Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Systematic Modifications of Substitution Patterns for Property Tuning of Photoswitchable Asymmetric Azobenzenes†

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- Supplemental Information -

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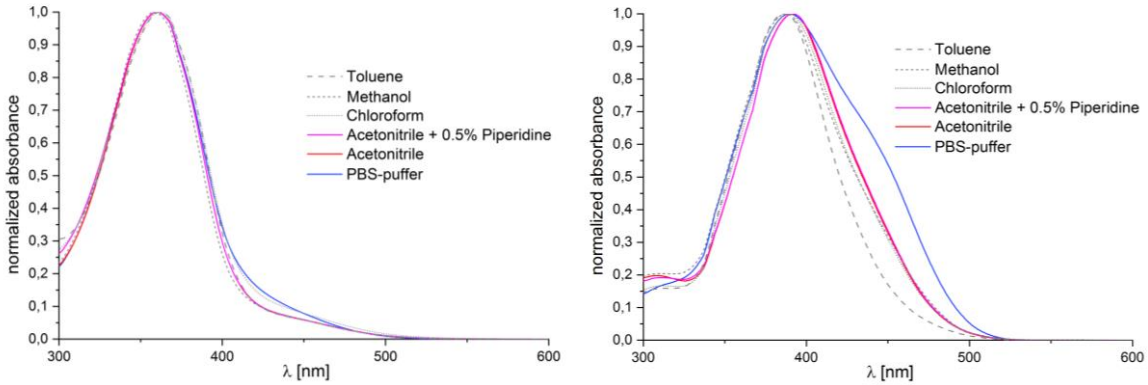


Figure S1. UV-Vis spectra of **9b** (left) and **1c** (right) in different solvents.

Table S1. PSS of azobenzenes in PBS-buffer.[a]

Entry	PSS [%][b]								λ_{max} [nm]
	370 nm	380 nm	390 nm	400 nm	420 nm	450 nm	470 nm	520 nm	
1e	96	94	88	67	44	32	26	15	360
1f	97	94	-	60	41	29	22	10	356
1g	93	87	79	46	32	28	26	21	352
4a	86	90	90	82	66	49	38	24	388
4b	85	90	92	90	80	66	55	32	400
4c	77	78	75	64	54	51	50	45	388
4d	83	88	90	88	81	70	59	30	407
5a	94	95	93	84	69	51	36	12	380
6	92	94	93	86	72	57	44	20	384
7a	93	92	88	72	50	40	37	33	368
9a	94	95	-	81	61	42	29	13	368
9b	96	94	90	71	49	36	30	18	360
9c	93	91	-	69	46	34	27	14	361
9d	95	94	-	72	47	34	27	14	360
9e	94	92	-	70	49	36	28	16	361
10a	95	96	-	79	55	37	28	13	369
10b	95	94	89	71	48	34	27	15	363
10c	81	86	83	71	54	41	32	16	368
10d	90	91	-	80	60	41	28	7	373
11a	90	93	93	87	75	61	45	15	390
11b	91	93	92	83	70	56	43	17	384
11c	81	80	77	67	55	49	48	40	360
12	96	94	88	67	44	32	26	15	370
26e	96	95	-	76	57	42	33	17	366
26f	99	97	-	74	51	35	25	10	361
26a	93	93	91	79	61	40	26	8	370
26b	94	95	91	75	55	40	30	15	365
26c	96	96	-	81	62	46	35	18	368
29a	96	96	94	86	71	53	39	14	380
29e	89	89	85	74	57	42	35	20	368
34	93	93	91	80	62	46	35	16	373
37a	91	94	94	84	67	50	36	15	381
37b	92	93	-	74	54	39	31	18	373
37c	94	94	91	74	48	32	25	16	368
39	82	82	78	64	47	39	38	34	360
47a	82	88	89	83	68	52	41	24	392
47b	78	85	88	87	79	67	58	32	406
47c	68	76	74	66	57	53	53	45	394
47d	75	83	87	88	83	73	64	32	415

[a] measured at 37 °C in PBS-buffer/ CH_3CN (2:1) mixture. [b] amount of *Z*-isomer after irradiation at referred wavelength.

Materials and Methods

Synthetic protocols

The Boc-protected anilines **23** and **32**, mono protected catechol **24a** and phenol **27** were synthesized using standard procedures.[1] TBS-protected catechol **43a** was synthesised following literature procedure of Stein.[2] Naphtols **45c** and **45d** were synthesized according to literature procedures of Deyris[3] and Ramkumar.[4] Oxazine **21** was synthesised according to literature procedures of Mofford[5] and Doherty.[6] All other reagents and solvents were purchased from vendors (Acros, Alfa Aesar, ChemPur, Fluka, Fluorochem, Sigma-Aldrich, Strem Chemicals, TCI Europe N.V., VWR) and were used without further purification unless noted otherwise.

All solvents, when not purchased in suitable purity or dryness, were distilled using standard methods,[7] or suitable dehydration procedures: tetrahydrofuran (THF) was distilled under a N_2 atmosphere from Na/benzophenone before use; dichloromethane (CH_2Cl_2) was distilled under a N_2 atmosphere from CaH_2 before use. Other anhydrous solvents such as toluene and dimethylformamide (DMF) were obtained in HPLC quality and passed through a solvent purification system equipped with Al_2O_3 (toluene) or molecular sieves 3 Å (DMF, Pure Solv, Innovative Technology, Inc., USA) by applying N_2 overpressure immediately before use. Commercial-grade distilled (iPr)$_2$NEt (99%) was used without additional distillation. The petroleum ether used had a boiling range of 40-60 °C. Phosphate buffer (pH = 7) was prepared by dissolving Na_3PO_4×12 H_2O (54.8 g, 0.14 mol) und NaH_2PO_4 (42.7 g, 0.36 mol) in water (1.0 L). Deionized water was used for all experiments.

Chromatography

Reaction progress was monitored by TLC on precoated, Merck Silica gel 60 F254 alumina-backed plates. TLC chromatograms were first visualized by UV irradiation at 254 nm or 320 nm, followed by staining with aqueous $KMnO_4$ (2 g $KMnO_4$, 13.2 g K_2CO_3, 165 mg NaOH, 200 mL H_2O) or ceric ammonium molybdate solution (0.5 g of $Ce(NH_4)_4(SO_4)_4 \times 2H_2O$, 12 g $(NH_4)_6Mo_7O_{24} \times 4H_2O$, 15 mL H_2SO_4, 235 mL H_2O) followed by gentle heating on air for detection. Primary and secondary amines were detected with ninhydrin (6% in EtOH).

Flash chromatography was performed using silica gel (SiO_2, particle size 40 – 63 µm) purchased from Macherey & Nagel, Düren (Germany) under a pressure of 0.3 – 0.5 bar.

Preparative HPLC purification was performed on a Varian system consisting of a ProStar 215 (pump), ProStar 340 (UV/VIS-detector) and a ProStar 701 (collector). A VP250/21 Nucleodur C18 Gravity 5µm column was used. A gradient of Water and Acetonitrile was applied as mobile phase.

NMR spectra

^{1}H- and ^{13}C-NMR spectra were recorded on Bruker Avance I 250 (250 MHz (^{1}H) and 63 Hz (^{13}C)), Bruker Fourier 300 (300 MHz (^{1}H) and 75 Hz (^{13}C)), Bruker Avance III 400 (400 MHz (^{1}H) and 100 MHz (^{13}C)), Bruker Avance III HD 500 (500 MHz (^{1}H) and 100 MHz (^{13}C)), and Bruker AC 600 (600 MHz (^{1}H) and 150 MHz (^{13}C)) spectrometers. Chemical shifts are expressed in parts per million (ppm). The spectra were calibrated to residual solvent signals of $CHCl_3$ (7.26 ppm (^{1}H) and 77.0 ppm (^{13}C)), DMSO-d_5 (2.50 ppm (^{1}H) and 39.43 ppm (^{13}C)), CHD_2OD (3.31 ppm (^{1}H) and 49.0 ppm (^{13}C)), DHO (4.79 ppm (^{1}H)), respectively. Coupling constants are given in Hertz (Hz) and the following notations indicate the multiplicity of the signals: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad signal). Owing to the *E*/*Z* equilibrium of some compounds containing an azobenzene functionality, more signals were observed in the ^{1}H and ^{13}C spectra than would be expected for a single isomer. Signals for the major *E*- isomer are reported. Signal identity and peak assignments were verified by 2D-NMR experiments (COSY, TOCSY, HSQC and HMBC) whenever necessary. NMR spectra are displayed in Supplementary Note 2.

UV–Vis analysis

UV-Vis spectra were recorded using a JASCO V-730 UV–Visible Spectrophotometer with Helma SUPRASIL precision cuvettes (5 mm light path). All compounds were dissolved as 10-30 mM stock solutions in DMF and diluted to the given concentrations using cosolvents and buffers as indicated. Switching was achieved by irradiating the cuvettes at 0.2 to 0.5 cm within the spectrometer for 10 to 30 s. For irradiation high power single chip SMD LEDs from Roithner Lasertechnik GmbH with a current of 350 mA were used. The LEDs show

their main intensity at the specified wavelength with a width of ± 5 nm. UV-spectra of all compounds are reproduced in Supplementary Note 1.

Table S2. LEDs from Roithner Lasertechnik GmbH used in this paper

Entry	λ [nm]	LED code
1	370	VL370-5050
2	380	VL380-5050
3	390	VL390-5050
4	400	VL400-5050
5	420	SMB1N-420H
6	450	SMB1N-D450
7	470	SMD1N-D470
8	520	SMD1N-D520

Relaxation rates were evaluated assigning first order kinetics of the *E*-*Z*-isomerization reaction. Samples were measured under dark (*E*) conditions at their absorption maximum, irradiated (*Z*) to reach photostationary equilibrium, followed by measuring the changing absorbance over time according to first order kinetics. Data were evaluated by fitting the rate equation [A] = $[A]_0$ e^(-*k*t) using the Excel program. Half-lives were obtained by: $t_{1/2}$ = ln(2)/*k*.

The determine the ratio α of the two isomers in the PSS *Fischer's* method was applied.[8] The absorbance (A) of the pure *E*- isomer (dark) and mixed spectra of *E*- and *Z*- isomer after irradiation with two different wavelengths (λ_1 and λ_2) are required. According to *Fischer's* formula:

$$\alpha_{\lambda 1} = \frac{\frac{\Delta A_{\lambda 1}}{A_{\lambda 1,\lambda 1}} - \frac{\Delta A_{\lambda 2}}{A_{\lambda 2,\lambda 2}}}{1 + \frac{\Delta A_{\lambda 1}}{A_{\lambda 1,\lambda 1}} - n\,(1 + \frac{\Delta A_{\lambda 2}}{A_{\lambda 2,\lambda 2}})} \qquad \text{with} \qquad n = \frac{A_{dark,\lambda 1} - A_{\lambda 1,\lambda 1}}{A_{dark,\lambda 1} - A_{\lambda 2,\lambda 1}}$$

the PSS (PSS = α * 100) at the irradiated wavelengths can be determined. In this work, irradiation was carried out at seven to eight different wavelengths. To determine the PSS, the wavelength that provided the largest percentage of (*Z*) isomers was chosen as the basis and the ratio α was determined with the other wavelengths. For this wavelength, the PSS was determined from the mean value of all received α. The other wavelengths were specified relative to it. The determined α values generally had a standard deviation of ± 0.01 – 0.03, for

some aniline derivatives the deviation was up to ± 0.05. Based on the obtained ratio α, the absorbance of the pure (Z) isomer can be calculated using the formula:

$$A_{Z-\mathrm{Isomer},\lambda} = A_{dark,\lambda} + \frac{A_{\lambda 1,\lambda} - A_{darkl,\lambda}}{\alpha_{\lambda 1}}$$

Infrared (IR) spectra

Fourier transform infrared spectroscopy (FT-IR) spectra were obtained by using an IR-Affinity-1 from Shimadzu (ATR, neat or as a thin film). Wave numbers are reported in cm^{-1}.

Microwave reactor

A Biotage Initiator Sixty microwave reactor with sealed glass vessels was used for the irradiation with microwaves. The temperature was measured using an IR sensor (accuracy ± 2%). Reaction times indicate how long the mixture was stirred at the specified temperature, not how long the mixture was irradiated overall.

Melting points

The melting points were measured on a Stuart Melting Point SMP 3 device.

Low- and high-resolution ESI mass spectra

Low- and high-resolution ESI mass spectra were obtained on Thermo-Finnigan LCQ (LR) and Bruker Maxis Impact (HR) spectrometers operating in either positive or negative ionization modes, respectively, fitted to Shimadzu AL-10 (LR-ESI-MS) or Dionex Ultima 3000 HPLC systems (HR-ESI-MS).

Chemical Synthesis and Characterisation

Standard Procedures

For Standard Procedures, the conditions and ratios of reactants/reagents employed were kept constant. Solvent volumes refer to 1.0 equiv. In general, the *E*- and *Z*- isomers of the azobenzenes were separable by silica-gel chromatography and on TLC when the thermal relaxation half-life time was in the range of minutes or longer. For improving separation, yields and purity of the desired product the crude materials were kept in the dark at room temperature overnight after isolation and protected from UV light during chromatographic separation (i.e. work under red light, wrapped/shielded column wherever possible).

Standard Procedure A: Diazo Coupling using isoamyl nitrite

To a solution of the aniline (1.0 equiv.) in MeOH (5.0 mL/mmol) conc. HCl (6.0 equiv.) was added and cooled to 0 °C (icebath). In case of Boc-protected anilines the amount of HCl was doubled and the solution was stirred at room temperature until TLC showed full deprotection before cooling down (approx. 2 h). A solution of isoamyl nitrite (1.02 equiv.) in methanol (1.0 mL/mmol) was added slowly and the mixture was stirred for 30 min in the cold.

A1: A cold solution of the phenol (1.05 equiv.) in methanol (2.0 mL/mmol) was added followed by addition of NaOH (2.0 M) until pH = 11 was reached (characteristic color change from yellow to deep red).

A2: A solution of the phenol (1.05 equiv.) in methanol (2.0 mL/mmol) was basified with NaOH (2.0 M, 7.2 equiv.) and cooled in an icebath. To it was added the solution of the diazonium salt prepared above dropwise over 1 minute.

After 30 minutes stirring at 0 °C, the pH was adjusted to 7 with phosphate buffer (30 mL/mmol) and $CHCl_3$ (30 mL/mmol) was added. The organic layer was separated followed by extraction of the aqueous layer with $CHCl_3$ (3 – 5 × 20 mL/mmol). The combined organic extracts were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica-gel chromatography or recrystallization provided the pure azobenzene.

Standard Procedure B: Phenol etherification in acetone

To a solution of the phenol (1.0 equiv.) and K_2CO_3 (4.0 equiv.) in anhydrous acetone (10 mL/mmol) the alkylhalogenide (1.0 – 10.0 equiv.) was added and stirred at reflux for 2 – 18 h until TLC indicated satisfactory conversion. The reaction mixture was concentrated under reduced pressure. The residue was dissolved in EtOAc (20 mL/mmol) and phosphate buffer (pH = 7, 30 mL/mmol). The organic layer was separated followed by extraction of the aqueous layer with EtOAc (3 × 20 mL/mmol). The combined organic extracts were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica-gel chromatography or recrystallization provided the arylether.

Standard Procedure C: Ester or Imine cleavage with LiOH

Ester or Imine (1.0 equiv.) was dissolved in THF (20 mL/mmol), treated with aqueous LiOH (2 M, 10.0 equiv.), and stirred for 2 h at room temperature. The solution was neutralized with aqueous HCl (1 M). Most of the THF was removed under reduced pressure and $CHCl_3$ (20 mL/mmol) was added. The organic layer was separated followed by extraction of the aqueous layer with $CHCl_3$ or EtOAc (3 – 12 × 20 mL/mmol). The combined organic extracts were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. If necessary, the residue was purified by silica-gel chromatography or prep. HPLC to obtain the carboxylic acid.

Standard Procedure D: Buchwald – Hartwig amination

A solution of bromoaryl azobenzene (1.0 equiv.) and Cs_2CO_3 (4.0 equiv.) in anhydrous acetonitrile (25 mL/mmol) was purged with N_2 in a microwave reaction vial over 20 minutes. Amine (2.0 equiv.), $Pd(dba)_2$ (0.1 equiv.) and RuPhos (0.2 equiv.) were added and the vial was capped under nitrogen flow. The resulting suspension was heated with stirring to 100 °C and kept at this temperature until TLC indicated satisfactory conversion (typically 16 h). The

mixture was cooled to RT, filtered, and concentrated under reduced pressure. Purification by silica-gel chromatography provided the aminated azobenzene.

Standard Procedure E: Reductive amination

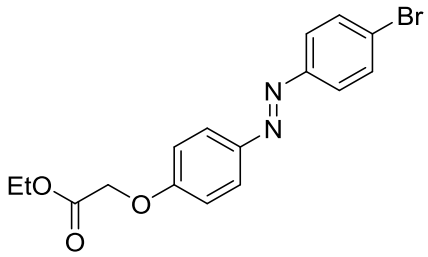
To a solution of amine (1.0 equiv.) in a mixture of AcOH and EtOH (1:9, 25 mL/mmol) aldehyde (3.0 equiv.) was added and stirred for 2 hours at room temperature. The mixture was cooled to 0 °C (icebath) and $NaCNBH_3$ (4.5 equiv.) was added. The icebath was removed and stirring was continued until TLC indicated satisfactory conversion (16 – 38 h). The solution was neutralized with aqueous NaOH (2 M) and most of the EtOH was removed under reduced pressure followed by extraction of the aqueous phase with $CHCl_3$ (3 × 20 mL/mmol). The combined organic extracts were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica-gel chromatography provided the pure azobenzene.

Standard Procedure F: Reduction of nitroaryl compounds

Nitrobenzene (1.0 equiv.) was dissolved in a mixture of EtOH, EtOAc and AcOH (5:10:1, 50 mL/mmol). Pd/C (10 m%, 55 mg/mmol) was added and H_2 was bubbled trough the solution until TLC indicates satisfactory conversion (6 – 24 h). The mixture was filtered through a pad of celite and the filter cake was washed with EtOH (~100 mL/mmol). Toluene (5 mL/mmol) was added and the mixture was concentrated under reduced pressure. The resulting crude product was dried under vacuum and used without further purification.

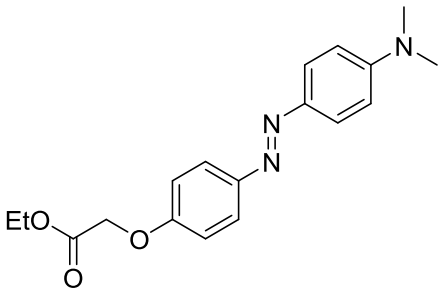
Syntheses

Ethyl-2-(4´-((4´´-bromophenyl)diazenyl)phenoxy)acetate **1a**



Standard Procedure **B** with azobenzene **31** (1.10 g, 4.0 mmol, 1.0 equiv.) and ethyl bromoacetate (1.45 mL, 13.1 mmol, 3,3 equiv.) gave azobenzene **1a** (1.20 g, 83 %) as a yellow solid after recrystallization (toluene/petroleum ether, 1:4). R_f = 0.55 (EtOAc/petroleum ether, 1:4); m.p. 203 °C; ^{1}H-NMR (300MHz, $CDCl_3$): δ = 7.92 (d, J = 9.0 Hz, 2 H), 7.77 (d, J = 8.6 Hz, 2 H), 7.64 (d, J = 8.5 Hz, 2 H), 7.03 (d, J = 9.0 Hz, 2 H), 4.71 (s, 2 H), 4.31 (q, J = 7.1 Hz, 2 H), 1.32 (t, J = 7.1 Hz, 3 H); ^{13}C-NMR (75MHz, $CDCl_3$): δ = 168.4, 160.3, 151.4, 147.4, 132.2, 124.9, 124.8, 124.1, 115.0, 65.5, 61.6, 14.2; IR: $\tilde{\nu}$ = 3167, 3024, 2816, 1740, 1570, 1473, 1409, 1219, 1060, 834; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε)= 464 nm (19800 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{16}H_{16}BrN_2O_3$: 363.0339/365.0320 $[M+H]^+$; found: 363.0344/365.0327.

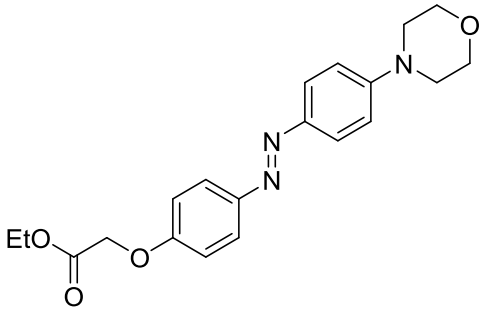
Ethyl-2-(4´-((4´´-(dimethylamino)phenyl)diazenyl)phenoxy)acetate **1b**



Standard Procedure **D** with azobenzene **1a** (50.0 mg, 0.14 mmol, 1.0 equiv.), dimethylamine hydrochloride (22.5 mg, 0.28 mmol, 2.0 equiv.) and Cs_2CO_3 (269 mg, 0.83 mmol, 6.0 equiv.) gave azobenzene **1b** (39.1 mg, 87 %) as a scarlet solid after silica-gel chromatography (CH_2Cl_2/MeOH, 20:1). R_f = 0.26 (CH_2Cl_2/MeOH, 20:1); m.p. 142 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, J = 3.3 Hz, 2 H), 7.83 (d, J = 3.1 Hz, 2 H), 7.00 (d, J = 8.9 Hz, 2 H), 6.77 (d, J = 9.1 Hz, 2 H), 4.69 (s, 2 H), 4.30 (q, J = 7.2 Hz, 2 H), 3.09 (s, 6 H), 1.32 (t, J = 7.1 Hz, 3 H); ^{13}C-NMR (101MHz, $CDCl_3$): δ = 168.7, 158.9, 152.1, 148.1, 143.6, 124.6, 123.3, 114.8,

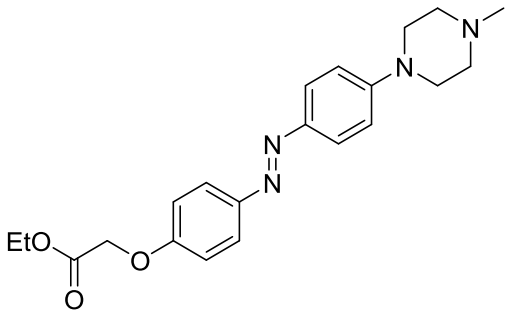
111.5, 65.6, 61.5, 40.3, 14.2; IR: $\tilde{\nu}$ = 3460, 3082, 2961, 2820, 1738, 1597, 1366, 1207, 1083, 838; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 409 nm (24700 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{18}H_{22}N_3O_3$: 328.1656 $[M+H]^+$; found: 328.1658.

Ethyl-2-(4´-((4´´-morpholinophenyl)diazenyl)phenoxy)acetate **1c**



Standard Procedure **D** with azobenzene **1a** (50.0 mg, 0.14 mmol, 1.0 equiv.) and morpholine (24.0 mg, 0.28 mmol, 2.0 equiv.) gave azobenzene **1c** (40.2 mg, 79 %) as an orange solid after silica-gel chromatography (EtOAc/petroleum ether, 1:4 → 1:2). R_f = 0.28 (EtOAc/petroleum ether, 1:4); m.p. 160 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 9.0 Hz, 2 H), 7.87 (d, *J* = 9.0 Hz, 2 H), 7.01 (d, *J* = 9.1 Hz, 2 H), 6.98 (d, *J* = 9.1 Hz, 2 H), 4.70 (s, 2 H), 4.30 (q, *J* = 7.2 Hz, 2 H), 3.95 - 3.82 (m, 4 H), 3.35 - 3.28 (m, 4 H), 1.32 (t, *J* = 7.2 Hz, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 168.6, 159.3, 152.8, 147.9, 145.8, 124.3, 124.1, 114.9, 114.5, 66.7, 65.5, 61.5, 48.2, 14.2; IR: $\tilde{\nu}$ = 3464, 2963, 2843, 1759, 1578, 1366, 1246, 1153, 921, 841; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 392 nm (26200 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{20}H_{24}N_3O_4$: 370.1761 $[M+H]^+$; found: 370.1766.

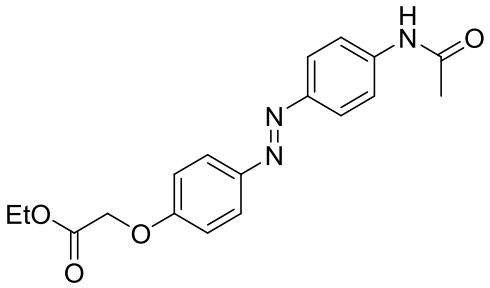
Ethyl-2-(4´-((4´´-(4´´´-methylpiperazin-1-yl)phenyl)diazenyl)phenoxy)acetate **1d**



Standard Procedure **D** with azobenzene **1a** (100.0 mg, 0.28 mmol, 1.0 equiv.) and 1-methylpiperazine (55.2 mg, 0.55 mmol, 2.0 equiv.) gave azobenzene **1d** (89.0 mg, 85 %) as a yellow solid after silica-gel chromatography (CH_2Cl_2/MeOH, 80:1 → 20:1). R_f = 0.25

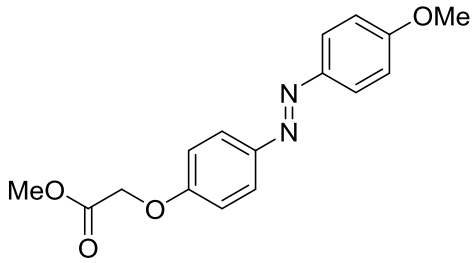
(CH_2Cl_2/MeOH, 20:1); m.p. 150 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 3.4 Hz, 2 H), 7.84 (d, *J* = 3.4 Hz, 2 H), 7.01 (d, *J* = 8.2 Hz, 2 H), 6.98 (d, *J* = 8.2 Hz, 2 H), 4.70 (s, 2 H), 4.30 (q, *J* = 7.2 Hz, 2 H), 3.43 - 3.34 (m, 4 H), 2.64 - 2.55 (m, 4 H), 2.38 (s, 3 H), 1.32 (t, *J* = 7.1 Hz, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 168.6, 159.2, 152.8, 148.0, 145.4, 124.3, 124.1, 114.8, 114.7, 65.5, 61.5, 54.9, 47.9, 46.1, 14.2; IR: $\tilde{\nu}$ = 3460, 2931, 2839, 2793, 1751, 1736, 1581, 1497, 1443, 1377, 1220, 834; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 396 nm (27300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{21}H_{27}N_4O_3$: 383.2078 $[M+H]^+$; found: 383.2084.

Ethyl-2-(4´-((4´´-acetamidophenyl)diazenyl)phenoxy)acetate **1e**



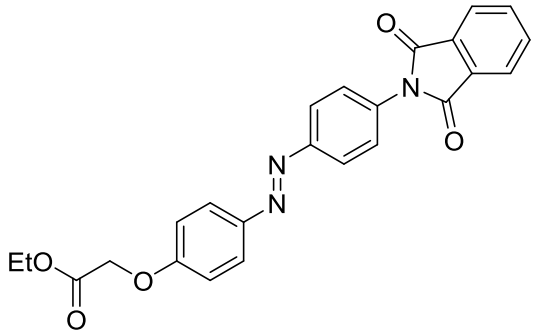
Standard Procedure **D** with azobenzene **1a** (100.0 mg, 0.28 mmol, 1.0 equiv.), and acetamide (32.5 mg, 0.55 mmol, 2.0 equiv.) gave azobenzene **1e** (61.2 mg, 65 %) as an orange solid after silica-gel chromatography (CH_2Cl_2/MeOH, 9:1). R_f = 0.40 (CH_2Cl_2/MeOH, 9:1); m.p. 192 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 6.7 Hz, 2 H), 7.90 (d, *J* = 6.7 Hz, 2 H), 7.68 (d, *J* = 8.5 Hz, 2 H), 7.34 (s, 1 H), 7.04 (d, *J* = 8.8 Hz, 2 H), 4.72 (s, 2 H), 4.32 (q, *J* = 7.2 Hz, 2 H), 2.25 (s, 3 H), 1.34 (t, *J* = 7.2 Hz, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 168.5, 168.2, 159.9, 149.1, 147.7, 140.0, 124.6, 123.7, 119.7, 114.9, 65.5, 61.6, 24.8, 14.2; IR: $\tilde{\nu}$ = 3005, 2913, 2322, 1717, 1601, 1504, 1377, 1203, 1076, 837, 714; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 361 nm (25700 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{18}H_{20}N_3O_4$: 342.1448 $[M+H]^+$; found: 342.1451.

Methyl-2-(4´-((4´´-methoxyphenyl)diazenyl)phenoxy)acetate **1f**



Standard Procedure **B** with azobenzene **25f** (30 mg, 0.10 mmol, 1.0 equiv.) and MeI (104 mg, 0.73 mmol, 7.0 equiv.) gave azobenzene **1f** (26 mg, 83 %) as a yellow solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:2). R_f = 0.58 (EtOAc/petroleum ether, 1:2); m.p. 149 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.86 (dd, J = 1.1, 9.0 Hz, 4 H), 6.99 (dd, J = 1.9, 8.9 Hz, 4 H), 4.70 (s, 2 H), 3.87 (s, 3 H), 3.81 (s, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.0, 161.7, 159.5, 147.8, 147.0, 124.5, 124.4, 114.9, 114.2, 65.4, 55.6, 52.4; IR: $\tilde{\nu}$ = 2955, 2322, 1766, 1578, 1493, 1211, 1026, 840; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 354 nm (26000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{16}H_{17}N_2O_4$: 301.1183 $[M+H]^+$; found: 301.1183.

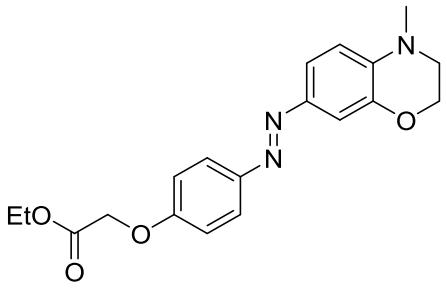
Ethyl-2-(4´-((4´´-(1´´´,3´´´-dioxoisoindolin-2´´´-yl)phenyl)diazenyl)phenoxy)acetate **1g**



Bromaryl azobenzene **1a** (50.0 mg, 0.14 mmol, 1.0 equiv.) CuI (39.3 mg, 0.21 mmol, 1.5 equiv.), and potassium phthalimide (38.3 mg, 0.21 mmol, 1.5 equiv.) were placed in a microwave reaction vial. The vial was sealed, and the atmosphere replaced by nitrogen. The solids were suspended in dry DMF (4 mL), and the vial was heated for 9 h to 160 °C. After cooling aqueous HCl (1 M, 3 mL) was added, followed by extraction with $CHCl_3$ (3 × 10 mL). The combined organic extracts were washed with H_2O (20 mL), and brine (20 mL), dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica-gel chromatography (EtOAc/petroleum ether, 1:9 → 1:1) provided pure azobenzene **1g** (42.0 mg, 71 %) as an ocher solid. R_f = 0.39 (EtOAc/petroleum ether, 1:2); m.p. 189 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.06 - 7.92 (m, 6 H), 7.84 - 7.80 (m, J = 3.1, 5.5 Hz, 2 H),

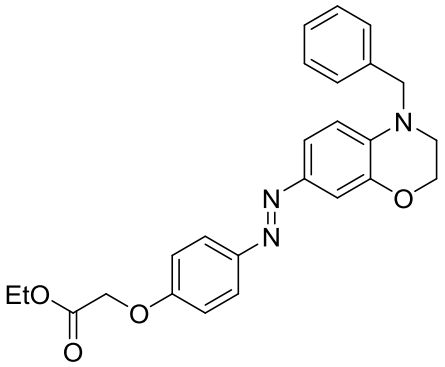
7.64 (d, J = 8.8 Hz, 2 H), 7.04 (d, J = 9.0 Hz, 2 H), 4.72 (s, 2 H), 4.31 (q, J = 7.2 Hz, 2 H), 1.33 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 168.4, 167.1, 160.3, 151.5, 147.6, 134.6, 133.5, 131.7, 126.8, 124.9, 123.9, 123.3, 114.9, 65.5, 61.6, 14.2; IR: $\tilde{\nu}$ = 3375, 2990, 2322, 1740, 1694, 1524, 1223, 1153, 1080, 841; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 351 nm (25300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{24}H_{20}N_3O_5$: 430.1397 $[M+H]^+$; found: 430.1410.

Ethyl -2-(4´-((4´´-methyl-3´´,4´´-dihydro-2´´*H*-benzo[b][1´´,4´´]oxazin-7-yl)diazenyl) phenoxy)acetate **2a**



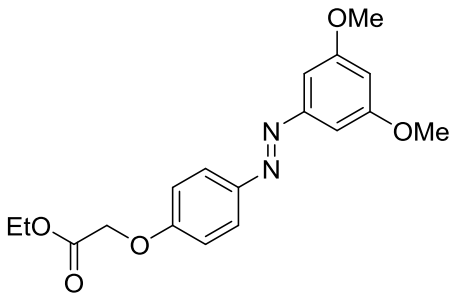
Standard Procedure **E** with azobenzene **19** (66 mg, 0.19 mmol, 1.0 equiv.) and paraformaldehyde (17 mg, 0.58 mmol, 3.0 equiv.) gave azobenzene **2a** (57 mg, 83 %) as an orange solid after purification by silica-gel chromatography ($CHCl_3$). R_f = 0.31 (CH_2Cl_2); m.p. 112 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.83 (d, J = 9.0 Hz, 2 H), 7.52 (dd, J = 2.2, 8.6 Hz, 1 H), 7.40 (d, J = 2.1 Hz, 1 H), 7.00 (d, J = 9.0 Hz, 2 H), 6.72 (d, J = 8.7 Hz, 1 H), 4.69 (s, 2 H), 4.36 - 4.24 (m, 4 H), 3.43 - 3.37 (m, 2 H), 3.02 (s, 3 H), 1.32 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 168.6, 159.0, 148.0, 144.8, 144.0, 139.1, 124.0, 120.6, 114.8, 110.8, 107.7, 65.6, 64.4, 61.5, 48.9, 38.5, 14.2; IR: $\tilde{\nu}$ = 3460, 2075, 2972, 1739, 1582, 1520, 1377, 1203, 810; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 419 nm (26800 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{22}N_3O_4$: 356.1605 $[M+H]^+$; found: 356.1606.

Ethyl-2-(4´-((4´´-benzyl-3´´,4´´-dihydro-2´´*H*-benzo[b][1´´,4´´]oxazin-7-yl)diazenyl) phenoxy)acetate **2b**



Standard Procedure **E** with azobenzene **19** (124 mg, 0.36 mmol, 1.0 equiv.) and benzaldehyde (116 mg, 1.09 mmol, 3.0 equiv.) gave azobenzene **2b** (105 mg, 68 %) as an orange solid after purification with silica-gel chromatography (CH_2Cl_2/petroleum ether, 1:1 → 2:1). R_f = 0.14 (CH_2Cl_2); m.p. 193 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.83 (d, J = 9.0 Hz, 2 H), 7.46 (qd, J = 2.3, 4.6 Hz, 2 H), 7.40 - 7.26 (m, 5 H), 7.00 (d, J = 9.0 Hz, 2 H), 6.74 (d, J = 9.2 Hz, 1 H), 4.69 (s, 2 H), 4.59 (s, 2 H), 4.36 - 4.25 (m, 4 H), 3.54 - 3.46 (m, 3 H), 1.32 (t, J = 7.1 Hz, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 168.6, 159.0, 148.0, 144.6, 143.8, 138.3, 137.1, 128.8, 127.4, 126.9, 124.0, 120.6, 114.8, 111.1, 108.5, 65.6, 64.3, 61.5, 54.5, 47.4, 14.2; IR: $\tilde{\nu}$ = 3460, 2909, 2870, 2326, 1763, 1582, 1246, 1080, 880, 810; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 420 nm (25300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{25}H_{26}N_3O_4$: 432.1918 $[M+H]^+$; found: 432.1921.

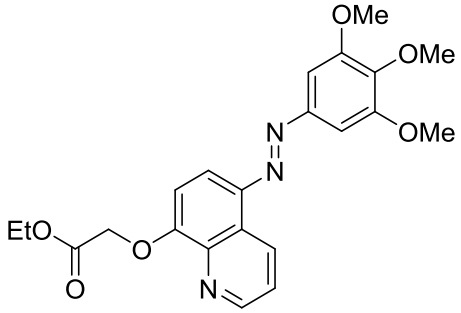
Ethyl-2-(4´-((3´´,5´´-trimethoxyphenyl)diazenyl)phenoxy)acetate **3**



Standard Procedure **B** with azobenzene **22** (199 mg, 0.77 mmol, 1.0 equiv.) and ethyl bromoacetate (282 µL, 13.4 mmol, 3.3 equiv.) gave azobenzene **3** (241 mg, 91 %) as an orange solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4). R_f = 0.40 (EtOAc/petroleum ether, 1:4); m.p. 93 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 9.1 Hz, 2 H), 7.11 (d, J = 2.3 Hz, 2 H), 7.05 (d, J = 9.1 Hz, 2 H), 6.60 (t, J = 2.3 Hz, 1

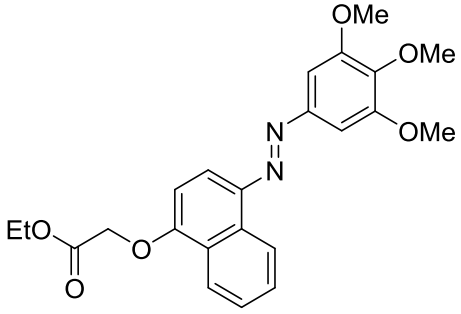
H), 4.72 (s, 2 H), 4.32 (q, J = 7.0 Hz, 2 H), 3.89 (s, 6 H), 1.33 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 168.5, 161.1, 160.2, 154.5, 147.4, 124.8, 114.9, 103.5, 100.7, 65.5, 61.6, 55.6, 14.2; IR: $\tilde{\nu}$ = 3062, 2908, 1762, 1582, 1412, 1210, 1145, 852, 829, 675; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 345 nm (20100 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{18}H_{21}N_2O_5$: 345.1445 $[M+H]^+$; found: 345.1450.

Ethyl-2-((5´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)quinolin-8´-yl)oxy)acetate **4a**



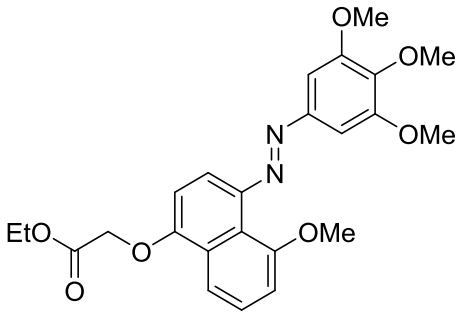
Standard Procedure **B** with azobenzene **46a** (359 mg, 1.06 mmol, 1.0 equiv.) and ethyl bromoacetate (0.47 mL, 4.23 mmol, 4.0 equiv.) gave azobenzene **4a** (362 mg, 80 %) as an orange solid after silica-gel chromatography (CH_2Cl_2/MeOH, 9:1). R_f = 0.41 (CH_2Cl_2/MeOH, 95:5); m.p. 114 °C; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 9.27 (d, J = 8.2 Hz, 1 H), 9.07 (d, J = 2.4 Hz, 1 H), 7.91 (d, J = 8.6 Hz, 1 H), 7.64 (dd, J = 3.8, 8.3 Hz, 1 H), 7.32 (s, 2 H), 7.05 (d, J = 8.6 Hz, 1 H), 5.06 (s, 2 H), 4.30 (q, J = 7.1 Hz, 2 H), 4.01 (s, 6 H), 3.96 (s, 3 H), 1.29 (t, J = 7.1 Hz, 3 H); ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 168.3, 156.1, 153.6, 150.1, 148.9, 141.6, 140.7, 139.8, 132.1, 127.9, 122.5, 113.1, 108.9, 100.5, 66.2, 61.6, 61.1, 56.2, 14.1; IR: $\tilde{\nu}$ = 2970, 2835, 1732, 1566, 1493, 1308, 1199, 1126, 999, 840; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 389 nm (20900 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{22}H_{24}N_3O_6$: 426.1660 $[M+H]^+$; found: 426.1666.

Ethyl-2-((4´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)naphth-1´-yl)oxy)acetate **4b**



Standard Procedure **B** with azobenzene **46b** (363 mg, 1.07 mmol, 1.0 equiv.) and ethyl bromoacetate (0.48 mL, 4.30 mmol, 4.0 equiv.) gave azobenzene **4b** (436 mg, 96 %) as an orange solid after silica-gel chromatography (EtOAc/petroleum ether, 1:4 → 1:2). R_f = 0.23 (EtOAc/petroleum ether, 1:4); m.p. 99 °C; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 8.93 (d, J = 8.1 Hz, 1 H), 8.47 (d, J = 7.9 Hz, 1 H), 7.84 (d, J = 8.4 Hz, 1 H), 7.73 (ddd, J = 1.3, 6.8, 8.1 Hz, 1 H), 7.65 (ddd, J = 1.3, 7.0, 8.2 Hz, 1 H), 7.37 (s, 2 H), 6.83 (d, J = 8.4 Hz, 1 H), 4.92 (s, 2 H), 4.35 (q, J = 7.1 Hz, 2 H), 4.04 (s, 6 H), 3.98 (s, 3 H), 1.35 (t, J = 7.1 Hz, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 168.4, 156.3, 153.6, 149.2, 142.5, 140.4, 132.5, 127.7, 126.2, 125.7, 123.0, 122.4, 112.5, 104.8, 100.4, 65.8, 61.6, 61.1, 56.3, 14.2; IR: $\tilde{\nu}$ = 2940, 2835, 1755, 1578, 1470, 1207, 1107, 991, 845, 768; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 397 nm (20100 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{23}H_{25}N_2O_6$: 425.1707 $[M+H]^+$; found: 425.1711.

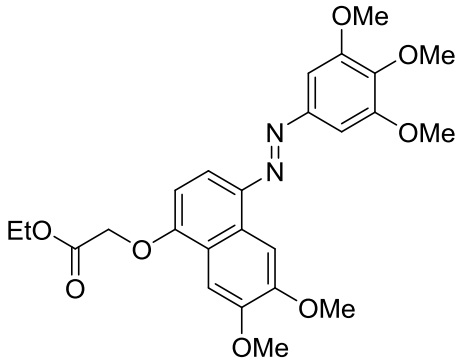
Ethyl-2-((4´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)-5´-methoxynaphth-1-yl)oxy)acetate **4c**



Standard Procedure **A1** with 3,4,5-trimethoxyaniline (183 mg, 1.0 mmol, 1.0 equiv.) and naphthol **45c** (183 mg, 1.05 mmol, 1.05 equiv.) gave crude azobenzene **46c** (185 mg) after evaporation of the solvent. The crude material was directly converted according to Standard Procedure **B** with ethyl bromoacetate (89 µL, 2.0 mmol, 4.0 equiv.). Azobenzene **4c** (61 mg, 13 %) was isolated as an orange solid after silica-gel chromatography (EtOAc/petroleum ether, 1:2). R_f = 0.64 (EtOAc/petroleum ether, 1:2); m.p. 143 °C; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 8.10 (d, J = 7.9 Hz, 1 H), 7.53 (t, J = 8.1 Hz, 1 H), 7.36 (s, 2 H), 7.27 (d, J = 8.4 Hz, 1 H), 7.08 (d, J = 7.7 Hz, 1 H), 6.79 (d, J = 8.4 Hz, 1 H), 4.87 (s, 2 H), 4.34 (q, J = 7.1 Hz, 2 H), 4.02 (s, 6 H), 3.98 (s, 3 H), 3.97 (s, 3 H), 1.34 (t, J = 7.1 Hz, 3 H); ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 169.4, 157.6, 155.7, 154.5, 150.0, 147.1, 141.0, 128.8, 127.4, 122.6, 116.1, 113.8, 109.7, 106.2, 101.4, 66.8, 62.4, 62.0, 57.4, 57.1, 15.1; IR: $\tilde{\nu}$ = 2909, 2839, 1759, 1593, 1412, 1207, 1084, 1002, 760; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 388 nm

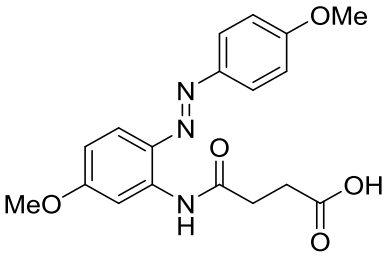
(20300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{24}H_{27}N_2O_7$: 455.1813 $[M+H]^+$; found: 455.1824.

Ethyl-2-((4´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)-6´,7´-dimethoxynaphth-1´-yl)oxy) acetate **4d**



Standard Procedure **B** with azobenzene **46d** (422 mg, 1.06 mmol, 1.0 equiv.) and ethyl bromoacetate (0.47 mL, 4.24 mmol, 4.0 equiv.) gave azobenzene **4d** (424 mg, 83 %) as an orange solid after silica-gel chromatography (EtOAc/petroleum ether, 1:2 → 1:1). R_f = 0.53 (EtOAc/petroleum ether, 1:2); m.p. 123 °C; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 8.25 (s, 1 H), 7.70 (s, 1 H), 7.71 (d, *J* = 8.4 Hz, 1 H), 7.32 (s, 2 H), 6.70 (d, *J* = 8.6 Hz, 1 H), 4.89 (s, 2 H), 4.32 (q, *J* = 7.1 Hz, 2 H), 4.09 (s, 3 H), 4.09 (s, 3 H), 4.00 (s, 6 H), 3.96 (s, 3 H), 1.33 (t, *J* = 7.1 Hz, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 168.5, 155.4, 153.5, 150.5, 149.6, 149.3, 141.5, 140.3, 129.0, 121.2, 111.5, 104.0, 101.9, 101.2, 100.3, 65.8, 61.5, 61.1, 56.1, 55.9, 55.7, 14.2; IR: $\tilde{\nu}$ = 2940, 2828, 1732, 1585, 1485, 1211, 1118, 1038, 1011, 818; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 408 nm (21300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{25}H_{29}N_2O_8$: 485.1918 $[M+H]^+$; found: 485.1927.

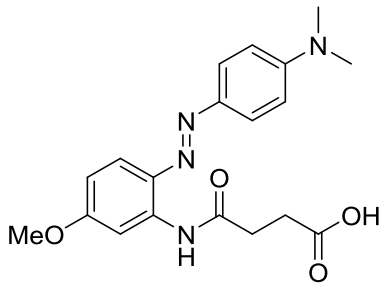
N-(5´-Methoxy-2´-((4´´-methoxyphenyl)diazenyl)phenyl)succinamic acid **5a**



Standard Procedure **C** with ester **29a** (60.0 mg, 0.16 mmol, 1.0 equiv.) gave carboxylic acid **5a** (57 mg, 99 %) as a chartreuse solid after evaporation of the solvent. R_f = 0.23 (CH_2Cl_2/MeOH, 95:5); m.p. 167 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 12.19 (s, 1 H), 10.22 (s, 1 H), 8.04 (d, *J* = 2.8 Hz, 1 H), 8.00 (d, *J* = 8.9 Hz, 2 H), 7.74 (d, *J* = 9.0 Hz, 1 H),

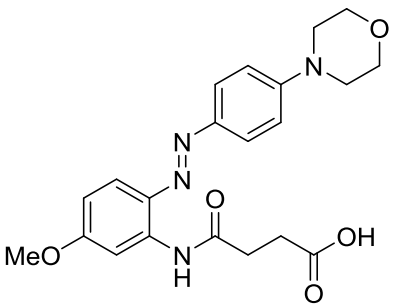
7.13 (d, *J* = 9.0 Hz, 2 H), 6.78 (dd, *J* = 2.8, 9.1 Hz, 1 H), 3.87 (s, 3 H), 3.84 (s, 3 H), 2.79 (t, *J* = 6.5 Hz, 2 H), 2.58 (t, *J* = 6.7 Hz, 2 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 174.3, 171.3, 162.5, 162.0, 146.9, 138.6, 134.9, 125.2, 119.1, 114.9, 110.4, 105.9, 56.1, 56.0, 32.1, 29.3; IR: $\tilde{\nu}$ = 3368, 2924, 2592, 1713, 1578, 1470, 1231, 1146, 1026, 833; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 386 nm (21400 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{18}H_{20}N_3O_5$: 358.1397 $[M+H]^+$; found: 358.1402.

N-(2´-((4´´-(Dimethylamino)phenyl)diazenyl)-5´-methoxyphenyl)succinamic acid **5b**



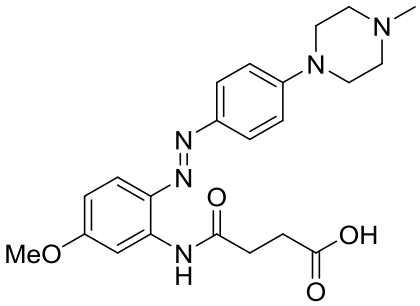
Standard Procedure **C** with ester **30b** (38 mg, 0.11 mmol, 1.0 equiv.) gave carboxylic acid **5b** (33 mg, 83 %) as an orange solid after purification by preparative HPLC (H_2O/CH_3CN, 70:30 → 0:100). R_f = 0.18 (CH_2Cl_2/MeOH, 8:2); m.p. 286 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 11.75 (s, 1 H), 8.16 (d, *J* = 2.7 Hz, 1 H), 8.10 (d, *J* = 9.0 Hz, 2 H), 7.66 (d, *J* = 9.0 Hz, 1 H), 6.79 (d, *J* = 9.1 Hz, 2 H), 6.66 (dd, *J* = 2.8, 9.0 Hz, 1 H), 3.79 (s, 3 H), 3.05 (s, 6 H), 2.50 - 2.48 (m, 2 H), 2.25 - 2.19 (m, 2 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 174.6, 173.8, 161.4, 152.3, 143.9, 139.2, 135.3, 126.0, 117.1, 112.0, 109.4, 105.5, 55.8, 39.4, 36.2, 34.8; IR: $\tilde{\nu}$ = 3345, 2920, 1654, 1589, 1362, 1280, 1141, 1030, 822; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 450 nm (21300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{23}N_4O_4$: 371.1714 $[M+H]^+$; found: 371.1718.

N-(5´-Methoxy-2´-((4´´-morpholinophenyl)diazenyl)phenyl)succinamic acid **5c**



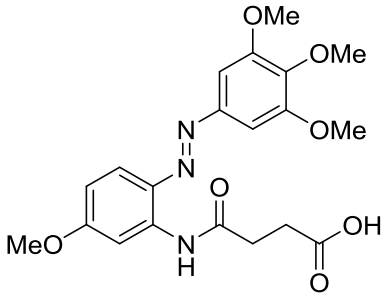
Standard Procedure **C** with ester **30c** (25 mg, 0.06 mmol, 1.0 equiv.) gave carboxylic acid **5c** (18 mg, 69 %) as a yellow solid after purification by preparative HPLC (H_2O/CH_3CN, 70:30 → 0:100). R_f = 0.22 (CH_2Cl_2/MeOH, 8:2); m.p. 207 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 10.23 (s, 1 H), 8.02 (d, J = 2.6 Hz, 1 H), 7.90 (d, J = 8.9 Hz, 2 H), 7.70 (d, J = 9.0 Hz, 1 H), 7.09 (d, J = 9.0 Hz, 2 H), 6.76 (dd, J = 2.6, 9.0 Hz, 1 H), 3.82 (s, 3 H), 3.79 - 3.72 (m, 4 H), 3.30 - 3.27 (m, 4 H), 2.76 (t, J = 6.2 Hz, 2 H), 2.56 (t, J = 6.8 Hz, 2 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 173.8, 170.7, 161.5, 152.7, 144.6, 137.6, 134.5, 124.5, 118.8, 114.0, 109.8, 105.3, 65.9, 55.5, 47.2, 31.7, 28.9; IR: $\tilde{\nu}$ = 3375, 2970, 1701, 1589, 1234, 1111, 1038, 918, 818; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 414 nm (28000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{21}H_{25}N_4O_5$: 413.1819 $[M+H]^+$; found: 413.1825.

N-(5´-Methoxy-2´-((4´´-(4´´´-methylpiperazin-1´´´-yl)phenyl)diazenyl)phenyl)succinamic acid **5d**



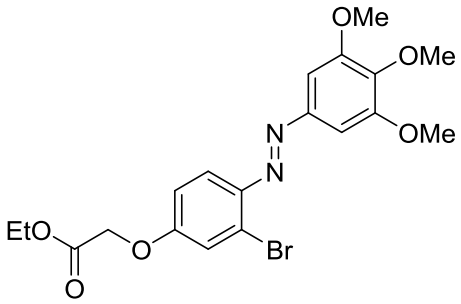
Standard Procedure **C** with ester **30d** (25 mg, 0.06 mmol, 1.0 equiv.) gave carboxylic acid **5d** (13 mg, 38 %) as a yellow solid after purification by preparative HPLC (H_2O/CH_3CN, 70:30 → 0:100). R_f = 0.12 (CH_2Cl_2/MeOH, 8:2); m.p. 160 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 10.26 (s, 1 H), 8.03 (d, J = 2.6 Hz, 1 H), 7.88 (d, J = 8.9 Hz, 2 H), 7.70 (d, J = 9.0 Hz, 1 H), 7.07 (d, J = 9.0 Hz, 2 H), 6.75 (dd, J = 2.7, 9.0 Hz, 1 H), 3.81 (s, 3 H), 3.40 - 3.27 (m, 4 H), 2.75 (t, J = 6.6 Hz, 2 H), 2.56 (t, J = 6.9 Hz, 2 H), 2.48 - 2.41 (m, 4 H), 2.23 (s, 3 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 173.9, 170.8, 161.4, 152.6, 144.3, 137.5, 134.5, 124.6, 118.7, 114.1, 109.7, 105.3, 55.5, 54.3, 46.9, 45.7, 31.8, 29.0; IR: $\tilde{\nu}$ = 3368, 2967, 2839, 1682, 1585, 1508, 1285, 1238, 1150, 1033, 829; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 417 nm (19300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{22}H_{28}N_5O_4$: 426.2136 $[M+H]^+$; found: 426.2139.

N-(5´-Methoxy-2´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)phenyl)succinamic acid **6**



Standard Procedure **B** with azobenzene **36b** (100 mg, 0.26 mmol, 1.0 equiv.) and MeI (32.3 µL, 0.52 mmol, 2.0 equiv.) gave crude azobenzene **37d** (99 mg) after evaporation of the solvent. The crude material was directly converted according to Standard Procedure **C** to give carboxylic acid **6** (77 mg, 71 %) as a yellow solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid). R_f = 0.19 (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid); m.p. 165 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 8.02 (d, J = 2.7 Hz, 1 H), 7.75 (d, J = 9.1 Hz, 1 H), 7.38 (s, 2 H), 6.79 (dd, J = 2.8, 9.1 Hz, 1 H), 3.91 (s, 6 H), 3.84 (s, 3 H), 3.75 (s, 3 H), 2.75 (t, J = 6.6 Hz, 2 H), 2.56 (t, J = 6.6 Hz, 2 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 174.4, 171.5, 163.0, 153.7, 148.6, 140.2, 139.3, 134.9, 118.5, 110.6, 106.1, 101.1, 60.7, 56.5, 56.1, 32.3, 29.7; IR: $\tilde{\nu}$ = 3291, 2940, 2361, 1732, 1597, 1458, 1231, 1119, 1006, 821; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 393 nm (20600 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{20}H_{24}N_3O_7$: 418.1609 $[M+H]^+$; found: 418.1617.

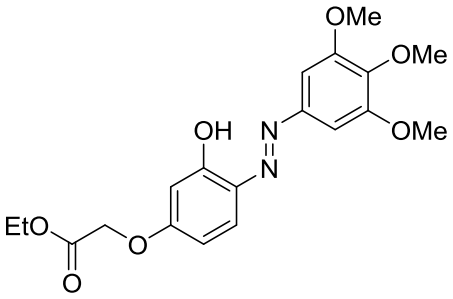
Ethyl-2-(3´-bromo-4´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)phenoxy)acetate **7a**



Standard Procedure **B** with azobenzene **41a** (453 mg, 1.24 mmol, 1.0 equiv.) and ethyl bromoacetate (0.55 mL, 4.94 mmol, 4.0 equiv.) gave azobenzene **7a** (471 mg, 84 %) as an orange solid after silica-gel chromatography (EtOAc/petroleum ether, 1:4 → 1:2). R_f = 0.57

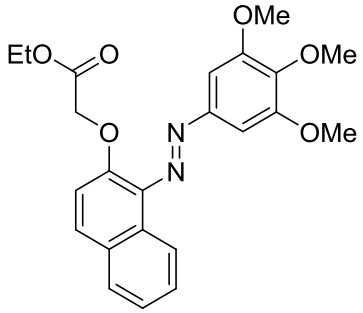
(EtOAc/petroleum ether, 1:2); m.p. 93 °C; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.75 (d, J = 9.0 Hz, 1 H), 7.30 (d, J = 3.1 Hz, 3 H), 6.98 (dd, J = 2.7, 9.0 Hz, 1 H), 4.71 (s, 2 H), 4.33 (q, J = 7.1 Hz, 2 H), 3.99 (s, 6 H), 3.96 (s, 3 H), 1.35 (t, J = 7.1 Hz, 3 H); ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 168.0, 160.0, 153.5, 148.6, 144.2, 140.8, 127.4, 118.9, 118.6, 114.8, 100.7, 65.5, 61.7, 61.0, 56.1, 14.1; IR: $\tilde{\nu}$ = 2982, 2839, 1763, 1589, 1416, 1200, 1126, 1076, 991, 841; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 369 nm (23000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{22}BrN_2O_6$: 453.0656/455.0635 $[M+H]^+$; found: 453.0660/455.0639.

Ethyl-2-(3´-hydroxy-4´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)phenoxy)acetate **7b**



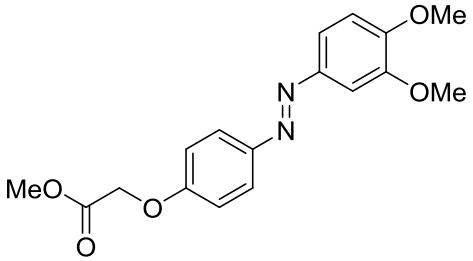
Standard Procedure **B** with azobenzene **41b** (115 mg, 0.38 mmol, 1.0 equiv.) and ethyl bromoacetate (42 µL, 0.38 mmol, 1.0 equiv.) gave azobenzene **7b** (110 mg, 75 %) as an orange solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4 → 1:2). R_f = 0.64 (EtOAc/petroleum ether, 1:2); m.p. 121 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 13.57 (br s, 1 H), 7.82 (d, J = 8.8 Hz, 1 H), 7.11 (s, 2 H), 6.66 (dd, J = 2.7, 8.9 Hz, 1 H), 6.45 (d, J = 2.7 Hz, 1 H), 4.68 (s, 2 H), 4.30 (q, J = 7.1 Hz, 2 H), 3.96 (s, 6 H), 3.93 (s, 3 H), 1.32 (t, J = 7.1 Hz, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 168.1, 161.6, 155.7, 153.8, 146.1, 140.2, 134.6, 133.2, 108.2, 102.3, 99.2, 65.3, 61.6, 61.1, 56.3, 14.2; IR: $\tilde{\nu}$ = 2940, 2639, 1724, 1597, 1423, 1280, 1219, 1114, 1006, 856, 825, 795; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 390 nm (27300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{23}N_2O_7$: 391.1500 $[M+H]^+$; found: 391.1503.

Ethyl-2-((1´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)naphth-2´-yl)oxy)acetate **8**



Standard Procedure **B** with azobenzene **49** (502 mg, 1.48 mmol, 1.0 equiv.) and ethyl bromoacetate (0.66 mL, 5.92 mmol, 4.0 equiv.) gave azobenzene **8** (449 mg, 71 %) as an orange solid after silica-gel chromatography (EtOAc/petroleum ether, 1:4 → 1:2). R_f = 0.30 (EtOAc/petroleum ether, 1:4); m.p. 126 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.6 Hz, 1 H), 7.85 (d, J = 8.7 Hz, 2 H), 7.54 (ddd, J = 1.4, 6.8, 8.4 Hz, 1 H), 7.47 (ddd, J = 1.3, 6.7, 8.1 Hz, 1 H), 7.37 (s, 2 H), 7.36 (d, J = 8.8 Hz, 1 H), 4.79 (s, 2 H), 4.23 (q, J = 7.1 Hz, 2 H), 4.00 (s, 6 H), 3.97 (s, 3 H), 1.25 (t, J = 7.1 Hz, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 168.8, 153.6, 149.3, 146.8, 140.8, 137.8, 130.6, 130.2, 128.2, 127.9, 127.7, 125.1, 123.4, 117.6, 100.4, 68.7, 61.3, 61.1, 56.3, 14.1; IR: $\tilde{\nu}$ = 2940, 2835, 1755, 1593, 1415, 1311, 1199, 1103, 991, 810; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 370 nm (26800 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{23}H_{25}N_2O_6$: 425.1707 $[M+H]^+$; found: 425.1713.

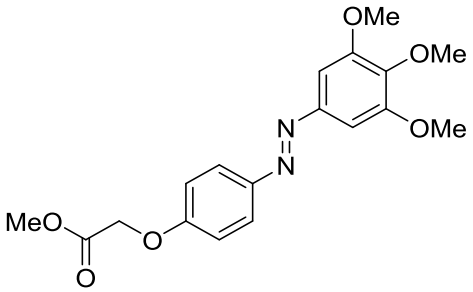
Methyl-2-(4´-((3´´,4´´-dimethoxyphenyl)diazenyl)phenoxy)acetate **9a**



Standard Procedure **B** with azobenzene **25a** (100 mg, 0.32 mmol, 1.0 equiv.), and MeI (94 mg, 0.66 mmol, 2.1 equiv.) gave azobenzene **9a** (83 mg, 80 %) as a yellow solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:2). R_f = 0.62 (EtOAc/petroleum ether, 1:2); m.p. 141 °C; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.92 (d, J = 9.0 Hz, 2 H), 7.62 (dd, J = 2.2, 8.4 Hz, 1 H), 7.52 (d, J = 2.0 Hz, 1 H), 7.09 - 6.98 (m, 3 H), 4.75 (s, 2 H), 4.01 (s, 3 H), 4.00 (s, 3 H), 3.86 (s, 3 H); ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 169.9, 160.5, 152.5, 150.5, 148.5, 147.8, 125.3, 121.4, 115.8, 111.3, 102.8, 66.3, 57.0, 56.9, 53.3; IR: $\tilde{\nu}$ = 2959, 2612, 1751, 1578, 1497, 1439, 1188, 1111, 1018, 856, 817; UV-VIS (CH_3CN +

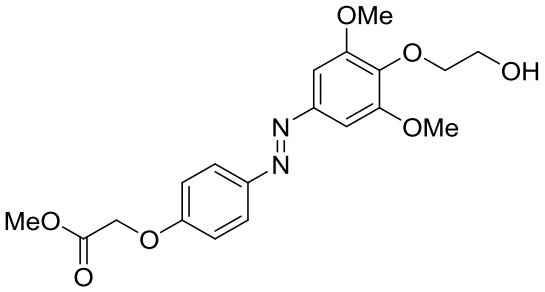
0.5 % piperidine): λ_{max} (ε) = 376 nm (19000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{17}H_{19}N_2O_5$: 331.1288 $[M+H]^+$; found: 311.1295.

Methyl-2-(4´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)phenoxy)acetate **9b**



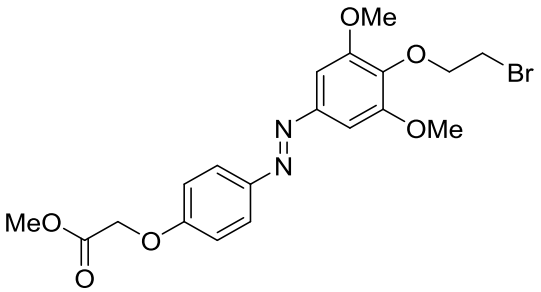
Standard Procedure **B** with azobenzene **25b** (222 mg, 0.64 mmol, 1.0 equiv.), and MeI (188 mg, 1.32 mmol, 2.1 equiv.) gave azobenzene **9b** (206 mg, 89 %) as a yellow solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:2). R_f = 0.62 (EtOAc/petroleum ether, 1:2); m.p. 51 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.5 Hz, 2 H), 7.23 (s, 2 H), 7.04 (d, J = 8.8 Hz, 2 H), 4.72 (s, 2 H), 4.31 (q, J = 7.2 Hz, 2 H), 3.98 (s, 6 H), 3.95 (s, 3 H), 1.33 (t, J = 7.9 Hz, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 168.4, 159.9, 153.5, 148.5, 147.4, 140.2, 124.5, 114.9, 100.1, 65.4, 61.5, 61.0, 56.1, 14.1; IR: $\tilde{\nu}$ = 2940, 2913, 2839, 1759, 1578, 1215, 1123, 1003, 845, 829; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 360 nm (22100 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{23}N_2O_6$: 375.1551 $[M+H]^+$; found: 375.1563.

Methyl-2-(4´-((4´´-(2´´´-hydroxyethoxy)-3´´,5´´-dimethoxyphenyl)diazenyl)phenoxy) acetate **9c**



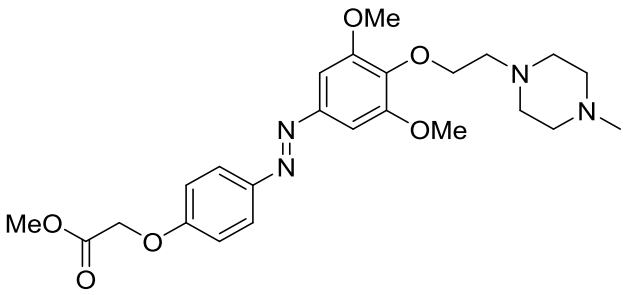
Standard Procedure **B** with azobenzene **25b** (100 mg, 0.28 mmol, 1.0 equiv.) and 2-bromoethanol (59 µL, 0.83 mmol, 1.0 equiv.) gave azobenzene **9c** (82 mg, 76 %) as a yellow solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:1). R_f = 0.38 (EtOAc/petroleum ether, 1:1); m.p. 91 °C; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.91 (d, J = 8.6 Hz, 2 H), 7.24 (s, 2 H), 7.03 (d, J = 8.6 Hz, 2 H), 4.73 (s, 2 H), 4.22 (t, J = 3.9 Hz, 2 H), 3.98 (s, 6 H), 3.84 (s, 3 H), 3.76 (t, J = 4.0 Hz, 2 H); ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 169.8, 160.9, 154.5, 149.7, 148.3, 139.3, 125.6, 115.8, 101.0, 76.5, 66.3, 62.3, 57.2, 53.3; IR: $\tilde{\nu}$ = 3510, 2951, 2322, 1751, 1582, 1497, 1207, 1126, 1072, 841; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 360 nm (19800 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{23}N_2O_7$: 391.1500 $[M+H]^+$; found: 391.1503.

Methyl-2-(4´-((4´´-(2´´´-bromoethoxy)-3´´,5´´-dimethoxyphenyl)diazenyl)phenoxy) acetate **9d**



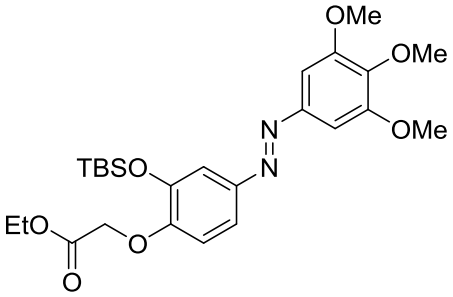
Standard Procedure **B** with azobenzene **25b** (100 mg, 0.28 mmol, 1.0 equiv.) and 1,2-dibromoethane (249 µL, 2.89 mmol, 10.0 equiv.) in anhydrous acetone (20 mL) gave azobenzene **9d** (119 mg, 91 %) as a chartreuse solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4). R_f = 0.57 (EtOAc/petroleum ether, 1:4); m.p. 179 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.7 Hz, 2 H), 7.21 (s, 2 H), 7.03 (d, J = 8.8 Hz, 2 H), 4.73 (s, 2 H), 4.34 (t, J = 7.0 Hz, 2 H), 3.96 (s, 6 H), 3.84 (s, 3 H), 3.64 (t, J = 7.0 Hz, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 168.9, 160.0, 153.5, 148.9, 147.5, 138.4, 124.7, 114.9, 100.0, 72.7, 65.3, 56.2, 52.4, 29.6; IR: $\tilde{\nu}$ = 2062, 2835, 1759, 1597, 1501, 1439, 1408, 1211, 1130, 1076, 991, 810; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 360 nm (27200 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{22}BrN_2O_6$: 453.0656/455.0638 $[M+H]^+$; found: 453.0658/455.0640.

Methyl-2-(4´-((3´´,5´´-dimethoxy-4´´-(2´´´-(4´´´´-methylpiperazin-1´´´´-yl)ethoxy)phenyl) diazenyl)-phenoxy)acetate **9e**



A microwave vial charged with azobenzene **9d** (60 mg, 0.13 mmol, 1.0 equiv.), 1-methylpiperazine (19 µL, 0.17 mmol, 1.3 equiv.), K_2CO_3 (24 mg, 0.17 mmol, 1.3 equiv.), and CH_3CN (4 mL) was heated to 140 °C for 10 min. in a microwave. After cooling the solvent was removed under reduced pressure, and the residue was redissolved in $CHCl_3$ (30 mL). The organic phase was washed with water (20 mL), and brine (20 mL), dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Azobenzene **9e** (45 mg, 72 %) was obtained as an orange oil without further purification. R_f = 0.31 (CH_2Cl_2/MeOH, 9:1); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, J = 8.9 Hz, 2 H), 7.18 (s, 2 H), 7.00 (d, J = 8.9 Hz, 2 H), 4.70 (s, 2 H), 4.16 (t, J = 5.8 Hz, 2 H), 3.91 (s, 6 H), 3.81 (s, 3 H), 2.79 (t, J = 6.1 Hz, 2 H), 2.63 (br s, 4 H), 2.49 (br s, 4 H), 2.27 (s, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 168.8, 159.8, 153.6, 148.5, 147.4, 139.3, 124.5, 114.8, 100.0, 70.6, 65.3, 57.9, 56.0, 55.0, 53.4, 52.3, 46.0; IR: $\tilde{\nu}$ = 2940, 2797, 2361, 1740, 1597, 1497, 1204, 1123, 1003, 841; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 362 nm (21600 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{24}H_{33}N_4O_6$: 473.2395 $[M+H]^+$; found: 473.2398.

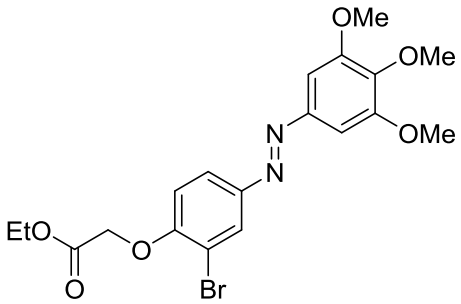
Ethyl-2-(2´-(*tert*-butyldimethylsilyl)oxy-4-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)phenoxy) acetate **10a**



A solution of phenol **44a** (100 mg, 0.24 mmol, 1.0 equiv.) in dry THF (10 mL) was cooled to -20 °C under an atmosphere of argon. Solid NaH (8.6 mg, 0.36 mmol, 1.5 equiv.) was added and stirred for 10 min followed by addition of ethyl bromoacetate (133 µL, 1.19 mmol,

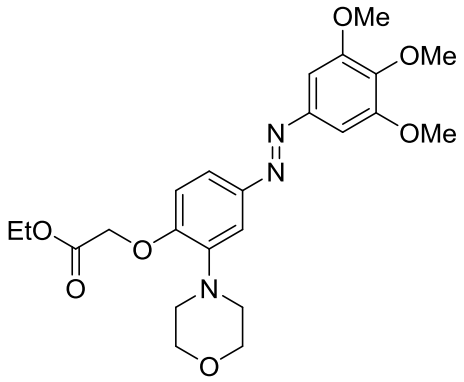
5.0 equiv.). The reaction mixture was stirred at 0°C for 1.5 h. After stirring for additional 1h at 20°C the pH was adjusted to 7 with phosphate buffer, and $CHCl_3$ (20 mL) was added. The aqueous layer was separated and extracted with $CHCl_3$ (3 × 10 mL). The combined organic extracts were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4) provided azobenzene **10a** (75 mg, 62 %) as a yellow solid. R_f = 0.42 (EtOAc/petroleum ether, 1:4); m.p. 101 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54 (dd, J = 2.3, 8.5 Hz, 1 H), 7.47 (d, J = 2.3 Hz, 1 H), 7.21 (s, 2 H), 6.90 (d, J = 8.5 Hz, 1 H), 4.70 (s, 2 H), 4.29 (q, J = 7.1 Hz, 2 H), 3.98 (s, 6 H), 3.93 (s, 3 H), 1.31 (t, J = 7.2 Hz, 3 H), 1.09 - 1.03 (m, 9 H), 0.26 (s, 6 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 168.4, 153.5, 151.9, 148.5, 147.8, 145.9, 140.2, 118.6, 114.2, 113.3, 100.2, 66.1, 61.4, 61.0, 56.2, 25.7, 18.4, 14.2, -4.6; IR: $\tilde{\nu}$ = 2932, 1759, 1593, 1493, 1416, 1277, 1192, 1122, 837, 783; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 369 nm (21300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{25}H_{37}N_2O_7Si$: 505.2365 $[M+H]^+$; found: 505.2359.

Ethyl-2-(2´-bromo-4´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)phenoxy)acetate **10b**



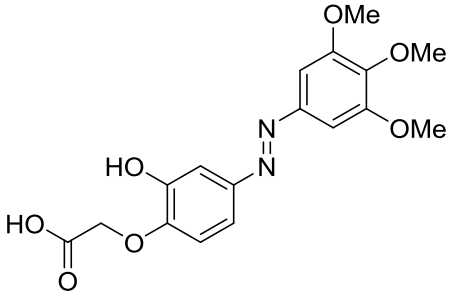
Standard Procedure **B** with azobenzene **44b** (305 mg, 0.83 mmol, 1.0 equiv.), and ethyl bromoacetate (0.37 mL, 3.33 mmol, 4.0 equiv.) gave azobenzene **10b** (338 mg, 89 %) as a yellow solid after silica-gel chromatography (EtOAc/petroleum ether, 1:4 → 1:2). R_f = 0.60 (EtOAc/petroleum ether, 1:2); m.p. 112 °C; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 8.19 (d, J = 2.4 Hz, 1 H), 7.88 (dd, J = 2.4, 8.8 Hz, 1 H), 7.23 (s, 2 H), 6.92 (d, J = 8.8 Hz, 1 H), 4.80 (s, 2 H), 4.31 (q, J = 7.1 Hz, 2 H), 3.97 (s, 6 H), 3.94 (s, 3 H), 1.32 (t, J = 7.1 Hz, 3 H); ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 167.9, 156.2, 153.5, 148.2, 147.6, 140.7, 126.5, 125.0, 113.2, 112.7, 100.4, 66.3, 61.7, 61.0, 56.2, 14.1; IR: $\tilde{\nu}$ = 2943, 2832, 1763, 1593, 1485, 1411, 1200, 1119, 1011, 849; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 364 nm (25700 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{22}BrN_2O_6$: 453.0656/455.0635 $[M+H]^+$; found: 453.0662/455.0642.

Ethyl-2-(2´-morpholino-4´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)phenoxy)acetate **10c**



Standard Procedure **D** with azobenzene **10b** (30.0 mg, 0.66 mmol, 1.0 equiv.) and morpholine (13.1 µL, 0.132 mmol, 2.0 equiv.) gave azobenzene **10c** (14.0 mg, 45 %) as an orange wax after silica-gel chromatography (CH_2Cl_2/MeOH, 9:1). R_f = 0.40 (CH_2Cl_2/MeOH, 9:1); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.62 (dd, J = 2.3, 8.5 Hz, 1 H), 7.57 (d, J = 2.2 Hz, 1 H), 7.23 (s, 2 H), 6.90 (d, J = 8.6 Hz, 1 H), 4.78 (s, 2 H), 4.31 (q, J = 7.1 Hz, 2 H), 3.98 (s, 6 H), 3.94 (s, 3 H), 3.99 - 3.92 (m, 4 H), 3.25 (t, J = 4.4 Hz, 4 H), 1.33 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR (75MHz, $CDCl_3$): δ = 168.3, 153.5, 152.6, 148.5, 147.7, 142.2, 140.3, 120.1, 112.4, 111.2, 100.1, 67.2, 65.6, 61.6, 61.0, 56.2, 51.1, 14.2; IR: $\tilde{\nu}$ = 3460, 2963, 2842, 1752, 1581, 1345, 1241, 1163, 911, 840; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 368 nm (22000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{23}H_{30}N_3O_7$: 460.2079 $[M+H]^+$; found: 460.2090.

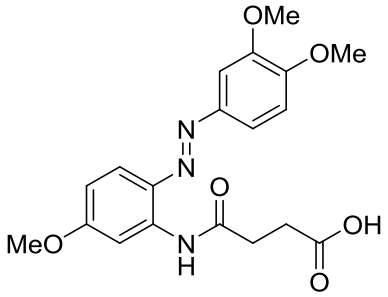
2-(2´-Hydroxy-4´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)phenoxy)acetic acid **10d**



Standard Procedure **C** with ester **10a** (60 mg, 0.12 mmol, 1.0 equiv.) gave carboxylic acid **10d** (40 mg, 94 %) as an orange solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 3:7 → EtOAc + 0.5 % formic acid). R_f = 0.15 (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid); m.p. 132 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = (br s, 1 H),

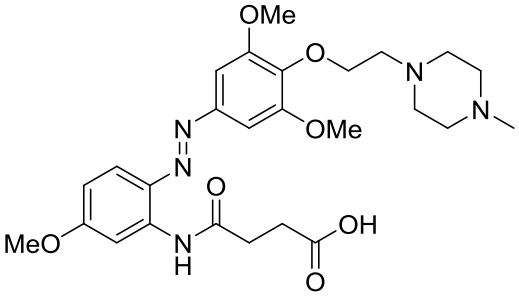
7.41 (dd, J = 2.3, 8.5 Hz, 1 H), 7.34 (d, J = 2.0 Hz, 1 H), 7.18 (s, 2 H), 7.00 (d, J = 8.5 Hz, 1 H), 4.77 (s, 2 H), 3.88 (s, 6 H), 3.75 (s, 3 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 170.1, 153.3, 149.5, 147.8, 147.5, 146.7, 139.8, 118.3, 113.4, 106.2, 99.9, 65.5, 60.2, 56.0; IR: $\tilde{\nu}$ = 3507, 3005, 2360, 1748, 1597, 1493, 1207, 1114, 995, 806; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 367 nm (21100 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{17}H_{19}N_2O_7$: 363.1187 $[M+H]^+$; found: 363.1194.

N-(2´-((3´´,4´´-Dimethoxyphenyl)diazenyl)-5´-methoxyphenyl)succinamic acid **11a**



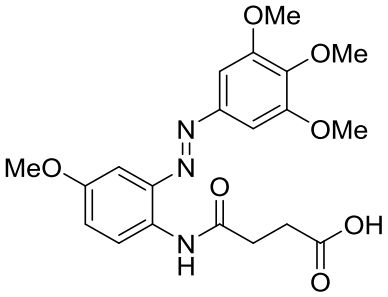
Standard Procedure **C** with ester **37a** (40.0 mg, 0.11 mmol, 1.0 equiv.) gave carboxylic acid **11a** (41 mg, 98 %) as a yellow solid after purification by silica-gel chromatography (CH_2Cl_2/MeOH, 98:2 → 95:5). R_f = 0.13 (CH_2Cl_2/MeOH, 95:5); m.p. 158 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 11.00 (s, 1 H), 8.32 (d, J = 2.6 Hz, 1 H), 7.85 (d, J = 9.0 Hz, 1 H), 7.51 (dd, J = 2.3, 8.5 Hz, 1 H), 7.47 (d, J = 2.1 Hz, 1 H), 7.03 (d, J = 8.5 Hz, 1 H), 6.76 (dd, J = 2.7, 9.0 Hz, 1 H), 4.01 (s, 3 H), 4.01 (s, 3 H), 3.93 (s, 3 H), 2.91 - 2.79 (m, 4 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 175.8, 170.3, 162.7, 151.6, 149.8, 146.6, 136.2, 133.3, 125.3, 119.4, 111.0, 110.6, 103.8, 102.0, 56.2, 56.0, 55.7, 32.5, 29.0; IR: $\tilde{\nu}$ = 2940, 2839, 2322, 1717, 1585, 1504, 1420, 1231, 1107, 1022, 856, 810; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 395 nm (24700 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{22}N_3O_6$: 388.1503 $[M+H]^+$; found: 388.1512.

N-(2´-((3´´,5´´-Dimethoxy-4´´-(2´´´-(4´´´´-methylpiperazin-1´´´´-yl)ethoxy)phenyl)diazenyl)-5´-methoxyphenyl)succinamic acid **11b**



Standard Procedure **C** with ester **37b** (36 mg, 0.07 mmol, 1.0 equiv.) gave carboxylic acid **11c** (35 mg, 94 %) as an orange solid after purification by preparative HPLC (H_2O/CH_3CN, 90:10 → 0:100). R_f = 0.24 (CH_2Cl_2/MeOH, 8:2); m.p. 208 °C; ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 10.37 (s, 1 H), 8.02 (d, J = 2.7 Hz, 1 H), 7.75 (d, J = 9.2 Hz, 1 H), 7.38 (s, 2 H), 6.79 (dd, J = 2.7, 9.2 Hz, 1 H), 4.04 (t, J = 6.0 Hz, 2 H), 3.90 (s, 6 H), 3.84 (s, 3 H), 2.75 (t, J = 6.6 Hz, 2 H), 2.64 (t, J = 6.0 Hz, 2 H), 2.56 (t, J = 6.6 Hz, 2 H), 2.46 (br. s, 4 H), 2.33 (br s, 4 H), 2.16 (s, 3 H); ^{13}C-NMR (126 MHz, DMSO-d_6): δ = 174.0, 171.1, 162.6, 153.4, 148.1, 138.9, 138.8, 134.5, 118.1, 110.1, 105.6, 100.7, 70.5, 57.4, 56.1, 55.6, 54.6, 52.8, 45.6, 32.0, 29.3; IR: $\tilde{\nu}$ = 3379, 2940, 2835, 1736, 1694, 1593, 1385, 1215, 1126, 1030, 845; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 393 nm (24100 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{26}H_{36}N_5O_7$: 530.2609 $[M+H]^+$; found: 530.2613.

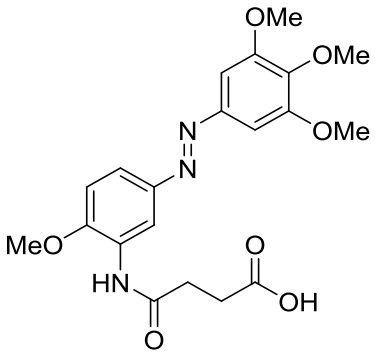
N-(4´-Methoxy-2´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)phenyl)succinamic acid **11c**



Standard Procedure **C** with ester **39** (80 mg, 0.19 mmol, 1.0 equiv.) gave carboxylic acid **11c** (58 mg, 75 %) as a yellow solid after purification by silica-gel chromatography (CH_2Cl_2/MeOH, 98:2 → 95:5). R_f = 0.11 (CH_2Cl_2/MeOH, 95:5); m.p. 163 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 10.03 (br s, 1 H), 8.05 (d, J = 9.0 Hz, 1 H), 7.40 (s, 2 H), 7.20 (d, J = 3.0 Hz, 1 H), 7.10 (dd, J = 3.0, 9.0 Hz, 1 H), 3.88 (s, 6 H), 3.77 (s, 3 H), 3.74 (s, 3 H), 2.66 (t, J = 6.7 Hz, 2 H), 2.51 (t, J = 6.5 Hz, 2 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 175.0, 170.9, 156.2, 153.7, 148.5, 142.3, 140.9, 131.8, 124.9, 119.7, 101.6, 98.9, 60.7, 56.5, 55.9, 29.8, 28.3; IR: $\tilde{\nu}$ = 3310, 2936, 2832, 1721, 1655, 1531, 1404, 1304, 1215, 1007, 833;

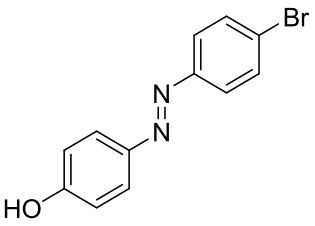
UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 393 nm (25500 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{20}H_{24}N_3O_7$: 418.1609 $[M+H]^+$; found: 418.1620.

N-(2-Methoxy-5-((3´,4´,5´-trimethoxyphenyl)diazenyl)phenyl)succinamic acid **12**



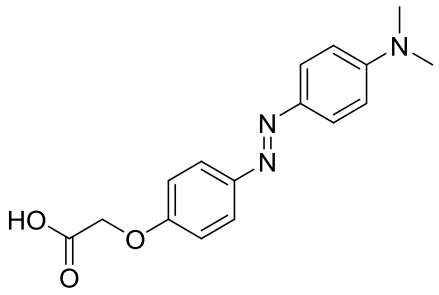
Azobenzene **34** (585 mg, 1.40 mmol, 1.0 equiv.) dissolved in a mixture of 1,4-dioxane and methanol (1:1, 10 mL) was treated with HCl (8.0 mL, 4 M in dioxan) and stirred at room temperature for 4 h. After evaporation of all solvents, K_2CO_3 (2.17 g, 15.7 mmol, 11.2 equiv.) and succinic anhydride (631 mg, 6.31 mmol, 4.5 equiv.) were added followed by DMF (8.0 mL). The resulting mixture was stirred for 16 h at 85 °C. After cooling water (30 mL) and EtOAc (20 mL) were added and the pH was adjusted to 10 with sat. $NaHCO_3$. The organic layer was discarded. The pH of the aqueous phase was adjusted to 3 with HCl (1 M), followed by extraction of the aqueous layer with EtOAc (3 × 150 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by silica-gel chromatography (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid) to provide azobenzene **12** (317 mg, 54 %) as an orange solid. R_f = 0.20 (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid); m.p. 88 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 12.12 (br s, 1 H), 9.36 (s, 1 H), 8.62 (d, J = 2.1 Hz, 1 H), 7.71 (dd, J = 2.4, 8.7 Hz, 1 H), 7.24 (d, J = 8.9 Hz, 1 H), 7.22 (s, 2 H), 3.95 (s, 3 H), 3.89 (s, 6 H), 3.75 (s, 3 H), 2.69 (t, J = 6.9 Hz, 2 H), 2.57 - 2.52 (m, 2 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 174.4, 171.2, 153.8, 152.2, 148.3, 145.9, 140.2, 128.7, 122.1, 113.6, 111.5, 100.3, 60.7, 56.6, 56.4, 31.4, 29.3; IR: $\tilde{\nu}$ = 3329, 2920, 2851, 1740, 1705, 1593, 1531, 1408, 1250, 1123, 991; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 373 nm (22600 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{20}H_{24}N_3O_7$: 418.1609 $[M+H]^+$; found: 418.1610.

4-((4´-bromophenyl)diazenyl)phenol **15**



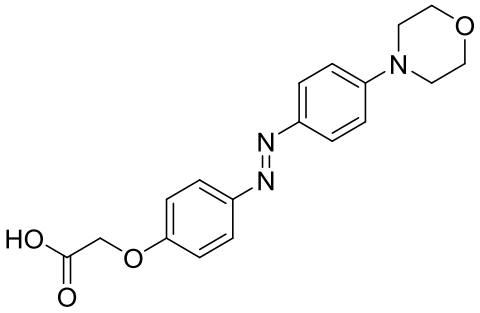
Standard Procedure **A1** with *p*-bromaniline (5.00 g, 29.1 mmol, 1.0 equiv.) and phenol (2.87 g, 30.5 mmol, 1.05 equiv.) gave azobenzene **15** (6.28 g, 78 %) as an ocher solid after recryztalisation (toluene/petroleum ether, 1:3). R_f = 0.40 (EtOAc/petroleum ether, 1:4); m.p. 160 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.8 Hz, 2 H), 7.77 (d, *J* = 8.8 Hz, 2 H), 7.63 (d, *J* = 8.8 Hz, 2 H), 6.96 (d, *J* = 8.8 Hz, 2 H), 5.19 (br s, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 158.4, 151.4, 147.0, 132.3, 125.1, 124.7, 124.1, 115.9; IR: $\tilde{\nu}$ = 3159, 2951, 2854, 1739, 1601, 1462, 1366, 1253, 837, 671; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 350 nm (23800 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{12}H_{10}BrN_2O$: 276.9971/278.9951 $[M+H]^+$; found: 276.9975/278.9954.

2-(4´-((4´´-(dimethylamino)phenyl)diazenyl)phenoxy)acetic acid **16b**



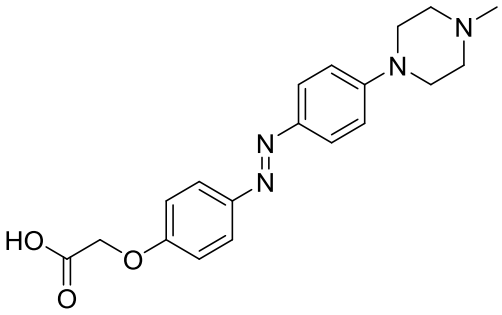
Standard Procedure **C** with ester **1b** (50.0 mg, 0.15 mmol, 1.0 equiv.) gave carboxylic acid **16b** (35.6 mg, 78 %) as an ocher solid after evaporation of the solvent. R_f = 0.19 (MeOH); m.p. 279 °C; ^{1}H-NMR (500 MHz, CD_3OD): δ = 7.77 (t, *J* = 7.6 Hz, 4 H), 7.03 (d, *J* = 8.2 Hz, 2 H), 6.82 (d, *J* = 8.5 Hz, 2 H), 4.45 (s, 2 H), 3.07 (s, 6 H); ^{13}C-NMR (126 MHz, CD_3OD): δ = 176.3, 161.8, 154.0, 148.8, 145.0, 125.6, 124.7, 116.1, 112.9, 68.7, 40.6; IR: $\tilde{\nu}$ = 3460, 2943, 2789, 1740, 1597, 1420, 1366, 1231, 1034, 826; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 408 nm (24400 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{16}H_{18}N_3O_3$: 300.1343 $[M+H]^+$; found: 300.1342.

2-(4´-((4´´-morpholinophenyl)diazenyl)phenoxy)acetic acid **16c**



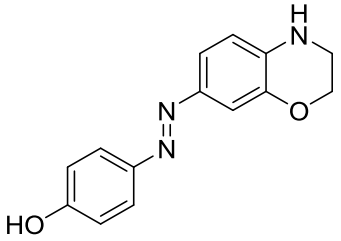
Standard Procedure **C** with ester **1c** (70.0 mg, 0.19 mmol, 1.0 equiv.) gave carboxylic acid **16c** (54.2 mg, 84 %) as a yellow solid after evaporation of the solvent. R_f = 0.20 (MeOH); m.p. 312 °C; ^{1}H-NMR (500 MHz, DMSO-d$_6$): δ = 7.76 (d, *J* = 9.2 Hz, 2 H), 7.73 (d, *J* = 9.2 Hz, 2 H), 7.08 (d, *J* = 9.2 Hz, 2 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 4.14 (s, 2 H), 3.78 - 3.74 (m, 4 H), 3.30 - 3.27 (m, 4 H); ^{13}C-NMR (126 MHz, DMSO-d_6): δ = 169.1, 161.9, 153.0, 146.1, 145.0, 124.2, 123.9, 115.4, 114.6, 68.9, 66.4, 47.8; IR: $\tilde{\nu}$ = 3464, 3205, 2970, 2851, 1740, 1574, 1423, 1377, 1346, 1227, 1123, 926, 841; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 392 nm (26200 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{18}H_{20}N_3O_4$: 342.1448 $[M+H]^+$; found: 342.1454.

2-(4´-((4´´-(4´´´-methylpiperazin-1´´´-yl)phenyl)diazenyl)phenoxy)acetic acid **16d**



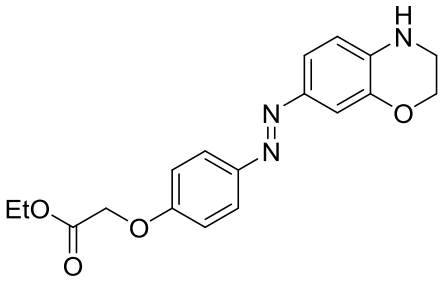
Standard Procedure **C** with ester **1d** (70.0 mg, 0.18 mmol, 1.0 equiv.) gave carboxylic acid **16d** (38.2 mg, 59 %) as a yellow solid after evaporation of the solvent. R_f = 0.20 (MeOH); m.p. 255 °C (decomp.); ^{1}H-NMR (500 MHz, D_2O): δ = 7.67 (d, *J* = 8.5 Hz, 2 H), 7.64 (d, *J* = 8.8 Hz, 2 H), 7.04 (d, *J* = 8.5 Hz, 2 H), 6.99 (d, *J* = 8.2 Hz, 2 H), 4.47 (s, 2 H), 3.22 (br s, 4 H), 2.55 (br s, 4 H), 2.24 (s, 3 H); ^{13}C-NMR (126 MHz, D_2O): δ = 176.2, 160.0, 152.9, 146.5, 145.4, 124.0, 123.9, 116.4, 115.0, 66.8, 53.4, 48.0, 44.4; IR: $\tilde{\nu}$ = 3460, 2947, 2843, 2681, 2596, 1744, 1597, 1234, 1080, 840; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 395 nm (26200 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{23}N_4O_3$: 355.1765 $[M+H]^+$; found: 355.1769.

4-((3´,4´-dihydro-2*H*-benzo[b][1´,4´]oxazin-7´-yl)diazenyl)phenol **18**



Standard Procedure **A1** with aniline **17** (156 mg, 1.04 mmol, 1.0 equiv.), phenol (103 mg, 1.09 mmol, 1.05 equiv.), and isoamyl nitrite (256 mg, 2.18 mmol, 2.1 equiv.) were converted to give a yellow solid (229 mg) that was dissolved in dry MeOH (12 mL), and HCl (4M in dioxane), and stirred at room temperature for 18 h. All solvents were removed under reduced pressure, and aq. $NaHCO_3$ (15 mL), $CHCl_3$ (20 mL), and acetone (2 mL) were added. The organic layer was separated, and the aqueous phase was extracted with $CHCl_3$ (3 × 20mL). The combined organic extracts were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Azobenzene **18** (145 mg, 55 %) was isolated as a brown oil after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4 → 1:1). R_f = 0.45 (EtOAc/petroleum ether, 1:1); ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 10.00 (br s, 1 H), 7.65 (d, J = 8.8 Hz, 2 H), 7.30 (dd, J = 2.0, 8.5 Hz, 1 H), 7.15 (d, J = 2.3 Hz, 1 H), 6.88 (d, J = 9.1 Hz, 2 H), 6.66 (d, J = 8.5 Hz, 1 H), 4.15 (t, J = 4.4 Hz, 2 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 159.8, 145.9, 143.6, 143.2, 138.7, 124.2, 120.1, 116.2, 113.8, 108.2, 64.6, 40.1; IR: $\tilde{\nu}$ = 3360, 2920, 2851, 1740, 1582, 1501, 1211, 840, 810; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 406 nm (24000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{14}H_{14}N_3O_2$: 256.1081 $[M+H]^+$; found: 256.1081.

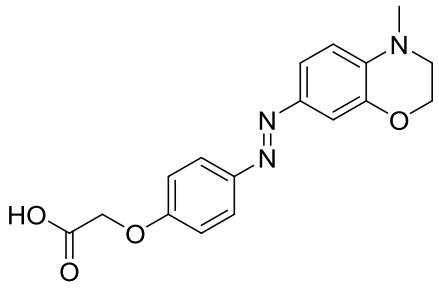
Ethyl-2-(4´-((3´´,4´´-dihydro-2´´*H*-benzo[b][1´´,4´´]oxazin-7´´-yl)diazenyl)phenoxy) acetate **19**



Standard Procedure **B** with azobenzene **18** (100 mg, 0.39 mmol, 1.0 equiv.), and ethyl bromoacetate (46 µL, 0.41 mmol, 1.05 equiv.) gave azobenzene **19** (124 mg, 93 %) as an orange solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4 →

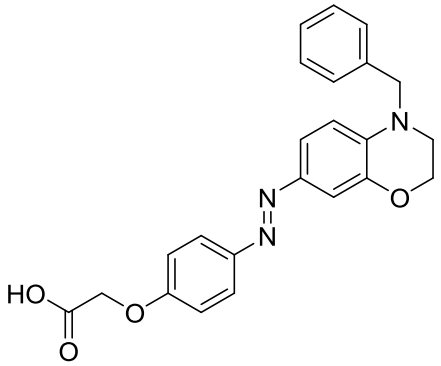
1:1). R_f = 0.35 (EtOAc/petroleum ether, 1:2); m.p. 76 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 7.73 (d, J = 9.1 Hz, 2 H), 7.34 (dd, J = 2.0, 8.5 Hz, 1 H), 7.18 (d, J = 2.0 Hz, 1 H), 7.06 (d, J = 9.1 Hz, 2 H), 6.80 - 6.76 (m, 1 H), 6.68 (d, J = 8.5 Hz, 1 H), 4.87 (s, 2 H), 4.19 (q, J = 7.1 Hz, 2 H), 4.16 (t, J = 4.4 Hz, 2 H), 3.43 - 3.37 (m, J = 2.3 Hz, 2 H), 1.23 (t, J = 7.2 Hz, 3 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 168.5, 158.8, 146.9, 143.0, 142.7, 138.8, 123.4, 120.2, 115.0, 113.2, 107.8, 64.8, 64.1, 60.7, 40.0, 14.0; IR: $\tilde{\nu}$ = 3356, 2970, 2928, 2870, 1751, 1597, 1500, 1315, 1261, 1080, 837, 810: UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 408 nm (24000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{18}H_{20}N_3O_4$: 342.1448 $[M+H]^+$; found: 342.1452.

2-(4´-((4´´-methyl-3´´,4´´-dihydro-2´´*H*-benzo[b][1´´,4´´]oxazin-7´´-yl)diazenyl)phenoxy) acetic acid **20a**



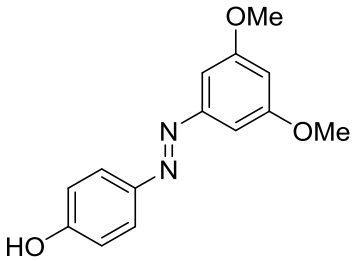
Standard Procedure **C** with ester **2a** (45.0 mg, 0.13 mmol, 1.0 equiv.) gave carboxylic acid **20a** (34 mg, 76 %) as a red solid after purification by silica-gel chromatography (CH_2Cl_2/MeOH, 10:1). R_f = 0.10 (CH_2Cl_2/MeOH, 10:1); m.p. 172 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 13.11 (br s, 1 H), 7.75 (d, J = 9.1 Hz, 2 H), 7.43 (dd, J = 2.3, 8.5 Hz, 1 H), 7.19 (d, J = 2.0 Hz, 1 H), 7.04 (d, J = 8.8 Hz, 2 H), 6.80 (d, J = 8.8 Hz, 1 H), 4.76 (s, 2 H), 4.29 - 4.19 (m, 2 H), 3.42 - 3.37 (m, 2 H), 2.98 (s, 3 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 170.4, 159.7, 147.2, 144.1, 143.9, 140.0, 124.0, 121.3, 115.4, 111.4, 106.7, 65.2, 64.5, 48.5, 38.4; IR: $\tilde{\nu}$ = 2916, 2851, 2326, 1736, 1520, 1215, 1080, 829, 795; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε)= 417 nm (26600 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{17}H_{18}N_3O_4$: 328.1292 $[M+H]^+$; found: 328.1296.

2-(4´-((4´´-benzyl-3´´,4´´-dihydro-2´´*H*-benzo[b][1´´,4´´]oxazin-7´´-yl)diazenyl)phenoxy) acetic acid **20b**



Standard Procedure **C** with ester **2b** (80.0 mg, 0.19 mmol, 1.0 equiv.) gave carboxylic acid **20b** (67 mg, 89 %) as an orange solid after purification by silica-gel chromatography (CH_2Cl_2/MeOH, 10:1). R_f = 0.31 (CH_2Cl_2/MeOH, 10:1); m.p. 87 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 13.11 (br s, 1 H), 7.74 (d, J = 9.1 Hz, 2 H), 7.40 - 7.25 (m, 6 H), 7.24 (d, J = 2.3 Hz, 1 H), 7.04 (d, J = 9.1 Hz, 2 H), 6.80 (d, J = 8.8 Hz, 1 H), 4.76 (s, 2 H), 4.66 (s, 2 H), 4.28 (t, J = 4.4 Hz, 2 H), 3.55 (t, J = 4.4 Hz, 2 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 170.4, 159.6, 147.2, 143.9, 143.6, 138.8, 138.0, 129.1, 127.5, 127.4, 124.0, 121.3, 115.4, 111.5, 107.3, 65.2, 64.3, 54.0, 47.5; IR: $\tilde{\nu}$ = 3460, 2920, 2866, 2578, 1736, 1597, 1315, 1234, 844, 725; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 418 nm (22700 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{23}H_{22}N_3O_4$: 404.1605 $[M+H]^+$; found: 404.1608.

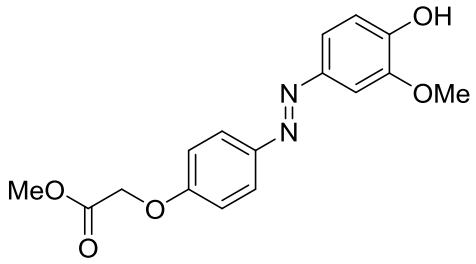
4-((3´,5´-dimethoxyphenyl)diazenyl)phenol **22**



Standard Procedure **A1** with 3,5-trimethoxyaniline (307 mg, 2.0 mmol, 1.0 equiv.) and phenol (198 mg, 2.1 mmol, 1.05 equiv.) gave azobenzene **22** (215 mg, 42 %) as an orange solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4). R_f = 0.38 (EtOAc/petroleum ether, 1:2); m.p. 129 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.8 Hz, 2 H), 7.10 (d, J = 2.2 Hz, 2 H), 6.95 (d, J = 8.8 Hz, 2 H), 6.59 (t, J = 2.2 Hz, 1 H),

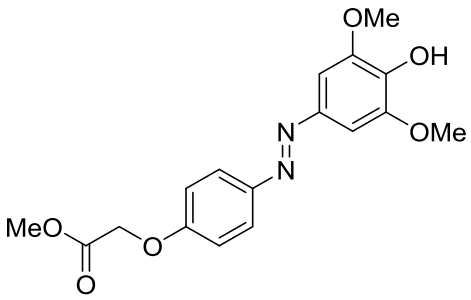
3.88 (s, 6 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 161.1, 158.4, 154.5, 147.0, 125.1, 115.8, 103.4, 100.7, 55.6; IR: $\tilde{\nu}$ = 3062, 2935, 1585, 1416, 1281, 1207, 1151, 1053, 942, 667; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 355 nm (21900 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{14}H_{15}N_2O_3$: 259.1077 $[M+H]^+$; found: 259.1082.

Methyl-2-(4´-((4´´-hydroxy-3´´-methoxyphenyl)diazenyl)phenoxy)acetate **25a**



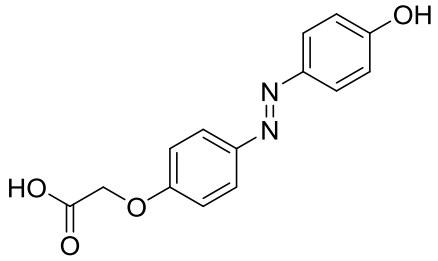
Standard Procedure **A1** with Boc-protected aniline **23** (200 mg, 0.68 mmol, 1.0 equiv.) and 2-methoxyphenol (88.3 mg, 0.71 mmol, 1.05 equiv.) gave after extraction, and evaporation of the solvent a residue that was redissolved in anhydrous MeOH (20 mL). Thionylchloride (1 mL) was added, and the mixture was stirred at room temperature for 2 h. The pH was adjusted to 7 with phosphate buffer, and $CHCl_3$ (30 mL) was added. The organic layer was separated followed by extraction of the aqueous layer with $CHCl_3$ (3 × 20 mL). The combined organic extracts were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica-gel chromatography (CH_2Cl_2/MeOH, 98:2) provided azobenzene **25a** (146 mg, 68 %) as an ocher solid. R_f = 0.47 (CH_2Cl_2/MeOH, 98:2 + 1.0 % formic acid); m.p. 133 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.7 Hz, 2 H), 7.67 (dd, *J* = 2.1, 8.4 Hz, 1 H), 7.60 (d, *J* = 2.1 Hz, 1 H), 7.16 (d, *J* = 8.6 Hz, 1 H), 7.13 (d, *J* = 9.1 Hz, 2 H), 6.06 (br s, 1 H), 4.83 (s, 2 H), 4.10 (s, 3 H), 3.95 (s, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.0, 159.5, 148.5, 147.6, 147.1, 146.7, 124.3, 121.0, 114.9, 114.2, 101.8, 65.4, 56.1, 52.4; IR: $\tilde{\nu}$ = 3190, 2916, 2851, 1771, 1582, 1501, 1207, 1022, 837; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 376 nm (19000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{16}H_{17}N_2O_5$: 317.1132 $[M+H]^+$; found: 317.1135.

Methyl-2-(4´-((4´´-hydroxy-3´´,5´´-dimethoxyphenyl)diazenyl)phenoxy)acetate **25b**



Standard Procedure **A1** with Boc-protected aniline **23** (500 mg, 1.69 mmol, 1.0 equiv.) and 2,6-dimethoxyphenol (274 mg, 1.78 mmol, 1.05 equiv.) gave after extraction and evaporation of the solvent a residue that was redissolved in dry MeOH (20 mL). Thionylchloride (1 mL) was added and the mixture was stirred at room temperature for 2 h. The pH was adjusted to 7 with phosphate buffer, and $CHCl_3$ (30 mL) was added. The organic layer was separated followed by extraction of the aqueous layer with $CHCl_3$ (3 × 20 mL). The combined organic extracts were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica-gel chromatography (EtOAc/petroleum ether, 1:1) provided azobenzene **25b** (397 mg, 68 %) as an ocher solid. R_f = 0.53 (EtOAc/petroleum ether, 1:1); m.p. 122 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.9 Hz, 2 H), 7.28 (s, 2 H), 7.03 (d, J = 8.9 Hz, 2 H), 5.82 (s, 1 H), 4.73 (s, 2 H), 4.01 (s, 6 H), 3.84 (s, 3 H); ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 169.0, 159.6, 147.5, 147.2, 145.5, 137.5, 124.3, 114.9, 100.2, 65.4, 56.4, 52.4; IR: $\tilde{\nu}$ = 3453, 2951, 1751, 1585, 1497, 1315, 1200, 1107, 841; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 384 nm (20000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{17}H_{19}N_2O_6$: 347.1238 $[M+H]^+$; found: 347.1242.

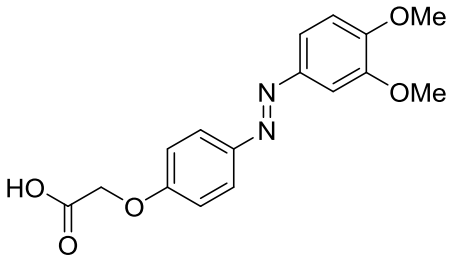
2-(4´-((4´´-hydroxyphenyl)diazenyl)phenoxy)acetic acid **25f**



Standard Procedure **A1** with Boc-protected aniline **23** (100 mg, 0.34 mmol, 1.0 equiv.) and phenol (33.5 mg, 0.35 mmol, 1.05 equiv.) gave azobenzene **25f** (47 mg, 51 %) as an orange solid after silica-gel chromatography (CH_2Cl_2/MeOH, 98:2 + 1.0 % formic acid). R_f = 0.17 (CH_2Cl_2/MeOH, 98:2 + 1.0 % formic acid); m.p. 186 °C; ^{1}H-NMR (300 MHz, CD_3OD): δ = 7.83 (d, J = 8.9 Hz, 2 H), 7.77 (d, J = 8.8 Hz, 2 H), 7.06 (d, J = 8.9 Hz, 2 H), 6.90 (d, J = 8.8 Hz, 2 H), 4.75 (s, 2 H); ^{13}C-NMR (101 MHz, CD_3OD): δ = 171.0, 160.2, 159.9, 147.4,

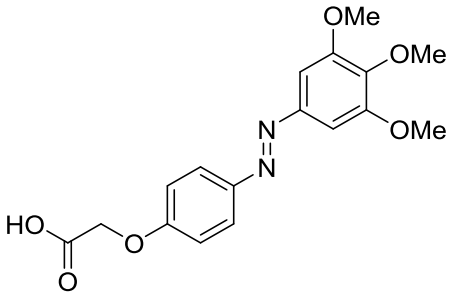
146.1, 124.2, 123.7, 115.3, 114.6, 64.7; IR: $\tilde{\nu}$ = 3406, 2924, 1728, 1585, 1497, 1435, 1215, 1146, 1080, 837; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 359 nm (16500 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{14}H_{13}N_2O_4$: 273.0870 $[M+H]^+$; found: 273.0874.

2-(4´-((3´´,4´´-dimethoxyphenyl)diazenyl)phenoxy)acetic acid **26a**



Standard Procedure **C** with ester **9a** (60 mg, 0.18 mmol, 1.0 equiv.) gave carboxylic acid **26a** (56 mg, 98 %) as a yellow solid after evaporation. R_f = 0.22 (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid); m.p. 190 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 7.83 (d, J = 9.0 Hz, 2 H), 7.53 (dd, J = 2.2, 8.5 Hz, 1 H), 7.42 (d, J = 2.2 Hz, 1 H), 7.14 (d, J = 8.7 Hz, 1 H), 7.07 (d, J = 8.8 Hz, 2 H), 4.77 (s, 2 H), 3.85 (s, 3 H), 3.84 (s, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.4, 160.3, 152.0, 149.9, 146.9, 146.5, 124.5, 120.2, 115.5, 111.7, 102.3, 65.2, 56.2, 55.9; IR: $\tilde{\nu}$ = 2916, 2851, 2577, 1736, 1705, 1578, 1497, 1231, 1018, 845; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 372 nm (25300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{16}H_{17}N_2O_5$: 317.1132 $[M+H]^+$; found: 317.1134.

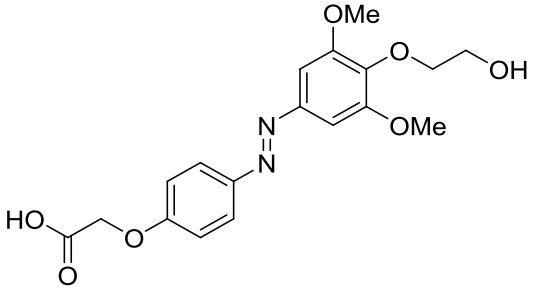
2-(4´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)phenoxy)acetic acid **26b**



Standard Procedure **C** with ester **9b** (135 mg, 0.37 mmol, 1.0 equiv.) gave carboxylic acid **26b** (106 mg, 82 %) as an orange solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid). R_f = 0.22 (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid); m.p. 110 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, J = 9.0 Hz, 2 H),

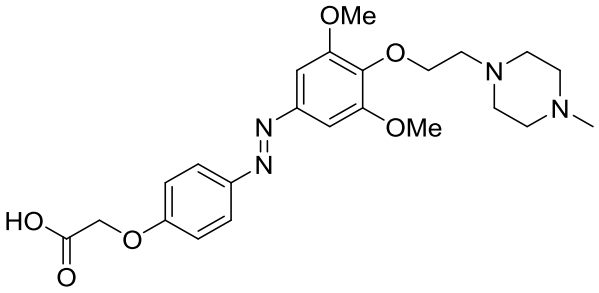
7.23 (s, 2 H), 7.06 (d, J = 9.0 Hz, 2 H), 4.79 (s, 2 H), 3.98 (s, 6 H), 3.94 (s, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 172.6, 159.4, 153.5, 148.5, 147.7, 140.4, 124.6, 114.9, 100.2, 64.8, 61.0, 56.2; IR: $\tilde{\nu}$ = 2943, 2839, 2573, 1732, 1585, 1416, 1219, 1126, 991, 845; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 368 nm (22100 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{17}H_{19}N_2O_6$: 347.1238 $[M+H]^+$; found: 347.1241.

2-(4´-((4´´-(2´´´-hydroxyethoxy)-3´´,5´´-dimethoxyphenyl)diazenyl)phenoxy)acetic acid **26c**



Standard Procedure **C** with ester **9c** (68 mg, 0.17 mmol, 1.0 equiv.) gave carboxylic acid **26c** (36 mg, 57 %) as a yellow solid after purification by preparative HPLC (H_2O/CH_3CN, 70:30 → 0:100). R_f = 0.31 (CH_2Cl_2/MeOH, 8:2); m.p. 183 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 7.86 (d, J = 9.0 Hz, 2 H), 7.21 (s, 2 H), 7.09 (d, J = 8.9 Hz, 2 H), 4.79 (s, 2 H), 3.96 (t, J = 5.6 Hz, 2 H), 3.87 (s, 6 H), 3.64 (t, J = 5.6 Hz, 2 H); ^{13}C-NMR (126 MHz, DMSO-d_6): δ = 170.4, 160.8, 153.8, 148.2, 146.8, 139.6, 124.8, 115.6, 100.5, 74.8, 65.3, 60.7, 56.5; IR: $\tilde{\nu}$ = 3410, 2932, 1593, 1493, 1258, 1126, 984, 826; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 369 nm (22000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{18}H_{21}N_2O_7$: 377.1343 $[M+H]^+$; found: 377.1347.

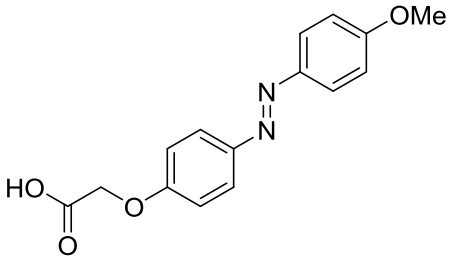
2-(4´-((3´´,5´´-dimethoxy-4´´-(2´´´-(4´´´´-methylpiperazin-1´´´´-yl)ethoxy)phenyl)diazenyl)-phenoxy)acetic acid **26e**



Standard Procedure **C** with ester **9e** (35 mg, 0.074 mmol, 1.0 equiv.) gave carboxylic acid **26e** (26 mg, 77 %) as a yellow solid after purification by preparative HPLC (H_2O/CH_3CN, 90:10 → 0:100). R_f = 0.22 (CH_2Cl_2/MeOH, 8:2); m.p. 128 °C; ^{1}H-NMR (300 MHz, D_2O): δ = 7.26

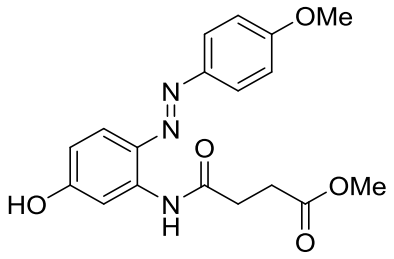
(d, J = 7.9 Hz, 2 H), 6.70 (d, J = 8.0 Hz, 2 H), 6.39 (s, 2 H), 4.31 (s, 2 H), 3.70 (s, 2 H), 3.45 (s, 6 H), 3.15 (br s, 4 H), 2.77 (s, 3 H), 2.88 - 2.66 (br s, 4 H); ^{13}C-NMR (101 MHz, D_2O): δ = 175.7, 160.4, 152.4, 147.8, 145.7, 137.3, 124.3, 114.7, 99.6, 68.8, 66.7, 56.1, 55.6, 52.4, 49.6, 42.9; IR: $\tilde{\nu}$ = 3422, 2997, 2634, 2361, 1597, 1412, 1219, 1126, 1042, 941, 840; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 368 nm (22900 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{23}H_{31}N_4O_6$: 459.2238 $[M+H]^+$; found: 459.2243.

2-(4´-((4´´-methoxyphenyl)diazenyl)phenoxy)acetic acid **26f**



Standard Procedure **C** with ester **1f** (24 mg, 0.08 mmol, 1.0 equiv.) gave carboxylic acid **26f** (22 mg, 96 %) as a yellow solid after evaporation. R_f = 0.22 (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid); m.p. 104 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 13.10 (br s, 1 H), 7.84 (t, J = 7.9 Hz, 4 H), 7.11 (t, J = 9.8 Hz, 4 H), 4.80 (s, 2 H), 3.86 (s, 3 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 170.3, 162.0, 160.4, 146.9, 146.6, 124.7, 124.5, 115.5, 115.0, 65.2, 56.1; IR: $\tilde{\nu}$ = 2916, 2569, 1736, 1705, 1597, 1578, 1497, 1234, 1146, 841; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 360 nm (25000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{15}H_{15}N_2O_4$: 287.1026 $[M+H]^+$; found: 287.1027.

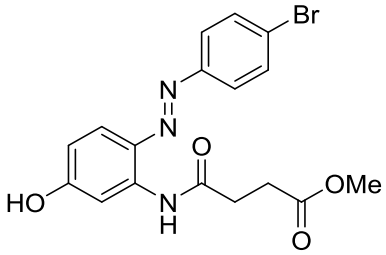
Methyl-*N*-(5´-hydroxy-2´-((4´´-methoxyphenyl)diazenyl)phenyl)succinamate **28a**



Standard Procedure **A1** with *p*-anisidine (123 mg, 1.00 mmol, 1.0 equiv.) and phenol **27** (201 mg, 1.05 mmol, 1.05 equiv.) gave after extraction and evaporation of the solvent a residue that was redissolved in anhydrous MeOH (20 mL). Thionylchloride (1 mL) was added and the mixture was stirred at room temperature for 2 h. The pH was adjusted to 7 with phosphate buffer and EtOAc (30 mL) was added. The organic layer was separated followed

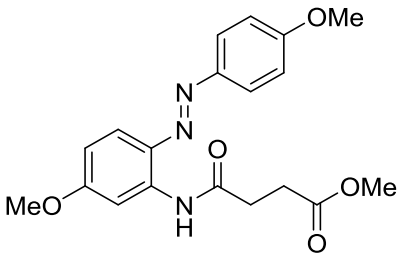
by extraction of the aqueous layer with EtOAc (3 × 20 mL). The combined organic extracts were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica-gel chromatography (EtOAc/petroleum ether, 1:2) provided azobenzene **28a** (201 mg, 56 %) as a yellow solid. R_f = 0.21 (EtOAc/petroleum ether, 1:2); m.p. 189 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 10.28 (br s, 1 H), 10.19 (s, 1 H), 7.95 (d, J = 8.9 Hz, 2 H), 7.86 (d, J = 2.5 Hz, 1 H), 7.64 (d, J = 8.9 Hz, 1 H), 7.10 (d, J = 9.0 Hz, 2 H), 6.57 (dd, J = 2.6, 8.9 Hz, 1 H), 3.85 (s, 3 H), 3.59 (s, 3 H), 2.80 (t, J = 6.5 Hz, 2 H), 2.63 (t, J = 6.9 Hz, 2 H); ^{13}C-NMR (126 MHz, DMSO-d_6): δ = 173.4, 170.8, 161.7, 161.7, 146.9, 138.6, 134.0, 125.0, 119.6, 114.9, 111.8, 107.6, 56.0, 51.9, 31.9, 29.1; IR: $\tilde{\nu}$ = 3113, 2951, 2839, 1720, 1663, 1597, 1454, 1242, 1172, 1111, 841; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 390 nm (23000 l·mol-1·cm-1); HRMS (ESI): *m/z* calcd for $C_{18}H_{20}N_3O_5$: 358.1397 $[M+H]^+$; found: 358.1401.

Methyl-*N*-(2´-((4´´-bromophenyl)diazenyl)-5´-hydroxyphenyl)succinamate **28e**



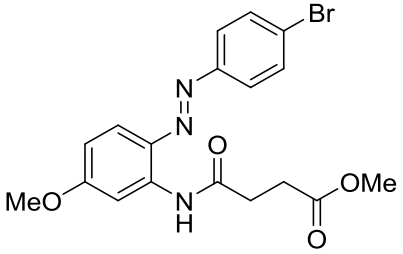
Standard Procedure **A1** with *p*-bromaniline (400 mg, 2.33 mmol, 1.0 equiv.), and phenol **27** (467 mg, 2.44 mmol, 1.05 equiv.) gave azobenzene **28e** (651 mg, 67 %) as an orange solid after recrystallization (toluene/petroleum ether, 3:1). R_f = 0.30 (CH_2Cl_2/MeOH, 95:5); m.p. 192 °C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 10.55 (br s, 1 H), 10.24 (s, 1 H), 7.92 (d, J = 8.8 Hz, 2 H), 7.89 (d, J = 2.6 Hz, 1 H), 7.77 (d, J = 8.5 Hz, 2 H), 7.70 (d, J = 8.8 Hz, 1 H), 6.61 (dd, J = 2.5, 8.9 Hz, 1 H), 3.61 (s, 3 H), 2.82 (t, J = 6.7 Hz, 2 H), 2.64 (t, J = 6.4 Hz, 2 H); ^{13}C-NMR (101 MHz, DMSO-d_6): δ = 173.4, 170.9, 162.9, 151.6, 139.5, 134.1, 132.7, 125.0, 124.1, 120.0, 112.1, 107.7, 51.9, 31.9, 29.0; IR: $\tilde{\nu}$ = 3012, 2951, 2322, 1736, 1458, 1366, 1207, 833; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 464 nm (19800 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{17}H_{17}BrN_3O_4$: 406.0397/408.0379 $[M+H]^+$; found: 406.0393/408.0375.

Methyl-*N*-(5´-methoxy-2´-((4´´-methoxyphenyl)diazenyl)phenyl)succinamate **29a**



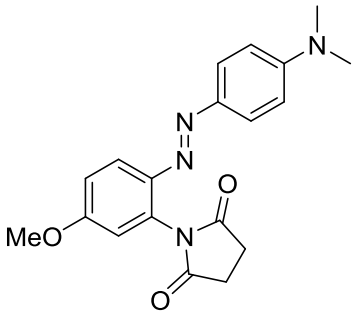
Standard Procedure **B** with azobenzene **28a** (70.0 mg, 0.20 mmol, 1.0 equiv.) and MeI (24.4 µL, 0.39 mmol, 2.0 equiv.) gave azobenzene **29a** (66 mg, 91 %) as an ocher solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4 → 1:2). R_f = 0.46 (EtOAc/petroleum ether, 1:2); m.p. 126 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.74 (br s, 1 H), 8.36 (d, *J* = 2.7 Hz, 1 H), 7.90 (d, *J* = 8.9 Hz, 2 H), 7.87 (d, *J* = 9.0 Hz, 1 H), 7.09 (d, *J* = 9.0 Hz, 2 H), 6.76 (dd, *J* = 2.7, 9.0 Hz, 1 H), 3.96 (s, 3 H), 3.95 (s, 3 H), 3.78 (s, 3 H), 2.87 (br. s, 4 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 173.2, 170.1, 162.8, 161.7, 146.7, 136.9, 133.4, 124.1, 123.7, 114.4, 110.9, 103.5, 55.7, 55.6, 52.0, 32.8, 29.1; IR: $\tilde{\nu}$ = 3337, 2932, 2835, 1744, 1670, 1582, 1470, 1227, 1168, 1034, 837; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 384 nm (24500 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{22}N_3O_5$: 372.1554 $[M+H]^+$; found: 372.1563.

Methyl-*N*-(2´-((4´´-bromophenyl)diazenyl)-5´-methoxyphenyl)succinamate **29e**



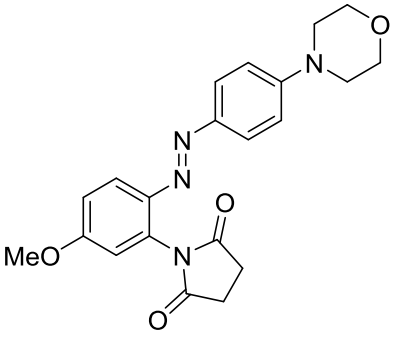
Standard Procedure **B** with azobenzene **28e** (555 mg, 1.37 mmol, 1.0 equiv.) and MeI (170 µL, 2.73 mmol, 2.0 equiv.) gave azobenzene **29e** (520 mg, 91 %) as a yellow solid after purification by silica-gel chromatography (CH_2Cl_2/MeOH, 98:2). R_f = 0.31 (CH_2Cl_2/MeOH, 98:2); m.p. 140 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.66 (br s, 1 H), 8.32 (d, *J* = 2.7 Hz, 1 H), 7.84 (d, *J* = 9.0 Hz, 1 H), 7.74 (d, *J* = 8.8 Hz, 2 H), 7.65 (d, *J* = 8.8 Hz, 2 H), 6.72 (dd, *J* = 2.7, 9.1 Hz, 1 H), 3.91 (s, 3 H), 3.72 (s, 3 H), 2.81 (s, 4 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 173.2, 170.3, 163.8, 151.2, 137.5, 133.4, 132.4, 124.7, 124.4, 123.8, 111.1, 103.5, 55.8, 52.0, 32.8, 29.0; IR: $\tilde{\nu}$ = 3329, 2943, 2322, 1732, 1604, 1527, 1474, 1219, 1157, 833; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 383 nm (19100 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{18}H_{19}BrN_3O_4$: 420.0553/422.0535 $[M+H]^+$; found: 420.0555/422.0537.

N-(2´-((4´´-(Dimethylamino)phenyl)diazenyl)-5´-methoxyphenyl)succinimide **30b**



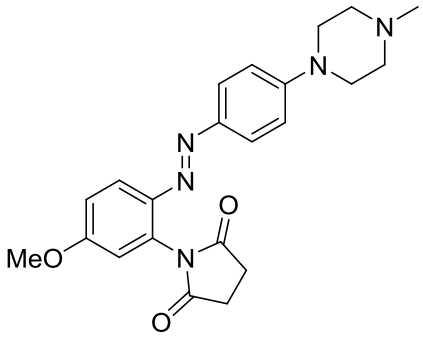
Standard Procedure **D** with azobenzene **29e** (100.0 mg, 0.24 mmol, 1.0 equiv.) and dimethylamine (92 µL, 5.2 M in EtOH, 0.48 mmol, 2.0 equiv.) gave azobenzene **30b** (73 mg, 88 %) as a yellow solid after silica-gel chromatography (EtOAc/petroleum ether, 1:4 → EtOAc). R_f = 0.29 (EtOAc/petroleum ether, 2:1); m.p. 94 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 9.1 Hz, 1 H), 7.69 (d, *J* = 9.0 Hz, 2 H), 7.05 (dd, *J* = 2.7, 9.1 Hz, 1 H), 6.82 (d, *J* = 2.7 Hz, 1 H), 6.72 (d, *J* = 9.1 Hz, 2 H), 3.88 (s, 3 H), 3.08 (s, 6 H), 2.97 (s, 4 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 176.4, 161.1, 152.3, 144.0, 141.8, 131.5, 124.7, 118.8, 116.3, 113.3, 111.5, 55.7, 40.3, 28.8; IR: $\tilde{\nu}$ = 2920, 2361, 1717, 1601, 1369, 1146, 826; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 421 nm (22400 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{21}N_4O_3$: 353.1608 $[M+H]^+$; found: 353.1610.

N-(5´-Methoxy-2´-((4´´-morpholinophenyl)diazenyl)phenyl)succinimide **30c**



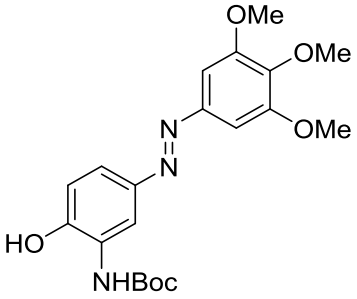
Standard Procedure **D** with azobenzene **29e** (80.0 mg, 0.19 mmol, 1.0 equiv.) and morpholine (33 µL, 0.38 mmol, 2.0 equiv.) gave azobenzene **30c** (76 mg, 94 %) as a dark red solid after silica-gel chromatography (CH_2Cl_2/MeOH, 98:2). R_f = 0.46 (CH_2Cl_2/MeOH, 98:2); m.p. 85 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 9.1 Hz, 1 H), 7.69 (d, J = 9.0 Hz, 2 H), 7.06 (dd, J = 2.7, 9.1 Hz, 1 H), 6.92 (d, J = 9.1 Hz, 2 H), 6.83 (d, J = 2.7 Hz, 1 H), 3.91 - 3.84 (m, 8 H), 3.33 - 3.26 (m, 4 H), 2.97 (s, 4 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.3, 161.6, 153.0, 146.0, 141.6, 132.0, 124.4, 118.9, 116.3, 114.4, 113.4, 66.6, 55.8, 48.1, 28.8; IR: $\tilde{\nu}$ = 2928, 2851, 2322, 1708, 1593, 1377, 1146, 926, 826; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 404 nm (24300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{21}H_{23}N_4O_4$: 395.1714 $[M+H]^+$; found: 395.1714.

N-(5´-Methoxy-2´-((4´´-(4´´´-methylpiperazin-1´´´-yl)phenyl)diazenyl)phenyl) succinimide **30d**



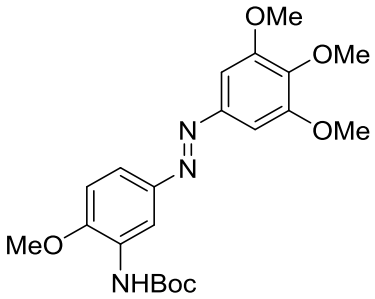
Standard Procedure **D** with azobenzene **29e** (100.0 mg, 0.24 mmol, 1.0 equiv.) and 1-methylpiperazine (53 µL, 0.48 mmol, 2.0 equiv.) gave azobenzene **30d** (94 mg, 97 %) as an ocher solid after silica-gel chromatography (CH_2Cl_2/MeOH, 98:2 → 93:7). R_f = 0.32 (CH_2Cl_2/MeOH, 95:5); m.p. 86 °C; ^{1}H-NMR (400 MHz, MeOD): δ = 7.85 (d, J = 9.1 Hz, 1 H), 7.69 (d, J = 9.1 Hz, 2 H), 7.12 (dd, J = 2.6, 9.1 Hz, 1 H), 7.03 (d, J = 9.1 Hz, 2 H), 6.96 (d, J = 2.9 Hz, 1 H), 3.89 (s, 3 H), 3.46 - 3.39 (m, 4 H), 2.96 (s, 4 H), 2.79 (t, J = 4.4 Hz, 4 H), 2.48 (s, 3 H); ^{13}C-NMR (101 MHz, MeOD): δ = 177.7, 161.8, 152.8, 145.7, 141.7, 132.4, 124.0, 117.9, 115.7, 114.7, 113.5, 55.0, 53.9, 46.7, 44.0, 28.3; IR: $\tilde{\nu}$ = 2932, 2839, 1709, 1597, 1373, 1234, 1138, 1007, 822; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 409 nm (21000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{22}H_{26}N_5O_3$: 408.2030 $[M+H]^+$; found: 408.2034.

tert-Butyl-2-hydroxy-5-((3´,4´,5´-trimethoxyphenyl)diazenyl)phenylcarbamate **33**



Standard Procedure **A2** with 3,4,5-trimethoxyaniline (1.0 g, 5.46 mmol, 1.0 equiv.) and phenol **32** (1.20 g, 5.73 mmol, 1.05 equiv.) gave azobenzene **33** (1.36 g, 62 %) as red solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4). R_f = 0.52 (EtOAc/petroleum ether, 1:4); m.p. 80 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.73 (br s, 1 H), 7.76 (d, *J* = 1.6 Hz, 1 H), 7.68 (dd, *J* = 2.0, 8.7 Hz, 1 H), 7.20 (s, 2 H), 7.08 (d, *J* = 8.8 Hz, 1 H), 6.79 (br s, 1 H), 3.96 (s, 6 H), 3.94 (s, 3 H), 1.56 (s, 9 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 154.8, 153.6, 148.4, 140.6, 129.9, 126.8, 122.1, 118.8, 112.6, 105.2, 100.2, 82.4, 61.1, 56.3, 28.2; IR: $\tilde{\nu}$ = 3260, 2970, 2361, 1736, 1597, 1493, 1366, 1219, 1123, 999; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 473 nm (27300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{20}H_{26}N_3O_6$: 404.1816 $[M+H]^+$; found: 404.1824.

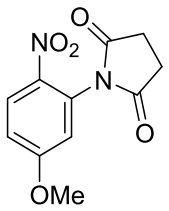
tert-Butyl-2-methoxy-5-((3´,4´,5´-trimethoxyphenyl)diazenyl)phenylcarbamate **34**



Standard Procedure **B** with azobenzene **33** (1.25 g, 3.10 mmol, 1.0 equiv.) and MeI (386 µL, 6.20 mmol, 2.0 equiv.) gave azobenzene **34** (1.18 g, 91 %) as a yellow solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4). R_f = 0.27 (EtOAc/petroleum ether, 1:4); m.p. 132 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.72 (s, 1 H), 7.62 (dd, *J* = 2.4, 8.6 Hz, 1 H), 7.26 (s, 2 H), 7.17 (s, 1 H), 6.98 (d, *J* = 8.7 Hz, 1 H), 3.97 (s, 9 H), 3.93 (s, 3 H), 1.57 (s, 9 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 153.4, 152.5, 149.7, 148.6, 146.9, 139.9, 128.7, 119.0, 111.1, 109.6, 100.1, 80.6, 61.0, 56.2, 56.0, 28.3; IR: $\tilde{\nu}$ = 2970, 2836, 2361, 1720, 1593, 1520, 1366, 1219, 1119, 992; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) =

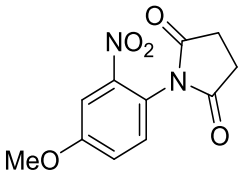
372 nm (22100 $l \cdot mol^{-1} \cdot cm^{-1}$); HRMS (ESI): *m/z* calcd for $C_{21}H_{28}N_3O_6$: 418.1973 $[M+H]^+$; found: 418.1978.

N-(5´-Methoxy-2´-nitrophenyl)succinimide ***p*-35**



Under an atmosphere of nitrogen 5-methoxy-2-nitroaniline (2.00 g, 11.9 mmol, 1.0 equiv.) and K_2CO_3 (4.11 g, 29.7 mmol, 2.5 equiv.) were suspended in dry THF (160 mL). Succinylchloride (1.31 mL, 11.9 mmol, 1.0 equiv.) was added dropwise and the reaction mixture was heated to 45 °C for 16 h. The reaction mixture was concentrated under reduced pressure. The residue was dissolved in EtOAc (100 mL) and washed with water (2 × 30 mL). The combined extracts were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by silica-gel chromatography (EtOAc/petroleum ether, 1:1) provided succinimide ***p*-35** (1.95 g, 66%) as a yellow solid. R_f = 0.34 (EtOAc/petroleum ether, 1:1); m.p. 176 °C; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 8.27 (d, J = 9.3 Hz, 1 H), 7.07 (dd, J = 2.7, 9.1 Hz, 1 H), 6.83 (d, J = 2.6 Hz, 1 H), 3.94 (s, 3 H), 3.16 - 2.82 (m, 4 H); ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 176.3, 164.9, 139.0, 129.3, 129.2, 116.9, 115.7, 57.2, 29.8; IR: $\tilde{\nu}$ = 3356, 2839, 1786, 1701, 1585, 1489, 1280, 1173, 1092, 825; HRMS (ESI): *m/z* calcd for $C_{11}H_{11}N_2O_5$: 251.0662 $[M+H]^+$; found: 251.0666.

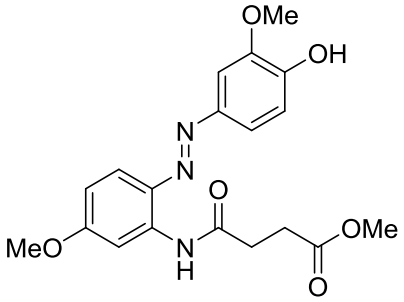
N-(4´-Methoxy-2´-nitrophenyl)succinimide ***m*-35**



Under an atmosphere of nitrogen 5-methoxy-2-nitroaniline (2.00 g, 11.9 mmol, 1.0 equiv.) and K_2CO_3 (4.11 g, 29.7 mmol, 2.5 equiv.) were suspended in dry THF (160 mL). Succinylchloride (1.31 mL, 11.9 mmol, 1.0 equiv.) was added dropwise and the reaction mixture was heated to 45 °C for 16 h. The reaction mixture was concentrated under reduced pressure. The residue was dissolved in EtOAc (100 mL) and washed with water (2 × 30 mL).

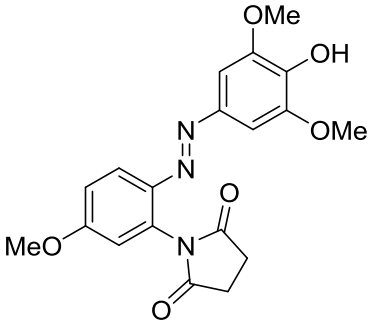
The combined organic extracts were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by silica-gel chromatography (EtOAc/petroleum ether, 1:1) provided succinimide ***m*-35** (1.94 g, 65%) as a yellow solid. R_f = 0.32 (EtOAc/petroleum ether, 1:1); m.p. 176 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.70 (dd, J = 1.2, 1.8 Hz, 1 H), 7.28 - 7.25 (m, 2 H), 3.92 (s, 3 H), 2.94 (d, J = 5.2 Hz, 4 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 175.7, 160.3, 145.7, 131.3, 120.3, 118.3, 110.9, 56.2, 28.7; IR: $\tilde{\nu}$ = 3348, 3089, 2939, 1774, 1705, 1539, 1357, 1280, 1171, 1030, 887, 664; HRMS (ESI): *m/z* calcd for $C_{11}H_{11}N_2O_5$: 251.0662 $[M+H]^+$; found: 251.0666.

Methyl-*N*-(2´-((4´´-hydroxy-3´´-methoxyphenyl)diazenyl)-5´-methoxyphenyl) succinamate **36a**



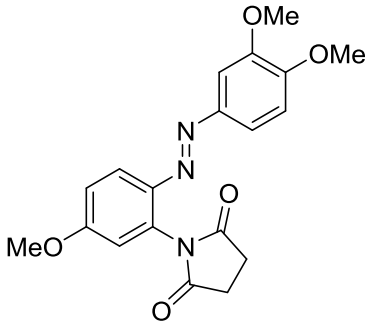
Nitrobenzene ***p*-35** (250 mg, 1.14 mmol, 1.0 equiv.) was reduced to the corresponding aniline (quant.) following Standard Procedure **F**. The crude material was converted according to Standard Procedure **A1** with 2-methoxyphenol (176 mg, 1.42 mmol, 1.05 equiv.) to give azobenzene **36a** (128 mg, 30 %) as chartreuse solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 7:3 → EtOAc). R_f = 0.39 (EtOAc/petroleum ether, 7:3); m.p. 104 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.85 (s, 1 H), 8.31 (d, J = 2.8 Hz, 1 H), 7.81 (d, J = 9.0 Hz, 1 H), 7.52 - 7.44 (m, 2 H), 7.06 (d, J = 8.9 Hz, 1 H), 6.71 (dd, J = 2.7, 9.0 Hz, 1 H), 4.01 (s, 3 H), 3.90 (s, 3 H), 3.71 (s, 3 H), 2.80 (s, 4 H); ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 174.1, 171.2, 163.6, 149.3, 148.1, 147.3, 137.5, 134.2, 125.5, 120.6, 115.3, 111.7, 104.6, 103.0, 57.0, 56.6, 52.9, 33.8, 30.1; IR: $\tilde{\nu}$ = 3348, 2940, 2322, 1728, 1585, 1431, 1200, 1157, 1111, 1022, 848, 806; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 401 nm (24100 $l \cdot mol^{-1} \cdot cm^{-1}$); HRMS (ESI): *m/z* calcd for $C_{19}H_{21}N_3O_6$: 388.1503 $[M+H]^+$; found: 388.1511.

N-(2´-((4´´-Hydroxy-3´´,5´´-dimethoxyphenyl)diazenyl)-5´-methoxyphenyl)succinimide **36b**



Nitrobenzene ***p*-35** (751 mg, 3.00 mmol, 1.0 equiv.) was reduced to the corresponding aniline (quant.) following Standard Procedure **F**. The crude material was converted according to Standard Procedure **A1** with 2,6-dimethoxyphenol (486 mg, 3.15 mmol, 1.05 equiv.) to give azobenzene **36b** (495 mg, 43 %) as a red solid after purification by silica-gel chromatography (CH_2Cl_2/MeOH, 98:2 → 95:5). R_f = 0.48 (CH_2Cl_2/MeOH, 97:3); m.p. 76 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, J = 9.0 Hz, 1 H), 7.09 (s, 2 H), 7.06 (dd, J = 2.6, 9.1 Hz, 1 H), 6.85 (d, J = 2.6 Hz, 1 H), 3.95 (s, 6 H), 3.90 (s, 3 H), 3.02 - 2.87 (m, 4 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 176.1, 162.0, 147.1, 146.0, 141.1, 137.8, 132.3, 118.8, 116.3, 113.5, 100.3, 56.2, 55.8, 28.8; IR: $\tilde{\nu}$ = 2940, 2839, 1705, 1604, 1508, 1377, 1234, 1176, 1026, 818; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 394 nm (16500 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{20}N_3O_6$: 386.1347 $[M+H]^+$; found: 386.1351.

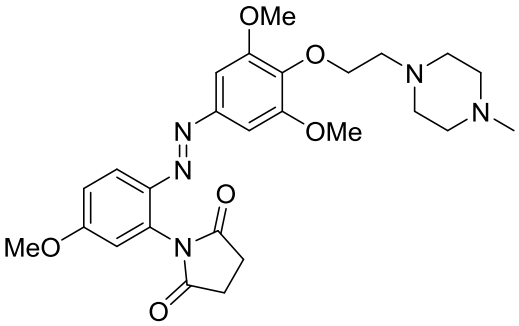
N-(2´-((3´´,4´´-Dimethoxyphenyl)diazenyl)-5´-methoxyphenyl)succinimide **37a**



Standard Procedure **B** with azobenzene **36a** (69.4 mg, 0.19 mmol, 1.0 equiv.) and MeI (25.4 µL, 0.41 mmol, 2.1 equiv.) gave azobenzene **37a** (47 mg, 68 %) as an orange solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:1 → EtOAc). R_f = 0.50 (EtOAc); m.p. 89 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, J = 9.0 Hz, 1 H), 7.46 (dd, J = 2.2, 8.5 Hz, 1 H), 7.29 (d, J = 2.1 Hz, 1 H), 7.07 (dd, J = 2.8, 9.1 Hz, 1 H), 6.97 (d, J = 8.6 Hz, 1 H), 6.86 (d, J = 2.8 Hz, 1 H), 3.97 (s, 3 H), 3.93 (s, 3 H), 3.90 (s, 3 H), 3.03 - 2.90 (m, 4 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 176.2, 162.0, 151.8, 149.4, 147.3, 141.2, 132.2,

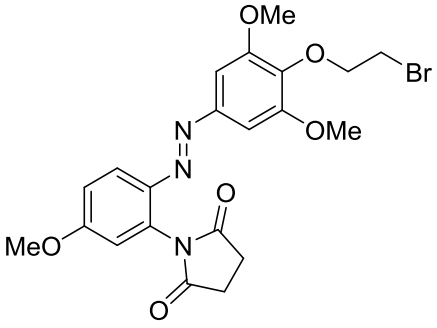
119.4, 119.1, 116.3, 113.5, 110.5, 102.9, 56.2, 55.8, 55.7, 28.8; IR: $\tilde{\nu}$ = 2943, 2322, 1713, 1504, 1373, 1234, 1177, 1015, 814; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 374 nm (20600 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{20}N_3O_5$: 370.1403 $[M+H]^+$; found: 370.1404.

N-(2´-((3´´,5´´-Dimethoxy-4´´-(2´´´-(4´´´´-methylpiperazin-1´´´´-yl)ethoxy)phenyl)diazenyl)-5´-methoxyphenyl)succinimide **37b**



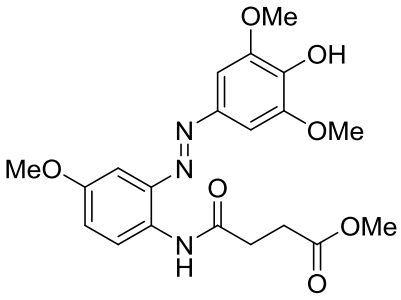
A microwave vial charged with azobenzene **37c** (64 mg, 0.13 mmol, 1.0 equiv.), 1-methylpiperazine (20 µL, 0.18 mmol, 1.3 equiv.), K_2CO_3 (25 mg, 0.18 mmol, 1.3 equiv.), and CH_3CN (4 mL) was heated to 140 °C for 10 min. in a microwave. After cooling the solvent was removed under reduced pressure, and the residue was redissolved in $CHCl_3$ (10 mL). The organic phase was washed with water (5 mL), brine (5 mL), dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Azobenzene **37b** (43 mg, 65 %) was obtained as an orange oil after purification by silica-gel chromatography (CH_2Cl_2/MeOH, 95:5 → 90:10). R_f = 0.35 (CH_2Cl_2/MeOH, 9:1); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 9.0 Hz, 1 H), 7.07 (dd, *J* = 2.7, 9.1 Hz, 1 H), 7.03 (s, 2 H), 6.87 (d, *J* = 2.7 Hz, 1 H), 4.17 (t, *J* = 5.8 Hz, 2 H), 3.90 (s, 3 H), 3.90 (s, 6 H), 3.03 - 2.87 (m, 4 H), 2.82 (t, *J* = 5.8 Hz, 2 H), 2.69 (br s, 4 H), 2.56 (br s, 4 H), 2.34 (s, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.1, 162.3, 153.6, 148.9, 141.0, 139.7, 132.7, 118.8, 116.3, 113.5, 100.2, 70.6, 57.9, 56.0, 55.8, 55.0, 53.3, 46.0, 28.8; IR: $\tilde{\nu}$ = 2936, 2797, 1713, 1601, 1454, 1223, 1123, 1003, 822; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 371 nm (26400 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{26}H_{34}N_5O_6$: 512.2504 $[M+H]^+$; found: 512.2510.

N-(2´-((4´´-(2´´´-Bromoethoxy)-3´´,5´´-dimethoxyphenyl)diazenyl)-5´-methoxyphenyl) succinimide **37c**



Standard Procedure **B** with azobenzene **36b** (200 mg, 0.52 mmol, 1.0 equiv.) and 1,2-dibromoethane (447 µL, 5.19 mmol, 10.0 equiv.) in anhydrous acetone (50 mL) gave azobenzene **37c** (108 mg, 43 %) as a red solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:2 → 2:1). R_f = 0.23 (EtOAc/petroleum ether, 1:1); m.p. 126 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J = 9.1 Hz, 1 H), 7.09 (dd, J = 2.6, 9.1 Hz, 1 H), 7.06 (s, 2 H), 6.89 (d, J = 2.6 Hz, 1 H), 4.35 (t, J = 7.2 Hz, 2 H), 3.93 (s, 6 H), 3.92 (s, 3 H), 3.65 (t, J = 7.3 Hz, 2 H), 3.06 - 2.87 (m, 4 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 176.1, 162.5, 153.4, 149.2, 141.0, 138.7, 132.8, 118.8, 116.3, 113.5, 100.1, 72.8, 56.1, 55.9, 29.6, 28.8; IR: $\tilde{\nu}$ = 2936, 2835, 2318, 1709, 1377, 1234, 1177, 1123, 856, 822; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 368 nm (24200 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{21}H_{23}BrN_3O_6$: 492.0765/494.0747 $[M+H]^+$; found: 492.0769/494.0750.

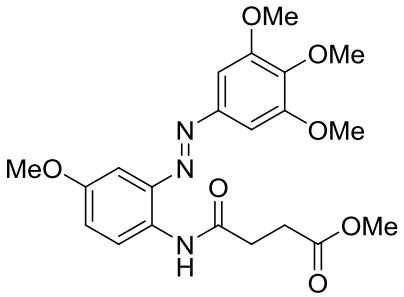
Methyl-*N*-(2´-((4´´-hydroxy-3´´,5´´-dimethoxyphenyl)diazenyl)-4´-methoxyphenyl) succinamate **38**



Nitrobenzene ***m*-35** (1.14 g, 4.56 mmol, 1.0 equiv.) was reduced to the corresponding aniline (quant.) following Standard Procedure **F**. The crude material was further converted according to Standard Procedure **A1** with 2,6-dimethoxyphenol (738 mg, 4.80 mmol, 1.05 equiv.). The resulting crude material was dissolved in anhydrous MeOH (20 mL). Thionylchloride (1 mL), was added and the mixture was stirred at room temperature for 2 h. The pH was adjusted to 7 with phosphate buffer, and $CHCl_3$ (40 mL) was added. The organic layer was separated followed by extraction of the aqueous layer with $CHCl_3$ (3 × 30 mL). The combined organic

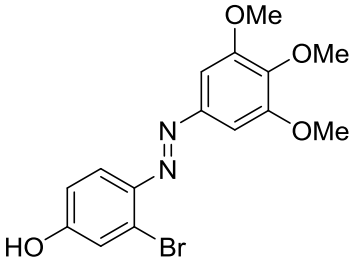
extracts were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica-gel chromatography (EtOAc/petroleum ether, 2:1 → EtOAc) provided azobenzene **38** (829 mg, 44 %) as an ocher solid. R_f = 0.21 (EtOAc/petroleum ether, 1:2); m.p. 159 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 9.67 (br s, 1 H), 8.54 (d, *J* = 9.1 Hz, 1 H), 7.32 (s, 2 H), 7.27 (s, 1 H), 7.03 (dd, *J* = 3.0, 9.1 Hz, 1 H), 5.98 (s, 1 H), 4.03 (s, 6 H), 3.86 (s, 3 H), 3.67 (s, 3 H), 2.84 - 2.72 (m, 4 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 173.4, 169.3, 155.8, 147.3, 145.5, 140.0, 138.4, 130.4, 121.6, 119.3, 101.4, 100.7, 56.5, 55.6, 52.0, 32.8, 29.5; IR: $\tilde{\nu}$ = 3360, 2947, 2361, 1732, 1609, 1504, 1462, 1308, 1107, 1033, 814; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 515 nm (19100 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{20}H_{24}N_3O_7$: 418.1609 $[M+H]^+$; found: 418.1622.

Methyl-*N*-(4´-methoxy-2´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)phenyl)succinamate **39**



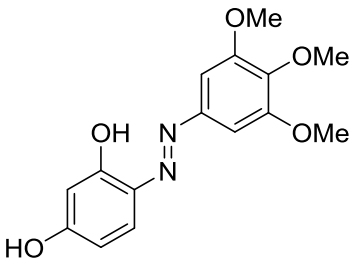
Standard Procedure **B** with azobenzene **38** (160 mg, 0.38 mmol, 1.0 equiv.) and MeI (47.7 µL, 0.77 mmol, 2.0 equiv.) gave azobenzene **39** (147 mg, 89 %) as a yellow solid after purification by silica-gel chromatography (acetone/petroleum ether, 1:4). R_f = 0.38 (acetone/petroleum ether, 1:3); m.p. 129 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 9.66 (br s, 1 H), 8.53 (d, *J* = 9.1 Hz, 1 H), 7.31 (d, *J* = 3.0 Hz, 1 H), 7.25 (s, 2 H), 7.04 (dd, *J* = 3.0, 9.2 Hz, 1 H), 3.97 (s, 6 H), 3.94 (s, 3 H), 3.84 (s, 3 H), 3.65 (s, 3 H), 2.81 - 2.68 (m, 4 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 173.4, 169.4, 155.8, 153.7, 148.4, 141.1, 139.9, 130.7, 121.7, 119.9, 101.5, 100.6, 61.1, 56.3, 55.6, 52.0, 32.8, 29.5; IR: $\tilde{\nu}$ = 3306, 2940, 2835, 1744, 1597, 1508, 1215, 1119, 1007, 845, 818; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 409 nm (23300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{21}H_{26}N_3O_7$: 432.1765 $[M+H]^+$; found: 432.1773.

3-Bromo-4-((3´,4´,5´-trimethoxyphenyl)diazenyl)phenol **41a**



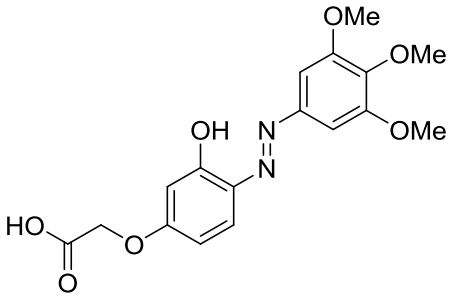
Standard Procedure **A1** with 3,4,5-trimethoxyaniline (366 mg, 2.0 mmol, 1.0 equiv.) and 3-bromphenol (363 mg, 2.1 mmol, 1.05 equiv.) gave azobenzene **41a** (516 mg, 70 %) as a dark green solid after purification by silica-gel chromatography (CH_2Cl_2/MeOH, 95:5 + 1.0 % formic acid). R_f = 0.45 (CH_2Cl_2/MeOH, 95:5 + 1.0 % formic acid); m.p. 221°C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 7.64 (d, J = 8.9 Hz, 1 H), 7.21 (s, 2 H), 7.21 (d, J = 2.5 Hz, 1 H), 6.88 (dd, J = 2.5, 8.9 Hz, 1 H), 3.86 (s, 6 H), 3.75 (s, 3 H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 162.1, 153.8, 148.5, 141.8, 140.5, 127.8, 120.0, 119.1, 116.4, 100.6, 60.7, 56.4; IR: $\tilde{\nu}$ = 3237, 2940, 1740, 1593, 1458, 1227, 1123, 984, 856; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 458 nm (28300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{15}H_{16}BrN_2O_4$: 367.0288/369.0267 $[M+H]^+$; found: 367.0295/369.0274.

4-((3´,4´,5´-Trimethoxyphenyl)diazenyl)resorcin **41b**



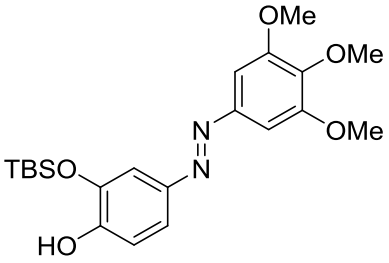
Standard Procedure **A1** with 3,4,5-trimethoxyaniline (366 mg, 2.0 mmol, 1.0 equiv.) and resorcin (231 mg, 2.1 mmol, 1.05 equiv.) gave azobenzene **41b** (347 mg, 57 %) as a red solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4 → 1:2). R_f = 0.42 (EtOAc/petroleum ether, 1:2); m.p. 95 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 13.83 (br s, 1 H), 7.76 (d, J = 8.8 Hz, 1 H), 7.10 (s, 2 H), 6.58 (dd, J = 2.5, 8.6 Hz, 1 H), 6.46 (d, J = 2.6 Hz, 1 H), 3.97 (s, 6 H), 3.95 (s, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 160.7, 156.6, 153.7, 145.9, 139.7, 135.1, 132.9, 108.9, 103.8, 99.0, 61.1, 56.3; IR: $\tilde{\nu}$ = 3360, 2940, 2832, 1724, 1597, 1215, 1115, 1006, 826, 783; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 350 nm (23800 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{15}H_{17}N_2O_5$: 305.1132 $[M+H]^+$; found: 305.1133.

2-(3´-Hydroxy-4´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)phenoxy)acetic acid **42b**



Standard Procedure **C** with ester **7b** (100 mg, 0.26 mmol, 1.0 equiv.) gave carboxylic acid **42b** (80 mg, 86 %) as a red solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 3:7 → EtOAc + 0.5 % formic acid). R_f = 0.17 (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid); m.p. 204 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 11.88 (br s, 1 H), 7.73 (d, J = 9.0 Hz, 1 H), 7.31 (s, 2 H), 6.60 (dd, J = 2.7, 9.0 Hz, 1 H), 6.50 (d, J = 2.6 Hz, 1 H), 4.71 (s, 2 H), 3.88 (s, 6 H), 3.74 (s, 3 H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 169.7, 162.2, 156.0, 153.4, 146.9, 139.6, 132.9, 126.9, 108.1, 102.2, 99.8, 65.2, 60.2, 56.1; IR: $\tilde{\nu}$ = 3545, 2943, 2839, 2530, 1751, 1600, 1226, 1130, 1060, 825; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 390 nm (27300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{17}H_{19}N_2O_7$: 363.1187 $[M+H]^+$; found: 363.1184.

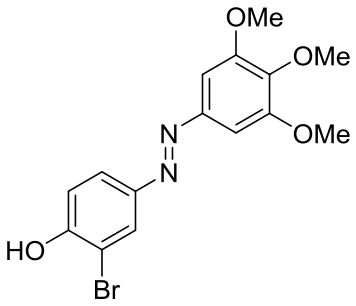
2-((*tert*-Butyldimethylsilyl)oxy)-4-((3´,4´,5´-trimethoxyphenyl)diazenyl)phenol **44a**



Standard Procedure **A1** with 3,4,5-trimethoxyaniline (366 mg, 2.0 mmol, 1.0 equiv.) and phenol **43a** (471 mg, 2.1 mmol, 1.05 equiv.) gave azobenzene **44a** (264 mg, 32 %) as a red oil after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4). R_f = 0.44 (EtOAc/petroleum ether, 1:4); ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.57 (dd, J = 2.2, 8.6 Hz, 1 H), 7.45 (d, J = 2.2 Hz, 1 H), 7.20 (s, 2 H), 7.06 (d, J = 8.6 Hz, 1 H), 5.81 (s, 1 H), 3.98 (s, 6 H), 3.93 (s, 3 H), 1.06 (s, 9 H), 0.36 (s, 6 H); ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 153.5, 150.3, 148.5, 147.8, 146.5, 142.8, 119.6, 117.5, 110.7, 100.1, 61.0, 56.2, 25.7, 18.2, -4.3; IR: $\tilde{\nu}$ = 2932, 2859, 2361, 1740, 1593, 1493, 1258, 1219, 1126, 829, 783; UV-VIS (CH_3CN + 0.5 %

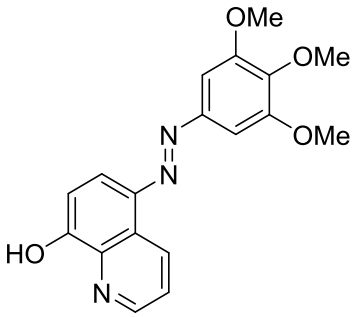
piperidine): λ_{max} (ε) = 375 nm (17300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{21}H_{31}N_2O_5Si$: 419.1997 $[M+H]^+$; found: 419.2004.

2-Bromo-4-((3´,4´,5´-trimethoxyphenyl)diazenyl)phenol **44b**



Standard Procedure **A1** with 3,4,5-trimethoxyaniline (366 mg, 2.0 mmol, 1.0 equiv.) and 2-bromphenol (363 mg, 2.1 mmol, 1.05 equiv.) gave azobenzene **44b** (402 mg, 55 %) as an ocher solid after purification by silica-gel chromatography (CH_2Cl_2/MeOH, 95:5 + 1.0 % formic acid). R_f = 0.45 (CH_2Cl_2/MeOH, 95:5 + 1.0 % formic acid); m.p. 161 °C; ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 2.2 Hz, 1 H), 7.88 (dd, *J* = 2.3, 8.7 Hz, 1 H), 7.23 (s, 2 H), 7.17 (d, *J* = 8.6 Hz, 1 H), 5.83 (s, 1 H), 3.97 (s, 6 H), 3.95 (s, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 154.4, 153.5, 148.2, 147.2, 140.6, 125.5, 116.1, 111.1, 100.3, 61.1, 56.2; IR: $\tilde{\nu}$ = 3325, 2955, 1740, 1597, 1334, 1207, 1130, 991; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 458 nm (28600 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{15}H_{16}BrN_2O_4$: 367.0288/369.0267 $[M+H]^+$; found: 367.0296/369.0275.

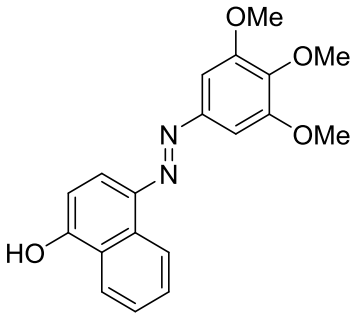
8-Hydroxy-5-((3´,4´,5´-trimethoxyphenyl)diazenyl)quinolin **46a**



Standard Procedure **A1** with 3,4,5-trimethoxyaniline (366 mg, 2.0 mmol, 1.0 equiv.) and 8-hydroxyquinoline (305 mg, 2.1 mmol, 1.05 equiv.) gave azobenzene **46a** (419 mg, 62 %) as a dark green solid after purification by silica-gel chromatography (CH_2Cl_2/MeOH, 95:5 + 1.0 % formic acid). R_f = 0.46 (CH_2Cl_2/MeOH, 95:5 + 1.0 % formic acid); m.p. 180 °C; ^{1}H-

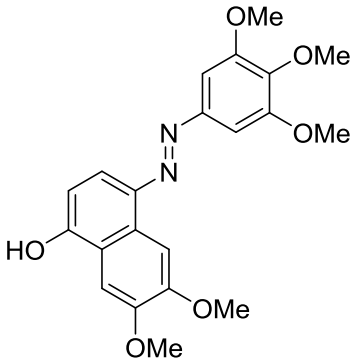
NMR (300 MHz, $CDCl_3$): δ = 9.22 (dd, *J* = 1.6, 8.5 Hz, 1 H), 8.84 (dd, *J* = 1.5, 4.1 Hz, 1 H), 7.98 (d, *J* = 8.5 Hz, 1 H), 7.59 (dd, *J* = 4.2, 8.6 Hz, 1 H), 7.23 (d, *J* = 8.5 Hz, 1 H), 7.22 (s, 2 H), 3.96 (s, 6 H), 3.91 (s, 3 H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 155.2, 153.6, 149.1, 148.5, 140.5, 139.9, 137.8, 132.8, 127.0, 122.8, 115.6, 110.0, 100.4, 61.1, 56.3; IR: $\tilde{\nu}$ = 2940, 2322, 1740, 1574, 1493, 1458, 1312, 1215, 1126, 999, 787; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 494 nm (17400 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{18}H_{18}N_3O_4$: 340.1292 $[M+H]^+$; found: 340.1298.

4-((3´,4´,5´-Trimethoxyphenyl)diazenyl)naphth-1-ol **46b**



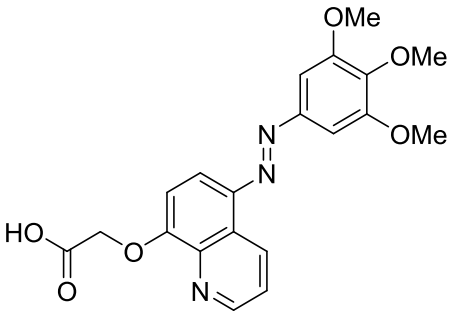
Standard Procedure **A1** with 3,4,5-trimethoxyaniline (366 mg, 2.0 mmol, 1.0 equiv.) and 1-naphthol (302 mg, 2.1 mmol, 1.05 equiv.) gave azobenzene **46b** (422 mg, 62 %) as an ocher solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4 → 1:2). R_f = 0.59 (EtOAc/petroleum ether, 1:4); m.p. 185 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 8.89 (d, *J* = 8.4 Hz, 1 H), 8.23 (d, *J* = 8.2 Hz, 1 H), 7.87 (d, *J* = 8.5 Hz, 1 H), 7.71 (ddd, *J* = 1.3, 6.9, 8.3 Hz, 1 H), 7.59 (ddd, *J* = 1.1, 7.0, 8.2 Hz, 1 H), 7.30 (s, 2 H), 7.00 (d, *J* = 8.6 Hz, 1 H), 3.93 (s, 6 H), 3.76 (s, 3 H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 157.8, 153.4, 148.3, 139.3, 132.6, 127.9, 125.5, 124.6, 122.7, 122.5, 114.4, 108.9, 99.7, 79.2, 60.2, 56.0; IR: $\tilde{\nu}$ = 3244, 2997, 2322, 1740, 1593, 1551, 1477, 1188, 1123, 1014, 814, 752; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 517 nm (18000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{19}N_2O_4$: 339.1339 $[M+H]^+$; found: 339.1342.

4-((3´,4´,5´-Trimethoxyphenyl)diazenyl)-6,7-dimethoxynaphth-1-ol **46d**



Standard Procedure **A1** with 3,4,5-trimethoxyaniline (366 mg, 2.0 mmol, 1.0 equiv.) and naphthol **45d** (429 mg, 2.1 mmol, 1.05 equiv.) gave azobenzene **46d** (488 mg, 62 %) as a dark red solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:2 → 1:1). R_f = 0.45 (EtOAc/petroleum ether, 1:2); m.p. 191 °C; ^{1}H-NMR (600 MHz, DMSO-d_6): δ = 8.22 (br s, 1 H), 7.73 (d, J = 8.3 Hz, 1 H), 7.49 (s, 1 H), 7.28 (br s, 2 H), 6.86 (d, J = 8.4 Hz, 1 H), 3.98 (s, 3 H), 3.92 (s, 3 H), 3.91 (s, 6 H), 3.75 (s, 3 H); ^{13}C-NMR (151 MHz, DMSO-d_6): δ = 157.0, 153.8, 150.9, 149.3, 139.6, 138.7, 129.7, 120.2, 112.8, 108.0, 102.1, 101.8, 100.1, 79.6, 60.7, 56.3, 55.8, 55.6; IR: $\tilde{\nu}$ = 2940, 2839, 1736, 1593, 1543, 1458, 1373, 1226, 1122, 1003, 779; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 517 nm (23000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{21}H_{23}N_2O_6$: 399.1551 $[M+H]^+$; found: 399.1561.

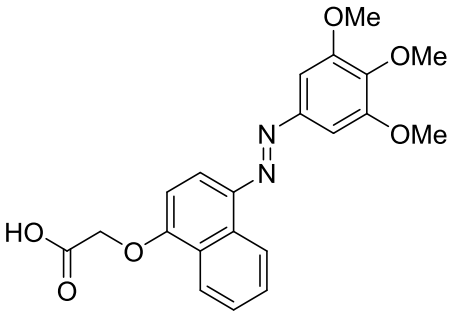
2-((5´-((3´´,4´´,5´´-Trimethoxyphenyl)diazenyl)quinolin-8´-yl)oxy)acetic acid **47a**



Standard Procedure **C** with ester **4a** (190 mg, 0.46 mmol, 1.0 equiv.) gave carboxylic acid **47a** (176 mg, 97 %) as a yellow solid after evaporation of the solvent. R_f = 0.20 (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid); m.p. 310 °C decomp.; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 9.33 (dd, J = 1.7, 8.6 Hz, 1 H), 9.01 (dd, J = 1.7, 4.1 Hz, 1 H), 7.93 (d, J = 8.7 Hz, 1 H), 7.77 (dd, J = 4.1, 8.6 Hz, 1 H), 7.37 (s, 2 H), 7.29 (d, J = 8.8 Hz, 1 H), 5.05 (s, 2 H), 3.94 (s, 6 H), 3.78 (s, 3 H); ^{13}C-NMR (126 MHz, , DMSO-d_6): δ = 171.5, 157.1, 153.8, 150.0, 148.9, 140.4,

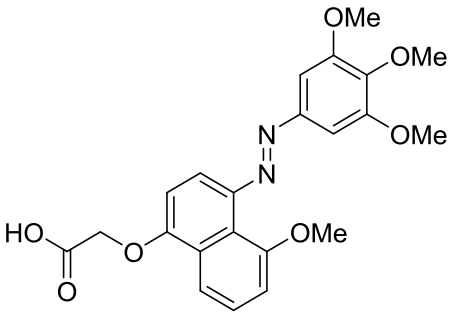
139.8, 138.9, 132.8, 127.7, 123.7, 114.5, 109.6, 100.7, 68.5, 60.9, 56.5; IR: $\tilde{\nu}$ = 2936, 2835, 1624, 1408, 1312, 1107, 991, 783; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 393 nm (25500 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{20}H_{20}N_3O_6$: 398.1347 $[M+H]^+$; found: 398.1357.

2-((4´-((3´´,4´´,5´´-Trimethoxyphenyl)diazenyl)naphth-1´-yl)oxy)acetic acid **47b**



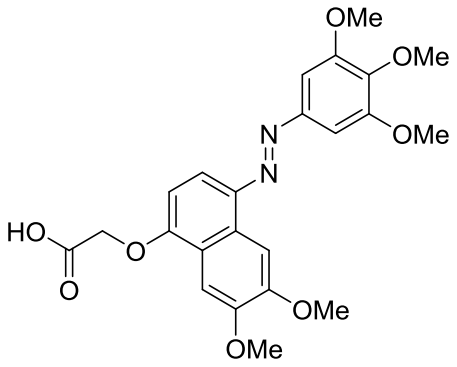
Standard Procedure **C** with ester **4b** (166 mg, 0.39 mmol, 1.0 equiv.) gave carboxylic acid **47b** (150 mg, 97 %) as an orange solid after evaporation of the solvent. R_f = 0.24 (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid); m.p. 295 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 8.91 (d, *J* = 8.3 Hz, 1 H), 8.32 (d, *J* = 8.2 Hz, 1 H), 7.84 (d, *J* = 8.6 Hz, 1 H), 7.71 (ddd, *J* = 0.9, 7.0, 8.4 Hz, 1 H), 7.61 (ddd, *J* = 0.9, 7.0, 8.4 Hz, 1 H), 7.33 (s, 2 H), 6.87 (d, *J* = 8.7 Hz, 1 H), 4.42 (s, 2 H), 3.93 (s, 6 H), 3.76 (s, 3 H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 169.1, 158.8, 153.8, 149.1, 140.1, 140.1, 132.4, 128.0, 126.0, 125.6, 123.1, 122.9, 113.8, 106.0, 100.5, 69.2, 60.7, 56.5; IR: $\tilde{\nu}$ = 3449, 2936, 2835, 1609, 1404, 1219, 1130, 984, 814, 760; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 409 nm (23300 l·mol-1·cm-1); HRMS (ESI): *m/z* calcd for $C_{21}H_{21}N_2O_6$: 397.1394 $[M+H]^+$; found: 397.1398.

2-((4´-((3´´,4´´,5´´-Trimethoxyphenyl)diazenyl)-5´-methoxynaphthalen-1´-yl)oxy)acetic acid **47c**



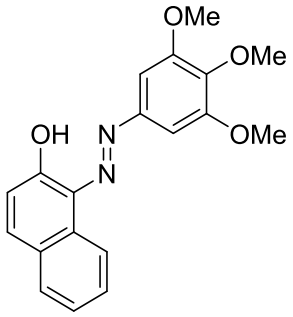
Standard Procedure **C** with ester **4c** (45 mg, 0.10 mmol, 1.0 equiv.) gave carboxylic acid **47c** (38 mg, 90 %) as an orange solid after evaporation of the solvent. R_f = 0.22 (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid); m.p. 196 °C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 7.94 (d, J = 8.4 Hz, 1 H), 7.55 (t, J = 8.1 Hz, 1 H), 7.30 (s, 2 H), 7.29 (d, J = 7.7 Hz, 1 H), 7.21 (d, J = 7.7 Hz, 1 H), 6.99 (d, J = 8.5 Hz, 1 H), 4.93 (s, 2 H), 3.92 (s, 3 H), 3.91 (s, 6 H), 3.77 (s, 3 H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 169.8, 156.4, 154.7, 153.3, 148.5, 144.3, 139.5, 127.0, 126.6, 121.0, 114.4, 113.0, 109.1, 105.6, 100.1, 65.4, 60.2, 56.4, 55.9; IR: $\tilde{\nu}$ = 2970, 2835, 1751, 1593, 1408, 1215, 1123, 1084, 748; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 398 nm (22000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{22}H_{23}N_2O_7$: 427.1500 $[M+H]^+$; found: 427.1505.

2-((4´-((3´´,4´´,5´´-trimethoxyphenyl)diazenyl)-6´,7´-dimethoxynaphth-1´-yl)oxy)acetic acid **47d**



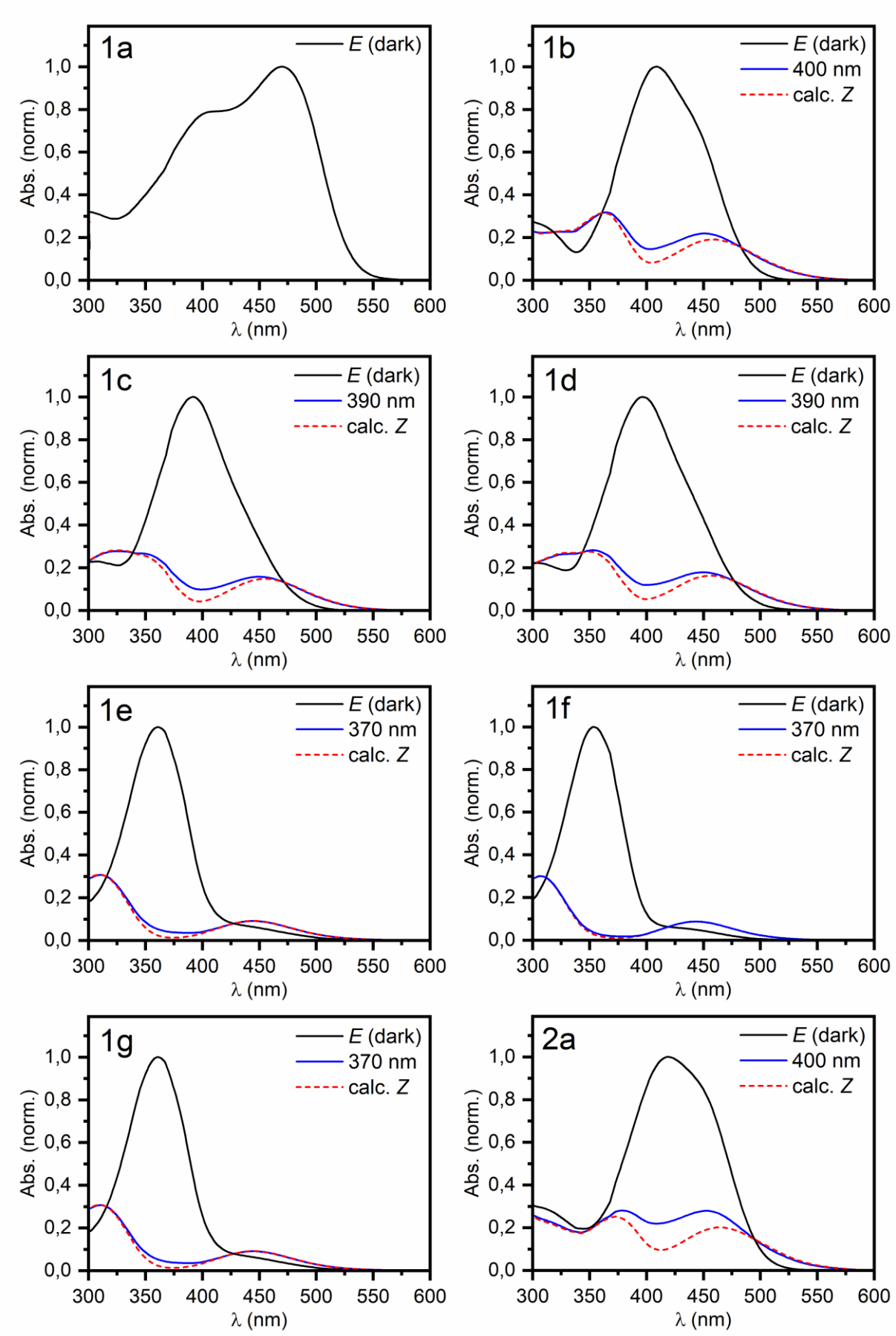
Standard Procedure **C** with ester **4d** (160 mg, 0.33 mmol, 1.0 equiv.) gave carboxylic acid **47d** (149 mg, 99 %) as an ocher solid after evaporation of the solvent. R_f = 0.23 (EtOAc/petroleum ether, 3:7 + 0.5 % formic acid); m.p. 235 °C; ^{1}H-NMR (250 MHz, DMSO-d_6): δ = 8.26 (s, 1 H), 7.73 (d, J = 8.6 Hz, 1 H), 7.58 (s, 1 H), 7.35 (s, 2 H), 6.91 (d, J = 8.6 Hz, 1 H), 4.99 (s, 2 H), 4.00 (s, 3 H), 3.95 (s, 3 H), 3.94 (s, 6 H), 3.78 (s, 3 H); ^{13}C-NMR (63 MHz, DMSO-d_6): δ = 171.3, 156.8, 154.7, 151.8, 150.7, 150.0, 141.1, 129.8, 121.6, 112.7, 105.8, 103.0, 102.1, 101.4, 66.5, 61.6, 57.3, 56.7, 56.6; IR: $\tilde{\nu}$ = 2932, 2832, 2361, 1732, 1481, 1312, 1211, 1168, 1111, 1002, 810; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 419 nm (26000 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{23}H_{25}N_2O_8$: 457.1605 $[M+H]^+$; found: 457.1611.

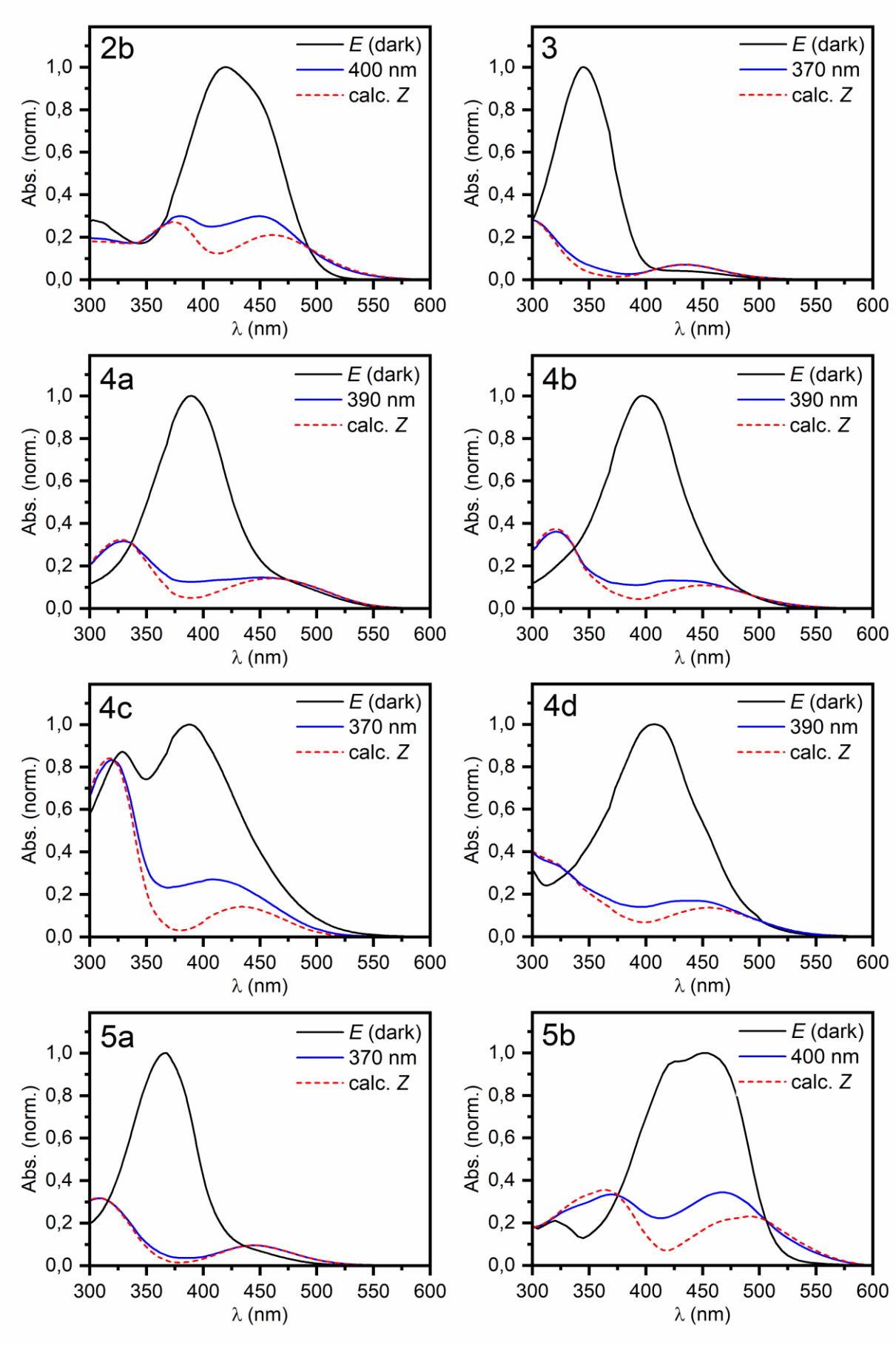
1-((3´,4´,5´-trimethoxyphenyl)diazenyl)naphth-2-ol **49**

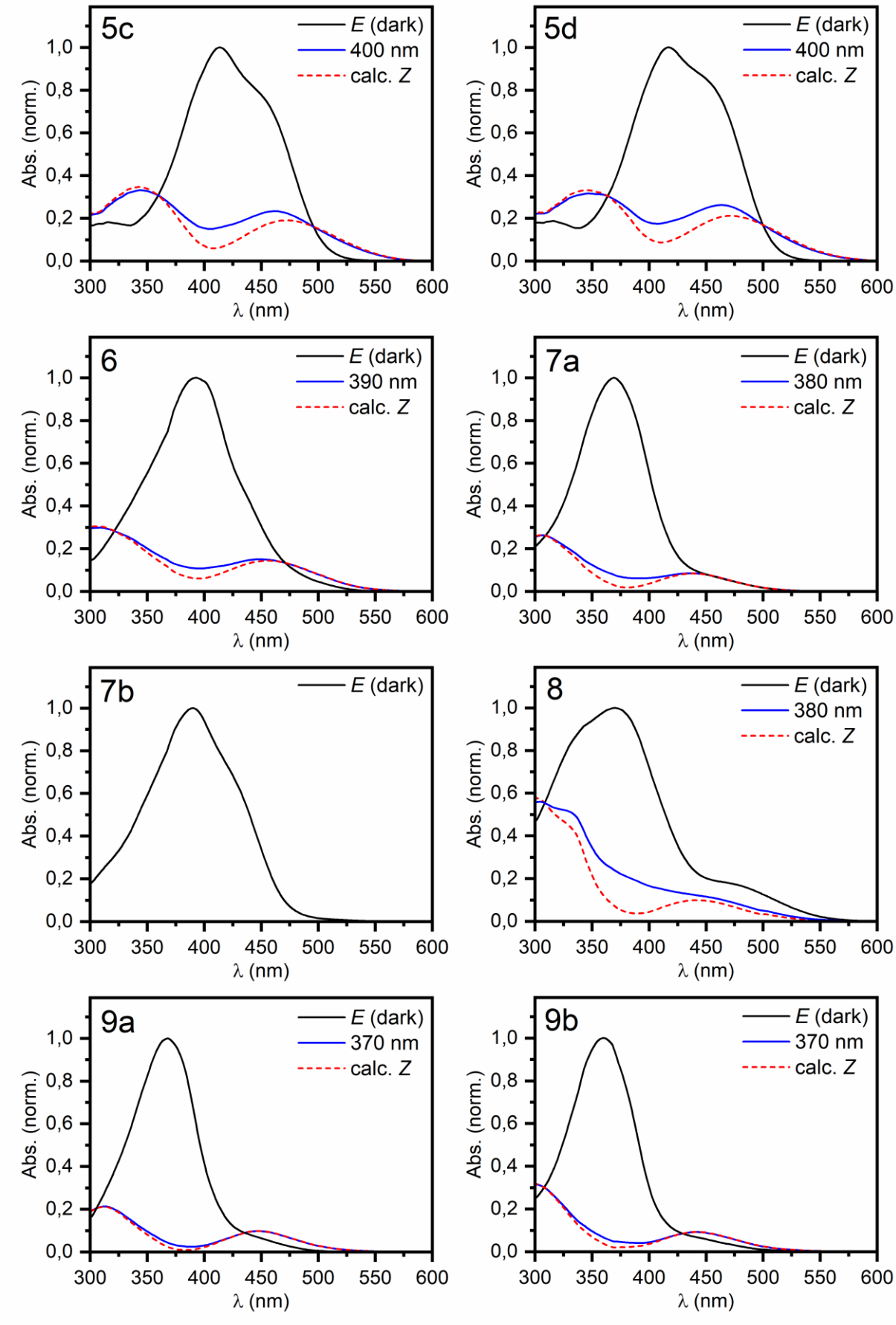


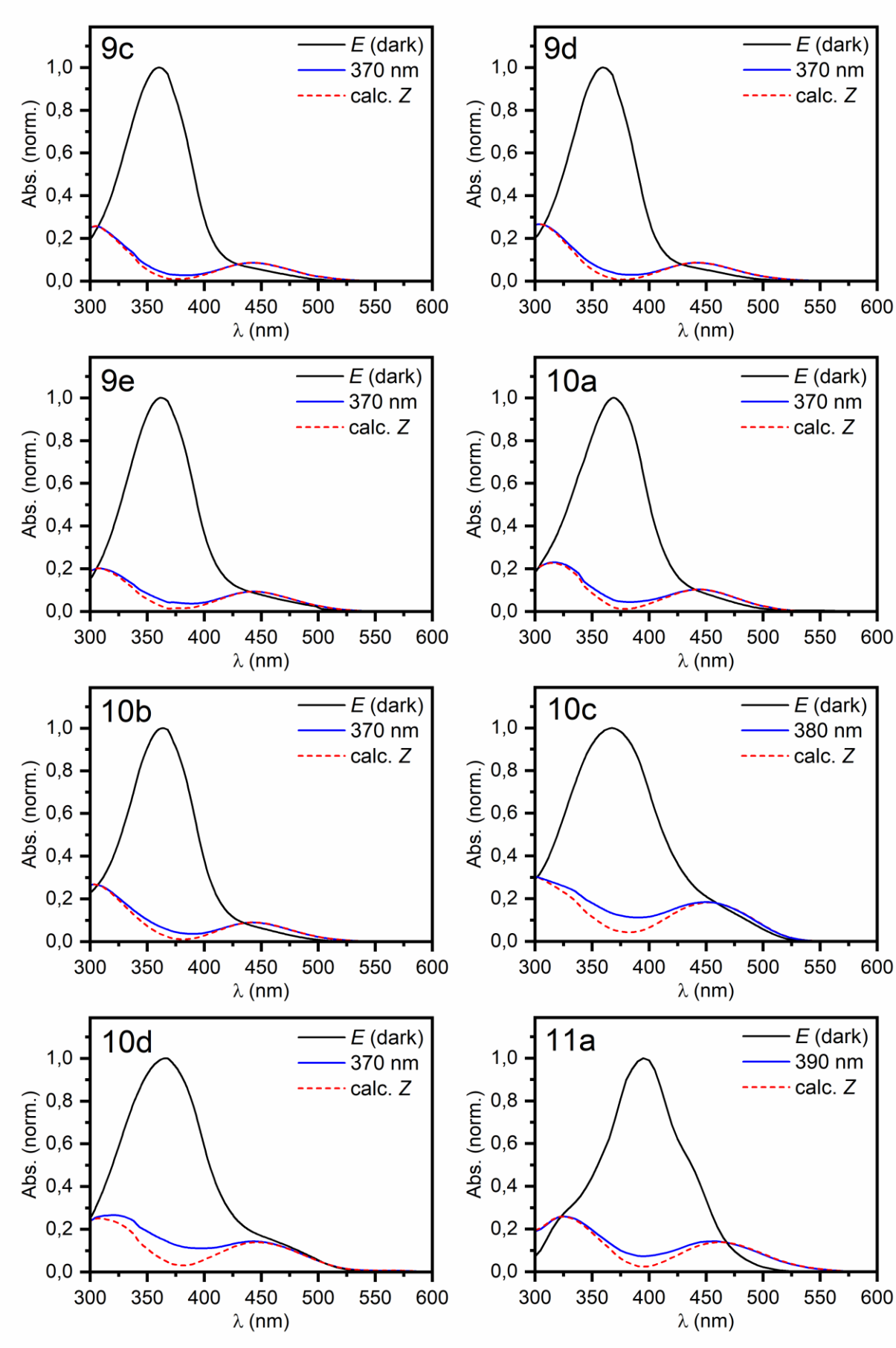
Standard Procedure **A1** with 3,4,5-trimethoxyaniline (366 mg, 2.0 mmol, 1.0 equiv.) and 2-naphthol (302 mg, 2.1 mmol, 1.05 equiv.) gave azobenzene **49** (574 mg, 85 %) as a red solid after purification by silica-gel chromatography (EtOAc/petroleum ether, 1:4 → 1:2). R_f = 0.41(EtOAc/petroleum ether, 1:4); m.p. 114 °C; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.58 (d, J = 8.3 Hz, 1 H), 7.74 (d, J = 9.4 Hz, 1 H), 7.65 (d, J = 7.9 Hz, 1 H), 7.58 (ddd, J = 1.1, 7.2, 8.3 Hz, 1 H), 7.41 (ddd, J = 0.9, 7.2, 7.9 Hz, 1 H), 7.04 (s, 2 H), 6.96 (d, J = 9.4 Hz, 1 H), 3.98 (s, 6 H), 3.93 (s, 3 H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 166.7, 154.0, 142.2, 138.6, 138.5, 133.3, 129.8, 128.6, 128.1, 125.4, 123.5, 121.5, 96.9, 61.1, 56.3; IR: $\tilde{\nu}$ = 2970, 2820, 1748, 1597, 1450, 1215, 1123, 991, 818, 752; UV-VIS (CH_3CN + 0.5 % piperidine): λ_{max} (ε) = 469 nm (26300 l·mol^{-1}·cm^{-1}); HRMS (ESI): *m/z* calcd for $C_{19}H_{19}N_2O_4$: 339.1339 $[M+H]^+$; found: 339.1344.

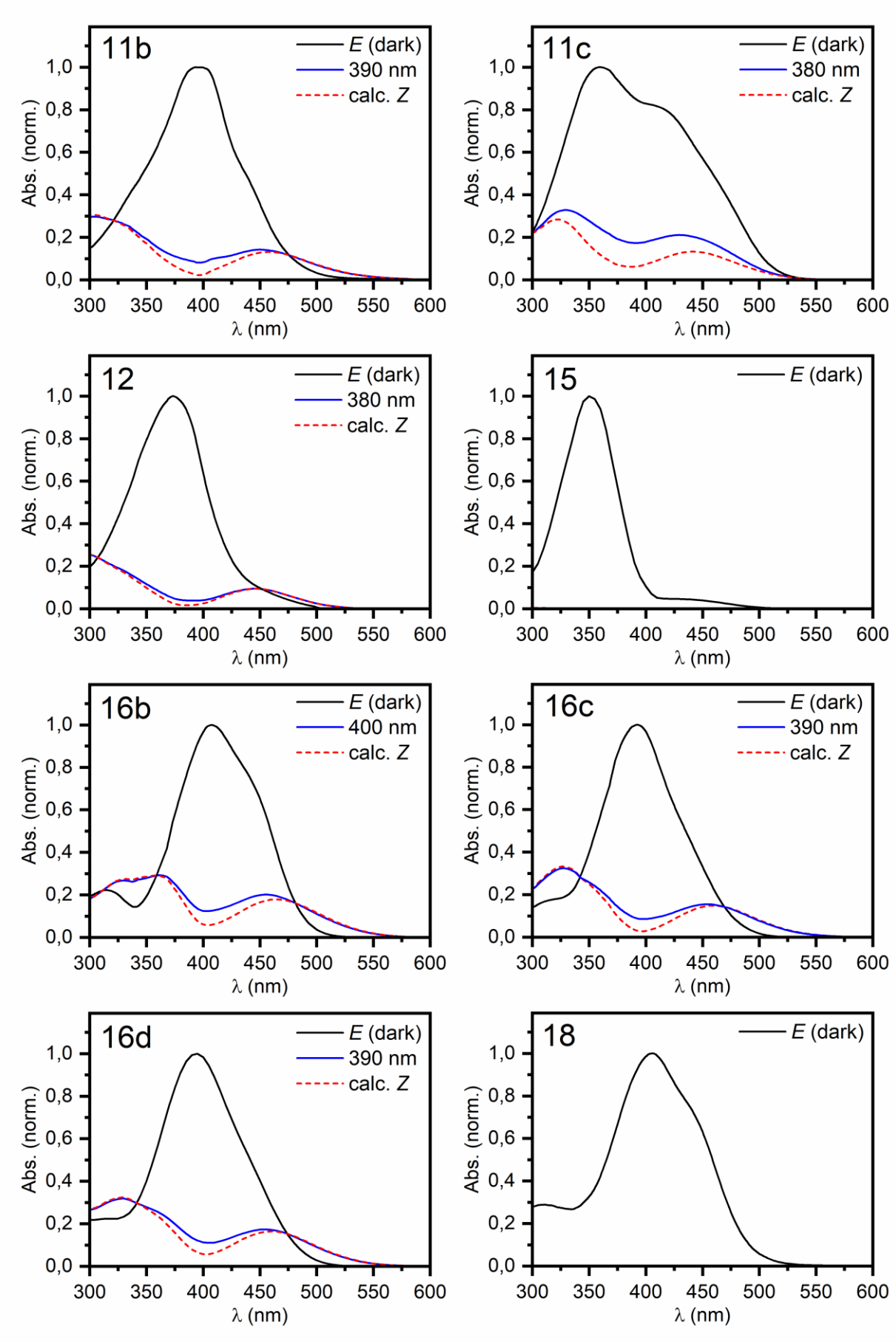
Supplementary Note 1.

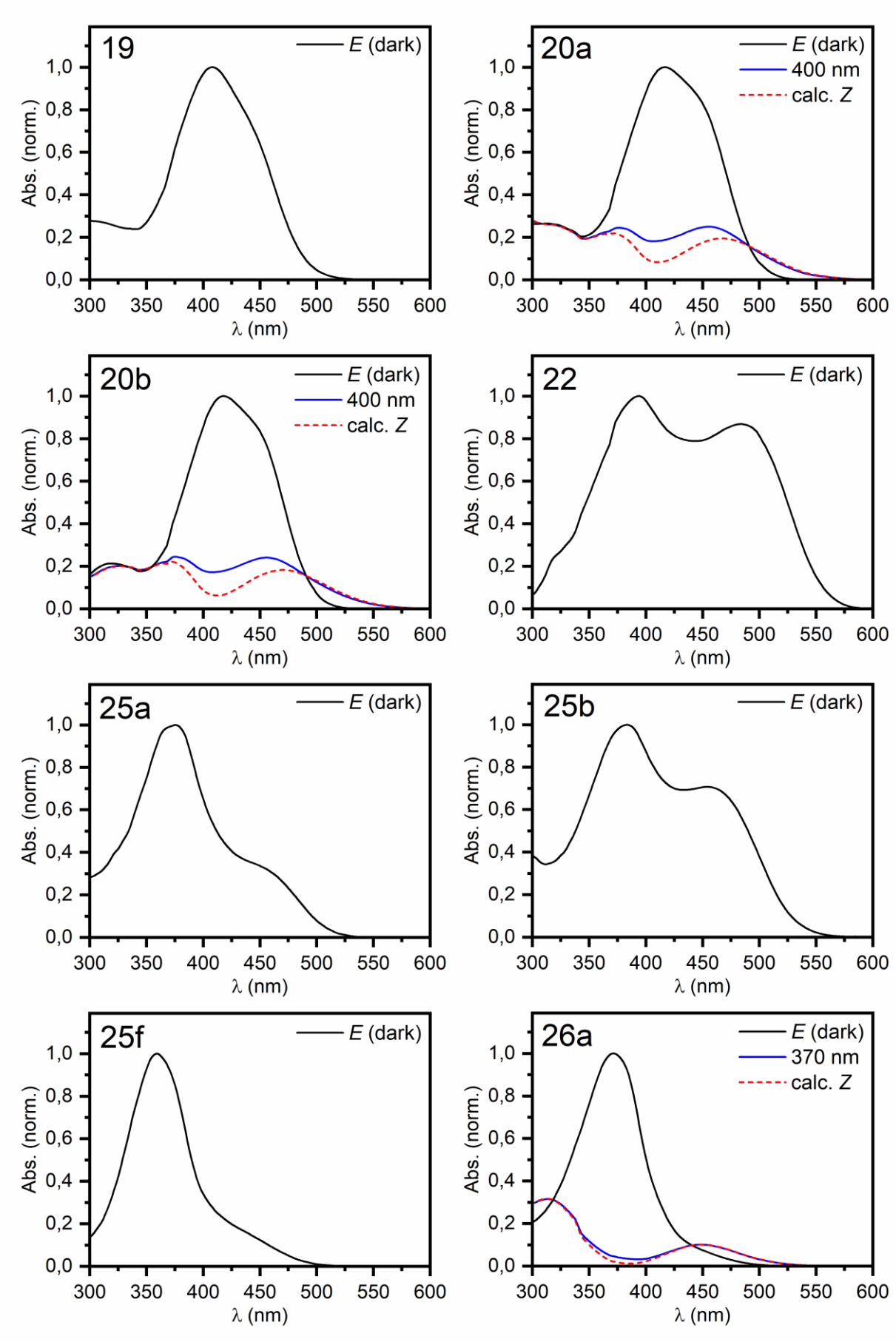


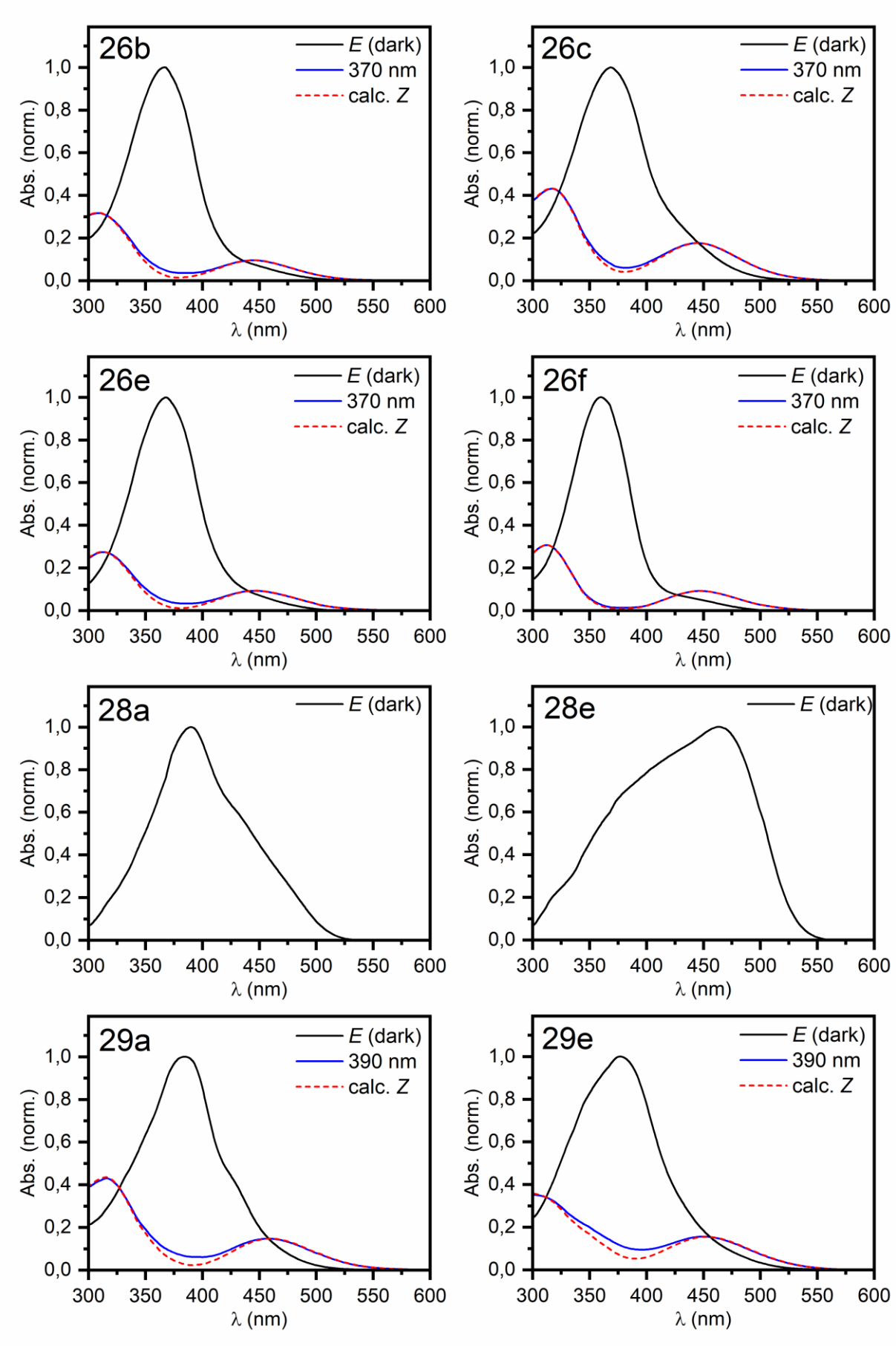

2b
E (dark)
400 nm
calc. Z
3
E (dark)
370 nm
calc. Z
4a
E (dark)
390 nm
calc. Z
4b
E (dark)
390 nm
calc. Z
4c
E (dark)
370 nm
calc. Z
4d
E (dark)
390 nm
calc. Z
5a
E (dark)
370 nm
calc. Z
5b
E (dark)
400 nm
calc. Z
Abs. (norm.)
λ (nm)

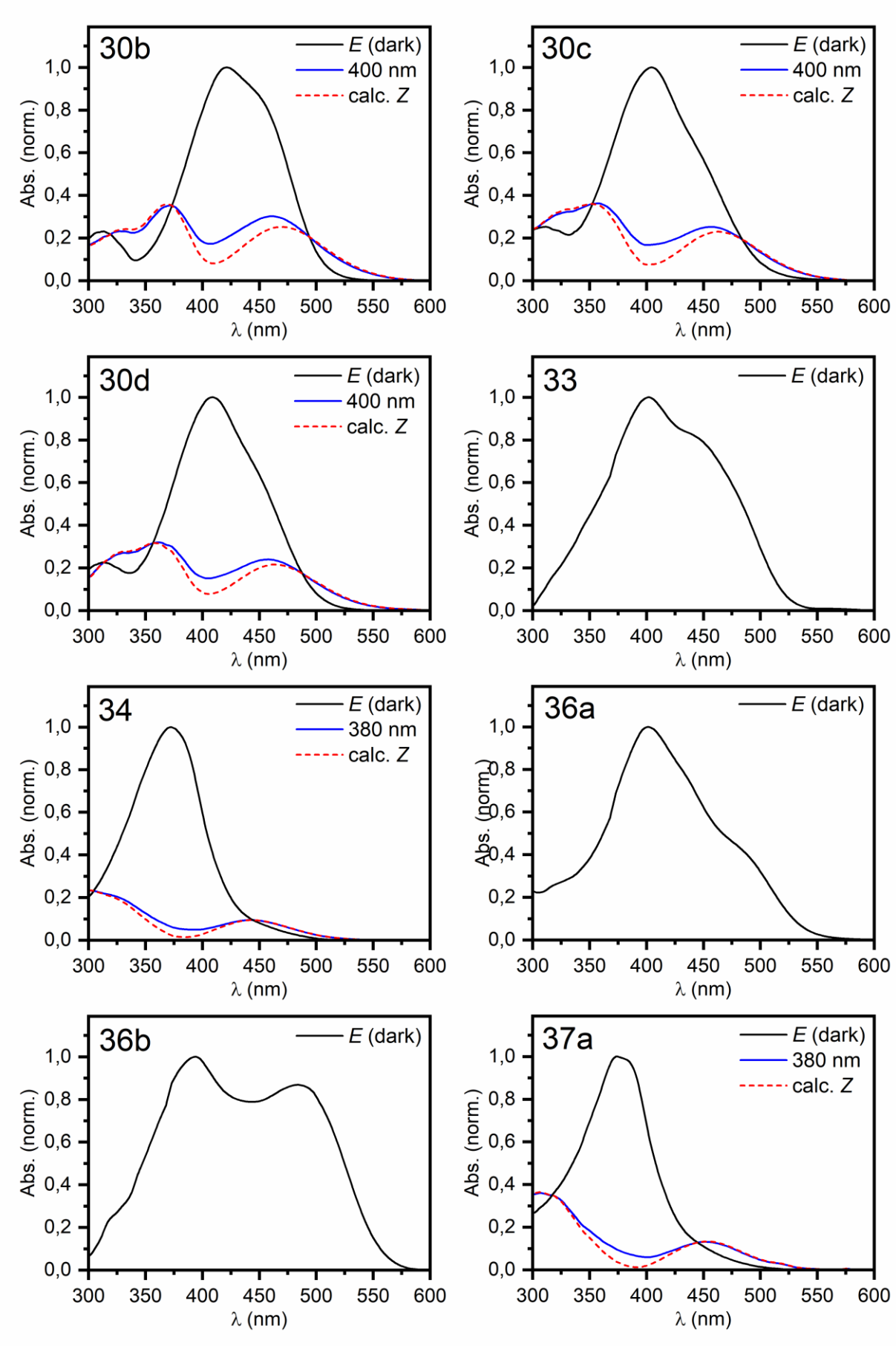

5c
E (dark)
400 nm
calc. Z
5d
E (dark)
400 nm
calc. Z
6
E (dark)
390 nm
calc. Z
7a
E (dark)
380 nm
calc. Z
7b
E (dark)
8
E (dark)
380 nm
calc. Z
9a
E (dark)
370 nm
calc. Z
9b
E (dark)
370 nm
calc. Z
Abs. (norm.)
λ (nm)

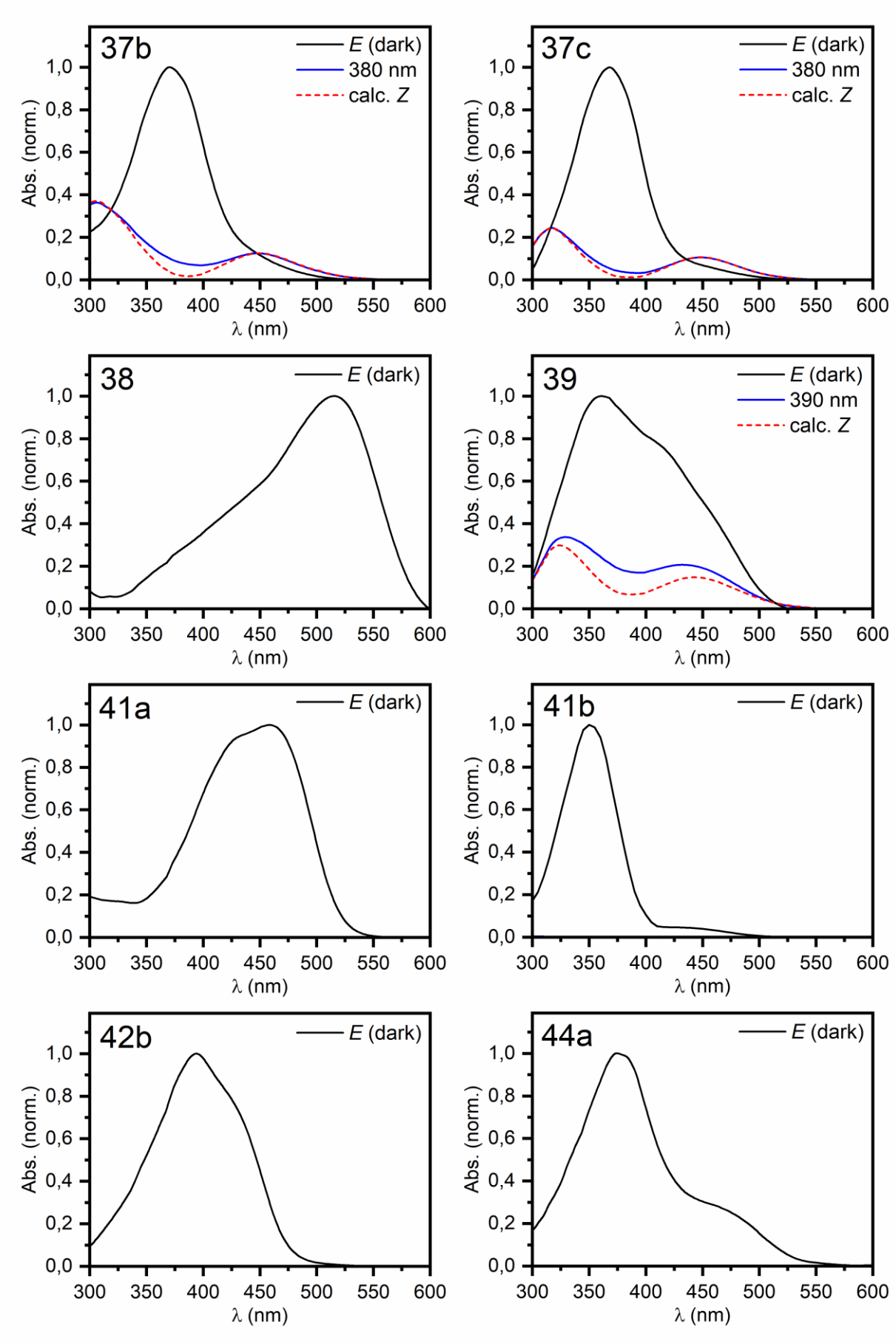

9c
E (dark)
370 nm
calc. Z
Abs. (norm.)
λ (nm)
9d
E (dark)
370 nm
calc. Z
Abs. (norm.)
λ (nm)
9e
E (dark)
370 nm
calc. Z
Abs. (norm.)
λ (nm)
10a
E (dark)
370 nm
calc. Z
Abs. (norm.)
λ (nm)
10b
E (dark)
370 nm
calc. Z
Abs. (norm.)
λ (nm)
10c
E (dark)
380 nm
calc. Z
Abs. (norm.)
λ (nm)
10d
E (dark)
370 nm
calc. Z
Abs. (norm.)
λ (nm)
11a
E (dark)
390 nm
calc. Z
Abs. (norm.)
λ (nm)

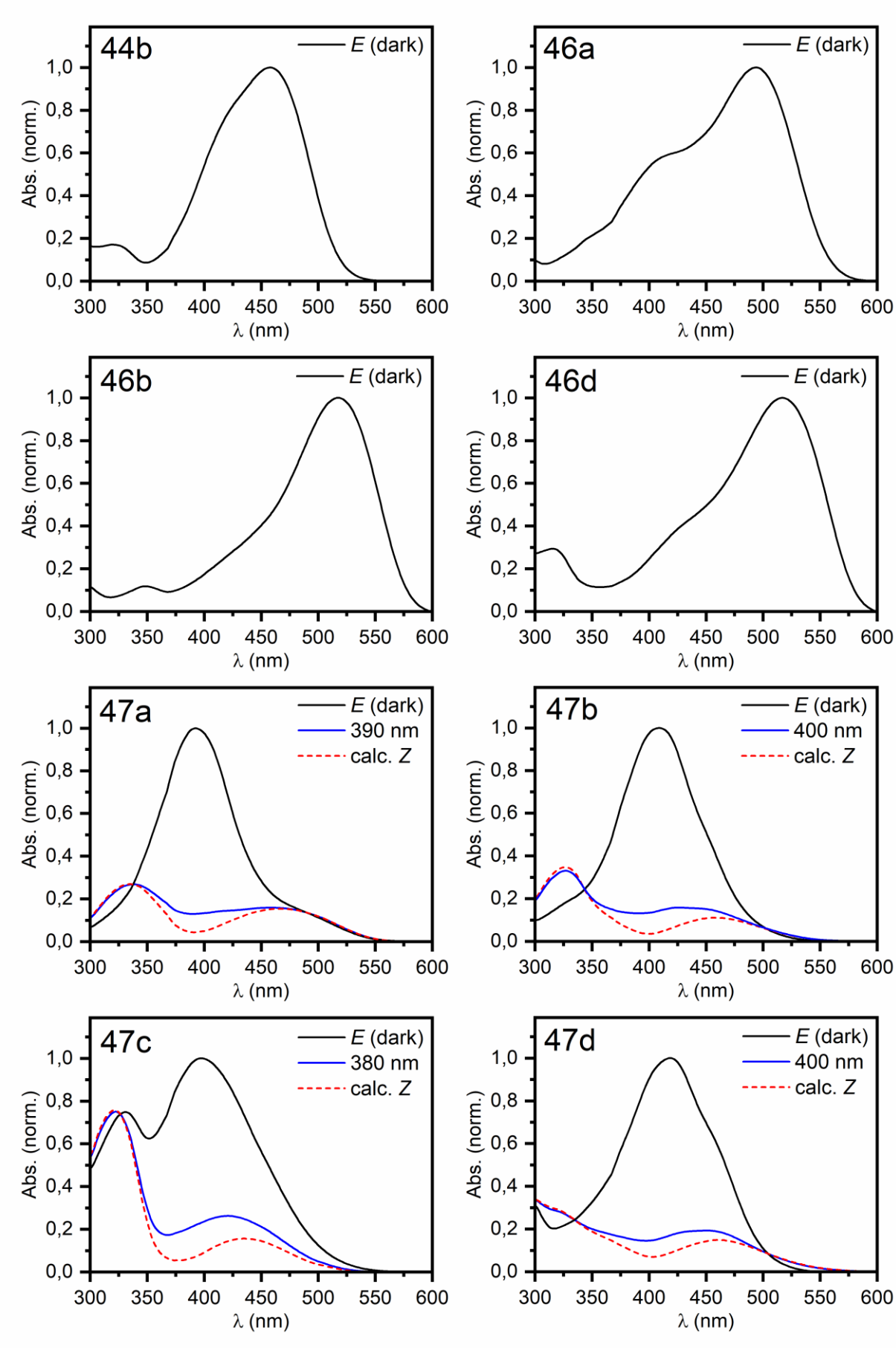

11b
E (dark)
390 nm
calc. Z
11c
E (dark)
380 nm
calc. Z
12
E (dark)
380 nm
calc. Z
15
E (dark)
16b
E (dark)
400 nm
calc. Z
16c
E (dark)
390 nm
calc. Z
16d
E (dark)
390 nm
calc. Z
18
E (dark)
Abs. (norm.)
λ (nm)

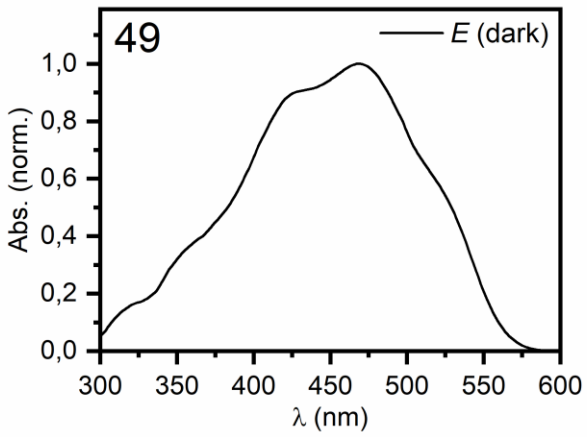

19
E (dark)
20a
E (dark)
400 nm
calc. Z
20b
E (dark)
400 nm
calc. Z
22
E (dark)
25a
E (dark)
25b
E (dark)
25f
E (dark)
26a
E (dark)
370 nm
calc. Z
Abs. (norm.)
λ (nm)
0,0
0,2
0,4
0,6
0,8
1,0
300
350
400
450
500
550
600


26b
E (dark)
370 nm
calc. Z
26c
E (dark)
370 nm
calc. Z
26e
E (dark)
370 nm
calc. Z
26f
E (dark)
370 nm
calc. Z
28a
E (dark)
28e
E (dark)
29a
E (dark)
390 nm
calc. Z
29e
E (dark)
390 nm
calc. Z
Abs. (norm.)
λ (nm)

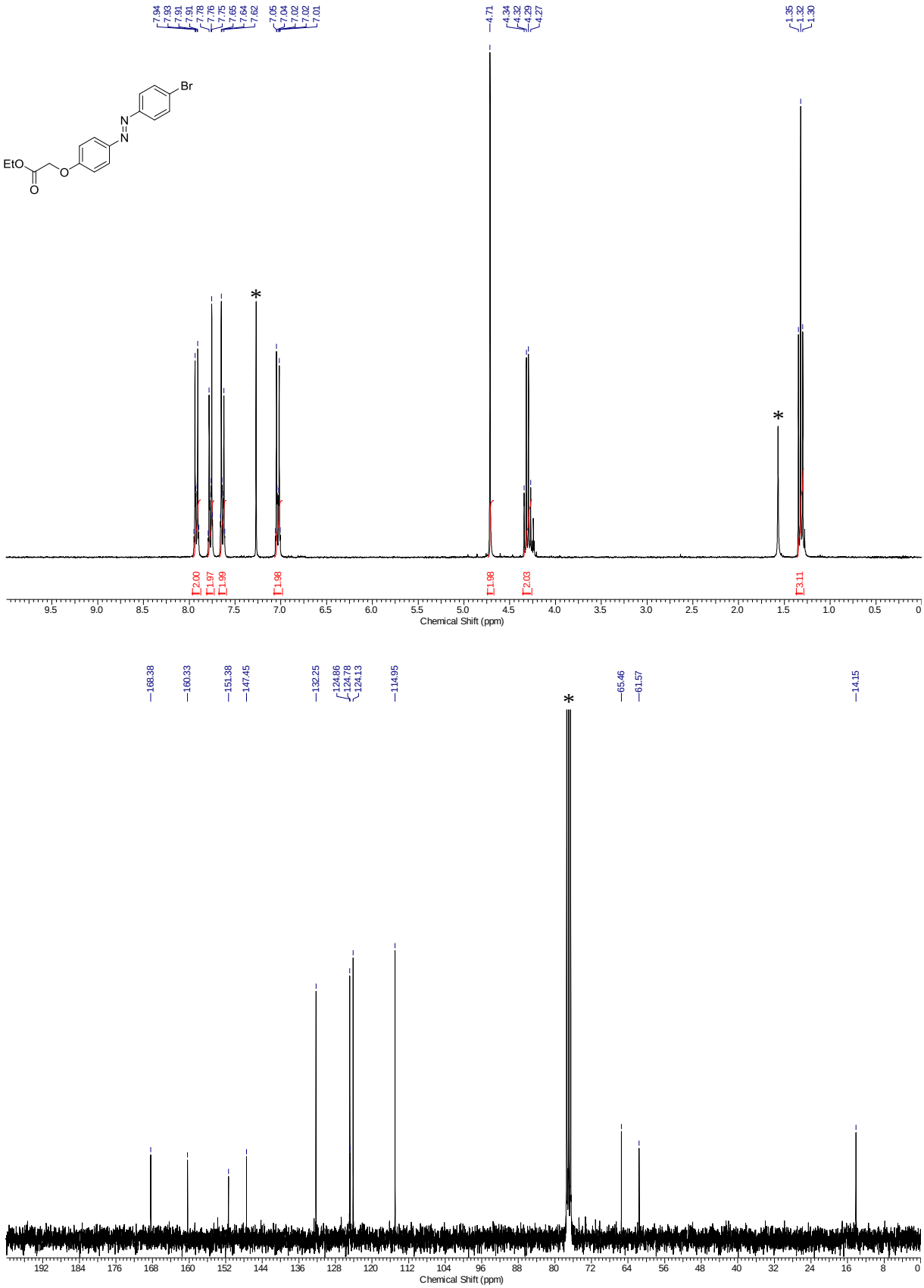

30b
E (dark)
400 nm
calc. Z
30c
E (dark)
400 nm
calc. Z
30d
E (dark)
400 nm
calc. Z
33
E (dark)
34
E (dark)
380 nm
calc. Z
36a
E (dark)
36b
E (dark)
37a
E (dark)
380 nm
calc. Z
Abs. (norm.)
λ (nm)
0,0
0,2
0,4
0,6
0,8
1,0
300
350
400
450
500
550
600


37b
E (dark)
380 nm
calc. Z
37c
E (dark)
380 nm
calc. Z
38
E (dark)
39
E (dark)
390 nm
calc. Z
41a
E (dark)
41b
E (dark)
42b
E (dark)
44a
E (dark)
Abs. (norm.)
λ (nm)
0,0
0,2
0,4
0,6
0,8
1,0
300
350
400
450
500
550
600

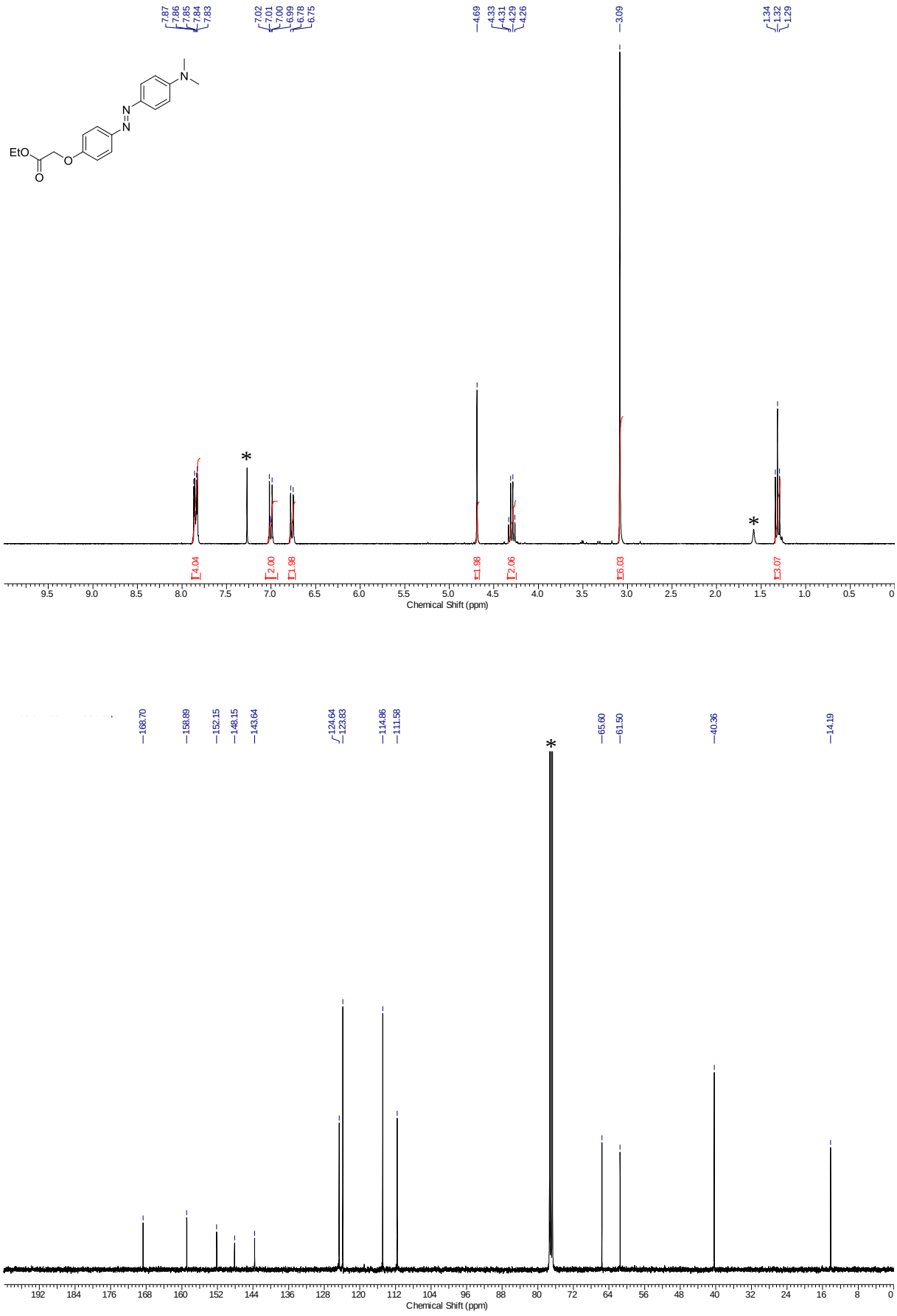

44b
E (dark)
46a
E (dark)
46b
E (dark)
46d
E (dark)
47a
E (dark)
390 nm
calc. Z
47b
E (dark)
400 nm
calc. Z
47c
E (dark)
380 nm
calc. Z
47d
E (dark)
400 nm
calc. Z
Abs. (norm.)
λ (nm)


49
E (dark)
Abs. (norm.)
1,0
0,8
0,6
0,4
0,2
0,0
300
350
400
450
500
550
600
λ (nm)

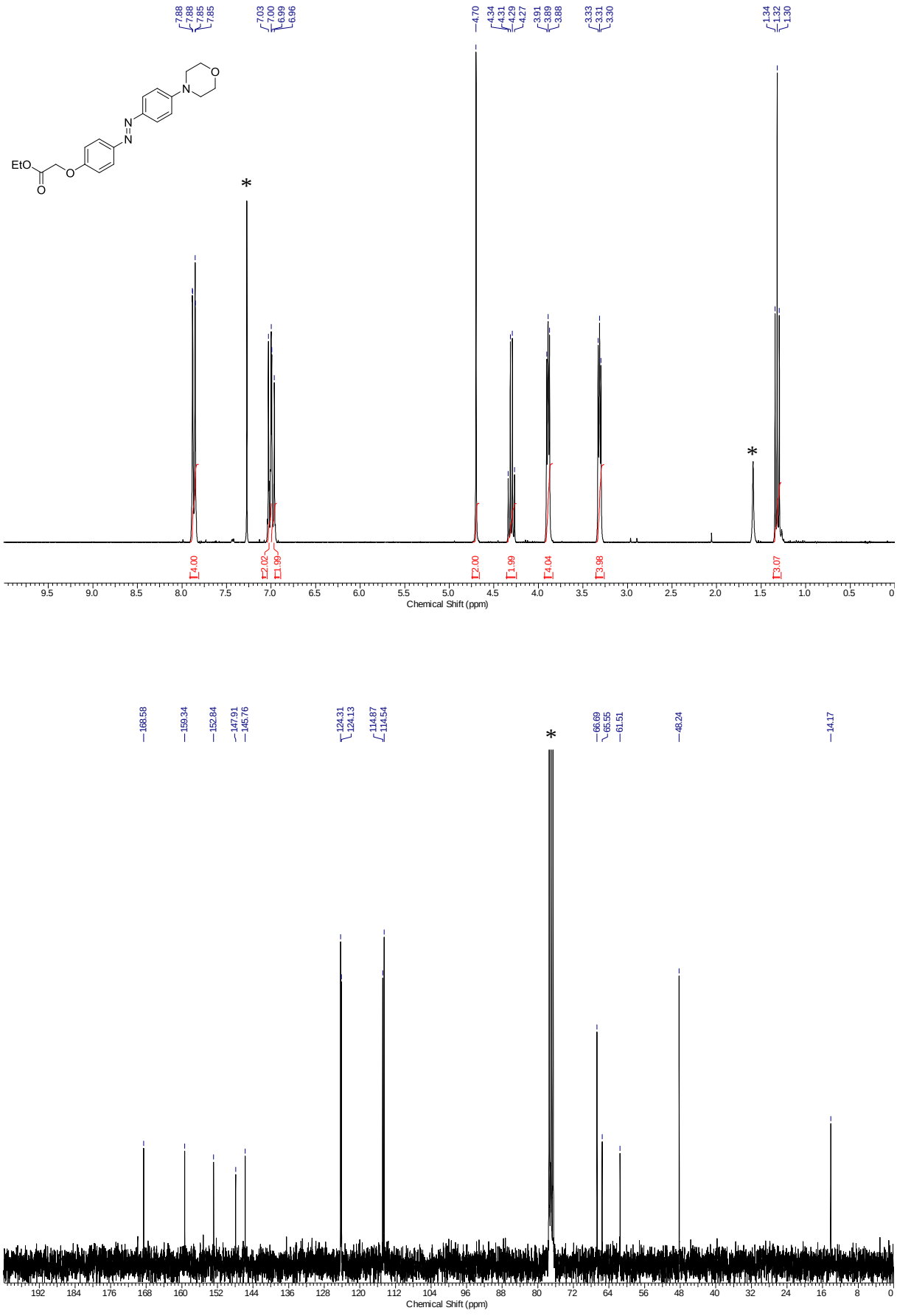
Supplementary Note 2.



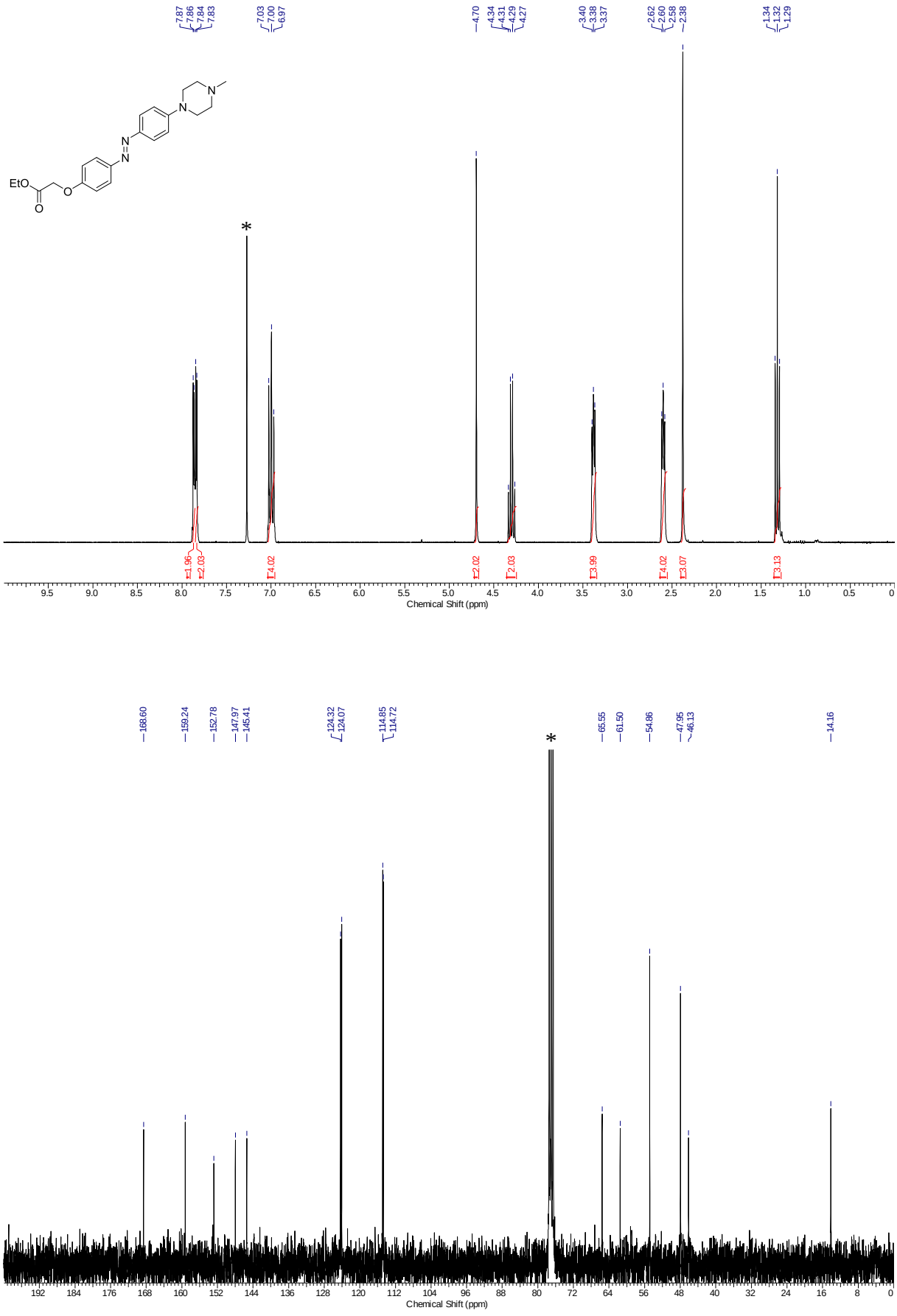
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **1a**. * = NMR-solvent, H_2O



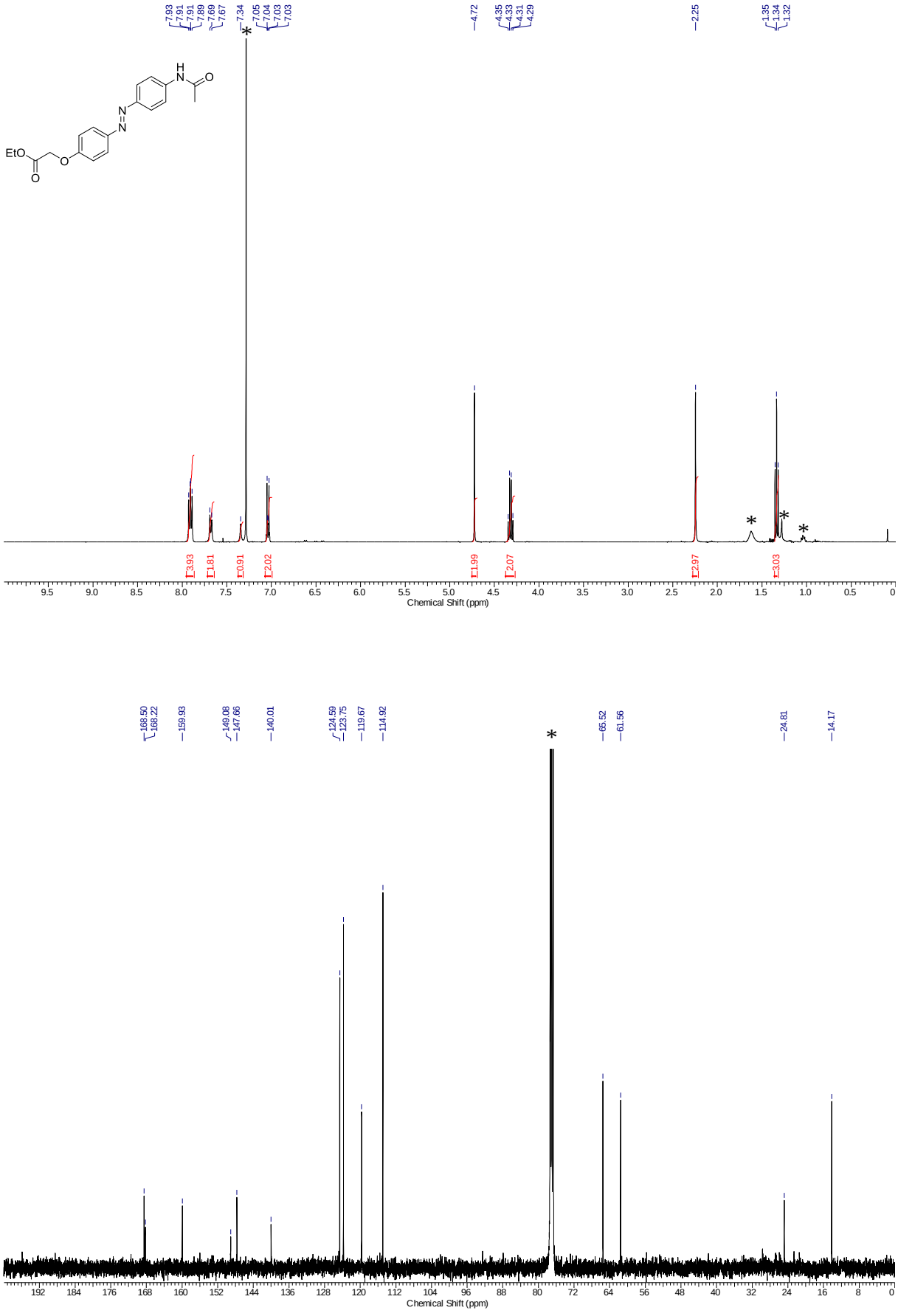
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **1b**. * = NMR-solvent, H_2O



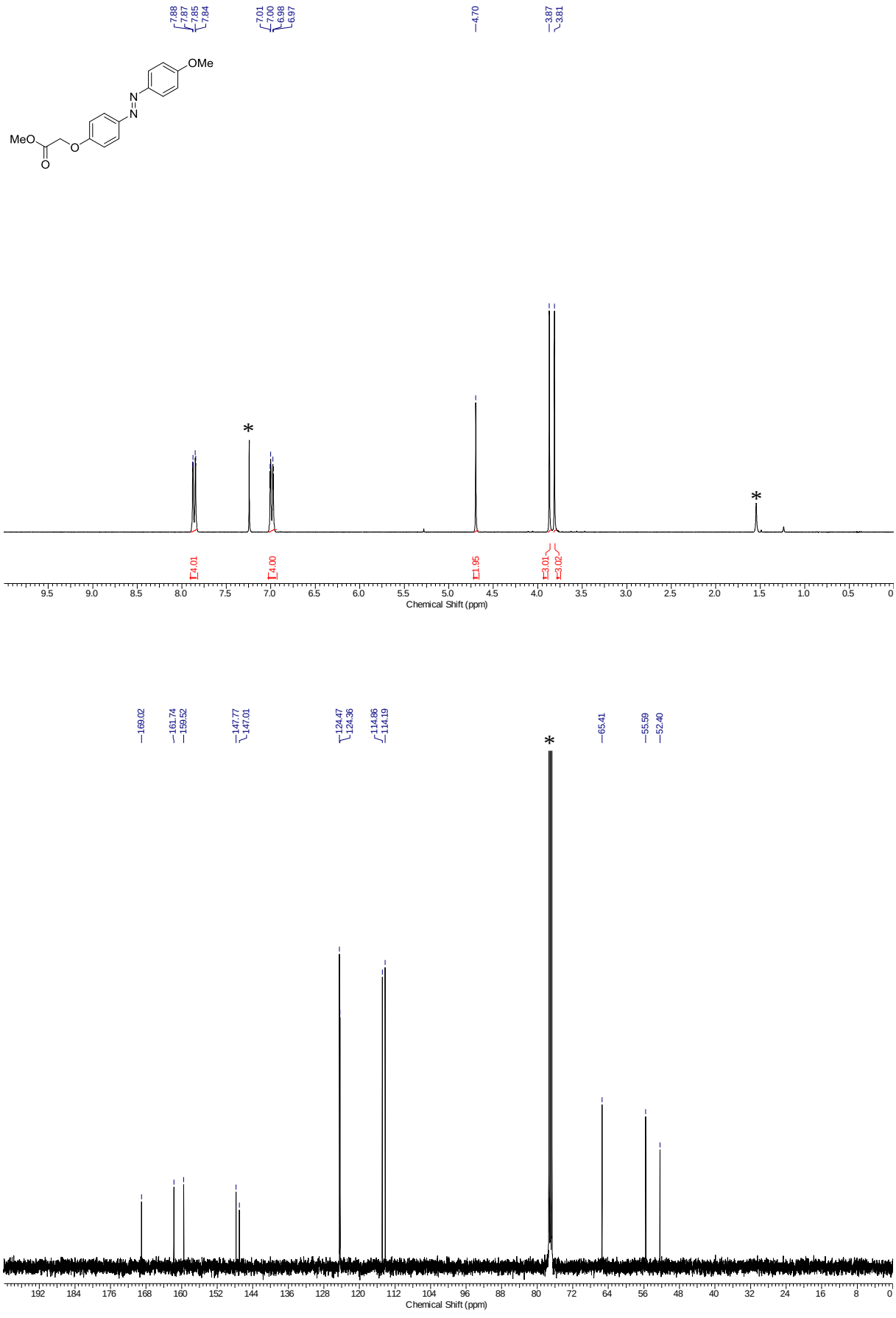
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **1c**. * = NMR-solvent, H_2O



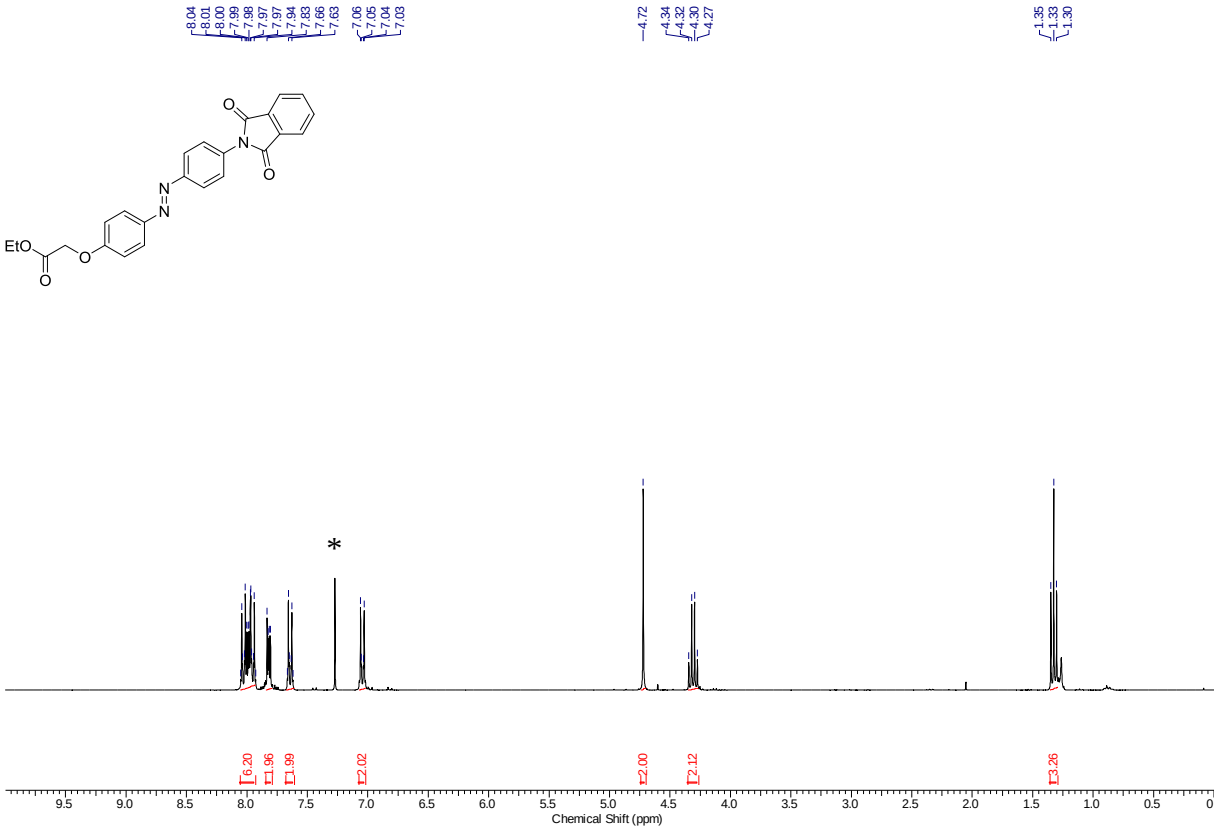
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **1d**. * = NMR-solvent

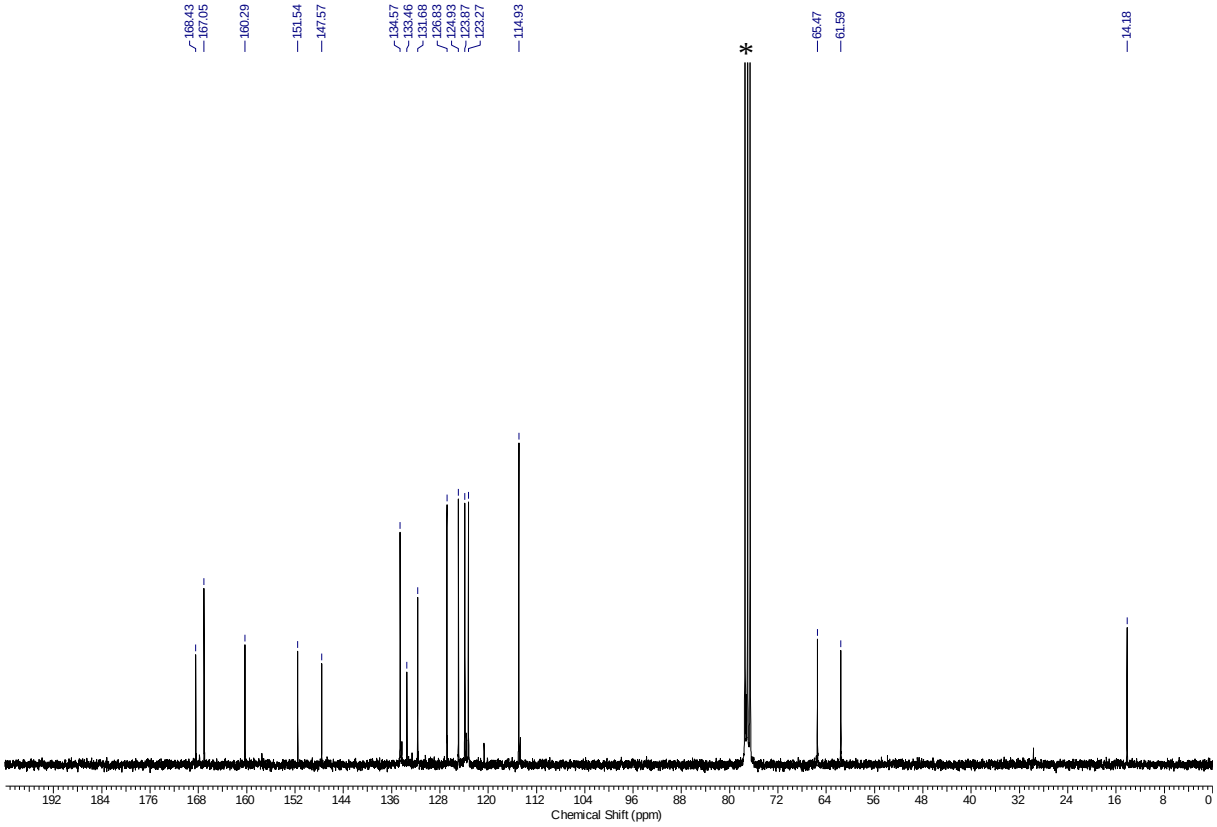


^{1}H-NMR (400 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **1e**. * = NMR-solvent, H_2O, grease

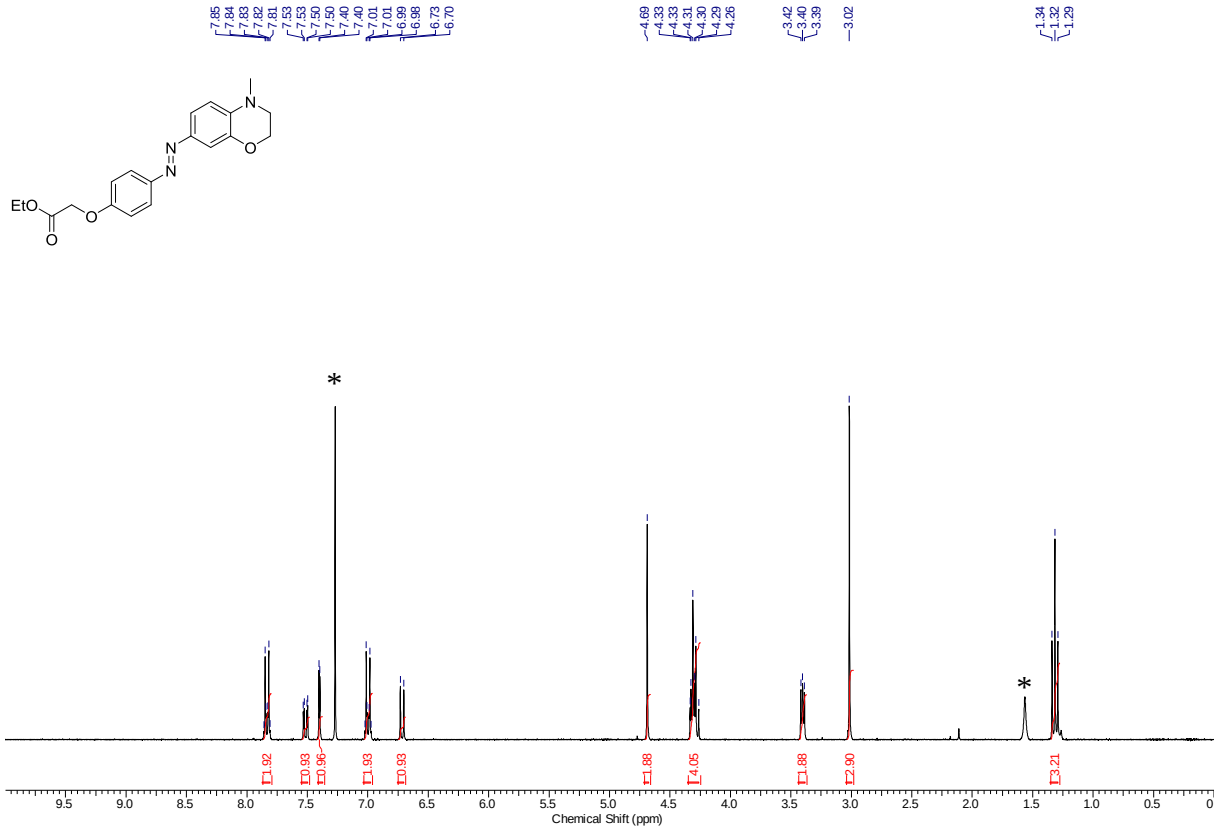


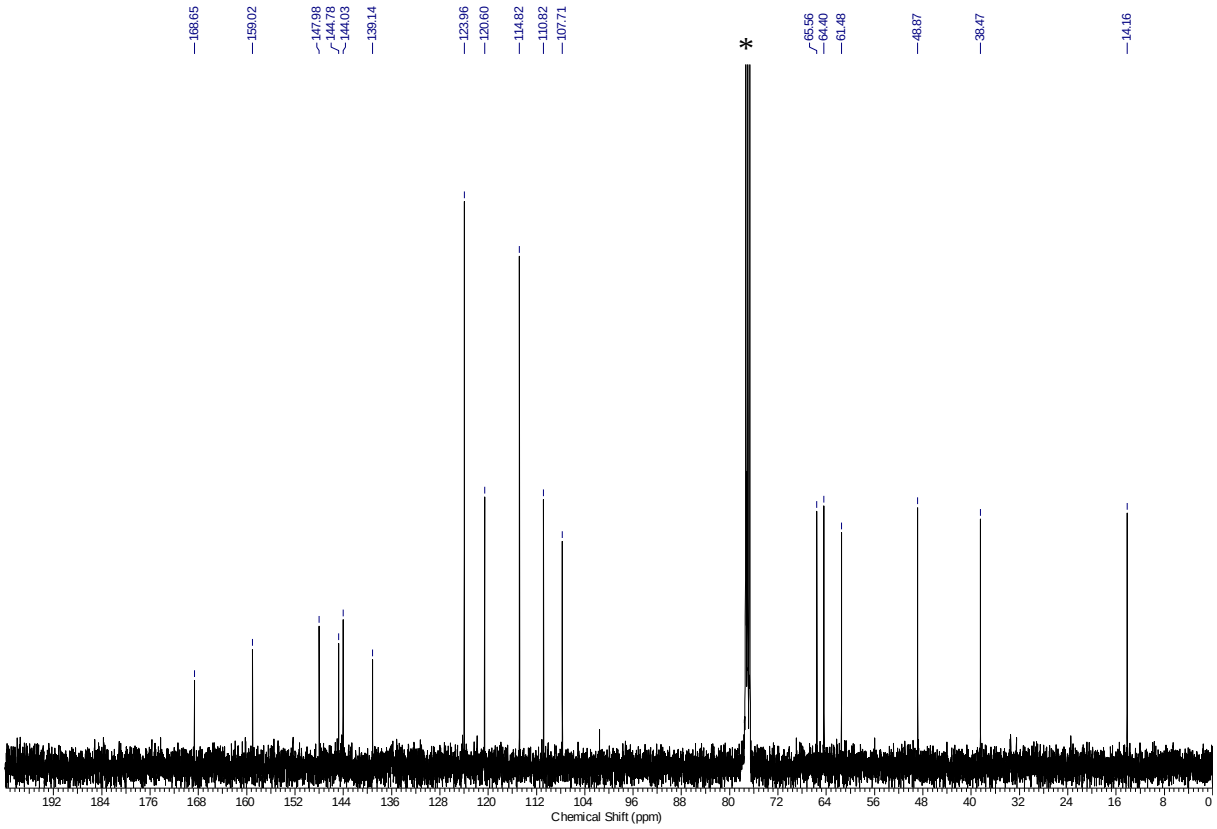
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **1f**. * = NMR-solvent, H_2O



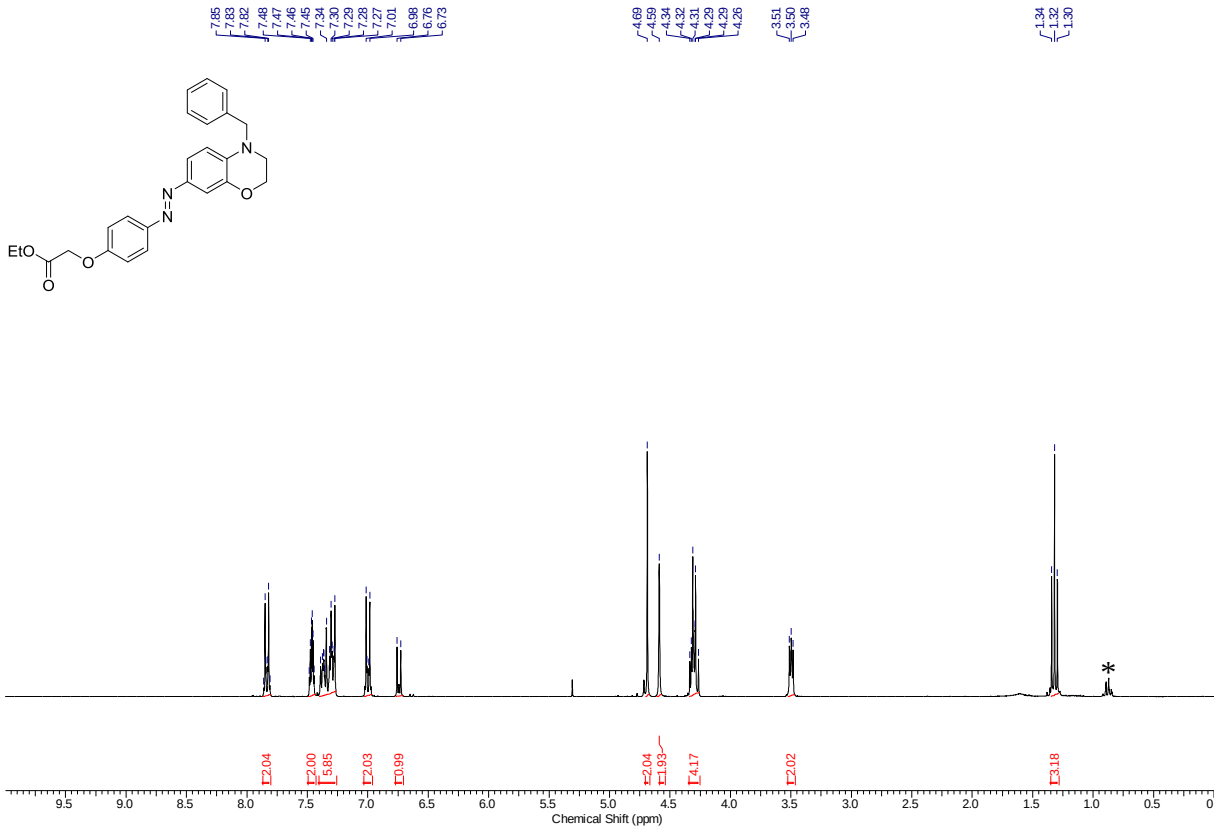


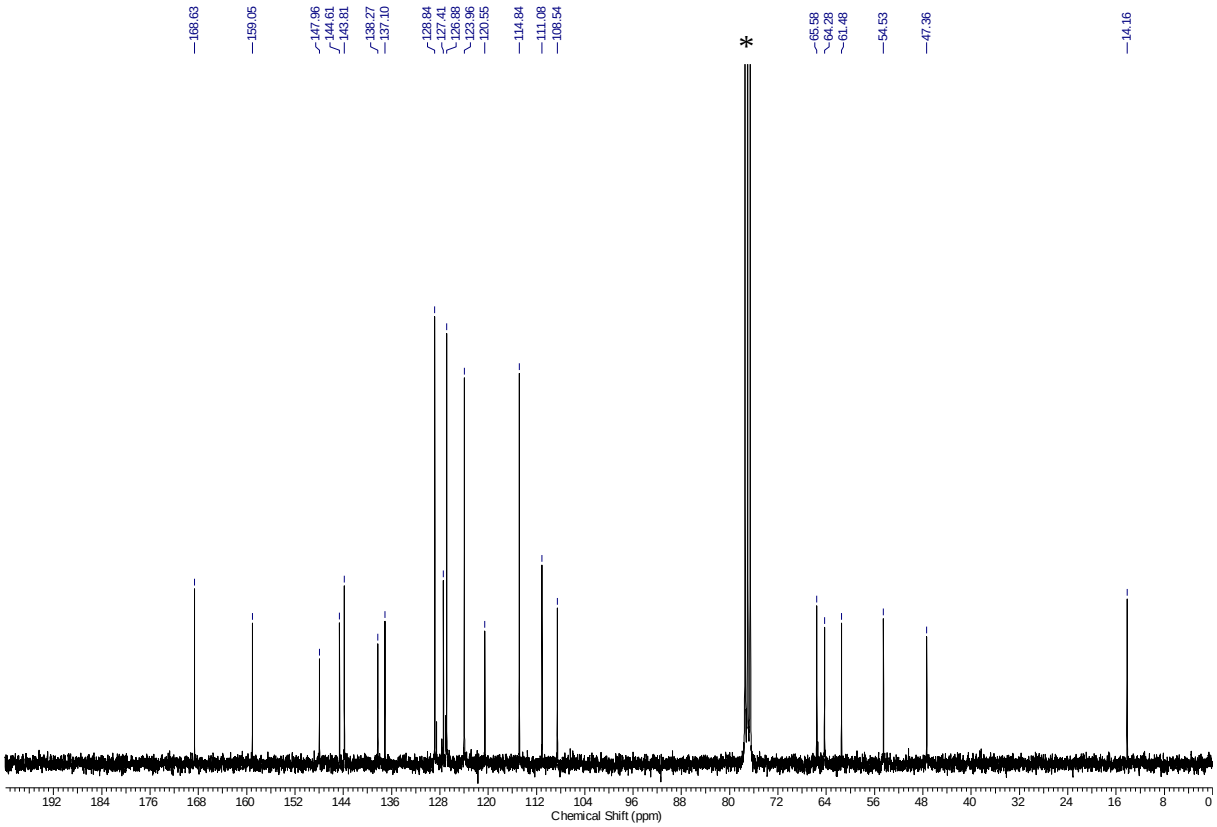
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **1g**. * = NMR-solvent


7.85
7.84
7.83
7.82
7.81
7.53
7.50
7.50
7.40
7.40
7.01
7.01
6.99
6.98
6.73
6.70
4.69
4.33
4.33
4.31
4.30
4.29
4.26
3.42
3.40
3.39
3.02
1.34
1.32
1.29
EtO
O
O
N
N
N
O
*
*
1.92
0.93
0.96
1.93
0.93
1.88
4.05
1.88
2.90
3.21
Chemical Shift (ppm)

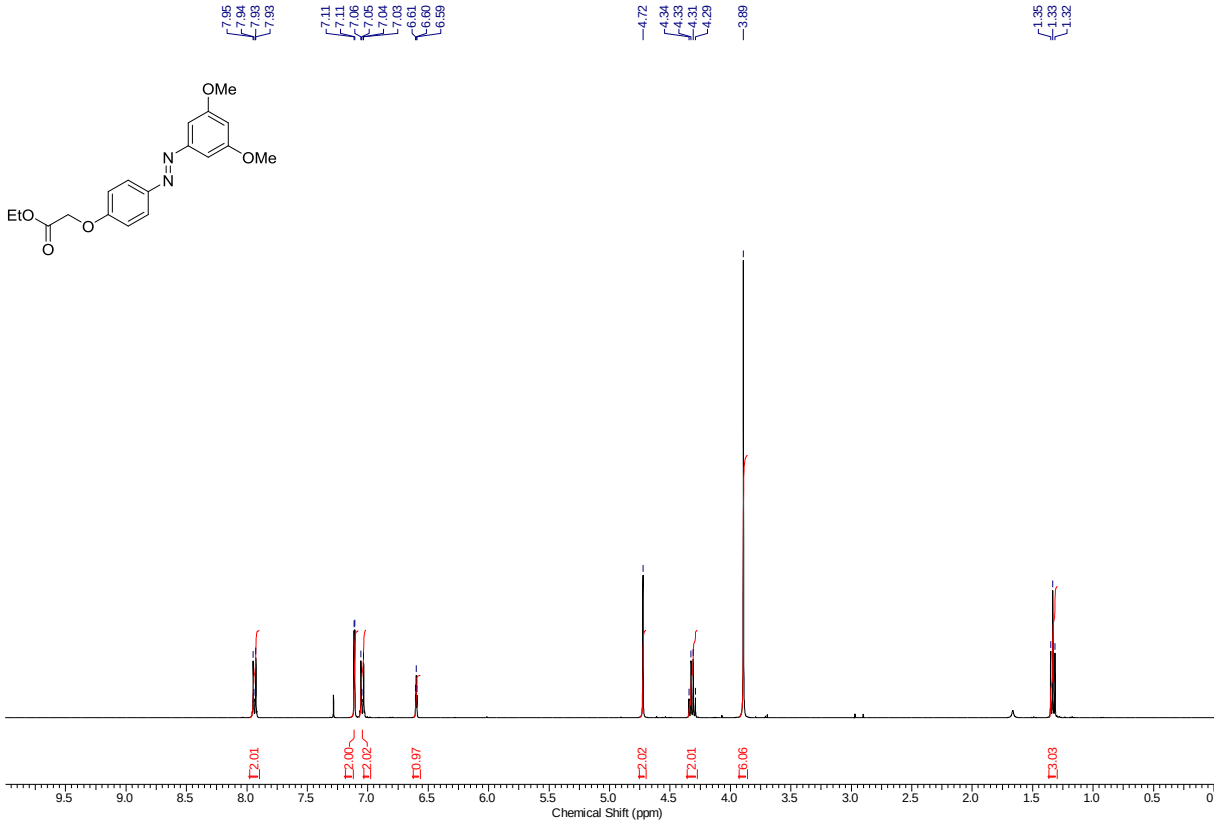

168.65
159.02
147.98
144.78
144.03
139.14
123.96
120.60
114.82
110.82
107.71
65.56
64.40
61.48
49.87
38.47
14.16
*
Chemical Shift (ppm)

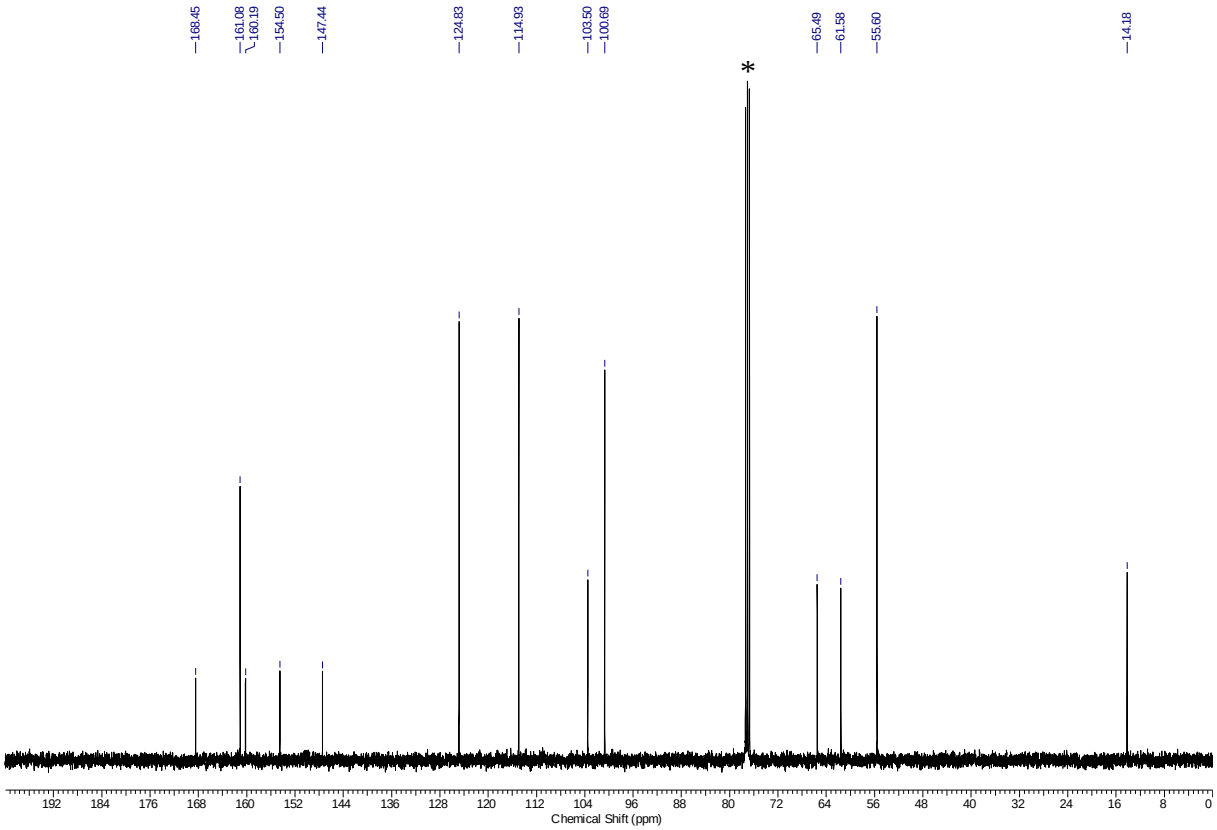
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **2a**. * = NMR-solvent, H_2O



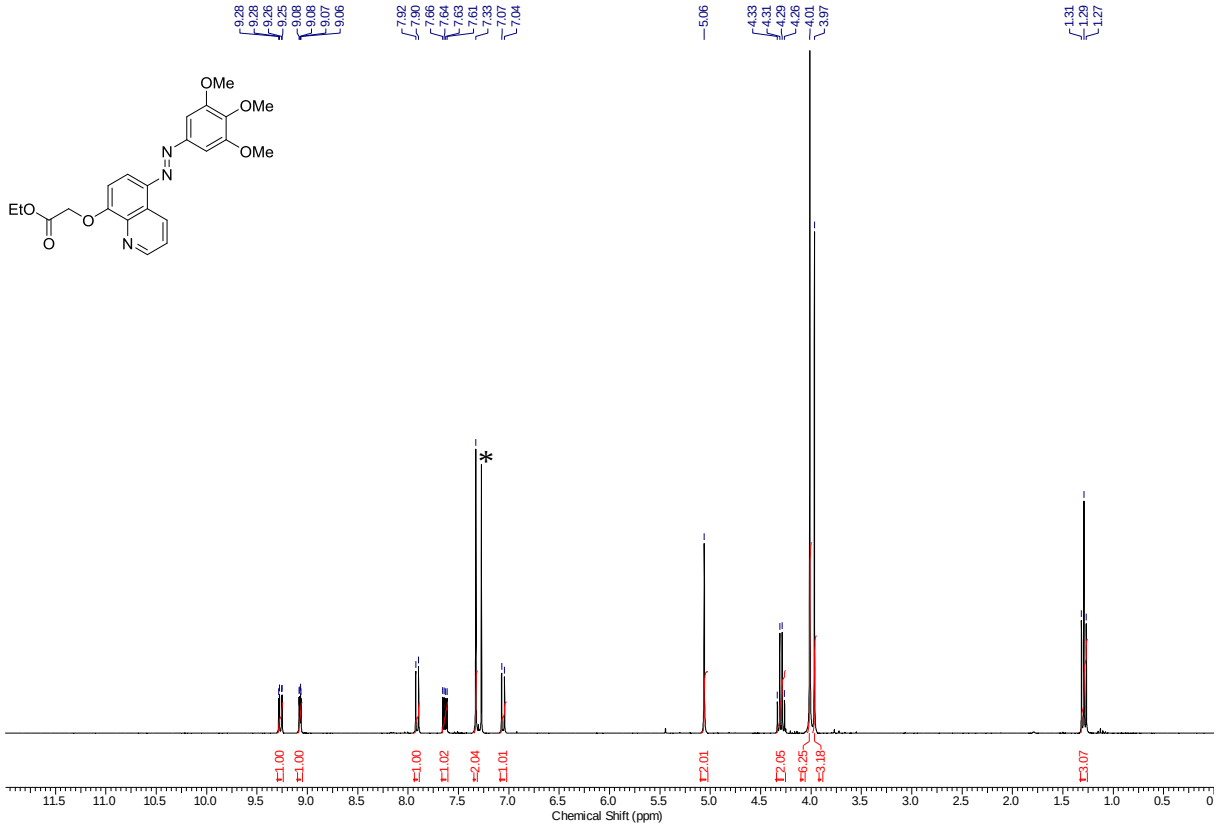


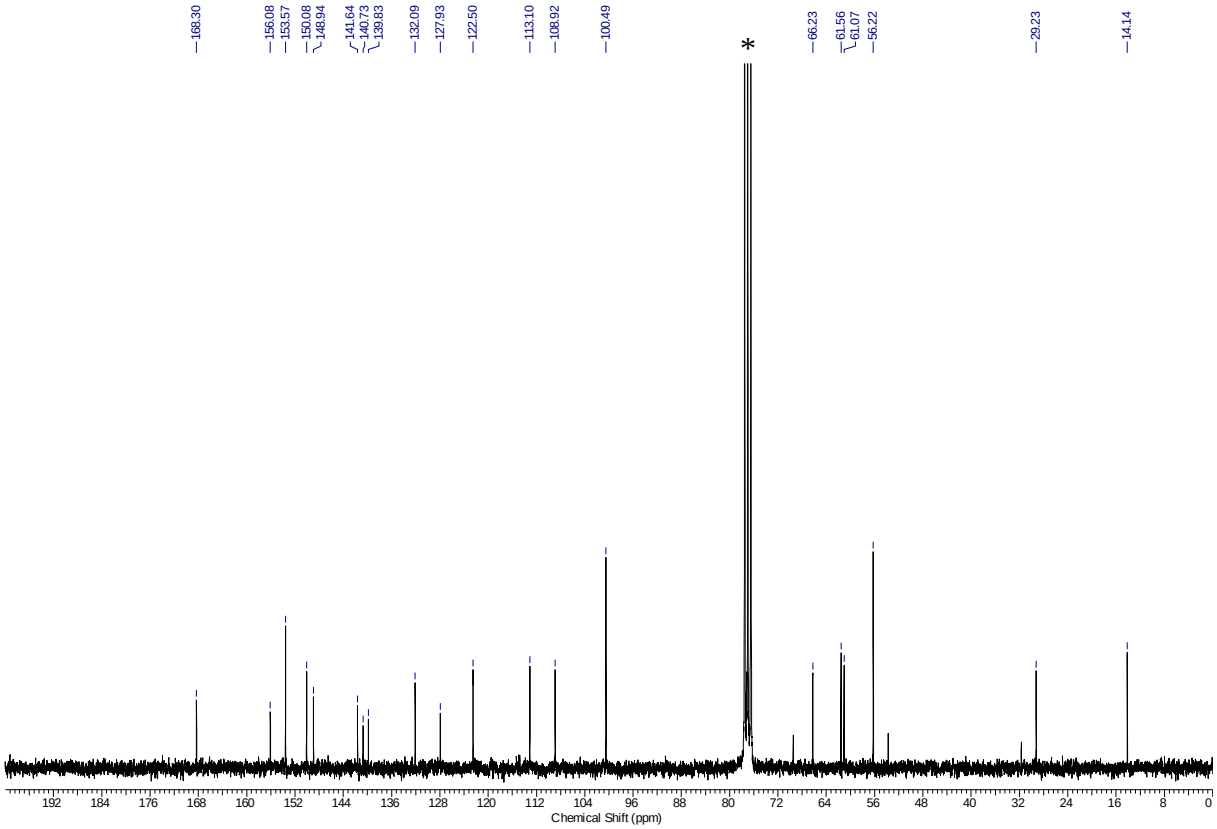
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **2b**. * = NMR-solvent, grease



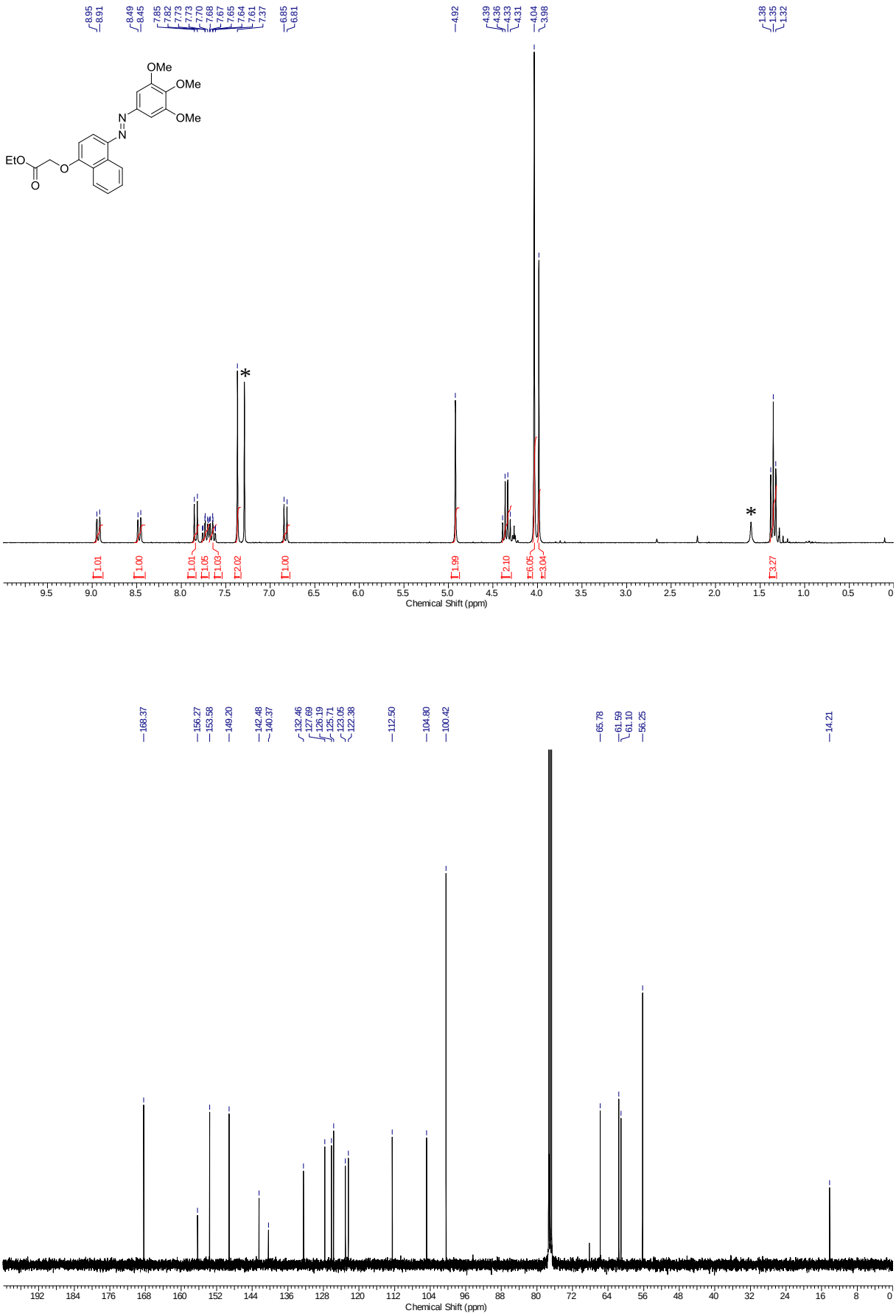


^{1}H-NMR (400 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **3**. * = NMR-solvent, H_2O

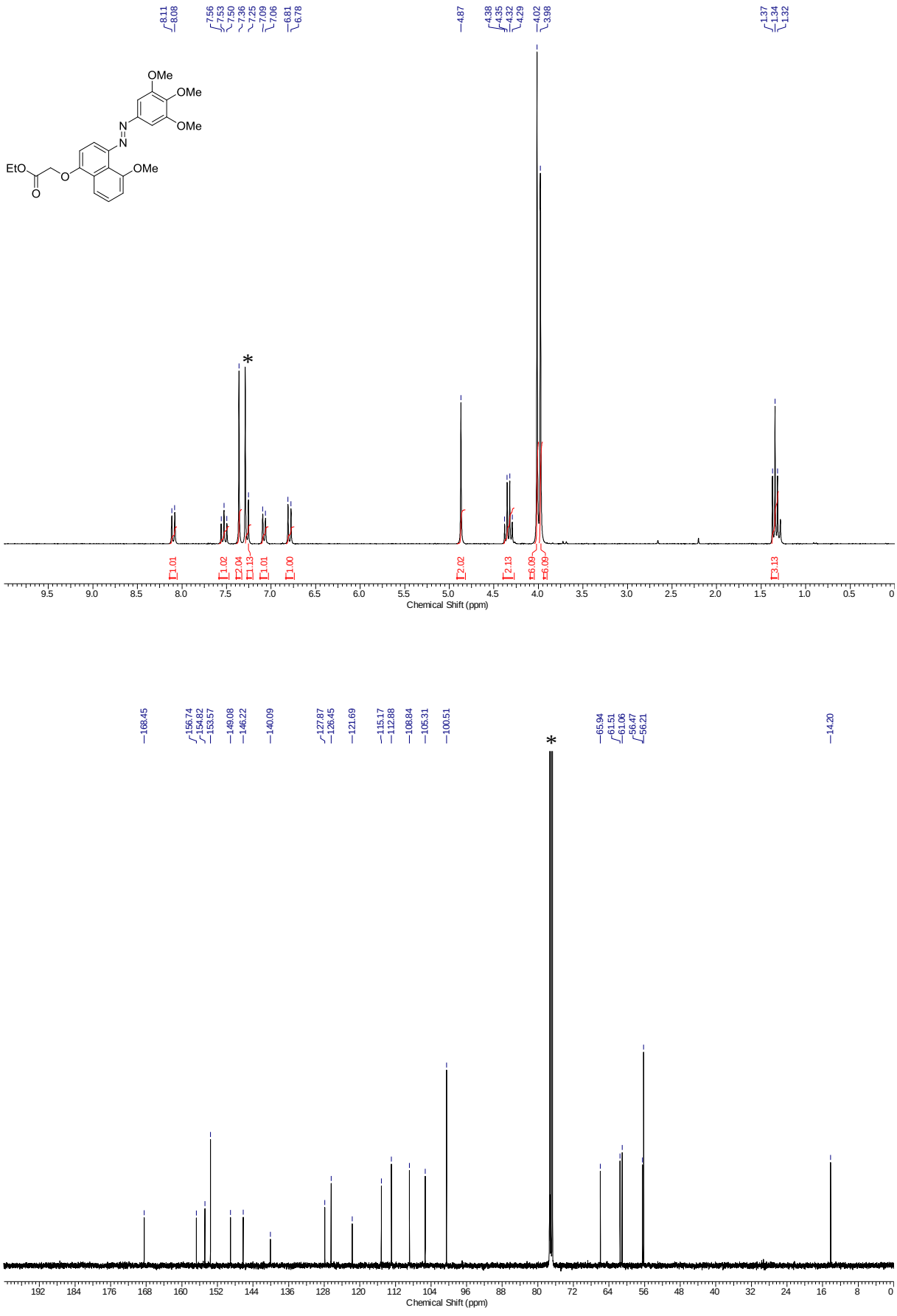




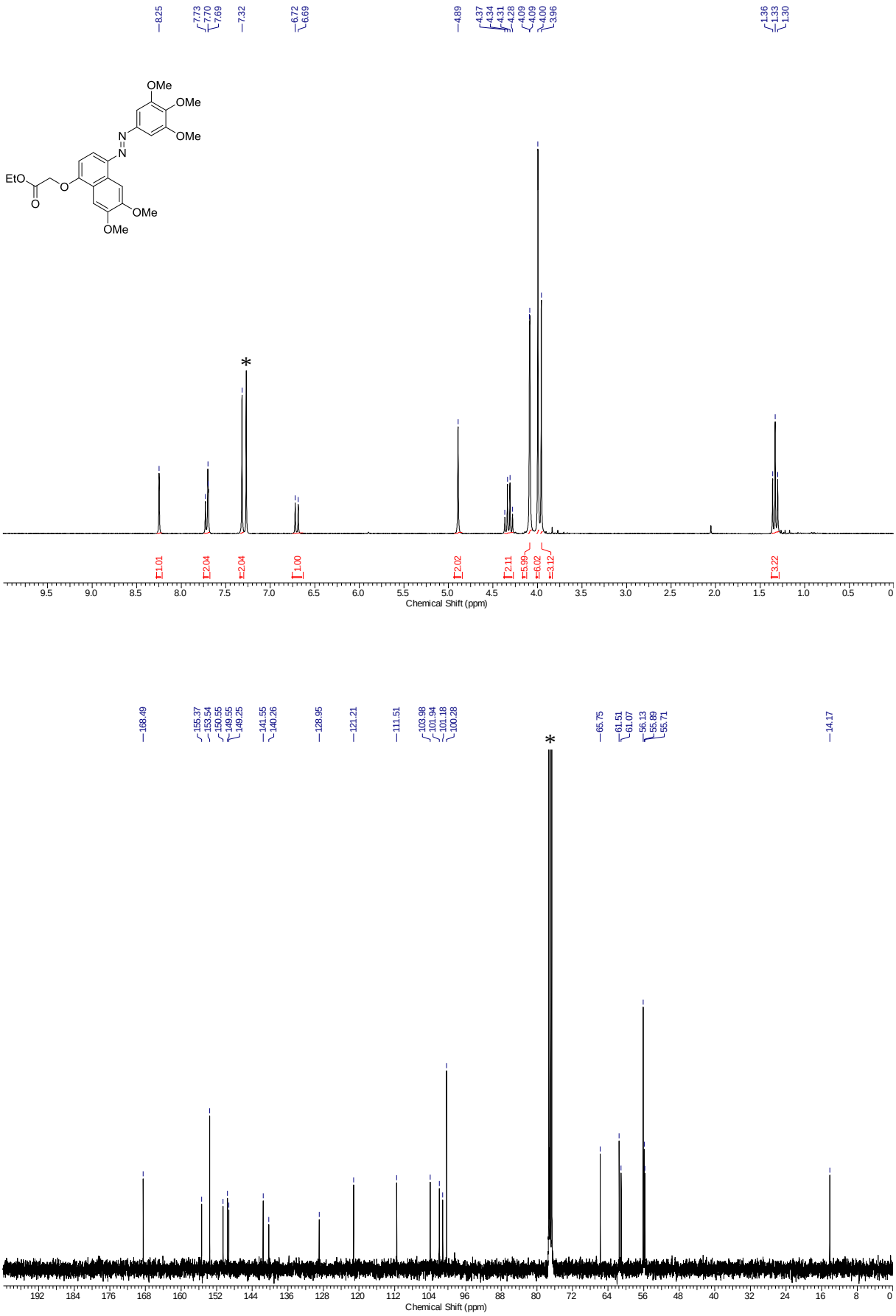
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (63 MHz, $CDCl_3$) spectrum of compound **4a**. * = NMR-solvent



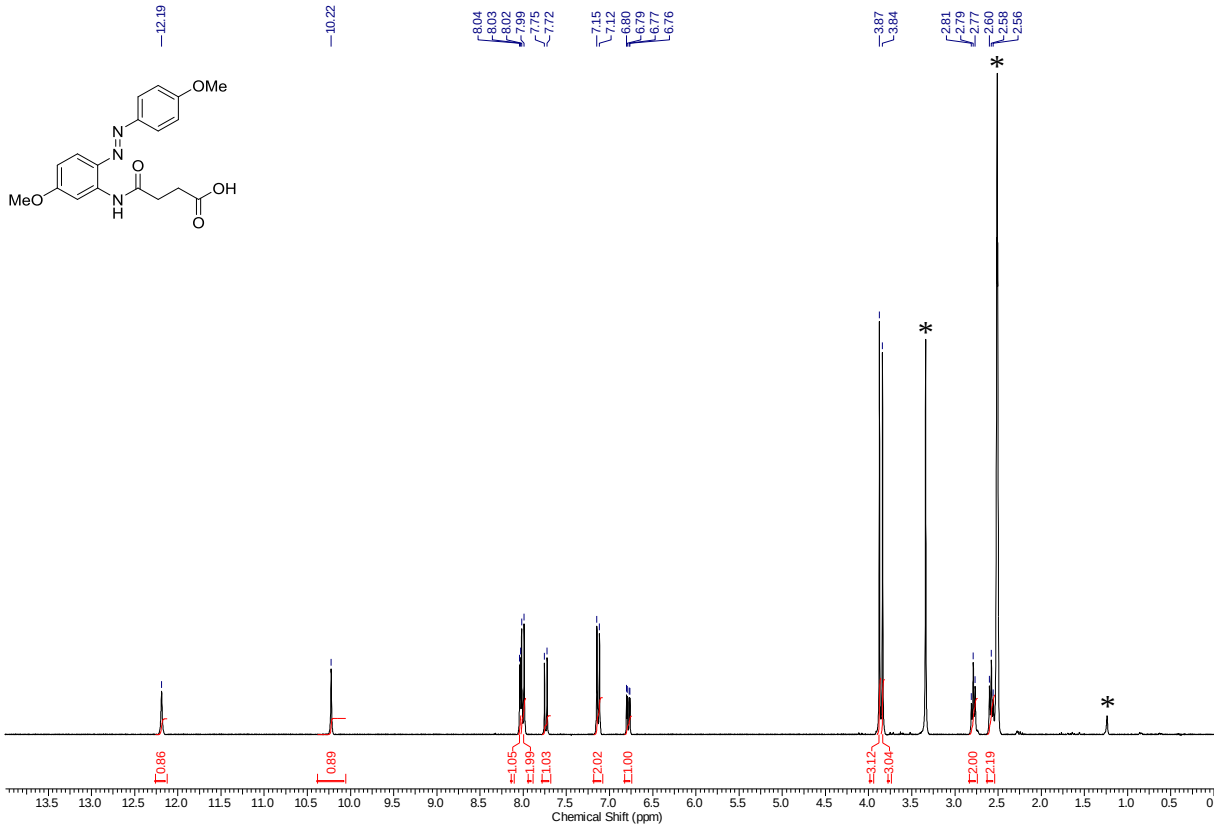
^{1}H-NMR (250 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **4b**. * = NMR-solvent, H_2O

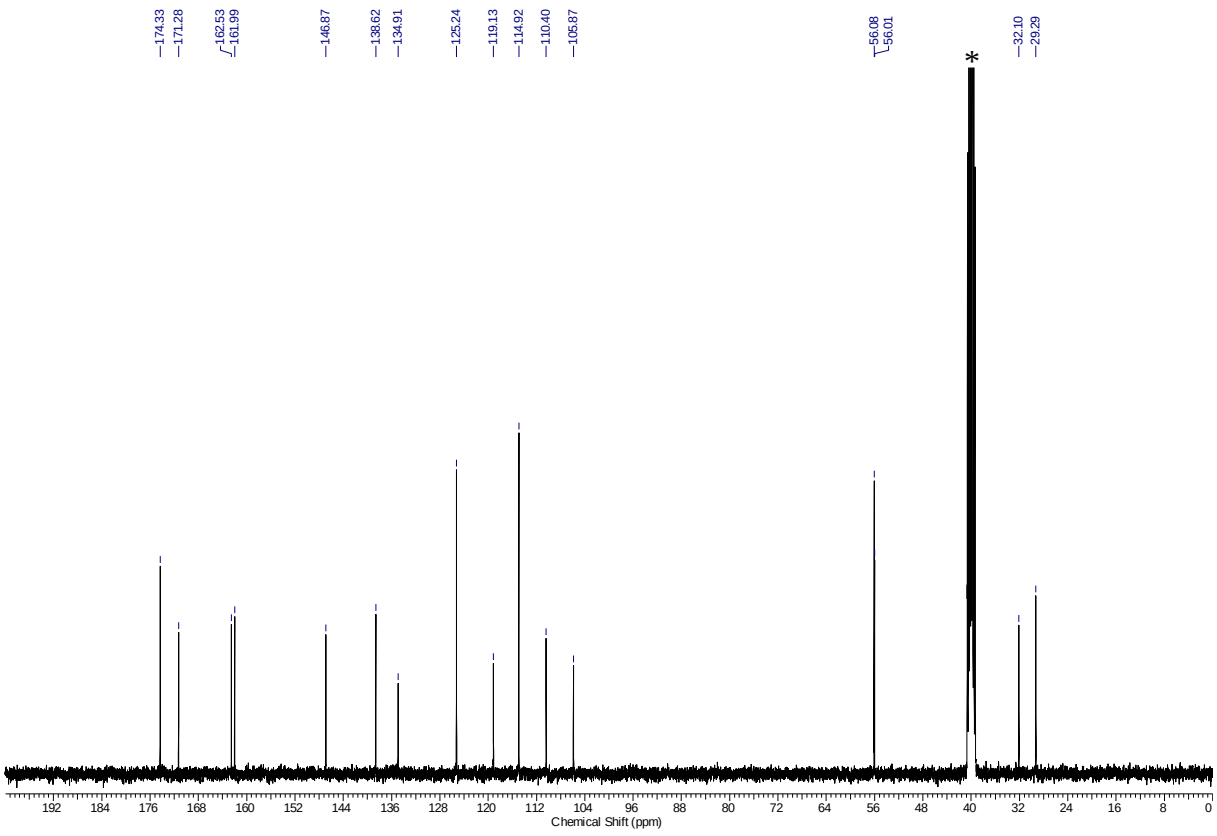


^{1}H-NMR (250 MHz, $CDCl_3$) and ^{13}C-NMR (63 MHz, $CDCl_3$) spectrum of compound **4c**. * = NMR-solvent

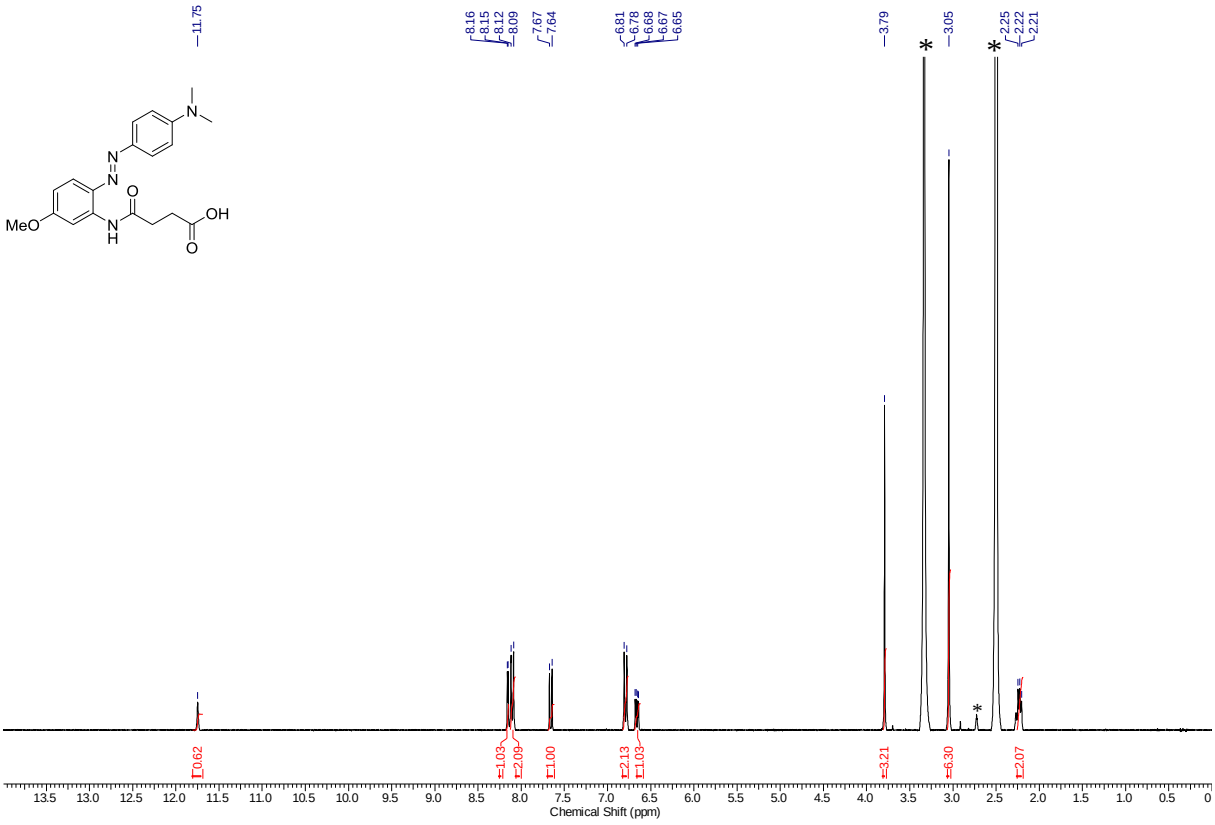


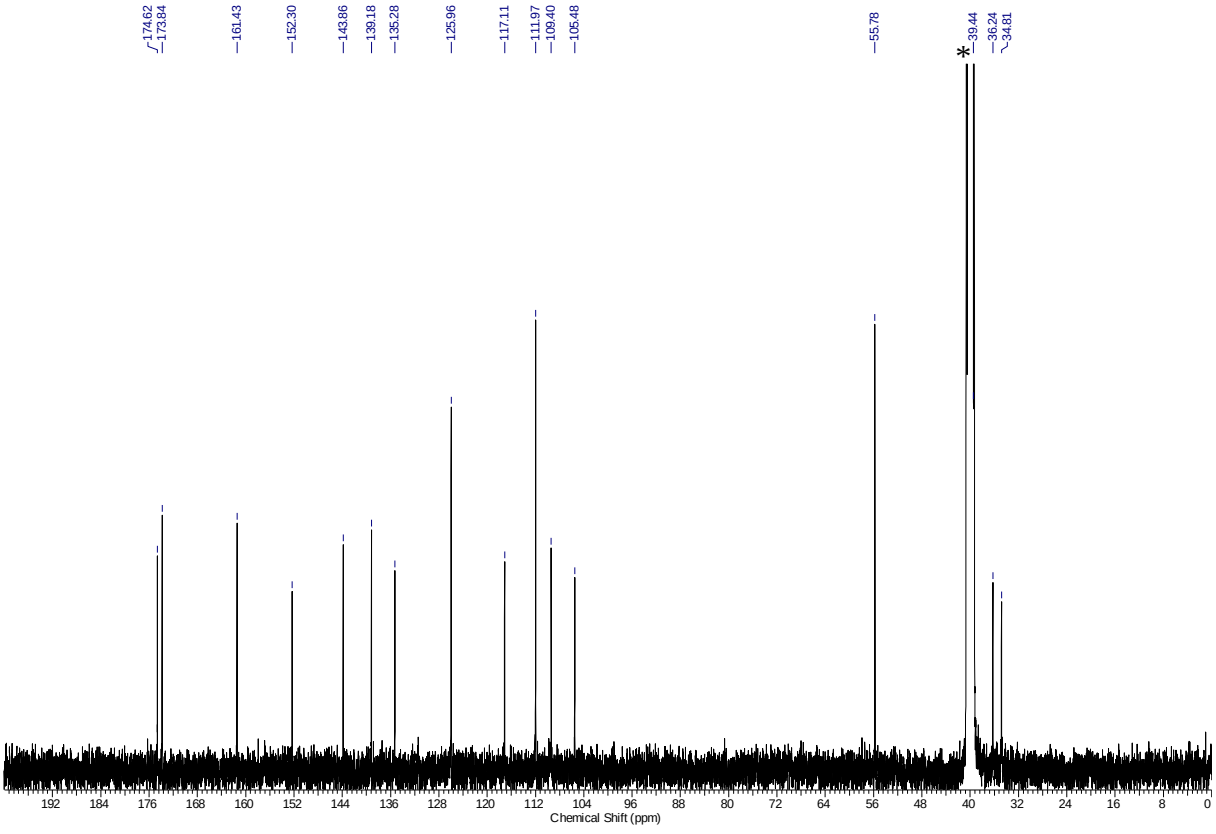
^{1}H-NMR (250 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **4d**. * = NMR-solvent



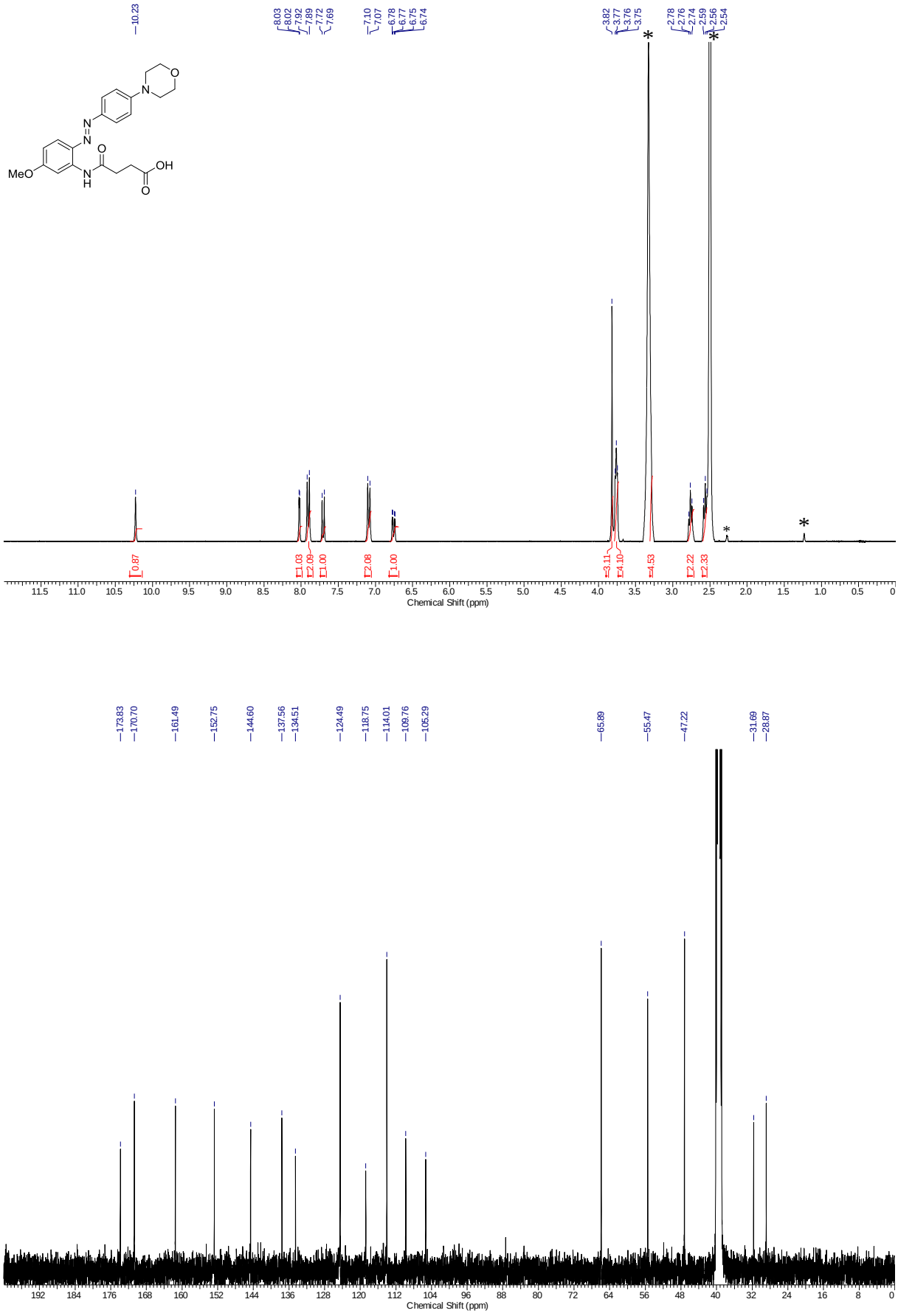


^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **5a**. * = NMR-solvent, H_2O, grease

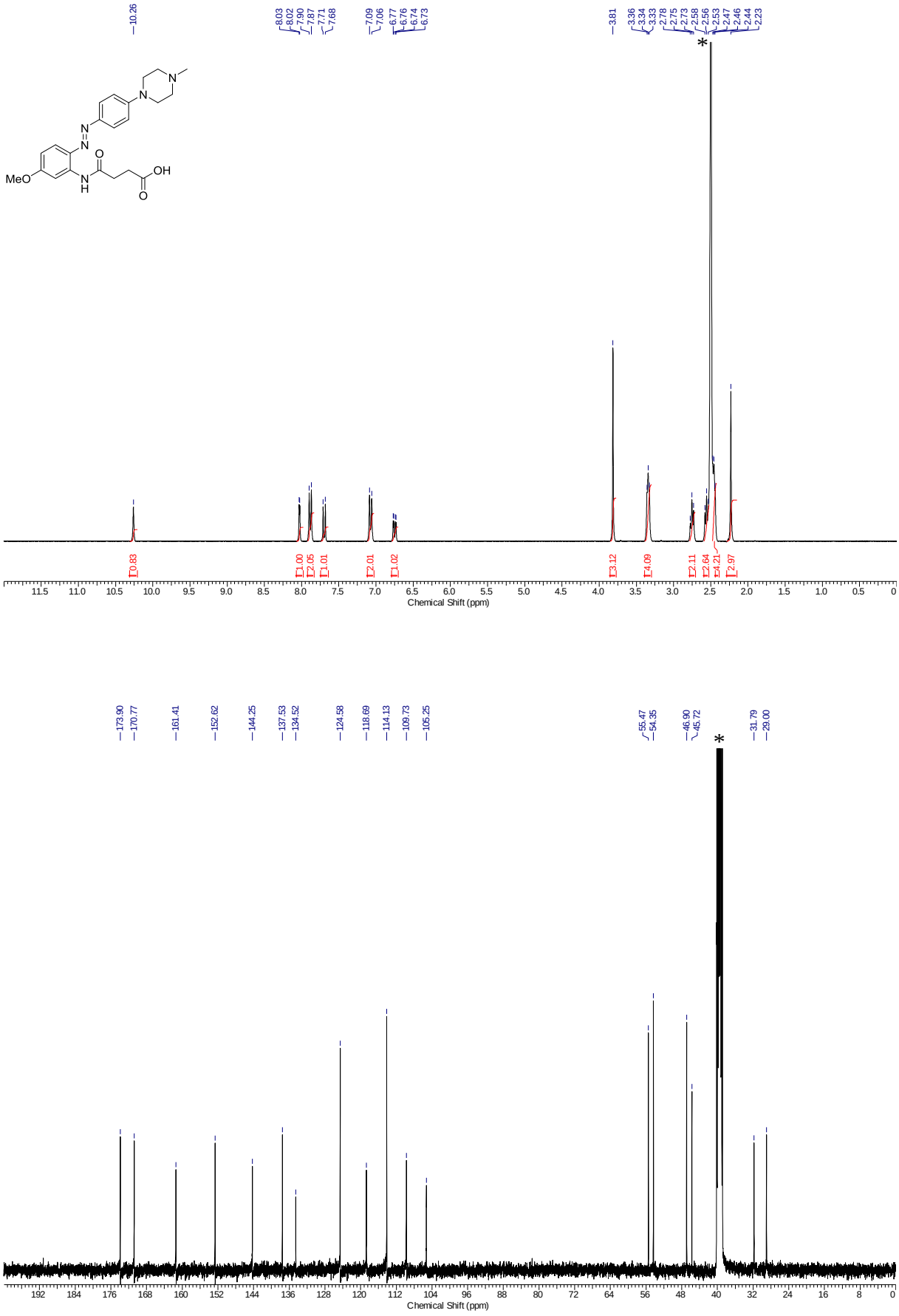




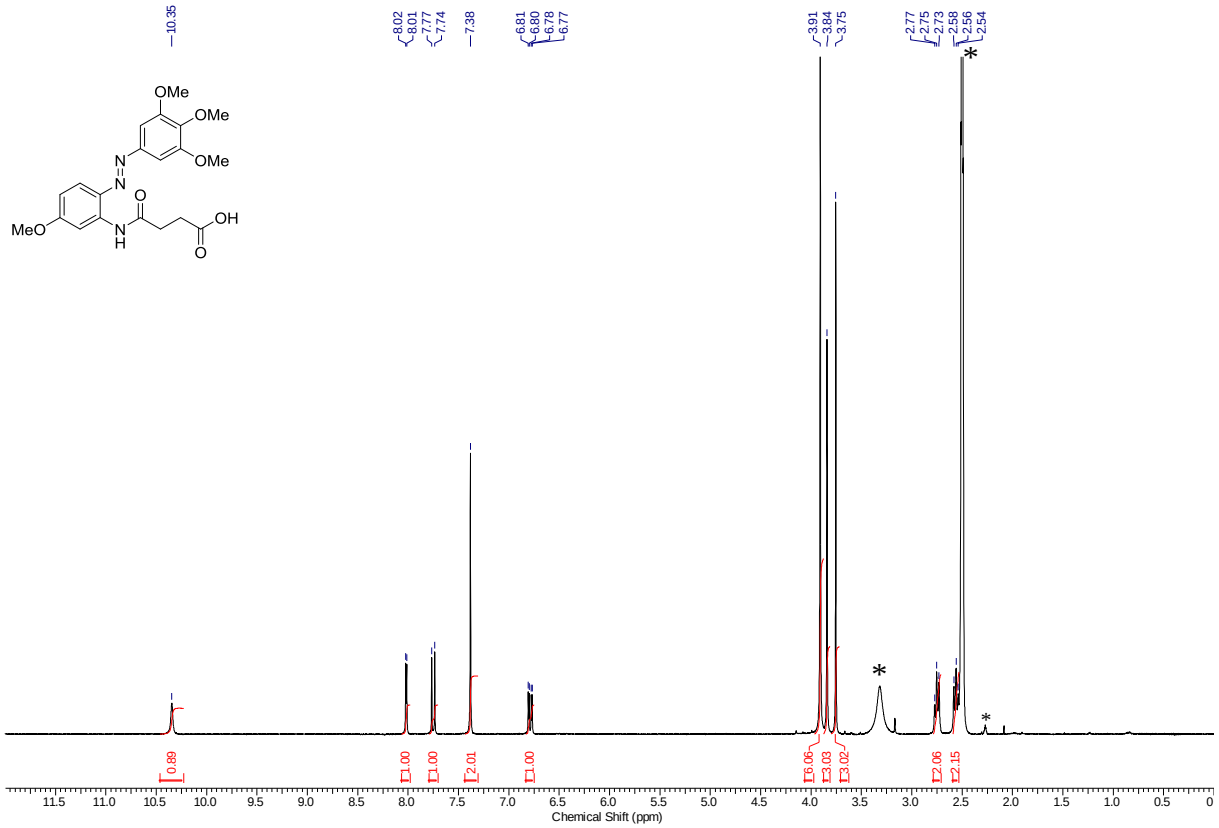
^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **5b**. * = NMR-solvent, H_2O

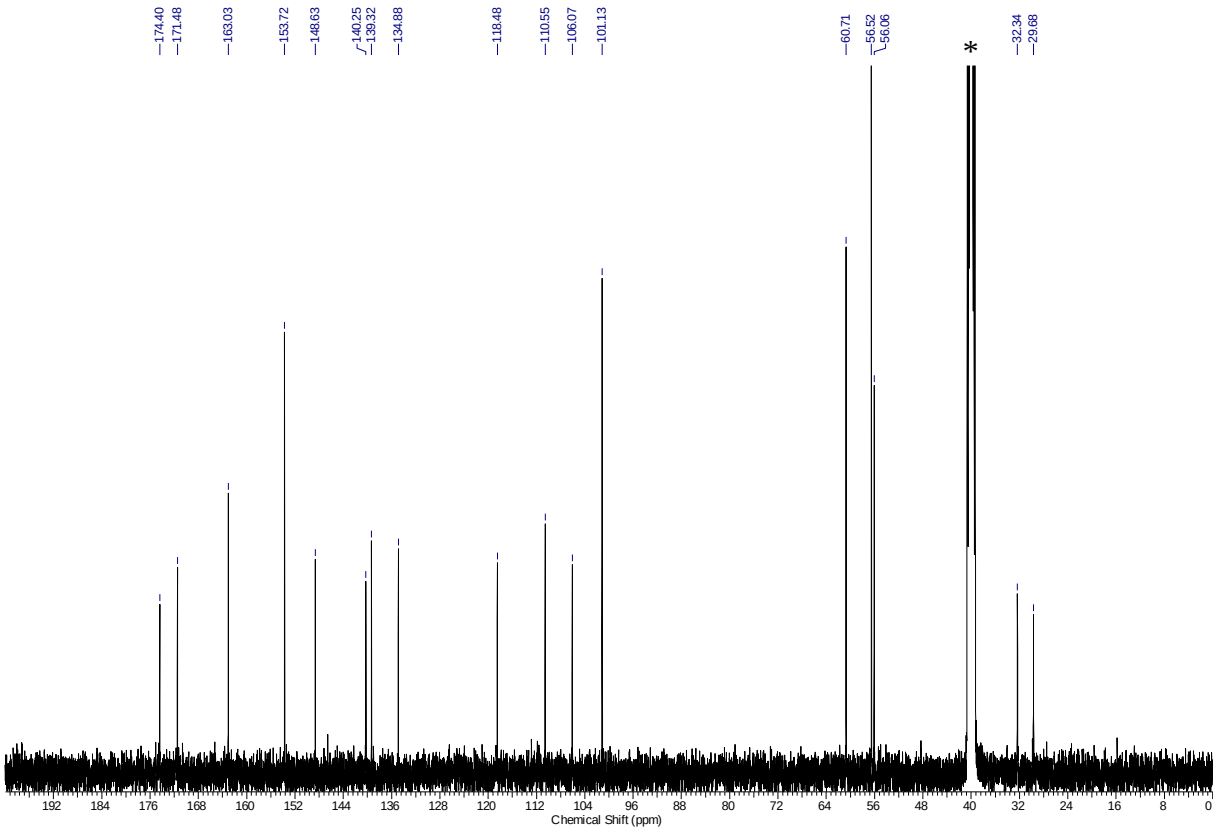


^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **5c**. * = NMR-solvent, H_2O, grease

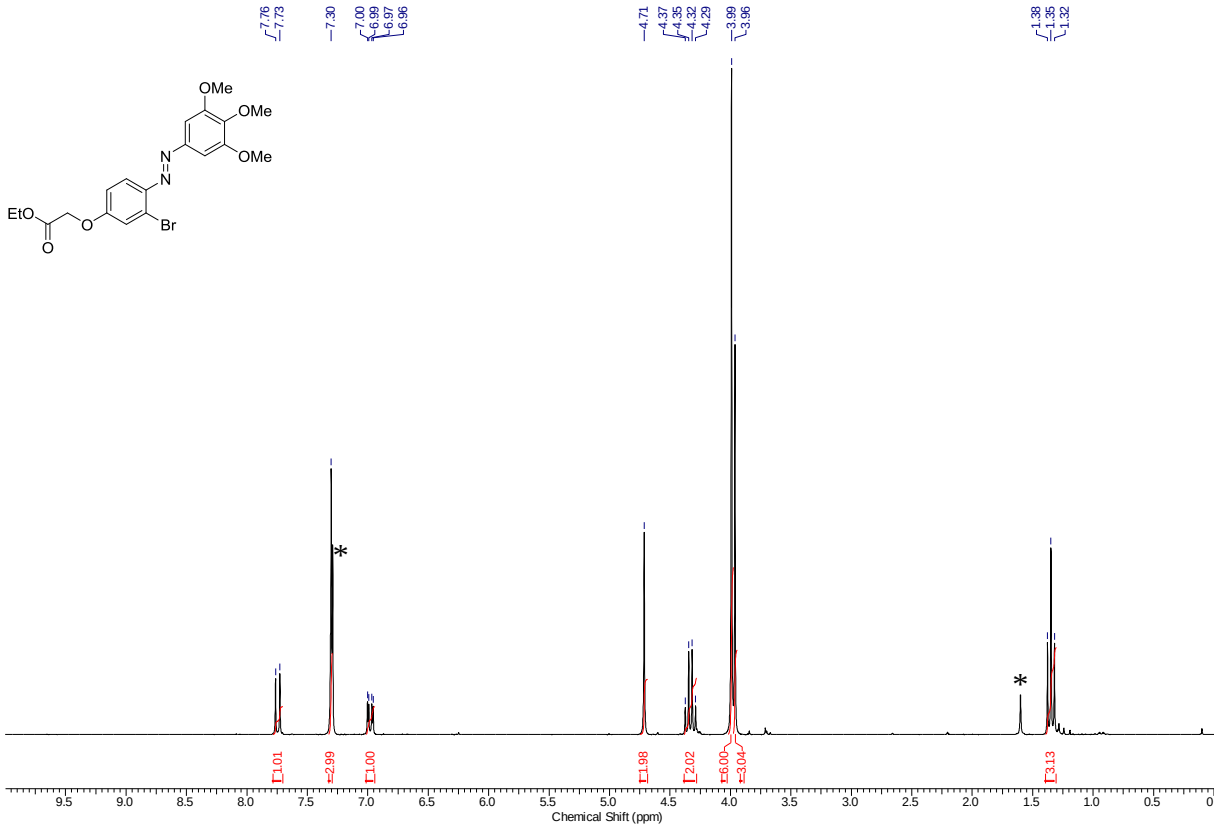


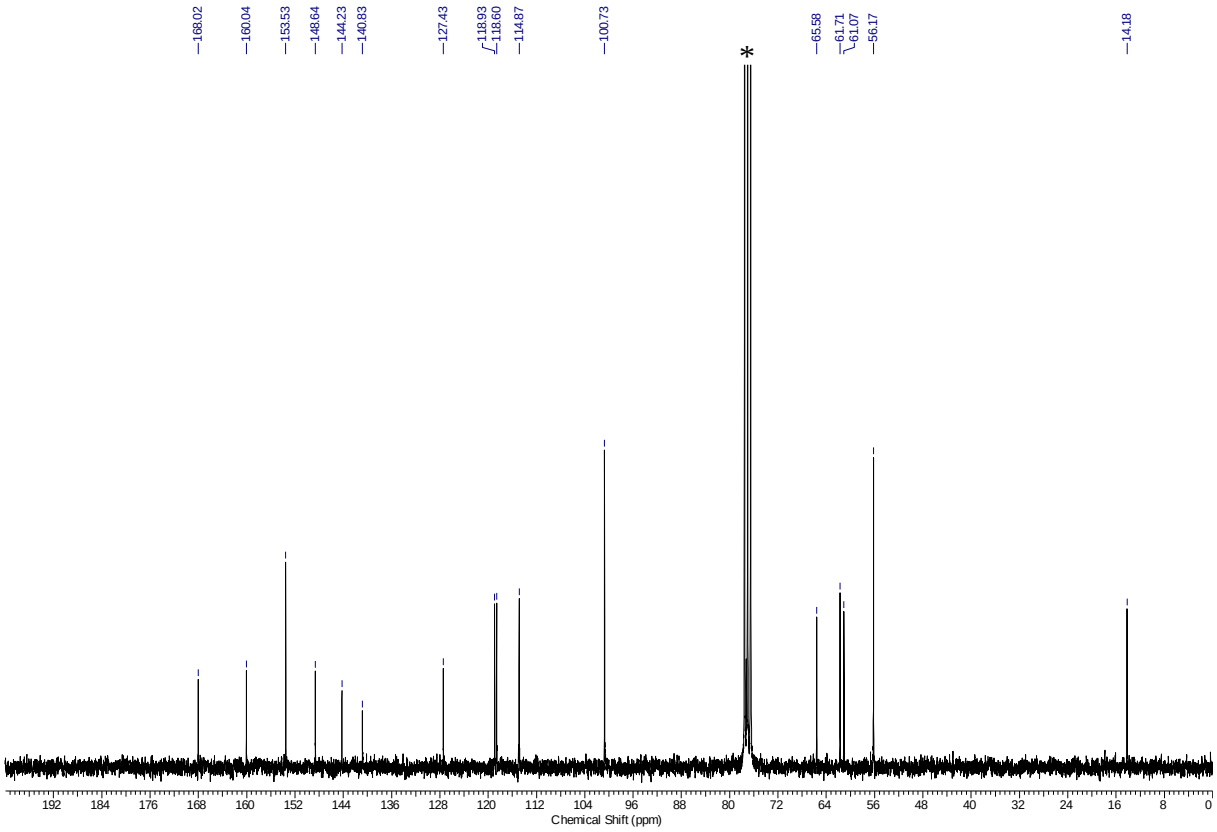
^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **5d**. * = NMR-solvent



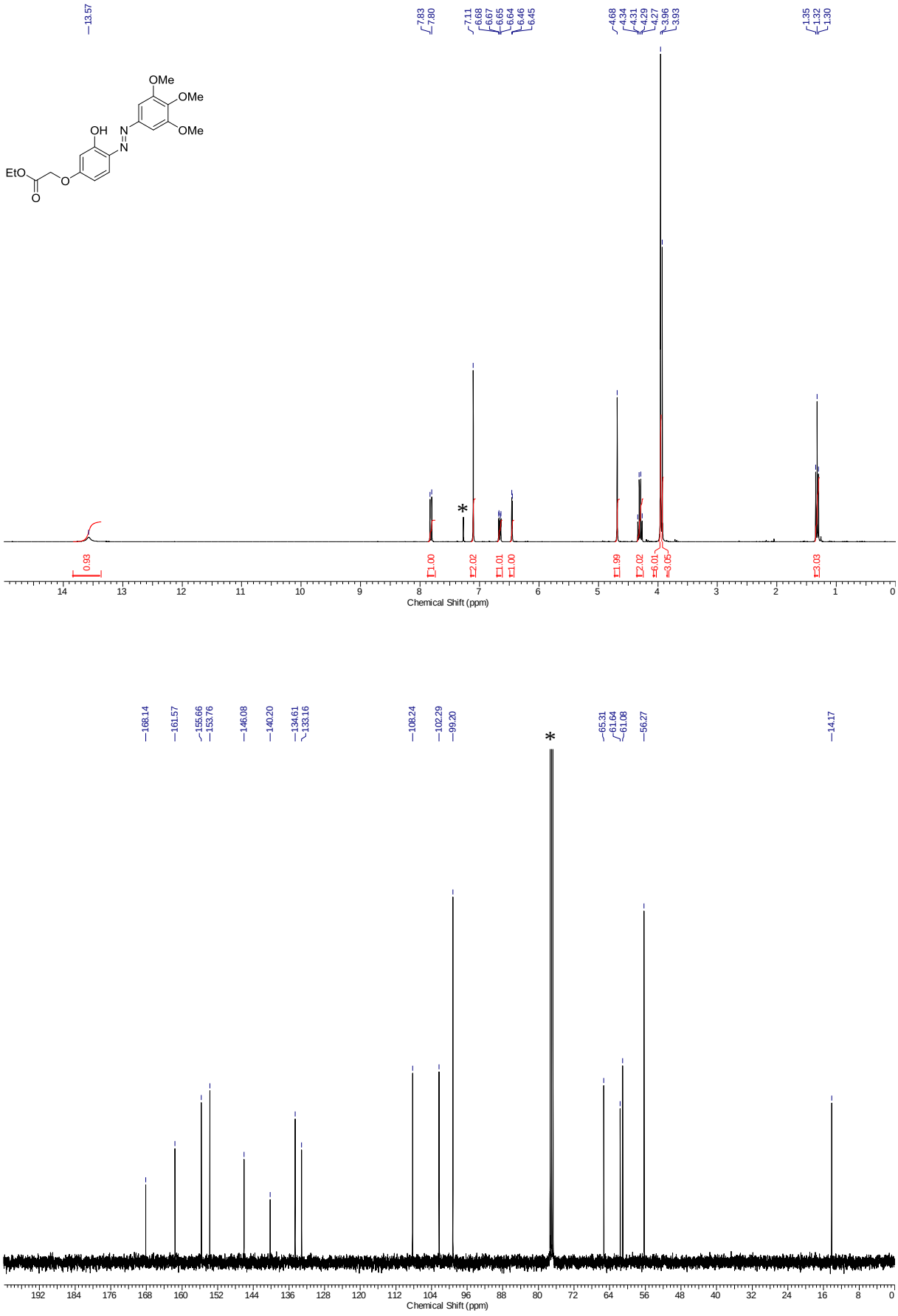


^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **6**. * = NMR-solvent, H_2O

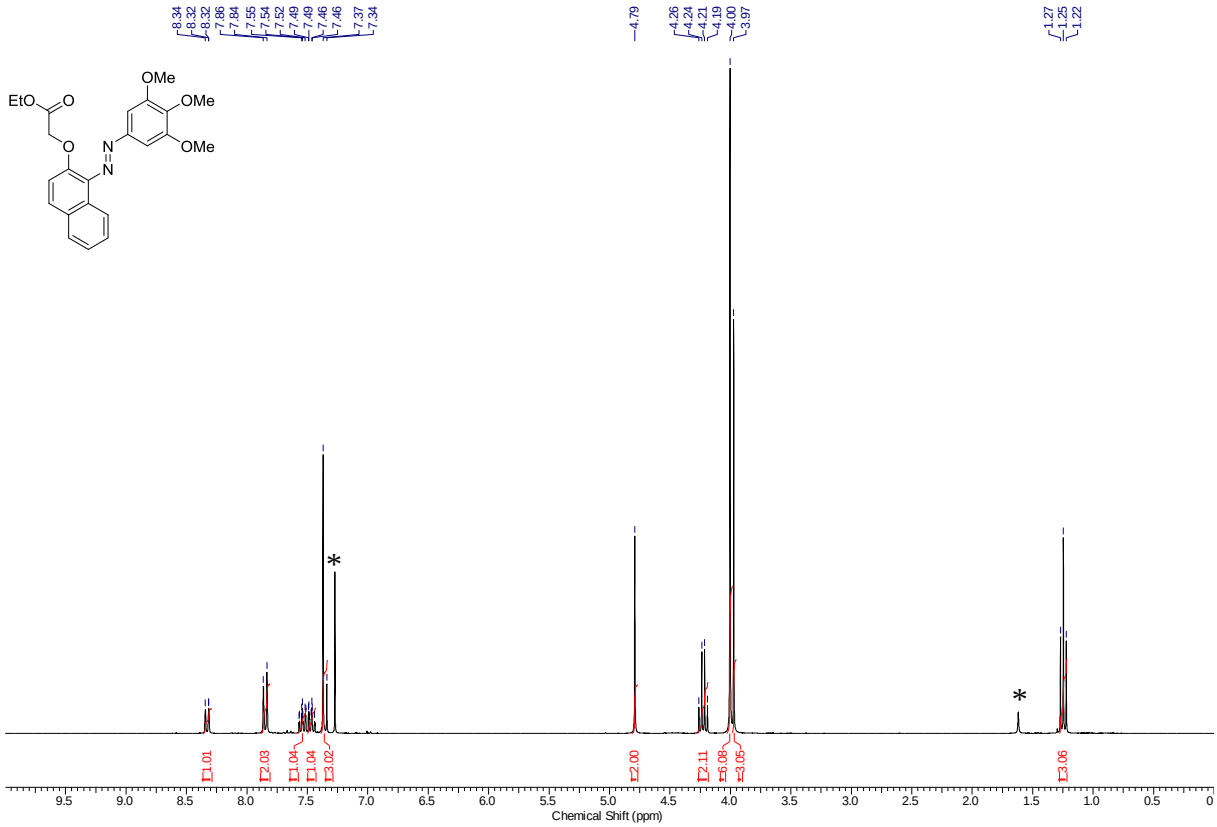


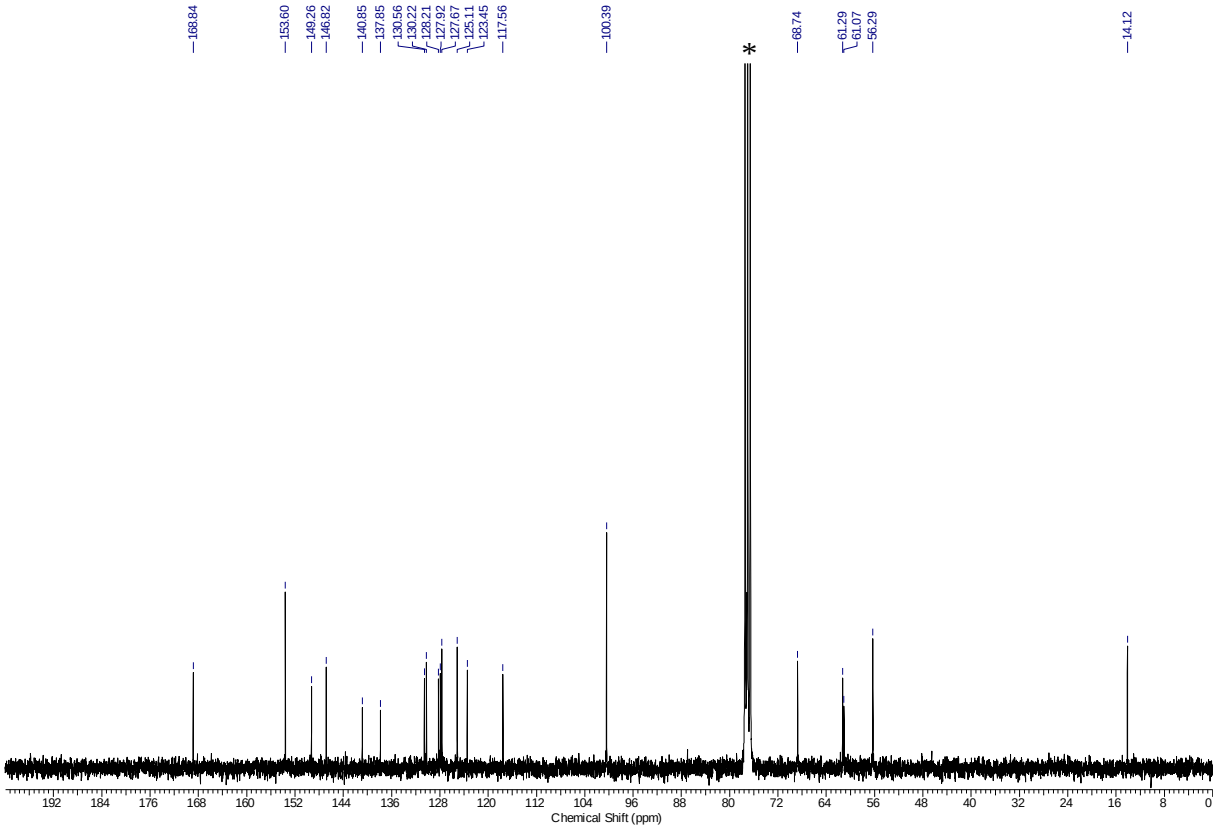


^{1}H-NMR (250 MHz, $CDCl_3$) and ^{13}C-NMR (63 MHz, $CDCl_3$) spectrum of compound **7a**. * = NMR-solvent, H_2O

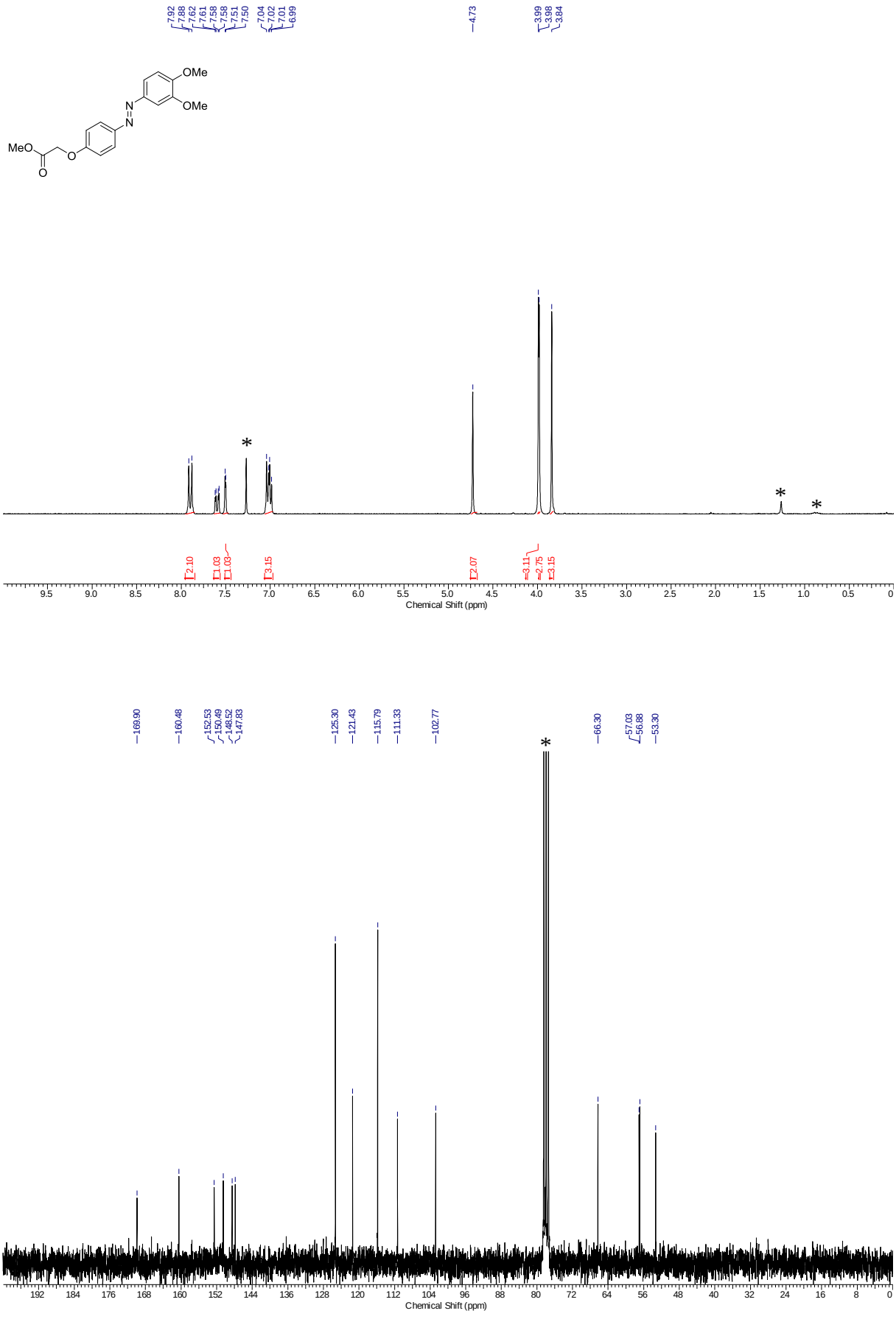


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **7b**. * = NMR-solvent

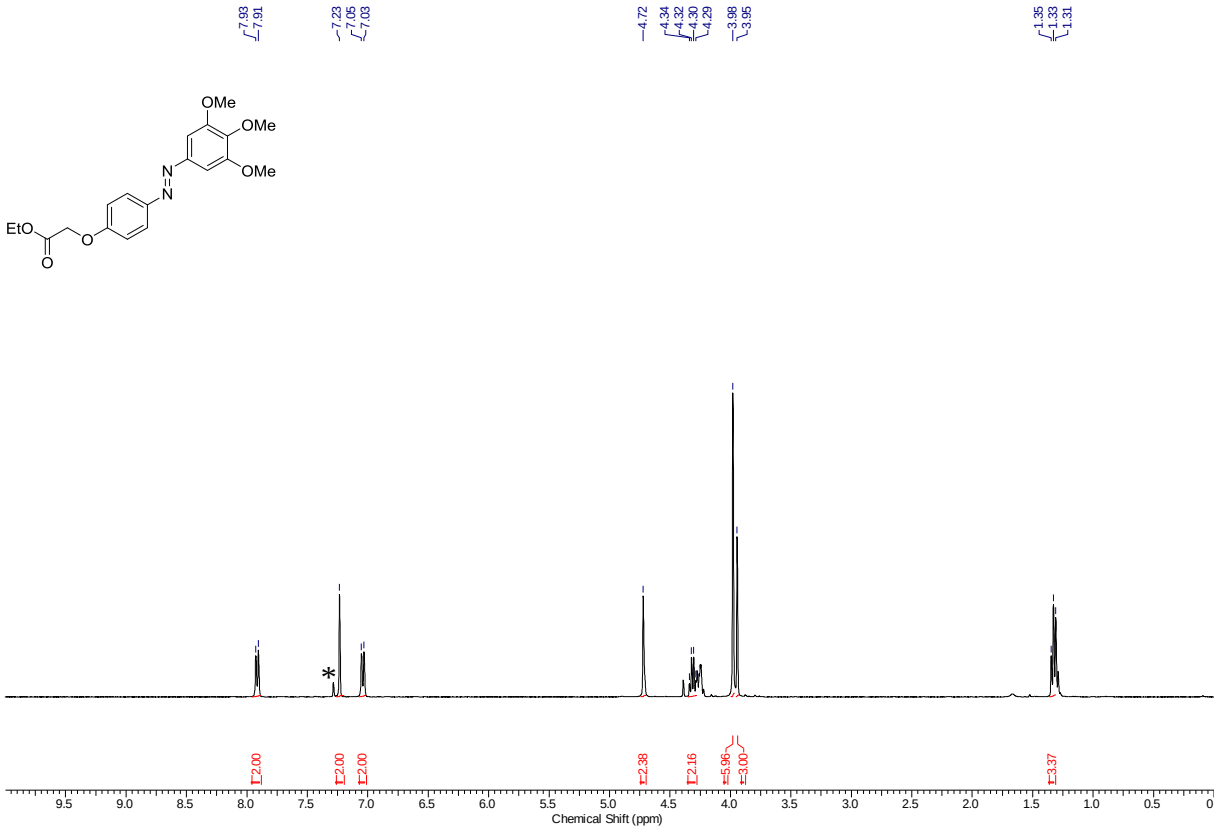


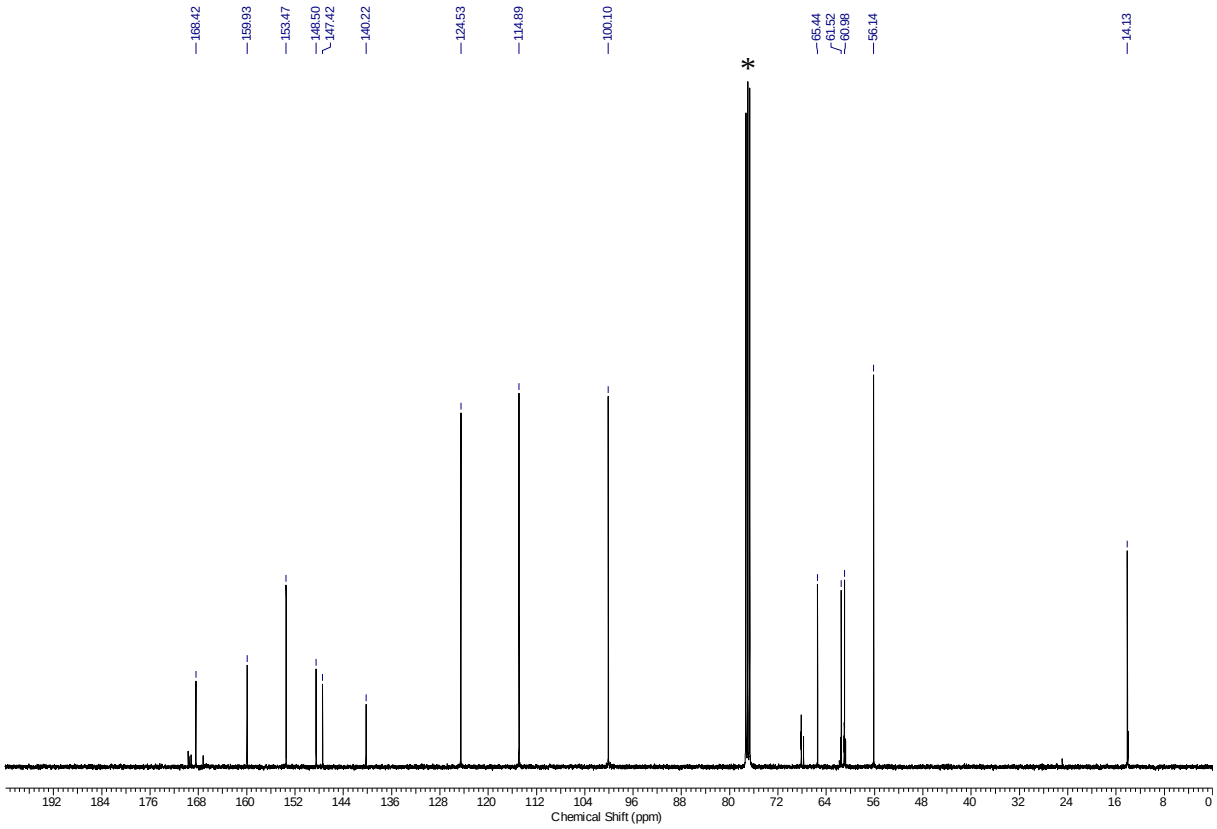


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **8**. * = NMR-solvent, H_2O

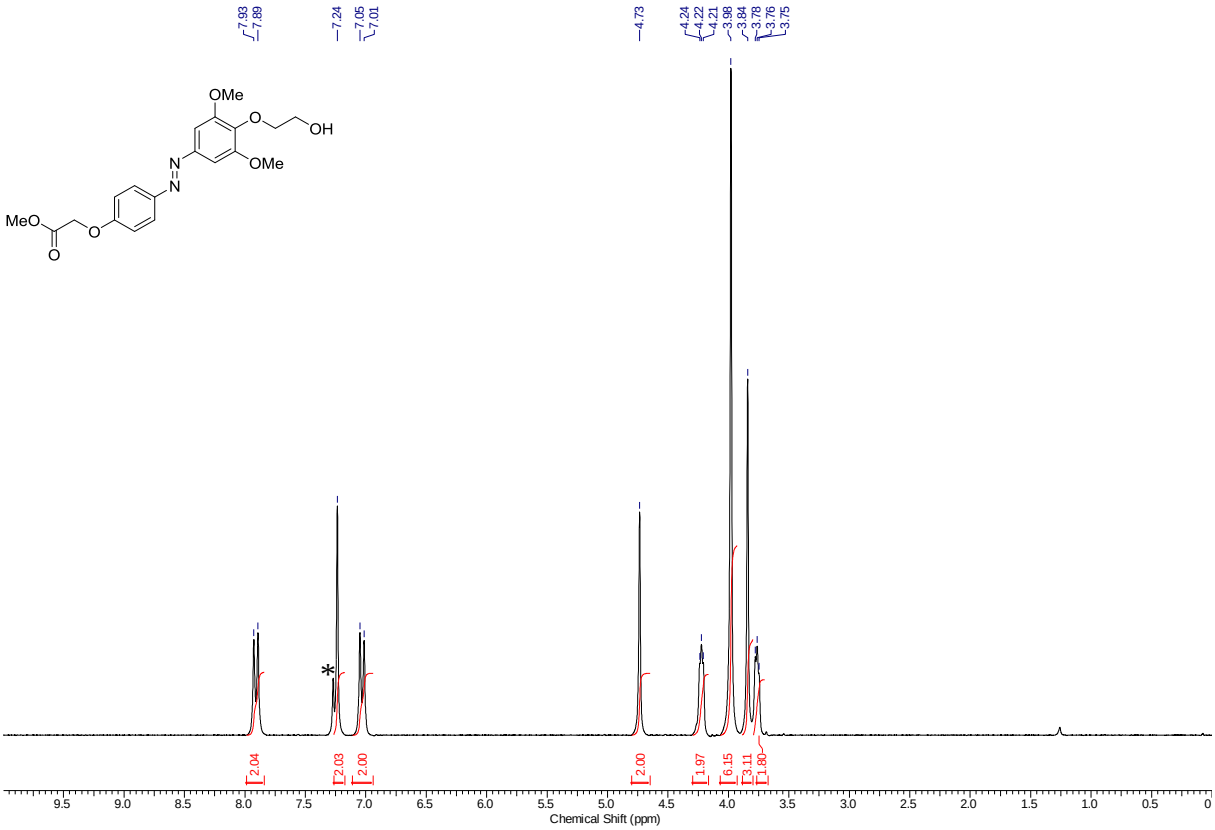


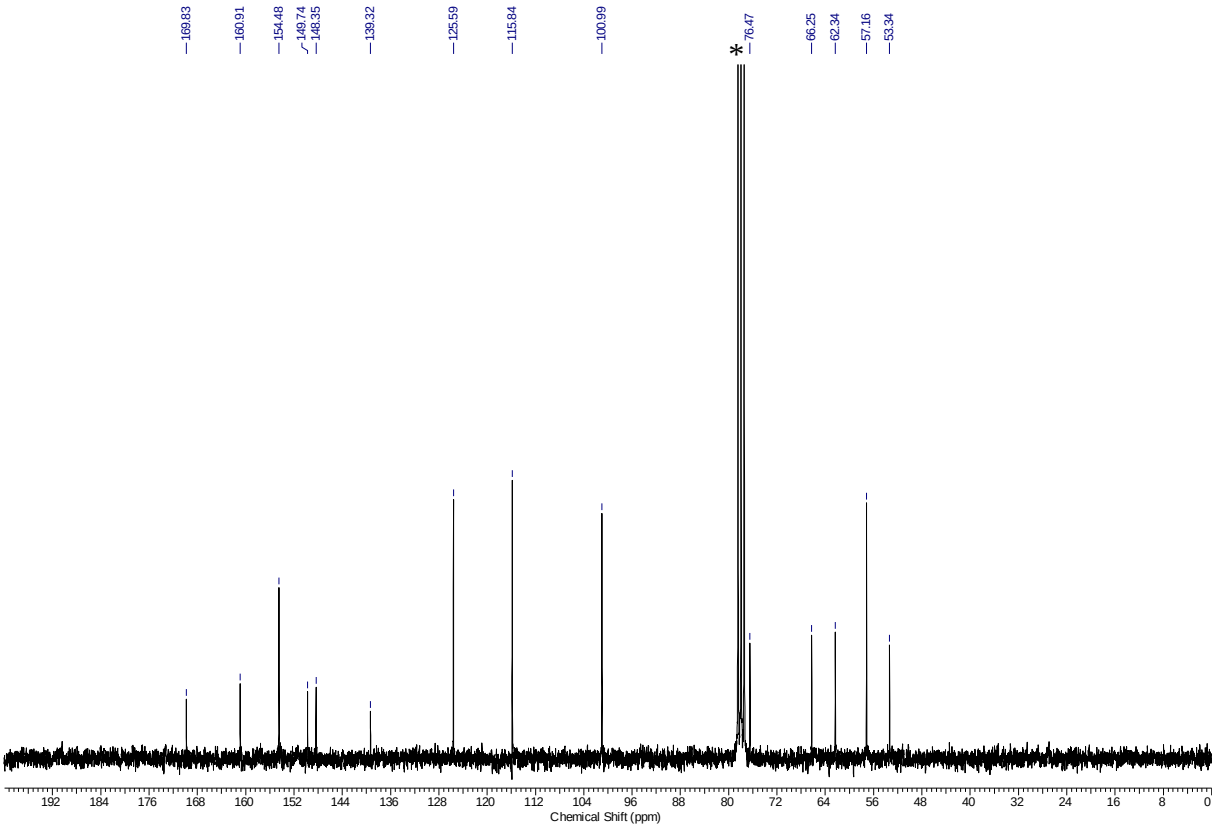
^{1}H-NMR (250 MHz, $CDCl_3$) and ^{13}C-NMR (63 MHz, $CDCl_3$) spectrum of compound **9a**. * = NMR-solvent, grease



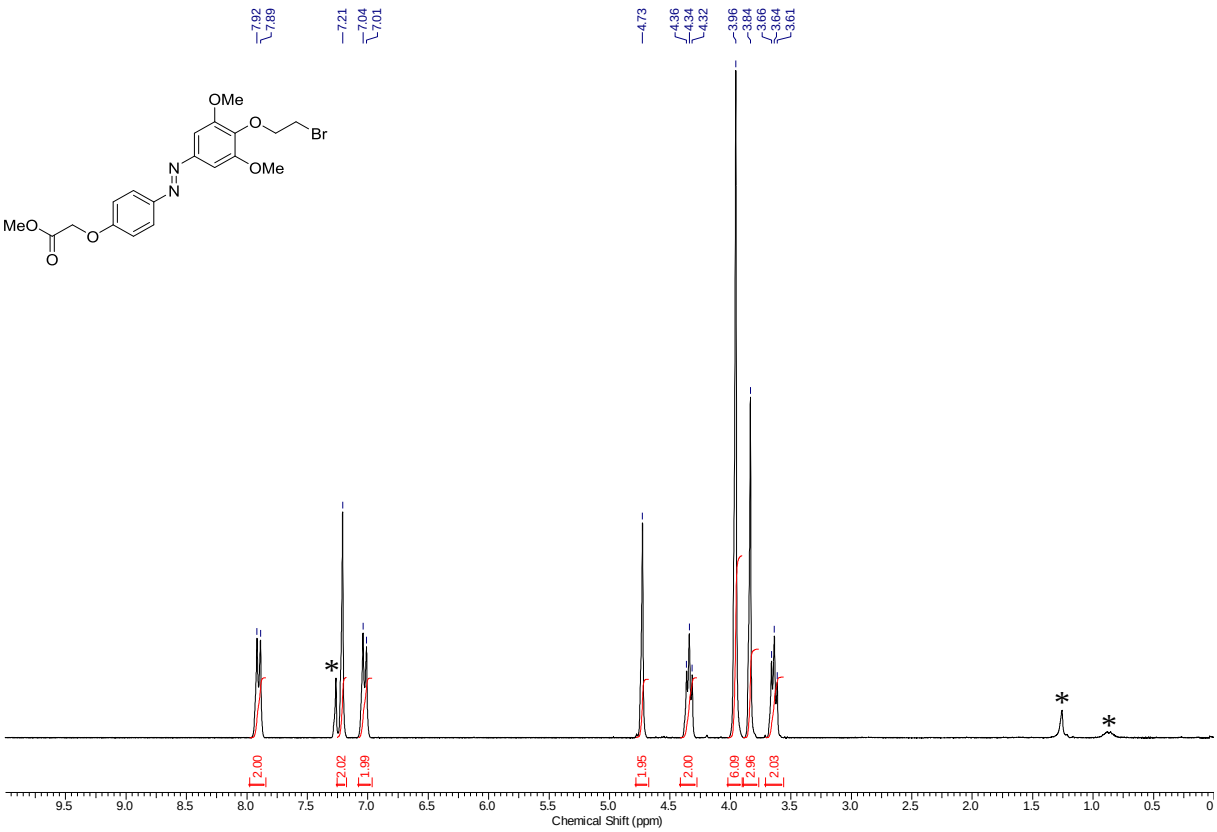


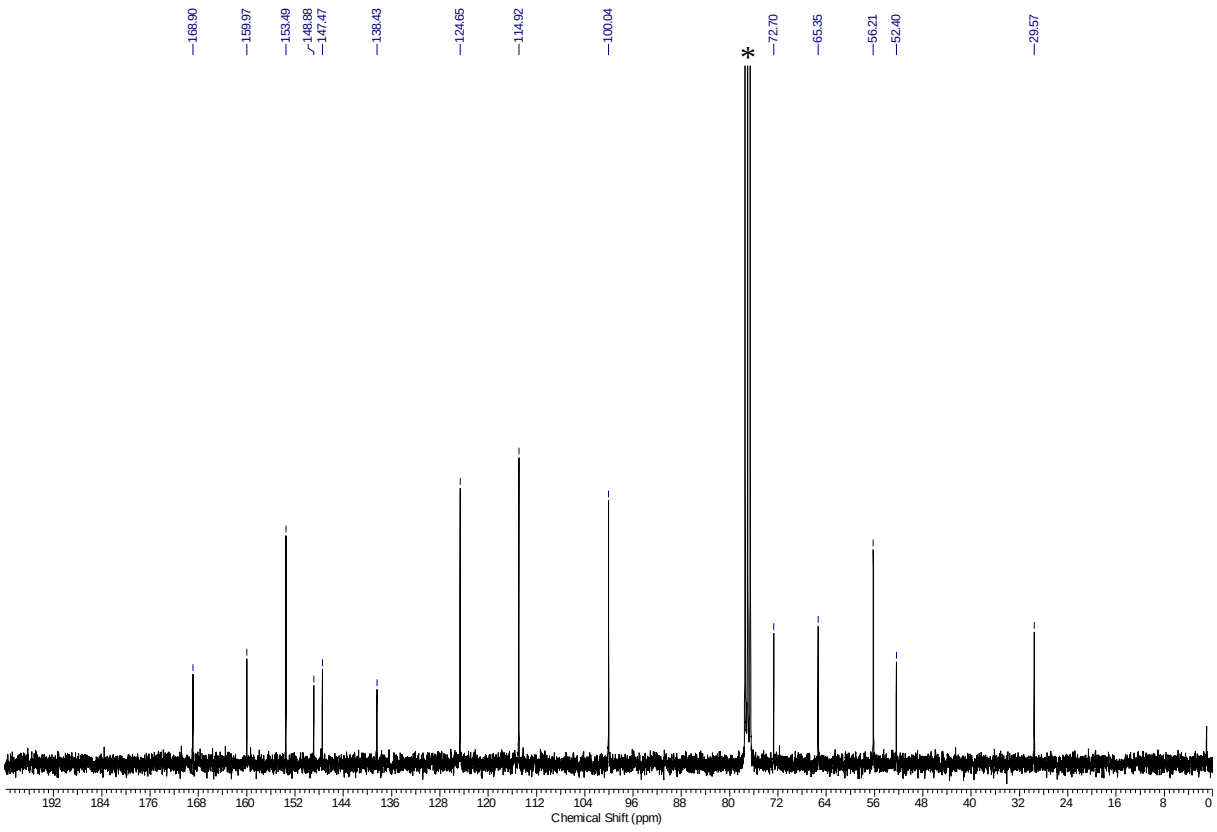
^{1}H-NMR (400 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **9b**. * = NMR-solvent



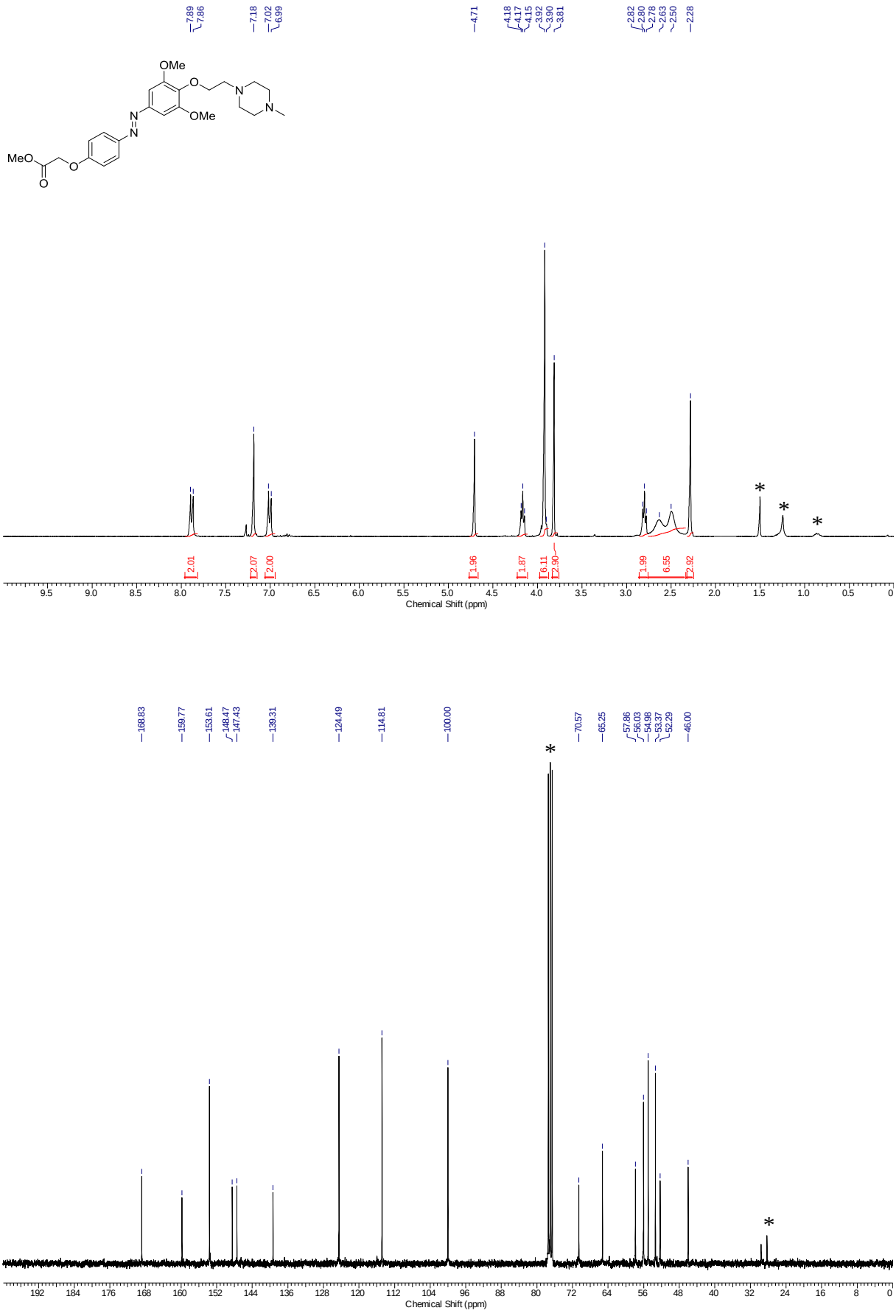


^{1}H-NMR (250 MHz, $CDCl_3$) and ^{13}C-NMR (63 MHz, $CDCl_3$) spectrum of compound **9c**. * = NMR-solvent

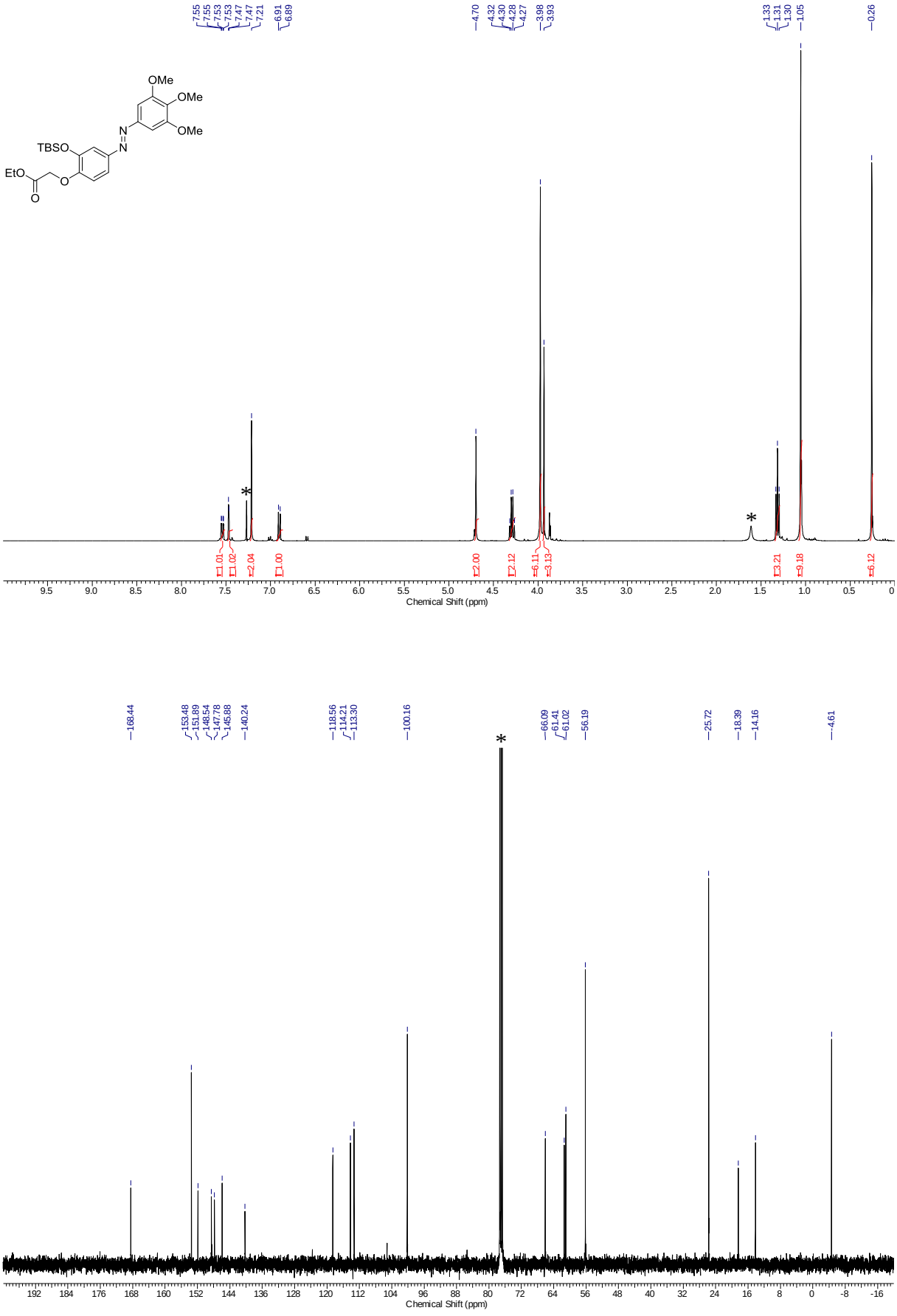




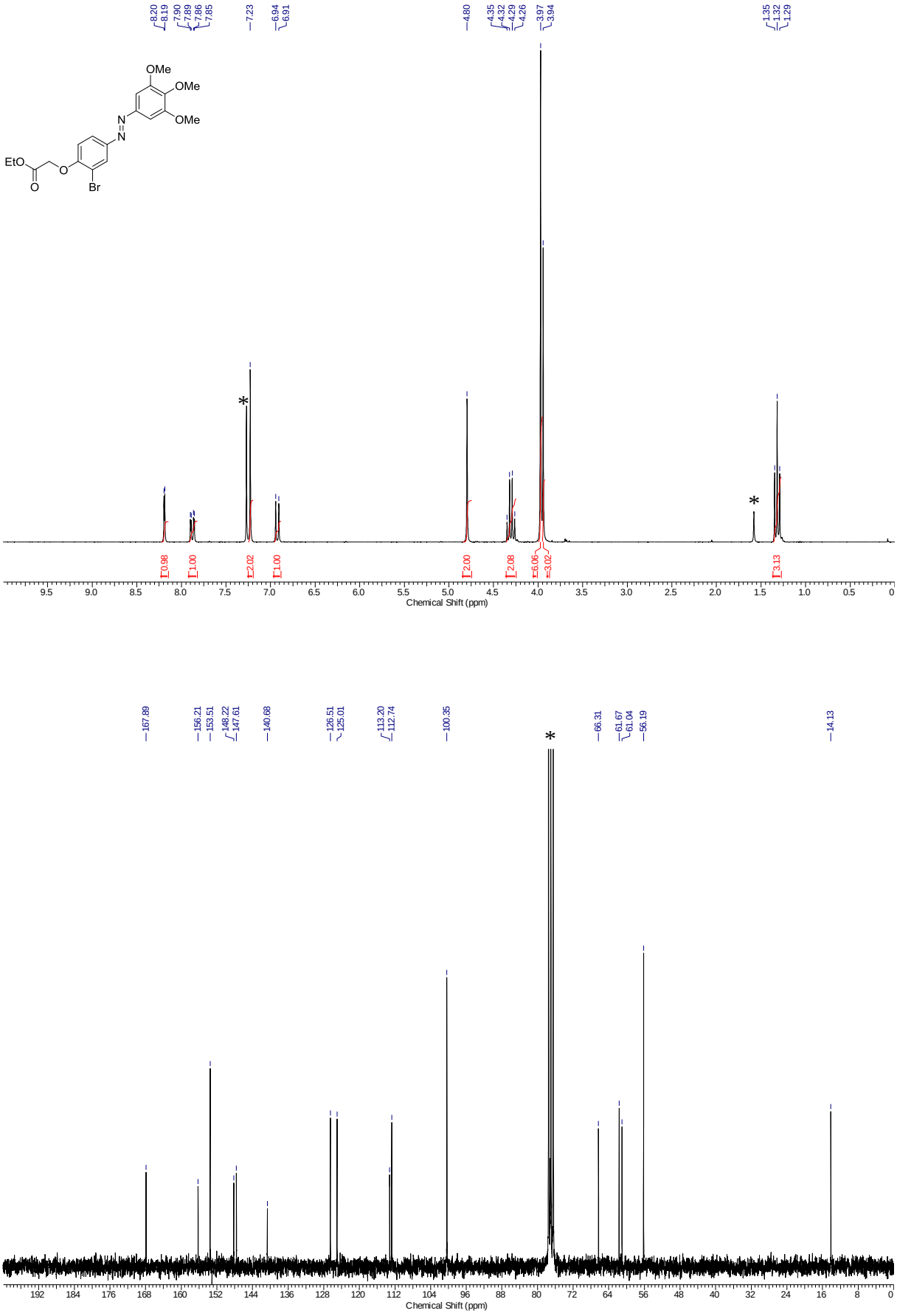
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **9d**. * = NMR-solvent, grease



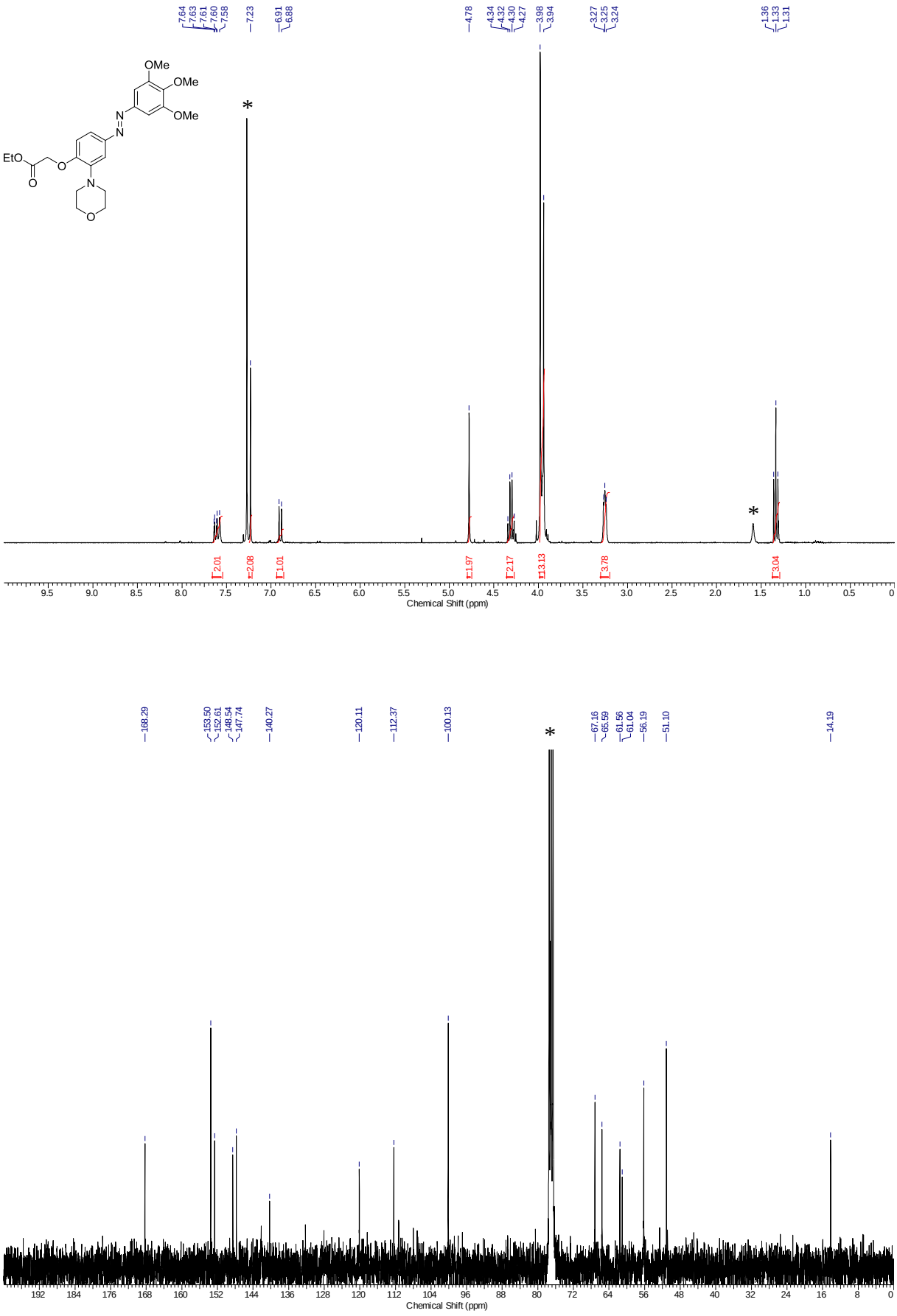
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **9e**. * = NMR-solvent, H_2O, grease



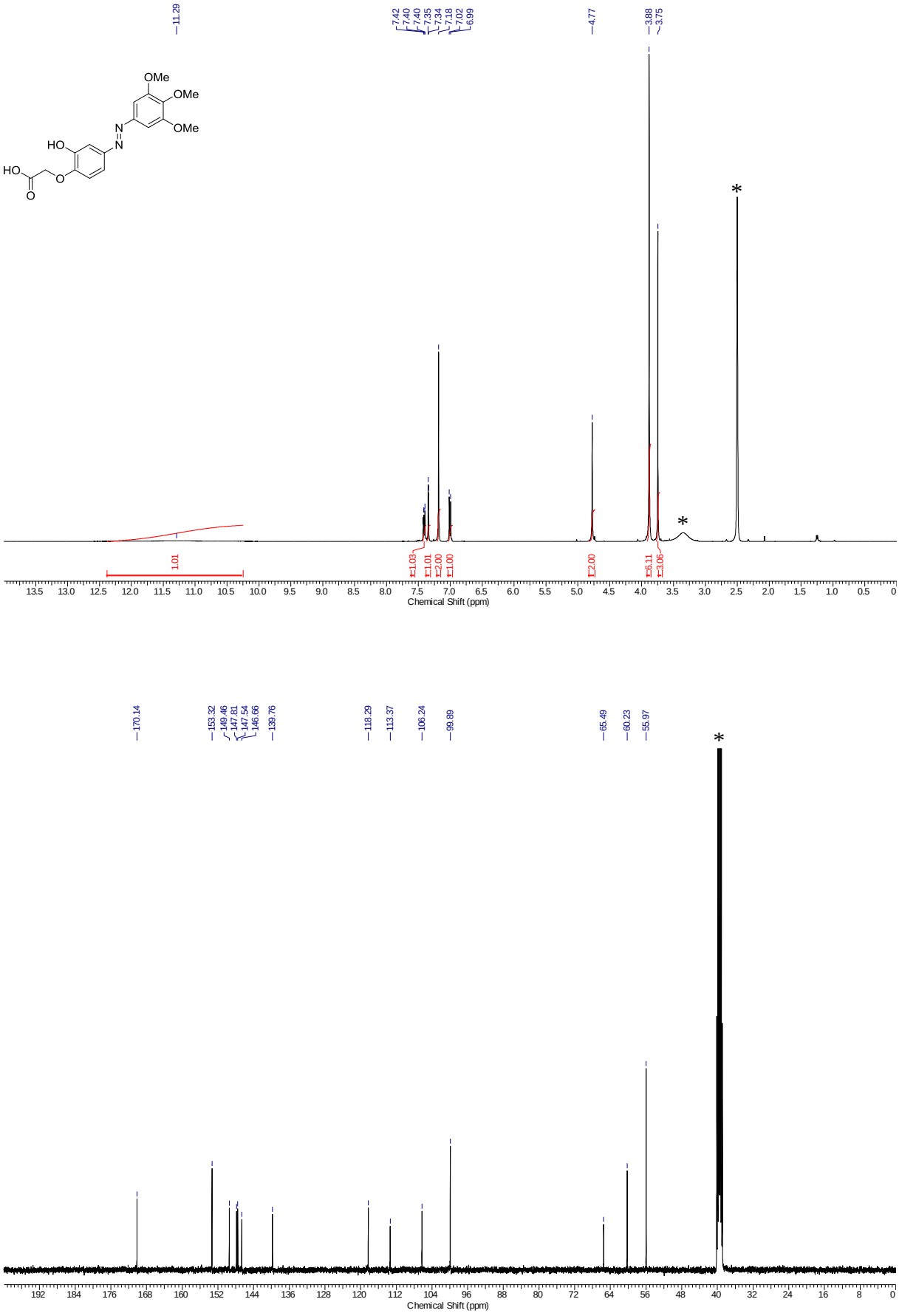
^{1}H-NMR (400 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **10a**. * = NMR-solvent, H_2O



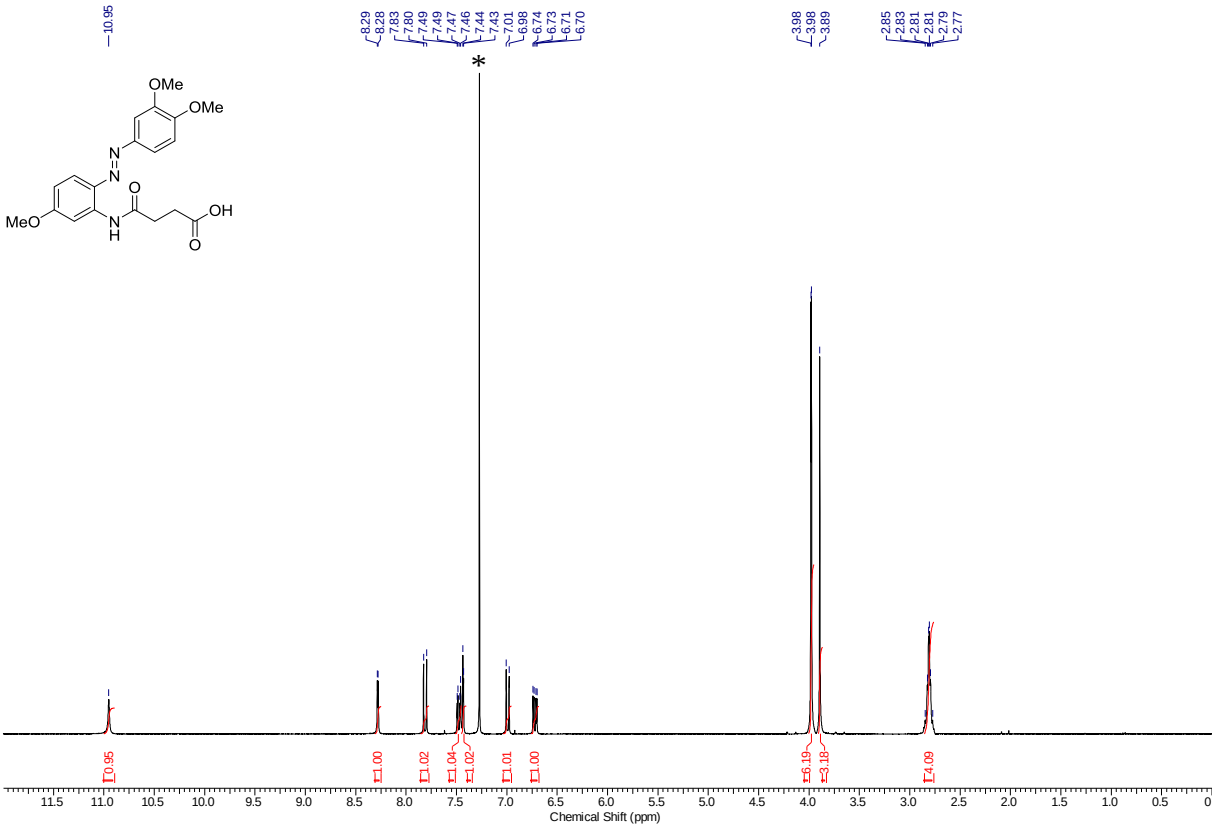
^{1}H-NMR (250 MHz, $CDCl_3$) and ^{13}C-NMR (63 MHz, $CDCl_3$) spectrum of compound **10b**. * = NMR-solvent, H_2O

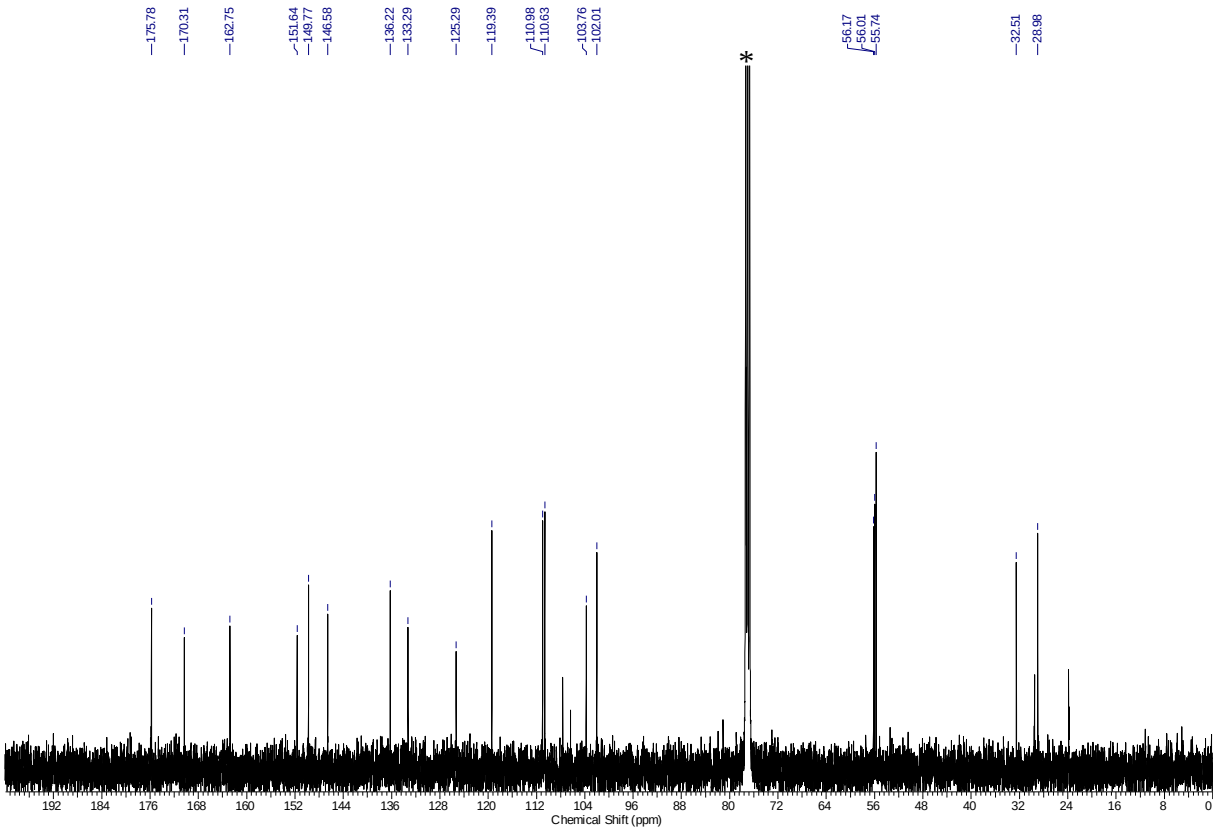


^{1}H-NMR (250 MHz, $CDCl_3$) and ^{13}C-NMR (63 MHz, $CDCl_3$) spectrum of compound **10c**. * = NMR-solvent, H_2O

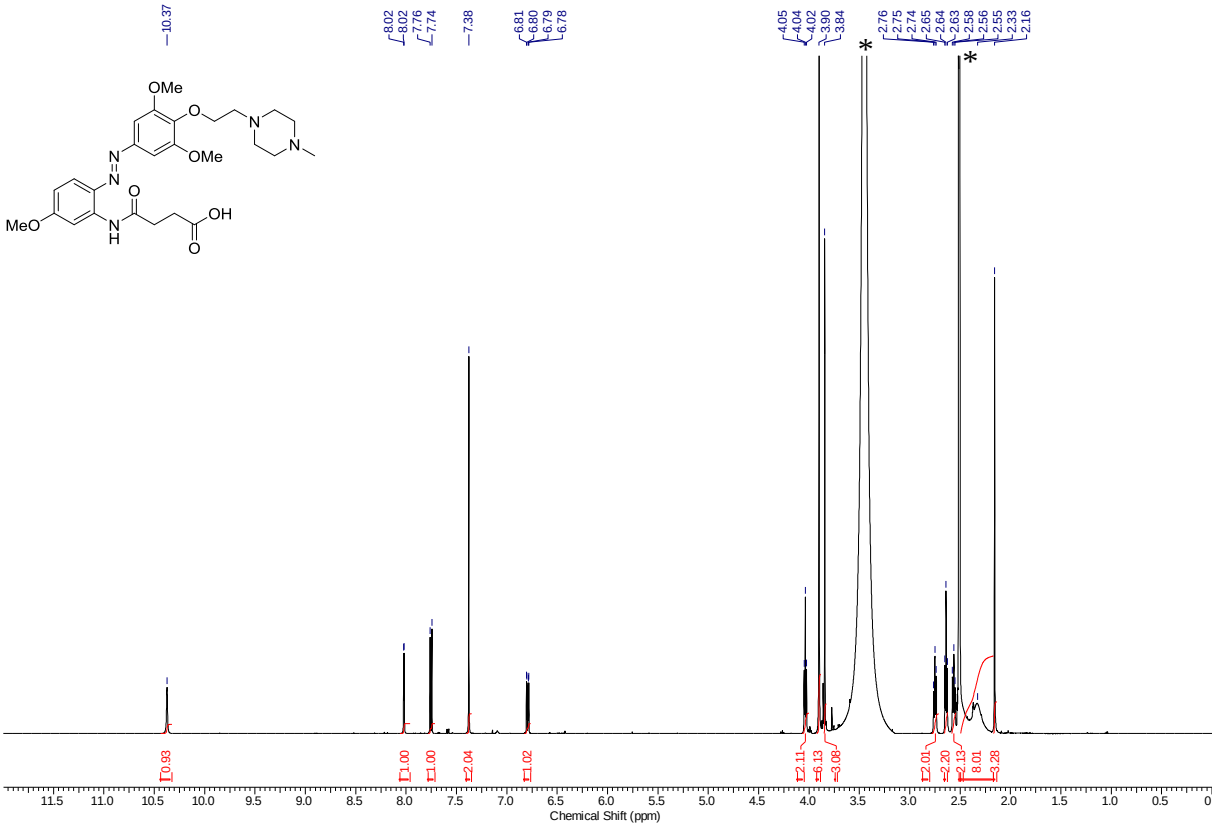


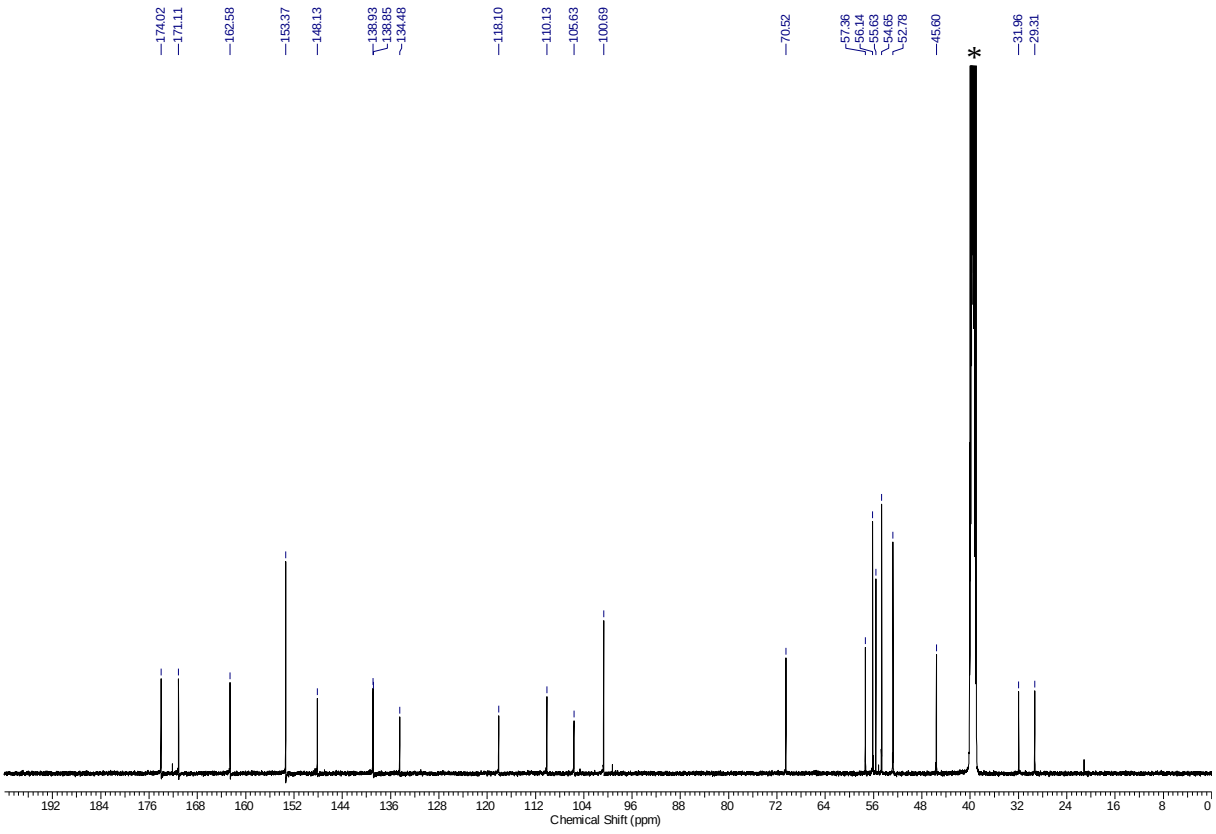
^{1}H-NMR (400 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **10d**. * = NMR-solvent, H_2O



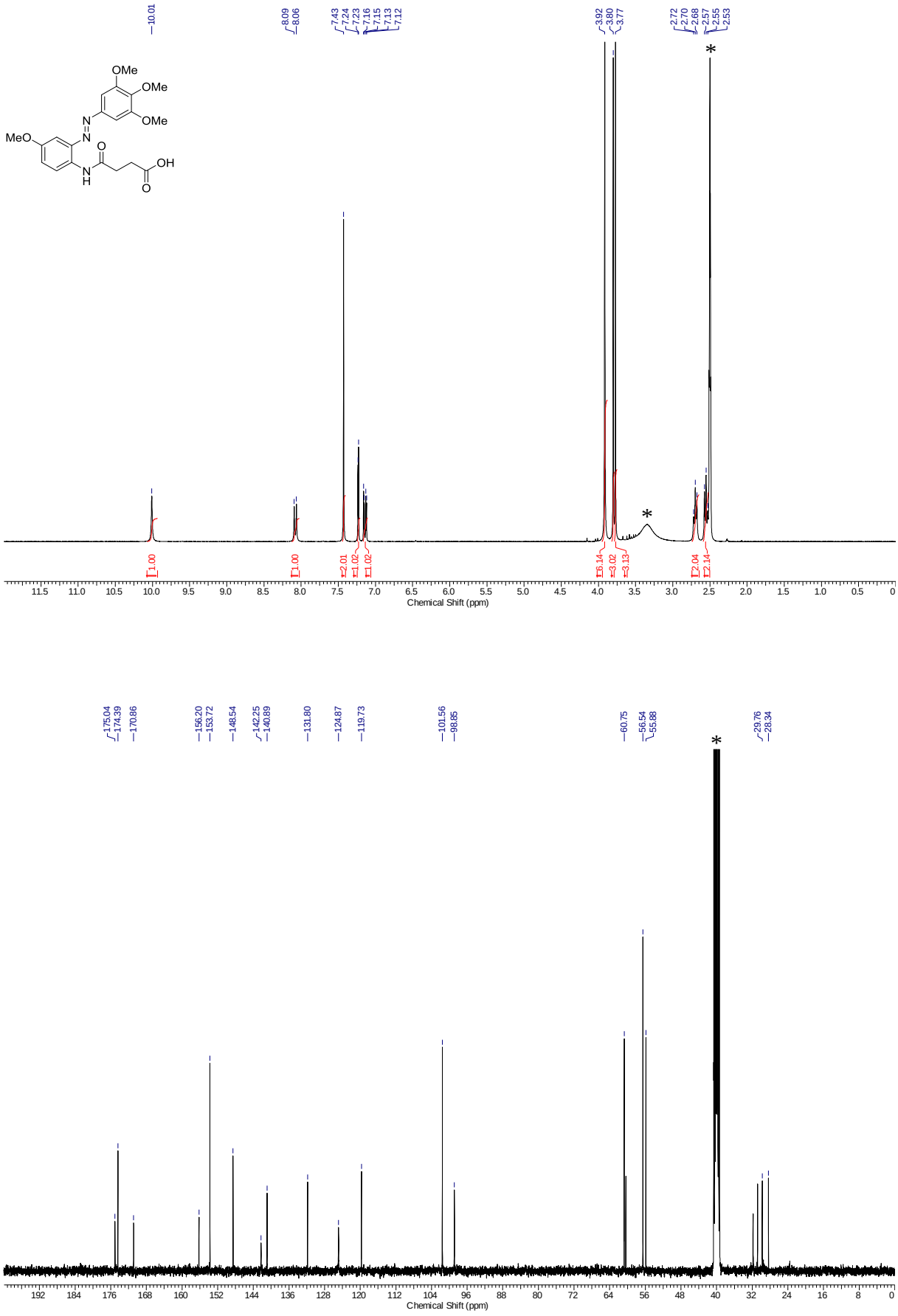


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **11a**. * = NMR-solvent

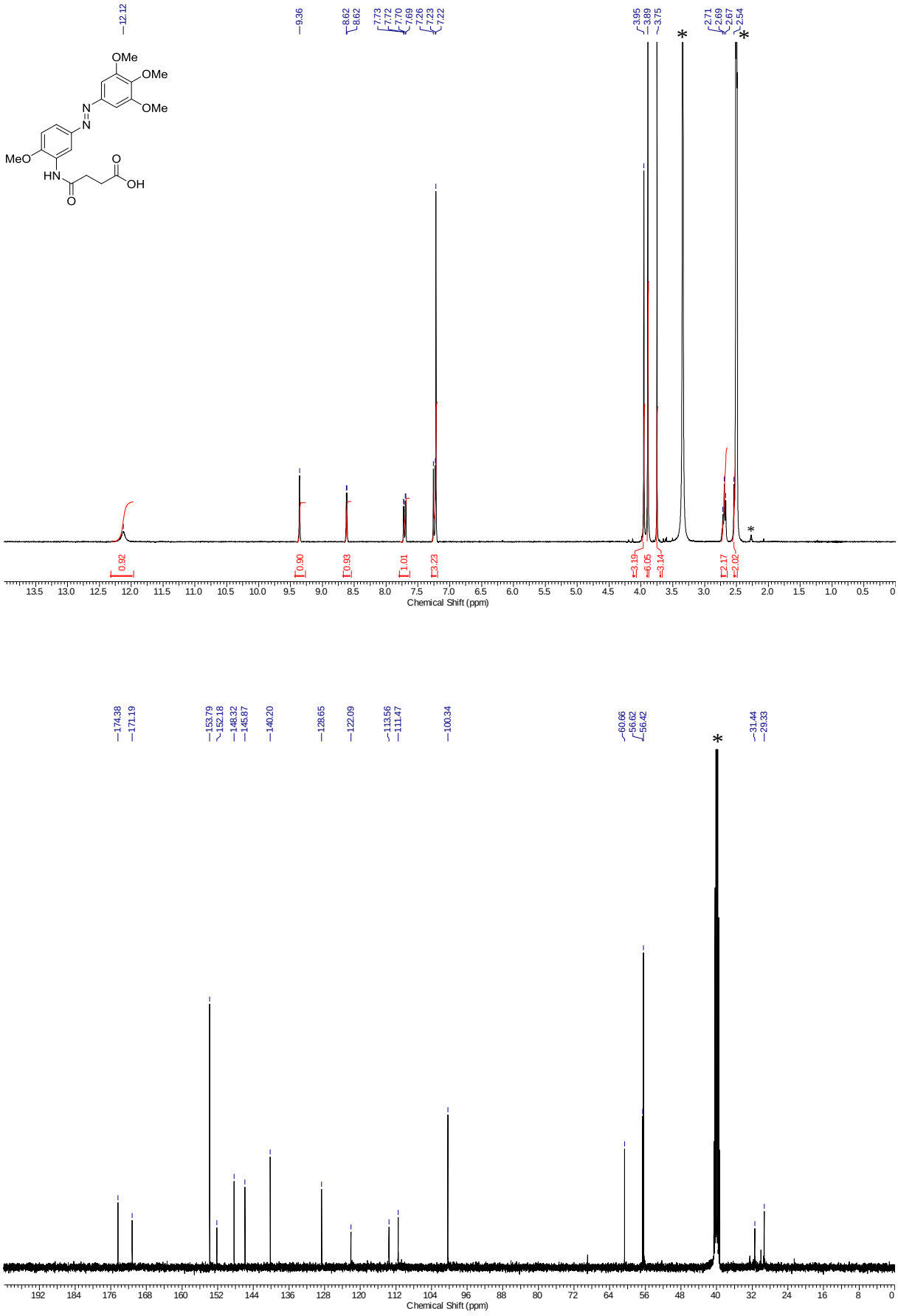




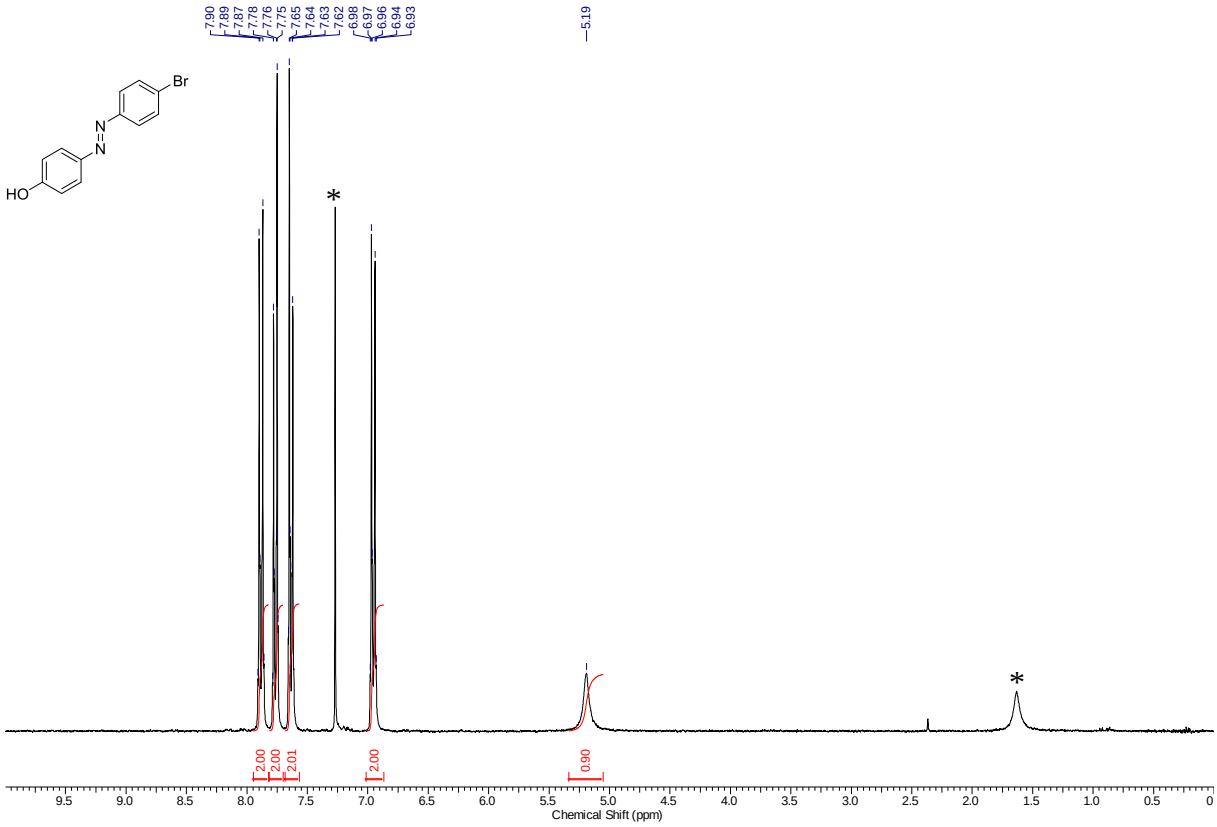
^{1}H-NMR (500 MHz, DMSO-d_6) and ^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of compound **11b**. * = NMR-solvent, H_2O

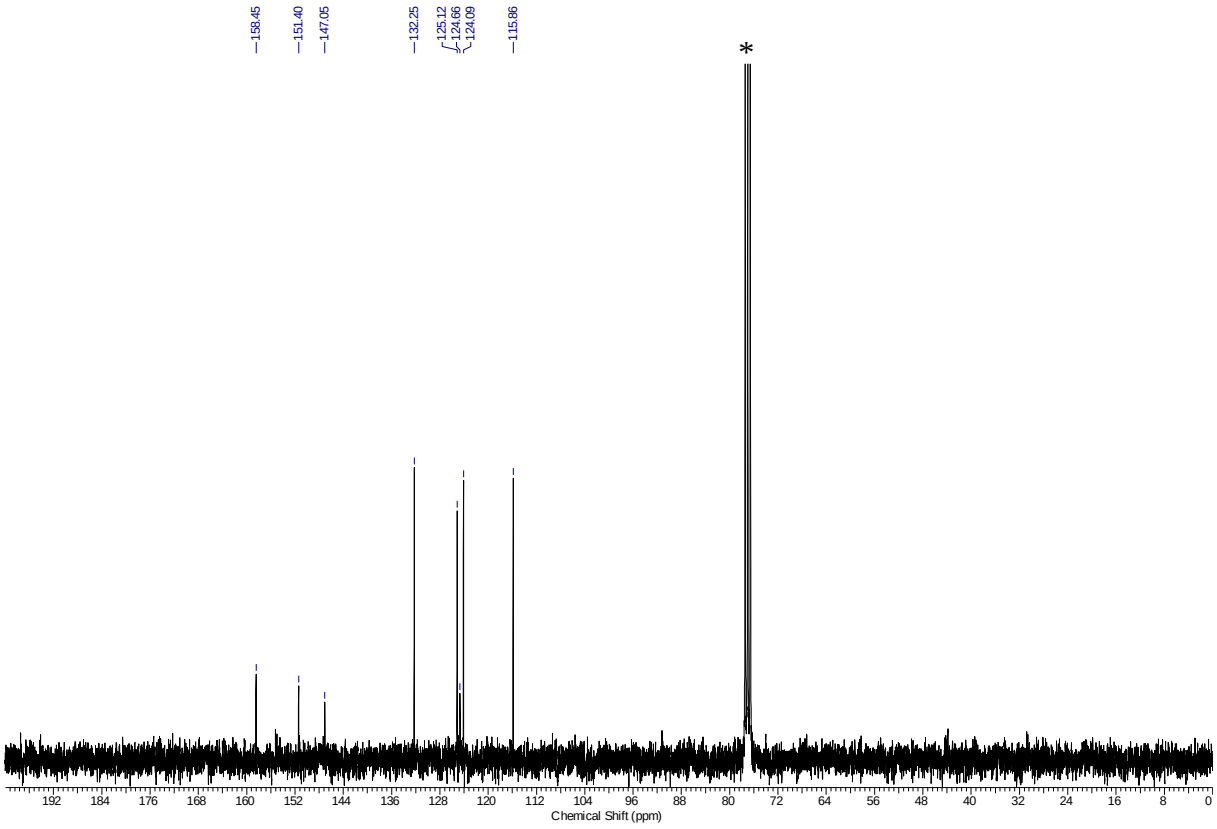


^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **11c**. * = NMR-solvent, H_2O

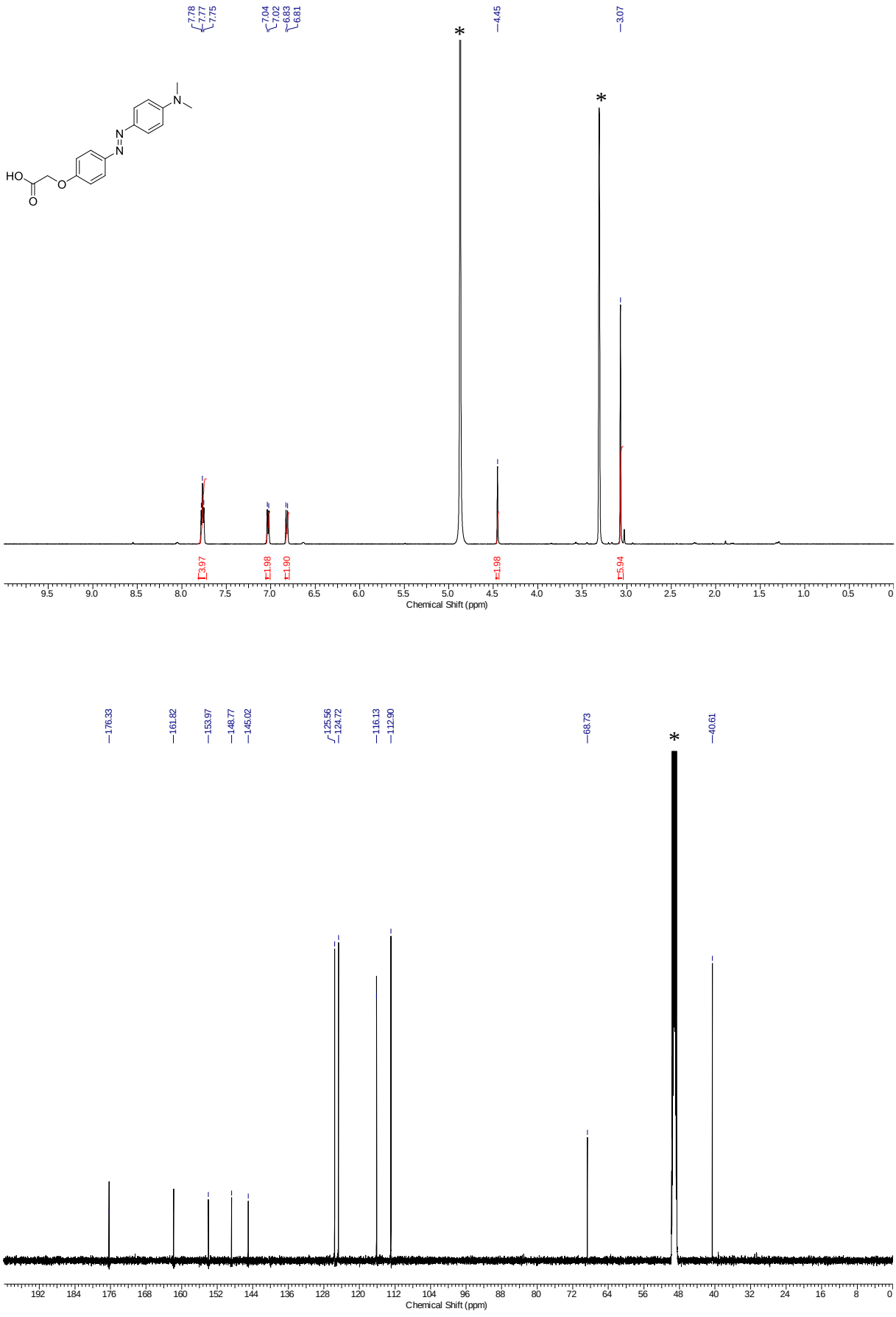


^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **12**. * = NMR-solvent, H_2O

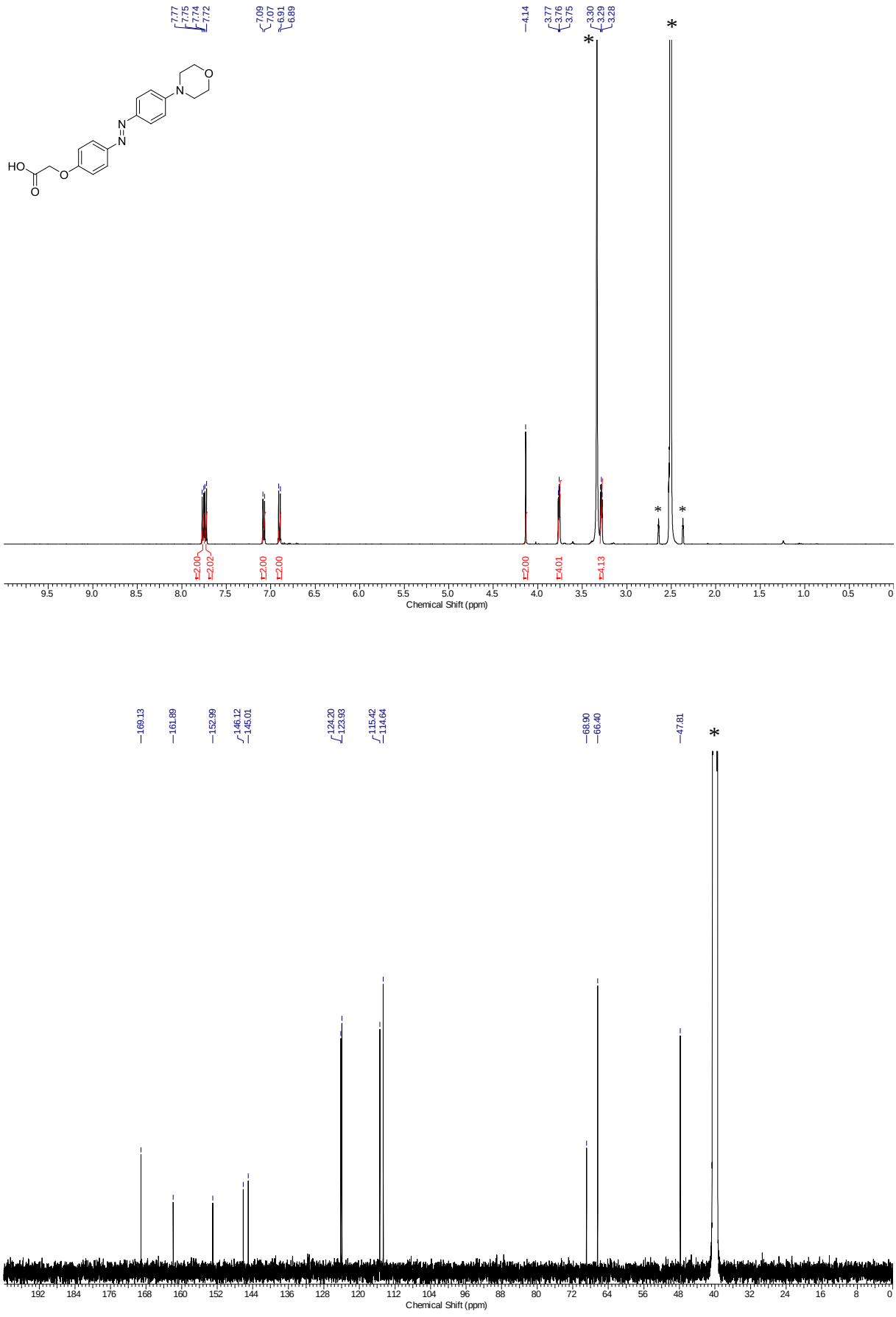




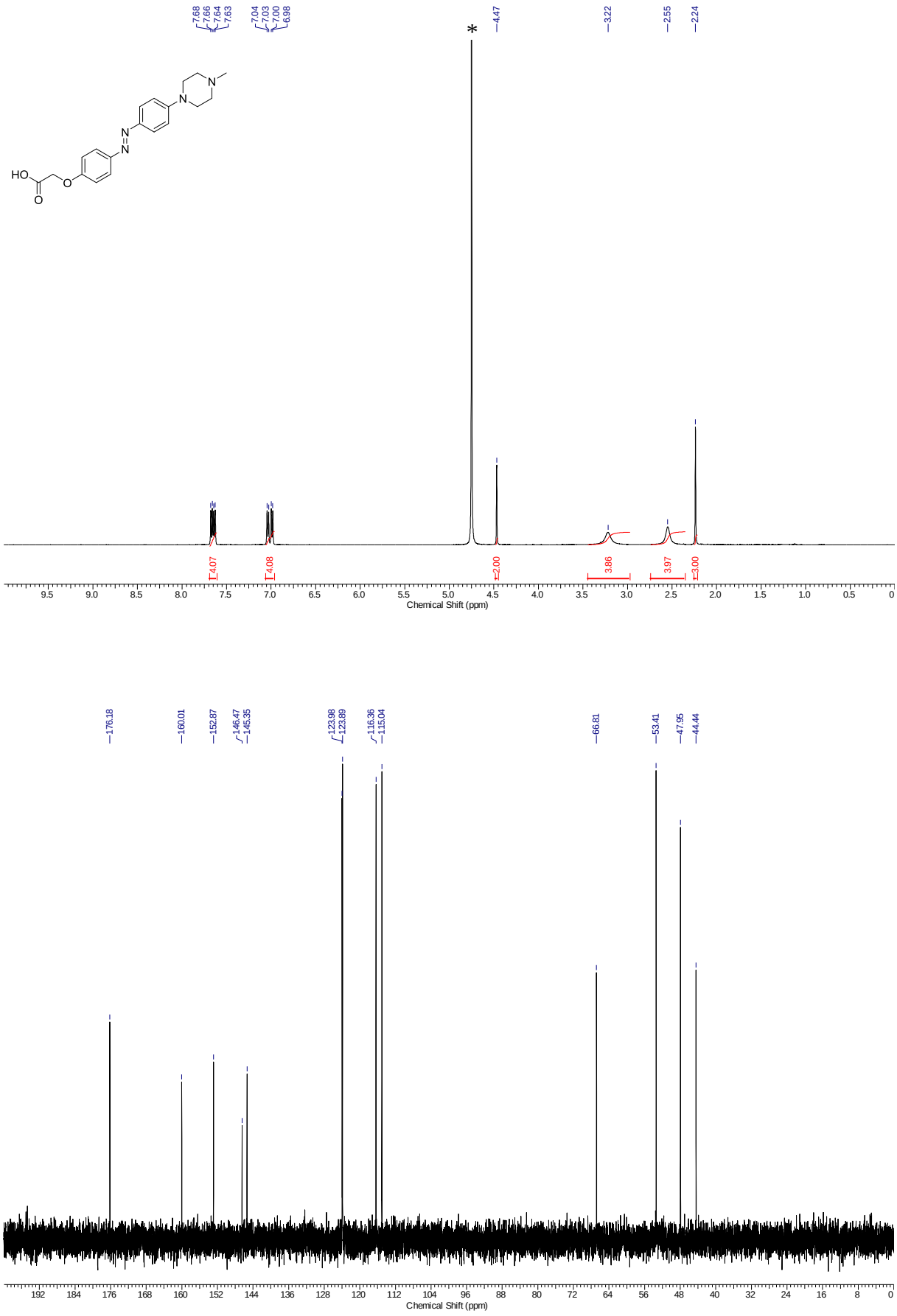
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **15**. * = NMR-solvent, H_2O



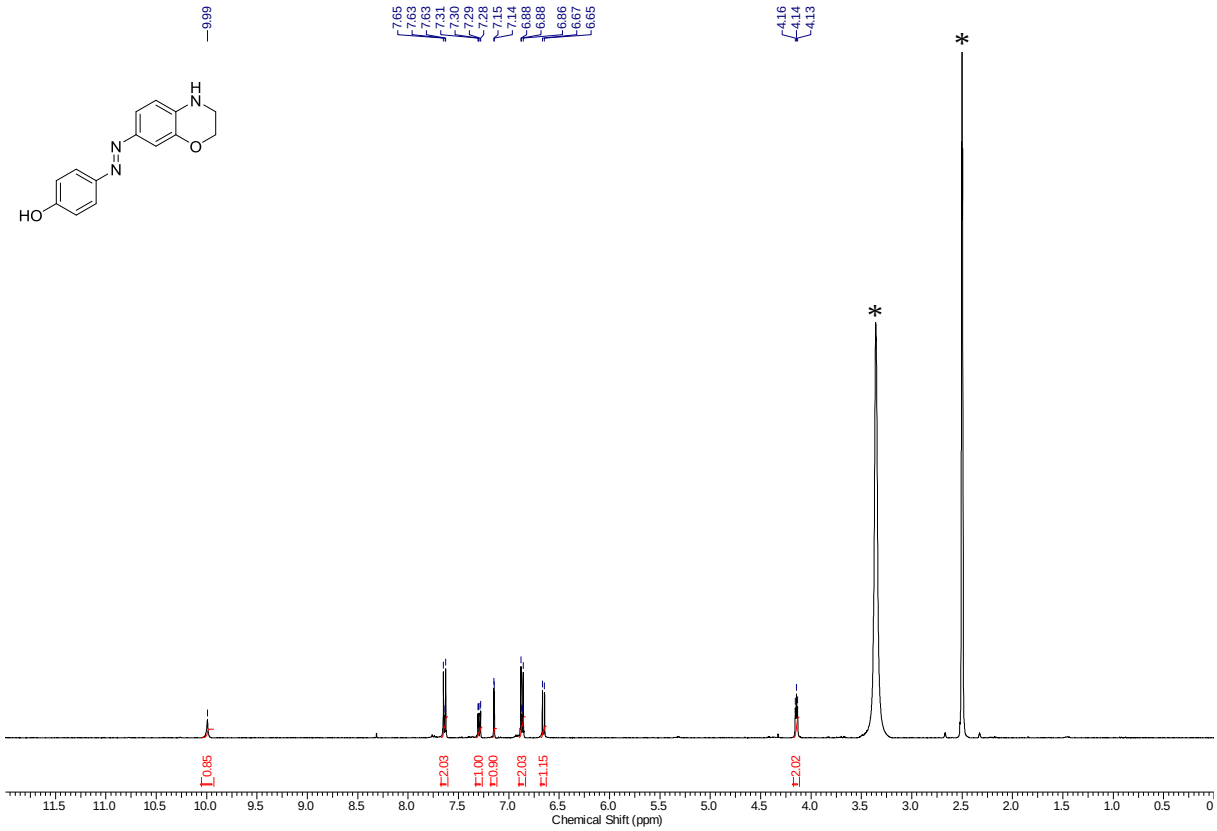
^{1}H-NMR (500 MHz, CD_3OD) and ^{13}C-NMR (126 MHz, CD_3OD) spectrum of compound **16b**. * = NMR-solvent, H_2O

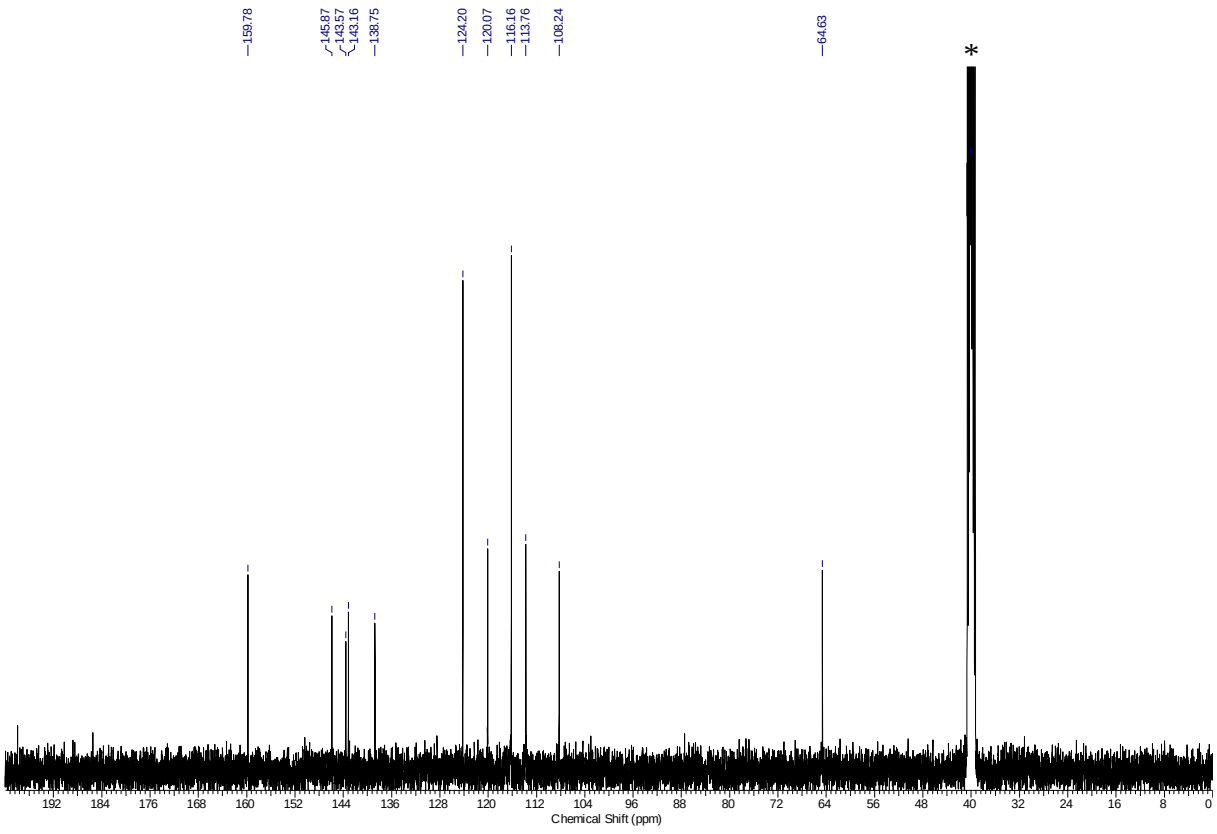


^{1}H-NMR (500 MHz, DMSO-d_6) and ^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of compound **16c**. * = NMR-solvent, H_2O

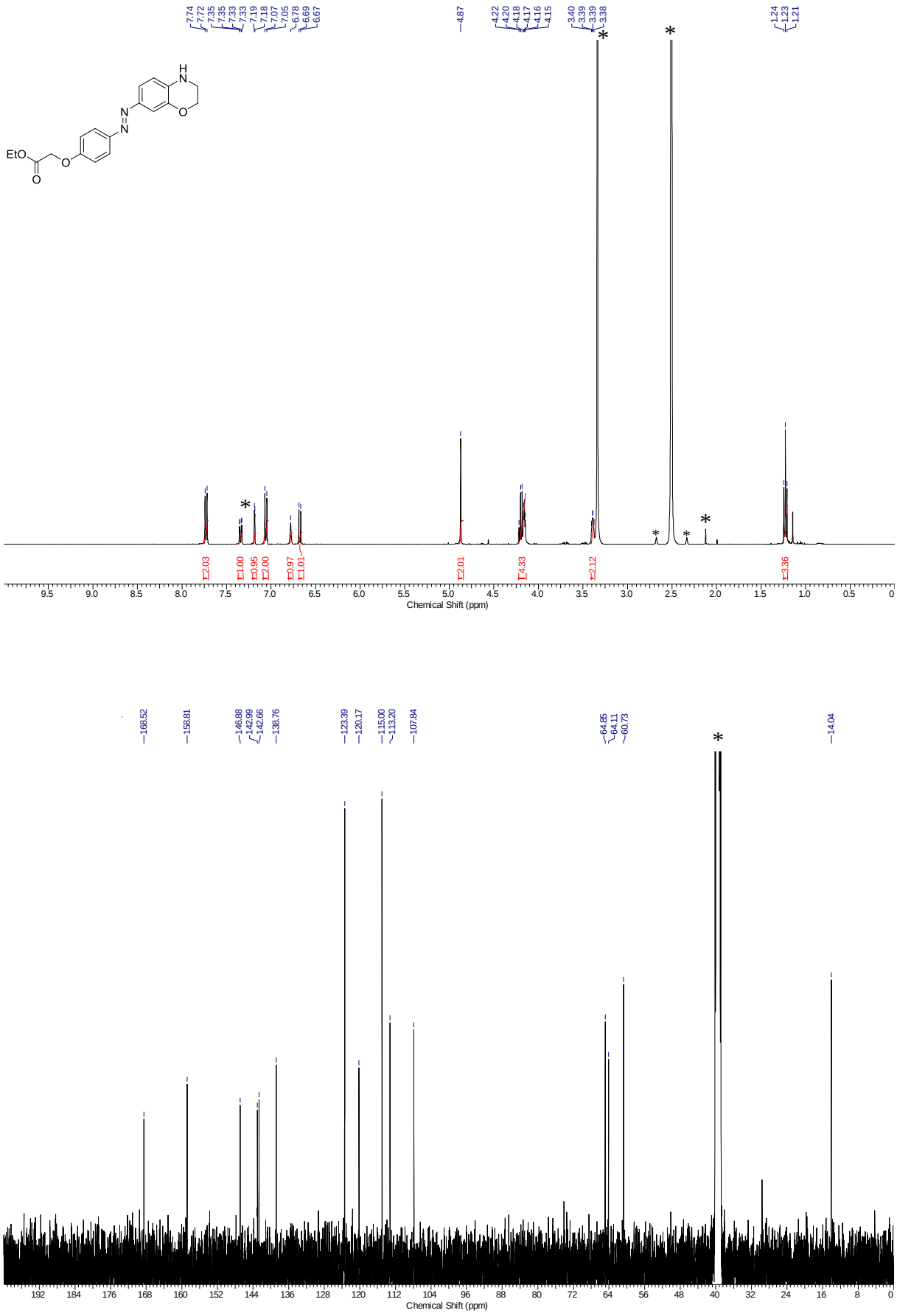


^{1}H-NMR (500 MHz, D_2O) and ^{13}C-NMR (126 MHz, D_2O) spectrum of compound **16d**. * = NMR-solvent

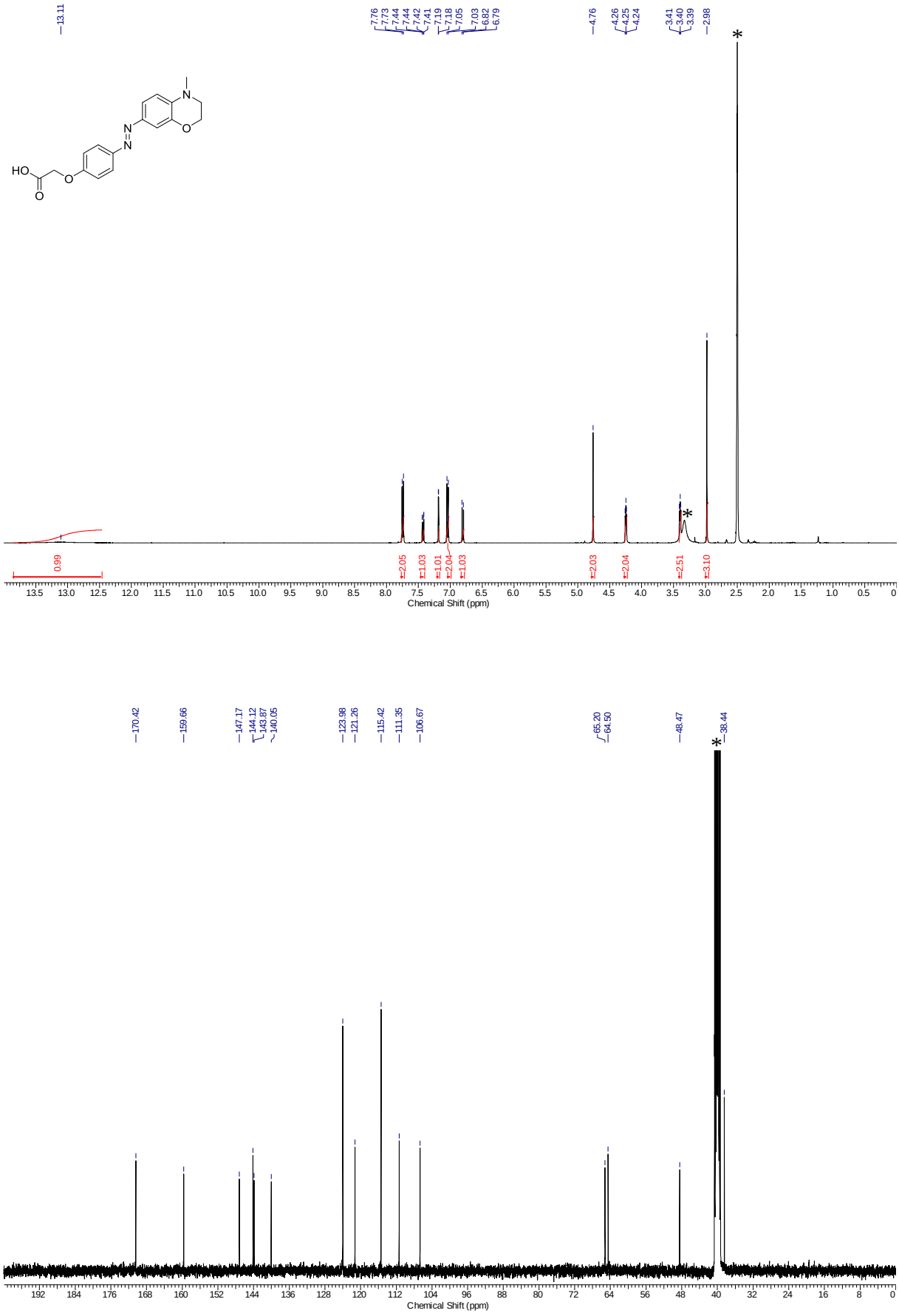




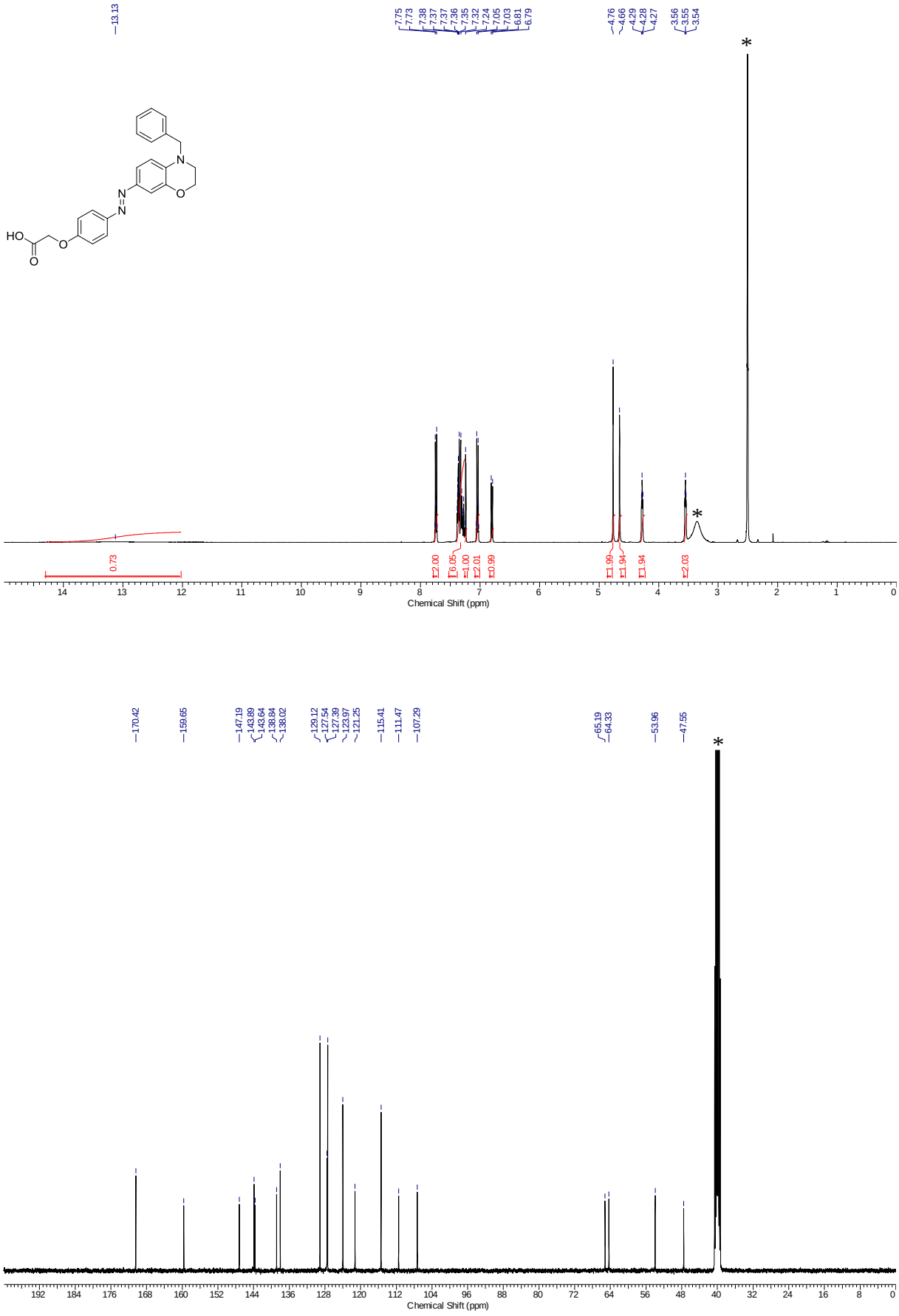
^{1}H-NMR (400 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **18**. * = H_2O



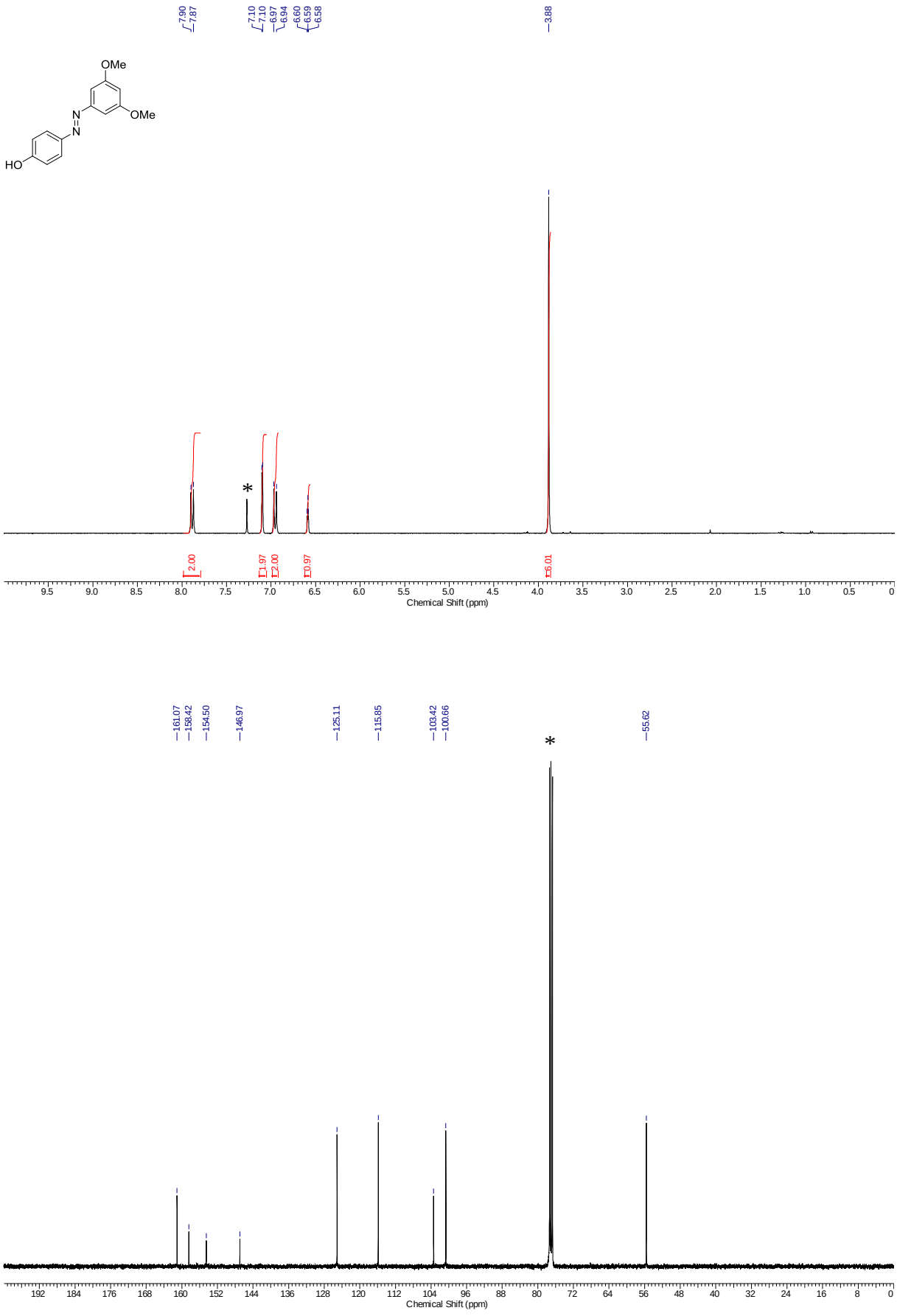
^{1}H-NMR (400 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **19**. * = NMR-solvent, H_2O, CH_3CN



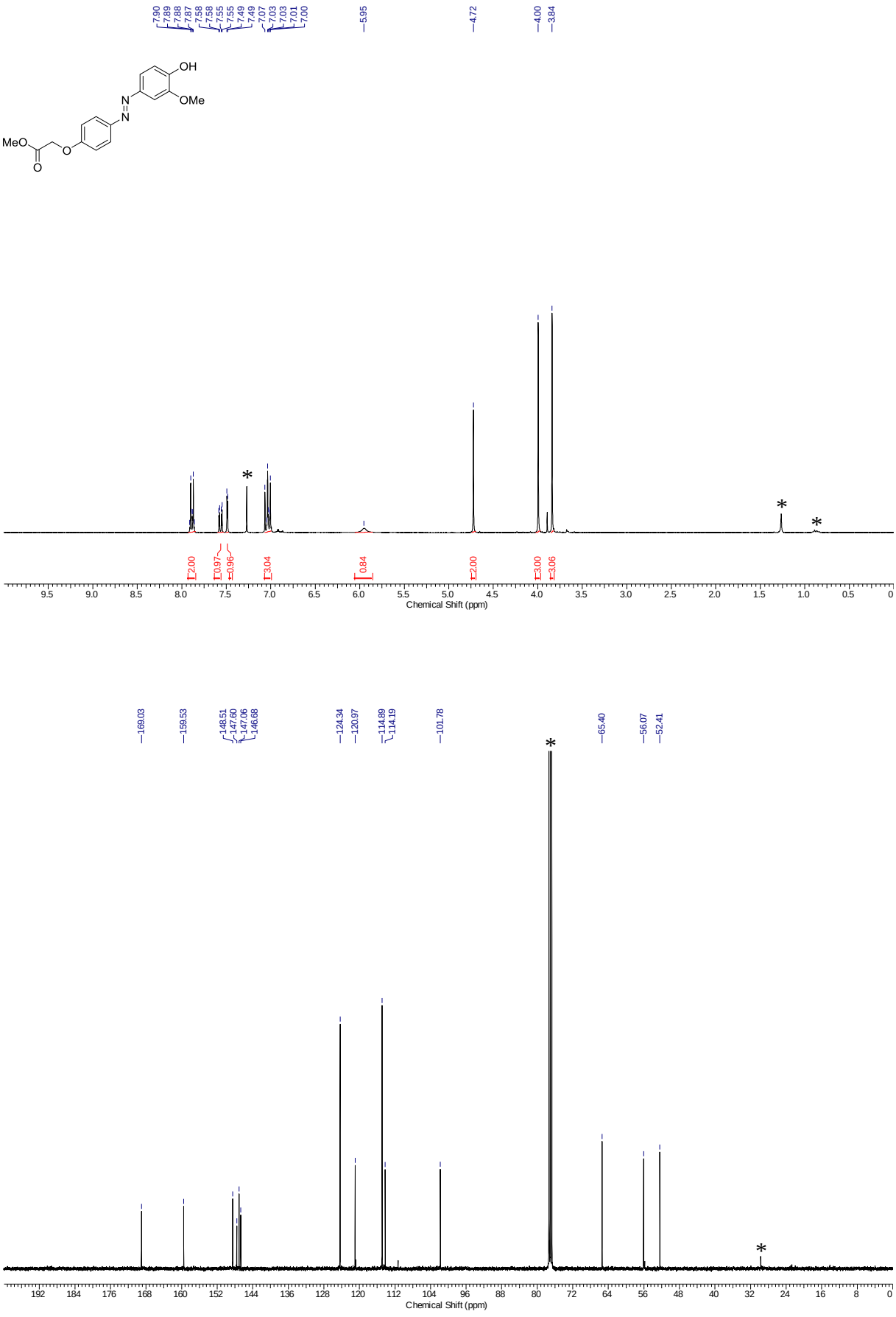
^{1}H-NMR (400 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **20a**. * = NMR-solvent, H_2O



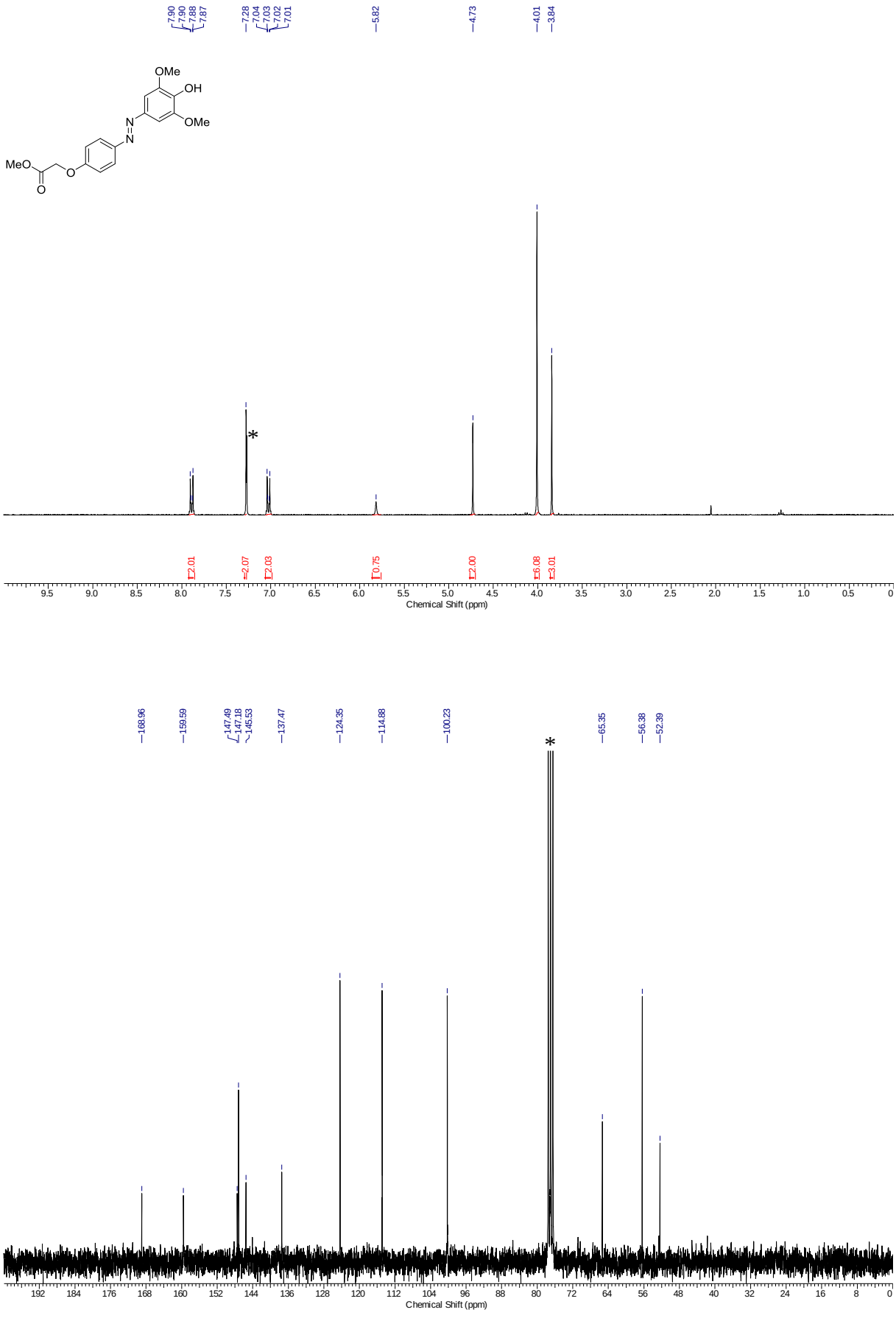
^{1}H-NMR (400 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **20b**. * = NMR-solvent, H_2O



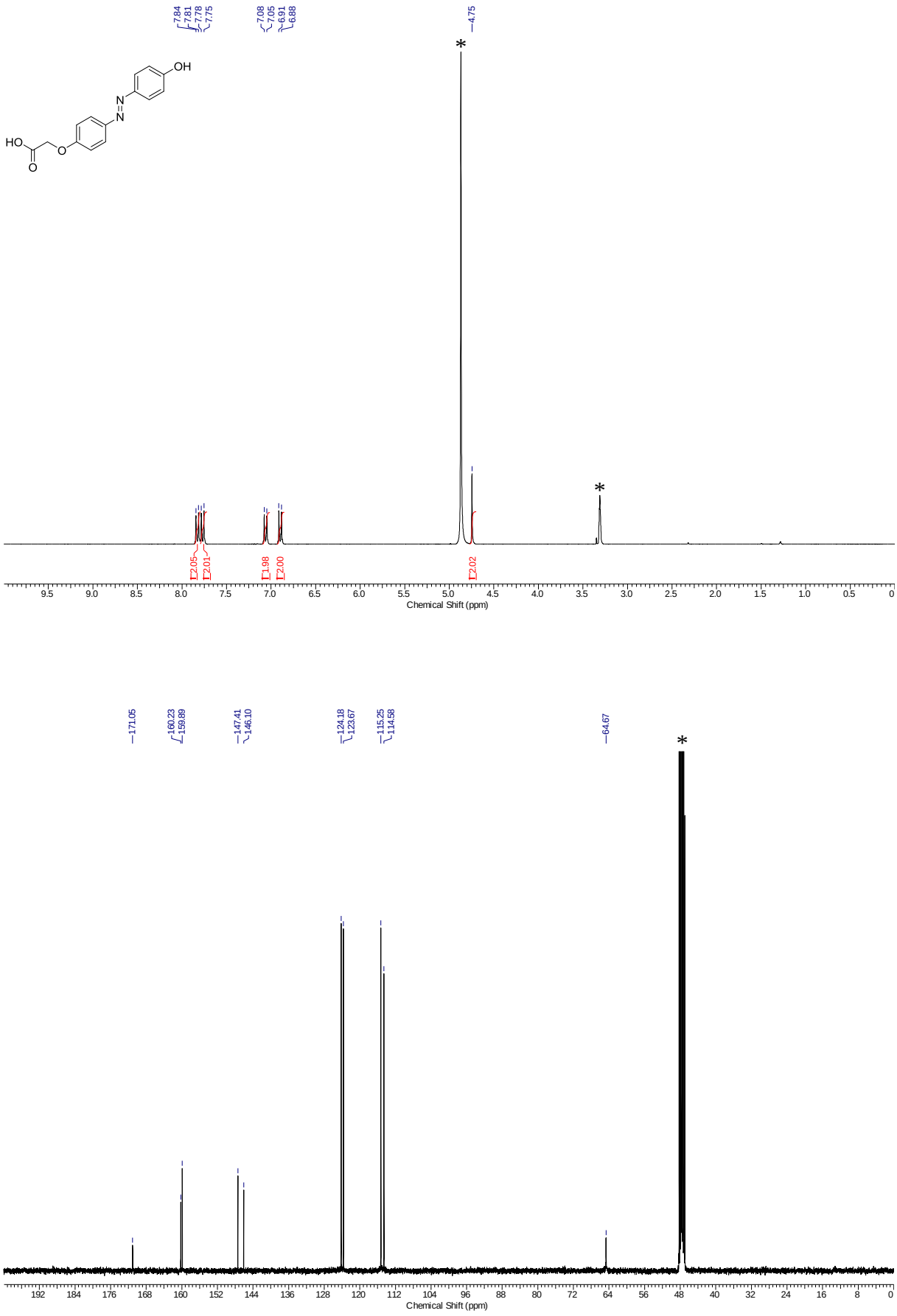
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **22**. * = NMR-solvent



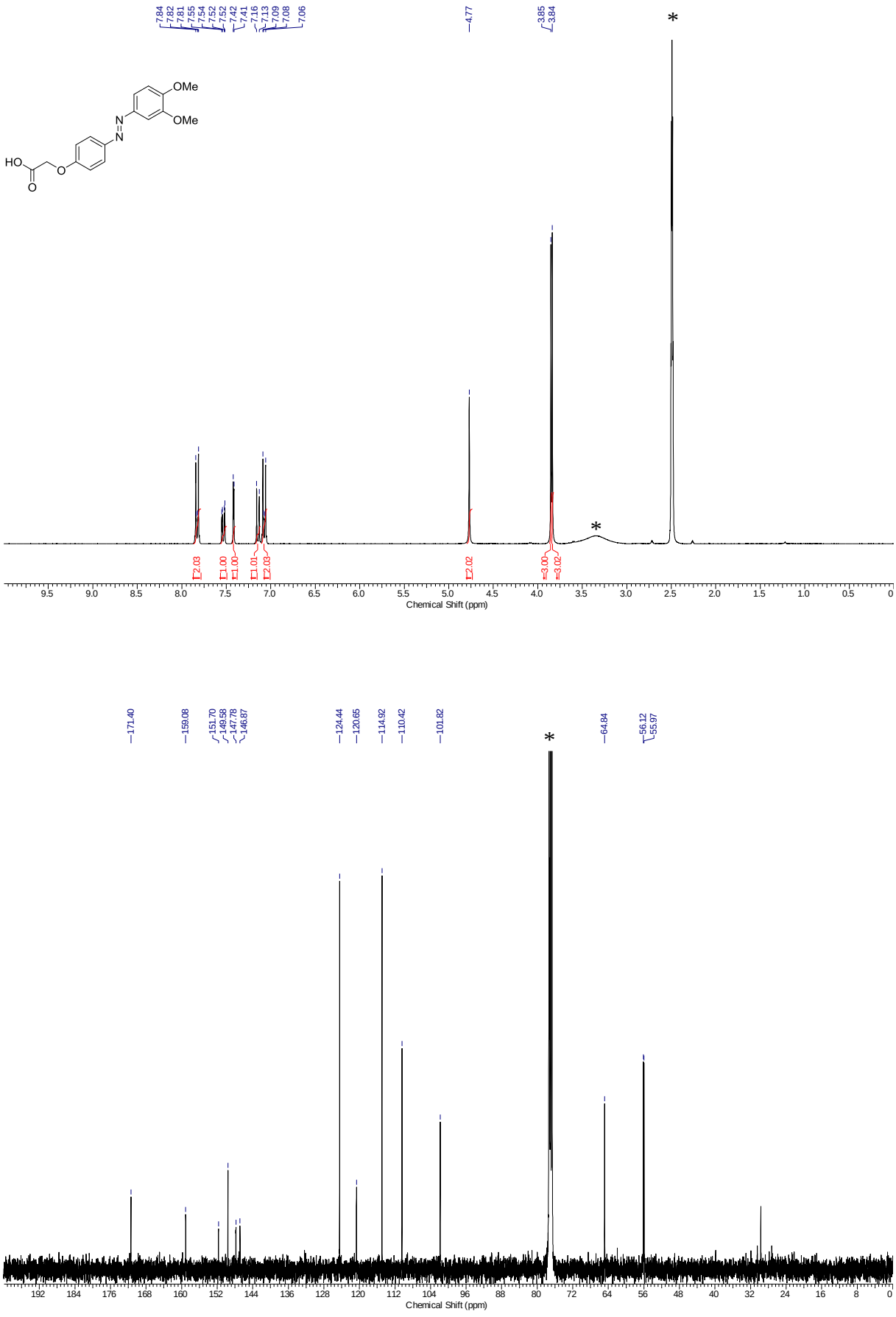
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **25a**. * = NMR-solvent, grease



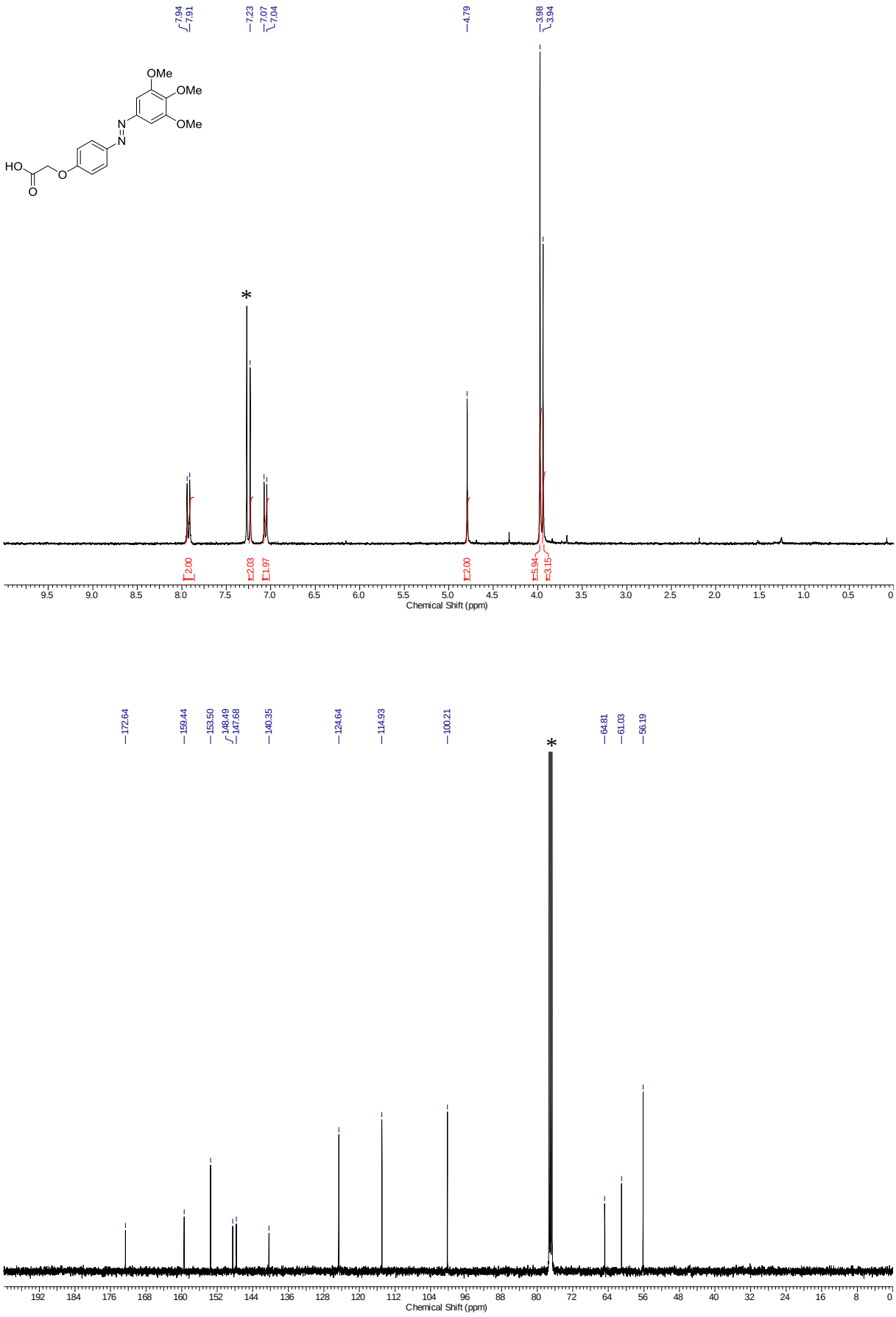
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (63 MHz, $CDCl_3$) spectrum of compound **25b**. * = NMR-solvent



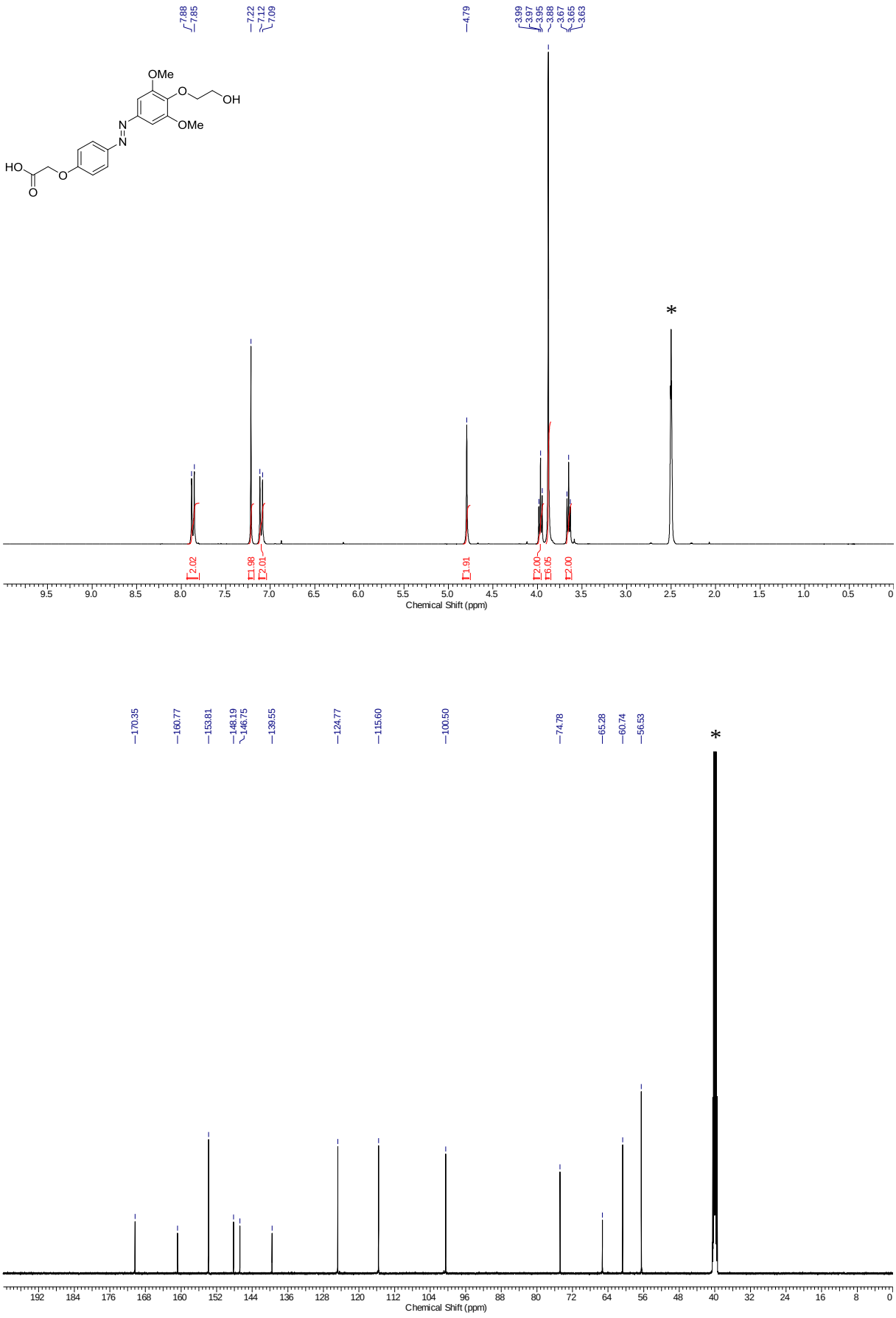
^{1}H-NMR (300 MHz, CD_3OD) and ^{13}C-NMR (101 MHz, CD_3OD) spectrum of compound **25f**. * = NMR-solvent, H_2O



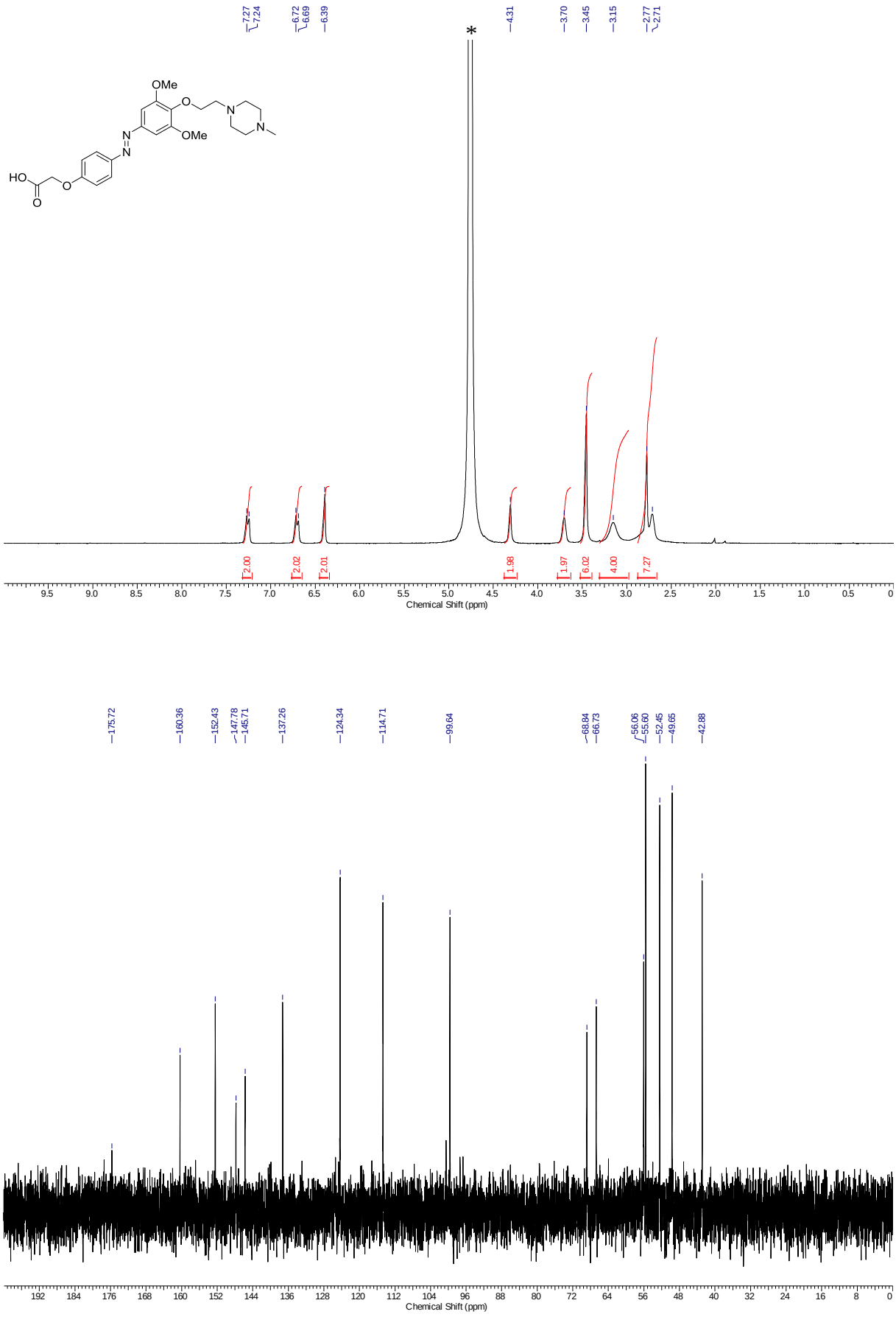
^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **26a**. * = NMR-solvent, H_2O



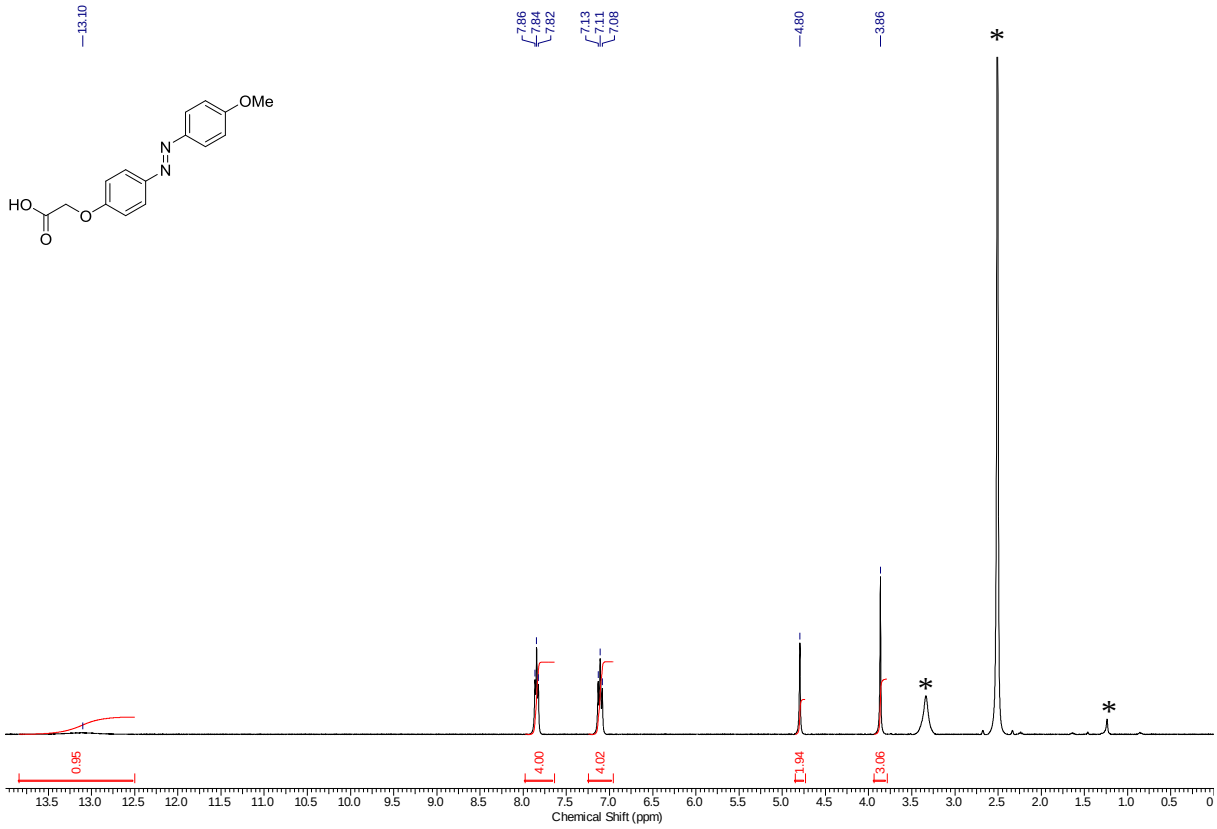
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **26b**. * = NMR-solvent

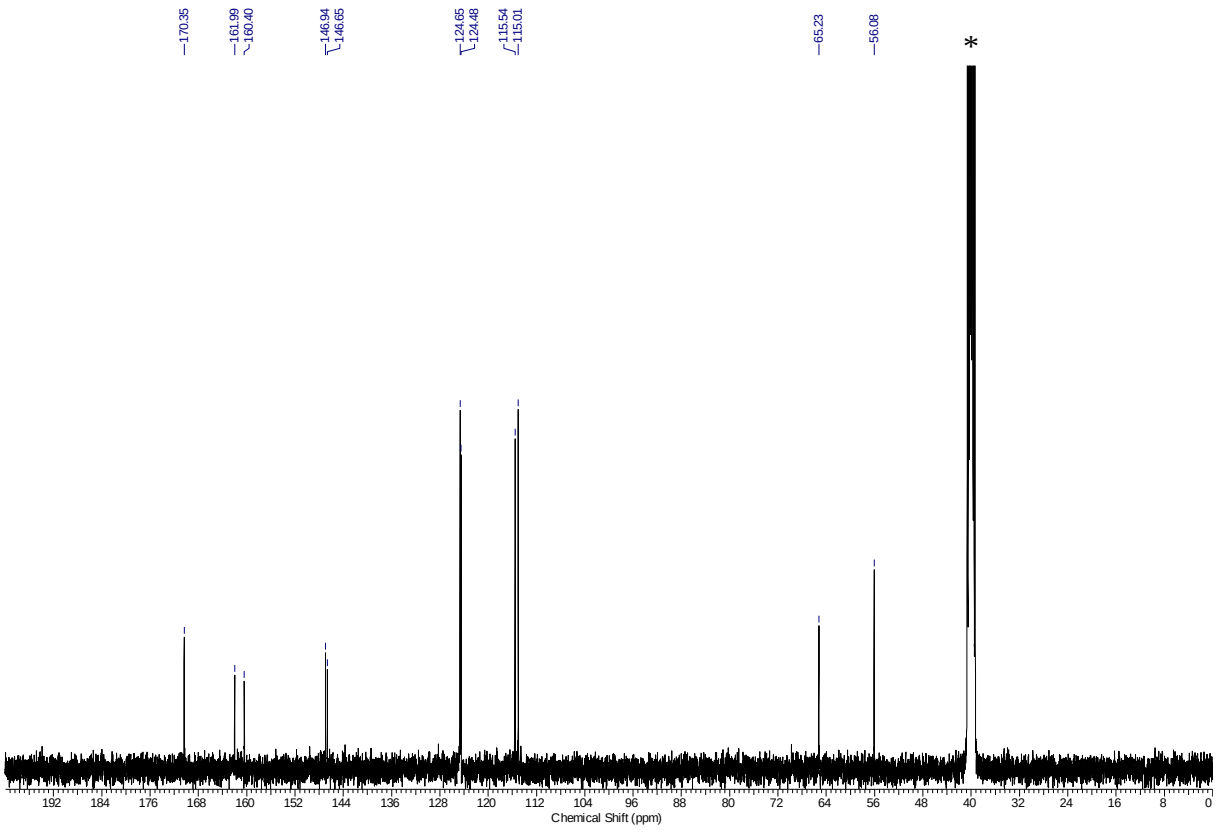


^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of compound **26c**. * = NMR-Solvent

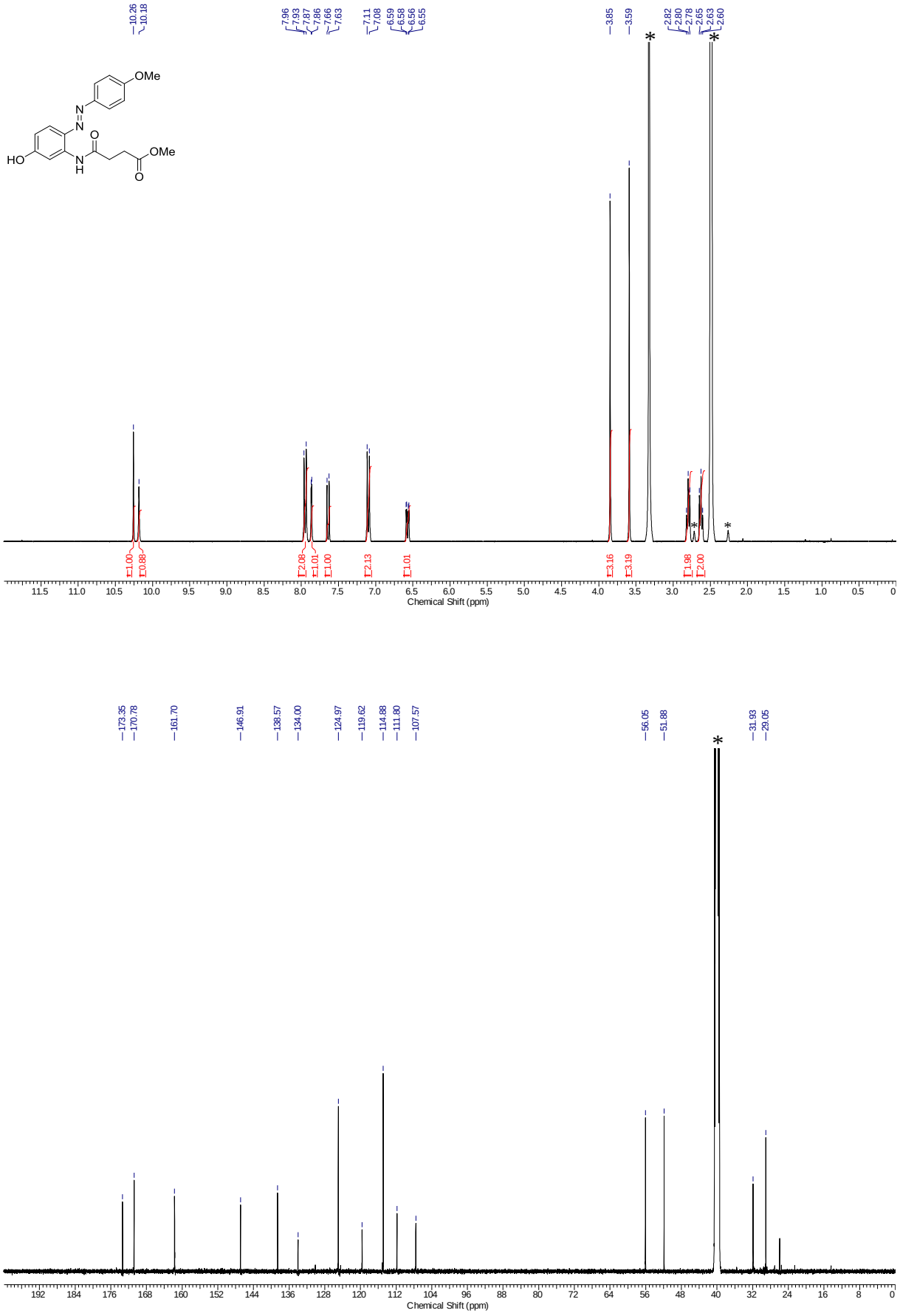


^{1}H-NMR (300 MHz, D_2O) and ^{13}C-NMR (101 MHz, D_2O) spectrum of compound **26e**. * = NMR-Solvent

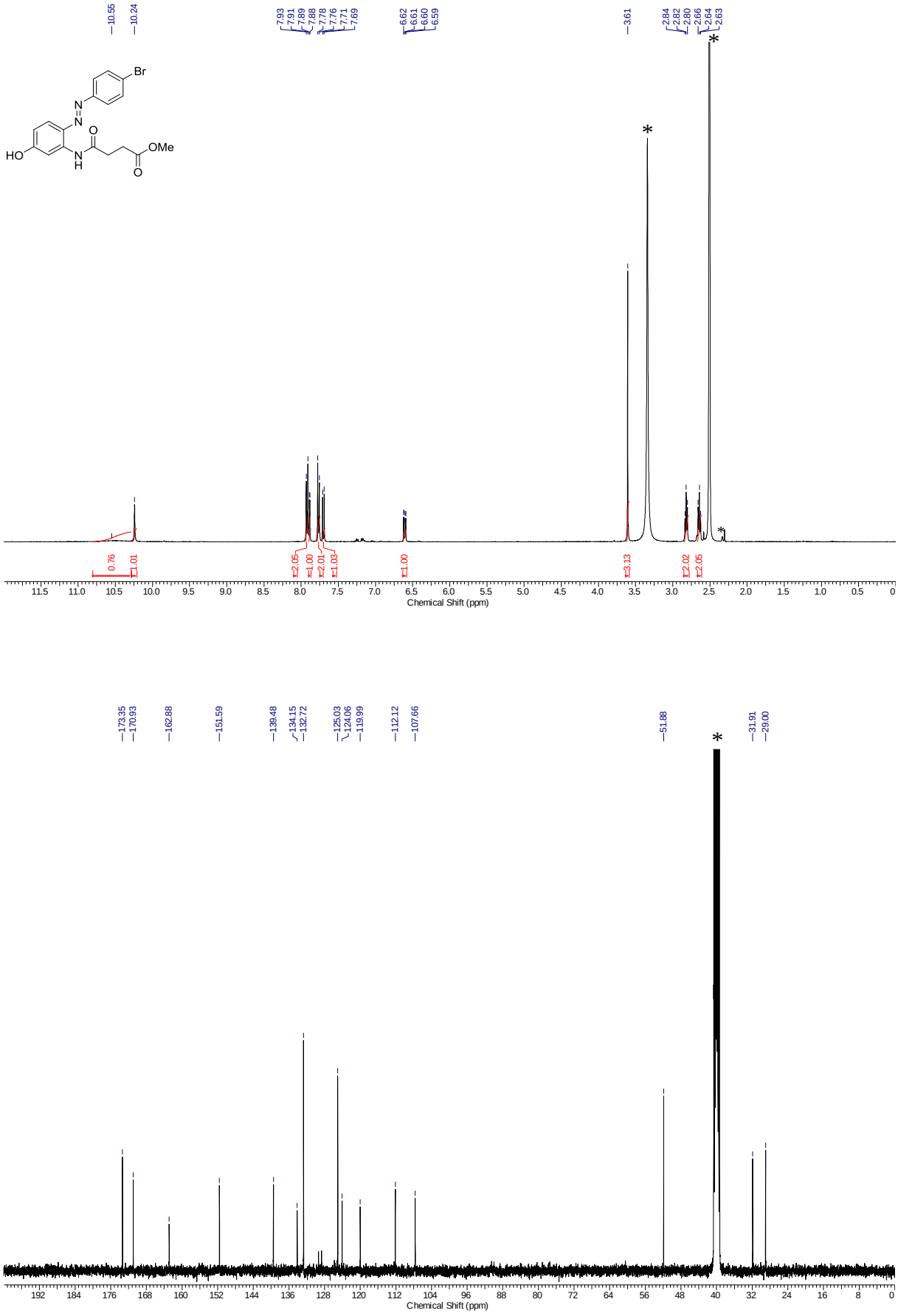




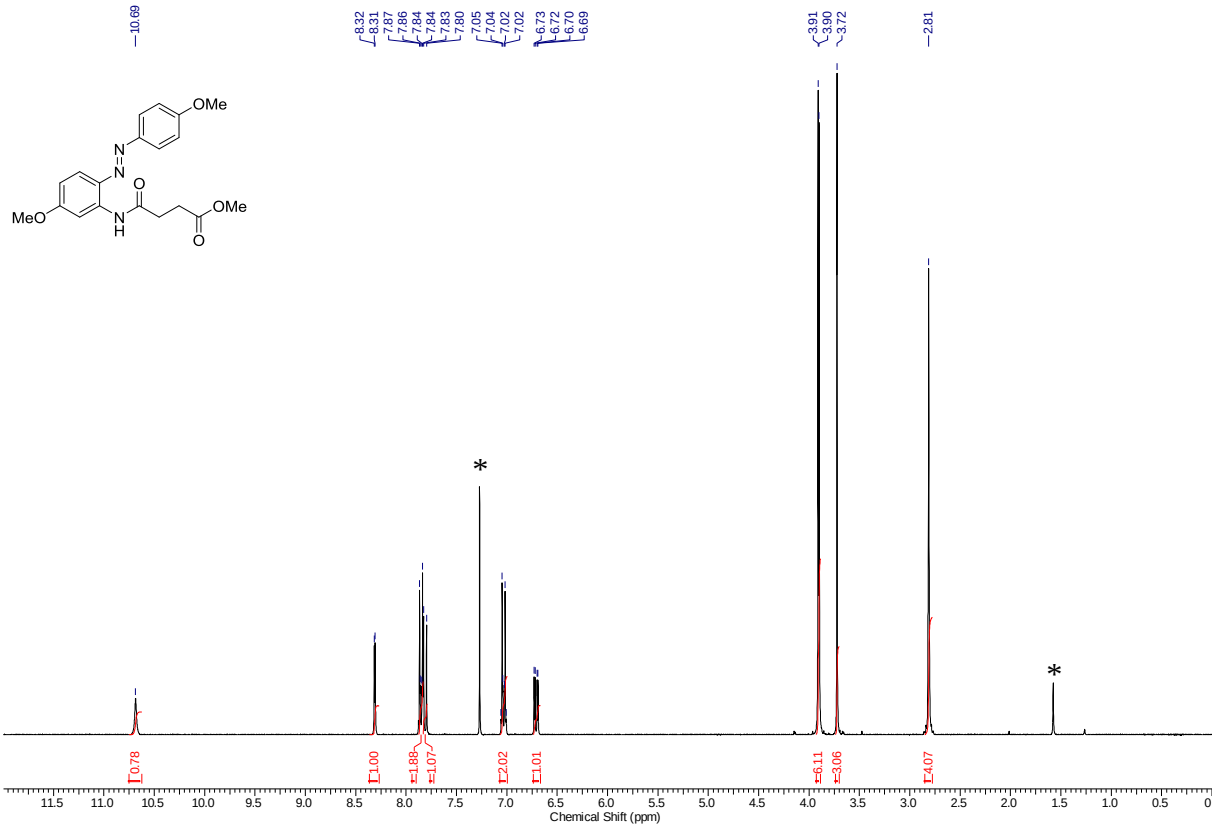
^{1}H-NMR (400 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **26f**. * = NMR-solvent, H_2O, grease

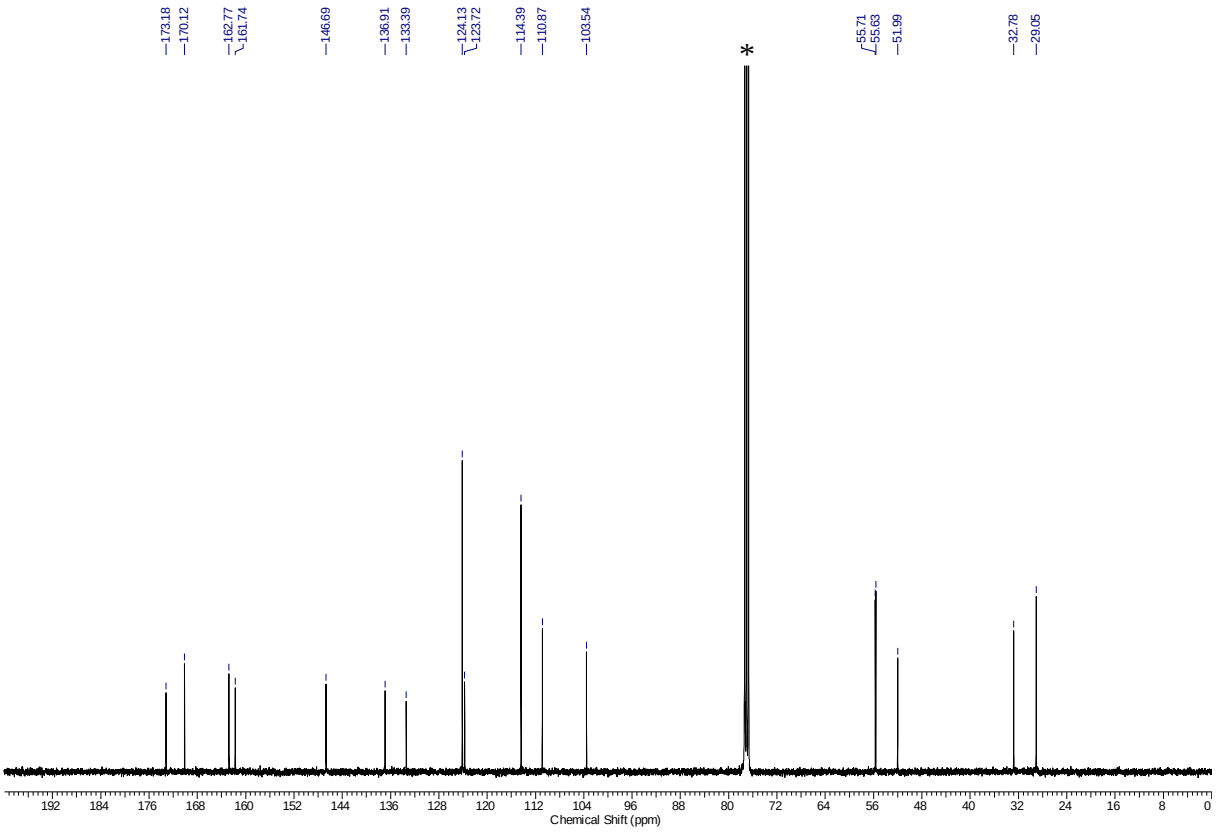


^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of compound **28a**. * = NMR-solvent, H_2O

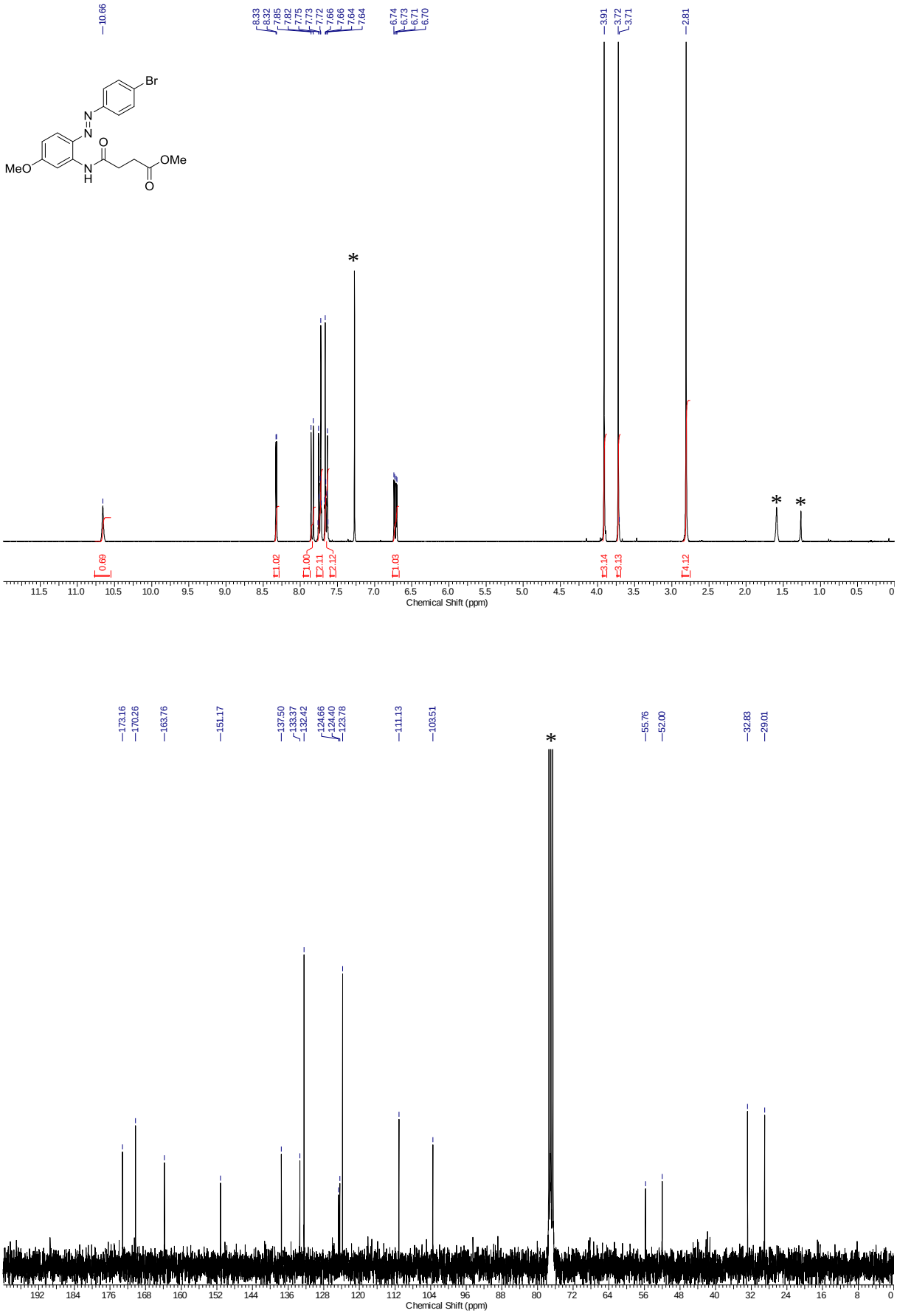


^{1}H-NMR (400 MHz, DMSO-d_6) and ^{13}C-NMR (101 MHz, DMSO-d_6) spectrum of compound **28e**. * = NMR-solvent, H_2O

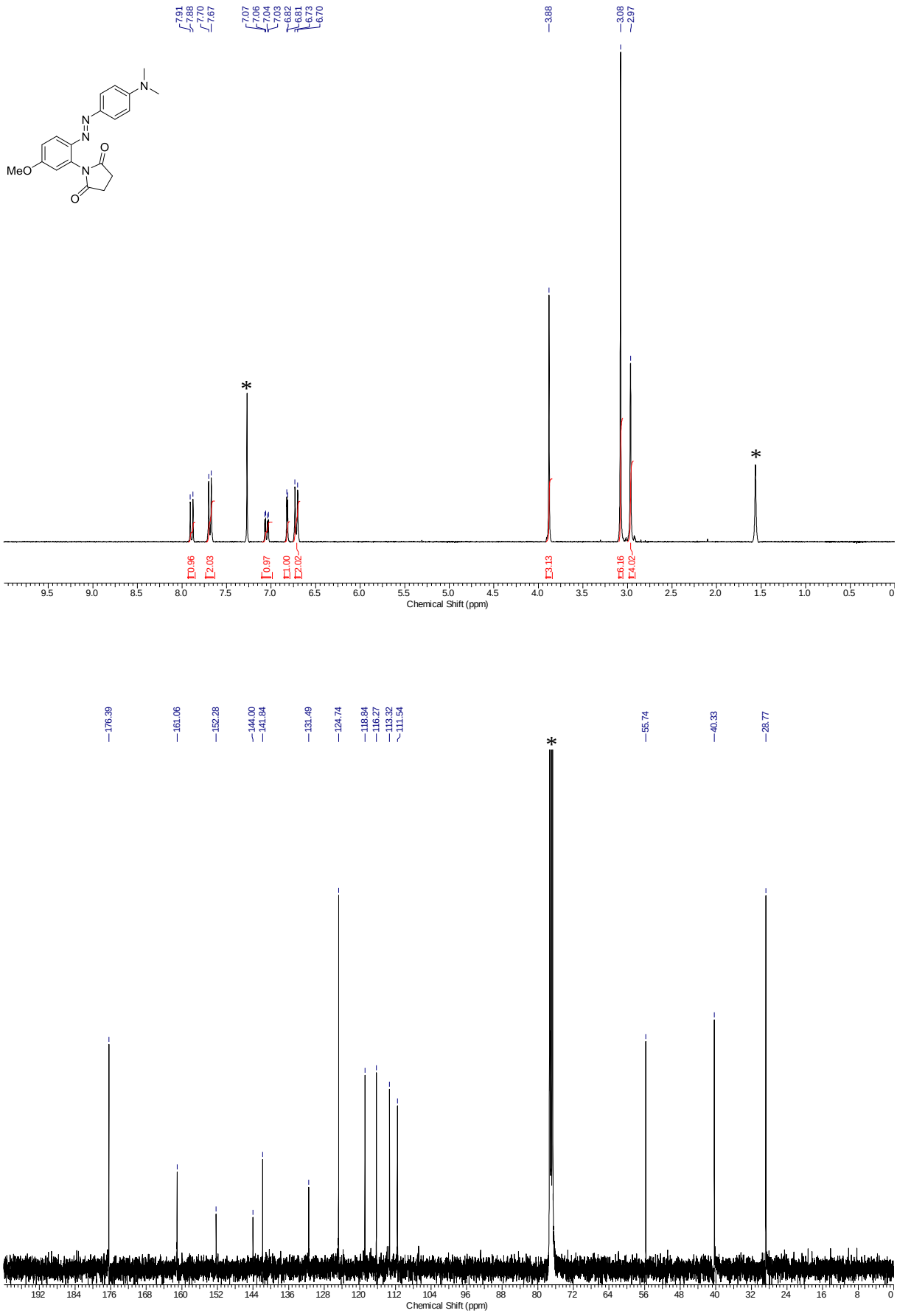




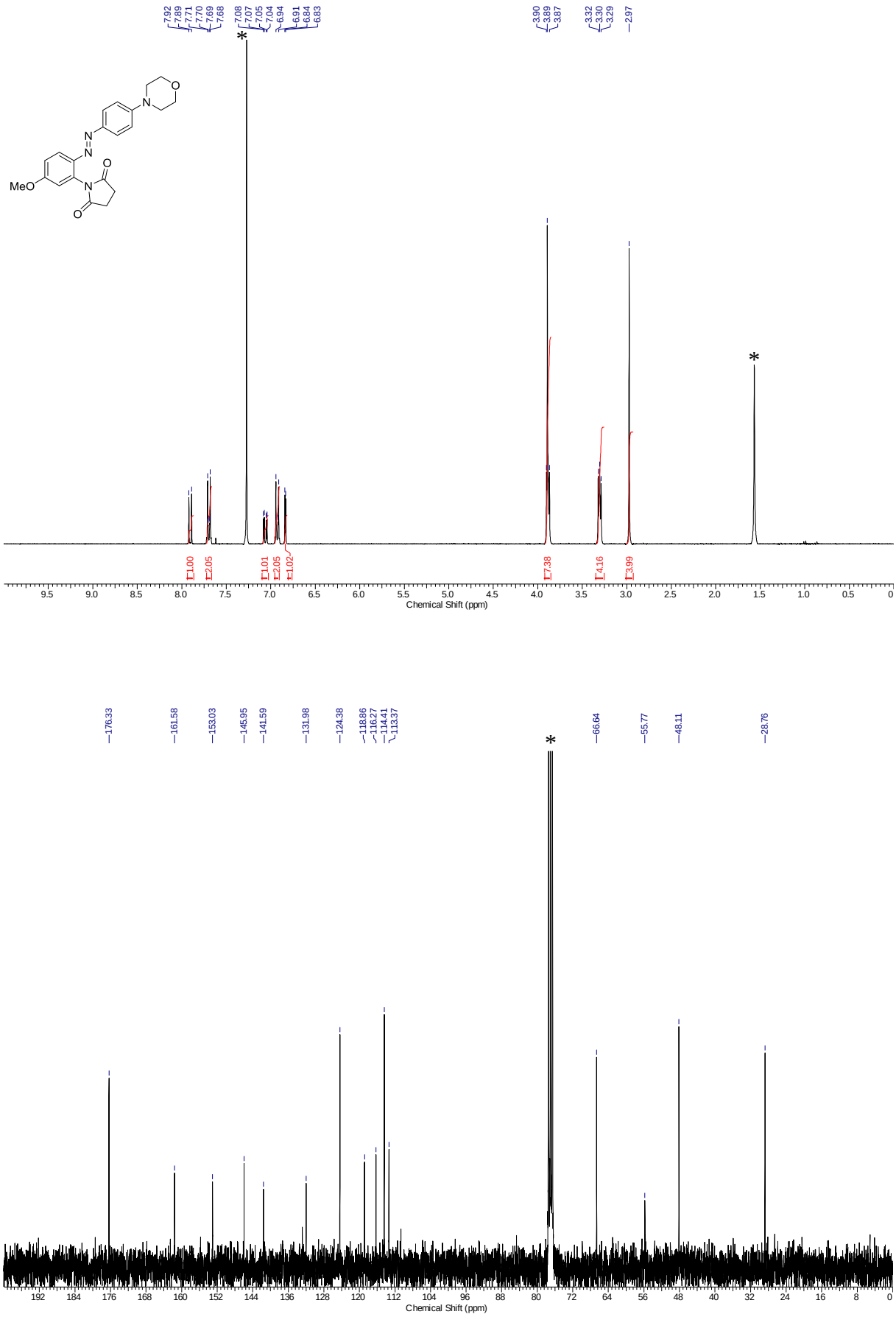
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **29a**. * = NMR-solvent, H_2O



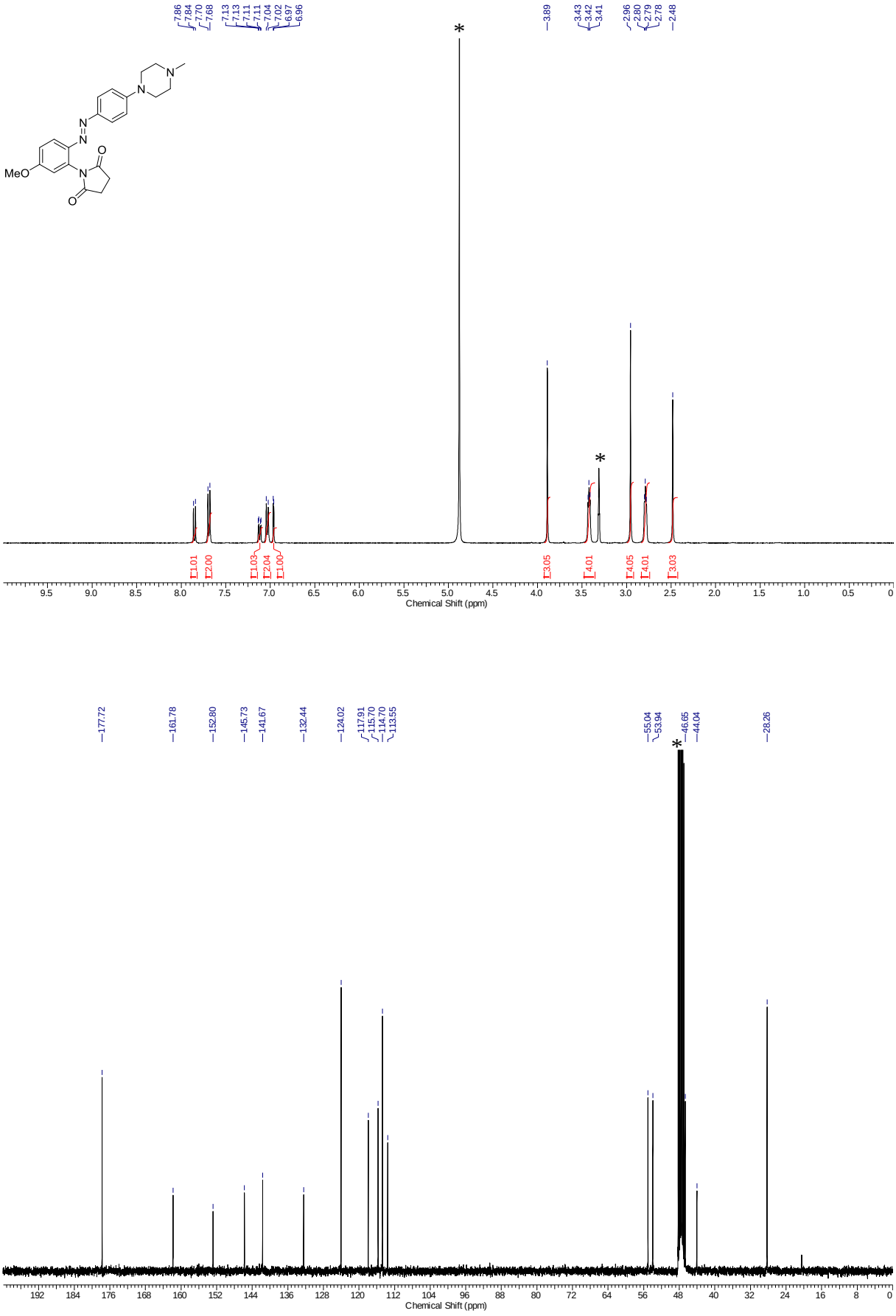
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **29e**. * = NMR-solvent, H_2O, grease



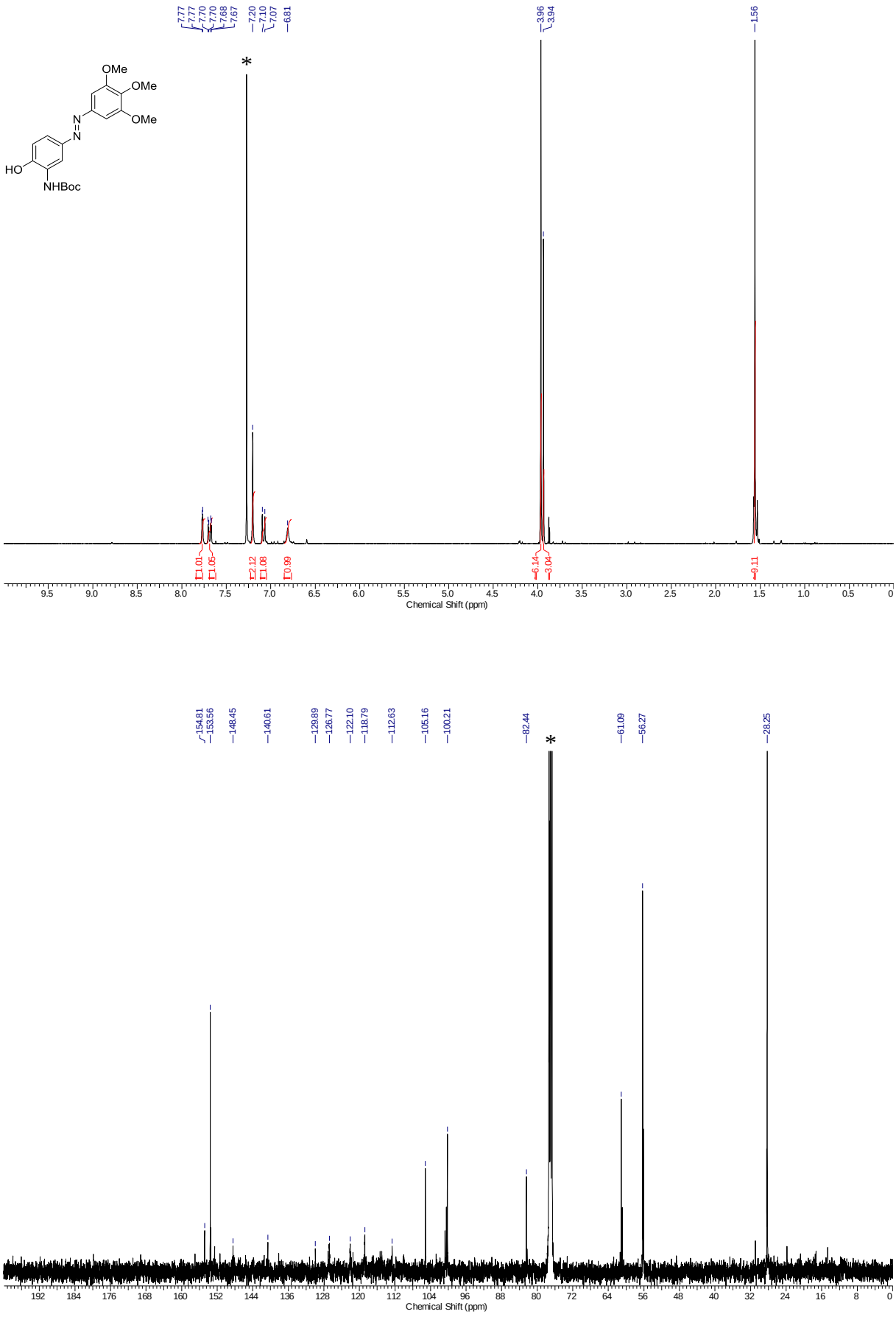
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **30b**. * = NMR-solvent, H_2O



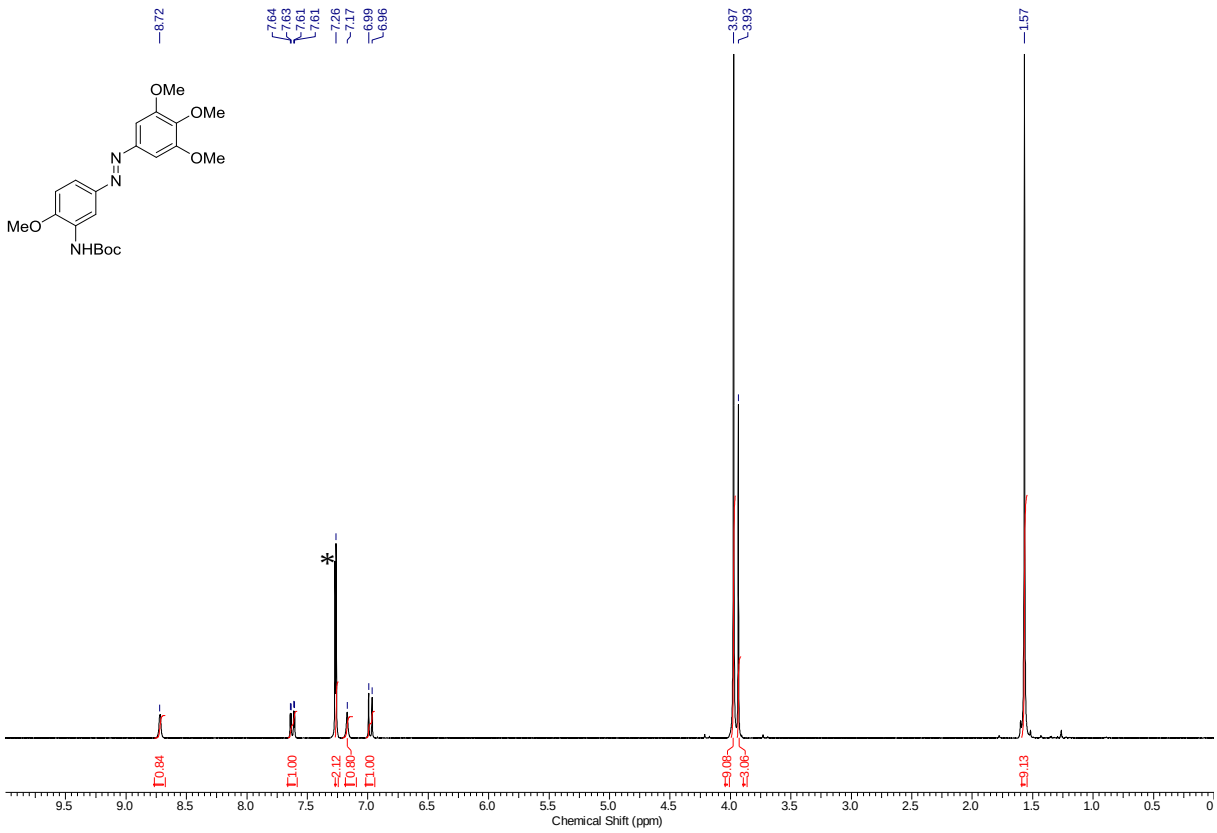
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **30c**. * = NMR-solvent, H_2O

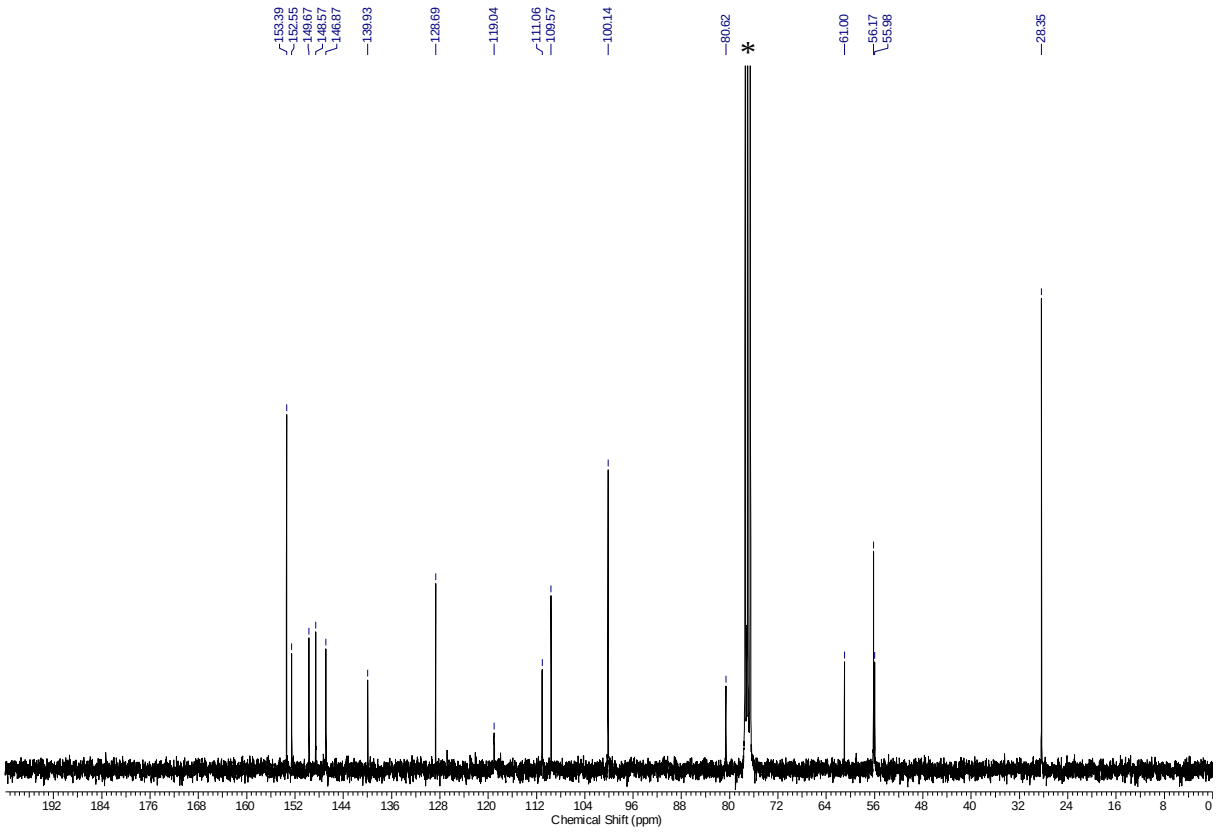


^{1}H-NMR (400 MHz, CD_3OD) and ^{13}C-NMR (101 MHz, CD_3OD) spectrum of compound **30d**. * = NMR-solvent, H_2O

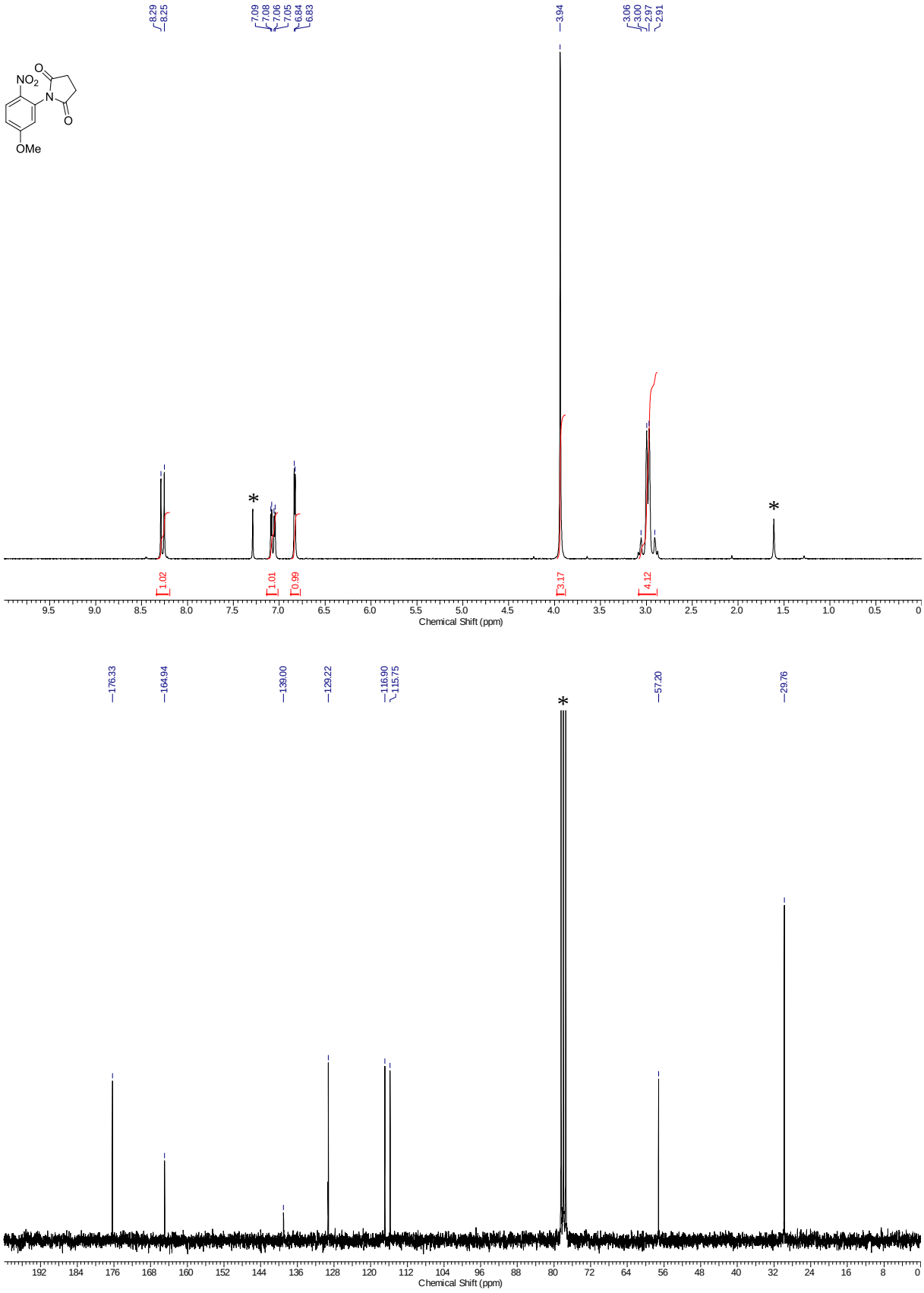


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **33**. * = NMR-solvent

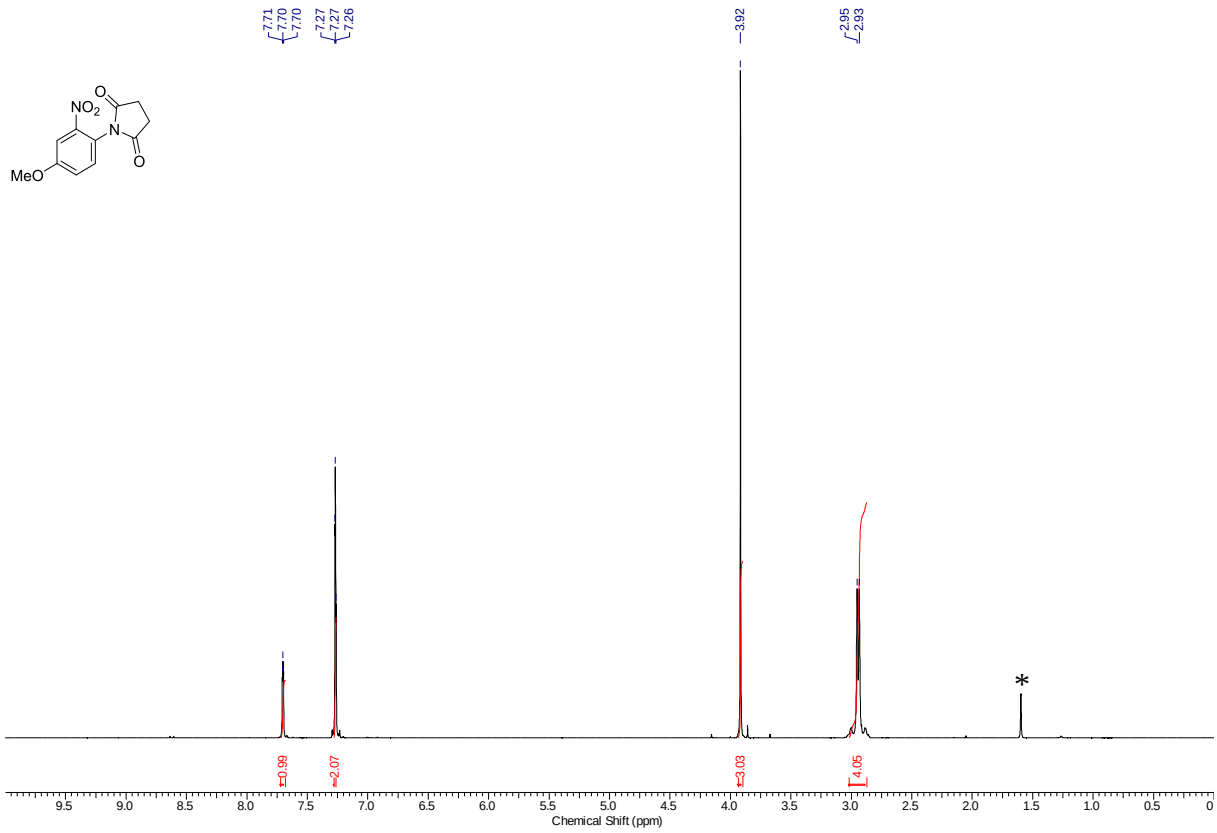


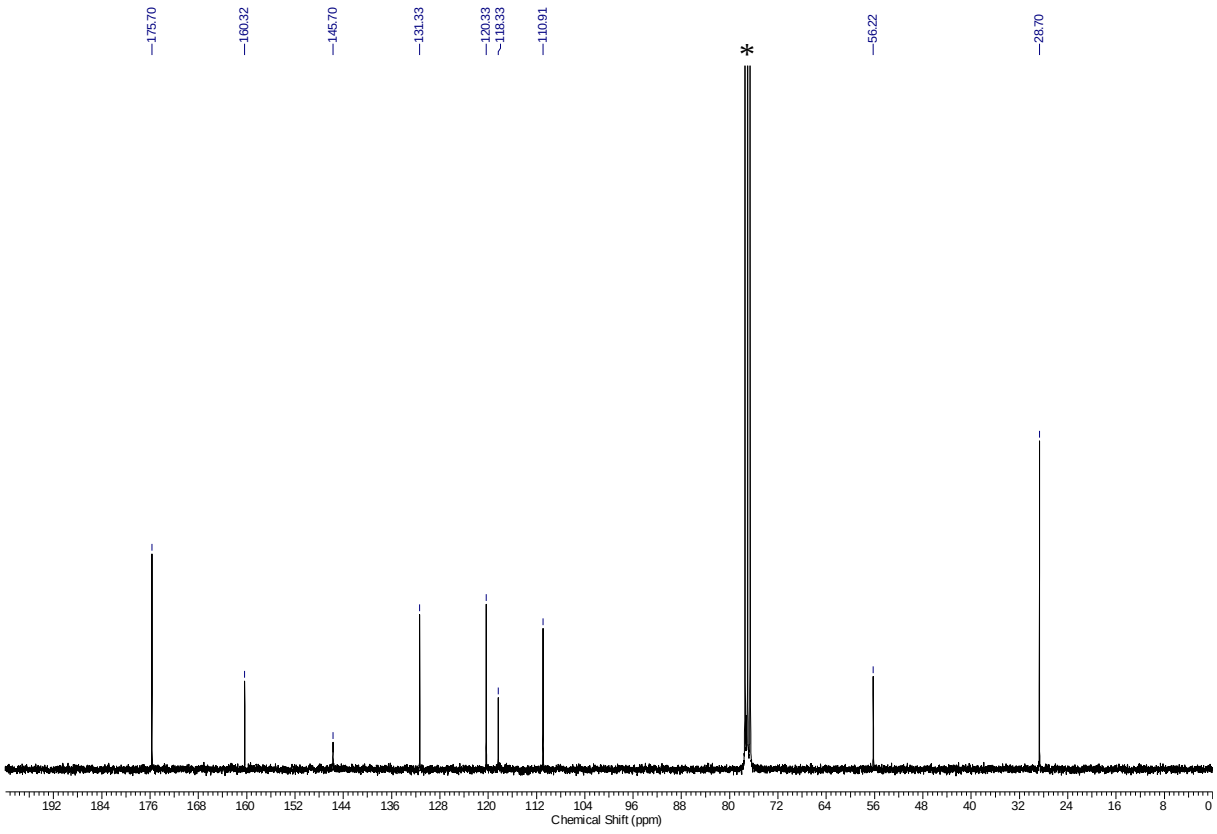


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **34**. * = NMR-solvent

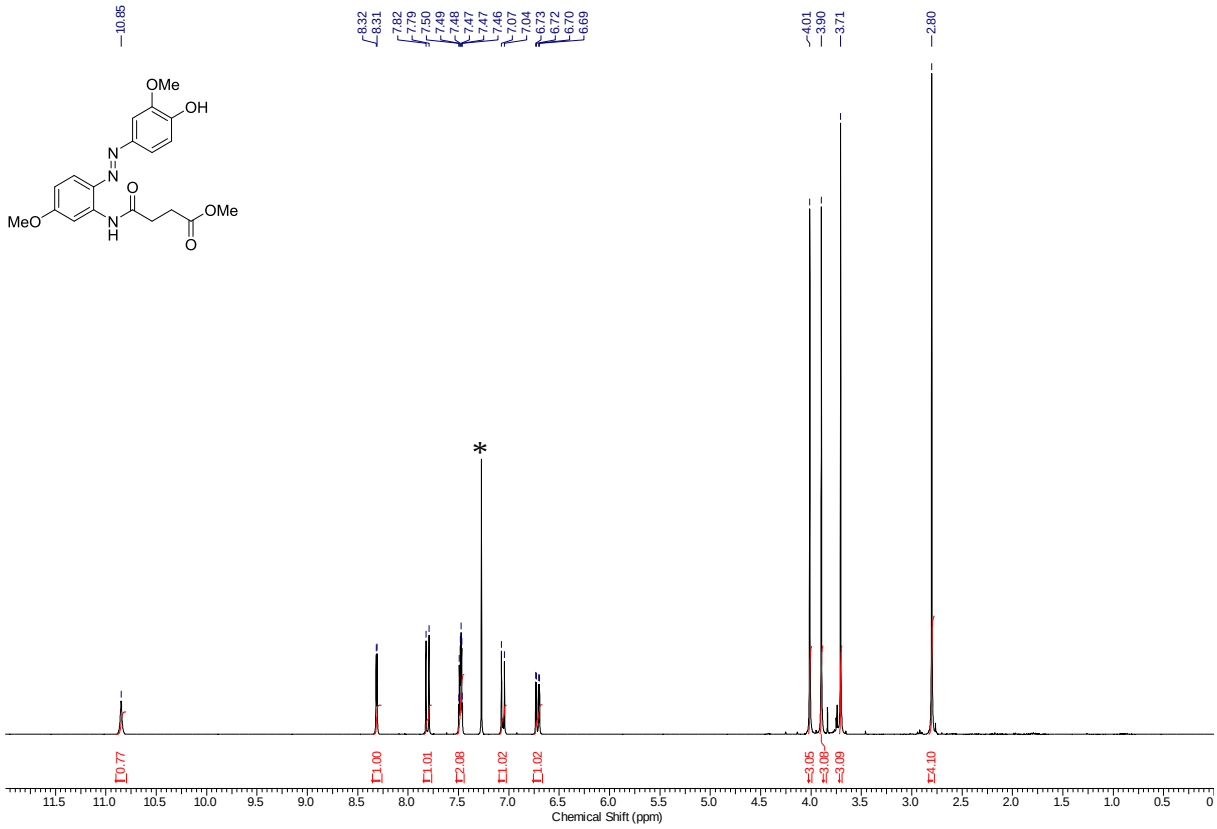


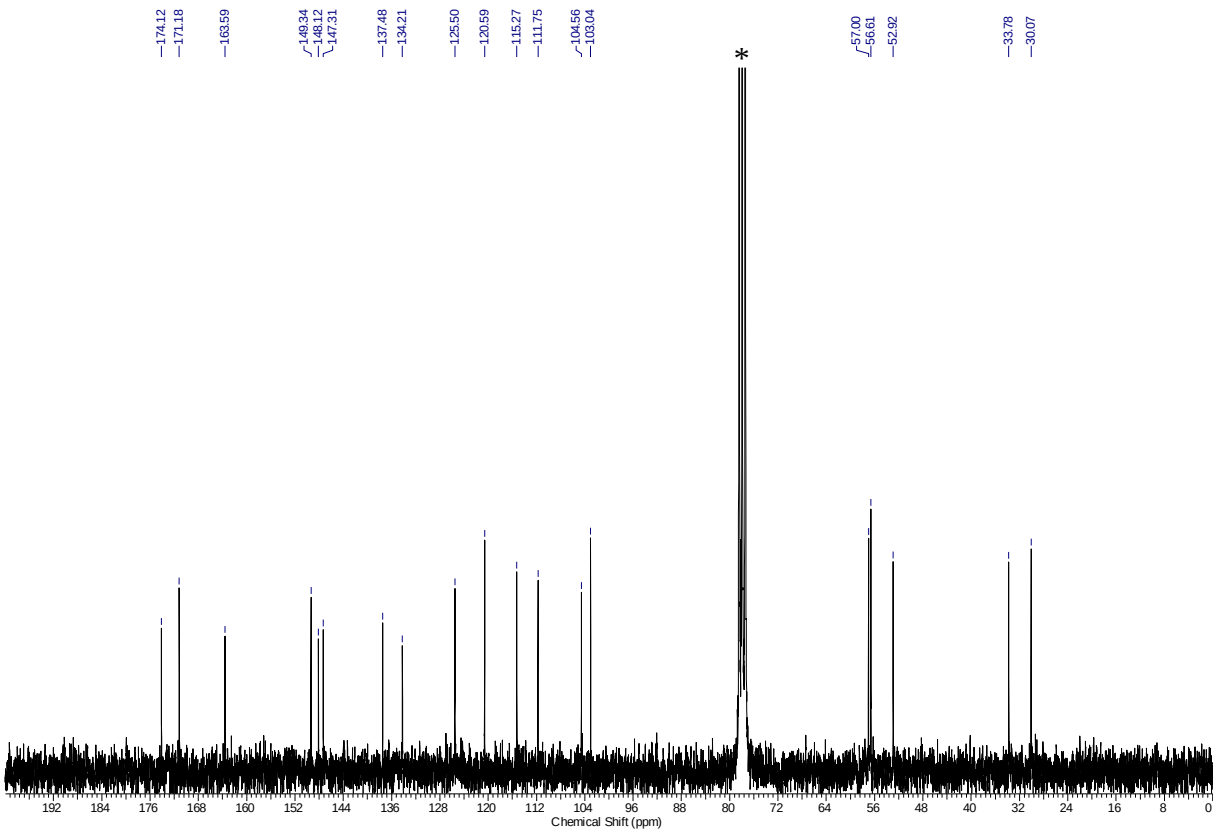
^{1}H-NMR (250 MHz, $CDCl_3$) and ^{13}C-NMR (63MHz, $CDCl_3$) spectrum of compound ***p*-35**. * = NMR-solvent, H_2O



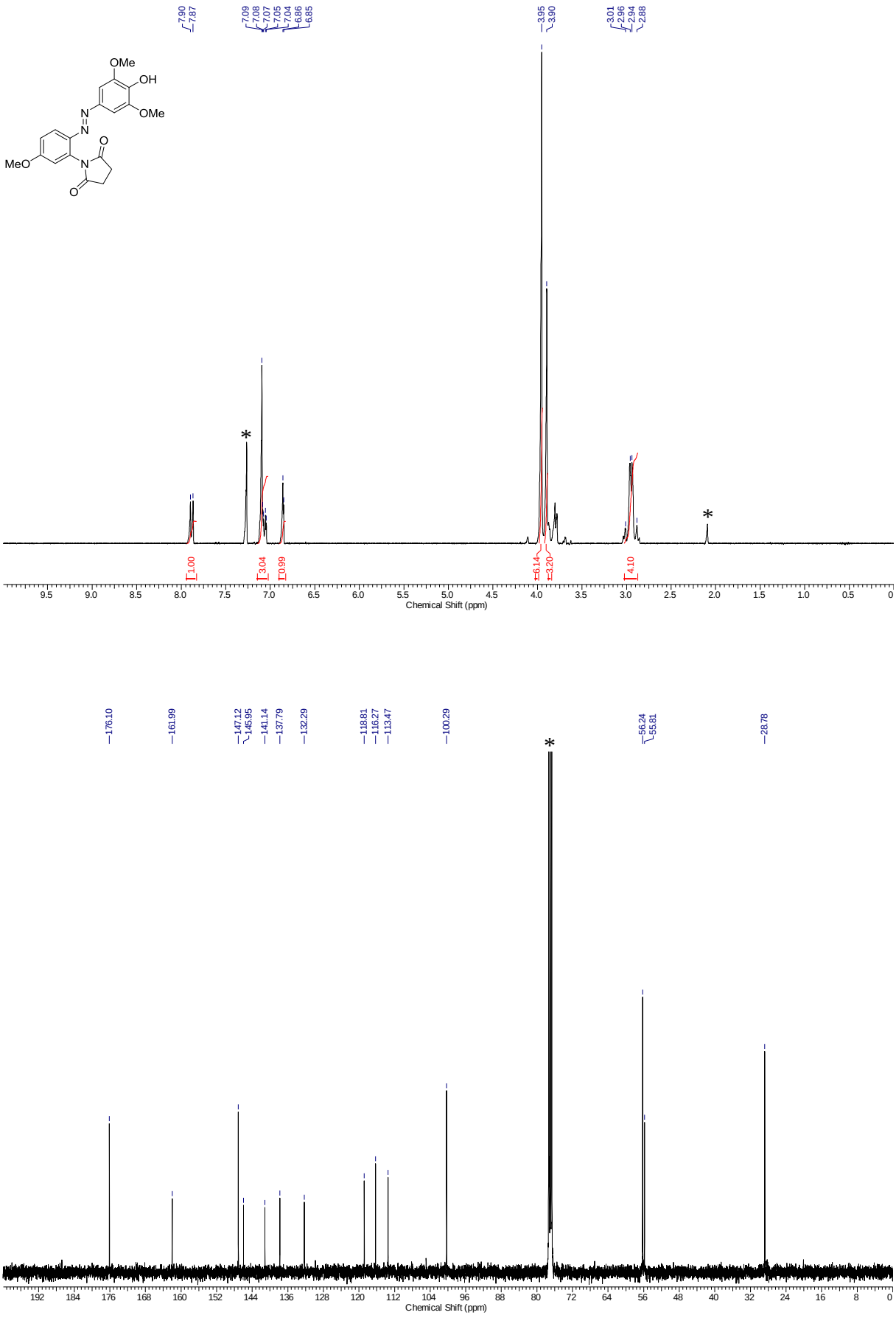


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound ***m*-35**. * = NMR-solvent, H_2O

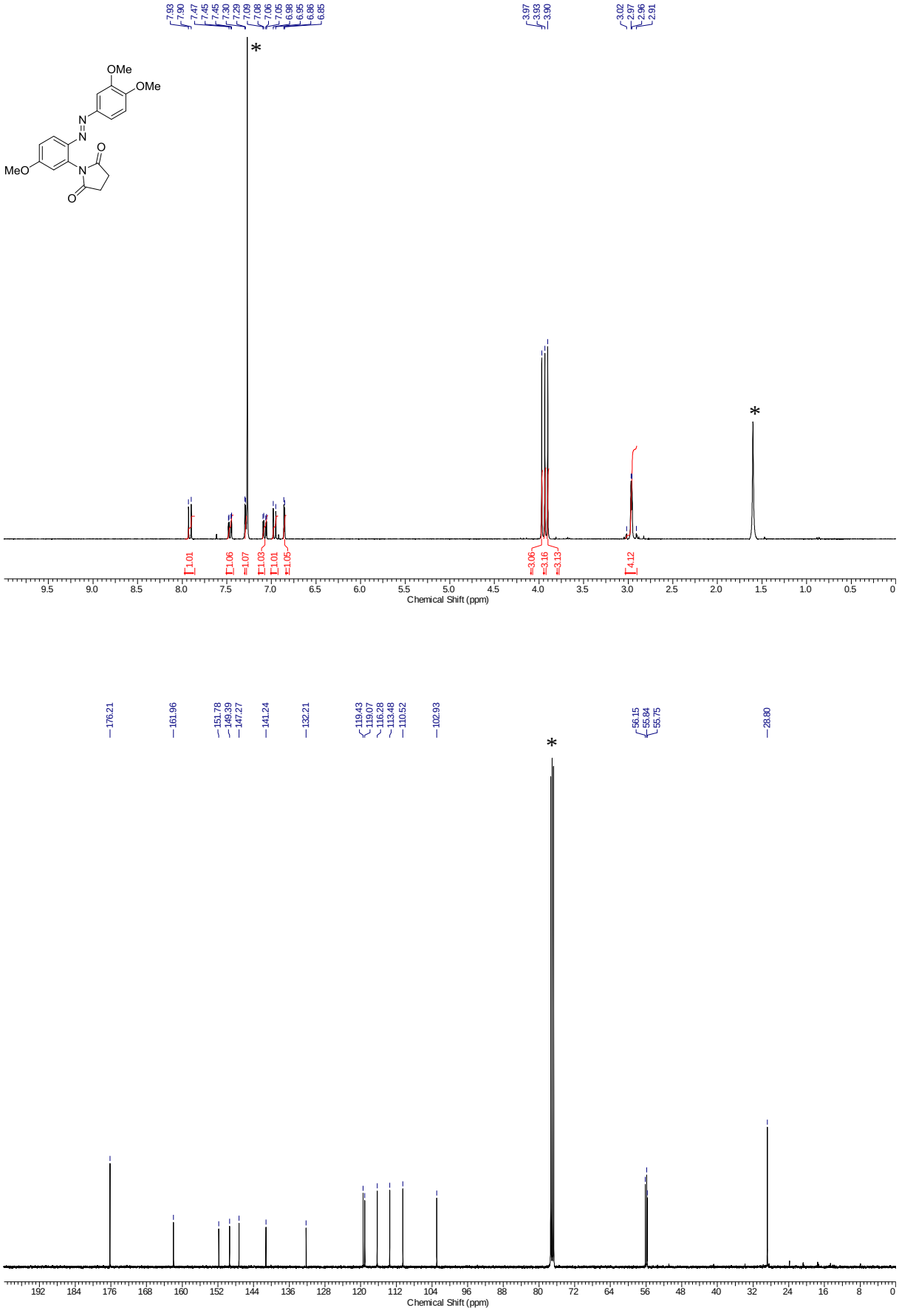




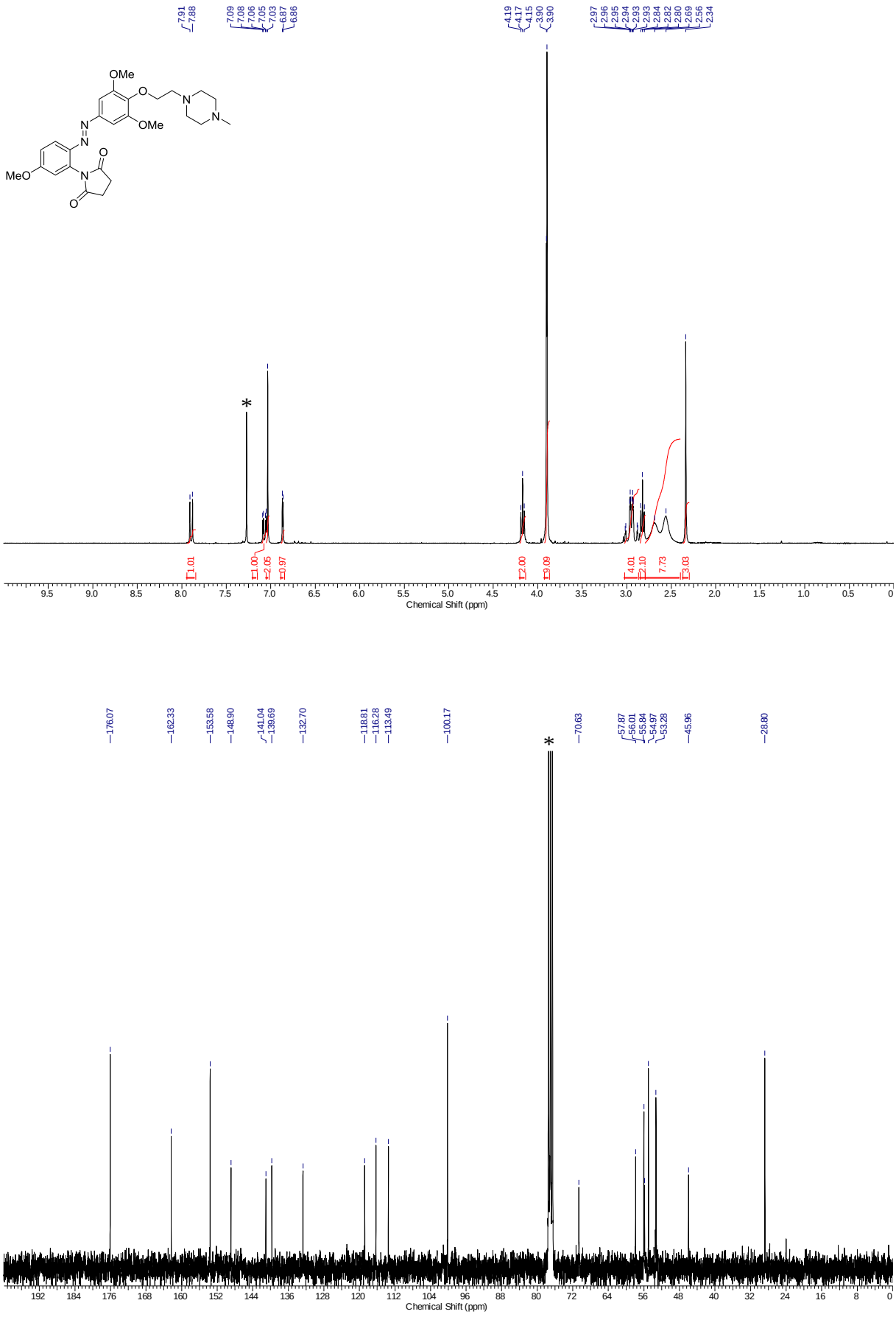
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (63 MHz, $CDCl_3$) spectrum of compound **36a**. * = NMR-solvent



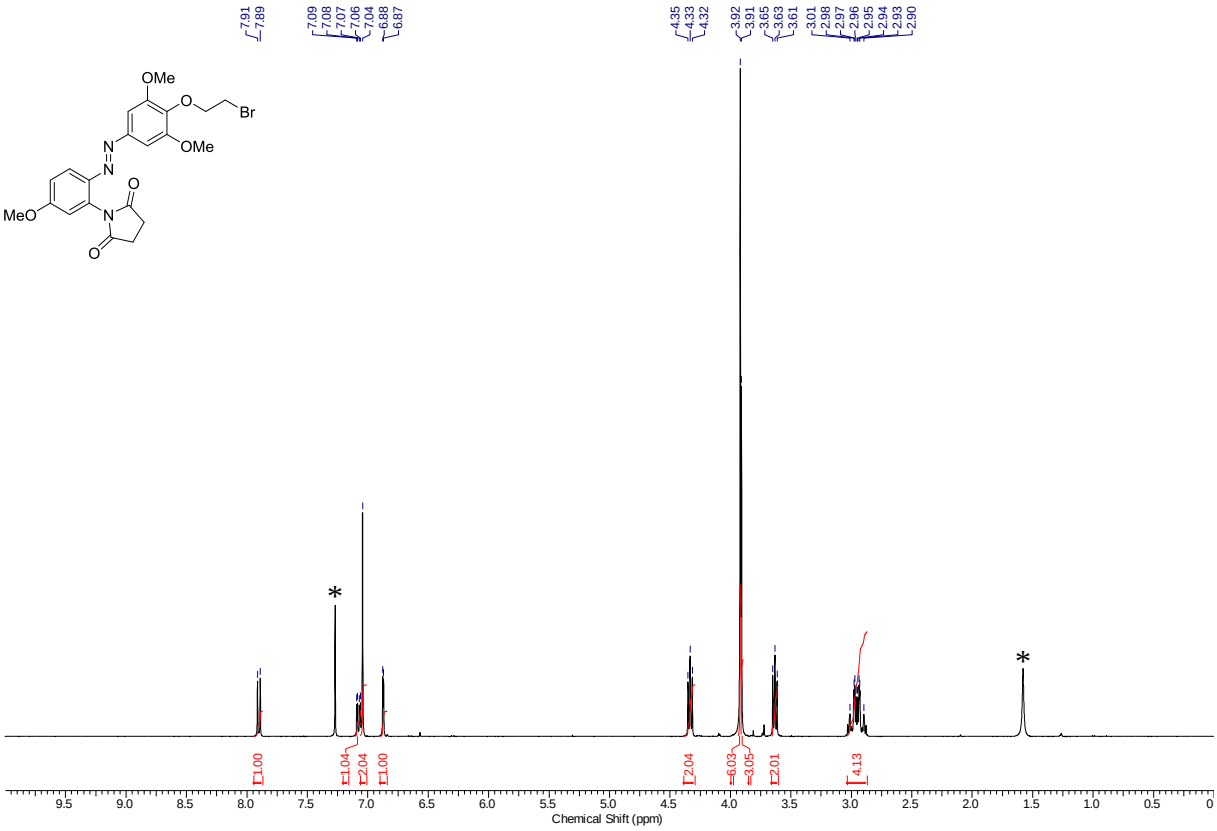
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **36b**. * = NMR-solvent, CH_3CN

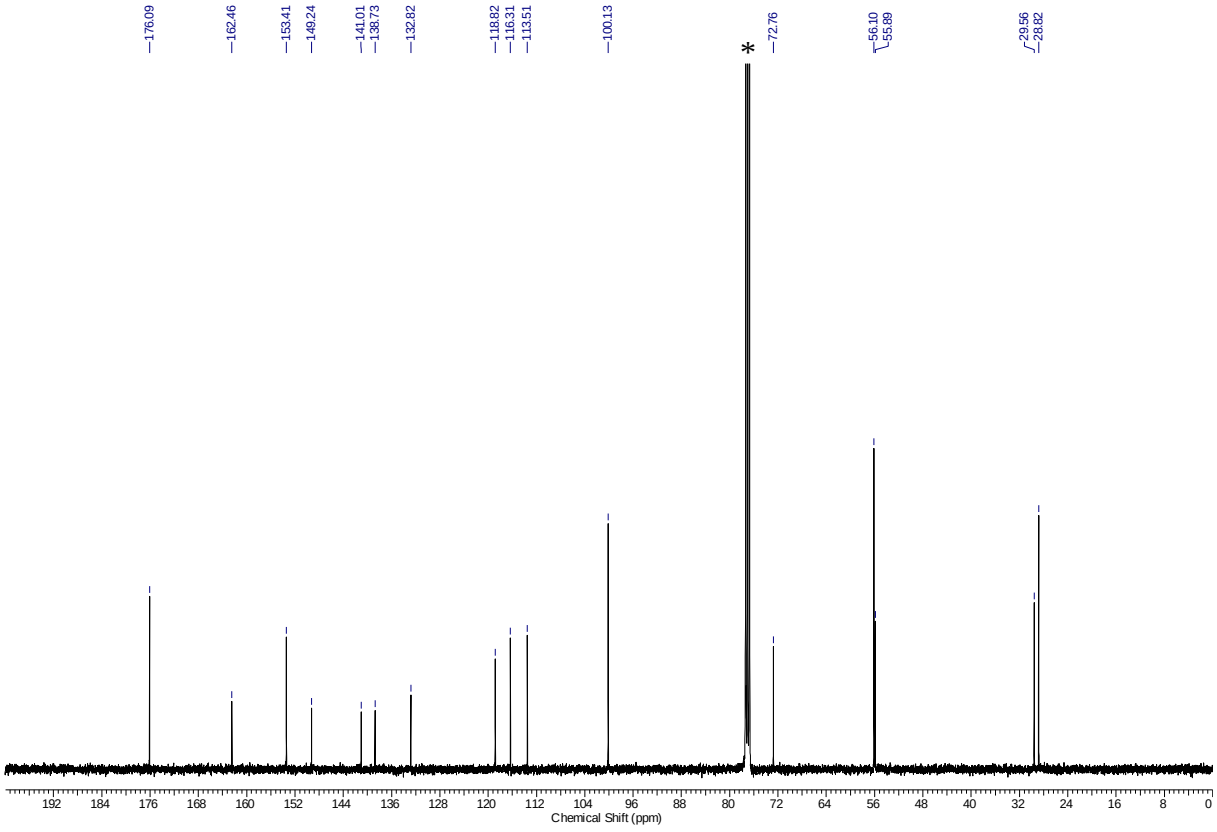


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **37a**. * = NMR-solvent, H_2O

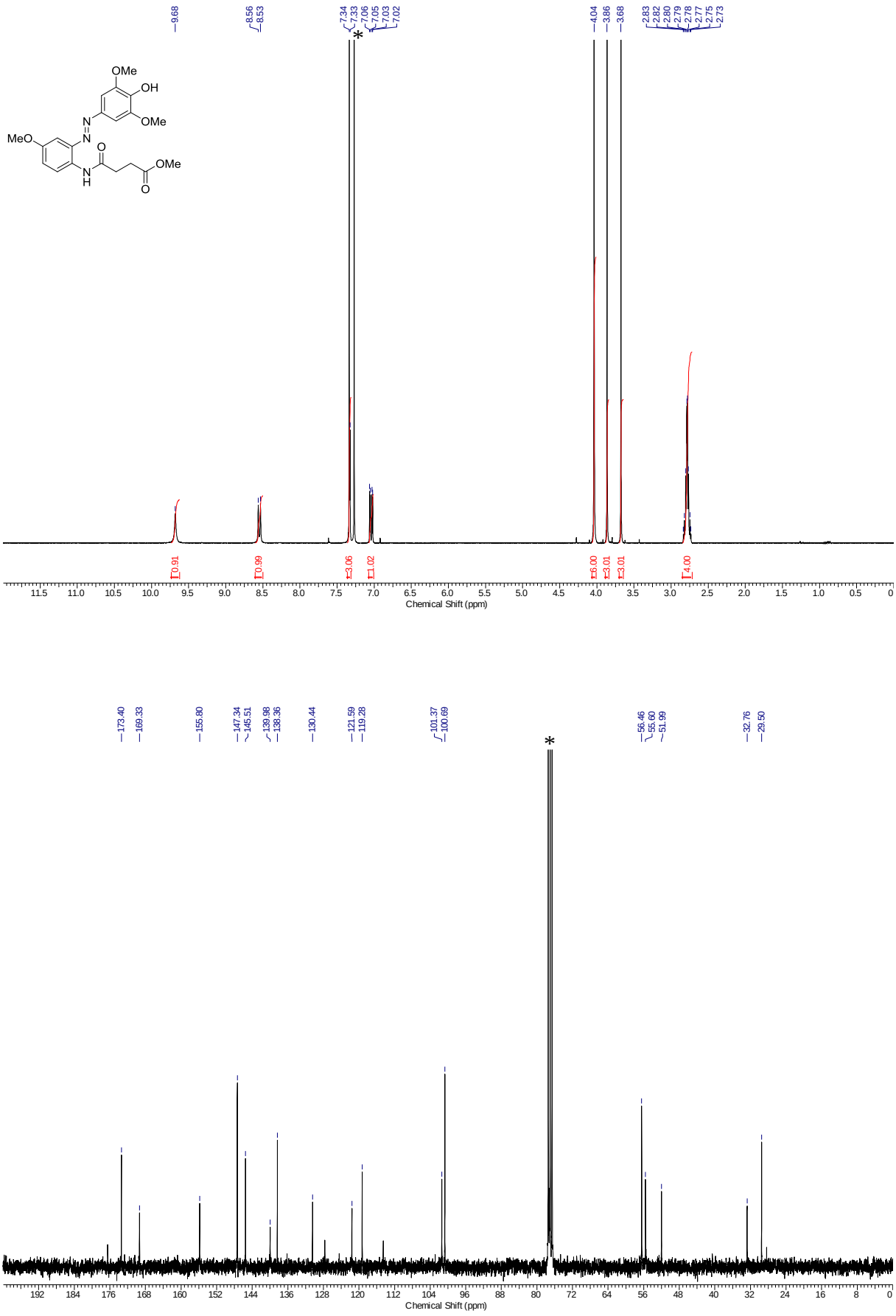


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **37b**. * = NMR-solvent

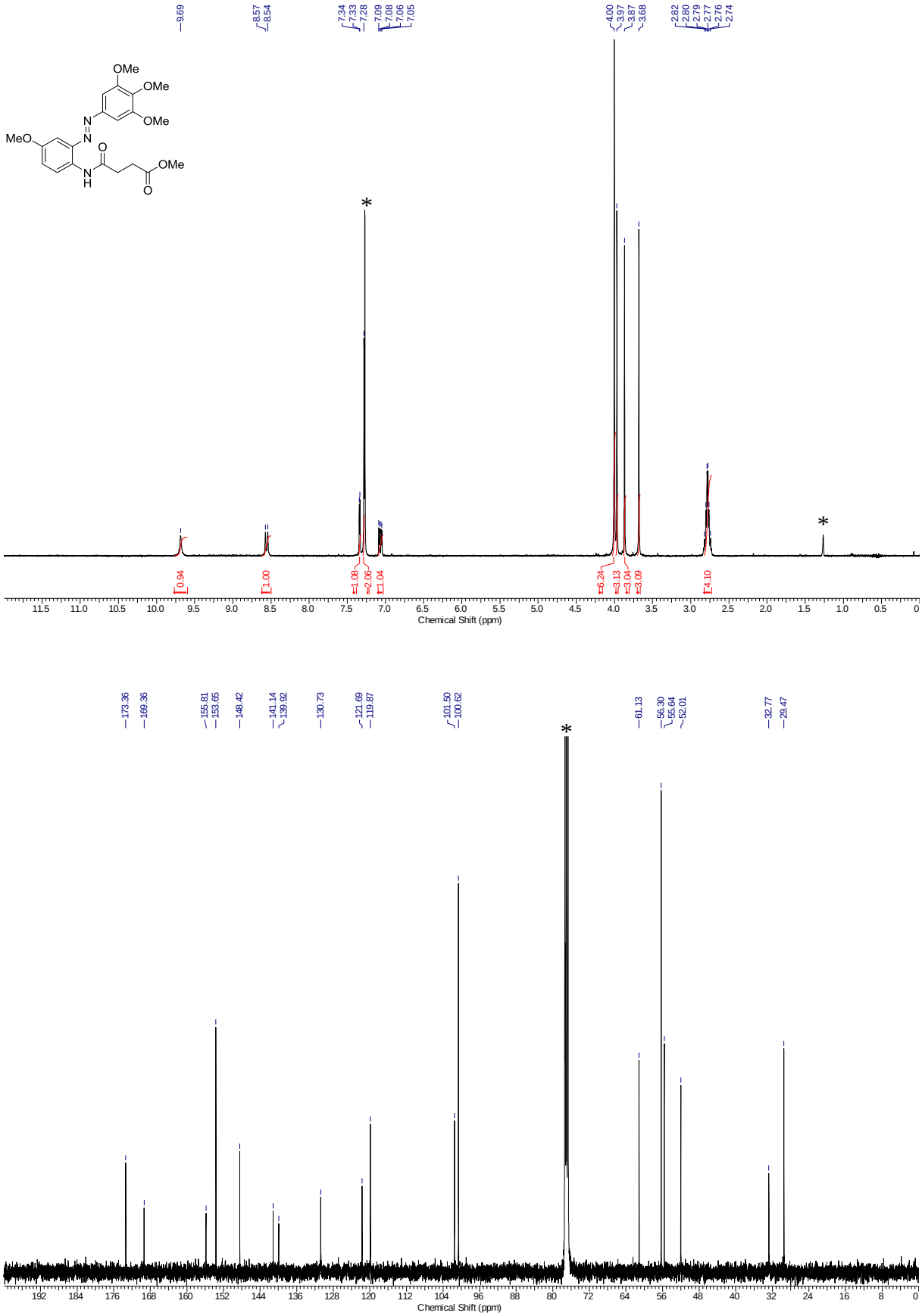




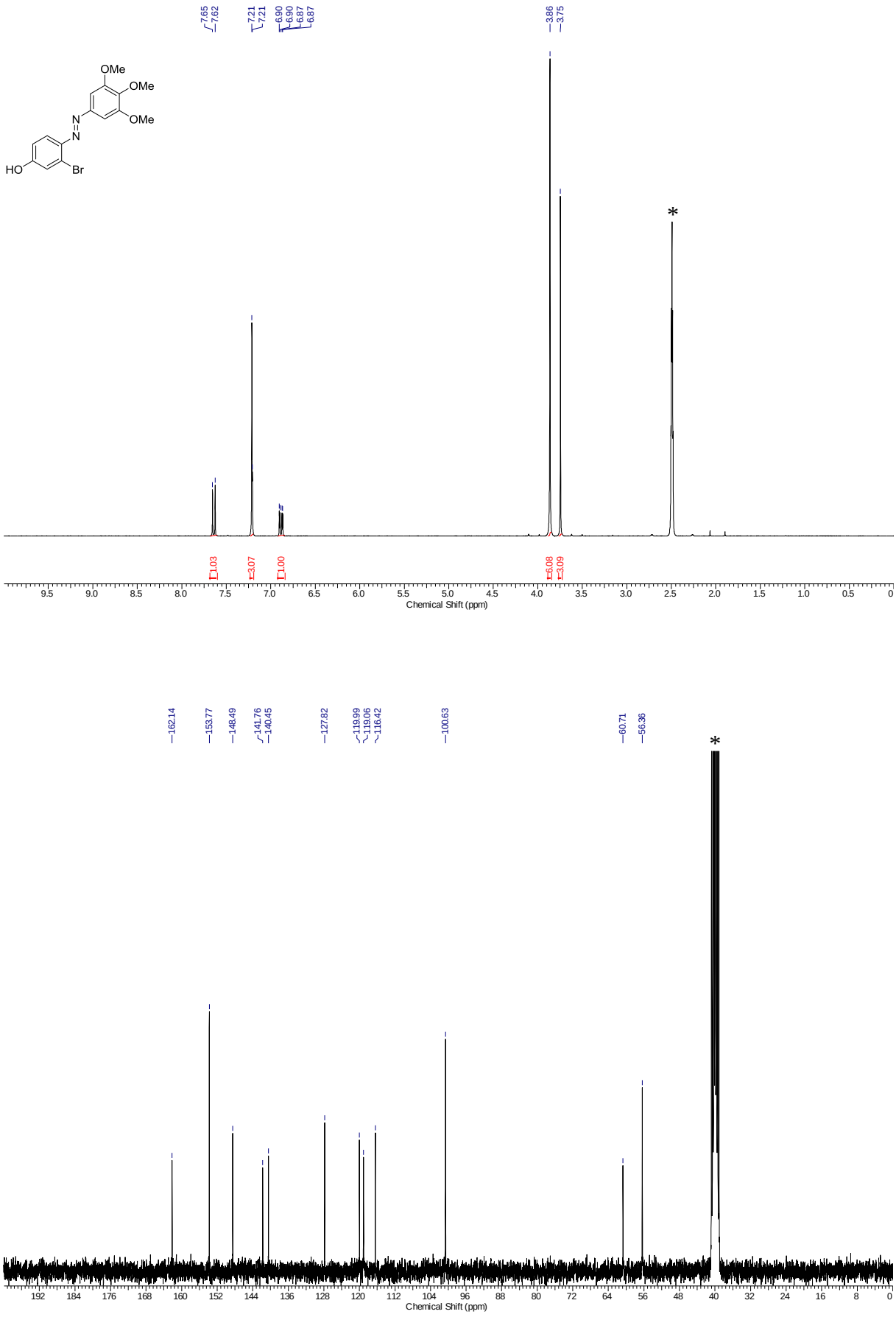
^{1}H-NMR (400 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **37c**. * = NMR-solvent, H_2O



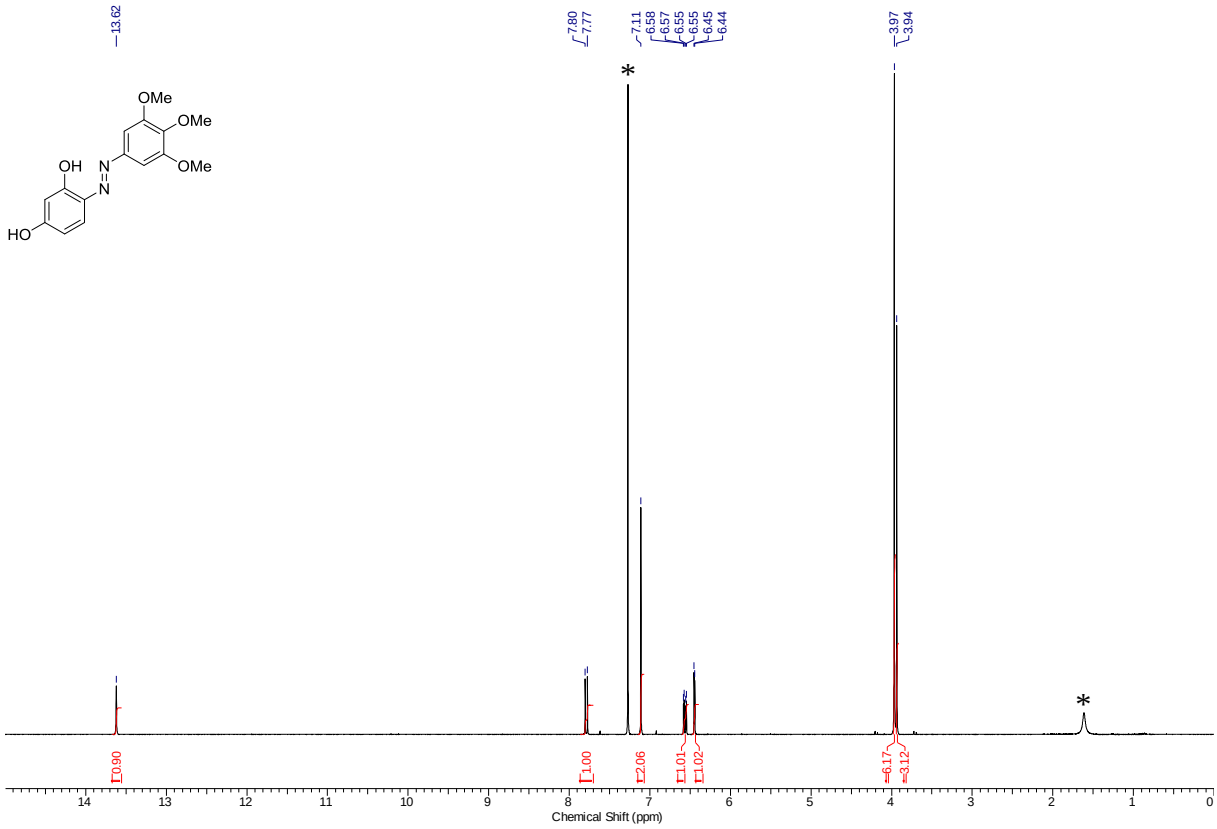
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of compound **38**. * = NMR-solvent

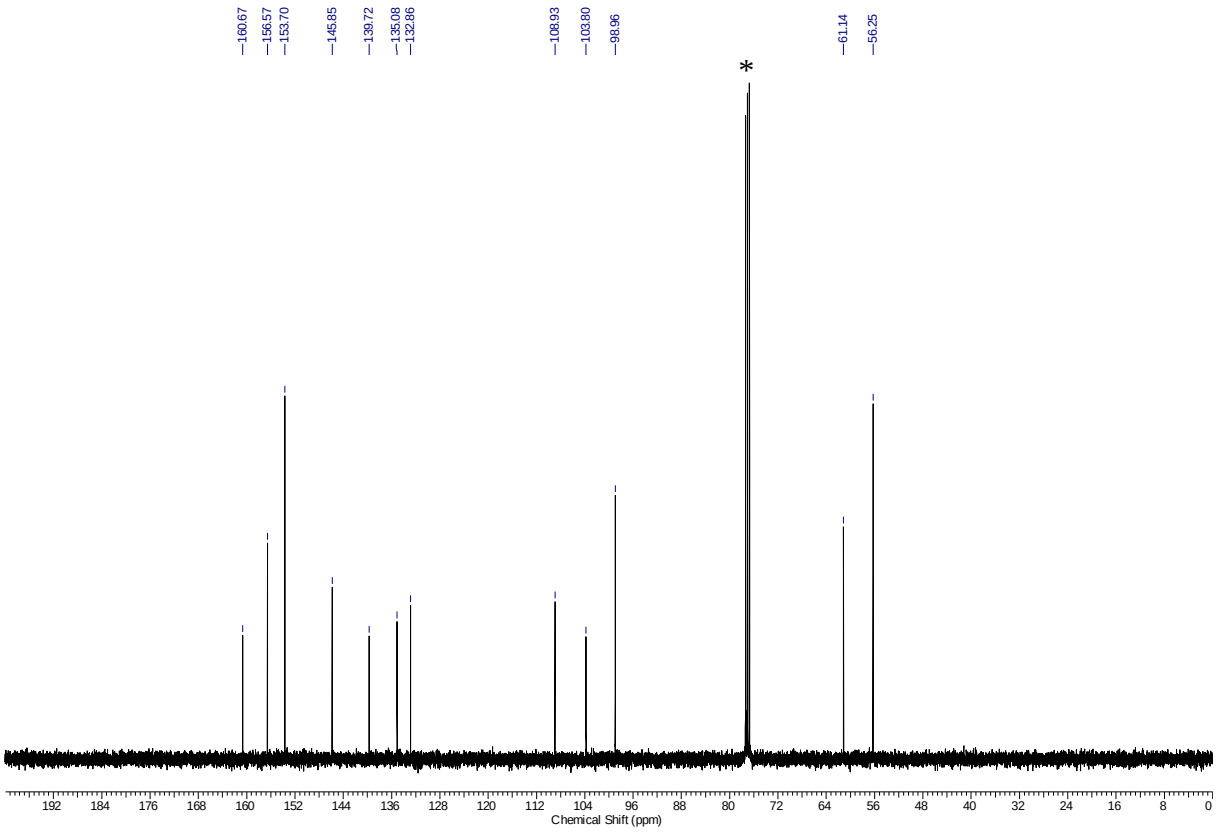


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **39**. * = NMR-solvent, grease

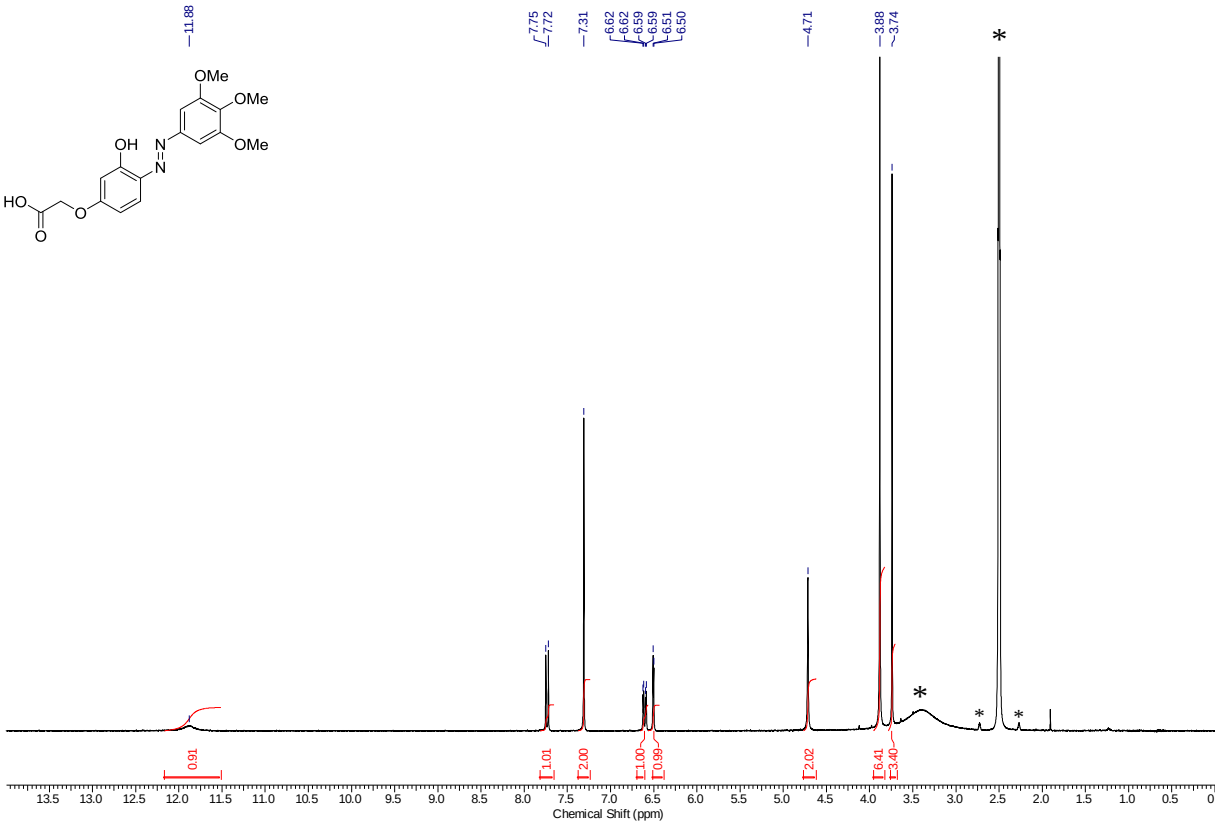


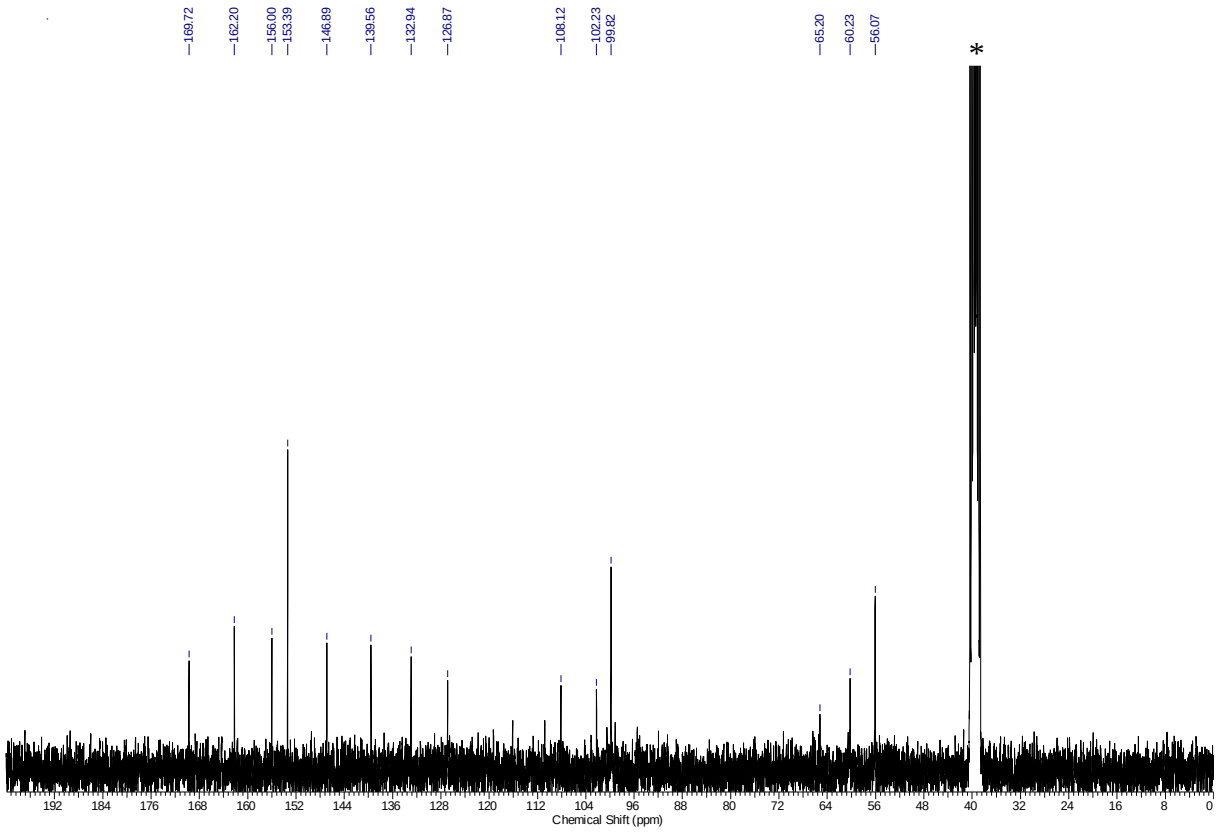
^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (75 MHz, DMSO-d_6) spectrum of compound **41a**.



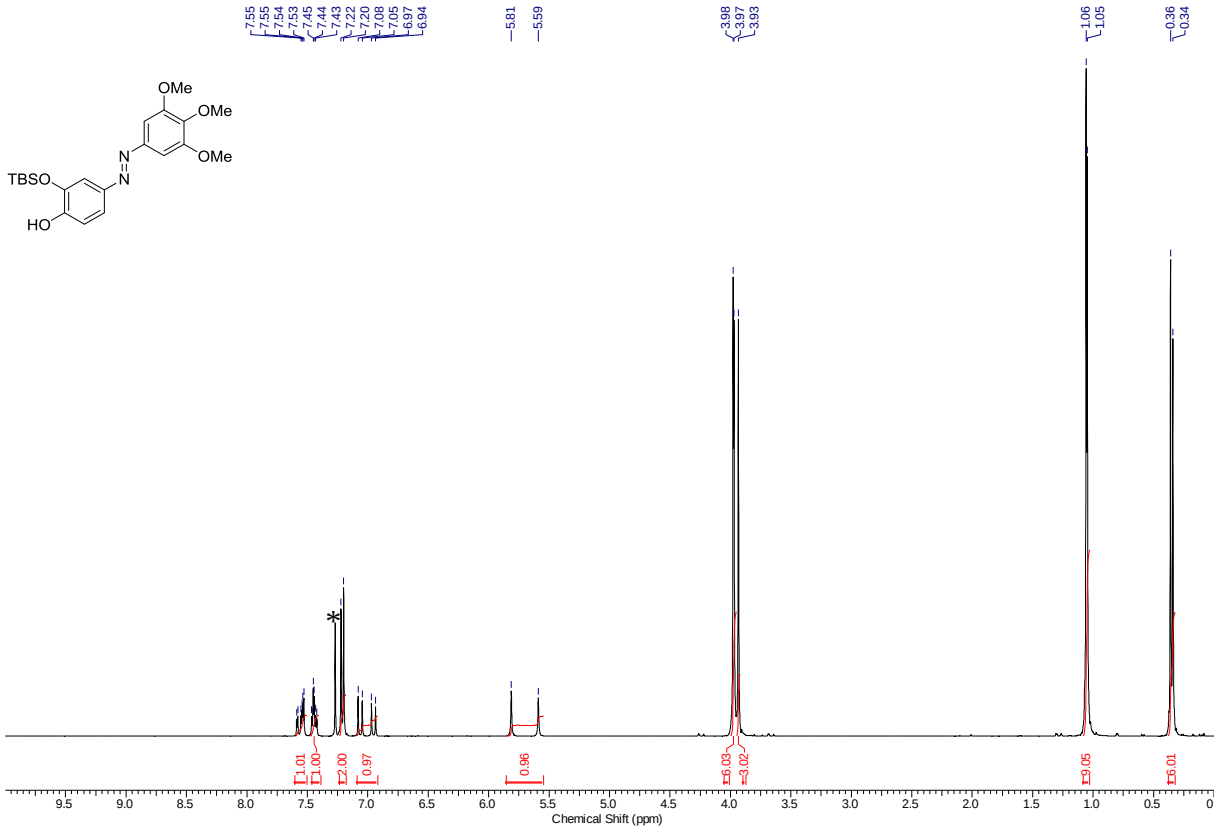


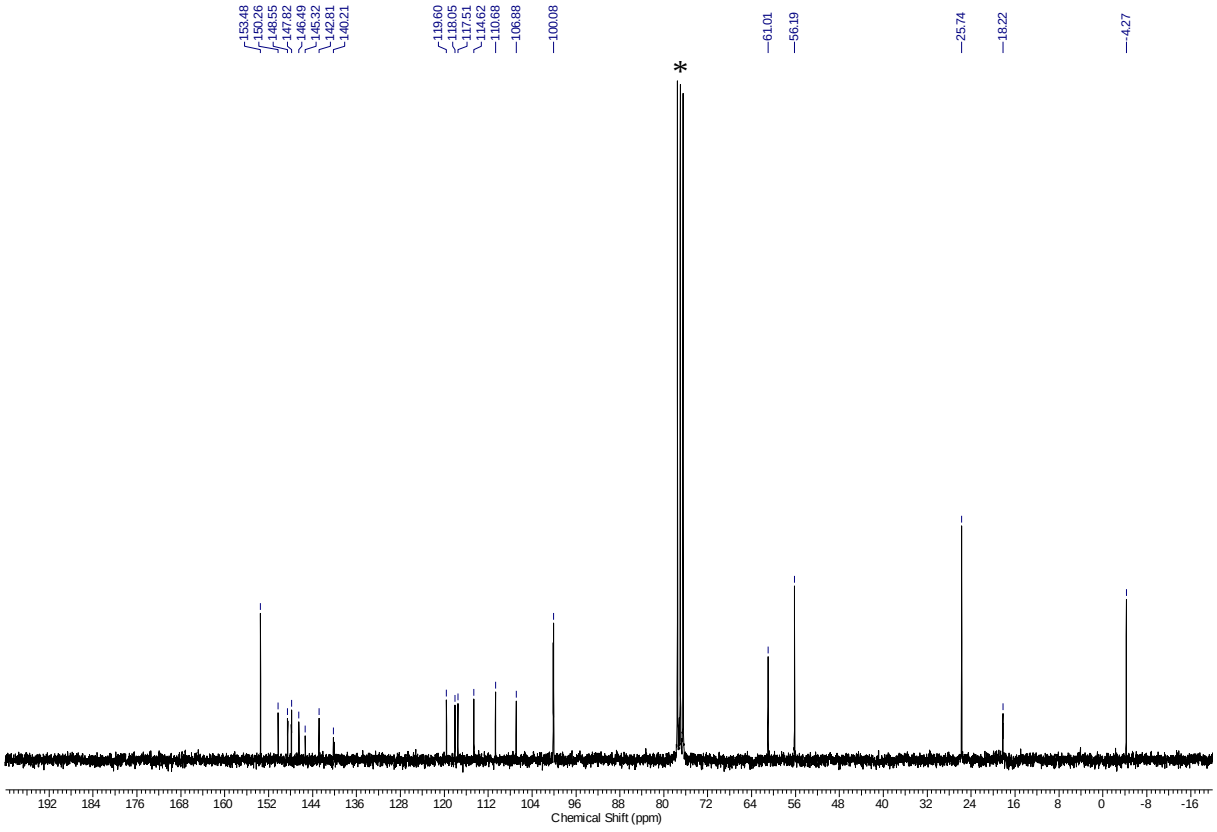
^{1}H-NMR (400 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **41b**. * = NMR-solvent, H_2O



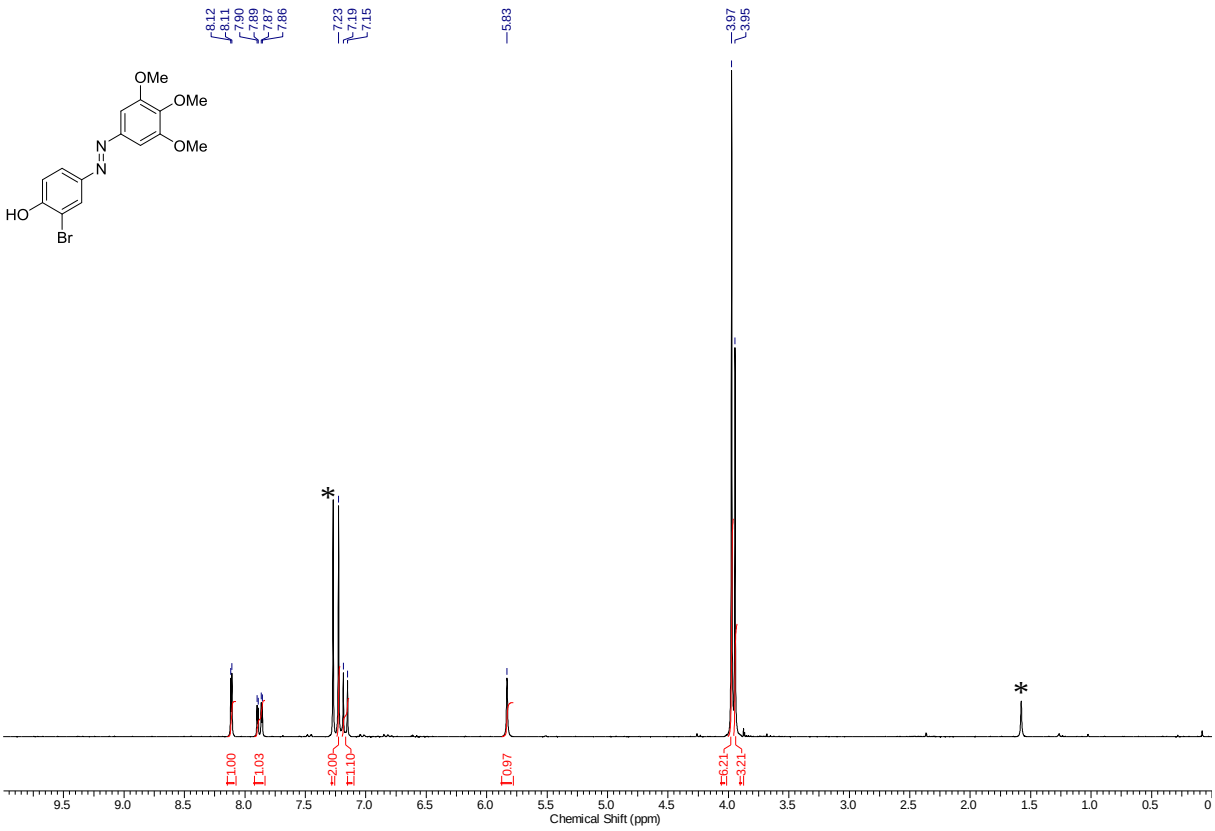


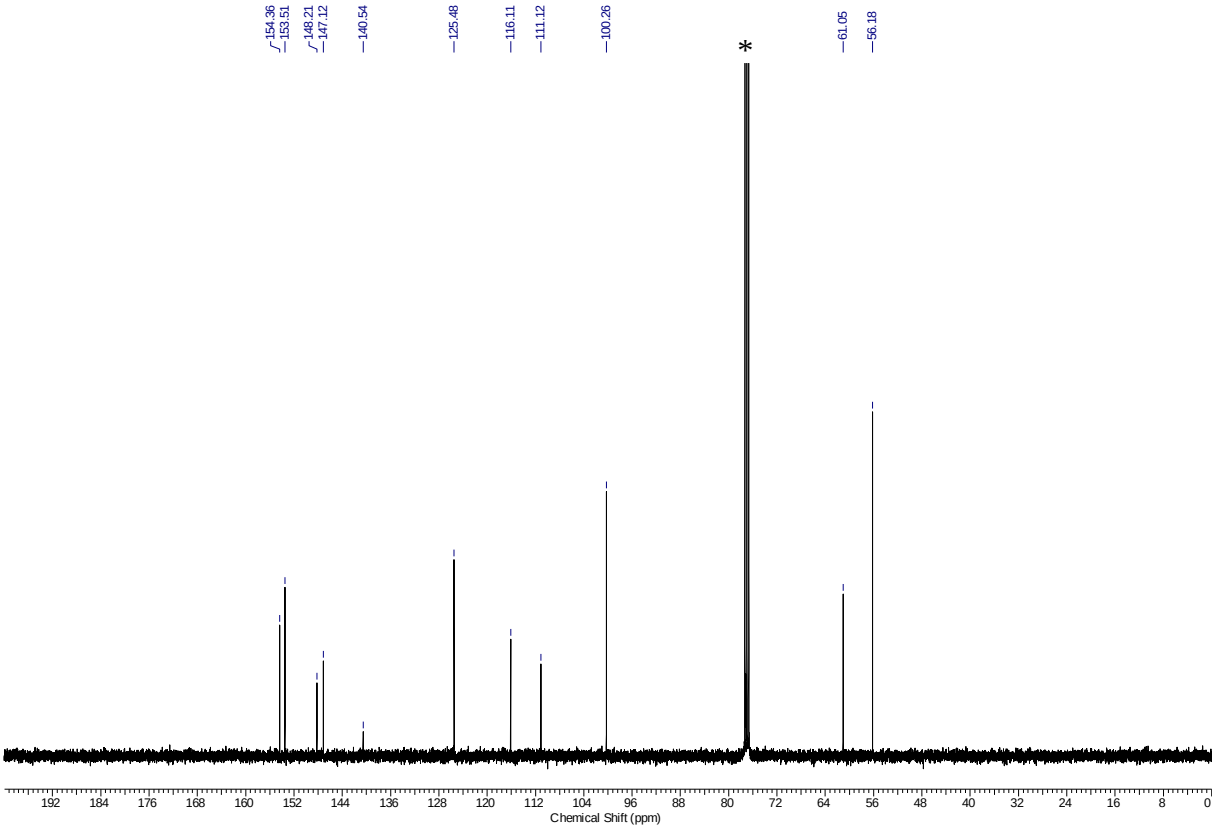
^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (75 MHz, DMSO-d_6) spectrum of compound **42b**. * = NMR-solvent, H_2O



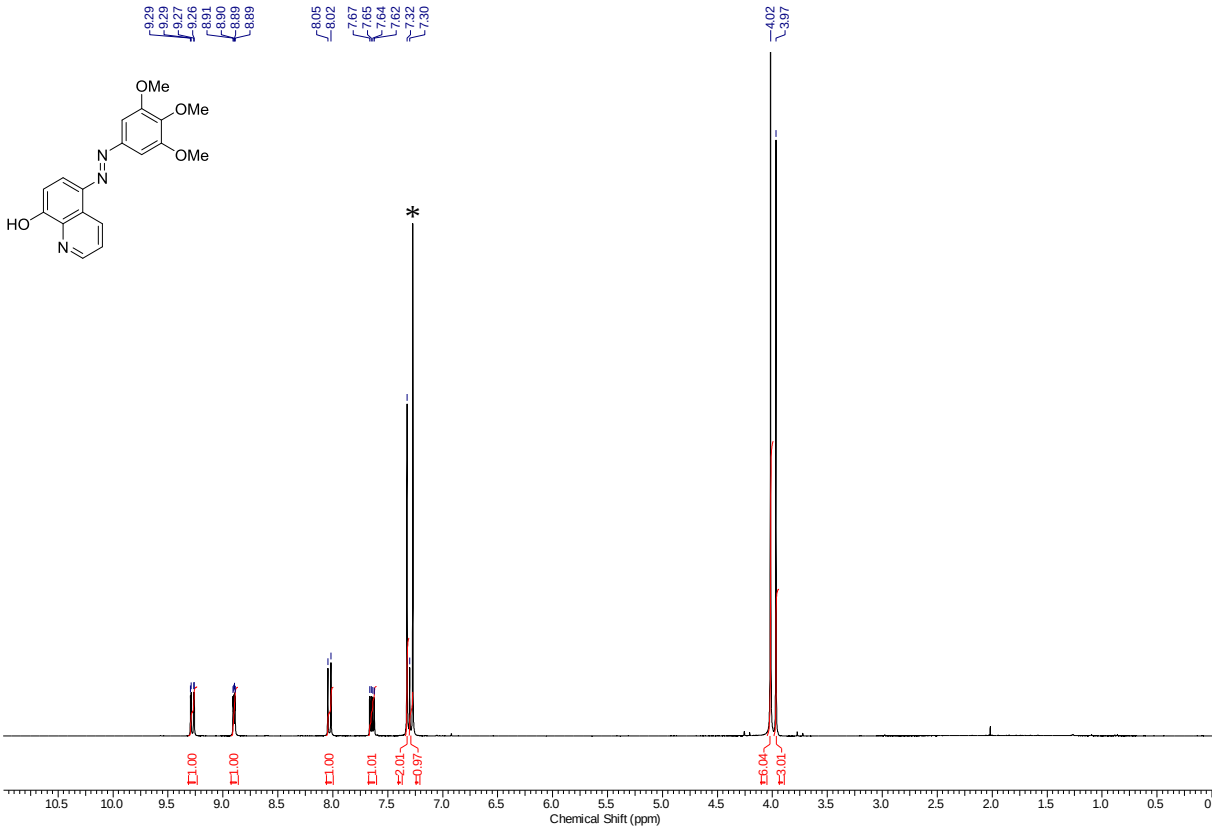


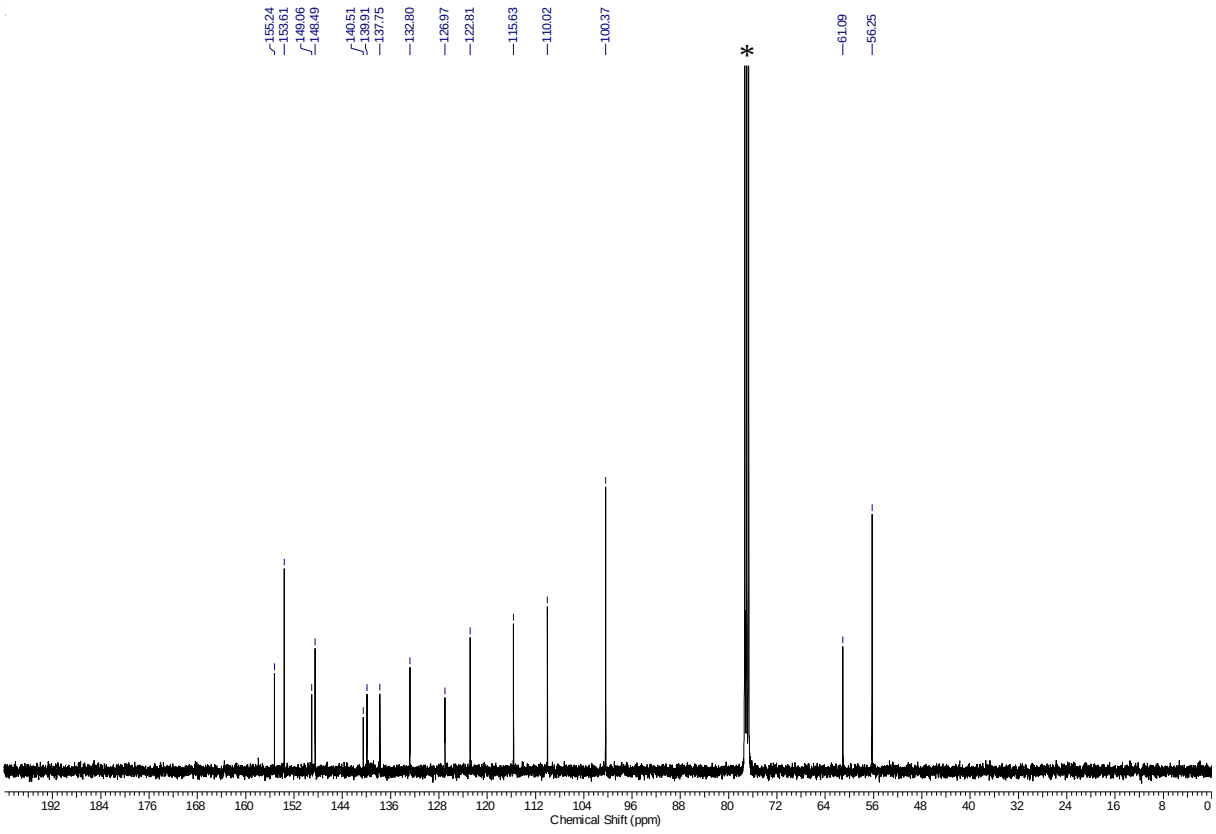
^{1}H-NMR (250 MHz, $CDCl_3$) and ^{13}C-NMR (63 MHz, $CDCl_3$) spectrum of compound **44a**. * = NMR-solvent



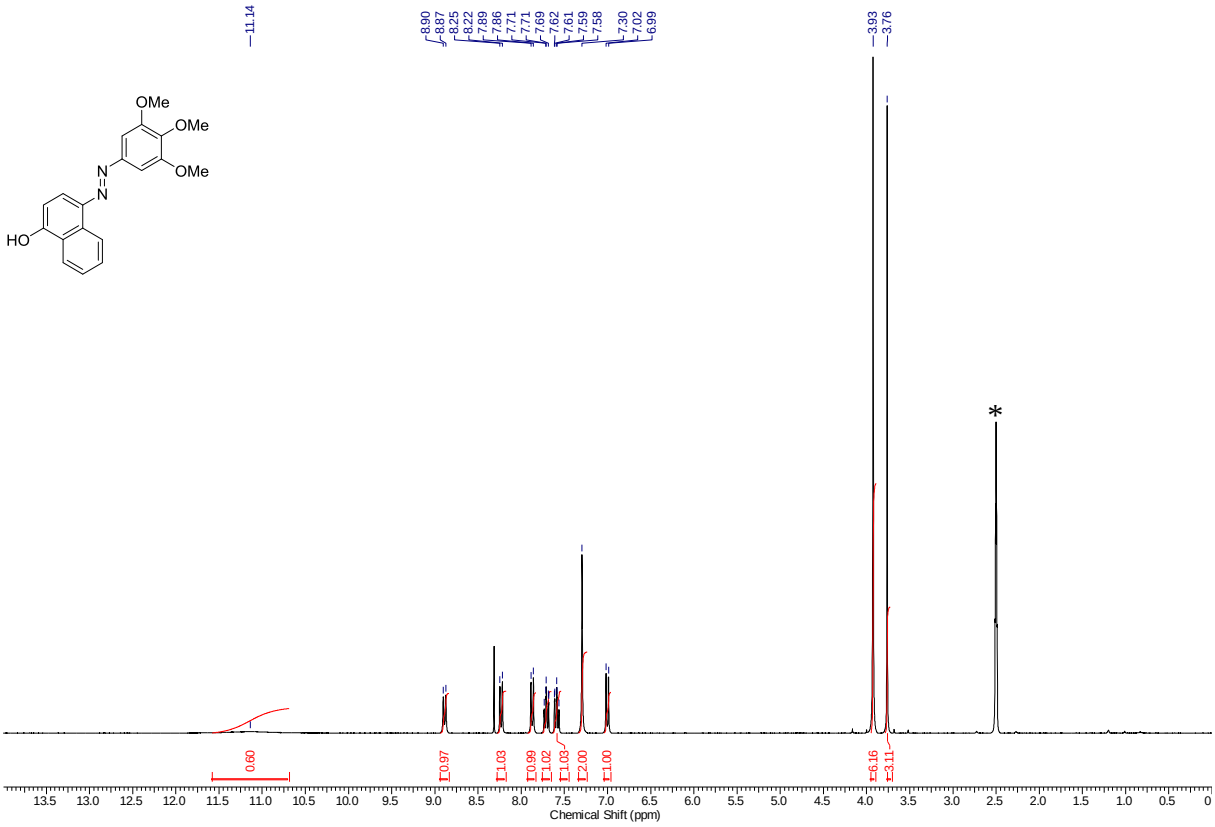


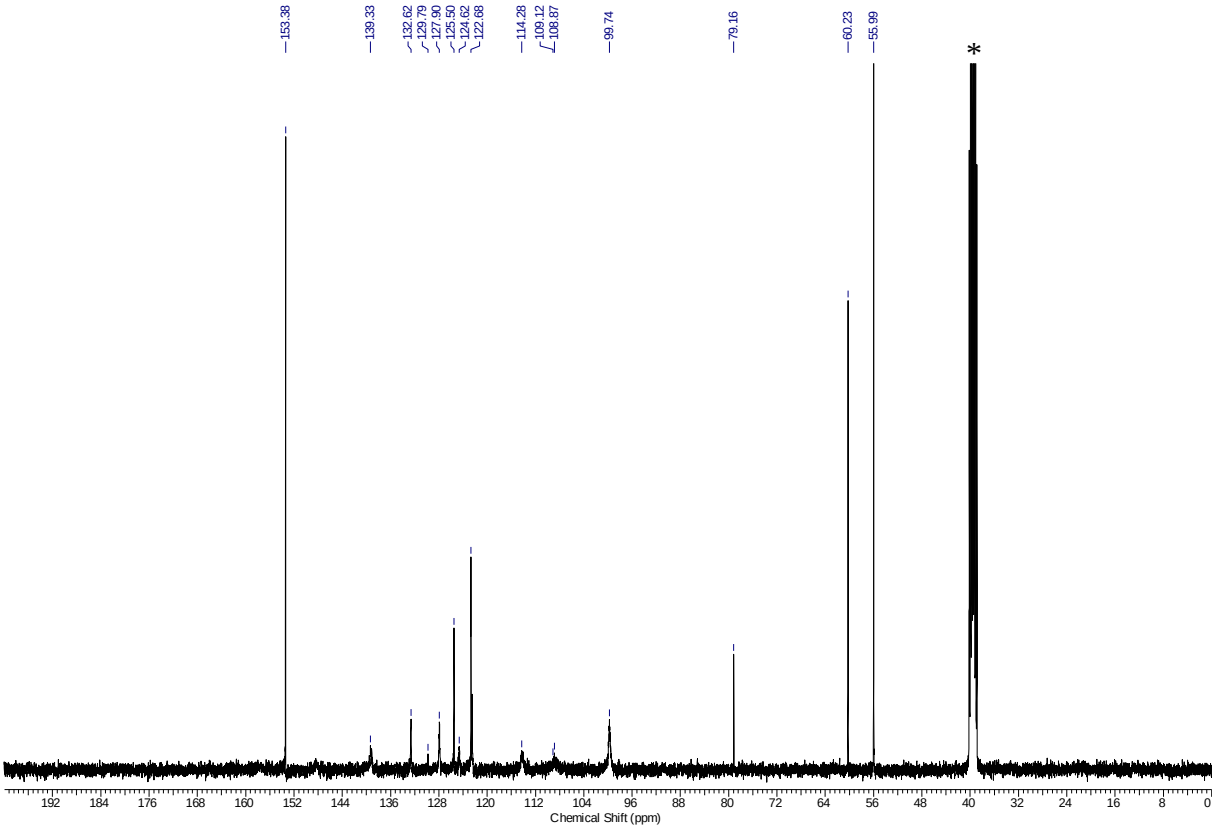
^{1}H-NMR (250 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **44b**. * = NMR-solvent, H_2O



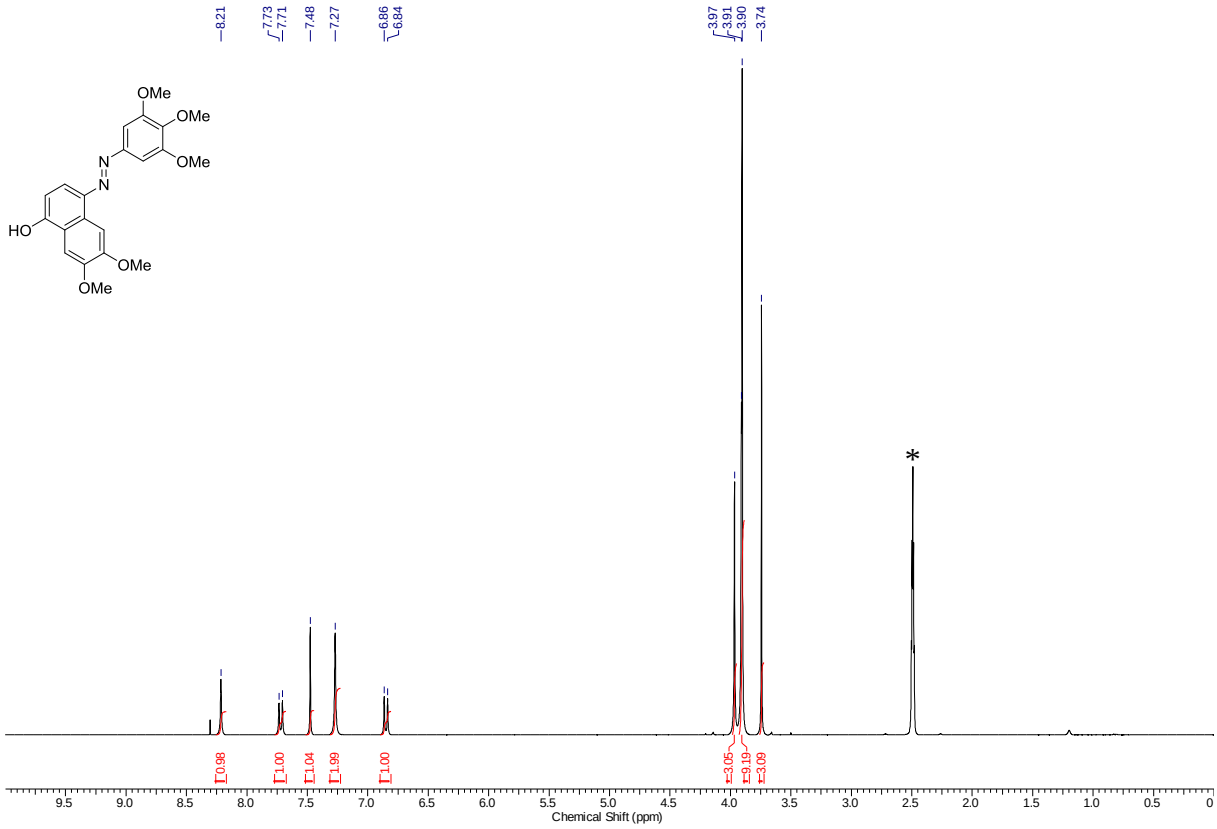


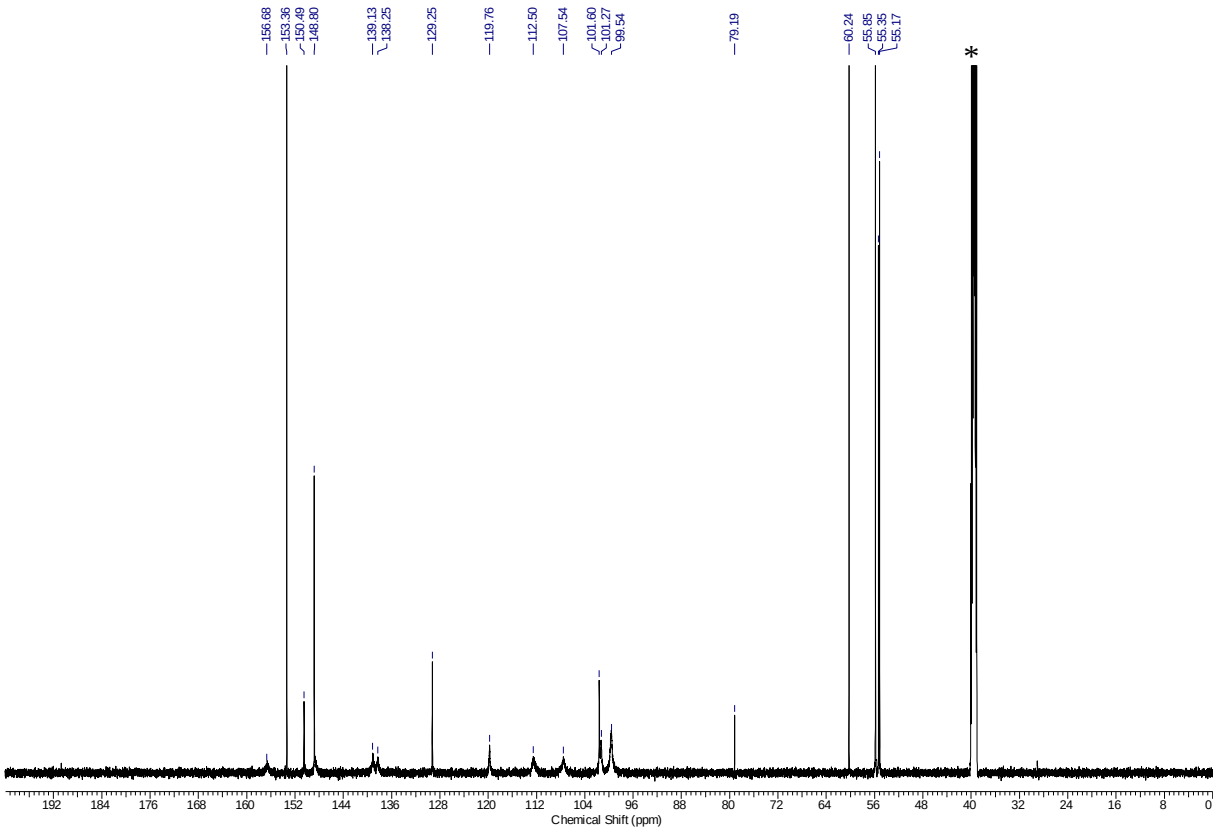
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of compound **46a**. * = NMR-solvent



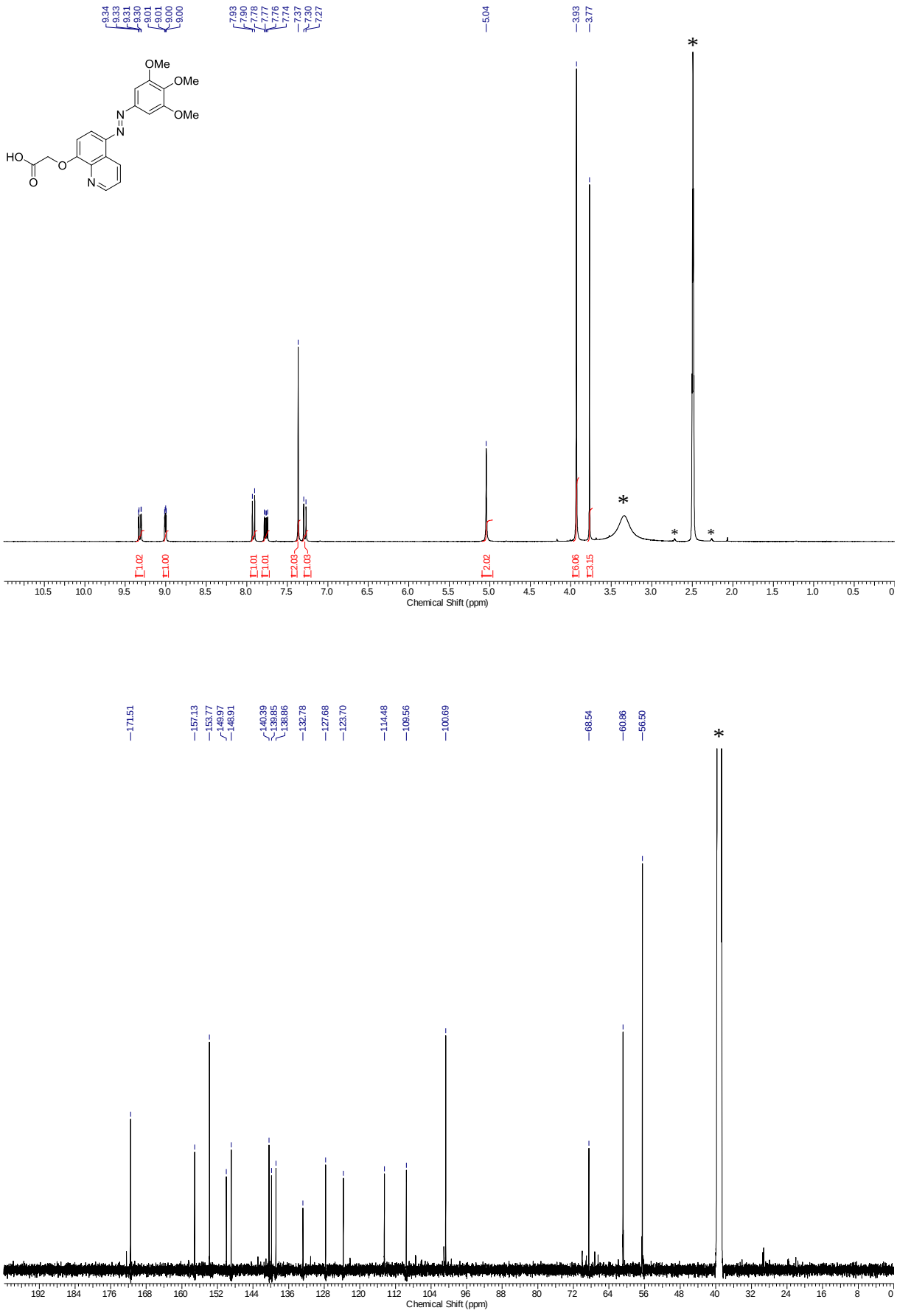


^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (75 MHz, DMSO-d_6) spectrum of compound **46b**. * = NMR-solvent

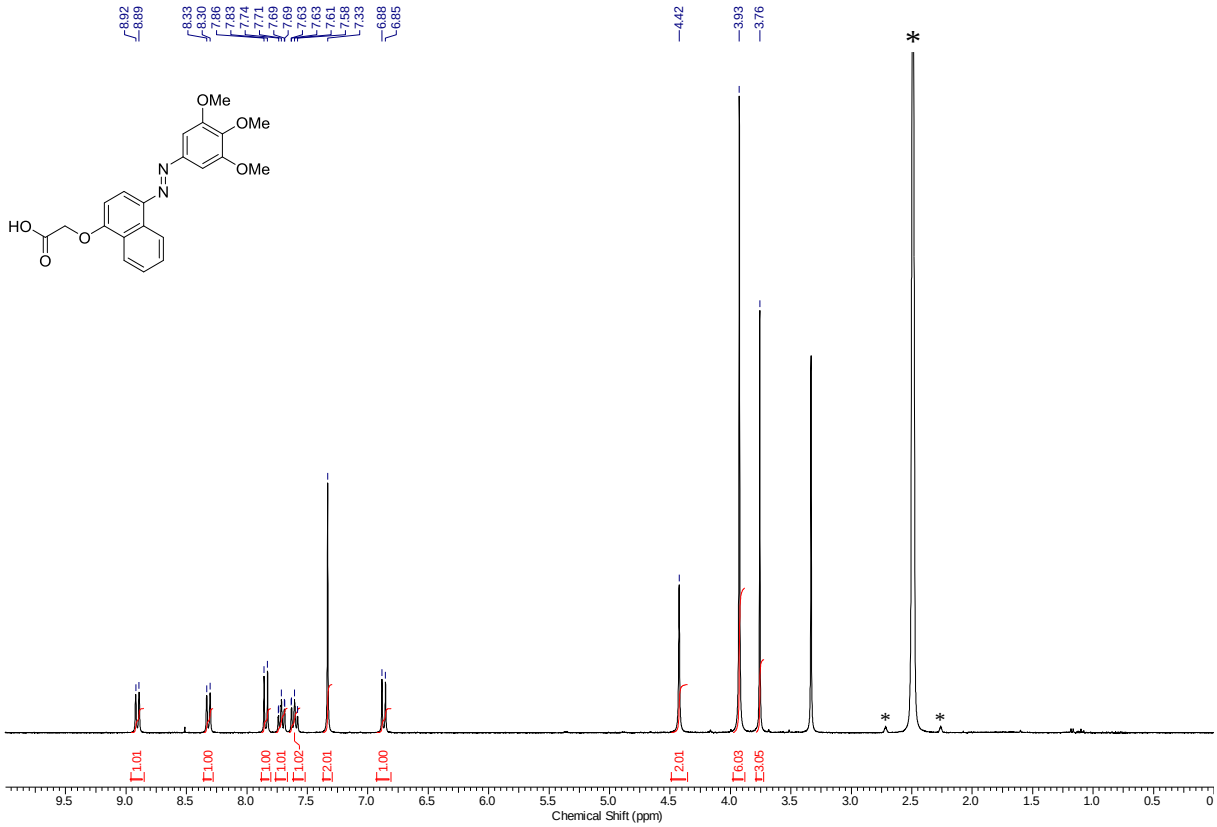


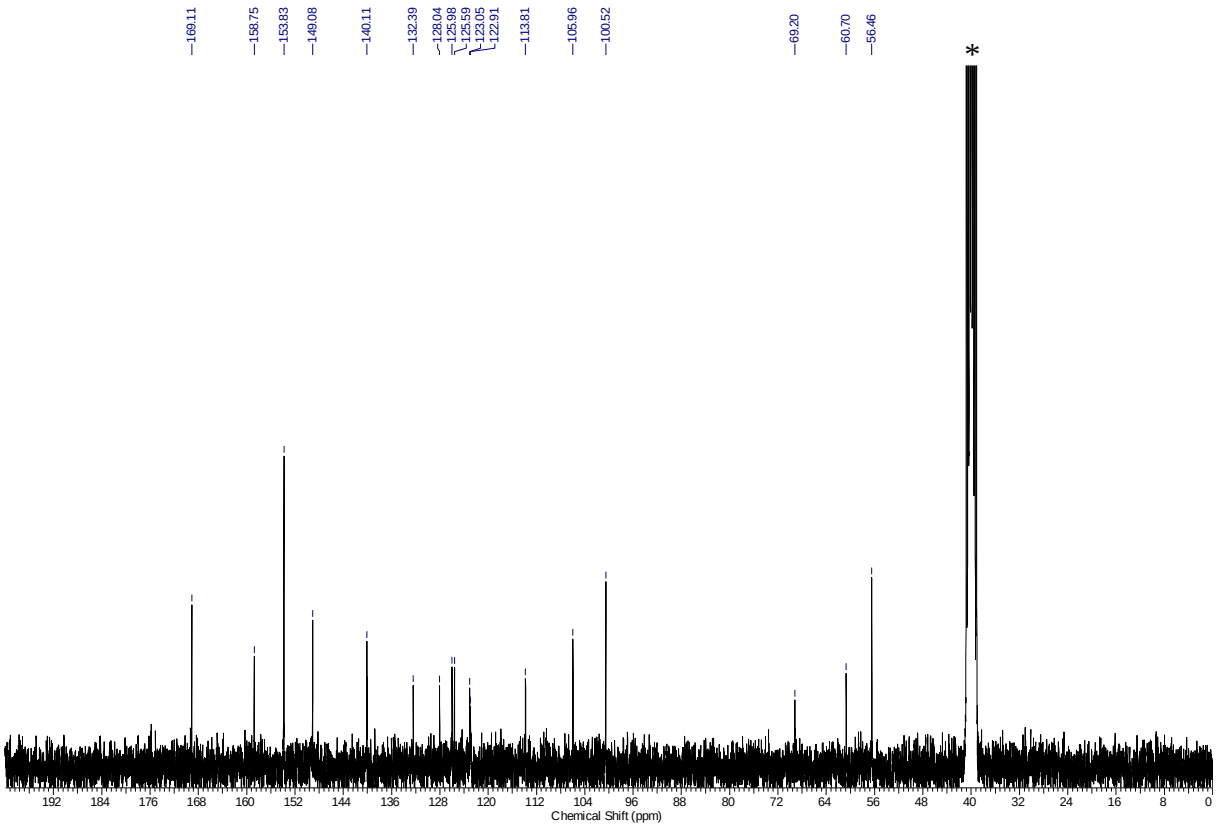


^{1}H-NMR (600 MHz, DMSO-d_6) and ^{13}C-NMR (151 MHz, DMSO-d_6) spectrum of compound **46d**. * = NMR-

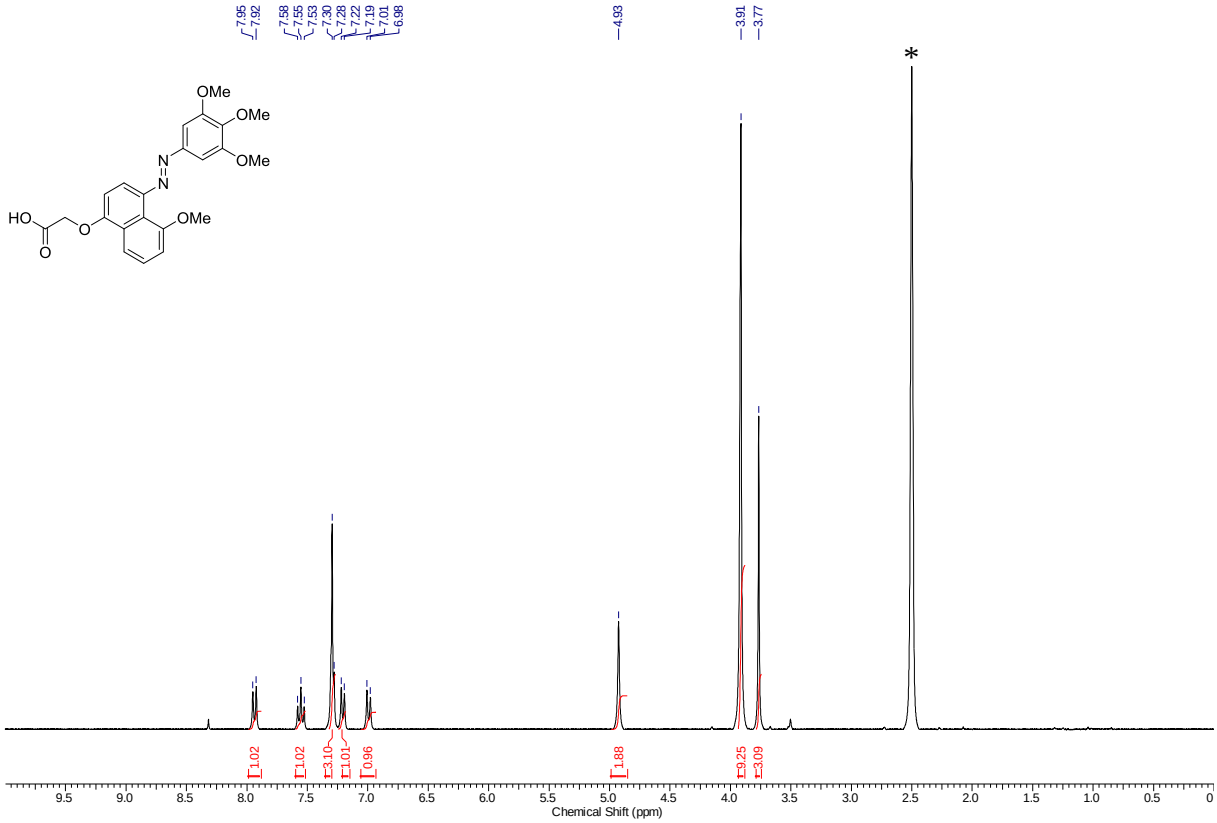


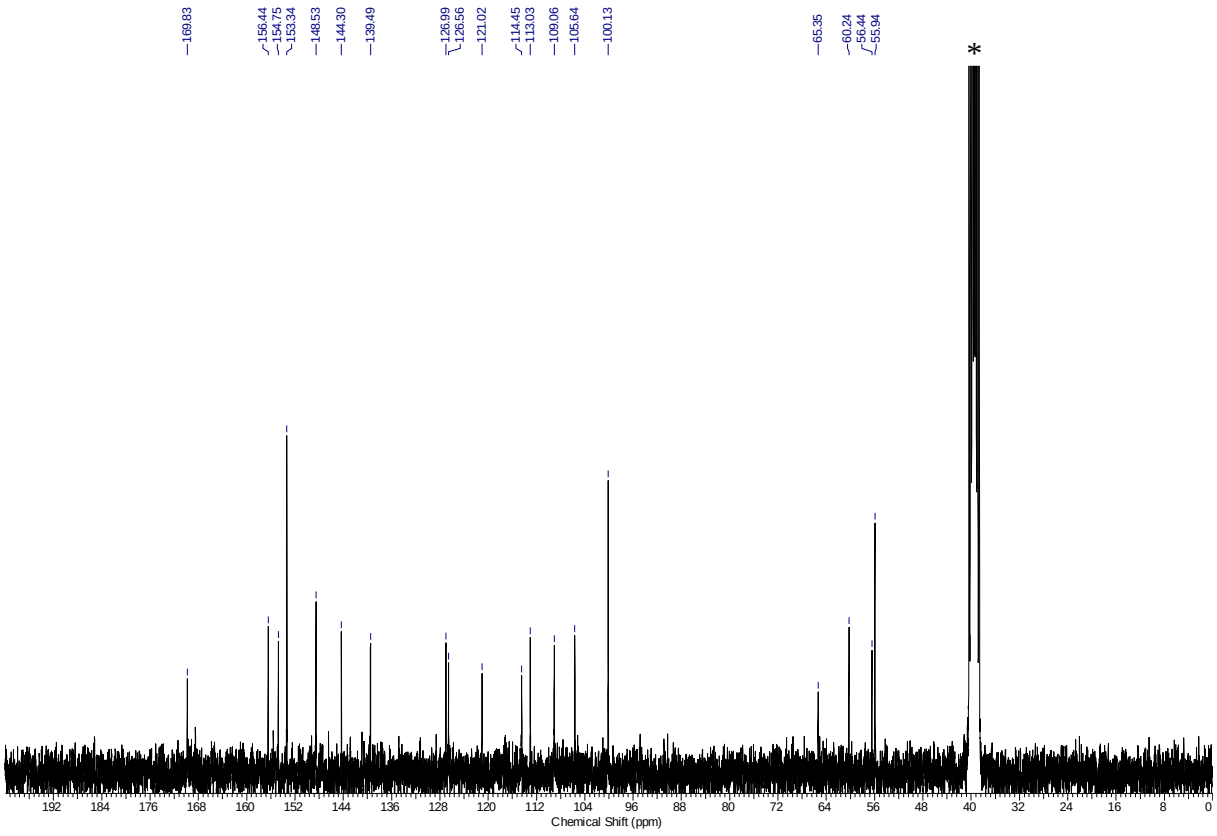
^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of compound **47a**. * = NMR-solvent, H_2O



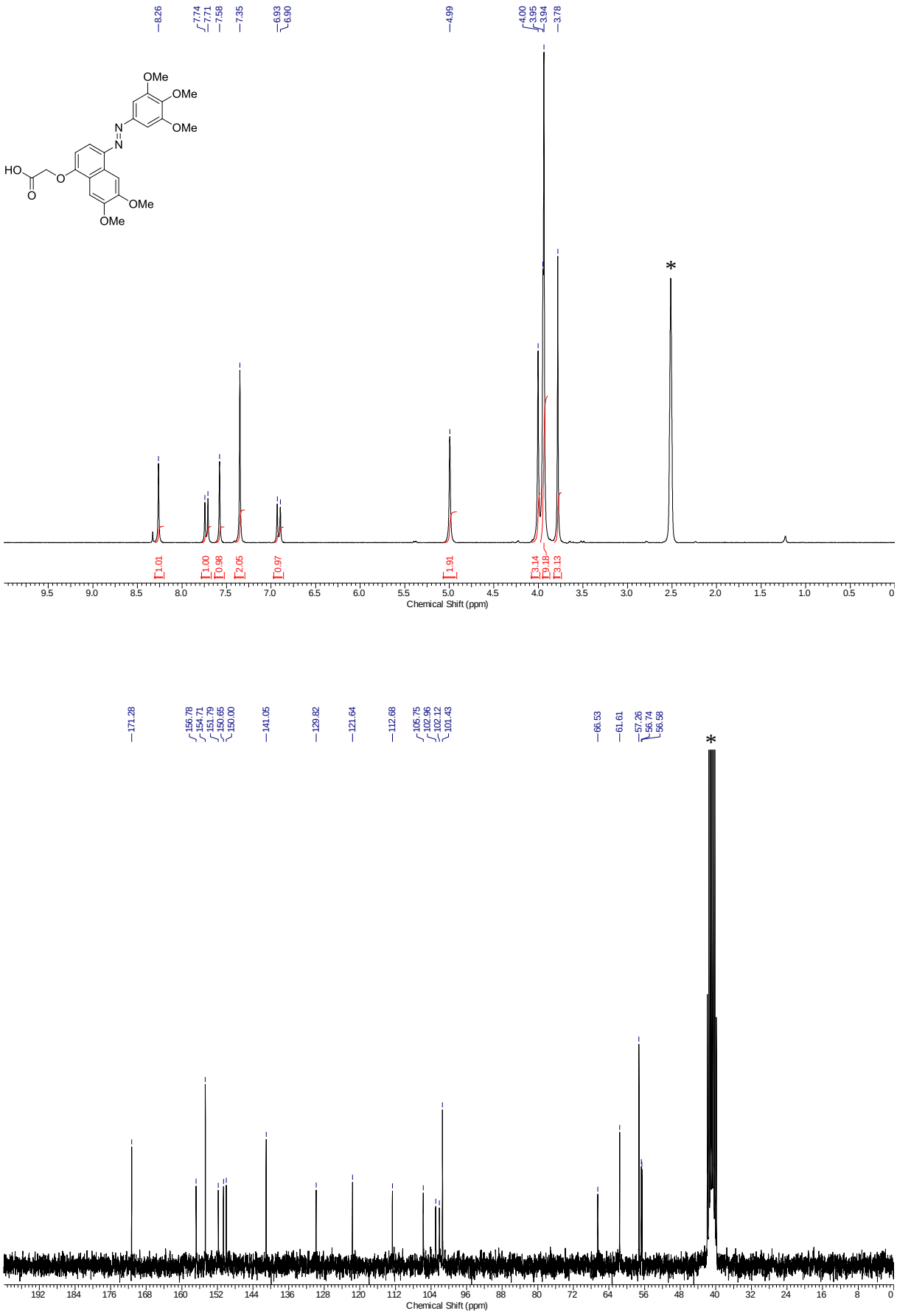


^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (75 MHz, DMSO-d_6) spectrum of compound **47b**. * = NMR-solvent

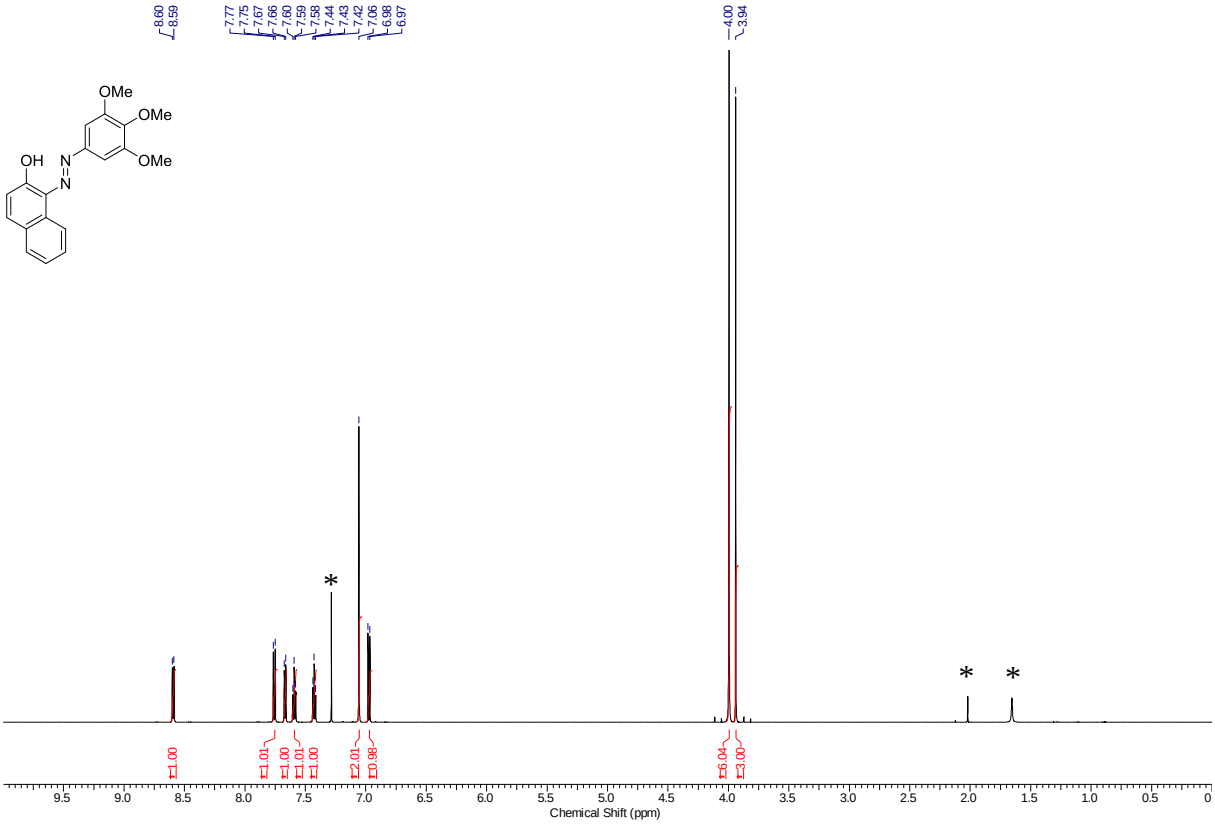


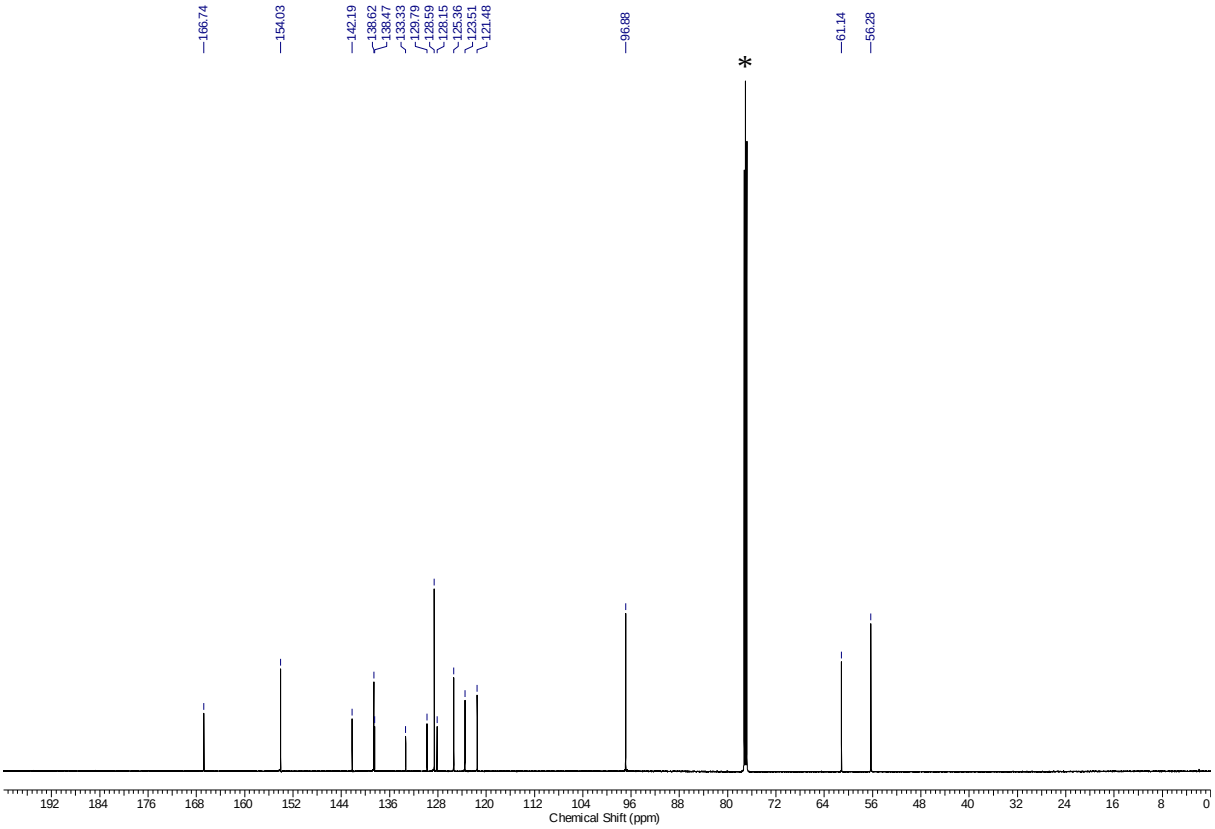


^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (75 MHz, DMSO-d_6) spectrum of compound **47c**. * = NMR-solvent



^{1}H-NMR (250 MHz, DMSO-d_6) and ^{13}C-NMR (63 MHz, DMSO-d_6) spectrum of compound **47d**. * = NMR-solvent





^{1}H-NMR (600 MHz, $CDCl_3$) and ^{13}C-NMR (151 MHz, $CDCl_3$) spectrum of compound **49**. * = NMR-solvent, CH_3CN, H_2O

Supplemental References

1 P. G. Wuts and T. W. Greene, *Greene's protective groups in organic synthesis*, John Wiley & Sons, 2006.

2 B. W. Stein, S. K. Cary, J. M. Berg, E. R. Birnbaum, S. A. Kozimor, V. Mocko and B. L. Scott, *J. Organomet. Chem.*, 2018, **857**, 170.

3 P.-A. Deyris, T. Cañeque, F. Gomes, V. Narbonne, G. Maestri and M. Malacria, *Heterocycles*, 2014, **88**, 807.

4. S. G. Ramkumar and S. Ramakrishnan, *Macromolecules*, 2010, **43**, 2307-2312.

5. D. M. Mofford, G. R. Reddy and S. C. Miller, *J. Am. Chem. Soc.*, 2014, **136**, 13277.

6. E. M. Doherty, C. Fotsch, Y. Bo, P. P. Chakrabarti, N. Chen, N. Gavva, N. Han, M. G. Kelly, J. Kincaid, L. Klionsky, Q. Liu, V. I. Ognyanov, R. Tamir, X. Wang, J. Zhu, M. H. Norman and J. J. S. Treanor, *J. Med. Chem.*, 2005, **48**, 71.

7 W. L. Armarego, *Purification of laboratory chemicals*, Butterworth-Heinemann, 2017.

8 E. Fischer, *J. Phys. Chem.*, 1967, **71**, 3704.