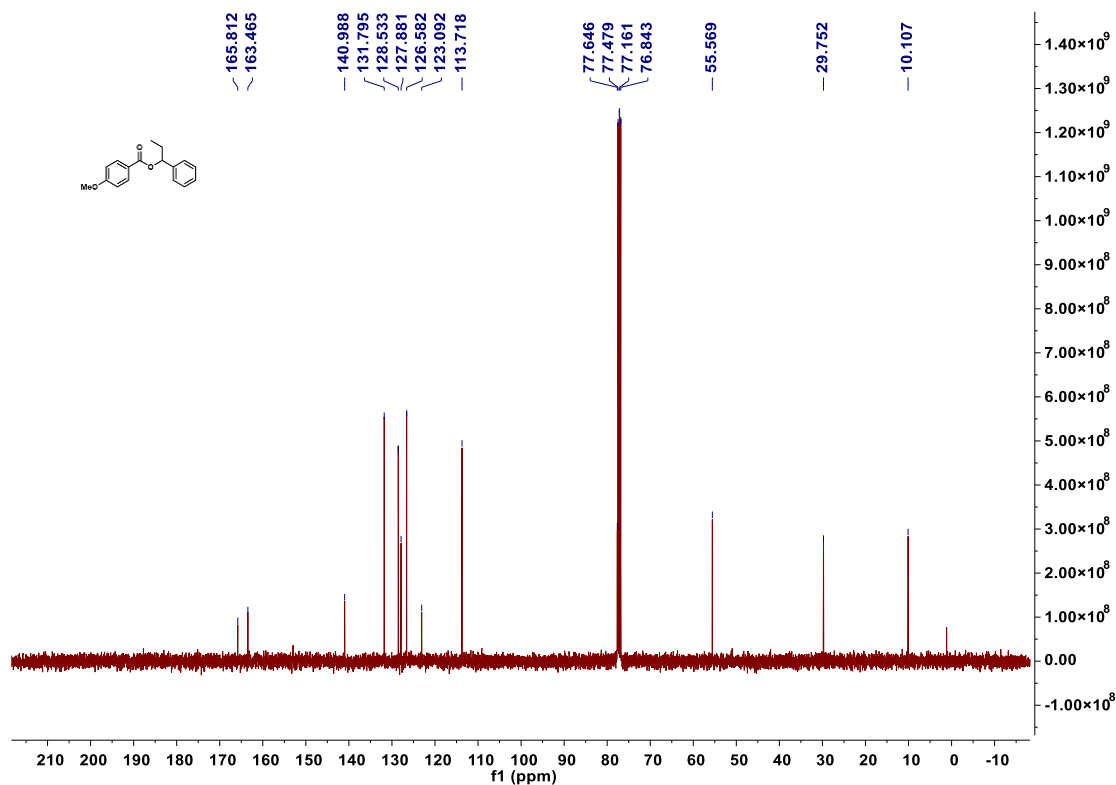
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3z**



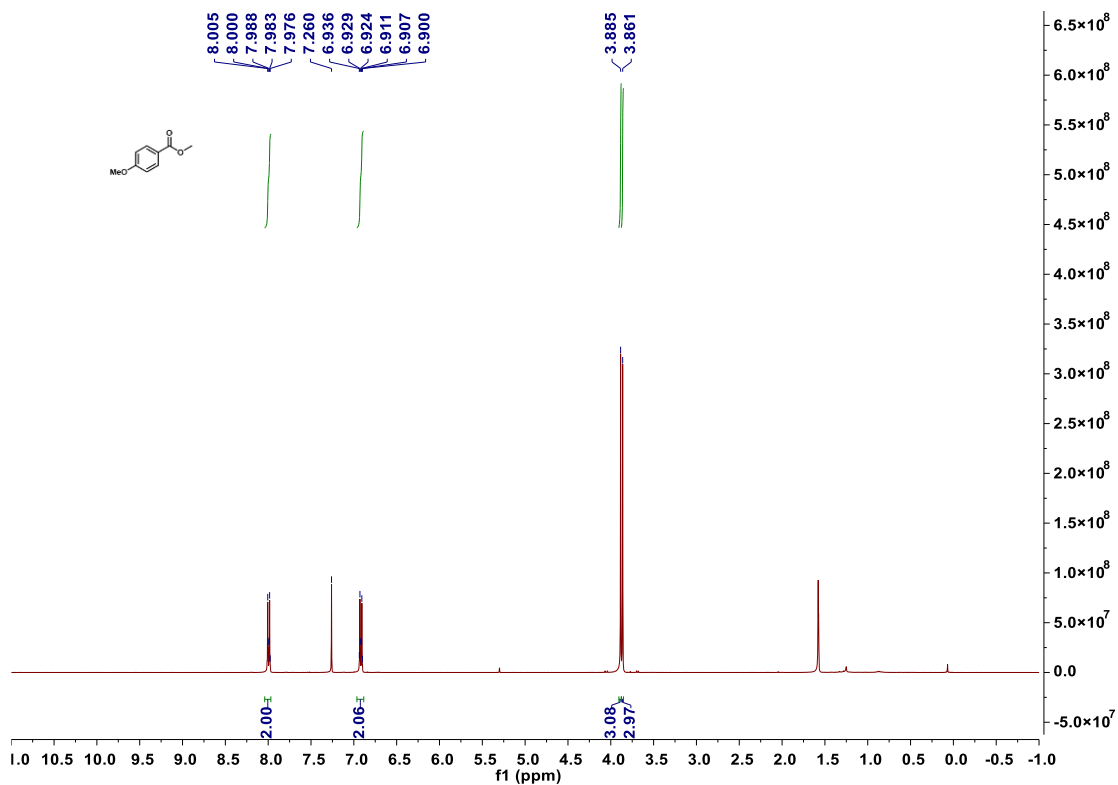
¹H NMR-spectrum (400 MHz, CDCl₃) of 3aa



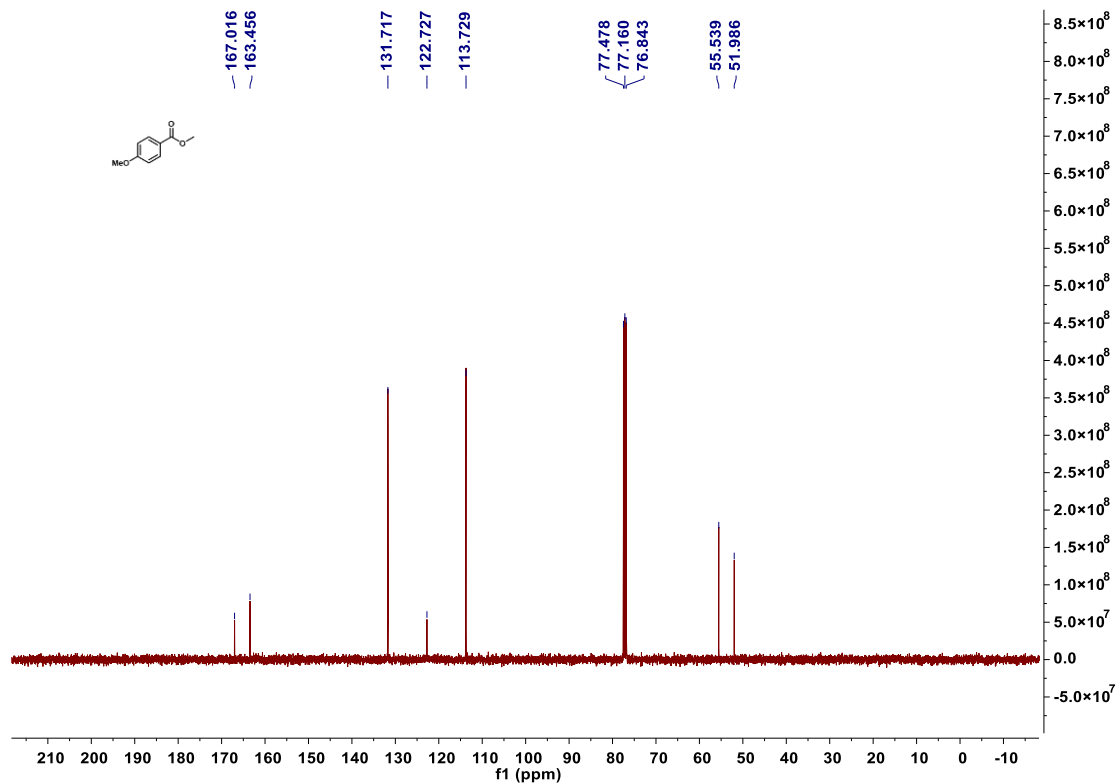
¹³C NMR-spectrum (100 MHz, CDCl₃) of 3aa



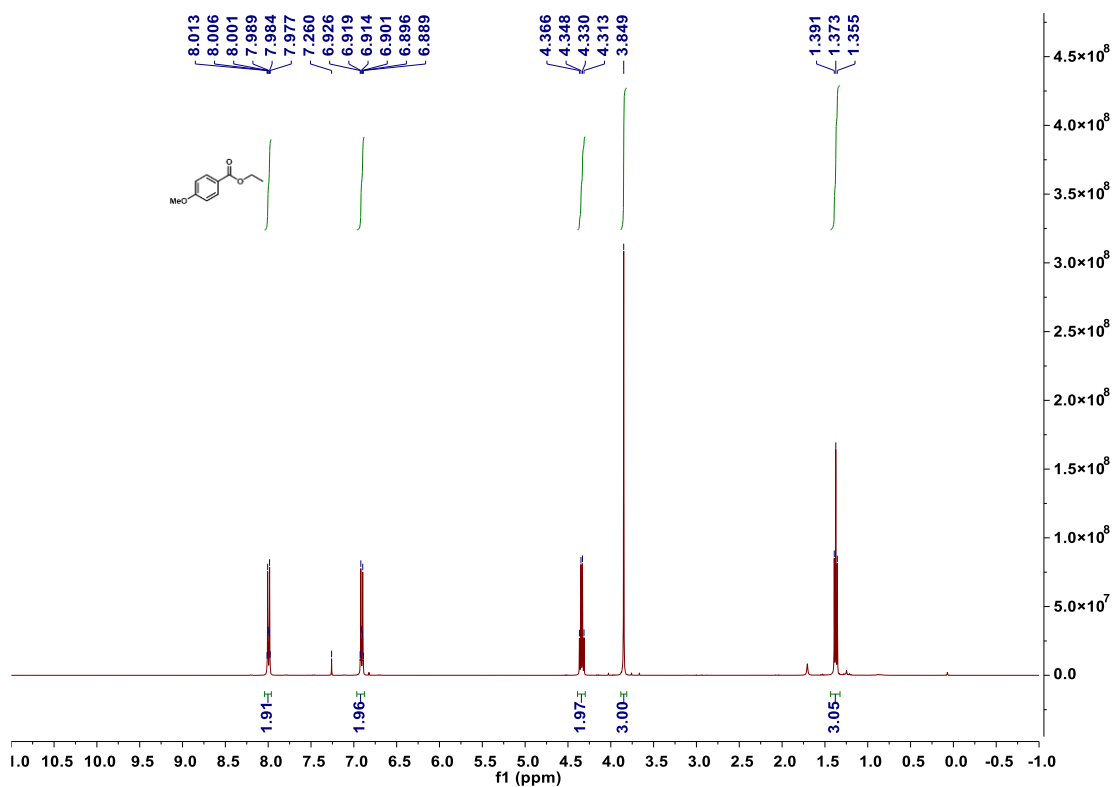
¹H NMR-spectrum (400 MHz, CDCl₃) of **3ab**



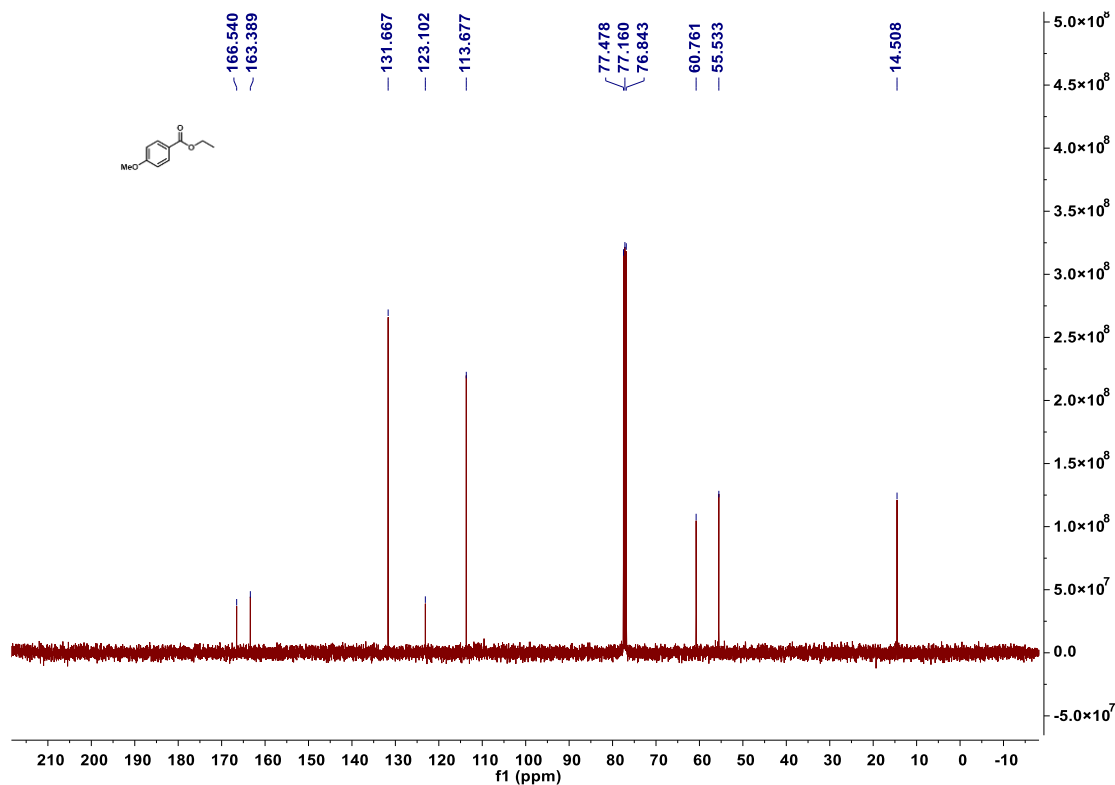
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3ab**



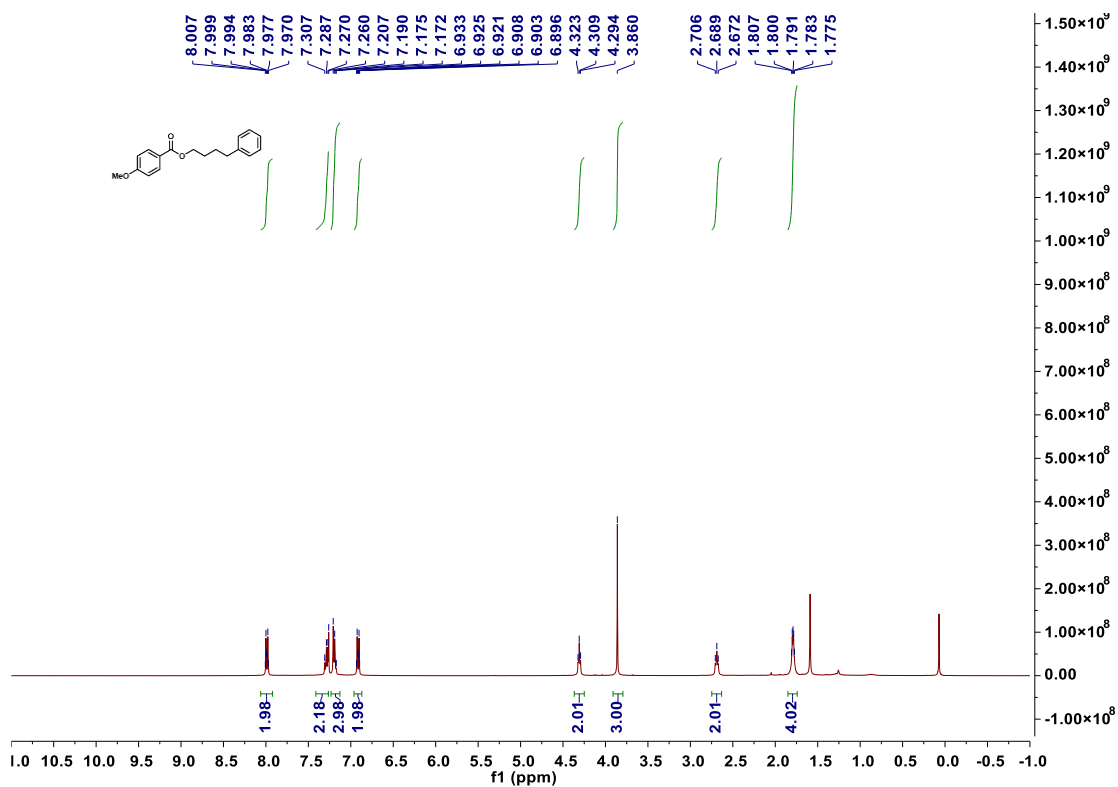
¹H NMR-spectrum (400 MHz, CDCl₃) of **3ac**



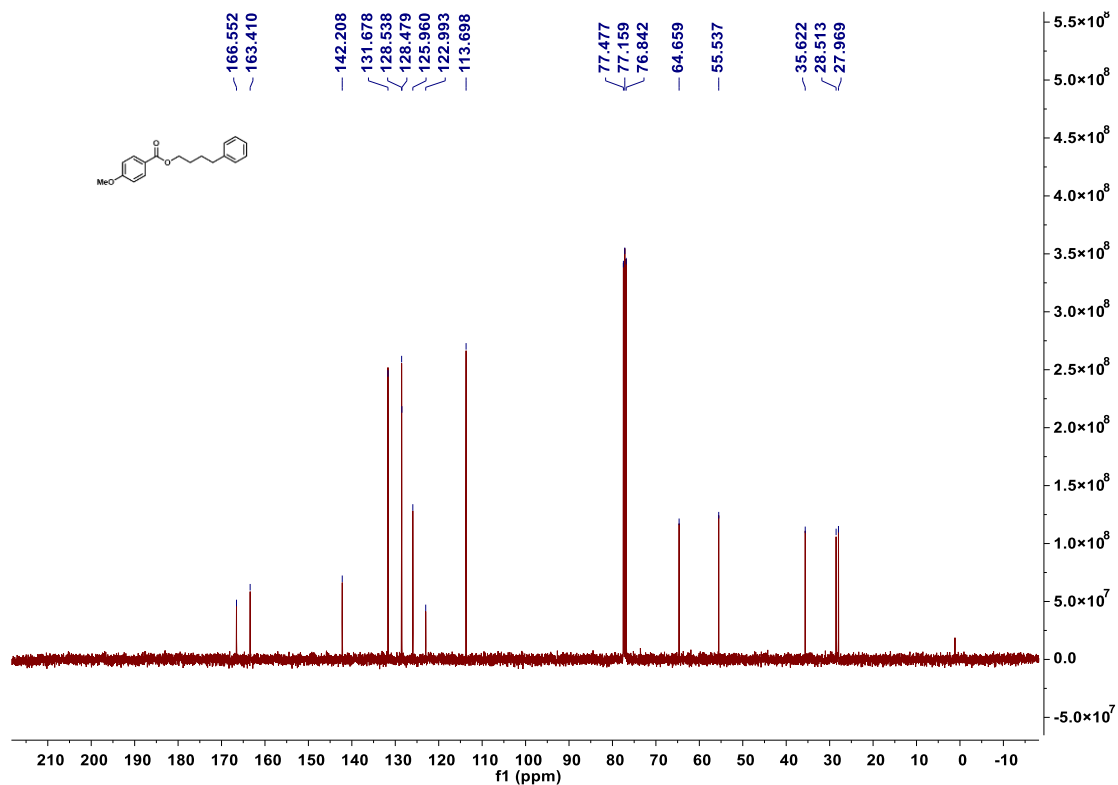
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3ac**



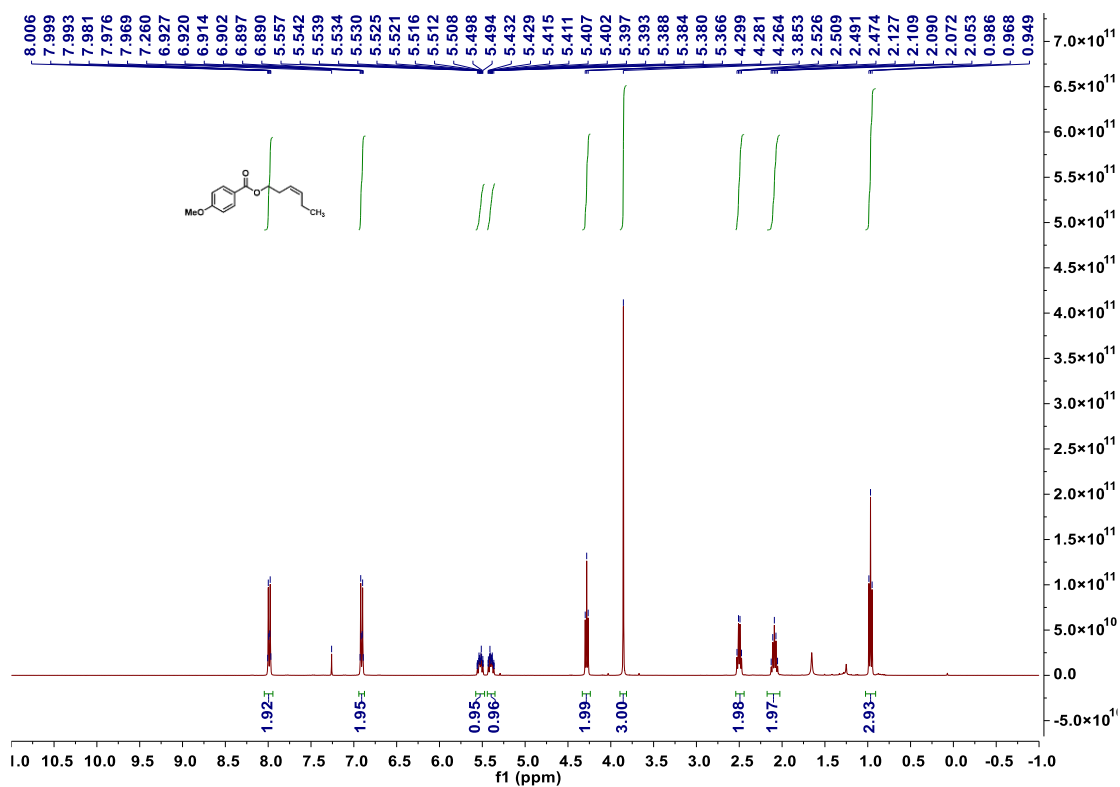
¹H NMR-spectrum (400 MHz, CDCl₃) of **3ad**



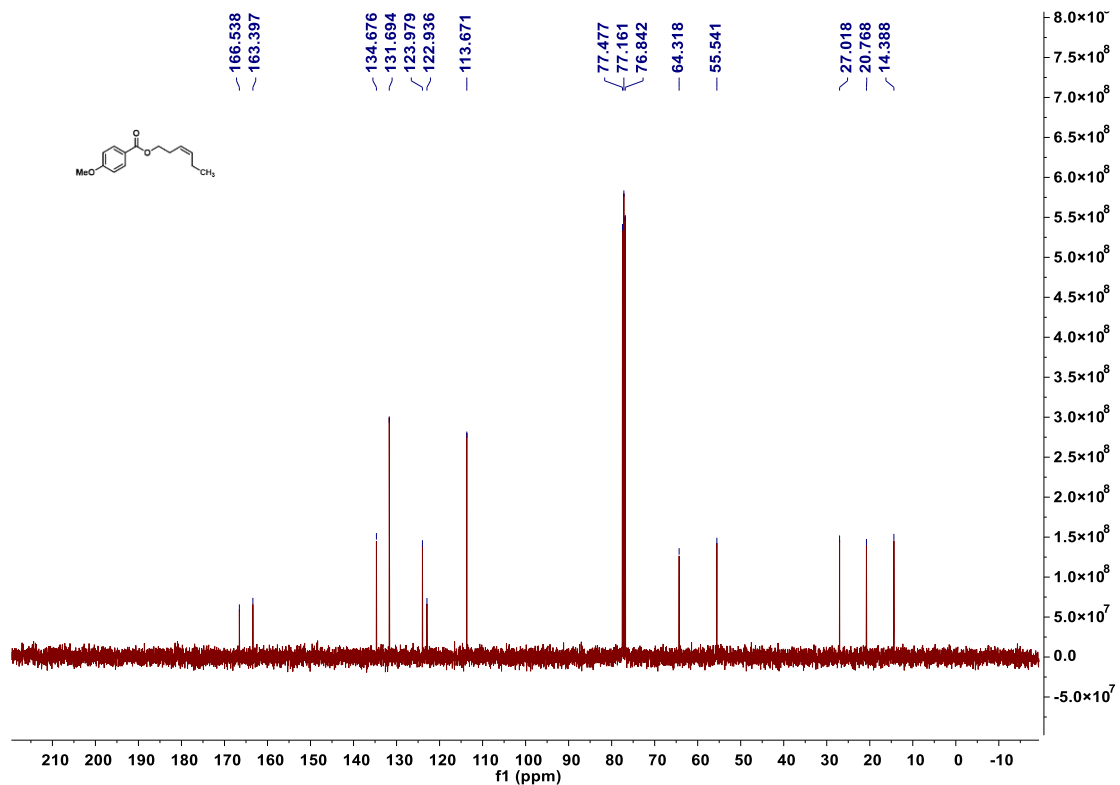
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3ad**



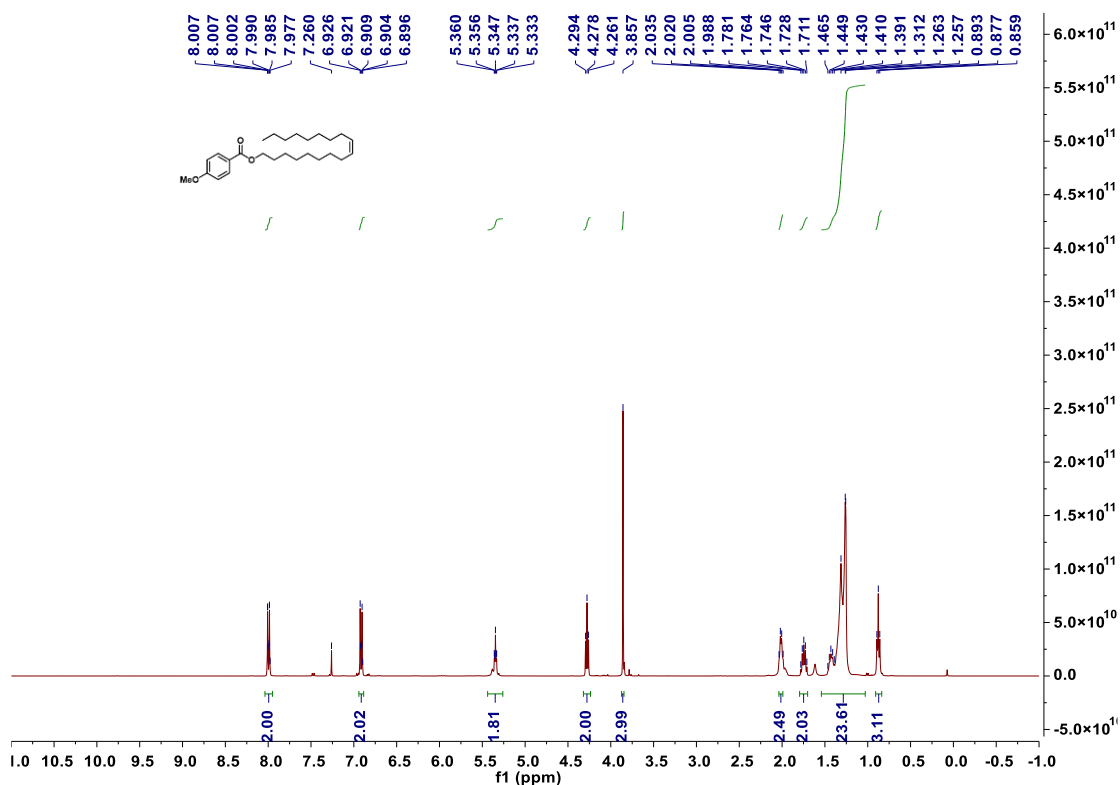
¹H NMR-spectrum (400 MHz, CDCl₃) of 3ae



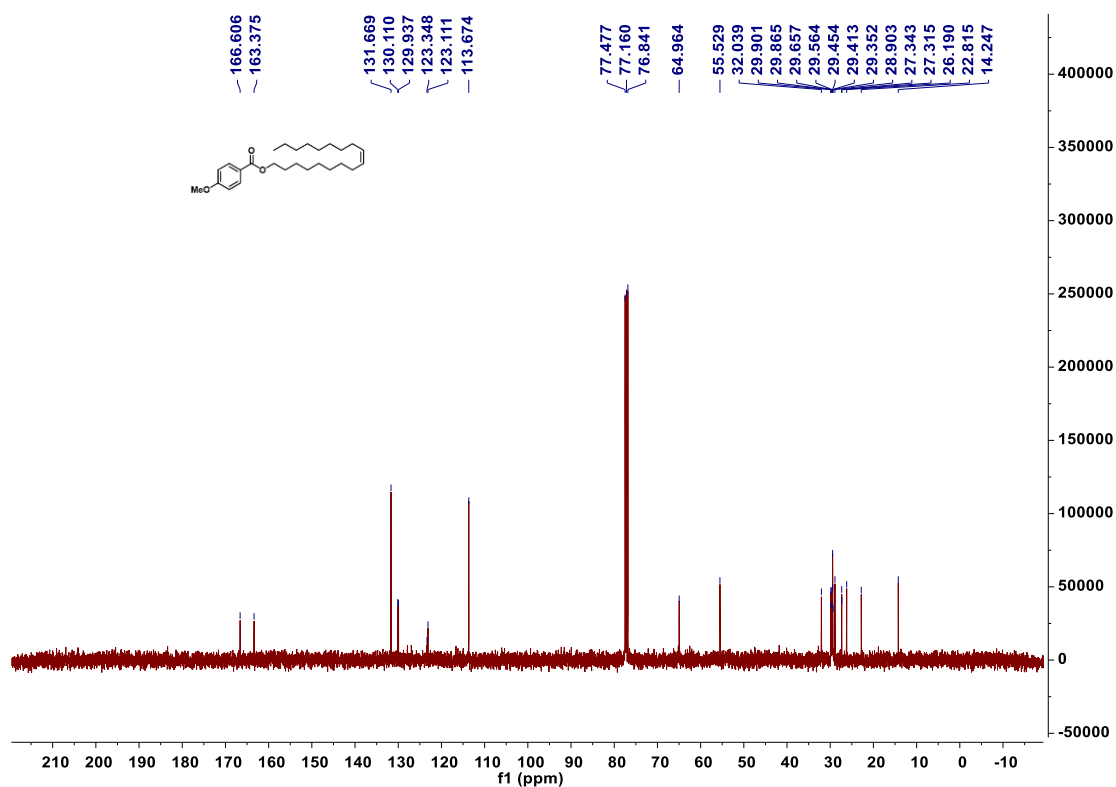
¹³C NMR-spectrum (100 MHz, CDCl₃) of 3ae



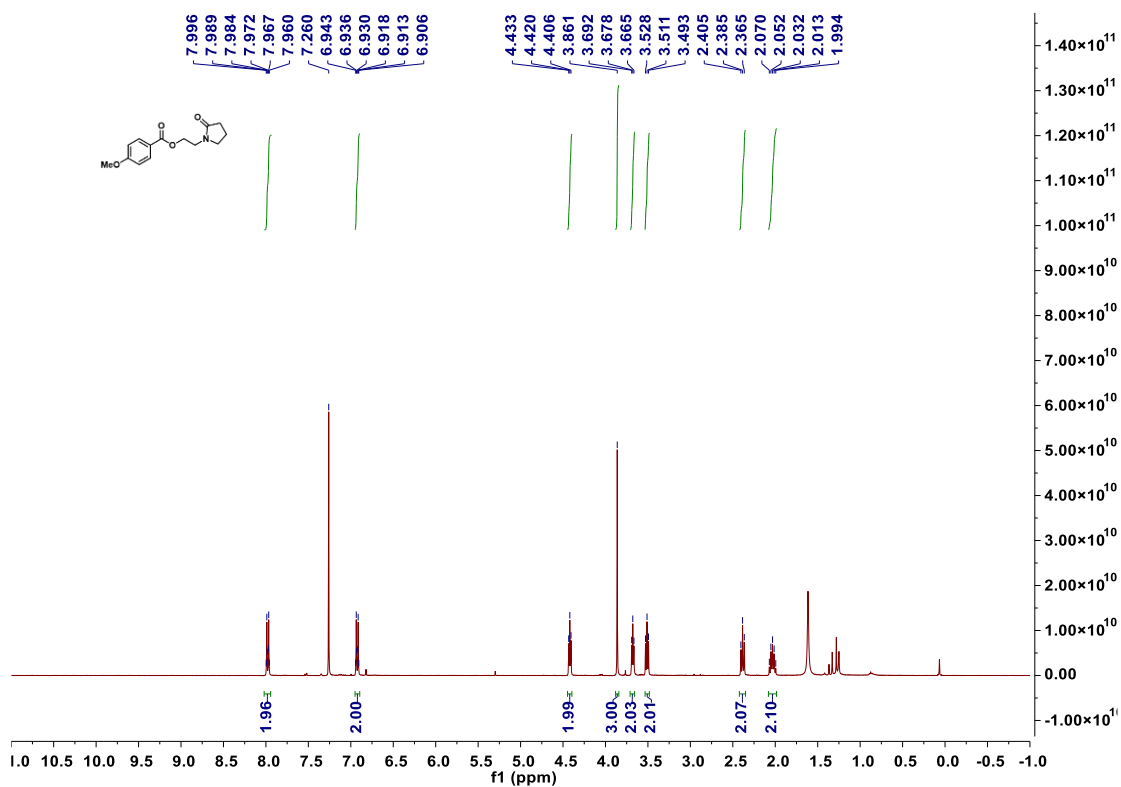
¹H NMR-spectrum (400 MHz, CDCl₃) of **3af**



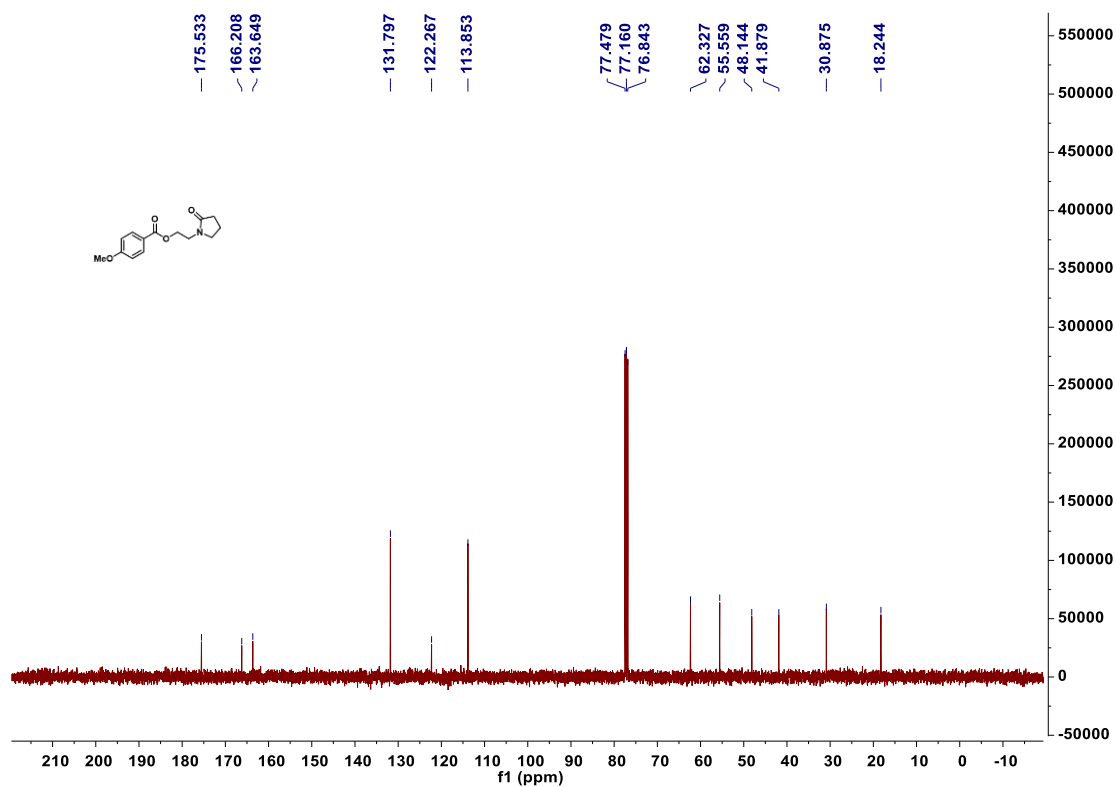
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3af**



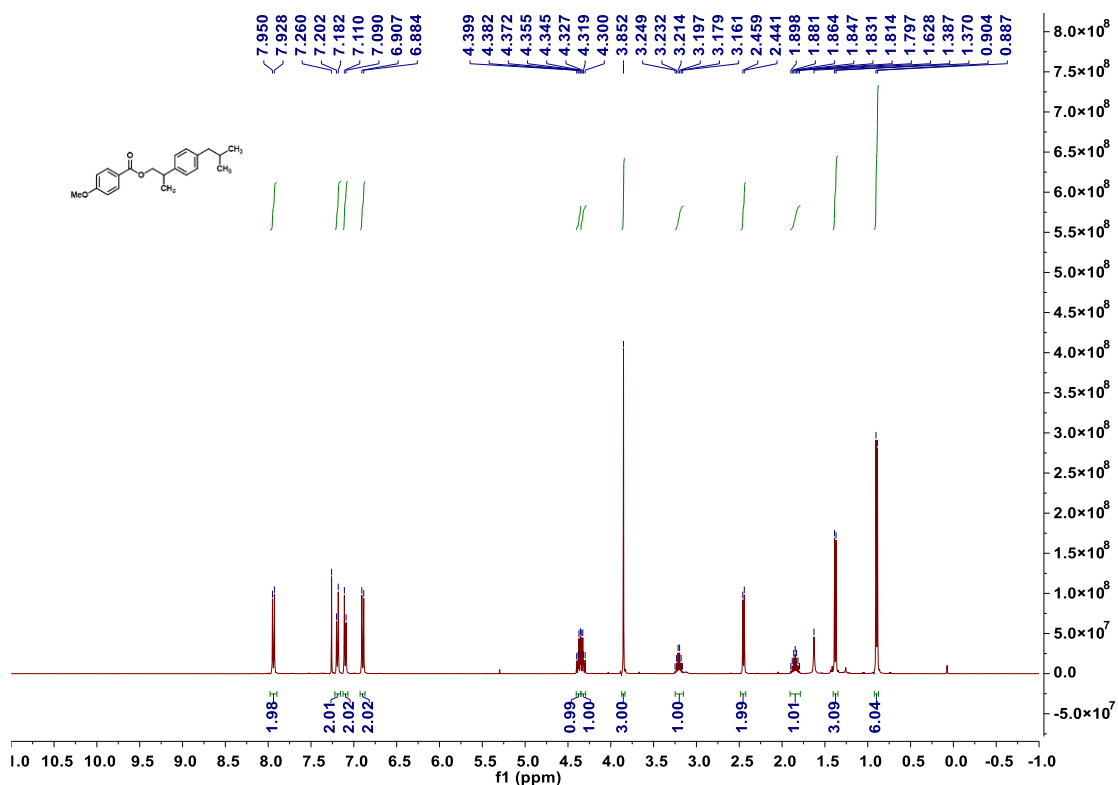
¹H NMR-spectrum (400 MHz, CDCl₃) of **3ag**



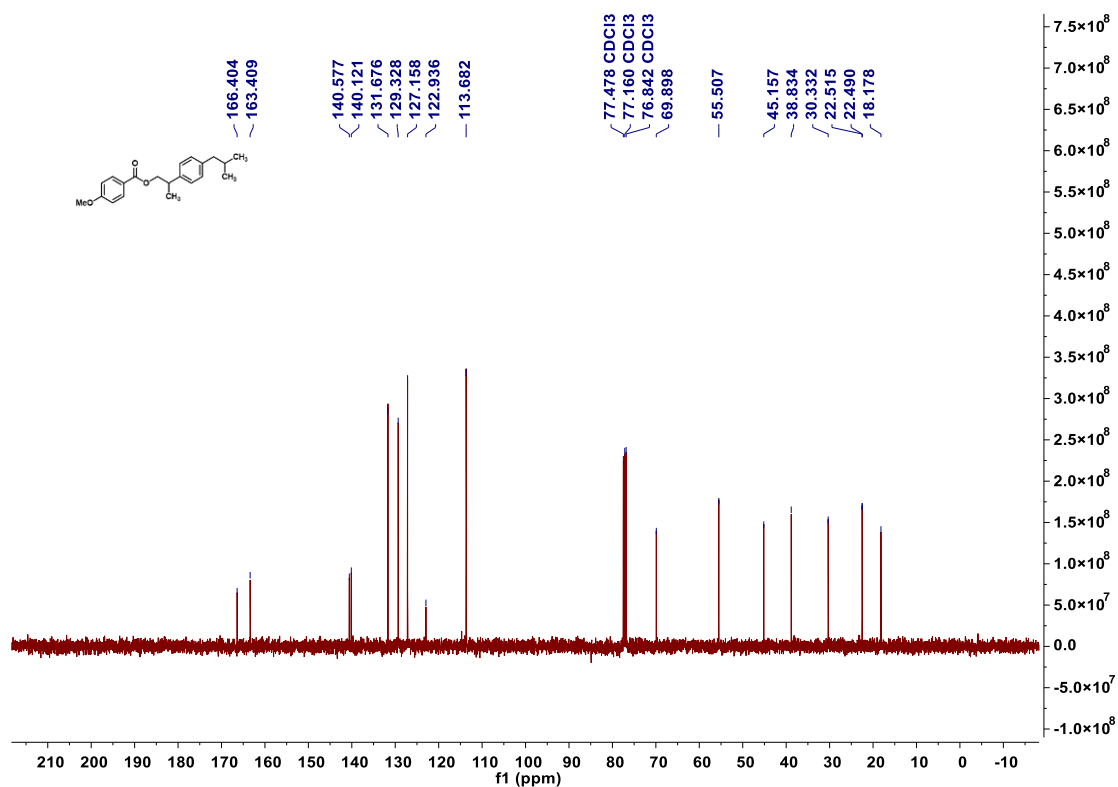
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3ag**



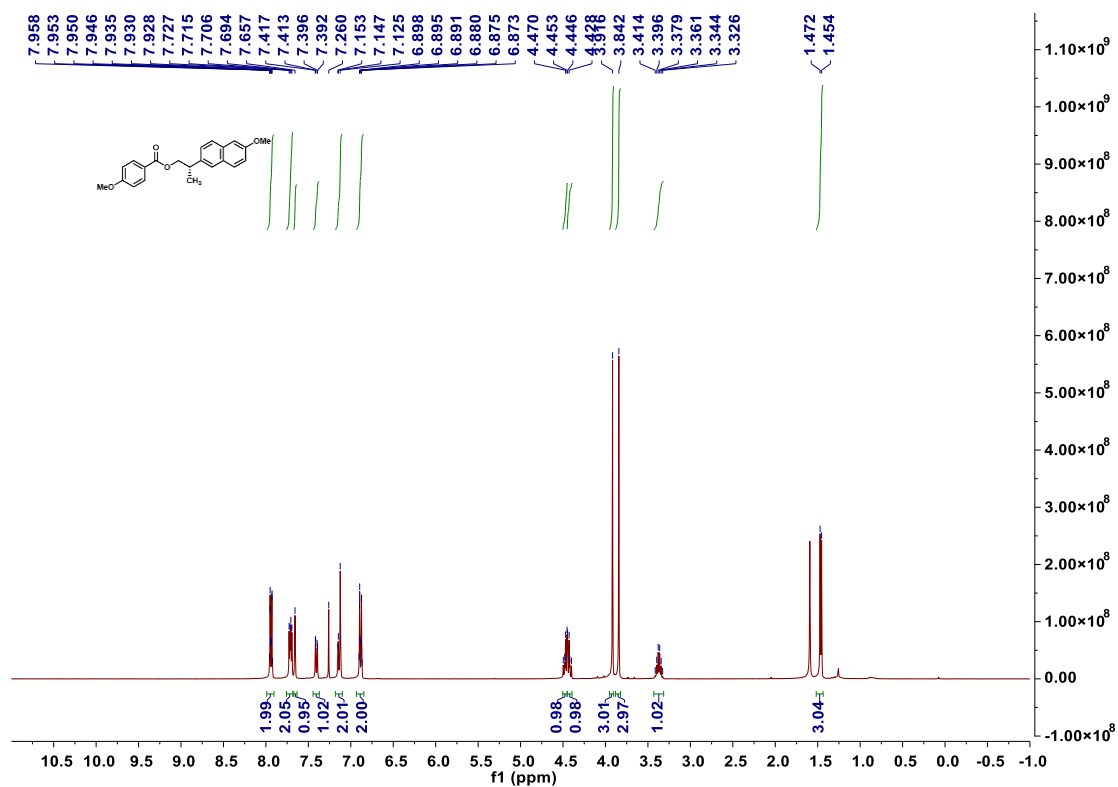
¹H NMR-spectrum (400 MHz, CDCl₃) of **3ah**



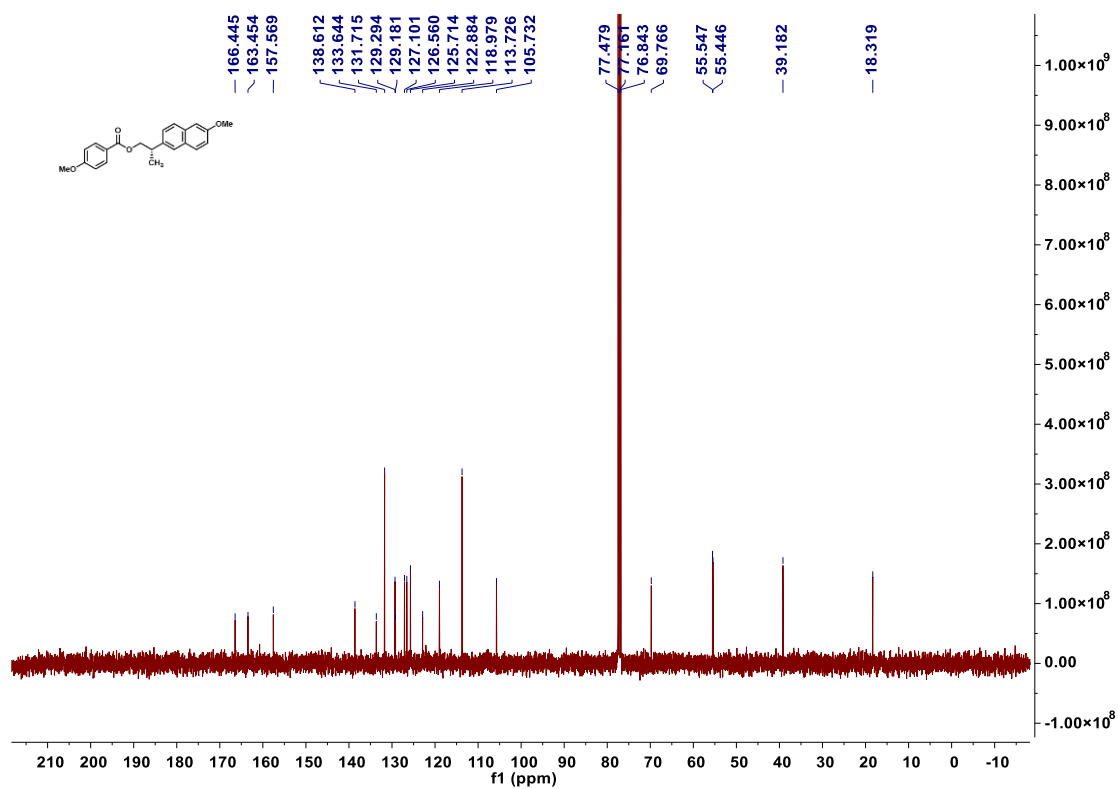
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3ah**



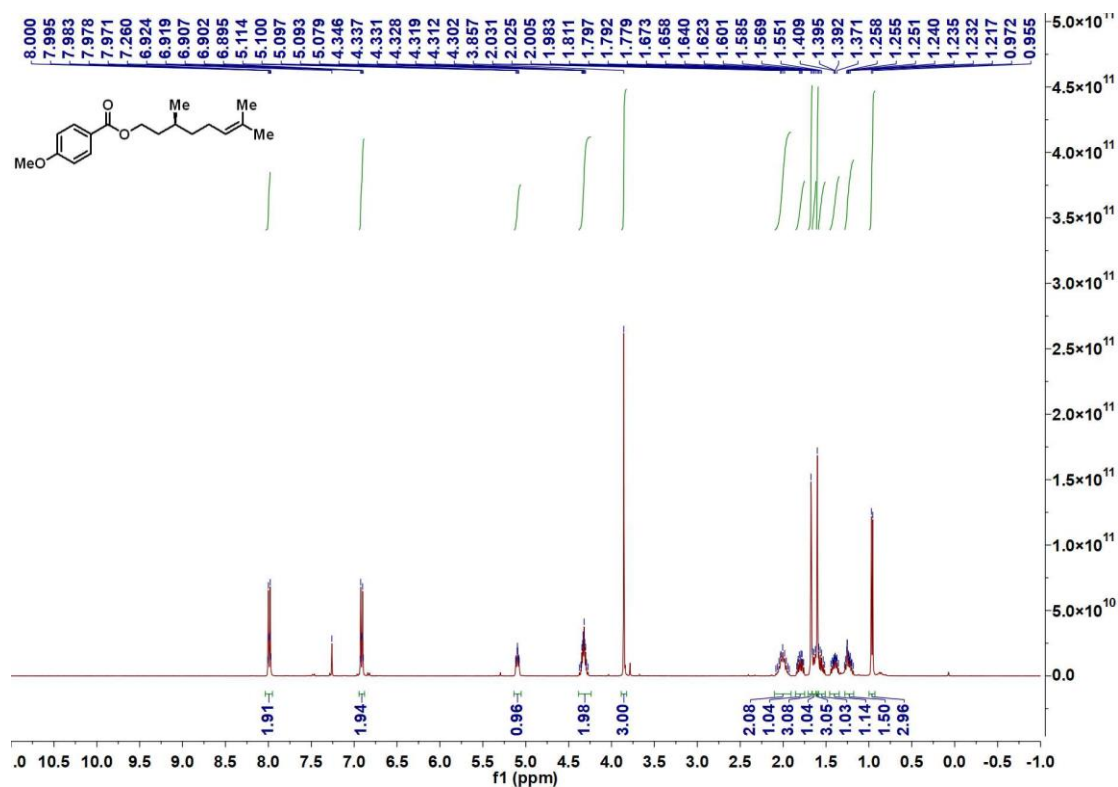
¹H NMR-spectrum (400 MHz, CDCl₃) of **3ai**



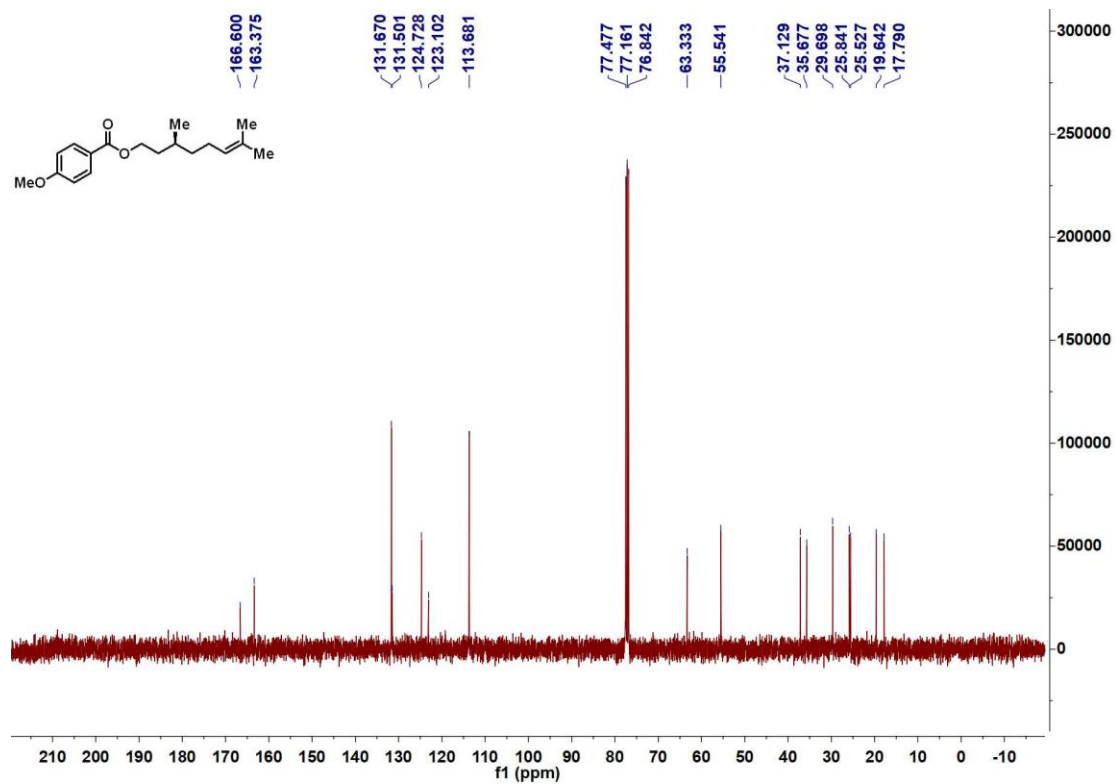
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3ai**



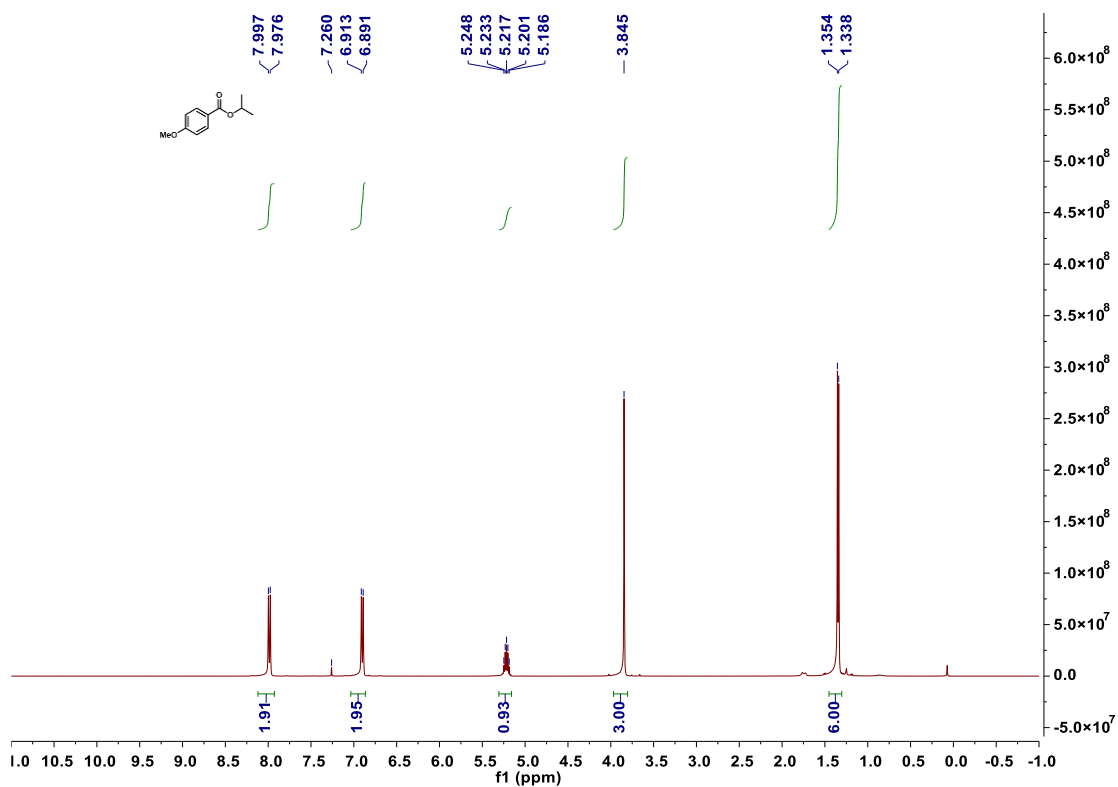
¹H NMR-spectrum (400 MHz, CDCl₃) of **3aj**



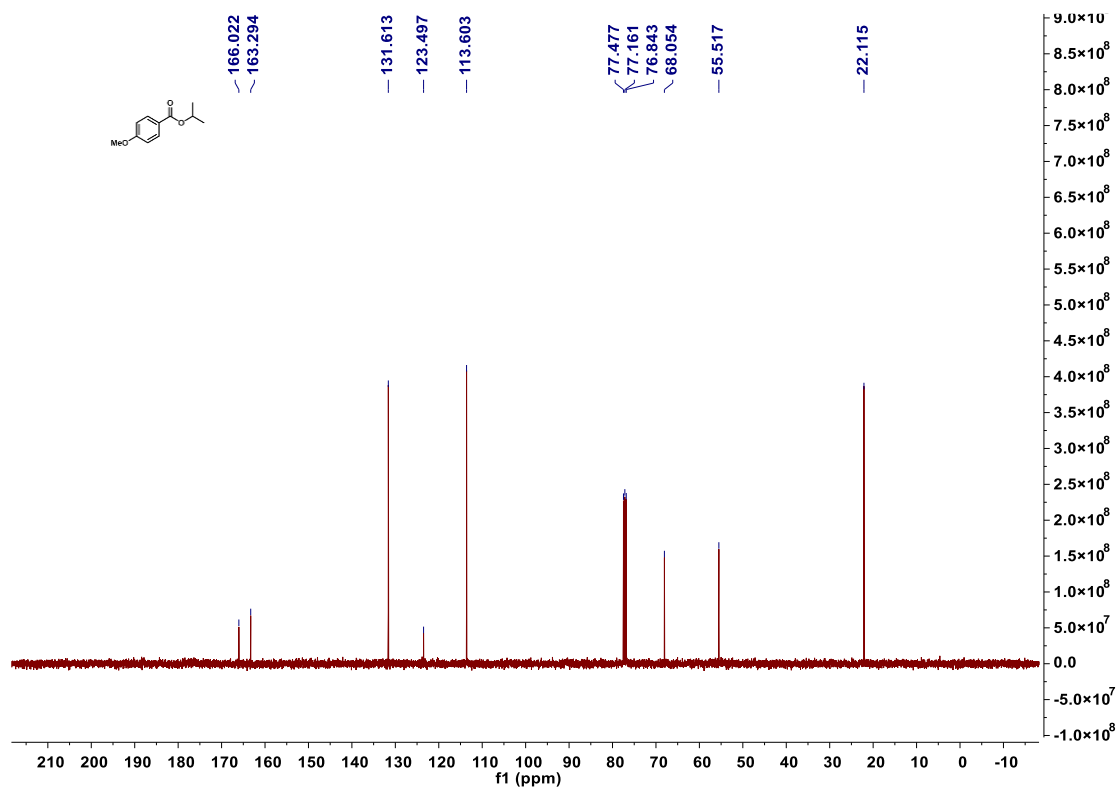
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3aj**



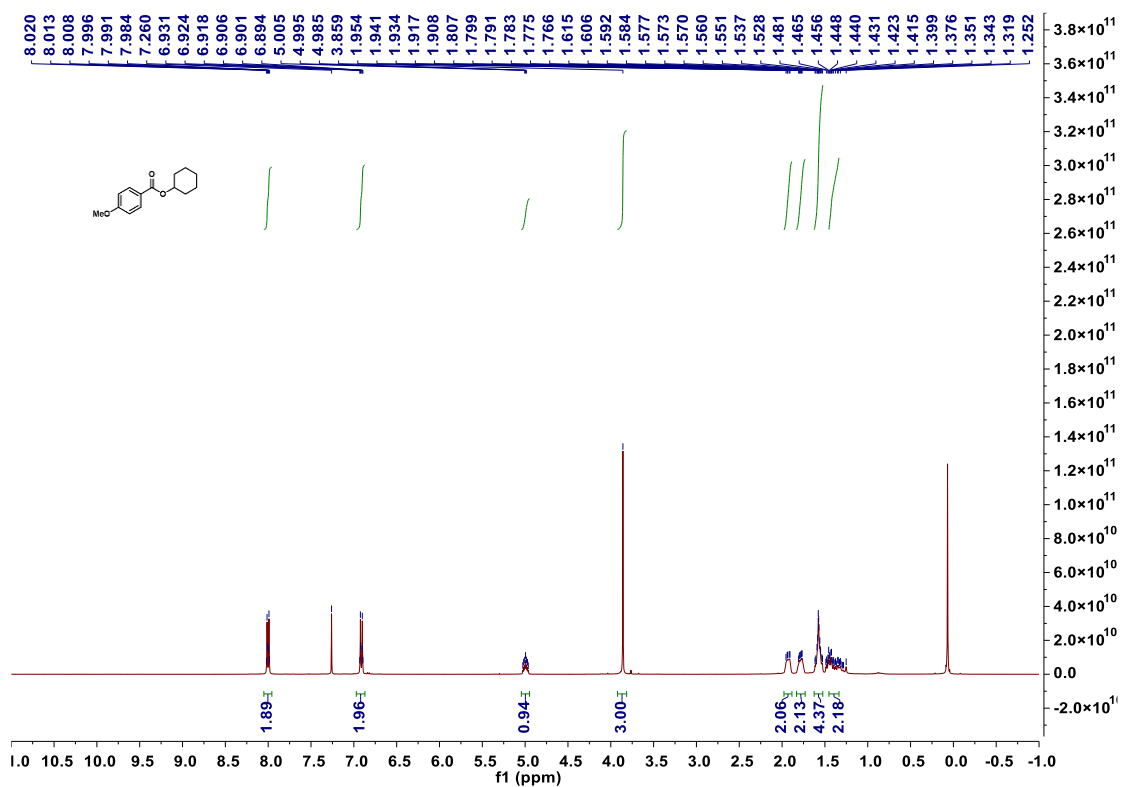
¹H NMR-spectrum (400 MHz, CDCl₃) of **3ak**



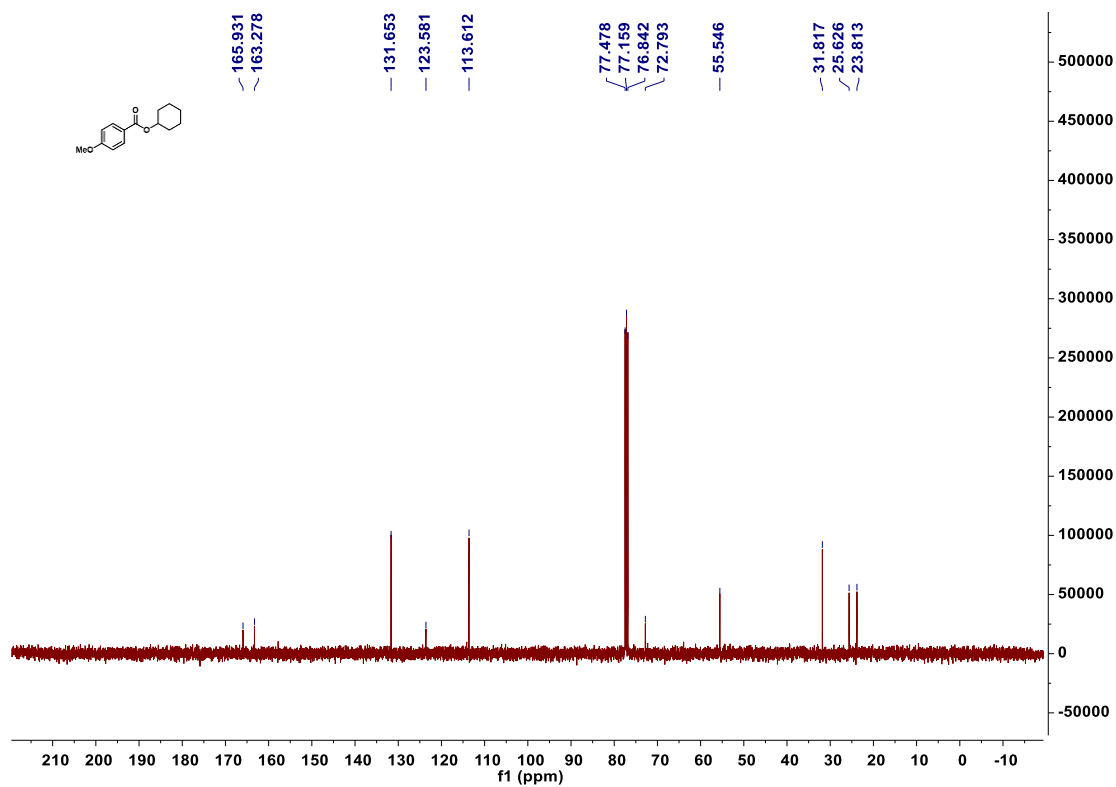
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3ak**



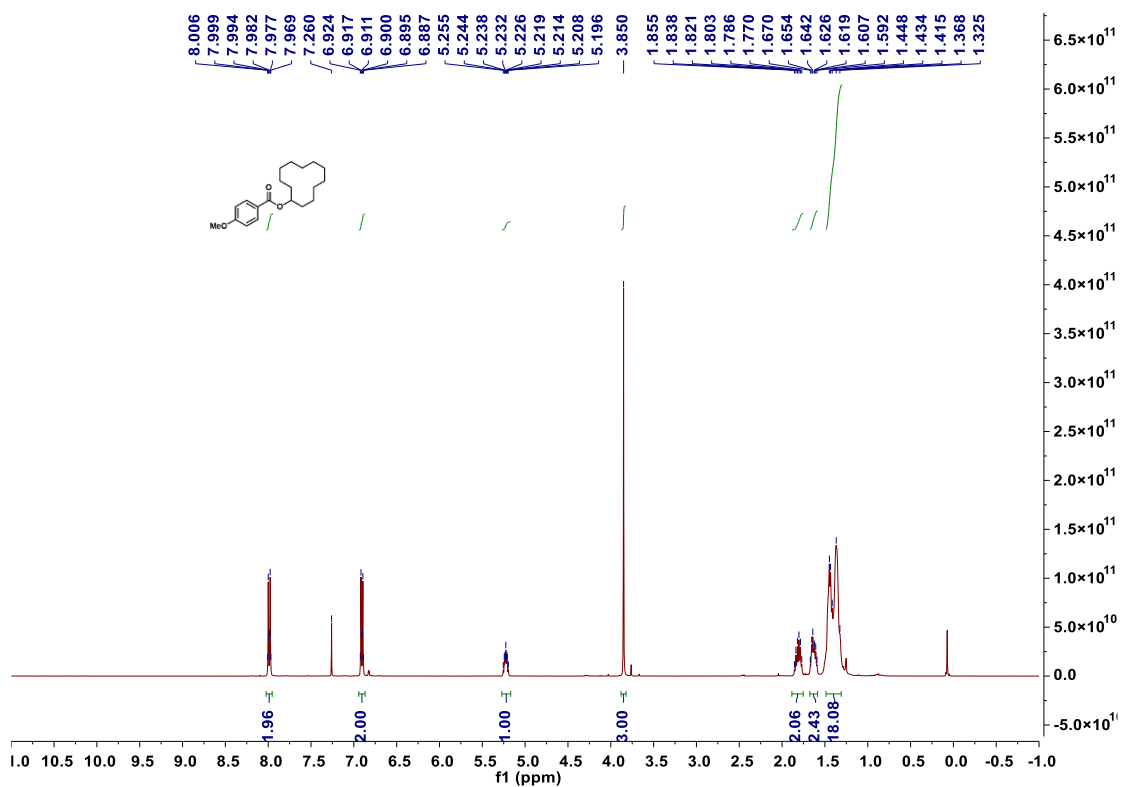
¹H NMR-spectrum (400 MHz, CDCl₃) of **3al**



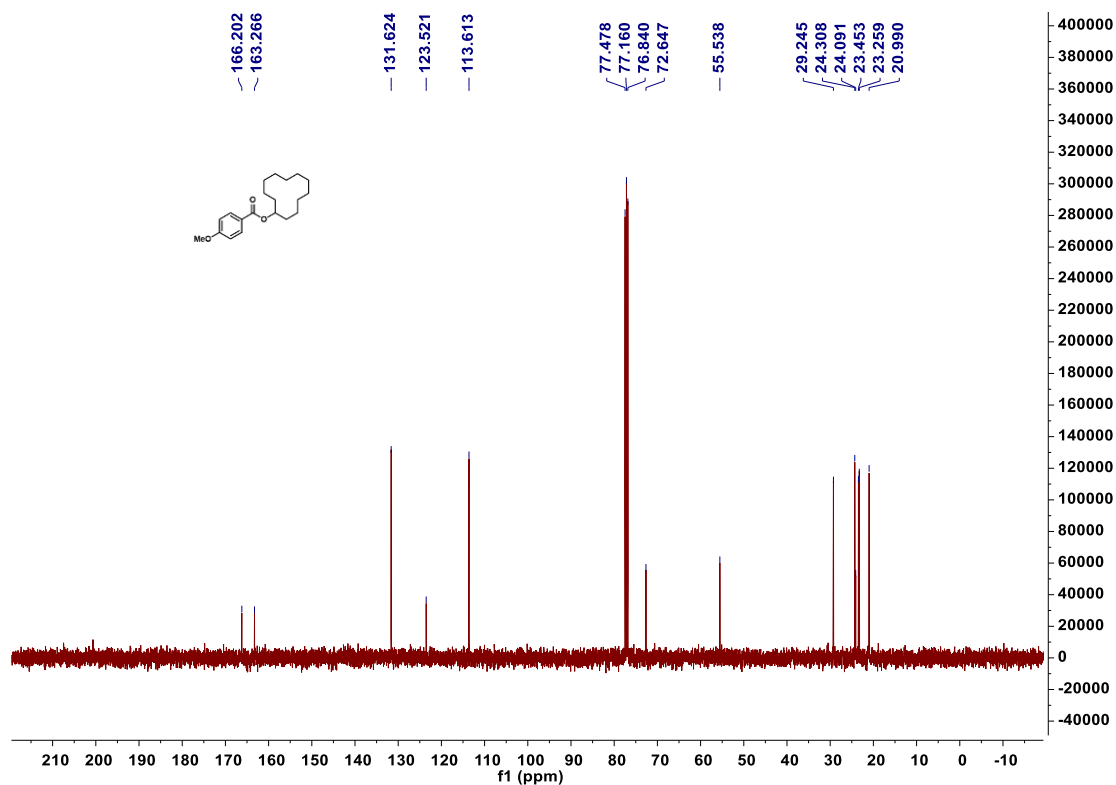
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3al**



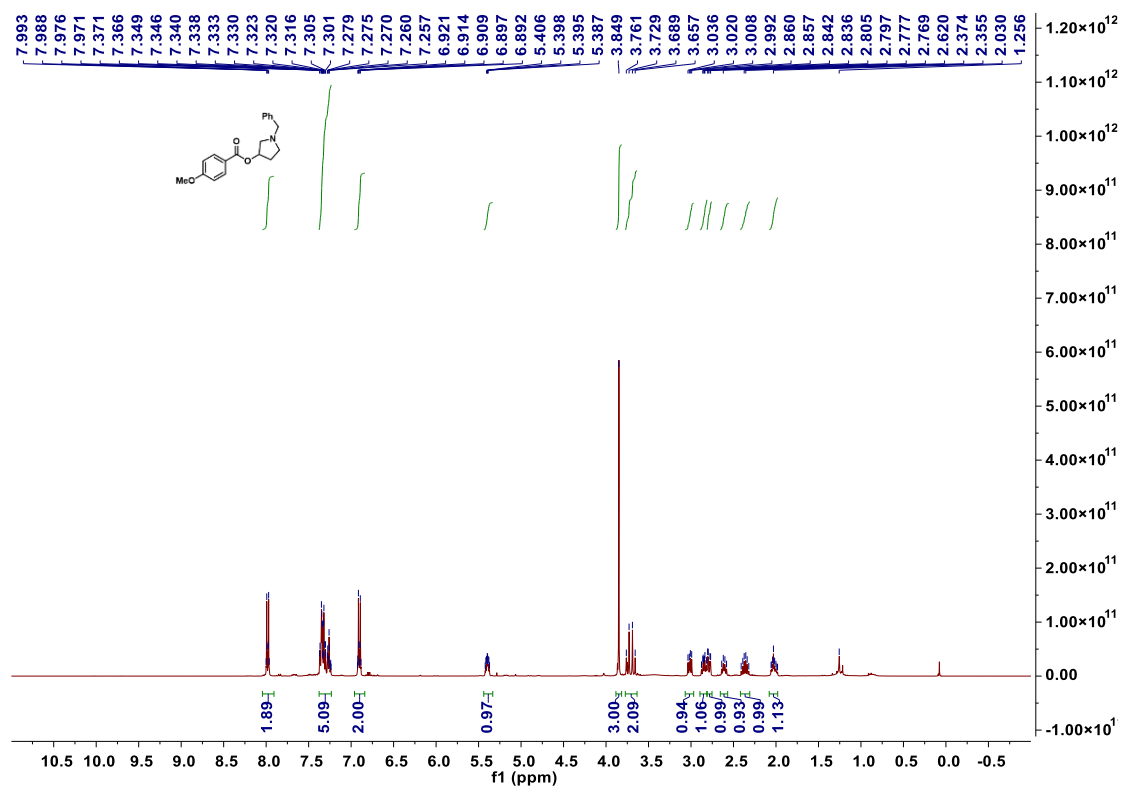
¹H NMR-spectrum (400 MHz, CDCl₃) of **3am**



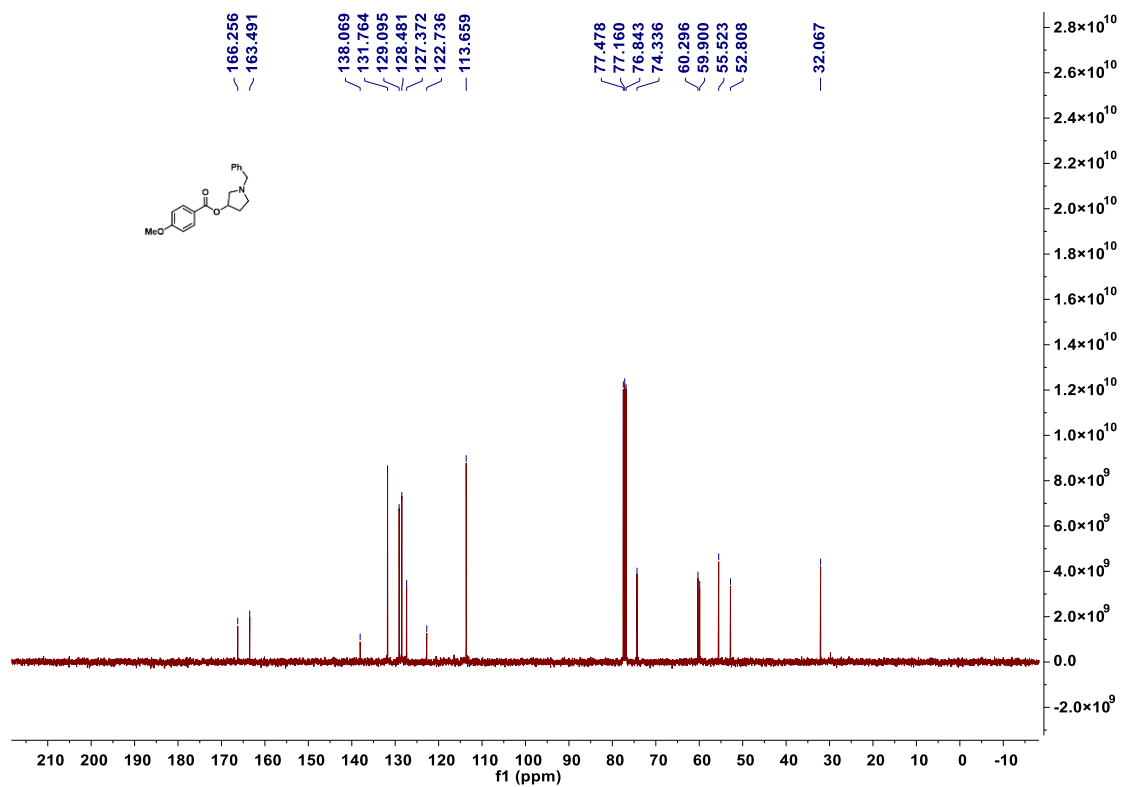
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3am**



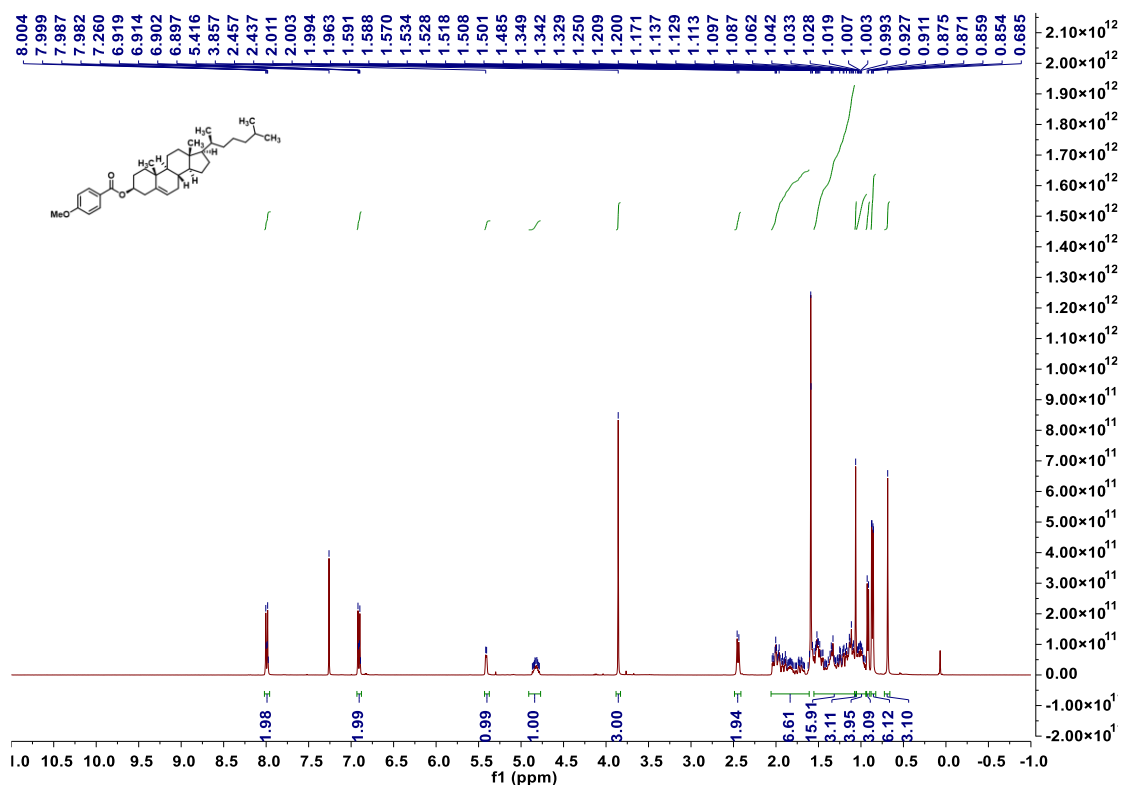
¹H NMR-spectrum (400 MHz, CDCl₃) of **3an**



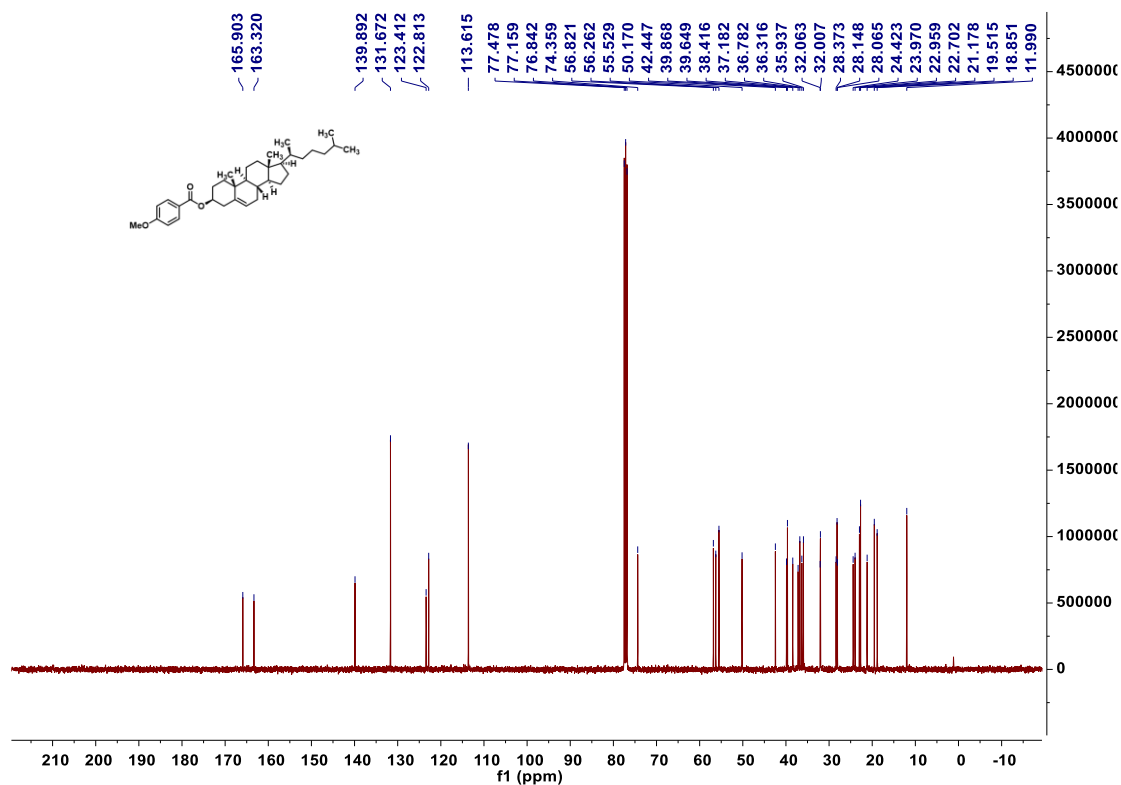
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3an**



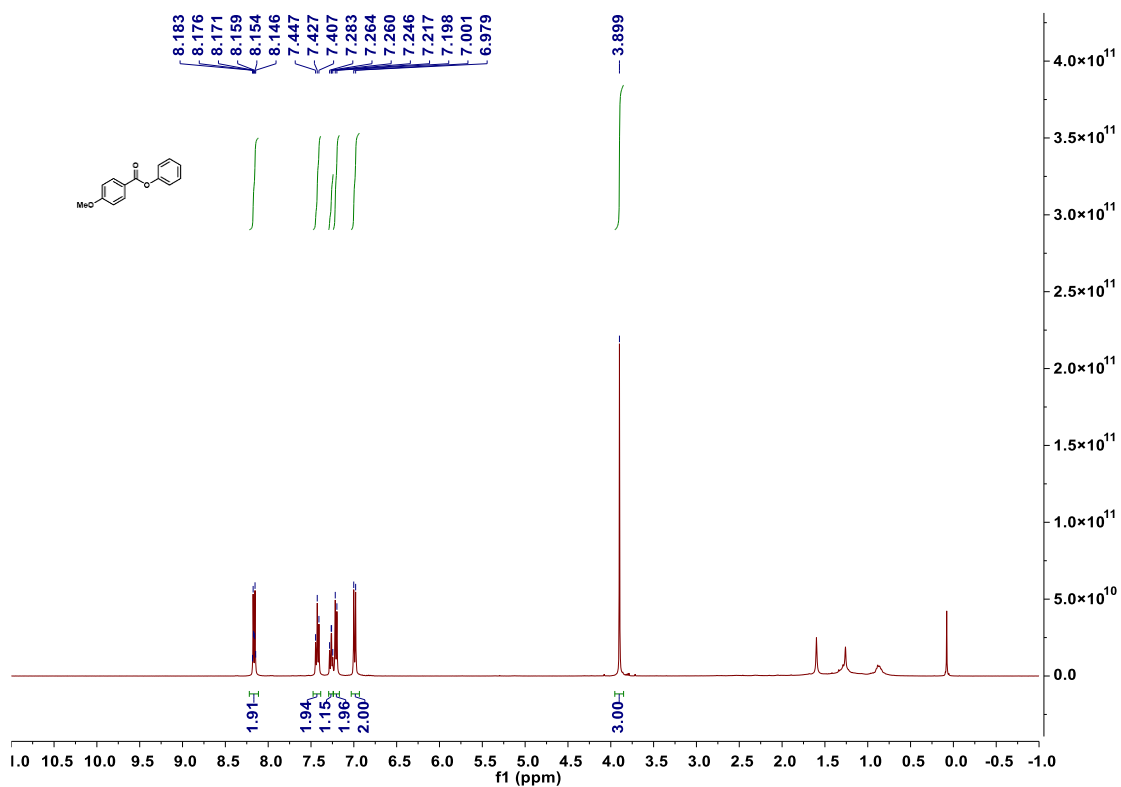
¹H NMR-spectrum (400 MHz, CDCl₃) of **3ao**



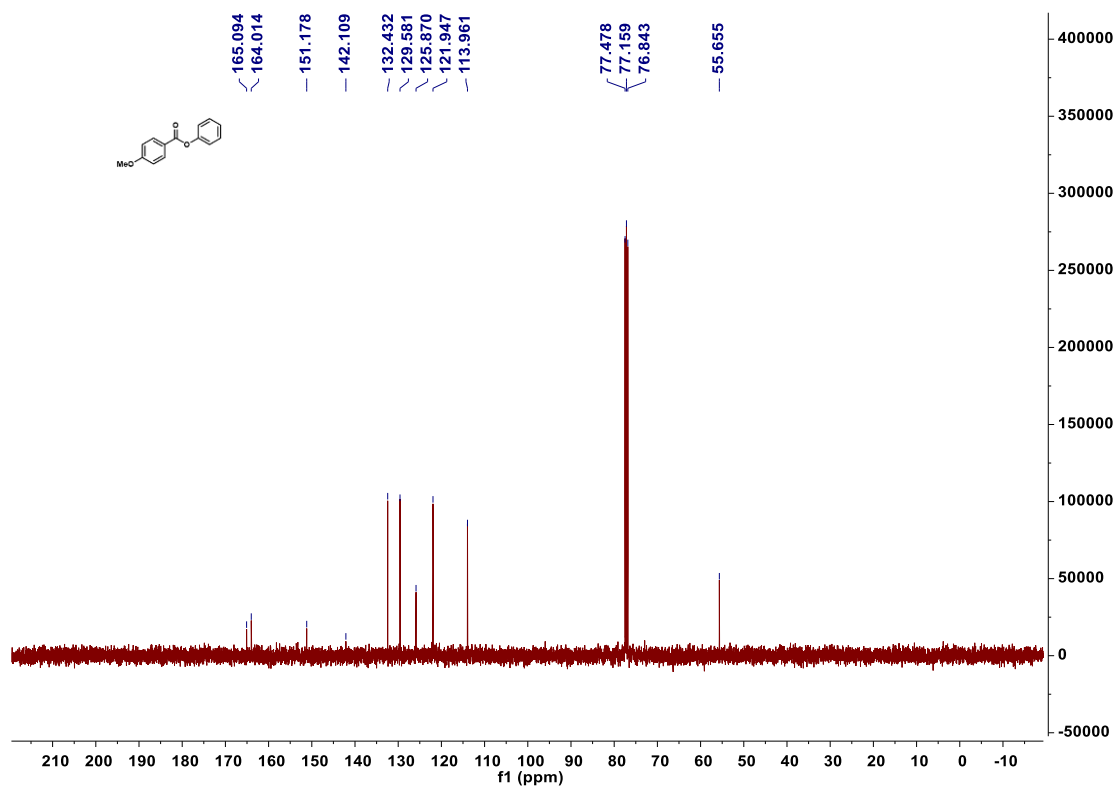
¹³C NMR-spectrum (100 MHz, CDCl₃) of **3ao**



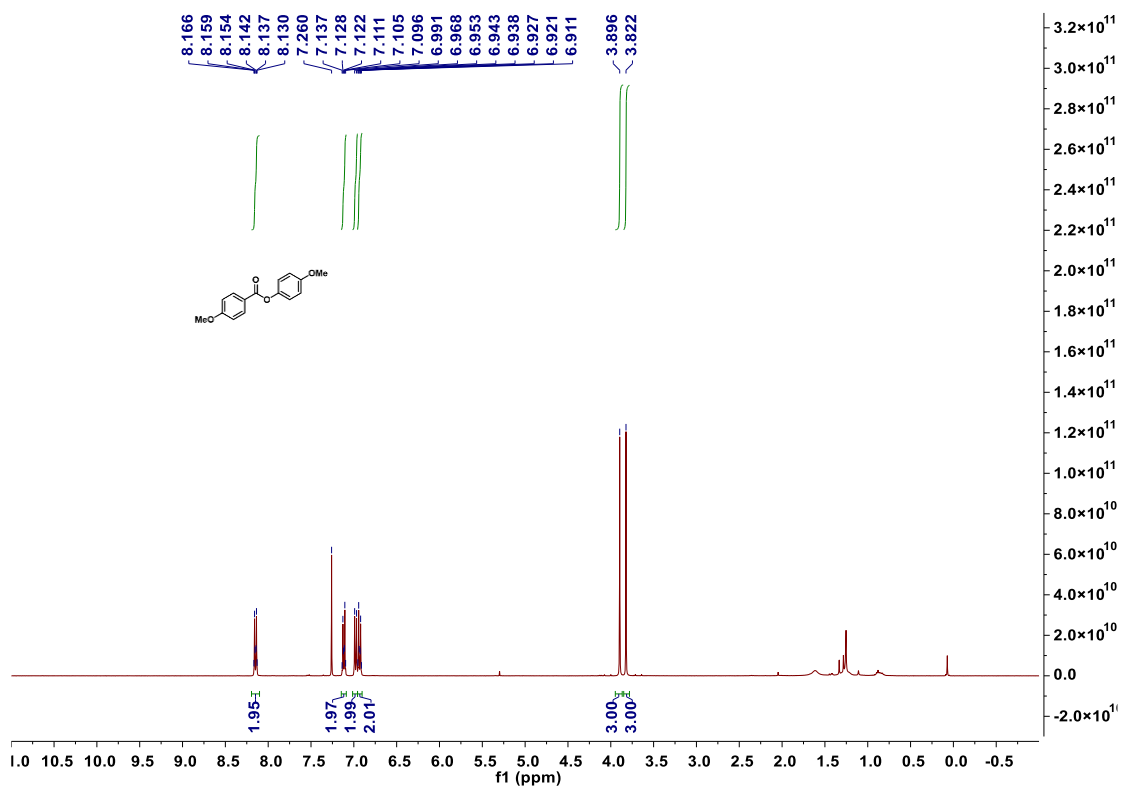
¹H NMR-spectrum (400 MHz, CDCl₃) of 3ap



¹³C NMR-spectrum (100 MHz, CDCl₃) of 3ap



¹H NMR-spectrum (400 MHz, CDCl₃) of **3aq**



¹³C NMR-spectrum (100 MHz, CDCl₃) of **3aq**

