

Solid Phase Synthesis of Selectively Deuterated Arenes

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Experimental Section

Instrumentation and reagents: ^1H NMR spectra were recorded on *Bruker AM 250* (250 MHz), *Bruker AM 400* (400 MHz) and *Bruker AM 500* (500 MHz) spectrometers. Chemical shifts are expressed in parts per million (δ /ppm) downfield from tetramethylsilane (TMS) and are referenced to chloroform (7.26 ppm) or methanol[d_4] (3.31 ppm) as internal standard. All coupling constants are absolute values and J values are expressed in Hertz (Hz). The description of signals include: s = singlet, d = doublet, bd = broad doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet. The spectra were analyzed according to first order. ^{13}C NMR spectra were recorded on *Bruker AM 250* (62.5 MHz), *Bruker AM 400* (100 MHz) and *Bruker AM 500* (125 MHz) spectrometers. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to CDCl_3 (77.4 ppm) or methanol[d_4] (49.1 ppm) as internal standard. For measurement of ^{13}C NMR-Gel-Spectra, 60-100 mg of the resin were swollen in a NMR-tube with the appropriate amount of solvent. All ^{13}C NMR signals are given except of those that derive from the polystyrene resin. Some of the expected signals of the attached molecules are superimposed by the polystyrene core and can therefore not be clearly attributed. The NMR-spectrometer was run with pulse program zgpg30 (relaxation delay D1 = 0.2 seconds, linebroadening LB = 9.0 Hz, 5120 scans). MS (EI) (electron impact mass spectrometry): *Finnigan MAT 90* (70 eV). The molecular fragments are quoted as the relation between mass and charge (m/z), the intensities as a percentage value relative to the intensity of the base signal (100%). The abbreviation $[\text{M}^+]$ refers to the molecule ion. IR (infrared spectroscopy): FTIR *Bruker IFS 88*. IR spectra of solids were recorded in KBr, and as thin films on KBr for oils and liquids. ATR spectra were recorded by diamond crystal on *Bruker ALPHA-IR*. Raman spectra were recorded on *Bruker Optics MultiRam* (30 scans, 1064 nm, 100–150 mW). The deposit of the absorption band was given in wave numbers in cm^{-1} . The intensity of the bands were characterized as follows: vs = very strong 0-10% T, s = strong 11-40% T, m = medium 41-70% T, w = weak 71–90% T, vw = very weak 91–100% T. Routine monitoring of reactions was performed using silica gel coated aluminium plates (*Merck*, silica gel 60, F₂₅₄) which were analyzed under UV-light at 254 nm and/or dipped into a solution of molybdate phosphate (5% phosphor molybdic acid in ethanol, dipping solution) and heated with a heat gun. Solvent mixtures are understood as volume/volume. Solid materials were powdered. Solvents, reagents and chemicals were purchased from *Aldrich*, *Fluka*, *ABCR* and *Acros*. Solvents, reagents and chemicals were used as purchased unless stated otherwise. Merrifield Resin was purchased from *Polymer Laboratories* (PL-CMS resin 0.995 mmol/g, 75–150 μm , CMS 191). If not stated otherwise, vials from *Macherey-Nagel* were used for all

reactions beyond room temperature (size 20-20 and 20-10, in combination with N20 oA and N20 TB/oA-M septa).

General remarks:

¹³C NMR signals:

The intensities of carbon signals are very low for carbons that are directly connected to deuterium owing to the lower sensitivity compared to ¹H (disadvantageous gyromagnetic ratio: $\gamma(^1\text{H})/\gamma(^2\text{H}) \sim 6.5$ and accordingly $^1J(^{13}\text{C}, ^1\text{H}) \approx 6.5 \cdot ^1J(^{13}\text{C}, ^2\text{H})$.) and the lack of Nuclear Overhauser Enhancement from the proton broad-band decoupling. Due to the occurrence of these signals as broad triplet (C-D) or septet (OCD₃), they are often hard to detect. The signals of the deuterated carbons are not given in here because of this disadvantage of deuterated compounds (compound **4z**: to prove the twofold deuteration all ¹³C signals are given, including C-D and OCD₃). In all cases we supply complete analytic datasets that identify all compounds doubtlessly.

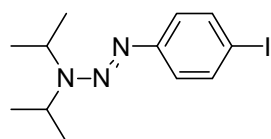
-Deuteration

If not otherwise stated, all purities were determined by mass spectroscopy

GP 1: Synthesis of diisopropyl triazenes in solution:

1.00 equiv. of aniline was dissolved in abs. THF (4 mL of THF for 1 mmol of aniline) at room temperature and 4.00 equiv. of BF₃•Et₂O were added. The mixture was cooled to -20 °C and stirring constantly, 3.50 equiv. of isoamyl nitrite were added dropwise. After 1 h at -20 °C the precipitate was filtered off, washed with cold diethyl ether, dissolved in acetonitrile, and then added to a solution of diisopropyl amine (1.00 equiv.), acetonitrile (5 mL MeCN for 1 mmol diisopropylamine) and pyridine (0.5 mL of pyridine for 1 mmol of diisopropyl amine) at -20 °C. After stirring for 48 h at room temperature water was added and the aqueous phase was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄, the solvent was removed under reduced pressure and the crude product was purified by column chromatography.

1-(4-Iodophenyl)-3,3-diisopropyltriaz-1-ene (precursor for triazene **1aa**):



2.86 g (13.1 mmol) of 4-iodoaniline were reacted with 1.83 mL (13.1 mmol) of diisopropylamine. Column chromatography (cyclohexane/ethyl acetate, 99:1) gave 1.53 g (4.63 mmol) of the

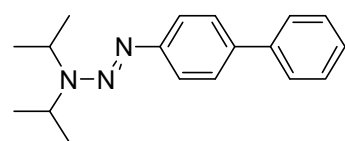
product as an orange solid in 35% yield. – R_f = 0.62 (cyclohexane/ethyl acetate, 20:1). – ¹H NMR (250 MHz, CDCl₃, ppm), δ = 1.30 (bs, 12 H), 3.62–4.44 (bs, 1 H), 4.79–5.58 (bs, 1 H),

7.13–7.19 (m, 2 H), 7.58–7.63 (m, 2 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 19.3–25.3 (bs, 4 C), 39.7–52.4 (bs, 2 C), 88.5, 122.3, 137.6, 151.4. – IR (DRIFT, ν): 2975, 2931, 2632, 1898, 1648, 1580, 1474, 1422, 1367, 1299, 1227, 1194, 1163, 1099. – EI (m/z): 331 (67) [M^+], 231 (95), 203 (100), 100 (60), 76 (47). – EA ($\text{C}_{12}\text{H}_{18}\text{N}_3$): calc. C 43.52, H 5.48, N 12.69; found C 43.98, H 5.43, N 12.60.

GP 2: Suzuki coupling in solution

1.00 equiv. of the triazene was dissolved in DMF and 1.50 equiv. of boronic acid, 1.50 equiv. of Na_2CO_3 as well as 0.044 equiv. of tetrakis triphenylphosphine palladium and 1.50 mL of H_2O were added. After stirring for 12 h at 80 °C, 5 mL of H_2O were added, the aqueous layer was extracted with CH_2Cl_2 three times, and the organic layer was dried over MgSO_4 and the crude product was purified by column chromatography.

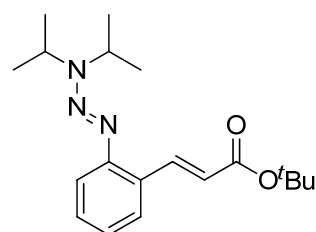
1-(Biphenyl-4-yl)-3,3-diisopropyltriaz-1-ene (1aa): According to GP 2, 350 mg of 1-(4-



iodophenyl)-3,3-diisopropyltriaz-1-ene (1.06 mmol, 1.00 equiv.) were reacted with 200 mg (1.50 mmol, 1.50 equiv.) of phenylboronic acid. Column chromatography (cyclohexane/ethyl

acetate, 50:1) gave 131 mg (0.46 mmol) of the target compound in 43% yield. – R_f = 0.48 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 1.34 (bd, 3J = 5.7 Hz, 12 H), 3.66–4.54 (bs, 1 H), 4.76–5.68 (bs, 1 H), 7.31–7.64 (m, 9 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 20.0–24.9 (bs, CH_3), 44.9–50.1 (bs, CH), 120.6 (CH), 126.7 (CH), 126.8 (CH), 127.5 (CH), 128.7 (CH), 137.4 (C), 141.2 (C), 151.0 (C). – EI (m/z): 281 (41) [M^+], 181 (31), 152 (100), 100 (35). – IR (ATR, $\tilde{\nu}$): 2974, 2930, 1599, 1511, 1482, 1449, 1396, 1379, 1364, 1306, 1270, 1224, 1162, 1147, 1130, 1027, 1005, 914, 844, 769, 758, 700 cm^{-1} . – EA ($\text{C}_{18}\text{H}_{23}\text{N}_3$): calc. C 76.83, H 8.24, N 14.93; found C 76.65, H 8.07, N 14.62.

***t*-Butyl-3-(2-(3,3-diisopropyltriaz-1-en-1-yl)phenyl)acrylate (1ab):** To a solution of 324 mg



(978 μmol) of 1-(2-iodophenyl)-3,3-diisopropyltriaz-1-ene in 5 mL of abs. THF were added 0.10 mL (72.6 mg, 0.73 equiv.) of triethylamine, 56.5 mg (4.89 mmol, 0.05 equiv.) of palladium-tetrakis(triphenylphosphine) and 128 mg (1.96 mmol, 2.00 equiv.) of *tert*-butyl acrylate. The mixture was stirred for 14 h at 120 °C, then

water was added, the aqueous layer was extracted three times with each 15 mL of ethyl

acetate, and the organic phase was dried over magnesium sulfate. Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 146 mg (0.441 mmol) of the target compound in 45% yield. – $R_f = 0.27$ (cyclohexane/ethyl acetate, 20:1). – $^1\text{H NMR}$ (250 MHz, CDCl_3 , ppm), $\delta = 1.31$ (bs, 6 H), 1.38 (bs, 6 H), 1.54 (s, 9 H), 4.02 (bs, 1 H), 5.24 (bs, 1 H), 6.39 (d, 1 H, $^3J = 16.2$ Hz), 7.10 (ddd, 1 H, $^3J = 7.9$ Hz, $^3J = 7.8$ Hz, $^4J = 1.2$ Hz), 7.26–7.33 (m, 1 H), 7.44 (dd, 1 H, $^3J = 8.2$ Hz, $^4J = 1.3$ Hz), 7.60 (dd, 1 H, $^3J = 7.9$ Hz, $^4J = 1.3$ Hz), 8.42 (d, 1 H, $^3J = 16.2$ Hz). – $^{13}\text{C NMR}$ (62.5 MHz, CDCl_3 , ppm), $\delta = 19.3$ (2 C), 23.8 (2 C), 28.2 (3 C), 46.8, 49.5, 79.8, 117.3, 119.5, 124.7, 126.7, 128.3, 130.3, 140.9, 149.9, 166.8. – IR (DRIFT, ν): 3067, 2977, 2929, 1697, 1619, 1595, 1568, 1477, 1456, 1409, 1379, 1362, 1299, 1254, 1227, 1197, 1157, 1127, 1103, 1036, 1003, 980, 890, 838, 785, 760, 740 cm^{-1} . – EI (m/z): 331 (13) [M^+], 231 (1), 147 (9), 119 (34), 100 (24), 91 (14), 57 (18), 43 (100). – HRMS ($\text{C}_{19}\text{H}_{29}\text{N}_3\text{O}_3$): calc. 331.2260, found 331.2258.

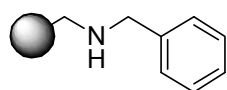
GP 3: Generation of D_3CO -derivatives in methanol

In a Crimptop vial the triazene is first evacuated and then flushed with nitrogen. Then methanol (1.0 mL/10 mg of triazene) and deuterated TFA (10 μL /10 mg of resin) are added. The vial is sealed, agitated for 14 h at 80 $^\circ\text{C}$, and then water is added and the aqueous phase extracted with ethyl acetate three times. The organic phase is concentrated *in vacuo* and the residue is purified by column chromatography.

General washing procedure for resins:

Using acetone the resins were transferred into a filter and subsequently washed according to the following procedure: (H_2O , THF, MeOH) 3 \times successive treatment, (CH_2Cl_2 , MeOH) 2 \times successive treatment, 2 \times CH_2Cl_2 .

***N*-Benzylaminomethyl polystyrene:** 40.0 g (loading: 0.995 mmol/g = 39.8 mmol, 1.00



equiv.) of Merrifield resin were swollen in 250 mL of abs. DMF. Then, 6.64 g (40.0 mmol, 1.00 equiv.) of KI and 43.7 mL (400 mmol, 10.0

equiv.) of benzyl amine were added. The mixture was shaken for 12 h at 80 $^\circ\text{C}$. The resin was filtered off the supernatant and then washed (according to washing procedure). After removal of the solvent *in vacuo* 39.7 g of benzylamine resin were obtained in quantitative yield (0.925 mmol/g). – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), $\delta = 53.2$, 125.8, 140.5. – IR (DRIFT, ν): 3647, 3618, 3324, 3161, 3032, 2846, 2603, 2336, 2311, 1944, 1871, 1803, 1746,

1721, 1669, 1601, 1494 cm^{-1} . – EA ($\text{C}_{83}\text{H}_{84}\text{N}$): calc. C 90.99, H 7.73, N 1.28; found C 89.78, H 7.62, N 1.10.

GP 4: Immobilization of anilines as triazene resin

The aniline (5.00 equiv.) was dissolved in THF, cooled to $-20\text{ }^{\circ}\text{C}$ and 7.50 equiv. of boron trifluoride diethyl etherate were added. Isoamyl nitrite (7.50 equiv.) was added under vigorous stirring and the mixture was stirred for another 2 h at $-20\text{ }^{\circ}\text{C}$. The residue was filtered off, washed with cold diethyl ether, dissolved in acetonitrile and added to the previously swollen *N*-benzylaminomethyl resin (1.00 equiv.) in THF/pyridine (9:1). The resin was allowed to warm slowly to room temperature and was shaken for 2 h at room temperature. The supernatant was filtered off, the resin was washed according to the general washing procedure, and was afterwards dried *in vacuo*.

Derivation of resin-bound triazenes:

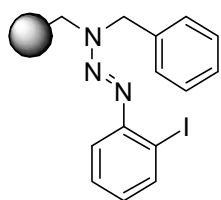
GP 5: Generation of *o*-diaryl ethers on solid supports

Under a nitrogen atmosphere 1.00 equiv. of the triazene resin, 5.00 equiv. of copper (I) bromide dimethyl sulfide complex and 6.00 equiv. of sodium carbonate were suspended in acetonitrile and pyridine, then 5.00 equiv. of the phenol were added. The vial was sealed and the mixture was shaken at $75\text{ }^{\circ}\text{C}$ for 48 h. After cooling down to room temperature the resin was first washed with water and then alternating with a solution of 5% of cupral (diethylaminodithiocarbamate in DMF) and acetone until the filtrate remained colorless. Then washing was continued following the general washing procedure and the resin was dried in high vacuum.

GP 6: Sonogashira coupling of immobilized aryl halogenides

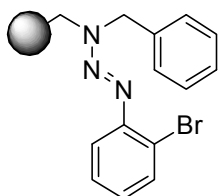
The aryl halogen resin (1.00 equiv.) was suspended in abs. DMF under a nitrogen atmosphere and was shaken for 30 minutes. Then at least 7.46 equiv. of the alkyne, 1.49 equiv. of NEt_3 , 0.746 equiv. of CuI as well as 0.0149 equiv. of tetrakis(triphenylphosphine) palladium were added. The mixture was degassed for 10 min, the vial was sealed and was shaken at $80\text{ }^{\circ}\text{C}$ for 48 h. The solvent was filtered off, the resin was washed according to the general washing procedure and was then dried in high vacuum.

3-Benzyl-(3-methylpolystyrene)-1-(2-iodophenyl)triaz-1-ene: According to GP 4, 2-



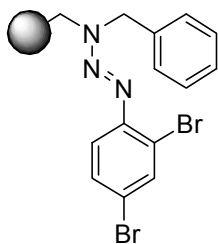
iodoaniline was immobilized on 3.00 g of *N*-benzylaminomethyl resin (2.78 mmol). After drying under high vacuum 3.95 g (2.78 mmol, 0.702 mmol/g) of the resin were obtained in quantitative yield. ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 48.7, 57.2, 97.0, 118.1, 139.4, 145.0. – IR (DRIFT, ν): 3583, 3034, 2856, 2337, 2312, 1945, 1878, 1805, 1748, 1723, 1600, 1529, 1494, 1349 cm^{-1} . Raman (60 mW, 1064 nm, ν): 3055, 2905, 2853, 1603, 1580, 1461, 1411, 1323, 1283, 1259, 1219, 1202, 1183, 1156, 1032, 1002, 796, 757, 622 cm^{-1} . – EA ($\text{C}_{90}\text{H}_{88}\text{N}_3$): calc. C 80.71, H 6.62, N 3.15; found C 80.54, H 6.7,3, N 2.63.

3-Benzyl-(3-methylpolystyrene)-1-(2-bromophenyl)triaz-1-ene: According to GP 4, 2-



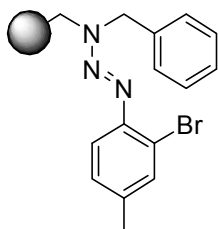
bromoaniline was immobilized on 6.00 g of *N*-benzylaminomethyl resin (5.55 mmol). After drying in high vacuum 6.90 g (4.94 mmol, 0.717 mmol/g) of the resin were obtained in 89% yield. – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 48.8, 57.3, 118.9, 133.3, 148.1. – Raman (60 mW, 1064 nm): 3057, 2907, 2853, 1677, 1602, 1476, 1443, 1413, 1327, 1236, 1216, 1183, 1156, 1033, 1002, 843, 796, 622 cm^{-1} . – EA ($\text{C}_{90}\text{H}_{88}\text{N}_3\text{Br}$): calc. C 83.66, H 6.86, N 3.27; found C 83.91, H 6.97, N 2.73.

3-Benzyl-(3-methylpolystyrene)-1-(2,4-dibromophenyl)triaz-1-ene: According to GP 4,



2,4-dibromoaniline was immobilized on 3.00 g of *N*-benzylaminomethyl resin (2.78 mmol). After drying in high vacuum 3.54 g (2.06 mmol, 0.581 mmol/g) of the resin were obtained in 74% yield. – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 48.9, 57.4, 118.7, 119.8, 125.8, 135.4, 147.2. – IR (ATR, $\tilde{\nu}$): 3059, 3025, 2918, 2849, 1601, 1492, 1449, 1375, 1347, 1153, 1076, 1028, 905, 816, 754, 695, 539 cm^{-1} . – Raman (60 mW, 1064 nm): 3056, 2914, 1603, 1573, 1461, 1447, 1417, 1376, 1251, 1223, 1185, 1133, 1082, 1033, 1003, 798 cm^{-1} . – EA ($\text{C}_{91}\text{H}_{90}\text{N}_3\text{Br}$): calc. C 83.68, H 6.94, N 3.23; found C 84.40, H 7.42, N 2.77.

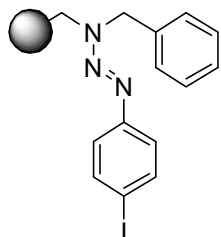
3-Benzyl-(3-methylpolystyrene)-1-(2-bromo-4-methylphenyl)triaz-1-ene: According to



GP 4, 2-bromo-4-methylaniline was immobilized on 3.00 g of *N*-benzylaminomethyl resin (2.78 mmol). After drying in high vacuum 3.23 g (1.19 mmol, 0.367 mmol/g) of the resin were obtained in 43% yield. – ^{13}C

Gel NMR (100 MHz, CDCl_3 , ppm), δ = 20.8. – Raman (60 mW, 1064 nm): 3055, 2908, 2848, 1602, 1584, 1483, 1449, 1426, 1389, 1264, 1225, 1184, 1155, 1031, 1003, 794 cm^{-1} . – IR (ATR, $\tilde{\nu}$): 3059, 3024, 2919, 2849, 1601, 1492, 1449, 1347, 1152, 1075, 1028, 981, 905, 818, 752, 695, 537 cm^{-1} . – EA ($\text{C}_{91}\text{H}_{90}\text{N}_3\text{Br}$): calc. C 83.68, H 6.94, N 3.23; found C 84.40, H 7.42, N 2.77.

3-Benzyl-(3-methylpolystyrene)-1-(4-iodophenyl)triaz-1-ene: According to GP 4, 4-



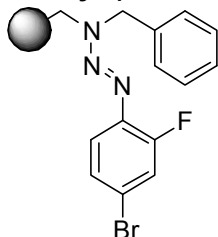
iodoaniline was immobilized on 6.00 g of *N*-benzylaminomethyl resin (5.55 mmol). After drying in high vacuum 6.57 g (2.48 mmol, 0.377 mmol/g) of the resin were obtained in 45% yield.

According to GP 4, 4-iodoaniline was immobilized on 9.00 g of *N*-benzylaminomethyl resin (8.33 mmol). After drying in high vacuum 10.3 g

(5.75 mmol, 0.557 mmol/g) of the resin were obtained in 69% yield.

– ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 25.8, 57.1, 68.1, 90.1, 113.7, 122.9, 138.0, 145.5, 150.3. – Raman (60 mW, 1064 nm, ν): 3055, 2906, 2853, 1603, 1582, 1479, 1447, 1425, 1391, 1322, 1268, 1218, 1182, 1162, 1057, 1031, 1002, 905, 842, 795, 622 cm^{-1} . – EA ($\text{C}_{90}\text{H}_{89}\text{IN}_3$): calc. C 80.69, H 6.70, N 3.14; found C 80.99, H 6.74, N 2.68.

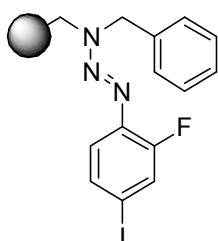
3-Benzyl-(3-methylpolystyrene)-1-(2-fluoro-4-bromophenyl)triaz-1-ene: According to GP



4, 2-fluoro-4-bromoaniline was immobilized on 9.00 g of *N*-benzylaminomethyl resin (8.33 mmol). After drying in high vacuum 10.0 g (5.18 mmol, 0.516 mmol/g) of the resin were obtained in 62% yield. –

^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 48.5, 57.2, 118.2, 120.1, 120.5, 125.9, 138.1, 155.2, 157.7. – IR (DRIFT, ν): 3650, 3650, 3589, 3029, 2903, 2337, 1944, 1873, 1804, 1746, 1721, 1670, 1602, 1542, 1492, 1156, 1114, 1068, 1029, 985, 942, 906, 855, 816, 708 cm^{-1} . – Raman (60 mW, 1064 nm, ν): 3055, 2901, 2852, 1596, 1481, 1448, 1425, 1400, 1323, 1251, 1226, 1202, 1183, 1156, 1116, 1068, 1031, 1002, 905, 798, 622 cm^{-1} . – EA ($\text{C}_{90}\text{H}_{87}\text{N}_3\text{FBr}$): calc. C 82.50, H 6.69, N 3.22; found C 81.77, H 6.73, N 2.64.

3-Benzyl-(3-methylpolystyrene)-1-(2-fluoro-4-iodophenyl)triaz-1-ene: According to GP 4,



2-fluoro-4-iodoaniline was immobilized on 2.34 g of *N*-benzylaminomethyl resin (2.17 mmol). After drying in high vacuum 2.78 g (1.76 mmol, 0.634

mmol/g) of the resin were obtained in 81% yield. – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 48.5, 57.4, 88.4, 120.9, 125.8, 133.4, 138.8, 155.1. – IR (DRIFT, ν): 3651, 3576, 3028, 2848, 2337, 2312, 1944, 1873, 1805, 1746, 1721, 1668, 1602, 1494, 1328, 1173, 1116, 1065, 1029, 907, 817, 708 cm^{-1} . – EA ($\text{C}_{90}\text{H}_{87}\text{N}_3\text{IF}$): calc. C 79.63, H 6.46, N 3.11; found C 80.35, H 6.64, N 2.51.

Resin 1a: According to GP 5, 500 mg of 3-benzyl-(3-methylpolystyrene)-1-(2-iodophenyl)triaz-1-ene (0.702 mmol/g, 351 μmol) were reacted with 1-methoxy-4-methylphenol in 4 mL of acetonitrile and 2 ml of pyridine. The resin was washed according to the washing procedure for diaryl ethers followed by the general washing procedure and was dried in high vacuum to give the product resin (0.697 mmol/g) in quantitative yield. – ^{13}C Gel NMR (100 MHz, CDCl_3): δ /ppm = 21.2, 56.1, 56.8, 113.5, 121.1, 126.4, 136.7, 142.2. – IR (ATR, ν): 3025, 2917, 2108, 1600, 1508, 1492, 1450, 1266, 1230, 1151, 1100, 1074, 1028, 905, 748, 695 cm^{-1} . – EA ($\text{C}_{98}\text{H}_{97}\text{N}_3\text{O}$): calc. C 88.31, H 7.34, N 3.15; found C 84.05, H 6.95, N 2.56.

Resin 1b: According to GP 5, 500 mg of 3-benzyl-(3-methylpolystyrene)-1-(2-bromophenyl)triaz-1-ene (0.717 mmol/g, 359 μmol) were reacted with pyrocatechol monoethyl ether in 4 mL of acetonitrile and 2 ml of pyridine. The resin was washed according to the washing procedure for diaryl ethers followed by the general washing procedure and was dried in high vacuum to give the product resin (0.689 mmol/g) in quantitative yield. – ^{13}C Gel NMR (100 MHz, CDCl_3): δ /ppm = 48.6, 57.2, 118.9, 125.9, 126.7, 133.3, 148.1. – IR (DRIFT, ν) = 3651, 3027, 2908, 2847, 2630, 2361, 2337, 1944, 1872, 1804, 1746, 1721, 1602, 1543, 1493, 1327, 1156, 1076, 1028, 984, 940, 907, 842, 762, 708 cm^{-1} . – EA ($\text{C}_{97}\text{H}_{95}\text{N}_3\text{O}_2$): calc. C 87.28, H 7.17, N 3.15; found C 85.16, H 7.11, N 2.48.

Resin 1c: According to GP 5, 500 mg of 3-benzyl-(3-methylpolystyrene)-1-(2-iodophenyl)triaz-1-ene (0.702 mmol/g, 351 μmol) were reacted with 3-hydroxybenzaldehyde, 4 mL of acetonitrile and 2 ml of pyridine. The resin was washed according to the washing procedure for diaryl ethers followed by the general washing

procedure and was dried in high vacuum to give the product resin (0.696 mmol/g) in quantitative yield. – ^{13}C Gel NMR (100 MHz, CDCl_3): δ/ppm = 47.8, 57.1, 116.5, 118.8, 122.7, 125.7, 137.5, 142.8, 147.9, 191.7. – IR (ATR, ν): 3025, 2920, 1703, 1585, 1493, 1481, 1451, 1434, 1355, 1251, 1220, 1152, 1095, 1027, 841, 745, 694 cm^{-1} . – EA ($\text{C}_{96}\text{H}_{91}\text{N}_3\text{O}$): calc. C 87.43, H 6.96, N 3.19; found C 83.25, H 6.80, N 2.62.

Resin 1d: According to GP 5, 500 mg of 3-benzyl-(3-methylpolystyrene)-1-(2-bromophenyl)triaz-1-ene (0.717 mmol/g, 359 μmol) were reacted with 3-methoxyphenol in 4 mL of acetonitrile and 2 ml of pyridine. The resin was washed according to the washing procedure for diaryl ethers followed by the general washing procedure and was dried in high vacuum to give the product resin (0.695 mmol/g) in quantitative yield. – ^{13}C Gel NMR (100 MHz, CDCl_3): δ/ppm = 55.2, 56.8, 119.4, 122.7, 160.8. – IR (ATR, ν): 3024, 2918, 1601, 1491, 1450, 1349, 1264, 1228, 1203, 1137, 1099, 1074, 1027, 904, 842, 749, 694, 622, 535 cm^{-1} . – EA ($\text{C}_{96}\text{H}_{93}\text{N}_3\text{O}_2$): calc. C 87.30, H 7.10, N 3.18; found C 81.71, H 6.74, N 2.53.

Resin 1e: According to GP 5, 500 mg of 3-benzyl-(3-methylpolystyrene)-1-(2,4-dibromophenyl)triaz-1-ene (0.581 mmol/g, 291 μmol) were reacted with 2-isopropylphenol in 4 mL of acetonitrile and 2 ml of pyridine. The resin was washed according to the washing procedure for diaryl ethers followed by the general washing procedure and was dried in high vacuum to give the product resin (0.563 mmol/g) in quantitative yield. – ^{13}C Gel NMR (100 MHz, CDCl_3): δ/ppm = 23.9, 34.0, 47.8, 56.7, 115.4, 120.4, 125.7, 141.8, 150.3, 158.7. – IR (ATR, ν): 3059, 3025, 2918, 2848, 1601, 1571, 1492, 1474, 1449, 1390, 1340, 1273, 1241, 1150, 1111, 1074, 1028, 982, 943, 902, 813, 754, 695, 537 cm^{-1} . – EA ($\text{C}_{98}\text{H}_{96}\text{N}_3\text{O}$): calc. C 83.38, H 6.85, N 2.98; found C 81.66, H 6.73, N 2.44.

Resin 1f: According to GP 5, 471 mg of 3-benzyl-(3-methylpolystyrene)-1-(2-bromo-4-methylphenyl)triaz-1-ene (0.367 mmol/g, 173 μmol) were reacted with 2-isopropylphenol in 4 mL of acetonitrile and 2 ml of pyridine. The resin was washed according to the washing procedure for diaryl ethers followed by the general washing procedure and was dried in high vacuum to give the

product resin (0.359 mmol/g) in quantitative yield. – IR (ATR, ν): 3566, 3024, 2920, 1748, 1601, 1542, 1491, 1448, 1363, 1266, 1152, 1109, 1027, 754, 694, 624, 533 cm^{-1} . – ^{13}C Gel NMR (100 MHz, CDCl_3): δ/ppm = 21.0, 23.9, 34.0, 56.3, 113.8, 115.1, 118.8, 119.6, 122.7, 125.6, 136.5, 140.3, 148.8, 150.3, 159.5. – EA ($\text{C}_{99}\text{H}_{100}\text{N}_3\text{O}$): calc. C 88.24, H 7.48, N 3.10; found C 79.10, H 6.59, N 2.35.

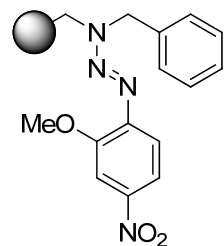
Resin 1g: According to GP 5, 490 mg of 3-benzyl-(3-methylpolystyrene)-1-(2-bromo-4-methylphenyl)triaz-1-ene (0.367 mmol/g, 180 μmol) were reacted with 2-phenylphenol in 4 mL of acetonitrile and 2 ml of pyridine. The resin was washed according to the washing procedure for diaryl ethers followed by the general washing procedure and was dried in high vacuum to give the product resin (0.355 mmol/g) in quantitative yield. – ^{13}C Gel NMR (100 MHz, CDCl_3): δ/ppm = 21.1, 57.1, 116.9, 119.0, 123.2, 126.7, 136.6, 140.6. – IR (ATR, ν): 3059, 3025, 2919, 2848, 1601, 1492, 1449, 1349, 1247, 1152, 1109, 1075, 1028, 906, 818, 757, 730, 695, 537 cm^{-1} . – EA ($\text{C}_{102}\text{H}_{98}\text{N}_3\text{O}$): calc. C 88.67, H 7.15, N 3.02; found C 87.09, H 7.00, N 2.52.

Resin 1h: According to GP 4, 2-phenoxyaniline was immobilized on 6.01 g of *N*-benzylaminomethyl resin (5.56 mmol). After drying in high vacuum 6.88 g (4.44 mmol, 0.6463 mmol/g) of the resin were obtained in 80% yield. For upscaling, resynthesis of 3.02 g of *N*-benzylaminomethyl resin gave 3.38 g of the product resin in 65% yield (0.536 mmol/g). – ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 56.8, 116.7, 119.4, 121.6, 122.7, 125.9, 126.7, 129.4, 143.1, 149.2, 159.6. – IR (KBr, ν): 3059, 3025, 2918, 2848, 1601, 1491, 1451, 1347, 1238, 1151, 1100, 1074, 1027, 748, 695, 538 cm^{-1} . – Raman (60 mW, 1064 nm): 3057, 2905, 2852, 1678, 1602, 1483, 1445, 1416, 1323, 1269, 1238, 1206, 1183, 1155, 1032, 1002, 797, 795, 755, 622 cm^{-1} . – EA ($\text{C}_{96}\text{H}_{93}\text{N}_3\text{O}$): calc. C 88.35, H 7.18, N 3.23; found C 87.53, H 7.27, N 2.79.

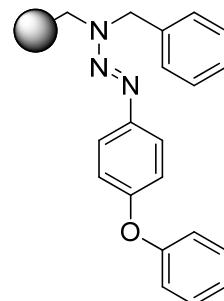
Resin 1i: According to GP 4, 5-chloro-2-phenoxyaniline was immobilized on 3.01 g of *N*-benzylaminomethyl resin (2.78 mmol). After drying in high vacuum the resin was obtained in quantitative yield (0.754 mmol/g). – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 48.2, 57.2, 116.6, 119.1, 122.0,

126.2, 143.9, 159.3. – Raman (60 mW, 1064 nm, ν): 3057, 3055, 2906, 2853, 1603, 1586, 1481, 1449, 1418, 1399, 1327, 1285, 1238, 1208, 1183, 1157, 1075, 1032, 1003, 796, 622 cm^{-1} . – IR (ATR, ν): 3059, 3025, 2918, 2847, 1600, 1491, 1479, 1450, 1346, 1251, 1153, 1109, 1073, 1027, 983, 906, 844, 750, 695, 537 cm^{-1} . – EA ($\text{C}_{96}\text{H}_{92}\text{N}_3\text{ClO}$): calc. C 86.07, H 6.92, N 3.15; found C 85.46, H 6.86, N 2.51.

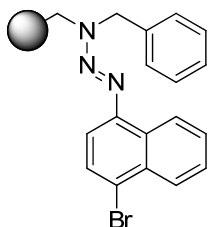
Resin 1j: According to GP 4, 2-methoxy-4-nitroaniline was immobilized on 2.00 g of *N*-benzylaminomethyl resin (1.85 mmol). After drying in high vacuum 2.20 g (0.99 mmol, 0.45 mmol/g) of the resin were obtained in 53% yield. – ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 48.8, 56.5, 107.7, 117.1, 118.0, 125.8, 153.2. – IR (ATR, ν): 3058, 3025, 2920, 2848, 1601, 1583, 1516, 1492, 1450, 1396, 1332, 1251, 1153, 1121, 1091, 1027, 906, 865, 799, 746, 695, 537 cm^{-1} . – Raman (60 mW, 1064 nm): 3055, 2906, 2858, 1603, 1584, 1488, 1446, 1422, 1399, 1334, 1253, 1183, 1157, 1094, 1032, 1002, 802, 622 cm^{-1} . – EA ($\text{C}_{91}\text{H}_{90}\text{N}_4\text{O}_3$): calc. C 84.85, H 7.04, N 4.37; found C 84.87, H 7.04, N 3.47.



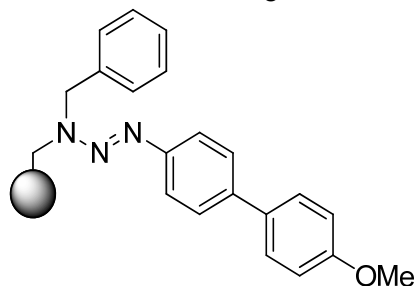
Resin 1k: According to GP 4, 4-phenoxyaniline was immobilized on 6.18 g of *N*-benzylaminomethyl resin (5.72 mmol). After drying in high vacuum 6.83 g (3.31 mmol, 0.484 mmol/g) of the resin were obtained in 56% yield. – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 56.5, 115.8, 119.8, 122.1, 123.0, 125.8, 129.8, 146.7, 155.0, 157.9. – Raman (60 mW, 1064 nm): 3056, 2905, 2853, 1604, 1585, 1497, 1450, 1407, 1324, 1214, 1183, 1152, 1032, 1003, 796, 622 cm^{-1} . – EA ($\text{C}_{96}\text{H}_{93}\text{N}_3\text{O}$): calc. C 88.35, H 7.18, N 3.23; found C 86.96, H 7.30, N 2.68.



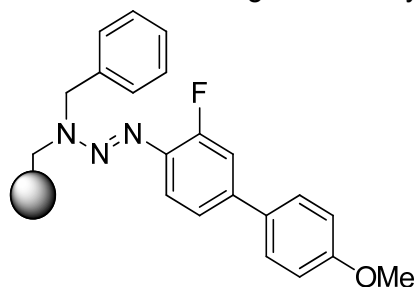
Resin 1l: According to GP 4, 1-amino-4-bromonaphthalene was immobilized on 5.86 g of *N*-benzylaminomethyl resin (5.42 mmol). After drying in high vacuum 6.80 g (4.05 mmol, 0.595 mmol/g) of the resin were obtained in 75% yield. – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 49.1, 57.7, 112.6, 119.6, 124.3, 125.8. – IR (ATR, $\tilde{\nu}$): 3058, 3024, 2917, 1601, 1492, 1450, 1319, 1276, 1171, 1139, 1024, 925, 826, 756, 695, 537 cm^{-1} . – EA ($\text{C}_{94}\text{H}_{90}\text{N}_3\text{Br}$): calc. C 84.12, H 6.76, N 3.14; found C 83.96, H 6.85, N 2.73.



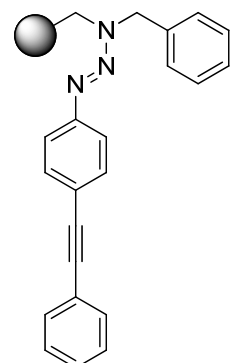
Resin 1m: 1.00 g of 3-benzyl-(3-methylpolystyrene)-1-(4-iodophenyl)triaz-1-ene (0.516 mmol/g, 0.516 μ mol) were swollen in DMF and 765 mg (5.00 mmol, 10.1 equiv.) of 4-methoxyphenylboronic acid, 530 mg (5.00 mmol, 10.1 equiv.) of Na₂CO₃, 40.0 mg (34.6 μ mol, 0.067 equiv.) of tetrakis(triphenylphosphine) palladium and 2 mL of H₂O were added. After shaking for 12 h at 120 °C the resin was washed according to the washing procedure and was dried in high vacuum (0.521 mmol/g). – ¹³C Gel NMR (100 MHz, CDCl₃, ppm), δ = 47.9, 55.3, 56.8, 114.2, 122.8, 125.7, 137.8, 149.3, 150.2. – IR (ATR, $\tilde{\nu}$): 3059, 3024, 2920, 2847, 1601, 1492, 1449, 1346, 1246, 1175, 1143, 1074, 1028, 1001, 904, 823, 753, 695, 536 cm⁻¹. – EA (C₉₆H₉₄N₃O): calc. C 88.30, H 7.26, N 3.22; found C 83.75, H 6.75, N 2.71.



Resin 1n: 500 mg of 3-benzyl-(3-methylpolystyrene)-1-(2-fluoro-4-bromophenyl)triaz-1-ene (0.516 mmol/g, 258 μ mol) were swollen in DMF and 184 mg (1.20 mmol, 2.33 equiv.) of 4-methoxyphenylboronic acid, 80.0 mg (755 μ mol, 1.46 equiv.) of Na₂CO₃, 20 mg (17.3 μ mol) of tetrakis(triphenylphosphine) palladium and 1.00 mL of H₂O were added. After shaking for 12 h at 120 °C the resin was washed according to the washing procedure and was dried in high vacuum (0.509 mmol/g). – ¹³C Gel NMR (100 MHz, CDCl₃, ppm), δ = 48.5, 55.5, 57.2, 114.4, 118.1, 120.5, 138.1, 155.2. – Raman (60 mW, 1064 nm): 3057, 2909, 2856, 1609, 1481, 1447, 1425, 1400, 1317, 1252, 1225, 1205, 1182, 1032, 1002, 901, 781, 622 cm⁻¹. – IR (ATR, $\tilde{\nu}$): 3058, 3025, 2921, 2848, 1601, 1491, 1449, 1397, 1347, 1249, 1152, 1113, 1074, 1027, 906, 818, 756, 729, 695, 538 cm⁻¹. – EA (C₉₆H₉₃FN₃O): calc. C 87.13, H 7.08, N 3.16; found C 76.03, H 6.14, N 2.39.



Resin 1o: According to GP 6, 512 mg of 3-benzyl-(3-methylpolystyrene)-1-(4-iodophenyl)triaz-1-ene (0.377 mmol/g, 193 μ mol) were reacted with phenylacetylene in 8 mL of DMF. The resin was washed following the general washing procedure and was dried in high vacuum to yield 502 mg of the product resin (0.381 mmol/g). – ¹³C Gel NMR (100 MHz, CDCl₃, ppm), δ = 57.2, 90.1, 121.0, 125.8, 132.5, 150.4. – IR (ATR, $\tilde{\nu}$): = 3025,

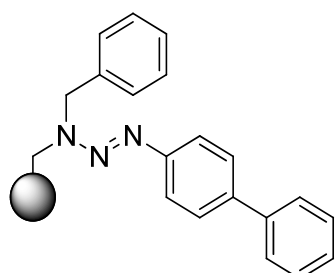


2918, 1600, 1493, 1449, 1399, 1346, 1148, 1072, 1028, 905, 839, 753, 695, 536, 408 cm^{-1} .
– Raman (60 mW, 1064 nm): 3060, 2923, 2855, 2215, 1595, 1428, 1401, 1224, 1163, 1137, 1031, 1002 cm^{-1} . – EA ($\text{C}_{98}\text{H}_{93}\text{N}_3$): calc. C 89.65, H 7.14, N 3.21; found C 87.03, H 7.00, N 2.49.

Resin 1p: According to GP 6, 504 mg of 3-benzyl-(3-methylpolystyrene)-1-(2-fluoro-4-iodophenyl)triaz-1-ene (0.634 mmol/g, 320 μmol) were reacted with phenylacetylene in 8 mL of DMF. The resin was washed following the general washing procedure and was dried in high vacuum to yield 483 mg of the product resin (0.600 mmol/g). – IR (ATR, ν): = 3025, 2920, 2851, 1601, 1492, 1449, 1399, 1347, 1145, 1074, 1028, 904, 840, 754, 695, 539 cm^{-1} . – ^{13}C Gel NMR (100 MHz, CDCl_3): δ/ppm = 48.4, 57.4, 119.5, 121.1, 125.8, 131.7, 139.0, 154.9. – Raman (60 mW, 1064 nm): 3055, 2920, 2211, 1609, 1599, 1498, 1428, 1405, 1325, 1252, 1216, 1100, 1032, 1002, 809, 746 cm^{-1} . – EA ($\text{C}_{98}\text{H}_{92}\text{N}_3\text{F}$): calc. C 88.43, H 6.96, N 3.17; found C 88.31, H 7.13, N 2.53.

Resin 1q: According to GP 6, 507 mg of 3-benzyl-(3-methylpolystyrene)-1-(4-iodophenyl)triaz-1-ene (0.377 mmol/g, 191 μmol) were reacted with 4-methoxyphenylacetylene in 8 mL of DMF. The resin was washed following the general washing procedure and was dried in high vacuum to yield 501 mg of the product resin (0.376 mmol/g). – ^{13}C Gel NMR (100 MHz, CDCl_3): δ/ppm = 43.6, 44.9, 54.9, 113.6, 120.2, 125.3, 131.8, 132.6, 149.7, 159.1. – IR (ATR, ν): 3025, 2918, 2848, 2161, 1602, 1512, 1492, 1448, 1399, 1286, 1247, 1172, 1146, 1073, 1028, 904, 831, 754, 695, 533 cm^{-1} . – Raman (60 mW, 1064 nm, ν): 3055, 2920, 2214, 1598, 1515, 1445, 1428, 1401, 1318, 1221, 1164, 1137, 1032, 1002, 779, 622 cm^{-1} . – EA ($\text{C}_{99}\text{H}_{95}\text{N}_3\text{O}$): calc. C 88.53, H 7.13, N 3.14; found C 85.64, H 6.97, N 2.46.

Resin 1r: 1.06 g of 3-benzyl-(3-methylpolystyrene)-1-(4-iodophenyl)triaz-1-ene (400 μmol , 0.377 mmol/g) were swollen in DMF. Then 420 mg (3.44 mmol) of phenylboronic acid, 183 mg (1.73 mmol) of Na_2CO_3 , 4.62 mg (4.00 μmol) of tetrakis(triphenylphosphine) palladium and 1.50 mL of H_2O were added. After shaking for 12 h at 120 $^\circ\text{C}$



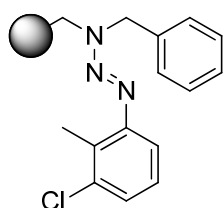
the resin was washed according to the washing procedure and was dried in high vacuum (0.400 mmol/g). – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 55.5, 57.0, 114.4, 123.0, 138.0. – IR (ATR, $\tilde{\nu}$): 3059, 3024, 2920, 2848, 1601, 1492, 1450, 1400, 1347, 1144, 1074, 1027, 905, 841, 755, 694, 534 cm^{-1} . – Raman (60 mW, 1064 nm): 3057, 2910, 2851, 1602, 1583, 1455, 1436, 1284, 1166, 1032, 1003, 622 cm^{-1} . – EA ($\text{C}_9\text{H}_9\text{N}_3$): calc. C 89.45, H 7.27, N 3.27; found C 86.64, H 7.03, N 2.49.

Resin 1s: According to GP 4, 2-aminobiphenyl was immobilized on 9.00 g of *N*-benzylaminomethyl resin (8.33 mmol). After drying in high vacuum 10.2 g (6.90 mmol, 0.674 mmol/g) of the resin were obtained in 83% yield. – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 57.1, 117.8, 125.9, 130.5, 136.8, 140.2, 147.6. – IR (DRIFT, ν): 3646, 3591, 2631, 2337, 2312, 1944, 1873, 1804, 1721, 1702, 1601, 1542, 1495 cm^{-1} . – EA ($\text{C}_9\text{H}_9\text{N}_3$): calc. C 89.44, H 7.27, N 3.29; found C 89.17, H 7.24, N 2.69.

Resin 1t: According to GP 4, 3-aminobenzylalcohol was immobilized on 6.41 g of *N*-benzylaminomethyl resin (5.93 mmol). After drying in high vacuum 7.03 g (4.64 mmol, 0.660 mmol/g) of the resin were obtained in 78% yield. – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 65.4, 124.4, 125.9, 151.0. – Raman (60 mW, 1064 nm, ν): 3056, 2908, 2853, 1602, 1487, 1453, 1421, 1402, 1322, 1214, 1196, 1135, 1093, 1032, 1002, 797, 622 cm^{-1} . – EA ($\text{C}_9\text{H}_9\text{N}_3\text{O}$): calc. C 87.93, H 7.38, N 3.40; found C 87.06, H 7.45, N 3.03.

Resin 1u: According to GP 4, 3-methoxyaniline was immobilized on 9.00 g of *N*-benzylaminomethyl resin (8.33 mmol). After drying in high vacuum 10.2 g (8.32 mmol, 0.816 mmol/g) of the resin were obtained in quantitative yield. – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 55.4, 105.9, 112.0, 152.2, 160.3. – IR (DRIFT, ν): 3575, 3027, 2908, 2847, 2629, 2337, 1945, 1873, 1806, 1748, 1720, 1603, 1493, 1450, 1329, 907, 845, 762 cm^{-1} . – Raman (60 mW, 1064 nm): 3055, 2906, 2854, 1603, 1585, 1452, 1414, 1322, 1265, 1196, 1183, 1156, 1032, 1002, 796, 622 cm^{-1} . – EA ($\text{C}_9\text{H}_9\text{N}_3\text{O}$): calc. C 87.81, H 7.61, N 3.32; found C 84.22, H 7.14, N 2.21.

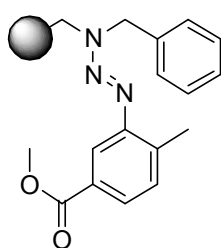
Resin 1v: According to GP 4, 3-chloro-2-methylaniline was immobilized on 6.00 g of *N*-



benzylaminomethyl resin (5.55 mmol). After drying in high vacuum 6.75 g (4.96 mmol, 0.725 mmol/g) of the resin were obtained in 77% yield. – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 14.4, 45.9, 57.5, 115.5, 135.3, 150.0. – IR (DRIFT, ν): 3589, 3024, 2904, 2337, 1944, 1871, 1803, 1722, 1672, 1602, 1494, 1424, 1349, 1154, 1076, 1005, 909, 844, cm^{-1} . –

Raman (60 mW, 1064 nm, ν): 3055, 2909, 2852, 1603, 1585, 1453, 1413, 1324, 1283, 1236, 1205, 1183, 1156, 1075, 1032, 1003, 800, 622 cm^{-1} . – EA ($\text{C}_{91}\text{H}_{81}\text{N}_3\text{Cl}$): calc. C 86.64, H 7.19, N 3.35; found C 85.45, H 7.29, N 2.84.

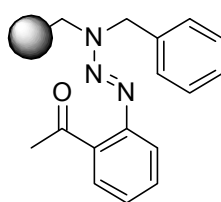
Resin 1w: According to GP 4, methyl 3-amino-4-methylbenzoate was immobilized on 3.02 g of



N-benzylaminomethyl resin (2.79 mmol). After drying in high vacuum 3.36 g (1.91 mmol, 0.570 mmol/g) of the resin were obtained in 69% yield. – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 18.2, 52.0, 57.5, 117.9, 167.0. – IR (ATR, $\tilde{\nu}$): 3025, 2918, 2848, 1718, 1602, 1493, 1450, 1284, 1260, 1154, 1120, 1091, 1028, 1004, 758, 695, 542 cm^{-1} . – Raman (1064 nm,

103 mW, ν): 3056, 2909, 2853, 1722, 1584, 1500, 1450, 1402, 1294, 1264, 1210, 1183, 1157, 1032, 1003, 819, 797, 764, 622 cm^{-1} . – EA ($\text{C}_{93}\text{H}_{93}\text{N}_3\text{O}_2$): calc. C 86.92, H 7.29, N 3.28; found C 86.03, H 7.17, N 2.75.

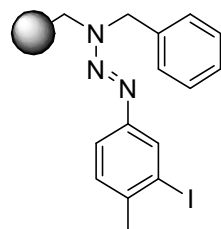
Resin 1x: According to GP 4, 2-aminoacetophenone was immobilized on 6.00 g of *N*-



benzylaminomethyl resin (5.55 mmol). After drying in high vacuum 6.61 g (4.16 mmol, 0.630 mmol/g) of the resin were obtained in 75% yield. – ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 32.2, 49.1, 57.8, 118.6, 125.7, 148.7. – IR (DRIFT, ν): 3650, 3022, 2904, 2339, 1945, 1872, 1806, 1680, 1601,

1439, 1349, 1234, 1153, 1110, 905, 843, 706 cm^{-1} . – Raman (60 mW, 1064 nm, ν): 3057, 2907, 2853, 1678, 1603, 1476, 1444, 1414, 1328, 1236, 1215, 1183, 1157, 1033, 1003, 796, 622 cm^{-1} . – EA ($\text{C}_{92}\text{H}_{91}\text{N}_3\text{O}$): calc. C 88.05, H 7.31, N 3.36; found C 87.68, H 7.38, N 2.82.

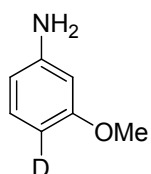
Resin 1y: According to GP 4, 3-iodo-4-methylaniline was immobilized on 3.05 g of *N*-



benzylaminomethyl resin (2.82 mmol). After drying in high vacuum 3.61 g (2.31 mmol, 0.639 mmol/g) of the resin were obtained in 82% yield. – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 27.7, 48.2, 57.0, 101.4, 121.2, 125.9,

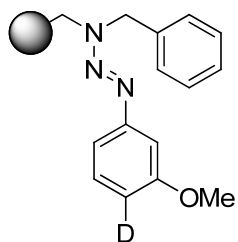
138.4, 149.6. – IR (ATR, $\tilde{\nu}$): 3025, 2920, 2849, 1601, 1492, 1449, 1347, 1151, 1073, 1025, 906, 819, 754, 695, 611, 535 cm^{-1} . – Raman (60 mW, 1064 nm, ν): 3054, 2913, 2850, 1592, 1448, 1425, 1379, 1321, 1218, 1198, 1156, 1031, 1003, 790, 622 cm^{-1} . – EA ($\text{C}_{91}\text{H}_{90}\text{N}_3\text{I}$): calc. C 80.76, H 6.70, N 3.12; found C 80.41, H 6.57, N 2.74.

3-Methoxy-4-deuteroaniline (precursor for resin 1z): 3-Methoxy-4-deuteronitrobenzene



(175 mg, 1.13 mmol) was dissolved in 5.00 mL of methanol, 20 mg of Pd/C (10% Pd) were added and the flask was evacuated and flushed with hydrogen three times. To guarantee hydrogen atmosphere the flask was equipped with a balloon filled with hydrogen and the mixture was stirred over night at room temperature. The catalyst was filtered off via syringe filter, silica gel was added to the filtrate and concentrated under reduced pressure. Column chromatography (cyclohexane/ethyl acetate/triethylamine, 5:1:0.025) yielded 97.6 mg (786 μmol , 70%) of the desired amine. – R_f : 0.20 (cyclohexane/ethyl acetate, 4:1).

Resin 1z: According to GP 4, 3-methoxy-4-deuteroaniline was immobilized on 320 mg of *N*-benzylaminomethyl resin (0.296 mmol). Due to the small amount of the aniline obtained from cleavage of resin 1j and subsequent reduction the number of equivalents of the aniline was reduced to two instead of five. As this might be a reason for incomplete attachment to the resin the yield of the cleavage was determined over two steps (attachment and cleavage). Theoretical loading: 0.821 mmol/g. – ^{13}C Gel NMR (100 MHz, CDCl_3 , ppm), δ = 55.4, 111.7, 114.0, 160.3. – IR (DRIFT, ν): 3060, 3025, 2916, 2847, 1600, 1493, 1450, 1400, 1345, 1252, 1135, 1075, 1028, 856, 753, 695, 541 cm^{-1} . – Raman (60 mW, 1064 nm, ν): 3056, 2906, 2853, 1603, 1585, 1449, 1404, 1322, 1256, 1197, 1184, 1156, 1032, 1002, 984, 622 cm^{-1} . – EA ($\text{C}_{91}\text{H}_{90}\text{DN}_3\text{O}$): calc. C 87.86, H 7.45, N 3.39; found C 87.46, H 7.27, N 2.90.



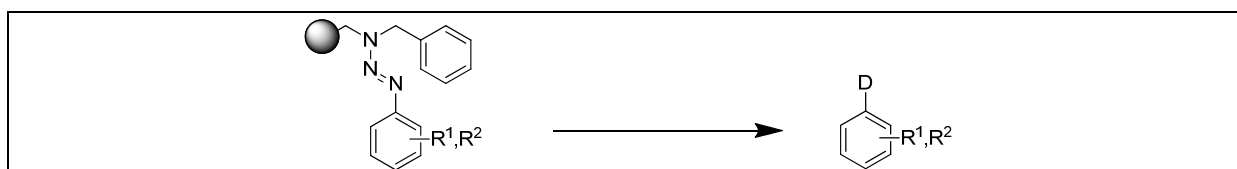
GP 7: Deuterating cleavage from the solid support in THF- d_8

In a Crimptop vial, the resin was first heated in a drying oven (93 °C), evacuated until adjusted to room temperature and was afterwards flushed with nitrogen. Then THF- d_8 (1.3 mL/100 mg of resin) and deuterated TFA (50 μL /100 mg of resin) were added. The vial was sealed, agitated for 14 h at 80 °C, and then the resin was filtered off and washed with

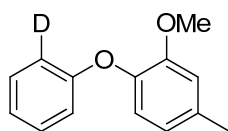
acetone, methanol and dichloromethane. The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography.

GP 8: Deuterating cleavage from the solid support in methanol-d₄

In a Crimptop vial, the resin was first heated in a drying oven (93°C), evacuated until adjusted to room temperature and afterwards flushed with nitrogen. Then methanol-d₄ (1.3 mL/100 mg of resin) and deuterated TFA (50 µL/100 mg of resin) were added. The vial was sealed, agitated for 14 h at 80 °C, and then the resin was filtered off and washed with acetone, methanol and dichloromethane. The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography.



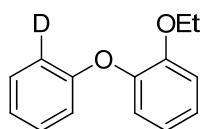
2-Methoxy-4-methyl-1-(2-deuterophenoxy)benzene (3a): Following GP 7, 110 mg (76.6



µmol) of resin **1a** (0.697 mmol/g) were reacted with TFA-d₁. Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 10.1 mg (46.9 µmol) of the product in 61% yield. – R_f: 0.39 (cyclohexane/ethyl acetate,

20:1). – ¹H NMR (400 MHz, CDCl₃, ppm), δ = 2.29 (s, 3 H), 3.74 (s, 3 H), 6.64–6.67 (m, 1 H), 6.74 (d, 1 H, ⁴J = 1.2 Hz), 6.85 (d, 1 H, ³J = 8.0 Hz), 6.89 (d, 1 H, ³J = 8.5 Hz), 6.96–7.00 (m, 1 H), 7.18–7.22 (m, 2 H). – ¹³C NMR (62.5 MHz, CDCl₃, ppm), δ = 21.3 (CH₃), 55.9 (CH₃), 113.7 (CH), 116.7 (CH), 121.2 (CH), 121.4 (CH), 122.1 (CH), 129.3 (CH), 129.4 (CH), 134.8, 142.4, 151.2, 158.3. – IR (ATR, ν): 3450, 3067, 2950, 2924, 1884, 1583, 1509, 1469, 1445, 1410, 1303, 1289, 1270, 1223, 1153, 1127, 1031, 827, 763, 742, 625 cm⁻¹. – EI (m/z): 215 (100) [M⁺], 214 (19), 200 (14), 185 (23), 172 (14), 144 (10), 129 (27), 109 (7), 92 (17), 78 (34). – HRMS (C₁₄H₁₃DO₂): calc. 215.1057, found 215.1056.

2-Ethoxy-2-(2-deuterophenoxy)benzene (3b): Following GP 7, 100 mg (68.9 µmol) of resin

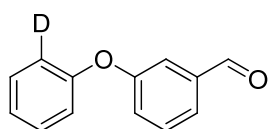


1b (0.689 mmol/g) were reacted with TFA-d₁. Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 14.8 mg (68.9 µmol) of the product

in quantitative yield.

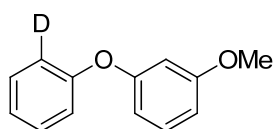
Cleavage of 142 mg (97.8 μmol) of resin **1b** (0.689 mmol/g) according to GP 8 gave 8.30 mg (38.5 μmol) of the product in 39% yield. – R_f : 0.59 (cyclohexane/ethyl acetate, 20:1) – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 1.25 (t, 3 H, 3J = 7.0 Hz), 4.20 (q, 2 H, 3J = 7.0 Hz), 6.85–7.11 (m, 6 H), 7.21–7.29 (m, 2 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 14.7 (CH_3), 64.6 (CH_2), 114.6 (CH), 117.1 (CH), 121.2 (CH), 121.5 (CH), 122.2 (CH), 124.8 (CH), 129.2 (CH), 129.3 (CH), 145.4 (C), 150.8 (C), 158.2 (C). – IR (ATR, ν): 3443, 3067, 2981, 2929, 1581, 1500, 1470, 1454, 1392, 1305, 1260, 1217, 1160, 1119, 1043, 927, 872, 747 cm^{-1} . – EI (m/z): 215 (100) [M^+], 214 (8), 187 (100), 170 (12), 158 (28), 129 (37), 78 (60). – HRMS ($\text{C}_{14}\text{H}_{13}\text{DO}_2$): calc. 215.1057, found 215.1056.

3-(2-Deuterophenoxy)benzaldehyde (3c): Following GP 7, 95.0 mg (66.1 μmol) of resin **1c**



(0.696 mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 11.1 mg (55.7 μmol) of the product in 84% yield. – R_f = 0.31 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 7.04 (dd, 1 H, 3J = 8.6 Hz, 3J = 1.2 Hz), 7.14–7.20 (m, 1 H), 7.29 (ddd, 1 H, 3J = 8.3 Hz, 3J = 2.6 Hz, 3J = 1.2 Hz), 7.35–7.42 (m, 2 H), 7.46–7.53 (m, 2 H), 7.59–7.63 (m, 1 H), 9.96 (s, 1 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 118.3 (CH), 119.6 (CH), 124.3 (CH), 124.7 (CH), 124.8 (CH), 130.1 (CH), 130.2 (CH), 130.6 (CH), 138.2, 158.2, 158.5, 191.8 (CH). – IR (ATR, ν): 3448, 3066, 2925, 2848, 2730, 1701, 1581, 1470, 1448, 1386, 1249, 1210, 1162, 1134, 1115, 1042, 942, 883 cm^{-1} . – EI (m/z): 199 (100) [M^+], 198 (39), 181 (8), 170 (34), 142 (33), 116 (13), 78 (17). – HRMS ($\text{C}_{13}\text{H}_9\text{DO}_2$): calc. 199.0744, found 199.0747.

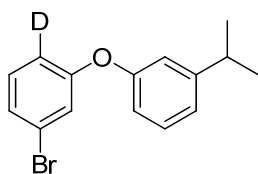
1-(3-Methoxyphenoxy)-2-deuterobenzene (3d): Following GP 7, 94.0 mg (65.3 μmol) of



resin **1d** (0.695 mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 13.1 mg (65.3 μmol) of the product in quantitative yield. – R_f = 0.61 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 3.78 (s, 3 H, OCH_3), 6.57–6.60 (m, 2 H), 6.64–6.67 (m, 1 H), 7.02–7.04 (m, 1 H), 7.09–7.13 (m, 1 H), 7.20–7.24 (m, 1 H), 7.31–7.38 (m, 2 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 55.3 (CH_3), 104.8 (CH), 108.8 (CH), 110.9 (CH), 119.1 (CH), 123.3 (CH), 129.6 (CH), 129.7 (CH), 130.1 (CH), 156.9, 158.5, 160.9. – IR (ATR, ν): 3443, 3068, 2937, 2836, 1584, 1488, 1469, 1384,

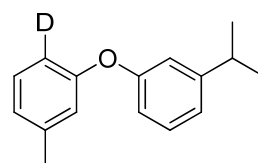
1304, 1278, 1217, 1140, 1076, 1042, 951, 848, 765, 688 cm^{-1} . – EI (m/z): 201 (100) [M^+], 200 (6), 170 (4), 158 (26), 142 (7), 130 (13), 116 (4), 92 (10). – HRMS ($\text{C}_{13}\text{H}_{11}\text{DO}_2$): calc. 201.0900, found 201.0898.

4-Bromo-2-(3-isopropylphenoxy)-1-deuterobenzene (3e): Following GP 7, 100 mg (56.3



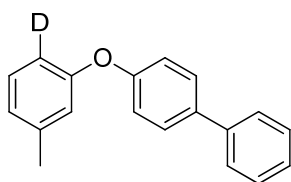
μmol) of resin **1e** (0.563 mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 13.4 mg (45.8 μmol) of the product in 81% yield. – R_f : 0.85 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 1.73 (d, 6 H, 3J = 6.9 Hz), 2.83 (sept, 1 H, 3J = 6.9 Hz), 6.74 (dd, 1 H, 3J = 8.1 Hz, 4J = 2.3 Hz), 6.84 (s, 1 H), 6.95 (d, 1 H, 3J = 7.8 Hz), 7.07–7.15 (m, 3 H), 7.15–7.22 (m, 1 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 23.9 (2 C, CH_3), 34.0 (CH), 116.6 (CH), 117.6 (CH), 121.5 (CH), 122.2 (CH), 122.8 (C), 125.9 (CH), 129.7 (CH), 130.6 (CH), 151.4 (C), 156.2 (C), 158.5 (C). – IR (ATR, ν): 3442, 3060, 2962, 2926, 2870, 1606, 1574, 1486, 1459, 1399, 1385, 1337, 1297, 1241, 1214, 1161, 1133, 1074, 981, 943, 883, 825, 790 cm^{-1} . – EI (m/z): 293 (46), 291 (100) [M^+], 290 (4), 278 (67), 276 (67), 213 (6), 197 (43), 182 (56), 169 (32), 153 (8), 142 (11), 119 (17), 104 (24), 91 (41), 77 (48). – HRMS ($\text{C}_{15}\text{H}_{14}\text{DOBr}$): calc. 291.0369, found 291.0367.

4-Methyl-2-(3-isopropylphenoxy)-1-deuterobenzene (3f): Following GP 7, 105 mg (41.3

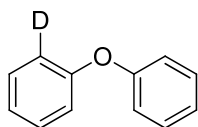


μmol) of resin **1f** (0.395 mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 8.70 mg (38.3 μmol) of the product in quantitative yield. – R_f : 0.72 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 1.24 (d, 6 H, 3J = 6.9 Hz), 2.33 (s, 3 H), 2.88 (sept, 1 H, 3J = 6.9 Hz), 6.80 (dd, 1 H, 3J = 8.0 Hz, 4J = 1.8 Hz), 6.84 (s, 1 H), 6.94–6.96 (m, 2 H), 6.97 (d, 1 H, 3J = 7.7 Hz), 7.13 (d, 1 H, 3J = 7.7 Hz), 7.17 (d, 1 H, 3J = 8.1 Hz). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 21.4 (CH_3), 23.9 (2 C, CH_3), 34.0 (CH), 116.1 (CH), 117.2 (CH), 119.4 (CH), 121.3 (CH), 123.8 (CH), 129.3 (CH), 129.4 (CH), 139.8 (C), 151.0 (C), 157.2 (C), 157.3 (C). – IR (ATR, ν): 2960, 2924, 1603, 1575, 1476, 1443, 1412, 1384, 1303, 1247, 1179, 1161, 1149, 1135, 1048, 954, 873, 824, 789, 700, 626 cm^{-1} . – EI (m/z): 227 (100) [M^+], 226 (7), 196 (2), 184 (5), 169 (3), 129 (1), 119 (6), 106 (6), 91 (13), 77 (7). – HRMS ($\text{C}_{16}\text{H}_{17}\text{DO}$): calc. 227.1420, found 227.1418.

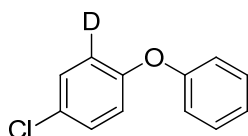
4-(2-Deutero-5-methylphenoxy)-1,1'-biphenyl (3g): Following GP 7, 101 mg (35.7 μmol) of resin **1g** (0.355 mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 9.10 mg (34.8 μmol) of the product in 98% yield. – R_f : 0.69 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 2.35 (s, 3 H), 6.89 (s, 1 H), 6.95 (dd, 1 H, $^3J = 7.6$ Hz, $^3J = 0.7$ Hz), 7.06–7.09 (m, 2 H), 7.24 (d, 1 H, $^3J = 7.6$ Hz), 7.31–7.35 (m, 1 H), 7.42–7.46 (m, 2 H), 7.55–7.59 (m, 4 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 21.4 (CH₃), 119.0 (2 C, CH), 119.7 (CH), 124.2 (CH), 126.9 (2 C, CH), 127.0 (CH), 128.4 (2 C, CH), 128.8 (2 C, CH), 129.4 (CH), 136.1, 140.0, 140.6, 156.9, 157.0. – IR (ATR, ν): 3033, 2918, 1904, 1594, 1574, 1515, 1474, 1401, 1302, 1264, 1235, 1167, 1144, 1129, 1106, 1004, 935, 880, 863, 847, 822, 768, 739, 724, 691, 623, 525, 484, 441 cm^{-1} . – EI (m/z): 261 (6) [M^+], 227 (17), 212 (12), 184 (2), 119 (2), 91 (4), 77 (4), 58 (19), 43 (100). – HRMS ($\text{C}_{19}\text{H}_{15}\text{DO}$): calc. 261.1264, found 261.1261.



1-Deutero-2-phenoxybenzene (3h): Following GP 7, 103 mg (66.7 μmol) of resin **1h** (0.646 mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 7.50 mg (54.4 μmol) of the product in 66% yield. – R_f : 0.65 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 7.01–7.03 (m, 3 H), 7.09–7.12 (m, 2 H), 7.32–7.36 (m, 4 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 118.9 (4 C, CH), 123.2 (2 C, CH), 129.6 (CH), 129.7 (2 C, CH), 157.2 (2 C, C). – IR (ATR, ν): 3442, 3068, 2925, 2854, 2427, 1581, 1490, 1469, 1445, 1384, 1273, 1234, 1197, 1162, 11116, 1072, 1042, 1023, 873, 838, 798 cm^{-1} . – EI (m/z): 171 (100) [M^+], 170 (14), 153 (42), 141 (30), 136 (16), 107 (19), 89 (15). – HRMS ($\text{C}_{12}\text{H}_9\text{DO}$): calc. 171.0794, found 171.0798

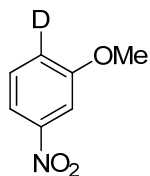


4-Chloro-2-deutero-1-phenoxybenzene (3i): Following GP 7, 101 mg (61.9 μmol) of resin **1i** (0.613 mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 50:1) gave 7.10 mg (34.5 μmol) of the product in 56% yield. – R_f : 0.59 (cyclohexane/ethyl acetate, 50:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 6.94 (d, 1 H, $^3J = 9.3$ Hz), 6.98–7.03 (m, 2 H), 7.09–7.16 (m, 1 H), 7.27–7.39 (m, 4 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 118.9 (2 C), 120.0 (2 C), 123.6 (2 C), 128.7, 129.6, 129.7, 129.9 (2 C), 155.9, 156.8. – IR (KBr, ν) = 3039, 2924, 2852, 1690, 1581, 1491, 1465, 1386, 1263, 1237, 1198, 1162, 1129, 1091, 1015, 897, 877, 825,



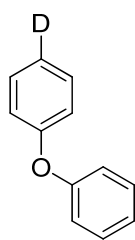
753, 692 cm^{-1} . – EI (m/z): 205 (8) [M^+], 153 (31), 125 (27), 111 (46), 97 (64), 85 (62), 71 (80), 57 (100). – HRMS ($\text{C}_{12}\text{H}_8\text{DCIO}$): calc. 205.0405, found 205.0403.

5-Deutero-3-nitroanisole (3j): Following GP 7, 98.0 mg (40.3 μmol) of resin **1j** (0.411



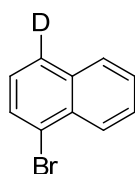
mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 10:1) gave 6.20 mg (40.3 μmol) of the product in quantitative yield. – R_f : 0.25 (cyclohexane/ethyl acetate, 10:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 3.90 (s, 3 H), 7.43 (d, 1 H, $^3J = 8.2$ Hz), 7.73 (d, 1 H, $^4J = 2.1$ Hz), 7.83 (dd, 1 H, $^3J = 8.2$ Hz, $^4J = 2.1$ Hz). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 56.0 (CH_3), 108.3 (CH), 115.9 (CH), 128.9 (C), 130.0 (CH), 160.2 (C). – IR (ATR, ν): 2922, 2853, 1740, 1654, 1522, 1465, 1263, 1101, 1023, 804 cm^{-1} . – EI (m/z): 154 (100) [M^+], 153 (11), 108 (40), 93 (77), 78 (72), 65 (56). – HRMS ($\text{C}_7\text{H}_6\text{DNO}_3$): calc. 154.0489, found 154.0487.

1-Deutero-4-phenoxybenzene (3k): Following GP 7, 95.8 mg (51.4 μmol) of resin **1k** (0.536



mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 5.00 mg (29.2 μmol) of the product in 57% yield. **Upscaling:** In a 20 mL vial 1.22 g (0.654 mmol) of resin **1h** (loading after upscaling: 0.536 mmol/g) were first evacuated, flushed with nitrogen, and then suspended in 6 mL of methanol- d_4 . After addition of 0.6 mL of deuterated trifluoroacetic acid the vial was sealed and the mixture was agitated for 15 h at 80 $^\circ\text{C}$. After cooling down to room temperature the resin was filtered off, washed with acetone and ethyl acetate and the residue was purified by column chromatography (100% cyclohexane \rightarrow cyclohexane/ethyl acetate, 10:1) to yield 67.3 mg (0.394 mmol, 60%) of a pale yellow oil. – R_f : 0.67 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 6.99–7.04 (m, 4 H), 7.07–7.14 (m, 1 H), 7.31–7.37 (m, 4 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 118.9 (4 C), 123.2, 129.6 (2 C), 129.7 (2 C), 157.2 (2 C). – IR (ATR, ν): 3041, 2217, 2069, 1503, 1488, 1227, 1110, 995, 870, 840, 756, 691 cm^{-1} . – EI (m/z): 171 (0.3) [M^+], 142 (0.2), 107 (0.8), 77 (2), 58 (15), 43 (100). – HRMS ($\text{C}_{12}\text{H}_9\text{DO}$): calc. 171.0794, found 171.0793.

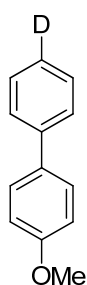
1-Bromo-4-deuteronaphthalene (3l): Following GP 7, 152 mg (90.7 μmol) of resin **1l** (0.595



mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 50:1) gave 9.20 mg (44.2 μmol) of the product in 49% yield. – R_f : 0.76 (cyclohexane/ethyl acetate, 10:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 7.29

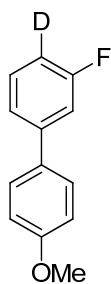
(d, 1 H, $^3J = 7.4$ Hz), 7.47–7.60 (m, 2 H), 7.79–7.83 (m, 1 H), 7.75 (d, 1 H, $^3J = 7.4$ Hz), 8.21 (dd, 1 H, $^3J = 8.0$ Hz, $^4J = 1.7$ Hz). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), $\delta = 122.8$ (C), 126.1 (CH), 126.7 (CH), 127.1 (CH), 127.3 (CH), 128.3 (CH), 129.9 (CH), 132.0 (C), 134.5 (C). – IR (ATR, ν): 3448, 3054, 2925, 1720, 1580, 1560, 1497, 1376, 1361, 1251, 1204, 1182, 1156, 1134, 1083, 1022, 956, 883, 844, 778, 760, 649, 501 cm^{-1} . – EI (m/z): 207/209 (42/31), 177 (57), 149 (100), 126/128 (49/40). – HRMS ($\text{C}_{10}\text{H}_6\text{DBr}$): calc. 206.9794, found 206.9789.

4-Methoxy-4'-deutero-1,1'-biphenyl (3m): Following GP 7, 102 mg (53.2 μmol) of resin **1m**



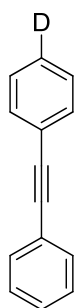
(0.521 mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 10:1) gave 3.00 mg (16.2 μmol) of the product in 30% yield. – R_f : 0.62 (cyclohexane/ethyl acetate, 10:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), $\delta = 3.86$ (s, 3 H), 6.97–6.99 (m, 2 H), 7.41–7.43 (m, 2 H), 7.52–7.57 (m, 4 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), $\delta = 55.3$ (CH₃), 114.2 (2 C, CH), 126.7 (2 C, CH), 128.1 (2 C, CH), 128.6 (2 C, CH), 133.8 (C), 140.8 (C), 159.1 (C). – IR (DRIFT) = 3004, 2961, 2925, 2854, 2279, 1892, 1786, 1739, 1607, 1581, 1522, 1483, 1464, 1398, 1288, 1252, 1202, 1184, 1038, 1014, 862, 829, 810, 602 cm^{-1} . – EI (m/z): 185 (100) [M^+], 184 (7), 170 (31), 142 (30), 116 (17), 95 (3). – HRMS ($\text{C}_{13}\text{H}_{11}\text{DO}$): calc. 185.0951, found 185.0953.

3-Fluoro-4'-methoxy-4-deutero-1,1'-biphenyl (3n): Following GP 7, 98.0 mg (48.9 μmol) of resin **1n**



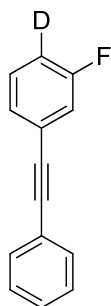
(0.509 mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 6.20 mg (30.5 μmol) of the product in 62% yield. – R_f : 0.53 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (500 MHz, CDCl_3 , ppm), $\delta = 3.86$ (s, 3 H), 6.95–7.01 (m, 2 H), 7.25 (dd, 1 H, $^3J = 10.7$ Hz, $^4J = 1.3$ Hz), 7.33 (d, 1 H, $^3J = 7.8$ Hz, $^4J = 1.3$ Hz), 7.35–7.38 (m, 1 H), 7.49–7.54 (m, 2 H). – ^{13}C NMR (125 MHz, CDCl_3 , ppm), $\delta = 55.4$ (s, 1 C, CH₃), 113.5 (d, 1 C, $^2J = 21.8$ Hz, CH), 114.3 (s, 2 C, CH), 122.2 (d, 1 C, $^4J = 1.7$ Hz, CH), 128.1 (s, 2 C, CH), 130.0 (d, 1 C, $^3J = 8.4$ Hz, CH), 132.4 (s, 1 C, C), 143.1 (d, 1 C, $^3J = 7.7$ Hz, C), 159.5 (s, 1 C, C), 163.2 (d, 1 C, $^1J = 245.2$ Hz, C). – IR (ATR, ν): 2962, 2934, 2840, 2044, 1733, 1603, 1582, 1567, 1518, 1455, 1432, 1397, 1288, 1247, 1182, 1142, 1115, 1025, 873 823, 813, 733, 722, 684, 647, 561, 520, 483, 453 cm^{-1} . – EI (m/z): 203 (100) [M^+], 202 (4), 188 (38), 160 (48), 134 (18). – HRMS ($\text{C}_{13}\text{H}_{10}\text{DOF}$): calc. 203.0857, found 203.0856.

1-Deutero-4-(phenylethynyl)benzene (3o): Following GP 7, 102 mg (39.0 μmol) of resin **1o**



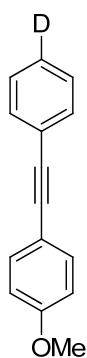
(0.381 mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 50:1) gave 4.00 mg (22.3 μmol) of the product in 57% yield. – R_f : 0.80 (cyclohexane/ethyl acetate, 10:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 7.34–7.37 (m, 5 H), 7.53–7.56 (m, 4 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 89.3 (2 C, C), 123.3 (2 C, C), 128.2 (2 C, CH), 128.2 (CH), 128.3 (2 C, CH), 131.6 (4 C, CH). – IR (ATR, ν): 3062, 1713, 1598, 1493, 1441, 1405, 1311, 1279, 1157, 1103, 1070, 1025, 916, 859, 753, 728, 688, 606, 532, 503 cm^{-1} . – EI (m/z): 179 (100) [M^+], 178 (11), 152 (6), 127 (2), 89 (5). – HRMS ($\text{C}_{14}\text{H}_9\text{D}$): calc. 179.0845, found 174.0844.

2-Fluoro-1-deutero-4-(phenylethynyl)benzene (3p): Following GP 7, 100 mg (51.1 μmol)



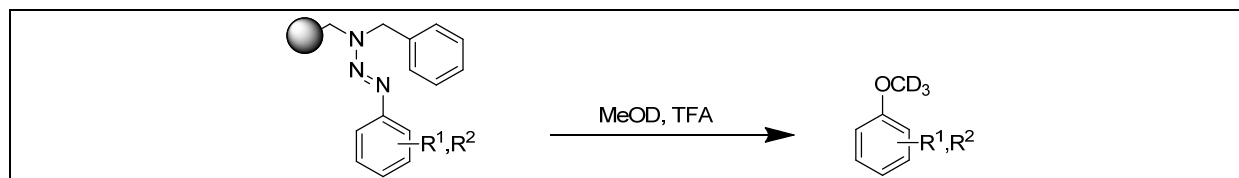
of resin **1p** (0.510 mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 4.40 mg (22.3 μmol) of the product in 43% yield. – R_f : 0.76 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (500 MHz, CDCl_3 , ppm), δ = 7.23 (d, 1 H, 3J = 9.5 Hz), 7.31–7.36 (m, 5 H), 7.53–7.54 (m, 2 H). – ^{13}C NMR (125 MHz, CDCl_3 , ppm), δ = 88.1 (d, 1 C, 4J = 3.0 Hz, C), 90.22 (s, 1 C, C), 114.9–115.7 (m, 1 C, C), 118.4 (d, 1 C, 2J = 22.6 Hz, CH), 122.8 (s, 1 C, C), 125.1 (d, 1 C, 3J = 9.4 Hz, C), 127.5 (d, 1 C, 4J = 1.4 Hz, CH), 128.4 (s, 2 C, CH), 128.6 (s, 1 C, CH), 129.8 (d, 1 C, 3J = 8.6 Hz, CH), 131.7 (s, 2 C, CH). 162.4 (d, 1 C, 1J = 246.5 Hz, C). – IR (ATR, ν): 3442, 3062, 2924, 2212, 1604, 1567, 1493, 1473, 1443, 1410, 1318, 1282, 1249, 1207, 1116, 939, 871, 840, 788, 755, 643, 556 cm^{-1} . – EI (m/z): 154 (100) [M^+], 153 (11), 124 (7), 108 (40), 93 (77), 78 (72), 65 (56). – HRMS ($\text{C}_{14}\text{H}_8\text{DF}$): calc. 197.0751, found 197.0748.

1-Methoxy-4-(*p*-deuterophenylethynyl)benzene (3q): Following GP 7, 108 mg (55.6 μmol)



of resin **1q** (0.515 mmol/g) were reacted with TFA- d_1 . Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 9.90 mg (47.3 μmol) of the product in 85% yield. – R_f : 0.68 (cyclohexane/ethyl acetate, 10:1). – ^1H NMR (500 MHz, CDCl_3 , ppm), δ = 3.83 (s, 3 H), 6.87–6.89 (m, 2 H), 7.33–7.34 (m, 2 H), 7.47–7.48 (m, 2 H), 7.51–7.52 (m, 2 H). – ^{13}C NMR (125 MHz, CDCl_3 , ppm), δ = 55.3 (CH_3), 88.1 (C), 89.3 (C), 114.0 (2 C, CH), 115.4 (C), 123.6 (C), 128.2 (2 C, CH), 131.4 (2 C, CH), 133.0 (2 C, CH), 159.6 (C). – IR (ATR, ν): 2935, 2836, 2284, 2214, 1920,

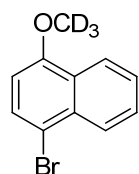
1603, 1589, 1508, 1455, 1405, 1286, 1245, 1203, 1173, 1138, 1107, 1026, 858, 832, 778, 758, 728, 690, 606, 541, 518 cm^{-1} . – EI (m/z): 209 (100) [M^+], 208 (6), 194 (35), 166 (25), 141 (98), 112 (23), 80 (17). – HRMS ($\text{C}_{15}\text{H}_{11}\text{DO}$): calc. 209.0951, found 209.0949.



GP 9: Generation of D₃CO-derivatives in methanol

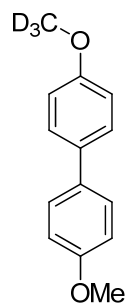
In a Crimptop vial, the resin was first heated in a drying oven (93°C), evacuated until adjusted to room temperature and afterwards flushed with nitrogen. Then methanol-d₄ (1.3 mL/100 mg of resin) and TFA-d₁ (50 μL /100 mg of resin) are added. The vial was sealed, agitated for 14 h at 80 °C, and then the resin was filtered off and washed with acetone, methanol and dichloromethane. The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography.

4-d₃-Methoxy-1-bromonaphthalene (4l): Following GP 9, 136 mg (81.0 μmol) of resin **1l**



(0.595 mmol/g) were reacted with TFA-d₁. Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 10.9 mg (45.4 μmol) of the product in 56% yield. – R_f : 0.76 (cyclohexane/ethyl acetate, 10:1). – ¹H NMR (400 MHz, CDCl_3 , ppm), δ = 6.69 (d, 1 H, ³J = 8.2 Hz), 7.52 (ddd, 1 H, ³J = 8.2 Hz, ³J = 6.9 Hz, ⁴J = 1.2 Hz), 7.52 (ddd, 1 H, ³J = 8.4 Hz, ³J = 6.9 Hz, ⁴J = 1.3 Hz), 7.66 (d, 1 H, ³J = 8.2), 8.16 (dd, 1 H, ³J = 8.4 Hz, ⁴J = 1.2 Hz), 8.16 (dd, 1 H, ³J = 8.2 Hz, ⁴J = 1.3 Hz). – ¹³C NMR (100 MHz, CDCl_3 , ppm), δ = 104.5 (CH), 113.2 (C), 122.4 (CH), 125.9 (CH), 126.7 (C), 126.8 (CH), 127.7 (CH), 129.4 (CH), 132.4 (C), 155.2 (C). – IR (ATR, ν): 3069, 2922, 2222, 2068, 1667, 1620, 1587, 1505, 1455, 1421, 1374, 1327, 1298, 1265, 1244, 1202, 1158, 1128, 1102, 1079, 1026, 973, 895, 806, 758, 613 cm^{-1} . – EI (m/z): 239/241 (100/95), 221/223 (38/38), 193/195 (48/48), 114 (33). – HRMS ($\text{C}_{11}\text{H}_6\text{D}_3\text{BOr}$): calc. 239.0025, found 239.0024.

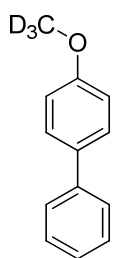
4-(d₃-Methoxy)-4'-methoxy-1,1'-biphenyl (4m): Following GP 9, 142 mg (53.4 μmol) of



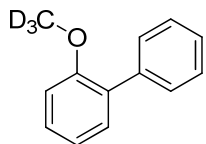
resin **1m** (0.376 mmol/g) were reacted with TFA. Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 6.40 mg (29.5 μmol) of the product in

55% yield. – R_f : 0.25 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 3.85 (s, 3 H), 6.94–6.98 (m, 4 H), 7.46–7.50 (m, 4 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 55.3 (CH_3), 114.1 (2 C, CH), 114.2 (2 C, CH), 127.7 (4 C, CH), 133.4 (C), 133.5 (C), 158.7 (2 C, C). – IR (ATR, ν): 2924, 2853, 2219, 2071, 1607, 1500, 1275, 1251, 1182, 1110, 1039, 990, 957, 824, 810, 771 cm^{-1} . – EI (m/z): 217 (100) [M^+], 202 (46), 174 (123), 156 (7), 128 (12), 108 (6). – HRMS ($\text{C}_{14}\text{H}_{11}\text{D}_3\text{O}_2$): calc. 217.1182, found 217.1184.

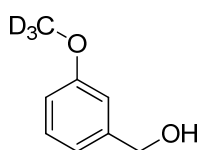
4-(d_3 -Methoxy)-1,1'-biphenyl (4r): Following GP 9, 123 mg (49.1 μmol) of resin **1r** (0.399 mmol/g) were reacted with TFA. Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 6.50 mg (34.7 μmol) of the product in 71% yield. – R_f : 0.64 (cyclohexane/ethyl acetate, 10:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 6.95–7.01 (m, 2 H), 7.30–7.34 (m, 1 H), 7.39–7.46 (m, 2 H), 7.51–7.58 (m, 4 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 114.1 (2 C), 126.6, 126.7 (2 C), 128.1 (2 C), 128.7 (2 C), 133.7, 140.8, 159.0. – IR (ATR, ν): 3034, 2924, 2253, 2221, 2069, 1604, 1520, 1482, 1269, 1201, 1105, 987, 955, 832, 757, 685 cm^{-1} . – EI (m/z): 187 (100) [M^+], 169 (30), 141 (29), 115 (20). – HRMS ($\text{C}_{13}\text{H}_9\text{D}_3\text{O}$): calc. 187.1076, found 187.1075.



2-(d_3 -Methoxy)-1,1'-biphenyl (4s): Following GP 9, 110 mg (74.1 μmol) of resin **1s** (0.674 mmol/g) were reacted with TFA. Column chromatography (cyclohexane/ethyl acetate, 50:1) gave 10.6 mg (56.6 μmol) of the product in 76% yield. – R_f : 0.56 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (500 MHz, CDCl_3 , ppm), δ = 7.00–7.08 (m, 2 H), 7.31–7.38 (m, 3 H), 7.39–7.46 (m, 2 H), 7.52–7.57 (m, 2 H). – ^{13}C NMR (125 MHz, CDCl_3 , ppm), δ = 111.1, 120.8, 126.9, 128.0 (2 C), 128.6, 129.5 (2 C), 130.7, 130.9, 138.5, 156.4. – IR (ATR, ν): 3059, 3026, 2925, 2217, 2069, 1596, 1583, 1503, 1481, 1435, 1270, 1240, 1125, 1108, 991, 753, 732, 714 cm^{-1} . – EI (m/z): 187 (100) [M^+], 169 (27), 141 (21), 115 (23). – HRMS ($\text{C}_{13}\text{H}_9\text{D}_3\text{O}$): calc. 187.1076, found 187.1078.

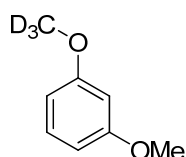


3-[(d_3 -Methoxy)phenyl]methanol (4t): Following GP 9, 130 mg (85.5 μmol) of resin **1t** (0.660 mmol/g) were reacted with TFA. Column chromatography (cyclohexane/ethyl acetate, 4:1) gave 6.20 mg (43.9 μmol) of the product in 51% yield. – R_f : 0.08 (cyclohexane/ethyl acetate, 10:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 4.57 (s, 2 H), 6.78–6.83 (m, 1 H), 6.89–6.93 (m, 2



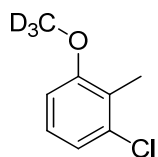
H), 7.20–7.26 (m, 1 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 65.3 (CH_2), 112.2 (CH), 113.3 (CH), 119.1 (CH), 129.6 (CH), 142.5 (C), 159.8 (C). – IR (ATR, ν): 3328, 2925, 2219, 2070, 1585, 1487, 1448, 1268, 1158, 1108, 1008, 857, 780, 728, 691 cm^{-1} . – EI (m/z): 141 (100) [M^+], 140 (38), 124 (19), 112 (84), 105 (28), 94 (28), 77 (37). – HRMS ($\text{C}_8\text{H}_7\text{D}_3\text{O}_2$): calc. 141.0869, found 141.0867.

1-(d₃-Methoxy)-3-methoxybenzene (4u): Following GP 9, 102 mg (83.1 μmol) of resin **1u**



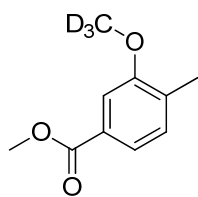
(0.816 mmol/g) were reacted with TFA. Column chromatography (cyclohexane/ethyl acetate, 10:1) gave 6.10 mg (43.2 μmol) of the product in 52% yield. – R_f : 0.37 (cyclohexane/ethyl acetate, 10:1). – ^1H NMR (400 MHz, CDCl_3 , ppm), δ = 3.80 (s, 3 H), 6.42–6.50 (m, 3 H), 7.17–7.21 (m, 1 H). – ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ = 55.3, 100.5, 106.1 (2 C), 129.8, 160.8, 160.8. – IR (ATR, ν): 3442, 2925, 2219, 2071, 1726, 1600, 1491, 1475, 1292, 1270, 1204, 1168, 1157, 1111, 1043, 835, 763, 687, 646, 561 cm^{-1} . – EI (m/z): 141 (100) [M^+], 112 (37), 80 (32), 65 (18).

1-Chloro-3-(d₃-methoxy)-2-methylbenzene (4v): Following GP 9, 221 mg (162 μmol) of



resin **1v** (0.735 mmol/g) were reacted with TFA. Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 9.40 mg (58.9 μmol) of the product in 36% yield. – R_f : 0.57 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 2.27 (s, 3 H), 6.74 (d, 1 H, 3J = 8.04 Hz), 6.97 (d, 1 H, 3J = 7.83 Hz), 7.05–7.11 (m, 1 H). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 12.6, 108.4, 121.3, 125.1, 126.6, 135.1, 158.5. – IR (ATR, ν): 3442, 2928, 2853, 2255, 2221, 2071, 1736, 1593, 1577, 1465, 1379, 1298, 1270, 1190, 1155, 1109, 1086, 1030, 957, 815, 798, 767, 706 cm^{-1} . – EI (m/z): 159 (100) [M^+], 149 (50), 141 (32), 124 (46), 105 (18), 92 (17), 77 (42). – HRMS ($\text{C}_8\text{H}_6\text{DClO}$): calc. 159.0530, found 159.0533.

Methyl 3-(d₃-methoxy)-4-methylbenzoate (4w): Following GP 9, 184 mg (104 μmol) of

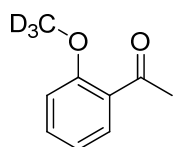


resin **1w** (0.570 mmol/g) were reacted with TFA. Column chromatography (cyclohexane/ethyl acetate, 20:1) gave 14.1 mg (77.0 μmol) of the product in 73% yield.

Upscaling: In a 20 mL vial 2.40 g (1.37 mmol) of resin **1w** (0.570 mmol/g) were first evacuated, flushed with nitrogen, and then suspended in 11 mL of methanol-d₄. After addition of 1.2 mL of trifluoroacetic acid the vial was sealed and the mixture was

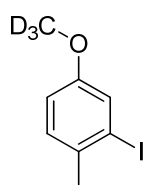
agitated for 15 h at 80 °C. After cooling down to room temperature the resin was filtered off, washed with acetone and ethyl acetate and the residue was purified by column chromatography (100% cyclohexane → cyclohexane/ethyl acetate, 10:1) to yield 206 mg (1.12 mmol, 82%) of a pale yellow oil. – R_f : 0.20 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 2.26 (s, 3 H), 3.90 (s, 3 H), 7.18 (d, 1 H, 3J = 7.7 Hz), 7.47 (d, 1 H, 4J = 1.5 Hz), 7.56 (dd, 1 H, 3J = 7.7, 4J = 1.5 Hz). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 16.5 (CH_3), 52.0 (CH_3), 110.4 (CH), 121.8 (CH), 129.9 (CH), 130.4, 132.5, 157.6, 167.2. – IR (ATR, ν): 3426, 2953, 2221, 2072, 1720, 1608, 1584, 1504, 1436, 1415, 1383, 1321, 1294, 1274, 1238, 1196, 1129, 1106, 1018, 986, 873, 791, 761 cm^{-1} . – EI (m/z): 183 (100) [M^+], 152 (116), 137 (2), 124 (20), 106 (8), 92 (20). – HRMS ($\text{C}_{10}\text{H}_9\text{D}_3\text{O}_3$): calc. 183.0975, found 183.0971.

2-(d₃-Methoxy)acetophenone (4x): Following GP 9, 114 mg (71.2 μmol) of resin **1x** (0.624



mmol/g) were reacted with TFA. Column chromatography (dichloromethane / methanol, 10:1) gave 6.90 mg (44.2 μmol) of the product in 62% yield. – R_f : 0.34 (dichloromethane / methanol, 10:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 6.95–7.03 (m, 2 H), 7.43–7.50 (m, 1 H), 7.74 (dd, 1 H, 3J = 7.7 Hz, 4J = 1.9 Hz). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 111.5 (CH), 120.5 (CH), 128.2 (C), 130.4 (C), 133.7 (CH), 158.9 (C), 200.0 (C). – IR (ATR, ν): 2937, 2228, 2073, 1666, 1596, 1480, 1449, 1295, 1247, 1164, 1126, 1104, 1049, 981, 953, 898, 755, 566, 516, 490 cm^{-1} . – EI (m/z): 156 (27) [M^+], 153 (18), 138 (100), 1107 (16), 89 (15), 77 (33). – HRMS ($\text{C}_9\text{H}_4\text{D}_6\text{O}_2$): calc. 156.1057, found 156.1060.

Iodo-4-(d₃-methoxy)-1-methylbenzene (4y): Following GP 9, 136 mg (86.6 μmol) of resin



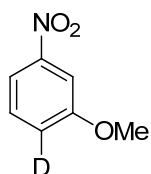
1z (0.639 mmol/g) were reacted with TFA. Column chromatography (cyclohexane/ethyl acetate, 50:1) gave 9.60 mg (38.2 μmol) of the product in 44% yield. – R_f : 0.58 (cyclohexane/ethyl acetate, 20:1). – ^1H NMR (250 MHz, CDCl_3 , ppm), δ = 2.36 (s, 3 H), 6.80 (dd, 1 H, 3J = 8.4 Hz, 4J = 2.7 Hz), 7.12 (d, 1 H, 3J = 8.4 Hz), 7.35 (d, 1 H, 4J = 2.7 Hz). – ^{13}C NMR (62.5 MHz, CDCl_3 , ppm), δ = 26.8 (CH_3), 100.8 (C), 114.2 (CH), 123.9 (CH), 129.7 (CH), 133.3, 157.8. – IR (ATR, ν): 3444, 2920, 2854, 2253, 2218, 2069, 1727, 1597, 1562, 1485, 1452, 1383, 1288, 1244, 1109, 1024, 1000, 960, 836, 803 cm^{-1} . – EI (m/z): 251 (59) [M^+], 217 (3), 184 (7), 157 (13), 124

(23), 105 (8), 90 (10), 77 (20), 58 (29), 43 (100). – HRMS (C₈H₆D₃OI): calc. 251.9886, found 251.9889.

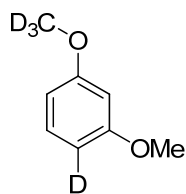
4-(d₃-Methoxy)1,1'-biphenyl (4aa): According to GP 3, 10.7 mg (34.6 μmol) of 1-(biphenyl-4-yl)-3,3-diisopropyltriaz-1-ene (**1aa**) were reacted with TFA-d₁ in methanol-d₄. Column chromatography (cyclohexane/ethyl acetate, 10:1) gave 5.10 mg (27.1 μmol) of the target compound in 79% yield. – R_f = 0.58 (cyclohexane/ethyl acetate, 10:1). – ¹H NMR (250 MHz, CDCl₃, ppm), δ = 6.95–7.01 (m, 2 H), (td, 1 H, ⁴J = 1.9 Hz, ³J = 4.7 Hz), 7.39–7.46 (m, 2 H), 7.51–7.58 (m, 4 H). – ¹³C NMR (62.5 MHz, CDCl₃, ppm), δ = 114.1 (2 C), 126.6, 126.7 (2 C), 128.1 (2 C), 128.7 (2 C), 133.7, 140.8, 159.0. – IR (ATR, ν): 3034, 2924, 2253, 2221, 2069, 1604, 1520, 1482, 1269, 1201, 1105, 987, 955, 832, 757, 685 cm⁻¹. – EI (m/z): 187 (100) [M⁺], 169 (30), 141 (29), 115 (20). – HRMS (C₁₃H₉D₃O): calc. 187.1076, found 187.1075.

tert-Butyl 3-(2-d₃-methoxyphenyl)acrylate (4ab): According to GP 3, 19.8 mg (59.7 μmol) of *tert*-butyl-3-(2-(–3,3-diisopropyltriaz-1-en-1-yl)phenyl)acrylate (**1ab**) were reacted with TFA-d₁ in methanol-d₄. Column chromatography (cyclohexane/ethyl acetate, 10:1) gave 11.4 mg (47.6 μmol) of the target compound in 80% yield. – R_f = 0.38 (cyclohexane/ethyl acetate, 10:1). – ¹H NMR (250 MHz, CDCl₃, ppm), δ = 1.53 (s, 9 H), 6.44 (d, 1 H, ³J = 16.1 Hz), 6.88–6.98 (m, 2 H), 7.33 (ddd, 1 H, ³J = 8.3 Hz, ³J = 7.5 Hz, ⁴J = 1.7 Hz), 7.49 (dd, 1 H, ³J = 7.5 Hz, ⁴J = 1.7 Hz), 7.91 (d, 1 H, ³J = 16.1 Hz). – ¹³C NMR (62.5 MHz, CDCl₃, ppm), δ = 28.2 (3 C), 80.2, 111.0, 120.5, 120.6, 123.6, 128.7, 131.1, 138.9, 158.2, 166.9. – IR (ATR, ν): 2977, 2930, 2221, 2072, 1705, 1631, 1599, 1487, 1457, 1391, 1367, 1324, 1258, 1151, 1112, 992, 875, 752 cm⁻¹. – EI (m/z): 237 (41) [M⁺], 181 (31), 152 (100), 100 (35). – HRMS (C₁₄H₁₅D₃O₃): calc. 237.1444, found 237.1445.

3-Methoxy-4-deutero-1-nitrobenzene (1j): According to general procedure 8, 6.05 g (3.70 mmol) of resin **1j** (0.612 mmol/g) were reacted with TFA-d₁. Column chromatography (cyclohexane/ethyl acetate, 10:1) gave 186 mg (1.21 mmol) of the product in 33% yield. Analytics are identical to compound **1j** via general procedure 7.



1-(D₃-Methoxy)-3-methoxy-4-deuterobenzene (4z): Following GP 9, 111 mg (90.9 μmol) of



resin **1z** were reacted with TFA. Column chromatography (cyclohexane/ethyl acetate, 50:1) gave 4.70 mg (33.1 μmol) of the product in 36% yield over two steps. – R_f: 0.39 (cyclohexane/ethyl acetate, 20:1). – ¹H NMR (400 MHz, CDCl₃, ppm), δ = 3.80 (s, 3 H), 6.47 (d, 1 H, ⁴J = 2.3 Hz), 6.51 (dd, 1 H, ³J = 8.2 Hz, ⁴J = 2.3 Hz), 7.12–7.19 (m, 1 H). – ¹³C NMR (100 MHz, CDCl₃, ppm), δ = 54.4 (sept, 1 C, ²J = 22.0 Hz), 55.3, 100.5, 105.8 (t, 1 C, ²J = 24.9 Hz), 106.1, 129.8, 160.8, 160.8. – IR (ATR, ν): 2922, 2851, 1734, 1596, 1472, 1375, 1245, 1170, 1110, 567. – EI (m/z): 142 [M⁺] (100), 95 (11), 78 (38), 53 (8).

Additional Literature:

Ref. 1 c) for a list of 260 available deuterated drugs as internal standard see: <http://www.lgcstandards.com/media/1014889491.pdf>.

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Ref. 5 b) E. Strandberg and A. S. Ulrich, *Concepts Magn. Reson. Part A* 2004, **23A**, 89–120 and references therein; c) S. Jankowski, *Annu. Reports NMR Spectroscopy* 2009, **68**, 149–191.

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Ref. 12 other methods. Reviews: c) J. Atzrodt, V. Derdau, T. Fey and J. Zimmermann, *Angew. Chem.* 2007, **119**, 7890–7911; *Angew. Chem. Int. Ed.* 2007, **46**, 7744–7765; d) W. J. S. Lockey, *J. Labelled Compd. Radiopharm.* 1983, **21**, 45–57; e) M. H. G. Prechtel, M. Hölscher, Y. Ben-David, N. Theyssen, R. Loschen, D. Milstein and W. Leitner, *Angew. Chem.* 2007, **119**, 2319–2322; *Angew. Chem. Int. Ed.* 2007, **46**, 2269–2272; f) M. Yamamoto, Y. Yokota, K. Oshima and S. Matsubara, *Chem. Commun.* 2004, 1714–1715; g) T. Itou, Y. Yoshimi, K. Nishikawa, T. Morita, Y. Okada, N. Ichinosec, M. Hatanakad *Chem. Commun.* 2010, **46**, 6177–6179; Metal-catalysed hydrogen isotope exchange: h) W. J. S. Lockey and J. R. Heys, *J. Labelled Compd. Radiopharm.* 2010, **53**, 635–644.

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