Supporting Information

3-Piperazinyl propenylidene indolone merocyanines – consecutive three-component synthesis and electronic properties of solid state luminophores with AIE properties

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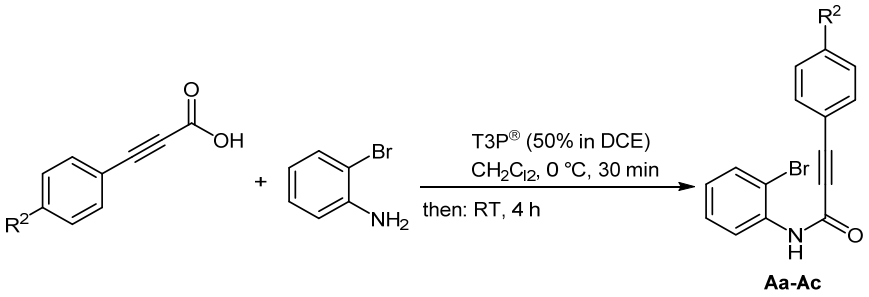
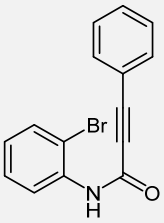
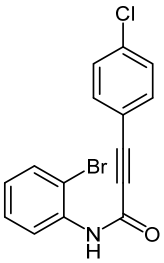
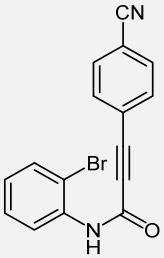
1.1.1 General procedure I (GP I) for the preparation of N-(2-bromophenyl)-3-arylpropiolamides A



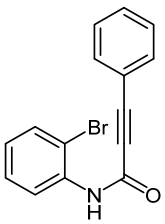
Aa-Ac

In a dry screw-cap Schlenk tube with a magnetic stir bar under nitrogen were placed the corresponding 3-arylpropiolic acids[1] (1.00 equiv) and dry dichloromethane (0.6 mL/mmol) and the solution was cooled to 0 °C (ice-salt bath) (for experimental details, see Table SI-1). Then 2-bromo aniline (1.10 equivs) was added to reaction mixture before T3P® (50 weight% i in 1,2-dichloroethane, 1.00 equiv) was slowly added dropwise at 0 °C. After complete addition the mixture was stirred at 0 °C for 30 min and then allowed to come to room temp where stirring was continued for 4 h. Then dichloromethane (20 mL) was added the organic phase was washed with 2 M aqueous hydrochloric acid (2 x 10 mL). The organic phase were washed with saturated an aqueous sodium carbonate solution and dried (anhydrous magnesium sulfate). After removal of the solvents in vacuo the crude product was adsorbed on celite® and chromatographed on silica gel (*n*-hexane-ethyl/acetate 7:1) to give the pure *N*-(2-bromophenyl)-3-arylpropiolamides **A**.

Table SI-1. Experimental details of the preparation of *N*-(2-bromophenyl)-3-arylpropiolamides **A** according to GP I.

entry	2-bromo aniline [g] (mmol)	3-arylpropiolic acid [g] (mmol)	*N*-(2-bromophenyl)propiolamide A [g] (%)
1	4.73 (27.5)	3.65 (25.0) of 3-phenylpropiolic acid (R^2 = H)	 6.45 (86) of **Aa**
2	1.29 (7.60)	1.37 (7.60) of 3-(*p*-chlorophenyl)propiolic acid (R^2 = Cl)	 1.83 (72) of **Ab**
3	0.47 (2.80)	0.43 (2.50) of 3-(*p*-cyanophenyl)propiolic acid (R^2 = CN)	 0.51 (62) of **Ac**

N-(2-Bromophenyl)-3-phenylpropiolamide (Aa)



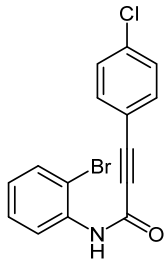
Aa
$C_{15}H_{10}BrNO$
300.16

According to GP I compound **Aa** was obtained as a colorless solid.

Mp 120 °C. R_f (*n*-hexane:EtOAc, 5:1): 0.41. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02 (t, *J* = 7.5 Hz, 1 H), 7.28-7.51 (m, 4 H), 7.51-7.68 (m, 3 H), 8.00 (s, 1 H), 8.37 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 83.4 (C_{quat}), 86.5 (C_{quat}), 113.2 (C_{quat}), 119.9 (C_{quat}), 122.4, 125.9, 128.7, 128.8, 130.7, 132.5, 132.9, 135.4 (C_{quat}), 151.0 (C_{quat}). IR (ATR): $\tilde{\nu}$ 3177 (w), 3146 (w), 3100 (w), 3019 (w), 2982 (w), 2959 (w), 2216 (m), 1622 (m), 1582 (m), 1530 (s), 1489 (m), 1470 (m), 1435 (s), 1412 (w), 1306 (s), 1273 (m), 1240 (m), 1188 (m), 1177 (m), 1157 (w), 1121

(w), 1047 (m), 1030 (m), 964 (m), 920 (w), 868 (m), 854 (w), 789 (w), 758 (m), 743 (s), 716 (m), 704 (m), 687 (s), 665 (s), 619 (m). GC-MS: *m/z* (%) 301 (M^+(^{81}Br), 2), 299 (M^+(^{79}Br), 2), 220 ($C_{15}H_{10}NO^+$, 33), 130 (10), 129 ($C_9H_5O^+$, 100), 101 ($C_8H_5^+$, 11), 75 (20). Anal. calcd. for $C_{15}H_{10}BrNO$ (299.0): C 60.02, H 3.36, N 4.67; Found: C 59.75, H 3.34, N 4.61.

***N*-(2-Bromophenyl)-3-(4-chlorophenyl)propiolamide (Ab)**

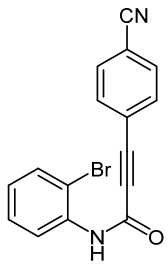


Ab
$C_{15}H_9BrClNO$
334.60

According to GP I compound **Ab** was obtained as a colorless solid.

Mp 132 °C. R_f (*n*-hexane:EtOAc, 5:1): 0.46. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.96-7.08 (m, 1 H), 7.29-7.43 (m, 3 H), 7.49-7.62 (m, 3 H), 7.98 (br, 1 H), 8.36 (d, *J* = 8.1 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 84.1 (C_{quat}), 85.3 (C_{quat}), 113.2 (C_{quat}), 118.3 (C_{quat}), 122.4, 126.0, 128.7, 129.2, 132.5, 134.1, 135.3 (C_{quat}), 137.0 (C_{quat}), 150.1 (C_{quat}). IR (ATR): $\tilde{\nu}$ (3225 (m), 3154 (w), 3102 (w), 3034 (w), 2930 (w), 2216 (m), 1639 (s), 1578 (m), 1522 (s), 1487 (m), 1466 (m), 1437 (s), 1396 (m), 1298 (s), 1271 (m), 1240 (m), 1190 (m), 1161 (w), 1088 (m), 1015 (m), 976 (m), 939 (w), 827 (s), 787 (m), 745 (s), 706 (m), 673 (s), 652 (s), 604 (m). EI-MS (70 eV): *m/z* (%) 335 (M^+(^{81}Br), 10), 333 (M^+(^{79}Br), 10), 256 (13), 254 (M^+-Br, 37), 219 ($C_{15}H_9NO^+$, 42), 165 (33), 164 (10), 163 ($C_9H_4ClO^+$, 100), 99 (10). Anal. calcd. for $C_{15}H_9BrClNO$ (333.0): C 53.84, H 2.71, N 4.19; Found: C 53.87, H 2.70, N 4.08.

***N*-(2-Bromophenyl)-3-(4-cyanophenyl)propiolamide (Ac)**



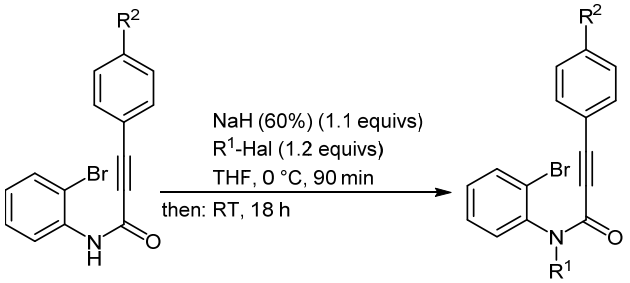
Ac
$C_{16}H_9BrN_2O$
325.17

According to GP I compound **Ac** was obtained as a colorless solid.

Mp 153 °C. R_f (*n*-hexane:EtOAc, 3:1): 0.42. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.05 (m, 1 H), 7.35 (ddd, *J* = 8.5, 7.7, 1.5 Hz, 1 H), 7.58 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.70 (br, 4 H), 8.02 (br, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 83.8 (C_{quat}), 86.3 (C_{quat}), 113.3 (C_{quat}), 114.0 (C_{quat}), 118.0 (C_{quat}), 122.5, 124.7 (C_{quat}), 126.3, 128.7, 132.4, 132.6, 133.3, 135.0 (C_{quat}), 150.1 (C_{quat}). IR (ATR) $\tilde{\nu}$ 3190 (w), 3144 (w), 3015 (w), 2220 (m), 1651 (m), 1632 (s), 1605 (m), 1578 (s), 1526 (s), 1499 (m), 1468 (m), 1441 (m), 1427 (m), 1406 (w), 1395 (w), 1300 (s), 1277 (m),

1236 (m), 1190 (s), 1161 (w), 1123 (w), 1105 (w), 1045 (m), 1026 (m), 966 (m), 943 (w), 837 (s), 812 (w), 760 (s), 721 (s), 691 (s), 660 (s). EI-MS (70 eV): *m/z* (%) 325.9 (M^+(^{81}Br), 4), 323.9 (M^+(^{79}Br), 4), 155 (14), 154 ($C_{10}H_4NO^+$, 100), 126 (9), 99 (9). Anal. calcd. for $C_{16}H_9BrN_2O$ (324.0): C 59.10, H 2.79, N 8.62; Found: C 59.05, H 2.85, N 8.46.

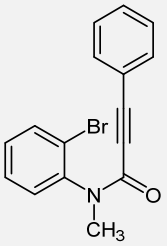
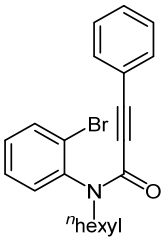
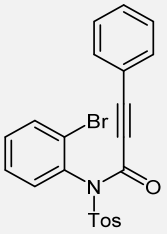
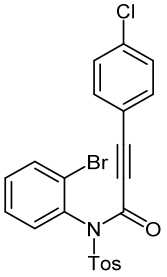
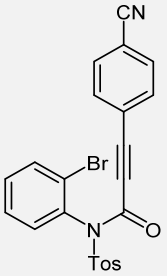
1.1.2 General procedure II (GP II) for the preparation of *N*-substituted *N*-(2-bromophenyl)-3 arylpropiolamides 1



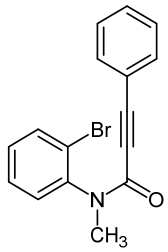
Aa-Ac **1a-c, 1g,h**

In a dry screw-cap Schlenk tube with a magnetic stir bar under nitrogen were placed sodium hydride (60% dispersion in petroleum, 1.1 equivs) and dry THF (2.7 mL/mmol) and the suspension was cooled to 0 °C (ice-salt bath). Then the corresponding secondary propiolamide **A** (1.0 equiv) dissolved in dry THF (2.0 mL/mmol) was slowly added dropwise to the sodium hydride suspension (for experimental details, see Table SI-2). After complete addition the mixture was stirred at 0 °C for 1 h. Then the electrophile R^1-Hal (1.2 equivs) was added and the mixture was stirred at 0 °C for 30 min and then allowed to come to room temp where stirring was continued for 18 h. Then the solvent was removed in vacuo and to the residue was added dichloromethane (20 mL/mmol). The organic layer was then washed with deionized water (2 x 20 mL/mmol) and saturated brine (2 x 20 mL/mmol) and dried (anhydrous magnesium sulfate). After removal of the solvents in vacuo the crude product was adsorbed on celite® and chromatographed on silica gel (*n*-hexane-ethyl/acetate) to give the pure *N*-substituted *N*-(2-bromophenyl)-3-arylpropiolamides **1**.

Table SI-2. Experimental details of the preparation of *N*-substituted *N*-(2-bromophenyl)-3-arylpropiolamides **1d-f** according to GP II.

Entry	propiolamide **A** [g] (mmol)	electrophile R^1-Hal [g] (mmol)	*N*-substituted *N*-(2-bromophenyl)-3-arylpropiolamides **1** [g] (%)	*n*-hexane:ethyl acetate (*v*/*v*)
1	0.30 (1.00) of **Aa** (R^2 = H)	0.18 (1.10) of methyliodide (R^1 = Me, Hal = I)	 0.29 (93) of **1a**	5:1
2	0.60 (2.00) of **Aa**	0.48 (2.20) of *n*-hexyliodide (R^1 = *n*-hexyl, Hal = I)	 0.66 (86) of **1b**	5:2
3	2.98 (9.90) of **Aa**	2.28 (11.9) of *p*-tosylchloride (R^1 = Tos, Hal = Cl)	 4.05 (90) of **1c**	6:1
4	0.82 (2.40) of **Ab**	0.57 (3.00) of *p*-tosylchloride	 0.95 (79) of **1g**	7:1
5	0.33 (1.00) of **Ac**	0.23 (1.20) of *p*-tosylchloride	 0.16 (54) of **1h**	7:1

***N*-(2-Bromophenyl)-*N*-methyl-3-phenylpropiolamide (1a)**

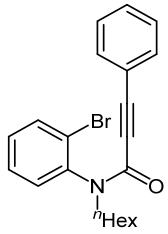


1a
$C_{16}H_{12}BrNO$
314.18

According to GP II compound **1a** was obtained as a colorless amorphous solid.

Mp 88 °C. R_f (*n*-hexane:EtOAc, 10:1): 0.17. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.32 (s, 3 H), 7.08 (dd, *J* = 8.4, 1.4 Hz, 2 H), 7.17-7.25 (m, 2 H), 7.27-7.37 (m, 2 H), 7.39-7.44 (m, 2 H), 7.67-7.77 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 35.2 (CH_3), 82.3 (C_{quat}), 90.5 (C_{quat}), 120.3 (C_{quat}), 124.0 (C_{quat}), 128.4, 128.6, 130.1, 130.2, 130.7, 132.6, 133.7, 142.2 (C_{quat}), 154.5 (C_{quat}). IR (ATR): $\tilde{\nu}$ 2980 (m), 2972 (w), 2932 (w), 2889 (w), 2212 (m), 1630 (s), 1582 (m), 1530 (w), 1491 (m), 1474 (m), 1433 (m), 1420 (m), 1360 (s), 1314 (m), 1242 (m), 1188 (w), 1159 (m), 1132 (m), 1115 (m), 1063 (m), 1026 (m), 964 (w), 935 (w), 914 (w), 802 (w), 772 (s), 754 (s), 723 (s), 708 (m), 681 (s), 650 (m), 604 (m). EI-MS (70 eV): *m/z* (%) 315 (M^+(^{81}Br), 0.3), 313 (M^+(^{79}Br), 0.3), 235 (17), 234 ($C_{16}H_{12}NO^+$, 100), 129 ($C_9H_5O^+$, 59), 77 ($C_6H_5^+$, 4). Anal. calcd. for $C_{16}H_{12}BrNO$ (313.0): C 61.17, H 3.85, N 4.46; Found: C 61.11, H 3.81, N 4.38.

***N*-(2-Bromophenyl)-*N*-(*n*-hexyl)-3-phenylpropiolamide (1b)**



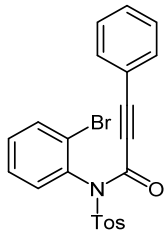
1b
$C_{21}H_{22}BrNO$
384.32

According to GP II compound **1b** was obtained as a crystalline pale yellow solid.

Mp 46 °C. R_f (*n*-hexane:EtOAc, 5:1): 0.38. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.78-0.97 (m, 3 H), 1.20-1.45 (m, 6 H), 1.46-1.80 (m, 2 H), 3.24-3.52 (m, 1 H), 4.13 (ddd, *J* = 13.5, 9.6, 6.5 Hz, 1 H), 7.03 (m, 2 H), 7.16-7.47 (m, 6 H), 7.74 (dd, *J* = 7.9, 1.4 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (CH_3), 22.7 (CH_2), 26.8 (CH_2), 27.8 (CH_2), 31.7 (CH_2), 47.8 (CH_2), 82.6 (C_{quat}), 90.3 (C_{quat}), 120.5 (C_{quat}), 124.7 (C_{quat}), 128.3, 128.4, 130.0, 131.9, 132.6, 133.8, 141.0 (C_{quat}), 154.4 (C_{quat}).[1] EI-MS (70 eV): *m/z* (%) 305 (22), 304 (M^+-Br, 90), 220 ($C_{15}H_{10}NO^+$, 46), 130 (10), 129 ($C_5H_9O^+$, 100), 43 ($C_3H_7^+$, 13).

***N*-(2-Bromophenyl)-3-phenyl-*N*-tosylpropiolamide (1c)**

[1] Signal of two chemical equivalent carbon atoms at δ 130.0.

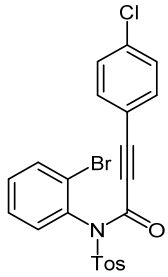


1c
$C_{22}H_{16}BrNO_3S$
454.34

According to GP II compound **1c** was obtained as a colorless amorphous solid.

Mp 142°C. R_f (*n*-hexane:EtOAc, 5:1): 0.24. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3 H), 7.01 (dd, *J* = 8.3, 1.3 Hz, 2 H), 7.20 (t, *J* = 7.6 Hz, 2 H), 7.27-7.41 (m, 4 H), 7.42-7.49 (m, 2 H), 7.73 (dd, *J* = 7.4, 1.3 Hz, 1 H), 8.04 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9 (CH_3), 81.7 (C_{quat}), 93.2 (C_{quat}), 119.2 (C_{quat}), 126.3 (C_{quat}), 128.55, 128.61, 129.5, 130.0, 131.1, 131.6, 132.8, 133.0, 133.9, 135.6 (C_{quat}), 136.0 (C_{quat}), 145.8 (C_{quat}), 152.1 (C_{quat}). IR (ATR): $\tilde{\nu}$ 3063 (w), 2222 (m), 1682 (s), 1468 (m), 1377 (m), 1362 (m), 1288 (m), 1281 (m), 1242 (w), 1157 (s), 1086 (m), 1055 (m), 1028 (m), 976 (m), 917 (m), 845 (w), 820 (m), 779 (m), 758 (m), 723 (m), 704 (s), 660 (s), 646 (m). EI-MS (70 eV): *m/z* (%) 374 (M^+-Br, 2), 284 ($C_9H_4(^{81}Br)NO_3S^+$, 17), 282 ($C_9H_4(^{79}Br)NO_3S^+$, 17), 220 ($C_6H_8NO_3S^+$, 15), 130 (10), 129 ($C_9H_5O^+$, 100), 91 ($C_7H_7^+$, 8). Anal. calcd. for $C_{22}H_{16}BrNO_3S$ (453.0): C 58.16, H 3.55, N 3.08, S 7.06; Found: C 58.12, H 3.51, N 2.91, S 7.13.

***N*-(2-Bromophenyl)-3-(4-chlorphenyl)-*N*-tosylpropiolamide (1g)**



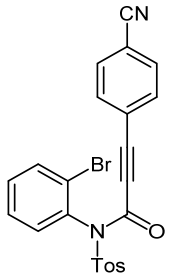
1g
$C_{22}H_{15}BrClNO_3S$
488.78

According to GP II compound **1g** was obtained as a colorless amorphous solid.

Mp 149 °C. R_f (*n*-hexane:EtOAc, 5:1): 0.30. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.47 (s, 3 H), 6.98 (d, *J* = 8.7 Hz, 2 H), 7.22 (d, *J* = 8.7 Hz, 2 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.39-7.45 (m, 1 H), 7.46-7.50 (m, 2 H), 7.71-7.81 (m, 1 H), 8.07 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9 (CH_3), 82.4 (C_{quat}), 91.8 (C_{quat}), 117.6 (C_{quat}), 126.3 (C_{quat}), 128.6, 129.1, 129.5, 130.0, 131.6, 132.8, 133.9, 134.2, 135.5 (C_{quat}), 135.9 (C_{quat}), 137.5 (C_{quat}), 145.9 (C_{quat}), 151.9 (C_{quat}). IR (ATR): $\tilde{\nu}$ 3120 (w), 3060 (w), 2851 (w), 2218 (m), 2197 (m), 1676 (s), 1591 (m), 1479 (m), 1466 (m), 1445 (w), 1431 (w), 1398 (w), 1362 (s), 1296 (s), 1242 (w), 1165 (s), 1119 (m), 1084 (s), 1053 (m), 1028 (w), 1011 (m), 976 (m), 914 (m), 856 (m), 827 (s), 808 (m), 783 (w), 756 (m), 723 (m), 704 (s), 660 (s), 642 (m). EI-MS (70 eV): *m/z* (%) 410 (M^+-Br, 1), 409 (1), 408 (2), 318 (25), 316 (20), 253 ($C_{15}H_8ClNO^+$, 8), 165 (33), 164 (10), 163

($C_9H_4ClO^+$, 100), 155 ($C_7H_7O_2S_2^+$, 9), 91 ($C_7H_7^+$, 13), 65 ($C_5H_5^+$, 4). Anal. calcd. for $C_{22}H_{15}BrClNO_3S$ (487.0): C 54.06, H 3.09, N 2.87, S 6.56; Found: C 53.90, H 2.83, N 2.83, S 6.79.

N-(2-Bromophenyl)-3-(4-cyanophenyl)-*N*-tosylpropiolamide (1h)

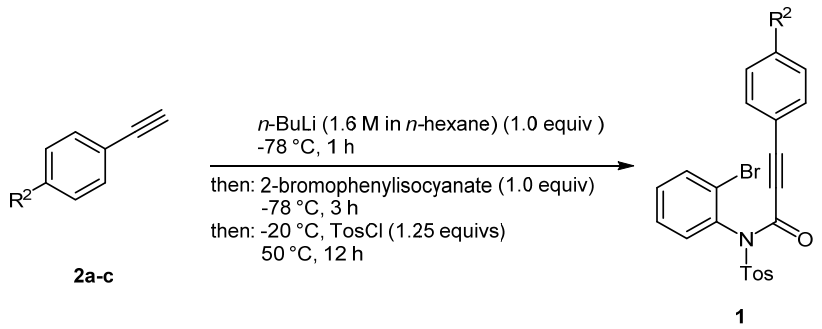


1h
$C_{23}H_{15}BrN_2O_3S$
479.35

According to GP II compound **1h** was obtained as a colorless amorphous solid.

Mp 162 °C. R_f (*n*-hexane:EtOAc, 2:1): 0.53. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.47 (s, 3 H), 7.16 (d, *J* = 8.6 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 7.40-7.46 (m, 1 H), 7.47-7.50 (m, 2 H), 7.54 (d, *J* = 8.6 Hz, 2 H), 7.74-7.80 (m, 1 H), 8.06 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9 (CH_3), 84.3 (C_{quat}), 89.8 (C_{quat}), 114.4 (C_{quat}), 117.8 (C_{quat}), 123.9 (C_{quat}), 126.1 (C_{quat}), 128.7, 129.6, 130.0, 131.8, 132.3, 132.8, 133.3, 133.9, 135.3 (C_{quat}), 135.6 (C_{quat}), 146.1 (C_{quat}), 151.4 (C_{quat}). IR (ATR): $\tilde{\nu}$ 3109 (w), 2922 (w), 2228 (m), 2205 (m), 1676 (s), 1593 (m), 1497 (m), 1470 (m), 1433 (w), 1396 (w), 1362 (s), 1346 (w), 1300 (s), 1244 (m), 1177 (s), 1161 (s), 1123 (m), 1105 (m), 1082 (s), 1059 (m), 1030 (m), 1015 (m), 978 (m), 916 (m), 847 (s), 814 (s), 758 (m), 725 (s), 702 (s), 681 (m), 660 (s), 642 (s). EI-MS (70 eV): *m/z* (%) 399 (M^+-Br, 2), 309 (19), 307 (19), 245 (20), 155 ($C_7H_7O_2S_2^+$, 26), 154 ($C_{10}H_4NO^+$, 100), 91 (20). Anal. calcd. for $C_{23}H_{15}BrN_2O_3S$ (478.0): C 57.63, H 3.15, N 5.84, S 6.69; Found: C 57.84, H 3.26, N 5.79, S 6.63.

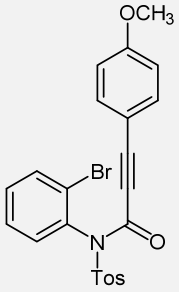
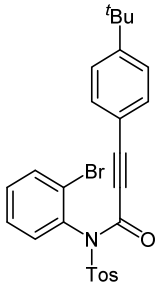
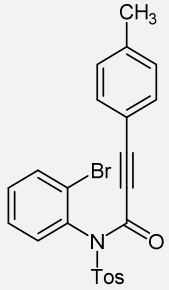
1.1.3 General procedure III (GP III) for the preparation of *N*-(2-bromophenyl)-3-aryl-*N*-tosyl propiolamides 1



2a-c **1**

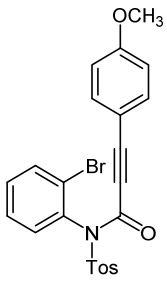
The corresponding terminal alkyne (2.20 mmol) **2** and dry tetrahydrofuran (6.0 mL) were placed in a dry screw-cap Schlenk tube with a magnetic stir bar under nitrogen and cooled to -78 °C by an external dry ice-acetone bath (for experimental details, see Table SI-3). Then *n*-butyllithium (1.6 M in *n*-hexane) (1.30 mL, 2.08 mmol) were added dropwise to the reaction mixture over a period of 20 min. Then the mixture was stirred at -78 °C for 1 h. Then 2-bromophenylisocyanate (0.40 g, 2.00 mmol) were added dropwise and stirring at -78 °C was continued for 3 h. Then the cooling bath was removed and the reaction mixture was allowed to come to -20 °C. To this mixture was added *p*-tosyl chloride (0.48 g, 2.50 mmol) under nitrogen. After the addition the reaction mixture was allowed to come to room temp before it was heated to 50 °C (oil bath) for 12 h. After cooling to room temp a saturated aqueous ammonium chloride solution (20 mL) was added to the reaction mixture. After addition of dichloromethane (30 mL) the phases were separated and the aqueous layer was extracted with dichloromethane (2 x 10 mL). The combined organic layers were then washed with saturated brine (30 mL) and dried (anhydrous magnesium sulfate). After removal of the solvents in vacuo the crude product was adsorbed on celite® and chromatographed on silica gel (*n*-hexane-ethyl/acetate) to give the pure *N*-tosyl *N*-(2-bromophenyl)-3-arylpropiolamides **1**.

Table SI-3. Experimental details of the preparation of *N*-tosyl *N*-(2-bromophenyl)-3-arylpropiolamides **1d-f** according to GP III.

entry	alkyne **2** [g] (mmol)	*N*-(2-bromophenyl)-3-aryl-*N*-tosyl propiolamides **1** [g] (%)	*n*-hexane:ethyl acetate (*v*/*v*)
1[a]	0.41 (3.10) of **2b** (R^2 = OMe)	 0.98 (84) of **1d**	6:1
2	0.36 (2.20) of **2c** (R^2 = ^{t}Bu)	 0.67 (65) of **1e**	7:1
3	0.27 (2.20) of **2d** (R^2 = Me)	 0.50 (51) of **1f**	7:1

[a] Performed with 9.0 mL of THF, 1.9 mL of *n*-BuLi (1.6 M in *n*-hexane) (3.10 mmol), 0.55 g (2.80 mmol) of 2-bromophenylisocyanate, and 0.66 g (3.50 mmol) of p-tosyl chloride.

N-(2-Bromophenyl)-3-(4-methoxyphenyl)-*N*-tosylpropiolamide (1d)



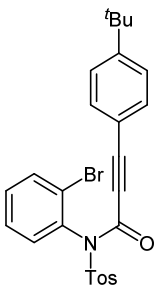
1d
$C_{23}H_{18}BrNO_4S$
484.36

According to GP III compound **1d** was obtained as a colorless amorphous solid.

R_f (*n*-hexane:EtOAc, 5:1): 0.29. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.46 (s, 3 H), 3.77 (s, 3 H), 6.74 (d, *J* = 8.9 Hz, 2 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.40 (td, *J* = 7.7,

2.0 Hz, 1 H), 7.47 (td, *J* = 7.5, 1.3 Hz, 1 H), 7.49 (dd, *J* = 7.8, 1.9 Hz, 1 H), 7.76 (dd, *J* = 8.1, 1.2 Hz, 1 H), 8.08 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 21.9 (CH_3), 55.5 (CH_3), 81.4 (C_{quat}), 94.4 (C_{quat}), 110.9 (C_{quat}), 114.4, 126.4 (C_{quat}), 128.5, 129.5, 130.0, 131.4, 132.8, 133.8, 135.1, 135.7 (C_{quat}), 136.2 (C_{quat}), 145.6 (C_{quat}), 152.3 (C_{quat}), 161.9 (C_{quat}). IR (ATR): $\tilde{\nu}$ 3150 (w), 3006 (w), 2980 (w), 2950 (w), 2191 (s), 1732 (m), 1672 (s), 1599 (s), 1558 (m), 1508 (s), 1470 (s), 1456 (m), 1441 (m), 1398 (w), 1364 (s), 1288 (s), 1254 (s), 1150 (s), 1121 (m), 1109 (m), 1086 (s), 1053 (m), 1026 (s), 976 (m), 953 (w), 920 (m), 862 (w), 833 (m), 812 (m), 762 (m), 736 (w), 723 (m), 704 (s), 660 (s), 646 (m). EI-MS (70 eV): *m/z* (%) 421 (M^+(^{81}Br), 1), 419 (M^+(^{79}Br), 1), 404 (M^+-Br, 2), 249 (14), 222 (12), 160 (11), 159 ($C_{10}H_7O_2^+$, 100), 43 (19). Anal. calcd. for $C_{23}H_{18}BrNO_4S$ (483.0): C 57.03, H 3.75, N 2.89, S 6.62; Found: C 57.08, H 3.88, N 2.84, S 6.35.

***N*-(2-Bromophenyl)-3-(4-(*tert*-butyl)phenyl)-*N*-tosylpropiolamide (1e)**

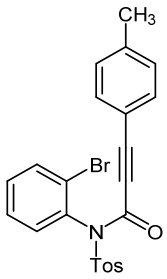


1e
$C_{26}H_{24}BrNO_3S$
510.45

According to GP III compound **1e** was obtained as a colorless amorphous solid.

Mp 86 °C, R_f (*n*-hexane:EtOAc, 5:1): 0.27. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 9 H), 2.47 (s, 3 H), 6.99 (d, *J* = 8.6 Hz, 2 H), 7.26 (d, *J* = 8.7 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.39-7.46 (m, 1 H), 7.47-7.52 (m, 2 H), 7.77 (dd, *J* = 7.7, 1.7 Hz, 1 H), 8.09 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9 (CH_3), 31.1 (CH_3), 35.2 (C_{quat}), 81.4 (C_{quat}), 93.9 (C_{quat}), 116.1 (C_{quat}), 125.7, 126.4 (C_{quat}), 128.5, 129.5, 130.0, 131.5, 132.8, 133.0, 133.9, 135.7 (C_{quat}), 136.1 (C_{quat}), 145.7 (C_{quat}), 152.2 (C_{quat}), 154.9 (C_{quat}). IR (ATR): $\tilde{\nu}$ 2964 (m), 2902 (w), 2868 (w), 2196 (s), 1678 (s), 1597 (m), 1504 (m), 1470 (s), 1435 (w), 1396 (w), 1366 (s), 1292 (s), 1269 (m), 1244 (w), 1163 (s), 1121 (m), 1105 (m), 1086 (s), 1055 (m), 1028 (m), 1018 (w), 977 (m), 953 (w), 920 (m), 837 (m), 814 (m), 783 (w), 752 (w), 723 (m), 704 (s), 660 (s), 642 (m). EI-MS (70 eV): *m/z* (%) 374 ($C_{22}H_{16}NO_3S^+$, 4), 327 ($C_{13}H_{11}$(^{81}Br)NO_2S^+, 2), 325 ($C_{13}H_{11}$(^{79}Br)NO_2S^+, 2), 186 (15), 185 ($C_{13}H_{13}O^+$, 100), 155 ($C_7H_7O_2S^+$, 20), 91 (12), 57 ($C_4H_9^+$, 5). Anal. calcd. for $C_{26}H_{24}BrNO_3S$ (509.1): C 61.18, H 4.74, N 2.74, S 6.28; Found: C 61.16, H 4.82, N 2.68, S 6.20.

***N*-(2-Bromophenyl)-3-(4-tolyl)-*N*-tosylpropiolamide (1f)**

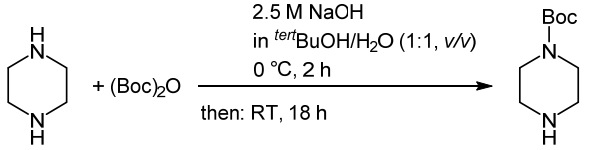


1f
$C_{23}H_{18}BrNO_3S$
468.37

According to GP III compound **1f** was obtained as a colorless amorphous solid.

Mp 125 °C. R_f (*n*-hexane:EtOAc, 5:1): 0.21. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.31 (s, 3 H), 2.47 (s, 3 H), 6.94 (d, *J* = 8.6 Hz, 2 H), 7.05 (d, *J* = 8.6 Hz, 2 H), 7.32-7.58 (m, 5 H), 7.76 (d, *J* = 7.4 Hz, 1 H), 8.08 (d, *J* = 7.0 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.85 (CH_3), 21.91 (CH_3), 81.5 (C_{quat}), 93.9 (C_{quat}), 116.1 (C_{quat}), 126.3 (C_{quat}), 128.5, 129.4, 129.5, 130.0, 131.5, 132.8, 133.0, 133.8, 135.7 (C_{quat}), 136.1 (C_{quat}), 141.9 (C_{quat}), 145.7 (C_{quat}), 152.2 (C_{quat}). IR (ATR): $\tilde{\nu}$ 3050 (w), 2985 (w), 2972 (w), 2922 (w), 2220 (m), 2193 (s), 1676 (s), 1595 (m), 1508 (m), 1470 (s), 1435 (m), 1400 (w), 1366 (s), 1292 (s), 1242 (m), 1186 (m), 1157 (s), 1121 (m), 1086 (s), 1053 (m), 1028 (m), 1018 (m), 976 (m), 951 (w), 920 (m), 862 (w), 814 (s), 762 (m), 737 (w), 723 (m), 704 (s), 660 (s), 644 (m). EI-MS (70 eV): *m/z* (%) 388 ($M\text{-}Br^+$, 1), 327 ($C_{13}H_{22}(^{81}Br)NO_2S^+$, 2), 325 ($C_{13}H_{22}(^{79}Br)NO_2S^+$, 2), 233 ($C_{16}H_{11}NO^+$, 10), 155 ($C_7H_7O_2S^+$, 12), 144 (11), 143 ($C_{10}H_7O^+$, 100), 91 (18), 43 (15). Anal. calcd. for $C_{23}H_{18}BrNO_3S$ (467.0): C 58.98, H 3.87, N 2.99, S 6.85; Found: C 58.73, H 3.96, N 2.91, S 6.55.

1.2 Synthesis of *tert*-Butyl piperazine-1-carboxylate (3)[2]



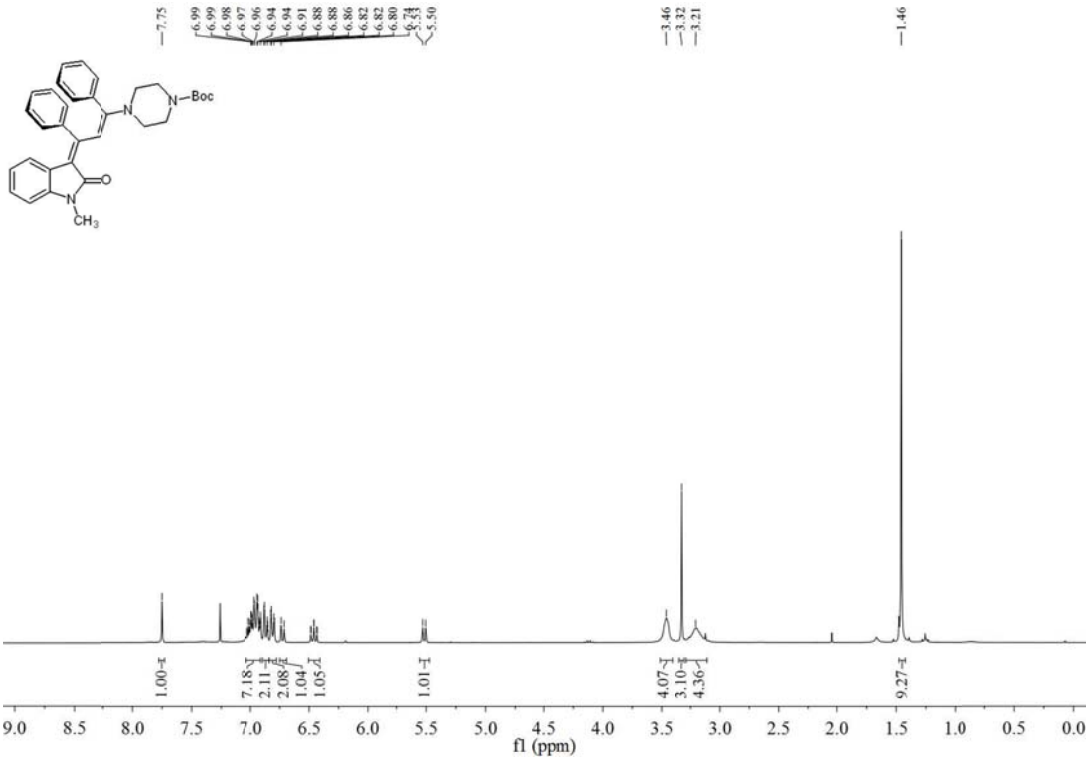
3a
$C_9H_{18}N_2O_2$
186.26

Piperazine (24.5 g, 284 mmol) was dissolved in a mixture of *tert*-BuOH (300 mL) and deionized water (300 mL) in a 1 L two-neck roundbottom flask with a dropping funnel under nitrogen and cooled to 0 °C (ice-salt bath). After stirring for 10 min an aqueous solution of 2.5 M sodium hydroxide (63.0 mL, 158 mmol) was added dropwise over 30 min. After the addition the reaction mixture was stirred at 0 °C for 30 min before di-*tert*-butyldicarbonate (24.9 g, 114 mmol) were added. After the addition the mixture was stirred at 0 °C for 2 h and allowed to come to room temp, where stirring was continued for 18 h. The reaction mixture was transferred to a 1 L roundbottom flask and *tert*-butanol was removed in vacuo. The remaining suspension was filtered and the filtrate was extracted with dichloromethane (4 x 150 mL). The combined organic phases were washed with brine and dried (anhydrous sodium sulfate). After filtration the solvents were removed in vacuo to give after drying in vacuo *tert*-Butyl piperazine-1-carboxylate (**3a**) (14.0 g, 33 %) as a crystalline colorless solid.

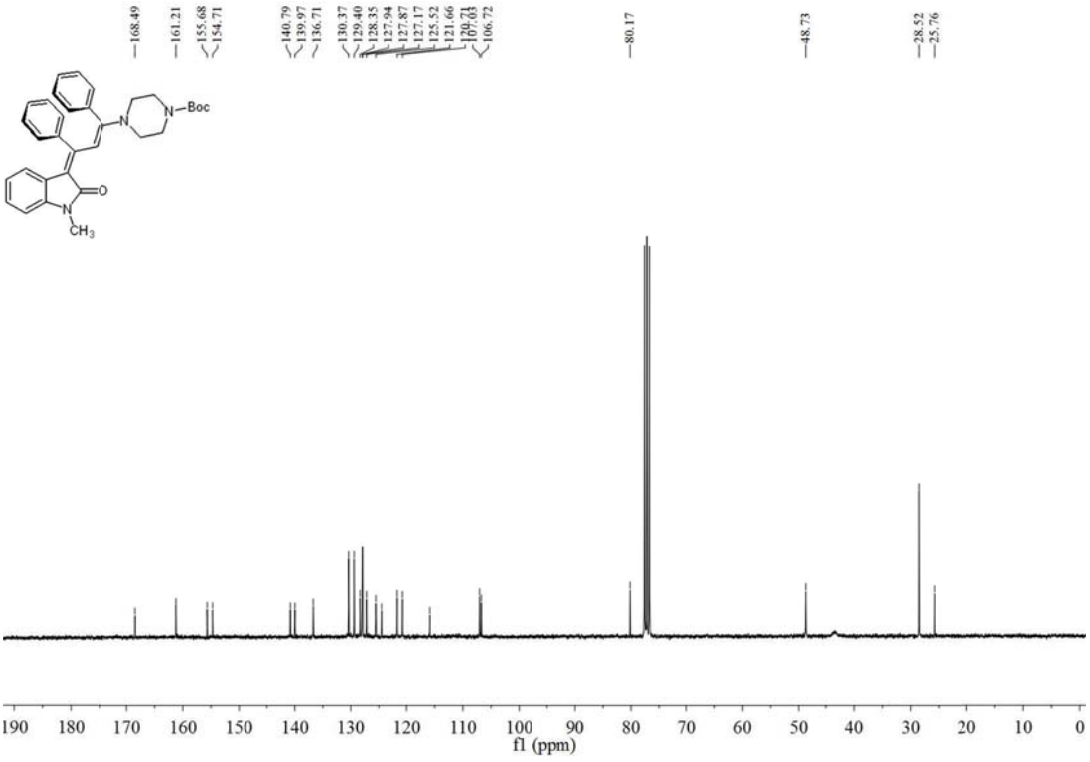
Mp 46 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (s, 9 H), 1.74 (s, 1 H), 2.72-2.83 (m, 4 H), 3.30-3.40 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.5 (CH_3), 46.0 (CH_2), 79.6 (C_{quat}), 154.9 (C_{quat}). IR (ATR): $\tilde{\nu}$ 3323 (w), 2976 (w), 2928 (w), 2860 (w), 2814 (w), 2737 (w), 1688 (s), 1476 (m), 1454 (m), 1418 (s), 1393 (m), 1364 (m), 1341 (w), 1317 (m), 1290 (m), 1242 (s), 1167 (s), 1121 (s), 1090 (m), 1053 (m), 1005 (m), 926 (w), 903 (w), 862 (m), 847 (m), 808 (m), 768 (m). EI-MS (70 eV): *m/z* (%) 186 (M^+, 19), 143 ($C_7H_{13}NO_2^+$, 63), 130 ($C_5H_{10}N_2O_2^+$, 47), 113 (32), 88 (16), 85 ($C_4H_9N_2^+$, 23), 57 ($C_4H_9^+$, 100), 56 (57), 55 (15), 44 (65), 43 ($C_2H_5N^+$, 17), 42 (15), 41 (28).

2 ^{1}H and ^{13}C NMR spectra of compounds 4

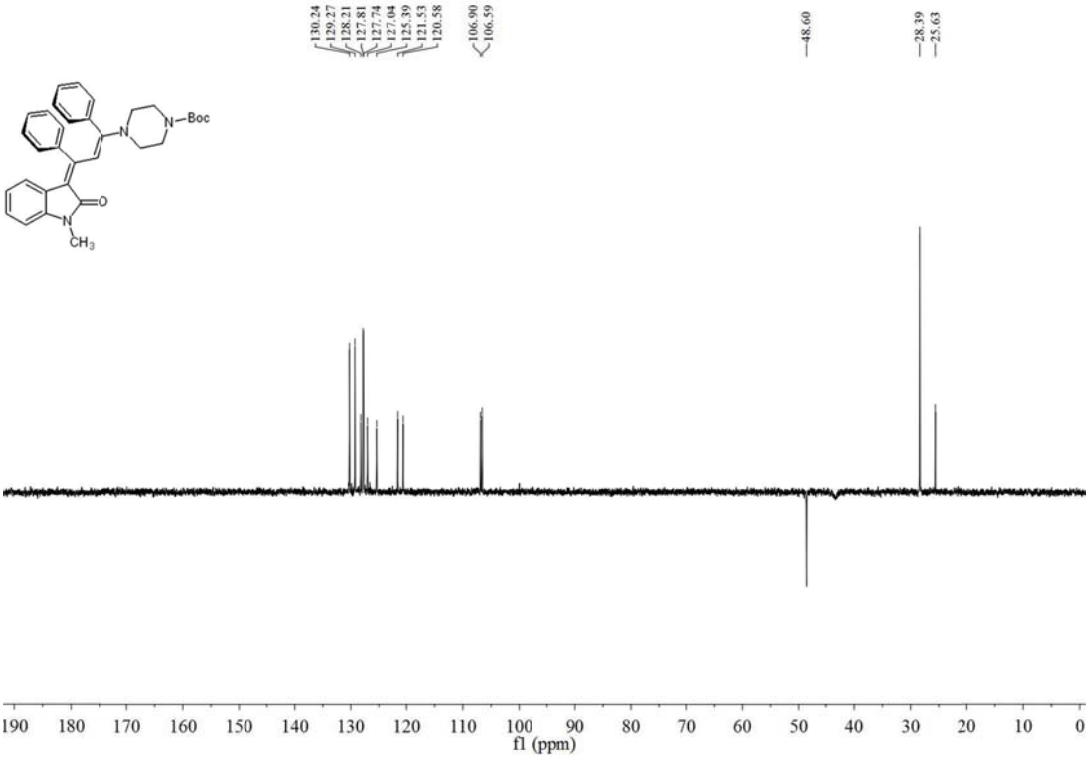
2.1 *tert*-Butyl-4-((*E*)-3-((*E*)-1-methyl-2-oxindolin-3-yliden)-1,3-diphenylprop-1-en-1-yl)piperazin-1-carboxylate (4a)



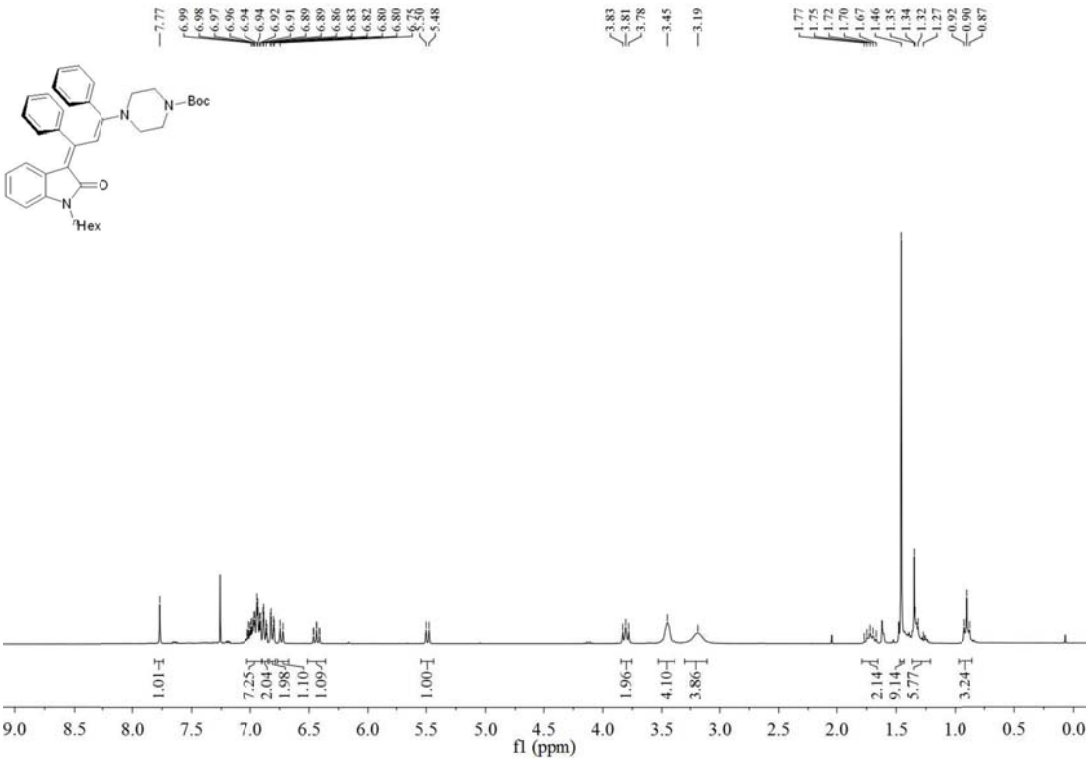
^{1}H NMR spectrum of **4a** ($CDCl_3$, 300 MHz, 293 K).



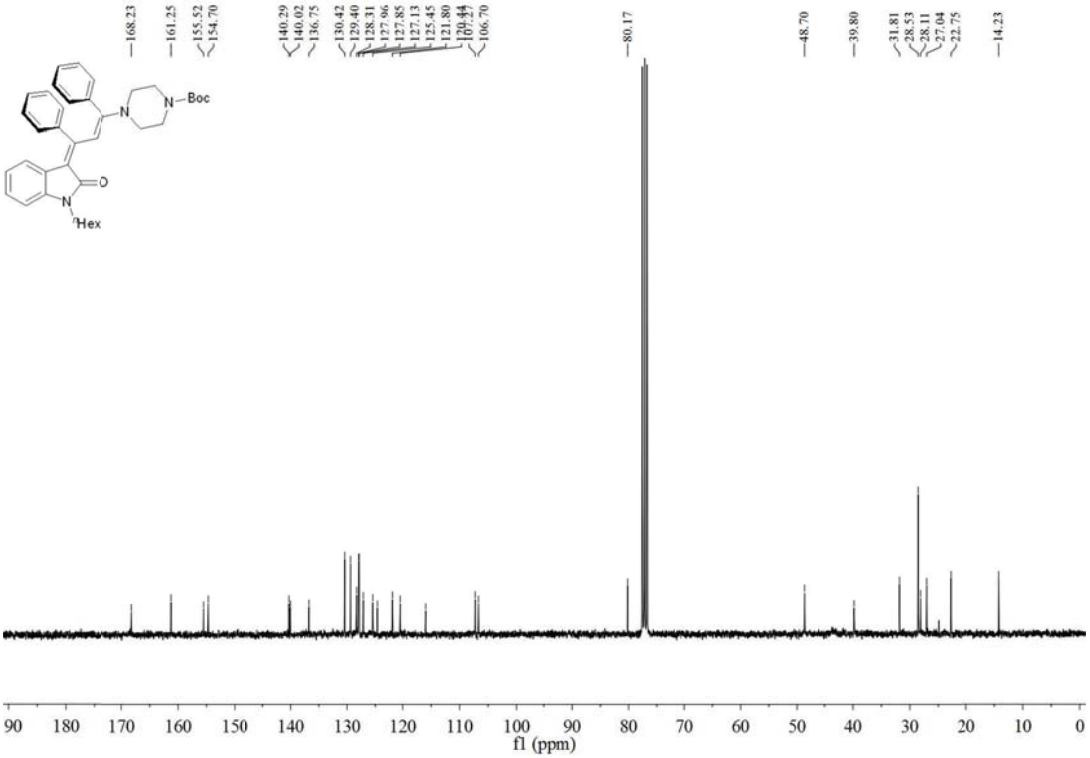
^{13}C NMR spectrum of **4a** ($CDCl_3$, 75 MHz, 293 K).



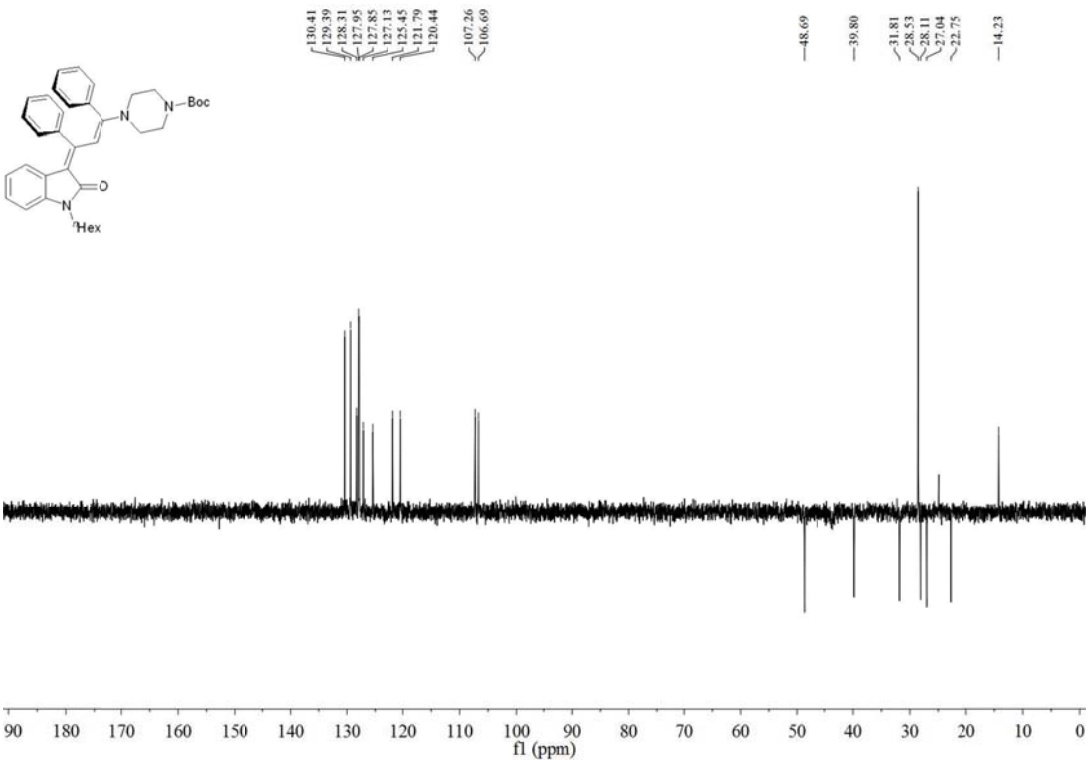
2.2 *tert*-Butyl-4-((*E*)-3-((*E*)-1-hexayl-2-oxindolin-3-yliden)-1,3-diphenylprop-1-en-1-yl)piperazin-1-carboxylate (4b)



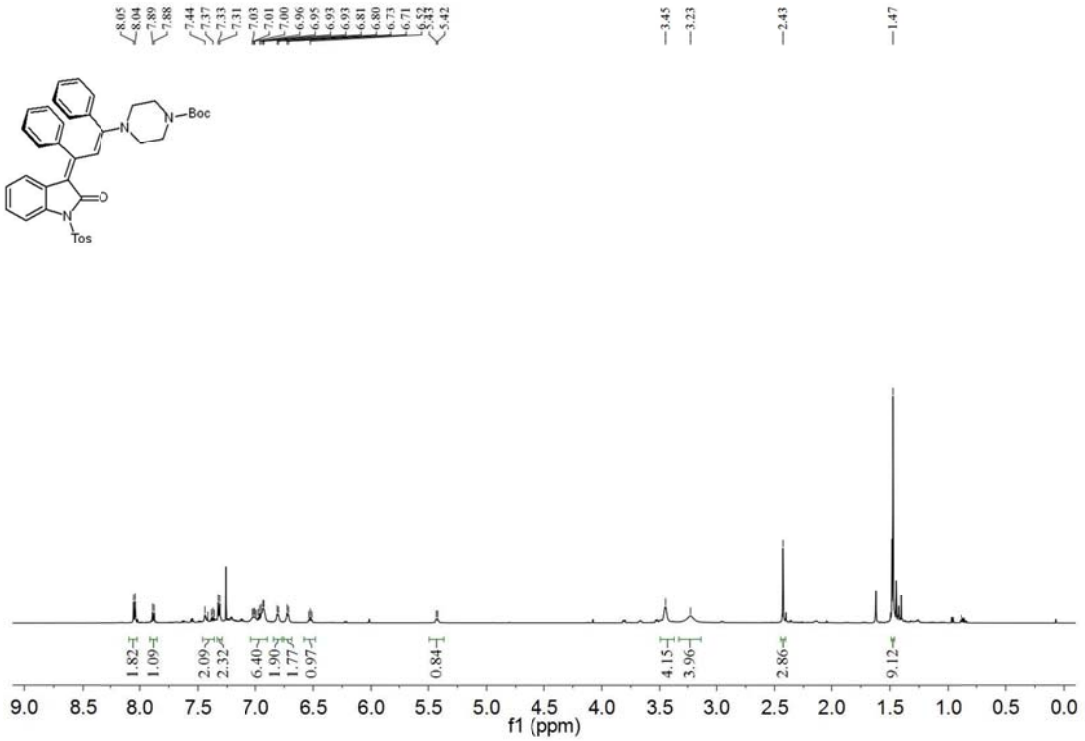
^{1}H NMR spectrum of **4b** ($CDCl_3$, 300 MHz, 293 K).



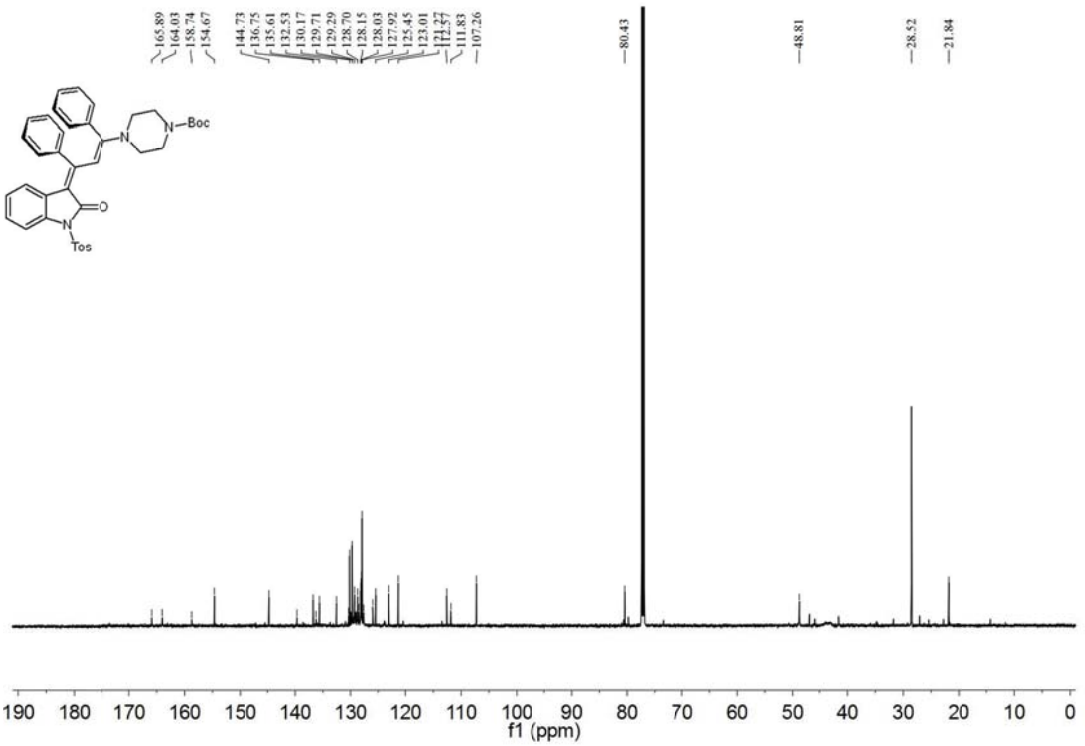
^{13}C NMR spectrum of **4b** ($CDCl_3$, 75 MHz, 293 K).



2.3 *tert*-Butyl-4-((*E*)-3-((*E*)-2-oxo-1-tosylindolin-3-yliden)-1,3-diphenylprop-1-en-1-yl)-piperazin-1-carboxylate (4c)

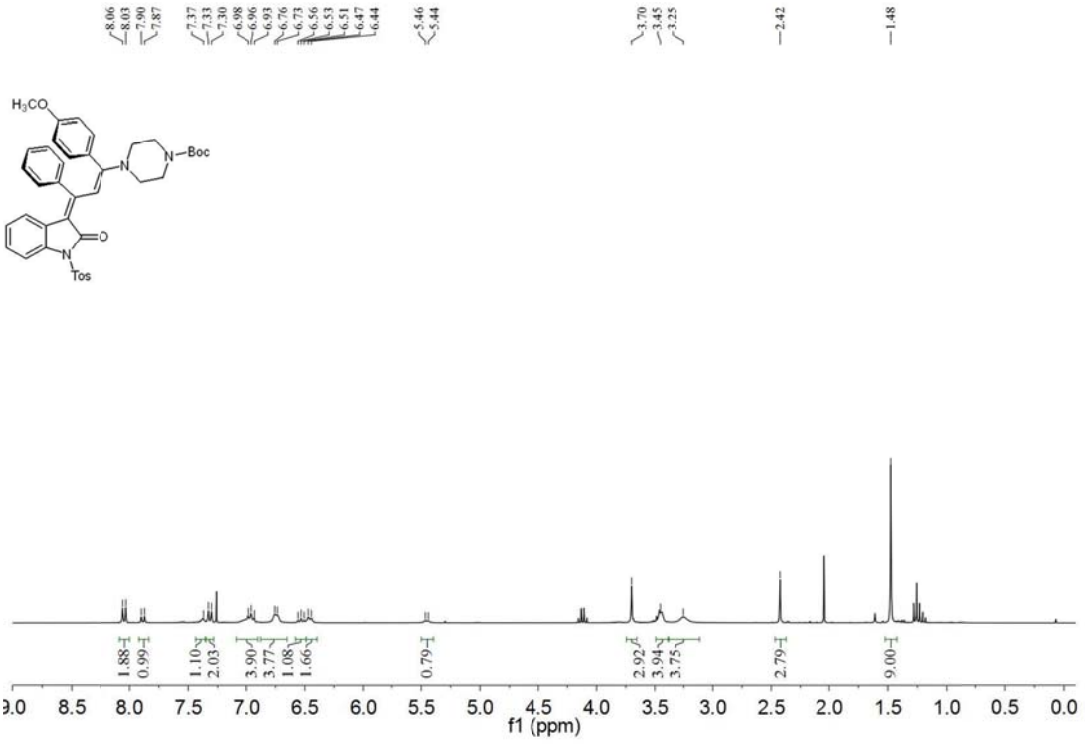


^{1}H NMR spectrum of **4c** ($CDCl_3$, 300 MHz, 293 K).

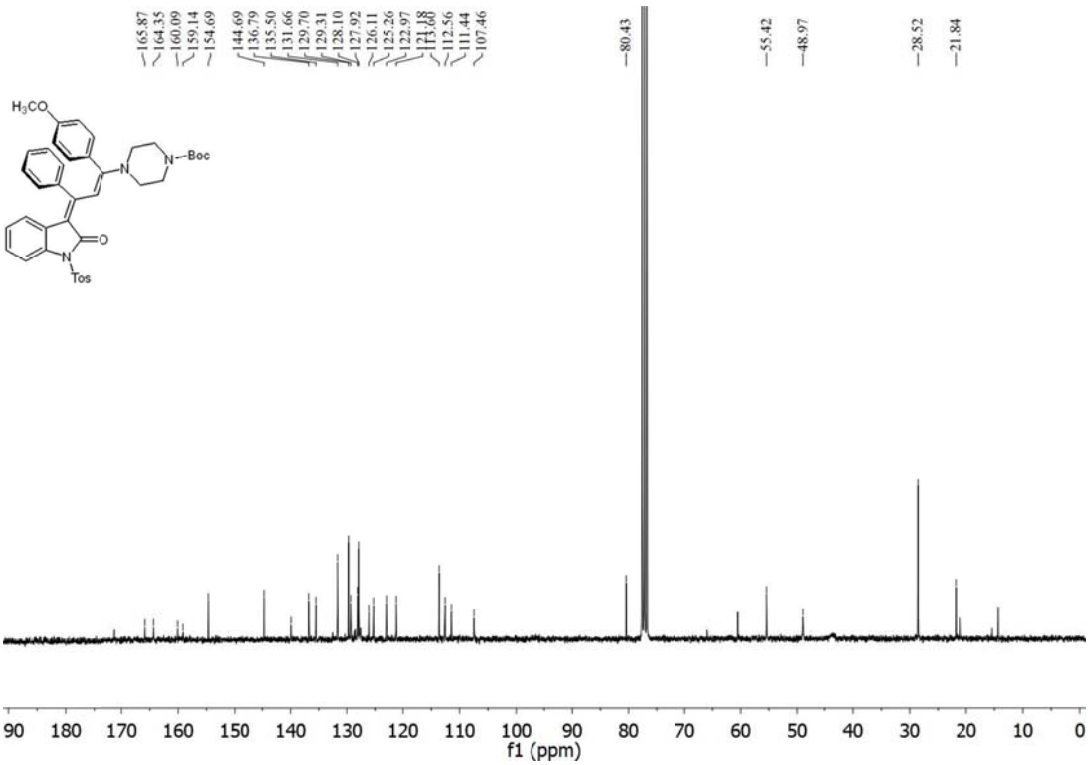


^{13}C NMR spectrum of **4c** ($CDCl_3$, 75 MHz, 293 K).

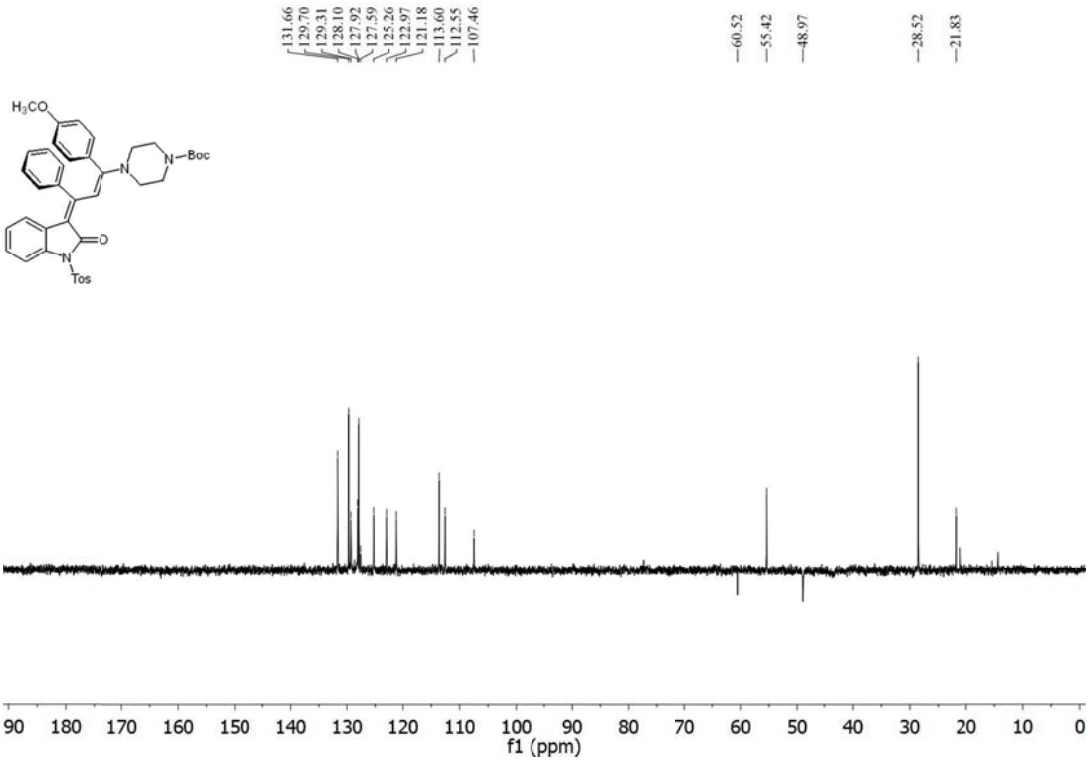
2.4 *tert*-Butyl-4-(1-(4-methoxyphenyl)-3-(2-oxo-1-tosylindolin-3-yliden)-3-phenylprop-1-en-1-yl)-piperazin-1-carboxylate (4d)



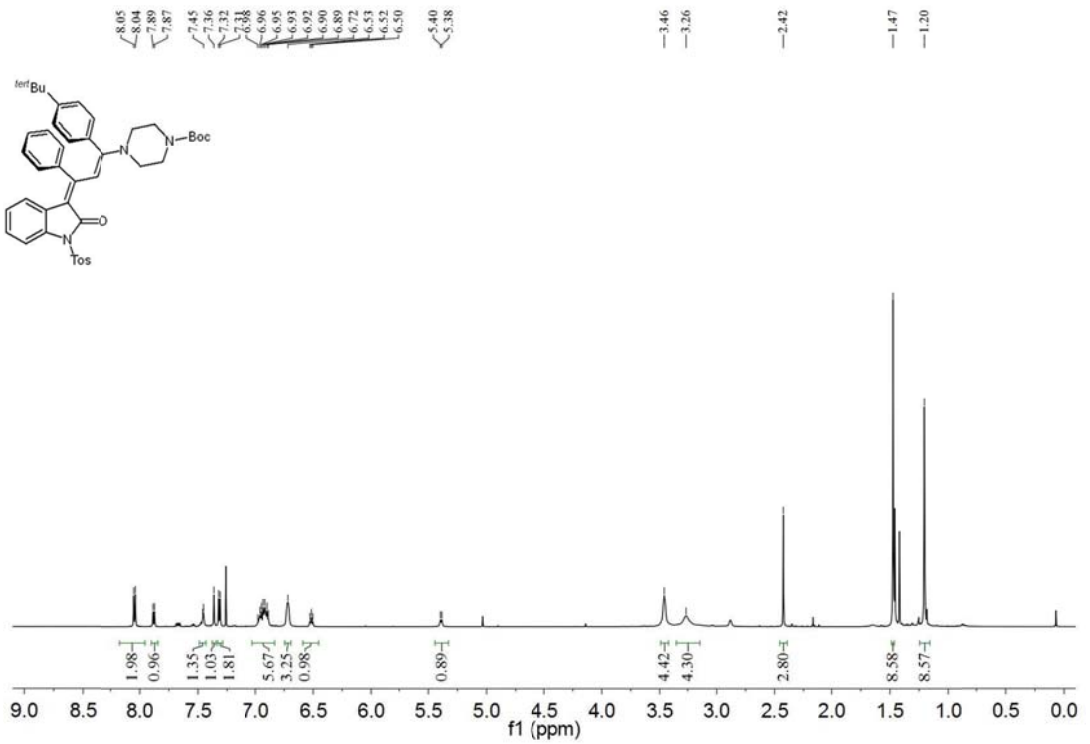
^{1}H NMR spectrum of **4d** ($CDCl_3$, 300 MHz, 293 K).



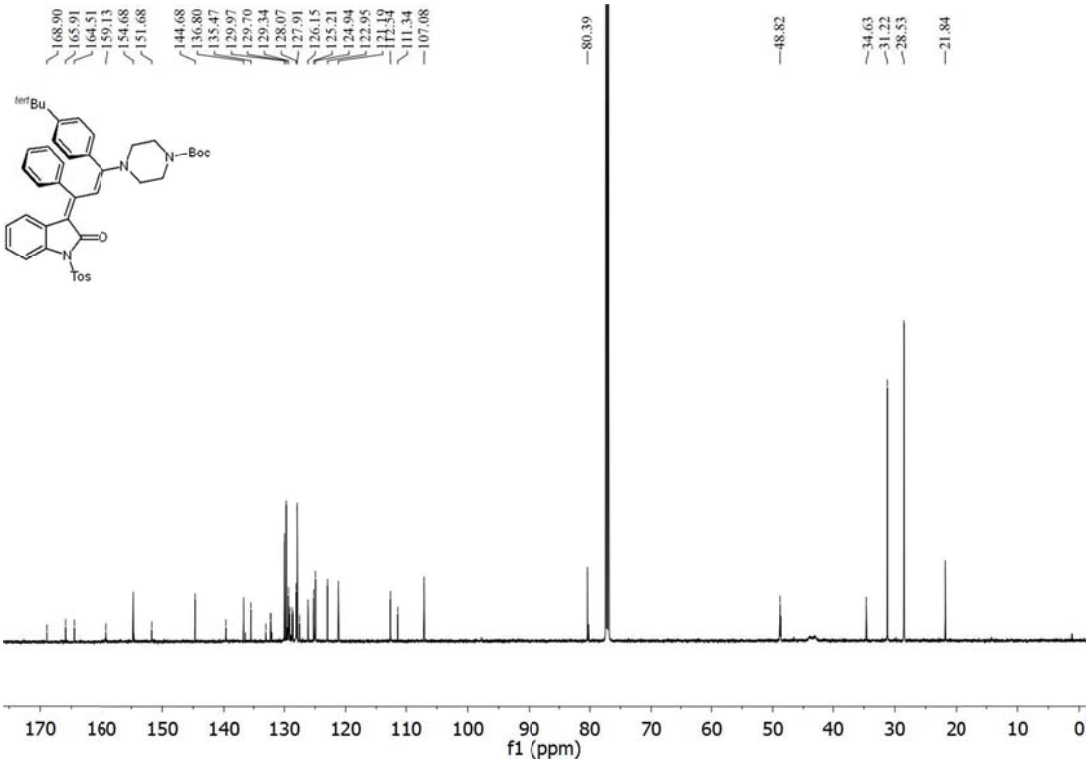
^{13}C NMR spectrum of **4d** ($CDCl_3$, 75 MHz, 293 K).



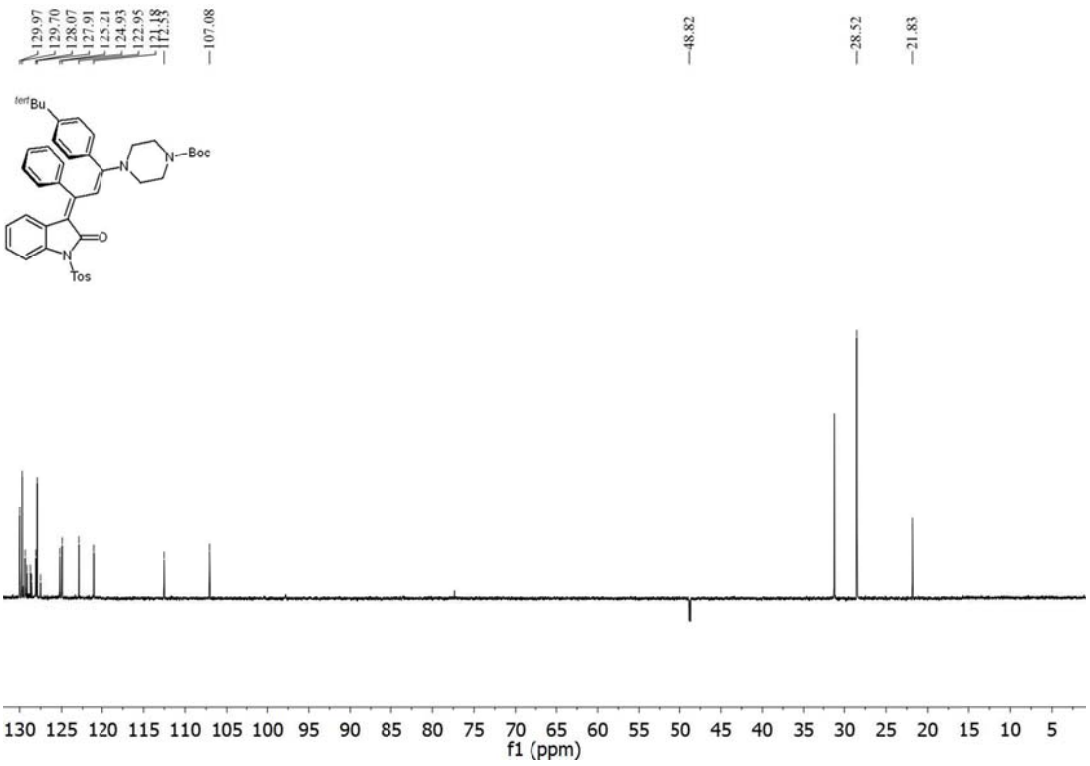
2.5 *tert*-Butyl-4-(1-(4-(*tert*-butyl)phenyl)-3-(2-oxo-1-tosylindolin-3-yliden)-3-phenylprop-1-en-1-yl)-piperazin-1-carboxylate (4e)



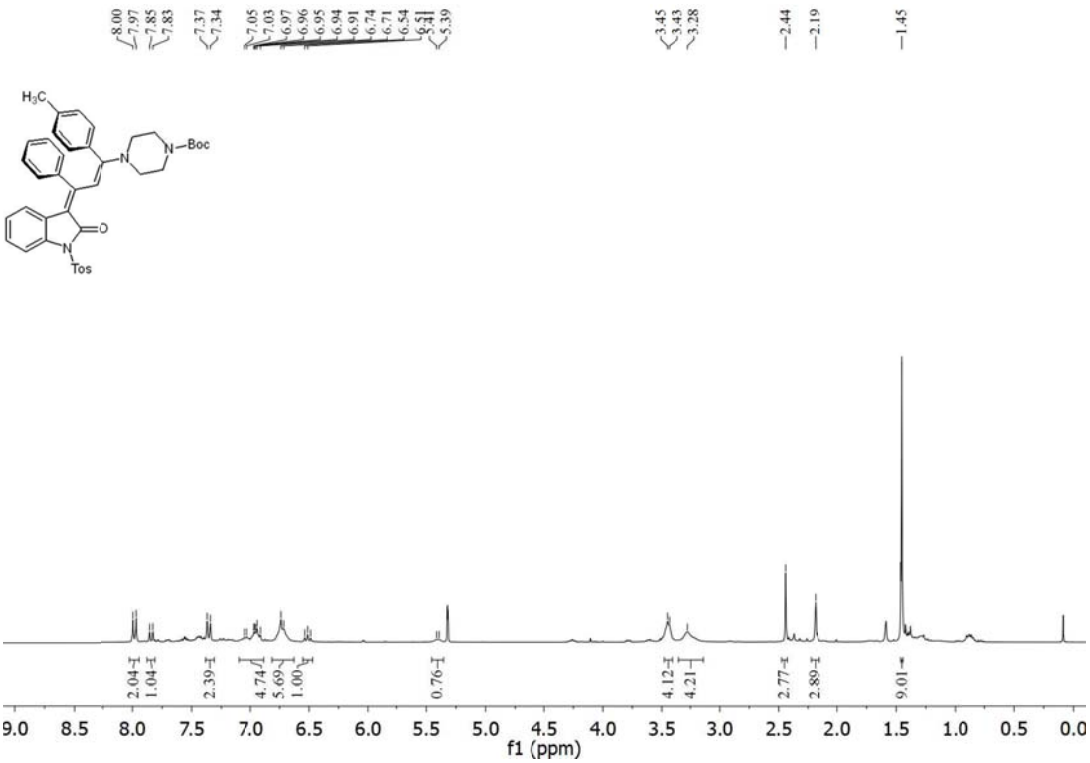
^{1}H NMR spectrum of **4e** ($CDCl_3$, 600 MHz, 293 K).



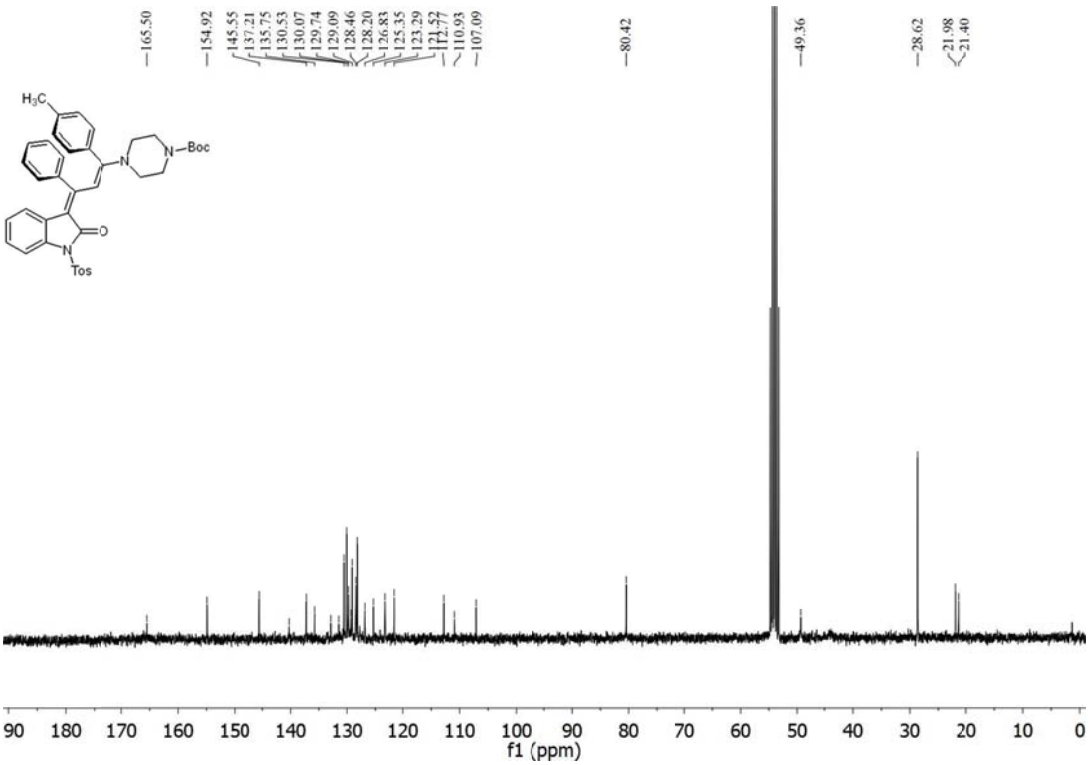
^{13}C NMR spectrum of **4e** ($CDCl_3$, 151 MHz, 293 K).



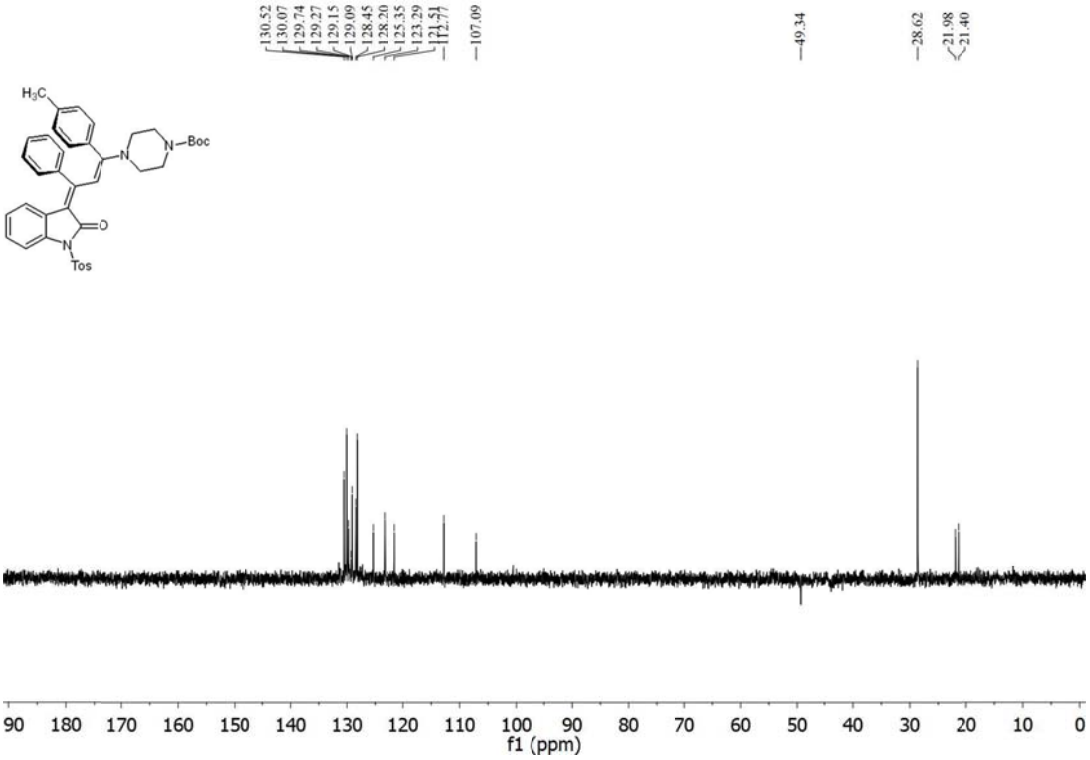
2.6 *tert*-Butyl-4-(3-(2-oxo-1-tosylindolin-3-yliden)-3-phenyl-1-(4-tolyl)prop-1-en-1-yl)-piperazin-1-carboxylate (4f)



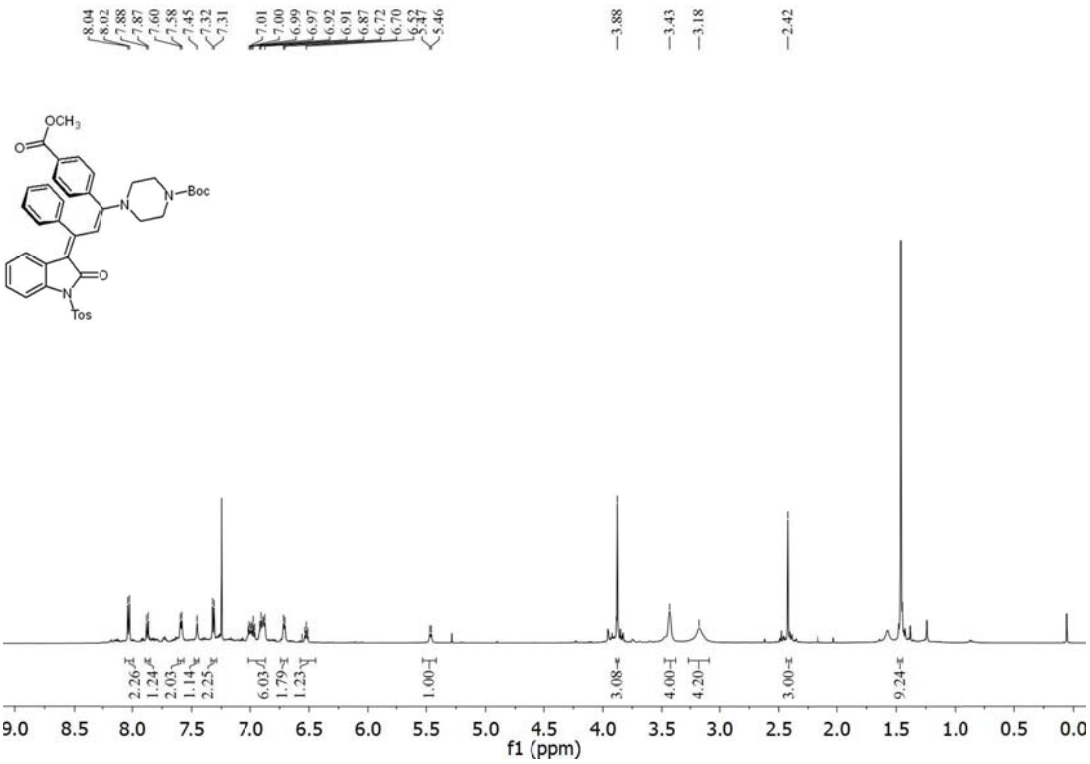
^{1}H NMR spectrum of **4f** ($CDCl_3$, 600 MHz, 293 K).



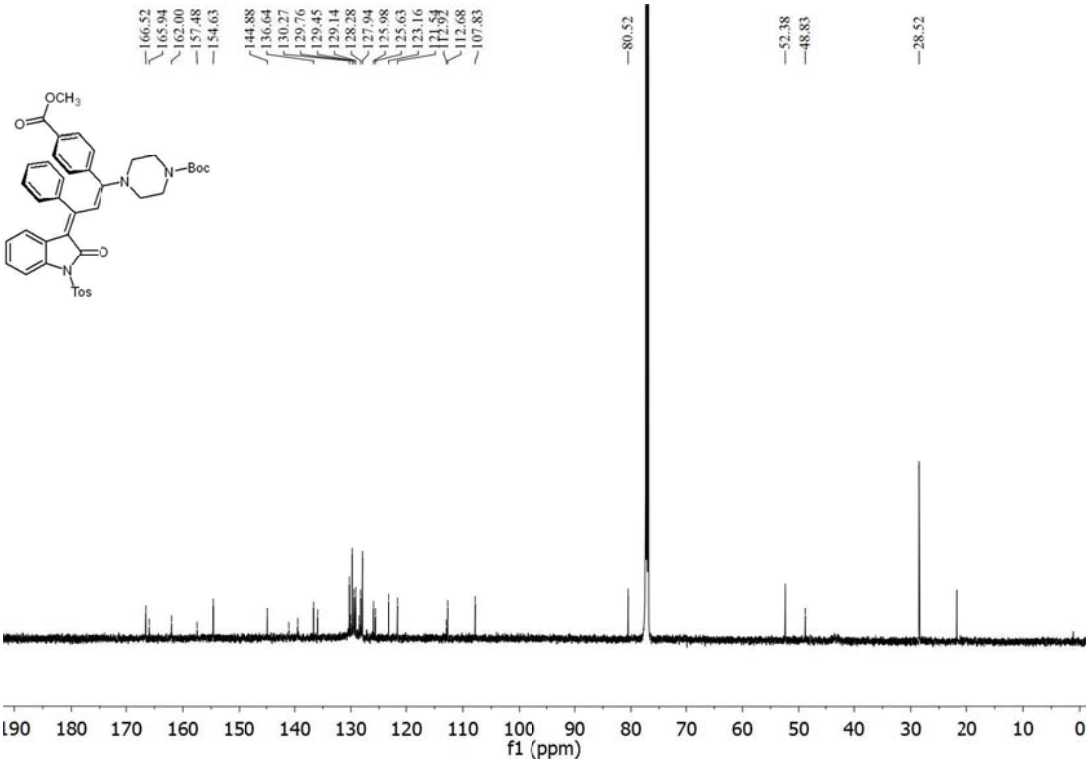
^{13}C NMR spectrum of **4f** ($CDCl_3$, 151 MHz, 293 K).



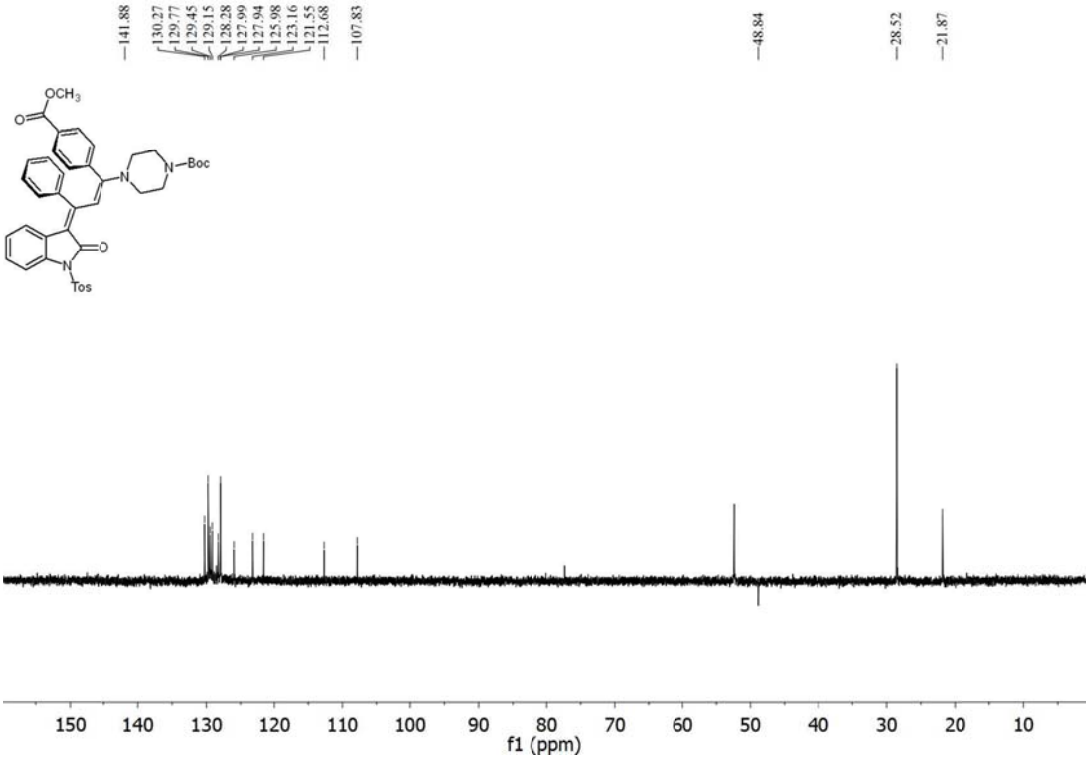
2.7 *tert*-Butyl-4-(1-(4-(methoxycarbonyl)phenyl)-3-(2-oxo-1-tosylindolin-3-yliden)-3-phenyl-prop-1-en-1-yl)piperazin-1-carboxylate (4g)



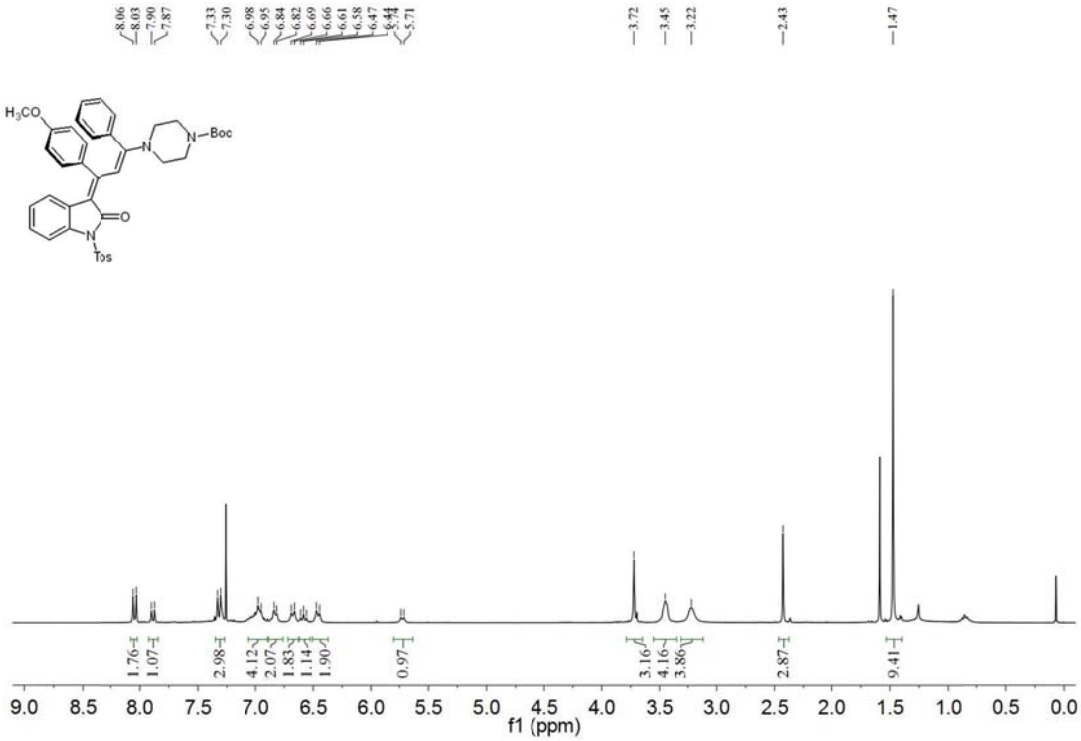
^{1}H NMR spectrum of **4g** ($CDCl_3$, 600 MHz, 293 K).



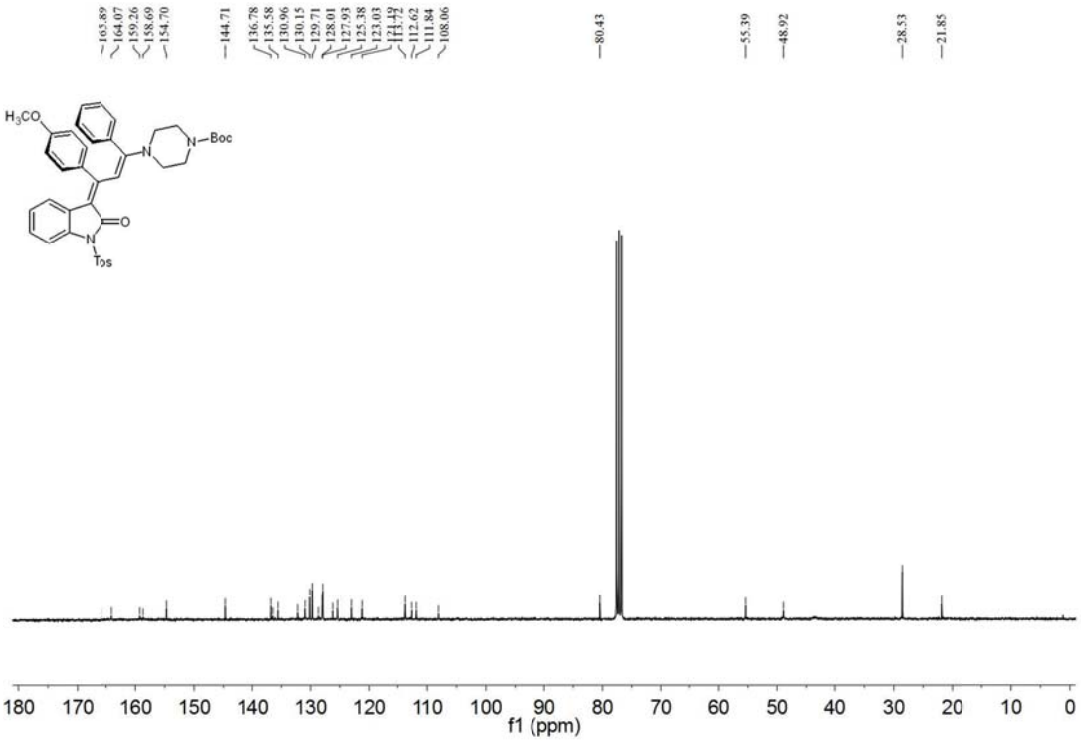
^{13}C NMR spectrum of **4g** ($CDCl_3$, 151 MHz, 293 K).



2.8 *tert*-Butyl-4-(3-(4-methoxyphenyl)-3-(2-oxo-1-tosylindolin-3-yliden)-1-phenylprop-1-en-1-yl)-piperazin-1-carboxylate (4h)

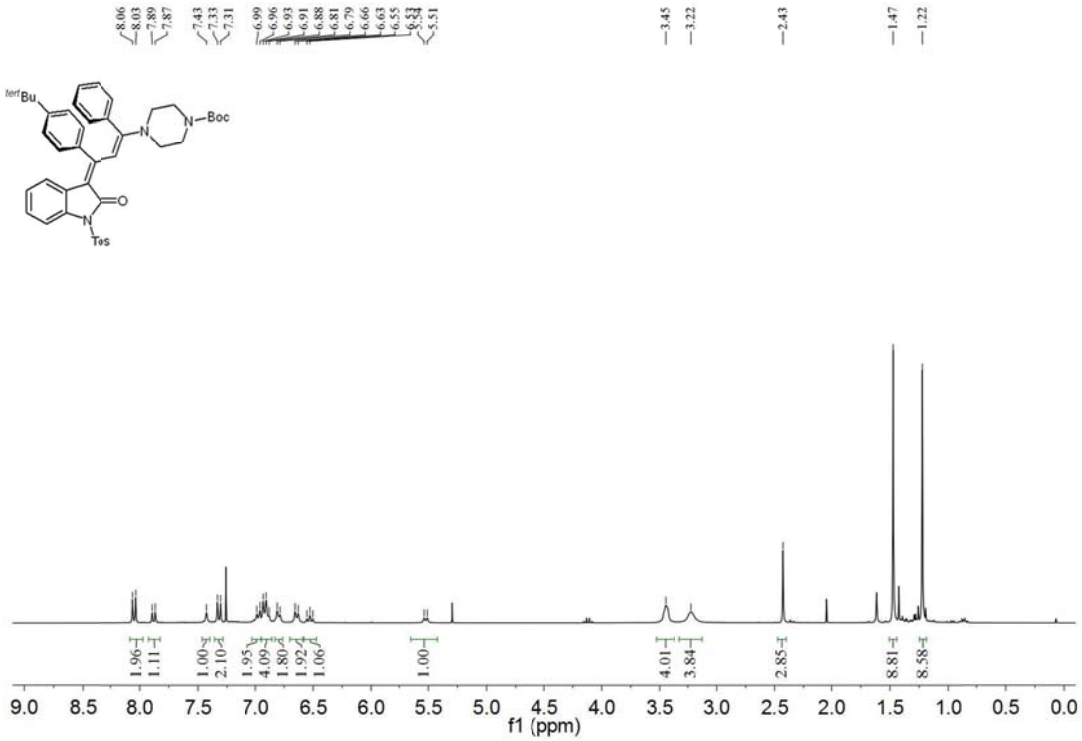


^{1}H NMR spectrum of **4h** ($CDCl_3$, 300 MHz, 293 K).

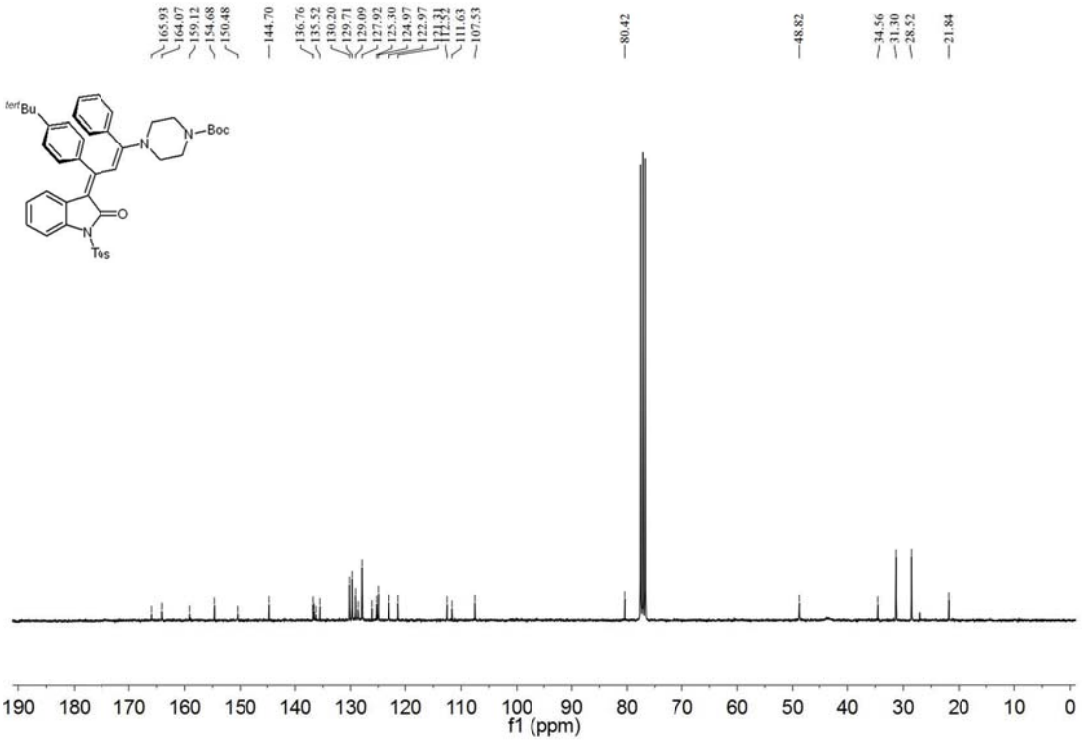


^{13}C NMR spectrum of **4h** ($CDCl_3$, 75 MHz, 293 K).

2.9 *tert*-Butyl-4-(3-(4-(*tert*-butyl)phenyl)-3-(2-oxo-1-tosylindolin-3-yliden)-1-phenylprop-1-en-1-yl)-piperazin-1-carboxylate (4i)

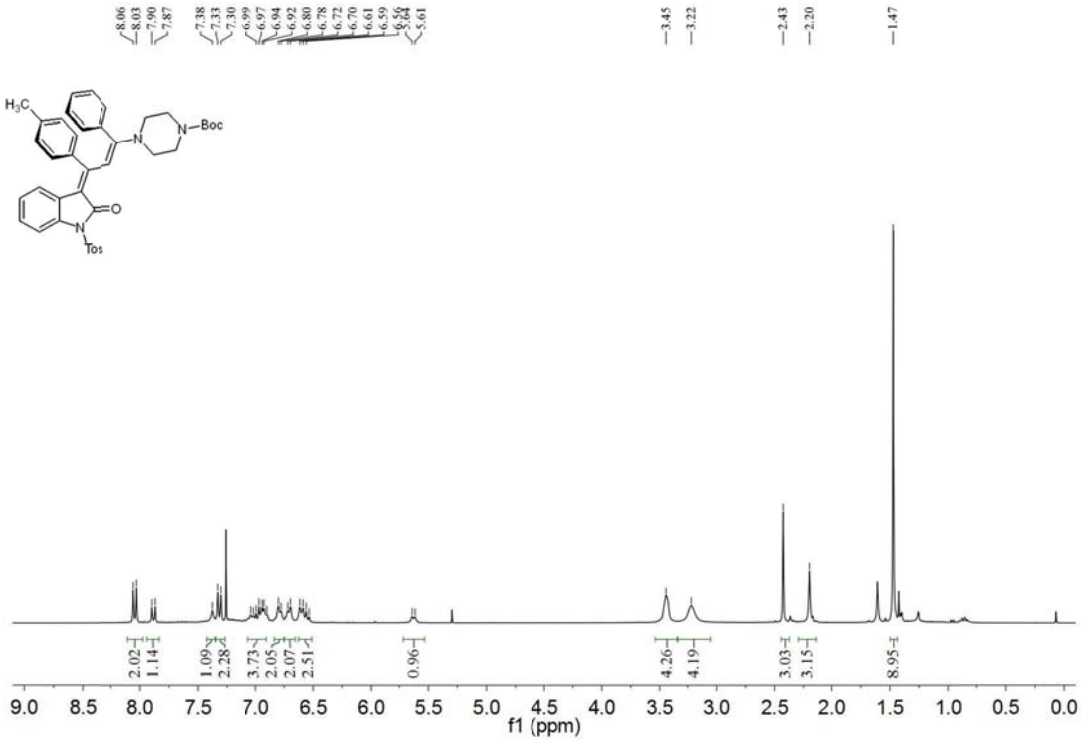


^{1}H NMR spectrum of **4i** ($CDCl_3$, 300 MHz, 293 K).

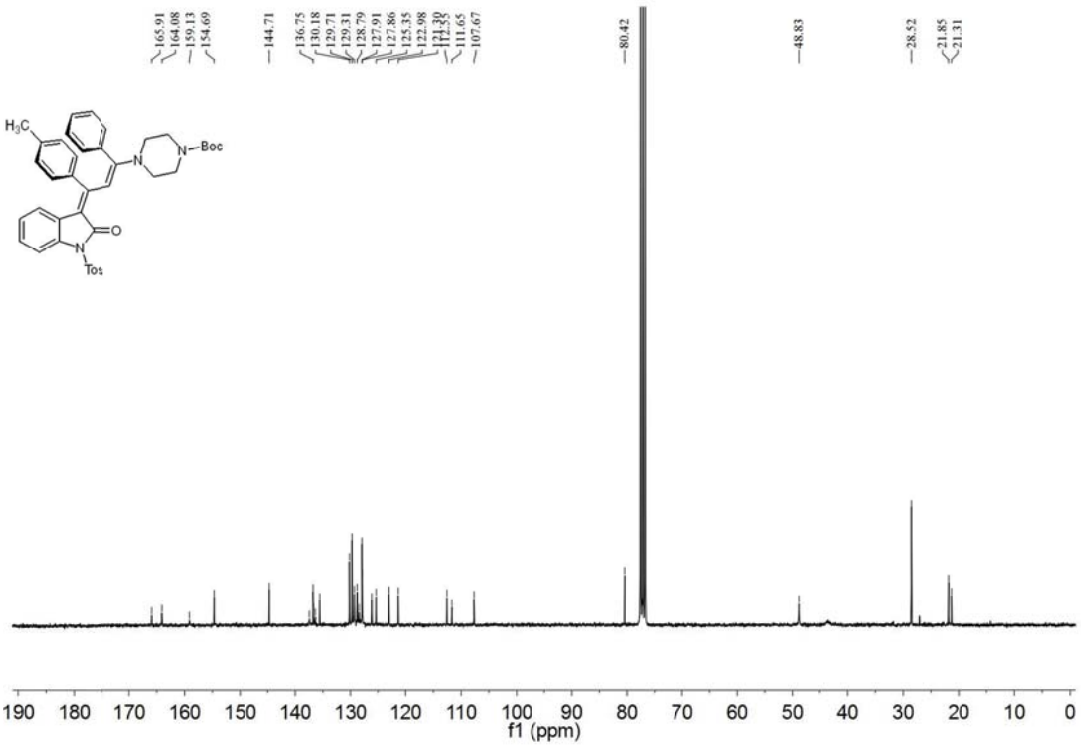


^{13}C NMR spectrum of **4i** ($CDCl_3$, 75 MHz, 293 K).

2.10 *tert*-Butyl-4-(3-(2-oxo-1-tosylindolin-3-yliden)-1-phenyl-3-(*p*-tolyl)prop-1-en-1-yl)-piperazin-1-carboxylat (4j)

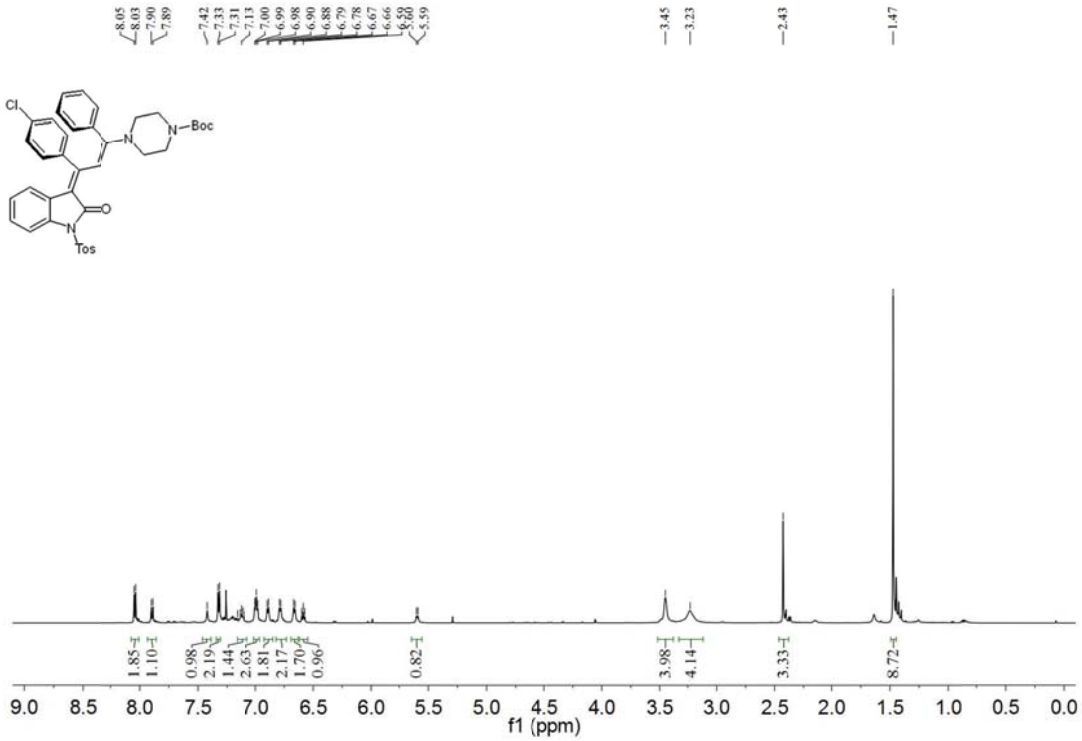


^{1}H NMR spectrum of **4j** ($CDCl_3$, 300 MHz, 293 K).

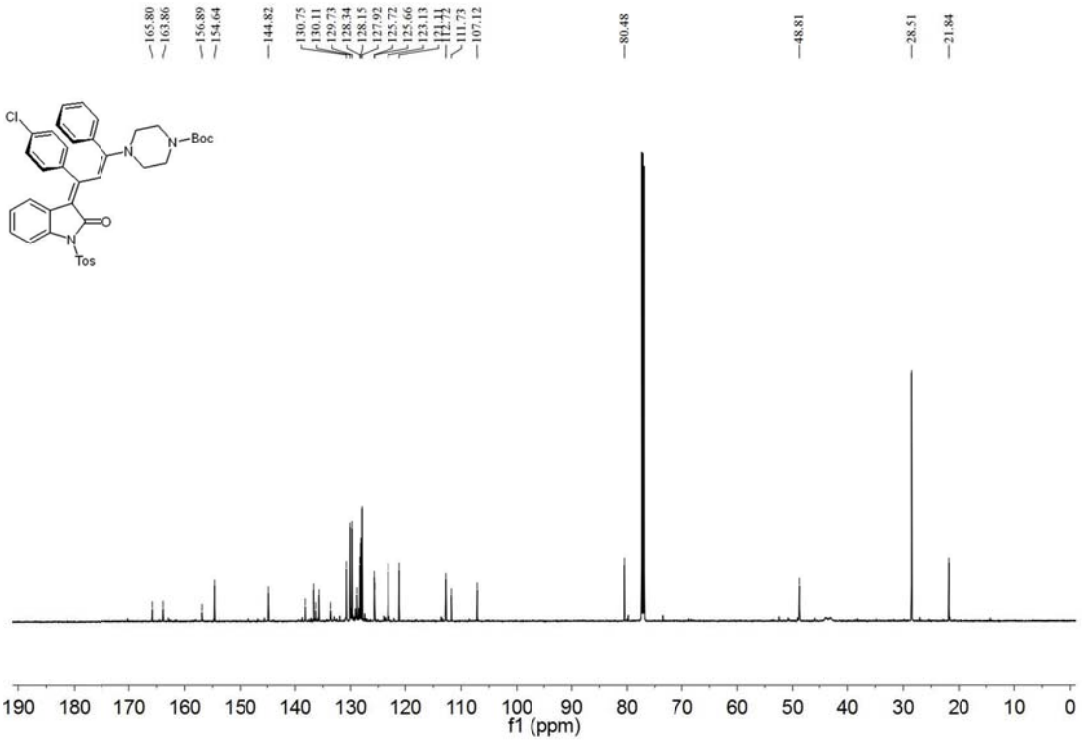


^{13}C NMR spectrum of **4j** ($CDCl_3$, 75 MHz, 293 K).

2.11 *tert*-Butyl-4-(3-(4-chlorphenyl)-3-(2-oxo-1-tosylindolin-3-yliden)-1-phenylprop-1-en-1-yl)piperazin-1-carboxylate (4k)

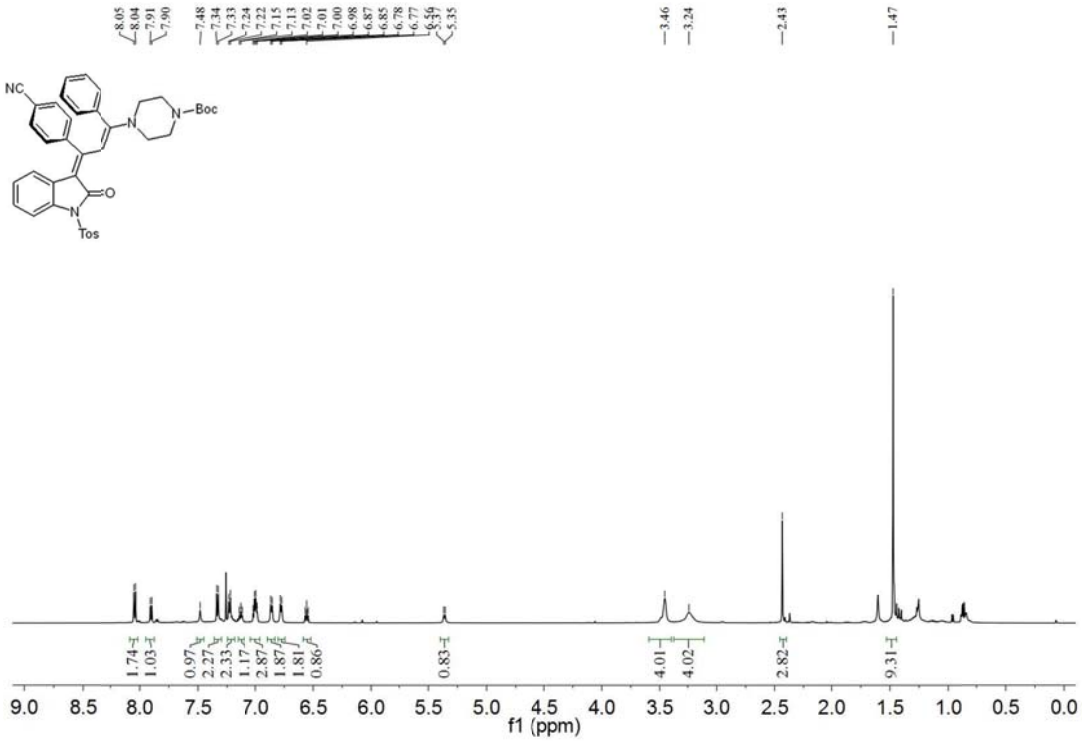


^{1}H NMR spectrum of **4k** ($CDCl_3$, 600 MHz, 293 K).

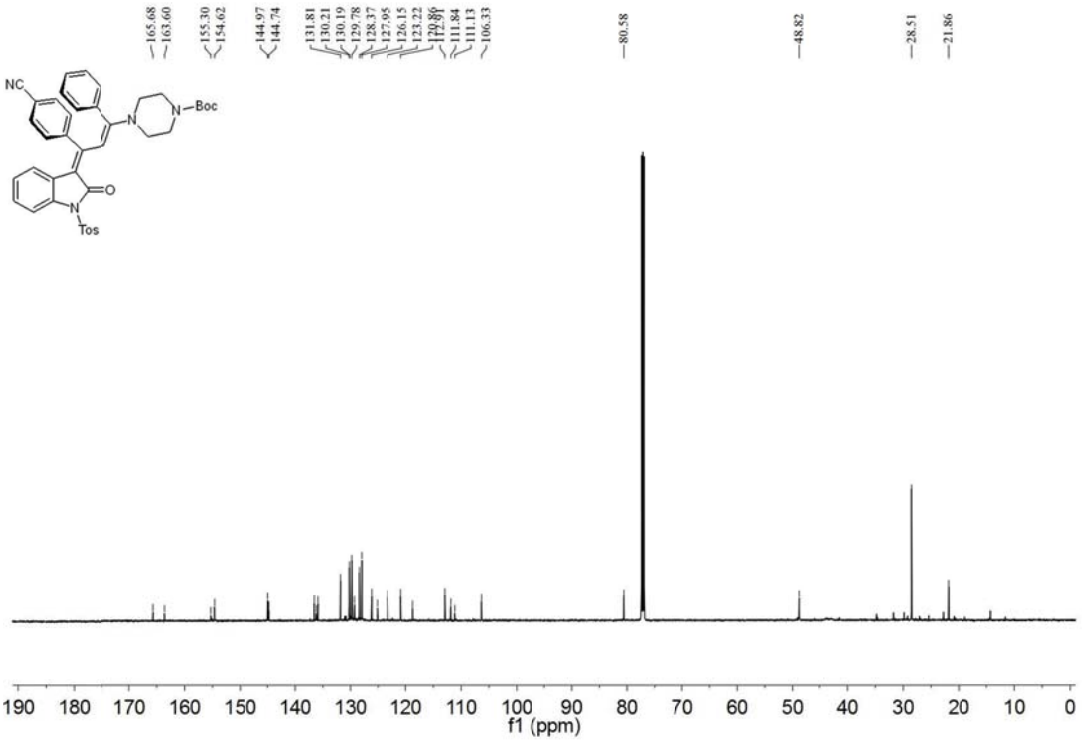


^{13}C NMR spectrum of **4k** ($CDCl_3$, 151 MHz, 293 K).

2.12 *tert*-Butyl-4-(3-(4-cyanophenyl)-3-(2-oxo-1-tosylindolin-3-yliden)-1-phenylprop-1-en-1-yl)piperazin-1-carboxylate (4l)



^{1}H NMR spectrum of **4l** ($CDCl_3$, 600 MHz, 293 K).



^{13}C NMR spectrum of **4l** ($CDCl_3$, 151 MHz, 293 K).

3 Solvatochromism of compound 4a

Table SI-4. Absorbance of compound **4a** in various solvents vs. $E_T(30)$.

solvent	λ_{max} [nm]	ε [L·(mol·cm)$^{-1}$]	$E_T(30)^a$ [kcal·mol^{-1}]
methylcyclohexane	423.5	20860	--
tetrahydrofuran	443.5	23940	37.4
ethyl acetate	440.5	23480	38.1
dichloromethane	444.0	25660	40.7
acetone	446.5	25050	42.2
dimethylsulfoxide	457.0	26730	45.1
acetonitril	448.0	25810	45.6
methanol	453.0	24850	55.4

4 Hammett correlations

4.1 Correlations of Substituent R^3

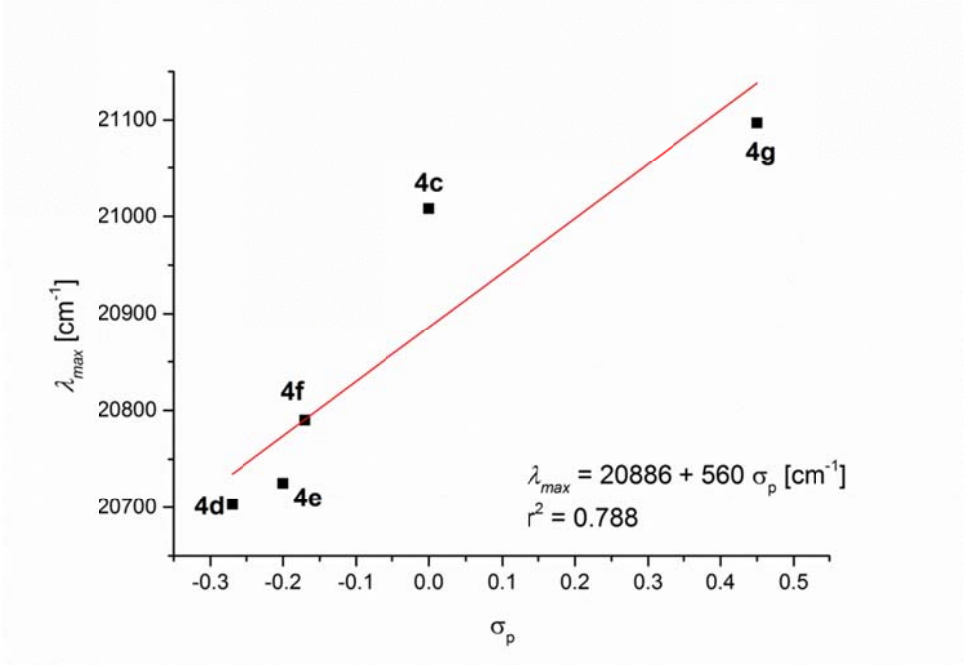


Figure SI-1. Hammett correlation of λ_{max} [cm^{-1}] vs σ_p for substituents R^3 in the consanguineous series **4c-g** (recorded in CH_2Cl_2 UVASOL® at T = 293 K).

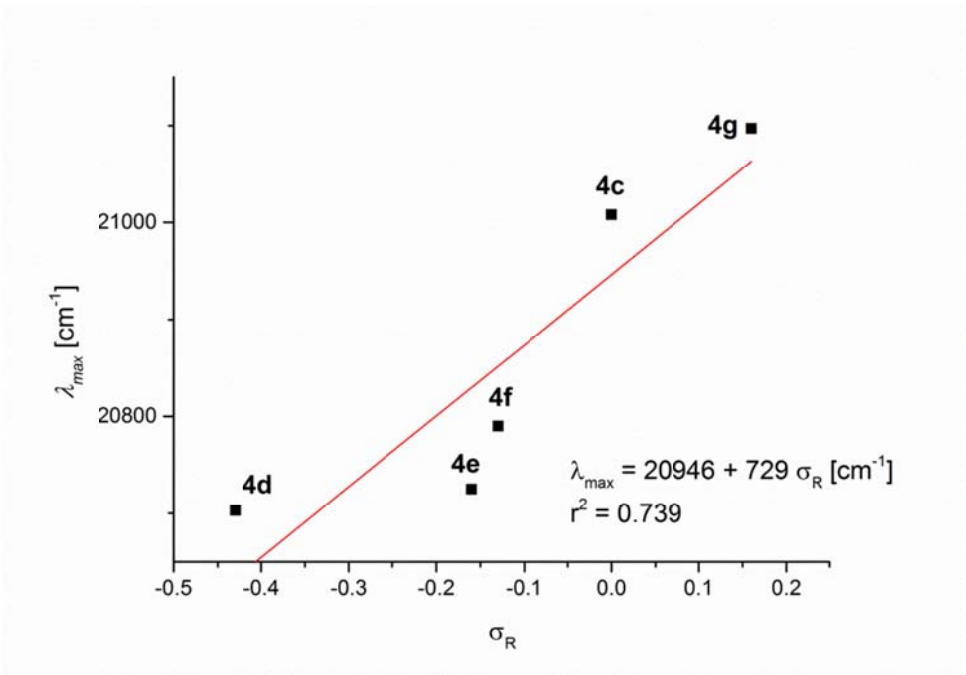


Figure SI-2. Hammett correlation of λ_{max} [cm^{-1}] vs σ_R for substituents R^3 in the consanguineous series **4c-g** (recorded in CH_2Cl_2 UVASOL® at *T* = 293 K).

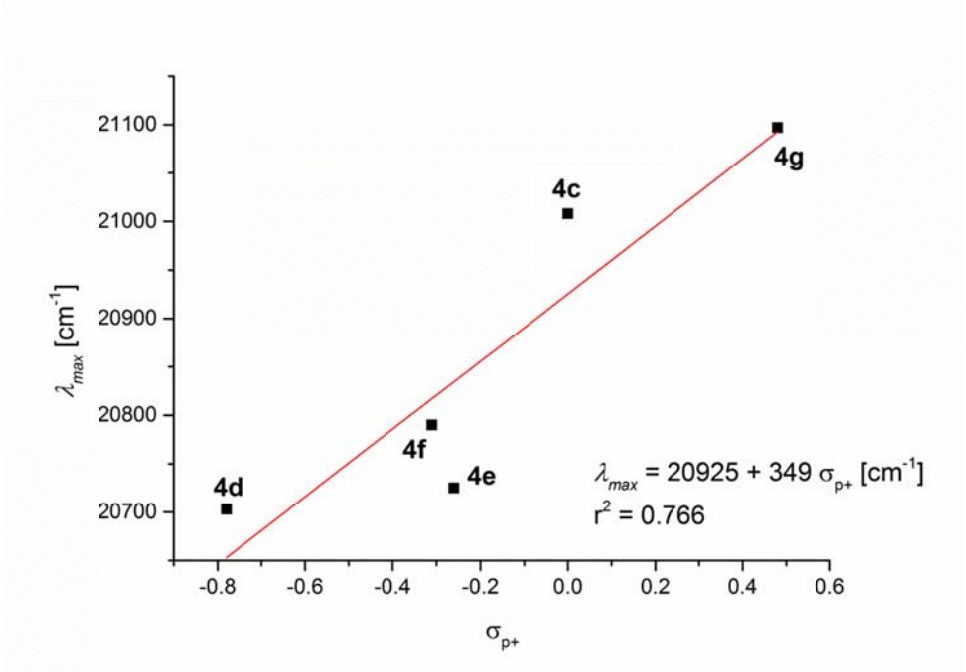


Figure SI-3. Hammett correlation of λ_{max} [cm^{-1}] vs σ_p+ for substituents R^3 in the consanguineous series **4c-g** (recorded in CH_2Cl_2 UVASOL® at *T* = 293 K).

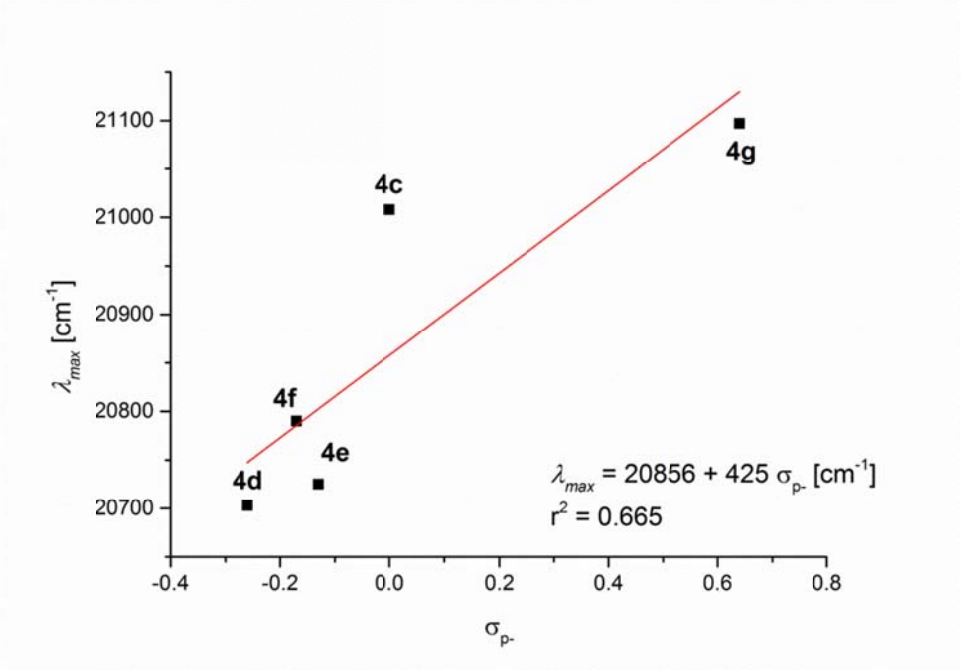


Figure SI-4. Hammett correlation of λ_{max} [cm^{-1}] vs σ_p- for substituents R^3 in the consanguineous series **4c-g** (recorded in CH_2Cl_2 UVASOL® at *T* = 293 K).

4.2 Correlations of Substituent R^2

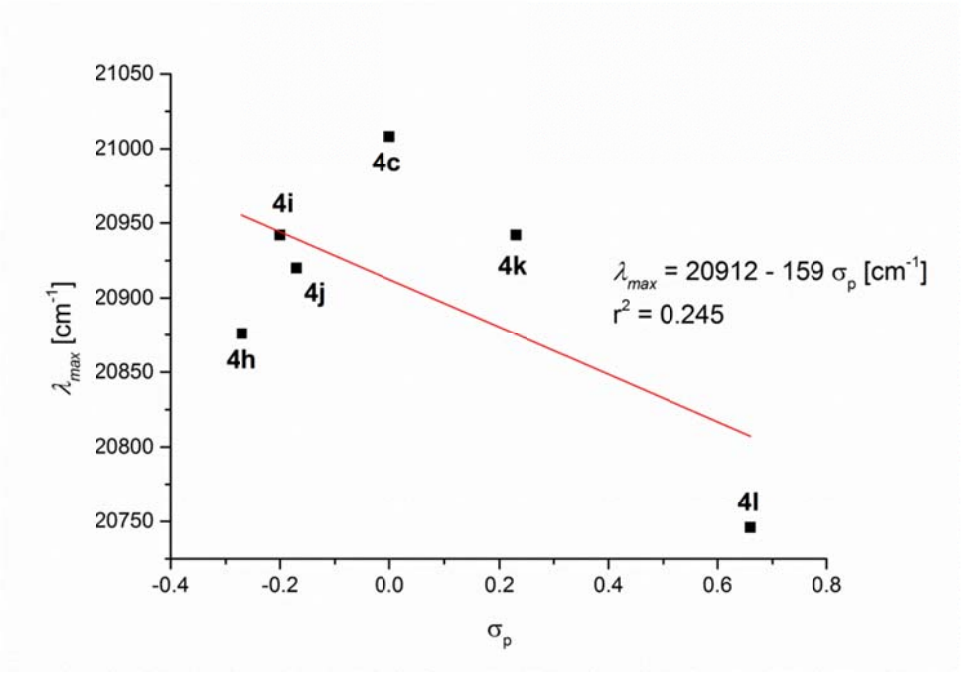


Figure SI-5. Hammett correlation of λ_{max} [cm^{-1}] vs σ_p for substituents R^2 in the consanguineous series **4c** and **4h-l** (recorded in CH_2Cl_2 UVASOL® at *T* = 293 K).

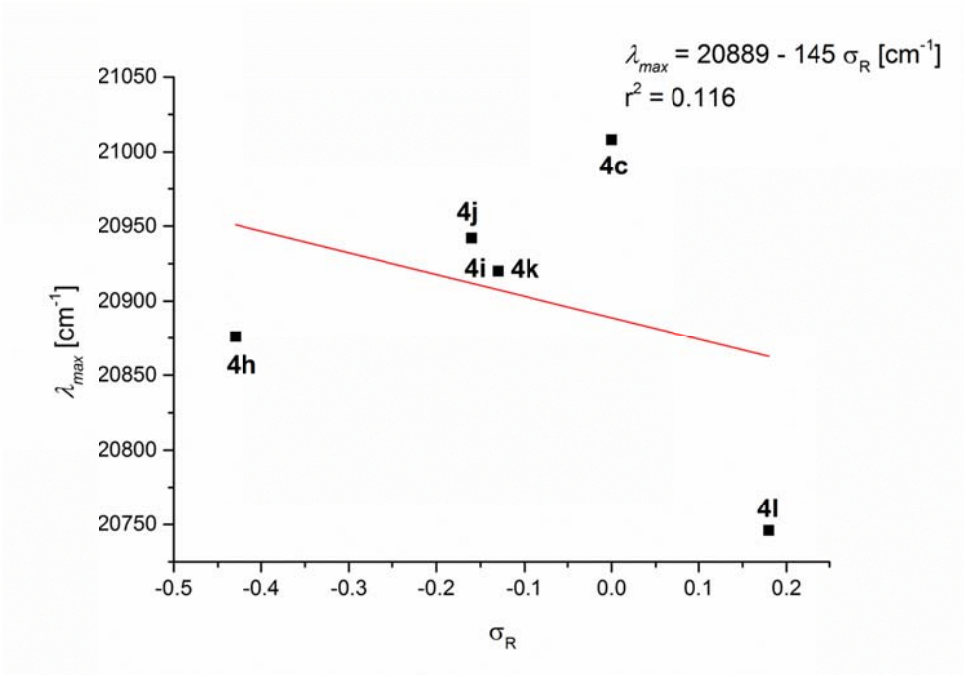


Figure SI-6. Hammett correlation of λ_{max} [cm^{-1}] vs σ_R for substituents R^2 in the consanguineous series **4c** and **4h-l** (recorded in CH_2Cl_2 UVASOL® at *T* = 293 K).

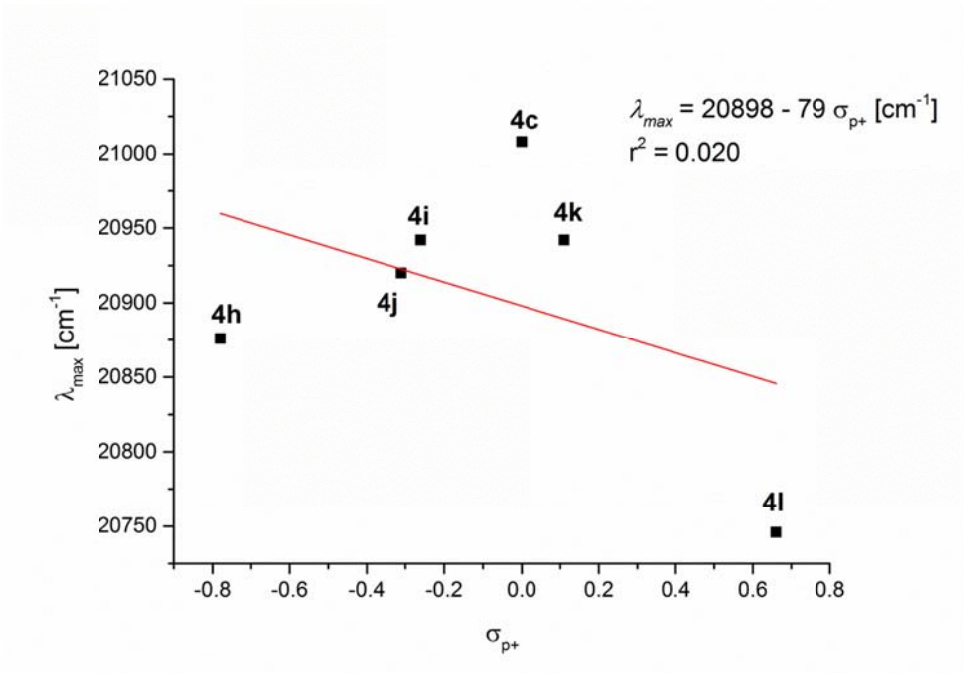


Figure SI-7. Hammett correlation of λ_{max} [cm^{-1}] vs σ_p+ for substituents R^2 in the consanguineous series **4c** and **4h-l** (recorded in CH_2Cl_2 UVASOL® at *T* = 293 K).

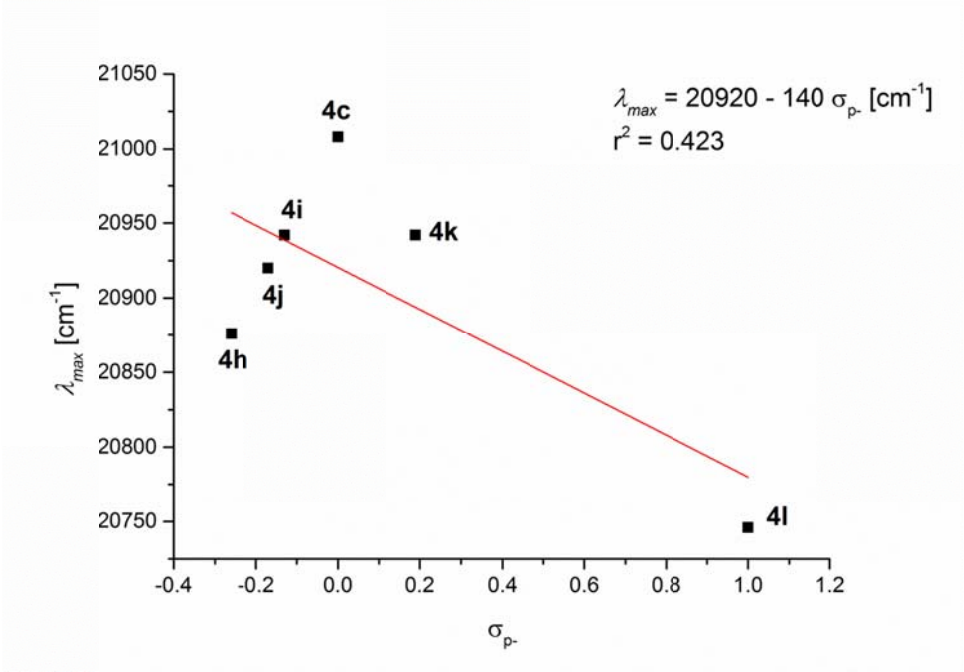


Figure SI-8. Hammett correlation of λ_{max} [cm^{-1}] vs σ_p- for substituents R^2 in the consanguineous series **4c** and **4h-l** (recorded in CH_2Cl_2 UVASOL® at *T* = 293 K).

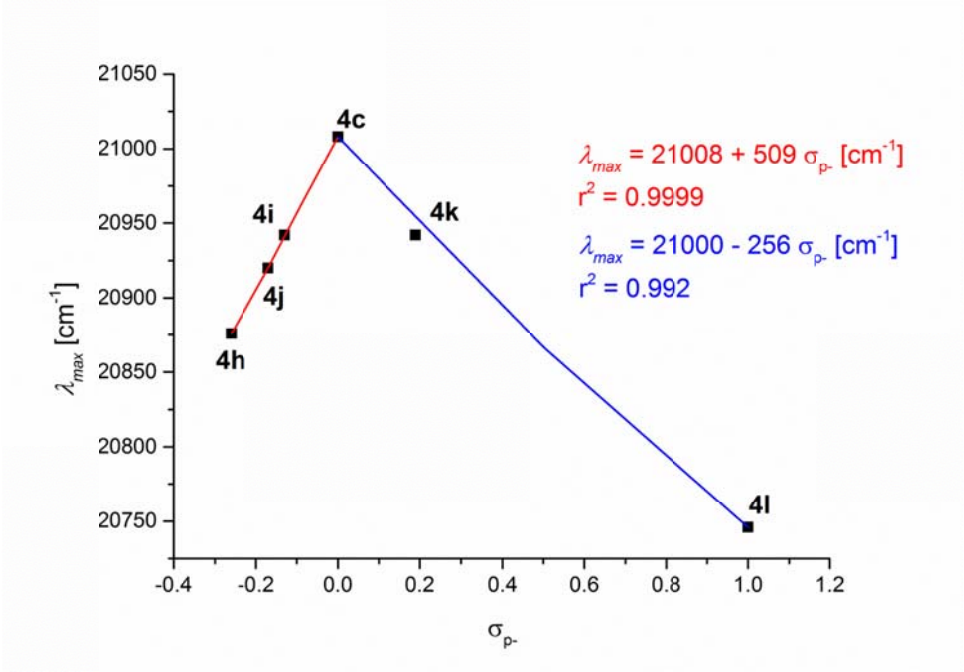


Figure SI-9. Discontinuous Hammett correlation of λ_{max} [cm^{-1}] vs σ_p for substituents R^2 in the consanguineous series **4c** and **4h-l** (recorded in CH_2Cl_2 UVASOL® at *T* = 293 K).

5 Computed XYZ coordinates and energies of *E*,*E*-4c and *E*,*Z*-4c

E,*E*-4c

B3LYP/6-311G(d,p) using the PCM model with acetonitrile as a solvent.

1	6	3.523381	2.214920	0.743021
2	7	2.432036	1.939894	-0.204059
3	6	2.911581	1.171279	-1.357655
4	6	3.531217	-0.162082	-0.926753
5	7	4.571935	0.087009	0.071625
6	6	4.158844	0.900405	1.212527
7	6	1.108762	2.094964	0.086516
8	6	0.781923	3.101050	1.137182
9	6	0.104231	2.700105	2.293938
10	6	-0.164381	3.617755	3.306930
11	6	0.228267	4.947393	3.167219
12	6	0.899235	5.356196	2.013510
13	6	1.184577	4.437112	1.008968
14	6	5.784986	-0.546641	0.104801
15	8	6.603963	-0.388538	0.997569
16	6	0.145105	1.300609	-0.530344
17	6	-1.251533	1.529433	-0.664769
18	6	-1.797645	2.916490	-0.564906
19	6	-1.390824	3.896605	-1.478034
20	6	-1.934325	5.179105	-1.429718
21	6	-2.873565	5.503960	-0.452623
22	6	-3.272505	4.537355	0.471752
23	6	-2.746837	3.250498	0.408954
24	6	-2.124743	0.485840	-0.990095
25	6	-3.500452	0.514804	-1.485855
26	6	-3.965466	-0.816621	-1.619712
27	7	-2.906933	-1.685072	-1.233963
28	6	-1.753289	-0.923475	-0.854962
29	6	-4.347844	1.551998	-1.896209
30	6	-5.620227	1.260881	-2.384765
31	6	-6.060453	-0.058514	-2.483132
32	6	-5.228935	-1.117696	-2.112179
33	8	-0.721187	-1.451437	-0.463459
34	8	5.951170	-1.346207	-0.968806
35	6	7.197881	-2.117021	-1.182836
36	6	8.384089	-1.162822	-1.336243
37	6	7.394428	-3.120804	-0.044899
38	6	6.913809	-2.841743	-2.498538
39	1	-6.269683	2.072007	-2.693835
40	1	-7.052223	-0.274551	-2.863244
41	1	-5.556805	-2.140245	-2.210803
42	1	-4.022971	2.580122	-1.837256
43	1	0.496215	0.371231	-0.952168
44	1	-0.658997	3.646406	-2.237351
45	1	-1.621040	5.923887	-2.152582
46	1	-3.290987	6.503519	-0.409187
47	1	-3.996662	4.785828	1.239367
48	1	-3.067094	2.498304	1.120288
49	1	-0.198536	1.665333	2.400861
50	1	-0.680778	3.293827	4.203130

51	1	0.014154	5.663060	3.952671
52	1	1.200888	6.390845	1.897927
53	1	1.710268	4.754081	0.115648
54	1	2.101173	1.014283	-2.064643
55	1	3.681064	1.774914	-1.850689
56	1	2.758161	-0.816401	-0.504387
57	1	3.969129	-0.659201	-1.786939
58	1	5.034937	1.106772	1.823057
59	1	3.433317	0.345997	1.822013
60	1	4.274278	2.831221	0.239368
61	1	3.146031	2.762967	1.600933
62	1	8.241989	-3.770095	-0.278285
63	1	7.588818	-2.614154	0.898556
64	1	6.505428	-3.747157	0.064204
65	1	7.771992	-3.457804	-2.775678
66	1	6.728410	-2.124413	-3.301108
67	1	6.039492	-3.488989	-2.400592
68	1	8.182898	-0.431915	-2.123624
69	1	8.587600	-0.635256	-0.406140
70	1	9.272792	-1.732199	-1.619983
71	16	-2.949365	-3.384687	-1.026058
72	8	-4.290432	-3.801618	-1.428893
73	8	-1.792507	-3.950409	-1.708013
74	6	-2.784359	-3.629684	0.734534
75	6	-3.926000	-3.538687	1.532185
76	6	-3.805642	-3.747166	2.900205
77	6	-2.566490	-4.049263	3.482231
78	6	-1.441424	-4.132812	2.653448
79	6	-1.537686	-3.922639	1.281516
80	1	-4.889991	-3.320133	1.091349
81	1	-4.688895	-3.677942	3.525281
82	6	-2.457792	-4.305227	4.963501
83	1	-0.473922	-4.362295	3.085642
84	1	-0.665141	-3.976168	0.646464
85	1	-2.721812	-5.343035	5.192991
86	1	-1.441751	-4.135758	5.323586
87	1	-3.138622	-3.664222	5.527420

Zero-point correction=	0.703509 (Hartree/Particle)
Thermal correction to Energy=	0.747587
Thermal correction to Enthalpy=	0.748532
Thermal correction to Gibbs Free Energy=	0.619049
Sum of electronic and zero-point Energies=	-2448.023119
Sum of electronic and thermal Energies=	-2447.979041
Sum of electronic and thermal Enthalpies=	-2447.978097
Sum of electronic and thermal Free Energies=	-2448.107579

***E,Z*-4c**

B3LYP/6-311G(d,p) using the PCM model with acetonitrile as a solvent.

1	6	-4.662941	-3.424048	0.052565
2	6	-3.716141	-2.419510	-0.101365
3	6	-2.502756	-2.405895	0.628137
4	6	-2.283027	-3.423240	1.564682
5	6	-3.229347	-4.432137	1.731914
6	6	-4.401988	-4.438078	0.977090
7	7	-3.741912	-1.255225	-0.919117
8	6	-2.589910	-0.441810	-0.659777
9	6	-1.753153	-1.201849	0.274734
10	6	-0.487875	-0.763113	0.674688
11	6	0.451309	-1.734104	1.306647
12	6	1.033464	-1.464918	2.552657
13	6	1.895572	-2.384565	3.147279
14	6	2.200273	-3.580915	2.499492
15	6	1.634630	-3.855162	1.253813
16	6	0.764267	-2.943017	0.666213
17	16	-4.977418	-0.734943	-1.985965
18	8	-2.424619	0.650244	-1.181343
19	6	-0.140472	0.619463	0.590843
20	6	1.090857	1.262748	0.674629
21	6	1.067535	2.702255	1.070544
22	6	0.327135	3.119644	2.184783
23	6	0.264983	4.467796	2.529135
24	6	0.932979	5.418490	1.758866
25	6	1.665411	5.015148	0.641885
26	6	1.737054	3.667696	0.303284
27	7	2.303083	0.741223	0.328456
28	6	2.473372	-0.364318	-0.617011
29	6	3.579362	-0.027965	-1.620855
30	7	4.816550	0.308498	-0.924487
31	6	4.690053	1.396724	0.042085
32	6	3.551004	1.101375	1.019600
33	6	6.003372	-0.211359	-1.365004
34	8	7.048466	0.306008	-0.686626
35	6	8.440500	-0.125925	-0.951730
36	6	9.240182	0.715794	0.042717
37	8	6.085552	-1.045915	-2.253382
38	6	8.594107	-1.616989	-0.645342
39	6	8.830769	0.221289	-2.390028
40	1	-3.048880	-5.217402	2.457037
41	1	-5.129242	-5.230857	1.108790
42	1	-5.575391	-3.419847	-0.522077
43	1	-1.383691	-3.430069	2.163263
44	1	-0.978153	1.294153	0.492182
45	1	0.793547	-0.540458	3.064256
46	1	2.326444	-2.166572	4.117863
47	1	2.873364	-4.294230	2.961159
48	1	1.870859	-4.780365	0.740662
49	1	0.326072	-3.160717	-0.300757
50	1	-0.188823	2.381170	2.786833
51	1	-0.303327	4.774937	3.399509
52	1	0.881159	6.468061	2.024705

53	1	2.174846	5.751153	0.030612
54	1	2.290007	3.360454	-0.576109
55	1	3.379146	1.961762	1.661450
56	1	3.835532	0.253783	1.656222
57	1	4.495387	2.338488	-0.486264
58	1	5.619614	1.501165	0.593686
59	1	3.766373	-0.885793	-2.262632
60	1	3.265661	0.815606	-2.249443
61	1	2.733717	-1.284169	-0.086315
62	1	1.535961	-0.522628	-1.146767
63	1	9.895649	0.021981	-2.534251
64	1	8.262174	-0.369491	-3.105871
65	1	8.653966	1.282331	-2.583852
66	1	10.304676	0.490502	-0.051693
67	1	8.929726	0.499800	1.067417
68	1	9.093191	1.780995	-0.149210
69	1	8.260727	-1.830625	0.373408
70	1	8.017973	-2.223485	-1.341893
71	1	9.647967	-1.895833	-0.724054
72	6	-5.728260	0.662218	-1.167139
73	8	-4.341322	-0.291456	-3.219005
74	8	-5.947162	-1.826113	-2.034802
75	6	-5.274978	1.951335	-1.441391
76	6	-5.887246	3.024910	-0.804464
77	6	-6.939602	2.830975	0.099417
78	6	-7.368130	1.521871	0.355675
79	6	-6.772447	0.433645	-0.270936
80	1	-4.455146	2.103558	-2.128443
81	1	-5.539145	4.030427	-1.012983
82	6	-7.615001	4.005792	0.758906
83	1	-8.181334	1.350429	1.051915
84	1	-7.120702	-0.572270	-0.076411
85	1	-8.032406	3.731545	1.729461
86	1	-6.919967	4.835569	0.900384
87	1	-8.439697	4.370892	0.137520

Zero-point correction=	0.703903 (Hartree/Particle)
Thermal correction to Energy=	0.747781
Thermal correction to Enthalpy=	0.748725
Thermal correction to Gibbs Free Energy=	0.621372
Sum of electronic and zero-point Energies=	-2448.020327
Sum of electronic and thermal Energies=	-2447.976450
Sum of electronic and thermal Enthalpies=	-2447.975505
Sum of electronic and thermal Free Energies=	-2448.102859

6 AIE studies of 4i and 4l in acetonitrile/water mixtures

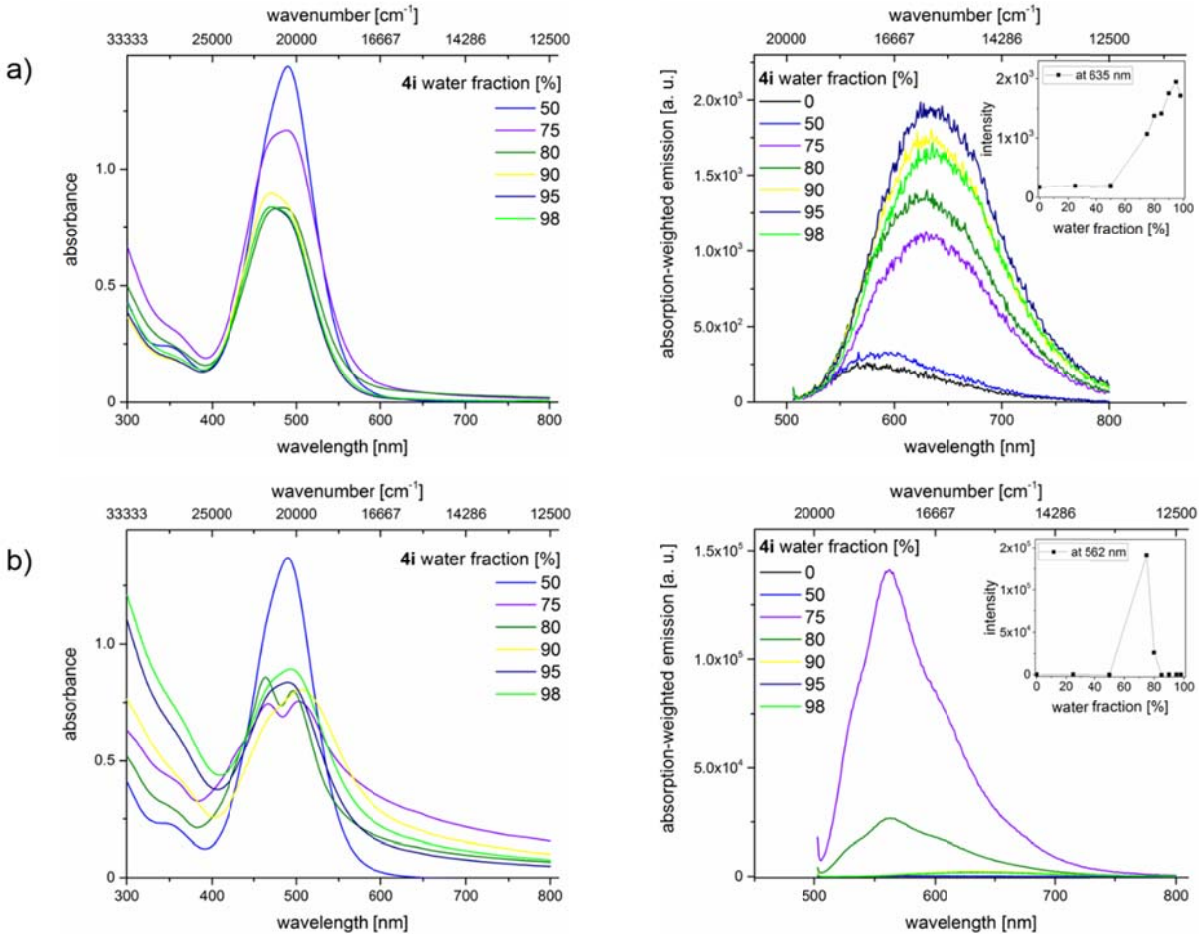


Figure SI-10. Absorption (left) and absorption-weighted emission spectra (right) of **4i** in acetonitrile/water mixtures containing different water fractions a) without sonication and b) with sonication at T = 293 K (λ_{exc} = 488 nm); the insets depict the change in emission intensity induced by different water fractions.

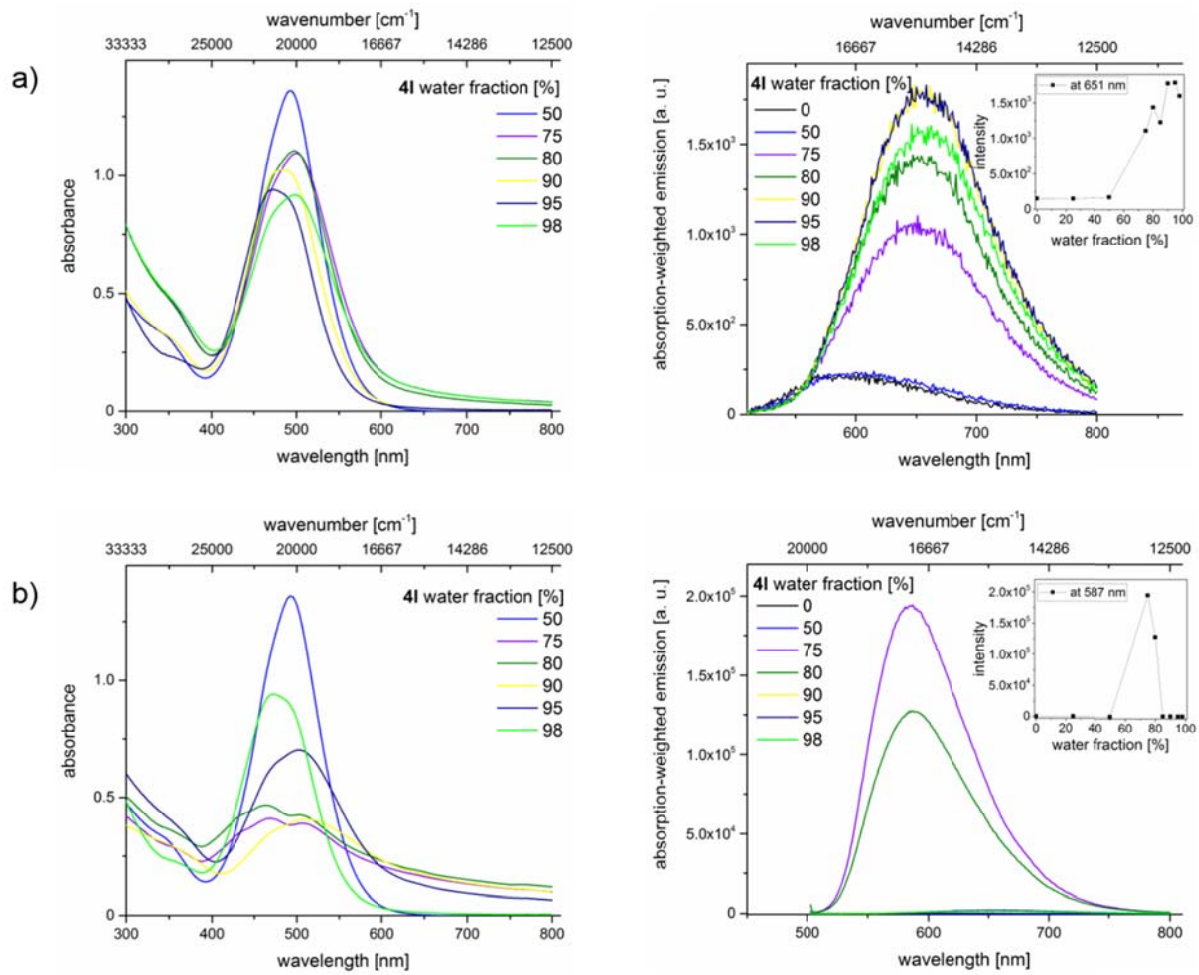


Figure SI-11. Absorption (left) and absorption-weighted emission spectra (right) of **4l** in acetonitrile/water mixtures containing different fractions of water a) without sonication and b) with sonication at T = 293 K (λ_{exc} = 484 nm); the insets depict the change in emission intensity induced by different water fractions.

7 AIE studies of 4i and 4l in THF/water mixtures

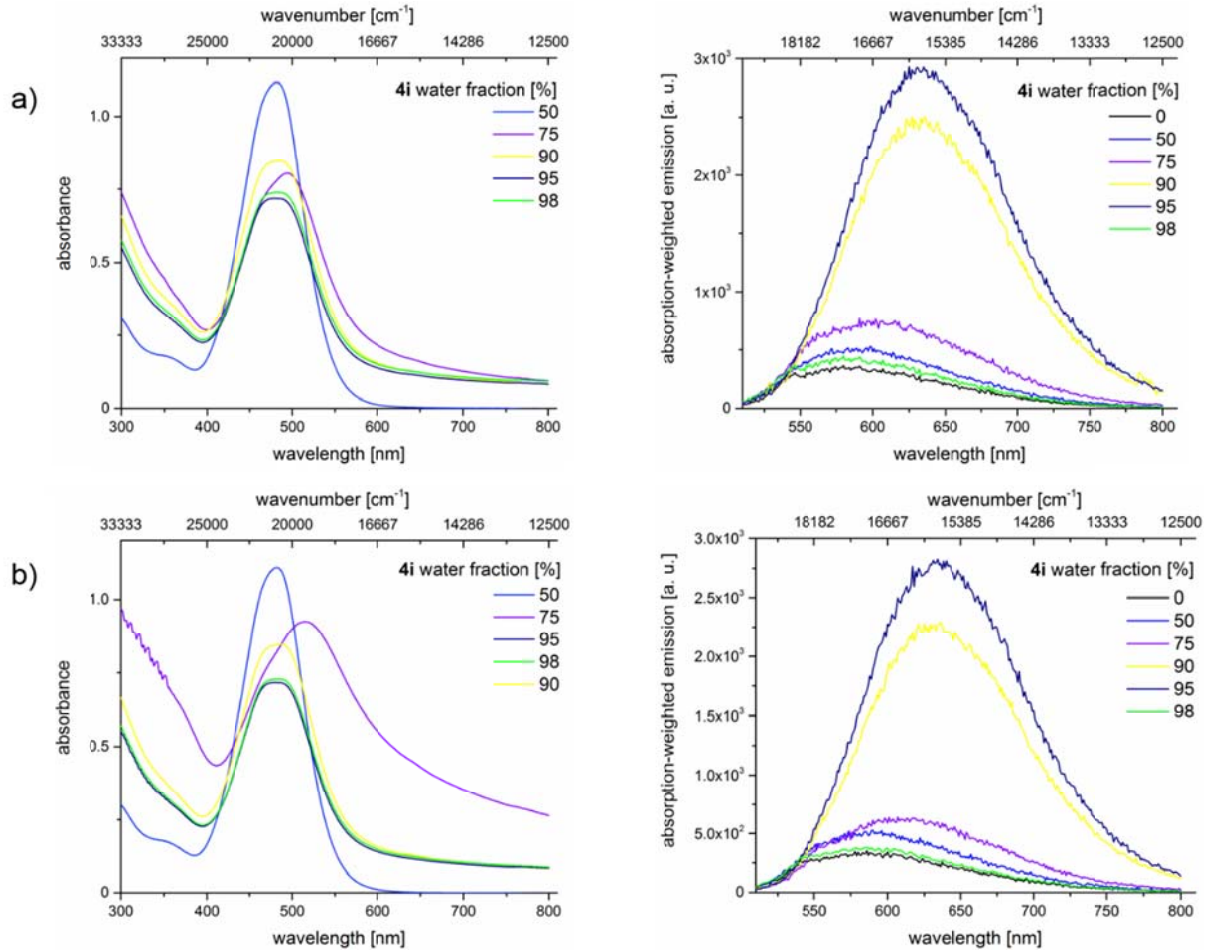


Figure SI-12. Absorption (left) and absorption-weighted emission spectra (right) of **4i** in THF/water mixtures with different water fractions a) without sonication and b) with sonication at T = 293 K (λ_{exc} = 475 nm); the insets depict the change in emission intensity with different water fraction.

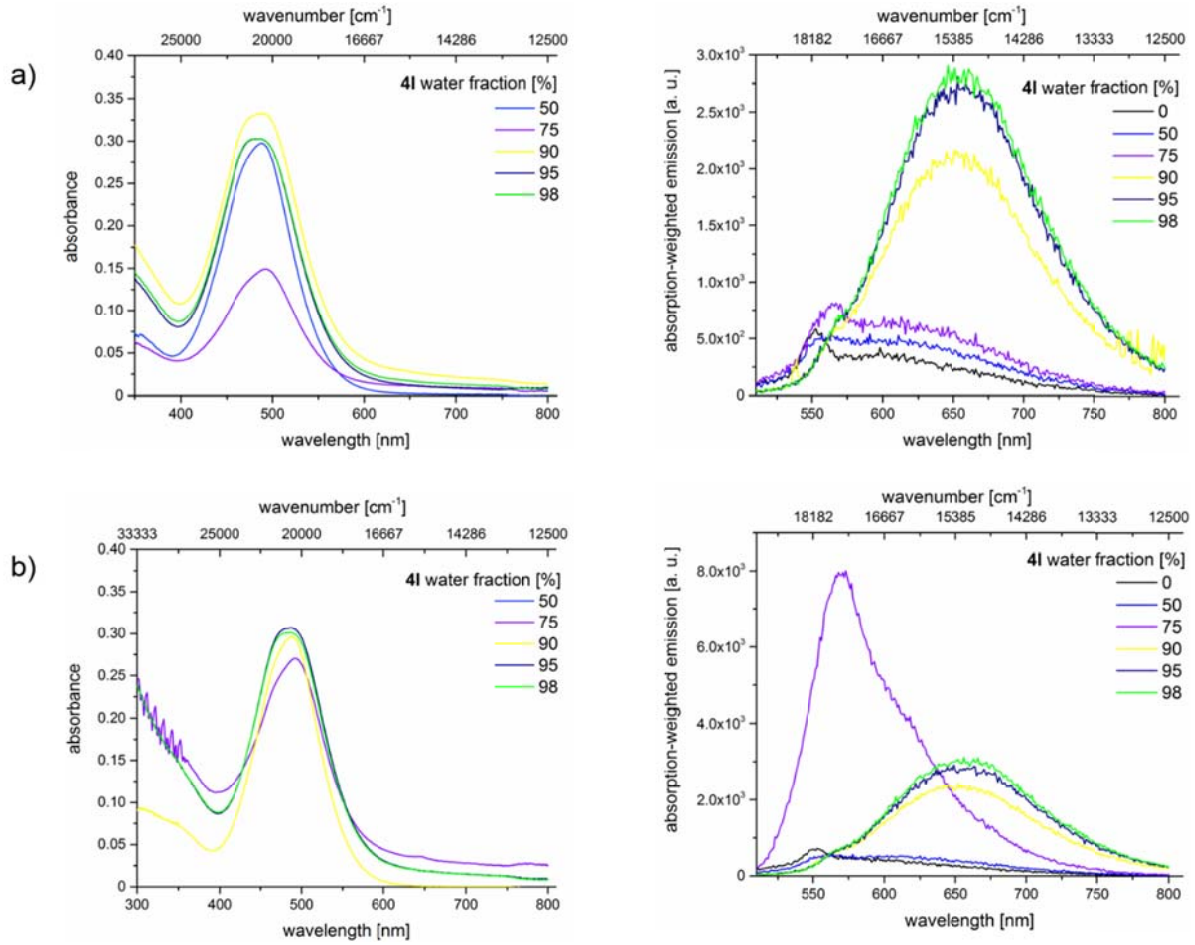


Figure SI-13. Absorption (left) and absorption-weighted emission spectra (right) of **4l** in THF/water mixtures with different water fractions a) without sonication and b) with sonication at T = 293 K (λ_{exc} = 467 nm); the insets depict the change in emission intensity with different water fraction.

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1 The aryl propiolic acids were prepared according to the following literature: (a) S. Tartaggia, O. De Lucchi and L. J. Gooßen, *Eur. J. Org. Chem.,* 2012, 1431–1438. (b) K. Park, J.-M. You, S. Jeon and S. Lee, *Eur. J. Org. Chem.,* 2013, 1973–1978.

2 K. Sundaresan, S. N. Raikar, S. R. Sammeta, G. Prabhu, H. Subramanya, A. Bischoff, United States Patent, 2011, US 8,039,463 B2.