Electronic Supporting Information (ESI)

Implications of rotational process of the flexible spacer on liquid crystals behavior of dimers 4,5-dihydroisoxazole benzoates.

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Experimental Section

Instruments and Techniques. Ethanol, diethyl ether, 4-bromobenzoic acid, copper(I) iodide (CuI), triphenylphosphine (PPh_3), 4-dimethylaminopyridine (DMAP) and 1,3- dicyclo hexylcarbodiimide (DCC) were used without further purification from Aldrich. 4-*n*-decyloxybenzoic acid[1] and 2-ethynyl-6-(octyloxy)naphthalene[2] were prepared according to modified literature methods. Bis(triphenylphosphine)palladium (II) chloride [$PdCl_2(PPh_3)_2$] was prepared following a literature procedure.[3] Triethylamine (Et_3N) was distilled over potassium hydroxide before use. Tetrahydrofuran (THF) was dried over sodium metal-benzophenone and distilled immediately before use. Anhydrous sodium sulphate (Na_2SO_4) was used as a drying agent for any organic phases. All reactions involving Sonogashira's coupling were performed in a one-neck round-bottom flask equipped with septum stoppers and charged with Et_3N, aromatic iodide and alkyne under argon atmosphere for 30 min. CuI, PPh_3 and [$PdCl_2(PPh_3)_2$] were then added.

Characterization. Nuclear magnetic resonance spectra were obtained using a Varian 300 MHz instrument. Chemical shifts (δ) are given in parts per million using tetramethylsilane (TMS) as a reference. ATR spectra were obtained using a Varian 640-IR spectrometer between 4000 and 500 cm^{-1} and with a resolution of 4 cm^{-1}. All spectra were performed with 16 scans and are given in wave numbers (cm^{-1}). Combustion (CHN) analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. The differential scanning calorimetry (DSC) traces were obtained using a DSC 2910 TA instrument. The melting points and liquid crystalline transition temperatures and textures of the samples were measured on a Mettler Toledo FP82HT Hot Stage combined with a FP90 Central Processor connected to an Olympus BX41 camera. The rate of heating or cooling was 10° C min^{-1}. The X-ray diffraction experiments were carried out with the X'PERT-PRO (PANalytical) diffractometer using Cu Kα radiation (λ = 1.5418 Å), with an applied power of 1.2 kVA. The scans were performed in continuous mode from 2° to 30° (2θ angle). The samples were prepared by prior heating (with a hot stage) of an amount of powder on a glass plate until the compound melted to the liquid state, followed by cooling to room temperature. As a result, we obtain a film approximately 1 mm thick. The films were then placed in the diffractometer chamber on the TCU2000 temperature control unit (Anton Paar), which allows control of the sample temperature during the measurement. The films were first heated until the isotropic phase and the diffraction patterns collected during cooling back through the mesophases.

Theoretical calculations. The energy and molecular geometry of all model systems were determined by full optimization without any constraint. The calculation was performed with the GAUSSIAN 98[4] program using the B3LYP hybrid functional[5] employing a 6-31G(d,p) basis set.

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Synthesis. The synthesis of the series {3-[4-(alkyloxy)phenyl]-4,5-dihydroisoxazol-5-yl} hydroxyalkyl (**3a-d**) was carried out according to modified literature methods.[6]

{3-[4-(Octyloxy)phenyl]-4,5-dihydroisoxazol-5-yl} methanol (3a): Yield: 219 mg, 36%; white solid; mp 94 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.89 (m, 3 H, CH_3), 1.41 (m, 10 H, $(CH_2)_5$), 1.78 (m, 2 H, C*H*$_2$CH$_2$O), 2.09 (broad, 1 H, OH), 3.24 (dd, $^{2}J_{gem}$ = 16.8 Hz, $^{3}J_{trans}$ = 8.1 Hz, 1 H, N=CC*H*HCH), 3.34 (dd, $^{2}J_{gem}$ = 16.8 Hz, $^{3}J_{cis}$ = 10.5 Hz, 1 H, N=CCH*H*CH), 3.67 (dd, $^{2}J_{gem}$ = 12.0 Hz, $^{3}J_{trans}$ = 4.8 Hz, 1 H, CHC*H*HOH), 3.83 (dd, $^{2}J_{gem}$ =12.0 Hz, $^{3}J_{cis}$ = 3.3 Hz, 1 H, CHCH*H*OH), 3.96 (t, *J* = 6.6 Hz, 2 H, CH$_2$O), 4.81 (m, 1 H), 6.87 (d, *J* = 9.0 Hz, 2 H, Ar), 7.56 (d, *J* = 8.7 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 13.9, 22.5, 25.8, 29.0, 29.1, 29.2, 31.7, 36.5, 63.4, 68.0, 80.9, 114.5, 121.4, 128.1, 156.5, 160.5; ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1606, 1594, 1515, 1255, 1181, 1045, 896, 819, 642; $C_{18}H_{27}NO_3$ (305.42): calcd. C 70.79, H 8.91, N 4.59; found C 70.65, H 8.86, N 4.80.

2-{3-[4-(Octyloxy)phenyl]-4,5-dihydroisoxazol-5-yl} ethanol (3b): Yield: 44 mg, 35%; white solid; mp 107 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.91 (m, 3 H, CH_3), 1.41 (m, 10 H, $(CH_2)_5$), 1.81 (m, 2 H, C*H*$_2$CH$_2$O), 1.97 (m, 2 H, CHC*H*$_2$CH$_2$OH), 3.06 (dd, $^{2}J_{gem}$ = 16.5 Hz, $^{3}J_{trans}$ = 7.8 Hz, 1 H, N=CC*H*HCH), 3.47 (dd, $^{2}J_{gem}$ = 16.5 Hz, $^{3}J_{cis}$ = 10.5 Hz, 1 H, N=CCH*H*CH), 3.88 (t, *J* = 6.3 Hz, 2 H, C*H*$_2$OH), 3.99 (t, *J* = 6.3 Hz, 2 H, CH$_2$O), 4.91 (m, 1 H), 6.92 (d, *J* = 9.0 Hz, 2 H, Ar), 7.60 (d, *J* = 9.0 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 160.7, 156.7, 128.2, 121.9, 114.7, 79.1, 68.2, 59.6, 40.8, 37.9, 31.9, 29.4, 29.3, 29.2, 26.1, 22.7, 14.2; ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1606, 1594, 1515, 1255, 1181, 1045, 896, 819, 642.

3-{3-[4-(Octyloxy)phenyl]-4,5-dihydroisoxazol-5-yl} propan-1-ol (3c): Yield: 48 mg, 36%; white solid; mp 97 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.91 (m, 3 H, CH_3), 1.41 (m, 10 H, $(CH_2)_5$), 1.70 (m, 6 H, CH(C*H*$_2$)$_2$CH$_2$OH, C*H*$_2$CH$_2$O), 2.89 (dd, $^{2}J_{gem}$ = 16.5 Hz, $^{3}J_{trans}$ = 7.8 Hz, 1 H, N=CC*H*HCH), 3.33 (dd, $^{2}J_{gem}$ = 16.0 Hz, $^{3}J_{cis}$ = 10.2 Hz, 1 H, N=CCH*H*CH), 3.64 (m, 2 H, C*H*$_2$OH), 3.90 (t, *J* = 6.6 Hz, 2 H, CH$_2$O), 4.67 (m, 1 H), 6.82 (d, *J* = 8.7 Hz, 2 H, Ar), 7.50 (d, *J* = 8.7 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 160.8, 156.4, 128.3, 122.2, 114.8, 81.0, 68.3, 62.6, 40.6, 32.0, 32.0, 29.5, 29.4, 29.3, 29.0, 26.2, 22.8, 14.3; ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1606, 1594, 1515, 1255, 1181, 1045, 896, 819, 642.

4-{3-[4-(Octyloxy)phenyl]-4,5-dihydroisoxazol-5-yl} butan-1-ol (3d): Yield: 45 mg, 33%; white solid; mp 102 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.91 (m, 3 H, CH_3), 1.60 (m, 18 H, $(CH_2)_5$, CH(C*H*$_2$)$_3$CH$_2$OH, C*H*$_2$CH$_2$O), 2.98 (dd, $^{2}J_{gem}$ = 16.5 Hz, $^{3}J_{trans}$ = 8.1 Hz, 1 H, N=CC*H*HCH), 3.40 (dd, $^{2}J_{gem}$ = 16.5 Hz, $^{3}J_{cis}$ = 10.5 Hz, 1 H, N=CCH*H*CH), 3.70 (t, *J* = 6.3 Hz, 2 H, C*H*$_2$OH), 4.00 (t, *J* = 6.3 Hz, 2 H, CH$_2$O), 4.73 (m, 1 H), 6.93 (d, *J* = 9.7 Hz, 2 H, Ar), 7.61 (d, *J* = 9.7 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 13.9, 21.7, 22.4, 25.8, 29.0, 29.1, 29.2, 31.6, 32.2, 34.8, 40.0, 62.1, 67.9, 80.8, 114.4, 121.9, 127.9, 156.0, 160.4; ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1606, 1594, 1515, 1255, 1181, 1045, 896, 819, 642.

Synthesis of the series **5a-d**. The corresponding alcohol (**3a-d**) (4.2 x 10^{-4} mol) and 4-decyloxybenzoic acid (4.2 x 10^{-4} mol) were dissolved in THF (5 mL) and the resultant solution stirred for 15 minutes under an inert atmosphere. Then DCC (5.8 x 10^{-4} mol) and DMAP (5.2 x

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10^{-5} mol) were added and the reaction stirred for 24 hours at room temperature. The white solid precipitate (DCU) was filtered off and the solvent evaporated under slightly reduced pressure. The pure product was obtained after recrystallization (three times) from ethanol.

{3-[4-(Octyloxyphenyl]-4,5-dihydroisoxazol-5-yl}methyl 4-(decyloxy)benzoate (5a): Yield: 192 mg, 81%; white solid; mp 103 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.89 (m, 6 H, $(CH_3)_2$), 1.38 (m, 24 H, $(CH_2)_{12}$), 1.79 (m, 4 H, $(CH_2CH_2O)_2$), 3.22 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ = 6.9 Hz, 1 H, N=CCHCH), 3.49 (dd, $^2J_{gem}$ = 16.8 Hz, $^3J_{cis}$ = 10.8 Hz, 1 H, N=CCHCH), 3.98 (t, *J* = 6.6 Hz, 4 H, $(CH_2O)_2$), 4.44 (m, 2 H, $CHCH_2OCO$), 5.05 (m, 1 H), 6.85 (d, *J* = 9.0 Hz, 2 H, Ar), 6.91 (d, *J* = 8.7 Hz, 2 H, Ar), 7.61 (d, *J* = 8.7 Hz, 2 H, Ar), 7.95 (d, *J* = 9.0 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 165.1, 162.1, 159.7, 154.8, 130.8, 127.2, 120.6, 120.5, 113.6, 113.0, 77.0, 67.2, 67.1, 64.2, 36.6, 30.9, 30.8, 28.5, 28.4, 28.3, 28.2, 28.1, 28.0, 25.0, 24.9, 21.7, 21.6, 13.1, 13.0 (2 carbon atoms signals are missing); ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1714, 1606, 1515, 1469, 1255, 1172, 1110, 1045, 896, 819, 767, 696, 642.

2-{3-[4-(Octyloxyphenyl]-4,5-dihydroisoxazol-5-yl}ethyl 4-(decyloxy)benzoate (5b): Yield: 69 mg, 30%; white solid; mp 72 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.89 (m, 6 H, $(CH_3)_2$), 1.38 (m, 24 H, $(CH_2)_{12}$), 1.82 (m, 4 H, $(CH_2CH_2O)_2$), 2.10 (m, 1 H, $CHCHCH_2OCO$), 2.23 (m, 1 H, $CHCHCH_2OCO$), 3.08 (dd, $^2J_{gem}$ = 16.2 Hz, $^3J_{trans}$ = 7.5 Hz, 1 H, N=CCHCH), 3.49 (dd, $^2J_{gem}$ = 16.2 Hz, $^3J_{cis}$ = 9.9 Hz, 1 H, N=CCHCH), 4.00 (t, *J* = 6.6 Hz, 2 H, CH_2O), 4.03 (t, *J* = 6.9 Hz, 2 H, CH_2O), 4.50 (m, 2 H, $CHCH_2CH_2OCO$), 4.93 (m, 1 H), 6.92 (d, *J* = 8.7 Hz, 4 H, Ar), 7.61 (d, *J* = 8.7 Hz, 2 H, Ar), 7.98 (d, *J* = 8.4 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 166.5, 162.8, 160.9, 156.4, 131.8, 129.3, 122.1, 122.0, 114.9, 114.4, 80.2, 68.1, 62.5, 40.8, 34.9, 32.4, 32.0, 31.9, 29.8, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 26.0, 22.6, 22.5, 21.8, 14.3 (2 carbon atoms signals are missing); ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1714, 1606, 1515, 1469, 1255, 1172, 1110, 1045, 896, 819, 767, 696, 642.

3-{3-[4-(Octyloxyphenyl]-4,5-dihydroisoxazol-5-yl}propyl 4-(decyloxy)benzoate (5c): Yield: 118 mg, 52%; white solid; mp 85 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.89 (m, 6 H, $(CH_3)_2$), 1.38 (m, 24 H, $(CH_2)_{12}$), 1.79 (m, 4 H, $(CH_2CH_2O)_2$), 1.93 (m, 4 H, $CHCH_2CH_2CH_2OCO$), 2.97 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ = 7.8 Hz, 1 H, N=CCHCH), 3.41 (dd, $^2J_{gem}$ = 16.2 Hz, $^3J_{cis}$ = 10.5 Hz, 1 H, N=CCHCH), 3.97 (t, *J* = 6.6 Hz, 2 H, CH_2O), 4.00 (t, *J* = 6.6 Hz, 2 H, CH_2O), 4.34 (m, 2 H, $CHCH_2CH_2CH_2OCO$), 4.80 (m, 1 H), 6.89 (d, *J* = 9.0 Hz, 4 H, Ar), 7.58 (d, *J* = 8.7 Hz, 2 H, Ar), 7.97 (d, *J* = 9.0 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 166.1, 163.3, 159.5, 155.7, 130.5, 128.0, 121.5, 121.4, 114.5, 114.2, 78.4, 68.2, 68.0, 65.1, 37.6, 31.8, 31.7, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 28.7, 25.4, 25.3, 22.5, 22.4, 14.1 (3 carbon atoms signals are missing); ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1714, 1606, 1515, 1469, 1255, 1172, 1110, 1045, 896, 819, 767, 696, 642.

4-{3-[4-(Octyloxyphenyl]-4,5-dihydroisoxazol-5-yl}butyl 4-(decyloxy)benzoate (5d): Yield: 81 mg, 36%; white solid; mp 68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.89 (m, 6 H, $(CH_3)_2$), 1.38 (m, 24 H, $(CH_2)_{12}$), 1.70 (m, 10 H, $CH(CH_2)_3CH_2OCO$, $(CH_2CH_2O)_2$), 2.87 (dd, $^2J_{gem}$ = 16.2 Hz, $^3J_{trans}$ = 8.1 Hz, 1 H, N=CCHCH), 3.30 (dd, $^2J_{gem}$ = 16.2 Hz, $^3J_{cis}$ = 10.2 Hz, 1 H, N=CCHCH), 3.90 (t, *J* = 6.9 Hz, 2 H, CH_2O), 3.92 (t, *J* = 6.6 Hz, 2 H, CH_2O), 4.23 (t, *J* = 6.3 Hz, 2H, $CH(CH_2)_3CH_2OCO$), 4.64 (m, 1 H), 6.82 (d, *J* = 9.0 Hz, 4 H, Ar), 7.51 (d, *J* = 8.7 Hz, 2 H, Ar), 7.90 (d, *J* = 9.0 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 166.4, 162.9, 160.4, 156.0, 131.5, 128.0, 122.1, 122.0, 114.5, 114.0, 80.8, 68.1, 62.6, 40.3, 35.0, 32.4, 31.8, 31.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 26.0, 25.9, 22.6, 21.8, 14.1 (4 carbon atoms signals are missing); ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1714, 1606, 1515, 1469, 1255, 1172, 1110, 1045, 896, 819, 767, 696, 642.

Synthesis of the series **7a-d**. The alcohol (**3a-d)** (1.1 x 10^{-3} mol) and the 4-bromobenzoic acid (1.1 x 10^{-3} mol) were dissolved in THF (13 mL) and the resultant solution stirred for 15 minutes under an atmosphere inert. Then DCC (1.5 x 10^{-3} mol) and DMAP (1.3 x 10^{-4} mol) were added. The reaction was stirred for 24 hours at room temperature. The white solid precipitate (DCU) was filtered and the solvent evaporated. The pure product was obtained after recrystallization (three times) from ethanol.

{3-[4-(Octyloxyphenyl]-4,5-dihydroisoxazol-5-yl}methyl 4-bromobenzoate (7a): Yield: 262 mg, 49%; white solid; mp 115 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.89 (m, 3 H, CH_3), 1.38 (m, 10 H, $(CH_2)_5$), 1.80 (m, 2 H, C*H*$_2$CH$_2$O), 3.21 (dd, $^2J_{gem}$ = 16.8 Hz, $^3J_{trans}$ = 6.6 Hz, 1 H, N=CC*H*HCH), 3.51 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{cis}$ = 10.8 Hz, 1 H, N=CCH*H*CH), 3.99 (t, *J* = 6.6 Hz, 2 H, CH$_2$O), 4.41 (dd, $^2J_{gem}$ = 11.7 Hz, $^3J_{trans}$ = 5.4 Hz, 1 H, CHC*H*HOCO), 4.50 (dd, $^2J_{gem}$ =11.7 Hz, $^3J_{cis}$ = 4.2 Hz, 1 H, CHCH*H*OCO), 5.10 (m, 1 H), 6.91 (d, *J* = 9.0 Hz, 2 H, Ar), 7.52 (d, *J* = 8.4 Hz, 2 H, Ar), 7.60 (d, *J* = 9.0 Hz, 2 H, Ar), 7.86 (d, *J* = 8.7 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 14.0, 22.5, 25.9, 29.0, 29.1, 29.2, 31.7, 37.5, 65.8, 68.0, 77.5, 114.5, 114.6, 121.2, 128.0, 128.1, 128.2, 128.3, 131.1, 131.2, 131.7, 131.8, 155.7, 160.7, 165.5; ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1720, 1606, 1591, 1515, 1438, 1388, 1255, 1172, 1110, 1068, 1045, 1012, 921, 896, 819, 755, 684, 642.

2-{3-[4-(Octyloxyphenyl]-4,5-dihydroisoxazol-5-yl}ethyl 4-bromobenzoate (7b): Yield: 308 mg, 56%; white solid; mp 89 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 0.90 (m, 3 H, CH_3), 1.38 (m, 10 H, $(CH_2)_5$), 1.81 (m, 2 H, C*H*$_2$CH$_2$O), 2.17 (m, 2 H, CHC*H*$_2$CH$_2$OCO), 3.07 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ = 7.5 Hz, 1 H, N=CC*H*HCH), 3.50 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{cis}$ = 10.2 Hz, 1 H, N=CCH*H*CH), 4.00 (t, *J* = 6.6 Hz, 2 H, CH$_2$O), 4.54 (m, 2 H, CHCH$_2$C*H*$_2$OCO), 4.92 (m, 1 H), 6.92 (d, *J* = 9.0 Hz, 2 H, Ar), 7.58 (d, *J* = 8.7 Hz, 2 H, Ar), 7.61 (d, *J* = 9.0 Hz, 2 H, Ar), 7.91 (d, *J* = 8.4 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 14.0, 22.5, 25.9, 29.0, 29.1, 29.2, 31.7, 34.3, 40.4, 61.7, 68.0, 77.5, 114.5, 114.6, 121.2, 128.0, 128.1, 128.2, 128.3, 131.1, 131.2, 131.7, 131.8, 155.9, 160.5, 165.5; ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1720, 1606, 1591, 1515, 1438, 1388, 1255, 1172, 1110, 1068, 1045, 1012, 921, 896, 819, 755, 684, 642.

3-{3-[4-(Octyloxyphenyl]-4,5-dihydroisoxazol-5-yl}propyl 4-bromobenzoate (7c): Yield: 323 mg, 57%; white solid; mp 98 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 0.89 (m, 3 H, CH_3), 1.38 (m, 10 H, $(CH_2)_5$), 1.80 (m, 2 H, C*H*$_2$CH$_2$O), 1.96 (m, 4 H, CHC*H*$_2$C*H*$_2$CH$_2$OCO), 2.97 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ = 7.8 Hz, 1 H, N=CC*H*HCH), 3.43 (dd, $^2J_{gem}$ = 16.2 Hz, $^3J_{cis}$ = 10.2 Hz, 1 H, N=CCH*H*CH), 3.98 (t, *J* = 6.6 Hz, 2 H, CH$_2$O), 4.39 (m, 2 H, CHCH$_2$CH$_2$C*H*$_2$OCO), 4.77 (m, 1 H), 6.90 (d, *J* = 9.0 Hz, 2 H, Ar), 7.56 (d, *J* = 8.4 Hz, 2 H, Ar), 7.59 (d, *J* = 9.0 Hz, 2 H, Ar), 7.90 (d, *J* = 8.7 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 13.9, 22.0, 25.8, 28.3, 28.9, 29.0, 29.1, 31.6, 34.7, 40.1, 64.8, 67.9, 80.5, 114.5, 114.6, 121.2, 128.0, 128.1, 128.2, 128.3, 131.1, 131.2, 131.7, 131.8, 155.8, 160.3, 165.5; ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1720, 1606, 1591, 1515, 1438, 1388, 1255, 1172, 1110, 1068, 1045, 1012, 921, 896, 819, 755, 684, 642.

4-{3-[4-(Octyloxyphenyl]-4,5-dihydroisoxazol-5-yl}butyl 4-bromobenzoate (7d): Yield: 286 mg, 44%; white solid; mp 73 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 0.89 (m, 3 H, CH_3), 1.38 (m, 10 H, $(CH_2)_5$), 1.80 (m, 2 H, C*H*$_2$CH$_2$O), 1.96 (m, 6 H, CHC*H*$_2$C*H*$_2$C*H*$_2$CH$_2$OCO), 2.97 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ = 7.8 Hz, 1 H, N=CC*H*HCH), 3.43 (dd, $^2J_{gem}$ = 16.2 Hz, $^3J_{cis}$ = 10.2 Hz, 1 H, N=CCH*H*CH), 3.98 (t, *J* = 6.6 Hz, 2 H, CH$_2$O), 4.39 (m, 2 H, CHCH$_2$CH$_2$C*H*$_2$OCO), 4.77 (m, 1 H), 6.90 (d, *J* = 9.0 Hz, 2 H, Ar), 7.56 (d, *J* = 8.4 Hz, 2 H, Ar), 7.59 (d, *J* = 9.0 Hz, 2 H, Ar), 7.90 (d, *J* = 8.7 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 13.9, 22.0, 22.4, 25.8, 28.3, 28.9, 29.0, 29.1, 31.6, 34.7, 40.1, 64.8, 67.9, 80.5, 114.5, 114.6, 121.2, 128.0, 128.1, 128.2, 128.3, 131.1, 131.2, 131.7,

131.8, 155.8, 160.3, 165.5; ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1720, 1606, 1591, 1515, 1438, 1388, 1255, 1172, 1110, 1068, 1045, 1012, 921, 896, 819, 755, 684, 642.

Synthesis of the series **9a-d**. *Sonogashira's coupling:* the ester **7a-d** (0.4 x 10^{-3} mol), 2-ethynyl-6-octyloxynaphthalene (**8**) (0.5 x 10^{-3} mol) and Et_3N (0.6 mL) were mixed in an one-neck round-bottom flask equipped with septum under argon atmosphere. The resultant reaction mixture was stirred for 20 minutes and then CuI (0.8 x 10^{-5} mol), PPh_3 (2.5 x 10^{-5} mol) and [$PdCl_2(PPh_3)_2$] (0.5 x 10^{-5} mol) were added and the resultant reaction mixture heated under reflux for 24 hours and then allowed to cool to room temperature and filtered through Celite®. The filtrate was washed with water (4 x 20 mL), dried over Na_2SO_4, filtered and then concentrated under slightly reduced pressure. The pure product was obtained after recrystallization (twice) from ethanol.

{3-[4-(Octyloxyphenyl]-4,5-dihydroisoxazol-5-yl}methyl 4-[(6-octyloxynaphthalen-2-yl)ethynyl]benzoate (9a): Yield: 230 mg, 66%; white solid; mp 150 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.82 (m, 6 H, $(CH_3)_2$), 1.22 (m, 20 H, $(CH_2)_{10}$), 1.74 (m, 4 H, $(CH_2CH_2O)_2$), 3.24 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ 7.2 Hz, 1 H, N=CC*H*HCH), 3.52 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{cis}$ = 10.8 Hz, 1H, N=CCH*H*CH), 3.99 (t, *J* = 6.6 Hz, 2H, CH_2O), 4.08 (t, *J* = 6.6 Hz, 2 H, CH_2O), 4.48 (m, 2 H, CHCH_2OCO), 5.09 (m, 1 H), 6.84 (d, *J* = 8.4 Hz, 2 H, Ar), 6.98-7.15 (m, 2 H, Ar), 7.38-7.74 (m, 8 H, Ar), 7.92 (d, *J* = 6.6 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 14.1, 22.6, 22.7, 26.0, 26.1, 29.0, 29.1, 29.2, 29.3, 29.4, 29.5, 31.8, 31.9, 37.6, 65.8, 68.1, 68.2, 77.9, 88.3, 93.4, 106.5, 114.7, 117.3, 119.9, 121.4, 126.9, 128.2, 128.3, 128.5, 128.6, 128.8, 129.3, 129.7, 131.4, 131.7, 134.5, 155.9, 158.1, 160.8, 165.8 (1 carbon atom signal are missing); ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1714, 1606, 1594, 1515, 1469, 1388, 1255, 1213, 1172, 1110, 1045, 943, 896, 858, 819, 767, 696, 642. Elem. anal. calcd for $C_{45}H_{53}NO_5$ (687.91): C 78.37, H 7.77, N 2.04; found C 77.49, H 7.93, N 2.15 $C_{30}H_{33}BrN_2O_2$: C, 67.54; H, 6,23; N, 5.25; found: C, 66.98; H, 5.14; N, 5.28. Repeated elemental analyses on a freshly recrystallized sample did not improve the agreement of the carbon found value with the calculated value.

2-{3-[4-(Octyloxyphenyl]-4,5-dihydroisoxazol-5-yl}ethyl 4-[(6-octyloxynaphthalen-2-yl)ethynyl]benzoate (9b): Yield: 222 mg, 65%; white solid; mp 130 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.90 (m, 6 H, $(CH_3)_2$), 1.24 (m, 20 H, $(CH_2)_{10}$), 1.80 (m, 4 H, $(CH_2CH_2O)_2$), 2.20 (m, 2 H, CHCH_2CH$_2$OCO), 3.07 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ 7.2 Hz, 1 H, N=CC*H*HCH), 3.48 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{cis}$ = 10.8 Hz, 1H, N=CCH*H*CH), 3.98 (t, *J* = 6.6 Hz, 2H, CH_2O), 4.08 (t, *J* = 6.6 Hz, 2 H, CH_2O), 4.53 (m, 2 H, CHCH_2OCO), 4.93 (m, 1 H), 6.90 (d, *J* = 9.0 Hz, 2 H, Ar), 7.07-7.21 (m, 2 H, Ar), 7.47-7.76 (m, 8 H, Ar), 8.01 (d, *J* = 8.4 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 14.1, 22.6, 26.0, 26.1, 29.0, 29.1, 29.2, 29.3, 29.4, 29.5, 31.7, 31.8, 34.4, 40.5, 61.7, 68.0, 77.7, 88.3, 93.3, 106.5, 114.5, 117.2, 119.8, 121.7, 126.8, 128.1, 128.2, 128.3, 128.7, 129.1, 129.3, 129.5, 131.4, 131.6, 134.4, 156.0, 158.0, 160.6, 165.8 (3 carbon atoms signals are missing); ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1714, 1606, 1594, 1515, 1469, 1388, 1255, 1213, 1172, 1110, 1045, 943, 896, 858, 819, 767, 696, 642. Elem. anal. calcd for $C_{46}H_{55}NO_5$ (701.93): C 78.71, H 7.90, N 2.00; found C 79.67, H 8.18, N 2.19. Repeated elemental analyses on a freshly recrystallized sample did not improve the agreement of the carbon found value with the calculated value.

3-{3-[4-(Octyloxyphenyl]-4,5-dihydroisoxazol-5-yl}propyl 4-[(6-octyloxynaphthalen-2-yl)ethynyl]benzoate (9c): Yield: 164 mg, 48%; white solid; mp 136 °C; ^{1}H NMR (300 MHz,

$CDCl_3$): δ (ppm) 0.88 (m, 6 H, $(CH_3)_2$), 1.30 (m, 20 H, $(CH_2)_{10}$), 1.70-2.08 (m, 8 H, $(CH_2CH_2O)_2$, $CHCH_2CH_2CH_2OCO$), 2.97 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ 7.2 Hz, 1 H, N=CCHHCH), 3.41 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{cis}$ = 10.8 Hz, 1H, N=CCHHCH), 3.97 (t, *J* = 6.6 Hz, 2H, CH_2O), 4.08 (t, *J* = 6.6 Hz, 2 H, CH_2O), 4.39 (m, 2 H, $CHCH_2OCO$), 4.78 (m, 1 H), 6.90 (d, *J* = 9.0 Hz, 2 H, Ar), 7.07-7.21 (m, 2 H, Ar), 7.47-7.76 (m, 8 H, Ar), 8.01 (d, *J* = 8.4 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 14.1, 22.6, 24.9, 25.9-26.0 (broad peak), 29.2-29.3 (broad peak), 31.7, 31.9, 40.3, 64.6, 68.0, 80.3, 88.3, 93.2, 106.5, 114.5, 117.2, 119.8, 121.8, 126.8, 128.0, 128.2, 128.7, 129.3, 129.5, 131.4, 131.6, 134.4, 156.0, 158.0, 160.5, 166.0 (10 carbon atoms signals are missing); ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1714, 1606, 1594, 1515, 1469, 1388, 1255, 1213, 1172, 1110, 1045, 943, 896, 858, 819, 767, 696, 642. Elem. anal. calcd for $C_{47}H_{57}NO_5$ (715.96): C 78.85, H 8.02, N 1.96; found C 79.11, H 8.44, N 2.09

4-{3-[4-(Octyloxyphenyl]-4,5-dihydroisoxazol-5-yl}butyl 4-[(6-octyloxynaphthalen-2-yl)ethynyl]benzoate (9d): Yield: 237 mg, 92%; white solid; mp 130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.90 (m, 6 H, $(CH_3)_2$), 1.28 (m, 20 H, $(CH_2)_{10}$), 1.62-1.92 (m, 10 H, $(CH_2CH_2O)_2$, $CHCH_2CH_2CH_2CH_2OCO$), 2.95 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ 7.2 Hz, 1 H, N=CCHHCH), 3.99 (dd, $^2J_{gem}$ = 16.5 Hz, $^3J_{cis}$ = 10.8 Hz, 1H, N=CCHHCH), 3.97 (t, *J* = 6.6 Hz, 2H, CH_2O), 4.08 (t, *J* = 6.6 Hz, 2 H, CH_2O), 4.36 (m, 2 H, $CHCH_2OCO$), 4.73 (m, 1 H), 6.90 (d, *J* = 9.0 Hz, 2 H, Ar), 7.07-7.21 (m, 2 H, Ar), 7.47-7.76 (m, 8 H, Ar), 8.01 (d, *J* = 8.4 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 14.1, 22.3, 22.6, 22.7, 26.0, 26.1, 28.6, 29.0, 29.1, 29.2, 29.3, 29.4, 29.5, 31.8, 31.9, 35.0, 40.3, 64.9, 68.1, 80.7, 88.4, 93.2, 106.5, 114.6, 117.3, 119.9, 122.0, 126.9, 128.1, 128.2, 128.3, 128.8, 129.3, 129.4, 129.5, 131.4, 131.6, 134.4, 156.0, 158.1, 160.5, 166.1 (2 carbon atoms signals are missing); ATR: ν (cm^{-1}) 2954, 2919, 2871, 2854, 1714, 1606, 1594, 1515, 1469, 1388, 1255, 1213, 1172, 1110, 1045, 943, 896, 858, 819, 767, 696, 642. Elem. anal. calcd for $C_{48}H_{59}NO_5$ (729.99): C 78.98, H 8.15, N 1.92; found C 78.97, H 8.39, N 2.05.

The absorption emission behavior of solutions of **9a-d** in dichloromethane was analyzed by UV-vis measurements. These materials exhibited absorption band at 328 nm assigned to π–π* transitions of the napthylethynylphenyl moiety. Absorption spectra are showed in the support information section (S30a and S30b). Also, an overlay of ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compounds **9a-d** between 6.0 – 2.0 ppm is presented in the support information section (S20). Attempts to correlate the length and parity of the flexible spacer with λ_{max} and chemical shift for compounds **9a-d** failed. The variation in the carbon atoms of the flexible spacer did not produce the alternation on the λ_{max} or in the chemical shift of the peaks in the ^{1}H NMR spectrum of compounds **9a-d**.

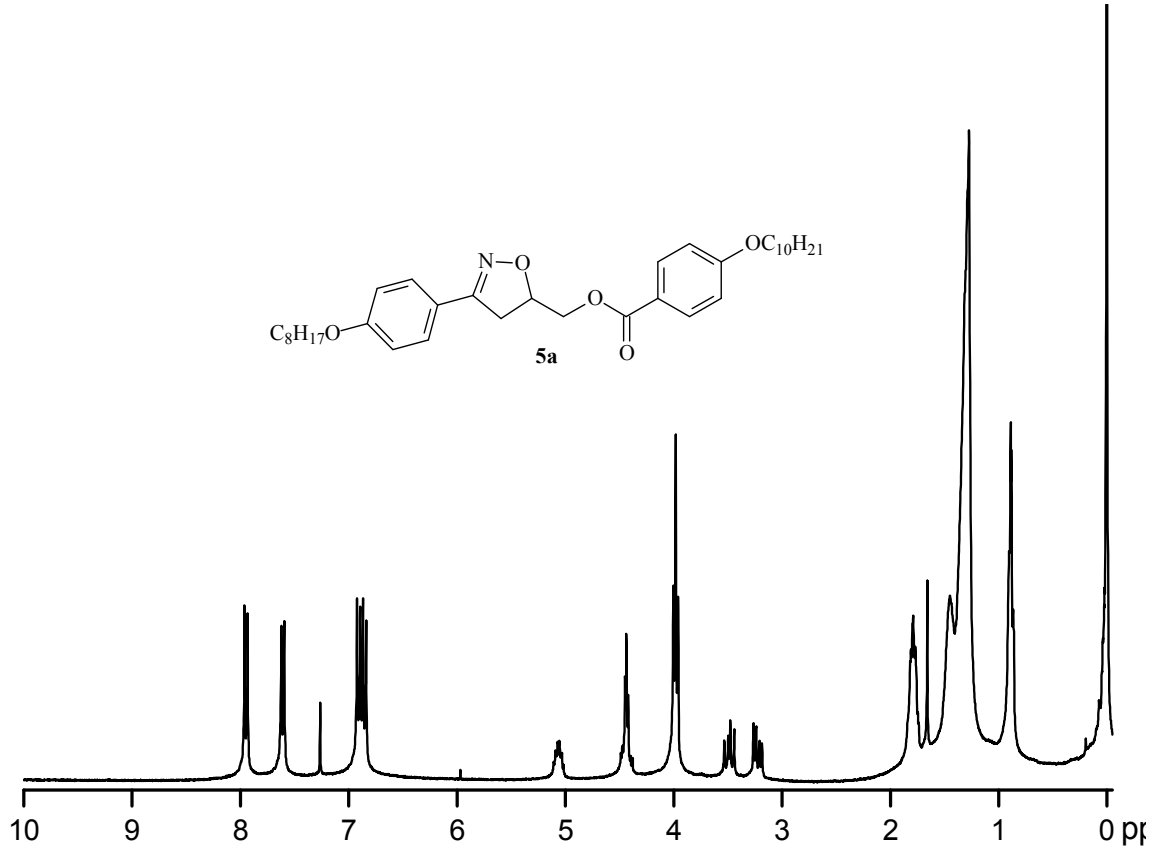


Figure S1. ^{1}H NMR spectrum of compound **5a** ($CDCl_3$, 300 MHz).

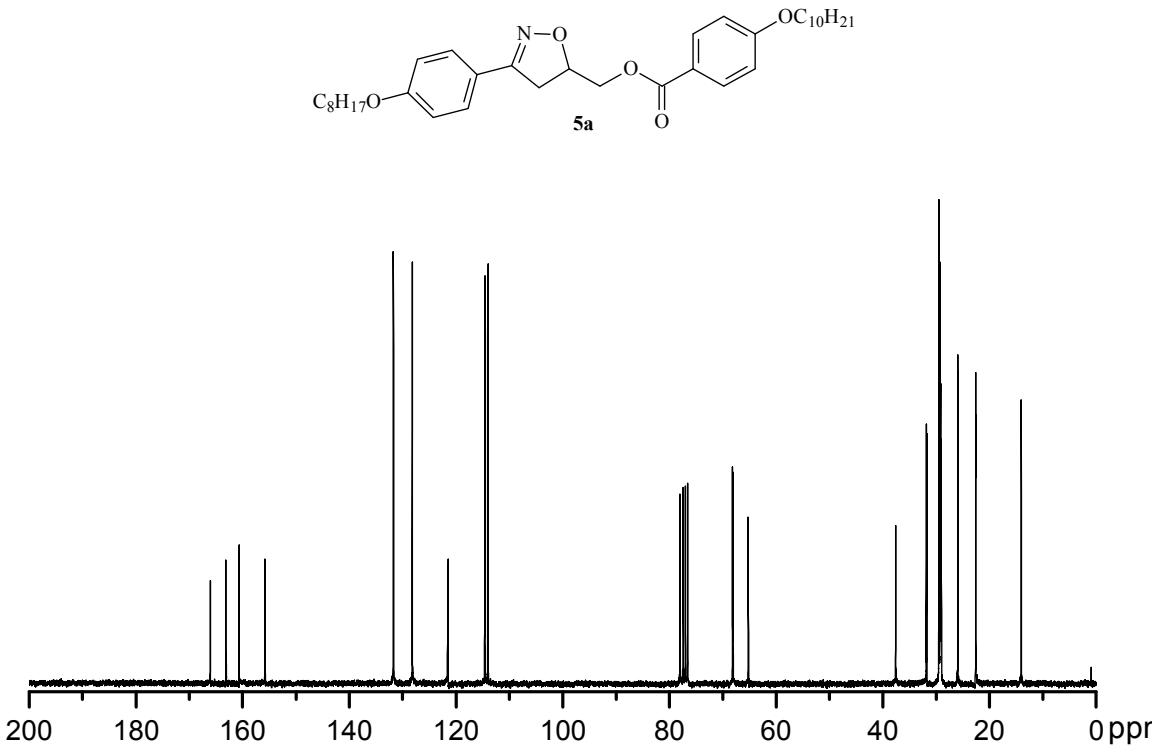


Figure S2. ^{13}C NMR spectrum of compound **5a** ($CDCl_3$, 75 MHz).

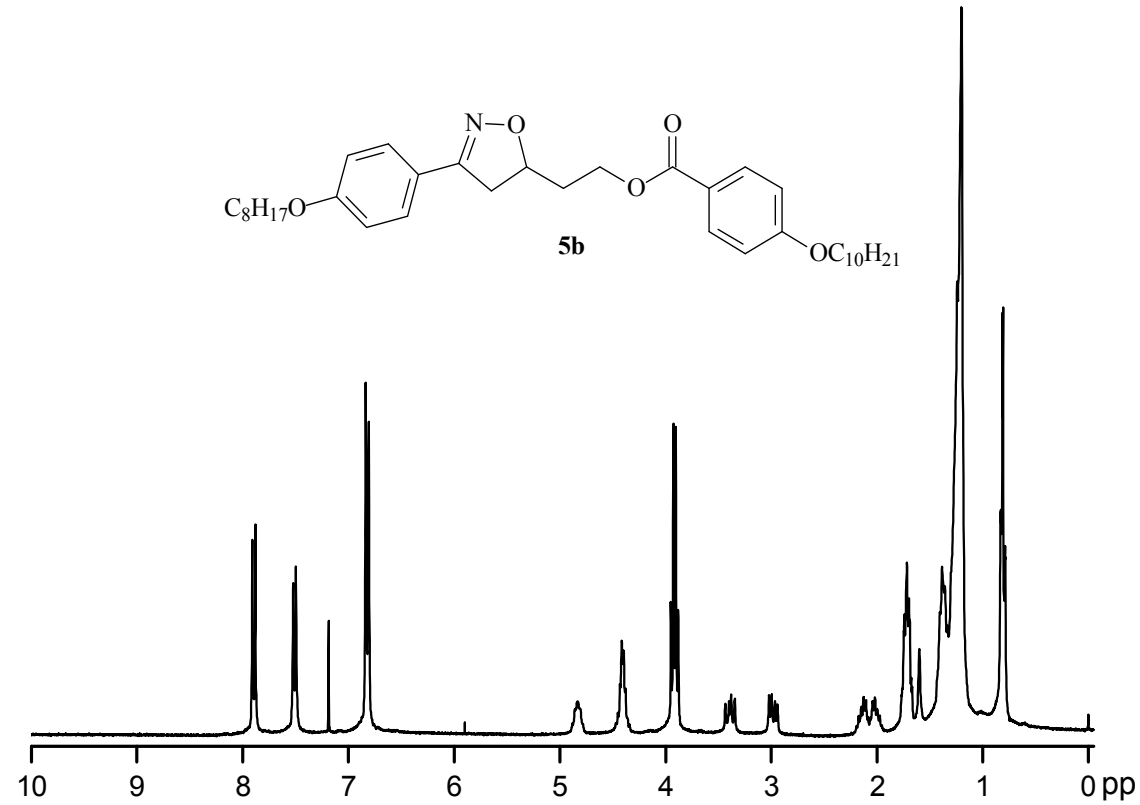


Figure S3. ^{1}H NMR spectrum of compound **5b** ($CDCl_3$, 300 MHz).

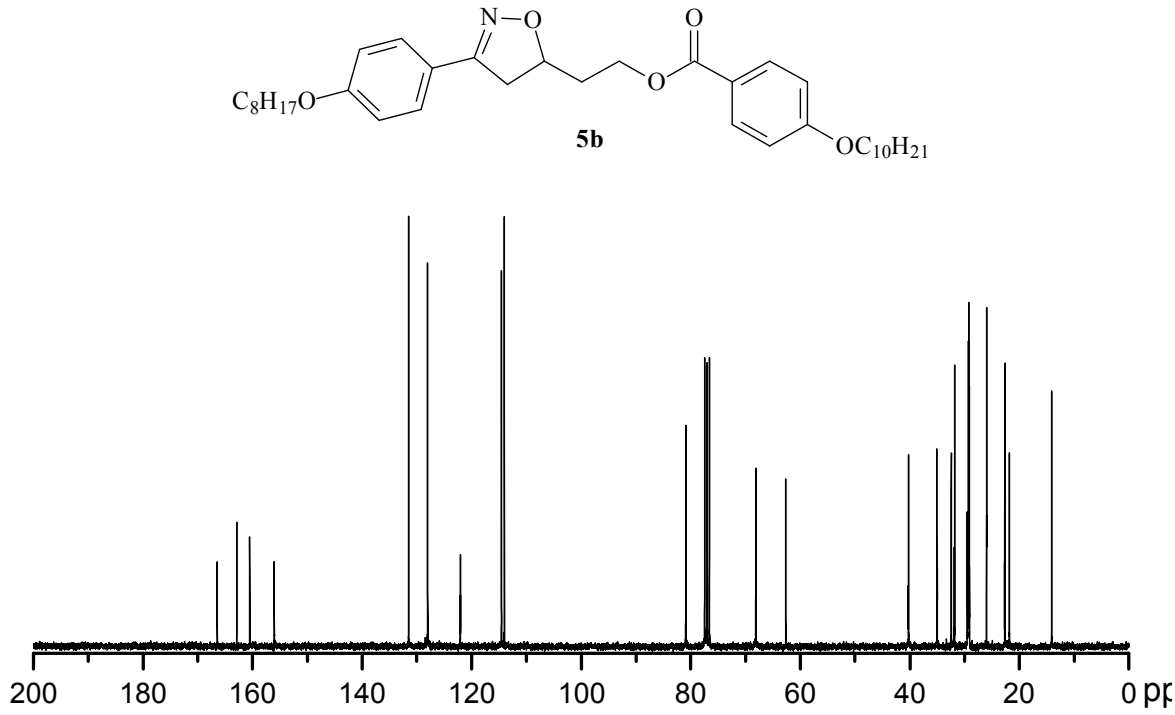


Figure S4. ^{13}C NMR spectrum of compound **5b** ($CDCl_3$, 75 MHz).

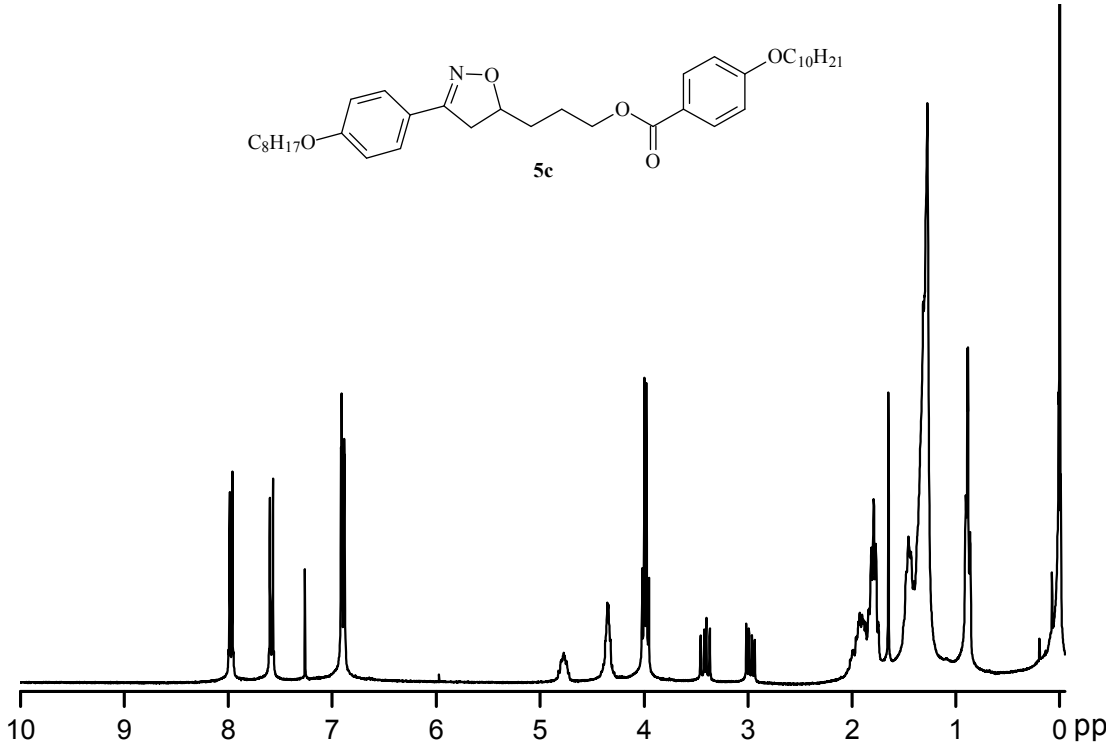


Figure S5. ^{1}H NMR spectrum of compound **5c** ($CDCl_3$, 300 MHz).

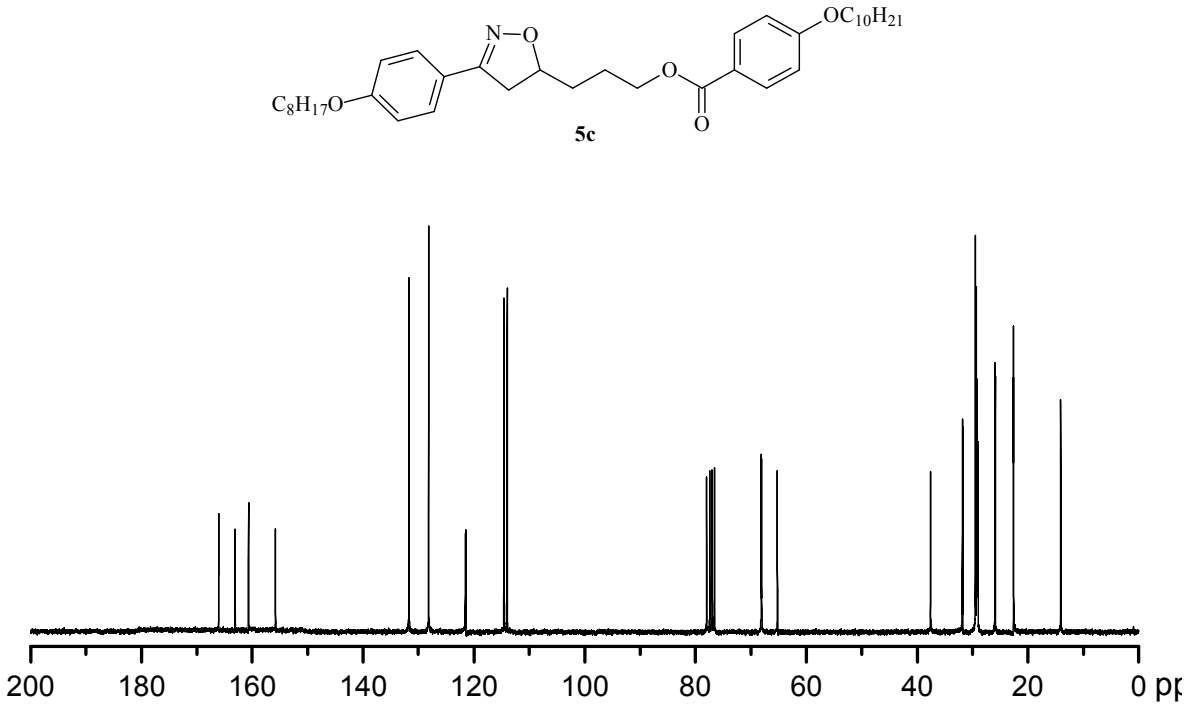


Figure S6. ^{13}C NMR spectrum of compound **5c** ($CDCl_3$, 75 MHz).

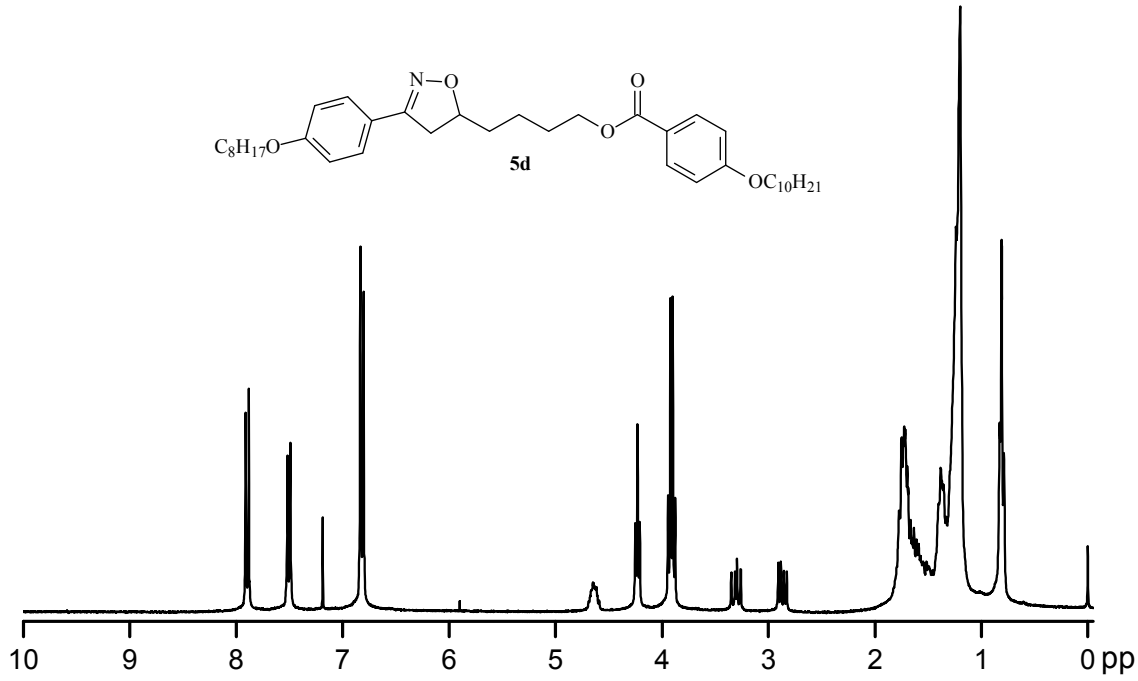


Figure S7. ^{1}H NMR spectrum of compound **5d** ($CDCl_3$, 300 MHz).

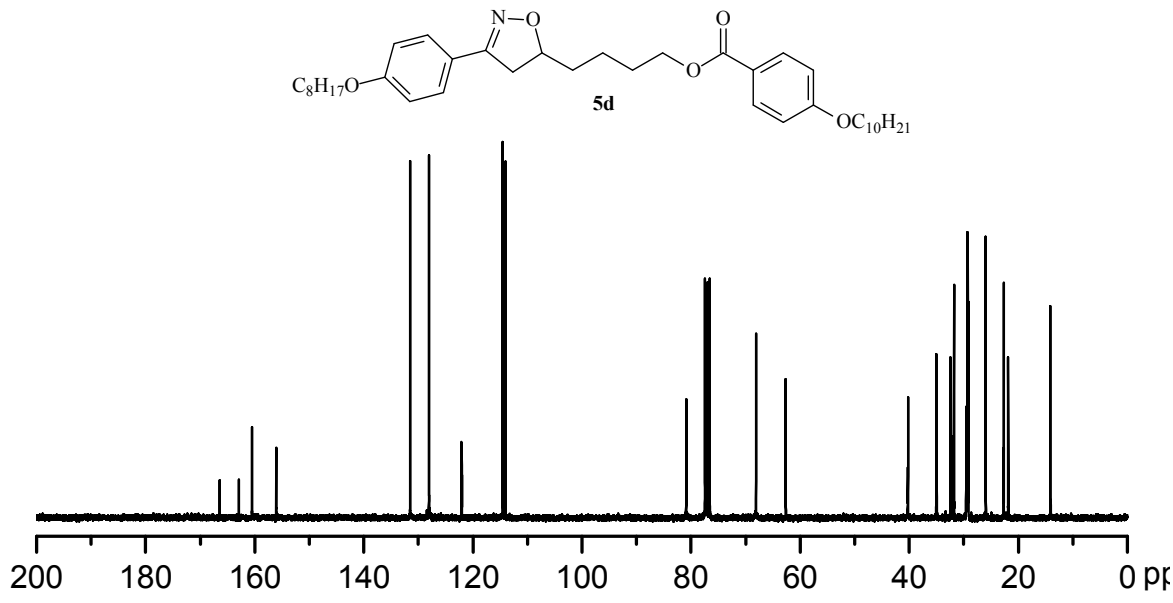


Figure S8. ^{13}C NMR spectrum of compound **5d** ($CDCl_3$, 75 MHz).

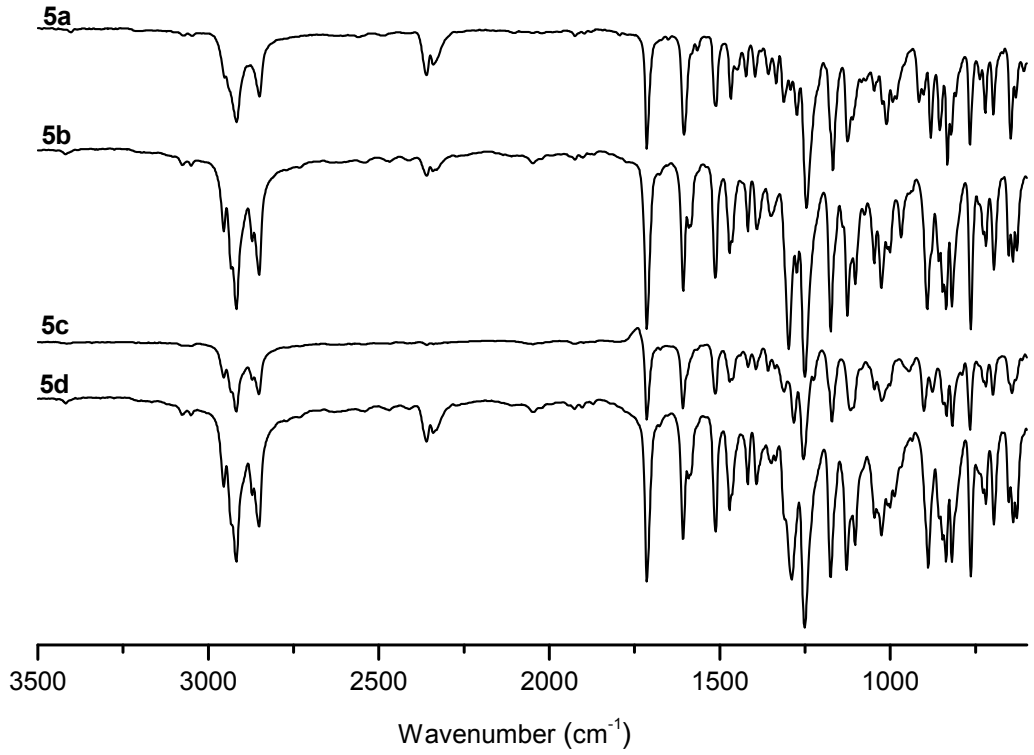


Figure S9. Overlay of FT-IR spectrum of compounds **5a-d**.

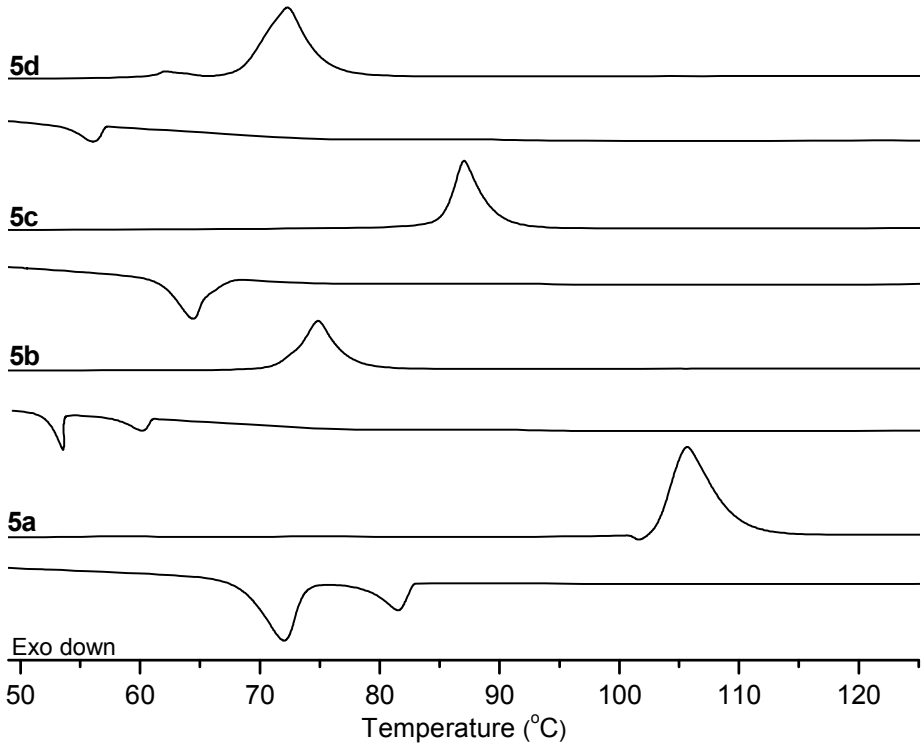


Figure S10. DSC thermograms of compounds **5a-d** on 2nd cycle at 10 ºC min-1.

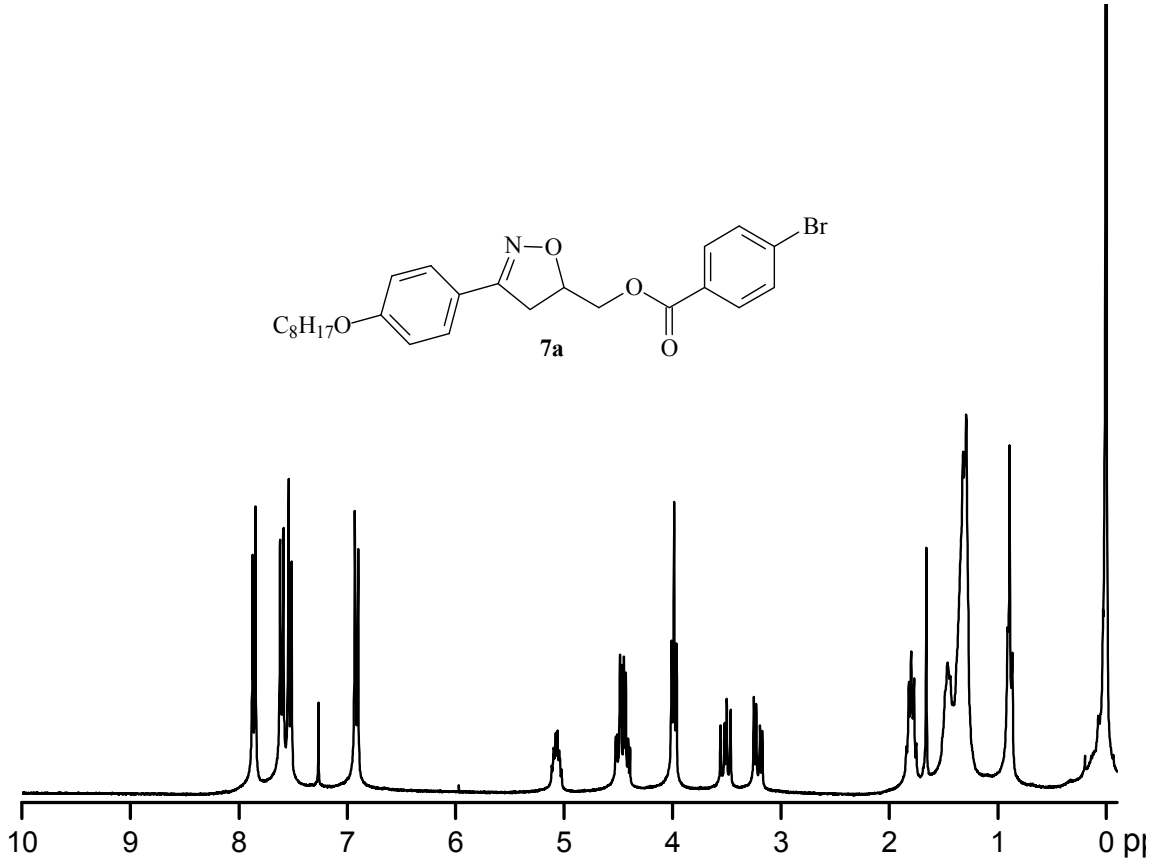


Figure S11. ^{1}H NMR spectrum of compound **7a** ($CDCl_3$, 300 MHz).

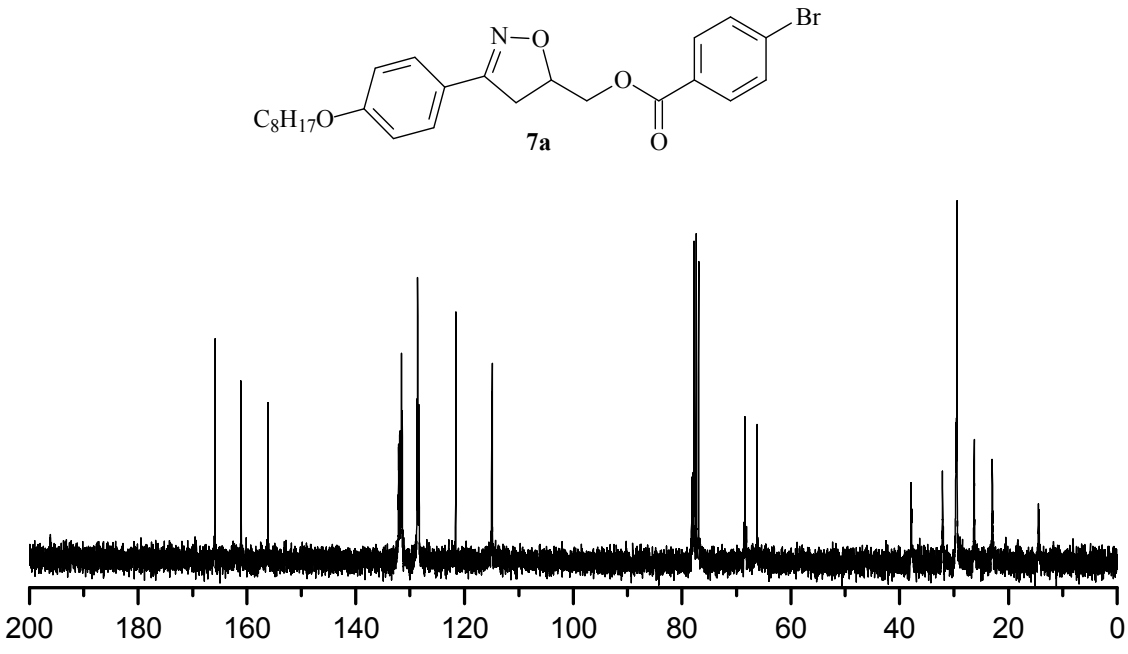


Figure S12. ^{13}C NMR spectrum of compound **7a** ($CDCl_3$, 75 MHz).

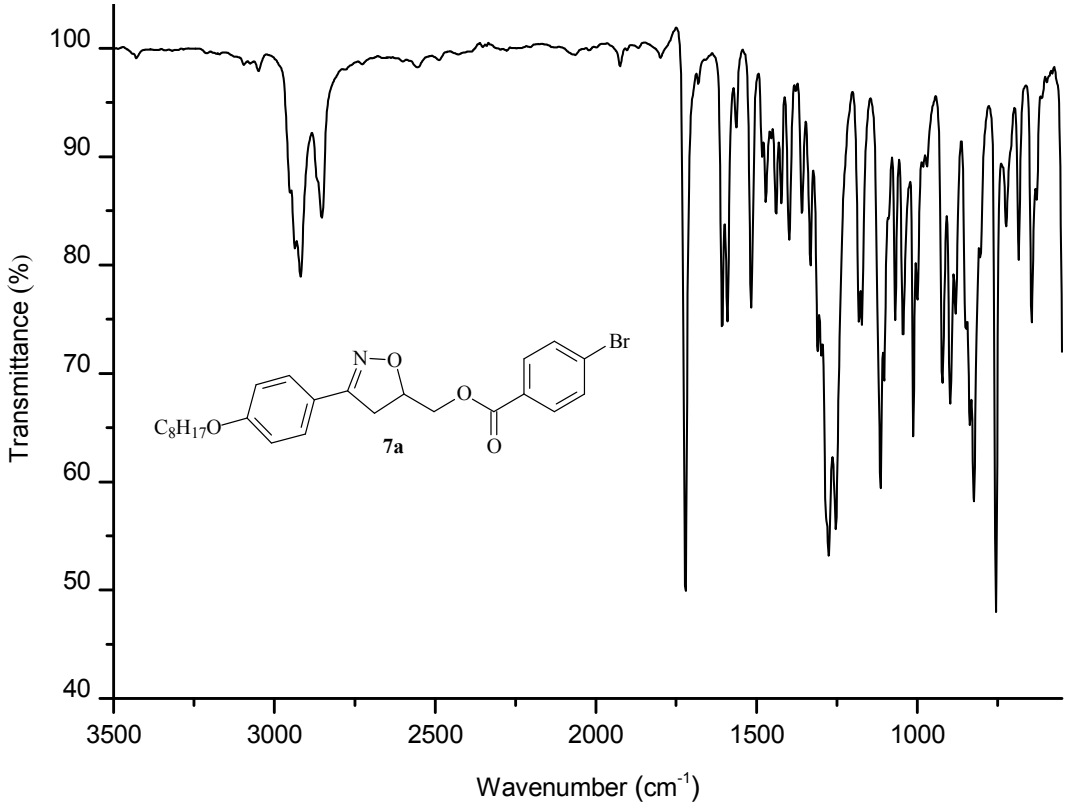


Figure S13. FT-IR spectrum of compound **7a**.

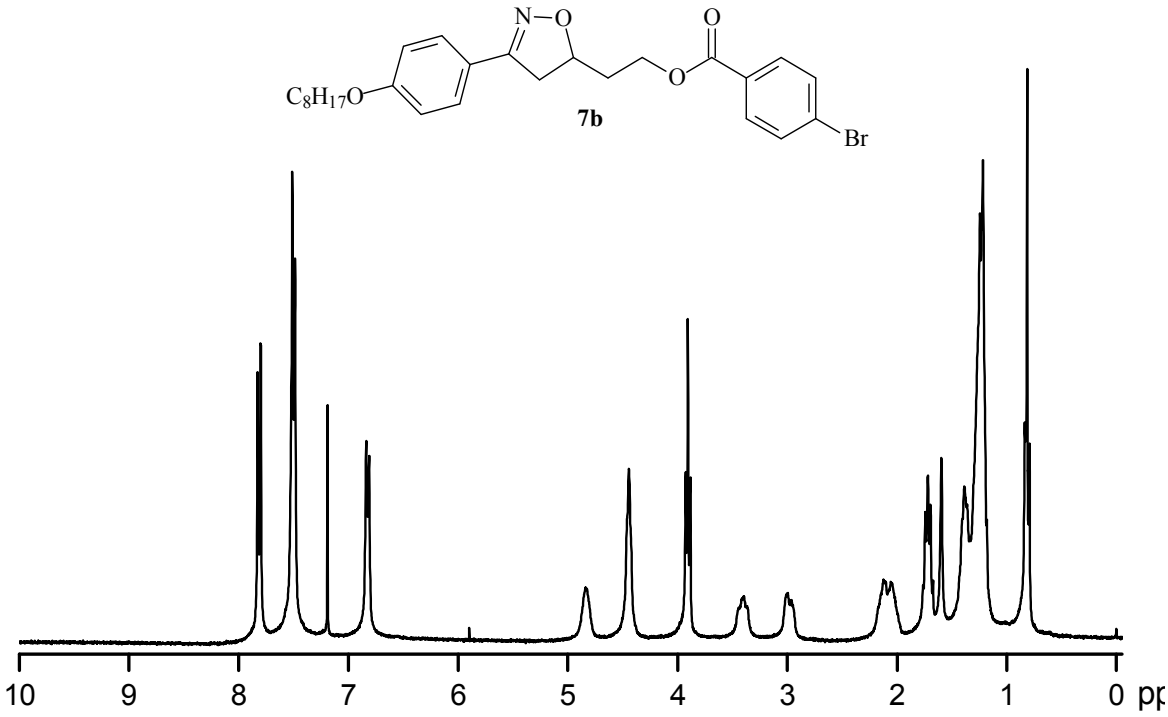


Figure S14. ^{1}H NMR spectrum of compound **7b** ($CDCl_3$, 300 MHz).

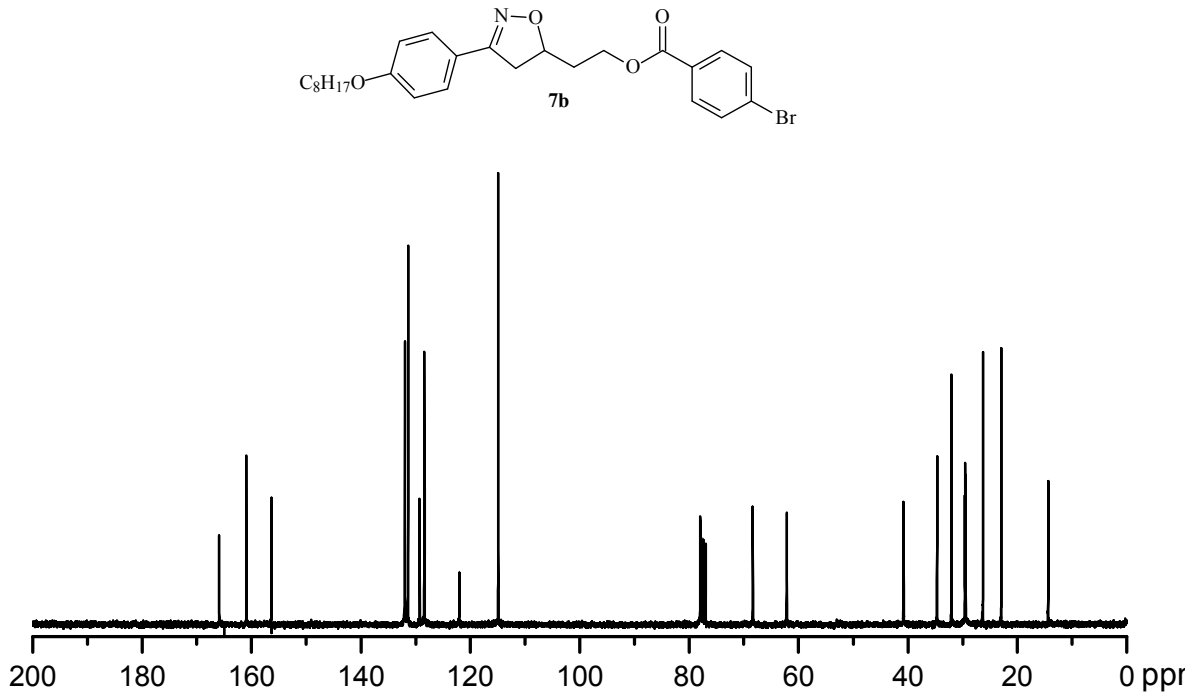


Figure S15. ^{13}C NMR spectrum of compound **7b** ($CDCl_3$, 75 MHz).

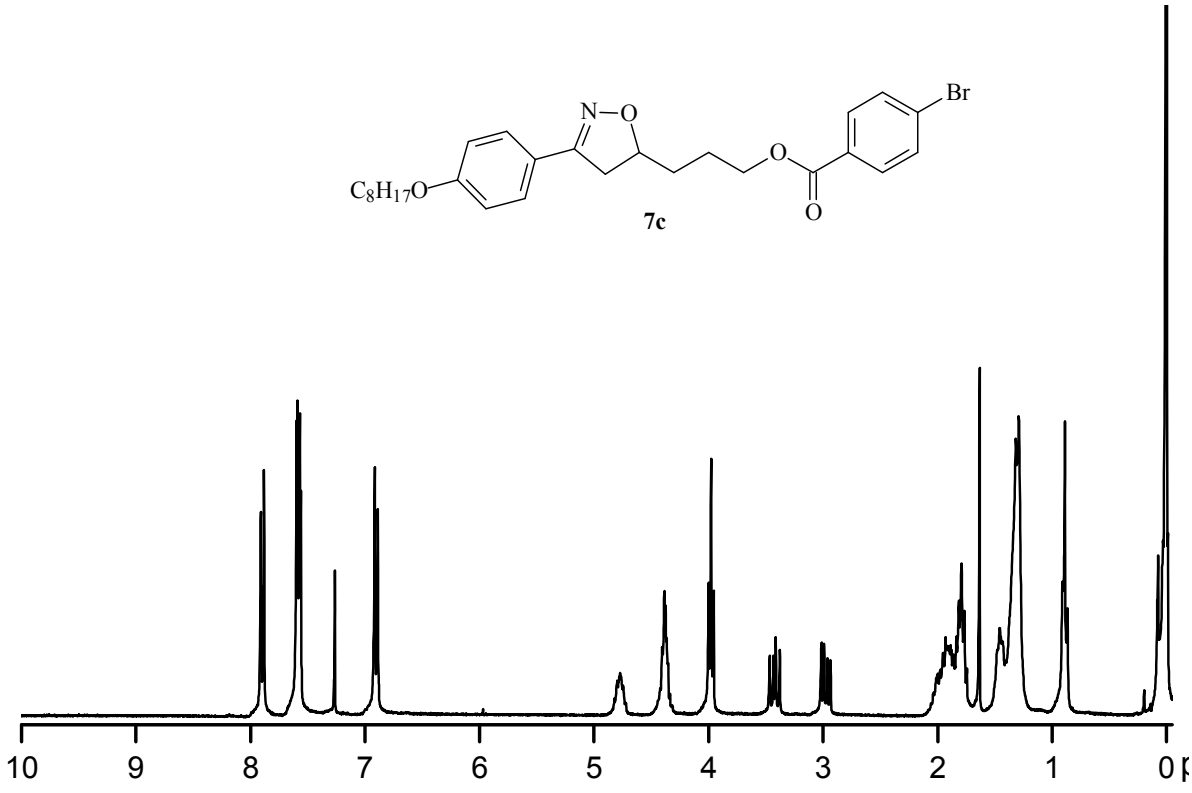


Figure S16. ^{1}H NMR spectrum of compound **7c** ($CDCl_3$, 300 MHz).

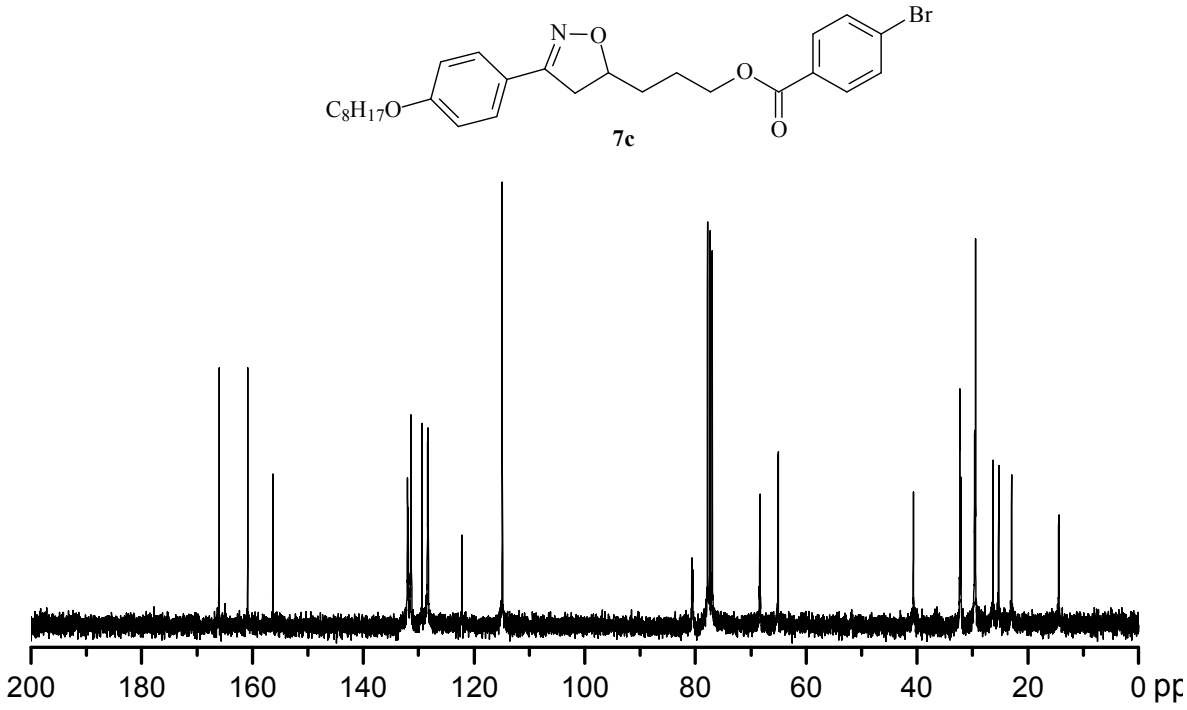


Figure S17. ^{13}C NMR spectrum of compound **7c** ($CDCl_3$, 75 MHz).

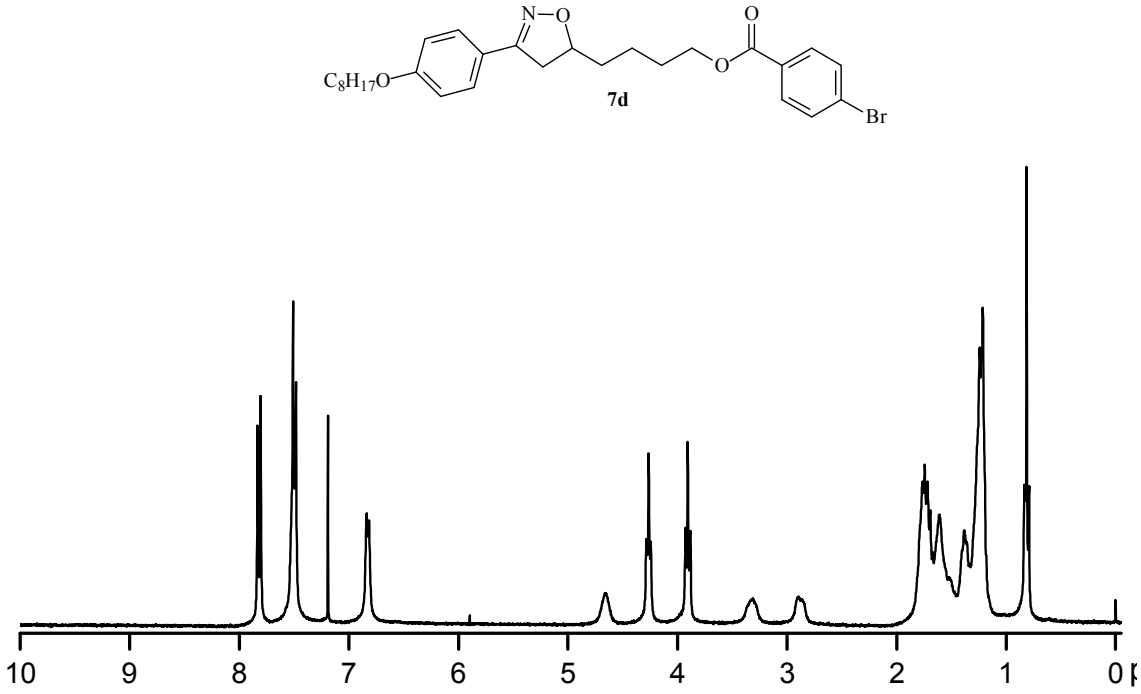


Figure S18. ^{1}H NMR spectrum of compound **7d** ($CDCl_3$, 300 MHz).

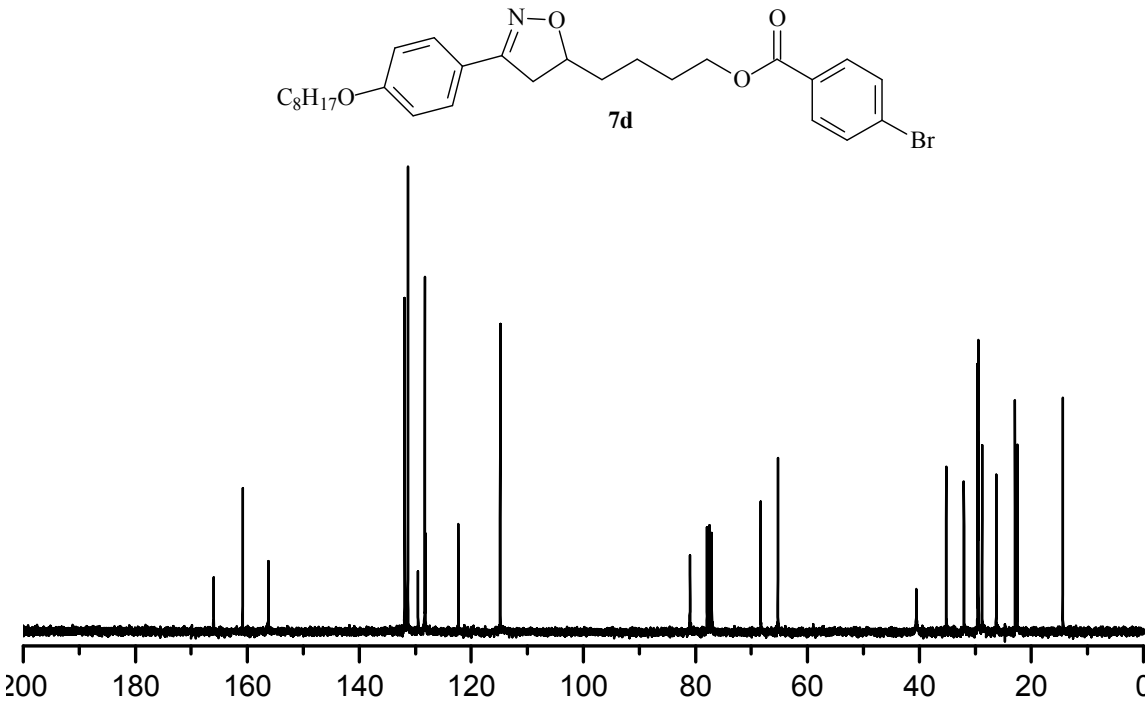


Figure S19. ^{13}C NMR spectrum of compound **7d** ($CDCl_3$, 75 MHz).

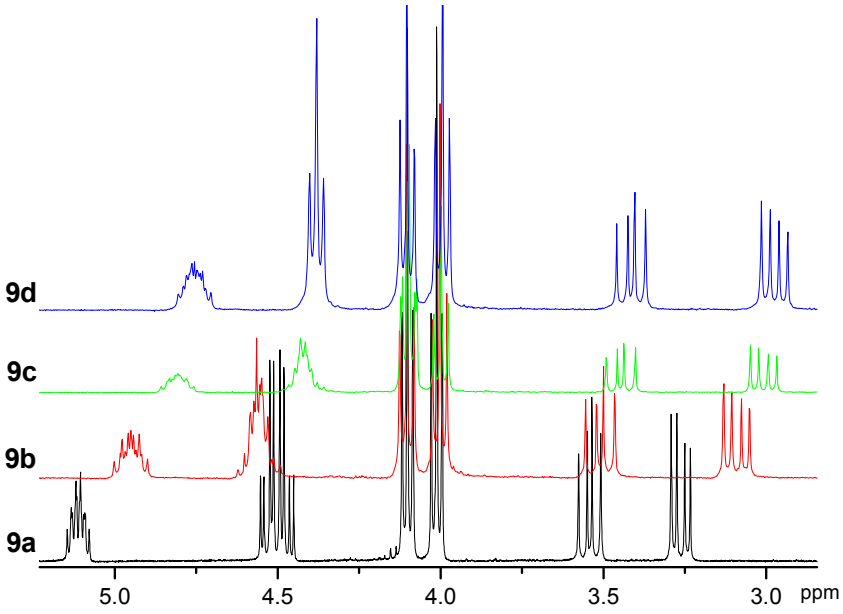


Figure S20. Overlay of ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compounds **9a-d** in the range of 6.0 – 2.0 ppm.

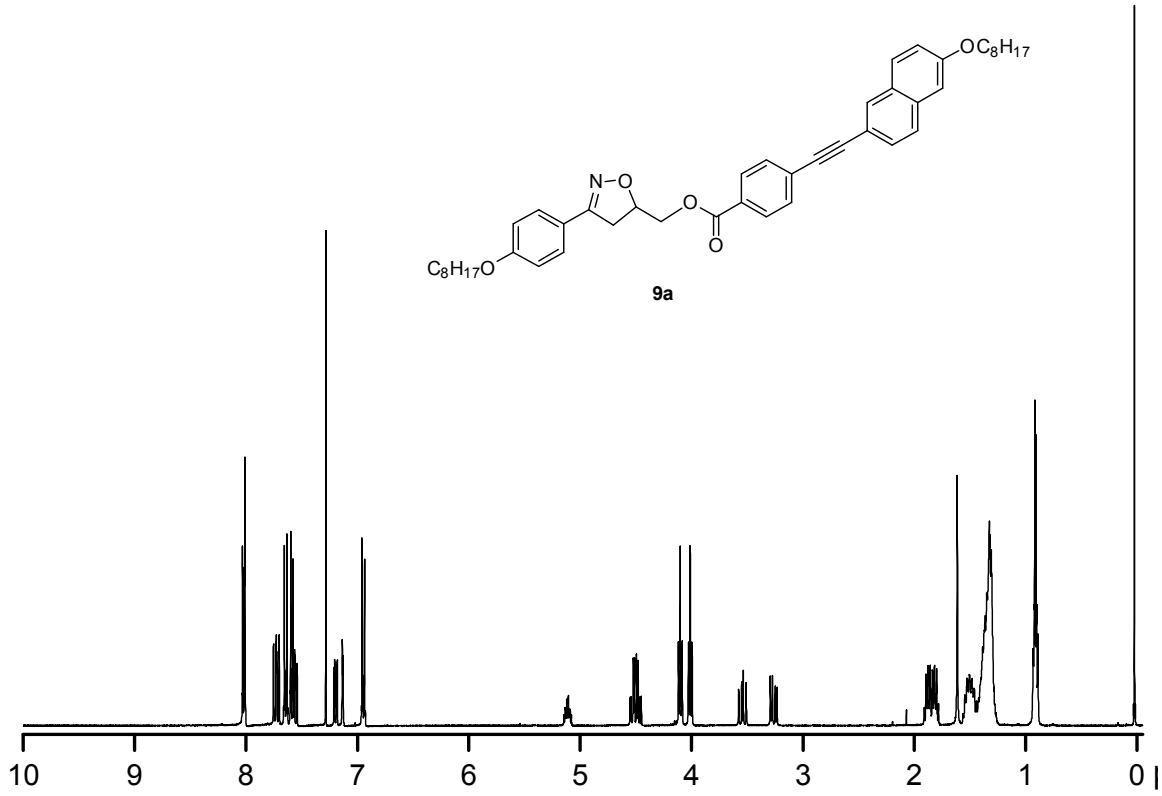


Figure S21. ^{1}H NMR spectrum of compound **9a** ($CDCl_3$, 300 MHz).

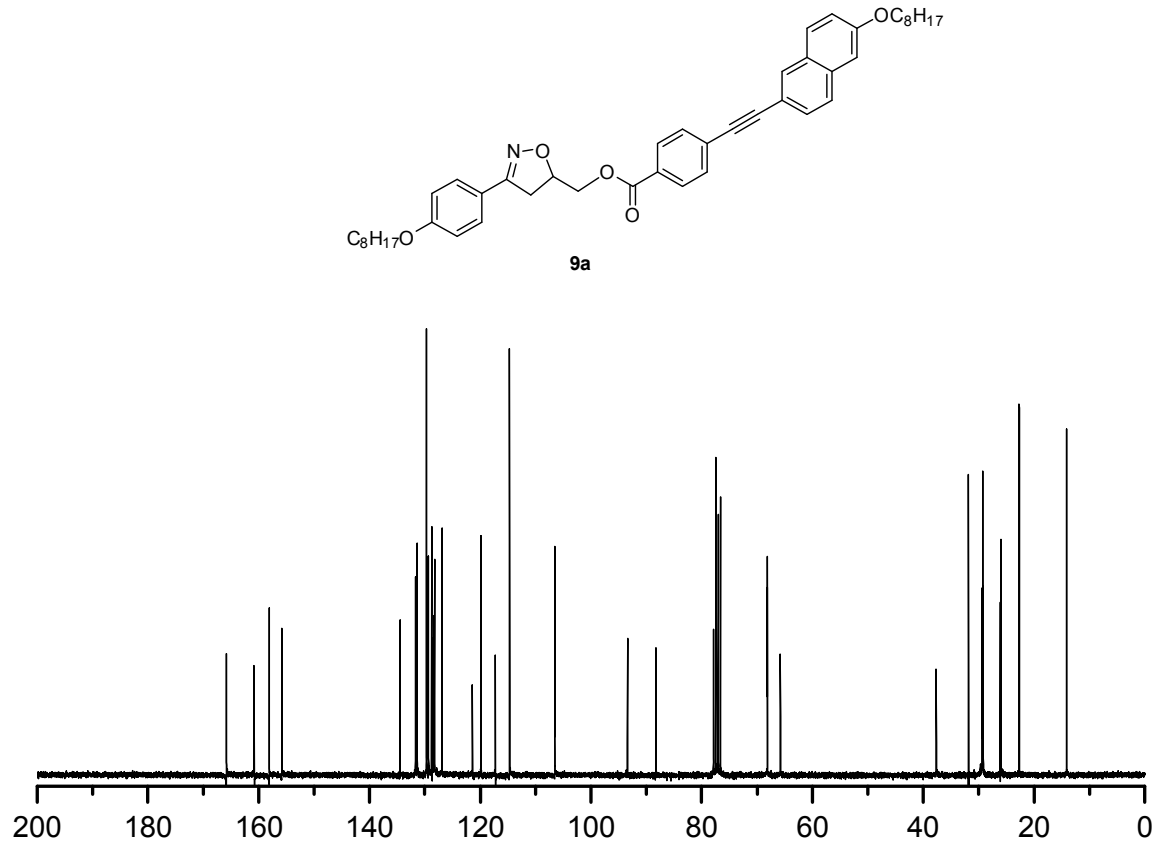


Figure S22. ^{13}C NMR spectrum of compound **9a** ($CDCl_3$, 75 MHz).

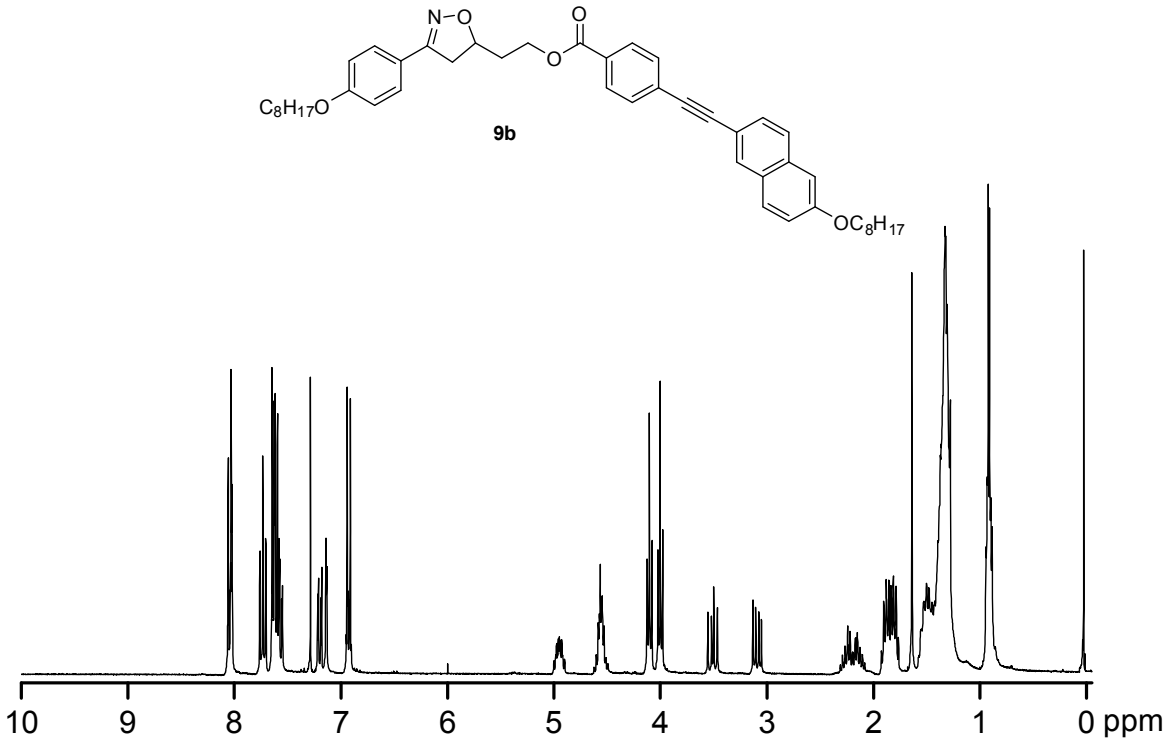


Figure S23. ^{1}H NMR spectrum of compound **9b** ($CDCl_3$, 300 MHz).

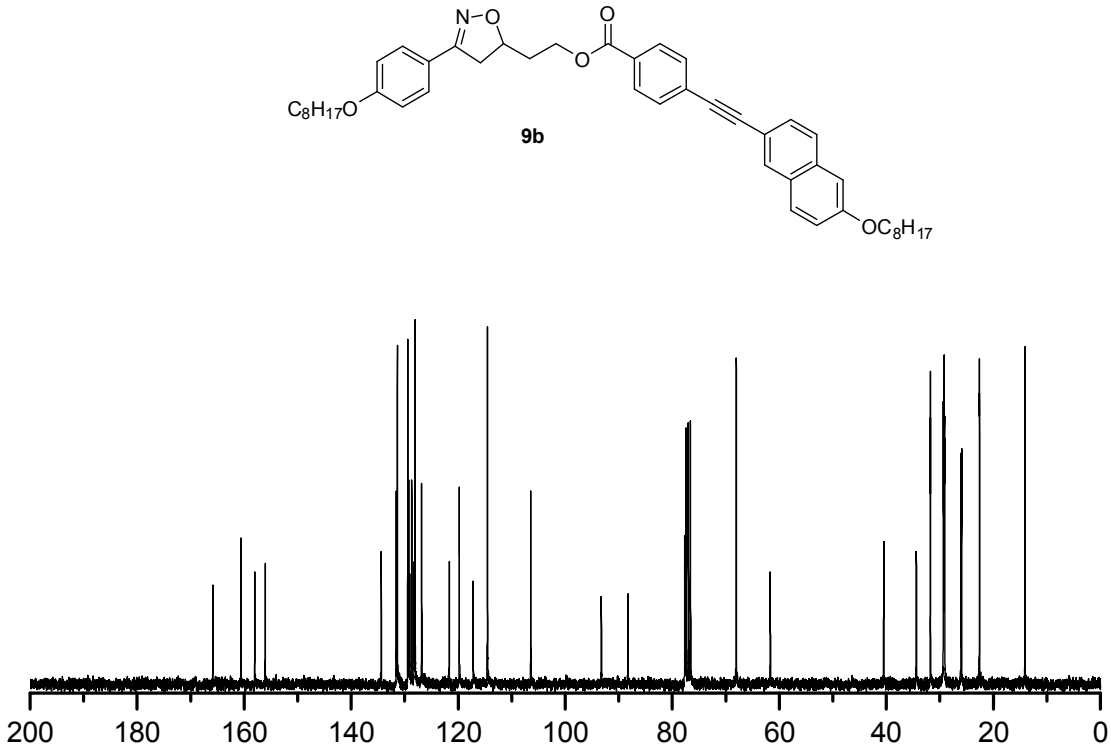


Figure S24. ^{13}C NMR spectrum of compound **9b** ($CDCl_3$, 75 MHz).

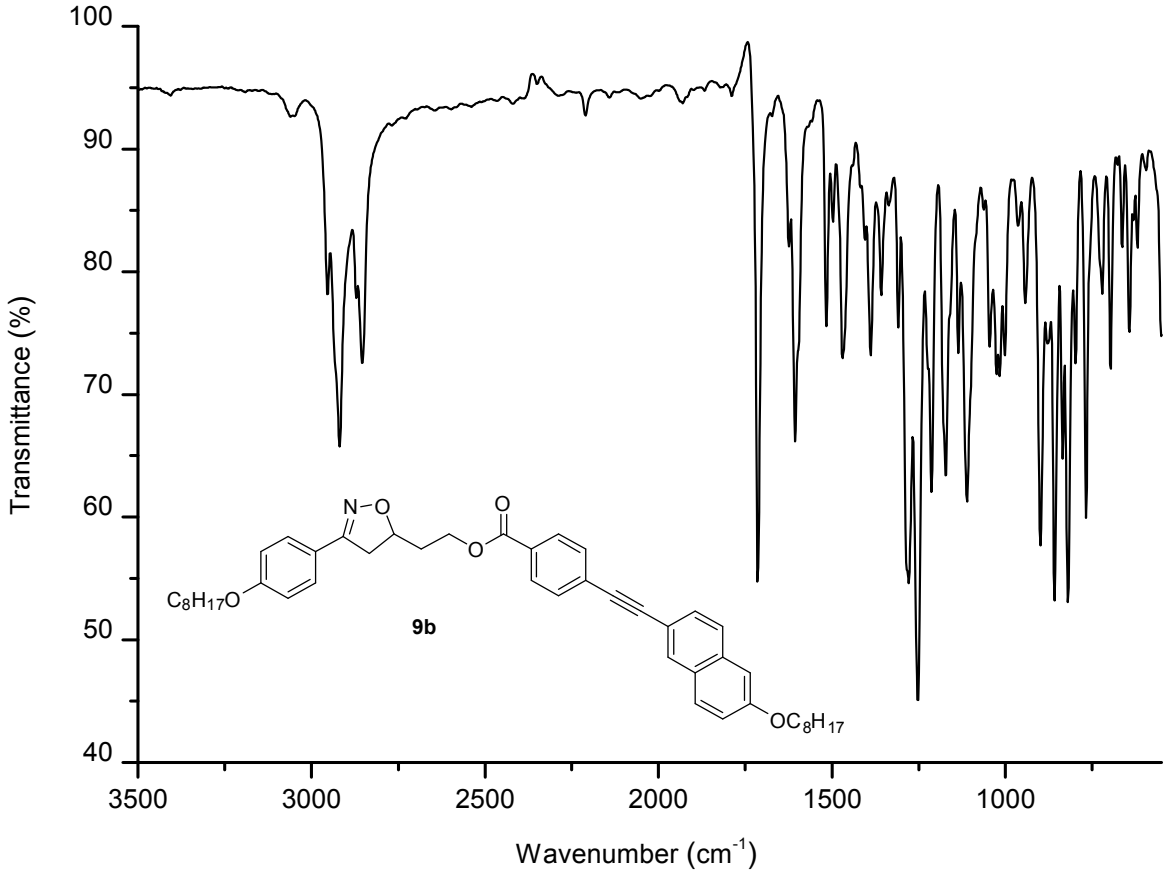


Figure S25. FT-IR spectrum of compound **9b**.

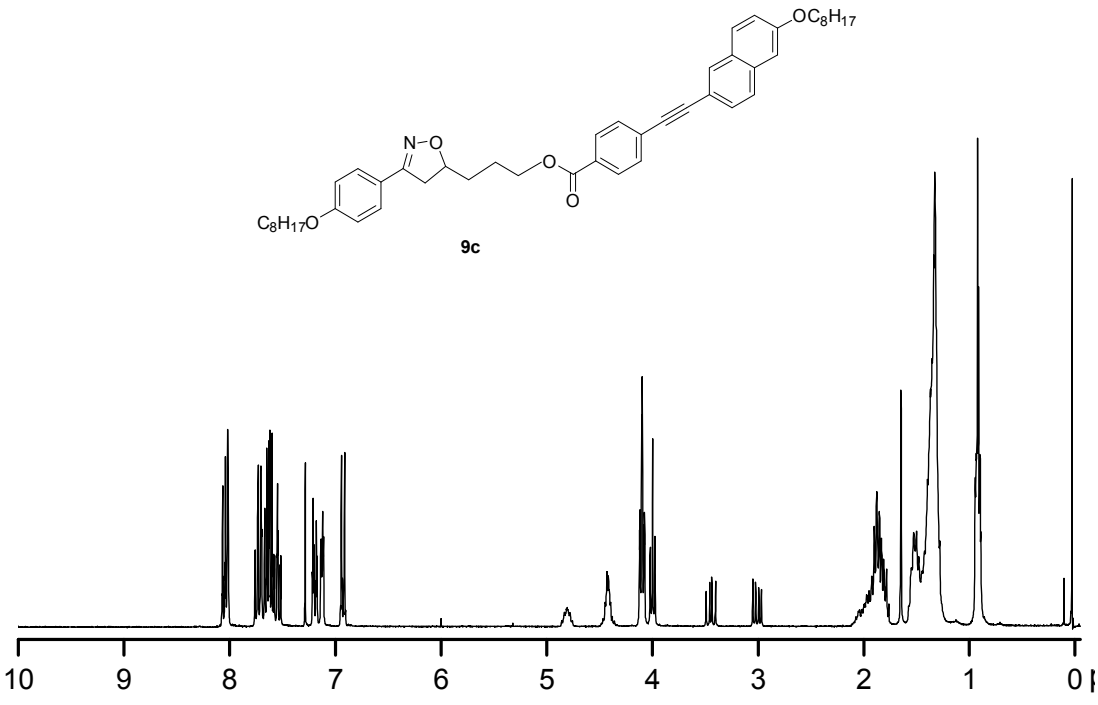


Figure S26. ^{1}H NMR spectrum of compound **9c** ($CDCl_3$, 300 MHz).

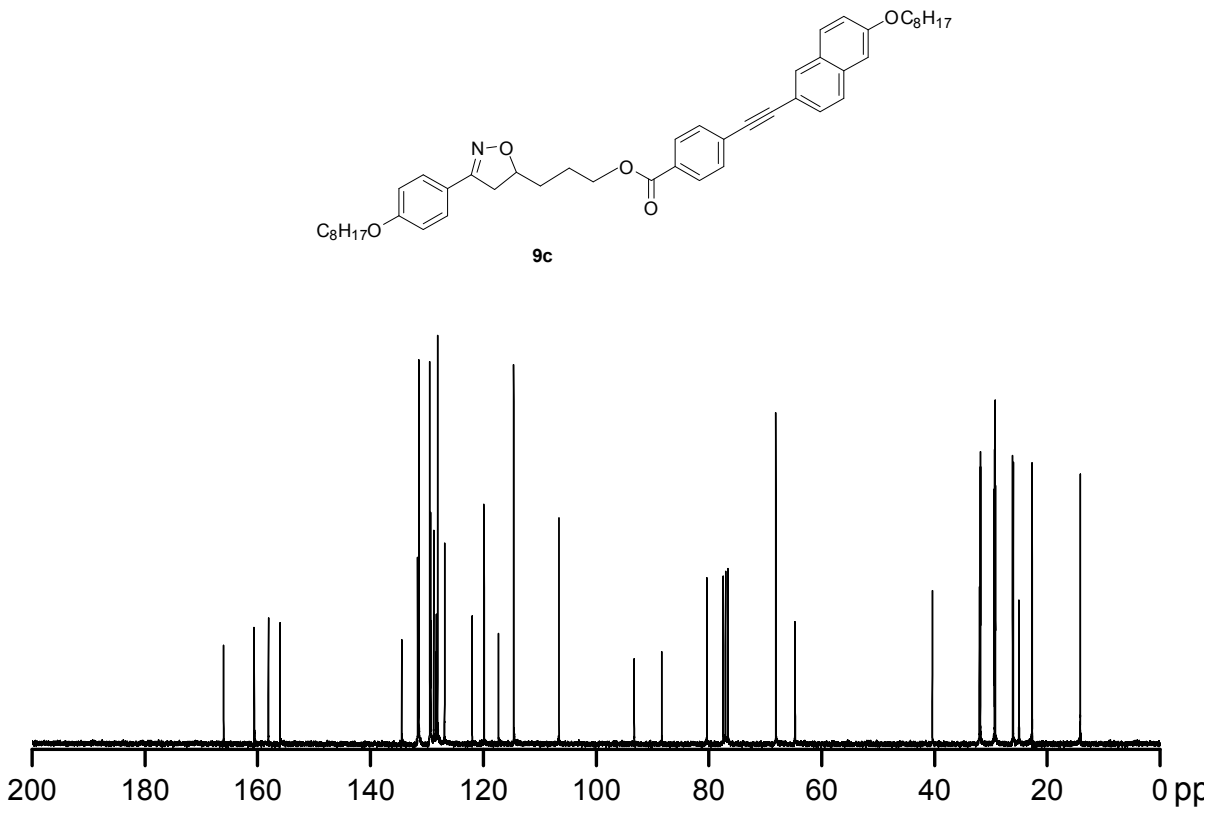


Figure S27. ^{13}C NMR spectrum of compound **9c** ($CDCl_3$, 75 MHz).

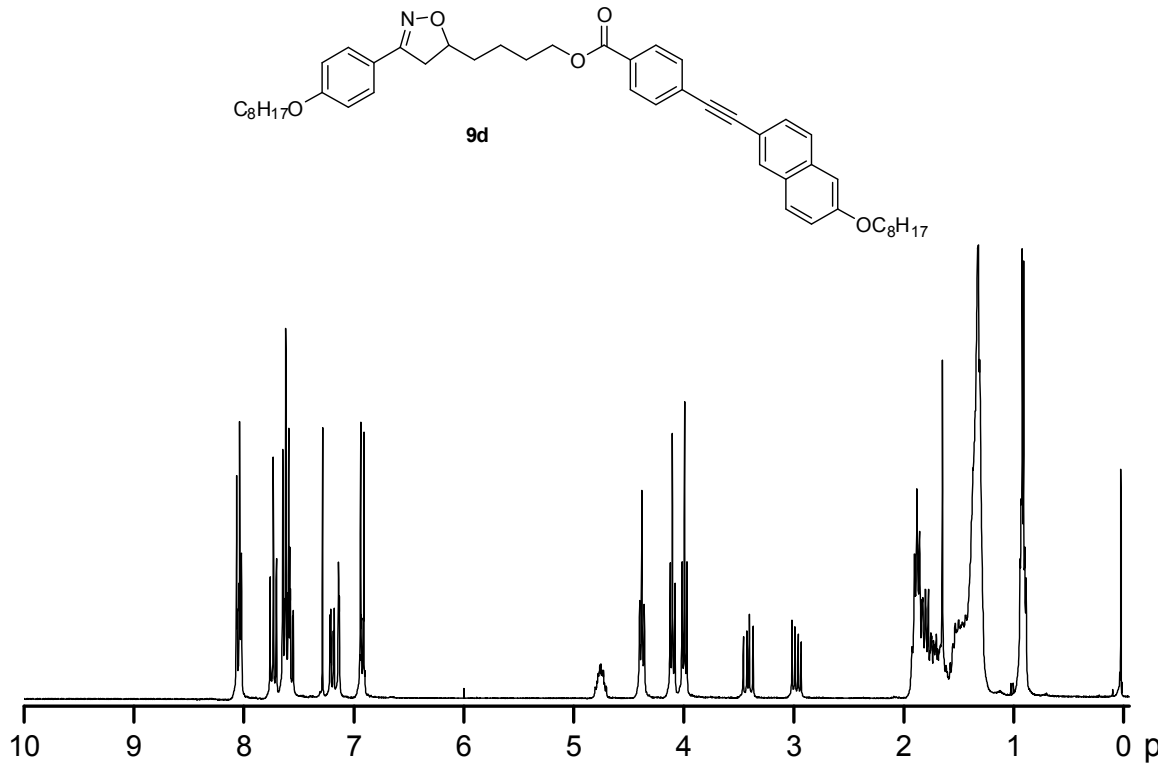


Figure S28. ^{1}H NMR spectrum of compound **9d** ($CDCl_3$, 300 MHz).

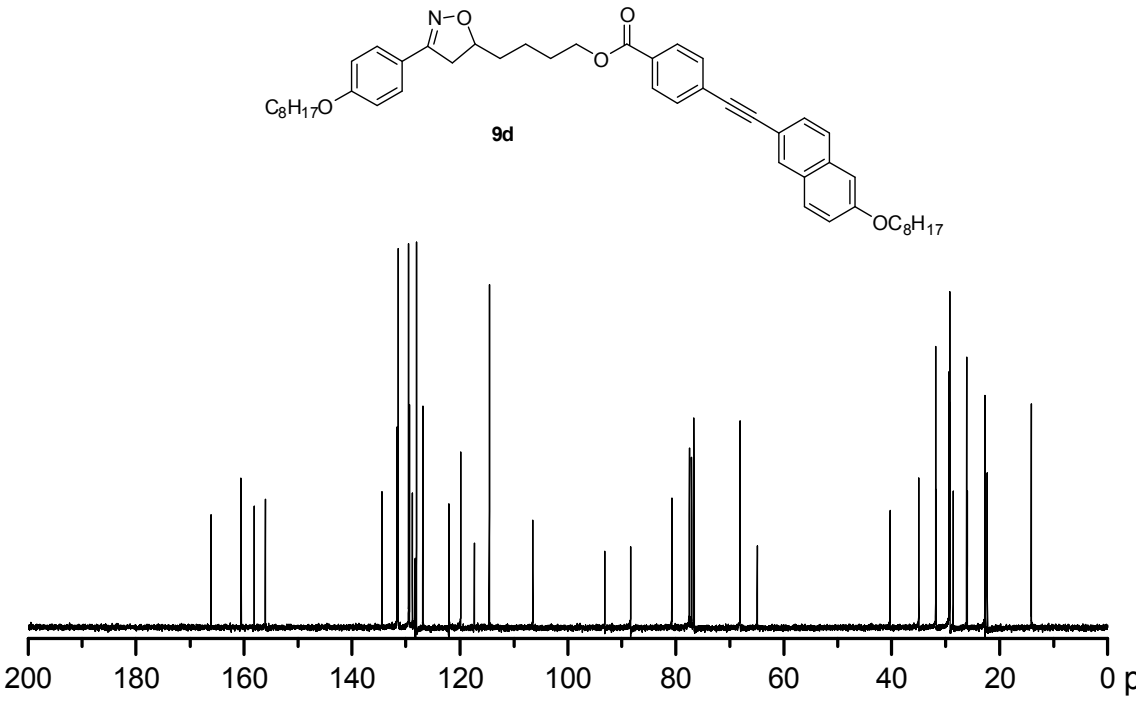


Figure S29. ^{13}C NMR spectrum of compound **9d** ($CDCl_3$, 75 MHz).

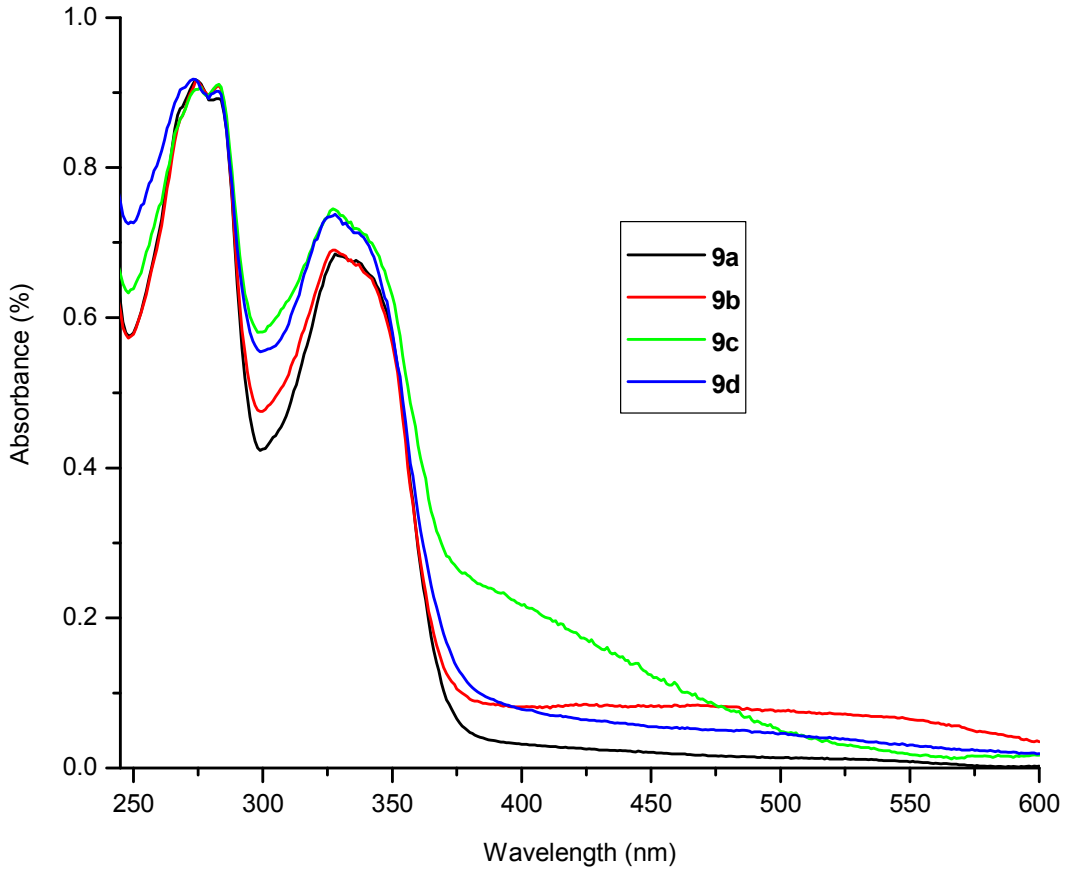


Figure S30a. UV-Vis absorption spectra of compounds **9a-d** in DCM solutions.

Figure S30b. Solutions of compounds **9a-d** excited under UV light at 365 nm.

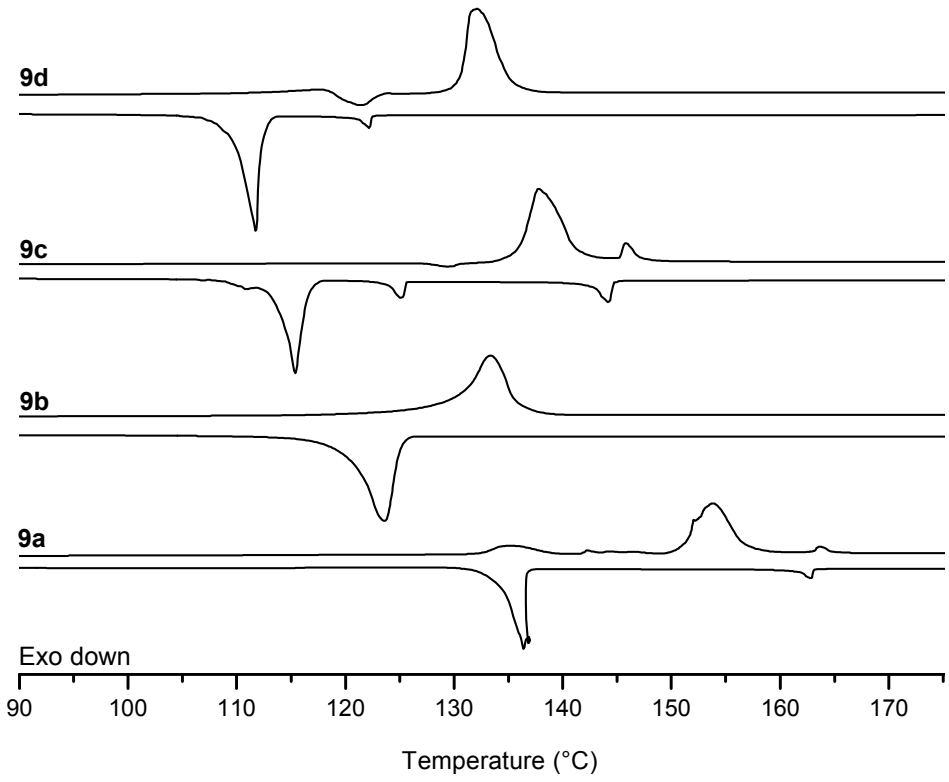


Figure S31. DSC thermograms of compounds **9a-d** on 2nd cycle at 10 ºC min^{-1}.

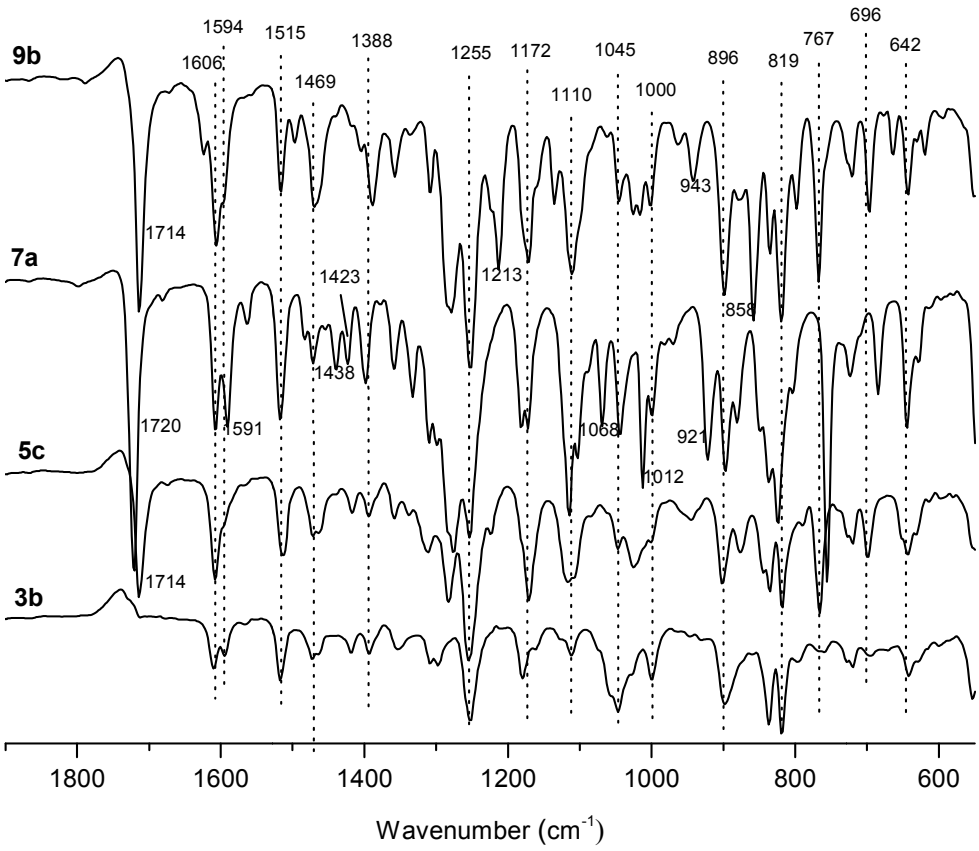


Figure S32. Overlay of IR spectra of **9b**, **7a**, **5c**, and **3b**.

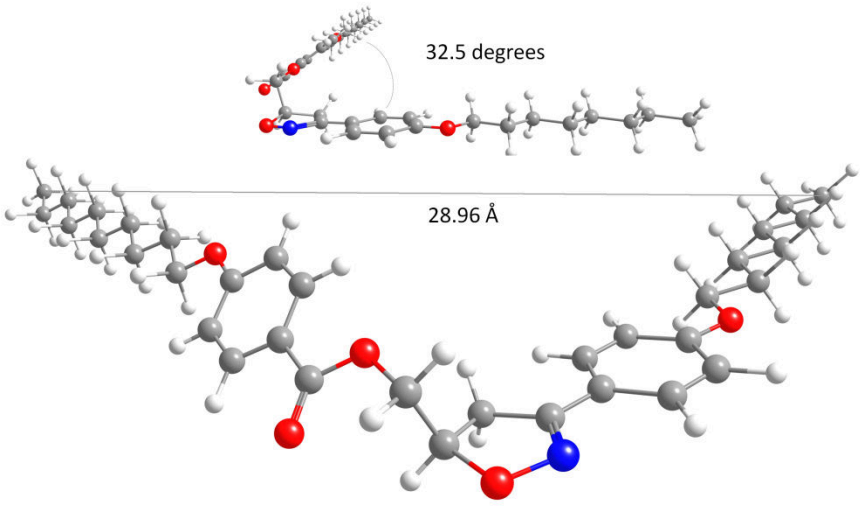


Figure S33. The most stable conformation (*anti*) for **5a,** molecular length and angle between molecular planes (above).

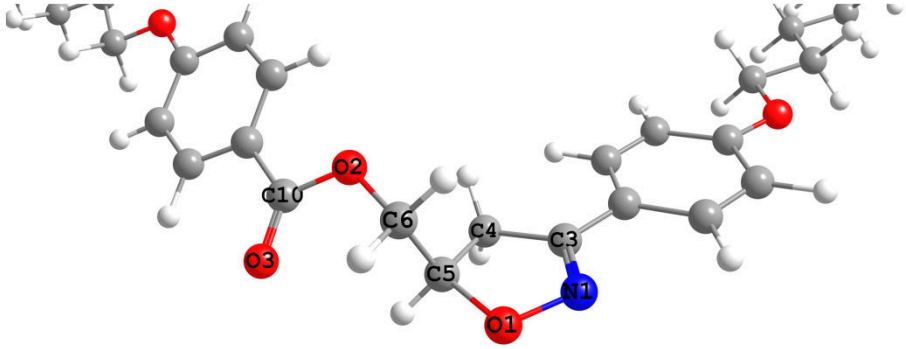


Figure S34. *Anti* conformer of **5a** structure. Dihedral angle ϕ_1 (O_1-C_5-C_6-O_2) is equal to 173.3 degrees.

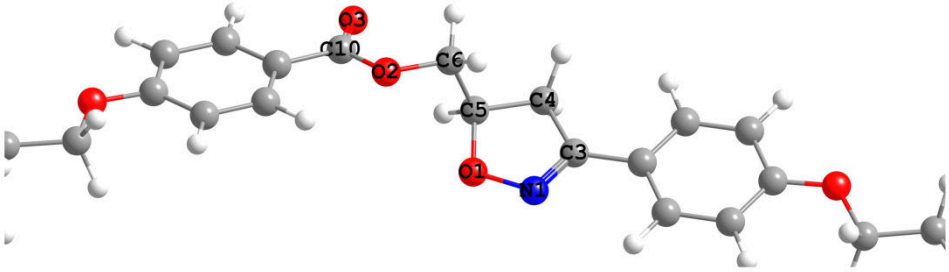


Figure S35. *Gauche* conformer of **5a** structure. Dihedral angle ϕ_1 (O_1-C_5-C_6-O_2) is equal to 61.83 degrees.

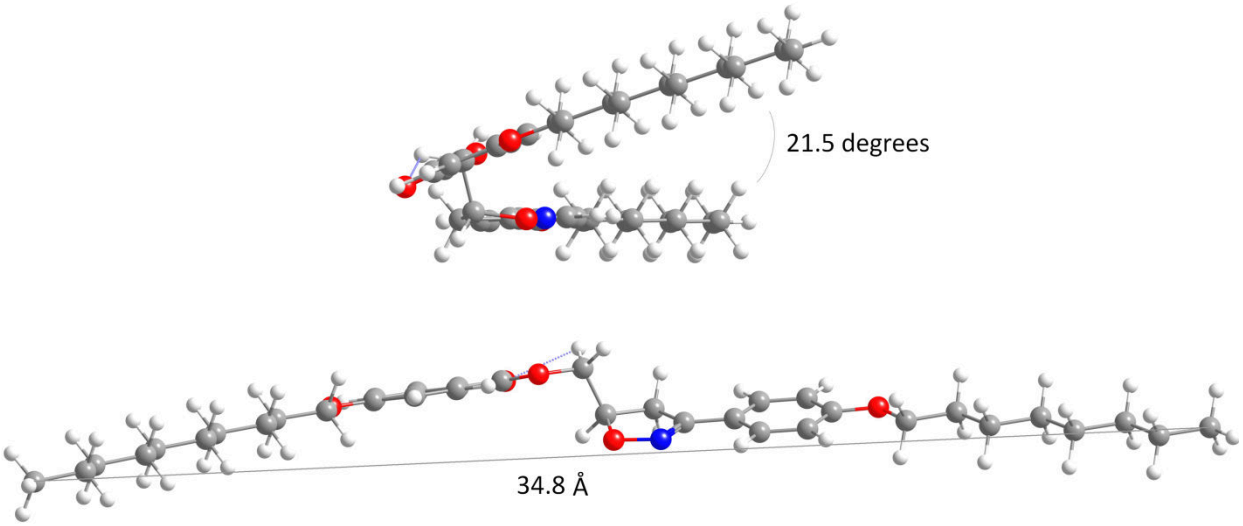


Figure S36. *Gauche* conformation for **5a,** molecular length and angle between molecular planes (above).

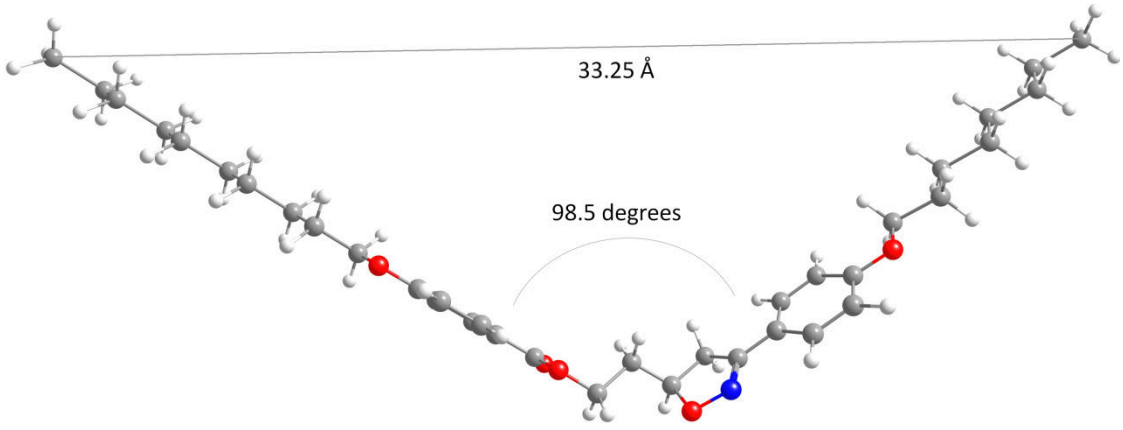


Figure S37. The most stable conformation for **5b,** molecular length and angle between molecular planes.

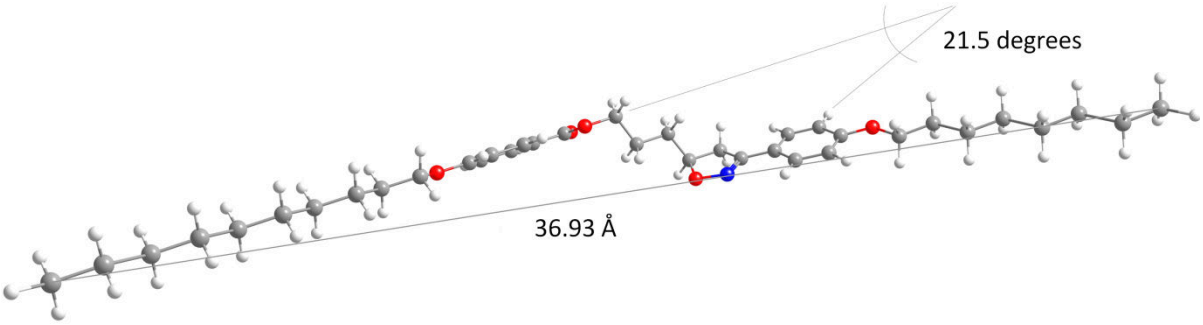


Figure S38. The most stable conformation for **5c,** molecular length and angle between molecular planes.

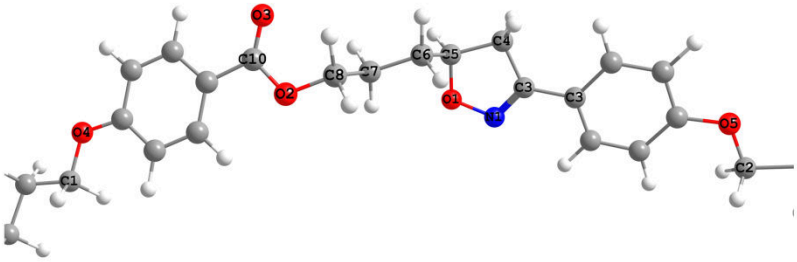


Figure S39. The most stable conformation for **5c.** Dihedral angle ϕ_1 (C_4-C_5-C_6-C_7) equal to 176.7 degrees.

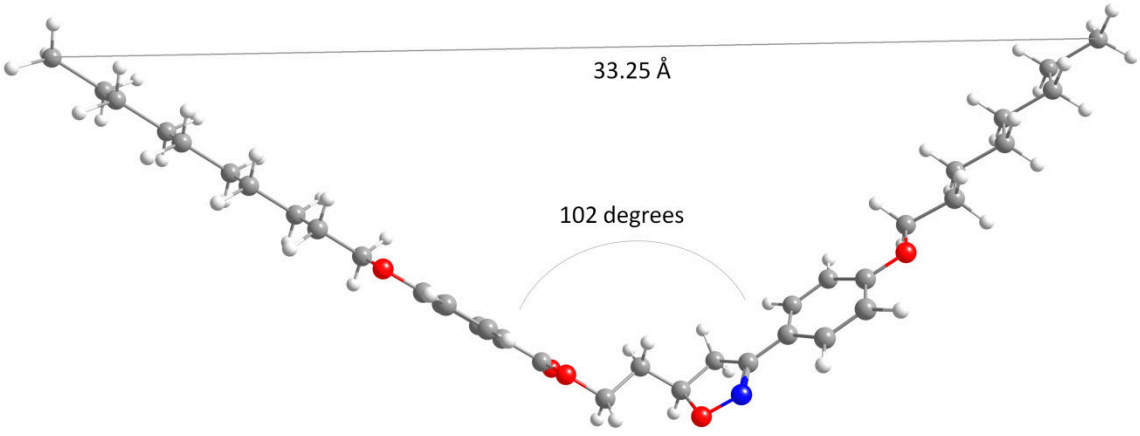


Figure S40. The most stable conformation for **5d,** molecular length and angle between molecular planes.

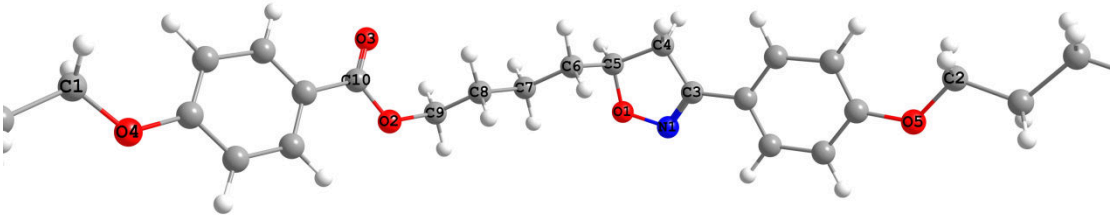
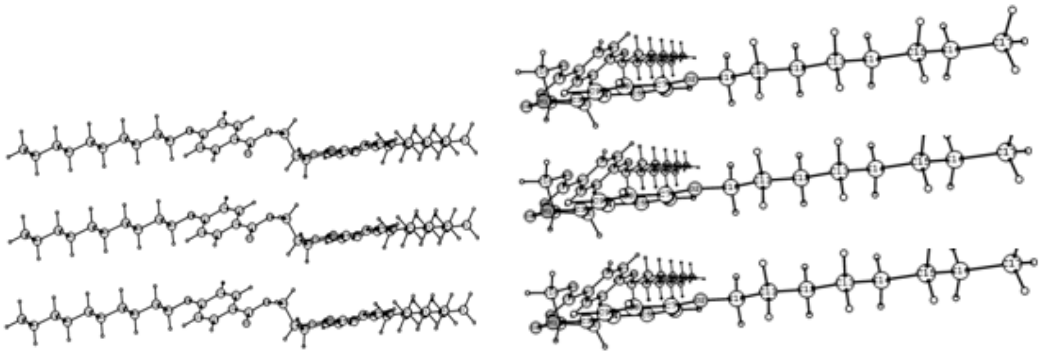
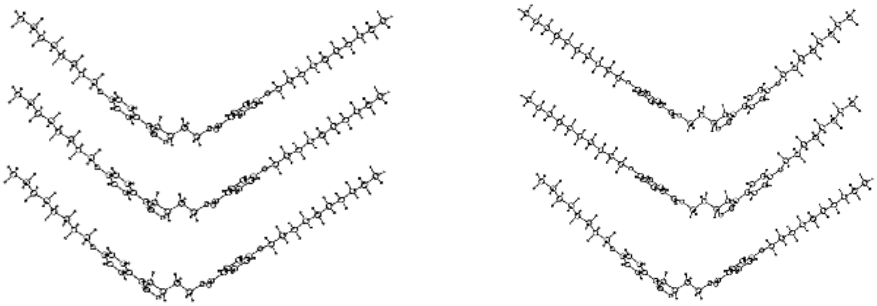


Figure S41. The most stable conformation for **5d.** Dihedral angle ϕ_1 (C_4-C_5-C_6-C_7) equal to 176.9 degrees.



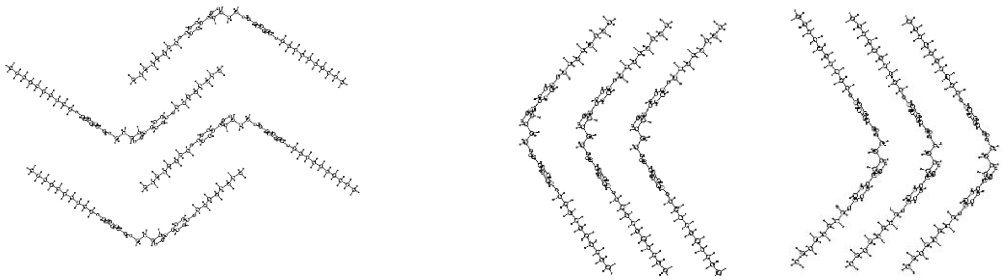
Frontal view **5a** Side view of **5a**

Figure S42. Frontal and side view of **5a**.



5b Face view head-head **5b** face view head-tail

Figure S43. Packing of **5b**: face view head-head and face view head-tail.



Zig-Zag view head-tail Chevron view

Figure S44. Packing of **5b**: zig-zag and chevron.

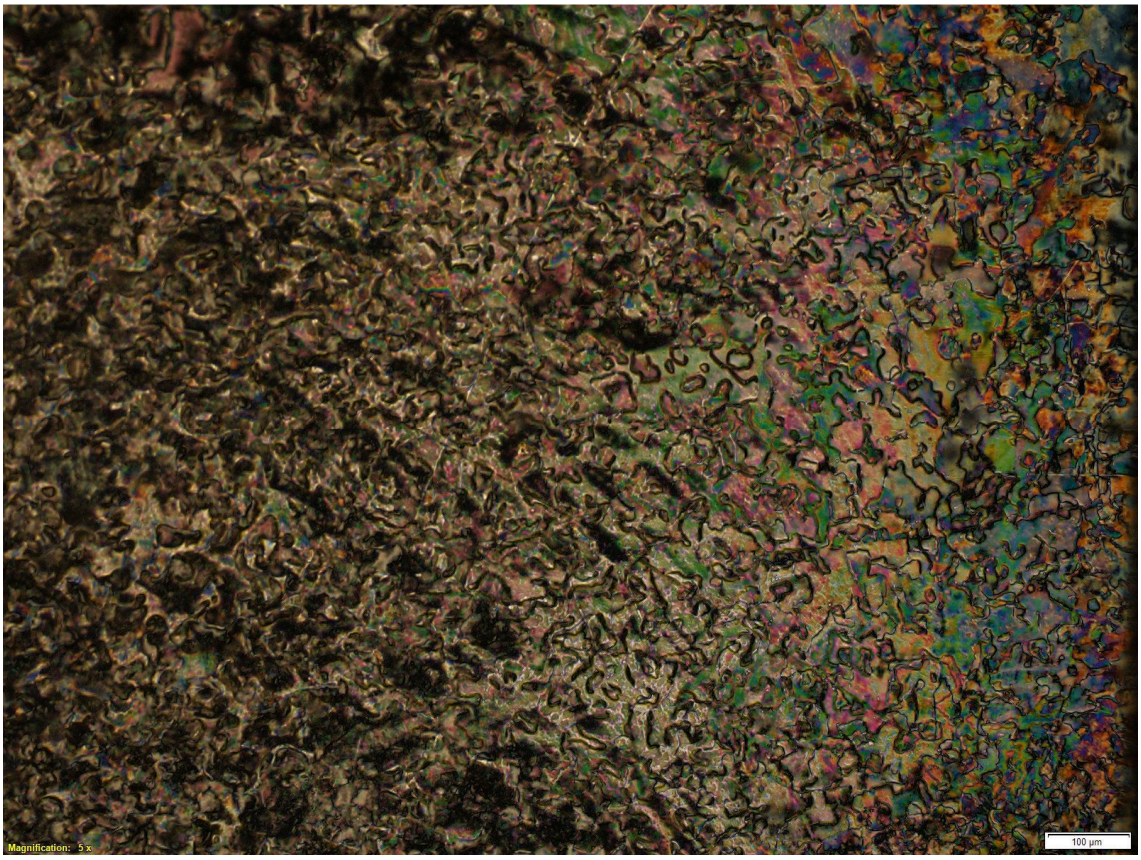


Figure S45. Nematic mesofase for **9a** upon cooling at 146 °C.

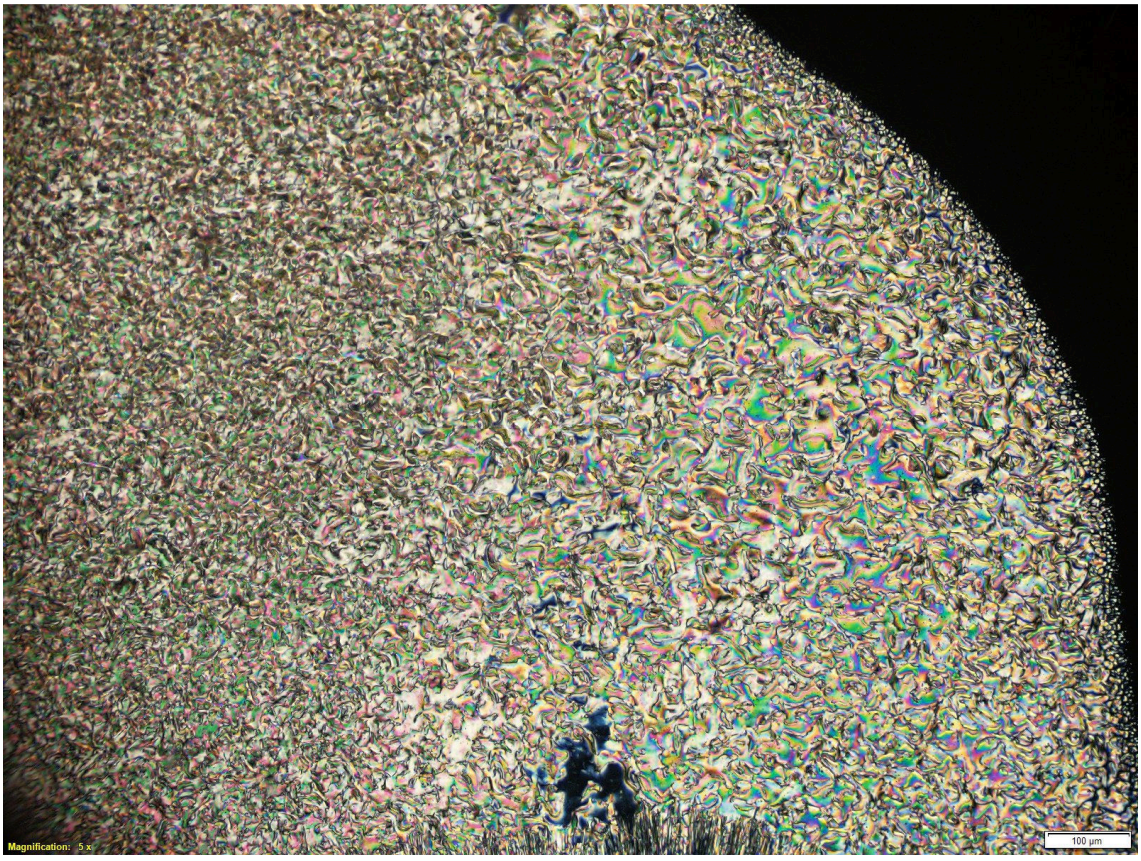


Figure S46. Nematic mesofase for **9d** upon cooling at 119 °C.