

## Supporting Information

### Sodium alginate-modified copper catalytic membrane for carbene N-H insertion

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## I. General

Unless otherwise noted, all reagents were used as received from commercial suppliers. Reactions were monitored by thin-layer chromatography (TLC). TLC plates were visualized with UV light (254 nm). Flash chromatography was performed using Merck silica gel 60 (0.040-0.063 mm) or SiliCycle silica gel F60 (0.040-0.063 mm). The dilute solvents usually used Ethyl Acetate/Petroleum Ether, which was abbreviated as EA/PE. <sup>1</sup>H NMR spectra were acquired on Bruker 400 MHz or Jeol 400 MHz spectrometers and chemical shifts were recorded relative to tetramethylsilane ( $\delta$  0.00) or residual protiated solvent (CDCl<sub>3</sub>:  $\delta$  7.26). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a J value in Hz. <sup>13</sup>C NMR spectra were obtained at 100 MHz on 400 MHz instruments and chemical shifts were recorded relative to solvent resonance (CDCl<sub>3</sub>:  $\delta$  77.16). Proof of purity of new compounds was demonstrated with copies of <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra. Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2010 plus instrument equipped with an FID detector and an Agilent J&W GC column DB-5MS-UI.

Glassware was dried in an oven at 120 °C for at least 2h before use. The GC standard, n-dodecane was degassed with argon bubbling and dried over activated 4 Å molecular sieve beads for a few days in the glove box before use.

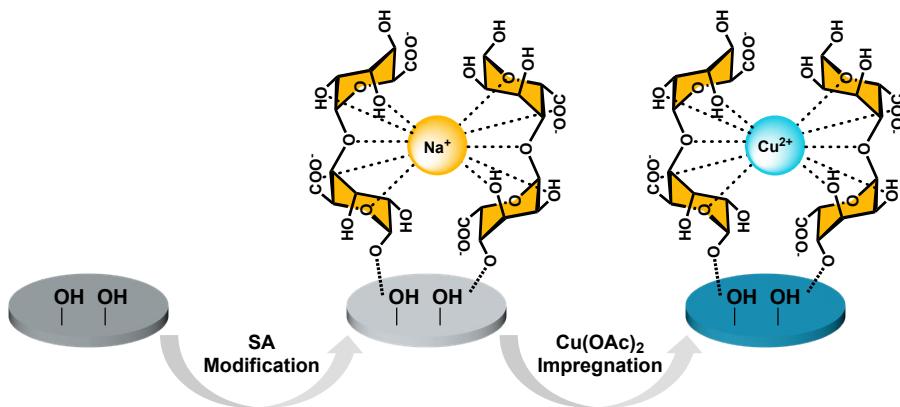
Functional group structures of the surface modified catalytic membranes were observed by Fourier transform infrared (FT-IR, Thermo Scientific Nicolet iS8). The morphologies of the catalytic membranes were obtained by a field-emission scanning electron microscope (FESEM, Hitachi S-4800II). The contents of Cu were determined from inductively coupled plasma emission spectroscopy (ICP-OES, Optima2000DV). The element composition and chemical state of the samples were characterized by X-ray photoelectron spectroscopy (XPS) using a Thermo ESCALAB 250 spectrometer equipped with a monochromatized Al KR radiation.

## II. Experimental apparatus and characterization

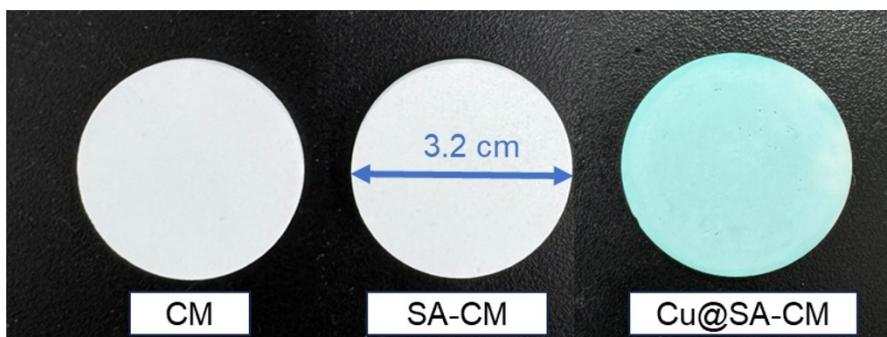
Alumina ceramic membranes were provided by Jiangsu Jiuwu High-Tech Co., Ltd., and sodium alginate was purchased from Tianjin Xiensi Biochemical Technology Co., Ltd. All other chemical reagents were obtained from commercial suppliers, and all reagents and solvents were used without

further purification unless otherwise specified.

**Preparation of Cu@SA-CM:** Initially, the ceramic membrane was submerged in bubbling water for 10 h, followed by drying in a stove at 110 °C for 12 h. The steps of modification and impregnation were then conducted to prepare copper@sodium alginate-ceramic membrane (named as Cu@SA-CM; **Scheme S1**). The detailed procedure was described as follows: Firstly, the ceramic membrane was submerged in 50 mL deionized water of 2 g/L SA solution at 45 °C for 12 h. Subsequently, the modified ceramic membrane was washed with deionized water to eliminate uncrosslinked SA and dried at room temperature (named SA-CM). Then, the modified membrane was impregnated with 0.04 mol/L Cu(OAc)<sub>2</sub> solution in 50 mL acetonitrile at 30 °C for 12 h. Finally, the ceramic membrane was washed with acetonitrile and dried at room temperature to obtain Cu@SA-CM.



**Scheme S1.** Procedure for preparing the Cu@SA-CM.



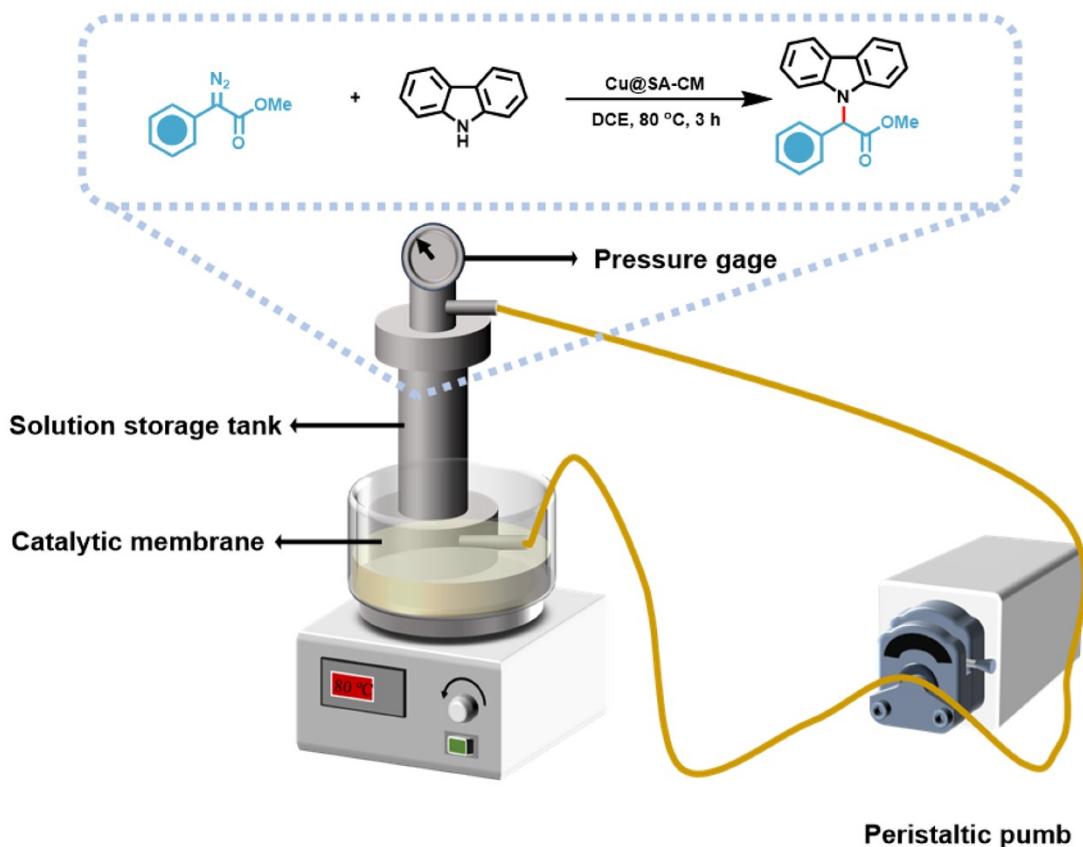
**Figure S1.** Digital photo of ceramic membrane.

**Preparation of Cu-KH792-CM:** Initially, the ceramic membrane was submerged in bubbling water for 10 h, followed by drying in a stove at 110 °C for 12 h. The steps of modification and impregnation were then conducted to prepare copper-N-[3-(trimethoxysilyl)propyl] ethylenediamine-Ceramic Membrane (named as Cu-KH792-CM). The detailed procedure was described as follows: Firstly, the ceramic membrane was submerged in 50 mL dichloromethane solution of 6 g/L N-[3-(trimethoxysilyl)propyl] ethylenediamine (KH792) at 25 °C for 60 minutes.

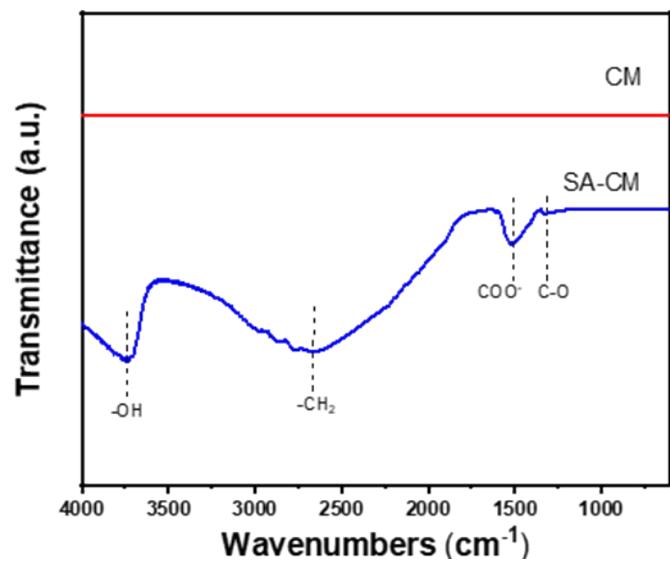
Subsequently, the modified ceramic membrane was washed with ethanol to eliminate unreacted KH792 and dried at room temperature (named as KH792-CM). Then, the modified membrane was impregnated with 0.04 mol/L Cu(OAc)<sub>2</sub> solution in 50 mL acetone at 30 °C for 12 hours. Finally, the Cu-loading ceramic membrane (named as Cu-KH792-CM) was entirely cleaned with acetone and dried at 25 °C.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was employed to quantify the copper content in the Cu@SA-CM catalytic membrane. Prior to ICP-OES analysis, the Cu@SA-CM catalytic membrane was first digested using a mixture of hydrochloric acid and nitric acid (volume ratio 3:1), and the resulting solution was then adjusted to a final volume of 50 mL with deionized water. The Cu content in Cu@SA-CM was determined to be 0.11 mg/cm<sup>2</sup> (equivalent to 0.85 mg Cu per membrane).

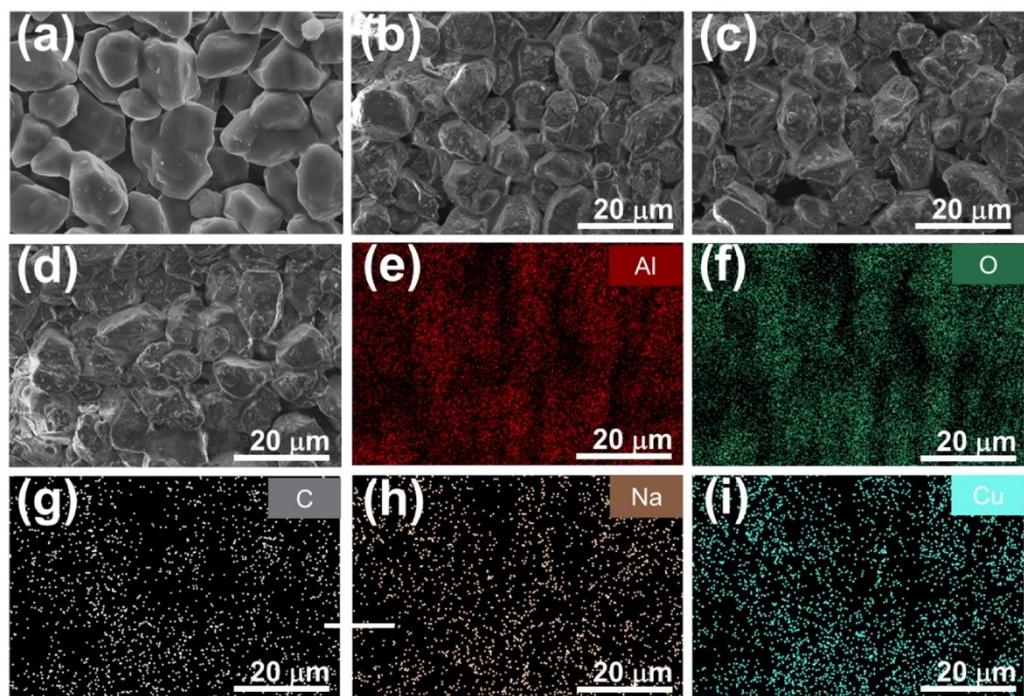
To evaluate the catalytic properties of the ceramic membrane-supported Cu catalyst that was newly prepared, we chose to investigate its performance in the carbene insertion N-H using  $\alpha$ -diazo ester as substrates. This reaction serves as a model reaction, as illustrated in **Figure S2**.



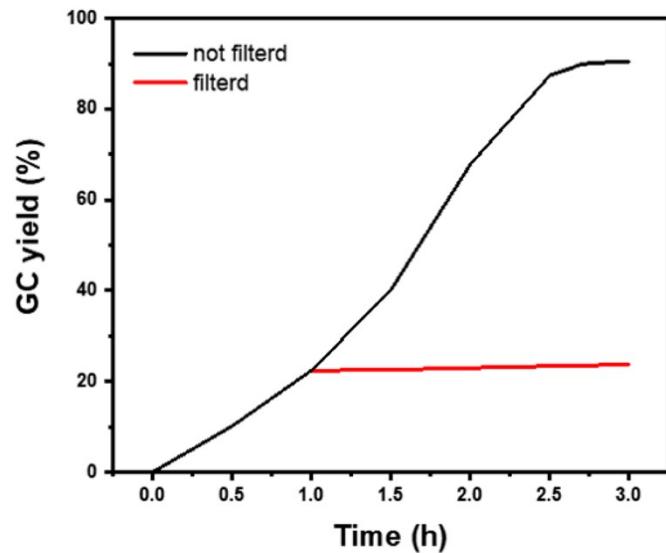
**Figure S2.** Schematic diagram of the flow-through membrane reactor



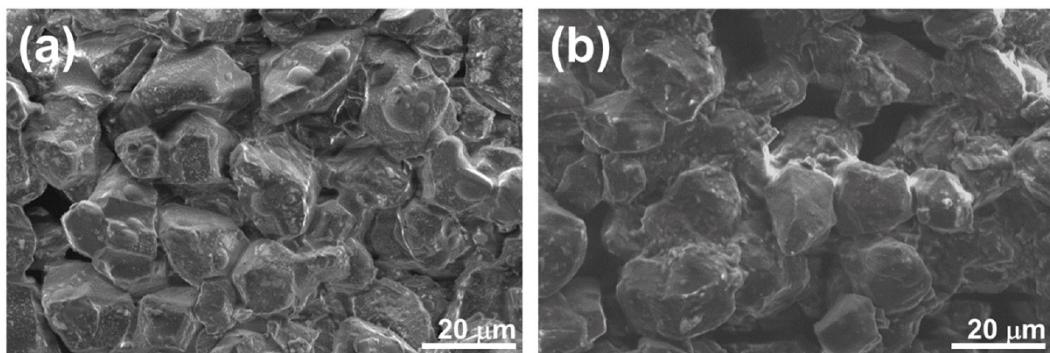
**Figure S3.** FT-IR spectra of CM and SA-CM



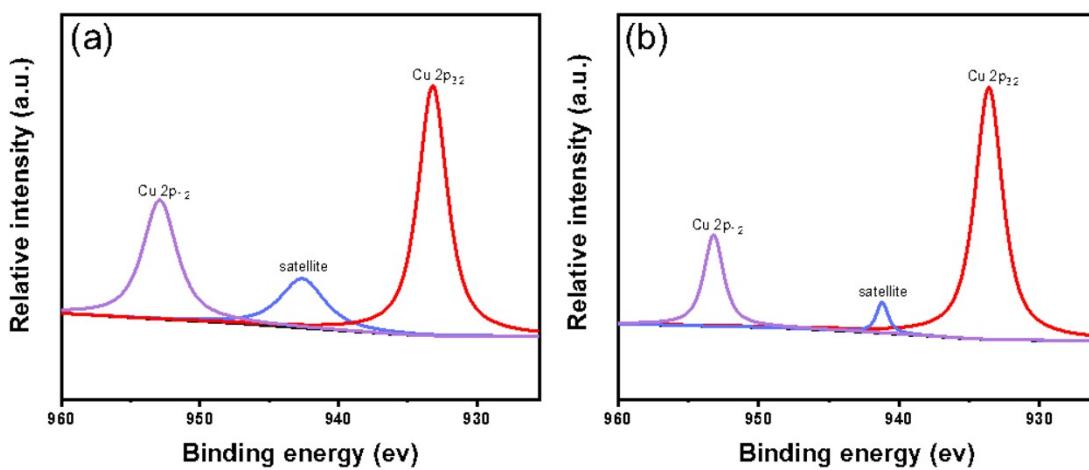
**Figure S4.** (a) SEM image of CM; (b) SEM image of SA-CM; (c) (d) SEM images of Cu@SA-CM; (e) (f) (g) (h) and (i) EDS images of Cu@SA-CM.



**Figure S5.** Hot-filtration experiments



**Figure S6.** SEM images of before (a) and after (b) reaction



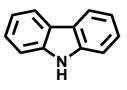
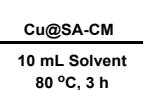
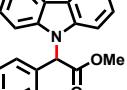
**Figure S7.** XPS spectra of Cu@SA-CM before (a) and after reaction (b)

### III. Condition optimization for the Model Reaction

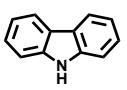
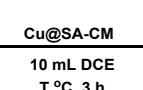
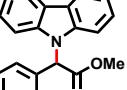
Typical procedure for condition optimization: A flow-through catalytic membrane reactor was designed and constructed based on the as-fabricated catalytic membrane. Typically, methyl 2-diazo-

2-phenylacetate (1.5 equiv, 0.75 mmol), carbazole (1.0 equiv, 0.5 mmol) and DCE (10 mL) were charged into the catalytic membrane reactor. Then the reactor was put in a pre-warmed to 80°C oil bath. The reaction mixture was forced through the catalytic membrane with the aid of a pump (100 mL/min), and the reaction started. The reaction progress was monitored by TLC as well as gas chromatography (GC). After 3 hours, 50  $\mu$ L dodecane was added in the tube. After filtering, the filtrate was subjected to GC analysis to determine the conversion of carbazole 2a, and the calibrated GC yield of the product was calculated.

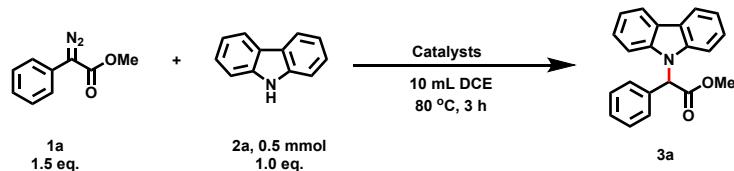
**Table S1 Effect of Solvent**

 <b>1a</b> 1.5 eq.		 <b>2a, 0.5 mmol</b> 1.0 eq.		 <b>3a</b>
Entry	Solvent	carbazole (2a) /Conversion (%)	Yield of 3a (%)	
1	MeOH	0	0	
2	EtOH	0	0	
3	MeCN	26	22	
4	THF	43	40	
5	DMF	0	0	
6	DCM	79	77	
7	<b>DCE</b>	<b>85</b>	<b>82</b>	
8	DMSO	0	0	
9	Toluene	56	53	
10	1,4-dioxane	65	60	

**Table S2 Effect of Temperature**

 <b>1a</b> 1.5 eq.		 <b>2a, 0.5 mmol</b> 1.0 eq.		 <b>3a</b>
Entry	T (°C)	carbazole (2a) /Conversion (%)	Yield of 3a (%)	
1	30	0	0	
2	40	0	0	
3	50	30	22	
4	60	54	48	
5	70	77	73	
6	<b>80</b>	<b>85</b>	<b>82</b>	

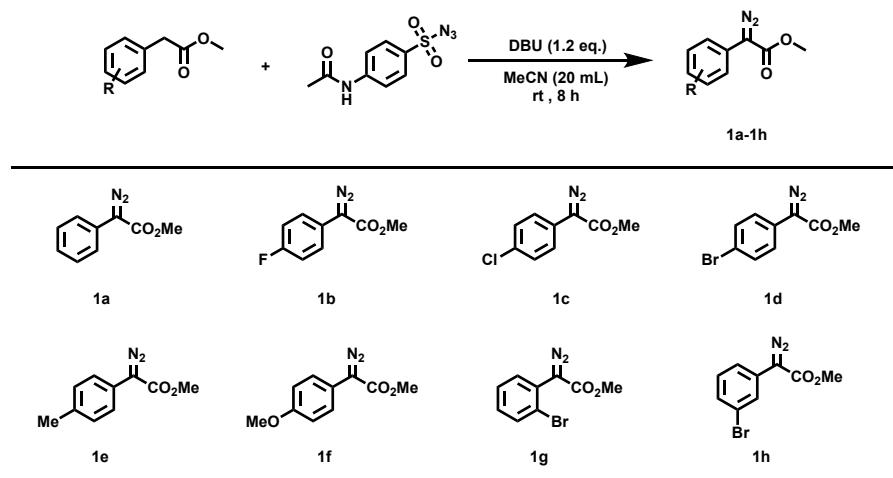
**Table S3 Effect of Catalysts**



Entry	Catalysts	carbazole (2a)	Yield of 3a
		/Conversion (%)	(%)
1	No Catalysts	0	0
2	CM	0	0
3	SA-CM	0	0
4	<b>Cu@SA-CM</b>	85	82

#### IV. Synthesis of aryl diazo esters

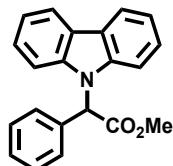
**General Procedure A :** All aryl diazo acetates were prepared by reported procedure. Aryl acetates (1 equiv, 5 mmol) were dissolved in acetonitrile (10 mL) in a clean oven dried round bottom flask, added DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) (1.2 equiv, 6 mmol), stirred for 10 minutes, pABSA (4-acetamidobenzenesulfonyl azide) (1.2 equiv, 6 mmol) was added, stirred for 8 hours in dark at r.t; after completion, acetonitrile was removed under vacuum, diluted with ethyl acetate (25 mL), washed with water and organic layer was dried with brine and sodium sulphate, purified with flash column chromatography in silica gel (100-200 mesh size) with 5% ethyl acetate in hexane to yield 98%.<sup>1</sup> All of these diazo compounds are stable under storage in refrigerator and dark condition.



#### V. The N–H insertion reaction catalyzed by Cu@SA-CM

**General Procedure B :** A flowthrough catalytic membrane reactor was designed and constructed based on the as-fabricated catalytic membrane. Typically, methyl 2-diazo-2-phenylacetate (1.5 equiv, 0.75 mmol), carbazole (1.0 equiv, 0.5 mmol) and DCE (10 mL) were charged to the catalytic membrane reactor. Then the reactor was put in a pre-warmed 80 °C oil bath. The reaction mixture

was forced through the catalytic membrane with the aid of a pump (100 mL/min), and the reaction started. The reaction progress was monitored by TLC as well as gas chromatography (GC). After 3 hours, the resultant mixture was cooled to ambient temperature and evaporated all the volatiles under reduced pressure. The residue was purified by flash chromatography (petroleum ether /EtOAc, 50:1) to afford the corresponding product. The structure of its pure product was determined by <sup>1</sup>H and <sup>13</sup>C NMR data characterization.



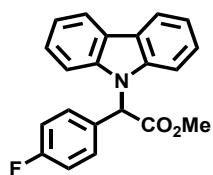
**Methyl-2-(9H-carbazol-9-yl)-2-phenylacetate (3a).**

The reaction was conducted according to **general procedure B**. The product was purified by flash chromatography (PE: EtOAc = 20:1) as colourless oil (129.3 mg, 82% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.13-8.11 (m, 2H), 7.39-7.35 (m, 2H), 7.34-7.32 (m, 3H), 7.28-7.27 (m, 2H), 7.25-7.23 (m, 4H), 6.63 (s, 1H), 3.78 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.0, 140.3, 134.1, 128.9, 128.5, 127.5, 125.9, 123.7, 120.4, 119.9, 110.3, 60.4, 53.0.

HRMS (ESI): Calcd for C<sub>21</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 316.1338, Found: 316.1334.



**Methyl-2-(9H-carbazol-9-yl)-2-(4-fluorophenyl)acetate (3b).**

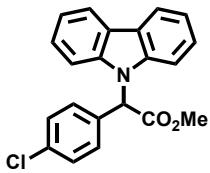
The reaction was conducted according to **general procedure B**. The product was purified by flash chromatography (PE: EtOAc = 20:1) as colourless oil (138.3 mg, 83% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.13-8.11 (m, 2H), 7.41-7.36 (m, 2H), 7.29-7.27 (m, 1.55H), 7.25 (s, 1.56H), 7.23-7.19 (m, 3H), 7.04-6.98 (m, 2H), 6.57 (s, 1H), 3.77 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 169.8, 140.6, 129.4, 129.3, 126.0, 123.7, 120.5, 120.0, 115.9, 115.7, 110.1, 59.7, 53.1.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -113.38 (td, *J* = 8.8, 4.8 Hz).

HRMS (ESI): Calcd for  $C_{21}H_{17}FNO_2$  [M+H] $^+$ : 334.1243, Found: 334.1249.



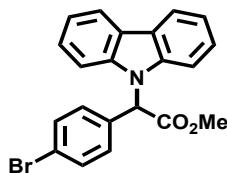
**Methyl-2-(9H-carbazol-9-yl)-2-(4-chlorophenyl)acetate (3c).**

The reaction was conducted according to **general procedure B**. The product was purified by flash chromatography (PE: EtOAc = 20:1) as colourless oil (152.2 mg, 87% yield).

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.13-8.11 (m, 2H), 7.41-7.36 (m, 2H), 7.30-7.27 (m, 4H), 7.25-7.22 (m, 2H), 7.18-7.16 (m, 2H), 6.55 (s, 1H), 3.76 (s, 3H).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  169.6, 140.1, 134.5, 132.7, 129.0(1), 128.9(7), 126.1, 123.8, 120.5, 120.1, 110.1, 59.7, 53.1.

HRMS (ESI): Calcd for  $C_{21}H_{17}ClNO_2$  [M+H] $^+$ : 350.0948, Found: 350.0952.



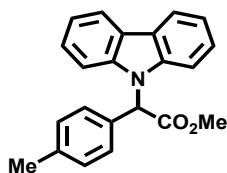
**Methyl-2-(4-bromophenyl)-2-(9H-carbazol-9-yl)acetate (3d).**

The reaction was conducted according to **general procedure B**. The product was purified by flash chromatography (PE: EtOAc = 20:1) as colourless oil (171.5 mg, 87% yield).

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.13-8.11 (m, 2H), 7.46-7.42 (m, 2H), 7.41-7.37 (m, 2H), 7.29-7.27 (m, 2H), 7.25-7.22 (m, 2H), 7.12-7.09 (m, 2H), 6.53 (s, 1H), 3.76 (s, 3H).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  169.5, 140.1, 133.2, 132.0, 129.3, 126.1, 123.8, 122.6, 120.5, 120.1, 110.1, 59.8, 53.1.

HRMS (ESI): Calcd for  $C_{21}H_{17}BrNO_2$  [M+H] $^+$ : 394.0443, Found: 394.0446.



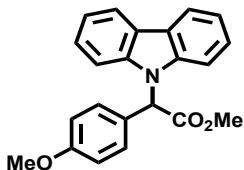
**Methyl-2-(9H-carbazol-9-yl)-2-(p-tolyl)acetate (3e).**

The reaction was conducted according to **general procedure B**. The product was purified by flash chromatography (PE: EtOAc = 20:1) as colourless oil (136.7 mg, 83% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.13-8.10 (m, 2H), 7.39-7.35 (m, 2H), 7.27(4)-7.27(1) (m, 2H), 7.25-7.23 (m, 2H), 7.13 (s, 4H), 6.59 (s, 1H), 3.78 (s, 3H), 2.33 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.1, 140.3, 138.3, 131.1, 129.5, 127.5, 125.9, 123.7, 120.4, 119.8, 110.3, 60.2, 52.9, 21.3.

HRMS (ESI): Calcd for C<sub>22</sub>H<sub>20</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 330.1494, Found: 330.1487.



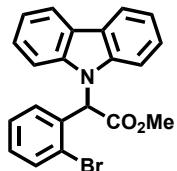
**Methyl-2-(9H-carbazol-9-yl)-2-(4-methoxyphenyl)acetate (3f).**

The reaction was conducted according to **general procedure B**. The product was purified by flash chromatography (PE: EtOAc = 20:1) as pale orange solid (139.8 mg, 81% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.13-8.11 (m, 2H), 7.40-7.35 (m, 2H), 7.27(3)-7.27(0) (m, 2H), 7.25-7.23 (m, 2H), 7.19-7.15 (m, 2H), 6.87-6.83 (m, 2H), 6.58 (s, 1H), 3.78 (s, 3H), 3.77 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.2, 159.6, 140.3, 128.9, 126.0, 125.9, 123.7, 120.4, 119.8, 114.2, 110.3, 59.9, 55.4, 52.9.

HRMS (ESI): Calcd for C<sub>22</sub>H<sub>20</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 346.1443, Found: 346.1447.



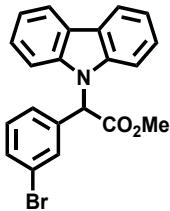
**Methyl-2-(2-bromophenyl)-2-(9H-carbazol-9-yl)acetate (3g).**

The reaction was conducted according to **general procedure B**. The product was purified by flash chromatography (PE: EtOAc = 20:1) as colourless oil (141.9 mg, 72% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.15-8.12 (m, 2H), 7.67-7.64 (m, 1H), 7.44-7.40 (m, 2H), 7.33-7.27 (m, 4H), 7.24-7.17 (m, 2H), 7.14-7.12 (m, 1H), 6.74 (s, 1H), 3.77 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 168.9, 140.5, 134.5, 133.3, 130.3, 128.7, 127.8, 126.3, 124.4, 123.7, 120.6, 120.1, 109.7, 61.6, 53.3.

HRMS (ESI): Calcd for C<sub>21</sub>H<sub>17</sub>BrNO<sub>2</sub> [M+H]<sup>+</sup>: 394.0443, Found: 394.0439.



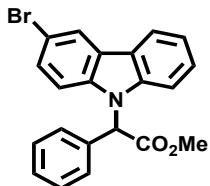
**Methyl-2-(3-bromophenyl)-2-(9H-carbazol-9-yl)acetate (3h).**

The reaction was conducted according to **general procedure B**. The product was purified by flash chromatography (PE: EtOAc = 20:1) as colourless oil (82.8 mg, 42% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.15-8.12 (m, 2H), 7.49-7.46 (m, 2H), 7.42-7.38 (m, 2H), 7.31-7.27 (m, 3H), 7.25-7.24 (m, 1H), 7.19-7.15 (m, 1H), 7.13-7.10 (m, 1H), 6.56 (s, 1H), 3.76 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 169.3, 140.1, 136.4, 131.7, 130.7, 130.3, 126.1, 123.7, 122.9, 120.5, 120.1, 112.5, 110.0, 59.7, 53.1.

HRMS (ESI): Calcd for C<sub>21</sub>H<sub>17</sub>BrNO<sub>2</sub> [M+H]<sup>+</sup>: 394.0443, Found: 394.0450



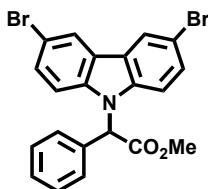
**Methyl-2-(3-bromo-9H-carbazol-9-yl)-2-phenylacetate (3i).**

The reaction was conducted according to **general procedure B**. The product was purified by flash chromatography (PE: EtOAc = 20:1) as colourless oil (153.8 mg, 78% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.21 (d, *J* = 2.0 Hz, 1H), 8.07-8.05 (m, 1H), 7.44-7.39 (m, 2H), 7.35-7.32 (m, 3H), 7.30-7.27 (m, 2H), 7.22-7.19 (m, 2H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.55 (s, 1H), 3.79 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 169.7, 140.8, 138.8, 133.7, 129.0, 128.7, 128.6, 127.5, 126.7, 125.5, 123.1, 122.6, 120.7, 120.4, 112.8, 112.2, 110.2, 60.5, 53.0.

HRMS (ESI): Calcd for C<sub>21</sub>H<sub>17</sub>BrNO<sub>2</sub> [M+H]<sup>+</sup>: 394.0443, Found: 394.0441.



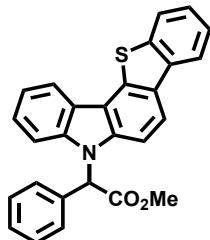
**Methyl-2-(3,6-dibromo-9H-carbazol-9-yl)-2-phenylacetate (3j).**

The reaction was conducted according to **general procedure B**. The product was purified by flash chromatography (PE: EtOAc = 20:1) as colourless oil (190.4 mg, 81% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.16 (d,  $J = 2.0$  Hz, 2H), 7.45 (dd,  $J = 8.8$  Hz, 2.0 Hz, 2H), 7.37-7.33 (m, 3H), 7.19-7.16 (m, 2H), 7.11 (d,  $J = 8.8$  Hz, 2H), 6.54 (s, 1H), 3.81 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.4, 139.3, 133.3, 129.4, 129.1, 128.9, 127.4, 124.4, 123.4, 113.2, 112.1, 60.6, 53.1.

HRMS (ESI): Calcd for  $\text{C}_{21}\text{H}_{16}\text{Br}_2\text{NO}_2$  [M+H] $^+$ : 471.9548, Found: 471.9553.



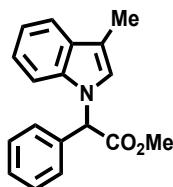
**Methyl-2-(5H-benzo[4,5]thieno[3,2-c]carbazol-5-yl)-2-phenylacetate (3k).**

The reaction was conducted according to **general procedure B**. The product was purified by flash chromatography (PE: EtOAc = 20:1) as colourless oil (153.9 mg, 73% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.31-8.29 (m, 1H), 8.19-8.17 (m, 1H), 8.14 (d,  $J = 8.8$  Hz, 1H), 7.99-7.97 (m, 1H), 7.52-7.46 (m, 2H), 7.45-7.43 (m, 2H), 7.41-7.37 (m, 2H), 7.36-7.34 (m, 3H), 7.28-7.27 (m, 2H), 6.75 (s, 1H), 3.81 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 169.8, 140.2, 139.4, 138.8, 136.0, 134.0, 133.0, 129.1, 128.9, 128.7, 127.5, 125.8, 125.5, 124.8, 123.1, 122.9, 121.9, 121.1, 120.6, 119.3, 117.5, 110.3, 108.3, 60.7, 53.1.

HRMS (ESI): Calcd for  $\text{C}_{27}\text{H}_{20}\text{NO}_2\text{S}$  [M+H] $^+$ : 422.1215, Found: 422.1218.



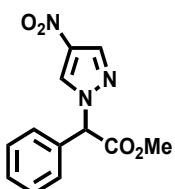
**Methyl-2-(3-methyl-1H-indol-1-yl)-2-phenylacetate (3l).**

The reaction was conducted according to **general procedure B**. The product was purified by flash chromatography (PE: EtOAc = 20:1) as pale orange oil (53.1 mg, 38% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.59-7.57 (m, 1H), 7.42-7.38 (m, 3H), 7.35-7.30 (m, 3H), 7.25-7.21 (m, 1H), 7.17-7.13 (m, 1H), 6.88 (s, 1H), 6.23 (s, 1H), 3.81 (s, 3H), 2.28(9)-2.28(6) (m, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.5, 136.9, 135.0, 129.3, 129.2, 129.0, 128.2, 124.2, 122.0, 119.6, 119.4, 111.8, 108.9, 61.8, 52.9, 9.9.

HRMS (ESI): Calcd for C<sub>18</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 280.1338, Found: 280.1341.



**Methyl-2-(4-nitro-1H-pyrazol-1-yl)-2-phenylacetate (3m).**

The reaction was conducted according to **general procedure B**. The product was purified by flash chromatography (PE: EtOAc = 20:1) as colourless oil (53.6 mg, 41% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.10 (d, *J* = 13.2 Hz, 2H), 7.51-7.46 (m, 3H), 7.43-7.40 (m, 2H), 6.19 (s, 1H), 3.85 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  168.3, 136.2, 131.8, 130.6, 130.0, 129.1, 128.7, 68.9, 53.6.

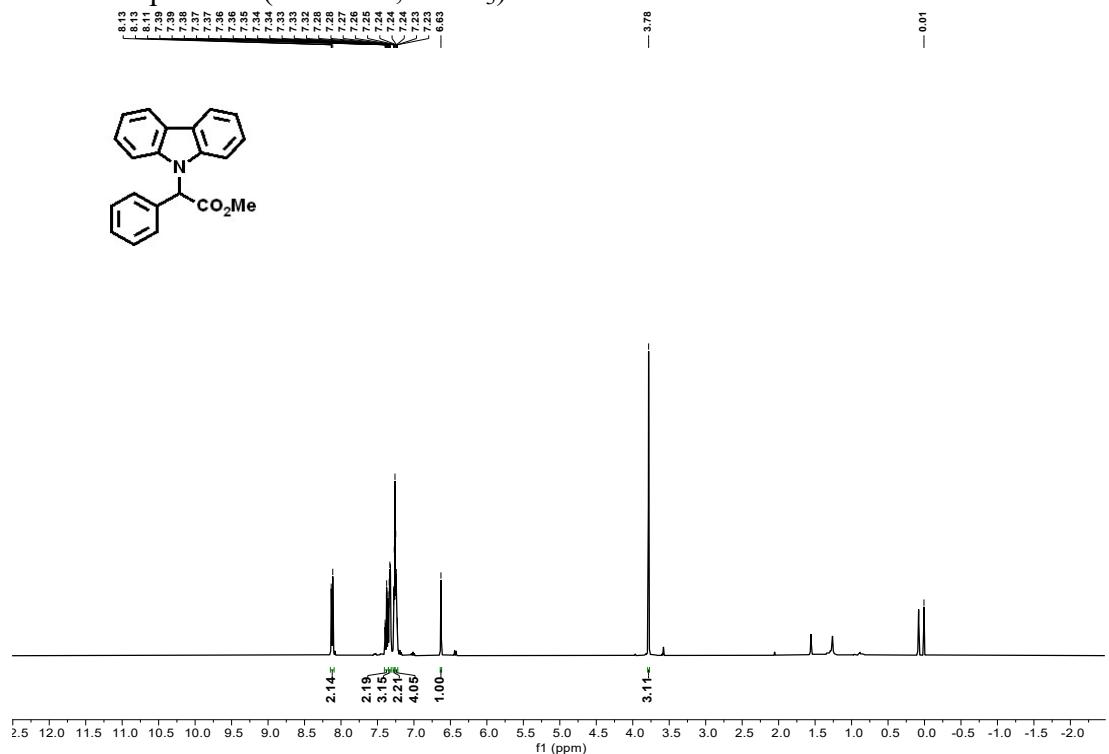
HRMS (ESI): Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>3</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 262.0828, Found: 262.0823.

## VI. Reference

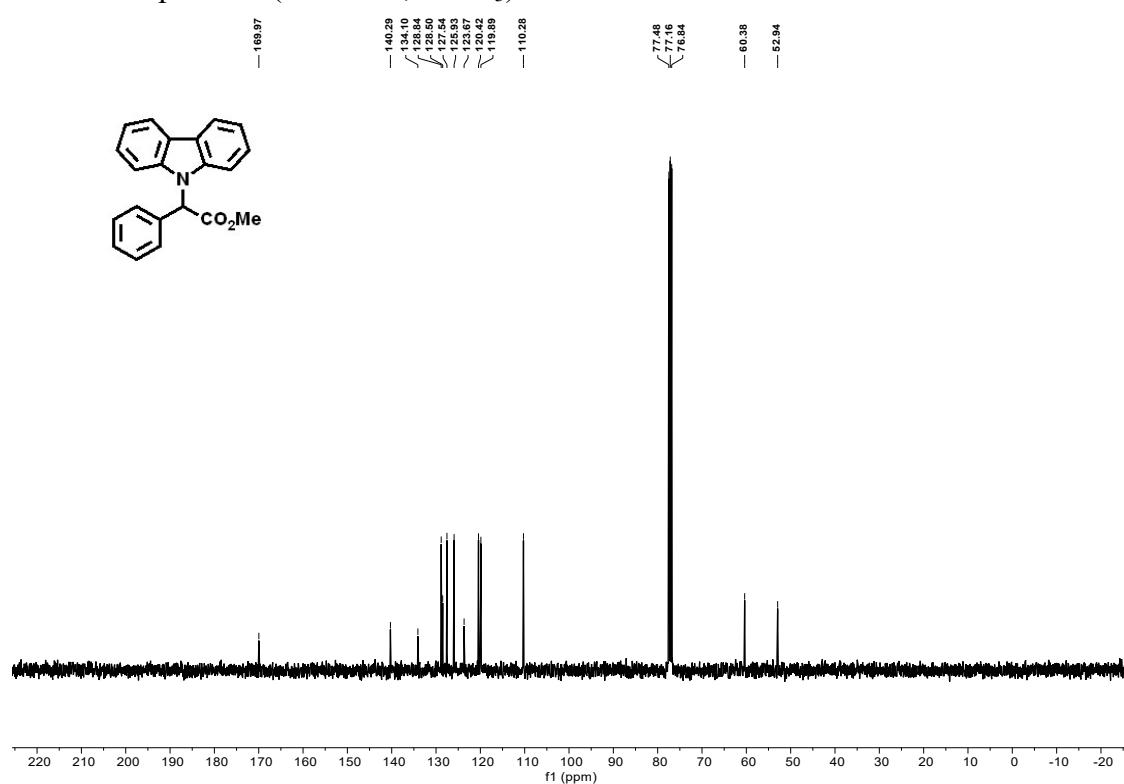
(1) Zhang, H.; Wang, H.; Luo, Y.; Chen, C.; Cao, Y.; Chen, P.; Guo, Y.-L.; Lan, Y.; Liu, G. Regioselective Palladium-Catalyzed C-H Bond Trifluoroethylation of Indoles: Exploration and Mechanistic Insight. *ACS Catalysis* **2018**, 8 (3), 2173-2180.

## VII. NMR spectra

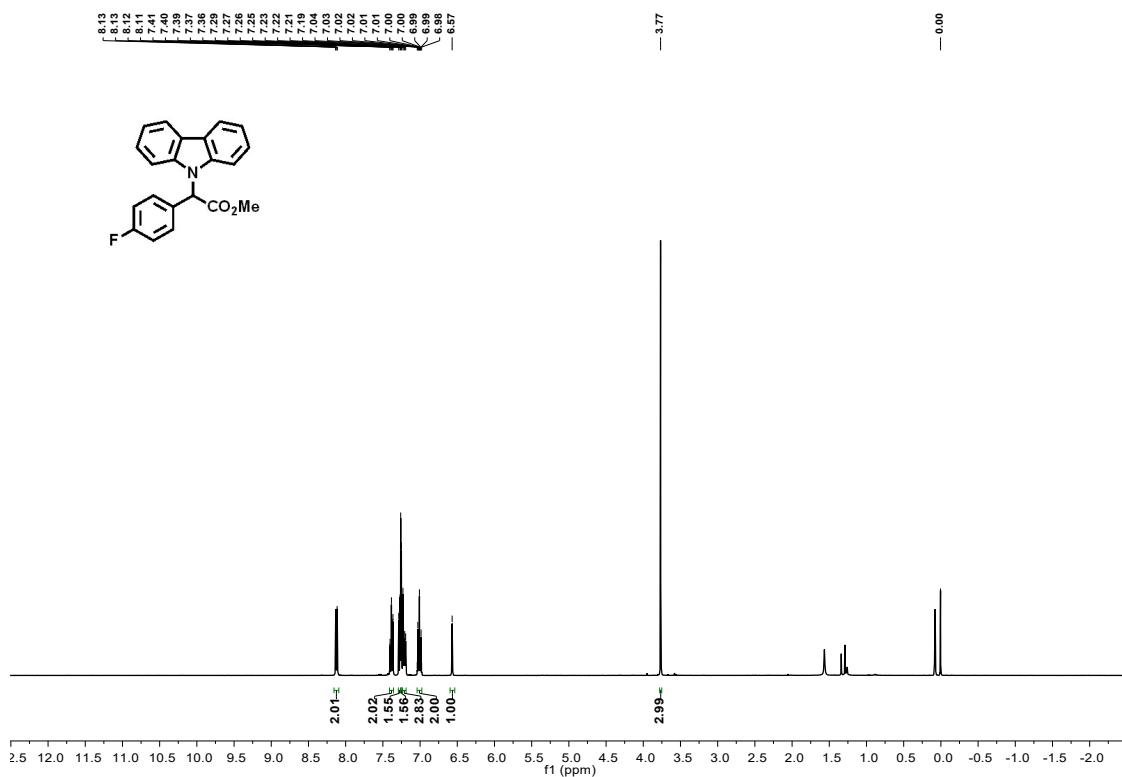
<sup>1</sup>H NMR-spectrum (400 MHz, CDCl<sub>3</sub>) of 3a.



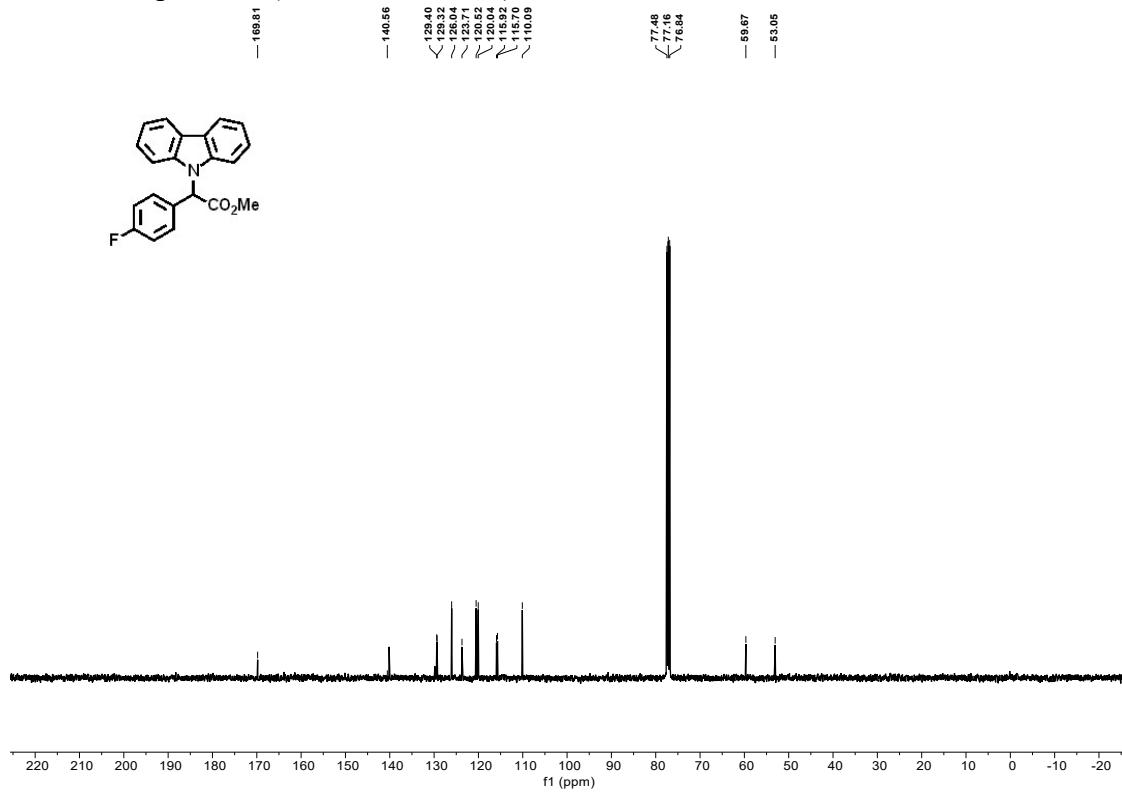
<sup>13</sup>C NMR-spectrum (100 MHz, CDCl<sub>3</sub>) of 3a.



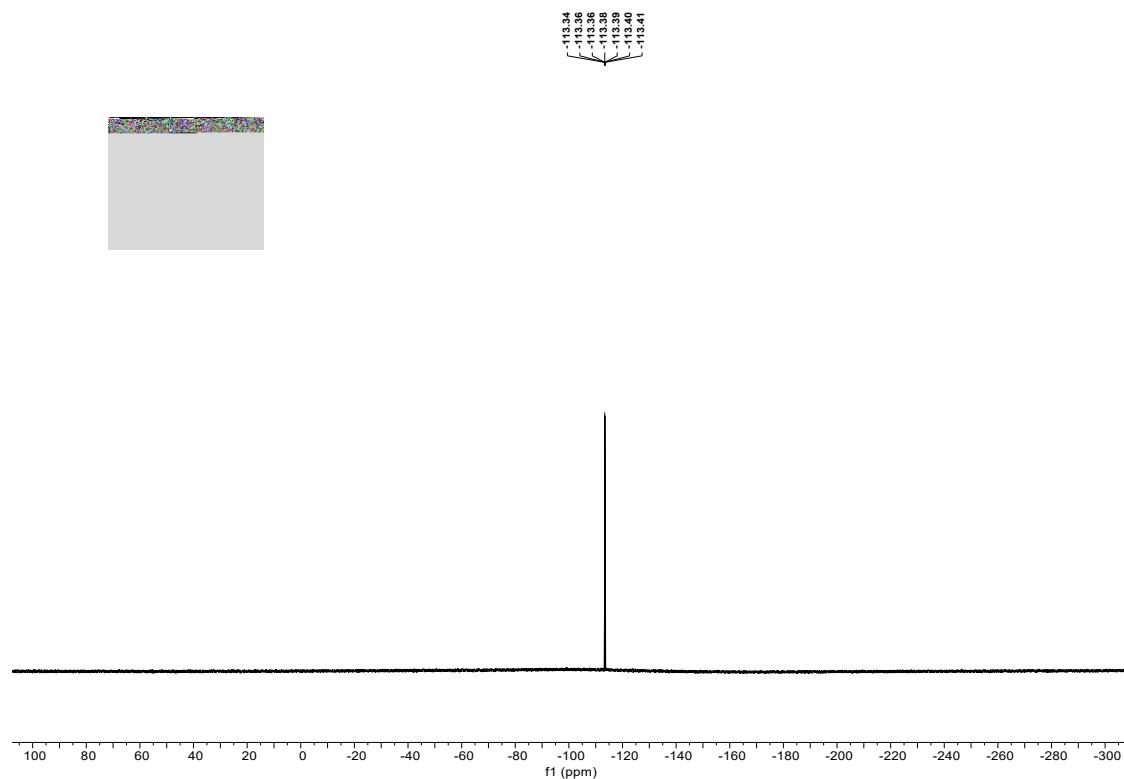
<sup>1</sup>H NMR-spectrum (400 MHz, CDCl<sub>3</sub>) of 3b.



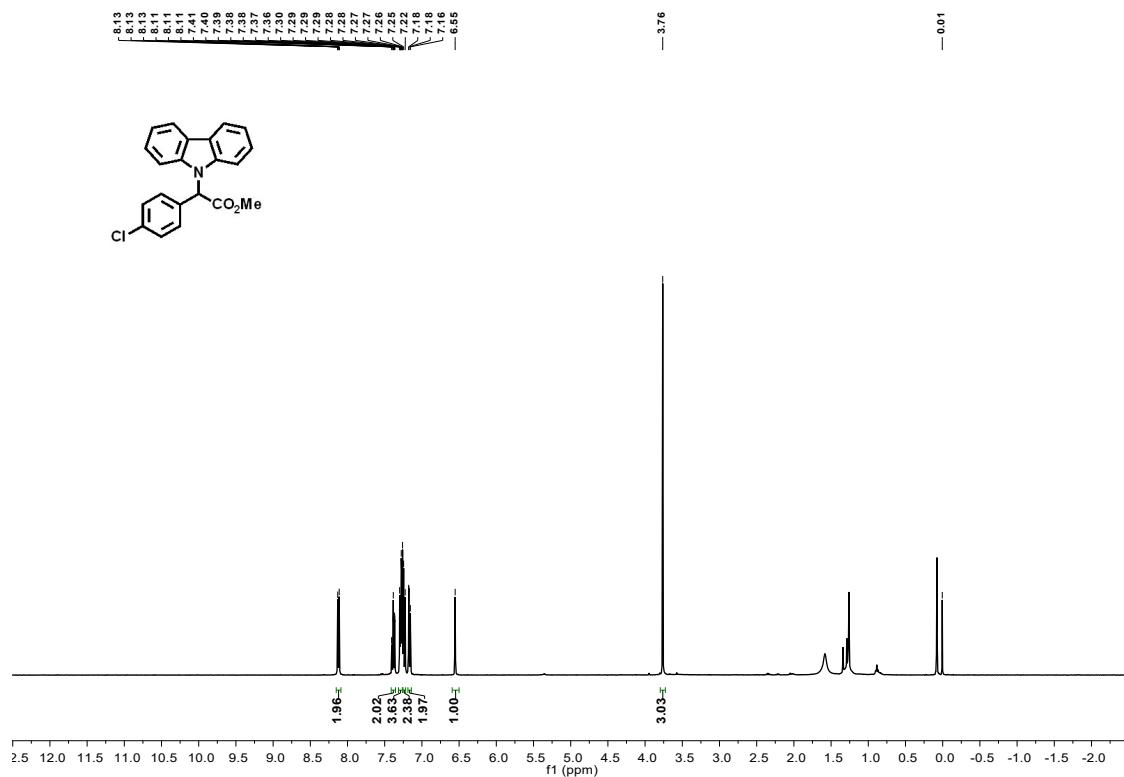
<sup>13</sup>C NMR-spectrum (100 MHz, CDCl<sub>3</sub>) of 3b.



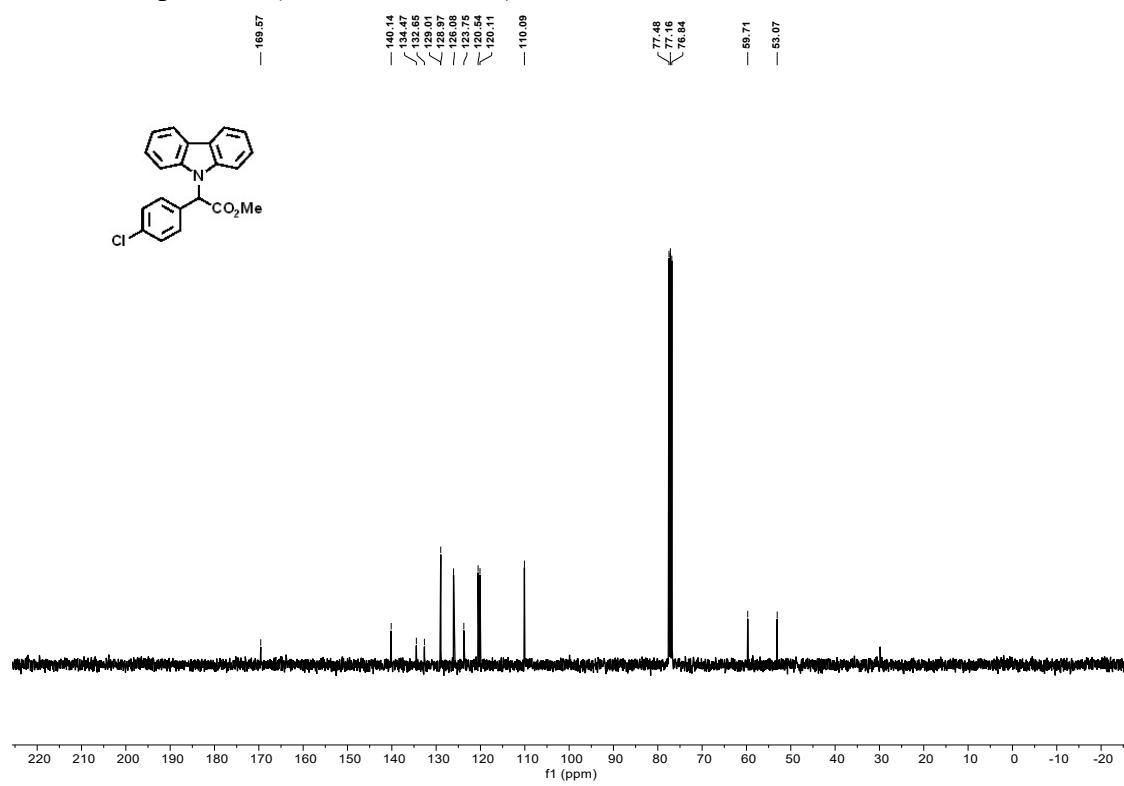
$^{19}\text{F}$  NMR-spectrum (376 MHz,  $\text{CDCl}_3$ ) of 3b



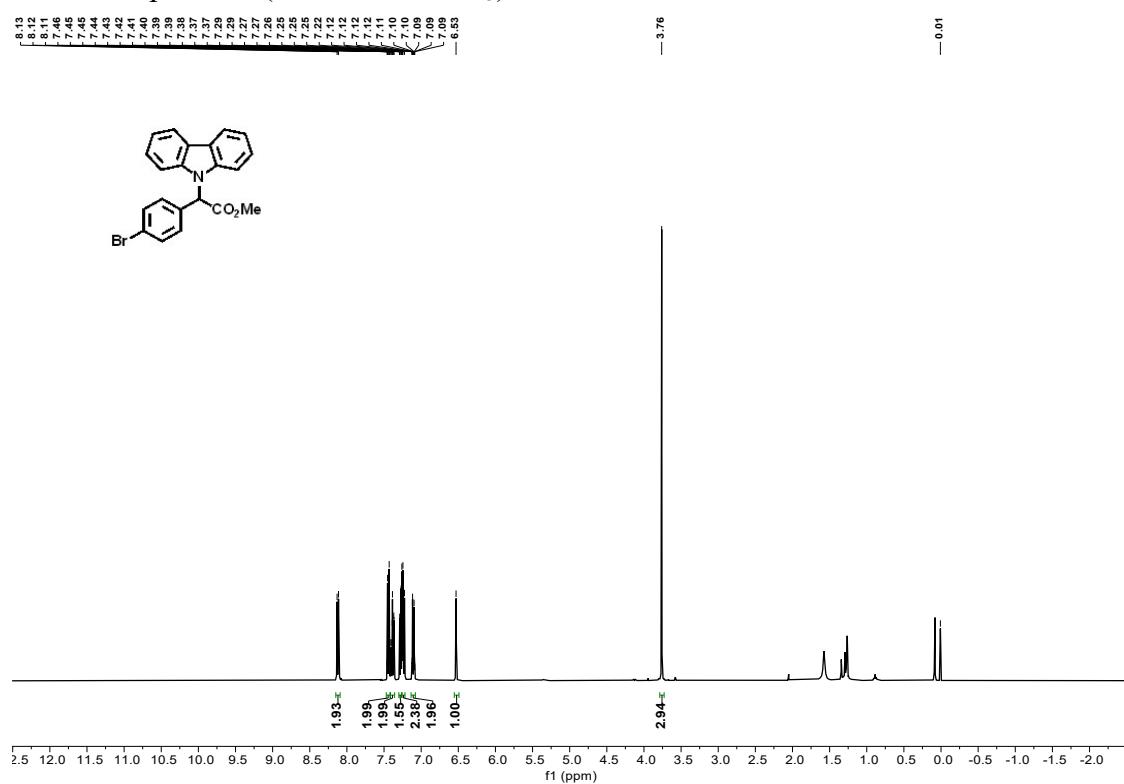
$^1\text{H}$  NMR-spectrum (400 MHz,  $\text{CDCl}_3$ ) of 3c.



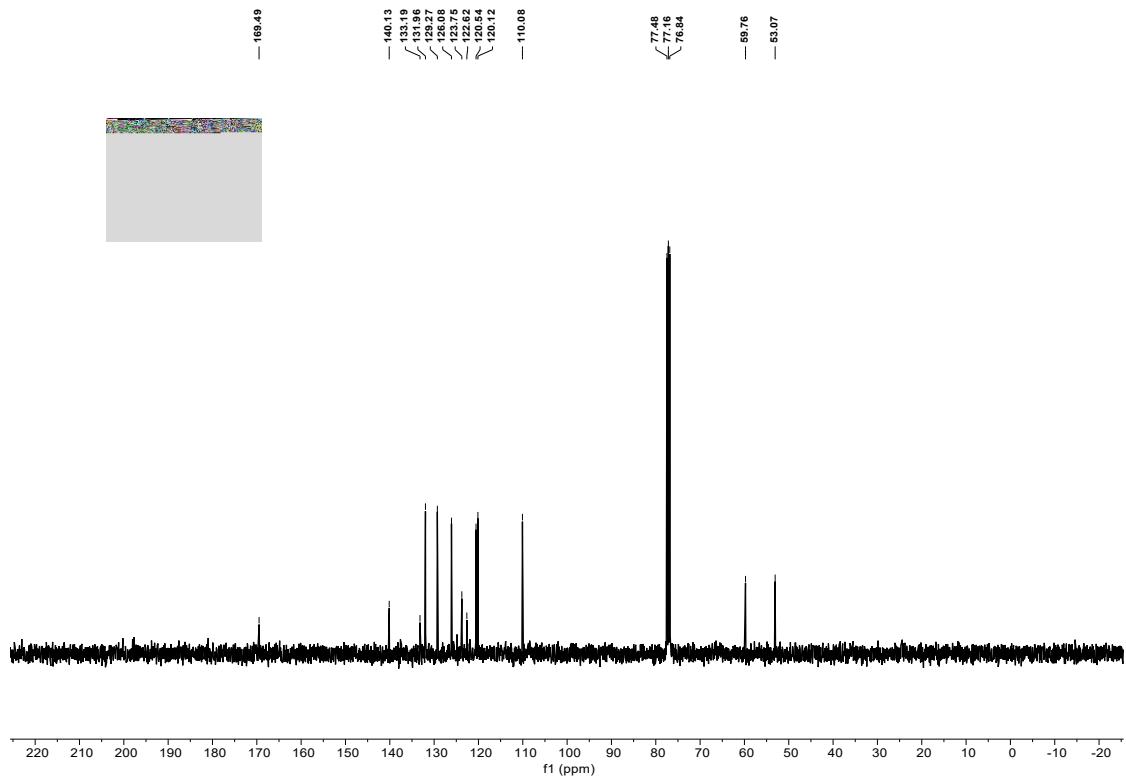
<sup>13</sup>C NMR-spectrum (100 MHz, CDCl<sub>3</sub>) of 3c.



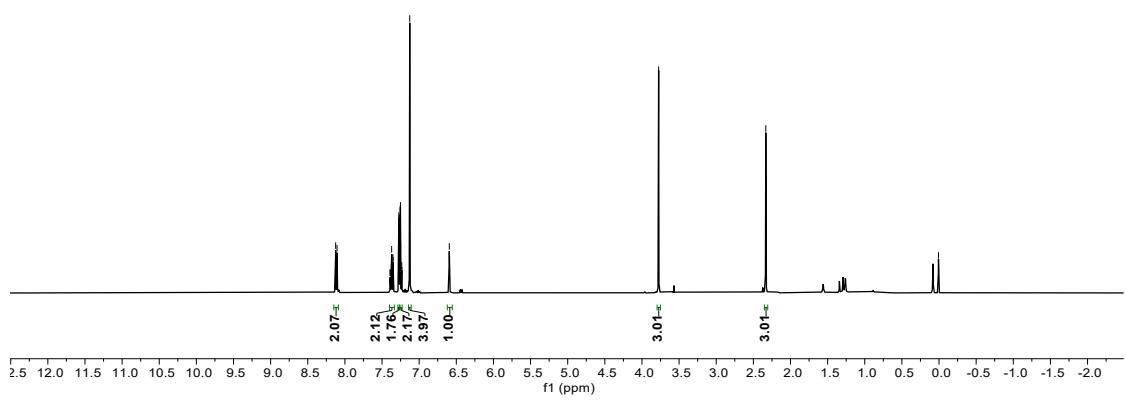
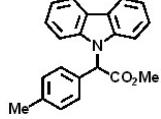
<sup>1</sup>H NMR-spectrum (400 MHz, CDCl<sub>3</sub>) of 3d.



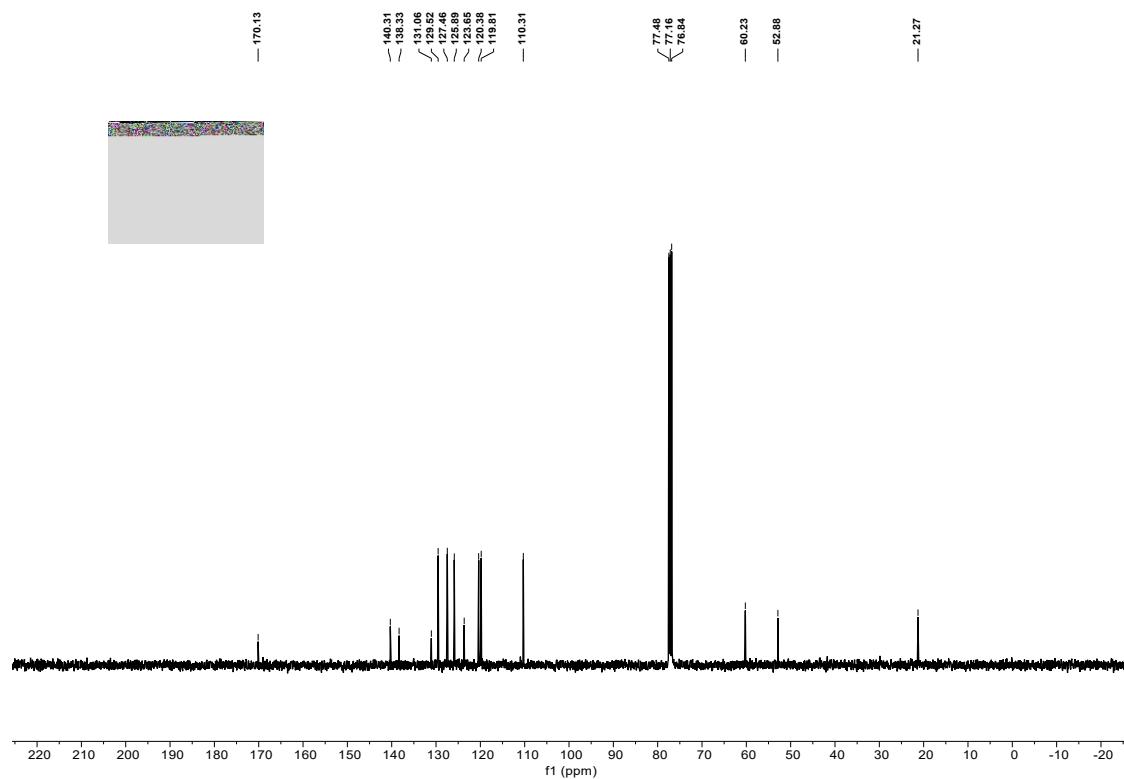
<sup>13</sup>C NMR-spectrum (100 MHz, CDCl<sub>3</sub>) of 3d.



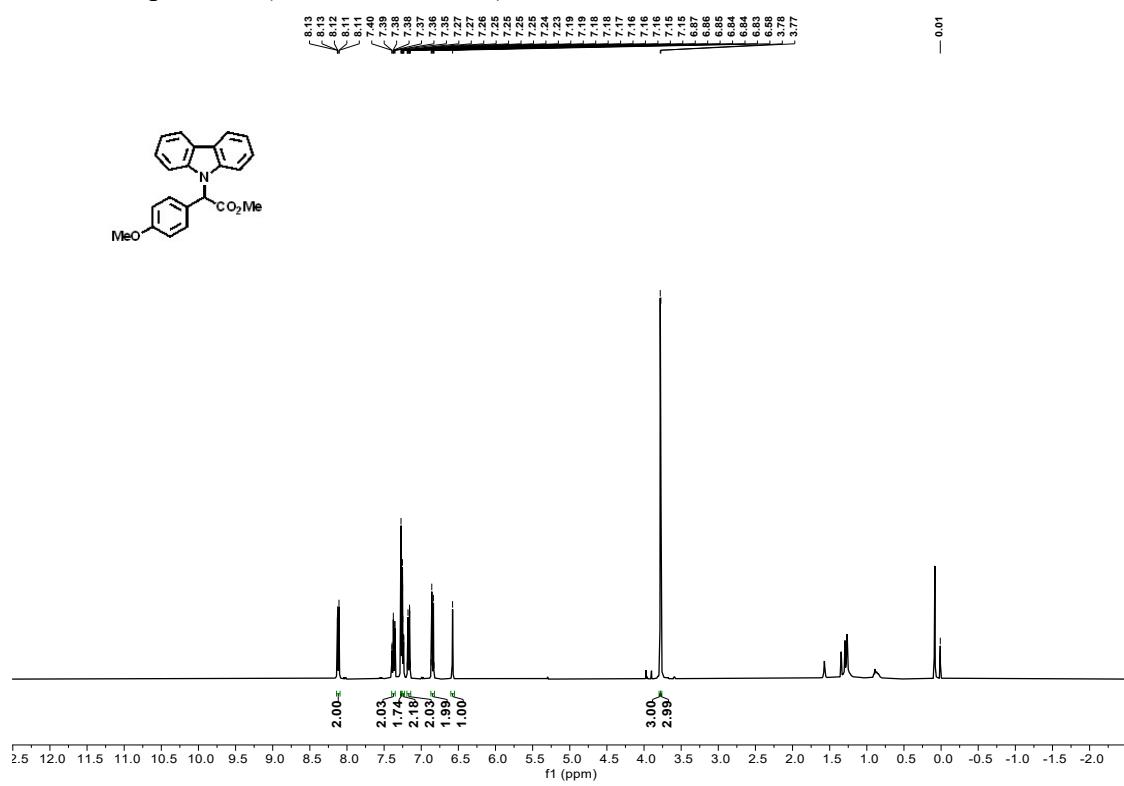
<sup>1</sup>H NMR-spectrum (400 MHz, CDCl<sub>3</sub>) of 3e.



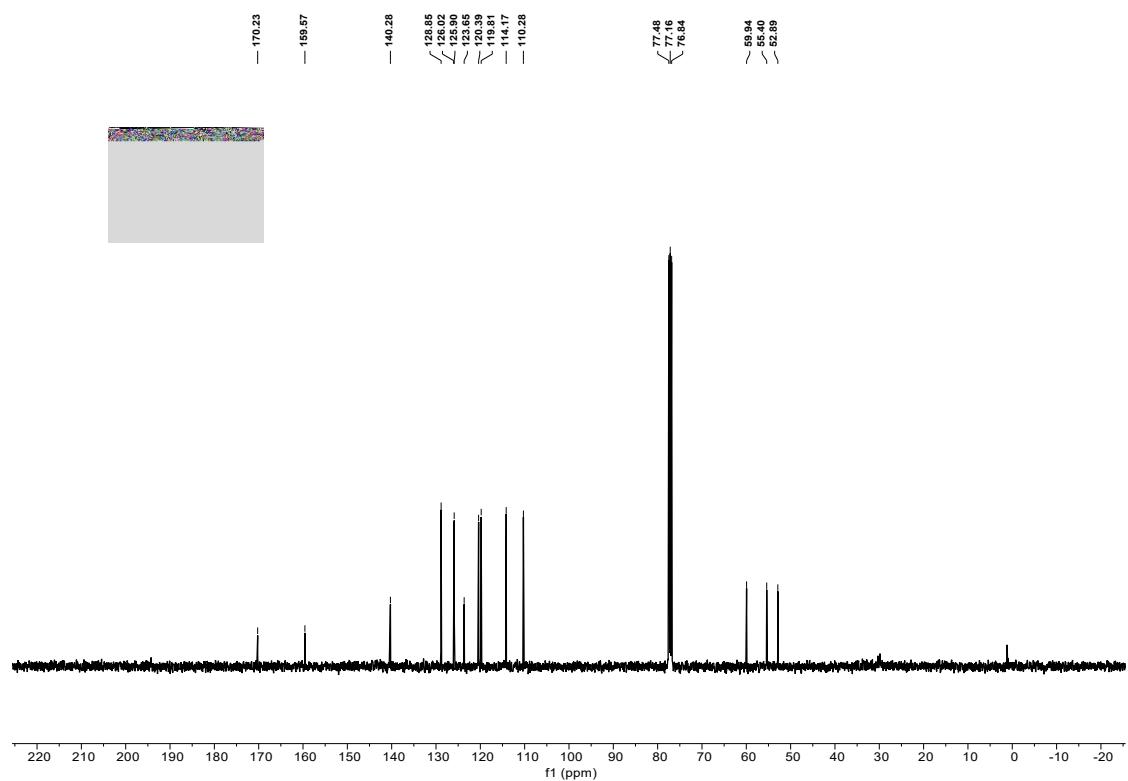
<sup>13</sup>C NMR-spectrum (100 MHz, CDCl<sub>3</sub>) of 3e.



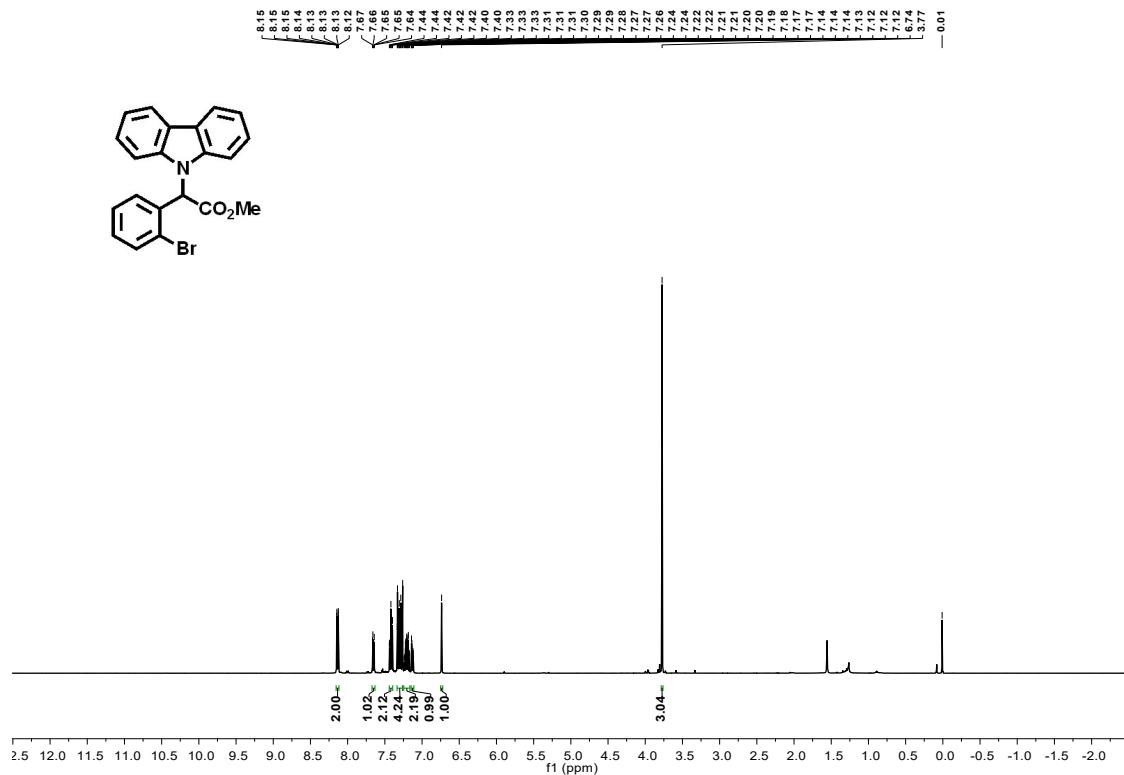
<sup>1</sup>H NMR-spectrum (400 MHz, CDCl<sub>3</sub>) of 3f.



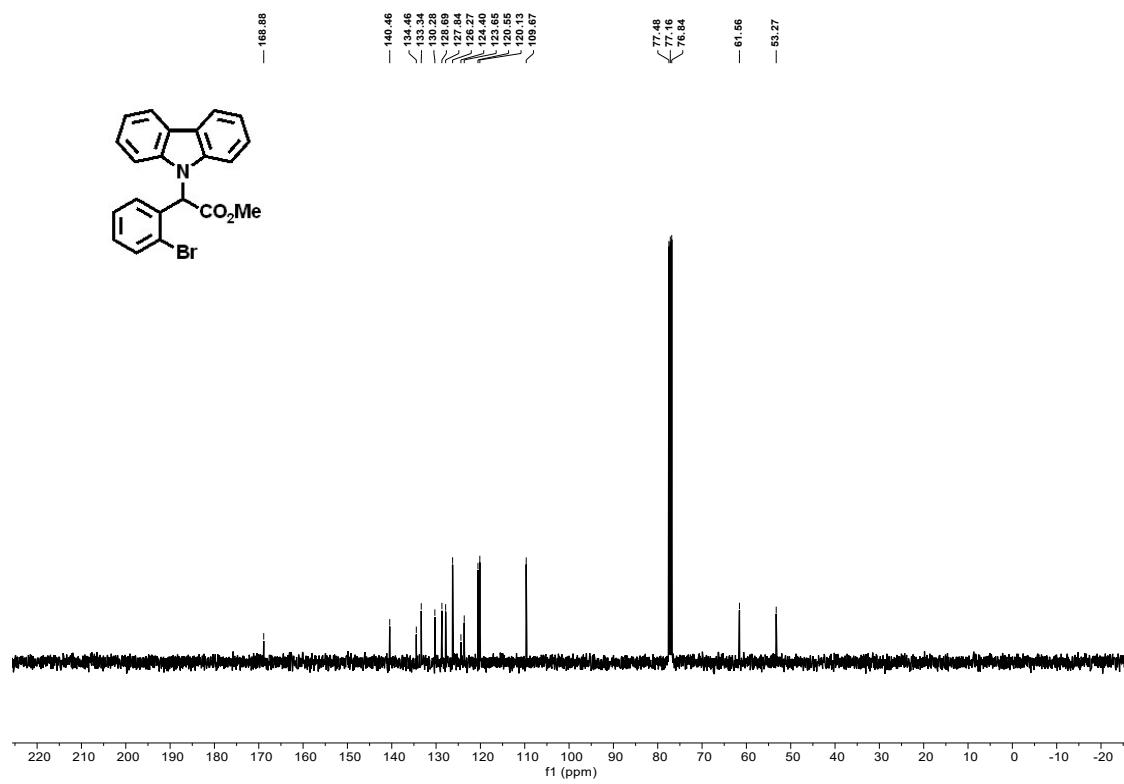
$^{13}\text{C}$  NMR-spectrum (100 MHz,  $\text{CDCl}_3$ ) of 3f.



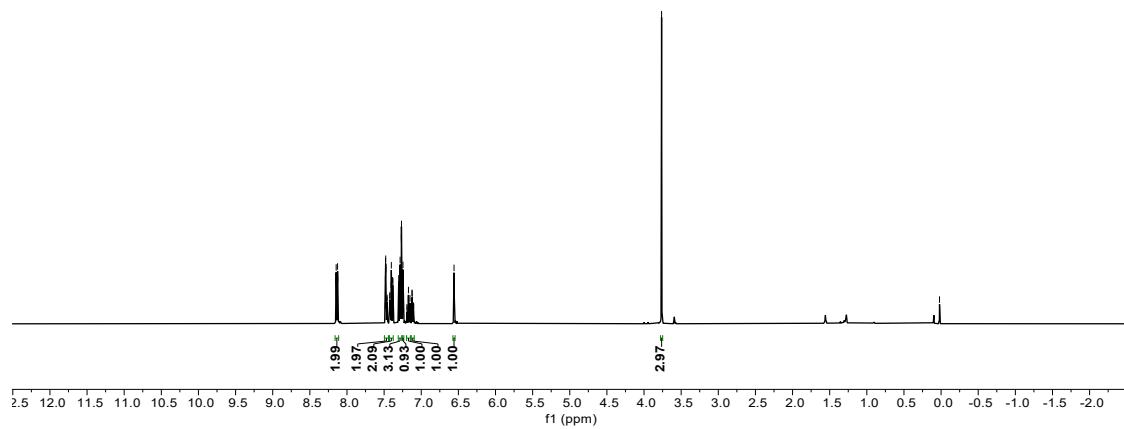
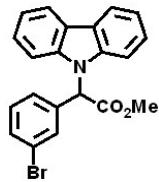
$^1\text{H}$  NMR-spectrum (400 MHz,  $\text{CDCl}_3$ ) of 3g.



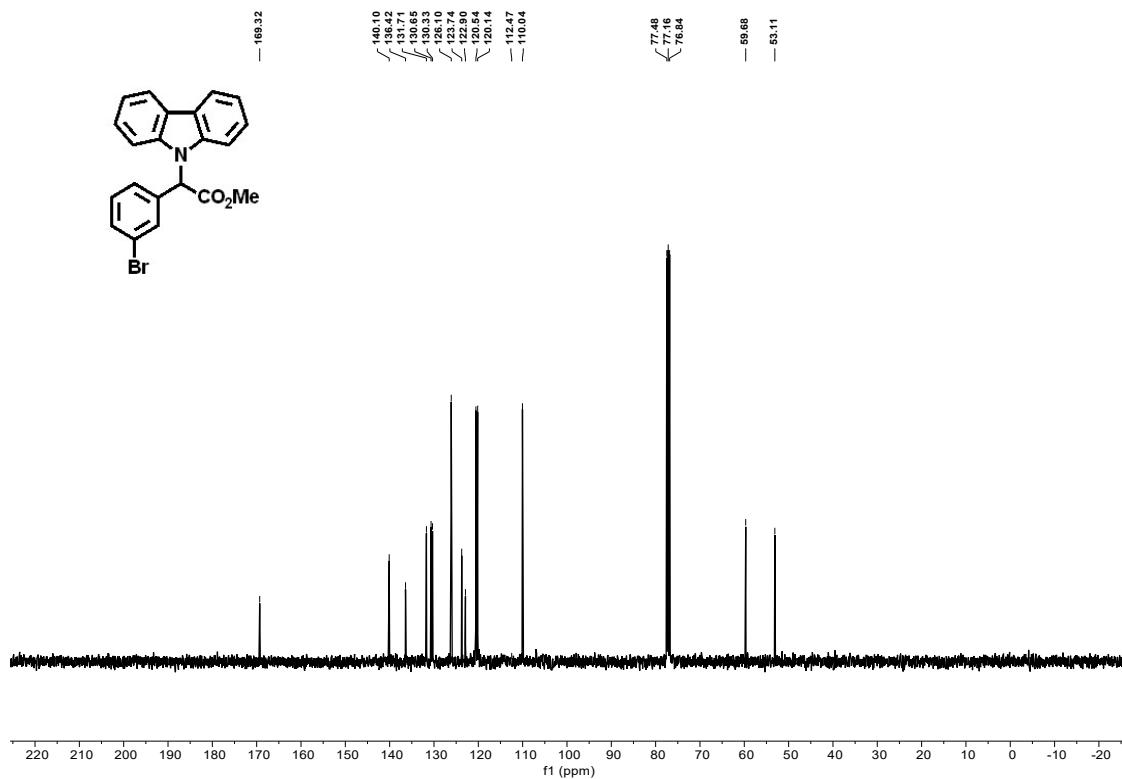
<sup>1</sup>C NMR-spectrum (100 MHz, CDCl<sub>3</sub>) of 3g.



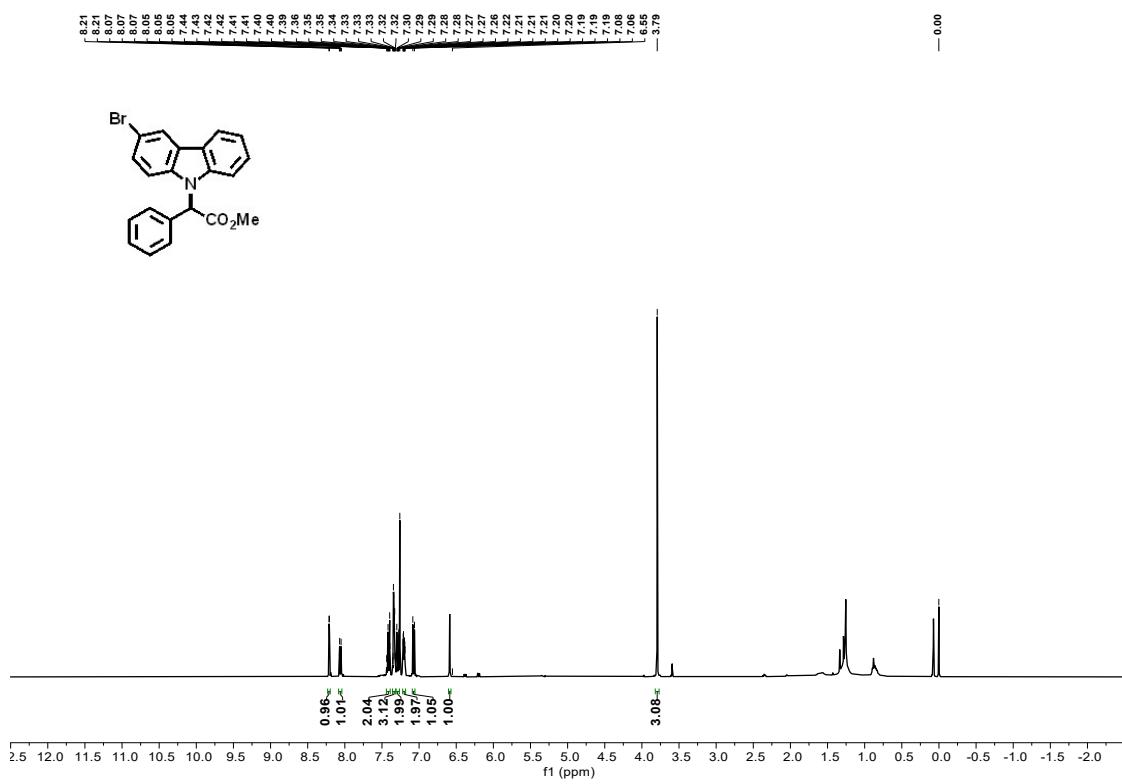
<sup>1</sup>H NMR-spectrum (400 MHz, CDCl<sub>3</sub>) of 3h.



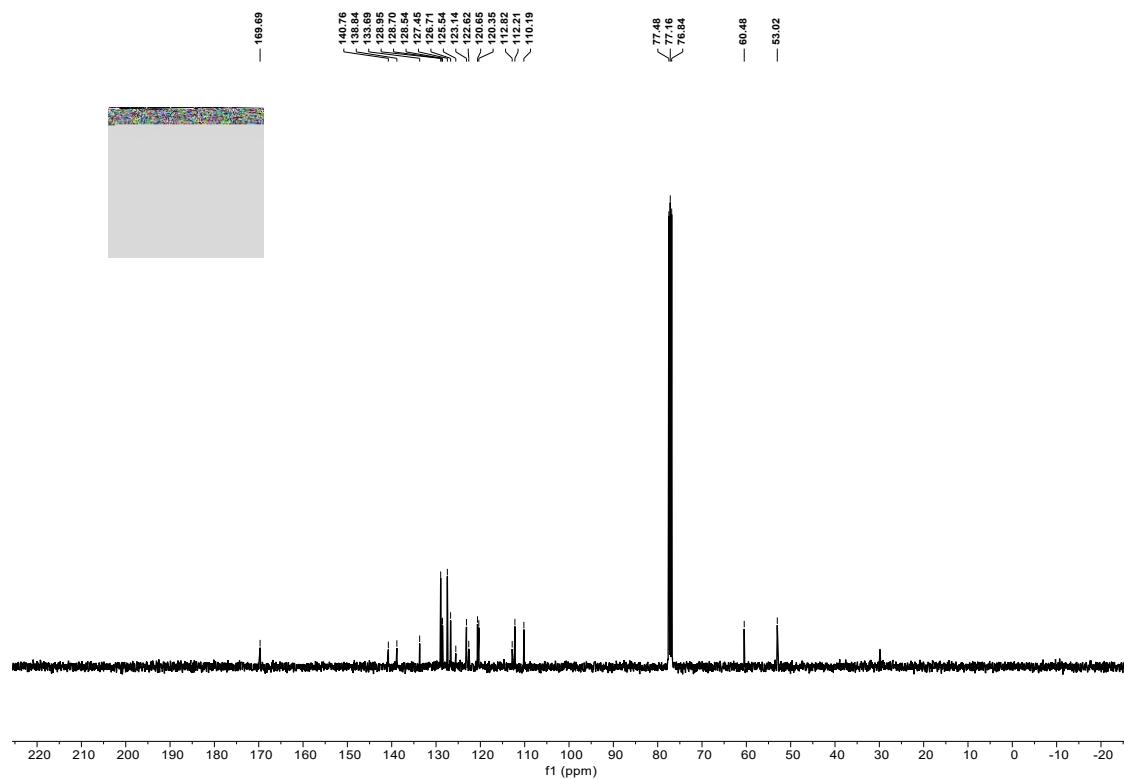
<sup>13</sup>C NMR-spectrum (100 MHz, CDCl<sub>3</sub>) of 3h.



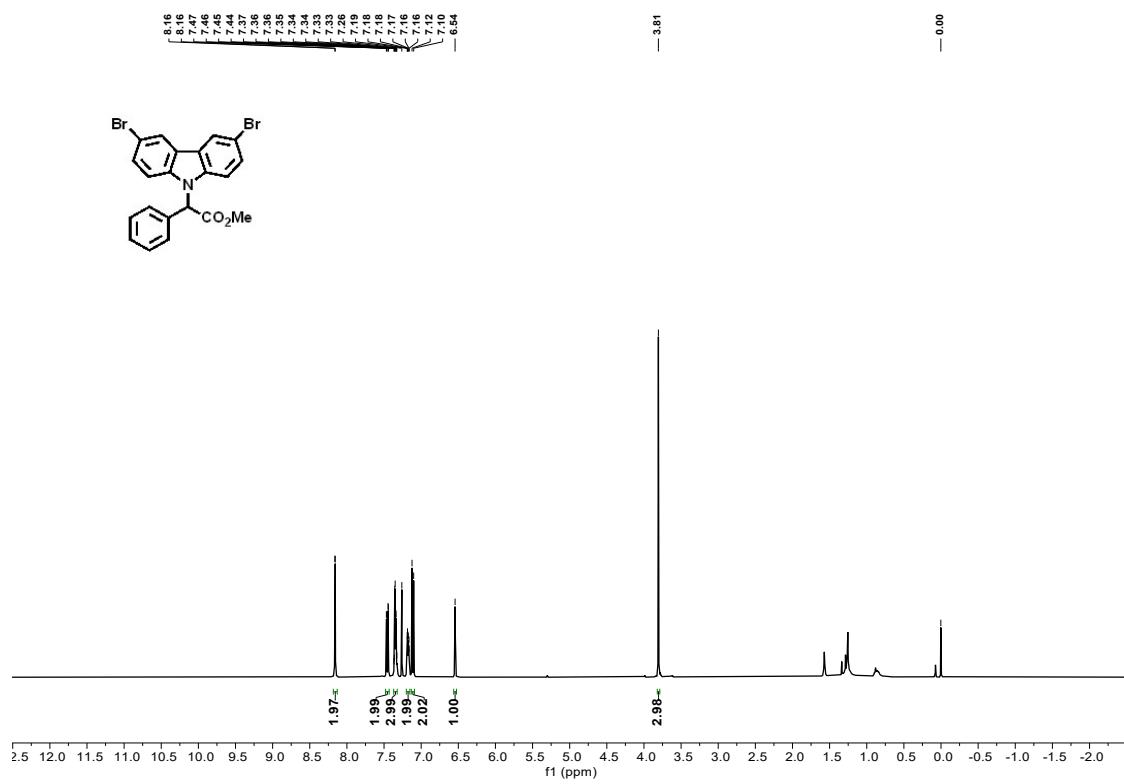
<sup>1</sup>H NMR-spectrum (400 MHz, CDCl<sub>3</sub>) of 3i.



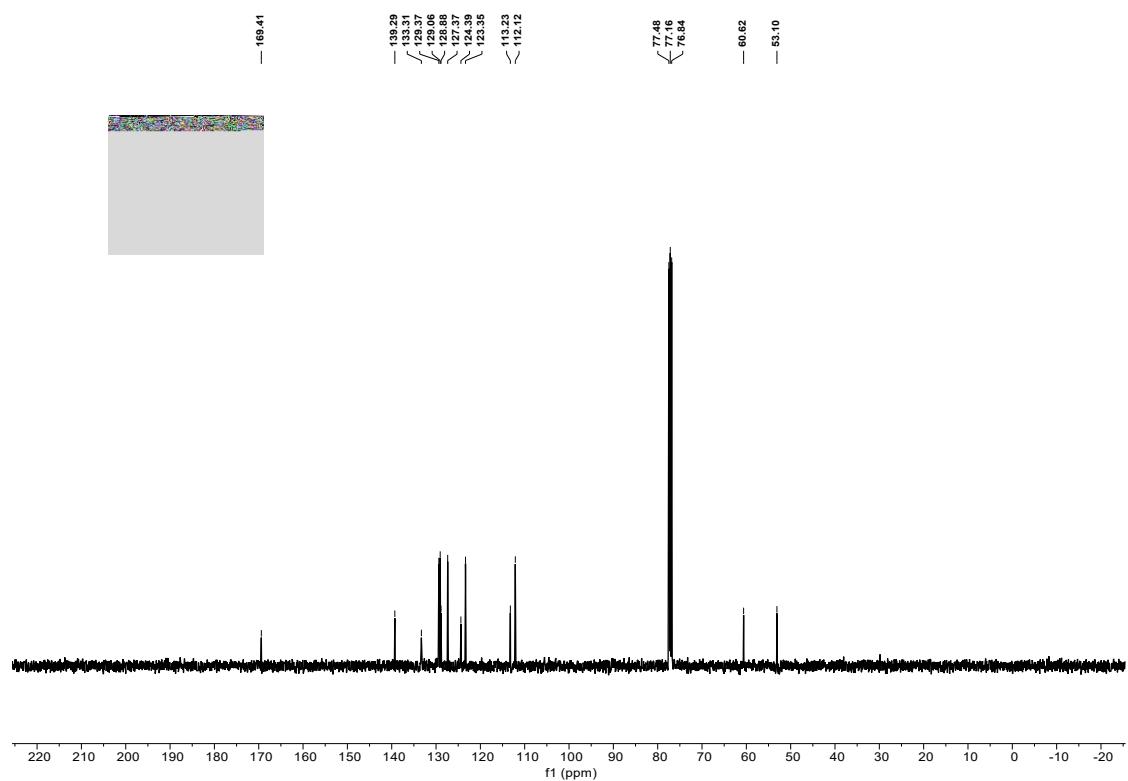
$^{13}\text{C}$  NMR-spectrum (100 MHz,  $\text{CDCl}_3$ ) of 3i.



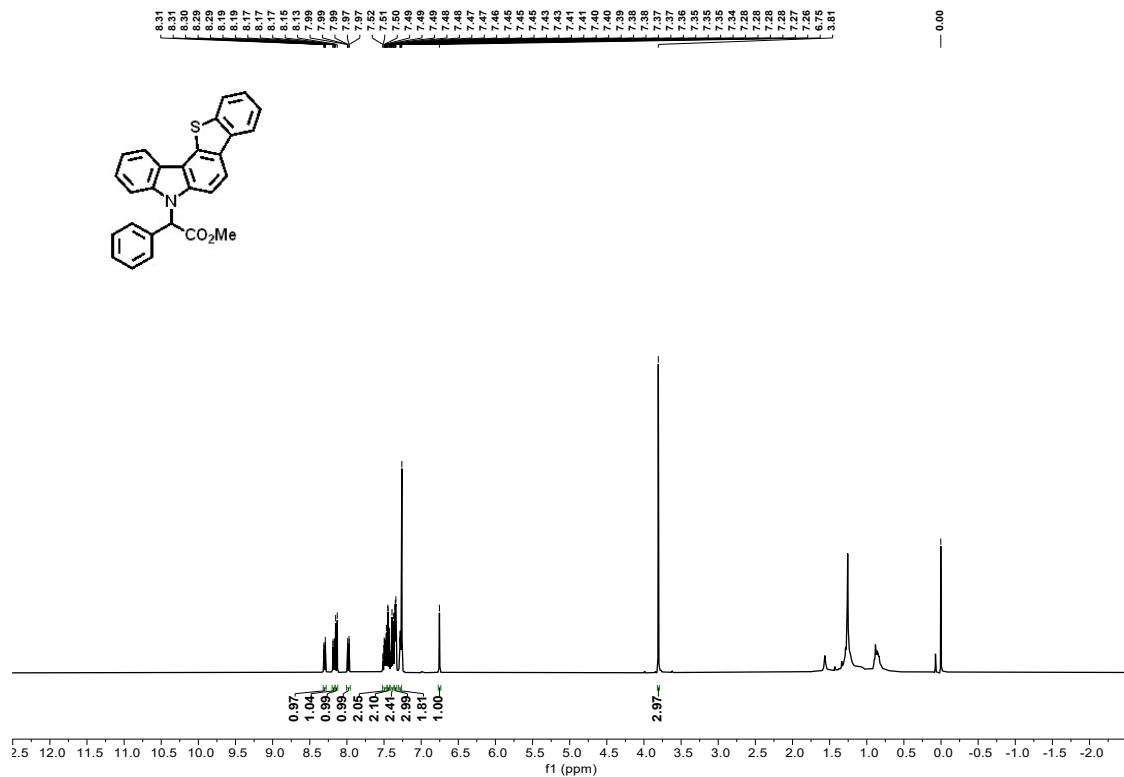
$^1\text{H}$  NMR-spectrum (400 MHz,  $\text{CDCl}_3$ ) of 3j.



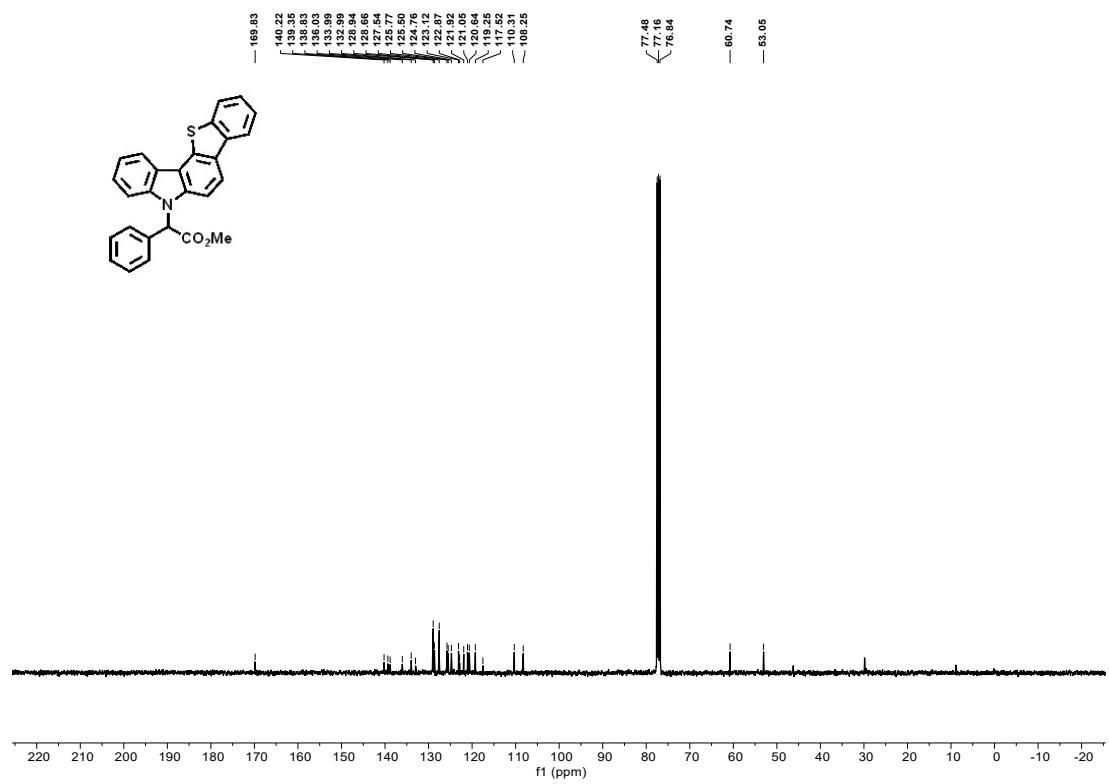
$^{13}\text{C}$  NMR-spectrum (100 MHz,  $\text{CDCl}_3$ ) of 3j.



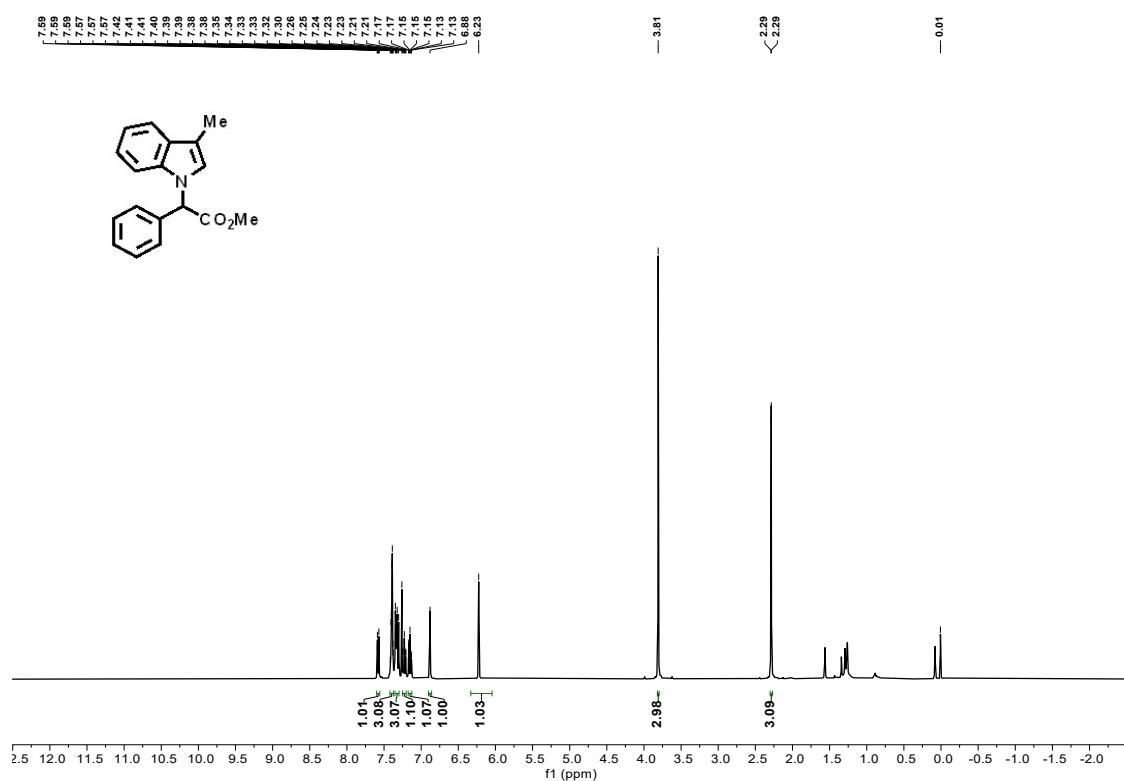
$^1\text{H}$  NMR-spectrum (400 MHz,  $\text{CDCl}_3$ ) of 3k.



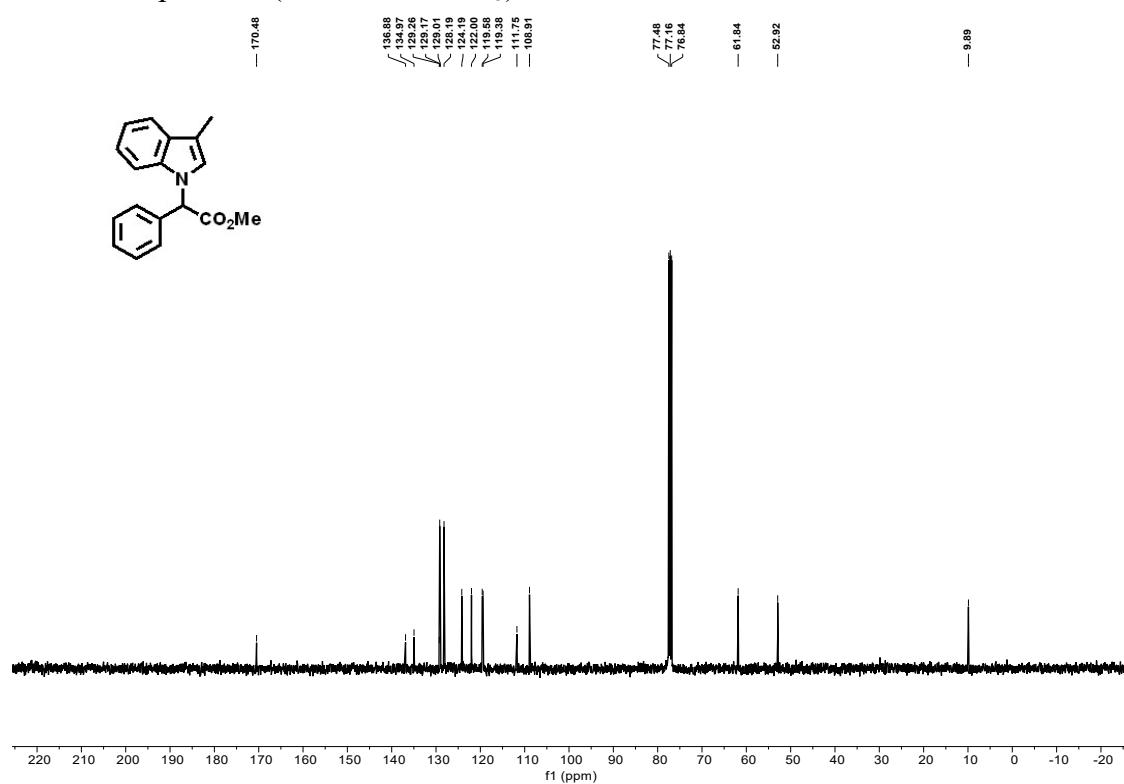
<sup>13</sup>C NMR-spectrum (100 MHz, CDCl<sub>3</sub>) of 3k.



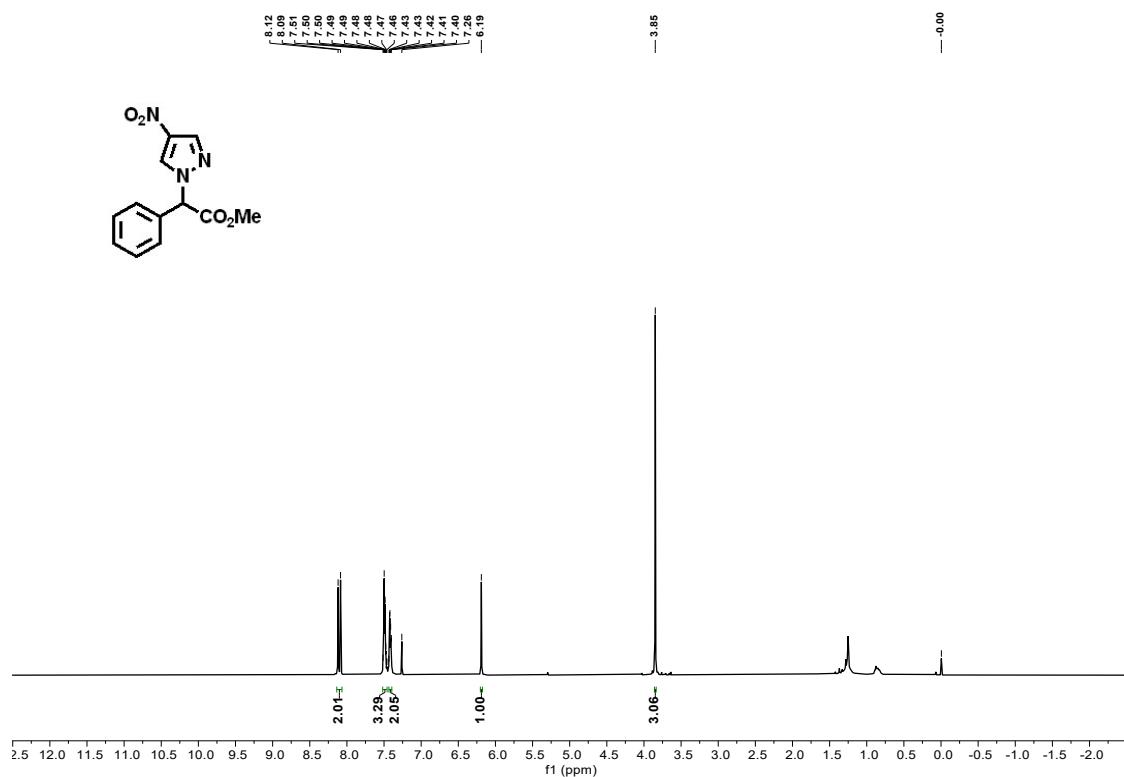
<sup>1</sup>H NMR-spectrum (400 MHz, CDCl<sub>3</sub>) of 31.



<sup>13</sup>C NMR-spectrum (100 MHz, CDCl<sub>3</sub>) of 31.



<sup>1</sup>H NMR-spectrum (400 MHz, CDCl<sub>3</sub>) of 3m.



<sup>13</sup>C NMR-spectrum (100 MHz, CDCl<sub>3</sub>) of 3m.

