Electronic Supplementary Information for:

Photocatalytic Esterification under Mitsunobu Reaction Conditions Mediated by Flavin and Visible Light

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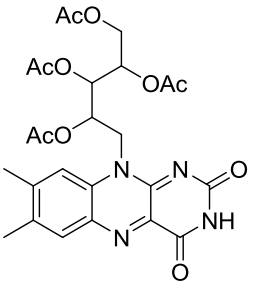
S1 Experimental – general comments

NMR spectra were recorded on a Varian Mercury Plus 300 (299.97 MHz for ^{1}H, 75.44 MHz for ^{13}C, and 282.23 MHz for ^{19}F) or Agilent 400-MR DDR2 (399.94 MHz for ^{1}H and 100.58 MHz for ^{13}C) at 298 K unless otherwise indicated. Chemical shifts δ are given in ppm, using residual solvent or tetramethylsilane as an internal standard. Coupling constants *J* are reported in Hz. **UV-VIS spectra** were recorded on a Varian Cary 50 spectrophotometer. **Fluorescence spectra** were recorded on Varian Cary Eclipse. High-resolution **mass spectra** were obtained on Q-Tof Micro (Waters), equipped with a quadrupole and TOF analyzers and MCP detector. TLC analyses were carried out on a DC Alufolien Kieselgel 60 F254 (Merck). Preparative column chromatography separations were performed on a silica gel Kieselgel 60 0.040-0.063 mm (Merck). **Melting points** were measured on a Boetius melting point apparatus and are uncorrected. **Quantum yields** of photocatalytic esterifications were measured by ferrioxalate actinometer.[1] Concentration of hydrogen peroxide in reaction mixtures was measured by iodometry.[2]

Starting materials, reagents and substrates were obtained from commercial suppliers and used without further purification. The solvents were purified and dried using standard procedures.[3] Riboflavin tetraacetate (**3**),[4,5] diacylhydrazines **2** (ref.)[6] and azo-compounds **1c** and **1d** (ref.[7]) were prepared according to previously reported procedures. NMR spectra of the prepared compounds are in agreement with previously reported data.[2-5]

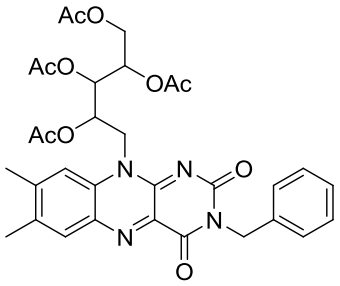
[1] S. L. Murov, I. Carmichael, G. L. Hug, *Handbook of Photochemistry*, 2. Edition, New York **1993**.
[2] R. D. Mair, A. J. Graupner, Anal. Chem. **1964**, 36, 194 –204.
[3] D. D. Perrin, W. L. F. A. *Purification of Laboratory Chemicals, 4th Ed.*; Elsevier Science Ltd., Oxford, 1996.
[4] Neveselý, T.; Svobodová, E.; Chudoba, J.; Sikorski, M.; Cibulka, R. *Adv. Synth. Catal.* **2016**, *358*, 1654.
[5] Schmaderer, H., et al., *Adv. Synth. Catal.* **2009**, 351, 163-174.
[6] Matveeva, E.D., et al., *Chem. Heterocycl. Compd.*, **2000**, 36(10), 1149-1153.
[7] Menard, F., C.F. Weise, and M. Lautens, *Org. Lett.* **2007**, 9(26), 5365-5367.

S2 Experimental – Synthetic procedures

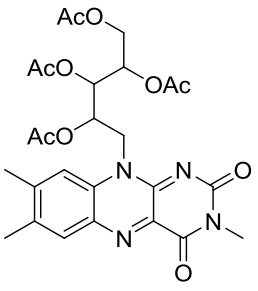


2',3',4',5'-Tetraacetylriboflavin (3b): Prepared according to described procedure.[2] ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.04 (s, 1H), 7.56 (s, 1H), 5.67 (d, *J* = 8.4 Hz, 2H), 5.46 (s, 2H), 5.41 (td, *J* = 6.1, 3.0 Hz, 2H), 4.43 (dd, *J* = 12.4, 2.8 Hz, 1H), 4.24 (dd, *J* = 12.4, 5.8 Hz, 1H), 2.57 (s, 4H), 2.45 (s, 4H), 2.28 (s, 3H), 2.21 (s, 3H), 2.08 (s, 3H), 1.76 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 170.4, 170.0, 159.4, 154.4, 150.9, 148.3, 137.2, 136.2, 134.8, 133.2, 131.4, 115.7, 70.7, 69.6, 69.2, 62.1, 45.2, 21.6, 21.2, 21.0, 20.86, 20.5, 19.6.

3-Benzyl-2',3',4',5'-tetraacetylriboflavin (**3c**): **3b** (1.1 mmol), benzylalcohol (1 mmol) and triphenylphosphine (2 mmol) were dissolved in CH_3CN (60 mL) under nitrogen atmosphere. Then DIAD (2 mmol) was added dropwise and the mixture was mixed 24 h at RT. After the reaction mixture was evaporated and the residue was purified by flash chromatography (silica gel, DCM/CH_3OH, 20:1) to give product **3c** (0,41 g, 63 %) as yellow solid; m.p: 90-92 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (s, 12H), 7.57 – 7.51 (m, 2H), 7.37 – 7.19 (m, 4H), 5.64 (d, J = 7.6 Hz, 2H), 5.48 – 5.36 (m, 2H), 5.26 (s, 2H), 5.03 – 4.61 (m, 2H), 4.42 (dd, J = 12.3, 2.8 Hz, 1H), 4.24 (dd, J = 12.4, 5.8 Hz, 1H), 2.54 (s, 3H), 2.43 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H), 2.06 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 170.4, 170.0, 169.8, 160.0, 155.4, 149.2, 147.6, 136.7, 135.7, 134.8, 133.0, 131.3, 115.5, 70.6, 69.1, 62.0, 44.7, 28.8, 21.5, 21.2, 20.9, 20.8, 20.5, 19.6; HRMS (ESI) calcd for $C_{32}H_{34}N_4O_{10}$ ($[M+Na]^+$) 657.21671, found 657.21655.



3-Methyl-2',3',4',5'-tetraacetylriboflavin (**3d**): **3b** (1 mmol) was dissolved in DMF (80 ml) and K_2CO_3 (10 mmol) was added. Methyl jodide (10 mmol) was added dropwise and the mixture was stirred 24h at RT. After evaporation of solvents, $CHCl_3$ (50 mL) was added and the mixture was washed with water (3 x 50 ml). The organic phase was dried with Na_2SO_4 and filtered. The solvent was evaporated and the residue was purified by flash chromatography (silica gel, $CHCl_3$/CH_3OH, 50:1) to give product **3d** (0.4 g, 72 %) as a orange solid. M.p. = 182 °C (ref.[8] 183 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.53 (s, 1H), 5.73 – 5.60 (m, 1H), 5.52 – 5.34 (m, 2H), 5.24 – 4.64 (m, 2H), 4.42 (dd, J = 12.4, 2.8 Hz, 1H), 4.24 (dd, J = 12.4, 5.8 Hz, 1H), 3.48 (s, 3H), 2.54 (s, 3H), 2.43 (s, 3H), 2.29 (s, 3H), 2.21 (s, 3H), 2.07 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 170.4, 170.0, 169.8, 160.0, 155.4, 149.2, 147.6, 136.7, 135.7, 134.8, 133.0, 131.3, 115.5, 70.6, 69.1, 62.0, 44.7, 28.8, 21.5, 21.2, 20.9, 20.8, 20.5, 19.6; HRMS (APCI) calcd for $C_{26}H_{30}N_4O_{10}$ ($[M+H]^+$) 559.20347, found 559.20329.

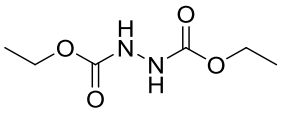


[8] Schmaderer, H., et al., *Adv.Synth. Catal.*, **2009**, 351(1-2), 163-174.

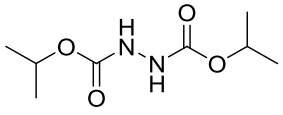
General procedure of preparation of hydrazines 2 (according to ref.[4]):

Alkyl chloroformate (0.05 mol) was added dropwise with stirring to a solution of hydrazine hydrate (1.37 g, 23.5 mmol) in ethanol (15 ml) cooled to 10 °C. After the addition of half of alkyl chloroformate, a solution of Na_2CO_3 (2.65 g, 25 mmol) in water (20 ml) was added and then second half of alkyl chloroformate was added dropwise. The mixture was stirred 30 min at 20 °C. The precipitate was then filtered, washed with water (15 ml) and ethanol (10 ml) and dried to give **2**.

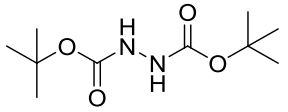
Diethyl hydrazine-1,2-dicarboxylate (**2a**): White solid (yield 65 %), M.p. = 131 °C (ref.[4] 131-132 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (s, 2H), 4.20 (q, J = 7.1 Hz, 4H), 1.27 (t, J = 7.1 Hz, 6H); 13C NMR (101 MHz, $CDCl_3$) δ 156.9, 62.4, 14.5; HRMS (ESI) calcd for $C_6H_{12}N_2O_4$ ($[M+Na]^+$) 199.06893, found 199.06911.



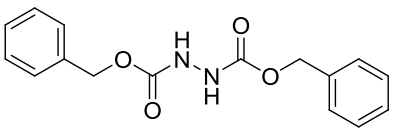
Diisopropyl hydrazine-1,2-dicarboxylate (**2b**): White solid (yield 33 %), M.p. = 106-108 °C (ref.[9] 107-108 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.32 (s, 1H), 4.98 (hept, J = 6.3 Hz, 1H), 1.26 (d, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 70.2, 22.1; HRMS (ESI) calcd for $C_8H_{16}N_2O_4$ ($[M+Na]^+$) 227.10029, found 227.10023.



Di-*tert*-butyl hydrazine-1,2-dicarboxylate (**2c**): Prepared according to described procedure.[10] White solid (yield 40 %), M.p. = 121 °C (ref.[9] 121-122 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (br, 1H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 81.7, 28.3; HRMS (ESI) calcd for $C_{10}H_{20}N_2O_4$ ($[M+Na]^+$) 255.13153, found 255.13181.



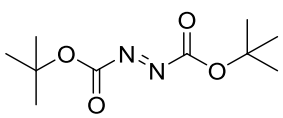
Dibenzyl hydrazine-1,2-dicarboxylate (**2d**): White solid (yield 70 %), M.p. = 106 °C (ref.[11] 106.5 °C); ^{1}H NMR (400 MHz, CD_3CN) δ 7.64 - 7.25 (m, 5H), 7.06 (br, 1H), 5.12 (s, 2H); ^{13}C NMR (101 MHz, cd_3cn) δ 157.5, 137.5, 129.5, 129.1, 128.9, 67.9; HRMS (ESI) calcd for $C_{16}H_{16}N_2O_4$ ($[M+Na]^+$) 323.10023, found 323.10065.



General procedure of preparation of azo-compounds[5] 1

Hydrazine (**2c** or **2d**; 0.7 mmol) and anhydrous pyridine (1.6 mmol) were dissolved in DCM (20 ml) under N_2 atmosphere and the mixture was cooled to 0 °C. The bromine (0.8 mmol) in DCM (6 ml) was added dropwise and the mixture was stirred for 90 min. After DCM (50 ml) was added and the mixture was washed with 1M HCl (2 x 15 ml), sat. $NaHCO_3$ (2 x 15 ml), H_2O (15 mL) and brine (15 mL). The organic phase was dried with $MgSO_4$ and filtered. The solvent was removed under reduced pressure to give **1c-d** as a yellow solid.

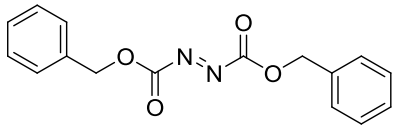
Di-*tert*-butyl azodicarboxylate (**1c**): Yellow solid (yield 92 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (s, 9H); ^{13}C NMR (101 MHz,



[9] Hughes, D.L. and R.A. Reamer, *J. Org. Chem.*, **1996**, 61(9), 2967-2971.
[10] Ling, K.B. and A.D. Smith, *Chem. Comm.un*, **2011**, 47(1), 373-375.
[11] Kenner, G.W. and R.J. Stedman, *J. Chem. Soc.*, **1952**, 2089-2094.

$CDCl_3$) δ 159.4, 87.0, 27.9; HRMS calcd for (ESI) $C_{10}H_{18}N_2O_4$ ($[M+Na]^+$) 253.11610, found 253.11588.

Dibenzyl azodicarboxylate (**1d**): Yellow solid (yield 90 %); ^1H NMR (400 MHz, CD_3CN) δ 7.51 – 7.37 (m, 5H), 5.45 (s, 2H); ^{13}C NMR (101 MHz, CD_3CN) δ 161.1, 135.1, 130.1, 129.8, 129.8, 71.9; HRMS (APCI) calcd for $C_{16}H_{14}N_2O_4$ (M^+) 298.09601, found 298.09591.



General procedure of preparation of chiral esters (standards)

3,5-dinitrobenzoic acid (**4h**) or 3-nitrobenzoic acid (**4a**) (1.2 mmol), 1-phenylethanol (**5l**) or ethyl lactate (**5m**) (1 mmol), DCC (1.5 mmol) and DMAP (0.1 mmol) were dissolved in dry CH_3CN (10 mL) and the mixture was stirred for 24h at RT. After the reaction mixture was evaporated, the residue was purified by flash chromatography (silica gel, Hexane/EtOAc, 10:1) to give the product.

(*R*)- and (*S*)-1-Phenylethyl 3-nitrobenzoate (**6r**): Yield 90 % (0.24 g, 0.9 mmol) for (*R*)- and 89 % (0,24 g, 0.89 mmol) for (*S*). Yellowish oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.98 – 8.81 (m, 1H), 8.48 – 8.25 (m, 2H), 7.68 – 7.62 (m, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.36 (m, 2H), 7.36 – 7.30 (m, 1H), 6.18 (q, *J* = 6.6 Hz, 1H), 1.72 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 148.4, 141.1, 135.5, 132.4, 129.7, 128.8, 128.4, 127.5, 126.3, 124.7, 74.3, 22.4; HRMS (APCI) calcd for $C_{15}H_{13}NO_4$ ($[M]^+$) 271.08501, found 271.08503. For (*R*)- $[\alpha]_D^{25}$ = -44.7° (*c* 0.380, $CHCl_3$), purity by HPLC 99 %; For (*S*)- $[\alpha]_D^{25}$ = 42.1° (*c* 0.329, $CHCl_3$), purity by HPLC 100 %.

Ethyl (S)- and (*R*)-2-((3,5-dinitrobenzoyl)oxy) propionate (**6s**): Yield 88 % (0.275 g, 0.88 mmol) for (*R*)- and 91 % (0.284 g, 0.91 mmol) for (*S*). White solid, m.p: 92-93 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.26 (t, *J* = 2.2, 1H), 9.20 (d, *J* = 2.1, 2H), 5.41 (q, *J* = 7.1, 1H), 4.27 (q, *J* = 7.1, 2H), 1.72 (d, *J* = 7.1, 3H), 1.31 (t, *J* = 7.1, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 162.1, 148.8, 133.4, 129.8, 122.8, 71.0, 62.1, 17.1, 14.3; HRMS (APCI) calcd for $C_{12}H_{12}N_2O_8$ ($[M]^+$) 312.05978, found 312.05991. For (*R*)- $[\alpha]_D^{25}$ = -10.4° (*c* 0.214, $CHCl_3$), purity by HPLC 100 %; For (*S*)- $[\alpha]_D^{25}$ = 8.2° (*c* 0.341, $CHCl_3$), purity by HPLC 99 %.

S3 Experimental – Photocatalytic esterification

General procedure for photocatalytic esterification under Mitsunobu reaction conditions

Preliminary experiments on esterification

A mixture of benzylalcohol (**5a**, 0.150 mmol), 3-nitrobenzoic acid (**4a**, 0.180 mmol), triphenylphosphine (0.30 mmol), diisopropyl hydrazine-1,2-dicarboxylate (**2b**) or DIAD (**1b**) (0.0150 mmol), catalyst (**3b-d**, **7** or **8**, 0.0150 mmol), in the presence or absence of phenylsilane (0.30 mmol) and activated MS 4 Å (150 mg) in CH_3CN (2 mL) was bubbled with oxygen (2 min) and then was stirred at 25 °C or 50 °C under O_2 (balloon) under irradiation with blue LEDs (450 nm, 1 W LED) for 24 hours (for details about experimental setup, see S14). Then, the reaction mixture was filtered and the solvent was evaporated. The conversion was determined by ^{1}H NMR.

Esterification on preparative scale

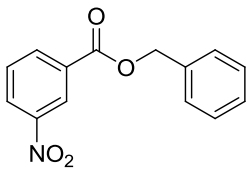
Method A

A mixture of alcohol (**5a-m**, 0.150 mmol), nucleophile (**4a-h**, or phthalimide, 0.180 mmol), triphenylphosphine (0.30 mmol), DIAD (**1b**, 0.0150 mmol), TARF^3-CH_3 (**3d**, 0.0150 mmol) and activated MS 4 Å (150 mg) in CH_3CN (2 mL) was bubbled with oxygen (2 min) and then was stirred at 25 °C under O_2 (balloon) under irradiation with blue LEDs (450 nm, 1 W LED) for 24 hours (for details about experimental setup, see S14). After irradiation, the reaction mixture was filtered and the solvent was evaporated. The residue was purified by flash chromatography (silica gel, *n*-hexane/EtOAc, 20:1 or $CHCl_3$) to give the product.

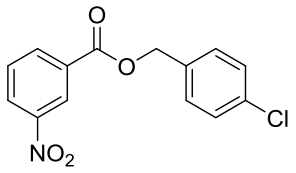
Method B

A mixture of alcohol (**5a-m**, 0.150 mmol), nucleophile (**4a-h**, or phthalimide 0.180 mmol), triphenylphosphine (0.30 mmol), diisopropyl hydrazine-1,2-dicarboxylate (**2b**, 0.0150 mmol), TARF^3-CH_3 (**3d**, 0.0150 mmol), phenylsilane (0.30 mmol) and activated MS 4 Å (150 mg) in CH_3CN (2 mL) was bubbled with oxygen (2 min) and then was heated at 50 °C under O_2 (balloon) under irradiation with blue LEDs (450 nm, 1 W LED) for 24 hours (for details about experimental setup, see S14). Then, the reaction mixture was filtered and the solvent was evaporated. The residue was purified by flash chromatography (silica gel, *n*-hexane/EtOAc, 20:1 or $CHCl_3$) to give the product.

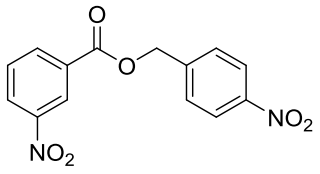
Benzyl 3-nitrobenzoate (**6a**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 – 8.87 (m, 1H), 8.45 – 8.36 (m, 2H), 7.66 (dd, *J* = 12.0, 4.2 Hz, 1H), 7.50 – 7.34 (m, 5H), 5.42 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 148.4, 135.5, 135.4, 132.1, 129.8, 128.9, 128.8, 128.6, 127.6, 124.8, 67.8; HRMS (APCI) calcd for $C_{14}H_{11}NO_4$ ($[M]^+$) 257.06936, found 257.06924.



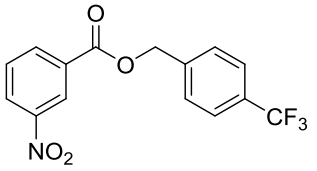
4-Chlorobenzyl 3-nitrobenzoate (**6b**): White solid, m.p: 85-87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (t, *J* = 1.8 Hz, 1H), 8.43 (ddd, *J* = 8.2, 2.2, 0.9 Hz, 1H), 8.40 – 8.36 (m, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.45 – 7.35 (m, 4H), 5.38 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 148.4, 135.5, 134.8, 133.9, 131.9, 130.1, 129.9, 129.1, 127.8, 124.8, 67.0; HRMS (APCI) calcd for $C_{14}H_{10}ClNO_4$ ($[M]^+$) 291.03038, found 291.03055.



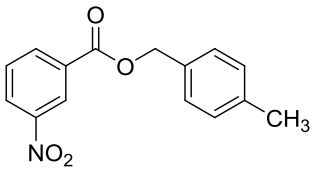
4-Nitrobenzyl 3-nitrobenzoate (**6c**): White solid, m.p: 142-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 – 8.84 (m, 1H), 8.50 – 8.43 (m, 1H), 8.43 - 8.38 (m, 1H), 8.27 (d, *J* = 8.6 Hz, 2H), 7.70 (m, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 5.52 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 148.6, 148.1, 142.5, 135.5, 131.4, 130.0, 128.9, 128.0, 124.9, 124.2, 66.2; HRMS (APCI) calcd for $C_{14}H_{10}N_2O_6$ ($[M]^+$) 302.04996, found 302.04969.



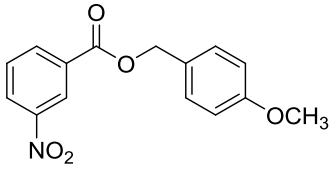
4-(Trifluormethyl)benzyl 3-nitrobenzoate (**6d**): White solid, m.p: 72-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 – 8.85 (m, 1H), 8.48 – 8.37 (m, 2H), 7.74 – 7.64 (m, 3H), 7.58 (d, *J* = 8.1 Hz, 2H), 5.47 (s, 2H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 164.3, 148.5, 139.3, 135.5, 131.6, 131.1, 129.9, 128.6, 127.9, 125.9 (q, *J* = 3.8 Hz), 124.8, 122.7, 66.8; HRMS (+EI) calcd for $C_{15}H_{10}F_3NO_4$ ($[M]^+$) 325,05832, found 325.05697.



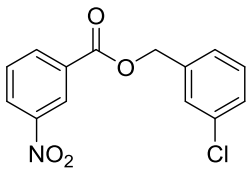
4-Methylbenzyl 3-nitrobenzoate (**6e**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 - 8.79 (m, 1H), 8.43 – 8.36 (m, 2H), 7.67 – 7.61 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 5.38 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 148.4, 138.7, 135.5, 132.4, 132.1, 129.7, 129.5, 128.8, 127.6, 124.8, 67.7, 21.4; HRMS (APCI) calcd for $C_{15}H_{13}NO_4$ ($[M]^+$) 271.08501, found 271.08502.



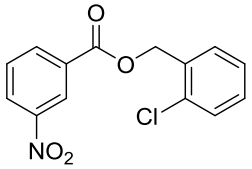
4-Methoxybenzyl 3-nitrobenzoate (**6f**): White solid, m.p: 75-77 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 – 8.73 (m, 1H), 8.48 – 8.27 (m, 2H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.44 – 7.38 (m, 2H), 6.96 – 6.90 (m, 2H), 5.35 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 160.1, 148.4, 135.5, 132.2, 130.6, 129.7, 127.5, 127.5, 124.8, 114.2, 67.7, 55.5; HRMS (APCI) calcd for $C_{15}H_{13}NO_5$ ($[M]^+$) 287.08053, found 287.08024.



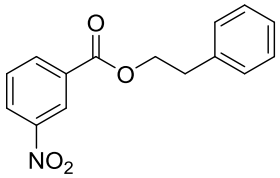
3-Chlorobenzyl 3-nitrobenzoate (**6g**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 – 8.79 (m, 1H), 8.56 – 8.25 (m, 2H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.45 (s, 1H), 7.38 – 7.31 (m, 3H), 5.39 (s, 2H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 164.2, 148.3, 137.2, 135.4, 134.6, 131.6, 130.1, 129.7, 128.8, 128.5, 127.6, 126.5, 124.7, 66.7; HRMS (APCI) calcd for $C_{14}H_{10}ClNO_4$ ($[M]^+$) 291.03038, found 291.03067.



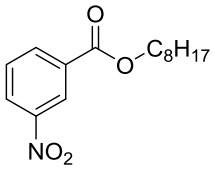
2-Chlorobenzyl 3-nitrobenzoate (**6h**): White solid, m.p: 71–72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 – 8.87 (m, 1H), 8.45 – 8.37 (m, 2H), 7.69 – 7.63 (m, 1H), 7.53 – 7.41 (m, 2H), 7.36 – 7.28 (m, 2H), 5.52 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 148.4, 135.6, 134.2, 133.1, 131.8, 130.5, 130.2, 129.9, 129.8, 65.2; HRMS (APCI) calcd for $C_{14}H_{10}ClNO_4$ ($[M]^+$) 291.03038, found 291.03053.



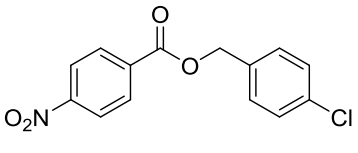
Phenethyl 3-nitrobenzoate (**6i**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 – 8.75 (m, 1H), 8.44 – 8.39 (m, 1H), 8.35 – 8.29 (m, 1H), 7.68 – 7.60 (m, 1H), 7.38 – 7.27 (m, 5H), 4.60 (t, J = 7.0 Hz, 2H), 3.12 (t, J = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 148.5, 137.5, 135.4, 132.2, 129.8, 129.1, 128.8, 127.5, 127.0, 124.7, 66.5, 35.3; HRMS (APCI) calcd for $C_{15}H_{13}NO_4$ ($[M]^+$) 271.08501, found 271.08500.



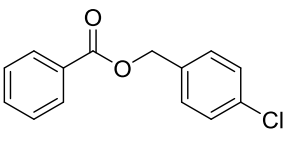
Octyl 3-nitrobenzoate (**6k**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.39 (dd, J = 17.1, 8.0 Hz, 2H), 7.66 (t, J = 8.0 Hz, 1H), 4.38 (t, J = 6.7 Hz, 2H), 1.92 – 1.62 (m, 2H), 1.66 – 1.10 (m, 10H), 0.88 (m, 3H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 164.7, 148.4, 135.4, 132.4, 129.7, 127.4, 124.7, 77.5, 66.3, 31.9, 29.4, 29.3, 28.8, 26.1, 22.8, 14.3; HRMS (APCI) calcd for $C_{15}H_{21}NO_4$ ($[M]^+$) 279.14761, found 279.14750.



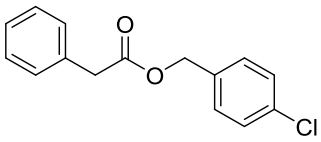
4-Chlorobenzyl 4-nitrobenzoate (**6l**): Yellowish solid, m.p: 110–111 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.26 (m, 2H), 8.26 – 8.20 (m, 2H), 7.43 – 7.36 (m, 4H), 5.38 (s, 2H); 13C NMR (101 MHz, $CDCl_3$) δ 164.56, 150.8, 135.4, 134.8, 133.8, 131.0, 130.0, 129.1, 123.8, 67.0; HRMS (APCI) calcd for C14H10ClNO4 ($[M]^+$) 291.03038, found 291.03046.



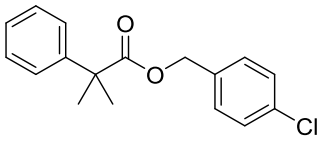
4-Chlorobenzyl benzoate (**6m**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.61 – 7.52 (m, 3H), 7.49 – 7.33 (m, 4H), 5.32 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 134.5, 134.1, 133.1, 129.9, 129.7, 129.6, 128.8, 128.4, 65.9; HRMS (APCI) calcd for $C_{14}H_{11}ClO_2$ ($[M]^+$) 246.04421, found 246.04544.



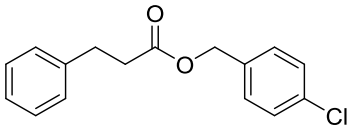
4-Chlorobenzyl 2-phenylacetate (**6n**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 - 6.94 (m, 9H), 5.10 (s, 2H), 3.67 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 134.5, 134.2, 133.9, 129.6, 129.4, 128.9, 128.8, 127.3, 65.9, 41.5; HRMS (APCI) calcd for $C_{15}H_{13}ClO_2$ ($[M]^+$) 260.05986, found 260.06006.



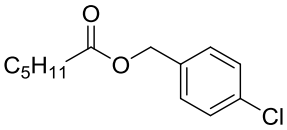
4-chlorobenzyl 2-methyl-2-phenylpropanoate (**6o**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 4H), 7.28 – 7.23 (m, 3H), 7.13 – 7.09 (m, 2H), 5.06 (s, 2H), 1.60 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.49, 144.4, 134.8, 133.9, 129.2, 128.7, 128.5, 126.9, 125.8, 65.7, 46.7, 26.5.



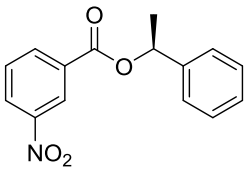
4-chlorobenzyl 3-phenylpropanoate (**6p**): Yellowish oil; ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.35 – 7.27 (m, 4H), 7.25 – 7.17 (m, 5H), 5.08 (s, 2H), 2.98 (t, J = 7.7 Hz, 2H), 2.70 (t, J = 9.1, 6.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 140.4, 134.5, 134.2, 129.7, 128.8, 128.6, 128.4, 126.4, 65.5, 35.9, 31.0; HRMS (+EI) calcd for $C_{16}H_{15}ClO_2$ ($[M]^+$) 256.06494, found 256.06670.



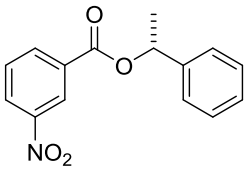
4-chlorobenzyl hexanoate (**6q**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.31 – 7.26 (m, 2H), 5.07 (s, 2H), 2.34 (t, J = 7.6 Hz, 2H), 1.78 – 1.49 (m, 2H), 1.40 – 1.20 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 134.8, 134.2, 129.7, 128.9, 65.4, 34.4, 31.4, 24.8, 22.4, 14.0; HRMS (+EI) calcd for $C_{13}H_{17}ClO_2$ ($[M]^+$) 240.09171, found 240.09134.



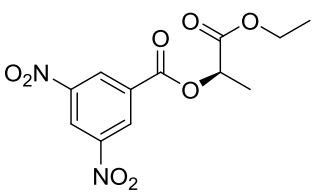
(*S*)-1-Phenylethyl 3-nitrobenzoate (**6r**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 - 8.81 (m, 1H), 8.48 – 8.25 (m, 2H), 7.68 – 7.62 (m, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.36 (m, 2H), 7.36 – 7.30 (m, 1H), 6.18 (q, J = 6.6 Hz, 1H), 1.72 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 148.4, 141.1, 135.5, 132.4, 129.7, 128.8, 128.4, 127.5, 126.3, 124.7, 74.3, 22.4; HRMS (APCI) calcd for $C_{15}H_{13}NO_4$ ($[M]^+$) 271.08501, found 271.08503.



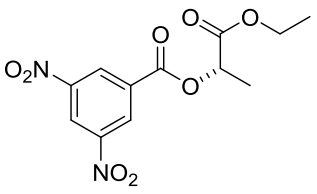
(*R*)-1-Phenylethyl 3-nitrobenzoate (**6r**): Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 - 8.81 (m, 1H), 8.48 – 8.25 (m, 2H), 7.68 – 7.62 (m, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.36 (m, 2H), 7.36 – 7.30 (m, 1H), 6.18 (q, J = 6.6 Hz, 1H), 1.72 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 148.4, 141.1, 135.5, 132.4, 129.7, 128.8, 128.4, 127.5, 126.3, 124.7, 74.3, 22.4; HRMS (APCI) calcd for $C_{15}H_{13}NO_4$ ($[M]^+$) 271.08501, found 271.08502.



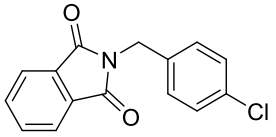
Ethyl (*R*)-2-((3,5-dinitrobenzoyl)oxy) propionate (**6s**): White solid, m.p: 92-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.26 (t, *J* = 2.2, 1H), 9.20 (d, *J* = 2.1, 2H), 5.41 (q, *J* = 7.1, 1H), 4.27 (q, *J* = 7.1, 2H), 1.72 (d, *J* = 7.1, 3H), 1.31 (t, *J* = 7.1, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 162.1, 148.8, 133.4, 129.8, 122.8, 71.0, 62.1, 17.1, 14.3; HRMS (APCI) calcd for $C_{12}H_{12}N_2O_8$ ($[M]^+$) 312.05978, found 312.05991.



Ethyl (*S*)-2-((3,5-dinitrobenzoyl)oxy) propionate (**6s**): White solid, m.p: 92-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.26 (t, *J* = 2.2, 1H), 9.20 (d, *J* = 2.1, 2H), 5.41 (q, *J* = 7.1, 1H), 4.27 (q, *J* = 7.1, 2H), 1.72 (d, *J* = 7.1, 3H), 1.31 (t, *J* = 7.1, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 162.1, 148.8, 133.4, 129.8, 122.8, 71.0, 62.1, 17.1, 14.3; HRMS (APCI) calcd for $C_{12}H_{12}N_2O_8$ ($[M]^+$) 312.05978, found 312.05991.



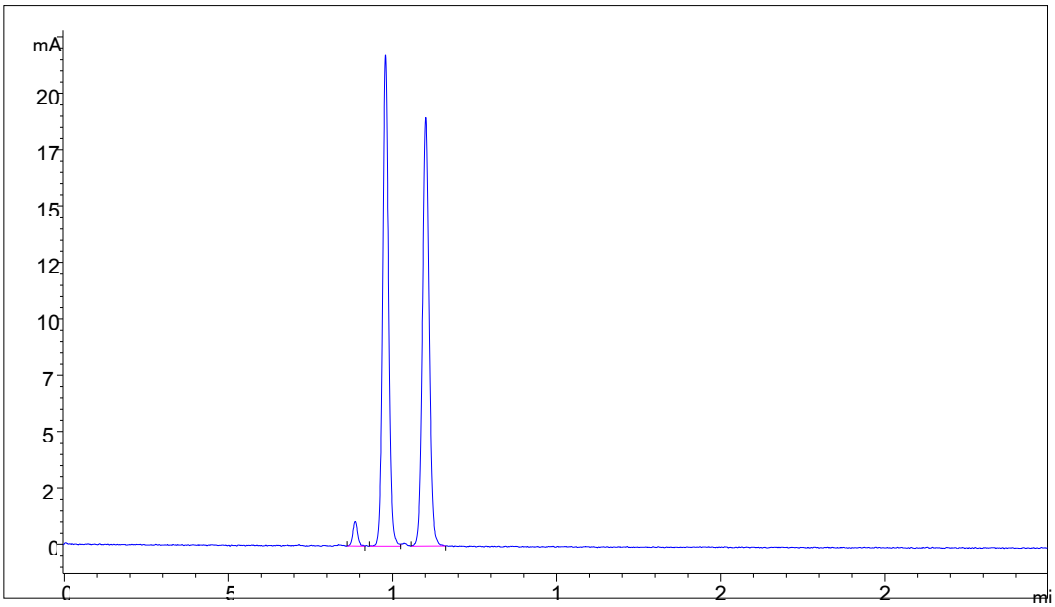
***N*-(4-Chlorobenzyl)-phthalimide** (**9**): White solid, m.p: 119–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2H), 7.75 – 7.68 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 4.81 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 135.0, 134.2, 133.9, 132.2, 130.2, 129.0, 123.6, 41.1; HRMS (APCI) calcd for $C_{15}H_{10}ClNO_2$ ($[M]^+$) 271.04055, found 271.04187.



S4 HPLC analysis of products (6i, 6k) of stereoselective esterification

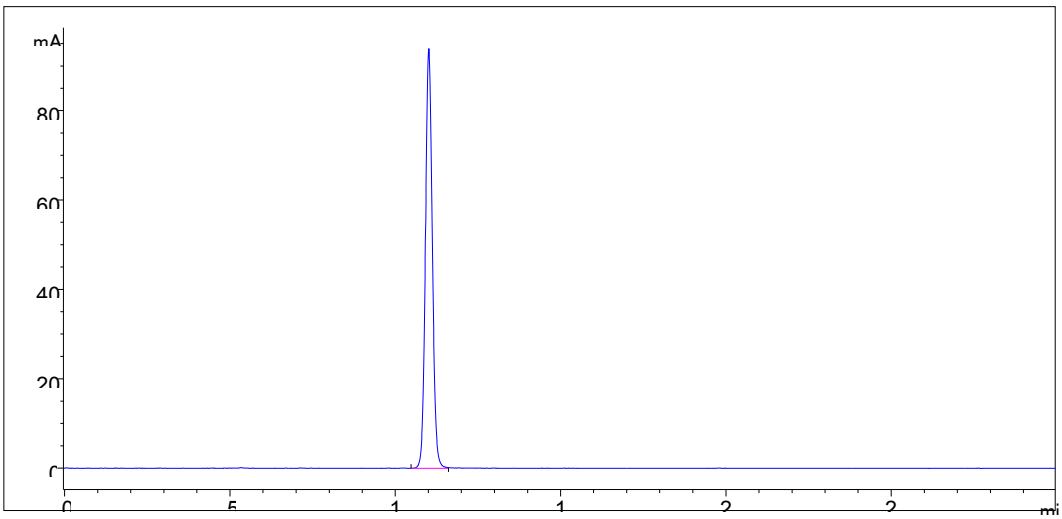
Analysis were performed on Agilent 1100 series (Agilent Technologies) using Chiral Art Amylose C column, heptane/isopropyl alcohol 9:1, flow 0,7 mL/min, temp. 15 °C, detection at 254 nm.

rac-1-phenylethyl 3-nitrobenzoate (*rac*-**6r**)



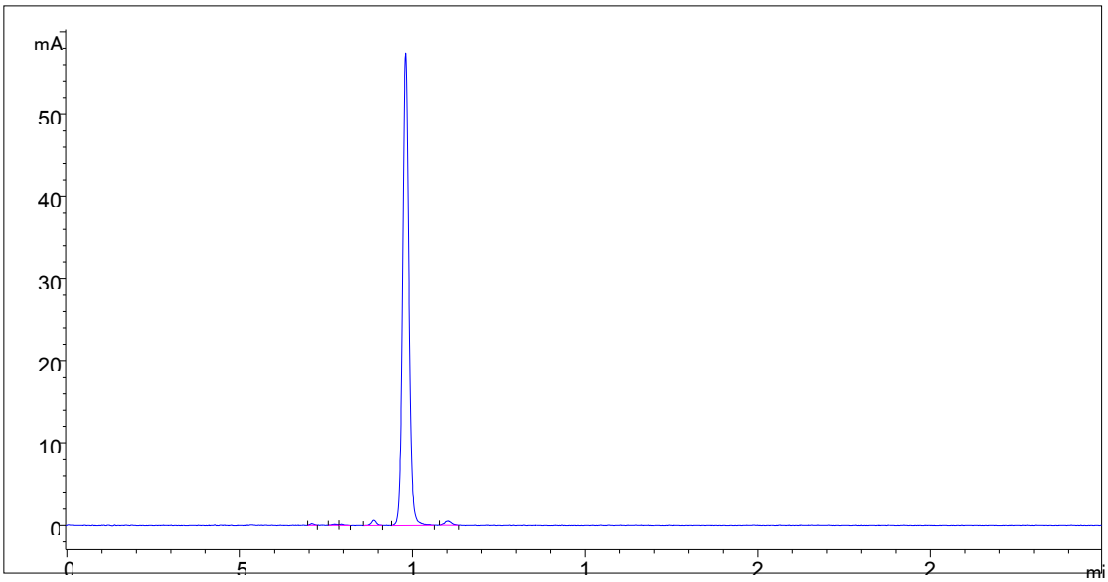
#	Time	Area	Height	Width	Area%	Symmetry
1	9.787	2716	218	0.1914	50.061	0.911
2	11.012	2709.4	190.1	0.2203	49.939	0.928

(*S*)-1-phenylethyl 3-nitrobenzoate ((*S*)-**6r**)



#	Time	Area	Height	Width	Area%	Symmetry
1	11.027	2709.4	190.1	0.2203	100	0.928

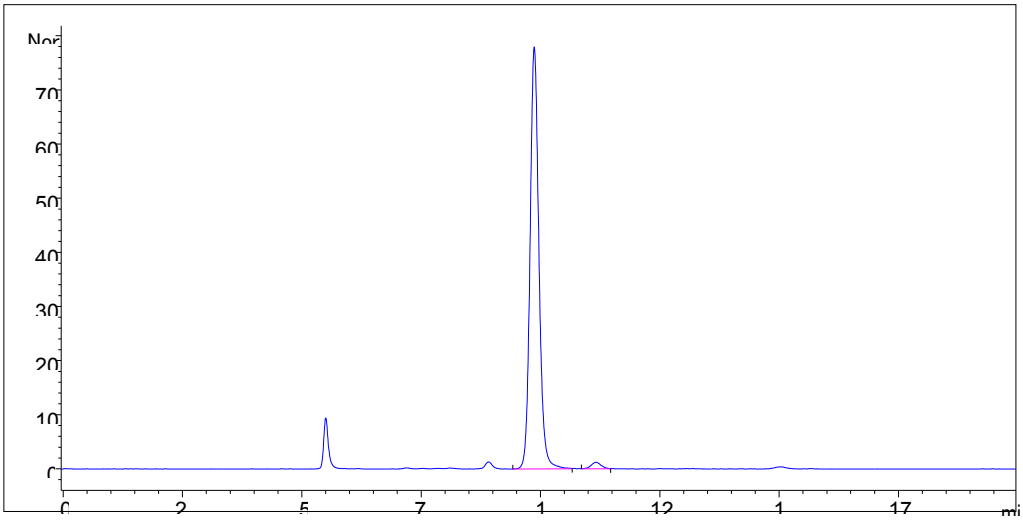
(*R*)-1-phenylethyl 3-nitrobenzoate ((*R*)-**6r**)



#	Time	Area	Height	Width	Area%	Symmetry
1	9.801	7223.7	574.5	0.1947	99.021	0.902
2	11.032	72.5	5.2	0.2046	0.979	0.915

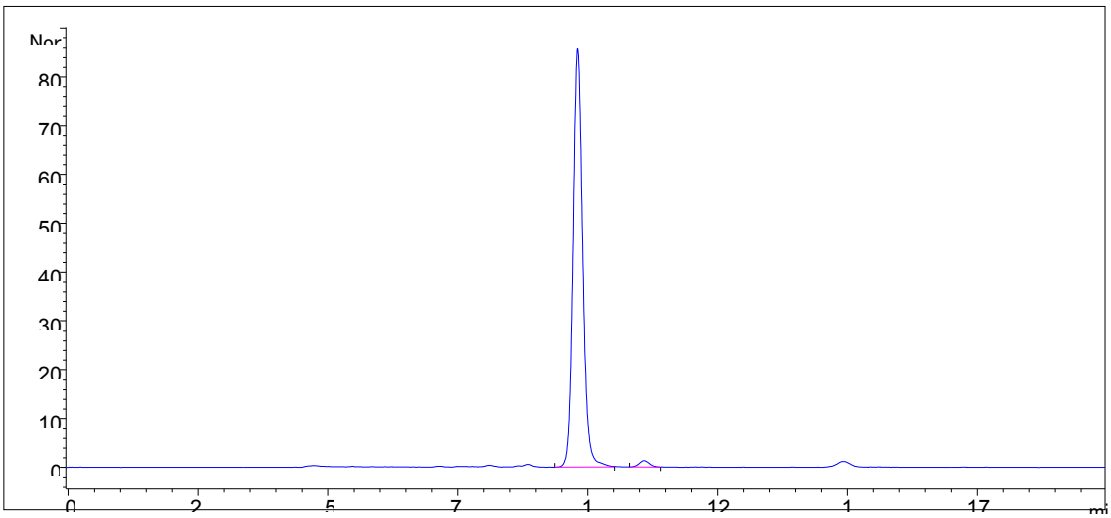
Results in Table 3 (main text)

(*R*)-**6r** (Method **A**)



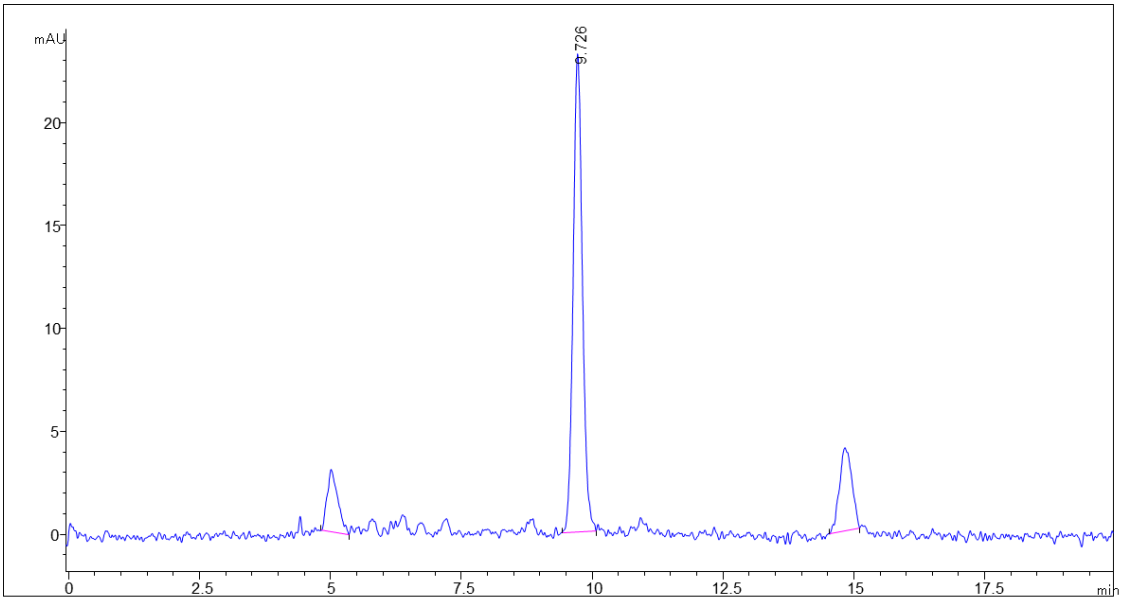
#	Time	Area	Height	Width	Area%	Symmetry
1	9.869	10041.1	780	0.1982	98.295	0.847
2	11.162	174.2	11.9	0.2229	1.705	0.891

(*R*)-**6r** (Method **B**)



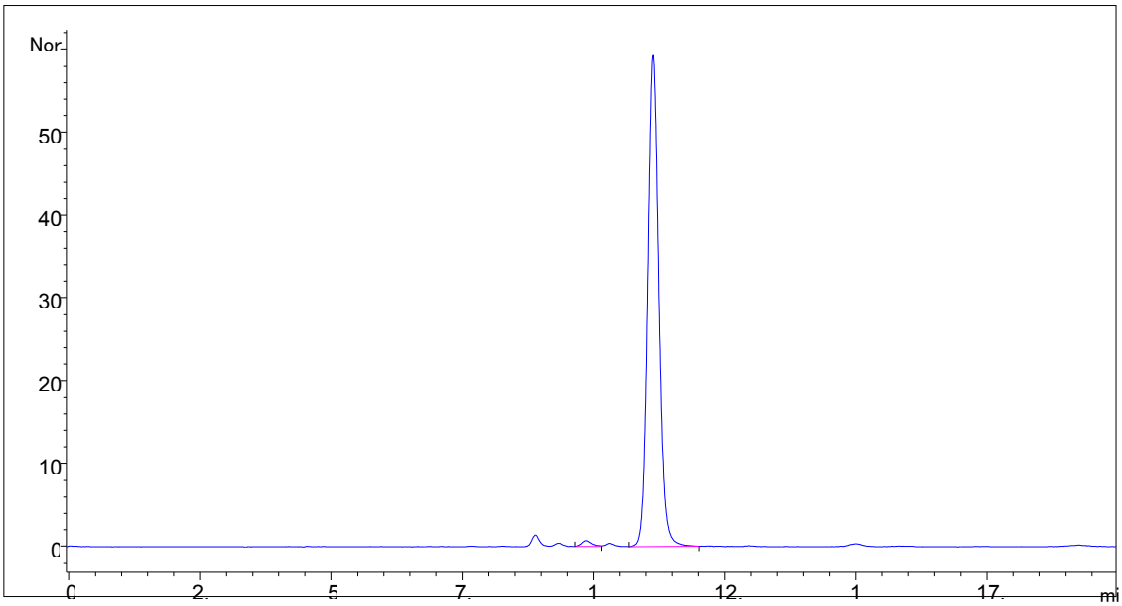
#	Time	Area	Height	Width	Area%	Symmetry
1	9.805	11066.8	858.5	0.2149	99.016	0.855
2	11.082	181.3	13.3	0.2268	0.984	0.837

(*R*)-**6r** (Method **B** – in the absence of **2b**)



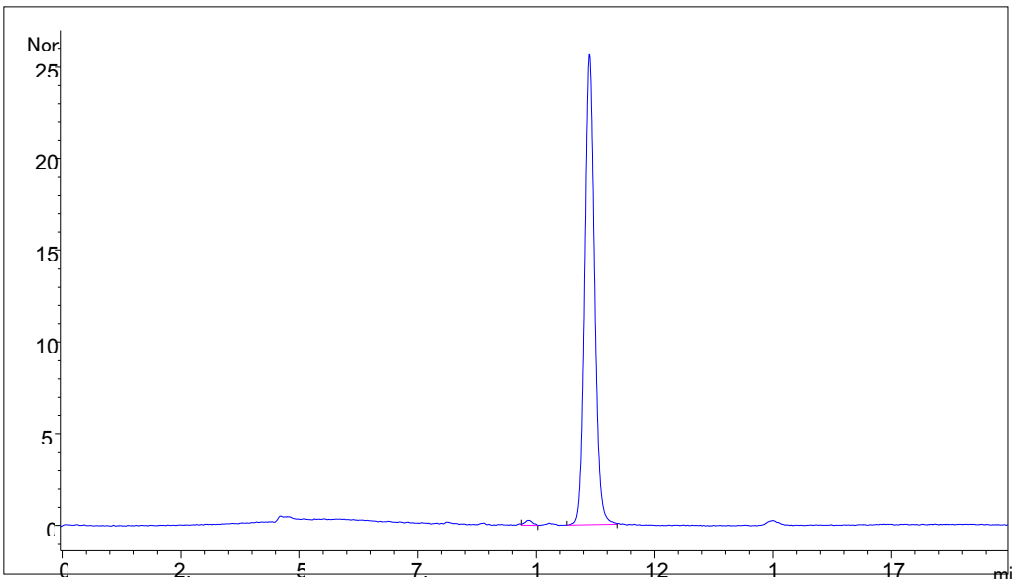
#	Time	Area	Height	Width	Area%	Symmetry
1	9.726	367.9	258.7	0.2215	98.882	0.894
2	11.137	41.8	2.9	0.1511	1.118	1.332

(*S*)-**6r** (Method **A**)



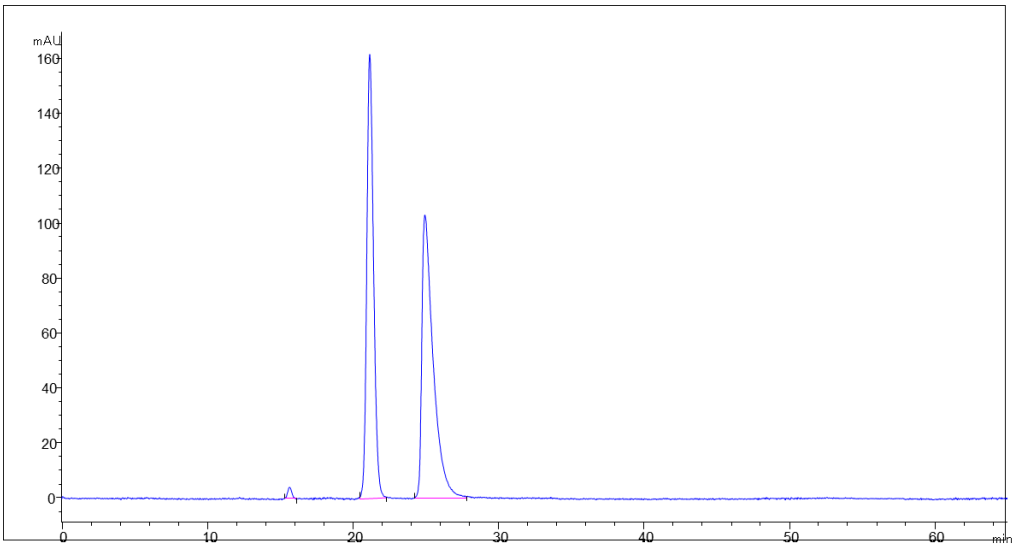
#	Time	Area	Height	Width	Area%	Symmetry
1	9.858	94.2	7.1	0.1832	1.070	0.719
2	11.134	8709.3	593.9	0.2251	98.930	0.875

(*S*)-**6r** (Method **B**)



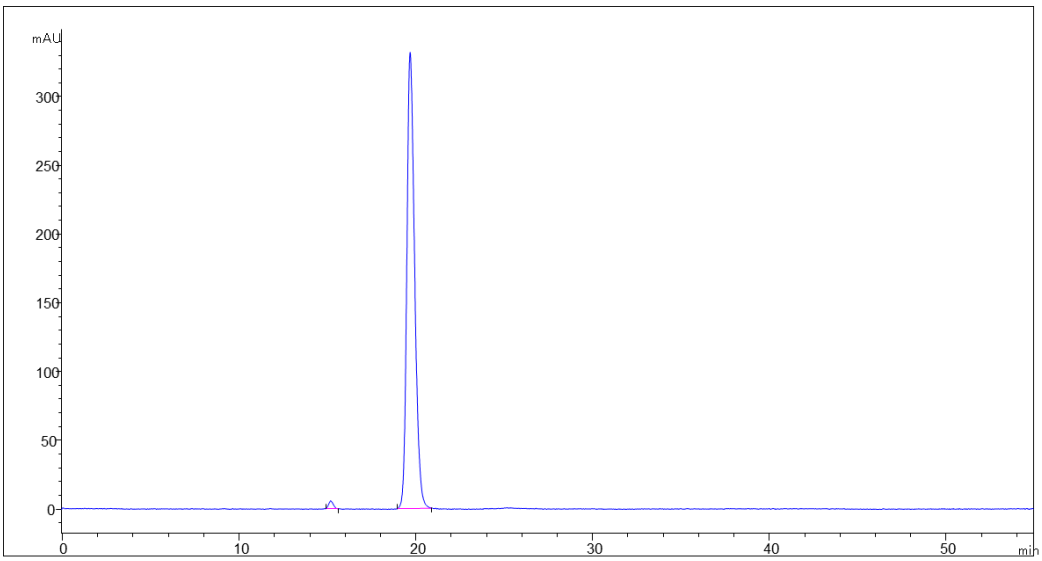
#	Time	Area	Height	Width	Area%	Symmetry
1	9.86	32.8	2.8	0.1501	0.873	1.342
2	11.124	3727.9	256.7	0.2214	99.127	0.884

Ethyl (*rac*)-2-((3,5-dinitrobenzoyl)oxy) propionate ((*rac*)-**6s**)



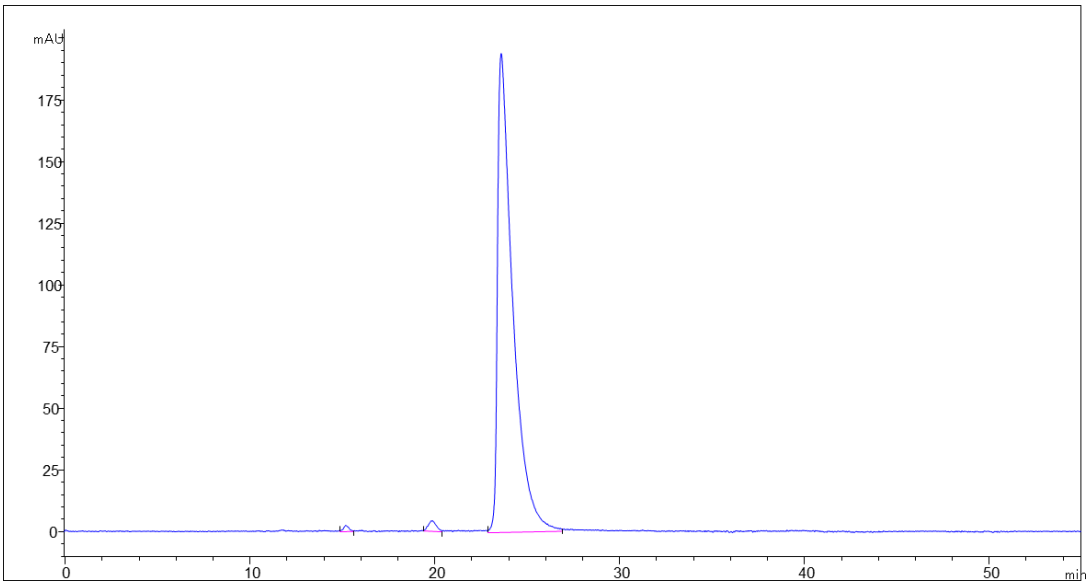
#	Time	Area	Height	Width	Area%	Symmetry
1	21.121	5203.4	161.8	0.4653	48.547	0.742
2	24.915	5601.9	103.4	0.9031	51.453	0.351

Ethyl (*R*)-2-((3,5-dinitrobenzoyl)oxy) propionate ((*R*)-**6s**)



#	Time	Area	Height	Width	Area%	Symmetry
1	19.676	10251.1	332.1	0.4661	100	0.704

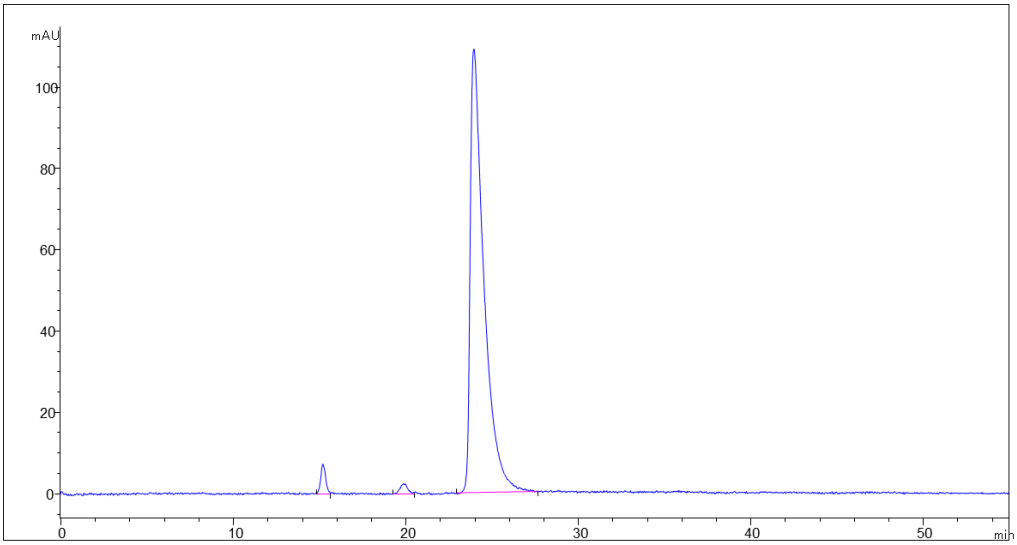
Ethyl (*S*)-2-((3,5-dinitrobenzoyl)oxy) propionate ((*S*)-**6s**))



#	Time	Area	Height	Width	Area%	Symmetry
1	19.868	131.4	4.5	0.3642	1.156	1.034
2	23.569	11192.5	194.3	0.9601	98.844	0.3

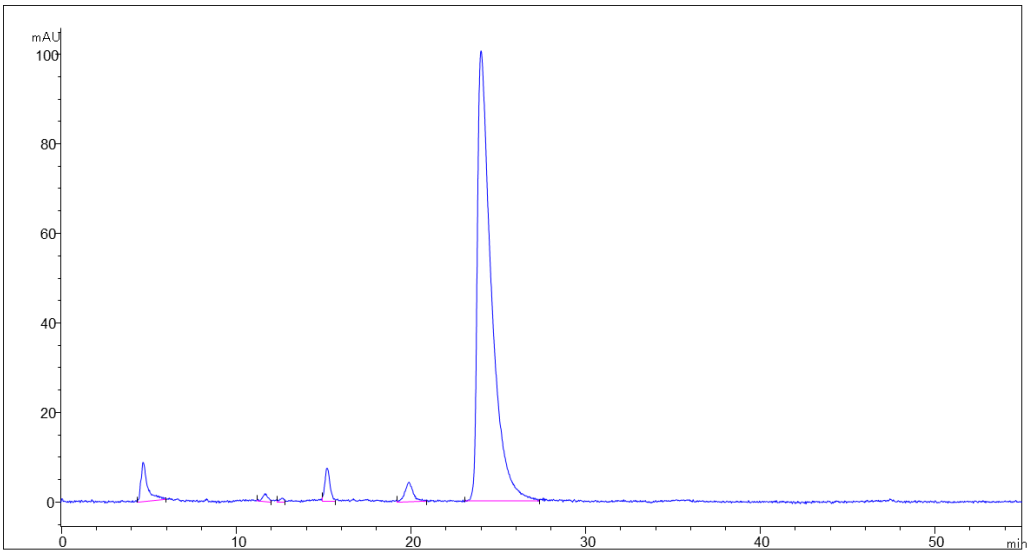
Results in Table 3 (main text)

(*S*)-**6s** (Method **A**)



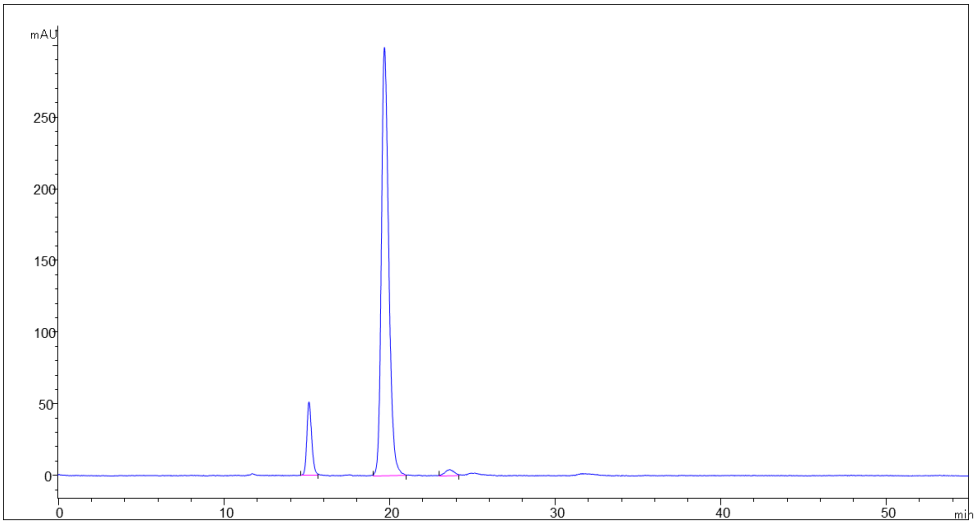
#	Time	Area	Height	Width	Area%	Symmetry
1	19.854	86.1	2.6	0.5457	1.402	0.788
2	23.925	6052.3	109.1	0.9246	98.594	0.36

(*S*)-**6s** (Method **B**)



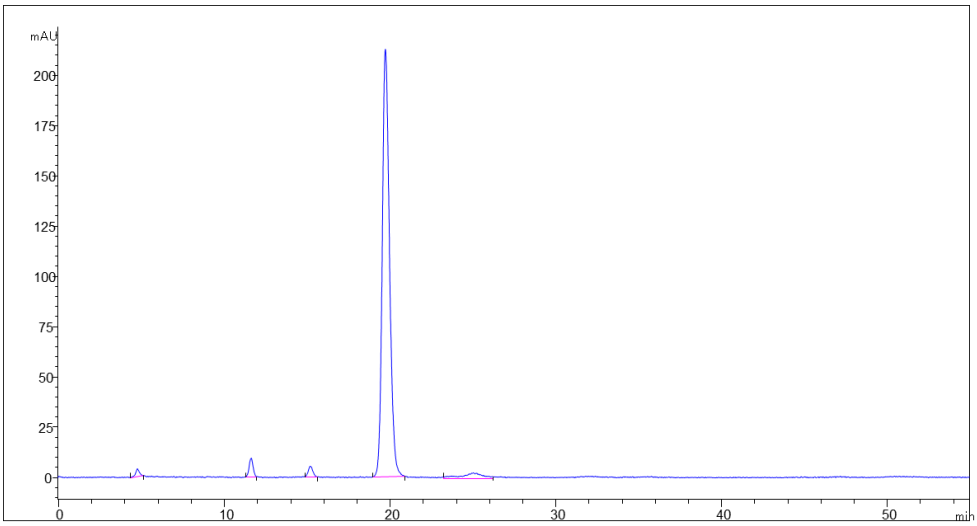
#	Time	Area	Height	Width	Area%	Symmetry
1	19.878	143.3	4.5	0.5352	2.216	0.972
2	23.983	5600.7	100.6	0.9278	97.784	0.344

(*R*)-**6s** (Method **A**)



#	Time	Area	Height	Width	Area%	Symmetry
1	19.678	9273.5	299	0.4699	98.331	0.703
2	23.602	157.4	4.4	0.4271	1.669	1.119

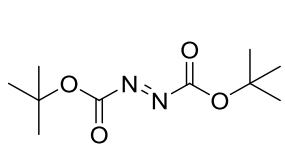
(*R*)-**6s** (Method **B**)

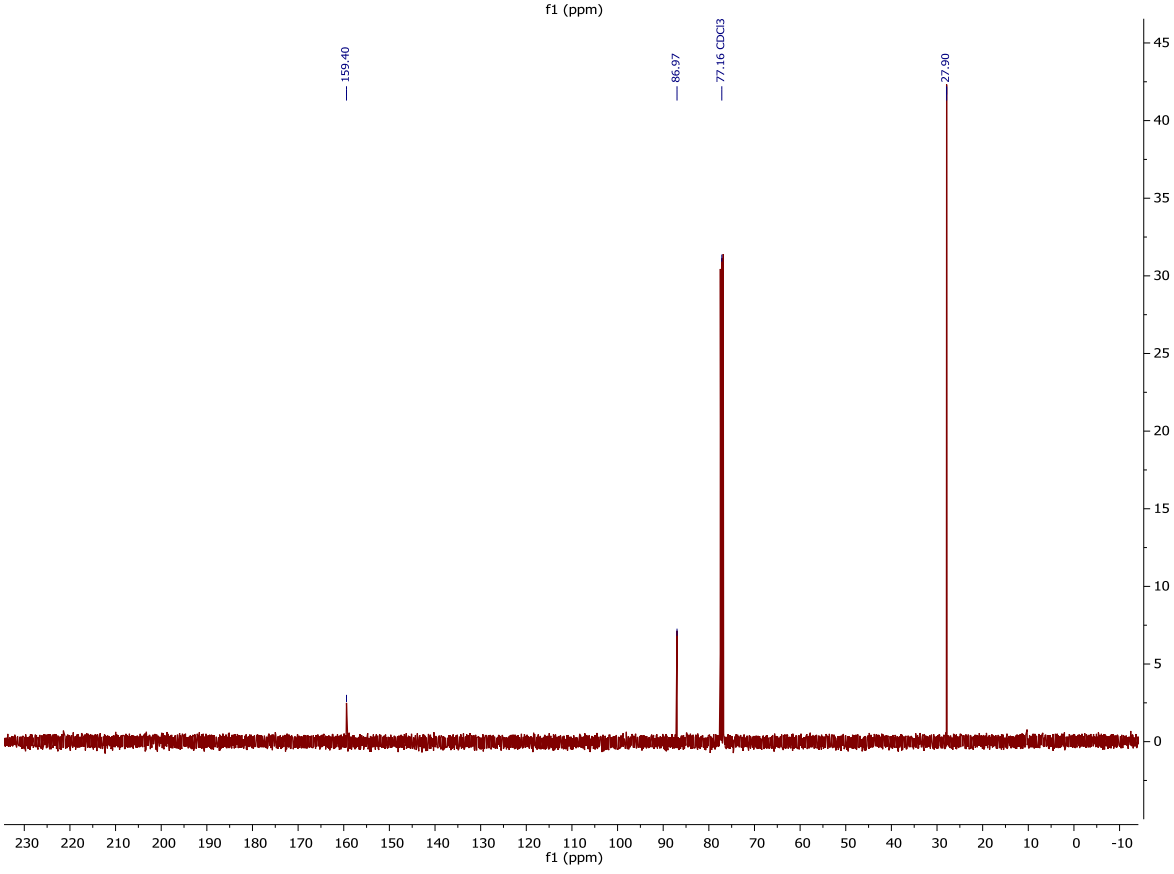


#	Time	Area	Height	Width	Area%	Symmetry
1	19.711	6484.1	212.8	0.4555	96.851	0.751
2	25.014	210.8	2.7	1.5865	3.149	1.359

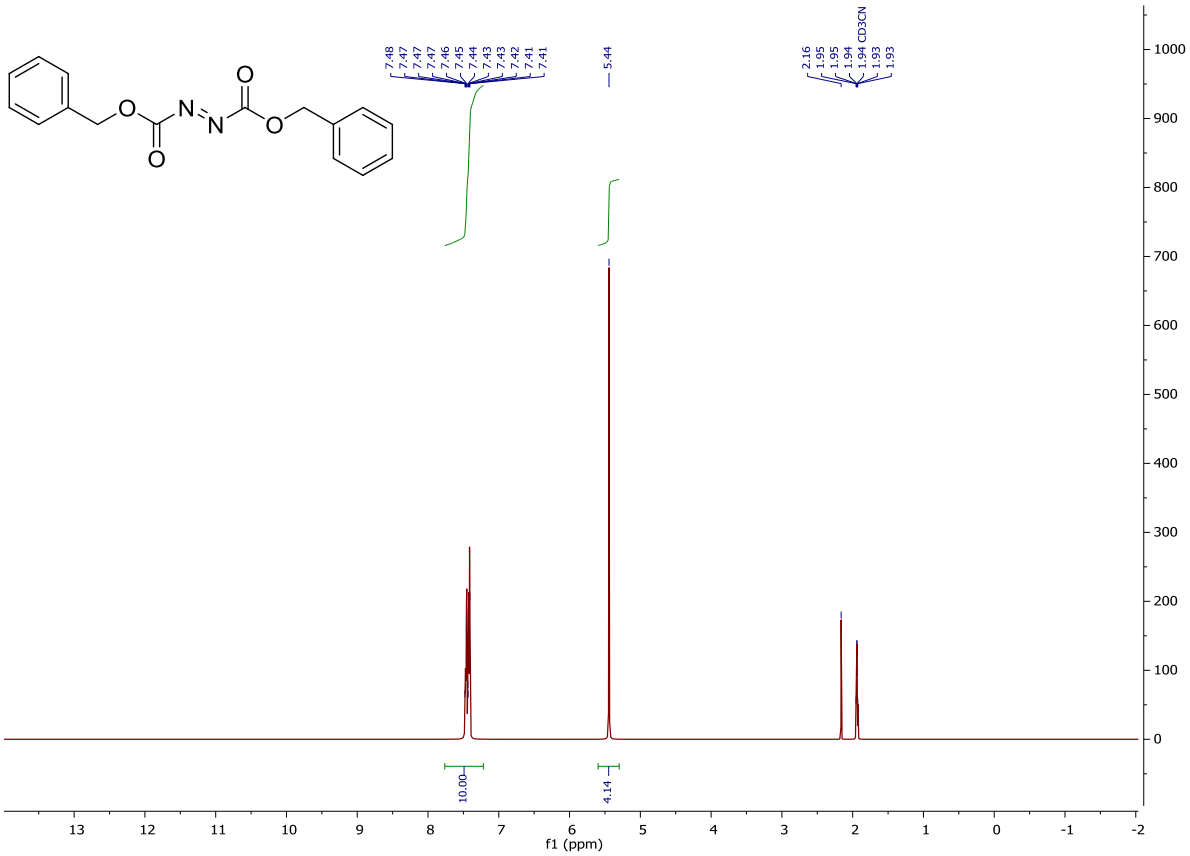
S5 ^{1}H and ^{13}C NMR spectra of 1 and 2

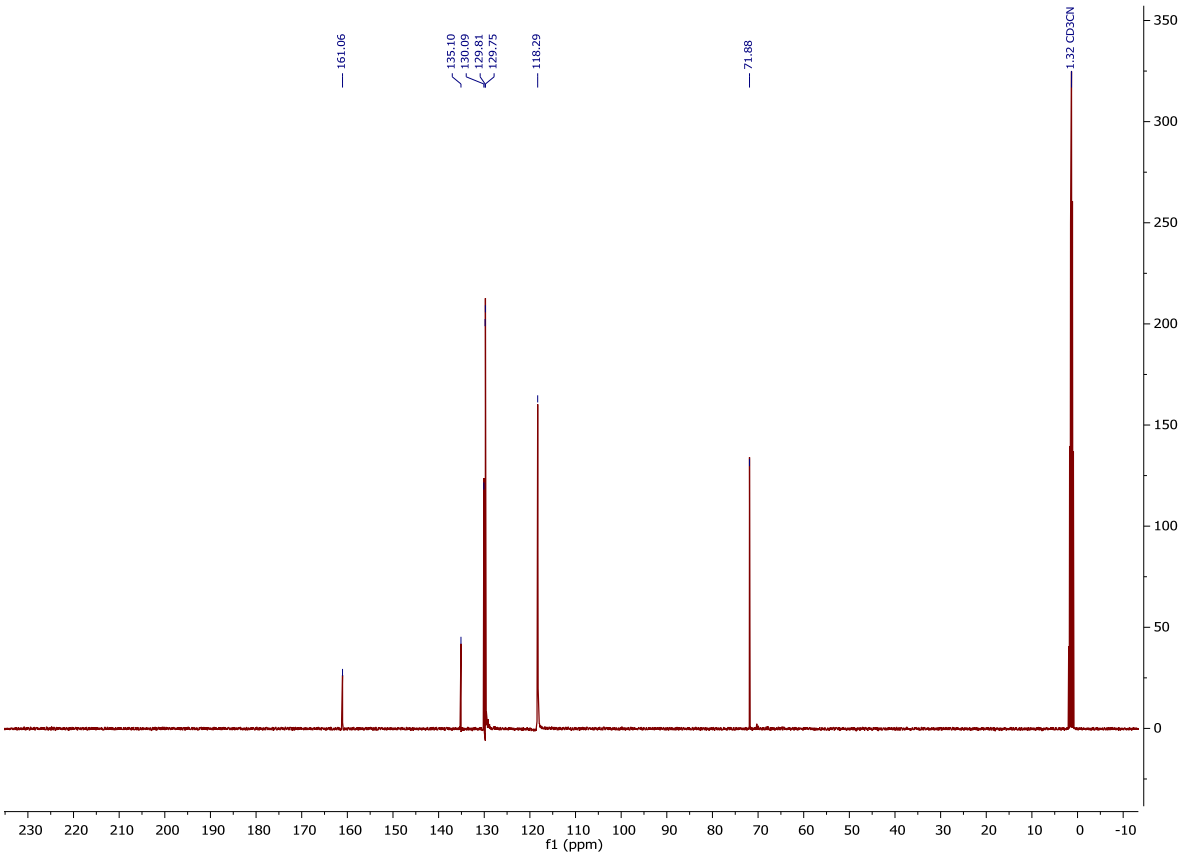
Di-*tert*-butyl azodicarboxylate (1c):



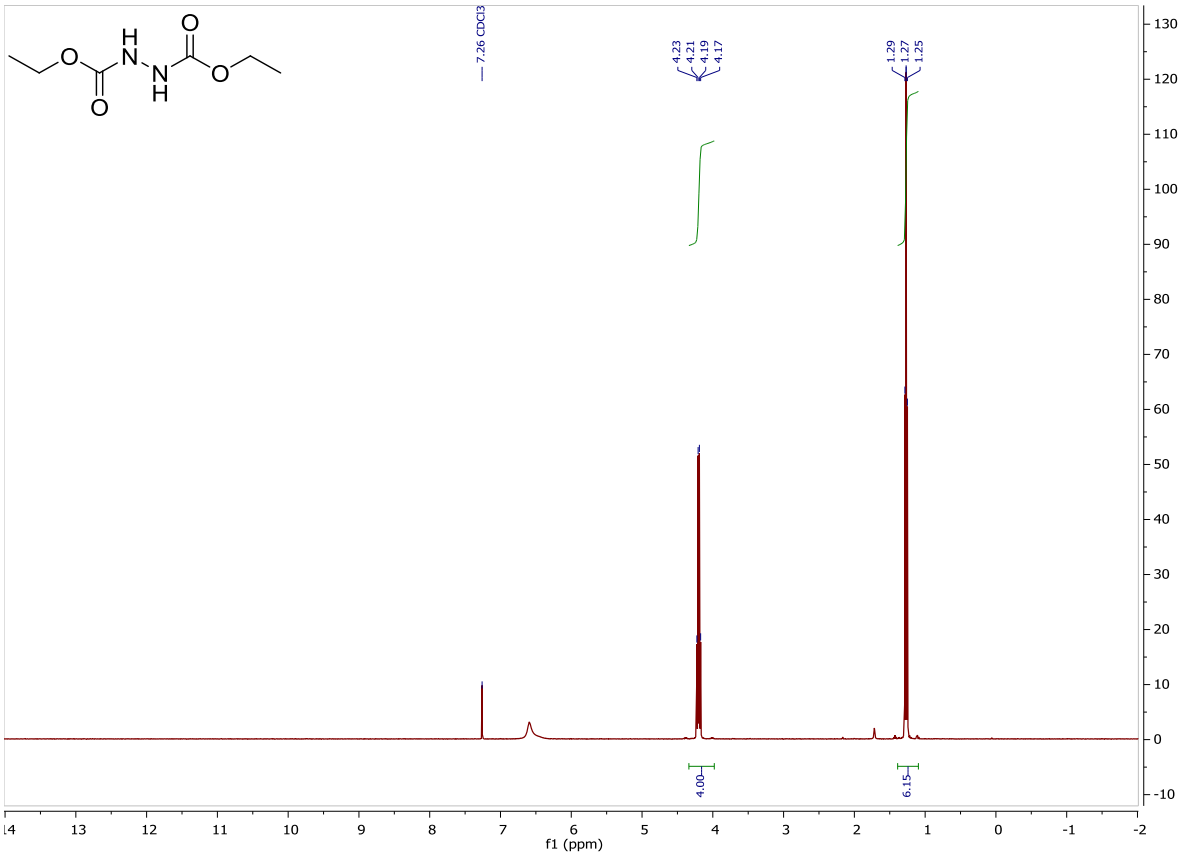


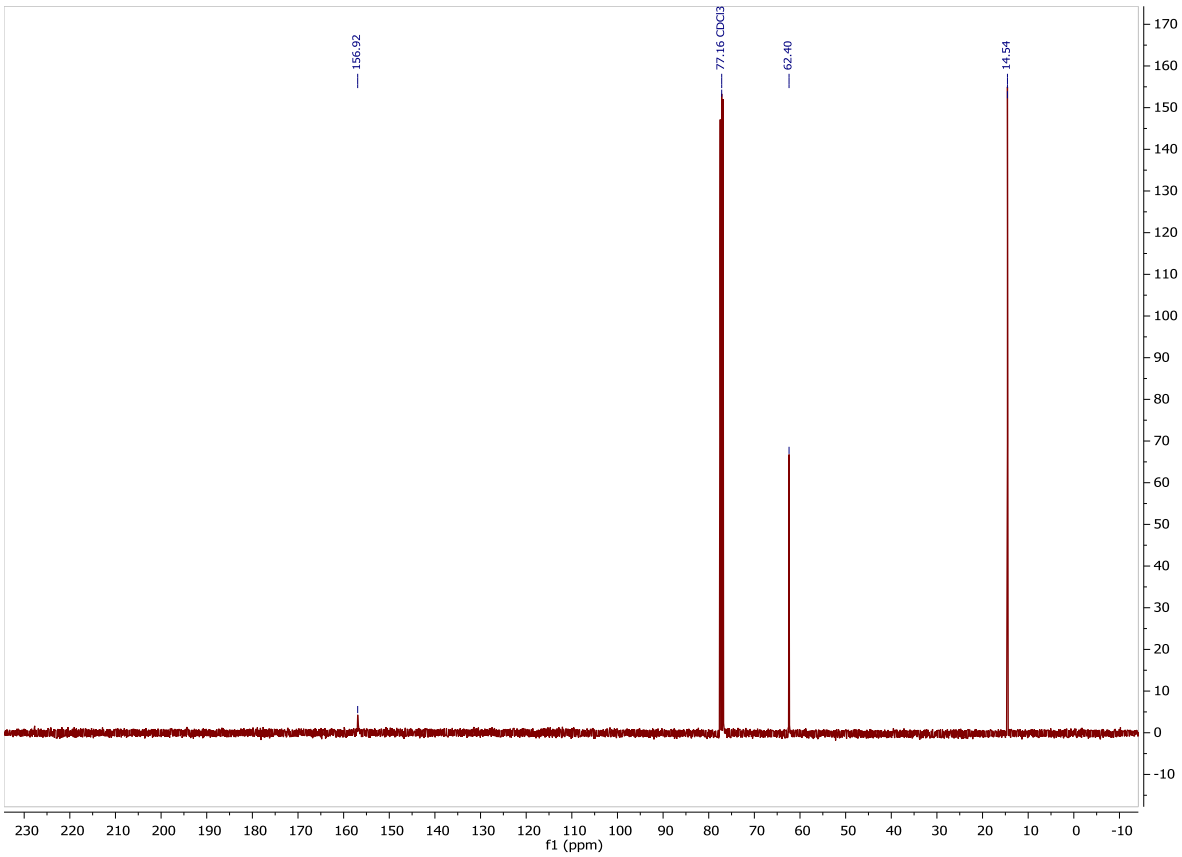
Dibenzyl azodicarboxylate (1d):



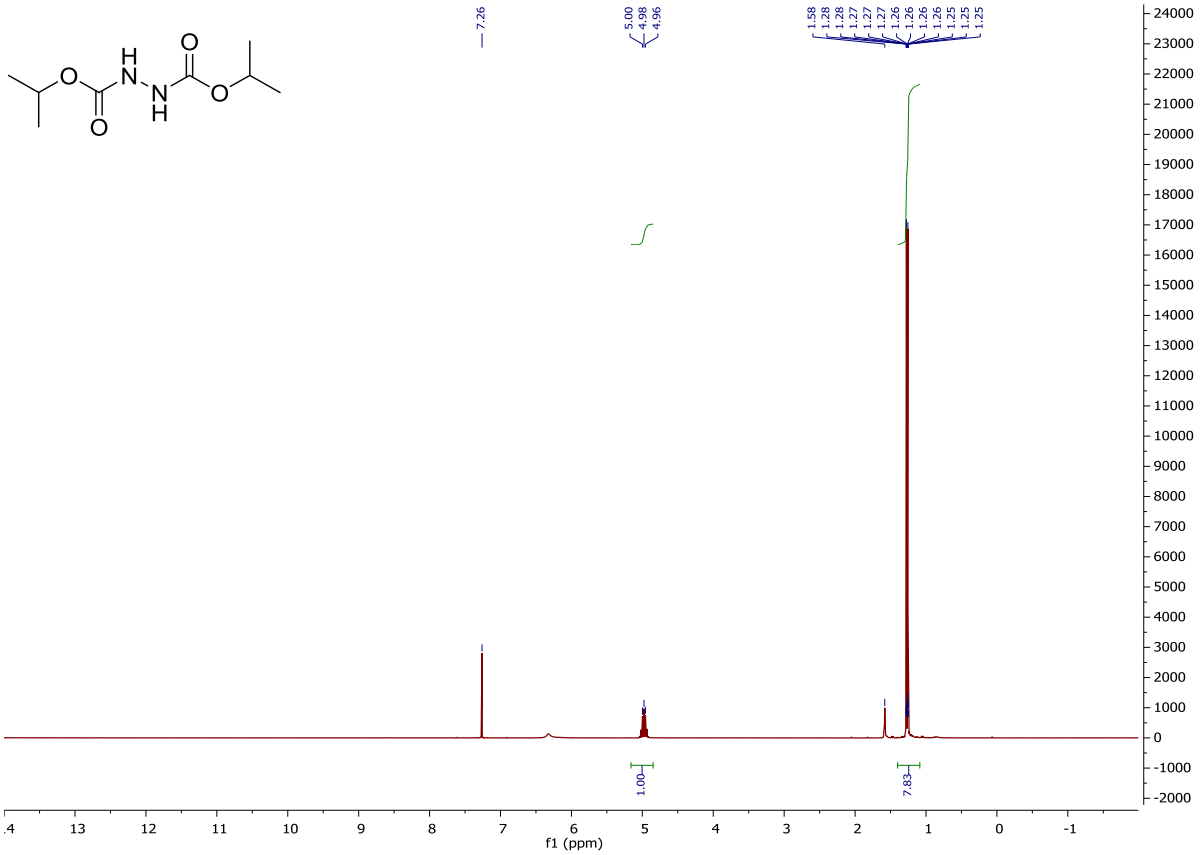


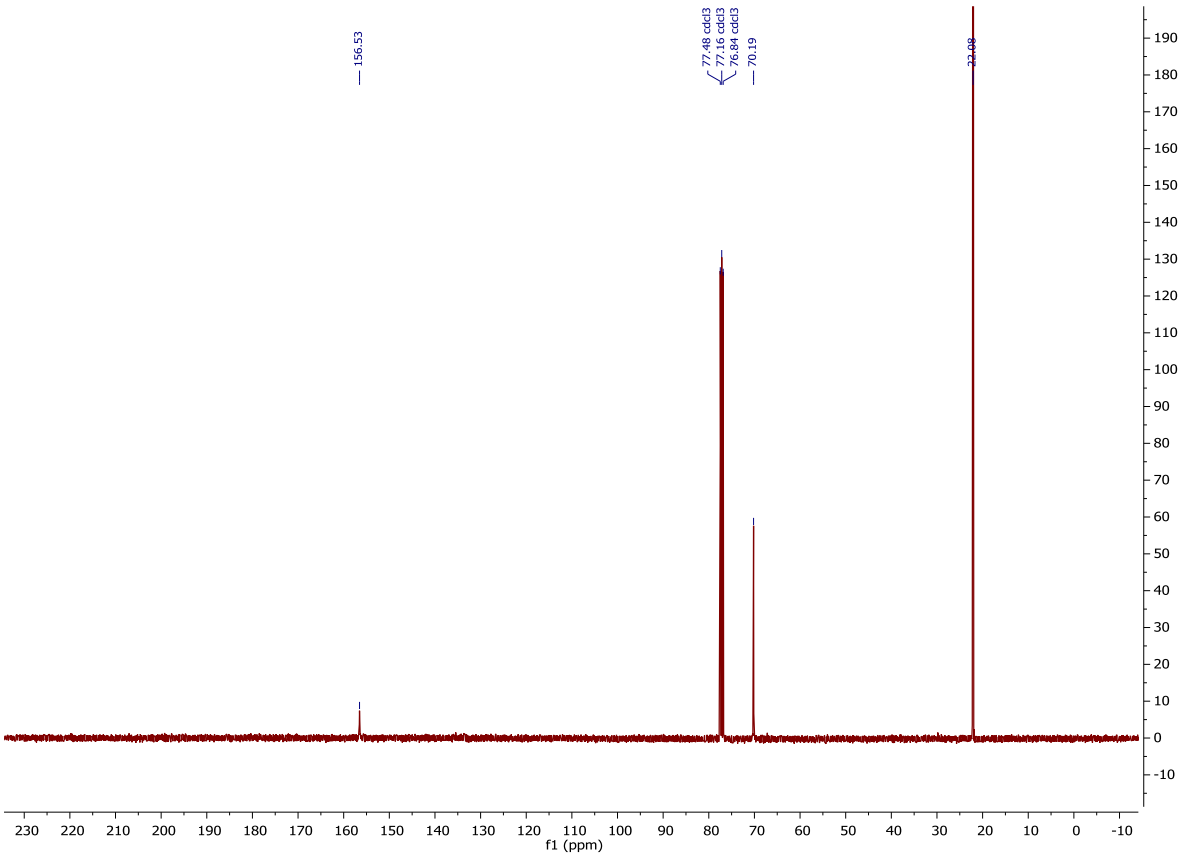
Diethyl hydrazine-1,2-dicarboxylate (2a):



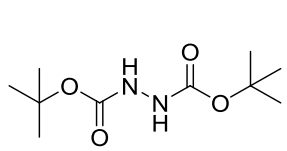


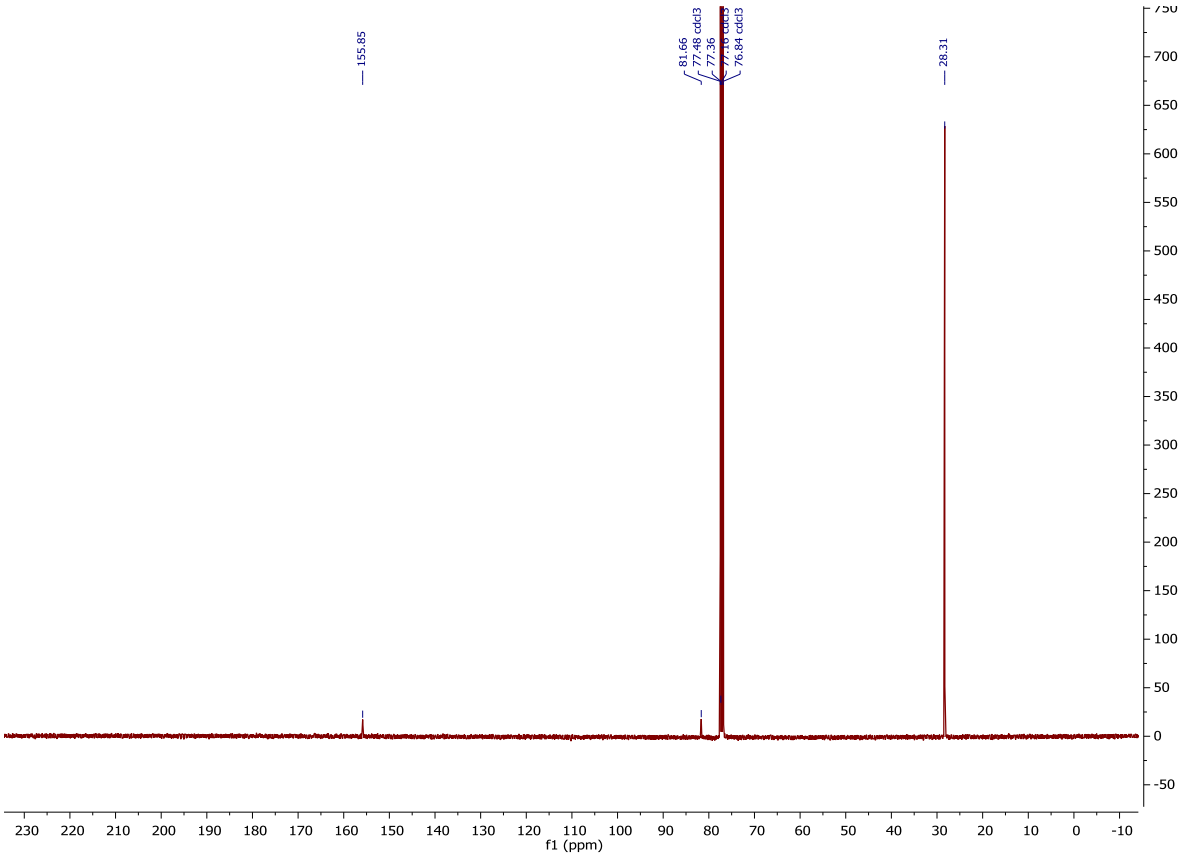
Diisopropyl hydrazine-1,2-dicarboxylate (2b):



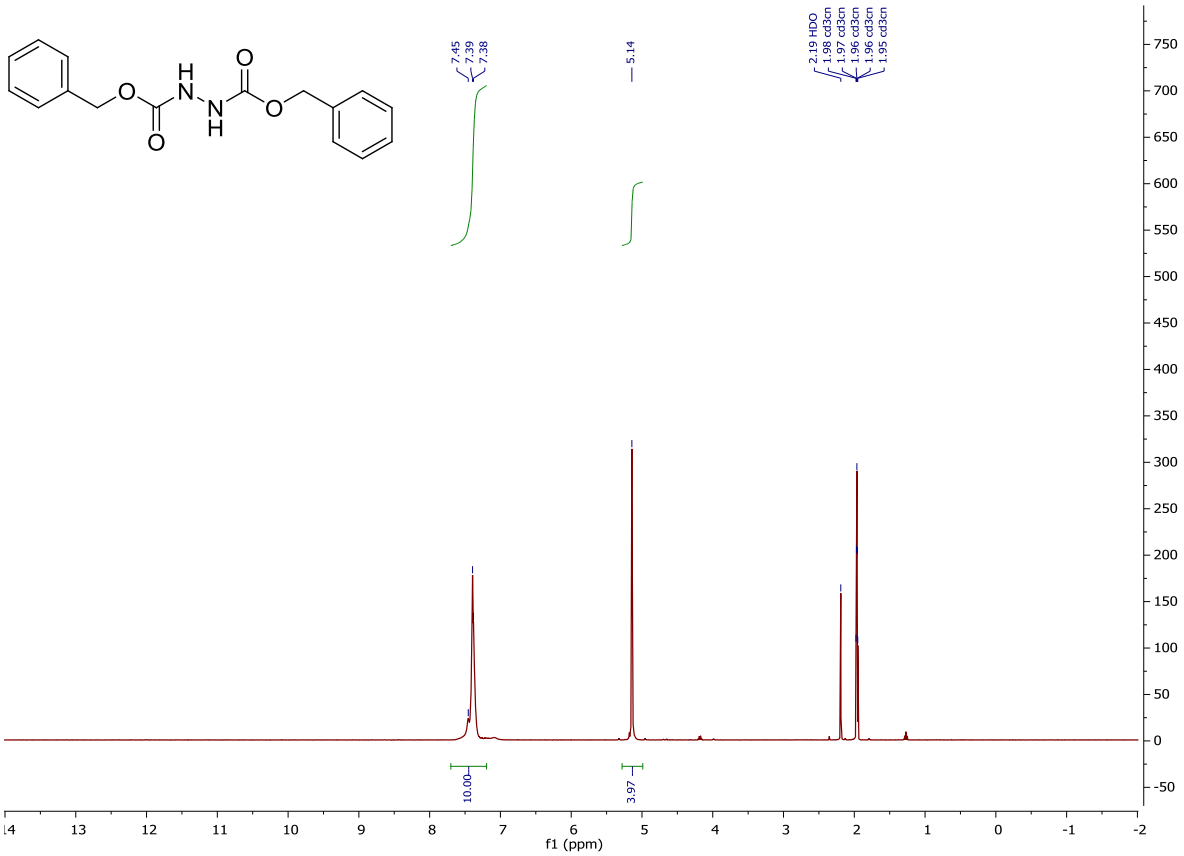


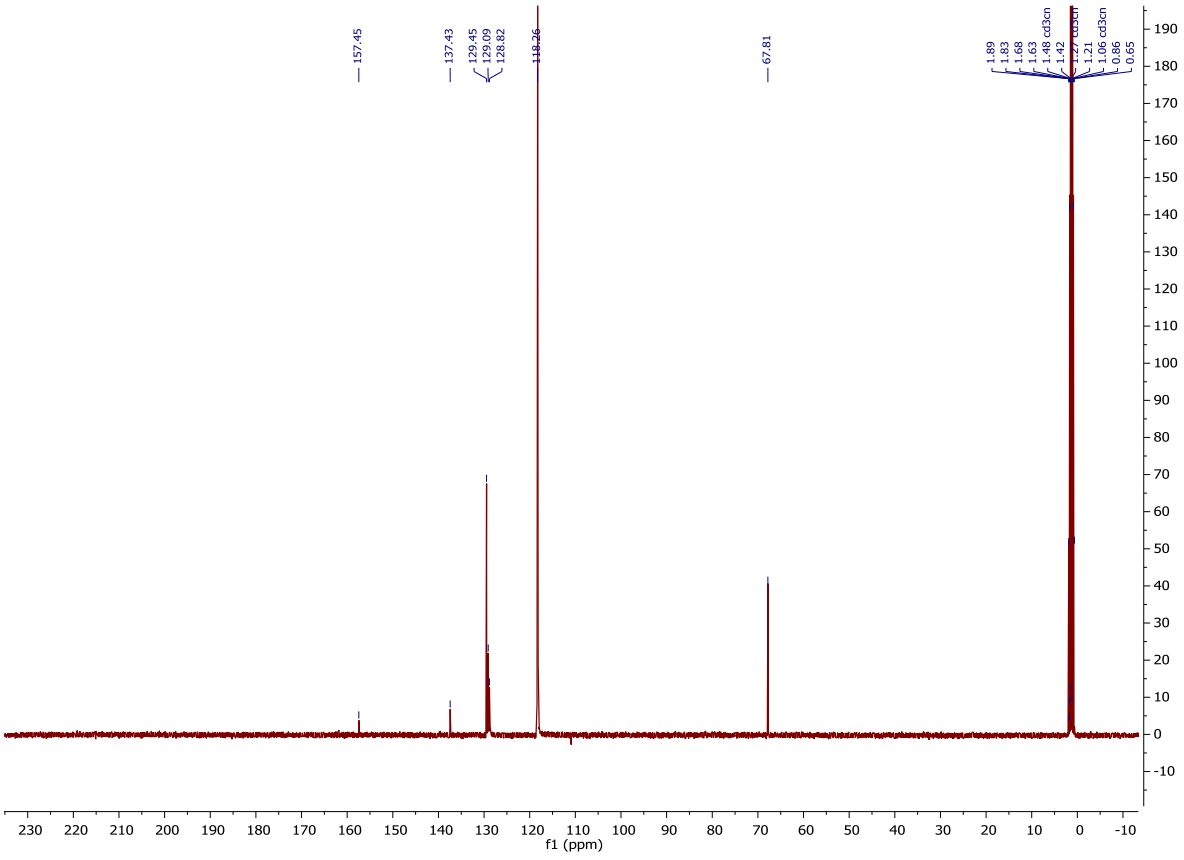
Di-*tert*-butyl hydrazine-1,2-dicarboxylate (2c):





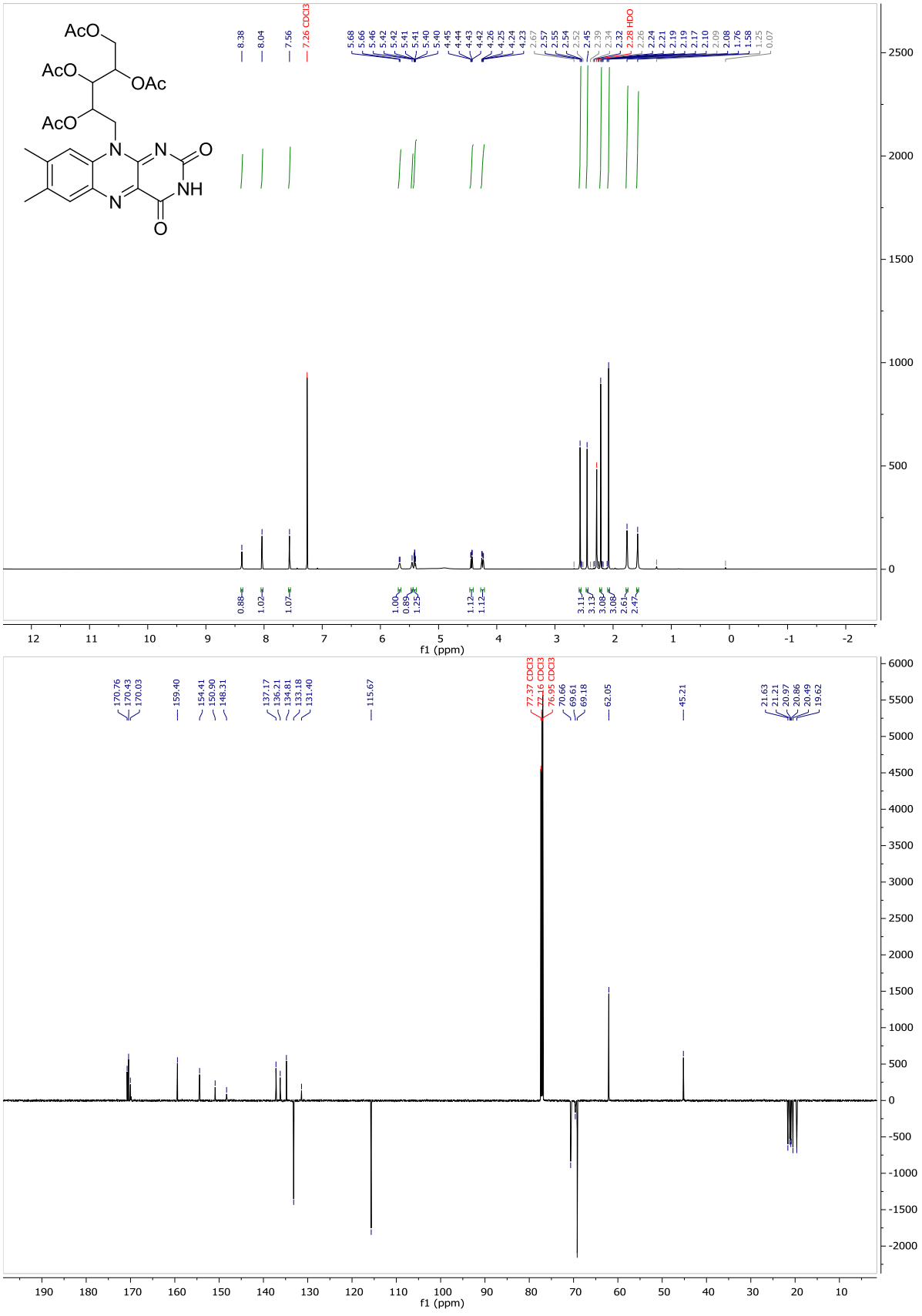
Dibenzyl hydrazine-1,2-dicarboxylate (2d):



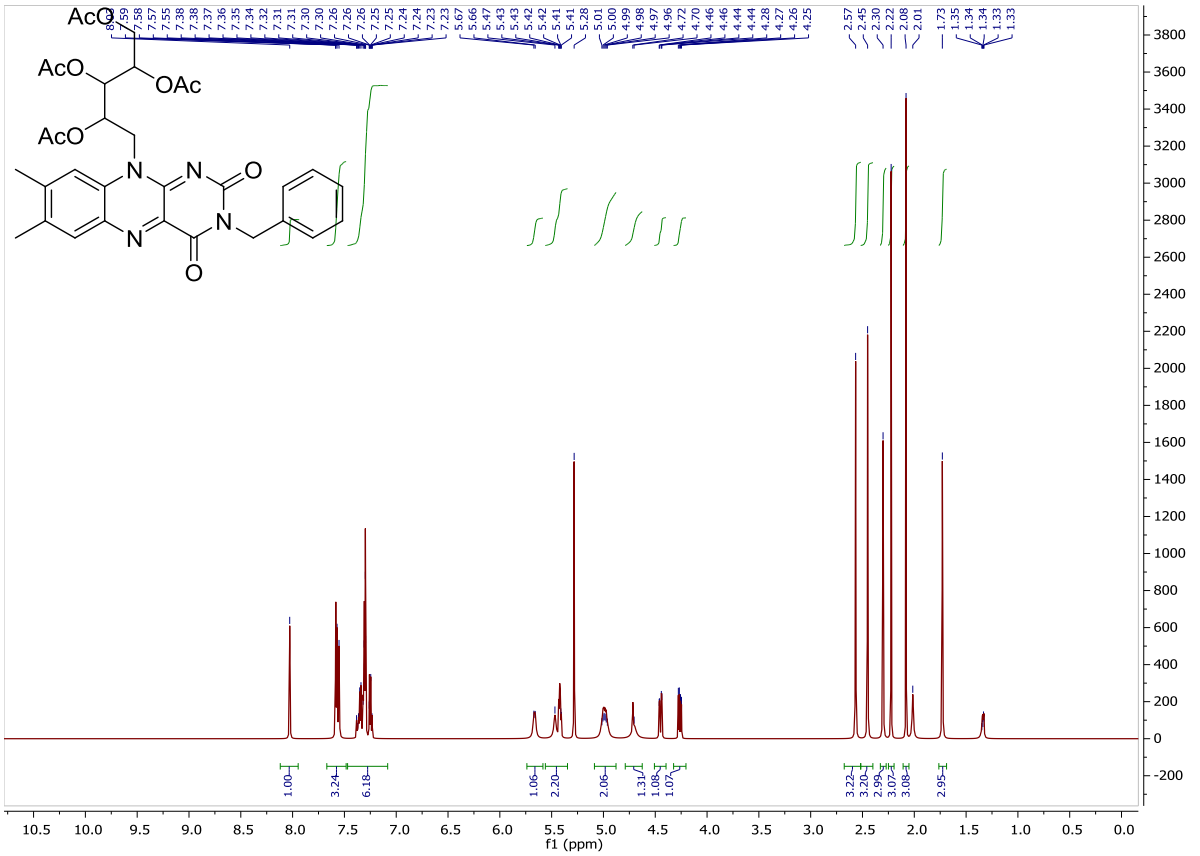


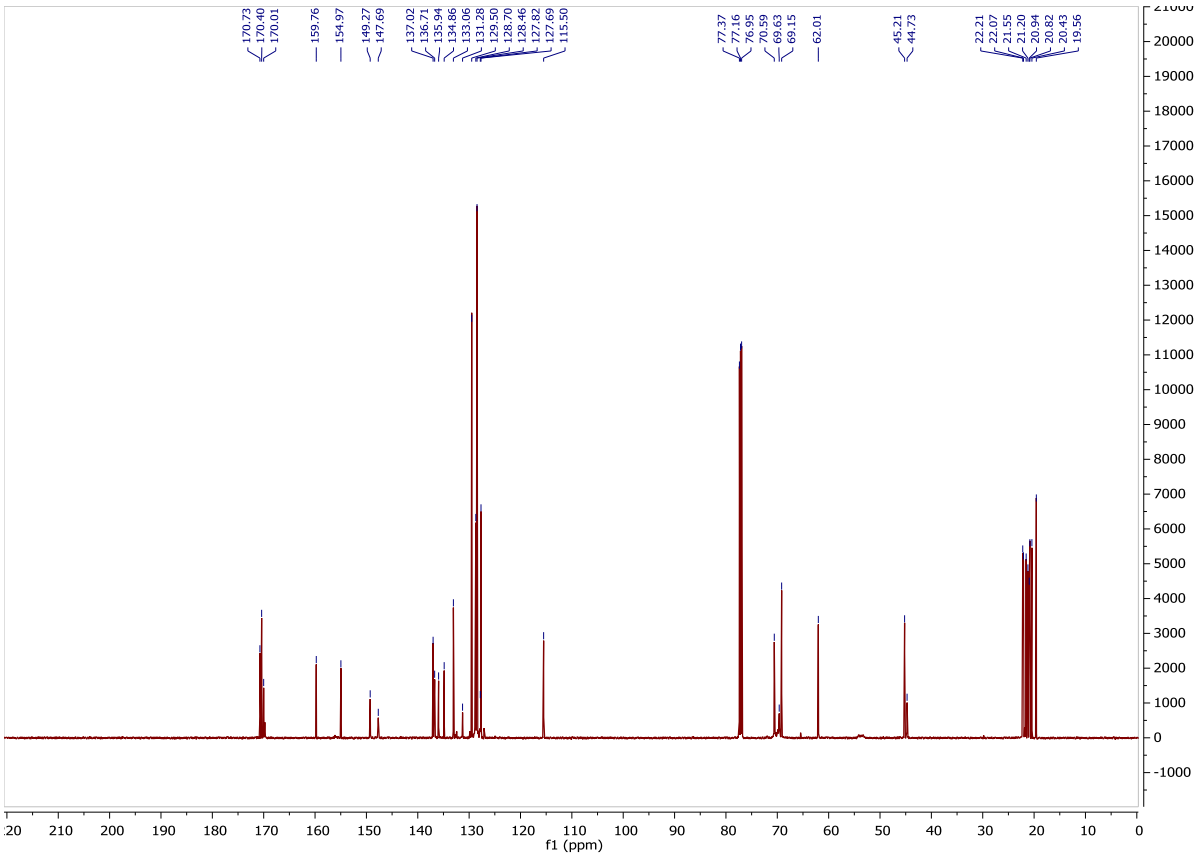
S6 ^{1}H and ^{13}C NMR spectra of 3

2',3',4',5'-tetraacetylriboflavin (3b)

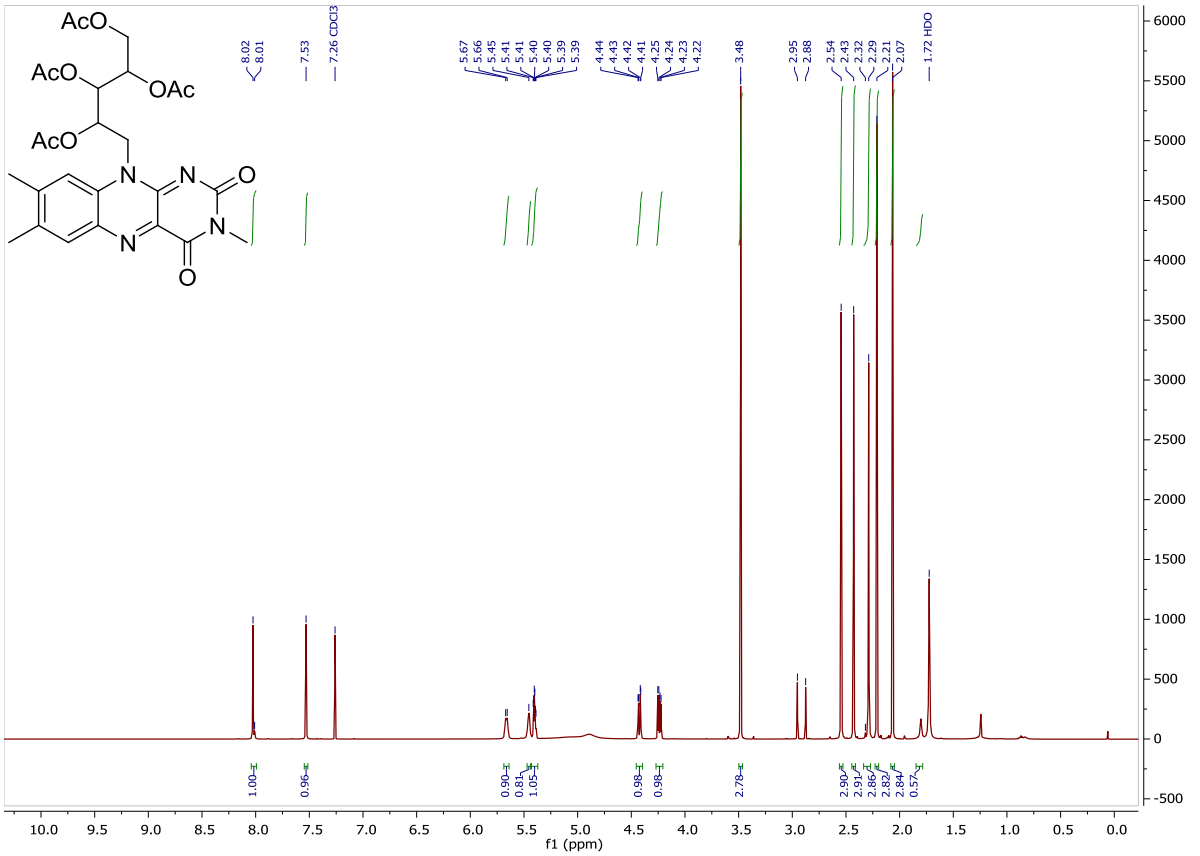


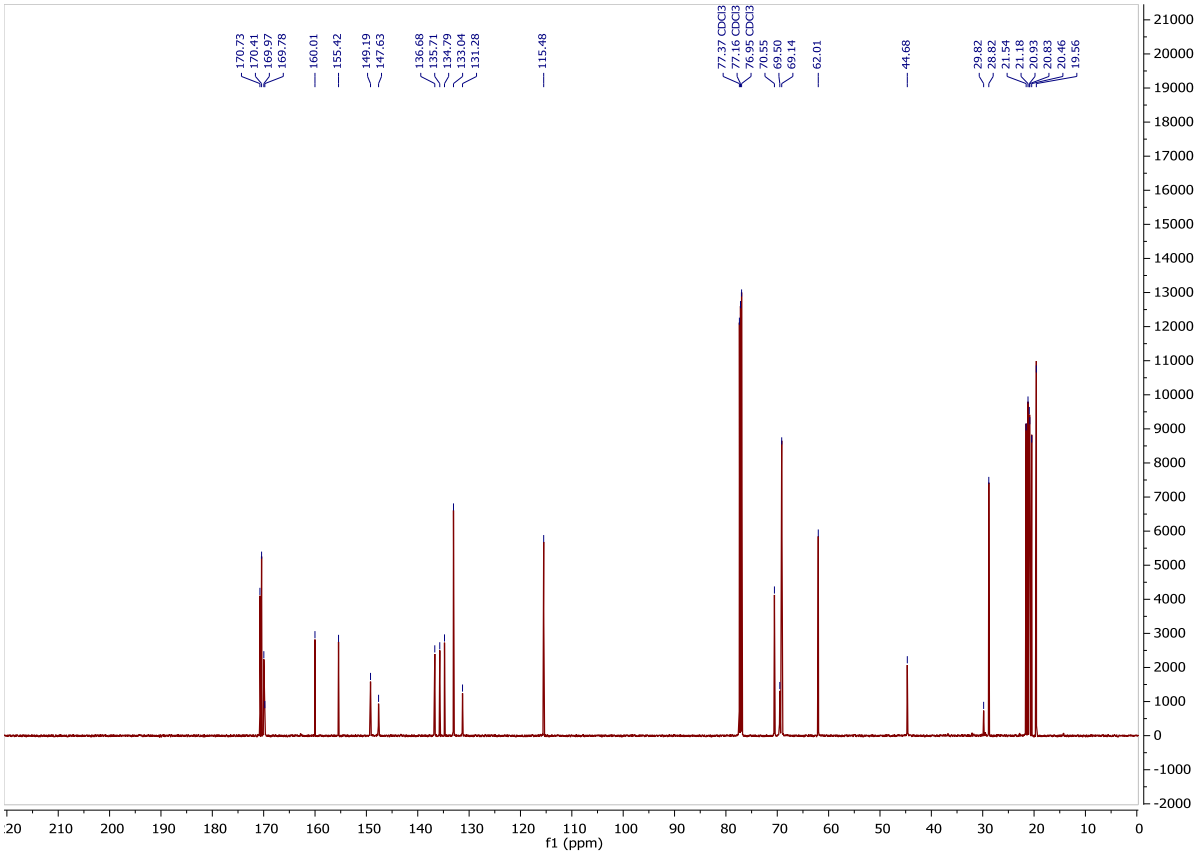
3-Benzyl-2',3',4',5'-tetraacetylriboflavin (3c)





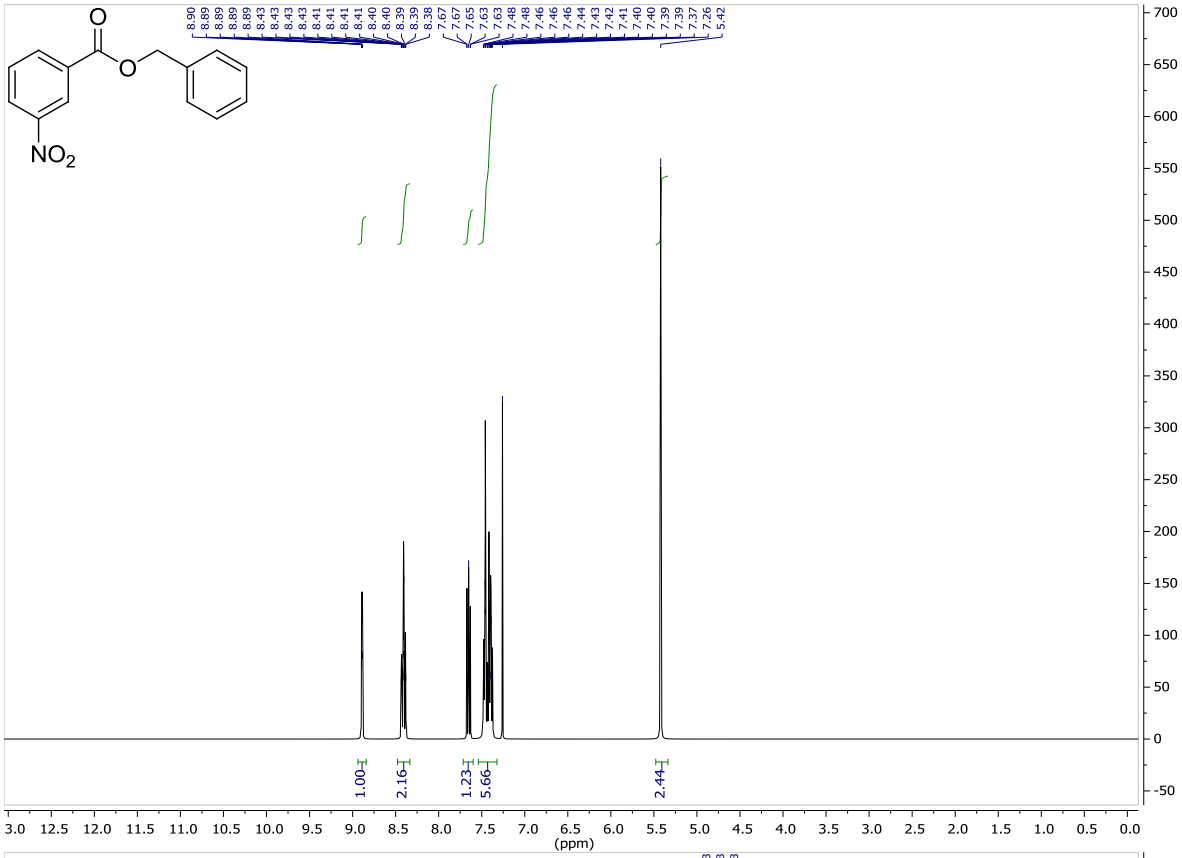
3-Methyl-2',3',4',5'-tetraacetylriboflavin (3d)

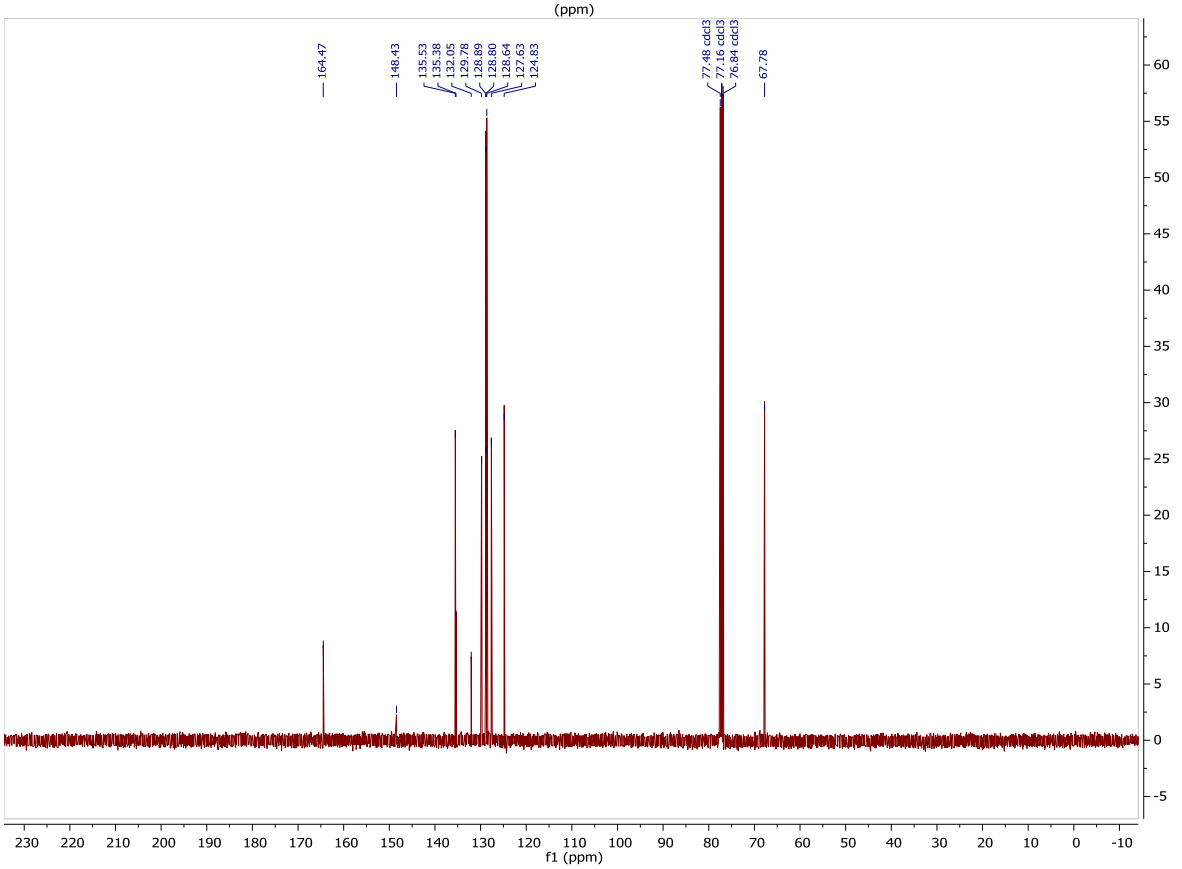




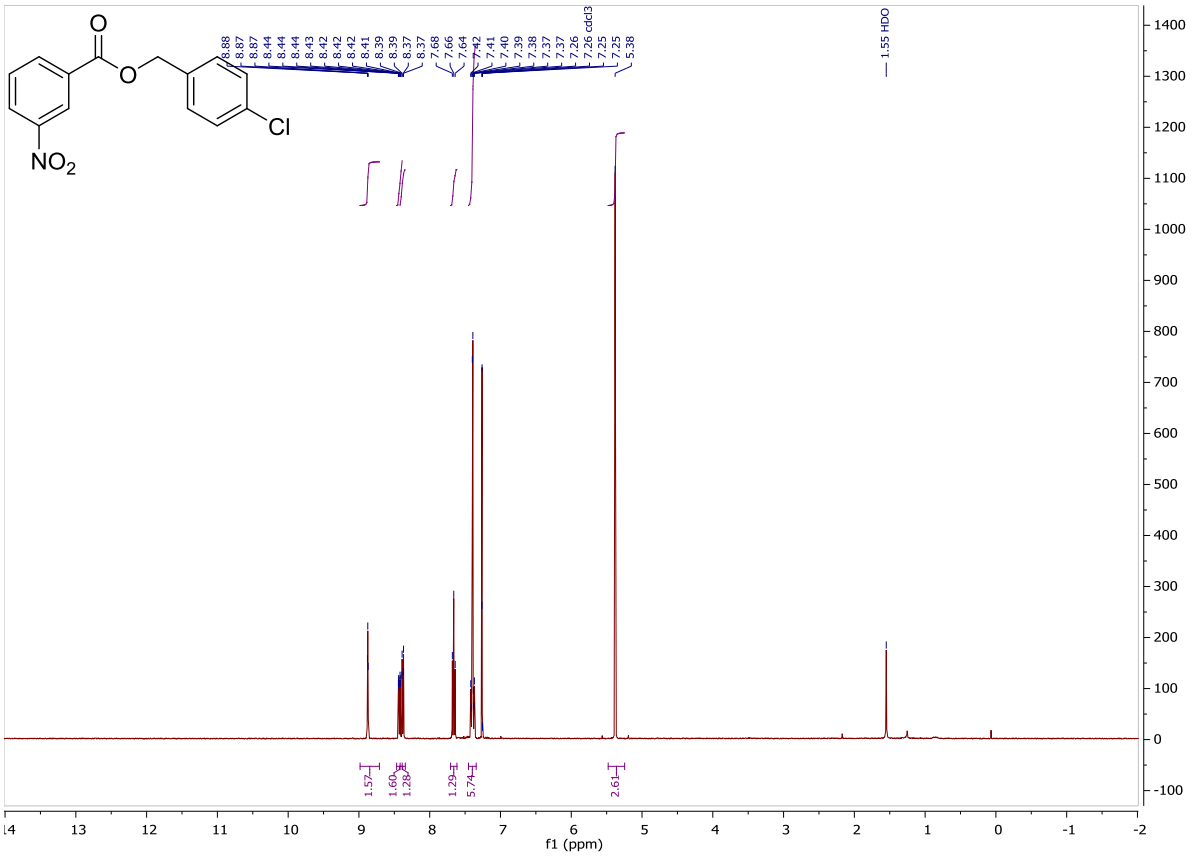
S7 ^{1}H and ^{13}C NMR spectra of 6

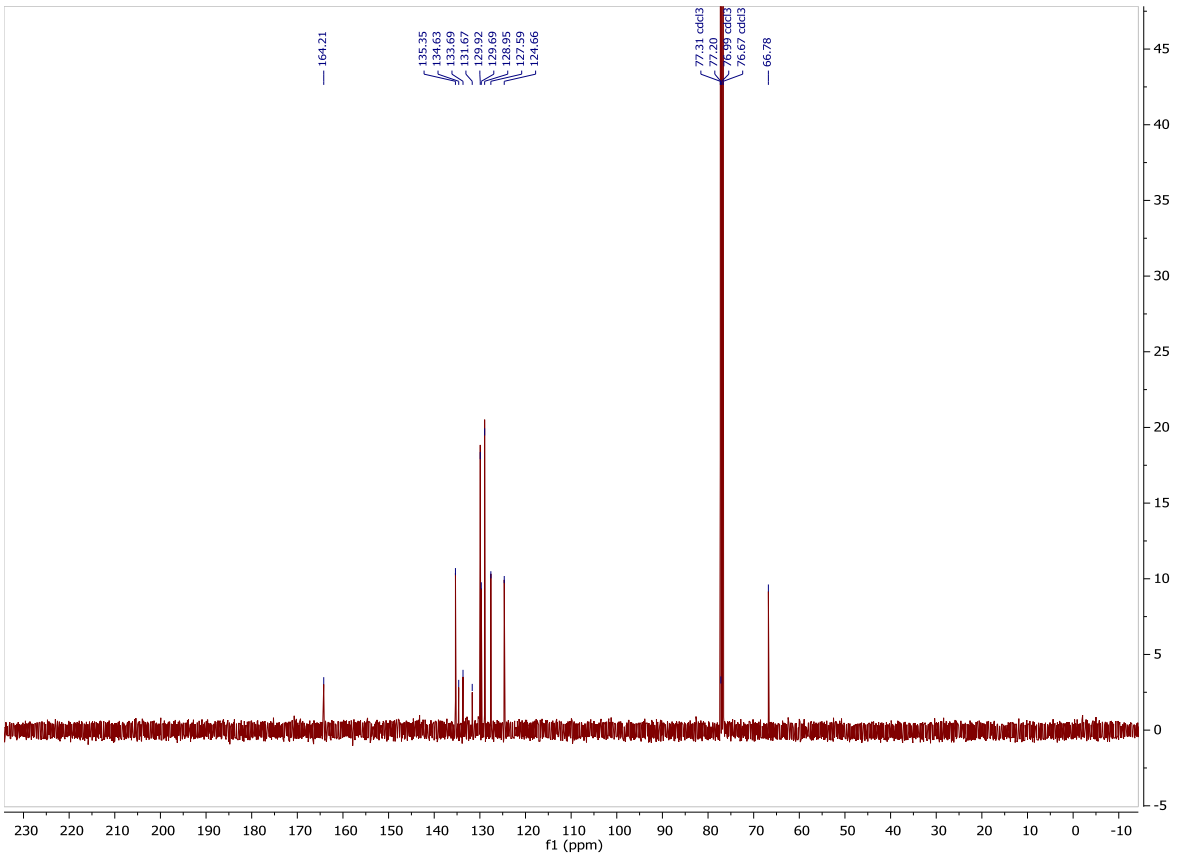
Benzyl 3-nitrobenzoate (6a)



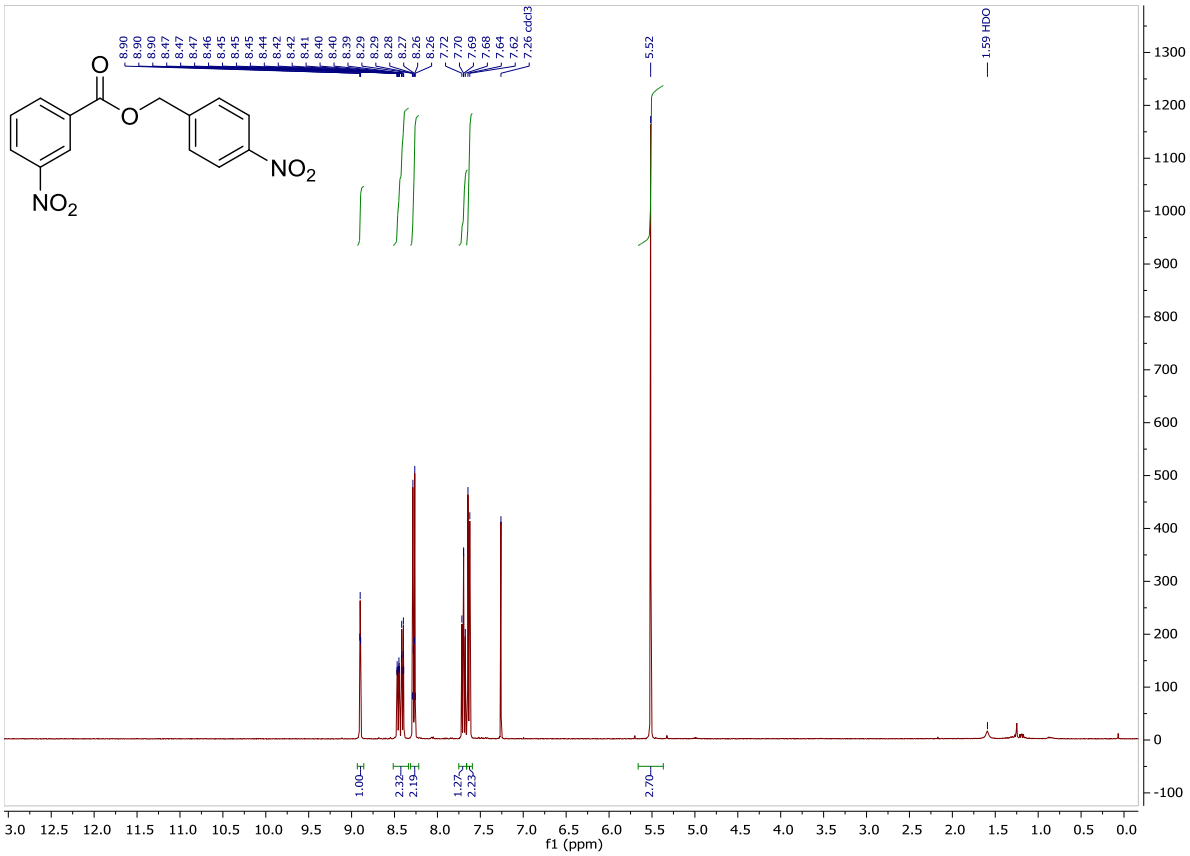


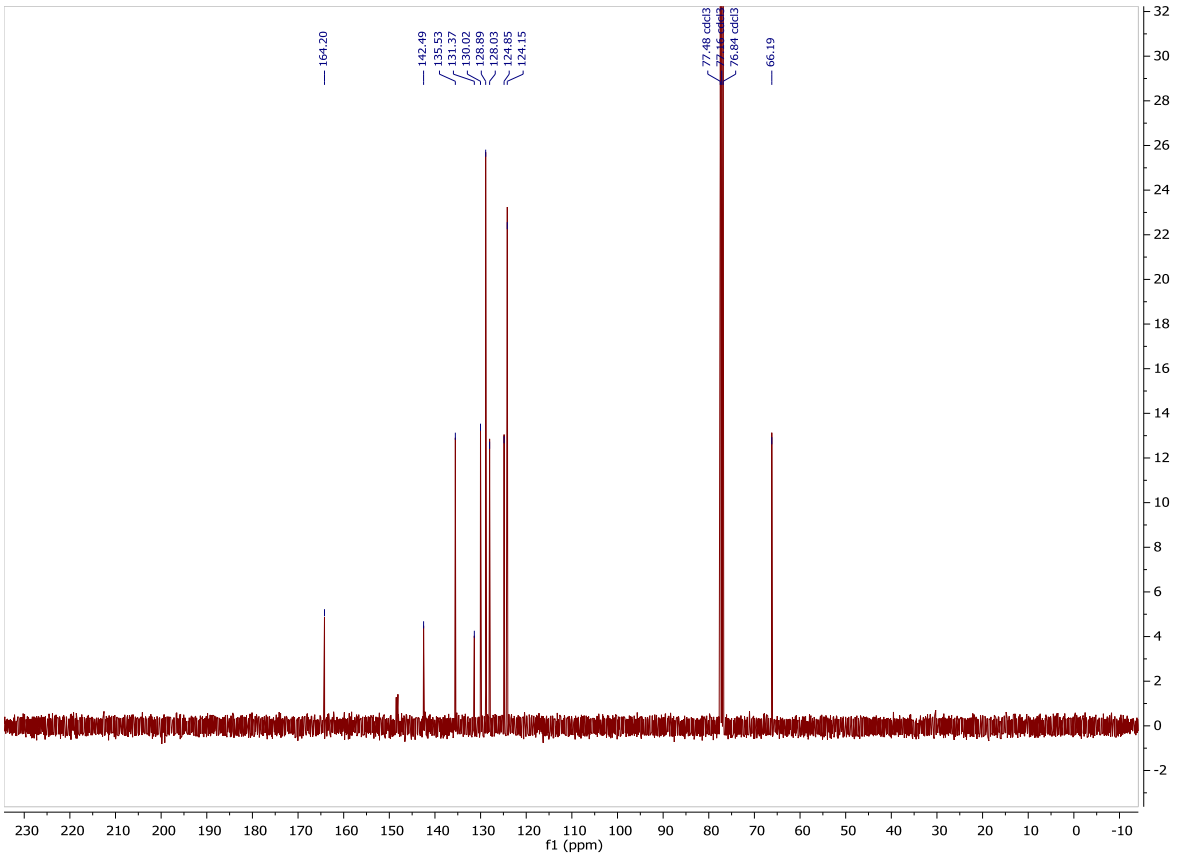
4-Chlorobenzyl 3-nitrobenzoate (6b)



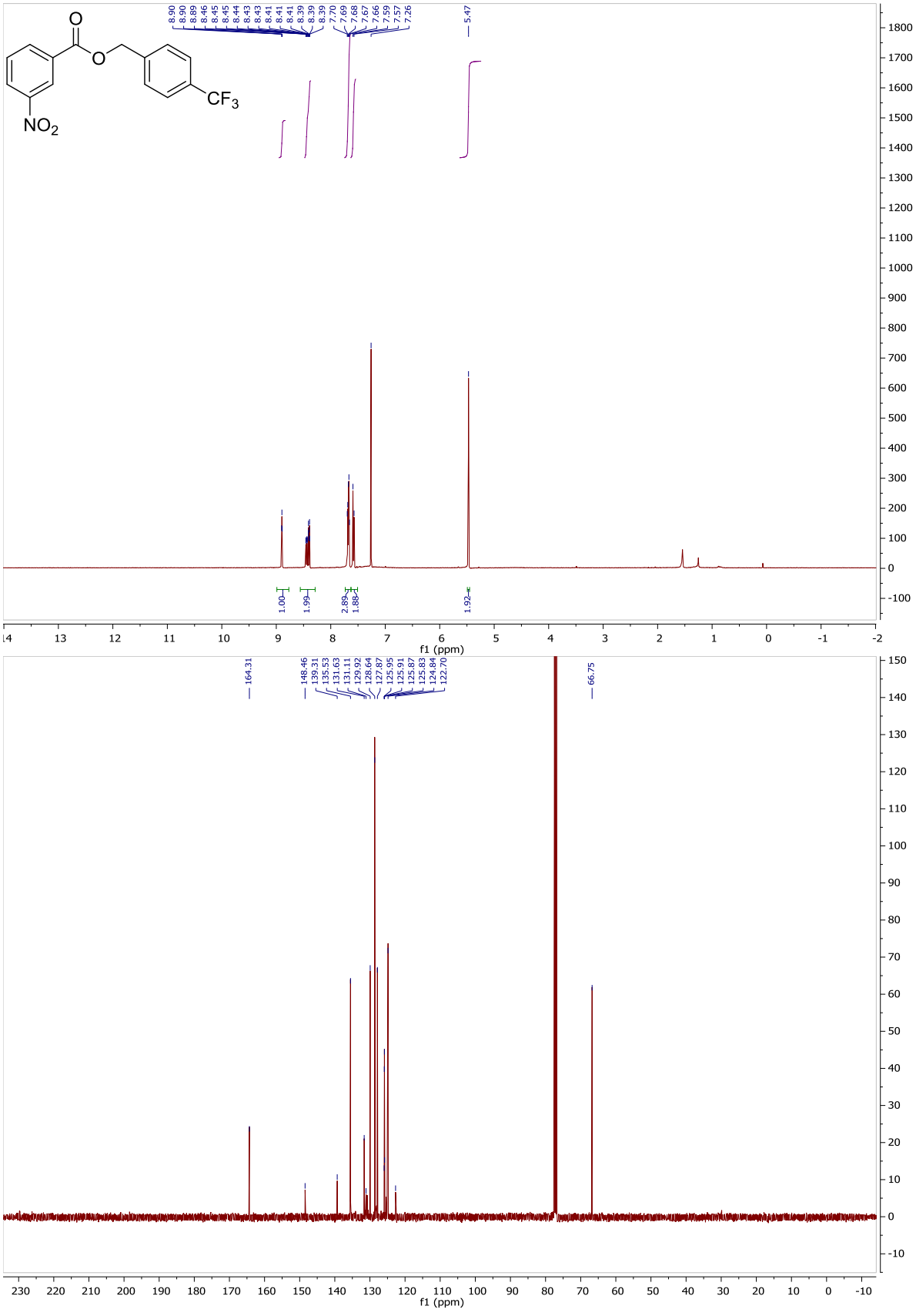


4-Nitrobenzyl 3-nitrobenzoate (6c)

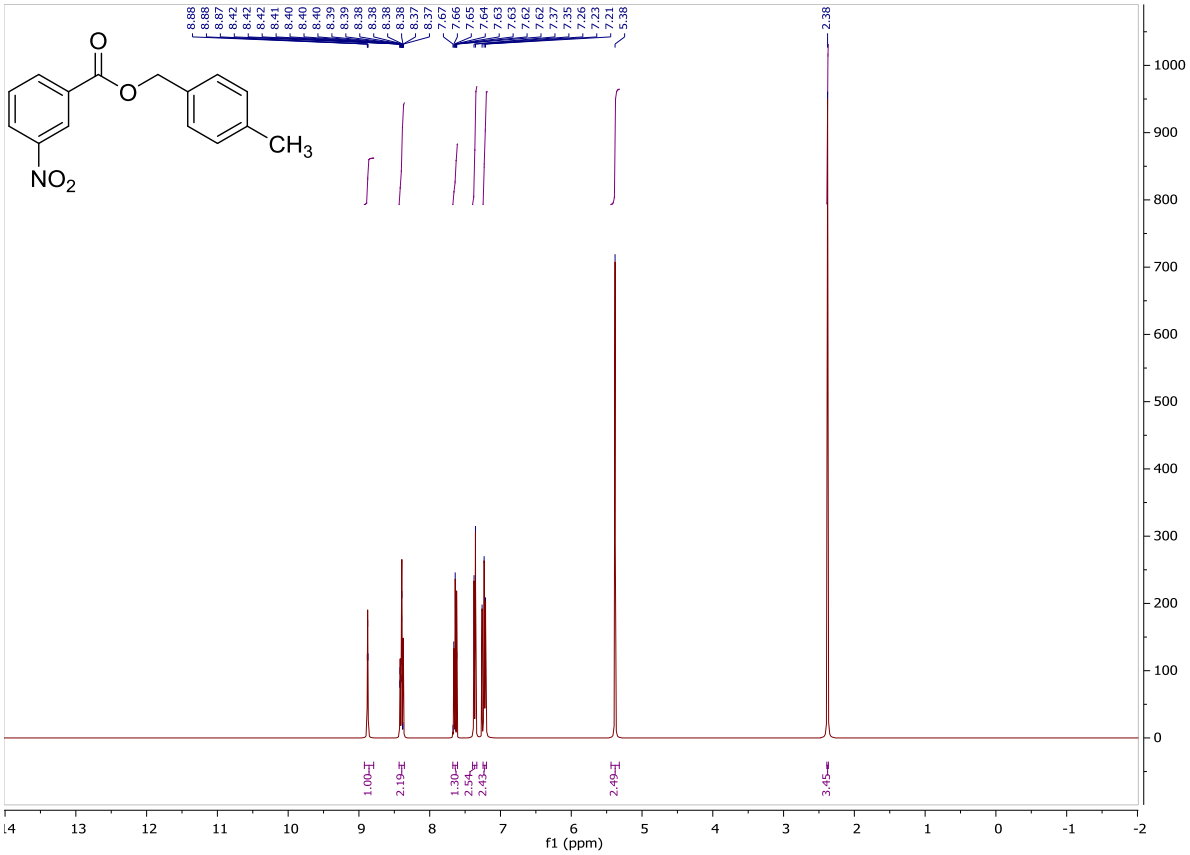


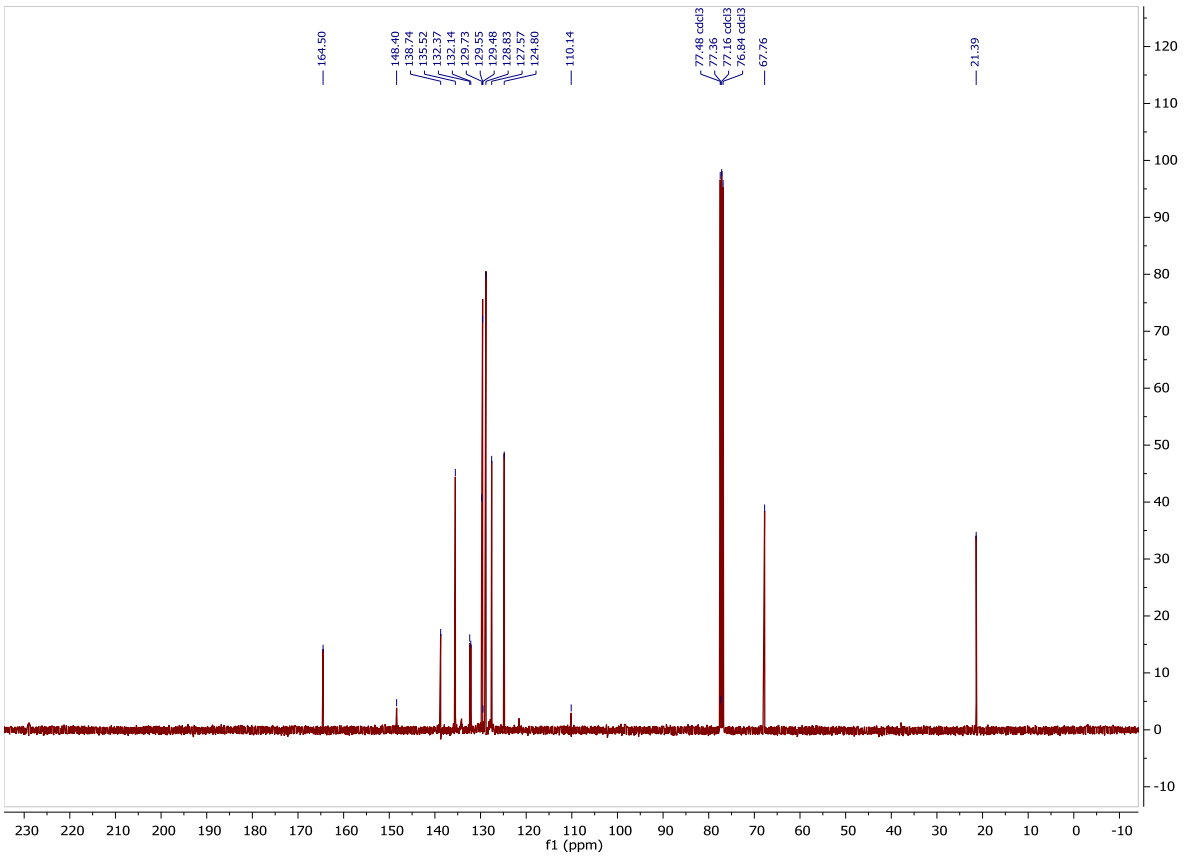


4-(Trifluoromethyl)benzyl 3-nitrobenzoate (6d)

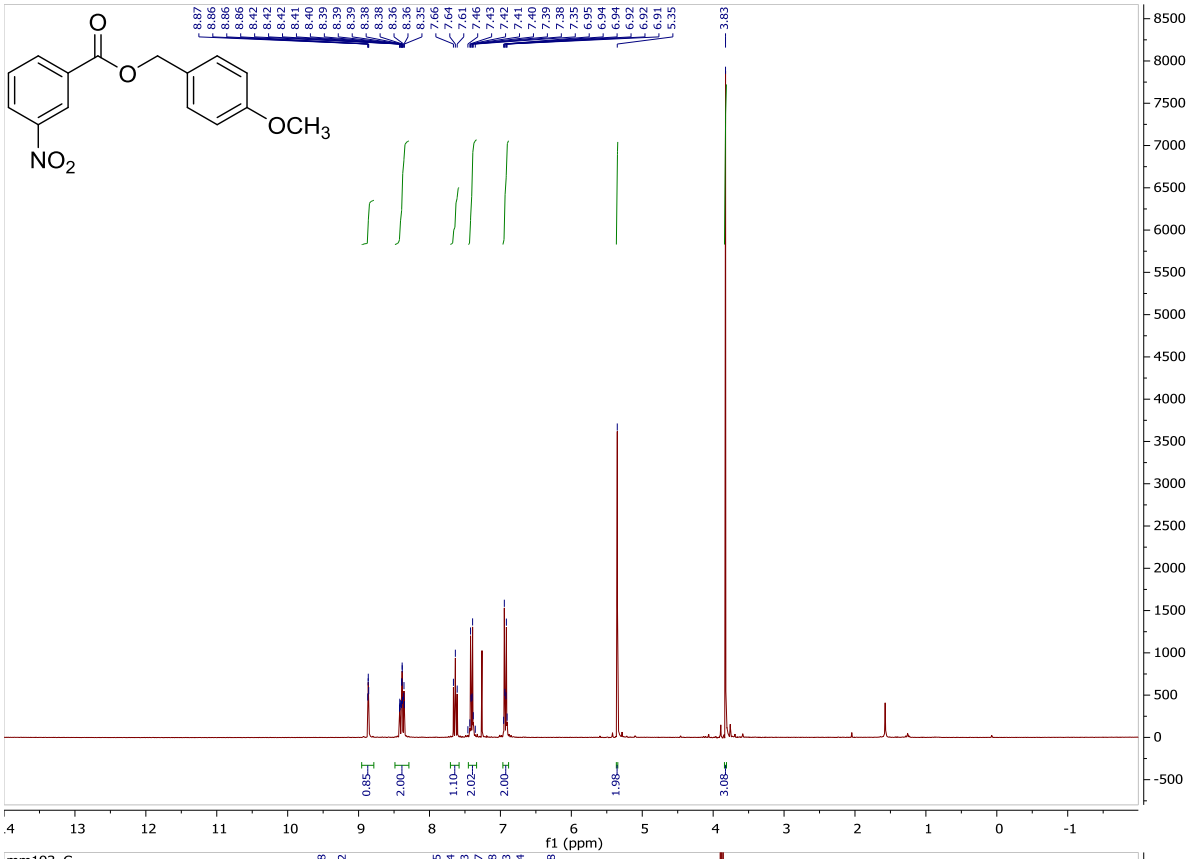


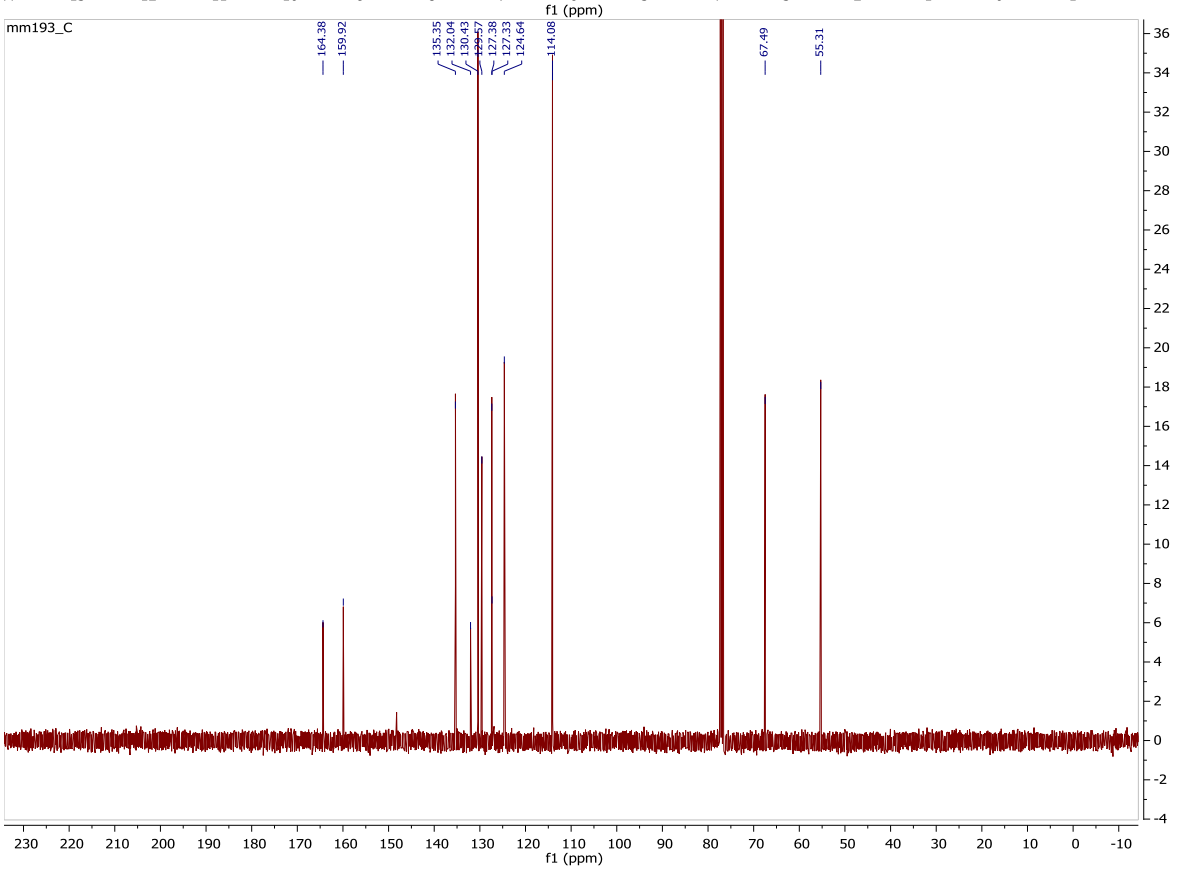
4-Methylbenzyl 3-nitrobenzoate (6e)



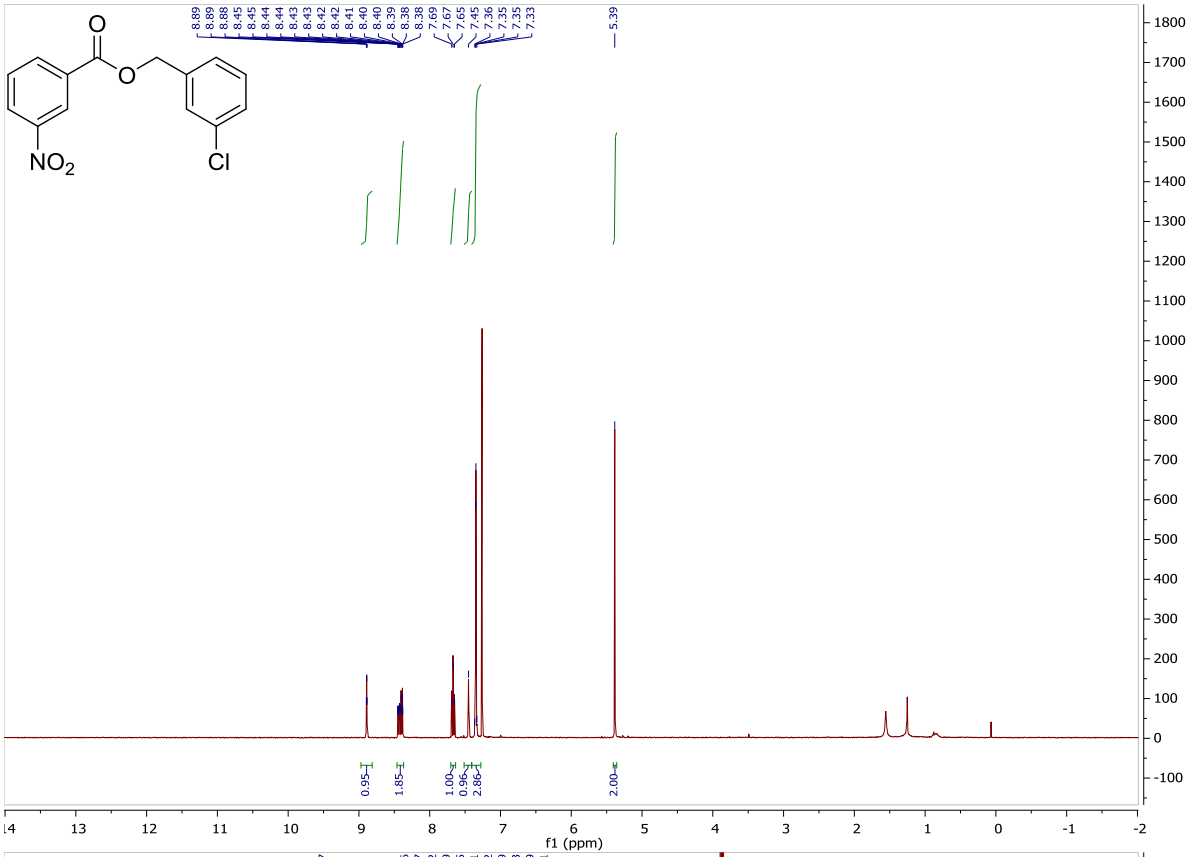


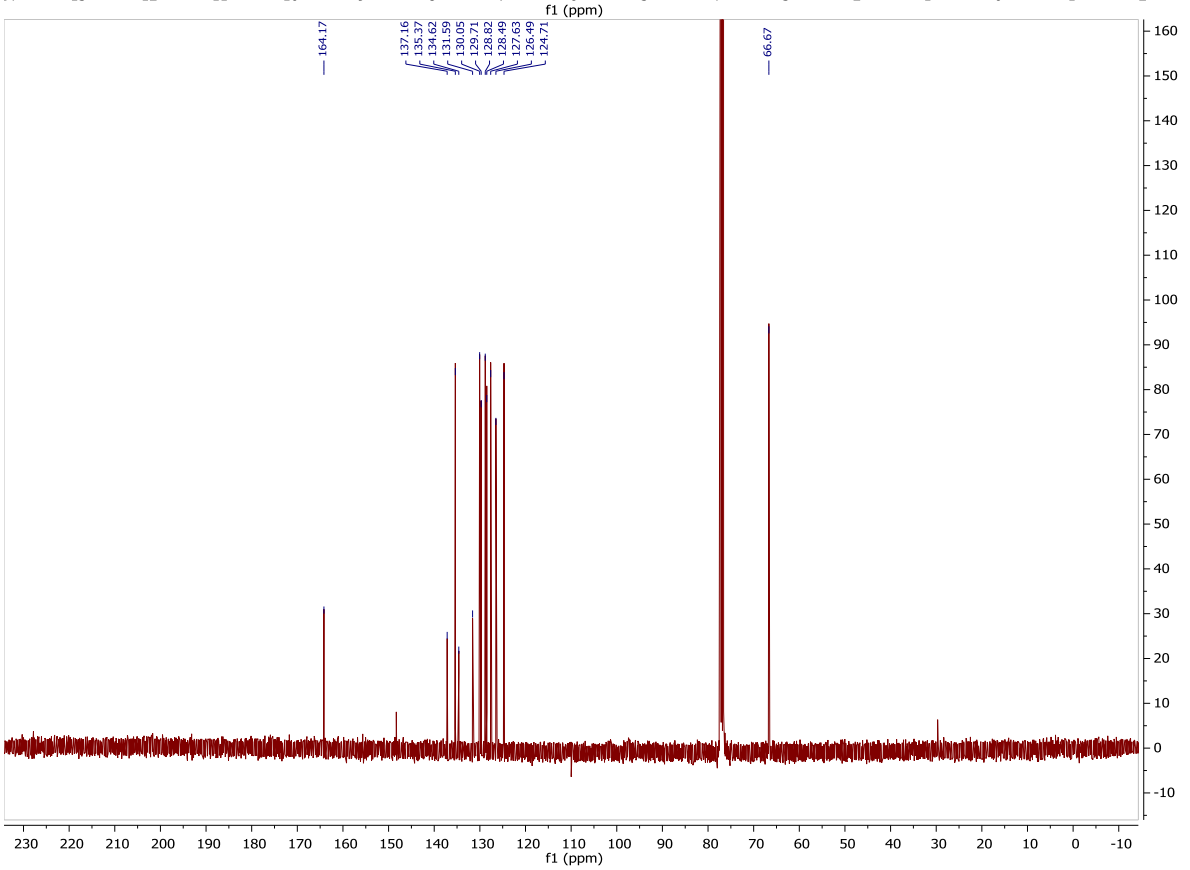
4-(Methoxy)benzyl 3-nitrobenzoate (6f)



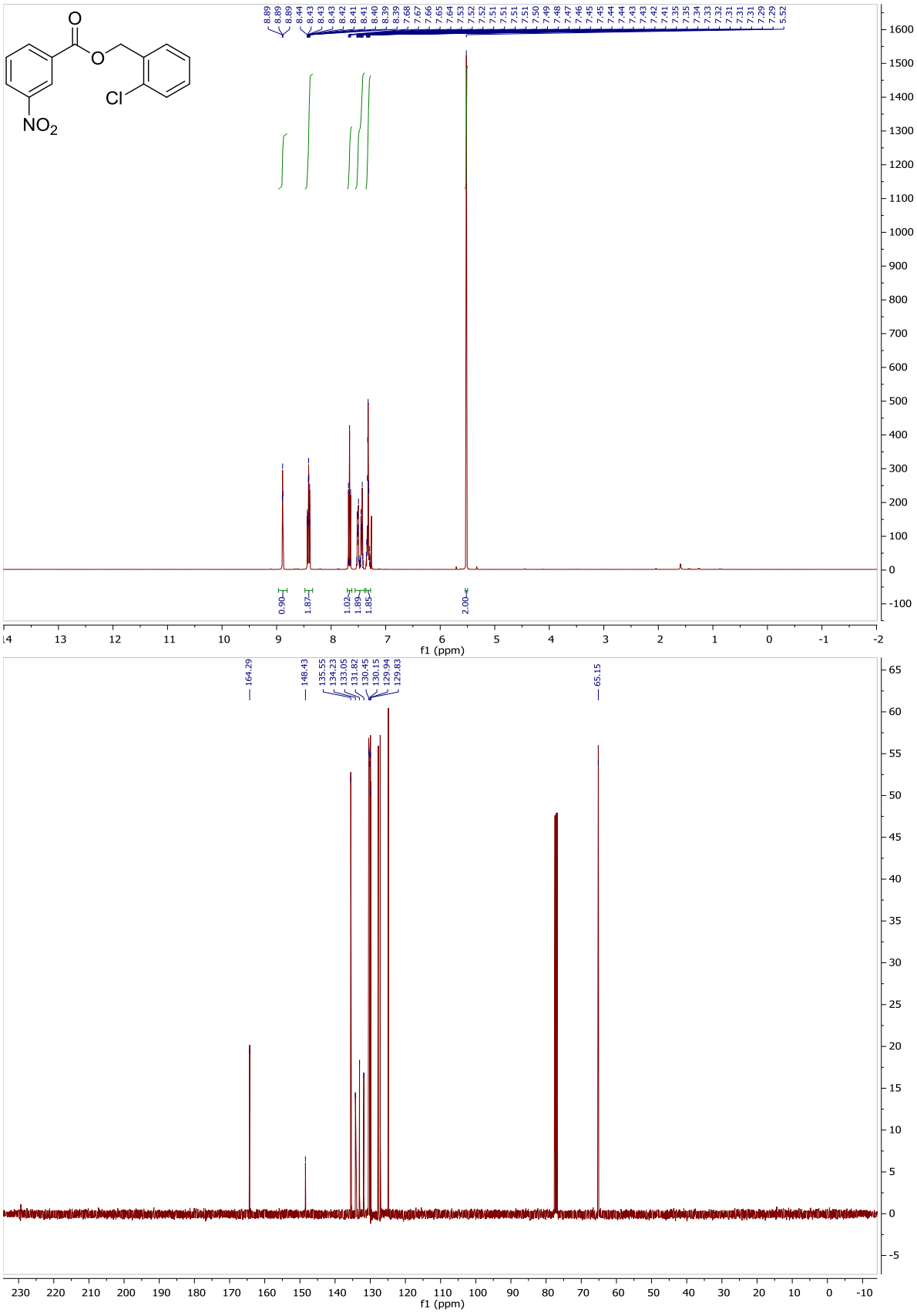


3-chlorobenzyl 3-nitrobenzoate (6g)

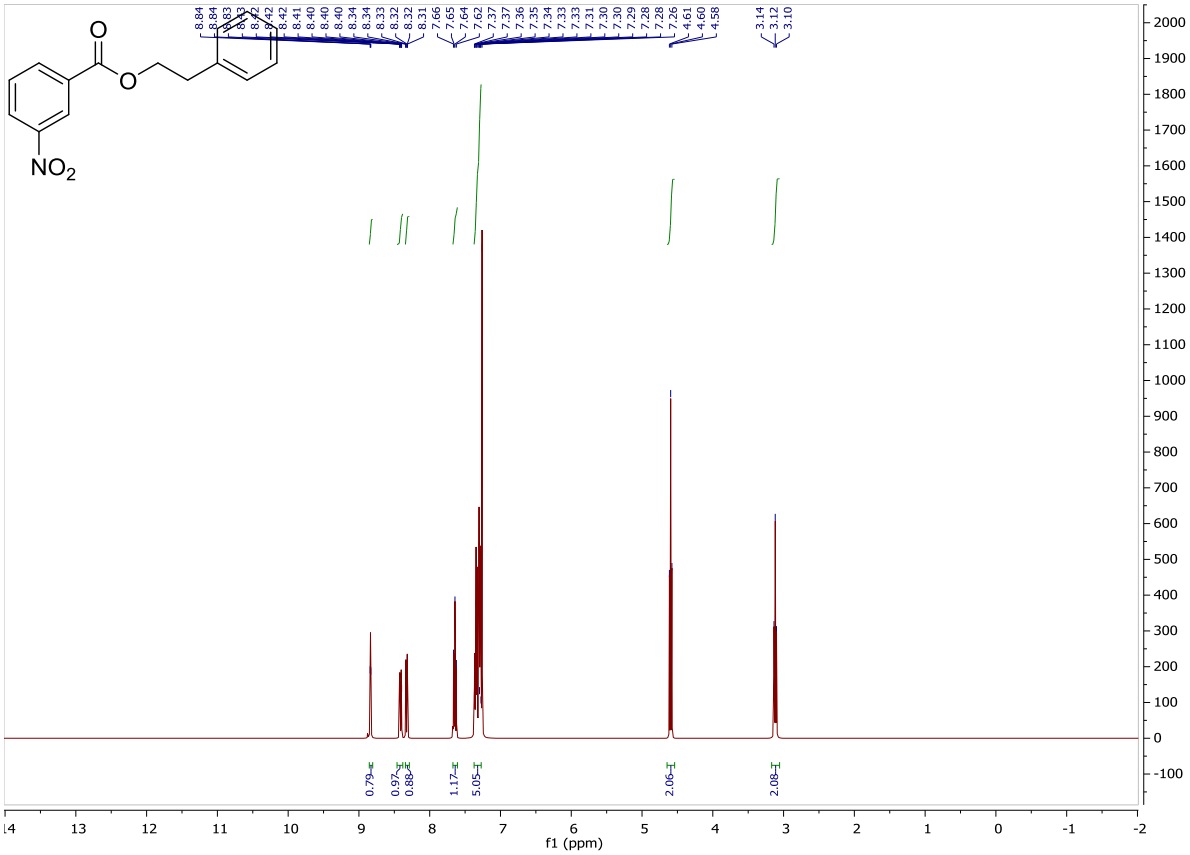


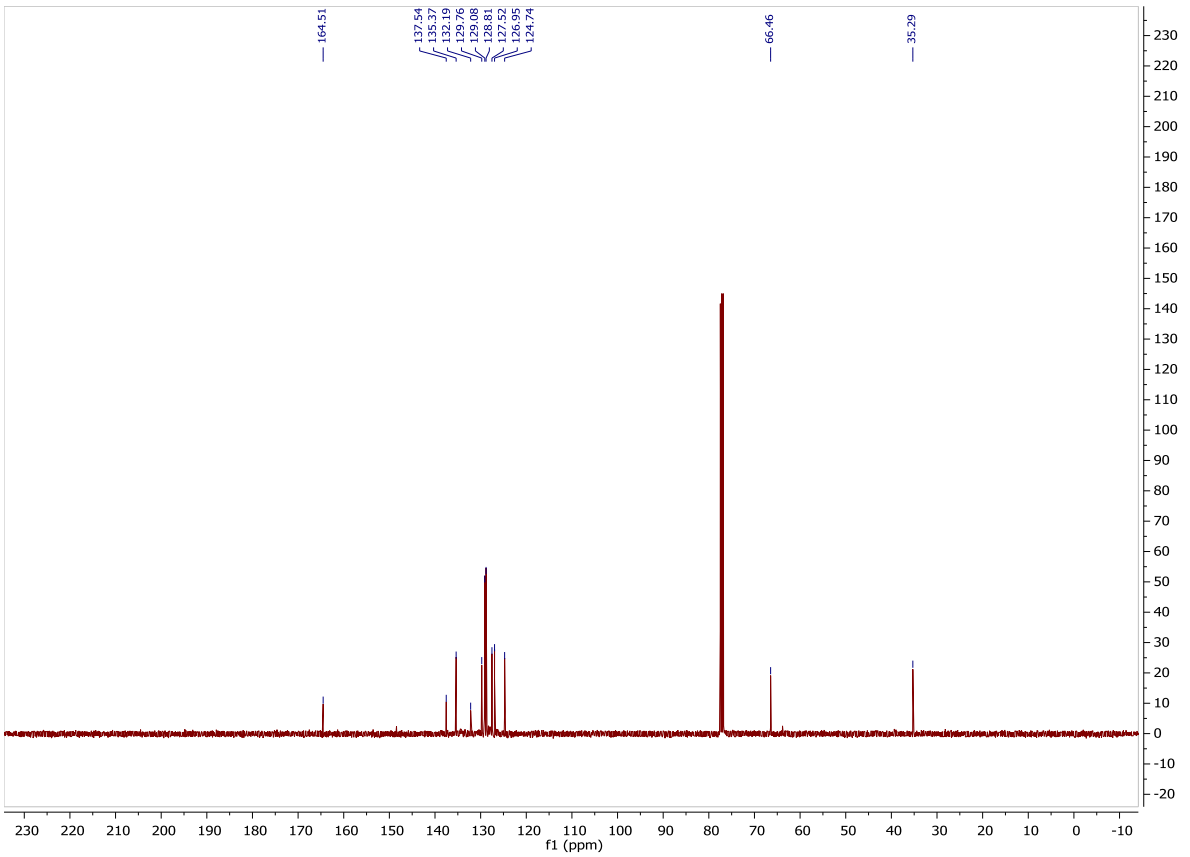


2-chlorobenzyl 3-nitrobenzoate (6h)

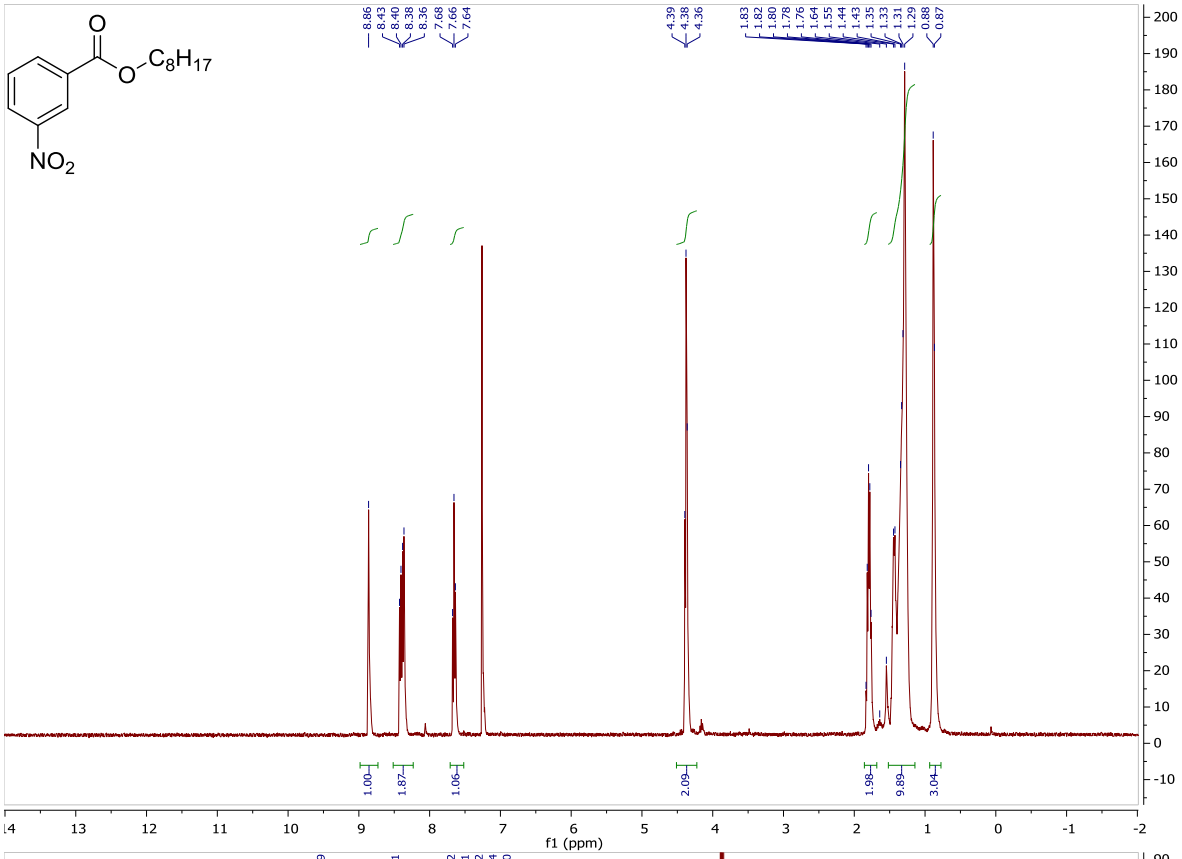


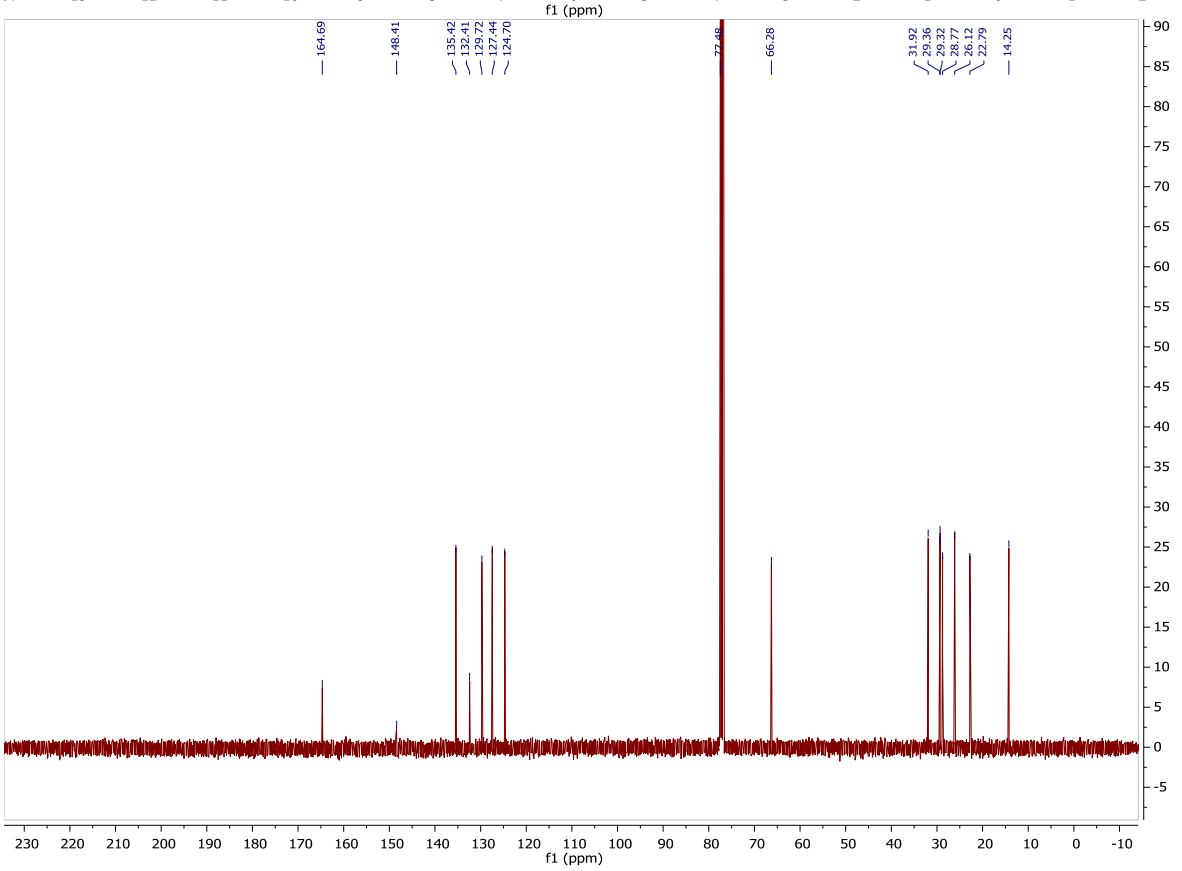
Phenethyl 3-nitrobenzoate (6i)



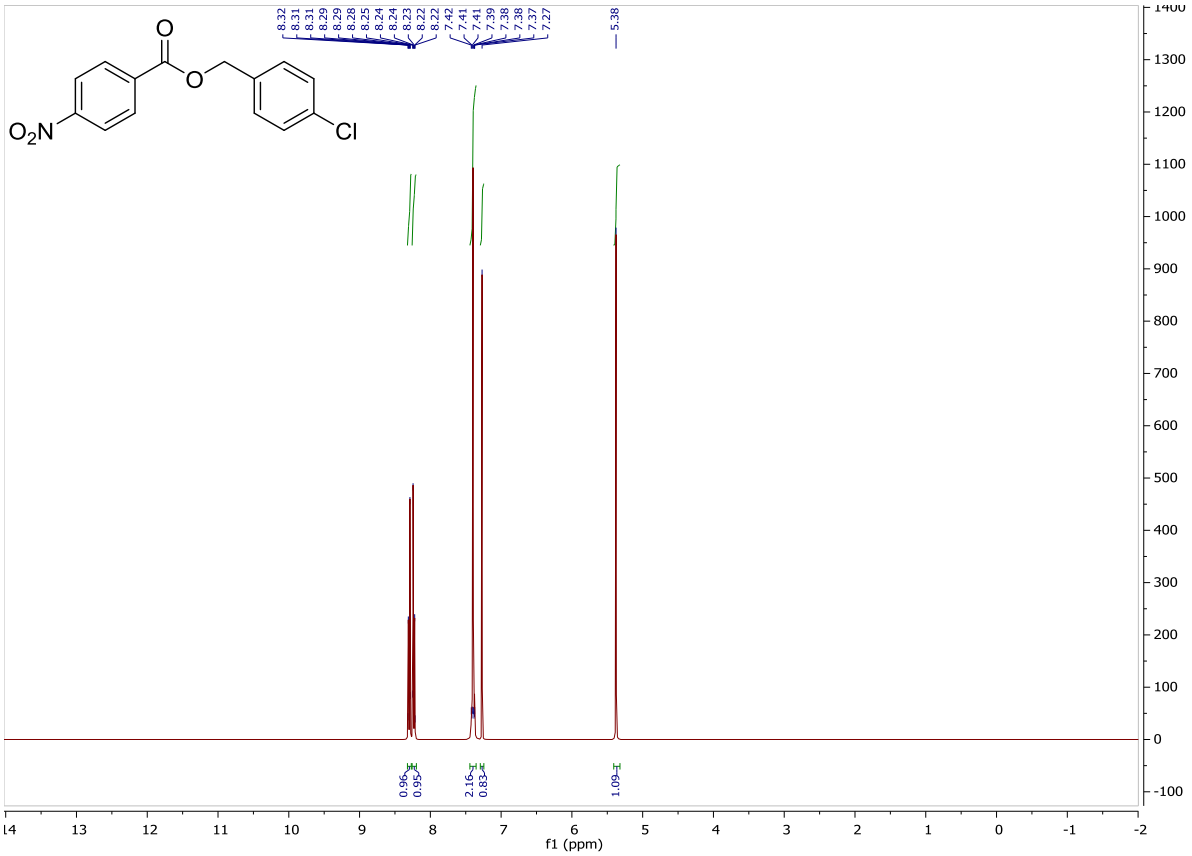


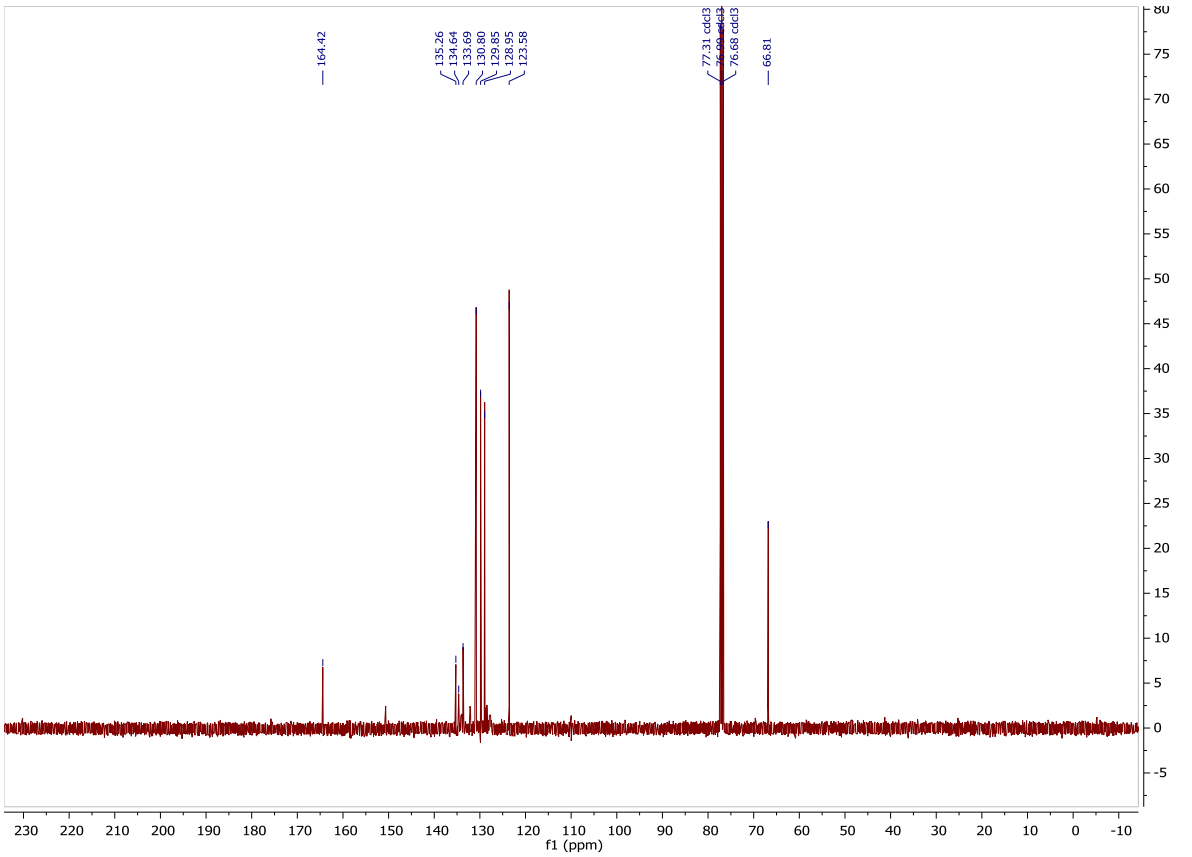
Octyl 3-nitrobenzoate (6k)



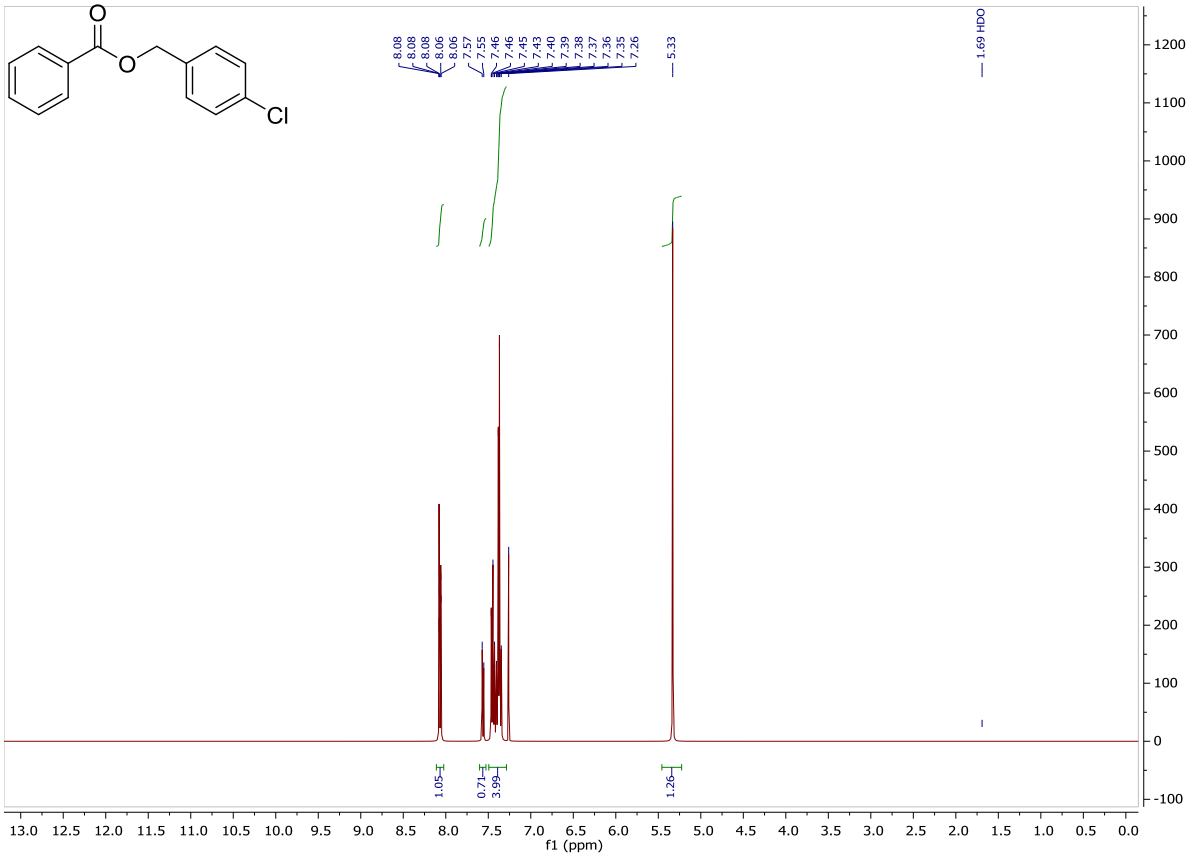


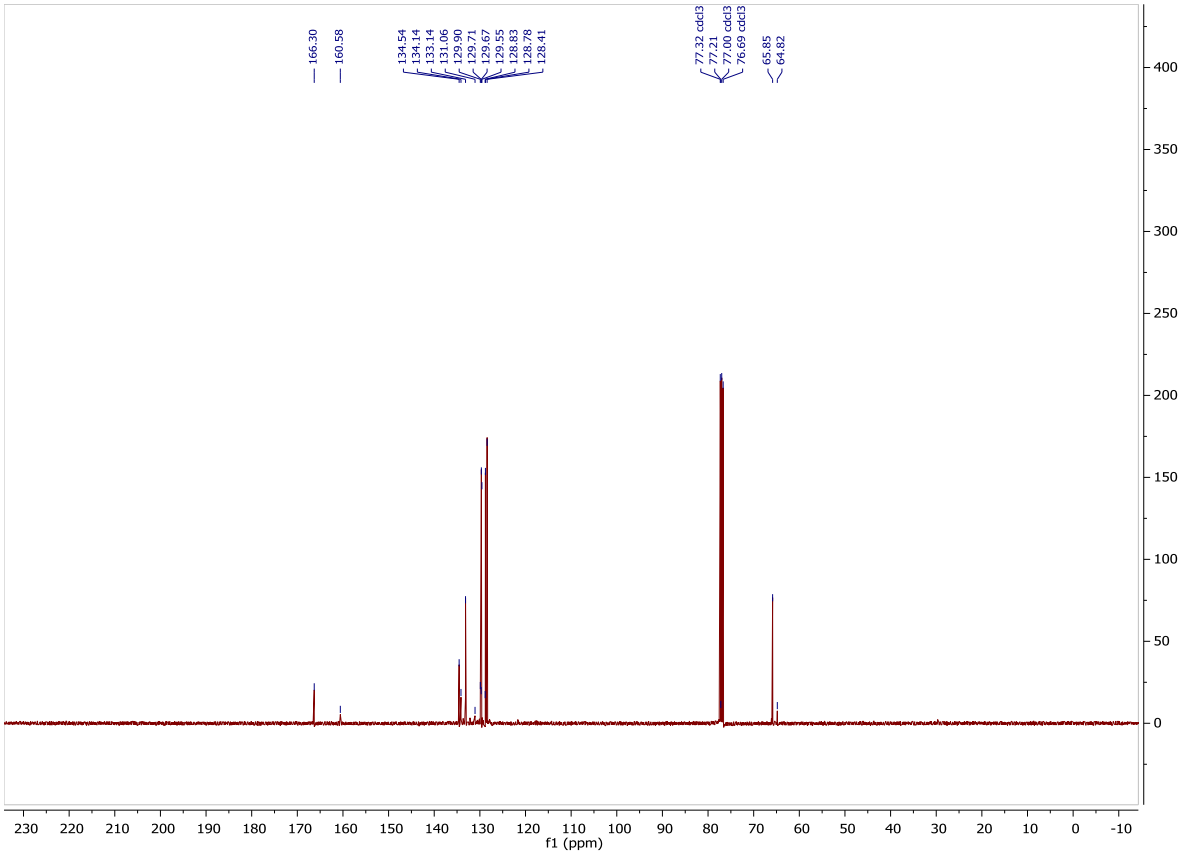
4-Chlorobenzyl 4-nitrobenzoate (6l)



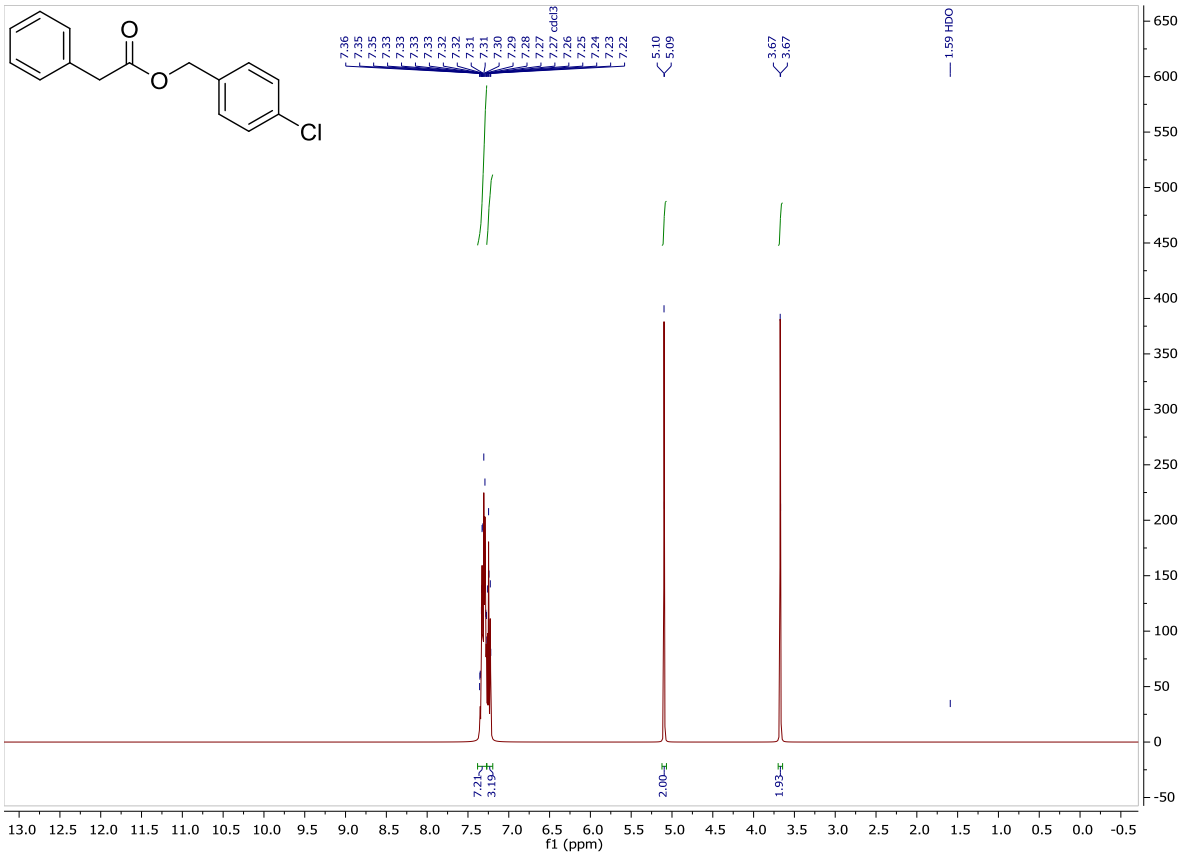


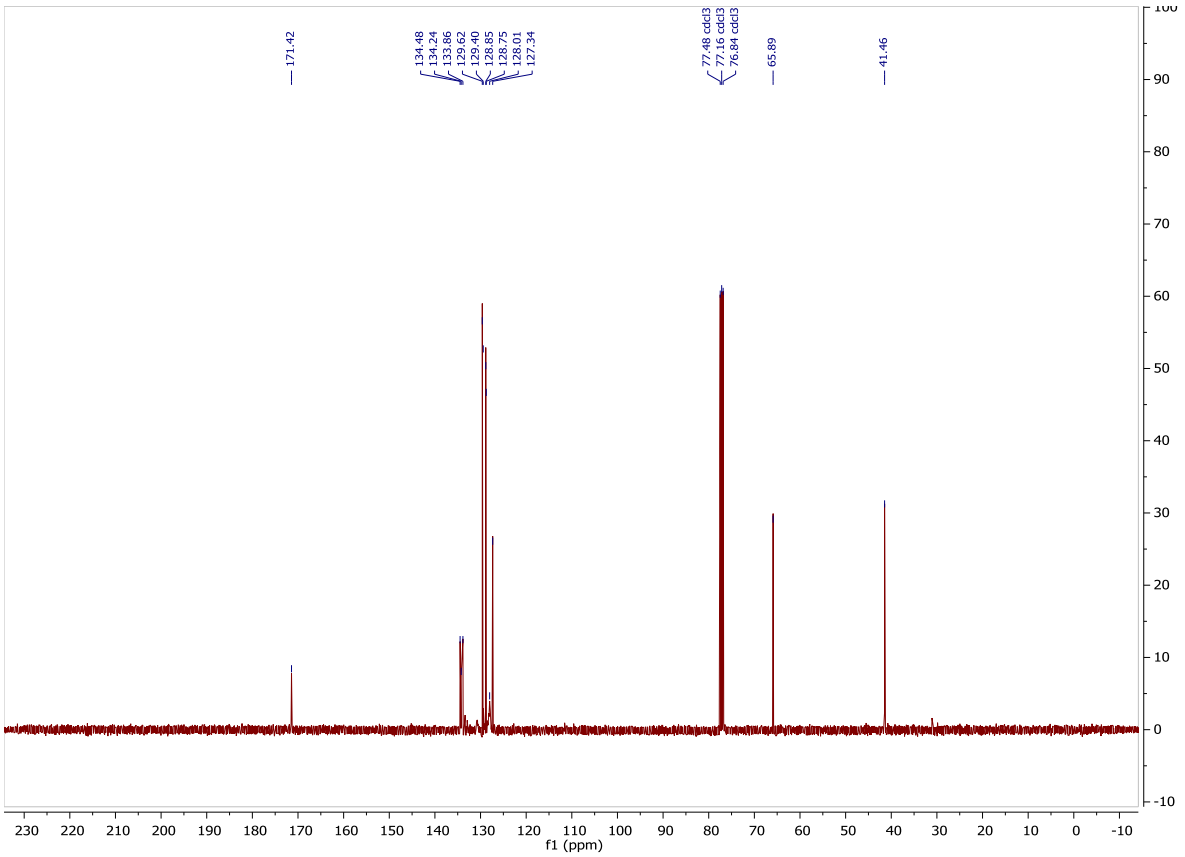
4-Chlorobenzyl benzoate (6m)



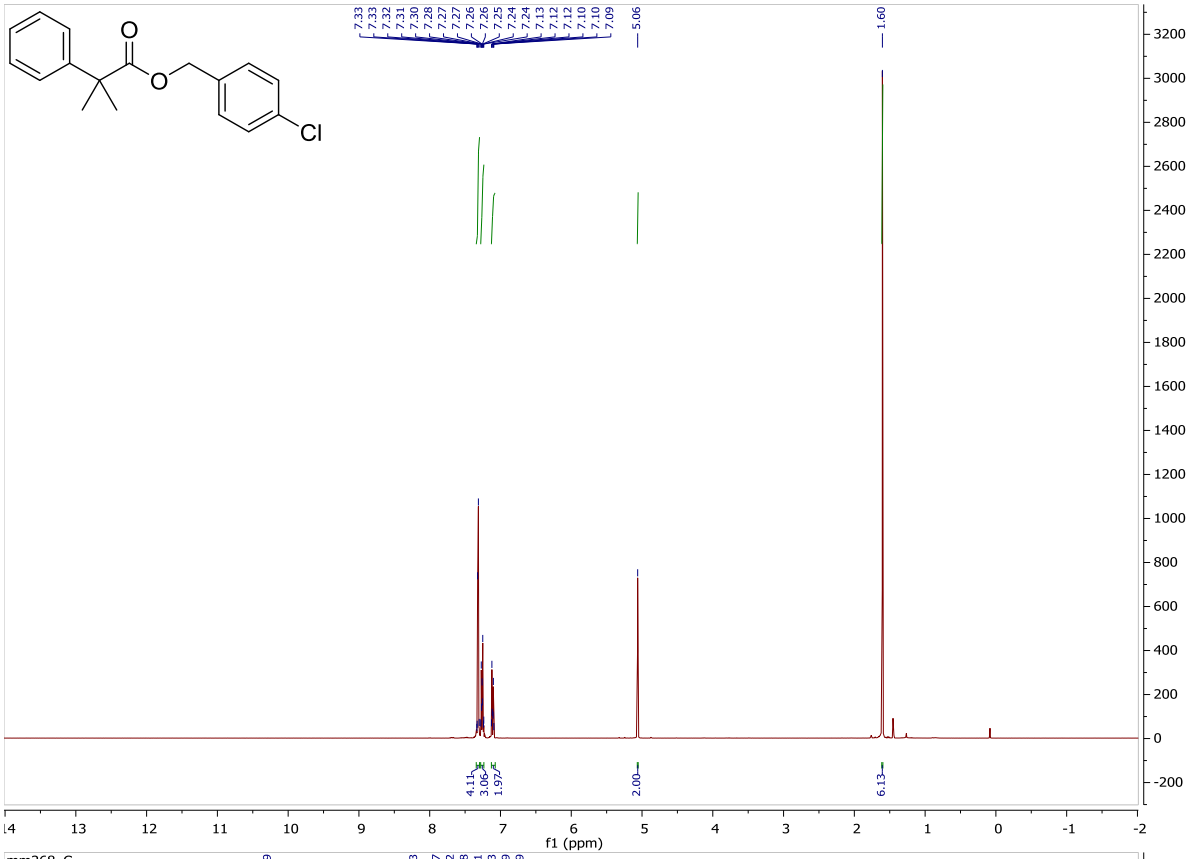


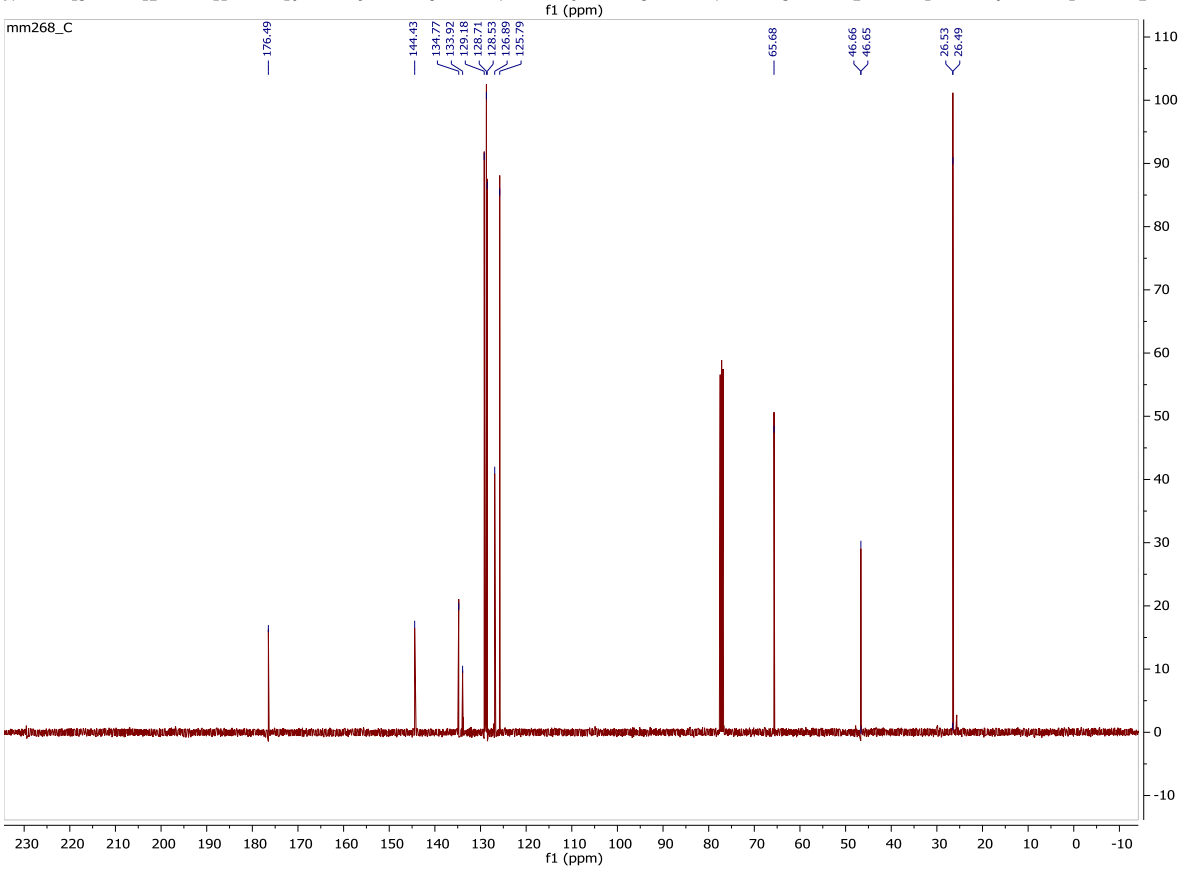
4-Chlorobenzyl 2-phenylacetate (6n)



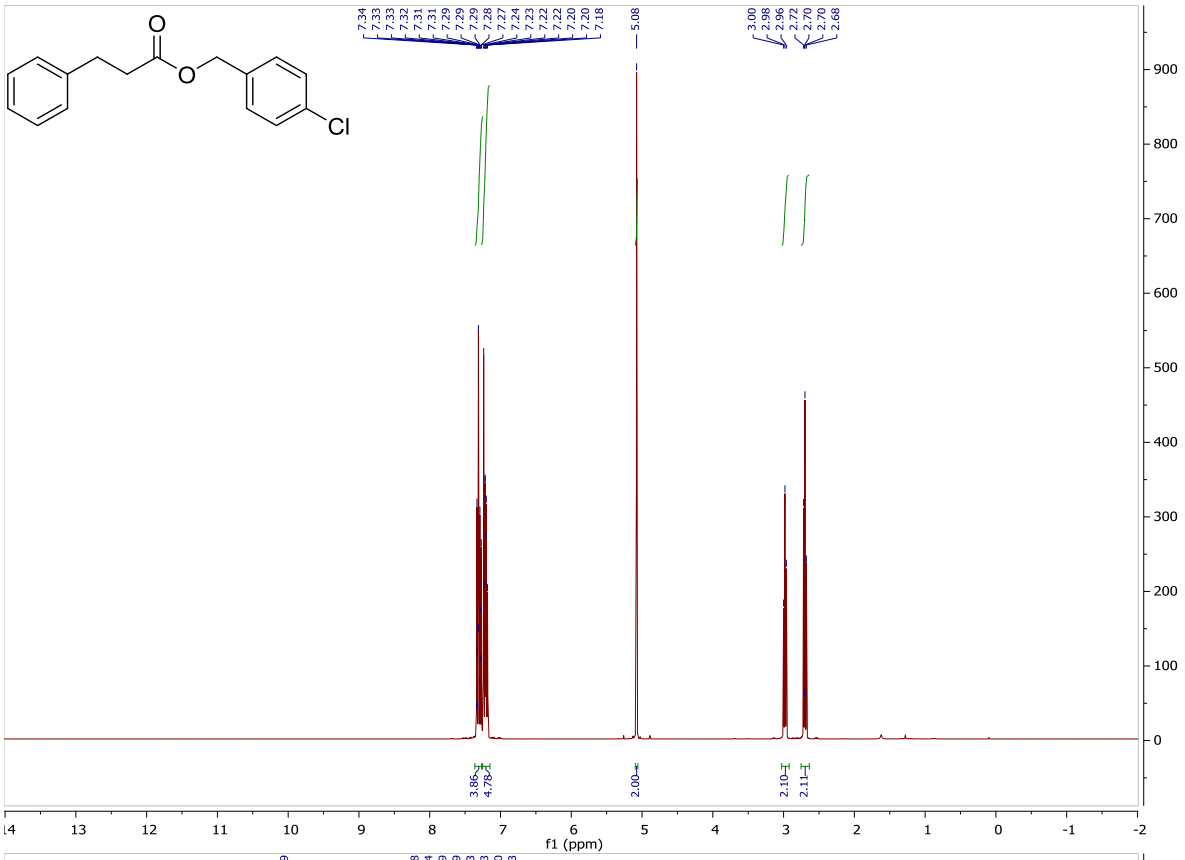


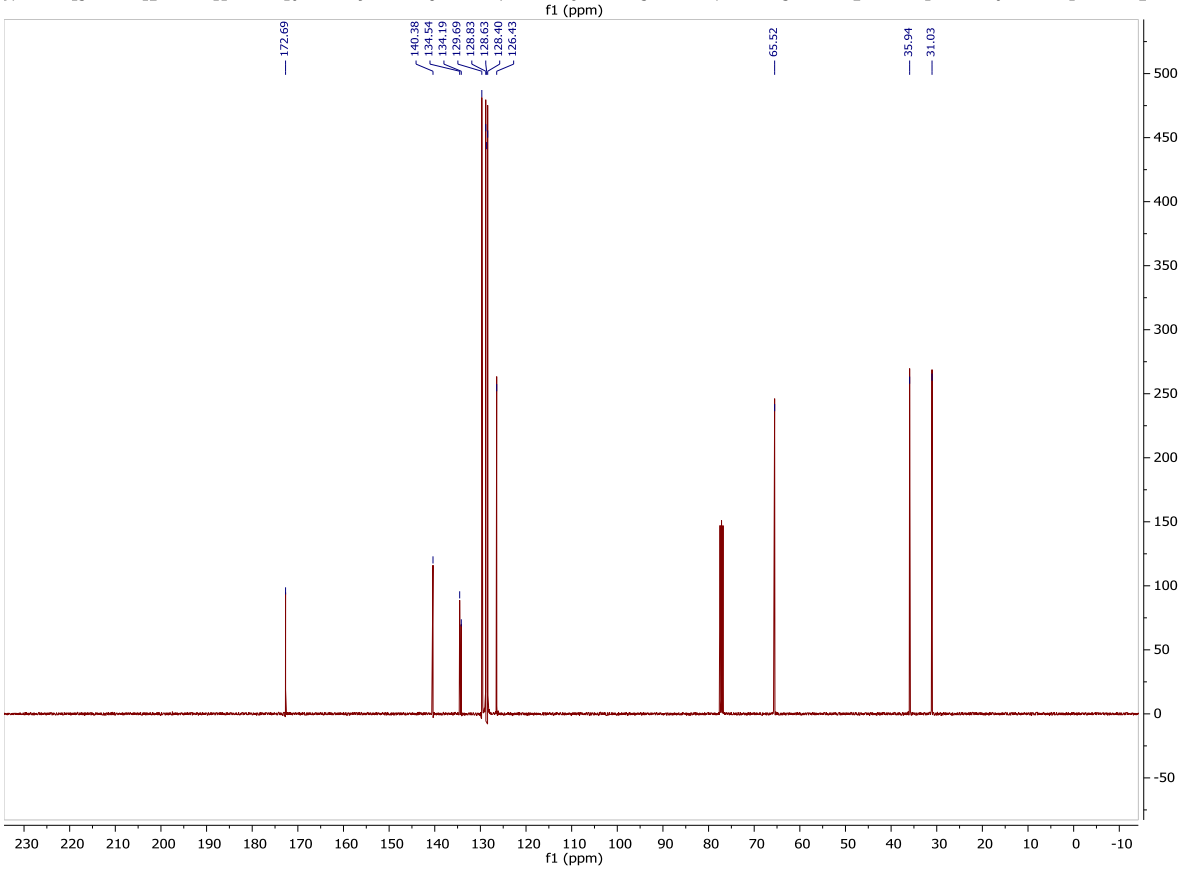
4-chlorobenzyl 2-methyl-2-phenylpropanoate (6o)



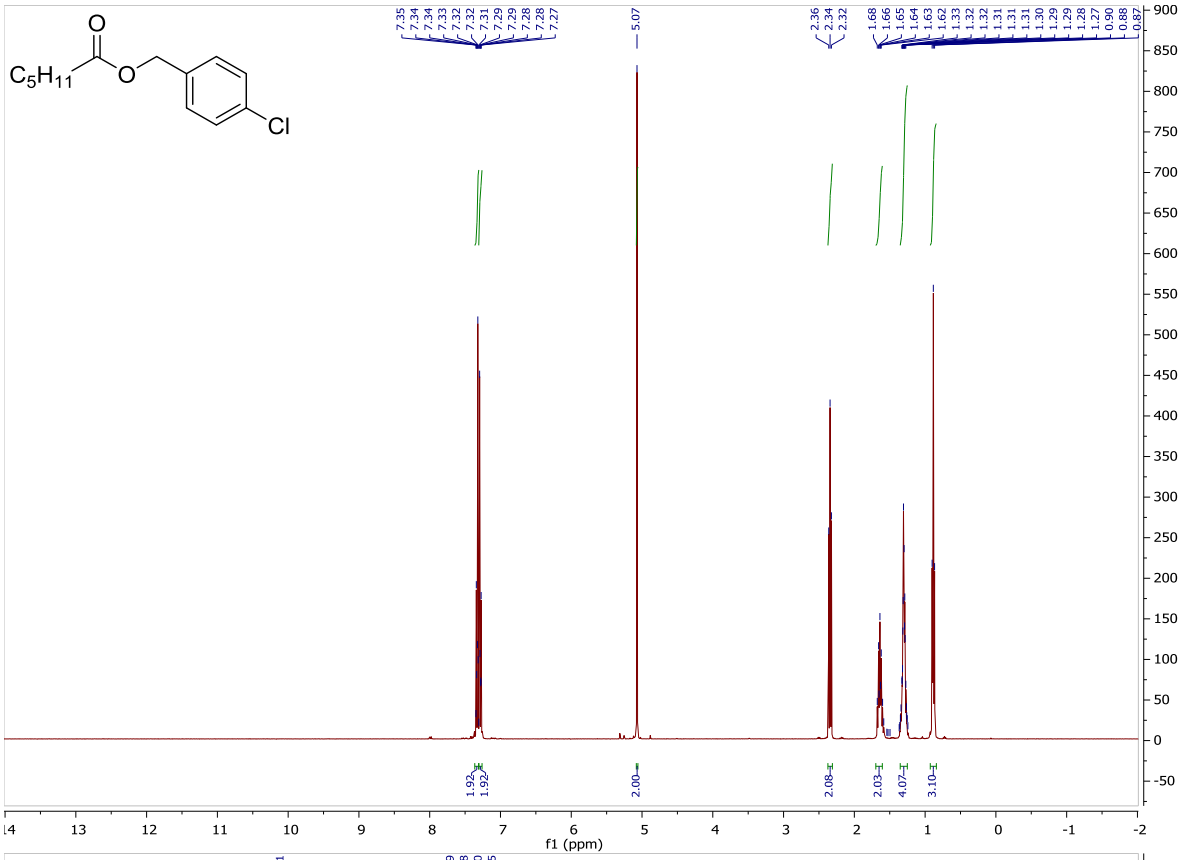


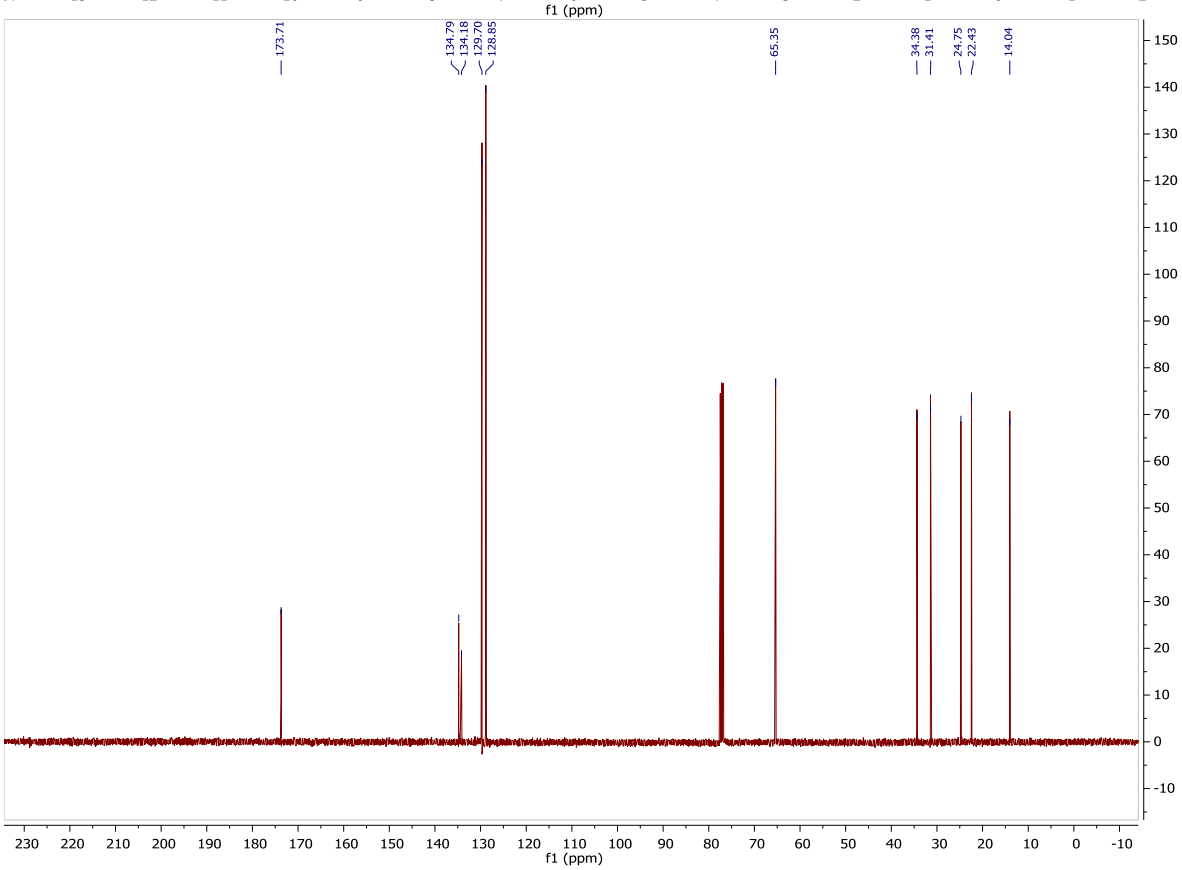
4-chlorobenzyl 3-phenylpropanoate (6p)



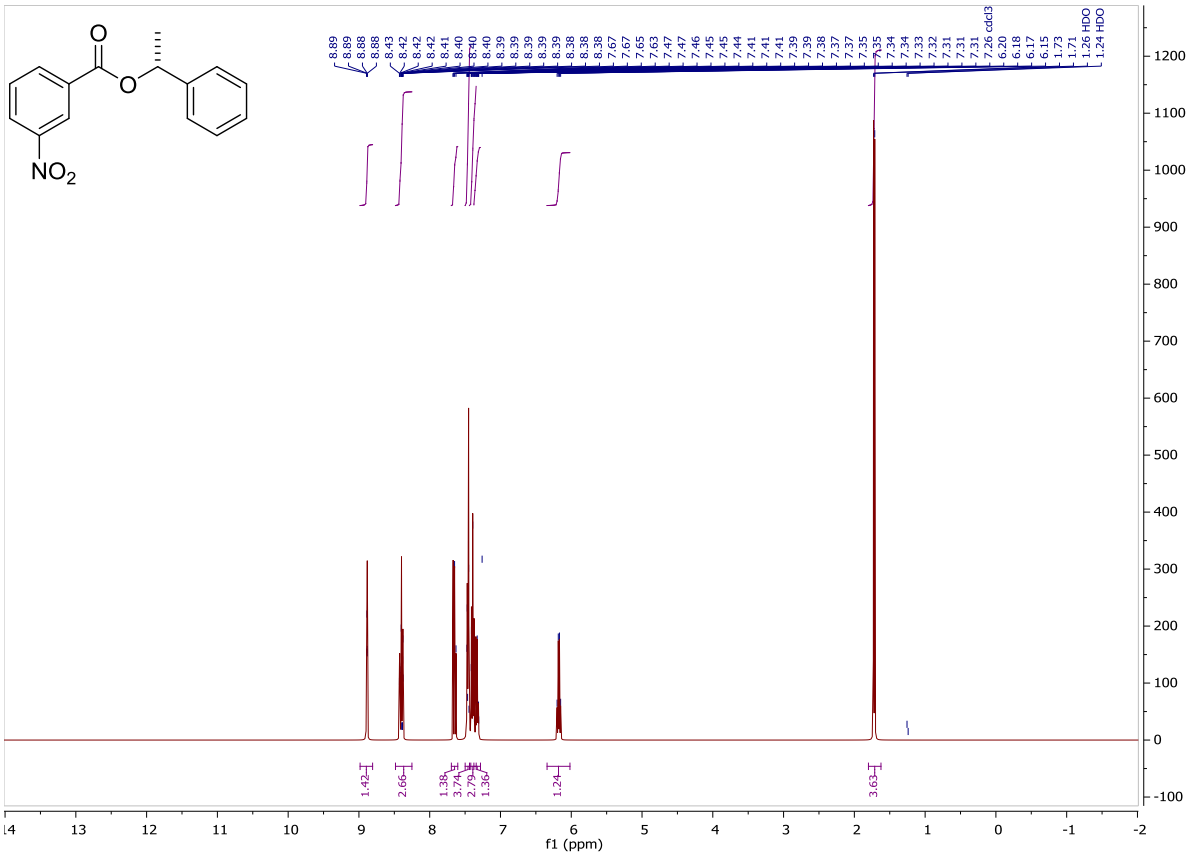


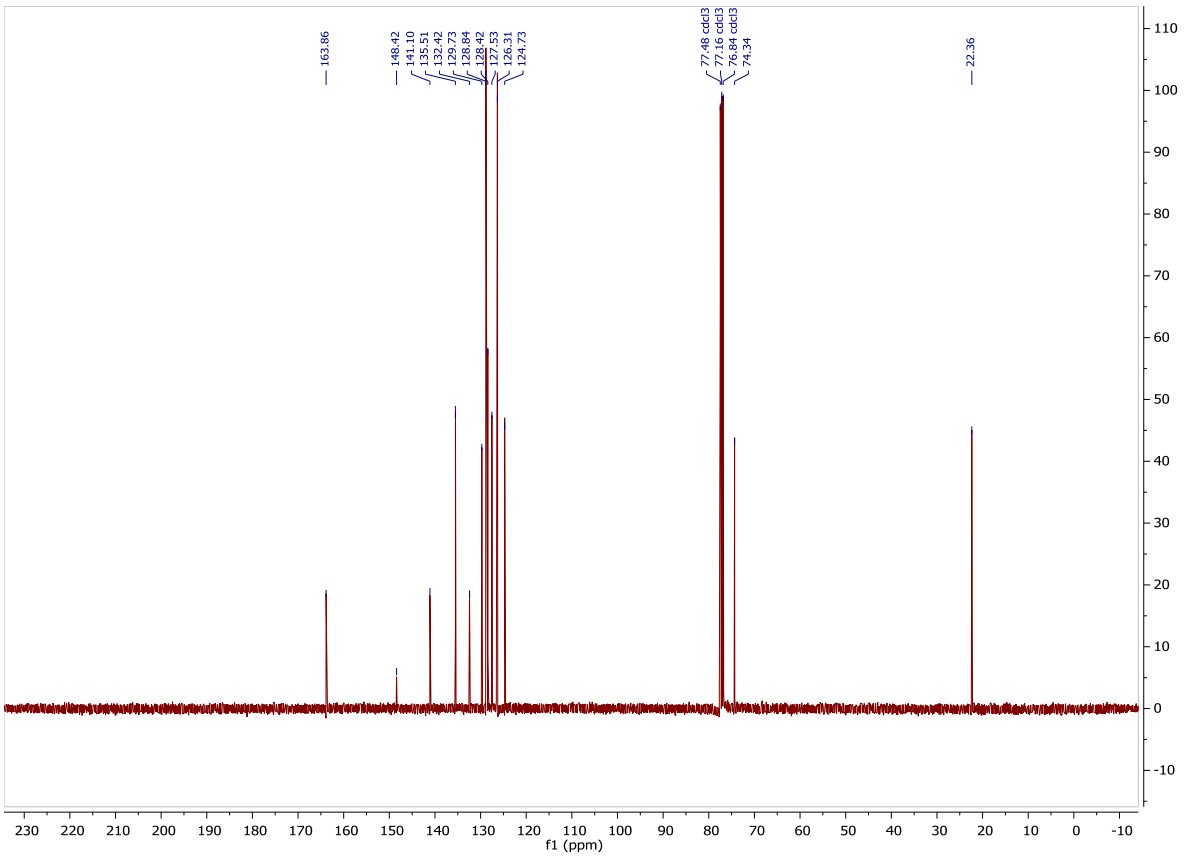
4-chlorobenzyl hexanoate (6q)



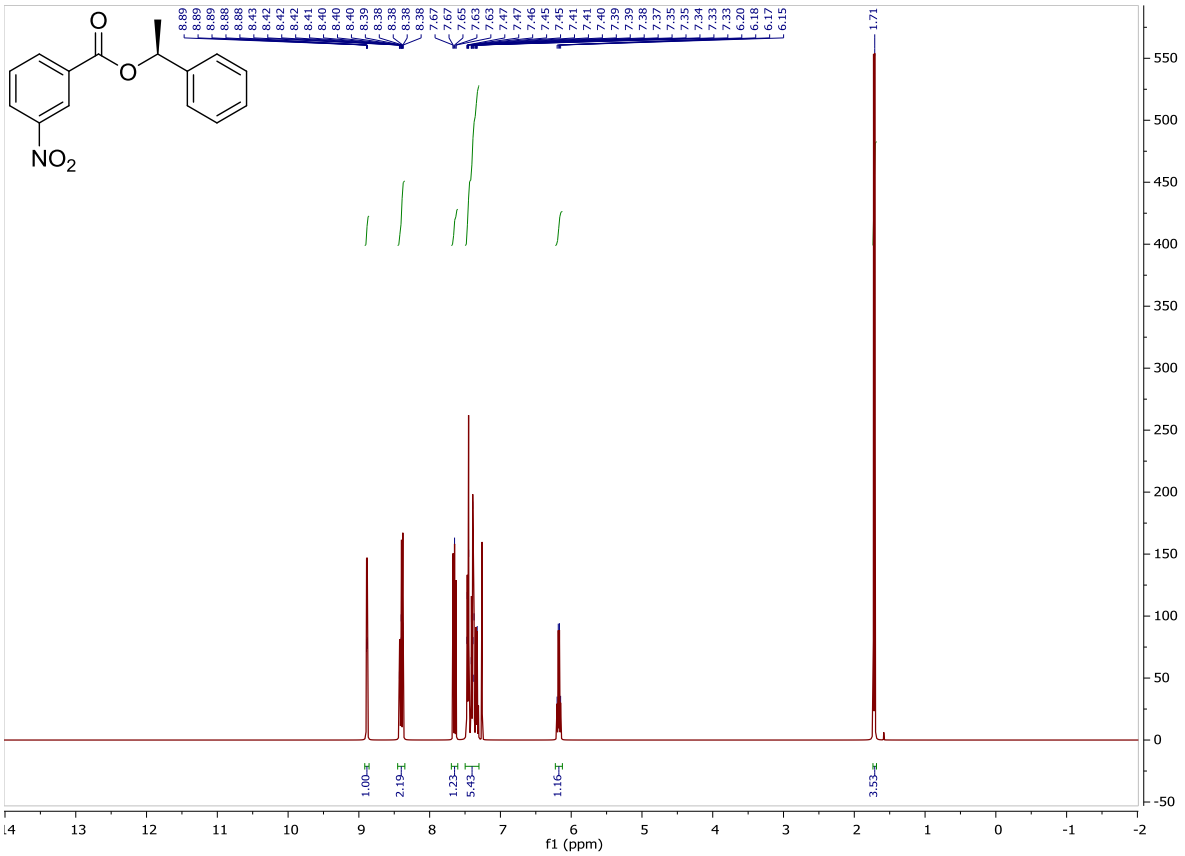


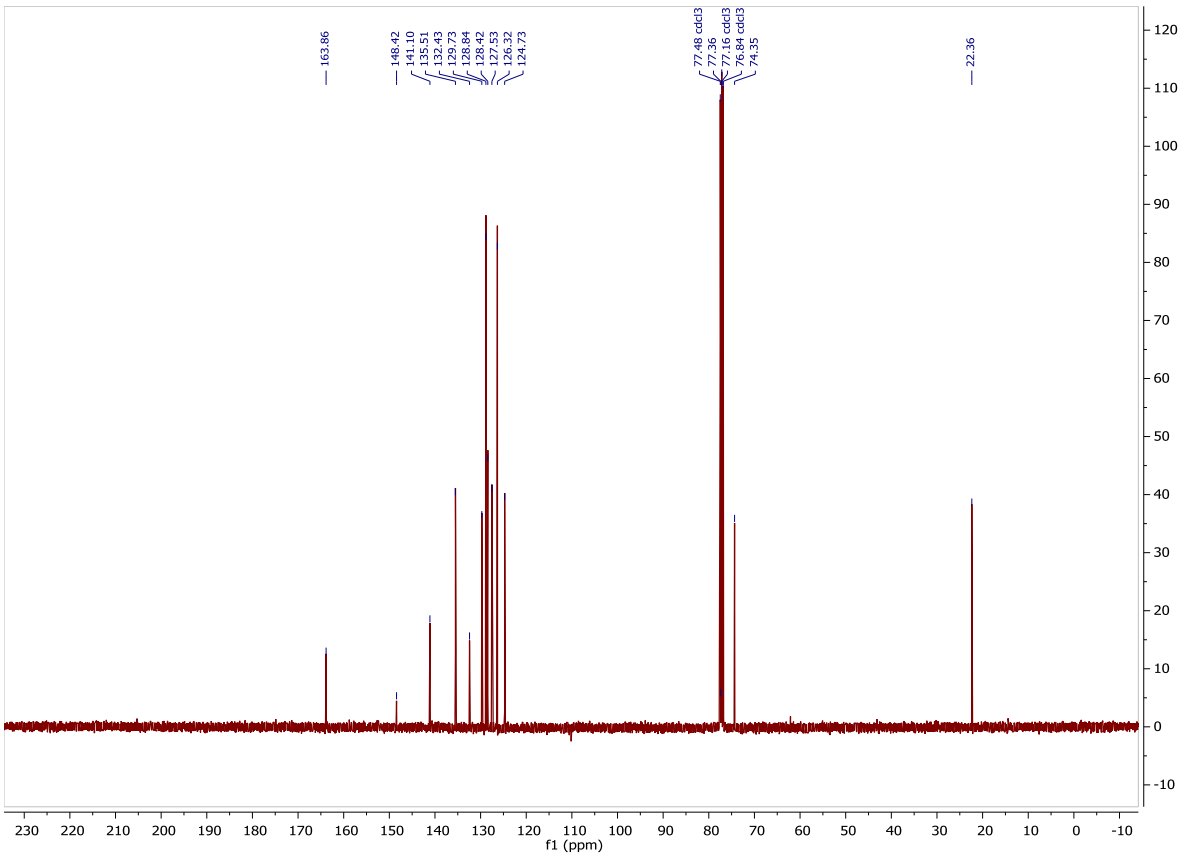
(*R*)-1-Phenylethyl 3-nitrobenzoate (6r)



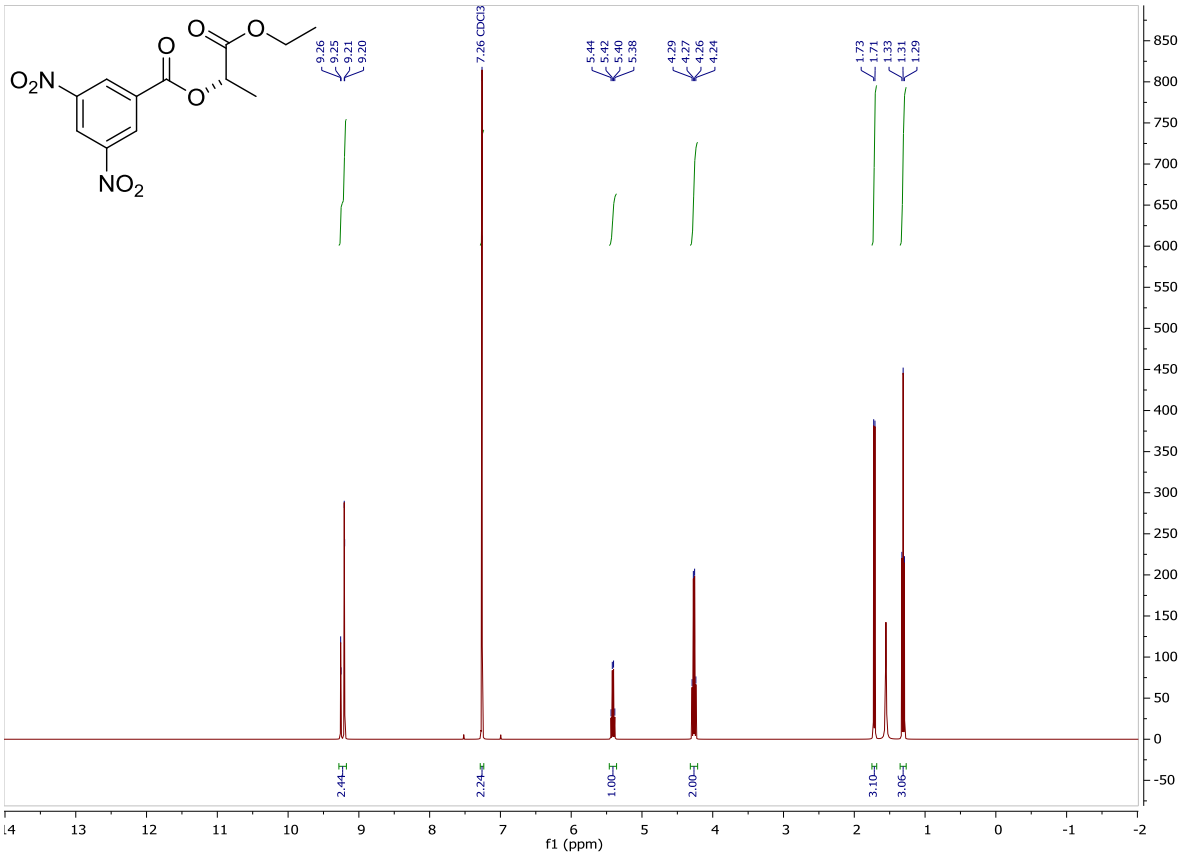


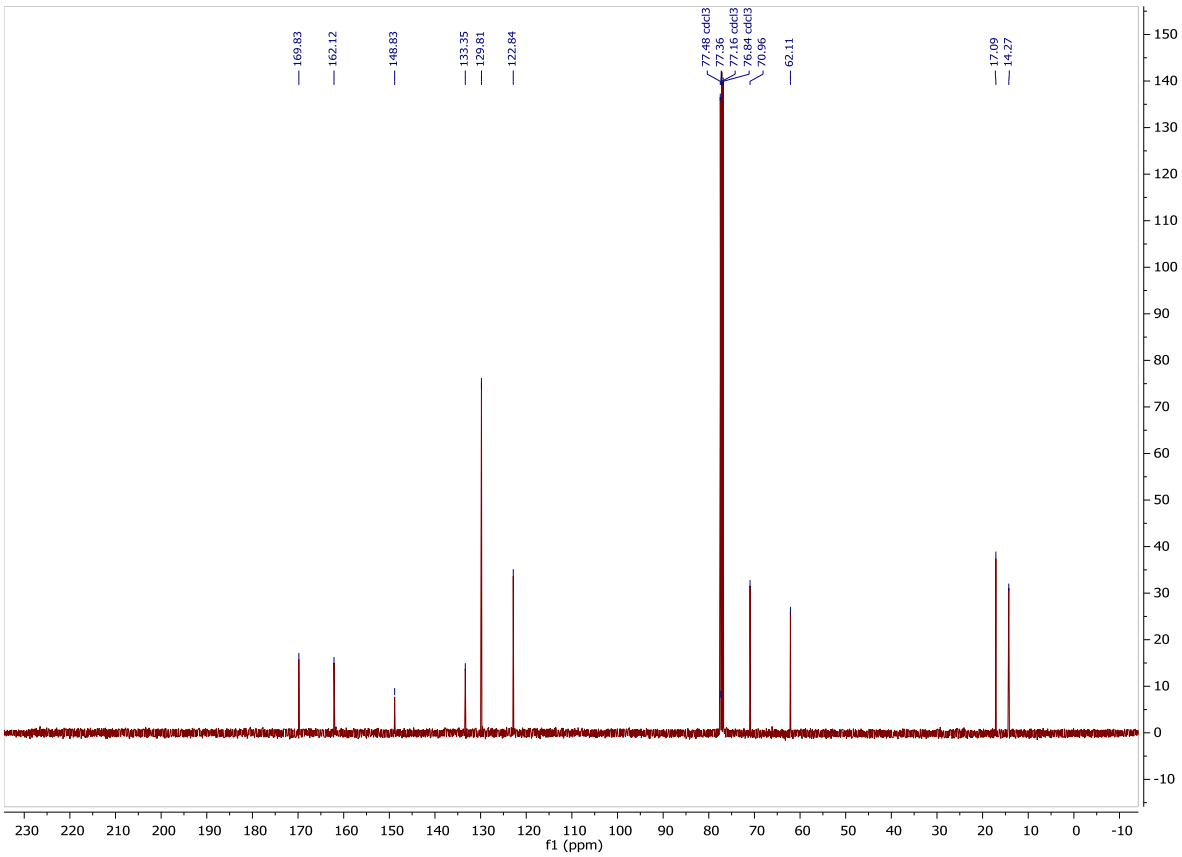
(*S*)-1-Phenylethyl 3-nitrobenzoate (6r)



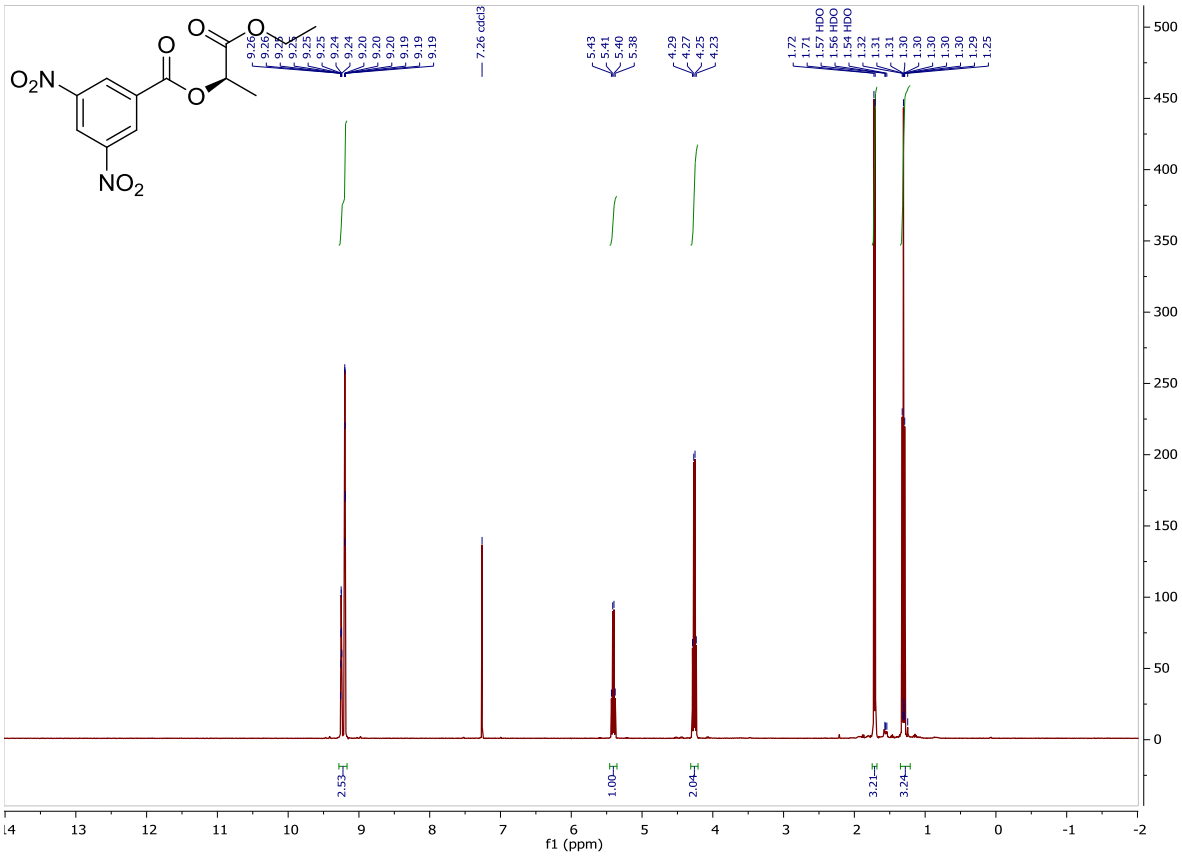


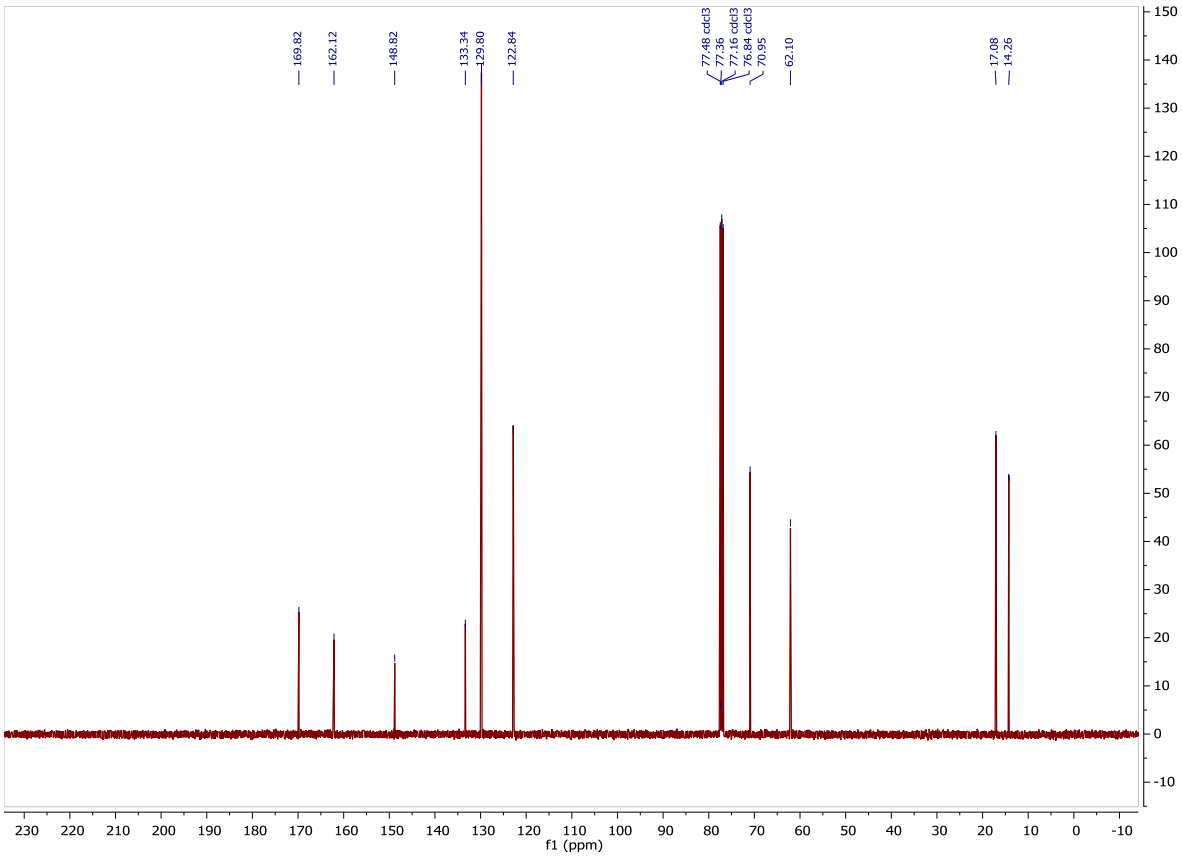
Ethyl (*S*)-2-((3,5-dinitrobenzoyl)oxy) propionate (6s)



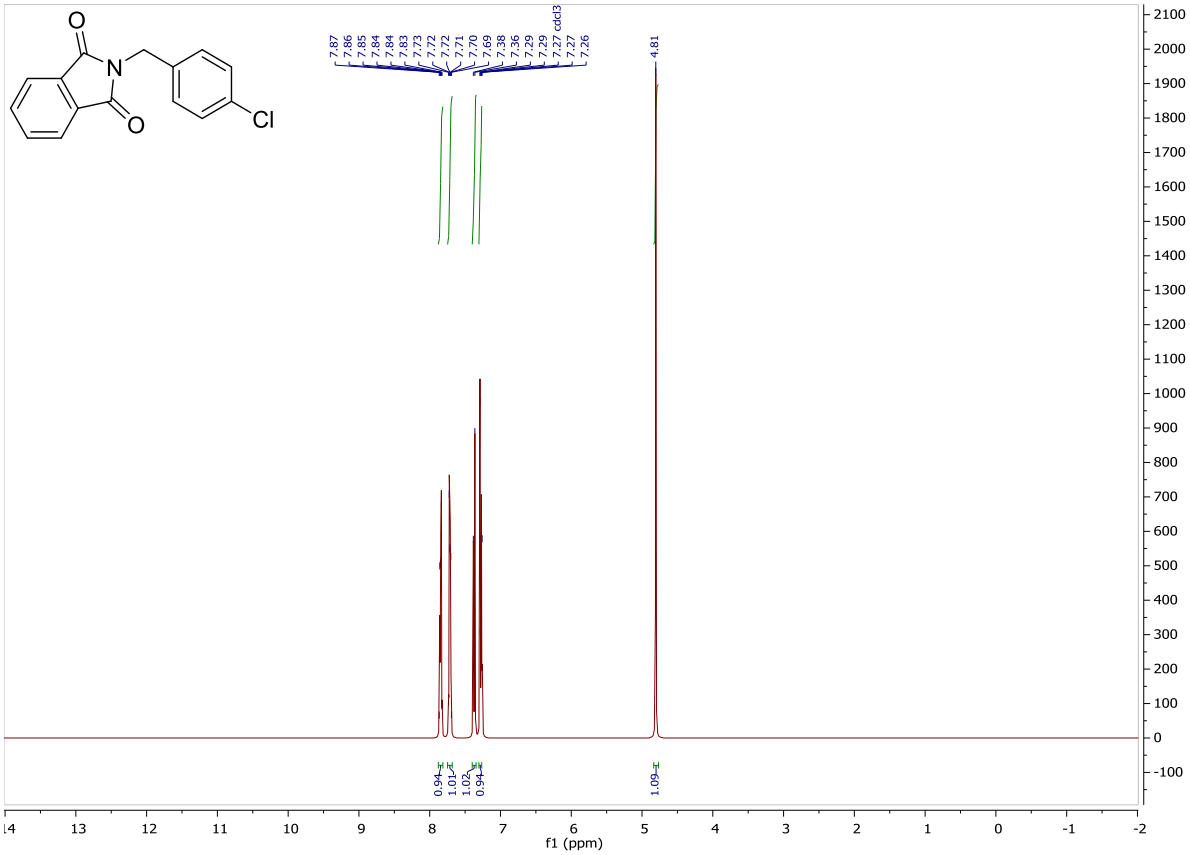


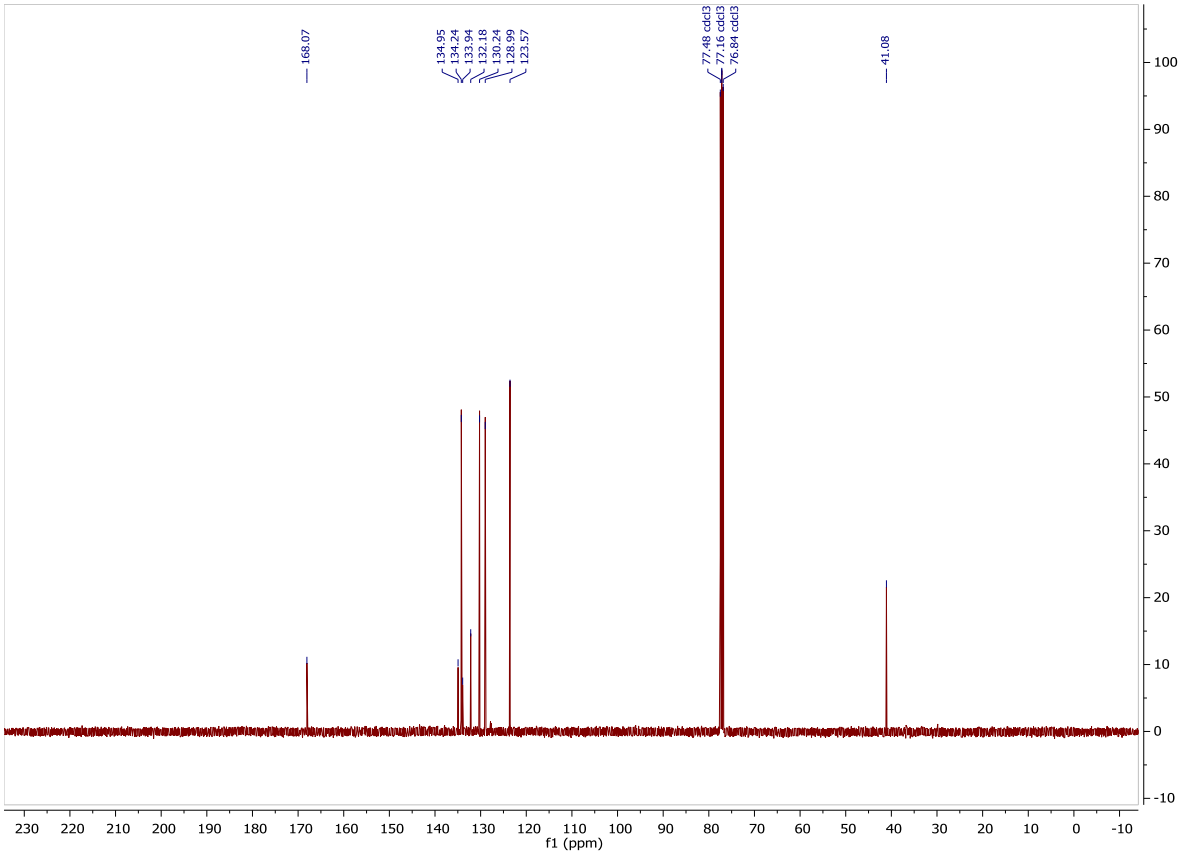
Ethyl (*R*)-2-((3,5-dinitrobenzoyl)oxy) propionate (6s)





N-(4-Chlorobenzyl)-phthalimide (9)



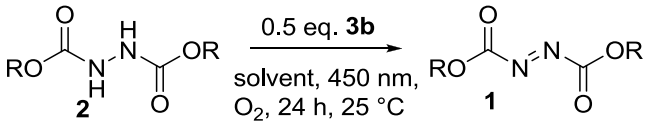


S8 Photooxidation of acylhydrazines 2 with 3

Photooxidation of 2 with 3b – solvent screening

A mixture of hydrazine **2** (c(**2**) = 1×10^{-3} M), flavin **3b** (c(**3b**) = 5×10^{-4} M), and alternatively of HBF_4 (c(HBF_4) = 5×10^{-4} M) in deuterated solvent (2 mL) was bubbled with oxygen (2 min) and then stirred for 24 hours at 25 °C under O_2 (balloon) under irradiation with blue LEDs (450 nm, 1 W LED). Reaction mixture was analysed by ^{1}H NMR.

Table. Photooxidation of **2** with **3d** – solvent screening[a]

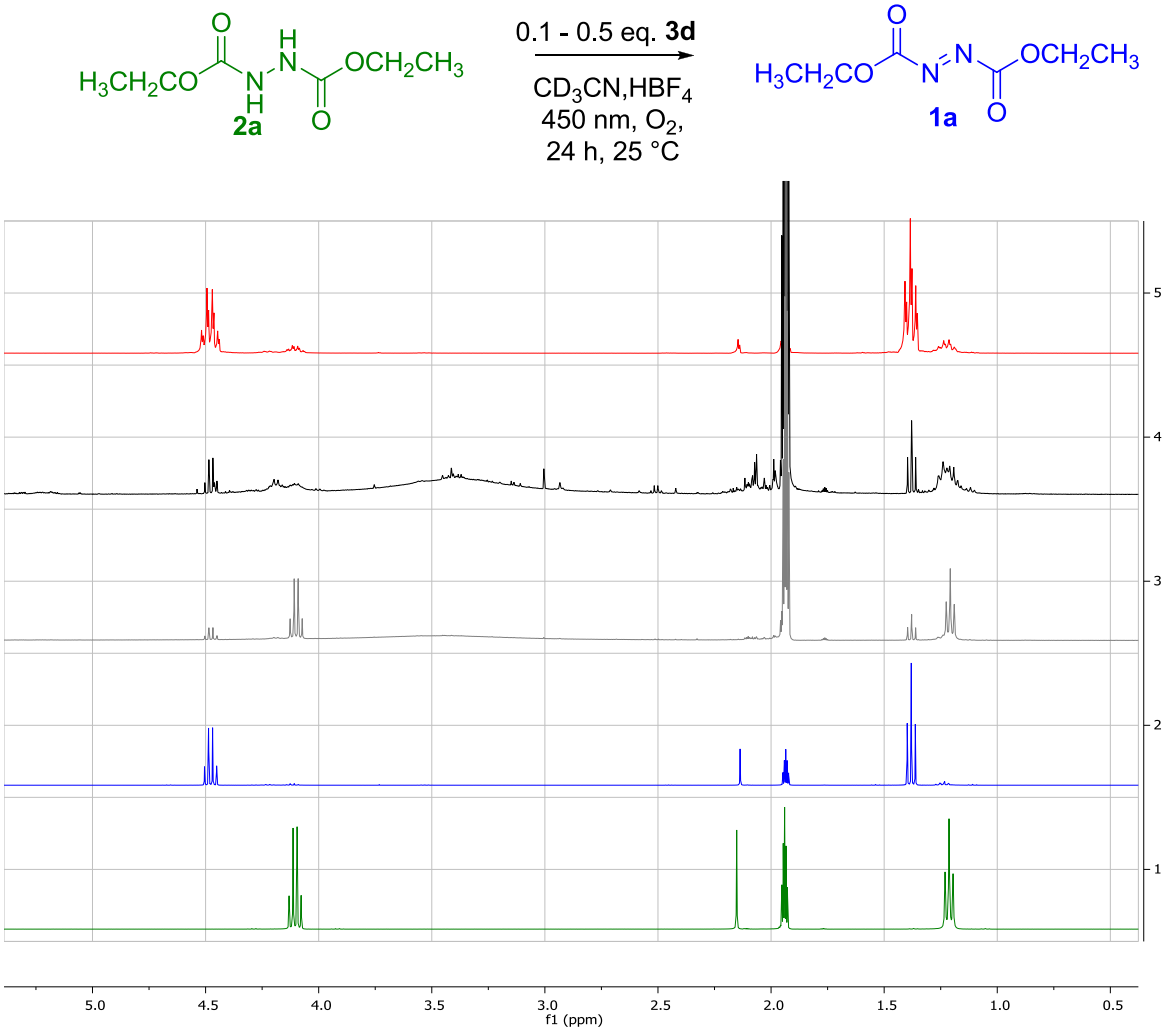


Solvents	R			
	Et	***i*Pr**	***t*Bu**	**Bn**
CD_3CN	18	21	39	35
CD_3CN + HBF_4	quant.	-	-	quant.
Chlofoform - d_1	44	-	-	48
DMSO - d_6	0[b]	-	-	0[b]
Nitromethane - d_3	13	-	-	53
Nitrobenzene - d_5	0	-	-	traces
DMF - d_7	0	-	-	0
THF - d_8	0	-	-	9

[a] c(**2**) = 1×10^{-3} M, c(catalyst **3b**) = 5×10^{-4} M; [b] HBF4 was added (1 equiv. relative to the substrate to simulate acidic conditions during esterification) [c] oxidation of solvent to dimethylsulfone

Photooxidation of 2a with 3d – semipreparative experiments

A mixture of hydrazine **2a** (0.01 mmol), flavin **3d** (0.001 or 0.005 mmol), and of HBF_4 (0.0150 mmol) in CD_3CN (2 mL) was bubbled with oxygen (2 min) and then stirred for 24 hours at 25 °C under O_2 (balloon) under irradiation with blue LEDs (450 nm, 1 W LED). Reaction mixture was analysed by ^1H NMR. Alternatively, after evaporation of solvents, crude product **1a** was purified by flash chromatography (see Figure below).

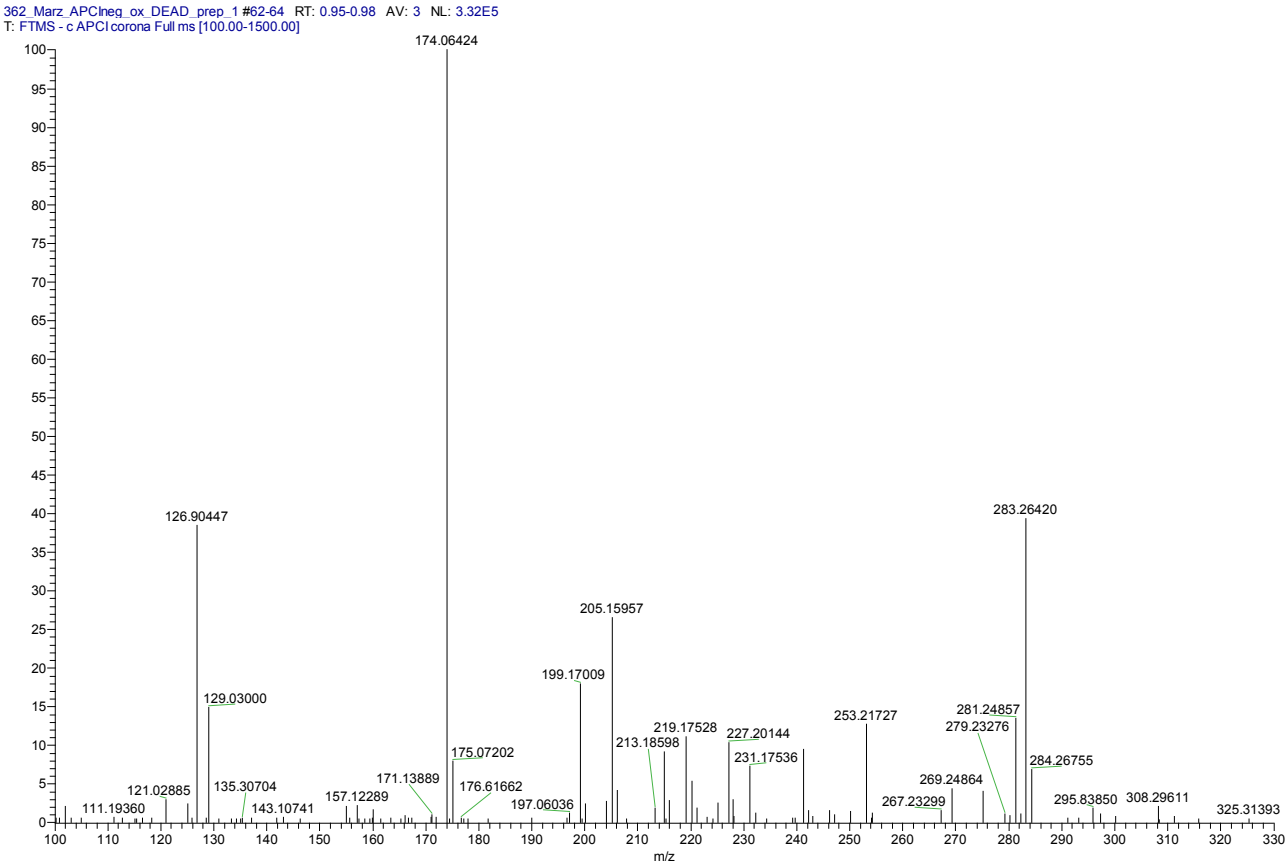


Red: oxidation with 25% of **3d** followed by flash chromatography to remove flavin **3d** and products of its decomposition

Black: oxidation with 25% of **3d**; impurities are mainly products of flavin **3d** decomposition
Grey: oxidation with 10% of **3d**
Blue: **1a**
Green: **2a**

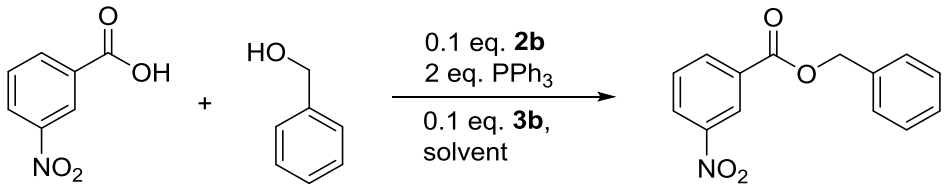
MS spectrum of fotooxidation of 2a with 3d

HRMS (APCI) calcd for $C_6H_{10}N_2O_4$ ([M]$^-$) 174.06461, found 174.06424.



S9 Preliminary screening of the reaction conditions

Preliminary screening of solvents[a]



Entry	Solvent	Conversion of ester/aldehyde [%]
1	CH_3CN	59/1
2	acetone	30/10
3	Ethyl-acetate	-/-
4	Toluene	50/2
5	THF	10/-
6	$CHCl_3$	34/10[b]
7	DMF	5/-

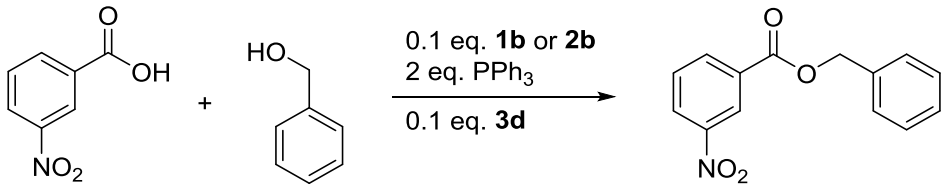
[a] *n*(**5a**) = 0.15 mmol; *n*(**4a**) = 0.18 mmol; *n*(**3b**) = 0.015 mmol; *n*(PPh_3) = 0.3 mmol; MS 4 Å (150 mg); *n*(**2b**) = 0.015 mmol; 450 nm; 25 °C; O_2; 24 h; [b] 44 % conversion of benzylchloride.

Preliminary screening of amounts of reagents[a]

Entry	Equivalents of reagents					Conv. [e]
	Acid	Alcohol	Hydrazine	PPh_3	Cat.	
1	1.2	1	0.1	2	0.1	48
2	1.2	1	0.1	2	0.1	45[b]
3	1.2	1	0.1	2	0.2	55
4	2.4	1	0.1	2	0.1	36
5	1.2	1	0.1	4	0.1	51
6	1.2	1	1	2	0.1	49
7	1	2	0.1	2	0.1	42
8	1.2	1	0.1	2	0.1	61[c]
9	1.2	1	0.1	2	0.1	70[d]

[a] *n*(**5a**) = 0.15 mmol; *n*(**4a**) = 0.18 mmol; *n*(**3b**) = 0.015 mmol; *n*(PPh_3) = 0.3 mmol; MS 4 Å (150 mg); 2 ml CH_3CN; *n*(**2b**) = 0.015 mmol; 450 nm; 25 °C; 24 h; [b] 2 x MS 4 Å; [c] 1 ml CH_3CN; [d] 0.5 ml CH_3CN; [e] determined by ^1H NMR.

S10 Blank experiments

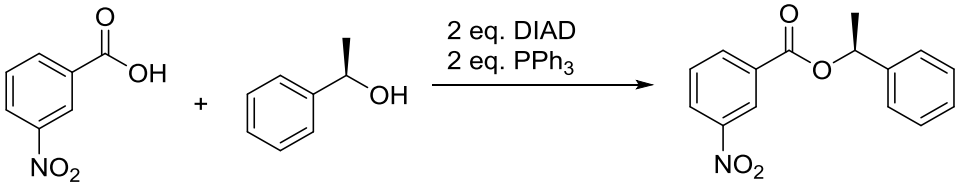


Blank experiments for photocatalytic esterification under Mitsunobu reaction conditions in the presence (✓) or absence (-) of catalyst **3d**, PPh_3, light or molecular sieves.[a]

Entry	Cat. (**3d**)	PPh_3	Light[b]	MS 4 Å	Conversion[c] 24 h [%]
1	-	✓	✓	✓	0
2	✓	-	✓	✓	0
3	✓	✓	-	✓	0
4	✓	✓	✓	-	0
5	✓	✓	✓	✓	64[d] (99[e])

[a] n(**5a**) = 0.15 mmol; n(**4a**) = 0.18 mmol; n(**2b**) = 0.015 mmol; n(**3d**) = 0.015 mmol; $n(PPh_3)$ = 0.3 mmol; 4 Å MS (150 mg); 2 ml CH_3CN; O_2; [b] 455 nm; [c] Determined by ^{1}H NMR; [d] method **A**: t = 25 °C; n(**1b**) = 0.015 mmol; [e] method **B**: t = 50 °C; n(**2b**) = 0.015 mmol; $n(PhSiH_3)$ = 0.3 mmol.

S11 Effect of adducts on stereoselectivity of Mitsunobu esterification



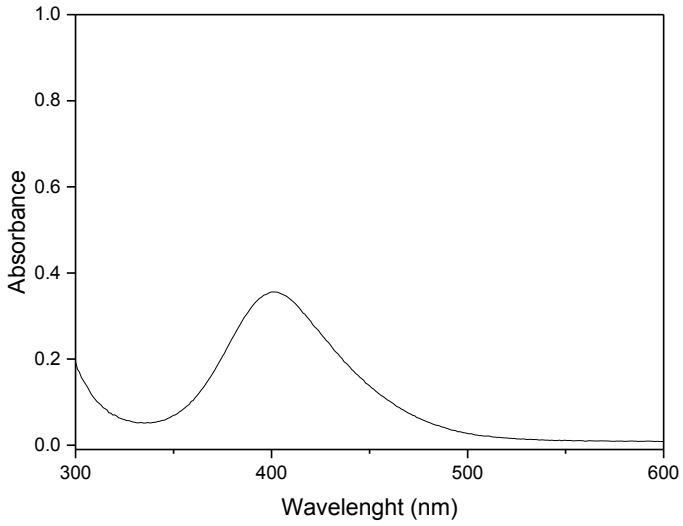
#		Yeild/conv.	*er*
1	-	71/84	85/15
2	10 % **3d**[b]	71/79	73/27
3	MS 4 Å[c]	67/75	86/14
4	*hv*[d]	69/80	78/22
5	*hv*, MS 4 Å[c,d]	70/78	87/13
6	10 % **3d**, MS 4 Å[b,c]	73/79	84/16
7	50 % **3d**[e]	72/82	81/19
8	10 % **3d**, *hv*[b,d]	68/76	79/21

[a] *n*((*R*)-**5l**) = 0.15 mmol; *n*(**4a**) = 0.18 mmol; *n*(**1b**) = 0.3 mmol; *n*(PPh_3) = 0.3 mmol; 2 ml CH_3CN; *t* = 25 °C; 24 h; [b] *n*(**3d**) = 0.015 mmol; [c] MS 4 Å (150 mg); [d] 450 nm; [e] *n*(**3d**) = 0.075 mmol.

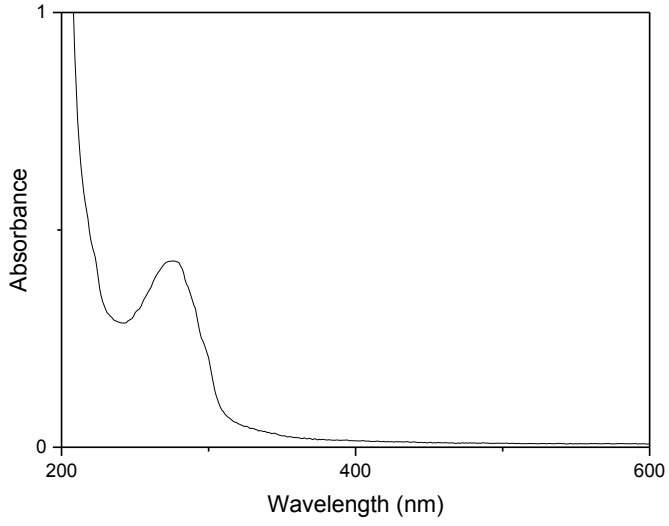
S12 UV-VIS and fluorescence spectra of 1, 2 and 3

Very small absorption of dialkyl azodicarboxylates **1** was observed thus **1** can undergo very slow photodecomposition

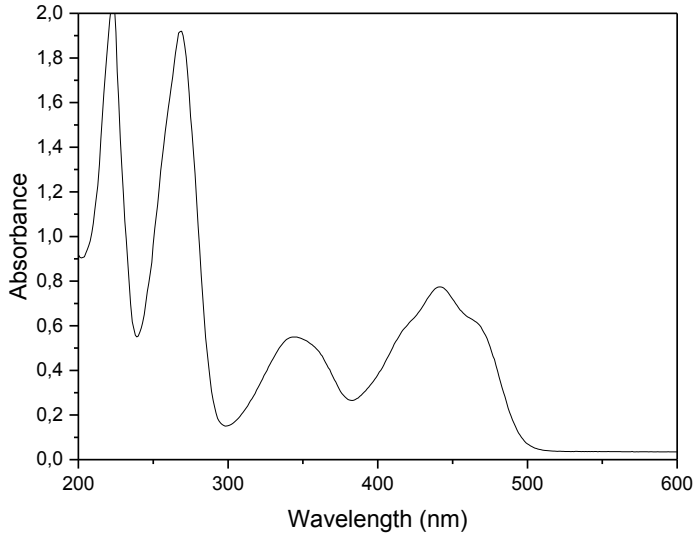
UV-VIS spectra of **1b** in acetonitrile (c(**1b**) = 1×10^{-2} M)



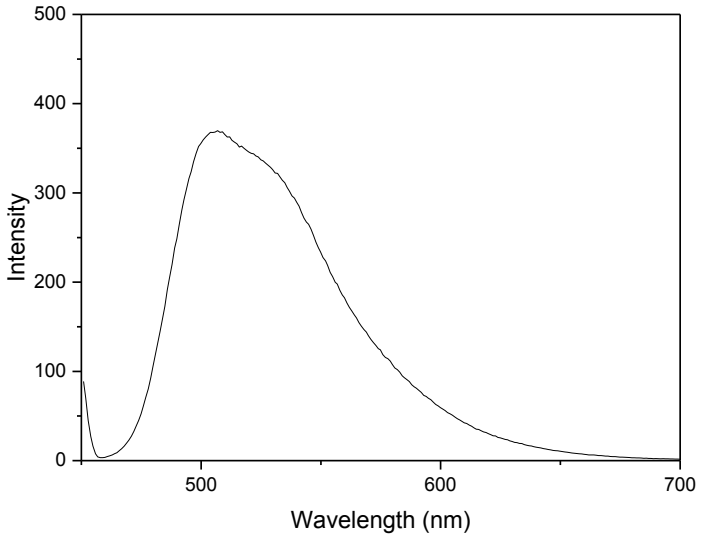
UV-VIS spectra of **2b** in acetonitrile (c(**2b**) = 1×10^{-2} M)



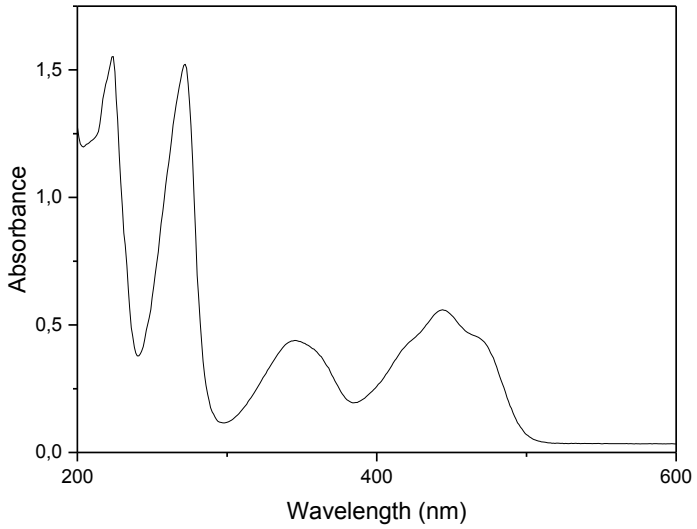
UV-VIS spectrum of **3b** in acetonitrile (c(**3b**) = 5×10^{-5} M)



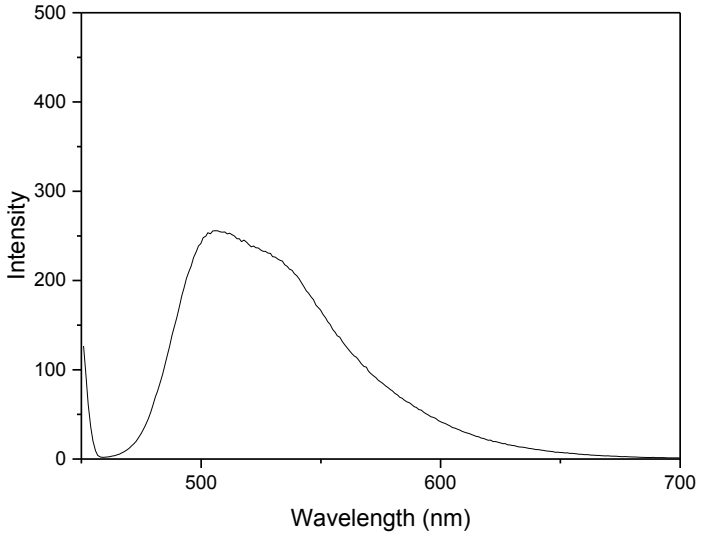
Fluorescence spectrum of **3b** in acetonitrile (c(**3b**) = 1×10^{-6} M); λ_{ext} = 507 nm



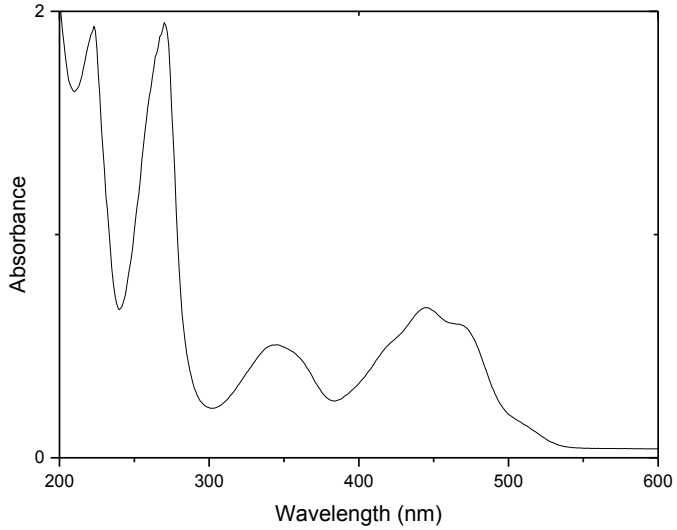
UV-VIS spectrum of **3c** in acetonitrile (c(**3c**) = 5×10^{-5} M)



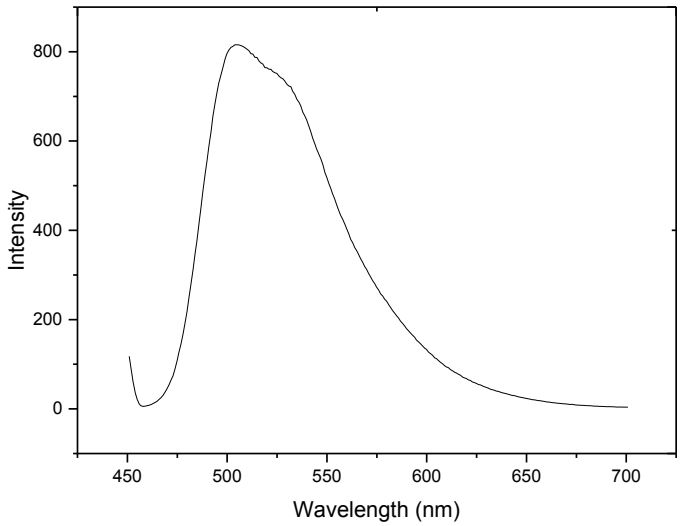
Fluorescence spectrum of **3c** in acetonitrile (c(**3c**) = 1×10^{-6} M); λ_{ext} = 506 nm



UV-VIS spectrum of **3d** in acetonitrile (c(**3d**) = 5×10^{-5} M)

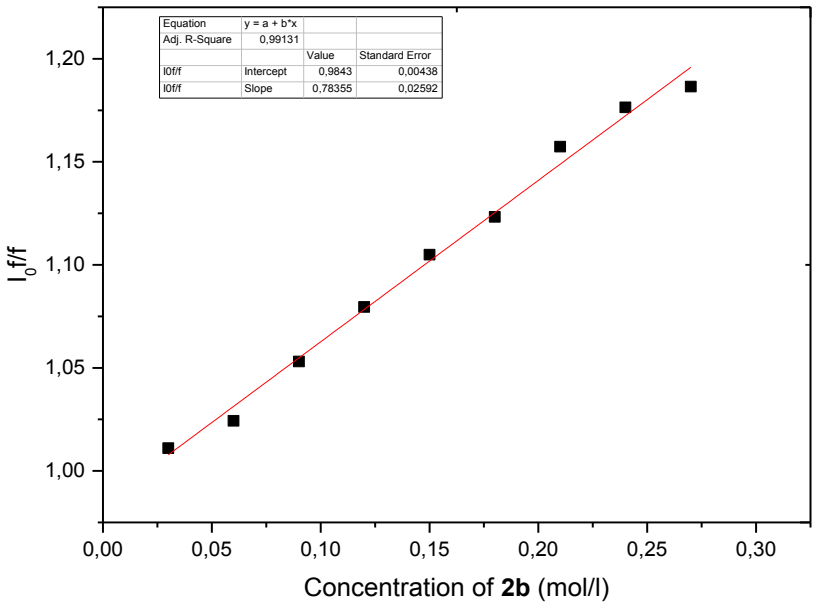


Fluorescence spectrum of **3d** in acetonitrile (c(**3d**) = 3×10^{-6} M); λ_{ext} = 504 nm

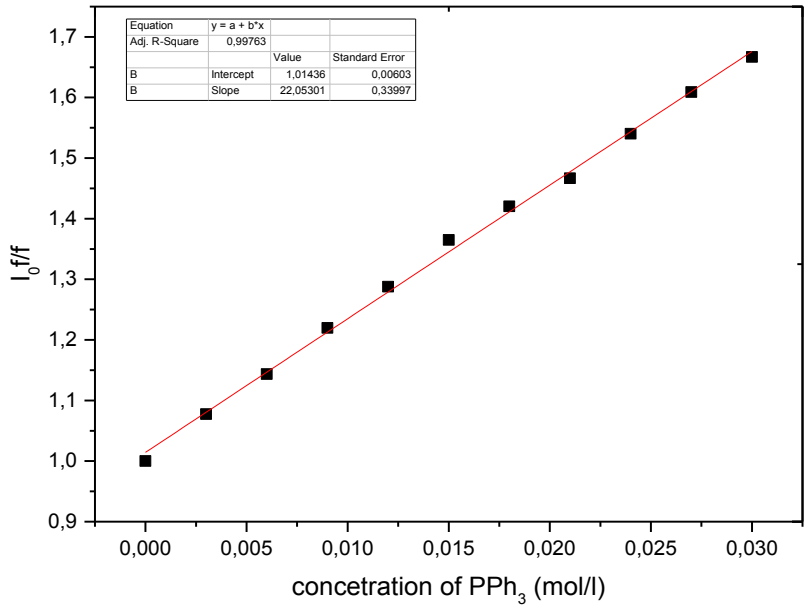


S13 Fluorescence quenching of 3d by diacylhydrazines 2b and Ph_3P

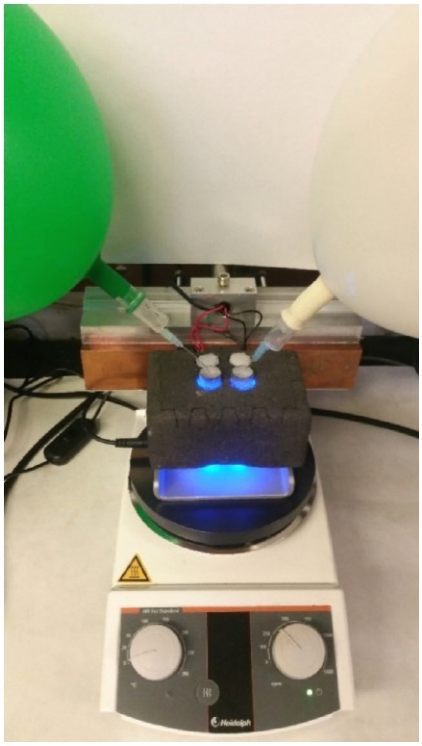
Quenching of **3d** with **2b**

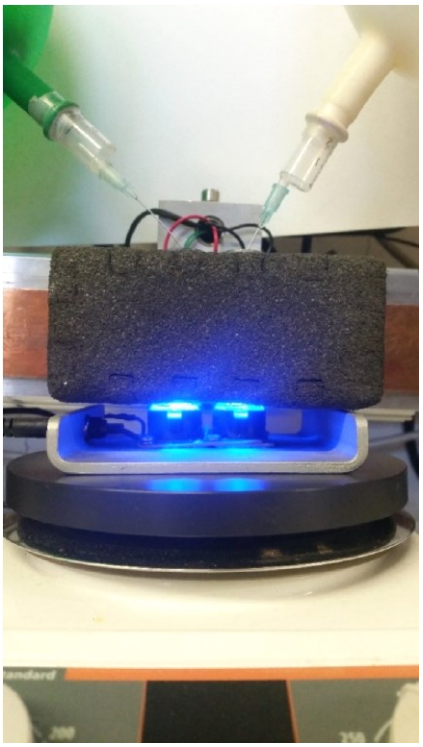


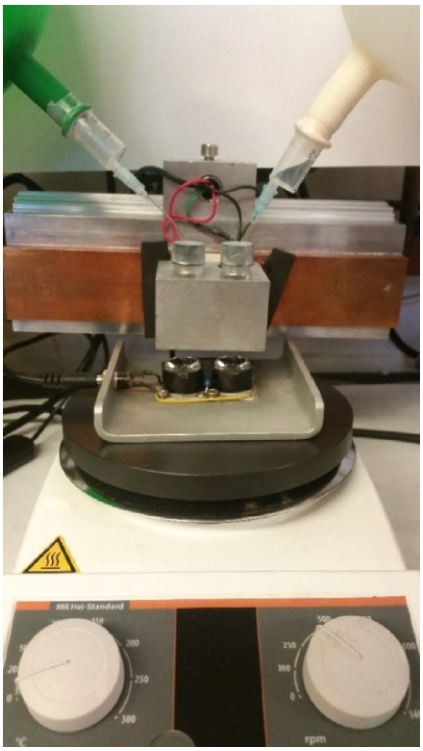
Quenching of **3d** with PPh_3



S14 Experimental setup







Reactions were performed in 4 mL vials irradiated at a distance 9 mm from the bottom by blue LED (Luxeon STAR/0, 1W; 220 mW@350 mA, 2.8-4 V, 440-460 nm, $\Delta\lambda_{1/2}$ = 20 nm). Vials were located in aluminium block which was tempered (±0.2 °C) by Peltier unit. Reaction mixtures were stirred (500 min^{-1}) with magnetic stirrer.