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$GaCl_3$-mediated acyclic dimerization of donor-acceptor cyclopropanes using 1,2-dipole reactivity

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Contents

General

^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX-III 400 (400.1 and 100.6 MHz, respectively) and Bruker AVANCE II 300 (300 and 75 MHz, respectively) spectrometers in $CDCl_3$ containing 0.05% Me_4Si as the internal standard. ^{19}F NMR spectra were recorded on a 300 MHz spectrometer (282.4 MHz), external standard — $CFCl_3$. Assignments of ^{1}H and ^{13}C signals, and determinations of structures and its stereochemistry were made with the aid of 1D DEPT-135 and 2D COSY, TOCSY, NOESY, HSQC and HMBC spectra.

*General procedure for the synthesis of dimers **6b–d***:

All operations were performed in dry argon atmosphere. To a solution of cyclopropane **1b–d** (0.6 mmol) in 5 ml of dry dichloromethane was added the solid $GaCl_3$ (0.36 mmol, 60 mol.%) in one portion at 20°C under vigorous stirring. Reaction mixture was stirred at the same temperature during 2 h. After that aqueous solution of HCl (5%) was added at room temperature until pH 3 was achieved and the reaction mixture was extracted with dichloromethane (3×10 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was separated by column chromatography on silica gel (eluent — benzene to benzene–EtOAc, 5:1) to afford cyclopropane dimers **6b–d**, **2b–d** and **3b–d** as a number of fractions with different purity. The target dimers **6b–d** were additionally purified on a Silufol chromatographic plate (20×20 cm) eluting with hexane–acetone, 5:1 or benzene–EtOAc, 10:1 to afford the pure product. NMR spectra of compounds **2b–d** and **3b–d** correspond to described earlier [Refs. 4,8].

*Tetramethyl 4-(4-fluorobenzyl)-3-(4-fluorophenyl)pent-2-ene-1,1,5,5-tetracarboxylate **6b***: The title compound was prepared according to the general procedure in 48 mg (32%) yield (mixture of *Z*- and *E*-isomers ~25:1): colorless thick oil. IR ($CHCl_3$) ν 3027, 2955, 2921, 2848, 2434, 2401, 1735 (C=O), 1606, 1511, 1437 cm^{-1}. HRMS calcd for $C_{26}H_{26}F_2O_8$: $[M+H]^+$, 505.1669; $[M+Na]^+$, 527.1488. Found: *m/z* 505.1681, 527.1494. *Z*-**6b**: ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 2.70 (dd, 1H, H(5a), ^{2}J = 14.0 Hz, ^{3}J = 9.4 Hz), 2.85 (dd, 1H, H(5b), ^{2}J = 14.0 Hz, ^{3}J = 4.3 Hz), 3.53 (ddd, 1H, H(4), ^{3}J = 9.5, 9.4 and 4.3 Hz), 3.65 (d, 1H, H(2′), ^{3}J = 9.5 Hz), 3.64, 3.68, 3.69 and 3.72 (all s, 4×3H, 4OMe), 3.87 (d, 1H, H(1), ^{3}J = 10.3 Hz), 5.66 (d, 1H, H(2), ^{3}J = 10.3 Hz), 6.86–7.11 (m, 8H, 2Ar). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 36.6 (CH_2(5)), 47.5 (CH(4)), 52.0 (CH(1)), 52.72 (OMe), 52.76 (3OMe), 55.7 (CH(2′)), 122.0 (CH(2)), 115.0 (d, 2 *m*-CH, $^{2}J_{CF}$ = 21.3 Hz), 115.4 (d, 2 *m*-CH, $^{2}J_{CF}$ = 20.5 Hz), 130.6 (d, 2 *o*-CH, $^{3}J_{CF}$ = 8.0 Hz), 131.1 (d, 2 *o*-CH, $^{3}J_{CF}$ = 7.8 Hz), 134.1 (d, *i*-C, $^{4}J_{CF}$ = 3.1 Hz), 134.4 (d, *i*-C, $^{4}J_{CF}$ = 3.3 Hz), 144.5 (C(3)), 161.67 (d, *p*-CF, $^{1}J_{CF}$ = 244.7 Hz), 161.73 (d, *p*-CF, $^{1}J_{CF}$ = 245.0 Hz), 168.1, 168.2, 168.3 and 168.4 (4COO). ^{19}F NMR ($CDCl_3$, 282.4 MHz): δ –117.6 (tt, 1F, $^{3}J_{HF}$ = 9.0 Hz, $^{4}J_{HF}$ = 5.1 Hz), –114.7 (tt, 1F, $^{3}J_{HF}$ = 9.1 Hz, $^{4}J_{HF}$ = 5.2 Hz). *E*-**6b**: part of ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 4.42 (d, 1H, H(1), ^{3}J = 10.6 Hz), 5.76 (d, 1H, H(2), ^{3}J = 10.6 Hz), other signals are overlapped with the signals of major isomer.

Tetramethyl 4-(4-chlorobenzyl)-3-(4-chlorophenyl)pent-2-ene-1,1,5,5-tetracarboxylate ***6c***: The title compound was prepared according to the general procedure in 59 mg (37%) yield (mixture of *Z*- and *E*-isomers ~20:1). Compound **6c** (mixture of *Z*- and *E*-isomers ~20:1): colorless thick oil. IR ($CHCl_3$) ν 3020, 2956, 2924, 2852, 2401, 1737 (C=O), 1659, 1519, 1476, 1423 cm^{-1}. MS (*m/z*, %): 505 (1) $[M–OMe]^+$ for ^{35}Cl, 473 (1), 441 (1), 404 (26), 373 (2), 345 (8), 313 (3), 272 (62), 237 (14), 205 (17), 167 (11), 149 (76), 125 (100), 115 (31), 100 (26), 89 (30), 69 (38), 59 (98), 43 (53). HRMS calcd for $C_{26}H_{26}{}^{35}Cl_2O_8$: $[M+H]^+$, 537.1077; $[M+Na]^+$, 559.0897. Found: *m/z* 537.1053, 559.0886. *Z*-**6c**: ^1H NMR ($CDCl_3$, 400.1 MHz): δ 2.70 (dd, 1H, H(5a), ^2J = 14.1 Hz, ^3J = 9.3 Hz), 2.85 (dd, 1H, H(5b), ^2J = 14.1 Hz, ^3J = 4.2 Hz), 3.53 (ddd, 1H, H(4), ^3J = 9.5, 9.3 and 4.2 Hz), 3.64 (d, 1H, H(2′), ^3J = 9.5 Hz), 3.65, 3.69, 3.70 and 3.73 (all s, 4×3H, 4OMe), 3.86 (d, 1H, H(1), ^3J = 10.4 Hz), 5.66 (d, 1H, H(2), ^3J = 10.4 Hz), 6.90–6.94 (m, 2H, 2 *o*-H, Ar at C(3)), 7.05–7.09 (m, 2H, 2 *o*-H, Ar at C(5)), 7.19–7.23 (m, 2H, 2 *m*-H, Ar at C(5)), 7.25–7.29 (m, 2H, 2 *m*-H, Ar at C(3)). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 36.5 (CH_2(5)), 48.2 (CH(4)), 52.0 (CH(1)), 52.77 (OMe), 52.80 (3OMe), 55.6 (CH(2′)), 122.3 (CH(2)), 128.4 (2 *m*-CH, Ar at C(5)), 128.7 (2 *m*-CH, Ar at C(3)), 130.2 (2 *o*-CH, Ar at C(3)), 131.0 (2 *o*-CH, Ar at C(5)), 132.3 (*p*-CCl, Ar at C(5)), 134.1 (*p*-CCl, Ar at C(3)), 136.76 (*i*-C, Ar at C(3)), 136.84 (*i*-C, Ar at C(5)), 144.2 (C(3)), 168.0, 168.1, 168.3 and 168.4 (4COO). *E*-**6c**: ^1H NMR ($CDCl_3$, 400.1 MHz): δ 2.54 (dd, 1H, H(5a), ^2J = 14.0 Hz, ^3J = 10.3 Hz), 2.76 (dd, 1H, H(5b), ^2J = 14.0 Hz, ^3J = 4.3 Hz), 3.63, 3.66, 3.72 and 3.75 (all s, 4×3H, 4OMe), 3.87–3.97 (m, 1H, H(4)), 4.41 (d, 1H, H(1), ^3J = 10.8 Hz), 5.78 (d, 1H, H(2), ^3J = 10.8 Hz), 6.98–7.30 (m, 8H, 2Ar), H(2′) signals are overlapped with the signals of major isomer. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 35.0 (CH_2(5)), 51.0, 52.2, 52.5, 52.7, 52.8 and 52.9 (CH(1), CH(4) and 4OMe), 55.9 (CH(2′)), 128.4, 128.5, 128.6 (2×2 *m*-CH, 2Ar, and CH(2)), 130.6 and 130.9 (2×2 *o*-CH, 2Ar), all signals of quaternary carbons are invisible due to its low intensity.

Tetramethyl 4-(4-chlorobenzyl)-3-(4-chlorophenyl)pent-1-ene-1,1,5,5-tetracarboxylate ***9c***: The title compound was isolated with ~70% purity in ~0.5 mg (~0.2%) yield as single diastereomer after a number of cascade separations and purifications (up to 3 times) on a Silufol chromatographic plates (20×20 cm, eluents — hexane–acetone, 5:1 and benzene–EtOAc, 10:1) of the obtained fractions from the main first column chromatography of the reaction mixture from general procedure for cyclopropane **1c**. Also the trace compounds **4c** and **5c** were detected in some obtained fractions. NMR spectra of compounds **4c** and **5c** correspond to described earlier [Refs. 4, 8]. Compound **9c** (single diastereomer, ~70% purity): colorless thick oil. IR ($CHCl_3$) ν 3020, 2955, 2922, 2851, 2434, 2400, 1734 (C=O), 1653, 1522, 1493, 1474, 1436, 1322 cm^{-1}. MS (*m/z*, %): 473 (1), 404 (3), 379 (8), 347 (15), 275 (46), 243 (90), 211 (100), 149 (71), 125 (68), 115 (40), 59 (51), 32 (33). HRMS calcd for $C_{26}H_{26}{}^{35}Cl_2O_8$: $[M+Na]^+$, 559.0897. Found: *m/z* 559.0889. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 2.55 (dd, 1H, H(5a), ^2J = 14.7 Hz, ^3J = 5.2 Hz), 2.76 (dd, 1H, H(5b), ^2J = 14.7 Hz, ^3J = 8.1 Hz), 2.98 (dddd, 1H, H(4), ^3J = 9.9, 8.1, 5.2 and 4.2 Hz), 3.50 (d, 1H, H(2′), ^3J = 4.2 Hz), 3.69, 3.71, 3.74 and 3.83 (all s, 4×3H, 4OMe), 4.15 (dd, 1H, H(3), ^3J = 11.6 and 9.9 Hz), 6.86–6.91 (m, 2H, 2 *o*-H, Ar at C(5)), 7.07 (d, 1H, H(2), ^3J

= 11.6 Hz), 7.12–7.16 (m, 2H, 2 *m*-H, Ar at C(5)), 7.16–7.20 (m, 2H, 2 *o*-H, Ar at C(3)), 7.24–7.29 (m, 2H, 2 *m*-H, Ar at C(3)). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 35.4 (CH_2(5)), 45.6 (CH(4)), 47.9 (CH(3)), 52.1, 52.2, 52.4, 52.5 and 52.6 (CH(2′) and 4OMe), 128.5 (2 *m*-CH, Ar at C(5)), 129.4 (2 *m*-CH, Ar at C(3)), 129.8 (2 *o*-CH, Ar at C(3)), 130.5 (2 *o*-CH, Ar at C(5)), 148.6 (CH(2)), all signals of quaternary carbons are not acquired due to very small quantity of substance.

Tetramethyl 4-(4-bromobenzyl)-3-(4-bromophenyl)pent-2-ene-1,1,5,5-tetracarboxylate ***6d***: The title compound was prepared according to the general procedure in 84 mg (45%) yield (mixture of *Z*- and *E*-isomers ~30:1): colorless thick oil. IR ($CHCl_3$) ν 3019, 2976, 2956, 2897, 2850, 1735 (C=O), 1589, 1513, 1487, 1436, 1392, 1297 cm^{-1}. MS (*m/z*, %): 494 (24), 463 (1), 435 (5), 375 (6), 362 (39), 323 (10), 295 (4), 277 (4), 265 (5), 249 (4), 215 (20), 169 (66), 139 (18), 115 (19), 90 (44), 59 (100). HRMS calcd for $C_{26}H_{26}{}^{79}Br_2O_8$: $[M+Na]^+$, 646.9887. Found: *m/z* 646.9882. *Z*-**6d**: ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 2.69 (dd, 1H, H(5a), ^2J = 14.1 Hz, ^3J = 9.3 Hz), 2.84 (dd, 1H, H(5b), ^2J = 14.1 Hz, ^3J = 4.1 Hz), 3.52 (ddd, 1H, H(4), ^3J = 9.6, 9.3 and 4.1 Hz), 3.64 (d, 1H, H(2′), ^3J = 9.6 Hz), 3.65, 3.69, 3.70 and 3.73 (all s, 4×3H, 4OMe), 3.85 (d, 1H, H(1), ^3J = 10.4 Hz), 5.67 (d, 1H, H(2), ^3J = 10.4 Hz), 6.82–6.88 (m, 2H, 2 *o*-H, Ar at C(3)), 6.99–7.05 (m, 2H, 2 *o*-H, Ar at C(5)), 7.34–7.39 (m, 2H, 2 *m*-H, Ar at C(5)), 7.40–7.45 (m, 2H, 2 *m*-H, Ar at C(3)). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 36.6 (CH_2(5)), 48.0 (CH(4)), 52.0 (CH(1)), 52.78 (OMe), 52.81 (3OMe), 55.6 (CH(2′)), 120.4 (*p*-CBr, Ar at C(5)), 122.3 (*p*-CBr, Ar at C(3)), 122.4 (CH(2)), 130.5 (2 *o*-CH, Ar at C(3)), 131.3 (2 *m*-CH, Ar at C(5)), 131.4 (2 *o*-CH, Ar at C(5)), 131.7 (2 *m*-CH, Ar at C(3)), 137.2 (*i*-C, Ar at C(3)), 137.3 (*i*-C, Ar at C(5)), 144.2 (C(3)), 168.0, 168.1, 168.3 and 168.4 (4COO). *E*-**6d**: ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 2.52 (dd, 1H, H(5a), ^2J = 13.5 Hz, ^3J = 10.3 Hz), 2.73 (dd, 1H, H(5b), ^2J = 13.5 Hz, ^3J = 4.3 Hz), 3.60, 3.62, 3.72 and 3.75 (all s, 4×3H, 4OMe), 3.84–3.96 (m, 1H, H(4)), 4.41 (d, 1H, H(1), ^3J = 10.9 Hz), 5.78 (d, 1H, H(2), ^3J = 10.9 Hz), 6.90–7.47 (m, 8H, 2Ar), H(2′) signals are overlapped with the signals of major isomer.

Dimerization of cyclopropane ***1e*** *in the presence of* $GaCl_3$: All operations were performed in dry argon atmosphere. To a solution of cyclopropane **1e** (167 mg, 0.6 mmol) in 5 ml of dry dichloromethane was added the solid $GaCl_3$ (127 mg, 0.72 mmol, 120 mol.%) in one portion at room temperature under vigorous stirring. Reaction mixture was heated to 40°C and refluxed with stirring during 3 h. After that aqueous solution of HCl (5%) was added at room temperature until pH 3 was achieved and the reaction mixture was extracted with dichloromethane (3×10 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was separated by column chromatography on silica gel (eluent — benzene to benzene–EtOAc, 5:1) to afford cyclopropane dimers **2e**, **6e** and minor dimers (**8e–10e**) as a number of fractions with different purity. The target dimers **2e** and **6e** were additionally purified on a Silufol chromatographic plates (20×20 cm) eluting with hexane–acetone, 5:1 or benzene–EtOAc, 10:1 to afford the pure products. Minor and trace dimers (**8e–10e**) were isolated with different purity

using a number of cascade separations and purifications (up to 4 times) on Silufol chromatographic plates (20×20 cm, eluents — hexane–acetone, 5:1 and benzene–EtOAc, 10:1) of the obtained fractions from the main first column chromatography and additional purifications of major dimers.

Dimethyl 2-(1,3-dimethoxy-1,3-dioxopropan-2-yl)-3,4-bis(4-nitrophenyl)cyclopentane-1,1-dicarboxylate ***2e***: The title compound was prepared in summary 84 mg (50%) yield (ratio of *trans,trans*- and *trans,cis*-isomers ~1.3:1), both isomers were completely separated to afford the pure diastereomers. *trans,trans*-**2e**: colorless thick oil. IR ($CHCl_3$): ν 3020, 2976, 2924, 2853, 1739 br (C=O), 1602, 1524, 1422 cm^{-1}. MS (*m/z*, %): 527 (3, M^+–OMe), 495 (1), 427 (5), 367 (11), 307 (3), 278 (5), 215 (13), 132 (100), 115 (21), 59 (61), 43 (30). HRMS calcd for $C_{26}H_{26}N_2O_{12}$: $[M+H]^+$, 559.1559; $[M+Na]^+$, 581.1378. Found: *m/z* 559.1533; 581.1357. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 2.53–2.64 (m, 1H, H_{anti}(5)), 3.06–3.19 (m, 2H, H_{syn}(5) and H(4)), 3.16, 3.64, 3.76 and 3.87 (all s, 4×3H, 4OCH_3), 3.94–4.07 (m, 3H, H(2), H(3) and H(2′)), 7.26–7.31 (m, 2H, 2 *o*-H, Ar), 7.31–7.36 (m, 2H, 2 *o*-H, Ar), 8.03–8.09 (m, 4H, 4 *m*-H, Ar). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 41.8 (CH_2(5)), 49.9 (CH(2)), 50.7 (CH(2′)), 52.3, 52.4, 53.08 and 53.7 (4OMe), 53.13 (CH(4)), 55.1 (CH(3)), 61.9 (C(1)), 123.6 and 123.9 (2×2 *m*-CH), 128.5 and 129.5 (2×2 *o*-CH), 147.2, 147.3, 147.7 and 148.1 (2 *i*-C and 2 *p*-C), 168.2, 168.7, 170.1 and 172.5 (4COO). *trans,cis*-**2e**: colorless thick oil. IR ($CHCl_3$): ν 3020, 2956, 2925, 2850, 2435, 2400, 1736 br (C=O), 1605, 1524, 1437, 1349, 1319, 1280, 1257 cm^{-1}. MS (*m/z*, %): 558 (1, M^+), 526 (4, M^+–$HOCH_3$), 495 (1), 466 (1), 427 (6), 382 (7), 367 (10), 278 (16), 247 (10), 215 (17), 145 (25), 132 (100), 100 (23), 59 (63), 43 (16). HRMS calcd for $C_{26}H_{26}N_2O_{12}$: $[M+Na]^+$, 581.1378. Found: *m/z* 581.1370. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 2.58–2.68 (m, 1H, H_{syn}(5)), 2.90–2.98 (m, 1H, H_{anti}(5)), 3.40, 3.47, 3.77 and 3.87 (all s, 4×3H, 4OCH_3), 3.96 (dd, 1H, H(2), ^3J = 7.5 and 5.7 Hz), 4.10–4.23 (m, 2H, H(3) and H(4)), 4.17 (d, 1H, H(2′), ^3J=5.6 Hz), 6.99–7.06 (m, 2H, 2 *o*-H, Ar), 7.06–7.12 (m, 2H, 2 *o*-H, Ar), 7.87–7.94 (m, 4H, 4 *m*-H, Ar). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 39.1 (CH_2(5)), 48.1 and 50.9 (CH(3) and CH(4)), 51.2 (CH(2)), 51.7 (CH(2′)), 52.3, 52.6, 52.9 and 53.5 (4OMe), 61.8 (C(1)), 123.2 and 123.3 (2×2 *m*-CH), 128.9 and 129.9 (2×2 *o*-CH), 146.62, 146.63, 146.9 and 148.7 (2 *i*-C and 2 *p*-C), 168.6, 168.8, 170.1 and 171.4 (4COO).

Tetramethyl 4-(4-nitrobenzyl)-3-(4-nitrophenyl)pent-2-ene-1,1,5,5-tetracarboxylate ***6e***: The title compound was prepared in 63 mg (38%) yield (mixture of *Z*- and *E*-isomers ~8:1): colorless thick oil. IR ($CHCl_3$) ν 3020, 2975, 2956, 2923, 2851, 2401, 2256, 1736 (C=O), 1601, 1524, 1495, 1436, 1348, 1318 cm^{-1}. MS (*m/z*, %): 527 (2, M^+–OMe), 495 (1), 426 (14), 367 (12), 307 (9), 290 (14), 278 (8), 232 (8), 215 (15), 145 (13), 132 (100), 100 (30), 59 (100), 43 (27). HRMS calcd for $C_{26}H_{26}N_2O_{12}$: $[M+H]^+$, 559.1559; $[M+Na]^+$, 581.1378. Found: *m/z* 559.1539; 581.1365. *Z*-**6e**: ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 2.89 (dd, 1H, H(5a), ^2J = 14.0 Hz, ^3J = 9.5 Hz), 3.07 (dd, 1H, H(5b), ^2J = 14.0 Hz, ^3J = 3.9 Hz), 3.61 (ddd, 1H, H(4), ^3J = 9.6, 9.5 and 3.9 Hz), 3.69 (d, 1H, H(2′), ^3J = 9.6 Hz), 3.68, 3.71, 3.72 and 3.78 (all s, 4×3H, 4OMe), 3.79 (d, 1H,

H(1), ^3J = 10.5 Hz), 5.84 (d, 1H, H(2), ^3J = 10.4 Hz), 7.13–7.18 (m, 2H, 2 *o*-H, Ar at C(3)), 7.32–7.36 (m, 2H, 2 *o*-H, Ar at C(5)), 8.10–8.14 (m, 2H, 2 *m*-H, Ar at C(5)), 8.12–8.16 (m, 2H, 2 *m*-H, Ar at C(3)). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 37.4 (CH_2(5)), 47.7 (CH(4)), 51.8 (CH(1)), 52.97 (OMe), 53.03 (3OMe), 55.5 (CH(2′)), 123.6 (2 *m*-CH, Ar at C(5)), 123.8 (CH(2) and 2 *m*-CH, Ar at C(3)), 129.7 (2 *o*-CH, Ar at C(3)), 130.5 (2 *o*-CH, Ar at C(5)), 143.3 (C(3)), 145.0 (*i*-C, Ar at C(3)), 146.0 (*i*-C, Ar at C(5)), 147.0 (*p*-C, Ar at C(5)), 147.6 (*p*-C, Ar at C(3)), 167.5 and 167.7 (2COO), 168.0 (2COO). *E*-**6e**: ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 2.64 (dd, 1H, H(5a), ^2J = 13.7 Hz, ^3J = 10.3 Hz), 2.98 (dd, 1H, H(5b), ^2J = 13.7 Hz, ^3J = 3.8 Hz), 3.63, 3.67, 3.76 and 3.80 (all s, 4×3H, 4OMe), 3.95–4.09 (m, 1H, H(4)), 4.50 (d, 1H, H(1), ^3J = 10.9 Hz), 5.90 (d, 1H, H(2), ^3J = 10.9 Hz), 7.22–7.27 (m, 2H, 2 *o*-H, Ar), 7.29–7.34 (m, 2H, 2 *o*-H, Ar), 8.07–8.12 (m, 2H, 2 *m*-H, Ar), 8.16–8.21 (m, 2H, 2 *m*-H, Ar), H(2′) signals are overlapped with the signals of major isomer.

Trimethyl 2-(4-nitrobenzyl)-3-(4-nitrophenyl)pent-3-ene-1,1,5-tricarboxylate ***10e***: The title compound was prepared in 8 mg (5%) yield (mixture of *E*- and *Z*-isomers ~1.2:1). Compound **10e** (mixture of *E*- and *Z*-isomers ~1.2:1): colorless thick oil. IR ($CHCl_3$) ν 3021, 2973, 2956, 2922, 1736 (C=O), 1600, 1523, 1494, 1437, 1403, 1348, 1320, 1264 cm^{-1}. MS (*m/z*, %): 500 (2), 468 (2), 368 (10), 350 (3), 332 (3), 309 (4), 295 (5), 272 (4), 232 (8), 215 (7), 202 (7), 286 (5), 168 (4), 141 (8), 132 (97), 115 (22), 100 (29), 90 (30), 74 (32), 59 (98), 43 (47), 30 (75), 15 (100). HRMS calcd for $C_{24}H_{24}N_2O_{10}$: $[M+H]^+$, 501.1504; $[M+Na]^+$, 523.1323,. Found: *m/z* 501.1502; 523.1326. *E*-**10e**: ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 2.64 (dd, 1H, H(5a), ^2J = 13.7 Hz, ^3J = 11.0 Hz), 3.98 (dd, 1H, H(5b), ^2J = 13.7 Hz, ^3J = 3.7 Hz), 3.05 (dd, 1H, H(1a), ^2J = 18.1 Hz, ^3J = 7.2 Hz), 3.27 (dd, 1H, H(1b), ^2J = 18.1 Hz, ^3J = 7.4 Hz), 3.64, 3.66 and 3.71 (all s, 3×3H, 3OMe), 3.81 (d, 1H, H(2′), ^3J = 11.3 Hz), 3.99 (ddd, 1H, H(4), ^3J = 11.3, 11.0 and 3.7 Hz), 5.84 (dd, 1H, H(2), ^3J = 7.4 and 7.2 Hz), 7.22–7.25 (m, 2H, 2 *o*-H, Ar at C(5)), 7.29–7.32 (m, 2H, 2 *o*-H, Ar at C(3)), 8.08–8.13 (m, 2H, 2 *m*-H, Ar at C(5)), 8.14–8.17 (m, 2H, 2 *m*-H, Ar at C(3)). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 33.7 (CH_2(1)), 37.4 (CH_2(5)), 42.1 (CH(4)), 52.1, 52.95 and 52.97 (3OMe), 55.8 (CH(2′)), 123.6 and 123.7 (2×2 *m*-CH, 2Ar), 129.4 (2 *o*-CH, Ar at C(3)), 129.88 (2 *o*-CH, Ar at C(5)), 129.89 (CH(2)), 139.1 (C(3)), 146.3, 147.0 and 147.3 (*i*-C, Ar at C(5), and 2 *p*-C, 2Ar), 148.0 (*i*-C, Ar at C(3)), 167.8, 168.1 and 171.1 (3COO). *Z*-**10e**: ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 2.79–2.87 (m, 2H, CH_2(1)), 2.84 (dd, 1H, H(5a), ^2J = 14.1 Hz, ^3J = 9.6 Hz), 3.05 (dd, 1H, H(5b), ^2J = 14.1 Hz, ^3J = 4.2 Hz), 3.60 (ddd, 1H, H(4), ^3J = 9.7, 9.6 and 4.2 Hz), 3.67 (d, 1H, H(2′), ^3J = 9.7 Hz), 3.67, 3.76 and 3.79 (all s, 3×3H, 3OMe), 5.79 (dd, 1H, H(2), ^3J = 7.4 and 7.4 Hz), 7.10–7.15 (m, 2H, 2 *o*-H, Ar at C(3)), 7.33–7.37 (m, 2H, 2 *o*-H, Ar at C(5)), 8.10–8.15 (m, 2H, 2 *m*-H, Ar at C(5)), 8.11–8.16 (m, 2H, 2 *m*-H, Ar at C(3)). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 34.4 (CH_2(1)), 37.7 (CH_2(5)), 47.7 (CH(4)), 52.1, 53.0 and 53.2 (3OMe), 55.9 (CH(2′)), 123.6 and 123.7 (2×2 *m*-CH, 2Ar), 124.5 (CH(2)), 129.8 (2 *o*-CH, Ar at C(3)), 130.4 (2 *o*-CH, Ar at C(5)), 141.1 (C(3)), 145.8 (*i*-C, Ar at C(3)), 146.2, 147.0 and 147.3 (*i*-C, Ar at C(5), and 2 *p*-C, 2Ar), 168.1, 168.2 and 171.0 (3COO).

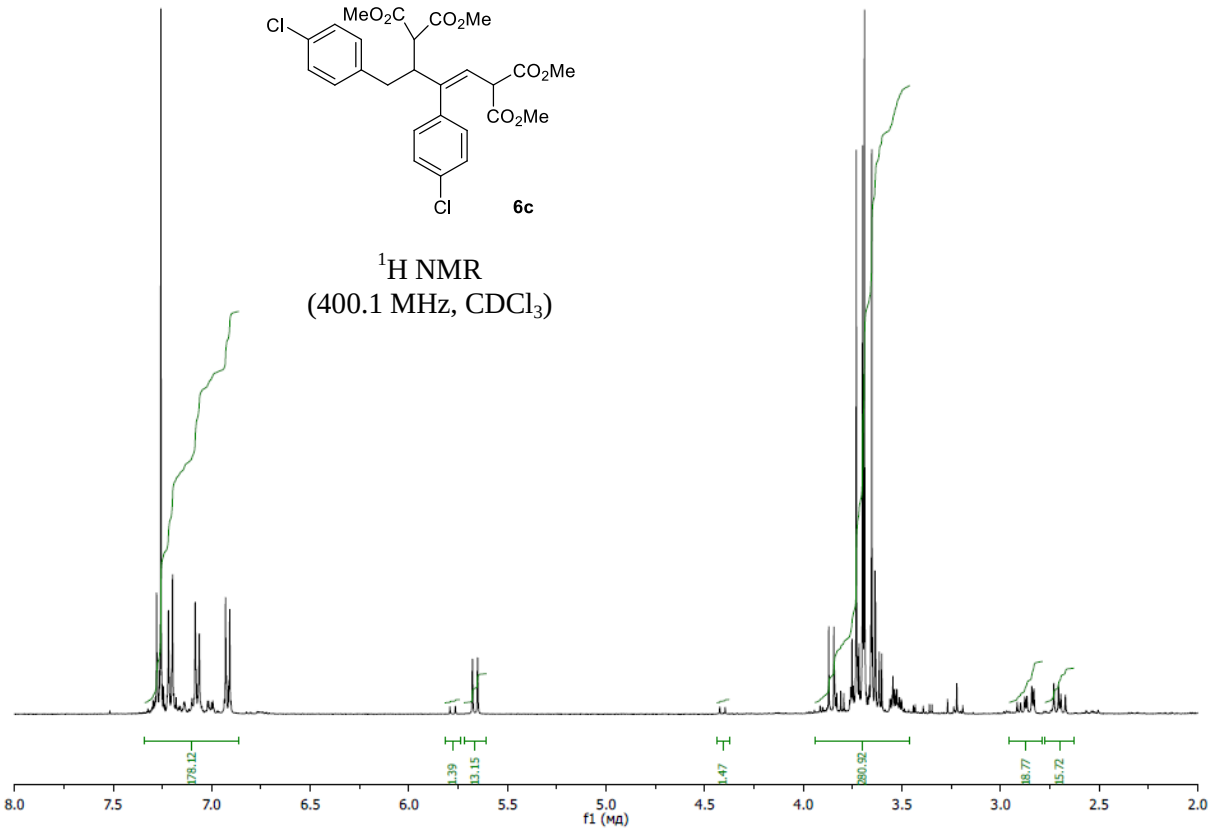
Trimethyl (5S,8S)-5,8-bis(4-nitrophenyl)-2-oxooxocane-3,6,6-tricarboxylate ***11e***: The title compound was prepared in summary 5 mg (3%) yield (mixture of 2 diastereomers at C(3) ~2:1): colorless thick oil. IR ($CHCl_3$) ν 3020, 2955, 2926, 2853, 2434, 2400, 1788, 1736 (C=O), 1651, 1527, 1468, 1436, 1350 cm^{-1}. MS (*m/z*, %): 220 (4), 202 (2), 160 (5), 149 (7), 132 (100), 115 (15), 100 (9), 59 (26). HRMS calcd for $C_{25}H_{24}N_2O_{12}$: $[M+Na]^+$, 567.1221. Found: *m/z* 567.1223. Diastereomers were partially separated, the minor diastereomer was isolated in pure form. Compound **11e** (major diastereomer): ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 2.31 (dd, 1H, H(7a), ^2J = 13.1 Hz, ^3J = 10.2 Hz), 2.24–2.34 (m, 1H, H(4a)), 2.50 (ddd, 1H, H(4b), ^2J = 14.5 Hz, ^3J = 12.2 and 4.8 Hz), 3.02 (dd, 1H, H(3), ^3J = 10.1 and 4.8 Hz), 3.17 (dd, 1H, H(7b), ^2J = 13.1 Hz, ^3J = 5.9 Hz), 3.55, 3.72 and 3.81 (all s, 3×3H, 3OMe), 3.75–3.81 (m, 1H, H(5)), 5.51 (dd, 1H, H(8), ^3J = 10.2 and 5.9 Hz), 7.35–7.39 (m, 2H, 2 *o*-H), 7.46–7.51 (m, 2H, 2 *o*-H), 8.16–8.20 (m, 2H, 2 *m*-H), 8.26–8.30 (m, 2H, 2 *m*-H). Part of ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 29.8 (CH_2(4)), 37.5 (CH_2(7)), 46.2 (CH(5)), 49.9 (CH(3)), 53.0, 53.1 and 53.8 (3OMe), 61.7 (C(6)), 77.7 (CH(8)), 124.2 and 124.4 (2×2 *m*-CH), 126.2 and 130.1 (2×2 *o*-CH), other signals of quaternary carbons are not acquired due to very small quantity of substance. Compound **11e** (minor diastereomer): Colorless thick oil. IR ($CHCl_3$) ν 3020, 2976, 2920, 2851, 2401, 1741 (C=O), 1658, 1602, 1525, 1477, 1422, 1331 cm^{-1}. MS (*m/z*, %): 468 (1), 351 (3), 336 (7), 306 (6), 276 (11), 217 (10), 204 (19), 167 (20), 149 (64), 115 (30), 105 (24), 83 (25), 71 (44), 57 (88), 43 (100). HRMS calcd for $C_{25}H_{24}N_2O_{12}$: $[M+Na]^+$, 567.1221. Found: *m/z* 567.1209. ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 2.23 (dd, 1H, H(7a), ^2J = 13.2 Hz, ^3J = 10.2 Hz), 2.29–2.40 (m, 2H, CH_2(4)), 2.96–3.03 (m, 1H, H(3)), 3.25 (dd, 1H, H(7b), ^2J = 13.2 Hz, ^3J = 6.1 Hz), 3.62, 3.75 and 3.86 (all s, 3×3H, 3OMe), 3.77–3.82 (m, 1H, H(5)), 5.50 (dd, 1H, H(8), ^3J = 10.2 and 6.1 Hz), 7.19–7.25 (m, 2H, 2 *o*-H), 7.50–7.56 (m, 2H, 2 *o*-H), 8.14–8.21 (m, 4H, 2×2 *m*-H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 29.6 (CH_2(4)), 37.4 (CH_2(7)), 45.9 (CH(5)), 49.3 (CH(3)), 52.92, 52.94 and 54.1 (3OMe), 61.7 (C(6)), 77.8 (CH(8)), 123.9 and 124.3 (2×2 *m*-CH), 126.0 and 131.4 (2×2 *o*-CH), 143.0, 143.4, 145.06 and 145.07 (2 *p*-C and 2 *i*-C), 168.1, 168.8 and 170.9 (3COO).

Trimethyl 4-(4-nitrobenzyl)-7-(4-nitrophenyl)-2-oxooxepane-3,5,5-tricarboxylate ***12e***: The title compound was detected in some fractions of compound **11e** without isolation in pure form, calculated yield ~0.2%, single diastereomer. ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 2.42–2.51 (m, 1H, CH_2(a) at C(4)), 2.68–2.79 (m, 1H, H(4)), 2.72 (dd, 1H, H(7a), ^2J = 14.0 Hz, ^3J = 5.8 Hz), 2.90 (dd, 1H, H(7b), ^2J = 14.0 Hz, ^3J = 7.4 Hz), 2.97–3.04 (m, 1H, CH_2(b) at C(4)), 3.59, 3.60 and 3.77 (all s, 3×3H, 3OMe), 3.63 (dd, 1H, H(3), ^3J = 12.4 Hz, ^4J = 1.6), 4.97 (dd, 1H, H(7), ^3J = 7.4 and 5.8 Hz), 7.35–7.40 (m, 2H, 2 *o*-H), 7.45–7.50 (m, 2H, 2 *o*-H), 8.18–8.23 (m, 2H, 2 *m*-H), 8.22–8.27 (m, 2H, 2 *m*-H).

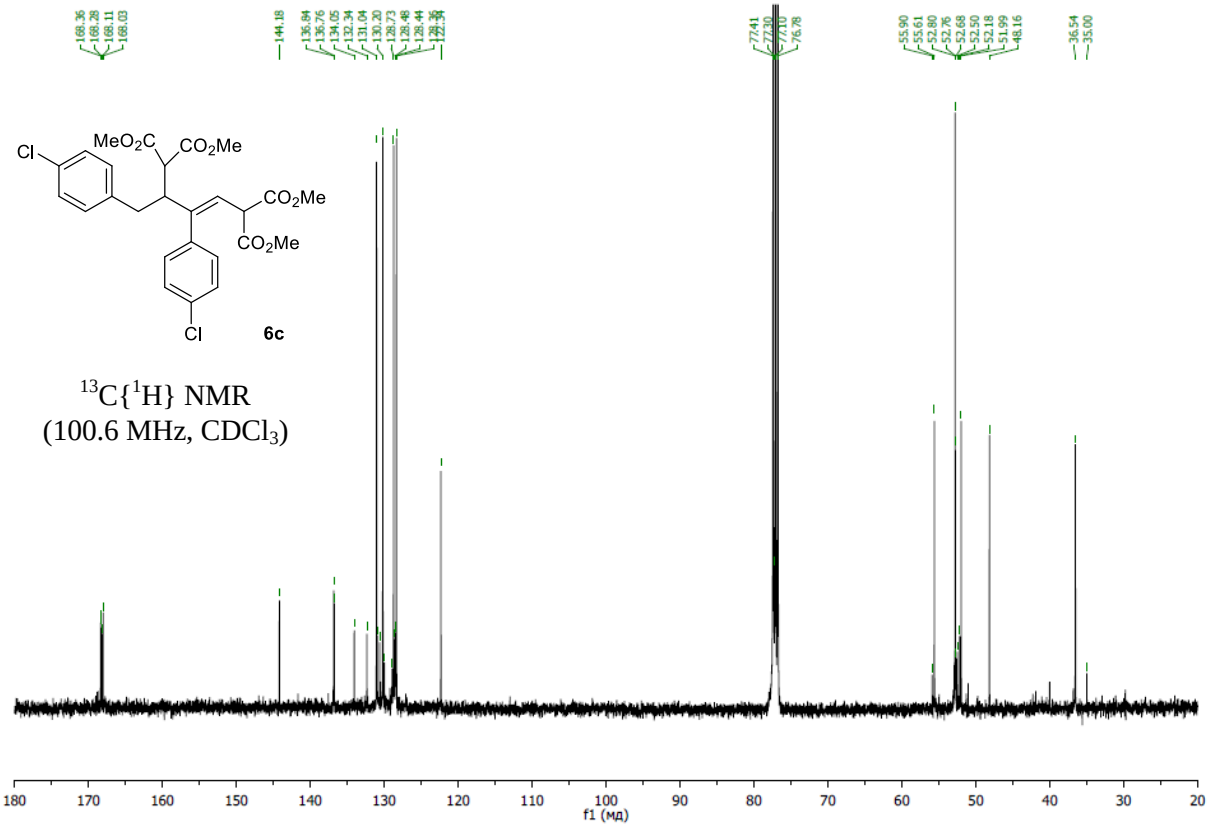
Tetramethyl 4-(3-bromobenzyl)-3-(3-bromophenyl)pent-1-ene-1,1,5,5-tetracarboxylate ***9f***: All operations were performed in dry argon atmosphere. To a solution of cyclopropane **1f** (125 mg, 0.4 mmol) in 5 ml of dry dichloromethane was added the solid $GaCl_3$ (70 mg, 0.4 mmol, 100 mol.%) in one portion at 20°C under vigorous stirring. Reaction mixture was stirred at the same

temperature during 4 h. After that aqueous solution of HCl (5%) was added at room temperature until pH 3 was achieved and the reaction mixture was extracted with dichloromethane (3×10 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was separated by column chromatography on silica gel (eluent — benzene to benzene–EtOAc, 5:1) to afford cyclopropane dimers **2f**, **3f** and **9f** as a number of fractions with different purity. NMR spectra of compounds **2f** and **3f** correspond to described earlier [Refs. 4, 8]. The target dimer **9f** was additionally purified on a Silufol chromatographic plate (20×20 cm) eluting with hexane–acetone, 5:1 or benzene–EtOAc, 10:1 to afford the pure **9f** in ~15 mg (~12%) yield as single diastereomer: colorless thick oil. IR ($CHCl_3$) ν 3020, 2956, 2926, 2853, 2433, 2400, 1738 (C=O), 1659, 1642, 1518, 1436, 1223 cm^{-1}. MS (*m/z*, %): 495 (3), 435 (3), 423 (3), 391 (3), 362 (25), 312 (18), 275 (31), 243 (70), 211 (82), 193 (31), 169 (34), 145 (37), 132 (32), 115 (87), 90 (30), 71 (40), 59 (100), 43 (58), 29 (43). HRMS calcd for $C_{26}H_{26}{}^{79}Br^{81}BrO_8$: $[M+H]^+$, 627.0047; $[M+Na]^+$, 648.9866. Found: *m/z* 627.0056; 648.9870. ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 2.55 (dd, 1H, H(5a), ^2J = 14.8 Hz, ^3J = 5.9 Hz), 2.82 (dd, 1H, H(5b), ^2J = 14.8 Hz, ^3J = 7.0 Hz), 2.99 (dddd, 1H, H(4), ^3J = 9.6, 7.0, 5.9 and 4.2 Hz), 3.53 (d, 1H, H(2′), ^3J = 4.2 Hz), 3.66, 3.73, 3.75 and 3.82 (all s, 4×3H, 4OMe), 4.12 (dd, 1H, H(3), ^3J = 11.4 and 9.6 Hz), 7.05 (d, 1H, H(2), ^3J = 11.4 Hz), 6.87–7.37 (m, 8H, Ar). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 35.9 (CH_2(5)), 45.3 (CH(4)), 48.4 (CH(3)), 52.39, 52.41, 52.47, 52.54 and 52.58 (CH(2′) and 4OMe), 122.2 and 122.3 (2 CBr), 126.0, 127.5, 129.5, 129.6, 131.0, 131.5, 132.0 and 132.1 (8 CH(Ar)), 130.4 (C(1)), 141.5 and 142.7 (2 *i*-C), 148.3 (CH(2)), 164.2 and 164.9 (2COO at C(1)), 167.7 and 170.8 (2COO at C(2′)).

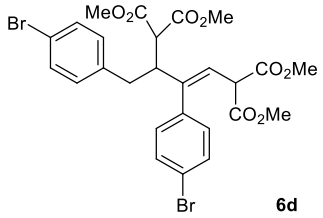
Selected NMR spectra



^{1}H NMR
(400.1 MHz, $CDCl_3$)

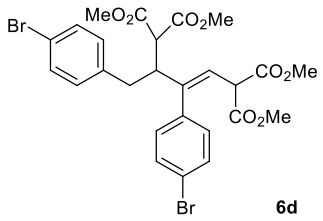


^{13}C{^{1}H} NMR
(100.6 MHz, $CDCl_3$)



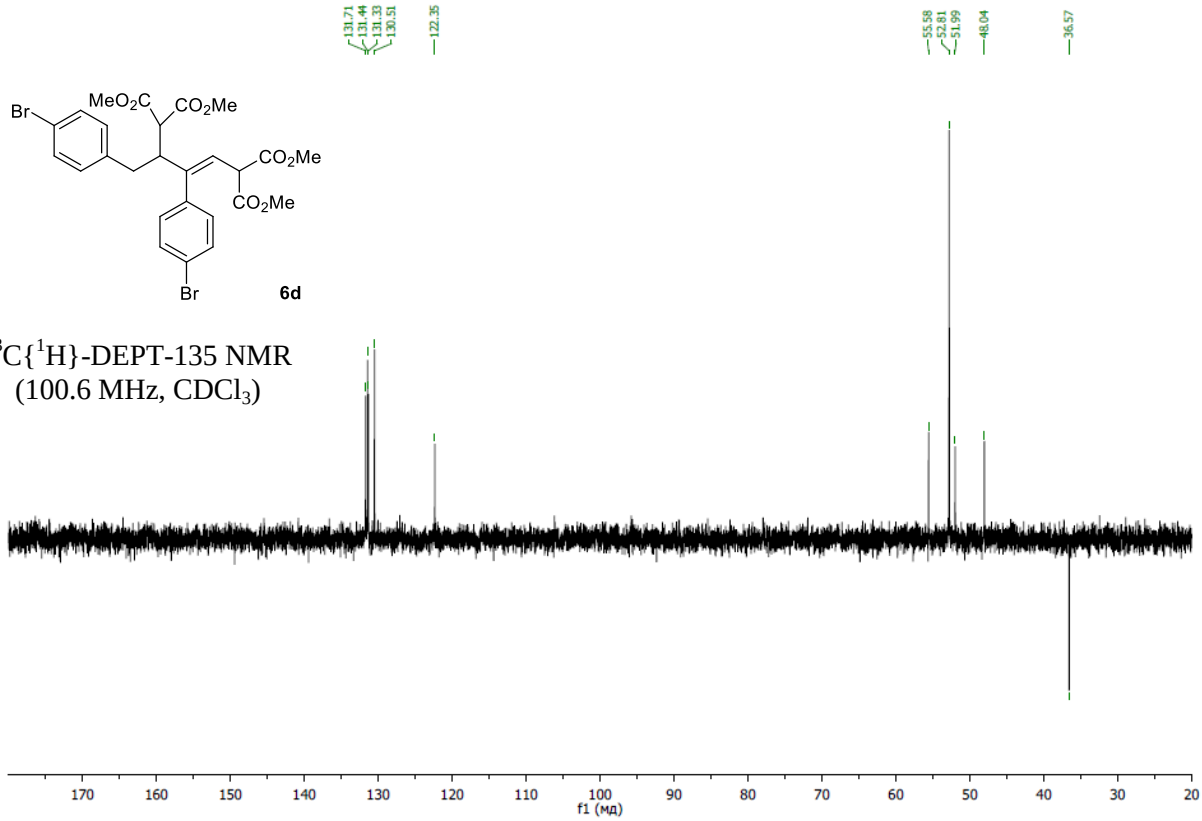
6d

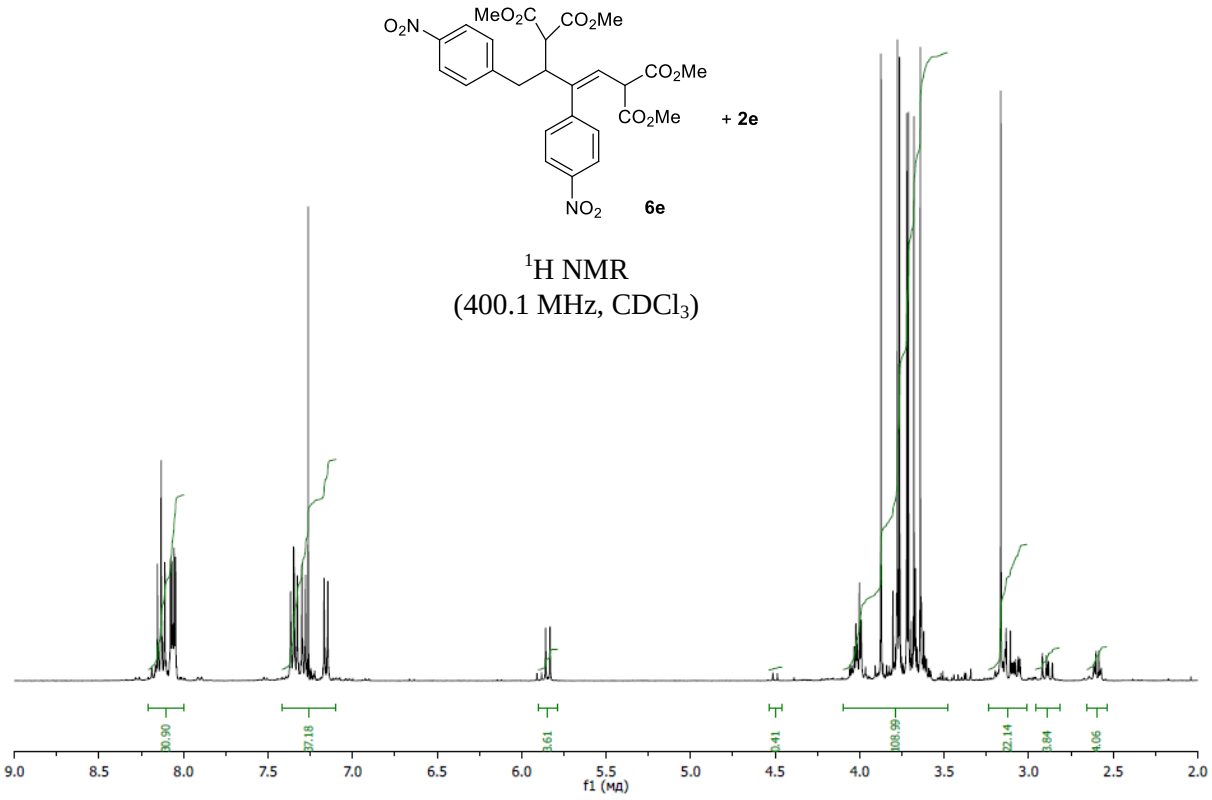
^{1}H NMR
(400.1 MHz, $CDCl_3$)



6d

^{13}C{^{1}H} NMR
(100.6 MHz, $CDCl_3$)


131.71
131.44
131.33
130.51
122.35
55.58
52.81
51.99
48.04
36.57
Br
MeO2C
CO2Me
CO2Me
CO2Me
Br
6d
13C{1H}-DEPT-135 NMR
(100.6 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (мд)


O2N
MeO2C
CO2Me
CO2Me
CO2Me
+ 2e
NO2
6e
1H NMR
(400.1 MHz, CDCl3)
30.90
37.18
3.61
0.41
108.99
22.14
3.84
4.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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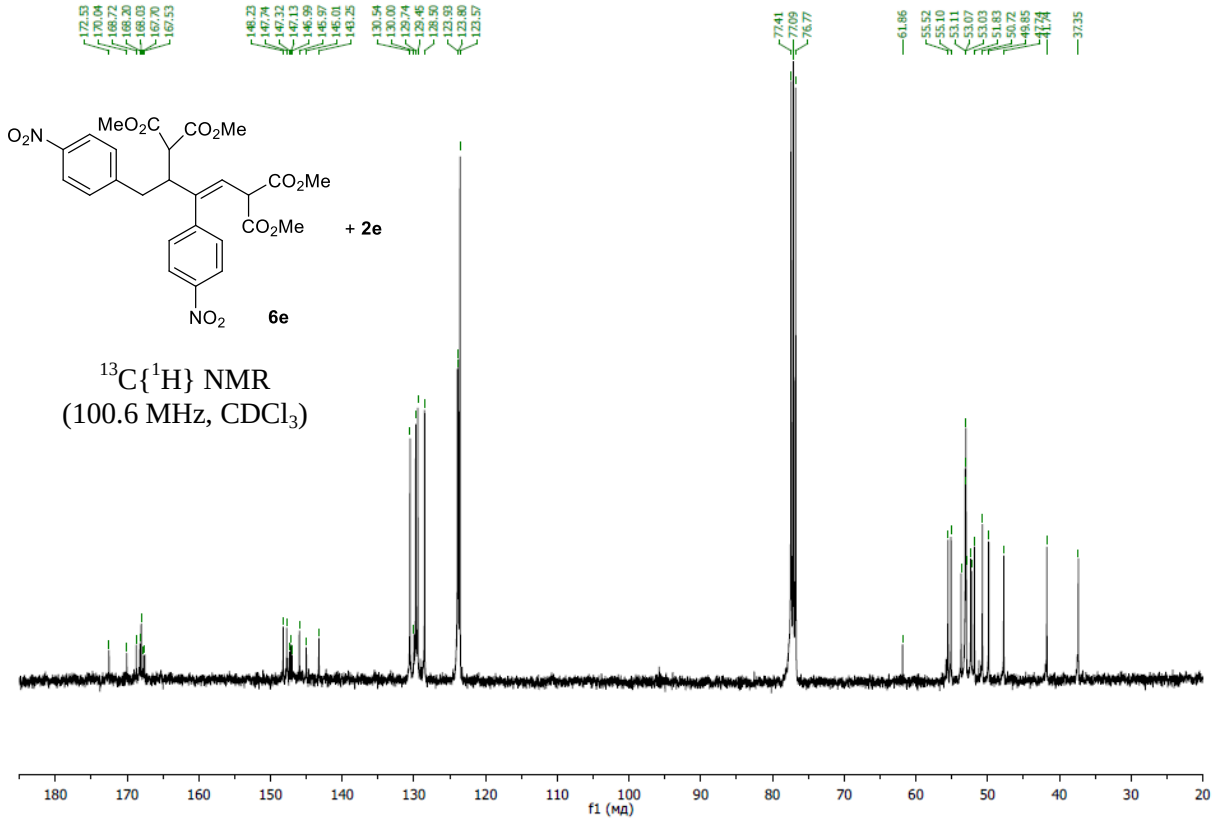
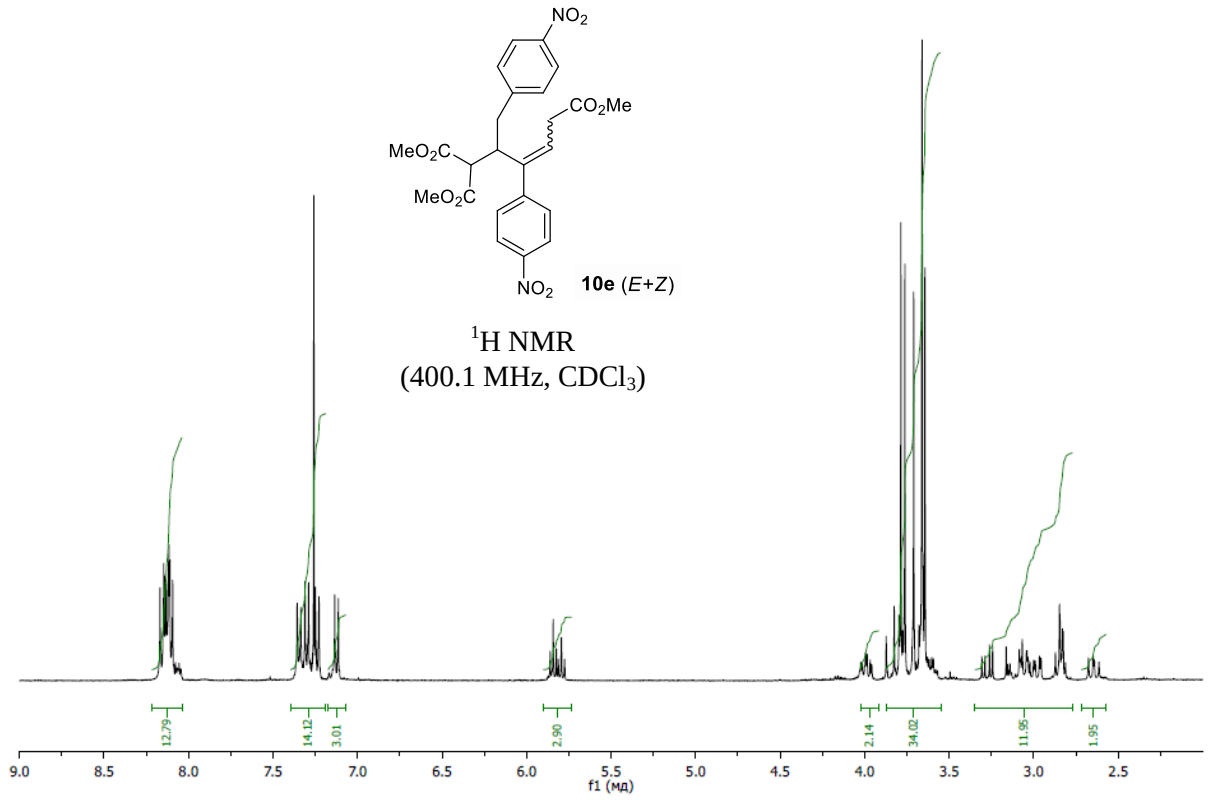
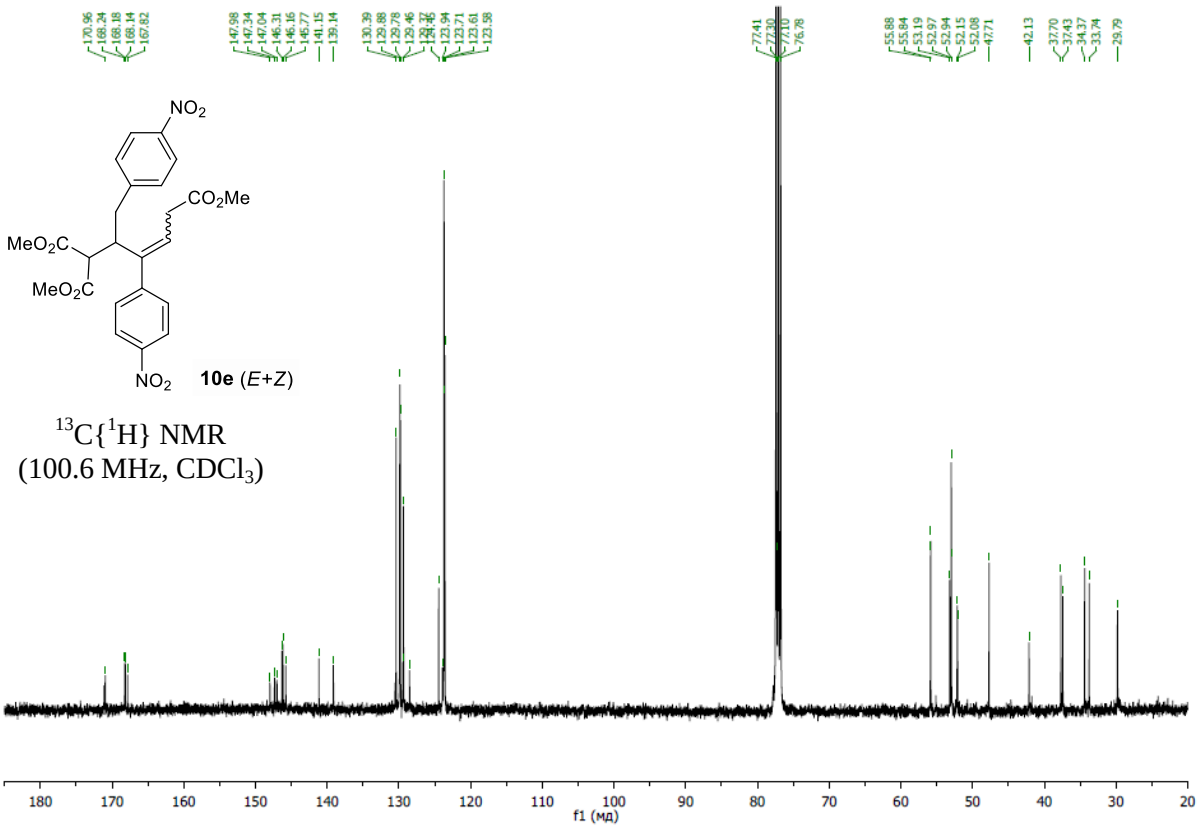
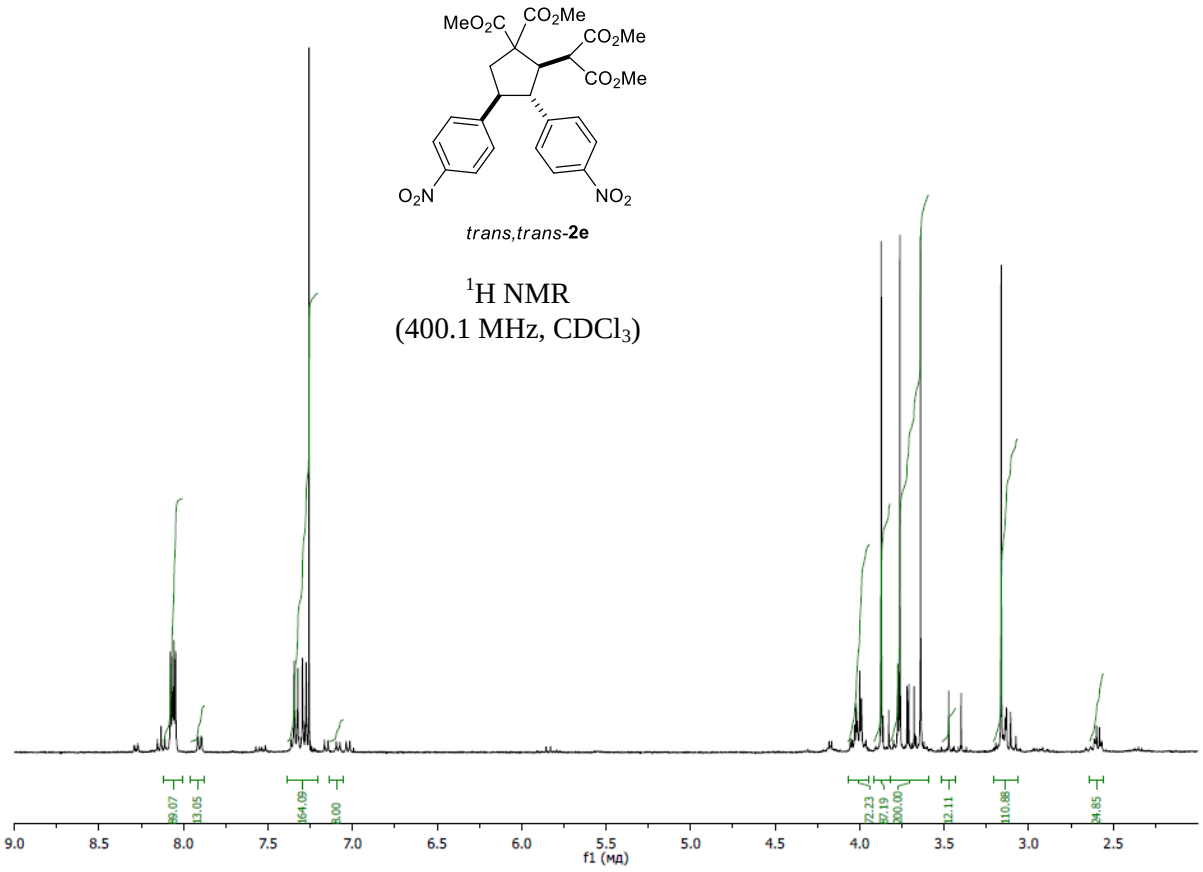
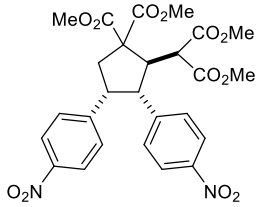
3.5
3.0
2.5
2.0
f1 (мд)


MeO2C
CO2Me
O2N
CO2Me
CO2Me
+ 2e
NO2
6e
13C{1H} NMR
(100.6 MHz, CDCl3)
f1 (мд)


NO2
CO2Me
MeO2C
MeO2C
NO2
10e (E+Z)
1H NMR
(400.1 MHz, CDCl3)
f1 (мд)

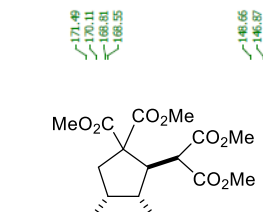

NO2
CO2Me
MeO2C
MeO2C
NO2
10e (E+Z)
13C{1H} NMR
(100.6 MHz, CDCl3)
f1 (мд)


MeO2C
CO2Me
CO2Me
CO2Me
O2N
NO2
trans,trans-2e
1H NMR
(400.1 MHz, CDCl3)
f1 (мд)



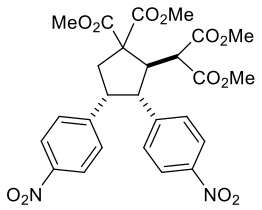
trans,cis-**2e**

^{1}H NMR
(400.1 MHz, $CDCl_3$)



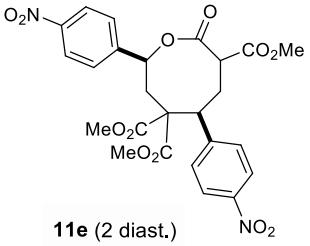
trans,cis-**2e**

^{13}C{^{1}H} NMR
(100.6 MHz, $CDCl_3$)



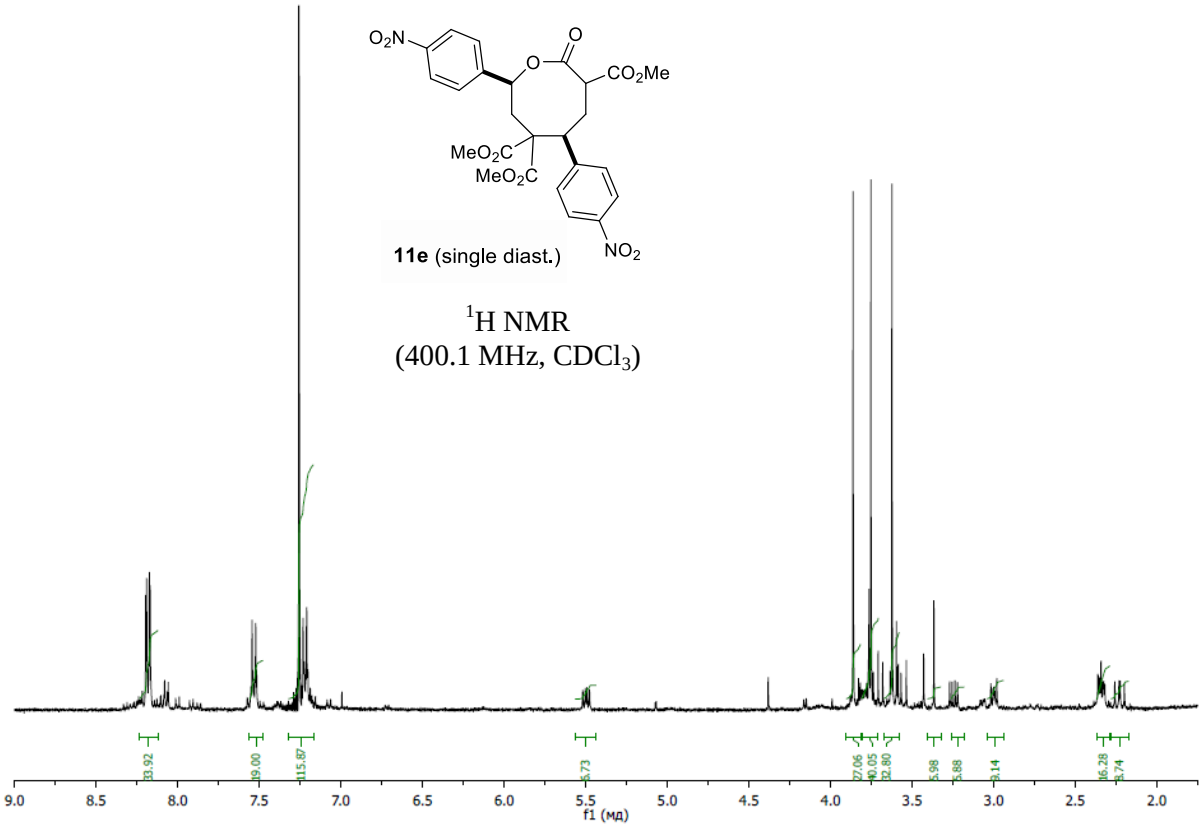
trans,cis-**2e**

$^{13}C\{^{1}H\}$-DEPT-135 NMR
(100.6 MHz, $CDCl_3$)

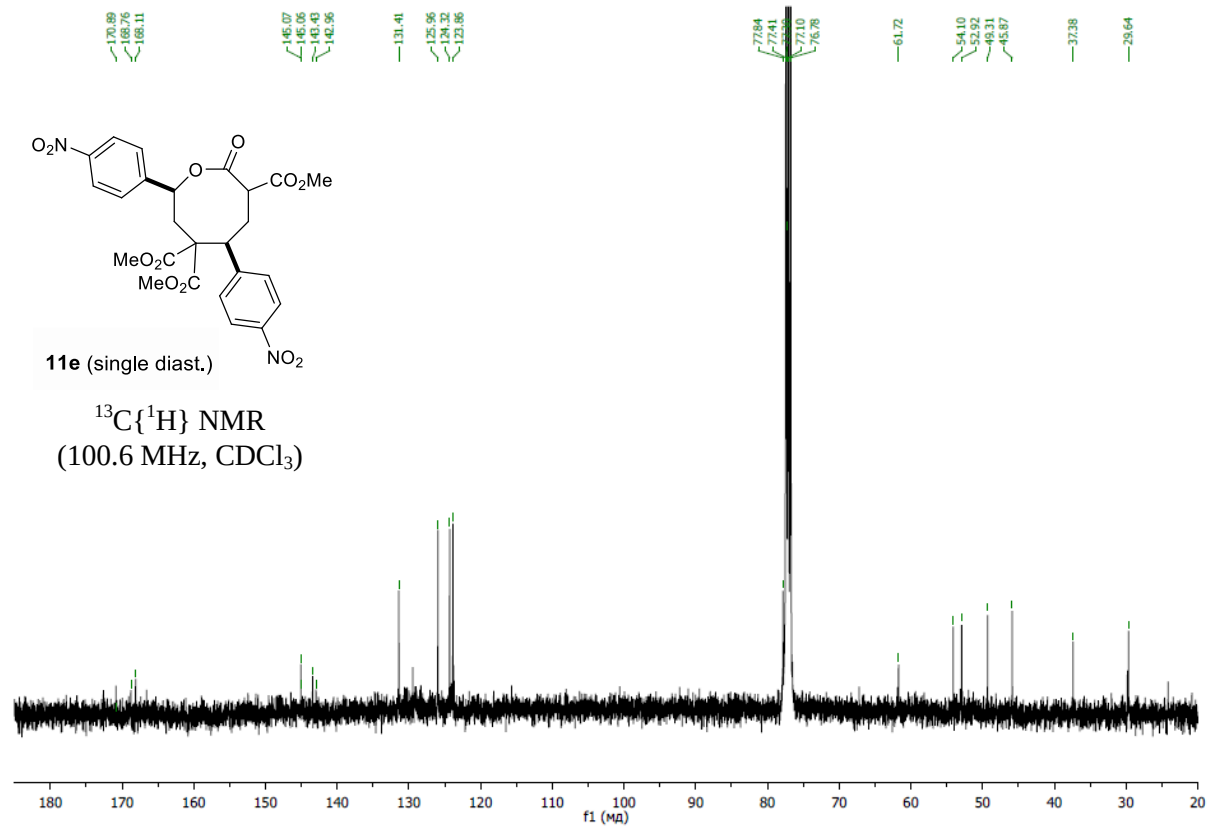


11e (2 diast.)

^{1}H NMR
(400.1 MHz, $CDCl_3$)

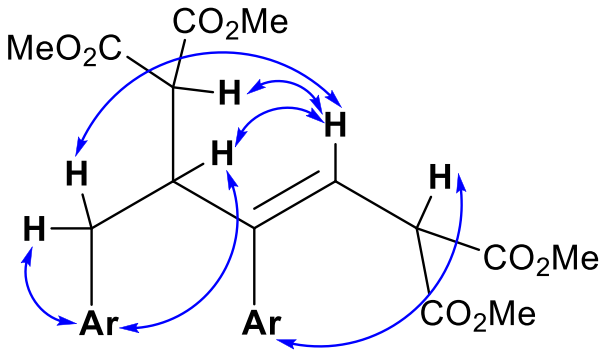


^{1}H NMR
(400.1 MHz, $CDCl_3$)

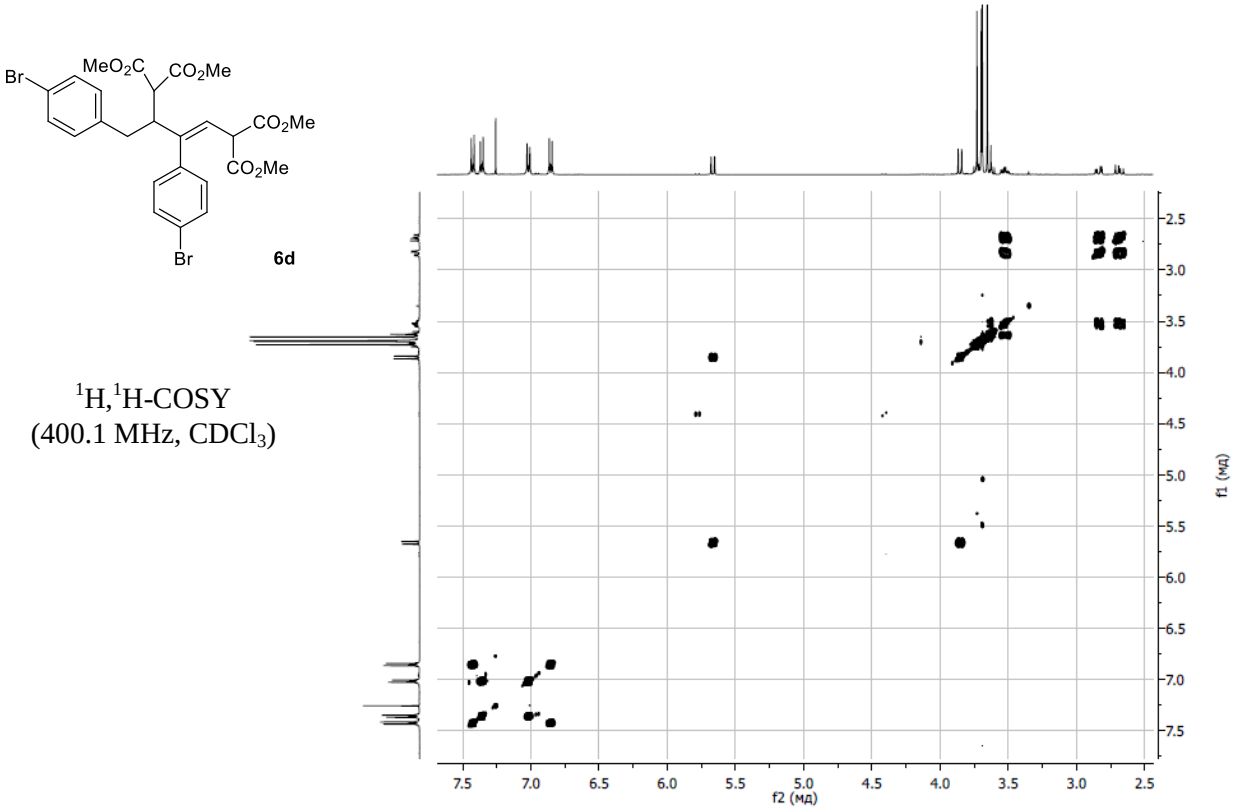


^{13}C{^{1}H} NMR
(100.6 MHz, $CDCl_3$)

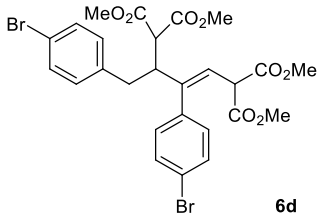
2D NOESY data for 6



Selected 2D NMR spectra

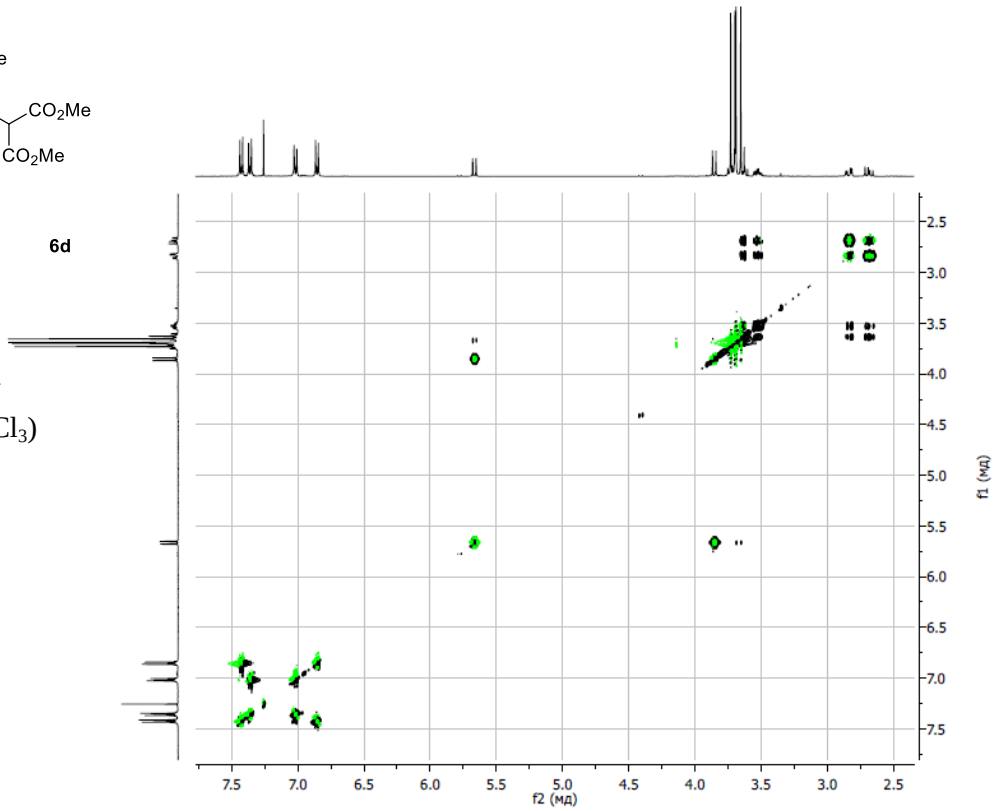


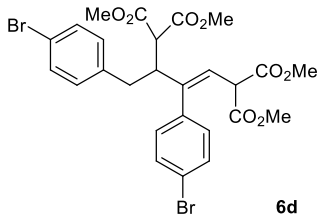
^{1}H,^{1}H-COSY
(400.1 MHz, $CDCl_3$)



6d

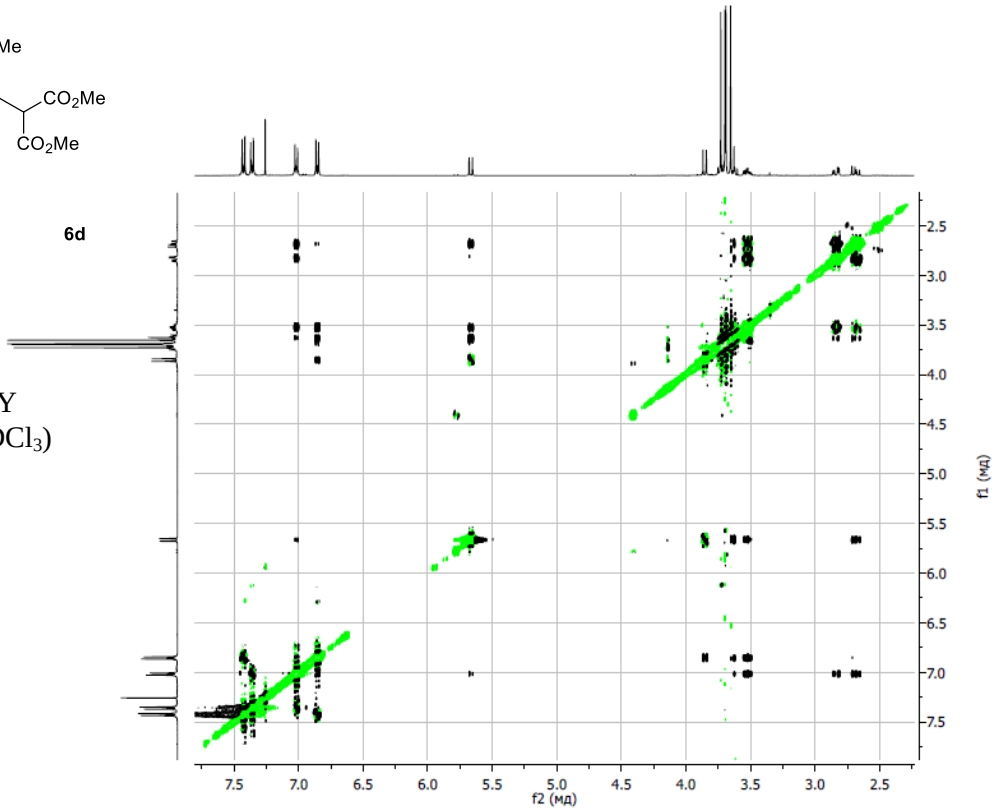
$^{1}H,^{1}H$-TOCSY
(400.1 MHz, $CDCl_3$)

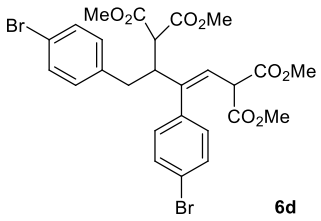




6d

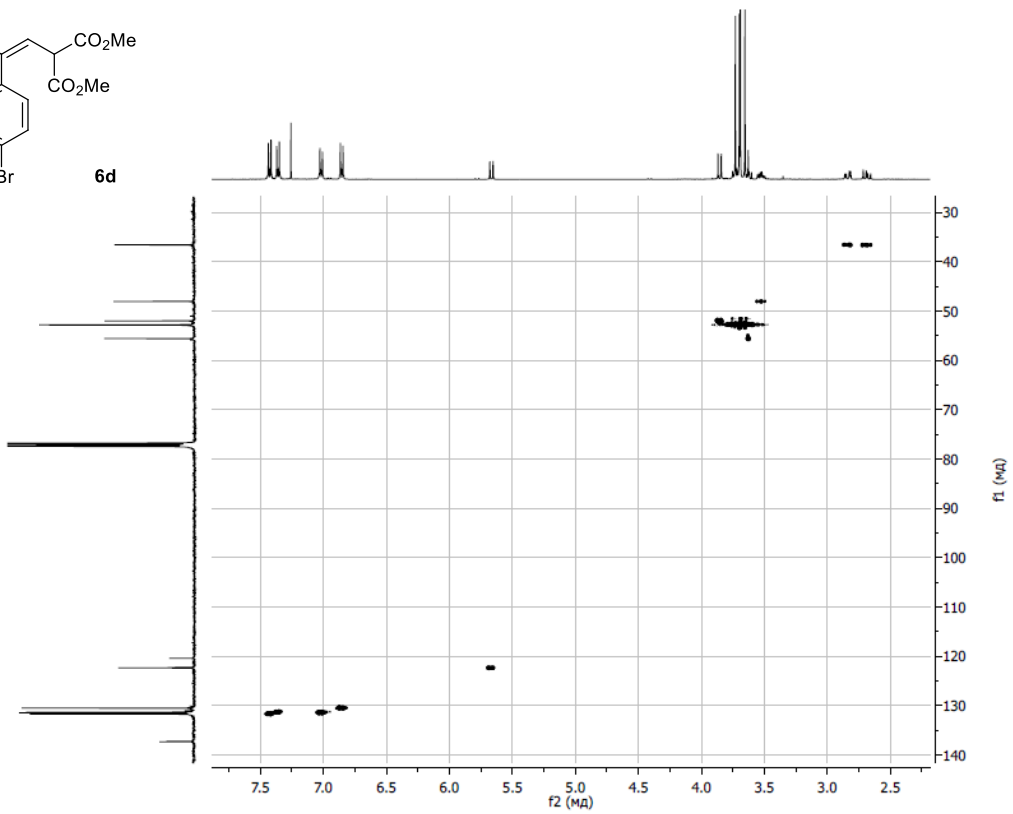
$^{1}H,^{1}H$-NOESY
(400.1 MHz, $CDCl_3$)

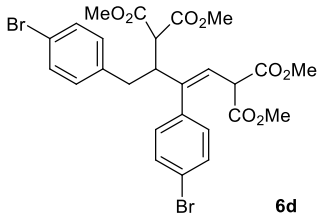




6d

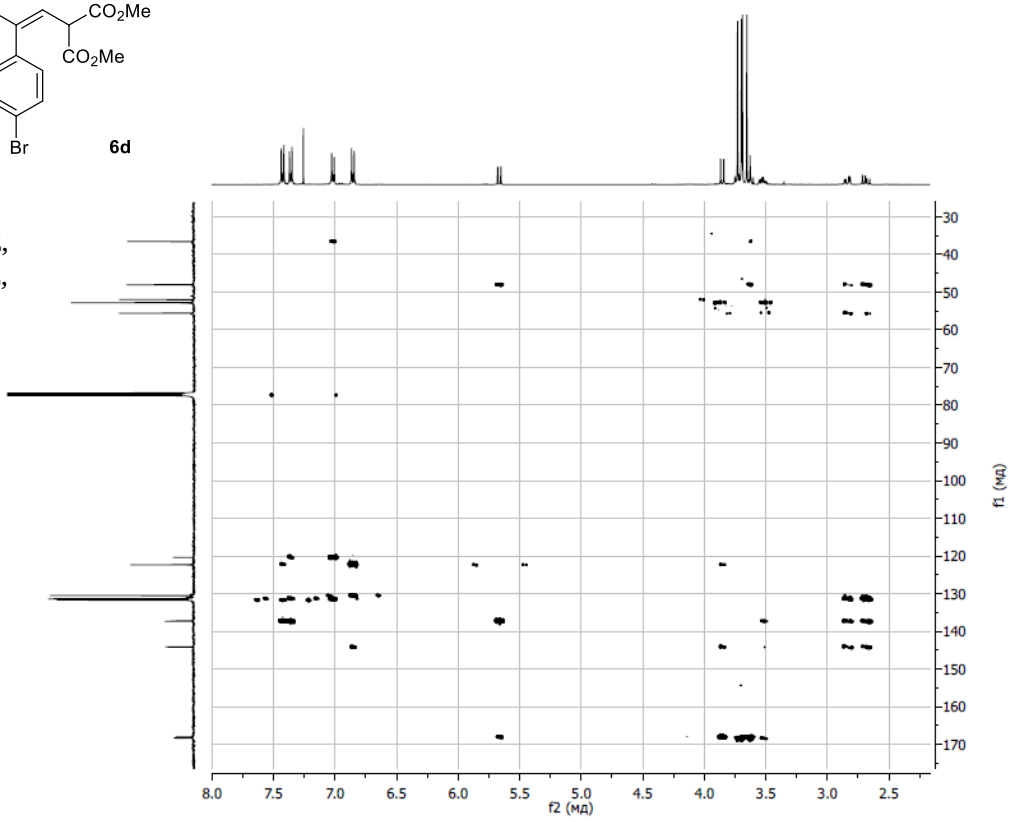
$^{1}H,^{13}C$-HSQC (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, $CDCl_3$)

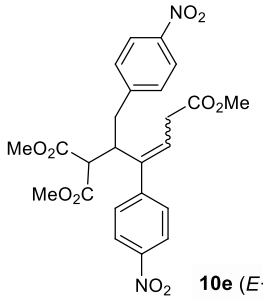




6d

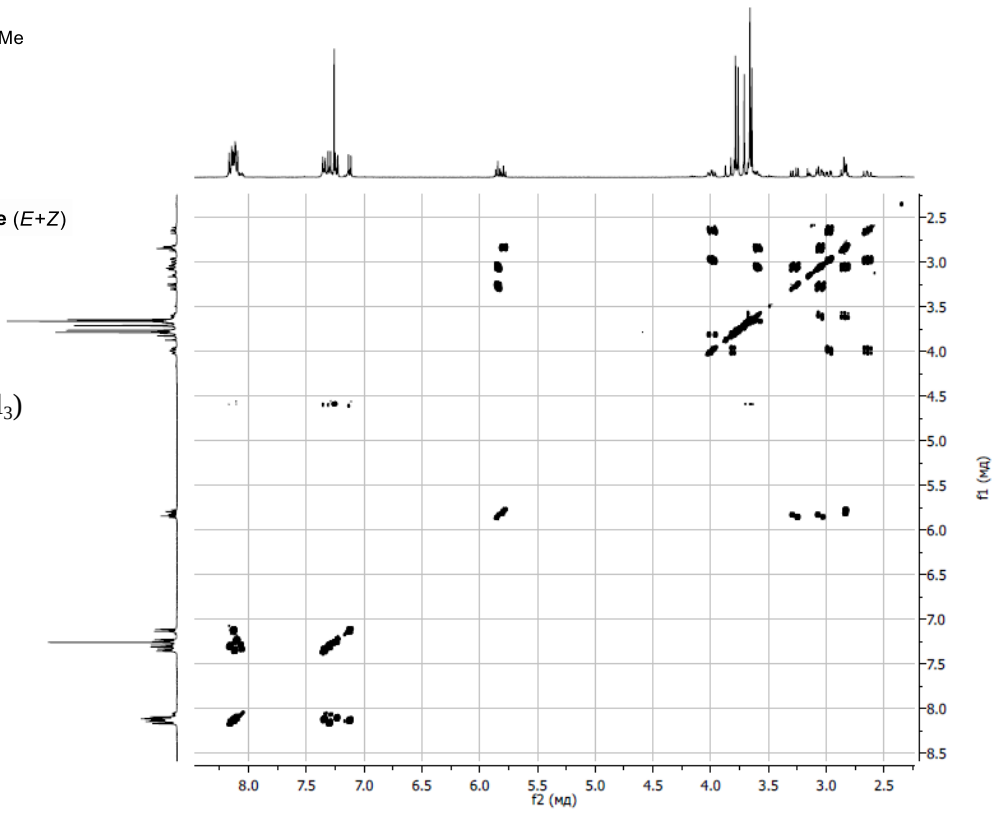
$^{1}H,^{13}C$-HMBC (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, $CDCl_3$)

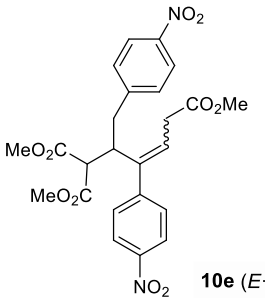




10e (*E*+*Z*)

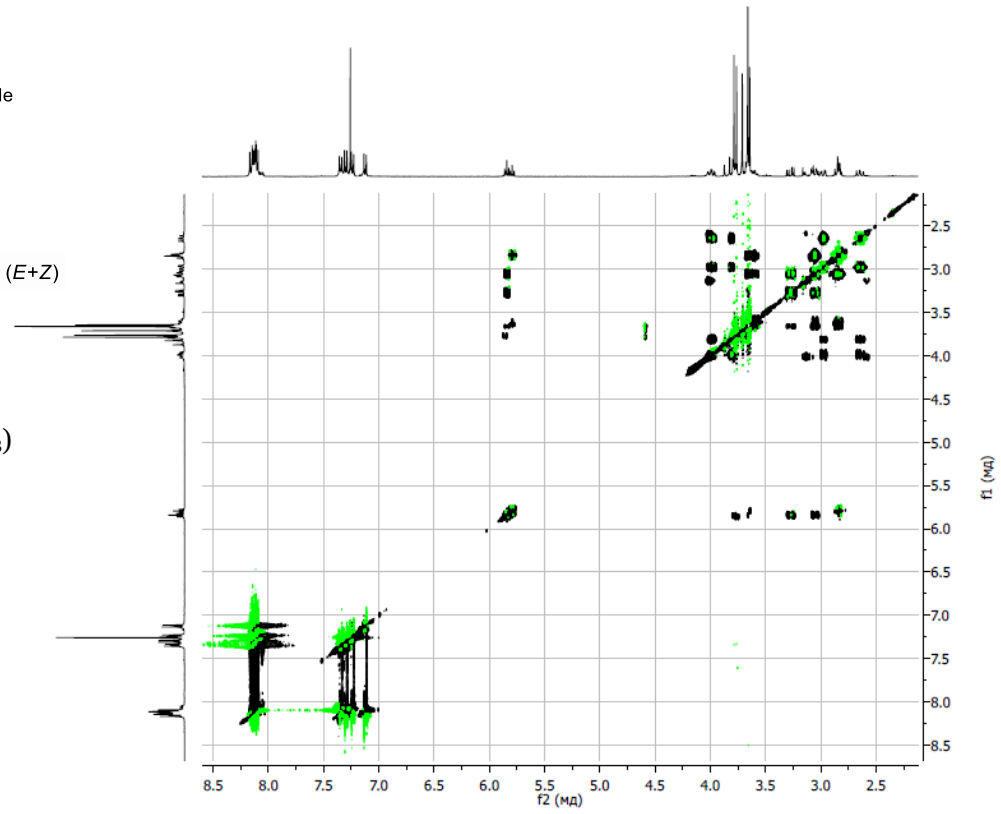
^{1}H,^{1}H-COSY
(400.1 MHz, $CDCl_3$)

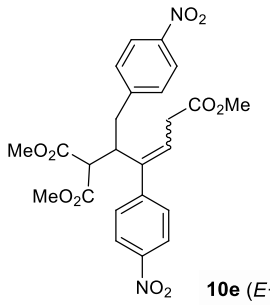




10e (*E*+*Z*)

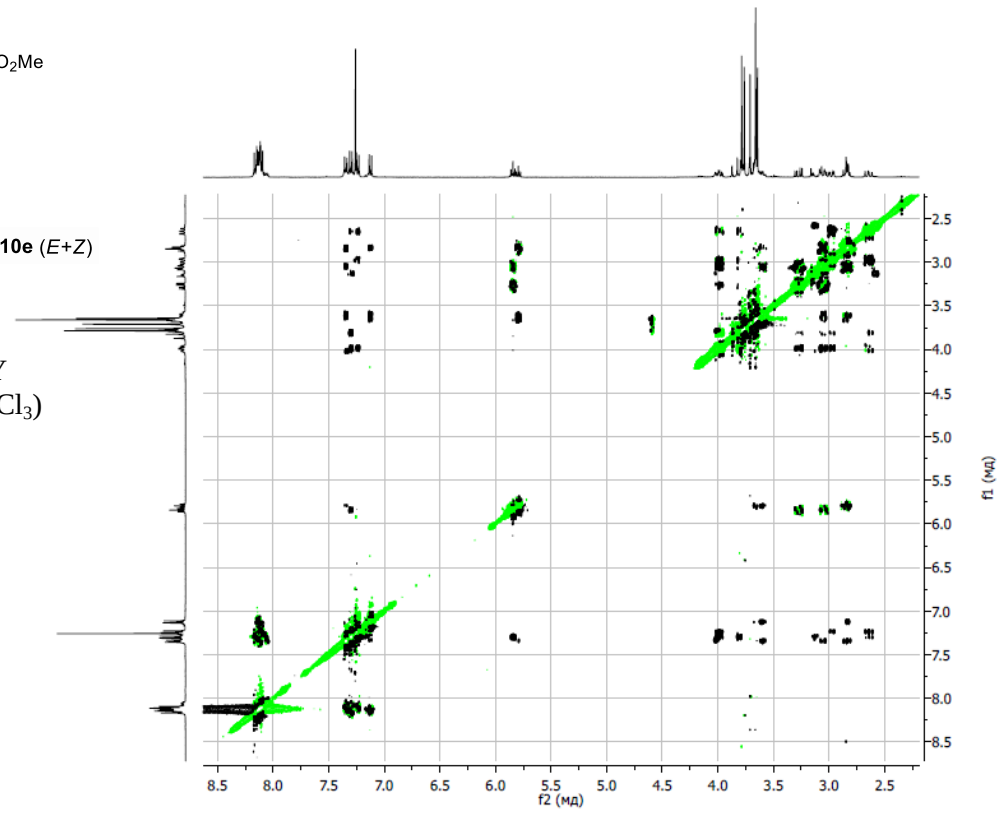
^{1}H,^{1}H-TOCSY
(400.1 MHz, $CDCl_3$)

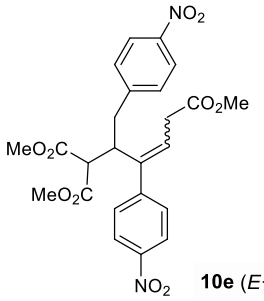




10e (*E*+*Z*)

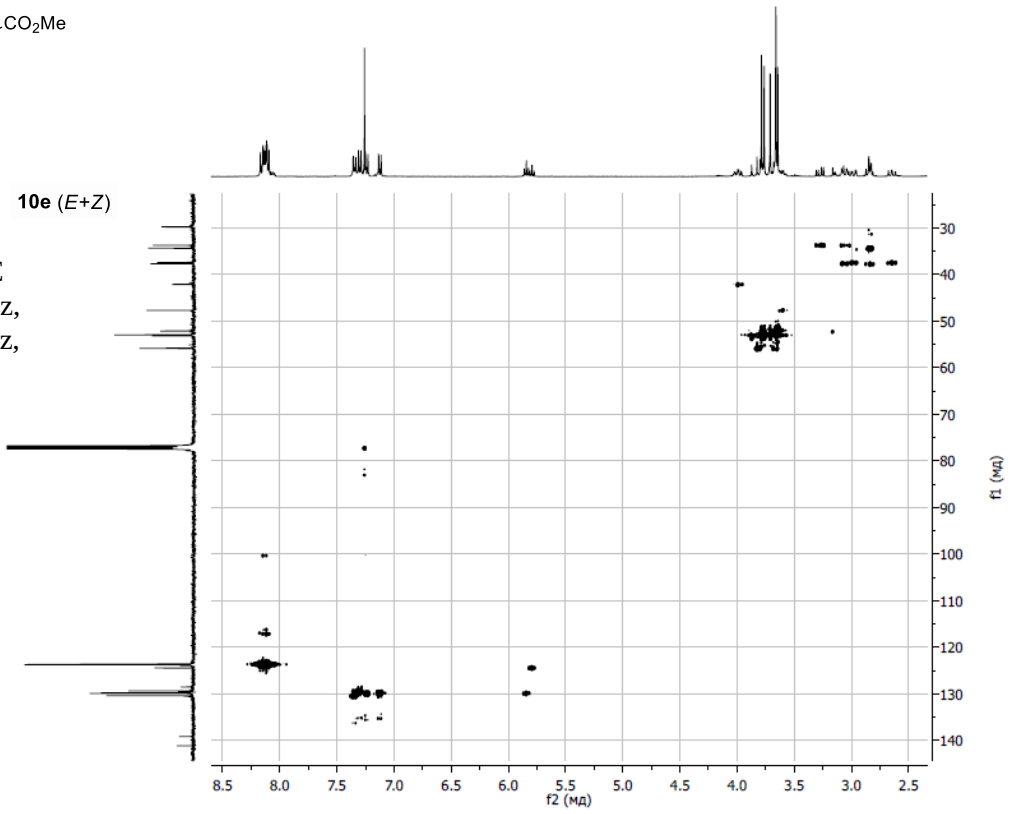
^{1}H,^{1}H-NOESY
(400.1 MHz, $CDCl_3$)

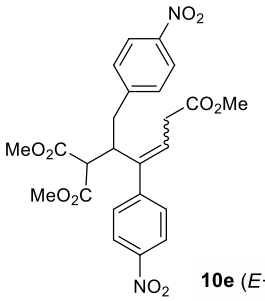




10e (*E*+*Z*)

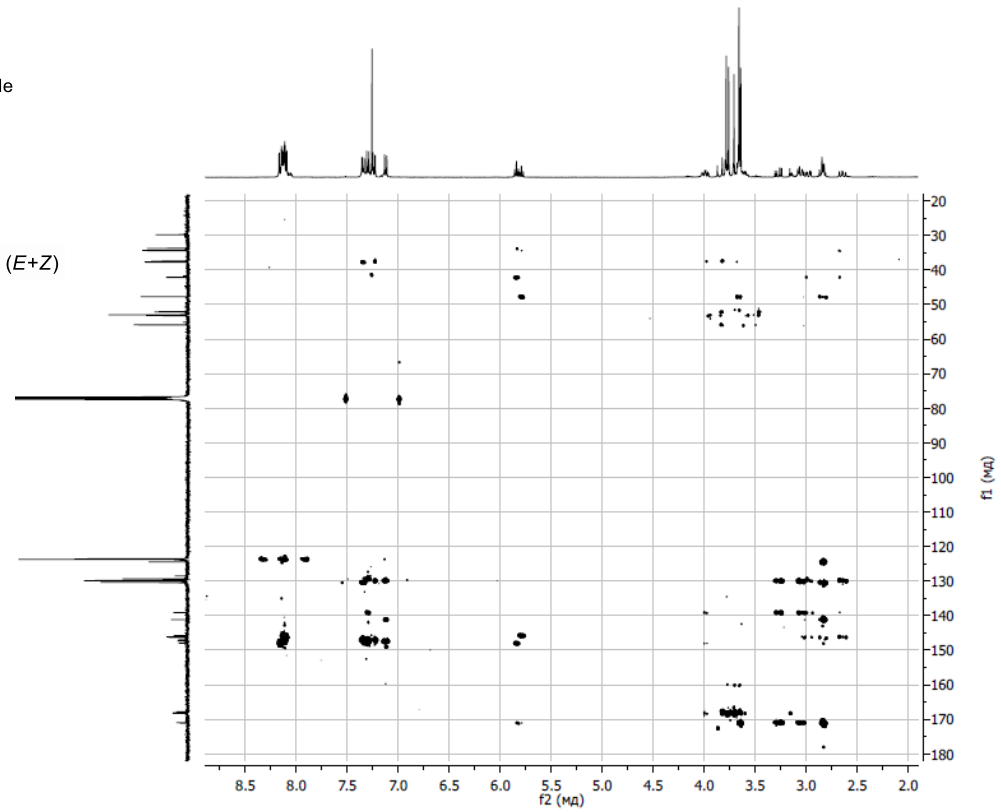
^{1}H,^{13}C-HSQC
(^{1}H: 400.1 MHz,
^{13}C: 100.6 MHz,
$CDCl_3$)

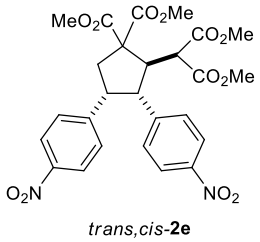




10e (*E*+*Z*)

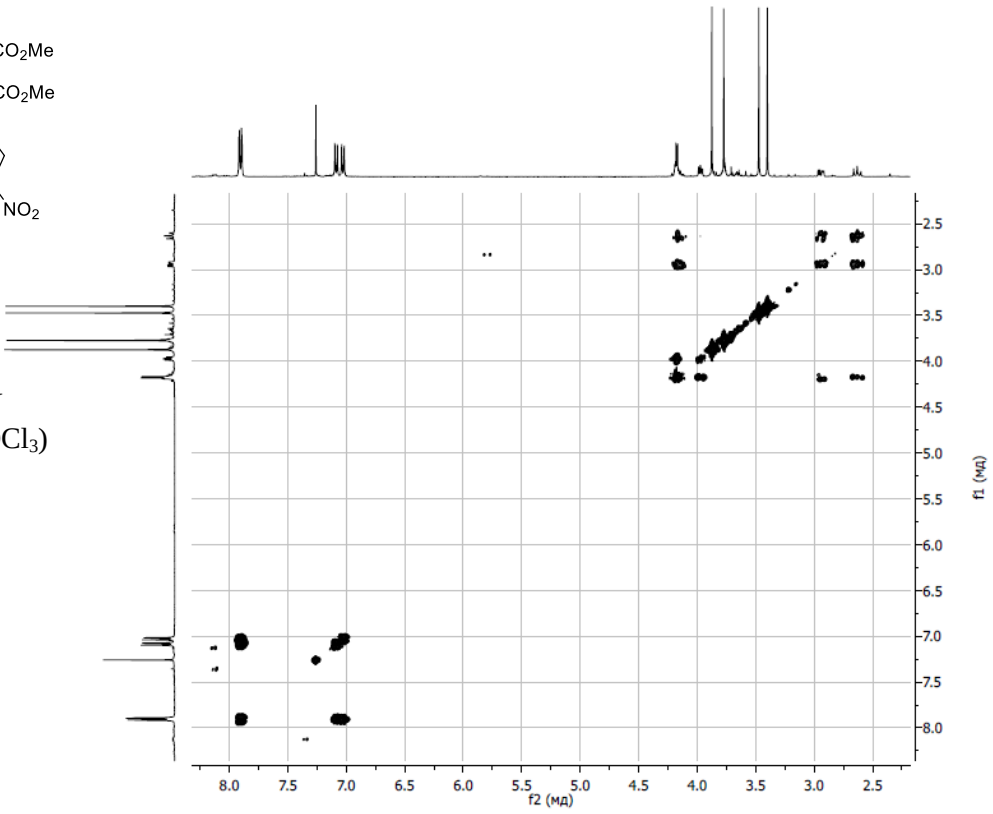
$^{1}H,^{13}C$-HMBC
(^{1}H: 400.1 MHz,
^{13}C: 100.6 MHz,
$CDCl_3$)

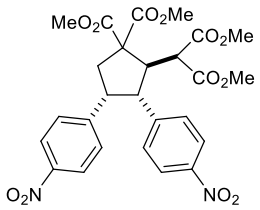




trans,cis-**2e**

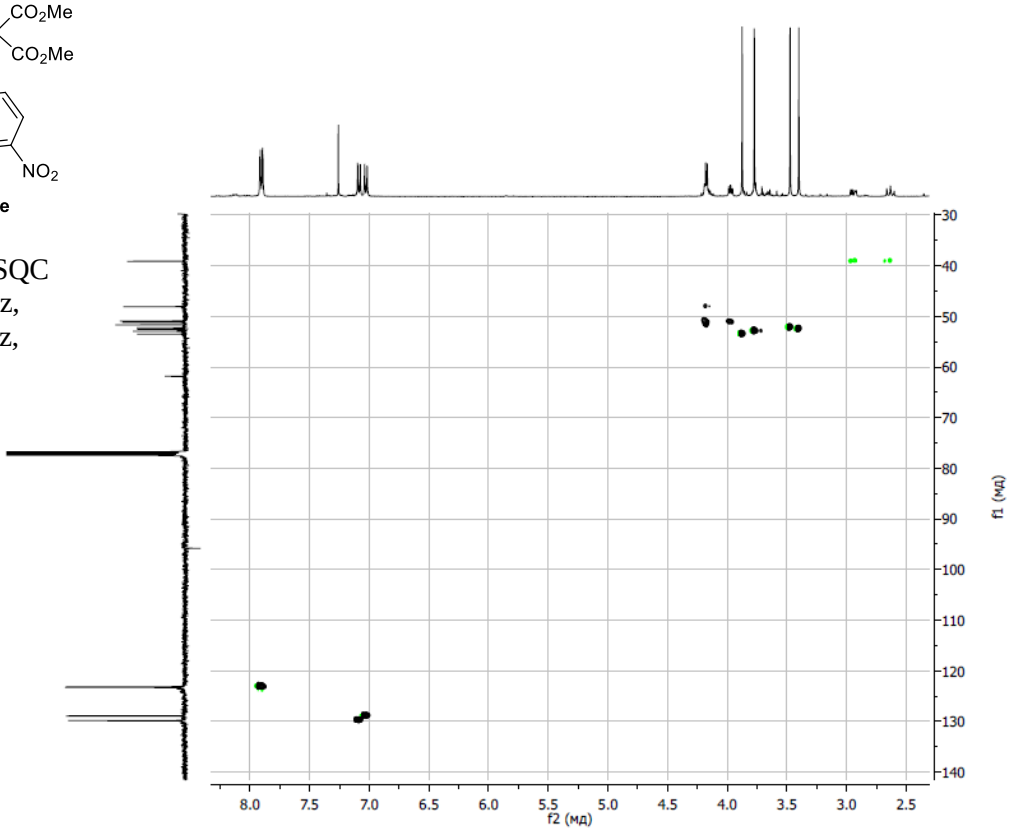
$^{1}H,^{1}H$-COSY
(400.1 MHz, $CDCl_3$)

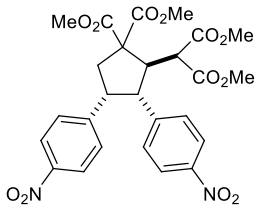




trans,cis-**2e**

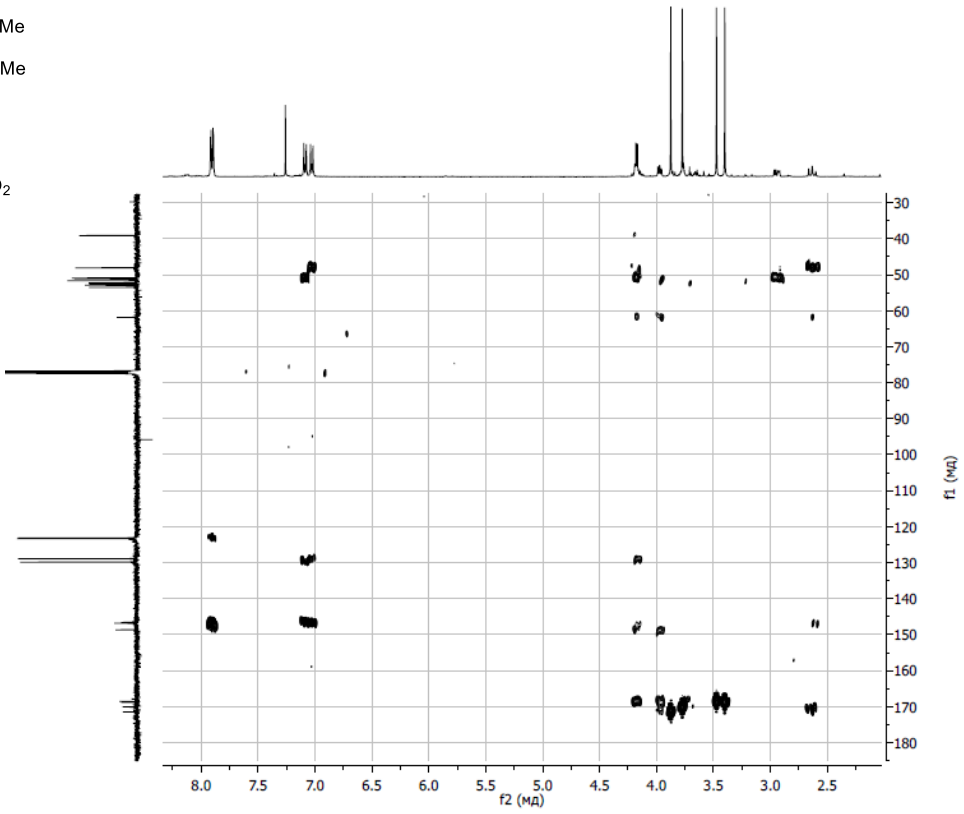
$^{1}H,^{13}C$-editing-HSQC (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, $CDCl_3$)

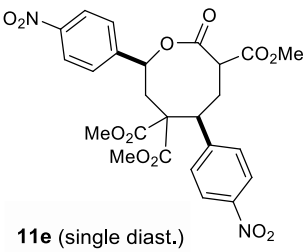




trans,cis-**2e**

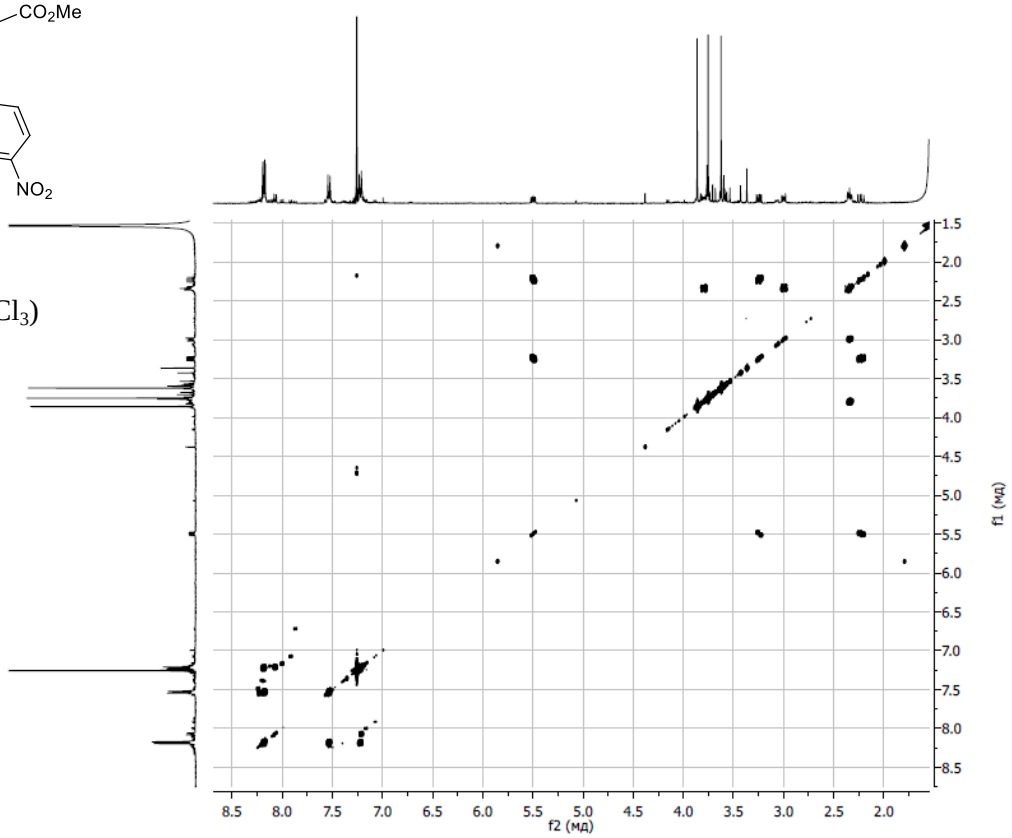
$^{1}H,^{13}C$-HMBC (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, $CDCl_3$)

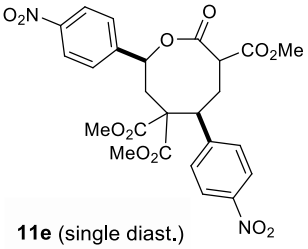




11e (single diast.)

^{1}H,^{1}H-COSY
(400.1 MHz, $CDCl_3$)





11e (single diast.)

^{1}H,^{13}C-HSQC
(^{1}H: 400.1 MHz,
^{13}C: 100.6 MHz,
$CDCl_3$)