Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Gold-Catalyzed Cascade Reactions of 4H-Furo[3,2-b]indoles with propargyl esters: Synthesis of 2-alkenylidene-3-oxoindolines

Elisa Brambilla,[*a] Valentina Pirovano,[a] Matteo Giannangeli,[b] Giorgio Abbiati,[a] Alessandro Caselli,[b] and Elisabetta Rossi,*[a]

[a] Dipartimento di Scienze Farmaceutiche - Sezione di Chimica Generale e Organica "A. Marchesini", Università degli Studi di Milano, Via Venezian 21, 20133 Milano, Italy

[b] Dipartimento di Chimica and ISTM-CNR, Università degli Studi di Milano, Via Golgi 19, 20133, Milano, Italy

*e-mail: elisabetta.rossi@unimi.it

Table of Contents

General Remarks

All chemicals and solvents are commercially available and were used after distillation or treatment with drying agents. Silica gel F254 thin-layer plates were employed for thin-layer chromatography (TLC). Silica gel 40–63 micron/60 Å was employed for flash column chromatography. Melting points were measured with a Perkin-Elmer DSC 6 calorimeter at a heating rate of 5 °C/min and are uncorrected. ^{1}H and ^{13}C-NMR spectra were determined with a Varian-Gemini 300, a Bruker 300 or Bruker 500 spectrometers at room temperature in $CDCl_3$, CD_2Cl_2 or DMSO with residual solvent peaks as the internal reference. The APT sequences were used to distinguish the methine and methyl carbon signals from those arising from methylene and quaternary carbon atoms. Two-dimensional NMR experiments were performed, where appropriate, to aid the assignment of structures. Low-resolution MS spectra were recorded with a Thermo-Finnigan LCQ advantage AP electrospray/ion trap equipped instrument using a syringe pump device to directly inject sample solutions.

Furoindole **1a-b** are known compound and were prepared according to literature procedures[1]

Indole **1f-g** are known compound and were prepared according to literature procedures[2]

Propargyl esters **2a-f** are known compounds and were prepared according to literature procedures.[3]

Catalysts **A-E** are known compounds and were purchased from commercial suppliers and used as received (**A** = JhonPhosAuSbF_6, **C** = tris(aryl)phosphiteSbF_6) or prepared following literature procedures (**B** = iPrAuNTf_2, **D** = Ph_3PAuNTf_2, **E** = JhonPhosAuNTf_2).[4]

[1] V. Pirovano, E. Brambilla, S. Rizzato, G. Abbiati, M. Bozzi and E. Rossi, *J. Org. Chem*., **2019**, *84*, 5150.

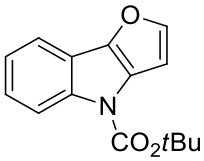
[2] *(a)* E. Rossi, G. Abbiati, V. Canevari, G. Celentano and E. Magri, *Synthesis*, **2006**, *2*, 299; *(b)* L.-J. Huang, J. Weng, S. Wang, and G. Lu, *Adv. Synth. Catal*.,. **2015**, *357*, 993.

[3]*(a)* A. Lepronier, T. Achard, L. Giordano, A. Tenaglia, G. Buono and H. Claviera, *Adv.Synth.Catal.*, **2016**, *358*, 631; *(b)* E. Rettenmeier, A. M. Schuster, M. Rudolph, F. Rominger, C.A. Gade and A. S. K. Hashmi, *Angew. Chem. Int. Ed.*, **2013**, *52*, 5880; *(c)* J. Zhao, S. Yang, X. Xie, X. Li and J. Liu, *J. Org. Chem.*, **2018**, *83*, 1287; *(d)* C. Brancour, T. Fukuyama, Y. Ohta, I. Ryu, A.-L. Dhimane, L. Fensterbank, and M. Malacria, *Chem. Commun.*, **2010**, *46*, 5470.

[4] (*a*) L. Ricard and F. Gagosz, *Organometallics*, **2007**, *26*, 4704; (*b*) N. Mézailles, L. Ricard and F. Gagosz, *Org. Lett.*, **2005**, *7*, 4133; (*c*) A. Homs, I. Escofet and A. M. Echavarren, *Org. Lett.*, **2013**, *15*, 5782.

Preparation and characterization data for 4*H*-furo[3,2-*b*]indole 1b-d

tert-butyl 4*H*-furo[3,2-*b*]indole-4-carboxylate (1b)



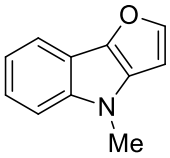
To a N_2-flushed solution of 4*H*-furo[3,2-*b*]indole[1] (157 mg, 1 mmol) in dichloromethane (5 mL), Boc_2O (659 mg, 3 mmol) and DMAP (12 mg, 0.1 mmol) were added at 0 °C. The mixture was warmed up to room temperature and stirred for 2.5 h. Then the solvent was evaporated and the crude was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 98:2) to yield **1b** (252 mg, 98%) as white solid (m.p. 82.4-84.6 °C).

^{1}H NMR (300 MHz, $CDCl_3$): 8.32 (bs, 1H), 7.66 (ddd, *J* = 6.7, 3.3, 2.1 Hz, 1H), 7.56 (t, *J* = 16.1 Hz, 1H), 7.38 – 7.19 (m, 2H), 6.79 (bs, 1H), 1.71 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 149.77 (C), 145.59 (CH), 143.24 (C), 138.80 (C), 129.67 (C), 123.74 (CH), 123.03 (CH), 117.88 (C), 116.33 (CH), 116.23 (CH), 103.07 (CH), 83.42 (C), 28.25 (3xCH_3).

ESI(+)-MS: m/z(%) = 258 (100) $[M+H]^+$; $C_{15}H_{15}NO_3$ [257.29]: calcd. for C, 70.02; H, 5.88; N, 5.44; found C, 70.15; H, 5.86, N 5.46.

4-methyl-4*H*-furo[3,2-*b*]indole (1c)



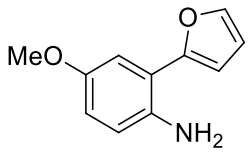
To a N_2-flushed solution of NaH (28 mg, 1.1 mmol) in DMF (6 ml) 4*H*-furo[3,2-*b*]indole[1] (157 mg, 1 mmol) was added in small portions at 0 °C and the mixture was stirred for 30 min at 0 °C. Then MeI (156 mg, 1.1 mmol) was added and the reaction was warmed to room temperature and stirred for 1 h before being quenched with water. The organic layer was extracted with ethyl acetate, dried over Na_2SO_4 and the solvent concentrated under reduced pression. The crude was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 98:2) to yield **1c** (153 mg, 89%) as pink oil.

^{1}H NMR (300 MHz, $CDCl_3$): 7.75 (dd, *J* = 7.1, 0.8 Hz, 1H), 7.56 (d, *J* = 2.1 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.09 (m, 2H), 6.61 (d, *J* = 2.1 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 145.69 (CH), 140.82 (C), 140.44 (C), 133.10 (C), 121.15 (CH), 118.94 (CH), 116.25 (CH), 113.96 (C), 109.63 (CH), 98.18 (CH), 31.21 (CH_3).

ESI(+)-MS: m/z(%) = 172 (100) $[M+H]^+$; $C_{11}H_9NO$ [171.20]: calcd. for C, 77.17; H, 5.30; N, 8.18; found C, 76.89; H, 5.33; N, 8.15.

2-(furan-2-yl)-4-methoxyaniline



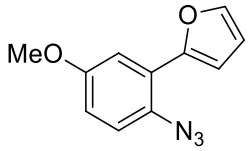
To a N_2-flushed solution of furan-2-ylboronic acid (1.24 g, 11.1 mmol), potassium carbonate (4.09 g, 29.6 mmol), $PdCl_2(PPh_3)_2$ (260 mg, 0.37 mmol) in DMF (33 mL) and water (7.5 mL), 2-bromoaniline (1.5 mg, 7.4 mmol) was added. The reaction mixture was heated at reflux for 3 h and then cooled at room temperature. The mixture was diluted with water and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4 and the solvent concentrated under reduced pression. The crude was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 9:1 to 8:2) to yield 2-(furan-2-yl)-4-methoxyaniline (1.34 g, 96%) as brownish oil.

^{1}H NMR (300 MHz, $CDCl_3$): 7.50 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.07 (dd, *J* = 2.5, 0.8 Hz, 1H), 6.74 – 6.71 (m, 2H), 6.61 (dd, *J* = 3.4, 0.8 Hz, 1H), 6.51 (dd, *J* = 3.4, 1.9 Hz, 1H), 3.86 (bs, 2H), 3.79 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 152.98 (C), 152.61 (C), 141.40 (CH), 136.87 (C), 118.23 (CH), 117.17 (C), 115.51 (CH), 112.02 (CH), 111.36 (CH), 106.88 (CH), 55.81 (CH_3).

ESI(+)-MS: m/z(%) = 190 (100) $[M+H]^+$; $C_{11}H_{11}NO_2$ [189.21]: calcd. for C, 69.83; H, 5.86; N, 7.40; found C, 69.65; H, 5.88; N, 7.37.

2-(2-azido-5-methoxyphenyl)furan



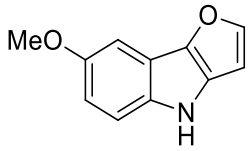
To a solution of 2-(furan-2-yl)-4-methoxyaniline (1.30 g, 6.9 mmol), an aqueous solution of hydrochloric acid (15%, 6.9 mL) was added dropwise at 0 °C. Then a solution of sodium nitrite (573 mg, 8.3 mmol) in water (19 mL) was added dropwise. The mixture was stirred for 1 h at 0 °C. Then a solution of sodium azide (728 mg, 11.2 mmol) in water (2.6 mL) was added dropwise at 0 °C and the mixture was stirred for 1 h at room temperature. The mixture was diluted with water, extracted with ethyl acetate, washed with sodium bicarbonate saturated solution and brine. The organic layer was dried over Na_2SO_4 and the solvent concentrated under reduced pression. The crude was purified by flash column chromatography (SiO_2, hexane 100%) to yield 2-(2-azido-5-methoxyphenyl)furan (1.47 g, 99%) as brownish oil.

^{1}H NMR (300 MHz, $CDCl_3$): 7.47 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.38 (d, *J* = 2.9 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 1H), 7.10 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.85 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.51 (dd, *J* = 3.4, 1.8 Hz, 1H), 3.85 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 156.89 (C), 149.47 (C), 141.74 (CH), 127.61 (C), 123.21 (C), 119.99 (CH), 114.44 (CH), 111.81 (CH), 111.21 (CH), 110.62 (CH), 55.61 (CH_3).

ESI(+)-MS: $C_{11}H_9N_3O_2$ [215.21]: calcd. for C, 61.39; H, 4.22; N, 19.53; found C, 61.67; H, 4.20; N, 19.48.

7-methoxy-4*H*-furo[3,2-*b*]indole



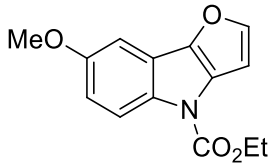
A solution of 2-(2-azido-5-methoxyphenyl)furan (1.34 g, 6.2 mmol) in 1,2-dichlorobenzene (4 mL) was added dropwise to 1,2-dichlorobenzene (8 mL) heated at 160 °C. The reaction mixture was stirred for 1 h. Then solvent was concentrated under reduced pression. The crude was purified by flash column chromatography (SiO_2, hexane/ ethyl acetate 95:5 to 9:1) to yield 7-methoxy-4*H*-furo[3,2-*b*]indole (279 mg, 24%) as brownish oil.

^{1}H NMR (300 MHz, CD_2Cl_2): 7.69 (bs, 1H), 7.56 (d, *J* = 2.1 Hz, 1H), 7.32 (dd, *J* = 8.9, 0.5 Hz, 1H), 7.19 (d, *J* = 2.5 Hz, 1H), 6.83 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.62 (d, *J* = 2.1 Hz, 1H), 3.87 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2):154.20 (C), 145.88 (CH), 142.22 (C), 135.10 (C), 131.10 (C), 114.49 (C), 112.91 (CH), 111.06 (CH), 99.52 (CH), 98.54 (CH), 55.71 (CH_3).

ESI(+)-MS: m/z(%) = 188 (100) $[M+H]^+$; $C_{11}H_9NO_2$ [187.19]: calcd. for C, 70.58; H, 4.85; N, 7.48; found for C, 70.84; H, 4.86; N, 7.45.

Ethyl 7-methoxy-4H-furo[3,2-b]indole-4-carboxylate (1d)



To a N_2-flushed solution of 7-methoxy-4*H*-furo[3,2-*b*]indole (250 mg, 1.3 mmol) in tetrahydrofuran (13 mL), a solution of *n*-butyllithium (1.6 M in hexane, 893 µL, 1.43 mmol), was added dropwise at -78 °C. The reaction mixture was stirred for 30 minutes. Ethyl chloroformate (186 µL, 1.95 mmol) was added dropwise and the reaction was brought to room temperature and stirred for 2 h before of being quenched with ammonium chloride saturated solution. The organic layer was extracted with ethyl acetate, dried over Na_2SO_4 and the solvent concentrated under reduced pression. The crude was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 95:5) to yield **1d** (288 mg, 86%) as orange solid (m.p. 74.5-76.2 °C).

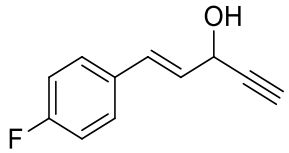
^{1}H NMR (300 MHz, $CDCl_3$): 8.20 (bs, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 2.6 Hz, 1H), 6.90 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.79 (s, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 156.31 (C), 151.04 (C) 145.85 (CH), 143.34 (C), 133.38 (C), 130.06 (C), 118.69 (C), 117.12 (CH), 111.80 (CH), 103.10 (CH), 99.87 (CH), 62.94 (CH_2), 55.72 (CH_3), 14.47 (CH_3)

ESI(+)-MS: m/z(%) = 260 (100) $[M+H]^+$; $C_{14}H_{13}NO_4$ [259.26]: calcd. for C, 64.86; H, 5.05; N, 5.40; found C, 65.09; H, 5.03; N, 5.42.

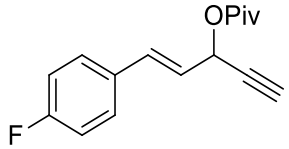
Preparation and characterization data for propargylic esters 2e,f

(*E*)-1-(4-fluorophenyl)pent-1-en-4-yn-3-ol



To a N_2-flushed solution of (*E*)-3-(4-fluorophenyl)acrylaldehyde (753 mg, 5 mmol) in tetrahydrofuran (10 mL), a solution of ethynylmagnesium bromide (0.5 M in tetrahydrofuran, 12 mL, 6 mmol) was added dropwise at 0 °C. The mixture was warmed up to room temperature and stirred for 1h before of being quenched with ammonium chloride saturated solution. The organic layer was extracted with ethyl acetate, dried over Na_2SO_4 and the solvent concentrated under vacuum. The crude was used directly for the next step, quantitative yield.

(*E*)-1-(4-fluorophenyl)pent-1-en-4-yn-3-yl pivalate (2e)



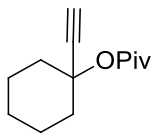
To a solution of (*E*)-1-(4-fluorophenyl)pent-1-en-4-yn-3-ol (889 mg, 5 mmol), triethylamine (1.52 g, 15 mmol), DMAP (61 mg, 0.5 mmol) in dichloromethane (21.5 mL), pivaloyl chloride (720 mg, 6 mmol) was added at 0 °C. The mixture was warmed up to room temperature and stirred for 2h before of being quenched with ammonium chloride saturated solution. The organic layer was extracted with dichloromethane, washed with brine, dried over Na_2SO_4 and the solvent concentrated under vacuum. The crude was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 98:2) to yield **2e** (1.3 g, quantitative) as an yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): 7.49 – 7.27 (m, 2H), 7.06 – 6.98 (m, 2H), 6.83 (d, *J* = 15.6 Hz, 1H), 6.14 (dd, *J* = 15.7, 6.3 Hz, 1H), 6.01 (ddd, *J* = 6.3, 2.2, 1.2 Hz, 1H), 2.61 (d, *J* = 2.2 Hz, 1H), 1.24 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 177.08 (C), 162.78 (d, *J* = 248.1 Hz, C), 133.18 (CH), 131.87 (d, *J* = 3.4 Hz, C), 128.51 (d, *J* = 8.2 Hz, 2xCH), 123.39 (d, *J* = 2.2 Hz, CH), 115.57 (d, *J* = 21.6 Hz, 2xCH), 79.48 (C), 74.99 (CH), 63.69 (CH), 38.76 (C), 26.98 ($3xCH_3$).

ESI(-)-MS: m/z(%) = 520 (100) $[dimer]^-$; $C_{16}H_{17}FO_2$ [260.30]: calcd. for C, 73.83; H, 6.58; found C, 73.57; H, 6.60.

1-ethynylcyclohexyl pivalate (2f)



1-Ethynylcyclohexanol (500 mg, 4 mmol) and pivalic anhydride (815 mg, 4.4 mmol) were stirred at 80 °C for 1h in presence of magnesium perchlorate (9 mg, 0.04 mmol). The mixture was diluted with water, saturated

solution of $NaHCO_3$ and extracted with Et_2O. the organic layers were washed with saturated solution of $NaHCO_3$, brine, dried over Na_2SO_4 and the solvent concentrated under vacuum. The crude was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 99:1 to 98:2) to yield **2f** (781 g, 94%) as an yellow oil.

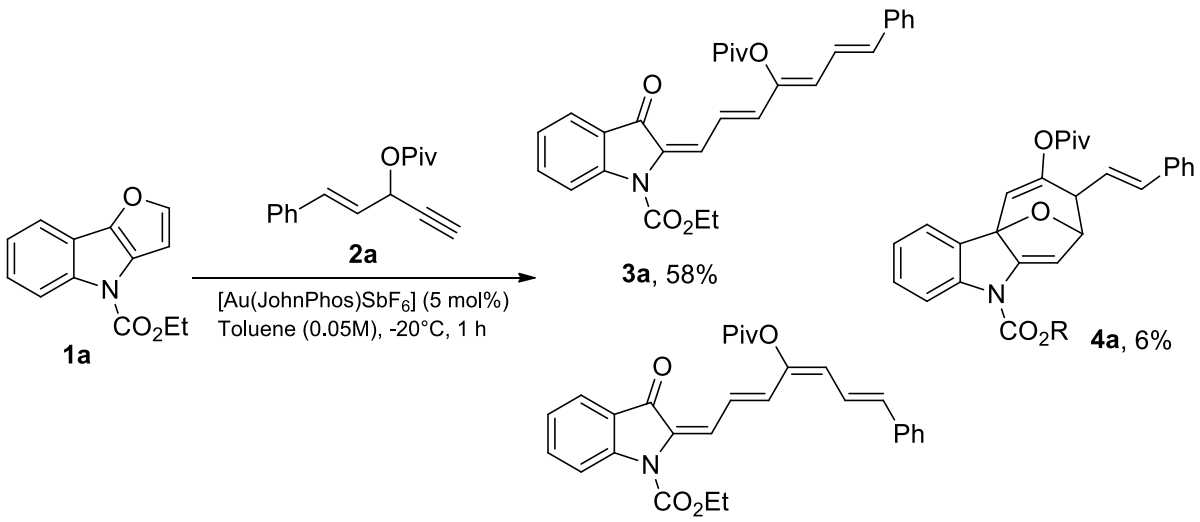
^{1}H NMR (300 MHz, $CDCl_3$): 2.54 (s, 1H), 2.06 – 1.90 (m, 4H), 1.66 – 1.52 (m, 4H), 1.51 – 1.34 (m, 2H), 1.19 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 176.43 (C), 84.08 (C), 74.15 (C), 73.44 (CH), 39.16 (C), 36.75 (2xCH_2), 27.08 (3xCH_3), 25.08(CH_2), 22.16 (2xCH_2).

ESI(+)-MS: m/z(%) = 209 (100) $[M+H]^+$; $C_{13}H_{20}O_2$ [208.30]: calcd. for C, 74.96; H, 9.68; found C, 75.23; H, 9.64.

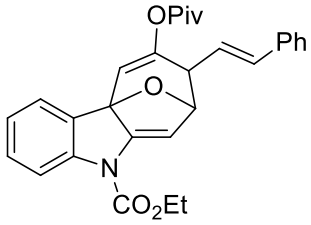
Preliminary reactions between 1a and 2a-c

Reaction between 1a and 2a



To a N_2-flushed solution of ethyl 4*H*-furo[3,2-*b*]indole-4-carboxylate **1a** (46 mg, 0.2 mmol) and [Au(JohnPhos)SbF_6] (5 mol%) in anhydrous toluene (2 mL), a solution of (*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate **2a** (58 mg, 0.24 mmol) in toluene (2 mL, final concentration 0.05 M) was added dropwise at -20 °C. The reaction mixture was stirred for 1 h at -20 °C and then quenched with PPh_3 (15 mol%). Purification by flash chromatography (SiO_2, toluene/ethyl acetate 99:1) yielded progressively **4a** (6 mg, 6%) as pale oil, **3'a** (34 mg, 36%) as a red solid (m.p. 174.2-176.3 °C) and **3a** (55 mg, 58%) as a red solid (m.p. 171.3-173.6 °C).

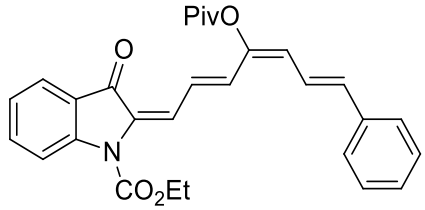
(*E*)-ethyl 9-(pivaloyloxy)-8-styryl-7,8-dihydro-5*H*-7,10a-epoxycyclohepta[*b*]indole-5-carboxylate (4a)



^{1}H NMR (300 MHz, $CDCl_3$): 7.92 (bs, 1H), 7.51 (d, *J* = 6.7 Hz, 1H), 7.44 – 7.20 (m, 6H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.44 (dd, *J* = 15.8, 8.8 Hz, 1H), 5.89 (d, *J* = 1.1 Hz, 1H), 5.68 (bs, 1H), 5.15 (d, *J* = 2.6 Hz, 1H), 4.58 – 4.21 (m, 2H), 3.29 (d, *J* = 9.0 Hz, 1H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.14 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): 176.43 (C), 156.41 (C), 151.50 (C), 146.87 (C), 146.03 (C), 136.84 (C), 133.13 (CH), 130.40 (CH), 128.81 (CH), 128.53 (2xCH), 128.45 (C), 127.54 (CH), 126.35 (2xCH), 124.86 (CH), 124.37 (CH), 120.74 (CH), 115.82 (CH), 104.10 (CH), 89.27 (CH), 62.75 (CH_2), 45.48 (CH), 39.05 (C), 29.66 (C), 26.99 (3xCH_3), 14.39 (CH_3).

ESI(+)-MS: m/z(%) = 472 (100) $[M+H]^+$; $C_{29}H_{29}NO_5$ [471.54]: calcd. for C, 73.87; H, 6.20; N, 2.97; found C, 73.76; H, 6.17; N, 2.98.

(*E*)-ethyl 3-oxo-2-((2*E*,4*E*,6*E*)-7-phenyl-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)indoline-1-carboxylate (3'a)



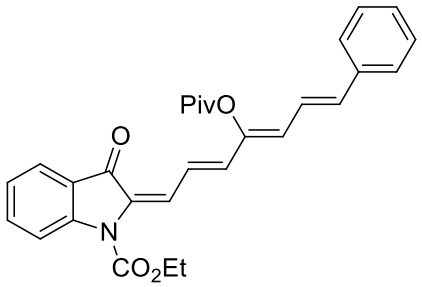
Elemental Analysis: C, 73.87; H, 6.20; N, 2.97; O, 16.96

^{1}H NMR (300 MHz, CD_2Cl_2): 8.23 (dd, *J* = 14.8, 12.1 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 12.1 Hz, 1H), 7.80 (m, 1H), 7.65 (ddd, *J* = 8.6, 7.3, 1.4 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.45 – 7.36 (m, 2) 7.35 – 7.14 (m, 4H), 6.74 (d, *J* = 15.3 Hz, 1H), 6.21 (d, *J* = 11.9 Hz, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 1.54 (t, *J* = 7.1 Hz, 3H), 1.50 (s, 9H).

^{13}C NMR (75 MHz, CD_2Cl_2): 184.10 (C), 176.76 (C), 151.75 (C), 146.88 (C), 146.85 (C), 136.95 (C), 135.53 (CH), 135.49 (CH), 132.57 (C), 130.62 (CH), 128.72 (2xCH), 128.23 (CH), 126.98 (CH), 126.71 (2xCH), 125.19 (CH), 125.07 (CH), 124.18 (CH), 123.87 (C), 123.58 (CH), 122.01 (CH), 117.28 (CH), 63.27 (CH_2), 39.11 (C), 27.07 (3xCH_3), 14.23 (CH_3).

ESI(+)-MS: m/z(%) = 472 (100) $[M+H]^+$; $C_{29}H_{29}NO_5$ [471.54]: calcd. for C, 73.87; H, 6.20; N, 32.97; found C, 74.15; H, 6.22; N, 2.96.

(*E*)-ethyl 3-oxo-2-((2*E*,4*Z*,6*E*)-7-phenyl-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)indoline-1-carboxylate (3a)

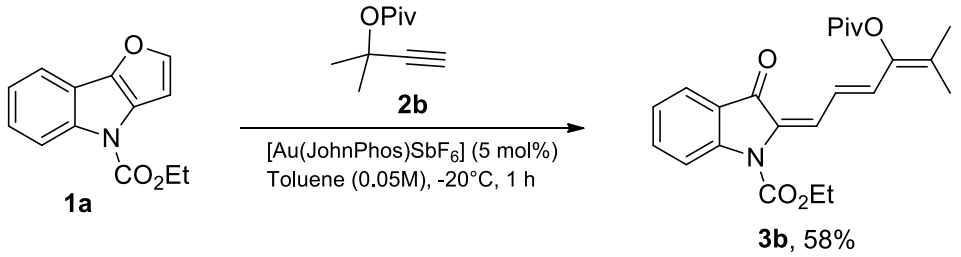


^{1}H NMR (300 MHz, CD_2Cl_2): 8.17 (dd, *J* = 15.1, 12.0 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.74 (m, 2H), 7.63 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.52 – 7.14 (m, 6H), 6.92 (dd, *J* = 15.6, 10.9 Hz, 1H) 6.81 (s, 1H), 6.68 (d, *J* = 15.1 Hz, 1H), 6.39 (d, *J* = 10.8 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 1.60 (s, 9H), 1.52 (d, *J* = 7.1, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2): 184.03 (C), 175.86 (C), 151.69 (C), 146.99 (C), 146.86 (C), 136.87 (C), 135.84 (CH), 135.78 (CH), 135.43 (CH), 132.15 (C), 128.73 (2xCH), 128.38 (CH), 127.11 (2xCH), 126.71 (CH), 124.87 (CH), 124.58 (CH), 124.22 (C), 123.81 (CH), 123.50 (CH), 121.79 (CH), 117.25 (CH), 63.21 (CH_2), 39.38 (C), 27.20 (3xCH_3), 14.16 (CH_3).

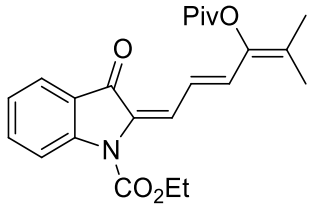
ESI(+)-MS: m/z(%) = 472 (100) $[M+H]^+$; $C_{29}H_{29}NO_5$ [471.54]: calcd. for C, 73.87; H, 6.20; N, 32.97; found C, 73.67; H, 6.18; N, 2.96.

Reaction between 1a and 2b



To a N_2-flushed solution of ethyl 4*H*-furo[3,2-*b*]indole-4-carboxylate **1a** (46 mg, 0.2 mmol) and [Au(JohnPhos)SbF_6] (5 mol%) in anhydrous toluene (2 mL), a solution of 2-methylbut-3-yn-2-yl pivalate **2b** (67 mg, 0.4 mmol) in toluene (2 mL, final concentration 0.05 M) was added dropwise at -20 °C. The reaction mixture was stirred for 1 h at -20 °C and then quenched with PPh_3 (15 mol%). Purification by flash chromatography (SiO_2, hexane/ ethyl acetate 95:5 to 9:1) yielded **3b** (46 mg, 58%) as a yellow solid (138.4 °C dec.).

(*E*)-ethyl 2-((*E*)-5-methyl-4-(pivaloyloxy)hexa-2,4-dien-1-ylidene)-3-oxoindoline-1-carboxylate (3b)

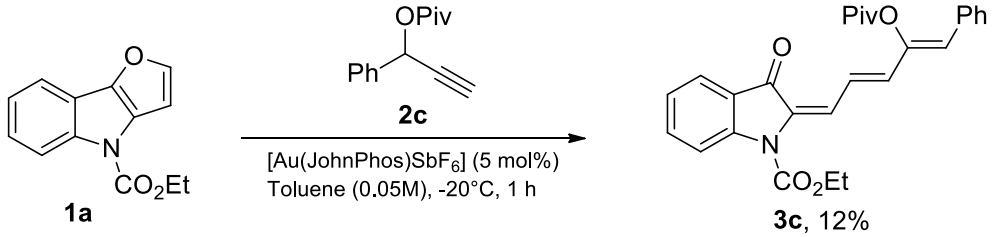


^{1}H NMR (300 MHz, $CDCl_3$): 8.06 – 7.93 (m, 2H), 7.90 – 7.74 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 14.7 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 1.99 (s, 3H), 1.75 (s, 3H), 1.61 – 1.42 (m, 12H).

^{13}C NMR (75 MHz, $CDCl_3$): 184.00 (C), 176.23 (C), 151.81 (C), 146.64 (C), 141.46 (C), 135.23 (CH), 133.11 (CH), 131.56 (C), 129.80 (C), 128.86 (CH), 124.45 (C), 123.79 (CH), 123.72 (CH), 122.36 (CH), 117.19 (CH), 62.98 (CH_2), 39.20 (C), 27.42 (3xCH_3), 19.27 (CH_3), 18.98 (CH_3), 14.41 (CH_3).

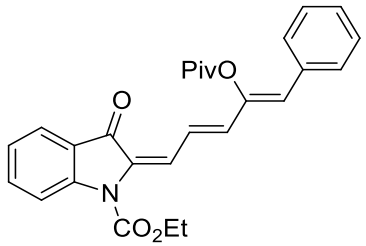
ESI(+)-MS: m/z(%) = 420 (100) $[M+Na]^+$; $C_{23}H_{27}NO_5$ [397.46]: calcd. for C, 69.50; H, 6.85; N, 3.52; found C, 69.36; H, 6.87; N, 3.54.

Reaction between 1a and 2c



To a N_2-flushed solution of ethyl 4*H*-furo[3,2-*b*]indole-4-carboxylate **1a** (46 mg, 0.2 mmol) and [Au(JohnPhos)SbF_6] (5 mol%) in anhydrous toluene (2 mL), a solution of 1-phenylprop-2-yn-1-yl pivalate **2c** (86 mg, 0.4 mmol) in toluene (2 mL, final concentration 0.05 M) was added dropwise at -20 °C. The reaction mixture was stirred for 1 h at -20 °C and then quenched with PPh_3 (15 mol%). Purification by flash chromatography (SiO_2, hexane/ ethyl acetate 95:5 to 9:1) yielded **3c** (11 mg, 12%) as a yellow oil.

(*E*)-ethyl 3-oxo-2-((2*E*,4*Z*)-5-phenyl-4-(pivaloyloxy)penta-2,4-dien-1-ylidene)indoline-1-carboxylate (3c)

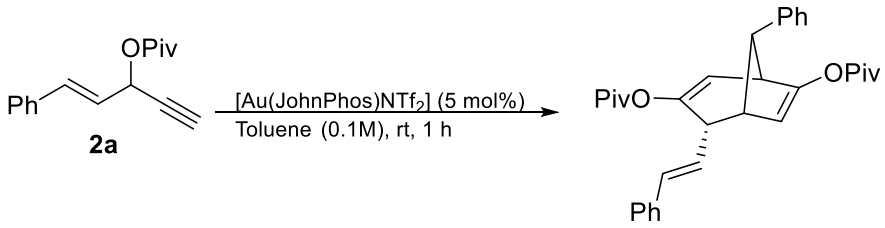


^{1}H NMR (300 MHz, $CDCl_3$): 8.15 (dd, *J* = 15.0, 11.8 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.81 (m, 2H), 7.58 (ddd, *J* = 8.6, 7.3, 1.4 Hz, 1H), 7.49 (m, 2H), 7.37 – 7.27 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.66 (s, 1H), 6.46 (s, 1H), 4.49 (q, *J* = 7.1 Hz, 3H), 1.58 – 1.41 (m, 12H).

^{13}C NMR (75 MHz, $CDCl_3$): 184.17 (C), 175.53 (C), 151.76 (C), 146.83 (C), 146.49 (C), 137.64 (CH), 135.48 (CH), 134.04 (C), 132.08 (C), 129.13 (2xCH), 128.38 (2xCH), 128.25 (CH), 127.64 (CH), 124.61 (CH), 124.37 (CH), 124.29 (C), 123.89 (CH), 117.24 (CH), 63.12 (CH_2), 39.30 (C), 27.47 (3xCH_3), 14.42 (CH_3). One CH is missing, probably overlapping.

ESI(+)-MS: m/z(%) = 468 (100) $[M+Na]^+$; $C_{27}H_{27}NO_5$ [445.51]: calcd. for C, 72.79; H, 6.11; N, 3.14; found 73.08; H, 6.09; N, 3.15.

Reaction of 2a under standard reaction conditions

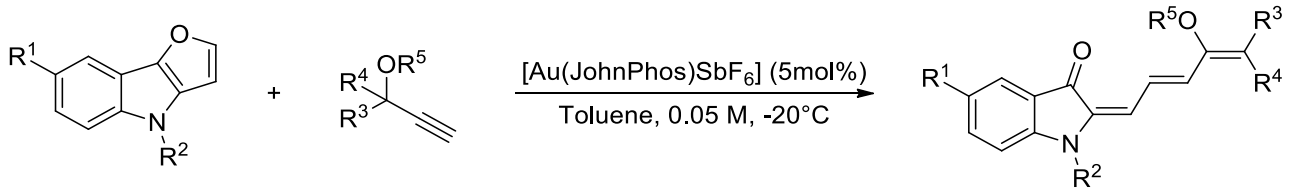


To a N_2-flushed solution of (*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate **2a** (97 mg, 0.4 mmol) in toluene (4 ml) was added [Au(JohnPhos)SbF_6] The reaction mixture was stirred for 1h at room temperature and then quenched with PPh_3 (15 mol%). Purification by flash chromatography (SiO_2, hexane/ ethyl acetate 98:2) yielded cycloadduc**t** (45 mg, 46%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): 7.45 – 7.06 (m, 10H), 6.52 (d, *J* = 15.7 Hz, 1H), 6.20 (dd, *J* = 6.9, 1.8 Hz, 1H), 6.07 (dd, *J* = 15.7, 9.8 Hz, 1H), 5.38 (d, *J* = 3.0 Hz, 1H), 3.95 – 3.76 (m, 1H), 3.55 (s, 1H), 3.19 (m, 1H), 3.12 (d, *J* = 7.0 Hz, 1H), 1.28 (s, 9H), 1.15 (s, 9H). Data are in agreement with those reported in literature.[5]

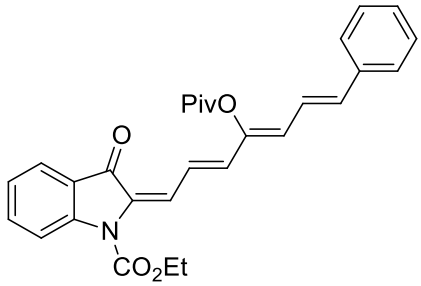
[5] J. Zhao, S. Yang, X. Xie, X. Li and Y. Liu, *J. Org. Chem.*, **2018**, *83*, 1287.

Preparation and characterization data for products 3a-n



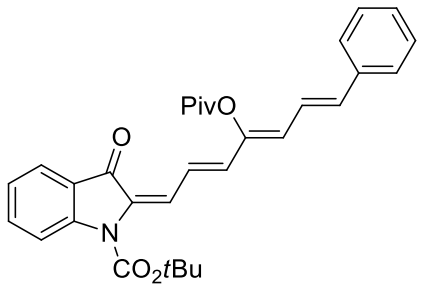
To a N_2-flushed solution of *N* protected 4*H*-furo[3,2-*b*]indole **1a-e** (1 equiv.) and [Au(JohnPhos)SbF_6] (5 mol%) in anhydrous toluene (2 mL), a solution of propargylic ester **2a-h** (1.2 or 2 equiv.) in toluene (2 mL, final concentration 0.05 M) was added dropwise at -20 °C. The reaction mixture was stirred for the stated time at -20 °C and then quenched with PPh_3 (15 mol%). Then the reaction mixture was warmed to room temperature and further stirred for 4 h in the presence of one crystal of I_2. The solvent was removed under reduced pression and the crude residue was purified by flash column chromatography to yield the desired product **3a-n**.

(*E*)-ethyl 3-oxo-2-((2*E*,4*Z*,6*E*)-7-phenyl-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)indoline-1-carboxylate (3a)



General procedure was followed using ethyl 4*H*-furo[3,2-*b*]indole-4-carboxylate **1a** (46 mg, 0.2 mmol), (*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate **2a** (58 mg, 0.24 mmol) and [Au(JohnPhos)SbF_6] (7.7 mg, 0.01 mmol) in anhydrous toluene (2+2 mL) at -20 °C for 1 h, followed by isomerization with I_2 for 4 h at rt. Purification by flash chromatography (SiO_2, toluene/ethyl acetate 99:1) yielded **3a** (89 mg, 98%). Data analysis are reported previously.

(*E*)-tert-butyl 3-oxo-2-((2*E*,4*Z*,6*E*)-7-phenyl-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)indoline-1-carboxylate (3d)



General procedure was followed using *tert*-butyl 4*H*-furo[3,2-*b*]indole-4-carboxylate **1b** (52 mg, 0.2 mmol), (*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate **2a** (58 mg, 0.24 mmol) and [Au(JohnPhos)SbF_6] (7.7 mg, 0.01

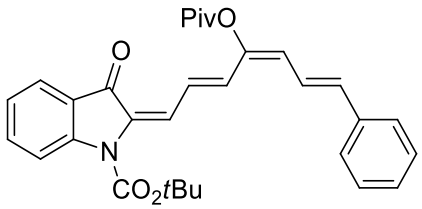
mmol) in anhydrous toluene (2+2 mL) at -20 °C for 1 h, followed by isomerization with I_2 for 4 h at rt. Purification by flash chromatography (SiO_2,toluene to toluene/ethyl acetate 98:2) yielded **3d** (75 mg, 75%) as a red solid (170.2 °C, dec).

^{1}H NMR (300 MHz, $CDCl_3$): 8.15 (dd, *J* = 14.9, 12.1 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.86 – 7.68 (m, 2H), 7.56 (m, 1H), 7.44 – 7.06 (m, 6H), 6.85 (dd, *J* = 15.5, 11.0 Hz, 1H), 6.71 (d, *J* = 15.7 Hz, 1H), 6.60 (d, *J* = 15.1 Hz, 1H), 6.31 (d, *J* = 11.0 Hz, 1H), 1.68 (s, 9H), 1.57 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 184.31 (C), 176.03 (C), 150.41 (C), 147.09 (C), 146.89 (C), 136.94 (C), 135.83 (CH), 135.75 (CH), 135.30 (CH), 132.32 (C), 128.74 (2xCH), 128.32 (CH), 127.54 (CH), 126.70 (2xCH), 124.88 (CH), 124.79 (CH), 124.19 (C), 123.80 (CH), 123.56 (CH), 121.89 (CH), 117.16 (CH), 84.21 (C), 39.50 (C), 28.32 (3xCH_3), 27.46 (3xCH_3).

ESI(+)-MS: m/z(%) = 500 (100) $[M+H]^+$; $C_{31}H_{33}NO_5$ [499.60]: calcd. for C, 74.53; H, 6.66; N, 2.80; found C, 74.78; H, 6.64; N, 2.79.

(*E*)-tert-butyl 3-oxo-2-((2*E*,4*E*,6*E*)-7-phenyl-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)indoline-1-carboxylate (3'd)



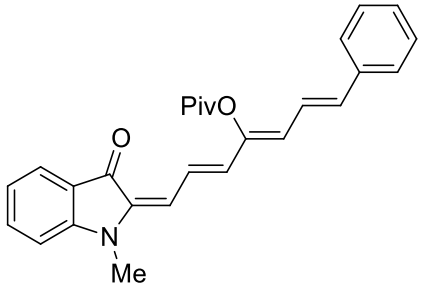
General procedure was followed using *tert*-butyl 4*H*-furo[3,2-*b*]indole-4-carboxylate **1b** (52 mg, 0.2 mmol), (*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate **2a** (58 mg, 0.24 mmol) and [Au(JohnPhos)SbF_6] (7.7 mg, 0.01 mmol) in anhydrous toluene (2+2 mL) at -20 °C for 1 h, avoiding the isomerization step with I_2. Purification by flash chromatography (SiO_2, toluene to toluene/ethyl acetate 98:2) yielded progressively **3'd** (35 mg, 35%) as red solid (177.3 °C, dec.) and **3d** (48 mg, 48%).

^{1}H NMR (500 MHz, $CDCl_3$): 8.24 (dd, *J* = 14.9, 12.1 Hz, 1H), 7.96 (dd, *J* = 22.2, 10.2 Hz, 2H), 7.82 (d, *J* = 7.0 Hz, 1H), 7.59 (m, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.31 (m, 1H), 7.26 – 7.15 (m, 2H), 7.12 (d, *J* = 14.9 Hz, 1H), 6.70 (d, *J* = 15.3 Hz, 1H), 6.19 (d, *J* = 11.7 Hz, 1H), 1.74 (s, 9H), 1.51 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): 184.35 (C), 177.00 (C), 150.50 (C), 147.05 (C), 146.76 (C), 137.00 (C), 135.52 (CH), 135.39 (CH), 132.77 (C), 130.72 (CH), 128.76 (2xCH), 128.20 (CH), 127.51 (CH), 126.74 (2xCH), 125.34 (CH), 125.20 (CH), 124.20 (C), 123.93 (CH), 123.65 (CH), 122.10 (CH), 117.18 (CH), 84.33 (C), 39.28 (C), 28.38 (3xCH_3), 27.37 (3xCH_3).

ESI(+)-MS: m/z(%) = 500 (100) $[M+H]^+$; $C_{31}H_{33}NO_5$ [499.60]: calcd. for C, 74.53; H, 6.66; N, 2.80; found C, 74.73; H, 6.68; N, 2.81.

(1*E*,3*Z*,5*E*,7*E*)-7-(1-methyl-3-oxoindolin-2-ylidene)-1-phenylhepta-1,3,5-trien-4-yl pivalate (3e)



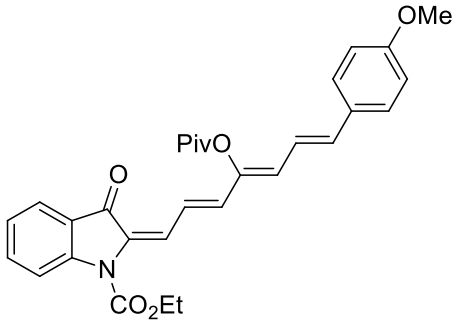
General procedure was followed using 4-methyl-4*H*-furo[3,2-*b*]indole **1c** (34 mg, 0.2 mmol), (*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate **2a** (58 mg, 0.24 mmol) and [Au(JohnPhos)SbF_6] (7.7 mg, 0.01 mmol) in anhydrous toluene (2+2 mL) at -20 °C for 1 h, followed by isomerization with I_2 for 4 h at rt. Purification by flash chromatography (SiO_2, toluene/ethyl acetate 99:1 to 98:2) yielded **3e** (33 mg, 40%) as a purple solid (m.p. 189.8-191.2 °C).

^{1}H NMR (300 MHz, $CDCl_3$): 7.99 (dd, *J* = 15.0, 12.0 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.13 (m, 6H), 6.99 – 6.77 (m, 3H), 6.67 (d, *J* = 15.6 Hz, 1H), 6.46 (d, *J* = 15.1 Hz, 1H), 6.25 (d, *J* = 11.2 Hz, 1H), 6.09 (d, *J* = 11.9 Hz, 1H), 3.22 (s, 3H), 1.60 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): 185.44 (C), 176.22 (C), 151.90 (C), 147.32 (C), 137.17 (C), 136.45 (C), 135.40 (CH), 134.61 (CH), 131.23 (CH), 128.75 (2xCH), 128.09 (CH), 126.60 (2xCH), 124.92 (CH), 124.47 (CH), 122.99 (CH), 122.12 (CH), 121.34 (C), 119.19 (CH), 115.14 (CH), 108.58 (CH), 39.53 (C), 28.53 (CH_3), 27.52 (3xCH_3).

ESI(+)-MS: m/z(%) = 414 (100) $[M+H]^+$; $C_{27}H_{27}NO_3$ [413.51]: calcd. for C, 78.42; H, 6.58; N, 3.39; found C, 78.35; H, 6.61; N, 3.38.

(*E*)-ethyl 2-((2*E*,4*Z*,6*E*)-7-(4-methoxyphenyl)-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)-3-oxoindoline-1-carboxylate (3f)



General procedure was followed using ethyl 4*H*-furo[3,2-*b*]indole-4-carboxylate **1a** (46 mg, 0.2 mmol), (*E*)-1-(4-methoxyphenyl)pent-1-en-4-yn-3-yl pivalate **2d** (109 mg, 0.4 mmol) and [Au(JohnPhos)SbF_6] (7.7 mg, 0.01 mmol) in anhydrous toluene (2+2 mL) at -20 °C for 1 h, followed by isomerization with I_2 for 4 h at rt. Purification by flash chromatography (SiO_2, hexane/ethyl acetate 9:1 to 8:2) yielded **3f** (89 mg, 89%) as a red solid (m.p. 154.3-156.8 °C).

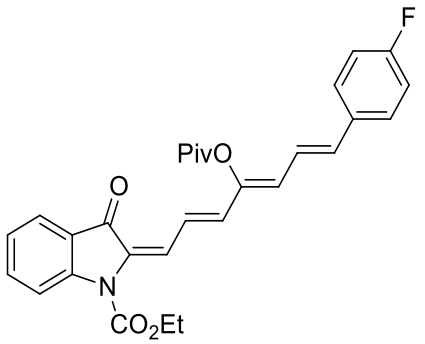
^{1}H NMR (300 MHz, $CDCl_3$): 8.11 (dd, *J* = 14.9, 11.9 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.81 (s, 1H), 7.78 (m, 1H), 7.57 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.19 (m, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.70

(d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 15.0 Hz, 1H), 6.30 (d, *J* = 9.9 Hz, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.57 (s, 9H), 1.49 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 184.01 (C), 176.01 (C), 159.95 (C), 151.75 (C), 146.65 (C), 146.05 (C), 136.40 (CH), 135.68 (CH), 135.28 (CH), 131.81 (C), 129.83 (C), 128.10 (2xCH), 127.97 (CH), 125.49 (CH), 124.40 (C), 124.09 (CH), 123.80 (2xCH), 119.90 (CH), 117.21 (CH), 114.28 (2xCH), 63.06 (CH_2), 55.30 (CH_3), 39.48 (C), 27.46 (3xCH_3), 14.40 (CH_3).

ESI(+)-MS: m/z(%) = 502 (100) $[M+H]^+$; $C_{30}H_{31}NO_6$ [501.57]: calcd. for C, 71.84; H, 6.23; N, 2.79; found C, 72.10; H, 6.25; N, 2.80.

(*E*)-ethyl 2-((2*E*,4*Z*,6*E*)-7-(4-fluorophenyl)-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)-3-oxoindoline-1-carboxylate (3g)



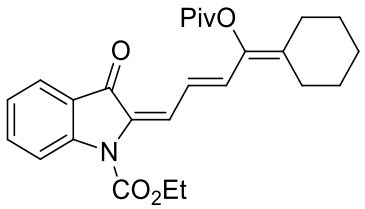
General procedure was followed using ethyl 4*H*-furo[3,2-*b*]indole-4-carboxylate **1a** (46 mg, 0.2 mmol), (*E*)-1-(4-fluorophenyl)pent-1-en-4-yn-3-yl pivalate **2e** (62 mg, 0.24 mmol) and [Au(JohnPhos)SbF_6] (7.7 mg, 0.01 mmol) in anhydrous toluene (2+2 mL) at -20 °C for 1 h, followed by isomerization with I_2 for 4 h at rt. Purification by flash chromatography (SiO_2, toluene/ethyl acetate 99:1) yielded **3g** (54 mg, 55%) as a red solid (m.p. 162.2-164.3 °C).

^{1}H NMR (300 MHz, $CDCl_3$): 8.16 (dd, *J* = 14.9, 12.1 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.88 – 7.73 (m, 2H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H),7.03 (t, *J* = 8.6 Hz, 2H), 6.85 – 6.56 (m, 3H), 6.32 (d, *J* = 10.3 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 1.59 (s, 9H), 1.51 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 184.14 (C), 176.09 (C), 162.69 (d, *J* = 249.1 Hz, C), 151.75 (C), 146.83 (d, *J* = 1.1 Hz, C),146.68 (C), 136.13 (CH), 135.46 (CH), 134.55 (CH), 133.15 (d, *J* = 3.4 Hz, C), 132.03 (C), 128.28 (d, *J* = 8.0 Hz, 2xCH), 127.72 (CH), 124.87 (CH), 124.71 (CH), 124.30 (C), 123.90 (CH), 123.87 (CH), 121.57 (d, *J* = 2.3 Hz, CH), 117.26 (CH), 115.83 (d, *J* = 21.9 Hz, 2xCH), 63.15 (CH_2), 39.53 (C), 27.47 (3xCH_3), 14.43 (CH_3).

ESI(+)-MS: m/z(%) = 490 (100) $[M+H]^+$; $C_{29}H_{28}FNO_5$ [489.53]: calcd. for C, 71.15; H, 5.77; N, 2.86; found C, 71.37; H, 5.79; N, 2.86.

(*E*)-ethyl 2-((*E*)-4-cyclohexylidene-4-(pivaloyloxy)but-2-en-1-ylidene)-3-oxoindoline-1-carboxylate (3h)



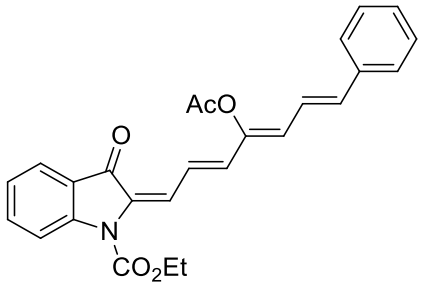
General procedure was followed using ethyl 4*H*-furo[3,2-*b*]indole-4-carboxylate **1a** (46 mg, 0.2 mmol), 1-ethynylcyclohexyl acetate **2f** (83 mg, 0.4 mmol) and [Au(JohnPhos)SbF_6] (7.7 mg, 0.01 mmol) in anhydrous toluene (2+2 mL) at -20 °C for 22 h, followed by isomerization with I_2 for 4 h at rt. Purification by flash chromatography (SiO_2, hexane/ethyl acetate 95:5 to 9:1) yielded **3h** (32 mg, 36%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): 8.06 – 7.94 (m, 2H), 7.86 – 7.72 (m, 2H), 7.56 (m, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 14.8 Hz, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 2.58 – 2.34 (m, 2H), 2.16 (d, *J* = 6.6 Hz, 2H), 1.77 – 1.01 (m, 18H).

^{13}C NMR (75 MHz, $CDCl_3$): 184.00 (C), 176.48 (C), 151.82 (C), 146.64 (C), 138.65 (C), 137.83 (C), 135.21 (CH), 132.88 (CH), 131.44 (C), 129.06 (CH), 124.47 (C), 123.79 (CH), 123.71 (CH), 122.64 (CH), 117.20 (CH), 62.98 (CH_2), 39.19 (C), 29.76 (CH_2), 28.89 (CH_2), 27.76 (CH_2), 27.46 (3xCH_3), 27.07 (CH_2), 26.29 (CH_2), 14.43 (CH_3).

ESI(+)-MS: m/z(%) = 438 (100) $[M+H]^+$; $C_{26}H_{31}NO_5$ [437.53]: calcd. for C, 71.37; H, 7.14; N, 3.20; found C, 71.18; H, 7.11; N, 3.22.

(*E*)-ethyl 2-((2*E*,4*Z*,6*E*)-4-acetoxy-7-phenylhepta-2,4,6-trien-1-ylidene)-3-oxoindoline-1-carboxylate (3i)



General procedure was followed using ethyl 4*H*-furo[3,2-*b*]indole-4-carboxylate **1a** (46 mg, 0.2 mmol), (*E*)-1-phenylpent-1-en-4-yn-3-yl acetate **2g** (48 mg, 0.24 mmol) and [Au(JohnPhos)SbF_6] (7.7 mg, 0.01 mmol) in anhydrous toluene (2+2 mL) at -20 °C for 2 h, followed by isomerization with I_2 for 4 h at rt. Purification by flash chromatography (SiO_2, hexane/ethyl acetate 9:1 to 8:2) yielded **3i** (48 mg, 56%) as a red solid (m.p. 88.2-90.1 °C).

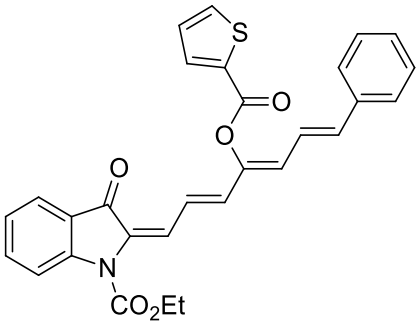
^{1}H NMR (300 MHz, $CDCl_3$): 8.21 (dd, *J* = 15.0, 12.0 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.77 (m, 2H), 7.61 (m, 1H), 7.53 – 7.41 (m, 2H), 7.37 – 7.17 (m, 4H), 6.87 (d, *J* = 10.9 Hz, 1H), 6.75 (d, *J* = 15.8 Hz, 1H), 6.62 (d, *J* = 15.0 Hz, 1H), 6.35 (d, *J* = 10.9 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 2.53 (s, 3H), 1.51 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 184.37 (C), 168.72 (C), 151.73 (C), 146.73 (C), 146.59 (C), 136.81 (C), 136.43 (CH), 135.79 (CH), 135.57 (CH), 132.08 (C), 128.72 (2xCH), 128.47 (CH), 127.74 (CH), 126.94 (2xCH),

125.39 (CH), 124.81 (CH), 124.31 (C), 123.99 (CH), 123.76 (CH), 121.92 (CH), 117.31 (CH), 63.18 (CH_2), (CH_3), 14.42 (CH_3).

ESI(+)-MS: m/z(%) = 452 (100) $[M+Na]^+$; $C_{26}H_{23}NO_5$ [429.46.

(*E*)-ethyl 3-oxo-2-((2*E*,4*Z*,6*E*)-7-phenyl-4-((thiophene-2-carbonyl)oxy)hepta-2,4,6-trien-1-ylidene)indoline-1-carboxylate (3j)



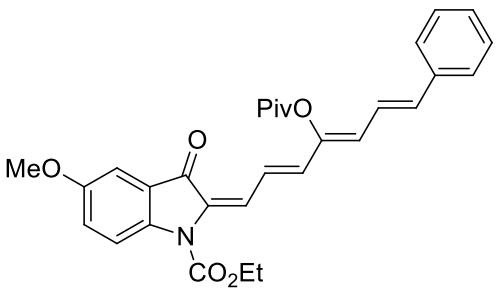
General procedure was followed using ethyl 4*H*-furo[3,2-*b*]indole-4-carboxylate **1a** (46 mg, 0.2 mmol (*E*)-1-phenylpent-1-en-4-yn-3-yl thiophene-2-carboxylate **2h** (65 mg, 0.24 mmol) and [Au(JohnPhos)SbF_6] (7.7 mg, 0.01 mmol) in anhydrous toluene (2+2 mL) at -20 °C for 22 h, followed by isomerization with I_2 for 4 h at rt. Purification by flash chromatography (SiO_2, hexane/ethyl acetate 9:1+1% dichloromethane) yielded **3j** (98 mg, 98%) as a red solid (m.p. 172.3-174.5 °C).

^{1}H NMR (300 MHz, $CDCl_3$): 8.29 (dd, *J* = 15.0, 12.0 Hz, 1H), 8.14 (dd, *J* = 3.7, 1.1 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 12.0 Hz, 1H), 7.79 – 7.70 (m, 2H), 7.56 (m, 1H), 7.43 – 7.36 (m, 2H), 7.34 – 7.14 (m, 5H), 6.95 (dd, *J* = 15.5, 11.0 Hz, 1H), 6.78 (d, *J* = 15.7 Hz, 1H), 6.71 (d, *J* = 15.1 Hz, 1H), 6.46 (d, *J* = 11.0 Hz, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 184.56 (C), 160.12 (C), 152.13 (C), 147.13 (C), 146.59 (C), 137.16 (C), 137.02 (CH), 136.58 (CH), 135.83 (CH), 135.61 (CH), 134.34 (CH), 132.45 (C), 132.40 (C), 129.06 (2xCH), 128.84 (CH), 128.71 (CH), 128.19 (CH), 127.38 (2xCH), 126.04 (CH), 125.39 (CH), 124.67 (C), 124.29 (CH), 124.22 (CH), 122.41 (CH), 117.65 (CH), 63.55 (CH_2), 14.81 (CH_3).

ESI(+)-MS: m/z(%) = 520 (100) $[M+Na]^+$; $C_{29}H_{23}NO_5S$ [497.56].

(*E*)-ethyl 5-methoxy-3-oxo-2-((2*E*,4*Z*,6*E*)-7-phenyl-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)indoline-1-carboxylate (3k)



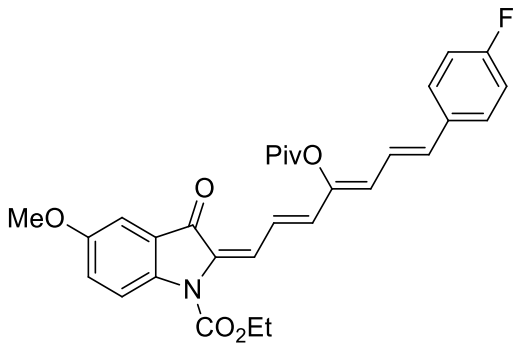
General procedure was followed using ethyl 7-methoxy-4*H*-furo[3,2-*b*]indole-4-carboxylate**1d** (52 mg, 0.2 mmol), (*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate **2a** (58 mg, 0.24 mmol) and [Au(JohnPhos)SbF_6] (7.7 mg, 0.01 mmol) in anhydrous toluene (2+2 mL) at -20 °C for 2 h, followed by isomerization with I_2 for 4 h at rt. Purification by flash chromatography (SiO_2, toluene/ethyl acetate 99:1 to 98:2) yielded **3k** (77 mg, 75%) as a red solid (m.p. 164.2-166.5 °C).

^{1}H NMR (300 MHz, $CDCl_3$): 8.12 (dd, *J* = 14.9, 12.1 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 12.2 Hz, 1H), 7.45 – 7.08 (m, 7H), 6.85 (dd, *J* = 15.6, 10.9 Hz, 1H), 6.76 – 6.56 (m, 2H), 6.32 (d, *J* = 10.8 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.58 (s, 9H), 1.48 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 183.92 (C), 175.96 (C), 156.43 (C), 151.60 (C), 146.85 (C), 141.25 (C), 136.93 (C), 136.20 (CH), 135.90 (CH), 132.52 (C), 128.73 (2xCH), 128.33 (CH), 127.92 (CH), 126.71 (2xCH), 125.05 (CH), 124.68 (CH), 124.13 (CH), 121.87 (CH), 118.40 (CH), 105.09 (CH), 62.92 (CH_2), 55.77 (CH_3), 39.49 (C), 27.46 (3xCH_3), 14.41 (CH_3), one quaternary carbon is missing, probably overlapping.

ESI(+)-MS: m/z(%) = 502 (100) $[M+H]^+$; $C_{30}H_{31}NO_6$ [501.57]: calcd. for C, 71.84; H, 6.23; N, 2.79; found C, 71.62; H, 6.20; N, 2.80.

(*E*)-ethyl 2-((2*E*,4*Z*,6*E*)-7-(4-fluorophenyl)-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)-5-methoxy-3-oxoindoline-1-carboxylate (3l)



General procedure was followed using ethyl 7-methoxy-4*H*-furo[3,2-*b*]indole-4-carboxylate**1d** (52 mg, 0.2 mmol), (*E*)-1-(4-fluorophenyl)pent-1-en-4-yn-3-yl pivalate **2e** (62 mg, 0.24 mmol) and [Au(JohnPhos)SbF_6] (7.7 mg, 0.01 mmol) in anhydrous toluene (2+2 mL) at -20 °C for 2 h, followed by isomerization with I_2 for 4 h at rt. Purification by flash chromatography (SiO_2, hexane/ethyl acetate 95:5 to 91) yielded **3l** (70 mg, 67%) as a red solid (m.p. 161.5-163.7 °C).

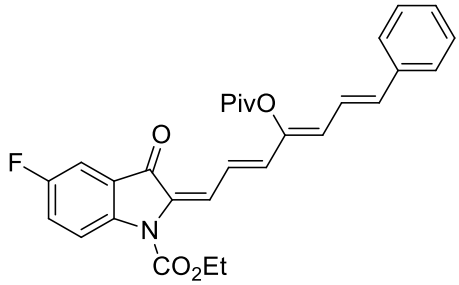
^{1}H NMR (300 MHz, $CDCl_3$): 8.12 (dd, *J* = 15.0, 12.1 Hz, 1H), 7.90 (d, *J* = 9.1 Hz, 1H), 7.79 (d, *J* = 12.1 Hz, 1H), 7.33 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.22 (d, *J* = 2.7 Hz, 1H), 7.15 (dd, *J* = 9.0, 2.8 Hz, 1H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.76 – 6.55 (m, 3H), 6.29 (d, *J* = 10.2 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.57 (s, 9H), 1.48 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 183.95 (C), 175.96 (C), 162.69 (d, *J* = 249.1 Hz, C), 156.45 (C), 151.61 (C), 146.86 (C), 141.26 (C), 136.07 (CH), 134.48 (CH), 133.18 (d, *J* = 3.4 Hz, C), 132.57 (C), 128.24 (d, *J* = 8.0 Hz, 2xCH), 127.85 (CH), 125.05 (C), 124.78 (CH),124.75 (CH), 124.17 (CH), 121.63 (CH), 118.41 (CH),

115.79 (d, *J* = 21.9 Hz, 2xCH), 105.10 (CH), 62.93 (CH_2), 55.77 (CH_3), 39.49 (C), 27.45 (3xCH_3), 14.41 (CH_3).

ESI(+)-MS: m/z(%) = 520 (100) $[M+H]^+$; $C_{30}H_{30}FNO_6$ [519.56]: calcd. for C, 69.35; H, 5.82; N, 2.70; found C, 69.13; H, 5.84; N, 2.69

(*E*)-ethyl 5-fluoro-3-oxo-2-((2*E*,4*Z*,6*E*)-7-phenyl-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)indoline-1-carboxylate (3m)



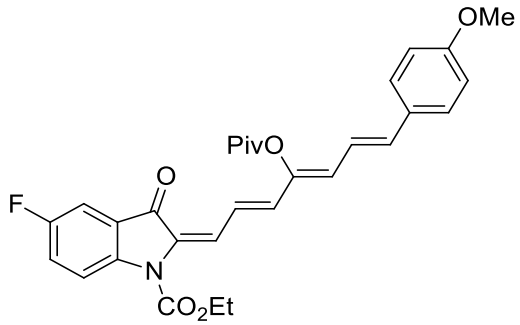
General procedure was followed using ethyl 7-fluoro-4*H*-furo[3,2-*b*]indole-4-carboxylate **1e** (49 mg, 0.2 mmol), (*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate **2a** (97 mg, 0.4 mmol) and [Au(JohnPhos)SbF_6] (7.7 mg, 0.01 mmol) in anhydrous toluene (2+2 mL) at -20 °C for 1 h, followed by isomerization with I_2 for 4 h at rt. Purification by flash chromatography (SiO_2, hexane/ethyl acetate 95:5 to 9:1) yielded **3m** (82 mg, 84%) as a red solid (m.p.144.6-146.1 °C).

^{1}H NMR (300 MHz, $CDCl_3$): 8.10 (dd, *J* = 14.9, 12.2 Hz, 1H), 7.98 (dd, *J* = 9.0, 3.9 Hz, 1H), 7.78 (d, *J* = 12.1 Hz, 1H), 7.44 (dd, *J* = 6.8, 2.7 Hz, 1H), 7.40 – 7.22 (m, 6H), 6.85 (dd, *J* = 15.6, 10.9 Hz, 1H), 6.76 – 6.59 (m, 2H), 6.33 (d, *J* = 10.9 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 1.57 (s, 9H), 1.48 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 183.00 (C), 175.98 (C), 159.27 (d, *J* = 245.6 Hz, C), 151.50 (C), 146.77 (C), 142.82 (C), 136.86 (C), 136.83 (CH), 136.20 (CH), 132.15 (C), 128.74 (2xCH), 128.58 (CH), 128.42 (CH), 126.74 (2xCH), 125.49 (d, *J* = 7.7 Hz, C), 125.50 (CH), 124.46 (CH), 122.46 (d, *J* = 24.3 Hz, CH), 121.81 (CH), 118.76 (d, *J* = 7.4 Hz, CH), 109.47 (d, *J* = 23.4 Hz, CH), 63.21 (CH_2), 39.50 (C), 27.43 (3xCH_3), 14.38 (CH_3).

ESI(+)-MS: m/z(%) = 490 (100) $[M+H]^+$; $C_{29}H_{28}FNO_5$ [489.53]: calcd. for C, 71.15; H, 5.77; N, 2.86; found C, 71.43; H, 5.75; N, 2.85.

(*E*)-ethyl 5-fluoro-2-((2*E*,4*Z*,6*E*)-7-(4-methoxyphenyl)-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)-3-oxoindoline-1-carboxylate (3n)



General procedure was followed using ethyl 7-fluoro-4*H*-furo[3,2-*b*]indole-4-carboxylate**1e** (49 mg, 0.2 mmol), (*E*)-1-(4-methoxyphenyl)pent-1-en-4-yn-3-yl pivalate **2d** (109 mg, 0.4 mmol) and [Au(JohnPhos)SbF_6] (7.7 mg, 0.01 mmol) in anhydrous toluene (2+2 mL) at -20 °C for 1 h, followed by isomerization with I_2 for 4 h at rt. Purification by flash chromatography (SiO_2, dichloromethane/hexane 95:5) yielded **3n** (102 mg, 98%) as a red solid (m.p. 175.9-177.6 °C).

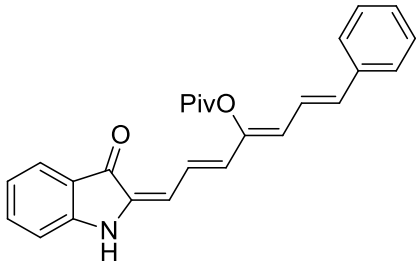
1H NMR (300 MHz, $CDCl_3$): 8.22 – 7.94 (m, 2H), 7.77 (d, *J* = 12.1 Hz, 1H), 7.43 (dd, *J* = 6.9, 2.7 Hz, 1H), 7.36 – 7.24 (m, 3H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.76 – 6.55 (m, 3H), 6.31 (d, *J* = 9.3 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.57 (s, 9H), 1.48 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 182.94 (C), 176.00 (C), 160.01 (C), 159.25 (d, *J* = 245.5 Hz, C), 151.49 (C), 145.98 (C), 142.74 (C), 137.10 (CH), 136.03 (CH), 131.92 (C), 129.75 (C), 128.86 (CH), 128.15 (2xCH), 126.05 (CH), 125.55 (d, *J* = 7.6 Hz, C), 123.87 (CH), 122.35 (d, *J* = 24.2 Hz, CH), 119.82 (CH), 118.73 (d, *J* = 7.4 Hz, CH), 114.28 (2xCH), 109.40 (d, *J* = 23.3 Hz, CH), 63.17 (CH_2), 55.28 (CH_3), 39.48 (C), 27.45 (3xCH_3), 14.38 (CH_3).

ESI(+)-MS: m/z(%) = 542 (100) $[M+Na]^+$; $C_{30}H_{30}FNO_6$ [519.56]: calcd. for C, 69.35; H, 5.82; N, 2.70; found C, 69.64; H, 5.80; N, 2.69.

Preparation and characterization data for products 3o, 5a-b, 6 and 7

(1*E*,3*Z*,5*E*,7*E*)-7-(3-oxoindolin-2-ylidene)-1-phenylhepta-1,3,5-trien-4-yl pivalate (3o)



To a solution of (*E*)-tert-butyl 3-oxo-2-((2*E*,4*Z*,6*E*)-7-phenyl-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)indoline-1-carboxylate **3d** (57 mg, 0.11 mmol) in dichloromethane (1 ml), trifluoroacetic acid (0.1 mL) was added. The mixture was stirred at room temperature for 2 h, then the reaction was quenched with 1 N sodium hydroxide aqueous solution and extracted with dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 3:1) to yield (1*E*,3*Z*,5*E*,7*E*)-7-(3-oxoindolin-2-ylidene)-1-phenylhepta-1,3,5-trien-4-yl pivalate **3o** (30 mg, 68%) as a red solid (m.p. 198.2-200.1 °C).

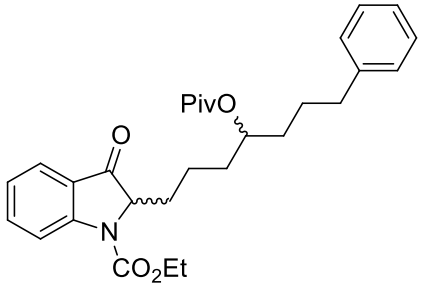
Alternatively, **3o** was prepared from **3a** according to the following procedure. To a solution of (*E*)-ethyl 3-oxo-2-((2*E*,4*Z*,6*E*)-7-phenyl-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)indoline-1-carboxylate **3a** (35 mg, 0.07 mmol) in methanol (0.7 ml), K_2CO_3 (10 mg, 0.07 mmol) was added. The mixture was stirred at 60 °C for 2 h, then the reaction extracted with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 3:1) to yield (1*E*,3*Z*,5*E*,7*E*)-7-(3-oxoindolin-2-ylidene)-1-phenylhepta-1,3,5-trien-4-yl pivalate **3o** (8 mg, 29%).

^{1}H NMR (300 MHz, DMSO): 10.06 (s, 1H), 7.63 – 7.23 (m, 7H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.94 – 6.65 (m, 4H), 6.64 – 6.52 (m, 1H), 6.51 – 6.42 (m, 2H), 1.43 (d, *J* = 24.0 Hz, 9H).

^{13}C NMR (75 MHz, DMSO): 185.70 (C), 175.93 (C), 152.89 (C), 146.98 (C), 136.99 (C), 136.49 (CH), 136.41 (C), 135.80 (CH), 133.25 (CH), 129.43 (2xCH), 128.92 (CH), 126.99 (2xCH), 124.47 (CH), 124.07 (CH), 123.09 (CH), 121.95 (CH), 121.16 (C), 120.00 (CH), 112.49 (CH), 110.94 (CH), 139.50 (C) 27.57 (3xCH_3).

ESI(+)-MS: m/z(%) = 400 (100) $[M+H]^+$; $C_{26}H_{25}NO_3$ [399.48]: calcd. for C, 78.17; H, 6.31; N, 3.51; found C, 77.95; H, 6.30; N, 3.53.

Ethyl 3-oxo-2-(7-phenyl-4-(pivaloyloxy)heptyl)indoline-1-carboxylate (5a)



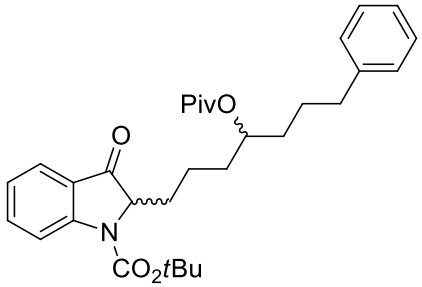
To a solution of (*E*)-ethyl 3-oxo-2-((2*E*,4*Z*,6*E*)-7-phenyl-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)indoline-1-carboxylate **3a** (70 mg, 0.15 mmol) in ethyl acetate, Pd/C (7 mg, 10% wt) was added. The reaction mixture was stirred under H_2 at room temperature overnight, then was filtered over a pad of celite and the solvent was evaporated under reduce pression. The crude residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 9:1) to yield ethyl 3-oxo-2-(7-phenyl-4-(pivaloyloxy)heptyl)indoline-1-carboxylate **5a** as a mixture of two diastereoisomers (45 mg, 63%, 1:1) as a pale oil.

^{1}H NMR (300 MHz, $CDCl_3$): 8.14 (s, 2H), 7.71 (dd, *J* = 7.7, 3.5 Hz, 2H), 7.68 – 7.58 (m, 2H), 7.33 – 7.22 (m, 4H), 7.22 – 7.08 (m, 8H), 4.86 – 4.74 (m, 2H), 4.44 – 4.22 (m, 6H), 2.67 – 2.49 (m, 4H), 2.32 – 1.96 (m, 4H), 1.66 – 1.45 (m, 12H), 1.41 (t, *J* = 7.1 Hz, 6H), 1.30 – 1.17 (m, 4H), 1.14 (s, 9H), 1.11 (s, 9H). Most signals are overlapped for two diastereoisomers.

^{13}C NMR (75 MHz, $CDCl_3$): 199.57 (C), 199.39 (C), 178.41 (2xC), 152.42 (2xC), 142.48 (4xC), 137.46 (CH), 137.34 (CH), 128.70 (3xCH), 128.67 (3xCH), 126.13 (4xCH), 124.63 (2xC) 124.15 (CH), 124.03 (CH), 123.71 (CH), 123.64 (CH), 117.28 (CH), 117.24 (CH), 73.24 (CH), 72.93 (CH), 65.54 (2xCH), 62.80 (CH_2), 62.76 (CH_2), 39.16 (C), 39.14 (C), 35.97 (2x CH_2), 34.40 (CH_2), 34.30 (CH_2), 34.13 (CH_2), 33.98 (CH_2), 31.14 (CH_2), 30.98 (CH_2), 27.52 (3xCH_3), 27.50 (3xCH_3), 27.32 (CH_2), 27.28 (CH_2), 19.29 (CH_2), 19.02 (CH_2), 14.92 (CH_3), 14.90 (CH_3).

ESI(+)-MS: m/z(%) = 502 (100) $[M+Na]^+$; $C_{29}H_{37}NO_5$ [479.27].

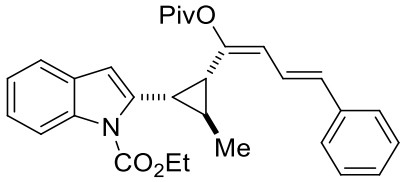
***Tert*-butyl 3-oxo-2-(7-phenyl-4-(pivaloyloxy)heptyl)indoline-1-carboxylate (5b)**



To a solution of (*E*)-tert-butyl 3-oxo-2-((2*E*,4*Z*,6*E*)-7-phenyl-4-(pivaloyloxy)hepta-2,4,6-trien-1-ylidene)indoline-1-carboxylate **3d** (88 mg, 0.17 mmol) in ethyl acetate, Pd/C (9 mg, 10% wt) was added. The reaction mixture was stirred under H_2 at room temperature overnight, then was filtered over a pad of celite and the solvent was evaporated under reduce pression. The crude residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 9:1 to 8:2) to yield **5b** as a mixture of two diastereoisomers (41 mg, 47%, 1:1) as a yellow oil.

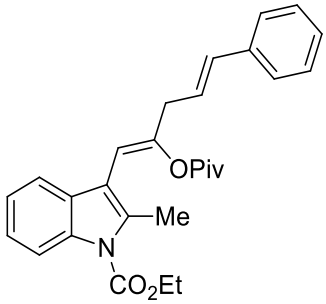
^{1}H NMR (300 MHz, $CDCl_3$): 8.09 (bs, 2H), 7.71 – 7.64 (m, 2H), 7.60 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 2H), 7.30 – 7.21 (m, 4H), 7.19 – 7.04 (m, 8H), 4.85 – 4.72 (m, 2H), 4.23 (bs, 2H), 2.60 – 2.51 (m, 4H), 2.16 – 2.00 (m, 4H), 1.64 – 1.43 (m, 34H), 1.11 (s, 9H), 1.08 (s, 9 H). Most signals are overlapped for two diastereoisomers.
^{13}C NMR (75 MHz, $CDCl_3$): 199.28 (2xC), 177.98 (2xC), 150.88 (2xC), 142.08 (2xC), 136.93 (2xCH), 128.29 (3xCH), 128.25 (3xCH), 125.70 (4xCH), 124.16 (2xC), 123.67 (CH), 123.58 (CH), 122.95 (CH), 122.89 (CH), 116.85 (CH), 116.75 (CH), 82.42 (2xC), 72.90 (CH), 72.82 (CH), 65.21 (2xCH), 38.74 (2xC), 35.58 (2xCH_2), 34.09 (CH_2), 34.02 (CH_2), 33.57 (2xCH_2), 30.84 (2xCH_2), 28.32 (6xCH_3), 27.11 (3xCH_3), 27.08 (3xCH_3), 26.86 (2xCH_2), 18.92 (CH_2), 18.82(CH_2). 2 quaternary carbons are missing, probably overlapped.
ESI(+)-MS: m/z(%) = 530 (100) $[M+Na]^+$; $C_{31}H_{41}NO_5$ [507.66].

Ethyl 2-(2-methyl-3-((1*Z*,3*E*)-4-phenyl-1-(pivaloyloxy)buta-1,3-dien-1-yl)cyclopropyl)-1*H*-indole-1-carboxylate (6)



To a N_2-flushed solution of (*E*)-ethyl 2-(prop-1-en-1-yl)-1*H*-indole-1-carboxylate **1f** (46 mg, 0.2 mmol) and [Au(JohnPhos)SbF_6] (5 mol%) in anhydrous toluene (2 mL), (*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate **2a** (97 mg, 0.4 mmol) in toluene (2 mL, final concentration 0.05 M) was added dropwise at -20 °C. The reaction mixture was stirred for 1 h at -20 °C and then quenched with PPh_3 (15 mol%). Purification by flash chromatography (SiO_2, hexane/ ethyl acetate 98:2) yielded **6** (41 mg, 43%) as a yellow oil.
^{1}H NMR (300 MHz, CD_2Cl_2): 7.99 (d, *J* = 8.3 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.42 – 7.34 (m, 2H), 7.31 – 7.10 (m, 4H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.37 (s, 1H), 5.89 (d, *J* = 11.3 Hz, 1H), 4.43 – 4.18 (m, 2H), 2.89 (dd, *J* = 8.1, 6.4 Hz, 1H), 2.35 (dd, *J* = 8.6, 5.6 Hz, 1H), 1.77 (m, 1H), 1.46 – 1.27 (m, 6H), 1.12 (s, 9H).
^{13}C NMR (75 MHz, CD_2Cl_2): 176.28(C), 151.80 (C), 148.19 (C), 139.13 (C), 137.63 (C), 136.42 (C), 131.81 (CH), 129.09 (C),128.55 (2xCH), 127.35 (CH), 126.27 (2xCH), 123.41 (CH), 123.24 (CH), 122.61 (CH), 120.37 (CH), 119.79 (CH), 115.42 (CH), 107.60 (CH), 63.06 (CH_2), 38.68 (C), 29.00 (CH), 27.95 (CH), 26.70 (3xCH_3), 19.65 (CH), 17.74 (CH_3), 13.99 (CH_3).
ESI(+)-MS: m/z(%) = 494 (100) $[M+Na]^+$; $C_{30}H_{33}NO_4$ [471.59]: calcd. for C, 76.41; H, 7.05; N, 2.97; found C, 76.25; H, 7.02; N, 2.98

Ethyl 2-methyl-3-((1*Z*,4*E*)-5-phenyl-2-(pivaloyloxy)penta-1,4-dien-1-yl)-1*H*-indole-1-carboxylate (7)



To a N_2-flushed solution of (*E*)-ethyl 2-(prop-1-en-1-yl)-1*H*-indole-1-carboxylate**1g** (46 mg, 0.2 mmol) and [Au(JohnPhos)SbF_6] (5 mol%) in anhydrous toluene (2 mL), (*E*)-1-phenylpent-1-en-4-yn-3-yl pivalate **2a** (97 mg, 0.4 mmol) in toluene (2 mL, final concentration 0.05 M) was added dropwise at -20 °C. The reaction mixture was stirred for 1 h at -20 °C and then quenched with PPh_3 (15 mol%). Purification by flash chromatography (SiO_2, hexane/ ethyl acetate 98:2) yielded **7** (44 mg, 50%) as a yellow oil.

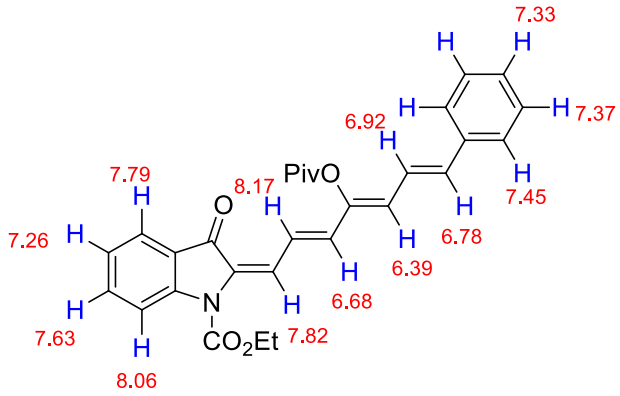
^{1}H NMR (300 MHz, C_6D_6): 8.52 (dd, *J* = 7.0, 1.8 Hz, 1H), 7.81 (dd, *J* = 6.5, 2.2 Hz, 1H), 7.53 – 6.90 (m, 7H), 6.58 (d, *J* = 15.7 Hz, 1H), 6.35 (dt, *J* = 15.8, 7.0 Hz, 1H), 6.09 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.47 (d, *J* = 7.0 Hz, 2H), 2.65 (s, 3H), 1.16 – 0.88 (m, 12H).

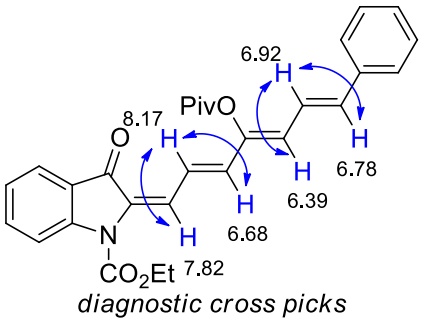
^{13}C NMR (75 MHz, C_6D_6): 175.46 (C), 151.78 (C), 151.07 (C), 137.39 (C), 136.09 (C), 134.69 (C), 133.53 (CH), 129.47 (C),128.64 (3xCH), 126.37 (2xCH), 125.15 (CH), 123.84 (CH), 122.90 (CH), 119.99 (CH), 115.72 (CH), 114.21 (C), 108.30 (CH), 62.47 (CH_2), 38.68 (C), 37.62 (CH_2), 26.75 (3xCH_3), 14.90 (CH_3), 13.75 (CH_3).

ESI(+)-MS: m/z(%) = 446 (100) $[M+H]^+$; $C_{28}H_{31}NO_4$ [445.55].

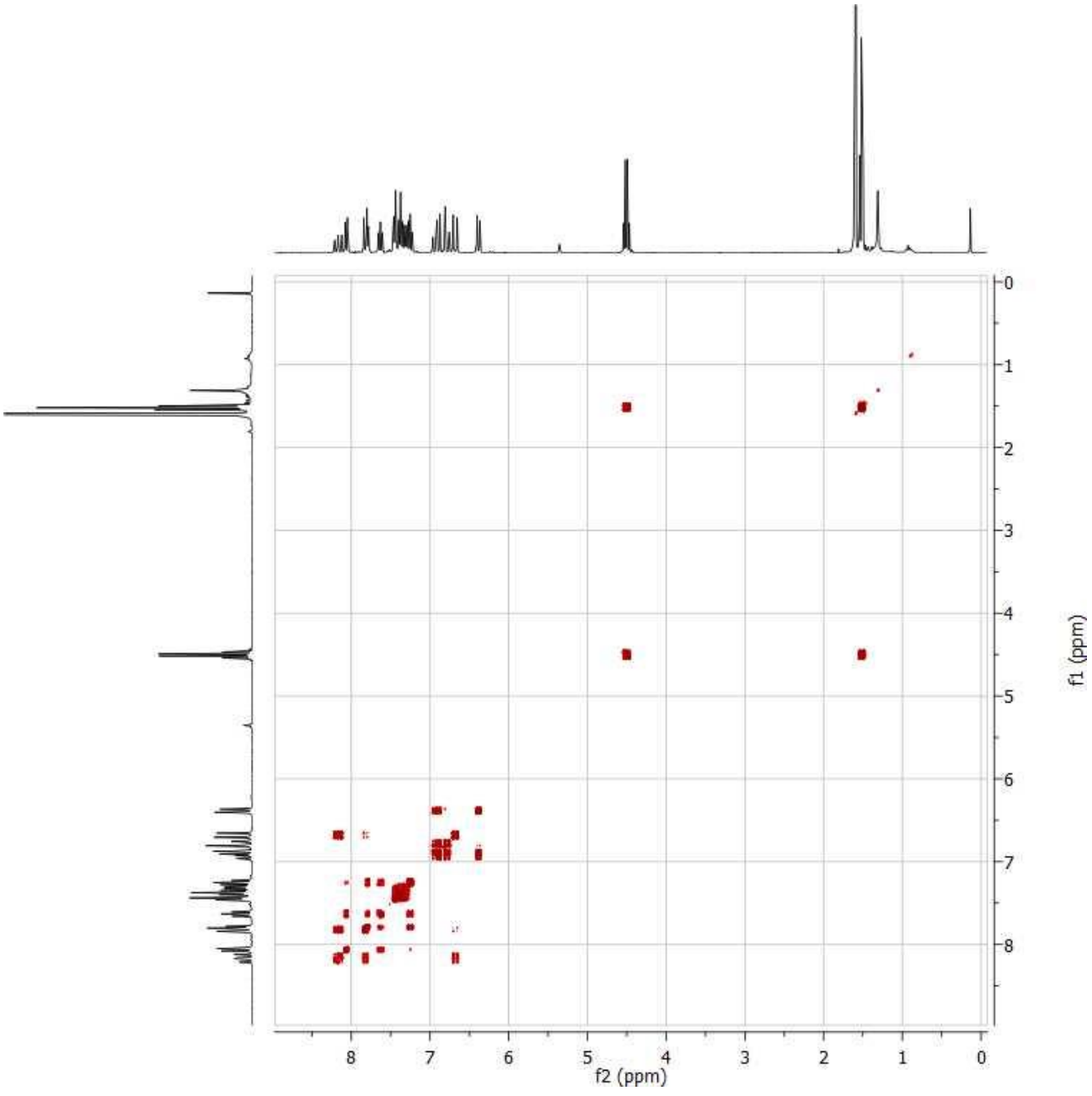
COSY, HSQC-and NOESY-NMR of product 3a,3'a, 3b, 4a, 5a, 6 and 7

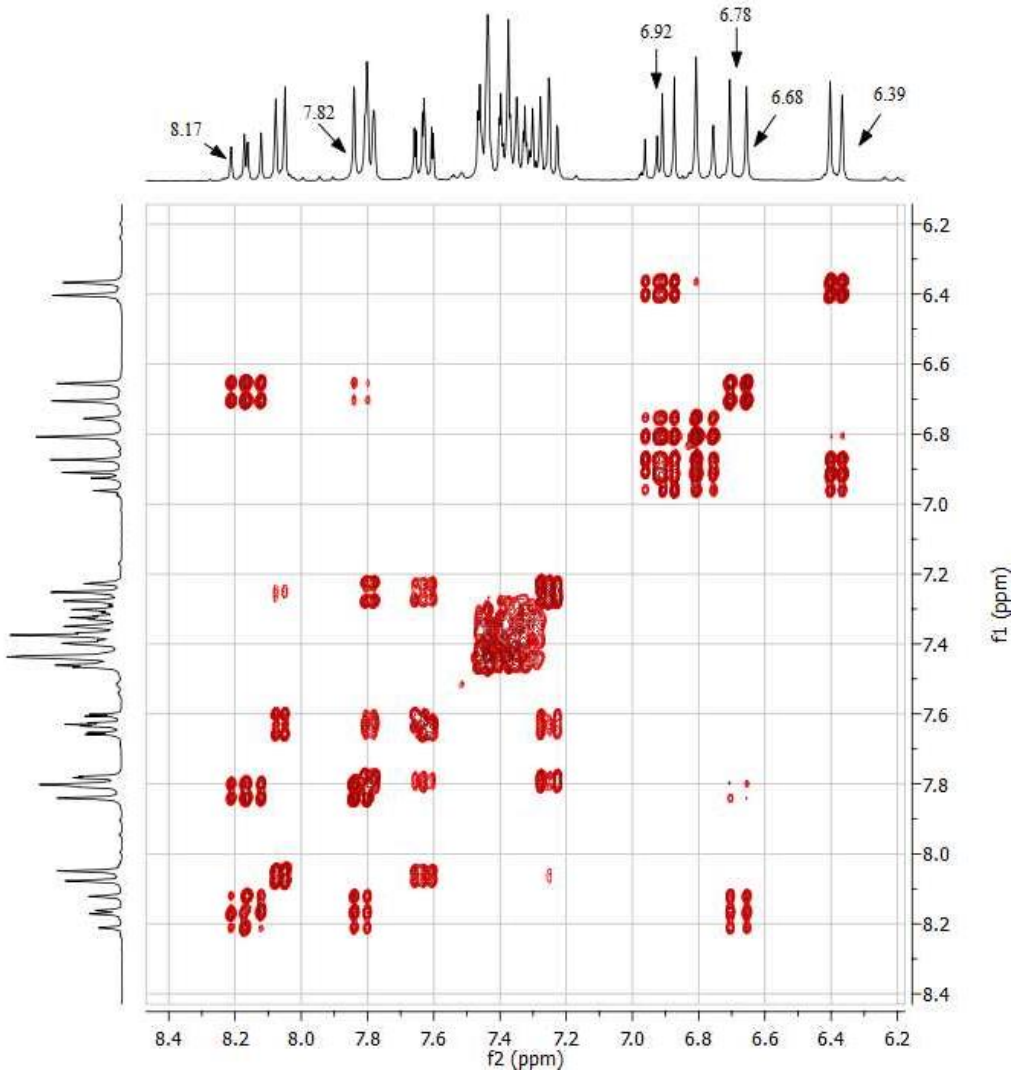
3a, *COSY in CD_2Cl_2 at T = 300 K*



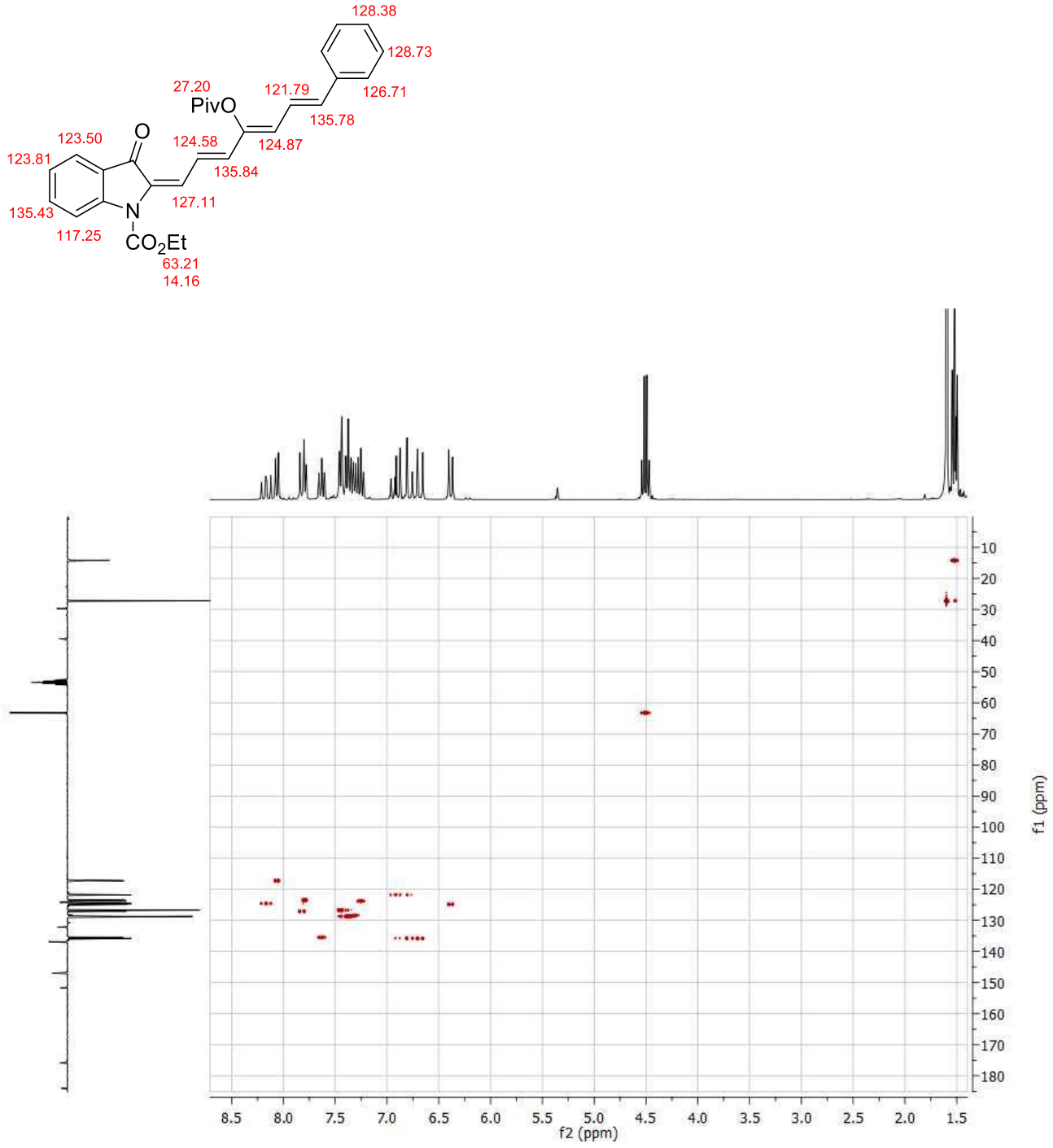


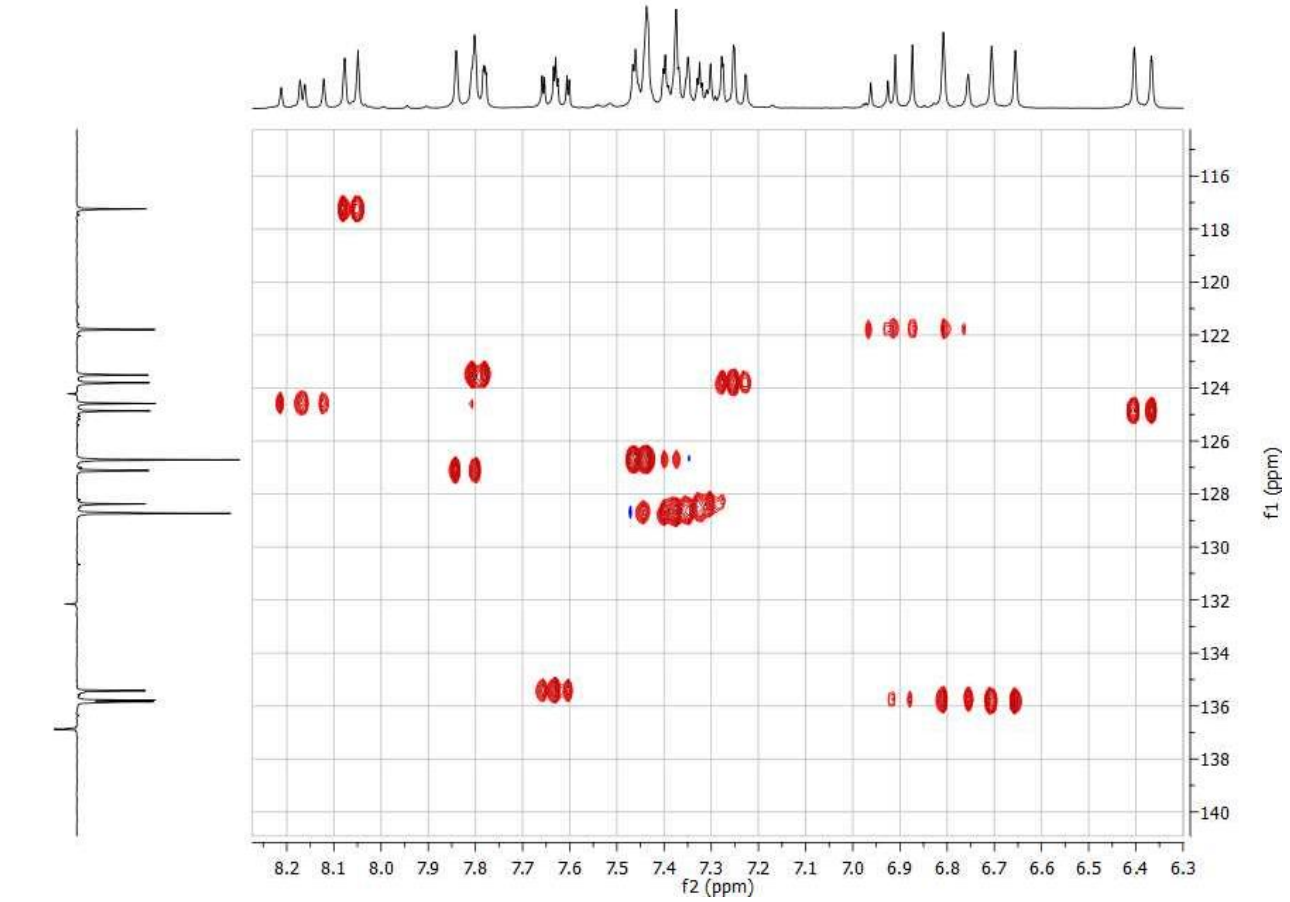
diagnostic cross picks

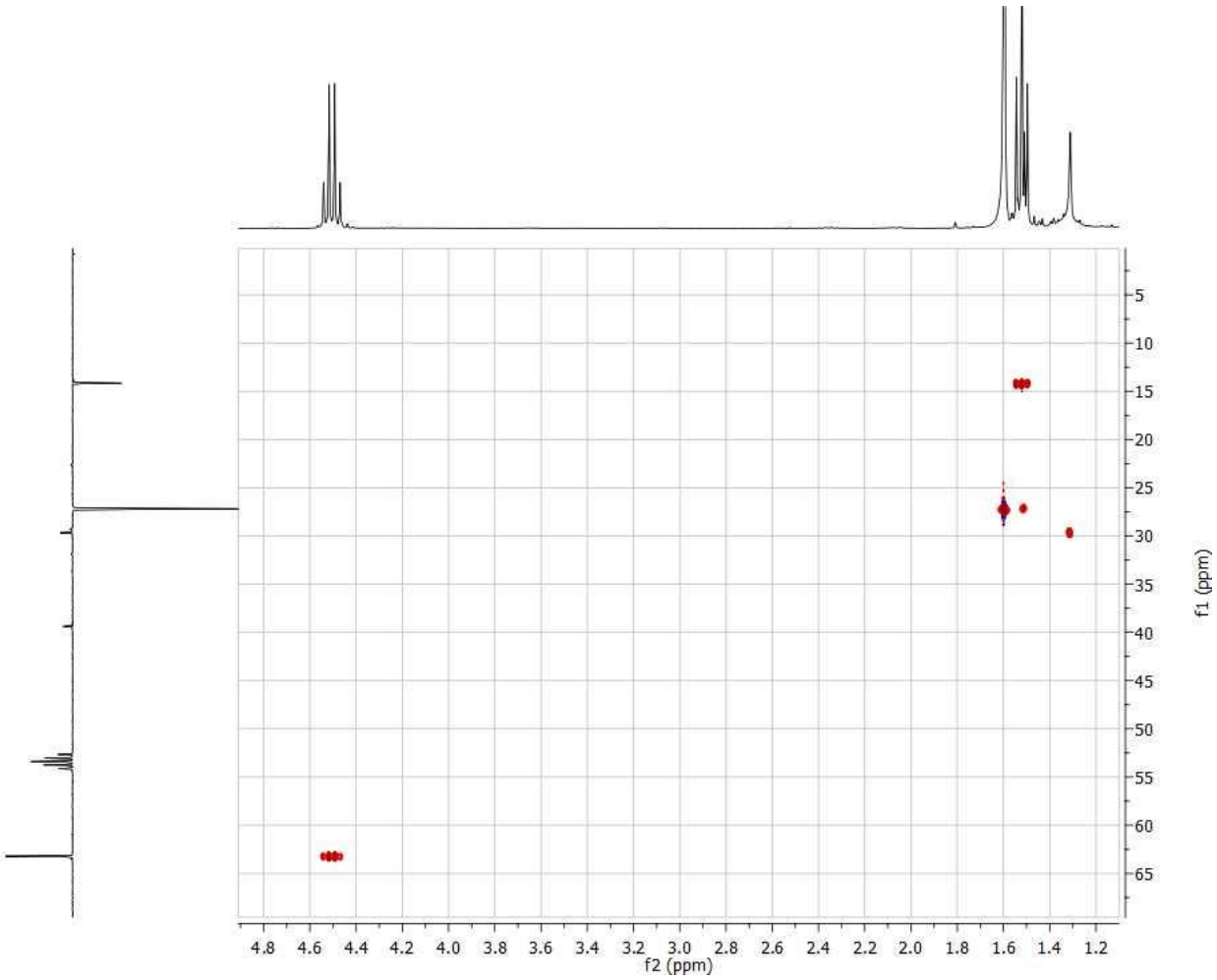



8.17
7.82
6.92
6.78
6.68
6.39
f2 (ppm)
f1 (ppm)

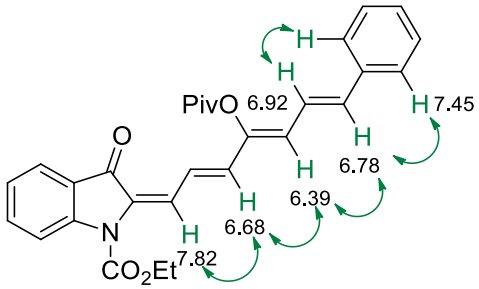
3a *HSQC in CD_2Cl_2 at T = 300 K*



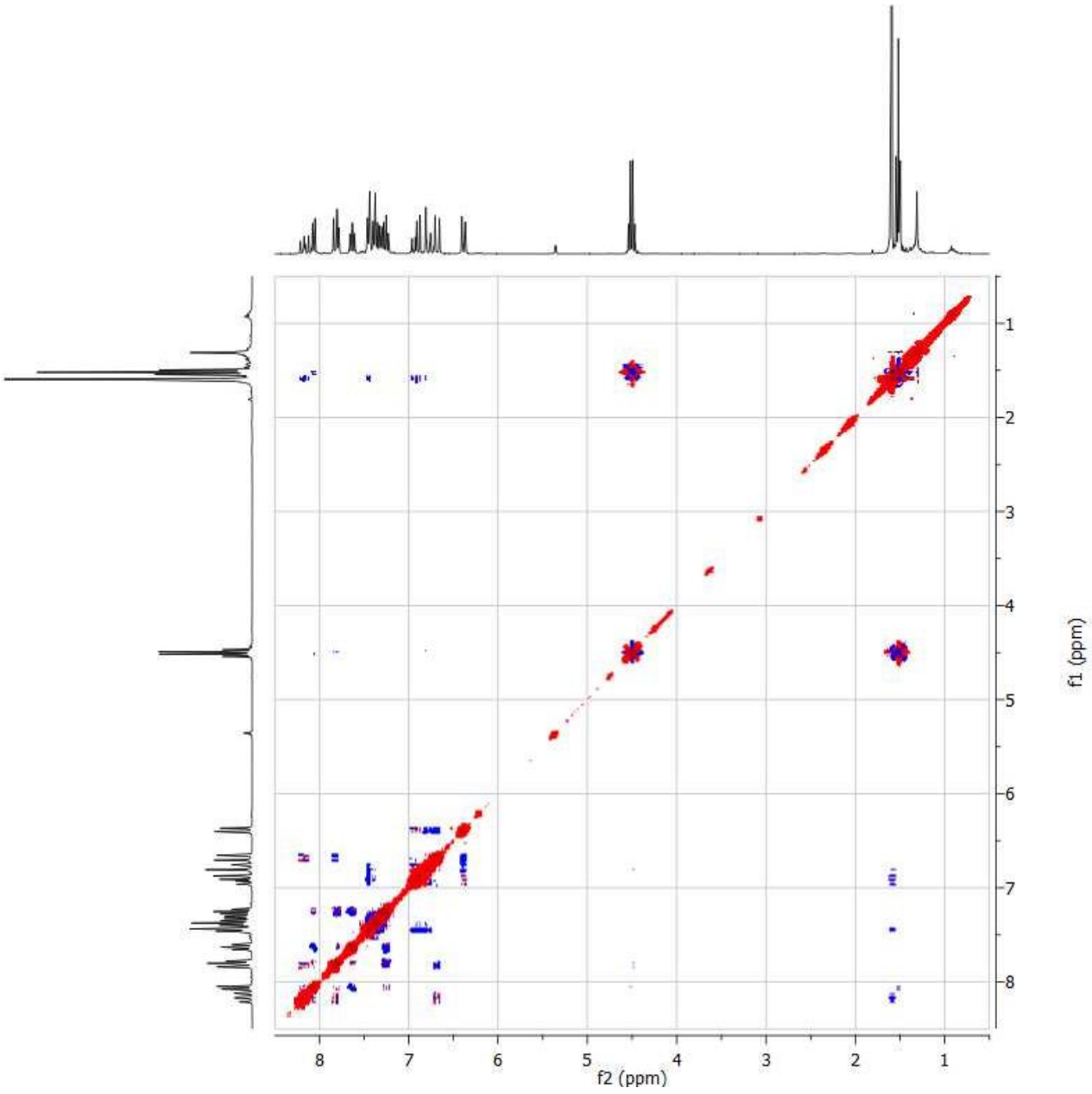

116
118
120
122
124
126
128
130
132
134
136
138
140
f1 (ppm)
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3
f2 (ppm)

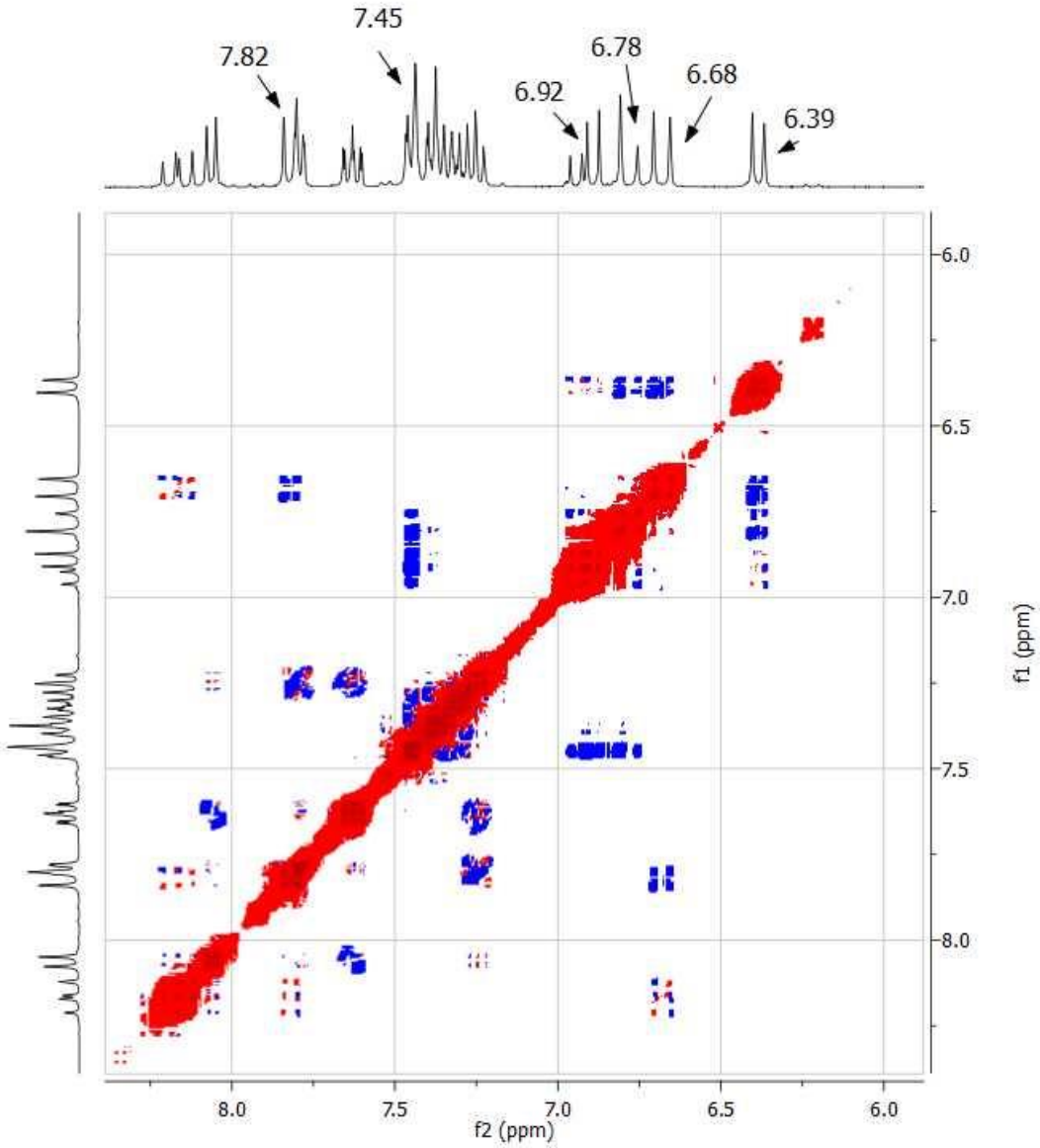

5
10
15
20
25
30
35
40
45
50
55
60
65
f1 (ppm)
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f2 (ppm)

3a *NOESY in CD_2Cl_2 at T = 300 K*

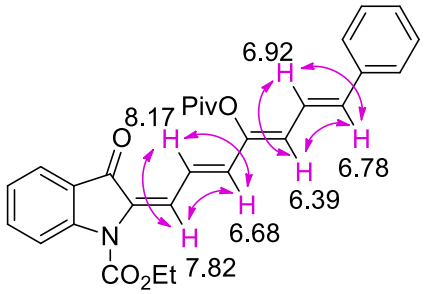


diagnostic cross picks

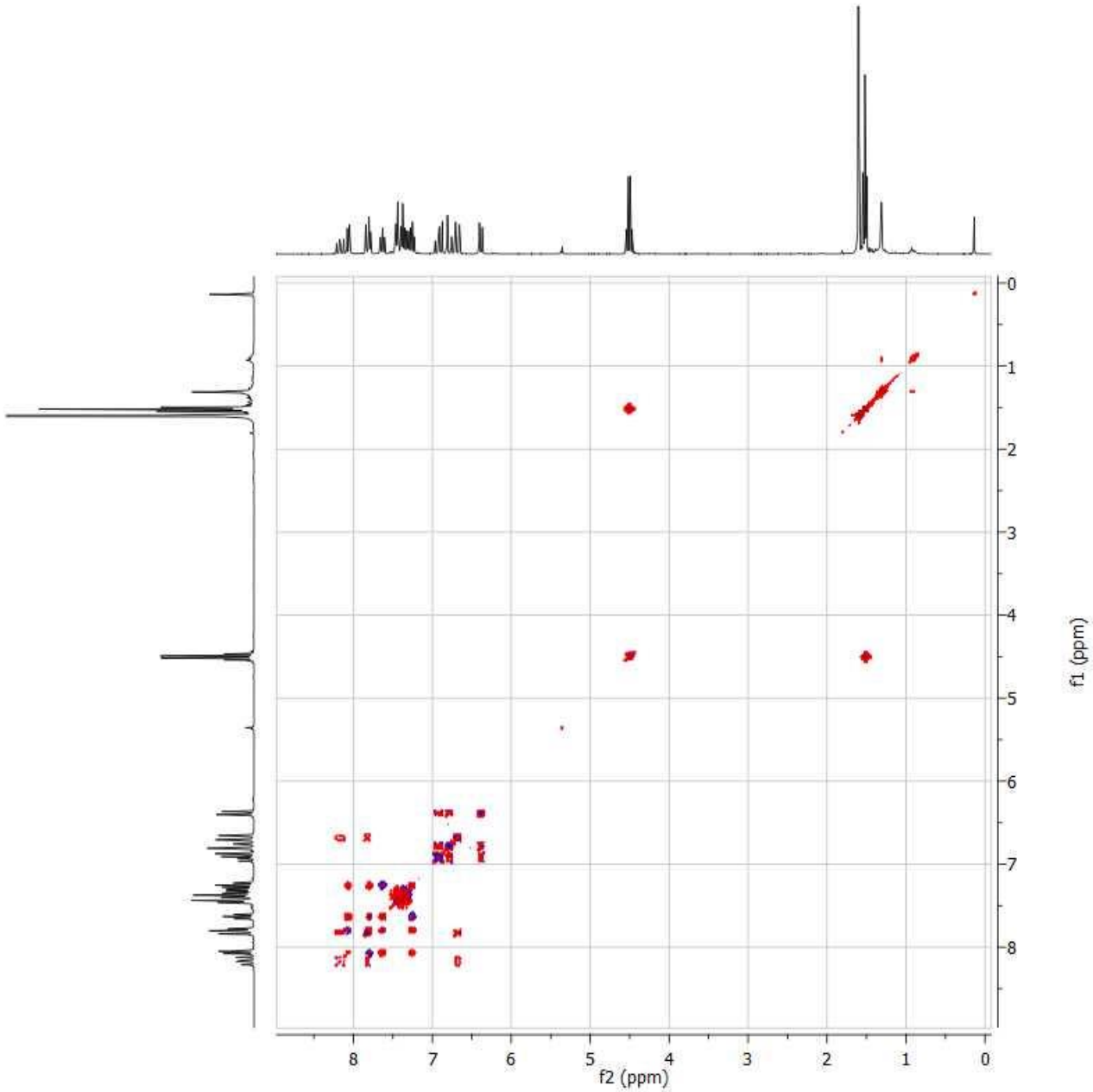


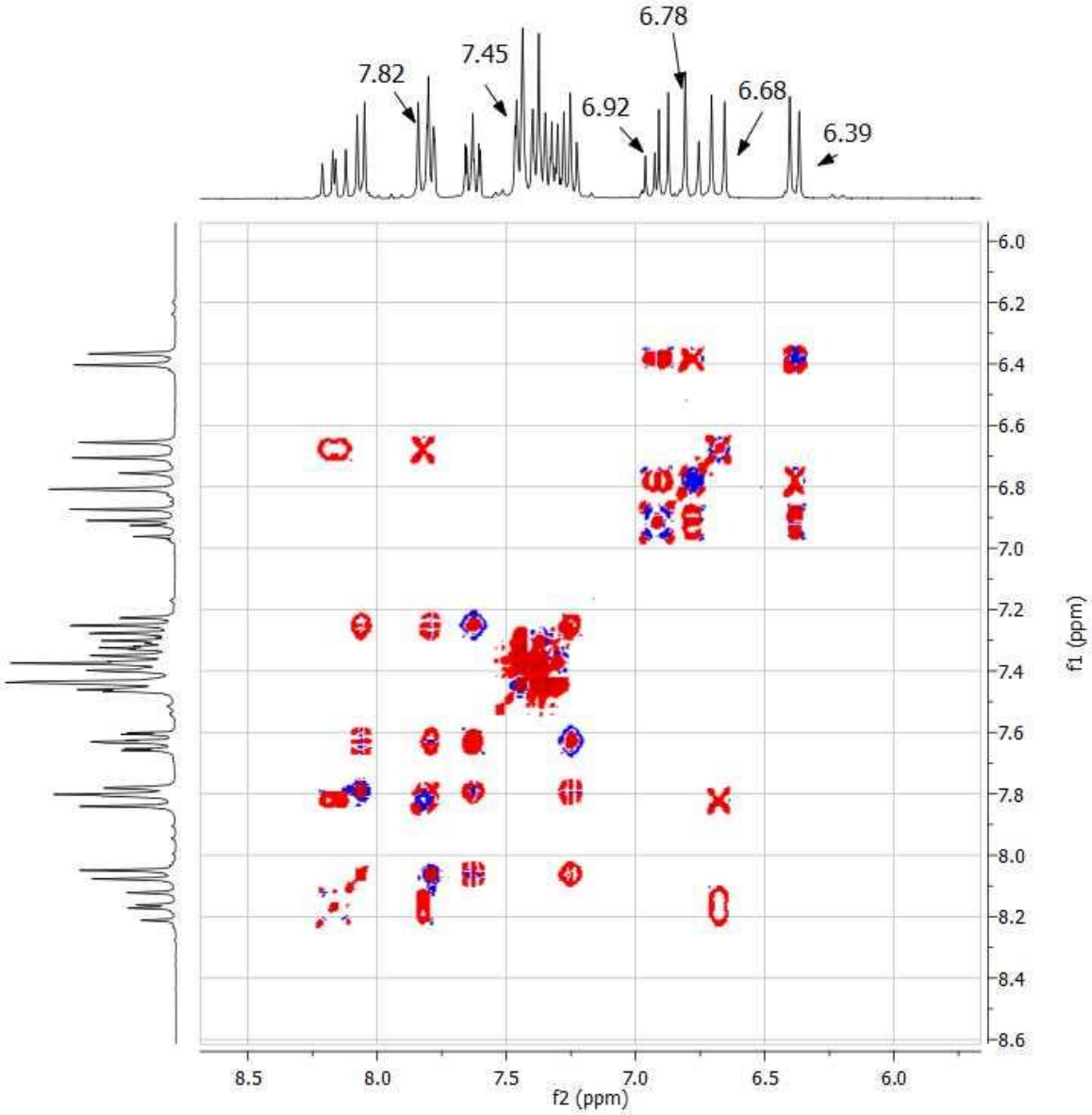

7.82
7.45
6.92
6.78
6.68
6.39
8.0
7.5
7.0
6.5
6.0
f2 (ppm)
f1 (ppm)

3a *TOCSY in CD_2Cl_2 at T = 300 K for the confirmation of stereochemistry*

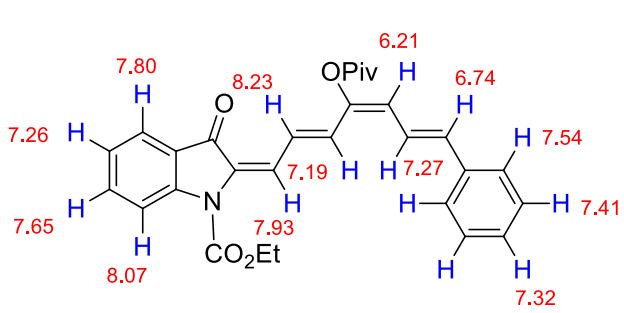


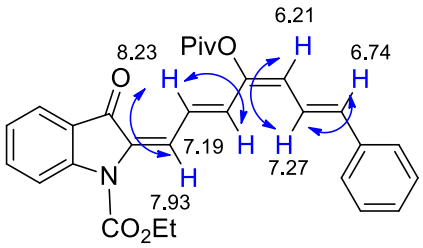
diagnostic cross picks



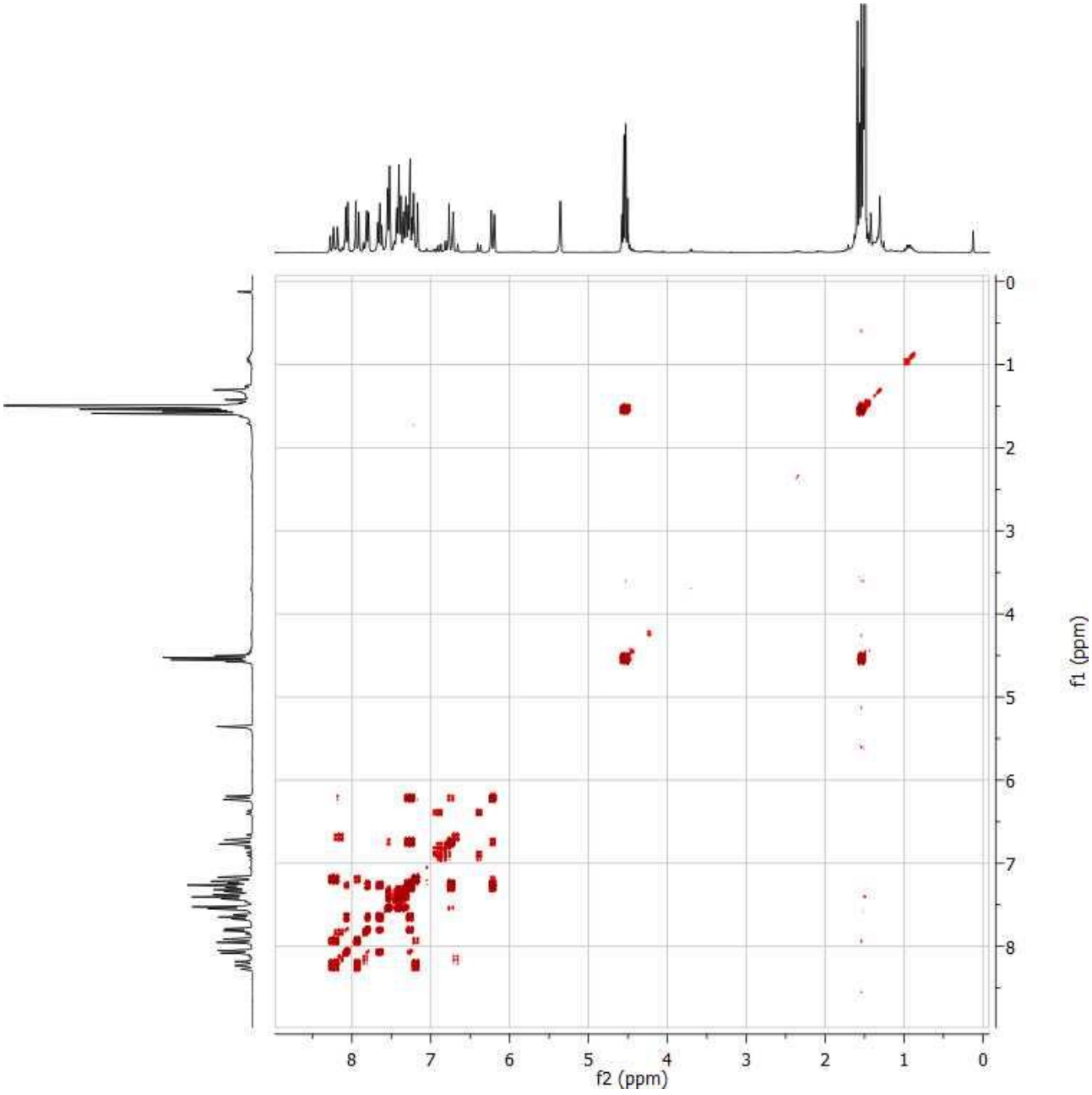

6.78
7.45
7.82
6.92
6.68
6.39
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
f2 (ppm)

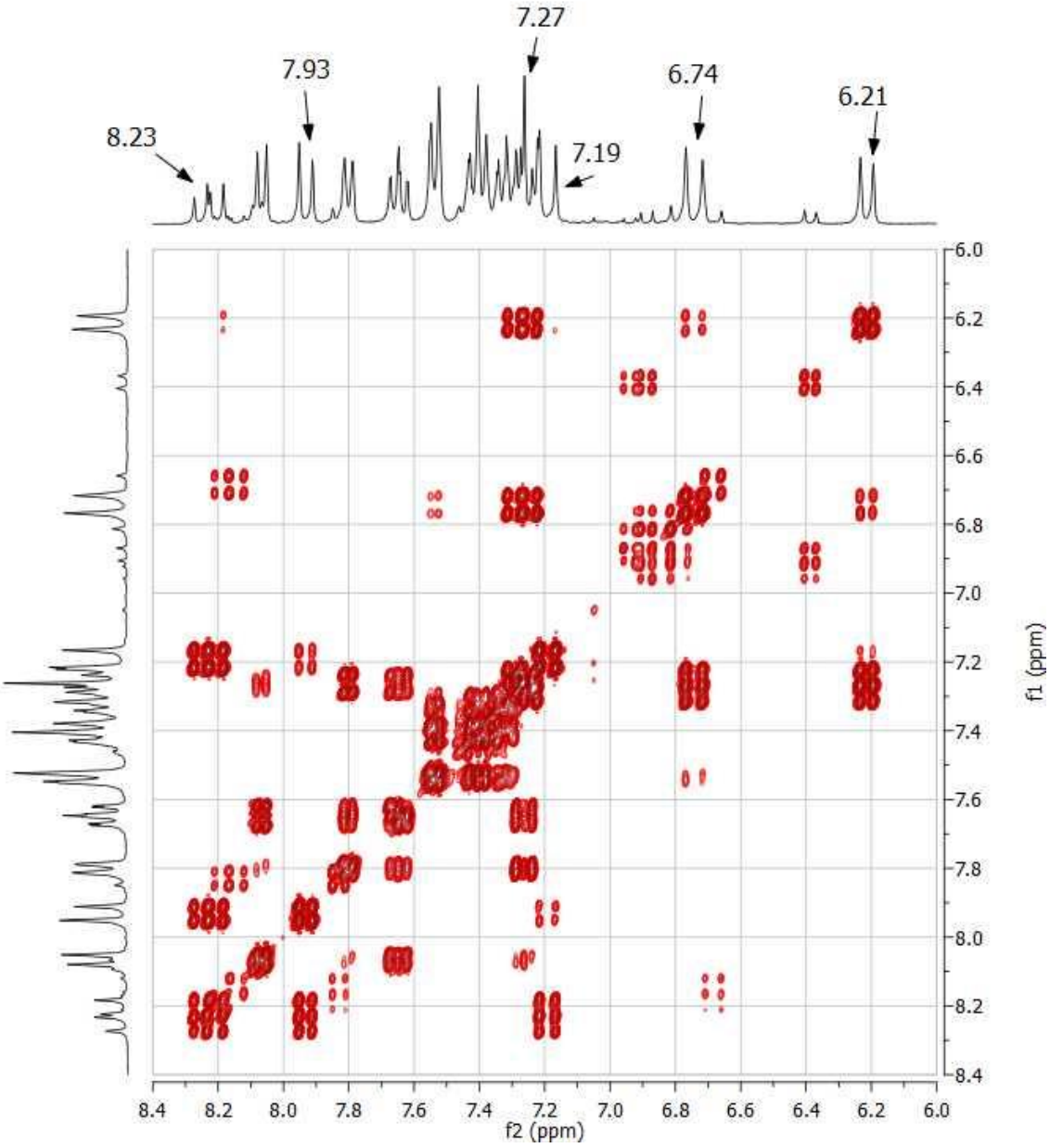
3'a, *COSY in CD_2Cl_2 at T = 300 K*



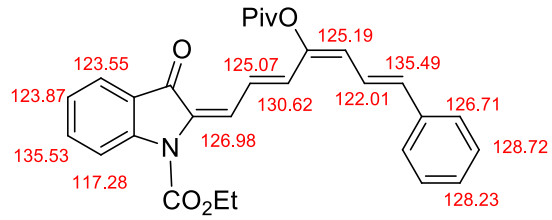


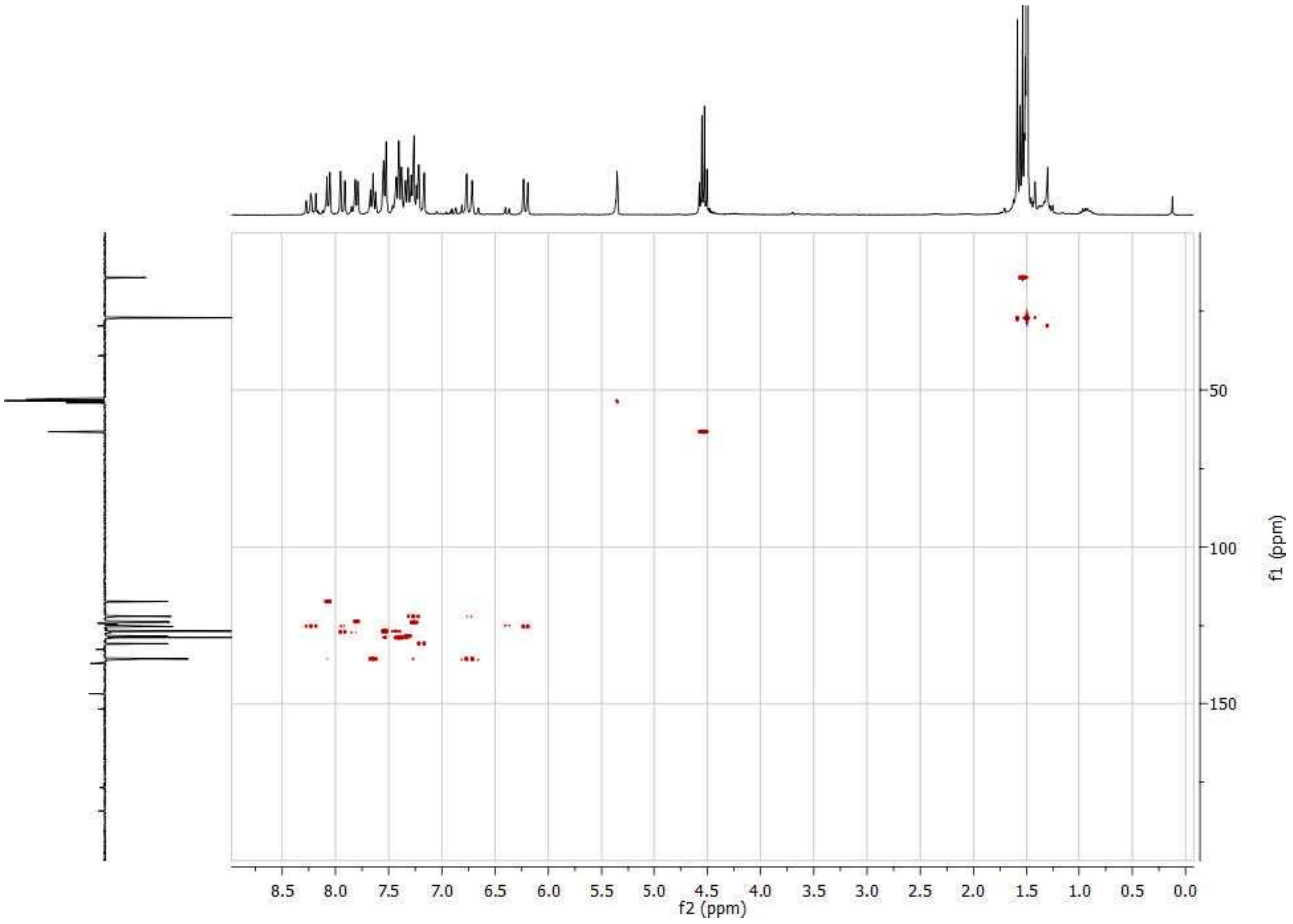
diagnostic cross picks

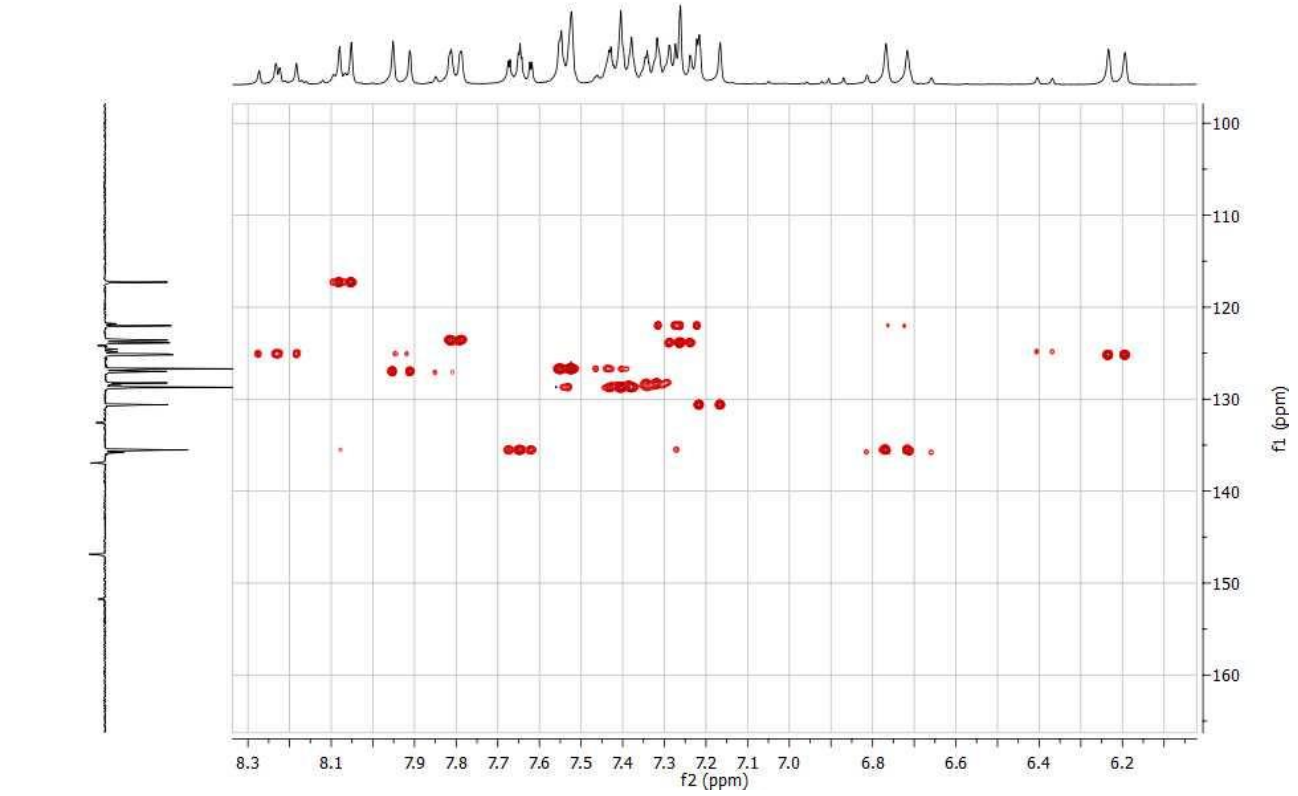


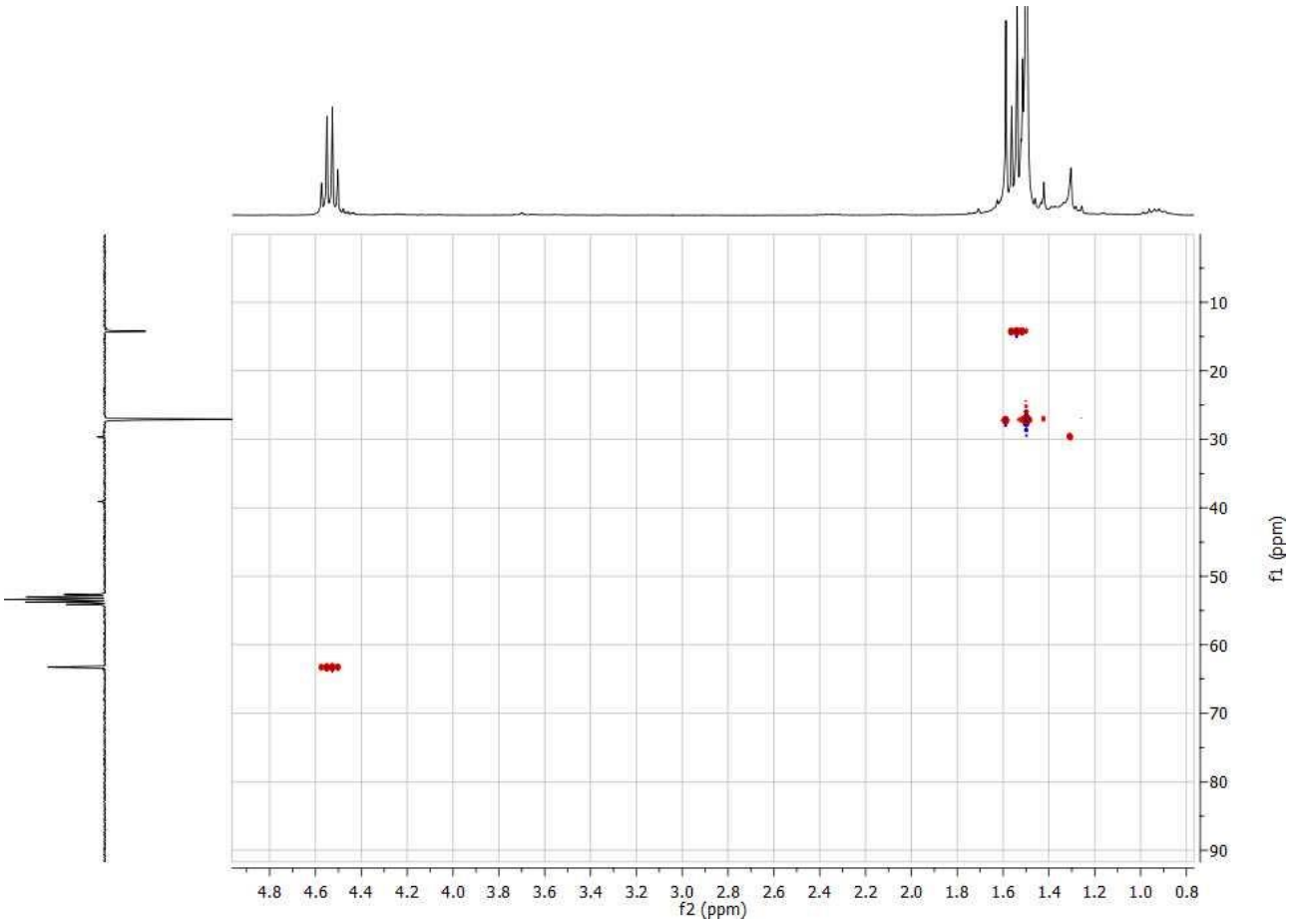

7.27
7.93
6.74
6.21
8.23
7.19
f1 (ppm)
f2 (ppm)

3'a, *HSQC in CD_2Cl_2 at T = 300 K*

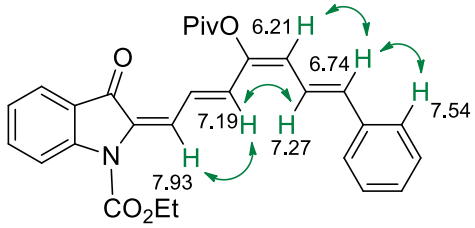




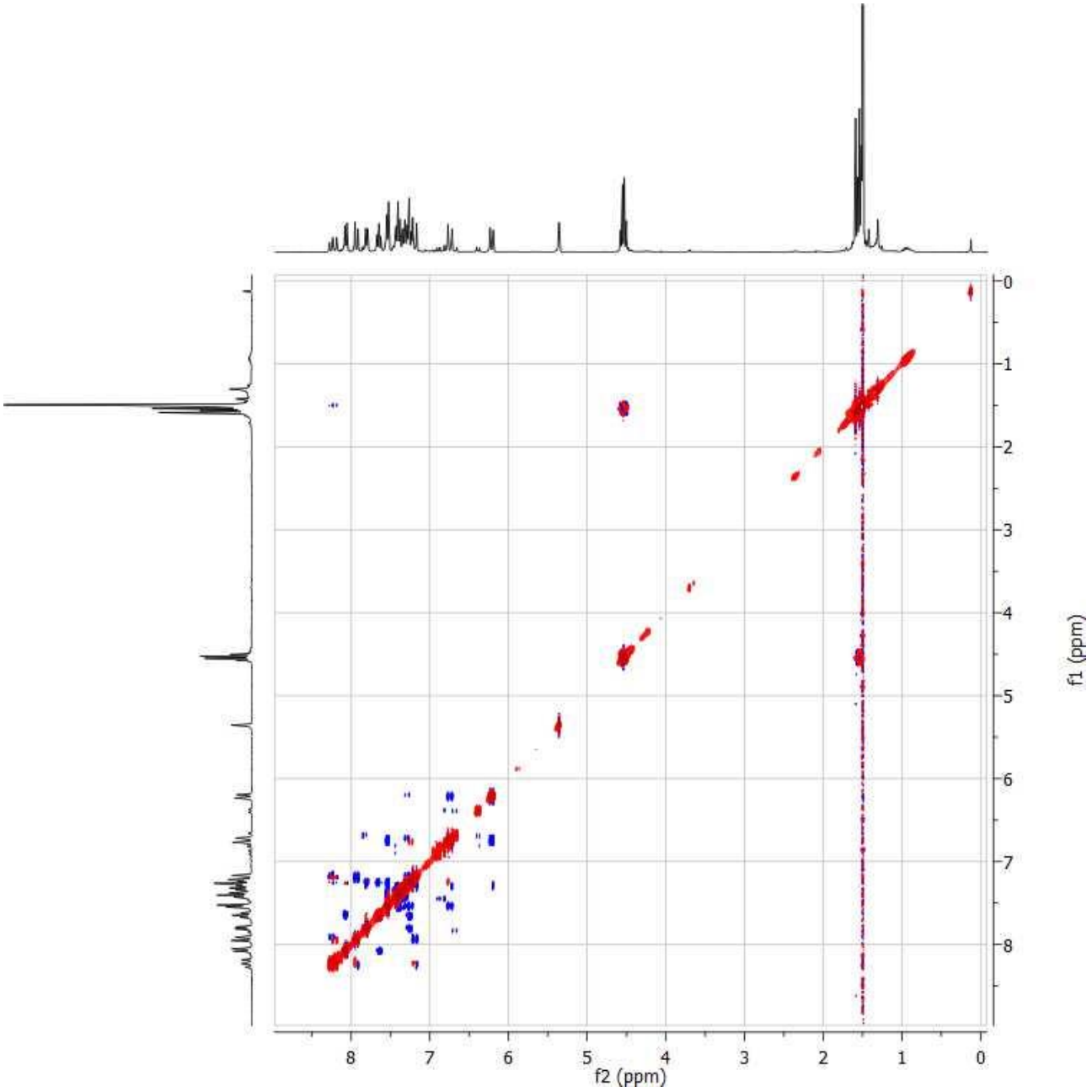

100
110
120
130
140
150
160
f1 (ppm)
8.3
8.1
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.8
6.6
6.4
6.2
f2 (ppm)

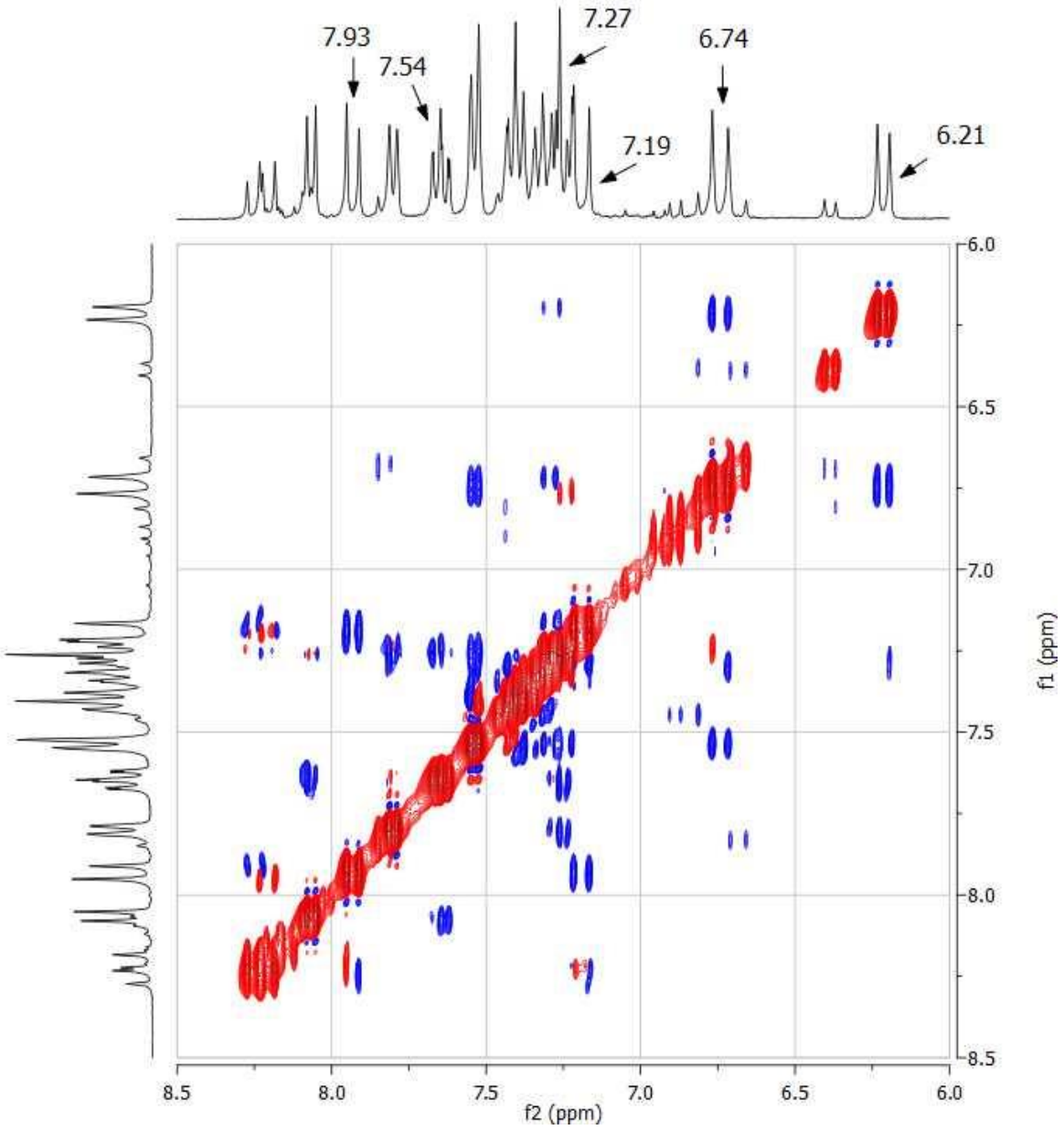

10
20
30
40
50
60
70
80
90
f1 (ppm)
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
f2 (ppm)

3'a, *NOESY in CD_2Cl_2 at T = 300 K*

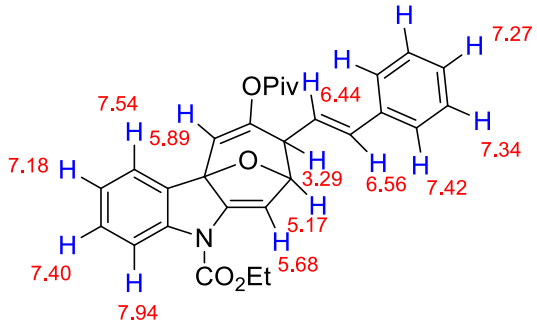


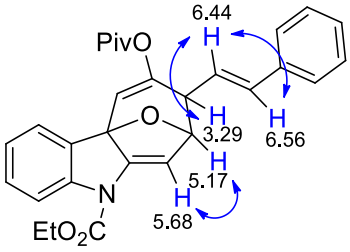
diagnostic cross picks



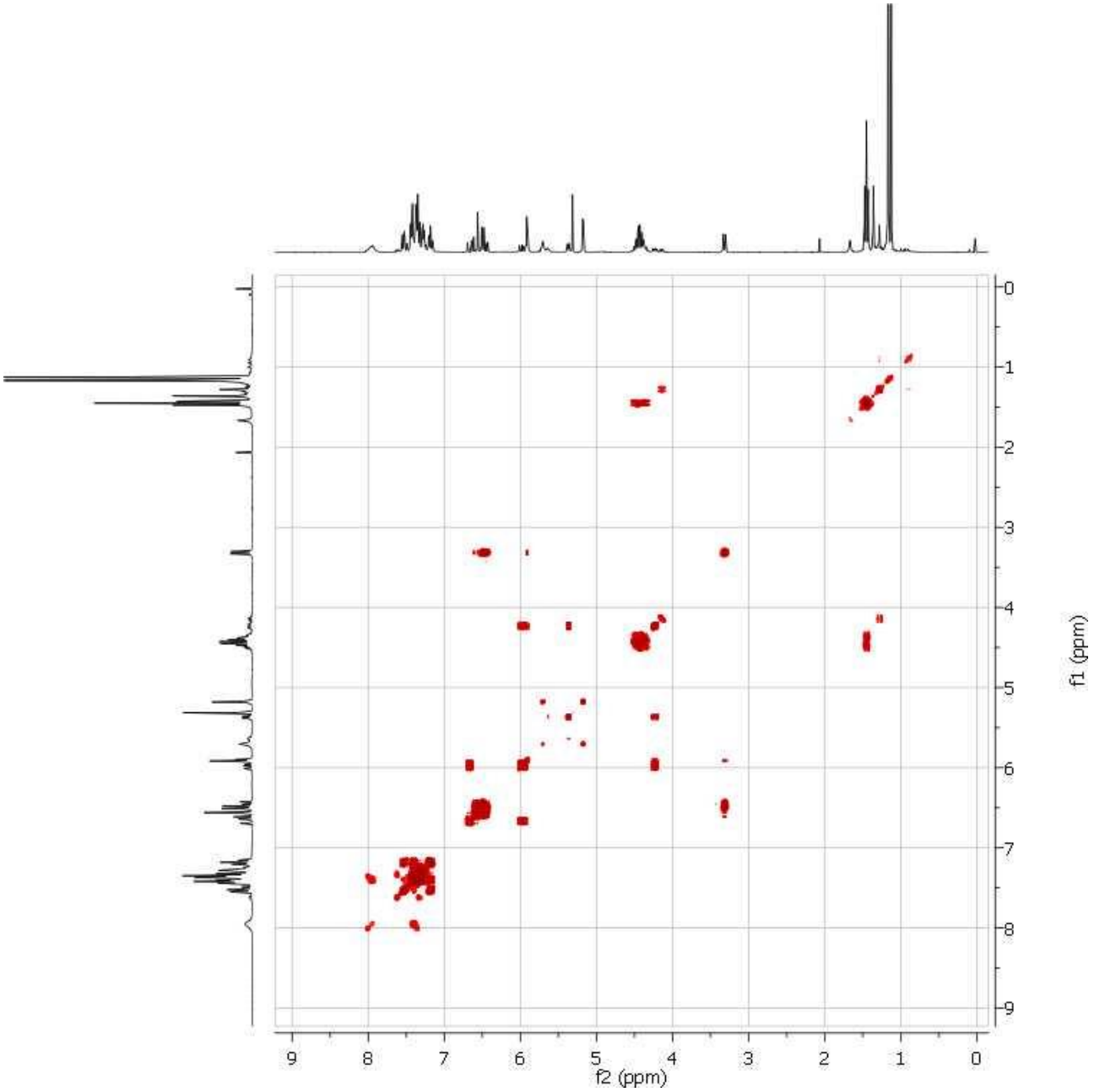

7.93
7.54
7.27
7.19
6.74
6.21
8.5
8.0
7.5
7.0
6.5
6.0
f2 (ppm)
6.0
6.5
7.0
7.5
8.0
8.5
f1 (ppm)

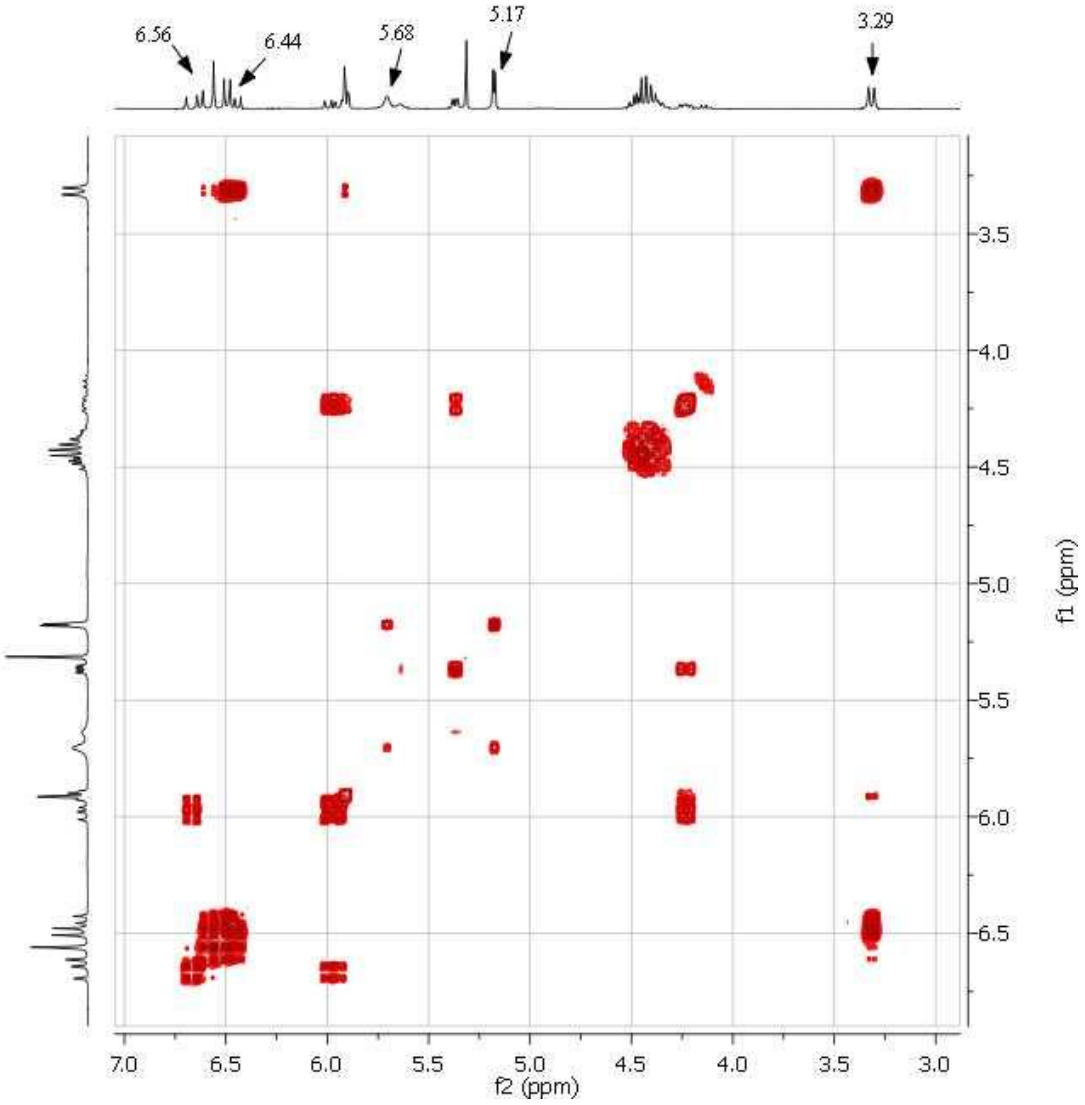
4a, *COSY in $CDCl_3$ at T = 300 K*



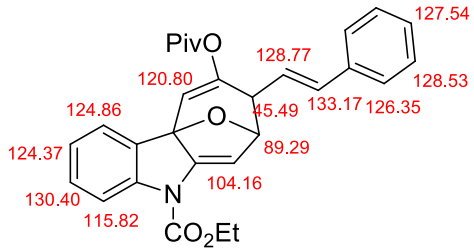


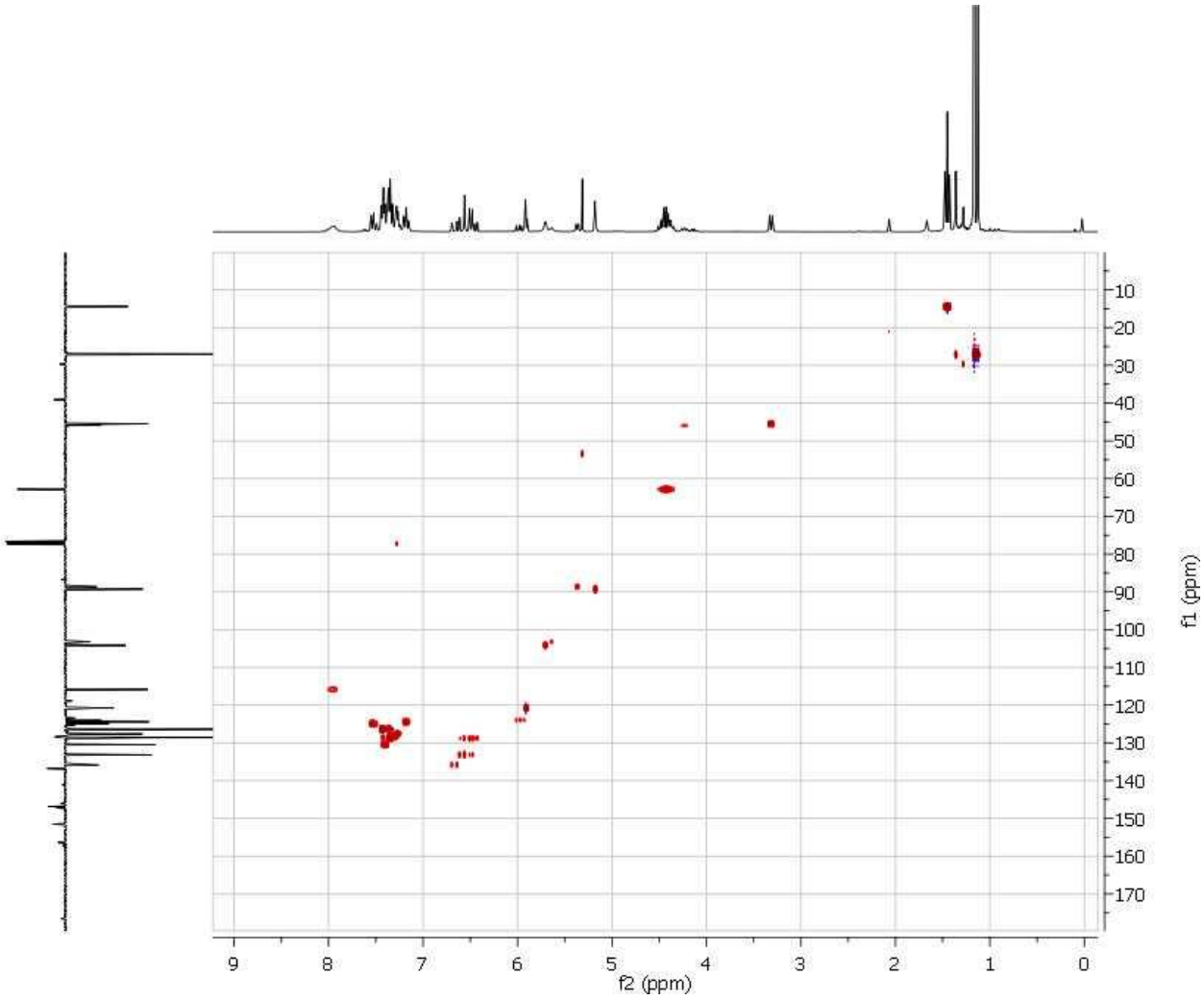
diagnostic cross picks

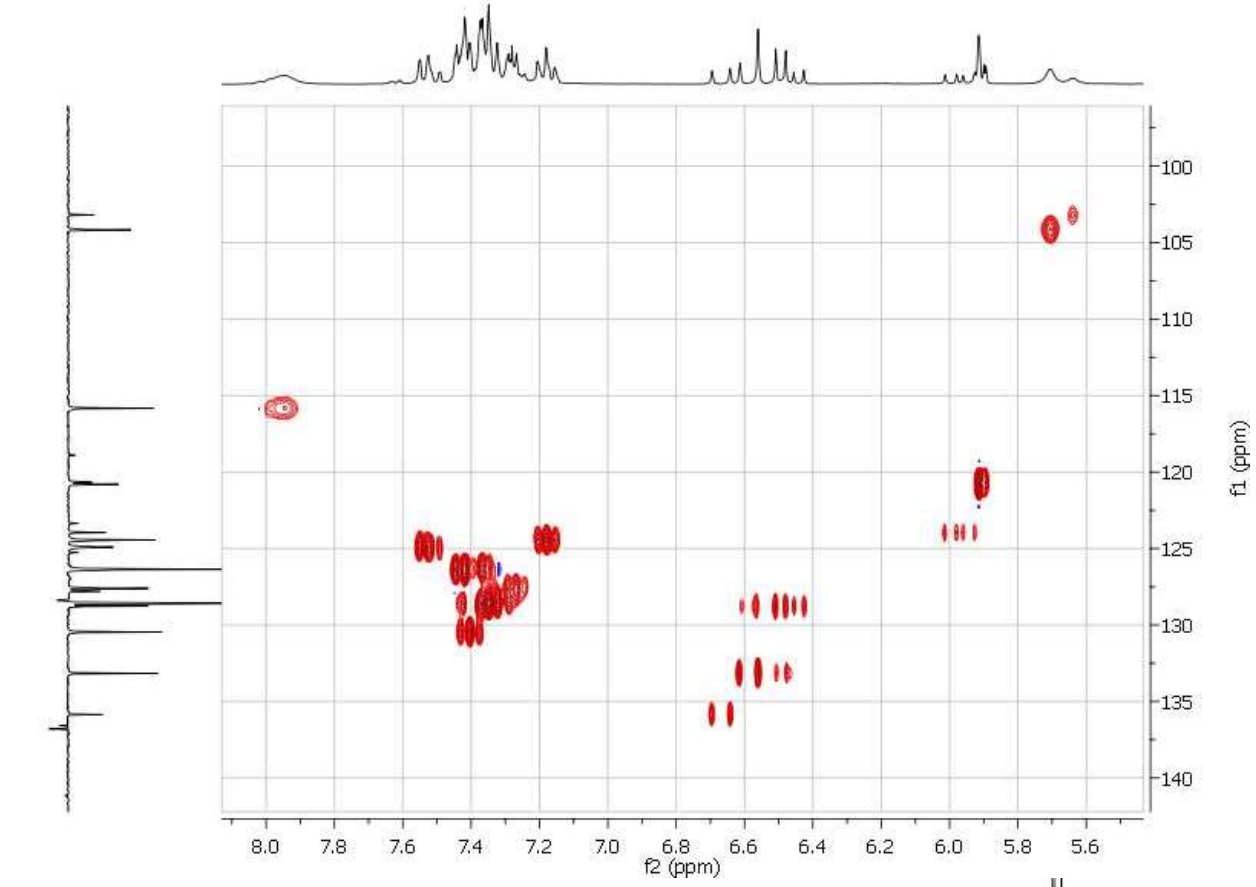


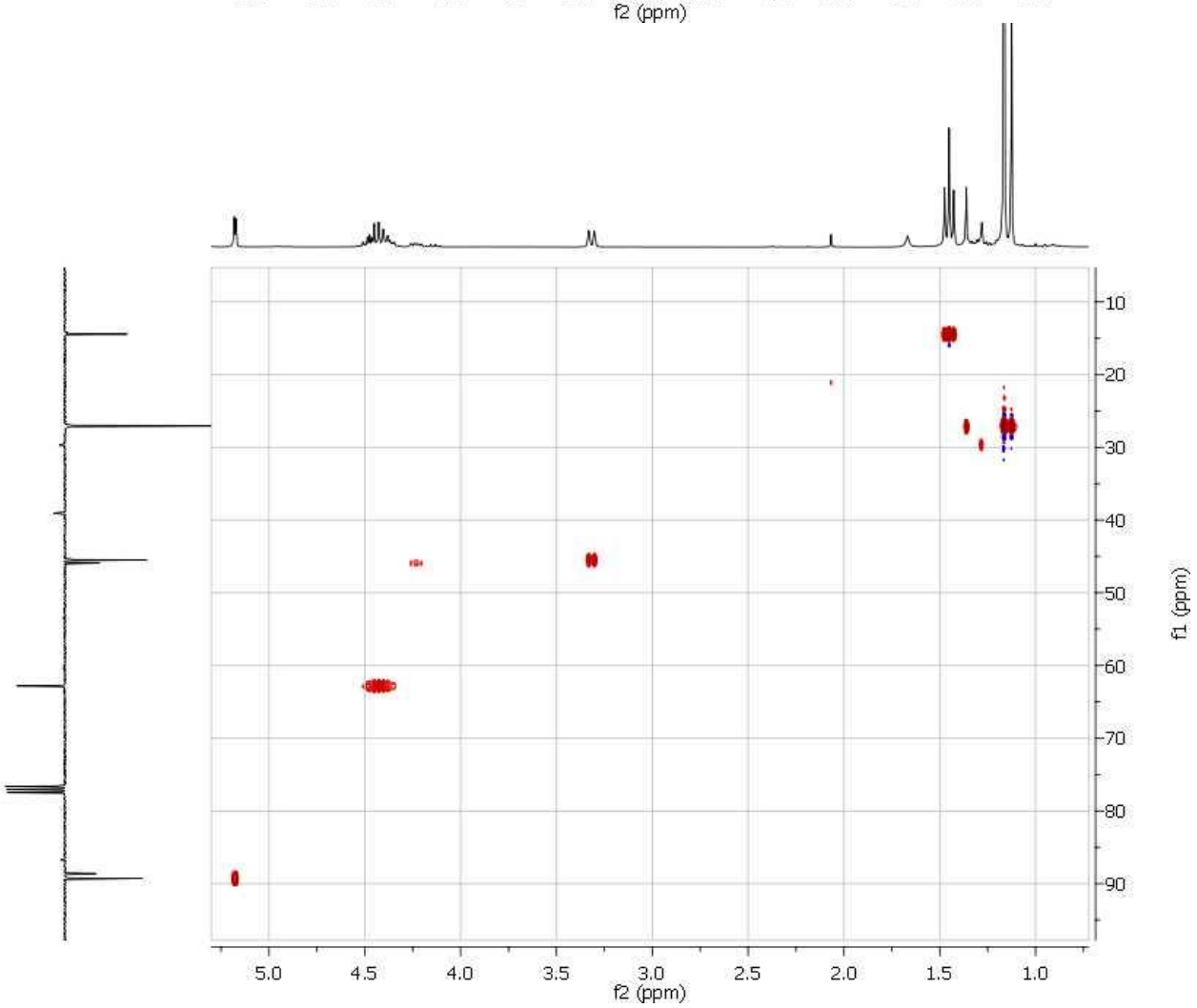

6.56
6.44
5.68
5.17
3.29
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f2 (ppm)
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)

4a, *HSQC in $CDCl_3$ at T = 300 K*

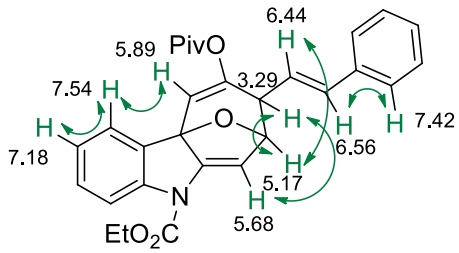




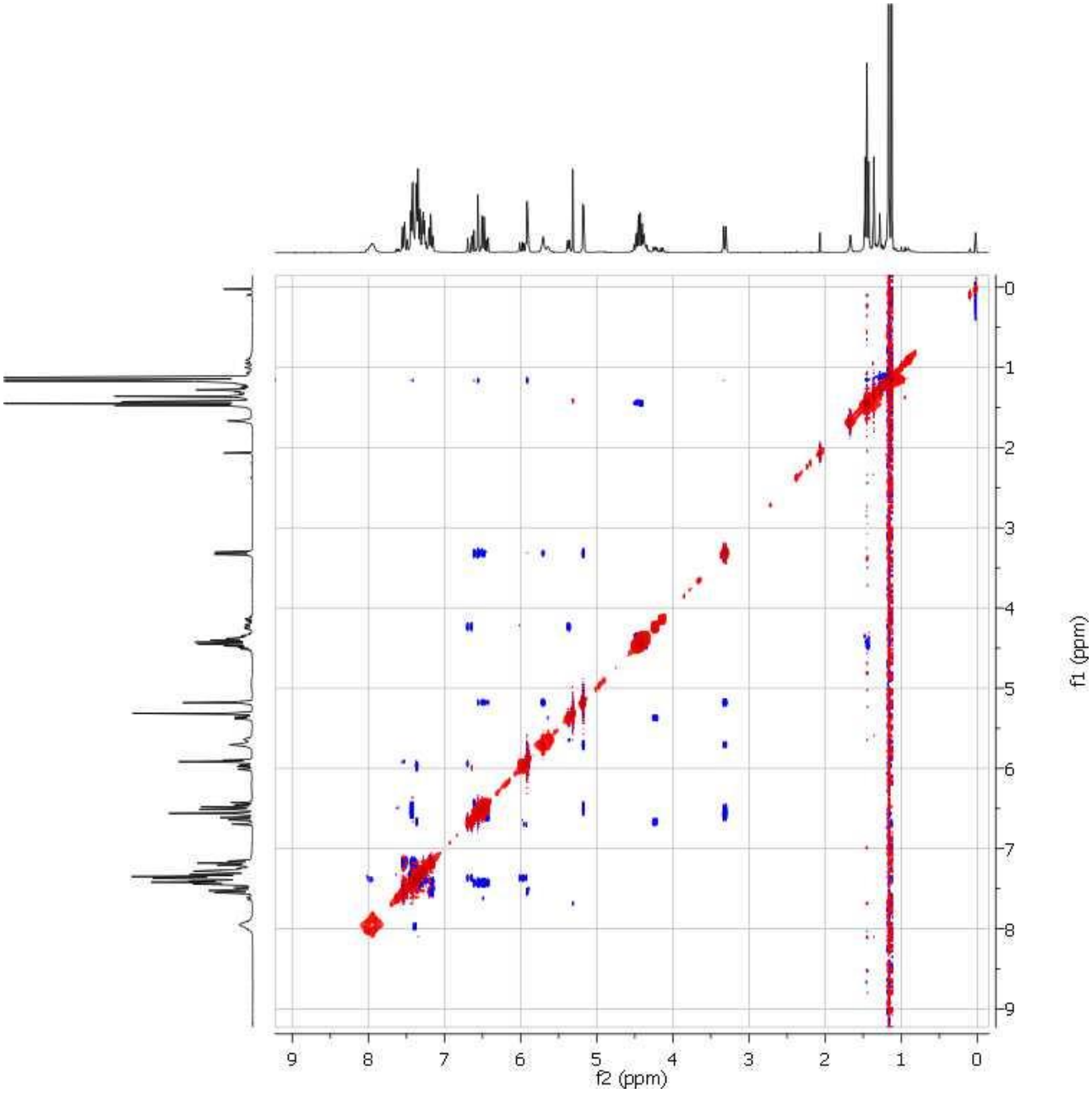

8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
f2 (ppm)
100
105
110
115
120
125
130
135
140
f1 (ppm)

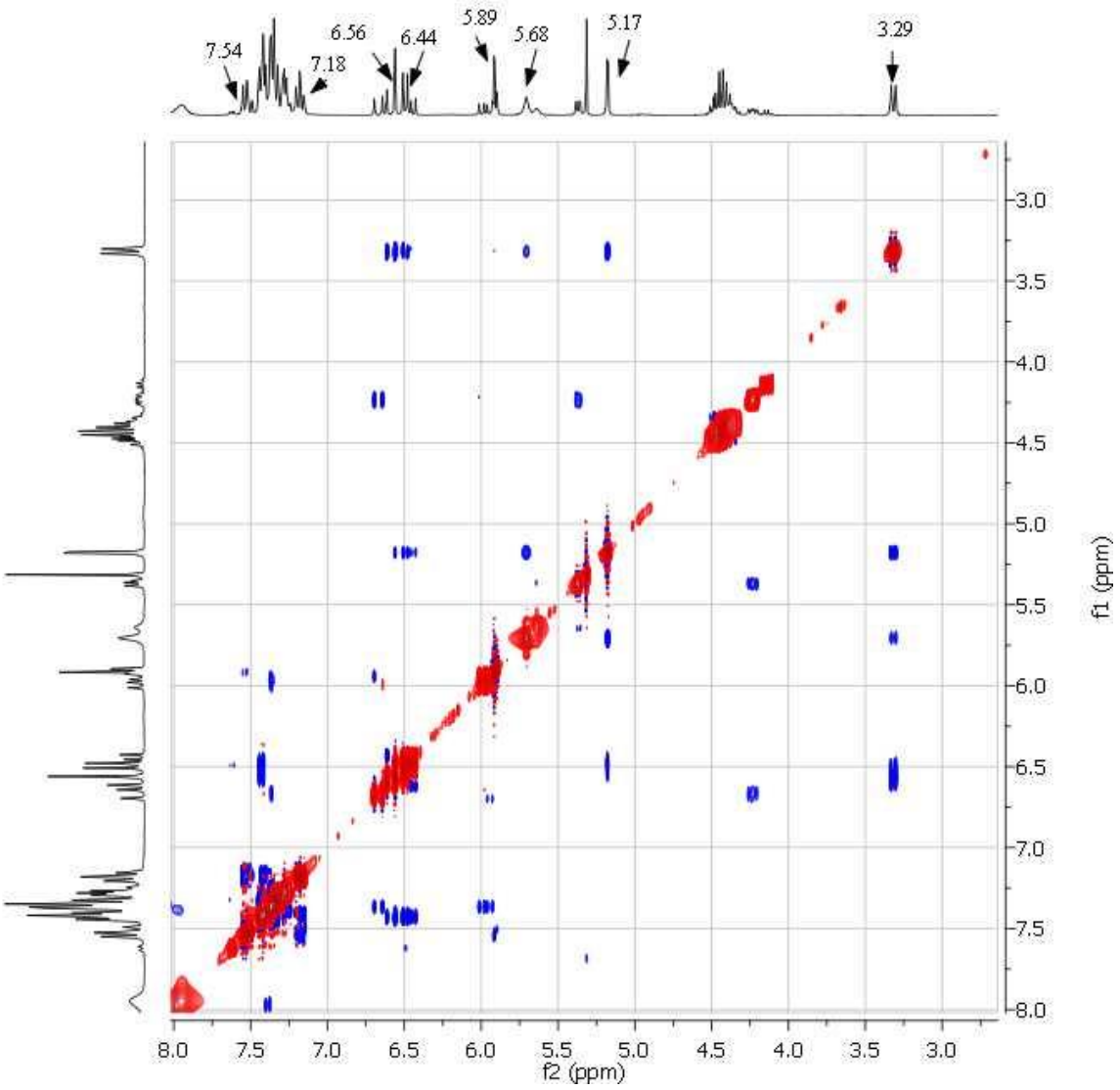

5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
f1 (ppm)

4a, *NOESY in $CDCl_3$ at T = 300 K*

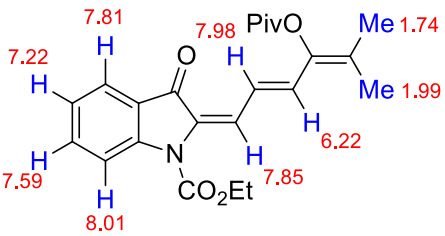


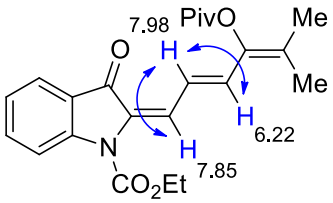
diagnostic cross picks



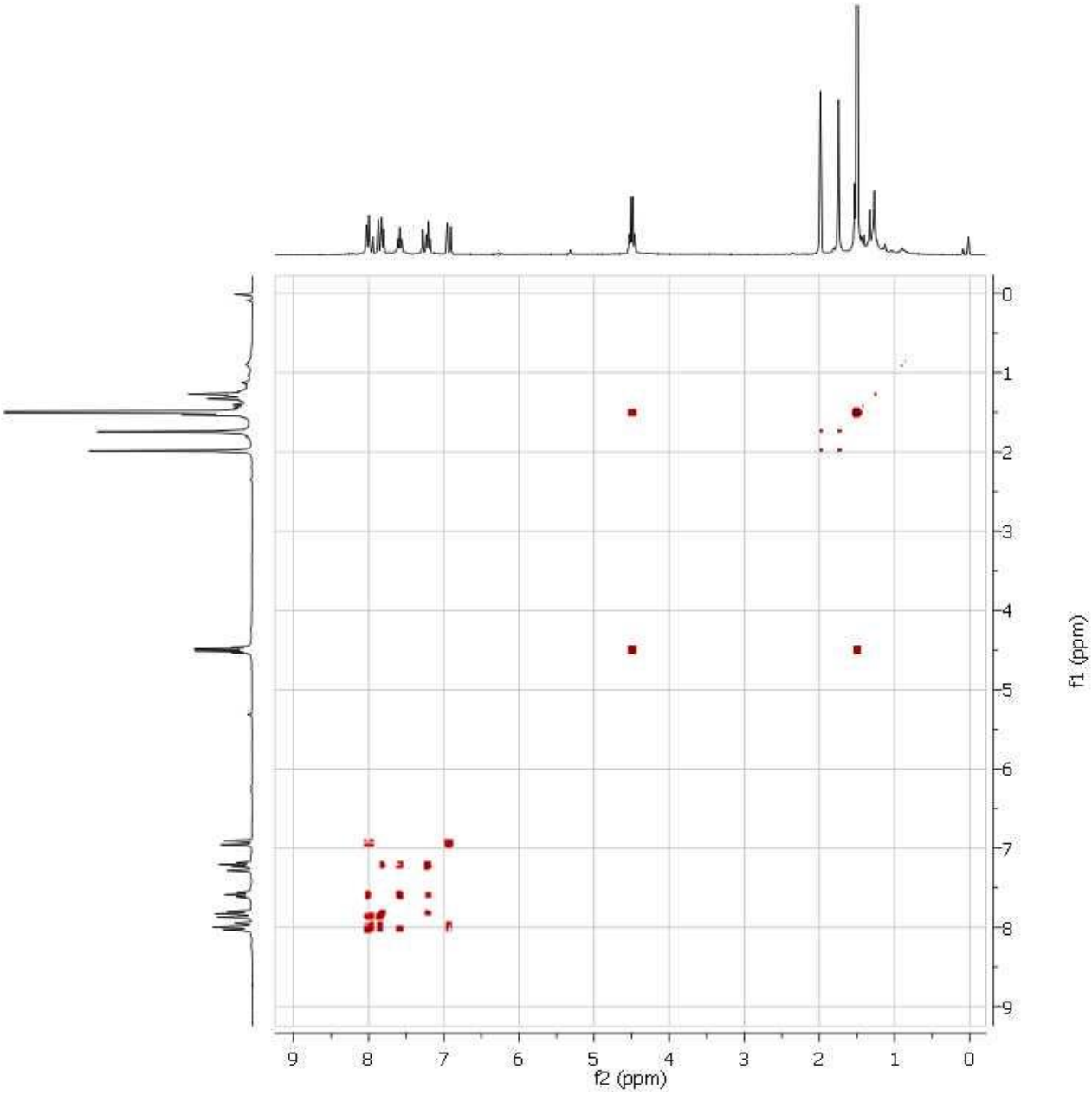

7.54
7.18
6.56
6.44
5.89
5.68
5.17
3.29
f2 (ppm)
f1 (ppm)

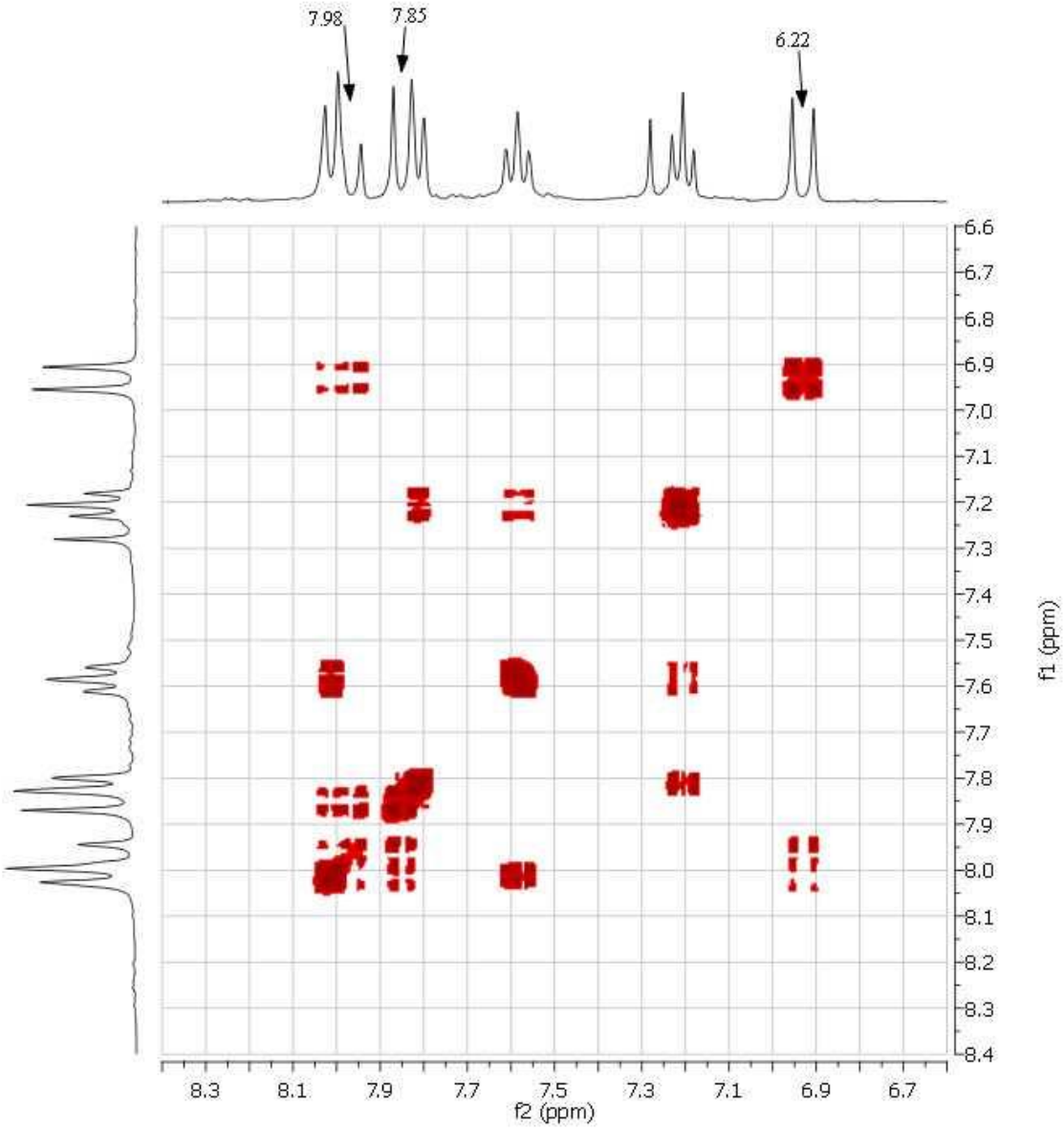
3b, *COSY in $CDCl_3$ at T = 300 K*



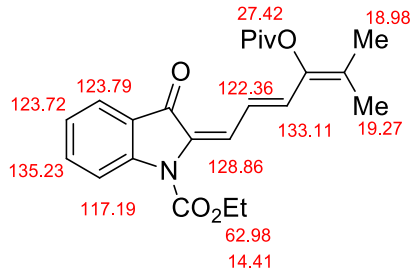


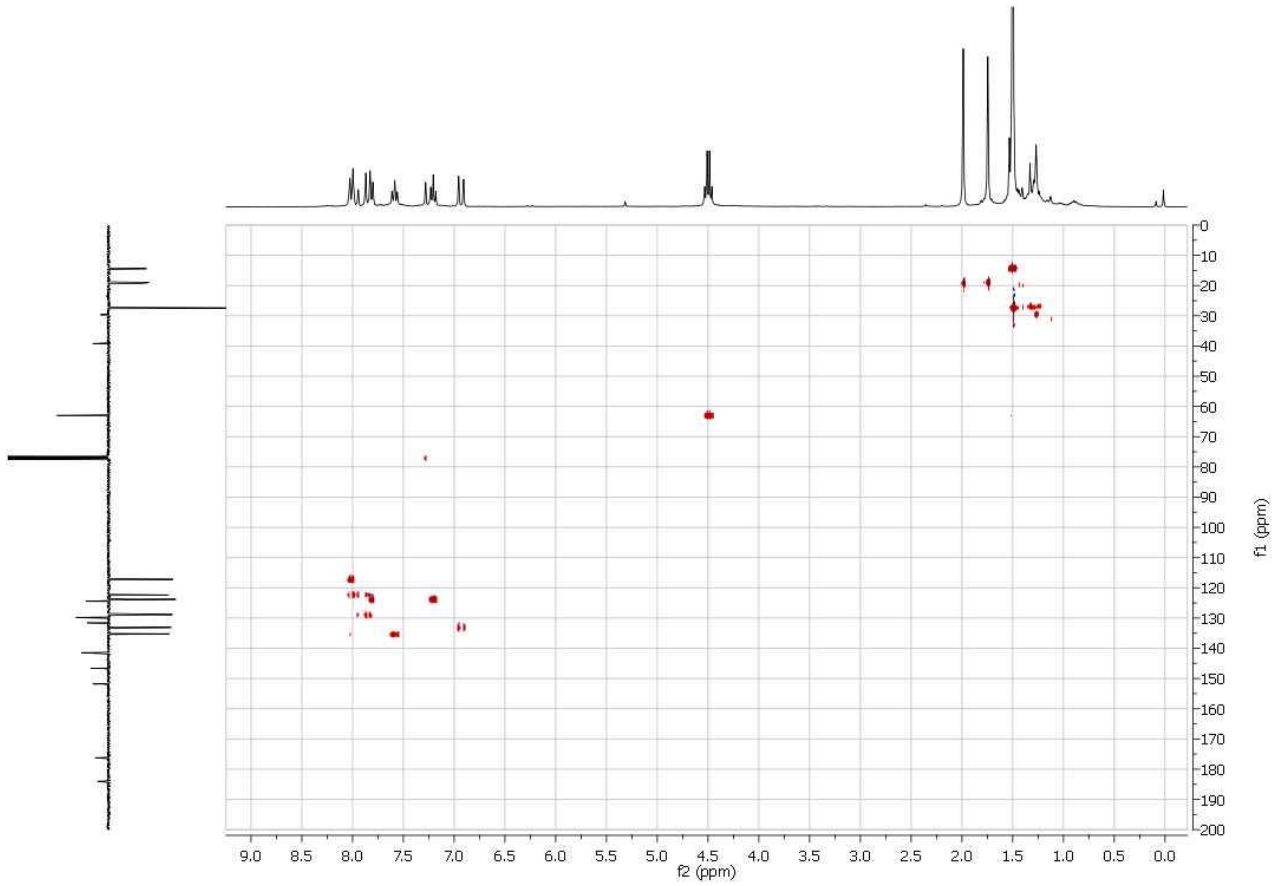
diagnostic cross picks

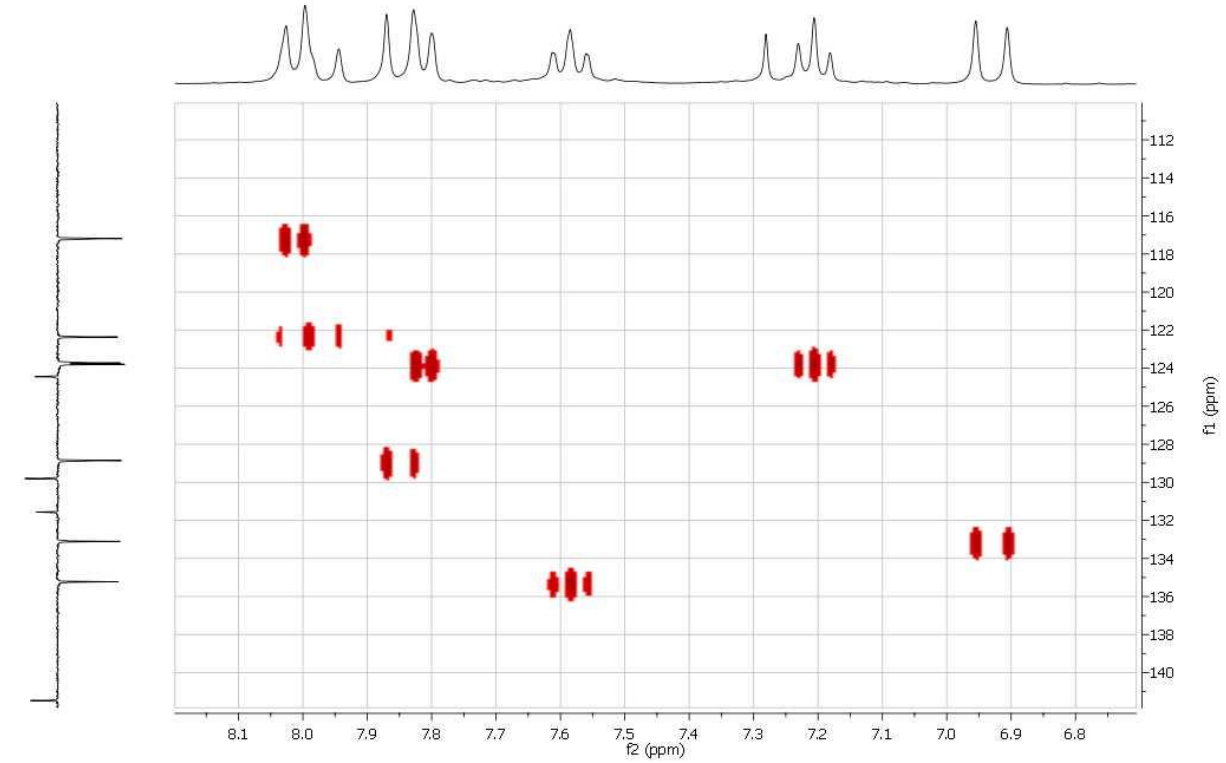


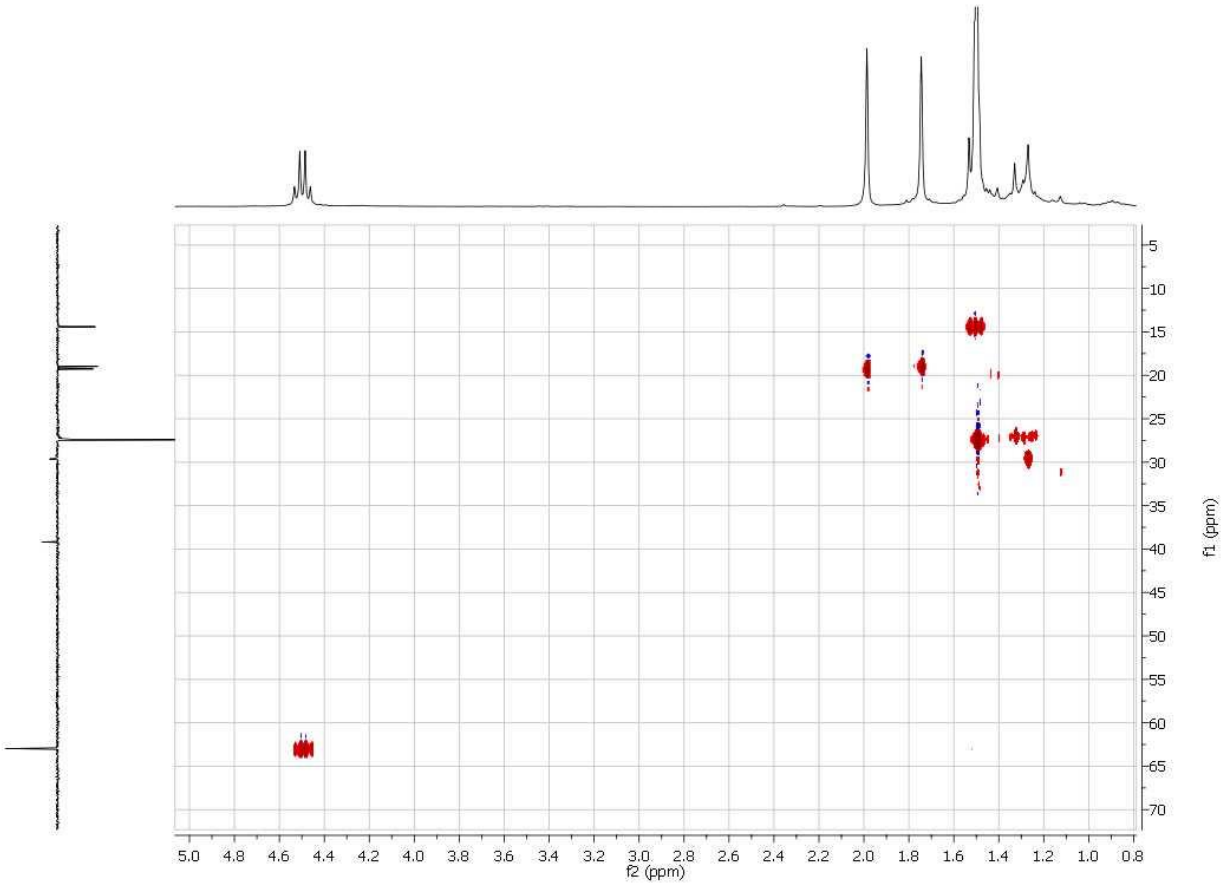

7.98
7.85
6.22
6.6
6.7
6.8
6.9
7.0
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8.0
8.1
8.2
8.3
8.4
f1 (ppm)
8.3
8.1
7.9
7.7
7.5
7.3
7.1
6.9
6.7
f2 (ppm)

3b, *HSQC in $CDCl_3$ at T = 300 K*

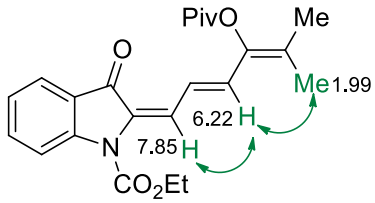




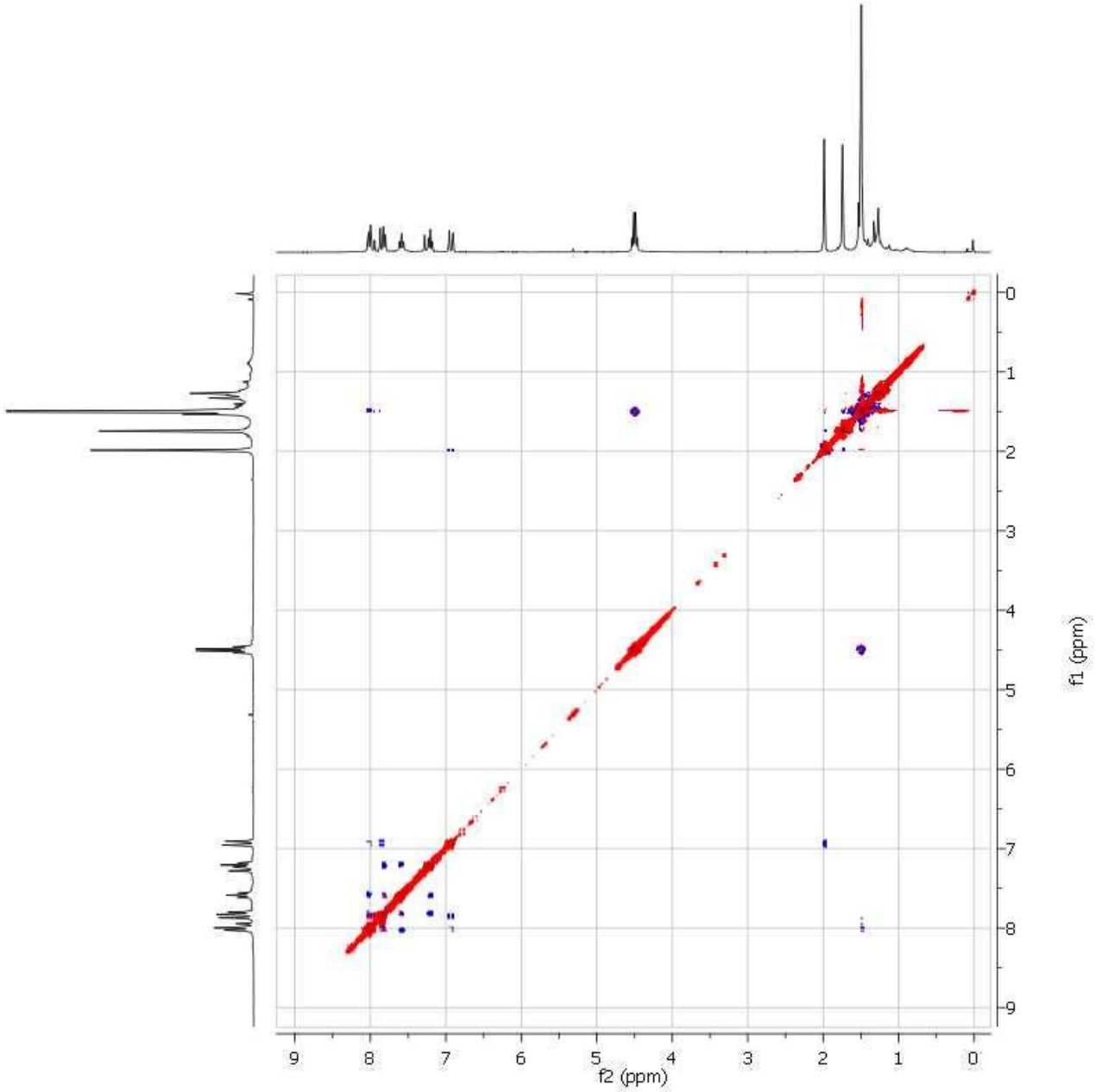

f2 (ppm)
f1 (ppm)

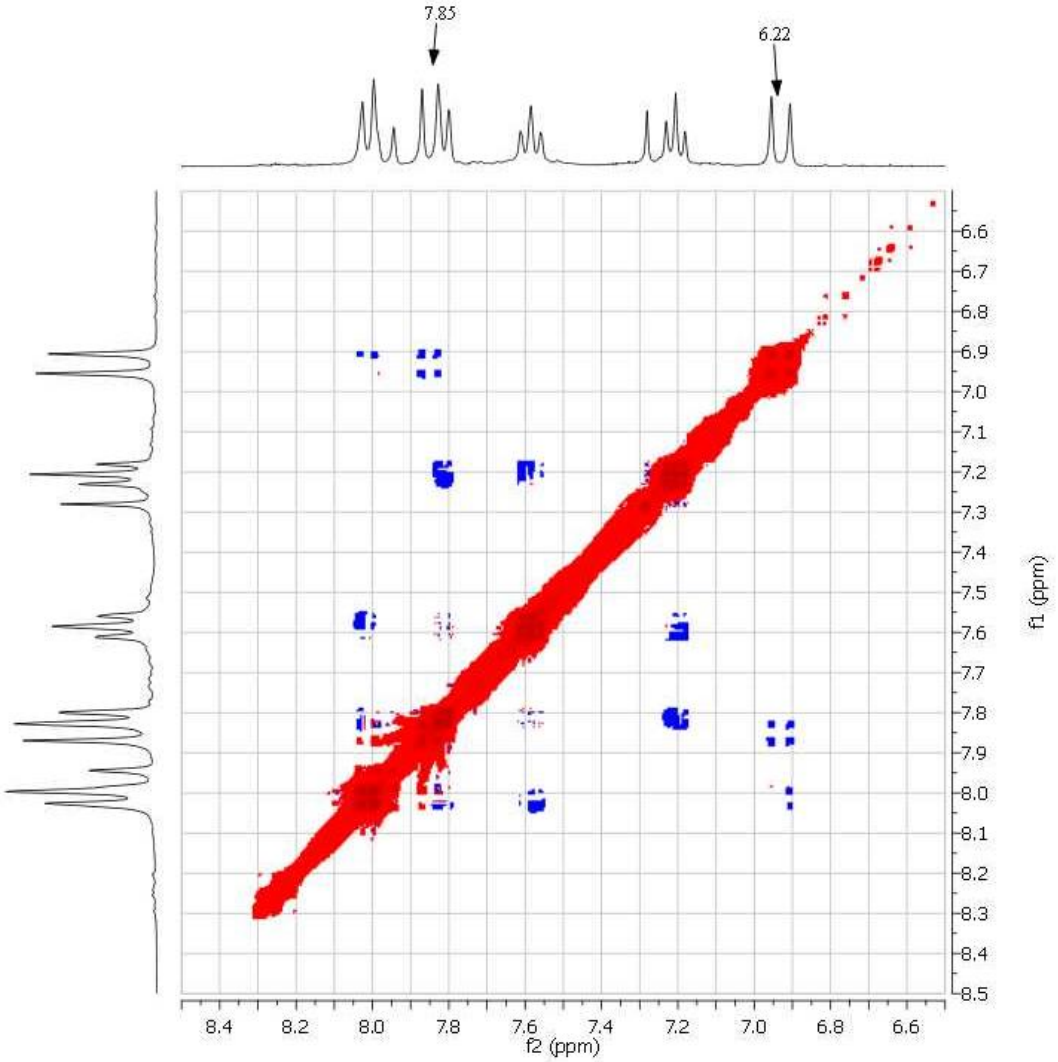

f2 (ppm)
f1 (ppm)

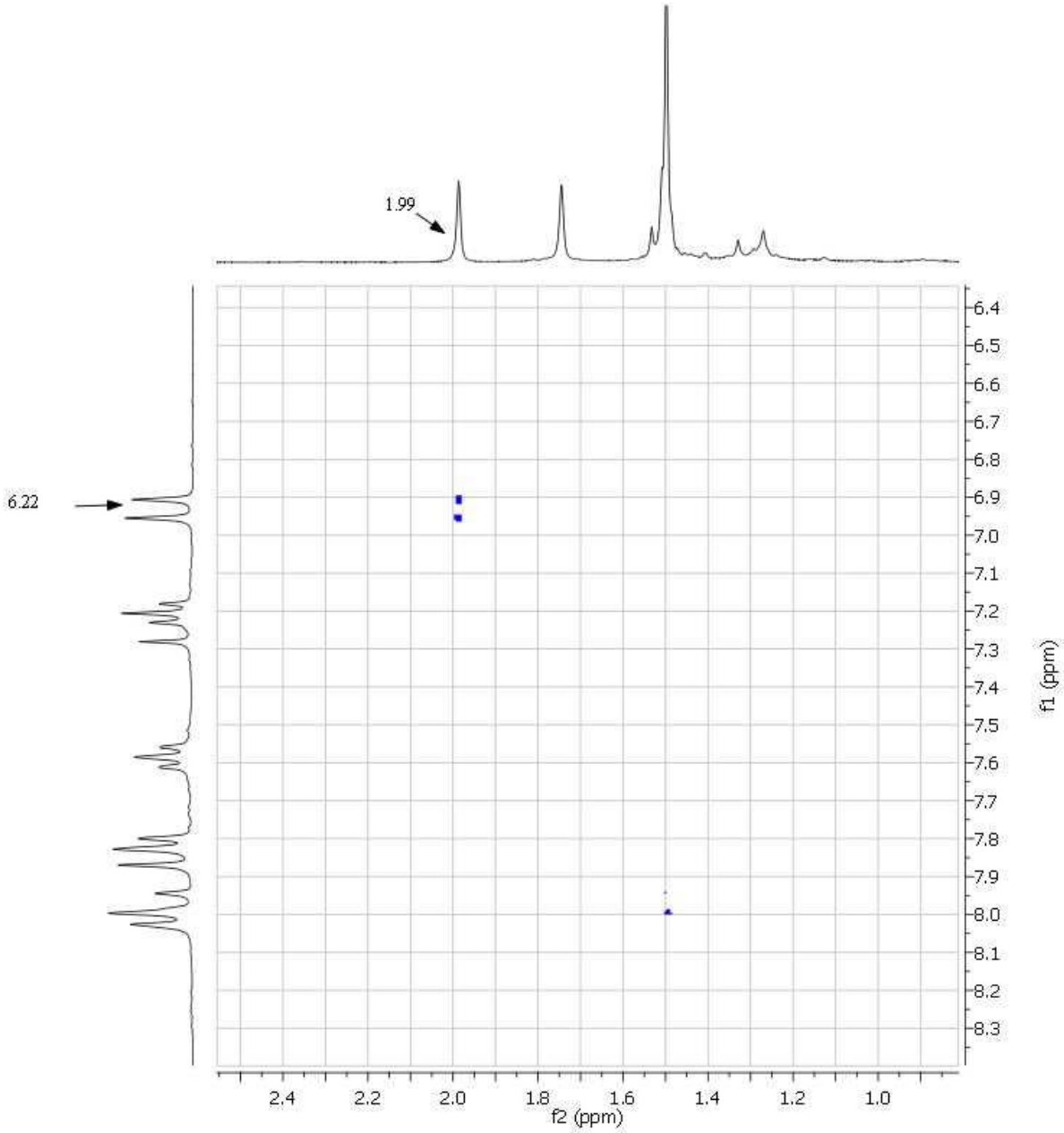
3b, *NOESY in $CDCl_3$ at T = 300 K*



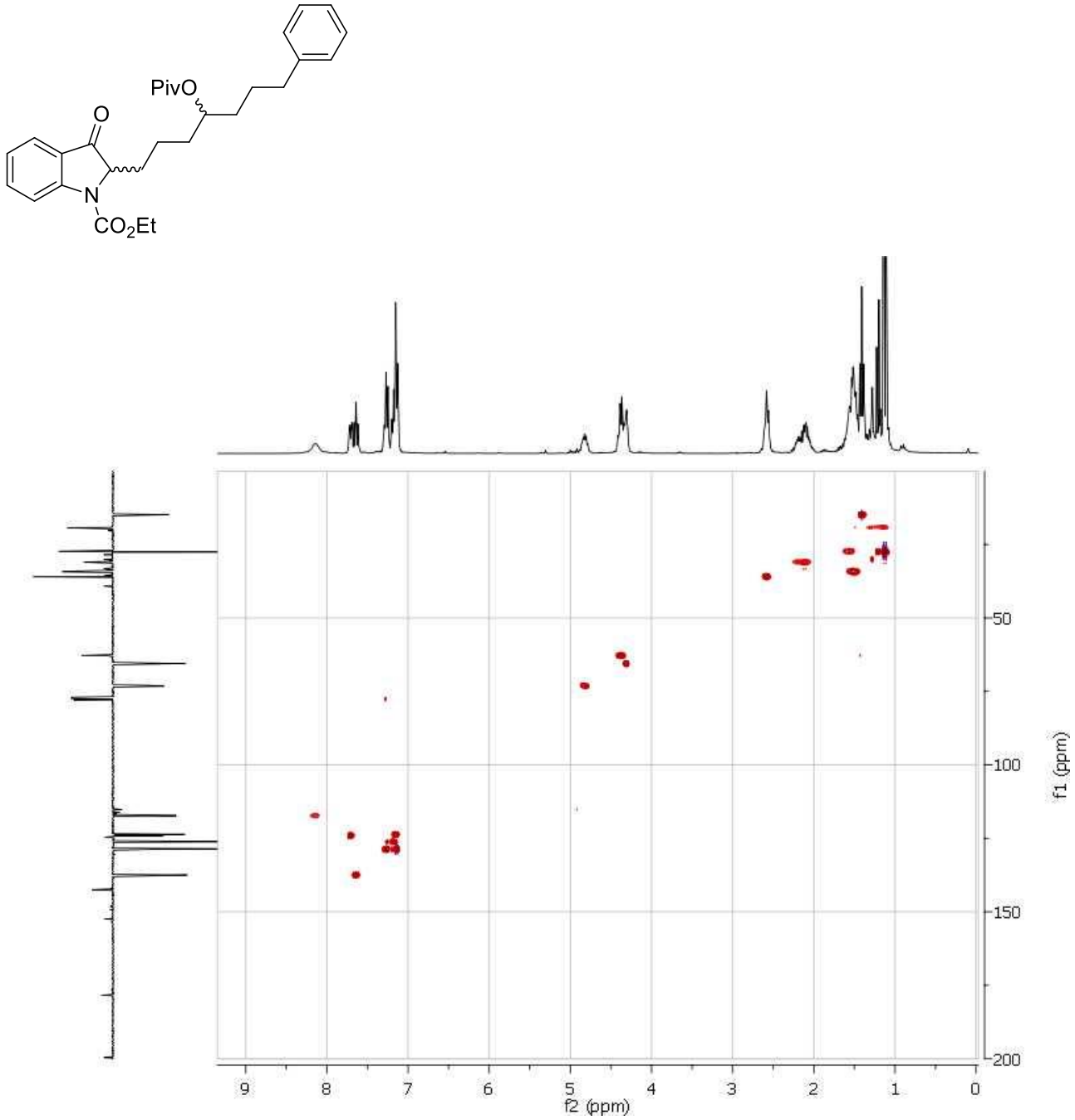
diagnostic cross picks

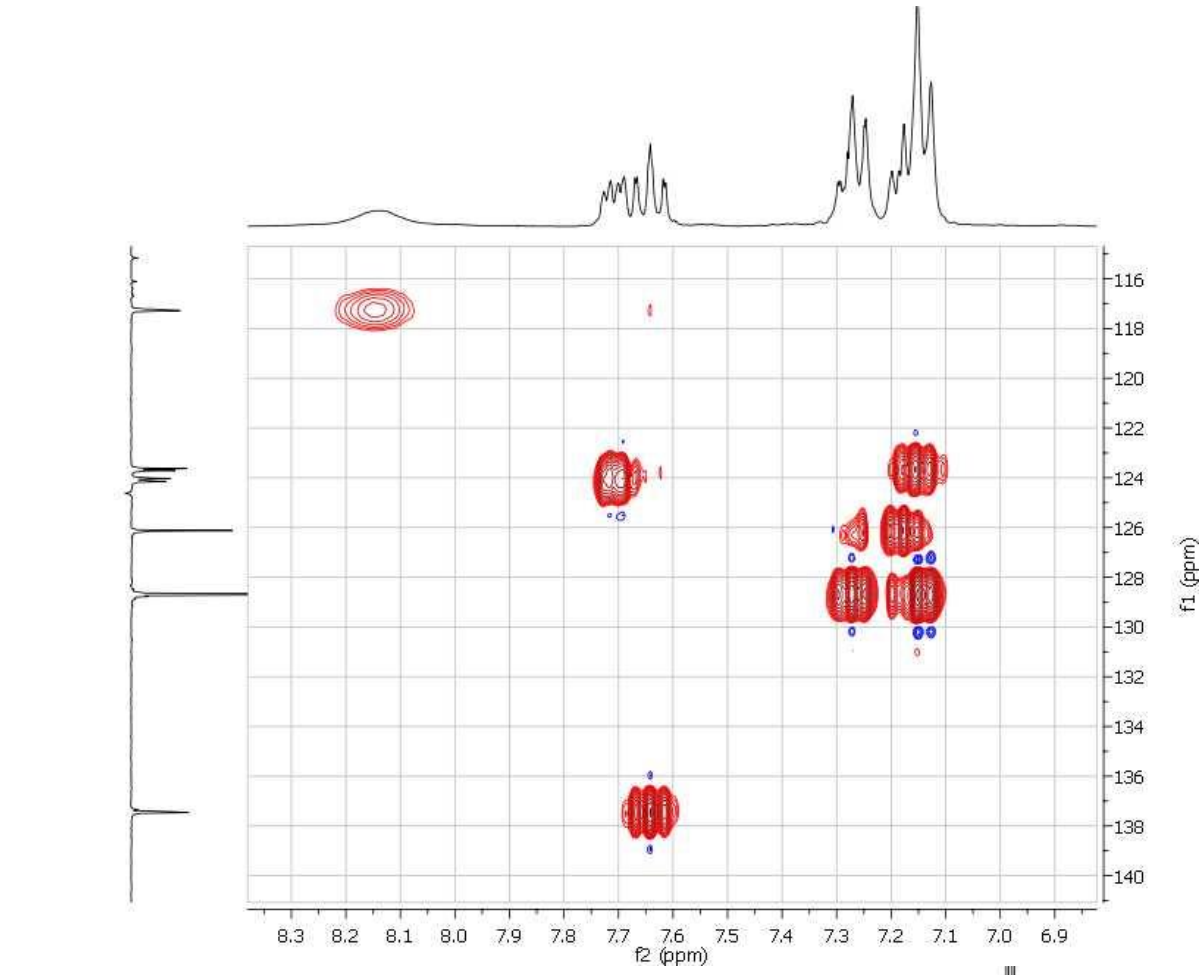


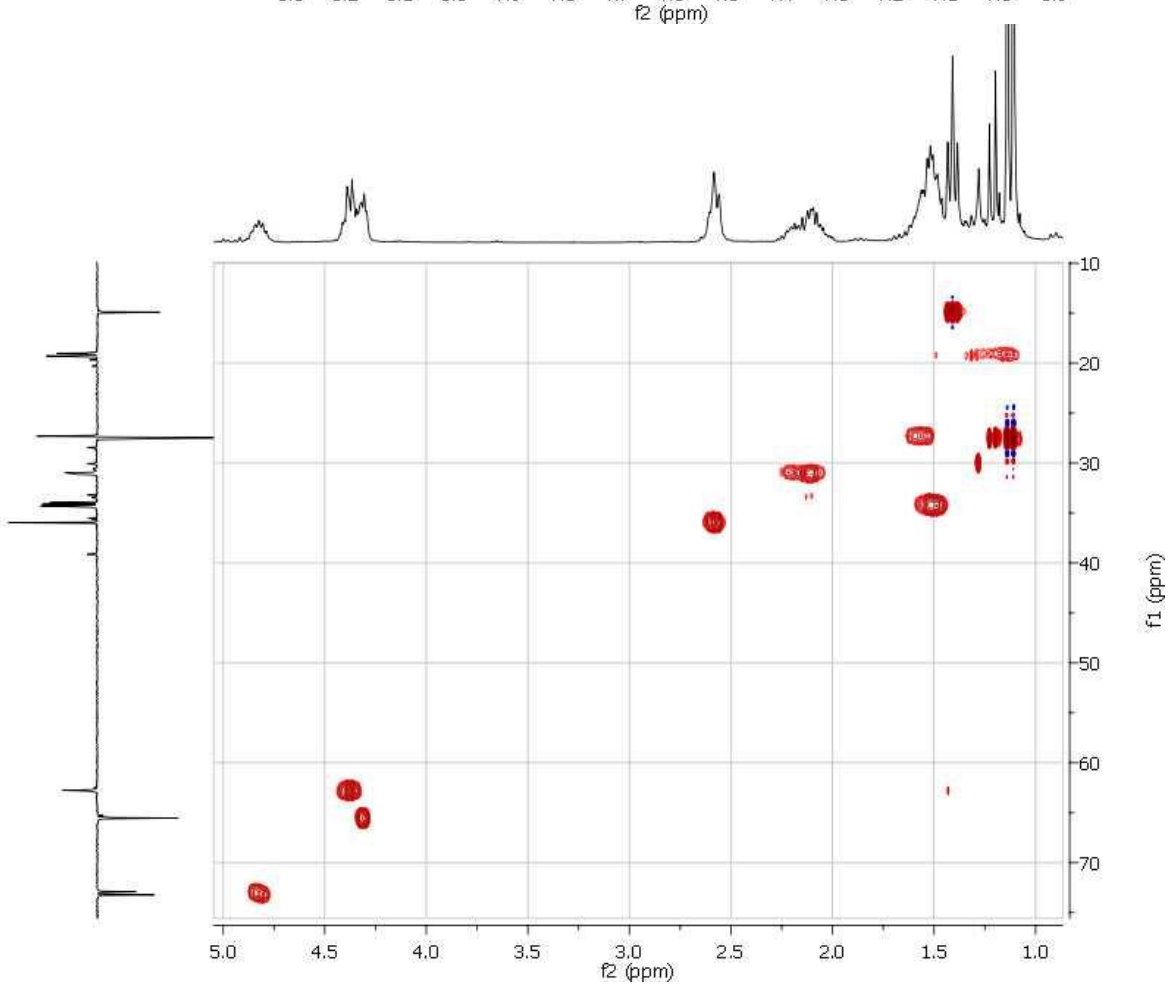

7.85
6.22
6.6
6.7
6.8
6.9
7.0
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8.0
8.1
8.2
8.3
8.4
8.5
f1 (ppm)
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
f2 (ppm)


1.99
6.22
6.4
6.5
6.6
6.7
6.8
6.9
7.0
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8
7.9
8.0
8.1
8.2
8.3
f1 (ppm)
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)

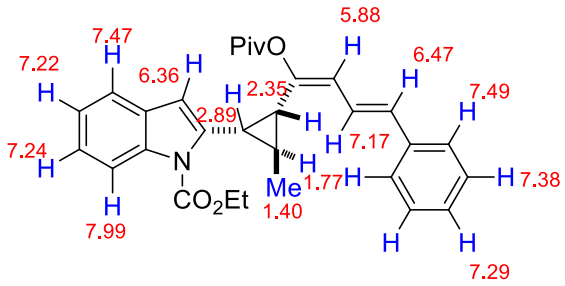
5a, *HSQC in $CDCl_3$ at T = 300*

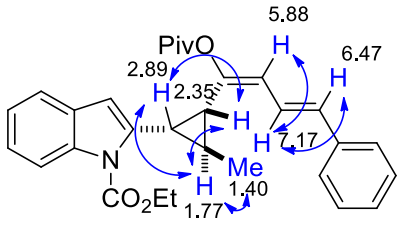


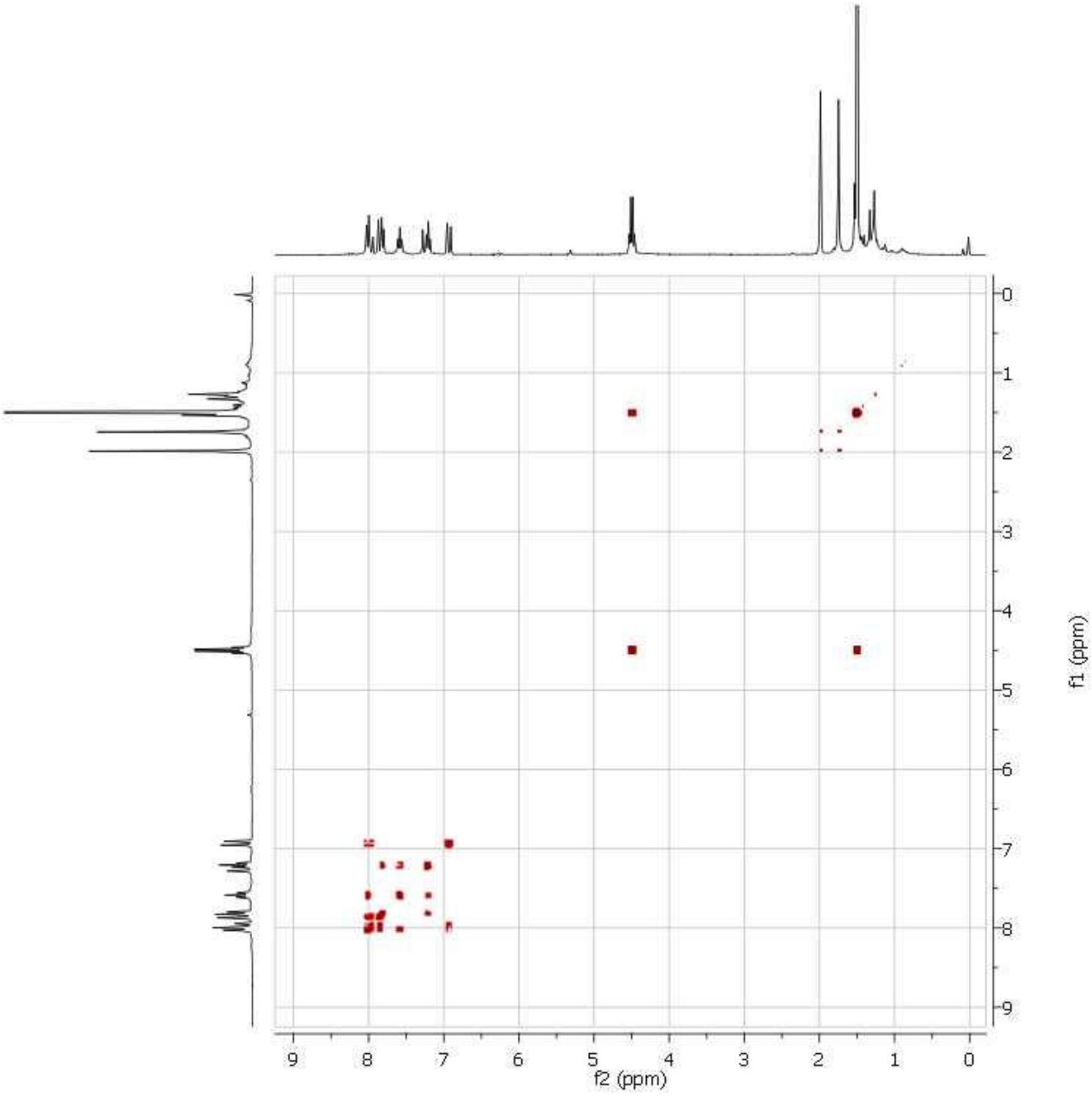

116
118
120
122
124
126
128
130
132
134
136
138
140
f1 (ppm)
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f2 (ppm)

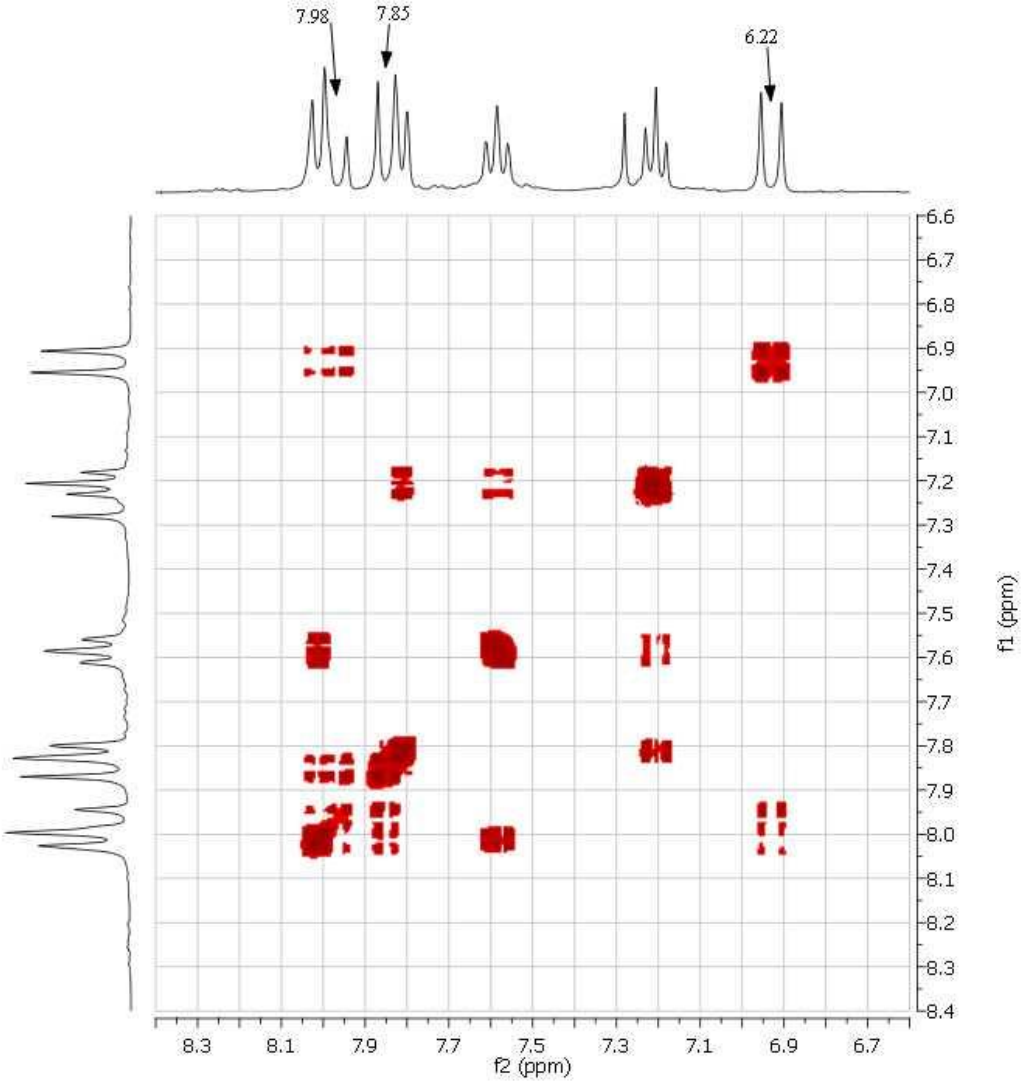

10
20
30
40
50
60
70
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)

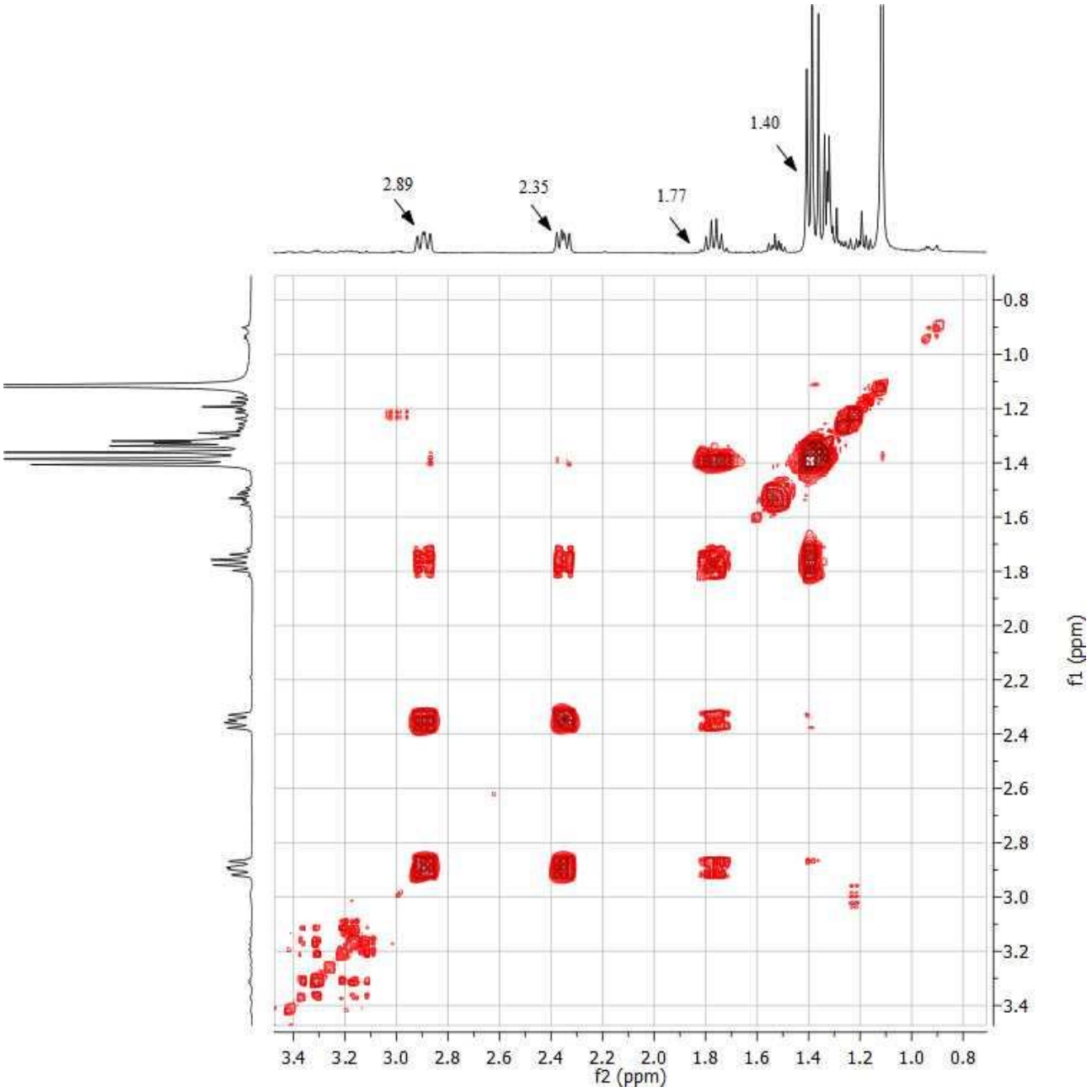
6, *COSY in CD_2Cl_2 at T = 300 K*



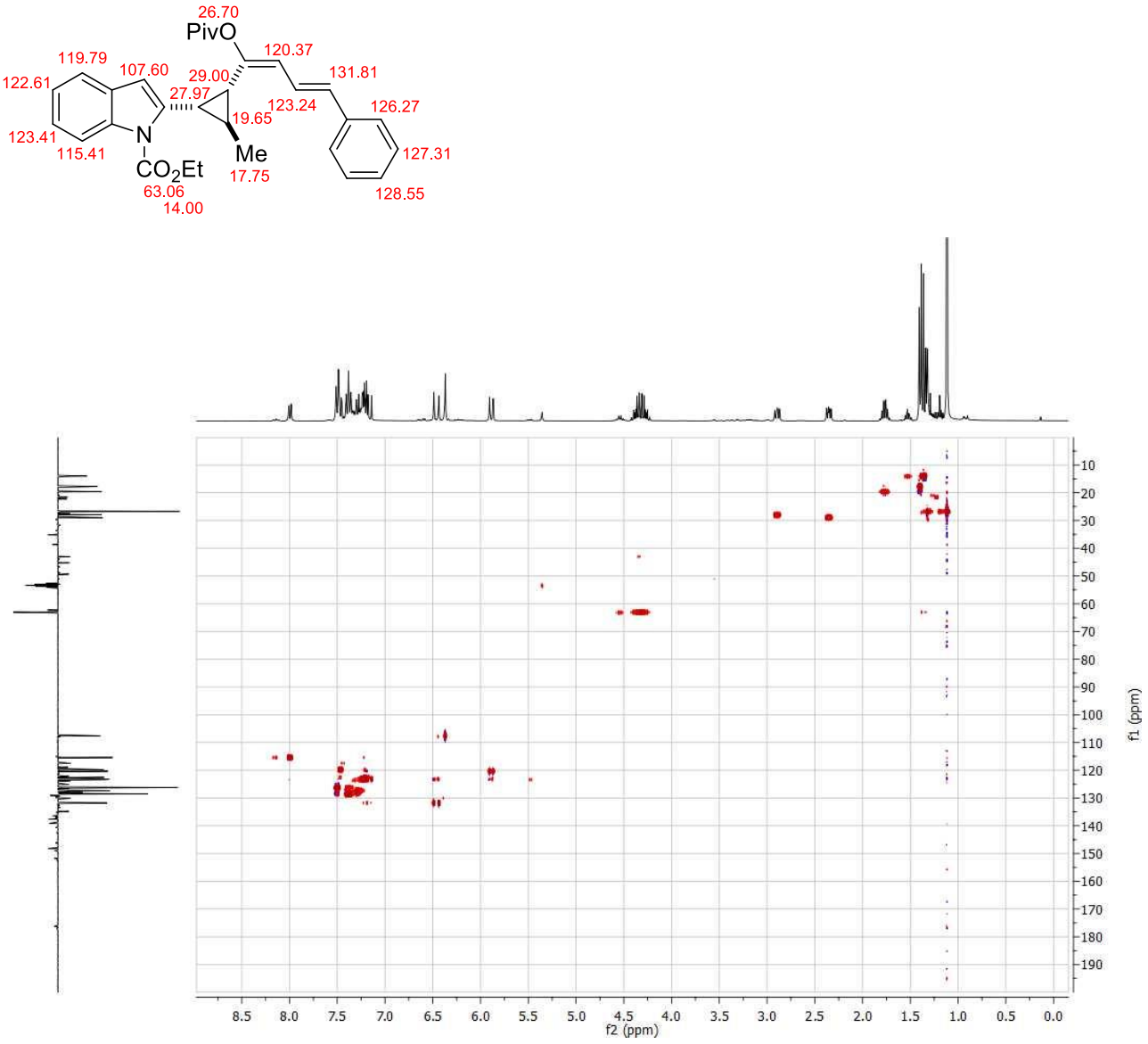


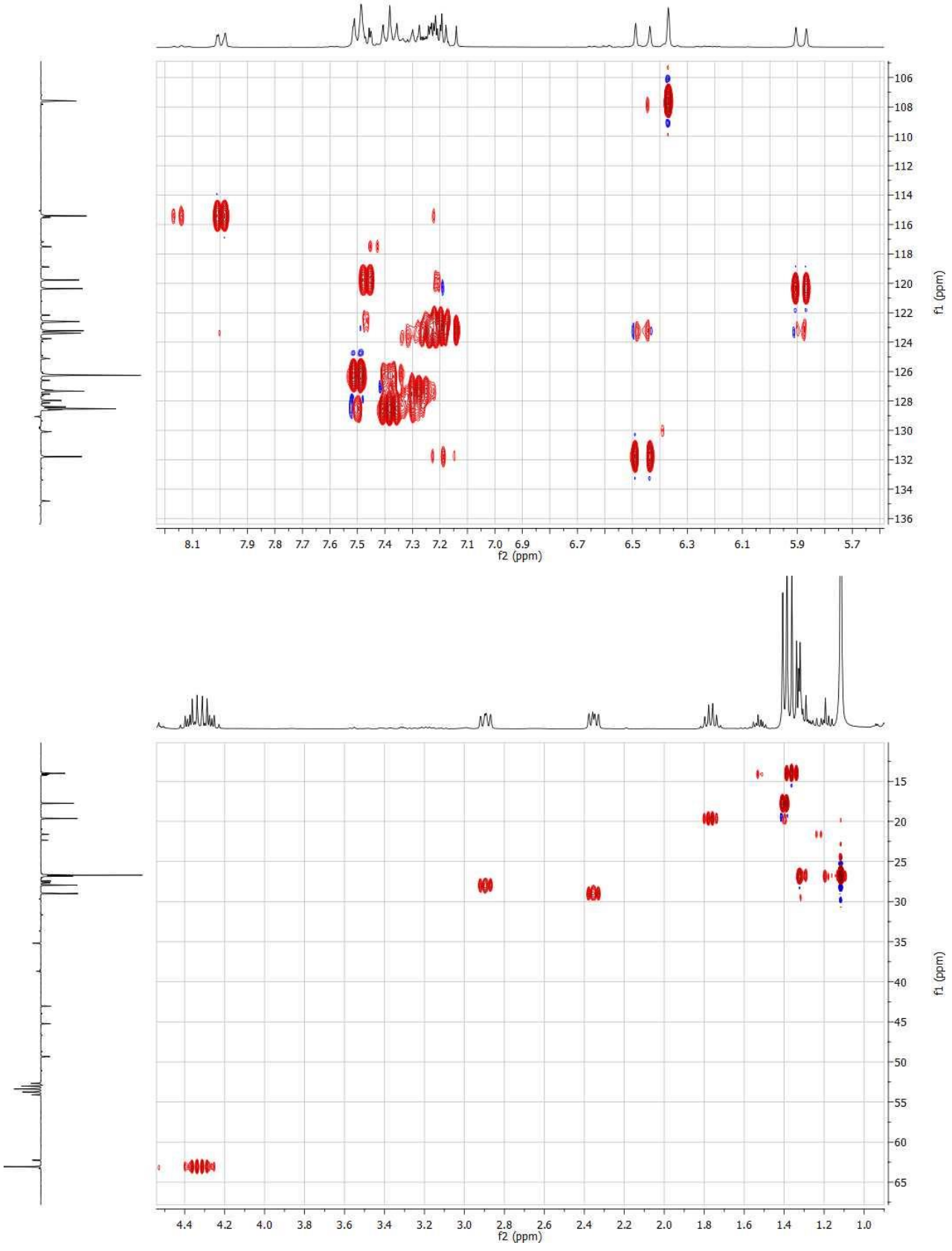



7.98
7.85
6.22
f1 (ppm)
f2 (ppm)

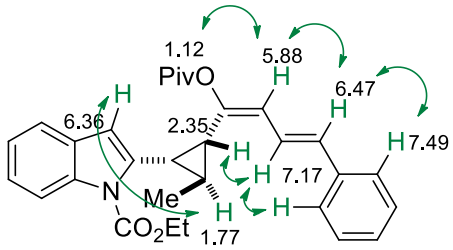

2.89
2.35
1.77
1.40
f1 (ppm)
f2 (ppm)

6, *HSQC in CD_2Cl_2 at T = 300 K*

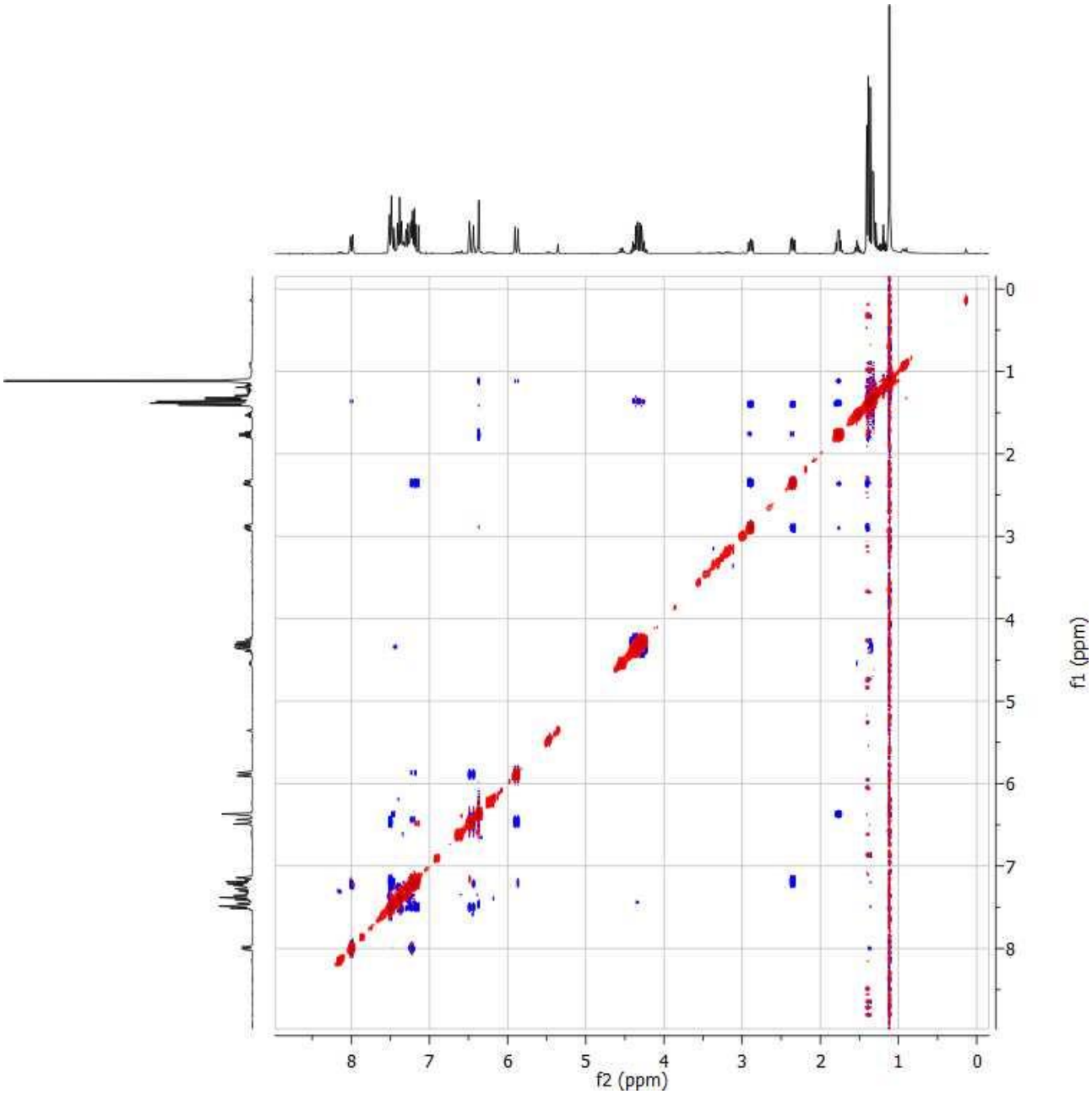



f1 (ppm)
f2 (ppm)
f1 (ppm)
f2 (ppm)

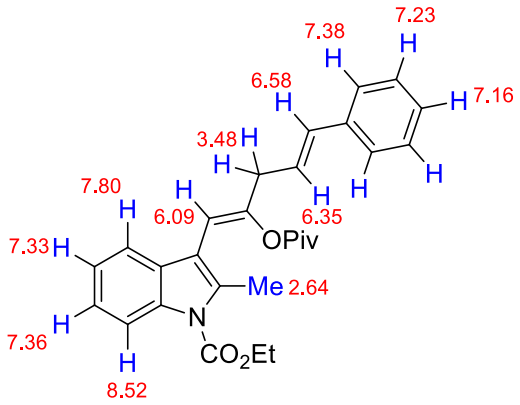
6, *NOESY in CD_2Cl_2 at T = 300 K*

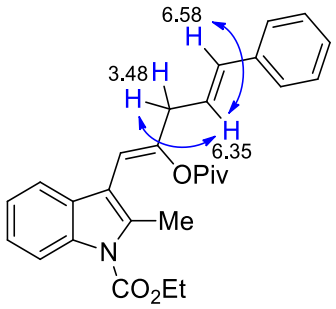


diagnostic cross picks

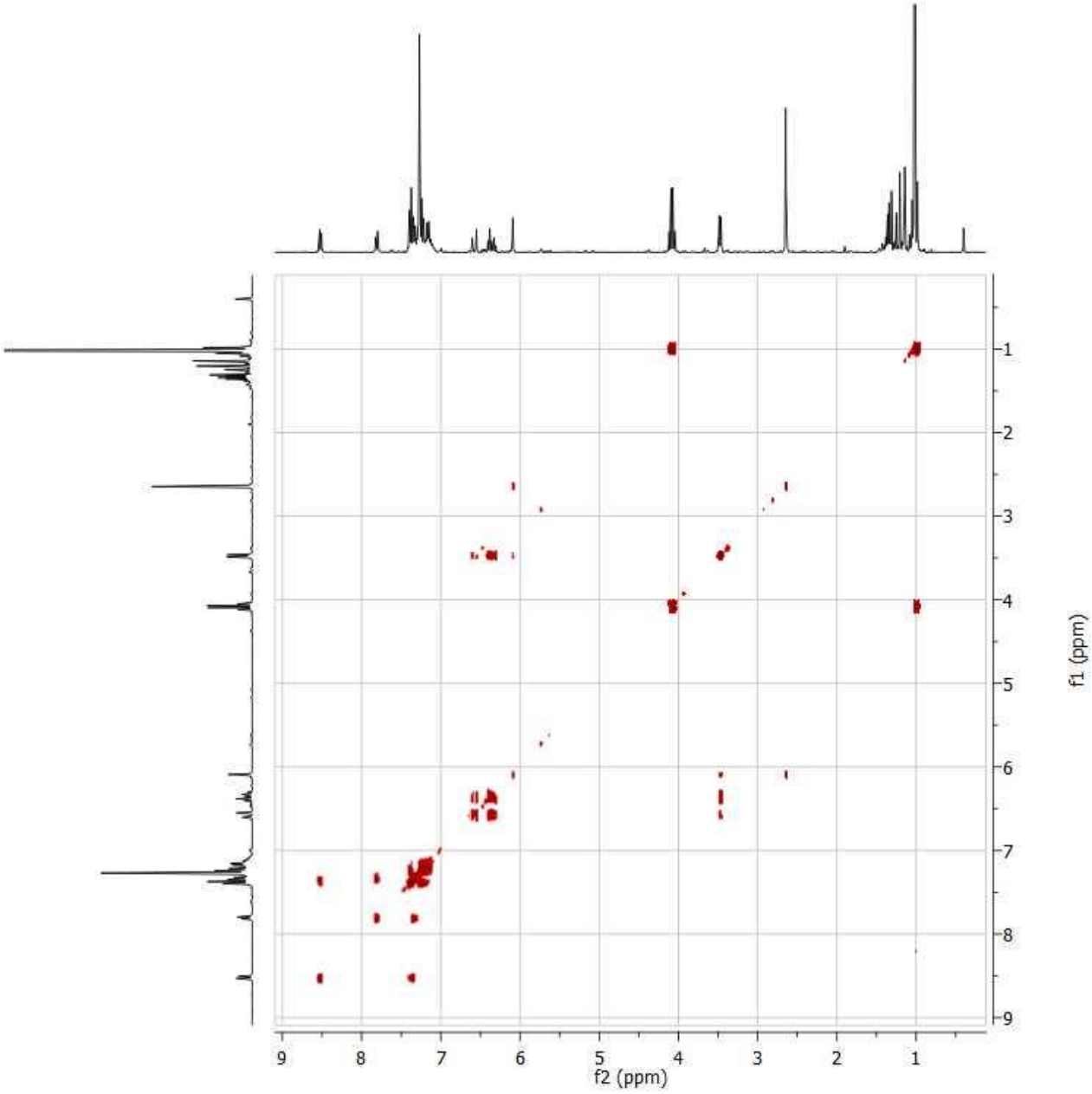


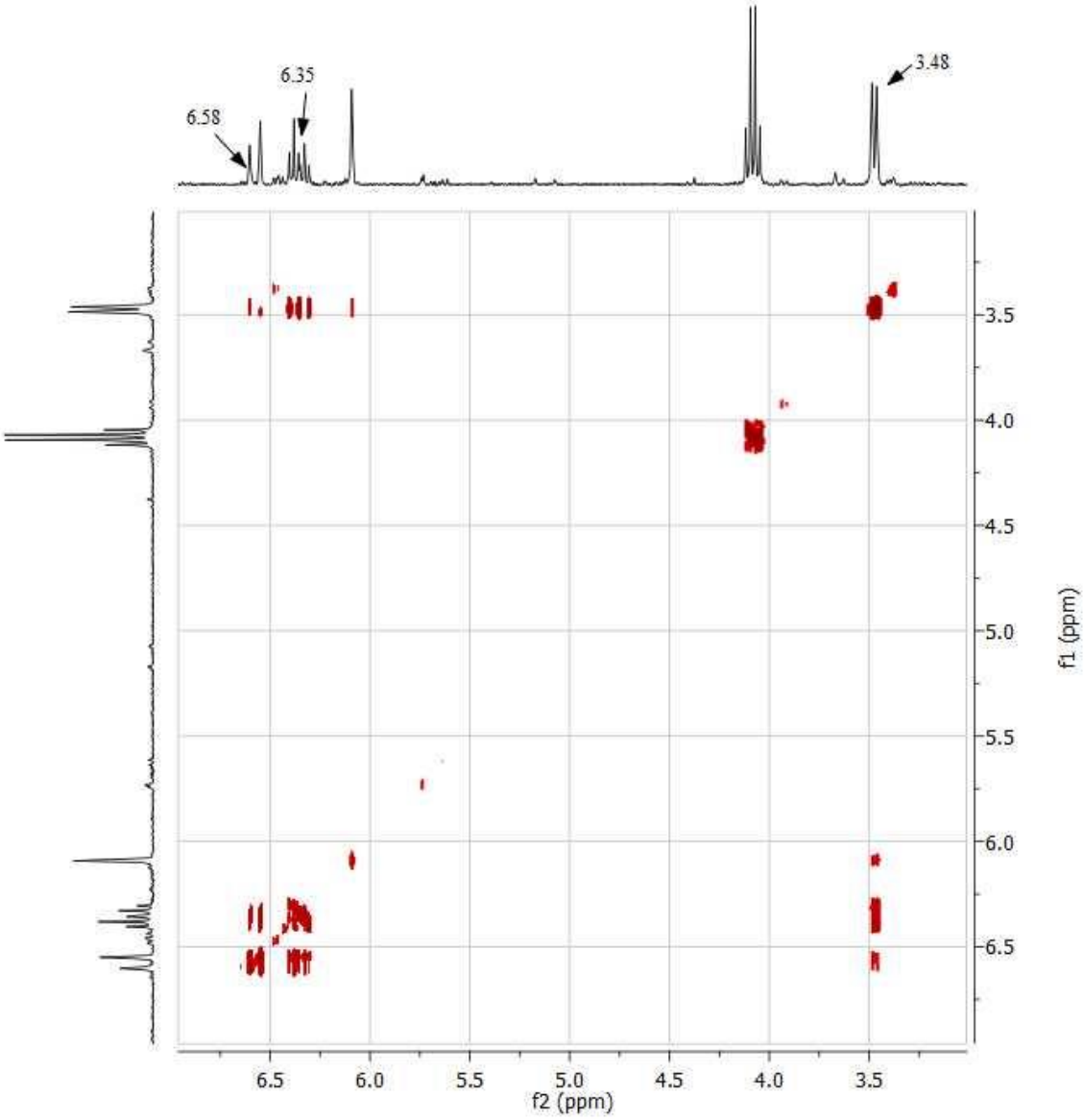
7, *COSY in C_6D_6 at T = 300 K*



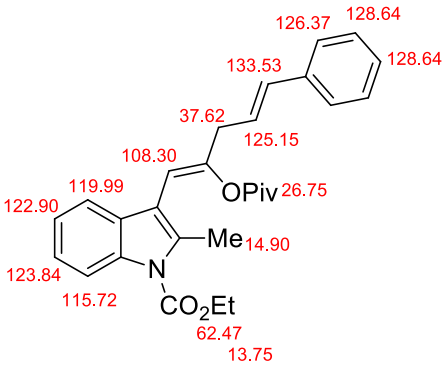


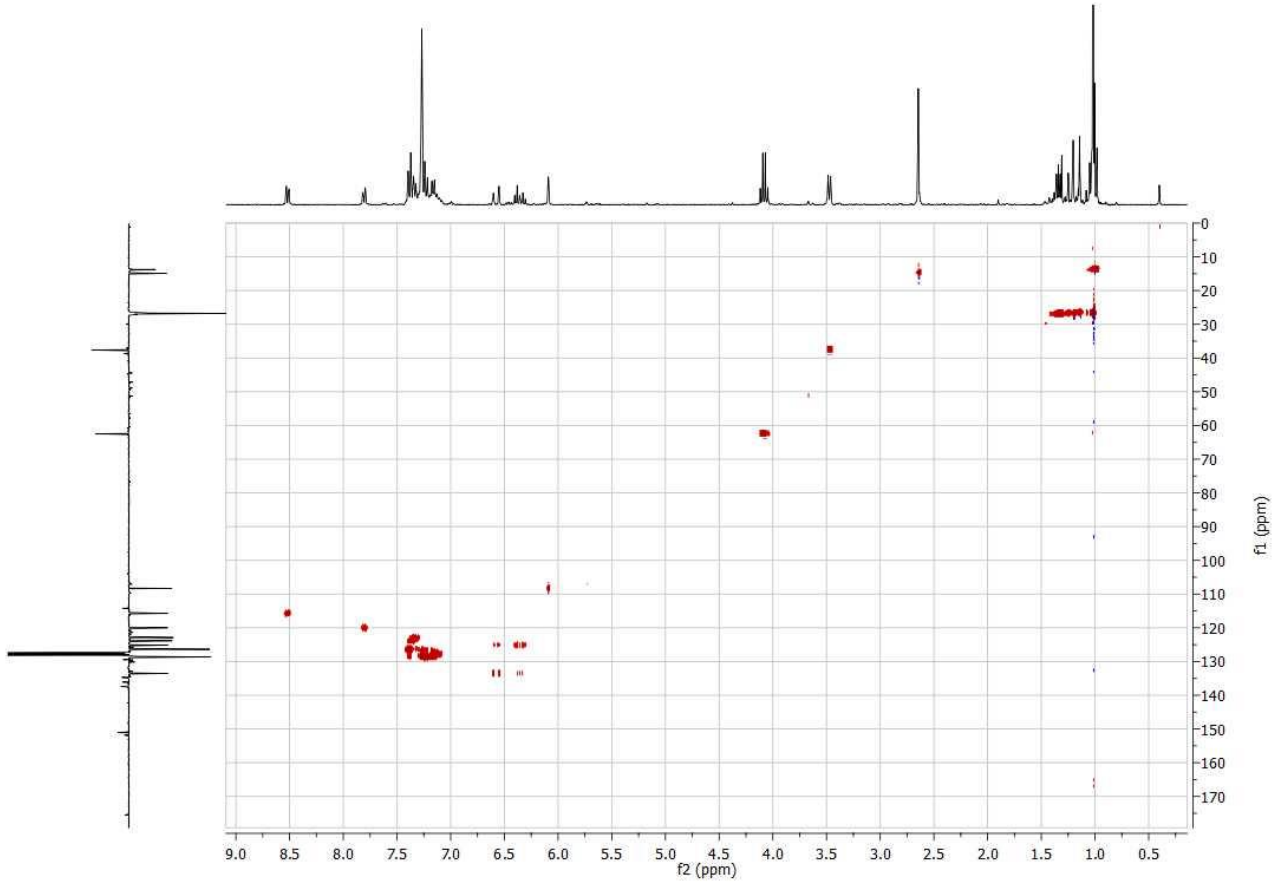
diagnostic cross picks

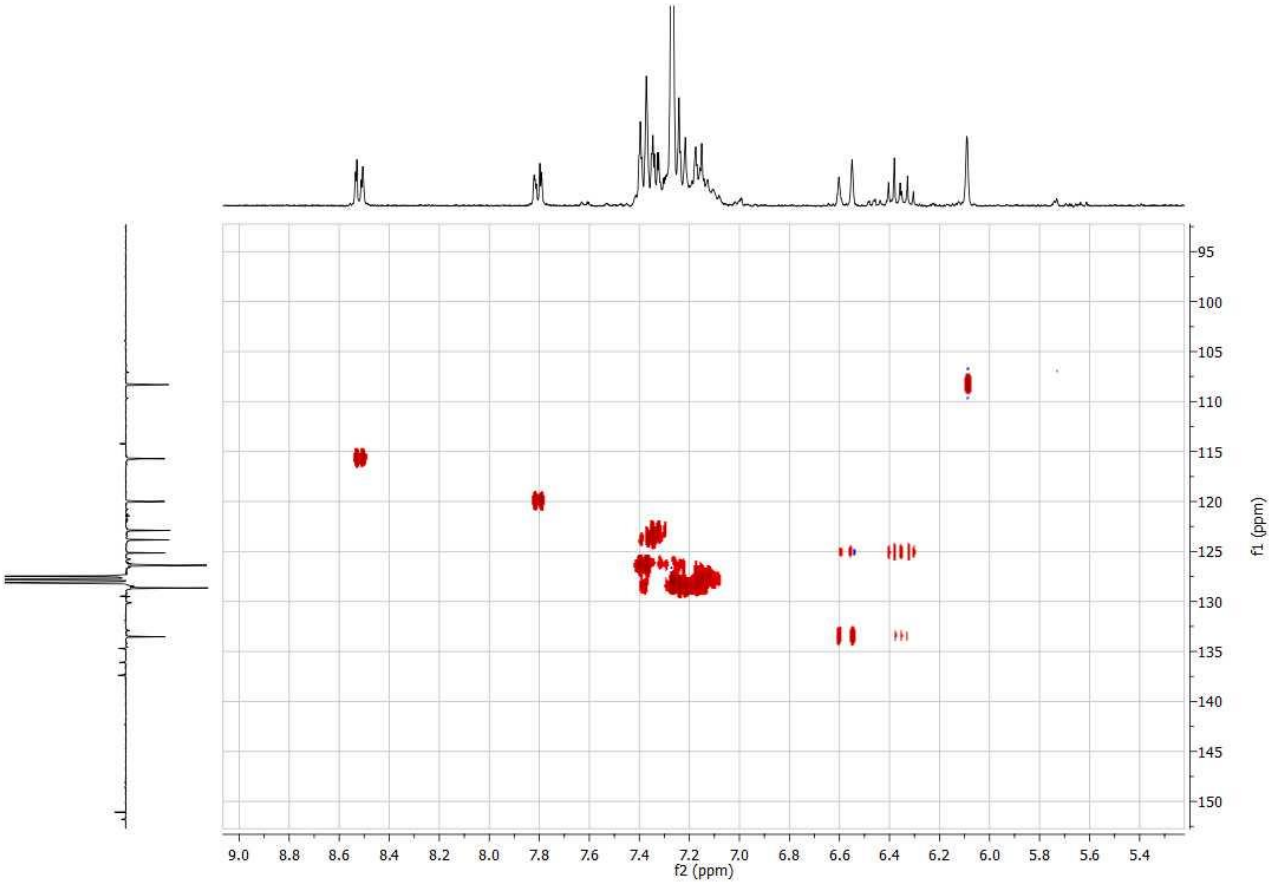


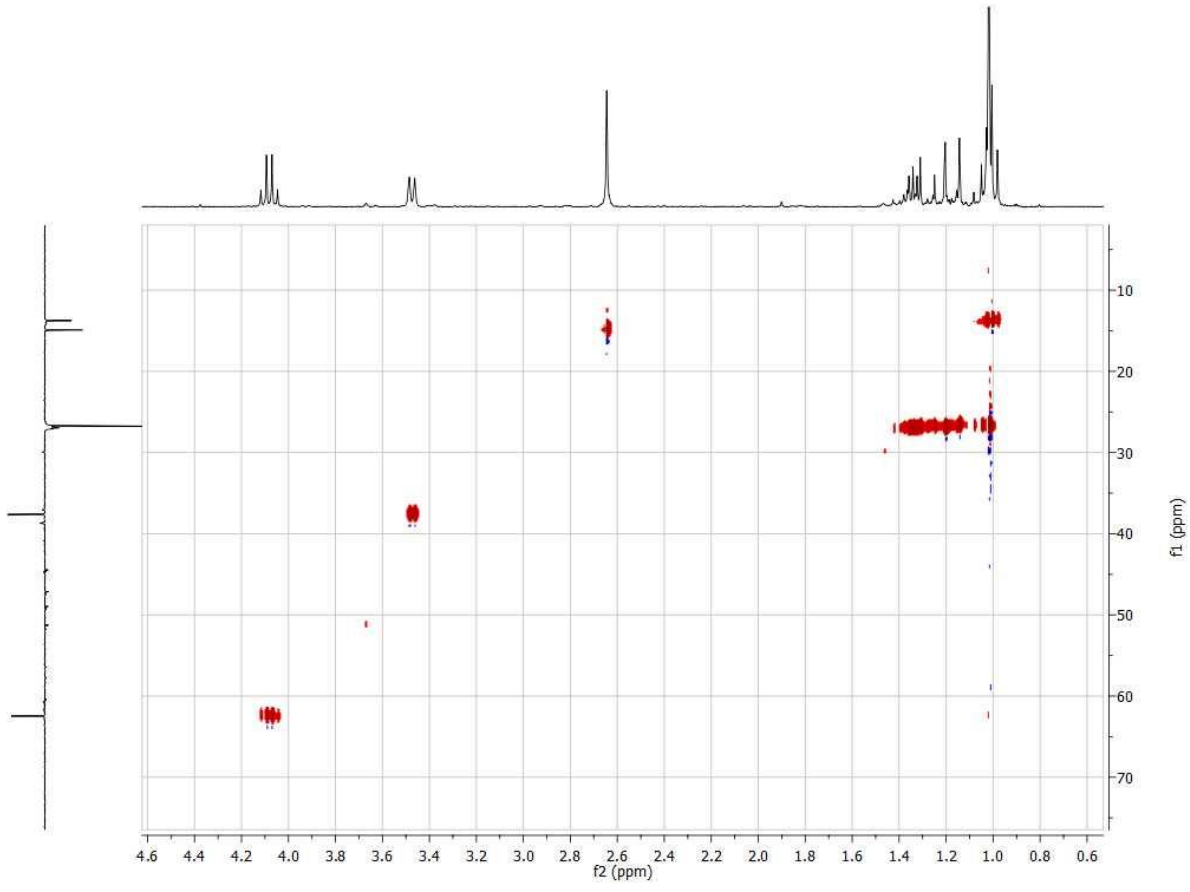

6.58
6.35
3.48
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f2 (ppm)

***7,** HSQC in C_6D_6 at T = 300 K*

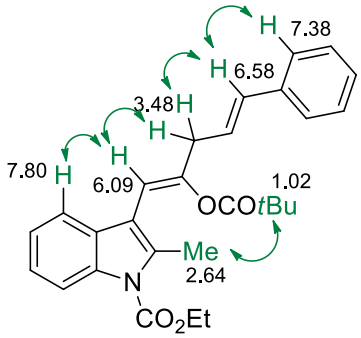




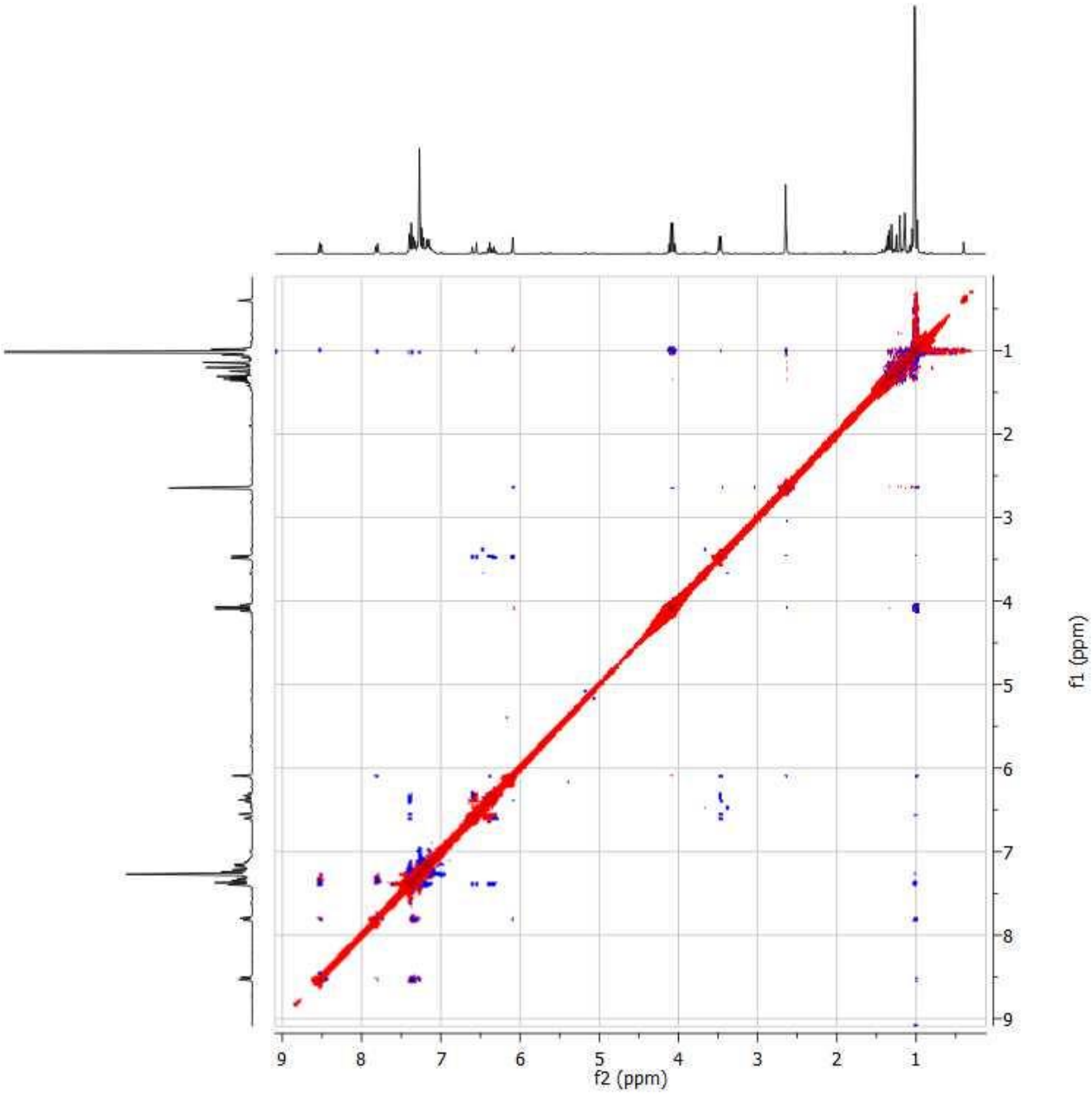

f1 (ppm)
f2 (ppm)

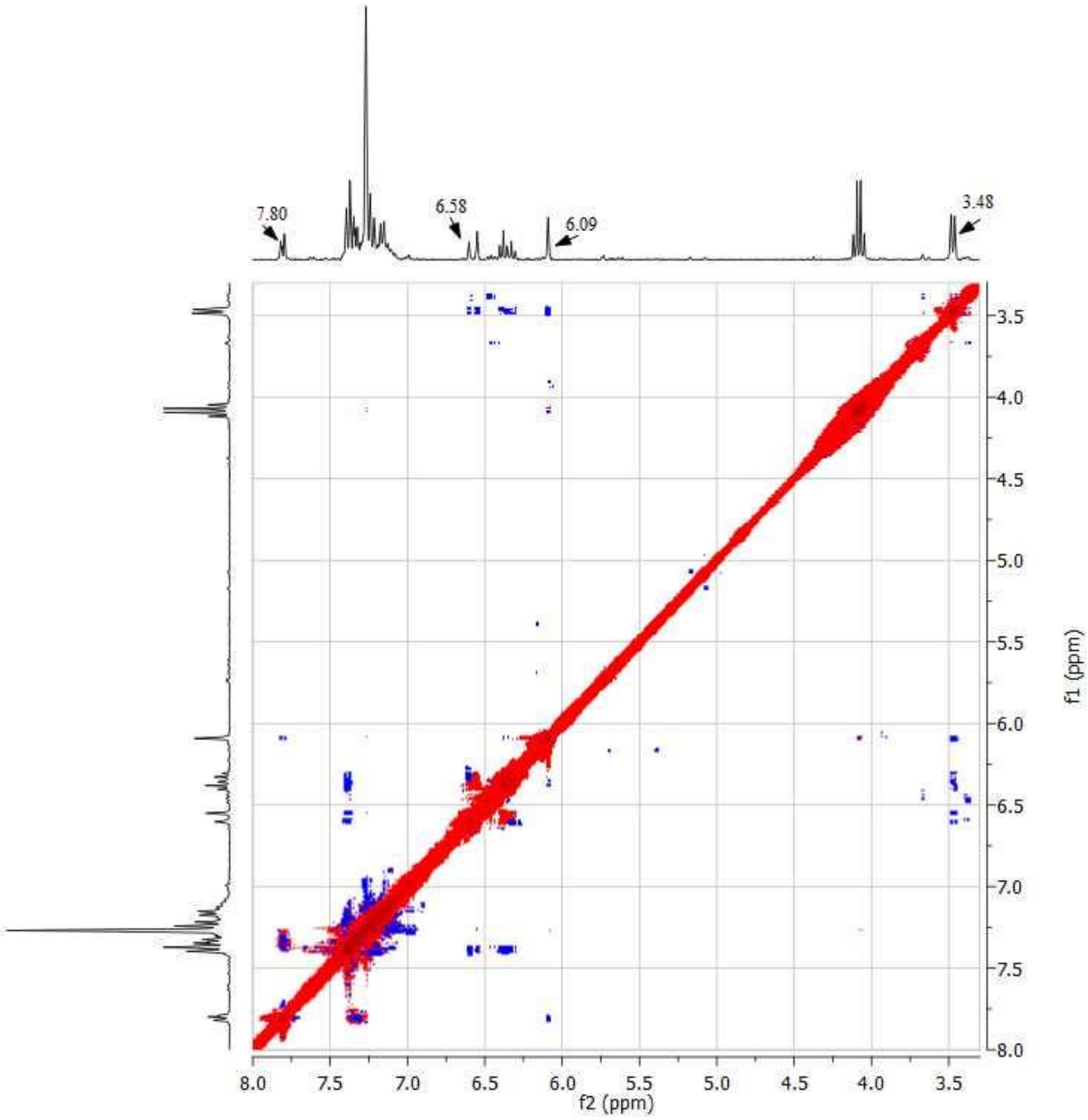

f1 (ppm)
f2 (ppm)

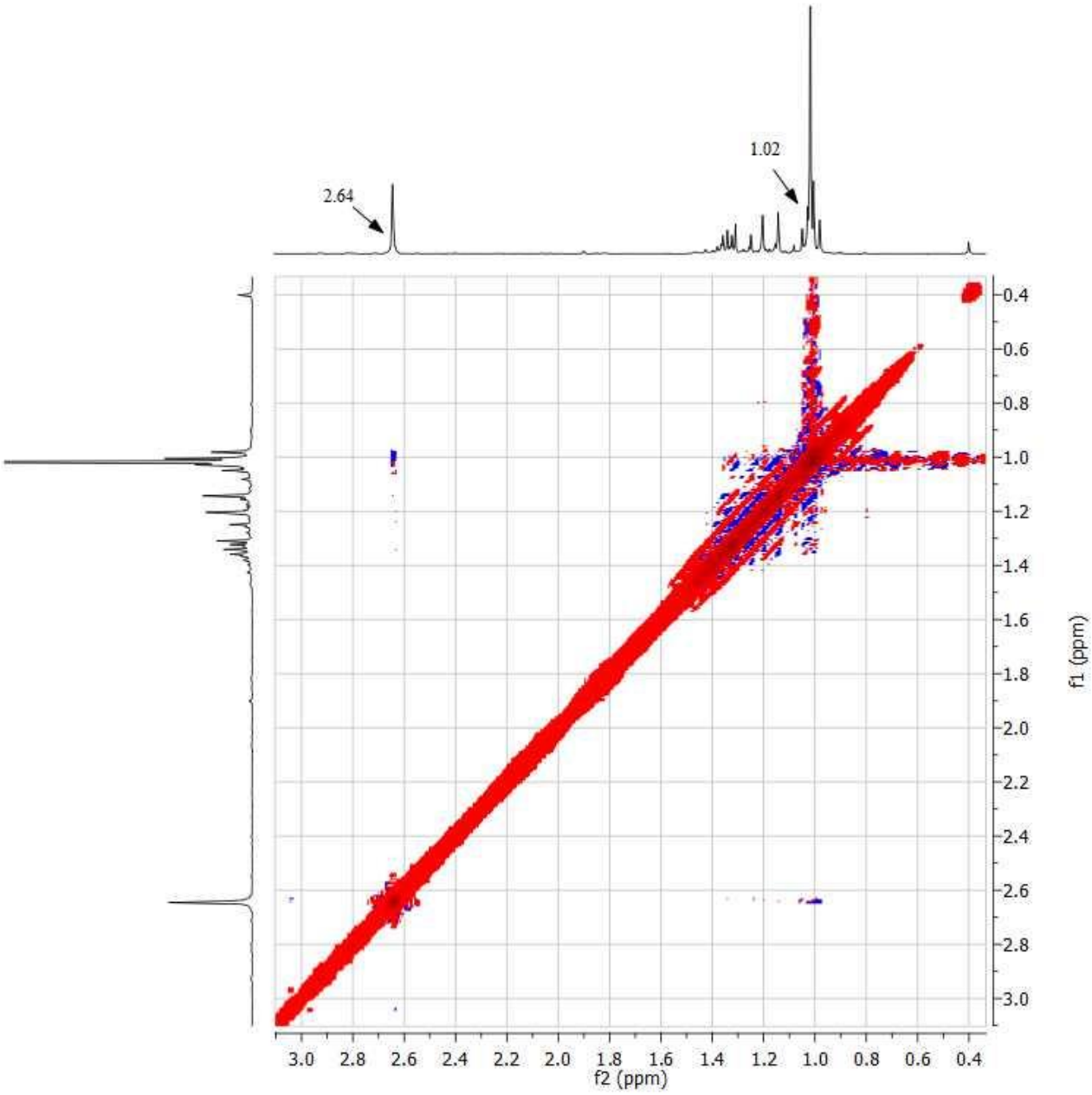
7, *NOESY in C_6D_6 at T = 300 K*



diagnostic cross picks




7.80
6.58
6.09
3.48
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f2 (ppm)
f1 (ppm)


1.02
2.64
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
f1 (ppm)
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4
f2 (ppm)

UV analysis for compound 3a, 3'a, 3d and 3'd

The determination of UV-Vis spectra was made for compounds **3a**, **3'a**, **3d** and **3'd**. In order to obtain the UV-Vis spectra, standard solution with 2.35 mg of **3a** and **3'a** in 10 mL volumetric flask and 1.25 mg of **3d** and **3'd** in 5 mL volumetric flask were prepared in toluene, thetrahydrofuran and dimethylsulfoxide. The standard solutions were used for the preparation of 10^{-4}-10^{-5} solutions of each compound. The extinction coefficients were determined using *Lambert-Beer* law after the determination of UV-Vis spectra using Agilnt 1453E and open top UV quartz cell, 10 mm, 3.0 ml vol.

In the conversion experiments two solutions of pure **3'a** and **3'd** at the concentration of $2 \cdot 10^{-5}$ M in dimethylsulfoxide were prepared. Experiments were conducted in a rotaflo equipped quartz cuvette and the cuvette was irradiated with a 200 W lamp for a period of 6h. Measurements have been taken every 20 minutes to monitor the isomerization. Relative concentrations of *E* and *Z* isomers in the reaction mixture were calculated using *Lambert-Beer* law by the following equation (1):

$$[E]_t = \frac{A_t - \varepsilon_Z C_0}{\varepsilon_E - \varepsilon_Z}$$

Where:

$[E]_t$ = concentration of the *E* isomer at time t;

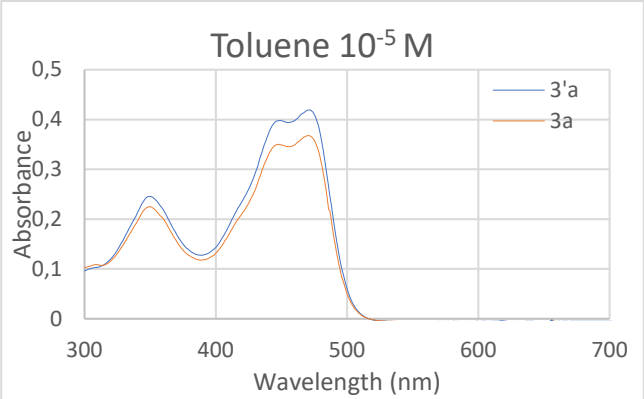
A_t = Absorbance at time t at 354 nm;

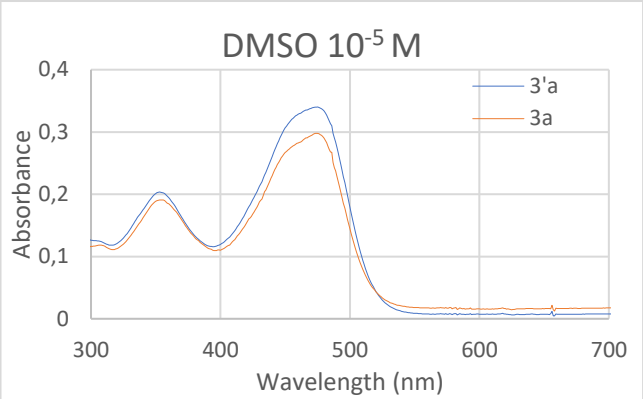
ε_Z = molar extinction coefficient for the isomer *Z* at 354 nm;

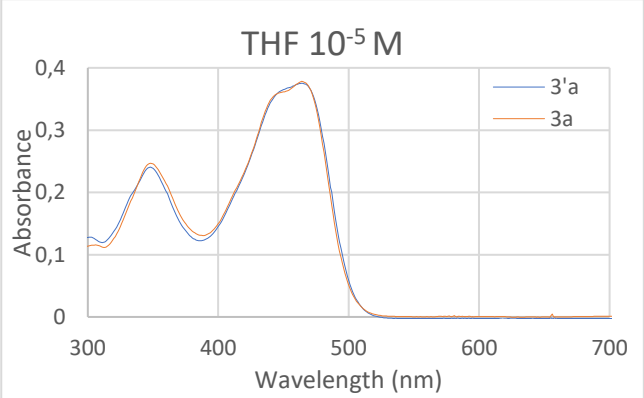
ε_E = molar extinction coefficient for the isomer *E* at 354 nm;

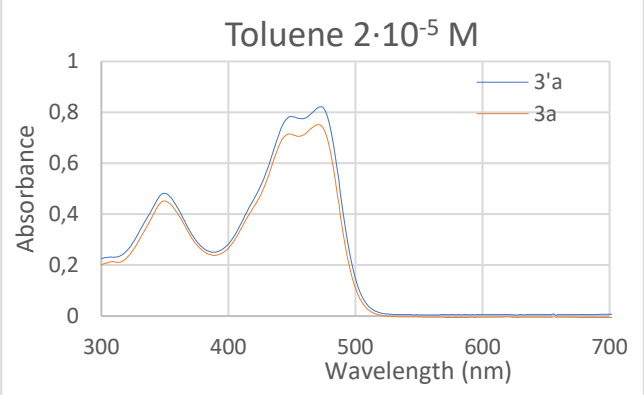
C_0 = starting concentration of **3'a** or **3'd**, respectively

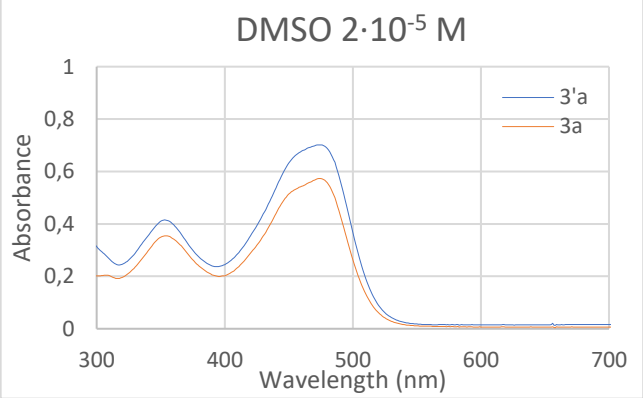
The following diagrams represent the absorbance spectra of **3a** and **3'a** in toluene, DMSO and THF at different concentrations

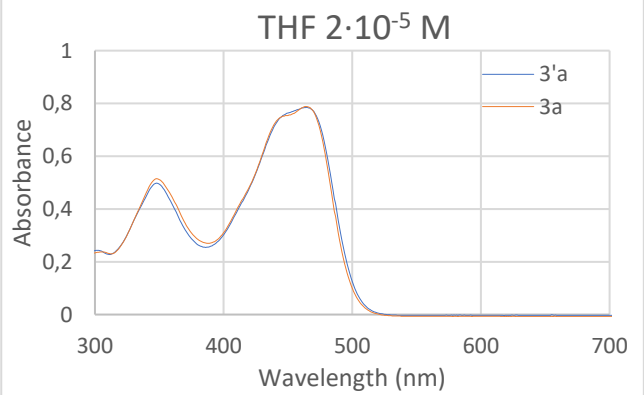

Toluene 10-5 M
Absorbance
Wavelength (nm)
3'a
3a

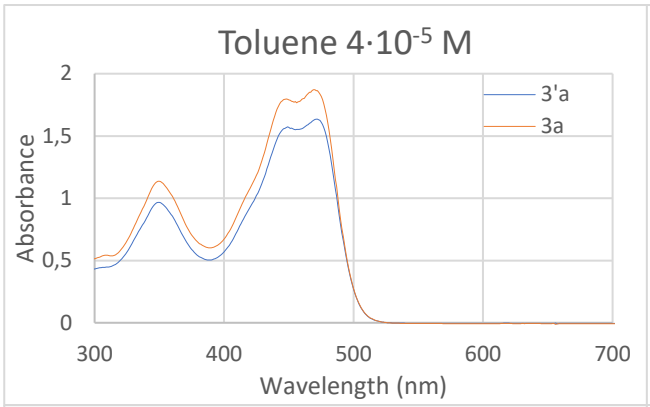

DMSO 10-5 M
Absorbance
Wavelength (nm)
3'a
3a

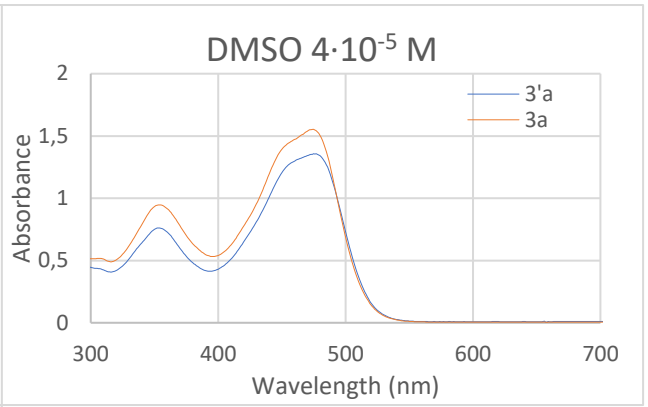

THF 10-5 M
Absorbance
Wavelength (nm)
3'a
3a

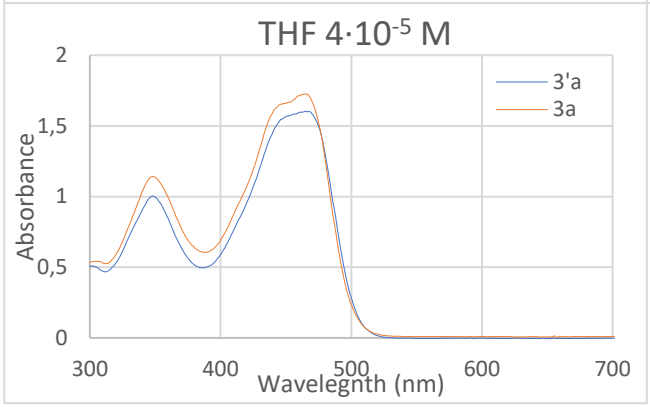

Toluene 2·10-5 M
Absorbance
Wavelength (nm)
3'a
3a

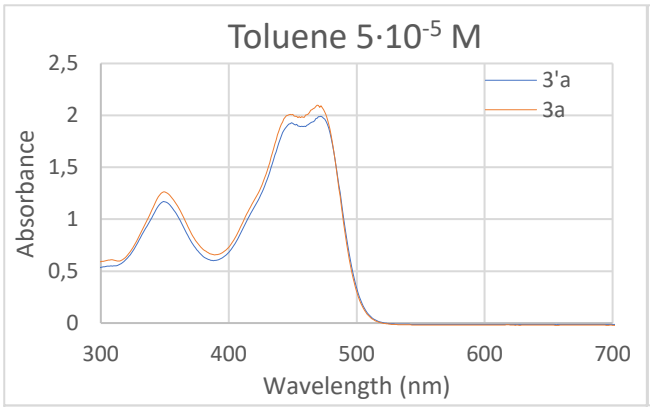

DMSO 2·10-5 M
Absorbance
Wavelength (nm)
3'a
3a

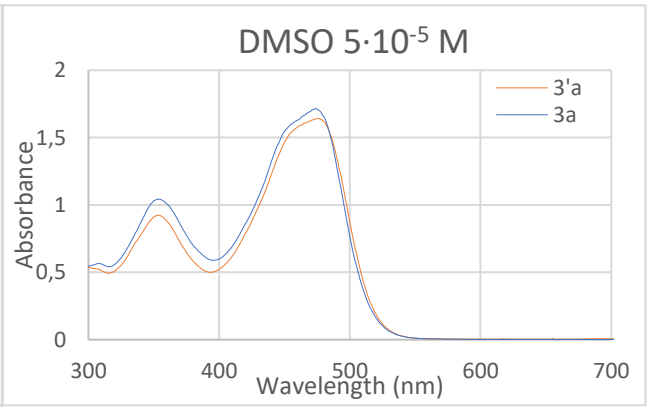

THF 2·10-5 M
Absorbance
Wavelength (nm)
3'a
3a

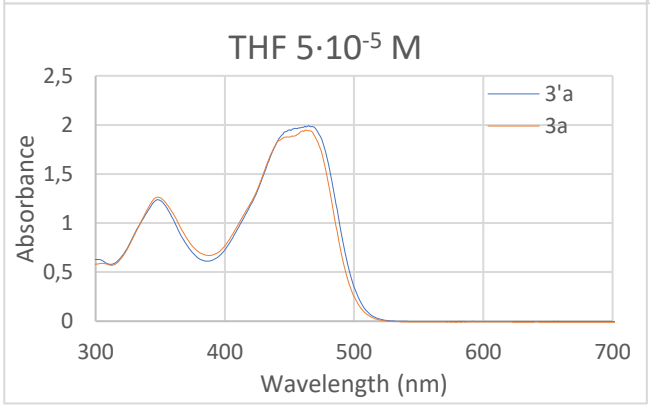

Toluene 4·10-5 M
Absorbance
Wavelength (nm)
3'a
3a


DMSO 4·10-5 M
Absorbance
Wavelength (nm)
3'a
3a

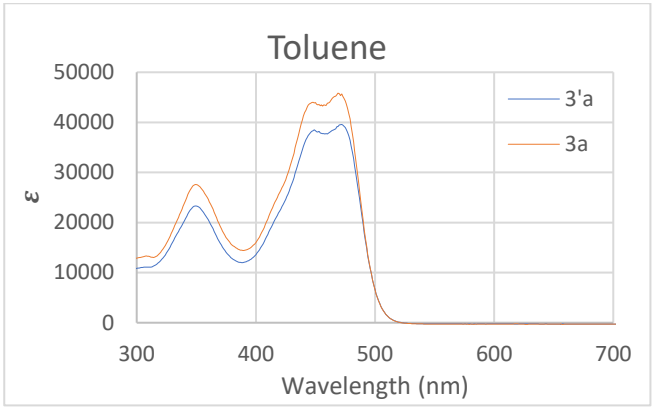

THF 4·10-5 M
Absorbance
Wavelegnth (nm)
3'a
3a

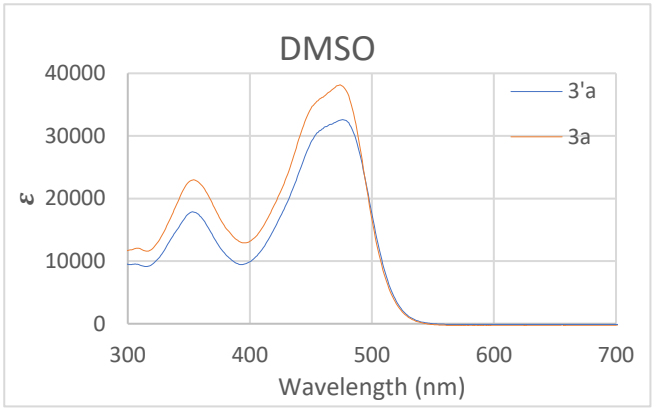

Toluene 5·10-5 M
Absorbance
Wavelength (nm)
3'a
3a

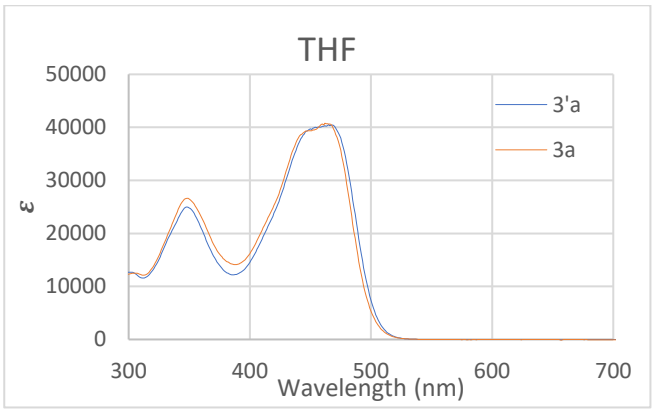

DMSO 5·10-5 M
Absorbance
Wavelength (nm)
3'a
3a


THF 5·10-5 M
Absorbance
Wavelength (nm)
3'a
3a

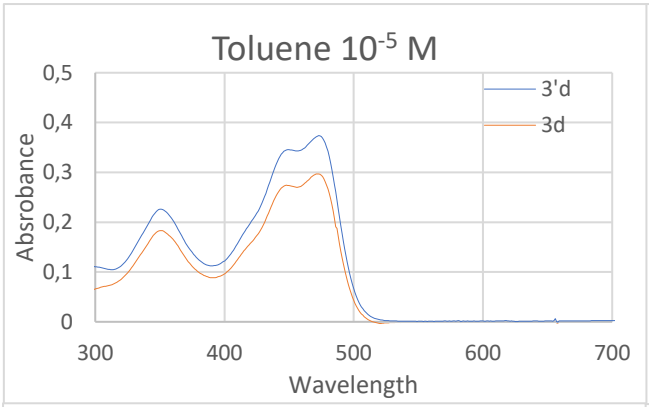
The following diagrams represent the molar extinction coefficient for **3a** and **3'a** in toluene, DMSO and THF obtained with linear regression method.

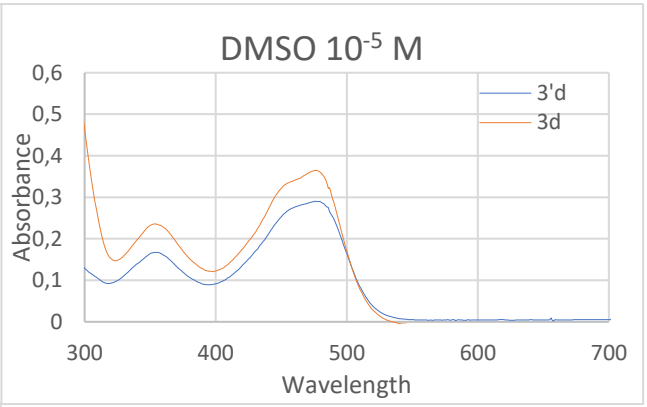


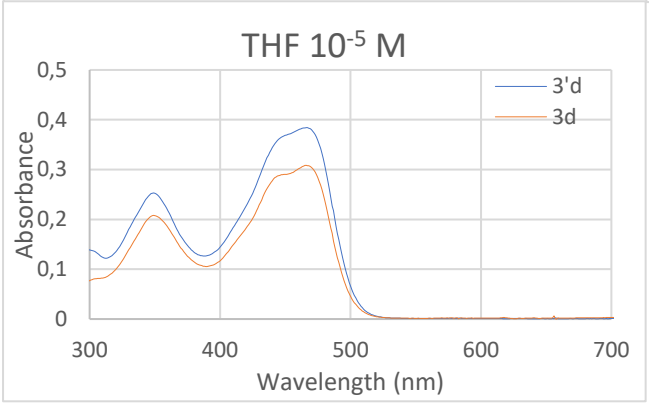


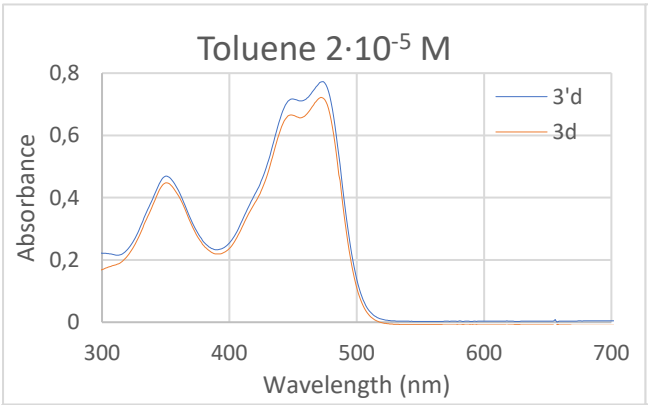


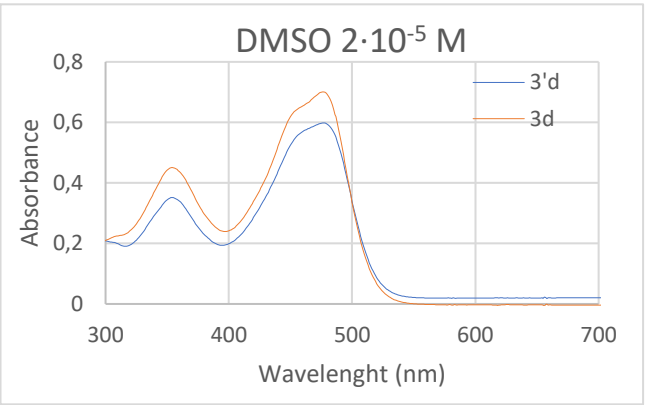
The following diagrams represent the absorbance spectra of compounds **3d** and **3'd** in toluene, DMSO and THF at different concentrations.

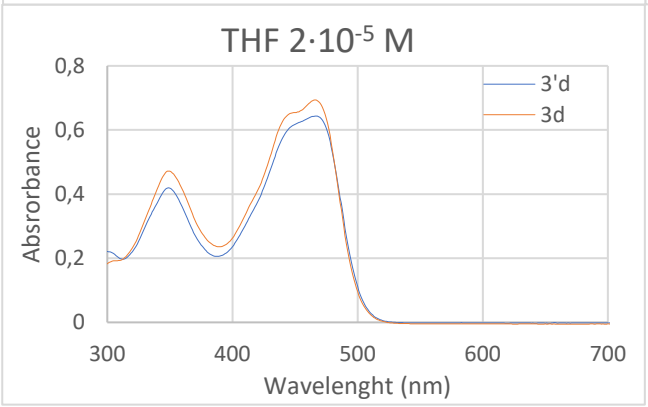


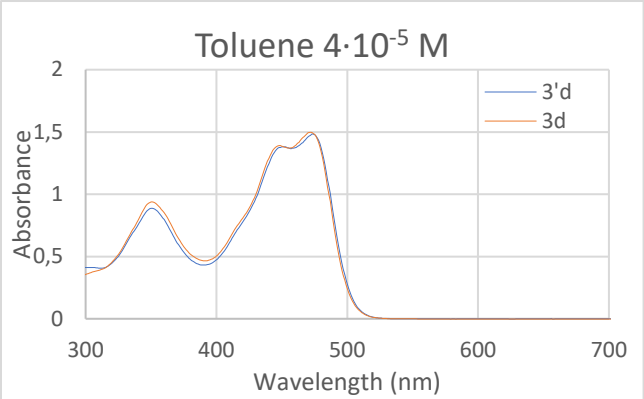


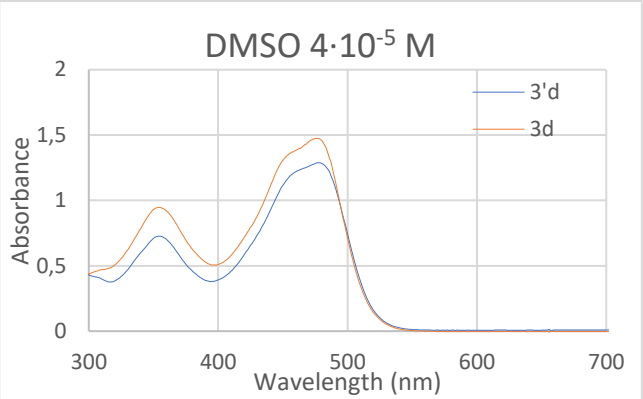


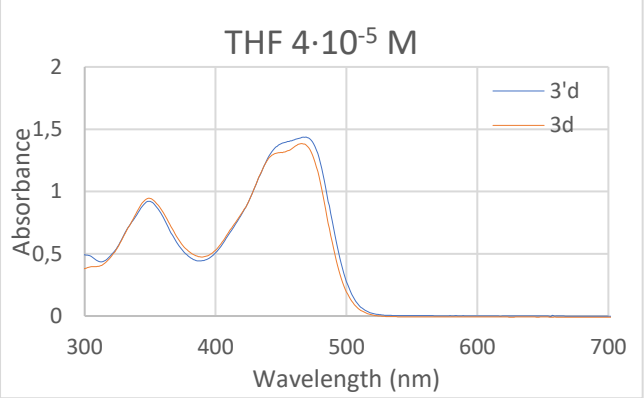


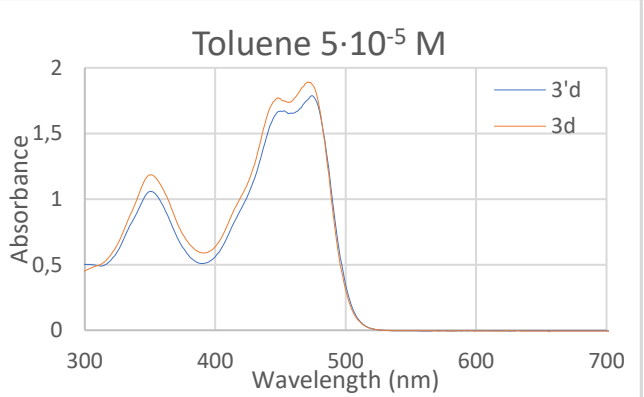


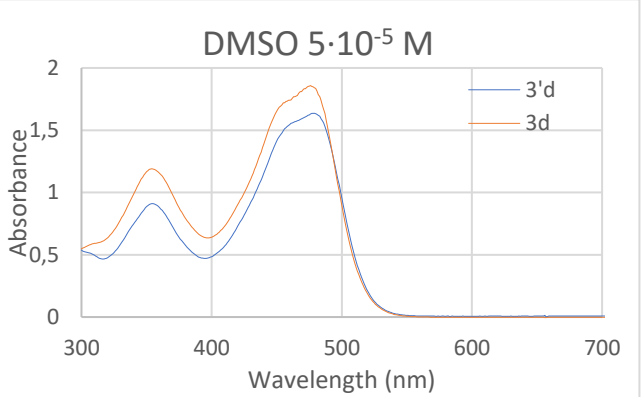


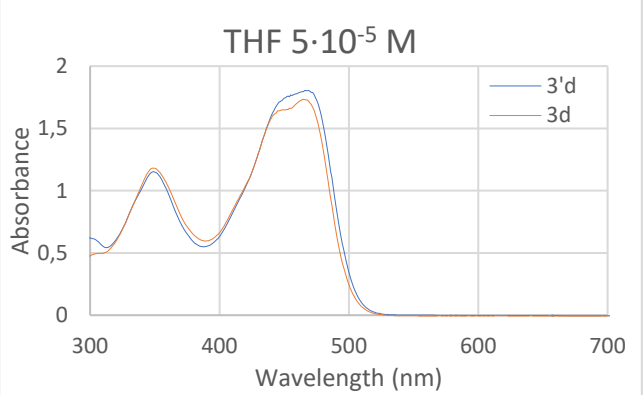

Toluene 4·10-5 M
Absorbance
Wavelength (nm)
3'd
3d


DMSO 4·10-5 M
Absorbance
Wavelength (nm)
3'd
3d

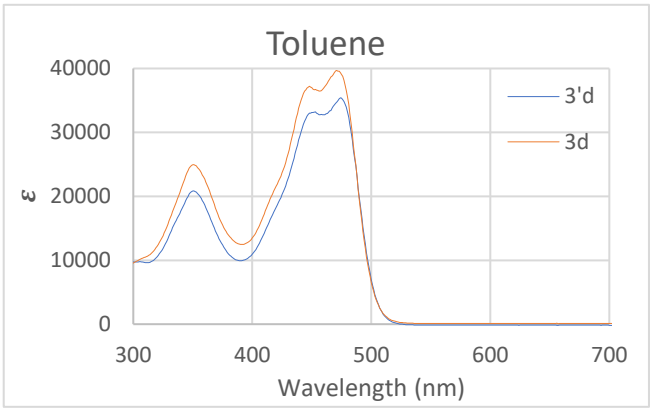

THF 4·10-5 M
Absorbance
Wavelength (nm)
3'd
3d

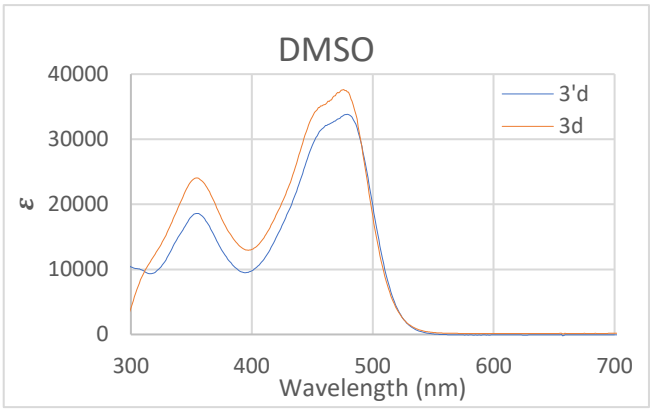

Toluene 5·10-5 M
Absorbance
Wavelength (nm)
3'd
3d

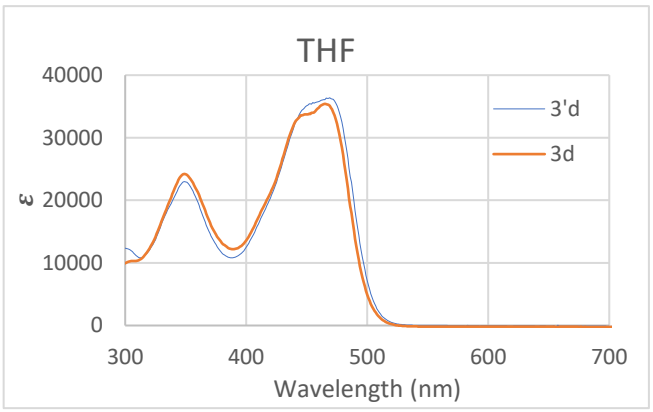

DMSO 5·10-5 M
Absorbance
Wavelength (nm)
3'd
3d


THF 5·10-5 M
Absorbance
Wavelength (nm)
3'd
3d

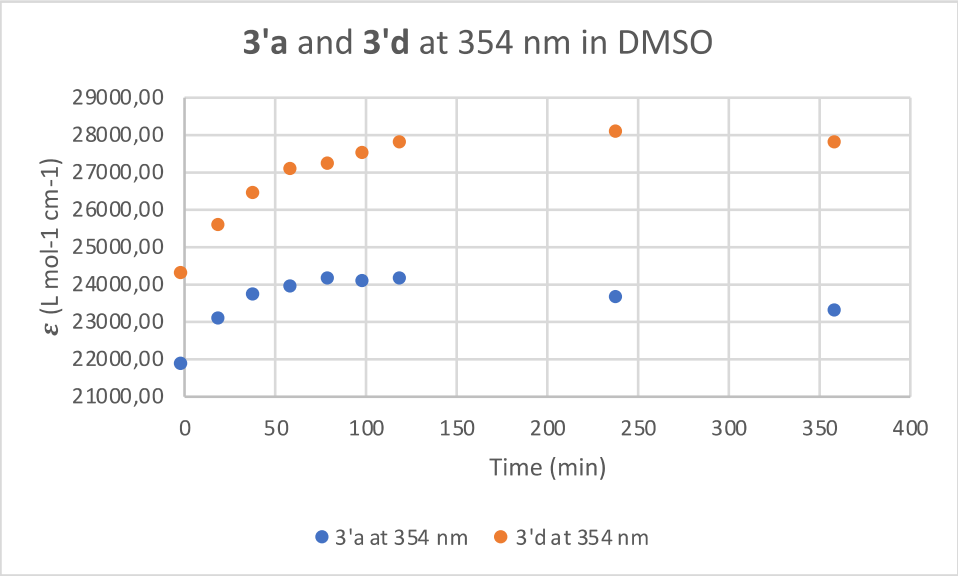
The following diagrams represent the molar extinction coefficient for **3d** and **3'd** in toluene, DMSO and THF obtained with linear regression method.

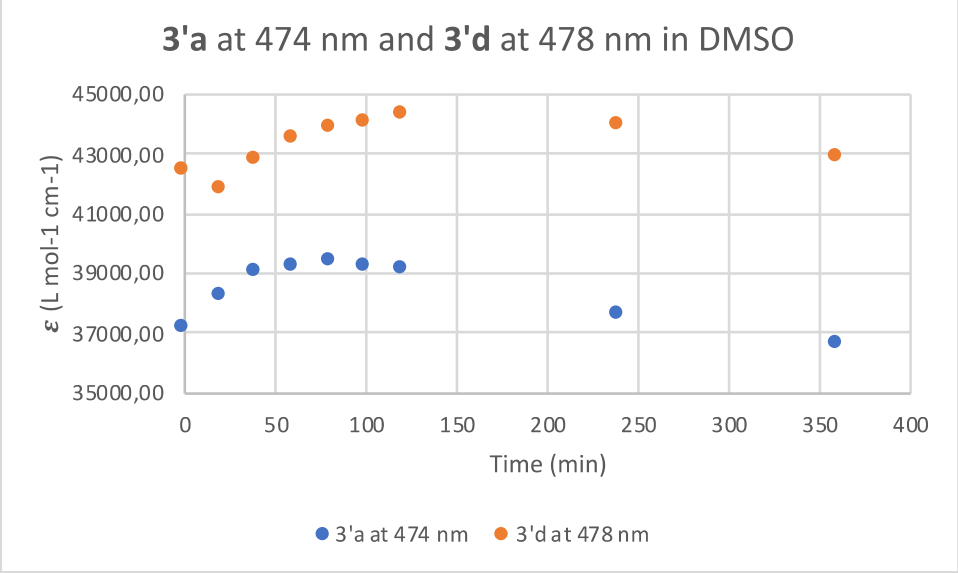




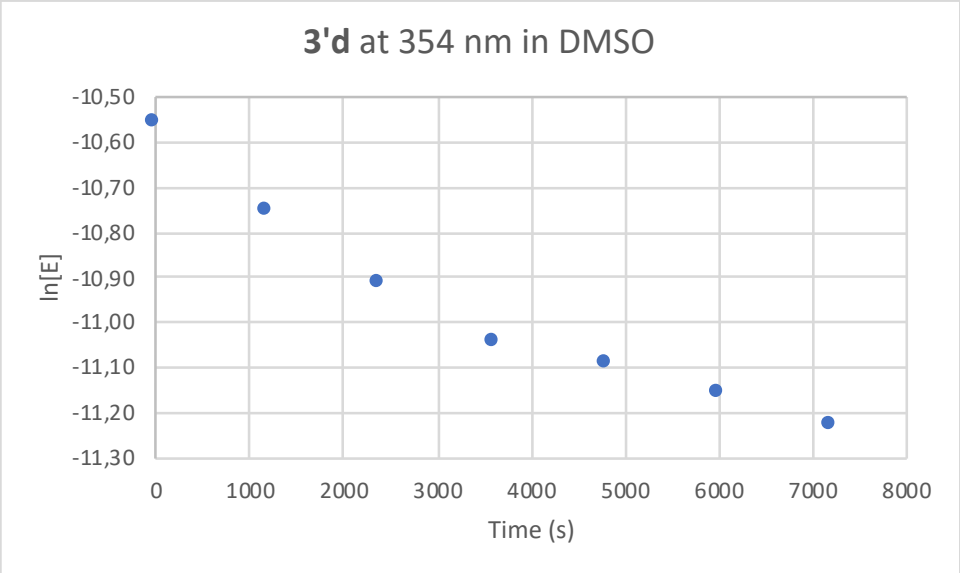


The following diagrams report the variation of the extinction coefficient *vs* time for **3a'/3a** (blue) and **3d'/3d** (orange) measured in DMSO at a concentration of $2x10^{-5}$ M at 354 and 474 nm for **3'a** and at 354 and 478 nm for **3'd**.





The following diagrams report the variation of ln[*E*] *vs* time for **3'a** and **3'd** at 354 nm in DMSO



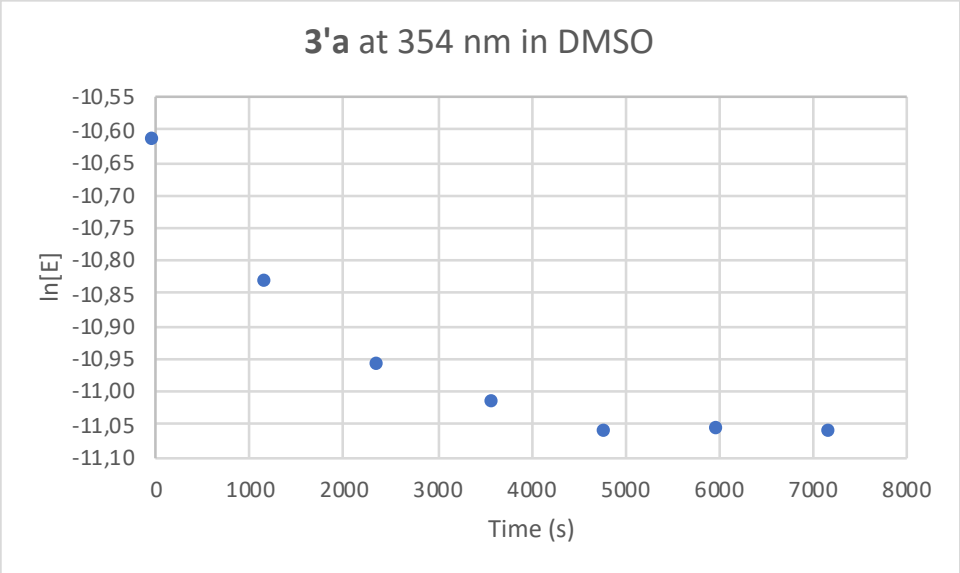


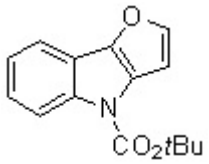
*Table 1. Relative concentrations of E and Z isomers in the reaction mixture for compound **3'a** calculated using equation (1)*

t (s)	ln[*E*] (mol L^{-1})	[*Z*] (mol L^{-1})	[*E*] (mol L^{-1})	[C_0] (mol L^{-1})	ε_E (354 nm)	ε_Z (354 nm)
0	-10,56	0	2,6E-05	2,6E-05	18596	24052
1200	-10,76	4,8E-06	2,1E-05	2,6E-05	18596	24052
2400	-10,92	7,9E-06	1,8E-05	2,6E-05	18596	24052
3600	-11,05	1,0E-05	1,6E-05	2,6E-05	18596	24052
4800	-11,09	1,1E-05	1,5E-05	2,6E-05	18596	24052
6000	-11,16	1,2E-05	1,4E-05	2,6E-05	18596	24052
7200	-11,23	1,3E-05	1,3E-05	2,6E-05	18596	24052

*Table 2. Relative concentrations of E and Z isomers in the reaction mixture for compound **3'd** calculated using equation (1)*

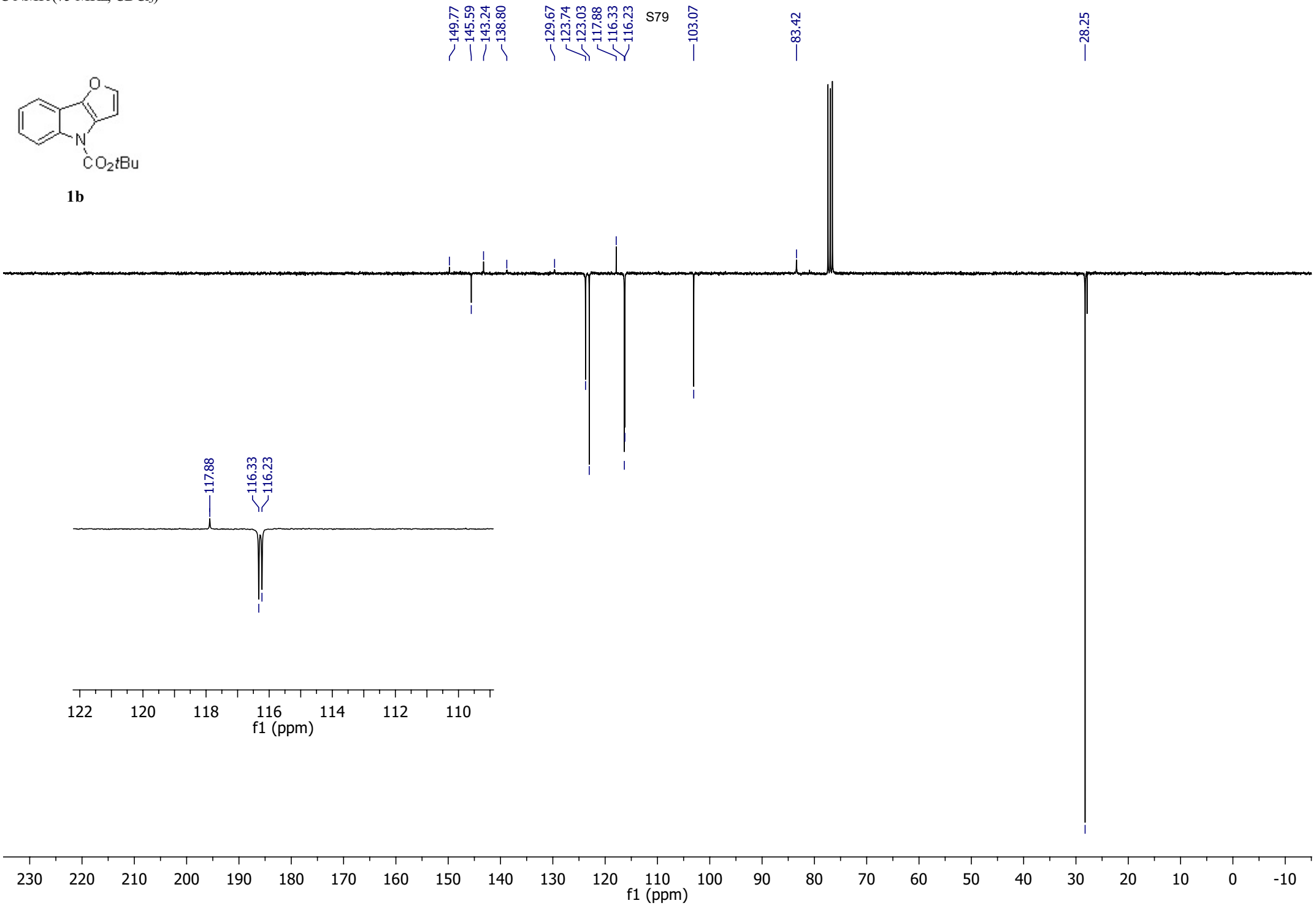
t (s)	ln[*E*] (mol L^{-1})	[*Z*] (mol L^{-1})	[*E*] (mol L^{-1})	[C_0] (mol L^{-1})	ε_E (354 nm)	ε_Z (354 nm)
0	-10,62	0	2,4E-05	2,4E-05	17859	22988
1200	-10,84	4,7E-06	2,0E-05	2,4E-05	17859	22988
2400	-10,96	7,1E-06	1,7E-05	2,4E-05	17859	22988
3600	-11,02	8,0E-06	1,6E-05	2,4E-05	17859	22988
4800	-11,06	8,8E-06	1,6E-05	2,4E-05	17859	22988
6000	-11,06	8,7E-06	1,6E-05	2,4E-05	17859	22988
7200	-11,06	8,7E-06	1,6E-05	2,4E-05	17859	22988

^{1}H NMR (300 MHz, $CDCl_3$)

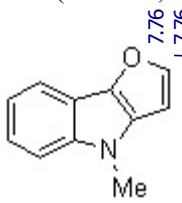


1b

^{13}C NMR (75 MHz, $CDCl_3$)

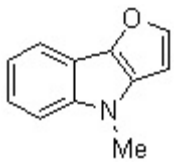


^{1}H NMR (300 MHz, $CDCl_3$)



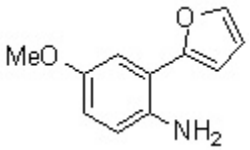
1c

^{13}C NMR (75 MHz, $CDCl_3$)

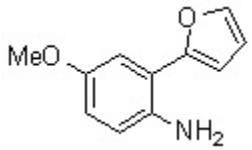


1c

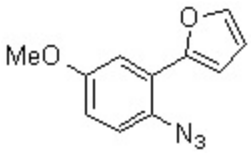
^{1}H NMR (300 MHz, $CDCl_3$)



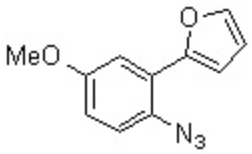
^{13}C NMR (75 MHz, $CDCl_3$)



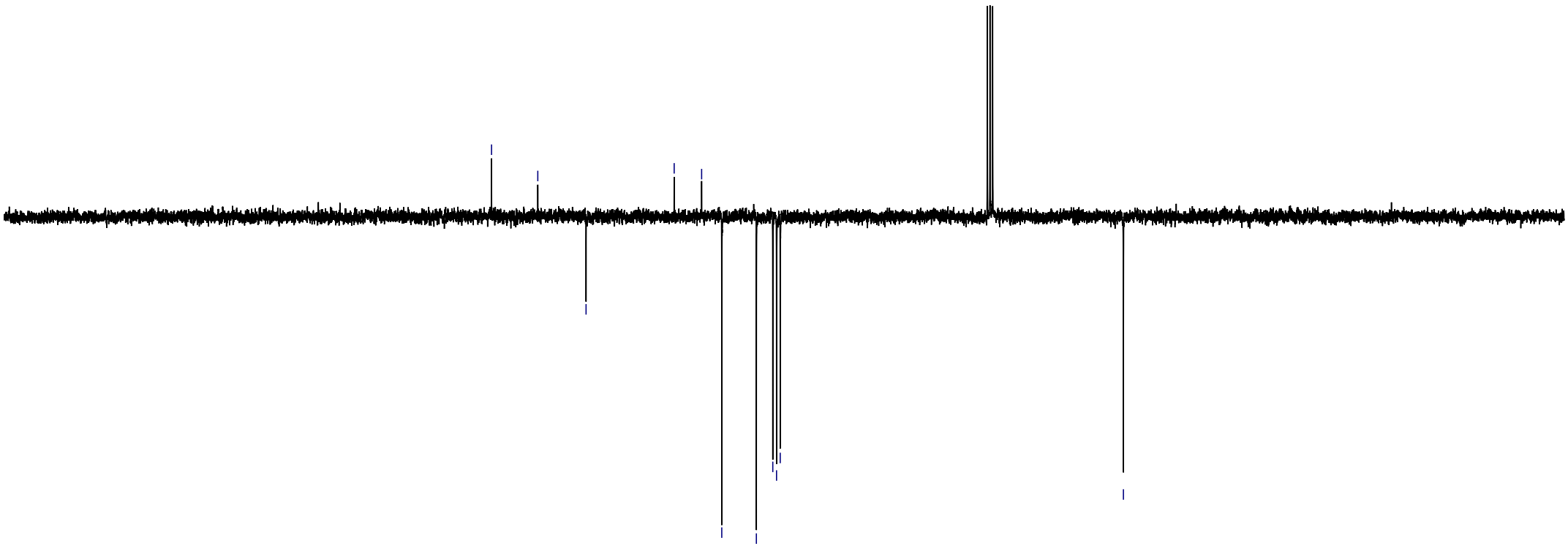
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



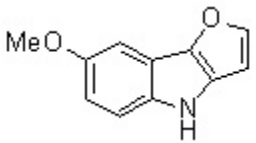
156.89
149.47
141.74
127.61
123.21
119.99
114.44
111.81
111.21
110.82
55.61



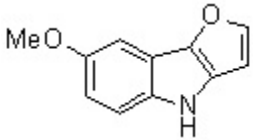
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

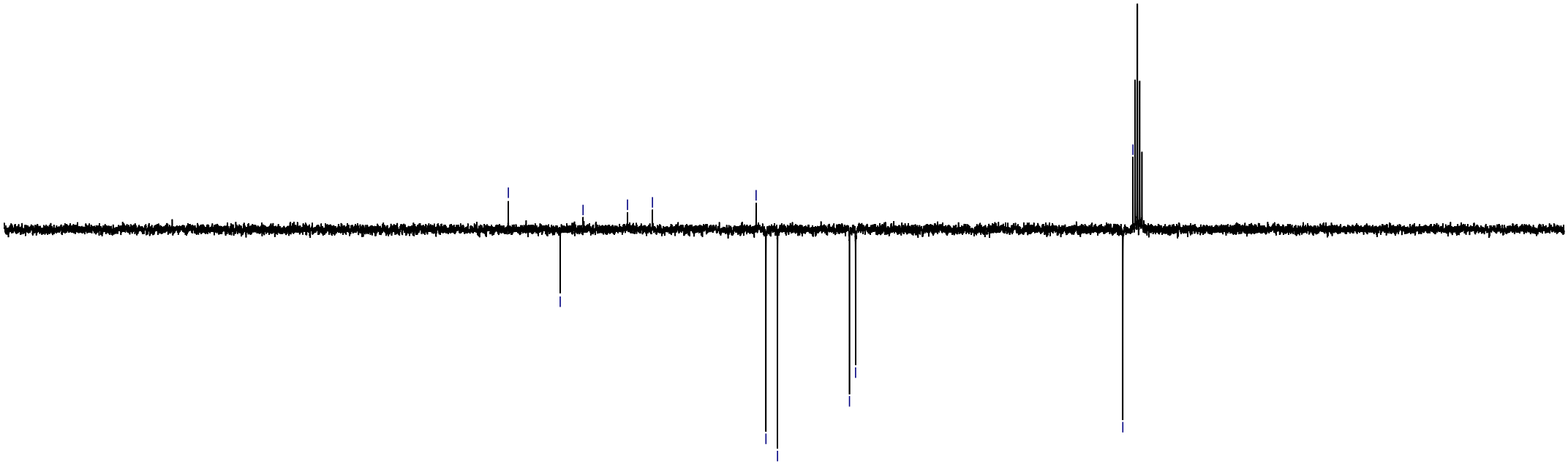
^{1}H NMR (300 MHz, CD_2Cl_2)



^{13}C NMR (75 MHz, CD_2Cl_2)



154.20
145.88
142.22
135.10
131.10
114.48
112.91
111.65
99.52
98.54
55.70
54.08

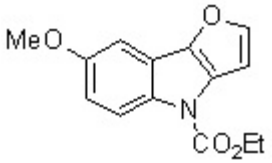


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

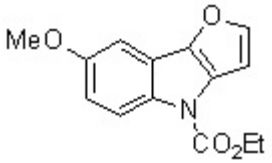
^{1}H NMR (300 MHz, $CDCl_3$)

S88

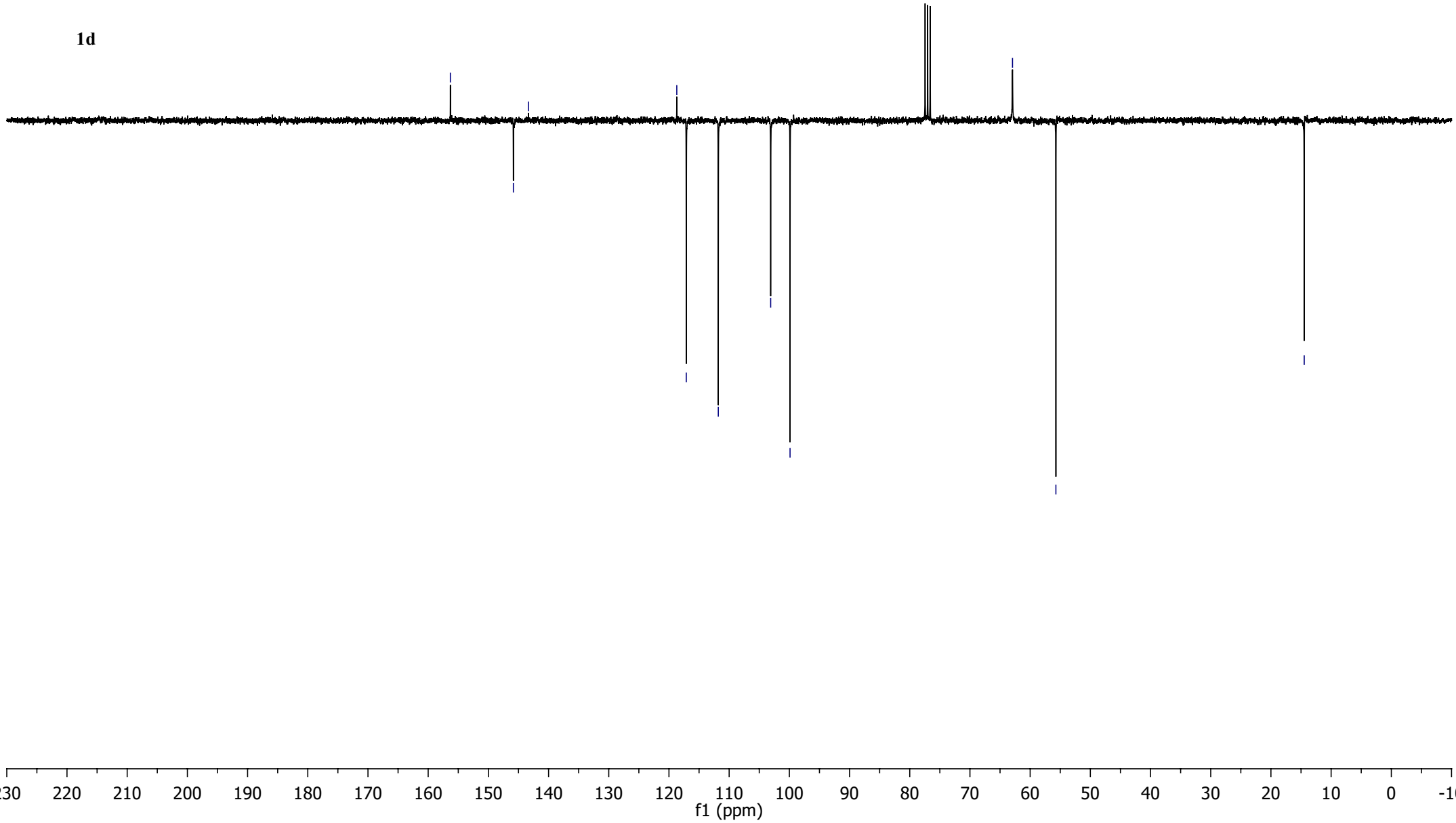


1d

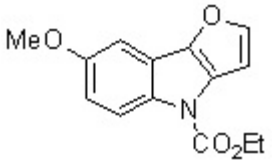
^{13}C NMR (75 MHz, $CDCl_3$)



1d

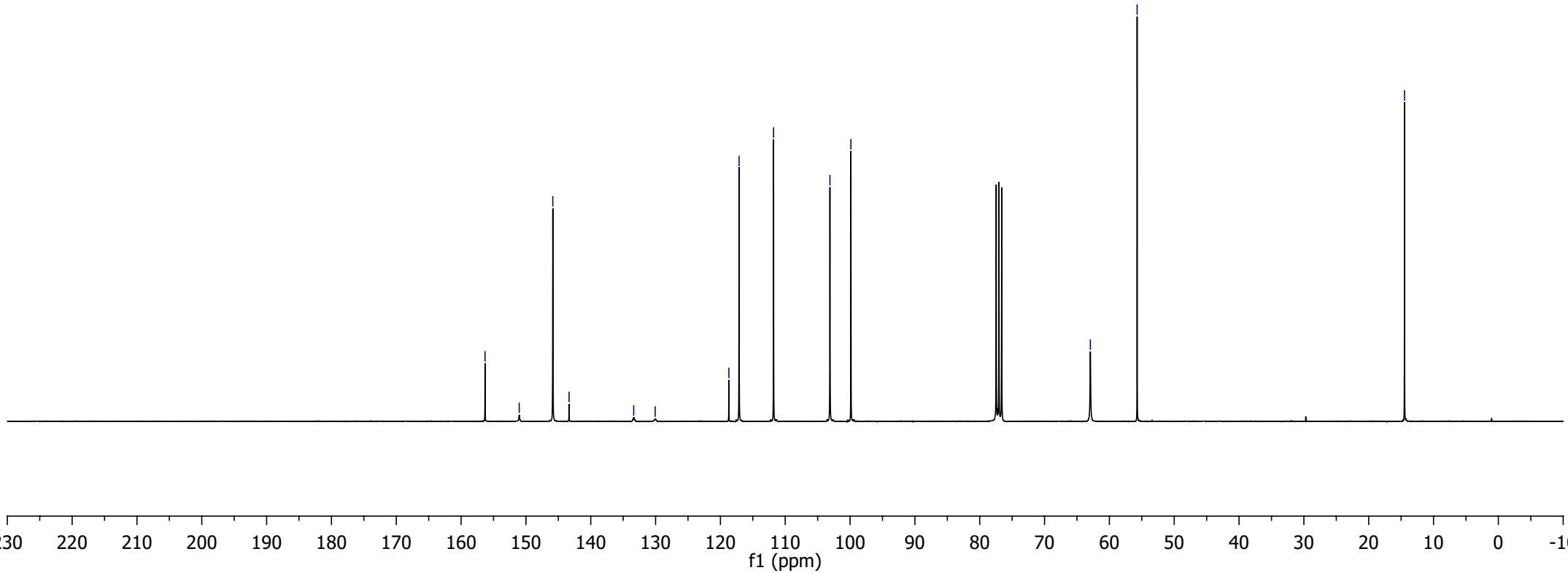


^{13}C NMR (75 MHz, $CDCl_3$)

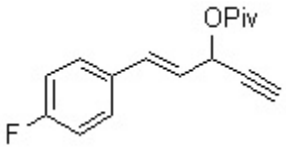


1d

156.31
151.04
145.85
143.34
133.38
130.06
118.69
117.12
111.80
103.10
99.87
62.94
55.72
14.47

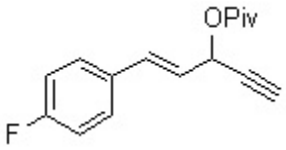


^{1}H NMR (300 MHz, $CDCl_3$)



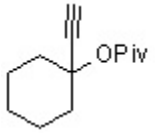
2e

^{13}C NMR (75 MHz, $CDCl_3$)



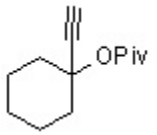
2e

^{1}H NMR (300 MHz, $CDCl_3$)



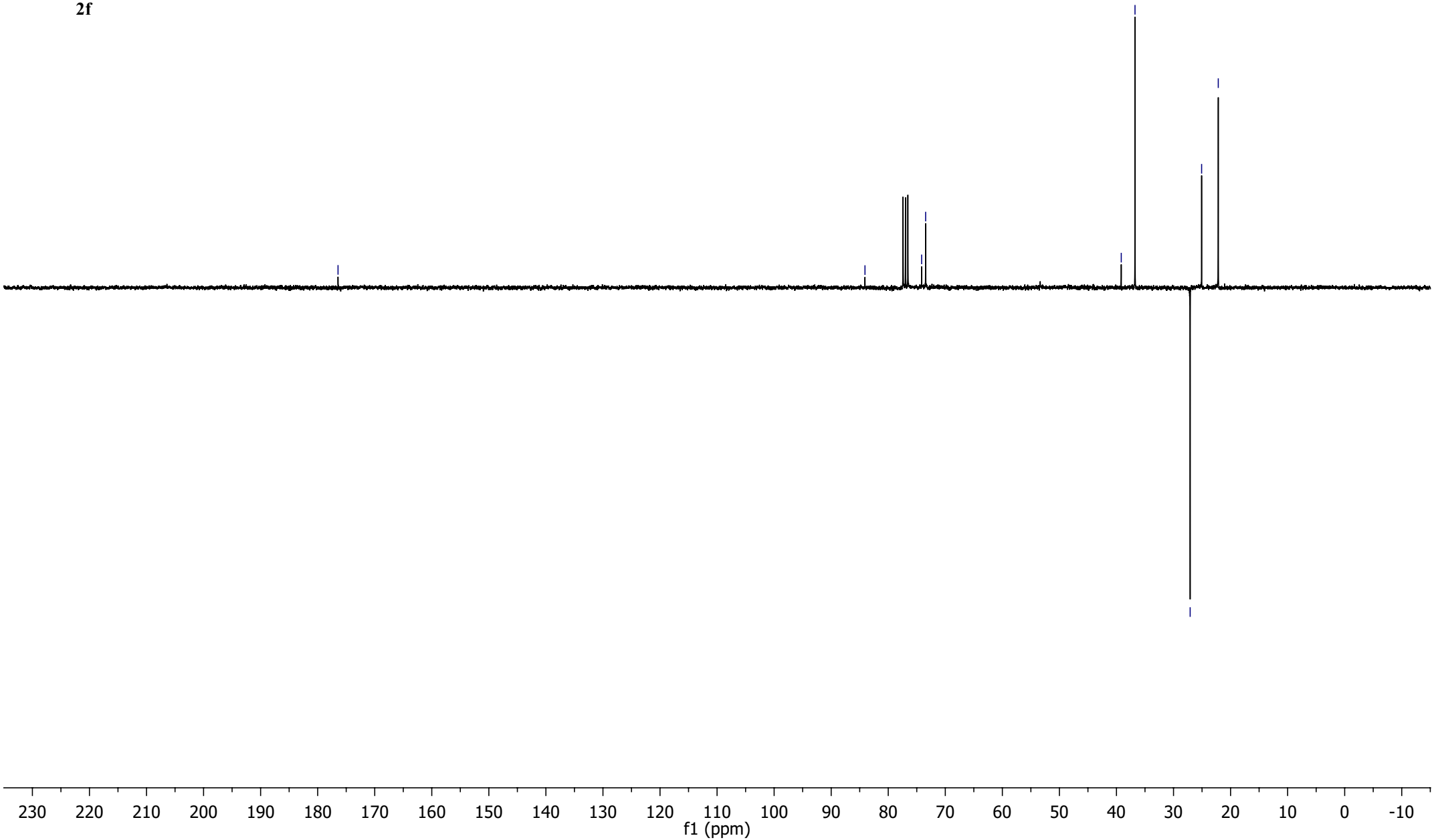
2f

^{13}C NMR (75 MHz, $CDCl_3$)



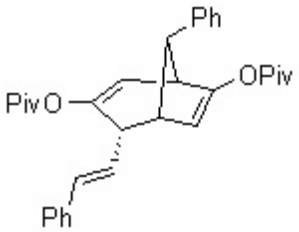
2f

176.43
84.08
74.15
73.44
39.16
36.75
27.08
25.08
22.16

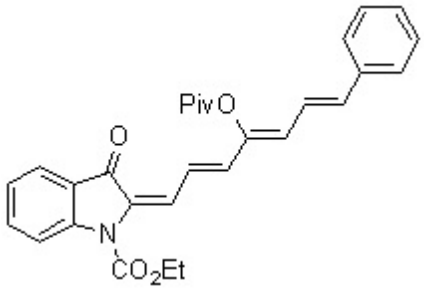


^{1}H NMR (300 MHz, $CDCl_3$)

S95

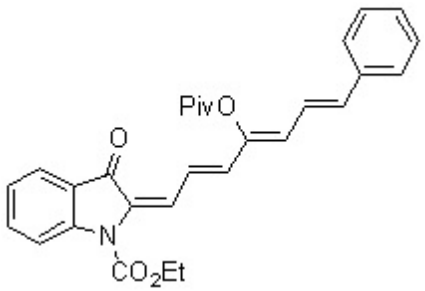


^{1}H NMR (300 MHz, CD_2Cl_2)



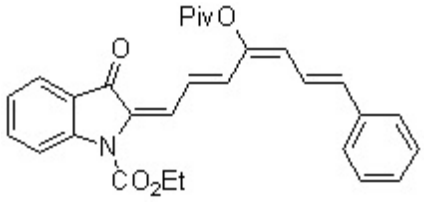
3a

^{13}C NMR (75 MHz, CD_2Cl_2)



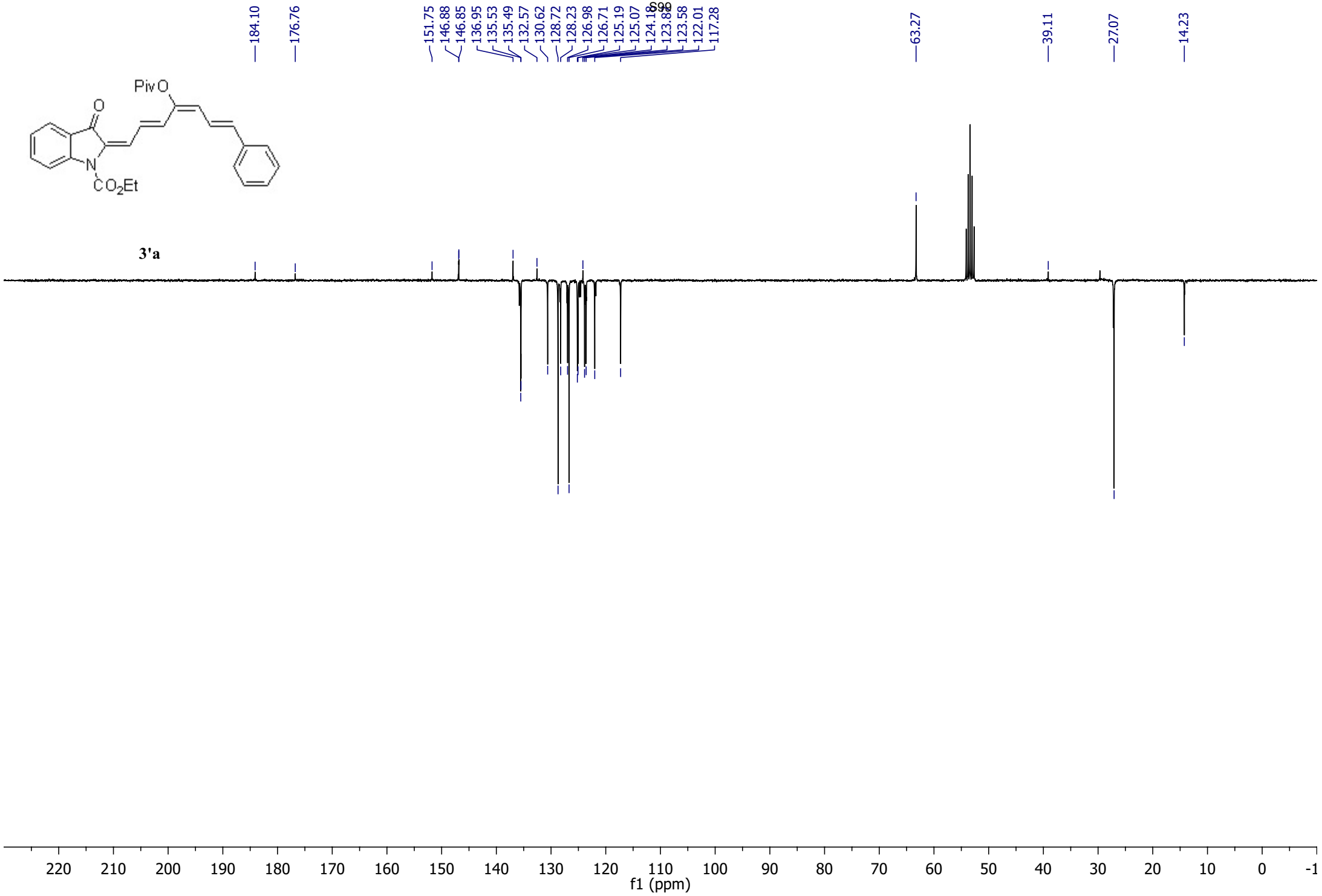
3a

^{1}H NMR (300 MHz, CD_2Cl_2)

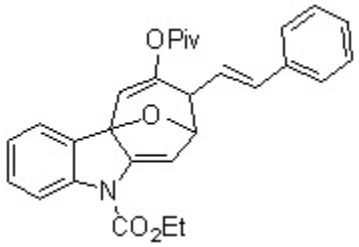


3'a

^{13}C NMR (75 MHz, CD_2Cl_2)

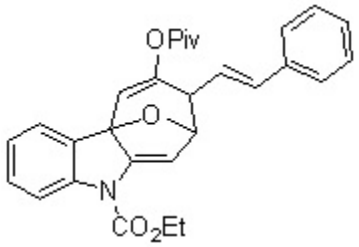


^{1}H NMR (300 MHz, $CDCl_3$)



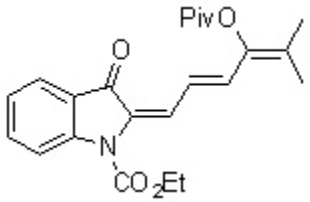
4a

^{13}C NMR (75 MHz, $CDCl_3$)



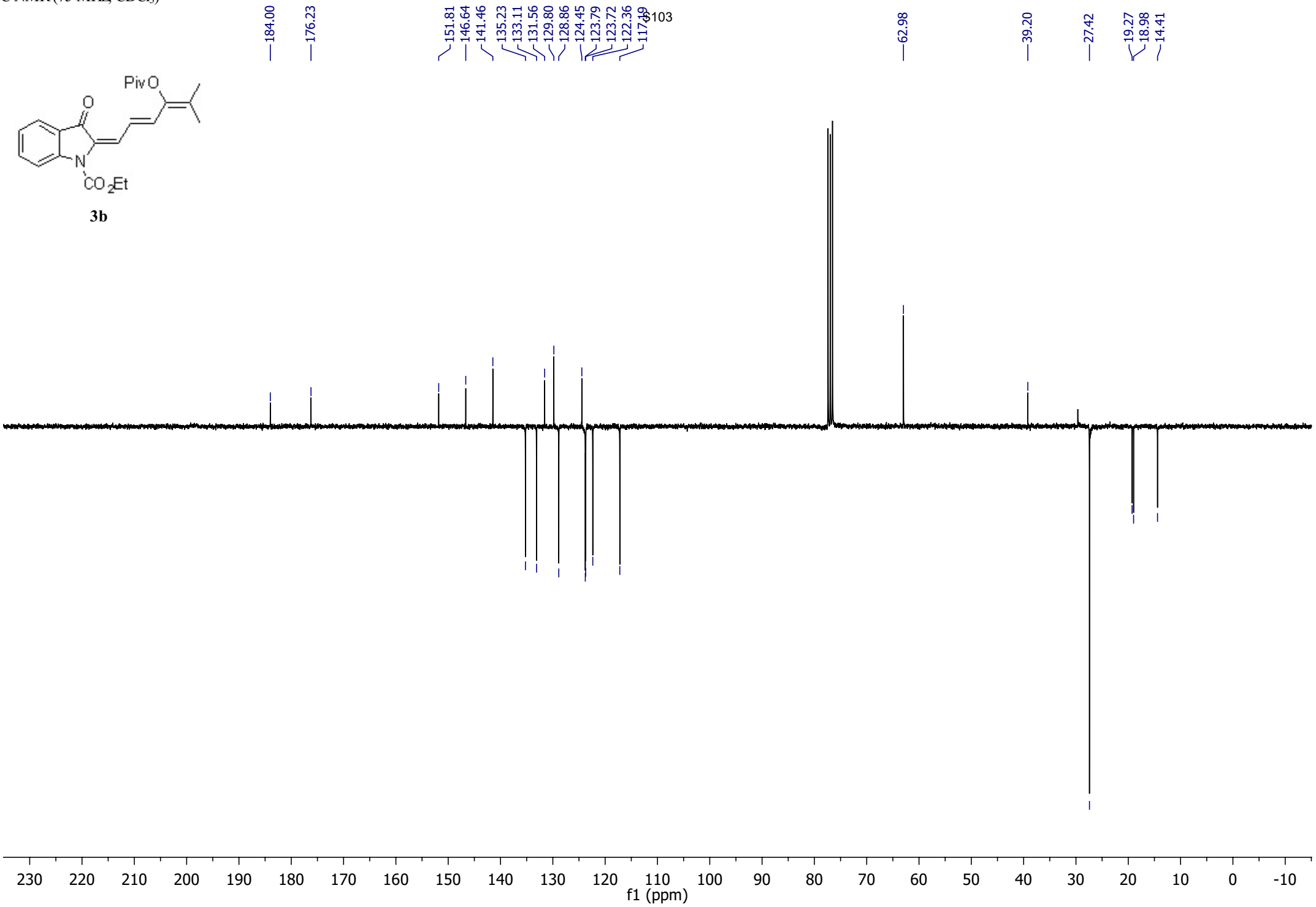
4a

^{1}H NMR (300 MHz, $CDCl_3$)



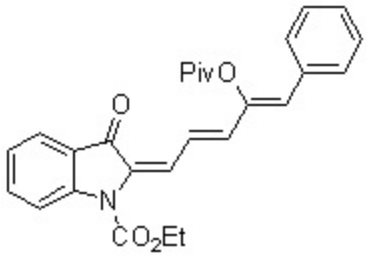
3b

^{13}C NMR (75 MHz, $CDCl_3$)



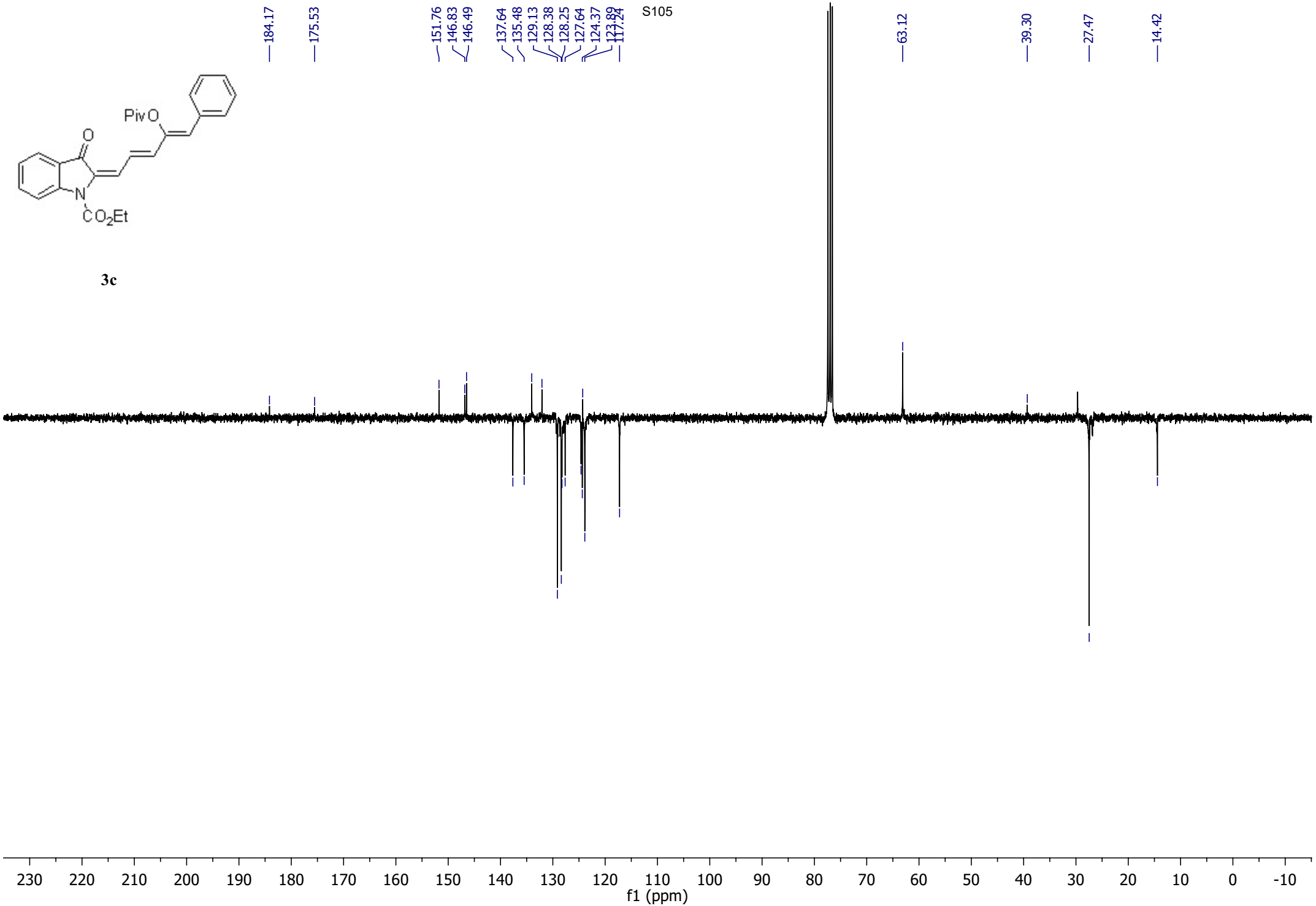
3b

^{1}H NMR (300 MHz, $CDCl_3$)



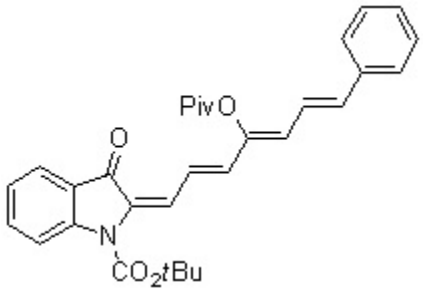
3c

^{13}C NMR (75 MHz, $CDCl_3$)



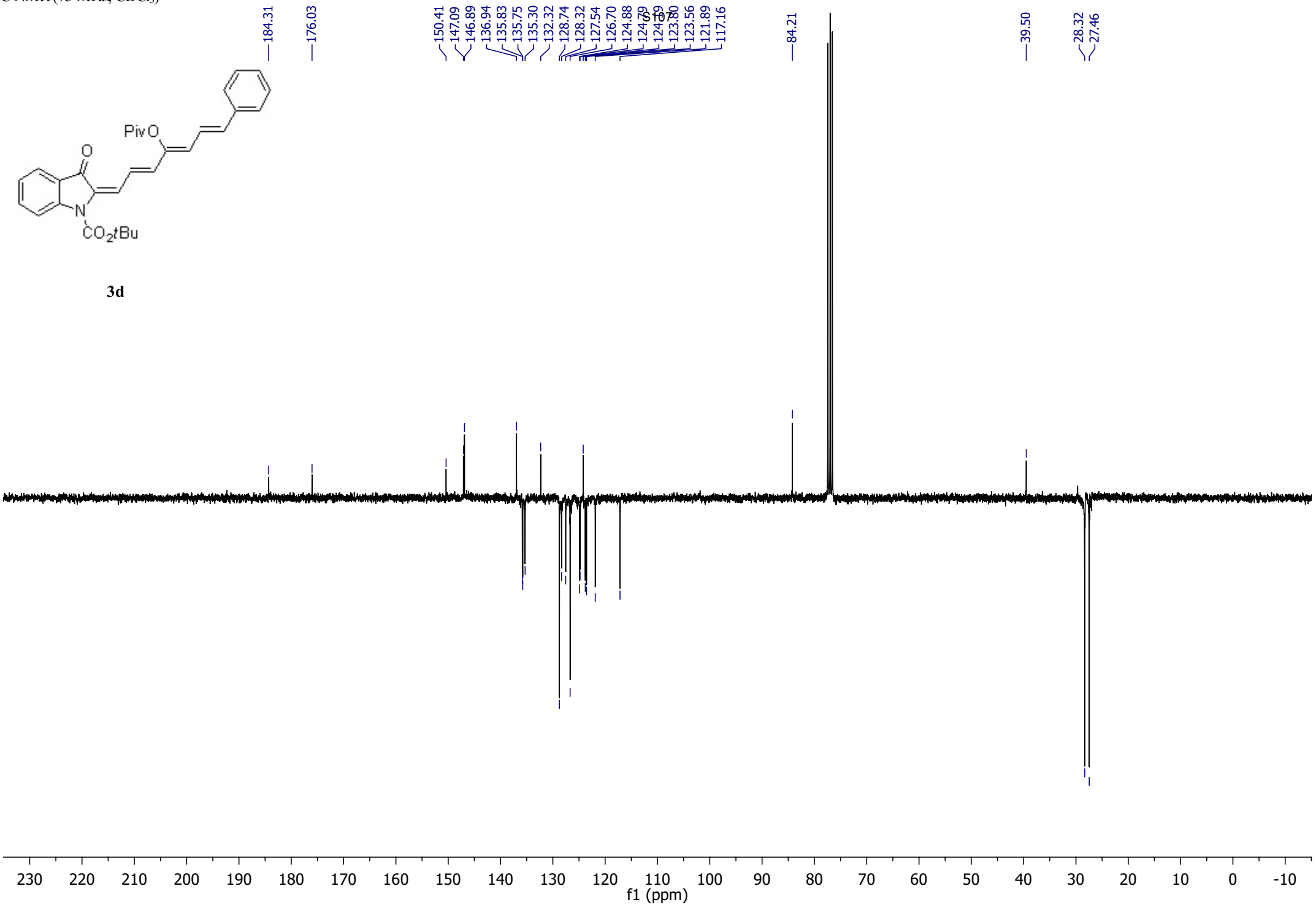
3c

^{1}H NMR (300 MHz, $CDCl_3$)



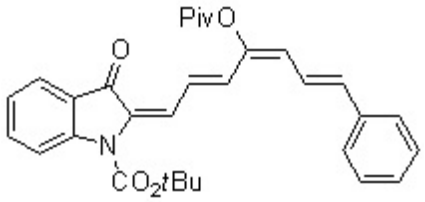
3d

^{13}C NMR (75 MHz, $CDCl_3$)



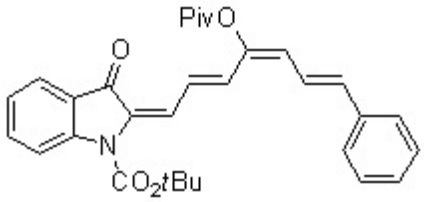
3d

^{1}H NMR (500 MHz, $CDCl_3$)



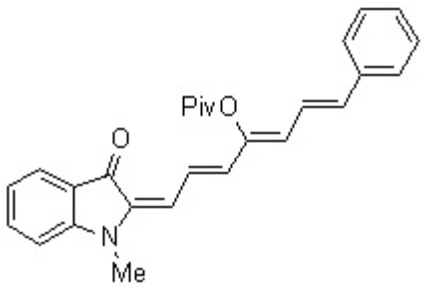
3'd

^{13}C NMR (126 MHz, $CDCl_3$)



3'd

^{1}H NMR (300 MHz, $CDCl_3$)



3e

S110

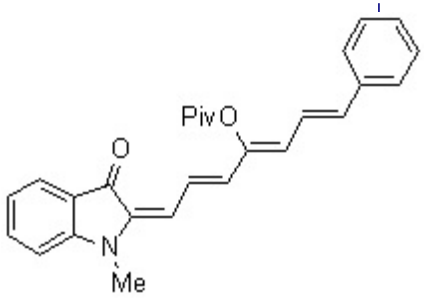
8.04 8.00 7.99 7.95 7.41 7.39 7.37 7.34 7.31 7.28 6.92 6.88 6.87 6.85 6.83 6.82 6.79 6.69 6.64 6.48 6.43 6.27 6.23 6.11 6.07 3.22 1.60

0.64 0.86 6.83 2.98 1.01 0.94 0.99 1.00 2.89 8.40

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

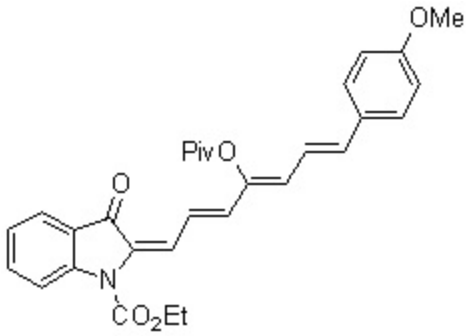
^{13}C NMR (75 MHz, $CDCl_3$)



3e

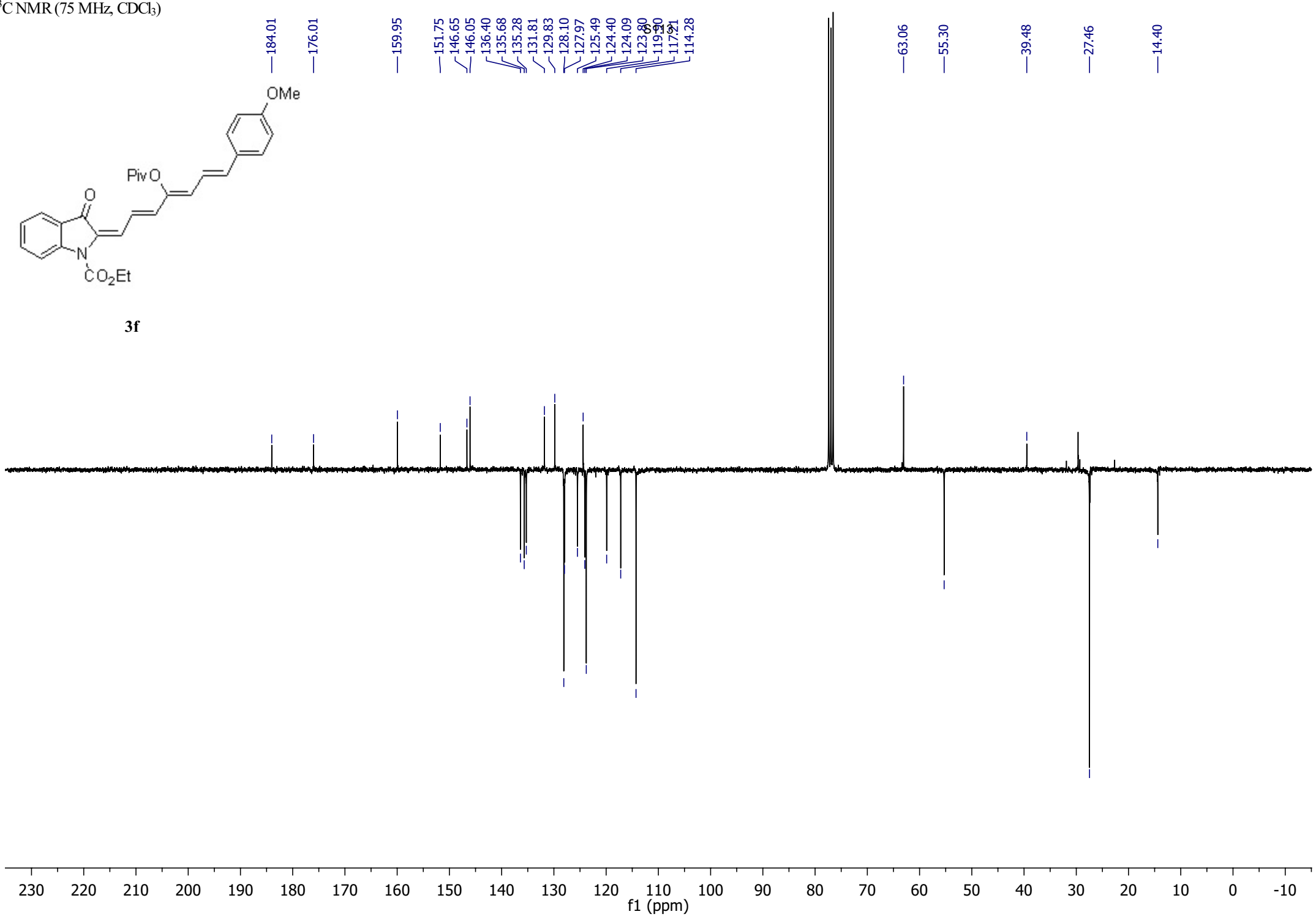
^{1}H NMR (300 MHz, $CDCl_3$)

S112



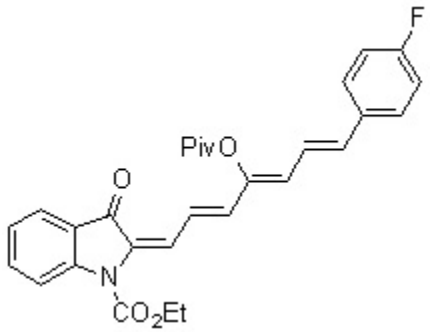
3f

^{13}C NMR (75 MHz, $CDCl_3$)



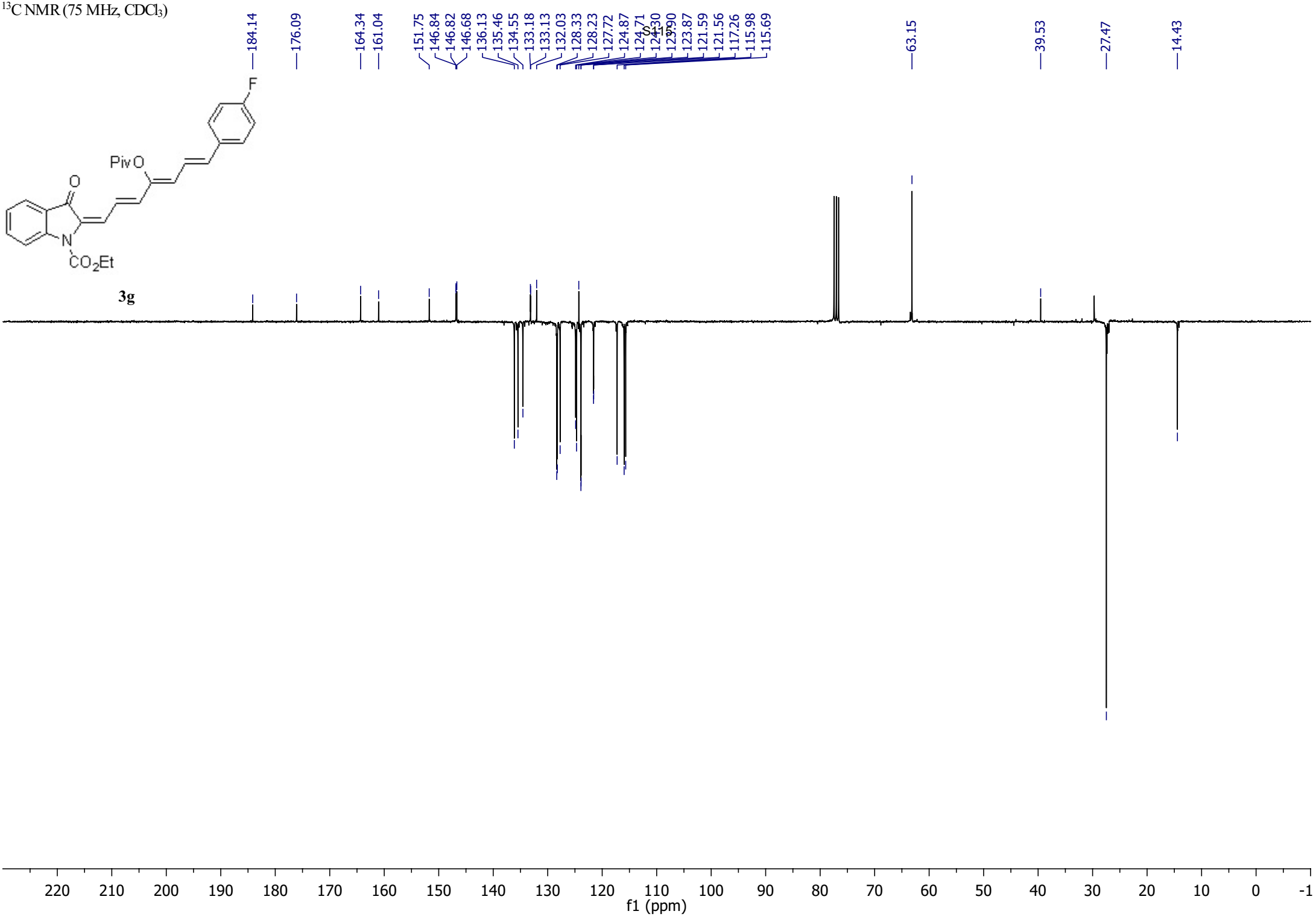
3f

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (t, J = 7.4 Hz, 1H).

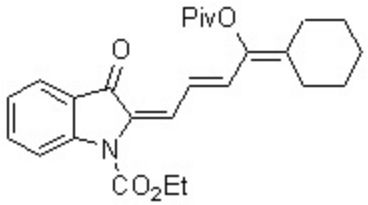


3g

^{13}C NMR (75 MHz, $CDCl_3$)

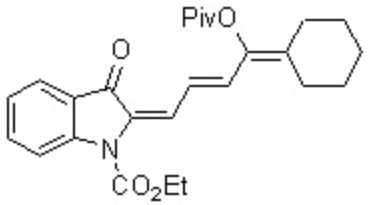


^{1}H NMR (300 MHz, $CDCl_3$)



3h

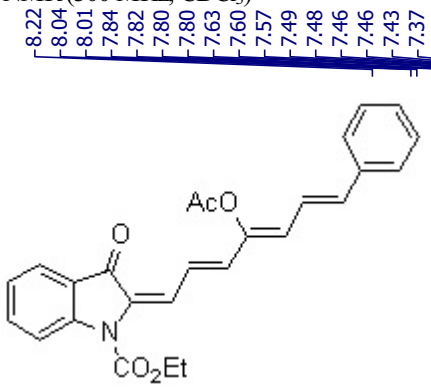
^{13}C NMR (75 MHz, $CDCl_3$)



3h

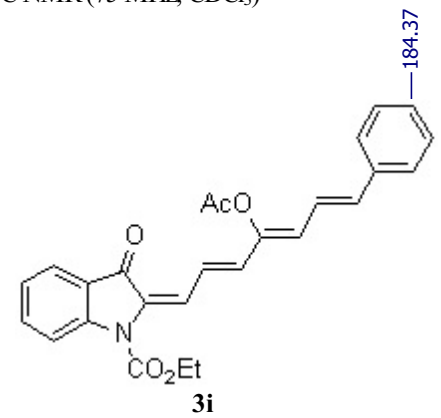
^{1}H NMR (300 MHz, $CDCl_3$)

S118



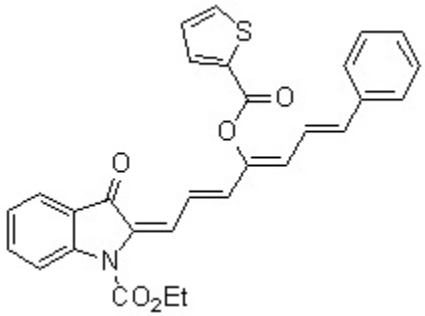
3i

^{13}C NMR (75 MHz, $CDCl_3$)



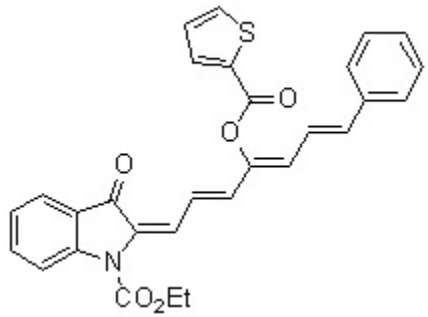
3i

^{1}H NMR (300 MHz, $CDCl_3$)



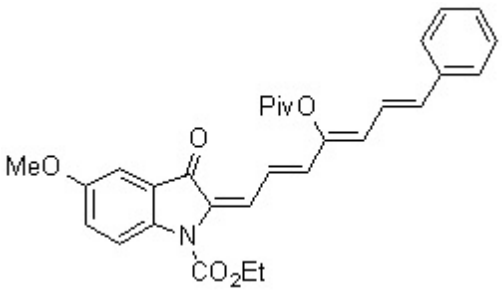
3j

^{13}C NMR (75 MHz, $CDCl_3$)



3j

^{1}H NMR (300 MHz, $CDCl_3$)



3k

S122

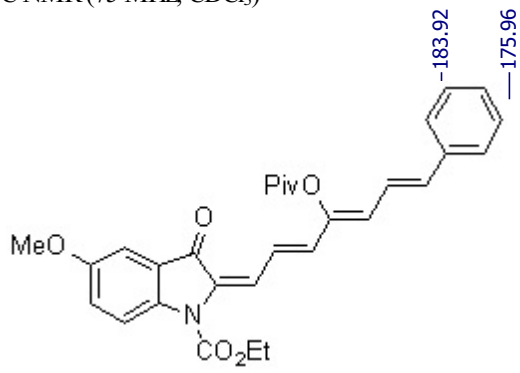
8.17 8.13 8.12 8.08 7.90 7.87 7.81 7.77 7.36 7.34 7.32 7.26 7.22 7.22 7.16 6.73 6.64 6.34 6.30 4.48 4.46 4.44 4.41 3.83 1.58 1.50 1.48 1.45

1.03 1.03 1.02 8.57 1.07 2.24 1.00 2.09 3.47 8.76 3.80

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

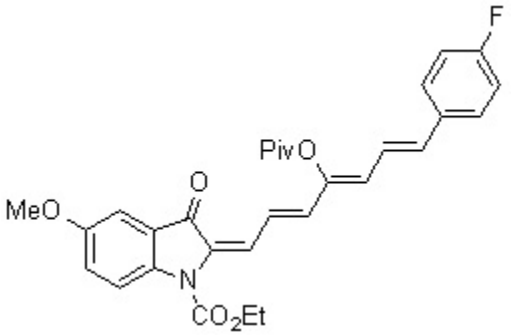
^{13}C NMR (75 MHz, $CDCl_3$)



3k

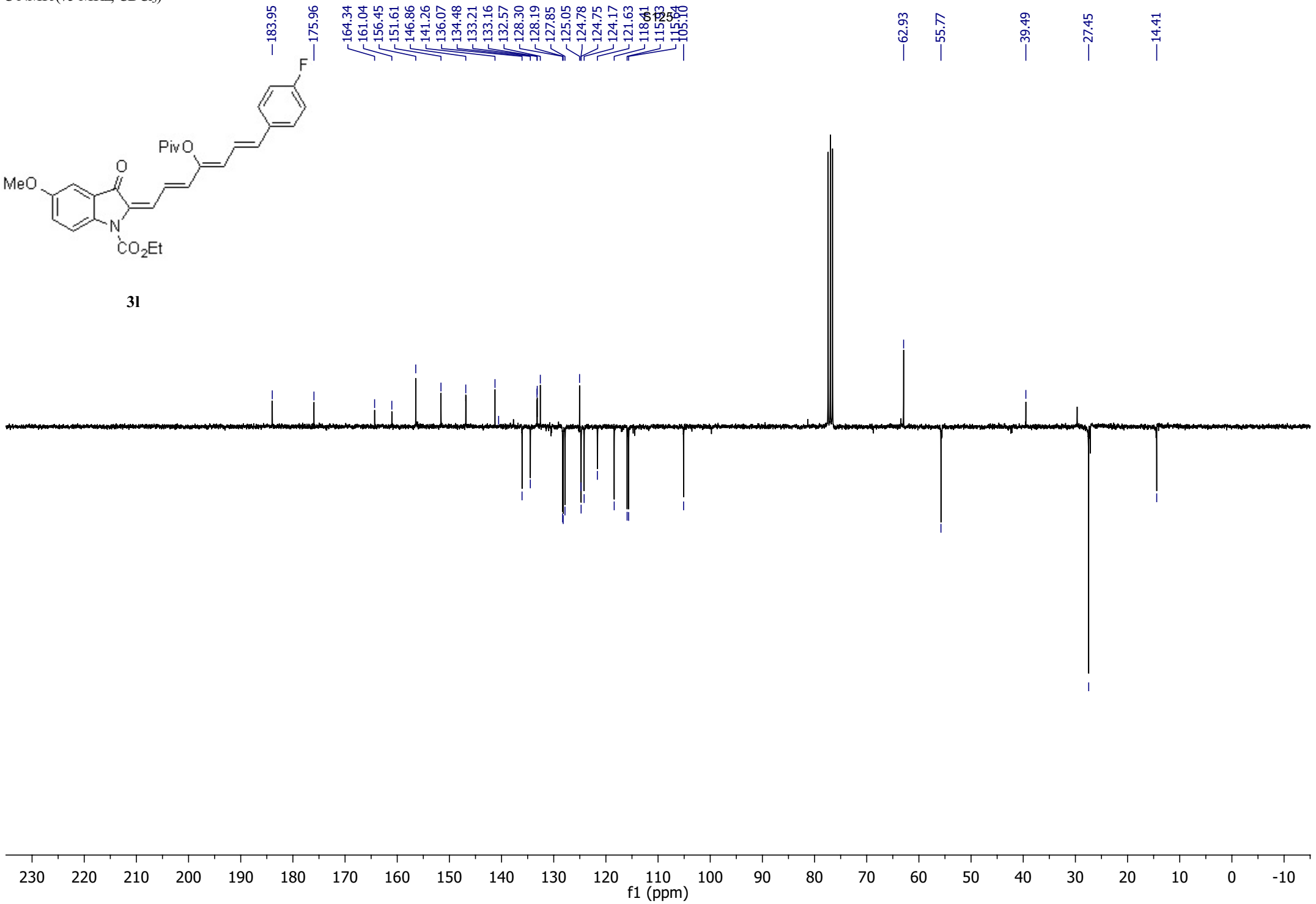
183.92
175.96
156.43
151.60
146.85
141.25
136.93
136.20
135.90
132.52
128.73
128.33
127.92
126.71
125.05
124.68
124.13
121.87
118.40
105.09
62.92
55.77
39.49
27.46
14.41

^{1}H NMR (300 MHz, $CDCl_3$)



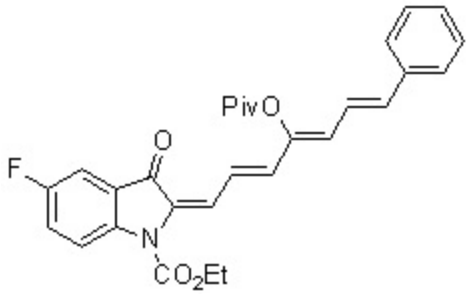
3l

^{13}C NMR (75 MHz, $CDCl_3$)



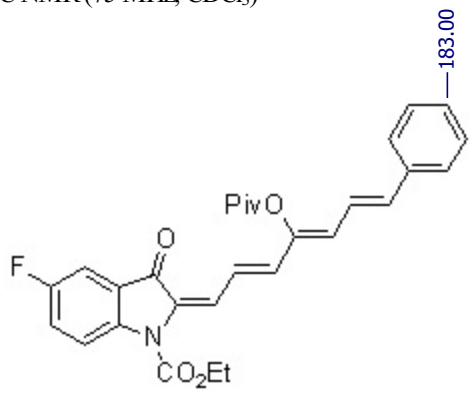
3l

^{1}H NMR (300 MHz, $CDCl_3$)



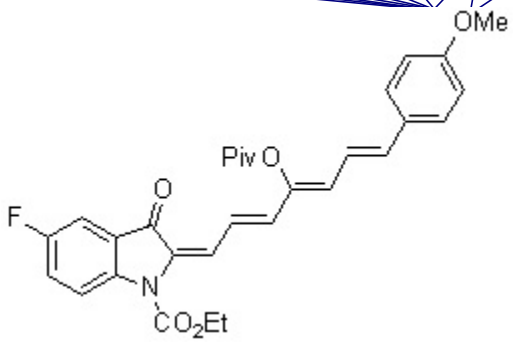
3m

^{13}C NMR (75 MHz, $CDCl_3$)



3m

^{1}H NMR (300 MHz, $CDCl_3$)



3n

S128

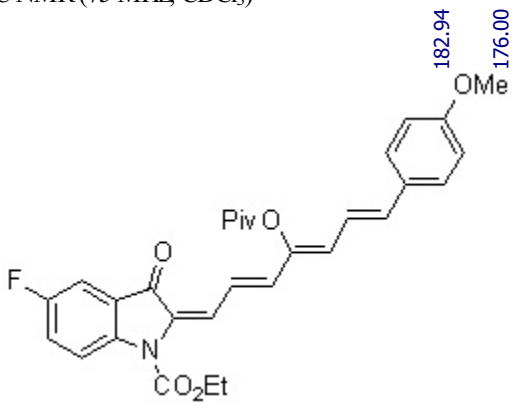
8.10 8.06 8.05 8.01 7.99 7.98 7.96 7.95 7.79 7.74 7.44 7.32 7.29 7.26 6.86 6.83 6.67 6.64 6.59 6.32 6.29 4.49 4.47 4.44 4.42 3.81 1.57 1.50 1.48 1.46

1.94 0.86 1.00 3.08 2.02 2.77 0.86 2.00 3.15 8.67 3.68

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

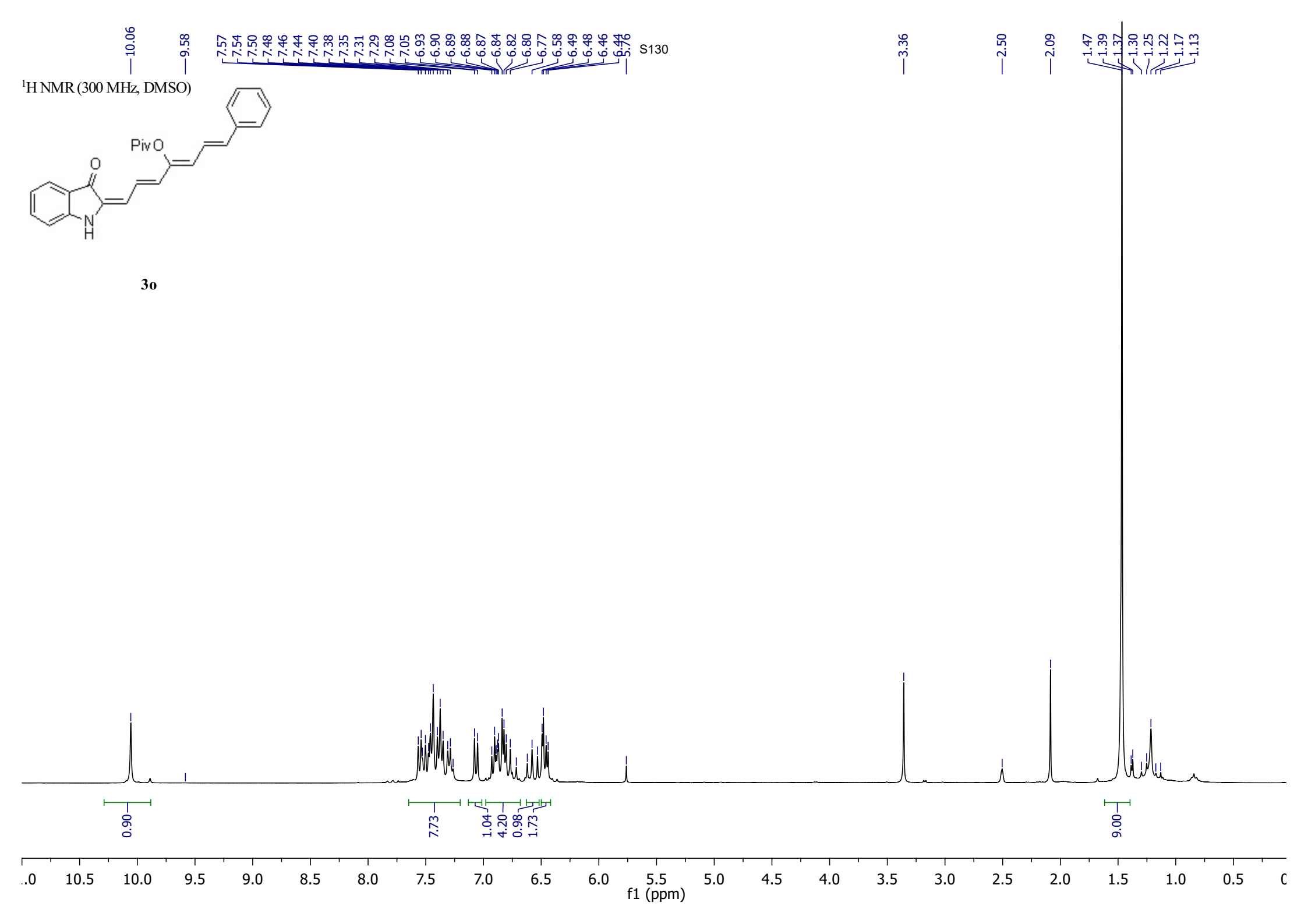
^{13}C NMR (75 MHz, $CDCl_3$)



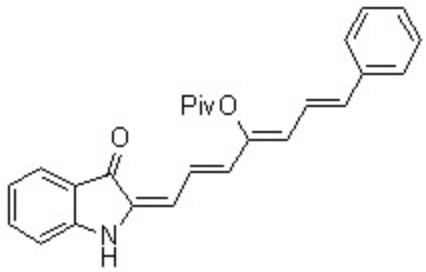
3n

182.94
176.00
160.88
160.01
157.63
151.49
145.98
142.74
137.10
136.03
131.92
129.75
128.86
128.15
126.05
125.60
125.50
123.87
122.51
122.49
122.42
119.02
118.78
118.68
114.28
109.55
109.24
63.17
55.28
39.48
27.45
14.38

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

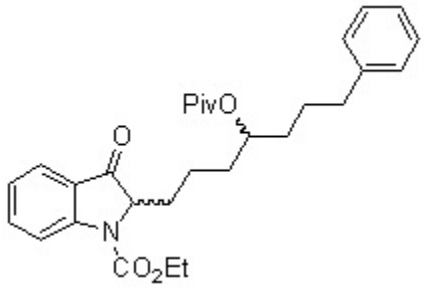

10.06
9.58
7.57
7.54
7.50
7.48
7.46
7.44
7.40
7.38
7.35
7.31
7.29
7.08
7.05
6.93
6.90
6.89
6.88
6.87
6.84
6.82
6.80
6.77
6.58
6.49
6.48
6.46
6.44
6.76
S130
3.36
2.50
2.09
1.47
1.39
1.37
1.30
1.25
1.22
1.17
1.13
[1]H NMR (300 MHz, DMSO)
PivO
O
N
H
3o
0.90
7.73
1.04
4.20
0.98
1.73
9.00
f1 (ppm)

^{13}C NMR (75 MHz, DMSO)



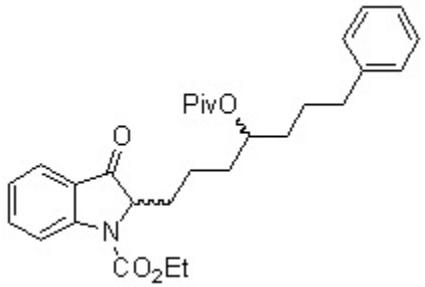
3o

^{1}H NMR (300 MHz, $CDCl_3$)



5a

^{13}C NMR (75 MHz, $CDCl_3$)



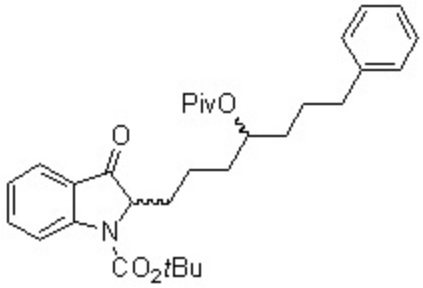
5a

199.57 199.39 178.42 176.51 153.44 152.42 149.32 148.20 142.48 137.46 137.34 128.70 128.67 126.13 123.71 123.64 117.28 117.24 116.11 115.17 S433 77.85 77.43 77.01 73.24 72.93 65.54 62.80 62.76 35.97 34.40 34.30 34.13 33.98 31.14 30.98 27.52 27.50 27.32 27.28 19.29 19.02 14.92 14.90

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

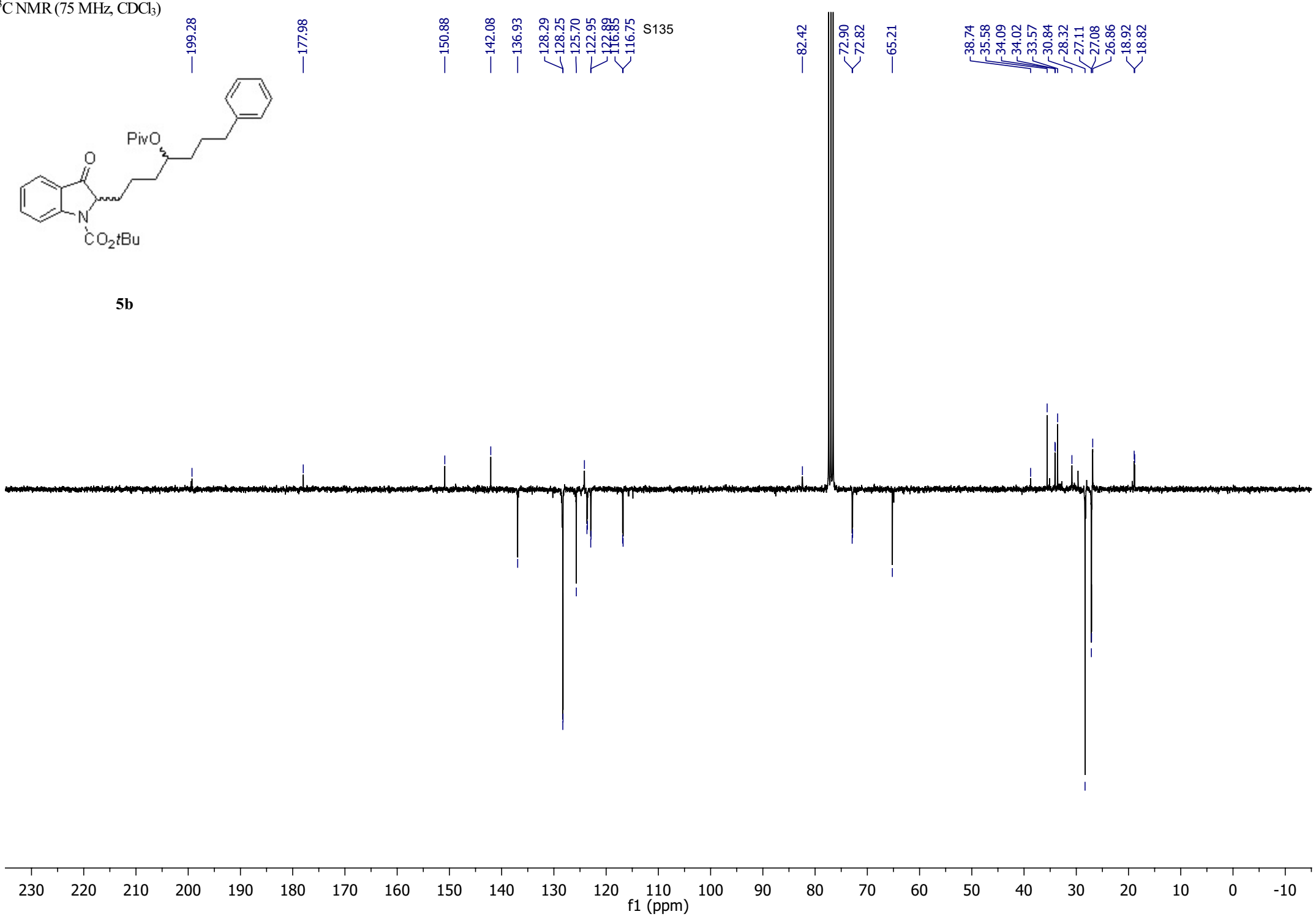
f1 (ppm)

^{1}H NMR (300 MHz, $CDCl_3$)



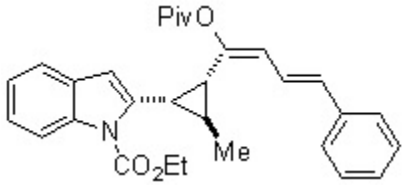
5b

^{13}C NMR (75 MHz, $CDCl_3$)



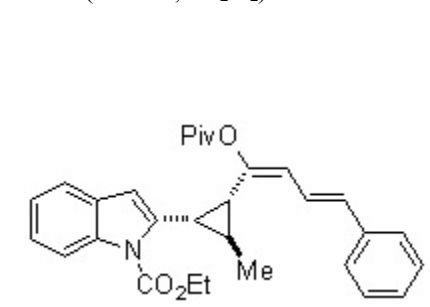
5b

^{1}H NMR (300 MHz, CD_2Cl_2)



6

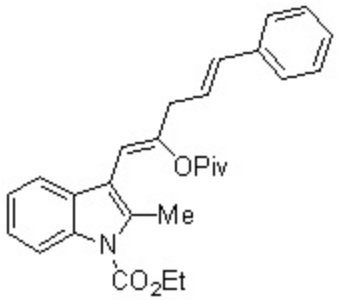
^{13}C NMR (75 MHz, CD_2Cl_2)



6

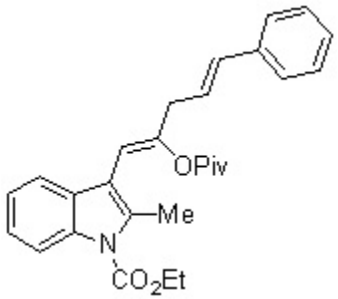
^{1}H NMR (300 MHz, C_6D_6)

S138



7

^{13}C NMR (75 MHz, C_6D_6)



7