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Visible Light Induced Metal-Free Carbene *N*-Carbazolation

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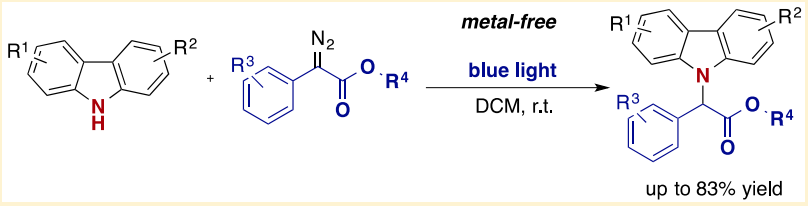
Supporting Information



ABSTRACT: Metal-free N−H functionalization reactions represent an important strategy for sustainable C−N coupling reactions. In this report, we describe the visible light photolysis of aryl diazoacetates in the presence of some *N*-heterocycles that enables mild, metal-free N−H functionalization reactions of carbazole and azepine heterocycles (15 examples, up to 83% yield).

Palladium, copper, or even iron catalysts have been utilized to enable the (enantioselective) insertion of carbenes into the N−H bond of carbazoles (Scheme 1) to yield *N*-functionalized carbazoles.[1,2] Although highly efficient, the limitations of these methods lie in the necessity of high catalyst loadings, the application of expensive ligands, and weakly coordinating anions (i.e., BAr^F), which impacts the atom efficiency of the overall process.[3] *N*-Functionalized carbazoles are particularly important as biologically active compounds and pharmaceuticals,[4] and are of prime interest in the fields of organic materials and polymers (Figure 1).[5] A broad array of synthetic methods exist to either *de novo* synthesize functionalized carbazole scaffolds,[6] or to selectively introduce new functional groups onto an appropriately prefunctionalized carbazole ring. The direct functionalizations of C−H or N−H bonds of the parent heterocycle via cross-dehydrogenative coupling, C−H activation, or the direct insertion of highly reactive carbenes or radicals are examples that allow the most atom-economic strategy to decorate the carbazole framework and is thus of major interest in organic synthesis.[7]

Metal-free carbene transfer reactions[8] represent a long-standing challenge in synthetic methodology, and typical approaches involve e.g. the UV photolysis[9] or the thermolysis of diazoalkanes,[10] yet with limitations to substrate scope and/or applicability. Only recently, the visible light photolysis of diazoalkanes[8,11−14] attracted the interest of synthetic chemists and is currently emerging as an attractive pathway toward sustainable carbene transfer reactions. This methodology now enables the selective photolysis of diazoalkanes in the presence of noncolored substrates under mild reaction conditions while other reaction partners and/or products remain untouched. In the past year, different groups reported on their efforts in metal-free cycloaddition,[11,12] rearrangement,[12,13] esterification,[11] N−H functionalization of basic amines,[11] or olefination reactions.[14] Indole was reported to undergo an efficient C−H functioanlization reaction with aryldiazoacetates under photochemical conditions.[11] In this context, the development of a (metal-free) insertion reaction of a carbene fragment into the N−H bond of carbazoles would open up new pathways to valuable compounds or late stage functionalization of well-known drugs (Scheme 1). In view of our interest in modern synthetic methods revolving around the strategic carbazole structure[7] and carbene transfer reactions,[12,13,15] we envisioned a metal-free synthetic scenario for the N−H functionalization of heterocycles via the visible light photolysis of diazoalkanes, which would avoid the usual transition metal complexes, ligands, and additives.

In a first step the model reaction of carbazole **4a** with methyl phenyldiazoacetate (**5a**) was investigated. Different solvents, concentrations, and equivalents were tested, to optimize the reaction conditions (Table 1). We identified DCM as a suitable solvent and verified that neither increasing nor decreasing the reaction concentration improved the yield (entries 13−14). Moreover, an excess of the diazo coupling partner was beneficial to the yield. The change to a slow addition protocol increased the yield slightly (entry 12). Importantly, no reaction was observed when the reaction mixture is kept in the dark (entry 15). Notably, in all reactions, exclusive N−H functionalization occurred and the product of a formal C−H functionalization was not observed.

With these very simple optimized conditions in hand (Table 1, entry 4), we next explored the functional group tolerance on both the carbazole **4** and the diazoalkane **5** (Scheme 2). Different phenyl diazoacetates were compatible with the optimized reaction conditions, and the N−H functionalization products were obtained in moderate to good yields (Scheme 2). Furthermore, diverse functional groups were tolerated, notably a number of halides (X = F, Cl, Br), leaving the possibility for further functionalization reactions. Notably, no

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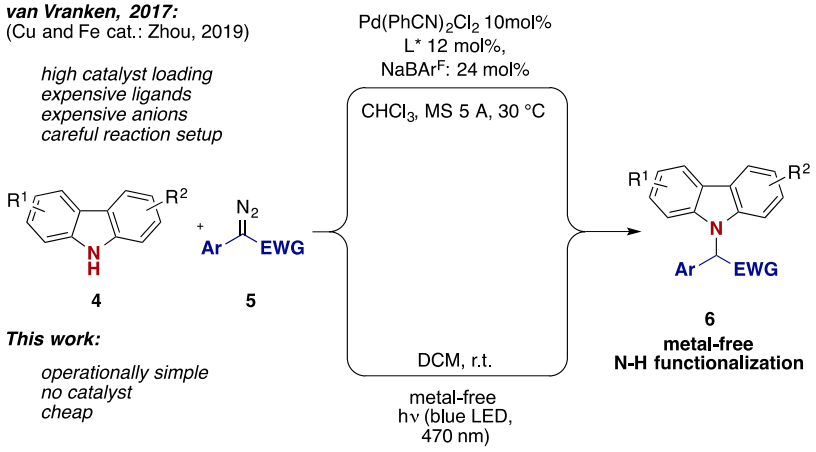
Scheme 1. Carbene *N*-Carbazolation



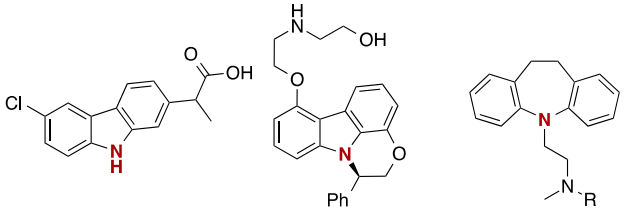
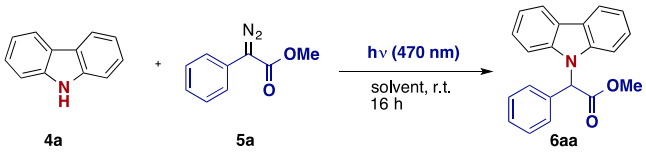


Figure 1. Bioactive compounds based on carbazole and dibenzoazepine.

Table 1. Reaction Optimization

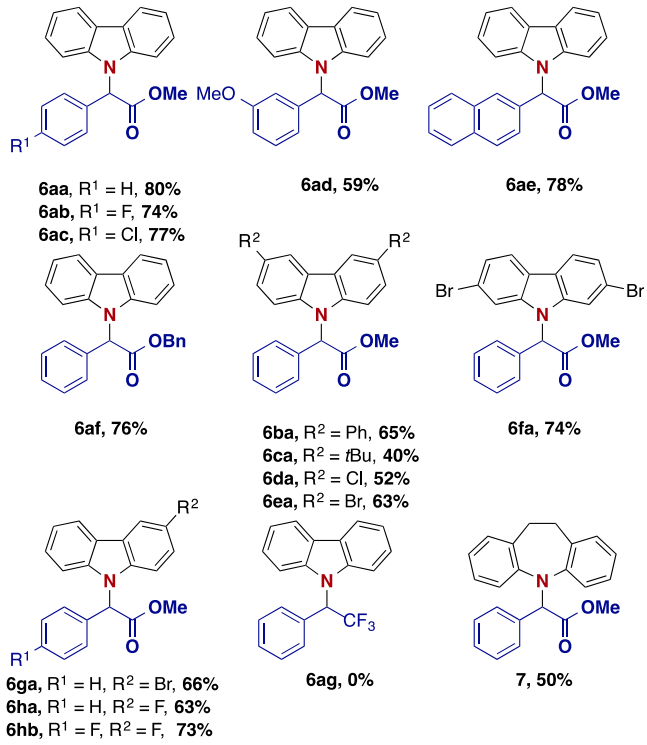


no.[a]	solvent	4a:5a ratio	other	yield (%)
1	toluene	1:2		50
2	*n*-hexane	1:2		24
3	$CHCl_3$	1:2		68
4	DCM	1:2		80
5	1,2-DCE	1:2		73
6	EtOAc	1:2		67
7	CH_3CN	1:2		69
8	THF	1:2		67
9	DCM	1:4		60
10	DCM	1:1		76
11	DCM	2:1		55
12[b]	DCM	1:2	slow add.	83
13	DCM	1:2	0.5 mL	76
14	DCM	1:2	2 mL	71
15[c]	DCM	1:2	dark	*no reaction*

[a]Reaction conditions: **4a** (0.4 mmol) and **5a** (0.8 mmol) were dissolved in 1 mL of solvent and were irradiated at room temperature with blue LEDs (1 W, 470 nm) overnight (16 h). [b]**4a** and **5a** were each dissolved in 0.5 mL of DCM, **5a** being slowly added over the course of 6 h by a syringe pump, under otherwise identical conditions. [c]The reaction mixture was stirred in the dark.

product formation was observed when changing the diazo compound to (1-diazo-2,2,2-trifluoroethyl)benzene. In a last

Scheme 2. Reaction Scope



step mono- and disubstituted carbazole derivatives were investigated, and the corresponding insertion products were isolated in moderate to good yield. To our delight 10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine, an important bioactive antidepressant drug precursor[16] showed promising reactivity (product **7**, 50%).

When using the *N*-methyl carbazole **8**, only the decomposition reaction of the diazoalkane, e.g. to the corresponding diazine, was observed and not even trace amounts of the C−H insertion reaction did occur under the optimized reaction conditions (Scheme 3a), which underlines the different reactivities of light-mediated and metal-catalyzed carbene transfer reactions.[1,12b] When changing the substrate from carbazole to diphenylamine **9**, no N−H insertion reaction was observed, which might be attributed to steric hindrance caused by the two phenyl rings.

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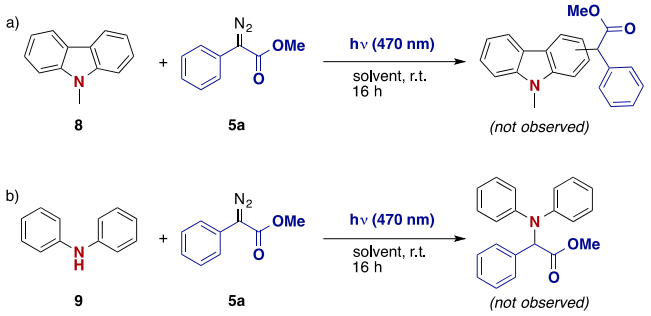
Scheme 3. Reaction with (a) *N*-Protected Carbazole and (b) Diphenylamine



Finally, we monitored the conversion of the starting materials **4h** and **5b**, and the formation of the N−H insertion product (**6hb**) over time, by means of ^{19}F NMR. The insertion reaction is almost complete within the first 2 h for those two substrates. Moreover, the excess of the diazo coupling partner disappears in about the same time, highlighting the competing decomposition processes (e.g., diazine formation) at play of the carbene intermediate and/or diazoalkane (Figure 2).

In summary, we reported on a metal-free insertion reaction of carbenes into the N−H bond of carbazoles, induced by low-energy blue light. The simple reaction protocol allows the direct functionalization of the carbazole backbone without the exclusion of moisture or air. This blue light induced reactivity certainly represents an important step in the field of metal-free intermolecular C−N bond forming reactions,[17] for possible applications in drug synthesis. Indeed, we expect it will inspire the development of future photochemical C−N bond forming methods.

EXPERIMENTAL SECTION

All commercially available compounds were used without further purification; chemicals were purchased from Fluorochem, TCI, Sigma-Aldrich, and Alfa Aesar. Solvents used for reactions were p.A. grade, and solvents for column chromatography were technical grade and distilled before use; solvent mixtures are understood as volume/volume.

^{1}H, ^{19}F, and ^{13}C NMR were recorded on a Varian AV600/AV400 or an Agilent DD2 400 NMR spectrometer in $CDCl_3$. HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization or on a Finnigan MAT 95 using EI ionization at 70 eV. IR spectra were recorded on a PerkinElmer-100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Syringe pump: Chemyx Inc. Model Fusion 710. LEDs used in this manuscript were purchased from Conrad Electronics: High Power LED-Module, 1 W, 23 lm, 10°, 470 nm, art.nr. 180711-62. Reactions were irradiated from 1.5 cm, the temperature was room temperature, and cooling was realized with a fan.

Important Safety Note. Handling of diazo compounds should only be done in a well-ventilated fume cupboard using an additional blast shield. No incidents occurred during the preparation of this manuscript, yet the reader should be aware of the carcinogenicity and explosiveness of the herein described diazo compounds. General safety precautions when working with diazo compounds should be followed. Any reactions described in this manuscript should not be performed without strict risk assessment and proper safety precautions.

Synthesis of Diazoalkanes. The aryldiazoacetates **5a**,[18] **5b**,[18] **5c**,[18] **5d**,[19] **5e**,[19] and **5f**[19] were prepared according to literature procedures. (1-Diazo-2,2,2-trifluoroethyl)benzene (**5g**) was prepared according to literature procedures.[20]

General Reaction Procedure. In a reaction tube carbazole **4** (0.4 mmol, 1.0 equiv) and diazo compound **5** (0.8 mmol, 2.0 equiv) were dissolved in 1.0 mL of DCM. The reaction mixture was irradiated with blue LEDs (470 nm; 1 W) overnight (16 h) at room temperature. The product was purified by column chromatography; eluent: *n*-hexane/EtOAc = 40:1 → 20:1. Solid products were recrystallized using *n*-pentane as solvent.

Procedure for Kinetic Measurements. For the kinetic measurements, carbazole **4b** (0.1 mmol, 18.5 mg, 1.0 equiv) and diazo compound **5g** (0.2 mmol, 38.8 mg, 2.0 equiv) were dissolved in 1.0 mL of DCM. Hexafluorobenzene (0.0167 mmol, 1.93 μL, 0.0167 equiv) was added as an internal standard. The reaction mixture was irradiated with blue LEDs (470 nm; 1 W) for different reaction times. The amounts of product **6gb**, the carbazole **4b**, and the diazo compound **5g** were then determined by ^{19}F NMR spectroscopy of the crude reaction mixture and quantified against the internal standard.

*Methyl 2-(9H-Carbazol-9-yl)-2-phenylacetate (**6aa**).* Compound **6aa** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 40:1 → 20:1) as a colorless solid in 80% yield (101.3 mg). ^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.16−8.07 (m, 2H), 7.39−7.35 (m, 2H), 7.35−7.31 (m, 3H), 7.29−7.21 (m, 6H), 6.63 (s, 1H), 3.78 (s, 3H) ppm. ^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*): δ = 169.8, 140.2, 134.0, 128.7, 128.4, 127.4, 125.8, 123.6, 120.3, 119.8, 110.2, 60.29*, 60.26*, 52.8 ppm. *Peaks belong to one Carbon; indication of two different conformers. Data according to literature.[1]

*Methyl 2-(9H-Carbazol-9-yl)-2-(4-fluorophenyl)acetate (**6ab**).* Compound **6ab** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 40:1 → 20:1) as a colorless solid in 74% yield (98.2 mg). ^{1}H NMR

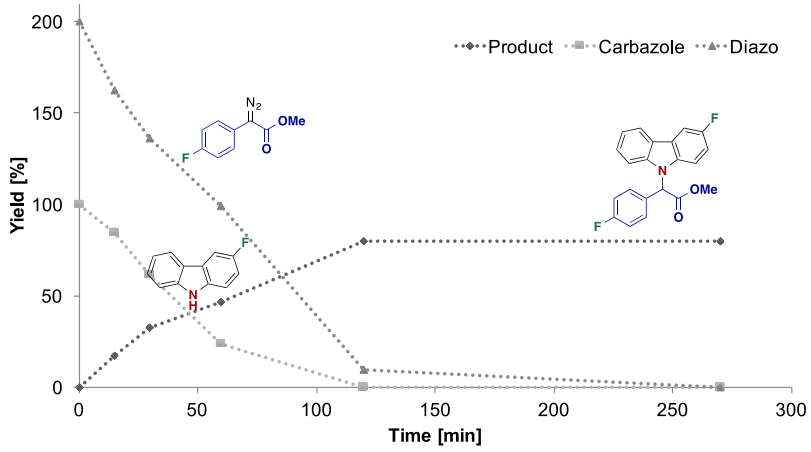


Figure 2. ^{19}F NMR conversion of **4h** and **5b** as well as formation of **6hb** over time, with hexafluorobenzene as the internal standard.

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(600 MHz, Chloroform-*d*): δ = 8.12 (dq, *J* = 7.8, 1.0 Hz, 2H), 7.38 (ddt, *J* = 8.3, 7.2, 1.2 Hz, 2H), 7.28−7.16 (m, 6H), 7.09−6.92 (m, 2H), 6.56 (s, 1H), 3.77 (d, *J* = 1.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*): δ = 169.6, 162.5 (d, *J* = 247.3 Hz), 139.9, 129.7 (d, *J* = 2.5 Hz), 129.21 (d, *J* = 8.2 Hz), 125.8, 123.5, 120.3, 119.8, 115.6 (d, *J* = 21.8 Hz), 109.9, 59.5, 52.8 ppm. ^{19}F NMR (564 MHz, Chloroform-*d*): δ = −113.5 ppm. HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{16}NFO_2Na^+$ 356.1057; Found 356.1057. IR (KBr): 3424, 3079, 2955, 2328, 2209, 2160, 2114, 2014, 1897, 1717, 1600, 1509, 1452, 1380, 1331, 1270, 1208, 1160, 1106, 1071, 1038, 1006, 932, 901, 838, 806, 747, 676 cm^{-1}.

Methyl 2-(9H-Carbazol-9-yl)-2-(4-chlorophenyl)acetate (**6ac**). Compound **6ac** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 40:1 → 20:1) as a colorless solid in 77% yield (108 mg). ^1H NMR (600 MHz, Chloroform-*d*): δ = 8.12 (dd, *J* = 7.7, 1.0 Hz, 2H), 7.38 (ddt, *J* = 8.1, 7.1, 0.9 Hz, 2H), 7.30−7.27 (m, 4H), 7.25−7.22 (m, 2H), 7.19−7.15 (m, 2H), 6.55 (s, 1H), 3.76 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*): δ = 169.4, 139.9, 134.2, 132.4, 128.8, 128.7, 125.9, 123.5, 120.3, 119.95, 109.92, 59.5, 52.9 ppm. HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{16}NClO_2Na^+$ 372.0761; Found 372.0766. IR (KBr): 3820, 3478, 3057, 2950, 2839, 2658, 2476, 2316, 2223, 2176, 2075, 2022, 1899, 1744, 1595, 1485, 1447, 1334, 1195, 1085, 999, 931, 888, 825, 748 cm^{-1}.

Methyl 2-(9H-Carbazol-9-yl)-2-(3-methoxyphenyl)acetate (**6ad**). Compound **6ad** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 40:1 → 20:1) as a colorless solid in 59% yield (81.1 mg). ^1H NMR (400 MHz, Chloroform-*d*): δ = 8.16−8.00 (m, 2H), 7.36 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 2H), 7.30−7.15 (m, 5H), 6.91−6.75 (m, 3H), 6.57 (s, 1H), 3.76 (s, 3H), 3.68 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*): δ = 169.6, 159.8, 140.2, 135.5, 129.7, 125.7, 123.6, 120.2, 119.7, 119.6, 113.6, 113.4, 110.2, 60.2, 55.2, 52.7 ppm. HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{22}H_{19}NO_3Na^+$ 368.1257; Found 368.1256. IR (KBr): 3852, 3504, 3048, 2981, 2942, 2837, 2660, 2316, 2170, 2072, 1984, 1873, 1756, 1596, 1484, 1448, 1386, 1336, 1291, 1257, 1159, 1051, 994, 933, 875, 803, 749 cm^{-1}.

Methyl 2-(9H-Carbazol-9-yl)-2-(naphthalen-2-yl)acetate (**6ae**). Compound **6ae** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 40:1 → 20:1) as a colorless solid in 78% yield (112 mg). ^1H NMR (600 MHz, Chloroform-*d*): δ = 8.14 (dt, *J* = 7.8, 0.9 Hz, 2H), 7.84−7.79 (m, 1H), 7.79−7.73 (m, 3H), 7.52−7.46 (m, 2H), 7.35 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 5H), 7.32−7.23 (m, 2H), 6.77 (s, 1H), 3.82 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*): δ = 169.8, 140.2, 132.98, 132.97, 131.4, 128.6, 128.2, 127.6, 126.5, 126.4, 126.3, 125.8, 125.1, 123.6, 120.2, 119.8, 110.1, 60.4, 52.8 ppm. HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{25}H_{20}NO_2^+$ 366.1488; Found 366.1475. IR (KBr): 3443, 3058, 2930, 2670, 2339, 2159, 2021, 1922, 1724, 1597, 1437, 1380, 1328, 1241, 1168, 1122, 1012, 953, 900, 860, 815, 744 cm^{-1}.

Benzyl 2-(9H-Carbazol-9-yl)-2-phenylacetate (**6af**). Compound **6af** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 40:1 → 20:1) as a red oil in 76% yield (119 mg). ^1H NMR (400 MHz, Chloroform-*d*): δ = 8.13−8.05 (m, 2H), 7.36−7.16 (m, 14H), 7.17−7.05 (m, 2H), 6.63 (s, 1H), 5.20 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*): δ = 169.1, 140.2, 134.9, 133.9, 128.6, 128.4, 128.32, 128.30, 128.2, 127.4, 125.7, 123.6, 120.2, 119.7, 110.3, 67.5, 60.5 ppm. HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{27}H_{21}NO_2Na^+$ 414.1464; Found 414.1467. IR (KBr): 3467, 3050, 2950, 2667, 2327, 2162, 1890, 1741, 1596, 1485, 1450, 1383, 1330, 1162, 1068, 970, 845, 809, 736 cm^{-1}.

Methyl 2-(3,6-Diphenyl-9H-carbazol-9-yl)-2-phenylacetate (**6ba**). Compound **6ba** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 40:1 → 20:1) as a colorless solid in 65% yield (122 mg). ^1H NMR (600 MHz, Chloroform-*d*): δ = 8.37 (d, *J* = 1.6 Hz, 2H), 7.73−7.69 (m, 4H), 7.63 (dd, *J* = 8.5, 1.9 Hz, 2H), 7.50−7.44 (m, 4H), 7.38−7.28 (m, 9H), 6.66 (s, 1H), 3.83 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*): δ = 169.7, 141.7, 140.1, 133.8, 133.4, 128.8, 128.7, 128.5, 127.4, 127.2, 126.6, 125.5, 124.2, 118.8, 110.5, 60.5, 52.8 ppm. HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{33}H_{25}NO_2Na^+$ 490.1777; Found 490.1770. IR (KBr): 3477, 3031, 2924, 2853, 2250, 2154, 1957, 1878, 1744, 1601, 1474, 1384, 1340 1270, 1201, 1163, 1073, 1004, 906, 882, 840, 811, 759, 730, 696, 658 cm^{-1}.

Methyl 2-(3,6-Di-tert-butyl-9H-carbazol-9-yl)-2-phenylacetate (**6ca**). Compound **6ca** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 80:1 → 40:1) as a colorless solid in 40% yield (67.6 mg). ^1H NMR (600 MHz, Chloroform-*d*): δ = 8.13−8.04 (m, 2H), 7.40 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.35−7.30 (m, 3H), 7.26 (s, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 6.56 (s, 1H), 3.77 (s, 3H), 1.44 (s, 18H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*): δ = 169.9, 142.4, 138.6, 134.3, 128.6, 128.2, 127.5, 123.4, 123.3, 116.1, 109.4, 60.3, 52.6, 34.6, 31.9 ppm. HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{29}H_{33}NO_2Na^+$ 450.2403; Found 450.2402. IR (KBr): 3418, 3057, 2956, 2905, 2868, 2323, 2168, 2124, 2034, 1952, 1874, 1743, 1691, 1604, 1473, 1388, 1360, 1327, 1296, 1260, 1291, 1166, 1106, 1057, 1031, 1003, 903, 878, 840, 806, 735, 696 cm^{-1}.

Methyl 2-(3,6-Dichloro-9H-carbazol-9-yl)-2-phenylacetate (**6da**). Compound **6da** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 40:1 → 20:1) as a colorless solid in 58% yield (88.8 mg). ^1H NMR (600 MHz, Chloroform-*d*): δ = 8.00 (d, *J* = 2.1 Hz, 2H), 7.37−7.30 (m, 5H), 7.21−7.16 (m, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.54 (s, 1H), 3.80 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*): δ = 169.2, 139.0, 133.2, 128.8, 128.7, 127.2, 126.5, 125.7, 123.8, 120.1, 111.5, 60.5, 52.8 ppm. Data according to literature.[1]

Methyl 2-(3,6-Dibromo-9H-carbazol-9-yl)-2-phenylacetate (**6ea**). Compound **6ea** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 40:1 → 20:1) as a colorless solid in 63% yield (120 mg). ^1H NMR (600 MHz, Chloroform-*d*): δ = 8.16 (d, *J* = 2.0 Hz, 2H), 7.45 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.39−7.30 (m, 3H), 7.21−7.14 (m, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.54 (s, 1H), 3.80 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*): δ = 169.2, 139.1, 133.1, 129.2, 128.9, 128.7, 127.2, 124.2, 123.2, 113.0, 111.9, 60.5, 52.9 ppm. HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{15}Br_2NO_2Na^+$ 493.9361; Found 493.9361. IR (KBr): 3470, 3201, 3063, 2951, 2847, 2654, 2520, 2335, 2193, 2110, 1972, 1903, 1861, 1823, 1742, 1592, 1469, 1434, 1380, 1332, 1280, 1204, 1172, 1112, 1054, 1007, 981, 944, 903, 863, 826, 790, 732, 696 cm^{-1}.

Methyl 2-(2,7-Dibromo-9H-carbazol-9-yl)-2-phenylacetate (**6fa**). Compound **6fa** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 40:1 → 20:1) as a colorless solid in 74% yield (141 mg). ^1H NMR (600 MHz, Chloroform-*d*): δ = 7.93−7.87 (m, 2H), 7.41−7.32 (m, 7H), 7.22−7.18 (m, 2H), 6.49 (s, 1H), 3.84 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*): δ = 169.1, 141.1, 132.9, 128.9, 128.8, 127.3, 123.5, 122.0, 121.3, 119.8, 113.5, 60.5, 53.0 ppm. HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{15}NBr_2O_2Na^+$ 493.9361; Found 493.9360. IR (KBr): 3872, 3399, 2951, 2325, 2093, 1990, 1887, 1810, 1739, 1688, 1589, 1498, 1477, 1446, 1419, 1368, 1325, 1237, 1205, 1173, 1135, 1054, 994, 961, 889, 849, 796, 731, 698, 665 cm^{-1}.

Methyl 2-(3-Bromo-9H-carbazol-9-yl)-2-phenylacetate (**6ga**). Compound **6ga** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 40:1 → 20:1) as a colorless solid in 66% yield (104 mg). ^1H NMR (600 MHz, Chloroform-*d*): δ = 8.21 (d, *J* = 2.0 Hz, 1H), 8.07−8.04 (m, 1H), 7.43−7.38 (m, 2H), 7.35−7.32 (m, 3H), 7.31−7.26 (m, 2H), 7.22−7.19 (m, 2H), 7.07 (d, *J* = 8.7 Hz, 1H), 6.58 (s, 1H), 3.79 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*): δ = 169.4, 140.6, 138.7, 133.5, 128.7, 128.5, 128.3, 127.3, 126.5, 125.4, 122.9, 122.5, 120.4, 120.2, 112.6, 112.0, 110.0, 60.3, 52.8 ppm. Data according to literature.[1]

Methyl 2-(3-Fluoro-9H-carbazol-9-yl)-2-phenylacetate (**6ha**). Compound **6ha** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc

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40:1 → 20:1) as a colorless oil in 63% yield (83.6 mg). ^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.06 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.75 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.40 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.36−7.33 (m, 3H), 7.31−7.24 (m, 2H), 7.24−7.21 (m, 2H), 7.14−7.11 (m, 1H), 7.07 (td, *J* = 9.0, 2.6 Hz, 1H), 5.30 (s, 1H), 3.79 (s, 3H) ppm. ^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*): δ = 169.6, 157.6 (d, *J* = 236.9 Hz), 141.1, 136.3, 133.8, 128.7, 128.4, 127.3, 126.3, 124.2 (d, *J* = 9.3 Hz), 123.1 (d, *J* = 4.1 Hz), 120.5, 119.7, 113.4 (d, *J* = 25.3 Hz), 111.1 (d, *J* = 8.9 Hz), 110.1, 105.9 (d, *J* = 23.8 Hz), 60.4, 52.7 ppm. ^{19}F NMR (564 MHz, Chloroform-*d*): δ = −124.2 ppm. HRMS (ESI) *m*/*z*: [M + Na]$^+$ Calcd for $C_{21}H_{16}NFO_2Na^+$ 356.1058; Found 356.1057. IR (KBr): 3418, 3059, 2951, 2849, 2661, 2329, 2086, 1739, 1592, 1484, 1452, 1388, 1330, 1275, 1206, 1165, 1066, 1000, 868, 800, 736, 694 cm^{-1}.

*Methyl 2-(3-Fluoro-9H-carbazol-9-yl)-2-(4-fluorophenyl)acetate (**6hb**).* Compound **6hb** was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 40:1 → 20:1) as a yellow oil in 73% yield (103 mg). ^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.12−8.02 (m, 1H), 7.75 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.43−7.39 (m, 1H), 7.29−7.22 (m, 2H), 7.21−7.16 (m, 2H), 7.14−7.07 (m, 2H), 7.04−6.99 (m, 2H), 6.54 (s, 1H), 3.78 (s, 3H) ppm. ^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*): δ = 169.4, 162.5 (d, *J* = 247.9 Hz), 157.7 (d, *J* = 236.9 Hz), 141.0, 136.2, 129.5 (d, *J* = 3.4 Hz), 129.1 (d, *J* = 8.3 Hz), 126.5, 124.2 (d, *J* = 9.4 Hz), 123.1, 120.6, 119.9, 115.7 (d, *J* = 21.8 Hz), 113.5 (d, *J* = 25.3 Hz), 110.9 (d, *J* = 9.0 Hz), 109.9, 106.0 (d, *J* = 23.7 Hz), 59.7, 52.8 ppm. ^{19}F NMR (564 MHz, Chloroform-*d*): δ = −113.24, −124.00 ppm. HRMS (ESI) *m*/*z*: [M + Na]$^+$ Calcd for $C_{21}H_{16}NO_2F_2^+$ 352.1143; Found 352.1143. IR (KBr): 3787, 3465, 3055, 2954, 2670, 2323, 2110, 2001, 1892, 1744, 1604, 1509, 1486, 1455, 1386, 1328, 1276, 1227, 1163, 1067, 1003, 905, 860, 834, 800, 732 cm^{-1}.

*Methyl 2-(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)-2-phenylacetate (**7**).* Compound 7 was prepared according to the general procedure and was obtained after column chromatography (*n*-hexane/EtOAc 40:1 → 20:1) as a colorless solid in 50% yield (68.5 mg). ^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.58−7.51 (m, 2H), 7.24−7.20 (m, 2H), 7.19−7.14 (m, 1H), 7.12−7.06 (m, 2H), 6.99−6.94 (m, 4H), 6.90−6.82 (m, 2H), 5.93 (s, 1H), 3.49 (s, 3H), 3.32 (br, 4H) ppm. ^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*): δ = 171.8, 147.4, 136.2, 135.1, 129.9, 128.7, 128.4, 128.2, 126.0, 123.5, 120.6, 68.1, 52.39*, 52.36*, 31.6 ppm. HRMS (ESI) *m*/*z*: [M + Na]$^+$ Calcd for $C_{23}H_{22}NO_2^+$ 344.1645; Found 344.1650. IR (KBr): 3059, 2928, 2671, 2330, 2242, 2115, 1913, 1820, 1738, 1587, 1486, 1444, 1345, 1297, 1235, 1195, 1164, 1030, 991, 905, 815, 722 cm^{-1}. *Peaks belong to one carbon; indication of two different conformers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b01753.

Copies of NMR spectra, picture of the reaction setup (PDF)

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Notes

The authors declare no competing financial interest.

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